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Concluding remarks: astrochemistry of dust, ice and gas

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In this closing article, we first introduce the subject of dust and ice chemistry and its role in astrochemistry. We then discuss the invited contributions and discussions concerning them, dividing the papers into groupings by subject: (i) astronomical sources, (ii) basic properties of dust, (iii) processes on bare grains, (iv) processes on and in ice mantles, (v) complex organic molecules. A sample of poster contributions is included in the text, when they complement the discussion. The article ends with some suggestions for future research.

1   Introduction

Although the title of this Faraday Discussion suggests that dust, ice and gas are three important environments for chemical reactions in the interstellar medium, the written contributions heavily emphasize the dust and ice environments. Readers more interested in the current state of research in gas-phase interstellar chemistry can look at a number of review articles.[1-4] The dust chemistry occurs on tiny particles of silicates and amorphous carbonaceous material of size range initially 5-250 nm until coagulation starts to occur during stellar and planetary formation. The dust particles comprise roughly 1% of the mass of an interstellar cloud and the dust-to-gas ratio by number is approx. 10^{-12}.[5]

The new emphasis on dust chemistry has been long in coming; for much of its existence as a research field, astrochemistry has been dominated by simulations in which the gas played the major role. But this domination began to ebb as it became reasonably clear that gas-phase reactions cannot explain the synthesis of the dominant species that constitute the ice mantles surrounding cold interstellar grains, as well as the partially saturated gas-phase organic molecules found in warm regions known as "hot cores."[6] In the last decade, laboratory studies of chemistry occurring on analogues of both bare grain surfaces and on and in ice mantles have grown in number and stature although we are still at an early stage of understanding these processes in great detail.

As brought out during the discussion sections, even the chemistry occurring on bare grain surfaces presents difficulties, and the chemistry on and in ice is even more complex. One problem is distinctly related to astrochemistry: the conditions in interstellar clouds are unlike those in the laboratory and extrapolations between laboratory and interstellar conditions for surface processes can be much more complex than in the gas-phase. In addition, unlike the situation in the gas-phase, there are three elementary mechanisms by which surface processes are thought to occur, although these pertain most exactly to systems in which adsorbed species constitute less than one full monolayer, as occurs most frequently for chemisorption.

With physisorption, on the other hand, multiple monolayers can be built up, as occurs, of course, to produce the ices on cold interstellar grains. In this case, chemistry can occur on the outer surface of the ices, which often cannot be regarded as a simple monolayer, and even inside the ices by a variety of mechanisms.

5 The three basic mechanisms[7] include the Langmuir-Hinshelwood process, where reactive species diffuse thermally on a surface until meeting each other; the Eley-Rideal process, in which a gas-phase species lands atop or near an adsorbed species and reacts with it; and the hot-atom mechanism, in which a non-thermal species moves a large distance along the surface to react with another species. The non-10 thermal species can achieve its condition by accreting from a gas higher in temperature than the grain, or as a product of an exothermic chemical reaction occuring on the grain, as mentioned by Dr. Cuppen and discussed in the paper by Lamberts et al (DOI: 10.1039/c3fd00136a).

Perhaps the simplest chemical process on interstellar dust grains is the formation 15 of molecular hydrogen from two hydrogen atoms, weakly bound on a bare silicate or carbonaceous grain, as occurs in diffuse interstellar clouds. In such clouds, the gas temperature is 50-100 K, the granular temperature ranges from 15-20 K, and the gas density is 10-100 $cm^{-3\#}$, consisting mainly of atomic and molecular hydrogen. The Langmuir-Hinshelwood mechanism occurs within a temperature range governed by 20 the flux of hydrogen atoms hitting and sticking to the grain surface and the mobility of these atoms afterwards.[8] The lower temperature limit is defined by the ability of H atoms to move appreciably while the upper temperature limit is defined by whether the two H atoms find one another before desorbing back into the gas. The range of temperatures for which the formation of H_2 is efficient can be very 25 narrow.[8-9] Although there is strong evidence from the laboratory studies of Vidali and co-workers that interstellar H_2 is indeed formed by such a mechanism[8], it is not clear from detailed theoretical studies that the process is sufficiently efficient to produce a significant fraction of the interstellar H_2.[10] Alternatives include a chemisorption-based Eley-Rideal process involving carbonaceous grains. Even the 30 hot-atom mechanism has been invoked to explain some of the data measured for H_2 reactions.[11] The removal of H_2 from the surface following formation can occur via simple thermal desorption but perhaps more rapidly by ejection into the gas, which requires only a small fraction of the exothermicity of the H + H reaction, which is over 4.5 eV. The efficiency of this ejection mechanism, sometimes called reactive 35 desorption, is unclear for the case of hydrogen formation, although a high efficiency has been measured for several other surface reactions.[12]

Although the chemistry of the formation of molecular hydrogen dominates the bare surface chemistry in diffuse interstellar clouds, other reactions are also possible. The detection of gaseous NH in diffuse clouds has often been ascribed to 40 the recombination of N and H atoms on a grain surface followed by desorption, and more recent suggestions of granular formation following the observation of NH_2 and NH_3 with the Herschel Space Observatory in spiral arm diffuse clouds have also been advanced.[13]

