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Studies of Interstellar Surface Chemistry

Experiment and Theory

Sean Antony Ayling

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Abstract

Astronomers seek information about the interactions occurring between complex organic molecules (COMs) and other common interstellar species. This information can help in understanding the conditions during star formation, and it is possible that this interstellar chemistry primes developing planetary systems with some of the essential compounds involved in the chemistry of life. Due to the conditions in interstellar space, the effects of particle bombardment, thermal processing and ultraviolet irradiation must be considered.

Laboratory surface science and theoretical modelling are employed because about 1 % of the mass of the interstellar medium (ISM) is in the form of dust grain particles, and these are considered to play an essential role in interstellar chemistry. In the experimental work, thin-layer ices of three COMs (2-propanol, dimethyl ether and acetaldehyde) were studied on a graphite surface, which served as the analogue for a carbonaceous dust grain, at ultra-high vacuum pressures and cryogenic temperatures. Observations of the ices were made via mass spectrometry and infrared spectroscopy. For the theoretical work, a number of adsorbing molecules were studied, and both cluster and periodic models of a graphite surface were considered.

Data for pure COM ices on graphite provided a reference point when observing more complex phenomena such as those COMs interacting with adsorbed water layers, and was also used to benchmark theoretical results. The amorphous-crystalline phase change of water was inhibited by the presence of 2-propanol, and this would be expected to affect the trapping and release of volatile chemical species in the ISM. Dimethyl ether and acetaldehyde had minimal effect on the water phase change, and showed broadly similar desorption from layered and mixed ices. Lastly, the theoretical model was established as consistently describing physisorption for a range of COMs on graphite.

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List of Abbreviations

ASW	amorphous solid water
BSSE	basis-set superposition error
CC	coupled cluster
CI	crystalline ice
CNM	cold neutral medium
СОМ	complex organic molecule
DFT	density functional theory
DIB	diffuse interstellar band
DME	dimethyl ether
DZ	double zeta
GGA	generalised gradient approximation
GTO	Gaussian-type orbital
HIM	hot ionised medium
HOPG	highly-oriented pyrolytic graphite
ISM	interstellar medium
ISRF	interstellar radiation field
LDA	local density approximation
LSDA	local spin density approximation
MCT	mercury cadmium telluride
OFHC	oxygen-free high-conductivity
PAH	polycyclic aromatic hydrocarbon
QMS	quadrupole mass spectrometer
RAIR(S)	reflection absorption infrared (spectroscopy)
STO	Slater-type orbital
SZ	single zeta
TPD	temperature-programmed desorption
ΤZ	triple zeta
UHV	ultra-high vacuum
UV	ultraviolet
WIM	warm ionised medium
WNM	warm neutral medium
XPS	x-ray photoelectron spectroscopy

Chapter I

Introduction

Space, in the popular imagination, is thought of as a great void, empty and inert. While a majority of the matter in a galaxy is indeed contained in the more familiar stars and planetary systems, a significant proportion exists in the 'space' between.¹ The proportion in the Milky way is ~10–15 %, and this tenuous matter is termed the interstellar medium (ISM). Ongoing astronomical observations of the ISM increasingly reveal a surprising richness at the molecular level, demonstrated well by large molecular clouds. Sagittarius B2 is a representative example, as illustrated in figure 1.1. Detection of new molecular species is ongoing, with the current inventory of interstellar molecules containing around 200; a list is provided here in table 1.1. In this context, molecules composed of six or more atoms are termed complex organic molecules (COMs). Referring to the table, it is notable that the larger molecular species are all based on carbon.



Figure 1.1. Colour-composite image of the Galactic Centre and Sagittarius B2 (middle-left bright, orange-red region) as seen by the ATLASGAL survey.² Image credit: ESO/APEX & MSX/IPAC/NASA

Sagitarrius B2 is among the largest molecular clouds in the Milky Way, sitting in a great belt around the Galactic Centre. As it is known to be particularly rich in chemical species, many observations have been made in this portion of the sky, and continue to reveal additional evidence of COMs. Detected

2 atoms	3 atoms	4 atoms	5 atoms	6 atoms	7 atoms	8 atoms
H_2	C ₃ *	<i>с</i> -С ₃ Н	C ₅ *	C_5H	C_6H	CH_3C_3N
AlF	C_2H	<i>l</i> -C ₃ H	C_4H	$l-H_2C_4$	CH ₂ CHCN	HC(O)OCH ₃
AlCl	C_2O	C_3N	C ₄ Si	$C_2H_4^{\star}$	CHC_2H	CH ₃ COOH
C_2^{**}	C_2S	C ₃ O	$l-C_3H_2$	CH ₃ CN	HC_5N	C ₇ H
СН	CH_2	C ₃ S	<i>c</i> -C ₃ H ₂	CH ₃ NC	CH ₃ CHO	C_6H_2
CH⁺	HCN	$C_2H_2^{\star}$	H_2CCN	CH ₃ OH	CH_3NH_2	CH ₂ OHCHO
CN	НСО	NH ₃	CH_4 *	CH ₃ SH	c-C ₂ H ₄ O	$l-HC_6H^*$
СО	HCO ⁺	HCCN	HC ₃ N	HC_3NH^+	H ₂ CCHOH	CH ₂ CHCHO (?)
CO^{+}	HCS ⁺	HCNH ⁺	HC ₂ NC	HC ₂ CHO	C ₆ H ⁻	CH ₂ CCHCN
СР	HOC+	HNCO	НСООН	NH ₂ CHO	CH ₃ NCO	H ₂ NCH ₂ CN
SiC	H_2O	HNCS	H ₂ CNH	C ₅ N	HC ₅ O	CH ₃ CHNH
HCl	H_2S	HOCO⁺	H_2C_2O	<i>l</i> -HC ₄ H*		CH ₃ SiH ₃
KCl	HNC	H ₂ CO	H ₂ NCN	<i>l</i> -HC ₄ N		
NH	HNO	H_2CN	HNC ₃	$c-H_2C_3O$		
NO	MgCN	H ₂ CS	SiH ₄ *	$H_2CCNH(?)$		
NS	MgNC	H_3O^+	H_2COH^+	$C_5 N^-$		
NaCl	N_2H^+	c-SiC ₃	C ₄ H ⁻	HNCHCN		
OH	N_2O	CH ₃ *	HC(O)CN	SiH ₃ CN		
PN	NaCN	C ₃ N ⁻	HNCNH			
SO	OCS	PH ₃	CH ₃ O			
SO ⁺	SO ₂	HCNO	NH_4^+			
SiN	c-SiC ₂	HOCN	H_2NCO^+ (?)			
SiO	CO_2^{\star}	HSCN	NCCNH ⁺			
SiS	NH_2	H_2O_2	CH ₃ Cl			
CS	$H_{3}^{+}(*)$	C_3H^+				
HF	SiCN	HMgNC				
HD	AlNC	НССО				
FeO?	SiNC					
O ₂	НСР					
CF^{+}	ССР	9 atoms	10 atoms	11 atoms	12 atoms	>12 atoms
SiH?	Aloh	CH ₃ C ₄ H	CH ₃ C ₅ N	HC ₉ N	<i>c</i> -C ₆ H ₆ *	C ₆₀ *
РО	H_2O^+	CH ₃ CH ₂ CN	(CH ₃) ₂ CO	CH ₃ C ₆ H	<i>n</i> -C ₃ H ₇ CN	C ₇₀ *
AlO	H_2Cl^+	(CH ₃) ₂ O	$(CH_2OH)_2$	C ₂ H ₅ OCHO	<i>i</i> -C ₃ H ₇ CN	C ₆₀ ⁺ *
OH⁺	KCN	CH ₃ CH ₂ OH	CH ₃ CH ₂ CHO	CH ₃ OC(O)CH ₃	C ₂ H ₅ OCH ₃ ?	c−C ₆ H ₅ CN
CN-	FeCN	HC ₇ N	CH ₃ CHCH ₂ O			
SH+	HO_2	C ₈ H	CH ₃ OCH ₂ OH			
SH	TiO ₂	CH ₃ C(O)NH ₂				
HCl+	C_2N	C ₈ H ⁻				
TiO	Si ₂ C	C_3H_6				
ArH ⁺	HS_2	CH ₃ CH ₂ SH (?)				
N_2		CH ₃ NHCHO?				
NO ⁺ ?		HC ₇ O				

Table 1.1. Detected molecules in various observed regions of the ISM as of January 2018.³ Dimethyl ether and acetaldehyde, which are significant molecules in this thesis, are highlighted in bold.

'?' denotes assignments that have reasonable chances of being correct

'(?)' denotes assignments where (partial) overlap of detection lines cannot be ruled out

* indicates molecules that have been detected by their rotation-vibration spectrum ** indicates molecules detected by electronic spectroscopy only

species include methanol, acetone, formaldehyde, dimethyl ether, acetaldehyde, acetic acid, methyl formate and glycolaldehyde.^{4–16} Over such vast regions, this complexity has potentially profound implications, as these organic molecular species could lead to widespread pre-biotic chemistry in the universe, as is shown by the formation of glycine, the simplest amino acid.¹⁷ Another notable detection of pre-biotic chemistry is the observation of glycolaldehyde, the simplest sugar.^{13–16} Further, and on a practical level, the complex structure of these molecules provide astronomers with greater insight into the nature of such remote environments. That is, detection of these molecules provides a probe into local physical conditions—especially with regard to temperature and radiation—with detection of some species thus able to act as chemical 'clocks' for star formation.¹⁸ Given the importance of this molecular environment, studies of relevant chemistry become essential to a complete understanding of these remote astronomical regions. The work presented in this thesis contributes toward this developing field of astrochemistry, using both laboratory experiments and theoretical models to better understand COM chemistry in the extremes of space.

I.I Interstellar Environments

Through the extinction of distant starlight, the general existence of interstellar matter was shown by Robert Trumpler in 1930.¹⁹ However, in the earliest observations, relatively dense regions of interstellar matter were mistakenly designated as areas of emptiness. In 1784 William Herschel—then the astronomer at the court of King George III—noted 'holes in the sky' where there were an apparent absence of stars.^{20,21} This is illustrated well by one such feature, the Bok globule Barnard 68 (B68), which is shown in figure 1.2. This feature takes its name from the American astronomer Edward Barnard who, in 1919, categorised B68 along with a number of other dark patches seen in astronomical images.²² He had shown through these and other observations that at least some of the dark features were not 'holes' but rather obscuring matter in space, blocking the starlight beyond, although at that time this was still a matter of debate.²¹ As shown in the figure, modern telescopes operating at far-infrared wavelengths have since clearly demonstrated that Barnard and others who held the same view were correct. In fact, far from being empty, dark clouds are now known to be the birthplace of new stars.²³ Although the process is not fully understood, it is there that matter condenses into hot-core protostars.

The cosmic proportion of elements is primarily hydrogen (90.8 % by number) and helium (9.1 %), with the remaining ~1 % comprised of heavier elements.¹ These rarer elements are termed 'metals' in astronomy, and notable examples include carbon, nitrogen, oxygen, silicon, magnesium and iron. The elemental composition of interstellar matter in terms of hydrogen and helium is very similar to the cosmic values, but observations of the gaseous content of the ISM have shown that there are significant depletions from the expected amounts of the heavier elements, especially in colder, more dense



Figure 1.2. Observations of the dark molecular cloud Barnard 68 at visible and infrared wavelengths.²⁴ The image to the right includes far-infrared wavelengths, shown in red colouration. Image credit: ESO

regions.^{1,25–28} The accepted rationalisation for these general depletions is that these elements are bound in solid forms as part of widespread microscopic dust grains.

Although only occupying <1 % of the volume of the galaxy, by mass about half of all interstellar matter is contained within clouds.^{1,29} These clouds can be divided into three general, overlapping categories. The coldest and most dense are the dark molecular clouds, of which B68 is an example. These clouds are mostly opaque to starlight, as seen visually in figure 1.2. They also have the most significant molecular content, and are therefore the primary interest for studying astrochemical complexity.^{1,30} In contrast, the diffuse clouds are, as the name indicates, much more diffuse, and these clouds are largely transparent to starlight. Diffuse clouds are primarily composed of atomic rather than molecular gases, due to greater exposure to the interstellar radiation field (ISRF).^{1,30,31} The third category is that of the translucent clouds, which have intermediate properties, containing both molecular and atomic gases.

Broad categorisation of clouds and other interstellar matter is shown in table 1.2. The categories are based on the model proposed by Field *et al.*, which was later extended by McKee and Ostriker.^{32,33} Briefly, the categories are the cold neutral medium (CNM), the warm neutral (or atomic) medium (WNM), the warm ionised medium (WIM) and the hot ionised medium (HIM). In the parameters of this model, the CNM category encompasses the diffuse clouds, which can condense under self-gravitation to form the dark clouds.³⁴ The remaining categories describe interstellar matter not contained within clouds. The WNM and WIM are intermediate regions.^{1,29} The most extreme regions described by this model are the HIM regions. The HIM, also referred to as coronal gas, is believed to originate from supernovae, as well as the intense stellar winds generated prior to supernova events.^{1,35}

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	Temperature / K	Number density / cm ⁻³
dark molecular clouds	10-20	$10^2 - 10^6$
CNM (diffuse clouds)	100	20-50
WNM + WIM	10 ⁴	0.2–0.5
HIM	10^{6}	10 ⁻⁴

Table 1.2. Categorisation of interstellar matter by approximate temperatures and number densities.

I.2 Dust in Space

Research into the exact composition of interstellar dust grains is still ongoing, though they are currently thought to be largely carbonaceous or silicaceous, and are believed to be formed in the relatively cool atmospheres of stars near the end of their lives.^{20,21,34,36–38} There are several sources of evidence for dust grains, and one such source is linked to the earliest direct demonstration of the existence of the ISM.¹⁹ Although the effects themselves had been seen earlier, Trumpler connected general extinction and the reddening of distant starlight to absorption and scattering by interstellar matter. These effects provide clues into the existence and nature of dust grains. An additional hint of the presence of dust grains is seen in the linear polarisation of starlight, explained by elongated dust grains aligned to a large-scale magnetic field.³⁹

Extinction curves plot interstellar extinction against wavelength, and many have been recorded in observations of the Milky Way. The example shown in figure 1.3 is representative of the common result in the UV-visible range.^{37,40} A steady increase toward shorter wavelengths is seen, along with a very distinct bump centred at 2175 Å ($4.6 \mu m^{-1}$). Fitted models attribute the slope of the extinction curve to dust particles ranging in size from a few nanometres up to almost a micrometre.^{1,20,21} Particles of this size scatter blue light more effectively than red light, causing the interstellar reddening seen in observations. Considering the composition of the grains, the prominent 2175 Å bump has been suggested as evidence of carbonaceous particles, potentially large polycyclic aromatic hydrocarbons (PAHs).^{1,20,37} Additional evidence for carbon content is seen in weak extinction features referred to as diffuse interstellar bands (DIBs), which may be indications of PAH structures in the ISM, with C₆₀⁺ confirmed as the carrier of two DIBs.^{41,42}

Additional spectroscopic information regarding dust grains is seen in the infrared region of the spectrum, illustrated in figure 1.4, which shows a spectrum of the W33A star-forming region recorded by the spectrometer on the Infrared Space Observatory satellite. The large absorption feature at ~10 μ m is readily observed and assigned to silicates in the literature.^{37,43} Many of the other features assigned in the figure are associated with icy mantles composed of molecular species adsorbed on the dust grain surfaces. More details on these ices are given in section 1.3.



Figure 1.3. Interstellar extinction in the Milky Way recorded in the UV-visible range. Adapted from results published by Fitzpatrick.⁴⁰



Figure 1.4. Infrared spectrum of the W33A star-forming region, recorded by the spectrometer on the Infrared Space Observatory satellite. Adapted from results published by Gibb *et al.*⁴³

As noted in section 1.1, the gas phase depletion of chemical elements provides indirect evidence of solid phase interstellar material.^{1,25–28} Depletions reported for several elements, based on observations of the star ζ Ophiuchi, are listed in table 1.3, which is adapted from results published by Snow and Witt.²⁸ Both carbon and silicon show substantial depletions versus the expected cosmic values. Although the fractional depletion of silicon is higher, carbon has a more than ten-fold greater absolute quantity, suggesting a larger total amount of carbon in the solid phase for this region, although the exact form of interstellar carbon is unknown. The results also have a bearing on dust grain structure, as Snow and Witt conclude that their findings imply a dust grain density suggestive of fluffy, porous or fractal structures. In considering the (Mg+Fe):Si ratio in interstellar dust—including results from ζ Ophiuchi—Sofa and Meyer suggested that olivine (MgFeSiO₄) is a reasonable approximation of interstellar silicates.⁴⁴ In general, olivine (Mg2xFe_{2-2x}(SiO₄)) and pyroxene (MgxFe_{1-2x}(SiO₃)) are both silicate structures of astrophysical interest.⁴⁵

Table 1.3. Gas phase abundances of several heavy elements in the ISM in the direction of the star ζ Ophiuchi, shown as fractions of the expected values to demonstrate depletion. The data listed are adapted from the literature.²⁸

Element	Stellar abundance*	Remaining gas phase fraction
С	2.1×10^{-4}	0.63
Ν	6.6×10^{-5}	~0
0	4.6×10^{-4}	0.72
Mg	2.5×10^{-5}	0.24
Si	1.9×10^{-5}	0.09
Fe	2.7 ×10 ⁻⁵	~1

* relative to hydrogen

Lastly, a potential source of information about interstellar dust is from the direct collection of dust grains in the vicinity of the Solar System. This presents challenges, as local interplanetary dust—thought to be similar to interstellar grains—will have been heavily processed during the evolution of the System. The objective of the recent Stardust spacecraft mission was to collect material from the coma of comet Wild 2 as well as to collect cosmic dust samples. Results of seven likely interstellar dust grains collected by the craft were reported by Westphal *et al.*⁴⁶ The composition of these potential interstellar particles was found to include crystalline and amorphous silicate, with magnesium and iron content. One of the particles showed a possible major carbon component, although it is uncertain whether this was a result of contamination, in this instance.

The inclusion of a comet in the Stardust mission highlights an important link that comets provide between the contemporary Solar System and the interstellar material from which it originated.^{34,47} Comets are now considered as aggregates of interstellar dust and ice, which formed in the early evolution of the System but were not incorporated into planetary bodies. As such, there is a potential for insight into pre-solar interstellar matter, especially from cometary cores.³⁷ Due to the relationship between the compositions of comet surfaces and icy dust grain mantles, the data from laboratory or theoretical investigations into processes on these surfaces are readily linked. However, it is important to consider that the degree to which individual comets have been altered by the environment of the Solar System is not completely known, and will depend both on the distance from the Sun at which they formed and how closely they have approached since.³⁴ Even so, additional interest in the chemistry of comets in its own right originates from the potential involvement of comets in delivering water and pre-biotic compounds to the early Earth.³⁴ A growing range of organic species has been detected in comets of the Solar System, including in the comets Halley (1P), Hale-Bopp (C/1995 O1), Lovejoy (C/2014 Q2) and Churyumov-Gerasimenko (67P).^{47–56}

1.2.1 Surface Chemistry on Dust Grains

Dust grains only account for 1 % by mass of interstellar clouds, yet they are proposed to be essential for driving many chemical processes in the ISM, including the production of COMs.^{4,20,57-59} Dust grains provide favourable conditions by reducing kinetic and thermodynamic barriers for reactive species, by removing excess energy as exothermic reactions occur, and by shielding resulting products from the degrading effects of interstellar radiation.

The ambient conditions of space present a problem for chemistry between gaseous species. Most reactions in interstellar space are thought to be associative in nature, producing a single product.^{20,60} In order for a reaction of this type to proceed in the gas phase, molecules must collide and release the excess internal energy to stabilise the product. In radiative association, this occurs through the emission of radiation

$$A + B \longrightarrow AB + h\nu$$

while for collisional stabilisation, the reaction proceeds due to rapid quenching by collision of a third particle. A general expression for collisional stabilisation is

$$A + B \Longrightarrow AB^*$$
$$AB^* + M \longrightarrow AB + M^*$$

where *M* is the third particle. The probability for radiative association proceeding is only ~ 10^{-5} or less per collision, and with gas phase concentrations so low in space, collisional stabilisation is very unlikely due to the negligible probability of a three-body collision.^{61,62} However, the surface of a dust grain can instead act as the third body in order to stabilise reaction products.⁶⁰ Moreover, the grain improves reaction kinetics by holding reactive species adsorbed on the surface, and has also been shown to lower the activation energy of reactions, as in the case of carbonyl sulphide (OCS) or carbon dioxide (CO₂) formation.^{63,64} This catalytic effect is potentially crucial because the temperatures in molecular clouds are ~10–20 K, such that only those processes with a minimal barrier (<10 kJ mol⁻¹) will proceed.⁶⁵

In terms of the kinetics, there are three commonly studied mechanisms for surface-mediated interstellar reactions: the Langmuir-Hinshelwood mechanism, the Eley-Rideal mechanism and the 'hotatom' mechanism.^{60,62,66} These are illustrated schematically in figure 1.5. The Langmuir-Hinshelwood mechanism is also called the 'diffusive' mechanism and describes the bimolecular reaction of two surfaceadsorbed species

$$\begin{array}{c} A_{(g)} \longrightarrow A_{(ads)} \\ \\ B_{(g)} \longrightarrow B_{(ads)} \\ \\ A_{(ads)} + B_{(ads)} \longrightarrow products \end{array}$$

Meanwhile, the Eley-Rideal mechanism describes a gas phase species reacting directly with an already adsorbed species

$$\begin{array}{c} A_{(g)} \longrightarrow A_{(ads)} \\ \\ A_{(ads)} + B_{(g)} \longrightarrow products \end{array}$$

Lastly, the 'hot-atom' mechanism considers an energetic gas phase species which adsorbs, diffuses and reacts with an adsorbed species without thermal relaxation

$$\begin{array}{c} A_{(g)} \longrightarrow A_{(ads)} \\ B_{(g)}^{*} \longrightarrow B_{(ads)}^{*} \\ A_{(ads)} + B_{(ads)}^{*} \longrightarrow products \end{array}$$

When comparing these mechanisms, two factors are essential to consider. One is the surrounding environment, as in all chemistry, while the other is the specifics of the species' adsorption. Adsorption is illustrated for reference by a generic potential energy diagram in figure 1.6. With respect to the environment, the Langmuir-Hinshelwood mechanism may seem more kinetically favourable than Eley-Rideal under interstellar conditions, as the surface-bound nature of the Langmuir-Hinshelwood mechanism improves the likelihood of two reactive species coming together. Surface mobility could be due to thermal hopping or quantum tunnelling, but allows the adsorbate to behave as a two-dimensional gas.^{68,69} However, the Langmuir-Hinshelwood mechanism does require this mobility on the surface, and the Eley-Rideal or 'hot-atom' mechanisms can be significant where there are higher grain surface



Figure 1.5. Illustration of the three common surface-mediated reaction mechanisms, with reactants 'A' and 'B' and the resulting association reaction product 'AB'. For the 'hot atom' and Eley-Rideal mechanisms in the illustration, reactant 'B' is assumed to already be adsorbed. In the figure, E_b is the energy barrier between surface binding sites and E_D is the desorption energy barrier. Adapted from an illustration published by Herbst.⁶⁷

temperatures or higher adsorbate concentrations, respectively.⁶² A weaker physisorption bond to the surface is necessary for adsorbate mobility, so the Langmuir-Hinshelwood mechanism is thus ruled out in cases where only chemisorbed species are found.⁷⁰ A physisorption bond, however, also increases the likelihood that the energy of reactions could cause desorption into the gas phase before a stable molecular product is formed. This then returns to a consideration of the surrounding environment, as temperature ranges which provide sufficient surface diffusion mobility—while limiting loss to the gas phase—will maximise the efficiency of the Langmuir-Hinshelwood mechanism.⁶⁹



Figure 1.6. Generic potential energy diagram for physisorption and activated chemisorption. In non-activated (barrierless) chemisorption, the crossing point lies below the zero level.

A notable example of the catalytic effects of dust grains is the formation of molecular hydrogen (H_2) . It was observed early on that the gas phase abundance of this most common interstellar molecule could not be explained by gas phase processes alone.^{71–73} Many studies have investigated the formation

'hot-atom'

of H₂ with respect to surface reaction mechanisms.^{70,74–81} The exact mechanism for H₂ formation may depend on the local conditions, including the position, structure and temperature of the adsorption site.^{80,81} Although H₂ is a common subject of study due to its simplicity and its prevalence in interstellar space, the role surfaces play in the formation of other chemical species in the ISM must be considered.⁵⁹ As is found for H₂, the observed abundances of other small, common molecular species—such as water are necessarily attributed to surface-bound processes.⁸² Due to the cosmic abundance of hydrogen and its mobility at dark cloud temperatures, successive hydrogen addition reactions are thought to generally play an important role.^{31,66} Apart from water, these reactions have been shown to produce ammonia and methane, as well as COMs such as methanol, glycolaldehyde and ethylene glycol.^{60,66}

Regardless of the mechanism, formation rates for species in molecular clouds must be balanced against destructive processes in the harsh environment of interstellar space. The effects of exposure to thermal changes due to cloud collapse or stellar shocks, as well as the effects of incident ultraviolet (UV), X-ray or cosmic radiation must be accounted for, although dust grains can be expected to shield products to some degree.^{67,83–86} Therefore, in order to fully understand the chemical evolution of interstellar matter, it is essential to understand the adsorption, the surface-bound processing, and the desorption of all molecular ices of astrophysical interest.

1.3 Ice Mantles and Processing in the ISM Environment

Although dust grains have effects on the temperature and radiation environment throughout the ISM, they are most important chemically in the molecular clouds and in the vicinity of protostars, where chemistry leading to the formation of larger molecules occurs.^{1,30,61} This is due to the relatively low temperatures and relatively high number densities within molecular clouds, which allow ices to accumulate on dust grain surfaces.⁸⁷ At such low temperatures, all impacting species are expected to stick to the surface, primarily through physisorption.²⁰ That is, they are held by van der Waals interactions rather than chemical bonds. Over time, ices of >100 monolayers can accrete onto a dust grain, built up from impacting gas phase molecules and from reactions on the surface.⁶⁰ Shielding effects of a dark molecular cloud limit penetration of the ISRF, allowing accumulation rates to exceed photodesorption rates of the ices, especially in the interior.²⁰

As shown by figure 1.4 previously, the composition of ices is commonly observed by infrared spectra, making use of astronomical radiation sources in the background of the observed region.^{40,88–90} The most common ices are H₂O, CO₂, CO, NH₃ and CH₃OH, though many other species are present.⁸⁷ Whether the ices are H₂O or CO dominated depends on the regional H/H₂ ratio.⁹¹ With a higher ratio, polar H₂O-dominated ices are formed, while in regions with a H/H₂ ratio less than 1, apolar CO-dominated ices are favoured. As these two types of ices are favoured at different times, interstellar ice mantles display two distinct phases: an inner H_2O -rich phase and an outer H_2O -poor phase.³¹

While the environment affects the composition of ice mantles, the composition can affect their structure. Water is thought to adsorb ballistically at dark cloud temperatures, sticking at the point of impact and in bulk forming a random, porous structure.⁹² However, when warmed to temperatures which allow surface mobility, intermolecular forces can take over, and ices may mix or segregate depending on those forces, a pattern which can be observed in laboratory work.^{93,94} The structure of the ice with respect to the surface also depends on the relative intermolecular forces available, with hydrogen bonding particularly influential due to the high proportions of water ice in dust grain mantles.^{88,95–100} This was illustrated well by Collings *et al.* on a model silica grain surface, as they showed that water ices dewet the surface to form multilayer island clusters, while O₂, N₂ and CO do not.¹⁰¹ This is explained by the strength of the intermolecular H₂O hydrogen bond forces exceeding those of the attraction forces between adsorbate H₂O molecules and the silica surface. As structures change, ices can trap components, with implications for processing over time.¹⁰²

Surface-bound processing of ices occurs through three major routes, summarised in figure 1.7. That is, the ices are subject to gas phase bombardment by radicals and energetic particles, to UV irradiation, and to thermal heating due to astrophysical phenomena.¹⁰³ Only thermally-driven processing is considered in the work presented in this thesis. Note that, as a result of this processing and the occurrence of surface-bound reactions, the ice composition does not necessarily reflect the gas phase abundances.⁸⁷



Figure 1.7. Schematic summary of the primary processing routes for ice mantles in the ISM, taken from a publication by Burke and Brown.¹⁰³

1.3.1 Temperature Effects and Interstellar Water Ice

Molecular clouds are the stellar nurseries, and the collapse of clouds and formation of new stars beginning as hot-cores—causes an increase in the local temperature to >100 K.^{67,103} Though chemistry of the pre-stellar dark cloud may survive accretion into planetary disks,¹⁰⁴ the temperature increases induce changes in ice morphology and ultimately contribute to significant sublimation of ice mantles. This sublimation drives rich gas phase chemistry in new star systems, including the formation of organic species such as methyl formate (HC(O)OCH₃) and dimethyl ether ((CH₃)₂O).^{29,105–107} It is this chemistry which allows COMs to be used as 'clocks', that is, as probes of evolving conditions around developing protostars.¹⁰⁸ Further, the rich organic chemistry of planetary disks likely distributes prebiotic chemistry to young planets.¹⁰⁹

In a pure system, the physics of adsorption for each molecular ice will directly determine the temperatures at which it desorbs into the gas phase. The quantity present as well as the rate of temperature increase will also have an effect.¹¹⁰ However, in molecular clouds the abundance of water ices—in many cases 60–70 %—as well as their ability to trap volatiles and form strong hydrogen bonds, indicates that often the desorption behaviour of water will have a significant effect on the temperatures at which molecules of other species are released into the gas phase.^{88,95–100} At the same time, the presence of other molecules has been shown to affect the thermal response and desorption of water, and methanol is a notable example of this.^{111,112} While the trapping capability of water can potentially limit gas phase chemistry which might otherwise occur, it has also been shown to possibly support additional chemistry within the ice matrix.^{113,114}

Water in space is predominantly in the amorphous solid water (ASW) form, having adsorbed at molecular cloud temperatures, although there is ordering in some ices where they have instead adopted a crystalline ice (CI) structure.^{82,92,115,116} The ASW structure has a significantly porous nature, with a higher surface area and a greater quantity of dangling O-H bonds at the surface.^{117,118} In this state, molecules adsorbing onto the water ice are capable of diffusing into the pores, although this is potentially limited by their molecular size, and the porosity can be affected by both irradiation and temperature changes.^{95,97,119} As illustrated in figure 1.8, heating of an ASW ice to sufficient temperature causes a transition, closing the pores off from the surface. The effect of this on other molecules co-adsorbed with water is that they may become trapped within the water ice beyond the temperature at which they would otherwise desorb. Above 140 K the ASW undergoes an irreversible transition to the CI form.^{95,120} During this transition the crystal structure becomes more ordered, but also segments in the process, potentially releasing trapped molecules in a sudden burst.^{95,97,99,121} This is often referred to as volcano desorption and has been observed for astrophysically relevant molecules.^{95,112} Further desorption may also occur at higher temperatures, coincident with desorption of water in the form of CI. Referred to as co-desorption, this particularly occurs where the other molecules have a strong intermolecular interaction with water. The way this process affects the desorption of other interstellar molecules varies, dependent on the strength of interaction with the water ice as well as the molecular size and volatility of a molecular species. General patterns can be seen however, and these have been categorised, first by Collings *et al.* in a preliminary study, then expanded to include COMs by Burke *et al.*, though the pattern has been noted by others.^{95,96,122}



Figure 1.8. Simple illustration of the adsorption of a volatile species on amorphous solid water, followed by trapping, volcano desorption and co-desorption as the temperature increases.

I.3.2 Radiation Effects

In addition to thermal effects, UV irradiation is another major driver of chemistry in space. The sources for incident UV light are the ISRF, the internal radiation field generated by secondary effects of cosmic rays and stellar effects within clouds, and the direct UV emissions of nearby stars.^{31,84,123–127} The energy delivered by UV irradiation can promote chemistry within ice mantles, and in laboratory studies of interstellar ice analogues, complex organic species have been observed following irradiation.^{31,83,86,102,128–137} Examples of such species include NH₂CHO, OCN and C₂H₅OH.^{86,138,139} In some cases, amino acids and molecules of pre-biotic interest have been produced.^{135–137} In addition to these chemical processes, UV irradiation can cause photodesorption through three general mechanisms: direct excitation of an adsorbate, excitation of the underlying substrate or through the reaction energy of chemistry occurring following UV photolysis.¹⁴⁰ Photodesorption is thought to be essential to maintaining gas phase concentrations of species where adsorption is favoured due to extremely low temperatures.^{141,142}

I.4 Complex Organic Molecules

As introduced at the start of the chapter, COMs are now known to form a significant and important component in the inventory of interstellar chemical species, through detections in interstellar space as well as in comets, which are contemporary links to pre-solar matter. While astrochemistry is ultimately concerned with understanding the behaviour and influence of all astrophysically relevant chemical species, COMs are of special interest for two principle reasons, both of which are related to their inherent complexity.

The first is that COMs are well-suited to act as probes of the remote, dynamic physical environments where they reside.^{18,67} These molecules can be found in an extensive variety of environments, including dark molecular clouds, star-forming regions, hot-core protostars, planetary discs and comets.^{7–12,48–51,54,55,143–161} They are thus involved in all stages of the development of new star systems, from the primordial pre-stellar clouds to the impact of comets and the characteristic 'snow lines' which determine planetary chemistry.^{34,37,47,89,104,162,163} Throughout these stages, with the application of rotational and vibrational spectra, they provide information on gas temperature, density, collapse and rotation, as well as the polar or non-polar nature of local dust grain mantles.⁶⁷ COMs also act indirectly as probes when included as part of model chemical reaction networks.⁶⁷ This is possible because COM abundances described by models are dependent on formation and destruction rates, which are in turn dependent on local conditions.^{4,164–166}

The second reason COMs are of interest is their connection to pre-biotic chemistry and the formation of life in the universe.^{167,168} Pre-biotic chemical species are organic compounds related to the fundamentals of biological chemistry, and as noted at the opening of the chapter, these species are already among the inventory of COMs detected in hot-core regions.^{13–17,67} These regions will develop into protoplanetary disks, and so an understanding of COM formation, interactions and stability in interstellar environments will inform our understanding of the possibilities for the chemistry of life in developing planetary systems.^{60,67,143}

The spectral character of COMs as well as their place in chemical reaction networks are thus important to quantify. This is necessarily complex due to the range of environmental variables in space, and additional difficulty arises from the remote and extreme nature of the environments, as summarised in sections 1.1 and 1.2. In recent years, astrochemical models have seen significant development. These models connect fundamental aspects of physical chemistry to astronomical observations of chemical species. As noted, these models take into account local conditions, but they are very broad and incorporate many variables such as accretion and desorption, thermal and non-thermal processing, and radical-radical reactions. This has been summarised in a recent review by Garrod and Widicus Weaver.¹⁶⁶ One area of focus is on the relative importance of gas-phase and surface-bound processes for the formation and processing of COMs. To investigate hot-core COM chemistry, work with COMs was included in gas-grain chemical codes and related chemical networks.^{4,164,165}

To inform such models, comprehensive studies must include a consideration of grain-surface chemistry. Such studies will incorporate the specifics of adsorption, surface processing and desorption, as outlined in section 1.3. The possibility for mixing or trapping must also be understood, as this will
affect residence times. While these types of studies have been undertaken for some molecular species of astrophysical relevance, studies of species among the growing list of detected COMs are limited, with respect to an astronomical context. As Garrod and Widicus Weaver note in their review, more laboratory data is needed.¹⁶⁶ With current knowledge of the interstellar environment and the nature of dust grains in the ISM, these aspects of COM astrochemistry are ready to be studied in the laboratory and in computational models, in order to build toward a chemical picture of the universe that relies on fewer assumptions than it does today.

1.4.1 Experimental and Theoretical Astrochemistry

In order to explore the chemistry of space in a laboratory, an apparatus is constructed to maintain high vacuum (HV) or ultra-high vacuum (UHV) pressures, within which is held a substrate surface. Some previous experiments have employed inert materials such as gold or CsI as the substrate.^{95,169,170} However, with interstellar dust expected to be carbon or silica-based, other experimental work has used materials meant to serve as more direct analogues for dust grain surfaces, such as amorphous silica, olivine, amorphous carbon and graphite.^{101,171–175} It is important to consider a range of relevant substrates, as they can affect the behaviour of adsorbed ices due to varying adsorbate-surface interactions. Theoretical models have also used dust grain analogues such as silica or graphene to represent dust grain surfaces.^{74,176} In models, these can be represented as small clusters or as infinite surfaces, depending on the modelling software that is used. Further details on the application of theoretical modelling to astrochemistry are provided in chapter 6.

In experimental work, ices can be grown *in situ*, adsorbing on a surface at cryogenic temperatures. Studies of pure ices form the basis for understanding more complex interactions when multiple ices are layered or co-deposited. These types of studies are especially applied to understanding the interactions of various molecules with water ice due to the relatively high proportion of water within dust grain mantles. A number of analytical surface science techniques can be applied to probe the surfacebound ices. Temperature-programmed desorption (TPD) and reflection absorption infrared spectroscopy (RAIRS) are common techniques.^{169,177–181} TPD and RAIRS are both used in the work presented here, though additional techniques such as X-ray photoelectron spectroscopy (XPS) or electron diffraction may be employed in other experimental apparatuses.^{117,182,183} Precise temperature control of the substrate provides insight into the adsorption and desorption kinetics of ices, and the effects of thermal processing over temperature ranges of astrophysical interest. Additionally, the substrate can be exposed to UV radiation to study the potential photoexcitation effects on surface-bound molecules. TPD and RAIRS are both applied in order to best examine any potential effects of thermal and UV processing.

TPD is a necessarily destructive technique, which detects desorption rates and can provide evidence of chemical reactions through comparisons of mass spectrometry fragments. The principle is simple: the temperature of the surface is increased linearly over time, while a mass spectrometer acts as a detector, observing molecules once they are released into the gas phase. Increasing the surface temperature imparts energy to adsorbed molecules, causing them to begin desorbing once a certain threshold is reached. The overall desorption rate increases as the temperature continues to rise, until there are no adsorbed molecules remaining. This causes a peak—or peaks—in the recorded mass spectrometer signal, and analysis of these peaks provides kinetic parameters for desorption: order, activation energy and pre-exponential factor. Further, as the experiment usually observes multiple mass fragments simultaneously, a comparison of mass fragment ratios between the sample as it is deposited and subsequently desorbed can provide evidence of chemical reactions having occurred. Because of the kinetic parameters it provides, TPD is used in several fields of chemistry. In astrochemistry the value is of course in quantifying interactions between molecules and dust grain or ice mantle surface analogues. These values can be incorporated into chemical models of interstellar environments.^{95,164,184}

RAIRS is non-destructive spectroscopy, and the infrared spectra produced can give information about ice structure and insight into ice and surface interactions.^{97,103,185} Broadly speaking, RAIRS is high resolution but low sensitivity, and it struggles to obtain useful spectra from thin monolayers.^{185–187} Laboratory-recorded ice spectra can however provide a reference for interpretation of astronomical spectra. From a surface science perspective, RAIRS can also provide data on desorption behaviour to compliment TPD results, and it can potentially reveal clues about molecular orientation of adsorbates on the substrate surface. RAIRS records an infrared spectrum of surface-bound ices by applying an infrared beam to the surface at a shallow angle.^{188,189} The beam reflects from the surface before being received by a detector opposite the source. Spectra are recorded as percent-reflectance, $\Delta R/R$, which allows the bands within the spectrum to be compared equally, regardless of variation in the baseline spectrum. In this work, RAIRS is used almost entirely qualitatively, but it is important to note that $\Delta R/R$ is not quantitative as it is a proportional measurement. The calculation of $\Delta R/R$ is explained in chapter 2 and is based on reflected transmittance values. These values are quantitative and are analogous to transmittance values found in typical transmission infrared spectroscopy, which relate to absorbance and the Beer-Lambert law as

$$T = \frac{I}{I_0}$$
$$-\log T = A = \epsilon c l$$

where *T* is the transmittance, *I* is the transmitted intensity, I_0 is the incident intensity, *A* is the absorbance, ϵ is the molar extinction coefficient, *c* is the concentration of the sample and *l* is the path length through the sample.

Ordered graphite is a semi-metal and as such the reflection of the beam imposes the metal-surface selection rule on the recorded spectra.^{185,187–189} That is, only dipoles with a vertical component relative the surface will be detected. This adds complications to the spectra, which both increase the difficulty of interpretation but also provide a potential source of information about the molecular orientation of adsorbed ices. Sharpening and changes in frequency can provide evidence of phase changes, and insight into the structure of those phases, particularly for crystalline transitions. However, these responses also place further constrains the ability to use RAIRS spectra quantitatively, as changes in ice structure or the orientation relative to the surface alter band intensities and peak areas. Like TPD, RAIRS finds use as a surface science technique in many areas, for example in the study of heterogeneous catalysis.^{187,190} One of the principle uses of RAIRS in this thesis makes use of its insights into surface ice structure. RAIRS is used to observe phase changes as amorphous interstellar ice analogues deposited at cryogenic temperatures are warmed and adopt different ordered structures. A phase change may see differing intensities due to orientation, as per the metal surface selection rule or additionally due to dipole coupling in the case of an ordered phase. Further evidence of ordering can in some cases be seen in band splitting.¹⁹¹

1.4.2 Thesis Overview

The primary aim of this thesis is to apply surface science techniques to expand the current knowledge of COM chemistry in conditions that are relevant to space, providing better information for astronomers studying the ISM and the development of new stars, protoplanetary discs and comets. The principle experimental objective of this work was thus to examine the response of COMs which had been adsorbed on graphite—a carbonaceous dust grain analogue—to thermal processing in the laboratory. This is linked to a parallel investigation into a theoretical model for studying adsorption on graphite. The COMs considered in the laboratory work are 2-propanol, dimethyl ether and acetaldehyde, and the results for these molecules are covered in chapters 3–5. A major portion of each chapter considers binary ices composed of COMs co-deposited or sequentially layered with bulk water ice. After having first quantified the kinetics of the pure ice, these additional experiments crucially examine the effects that the COMs and water have on each other as they are exposed to heat.

In chapter 3, 2-propanol is studied with a particular interest on its affects on the behaviour of water ice. As an alcohol it is expected to have a strong hydrogen-bonding interaction with water. Due to the predominance of water ice in space, changes in its behaviour would have wide-reaching effects. Other alcohol COMs have previously been studied in the laboratory, and 2-propanol is compared to these in particular. Note that 2-propanol has not currently been detected as a COM in interstellar space, but can be expected to be a component.

In chapter 4, dimethyl ether is studied with a similar range of experiments as for 2-propanol. With weaker intermolecular interactions it is considered in contrast with the results for 2-propanol. Along

these lines, results here are considered in the context of the broad classification of COMs into the 'complex intermediate' and 'complex water-like' categories.

In chapter 5, acetaldehyde is studied experimentally, again with a similar combination of TPD and RAIRS examining its interaction with HOPG and with water ice. A close look is taken at the deposited ice structure and variable phase change behaviour of acetaldehyde, and whether there is evidence for low-temperature polymerisation, both with and without water present. The behaviour is also compared closely with that of dimethyl ether and contrasted with that of 2-propanol.

The final results chapter of the thesis, chapter 6, differs in that it concerns theoretical modelling work which was undertaken alongside the laboratory experiments. The aim of this model was to use density functional theory (DFT) to construct a general computational framework for the adsorption of COMs on a graphite surface. A number of COMs were included in the model, as well as some smaller molecules of astrophysical interest. The results are benchmarked against existing laboratory values from the literature that have quantified surface adsorption experimentally. Once established, this model should provide additional information to compliment experimental results, and gain further insight into astrochemistry.

Chapter 7 concludes the thesis with a broad comparison of the three COMs studied experimentally. This is followed by illustrations connecting the results here to the astrophysical context, and finally there is a brief consideration of potential future experimental and theoretical work.

Chapter 2

Experimental Methodology

The purpose of the laboratory experiment was to study the surface-adsorbed behaviour of organic molecules within an environment that is as close as possible to the conditions found in interstellar space. This principally required reproducing extremely low pressures and temperatures. In addition to creating an analogue for interstellar conditions, the ultra-high vacuum (UHV) pressures provided a clean environment for the duration of the experiments, which could be up to a few hours, improving signal-to-noise ratios in recorded spectra. Within the vacuum, a graphite surface was fixed as the analogue for a carbonaceous interstellar dust grain onto which ices could be deposited as thin films. Through the use of additional components attached to the apparatus, the surface could be heated or exposed to ultraviolet irradiation. As illustrated in figure 2.1, mass and infrared spectrometers were also aligned with the surface in order to probe the resulting behaviour of the adsorbed ices.



Figure 2.1. Schematic illustration of the UHV chamber and instrument layout.

Theoretical modelling, intended to complement the laboratory work, can provide insight which is otherwise difficult to extract from experimental data. In addition, models are often used to suggest avenues for laboratory research that are likely to yield promising results. For the current work, computational modelling began with calculating theoretical binding energies (allowing direct, quantitative comparison to experiment) and then progressed to attempt predictions for the energetics of a surfacebound reaction pathway. The methodologies considered for this theoretical work will be described in chapter 6, along with the results.

2.1 Ultra-High Vacuum

The experiment was contained within a stainless steel chamber (pictured in figure 2.2), where base UHV pressures of 10^{-10} mbar were achieved by two primary pumps: a turbo-molecular pump (TurboVac 361, Oerlikon Leybold) and an ion pump (TiTan, Gamma Vacuum), as illustrated in the schematic figure 2.3. The turbo-molecular pump contains fan blades which rotate at extreme velocity (approximately 45,000 times per minute), forcing molecules that contact the blades from the chamber, and is backed by a ballast volume evacuated to around 5×10^{-3} mbar via a dedicated 17 m³ h⁻¹ rotary vane pump (E2M18, Edwards). Provided that the turbo-molecular pump is backed, it can be switched on while the chamber is at only mild vacuum (<1 mbar), and it alone can ultimately pump the chamber to pressures <10⁻⁸ mbar.



Figure 2.2. The UHV chamber, pictured within the laboratory.



Figure 2.3. UHV pumping and pressure monitoring schematic diagram.

