Faraday Discuss., 1998, **109**, 493–516

General Discussion

The Chairman introduced the last session of the Discussion by commenting that it was hoped it would prove possible to draw many topics together and, in particular, to explore planetary–interstellar connections.

Prof. Irvine began the discussion by asking: Would Prof. Zare tell us about the status of searches for organic material in other Martian meteorites and about the prospects for carbon isotope measurements of such organics.

Prof. Zare and **Dr Clemett** replied: The search for indigenous organic material in two other Martian meteorites, EETA79001 and Nakhla, is actively underway by both ourselves and other researchers. The C isotopic measurement of such organics ultimately provides the strongest evidence of an indigenous *vs.* terrestrial origin. Unfortunately, molecule–specific isotopic measurements are complex due to the limited sample material and the low concentrations of organic material. Nevertheless we note, we have already been able to demonstrate successfully the application of molecule-specific C isotope measurements to the analysis of interstellar graphite grains isolated from the Murchison (CM2) meteorite.[1]

[1] S. Messenger, S. Amari, X. Gao, R. M. Walker, S. J. Clemett, X. D. F. Chillier, R. N. Zare and R. S. Lewis, *Astrophys. J.*, 1998, **502**, in press.

Prof. Pillinger commented: Carbon isotope measurements have already been made by the Open University on material recognised as organic by virtue of its low temperature of combustion. Unfortunately the values do not distinguish terrestrial from martian sources.

Prof. Sedlmayr introduced discussion of Prof. Pillinger's paper: Krueger *et al.*[1] have shown that under certain conditions in the pressure–temperature plane preferentially sp^3 dangling bonds are formed by hydrogen abstraction from hydrogen covered graphitic surfaces. This could possibly be a key to micro-diamond formation.

[1] D. Krüger, A. B. C. Patzer and E. Sedlmayr, *Astron. Astrophys.*, 1996, **313**, 891.

Prof. Pillinger responded: It should be appreciated that our diamonds are nano rather than micro, therefore, the mechanisms of chemical vapour deposition are indeed applicable. This means that if the diamonds are produced in a stellar environment as we imagine they are then hydrogen will be available to etch away co-produced graphite.

Dr Ehrenfreund commented: In Prof. Zare's paper the controversy about the extraterrestrial origin of PAHs in the Martian meteorite ALH84001 has been extensively discussed and it was concluded that contaminations are negligible. A search for endogenous amino acids in Martian Meteorite ALH84001 indicated that those amino acids appear to be terrestrial in origin.[1] What is the evidence here against terrestrial contamination and how is this result connected to the origin of the PAHs?

[1] J. L. Bada, D. P. Glavin, G. D. McDonald and L. Becker, *Science*, 1998, **279**, 362.

Prof. Zare and **Dr Clemett** responded: Recent measurement of water-soluble amino acids by Bada *et al.*[1] in ALH84001 demonstrated the presence of trace amounts of glycine, serine and alanine in concentrations ranging from 0.1 to 7 ppm. They argue that these are terrestrial contaminants based on three observations: (1) no nonprotein α-amino acids such as α-amino isobutyric acid (AIB) were observed in contrast to in the carbonaceous chondrite Murchison (CM2) in which AIB is abundant; (2) the observed amino acids are similar to the distribution Bada *et al.*[1] find in Antarctic meltwater from the Allan Hills region; and (3) the predominant enantiomer observed was 'L'.

The results of Bada *et al.*[1] need to be interpreted with some caution. Firstly, their acid treatment, which was designed to dissolve only carbonate minerals, dissolved 20% of their carbonate-free sample of lunar rock. Therefore it is unclear what actually dissolved and how this might influence their conclusions. Secondly, their acid treatment appears to have increased the masses of their samples. In the treatment of their sample 2, the initial mass of rock is listed at 463 mg, yet the total mass of the three extracts they prepare from this sample is 472.5 mg. We wonder what this extra mass is and whether it could represent a source of laboratory amino acid contamination. This question is particularly relevant in light of the 'serpentine blanks' they concurrently ran with ALH84001, which in at least one case had a higher concentration of amino acids than on ALH84001, with the dominant amino acids being identical in both cases. Nevertheless, amino acids are considerably more soluble than the PAHs we studied (see Fig. 1A) and therefore their transport into this meteorite would be more facile.

We wish to emphasize that our study concerns the indigeneity of PAHs in ALH84001, for which PAHs represent a hydrophobic, more refractory organic phase, constituting less than 1% of the total organic content of this meteorite.[2] In this regard we take this opportunity to present additional data supporting the claim that these PAHs are found inhomogeneously in the meteorite, being particularly concentrated in the rims of the carbonate globules. The globule is approximately 250 μm in diameter, which should be compared to the laser desorption spot size of less than 40 μm in diameter. Fig. 1B shows a two-step laser desorption/laser ionization mass spectrum taken on a fresh cleaved fracture of ALH84001 containing a single large carbonate globule. Three regions of the surface were analyzed: (1) a region exterior to the carbonate globule consisting primarily of orthopyroxenite, which is the dominant mineral phase in the meteorite; (2) a region located on the carbonate rim; and (3) a region inside the carbonate globule. The highest concentration of PAHs occur in the carbonate rim and this

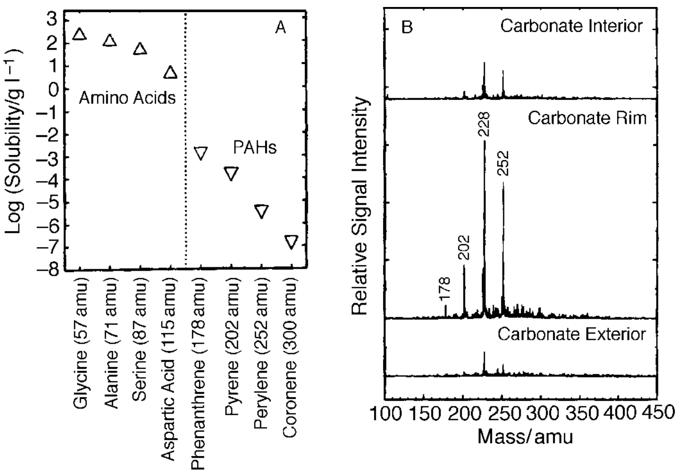

Fig. 1 A, Solubility (g l^{-1} at 25 °C) comparison between the 'terrestrial' amino acids observed by Bada *et al.*[1] in ALH84001 and the PAHs observed by McKay *et al.* in ALH84001. B, Three PAH spectra from a fresh cleaved interior (> 1 cm) chip of ALH84001 containing a single large carbonate globule.

concentration is seven times larger than that found external to the carbonate rim. Once again these findings are inconsistent with the hypothesis of terrestrial contamination.

[1] J. L. Bada, D. P. Glavin, G. D. McDonald and L. Becker, *Science*, 1998, **279**, 362.

[2] D. S. McKay, E. K. Gibson, Jr., K. L. Thomas-Keprta, H. Vali, C. S. Romanek, S. J. Clemett, X. D. F. Chillier, C. R. Maechling and R. N. Zare, *Science*, 1996, **273**, 924.

Prof. Pillinger commented: The amounts of contamination considered by the amino acid analyses are minute *ca.* 1 ppm or less. Some samples of Martian meterorites contain amounts of organic carbon up to 1000 ppm which cannot have been added by the mechanism proposed for amino acids.

Prof. Sarre said: Diamonds with impurities such as nitrogen have optical absorption lines with very well characterised wavelengths and widths. I would like to ask what role optical spectroscopy might play in the analysis of meteoritic samples, and, possibly, in the detection of small diamonds in circumstellar or interstellar environments.

Prof. Pillinger responded: Some work has been done in this area. However, there is clear potential for using meteroritic diamonds as laboratory analogues to guide further studies.

Dr Leach asked: (1) Has microRaman spectroscopy been used to analyse the sp^2/sp^3 carbon content, and its spatial variation in meteoritic materials? (2) Fluorescence spectroscopy should be a good technique for studying meteoritic diamonds. Doped diamond fluorescence studies have been made for many years and permit characterization of diamond materials and their inclusions.

Prof. Pillinger responded: As far as I know Raman has not been used in this context but the diamonds are isolated by techniques which eliminate sp^2 type bonding; graphite is destroyed by perchloric acid. There have been studies of diamonds for trace elements but these were by solid source mass spectrometry. Of course the most abundant trace elements investigated are N and the noble gases (the latter which have no spectral characteristics) using mass spectrometry.

A. K. Speck said: I have two questions. The first is a general enquiry to everyone regarding the nature of diamonds. Spectra have been obtained from meteoritic diamonds and synthetic analogues.[1–5] These are not spectra related to the nitrogen impurities in these grains discussed by Prof. Sarre, however they do exist and therefore we should be able to use them to find evidence of diamonds in interstellar and circumstellar observations. In order to do this, I would like to know what environmental factors are necessary for the diamonds to produce absorptions and emissions. For instance, they do not absorb a great deal in the visible light, so do they need an ultraviolet source in order to produce infrared emission spectra? If this is the case, detecting them around carbon stars will problematic even if they are abundant. I would also like to address a question to Prof. Pillinger. One of the published diamond spectra includes a model for the formation of diamonds around carbon stars.[5] Could you tell me which specific stellar sources for meteoritic diamonds are implied from your isotopic studies, and whether carbon stars are likely formation sites?

[1] R. S. Lewis, E. Anders and B. T. Draine, *Nature* (*London*) 1989, **399**, 117.

[2] C. Koike, N. C. Wickramasinghe, N. Kano, K. Yamakoshi, T. Yamamoto, C. Kaito, S. Kimura and H. Okuda, *Mon. Not. R. Astron. Soc.*, 1995, **277**, 986.

[3] H. Mutschke, J. Dorschner, Th. Henning and C. Jäger, *Astrophys. J. Lett.* 1995, **454**, L157.