In addition to the surface chemistry that occurs in diffuse clouds, two additional 45 environments have been discussed, all of which occur during the evolutionary stages of star and planetary formation. The first of these occurs on cold dust grains in so-called pre-stellar cold cores found in dense interstellar clouds, which are dense agglomerations formed by gravitational contraction from more diffuse sources. These cores have a temperature of 10 K, appropriate to both the gas and the dust,

and a gas density of 10^4 cm^{-3}, which is overwhelmingly molecular hydrogen. Here some molecular hydrogen is still being produced via the surface H + H process, but the unique processes occurring on these cold grains are reactions involving atomic hydrogen and other atoms and small molecules that combine, probably via a Langmuir-Hinshelwood-type diffusive mechanism, to form icy mantles, dominated by water ice, which can grow to over 100 monolayers of material. The major reactants are atoms and diatoms because they are typically bound less strongly to the bare and ice surfaces and so can diffuse more appreciably at the low temperature of 10 K. A diagram of the various reactions leading to the formation of water ice on grains is shown in a recent review by van Dishoeck et al.[14] and was discussed at the meeting. Other major species formed by surface/ice chemistry and detected via infrared absorption include CO_2, H_2CO, CH_3OH, NH_3, CH_4, and OCN^-, the anion presumably attached to a suitable cation. Possible synthetic routes to more complex molecules can be found in a diagram by S. Charnley in the review article by Herbst and van Dishoeck.[6] According to current simulations, CO ice is formed via direct accretion from the gas, where it is quite abundant. Details of the line shapes of infrared absorption spectra indicate the ices to be composed of both inner polar layers, dominated by water, and outer non-polar layers, in which a significant amount of CO exists, while CO_2 is found in both layers. The large mantles that form indicate that non-thermal desorption mechanisms, which are needed to desorb molecules that bind more strongly than H_2 and He, are not exceedingly efficient in this environment. Simulations of the nature of the ice indicate it to be rather amorphous with significant porosity at higher densities, as discussed at the meeting. Measurements of ice porosity are discussed in poster abstract P14 by Bossa et al.

The next environment to occur sequentially is one that is warming to a temperature of perhaps 300 K as the initially cold material of a pre-stellar cold core collapses towards a star-in-formation, labelled a protostar or young stellar object (YSO). As the temperature increases from 10 K to 100 K, the surface chemistry changes as atomic hydrogen can no longer reside on grains long enough to be a major reactant and the larger molecules formed at 10 K begin to diffuse. With some exceptions, however, these larger moving species are non-reactive, and must be activated by some mechanism, most likely to form reactive radicals. One suggestion[15-17] is that photons, produced via the interaction of cosmic rays and hydrogen molecules, can indeed produce radicals by photodissociation of species throughout the ice mantles. The radicals then recombine to form the so-called complex organic molecules, consisting of six or more atoms, which can undergo non-thermal desorption at lower temperatures, but eventually desorb thermally and fully into the gas at temperatures exceeding 100 K. Detailed predictions of abundances with this model are rendered difficult by the physical complexity and dynamics of hot-core sources. Nevertheless, as discussed by Öberg et al. (DOI: 10.1039/c3fd00146f), analysis of inteferometric observations buttressed by single-dish measurements can yield information on the abundances of these complex species as functions of temperature. These observations have been compared with current models supplied by Garrod. Studies of thermal desorption, however, with temperature programmed desorption (TPD) show that even this process on mixed ices is complex (see poster abstract P08 by Martin-Doménech and Muñoz Caro) and must be treated in some detail in simulations.[18]

As will be discussed in more detail later in this closing paper, there are other forms of energy that can be used to activate granular molecules to become reactive.

Perhaps the best studied are interactions between non-thermal electrons and molecules on and in ices.

2   Papers

In the following section, we group papers according to their subject content, and discuss some important aspects of the individual papers and related posters.

Astronomical source types

The paper by Guzmán et al. (DOI: 10.1039/c3fd00114h) concerns the famous photon-dominated region (PDR) known as the Horsehead Nebula, which is located in the larger Orion Nebula. The authors announce that, for the first time, complex organic molecules (COMs) have been detected in such a region, in particular $HCOOH$, CH_2CO, CH_3CHO, CH_3CCH, and CH_3CN. These molecules can be classified as COMs using the definition advanced by Öberg et al. (DOI: 1039/c3fd00146f) in their paper presented here, where COMs are defined as "hydrogen-rich organics with three or more heavy atoms." In the older definition of six or more atoms, only acetaldedhye, acetonitrile, and methyl acetylene would be counted as complex. Nevertheless, the discovery of these species is of great interest, since COMs are now being found in a multitude of different sources, suggesting that more than one mechanism is needed to explain their formation. In other sources, however, the major COMs include dimethyl ether (CH_3OCH_3) and methyl formate ($HCOOCH_3$), and these have not yet been detected in PDRs. Also, interestingly, of the two portions of the PDR studied, the abundances are found to be enhanced in the warm PDR nearer to the edge and richer in UV photons than in the dense cold core. According to the authors, this difference suggests that photodesorption of COMs produced on grains is an efficient mechanism for releasing them into the gas, where they are observed. There is also the possibility that the enhanced photon field is instrumental in the formation of surface radicals, which can then react to form the COMs on grain mantles.[15-17]

Öberg et al. (DOI: 1039/c3fd00146f) are also interested in the topic of complex organic molecules, but in the more standard environment of hot cores, or more generally, massive young stellar objects (MYSOs). These authors studied three MYSOs using the Submillimeter Array to achieve high spatial resolution, along with single-dish data, and were able to determine how molecular abundances and ratios depend on the temperature, which itself is dependent on the proximity to the forming star. For example, acetaldedyde (CH_3CHO) is typically found in "lukewarm" regions whereas acetonitrile (CH_3CN) is found in warmer regions. Their results are consistent with theoretical models of grain photolysis in warming regions[16], in which different processes are likely to occur at different temperatures.

Three papers were written on the subject of the chemistry that occurs in protoplanetary disks. The paper by Pontoppidan and Bevins (DOI: 10.1039/c3fd00141e) concerns molecular observations and modelling (with radiative transfer) of the inner, planet-forming, portion of the protoplanetary disk RNO 90, near to the budding star, which is much warmer than dense clouds and protostellar envelopes. The authors show that the molecular inventory and abundances do not resemble those of the colder regions. The case of CO_2 is particularly strong; this molecule has a particularly low gaseous abundance in the inner disk compared with

its high concentration in dense clouds, and protostellar envelopes, although here the carbon dioxide is mainly found in ice mantles.