The ion pump has a different principle of operation, maintaining an electron cloud within a strong magnetic field in order to ionise molecules that enter the ion pump chamber. These ions are then attracted toward a titanium surface which they bind with chemically, sequestering them from the gas phase permanently. Because the ion pump traps the molecules it pumps, it has a limited capacity and should only be operated at pressures well into high vacuum (<10⁻⁴ mbar), but once active, it will operate in combination with the turbo-molecular pump to bring the chamber down to UHV. For the work described here, the ion pump was never operated above 10^{-6} mbar for any significant length of time.

The two primary pumps were aided by a liquid-nitrogen-cooled titanium sublimation pump, a type of pump that is particularly effective at sequestering otherwise difficult-to-eliminate hydrogen (H₂) gas. This pump was fired at 30.5 amperes for 30 sec at least once a day, during the initial surface flash-heating, but only once the surrounding shield had been filled with liquid nitrogen. The current causes sublimation of a titanium filament, coating the nearby chamber surfaces with fresh, highly-reactive titanium material. The liquid nitrogen cooling increases the reactivity further, such that incident gas molecules will readily react to chemisorb with the surface, removing them from the gas phase and further lowering the UHV chamber pressure. The pressure within the main chamber was measured by a Pirani thermal conductivity pressure gauge (BOC Edwards). In typical operation, a base pressure of less than 2×10^{-10} mbar was regularly achieved in the main chamber.

Acquiring ultra-high vacuum is non-trivial, and special considerations must be made that are not necessary for applications implementing only moderate vacuums. The materials and construction were selected to avoid potential outgassing, which would preclude UHV. Additionally, the interior surfaces were cleaned carefully with acetone or methanol. Care was taken to avoid skin oils being deposited within the chamber, and clean nitrile gloves were worn at all times. Dust contamination was also minimised. The chamber components were connected using ConFlat (CF) flanges which are sealed with single-use copper gaskets compressed between twin knife-edges. The infrared window mounts and the rotating flange have small internal volumes within their structures. These volumes were differentially pumped to approximately 5×10^{-3} mbar by a 3.3 m³ h⁻¹ rotary vane pump (RV3, Edwards) to protect the UHV conditions in the main chamber.

When the chamber was vented, or otherwise removed from UHV conditions, it became necessary to bake it to reattain UHV pressures. Once all heat-sensitive components had been detached, the full apparatus was encased in insulated covers, forming a box within which ceramic heaters were placed. These heaters were switched on and off automatically by a controller linked to a thermocouple, to achieve a set temperature. Typically the apparatus was baked for 3 to 5 days, during which time the raised temperatures would promote contaminants from the chamber surfaces into the gas phase so that they could be actively pumped away via the turbo-molecular pump. Maintaining the temperature at approximately 100 °C was necessary, primarily to remove atmospheric water contamination. Typically the chamber pressure would rise to the 10^{-7} mbar range during the initial warm-up, gradually falling to around 9×10^{-8} mbar by the end of the bake. While the turbo-molecular pump ran continuously during the bake, the ion pump was disabled and heated to around 140 °C using dedicated, built-in heaters, in order to refresh its function.

A degassing procedure immediately followed each bake, while the chamber was cooling but still above room temperature. During this procedure the ion gauge, graphite surface, titanium sublimation pump and mass spectrometer were each degassed in turn to be ready for normal usage. In sequence, each ion gauge filament was degassed for five cycles of approximately one minute each, the graphite surface was flashed to >500 K twice, the titanium sublimation pump filaments were each degassed at 25 A for 20 min, and finally each mass spectrometer filament was run at 1000 μ A and 0 V for 45–60 min. The degassing procedure described here for the mass spectrometer filaments was a manual method specified by the manufacturer, as the automated degas was non-functional. Following the degassing procedure, and once the apparatus had cooled to a level close to room temperature, the active cooling system (described in detail in the next section) could be switched on to bring the temperature down to base level, ready for experiments.

2.2 Highly-Oriented Pyrolytic Graphite

The central component of the laboratory apparatus was the highly-oriented pyrolytic graphite (HOPG) surface, an idealised analogue for a carbonaceous dust grain surface, measuring approximately 2 cm². It was here that thin-film ices were deposited for study. The HOPG surface (illustrated in figure 2.4) has a high degree of ordering and purity, with a 0.34 nm distance between layered graphene sheets.¹⁹² The

surface was cleaved by the 'Scotch tape' method prior to the sample being mounted within the chamber, providing a surface which allowed for consistent collection of data on the interaction of various ices with solid carbon and limiting the complicating variations that might occur with impurities or deformities in the graphite surface. Additionally, this ordered surface invites more direct comparison to the results of theoretical models.



Figure 2.4. Structure of a segment of the highly-oriented pyrolytic graphite (HOPG) surface.

The HOPG sample mount—pictured in figure 2.5 and illustrated schematically in figure 2.6—was held at the end of a cold finger, which was fixed on a rotatable flange, itself mounted on a threedimensional shift. This allowed a large degree of flexibility and precision in the alignment of the HOPG surface within the central chamber. The cold finger was cooled by a closed-cycle helium gas refrigeration system (SHI-APD Cryogenics), where the expansion of compressed helium (99.999 %, BOC) facilitates rapid cooling to extremely low temperatures. A copper shield surrounded the cold finger, limiting its exposure to the black-body radiation from the surrounding, room-temperature chamber walls. The HOPG sample mount at the end of this structure was designed to provide op-timal thermal characteristics, with real-time control and monitoring of the sample surface temperature provided by a resistive heating circuit and a spot-welded E-type (nickel-chromium/constantan) thermocouple, respectively. The resistive heating circuit was powered by a DC power supply (LP 40-30, Glassman Europe), while the thermocouple was connected via a feedthrough to an external Eurotherm unit. Both units were linked to a computer running the iTools software for smooth digital control and monitoring of the temperature, and an example of the heating and cooling during and after a typical 1 min flash, as monitored by iTools, is displayed in figure 2.7.

The central structure of the sample mount was an oxygen-free high-conductivity (OFHC) copper plate attached to the end of the cold finger, with several layers of silver foil between the plate and the cold finger, to improve thermal conductivity. The resistive heating circuit ran through a separate structure on the back of the OFHC copper plate. This structure was comprised of two OFHC copper blocks, separated by a insulating ceramic spacer and electrically isolated from the main plate by a sapphire



Figure 2.5. Photo of the HOPG mount on the cold finger, within the UHV chamber.



Figure 2.6. Schematic representation of the major components of the HOPG mount on the cold finger.



Figure 2.7. Heating and cooling of the HOPG sample as a function of time, during and after a typical 1 min flash.

spacer. This was secured by molybdenum screws, each insulated with a ceramic sleeve and hat. Kapton insulated, silver plated copper heating wire was fixed to each OFHC copper block to form the first stage of the heating circuit. A tungsten stud was recessed into a hole in the bottom of each block and held in place by molybdenum screws. Into each stud a smaller hole was bored, within which a 0.5 mm tungsten-rhenium (W 75 %, Re 25 %) alloy filament was fixed by silver solder. These two filaments completed the resistive heating circuit when attached to the tantalum foil which backs the HOPG itself.

On the front of the OFHC copper plate, a smaller sapphire plate was placed, with silver foil between the two. The use of sapphire here was due to its beneficial thermal and electrical properties. Its thermal conductivity at low temperatures allows efficient cooling, while its thermal insulation at higher temperatures allows the HOPG sample to be heated to higher temperatures despite the cryostat system being in continuous operation. Additionally, it is electrically insulating, preventing the heating circuit from shorting through the OFHC copper plate and the cold finger. The HOPG sample was mounted onto the sapphire plate, with the previously-mentioned tantalum foil sheet, as well as the ends of the tungsten-rhenium filaments sandwiched between. The thermocouple was spot welded to this tantalum sheet to give the best possible measurement of the HOPG surface temperature. Grooves cut into the back of the HOPG sample formed a close contact between the graphite and the heating filaments and thermocouple wire. Lastly, the HOPG sample, sapphire plate and other components on the front of the OFHC copper plate were held in place by tension wires linked to an electrically insulated tension mechanism on the back of the plate.

Prior to beginning experiments, the surface was flashed to 250 K and held at that temperature for 1 min. This is sufficient to clean the surface, as confirmed by running a zero-dose temperatureprogrammed desorption trace following the flash (see the following section for an explanation of the temperature-programmed desorption technique). Once the surface temperature had recovered to \leq 30 K, the desired ices could be dosed onto the graphite. Doses were measured in Langmuir (L_m), a unit of exposure, where 1 L_m = 10⁻⁶ mbar s. Dosing was accomplished via a pair of leak valves (VG Scienta), each linked to a gas line, as illustrated in figure 2.8. The two gas lines were both pumped through a single diffusion pump (E02, Edwards), which was backed by a 8.5 m³/h rotary vane pump (RV8, Edwards). Each gas line had multiple ports, allowing the easy attachment of liquid and solid sample vessels or regulated gas cylinders, as needed, via Swagelok connections and valves.



Figure 2.8. Schematic diagram of the dose line and pumps.

2.3 Temperature-Programmed Desorption

The temperature-programmed desorption (TPD) technique, also known as thermal desorption spectroscopy, is straightforward in principle and provides an essential analytical method in surface science.¹⁹³ A simple illustration of the technique is provided in figure 2.9. In brief, the TPD applies a linear heating rate to the graphite surface. For the current work this is a rate of 0.50 ± 0.01 K s⁻¹ from ~30–250 K. The temperature is held at 250 K for 1 min in order to leave a clean surface for the next run. During the temperature ramp, a pulse-counting quadrupole mass spectrometer (QMS) (3F-PIC, Hiden Analytical) records the intensity, in real-time, for chosen mass fragments of desorbing molecules. These data are used to plot a TPD trace of fragment intensity relative to temperature: a TPD spectrum. Because this technique relies on the active desorption of the sample ice, it is a wholly destructive technique, and this is a potential concern which must be considered when employing it.

Raw TPD traces were first corrected by subtracting a fitted baseline, most commonly a Gaussian curve, though a linear function was more appropriate in some cases. Careful analysis of these corrected TPD spectra can reveal substantial information on the surface-adsorbed properties and behaviour of molecules, especially the characteristic phase transitions and desorption kinetics — desorption order, activation energy and pre-exponential factor — for various ices. To obtain the kinetic parameters, a



Figure 2.9. Simple illustration of the TPD technique.

leading-edge analysis based on the lineshape analysis method, previously reviewed by King and by de Jong and Niemantsverdriet, was used.^{194,195}

The Polanyi-Wigner equation forms the basis for the leading-edge analysis, and describes the desorption rate of molecules from a surface with an Arrhenius expression:

$$-\frac{d\theta}{dt} = \nu_n \,\theta^n \,\exp\left(\frac{-E_{des}}{RT}\right) \tag{2.1}$$

where v_n is the pre-exponential factor, θ is the surface adsorbate coverage, n is the order of desorption, E_{des} is the desorption activation energy, R is the gas constant, T is the temperature and t is time. Physically, the desorption activation energy is the energy barrier which must be overcome for a molecule to desorb, while the pre-exponential factor here relates to the attempt frequency of desorption due to the motion of the adsorbed molecule on the surface. We must consider that the surface coverage actually changes with respect to changes in temperature

$$-\frac{d\theta}{dt} = -\frac{d\theta}{dT} \times \frac{dT}{dt}$$
(2.2)

such that with a linear heating rate, β , this simplifies to

$$-\frac{d\theta}{dt} = -\beta \,\frac{d\theta}{dT} \tag{2.3}$$

Substituting equation 2.3 into equation 2.1 and rearranging, with $r_{des} = -d\theta/dT$, gives

$$r_{des} = \frac{\nu_n}{\beta} \,\theta^n \, \exp\left(\frac{-E_{des}}{RT}\right) \tag{2.4}$$

In practice, the desorption rate is measured by proportional QMS signal intensity, I(T), recorded in counts per second, and the integrated area of the trace, θ_{rel} , is proportionally representative of coverage.

$$I(T) \propto r_{des} \tag{2.5}$$

$$\theta_{rel} = \int_{T}^{T_{max}} I(T) \, dT \propto \theta \tag{2.6}$$

Because the only information recorded is the QMS signal intensity, the exact coverage, θ , is unknown. However, due to its direct proportionality with the surface coverage, the relative coverage value, θ_{rel} , is sufficient for the calculations here. As both I(T) and θ_{rel} are derived directly from the QMS signal, the constant of proportionality, z, is the same for each, so equation 2.4 then takes the practical form

$$I(T) = \frac{\nu_n}{\beta} z^{n-1} \theta_{rel}^n \exp\left(\frac{-E_{des}}{RT}\right)$$
(2.7)

$$\ln[I(T)] = \ln\left[\frac{\nu_n}{\beta} z^{n-1}\right] + n \ln[\theta_{rel}] - \frac{E_{des}}{RT}$$
(2.8)

For a given *T*, assuming that v_n and E_{des} do not vary significantly with coverage, equation 2.8 shows clearly that a plot of $\ln[I(T)]$ versus $\ln[\theta_{rel}]$ will produce a linear trend with slope *n*. This plot is composed from a set of TPD data of varying coverage, as illustrated in figures 2.10 and 2.11. Several of these plots are made at different temperatures along the leading edge, and the average result is reported as the desorption order. As the error in the QMS intensity is taken to be negligible, the only possible source of error for individual order values lies in the manual baseline correction and in the selection of a cut-off for calculating θ_{rel} . The variation in $\ln[I(T)]$ and $\ln[\theta_{rel}]$ arising from these sources is estimated to be well below 1 %, even for the lowest coverages which are most susceptible to changes in baseline. As such this error is omitted from figure 2.11 and indeed from calculations of the order values.

With the desorption order established, a rearrangement of the same equation can be used to find the desorption activation energy.

$$\ln[I(T)] - n \ln[\theta_{rel}] = \ln\left[\frac{\nu_n}{\beta} z^{n-1}\right] - \left(\frac{E_{des}}{R}\right) \left(\frac{1}{T}\right)$$
(2.9)

Thus, plotting $\ln[I(T)] - n \ln[\theta_{rel}]$ against 1/T will show another linear trend, now with a slope of $-E_{des}/R$, from which the desorption activation energy is easily calculated (figure 2.12). This plot is made from the leading edge of each TPD of the set, giving several calculated desorption energy values. The average of these values can then be reported as E_{des} for that desorption regime.

Alternatively, if the activation energy of desorption and/or pre-exponential factor is thought to vary significantly with coverage, the leading edge of the TPD traces can be evaluated just at the onset of detected desorption. This region of the trace represents a range where the surface adsorbate coverage



Figure 2.10. Example TPD traces from the desorption of $1-5 L_m 2$ -propanol, dosed on HOPG at 26 K, illustrating application of leading-edge analysis and the Polanyi-Wigner equation at T = 135 K.



Figure 2.11. Example order plot from TPD data for 2-propanol dosed on HOPG at 26 K, with fitted slope providing the order of desorption, *n*. The two fits clearly show the two coverage regimes with exclusive linear fits. The blue arrow highlights the transition point, which falls between 10 and 15 L_m in this case. The data points here were taken using T = 135 K, as illustrated for 5 L_m in figure 2.10.



Figure 2.12. Example desorption energy plot (Arrhenius plot) with fitted slope providing the value $-E_{des}/R$ from which the desorption activation energy is calculated.

is largely unchanged (<5 % difference) and can be approximated as constant. Within this limit, equation 2.8 can be used to evaluate E_{des} from the slope of a plot of $\ln[I(T)]$ versus 1/T, which does not rely on the value of the desorption order, as shown by Habenschaden and Küppers.¹⁹⁶ However, it is important to note that, as the detected intensity in this region is relatively small, high-quality data are needed to maximise the signal-to-noise ratio.

If the activation energy of desorption is evaluated in this way, the order of desorption could be determined from an alternate rearrangement of equation 2.8:

$$\ln[I(T)] + \left(\frac{E_{des}}{RT}\right) = \ln\left[\frac{\nu_n}{\beta} z^{n-1}\right] + n\ln[\theta_{rel}]$$
(2.10)

That is, a plot of $\ln[I(T)] + (E_{des}/RT)$ versus $\ln[\theta_{rel}]$ will have a slope of *n*.

For both desorption order (*n*) and desorption energy (E_{des}) values, the error estimates are derived simply from the linear fits, as the error in the QMS signal is negligible. Each linear fit has an associated 95 % confidence interval, which is used here as the error estimate for each fit. In practice, the reported values for both desorption order and desorption energy are averages derived from a number of such fits. To estimate the error in these average values, two methods are considered and the more conservative result is reported. The first method is the propagation of the individual errors through the mean calculation. That is

$$\sigma_{avg} = \frac{\sqrt{x_1^2 + x_2^2 + \dots + x_n^2}}{n}$$
(2.11)

where σ_{avg} is the error in the mean, x are the individual errors (95 % confidence intervals) and n is the number of values. The second method is to use twice the standard error of the mean, σ_m , which is

calculated by

$$\sigma_m = \frac{\sigma}{\sqrt{N}} \tag{2.12}$$

where σ is the sample standard deviation and N is the sample size. The considered value is then $2 \times \sigma_m$.

Lastly, with values and error estimates for n and E_{des} obtained, an approximate value for the preexponential factor can be calculated through a rearrangement of equation 2.4:

$$\nu_n = \frac{r_{des}\,\beta}{\theta^n\,\exp\left(\frac{-E_{des}}{RT}\right)}\tag{2.13}$$

As expressed in the equation, while proportional values were permissible in the previous calculations due to the trends' non-reliance on the specific quantities, for the pre-exponential calculation reasonable values for the actual coverage and desorption rate, θ and r_{des} , must be determined.

To do so, the theoretical total number of molecules adsorbing on the surface, N_m , must first be calculated from the rate of impingement and sticking probability by

$$N_m = jAtS \tag{2.14}$$

where *j* is the flux per unit area per unit time, *A* is the surface area, *t* is the time, and *S* is the sticking probability. Through the kinetic theory of gases and the ideal gas law, the physical equation for flux can be expressed in terms of pressure:

$$j = \frac{\rho_N}{4} v_{avg} = \frac{\rho_N}{4} \sqrt{\frac{8k_BT}{\pi m}}$$
(2.15)

$$=\frac{\Gamma}{\sqrt{2\,\pi\,m\,k_B\,T}}\tag{2.16}$$

where ρ_N is the number density of the gas molecules, v_{avg} is the average velocity of the gas molecules, k_B is the Boltzmann constant, T is the gas temperature (295 K), m is the molecular mass of the gas molecules, and P is the gas pressure. Substituting equation 2.16 into equation 2.14, and assuming a sticking probability of S = 1 due to the extremely low surface temperature, results in

$$N_m = \frac{PAt}{\sqrt{2\pi m k_B T}}$$
(2.17)

As noted previously, the doses were measured as exposure in Langmuir (L_m), a convenient unit representing pressure over time, where 1 L_m = 10⁻⁶ mbar s. Exposure in Langmuir can be directly substituted for pressure and time in equation 2.17 with the inclusion of a 10⁻⁴ conversion factor (1 L_m = 10⁻⁴ Pa s),

such that all units will properly cancel if SI base units are otherwise used:

$$N_m = \frac{(10^{-4}) X A}{\sqrt{2 \pi m k_B T}}$$
(2.18)

where X is exposure in Langmuir (L_m). With X = 1, the resulting value for N_m represents a calculated number of adsorbed molecules per Langmuir of exposure.

A plot of integrated TPD trace area versus exposure in Langmuir provides a linear trend where, naturally, the slope is the ratio of TPD area to measured exposure. Dividing the value for molecules per Langmuir from equation 2.18 by this ratio provides a scaling factor—the constant of proportionality introduced in equation 2.7—which can directly convert QMS data into a number of molecules and therefore convert θ_{rel} to θ and I(T) to r_{des} . The pre-exponential factor can then be calculated using equation 2.13, taking a range of data points from the leading edge. The error for this calculation is estimated by evaluating v_n with the minimum and maximum values for E_{des} and n, within their respective error limits.

Through leading-edge analysis, TPD can thus provide the kinetic parameters for desorption, yet with further consideration, more can be learned from the TPD spectra qualitatively and quantitatively. Various aspects of this are discussed in detail in the relevant chapters later in the text.

2.4 Reflection Absorption Infrared Spectroscopy

The reflection absorption infrared spectroscopy (RAIRS) technique, illustrated in figure 2.13, is a type of infrared spectroscopy adapted especially for studying surface-adsorbed compounds.¹⁹⁷ As with other types of IR spectroscopy, this technique detects molecular bonds within a sample, where a reduction in reflection at characteristic IR frequencies identifies these bonds. For this work, a Fourier transform infrared spectrometer (Nexus, Thermo Nicolet) was used, linked to a mercury-cadmium-telluride (MCT) detector (Thermo). Within the chamber, the infrared beam reflects from the graphite surface at a grazing angle of 80°. The reflected beam is collected by the MCT detector, which transmits to the spectrometer through a data link. The beam enters and exits the chamber through KBr windows, which are transparent to infrared wavelengths. The signal is optimised following each bake of the apparatus, before any experiments are undertaken, by aligning the reflecting and focusing mirrors as well as the HOPG surface position and angle to maximise the peak-to-peak reading. This optimisation typically resulted in a peak-to-peak of ~2.1 V.

As a semi-metal, HOPG has been shown to obey the metal surface selection rule, making this is an important consideration for the application of RAIRS to ices adsorbed on HOPG.^{185,187–189,198} This rule holds that only dipoles with a component perpendicular to the plane of the surface will interact with the reflected light. Additionally, the interaction is enhanced at grazing beam angles, which is why



Figure 2.13. Overview of the reflection absorption infrared spectroscopy (RAIRS) equipment set-up.

an 80° angle is built into the apparatus layout.^{188,189} To understand why this enhancement occurs, the incident radiation can be considered in terms of the—in relation to the plane of incidence—parallel and perpendicular polarised components of the electric field, as illustrated in figure 2.14. The s-polarised electric field (E_s incident and E'_s reflected), perpendicular to the plane of incidence, undergoes a phase shift close to 180°, reducing this electric field to almost nothing upon reflection. At the same time, the p-polarised field (E_p incident and E'_p reflected), parallel to the plane of incidence—and perpendicular to the surface—is enhanced, dependent on the angle of incidence.



Figure 2.14. Diagram illustrating the electric field vectors for incident and reflected light, where *I* is the incident and *R* is the reflected. Note the opposing (cancelling) vectors E_s and E'_s for the s-polarised electric field, while the p-polarised electric field, represented by E_p and E'_p , is enhanced.

The effect of the metal surface selection rule is that molecular orientation influences band intensity, with orientations that result in a larger component of the dipole being perpendicular to the surface resulting in greater intensity. In this way RAIRS can provide insight into the orientation of molecules adsorbed on a surface. Because HOPG is only a semi-metal, it does not obey the surface selection rule completely as a true metal surface does.¹⁸⁹ This results in varying degrees of asymmetry in recorded peaks, dependent on orientation of the dipoles. The asymmetry can therefore potentially be used as an additional source of information regarding molecular orientation in the ices.¹⁸⁹

The spectrometer was connected to a desktop computer with the OMNIC software package (Thermo Scientific), which provided visualisation as well as tools for manipulation of spectra. Following a flash, but prior to dosing, a background spectrum was taken of the graphite surface. Once an ice had subsequently been deposited, spectra were collected and displayed as percent-reflectance, $\Delta R/R$, versus wavenumber:

$$\Delta R / R = \frac{R_{base} - R_{sample}}{R_{base}} \times 100\%$$
(2.19)

where R_{base} is the reflectance of the baseline clean HOPG baseline and R_{sample} is the reflectance once the sample has been dosed onto the surface. Because the baseline varies in intensity over the wavenumber range (800–4000 cm⁻¹), using the proportional $\Delta R/R$ to display the percent-reflectance ensures that the various bands in the spectrum are represented equally. All spectra were baseline corrected manually, using best judgement.

As both the spectrometer and detector were outside of the UHV chamber, the infrared beam had to pass through atmospheric pressures for part of its path. In order to reduce the interference from atmospheric CO_2 and H_2O , which have strong infrared signals, the beam path was enclosed within a sealed volume which was purged by a constant flow of dried, CO_2 -scrubbed air. The seal was not airtight and allowed the positive pressure to constantly flush the enclosed volume. The flow rate for the purge was set to 22–24 L/min to match the scrubber capacity. Adding an additional valve to limit flow to the purge enclosures allowed 14 L/min of this total flow rate to be directed through the spectrometer itself, in accordance with the manufacturer's recommendation, while the remainder was directed to pass through the purge enclosures. In some experiments, the OMNIC software atmospheric suppression feature was used, although spectrum artefacts were a concern when using this feature. It was discovered that, during the course of an experiment, fluctuations in the purge—especially the level of atmospheric H_2O —could be compensated for to some degree by adjusting the total purge flow rate. Once this manual adjustment was included in the experimental procedure, software atmospheric suppression was no longer used in any experiments.

For RAIRS experiments, spectra were recorded first at base temperature, then following thermal or irradiative processing. The application of RAIRS to studying irradiative processing is explained in detail in chapter 5. For thermal processing, the sample was annealed at increasing temperatures above base temperature. Each annealing temperature was held for 3 minutes to ensure that the sample had reached a new stable state. The RAIR spectra that were collected were then primarily considered qualitatively, as a set. The effects that ice phase and the orientation of molecules have on the spectra add complexity to this

analysis. When the amount of ice on the surface can be assumed to be approximately constant—that is, below the desorption temperature—changes in peak area and character are likely to be due to a change in molecular orientation or ice structure. Changes in orientation of the dipole would affect intensity as per the metal surface selection rule, while in the case of adoption of a crystalline phase, changes are likely due to coupling in an ordered structure. Band splitting can also be observed in the case of an ordered structure, caused by Fermi resonance or by non-equivalent components in the crystalline unit cell.¹⁹¹ At sufficiently high temperatures, likely following visible changes in character, even the most intense bands in the spectrum disappear as the annealing temperature reaches the desorption temperature of the ice. This can be compared closely with desorption results from TPD experiments, although it is not necessarily identical due to the different heating profile.

Chapter 3

2-Propanol and Water Ice on HOPG

The behaviour of simple alcohols on a graphite surface is thought to be of direct importance to the chemistry of the interstellar medium (ISM), where dust grain surfaces play a substantial role in chemical processes.^{103,107} Methanol, ethanol and 1-propanol have previously been studied using surface science methods, in several cases with a view to the astrophysical context in mind.^{111,112,173,175,199-204} Broadly, the results show a significant interaction with water ice when present together on a surface, predominantly influenced by hydrogen bonding. The presence of alcohols affects the structure and temperature-dependent behaviour of water ice, especially the amorphous solid water (ASW) to crystalline ice (CI) phase transition. This work investigating surface-bound alcohols is extended here by studying the behaviour of 2-propanol, with and without water ice present, with the overall goal being to further understand the behaviour for this group of molecules adsorbed on model carbonaceous dust grains. When compared with the results previously obtained for methanol and ethanol, data for 2-propanol will add to our fundamental knowledge of the surface chemistry of alcohols, in particular the intermolecular and surface interactions of these species on astronomically relevant surfaces.

Methanol and ethanol are included amongst the large number of complex organic molecules observed in the ISM.^{43,67,147,205,206} Methanol has also been detected in the comets Hale-Bopp (C/1995 O1) and Churyumov-Gerasimenko (67P), as well as in the protoplanetary disk TW Hya, and on the surface of minor bodies in the Solar System.^{48–50,143,144} Ethanol has been detected in comet Lovejoy (C/2014 Q2) along with other organic molecules.⁵¹ Methanol, ethanol and propanol were found to fit with mass spectrometry data from comet 67P, detected by the ROSINA double focusing mass spectrometer of the European Space Agency's *Rosetta* mission.⁵⁴ Although 2-propanol is as yet undetected in ISM regions, the C₃H₈O isomer methoxyethane has been detected, and theory indicates that 2propanol would be more stable than methoxyethane under interstellar conditions.²⁰⁷ It therefore seems likely that 2-propanol will be found, and models predict that it would have chemistry similar to that of ethanol.¹⁰⁷ That is, it would lead to the production of mixed and pure ethers when released into the gas phase of hot-core (proto-star) regions. In addition to generating this chemistry, if the presence of 2-propanol affects water—as the other alcohols previously studied do—its presence could have additional implications for the development of the chemical environment of the ISM due to water's ability to trap other molecules in ice grain mantles.^{95–100} Lastly, studies have shown the production of 2-propanol and other organic species from acetaldehyde following low-energy electron impacts at cryogenic temperatures, linking the results here to those of chapter 5.^{208,209}

As illustrated in chapter 2, the surface chemistry and adsorption behaviour of thin-layer ices can be probed with surface science techniques, providing qualitative information as well as quantitative parameters. These parameters can be used to apply laboratory data to astronomical models.¹⁷³ Previously, 2-propanol has been studied using temperature-programmed desorption (TPD), X-ray photoelectron spectroscopy (XPS) and reflection absorption infrared spectroscopy (RAIRS) by Gleason et al. in order to characterise the thermal chemistry of 2-propanol on a Ni(100) surface at 100 K.182 They found that 2-propanol adsorbs intact and noted evidence of extensive hydrogen bonding occurring between the adsorbed molecules. Shorthouse et al. looked at reactions of 2-propanol on a Ni(111) surface, using RAIRS and TPD.¹⁷⁷ Like Gleason et al., they observed molecular adsorption of 2-propanol as part of their study. They report formation of multilayer 2-propanol at 110 K on the Ni surface. RAIRS was also used by Camplin and McCash to look at multilayer 2-propanol on an oxygen-modified Cu(100) surface, dosed at 78 K.¹⁷⁸ Their infrared spectrum was in good agreement with that of the liquid alcohol, as was the RAIR spectra recorded by Vannice et al. for 2-propanol on Pt(111).²¹⁰ Schaff and Roberts used both RAIRS and TPD techniques to study the interaction of 2-propanol with multilayer amorphous and crystalline ice on a metal substrate with a base temperature of ~95 K.¹¹⁸ Deuterium isotopes were employed to probe the role of hydrogen bonding in this interaction, with the result that it was found to be a significant factor. TPD gave desorption temperatures of 166 K and 175 K on amorphous ice, and 175 K on crystalline water ice. Desorption was pseudo-zero order with an energy of 56 ± 1 kJ mol⁻¹. Desorption of 2-propanol from a carbon surface in the form of single-walled carbon nanotubes (CNTs) was studied by Goering et al., determining a multilayer desorption energy of $31 \pm 2 \text{ kJ mol}^{-1}$ but with first-order kinetics.²¹¹

While the importance of hydrogen bonding is established for surface-bound 2-propanol, as seen in some of the literature outlined above, this effect also influences other complex organic molecules (COMs) and their interactions with water. For instance, Methikkalam *et al.* used RAIRS to investigate the interaction of acetonitrile with water, methanol and ethanol.²¹² In all three cases, hydrogen bonding was found to be the dominant interaction, and the energetics of this was considered. Additionally, they saw that this interaction was able to limit the phase transition of ethanol. Bertin *et al.* compared the desorption of the isomers methyl formate and acetic acid from a water ice surface.²¹³ Methyl formate desorbed at a significantly lower temperature, a behaviour attributed to hydrogen bonding with water surface dangling O-H bonds. Another study also looked at methyl formate and acetic acid, as well as the isomer glycolaldehyde.⁹³ In this case, hydrogen bonding was implicated in the way in which ices grow on a highly-oriented pyrolytic graphite (HOPG) surface, with strong intermolecular forces promoting clustering. Hydrogen bonding was also proposed as the reason for the relatively elevated desorption energies for acetic acid and glycolaldehyde. Additional work with these three isomers showed that the intermolecular interactions affected the crystallisation of water ice, and therefore the trapping and general desorption behaviour of the molecules when water ice was present.⁹⁶ Lastly, Etim and Arunan, in a quantum chemical study of the relationship between energy, stability and interstellar abundance—with lower enthalpies of formation correlating with higher abundance—noted that hydrogen bonding readily explained anomalous abundances in the ISM.²¹⁴ In summary, hydrogen bonding clearly has an important role in the surface behaviour of COMs which are capable of this intermolecular interaction, and therefore it must be considered when exploring the nature of interstellar dust grain mantles, which contain many of these molecular species.

The work presented in this chapter considers the thermal annealing of 2-propanol thin-layer ices adsorbed on a HOPG surface, studied by TPD and RAIRS methods. Pure samples of 2-propanol are studied, as well as binary ice samples composed of 2-propanol of water, which are either layered or mixed. The results should provide information about the surface interaction of these ices, and the effects that they have on each other with regard to structure and retention on the surface in response to increasing temperatures.

3.1 Experimental

The behaviour and properties of 2-propanol (≥99.7 %, BDH Laboratory Supplies Ltd.) on an HOPG surface were investigated. Mixed and layered binary ices of 2-propanol and water on HOPG were also studied, probing the intermolecular interactions of the two species. The ices were dosed at ~26 K which, while slightly above the 10–20 K temperatures of the ISM, is a sufficiently low temperature to ensure that the sticking probability is near unity.

The exception to this dosing temperature was when dosing water in the crystalline ice (CI) phase. In those experiments, water was dosed at 120 K then annealed at 125, 130, 135 and 140 K for 3 minutes each. At this dosing temperature the sticking probability is lower, and the subsequent annealing causes partial desorption, so a slightly higher exposure of 60 L_m was used to achieve a bulk multilayer ice sufficient to cover the HOPG surface, as is provided by 50 L_m ASW dosed at base temperature. Later comparison of TPD integrated areas indicated that this dosing method ultimately produced a dose equivalent to that of amorphous solid water (ASW) ice deposited with an exposure of 35 L_m at base temperature. The results for the 2-propanol layered on CI are comparable however, as 35 L_m is still sufficient to cover the graphite with a multilayer ice, such that 2-propanol will be interacting with water only.

All ices were background dosed onto the HOPG by exposure of $10^{-8}-10^{-7}$ mbar of the vapour, with the HOPG surface directly oriented toward the active leak valve (or half-way between the two leak valves in the case of mixture dosing). Mixtures were dosed by simultaneous co-deposition of 2-propanol and water. As two gases are being introduced into the chamber, use of the pressure gauge alone is not reliable. Instead, the pressure was used to set the dose of water according to the usual method, in order to achieve an exposure of 50 L_m (2 × 10^{-7} mbar for 250 s). Once the water dose was set, the 2-propanol dose was immediately begun, tracked in real time by the QMS signal. As the signal intensity corresponding to exposures of pure water and 2-propanol was already known, calculating the intensity to achieve a desired 2-propanol proportion was straightforward.

During initial preparation, the 2-propanol sample was purified within a Pyrex borosilicate glass cell attached to the dose line. The vapour over the liquid was pumped briefly, then the liquid itself was subjected to two freeze-pump-thaw cycles, evacuating any residual contaminant gases each time the 2-propanol was frozen. The same purification procedure was applied to the water sample. At least once a day, prior to any dosing, the vapour pressure over each liquid sample was briefly pumped to <1 mbar. Once deposited on the HOPG surface, the ices were studied with TPD and RAIRS. In the case of TPD, the quadrupole mass spectrometer (QMS) was set to monitor the most prominent fragments of 2-propanol (45, 43 and 31 m/z), as well as the 18 and 17 m/z water and OH ions. Traces for the 45 and 18 m/z fragments are used for plotting and analysis of 2-propanol and water, respectively, as these are detected at the highest intensity and give the best signal-to-noise ratio. An example illustration of the set of fragment traces for 2-propanol is shown in figure 3.1. All TPD traces were recorded during a surface temperature increase from ~30-250 K at a constant rate of 0.50 ± 0.01 K s⁻¹. RAIR spectra were obtained from the coaddition of 256 scans at a resolution of 4 cm⁻¹. In all cases, thermal processing and subsequent desorption occurred at high temperatures (>100 K) which are within the realm of hot-core temperatures (100–300 K).



Figure 3.1. The mass fragment traces for 20 L_m 2-propanol during a TPD experiment.

3.2 Results and Discussion

3.2.1 TPD Results for Pure 2-Propanol on HOPG

TPD traces were recorded for 2-propanol dosed on HOPG at 26 K from 1–50 L_m , shown in figure 3.2. For exposures up to 10 L_m , the rate of desorption clearly increases with coverage, and shares a common peak temperature of ~141 K. A coverage-dependent rate of desorption and constant peak temperature suggests that 1–10 L_m of 2-propanol gives rise to the formation of monolayer coverages on the HOPG surface. At 10 L_m a second feature becomes apparent at a lower temperature of ~137 K, growing as a peak and increasing in temperature as the dose increases. By 50 L_m this peak is seen at ~144 K. This is similar to the ~150–160 K desorption temperature for multilayer 2-propanol reported by Burean and Swiderek.²⁰⁹ Overall, desorption temperatures in this range indicate that the 2-propanol does not bond strongly to the surface and is likely physisorbed on the surface.²⁰¹

The relationship between exposure, measured in L_m , and the number of adsorbed molecules was shown previously by equations 2.13–2.18, in section 2.3. This allows the number of molecules adsorbed during a dose, N_m , to be calculated directly from the exposure (L_m). A fast, approximate calculation of the van der Waals volume of an organic molecule can be obtained, as shown by Zhao *et al.*, using

$$V_{vdW} = \sum A_V - 5.92N_B - 14.7R_A - 3.8R_{NA}$$
(3.1)

where A_V are the atomic van der Waals volume contributions, N_B is the number of bonds, R_A is the number of aromatic rings and R_{NA} is the number of nonaromatic rings.²¹⁵ As 2-propanol has no rings in its structure, the calculation is simple, and here it is carried out using values for the van der Waals radii of elements as determined by Alvarez.²¹⁶ The calculated van der Waals volume of 2-propanol



Figure 3.2. TPD (mass 45) data for pure 2-propanol dosed on HOPG at 26 K, showing higher exposure 10, 15, 20, 30 and 50 L_m (top figure) and lower exposure 1, 2, 5, and 10 L_m (bottom figure) regimes. Though regarded as part of the monolayer regime, 10 L_m is shown in both the upper and lower figures to provide a reference for the scale.

using this method is V_{vdW} = 0.077 nm³ per molecule. Multiplying this value by the calculated number of adsorbed molecules

$$V_{tot} = V_{vdW} N_m \tag{3.2}$$

gives the total volume of the ice, V_{tot} . In turn, dividing the total volume by the 2 cm² HOPG surface area provides an estimate of the average ice thickness. For 2-propanol, this results in an estimated average ice thickness of ~0.06–2.96 nm, corresponding directly with 1–50 L_m exposures, as shown in table 3.1. Note that this assumes a constant sticking probability of S = 1, as per equation 2.14. This is a reasonable assumption for physisorbed ices dosed at cryogenic temperatures, so the thickness estimates are appropriate.

exposure / L _m	N_m / 10^{15} molec	V_{tot} / 10^{14} nm ³	avg. thickness / nm
1	0.15	0.12	0.06
2	0.31	0.24	0.12
5	0.77	0.59	0.30
10	1.54	1.18	0.59
15	2.32	1.77	0.89
20	3.09	2.36	1.18
30	4.63	3.55	1.77
50	7.72	5.91	2.96

Table 3.1. Comparison of average ice thickness for adsorbed 2-propanol for each dose, assuming a constant sticking probability of S = 1.

The appearance and behaviour of the peaks in figure 3.2 can be used to qualitatively assign the coverages to either a monolayer or multilayer regime. The shared peak temperature at 1–10 L_m points toward first-order desorption, which is expected for physisorbed monolayer coverages.¹⁷³ Meanwhile, the shared leading-edge and increasing peak desorption temperature seen for the peak that appears at \geq 15 L_m exposures is likely zero-order behaviour, which is generally seen for multilayer coverages.¹⁷³ Although 10 L_m shows the beginnings of multilayer behaviour, the trace is still dominated by the monolayer peak. 10 L_m is therefore grouped with the monolayer traces. With reference to table 3.1, this indicates saturated monolayer behaviour for an ice with an average thickness of ~0.6 nm. If 2-propanol is approximated as a sphere, with $V_{vdW} = 0.077$ nm³, simple geometry would give a diameter of ~0.5 nm. So, to a rough approximation, 10 L_m can be reasonably correlated with a single molecule-thick layer on the surface, on average. However, this is only true if 2-propanol wets the HOPG surface, and it seems that this may not be so, as will be discussed in section 3.2.1.3.

The qualitative assignments can be supported more rigorously by the quantitative analysis of desorption kinetics described in the following section. Analysis of the TPD spectra provides the order of desorption, allowing confirmation of the assignments of these peaks. The assignments are supported by the goodness of the linear fits used to derive order values during analysis. 15 L_m will be shown to fit poorly with the data for 1–10 L_m and hence doses ≥15 L_m are ascribed to multilayer.

3.2.1.1 Monolayer Desorption Order

The Polanyi-Wigner equation^{194,195} was used as the basis for a leading-edge analysis¹⁹⁶ applied to the TPD traces, providing values to characterise the kinetics of desorption. For full details of this analysis method, see section 2.3. Errors for the values of order and desorption energy were estimated both by propagation of individual fit errors—95 % confidence intervals—and as twice the standard error of the mean. The latter value was larger in these cases, and so it was chosen as a conservative error estimate. Kinetic analysis, illustrated in figure 3.3, reveals that the desorption order from 1–10 L_m has a fractional order of 1.23 ± 0.03. This value is an average. See table 3.2 for the individual values as evaluated at different temperatures along the leading edges for three sets of TPD spectra.



Figure 3.3. Illustration of linear fits where slopes provide the desorption order for monolayer and multilayer 2-propanol adsorbed on HOPG at 26 K. For illustration here, a single fit for is applied to all three sets of TPD spectra, evaluated at 135 K. In the analysis each set was analysed separately, as shown in table 3.2 for the monolayer regime.

The value for the desorption order being close to 1 supports the assignment of this range of doses as being within the monolayer regime, but the fractional component points to the influence of an intermolecular interaction. This is not surprising due to the presence of the hydrogen bonding alcohol group in 2-propanol. This functional group has a strong influence on the behaviour of 2-propanol ices, as evidenced by the central role it takes when 2-propanol crystallises into helical chains, linked by repeating hydrogen bonds..²¹⁷ The crystal structure will be discussed further with regard to RAIRS data, later in the chapter. Although non-ideal, fractional order behaviour has precedent in the literature, and has been seen previously for both methanol, ethanol and water in similar studies.^{201,202,218} Other TPD

Temperature / K		Order, <i>n</i>	
131	1.29	1.21	1.20
132	1.22	1.17	1.34
133	1.06	1.35	1.35
134	1.18	1.25	1.20
135	1.25	1.23	1.26
136	1.16	1.31	1.20
137	1.15	1.30	1.26

Table 3.2. Monolayer desorption order values derived from the three sets of 2-propanol TPD spectra—one set per column—recorded during the course of this study. These values were obtained from order plots like those shown in figure 3.3.

data for hydrogen-bonding organic species have also shown fractional order behaviour, as in results from Wu *et al.*, Nishimura *et al.* and Burke *et al.*.^{93,219,220}

3.2.1.2 Monolayer Desorption Energy and Pre-exponential Factor

With the order value known, the quantitative analysis continued with construction of plots to determine the desorption energy. An example of one of these plots, for a dose of 5 L_m , is shown in figure 3.4. The desorption energy for the monolayer coverages ranges from ~45–49 kJ mol⁻¹, increasing with dose, as seen in figure 3.5. This slight increase is likely due to relatively strong intermolecular forces between individual 2-propanol molecules providing an increased stability as the monolayer approaches saturation. Overall, the resulting average desorption energy for the monolayer regime is 47 ± 2 kJ mol⁻¹, a reasonable value consistent with a strong physisorption interaction on the surface.



Figure 3.4. Linear fit providing desorption energy for a single trace of 5 L_m 2-propanol adsorbed on HOPG at 26 K. The energy evaluated from this slope is 50 ± 5 (95 % confidence interval) with r^2 = 0.9880.

This value for the energy is very similar to the 45.4 kJ mol⁻¹ and 52.0 kJ mol⁻¹ found for monolayer methanol and ethanol, respectively, on graphene-covered Pt(111) in a study by Smith *et al.*²⁰⁴ How-



Figure 3.5. Desorption energy (E_{des}) versus dose (L_m) for 1–50 L_m 2-propanol adsorbed on HOPG at 26 K.

ever, it is interesting to note that in their study monolayer (and bilayer) desorption orders for both methanol and ethanol were zero-order. This desorption order for a monolayer regime was attributed to a fast equilibrium (relative to the desorption rate) between clustered and individual molecules on the surface. Similar results were reported by Ulbricht *et al.*, with zero-order desorption and energies of 48 ± 3 kJ mol⁻¹ and 50 ± 3 kJ mol⁻¹ for methanol and ethanol, respectively.¹⁷⁵ In that case the desorption order was evaluated qualitatively.

The desorption energy value determined here for 2-propanol also falls in the range of ~33–48 kJ mol⁻¹ found in previous work by our own group for monolayer methanol on HOPG.²⁰¹ The results of that work showed a fractional desorption order for methanol of 1.23, which is the same as seen here for 2-propanol. The significant difference between the literature methanol results is unclear, but Smith *et al* suggest they could be attributed to differences in the surface (graphene versus graphite), the dosing method or the detection apparatus.²⁰⁴ It seems less likely that the surface itself is the cause, as the results shown by Ulbricht *et al.* were for the alcohols on an HOPG surface.¹⁷⁵ Regardless, the same disparity could potentially occur for 2-propanol, as the work here was done using the same type of surface and methods as the previous methanol work from our group.

With the desorption energy as 47 ± 2 kJ mol⁻¹, the monolayer pre-exponential factor is calculated as $10^{13 \pm 1}$ s⁻¹ via equation 2.13. First-order units are reported here for simplicity. As noted previously in chapter 2, the error for the pre-exponential factor is estimated by considering the minimum and maximum values possible given the respective error limits of the order and desorption energy. This preexponential value is very reasonable for a monolayer regime, where values of 10^{12} – 10^{13} s⁻¹ are expected for first-order desorption generally.¹⁹⁵ However, previous work found pre-exponential factors in the range 10^{15} – 10^{16} s⁻¹ for methanol and ethanol. While these values differ, there is still overlap when error estimates are taken into consideration.^{175,204}

3.2.1.3 Monolayer Growth

Combining the kinetic parameters derived from the current data along with further qualitative consideration of the TPD results, it is possible to speculate on the growth pattern of the ice to some degree. The growth of a thin-film ice falls into one of three categories, as classified by Ernst Bauer in 1958.²²¹ When the intermolecular forces between adsorbing molecules are stronger than those between the molecules on the surface, the molecules preferentially cluster, forming 'islands'. This is the Volmer– Weber growth mode. Conversely, in cases where the interaction between the molecules and the surface is stronger, the thin-film will wet the surface, growing layer-by-layer in what is referred to as Frank– van der Merwe growth. Stranski–Krastanov growth is the third category and is intermediate between the other two categories. In this growth mode, initial layer-by-layer growth of the thin-film is followed by the formation of islands above.

