Faraday Discuss., 1998, **109**, 83–108

General Discussion

Dr Bergin opened the discussion of Prof. Millar's and Prof. van Dishoeck's papers: ISO observations of H_2O towards the BN/KL star forming core in Orion[1] have recently confirmed the astrochemical prediction that water will be produced in abundance ($[H_2O]/[H_2] > 10^{-4}$) in shocked molecular gas. Since the cooling timescale after the shock passage is rather short (on the order of 100 years) an important question is what happens to this large water abundance once the gas cools to typical values of $T_k \approx$ 10–40 K. One likely possibility is that the H_2O molecules will deplete onto the surfaces of cold dust grains. Chemical models have shown that this depletion will occur prior to the re-assertion of the normal quiescent time-dependent chemistry.[2] Thus this offers an alternate method to create the abundant water ice mantles that are observed in molecular clouds. This method is quite robust and is able to reproduce the $[HDO]/[H_2O]$ ratios observed both in hot cores and in cometary ices. Furthermore, due to an imbalance created in the chemistry by the high water abundance, there is a significant increase in the abundance of OH in the post-shock gas which allows for the production of CO_2 in the gas phase. The carbon dioxide molecules will deplete onto the grain mantles with an abundance that is 1–30% of H_2O ice, again an amount that is quite similar to observed values. These results do not suggest that surface chemistry does not occur, but rather argue that care must be applied in the interpretation that ISM ices are the sole result of grain surface chemistry; instead they may be created in shocks.

1 Harwitt *et al.*, *Astrophys. J. Lett.*, 1998.
2 Bergin, Melnick and Neufeld, *Astrophys. J. Lett.*, 1998, **499**, 777.

Prof. Millar responded: Shocks may not play a dominant role in determining the composition of molecular ices because the degree of deuterium in hot cores appears to be relatively large, *e.g.*, for HDO and, perhaps more importantly for D_2CO. However, we need a much more detailed study of D-bearing molecules in hot cores to be certain of this.

Dr Hatchell said: The shock tracer SiO is detected in single dish observations of many hot core regions. High resolution VLA† observations of one such hot core, G34.26 show that the SiO traces a possible outflow and a widespread, extended component but that no SiO is seen in the direction of the ammonia core (see Fig. 1).

Prof. Irvine said: Last year my student Jimmy Dickens, and I and colleagues in Sweden and Japan reported the identification of a new 'hot core' molecule, ethylene oxide, in the Galactic center cloud Sgr B2 (N).[1] This 3-membered ring, c-C_2H_4O, is only the third cyclic molecule discovered in interstellar clouds. However, the richness of the Sgr B2 spectra and the width of the lines left some lingering doubt about the assignment. Quite recently, additional observations at SEST have detected ethylene oxide in several other hot core sources, thus absolutely confirming the presence of this molecule in such regions. Fig. 2 shows seven transitions of ethylene oxide labeled with the relevant energy levels, observed in the source NGC 6334F by Albert Nummelin from the Onsala Space Observatory and Jimmy Dickens from the University of Massachusetts.[2] In addition, several other large oxygen-containing organic molecules were observed in several transitions, including acetaldehyde (CH_3CHO), a lower energy isomer of ethylene oxide (Fig.

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† The VLA is part of the National Radio Astronomy Observatory, a facility of the National Science Foundation operated under co-operative agreement by Associated Universities, Inc.

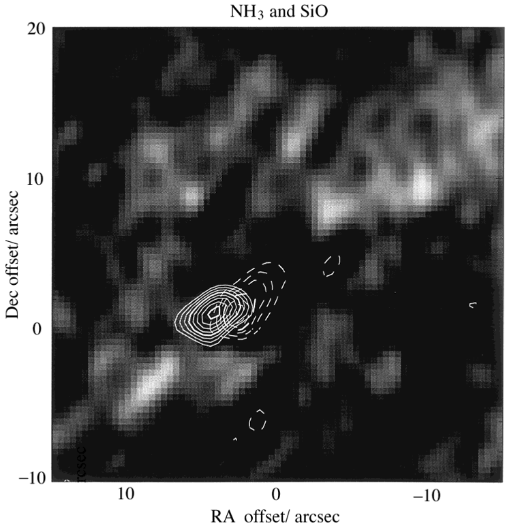

Fig. 1 SiO absorption (– – –) and emission (greyscale) towards the G34.26 hot core. The hot core itself is detected in NH_3 (——).

3). It is interesting that the ratio of c-C_2H_4O to CH_3CHO is quite well determined and is rather constant in the sources observed to date (in the range CH_3CHO/c-$C_2H_4O \approx$ 2–8). Hopefully, these data will stimulate the modelers to include ethylene oxide in their calculations and to see what constraints these observed values put on the models.

1 J. E. Dickens, W. M. Irvine, M. Ohishi, M. Ikeda, S. Ishikawa, A. Nummelin and Å. Hjalmarson, *Astrophys. J.*, 1997, **489**, 753.
2 A. Nummelin, J. E. Dickens, P. Bergman, Å. Hjalmarson, W. M. Irvine, M. Ikeda and M. Ohishi, *Astron. Astrophys.*, 1998, in press.

Dr Schutte communicated: Some of the more complex molecules seen in hot cores, such as CH_3CH_2OH and $(CH_3)_2O$ could first be produced by grain surface chemistry and later released into the gas phase. In addition to surface chemistry complex species could be produced by UV irradiation of the ice mantles. As an example, it was found that methyl formate ($HCOOCH_3$), one of the products seen in hot cores which is not accounted for by the surface chemistry model, is produced by irradiation of methanol ice.[1] The production of ethanol was reported for UV irradiated H_2O–CH_3OH mixtures.[2] In this context it must be noted that methanol-rich ice is often observed in the direction of protostars.[3,4] Thus, photochemistry should be considered as a mechanism for the production of some of the more complex species seen in hot cores.

1 P. A. Gerakines, W. A. Schutte, P. Ehrenfreund and E. F. van Dishoeck, 1996, *Astron. Astrophys.*, 1996, **312**, 289.
2 M. P. Bernstein, S. A. Sandford, L. J. Allamandola, S. Chang and M. A. Scharberg, *Astrophys. J.*, 1995, **454**, 327.
3 C. J. Skinner, A. G. G. M. Tielens, M. J. Barlow and K. Justanont, *Astrophys. J.*, 1992, **399**, L79.
4 M. E. Palumbo, A. G. G. M. Tielens and A. T. Tokunaga, *Astrophys. J.*, 1995, **449**, 674; M. E. Palumbo, T. R. Geballe and A. G. G. M. Tielens, *Astrophys. J.*, 1997, **479**, 839.

Dr Palumbo asked: In your paper you discuss that S-bearing molecules can be used to derive the age of HMCs. In this picture H_2S is formed in the mantles and then evaporates. As far as I know H_2S has never been detected in the solid phase. Why do you start with H_2S? Why do you not consider OCS which has been identified in the solid phase?

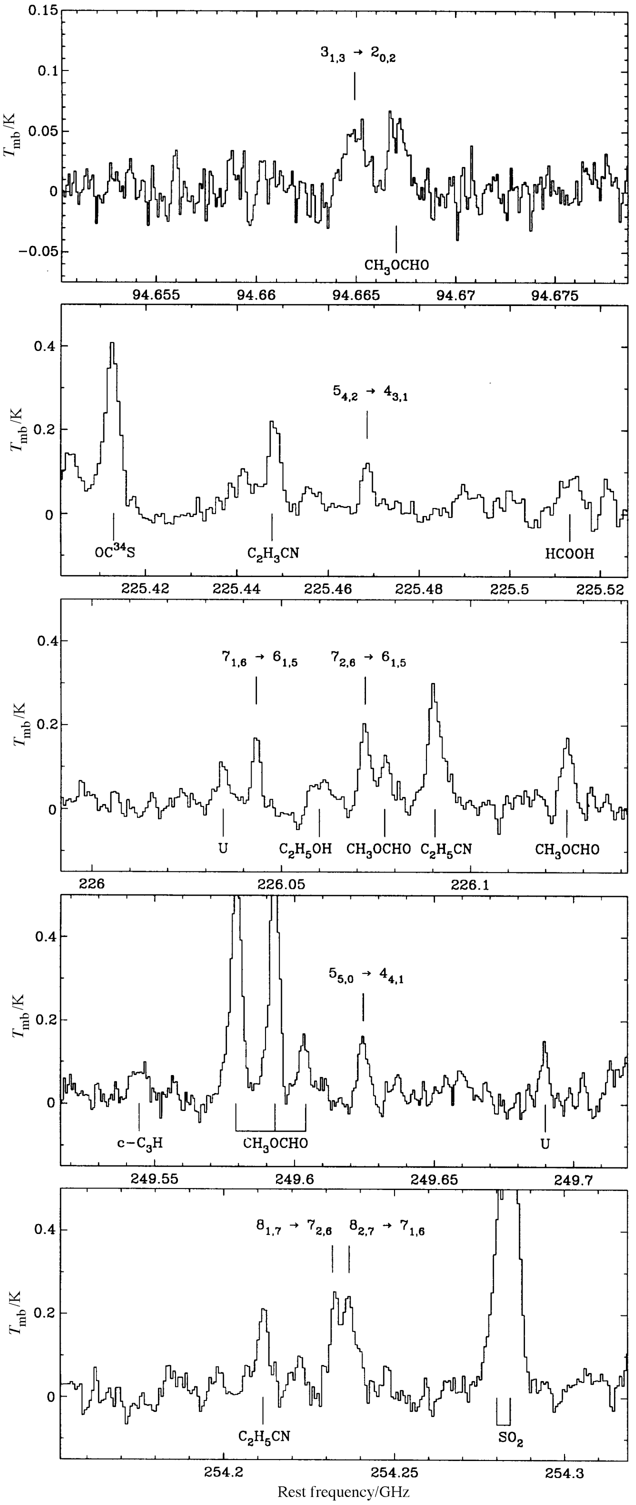

Fig. 2 Spectra towards NGC6334F, with all seven detected c-C_2H_4O transitions indicated

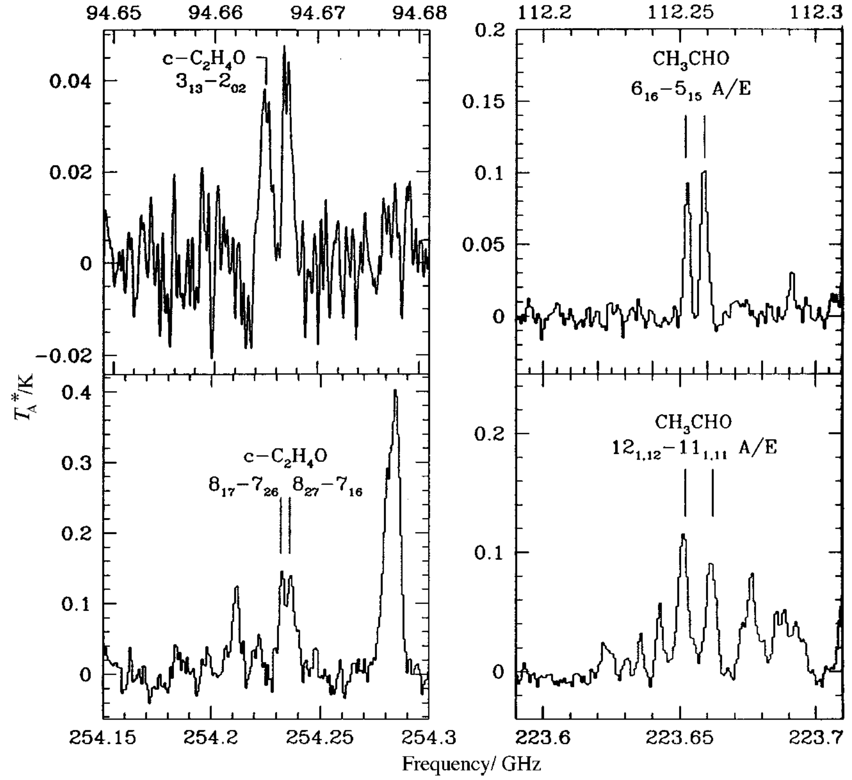

Fig. 3 Three rotational transitions of ethylene oxide (c-C_2H_4O) and four of acetaldehyde (CH_3CHO) observed toward the hot core NGC 6334 (F) with the SEST telescope by A. Nummel in (Onsala, Space Observatory) and J. Dickens (University of Massachusetts). Both these isomers have very recently been found to be commonly present in such regions.