Bergin et al. (DOI: 10.1039/c4fd00003) have looked at the origins of carbon in terrestrial worlds such as our own. It is clear that CO is lower in abundance in meteorities, comets, and the disk TW Hya than in the interstellar medium. The explanation for TW Hya is found in gas-phase reactions starting from the destruction of gaseous CO by reaction with He^+, which, given enough time, can lead to the conversion of CO into more complex organic material under certain conditions; the material can then be incorporated into comets and planets. This type of process can also occur in cold dense clouds but only after non-physically long periods of time.

No COMs have yet been found in the gas of protoplanetary disks, although these molecules are found in many other sources. Two major reasons are that the disks are small and that the high densities lead to much of the material accreting onto ices or remaining there from an earlier evolutionary stage. The chemistry of these species in disks has been studied by Walsh et al (DOI: 10.1039/c3fd00135k) along an inward accretion flow with a gas-grain chemical model. Two situations were considered: in one the disk is isolated, but in the other, the disk is located near a massive star, the radiation from which affects the disk. In addition, two different initial conditions were used: simple ices and ices containing COMs. The different initial conditions and the proximity of a massive star can affect the balance between the chemistry occurring in the disk and that resulting simply from the initial conditions. Under some conditions, reasonable abundances of gas-phase COMs are predicted, leading to the hope that observations with ALMA will soon result in their detection.

Basic Properties of Dust

Jones et al. (DOI: 10.1309/c3fd00128h) have considered the cycling of carbon in dust particles in the interstellar medium, and deduced that this cycling is rapid in astronomical terms, especially for small hydrocarbon grains. In other words, carbonaceous dust cannot survive indefinitely in the ISM and its re-formation must be considered under low density conditions. In particular, the stage from diffuse cloud to outer portions of dense clouds is looked at carefully. In diffuse clouds, the major form of carbon in outer layers of the dust is likely to be aromatic in nature, whereas the core is more likely to be aliphatic-rich material. In the outer layers of dense clouds, the amount of aliphatic carbon becomes more dominant, whereas in the inner regions of dense clouds, accreting carbon will form aromatic species once again. Despite the nature of the carbon, it is clear that this model posits layers of carbonaceous material below the ice that form in the cold core stage. Discussion has brought out the possibility that the carbon can play a role in the formation of complex organic molecules during star formation.

The condensation of tiny dust particles into much larger solid objects such as comets, planetesimals, meteors, and eventually planets is a complex process, with many poorly understood facets. Rouillé et al. (DOI: 10.1309/c4fd00010b) have reported experiments to understand aspects of condensation. In their experiments, refractory species accrete onto cold substrates; the process does not mimic condensation from the gas, but represents the growth of dust particles from smaller ones, perhaps those that survived a shock wave or other catastrophic event.

Processes on Bare Grains

Although much grain chemistry in the ISM occurs on ices, it is still useful to understand reactions on bare grain surfaces, especially if these surfaces are rough or amorphous; i.e., have a variety of different types of binding sites or a distribution of
5 such sites, so that normal rate equations are inadequate. The use of microscopic kinetic Monte Carlo methods solves the problem of diffusion with different types of sites quite easily, and also can be used with distributions of binding energies[19], but is very computer intensive and difficult to use in simulations where a large number of different molecules are undergoing reactions.[20] So, the use of a rate equation
10 treatment that treats diffusion properly in the presence of different types of binding sites is a useful advance, and this is what has been accomplished by He and Vidali (DOI: 10.1309/c3fd00113), whose paper contains their method.   These authors are also able to obtain distributions of desorption energies and diffusion barriers from TPD profiles with their approach.
15 Despite its role as the most basic surface reaction in the universe, even the production of H_2 on bare grain surfaces in diffuse interstellar conditions is still not fully understood, as briefly discussed above. On grains within the normal size range, current microscopic Monte Carlo calculations involving physisorption of atomic hydrogen on flat silicate surfaces indicate that the efficiency of the process is
20 probably insufficient to account for the abundance of molecular hydrogen in diffuse clouds. The basic problem is the estimated temperature of the dust particles (20 K), which is higher than the temperature range of optimum efficiency for silicate grains.[8]   The efficiency can be improved with carbonaceous grains.[10] One method of broadening the temperature range of high efficiency for silicate grains is to
25 consider rough or amorphous surfaces,[8-9] in which sites of different energy are used, as in the He and Vidali paper discussed above. However, it is unclear that the effect of roughness is strong enough to fully account for H_2 formation. Another possibility is to invoke chemisorption, which can be efficient only if the barrier to production of the chemisorption bond is sufficiently low.[10] The utility of chemisorption at dust
30 temperatures relevant to diffuse clouds has been debated for some time now with no clear answer, because the barrier is still not well determined and the role of tunnelling under this barrier poorly constrained. The formation of molecular hydrogen on crystalline models of forsterite has been studied theoretically by Rimola et al. (Poster P03) who find both physisorption and chemisorption pathways.
35 The group of Hornekaer has studied the role of chemisorption for the production of H_2 first on graphite surfaces and subsequently on polycyclic aromatic hydrocarbons (PAHs), where the mechanism appears to be at least partially an Eley-Rideal one, in which H atoms stick to the PAH to make it supersaturated, and subsequent H atoms abstract the H atoms from the PAH into the gas.   The paper
40 from this group (Skov et al. DOI: 10.1309/c3fd00151b) contains a discussion of experiments with hot deuterium atoms and the PAH coronene; the results are interpreted in terms of warm interstellar regions such as photon-dominated regions, where the hindering effect of barriers is less constraining. There appears to be little to no barrier for the abstraction step. These interesting results are not directly
45 applicable to diffuse clouds, where H_2 is first produced. The role of PAHs as catalysts for H_2 production is also discussed in a poster abstract (P05) by Mennella with similar conclusions to those of Skov et al.