The conspicuous fractional desorption order has been attributed to intermolecular hydrogen bonding in earlier discussion. The strength of these interactions could promote the formation of islands, preventing lower exposures of pure 2-propanol from fully wetting the graphite surface. Indeed, the O–H···O hydrogen bonding strength is in the region of ~20–25 kJ mol⁻¹ while the monolayer desorption energy of 2-propanol is only ~47 kJ mol⁻¹.²²² With each 2-propanol potentially associated with two hydrogen bonds, clearly these interactions are going to have a significant relative contribution to the behaviour of the ice. Two further pieces of evidence for islanding are seen as trends in the TPD results. The first is that the peak assigned to the monolayer continues to develop beyond the point where the multilayer first appears, a behaviour previously shown for methanol.^{201,223} The second is the increasing value of the desorption energy as exposure increases, shown previously in figure 3.5, which suggests that intermolecular forces between adsorbed 2-propanol molecules are stronger than those between the 2-propanol molecules and the HOPG surface.

It is worth considering that using TPD results to discuss ice structure brings caveats with regard to temperature, due to the dynamic nature of the experiments. Desorption of 2-propanol from HOPG occurs at temperatures >120 K. Prior to this, during the linear temperature increase, the ice can undergo significant thermal processing, so there is some uncertainty when drawing conclusions from TPD about the nature of the ice at the experimental base temperature 30 K, or indeed at interstellar temperatures of 10–20 K. Due to the limitations of RAIRS, the 30 K morphology of sub-monolayer 2-propanol on HOPG could not be studied directly. However, it is important to note that effects attributed to both coverage-dependent intermolecular interactions and islanding have also been assigned to results for methanol and ethanol on HOPG, lending support to the suggestion of Volmer–Weber growth mode for 2-propanol ices adsorbing on HOPG.^{201,202}

3.2.1.4 Multilayer Desorption Kinetics

While the doses from 15–50 L_m are assigned to the formation of a multilayer, the leading edges of these traces are not shared. That is, the rate of desorption is not coverage independent as would be expected for a perfectly zero-order process. In fact, the leading edges shift to a higher temperature as dose increases, as seen in figure 3.2 for 30 and 50 L_m . Numerical analysis of the desorption order for these traces results in a negative order of desorption, which is clearly not physical. The non-shared leading edges may be due to the increasing influence of hydrogen bonding between 2-propanol molecules in the ice as the dose increases, or may indicate that a thermally driven phase change of the 2-propanol occurs during the annealing. For the purpose of further numerical analysis, the order of desorption was assumed to be zero in the multilayer regime. This assumption is reasonable as with the bulk multilayer the surface is saturated and there should be no coverage dependence for the desorption rate.¹¹⁸ Furthermore, other alcohols have previously been determined to show zero-order desorption at multilayer coverages.^{175,201,202,204,224} Errors for the multilayer calculation were estimated in the same way as for the monolayer values, and again, twice the standard error of the mean was used as the more conservative error estimate.

The average desorption energy for the multilayer 2-propanol ice is 52 ± 1 kJ mol⁻¹, varying from ~51–54 kJ mol⁻¹ (see again figure 3.5). As this is higher than the energy for the monolayer, it may point to stronger interactions between molecules within the bulk ice than between the ice monolayer and the HOPG surface. Such an effect was also seen for another hydrogen bonding species, NH₃, in a previous study, where the growing multilayer peak appeared at higher temperatures than monolayer desorption.²²⁵ The pre-exponential factor for the multilayer 2-propanol is then $10^{35.8 \pm 0.5}$ molecules m⁻² s⁻¹, if the desorption kinetics are again assumed as zero-order.

The multilayer desorption energy is similar to the 50.8 kJ mol⁻¹ found by Smith *et al.* for multilayer ethanol.²⁰⁴ However, it is somewhat higher than the 44.6 kJ mol⁻¹ energy they determined for methanol. It is also higher than the multilayer desorption energy Goering *et al.* reported for 2-propanol on CNTs (31 \pm 2 kJ mol⁻¹), though they did assume first-order kinetics.²¹¹ Acetic acid, another interstellar COM capable of hydrogen bonding, was found to have a multilayer desorption energy at 55 \pm 2 kJ mol⁻¹ which is closer to the value determined here for 2-propanol.²²⁶ Previous results for ethanol and methanol obtained by our group are summarised in table 3.3. Studies from our group are used for comparison here due to the directly comparable experimental method.

Table 3.3. Calculated desorption kinetic parameters for 2-propanol on HOPG, obtained from the TPD spectra shown in figure 3.2. Values previously obtained by our group for ethanol²⁰² and methanol^{201,224} are included for comparison.

	2-Propanol		Ethanol		Methanol	
	monolayer	multilayer	monolayer	multilayer	monolayer	multilayer
Order, <i>n</i>	1.23 ± 0.03	~0	0.98 ± 0.13	0.08 ± 0.07	1.23 ± 0.14	0.35 ± 0.21
Energy, E _{des} / kJ mol ⁻¹	47 ± 2	52 ± 1	53.3 ± 3.1 †	56.3 ± 1.7	~33-48	~31-40
Pre-exponential, v_n	10 ^{13 ± 1} s ⁻¹	$10^{35.8 \pm 0.5}$ molec m ⁻² s ⁻¹	-	2.2×10 ^{37±2} molec m ⁻² s ⁻¹	9×10 ^{9±3} s ⁻¹	6×10 ^{25±3} molec m ⁻² s ⁻¹

[†] bilayer energy of desorption

3.2.2 RAIRS Results for Pure 2-Propanol on HOPG

The RAIRS technique was employed to investigate the structure of the ice as well as its behaviour on the surface. In addition to providing their own potential insights, these infrared data can offer powerful corroborating evidence for the conclusions drawn from the TPD results. Adsorption of increasing doses of 2-propanol at 26 K, as in figure 3.6, shows bands increasing in intensity as the dose grows, but no shifts in the bands are observed and none of the bands saturate. This indicates that the structure of the adsorbed ice is not affected by the quantity dosed and that the monolayer and growing multilayer are physisorbed on the surface, as seen for methanol and ethanol.^{201,202} Due to the high signal-to-noise ratio, the 100 L_m spectrum shown in figure 3.6 was used to assign peaks with reference to previous spectra of 2-propanol on metal surfaces as well as in the liquid and gas phase.^{178,182,227} A summary of the assignments is shown in table 3.4.

Most substantial in the spectrum are several peaks associated with methyl and hydroxyl groups. The main v(O-H) band at ~3350 cm⁻¹ is very broad at base temperature, supporting the picture of hydrogen-bonded 2-propanol ice networks, as suggested by the quantitative kinetics discussed in the previous section. There are strong, sharp peaks at 2976 cm⁻¹ assigned to v(C-H), at 1169 and 1134 cm⁻¹ jointly assigned to v(C-C) and $\rho(CH_3)$, and at 960 cm⁻¹ assigned to the $\rho(CH_3)$ mode. More moderate in intensity, but still clearly defined, are peaks at 1475 and 1383 cm⁻¹ assigned to the $\delta(CH_3)$ band. These bands are expected for condensed-phase 2-propanol and are in good agreement with the previous spectra.^{178,182,227}

3.2.2.1 Annealing and 2-Propanol Crystallisation

Following adsorption, the deposited ice was annealed, in controlled 3 minute intervals, to study the effects of thermal processing of the ice. Selected temperatures are shown in figure 3.7 to highlight the changes that occur during the course of the annealing sequence. The sequence occurred in steps of 5–15 K, but in order to focus on the changes, only some of the spectra are shown in the figure. Between 110 and 120 K there is a dramatic change across the entire spectrum, as seen very clearly in figure 3.7,



Figure 3.6. RAIR spectra for adsorption of 100 L_m 2-propanol at 26 K at 10, 20, 50 and 100 L_m (top to bottom). The region 1600–2800 cm⁻¹ is omitted as there are no visible peaks in this region. Assignment of the main bands is given in the figure.

mode	present study	on Ni(100) ¹⁸²	on Cu(100) ¹⁷⁸	liquid ²²⁷
v(C-C)	822		820	818
ρ(CH ₃)	960	956	960	952
v(C-O)	1117	1108	1114	1108
ν(C-C), ρ(CH ₃)	1134	1130	1133	1130
ν(C-C), ρ(CH ₃)	1169	1166	1168	1162
δ(CH)	1325	1313	1322	1312
δ(CH)	1344		1342	1346
δ(CH ₃)	1383	1382	1381	1380
δ(CH ₃)	1412		1418	1410
δ(CH ₃)	1475	1460	1473	1475 (gas)
ν(С-Н)	2889	2885	2882	2875
	2922			
ν(С-Н)	2931	2940	2940	2933
ν(С-Н)	2976	2967	2972	2976
v(O-H)	3350 (broad)	3300 (broad)		
v(O-H)	3650			3650 (gas)
1. 1. 1. 5	1.0 .			

Table 3.4. Vibrational wavenumber (cm⁻¹) values and their assignments for 100 L_m 2-propanol adsorbed on HOPG at 26 K. Data from the literature are included for comparison.

v = stretching, $\rho =$ rocking, $\delta =$ deformation

50

with most peaks increasing in intensity and some peaks developing shoulders. Prior to the significant changes seen at 120 K, the sequence shows a clear but gradual alteration in the v(O-H) band as it shifts from base temperature up to 110 K, perhaps indicating that a partial change is occurring. Other changes in the temperature range 26–110 K are relatively minor.



Figure 3.7. Selected RAIR spectra recorded at annealing temperatures of 26–140 K for 50 L_m pure 2-propanol dosed on HOPG at 26 K. The region from 1600–2800 cm⁻¹ was omitted as there are no peaks visible within this region.

The significant behaviour of the spectrum at 120 K is most evident in the v(O-H) band at ~3350 cm⁻¹, which shifts and sharpens substantially, splitting into distinct peaks at 3288 cm⁻¹ and 3169 cm⁻¹. Similar behaviour is also seen for methanol, ethanol and acetic acid, where it is attributed to a bulk crystallisation phase change.^{93,201,202} Both ethanol and methanol show comparable spectral features in the v(O-H) band region following annealing.^{201,202} For ethanol these were at 3238 and 3161 cm⁻¹, while for methanol they were at 3290 and 3174 cm⁻¹. For 2-propanol during this assumed crystallisation process, in addition to the sharpening of the v(O-H) band, the 960 cm⁻¹ band blueshifts and the 1134 and 1169 cm⁻¹ bands start to split or shift, with a shoulder appearing on each. The 1383 cm⁻¹ band redshifts slightly and the 2976 cm⁻¹ band begins to shift, a shoulder remaining where the peak originated.

As previously noted, Cirkel and Boese found a helical chain crystal structure for 2-propanol.²¹⁷ In this structure, the chain is linked by repeating O–H···O hydrogen bonds. Considering that the change seen at 120 K is likely crystallisation, we may intuit that the alignment of the hydrogen bonds as the central element of these chains is the reason why the v(O-H) band is altered so significantly while other bands in the spectrum remain relatively unchanged. In support of this, it has been shown that the character of the v(O-H) band of solid water is indicative of the phase as a result of hydrogen bonding behaviour.^{228,229} Further, a pattern of thermally-driven formation of hydrogen-bonded chain struc-
tures has been previously demonstrated by methanol, ethanol and acetic acid on graphite surfaces, with intermolecular coupling effects implicated in the profound splitting of the v(O-H) band.^{93,201,202,230–235} Given the chain crystal structure resolved by Cirkel and Boese, it seems clear that 2-propanol is following this pattern. Beyond this, the data at present does not appear to provide clear evidence for the broader ice structure or relative orientation of the 2-propanol chains.

3.2.2.2 Annealing Trends

Figure 3.8 shows a plot of peak area and wavenumber values for the $\rho(CH_3)$ 960 cm⁻¹ and $\nu(C-H)$ 2976 cm⁻¹ bands, illustrating the general trends seen in the RAIR spectra during the annealing sequence. These bands were chosen as they are particularly intense and well-defined in the spectrum. Figure 3.8(a) shows that the 960 cm⁻¹ peak area and wavenumber both increase at 120 K, while figure 3.8(b) shows the 2976 cm⁻¹ band decreasing in wavenumber at 120 K but maintaining a relatively constant peak area. As is the case for the whole spectrum, both peaks disappear for temperatures >140 K due to desorption of 2-propanol, in agreement with the TPD traces which show a maximum desorption rate between 140 and 145 K.



Figure 3.8. Peak area and wavenumber for selected peaks a) $\rho(CH_3)$ at 960 cm⁻¹ and b) $\nu(C-H)$ at 2976 cm⁻¹ illustrating the general trend observed during the annealing sequence of 50 L_m of pure 2-propanol dosed on HOPG at 26 K (see figure 3.7).

3.2.2.3 RAIRS Evidence of Coverage-dependent Behaviour

The TPD data for 2-propanol on HOPG showed non-ideal behaviour at higher doses, as the leading edges for the traces were not shared (figure 3.2) as they would be for an ideal zero-order process. This was especially noticeable at 50 L_m , suggesting a coverage-dependent phase change occurring simultaneously with, or just prior to, desorption in the region of 120–140 K. The RAIR spectra for the annealing sequence of 20 L_m 2-propanol—shown in figure 3.9—appear to support this, displaying

less distinct spectral changes than shown in the spectra for 50 L_m 2-propanol in figure 3.7. This lack of significant phase change for 20 L_m may be related to the degree that 2-propanol forms islands on the graphite surface, which might affect its ability to undergo the phase change at lower doses. Other species that can hydrogen bond also show behaviour of this sort. Water does not wet the graphite surface, nor does methanol, which like 2-propanol shows a coverage-dependent crystallisation phase change.^{201,218,236}



Figure 3.9. Selected RAIR spectra recorded at annealing temperatures of 26–140 K for 20 L_m pure 2-propanol dosed on HOPG at 26 K. The region from 1600–2800 cm⁻¹ was omitted as there are no peaks visible within this region.

3.2.3 TPD Results for 2-Propanol/Water Binary Ices

As an abundant and reactive species in the ISM, water plays an important role in the chemical environment of these regions of space.¹¹⁶ The surface interaction of water ice with other molecules is therefore of significant interest, as is the proven ability for water to trap volatile species. The TPD spectra in the figures that follow show traces for the main fragment of 2-propanol (45 m/z), illustrating how the alcohol behaves when dosed in three different configurations with water: layered on crystalline ice, layered on amorphous ice, and in a mixture with amorphous ice. While a mixed ice is the most directly relevant to the chemistry of the ISM, looking at layered systems in the laboratory can serve to better understand the interaction between the two ices. Because of the complex interactions between the two ices, it is not possible to apply quantitative analysis in order to derive kinetic values, as was undertaken for the pure 2-propanol ices. Instead, the discussion in this section focuses on qualitative observations.

3.2.3.1 2-Propanol on CI

Figure 3.10 shows TPD data for 1–30 L_m 2-propanol dosed on multilayer crystalline water ice. Because of the method used to generate a CI layer on the HOPG surface, the effective exposure of the CI is not known exactly. It is determined to be approximately 35 L_m , by comparison of the proportional TPD peak area to that of 50 L_m ASW. While this is lower than the amorphous ice, ~35 L_m still ensures a bulk multilayer fully covering the HOPG surface. As such the results for 2-propanol layered on CI and ASW can still be directly compared. At the lowest dose, 1 L_m , a single peak appears at ~155 K, while for doses of 5–30 L_m a second, lower temperature, peak at 141–142 K grows into the spectrum. As the dose increases, the lower temperature peak grows much more rapidly than the peak seen at 155 K, which saturates. This is illustrated more clearly in figure 3.11 which shows fitted peaks for the TPD spectra. The desorption temperatures are significantly lower than reported previously by Schaff and Roberts, but this can be explained due to the different heating rates during the TPD data collection.¹¹⁸ The significantly more rapid 3–5 K s⁻¹ used in the previous work would be expected to show higher desorption temperatures.



Figure 3.10. TPD spectra of 1, 5, 10, 20 and 30 L_m 2-propanol dosed at ~26 K on ~35 L_m multilayer CI. The trace for water is shown as a dotted line for reference only (not to scale).

3.2.3.2 2-Propanol on ASW

Figure 3.12 shows TPD spectra for 1–20 L_m 2-propanol dosed on 50 L_m amorphous water. As with 2-propanol adsorbed on CI, the spectra for the lowest doses show an initial peak at ~155 K. This peak decreases in temperature with increasing dose of 2-propanol, as well as apparently saturating following doses of 10–15 L_m . A second, lower temperature peak is also observed following doses of 5 L_m of



Figure 3.11. Illustration of fitted peaks for the TPD spectra shown in figure 3.10 of 1, 5 and 10 L_m 2-propanol dosed at ~26 K on ~35 L_m multilayer CI. Voigt profiles are used as these capture the leading-edge better than a simple Gaussian curve. Fit residuals are shown in the upper section of the figure.

2-propanol. Following 10 L_m doses this peak grows into the spectrum at ~148 K. Finally, at 10 L_m a third peak appears at a low temperature of ~138 K. This last peak is similar to that seen for higher doses of 2-propanol on CI and for multilayer 2-propanol on HOPG.

As the last to appear, closely following the water peak, the highest temperature peak can be reasonably assigned to 2-propanol co-desorbing with water. The similarity between this peak and the lowest dose peak in figure 3.10 could suggest that the water may not be completely crystalline in the CI experiments. However, the rapid saturation of this peak at low doses on CI would seem to indicate that the bulk of the water layer is properly crystalline in those systems. The explanation for this peak appearing in the CI experiments at all is attributed to the dangling O-H bonds exhibited by CI which are known to be present, though at only 1/6 the amount seen for ASW.¹¹⁸ For 2-propanol and ASW, the increasing presence of alcohol inhibits the ASW-CI phase change, causing more rapid desorption of water and at lower temperatures. The water behaviour is further discussed in section 3.2.5 of this chapter, but here it is seen as a shift in the high temperature peak to slightly lower temperatures with increasing 2-propanol dose.

The low temperature peak of figure 3.10 must represent pure multilayer 2-propanol not directly interacting with the water, as does the similar peak in figure 3.12, appearing at the same temperature as the peak for multilayer 2-propanol on HOPG. In both cases this peak grows quickly once it appears in the TPD spectrum, showing no saturation at the doses studied. While the low temperature feature is assigned as multilayer desorption in both the crystalline and ASW systems, it peaks at different tem-



Figure 3.12. TPD spectra of 1, 2, 5, 10, 15 and 20 L_m 2-propanol dosed at ~26 K on 50 L_m multilayer ASW. The trace for water is shown as a dotted line for reference only (not to scale).

peratures. However, it is clear from the comparable leading edges that this difference is very likely due to there simply being less multilayer 2-propanol on ASW than on CI at equivalent doses due to thermally-driven mixing.

The origin of the additional peak at ~148 K for the 2-propanol on ASW system is not certain. As it only appears in this system, it may represent 2-propanol that has penetrated within the porous amorphous water but is not directly interacting-that is, co-desorbing—with the water. Supporting this physical interpretation is the fact that the peak appears at a slightly lower temperature than that of the water peak. Due to the inhibition of the water phase change the 2-propanol is not released as a sudden volcano, but as a smaller peak in the region of the earlier part of water desorption.

3.2.3.3 2-Propanol/Water Mixtures

Figure 3.13 shows TPD spectra for 2-propanol in 5, 6, 15 and 28 % mixtures with 50 L_m multilayer amorphous water. These proportions were chosen as they are similar to the proportions used in the layer systems. The TPD spectra show a single desorption peak for this system at all doses. The peak appears initially at ~155 K for a low percentage of 2-propanol, and at higher percentages it shifts to 151–152 K in a similar manner to that seen for the 2-propanol on ASW peak shown in figure 3.12, although it does not saturate at the compositions investigated. Due to the mixture dosing method, the traces in figure 3.13 can be confidently assigned as 2-propanol intimately interacting and co-desorbing with water. The similarity of the high temperature peak of figure 3.12 to these traces seems to indicate that there is significant thermally-induced mixing during the annealing of 2-propanol layered on ASW. In both cases this peak appears to follow a corresponding shift in the water desorption trace, supporting the view that these peaks represent co-desorbing 2-propanol. The same conclusions have previously been drawn for ethanol.²⁰³ As with the ASW layer system, the presence of 2-propanol in a co-deposited mixture has a significant effect inhibiting the ASW-CI phase transition. No abrupt volcano desorption was observed for any of the binary 2-propanol/water systems, although this result is not unexpected with the desorption temperatures of 2-propanol and water being very similar, and the expected intermolecular forces between them being particularly strong due to hydrogen bonding.



Figure 3.13. TPD spectra of 2-propanol dosed at ~26 K in 6, 8, 15 and 26 % mixtures with ~50 L_m multilayer ASW. The trace for water is shown as a dotted line for reference only (not to scale).

3.2.3.4 Comparison of the Three Binary Ice Systems

Figure 3.14 directly compares pure 2-propanol on HOPG and 2-propanol in the three configurations of binary ices with water. TPD peaks for amorphous and crystalline water are shown in figure 3.14(a) for reference. Figure 3.14(b), 3.14(c) and 3.14(d) show TPD peaks for 20 L_m , 10 L_m and 5 L_m 2-propanol, respectively. In comparing mixtures to layers, mixtures were chosen that closely matched the proportions for the associated layered configurations, allowing for the best comparison despite the different dosing methods. For example, for 20 L_m 2-propanol layered on 50 L_m ASW, 2-propanol represents ~29 % of the total 70 L_m dose. As such, the 26 % mixture data was used for comparison in figure 3.14(b). When considering peak assignments, the pure and mixed ices can be considered as two 'extremes', while the layers are intermediate. This viewpoint highlights the inferred interaction of the two ices in the layered systems as they are deposited and as heat is subsequently applied during the TPD process.



Figure 3.14. TPD traces for a) multilayer ASW and CI (shown for reference), b) 20 L_m , c) 10 L_m and d) 5 L_m 2-propanol on HOPG, as well as in binary layers and mixtures with multilayer water, adsorbed at 26 K.

In the case of 20 L_m , shown in figure 3.14(b), two major regimes are evident. One appears at ~140 K and is present for the pure and layered systems. In the pure system this is already assigned to multilayer desorption, as described previously. It is reasonable that the multilayer 2-propanol ice would be minimally affected by the underlying layer and, given the similarity, this peak can be assigned to multilayer 2-propanol desorbing in bulk for both the CI and ASW layered systems. That it does not appear at all in the mixed system also supports this, as a multilayer would not be expected to form when the two ices are being deposited simultaneously. The second regime is in the range 151–155 K is assigned to 2-propanol co-desorbing with water. This assignment is strongly supported by this being the only peak appearing in the pre-mixed system. For the layered systems it is assumed that this represents 2-propanol which has become mixed or trapped by water due to thermally-driven mixing. Finally for this figure, there is the third peak at ~148 K only visible for 2-propanol layered on ASW. As discussed previously, this possibly represents 2-propanol at or near the amorphous water surface.

Considering then the comparison of 10 L_m in figure 3.14(c), the ~140 K regime remains for 2propanol on HOPG and on CI, but is no longer present for 2-propanol on ASW. This remains assigned to upper surface desorption. Although it appears at a very similar temperature as the peak for 20 L_m 2-propanol, as shown by the pure system in section 3.2.1 this now primarily represents a monolayer. At 10 L_m , 2-propanol on ASW demonstrates primarily the two features ascribed to surface or near-surface desorption and to co-desorption. This indicates that there is insufficient 2-propanol at this dose for a surface layer to remain after thermally-driven mixing. For the 2-propanol on CI system at this dose, the co-desorption and surface desorption are both still visible, though the surface layer represents a smaller proportion of the total here. This makes sense, as although there is less 2-propanol in this system also, thermally-driven mixing is limited due to the irreversibly crystalline ice lower layer.

Lastly, the 5 L_m traces in figure 3.14(d) continue the trend shown by the previous two figures. There is now only a minor amount of surface desorption for 2-propanol on CI and on ASW. For both, the co-desorption is most significant, particularly for 5 L_m 2-propanol on ASW which, by comparison with the 8 % mixture trace, appears to have been almost completely mixed by the annealing of the ices occurring during the TPD heating.

3.2.4 RAIRS Results for 2-Propanol/Water Binary Ices

RAIR spectra at base temperature are shown in figure 3.15 for ~20 L_m of 2-propanol in layers and mixtures with water, as well as 20 L_m 2-propanol on HOPG for comparison. The 960 cm⁻¹ ρ (CH₃) band is visible as a sharp peak in each case. Compared to 2-propanol on HOPG, the peak is redshifted slightly for the layered ices and significantly for the mixed ice. The 1134 cm⁻¹ and 1169 cm⁻¹ ν (C-C)/ ρ (CH₃) bands for the layered ices appear quite similar to the bands for 2-propanol on HOPG. These bands occur at the same wavenumber values and are of similar relative intensity in each case. For the mixture, however, there is a clear change as the 1169 cm⁻¹ band shows about half the intensity of the 1134 cm⁻¹ band and, additionally, the 1134 cm⁻¹ band is shifted to a slightly lower wavenumber. The 960, 1134 and 1169 cm⁻¹ bands therefore appear to show a fundamental difference between the mixed and layered systems even at base temperature. The small band at 1270 cm⁻¹ is much more noticeable for 2-propanol layered on CI than for the other systems. The δ (CH) bands at 1319 and 1342 cm⁻¹ appear more intense for the amorphous water layer and mixture, and they are sharpest in the mixture. The bands at 1369 cm⁻¹ and 1381 cm⁻¹ show a similar pattern, additionally showing a significant blueshift in the case of the mixture. The 1477 cm⁻¹ δ (CH₃) band is not clear at 20 L_m for 2-propanol on HOPG, but becomes more distinct when 2-propanol is layered or mixed with water. This band occurs at a similar wavenumber value for the layered ices but appears at a lower wavenumber in the mixture. The broad band at 1650 cm⁻¹ is associated with the water ices and so does not appear in the spectrum for 2-propanol on HOPG. The band has a slightly different character for the crystalline ice, shifted to a lower wavenumber.



Figure 3.15. RAIR spectra in the 1050–1800 cm⁻¹ region comparing 20 L_m of 2-propanol adsorbed at ~27 K on HOPG, on CI, on ASW and in a 27 % mixture with water.

Annealing the 2-propanol/water ices reveals relatively few details, although small changes for 2propanol bands are visible from 120 K in the form of peak shifts. Doses of ~20 L_m are shown in figure 3.16 while doses of ~10 L_m are shown in figure 3.17. For 20 L_m 2-propanol on HOPG the 1134 cm⁻¹ and 1169 cm⁻¹ bands started at similar intensity at base temperature but the 1134 cm⁻¹ signal then grew with increasing annealing temperature up to 125 K. This growth does not appear for 2-propanol in the binary ices. For the mixtures, shown in figure 3.16(c) and figure 3.17(c), at all temperatures the 1169 cm⁻¹ signal is greatly reduced relative to the one at 1134 cm⁻¹, and in fact is not readily distinguishable from noise for the 16% mixture in the latter figure. Also noteworthy for the mixtures is that the 960 cm⁻¹ ρ (CH₃) band is reduced at all temperatures for both doses of 2-propanol. In comparison to the other bands shown, the 2976 cm⁻¹ v(C-H) band is also reduced in the case of the 27% mixture and, like the 1169 cm⁻¹ signal, is very minimal in the 16% mixture. These are the most substantial differences between the binary ice spectra, apart from the crystalline v(O-H) band seen for the CI layers, which is shown and discussed in the following section.



Figure 3.16. RAIR spectra highlighting the 2976 cm⁻¹, 1169 cm⁻¹, 1134 cm⁻¹ and 960 cm⁻¹ bands for the annealing of 20 L_m of 2-propanol a) layered on multilayer CI, b) layered on multilayer ASW, and c) in a 27 % mixture with water ice.

None of the spectra for the 1169 cm⁻¹ and 1134 cm⁻¹ bands of the layered ices approach that of the mixture during annealing, as might be expected from the TPD data of the previous section. This may be because—at ~20 L_m —there is a large proportion of multilayer, non-mixed 2-propanol, as discussed previously, which presents the majority of the RAIRS band intensity. The principle effect seen during annealing is a gradual reduction in intensity due to desorption. The v(C-H) peak at 2976 cm⁻¹ provides a good marker for the presence of 2-propanol on the surface. For 2-propanol on HOPG this peak is no longer visible after annealing at 140 K, while spectra for the binary ices show a delayed desorption and do not disappear until following annealing at 145 K. This delay seems to indicate prolonged adsorption due to interaction with water, and correlates well with the TPD in figure 3.14, which show higher temperature desorption peaks when water is present.



Figure 3.17. RAIR spectra highlighting the 2976 cm⁻¹, 1169 cm⁻¹, 1134 cm⁻¹ and 960 cm⁻¹ bands for the annealing of 10 L_m of 2-propanol a) layered on multilayer CI, b) layered on multilayer ASW, and c) in a 16 % mixture with water ice.

3.2.5 Effects of 2-Propanol on H₂O

Methanol was previously demonstrated to affect the crystallisation kinetics of co-adsorbed amorphous water.^{111,237} This effect was shown to modify the trapping of volatiles when Burke *et al.* concluded that the phase change temperature of water, in a ternary ice with methanol and OCS, was reduced by the presence of the alcohol.¹¹² Ethanol has also been shown to affect co-adsorbed water, though the effects were limited for 50 L_m of H_2O .²⁰³

3.2.5.1 TPD Data

The water TPD corresponding to the 2-propanol TPD shown in figures 3.10, 3.12 and 3.13 are shown in figure 3.18. These traces clearly illustrate that just as the presence of water influences 2-propanol, the alcohol also influences the behaviour of water. In particular, the 2-propanol affects the peak desorption rate as well as the crystallisation phase change for ASW. Unlike ASW, CI has no phase change to influence for this temperature range and its structure allows only simple surface interaction with the 2-propanol. As such, the desorption rate and peak for water dosed as CI are unaffected by the 2-propanol layers above, the peak remaining at ~153 K for all coverages of 2-propanol. Contrast this with the experiments where the water ice is amorphous, shown in figure 3.18(b) and 3.18(c). As the proportion

of 2-propanol on ASW increases, the temperature at which the amorphous to crystalline phase change feature appears increases. This indicates that 2-propanol is inhibiting the phase change, resulting in decreasing proportions of CI and greater proportions of ASW at higher temperatures.

This is notably different from the case with methanol where the peak broadens and shifts to a higher temperature with increasing amounts of the alcohol. With methanol present, water evidently undergoes the phase change at a lower temperature and desorbs at a higher temperature, from the crystalline phase. Here the smallest proportion of 2-propanol studied is sufficient to have the opposite effect and shift the shoulder associated with the phase change ~5 K higher, indicating a greater proportion of amorphous water at the point of desorption. The effect being present to such a degree—for what is initially a layered system—further suggests significant thermal mixing of the two ices. The limiting of the phase change causes the desorption profile of the water to shift to a lower temperature, and also exhibit a significantly higher desorption rate overall, as indicated by increasing integrated peak areas for the water trace with increasing amounts of 2-propanol. This suggests that in interrupting the phase change, 2-propanol alters the effective desorption kinetics for water ices. This in turn has effects on the behaviour of the 2-propanol, as discussed previously and as shown in figures 3.12 and 3.13.

3.2.5.2 RAIRS Data

Figure 3.19 compares the 2900-3800 cm⁻¹ region (dominated by the water v(O-H) band) for each of the binary ices and for pure amorphous water, as they are thermally processed through their respective annealing sequences. Note the comparatively small v(C-H) 2976 cm⁻¹ band of 2-propanol in figure 3.19(b), (c) and (d). The large v(O-H) band strongly indicates the phase of water, and figure 3.19(a) shows the amorphous to crystalline phase change for pure water, recorded under the same conditions as the binary ices. The general behaviour is similar to what has been seen previously, fully adopting the crystalline phase at ~140 K.^{218,238,239} This compares well with the crystalline ice band in figure 3.19(b) which shows very little change during annealing, displaying the crystalline character throughout, as expected. The amorphous water in the layered system in figure 3.19(c) shows only slight crystallisation and the mixture system in figure 3.19(d) shows almost none. As with the pure water in figure 3.19(a), these two have begun to slightly change character by 125 K, but beyond this they do not continue to crystallise in the manner seen clearly for the pure system. In agreement with the TPD, it appears that 2-propanol inhibits the crystallisation of water, with the effect seen to a greater degree when the 2-propanol and water are mixed from the start rather than layered. Apart from the clear difference in character there is also a significant reduction in peak area for the 140 K v(O-H) band in both figure 3.19(c) and (d).

The effect of ~10 L_m 2-propanol on water can also be considered, as illustrated in figure 3.20. Again the water layer which was pre-prepared as crystalline ice (figure 3.20(b)) shows crystalline character



Figure 3.18. TPD spectra of multilayer water, corresponding to the 2-propanol traces in figures 3.10, 3.12 and 3.13. The water traces represent: a) \sim 35 L_m CI under 1, 5, 10, 20 L_m 2-propanol, b) \sim 50 L_m ASW under 1, 2, 5, 10, 15 and 20 L_m 2-propanol and c) \sim 50 L_m ASW mixture dosed with 6, 8, 15, 26 % 2-propanol. Pure ASW on HOPG is shown in each graph (dotted line) for comparison.



Figure 3.19. The 2900–3800 cm⁻¹ region of RAIR spectra, to scale, for a) 50 L_m ASW on HOPG, b) ~35 L_m CI on HOPG with 20 L_m 2-propanol layered on top, c) 50 L_m ASW on HOPG with 20 L_m 2-propanol layered on top and d) 50 L_m ASW in a 26 % mixture with 2-propanol. All ices were dosed at ~27 K and the annealing sequence is the same in each case. The selected annealing temperatures shown are (top to bottom) 27, 125, 135 and 140 K. Credit and thanks to Tara Salter for the spectra of pure ASW in shown in (a).

through the annealing sequence. The effect of 10 L_m 2-propanol on the crystallisation of multilayer ASW is shown in figure 3.20(c), and it appears to have a very similar effect to 20 L_m 2-propanol. This may seem surprising, but with reference to figure 3.12, it has already been shown that 10 and 20 L_m 2-propanol both ultimately result in a comparable proportion of mixed ices, as the thermally driven mixing effect saturates at around 10-15 L_m of layered 2-propanol. Finally, as shown in figure 3.20(d), 16 % 2-propanol has a very similar effect on the crystallisation of ASW as the 10 L_m layer. Again this makes sense in light of the TPD data already shown because, as seen in figure 3.14(b), a similar mixture (15 %) shows approximately the same amount of co-desorption as the 10 L_m layer. The effect is clearly not as strong as the 26 % mixture.



Figure 3.20. The 2900–3800 cm⁻¹ region of RAIR spectra, to scale, for a) 50 L_m ASW on HOPG, b) ~35 L_m CI on HOPG with 10 L_m 2-propanol layered on top, c) 50 L_m ASW on HOPG with 10 L_m 2-propanol layered on top and d) 50 L_m ASW in a 16 % mixture with 2-propanol. All ices were dosed at ~28 K and the annealing sequence is the same in each case. The selected annealing temperatures shown are (top to bottom) 27, 125, 135 and 140 K. Credit and thanks to Tara Salter for the spectra of pure ASW in shown in (a).

3.3 Summary and Conclusions

Alcohols are common complex molecules in space, and they are known to play a significant role in the chemistry that occurs there.^{43,49,51,67,107,144,147,205} Although 2-propanol has not yet been detected in the ISM, it can be expected in such environments.²⁰⁷ A range of surface science experiments have been applied here to better understand how it is likely to behave under such conditions.

The growth of pure 2-propanol on graphite was found to have two distinct regimes. Doses generated by up to 10 L_m were assigned to monolayer coverages, while those >10 L_m generate bulk multilayer ices. Patterns of behaviour observed in subsequent TPD experiments with the pure ices suggest that monolayer coverages of 2-propanol are in fact forming islands, rather than wetting the graphite surface. This is proposed to be due to the greater strength of interactions between 2-propanol molecules when compared to the interaction between 2-propanol and the substrate surface, with the former likely being enhanced due to the ~20–25 kJ mol⁻¹ hydrogen bonding available to 2-propanol through its O-H group.²²² This is in good agreement with results previously seen for both methanol and ethanol, supporting this conclusion.^{201,202,223}

A phase change was observed at 120 K, which was favoured at coverages associated with higher exposures. The effects of this were seen in both TPD and RAIRS results and attributed to crystallisation of the amorphous 2-propanol. A consideration of the helical chain crystal structure determined by Cirkel and Boese shows that it is a good rationalisation for the effects seen in the spectra, particularly the substantial sharpening of the v(O-H) band.^{217,228,229} While further showing the importance of hydrogen bonding to the behaviour of 2-propanol, this also supports the conclusion that 2-propanol forms islands at low coverages, as this could inhibit crystallisation.^{201,218,236} As with the structural conclusion, this crystallisation—and its coverage-dependence—again showed a strong correlation with results seen for ethanol and methanol, as well as acetic acid: all COMs with the ability to hydrogen bond.^{93,201,202}

Kinetic analysis of TPD produced results consistent with physisorption.¹⁷³ An average monolayer desorption order of 1.23 ± 0.03 , average desorption energy of 47 ± 2 kJ mol⁻¹ and average pre-exponential factor of $10^{13 \pm 1}$ s⁻¹ were obtained through leading-edge analysis. The non-ideal, fractional order of desorption is another commonality between 2-propanol and other interstellar alcohols.^{201,202} For multilayer kinetic analysis it was necessary to assume zero-order desorption, allowing evaluation of a multilayer binding energy of 52 ± 1 kJ mol⁻¹ and multilayer pre-exponential factor of $10^{35.8 \pm 0.5}$ molecules m⁻² s⁻¹. While the desorption energies determined here are reasonably comparable to those for the other alcohols, there are clear differences in the desorption temperatures. For lower coverages, methanol desorption peaks at around 144 K while the larger ethanol peaks at about 151 K.^{201,202} Although 2-propanol is larger still, desorption peaks at a similar temperature to methanol, at ~143 K. The possibility is suggested that this is due to hindrance of the isopropyl group having a limiting effect on the ability to form intermolecular hydrogen bonds, suggesting these interactions are more important than molecular size in determining desorption temperature, though further work is likely needed to confirm this hypothesis.

The interaction between 2-propanol and water on HOPG was shown to be complex and significant. Broadly the effects can be attributed to the dominant hydrogen bonding interaction these molecules share. In binary ice systems with 2-propanol and ASW, multiple experimental results point to thermal mixing of the two ices, with co-desorption predominant at low proportions of 2-propanol. The presence of water is shown to inhibit the crystallisation of the alcohol, in good agreement with previous results for methanol and ethanol.^{111,202} This is the case whether it is present as a layer or in a co-deposited mixture with 2-propanol. Perhaps one of those most significant results is the observation that a relatively small amount of 2-propanol is sufficient to affect the phase change kinetics of water. From this it can be concluded that 2-propanol and other hydrogen-bonding species could have significant implications for astrophysical models of chemical evolution. This and other conclusions relevant to astrochemistry will be considered in the concluding chapter.

Chapter 4

Dimethyl Ether and Water Ice on HOPG

As demonstrated by the results for 2-propanol in the previous chapter, the intermolecular interactions between complex organic molecules (COMs) and water ice on graphite surfaces can have significant implications for the desorption behaviour of both. However, even in the absence of strong intermolecular interactions there are indications that the porosity of water ice allows it to trap interstellar molecules including COMs, which are formed within or deposited on the bulk ice mantles of dust grains.^{95–100} Thus, in interstellar space the kinetics of the phase change and desorption of the water ice ultimately control the release of these molecules into the gas phase. With water comprising 60–70 % of interstellar ices in many cases, it is critical to understand the interaction between molecular species and water in order to develop accurate astrophysical models of interstellar chemistry.^{88,89,166}

The desorption of a number of small, astrophysically-relevant molecules—in pure forms and codeposited or layered with water ice—was considered by Collings *et al.* in a broad survey using a gold substrate.⁹⁵ While each molecular species was not investigated in detail, by using temperatureprogrammed desorption (TPD) at 0.08 K s⁻¹ to study a range of molecules, they were able to propose assignment of the molecular species into three categories based on desorption behaviour: 'CO-like', 'water-like' and 'intermediate'. The assignments were made by grouping molecules into categories based on the qualitative nature of their desorption traces, as well as their response to the presence of water ice and especially their tendency to being trapped within the porous structure. These categories were subsequently used for astrophysical modelling work.¹⁸⁴

Spectra for pure ices of CO-like species displayed both multilayer and monolayer peaks, with a long trailing edge. When interacting with water ice, these species showed both volcano and co-desorption, indicative of trapping within the water ice. In contrast, water-like species show a single peak for pure spectra, attributed to a multilayer. This dominates for these molecular ices due to the relative strength of adsorbate-adsorbate interactions relative to adsorbate-surface interactions favouring bulk ice cluster-ing, as discussed previously in section 3.2.1.3 regarding growth patterns. As a related phenomenon,

when these molecules are deposited along with water, a desorption peak is seen coincident with that of water due to the strong intermolecular hydrogen bonding interaction with the water molecules. For the intermediate category, species show volcano and co-desorption peaks, as well as a small monolayer feature due to diffusion through the water ice matrix. In their discussion, the authors make the important point that, because of the dominant effects of the water ice, it may be important to consider what type of deposited ice in the laboratory is most relevant to the expected astrophysical conditions. In particular, it should be considered whether the species is expected to be deposited on top of the icy mantle, after forming in the gas phase, or whether it would form within the mantle. In the former case it would likely be better modelled by sequentially-deposited, layered ices, while in the latter it would probably be better represented by a co-deposited, mixed ice.

However, the survey of Collings *et al.* has some limitations. It considered only very small molecules, and as the authors note, was only a preliminary investigation, which did not investigate a range of coverages for each species. A much more recent publication by Burke *et al.* has taken the idea of categorising astrophysically-relevant molecules further, considering the chemistry of desorption in greater detail by incorporating data for COMs.⁹⁶ This comparative study used laboratory TPD and reflection absorption infrared spectroscopy (RAIRS) data for the $C_2H_4O_2$ isomers methyl formate, glycolaldehyde and acetic acid.^{93,226} The importance of functional groups and the intermolecular interactions that they can mediate was used as the basis for extending the categories of Collings *et al.*⁹⁵

The data for these isomers showed that COMs can be categorised based on COM-COM and COMwater interactions, as well as the relative temperatures at which desorption occurs for each species. It was noted that both the desorption and crystallisation of water can potentially be affected by COM-water interactions, which in turn would affect the trapping and release of volatiles by the water ice, having significant implications for interstellar chemistry. This led to the definition of two classifications based on the earlier work but accounting for the more complex behaviour of COMs: 'complex intermediate' and 'complex water-like'. The complex intermediate molecules are those which do not form hydrogen bonds (e.g. ketones, esters, ethers, aldehydes and epoxides) and primarily exhibit volcano desorption in the presence of water ice. In contrast, the complex water-like molecules can form hydrogen bonds (e.g. carboxylic acids and alcohols), and further, because of their naturally high desorption temperatures similar to that of pure water—they primarily exhibit co-desorption. Thermally-driven mixing can also be seen for species in this category, due to their stronger intermolecular interaction with water, and they may also affect the crystallisation of water ice for the same reason.

A similar pattern was recognised in work by Souda, studying desorption of water and organic species from graphite.¹²² This work included non-polar *n*-hexane, as well as the polar molecules form-aldehyde, acetone and methanol. Hydrophobic trapping of *n*-hexane caused rapid desorption during the phase change of water, and a similar behaviour was seen for formaldehyde, in spite of its polar car-

bonyl group. Methanol displayed similar desorption behaviour to water and a broadened desorption profile attributed to hydrophilic and hydrogen-bonding interactions. Acetone showed an intermediate behaviour, and the character of its desorption was linked to the structure of the water ice as well as the nature of the underlying graphite substrate.

Both dimethyl ether (DME) and 2-propanol are oxygen-containing COMs, and from preliminary data DME has been assigned to the complex intermediate species, while 2-propanol is categorised as a complex water-like species.⁹⁶ Ethanol is also classified as part of the complex water-like category, and as an isomer of DME, it provides another point of comparison. This is particularly interesting as the comparison of the $C_2H_4O_2$ isomers was used to initially derive the new classifications. Previous experimental work for ethanol was included in the preceding chapter to compare the behaviour of 2-propanol and ethanol as alcohols, but here these data can be compared to the behaviour of DME as an isomer of C_2H_6O .^{175,202–204,211,212}

4.1 Interstellar Dimethyl Ether and Previous Experimental Work

DME has been detected in interstellar space in a variety of contexts showing it to be relevant during star formation processes. It has been observed in molecular clouds, including the large Sagittarius B2, and in star-forming regions.^{7,8,145–147} A number of astronomical studies have also detected DME in hot or prestellar cores.^{148–153,160} Millar *et al.* concluded that surface processes were important for the formation of the isomers ethanol and DME, due to their abundance in the W51M star-forming region.²⁰⁵ However, from recent observation of DME—also in a star-forming region—Bisschop *et al.* concluded that DME forms in the solid and gas phase, dependent on the local temperature.¹⁵⁴ DME has been considered in astrophysical gas-grain reaction models, by Garrod *et al.*, for the developing chemistry of star-forming regions.^{4,164} The models also showed that, as temperatures increase, both grain surface and gas phase reactions play a role in the formation of DME in space.