[4] H. G. M. Hill, L. B. D'Hendecourt, C. Perron and A. P. Jones, *Meteoritics Planet. Sci.*, 1997, **32**, 713.

[5] A. C. Andersen, U. G. Jørgensen, F. M. Nicolaisen, P. G. Sørensen and K. Glejbol, *Astron. Astrophys.*, 1998, **330**, 1080.

Prof. Pillinger responded: Type II supernovae are the suggested source. The paper already includes a reference to our work by Clayton *et al.*, 1995.

Prof. Papoular asked: What is the compostional and structural data behind the term 'diamonds' in relation to meteorites? What is the size range of these diamonds? What are the observed types of hybridization?

Prof. Pillinger responded: The structure of diamonds has been identified by diffraction patterns. Their size is very small < 2 nm (the text of the paper has much discussion on this point). We have recognised the diffraction patterns of chaoite believed by some to be sp hybridization.

Prof. Irvine said: Would Dr Crovisier comment on the significance of the water *ortho*/*para* ratio in comets?

Dr Crovisier responded: This topic is already discussed in my paper. Since this paper was written, ISO observed comet 103P/Hartley 2 (ref. 1), which is a short-period, Jupiter-family comet which presumably migrated from the Kuiper–Edgeworth belt. The first analysis of the water spectrum of this comet gives an *ortho*-to-*para* ratio of *ca.* 2.7, corresponding to a spin temperature of *ca.* 35 K. This shows that low spin temperatures are common in comets, whatever their origin and history.

[1] J. Crovisier *et al.*, *XXIIIth EGS General Assembly*, Nice, 1998, poster presentation.

Dr Vigasin said: I would like to comment on the *ortho*-to-*para* ratio of water molecules. It has been well established that *ortho*- and *para*-water molecules possess different associative abilities. In other words *ortho* and *para* molecules condense with various rates. For instance, in laboratory controlled supersonic jet expansions *ortho*-enriched liquid water can be readily prepared *via* the spin-selective condensation effect.

Dr Crovisier responded: It will be important to consider such fractionation processes when trying to understand the water *ortho*-to-*para* ratios observed in comets.

Prof. van Dishoeck said: The question was asked as to whether there are any observational data on the *ortho*-to-*para* ratio of H_2O in interstellar clouds. This gives me an opportunity to present our recent ISO SWS full grating scan of the Orion BN/KL region.[1] The aperture was centered near IRc2, and includes both the hot core, low-velocity plateau and quiescent ridge gas. A wealth of emission and absorption features is found, (see Fig. 2) including H_2 vibration–rotation lines, the full set of H_2 pure rotational lines (0,0) S(1)–S(17), H recombination lines, ionic fine-structure lines, PAH emission features, and absorption and emission bands by interstellar ices and gas-phase molecules, including CO_2, CH_4 and SO_2. Particularly relevant for this discussion is the detection of strong emission and absorption lines in the H_2O ν_2 bending mode at 6.2 μm, and the observation of highly excited pure rotational lines of H_2O in absorption at 25–45 μm. Fabry–Perot observations of several of the pure rotational lines of both *ortho*- and *para*-H_2O have been obtained by Wright *et al.*[2] The line profiles are resolved so that accurate optical depths can be measured. Initial analysis indicates an *ortho*-to-*para* ratio consistent with the high-temperature limit of 3, but more detailed modelling including pumping by infrared radiation is needed.

[1] E. F. van Dishoeck, C. M. Wright, J. Cernicharo, E. Gonz'alez-Alfonso, Th. de Graauw, F. P. Helmich and B. Vandenbussche, *Astrophys. J.*, 1998, **502**, L173.

[2] C. M. Wright, E. F. van Dishoeck, H. Feuchtgruber, J. Cernicharo, E. Gonz'alez-Alfonso and Th. de Graauw, in preparation.

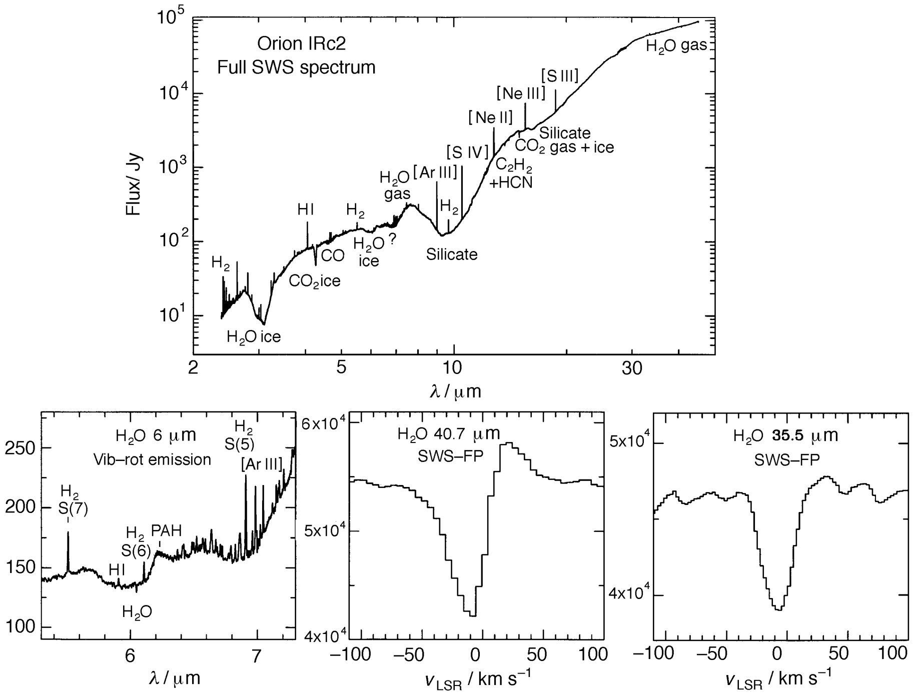

Fig. 2 The top panel shows the ISO–SWS grating spectrum of Orion-IRc2. The left bottom panel shows a blow-up of the H_2O ν_2 6 μm band seen in emission. The middle and right bottom panels show Fabry–Perot observations of the *o*-H_2O 4_{32}–3_{03} 40.7 and *p*-H_2O 5_{33}–4_{04} 35.5 μm pure rotational lines (reproduced with permission from ref. 1).

Dr Ehrenfreund asked: For abundance calculations of cometary volatiles as well as for interstellar ices the abundances of all other species are calculated relative to water. However the production rates of water seem to be very difficult to establish in comets, since only indirect measurements can be made. For interstellar water ice we have very accurate measurements as well as for other ice species, because the cross sections can be measured in the laboratory. How could this problem to achieve a correct water production rate influence the abundance scale and the comparison with interstellar ice abundances?

Dr Crovisier responded: Cometary water production rates derived from different methods may differ by as much as a factor of two or so. I believe that these discrepancies could be significantly reduced in the near future by improving cometary models as well as from better known molecular data. To achieve this goal, an investigation, coordinated by Prof. W. F. Huebner, has been requested by IAU Commission 15.

As for other cometary species, the abundances reported in Table 1 of my paper are probably known to much better than an order of magnitude (to be conservative). Most of them are based upon preliminary reports from the observers of comet Hale–Bopp. They will also be improved in the near future when fully reduced observations will be available, using consistent cometary models.

On the other hand, I am not so sure that the prospect is really better for the determination of abundances in interstellar ices. Whereas cross sections from laboratory measurement of ices could be precisely known, it is likely that interstellar ices are much more complex than laboratory analogues, yielding blended spectral patterns difficult to interpret. The situation is different from the gas phase where individual rotational or ro-vibrational lines may be resolved, unambiguously identified and measured.

Prof. Bernath said: In response to the question 'what is the situation with respect to the intensities of water lines', for most astronomical applications involving the relatively cool objects observed by ISO, the available line positions and intensities for water are adequate. They can most conveniently be found in the HITRAN 96 database.[1] For relatively hot water (in excess of 1000 K) as found in stellar atmospheres and sunspots as well as for a near infrared band seen in emission from Comet Hale–Bopp,[2] the situation is not so favourable. We have measured and assigned a large number of hot water lines in laboratory emission spectra and in sunspot absorption spectra,[3–4] including the $\nu_1 + \nu_2 + \nu_3 - \nu_1$ hot band[5] seen in Hale–Bopp. The intensities of these lines, however, are probably best derived by calculation using a high quality *ab initio* dipole moment surface.[6]

1 L. S. Rothman, *et al.*, *J. Quant. Spectros. Radiat. Transfer*, 1998, in press.
2 J. Crovisier, *Faraday Discuss.*, 1998, **109**, 437.
3 L. Wallace, P. Bernath, W. Livingston, K. Hinkle, J. Busler, B. Guo and K-Q. Zhang, *Science*, 1995, **268**, 1155.
4 O. L. Polyansky, N. F. Zobov, S. Viti, J. Tennyson, P. F. Bernath and L. Wallace, *Science*, 1997, **277**, 346.
5 O. L. Polyansky, N. F. Zobov, S. Viti, J. Tennyson, P. F. Bernath and L. Wallace, *Astrophys. J. Lett.*, 1997, **489**, L205.
6 J. Tennyson, personal communication.

Dr Crovisier responded: The HITRAN and GEISA[1] databases are a convenient and appreciated source for modelling infrared spectra of comets. However, they do not yet contain the $\nu_1 + \nu_2 + \nu_3 - \nu_1$ band of water nor several other hot bands which are now of interest for comets. I learned at this meeting from Dr Schwenke that a new database of water lines containing such hot bands, based upon *ab initio* calculations, is now available.[2]

1 N. Jaquinet-Husson *et al.*, *J. Quant. Spectrosc. Radiat. Transfer*, 1998, **59**, 511.
2 H. Partridge and D. W. Schwenke, *J. Chem. Phys.*, 1997, **106**, 4618.