Congiu et al. (DOI: 10.1039/c4fd00002a) have looked carefully at the diffusive

motion of another atom – atomic oxygen – in the laboratory, and found that this atom moves unexpectedly quickly on a variety of surfaces – and so can be an important reactant. The mechanism for the rapid diffusion is thought to be tunnelling, although this suggestion met with some disagreement in the discussion
5 following the introduction of the paper.

Processes on and in Ice Mantles

Physical Processes

10 The diffusion of atomic oxygen on water ice was found to be even faster than on silicate by Congiu et al. (DOI: 10.1039/c4fd00002a), suggesting that the mechanism does not depend entirely upon the structure of the surface, and might indeed be tunnelling. Molecular dynamics simulations have been reported by Lee and Meuwly (DOI: 10.1309/c3fd00160a) on the diffusion of atomic oxygen in amorphous ice at
15 temperatures between 50 K and 100 K. These authors found that atomic oxygen is mobile "to a certain degree" without the need for tunnelling.

The process of photodesorption from ice mantles has been studied in the laboratory for a number of years, especially in Leiden.[20-21] Fillion et al. (DOI: 10.1309/cf3d00129f) reported the latest laboratory work on the subject regarding
20 CO_2 ice utilizing the vacuum UV beamline DESIRS at SOLEIL. Their work reveals a complex situation in which both direct photodesorption and photodesorption via photodissociation play a role. On CO_2 ice, photodissociation leads to CO, which can then undergo the indirect process of photodesorption, which occurs via its excited $a^1\Pi$ state. The direct desorption of CO_2 ice occurs at higher photon energies than
25 the indirect process. One other possible distinction between indirect photodesorption initiated by photodissociation and photodesorption without photodissociation would be the depth dependence of the process originating in the ice mantle.

30 *Chemical Processes*

Cuppen et al. have been exploring the use of microscopic Monte Carlo techniques both for physical and chemical processes involving interstellar grains and mantles for some time now.[9,19,23-24] For their paper here, the group presents a new facet of
35 this approach: a departure from the Markovian, or stochastic, approximation (Lamberts et al. DOI: 10.1039/c3fd00136a). In particular, they look at the non-equilibrium chemical process in which the products of a chemical reaction retain some of the exothermicity of the reaction long enough to move with considerable momentum. This process has an analogue in gas-phase reactions. In the interstellar
40 medium, gaseous reaction products will most likely lose their excess rotational and vibrational energy via radiative and collisional processes and, by the time of their next reaction, these modes will be at local thermodynamic equilibrium. On the other hand, translational energy takes longer to relax and collisional relaxation may well lose out to chemical reaction in the disposal of energy. Other forms of energy that
45 relax very slowly are nuclear spin (ortho-para forms) and atomic fine structure. In current gas-phase chemical simulations, the most important molecules with abundances affected by non-thermal considerations are ammonia and the deuterated isotopomers of H_3^+. For ammonia, the reaction between N^+ and H_2 leading to the

products NH^+ + H has a small barrier, which, at low temperatures, can be surmounted by excess fine-structure energy of N^+ or excess (non-thermal) energy of of the $J=1$ ortho rotational state of H_2.[25-26]

Lamberts et al. consider the granular case of H + HO_2 leading to two OH radicals, which can then recombine to form hydrogen peroxide, written as HOOH or H_2O_2. The initial reaction is exothermic by 1.5 eV, or 1800 K, so that if a significant fraction of this energy remains in translation of the OH products for some time, the dynamics of the reaction to form H_2O_2 will certainly change due to the competing effects of directionality and energy dissipation. Lamberts et al constrained the dynamics with experimental results, and used the resulting parameters to constrain the larger problem of the interstellar formation of water ice.

Two other papers presented here are concerned with HOOH, perhaps the simplest internal rotor in the interstellar gas, and how it possibly affects the rather complex synthesis of water ice at low temperatures in the ISM. A recent review of this synthesis in contained in a review article on water in the ISM by van Dishoeck et al.[14] Oba et al. (DOI: 10.1039/c3fd00112a) studied the reaction between H atoms and H_2O_2 and their deuterated counterparts at 10 – 30 K using hydrogen peroxide ice. These authors found that despite an activation energy of 2000 K to form the products H_2O and OH, the reaction occurs appreciably. They also found that the reaction with deuterated reactants is significantly slower, suggesting a tunnelling mechanism. Yet, the reaction rate coefficients decrease with increasing temperature, whereas a simple tunnelling mechanism should show little if any change. Moreover, it is not obvious whether the detailed mechanism involves diffusion or not. The hydrogenation of H_2O_2 with deuterium atoms in a neon matrix was studied by Zins et al. (Poster P02) and found to occur slowly.

Parise et al. (DOI: 10.1039/c3fd00115f) discuss the observation of H_2O_2 in space, in particular the fact that in the gas phase it is found only in one source – ρ Oph A. This seems peculiar because H_2O_2 in ice is a key intermediate in the formation of water ice. But it should be noted that although the ice mantle is dominated by water, there is little water in the gas in cold regions. The gas-grain chemical simulations done by these authors indicate that hydrogen peroxide production is very sensitive to temperature, with the ideal temperature for its observation in the gas to be in the 20 K – 30 K range. The analysis suggests that much of the gas in ρ Oph A lies in this temperature range, and that this situation is unusual.