As in terrestrial chemistry, DME was proposed by Blake *et al.* to form in interstellar space principally from methanol, in a gas phase process.²⁴⁰ For this reason interstellar DME may be useful as a 'chemical clock' for developing star systems.¹⁸ In considering this astrochemistry, Peeters *et al.* investigated the ultraviolet irradiation of DME in an argon matrix.¹⁸ They suggested formation of DME by radical groups such as methoxy and methyl radicals generated by incident radiation, but ultimately concluded that grain-surface reactions are a minor source of DME in the ISM. Considering the breakdown of DME, Schriver *et al.* used FTIR to study the photo-dissociation by vacuum ultraviolet irradiation of DME trapped in ice at 10 K, finding that the primary products were formaldehyde and methane.²⁴¹

Experimental work considering adsorption of DME in an interstellar context is relatively limited. A reflection infrared spectroscopy based study by Schriver-Mazzuoli *et al.* investigated the spectra and the

thermally driven behaviour of thin-film DME and DME:H₂O ices, building on earlier infrared observations of DME films by Allan *et al.*^{169,191} These experiments were carried out on a gold substrate under vacuum conditions (10^{-7} mbar) and through the temperature range 10-160 K. The results showed two solid phases of DME: an amorphous phase below 65 K and a crystalline phase above 65 K. Additionally, through analysis of changes in the integrated area of the bands, a multilayer binding energy of 20 ± 2 kJ mol⁻¹ was calculated. Sublimation occurred above 90 K and the kinetics were zero-order, as expected for a multilayer ice. They also especially noted hydrogen bonding to water below 120 K, as well as behaviour suggesting the formation of clathrate hydrates. DME was also studied by Lattelais *et al.* as part of a concerted experimental and theoretical investigation into interstellar isomer pairs, specifically DME/ethanol and acetic acid/methyl formate.¹⁷⁹ For DME adsorbed on a crystalline ice (CI) surface, they determined a theoretical desorption energy of ~ 36 kJ mol⁻¹ and an experimental desorption energy of 34 ± 4 kJ mol⁻¹. They noted a stronger interaction between ethanol and CI, though they were not able to experimentally quantify the desorption energy for ethanol due to the overlap in desorption temperature with that of the water ice. The theoretical desorption energy for ethanol due to the overlap in desorption temperature with that of the water ice. The theoretical desorption energy for ethanol due to the overlap in desorption temperature with that of the water ice.

The present study builds on previous work—especially that by Schriver-Mazzuoli *et al.*, Peeters *et al.* and Lattelais *et al.*—by considering the temperature-dependent kinetic behaviour of DME on a graphite surface, which represents solid dust grain components of the interstellar medium.^{18,169,179} Importantly, the TPD technique is used alongside RAIRS data to explore the interaction between DME and water ice on these surfaces. Presented in this chapter are studies of pure DME as well as DME layered and mixed with water ice. The resulting data are considered especially in the context of the extended COM classifications proposed by Burke *et al.*, and with comparison to the results of the previous chapter.⁹⁶

4.2 Experimental

The behaviour and properties of DME (>99 %, Aldrich Chemical Company) were investigated in the laboratory on highly-oriented pyrolytic graphite (HOPG) using surface science methods. The general experimental procedure as well as the subsequent analysis were the same as described previously for 2-propanol, in section 3.1. Pure thin-film DME was studied on the graphite surface, as well as in layered and mixed ices with water. DME was introduced into the dosing line from the source cylinder to a pressure of ~0.4 mbar, prior to experiments. It was then background dosed by exposure of 10⁻⁸–10⁻⁷ mbar pressures within the UHV chamber via a precision leak valve. As in the 2-propanol experiments, water was purified by at least two freeze-pump-thaw cycles. It was then introduced into the chamber, via a precision leak valve, from the vapour within the dose line. Mixed ices were co-deposited using the same method as for 2-propanol, described in section 3.1. For DME, intensity traces of the parent molecule and mass fragments CH_3OCH_2 , CH_3O and CH_3 (46, 45, 29 and 15 m/z) were detected by the quadrupole mass spectrometer (QMS). Intensity was recorded versus time during dosing and versus temperature during the subsequent temperatureprogrammed desorption experiments. Mass 46 is the parent fragment for DME, but for analysis, traces for the mass 45 (highest intensity) fragment were used in order to maximise the signal-to-noise ratio. See figure 4.1 for a comparison of the mass fragment intensities as detected by the QMS during a TPD experiment for 20 L_m DME. All TPD traces were recorded during a surface temperature increase from base temperature (<30 K) to 250 K at a linear rate of 0.50 ± 0.01 K s⁻¹. For infrared spectroscopy experiments, the region 800–4000 cm⁻¹ was recorded with a resolution of 4 cm⁻¹, co-adding 256 scans to provide good signal-to-noise ratio for the spectra.



Figure 4.1. The mass fragment traces for 20 L_m DME, dosed on HOPG at <30 K, during a TPD experiment.

4.3 Results and Discussion

4.3.1 TPD Results for Pure DME on HOPG

The TPD spectra for 5–50 L_m pure DME dosed on HOPG at 27 K are shown in figure 4.2. By making use of the approximate calculation method that was described in detail in section 3.2.1, these exposures can be estimated to produce corresponding DME ices of 0.25–2.50 nm average thickness over the 2 cm² surface.^{215,216} The traces for 15–50 L_m approximately share leading edges, and further, exhibit increasing peak desorption temperatures (90–92 K). Partial sharing of the leading edge is seen as low as 5 L_m . However for 5 and 10 L_m DME, while the leading edge is shared initially, it falls away before the peak (significantly so for 5 L_m), suggesting that these exposures do not wholly fit with those ≥15 L_m .

The TPD for 0.5–5 L_m pure DME dosed on HOPG at 27 K are shown in figure 4.3 and exhibit more complex behaviour than the higher exposure regime. As for the multilayer, the average ice thickness



Figure 4.2. TPD spectra for 5–50 L_m pure DME adsorbed on HOPG at 27 K.

on the surface corresponding to these doses can be estimated, showing that 0.02-0.25 nm ices can be expected for these exposures.^{215,216} At the lowest coverage, 0.5 L_m, desorption starts around 85–90 K and peaks at ~98 K. As the coverage increases to 1 and 1.5 L_m, the desorption temperature for this peak decreases to ~91 K, while a second peak appears at ~87 K. Precise location of the peaks is hindered by the high degree of noise in the spectra. For exposures of 1 L_m and greater, the second peak grows in with increasing exposure, showing a constant peak temperature at ~87 K. The ~91 K peak appears to saturate at ~2 L_m, especially highlighted by the proposed peak fits, two examples of which are shown in figure 4.4. The lower temperature peak overtakes the ~91 K peak in intensity at 3 L_m, but as shown in figure 4.5, the feature does not dominate the traces until >4 L_m.

Even at the lowest coverages, the traces show an unusually long trailing edge, a non-ideal behaviour which complicated the peak fitting. The nature of the feature is uncertain, though it appears to be similar to those seen by Collings *et al.* for CO and CO-like molecules.^{95,97} However, DME is a COM and desorbs at a much higher temperature than the CO-like species, which have desorption peaks between 20–40 K, so it is difficult to draw a strong conclusion from this comparison. A consideration of the TPD for the lowest coverages shown in fig 4.3 provides a potential explanation for the trailing edge. With decreasing coverage at the lowest exposures $\leq 1.5 L_m$, the peak is seen to shift to higher temperatures. This shift may indicate a coverage-dependent desorption energy, with generally higher effective desorption energy originating from greater stability of adsorbate molecules caused by decreasing repulsion between adsorbates at lower coverages. Following this trend, the minimal coverage present toward the end of a TPD experiment is expected to see increasing desorption energy as desorption of the ice progresses. This effect may be responsible for extending the trailing edge. As



Figure 4.3. TPD spectra for $0.5-5 L_m$ pure DME adsorbed on HOPG at 27 K. The inset increases the vertical scale to highlight the peak shift which occurs at the lowest exposures.



Figure 4.4. Proposed peak fits (coloured lines) for the TPD spectra (black lines) for 1 and 3 L_m DME adsorbed on HOPG at 27 K (representative of 0.5–5 L_m). The individual fitted peaks are shown as dotted lines. A Voigt profile is used to fit the lower temperature peak, while an exponentially-modified Gaussian distribution fits the higher temperature peak and the long trailing edge.



Figure 4.5. Peak areas for the fitted peaks shown for 0.5–5 L_m DME adsorbed on HOPG at 27 K, as illustrated in figure 4.4. Third degree polynomial fits (lines) are overlaid for illustrative purposes.

a final note, this suggestion of repulsion would preclude islanding at low coverages, indicating that monolayer growth follows a Frank–van der Merwe or Stranski–Krastanov pattern, with a monolayer first wetting the surface, as outlined previously in section 3.2.1.3.²²¹

4.3.1.1 Multilayer Desorption Kinetics

The pattern of shared leading edges for the 15–50 L_m traces fits zero-order behaviour and therefore likely a bulk multilayer ice. This qualitative assessment is supported by the leading-edge kinetic analysis, with 10–50 L_m providing a desorption order of 0.11 ± 0.09 with good linear fits, as shown in figure 4.6 and in table 4.1. A multilayer desorption order of ~0.1 is slightly above ideal zero-order, but is similar to that seen for other multilayer ices, including water, methanol, ethanol and acetic acid.^{93,201,202,218} The order analysis was performed in the temperature range 81.5–85 K, where 10 L_m also shares the leading edge.

Table 4.1. Multilayer order values from the individual TPD spectra represented by figure 4.2, and obtained from linear fits like that illustrated for the higher coverages in figure 4.6. Each of the two columns represents a set of TPD data for $10-50 L_m$.

Temperature / K	Order, <i>n</i>	
81.5	0.05	-0.10
82	0.00	0.00
82.5	0.17	-0.10
83	0.24	0.01
83.5	0.09	0.10
84	0.40	0.15
84.5	0.13	0.26
85	0.18	0.13



Figure 4.6. Order plots showing the two desorption regimes for DME which has been adsorbed on HOPG at 27 K. Points for two sets of data are shown, but (for illustrative purposes) only a single fit is applied to each. Note that, in the analysis, each set was evaluated separately, as outlined in table 4.1. The sets of data points in this figure were calculated at 86 K.

With an order established for the multilayer, further analysis utilising Arrhenius plots obtained an average multilayer desorption energy of 30 ± 2 kJ mol⁻¹ from the individual values presented in table 4.2. An example Arrhenius plot is shown in figure 4.7. A multilayer pre-exponential factor of $10^{31\pm3}$ molec m⁻² s⁻¹ was then calculated. For simplicity, zero-order units are given for the preexponential factor. As with the 2-propanol analysis, errors are estimated as twice the standard error of the mean or by propagation of the individual fit errors, whichever is greater. In this case the reported errors for both the order and desorption energy are from propagation. The error for the pre-exponential factor is estimated by varying the values for the order and desorption energy within their respective error limits, which again is the same method used to estimate error during the analysis of the 2-propanol data.

Table 4.2. Multilayer desorption energy values from the individual TPD spectra represented by figure 4.2, and obtained from linear fits like that illustrated in figure 4.7. Two TPD traces were recorded at each multilayer coverage and these are presented in two columns.

Exposure / L _m	E _{des} / kJ mol ⁻¹		
10	28.6	28.2	
15	30.9	30.8	
20	30.7	30.4	
30	31.5	30.9	
50	30.4	31.9	

The values determined for desorption energy and pre-exponential factor are reasonable for a physisorbed, multilayer organic species. They compare well with, for example, acetaldehyde in the following chapter or methyl formate in Burke *et al.*⁹³ However, the desorption energy here disagrees



Figure 4.7. Example energy Arrhenius plot illustrating the analysis of TPD data from 30 L_m DME adsorbed on HOPG at 27 K. For this particular example, the energy is evaluated from the slope as 31 ± 6 kJ mol⁻¹ (95% confidence interval) with r² = 0.9963.

significantly with the previous value found by Schriver-Mazzuoli *et al.* $(20 \pm 2 \text{ kJ mol}^{-1})$.¹⁶⁹ This may be due to their use of infrared data for the analysis. A desorption energy of 20 kJ mol⁻¹ would seem to be too low for DME, which desorbs at temperatures >80 K. Desorption energy correlates to desorption temperature, and molecules with desorption energies this low—such as CO, C₂H₄ or N₂—are typically small, low-mass molecules which desorb at temperatures <40 K.⁹⁵

In comparison to the multilayer desorption energies for the C_2H_6O isomer ethanol (~51–58 kJ mol⁻¹) the value for pure DME is quite small.^{202,204} This can be rationalised by the inability for DME molecules to form hydrogen bonds with each other, precluding this stabilising effect. In the comparison of the $C_2H_4O_2$ isomers by Burke *et al.* this pattern was also seen, with glycolaldehyde and acetic acid having higher desorption energies and temperatures than methyl formate.⁹³ More broadly, this lower desorption energy is a feature which was ascribed to the complex intermediate species in the classification of COMs.⁹⁶

4.3.1.2 Monolayer Desorption: Stochastic Simulations

Directly applying a leading-edge analysis to the lower coverages in figure 4.6, $0.5-5 L_m$, results in an order value of ~3.4. This value is clearly non-physical and indicates that the desorption behaviour is more complex than can be directly accounted for through this type of analysis. Despite the slope being far from an ideal zero or first-order, the coverages represented can be ascribed to monolayer or sub-monolayer coverages from a qualitative consideration of the TPD. With reference to figures 4.4 and 4.5, the first peak is seen to saturate from about 2 L_m , just as the second peak grows in. Further, these peaks become approximately equivalent at 4–5 L_m , which is twice the exposure at which the first peak saturates. This is also the start of the multilayer regime, as seen in figure 4.2. Together, these trends suggest that these two low exposure peaks represent a monolayer and the start of a multilayer or possibly an intermediate bilayer, as seen for methyl formate.⁹³ Therefore, the order value evaluated above is not actually associated with the monolayer peak. However, even attempting to apply leadingedge analysis to the monolayer fitted peaks results in an order value of ~3.5. While the peak fitting appears qualitatively reasonable, this may indicate that the fit function captures the leading edge of the monolayer peak poorly, or it may be that even the isolated monolayer behaviour is too complex for a straightforward analysis of this type, due to adsorbate-adsorbate interactions.

Because of the non-ideal desorption at lower exposures, a stochastic kinetic simulation was fitted to the TPD traces for the coverages 0.5–1.5 L_m , in order to extract a monolayer desorption energy. In this range of exposures, the peak behaviour is thought to have a major component showing monolayer and sub-monolayer interactions based on the peak fits. The procedure used was that employed by Thrower *et al.* in their work with benzene on a silicate surface.²⁴² This was achieved through use of the Kinetiscope (Columbia Hill Technical Consulting) simulation software.²⁴³ The software requires an initial surface concentration, a pre-exponential factor (ν), an energy of desorption (E_{des}) and an order of desorption (n). The latter three kinetic parameters are assumed to be constant. Within the software, a simple reaction scheme is constructed

$$DME(ads) \longrightarrow DME(g)$$
$$DME(g) \xrightarrow{k} DME(p)$$

where DME(ads) is the concentration of adsorbed DME in molec cm⁻², DME(g) is DME which has desorbed, DME(p) is DME which has been pumped from the chamber, and k is the pumping rate. An example simulation based on this scheme is illustrated in figure 4.8.



Figure 4.8. Illustration of the three components of the reaction scheme during a simulation of the desorption of 1 L_m DME. The DME(g) peak has very low intensity on this scale and has been increased by a factor of 100, for visibility.

First, the simulation was applied to the multilayer regime, where the kinetics had already been established via leading-edge analysis of the experimental results. The initial surface concentration was determined by the equation for the number of molecules adsorbing on the surface, equation 2.18 (page 33), which is also used during Polanyi-Wigner pre-exponential factor analysis. The values for v, E_{des} and n were varied within the previously calculated experimental error limits until a good fit was achieved (evaluated visually). A pumping rate of 30 s⁻¹ was used. Varying this value appeared to affect the intensity of the simulated TPD trace, but not the peak shape. By comparison to the experimental TPD (previously shown in figure 4.2), simulation parameters were found which provided a reasonable fit, as illustrated in figure 4.9. The parameters were $v = 10^{30}$ molec m⁻² s⁻¹, $E_{des} = 30.3$ kJ mol⁻¹ and n = 0.08, with a pumping rate of 30 s⁻¹. Note that while the leading edges and peak positions of the simulated traces match reasonably with their experimental counterparts, the tail portion of these traces falls off very sharply in comparison to the laboratory data. This may be primarily due to the idealised description of the pumping behaviour in the simulation.



Figure 4.9. Comparison of experimental (dotted lines) and simulated (solid lines) TPD spectra for multilayer DME. The parameters used for the simulation were $\nu = 10^{30}$ molec cm⁻² s⁻¹, $E_{des} = 30.3$ kJ mol⁻¹ and n = 0.08, with a pumping rate of 30 s⁻¹.

For the monolayer TPD simulations, a desorption order of n = 1 was assumed in order to simplify the analysis, as this is a typical order for simple molecular monolayer—or sub-monolayer—desorption. The pre-exponential factor was set to 10^{13} s⁻¹. As noted in the previous chapter, this value is in the general $10^{12}-10^{13}$ s⁻¹ range expected for first-order desorption.¹⁹⁵ In the physical model, this factor is interpreted as a desorption attempt frequency related to vibration of the molecules.^{225,244} The main source of the substantial difference in magnitudes for the multilayer and monolayer pre-exponential factors stems from the different units resulting from the calculation. For multilayer coverages, expressed in molec cm⁻² s⁻¹, a concentration factor on the order of 10^{15} molec cm⁻² is included. With the chosen pre-exponential value, desorption energies of ~28, 27 and 26 kJ mol⁻¹ provide good fits to the leading edge and peak positions between simulation and experiment for 0.5, 1 and 1.5 L_m, respectively. The comparison between the simulation and laboratory TPD traces is shown in figure 4.10. Variation of the pre-exponential factor in the range $10^{12}-10^{14}$ s⁻¹, to represent an order of magnitude error, causes a significant change in the simulated desorption temperature. By adjusting the corresponding desorption energies to maintain the simulation fit, approximate error estimates for the energy values were determined as ±2 kJ mol⁻¹. The trailing edges match very poorly between simulation and experiment, but this is not unexpected when considering the complex behaviour attributed to low DME coverages. The simulation assumes that desorption energy is independent of coverage, as well as an ideal desorption order of n = 1, both of which likely contribute to the discrepancies seen.



Figure 4.10. Comparison of fitted peaks (dotted lines) for 0.5, 1 and 1.5 L_m DME (as in figure 4.4) and simulated TPD spectra (solid lines). The parameters used for the simulation were $\nu = 10^{13}$ s⁻¹, n = 1, and $E_{des} = 28$, 27 and 26 kJ mol⁻¹, with a pumping rate of 30 s⁻¹.

4.3.2 RAIRS Results for Pure DME on HOPG

A RAIR spectrum for 50 L_m DME adsorbed on HOPG at 27 K is shown in figure 4.11 with several band assignments highlighted. A 50 L_m spectrum was chosen to consider band assignments as this was the highest coverage of pure DME studied by infrared and thus provides the best signal-to-noise ratio. The full list of assignments is given in table 4.3, with reference to the literature.^{169,191,245–247} The peak positions here can be readily matched with the previous results, though there are differences of up to ~10 cm⁻¹ in some cases. This may be due to the different substrates used in the previous work: a gold surface and an argon matrix, as opposed to the graphite surface employed here. As with this investigation, in both of the previous studies DME was deposited at cryogenic temperatures.

Between 3100–2750 cm⁻¹ there are three stretching modes associated with the CH₃ groups. With moderate intensity, there appears a v'_{s} (CH₃) symmetric stretch at 2993 cm⁻¹ and about twice as intense



Figure 4.11. Band assignments for the pure DME infrared spectrum in the 900–3050 cm⁻¹ region, based on the RAIR spectrum of 50 L_m DME adsorbed on HOPG at 27 K. The region 1550–2750 cm⁻¹ is omitted as there are no distinct bands for DME visible in this range, at base temperature.

Table 4.3. Vibrational wavenumber (cm⁻¹) values and their assignments for 50 L_m DME adsorbed on HOPG at 27 K. Data from the literature are included for comparison.^{169,245} Note that the 1250 cm⁻¹ ρ (CH₃) mode is not visible at base temperature in figure 4.11, due to an artefact in the baseline of the raw spectrum.

mode	present study	on Au (11 K) ¹⁶⁹	Ar matrix (17 K) ²⁴⁵
v _s (COC)	926	916	926
$\nu_a(COC), \rho(CH_3)$	1099	1089	1098
	1167	1159	1172
ρ(CH ₃)	~1250	1247	1244
δ(CH ₃)	1466	1458	1455
	1483	1480	
$v_s(CH_3)$	2819	2814	2821
2δ(CH ₃)	2870	2867	2869
	2890	2884	2890
$v_a(CH_3)$	2929	2921	2942
$v'_{s}(CH_{3})$	2992	2987	2986

v = stretching, $\delta =$ deformation, $\rho =$ rocking

is the $v_s(CH_3)$ symmetric stretch at 2819 cm⁻¹. The origin of these two bands are the non-equivalent inplane $v_s(CH)$ and out-of-plane $v_s(CH_2)$ stretches, with the 2993 cm⁻¹ band primarily in-plane and the 2819 cm⁻¹ band primarily out-of-plane.^{191,247} Between the symmetric stretch modes are the $v_a(CH_3)$ antisymmetric stretch at 2929 cm⁻¹ and a band at 2891 cm⁻¹ with a small shoulder visible at 2870 cm⁻¹. With reference to previous work, is should be noted that the bands in this region of the spectrum are expected to be affected by Fermi resonance with higher-frequency modes.^{169,191}

The 2891 cm⁻¹ and 2870 cm⁻¹ features are assigned to overtones or combinations of the fundamental $\delta(CH_3)$ deformation modes, which are found in the lower region of the spectrum as a moderate peak and shoulder at 1466 cm⁻¹ and 1483 cm⁻¹, respectively. Also in the lower 1550–900 cm⁻¹ region, the most intense features are the peaks at 1169 cm⁻¹ and 1099 cm⁻¹, which arise from coupling of the $\rho(CH_3)$ rocking and $v_a(COC)$ antisymmetric stretching. A slight shoulder feature is seen on one side of the 1169 cm⁻¹ peak, though it is not distinct at base temperature. Also quite intense is the $v_s(COC)$ symmetric stretching peak at 926 cm⁻¹, which is the lowest energy mode visible. As a final note, the ~1250 cm⁻¹ $\rho(CH_3)$ mode that is expected in this region of the spectrum is not visible at base temperature due to an artefact which masks it. It does become visible once it sharpens, following annealing, as will be shown later.

4.3.2.1 Symmetry Analysis Notes

Gas phase DME has C_{2v} symmetry, as illustrated in figure 4.12. A total of 3N - 6 = 21 normal modes are expected for a molecule composed of N = 9 atoms and having 3N = 27 degrees of freedom. As noted by Kanazawa and Nukaza in the discussion of assignments for their recorded infrared spectra of gas phase DME, symmetry analysis classifies the vibrational modes into four types as represented by

$$\Gamma_{vib} = 7A_1 + 4A_2 + 6B_1 + 4B_2$$

with the A_2 modes being infrared inactive.²⁴⁶ This leaves 17 infrared active modes, although some overlapping is expected, and three previously seen bands are not within the recorded wavenumber range of the current work.^{191,246,247} The 11 reported modes at base temperature outlined in table 4.3 therefore seem reasonably in line with the molecular symmetry. Further, the similarity between the gas phase and the base temperature surface results suggests a disordered structure relative to the graphite surface, as the surface selection rule is not a significant factor.

4.3.2.2 Annealing Multilayer DME

Spectra from annealing series for 50 L_m and 20 L_m multilayer DME through the temperature range 30–90 K are shown in this section, with selected temperatures shown to highlight the thresholds for structural change and for desorption. Overall, the results seen match very closely with those reported



Figure 4.12. Illustration of the application of the C_{2v} point group assignment to dimethyl ether, with the associated character table shown to the right.

by Schriver-Mazzuoli *et al.* in their study of DME on the Au surface.¹⁶⁹ Notably, the ice exhibits a distinct change from a disordered, amorphous phase to a more ordered, crystalline structure. These changes are described in detail below.

As shown in figure 4.13, the v'_{s} (CH₃) band—which appears at 2997 cm⁻¹ at base temperature—shifts to a slightly lower wavenumber in the spectrum after the 70 K anneal. The band also splits, resulting in two roughly equivalent peaks which are seen at 2993 and 2985 cm⁻¹. The $v_a(CH_3)$ 2929 cm⁻¹ and $2\delta(CH_3)$ 2890 cm bands do not show substantial changes during the phase change, though the 2869 cm⁻¹ shoulder moves slightly to 2873 cm⁻¹ while also becoming noticeably distinct from the larger band. The stronger 2819 cm⁻¹ v_s(CH₃) peak splits into two peaks of similar intensity, much like the v's(CH3) band. These appear at 2825 and 2816 cm⁻¹. Two very small peaks, which are difficult to distinguish from noise at base temperature, become clearly visible at 2077 cm⁻¹ and 2002 cm⁻¹. While these two peaks appear to respond to the phase change, and thus can be associated with DME, they were not reported in previous results and it is not clear what they represent. It is possible that they are weak combination bands of lower frequency modes. The broad $\delta(CH_3)$ deformation band at ~1466 cm⁻¹ splits into several sharp peaks. Only three of these-at 1485, 1470 and 1458 cm⁻¹-are clearly visible amid the interference of the atmospheric water in this part of the spectrum. Close inspection tentatively puts two additional crystalline DME peaks at 1437 and 1419 cm⁻¹. In the lower part of the spectrum, a small $\rho(CH_3)$ 1250 cm⁻¹ band appears. This band is likely present prior to the phase change also, but the baseline of this segment of the spectrum is partly obscured by an artefact. As such it is not able to be separated from the effective baseline at the lower temperatures. The large $v_a(COC)$ and $\rho(CH_3)$ coupled peaks grow dramatically at 75 K, approximately doubling in intensity. Additionally, the shoulder at ~1178 cm⁻¹ shifts to 1182 cm⁻¹, becoming more distinct, while the band at 1099 cm⁻¹ shifts slightly to 1097 cm⁻¹. Lastly, the v_s(COC) peak at 926 cm⁻¹ also increases in intensity and shifts to ~922 cm⁻¹. Unlike the results presented by Schriver-Mazzuoli *et al.*, no splitting is seen for this band in the results presented here.¹⁶⁹

As the temperature is increased beyond 70 K, additional subtle changes occur in the spectra. This potentially shows that—for anneal times of 3 min, as used here—higher temperatures are needed to complete the phase change. Looking at the spectrum following the 85 K anneal, the relative intensity of the peaks within split bands has shifted. For the $v'_s(CH_3)$ peaks at 2993 and 2985 cm⁻¹, the lower wavenumber peak has decreased in intensity. Conversely, for the 2825 and 2816 cm⁻¹ $v_s(CH_3)$ peaks, the higher wavenumber peak has decreased. The 1485 cm⁻¹ peak appears to grow while the 1458 cm⁻¹ peak appears to shrink. Lastly, the $v_a(COC)$ and $\rho(CH_3)$ coupled peaks shrink slightly and the $v_s(COC)$ peak shifts even further to ~920 cm⁻¹. The decrease in intensity for the coupled peaks may be evidence of some desorption occurring, which only causes a significant change in these strongest peaks. Further annealing to 90 K causes complete desorption, as seen in the last spectrum of figure 4.13. This is in line with the results in Schriver-Mazzuoli *et al.* as well as the TPD results shown in the previous section, allowing for differences due to the differing heating patterns between RAIRS and TPD.¹⁶⁹

Selected RAIR spectra are shown in figure 4.14 for the annealing of 20 L_m multilayer DME. The TPD results previously illustrated that a 20 L_m exposure also gives a multilayer ice, yet the effects of annealing are somewhat different from those seen for 50 L_m . While the same patterns are seen for all bands, the temperature-dependence is different. The phase change to the crystalline form still occurs between 65–70 K, but looking at the spectrum following 70 K annealing it clearly has a different character than the spectrum at the same point in the 50 L_m annealing sequence. In fact, it more closely resembles the 85 K spectrum shown in figure 4.13, which was ascribed to a more complete phase shift. This suggests that 20 L_m bulk DME undergoes the phase change more readily. This is further supported by the fact that there are no further substantial changes as the temperature is increased to 80 K. Apart from the phase change, another clear difference in the last spectrum of figure 4.14. In comparison, the 50 L_m ice was largely unaffected at this temperature.

4.3.2.3 DME Crystallisation Discussion

The adoption of a crystalline structure is seen both in the present work as well as in Schriver-Mazzuoli *et al.*, occurring between 65–70 K, and appearing most clearly as an increase in the sharpness of several bands, as well as splitting in bands associated with the CH₃ groups.¹⁶⁹ The previous study suggested non-equivalence of the methyl groups—that is, symmetry less than C_{2v} —as the cause of this splitting, citing much earlier work by Allan *et al.* looking at DME films on CsI or KBr windows at 78 K, which concluded such.^{169,191} However, Schriver-Mazzuoli *et al.* also allowed that it could be due to two types of molecule within each unit cell of the crystal, a conclusion which Allan *et al.* did not favour.



Figure 4.13. Spectra (30, 65, 70, 85 and 90 K) from the annealing sequence for 50 L_m DME adsorbed on HOPG at 30 K. Only wavenumber ranges with visible bands are shown: 3050–2775 cm⁻¹, 2100–1950 cm⁻¹, 1650–1200 cm⁻¹ and 1200–900 cm⁻¹.



Figure 4.14. Spectra (27, 65, 70, 80 and 85 K) from the annealing sequence for 20 L_m DME adsorbed on HOPG at 27 K. Only wavenumber ranges with visible bands (the same as for 50 L_m DME) are shown: 3050–2775 cm⁻¹, 2100–1950 cm⁻¹, 1650–1200 cm⁻¹ and 1200–900 cm⁻¹.

While the current work shows that the same phenomena occur on a graphite surface, which is of relevance to an interstellar context, the data do not appear to provide further insight into the physical origin of the splitting. Instead we may look to a slightly more recent work published by Vojinović *et al.* which has resolved the crystal structure via low-temperature x-ray crystallography, and is shown here in figure 4.15.²⁴⁸ The resolved structure exhibits one molecule in the asymmetric unit of the cell. This suggests that the splitting in the crystalline bands associated with the CH₃ groups is due to non-equivalence of the environments of the two methyl groups, rather than being due two types of molecule in the unit cell.



Figure 4.15. The crystal structure of DME, as determined by Vojinović *et al.* using low-temperature x-ray crystallography.²⁴⁸ The figure shown here is taken from the reference.

At low temperature the amorphous phase of DME exhibits a similar spectrum to the gas phase, as noted in section 4.3.2.1. The previous two figures have clearly illustrated the changes visible following annealing and attributed to crystallisation. The annealing causes no appearances or disappearances, however, and no effects which can be attributed to intermolecular coupling.¹⁹¹ This suggests that the DME molecules do not adopt a particular orientation relative to the HOPG surface, even in the ordered phase. This is clearly in good agreement with the previously recorded x-ray crystal structure, illustrated in figure 4.15, which exhibits DME molecules oriented in multiple directions.²⁴⁸

The apparent favouring of the phase change seen here at lower coverages contrasts directly with the results for 2-propanol and ethanol.²⁰² For these molecules—complex water-like species—phase changes are favoured with increasing coverage. This is proposed to be due to clustering as a result of their ability to hydrogen bond, which DME lacks. This supports the suggestion that DME does not island but rather
wets the graphite surface. The lack of strong DME-DME interactions will also have implications for the interaction of DME with water, which is considered in the following sections.

4.3.3 TPD Results for DME/Water Binary Ices

Understanding the interaction of COMs with water ice is crucial to understanding their behaviour within the ISM and other astronomical environments, and was considered as a major component in the classification of COMs by Burke *et al.*⁹⁶ Here the interaction between DME and water has been probed through experiments observing layered and mixed ices, in much the same way as it was investigated with 2-propanol. In figure 4.16, a set of TPD traces is shown for DME layered on top of multilayer CI. For each TPD, the CI was dosed using the previous method established for 2-propanol, and the DME was then deposited once the surface had cooled to \leq 30 K. Although a majority of ice in space is thought to be amorphous solid water (ASW), studying DME on CI is useful because CI presents an ordered surface without porosity, allowing a more straightforward consideration of the interaction between the DME and water ices.^{115,116} This can be useful for modelling a component of desorption from astrophysical ice surfaces, such as in Burke *et al.*²²⁶

4.3.3.1 Multilayers of DME on CI

The higher exposures of DME layered on CI, 10–30 L_m, are shown in figure 4.16(a). These appear at approximately the same temperatures as the peaks for the matching DME exposures on HOPG, with increasing coverage showing increasing peak temperature. Desorption becomes apparent at ~76 K and peaks from 88-92 K, rising as the coverage increases. Further, the TPD traces exhibit a common leading edge indicating zero-order behaviour. Leading-edge kinetic analysis for these DME layers results in a desorption order of 0.0 \pm 0.2. As such, exposures of 10–30 L_m DME on CI are considered the multilayer regime for further analysis. Because zero lies within the error limits, and the order should not be negative, the desorption energy of the multilayer DME was calculated assuming n = 0. This value is different than the fractional order (0.11 ± 0.09) used for multilayer DME on HOPG, but it is worth noting that with their respective errors the two values do overlap. Using n = 0 in the construction of Arrhenius plots for the 10–30 L_m traces resulted in an average value of 29 ± 2 kJ mol⁻¹ for the multilayer desorption energy. This value is very similar to the $30 \pm 2 \text{ kJ}$ mol⁻¹ average desorption energy for multilayer DME on HOPG, which is not surprising for the bulk DME ice, and confirms that the DME in this layered system is a multilayer. The multilayer pre-exponential factor was then calculated as $10^{31.5\pm1.4}$ molec m⁻² s⁻¹, which is very similar to the $10^{31\pm3}$ molec m⁻² s⁻¹ pre-exponential factor of the pure system. Again, this is expected as a bulk multilayer should not be significantly affected by the substrate.



Figure 4.16. TPD traces for a) 5–30 L_m and a) 0.5–5 L_m DME dosed at 27 K on top of multilayer CI. The CI peak shown is not to scale.

4.3.3.2 Monolayer DME on CI

While there is similarity in both the kinetics and the exposure range associated with the multilayer regimes of the DME on CI and the DME on HOPG systems, the behaviour of lower exposures shows significant differences. TPD for the lower exposures of DME on CI are shown in figure 4.16(b). A significant feature is immediately apparent which was not seen for DME on HOPG. This feature appears at a higher temperature in the TPD spectrum, relative to the multilayer peak. While desorption occurred predominantly between 80–100 K in the pure system, in this case a clearly separate peak is evident from the lowest exposures. This peak is roughly symmetrical with a maximum of ~120 K, and it grows in with increasing exposure, appearing to saturate between 3 and 5 L_m exposures, while also shifting the maximum slightly to ~119 K. Because of the approximately constant peak temperature and the overall higher desorption temperature, and because it saturates as the multilayer peak begins to appear, this peak is ascribed to a monolayer of DME interacting with the CI surface.

Unlike the monolayer coverages on HOPG, there is no extended trailing edge visible here. Considering this in combination with the nearly constant peak temperature indicates that DME does not have a significant coverage-dependence for its desorption energy, when interacting with water ice. The stronger adsorbate-surface interactions may limit the relative influence of adsorbate-adsorbate repulsion. Lastly, the significantly higher desorption temperature for the monolayer suggests a strong intermolecular interaction between DME and the water molecules at the surface of the CI layer. This is likely mediated by hydrogen bonding between water O–H and the DME oxygen. As noted in the previous chapter, while they are reduced in number relative to the ASW surface, CI does expose dangling O–H groups to allow hydrogen bonding to occur.¹¹⁸ A similar pattern was shown for methyl formate in previous work.^{96,226}

Applying kinetic analysis to 0.5–1 L_m resulted in a desorption order of 1.8 ± 0.5. This is significantly removed from the ideal n = 1, indicating additional complexity, presumably a consequence of the hydrogen bonding occurring between the CI surface and DME. The error range for this value is also very significant, and causes calculation of the desorption energy to have a very large error (38 ± 22 kJ mol⁻¹). A value of ~38 kJ mol⁻¹ is qualitatively reasonable. That is, it is somewhat higher than the desorption energy for the multilayer on CI and the desorption energy for the pure monolayer on HOPG, which both desorb at lower temperatures, as evidenced in figures 4.16 and 4.3, respectively. The value also compares well with the previous results for desorption of DME from CI reported by Lattelais *et al.* which showed desorption energies of ~34–36 kJ mol⁻¹ through theory and experiment.¹⁷⁹ As such it also contrasts with the much higher desorption energy they found for ethanol on CI (~56 kJ mol⁻¹).

Due to the substantial error and the non-ideal behaviour at the lowest coverages, straightforward leading edge analysis appears to be inappropriate for this system. Instead, the stochastic kinetics simulation previously used to fit the low coverages of pure DME on HOPG was also adapted to these data to evaluate the desorption energy.^{242,243} As before, the monolayer—represented by the 0.5 L_m TPD trace—was approximated as first-order (n = 1). With a pre-exponential factor of 10^{13} s⁻¹, the fitted desorption energy was 32 kJ mol⁻¹. This value for the energy also provided a good fit to the 1 L_m trace. Both fits are shown in figure 4.17. Like the leading edge analysis result, this value is higher than the multilayer on CI and monolayer on HOPG desorption energies, as would be expected. Varying the pre-exponential factor by an order of magnitude ($10^{12}-10^{14}$ s⁻¹) again provided an estimate for the error in the desorption energy (± 2 kJ mol⁻¹). Because of the clear non-ideal behaviour, the simulated result (32 ± 2 kJ mol⁻¹) is taken as the most accurate analysis of the data, supported by being close to the published ~34–36 kJ mol⁻¹ desorption energy.¹⁷⁹



Figure 4.17. Comparison of experimental (dotted lines) and simulated (solid lines) TPD spectra for 0.5 and 1 L_m sub-monolayer DME on multilayer CI. The parameters used for the simulation were $\nu = 10^{13} \text{ s}^{-1}$, n = 1, and $E_{des} = 32 \text{ kJ mol}^{-1}$, with a pumping rate of 30 s⁻¹.

4.3.3.3 Comparison of Intermolecular Interactions

The desorption energies and peak desorption temperatures for pure monolayer DME on HOPG, multilayer DME on CI and monolayer DME on CI are compared in table 4.4. The DME-graphite and DME-DME interactions are represented by monolayer DME on HOPG and multilayer DME on CI, respectively. The interaction energies must be quite similar as, allowing for uncertainty, the desorption energies actually overlap, while the desorption peak temperature ranges are very close. In contrast, the DME-H₂O interaction, represented by monolayer DME on CI, is clearly stronger. The desorption energy for this system appears to be the highest, although there is some overlap with the error margin. However, when considering the peak temperature also, the difference becomes clear. As noted earlier in the qualitative description of the TPD spectra, the desorption peak for monolayer DME on CI is much higher, at ~120 K. Overall then, this provides a picture of a relatively strong DME-H₂O interaction energy, with DME-DME being somewhat weaker, while DME-graphite is the weakest interaction, although the latter two are quite similar. Additional qualitative evidence of the strength of the DME-H₂O interaction is seen in the lack of the coverage-dependent effects in the monolayer desorption. In contrast to the monolayer DME on HOPG behaviour, this suggests the dominance of the DME-H₂O interaction over coverage-dependent effects.

Table 4.4. Comparison of desorption energies and desorption peak temperatures for consideration with respect to DME-graphite, DME-DME and DME- H_2O interaction.

System	E_{des} / kJ mol ⁻¹	T / K
monolayer on HOPG	~26-28	~92-100
multilayer on CI	29 ± 2	88-92
monolayer on CI	32 ± 2	~120

In particular, for the DME on CI system considered here, the strength of the interaction energy is expected to have a bearing on the structure of DME on the CI surface. The evidence that the DME- H_2O interaction is stronger than the DME-DME interaction is reinforced by referring again to the crystal structure of DME obtained by Vojinović *et al.*²⁴⁸ They found that oxygen interacts through five weak hydrogen bonds to neighbouring molecules, as seen in figure 4.18.^{248–250} Not only are these methyl C–H…O hydrogen bonds significantly weaker than the O–H…O hydrogen bonds water is capable of, they can be expected to be less stable due to the over-coordination of oxygen, which would optimally form two hydrogen bonds.^{222,251,252} The result of these relative interactions is that the DME- H_2O interaction is favoured, mediated by hydrogen bonding. As such, the DME is not likely to form islands at monolayer coverage or lower.



Figure 4.18. Illustration of the five C-H···O hydrogen bonds in the crystal structure of DME, as determined by Vojinović *et al.* using low-temperature x-ray crystallography.²⁴⁸ The figure shown here is taken from the reference.

4.3.3.4 DME on ASW

Traces for DME layered on 50 L_m multilayer ASW are shown in figure 4.19, with higher exposures of DME displayed in part (a) of the figure and lower exposures in part (b). For these TPD traces, the lowest temperature feature is a large peak which appears for all of the exposures >5 L_m . This peak

partially shares leading edges, with peak desorption rates appearing from 86–90 K. There is a much smaller peak at ~120 K, which is very similar in appearance to the peak at ~120 K in the TPD spectra for the DME-CI layered system. At ~140 K there is a volcano peak, coincident with the ASW-CI phase change shoulder feature in the TPD trace of the water ice.



Figure 4.19. TPD traces for a) 15–50 L_m and b) 2–15 L_m DME dosed at 27 K on top of 50 L_m multilayer ASW. The ASW peak is not shown to scale.

Based on the results for DME on CI, and the similarity of the ~120 K peak here, this feature is assigned to DME interacting with the water ice directly. Further, as both this feature and the volcano feature are close to saturation for exposures >5 L_m , the growing peak which appears at 86–90 K is assigned to multilayer DME. Additionally, this peak appears at approximately the same temperature as the multilayer DME features in both the pure DME and DME layered on CI systems. However, as this multilayer grows at 20 and 30 L_m , the behaviour shows some complication. While the leading edges are initially shared, the 90 K peak remains significant at 30 L_m . It is possible that the presence of the amorphous structured water interferes with the normal phase change which occurs prior to desorption, causing this shifting peak behaviour. The RAIRS results support this conclusion to some degree, as will be shown shortly. Finally, the highest temperature feature, visible at ~154 K, appears near the peak of water desorption and is therefore assigned to a small proportion of co-desorbing DME.

The multilayer and monolayer features appear at similar temperatures to those seen for the CI layers, yet the growth of the multilayer does not occur at the same exposures as for the DME:CI system, requiring higher exposures to appear here (>15 L_m for DME:ASW versus >10 L_m for DME:CI). The reason for this is demonstrated by the volcano peak at ~140 K, which is a clear indicator of trapping. The volcano feature grows with increasing dose until saturating at 10–15 L_m . This means that DME is able to penetrate into the porous ASW surface, becoming trapped during the temperature increase until its sudden release when the crystallisation of the water lattice disrupts the amorphous pores. This is significant in the context of the ISM, as it indicates that DME deposited or formed on the surface of an icy mantle might not be released into the gas phase until higher temperatures than otherwise expected. This is a behaviour seen for the other species in the complex intermediate classification, and is another result which points to the importance of water and its phase change behaviour in determining interstellar chemical evolution.⁹⁵⁻¹⁰⁰

4.3.3.5 DME/Water Mixtures

The last full set of binary ices in which DME was studied were mixed (co-deposited) ices. These ices were composed of 50 L_m ASW co-deposited with 9–50 % proportions of DME, comparable to the proportions used in the layered systems. The TPD traces for these mixed ices are shown in figure 4.20. A scaled-up view of the the spectra is inset in order to highlight the less intense features. The TPD are clearly dominated by the volcano, though in light of the DME:ASW layered ice results, this behaviour is not unexpected because the co-deposited water ice will trap a large proportion of DME from the start. The volcano peak appears initially at ~142 K, but grows and continues to shift to lower temperatures with increasing proportions of DME, appearing at ~138 K for 50 % DME. This differs somewhat from the DME-ASW layered system, where the volcano peak stabilised at ~140 K as it saturated. The shift appears to follow a corresponding shift in the ASW-CI transition shoulder feature of the water peak.

The ASW-CI feature appears at ~142 K when ASW makes up 81 % of the mixture, but this is shifted to ~138.5 K when ASW makes up only 64 % of the mixed ice, an effect illustrated in figure 4.21(c). This indicates that the increasing presence of the DME in the mixture has a small effect on the phase change of water, causing it to complete at slightly lower temperatures. The effect is also seen for the DME:ASW layered system, shown in figure 4.21(b), although to a lesser degree. This correlates with the smaller proportion of trapped DME in this system as seen in both the saturation and stabilisation of the volcano peak in the layered system. Overall, the effect of DME on the ASW-CI transition contrasts with that seen in the presence of the complex water-like species 2-propanol, where increasing amounts of the alcohol had a substantial inhibiting effect, shifting the phase change to higher temperatures to



Figure 4.20. TPD traces for DME dosed at 27 K simultaneously with ASW, with DME proportions of 9–50 %. The ASW trace corresponding to 22 % DME (78 % ASW) is shown for reference, but is not shown to scale.

the degree that it was no longer visible in the TPD (see section 3.2.5). Regardless, DME does have a small effect on the thermal processing of water, unlike methyl formate, despite other similarities seen for their surface behaviour.^{96,226}

In addition to the volcano peak there are three other, smaller features in the spectra for the mixed systems: a variable peak at ~100–110 K, a roughly symmetrical peak at ~120 K and a minor feature at ~151 K. For the 9 % DME mixture, only the latter two of these are apparent. The peak at ~120 K again appears very similar to the peak seen at this temperature for DME on CI and on ASW, which were ascribed to monolayer DME interacting with the water ice, principally via hydrogen bonding. As with the layered systems, this grows with increasing amounts of DME, although for the 50 % DME mixture it shifts to a slightly higher temperature of ~123 K. The reason for this shift is unknown, though it may be the influence of the very large volcano seen for this exposure. Although the ~120 K peak was assigned to monolayer DME in the other two DME:water systems, a monolayer does not make physical sense in the same way for a mixture. Instead it is proposed that this is representative of DME interacting with water on the interior surface of amorphous pores, close to the surface of the mixed of the mixed spectra.

For DME proportions of 22 % and greater, an additional feature is seen overlapping with the ~120 K peak. This feature starts at ~110 K for 22 % DME, and progresses to lower temperatures of ~100 K and ~95 K for 36 % and 50 % DME, respectively. While the ~120 K peak is thought to represent DME interacting with water within surface pores, this shifting feature is similarly proposed as a partial pocket of bulk pure DME within surface pores. The smallest feature, at ~151 K, coincides approximately with the peak desorption of the water ice. This feature again likely represents co-desorption and appears to



Figure 4.21. The TPD trace for a) pure ASW compared to traces for ASW in b) layered and c) mixed binary systems with DME, comparing the relative effects of the presence of DME on the ASW-CI phase change.

grow slightly with increasing DME proportion, although this may be due to overlap with the tail of the large volcano peak.