Prof. Millar replied: I believe that there is a claim for solid H_2S along one line of sight, but it is clear that it is not a major component of interstellar ices. In our models of hot molecular cores, we find that our observations of many sulfur-bearing molecules are best fit by assuming an initial H_2S abundance of *ca.* 10^{-7}, that is about 100 times less than the cosmic abundances of sulfur.

Prof. Black said: The Introductory Lecture by Prof. Williams has called attention to a 'sulfur problem'; *viz.*, our current inability to explain simultaneously the high abundance of atomic sulfur observed in diffuse molecular clouds, the chemistry of simple sulfur-bearing molecules (CS, SO, SO_2, H_2S, and SO^+) in dense clouds, and the absence of large quantities of sulfur-containing ices (*e.g.* OCS and H_2S).

Prof. Millar's paper cites a possible role of H_2S-ice in the chemical evolution of interstellar gas. Do the recent ISO data on ices (Prof. van Dishoeck's paper) provide an improved limit on the abundance of solid H_2S? A reason for raising this question is that Prof. Millar's paper discusses the evaporation of solid H_2S in regions where H-atom reactions

$$H_2S + H \rightarrow SH + H_2$$

$$SH + H \rightarrow S + H_2$$

subsequently introduce S, which in turn leads to formation of the widely observed CS, SO, and SO_2. If this scheme is important, shouldn't the SH/H_2S abundance ratio approach unity? Although SH has Λ-doubling and rotational transitions at unfavourable frequencies for ground-based astronomy, searches for it might afford useful tests of this scheme.

It is worth noting that the gaseous sulfur abundance may play a key role in controlling the electron abundance in dense clouds, since atomic S is rather easily ionized and sulfur may not appear in molecular form to the extent that carbon does.

Dr Schutte responded: Several questions have been asked here, but I will only address the solid phase abundance of H_2S. The strongest feature of H_2S is the combined ν_3/ν_1 mode around 3.85 μm. Since this spectral region is accessible from the ground, the most sensitive search for this feature can be obtained with ground-based telescopes. No feature that can be ascribed to solid H_2S has yet been found in this spectral region. An earlier assignment of the weak absorption feature at 3.91 μm seen towards the high-mass young stellar object W33A to solid H_2S (ref. 1) was revised by Allamandola *et al.*,[2] who convincingly showed that the band can be accounted for by solid methanol. So as of yet no evidence for H_2S in dense cloud ices is available. Unfortunately, quantitative spectroscopic data of H_2S in astrophysically relevant ice matrices is not yet available so no upper limit can be quoted here.

[1] T. R. Geballe, F. Baas, J. M. Greenberg and W. Schutte, *Astron. Astrophys.*, 1985, **L6**, 146.
[2] L. J. Allamandola, S. A. Sandford, A. G. G. M. Tielens and J. M. Herbst, *Astrophys. J.*, 1992, **134**, 399.

Prof. van Dishoeck added: The ISO spectra do indeed provide the first opportunity to put quantitative limits on any sulfur-bearing ices, because of the complete wavelength coverage (e.g., Whittet *et al.*,[1] and d'Hendecourt *et al.*[2]). Apart from the 6.8 μm feature discussed by Schutte *et al.*,[3] the ISO spectra do not show any strong unidentified bands. Thus, if the sulfur is primarily in the solid phase in cold dense clouds, it must be in a compound which does not have any strong IR bands. This conclusion was also reached by Palumbo *et al.*[4] in their study of solid OCS. Detection and analysis of any weaker bands in the ISO spectra awaits improved data reduction software.

[1] D. C. B. Whittet, W. A. Schutte, A. G. G. M. Tielens *et al.*, *Astron. Astrophys.*, 1996, **315**, L357.
[2] L. d'Hendecourt, M. Jourdain de Muizon, E. Dartois *et al.*, *Astron. Astrophys.*, 1996, **315**, L365.
[3] W. A. Schutte, A. G. G. M. Tielens, D. C. B. Whittet *et al.*, *Astron. Astrophys.*, 1996, **315**, L365.
[4] M. E. Palumbo, T. R. Geballe and A. G. G. M. Tielens, *Astrophys. J.*, 1997, **479**, 839.

Dr Hatchell commented: I would like to show two figures to illustrate the discussion on sulfur chemistry: Fig. 4 shows a plot of the abundances in a number of hot core sources of several sulfur-bearing molecules; Fig. 5 is an illustration of the chemical evolution of sulfur species under typical hot core conditions.

Prof. Thaddeus said: The abundance ratio of most sulfur molecules in molecular clouds to their oxygen analogues is about that of the cosmic S : O ratio, 1 : 42. The most notable exception is CS, which is very deficient relative to CO. Taking into account limits which have been obtained for solid H_2S, how deficient do you think H_2S is relative to H_2O?

Prof. Millar responded: In cold clouds, the ratio of H_2S to H_2O is hard to determine because the abundance of H_2O is difficult to estimate. However, H_2O is likely to be reasonably abundant, at least 1% of the total oxygen not locked up in CO and grains. Upper limits to the H_2S fractional abundance are very low and imply a ratio of H_2O : H_2S on the order of 10000–100000.

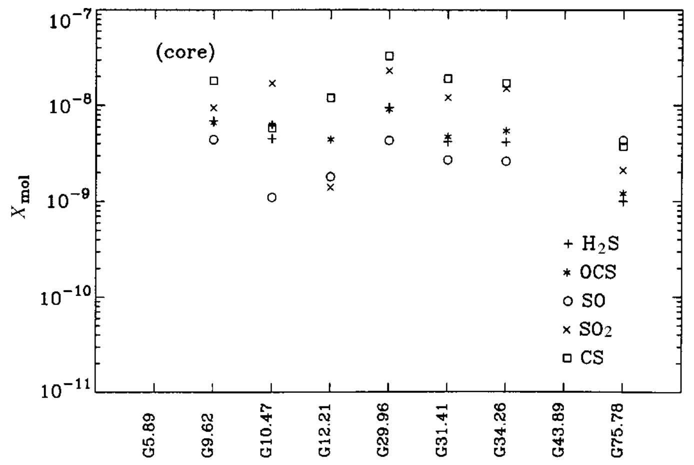

Fig. 4 Abundances of sulfur-bearing molecules in a number of hot cores associated with ultracompact HII regions

In warm clouds, H_2S is detectable but still appears to be a factor of at least 100 less abundant than H_2O.

Dr Palumbo asked: In your paper you discuss the formation of ice mantles during the collapse phase of a cloud. We know that ice mantles exist in quiescent molecular clouds. Reading other papers I understood that ice mantles already exist at the time the collapse starts. Why do you not consider pre-existing ice mantles? Alternatively, is the scientific community changing its view on this subject?

Prof. Millar responded: My belief is that the ice mantles in both cold dense clouds and in (pre-) hot molecular cores are very similar. Unfortunately, IR observations are not sensitive to material with fractional abundances $\leqslant 10^{-6}$–10^{-7} relative to hydrogen. In cold clouds material is not returned to the gas whereas in hot cores we can see *via* gas-phase spectroscopy, the ice mantles when they are returned to the gas phase.

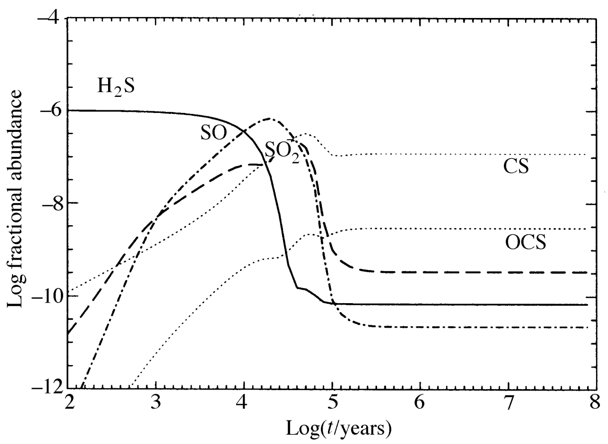

Fig. 5 Model of time evolution of sulfur species abundances for typical hot core conditions: $T_{\mathrm{kin}} = 100$ K; $n_{H_2} = 2 \times 10^5$ cm^{-3} and cosmic ray rate $Z = 1.2 \times 10^{-16}$ s^{-1}

Dr Ehrenfreund said: ISO allowed a new definition of the composition of interstellar ices, thermal processing in the protostellar vicinity and gas–grain chemistry. An important result of ISO was the ubiquitous presence of abundant CO_2 ice in space. From the triple-peaked bending mode of CO_2 ice we could derive for the first time that extensive ice segregation is occurring in the environment of protostars. H_2O, CO_2 and CH_3OH ice seem to exist towards many protostars in temperature zones of ≈ 60 K in fragile ice layers where these molecules are loosely bound to each other. This has important consequences for their desorption in the gas phase as well as for outgassing of cometary ices.