What can happen to deuterated water ice bombarded by XUV photons has been studied by Siemer et al. (DOI: 10.1039/c3fd00116d) using the free electron laser at Hamburg (FLASH). Photo-ionisation is one possibility, and it can be followed by dissociative recombination, a well-known gas-phase process, to form OD and D, as well as the higher energy channels OD + D^+ + e and OD^+ + D + e. The OD radicals can recombine to form DOOD, as also discussed by Lamberts et al., which can then suffer photo-dissociation and photo-ionisation.

Complex Organic Molecules (COMs)

The production of COMs is thought to occur mainly on and in icy grain mantles, although gas-phase processes can also be of importance.[6,15] Although a variety of grain mechanisms have been discussed in the literature, the currently dominant one involves photolysis of warming grains leading to radicals, which recombine to form

more complex species.[6,15-17] An interesting variant on this idea was presented here by Rawlings et al. (DOI: 10.1039/c3fd00155e), who amplify their earlier theory in which gas-phase three-body association reactions occur in the transitory dense gas surrounding an interstellar dust particle that has just undergone an explosive event, catalysed by an ice mantle explosion caused by the catastrophic recombination of trapped hydrogen atoms and other radicals in the ice. Recent kinetic Monte Carlo calculations of ice mantle chemistry indicate that the radical abundances are higher than previously thought, lending some support to this theory.

With the exception of photon-dominated regions, the recent detection of complex organic molecules in a variety of new sources – cold cores, protostellar enveopes, infrared dark clouds, and circumnuclear disks of active galaxies – is not discussed in detail in any of the invited papers. But this diversity of sources shows that it is likely that more than one mechanism for the formation of complex organic molecules is at play. Several poster abstracts report observations of COMs or discussions of the chemistry leading to complex organic molecules. Jaber et al. (poster abstract P19) discuss a census of COMs towards the solar type protostar IRAS 16293-2422. Their observations provide evidence that at least some of the COM spectra arise from cold regions. Fayolle et al. (poster abstract P57) have observed high abundances of COMs with respect to methanol in massive young stellar objects that do not possess strong hot core features. A new model for the formation of COMs under low temperature conditions is discussed in poster abstract P68 by Vasyunin et al. Their network contains enhanced rates for reactive desorption and radiative association reactions in the gas not previously studied. Observations of complex organics and deuteration in the inner regions of low-mass protostars are reported by Taquet et al. (poster abstract P29). Furuya and Aikawa (poster abstract P37) discuss the role of turbulence in affecting the chemistry of COMs.

The molecule glycolaldehyde has been singled out by several authors. Woods et al. (poster abstract P67) discuss theoretical approaches to its formation, while Brown et al. (poster abstract P60) report experimental studies on its thermal and UV processing. Maity et al. (DOI: 10.1039/c3fd00121k) discuss the formation of glycolaldehyde in ices exposed to ionizing radiation.

Although COMs usually refer to oxygen-containing and nitrogen-containing molecules, it is also important to point out that the syntheses of species as complex as PAHs can also occur on solid surfaces. The poster abstract by Tian et al. (P71) contains the report that PAHs can be synthesized on silicates and silicon carbide by reactions starting from acetylene. The formation of PAHs in so-called planetary nebulae (PNe) is linked to small hydrocarbon precursors by Guzman-Ramirez et al. (poster abstract P01). The gas-phase chemistry of PAH cations and nitrogen-containing analogs is discussed in poster abstract P58 by Demarais et al.

One problem with confirmation of granular hypotheses is that it is hard to detect complex molecules on ice mantles because the infrared spectroscopy needed consists of broad bands and is not very sensitive even with satellite observations. Measurements are normally made on complex molecules after their post-synthesis desorption into the gas. A new approach has been discussed here by Ioppolo et al. (DOI: 10.1039/c3fd00154g) in which THz spectra of solid objects have been studied in the laboratory and the preliminary results do indicate that such spectra might be able to distinguish chemically some aspects of the chemistry that occurs on and in ice matrices.

A variety of processes are thought to occur on ices. At low temperatures, organic molecules can possibly be produced by single atoms diffusing rapidly on 10 K grains and adding chemically to smaller species to produce larger ones.[6] Methanol is formed in this manner, and some larger species might be formed also. Duflot et
5 al. (Poster P06) have recalculated the barrier to the initial reaction in the formation of methanol ice: the hydrogenation of CO by reaction with atomic hydrogen. Subsequent reactions involving H atoms and HCO, H_2CO, and CH_3O (CH_2OH) lead to methanol. Kobayashi et al. (Poster abstract P17) find evidence for saturation of hydrocarbons on grains by reactions with atomic hydrogen.
10 The importance of adsorbed O atoms to form water ice in cold sources is well-known:

$$O(ads) + H(ads) \rightarrow OH(ads); OH(ads) + H(ads) \rightarrow H_2O(ads)$$
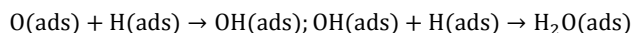
but atomic oxygen is reactive with other species than hydrogen atoms on ices,
15 including organic molecules. The formation of CO_2 on ices has been a weak link in chemical simulations of ices, although a number of possible simulations, both thermal and requiring activation, have been suggested. Minissale et al. (poster abstract 59) report experimental evidence for the formation of CO_2 via the reaction of O and H_2CO. Following earlier low-temperature experiments between O atoms
20 and ethylene to form ethylene oxide, the UCL group (Kimber et al. DOI: 10.1039/c3fd00130j) report here a study of the reaction between O atoms and propyne (C_3H_4) to form C_3H_4O. In both cases, the kinetic model for reaction involves a diffusive (Langmuir Hinshelwood) channel and an Eley-Rideal channel. The kinetic parameters obtained for O + C_3H_4 include a small reaction barrier of 160
25 K for both processes, which, in the diffusive case, probably consists of some sort of chemical barrier plus a diffusion barrier (presumably for the more mobile O atoms), and desorption energies of 2500 K for propyne and 1700 K for O atoms. For the diffusive case, the amount of energy left for the diffusion barrier is unphysically small. In fact, a newly measured value for the diffusive barrier of O on amorphous
30 silicates is 1785 K, which is considerably greater than the standard assumption of a fraction of the desorption energy.[28] Even if this value is somewhat large, it is likely that the process measured by the UCL does not involve diffusion. This hypothesis can possibly be checked by using sub-monolayer quantities of reactants to see if any role for diffusion can be found. In addition, the unusual temperature dependence
35 might suggest a tunnelling mechanism. In an earlier study of the O + C_2H_4 reaction, the reaction barrier reported (190 K) for the LH mechanism is once again lower than the diffusive value for O.

