

# Towards a Laboratory Strategy for the Study of Heterogeneous Catalysis in Stratospheric Ozone Depletion

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## 1 Introduction

In 1985, Farman, reporting on a series of measurements of austral spring average stratospheric ozone concentrations made at the British Antarctic Survey (BAS) Halley Bay facility and stretching back to International Geophysical Year (1957), clearly demonstrated a decline in these levels.<sup>1,2</sup> The decline appeared to be accelerating in the late 1970s and early 1980s, as shown by the data reproduced in Figure 1. The trend exhibited by Farman's more recent data was soon to be corroborated by a re-analysis of historical data from the *Total Ozone Mapping Spectrometer* (TOMS) mounted on the Nimbus 7 satellite.<sup>2</sup> Subsequently, a number of large-scale coordinated field campaigns such as the Airborne Antarctic Stratosphere Experiments (AASE I and II) and the European Arctic Stratospheric Ozone Experiment (EASOE) have made measurements of global stratosphere ozone concentrations using a variety of complementary techniques and have highlighted a small but significant decline in recent years in both the Antarctic and the Arctic. These studies have also served to enhance our understanding of the composition of the polar stratosphere and its perturbation by pollutants. Although Arctic and mid-latitude perturbations are not as drastic as the Antarctic phenomenon, depletion of stratospheric ozone levels on a global scale is now known to be occurring and is clearly of significant concern to mankind.

While the chemistry of stratospheric ozone formation and destruction in the homogenous gas phase is well established,<sup>3–5</sup> sophisticated atmospheric models, constructed in an attempt to explain the geochemical field observations and including all known homogeneous chemistry and appropriate meteorological processes of relevance, do not appear to do so. New chemistry or new meteorology must be proposed to develop these models. Since a discussion of atmospheric physics is beyond the scope of this review, we will concentrate on possible new chemistry of relevance to global stratospheric ozone depletion.

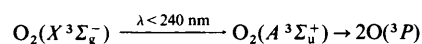
Field observations in the Antarctic indicate that the enhanced ozone depletion each austral spring is a result of the ultra-low temperatures (< 200 K) attained within the trapped airmass of the polar vortex and the consequent formation of *Polar Stratos-*

*pheric Clouds* (PSCs).<sup>6</sup> Such clouds consist of either small ice particles (Type II PSC) or solid nitric acid trihydrate (NAT) particles (Type I PSC). The new chemistry that has come to light is the catalytic regeneration of ozone depleting species from stable reservoir materials on cold solids. In global terms, the rôle of PSCs is clearly negligible as the low temperatures necessary for their formation are rarely achieved outside the polar vortices. However, the low temperature (190–230 K) sulfuric acid (40–60% H<sub>2</sub>SO<sub>4</sub>) aerosol, always present in the stratosphere, may provide a suitable surface for such chemistry at other latitudes. The study of cold, acidic solid and liquid surfaces will therefore be of relevance in widening our understanding of stratospheric ozone depletion and it is the aim of this brief review to highlight some of the techniques that have been brought to bear on this problem.

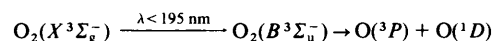
## 2 Background

### 2.1 The Chemistry of Stratospheric Ozone

The chemistry of ozone formation and destruction in the homogenous gas phase is well documented.<sup>3–5</sup> Oxygen is known to photodissociate at all wavelengths shorter than 240 nm, producing both ground state O(<sup>3</sup>P) and excited O(<sup>1</sup>D) atoms. The former are produced both by the photodissociation of the A <sup>3</sup>Σ<sub>g</sub><sup>+</sup> state populated by excitation in the weak, forbidden Herzberg I band system in the 195 to 240 nm region,



and by excitation into the B <sup>3</sup>Σ<sub>u</sub><sup>+</sup> state via the well-known Schumann–Runge bands at wavelengths below 195 nm.

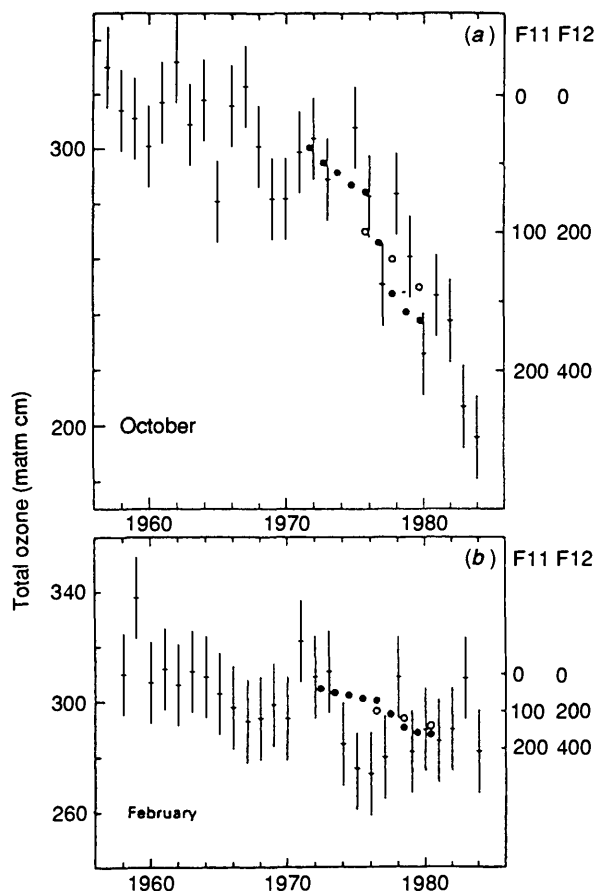


Andrew Horn obtained his B.Sc. (Chemistry) and Ph.D. (Surface Science) from the University of East Anglia in 1986 and 1989, respectively, before holding a postdoctoral fellowship there studying reactions on ruthenium surfaces. In 1990, he moved to the Physics Department of the Loughborough University of Technology where he undertook studies of mixed metal alloys. Since returning to EUA in 1992, he has developed techniques for the laboratory study of heterogeneous reactions relevant to ozone chemistry, and was appointed to a lectureship in physical chemistry in 1993.



Dr. Martin McCoustra was born in September 1962 in Falkirk, Stirlingshire. He gained his Ph.D., through a scholarship from the Carnegie Trust for the Universities of Scotland, on the study of the photodissociation dynamics of NO-containing molecules from Heriot-Watt University in 1987. In April 1988, after a short postdoctoral period with his former supervisor (Professor J. Pfab), he was appointed to a lectureship in physical chemistry at the School of Chemical Science of the University of East Anglia. There he has developed new research interests in the study of dynamics at the gas–solid interface and in the heterogeneous aspects of the chemistry involved in stratospheric ozone loss as well as retaining an interest in free jets and their use in spectroscopy.

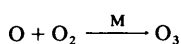




**Figure 1** (a) Austral Spring (October) and (b) Summer (February) monthly means of total ozone (crosses) at Halley Bay, and Southern Hemisphere measurements of  $\text{CFCl}_3$  (F11, filled circles) and  $\text{CF}_2\text{Cl}_2$  (F12, open circles) in p.p.t.v. over the period 1957–84. Note that the F11 and F12 amounts increase down the figure to emphasize the correlation with ozone loss.