Prof. Owen asked: Given the strength of the CN bond is there an alternative parent molecule for C_3 other than HC_3N? Perhaps amorphous carbon or a C_3 hydrocarbon?

Dr Crovisier responded: If C_3 is coming from amorphous carbon, there should be a desorption mechanism whose efficiency is large enough to produce the radical with its observed abundance. Such a mechanism is yet unknown. It is unlikely that HC_3N is the only parent for C_3 (although C_3 and HC_3N are produced with similar abundances—about 0.02% relative to water). The presence of C_2H_2 and C_2H_6 points to the existence of more complex hydrocarbons, and that of HC_3N, of carbon-chain molecules, that are all potential parents for C_3.

Prof. Irvine commented: Concerning the parent of C_3 in comets, the Giotto mass spectrometers had a peak that has been interpreted as $C_3H_3^+$, the parent of C_3H_2, which is widespread in the interstellar medium. Has anyone looked for C_3H_2 in comet Hale–Bopp?

Dr Crovisier responded: We looked for C_3H_2 in the radio spectra of comets Hyakutake and Hale–Bopp but we only obtained upper limits.

Dr Kaiser said: Concerning potential C_3 parent molecules in comets, very recent (hitherto unpublished) work at UC Berkeley shows that photodissociation of methylacetylene/allene produces C_3H_2 isomers, which can either undergo secondary decomposition or secondary photon absorption to form C_3H/C molecules.

Dr Palumbo commented: Here I present recent laboratory experiments on irradiation with 3–30 keV He^+ ions of $H_2O : NH_3 : CH_4$ and $H_2O : N_2 : CH_4$ ice mixtures at 10 K.[1] A description of the experimental apparatus can be found in ref. 2. From Fig.3 it is evident that new absorption bands appear in the 2300–2000 cm^{-1} spectral range (these bands are not present before irradiation). The band at 2140 cm^{-1} is easily attributed to solid CO. The band at about 2170 cm^{-1} is attributed to a CN group. In order to identify the species to which the CN group is bonded we note that: (1) the 2170 cm^{-1} band is also present after warm up to 250 K and that is it is not a simple volatile molecule; (2) the band does not appear after ion irradiation of the binary mixtures $NH_3 : CH_4$ and $N_2 : CH_4$ thus it should be sensitive to the presence of oxygen or at least water in the irradiated mixture; (3) it is well known that after ion irradiation of ice mixtures which contains hydrocarbon a tridimensional disordered organic residue is formed. Thus at present we attribute the band at about 2170 cm^{-1} to a CN group bonded to oxygen containing end groups of the disordered tridimensional structure (often referred to as refractory organic residue) that is formed upon irradiation of hydrocarbon containing ices.

Finally, laboratory experiments have shown that the profile (shape, width and peak position) of the 2170 cm^{-1} band does not depend on the initial composition (molecular nitrogen or ammonia). This result is particularly interesting in view of the comparison with astronomical observations. In fact, a detailed comparison of the laboratory results with astronomical data of the so-called XCN band in protostellar spectra shows good agreement in peak position and profile.

[1] M. E. Palumbo, G. Strazzulla, Y. J. Pendleton and A. G. G. M. Tielens, *Astrophys. J.*, 1998, submitted.
[2] M. E. Palumbo, *Adv. Space Res.*, 1997, **20**, 1637 and references therein.

Dr Crovisier responded: This X—CN product is probably closely related to the HNCO molecule (isocyanic acid) recently identified in comets.

Prof. Irvine asked: There has been some suggestion that the interstellar feature might be due to an isonitrile. Could you distinguish nitriles from isonitriles in your lab work?

Dr Palumbo responded: A band at about 2170 cm^{-1} appears after ion irradiation of $H_2O : NH_3 : CH_4$ and $H_2O : N_2 : CH_4$ ice mixtures at 10 K. We attribute this band to a —CN group bonded to the oxygen containing end group of the disordered tridimensional structure of the organic refractory residue that is formed upon irradiation of hydrocarbon containing ices.[1] At this stage we are not able to exclude the fact that an isonitrile compound could also be the carrier of that band observed in laboratory spectra.

[1] M. E. Palumbo, G. Strazzulla, Y. Pendleton and A. G. G. M. Tielens, *Astrophys. J.*, submitted.

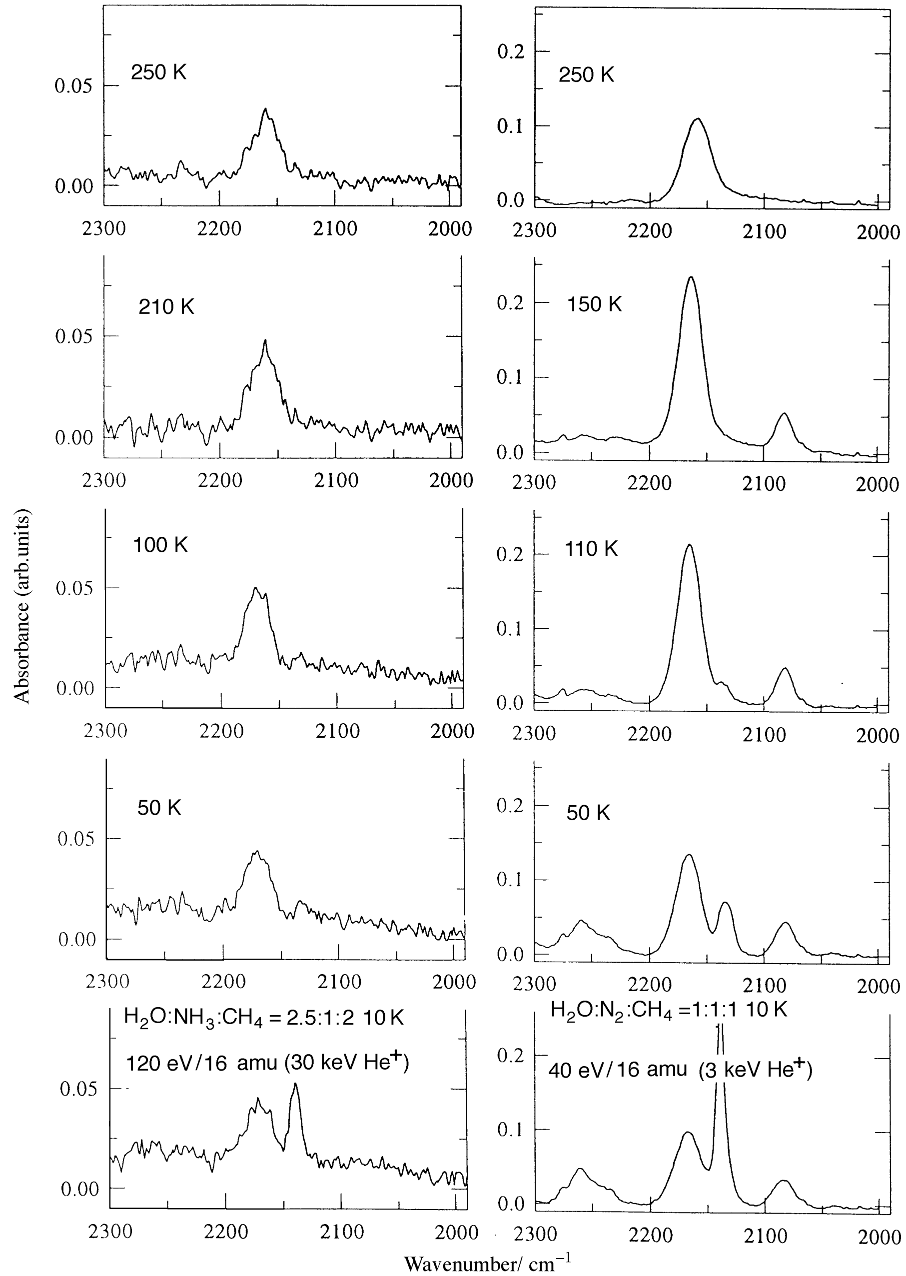

Fig. 3 Infrared spectra of $H_2O:NH_3:CH_4$ ($\approx 2.5:1:2$) (left panels) and $H_2O:N_2:CH_4$ ($\approx 1:1:1$) (right panels) mixtures in the 2300–2000 cm^{-1} spectral range. Mixtures were irradiated with 30 keV He^+at 120 eV/16 amu and 3 keV He^+ at 40 eV/16 amu at 10 K, respectively. The mixtures were then warmed and spectra taken at the different temperatures are shown.

Dr Schutte said: Dr Palumbo proposes that the 4.62 μm band is due to 'R—OCN', where R stands for some kind of molecular organic structure.

UV photolysis of ice mixtures containing NH_3 and CO leads to the formation of a band near 4.62 μm which corresponds well with the interstellar 'XCN' band.[1–3] To identify the laboratory feature, isotope shifts were measured by including labelled compounds in the ice mixture. The magnitudes of such shifts are highly characteristic of the nature of the carrier. The ^{13}C, ^{18}O, ^{15}N shifts are all matched by OCN^- (see ref. 1 and 4; and Table 1). This assignment is supported by the presence of a total of four features in the infrared spectrum of photolysed NH_3/CO ice that can be assigned to this ion.[4] It was proposed that OCN^- can be produced in the ice by the photochemical production of isocyanic acid (HNCO), followed by proton transfer to the base NH_3 (ref. 5). Support to this mechanism is provided by Keane and Schutte[6] who showed that OCN^- is readily formed by 10 K deposition and warm-up of an ice consisting of isocyanic acid and NH_3 (Fig. 4). Since the feature found by Palumbo *et al.* matches the OCN^- feature both in position and width, and moreover is produced from an ice mixture which contains the same elements (C, N, O), it seems that OCN^- should be considered a good candidate for its assignment. While no base is included in the initial ice mixture, break-up of the N_2 molecule and subsequent hydrogenation of the resulting nitrogen atoms could result in the NH_3 necessary to initiate the acid–base reactions. Alternatively, hydrogenation of N_2 could lead to the production of the strong base hydrazine (N_2H_4).