Although the surface reactions between O and organic molecules do not require anything but thermal energy, the syntheses of most organic molecules on grains are
40 expected to be non-thermal in nature, and to require activation of some kind. Photolysis has been studied most extensively; as discussed above, photons, produced indirectly via cosmic ray bombardment, activate precursor species on grains such as methanol into radicals and the radicals recombine into larger species. Some laboratory evidence for this mechanism exists.[29]
45 In this Discussion however, more emphasis has been placed on electron bombardment upon surfaces to produce complex organic molecules in ice mantles. Although effective cross sections for such processes can be high, it is not easy to simulate what is actually happening on grains and ice mantles despite a number of

interesting experiments. Problems include an incomplete knowledge of the flux of non-thermal electrons interacting with the ice mantle of a grain. Energetic electrons can arise from interactions in the gas and in the ice mantle. Non-thermal electrons produced in the gas, however, may relax appreciably before striking grains.[30] For
5 visible and UV photons, the major cause of extinction is interaction with dust grains, since most gas-phase processes are discrete in character to a significant extent. For electrons, on the other hand, inelastic processes in the gas tend to be continuous, so that the electrons that strike dust particles have been significantly relaxed by collisions with gas-phase species such as H, He, and H_2.[30]
10 For low-energy non-thermal electrons, formation in diffuse regions is mainly by the photoelectric effect between photons and grains. For significantly higher energy electrons, cosmic rays, with energies from MeV – GeV, are involved in a variety of ways. Although protons represent most of the cosmic ray flux, electrons are also present at the 1% level, presumably with energies reduced by about a factor of 2000
15 by the mass factor. Cosmic rays can also produce secondary electrons, both in the gas and as they traverse through grains. The gas-phase secondary electrons initially have perhaps 30 eV of energy. As discussed by Mason et al. (DOI: 10.1039/c4fd00004h), cosmic rays interacting with ice-covered dust particles can produce up to 10^4 secondary electrons, with a mean kinetic energy under 20 eV.
20 Simulations indicate that cosmic ray bombardment of grains leads to both thermal and ionization effects, with heavy cosmic rays playing an important role.[31] The thermal effect is utilized as a desorption mechanism in interstellar gas-grain chemical simulations.[32]

So experiments utilizing a variety of energy ranges for electrons are useful. Of
25 course, it must be mentioned that both photon-irradiation and electron-irradiation experiments performed in the laboratory cannot be compared directly with interstellar processes, because the laboratory work utilizes much higher fluxes over much shorter periods of time. So, simulations must be constructed for the laboratory work and, if successful, perhaps carried over into the different physical conditions of
30 the ISM. These simulations will not be facile.

There are a number of papers in this Discussion on electron-induced chemistry, with an introductory work by Mason et al., who give a simple example of the formation of ozone on O_2 ice. Irradiation of the ice by electrons of energy 10 eV or more dissociates the oxygen to produce atoms, which then recombine with
35 molecular oxygen to form ozone with the bulk ice acting as the third body. Mason et al. also discuss the production of anions on ices via dissociative attachment leading to an interesting chemistry.

The interstellar synthesis of pre-biotic molecules via low-energy-induced chemistry in ices is discussed in the paper by Boamah et al. (DOI:
40 10.1039/c3fd00158j), who use condensed methanol as the target. With 7 eV and 20 eV electrons under high-vacuum conditions, these authors produced a number of organic molecules also detected in the interstellar medium and thought to be produced via photolysis. The molecules include formaldehyde, dimethyl ether, methyl formate, acetaldehyde, glycolaldehyde, acetic acid, ethanol, and ethylene
45 glycol.

Experiments using keV electrons are reported in papers by Maté et al. (DOI: 10.1039/c3fd00132f) and Maity et al. (10.1039/c3fd00121k) Maté et al. are interested in the stability of carbonaceous dust analogues and glycine against both photon and electron bombardment. The authors find that for glycine, 2 keV

electrons are less efficient than both UV photons and MeV protons for its destruction, and caution investigators who use keV electrons to simulate cosmic ray effects, given the low penetration depth of the electrons. Maity et al, on the other hand, are interested in the synthesis of glycolaldehyde from methanol ice and
5 methanol-carbon monoxide ices exposed to 5 keV electron irradiation. Evidence is found for three mechanisms involving radical-radical recombination (similar to the photolysis mechanism suggested in hot cores).

One concludes from a perusal of the papers on electron-induced chemistry that initial chemical simulations will have to make some drastic simplifying
10 assumptions. It would be useful to find signatures to distinguish among thermal reactions, photolysis, and electron-induced processes. For example, the isomeric abundances of complex organic molecules may well betray how the molecules are formed.