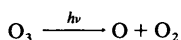
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The excited  $\text{O}(^1D)$  atoms are produced only by the latter mechanism. These excited-state atoms are rapidly relaxed collisionally. The subsequent ozone formation step,

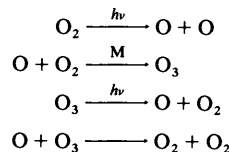


where M is a third body required to remove excess internal energy in the nascent  $\text{O}_3$  molecule by collisional energy transfer, involves only the ground-state  $\text{O}(^3P)$  atoms.

The primary destructive mechanism is photochemical. Ozone itself is known to be highly photochemically active, absorbing light at all wavelengths below 1180 nm. It absorbs most strongly in the near-UV region below 350 nm, producing oxygen atoms and molecules in a variety of electronic states dependent upon the excitation wavelength.

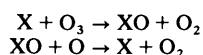


As such, ozone effectively blocks all UV radiation in the range 240 to 290 nm. It is this, in combination with the blocking of shorter wavelengths by molecular oxygen absorption, that prevents any significant flux of UV radiation of wavelength shorter than 290 nm reaching the surface of the Earth. In addition, however, the reaction of free O atoms with ozone leading to the formation of molecular oxygen is known to occur. In 1930, the combination of the ozone-forming process and the two ozone destroying processes discussed above,

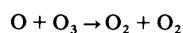


was proposed by Chapman to be primarily responsible for the formation of the thin, stable ozone layer in the stratosphere<sup>7</sup> and now bears his name – *The Chapman Cycle*. However, simple atmospheric models using only this chemical mechanism with an appropriate incident solar UV flux and suitable thermal and mass balance relationships overestimate the concentration of ozone in the ozone layer by a factor of as much as five. Clearly, even in the unperturbed stratosphere, there must be additional ozone-loss mechanisms in operation.

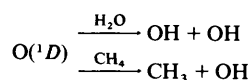
The additional loss mechanisms can in part be summarized by the simple catalytic cycle,



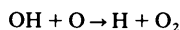
This has the net effect of removing two *odd* oxygen species (O and  $\text{O}_3$ ) and producing two *even* species (two  $\text{O}_2$ ),



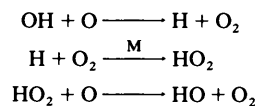
Various catalysts X are available within the stratosphere. At altitudes above 50 km, the dominant catalysts are OH radicals and H atoms. This is the  $\text{HO}_x$  Catalytic Cycle. The OH radicals are produced by reaction of  $\text{O}(^1D)$  with water and methane present in the stratosphere,



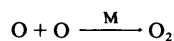
and the H atoms by the subsequent reaction,



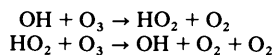
In addition to the simple  $\text{HO}_x$  cycle, more complex odd oxygen-removing cycles involving  $\text{HO}_x$  species are known to occur such as,



which has the net effect,

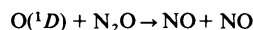


and,



which has the overall effect of removing two ozone molecules and generating three oxygen molecules.

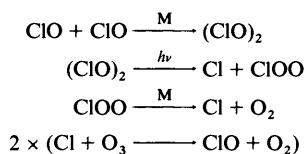
At somewhat lower altitudes, around 40 to 45 km, the dominant catalyst is NO, giving the  $\text{NO}_x$  Catalytic Cycle. NO is produced from the reaction of nitrous oxide with  $\text{O}(^1D)$ ,



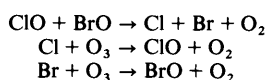
In the late 1960s and early 1970s, considerable concern was expressed about the potential perturbation of the  $\text{NO}_x$  cycle by the injection of substantial quantities of NO directly into the stratosphere by high-flying supersonic stratospheric transport (SST) aircraft. The failure of the envisaged fleets of these aircraft to appear alleviated the concern. However, this potential

problem may yet return as there appears to be growing interest in the further development of such stratospheric SST vehicles. In addition, increasing  $N_2O$  concentrations as a consequence of the increased use of nitrogen-based fertilizers to maintain high crop yields across the globe is of concern, since this may subsequently lead to an increase in the stratospheric NO concentration. NO from this indirect source is not as readily controlled as NO emission from SSTs and may therefore be more of a problem.

At lower altitudes still, above 30 km, the catalytic cycles involving chlorine and bromine atoms, the *Hal<sub>x</sub> Catalytic Cycle*, become important. At low temperatures and high halogen monoxide concentrations additional steps involving the so-called *Dimer Cycle*,



and the reactions,

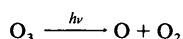


both of which have the net effect of converting two molecules of ozone into three oxygen molecules, must be considered. In the clean stratosphere, the only source of Cl and Br atoms is the photolysis of the corresponding methyl halide which originates from biogenic sources. Under such conditions, the concentrations of ClO and BrO are too low for the ClO dimerization and ClO–BrO reactions to be significant. Any additional anthropogenic source of halogen atoms will clearly perturb these catalytic cycles. This was recognized in the early 1970s by Molina and Rowland in their consideration of the potential impact of the increasing use of chlorofluorocarbons (CFCs;  $\text{CCl}_x\text{F}_y$  and  $\text{C}_2\text{Cl}_x\text{F}_y$ ) and their brominated counterparts.<sup>8</sup> Whilst these materials are photochemically stable in the troposphere, they undergo rapid photodissociation in the presence of the shorter wavelength UV radiation present above the ozone layer. This releases a substantial and growing quantity of halogen atoms directly into the stratosphere. It is significant that the increase in atmospheric loading of CFC over recent decades almost mirrors the ozone depletion data reported by Farman as shown in Figure 1. Quite clearly, the additional halogen loading and perturbation of the *Hal<sub>x</sub> cycle* is of significance in explaining both the Antarctic ozone depletion and also more global depletion phenomena.

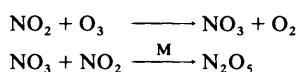
In addition to the ozone-destroying catalytic cycles, a number of reaction cycles exist that simply interconvert  $\text{O}_3$  molecules and O atoms. Consequently, these do not affect the overall balance of the ozone chemistry but simply trap the destructive catalytic species in a non-destructive channel. This is exemplified by the process,



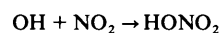
which has the net effect,



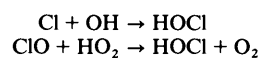
*i.e.* simply photosensitizing the decomposition of  $\text{O}_3$ . In addition to such *null cycles*, the catalytically-active species can be trapped into relatively stable and unreactive *reservoir* species. For the  $\text{NO}_x$  cycle, up to about 10% of the  $\text{NO}_x$  is trapped as the stable reservoir species  $\text{N}_2\text{O}_5$ , produced by the sequence of reactions,



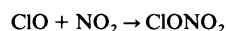
These become important at night when substantial concentrations of  $\text{NO}_3$  can be built up. A further 50% of the  $\text{NO}_x$  is trapped in the form of nitric acid ( $\text{HONO}_2$ ),



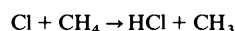
which, in addition, traps a substantial proportion of the active  $\text{HO}_x$  and provides a link between two of the important destructive catalytic cycles. Similar links between the destructive  $\text{Hal}_x$  and other destructive cycles are to be found in the reservoir species hypochlorous acid, HOCl, formed by reactions such as



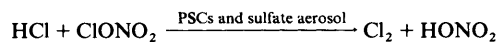
and chlorine nitrate,  $\text{ClONO}_2$ ,



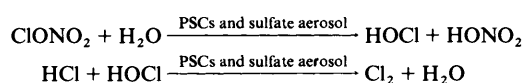
The principal reservoir for the *Hal<sub>x</sub> cycle* is the corresponding hydrogen halide, formed by reaction of the halogen atom with stratospheric methane,



Any new chemistry which affects the stability of these reservoir species will obviously therefore alter the overall balance of the chemistry within the stratosphere. It has been demonstrated that the presence of the cold, acidic surfaces described above (PSC particles and sulfate aerosol particles) plays the major rôle in perturbing the steady state by more rapidly regenerating the destructive halogen atoms from their relatively stable reservoirs than by normal gas-phase photochemical routes.<sup>6</sup> This is believed principally to involve the reaction



which is thought to occur in two steps,



generating molecular chlorine, which is rapidly photolysed to yield free chlorine atoms. Additionally, this process traps nitric acid within a solid or liquid matrix from which it is unlikely to escape and therefore will subsequently be unable to participate in the normal photoinitiated gas-phase stratospheric chemistry of nitric acid. This effectively reduces the overall concentration of trapping partners ( $\text{HO}$  and  $\text{NO}_2$ ) for the active Cl and ClO in the stratosphere, enhancing the effect of the destructive catalytic cycles involving these species.