Table 1 ^{18}O, ^{13}C and ^{15}N isotope shifts of the 4.62 μm feature produced by UV photolysis of ices containing CO and NH_3

isotope	shift/ cm^{-1}	shift(OCN^-)/ cm^{-1}
^{13}C	57	57
^{15}N	18	17
^{18}O	8.7	8.3

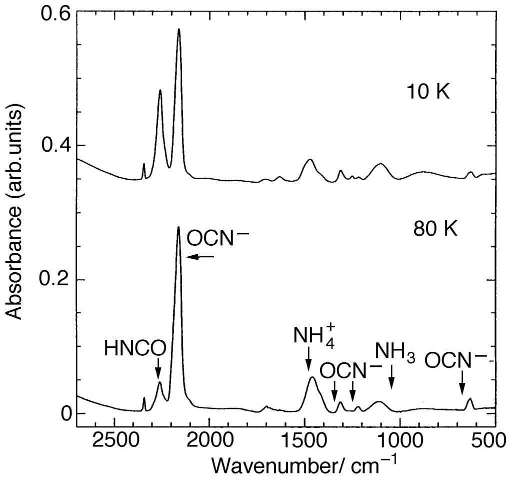

Fig. 4 Infrared spectrum of a mixture of (independently deposited) isocyanic acid (HNCO) and ammonia (NH_3); just after deposition (10 K), and following warm-up to 80 K. Immediately after deposition features of OCN^- and NH_4^+ are already present. These grow during the warm-up, while the HNCO and NH_3 become smaller, showing the occurrence of acid–base chemistry (from Keane and Schutte, 1998, in preparation).

An easy test of the OCN^- assignment would be isotopic labelling of the original ice mixture. Additionally, the spectrum could be inspected for features of positive ions, *i.e.*, NH_4^+ (1500 cm^{-1}; ref. 5), or $N_2H_5^+$ (981, 1136 and 2096 cm^{-1}; ref. 7).

[1] J. H. Lacy, F. Baas and L. J. Allamandola, *et al.*, *Astrophys J.*, 1984, **276**, 533.

[2] R. J. A. Grim and J. M. Greenberg, *Astrophys. J.*, 1987, **321**, L91.

[3] S. C. Tegler, D. A. Weintraub, T. W. Rettig, Y. J. Pendleton, D. C. B. Whittet and C. A. Kulesa, *Astrophys. J.*, 1995, **439**, 279.

[4] W. A. Schutte and J. M. Greenberg, *Astron. Astrophys.*, 1997, **317**, L43.

[5] R. J. A. Grim, J. M. Greenberg, M. S. de Groot, F. Baas, W. A. Schutte and B. Schmitt, *Astron. Astrophys. Suppl. Ser.*, 1989, **78**, 161.

[6] J. Keane and W. A. Schutte, 1998, in preparation.

[7] N. Boudin, W. A. Schutte and J. M. Greenberg, *Astron. Astrophys.*, 1998, **331**, 749.

Dr Palumbo commented: Ion irradiation experiments show that N_2, which is a more likely interstellar ice component than NH_3, can be the molecular progenitor of the carrier of the interstellar XCN band. In fact, FUV laboratory experiments have exclusively considered NH_3 (N_2 is not photolyzed by FUV photons) as the molecular precursor, despite the apparent absence of the IR absorption feature of this molecule in interstellar ice spectra (*e.g.*, Whittet *et al.*[1])

Thus, these laboratory results will probably help solve the case of the missing nitrogen in dense molecular clouds. In fact interstellar ices are likely to contain substantial amounts of solid N_2, as nitrogen is depleted from the gas phase in molecular clouds and no other reservoir of solid nitrogen has emerged.

[1] D. C. B. Whittet, W. A. Schutte, A. G. G. M. Tielens, A. C. A. Boogert, Th. de Graauw, P. Ehrenfreund, P. A. Gerakines, F. P. Helmich, T. Prusti and E. F. van Dishoeck, *Astron. Astrophys.*, 1996, **315**, L357.

Prof. Bernath commented: Although the Comets Hale–Bopp and Hyakutake were very bright, there is another reason that several new molecules were identified by infrared spectroscopy. In the past few years cryogenic echelle spectrographs have become available to astronomers. Because these new instruments are based on large format infrared array detectors, they are much more sensitive than Fourier transform spectrometers. One such instrument is Phoenix, developed by K. Hinkle at Kitt Peak National Observatory in Tucson, Arizona. Phoenix was used to record infrared spectra of Comet Hale–Bopp at a resolving power of about 50 000. These spectra revealed cometary emission features that could be assigned to OCS, C_2H_6 and CH.[1]

[1] D. Reuter, D. Jennings, P. Sada, K. Hinkle, S. Ridgway, L. Wallace, P. Bernath and J. Waller, *IAU Circular 6681*, 1997.

Prof. Sarre said: In his paper Dr Crovisier mentions the possibility of diffuse band carriers being present in comets. Diffuse interstellar bands have been sought in absorption in cometary spectra using a background star,[1] but not confirmed. In the Red Rectangle (and the R CrB star V854 Cen) a subset of the diffuse bands have been observed in emission[2] but they do not appear in cometary emission spectra.

As this morning's session is meant to explore links between stellar, interstellar and planetary topics, I would remark that ten years ago Duley drew attention to the general similarity between the optical Red Rectangle emission bands and luminescent features of impure diamonds[3] which were touched on during the discussion of Prof. Pillinger's paper. If diamonds were indeed responsible for the Red Rectangle emission features, it would follow from ref. 2 that some of the diffuse bands would also arise from impure diamonds. Much research, especially in the laboratory, is needed to evaluate this and we are beginning such a programme to explore this possibility. I would finally comment that although most current evidence strongly suggests that free gas phase molecules are responsible for the diffuse band spectrum, this is not yet proven.

1 I. A. Crawford and D. McNally, *Observatory*, 1987, **107**, 20.
2 P. J. Sarre, J. R. Miles and S. M. Scarrott, *Science*, 1995, **269**, 674.
3 W. W. Duley, *Astrophys. Space Sci.*, 1988, **150**, 387.

Dr Aikawa asked: Are there any phenomena which indicate the inhomogeneity within the nucleus caused by the thermal history (*e.g.* migration of molecules within the nucleus)?

Dr Crovisier responded: The ultimate answer to this question will be given by deep drilling experiments on a cometary nucleus. Unfortunately, the landers of ROSETTA and Champollion missions to comets will only skim and sample the very outer part of their nuclei. We thus have to rely upon remote sensing studies, which allow us to study the production rates of various molecular species as a function of heliocentric distances, for comets experiencing different thermal histories. Unprecedented data were gathered on comet Hale–Bopp, from 7 AU pre-perihelion from the Sun to perihelion at 0.9 AU, and again when it receded from the Sun. Other interesting results could be obtained if we can achieve a similar study on a comet making its first return from the Oort cloud, or on a comet which recently underwent a change of orbit, or if we can compare data from successive returns of a comet to the Sun. These are long-term projects, whereas the possibility of observing directly cometary parent molecules is very recent! On the other hand, the interpretation of such observations in terms of volatile molecule segregation within the nucleus will undoubtedly need the use of realistic models of the evolution of sublimation within cometary nuclei.

Prof. van Dishoeck said: In your paper, you do not mention your beautiful ISO SWS01 spectrum of comet Hale–Bopp showing crystalline silicate features, many of which can be ascribed to forsterite (Mg_2SiO_4).[1] This spectrum is remarkably similar to the SWS01 spectrum of the circumstellar disk around the young Herbig Ae/Be star HD 100546 measured by Waelkens *et al.*[2] However, crystalline silicates have not yet been detected in the interstellar medium, suggesting that they must be made during the star-formation process. Could you comment on the origin of the crystallinity in comets, which spent most of their lifetime in the cold outer parts of our solar system?

1 J. Crovisier, K. Leech, D. Bockelée-Morvan, T. Y. Brooke, M. S. Hanner, S. Altieri, H. U. Keller and E. Lellouch, *Science*, 1997, **275**, 1904.
2 C. Waelkens, L. B. F. M. Waters, Th. de Graauw *et al.*, *Astron. Astrophys.*, 1996, **315**, L245.

Dr Crovisier responded: As mentioned by Prof. van Dishoeck, the 7–45 μm spectrum of comet Hale–Bopp observed at 3 AU from the Sun shows features which are closely matched by crystalline magnesium-rich olivine (forsterite) (see Fig. 5 here).

This does not mean that forsterite is the main constituent of cometary dust, but that the spectral features of this species are dominating the cometary spectrum at this distance (3 AU) from the Sun. Indeed, in a recent analysis of Hale–Bopp infrared spectra, Wooden *et al.*[1] found that spectra closer to the Sun ($<$ 1.7 AU) show a peak at 9.3 μm that they attribute to pyroxene. These authors ascribe the non-detection of pyroxene at large heliocentric distances to a temperature effect. The spectra are also consistent with the presence of amorphous silicates. With the presence of both olivine and pyroxene, the dust of Hale–Bopp appears to be akin to interstellar dust particles.

In any case, scenarios of cometary formation now have to explain how and when crystalline silicates have been incorporated, whereas interstellar grains only show amorphous silicates and whereas the cometary volatile phase is akin to (by its chemical and isotopic composition) interstellar matter. This is one of the new engimas brought up by recent cometary observations.