4.3.4 RAIRS Results for DME/Water Binary Ices

The interaction between DME and water was also investigated by RAIRS. While small changes were noticeable in the behaviour of ASW in the presence of DME (figure 4.21), the effects are not seen clearly in RAIRS data. The RAIRS results discussion here will therefore focus on DME behaviour in the binary ices. Although no additional findings arise from these data, it does support the picture of DME interaction with water derived from the TPD observations of the previous section, as will be shown. In the RAIR spectra for pure DME on HOPG, base temperature and 70 K were most significant, but in the more complex DME-water systems, other temperatures demonstrate key behaviour.

Shown in figure 4.22, represented by some of the stronger features of the spectra, 20 L_m DME on CI behaves in RAIRS quite similarly to 20 L_m DME on HOPG (shown previously in figure 4.14). Several spectra from the annealing sequence are shown in the figure. As the phase change appears at 70 K, the bands show essentially the same sharpening and splitting as they do for the pure system. The split $v_s(CH_3)$ band again shows greater intensity for the 2816 cm⁻¹ peak than for the 2823 cm⁻¹ peak. The 1250 cm⁻¹ $\rho(CH_3)$ feature again becomes distinct from the baseline at 70 K. Lastly, the $v_a(COC)$ and $\rho(CH_3)$ 1169 cm⁻¹ and 1097 cm⁻¹ coupled peaks sharpen and increase in intensity, with the shoulder of the former becoming more apparent, as was seen for the pure system.



Figure 4.22. RAIR spectra for the annealing of 20 L_m DME deposited on multilayer CI at 27 K. The 2925–2775 cm⁻¹ and 1300–1050 cm⁻¹ regions of the spectra are shown, to highlight the relatively strong bands at these wavenumbers.

However, following further annealing the 85 K spectrum—which for the pure system showed complete desorption—contains remaining features associated with the $v_a(COC)$ and $\rho(CH_3)$ coupled peaks. Here the bands now appear as a small peaks redshifted to 1163 cm⁻¹ and 1086 cm⁻¹. A minor shoulder remains at 1097 cm⁻¹. These features remain until following annealing at 120 K. In comparison to the TPD results for DME-CI layered system, these small, shifted peaks appear to represent the monolayer DME. Their appearance is largely obscured by the intense multilayer peaks until desorption of the multilayer at temperatures >80 K, and then they are seen to desorb at 120 K. These temperatures agree well with the desorption temperatures seen in the TPD for the multilayer and monolayer DME. This redshifting of the $v_a(COC)$ and $\rho(CH_3)$ modes is in line with previous matrix-isolation work which showed these effects for hydrogen-bond mediated complexation, providing strong support for the interpretation that these are bands for the monolayer.^{253,254}

The annealing sequences for DME layered on ASW are shown in figure 4.23, highlighting the same regions of the spectra as for the DME-CI layered system. The spectra in this case are seen to diverge more substantially from the pure results. The $v_s(CH_3)$ band does not split so clearly in this case, appearing instead as two broader overlapping peaks at 70 K, then as a blueshifted, single 2831 cm⁻¹ peak at 85 K. Additionally, the significant sharpening and increase in intensity is not seen for the $v_a(COC)$ and $\rho(CH_3)$ coupled peaks, however both peaks redshift slightly at 85 K, before returning to their original position at 120 K. The general intensity of the spectrum features decreases slightly at 85 K, then more substantially at 120 K, finally showing complete desorption at 140 K. As noted above, redshifting is indicated for the direct hydrogen-bonding interaction of DME and water. The same work additionally saw blueshifting of the $v_s(CH_3)$ modes.^{253,254} This supports a picture of thermally-driven interaction and mixing up to 120 K.

Comparison to the TPD results is not as distinct for the DME-ASW layered system, though the patterns in the spectra reveal a delayed and limited phase change for 20 L_m DME. This appears to be potentially consistent with the TPD data observed, for which examples were shown in figure 4.19(a). Unusual multilayer behaviour was attributed to inhibited DME crystallisation. Detected signal remains until at least 120 K, likely representing trapped DME. Complete desorption at 140 K coincides with the temperature at which volcano desorption would have occurred due to the crystallisation of water.

The mixture annealing spectra, shown for 24 % DME in figure 4.24, are the most removed from those of the pure system. The $v_s(CH_3)$ band remains broad at all annealing temperatures. This band appears to possibly shift following annealing at 130 K, however this may be an artefact of the baseline, as intensity is very small. The $v_a(COC)$ and $\rho(CH_3)$ coupled peaks appear at 1163 cm⁻¹ and 1090 cm⁻¹ — compared to 1169 cm⁻¹ and 1099 cm⁻¹ in the pure system. Unlike the layered systems, here a steady shift in the spectrum is seen prior to 70 K, for the lower frequency band of this pair. This appears as a large shoulder or second peak at 1078 cm⁻¹, which decreases in intensity with increasing annealing



Figure 4.23. RAIR spectra for the annealing of 20 L_m DME deposited on multilayer ASW at 27 K. The 2925–2775 cm⁻¹ and 1300–1050 cm⁻¹ regions of the spectra are shown, to highlight the relatively strong bands at these wavenumbers.

temperature. The appearance of this feature which is not seen in the other systems was also noted in the infrared spectra taken by Schriver-Mazzuoli *et al.*¹⁶⁹ Following annealing at 120 K, the $v_a(COC)$ and $\rho(CH_3)$ coupled peaks are shifted to 1167 cm⁻¹ and 1097 cm⁻¹, which appears to be more similar to the pure and layered systems, especially the DME-ASW layered system.

The mixture RAIR spectra overall do not show evidence for a significant phase change shift at 70 or 85 K. This appears to generally agree with the TPD, where only a minor component of the TPD trace is associated with multilayer, while the majority of the DME is seen trapped or interacting with porous ASW. Desorption is delayed even more so than for the DME layered on ASW, correlating with a greater proportion of trapped DME in the mixture ice. However, as also seen in the DME-ASW layered system, DME is fully desorbed at 140 K. This is again proposed to coincide with the volcano desorption which occurs at this temperature, representing the final major component of DME on the surface. The significant shift seen at 130 K or 120–130 K was considered by Schriver-Mazzuoli *et al.* to potentially represent the formation of clathrate hydrates, although it is not clear that this is the case at present.¹⁶⁹



Figure 4.24. RAIR spectra for the annealing of 24 % DME co-deposited with multilayer ASW at 27 K. The 2925–2775 cm⁻¹ and 1300–1050 cm⁻¹ regions of the spectra are shown, to highlight the relatively strong bands at these wavenumbers.

4.4 Summary and Conclusions

As in chapter 3, TPD and RAIRS have been applied to study the surface behaviour of a COM. Beginning with pure DME on graphite to understand the behaviour on a bare dust grain analogue—and without the complications of water interactions—TPD results showed the formation of a monolayer up to approximately 2 L_m exposures. The behaviour was non-ideal, with a coverage-dependent desorption energy which decreased as the monolayer approached saturation, suggestive of a repulsive interaction between the adsorbate DME molecules. This was taken as an early indication that DME is unlikely to form islands and instead initially adsorbs as a single monolayer on the HOPG surface.²²¹

The appearance of a new, low-temperature feature at ~1.5 L_m exposure, as the peak temperature begins to stabilise, suggests the start of a multilayer or possibly bilayer. Bulk multilayer behaviour, as indicated by zero order desorption, is not clearly seen until ~10 L_m , but there is no clear evidence of a bilayer at this stage. Kinetic analysis found a quantitative desorption order of 0.11 ± 0.09 for the multilayer. Although non-ideal, it was noted that this has been seen for other multilayer ices.^{93,201,202,218} Additional analysis gave a multilayer desorption energy of 30 ± 2 kj mol⁻¹ and a pre-exponential factor of $10^{31\pm3}$. Similar analysis for the monolayer was not possible due to the non-ideal behaviour, but a combination of peak fitting and the use of stochastic simulations provided an approximate monolayer desorption energy range of 26–28 kJ mol⁻¹.^{242,243} RAIRS data show the development of a crystalline phase at 70 K for 50 L_m DME ices, while for a smaller multilayer of 20 L_m there are indications of this phase starting at 65 K. This is in good agreement with previous results.¹⁶⁹ Additionally, the coverage-dependence of this phase change is taken as further evidence that DME does not interact strongly, supporting the suggestion that it could wet the graphite surface at lower coverages. This contrasts with 2-propanol and other hydrogen-bonding species, where low coverages limited phase change due to clustering of the ices as a result of strong hydrogen bonding and evidence points to the formation of islands.^{201,202}

The spectra of the crystalline phase are shown to be in good agreement with the literature experiments, with clear splitting of the methyl bands.¹⁶⁹ The results are also readily rationalised with regard to the published x-ray crystal structure.²⁴⁸ However, the nature of the crystal structure appears to limit the ability to gain insight into the ice orientation on the surface. The presence of amorphous water is shown to have an limiting effect on the ability for DME to crystallise, and this is linked to its ability to be a hydrogen-bond acceptor. Matrix-isolation experiments in the literature strongly support this conclusion.^{253,254} Additionally, the pattern seen in the spectra suggests that thermally-driven mixing occurs for DME/ASW binary ices, although this pattern shifts at ~120 K, the reason for which is not yet understood. The literature interpretation is formation of clathrate hydrates.¹⁶⁹ However, it also seems reasonable to attribute it to possible segregation of trapped DME ice, as the spectra shift away from the previous strong indication of hydrogen bonding, approaching the frequencies associated with the pure ice.

It seems certain that water kinetics will impact the surface retention and thus evolution of relative gas phase concentrations of DME in the ISM, which must be considered. Further conclusions, especially with regard to astrophysical implications, are addressed in the final chapter of the thesis.

Chapter 5

Acetaldehyde and Water Ice on HOPG

Acetaldehyde (CH₃CHO) is a COM that has been detected, along with other organic compounds, in a number of interstellar regions. It has been detected in translucent molecular clouds,¹⁵⁵ in cold molecular clouds,^{155,156} and in hot-cores and star-forming regions.^{9–12,147,148,152,153,157–161} Ikeda *et al.* report acetaldehyde showing an enhanced abundance relative to its isomer c-C₂H₄O in hot-cores.¹⁴⁷ The C₂H₄O isomers are of astrobiological interest, with acetaldehyde itself linked to the pre-biotic formation of amino acids.^{167,168} Acetaldehyde was also detected in the comet Hale-Bopp (C/1995 O1).⁵⁵ Together, these findings suggest acetaldehyde as a link between pre-biotic chemistry and the early Solar System.

As previously noted, ice mantle rather than gas phase chemistry is thought to be the main source of COMs in interstellar space.^{4,58,67} Organic species are proposed to be formed by successive hydrogenation reactions, possible due to the mobility of H atoms at low temperature. Several gas phase formation routes for acetaldehyde have been proposed.^{106,255–258} These do not generally explain the recorded abundances, however, though Nomura and Millar found that the reaction C_2H_5 + O could reasonably explain the abundance toward the hot-core G34.3+0.15.^{106,161,259} Grain-surface reactions followed by evaporation were proposed to explain the observations, but also failed to model the enhanced quantities of acetaldehyde seen in star-forming regions.^{147,161,167,258} Even so, as abundances are much higher than predicted by gas-phase reactions, solid state processes are thought to play an important role.^{147,161}

5.1 Previous Work

Many laboratory and theoretical studies have considered acetaldehyde on metal surfaces, using a range of surface science techniques, including temperature-programmed desorption (TPD) and reflection absorption infrared spectroscopy (RAIRS).^{180,181,260–268} These are not inert surfaces however, and both chemisorption and other reactions are observed, including helical chain polymerisation, which was fa-

voured by the deposition of bulk multilayers.^{180,262} Such polymerisation has a long history of study for acetaldehyde, where it was first observed forming in a low-temperature reaction by both Travers and Letort in 1936.^{269,270} Further work soon followed in order to understand the structure of the chain and the temperature-dependence of the polymerisation. It was shown that it was likely a polyoxymethylene—a structure first proposed by Staudinger—and that super-cooling and rapid freezing inhibited the polymerisation, as did the presence of water and alcohol.^{271–274} Both amorphous and crystalline polymers were observed spectroscopically and the catalysis of the polymerisation investigated.^{275–278} The first high vacuum observation of the production of acetaldehyde polymer was made by Madix *et al.* by detection of desorption from a Ni(100) surface.²⁶⁶

Although the infrared spectra are similar, there are key differences from the monomer that should allow production of the polymer to be determined spectroscopically.^{181,263,265,276,278} In addition, several studies have shown that the desorption temperature of acetaldehyde dissociating from the polymer is much higher than desorption of the monomer, such that desorption evidence of the polymer is expected at >200 K.^{180,181,260,262,263,266} Infrared spectra have been analysed by theory and experiment in several studies, including matrix-isolation work, although these and other modern papers often use the band assignments of Hollenstein and Günthard as a basis.^{94,279–284} Crystallisation has been observed at 70–80 K following annealing from lower temperatures by Ennis *et al.* and Ioppolo *et al.*^{94,284} The crystal structures of monomeric acetaldehyde were determined directly only relatively recently by neutron powder diffraction, confirming heat capacity evidence and suggestions from earlier work for two distinct crystalline phases: monoclinic P2₁/c, stable at low temperatures, and orthorhombic Pna2₁, metastable at higher temperatures.²⁸⁵

While studies such as those outlined above will aid in interpreting results here, it is essential to understand the surface-bound properties of acetaldehyde with a view to astrophysical conditions. In this regard, experimental and theoretical work by Bennett *et al.* has shown that acetaldehyde can be formed under interstellar conditions through the high-energy (5 keV) processing of CO:CH₄ and $CO_2:C_2H_4$ ices.^{167,286} Meanwhile, electron-induced reactions of acetaldehyde at cryogenic temperatures have shown the production of propionaldehyde and ethanol, as well as 2-propanol, linking acetal-dehyde to the work presented in chapter 3.²⁰⁹ These reactions were further explored particularly with regard to 2-propanol in a recent theoretical study, especially with respect to dimer interactions.²⁰⁸ As discussed in previous chapters, intermolecular forces have significant implications for physisorbed ices, and further work with acetaldehyde and related dimers has shown that C–H…O interactions can be significant.^{287,288}

A consideration of the interactions with water is important for the interstellar context, and the adsorption of acetaldehyde on water ices has been investigated by Darvas *et al.* due to its relevance to atmospheric chemistry on Earth.²²² They found that a monolayer of acetaldehyde forms hydrogen

bonds to dangling hydrogen atoms at the water surface, with individual molecules adopting a tilted orientation. A minimal coverage desorption energy of 36 ± 2 kJ mol⁻¹ was determined experimentally, supported by a simulated value of 34 kJ mol⁻¹. In related earlier work, Hudson *et al.* found an adsorption energy of 34.7 kJ mol⁻¹ for acetaldehyde on water between 120 and 180 K.²⁸⁹ More recently, Ioppolo *et al.* studied acetaldehyde along with other interstellar molecules using THz spectroscopy.⁹⁴ In addition to showing evidence of crystallisation, as already noted, they demonstrated that the acetaldehyde and water do not mix extensively, with results suggesting that acetaldehyde segregates and crystallises within amorphous water pores.

The aim of the present study will be to add to these studies and observe the thermal processing of acetaldehyde ices adsorbed on a graphite surface, which serves as an analogue for a carbonaceous interstellar dust grain, and to consider the interaction with water ices, which are common in many astronomical environments.^{87,88,95} Studying acetaldehyde in a surface-bound context is essential due to the importance of surface processes in the creation of COMs in space.^{4,20,57–59} Pure ices as well as binary ices with water will provide important quantitative and qualitative data for considering acetal-dehyde with respect to other COMs and to enable acetaldehyde to be more accurately incorporated into astrochemical models.^{166,226}

5.2 Experimental

The adsorption of acetaldehyde (\geq 99.0 %, Fluka Analytical) was studied in the laboratory on highlyoriented pyrolytic graphite (HOPG). TPD and RAIRS surface science methods were employed in the previously described studies of 2-propanol and dimethyl ether (DME), and these same methods were applied here. General procedures for deposition of thin-film ices and the analysis of TPD data were the same as described previously. The exception is that a modified procedure for the dosing of crystalline ice (CI) was used for this study. Rather than dosing at 120 K and subsequently annealing, it was found that dosing at base temperature and annealing to 135 K for 3 minutes produced CI. The crystallinity of the water ice was confirmed by the character of the ~3250 cm⁻¹ v(O-H) infrared band. This dosing procedure for CI has the advantage of being quicker, as well as leaving a greater quantity of water ice on the surface.

Pure acetaldehyde ices were studied on graphite, in addition to layered and mixed binary ices of acetaldehyde and water. Acetaldehyde was attached to the dosing line as a liquid sample, and the vapour above the liquid was used to fill the line prior to dosing. It was found that it was unnecessary to purify the acetaldehyde with freeze-pump-thaw cycles, as it did not improve purity. As before, the water samples were purified with two freeze-pump-thaw cycles. Acetaldehyde and water were introduced into the ultra-high vacuum (UHV) chamber via precision leak valves. All ices were created

by background dosing, with exposure of the graphite surface to $10^{-8}-10^{-7}$ mbar pressures. Mixed ices were co-deposited using the same method as for 2-propanol, described in section 3.1. The effects of thermal processing were explored—as done for 2-propanol and DME—by heating the surface.

For acetaldehyde, intensity traces of the mass fragments 44, 43, 29 and 15 m/z were detected by the quadrupole mass spectrometer (QMS). Intensity was recorded versus time during dosing and versus temperature during temperature-programmed desorption experiments. Mass 44 is the parent fragment for acetaldehyde, but for analysis, traces for the mass 29 (highest intensity) fragment were used, in order to maximise the signal-to-noise ratio. See figure 5.1 for a comparison of the mass fragment intensities as detected by the QMS during a TPD experiment for 20 L_m pure, non-irradiated acetaldehyde. All TPD traces were recorded during heating from ~30-250 K at a linear rate of 0.50 ± 0.01 K s⁻¹. For infrared spectroscopy experiments, a range of 800–4000 cm⁻¹ was recorded with a resolution of 4 cm⁻¹, co-adding 256 scans to provide a good signal-to-noise ratio in the spectra.



Figure 5.1. The mass fragment traces for 20 L_m acetaldehyde desorbing from HOPG during a TPD experiment.

5.3 Results and Discussion

5.3.1 TPD Data for Pure Acetaldehyde on HOPG

Figure 5.2 shows the TPD spectra (29 m/z) for 2–50 L_m pure acetaldehyde dosed on HOPG at 28 K. Using the approximate calculation method that was described in section 3.2.1, these exposures can be estimated to generate corresponding acetaldehyde ices of 0.10–2.43 nm average thickness over the 2 cm² surface.^{215,216} The traces exhibit partially shared leading edges from 10–50 L_m , with desorption peaks increasing with dose from ~104 K for 10 L_m to ~108 K for 50 L_m . A very clear exception is seen at 30 L_m , however this is partly thought to be experimental error, which will explained momentarily. Highlighted by the figure inset, both the 2 and 5 L_m traces exhibit slightly different desorption profiles.

This is especially noticeable for the 5 L_m trace, which clearly shows two overlapping features: a higher temperature peak at ~104 K and a lower temperature shoulder at ~99 K. At higher exposures, the 30 and 50 L_m traces also display complicating aspects. At 30 L_m , there are again two overlapping features: a peak at ~106 K and a significant shoulder at ~108 K. Although 50 L_m does not exhibit two distinct features, it does appear to have a distorted, convex shape to its trailing edge. In light of the 30 L_m result, this suggests a second feature that is masked by the large first peak. Additionally, another 50 L_m TPD spectrum—not shown—does exhibit what appears to be a slight shoulder on the trailing edge, though it is less distinct than the shoulder at 30 L_m .



Figure 5.2. TPD spectra for 2–50 L_m acetaldehyde dosed on HOPG at <30 K. The inset highlights the smaller peaks, for clarity.

It important to note here that the 30 L_m trace was recorded at a different time from the other spectra, which may have caused a slight shift in the temperature response. This is suggested by a comparison of the offset between the 20 L_m trace shown here and 20 L_m traces recorded at the same time as the 30 L_m trace. Such traces are shown later, in figure 5.18, as part of the discussion of coverage effects. They suggest that the 30 L_m shown in figure 5.2 should have a more similar leading edge to the other multilayer traces, but it is difficult to be certain. As such, the 30 L_m trace is presented here for qualitative comparison only and is not included in the quantitative analysis.

TPD spectra (29 m/z) for 0.5–2 L_m exposures of acetaldehyde are displayed in figure 5.3. Using the same calculation as for the larger exposures provides corresponding estimates of dosed ices with 0.02–0.10 nm average thickness deposited following these exposures.^{215,216} The traces in the figure show somewhat broad peaks, which appear at ~101 K for 0.5 L_m and at ~99 K for 1 and 2 L_m . The intensities of the leading edges for 0.5–2 L_m correlate with exposure, indicating a coverage-dependent desorption rate at these exposures. For all exposures, 0.5–50 L_m, no visible desorption is seen beyond the temperature ranges presented here, up to the 250 K maximum.



Figure 5.3. TPD spectra for 0.5–2 $L_{\rm m}$ acetaldehyde dosed on HOPG at <30 K.

The uptake of acetaldehyde on the surface during each exposure is illustrated by figure 5.4, which plots the integrated 29 m/z TPD areas against exposure. In figure 5.4(a) these values are plotted against the target exposure, while in figure 5.4(b) they are plotted against normalised relative exposures, as calculated by recorded dose traces. In both cases there is a very linear trend, though the fit is slightly better when the variation in exposure is accounted for by the use of relative exposure values. This linear trend indicates that the dose is linearly related to the exposure, and implies a constant sticking probability from the lowest coverages through to a bulk multilayer, suggestive that the monolayer is physisorbed on the surface.

Figure 5.5 illustrates in detail the shift in behaviour as exposure increases beyond $2 L_m$. Unlike other figures presented in this chapter, the TPD in this figure are labelled by their normalised relative exposures, rather than the intended target exposures. This is important because variations in the dose have significant effects on character of the TPD trace for this range of exposures. With that in mind, peak fitting strongly suggests that a low temperature feature at approximately 99 K remains for intermediate 6 and 7 L_m relative exposures. Even without peak fitting, this is particularly evident as a shoulder in the 7 L_m TPD spectrum. It is difficult to be certain about the fitted peaks due to the high degree of overlap, however, with the fits shown, the low temperature feature for both 6 and 7 L_m has very similar integrated areas to that of the 2 L_m peak, suggesting that they represent the same component of the adsorbed acetaldehyde. Meanwhile, though the low temperature feature shows minimal change between 6 and 7 L_m , the area of the higher temperature feature clearly increases in correlation with the relative



Figure 5.4. Integrated (80–140 K) TPD areas for 0.5–50 L_m acetaldehyde dosed on HOPG at <30 K, versus a) target exposure (r² = 0.991) and b) normalised exposure (r² = 0.998).

exposure. Altogether, this is strong evidence that the component of the acetaldehyde represented by the lower temperature feature is saturated for approximately $2 L_m$ exposures and greater.



Figure 5.5. TPD spectra for 1, 2, 6 and 7 L_m relative exposures of acetaldehyde, dosed on HOPG at <30 K. Peak fits are applied to 6 and 7 L_m , illustrating the development of an intermediate regime at ~5 L_m and potential saturation of the low temperature feature.

5.3.1.1 Discussion of Pure TPD Results

A primarily qualitative consideration of the spectra in figures 5.2 and 5.3 appears to indicate that there are three desorption regimes for the range of exposures presented. These are summarised by the illustration in figure 5.6. The first, appearing at the lowest exposures of $0.5-2 L_m$, is assigned to monolayer coverages of acetaldehyde on the HOPG surface. It is the first feature to appear at minimum exposure and therefore must be a result of acetaldehyde interacting directly with the graphite. Additionally, the approximately similar peak temperatures, coverage-dependent leading edges and the roughly symmetrical peak shapes are suggestive of first-order desorption, which is also expected for monolayer and sub-monolayer coverages.¹⁷³ The desorption temperature at 99–101 K appears reasonable and indicates physisorption. This temperature is slightly lower than the ~104 K temperature previously reported for the desorption of monolayer methyl formate on HOPG.⁹³ In contrast, it is significantly lower than values of ~160–190 K reported from TPD of acetaldehyde monolayers on metal surfaces.^{181,265} This highlights the weak interaction that graphite has with physisorbed monolayers. Lastly, it is interesting to compare the saturation of the monolayer at ~2 L_m with 2-propanol, which saturated a 'monolayer' at doses of ~10 L_m . Looked at another way, the 2-propanol monolayer was associated with an average

ice thickness of ~0.6 nm while the acetaldehyde monolayer is connected with a calculated average ice thickness of only ~0.1 nm. Based on molecular weight alone, such a large difference in dose response is not expected. In light of other evidence, it suggests that, unlike 2-propanol, acetaldehyde is wetting the surface and is therefore able to saturate a low coverage regime—a monolayer—at lower exposures.



Figure 5.6. Schematic representation of the proposed desorption regimes for pure acetaldehyde dose on HOPG at <30 K. Simplified depictions of the TPD trace character associated with each regime are shown to the right.

The second regime appears for exposures of around 5 L_m and is identified by the appearance of two discernible features. The two features, isolated by peak fitting as described at the end of the previous section and illustrated in figure 5.5, indicate a more complex structure as exposure increases. The similarity between the low temperature feature at 6 and 7 L_m and the desorption peak seen for 2 L_m acetaldehyde suggests that the monolayer saturates at ~2 L_m , allowing the assignment of the monolayer regime at 0.5–2 L_m as described. However, the saturated monolayer clearly remains a significant component in the TPD in this intermediate regime. That the monolayer is able to continue to desorb at ~99 K—even beyond the point where two monolayer-equivalents (~4 L_m) have been added to the surface—implies that it is not trapped and there must therefore be gaps in the overlayer. This complex desorption regime is attributed to the formation of islands above the saturated monolayer, as described by the Stranski–Krastanov intermediate growth mode, previously noted in section 3.2.1.3.²²¹ Such a growth mode indicates an intermediate strength for adsorbate-adsorbate intermolecular interactions

relative to adsorbate-surface interactions. This would seem to be consistent with the chemical structure of acetaldehyde, which has a moderate ability to hydrogen bond and a relatively unhindered polar carbonyl group.^{208,287,288} As such assignment of the intermediate growth mode is appropriate, distinct from the islanding suspected for 2-propanol and comparable to the surface-wetting behaviour indicated by DME. Similar TPD profiles to those demonstrated by this regime were observed for intermediate exposures of benzene on Cu(111) and methyl formate on graphite.^{93,290} These were attributed to bilayer formation by those species, and in the case of the methyl formate work this was also with reference to similar results for ethanol.^{93,202}

The third regime is clearly in effect at exposures of 10 L_m and above. Although the onset of desorption is at a very similar temperature, the profile of the leading edge is subtly distinct from that of the lower exposures. This can be observed with close attention to the figure 5.2 inset. Additionally, there are no longer two distinct desorption features, and the TPD spectrum is dominated by a single peak, as seen for methyl formate.⁹³ This single, asymmetrical peak, which increases with temperature, suggests that from this exposure the majority of the acetaldehyde is a bulk multilayer above the surface. The TPD leading edge is also shared-at least for 10 and 20 Lm-which also indicates a bulk multilayer.¹⁷³ The initial appearance of the peak for this regime is at a very similar temperature to the high-temperature feature seen in the intermediate regime, supporting the assignment of the feature in the intermediate regime to clustered islands. That is, they are both representative of bulk condensed acetaldehyde. The peak temperature for the multilayer is similar to that of methyl formate, appearing at a slightly lower temperature, following the same pattern as previously shown for comparison of the monolayer desorption temperature.⁹³ In surface science work on metal surfaces, multilayer desorption of acetaldehyde is seen at ~113–150 K. 181,260,265,268 This is generally higher than the ~108 K for 50 L_m acetaldehyde on graphite seen in the present work, but may be primarily due to the different heating rates employed, which vary from 1-13 K s⁻¹. This rationalisation is supported by the fact that the most comparable heating rate to the present work is the 1 K s⁻¹ employed by Li et al.²⁶⁵ This produced a multilayer desorption temperature of ~113 K, which is quite similar to the result here.

For 30 and 50 L_m new complications arise, and the trace diverges from the behaviour of an ideal multilayer. At these highest exposures studied, there is again the appearance of two features in the TPD spectra. Rather than being related to the layer structure as in the intermediate regime, the cause of this is proposed to be due to coverage-dependent phase change behaviour in acetaldehyde, which was also previously seen for 2-propanol as well as other molecules, as discussed in chapter 3.^{201,218,236} This behaviour is quite significant and will be explored later in the chapter, with additional data from infrared spectroscopy experiments.

In previous work, TPD evidence of polymerisation has been generally seen in the form of desorption peaks at high temperatures.^{181,263,265} TPD peaks beyond the ~108 K temperature of the multilayer

desorption peak are not evident in the present work. As such, no polymerisation is thought to occur on graphite, even with multilayer coverage, which previous work found favours polymerisation. This is not unexpected as the graphite surface is inert, whereas surface-induced polymerisation so far has been seen for transition metal surfaces, where stronger interactions and chemisorption are possible.^{181,263,291} Additionally, there is no evidence to suggest that paraldehyde is forming, as was concluded by Sim *et al.* for their results.²⁶³ Desorption of the oligomer would be indicated with a low relative intensity of the mass fragment 29 m/z detected by QMS, which is counter to the results here, as seen in figure 5.1.

5.3.1.2 Pure Acetaldehyde Desorption: Kinetic Analysis and Discussion

Kinetic analysis was performed, as was done for 2-propanol and DME, beginning with the construction of linear order plots. The overall pattern seen for these plots is illustrated in figure 5.7. The 50 L_m exposures are not included in the fit, as they do not follow the linear pattern of the other high coverages. As noted previously, 30 L_m results can not be included in the quantitative analysis because they were recorded at a different time, such that the recorded temperatures were slightly offset. However, based on the poor fit of the 50 L_m data indicated here, the 30 L_m data would also likely be problematic, as it displayed two distinct features in the TPD spectra.



Figure 5.7. Illustration of fits to the two desorption regimes for pure acetaldehyde adsorbed on HOPG at <30 K, showing points for all recorded spectra, analysed at 98.5 K. The linear fit for higher coverages does not include the data points for $50 L_m$, due to the anomalous behaviour.

While figure 5.7 provides an illustration using data points at 98.5 K, for the actual analysis the spectra were considered at several different temperatures along the shared leading edge. The results of this analysis applied to the TPD for three 10 L_m and five 20 L_m exposures are presented in table 5.1 and provide an average desorption order of 0.0 ± 0.1 for this regime. Because n = 0 falls within the estimated error limits—and the order should not be negative—the desorption order is assumed to be zero. If 50 L_m is included in the analysis for this regime, the resulting value is negative (-0.2 ± 0.1), in

which case it would also be necessary to assume that the desorption order is zero. An approximately zero-order desorption, combined with the previously stated observation of shared leading edges and increasing peak heights, allows this regime to be confirmed as a bulk multilayer, as was also seen for both 2-propanol and DME multilayer coverages.¹⁷³ As noted previously in chapters 3 and 4, this is commonly observed and is expected for multilayer desorption.^{93,118,175,201,202,204,218,224}

Table 5.1. Multilayer order of desorption values for acetaldehyde on HOPG, evaluated from TPD spectra following 10 and 20 L_m exposures, which were previously shown in figure 5.2. The values were obtained from linear fits like the one illustrated for the higher coverages in figure 5.7. Errors are 95 % confidence intervals for the individual linear fits.

Temperature / K	Order, <i>n</i>
97	0.1 ± 0.4
98	-0.1 ± 0.3
99	-0.1 ± 0.2
100	-0.1 ± 0.2
101	0.0 ± 0.2
102	0.0 ± 0.2
103	-0.1 ± 0.1
104	0.0 ± 0.2

The lower exposures of 0.5–2 L_m were assigned as monolayer coverages from qualitative observations. This is supported by the goodness of the linear fits in the order plots, as illustrated here by figure 5.7. The desorption order for this regime can therefore be confidently evaluated from the TPD spectra for 0.5–2 L_m . The analysis was applied to TPD results for two each of 0.5, 1 and 2 L_m exposures. The results are given in table 5.2, and provide an average monolayer desorption order of 1.4 ± 0.2. This is non-ideal ($n \neq 1$) but approximates a first-order desorption process.¹⁷³ However, it is not unreasonable as similar fractional order values have been seen for low coverages of other interstellar molecules, resulting from their molecular interactions.^{93,201,202,218–220} This was also observed for 2-propanol in the results presented in chapter 3, and as in that case, the fractional order is usually attributed to hydrogen bonding. Historically, hydrogen bonding is not expected to be as significant for acetaldehyde.²⁹² However, the previously noted shift in peak temperature between 0.5 and 1 L_m indicates complicating factors related to coverage, suggesting the influence of adsorbate-adsorbate intermolecular forces. This could be another result that can be attributed to C–H…O interactions, which recent work has shown to be important for molecules such as acetaldehyde.^{208,287,288}

Using the calculated values for desorption order, Arrhenius plots were constructed to quantify the energies of desorption, in each case assuming a constant desorption order value. For the multilayer 10 and 20 L_m TPD analysis, a single plot was made for each TPD trace, using an order of n = 0. For the monolayer 0.5–2 L_m analysis, two plots were made for each TPD trace, using order values of n = 1.2

Temperature (K)	Order, <i>n</i>
93	1.5 ± 0.3
93.5	1.0 ± 1.0
94	1.5 ± 0.7
94.5	0.9 ± 0.6
95	1.1 ± 0.9
95.5	1.2 ± 0.3
96	1.7 ± 0.3
96.5	1.6 ± 0.3
97	1.7 ± 0.4
97.5	1.6 ± 0.1
98	1.3 ± 1.0
98.5	1.5 ± 0.5

Table 5.2. Monolayer order of desorption values for acetaldehyde on HOPG, evaluated from TPD spectra following 0.5–2 L_m exposures, which were previously shown in figure 5.3. The values were obtained from linear fits like the one illustrated for the lower coverages in figure 5.7. Errors are 95 % confidence intervals for the individual linear fits.

and n = 1.6 to account for the error in the monolayer desorption order ($n = 1.4 \pm 0.2$). Examples of these plots are shown in figure 5.8 and the set of desorption energy values evaluated for both the multilayer and monolayer regimes is listed in table 5.3. The multilayer analysis results in an average value of 35.4 ± 0.8 kJ mol⁻¹ for the desorption energy, and the pre-exponential factor for the multilayer is then $10^{32.1\pm0.4}$ molec m⁻² s⁻¹. For monolayer coverages, the average energies are 28 ± 3 kJ mol⁻¹ and 29 ± 3 kJ mol⁻¹ for n = 1.2 and n = 1.6, respectively. The overall desorption energy for the monolayer is therefore approximately 28 ± 4 kJ mol⁻¹ with the combined error limits. Currently, the uncertainty for the monolayer desorption order and desorption energy prevent calculation of a precise pre-exponential factor for the kinetics of this desorption regime. Using the established minimum-maximum method, varying the desorption order and energy within their respective error limits, the calculated factor is $10^{8\pm5}$ s⁻¹. Although this covers the expected $10^{12}-10^{13}$ s⁻¹ expected for a physisorbed monolayer, the uncertainty is too large for the calculated value to be meaningful.¹⁹⁵ As in previous chapters, ideal first-order units are given here, for simplicity.

In general, the desorption energy values calculated here are reasonable for a pure ice physisorbed on graphite.²⁰¹ This is readily seen with broad comparison to values for 2-propanol and DME reported in chapters 3 and 4, which ranged from ~26–52 kJ mol⁻¹. In turn, the values therefore compare well with many previous similar results for physisorbed ices, as discussed in chapters 3 and 4. However, in particular, as noted in section 5.3.1.1, the desorption temperatures for the monolayer and multilayer regimes are quite comparable to methyl formate.⁹³ As such they are more similar to DME than to 2-propanol. Considering the kinetic parameters determined here supports this association. The 35.4 ± 0.8 kJ mol⁻¹



Figure 5.8. Example Arrhenius plots illustrating the analysis of TPD data for 2 L_m (upper) and 10 L_m (lower) acetaldehyde adsorbed on HOPG at < 30 K. As shown in the upper figure for 2 L_m , for each monolayer TPD trace, two Arrhenius plots are constructed in order to determine the variation in the slope caused by the uncertainty in the evaluated desorption order.

Table 5.3.	Desorption	energy 7	values fo	r acetalde	hyde on	HOPG,	evaluated	from	the	individual	TPD	spectra
represented	by figure 5.	2, and ol	otained fi	om linear	fits like	those illu	strated in I	figure	5.8.			

mult	ilayer	monolayer			
Exposure / L_m	$E_{des} / kJ mol^{-1}$ (n = 0)	Exposure / L _m	$E_{des} / \text{kJ mol}^{-1}$ (n = 1.2)	E_{des} / kJ mol ⁻¹ (n = 1.6)	
10	34 ± 1	0.5	24 ± 5	25 ± 5	
10	36 ± 2	0.5	26 ± 4	26 ± 4	
10	36 ± 1	1	24 ± 4	25 ± 4	
20	34 ± 1	1	31 ± 4	32 ± 4	
20	36 ± 1	2	31 ± 3	32 ± 3	
20	36 ± 1	2	30 ± 3	31 ± 3	
20	37 ± 1				
20	36 ± 1				

desorption energy for multilayer acetaldehyde is very comparable to previous literature values of ~35 and 34 kJ mol⁻¹ for multilayer methyl formate.^{93,293} Similarly, the monolayer desorption energy of 28 ± 4 kJ mol⁻¹ compares with the ~26–28 kJ mol⁻¹ evaluated for DME, in the previous chapter. These comparisons are not surprising following the earlier qualitative analysis, as the desorption energy is expected to correlate with desorption temperature. With reference to the discussion of the previous chapter, this then suggests that, like DME, acetaldehyde may be placed in the complex intermediate classification, which agrees with the prediction made by Burke *et al.*⁹⁶ The behaviour demonstrated by the interaction of acetaldehyde and water ices is essential to confirm such an assignment, however, and will be discussed later in this chapter.

Lastly, considering the general thermodynamics of acetaldehyde, the enthalpy of vaporisation is reported as ~26 kJ mol⁻¹.²⁹⁴ This is lower than the ~35 kJ mol⁻¹ desorption energy for sublimation from the bulk multilayer solid, as expected. However, it compares quite closely to the monolayer desorption energy, perhaps being slightly lower, suggesting that the interaction strength between acetaldehyde molecules is similar to the interaction between acetaldehyde and graphite. This is in line with the qualitative discussion of section 5.3.1.1, which concluded an intermediate interaction strength and growth mode for acetaldehyde on graphite.

5.3.2 RAIRS Data for Pure Acetaldehyde on HOPG

RAIRS spectra for the adsorption of pure acetaldehyde at base temperature were recorded for 5, 10, 20 and 50 L_m cumulative exposures. Following the initial 5 L_m exposure, sequential exposures of 5, 10 and 30 L_m were additionally dosed to generate the totals shown. This is illustrated in figure 5.9, which demonstrates an increase in band intensity but no clear differences otherwise. This is then quantified in figure 5.10 by plotting integrated peak areas versus cumulative exposure. The peak areas are calculated from the absorbance spectrum, which is not shown, rather than the $\Delta R/R$ spectrum presented here in figure 5.9. This indicates that—for up to 50 L_m exposures—there are no coverage-dependent adsorption effects for pure acetaldehyde ices on HOPG at base temperature, in good agreement with the uptake previously measured by TPD. This was also generally true for 2-propanol, as shown previously, as well as for other astrophysically relevant molecules adsorbed at cryogenic temperatures.^{201,202} This provides additional confirmation that acetaldehyde is in the form of physisorbed bulk multilayers on graphite at >5 L_m exposures, which is further supported by the very good agreement between the cumulative and single–exposure 50 L_m doses, as illustrated in figure 5.9.

The RAIR spectrum of pure acetaldehyde on HOPG, at base temperature (<30 K), is illustrated in figure 5.11. Band assignments are labelled in the figure and listed in table 5.4 with reference to the literature.^{180,181,265,279,281–283} Much of the recent infrared work with acetaldehyde, including the Ar matrix and $WO_3/Pt(111)$ surface work listed in the table, assigns bands at least to some degree based on



Figure 5.9. RAIR spectra, in the region 1000–3100 cm⁻¹, for acetaldehyde cumulatively adsorbed on HOPG at <30 K. The spectrum (dotted line) for 50 L_m dosed in a single exposure is included for comparison.



Figure 5.10. Uptake of acetaldehyde, adsorbed cumulatively on HOPG at <30 K to produce total doses equivalent to 5, 10, 20 and 50 L_m exposures, as measured by integrated peak area of infrared absorbance bands.

an infrared study published by Hollenstein and Günthard, which investigated gas phase and crystalline acetaldehyde.^{265,282,283} Overall, the appearance of the spectrum is in very good agreement with that recorded by Li *et al.* for multilayer acetaldehyde on $WO_3/Pt(111)$ at 25 K.²⁶⁵ As they state, all peaks are attributed to acetaldehyde at base temperature, indicating monomeric molecular adsorption on the surface.^{265,283}



Figure 5.11. RAIR spectrum in the region $850-3050 \text{ cm}^{-1}$ for 50 L_m acetaldehyde dosed on HOPG at <30 K. Only those regions of the spectrum which show clear bands are displayed.

At 3005 cm⁻¹ there is a small band assigned to the $v_a(CH_3)$ antisymmetric stretch, while at 2918 cm⁻¹ there is a minimal band assigned to the $v_a(CH_3)$ symmetric stretch. The latter assignment is somewhat tentative because it is close to the noise level in the spectrum, but it is in good agreement with previous work, as shown in the table. The region 2900–2700 cm⁻¹ is difficult to assign precisely due to combination bands arising from the $\delta_a(CH_3)$, $\delta(CH)$ and $\delta_s(CH_3)$ deformation modes at 1435, ~1400 and 1350 cm⁻¹, respectively.^{279,283} The v(CH) fundamental is also in this range, however, and here it is assigned to the 2764 cm⁻¹ band, although this band is also likely influenced by combinations. Below 2764 cm⁻¹ there are no peaks visible until the very strong band at 1730 cm⁻¹, which is assigned to the v(C=O) carbonyl stretch mode. Between 1500 and 1300 cm⁻¹ are the previously-mentioned deformation modes, then at 1126 cm⁻¹ is the v(CC) stretch mode. Although not assigned as such in the figure or table, this band likely has a contribution from the $\rho(CH_3)$ methyl rocking mode, as the v(CC) and p(CH₃) modes are strongly coupled.^{263,283} Lastly, there is a very small but distinct band at 887 cm⁻¹, resulting from the $\rho(CH_3)$ rocking mode. Due to the stated coupling, though not listed as such in the figure or table, this band likely has a contribution from the v(CC) stretch.^{263,283}

mode	this work	Ar matrix ²⁸²	WO ₃ /Pt(111) ²⁶⁵	$Ag(111)^{181}$	liquid ²⁷⁹	gas ²⁸³			
$v_a(CH_3)$	3005	3022	3002		2964	3014			
$v_s(CH_3)$	~2918	2921	2860		2917	2923			
comb.	~2866				2843-2731	2830-2716			
v(CH)	2764	2736	2760		2843	2716			
v(C=O)	1730	1729	1727	1728	1714	1743			
$\delta_a(CH_3)$	1435	1427	1432	1426	1426	1433			
δ(CH)	~1400	1399	1392	1390	1391	1395			
$\delta_{s}(CH_{3})$	1350	1349	1347	1348	1342	1352			
v(CC)	1126	1111		1122	1109	1114			
ρ(CH ₃)	887	873	888		885	867			
v = stretching, δ = deformation, ρ = rocking, comb. = combination									

Table 5.4. Vibrational wavenumber (cm⁻¹) values and their mode assignments for 50 L_m acetaldehyde adsorbed on HOPG at <30 K. Data from the literature are included for comparison.^{181,265,279,282,283}

5.3.2.1 Symmetry Analysis Notes

Gas phase acetaldehyde has C_s symmetry, as illustrated in figure 5.12. So far there is good evidence that acetaldehyde physisorbs on clean graphite. This means that minimal perturbation of the internal mode frequencies is expected with respect to the gas phase.²⁹⁵ Although changes to the already low symmetry are not expected due to lack of bonding with the surface, the interaction of the dipole moments with the surface selection rule can be considered, as discussed by Sim *et al.*²⁶³ That is, the infrared response is expected to scale with the normal component of dynamic dipole moments, relative to the surface. This can provide information on the orientation of the acetaldehyde molecules with respect to the graphite, and will be used to interpret results as part of the discussion presented in section 5.3.2.4.



Figure 5.12. Illustration of the application of the C_s point group assignment to acetaldehyde, with the associated character table shown to the right.

A total of 3N - 6 = 15 normal modes are expected for a molecule composed of N = 7 atoms and having 3N = 21 degrees of freedom. As noted by Evans and Bernstein in the discussion of assignments for their recorded infrared spectra of acetaldehyde, symmetry analysis classifies the vibrational modes into two types as represented by

$$\Gamma_{vib} = 10A' + 5A''$$

with all modes being infrared active.²⁷⁹ Three modes previously recorded in other studies are expected at <800 cm⁻¹, which is out of the range presented here.^{279,283} Of the remaining twelve modes, nine are A' and three are A''. The currently assigned modes, as given in table 5.4, are all A' modes. However, there is some ambiguity that allows for the A'' modes to be present but obscured. In particular, the $\delta_a(CH_3)(A')$ and $\delta(CH_3)(A'')$ modes are expected to directly overlap at ~1430 cm⁻¹.^{279,283} Although not clearly visible in the base temperature spectra, the next two sections consider the thermal processing of acetaldehyde and will show the relevance of the A'' modes and their relationship to the molecular geometry and the understanding of the acetaldehyde solid structure.

5.3.2.2 Annealing Multilayer Acetaldehyde

The infrared spectrum recorded following the 75 K annealing of 50 L_m acetaldehyde, which had been adsorbed on HOPG at <30 K, is shown in figure 5.13. The base temperature (28 K) spectrum is also included, for comparison. The 75 K anneal is chosen for display here because it is the lowest temperature that shows evidence of significant changes in the spectrum relative to the base temperature. The acetaldehyde had been annealed to both 50 and 70 K prior to being annealed to 75 K, but the spectrum did not show any significant response. At 75 K, sharpening and splitting are seen across the spectrum, and some of the new features are assigned to A'' modes. These assignments, and the assignment of a small new combination mode at 1408 cm⁻¹, are based on the assignments of Hollenstein and Günthard.²⁸³ The tentative new combination mode is very weak and is not labelled in the figure.