## 2.2 Databases of Relevant Chemical Information

Many of the important chemical species mentioned in the previous section have been identified by field studies as being present in the stratosphere and have been characterized in the laboratory by a number of techniques in the course of other diverse investigations. We are therefore already provided with a large database of chemical and physical information which may be exploited. Perhaps the largest database that exists is that of spectroscopic information. Techniques such as infrared, microwave, and UV/visible spectroscopy are frequently applied as a matter of course during chemical experiments in virtually every laboratory. Whilst the conditions under which these spectra have been obtained are generally not directly relevant to the chemistry of the stratosphere, they do serve to provide an extensive reference library for the assignment of spectra obtained in laboratory studies of ozone loss in the presence of cold surfaces.

### 2.2.1 Matrix Isolation Techniques

The low-temperature chemistry of the stratosphere involves many species which are extremely unstable at room temperatures. One of the most significant techniques for the stabilization of reactive compounds and photolytic intermediates for spectroscopic study is matrix isolation (MI). A compound (or its precursor) is mixed in the gas phase with a supporting gas such as argon, nitrogen, or oxygen and is then condensed on a cold window. Typical matrix ratios are in the range 1:100 to 1:10,000, depending upon the nature of the compound and its tendency to aggregate. Window temperatures of between 4.2 and 20 K are easily obtained using a helium cryostat. At these ultra-low temperatures and with high dilution ratios, the trapped molecules are sufficiently far apart to be unable to react with each other. By decreasing the matrix ratio, we can also adjust the conditions to investigate the formation of dimers and higher aggregates. The species trapped in the matrix can be studied using a variety of methods including infrared, UV/visible, and Raman spectroscopy.<sup>9</sup>

As an example of potential relevance, the formation and stability of HCl:H<sub>2</sub>O aggregates has been studied extensively in low temperature matrices.<sup>10</sup> Below 50 K, the number of water molecules available per HCl unit determines whether or not proton transfer occurs to produce an ionic hydrate: the limit appears to be three water molecules. Warming above 60 K results in the formation of amorphous ionic hydrates for all water:HCl ratios. Low-temperature matrices therefore appear to assist in the stabilization of an unstable molecular complex. Extrapolating such measurements to higher temperatures, the adsorption of HCl on ice at stratospheric temperatures will initially involve the arrival of an intact molecule of HCl at the surface, followed by the formation of a weak bond to the surface and subsequent dissociative adsorption. Whilst the resulting surface species can be analysed using the spectroscopic methods described below, the weak initial interaction occurs on too short a timescale for this approach to be useful. Experimentally, MI studies at low temperatures have shown that the interaction is a weak hydrogen bond between the HCl molecule and the oxygen atom of the surface water.<sup>11</sup> Theoretically, and in excellent agreement with detailed experiments, Clary and co-workers<sup>12,13</sup> have modelled the interaction of HCl with an ice crystal by the use of classical trajectory calculations, employing both *ab initio* potentials for the interactions of HCl with a single H<sub>2</sub>O molecule in the ice surface and molecular dynamics potentials for the behaviour of the ice, assuming both dissociative and non-dissociative adsorption mechanisms. Their results suggest that the molecular interaction is very weak, leading to a low equilibrium surface concentration of physically adsorbed molecular HCl.

### 2.2.2 Condensed Phase Vibrational Spectra

Classical methods for the characterization of molecular vibrations, such as Raman and infrared spectroscopy, provide perhaps the most useful information in the context of PSC chemistry. Vibrational spectra are extremely sensitive to both inter- and intra-molecular bonding in the condensed phase, and can provide a great deal of information about molecule–molecule and molecule–surface interactions. There are in the literature many studies, some dating back to the early days of infrared and Raman measurements, of the structure and bonding of important stratospheric species such as HCl, HBr, and HONO<sub>2</sub> with water. These studies cover a broad range of conditions, from gas-phase molecular complexes to solid films of ionized polyhydrates<sup>14,15</sup>

### 2.2.3 Photolysis and UV/Visible Studies

As discussed above, short wavelength UV photolysis plays an important role in the homogeneous chemistry of the stratosphere. Determination of the yields of products from such photolyses and the variation of these yields with wavelength are

crucial to our understanding of photo-initiated chemistry. Whilst such measurements are routine in the gas phase, analogous measurements on the potentially perturbed species adsorbed on cold surfaces have yet to be made in detail and are likely to be highly significant. Photochemical studies in low-temperature matrices have gone some way to providing this information and have indicated that alternative reaction channels may become available to species trapped at or near a surface.<sup>16</sup>

### 2.2.4 Crystallographic Methods

X-Ray crystallography of the structure of ionic hydrate single crystals can provide information about the nature of the hydrogen bonding in H<sub>3</sub>O<sup>+</sup> ions.<sup>17</sup> This information can be used in the spectroscopic identification of a number of acid polyhydrates, for which the infrared and Raman spectra indicate a number of O–H bond lengths and environments. Additionally, the structure of adsorbates such as N<sub>2</sub>O<sub>5</sub> and N<sub>2</sub>O<sub>4</sub> in the solid state can be used to interpret trends in their surface packing and ordering.

### 2.2.5 Other Techniques

Other analytical techniques can provide useful information for the interpretation and analysis of ice/adsorbate chemistry. Weak hydrogen-bonding interactions have been studied extensively using methods such as microwave (rotational) spectroscopy to investigate the bonding to water in molecular complexes<sup>18</sup> and NMR to study hydroxonium ion structure. Molecular beam methods for the study of molecule–ion interactions and laser-based spectroscopy for the investigation of state-resolved molecular energy partitioning also provides insights into the internal energy distribution of atmospheric species and its possible influence on reaction mechanisms.

## 3 Theoretical Modelling of Surface Processes of Relevance to Stratospheric Particles

Interpretation of results in science frequently involves the use of models. Experimental observations are compared against theoretical predictions based upon a particular model, with discrepancies being used to further refine the model until a better fit is achieved. This phenomenological approach has been used very effectively in the prediction of the homogeneous gas-phase chemistry of the stratosphere, and its logical progression into heterogeneous processes is described below. Additionally, the inclusion of accurate heterogeneous chemistry models into global stratospheric ozone prediction programs have dramatically improved their accuracy in predicting ozone trends.