Prof. Chakarov said: Photochemical reactions on the grain surfaces play an important role in the material evolution in space. Unfortunately, the potential of photoinduced processes on surfaces is not yet fully understood and applied in the models attempting to reproduce the observed abundances. In the case of graphite (carbon) grains, surface photoprocesses are especially efficient (much more than in the gas phase) due to the strong light absorption by the substrate and its relatively weak quenching of the excitations. Thus the surface photochemistry is driven by an efficient, substrate mediated mechanism based on the creation, transport and resonant scattering of hot charge carriers, created in the bulk. Here (Fig. 6) we show experimental evidence for the photoproduction of a number of new products, as well as photodesorption of the primary species during photon irradiation of water (ice) on potassium precovered graphite surface. These observations adequately support the model predictions from Prof. van Dishoeck's paper. We found that UV irradiation ($\lambda < 400$ nm) of H_2O and K coadsorbed on graphite (0001) at 85 K leads to the photodesorption of H, H_2, CH_4, CO, K and CO_2 and the formation oxygen-rich K—O—C complexes on the surface. The primary step of these photoreactions involves selective photodissociation of H_2O, generating hot H atoms (significantly more energetic than in thermal equilibrium) and OH in ground and excited vibrational states. Subsequent collisions with coadsorbed H_2O, K and with substrate (C) give rise to the observed photoproducts. It is worth noting that these reactions are possible in the dark only at temperatures above 1100 K.

Dr Ehrenfreund communicated: The results of photon-induced crystallization of thin ice films are very interesting and challenging and could have important consequences for gas–grain chemistry in the interstellar medium. It would be important to quantify how

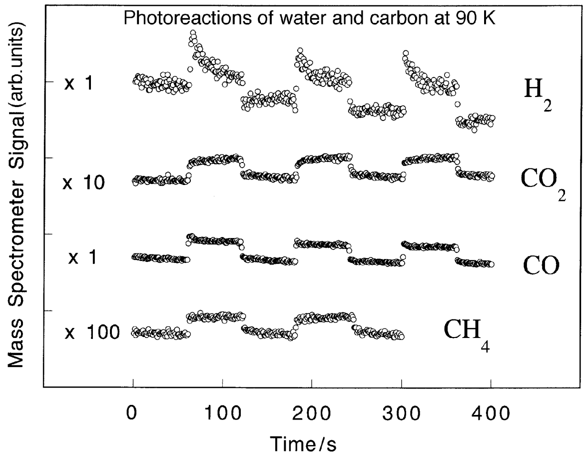

Fig. 6 Direct observations of the products of photoinduced surface reactions in H_2O–K coadsorbed layer on graphite surface at 85 K. $\theta_{H_2O} = 0.75$ monolayers; $\theta_K = 0.13$ monolayers. Photon energy: 4.3 eV (289 nm); flux: 1.6×10^{16} photons cm^{-2} s^{-1}.

much H_2O ice can be converted into the crystalline form and to combine those experiments in the future with spectroscopic studies. In astronomical spectra our only possibility of proving the crystallization of water ice is to monitor the change in the IR spectrum.

Prof. Chakarov added: Astronomers believe that water ice forming the mantles covering interstellar dust particles is mainly in amorphous form. The belief is based not so much on spectroscopic evidence as on the well established fact that amorphous–crystalline [$I_a \rightarrow I_c$, I_c stands for ice (cubic)] phase transition takes place at temperatures around 140 K *in vacuo*. This may turn out to be wrong taking into account the recent discovery of photon-induced crystallization of thin ice films. A new photoinduced surface process is observed under UV irradiation of thin ice films on graphite surface: transition from amorphous to crystalline phase. The effect is confirmed on the graphite/ice interface and first 3–4 monolayers. It has clear coverage and wavelength dependence with a threshold at *ca.* 4 eV. The mechanism we propose for the excitation of lattice vibrational modes includes both energy dissipation by the transient anion state and polarization effects. The observed effect has (at least) two important consequences: (i) the sublimation rate of the crystalline ice is almost twice as low as those for amorphous ice (see Fig. 7), thus directly affecting the H_2O abundance; (ii) the surface structure (the termination) of the ice layer is different for the two phases, thus dramatically changing the ability of water molecules to participate in reactions/transformations. The crystallization process can be called 'accumulative', since ice grown (condensed) on already crystalline ice surfaces continues to grow as crystalline.

Prof. van Dishoeck responded: I do not agree with your statement that there is not much spectroscopic evidence for the fact that the water ice is in amorphous form. This has been demonstrated extensively through laboratory experiments, starting with the work of Hagen *et al.*[1] Crystalline and amorphous ice can clearly be distinguished at the spectral resolving power and signal to noise ratio of the observed IR spectra.

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[1] W. Hagen, J. M. Greenberg and A. G. G. M. Tielens, *Astron. Astrophys. Suppl.*, 1983, **51**, 389.

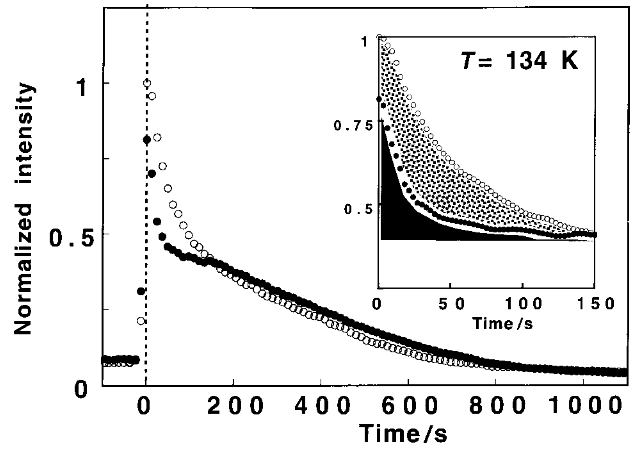

Fig. 7 Mass spectrometer ($m/z = 18$) trace of the isothermal sublimation of 2.2 monolayers of water ice deposited on graphite (0001) surface at 89 K. The sublimation temperature of 134 K is approached by a linear T-ramp with $\beta = 0.1$ K s^{-1}. ○, trace recorded directly after the deposition; ●, UV light irradiated layer (dose 5.5×10^{18} photons cm^{-2}). The inset shows changes of the sublimation rate that are specific for the transition from amorphous to the crystalline state.

Ms Trakhtenberg said: We have investigated the adsorption of water ice on substrates of various roughness and chemical composition at 100 K. Amorphous quartz, amorphous quartz covered with octadecyltrichlorosilan monolayer (OTS), amorphous quartz covered with mixed octadecyltrichlorosilan-docosyltrichlorosilan monolayer (OTS–DTS), single crystal silicon (100) wafer, silicon wafer covered with OTS, and silicon wafer covered with OTS–DTS were studied.

It was found that on smooth substrates partially crystalline ice is formed, however on rough substrates ice is amorphous. Hence, the ice structure can provide information about the morphology of substrate on which ice is adsorbed.

After the adsorption, the samples were heated and the desorption of ice was observed. It was found that desorption of ice from smooth surfaces occurs at lower temperatures than from rough surfaces. In Fig. 8 the correlation between the ice desorption temperature and the substrate roughness is presented.

These results can be rationalized in the following way. An ice cluster adsorbed on a rough substrate interacts with a larger number of sites than the ice cluster adsorbed on a smooth substrate. Therefore, the interaction between the ice and the rough substrate is stronger than that between the ice and the smooth substrate. The ice clusters adsorbed on a smooth substrate are more mobile and they can rearrange themselves to a more stable crystalline state. Ice clusters adsorbed on rough substrates are trapped in the potential wells and therefore desorbed from the substrate at higher temperatures.

Prof. van Dishoeck responded: Thank you for presenting your interesting experiments on the dependence of the adsorbed ice phase on the roughness of the substrate. In the interstellar medium, most of the silicate grains are amorphous and therefore have rough surfaces. The observed ices are indeed predominantly amorphous (*e.g.* Hagen *et al.*[1]).

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[1] W. Hagen, J. M. Greenberg and A. G. G. M. Tielens, *Astron. Astrophys. Suppl.*, 1983, **51**, 389.

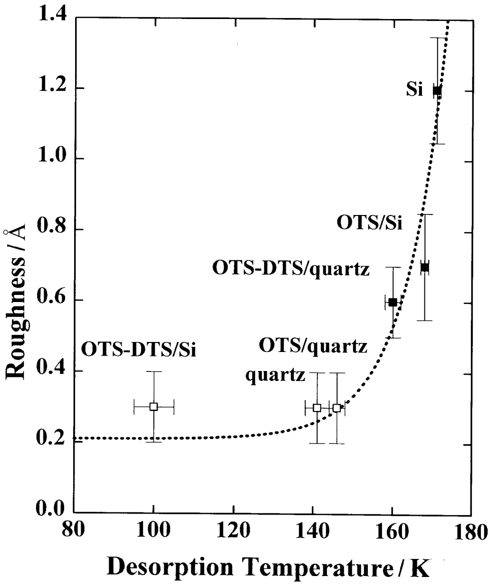

Fig. 8 Correlation between the substrate roughness, ice phase and ice desorption temperature. Quartz slides and silicon wafers either bare or covered by self-assembled monolayers of octadecyltrichlorosilane, pure (OTS) or mixed with decosyltrichlorosilane (OTS-DTS) were used as substrates. □, Deposited ice was partially crystalline; ■, deposited ice was amorphous.

Dr McCoustra communicated: The water ice temperature programmed desorption (TPD) data presented by Ms Trakhtenberg and co-workers contrasts markedly with measurements comparing the behaviour of amorphous and crystalline water ices that we have previously reported.[1] Therein, we presented evidence that clearly showed that a crystalline water ice film desorbs at a temperature typically 10 to 15 K above that of an amorphous film. Perhaps Ms Trakhtenberg would care to comment on this difference.

[1] P. Jenniskens, S. F. Banham, D. F. Blake and M. R. S. McCoustra, *J. Chem. Phys.*, 1997, **107**, 1232.

Ms Trakhtenberg responded: The fact that the desorption rate of amorphous ice is higher than that of crystalline ice is well known.[1] The reason is the excess free energy of the metastable amorphous ice phase *vs.* the crystalline ice phase. The hydrogen bonding within the ice crystal is known to be stronger than within the amorphous ice. However, in this consideration one assumes that the interaction between the ice and the substrate is the same for both phases. Hence, it is reasonable that in the study undertaken by Jenniskens *et al.*[2] it was found that the desorption temperature of freshly deposited ice is lower than that of annealed ice, due to the larger fraction of crystalline component in the latter. In both cases the same substrate has been used. On the contrary, in our work[3] we compared the desorption of ice which were deposited on substrates of various roughness. The substrate effect was enhanced by using thin ice films (5–10 monolayers thick, *vs.* 70 monolayers thick films used in the study by Jenniskens *et al.*[2]). We found that the ice deposited on rough substrates was amorphous, while ice deposited on smoother substrates was partially crystalline. From smooth surfaces ice was found to desorb at lower temperature than from rough surfaces. However, it is important to realise that the desorption occurs after the onset of ice crystallisation. Therefore, the ice which was deposited as amorphous became partially crystalline prior to desorption. It means that in both cases the desorption of partially crystalline ice was observed. We suggest that the desorption which we observed is the desorption of ice clusters. Therefore, the main factor in this process is the interaction between the ice cluster and the substrate and not the interactions between the water molecules. The changes in desorption temperature of ice result from its interaction with the substrate and not from differences in the ice phase during desorption.