The role of gas-phase processes in the chemistry of interstellar COMs and smaller
15 species has not been fully represented in this Faraday Discussion, but some posters have reported exciting new results in this area. de Ruette et al. (poster abstract P21) have studied the reaction between C and H_3^+, one of the primary reactions in the initial syntheses of organic molecules in cold clouds. Novotny et al. (poster abstract P22) have measured dissociative recombination rate coefficients for the ions HCl^+,
20 D_2Cl^+, HF^+, D_2F^+, and CF^+. Caravan et al. (poster abstract 29) have measured enhanced rates of gas phase neutral-neutral reactions involving OH at very low temperatures due to a potential surface with a well in the entrance channel and a subsequent barrier that can be tunnelled under.[33] Harada et al. (poster abstract P36) have observed and analysed via a gas-grain simulation the chemistry that occurs in
25 the circumnuclear disk at the center of our galaxy. Hincelin et al. (poster abstract 31) have assembled a huge new gas-grain chemical network for deuterated species that takes into account the ortho, para, and meta spin states of simple hydrogen/deuterium species. Quantum chemical calculations have been performed by Zicler et al. (poster abstract P12) to understand why HeH^+ has not been observed,
30 while Ellinger et al. (poster abstract P41) have studied the survival of glycine and alanine both experimentally and theoretically under irradiation. The gas-phase chemistry of carbon chains in dark cloud models has been reviewed by Loison et al. in poster abstract P43. The low temperature reactivity of water and of methanol in the gas-phase has been studied by Hickson and Loison (poster abstract P45).

35 3   Towards the future: What remains to be done?

It is always difficult to predict the future. Both Nigel Mason and I quoted Donald Rumsfeld, who divided knowledge into "known knowns, known unknowns, and unknown unknowns." A prediction of the future is normally a list of known unknowns. But the path of science is in reality more complex. Nevertheless, here is
40 my list of known unknowns, divided into topics within two areas of research: observations/simulations, and laboratory and theoretical treatments of individual processes.

Topics in Observations/Simulations

(i)   To determine the extent of homogeneity in different types of sources,
45 (ii)   To understand the chemistry at high spatial resolution and high sensitivity,

(iii)   To understand the chemistry in external galaxies to the extent obtained from single-dish observations of our own galaxy,

(iv)   To obtain an increased understanding of the synthesis and distribution of complex organic molecules,

(v)   To increase the use of molecular dynamics and kinetic Monte Carlo methods in simulations if needed.

Molecular observations are undergoing a revolutionary transformation because of the construction of a number of new and more powerful telescopes for the observations of molecules throughout much of the known universe. The telescopes are of two types, (i) "space" telescopes designed to look at frequencies higher than observable from the ground so that rotational transitions of light hydrides or low frequency vibrations such as torsional motions can be explored, and (ii) interferometers, which consist of arrays of radio telescopes at excellent ground-based sites acting in a coherent manner. Interferometers have the capability of high sensitivity given their large combined surface area, but also have ultra-high spatial resolution, which enables them to observe the details of small nearby objects in molecular lines such as protoplanetary disks as well as to see structure in distant galaxies. The space telescopes include the Herschel Space Telescope, which operated in solar orbit at frequencies through 1910 GHz until recently exhausting its supply of liquid helium, and SOFIA (Stratospheric Observatory for Infrared Astronomy), which operates from an airplane above most of the atmosphere. These telescopes have enabled astronomers to detect a number of new and exotic molecules and to probe environments not fully probed before. The interferometers include the mother-of-all-such instruments, the so-called ALMA (Atacama Large Millimeter/Submillimeter Array), which is undergoing construction in a high desert site in the Andes. When complete, it will consist of 60 dishes and probe the sky with ultra-high spatial resolution and unheard of sensitivity.

Keeping up with the advances from such telescopes will keep molecular astronomers quite occupied. Observations from ALMA made even before its completion show that sources treated as nearly homogeneous can turn out to be dramatically inhomogeneous in molecular intensities.[34] The inhomogeneity can be caused by differences in physical conditions, which cause excitation differences, such as large variations in density over small distances, or can be caused by differences in chemistry, which can themselves stem from density and temperature differences as well as diverse time scales. In other words, chemical simulations will have to be much more detailed in their treatment of physical conditions on small distance scales, with three-dimensional hydrodynamic calculations[35] or semi-analytic methods[36] to understand dynamics combined with the chemistry. Such considerations lie behind my inclusion of research areas (i), (ii), and (iii) above. This viewpoint is not universal, with some investigators still preferring simplicity over what might be regarded as excess detail. But, how can simple homogeneous time-independent models obtain correct molecular abundances of different molecules if the molecules are not even totally located in the same regions of space, and if the physical conditions are different, either statically or dynamically? Even the well-studied "homogeneous" cold core source TMC-1, is certainly not homogeneous on scales already studied. The study of so-called "data cubes," consisting of spatial resolution across the sky and Doppler resolution in the direction towards the observer, seems to be the path many will follow.

Topics (iv) and (v) above concern the chemistry of simulations, which still must be improved in several areas including the pathways leading to complex molecules, especially in new types of sources, such as the atmospheres of extra-solar planets, and improvements in how surface chemistry, especially the chemistry occurring on

5 and in ice mantles, is treated. As computers become more powerful, it should be possible to replace approximate methods, such as the use of rate equations, with more exact treatments, such as microscopic stochastic approaches, including the new "off-lattice" approaches mentioned here.[37]

10 **Topics in laboratory and theoretical treatments of individual processes**

(i) To obtain absolute rate coefficients for processes on surfaces and in ice mantles with understanding of the mechanism and reasonable agreement among different research groups,

(ii) To simulate laboratory rate experiments to allow subsequent

15 extrapolation to rates under interstellar conditions,

(iii) To understand the differences between processes on surfaces and processes inside ices,

(iv) To include electron-induced processes on grain mantles into simulations,

20 (v) To improve understanding of poorly known gas-phase reactions, particularly those involving radiative emission.