### 3.1 Definition of Terms

In order for information gathered in separate experiments to be consistent, it is necessary to define the terms in which adsorption, reaction, and release of product can be quantified. Many studies have used terms to express the amount of material which either remains adsorbed on the surface, the amount of material removed from the gas flow, describing such processes using 'mass accommodation', 'uptake', and 'sticking' coefficients. Such terms frequently have established definitions in classical surface science, although the quantities actually measured usually depend upon the nature of the experiment. The following definitions may be of use. The *accommodation coefficient* simply reflects whether a molecule can be accommodated by the surface or not.<sup>19</sup> For a molecule in collision with a surface with which it does not interact, then the accommodation coefficient is zero and the molecule rebounds with its original energy: consequently, no adsorption has occurred. If an attractive force exists between the surface and the molecule such that the molecule is accommodated at the surface for sufficient time for energy exchange to occur, then the accommodation coefficient is unity

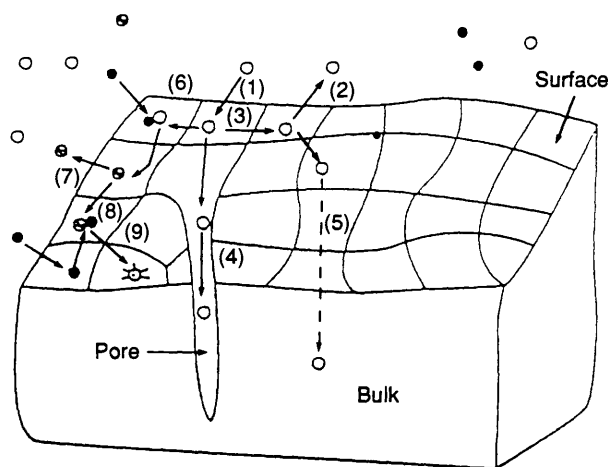
and either physical or chemical adsorption has occurred. The *sticking coefficient* is usually defined for a specific experiment. Generally, it is based upon the ratio of the number of molecules which stick to the surface and equilibrate per unit time and the total number of molecules incident per unit time. In a system where the rate of desorption is low (*i.e.* most of the equilibrated molecules remain attached to the surface), then the sticking coefficient can be determined using the technique of King and Wells.<sup>20</sup> The partial pressure of the reagent of interest in the reaction chamber is measured with an unreactive flag between the gas jet (molecular beam) and the sample. The partial pressure is then monitored as the flag is withdrawn. The adsorption of gas results in a second pressure which is lower than the first, and the ratio can be related to the sticking probability. This technique works best for chemisorption processes with a relatively high sticking probability. The sticking coefficient is often a function of coverage in a chemisorption system because the number of molecules adsorbing decreases as the number of available sites falls. Other effects may be observed if the rate of desorption is high, in which case the sticking coefficient may be high with an equilibrium surface concentration close to zero.

The extent of a reaction is often quantified using an *uptake coefficient* or a *reaction probability*. The existence of these two extremes for the sticking coefficient can cause confusion when the detailed nature of the surface processes in the system under study is not known. For example, in a system where the sticking coefficient is high and the rate of desorption is low, the uptake coefficient would be high at first and would decrease with exposure, leading to a correct assumption about the nature of the sticking coefficient. However, at the other extreme with a high sticking coefficient and a low equilibrium concentration, the uptake coefficient would be observed to be low for all exposures and the sticking coefficient may incorrectly be inferred to be low. This may well be the case, but if a small surface concentration of one reactant is required for another reaction channel to become favourable, such as appears to be the case for the HCl/ice system, then incorrect assumptions may be made about the surface processes. In other words, the use of such macroscopic parameters to describe the amount of reaction which is observed to occur should be treated with caution because they do not take into account any of the microscopic details of the reaction scheme.

### 3.2 Processes Involved in Gas/Surface/Bulk Chemistry

The mechanisms involved in the transport of reactants from the gas-phase to the surface, the surface adsorption/desorption equilibria, and the subsequent desorption of reaction products and their transport away from the surface are often considered to be the most important factors in heterogeneous catalysts. An additional, equally important factor to be considered in the case of reactions which occur between adsorbates and a surface which may be mobile, and which consume some of the surface material, is the rate at which these surface species can be replaced from either other surface sites or from the bulk. This behaviour necessarily also includes the transport of reaction products away from the reaction site. Figure 2 shows a schematic of all the processes to be considered. These diffusion processes can be divided into a number of types. Lateral diffusion may occur along a surface where residence times are long. Surface/bulk diffusion is expected to play an important role in stratospheric heterogeneous catalysis, particularly in liquid and quasi-liquid systems such as aerosols. In more solid systems such as microcrystalline ice and NAT, where the surface is rough and pitted, pore diffusion and grain boundary diffusion may also be important.

The development of a comprehensive model including all of the processes observed to occur on and in PSC particles has been addressed by Tabazadeh and Turco.<sup>21</sup> Although this introduces a much greater degree of complexity into the overall models for global stratospheric ozone, and increases computation time, the results already appear to vindicate this approach.



**Figure 2** Gas-surface interactions in heterogeneous chemistry model. Molecular species are indicated by circles. The processes depicted are (1) molecular adsorption, (2) molecular desorption, (3) surface diffusion, (4) pore diffusion, (5) bulk crystalline diffusion, (6) surface activation and reaction, (7) reactive product desorption, (8) secondary reaction, and (9) surface poisoning. (Reproduced with permission from *J. Geophys. Res.*, 1993, **98**, 12727.)

## 4 Composition and Characterization of Stratospheric Substrates

Although the approximate composition of particles found in the stratosphere is known, the detailed nature is the subject of some conjecture. We do however have an accurate idea of the pressure, temperature, and component partial pressure conditions in the stratosphere. Using this information, we can exploit widely available thermodynamic information such as phase diagrams and vapour pressure/composition data to extrapolate likely PSC composition. This approach can also be used to estimate and measure the extent of acid absorption (HCl, HONO<sub>2</sub> *etc.*) into bulk particles by measuring the vapour pressure of a particular component over the sample.

Since no experiment has yet been devised for either the production of polar stratospheric clouds in the laboratory or *in situ* surface spectroscopic measurements in the stratosphere, it is necessary to devise a technique to mimic the relevant aspects of the physics and chemistry of such particles in the laboratory. For processes which are primarily concerned with gas/surface interactions, studies of heterogeneous stratospheric chemistry are most easily performed using apparatus in which only the surface functionality of PSC particles is simulated. As in the use of all model, idealized systems, the nature of the mimic will obviously affect the experimental results. As discussed in the previous section, the nature of the PSC particle composition and structure can be inferred from phase diagrams of the relevant constituents and the surface functionality can be inferred from what is known about the physical chemistry of ice and solid acid polyhydrates. The task which remains is to develop experimental apparatus to generate and maintain PSC mimics in a controlled laboratory environment, within which meaningful measurements can be made.

### 4.1 Stratospheric Particle Compositions from Phase Diagrams

There is a great deal of speculation as to the nature of the formation of stratospheric particles from a wide variety of stratospheric species. The condensation at different temperatures of various sulfuric acid/nitric acid/water mixtures as solids has been suggested as the most likely scenario. This rationale is supported by a number of studies of the phase diagrams of binary systems such as HONO<sub>2</sub>/H<sub>2</sub>O and H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O and ternary systems such as HONO<sub>2</sub>/H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O. Perhaps the most convincing evidence for this is presented in a recent report by Molina *et al.*<sup>22</sup>

#### 4.2 Vapour Pressure Measurements of Liquid/Solid Systems

The uptake of HCl by ice, NAT, and sulfuric acid aerosol has also been studied using vapour pressure measurements and related to bulk concentrations by the Gibbs–Duhem equation.<sup>23</sup> A number of conclusions can be drawn from trends in vapour pressure/composition measurements, with the most noticeable being that the bulk solubility of HCl varies quite widely in all of these systems, although it is never particularly high. NAT appears to have a significantly higher affinity for HCl than does ice.