1 D. H. Wooden *et al.*, *Astrophys. J.*, 1998, submitted.

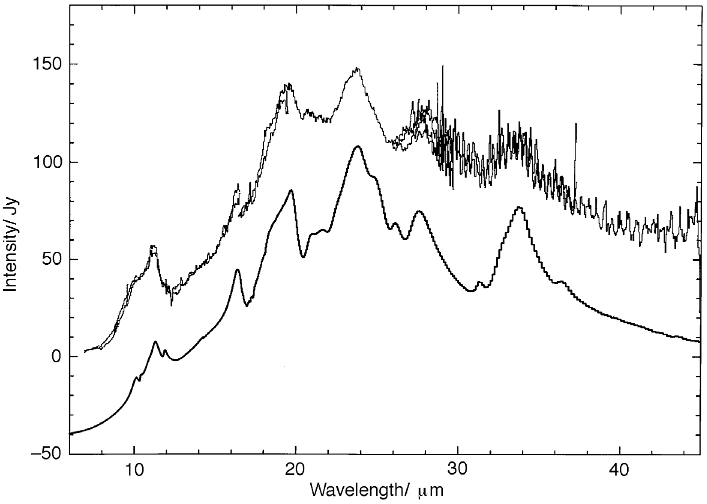

Fig. 5 ISO–SWS spectrum of C/1995 O1 (Hale–Bopp) and a spectrum of forsterite modelled from a laboratory spectrum provided by W-F. Thi and L. d'Hendecourt (reproduced with kind permission from Crovisier *et al.*[2]).

[2] J. Crovisier *et al.*, in *First ISO Workshop on Analytical Spectroscopy*, ed. A. M. Heras, K. Leech, N. R. Trams and M. Perry, ESA SP-419, 1997, p. 259.

Dr Ehrenfreund and **Prof. J. Nuth** (in part communicated): ISO has revealed for the first time the presence of crystalline silicates, such as olivines and pyroxenes in AGB stars, Planetary Nebulae, as well as young stellar objects.[1,2] In the interstellar medium silicates are only observed in amorphous form. Note that it could be very difficult to detect a 5% crystalline silicate contribution against most sources such as the galactic center that are used to characterize the interstellar silicate grain population. Crystalline silicates can be converted into amorphous silicates due to the cosmic ray irradiation in the interstellar medium.[3–5] In the Solar System, in interplanetary dust particles and comets (see ref. 6), crystalline silicates are observed. As mentioned by Dr. Crovisier, ISO revealed a striking identification of fosterite around young Herbig Ae/Be stars which matches well the spectrum of comet Hale–Bopp, indicating a link between dust around young stars and comets.[7] In the cold environment of the Oort cloud the density and temperature do not in general allow the formation of crystalline silicates. Annealed silicates may have been formed in the hot and very turbulent environment of the nebula[8] and thereafter incorporated into comets. Radiation damage silicate grains, which were previously crystalline may be re-annealed on a shorter time scale and at a lower temperature. However, laboratory studies indicate that the temperature conditions in the cometary coma do not seem sufficient to allow this process. It has to be noted that the fraction of crystalline silicates in the circumstellar environments account only for a few percent. To study the relation between circumstellar and cometary silicates should however provide important constraints for the formation of the Solar System.

[1] R. Waters *et al.*, *Astron. Astrophys.*, 1996, **315**, L361.
[2] C. Waelkens *et al.*, *Astron. Astrophys.*, 1996, **315**, 245.
[3] G. Day, *Mon. Not. R. Astron. Soc.*, 1977, **178**, 49.
[4] W. Kratschmer and D. R. Huffman, *Astrophys. Space Sci.*, 1979, **61**, 195.
[5] J. Nuth, *Earth Moon Plan.*, 1989, **47**, 33.
[6] D. Wooden *et al.*, *Astrophys. J.*, 1998, submitted.
[7] K. Malfait *et al.*, *Astron. Astrophys.*, 1998, **332**, L25.
[8] S. L. Hallenback, J. A. Nuth and P. L. Daukantas, *Icarus*, 1998, **131**, 198.

Dr Schutte communicated: Since the re-crystallization rate of the silicates should increase steeply with temperature, such a mechanism would imply that the ratio of crystalline to amorphous silicates should be a strong function of heliocentric distance. Is there any observational evidence for such a dependence?

Dr Crovisier responded: It must be first noted that the ISO observations of comet Hale–Bopp have shown the presence of crystalline silicates as far as 4.6 AU from the Sun, where the dust temperature is too low to permit re-crystallisation of amorphized silicates.[1] Thus, crystalline silicates must have been incorporated at the moment of cometary formation.

It is interesting to investigate silicate crystallinity in comets as a function of the heliocentric distance of their formation. Comets from the Oort cloud are believed to have formed in the Jupiter–Uranus region. Observations of P/Halley, Hale–Bopp and other bright comets from the Oort cloud has revealed the presence of crystalline olivine. Comets from the Edgeworth–Kuiper belt formed beyond Neptune, in a cooler region. Unfortunately, Jupiter-family comets, believed to have migrated from the Edgeworth–Kuiper belt, are relatively faint objects and observations of their silicates have been inconclusive up to now (see *e.g.* ref. 2). However, 103P/Hartley 2, a Jupiter-family comet, could be observed recently by ISO (ref. 3): its silicate band shows the 11.3 μm feature characteristic of crystalline olivine. Thus, present observations do not show any dependence of the presence or not of crystalline silicates on their presumed site of formation.

1 J. Crovisier, *Astron. Astrophys.*, 1996, **315**, L385.
2 M. S. Hanner, D. K. Lynch, R. W. Russell, J. A. Hackwell, R. Kellogg and D. Blaney, *Icarus*, 1996, **124**, 344.
3 J. Crovisier *et al.*, XXIIIth EGS General Assembly, Nice, 1998, poster presentation.

Prof. Papoular asked: Is it possible to infer, from the ISO spectra, the fraction of total silicates which is in a crystalline state?

Prof. van Dishoeck responded: The fraction of silicates in crystalline form in AGB stars and in the disks around young stars estimated by Waters *et al.*[1] and Waelkens *et al.*[2] ranges from a few percent to 13% of the total amount of silicates. Thus, the majority of the silicates is still in amorphous form. Detailed analysis is still in progress using new laboratory data obtained at the University of Jena.

1 L. B. F. M. Waters, F. J. Molster, T. de Jong *et al.*, *Astron. Astrophys.*, 1996, **315**, L361.
2 C. Waelkens, L. B. F. M. Waters, Th. de Graauw *et al.*, *Astron. Astrophys.*, 1996, **315**, L245.

Mr Gounelle asked: Is it possible to measure the pyroxene : olivine ratio in cometary spectra? (It is interesting because it distinguishes micrometeorites from carbonaceous meteorites.) Is it possible to detect refectory material (CAIS) in ISO spectra? Shu's model[1] shows that it is possible to send silicates from the inner solar system to the outer solar system *via* x-winds produced during the T. Tauri phase which leads to an explanation for solar system silicates in comets.

1 F. Shu, *et al.*, *Science*, 1996, **271**, 1545.

Dr van Winkel said: In the young stellar objects observed with ISO–SWS–LWS and analysed so far, both crystalline olivines and pyroxenes could be identified. The silicates are up to 10% in crystalline form. The main difficulty in determining the ratio between the olivines the pyroxenes is the decomposition and identification of the different contributors to the whole spectrum (see *e.g.* Malfait *et al.*[1] on the spectrum of the isolated Herbig Ae/Be star HD 100546). The striking similarity between the spectrum of the object and the spectrum of Hale–Bopp suggests also a similar content.

A very preliminary estimate is a higher olivine than pyroxene content with a ratio of olivine to pyroxene similar to that in comets (up to 10 : 1). The same is true for the dust-disk of the Red Rectangle: there the SWS (2.4 to 40 μm) spectrum is even more difficult since the separated chemistry (a strong C-rich and O-rich contribution) makes the decomposition of the different contributors even more difficult.

1 K. Malfait, C. Waelkens, L. P. F. M. Waters, B. Vandenbussche, E. Huygen and M. S. De Graauw, *Astron. Astrophys.*, 1998, **332**, L25.

Dr Palumbo commented: Among the suggested formation mechanisms of solid CO_2 in dense molecular clouds is cosmic ray irradiation of icy mantles. Here I would like to show some recent laboratory experiments[1] on the formation of solid CO_2 after ion irradiation (3–60 keV He^+, Ar^{2+}) of CO and CH_3OH ices (10 K) and mixtures ($CO:O_2$, $CO:N_2$ (apolar mixtures) and $H_2O:CO$, $H_2O:CH_3OH$, $H_2O:CH_4$, $H_2O:CH_4:NH_3$ (polar mixtures).

A description of the experimental apparatus can be found in Palumbo.[2] Fig. 6 and 7 show the profile of the CO_2 stretching mode produced after ion irradiation of apolar and polar mixtures, respectively. The dotted line at 2343 cm^{-1} which indicates the peak position of pure CO_2 ice,[3] has been drawn for reference.

Furthermore we have studied the $CO:CO_2$ molecular number ratio as a function of initial mixture and dose (eV/16 amu) at 10 K. We found that a ratio equal to (or close to) 1 (which in fact has been observed towards the field star Elias 16) is obtained after irradiation of some mixtures such as $CO:O_2$ (1 : 1) and $H_2O:CH_3OH$ (2 : 1 to 10 : 1). A ratio of less than 1 is obtained for the $H_2O:CO$ (10 : 1) mixtures studied. Moreover, owing to the different volatility of these two molecules the $CO:CO_2$ ratio decreases after warm-up.