[1] R. J. Speedy, P. G. Debenedetti, R. S. Smith, C. Huang and B. D. Kay, *J. Chem. Phys.*, 1996, **105**, 240.
[2] P. Jenniskens, S. F. Banham, D. F. Blake and M. R. S. McCoustra, *J. Chem. Phys.*, 1997, **107**, 1232.
[3] S. Trakhtenberg, R. Naaman, S. R. Cohen and I. Benjamin, *J. Phys. Chem. B*, 1997, **101**, 5172.

Dr Kaiser said: From the chemical viewpoint, the postulation of grain–surface diffusion processes in the formation of methanol, CH_3OH, ethanol, C_2H_5OH, carbon dioxide, CO_2, carbon monoxide, CO, formaldehyde, H_2CO, ethane, C_2H_6, is very surprising and until now without scientific proof. Based on laboratory studies on the interaction of MeV cosmic ray particles such as protons (H^+) and helium nuclei (He^{2+}) and computer calculations of these processes, there are strong alternative pathways to these grain surface processes. Inside dark clouds, the ice mantle condensed on interstellar grains at about 10 K is processed by particles of the galactic cosmic radiation field leading to new molecules synthesized in the solid state. Since, however, typical carbon–hydrogen and carbon–carbon bond strengths in organic molecules range between 3 and 10 eV, the cosmic ray particles are too energetic to form a stable chemical bond as implanted into the icy mantle. But upon interaction with the solid target, each cosmic ray particle releases its excess energy to the target atoms in successive collisions *via* elastic and inelastic interactions. Here, the elastic process transfers energy to the nuclei of the target atoms igniting primary knock-on particles (PKOs; 1st generation of knock-on particles) if this amount is larger than the binding energy of the atom. MeV α-particles, for example, generate carbon PKOs with kinetic energies up to 10 keV. These knock-on particles can transfer their energy in consecutive encounters to the target

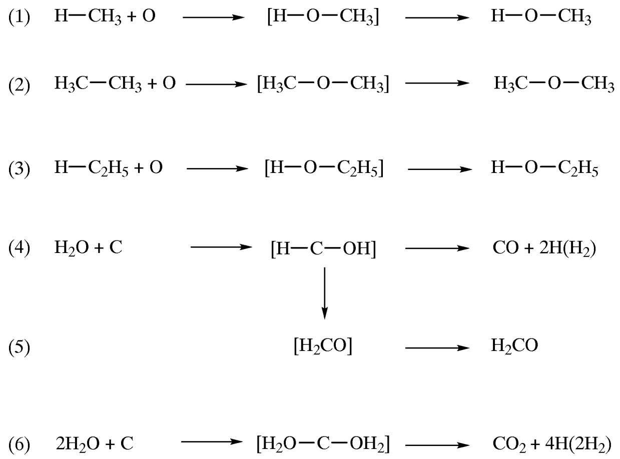

Fig. 9 Derived pathways to form methanol (1), dimethylether (2), ethanol (3), carbon monoxide (4), formaldehyde (5) and carbon dioxide (6)

atoms resulting in a collision cascade of secondary, tertiary, *etc.*, knock-on atoms. Moderated to about 1–10 eV (the so-called chemical energy range) these atoms are not in thermal equilibrium with the 10 K target (hence: non-equilibrium or suprathermal particles) and can react finally with the target molecules *via* elementary steps of bond insertion, addition to double or triple bonds, or hydrogen abstraction. The power of these suprathermal reactions to form new molecules at temperatures even as low as 10 K is based on their ability to overcome reaction barriers in the entrance channel easily, since suprathermal species can impact their excess kinetic energy into the transition state of the reaction. Even reactions endothermic at 10 K are feasible and extend the synthetic power of this reaction class further beyond thermal processes of diffusion controlled chemistry on interstellar grains. These unique aspects of suprathermal reactions result in reaction rate constants, *k*, orders of magnitude larger than their thermal counterparts. Detailed calculations on the reactions of, *e.g.*, 1 eV suprathermal hydrogen atoms with H_2O and CH_4 to form H_2 and OH as well as CH_3, respectively, depict k (1 eV H, H_2O) $= 1.7 \times 10^{-11}$ cm^3 s^{-1} and k (1 eV H, CH_4) $= 5.0 \times 10^{-11}$ cm^3 s^{-1} *vs.* thermal rate constants of k (293 K, $H + H_2O$) $= 9.6 \times 10^{-27}$ cm^3 s^{-1} and k (293 K, $H + CH_4$) $= 2.5 \times 10^{-19}$ cm^3 s^{-1}, a difference of up to 16 orders of magnitude. An order of magnitude calculation shows that although the internal UV flux in dense, molecular clouds ($\phi = 10^3$ cm^{-2} s^{-1}) ranges two orders of magnitude higher than the cosmic ray particle flux distribution maximum of $\phi = 10^1$ cm^{-2} s^{-1} for 1–10 MeV protons and α-particles, each MeV particle can generate about 100 suprathermal species in a 0.2 μm thick icy layer and 0.3 μm thick grain core. The flux advantage of the internal UV field deep inside molecular clouds is clearly eliminated by the ability of a single MeV particle to induce collision cascades with up to 100 suprathermal species. Therefore, an opening from 'photon-only universe' to process interstellar grains to include MeV ion synthesis is strongly encouraged. Fig. 9 summarizes derived pathways to form methanol (1), dimethylether (2), ethanol (3), carbon monoxide (4), formaldehyde (5) and carbon dioxide (6) in ices condensed on interstellar grains. The spin states of the carbon (C) and oxygen (O) atoms are not indicated. Square brackets indicate an internally/electronically excited intermediate which can transfer its excess energy to the surrounding matrix.

Dr Schutte responded: I agree that the matter of the mechanism for the formation of relatively complex species like formaldehyde, methanol, ethanol, carbon dioxide *etc.* on interstellar grains is far from settled. Indeed, though widely postulated in chemical models of gas–grain chemistry, experimental proof (or disproof) for the required surface chemical reactions is still lacking. Therefore, energetic processing, *i.e.*, by energetic ions or UV, is often mentioned as an alternative. Such processing would involve very simple starting mixtures of H_2O, CO and possibly NH_3, CH_4, O_2 and N_2. These species can either accrete directly from the gas phase (CO, O_2, N_2), or be produced by a very basic surface chemistry network (H_2O, CH_4, NH_3). While experiments have shown that irradiation of such ices either by UV or energetic ions efficiently produces CO_2, and some formaldehyde, no indication of the formation of significant quantities of CH_3OH or ethanol has yet been found.[1–3] It must be noted however that the energy of the ions in these experiments (≈ 1 MeV) was considerably lower than expected for cosmic rays. Nevertheless, the experimental evidence at this point does not support the theoretical prediction that the formation of methanol and ethanol through energetic processing is feasible, although carbon dioxide may be produced in this way.

The matter of the relative importance of UV and ion processing is still open. Opposite opinions in this respect have been expressed, with unfortunately, so far little substantial evidence in the form of detailed published calculations from either side. What is necessary to address this matter is a self-consistent calculation which compares the energy deposited in dense cloud ices by an appropriate energy distribution of charged particles, with the energy deposited by the UV radiation produced by the excitation of H_2 by these charged particles, as was described by Prasad and Tarafdar.[4]

[1] W. Hagen, 1982, PhD Thesis, University of Leiden, The Netherlands.
[2] W. A. Schutte, P. A. Gerakines, T. R. Geballe, E. F. van Dishoeck and J. M. Greenberg, *Astron. Astrophys.*, 1996, **309**, 633.
[3] M. H. Moore, R. Uhanna and B. Donn, *J. Geophys. Res.*, 1991, **966**, 17541.
[4] S. S. Prasad, S. P. Tarafdar, *Astrophys. J.*, 1983, **267**, 603.

Dr Kaiser commented: I strongly recommend a report by Nebeling.[1] Nebeling found that atomic carbon knock particles react with solid H_2O, and the following products are formed: CH_4, CO, CO_2, CH_2O, HCOOH, and up to 60% CH_3OH. So, there is experimental evidence that cosmic ray particle induced knock on carbon atoms could produce methanol in solid H_2O in the icy mantles on interstellar grains. Regarding the C_2H_5OH synthesis: this is only a theoretical, but logical, prediction based on collision cascade simulations (TRIM and MARLOWE code) and experiments in Juelich.[1]

[1] B. Nebeling, *Forschungszentrum Juelich*, 1998, 2245.

Prof. Field commented: One suggestion has been made that fast neutrals striking grains may influence the chemistry associated with grains. I should like just to mention that there is indeed an important astrophysical context in which fast neutrals may strike grains with many eV of energy. In magnetohydrodynamic shocks (MHD) there exists an extensive region in which there is differential motion of the charged grains and the neutrals. This motion typically is a large factor of the shock velocity. In this regime therefore fast neutrals do indeed strike grains. One may however doubt that the grains maintain their molecular mantles in this environment.

Prof. Smith said: I wonder if Prof. Millar could clarify the kinetic information given in his paper for $H + DCN \rightarrow HCN + D$. An activation energy of $E_A/k \approx 200$ K is given but, for the reaction as written, the endothermicity based on zero-point energy differences corresponds to *ca.* 800 K. In the light of this, is this reaction still likely to be important and would measurements of its rate coefficient at low temperature be valuable?

Prof. Herbst commented: Talbi and Herbst[1] have shown that the reaction $H + DCN \rightarrow HCN + D$ has large activation energy barriers in both the entrance and exit channels. This reaction, which is endothermic by 800–850 K, cannot occur efficiently in hot molecular cores unless the barriers do not exist.

[1] D. Talbi and E. Herbst, *Astron. Astrophys.*, submitted.

Prof. Millar responded: The factor of importance for determining whether atomic H can alter the DCN/HCH ratio is E_A/kT. As long as this factor is smaller than about 5, then the reaction can proceed at a fast enough rate to alter the DCN/HCN ratio on a time-scale less than those estimated for the ages of hot molecular cores. Thus for an endothermicity of *ca.* 800 K, kinetic temperatures of greater than *ca.* 160 K are needed, not a drastic constraint in terms of the temperatures of hot cores. However, if the reaction posseses an energy barrier of the size discussed by Talbi and Herbst, then this route will be unimportant in destroying DCN in hot cores.

Prof. Zare said: What kind of dust should we consider in gas–dust chemistry? Can we define a 'standard dust' or a series of standard dusts?

Prof. Papoular responded: It is clear that a deep mental gap separates the large 'molecular' community from the small 'dust' community. The former builds upon a solid foundation of well established facts and theories and can perform impressive computations, none of which, however, applies to the solid state. The 'dust' community, on the other hand, has not yet managed to bring to the forefront of the astrophysical literature the wealth of new experimental and theoretical results which are found in the general physical, chemical and solid state literatures, and may now profitably complement the seminal calculations of Salpeter.[1] This conference is an opportunity to help bridge the gap.