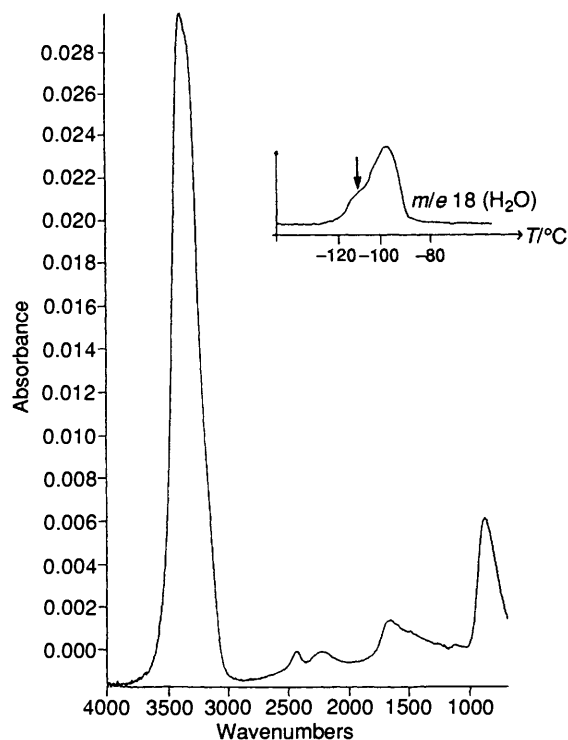
#### 4.3 Spectroscopic Characterization of Water Ices

Perhaps the simplest system upon which representative measurements can be made in the laboratory is that of type II PSCs, which consist of ice particles of between 1.0 and 10  $\mu\text{m}$  diameter.<sup>6</sup> Two possibilities exist for generating ice surfaces: thin films and particles. The literature is rich with examples of spectroscopic and crystallographic studies of the structure of many of the phases of solid water.

Small clusters of ice can be generated in an infrared cell using the method of Devlin.<sup>24</sup> Ice clusters are formed by introducing a mixture of water and either argon or nitrogen into a pre-cooled optical cell, mounted in the sample compartment of a spectrometer. At 77 K, aggregation of the water into small clusters ( $10^2$ – $10^3$  molecules) occurs whilst the carrier gas remains unaffected. These clusters remain stable and in suspension for several hours. Infrared spectra of these clusters has led to the identification of a particular feature that has been assigned to the vibration of surface water molecules, relatively unaffected by bulk hydrogen bonding. This ‘dangling’ OH bond is particularly prominent because of the small bulk:surface water molecule ratio.

The generation of thin solid films of ice at low temperature is of more widespread applicability in many of the techniques discussed below, and which we have adopted in our own studies.<sup>25,26</sup> We have concentrated on producing a well characterized, easily reproducible substrate for such studies. The experimental apparatus consists of a circular stainless steel vacuum system, capable of evacuation to pressures of less than  $1 \times 10^{-9}$  torr. Ice films are grown on a thermostatted flat gold foil, upon which infrared spectroscopic measurements can be made simultaneously. The substrate can be held at any temperature in the range 80–500 K with a stability of better than 1 K. The substrate, held at 80 K, is exposed to gas-phase water at a pressure of  $1 \times 10^{-7}$  torr for 60 seconds from a precision leak valve. This generates an amorphous film of approximately 50 nm thickness. A surface ‘dangling’ OH bond feature similar to that observed in small clusters can be discerned in the infrared spectrum. When this film is then heated *in vacuo*, the partial pressure of water in the chamber starts to increase, as measured by a quadrupole mass spectrometer. This water desorption corresponds to the low-temperature shoulder in the thermal desorption spectrum (Figure 3, inset), which is due to an ordering of the amorphous film into a polycrystalline structure. The substrate temperature is then stabilized at this value until the desorption ceases. The substrate can then be cooled to the required temperature. Figure 3 shows a typical infrared spectrum of an ice film grown by this method.

Ice films for use in flow tube experiments are normally deposited by flowing the carrier gas (generally He) through water and passing the resultant mixture over the cold walls of the reaction chamber. There is some debate in the literature concerning the physical state and surface area of ice films deposited in this manner. Many early studies have used the geometric surface area of the film, but recent evidence suggests that, because of the highly porous nature of the layer, the actual area may be as high as fifty times this value.<sup>27,28</sup> The reasonable degree of reproducibility observed using this method, however, suggests that such films are a valid substrate for measurement.



**Figure 3** RAIR spectrum of a typical thin ice layer at 80 K, formed by low temperature water deposition from the gas phase onto a cold gold substrate and annealing to the low temperature desorption shoulder (inset TDS). (Reproduced with permission from *J. Phys. Chem.*, 1994, **98**, 946.)

#### 4.4 Spectroscopic Characterization of Nitric Acid Hydrates

Examination of the  $\text{HONO}_2/\text{H}_2\text{O}$  phase diagrams under stratospheric conditions suggests that type I PSC particles are composed of nitric acid trihydrate (NAT), as discussed previously. A number of authors have spectroscopically characterized thin films of nitric acid hydrates, condensed from the vapour above aqueous nitric acid solutions of various composition, and have identified three distinct hydrates; nitric acid monohydrate (NAM), dihydrate (NAD), and NAT.<sup>29</sup> On annealing to 180 K, typical of the polar stratosphere in winter, the lower hydrates appear to convert into the stable trihydrate. Recent evidence suggests that there are two structural modifications of NAT,  $\alpha$ -NAT and  $\beta$ -NAT, and that  $\beta$ -NAT is the more stable high temperature form. Transitions between the phases appear to be irreversible.<sup>30</sup>

The simulation of sulfuric acid aerosol surfaces has recently been addressed by a number of groups. Molina *et al.* have investigated the inclusion of  $\text{HONO}_2$  into aerosols of varying  $\text{H}_2\text{SO}_4$  composition and subsequent crystallization.<sup>22</sup> The generation of such surfaces in flow tubes and Knudsen cells has also been performed.

### 5 Probing Stratospheric Reactions

Once a mimic for a particular stratospheric substrate has been generated, a technique for the investigation of its surface chemistry needs to be devised. The popular methods available for this can be divided into two types. Non-surface-specific techniques generally tend to probe the gaseous composition over a substrate or ‘downstream’ from it in a gas flow. Surface-specific techniques are generally spectroscopic probes which have been adapted to be surface sensitive rather than surface specific in the sense of classical surface analysis.

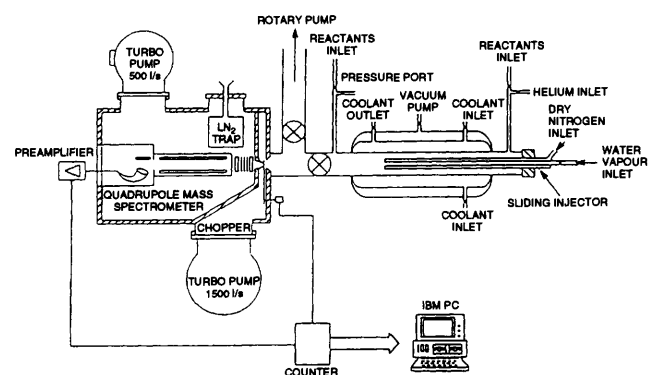
#### 5.1 Non-surface-specific Techniques

All the techniques currently in use for the investigation of

heterogeneous stratospheric chemistry can roughly be divided into two groups: those which use a surface-sensitive probe, and those which do not. The use of mass spectrometry as a detection method in fast-flow systems we class as a non-surface method, whereas its use in thermal desorption spectroscopy we class as a surface-sensitive method. In this section, the two major non-surface-specific techniques using flow tubes and Knudsen cells are reviewed. These techniques rely on the use of models for the interpretation of data; consequently, the quality of the result depends upon the accuracy of the model.