Finally, I present an alternative to the segregation model proposed here by Dr Ehrenfreund. Fig. 8 shows a comparison of the profile of the CO_2 bending mode observed by ISO towards the embedded source NGC7538 IRS1 (ref. 4) with laboratory spectra. The dashed line is the spectrum of CO_2 produced after ion irradiation of CO at

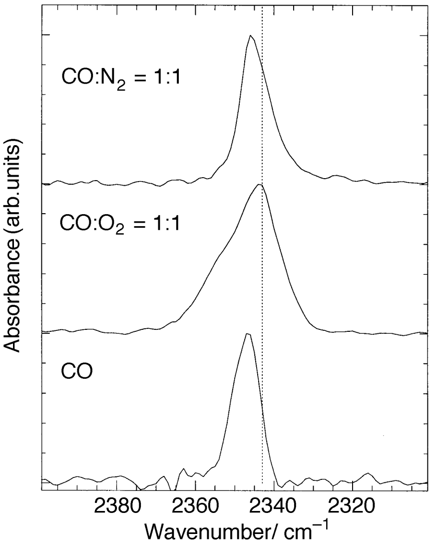

Fig. 6 Profile of the CO_2 asymmetric stretching mode, at about 2340 cm^{-1} (4.27 μm) produced after ion irradiation of non-polar mixtures at 10 K. Pure CO has been irradiated with 3 keV He^+ ions while the mixtures have been irradiated with 60 keV Ar^{2+} ions. The irradiation dose for all samples is *ca.* 20 eV/16 amu. A dotted line at 2343 cm^{-1}, which indicates the peak position of pure CO_2 has been drawn for reference.

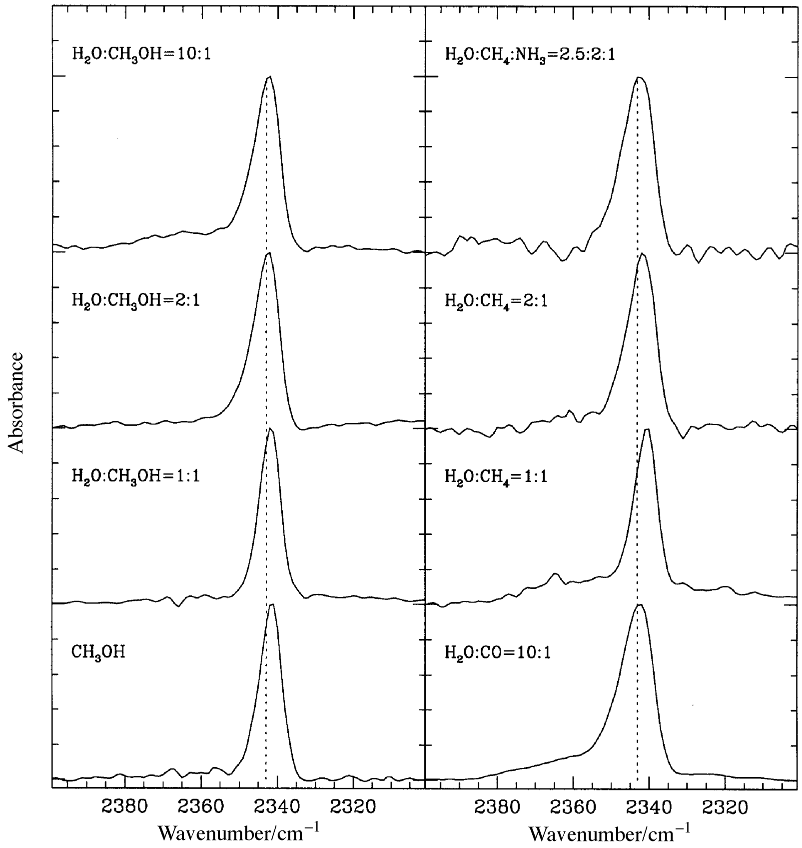

Fig. 7 Profile of the CO_2 asymmetric stretching mode, at about 2340 cm^{-1} (4.27 μm) produced after ion irradiation of polar mixtures at 10 K. Mixtures with methanol have been irradiated with 3 keV He^+ at *ca.* 40 eV/16 amu; $H_2O : CO$ and $H_2O : CH_4 = 1 : 1$ mixtures have been irradiated with 3 keV He^+ at *ca.* 20 eV/16 amu; $H_2O : CH_4 = 2 : 1$ and $H_2O : CH_4 : NH_3 = 2.5 : 2 : 1$ mixtures have been irradiated with 30 keV He^+ at *ca.* 80 eV/16 amu. A dotted line at 2343 cm^{-1}, which indicates the peak position of pure CO_2 has been drawn for reference.

10 K and warmed up to 40 K (apolar component). The dotted line is the spectrum of CO_2 produced in an $H_2O : CH_3OH$ mixture (polar component).

It is important to note that these laboratory spectra are the same used to fit the observed CO band at about 2140 cm^{-1} (ref. 5 and 6).

1 M. E. Palumbo, G. A. Baratta, J. R. Brucato, A. C. Castorina, M. A. Satorre and G. Strazzulla, *Astron. Astrophys.*, 1998, **334**, 247.
2 M. E. Palumbo, *Adv. Space Res.*, 1997, **20**, 1637 and references therein.
3 S. A. Sandford and L. J. Allamandola, *Astrophys. J.*, 1990, **355**, 357.
4 G. Strazzulla, B. Nisini, G. Leto, M. E. Palumbo and P. Saraceno, *Astron. Astrophys.*, 1998, **334**, 1056.
5 T. C. Teixeira, J. P. Emerson and M. E. Palumbo, *Astron. Astrophys.*, 1998, **330**, 711.
6 M. E. Palumbo and G. Strazzulla, *Astron. Astrophys.*, 1993, **269**, 568.

Dr Ehrenfreund responded: Solid CO_2, ubiquitously observed in the interstellar medium, may be formed by grain surface reactions or by energetic processing such as UV photolysis and/or cosmic rays. In models of surface chemistry accreted CO reacts with accreted O to form CO_2. The long timescales between successive accretion events

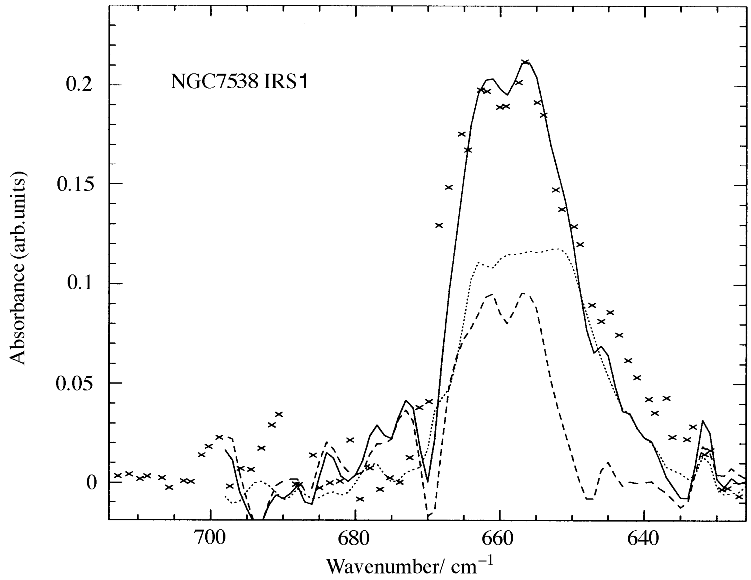

Fig. 8 Comparison of the observed bending mode (crosses) with laboratory spectra of CO_2 produced after ion irradiation of CO at 10 K and warmed to 40 K (dashed line) and of CO_2 produced in an $H_2O:CH_3OH$ mixture (100 K; dotted line). The solid line is the sum of the two components.

may allow the reaction to proceed. Laboratory measurements report the rapid production of CO_2 from UV irradiated H_2O–CO mixtures. Throughout the whole cloud a constant UV field of *ca.* 10^3 photons s^{-1} cm^{-2} (induced by cosmic rays) may act as a source of irradiation products. Impact of cosmic rays may form CO_2 from simple ices. Only future observations and quantitative laboratory results will reveal the origin and evolution of this important ice constituent.

ISO observations show that CO_2 resides predominantly in water-rich ices and provide evidence for 'annealed' CO_2 towards 20 protostars. The narrow width of the CO band towards many of these targets also indicates that little or no CO_2 is mixed with apolar CO.[1] The remarkable triple structure observed in the CO_2 bending mode throughout the interstellar medium can be well reproduced in the laboratory, see Fig. 5 in Dr Ehrenfreund's paper. The best fits are currently obtained with ice mixtures containing H_2O, CH_3OH and CO_2, which are simply thermally processed (slow warm-up to temperatures above 100 K). We assume that this particular triple structure is formed when the matrix is rearranged and molecules start to be mobile within the ice matrix (a process which can also be introduced by irradiation). The best current explanation for the multipeak is the formation of special bonds (T-shaped complexes) between CO_2 and specific polar neighbour molecules (such as CH_3OH, NH_3 or maybe other less abundant species). The comparison of astronomical data with spectra of thermal processed CO_2 in CH_3OH/H_2O matrices show a perfect match[2] and are currently much more convincing than any other attempts involving irradiation. However, future laboratory studies will show whether this remains the best possible explanation and whether other mechanisms and other polar molecules could be involved in the formation of this particular CO_2 feature at 15.2 μm.

1 P. Ehrenfreund, A. C. A. Boogert, P. Gerakines, A. G. G. M. Tielens and E. F. van Dishoeck, *Astron. Astrophys.*, 1997, **328**, 649.

2 P. Gerakines *et al.*, *Astron. Astrophys.*, 1998, in preparation.

Prof. Vidali said: Dr Ehrenfreund mentioned CO + O reactions on grains. Are these grains bare or are they covered by ices?

Dr Ehrenfreund responded: Surface reactions such as CO + O occur on icy grain mantles in dense cold clouds and lead eventually to the formation of solid CO_2.

Dr Schutte commented: Grains in dense clouds are covered by accreted icy mantles, as can be seen observationally from the presence of absorptions of frozen molecules in the spectra of obscured objects (*e.g.*, Smith *et al.*[1] and Willner *et al.*[2]).