Most bands in the spectrum are affected after the annealing at 75 K, though for the very small $v_s(CH_3)$ and $p(CH_3)$ bands there is some uncertainty due to noise. At the high end of the spectrum, the $v_a(CH_3)$ band shifts from 3005 cm⁻¹ to 2999 cm⁻¹ and both sharpens and grows in intensity. A weak feature at 2964 cm⁻¹ is tentatively assigned to the $v(CH_3)(A'')$ stretch mode. The $v_s(CH_3)$ band at 2918 cm⁻¹ shows minimal change at 75 K, though there may be a slight sharpening of the feature. The adjacent combination band splits into two distinct, sharp features: a relatively strong band at 2883 cm⁻¹ and a much weaker band at 2858 cm⁻¹. The v(CH) stretching mode band narrows slightly, with a small sharp peak at 2771 cm⁻¹ and a small shoulder feature at 2764 cm⁻¹.

Looking to the middle of the spectrum, the v(C=O) stretch band splits into a broad band at 1728 cm⁻¹ and a sharp band at 1714 cm⁻¹. Notably, the intensity and peak area of the bands are greatly decreased relative to the base temperature band, which is at 1730 cm⁻¹. The 1435 cm⁻¹ δ_a (CH₃) methyl deforma-



Figure 5.13. RAIR spectrum for 50 L_m acetaldehyde dosed on HOPG at <30 K, following annealing to 75 K for 3 minutes. Only those regions of the spectra that exhibit acetaldehyde bands are shown. The base temperature spectrum (dotted line) is included for reference.

tion mode splits into a small sharp peak at 1450 cm⁻¹ and a more intense, sharp peak at 1425 cm⁻¹. The 1450 cm⁻¹ band is tentatively assigned to the $\delta(CH_3)(A'')$ mode. A very weak feature at 1408 cm⁻¹ may be a $\rho(CH_3) + \delta(CCO)$ combination band.²⁸³ At 1392 cm⁻¹ the $\delta(CH)$ band is still quite small but has grown in intensity, such that it can be assigned to a precise frequency. The lowest frequency deformation band, $\delta_s(CH_3)$, splits into a strong, sharp band at 1354 cm⁻¹ and a very small, but sharp, band at 1348 cm⁻¹.

Finally, at the lower section of the spectrum the v(CC) stretch mode sharpens and grows in intensity, shifting to 1122 cm⁻¹. The appearance of a similar sharp band at 1111 cm⁻¹ could simply be the result of splitting and shifting of the v(CC) band. However, here it is assigned to the significant intensifying of the $\rho(CH_3)(A'')$ rocking and $\pi(CH)(A'')$ bending out-of-plane coupled modes, with reference to the literature.²⁸³ This assignment is also supported by spectra for lower coverages, which will be explored in the next section. Close to the limit of the spectrum, the $\rho(CH_3)$ band appears to shift from 887 cm⁻¹ to 897 cm⁻¹.

When annealed to temperatures above 75 K, the infrared spectrum reveals gradual changes up to 95 K. These are illustrated in figure 5.14 by spectra recorded following annealing at 85 and 95 K. No significant changes are seen in the bands for the deformation modes at these temperatures, so they are not shown in the figure. The $\rho(CH_3)$ band at ~897 cm⁻¹ is also not shown due to uncertainty caused by its weak intensity.



Figure 5.14. RAIR spectra for 50 L_m acetaldehyde adsorbed on HOPG at <30 K, following annealing to 75, 85 and 95 K, for 3 minutes each. Only those regions of the spectra that have clearly changing acetaldehyde bands—at the temperatures listed—are shown. Vertical lines mark the 75 K peaks.

For most of the spectrum, no significant change is seen until 95 K, where a number of features are altered. The $v_a(CH_3)$ band shifts to 3005 cm⁻¹ at this temperature. Also, the relative intensity exhibited by the two peaks of the split combination band changes, with the 2883 cm⁻¹ band reduced and the 2858 cm⁻¹ band increased, such that they show similar intensities. The relative intensities of the features of the v(CH) band are also altered. Here the shoulder at 2764 cm⁻¹ grows in intensity to become the main peak of the band, while the former peak at 2771 cm⁻¹ remains at a similar intensity, becoming a shoulder feature. Changes seen in the v(C=O) stretch band are the exception in that there is an observable significant difference between the 75 and 85 K spectra. While the sharp 1714 cm⁻¹ band is unchanged, the broad band at 1728 cm⁻¹ grows, and begins to show evidence of a third peak at 1724 cm⁻¹. This third peak grows to become the most intense at 95 K, with the 1728 cm⁻¹ peak becoming a shoulder. Also at 95 K, there is a small reduction in the intensity of the 1714 cm⁻¹ band. Lastly, while there was no significant change at 85 K, the v(CC) band shows a slight increase and the $\rho(CH_3)(A'')$ band shows a moderate decrease.

Spectra were also recorded following annealing at 100 and 105 K but are not shown. At 100 K the bands are significantly reduced, a response that is ascribed to the onset of desorption. This makes it difficult to consider structural changes beyond 95 K. The character appears quite similar to the 95 K spectrum, albeit reduced in intensity. The subsequent 105 K spectrum displays no evidence of any acetaldehyde bands, indicating complete desorption during the course of annealing at this temperature.

This is consistent with the TPD results for 50 L_m acetaldehyde, which showed the onset of minor desorption at ~90 K and a peak desorption rate at ~109 K, as shown previously in figure 5.2.

5.3.2.3 Coverage-Dependence Effects

Annealing experiments were also performed on 20 L_m acetaldehyde ices. In light of the anomalous TPD results at high exposures, the behaviour of this thinner multilayer ice was predicted to be different from that of the 50 L_m ice. While this proved to be so, it was observed during repeat experiments at 20 L_m that there was significant variation in the response to thermal processing by the spectra recorded for different 20 L_m doses. There is expected to be some variation in exposure due to experimental error. As such, it was hypothesised that small changes in multilayer ice thickness around this exposure had a critical effect on the behaviour of the ice.

In order to test the hypothesis more deliberately, additional annealing experiments were conducted at 25 and 30 L_m . Select bands from the annealing sequences for 20, 25 and 30 L_m are included in the comparison shown in figure 5.15. The bands chosen are those for the v(C=O) stretch mode; the $\delta(CH_3)(A'')$, $\delta_a(CH_3)$, $\delta(CH)$ and $\delta_s(CH_3)$ deformation modes; the v(C-C) stretch mode; and the $\rho(CH_3)(A'')$ mode. The spectra as presented have been scaled relative to the initial exposures. This is only approximate and is not meant to impart a strict quantitative meaning, but it is done here to simplify qualitative visual comparison. Additionally note that the parts (a), (b), (c) and (d) of the figure are not toscale relative to each other. The spectra shown follow 75, 85 and 95 K annealing temperatures, although 85 K anneal spectra are omitted where they do not show a significant change from the respective 75 K spectra. Spectra following annealing at 100 and 105 K were also recorded, though they are not shown here. It was previously noted for 50 L_m that the 100 K spectrum primarily indicates the onset of desorption, while 105 K shows complete desorption. This pattern holds for 20, 25 and 30 L_m also.

The v(C=O) band is shown in figure 5.15(a). As seen in the annealing of 50 L_m , the band splits into peaks at 1728 and 1714 cm⁻¹ at 75 K. For all three exposures, increasing temperature favours increased relative intensity of the 1728 cm⁻¹ peak, which develops a discernible feature at 1724 cm⁻¹ as the intensity increases. However, there is a clear coverage-dependence. At 75 K the 25 and 30 L_m spectra are comparable, showing greatly reduced peak areas and a slightly stronger peak intensity in the sharp 1714 cm⁻¹ band relative to the intensity of the 1728 cm⁻¹ band. On the other hand, at 75 K the 20 L_m spectrum already shows a moderately strong band at 1728 cm⁻¹. As seen for 50 L_m , there is no significant change in the bands for 30 L_m at 85 K. At this temperature, the 25 L_m spectrum begins to show growing relative intensity of the 1728 cm⁻¹ band, while 20 L_m exhibits a substantial increase in the intensity of the 1728 cm⁻¹ band for 20 L_m , with the appearance of a slight shoulder feature at ~1724 cm⁻¹. The band for 25 L_m undergoes a substantial change at 95 K, adopting a very


Figure 5.15. RAIR spectra of select bands for 20, 25 and 30 L_m acetaldehyde adsorbed on HOPG at <30 K, following annealing to 75, 85 and 95 K, for 3 minutes each. The base temperature spectra (dotted lines) are included for reference. The 85 K anneal spectra are omitted where they do not show a significant difference relative to 75 K.

comparable profile to that of the 20 L_m band. Although unchanged at 85 K, the 30 L_m band starts to show a significant modification at 95 K with the 1728 cm⁻¹ band starting to grow and exhibiting a shoulder at ~1724 cm⁻¹. However, it does not approach the relative intensity seen in the 20 and 25 L_m , and for 30 L_m some intensity is retained in the 1714 cm⁻¹ band, even at 95 K.

The deformation bands for $\delta(CH_3)(A'')$, $\delta_a(CH_3)$ and $\delta(CH)$ are shown in figure 5.15(b). At these frequencies, the influence of atmospheric water bands must be considered, especially with regard to the small 1450 cm⁻¹ band assigned to the $\delta(CH_3)(A'')$ mode. However, at all three coverages this feature consistently follows the behaviour pattern of the more intense peaks. That is, it disappears for both 20 and 25 L_m upon adoption of the final state at 85 and 95 K, respectively, while for 30 L_m, which does not show that character at any temperature, the 1450 cm⁻¹ feature is retained. This feature is therefore assigned to acetaldehyde rather than water. This contrasts with the small feature seen at ~1456 cm⁻¹ in some of the spectra, which does not show such a correlation and—unlike the 1450 cm⁻¹ feature—is also found in the background spectrum.

Returning to observations of the overall pattern in figure 5.15(b), at 75 K the spectra are similar at all three coverages, though the 20 L_m spectrum shows slightly stronger relative intensity in the 1425 cm⁻¹ band and a feature which suggests a small shoulder at ~1432 cm⁻¹. At 85 K neither 25 nor 30 L_m show significant change, while 20 L_m does, as the shoulder feature grows in intensity to become a sharp peak at 1432 cm⁻¹. The peak at 1425 cm⁻¹ is retained as a clearly defined shoulder. At 95 K the 20 L_m spectrum shows minimal change, while the 25 L_m spectrum shows a substantial change to adopt a very similar spectral profile to that seen for 20 L_m . This is similar to the results shown for the v(C=O) band in part (a) of the figure. The bands in this section of the spectrum for 50 L_m remained unchanged until desorption, when annealed >75 K, but some slight changes are evident for the 30 L_m spectrum at 95 K here, indicating there is a little variation between these two large exposures.

The $\delta_s(CH_3)$ deformation band is shown in figure 5.15(c) and shows a similar pattern to the deformation bands in figure 5.15(b), but with a slightly more pronounced coverage dependence. At 75 K the 1354 cm⁻¹ band shows increasing relative intensity with increased coverage, while the 1348 cm⁻¹ band shows decreasing relative intensity. At both 85 and 95 K the 20 L_m bands show small changes. Again, neither 25 nor 30 L_m exhibit significant changes at 85 K, and again, at 95 K the 25 L_m spectrum shows a significant change to adopt a similar profile to the 20 L_m spectrum, while the 30 L_m spectrum shows only a minor change. For both 25 and 30 L_m, changes are seen in the 1348 cm⁻¹ band but not in the 1354 cm⁻¹ band for these temperatures.

Lastly, the bands for the v(CC) and $\rho(CH_3)(A'')$ modes are shown in figure 5.15(d). Notably, the base temperature spectrum shows a weak feature at ~1109 cm⁻¹ at all three coverages. This supports the assignment of the 1111 cm⁻¹ band to $\rho(CH_3)(A'')$ rather than a crystalline mode of v(CC). The reason this feature was not seen in the base temperature spectrum for 50 L_m acetaldehyde may be that at

such a high exposure it is masked by the adjacent broad and relatively strong amorphous v(CC) band. Returning to observations of coverage-dependence, overall the v(CC) does not show temperaturedependent effects above 75 K nor does it show coverage-dependent effects. The small exception is a slight increase in intensity for the 20 L_m band, but only at 95 K. This contrasts with the $\rho(CH_3)(A'')$ band, which shows both temperature-dependent and coverage-dependent effects. At 75 K, the relative intensity of this band correlates with increased exposure. Following a similar pattern to the coveragedependent pattern seen so far, at 85 K this band is unchanged for both 25 and 30 L_m , while for 20 L_m it is has changed substantially. In this case the change is such that it is no longer distinguishable in the spectrum. At 85 K the 25 L_m band exhibits a significant change and adopts a similar profile to that of the 20 L_m spectrum. This is also in line with the general pattern of coverage-dependence, that is, the band is no longer significant in the 25 L_m spectrum at 95 K. The 30 L_m band shows moderate change but as with other bands shown for the 30 L_m exposure, its spectrum does not match the spectra of the lower 25 and 20 L_m exposures, and it desorbs before it could potentially do so.

5.3.2.4 Discussion of Pure RAIRS Results

Firstly, the RAIRS results confirm the earlier conclusion, drawn from the TPD data, that polymerisation of acetaldehyde is not seen on bare graphite at UHV. The infrared spectra of both amorphous and crystalline polyacetaldehyde have been obtained by a number of groups.^{181,263,265,276,278} While reduction in v(C=O) is seen in the results of the present work—as would be expected in polymerisation—this is instead attributed to surface-relative orientation effects, which will be discussed shortly. In particular, the subsequent growing intensity of v(C=O) at higher temperatures—but not so high as to allow depolymerisation—disfavours attributing the changes seen in the v(C=O) band to polymerisation.^{181,262,263,265}

Of the evidence that would be expected if acetaldehyde polymer were present, the most unambiguous is the appearance of distinct $v_a(O-C-O)$, $v_s(O-C-O)$ and $\rho(CH_3)$ bands in the ranges 1146– 1199 cm⁻¹, 1040–1099 cm⁻¹ and 915–973 cm⁻¹, respectively, as shown in table 5.5. No such bands are seen in the current work. The possibility that polymerisation occurs but these bands are excluded by surface-selection is rejected due to the established helical structure of polyacetaldehyde.^{263,264,275} The structure would not be expected to be significantly perturbed on graphite, yet with such a structure, most of the dipole moments would necessarily have a component normal to the surface.^{263,291}

The RAIR spectra for pure acetaldehyde adsorbed on HOPG show very complex modification in response to thermal processing, with additional complications added by the observed coverage-dependent behaviour. The variable effects relative to exposure are confidently assigned to different temperature responses, rather than differences in base temperature structure, with reference to figures 5.4, 5.9 and 5.10, which illustrate linear adsorption. Base temperature acetaldehyde is assigned to amorphous mono-

mode	(CH ₃ CHO) _n crystalline ^{276*}	(CH ₃ CHO) _n crystalline ²⁷⁸	(CH ₃ CHO) _n ²⁶³	³ (CH ₃ CHO) _n ¹⁸¹	$(CH_3CHO)_n^{265}$
v _a (O–C–O)	1187	1187, 1158	1175, 1160	1189, 1173	1199, 1146
v _s (O–C–O)	1085, 1040	1083, 1040	1090, 1084	1034	1099, 1043
ρ(CH ₃)	970, 935	973, 933	915	946	97 0
1.	1.				

Table 5.5. Data from the literature indicating vibrational wavenumber (cm^{-1}) values, and their assignments, formodes of crystalline and amorphous polyacetaldehyde that are distinct from the monomer modes.181,263,265,276,278

v = stretching, $\rho =$ rocking

* assignments made by Sim et al.²⁶³

meric multilayers physisorbed during dosing, as evidenced by the broad bands in the spectra, and with support from literature results, which demonstrate that acetaldehyde adsorbs in an amorphous state at cryogenic temperatures.^{94,265,284} Close agreement with gas phase and Ar matrix isolation results, in particular, support the conclusion of physisorption, as previously shown in table 5.4.^{282,283}

Changes are first observed following 75 K annealing, for all multilayer coverages studied, in the form of general sharpening of bands across the spectra and the appearance of newly-distinct features. As observed in previous chapters, the former behaviour in particular is suggestive of a more ordered structure. The spectra at 75 K are therefore attributed to crystallisation of the amorphous acetaldehyde ice. This is supported by the existing literature, which shows evidence of crystallisation at 70–80 K.^{94,284} Polymerisation is also observed at this temperature, in previous work.²⁶⁵ Although polymerisation is not seen on graphite, the temperature is relevant as it indicates that acetaldehyde is able to diffuse on the surface and propagate polymerisation.²⁶⁵ On graphite, this mobility could instead simply allow a phase change to occur, supporting the assignment.

The interpretation of the behaviour seen for subsequent annealing at 85 and 95 K is the shift to a second crystalline phase. Although certainly different in character, the spectra seen at these temperatures, particularly for 20 and 25 L_m , continue to show a clearly crystalline profile in comparison to the base temperature spectra, with relatively intense peaks and splitting of bands. For this reason, the changing character >75 K is not attributed to a return to an amorphous state, although band frequencies do shift closer to the base temperature frequencies, as seen in figure 5.15. Hollenstein and Günthard previously found that there were two solid phases occurring for acetaldehyde, but their ability to draw conclusions was limited by available X-ray data at the time.²⁸³ However, they did show clear evidence of hysteresis effects, as did Schneider and Bernstein.²⁹² The coverage-dependent behaviour seen in the present work may be related to this. The existence of two crystalline phases was confirmed in more recent work by Ibberson *et al.*, using neutron powder diffraction.²⁸⁵ Additionally, it is notable that two crystalline phases have also been indicated for methyl formate and ethyl formate in previous infrared studies, and there are similarities in the spectra for those ices to the spectra presented here, particularly with regard to the character of the v(C=O) band, which shows overlapping features and a sharp peak at slightly lower frequency.^{296,297}

The second crystalline phase appears to be best represented by ices dosed at lower exposures, with 20 L_m adopting an approximately stable spectral character at ~85 K. In combination with the complete disappearance of some 75 K features such as the sharp 1714 cm⁻¹ v(C=O) and 1111 cm⁻¹ ρ (CH₃)(*A''*) modes, this suggests that the 85 K spectrum is indicative of a complete phase change. The proposed two phases are here termed 'phase I' and 'phase II'. Acetaldehyde from a 30 L_m —or more so, 50 L_m —exposure appears to demonstrate the phase I features most strongly. That is, it emphasises the features seen particularly at 75 K in the spectra. However, like all doses observed, it appears to show some phase II character at 75 K also. In contrast, acetaldehyde from a 20 L_m exposure appears to readily adopt significant phase II structure even at 75 K, though it does retain some phase I character until 85 K. Phase I and phase II are illustrated for reference in figure 5.16, where phase I is represented by 30 L_m after annealing to 75 K and phase II is represented by 20 L_m after annealing to 85 K.



Figure 5.16. RAIR spectra directly comparing representative examples of 'phase I' and 'phase II' acetaldehyde on HOPG. Phase I is represented by $30 L_m$ after annealing to 75 K and phase II is represented by $20 L_m$ after annealing to 85 K. A spectrum of amorphous acetaldehyde is included underlaid below phase I, for comparison, and is represented by $30 L_m$ after dosing on HOPG at base temperature.

Recent spectroscopic work looking at acetaldehyde has clearly shown crystallisation but has not investigated multiple phases.^{94,284} In particular, Ennis *et al.* expected to only see a stable monoclinic P2₁/c phase at ~70 K, based on the previous results by Ibberson *et al.*^{284,285} The identified structures are monoclinic P2₁/c, stable at low temperatures, and orthorhombic Pna2₁, metastable at higher temperatures.²⁸⁵ These are illustrated in figure 5.17, which is taken from the reference. Ibberson *et al.* noted that

the orthorhombic Pna2₁ structure is consistent with much earlier X-ray work.^{285,298} Referencing the X-ray data, Hollenstein and Günthard attributed their crystalline infrared spectra, acquired following deposition at 77 K and annealing to 110 K, to this Pna2₁ crystal structure. However, as noted previously the available structure data was limited at the time, and they also observed a higher temperature metastable phase following deposition at 110 K, which they were unable to assign.²⁸³ Both Ibberson *et al.* and Hollenstein and Günthard saw some stable phase combined with the metastable phase.^{283,285} For the latter, this was especially seen for thicker ices. This correlates well with the coverage-dependent behaviour seen in the current work, where overlapping phase I and phase II character is particularly seen for thicker ices. Based on the previous results, the phase I spectra are thus assigned as monoclinic P2₁/c, while the phase II spectra that appear particularly at higher temperatures are assigned to the orthorhombic Pna2₁ crystal. However, it is notable that the orthorhombic phase is observed at a significantly lower temperatures for the thin-film ices studied in the present work.



Figure 5.17. Crystal structures for a) monoclinic $P2_1/c$ and b) orthorhombic $Pna2_1$ acetaldehyde, determined by high-resolution neutron powder diffraction by Ibberson *et al.*²⁸⁵ The figure is adapted from the reference.

Consideration of the monoclinic crystal suggests that the character of the phase I spectra can be reasonably explained by its structure. As illustrated by the figure, all carbonyl bonds are similar within the crystal, which would be expected to sharpen the v(C=O) band. At the same time, if the crystal were oriented relative to the graphite such that the aligned carbonyl bonds were parallel to the surface, the v(C=O) band would be greatly reduced due to surface selection. This could explain the appearance of the sharp, weak 1714 cm⁻¹ v(C=O) band—and the reduced peak area of the v(C=O) bands in general—in phase I spectra. Additionally, the redshift is quite significant, at -16 cm⁻¹ relative to the gas-phase frequency from the literature.²⁸³ Previously, Darvas *et al.* observed overlapping bands at 1728 and 1717 cm⁻¹ for an acetaldehyde layer interacting with water ice.²²² The 1717 cm⁻¹ band was assigned to O–H…O hydrogen bonds due to interaction with the water, while the redshifted frequency—relative

to the gas phase—of the 1728 cm⁻¹ band was attributed to C–H···O hydrogen bonds. This is consistent with matrix-isolation studies of carbonyl-containing molecules that observe redshifting of the v(C=O) stretch in response to hydrogen bonding with water.^{299–302} Such a shift is seen for acetone, formaldehyde, formamide and acetic acid in these studies, so it is reasonable to expect a similar effect for acetaldehyde.

However, O–H…O hydrogen bonding is precluded in the pure acetaldehyde. The redshift of the 1714 cm⁻¹ band here may instead be due to a combination of moderate C–H…O hydrogen bonds and the favourable C=O…C=O alignment in the monoclinic P2₁/c crystal structure. Both types of intermolecular association were shown to be important to the interaction energy in studies of acetaldehyde dimers.^{208,287,288} For the time being, the 1728 cm⁻¹ seen here is not associated specifically with the monoclinic P2₁/c structure. It appears to represent the appearance of phase II in addition to phase I at 75 K. This is supported by the frequency agreement with the strong main peak of the band seen in the phase II spectra at higher temperatures.

The monoclinic P2₁/c structure may also explain the appearance of the A'' modes, which are antisymmetric with respect to the σ_h symmetry plane, as illustrated in figure 5.12. If the crystal were oriented such that the symmetry planes of the acetaldehyde molecules were approximately parallel to the surface, the bands arising from the dipole moment changes associated with the A'' modes would be enhanced. Such an orientation would also explain the relative weakness of the v(CH) and δ (CH) bands in phase I. The v(CH) band in particular is expected to be strong for acetaldehyde.²⁸³

Lastly, the relationship to the anomalous behaviour seen in the TPD can be considered in light of these two phases. A few additional TPD spectra were recorded following 20 and 30 L_m acetaldehyde exposures dosed both at base temperature and at 75 K, as illustrated in figure 5.18. These experiments show that the dosing temperature does not affect the TPD spectra of 20 L_m acetaldehyde on HOPG. This can be understood with reference to the RAIRS results, which showed that 20 L_m acetaldehyde readily adopts phase II before desorption. That is, regardless of adsorption temperature, the TPD is expected to only detect desorption of phase II for 20 L_m acetaldehyde.

The same desorption profile is seen for 30 L_m adsorbed at 75 K, indicating it is likely deposited as phase II at this temperature. However, for the 30 L_m exposure dosed at base temperature, the intermediate phase I state is expected to be retained to some degree at the point of desorption, as shown clearly by the 30 L_m spectra in figure 5.15. The high temperature retention of this phase for >30 L_m exposures is then readily ascribed to the origin of the high temperature shoulder seen in the 30 L_m TPD spectrum, and to the anomalous desorption kinetics seen in the quantitative analysis of 50 L_m TPD.



Figure 5.18. TPD spectra for 20 L_m and 30 L_m exposures of acetaldehyde, dosed on HOPG at base temperature <30 K and at 75 K.

5.3.3 Acetaldehyde/Water Binary Ices

It has been well-demonstrated in the previous chapters that it is vital to consider the interaction of COMs with water ice. The functional groups in acetaldehyde, as well as the desorption temperature observed for the pure ice on graphite, indicate that it will most probably follow the behaviour of other complex intermediate COM species, and it will therefore interact with water in a broadly similar pattern to that shown by DME in the previous chapter, as described in sections 4.3.3 and 4.3.4.⁹⁶

5.3.3.1 TPD Data for Acetaldehyde on CI

The results for acetaldehyde layered on CI are shown first, in figure 5.19. This surface is most similar to the ordered surface of HOPG and its simplicity allows for a focus on the interaction between acetaldehyde and water molecules, without the complications of temperature-driven changes in the bulk structure of the water ice. Figure 5.19 shows TPD spectra for acetaldehyde layers deposited on top of pre-dosed multilayer CI at <30 K. Figure 5.19(a) shows the spectra for higher 5–30 L_m doses of acetaldehyde, while figure 5.19(b) shows TPD following exposures of 0.5–5 L_m. A single representative trace for multilayer CI is also shown, in part (a) of the figure, for reference.

All TPD for the larger exposures, in figure 5.19(a), exhibit two observable peaks. The lower temperature peak (α) grows rapidly with increasing exposure, while the peak temperature progresses from ~101 K to ~104 K. This peak demonstrates shared leading edges for these exposures, although for 5 L_m the desorption rate falls away before the maximum. For these spectra, the second peak (β) is evident as a significant shoulder feature on the trailing edge of peak α . Although the character of peak β is partially masked by the much larger peak α , it appears to be saturated for these exposures. This is demonstrated by the 5 and 10 L_m TPD traces in the figure 5.19(a) inset.



Figure 5.19. TPD spectra for a) $5-30 L_m$ and b) $0.5-5 L_m$ acetaldehyde dosed on multilayer CI at <30 K. A trace for CI (not to scale) is shown in section (a) of the figure, for reference. Peak fits (dotted lines) for 2 and 5 L_m are included.

For the lower doses in figure 5.19(b) the 5 L_m TPD trace is shown again, providing a reference for scale. In TPD for 0.5 and 1 L_m , peak β appears as the only desorption feature. At 0.5 L_m the maximum is at 128 K, but as the exposure increases to 1 L_m and greater, this peak appears to shift to a slightly lower temperature of ~124–125 K. At 1–2 L_m an additional feature grows in, deforming the leading edge of peak β , which appears to saturate at these doses. By 5 L_m the additional feature appears to grow into the dominant peak α . Because peak β appears at the lowest exposures, demonstrates coverage-dependent desorption rates and then saturates at only 1–2 L_m , it can be assigned to monolayer acetaldehyde saturated at ~2 L_m and, as noted, CI and HOPG are both ordered substrates and will present a similar surface area. Meanwhile, peak α appears just as peak β saturates, and then continues to grow with larger doses, suggesting that it is multilayer acetaldehyde above the CI surface. The shared leading edge and the similarity with the TPD peaks for pure multilayer acetaldehyde on HOPG support this assignment.

The same method of kinetic analysis shown in section 5.3.1.2 for the pure TPD was applied to the traces shown here. Constructed order plots over the temperature range 97–103 K for peak α in the 10–30 L_m high-exposure traces, as listed in table 5.6, provide an average desorption order value of 0.1 ± 0.1. Because zero is within the error limits, the desorption order is assumed to be zero. This helps to confirm that peak α represents bulk multilayer acetaldehyde above the CI surface.¹⁷³ With n = 0, Arrhenius plots were made for peak α from three 10 L_m, two 15 L_m, four 20 L_m and two 30 L_m TPD traces. The evaluated desorption energies are tabulated in table 5.7 and provide a calculated average of 37.4 ± 0.9 kJ mol⁻¹ for multilayer acetaldehyde on CI. The calculated multilayer pre-exponential factor is 10^{33.1±0.5} molec m⁻² s⁻¹. The uncertainty in the pre-exponential factor is determined by varying the desorption energy through its error limits, as in previous analyses.

Table 5.6. Multilayer order of desorption values for acetaldehyde on CI, evaluated from peak α in 10–30 L_m TPD spectra, such as illustrated in figure 5.19(a). Errors are 95 % confidence intervals for the individual linear fits.

Temperature (K)	Order, <i>n</i>
97	-0.1 ± 0.2
98	0.1 ± 0.2
99	0.1 ± 0.1
100	0.1 ± 0.2
101	0.1 ± 0.2
102	0.1 ± 0.2
103	0.2 ± 0.1

Because only 0.5 L_m exposures display peak β as a single, unmodified feature, it is the only exposure appropriate for use in leading-edge analysis of this peak. As such, at the present time quantitative analysis is very limited for these small coverages of acetaldehyde on CI. By assuming that n = 1, Arrhenius

Exposure / L _m		E _{des} / k	J mol ⁻¹	
10	35 ± 2	36 ± 2	35 ± 2	
15	39 ± 1	38 ± 1		
20	37 ± 1	37 ± 1	39 ± 2	37 ± 1
30	39 ± 1	39 ± 2		

Table 5.7. Desorption energy values for acetaldehyde on CI, evaluated from peak α in 10–30 L_m TPD spectra, such as illustrated in figure 5.19(a). Errors are 95 % confidence intervals for the individual linear fits.

plots for peak β from the two recorded 0.5 L_m TPD traces provide an average energy of desorption of ~42 kJ mol⁻¹. As noted in previous chapters, such a value is reasonable for physisorption. Assuming ideal first-order desorption for this analysis seems reasonable because the lowest coverages of acetaldehyde on CI show similar peak desorption temperatures and coverage-dependent desorption rates, which approximate the characteristics of first-order desorption.¹⁷³ Also, qualitative observations suggest peak β represents monolayer acetaldehyde desorption, providing additional justification for the assumption. The pre-exponential factor was not evaluated for peak β because the calculated desorption energy is only an approximation.

5.3.3.2 TPD Data for Acetaldehyde on ASW

TPD spectra for 0.5–30 L_m acetaldehyde layered on multilayer amorphous solid water (ASW) were also recorded. As seen in previous chapters, this binary ice system can help to show evidence of mixing or trapping of the COM by the water ice as the latter undergoes structural changes in response to thermal processing. Smaller exposures of acetaldehyde (0.5–10 L_m) are displayed first, in figure 5.20.

For 0.5–2 L_m , enhanced in the figure inset, there are two principle peaks. The low temperature peak appears first at ~127 K and shifts to ~125 K as the exposure increases. This is very comparable to peak β from the previous section and the same designation is used here. This suggests that this is also acetaldehyde desorbing from the water ice surface, supported by the presence of this peak from the lowest exposures. The higher temperature peak (γ) visible for 0.5–2 L_m is very sharp and coincident with the ASW-CI shoulder feature in the water trace. This is clearly demonstrated in figure 5.21. Peak γ is therefore assigned to volcano desorption of trapped acetaldehyde.

As exposure increases to 2 L_m and greater, two additional features become apparent. At 2 L_m the leading edge of peak β is clearly distorted by an additional feature. This is followed by the appearance of a significant low-temperature peak at ~108 K. By comparison with the TPD of the previous section, this is again designated peak α , representative of rapidly-growing multilayer acetaldehyde. The second new feature as exposures increase is a very small, high-temperature peak (δ), which appears at ~152–154 K. This feature is partially masked by the trailing edge of peak γ , but it does not appear to grow significantly with exposure. The temperature for this peak is at or slightly following that of the water



Figure 5.20. TPD spectra for 0.5–10 L_m acetaldehyde dosed on multilayer ASW at <30 K. A representative trace for ASW (not to scale) is shown, for reference.



Figure 5.21. Comparison between the shift in volcano peak γ temperature for acetaldehyde layered on ASW and the corresponding shift in the ASW-CI shoulder feature. TPD for 0.5 and 5 L_m acetaldehyde, dosed on 50 L_m multilayer ASW at base temperature <30 K, are used here as examples.

desorption peak, indicating that this can likely be assigned to co-desorption of acetaldehyde. Overall, the arrangement and development of peaks in figure 5.20 is broadly very similar to the pattern seen for DME, with reference to figure 4.19 on page 93 in the previous chapter.

Larger exposures of 10–50 L_m acetaldehyde on ASW are represented in figure 5.22. The evolution >10 L_m primarily demonstrates the continuing growth of the low-temperature peak α dominating the spectra. This peak exhibits shared leading edges for this range of exposures, especially for >20 L_m , further confirming that this is again evidence of multilayer desorption. The intermediate peak β at 126–128 K is also seen, shifting to ~130 K as exposure increases. It is difficult to discern the character of this peak due to the strong peak α and peak γ trailing and leading edges, respectively. The shift in the volcano peak γ appears to stabilise for acetaldehyde exposures >25 L_m , while at the same time saturating and showing a consistent intensity for 30–50 L_m . At the highest-temperature end of the spectra, the co-desorption peak δ remains visible at 152 K for all TPD in this range.



Figure 5.22. TPD spectra for 10–50 L_m acetaldehyde dosed on multilayer ASW at <30 K. A representative trace for ASW (not to scale) is shown, for reference.

The low-temperature peak α presented by the 5–30 L_m range of exposures is the only peak that presents a leading edge appropriate for quantitative kinetic analysis. As noted, this peak exhibits a shared leading edge, particularly for 25–50 L_m, suggesting zero order kinetics. Leading-edge analysis was performed, as was done for peak α in the acetaldehyde-on-CI TPD of the previous section. Here two 20 L_m, two 25 L_m, two 30 L_m, two 40 L_m and one 50 L_m trace were used for the analysis. Order plots were constructed using these data, over the temperature range 97–102 K, providing an average order of desorption value of 0.0 ± 0.1 from the individual values as listed in table 5.8. As in previous analyses, the order is therefore assumed to be zero. Peak α is thus confirmed as multilayer desorption for this binary ice system also. With n = 0, evaluation of the energy of desorption via Arrhenius plots resulted in an average value of 35 ± 1 kJ mol⁻¹, from the individual values given in table 5.9. The pre-exponential factor for multilayer desorption is then $10^{31.9\pm0.5}$ molec m⁻² s⁻¹, where again the uncertainty is determined by varying the desorption energy through its error limits.

Table 5.8. Multilayer order of desorption values for acetaldehyde on ASW, evaluated from peak α in 20–50 L_m TPD spectra, such as illustrated in figure 5.22. Errors are 95 % confidence intervals for the individual linear fits.

Temperature (K)	Order, <i>n</i>
97	-0.2 ± 0.3
97.5	-0.1 ± 0.4
98	0.0 ± 0.2
98.5	-0.2 ± 0.3
99	0.0 ± 0.3
99.5	0.0 ± 0.3
100	0.0 ± 0.3
100.5	0.1 ± 0.3
101	0.1 ± 0.3
101.5	0.2 ± 0.4
102	0.3 ± 0.4

Table 5.9. Desorption energy values for multilayer acetaldehyde on ASW, evaluated from peak α in 20–50 L_m TPD spectra, such as illustrated in figure 5.22. Errors are 95 % confidence intervals for the individual linear fits.

Exposure / L _m	E _{des} / k	J mol ⁻¹
25	33 ± 1	34 ± 2
30	34 ± 1	34 ± 1
40	37 ± 1	37 ± 1
50	36 ± 1	

5.3.3.3 TPD Data for Acetaldehyde/ASW Mixtures

Lastly, TPD were recorded for a range of mixed acetaldehyde/water ices. Expected to be the most astrophysically-relevant, these were co-deposited on the graphite, as was done for 2-propanol/water and DME/water mixed binary ices. In each case, 50 L_m of water is dosed, creating a bulk multilayer ASW ice, along with a proportion of acetaldehyde selected in order to create mixtures of 4–34 % acetaldehyde. This range of mixed ice compositions was chosen as it approximately corresponds to the proportions used in the layered ice experiments. The TPD spectra are shown in figure 5.23, with a representative trace for ASW included for reference. In these spectra the volcano peak γ dominates, as expected for a mixed ice. The volcano peak appears at 142 K for 4 % acetaldehyde, decreasing steadily in temperature as acetaldehyde proportion increases, to reach 138 K at 34 % acetaldehyde.

the volcano behaviour in the layered ASW system of the previous section, this decrease in temperature coincides with a small but significant shift in the ASW-CI phase change, as evidenced by a shift in the shoulder feature in figure 5.24. This is very comparable to the results seen in the previous chapter for DME/water binary ice mixtures on HOPG (figure 4.20, page 95).



Figure 5.23. TPD spectra for 4–34 % acetaldehyde co-deposited with multilayer ASW at <30 K. A trace for ASW (not to scale) is shown, for reference.

Following the volcano desorption of peak γ , a small co-desorption peak (δ) is seen in the mixtures system. This appears at the same ~152–154 K temperatures as it does for acetaldehyde layered on ASW. Meanwhile, at lower temperatures in the spectra, a small peak at 125 K is visible even in the 4 % TPD spectrum. This is similar to the peak ascribed to surface water interaction in the TPD for the ASW and CI layered systems, and is again designated peak β , representing acetaldehyde interacting with water molecules at the water ice surface. This peak appears to remain in the spectra with increasing acetaldehyde proportions, but becomes obscured by the growing volcano peak γ as well as a lower-temperature feature (ϵ), which appears for acetaldehyde proportions >4 %. The temperature at which this growing peak reaches a maximum (~106–110 K) is similar to the multilayer acetaldehyde peak α seen in the layered binary ice systems. Based on this, the low-temperature peak ϵ is thought to be due to desorption of segregated acetaldehyde, within the porous ASW surface but not interacting directly with water. As with the results for the layered systems, the patterns represented in the mixture TPD do generally resemble those seen in the previous DME experiments of chapter 4.



Figure 5.24. Comparison between the shift in volcano peak γ temperature for acetaldehyde mixed with ASW and the corresponding shift in the ASW-CI shoulder feature. TPD for 4 and 34 % acetaldehyde, dosed with 50 L_m multilayer ASW at base temperature <30 K, are used here as examples.

5.3.3.4 Discussion of Binary Ice Desorption and Kinetics

The adsorption, thermal processing and desorption of acetaldehyde exhibit significant modification in the presence of either CI or ASW. The monolayer or surface interaction peak β is very comparable between the systems, particularly the layer systems. This is illustrated by figure 5.25, which shows a direct comparison of minimal 0.5 L_m acetaldehyde exposures dosed on CI and on ASW, with TPD for acetaldehyde on HOPG and acetaldehyde in a 4 % mixture also shown, for reference. The similarity of this peak between the two layer systems suggests that the interaction at the surface is primarily influenced by the intermolecular forces rather than the large scale structure of the water ice. Although the monolayer peak β features have a simple profile, which is similar to TPD traces for monolayer acetaldehyde on HOPG, the peak for this regime is seen to saturate at ~1 L_m. This differs from acetaldehyde adsorbed on graphite, for which the monolayer TPD saturated at ~2 L_m. A possible reason for this is due to the favourable interaction between acetaldehyde and water. Monolayer growth in particular is dependent on the relative strength of adsorbate-adsorbate and adsorbate-substrate interactions.²²¹ With the ability of water to form hydrogen bonds (~20–25 kJ mol⁻¹), the adsorbate-substrate interaction is expected to be stronger.²²² Further evidence of this effect is apparent in the lack of intermediate desorption regime behaviour, which was seen in the pure system, as highlighted in figures 5.5 and 5.6.



Figure 5.25. TPD for 0.5 L_m acetaldehyde adsorbed on multilayer ASW and on multilayer CI. TPD for 0.5 L_m acetaldehyde on HOPG and in a 4 % mixture (dotted lines) are included for comparison. The TPD for acetaldehyde in a 4 % mixture is not to scale, as this is a somewhat larger exposure than the other examples.

For the layered ice systems, the slight shift of the monolayer peak β to lower temperature as exposure increases is qualitatively similar to the slight shift seen in the TPD for the lowest coverages of acetaldehyde on HOPG. However, the desorption temperature seen for peak β in the binary systems is >20 K higher than for the monolayer on HOPG, again indicating a much stronger interaction between acetaldehyde and water than between acetaldehyde and graphite. Considering the interac-

tion kinetically, a monolayer energy of desorption was obtained for acetaldehyde layered on CI. At ~42 kJ mol⁻¹ it is indicative of physisorption, but it appears higher than the same value for monolayer acetaldehyde on HOPG, which was calculated as 28 ± 4 kJ mol⁻¹ in section 5.3.1.2. A desorption energy of ~42 kJ mol⁻¹ is somewhat higher than the 34.7 kJ mol⁻¹ for acetaldehyde on water at 120–180 K reported by Hudson *et al.* and the 36 ± 2 kJ mol⁻¹ reported by Darvas *et al.*^{222,289} However, ~42 kJ mol⁻¹ is also slightly higher than the desorption energy for DME on CI (~34–36 kJ mol⁻¹) reported by Lattelais *et al.* in the literature.¹⁷⁹ This correlates with the slightly higher desorption temperature seen here (~126 K) compared to the desorption temperature shown for DME in the previous chapter (~120 K, figure 4.16). In comparison with the desorption energy for pure acetaldehyde on HOPG, the previous and current desorption energy values for acetaldehyde interacting with water.^{222,289} Overall, both of these quantitative measures—desorption temperature and desorption energy—indicate a relatively strong interaction between acetaldehyde and the water surface, likely influenced by the surface hydrogen bonding previously described in detail by Darvas *et al.*²²²

With reference again to figure 5.25, the volcano peak γ is clearly present even from the lowest coverage measured, indicating that ASW readily traps small amounts of acetaldehyde. For both the layered and mixed ASW systems, the volcano grows substantially with increasing exposure, as shown in sections 5.3.3.2 and 5.3.3.3. Additionally, the peak temperature for volcano desorption shifts consistently with the ASW-CI shoulder feature in the corresponding water TPD traces. This was previously shown by the examples in figures 5.21 and 5.24. These trends are summarised here in figure 5.26. Peak areas for the volcano peak γ are approximated by peak fitting the convoluted TPD spectra. Although only an approximation, it clearly shows that the ability for ASW to trap an adsorbed overlayer saturates at ~29 % proportion of acetaldehyde exposure (~20 L_m). In contrast, for a co-deposited mixture, no limit is seen for the amount of trapped acetaldehyde at the proportions studied. In both cases this suggests that the ability for acetaldehyde to diffuse through ASW is limited. Meanwhile, the lower part of the figure shows that the stabilising of the peak γ temperature position correlates with the saturation of the trapped quantity. As this was previously shown to correspond with the ASW-CI shoulder, it suggests that the change in the water behaviour is due to the trapped acetaldehyde.

For higher exposures in both layered systems, the low-temperature multilayer peak α feature grows into the dominant peak. This occurs at ~5 L_m on CI and ~25 L_m on ASW. The initial appearance of a higher-temperature monolayer peak, followed by growth of a lower-temperature bulk multilayer peak, is very comparable to the results seen for DME on CI in chapter 4. TPD traces assigned to multilayer for the pure, CI layer and ASW layer systems are compared in figure 5.27. While 10 and 20 L_m acetaldehyde TPD are shown for the pure acetaldehyde and acetaldehyde layered on CI, it is necessary to include 30 and 40 L_m acetaldehyde exposures for the ASW layered system in order to display a



Figure 5.26. Summary of trends seen for the evolution of the volcano peak γ size and position relative to proportion of acetaldehyde in the binary ice. Trends are shown for acetaldehyde layered on ASW as well as acetaldehyde mixed with ASW binary systems. The lines in the figure are polynomial fits serving as a guide for the eye and do not have strict meaning.

consistent leading edge. This is because a significant component of the acetaldehyde is trapped within the porous ASW for this system, as evidenced by the volcano peak noted previously.



Figure 5.27. TPD spectra for 20 L_m multilayer acetaldehyde on multilayer CI and on HOPG and 40 L_m multilayer acetaldehyde on multilayer ASW. All ices were dosed at <30 K.

Firstly, without the convolution of the overlapping monolayer and bilayer complexity seen for the pure system, the CI multilayer peak provides additional certainty that the peak seen for 10 L_m pure acetaldehyde on HOPG is indeed a single peak representing a bulk multilayer. Further, evaluated desorption energies for all three systems are very similar, as shown in table 5.10, supporting the accuracy of the calculations as well as the assertion that these exposures all represent bulk multilayers in their respective systems. However, as suggested by figure 5.27, the crystallisation behaviour of acetaldehyde appears to be affected by the presence of water substrate. This was also previously hinted at in the TPD for acetaldehyde layered on CI, in figure 5.19(a), where—unlike in the pure TPD results—the 30 L_m TPD trace does not display anomalous behaviour. Taken together, this suggests that a CI underlayer promotes adoption of phase II, and possibly that ASW inhibits it.

Table 5.10. Comparison of the desorption energy values for multilayer acetaldehyde on HOPG, on CI and on ASW. For the binary ice systems, this is evaluated from peak α in the respective TPD spectra.

system	E_{des} / kJ mol ⁻¹
on HOPG	35.4 ± 0.8
on CI	37.4 ± 0.9
on ASW	35 ± 1

5.3.3.5 RAIRS Data for Acetaldehyde/Water Binary Ices

RAIR spectra were recorded during annealing sequences applied to all three binary systems. Figure 5.28 shows the distinct carbonyl stretch band and the deformation region from these spectra for 20 L_m acetaldehyde on multilayer CI, 20 L_m acetaldehyde on multilayer ASW, and a mixed ice composed of 25 % acetaldehyde. The v(C=O) band in particular was previously shown in the pure system to clearly respond to the phase of the acetaldehyde. The figure is limited to the temperatures prior to both the desorption of multilayer acetaldehyde and the ASW-CI phase transition of water. For the layered systems, effects are seen following annealing at several temperatures, and both exhibit the onset of desorption at 95 K. The spectra for the layered systems at this temperature are therefore not included in the figure.