### 5.1.1 Flow Tube Experiments

Figure 4, reproduced from reference 31, shows a schematic diagram of a modern flow tube experiment. The flowing gas composition is measured using a differentially pumped quadrupole mass spectrometer (QMS). Such reactors are generally constructed from glass. The principle of operation is a simple modification of the chemical gas kinetic technique.<sup>32</sup> A carrier gas, usually an inert gas such as helium, is passed through the reaction cell. A high flow rate is maintained with a large capacity vacuum pump. The substrate of interest is deposited onto the walls of the cell, which can be cooled to the required temperature. Reactant gases are introduced into the carrier flow at the upstream end of the cell via a moveable injector and the composition of the eluted gas is measured by the QMS at the downstream end. The detected composition is compared to that measured in the absence of a substrate to yield information about the reaction probability on the substrate.



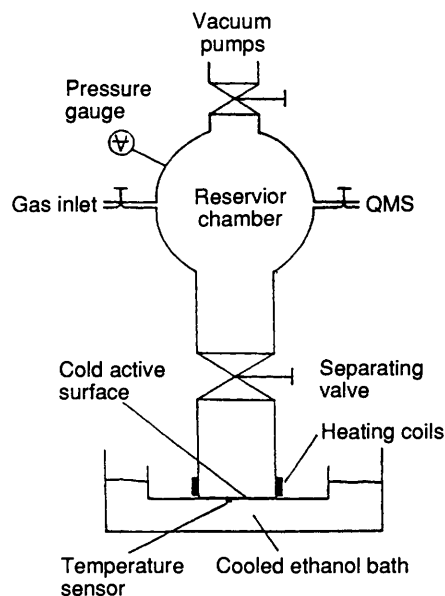
**Figure 4** Schematic diagram of a typical flow tube system. Gases are introduced *via* the moveable injector and the composition of the eluted gas is measured using the differentially pumped quadrupole mass spectrometer.

(Reproduced with permission from *J. Phys. Chem.*, 1993, **97**, 7779.)

Flow tube measurements provide the bulk of laboratory studies of heterogeneous stratospheric chemistry to date. The interactions of single reactants such as ClONO<sub>2</sub>, ClO, N<sub>2</sub>O<sub>5</sub>, HCl, HBr, HF, and HOCl with ice and various nitric acid hydrates have been studied under a variety of pressure and temperature regimes applicable to the stratosphere. The information obtained using this technique is useful for the determination of reaction probabilities and reaction rates. Reactions such as ClONO<sub>2</sub> + HCl → Cl<sub>2</sub>(g) + HONO<sub>2</sub>(s) have also been studied on ice and NAT.

### 5.1.2 Knudsen Cell Partial Pressure Methods

Uptake measurements can be made using a static reaction chamber comprising two separate compartments, separated by a valve (Figure 5).<sup>33</sup> In one of the compartments, a cold reaction surface is deposited. The reactive mixture of interest is held in the second compartment. The composition of this mixture is measured using a differentially pumped QMS. When the valve is opened, the gas mixture comes into contact with the cold surface



**Figure 5** Schematic diagram of a typical Knudsen cell gas uptake system. The composition of the gas in the reservoir chamber is measured using the quadrupole mass spectrometer as a function of time after the separating valve has been opened. (Reproduced with permission from *Geophys. Res. Lett.*, 1993, **20**, 1191.)

and the evolution of the reaction between the gas components and the surface can be monitored using the QMS.

An example of the use of such a chamber is in the evaluation of reaction potentiality. It has been suggested that the reaction of NO and NO<sub>2</sub> with sulfuric acid aerosol may lead to the formation of nitrosylsulfuric acid (NOHSO<sub>4</sub>), with a potential for further chlorine reservoir reactivation.<sup>33</sup> Knudsen cell studies however, indicate that the reaction probability for this reaction is less than  $5 \times 10^{-5}$ , thereby eliminating it as an important process.

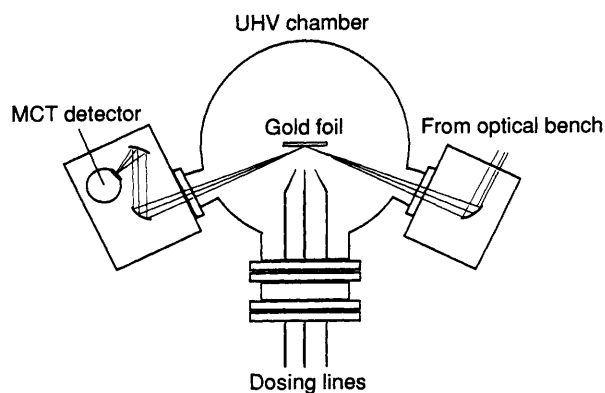
## 5.2 Surface-specific Methods

By far the most informative method for the investigation of PSC surface chemistry is spectroscopic probing. Common techniques such as UV/visible (electronic), infrared, and Raman (vibrational) spectroscopy can be adapted to probe the surface and to provide direct information about the electronic states of adsorbates, details of the bonding environments, and direct surface fragment identification. Surface sensitivity can be attained by either reducing the amount of material present whilst retaining the surface area; *e.g.* by the use of ultrathin films, or by adapting the optics of the system using waveguides or underlying metal substrates.<sup>34</sup>

### 5.2.1 In situ Surface Techniques

A number of spectroscopic techniques are currently in use for the study of ice and NAT surface chemistry using thin solid films. Figure 6 shows a schematic of our experimental apparatus. This consists of a cylindrical stainless steel chamber pumped by an oil-vapour diffusion pump. The vacuum system is optically coupled to a Bio-Rad FT infrared spectrometer (model FTS60A/896) and the IR beam is focused onto the substrate at an angle of 75° to the surface normal. The reflected beam is detected using a HgCdTe photoconductive detector cooled to 77 K. The substrate upon which ice films are condensed consists of a flat foil of gold or nickel mounted between a pair of tungsten supports. These supports are in thermal contact with a liquid nitrogen reservoir. The temperature is controlled by balancing the reservoir cooling against the resistively heated foil. Sample gases are dosed onto the vacuum chamber from one of three independent gas reservoirs to ensure sample purity. Gas samples





**Figure 6** Schematic diagram of the UEA RAIRS/ultra-high vacuum system. Ice films are deposited upon the cooled gold substrate. Reactions between impinging gases and the ice film are monitored using the infrared spectroscopic probe.