[1] R. G. Smith, K. Sellgren and A. J. Tokunaga, *Astrophys. J.*, 1989, **344**, 413.

[2] S. P. Willner, F. C. Gillett, B. Herter *et al.*, *Astrophys. J.*, 1982, **253**, 174.

Prof. Smith commented: I wanted to make a brief comment on the experiments undertaken in Leiden on the formation of CO_2 when CO and O_2 are irradiated in low temperature matrices. I believe that it is important that these experiments mimic, as far as is possible, the conditions in those regions of space where CO_2 ices are formed. In particular, I have in mind the wavelengths of ultraviolet light that are used in the illumination. At wavelengths above *ca.* 174 nm, O_2 will dissociate, largely through predissociation of the $B\,{}^3\Sigma_u^-$ state, to two ground state $O(^3P)$ oxygen atoms. Below that wavelength, $O(^1D)$ atoms will be produced. The latter, although they may be efficiently quenched, will combine much more readily with CO than $O(^3P)$ since no spin change is involved in form CO_2 in its ground electronic state. Can I ask if any attempt has been made to study the effect in these experiments of changing the wavelength of the light which is initiating change?

Prof. Vidali commented: CO oxidation on grains can occur by reaction of O coming from the gas phase. Is it possible that this reaction occurs in astrophysical environments? It might give different results than a reaction done in the laboratory where O_2 is split by UV, since kinetic factors and/or the state of excitation of oxygen atoms might play a role.

Dr Ehrenfreund and **Dr Schutte** responded: UV irradiation is usually performed using a microwave-excited hydrogen flow lamp. This source has a sharp emission peak at 1216 Å (Lyman alpha) and additional bands centered at 1360, 1450, 1600 and 2800 Å, which produce a total UV flux of approximately 10^{15} photons cm^{-2} s^{-1}. So far we are not aware of experiments that study the wavelength dependence of CO_2 formation. It is certainly correct that if the laboratory experiments are to give relevant simulation, we should produce triplet O_2, *i.e.*, the lowest state, since in space the atomic oxygen would have plenty of time to relax after dissociation before it would accrete on a grain surface. Methods of doing this would be, as already noted, tuning of the spectral output of the UV lamp, or, alternatively, storage of the oxygen atoms in the inert matrix for sufficiently long time to ensure relaxation prior to diffusion and meeting CO.

Prof. Irvine asked: How do you distinguish for the interstellar ices between segregation of different molecular species on the same grain and differing mantle compositions on grains along the line of sight?

Dr Ehrenfreund responded: We are not able to distinguish whether interstellar ices are arranged in different ice layers on grains or whether they reside on different grain populations. We can however determine differences in the chemical composition of grains towards several protostars: The presence of apolar CO, which evaporates below 20 K in astronomical environments is used as a tracer for dense, cold and quiescent regions. The multipeak bending mode of CO_2 indicates a higher temperature of about

60 K in the line of sight. In many cases we can deconvolve the profiles of the strong bands of H_2O, CO, CO_2, CH_3OH and other species and determine the composition as well as the radiation and temperature history of interstellar ices. Those laboratory studies have shown the existence of water-dominated and water-poor ices and ISO observations have revealed many more different phases. Only the complete ice spectrum in combination with the knowledge of the prevailing physical conditions (such as temperature and irradiation) in the environments of protostars will allow us to distinguish the processes on interstellar grains.

Mr Liu said: I have two comments and a question: (1) In addition to being identified in cometary and interstellar ices, formic acid (HCOOH) is also observed in hot molecular cores. We have surveyed several molecular core regions including Sgr B2, Orion, W51, G34.4 + 0.2 and NGC7538 for HCOOH. Preliminary results show HCOOH abundance in the gas phase varies from core to core. (2) The BIMA (Berkeley–Illinois–Maryland Association) Array now operates at 3 mm as well as 1 mm wavelength. With its longest baseline, which extends over 1 km, we can observe at a very high angular resolution (0.5 arcsec). The physical resolution, for example, for a source at the galactic center is thousands of AU, which is comparable to size of the Oort cloud. Observations with BIMA can therefore probe objects from interstellar clouds down to possibly planet-forming disks.

My question to Dr Ehrenfreund is: Solid state experiments of interstellar ices are conducted in a time scale which is significantly shorter than the cosmic time scale. Some slow but important processes are probably not considered in this case. Is there any concern or future plan regarding this? Would you please comment?

Dr Ehrenfreund and **Dr Schutte** responded: In the laboratory we can simulate the following conditions: (1) a limited vacuum of 10^{-8} mbar; (2) temperature *ca.* 10 K; (3) the UV radiation field in the interstellar medium: one hour UV irradiation in the laboratory corresponds to a radiation of *ca.* 10^3 years in cloud outskirts (assuming a UV irradiation of 8×10^7 photons cm^{-2} s^{-1} and to *ca.* 10^8 years in dense clouds (with a UV flux of 10^{-3} photons cm^{-2} s^{-1}).

Owing to the limited lifetime of scientists we need in the laboratory to simulate grain surface reactions with an H-atom flux which exceeds that in the interstellar medium by many orders of magnitude. At these high fluxes recombination of the H atoms on the icy surface may strongly compete with hydrogenation of the surface molecules. Therefore laboratory experiments will be difficult to interpret in a quantitative way, but the relative efficiency of surface hydrogenation of various molecules may be readily determined.

Introducing the paper 'Chemistry in cometary comae', **Prof. Irvine** said: There have been a number of interesting developments relevant to our paper since it was submitted last December.

The chemical model employed has a number of somewhat uncertain parameters, including the chemical composition of the cometary nucleus, certain reaction rates and branching ratios, and the particular set of molecular species and reactions included. Although the absolute abundances of some species in the coma may depend on the choice of such parameters, the calculated HNC : HCN ratio is surprisingly insensitive to most such choices. For example, we varied the initial (nuclear) abundances of the nitrogen-containing molecules N_2 and NH_3 over rather broad ranges ($O < N_2 < 0.3$ and $0 < NH_3 < 0.05$, relative to $H_2O = 1$) without significantly changing the calculated HNC/HCN ratio.[1] Likewise, the corresponding model by Rodgers and Charnley[2] includes some potentially important reactions which we have omitted, but those authors agree with our conclusion that gas phase chemistry is responsible for the production of HNC in Comet Hale–Bopp.

There is one reaction, however, which we find does significantly affect the HNC : HCN ratio, and that is the dissociative recombination $HCNH^+ + e$, for which the products and the branching ratios have not been measured in the laboratory. Models of interstellar chemistry traditionally assume that this reaction yields HCN : HNC : CN in the ratios 0.25 : 0.25 : 0.50, based on estimates made some 20 years ago.[3] Recent quantum chemical calculations, however, indicate that there will be little CN produced and that the production of HNC should exceed that of HCN.[4] This result agrees with conclusions derived from an extensive set of observations of HCN and HNC in cold interstellar cloud cores.[5] We therefore re-ran our chemical model using the branching ratios HCN : HNC : CN = 0.45 : 0.55 : 0.0, and the results are shown in Fig. 9.[6] It may be seen that the model now matches the observations even better than before. Clearly, laboratory measurement of the branching ratios for this dissociative recombination would be extremely valuable to astrochemistry, both in its applications to cometary science and to the interstellar medium.

We have also investigated further the question of whether HNC could be a direct product of photodissociation of an unknown parent. We considered such parents to have lifetimes in the solar radiation field of either 0.1 or 1.0 times that of HCN, and chose nuclear abundances that would give the observed HNC : HCN ratio at a heliocentric distance of 1 AU. The variation of HNC : HCN with heliocentric distance can then be calculated, and the results are displayed in Fig. 9. It is clear that such a source of HNC does not match the observed heliocentric dependence of the HNC/HCN ratio.[1]

Unfortunately, the proposed mapping of the HNC : HCN ratio in the coma of Comet Temple–Tuttle, mentioned in the last sentence of the paper, was not successful because of the weak emission from that comet. However, there have been new reports of

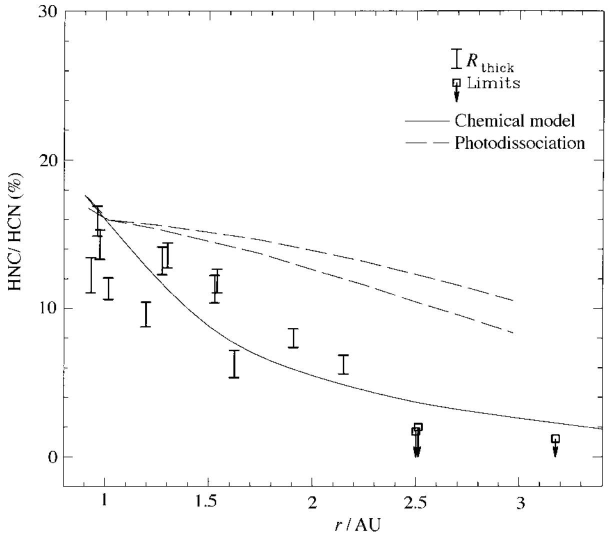

Fig. 9 Dependence of the HNC : HCN ratio on heliocentric distance, *r*. R_{thick} is the observed ratio of column densities after correcting for optical depth using the homogeneous slab model. Open squares are 3σ upper limits (see main text and Fig. 4 in our paper). Chemical model results using new branching ratios for $HCNH^+ + e$ are given as the filled line, assuming a water production rare of 10^{31} $r(AU)^{-1.6}$ molecules s^{-1} [the approximate rate reported at the First International Conference on Comet Hale–Bopp, February, 1998 (to be published in *Earth, Moon, Planets*)]. Dashed lines give the calculated[10] HNC : HCN ratio for the case where HCN is sublimating from the nucleus while HNC is formed by photodissociation of an unknown nuclear parent; upper and lower curves for parent lifetimes in the solar radiation field equal to 0.1 and 1.0 times that of HCN, respectively.