Figure 5.28. RAIR spectra following annealing at selected temperatures, highlighting the distinct v(C=O), $\delta_a(CH_3)$, $\delta(CH)$ and $\delta_s(CH_3)$ bands during annealing sequences for a) 20 L_m acetaldehyde on CI, b) 20 L_m acetaldehyde on ASW and c) acetaldehyde in a 25 % mixture with ASW.

The spectra for 20 L_m acetaldehyde adsorbed on multilayer CI, shown in figure 5.28(a), exhibit some similarity to the behaviour seen for acetaldehyde on HOPG (figure 5.15(b) and (c)). This is consistent with the fact that both HOPG and CI are ordered surfaces.^{115,116} As was the case for acetaldehyde on

HOPG, no changes are seen following either 50 or 70 K anneals. At 75 K a significant increase in intensity is exhibited, with a peak shift for v(C=O) from 1730 cm⁻¹ to 1726 cm⁻¹. A small additional increase in intensity for this band is seen at 80 K. At 75–80 K, the $\delta_a(CH_3)$ and $\delta_s(CH_3)$ deformation bands show shifts and slight peak splitting, while the $\delta(CH)$ shows a substantial increase in peak area. No further significant change is seen until the onset of multilayer desorption at 95 K.

In figure 5.28(b), the spectra for 20 L_m acetaldehyde adsorbed on multilayer ASW exhibit a different pattern. Changes are initially seen at 70 K rather than 75 K, and in this case a partial reduction in v(C=O) band intensity is shown. This is followed by a gradual shift in the peak frequency from 1730 cm⁻¹ to 1726 cm⁻¹ at 80–85 K. In the deformation region, there is evidence of slight peak splitting, particuarly at 85 K. Roughly consistent with acetaldehyde on CI, the onset of desorption is seen at 95 K, which again is not shown.

Lastly, in figure 5.28(c), the spectra for a 25 % acetaldehyde mixture are presented. Unlike the layer systems, the base temperature v(C=O) band peaks at 1722 cm⁻¹ initially. The spectra for subsequent anneals also demonstrate a unique pattern. As for acetaldehyde layered on ASW, changes are seen from 70 K. In this case, a gradual reduction in band intensity is seen at each temperature, which continues until only the trapped acetaldehyde remains, at 120 K, as will be shown in the next figure.

Figure 5.29 demonstrates the end result of the sequential annealing. The v(C=O) stretch mode and the δ_a (CH₃), δ (CH) and δ_s (CH₃) deformation modes are again highlighted, and crystalline spectra from the pure system are shown in the lower part of the figure for reference. Note that a 25 % mixture acetaldehyde dose is expected to be larger than a 20 L_m layered dose, which may account for the larger peak areas. However, the observations will focus on peak frequencies. The mixture displays a band at 1734 cm⁻¹, suggesting that this is representative of trapped acetaldehyde. Following 110 K anneals, the acetaldehyde layered on CI shows a small band at 1714 cm⁻¹, while the acetaldehyde layered on ASW shows a band at 1734 cm⁻¹. With respect to the desorption temperatures previously shown in the binary ice TPD results, these bands are assigned to monolayer acetaldehyde interacting with the CI surface and acetaldehyde trapped by ASW as a result of thermal processing, respectively. The volcano peaks in the TPD are clear evidence that the acetaldehyde is primarily trapped at these temperatures for the ASW layer and mixture systems, so these assignments can be made confidently.

5.3.3.6 Additional Discussion of Acetaldehyde and Water Interactions

With regard to the phase behaviour, the infrared spectra for binary ices—as shown in the preceding section—show variation between the systems, but are not as clearly defined as the counterparts for pure acetaldehyde on HOPG. The spectra do reflect the nature of the adsorption, trapping and desorption in each system, in agreement with TPD. However, some speculation can be made with regard to the patterns seen. At lower temperatures, as in figure 5.28, it seems the increase in intensity and the



Figure 5.29. RAIR spectra highlighting the v(C=O) stretch mode and the $\delta_a(CH_3)$, $\delta(CH)$ and $\delta_s(CH_3)$ deformation modes at high temperatures during the respective annealing sequences for 20 L_m acetaldehyde on CI, 20 L_m acetaldehyde on ASW, and acetaldehyde in a 25 % mixture with ASW. Spectra were recorded at base temperature, following annealing for 3 min at the temperatures indicated in the figure. The upper and lower parts of the figure are not to scale. Additionally, the v(C=O) band for the 'phase II' spectrum has been scaled by a factor of 0.25.

redshift seen for the v(C=O) band in the RAIR spectra for the CI layer system are due to phase II crystallisation. Redshifting of this band can also be expected for hydrogen bonding with water, as noted in earlier discussion, but 20 L_m is confirmed as a bulk multilayer by TPD.²⁹⁹⁻³⁰² As such, only the monolayer would be affected in this way, and then only to a limited degree, as CI presents relatively few dangling O-H groups.¹¹⁸ A redshift and increase in intensity is the general pattern seen in the pure results for the spectral character of phase II relative to amorphous acetaldehyde, as shown in figure 5.16. Additionally, figure 5.27 suggests that acetaldehyde multilayers above CI adopt a primarily phase II structure prior to desorption, due to the close agreement with 20 L_m TPD traces for the pure system. The character of 20 L_m was shown to be the result of desorption from phase II, as discussed earlier and seen in figure 5.18. Meanwhile, the effects seen in the RAIR spectra for the ASW layer system also show crystallisation, though at different temperatures, and from the character of the bands, the ordering appears to be hindered by the porous surface of the ASW layer beneath. This is again in agreement with binary ice TPD, with reference to figure 5.27. Lastly, for the lower annealing temperatures, the cause of the effects seen in the mixture system are not certain, and crystallisation is not clearly indicated by the results. There is clearly a reduction in peak areas for the v(C=O) and $\delta_s(CH_3)$ bands. The sharpening seen may indicate reduced interaction with the water ice due to segregation, as the frequency of both bands shifts toward the expected pure frequencies for these features.

Trapping is clearly observed to some degree for the ASW layer system, as integrated TPD peak areas in the present work indicate that around ~25–30 % of the acetaldehyde is trapped for a 20 L_m exposure dosed onto ASW. This is represented by the clear volcano peak in the TPD for the system. However, as seen by comparison to the infrared spectra of the mixture system, as in figure 5.29, trapped acetaldehyde appears to be indicated by a frequency of around 1733 cm⁻¹. As has been stated, hydrogen bonding with water would be expected to create a more redshifted band.^{222,299-302} Looking again to figure 5.28(b), the distorted band edge at ~1718 cm⁻¹ appears along with clear indicators of crystallisation in the deformation bands. This feature is also visible as a shoulder in the spectra for both the ASW layer and mixture systems in figure 5.29, and compares well with the low frequency features seen for this band in the pure crystalline spectra, so it may be that some crystallisation is observed for these systems. Previous work by Ioppolo et al. showed that acetaldehyde and water are not extensively mixed up to 125 K.94 They also found evidence for crystalline acetaldehyde in mixtures, suggesting that it segregates into the pores of the water ice. However, in the data seen here it could also simply be due to hydrogen bonding rather than crystallisation, as this shoulder is similar to the peak seen for monolayer acetaldehyde on CI, also shown in figure 5.29, and to the infrared band seen at 1717 cm⁻¹ by Darvas et al., who showed it could be attributed to interaction with water.²²²

5.4 Summary and Conclusions

Initial pure TPD results analysed by peak-fitting indicate that pure acetaldehyde dosed on HOPG forms a saturated monolayer with exposures of 2 L_m , as was the case for DME in the previous chapter. Kinetic analysis as well as infrared spectra indicate the monomeric molecular deposition of acetaldehyde, with uptake patterns indicating physisorption on the surface. During TPD experiments, the appearance of two overlapping peaks at intermediate coverages is attributed to an initial monolayer with clustered islands as exposures increase, as described by the Straski-Krastanov growth mode, where both have similar desorption energies.²²¹ This appears to be intermediate between the islanding behaviour for 2-propanol and surface-wetting for DME. This is rationalised based on the moderate intermolecular forces available to acetaldehyde adsorbate-adsorbate interactions due to C–H…O hydrogen bonds.^{208,287,288} Both the monolayer and multilayer desorption temperatures are comparable to methyl formate, from previous work.⁹³ Multilayers initially show ideal zero-order desorption but at >30 L_m appear to diverge. This is attributed to the existence of two crystalline phases, phase I and phase II, where the adoption of the second phase is inhibited at higher doses. The production of acetaldehyde polymer was ruled out based on a lack of >200 K peaks in the TPD spectra, and the absence of clear infrared bands expected for the polymer.^{180,181,260,263,265,266,276,278}

The two phases were observed spectroscopically and are linked to the two crystalline phases that were resolved by neutron powder diffraction in work published by Ibberson *et al.*: monoclinic $P2_1/c$ and orthorhombic Pna21.285 Infrared spectra for phase I suggest the adoption of the monoclinic structure, with the molecular plane of symmetry of the repeating acetaldehyde molecules oriented approximately parallel to the graphite surface. This is suggested by the weakening of the v(C=O) band and the strengthening of bands assigned to A" modes. The distinct character of the v(C=O) band at ~75 K is proposed to be due to the alignment of carbonyl bonds in the monoclinic crystal structure, and the influence of C-H···O hydrogen bonds, which as noted are also implicated in the nature of the growth of low coverage acetaldehyde ices on graphite. The hypothesis that the coverage dependence of the phase change varies significantly was shown to be correct by comparison of the response of acetaldehyde doses of 20, 25 and 30 L_m to annealing. The adoption of the phase II structure was shown to be favoured at coverages produced by a dose of 20 Lm, with the spectrum indicating a significant shift to this phase already evident at as low as 75 K, which is much lower than expected.^{284,285} The assignment of the orthorhombic crystalline structure was based on agreement with the literature.^{283–285} Lastly, the two phase changes and the complex response of the v(C=O) band suggest similarities with previous results for methyl formate and ethyl formate.^{296,297}

The interaction with water was investigated for binary layers and mixtures, as in previous chapters. There is a clear surface desorption in the TPD at 124–128 K, significantly higher than the pure 99– 101 K of the monolayer on HOPG. This is consistent with the ability of the water ice to hydrogen bond to the acetaldehyde monolayer. Evidence of trapping was seen in both TPD and RAIRS, and appeared to a similar degree as seen in the TPD of DME/water binary ices in the previous chapter. In order to understand the interaction of the two ices at increasing temperatures, infrared data was compared to results from layered ice results presented by Darvas *et al.* and to matrix-isolation studies investigating the effect of hydrogen bonding on the v(C=O) stretch.^{222,299–302} These comparisons suggest that hydrogen bonding becomes less favoured during annealing, and therefore that thermally-driven mixing is not favoured and the ices segregate. This is in agreement with previous far-infrared work which shows segregation and crystallisation up to 125 K.^{94,284} The results here are uncertain with regard to crystallisation of trapped acetaldehyde, at present. This is due to the similar ~1714–1717 cm⁻¹ frequency expected for both crystalline acetaldehyde and acetaldehyde hydrogen bonding with water.

Full kinetic analysis of pure acetaldehyde ices on HOPG was completed, using leading-edge analysis as in the previous chapters. This revealed approximate first-order desorption at low coverages and zero-order desorption at higher coverages, supporting the assignment of monolayer and multilayer regimes.¹⁷³ Evaluated energies of desorption fall between the values for 2-propanol and DME, confirming physisorption of the ice, and adding another indication that acetaldehyde has intermediate behaviour between 2-propanol and DME. Even so, the general pattern of interaction exhibited by acetaldehyde is far more similar to DME, with similarities noted in places throughout the chapter.

Chapter 6

A DFT Model for the Surface Behaviour of COMs

The adsorption and desorption of molecules in the interstellar medium is core to much of the chemistry that occurs, and how that chemistry develops in response to changes in the environment, especially increasing temperature.⁴ Additionally, molecules sequestered on the surface of dust grains react more frequently than in the gas phase. The surface improves kinetics due to concentration of the reagents in an otherwise diffuse environment, and the resulting products are additionally stabilised by the surface as it acts as a thermal sink.^{20,57} There is a growing body of experimental laboratory data concerning the kinetic and energetic properties of these adsorbed molecules. Examples of this were previously shown in chapters 3–5 and references therein. The aim here is to develop a theoretical model which can be applied broadly to provide further insight into the surface adsorption and chemical behaviour—under interstellar conditions—of these molecules of astrophysical interest. All work presented in this chapter is my own but was undertaken in collaboration with Prof. Anthony J. H. M. Meijer, Professor of Theoretical Chemistry in the Department of Chemistry at the University of Sheffield.

As discussed in section 1.2, there is evidence that many interstellar dust grains are made up of amorphous carbon.^{20,37,303} As with laboratory experiments, a model graphite or graphene surface can provide a useful—if idealised—surface for the theoretical study of the adsorption and surface-bound behaviour of molecular species.^{74–77,304–306} In many computational model systems, this surface takes the form of a repeating unit cell. However, in a similar manner, larger planar polycyclic aromatic hydrocarbon (PAH) molecules can also be used as a substitute for the carbonaceous surface, as they are electronically very similar to a graphene sheet.³⁰⁷

An essential aspect of a model is its treatment of the adsorption of molecular species on the carbon surface. This is an important characteristic in its own right, but also necessarily must be accurate in order to reasonably model further surface processes. In experimental work the stability of molecules adsorbed on the surface is investigated through the kinetics of the desorption process. Analysis of this process reveals energies of desorption (among other parameters), as described in previous chapters. Meanwhile, in the most straightforward case, the theoretical model can provide a binding energy by calculating the reduction in total energy of the adsorbate–surface system versus the isolated components. This binding energy is subtly different from a practical energy of desorption, as it neglects any energy barriers, as shown in figure 6.1. For the case of physisorption, however, there is generally no barrier, or else a minimal one. Therefore, a theoretical binding energy, calculated in this simple way, can be expected to match the experimental energy of desorption closely.



Figure 6.1. Illustration of the difference between theoretical binding energies as calculated in the present work, E_{bind} , and experimental energies of desorption, E_{des} .

Computational chemistry can generally provide useful insight to supplement and complement many areas of experimental work. When applied to the properties of adsorption it has the advantage of being able to look at far lower effective coverages (fractions of a monolayer) than is readily detectable experimentally. The interaction of a single adsorbing molecule with the surface can be considered. Calculating theoretical infrared spectra is also possible, and is useful as it provides information to help interpret measured infrared spectra.^{308–312} Further, although it is more computationally difficult, chemical reactions can be modelled by considering stable and transition geometries and their relative energies. This can suggest likely chemical products, prior to carrying out experiments.^{63,64,313–318} In addition to providing supporting data for insight into the reaction mechanisms, this confers the advantage of suggesting products to look for in the laboratory.

6.1 Theoretical Chemistry

At its core, theoretical chemistry is concerned with determining the properties of chemical systems through mathematical models. A proper description of the electronic structure of a system requires quantum mechanics, and at the heart of this are the methods which evaluate the wave function of a system. These are termed *ab initio* methods, as they attempt to calculate the properties of model systems

through physical principles alone, without incorporating empirically-derived parameters. The Hartree-Fock (HF) method^{319–322} is an *ab initio* method, which solves—with several key approximations—the time-independent Schrödinger equation³²³

The variational principle holds that an approximate wave function will always have energy greater than or equal to the exact energy.³²⁴ The HF method makes use of this, beginning with an *ansatz*—trial wave function—and then minimising the energy to achieve a self-consistent result. The wave function is constructed from a single Slater determinant, which is a product of single-electron wave functions that is, orbitals—and intrinsically satisfies the antisymmetry requirement of the Pauli exclusion principle.

A popular alternative to using the wave function based methods is the use of density functional theory (DFT) methods. These are based on the theory that the electronic energy corresponds to the electron density, as shown by Hohenberg and Kohn.³²⁵ Within DFT the electron density, ρ , is itself a function of radial distance from the nuclei, and the energy is thus a function of a function: a functional. Making use of the electron density is computationally advantageous, as while the HF methods, which are based on wavefunctions, scale with 3N variables, the DFT methods only have three. The Born-Oppenheimer approximation is used here, and the exact electronic energy functional can be described by three components as

$$E[\rho] = T[\rho] + E_{ne}[\rho] + E_{ee}[\rho]$$
(6.1)

where $T[\rho]$ is the kinetic energy functional, $E_{ne}[\rho]$ is the potential energy functional of the nucleielectron attraction and $E_{ee}[\rho]$ is the potential energy functional of the electron-electron repulsion.

In all contemporary computational chemistry work, DFT methods are based on the methods proposed by Kohn and Sham.³²⁶ DFT in its original implementation was still difficult to solve, a problem that the Kohn-Sham methods were invented to address. In Kohn-Sham DFT, an auxiliary wave function and orbitals are introduced, and the electronic kinetic energy is calculated from a single Slater determinant. This avoids the many-body problem by assuming non-interacting electrons: the Kohn-Sham *ansatz*. This means that the energy is an approximation to the exact kinetic energy, though the difference is small.³²⁴ The DFT energy is now expressed as

$$E_{DFT}[\rho] = T_{S}[\rho] + E_{ne}[\rho] + J[\rho] + E_{XC}[\rho]$$
(6.2)

where $T_S[\rho]$ is the kinetic energy calculated via the Slater determinant, $J[\rho]$ is the electron-electron repulsion potential energy and $E_{XC}[\rho]$ is an exchange-correlation term which accounts for the remaining energy—kinetic and Coulomb correlation—as well as non-classical electron interactions.

The exact form of the exchange-correlation functional is not known, except for special cases, and it is therefore an ongoing area of research in theoretical chemistry.³²⁴ The development of exchange-correlation functionals cannot be approached systematically in the same way as the wave function based

methods. However, Perdew has suggested a 'Jacob's ladder' which represents expected improvements in accuracy based on the variables used to define the functional.^{327,328} In this scheme the lowest 'rung' consists of the local density approximation (LDA) and local spin density approximation (LSDA) which directly correlate the exchange-correlation energy to the electron density. This effectively assumes that the density is locally uniform and does not vary suddenly. While this is reasonable for extended systems such as metals, it is poor at describing molecular systems. The next step beyond LDA and LSDA is the generalised gradient approximation (GGA), which incorporates the first derivative of the density as an additional variable. Beyond GGA are refinements which attempt to improve accuracy further. These refinements include meta-GGA and hyper-GGA, among other methods.

6.2 Basis Sets

In both wave function and electron density based methods, basis sets are used to provide a mathematical basis for describing molecular orbitals. These sets of basis functions are necessarily finite, and only approximate the ideal infinite, complete basis set. The number and type of basis functions which comprise the basis set affect its relative accuracy.³²⁴

For modelling extended, periodic systems, plane waves can be utilised to model the system as a whole, rather than using nucleus-centred Gaussian-type orbitals. While these periodic functions are useful for describing infinite systems and the valence region, they are not well-equipped to describe local core electrons. When using a plane wave basis, the core electrons are instead described non-explicitly by a pseudo-potential function. In terms of Gaussian-type basis sets, the error introduced by the use of pseudo-potentials in plane wave basis DFT calculations is roughly equivalent to the use of a triple zeta basis with additional functions to describe polarisation (TZP).^{324,329}

Due to computational cost, the extent of the plane wave basis must be limited by a cut-off energy. A larger cut-off energy is more accurate, but it entails a much higher computational cost. This cut-off kinetic energy defines the cut-off radius as

$$G_{cut} = \sqrt{2 E_{cut}} \tag{6.3}$$

where G_{cut} is the cut-off radius and E_{cut} is the cut-off energy. At larger radii, the plane-wave components become negligible and the evaluated energy converges to a minimum, such that a modest cut-off can be determined which gives a reasonably accurate result. A calibration can be considered prior to a given study to determine an appropriate cut-off energy, which determines the corresponding cut-off radius. This allows for sufficient accuracy while minimising the computational cost.

6.3 Previous Work

A major portion of current literature looking at adsorption in an astrophysical context uses DFT to consider atoms and molecules of hydrogen. Due to its high abundance, hydrogen is a key component of the chemistry of the interstellar medium (ISM), commonly acting as a source of protons. While hydrogen is a relatively simple case, there have been several key conclusions from this body of work which have implications for approaching theoretical models of adsorption in general. In particular, the limitations of DFT with respect to dispersion interactions as well as the complicating artificial effects of basis-set superposition error (BSSE) need to be addressed.

The first theoretical work to look at adsorption on graphite with DFT was a cluster model study by Jeloaica and Sidis in 1999.³⁰⁷ This work considered hydrogen atoms, and it noted chemisorption above surface carbons as well as the ability for the atoms to physisorb and remain mobile, allowing for reactions based on the Langmuir-Hinshelwood mechanism in addition to Eley-Rideal. They noted concerns that GGA-based calculations may not correctly predict van der Waals interactions. More recently, Ferullo *et al.* considered the importance of dispersion corrections for modelling physisorption of hydrogen on graphite.³³⁰ They concluded that these corrections should be included with DFT in order to obtain accurate results.

The adsorption of molecular hydrogen was looked at in a periodic model by Arellano *et al.* using the LDA for electron exchange and correlation.³³¹ This study focused on the energetics of physisorption at different points above the carbon lattice, finding the most stable position for adsorption at the centre of the graphene hexagon. Pauzat *et al.* also used a periodic model in a study of the physisorption of H₂ on graphite.³³² They noted the advantages of the periodic model in avoiding the influences of BSSE and avoiding the finite size of the cluster model. Tran *et al.* also considered the adsorption of H₂ molecules, instead using a cluster model with PAH substrates of varying size.³³³ Similar considerations were made with a study of H atom adsorption by Ferro *et al.*³⁰⁵ In both studies, the effect of a second substrate layer was investigated by addition of a second PAH beneath the first. This was found not to be a significant influence in either case. Tran *et al.* showed significant effects on the interaction distance and energy due to BSSE, and the authors noted the importance of applying a correction (counterpoise) during optimisation. Meanwhile, Ferro *et al.* noted the advantages of the periodic model, and used it as a basis for selecting an appropriate graphite cluster, employed due to the reduced computational cost.

Theory can also probe chemical and physical effects beyond simple adsorption. For example, models have been used to consider the effects an initial chemisorbed H atom had on the adsorption of a subsequent H atom in nearby positions, ultimately looking to model H_2 formation.^{77,334–336} Adsorption of the first H atom effectively forms a surface defect. It is found that a second H atom chemisorbs with no barrier at the para position, noting that this provides a favourable condition for formation of H_2 via

the Eley-Rideal mechanism.^{174,336} Teillet-Billy *et al.* also showed this for the two-sided chemisorption of hydrogen atoms (on opposing sides of the graphene layer), which could be significant for the ISM where graphenic platelets form part of the available carbon surfaces.³³⁷ The ortho and para positions are shown to be stable for hydrogen dimers, important for hydrogen recombination in the ISM.³³⁸

The formation of H₂ via the Eley-Rideal mechanism—and the subsequent associative desorption was plotted as a potential energy surface with GGA DFT by Farebrother et al.⁷⁴ This showed barrierless formation of H₂, with vibrationally excited product dominant. It was noted that this is favourable for driving further chemistry in the ISM that might otherwise not be feasible. Further work considering the Eley-Rideal mechanism following from this was published by Meijer et al..75,76 Ferro et al. undertook two theoretical studies where H2 formation was studied on model graphite.^{305,306} In the first study, both the periodic and cluster models were employed, and the H + H surface recombination via the Eley-Rideal mechanism was investigated, showing exothermic reactions for both physisorbed and chemisorbed hydrogen. In the second study, only the cluster model was utilised, in this case to consider the surface H + H recombination via the Langmuir-Hinshelwood mechanism, concluding that this mechanism is an important component in experimental results. Sha and Jackson also looked at Eley-Rideal reactions.⁷⁷ Adsorption of hydrogen atoms and formation of H₂ was also investigated on a model crystalline forsterite (010) surface.³³⁹ This surface is representative of a silicate dust grain, and barrierless physisorption of hydrogen was seen. In comparison to laboratory results, the model overestimated both the adsorption energy and the barrier for moving between surface sites. Using a nanoscale slab model of the surface, they were able to estimate that half the energy released by H_2 formation on the surface could be dispersed by the surface through a 53 K temperature increase, which would radiate in ~0.02 s.

In addition to hydrogen, a number of theoretical studies have looked at the adsorption of other molecules of astrophysical interest. With more complex molecules, additional factors are significant. Allouche investigated the hydrogen bonding interactions of formic acid dimers and trimers in two different water clusters.³⁰⁸ Adsorption and resulting spectroscopic effects were modelled. Observed differences in the spectrum dependent on orientation to the surface were noted for their experimental value. Significant for adsorption in the ISM, the formic acid was shown to adsorb more strongly to the simulated amorphous ice than water molecules do.³⁰⁸ Subsequently, Allouche and Bahr modelled adsorption of acetic acid on a periodic water ice surface, comparing results with spectroscopic data.³⁴⁰ They were concerned about the modelling of hydrogen bonds by the PBE functional, and also the poor representation of dispersion interactions of DFT, though they also noted the advantages of the periodic model. Rubeš *et al.* used coupled cluster (CC) theory in addition to DFT to calculate DFT/CC interaction energies (comparing well with experiment) for several small molecules on a coronene cluster model of graphite.³⁴¹ The molecules included relatively common interstellar ices such as H₂O, NH₃

and CO₂, while the largest molecule modelled was benzene (C_6H_6). An investigation incorporating periodic DFT as well as laboratory studies was carried out by Lattelais *et al.* to compare adsorption of organic isomers.¹⁷⁹ This showed that the occurrence of hydrogen bonding could explain exceptions to the 'minimum energy principle' for determining interstellar abundance of isomers. A broad study by Lazar *et al.* modelled each of seven organic molecules (acetone, acetonitrile, dichloromethane, ethanol, ethyl acetate, hexane and toluene) on both cluster and periodic representations of graphene.³⁴² This study compared DFT as well as non-DFT methods to experimental results. Only DFT functionals including dispersive effects provided reasonable results. Recently, Lattelais *et al.* considered adsorption of HCON isomers on a periodic model of graphene, in addition to on water ice and silica surfaces.¹⁷⁶ From their results, they noted the importance of hydrogen bonding interactions between adsorbates. Lastly, Bertin *et al.* modelled adsorption of nitrile and isonitrile with a view to understanding the effects of the functional groups.³⁴³ They employed a periodic model for the surface and found that theory gave similar results to experimental work.

As seen for hydrogen recombination, additional work has been done with the computational models to investigate surface-bound reactions for other molecules of interstellar interest, exploring possible catalytic effects of the surface. Goumans et al. studied three routes for CO2 formation on a coronene model carbonaceous surface.⁶⁴ They noted the reduced energy barriers on the surface relative to the gas phase. This was also seen by Adriaens et al. in an investigation of four pathways to the formation of carbonyl sulfide (OCS) on coronene.⁶³ Similar results were found for formation of water and H₂ on a forsterite (010) surface.^{313,314} Bergeron et al. considered the formation of OH through the Langmuir-Hinshelwood reaction mechanism on a graphitic surface, using both DFT and Møller-Plesset (MP2) calculations.³¹⁵ Chemisorption and physisorption were shown for oxygen atoms, with the latter used in calculations for the reaction dynamics. The OH product was shown to form with a large amount of energy, desorbing from the surface. DFT was used as part of a study by Woods et al. modelling the reaction pathway for formation of glycolaldehyde in the interstellar medium.³¹⁶ Dispersion correction was included and a barrier for the reaction was evaluated and compared to the gas phase, showing a reduction at the same level of theory. This was then incorporated into a chemical model of astrophysical conditions. Rimola et al. investigated the formation of glycine catalysed by water ice.^{317,318} They found that the barrier for a Strecker-type reaction was too high for interstellar conditions. However, processes driven by water radicals (which would be generated by ultraviolet irradiation in the ISM) are shown to potentially lead to glycine at hot core temperatures.

As a first step to building on this work which investigates interstellar chemistry through theory, the work presented here employs DFT to construct a model framework which can be applied broadly to describe the adsorption of complex organic molecules (COMs). As the previous work indicates, this will have to account for intermolecular forces (especially hydrogen bonding, for the oxygen-containing COMs studied here), will likely require empirical dispersion corrections, and will have to account for BSSE either by correcting or by using a mathematical basis that does not suffer from this error. The first step to establishing this framework is simply modelling adsorption of molecular species on a graphite surface. If this essential characteristic can be captured well by the model, further work can then make use of the framework to gain insights into the surface behaviour of COMs, as well as to model surfacebound reaction pathways.

6.4 Computational Methodology

Two models and three software packages were considered, which are covered in detail in the next two sections. The first model was a cluster model using Gaussian 09 software, where the PAH species pyrene and coronene were used as analogues for a carbon surface in a vacuum.³⁴⁴ The basis sets used in this model were localised Gaussian-type basis sets. The second model employed was a repeating supercell containing two layers of graphite crystal with several angstroms of empty vacuum above, in which model surface-bound molecules were placed. Computations for the repeating supercell were done with the same functional in all cases, but were attempted with both the CRYSTAL and CASTEP software packages.^{345–347} CRYSTAL utilises Gaussian-type basis sets while the CASTEP uses a plane wave basis. The original aim of using two software packages for periodic models was to compare their effectiveness in describing these adsorbing chemical systems, particularly due to this difference in basis sets. Previous theoretical work has compared well with experiment, and experimental results are used as a benchmark for the performance of the models considered here, particularly with regard to modelling physisorption.^{179,341,343}

Where Gaussian-type basis sets were used, BSSE was found to be a concern, as is common with weakly-interacting systems. The counterpoise correction method was chosen to attempt to limit this source of error.^{348–353} Because of the finite basis, BSSE occurs when the model orbitals of the adsorbate and substrate fragments are close to each other, allowing non-physical artificial relaxation and lowering of the total energy to occur. The counterpoise correction is one method to counteract this, but it is not an exact solution. The counterpoise method works by repeating calculations for each fragment using the basis of the full system. In these calculations, the orbitals without their associated atoms or electrons—so-called ghost orbitals—allow the energy change associated with BSSE to be isolated. This energy is then subtracted as a correction to the original result.

At the present time, DFT methods are known to be poor at describing dispersion interactions because of their use of electron exchange-correlation approximations.³⁵⁴ However, dispersion interactions are naturally critical when considering physisorbed molecules. In lieu of a DFT method that can achieve a good model of this phenomenon, additional empirical corrections devised by Grimme were used to properly model these systems.^{355,356} Previous published work has recognised this limitation and included empirical corrections to achieve good results.^{176,330,343} The Grimme correction is applied as a correction to the DFT energy

$$E_{DFT-D} = E_{DFT} + E_{disp} \tag{6.4}$$

where E_{DFT-D} is the corrected value, E_{DFT} is the normal density functional determined energy and E_{disp} is the dispersion correction energy. The value for E_{disp} is obtained by empirical scaling factors.

6.4.1 Evaluating the Cluster Model: Gaussian 09

The Gaussian 09 software package³⁴⁴ was used for all cluster model calculations, and was run on the dedicated high-performance computer systems 'sol' at the University of Sheffield and 'apollo' at the University of Sussex. In these cluster model calculations, pyrene and coronene were used as representatives for a graphite surface, as illustrated by examples in figure 6.2. While pyrene was quickly deemed unsuitable due to its small size, coronene was employed for a number of intermolecular binding tests with triatomic species: H₂O, CO₂, CS₂, H₂S, OCS and SO₂. These molecules were chosen for tests due to their small size, the availability of experimental values for comparison, and because all are molecules which are detected in interstellar ices.³⁵⁷



Figure 6.2. Illustration of the coronene (left) and pyrene (right) cluster models, with CO_2 and H_2S molecules included for comparison on coronene and pyrene, respectively.

Both the B3LYP functional with Grimme's dispersion correction and the WB97XD functional were trialled.^{356,358,359} B3LYP is a very popular hyper-GGA functional, while WB97XD is a newer functional constructed to better account for dispersion interactions. The cluster model has previously

been used successfully with a range of molecules, as evidenced in the literature. However, within the scope of the present work, inconsistent results and frequent adsorbate interactions with the edge hydrogen atoms of coronene appear to indicate that this model is not suitable for describing a range of molecules adsorbing on a carbon surface. With larger or multiple adsorbate molecules, this was expected to be an even greater problem. Due to this behaviour, and the added complication of BSSE in the cluster model, the two periodic models were pursued instead.

6.4.2 Evaluating the Periodic Model: CRYSTAL and CASTEP

The CRYSTAL and CASTEP software packages were used to model a repeating supercell containing layers of graphite.^{345–347} These software packages were run on the high-performance computer system 'slater' at the National Service for Computational Chemistry Software, with some additional CASTEP calculations run on the 'sol' system at the University of Sheffield. Unlike the cluster model, there is no edge for the adsorbate to interact with, but the size of the supercell must be considered to avoid unwanted interactions between adsorbates in adjacent cells.

The initial structure for the graphite was taken from the literature.¹⁹² A 3×3 or 4×4 supercell of this crystallographic primitive cell was used, with a 10 Å vacuum space added above the top layer of graphite to prevent any interaction along the vertical axis. This is illustrated for the 3×3 supercell in figures 6.3 and 6.4. The PBE functional was chosen as a well-established DFT GGA functional which was, most importantly, available in both software packages.³⁶⁰ An empirical dispersion correction was included, much like that added to the cluster models. In this case Grimme 06 was used, which was available for both CRYSTAL and CASTEP.³⁵⁵ By using the same functional and dispersion correction, a more direct comparison could be made between the two software packages. However, while CASTEP uses a plane wave basis, CRYSTAL does not, so it was necessary to choose a basis set for the CRYSTAL calculations. The basis set chosen for CRYSTAL was Peintinger-Oliveira-Bredow triple zeta valence with polarisation (POB-TZVP).³⁶¹ This was chosen because it was one of the built-in basis sets within the software that should be roughly comparable to a plane wave basis, as noted in section 6.2. However, because CRYSTAL uses localised basis sets, BSSE becomes a complicating factor in this model.

Initial adsorbate molecule geometries were generated using the default parameters of the GaussView (Gaussian, Inc.) program. For each molecule, the starting geometry was first optimised in an otherwise empty cell of the same dimensions as the graphite supercell. This is essentially the 'gas phase' molecule. The optimised molecule was then placed above the upper layer of graphite in the supercell at a distance of \sim 2–3 Å. This adsorbate/graphite system, as illustrated for methanol in figure 6.5, was then optimised. The energies of the optimised geometries were compared, and the difference was taken as the binding energy. That is

$$E_{bind} = E_{adsorbed} - (E_{mol} + E_{graphite})$$
(6.5)


Figure 6.3. Illustration of the 3×3 supercell used in the CRYSTAL and CASTEP models, with two graphite layers (CO₂ molecule included for comparison), and a top-down view of four repeats (2×2) of the 3×3 supercell.



Figure 6.4. Illustration of the construction of the 3×3 supercell used in the CRYSTAL and CASTEP models, with two graphite layers. The crystallographic unit cell forms a 3×3 grid which is merged, and a 10 Å vacuum space is then added to the upper part of the merged cell.

where $E_{adsorbed}$ is the energy of the adsorbate/graphite system, E_{mol} , is the energy of the isolated molecule within a cell and $E_{graphite}$ is the energy of the isolated graphite within the supercell.



Figure 6.5. Illustration of methanol on the graphite surface within the 3×3 supercell, optimised with the PBE functional and the Grimme 06 dispersion correction.

6.4.2.1 Benchmarking CRYSTAL

As with Gaussian, astrophysically relevant molecules that would be relatively simple for calculations were chosen for initial tests. In the first tests, CRYSTAL found a binding energy of 64 kJ mol⁻¹ for dimethyl ether (DME) and 45 kJ mol⁻¹ for carbon dioxide (CO₂). As these values were dramatically higher than experimental values of 28 kJ mol⁻¹ for DME, from the present work, and 24 ± 2 kJ mol⁻¹ and 20 ± 2 kJ mol⁻¹ for CO₂ from Ulbricht *et al.* and Edridge *et al.*, the test was repeated without the Grimme 06 correction.^{175,362} This resulted in binding energies of 28 kJ mol⁻¹ for methanol, 23 kJ mol⁻¹ for DME and 22 kJ mol⁻¹ for CO₂.

Thus the model agrees that methanol binds more strongly to the carbon surface than DME does, which binds more strongly than CO₂. The results without the inclusion of Grimme 06 are more reasonable, quantitatively, for DME and CO₂, which was not expected. Without further study it is uncertain if this is coincidental, and the value for methanol is still somewhat poor compared to experimental values. In experiments, values of $45 \pm 2 \text{ kJ} \text{ mol}^{-1}$, $48 \pm 3 \text{ kJ} \text{ mol}^{-1}$ and $48 \pm 1 \text{ kJ} \text{ mol}^{-1}$ are reported for monolayer methanol.^{175,204,224} A somewhat closer value of ~33 kJ mol⁻¹ was given for the lowest coverage of methanol studied experimentally.²⁰¹

An attempt was made to implement a counterpoise correction for BSSE by using ghost atoms. Unfortunately, this functionality cannot be used in conjunction with dispersion corrections in the CRYSTAL software package. Because of this limitation and the unexpected behaviour of the model with regard to the Grimme 06 corrections, CRYSTAL was abandoned for the rest of this work. Further investigation may be warranted, in the future, in order to understand the behaviour of adsorption and dispersion corrections in CRYSTAL.

6.4.2.2 Calibration of CASTEP

Unlike CRYSTAL and Gaussian, computational methods in CASTEP do not incur BSSE due to the use of a plane wave basis. As outlined in section 6.2, the basis is calibrated by convergence of the energy. To calibrate, initially a single layer of graphite (graphene) was optimised, within a supercell similar to the one illustrated previously in figure 6.3. Optimisations were calculated with cut-off energies of 300–600 eV in 100 eV steps, using $3\times3\times1$, $4\times4\times1$, $5\times5\times1$ and $6\times6\times1$ *k*-point meshes. The results are shown in figure 6.6, illustrating the convergence to a minimum energy. The improvement in energy beyond a 500 eV cut-off is very small (<0.1 eV), so this cut-off energy was chosen. Further, the difference between the $5\times5\times1$ and $4\times4\times1$ *k*-point meshes was minimal. Therefore the $4\times4\times1$ *k*-point mesh with a 500 eV cut-off was used for the calculations to follow. An additional calculation, using the $4\times4\times1$ *k*-point mesh only, was made with a 450 eV cut-off to confirm 500 eV was appropriate, as seen in figure 6.6. The built-in 'on-the-fly' pseudopotentials in CASTEP were used for all calculations.



Figure 6.6. Initial calibration of the CASTEP cut-off energy, with a single graphite layer, using the RPBE functional. The 300 eV value is not shown due to scale.

Initial tests, with methanol adsorbed on a single graphite layer, gave a binding energy of 21 kJ mol⁻¹. As was done in evaluating the CRYSTAL model, this result compares with the minimum experimental value of ~33 kJ mol⁻¹.²⁰¹ Following this initial test, it was considered that a two-layer graphite surface might provide better results. This two-layer graphite was illustrated previously in figures 6.3 and 6.4. Evaluating the binding energy of methanol above two layers of graphite gave a value of 24 kJ mol⁻¹. Previous work has concluded—or assumed—that the ~3.4 Å separation of the layers in graphite meant

that multiple layers were unnecessary when modelling physisorption.^{305,307,333} In the interest of computational efficiency, this may be worth considering for future work with this model, but here the double layer appeared to slightly improve the methanol binding energy with respect to the experimental value. This may be due to an energetic change in the graphite, as small inter-layer variation is seen in response to the proximity of model adsorbates. As a result, the two-layer model of graphite—in 3×3 and 4×4 supercells—was used going forward.

Since the initial calibration was done with single-layer graphite, a convergence test was again applied to confirm an appropriate cut-off energy, as shown in figure 6.7. This calibration used a $4\times4\times1$ *k*-point mesh and cut-off energies of 200–600 eV. As with the single layer, 500 eV proved to be a good cut-off value and was thus used for all subsequent modelling. This is a reasonable value when compared to previous literature, and indeed, a 500 eV cut-off has been used in previous modelling of adsorption of COMs and H₂ on surfaces relevant to astrochemistry.^{179,332} Thus the final parameters for the model were established, as listed in table 6.1. Geometry optimisation of the graphite using these parameters showed no significant change from the crystallographic input geometry. This provided an initial confirmation that the choice of functional and other parameters for the model were appropriate.



Figure 6.7. Further calibration of the CASTEP cut-off energy, with a double graphite layer, using the PBE functional and a $4 \times 4 \times 1$ *k*-point mesh. The 200 eV value is not shown due to scale.

6.4.2.3 Initial Benchmarking of CASTEP

As it was used for calibration, methanol was effectively the first molecule for which adsorption was modelled in CASTEP with the established parameters. The optimised geometry of the isolated, 'gas phase', molecule was very close to the established geometry for methanol. This had then been originally placed at a distance of ~2.0 Å from the upper graphite layer in the supercell. Following optimisation of the combined system, the molecule shifted to a distance of ~2.4 Å. Additionally, optimisation de-

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Table 6.1. Summary of the final parameters for the CASTEP model.

parameter	selection
functional	PBE
correction	Grimme 06
cut-off energy	500 eV
pseudopotentials	'on-the-fly'
<i>k</i> -point mesh	4×4×1
supercell	3×3 or 4×4

creased the separation of the two graphite layers from the initial 3.36 Å to 3.23 Å, though there was no deformation of the layers. Optimisation of the system caused no significant changes in the geometry of the methanol molecule itself. As previously noted in the discussion of calibration, the resulting binding energy (24 kJ mol⁻¹) showed poor agreement with experiment (~33 kJ mol⁻¹), similar to the results in CRYSTAL.²⁰¹ The model value for methanol here is very different in comparison to the previous computational result of 52 kJ mol⁻¹ reported by Adriaens using the PW1K DFT functional.³⁶³ While the result here seems to underestimate the binding energy, the functional employed by Adriaens appears to overestimate it. However it can be noted that the result from Adriaens is similar to the experimental values for the saturated monolayer energy.^{175,204,224}

Another small molecule, CO_2 , was modelled in the same way, as an additional simple test of the parameters. Again the model gave an accurate optimised geometry for the isolated CO_2 molecule. In this case, in the combined system there was then an initial distance of ~2.4 Å between the adsorbate CO_2 and the upper layer of the graphite. This shifted to a distance of ~3.2 Å following optimisation. As was the case with the methanol model, the separation of the two graphite layers decreased from the initial 3.36 Å. Following optimisation the separation was 3.22 Å, which is very close to the 3.23 Å separation of the graphite layers in the optimised methanol adsorption system. Again there was no deformation of the graphite and no significant change to the geometry of the adsorbate itself. The result was a binding energy of 18 kJ mol⁻¹. This value corresponds reasonably well with experimental values (24 ± 2 kJ mol⁻¹ and 20 ± 2 kJ mol⁻¹).^{175,362} Previous theoretical work for CO_2 interaction with a carbon surface, by Rubeš *et al.*, has had similar results to the model here.³⁴¹ They found a DFT/CC interaction energy of 16 kJ mol⁻¹ for CO_2 on coronene. They also found an MP2 interaction energy of 21 kJ mol⁻¹ for the same complex, but the authors note that MP2 generally overestimates the strength of weak intermolecular interactions.

So at this early stage, optimisation calculations could complete successfully and one binding energy result agreed reasonably with experiment while the other did not. A common theme in previous chapters has been the importance of intermolecular forces, and it can already be noted here that CO_2 molecules do not hydrogen bond with each other, while methanol molecules do. This was an early

indication of the complicating effect functional groups that have strong dispersive forces would have on the behaviour of the model. However, conversely, because CO_2 is relatively small and has limited intermolecular interactions, the good agreement with experimental desorption energy values indicates that the CASTEP model is appropriate for modelling simple adsorption on graphite. Accounting for intermolecular forces is explored more purposefully shortly, as it will be essential for modelling a broad range of COMs accurately.

6.5 CASTEP Results and Discussion

Provided that dispersion corrections were included, initial results for CASTEP binding energies were promising, so a general model for adsorption of astrophysically relevant molecules—especially COMs was pursued utilising this software package.

6.5.1 Monomer Adsorption

DME was one of the initial COMs modelled using CASTEP, once the parameters were established. Like methanol, it was placed above the two layer graphite model within the 3×3 supercell. Dimethyl ether was chosen for initial work because there were experimental results available for comparison from the current work, its geometry is relatively simple, and like CO₂, adjacent DME molecules do not have strong intermolecular interactions. It was considered with two different orientations relative to the graphite surface, as shown in figure 6.8. The vertical orientation shown in figure 6.8 (left) results in a binding energy of 28 kJ mol⁻¹ at a distance of ~2.8 Å, while the horizontal orientation in figure 6.8 (right) gives a value of 32 kJ mol^{-1} at a distance of ~3.0 Å. The carbon atoms of the dimethyl ether are at approximately the same distance from the surface (~3.8 Å) in both cases, but the oxygen being closer to the surface in the horizontal orientation appears to result in a more stable bound system. Both binding energy values are fairly close to the experimental value of $28 \pm 2 \text{ kJ mol}^{-1}$ from the current work, with the value for the less stable vertical orientation matching exactly. Regardless, it is clear that orientation relative to the graphite surface must be considered.

Other adsorbate molecules modelled in the 3×3 supercell were ethene, ethylene oxide, ethenol and toluene. The computational binding energy result for ethene was 18 kJ mol⁻¹, with an optimised adsorbate distance of 3.2 Å from the surface. The binding energy value is similar to the experimental value of 16.8 ± 0.1 kJ mol⁻¹, though it is not within the small experimental error limits.³⁶⁴ It is also similar to the 17 kJ mol⁻¹ theoretical DFT/CC value Rubeš *et al.* calculated for the interaction energy of ethene with coronene.³⁴¹ Values for ethylene oxide (23 kJ mol⁻¹ at a distance of 2.9 Å) and ethenol (27 kJ mol⁻¹ at a distance of 3.2 Å) are included in the summary in the following section—and appear reasonable for COMs—but there are no experimental values available for comparison at the present time for these



Figure 6.8. Illustration of the two dimethyl ether orientations on the model two layer graphite surface within the 3×3 supercell. The vertical (left) and horizontal (right) orientations were each optimised with the PBE functional and the Grimme 06 dispersion correction.

two molecules. In both cases the presence of the oxygen atom seems to cause the binding energy to increase significantly relative to the value for ethene. This appears to follow the pattern of results seen with respect to the orientation of dimethyl ether, which showed a favourable interaction between oxygen and graphite. Rather than being primarily intended for comparison to experimental adsorption as most of the results were, the binding energy values for ethylene oxide and ethenol were calculated for use in investigating surface-bound reactions. Lastly, the binding energy value for monomeric toluene was 44 kJ mol⁻¹, with a corresponding optimised adsorption distance of ~3.3 Å. This binding energy compares well with an experimental value of 42 kJ mol⁻¹ communicated by Stubbing, but is significantly lower than the 68 ± 7 kJ mol published by Ulbricht *et al.*^{175,365} However, it is important to note that toluene is a very bulky molecule relative to the confines of a 3×3 graphite supercell, and this aspect of the model will be explored further, particularly in section 6.5.5.