The most solidly established dust types are silicon carbide (SiC) and silicates: crystalline and amorphous SiO_3(Mg, Fe) and SiO_4(Mg, Fe)$_2$. It does not seem that such dust, when bare, enters into gas–solid reactions. Deep in molecular clouds, however, it may be covered with condensed gases, forming ices of H_2O, CO, CO_2, CH_4, $\cdots$. It is possible, in turn, that these ices interact chemically with the help of cosmic rays (see remarks by Dr Kaiser at this meeting).

The most reactive dust may turn out to be carbonaceous and hydrogenated, like coal, kerogen and hydrogenated amorphous carbon (HAC). A comparison of laboratory, solid state carbonaceous models of cosmic dust can be found in Papoular *et al.*[2] In view of the consensus that seems to have now been reached as to the functional groups associated with the UIBs (see ref. 3 and comments by Bernstein and Papoular at this meeting), a carbonaceous dust could be viewed macroscopically as fluffy and porous. Microscopically, it should include (in various proportions, according to age and environment) conjugated aliphatic carbon chains and clusters of a few benzenic rings; the rings would be more or less hydrogenated and substituted with aliphatic groups and heteroatoms (O, N, S ...), and the clusters (graphenes) would be linked by oxygen bridges and more or less stacked together in turbostratic disorder. A schematic view of a model dust is presented by Papoular in a comment at this meeting. Such materials have been studied at length by coal and oil experts, and their behaviour under heat and chemical treatments is now well documented. Banks of typical materials ('standards') were established in the US and Europe.

Clearly, impinging atoms can react, with attached H atoms and recombine into a molecule which is then easily expelled, leaving behind a very reactive dangling bond.

[1] E. E. Salpeter, *Astrophys. J.*, 1974, **193**, 579; 585.

[2] R. Papoular, J. Conard, O. Guillors, I. Nenner, C. Reynaud and J-N. Rouzard, *Astron. Astrophys.*, 1996, **315**, 222.

[3] C. Joblin, *Faraday Discuss.*, 1998, **109**, 349.

Dr Ali commented: Professor Zare asked what the chemical composition and structure of interstellar dust is? I think the question is very timely and most appropriate. We yet do not have any single definitive answer to this. Mass return from cool high luminous red giants and supergiants, and more specifically from evolved thermally pulsing AGB stars, is probably the single most important source of interstellar primary dust. Physical and chemical evolution of these stellar ejecta in the interstellar medium is far from being understood. The chemical composition and structure of interstellar primary grains will have a strong influence on the physics of gas–grain interaction in the interstellar medium. The problem of heterogeneous nucleation or particle growth in return addresses a question: What does the surface of pertinent condensation nuclei look like? At best we could expect that condensation at low temperature would result in a disordered molecular surface in dense molecular clouds.

There is an uncertainty to a large extent in composition and structure of grains formed in stellar outflows. M-type stars: $C/O < 1$, oxygen-rich element composition which may form some kind of iron–magnesium–silicate dust in expanding circumstellar shells around the stars. C-type stars: $C/O > 1$, carbon-rich systems which may form amorphous carbon grains, perhaps the carbonaceous particles. We understand how gas phase small molecules are formed in interstellar clouds (see the papers by Lee and co-workers, and Smith *et al.* presented at this meeting). These are certainly going to add another dimension to our knowledge of formation of small molecules in space. Yet, there are no proper descriptions that take account of how dust grains are formed out of the small molecules in stellar outflows. A theory guided by laboratory experiments on nucleation: Cluster dynamics, coupled with future observations at an increased resolution in spectroscopy and interferometric imaging with fine spatial analysis of both scattered and emitted radiation from nucleation zone in circumstellar shells of evolved stars, would be able to decide the size distributions, chemical compositions and structures of grains formed. Inference on chemical and structural state of primary grains is crucial if we want to make further progress on chemical and physical evolution of interstellar dust.

A. K. Speck said: Many people ask what sort of grains should we be investigating. What are the grain surfaces where chemistry takes place? No one seems to have caught onto the fact that we can get the answers to these questions from meteorites. There are samples of interstellar dust in the form of SiC (see ref. 1), diamond and graphite[2] and even aluminium oxide[3] found in meteorites. From the isotopic studies it is clear that they are presolar. We can therefore study these grains in order to understand in detail which grains survive or are formed in the interstellar medium, and what sort of grain surfaces are available.

1 P. Hoppe and U. Ott, in *Astrophysical Implications of the Laboratory Study of Presolar Materials*, ed. T. Bernatowicz and E. Zinner, AIP Conference Proceedings, American Institute of Physics, New York, 1997.
2 E. Anders and E. Zinner *Meteoritics*, 1993, **28**, 490.
3 L. Nittler, C. M. O'D. Alexander, X. Gao, R. M. Walker and E. Zinner, *Astrophys J.*, 1997, **483**, 475.

Dr Ali responded: The isotopic composition of a few elements in some meterotic minerals, which is distinctly different from that in terrestrial samples, of course bears the unambiguous evidence of heterogeneity of the solar nebula. However, we do not have any clues as to what fraction of overall interstellar grain population constitutes such chemically distinct isotopically anomalous grains. The large degree of variations in cosmic abundances and physico-chemical conditions among various astrophysical objects lead to a question on the mechanism of formation of such grains (see the paper by Gail and Sedlmayr presented at this meeting) before passing a judgment based on isotopic anomalies in meteorites on the source medium where grains are formed. The presolar SiC has been astronomically observed and also graphite has been predicted in the interpretation of the hump at about 200 nm in the average interstellar extinction curve long before any meteoritic evidence of these grains.[1] There are some major problems that concern most of us here in our understanding of the chemical and physical evolution of interstellar 'primitive' dust and, most notably, what does the grain surface where chemistry occurs represent?

Immediate answers exist, while it is hard to justify that graphites and diamonds are dominant as interstellar grains from such arguments based on nucleosynthetic isotopic anomalies alone.

The ^{16}O enrichments in refractory calcium–aluminum inclusions (CAI) in meteorites have been interpreted in terms of presolar grains with a separate history of nucleosynthesis for more than twenty years of research.[2] An appeal was made that because chemical reactions could not produce such mass independent isotope effects, the observed oxygen isotopic anomalies are purely correlated with nuclear astrophysical processes in the source medium. Now that it is known that the dynamics of nonequilibrium chemical reactions could indeed produce mass-independent isotopic anomalies strikingly similar to that observed in ^{16}O-rich minerals in carbonaceous meteorites, it is no longer possible to accept the notion that the ^{16}O anomalies have always had a nuclear origin.[3] In the light of this current understanding, many of the ^{16}O-rich thermodynamically stable refractory phases such as corundum (Al_2O_3), spinel ($MgAl_2O_4$), *etc*., could be formed in the solar nebula by chemical processing and need not be considered as condensates in extrasolar system environments, though it was originally proposed.[4]

Consider a specific reaction in solar nebular environment such as $^{18}O + Si^{16}O \rightarrow O^{16}{=}Si{=}O^{18}$. The molecular symmetry induced stabilization of a non-symmetric refractory trimer through short-lived transition state during a collision event at a certain energy would extract ^{17}O and ^{18}O from the gas-phase reservoir containing all three oxygen isotopic systems *via* preferential reaction of the SiO dimer to form the $O^{16}{=}Si{=}O^{18}$ (or O^{17}) trimer. The end result would be a gas phase enriched in ^{16}O. Such an effect produces both positive and negative isotopic reservoirs and may account for the meteoritic O observations. Specific laboratory experiments would be required to demonstrate how symmetry could play a crucial role on the lifetimes of transition states during a chemical reaction event. The longer the transition states lifetimes, the greater the probability of stabilization [see ref. 3(*b*)]. If a chemically produced non-mass dependent oxygen isotopic fractionation does indeed occur in the presolar nebula, it establishes a direct link between observed refractory grains in meteorites with early solar system history. Oxide grains primarily corundum Al_2O_3 in primitive meteorites are recently reported to have a large excess of ^{17}O (rather than ^{16}O-rich) and a deficit of ^{18}O relative to solar system oxygen. From these unusual isotopic ratios and the presence of ^{26}Al in grains, it is conjectured that these grains are of circumstellar condensates from red giant and AGB stars. Many distinct nucleosynthetic sources with different masses and initial oxygen compositions were required to explain the range of isotopic differences.[5] However, it is far from clear how the thermodynamically stable mineralogical solids such as corundum (Al_2O_3), spinel ($MgAl_2O_4$), *etc*., emerge from gas phase species as stellar condensates. There is not yet any definitive laboratory experiment on the formation of grains with variations in cosmic abundances and appropriate physicochemical conditions. No one has ever proposed an *ab initio* predictive theory of how dust formation occurs based on basic chemical processes in circumstellar shells of evolved stars.

The study of isotopic anomalies and grain systematics in primitive meteorites is connected elsewhere both in testing models of nucleosynthesis and in the construction of models of origin and evolution of the solar system. However, it is important to recognize that cosmic dust complex is primarily a many component system, chemical details of which remain largely unknown. First, dust in stellar outflows: grains are not primitive. The molecule/solid phase transition, *i.e*., the formation of grains out of the gas phase

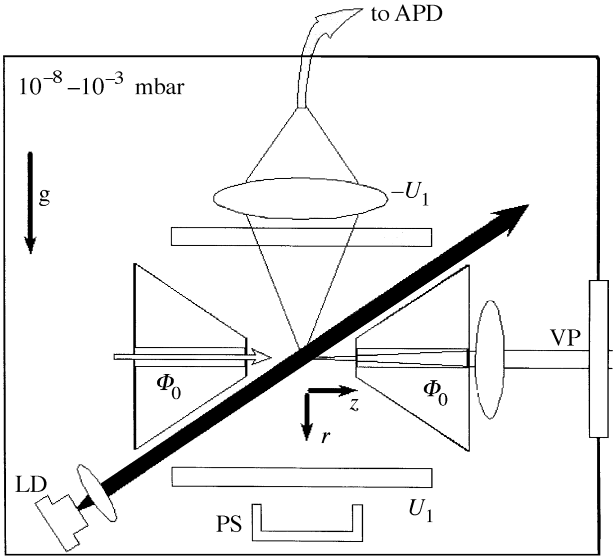

Fig. 10 Schematic view of the UHV Paul-type trap used for the non-destructive mass determination of individual nm-sized grains. APD: avalanche photo-diode, PS: particle source, VP: view port, LD: diode laser, $\Phi_0 = V\cos(\Omega_{\rm HF}t)$: applied potential (typically $V = 1$–2 kV, $\Omega_{\rm HF}/2\pi = 0.2$–$2$ kHz), U_1: gravitational compensation voltage ($U_1 = 0.40$ V).

atomic and molecular species. Second, dust in dense cool molecular clouds and in the diffuse interstellar medium: grain transformation and metamorphism, *i.e.*, the modification of existing primary dust by heterogeneous nucleation, sputtering and recondensation, coagulation, *etc.* Third, circumstellar dust around young stellar objects: largely fluffy and inhomogeneous aggregates. Structure and chemical composition of dust are expected to be different from those of dust in the diffuse medium and the circumstellar shells around evolved stars. Dust grains play an important role for both the spectral appearance and the thermal, dynamical, and chemical evolution of astrophysical objects. Chemistry of interstellar dust is one of the exciting fields of science and much remains to be learned from infrared observations, specific laboratory experiments, and theory on grain formation, as well as evolution by interstellar surface processes. We still need answers to a difficult question relating to physics of interstellar grain surfaces.[6]

1 T. Stecher and B. Donn., *Astrophys. J.*, 1965, **142**, 1682.
2 R. N. Clayton, L. Grossman and T. K. Mayeda, *Science*, 1973, **182**, 485.
3 (*a*) M. H. Thiemens and J. E. Heidenreich III, *Science*, 1983, **219**, 1073; (*b*) M. H. Thiemens, *Meteorites and the Early Solar System*, ed. J. F. Kerridge and M. S. Matthews, University of Arizona Press, Tuscson, AZ, 1988, p. 899.
4 D. D. Clayton, in *Cosmogonical Processes*, ed. W. D. Arnett, C. Hansen, J. Truran and S. Tsuruta, VNU Science, Utrecht, 1986, p. 101.
5 I. D. Hutcheon, G. R. Huss, A. J. Fahey and G. J. Wasserburg, *Astrophys. J.*, 1994, **425**, L97; G. R. Huss, A. J. Fahey, R. Gallino and G. J. Wasserburg, *Astrophys. J.*, 1994, **430**, L81.
6 V. Buch and J. P. Devlin in *Molecules in Astrophysics: Probes and Processes*, ed. E. F. van Dishoeck, IAU, Kluwer, Dordrecht, 1997, p. 321.