Astronomical problems and problems in kinetic treatments are not the only difficulties faced when attempting to simulate the chemistry of regions alien to the

25 earth. Some of the processes thought to be of importance in interstellar clouds, for example, cannot easily be studied in the laboratory and require quantum chemical treatments. Others can be studied in the laboratory but not at temperature regions much lower or higher than room temperature, leading to the problem of whether long temperature extrapolations of experimental work are accurate. An example of

30 the problem in extrapolations to low temperature (topic ii) has been highlighted recently with the discovery that the so-called Arrhenius rate law, which typically governs the temperature dependence of rate coefficients for gas-phase reactions with activation energy barriers, can be quite wrong at low temperatures where quantum mechanical tunnelling under barriers can increase the rate coefficient by many

35 orders of magnitude.[33] In collaboration with the Leeds group, we are currently beginning an investigation of how important this effect will be in cold interstellar clouds. Similar laboratory sresearch is also being undertaken in Rennes and Ciudad Real. At present, only the reaction

$$NH_3^+ + H_2 \rightarrow NH_4^+ + H$$
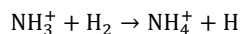
40

which occurs with a high rate coefficient at low temperatures because of an entrance channel potential minimum and tunnelling through a small barrier, is included in standard networks to the best of our knowledge.[38]

Perhaps the most difficult problem facing modellers at present is to utilize the

45 fascinating results being obtained on chemical reactions on and in ice mantles, as we have heard during this Discussion. This difficulty underlies topics (i)-(iii). Such utilization requires first that the laboratory scientists understand the mechanism for

the reaction being studied in the laboratory. If a process occurring via an Eley-Rideal mechanism is instead labelled diffusive in nature, astrochemists will certainly not utilize these results correctly when they incorporate the rate coefficient into their networks. Similarly, if a process thought to be occurring on a flat source is really
5 occurring in pores in the ice, the interstellar transformation will not be successful. In addition, laboratory scientists must understand differences that arise among measurements in different laboratories and must be able to obtain absolute rate coefficients based on well-determined parameters such as diffusion barriers and desorption energies. Finally, a collaboration between laboratory scientists and
10 astrochemists is needed to transfer the laboratory results to interstellar conditions, where physical conditions are likely to be significantly different. In our estimation, the best manner in which to achieve this transfer is to first simulate the results of the laboratory experiments using stochastic treatments if necessary and, in so doing, achieve a sufficiently detailed understanding of the process or processes occurring
15 so that the rate coefficient can be extrapolated to very different conditions. The closest we have come to success in this area appears to be our understanding of the synthesis of water ice.

There are some processes that we understand sufficiently poorly that it is currently exceedingly difficult to incorporate them into chemical simulations. Of
20 these, the most important in the area of ice chemistry concerns electron-induced processes (topic iv). A variety of experiments discussed here show that electron bombardment of ices can indeed lead to new chemical pathways both for simple and complex molecule formation, but our detailed understanding of what exactly happens chemically as electrons penetrate ices is less than needed. Perhaps it might
25 be possible to incorporate chemical processes and the details of Monte Carlo calculations that can follow the penetration into the ice mantles of cosmic rays and secondary electrons of various energies.

Finally, although much of the emphasis here has been on dust chemistry, there are some critical gas-phase processes that are very poorly understood. Topic (v)
30 concerns our understanding of exotic chemical processes that are based on the emission of radiation. Known as radiative association in the atomic/molecular community and radiative capture in the nuclear physics community, the recombination of two heavy species to form one compound product can occur at low densities only by the emission of radiation. If we consider two molecules A and B,
35 radiative association can be modelled as

$$A + B \leftrightarrow AB^* \rightarrow AB + h\upsilon$$

where AB^* is referred to as a complex, and sits atop a potential minimum. Depending upon the competition between radiative stabilisation, typically via
40 vibrational relaxation, and re-dissociation of the complex, the rate coefficient can vary over 10 orders of magnitude. Very few experimental studies of radiative association have been undertaken, because the process requires very low densities, such as pertain in ion traps, or three-body association will dominate, where collision with a third body stabilizes the complex.[39] Moreover, to the best of our knowledge,
45 no experiment has resulted in unambiguous measurement of any emitted radiation. In addition, detailed quantum treatments have not been applied except in rare instances. Simple statistical theories are customarily used; these do show a strong inverse temperature dependence to the rate coefficients, and very strong direct

dependencies on the bond energy of the complex and its size, essentially because these parameters determine the complex lifetime.[40] According to a number of studies, radiative association is likely to help in the synthesis of complex organic molecules under cold conditions.[41] An analogous process, radiative attachment:

$$A + e^- \leftrightarrow A^{-*} \rightarrow A^- + h\upsilon$$
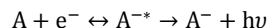
is thought to be a major process leading to the formation of negative molecular ions in cold sources.[42] Yet, there have been only a few studies of this process, and, to the best of our knowledge, no recent ones. Again, simple statistical approximations are used, and, when included in simulations of dense clouds and the AGB star IRC+10216, seem to be adequate to reproduce the abundances of the larger anions; e.g. C_6H^-.[43]

In summary, the future promises to be a time of rapidly increasing knowledge of molecules throughout the universe, which will aid both our understanding of chemistry under exotic conditions as well as our understanding of the physical conditions of the sources through both molecular spectroscopy and chemical simulations. When my research in this field started, in 1972, there were probably fewer practitioners throughout the world than there were in the auditorium where our discussions were held. The growth since then has been phenomenal. To maintain the growth in astrochemistry, further research in molecular observations, simulations, experiments in both spectroscopy and kinetics, and quantum chemical theory will be needed. As we have seen in this Discussion, astrochemistry is already a vibrant subject in which all of these modes of research are being employed.

Acknowledgments

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[#] The units used throughout the paper are those in common use in astronomy, which are mainly cgs units.

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