6.5.2 Model Overview

Table 6.2 summarises the results of the CASTEP model, while figure 6.9 visually shows the correlation to experimental values. To represent the CASTEP model on the lower axis, the figure uses the averaged values of adsorbate pairs, where available, or values for single adsorbed molecules otherwise. As seen in the figure, the correlation is good, with a ratio close to 1:1, supporting the general accuracy of the model with the chosen parameters. The early part of the process of developing the model has so far been described and the principle results will be discussed in further detail, with the following sections

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investigating different aspects of the model that have an influence on the evaluated binding energies

for each molecule.

Table 6.2. Comparison of theoretical binding energies with experimental monolayer or sub-monolayer energies of desorption. All values are in units of $kJ \text{ mol}^{-1}$. Where pairs of adsorbates are modelled, 'pair A' is the pair favouring interaction and 'pair B' is the pair not favouring or less favouring interaction. The 'average' is the simple average of these two values. Note that some species have multiple experimental results in the literature, which are given on separate rows in the table.

	CASTEP				Experiment
	single	pair A	pair B	average	
carbon dioxide	18	-	18	_	20 ± 2^{362}
					24 ± 2^{175}
ethene	18	-	_	-	16.8 ± 0.1^{364}
ethylene oxide	23	-	-	_	
ethenol	27	-	-	_	
dimethyl ether	32	_	28	_	$28 \pm 2^{\ddagger \star}$
methanol	24	40	25	33	~ 33 ²⁰¹
					45 ± 2^{204}
					48 ± 3^{175}
methyl formate	36	44	31	37	18 ± 1^{93}
acetaldehyde	27	39	-	-	$28 \pm 4^{\star}$
ethanol	32	44	35	39	53 ± 3^{202}
					52 ± 3^{204}
					50 ± 3^{175}
toluene	44	_	-	_	42 ³⁶⁵
					68 ± 7^{175}
glycolaldehyde	37	54	34	44	$47 \pm 8^{+93}$
2-propanol	37	51	43	47	$47 \pm 2^{\star}$
formic acid	23	61	34	47	48 ± 5^{366}
acetone	48	51	47	49	$39 \pm 1^{\ddagger 367}$
					56 ± 3^{368}
acetic acid	32	73	36	54	$55 \pm 2^{+93}$

[†] indicates bilayer or multilayer experimental desorption energy value

[‡] indicates desorption energy value from fitted stochastic models

* indicates experimental value from the present work



Figure 6.9. Graph showing the correlation of experimental to theoretical binding energy values with a linear fit (blue line). Unlike the table, bilayer and multilayer experimental values are not included in the figure. Poorly-fitting results for methanol, ethanol, methyl formate and toluene are highlighted in red. The linear fit is applied for all results, weighted by experimental error estimates. The dashed line indicates a 1:1 ratio, for reference.

6.5.3 Geometry Notes

Some general observations can be made with regard to the optimised geometries produced by the model calculations. Firstly, the separation of the graphite layers is measured as 3.21–3.25 Å when adsorbate molecules are present in the supercell. This differs from the 3.36 Å separation of the crystallographic source structure, which is maintained when the graphite is optimised alone within the supercell.¹⁹² Although this modification to the layer separation consistently appears when an adsorbate is introduced into the model, no significant deformation of the graphite layers themselves is observed. Even so, the variable inter-layer geometry seems to support the use of two-layer graphite for the model, as without the second layer this aspect would be lost. Further study is needed to quantify the effect. Another general observation is that the model is reasonably accurate when optimising the isolated 'gas phase' molecules. Select geometry values are compared to experimentally derived values from the literature in table 6.3. The values match well, in most cases with differences of ~1 % or less.

Additionally, following subsequent inclusion of the molecules as adsorbates in the supercells, the geometries of the molecules do not generally change significantly when optimised as part of the combined adsorbate/graphite systems. This indicates that physisorption and inter-adsorbate forces are the principle variable effects. This is taken as an indicator that physisorption is being modelled appropriately, as graphite should not significantly perturb physisorbed species.²⁹¹ One exception is seen in the rotation of the methyl groups for acetone upon adsorption, although bond lengths and bond angles are retained.

acetaldehyde	theory	expt ²⁸³	methyl formate	theory	expt ³⁶⁹
C-C	1.510	1.501	C=O	1.205	1.200
C=O	1.215	1.216	C-O	1.351	1.334
C-H	1.121	1.114	C-H	1.115	1.101
ethanol	theory	expt ³⁷⁰	acetic acid	theory	expt ³⁶⁹
C-O	1.436	1.431	C=O	1.215	1.212
O-H	0.973	0.971	C-O	1.365	1.361
C-C	1.517	1.512	C-C	1.505	1.517
dimethyl ether	theory	expt ³⁷¹	acetone	theory	expt ³⁷²
C-O	1.417	1.411	C-O	1.221	1.214
aCOC	111	111.2	C-C	1.519	1.520
			aCCC	117.7	116.0
formic acid	theory	expt ³⁷³	methanol	theory	expt ³⁷⁴
C=O	1.209	1.202	О-Н	0.972	0.956
C-O	1.353	1.343	C-O	1.431	1.427
О-Н	0.984	0.972	aHOC	107.3	108.9

Table 6.3. Comparison of select CASTEP PBE/500 eV gas-phase geometries with experimental values from the literature. All C-H bonds listed are associated with the carbonyl group of their respective molecules.

Other exceptions are seen in peripheral aspects of the molecule that are expected to change. These can be seen for adsorbate pairs where hydrogen bonding is favoured. In these cases, the C–O–H bond angles can shift by up to 5 degrees, and there can be rotation of -O-H groups to facilitate O–H…O links. Adsorbate pairs are discussed in more detail in section 6.5.4. As a final general note, adsorbate-graphite distances range from ~2.4–3.3 Å, but there does not appear to be a clear correlation between the binding energy and the distance between the adsorbate and the graphite surface. Further, from an examination of the optimised geometries, the adsorbate-graphite distance exhibited by single molecules is not significantly perturbed by interaction as part of a pair, indicating that both the surface and adsorbate interactions are modelled for dimers. These paired dimers are discussed in the following section.

6.5.4 Adsorbate-Adsorbate Interactions

From the early development of the model, it was quickly shown by methanol that accounting for adsorbate interactions is essential, and as shown in the experimental work, hydrogen bonding proves to have a very significant affect on the stability of adsorption, while other species of astrophysical interest are able to form dimers. In order to model 2-propanol and other larger COMs on the graphite surface, a 4×4 supercell of the two-layer graphite primitive cell was used, rather than the 3×3 supercell illustrated previously. This significantly increased the computational cost, but gave sufficient space for these species to adsorb. Additionally, with reference to table 6.2, there is a need to directly model adsorbate-adsorbate interactions on the model surface in order to enable better comparison to experiment. This is particularly true for molecules which have stronger intermolecular interactions. The importance, therefore, of modelling two molecules on the surface further necessitated using the larger supercell, in order to avoid unwanted interactions with image particles on the periodic surface.

In experimental work, the effects of adsorbate-adsorbate interaction on the desorption energy at monolayer or sub-monolayer coverages are common, as discussed in previous chapters. When considering the theoretical model as originally conceptualised—to isolate the interaction of a single adsorbate molecule with graphite—the effects of other adsorbate molecules will naturally be neglected. If the model is shown to work well, then this could be useful with regard to astrophysical environments. However, for comparison to experiment it will potentially fail. The first column of table 6.2 suggests this, as there is poor agreement between the results for single molecules and the experimental values.

6.5.4.1 Testing Adsorbate Pairing With 2-Propanol

The 2-propanol pair was the first model attempted that included adsorbate-adsorbate interactions, and it is shown in figure 6.10, oriented both to favour and disfavour hydrogen bonding. The hydrogen bonding of the alcohol makes its intermolecular interaction relatively straightforward to approach. Importantly, for this first case, the relative orientation of the 2-propanol molecules in the pair favouring hydrogen bonding was initialised with reference to the crystal structure, obtained by Cirkel and Boese, which is dominated by hydrogen bonding chains.²¹⁷ The 2-propanol molecules in the pair not favouring hydrogen bonding are oriented relative to the surface based on the optimised geometry of a single 2-propanol adsorbate, which had previously been modelled. The relative orientation of the 2-propanol molecules was arranged such that the distance between the alcohol groups prevented the formation of a hydrogen bond. For both pairs, the binding energy, *E*_{bind}, is then calculated by

$$E_{bind} = \frac{E_{adsorbed} - (2 E_{mol} + E_{graphite})}{2}$$
(6.6)

where $E_{adsorbed}$ is the energy of the system containing the two adsorbed 2-propanol molecules, E_{mol} is the energy of an isolated 2-propanol molecule within the supercell and $E_{graphite}$ is the energy of the isolated graphite within the supercell.



Figure 6.10. Illustration of two 2-propanol molecules, in the larger 4×4 supercell, favouring (left) and not favouring (right) hydrogen bonding interaction. The geometry of the system favouring interaction was initialised based on the 2-propanol crystal structure found by Cirkel and Boese.²¹⁷

For the 2-propanol pair interacting favourably via hydrogen bonding, illustrated in figure 6.10 (left), the binding energy was calculated as 51 kJ mol⁻¹, with a hydrogen bond length of ~1.85 Å and an adsorbate-surface distance of ~2.6 Å. Notably, the structure changed very little during optimisation, suggesting that the crystal structure used for the initial geometry was close to ideal. This consistency is another strong indicator that the chosen software and parameters are accurate. For the 2-propanol pair without hydrogen bonding, as in figure 6.10 (right), the result for the binding energy per molecule was 43 kJ mol⁻¹ and the result for the adsorbate-surface distance was ~2.5 Å. It was noticed that the average

of the two values (47 kJ mol⁻¹) compares very well with the 47 \pm 2 kJ mol⁻¹ experimental monolayer energy of desorption for 2-propanol from the current work.

This comparison of experimental results to an average theoretical value can be rationalised by considering the experimental conditions. For ices deposited at cryogenic temperatures the orientation of the molecules is distributed randomly initially, due to the extreme low temperature of the surface. There will be limited or no rotation following adsorption. Due to random probability, the effective binding energy will then be close to the average of a 50:50 split between orientations that most and least favour association. However, complications will arise in the experiment as the temperature increase during temperature-programmed desorption allows potential phase changes to occur. Crystallisation or the formation of dimers, for example, can cause ordering in the ice. This will lead to less randomness in the molecular orientation as certain orientations are energetically favoured. This will shift the experimental value away from the assumptions of the theoretical pair model. With consideration of the functional groups of each molecule and the intermolecular forces that result, this explains why molecules such as ethanol, which has a strong interaction due to hydrogen bonding, diverge from the average. At the same time molecules like DME are less affected, and even the theoretical monomer binding energies agree reasonably with the experimental desorption energies.

6.5.4.2 Expanding the Pair Model to Other COMs

Due to the apparent success of modelling 2-propanol pairs on the 4×4 surface, additional molecules were considered in the same way to see if it was a good general model. That is, binding energies were calculated via equation 6.6 by looking at two geometries, one favouring and one not favouring—or, at least, less favouring—intermolecular forces. Astrophysically relevant molecules were chosen for which experimental data already exist, as was done for the previously discussed theoretical work in the 3×3 supercell. In this case, these additional molecules were all COMs. Optimisations were considered with acetone, formic acid and ethanol, in addition to three isomers of $C_2H_4O_2$: acetic acid, glycolaldehyde and methyl formate. The resulting average binding energies for each of these chemical species—with the exception of ethanol and methyl formate—were in good agreement with experiment, as previously illustrated in figure 6.9.

For acetone, there was very little variation between the calculated binding energies for the two pair configurations. This seems reasonable as the intermolecular interactions for acetone are relatively weak. The initial orientation of the adsorbate acetone molecules was set using best judgement, with the molecular dipoles aligned for the pair favouring interaction and reversed for the pair less favouring interaction. Following optimisation, the binding energies were evaluated as 47 and 51 kJ mol⁻¹, while the adsorbate-graphite separations were ~2.8–3.0 Å. The average calculated binding energy for the acetone pairs is 49 kJ mol⁻¹, which falls between the known experimental values of 39 ± 1 kJ mol⁻¹ and

 $56 \pm 3 \text{ kJ mol}^{-1}$.^{367,368} The average is similar to the value for a single adsorbed acetone (48 kJ mol⁻¹), which also suggests that there is very minimal interaction between acetone adsorbates.

Compared to acetone, methyl formate showed somewhat more variation between the two pairs, with model binding energies of 31 and 44 kJ mol⁻¹ and corresponding adsorption distances of ~2.5 and ~2.7 Å. As with acetone, best judgement was used in choosing initial orientations for the molecules. For the pair favouring interaction, the pair were aligned such that the lone hydrogen from one ester group was 1.75 Å from the carbonyl oxygen of the other ester group. This could not be a true hydrogen bond however, which is clearly supported by the model, as this distance increases to 2.42 Å following optimisation. For the pair less favouring interaction, the two molecules were oriented such that hydrogen and methyl groups were closest. From the two optimised pairs, the calculated average binding energy is 37 kJ mol⁻¹, versus a much lower energy of desorption value of 18 ± 1 kJ mol⁻¹ from minimal experimental coverage.⁹³ The theoretical average here does compare well with more saturated experimental monolayer desorption energies, which reach a maximum of 35 ± 4 kJ mol⁻¹.⁹³ The experimental work found that desorption energy increases with exposure within the sub-monolayer regime. As the pair model here is simulating interacting methyl formate molecules, it is tempting to conclude that the model is accurate for methyl formate. However, it is important to note that the model is not consistent with respect to experiment because optimisation of a single adsorbate methyl formate, which has no adsorbate-adsorbate interactions, gives a binding energy of 36 kJ mol⁻¹. Overall it is difficult to draw a strong conclusion from the comparison between theory and experiment for methyl formate at this time.

In spite of its ability to hydrogen bond, ethanol also exhibited only modest variation between its two pairs, with model binding energy values of 35 and 44 kJ mol⁻¹. This is similar to the variation seen between the two 2-propanol pairs. The ethanol graphite distance was ~2.5 Å for both pairs, and for the pair favouring interaction the hydrogen bond length was 1.90 Å. The model average binding energy value of 39 kJ mol⁻¹ for ethanol significantly underestimates the binding energy when compared to experimental energies of desorption, which are fairly similar for two studies of ethanol monolayers, at 52 ± 3 and 50 ± 3 kJ mol⁻¹.^{175,204} In light of this poor result, contrasting with the good agreement of the 2-propanol model average, methanol was also modelled in pairs in order to consider adsorbate-adsorbate interactions for an additional alcohol. Due to the small size of methanol molecules, this was possible to investigate using the 3×3 supercell. The calculated binding energies for the methanol pairs were 40 and 25 kJ mol⁻¹. These average to 33 kJ mol⁻¹, which compares well with the lowest reported experimental energy of desorption for methanol (~33 kJ mol⁻¹).²⁰¹ However, it is a poor match for the monolayer values reported otherwise (~48, 45 ± 2 and 48 ± 3 kJ mol⁻¹).^{175,204,224} This illustrates the importance of considering the experimental conditions, while the good agreement with minimal coverage methanol in spite of its ability to hydrogen bond, supports the accuracy of the model, as

deviations can be attributed to large scale effects which occur in experiment. With regard to 2-propanol and acetaldehyde in previous chapters, for example, both showed non-ideal desorption order.

Other hydrogen bonding species showed more dramatic variation between the two geometries. There is a range of 20 kJ mol⁻¹ between the two glycolaldehyde pairs, which exhibit binding energies of 34 and 54 kJ mol⁻¹ at distances of ~2.5 and ~3.0 Å. For formic acid the distances are ~3.0 Å for both pairs, with binding energies of 34 and 61 kJ mol⁻¹, giving a larger range of 27 kJ mol⁻¹ between the two pairs. The greatest difference between adsorbate pairs is for acetic acid, which has binding energies of 36 and 73 kJ -mol⁻¹ at distances of ~3.1 and ~2.5 Å, and therefore has a range of 37 kJ mol⁻¹. Formic acid is the only one of these three with a recorded experimental monolayer desorption energy. The average theoretical binding energy value for formic acid here is 47 kJ mol⁻¹, which compares closely with the experimental value of 48 ± 5 kJ mol⁻¹, lying within the error limits.³⁶⁶

The reason why these three molecules exhibit such high ranges between the two pairs is due to the relatively strong interactions that are possible when they are oriented to favour those interactions. With reference to table 6.2, the binding energy for single molecules of these species are similar to those for the other species, but the 'pair A'-favouring interaction-binding energies are the highest overall. When considering the orientation of the adsorbates relative to each other, it is clear why this is so for the acids: each pair can form two hydrogen bonds, something that is not possible with the pairs of simple alcohols. For the acetic acid and formic acid pairs this occurs because the acidic hydrogen of each molecule interacts with the carbonyl oxygen of the other. For acetic acid the hydrogen bond lengths are 1.73 and 1.81 Å, and for formic acid they are both 1.56 Å. The case of glycolaldehyde is not quite as extreme, with only a single hydrogen bond of length 1.8 Å. The enhanced binding energy may be due to favourable interactions between glycolaldehyde molecules in adjacent supercells of the periodic system, where there is only a 2.6 Å separation between the hydrogen of one aldehyde group and the carbonyl oxygen of another. Though not as strong as hydrogen bonding, this could help stabilise the adsorbates, giving a relatively high binding energy per molecule. This result for glycolaldehyde suggests the importance of supercell size and the need to consider interaction with adjacent cells. However, this sort of interaction may be beneficial if aiming to better match experimental values.

6.5.5 Supercell Size Effects

As noted, the size of the supercell is an important consideration in general, but in the current work this is demonstrated especially well in the case of toluene. A single toluene molecule was optimised, adsorbed on the surface, both in the 3×3 and 4×4 supercells, as illustrated in figure 6.11. In the smaller supercell the effective coverage is 2.11×10^{14} molecules cm⁻² based on the dimensions of the supercell. The intermolecular distance between adsorbates is then only ~2 Å. The resulting binding energy for toluene in this supercell was 44 kJ mol⁻¹.



Figure 6.11. Illustration of toluene optimised within the larger 4×4 and smaller 3×3 supercells, showing the variation in the effective surface coverage on the model graphite substrate beneath.

In contrast, the binding energy calculated was 60 kJ mol⁻¹ in the larger supercell, where the effective coverage is 1.19×10^{14} molecules cm⁻² and the intermolecular distance >4 Å. This is presumably due to toluene in the smaller supercell interacting with its neighbours because of the relative proximity. This interaction reduces adsorption stability and therefore reduces the binding energy. This lower value for binding energy is in better agreement with the experimental desorption energy value for submonolayer toluene (~42 kJ mol⁻¹).³⁶⁵ This seems to suggest that, in order to correlate with experiment, eliminating all interaction on the horizontal axes between adjacent supercells may not be desirable. As previously noted, a separate experimental result has a significantly different energy of desorption at 68 ± 7 kJ mol⁻¹, in this case for a saturated monolayer.¹⁷⁵ The discrepancy in experimental results makes the importance of the supercell size to the theoretical results clear. As with the results for methanol and ethanol in the previous section, with consideration of the experimental conditions it illustrates that the model is appropriate and that the larger supercell reflects the low coverage adsorption, as it should.

6.6 Summary and Conclusions

The results for the range of molecules studied in the CASTEP model are promising, and they suggest that with further development it should be broadly applicable for studying adsorption of COMs on graphite. As previous computational research has shown, allowing for proper treatment of dispersion interactions and correction-or elimination-of BSSE also proved to be essential for the calculations to be accurate in general. Several aspects of the results provide good support for the baseline behaviour of the model. For example, in the first instance the optimised graphite structure agrees with the crystallographic reference, maintaining the correct layer separation.¹⁹² The good agreement for the simple case of CO₂, which is small and lacks significant intermolecular interaction, also add support for the baseline modelling of adsorption on graphite. Returning to literature crystal structures, the relative orientation of the pair of optimised 2-propanol molecules favouring interaction is maintained in agreement with the crystal structure, even when this is complicated by the pair also interacting with graphite.²¹⁷ This in particular helps to support the use of paired molecules in the model. Of course this is further supported, importantly, by the good agreement of the average binding energy from the two pairs. Lastly, the 'gas phase' geometries are reasonable, and both these geometries and the geometries of the graphite layers are generally retained during adsorption optimisation, suggesting that the model is capturing physisorption behaviour.

However, there are many considerations in order to allow adsorption in the DFT model to compare well with experiment. In particular there are a number of variables, which have not yet been fully explored, with regard to orientation on the surface and the relative importance of adsorbate-adsorbate interactions. This also implicates considerations for the size of the supercell. Adsorbate interactions are particularly clear in table 6.2, where results for a number of molecules are affected dramatically by the presence of a second adsorbate. This was emphasised by the 'pair model' developed during the course of this work. The effectiveness of the pair model was rationalised in the discussion, but there is nevertheless variation. When comparing directly to experiment, a simple average may be too simplistic. Even so, the generally good correlation—along with the promising baseline behaviour outlined in the previous paragraph—suggests that the model can be applied to study the small scale, even if it does not exactly match the large scale behaviour represented by experimental results.

It should be noted that there are practical complications in comparing theory and experiment simply due to the nature of the experimental results available, some of which have affected the comparison here. In some cases there was significant disagreement between the available experimental results from the literature. Also, for several molecules only full monolayer coverage—or multilayer coverage—desorption energies were available from experiments, preventing comparison to minimal coverage results. In a related limitation, some experimental work can provide energies from fitted stochastic models only, rather than directly from the experiment.

It is also noteworthy that when opting to model a single molecule with no inter-adsorbate interactions possible—something that is not easily accomplished in the laboratory—-there is significant disagreement with experiment. If this is accurate, it suggests that the type of experimental work used for comparison here is not always ideal for evaluating the astronomical conditions of isolated molecules, when those molecules are expected to exhibit significant inter-adsorbate effects in the lab. Whether comparing paired or single molecules, understanding why the experiments diverge from the results shown here may provide new insight into the adsorbed ices. In earlier discussion it has been shown that, provided consideration is given to the experimental conditions, the model compares well with experiment and should be pursued further, with clear utility for studying theoretical minimal coverages such as those important in astrochemistry.

Chapter 7

Conclusions and Astrophysical Implications

This chapter concludes the thesis with summarised key and general conclusions from the laboratory studies of complex organic molecules (COMs) and from the parallel work benchmarking a new density functional theory (DFT) based model for the adsorption of COMs on graphite. Examples of how the data gathered here may inform astrochemistry are illustrated, and finally, there will be a consideration of avenues for future work.

7.1 Experiment and Theory

In chapters 3–5, the COMs 2-propanol, dimethyl ether (DME) and acetaldehyde were studied on a graphite surface, that is, the analogue for a carbonaceous interstellar dust grain.^{20,21,37} Results were interpreted to provide indications of the adsorbed structures of low coverages, the development of multilayers, the patterns of crystallisation and kinetics of desorption. Experimentally-determined kinetic parameters can be directly incorporated into astrophysical gas-grain models.^{4,164} Additionally, knowing that dust grains develop icy mantles, and that comets often contain large quantities of water ice, the interaction between each COM and water was investigated.^{34,37,47,95,184}

In chapter 3 the hydrogen-bonding ability of 2-propanol was evident, and monolayer saturation at approximately 10 L_m exposures was taken as a probable indication of the formation of islands on the graphite surface.^{101,201,202,223} The limited ability for the ice to crystallise until higher exposures helps to confirm this.^{111,202} The strong hydrogen bond-mediated interactions cause 2-propanol to mix significantly with water during thermal processing, and co-deposited mixtures of 2-propanol and water showed entirely co-desorption. The ability for 2-propanol to affect the phase change of water itself was clearly evident in both TPD and RAIRS results. This has substantial implications for the interstellar context and associated models, which will be discussed shortly. In contrast, the results from chapter 4 initially showed that the repulsive interactions between DME adsorbates likely cause it to wet the graphite surface. With increasing exposure, there appears to be an intermediate desorption regime between the monolayer at ~2 L_m and multilayer at ~10–15 L_m , but there is no clear evidence of a bilayer. The significantly non-ideal behaviour necessitated the use of stochastic simulations to extract kinetic data.^{242,243} DME displayed an opposite trend to 2-propanol, with crystallisation favoured at lower coverages. The interaction with water was much weaker, though the ability for DME to act as a hydrogen bond acceptor was clearly evident. Infrared data showed hydrogen bonding at the DME-CI monolayer interface, with support from literature data.^{169,253,254} While evidence of trapping was seen in the presence of ASW, RAIRS results suggest that hydrogen bonding is lessened at ~120 K.^{253,254} This may be due to segregation of the ices, or due to the formation of clathrate hydrates, as suggested in previous work.¹⁶⁹ The weak interaction of DME with water ice indicates that it will likely behave similar to a volatile like CO₂, and therefore be controlled by the behaviour of the ice mantle where it resides. The model shown in section 7.2 will illustrate this.

The laboratory work presented in chapter 5 broadly followed the pattern seen for DME, and as such also contrasted the behaviour of 2-propanol. Like DME, acetaldehyde monolayers appear to saturate at ~2 L_m, supported by peak-fitting. The complex desorption at intermediate exposures is attributed to the formation of a monolayer plus subsequent islands in an intermediate growth mode.²²¹ This may be helped by weak aldehyde hydrogen bonding or the interaction of carbonyl groups.^{208,287,288} Unique among the three COMs studied here, acetaldehyde showed strong evidence of two crystalline phases. This is supported by the infrared data, with comparison to work in the literature, and the RAIRS data was shown to fit the known crystal structures of the two phases.^{222,284,285,299–302} The pure ice appears to adopt a monoclinic structure at ~75 K and an orthorhombic structure at higher temperatures. There was complex coverage-dependence for the phase-change behaviour, but the hypothesis that small changes in multilayer ice thickness at ~20 L_m exposures had a significant effect was confirmed by studying 25 and 30 L_m also. The adoption of the second crystalline phase was shown to be limited for 30 L_m and greater exposures. In contrast, for acetaldehyde dosed by a 20 Lm exposure, there was evidence of this phase at 75 K. This compares with the results for DME, which also saw crystallisation favoured at lower coverages, although the behaviour for DME was not complicated by two crystalline phases. The small quantities and long time scales in astrochemistry suggest that if acetaldehyde molecules were able to cluster, they could adopt the orthorhombic crystal structure at temperatures at least as low as 75 K. While this temperature is far too high for interstellar dark clouds, such temperatures are available around young protostars.^{67,103} For binary ice experiments with acetaldehyde and water, the infrared results suggest the segregation of acetaldehyde. This is concluded based on comparison with literature matrixisolation data and previous binary ice work with acetaldehyde, and is in agreement with recent farinfrared work which concluded observation of both segregation and crystallisation within the porous

water structure.^{94,222,284,299–302} Although the TPD pattern of acetaldehyde indicates that it will act as a volatile species—in a manner similar to DME, as shown in the next section—under astronomical conditions the ability for it to segregate and possibly even crystallise may cause unexpected behaviour as well as a modified spectrum.

7.1.1 Classifying the COMs

While rigorous experimental investigations into surface chemistry have value in their own right, the major motivation for this work was to contribute to the current effort to understand how COMs interact with surfaces relevant to astrochemistry and in the presence of water ice. The broad classifications introduced by Collings et al. and extended by Burke et al. are concerned with these interactions.95,96 These classifications were discussed in the introduction to chapter 4 because the contrast between DME and 2-propanol was clearly in line with the two extended classifications proposed by Burke et al., as indicated by previous preliminary results.⁹⁶ The extended classifications are particularly focused on describing the pattern of desorption seen for COMs with respect to their component functional groups.⁹⁶ Molecular species associated with the complex water-like classification have pure desorption temperatures similar to water, show evidence of thermally-driven mixing, and exhibit mainly co-desorption in mixed binary ices with water. On the other hand, species assigned to the complex intermediate classification have lower pure desorption temperatures than water and exhibit primarily volcano desorptionwith a minor co-desorption component—from mixed binary ices with water. In addition to revealing the dominance of the water interaction, the utility of these classifications for astronomers is in their application to astrochemical models and observations.^{154,184,357} They allow the modelling of desorption on astrophysical time-scales, even for molecules which have limited or no experimental data currently available, as the predicted general behaviour is shown to be reliable.

A simple summary of the interaction of each of the three COMs with water, from the current work, is shown here in figure 7.1. The COMs are represented by moderate multilayer TPD data, and exhibit two distinct categories, as illustrated in the figure. The patterns shown by these two categories clearly demonstrate that the results presented here support the preliminary classifications of DME and 2-propanol, as well as the predicted classification for acetaldehyde.⁹⁶ To the left of the figure, 2-propanol shows a pattern expected for the complex water-like classification, while to the right of the figure, both DME and acetaldehyde show behaviour consistent with the complex intermediate classification. Considering the binary ice work from chapters 3–5 as a whole, as summarised here, it can be concluded that the results in this thesis strongly support the use of these classifications for future work.



Figure 7.1. Summary of the patterns seen for the three COMs studied during the course of the laboratory work presented in this thesis. Multilayer 2-propanol, DME and acetaldehyde are shown, first as pure ices on HOPG and then in each of the studied binary ice systems with water. The left and right sides of the figure are not to scale with each other.

7.1.2 A DFT Model of Adsorption on Graphite

Chapter 6 made use of the evaluated desorption energies for the COMs on graphite to help benchmark the development of a computational model of graphite adsorption. Based on DFT, both cluster models and periodic models were initially trialled, with mixed results. Periodic model surfaces implemented with CASTEP software gave the best preliminary results and were therefore selected for the model.³⁴⁷ The general comparison with experimental results from this work and from the literature showed a good linearity. In addition, the model was consistent with physisorption, showing minimal perturbation of the optimised gas-phase geometries and the carbon surface, in good agreement with the expectation for inert graphite.²⁹¹ The comparison to literature data was enhanced by modelling adsorbate pairs on the surface, although not all permutations have been explored.

Results from chapters 3–5 were used, along with additional experimental data from the literature, in order to benchmark the results of the DFT model. As highlighted in the previous section, the ability for 2-propanol to act as both a hydrogen bond donor and acceptor sets it apart from the behaviour of DME and acetaldehyde, placing the COMs into two different classifications. The importance of these differences in intermolecular forces was seen when benchmarking the model also. For DME and acetaldehyde, the agreement between the theoretical binding energy of a single adsorbate and the experimental desorption energy from TPD was reasonable, and only relatively small changes were seen in pair models for these two COMs. In contrast, incorporating the contribution of the strong intermolecular interactions of 2-propanol—by modelling paired adsorbates—was essential to show good agreement between experiment and theory. Overall, it is concluded that the model can be a useful tool for helping to understand complex experimental results and for considering low effective coverages, which has particular relevance to astrochemistry where the relative concentrations of most complex molecular species are small.

7.2 Interstellar Chemistry

As explored in the introductory chapter, dust grain and ice surfaces are thought to be essential to the production and release of these molecules in astronomical environments.^{4,20,57–59} However, there are many unknowns that need to be understood in order to gain a complete understanding of these processes.⁹⁴ The nature of the surface processes is important with regard to the residence time of molecules adsorbed on the surface or trapped within ices, as different chemistry is expected in the solid and gas phases. Also related to residence time, from an astronomical point of view, it is important to know when molecules are released into the gas phase during the warm-up period of a young stellar object.¹⁰⁸ In addition to having a bearing on the possible processing of these molecules, and the generation of prebiotic species, it informs astronomical spectroscopic observations for which COMs are well-suited.⁶⁷ If

the specifics of adsorption and trapping processes are understood in laboratory or computational models, observation of these molecular species can thus provide astronomers with information about the environment around newly developing star systems.

The laboratory TPD data that have been shown throughout this thesis are recorded during a temperature increase at a rate of 0.5 K s⁻¹. This is slow enough to produce accurate results for potential kinetic analysis, but it is many orders of magnitude faster than heating rates in the vicinity of young stars, where temperatures rise at rates of approximately 1 K century⁻¹ to 1 K millenium⁻¹.^{98,103,173} Such rates are naturally impractical for laboratory work, yet the rate applied is known to affect the observed desorption temperature.¹⁰³ This effect can be illustrated through the use of stochastic simulations, where heating rate is simply a parameter of the simulation, as shown in figure 7.2. Such simulations were used earlier, in chapter 4, to estimate desorption energies where laboratory data was too non-ideal for leading-edge analysis.^{242,243}



Figure 7.2. Simulated TPD traces for monolayer DME on CI, using the parameters derived in chapter 4, but varying the linear heating rate from 0.5 K s⁻¹ to 1 K millenium⁻¹. The 0.5 K s⁻¹ trace was previously shown in figure 4.17.

While the effect is clear, it is still too simplistic to appropriately model desorption in the region of stars, which have non-linear heating rates dependent on their mass.¹⁸⁴ Viti *et al.* derived a heating rate

$$T = A t^B$$

where *T* is temperature (K), *t* is time (years) and the parameters *A* and *B* are determined by the mass of the star.¹⁸⁴ By combining this temperature evolution with the Polanyi-Wigner equation, Burke *et al.* showed that it was possible to simulate astrophysical desorption with a simple model, using kinetic parameters extracted from TPD data.^{194,226} They used 25 M_{\odot} (*A* = 1.766 × 10⁻⁴ and *B* = 1.289) and 5 M_{\odot} (*A* = 4.856 × 10⁻² and *B* = 0.6255) mass stars to show how the variation in heating rate affects the simulated desorption. For illustrative purposes, these same heating profiles are used here along

with the kinetic data—desorption order, desorption energy and pre-exponential factor—gathered from DME and acetaldehyde, as previously shown in chapters 4 and 5. The use of 5 and 25 M_{\odot} mass stars as examples is justified, as it was for Burke *et al.*, because DME and acetaldehyde are found in a range of interstellar environments. For example, both DME and acetaldehyde have been detected in the hot core around the low-mass protostar IRAS 16293–2422, and both have been detected in high-mass star-forming regions.^{147,153,154,160}

For the model, the ice coverage is set as 9.5×10^{21} molec m⁻², which corresponds to an amorphous solid water (ASW) ice of ~0.3 µm thickness, similar to interstellar ices.²²⁴ The parameters used for DME and acetaldehyde surface desorption were taken from the kinetic analysis of multilayers of each COM on crystalline ice (CI), as in sections 4.3.3.1 and 5.3.3.1. However, in a mixture there are three general components of desorption possible: surface desorption, volcano desorption and co-desorption. All three were seen for both DME and acetaldehyde when they were mixed with ASW. The key is that volcano and co-desorption are dominated by the behaviour of water, and for this reason the model uses kinetic parameters for ASW and CI to determine the desorption temperature for the volcano and co-desorption components, respectively, of the mixed model ice. Burke *et al.* sourced these values from previous work, and the same will be done here.^{116,226}

A mixed model ice, with COM species as dilute components, is proposed to be the most astrophysically relevant comparison, and the basis for this, as explained by Collings et al. is the current understanding of how both water and other hydrogenated species are formed.^{95,226} These species are all believed to be generated by reaction of astronomically-abundant hydrogen in combination with C, O, N and S atoms on dust grain surfaces and by subsequent radical chemistry driven by photoexcitation.^{87,95} Meanwhile, observations of COMs in cold regions, such as demonstrated by Bacmann et al. for the L1689B pre-stellar core, show that these complex species can be present prior to the warm-up that occurs during protostar formation.¹⁵² Laboratory ices co-deposited at cryogenic temperatures thus provide a reasonable analogy. The COM is assumed to be in a 1 % mixture as an initial approximation, with the proportions of each desorption sub-component determined by integrated areas from previously recorded mixture TPD data, as illustrated in figure 7.3. For both DME and acetaldehyde, the proportions of these three components are approximately consistent across a range of mixtures where the COM is a relatively small component: 9-22 % for DME and 4-15 % for acetaldehyde. Therefore, the proportions can be reasonably approximated for a 1 % mixture by extrapolation. The parameters for the model, including these derived proportions, are shown in table 7.1, and the resulting simulated gas-phase concentration profiles are shown in figure 7.4.



Figure 7.3. An illustrative example of evaluating the desorption component proportions for acetaldehyde. The TPD used here is a 4 % mixture of acetaldehyde in multilayer amorphous water. This TPD was previously shown in figure 5.23.

Table 7.1. Parameters used to simulate the gas-phase evolution of 1 % DME and acetaldehyde interstellar ices in the vicinity of 25 and 5 M_{\odot} stars. The values for ASW and CI are taken from the literature. ¹¹⁶

molecule	surface	volcano	co- desorption	E _{des} / kJ mol ⁻¹	n	v_n / molec m ⁻² s ⁻¹
DME	30 %	64 %	6 %	29	0	10 ^{31.5}
acetaldehyde	33 %	62 %	5 %	37	0	10 ³³
ASW^{116}				46.6	0.01	10 ³⁴
CI ¹¹⁶				47.9	0.01	10 ³⁴
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 E_{des} = desorption energy, n = desorption order, ν_n = pre-exponential factor



Figure 7.4. Gas-phase concentration profiles for DME and acetaldehyde in the vicinity of 25 M_{\odot} (upper) and 5 M_{\odot} (lower) stars, based on the model of thermal desorption at astronomical heating rates developed by Burke *et al.*²²⁶ Note that the bottom and top axes show significantly different time and temperature ranges for the two parts of the figure, while the vertical scales are identical.

7.2.1 Surface Science and Astrochemistry

While a full consideration of incorporating the results into astrochemical models, in collaboration with astronomers, is beyond the scope of the current work, these illustrations are a straightforward example of how the laboratory results may be applied to the astrophysical context. There are many factors to astrochemical models, including the nature of the formation and destruction of molecules, mobility of species on the surface and the influence of both thermal and non-thermal desorption processes, all of which can generate a complex chemical network.^{4,166} Many aspects of these models are still uncertain and therefore matters for debate. One concern which models and astronomical observations attempt to clarify is the relative importance of dust grain and gas phase formation mechanisms regarding the production of complex organics. Although grain surface reactions are known to be essential to the general chemistry of the interstellar medium, the relative influence for particular species is still a matter of ongoing study.^{18,154,165} This was previously illustrated, for example, in the introduction of chapter 4, where a review of observational and modelling literature highlights respective conclusions that surface reactions, gas-phase reactions or both are important in the formation of DME.^{4,18,147,153,154,164,205,375}

The gas-phase concentration of species with respect to the developing temperature during warm up around a protostar is one measure used to understand this.^{147,154} However, as noted in the previous section, Bacmann *et al.* showed a pre-stellar origin of COMs, and as the model presented in figure 7.4 shows, the gas-phase evolution during subsequent warm-up can be significantly affected by water ice.¹⁵² This will therefore need to be taken into account when astronomers draw conclusions from their observations, and shows the value of studying these binary ices in the laboratory. It is important to note that only thermally-driven processes are studied here and photo-driven processes are also expected. Indeed, Bacmann *et al.* propose this as an explanation for the formation and desorption of COMs in the cold L1689B pre-stellar core.¹⁵² Laboratory work has also been used to show that photochemistry occurs for adsorbed molecules, generating varied chemistry.^{31,83,86,102,128–137} With reference again to the results shown in the present work by figure 7.4, the extended residence time and the coincident shielding provided by dust grains and enforced by water ice trapping will influence the available photochemistry for retained molecules. This is important for volatiles such as DME and acetaldehyde, which would otherwise be released into the gas phase much earlier, and likely be subjected to more significant photodestruction in addition to a different range of favoured reactions once in the gas-phase.^{18,166}

Conspicuously, 2-propanol was not included in the modelling in the previous section. Astrophysical implications for 2-propanol are necessarily limited by the fact that it has yet to be detected. It would be possible to include 2-propanol in the model, and with its high proportion of co-desorption from a mixture, as seen in figure 7.1, it would have similar simulated gas-phase concentration profiles as those shown for acetic acid and glycolaldehyde by Burke *et al.*, which show no gas-phase concentration increase at all until ~105–110 K.²²⁶ Although it has been excluded from the simulation, there is a significant parallel to note here with regard to the favouring of co-desorption. Burke *et al.* speculate, in their conclusions from the model, that the early appearance of gas-phase methyl formate—relative to acetic acid and glycolaldehyde—may explain the fact that it is more widely detected.²²⁶ The same rationale could be applied to 2-propanol, as it was previously noted that its isomer methoxyethane has been detected, in spite of being less stable under interstellar conditions.²⁰⁷ The structure of methoxyethane would expect it to show complex intermediate behaviour, similar to methyl formate, so it can be concluded that at least one factor in the lack of 2-propanol detection so far may indeed be its strong interaction with water.

7.2.2 COMs and the ASW-CI Phase Change

While water can hydrogen bond to DME and acetaldehyde—and the effects of this were clearly seen in the data presented in the thesis—the influence of these COMs on the behaviour of water appears to be limited compared to a complex water-like molecule such as 2-propanol. In an interstellar context, low relative proportions of DME and acetaldehyde may limit their effect on water ice, as the strength of the effect was shown in the laboratory results to correlate with the proportion of each COM relative to the amount of water. However, 2-propanol showed significant influence on the ASW-CI transition for both layered and co-deposited water (figure 3.18). As discussed in section 7.2, the model of astrophysical heating makes use of the desorption profiles of pure ASW and CI to determine the temperature at which volcano and co-desorption can occur in astronomical environments.²²⁶ For this reason it is not thought to be sufficient to model 2-propanol in the same way as DME and acetaldehyde.

Instead this points to the last significant conclusion of this thesis. When considering that methanol and ethanol have also been shown to affect the behaviour of water under astrophysical conditions, it seems that the effects of the alcohols—and most likely many complex water-like species—must be fully accounted for when describing the chemistry of the ISM, to which water is highly central.^{87,88,95} Though the alcohols all have an effect on the phase change of water, 2-propanol and ethanol in particular show evidence of inhibiting this process, while methanol promotes it.^{111,112,202,237} This will in turn affect the release of volatiles and weakly-interacting species, which is primarily dependent on the phase and desorption of water ice.^{95,97,99,100,226} This is illustrated in the current work by the complex intermediate species DME and acetaldehyde, with reference again to figures 7.1 and 7.4. Though any given species of COM will only represent a small fraction of ices bound on dust grains, it appears reasonable that the cumulative effects of hydrogen-bonding species could have significant implications for the behaviour of solid water phases in the ISM, and therefore the chemical environment in those regions of space.^{93,95,184,212-214} Further, in connection with the discussion of the previous section, the modified trapping will constrain the possible gas-phase chemistry that can occur for these species, having significant implications for the chemical development of young star systems as temperatures rise.¹⁶⁶ As planetary discs form, the 'snow line' where molecular species can freeze out and be adsorbed onto dust grains is known to have a direct bearing on the eventual make up of the planets themselves.^{89,162,163} Modified trapping could affect the make-up of comets also, which are formed of dust and ice, and are themselves implicated in the further development of planetary chemistry through impacts.^{34,37,47,104} The effects of hydrogenbonding COMs could thus be far-reaching, and they should therefore be considered in greater detail in the development of astrophysical models of chemical networks, where the behaviour of molecules clearly can not be considered in isolation.¹⁶⁶

7.3 Future Work

Future work following the results presented here should continue to consider the similarities and differences between the two apparent classes of COMs, as the dichotomy is quite strong, and for COMs appears to continue to be primarily dependent on the ability of a molecular species to form strong O–H···O hydrogen bonds. Along the same lines, the demonstrated affect that hydrogen-bonding species have should be investigated in greater detail as a matter of priority with regard to implications for astrochemical models. While some molecules such as methanol cause earlier onset of crystallisation, others such as 2-propanol significantly delay the phase change. The effects should be quantified further with regard to particular molecules and relative proportions in binary ices. Although substantially more complex, it may also be worth considering mixed ices with three components or more. For example, combining methanol and 2-propanol which have opposing effects on the behaviour of water. This may help to better understand effects that could be seen in multi-component astrophysical ices. Additional investigations of isomers could help to understand the role that molecular size and other functional groups have, and how these aspects of molecular structure might be significant against the apparently dominant influence of hydrogen bonding, in order to further understand the dichotomy of the complex intermediate and complex water-like classifications.^{93,95,96,179}

Better understanding of the structure and growth of small coverages was limited in the work here due to the relatively low sensitivity of RAIRS, particularly when applied to a graphite surface. While patterns of behaviour as presented here are strongly suggestive, it may be possible to gain greater insight through the use of probe molecules. This could enable the sensitivity of TPD data to support an understanding of monolayer growth and how ices develop at coverages intermediate between the monolayer and bulk multilayer. In addition, to better understand phase changes it may be worth performing experiments at varying deposition temperature or with longer annealing times. This could be particularly relevant for astrochemistry, with regard to re-adsorption on dust grains and the long heating time scales, respectively.

The theoretical work has established an effective DFT-based description of adsorption on graphite through the use of CASTEP and a periodic model. Beyond the scope of this work, if further modelling continued with CASTEP and the parameters established here, but without a need to compare to CRYSTAL, the RPBE functional could perhaps be explored as well. This functional is not available in CRYSTAL but is thought to be better at describing adsorption and could therefore potentially yield more accurate results. At the same time, the results presented here showed unexpected behaviour in CRYSTAL which deserves further exploration. It would also be worth optimising molecule pairs in the gas phase and calculating dimer binding energies. Additionally, the interactions between adsorbed COMs and water molecules could be investigated on the theoretical graphite, benchmarking the behaviour against matrix isolation work with such complexes could provide insight into the interactions of COMs and water, which are essential to a complete view of astrochemistry. Other important avenues to continue investigating-both with the molecules included in chapter 6 and any additional COMs which are modelled—are the effects of cell size, as was seen for toluene, and the effects of orientation on the surface, as was seen with DME. Orientation of dimers and the different possible intermolecular interactions should be quantified within the model. Lastly, although software limitations appear to be a factor, the model captures physisorption well and could be appropriate for studying surface-bound reactions theoretically, in order to inform laboratory experiments in this area.

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