Dr Schlemmer commented: In the first two papers in this session and in the Introductory Lecture by Prof. Williams the importance of gas–grain interaction was pointed out as one of the key frontiers in astrophysical chemistry. At the Technical University of Chemnitz we have built a new apparatus to carry out experiments answering some of the questions raised in the papers mentioned. The basic idea of this experimental set-up is to investigate individual, single, charged nm-sized particles which can be stored very well localized in an electrodynamical trap over days. Fig. 10 shows a schematic view of the apparatus. It is a modified Paul-type trap[1] mounted in an ultra-high-vacuum

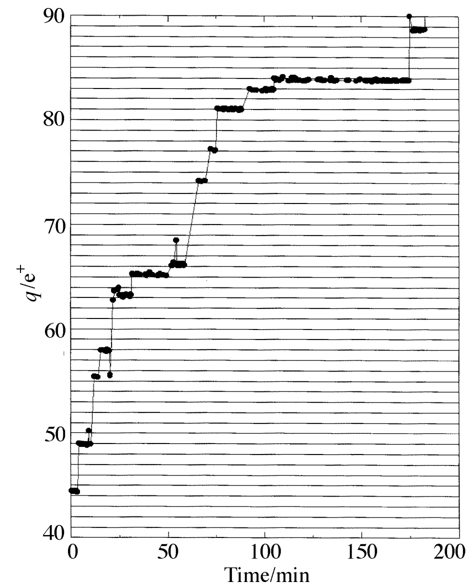

Fig. 11 Charge state of a single 500 nm diameter SiO_2 particle as a function of time

chamber. Test particles are 500 nm in diameter SiO_2 spheres. These particles are injected from the source (PS) into the trap. For injection the pressure is increased up to 10^{-3} mbar. Owing to collisions with residual gas, particles are decelerated into the effective potential of the electrodynamical trapping field. The apparatus will be described in detail in a forthcoming publication.[2] For continuous monitoring a diode laser (LD) is focused into the center of the trap. Scattered light from the particle is collected with a lens through a fibre and detected by an avalanche photo-diode (APD). The scattered light is modulated by the motion of the particle in the center of the trap. Due to the harmonic effective potential of the trap the modulation is characterized by two secular frequencies, ω_z for the particle's motion in the z-direction and ω_r for the particle's motion in the r-direction. These frequencies are proportional to the charge to mass ratio of the stored particle. They are extracted from the raw data by fast Fourier transform of the signal. By this method the particles charge to mass ratio can be followed over a long period of time with a current resolution of 3×10^{-4}. In a first experiment the particle's charge (mostly positive) has been changed with the aid of an electron gun. Due to the high resolution of the frequency measurement changing in steps of elementary charges can be observed. With this additional information the particle's charge and thus also its mass can be determined. Fig. 11 shows the charge state of a single particle with a mass of 2.4×10^{-16} kg as a function of time. This experiment demonstrates that a mass determination of single particles in a mass range of $< 10^{-16}$ kg has become possible. In the future this technique of non-destructive mass determination will be used to detect the adsorption and desorption from single nano-grains with the aim of determining sticking coefficients under conditions relevant to astrophysical chemistry.

[1] W. Paul, *Rev. Mod. Phys.*, 1990, **62**, 531 and references therein.

[2] S. Schlemmer, J. Illemann, S. Wellert and D. Gerlich, in preparation.

Prof. Herbst opened the Discussion of Dr Plume's paper: Your results indicate that the electron abundance in dense cloud cores is rather constant. Could you comment on the results of Caselli *et al.*,[1] which indicate a much wider range of electron abundances? These authors varied both ζ (the cosmic ray ionization rate) and elemental depletions.

[1] P. Caselli, C. M. Walmsley, R. Terzieva and E. Herbst, *Astrophys. J.*, 1998, **499**, 234.

Dr Plume responded: Our approach and that of Caselli *et al.* differed in the way that cosmic rays were handled. Caselli *et al.* varied the cosmic ray flux by two orders of magnitude, using the cosmic ray flux as a true variable in their model calculations (*i.e.* each core in their sample was fit with a different value). On the other hand, we only varied the cosmic ray flux to fit the entire sample. By constraining the gas temperature to a range of 8–20 K, we used the thermal balance model of Neufeld *et al.*[1] to limit the cosmic ray flux to a range of $1\text{–}15 \times 10^{-17}$ s^{-1}. A cosmic ray flux of 5×10^{-17} s^{-1} fit our sample of cores best. Therefore, in our subsequent modeling, we varied the density, temperature, and chemical abundances for each core individually, but held the cosmic ray flux constant at 5×10^{-17} s^{-1}. We feel that this is a more appropriate approach for our cores since they lie in similar regions of the Galaxy (the low-mass cores all lie within a few hundred parsecs of each other and the high-mass cores are all in Orion). Therefore, we believe there is no reason to assume that the cosmic ray flux changes significantly from core to core. Thus, it is only natural that our derived electron abundances show much less scatter than those in the paper as Caselli *et al.*, since we have removed a free parameter whose value can change by two orders of magnitude.

[1] D. A. Neufeld, S. Lepp and G. J. Melnick, *Astrophys. J. Suppl.*, 1995, **100**, 132.

Prof. van Dishoeck asked: In order to resolve the ambiguity in the modelling between varying the cosmic ray ionization rate or electron density, it helps to have observations of other ions in the same clouds, such as N_2H^+, HCS^+. Do you have data on any of these species, and are they consistent with the DCO^+/HCO^+ analysis?

Dr Bergin responded: In the low mass cores we have a sub-sample of eight cores in which we have reliable detections of optically thin N_2H^+ emission (opacities are estimated from the ratios of the hyperfine components). A comparison of the $H^{13}CO^+$ and N_2H^+ abundances demonstrates that the regions with low $H^{13}CO^+$ abundance (high electron fraction) also have low concentrations of N_2H^+. The opposite is true for sources with high $H^{13}CO^+$ abundance. Thus, for low mass cores the N_2H^+ data support our derived electron fractions, although the sample is not large. For high mass sources we have corresponding N_2H^+ observations for five cores. For this small sample the N_2H^+ abundance is also correlated with the $H^{13}CO^+$ abundance.

Dr Roueff commented: Fractional ionisation may not be uniquely determined from the DCO^+/HCO^+ ratio. The non-linear character of the chemical equation gives rise to possible multiple solutions reflecting the sensitivity of the system to the initial conditions.[1] Fig. 12 shows the evolution of the ionisation fraction for eight different initial conditions whereas Fig. 13 displays the ensemble of the steady state solutions for ξ/n_H ranging between 2×10^{-22} and 4×10^{-20} s^{-1} cm^3. The vertical line corresponds to Fig. 12. In which way can this complex behaviour be taken into account in the analysis discussed by Plume *et al.*?

[1] J. Le Bourlot, G. Pineau des Forèts and E. Roueff, *Astron. Astrophys.*, 1995, **297**, 251; H. H. Lee, E. Roueff *et al.*, *Astron. Astrophys.*, 1998, **334**, 1047.

Dr Bergin responded: We agree that complex bistable solutions discussed in ref. 1 have dramatic effects on the ionization fraction and, therefore, on the coupling between ion and neutrals in cloud cores. In our models we varied the abundances of metals, the cosmic ray ionization rate, the temperature, and the density. In all, over 1200 models were run to find the best match to the data. In no case was a bistable solution found, instead our results are consistent with the low ionization phase (LIP) solution.

[1] J. Le Bourlot, G. Pineau des Forêts and E. Roueff, *Astron. Astrophys.*, 1995, **297**, 251.

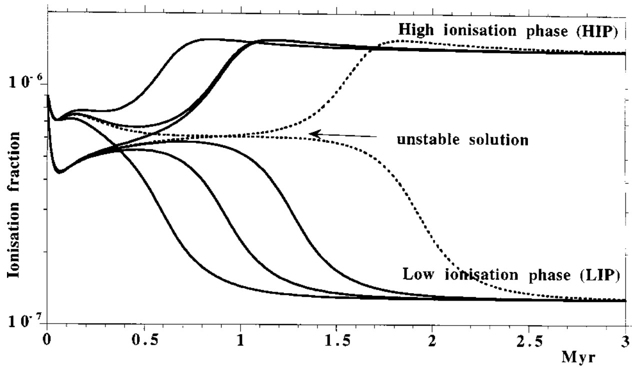

Fig. 12 Evolution with time of the ionisation fraction for $\zeta/n_H = 4 \times 10^{-21}$ s^{-1} cm^3. Eight evolution curves are displayed each one corresponding to different initial conditions.

Prof. Herbst commented: In addition to the work of Plume *et al.* on the ionisation fraction in dense cores, a paper by Caselli *et al.*[1] will shortly appear on the subject. In this paper, the subject of bistability is mentioned and the following statement made: 'We point out that the parameter range (and in particular the abundances for refractory species) studied by us has the consequence that our solutions are not in general affected by conditions of bistability'. The range of parameters in which bistability appears has been studied in great detail by Lee *et al.*[2] and normally involves higher gas-phase elemental abundances of sulfur than used in most dense cloud models.

[1] P. Caselli, C. M. Walmsley, R. Terzieva, and E. Herbst, *Astrophys. J.*, 1998, **499**, 234.

[2] H-H. Lee, E. Roueff, G. Pineau des Forêts, O. M. Shalabiea, R. Terzieva, and E. Herbst, *Astron. Astrophys.*, 1998, **334**, 1047.