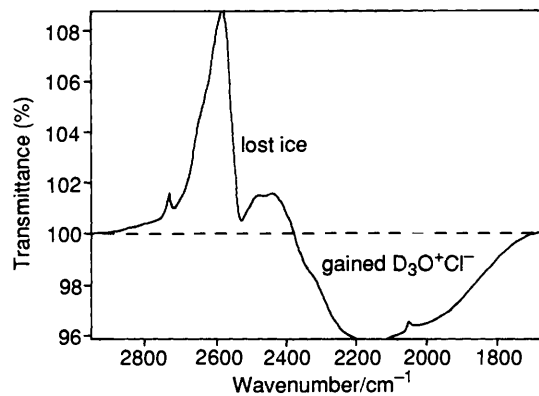
inside the chamber are directed at the sample position by glass guide tubes. The spectra recorded in this configuration are reflection-absorption infrared (RAIR) spectra.

An alternative reflection technique, used by Schrems *et al.*,<sup>29</sup> utilises a normal incidence reflection from a cold substrate. This has the advantage of a more convenient optical arrangement for use with more conventional cryostat cold fingers. This method, which requires a much thicker film, can be used to provide complementary information to grazing incidence reflection. In a grazing incidence RAIRS experiment, only vibrational modes polarized perpendicular to the metal surface are detected, by virtue of the *metal surface selection rule*. The origin of this phenomenon is beyond the scope of this review, but a comprehensive treatment can be found in reference 35. In the normal incidence RAIR configuration, the electric field vector of the incident radiation is confined to the surface plane. Species close to the metal surface cannot be detected because of the metal surface selection rule, hence the requirement for thick films, for which parallel-polarized modes can be obtained.

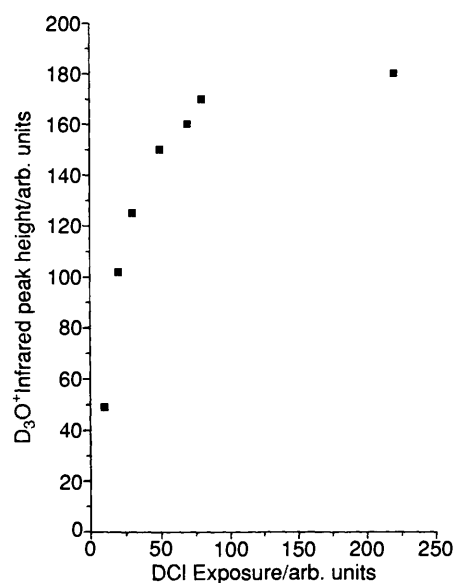
Transmission infrared spectroscopic studies of thin films have been performed using thin, transparent optical windows as a substrate, in a similar manner to matrix isolation spectroscopy. Although this method samples both the bulk and the surface of the film simultaneously and is relatively insensitive to monolayer quantities, it has the benefit of experimental simplicity. Good quality spectra can be obtained for reasonably thick surface layers on thin substrates, with several examples in the literature of its application to the characterization of NAT films and HCl uptake.<sup>36</sup>

### 5.2.2 Applications to Surface Reactions: HCl and N<sub>2</sub>O<sub>5</sub> on Ice

Our own studies have concentrated on the infrared spectroscopic study of the adsorption and reaction of stratospheric species such as HCl, Cl<sub>2</sub>, HONO<sub>2</sub>, and N<sub>2</sub>O<sub>5</sub> on thin film ice surfaces. Initial experiments in which the adsorption of HCl on ice at 100 K was monitored indicated that there is little or no molecular adsorption at this temperature. This is in agreement with the results of MI studies and theoretical predictions. What is observed is the formation of a thin surface film of an amorphous ionic hydrate. Figure 7 shows the result of exposing a D<sub>2</sub>O ice film at 100 K to a pressure of 1 × 10<sup>-7</sup> torr DCl for 10 seconds. The positive absorbance bands are characteristic of the hydroxonium ion, D<sub>3</sub>O<sup>+</sup>, whereas the negative absorbance features are due to both the removal and conversion of water from the original ice film. Studies of the uptake of DCl as a function of exposure (Figure 8) suggest that the adsorption increases to a saturation level, due to the depletion of surface water to such a level that no further dissociative adsorption can occur. Studies of the rate of uptake as a function of temperature

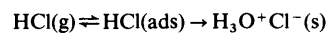


**Figure 7** RAIR difference spectrum of DCl uptake by a D<sub>2</sub>O ice film at 90 K. The spectrum shows upward bands due to the loss of water from the film and downward bands from the formation of D<sub>3</sub>O<sup>+</sup>. (The behaviour of HCl and H<sub>2</sub>O ice at 90 K is qualitatively similar.) (Reproduced with permission from *J. Chem. Soc., Faraday Trans.*, 1992, **88**, 1077.)



**Figure 8** Intensity of the D<sub>3</sub>O<sup>+</sup> peak from Figure 7 as a function of exposure to DCl. It can clearly be seen at this temperature that the uptake falls off as exposure increases, indicating a saturation of the ice film. This is believed to be due to the consumption of all the available surface water. (The behaviour of HCl and H<sub>2</sub>O ice at 90 K is qualitatively similar.)

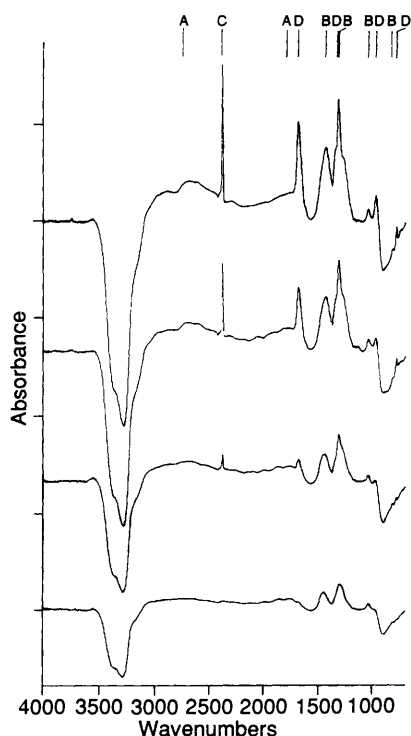
indicate that the adsorption is likely to be controlled by a precursor-mediated scheme such as that shown below.



The reaction requires a pre-equilibrium of physically adsorbed HCl with a sufficiently long surface residence time for reaction into the ionic hydrate to occur. This process does not require a high instantaneous surface concentration, and indeed, the molecular, physically adsorbed state cannot be detected by reflection absorption infrared spectroscopy, despite its sub-monolayer sensitivity. This is consistent with calculations by Clary and co-workers.<sup>12,13</sup>

The reaction of increasing doses of gas-phase covalent N<sub>2</sub>O<sub>5</sub> with a thin ice film at 140 K is shown in Figure 9. At low doses, the first observation is a water loss, evidenced by the negative bands at *ca.* 3400, 1600, and 800 cm<sup>-1</sup>. Concurrently, strong broad features centred on *ca.* 2900 and 1750 cm<sup>-1</sup> and sharper bands at *ca.* 1450, 1300, 1040, and 810 cm<sup>-1</sup> start to grow in, labelled species A and B respectively. Increasing doses result in

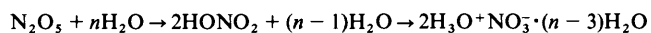




**Figure 9** RAIR difference spectra of successive doses of  $\text{N}_2\text{O}_5$  onto an ice film at 140 K. The spectra show, from the bottom, the build-up of amorphous  $\text{H}_3\text{O}^+\text{NO}_3^-$ , the onset of molecular nitric acid and nitronium ions, and the eventual domination of the spectrum by a mixture of  $\text{H}_3\text{O}^+$ ,  $\text{NO}_2^+$ ,  $\text{NO}_3^-$ , and  $\text{HONO}_2$ .