Dr Roueff communicated: The sulfur elemental abundance is an open problem as mentioned by Prof. Williams in his Introductory Lecture. No definitive statement can thus be derived on the absence of bistability.

Dr Yates commented: One of the most difficult problems we face in molecular line astrophysics is converting the photons we collect to abundances. Most of the molecular Universe is not in local thermodynamic equilibrium (LTE) and molecular clouds or

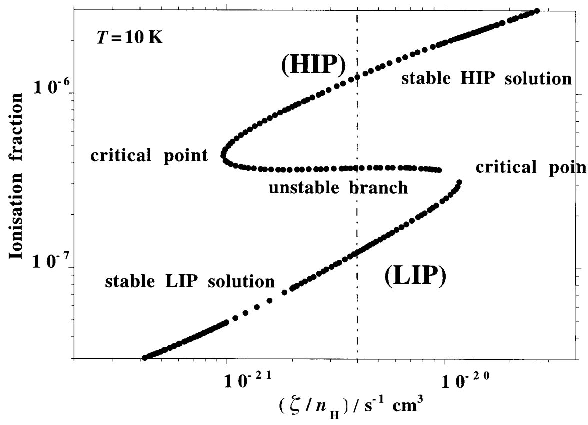

Fig. 13 Steady state values of the ionisation fraction as functions of ζ/n_H, the ratio of the cosmic ionisation ratio to proton density. Each point is a solution of the steady state equations. The ensemble of solutions displays a 'hysteresis curve'.

envelopes around stars are radiatively coupled over most or all of their spatial extent. This should preclude the use of approximations such as LTE or the large velocity approximation. The historical need for these approximations is noted, but there is no excuse for not using non-LTE radiation transport codes which are coupled to the kinetic master equations, to compute simulated spectra/maps for comparison with your observed data.

My question is therefore: What radiation transport methods were used in interpreting the observed data and why are they valid?

Dr Yates added: Using a spherical ALI code on a modern computer platform such as a Pentium 200-MHz machine one can compute a solution in minutes even if your observed data contains optically thick transitions as well as optically thin transitions. As an example see Fig. 14 which shows the computed line-shapes for HCO^+ emission from the protostar B335. The line-shapes show optically thick emission from the low lying J-state transitions and optically thinner emission from the high J-state transitions. Yet these spectra took 426 s to compute. A final plea: Would modellers please remember that dust continuum emission is a very important source of photons and opacity and should never be excluded from molecular line radiation transport calculations.

Prof. van Dishoeck commented: I fully agree with Dr Yates that a non-local thermal equilibrium (LTE), non-local radiative transfer code is essential for the analysis of (sub)millimeter data of molecules and the derivation of abundances. For this reason, we have developed a 1D and 2D Monte Carlo code,[1] which has been tested extensively against the code by Choi *et al.*[2] and is substantially faster. Comparison with your spherical ALI code would be very interesting as well. This new code will be used in all our subsequent analyses on molecular abundances, and excitation by far-infrared radiation due to warm dust will be included. In general, we derive abundances from optically thin lines, wherever available.

The situation for the near-infrared absorption lines presented in my paper is somewhat different from the case for millimeter lines discussed by Dr Yates. Here the analysis follows that commonly used for optical and ultraviolet absorption lines. Because of the low spectral resolving power of the ISO spectrometers, the lines are unresolved and a curve-of-growth method or profile synthesis analysis must be used. The latter method requires specification of the Doppler parameter (constrained by higher resolution ground-based CO data), the spectral resolution, the total column density of the molecule and the populations in each of the rotational energy levels of the lowest vibrational state. In first approximation, these are indeed assumed to be in LTE because of the high temperatures and densities in the regions, but they could be further refined using the Monte Carlo program discussed above to obtain non-LTE values. This will indeed be the next step in our analysis. At the current signal-to-noise level of the data, however, no major departures from LTE are observed, so that the column densities for the warm gas component should be reliable within the quoted errors of typically a factor of two. Note also that most infrared lines of *e.g.* H_2O and CO_2 for the warm component are not very optically thick, except those arising from the lowest rotational energy levels.

[1] M. R. Hogerheijde, PhD Thesis, University of Leiden, 1998.

[2] M. Choi, N. J. Evans, E. M. Gregersen and Y. Wang, *Astrophys. J.*, 1995, **448**, 742.

Dr Hatchell commented: In calculating the excitation conditions we have assumed a homogeneous slab in local thermal equilibrium (LTE). For most molecules the assumption of LTE is reasonable at the high densities of these cores (10^5–10^9 cm^{-3}). It would be nice to use a radiative transfer approach to unravel the temperature/density gradients in the cores. This may be possible for some of the simpler species but unfortunately for

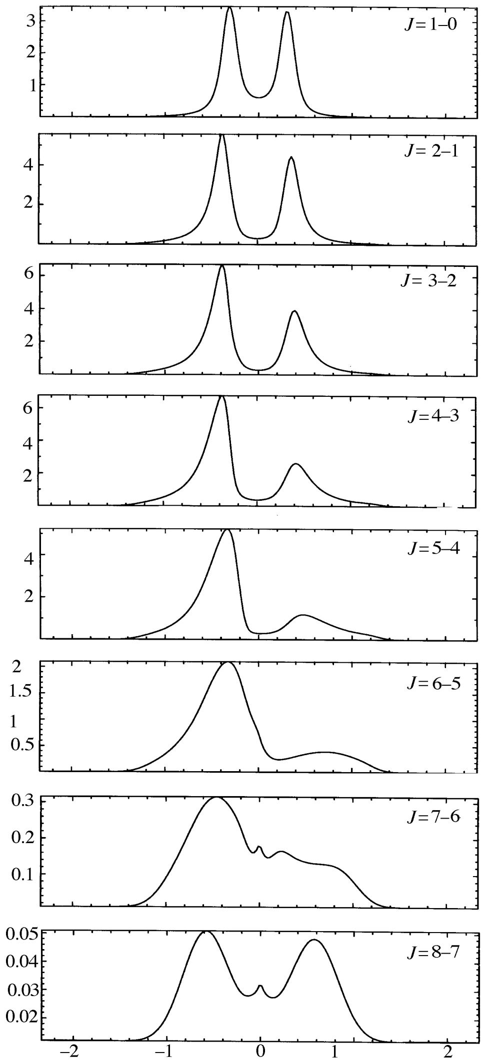

Fig. 14 Simulated multi-transition spectrum of the HCO^+ emission from the protostar B335. The first eight rotational transitions are shown here. The intensities are given as JCMT antenna temperatures assuming a dish efficiency of 0.6. The velocities are in km s^{-1}. The physical model was kindly provided by Neal Evans (Austin, Texas).

more complex molecules such as CH_3OH, which should give the most information on the excitation, the collision cross-sections are not known.

Dr Plume responded: For $C^{18}O$, DCO^+, and $H^{13}CO^+$ we used a simple optically thin LTE approach. This is likely true for $C^{18}O$ (due to its low isotopic abundance and the small critical density of this transition) but, to test this assumption for DCO^+ and $H^{13}CO^+$, we also observed the rarer isotopes of $D^{13}CO^+$ and $HC^{18}O^+$ in a small sub-sample of our cores. Comparing the isotopic lines ratios suggested that the opacities were less than unity for DCO^+ and $H^{13}CO^+$. We, therefore, assumed it to be true for all of our cores. To account for deviations from LTE due to the low densities used in our model calculations, we used a statistical equilibrium calculation to correct the LTE derived column densities. For CS, however, we used a large velocity gradient (LVG) model to calculate the coupled equations of radiative transfer and statistical equilibrium.

I agree that the more sophisticated Monte Carlo and accelerated lambda iteration techniques are better able to model the radiative transfer through clouds with realistic physical conditions. We are working on our own versions of these codes at the Harvard–Smithsonian Center for Astrophysics. I would like to point out, however, that the radiative transfer is only crucial if the opacities are large, and our supplementary data indicates that they are likely to be quite small. Additionally, since the observed spectral lines were weak (making a meaningful line-shape comparison between the observations and the models difficult) and the physical model for the cores (*e.g.* density and temperature profile) is unknown, we feel that our approach is justified.

Prof. Irvine asked Dr Rowe: In your paper you mention plans to carry out experiments with substituted PAHs. I wonder whether any such experiments have yet been made?

Dr Rowe responded: A heated nozzle is currently being developed and once this is in operation and characterised, experiments on other condensable species such as substituted PAHs will commence. This should be in the next few months.

Prof. Sarre said: The experimental study of electron attachment to substituted PAHs would be interesting, especially for those neutral molecules with large electric dipole moments which can support dipole-bound states of the molecular anions. These dipole-bound excited states could also be important in the calculation of radiative association rates.

Dr Rowe responded: This is a very interesting suggestion and we shall bear it in mind in planning our future experimental programme.

Prof. Clary commented: A molecule with a dipole moment larger than 2.5 D can form an 'electron-dipole bound state' in which the geometry and rotational constants of the molecular anion are almost the same as the parent molecule.[1] Over 30 such dipole bound anions have now been observed for systems ranging from acetone to uracil.[2] These anions have very small electron ionisation potentials (typically less than 50 meV). The rotational spectra of these anions will be almost identical to the parent neutral molecules and vibrational excitation will normally dissociate the weakly bound electron. Therefore, detection of these anions in the interstellar medium through their emission spectra is likely to be difficult, even if there are conditions that enable them to be formed.

1 D. C. Clary, *J. Phys. Chem.*, 1998, **92**, 3123.
2 C. Defrancois, H. Abdoul-Carime and J-P. Schermann, *Int. J. Mod. Phys. B*, 1996, **10**, 1339.

Prof. Herbst commented: The existence of excited electronic states of negative molecular ions can indeed increase calculated rates of radiative attachment if the excited states are connected by dipole transitions to the ground state. A theory concerning the amount of enhancement to be expected for the analogous process of radiative association has been published by Herbst and Bates.[1]

In the standard mechanism for radiative attachment and radiative association, a complex is formed which can only be stabilized by the emission of vibrational (infrared) photons. The existence of bound electronic excited states permits stabilization by the emission of electronic (visible, ultraviolet) photons, which is generally far more rapid although Franck–Condon effects have to be considered. We propose to undertake calculations on the radiative attachment of electrons to bare carbon chains (*e.g.* $e^- + C_7 \rightarrow C_7^-$) since the negative ions are known to possess bound excited electronic states.

[1] E. Herbst and D. R. Bates, *Astrophys. J.*, 1988, **329**, 410.

Prof. Herbst added: We have used a statistical theory of radiative attachment reactions to calculate rates of such reactions involving small radicals with large electron affinities. In general, results for reactions such as $C_3N + e^- \rightarrow C_3N^- + h\nu$ show that abundances of small negative molecular ions in interstellar clouds are small. The electron-controlled catalytic reaction $1\text{-}C_3H + e^- \rightarrow 1\text{-}C_3H^- \rightarrow c\text{-}C_3H^- \rightarrow c\text{-}C_3H + e^-$ may be important in regulating the isomeric balance between 1-C_3H and c-C_3H in dense clouds.[1]

[1] S. Petrie and E. Herbst, *Astrophys. J.*, 1997, **491**, 210.

Prof. Zare asked: What might be the role of dissociative electron attachment in generating negative ions? How important might this process be as a function of the state of internal excitation of the target?

Prof. Herbst responded: In cool molecular clouds, the kinetic energy distribution of the electrons is nearly thermal. Under these conditions, dissociative attachment must be exothermic to be rapid. This condition implies that the electron affinity of the negative ion product must be greater than the bond energy of the bond being broken. Although some such reactions[1] have been suggested to occur in the low temperature interstellar medium and/or circumstellar envelopes: *viz.*, $MgCN + e^- \rightarrow CN^- + Mg$, they do not appear to produce copious quantities of negative ions. In regions where the electrons possess a significant amount of kinetic energy, then dissociative attachment will undoubtedly be more important especially if the targets are internally excited.

[1] S. Petrie, *Mon. Not. R. Astron. Soc.*, 1996, **282**, 807.

Prof. Field commented: Dissociative attachment may in principle be of importance in the ISM. Many small species, such as H_2 or CO_2, undergo electron attachment *via* a shape resonance at a few eV electron energy, resulting in decay either to negative ion products (H^- or O^- for example) or in vibrational excitation of the target. Cross-sections tend however to be rather small, especially for H_2.

Prof. Field added: May I take the opportunity to complement the excellent CRESU data from Rennes with data of our own, which corroborates the electron attaching behaviour of PAHs. We have an experiment, working on the ASTRID synchroton at ISA Aarhus and the Daresbury Synchrotron Radiation source which allows us to form electron beams down to a few meV energy with a few meV energy resolution. Data, which are shown in Fig. 15, demonstrate that electrons are very strongly scattered out of the incident beam as they pass, in this case, through naphthalene vapour. Cross-sections are several hundred Å^2 at 10–20 meV electron energy. Scattering events are very likely due to electron attachment. Further details may be found in a paper shortly to appear[1] showing similar behaviour in benzene. We have similar data for a number of PAHs.

[1] R. J. Gulley, S. L. Lunt, J-P. Ziesel and D. Field, *J. Phys. B.*, 1998, **31**, 2735.

Prof. Smith said: The cross-sections for electron capture by naphthalene shown by Prof. Field exhibit a strong decrease with collision energy. Could he comment on the expected temperature dependence of the corresponding rate coefficients in the light of the result of Rowe and his co-workers of a temperature independent rate coefficient in the case of anthracene?

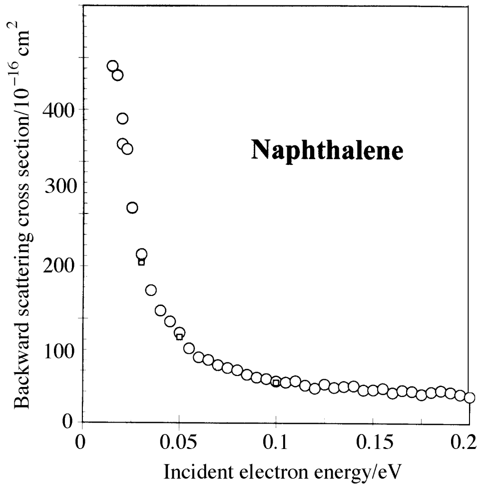

Fig. 15 Variation of the backward scattering cross-section for scattering of electrons by naphthalene as a function of electron impact energy.

Prof. Field replied: We do indeed find that the cross-section drops quite sharply in higher energy collisions between electrons and naphthalene. Of course we are looking at a temporary attachment process. The lifetime of the negative ion is however certainly increasing as the electron impact energy drops. The data of Rowe and co-workers involves the measurement of a third order rate coefficient as a function of temperature. In the low pressure limit, of true third order, the behaviour of this rate coefficient should indeed reflect the lifetime of the anthracene negative ion (in this case). Therefore one might expect the third order rate coefficient to rise at very low temperatures. There are two points to consider however. Is it certain that the data of Rowe are in the third order limiting region? (This is a question, not a statement!) Also bulk data do need to be convoluted with the thermal spread, of course. I would therefore not say at this stage that there is a clear discrepancy here, but we should certainly look into it.

The Chairman then invited discussion on any of the papers in the afternoon session and on the Introductory Lecture.

Prof. Zare said to Prof. Williams: I would like to encourage you to sharpen your definitions of astrochemistry. In your talk you defined astrochemistry as the intersection of observations, processes, and modeling. What difference is there in your mind between astrophysics, astrochemistry and astrobiology? Is that difference an important one?

Prof. Williams responded: Yes, in my own mind I do make a distinction between astrophysics and astrochemistry. In astrophysics, I regard the emphasis as being on using models to determine astronomical parameters such as density, temperature, mass, dynamics etc. In astrochemistry, I regard the emphasis as being on anything to do with molecules. The two do not entirely overlap. Astrobiology is surely an extension of both, but there must be a great deal of commonality between the three.

Prof. Vidali said: I would like to make a few comments about the experimental results mentioned in Prof. William's Introductory Lecture. We have built an apparatus to study hydrogen recombination reactions on surfaces in astronomically relevant conditions. Experiments were conducted using two low energy hydrogen and deuterium atomic beams impinging on a sample kept at 6–20 K in an ultra-high vacuum chamber. Our main results are: (1) Recombination kinetics depend quadratically on reactant concentration at low coverage. (2) Mobility is dominated by thermally activated processes.

Based on these results, we propose a model consisting of a set of rate equations for the recombination of hydrogen in different astrophysical environments.[1] The results quoted by Prof. Williams[2] were for an olivine natural polycrystalline sample. Qualitatively similar results are found for a sample of amorphous carbon.[3] The evidence is strong that thermal activation is the primary agent for diffusion of H and D atoms. A somewhat longer recombination efficiency is seen for amorphous carbon with respect to olivine.

[1] O. Biham, I. Furman, N. Katz, V. Pirronello and G. Vidali, *Mon. Not. R. Astron. Soc.*, 1998, **296**, 869.

[2] V. Pirronello, O. Biham, C. Liu, L. Shen and G. Vidali, *Astrophys. J.*, 1997, **483**, L131; V. Pirronello, C. Liu, L. Shen and G. Vidali, *Astrophys. J.*, 1997, **475**, L69.

[3] V. Pirronello, J. Roser and G. Vidali, in preparation.

Prof. Bréchignac commented: Prof. Williams in his lecture has addressed the problem of the formation of molecular hydrogen at the surface of grains, pointing out the experimental efforts being made in London, as well as the results on the recombination efficiency obtained in Syracuse (USA) by Professor Vidali and his co-workers. He has shown some results of theoretical simulations for the case of an H_2O-ice surface by Takahashi *et al.*, and of preliminary quantum calculations for the case of a graphite surface in Prof. Clary's group. In both cases the vibrational distribution of the newly formed molecule seems to peak at some vibrational quantum number of the order of 3 to 4. He also mentioned the poster by Dr Parneix and myself presenting the results of classical trajectory simulations for the recombination of a graphite surface. Since our results for the vibrational distribution seem to differ from those, I wish to tell you more about what we did.[1]

We used a model potential energy surface for both the sticking of a single H atom to the graphite surface, considered as a rigid hexagonal pavement of C atoms, and the reactive part when a second H atom approaches. The model was adjusted on some available *ab initio* data for particular geometries. The Eley–Rideal process, *i.e.* the reactive collision between an atom from the gas phase and a previously chemisorbed atom

$$H + S{-}H \rightarrow H_2 + S$$

was simulated by running classical trajectories on this potential energy surface. Statistical averages were done over a large number of trajectories probing all the possible initial conditions. The results have been analysed, as a function of the collision energy

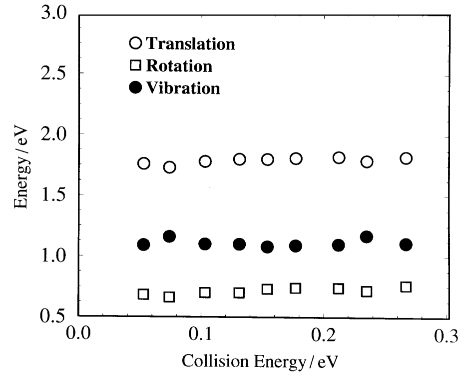

Fig. 16 Ensemble averages of the translational, vibrational and rotational energies of the H_2 molecule as a function of the initial collision energy of the impinging H atom

(gas phase temperature) and of the initial coverage of the surface, for the efficiency (reaction probability), the distribution of the excess energy among the various degrees of freedom, and some observables which could be measured experimentally such as the angular distribution.

The efficiency of the reaction has been found to be large (probability ranging from 0.3 to 0.6 in case of a 5% coverage) with a threshold in collision energy associated to the presence of a small barrier in the potential surface. It grows up to saturation as the coverage is increased. Fig. 16 shows the partitioning of the excess energy in the different degrees of freedom of the nascent H_2 molecule. Clearly the distribution is almost independent of the collision energy, which is consistent with the fact that most of the available energy comes from the binding energy of the H_2 molecule. About 50% of the energy is transferred into the translation of the ejected molecule, which, in astrophysical conditions, must have an effect in the heating of the interstellar gas. About 20% of the energy is found in excited rotational states (peaking near $J = 10$ or more), which may have a spectroscopic importance for the comparison with either experiment or astrophysical observations. The remaining 30% is found in vibrational excitation.

The relative vibrational population distribution is shown in Fig. 17. Excitation up to the level $v = 6$ is observed, but with a smoothly decreasing distribution, and no sign of any inversion. However, I should mention that we have investigated the effect of a little change in the shape of the potential energy surface. Although no dramatic change was found, an effect was seen on the vibrational distribution. Then these results on the vibrational distribution of H_2 formed by recombination of H atoms at a graphite surface seem very different from the ones obtained by Prof. Clary. Many points seem to differ in the two approaches (the potential energy surface, the restricted geometry, the quantum/classical treatment of the dynamics), which will have, in view of the strong astrophysical interest of the process, to be considered in order to clear up possible discrepancies. It may be the beginning of a debate around this question, on the theoretical expectations first, with the hope that the experiment will help to approach the physical reality, for the best of astrochemistry.

1 P. Parneix and Ph. Bréchignac, *Astron. Astrophys.*, 1998, **334**, 363.

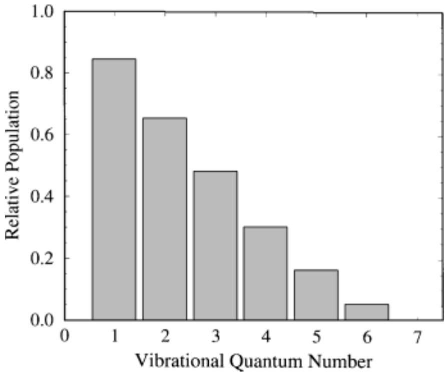

Fig. 17 Vibrational population distribution of the newly formed H_2 molecule, relative to the population in $v = 0$