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further water loss and new features at  $2380\text{ cm}^{-1}$  (species C) and  $1682$ ,  $1318$ ,  $965$ , and  $778\text{ cm}^{-1}$  (species D). By comparison with literature spectra of hydrated acid ices,<sup>14</sup> species A can be identified as being a hydroxonium ion. Species B is assigned to a solvated nitrate ion for which the bands at *ca.*  $1450$  and  $1300\text{ cm}^{-1}$  are the two components of the normally degenerate asymmetric stretching mode, where the degeneracy is lifted due to the low symmetry of the planar nitrate environment. The weak feature at  $1040\text{ cm}^{-1}$  is the formally forbidden symmetric stretch which is often observed in disordered films. The weak feature at  $810\text{ cm}^{-1}$  is the  $\text{NO}_3^-$  bending mode. The presence of species A and B are evidence for the formation of an amorphous nitric acid hydrate, for which we propose the reaction scheme:



The number of water molecules,  $n$ , involved in the reaction will be determined principally by the preferred stoichiometry of the hydrate formed, *i.e.* NAT, NAM, *etc.* and the availability of water in the region of reaction. Studies of the formation of nitric acid hydrates as a function of temperature suggest that the monohydrate and the dihydrate may be favoured at 140 K. However, we are unable unequivocally to assign our spectra as anything other than an amorphous hydrate. As the amount of surface water available for reaction is reduced on further dosing of  $\text{N}_2\text{O}_5$ , a change occurs with the simultaneous growth of species C and D. By comparison with the solid  $\text{N}_2\text{O}_5$  film spectra, species C can be assigned to linear  $\text{NO}_2^+$ . The remaining bands (species D) are due to molecular nitric acid, confirmed by comparison with matrix isolated nitric acid at 4.2 K.<sup>37</sup> The formation of molecular nitric acid as the amount of available surface water decreases is not surprising. From the point at which the formation of the amorphous nitric acid hydrate reaches a saturation coverage, further reaction requires that either diffusion of the water to the surface occurs to release more water or that the reaction scheme must change. Our spectra suggest that the latter is the case. Since the bands due to the

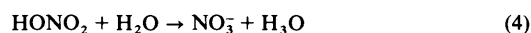
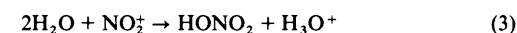
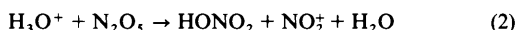
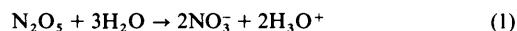
nitronium ion and molecular nitric acid grow in together, it seems likely that they are formed concurrently from the partial hydrolysis of gas phase  $\text{N}_2\text{O}_5$ , as it impinges upon the surface. Considering the likely surface species in the saturated layer ( $\text{NO}_2^+$ ,  $\text{H}_3\text{O}^+$ ,  $\text{HONO}_2$  *etc.*) and the scarcity of water, it seems likely that the hydrolysis occurs by reaction of  $\text{N}_2\text{O}_5$ , not with water but rather with the hydroxonium ion. The products from such a reaction would be  $\text{HONO}_2$ , water and  $\text{NO}_2^+$ .



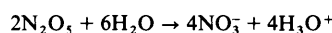
This generation of more surface water, able to undergo further reaction with  $\text{N}_2\text{O}_5$ , to produce more partially hydrated nitric acid and therefore more nitrate ions, accounts for the growth of the nitrate bands during the formation of molecular nitric acid.

Annealing this composite film to 160 K results in the production of a thicker film of molecular nitric acid and a small amount of nitric acid hydrate. This occurs because the increase in mobility of the ice film allows water to diffuse. As more water becomes available for reaction with the molecular nitric acid and  $\text{NO}_2^+$ , further changes occur.  $\text{NO}_2^+$  and water are both consumed to produce more nitric acid and a proton. The proton becomes hydrated and this can be seen in the growth of the broad  $\text{H}_3\text{O}^+$  absorption in the difference spectrum (Figure 9). The charge associated with this ion is balanced by the negative charge on the nitrate ion originally associated with the  $\text{NO}_2^+$ , thus maintaining overall neutrality. The fact that there is only a slight increase in the nitrate ion absorptions indicates that the rate of solvation of molecular nitric acid is slower than that for reaction of the nitronium ion. Annealing above 180 K results in the loss by evaporation of this film.

To summarize, the reaction of gas-phase  $\text{N}_2\text{O}_5$  with a thin ice film occurs through a complex interplay of ionic chemistry involving nitrate, nitronium, and hydroxonium species, for which we suggest the following scheme:



overall,



During the initial uptake, reaction 1 prevails until saturation occurs. Beyond this limit, dictated by the water availability which prevents complete hydration of  $\text{NO}_2^+$  and nitric acid and effectively eliminates steps 3 and 4, there is a competition between nitrogen-containing entities for the surface water.  $\text{N}_2\text{O}_5$  arriving from the gas phase forms molecular nitric acid and  $\text{NO}_2^+$  from the hydrolysis of  $\text{N}_2\text{O}_5$  on the hydroxonium-rich surface, 2. The charge balance is maintained by the presence of the  $\text{NO}_3^-$  counter-ion released by the reaction of its accompanying hydroxonium ion. On annealing, more water becomes available as the ice film becomes mobile and is consumed by the above reaction scheme to reduce the concentration of  $\text{NO}_2^+$  which produces more molecular nitric acid and hydroxonium species. There is a competition between the  $\text{NO}_2^+$  and the molecular nitric acid for the water in steps 3 and 4, and our observation that the  $\text{NO}_2^+$  band is depleted and more  $\text{HONO}_2$  is formed suggests that 3 occurs in preference to 4. The pH of the surface layer is likely to control the relative contributions of these four surface reactions and further investigations are in progress.

## 6 New Directions

There are a large number of classical surface science techniques that are of possible application to the study of stratospheric

chemistry.<sup>34</sup> Although many electron-based spectroscopies such as X-ray photoelectron spectroscopy, Auger electron spectroscopy, and ultraviolet spectroscopy are extremely surface-specific and sensitive, they are limited in their application to higher pressure systems by the short inelastic mean free path of electrons in high pressure gases. However, these techniques may be rendered useful by the application of differential pumping and cryogenic trapping. Nuclear magnetic resonance, which can be extremely sensitive to proton environments, may also be of use in the determination of the mobility of acidic protons and their role in bulk PSC structure.

An example of the recent application of a classical surface analysis to the study of PSC chemistry which shows great promise is the use of secondary ion mass spectrometry (SIMS).<sup>38</sup> In this technique, inert ions (Ar, Ne) are fired at the surface. The sputtered material is analysed using mass spectrometry. Modern instrumentation makes it possible to observe negative ions and neutrals as well as positive species. This technique can be used in two regimes. Static SIMS uses a low power beam to probe the surface layer with little disruption. Dynamic SIMS uses higher powers to ablate the surface, and can be used to extract bulk concentration gradients. This is currently being applied to the determination of chloride ion diffusion in ice by Vickerman *et al.*

Recent trends in ozone depletion in mid-latitudes have been linked to rising concentrations of stratospheric particulates, particularly in the Northern hemisphere. There is mounting evidence that low-temperature heterogeneous reactions can occur on the surface of sulfuric acid aerosol droplets and volcanogenic dust particles in addition to PSC particles. New techniques are required to investigate the surface chemistry of such systems and some of the techniques discussed above will find application in this area. Clearly, there is scope for the use of other surface analytical techniques to be applied to this problem.

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