the HNC : HCN ratio at several positions in the coma of Comet Hale–Bopp which are consistent with the chemical model in the present paper, although the signal-to-noise left the results somewhat ambiguous.[7]

In regard to HCO^+, a simple model has been developed to simulate the acceleration of such ions due to interaction with the solar wind, and the results qualitatively reproduce the observed offset of the peak HCO^+ emission in the anti-sunward direction and the increasing redshift of the emission in this direction.[8] We have also made a preliminary analysis of the excitation of HCO^+ in the coma of comet Hale–Bopp and analysed the maps including both radiative and collisional effects.[9]

1 W. M. Irvine, E. A. Bergin, J. E. Dickens, D. Jewitt, A. J. Lovell, H. E. Matthews, F. P. Schloerb and M. Senay, *Nature* (*London*), 1998, **393**, 547.
2 S. D. Rodgers, and S. B. Charnley, *Astrophys. J. Lett.*, 1998, **501**, L227.
3 E. Herbst, *Astrophys. J.*, 1978, **222**, 508.
4 Y. Shiba, T. Hirano, U. Nagashima and K. Ishii, *J. Chem. Phys.*, 1998, **108**, 698.
5 T. Hirota, S. Yamamoto, H. Mikami and M. Ohishi, *Astrophys. J.*, 1998, in press.
6 W. M. Irvine, J. E. Dickens, A. J. Lovell, F. P. Schloerb, M. Senay, E. A. Bergin, D. Jewitt and H. E. Matthews, *Earth*, *Moon*, *Planet*, 1998, in press.
7 T. Hirota, S. Yamamoto, K. Kawaguchi, A. Sakamoto and N. Ukita, *Astrophys. J.*, 1998, in press.
8 A. J. Lovell, F. P. Schloerb, E. A. Bergin, J. E. Dickens, C. H. DeVries, M. C. Senay and W. M. Irvine, *Astrophys. J. Lett.*, 1988, **497**, L117.
9 A. J. Lovell, F. P. Schloerb, E. A. Bergin, J. E. Dickens, C. H. DeVries, M. C. Senay and W. M. Irvine, *Earth*, *Moon*, *Planets*, 1998, in press.
10 L. E. Tacconi-Garman, F. P. Schloerb and M. J. Claussen, *Astrophys. J.*, 1990, **364**, 672.

Dr Crovisier commented: We have independently monitored HNC in comet Hale–Bopp.[1] It was detected pre-perihelion as far as 2.4 AU from the Sun. The evolution of HNC : HCN is very similar to that observed by Irvine *et al.* in their Discussion paper.

In addition, we mapped the HNC and HCN $J = 1–0$ lines with the IRAM interferometer at Plateau de Bure in March, 1997 (ref. 2). Our preliminary analysis shows that the HNC : HCN visibility ratio is larger for short interferometer baselines than for long baselines. This demonstrates that HNC has a distributed origin. We hope to derive the scale length of the HNC source from further analysis of the data. This will provide a crucial test of chemical models for the formation of HNC.

1 N. Biver *et al.*, *Earth Moon Planets*, 1998, in press.
2 J. Wink *et al.*, *Earth Moon Planets* 1998, in press.

Prof. Herbst commented: Storage ring measurements on a variety of molecular ions (H_3O^+, $CH_5{}^+$, $CH_2{}^+$, $NH_4{}^+$) show strong three-body product channels in most (but not all) cases. Assuming this to be the case for $HCNH^+$, the channel $HCNH^+ + e \rightarrow CN + H + H$ may be dominant.

Dr Stancil said: The authors modelled the formation of HCO^+ in the coma of comet C/1995 O1 (Hale–Bopp) and found that the primary formation path was through the reaction $CO^+ + H_2O \rightarrow HCO^+ + OH$. They assumed that CO^+ was produced by photoionization of CO due to the solar radiation field.

However, X-ray emission has recently been observed in a number of comets (*e.g.* C. M. Lisse *et al.*[1]). One of the most successful models for producing the X-ray emission involves charge transfer by heavy solar wind ions due to collisions with cometary neutrals such as H_2O, CO, *etc.* (*e.g.* T. E. Cravens[2]). Further, the X-ray emission radial profile peaks at nearly the same radius (10^5 km) as the observed HCO^+ column density.[3] This suggests that two other mechanisms may contribute to the ionization of CO and affect the HCO^+ abundance: $CO + \text{X-ray} \rightarrow CO^+ + e$ and $A^{q+} + CO \rightarrow A^{(q-1)+} + CO^+$ where A^{q+} is a heavy solar wind ion.

1 C. M. Lisse *et al.*, *Science*, 1996, **274**, 205.
2 T. E. Cravens, *Geophys. Res. Lett.*, 1997, **24**, 105.
3 M. J. Mumma *et al.*, *Astrophys. J.*, 1997, **491**, L125.

Prof. Owen asked: Does the gas phase chemistry model explain HNC/HCN in Hyakutake? If not, is it possible that HCN was present as such in the nucleus? Also, does the model exclude the presence of some original HNC in Hale Bopp (in addition to whatever gets made in the coma)?

Prof. Irvine replied: It is certainly interesting that neither our chemistry model nor the independent coma model developed by Rodgers and Charnley produce enough HNC to match the observations of Comet Hyakutake, in which HNC was first detected. The much lower gas production rate in this comet, compared to Hale–Bopp, results in much lower gas densities and hence less chemical processing in the coma. It is thus possible that HNC was present in the nucleus of Comet Hyakutake. However, our low limits at large heliocentric distances for the HNC : HCN ratio in Comet Hale–Bopp indicate that there was little intrinsic HNC in the nucleus of Hale–Bopp.

It would be very valuable for these investigations if laboratory experiments could be carried out to determine: (1) whether HNC might be produced by ultraviolet irradiation of HCN in a water ice matrix at temperatures typical of cometary nuclei (as low as 5 K in the Oort cloud, warmer as the comet approaches the sun); (2) whether HNC in a water ice matrix would be stable over long periods of time, or whether it would isomerize to HCN; (3) whether HNC in water ice matrix would isomerize upon sublimation; and (4) the lifetime and the photodissociation products in the solar radiation field of potential HNC precursors such as CH_2NH.

Dr Kaiser said: Concerning the formation of HNC in comets, although the reaction of HCN with H atoms *via* an H_2CN/HCNH intermediate to form HNC + H is endothermic, suprathermal H atoms, *i.e.* those with a high kinetic energy to compensate the endothermicity, can induce this isomerization. In comets, for example, the photodissociation of water molecules by solar photons produces suprathermal H atoms[1] which can react in this way. The reaction rate constant can be obtained by convoluting over (a) the wavelength and radius dependent solar photon flux, (b) the radius dependent production rate of H_2O molecules and (c) the kinetic energy of the produced H atoms.

[1] M. Heyl, Report Jül-2409, 1990.

Prof. Millar said: The fast H atom route to produce HNC from HCN is precisely the mechanism used by Rodgers and Charnley.[1] They follow the de-excitation of H atoms but still find good agreement with the observations of Comet Hale–Bopp. Unfortunately, the same process fails to account for the HNC : HCN ratio in Comet Haymaker.

[1] S. D. Rodgers and S. B. Charnley, *Astrophys. J.*, 1998, **501**, L227.

Dr Hatchell and **Prof. Millar** commented: DCN : HCN ratios similar to those in comets (0.1%) are seen in hot-cores, yet if these simply reflected the gas phase DCN : HCN ratios when ice mantles formed then we might expect to see the higher DCN : HCN ratios observed in cold dark clouds (10%) at 20 K. We have determined this ratio 'off-core' by 20 arcsec and find larger DCN : HCN ratios, more consistent with cold gas.

How do you know that the observed terrestrial and cometary DCN : HCN ratios reflect the composition of the protosolar nebula and are not altered by subsequent processing?

Prof. Owen replied: Hatchell, Millar and Rodgers[1] have found DCN : HCN values of a few $\times 10^{-3}$ in hot cores of molecular clouds. The authors favour gas-phase reactions after evaporation of gas frozen out on grains at lower temperatures to explain these ratios. They point out that values of DCN : HCN $\approx 3 \times 10^{-3}$ are consistent with ion–molecule reactions at 30–70 K (ref. 2) a point we also made.[3] We suggest the solar system formed from a clump of interstellar gas that was at a temperature of 50 ± 20 K. This temperature could be preserved in the outer solar nebula, as it corresponds to the temperature in the Uranus–Neptune region in standard models. We have demonstrated that observed ratios of $CO^+ : N_2^+$ and $CH_4 : C_2H_6$ in comets correspond to this same temperature range. This suggests that little processing occurred in comets or in the nebula prior to comet formation, a conclusion that is also consistent with the coexistence of CO_2, CH_4, CO, N_2 and NH_3 in comet ices.

1 J. Hatchell, T. J. Millar and S. D. Rodgers, *Astron. Astrophys.*, 1998, **332**, 695.
2 T. J. Millar, A. Bennett and E. Herbst, *Astrophys. J.*, 1989, **340**, 906.
3 Meier *et al.*, *Science*, 1998 and references therein.

Prof. Thaddeus commented: I believe Comet Halley was known in antiquity. If so, it has entered the inner solar system dozens or hundreds of times, and has outgassed many times. Have you considered the possibility that the lighter isotopic species (*e.g.*, H_2O, HCN) boiled off preferentially, leaving the remaining volatiles enriched in D, so that the D : H ratio today is higher than when the comet was in the Oort belt?

Prof. Owen responded: The sublimation of a solid into space is not expected to change the isotope ratio in the residual solid. This expectation has just been demonstrated in the laboratory for H_2O and HDO by Bar-Nun and his colleagues at the University of Tel Aviv. Evidently the D/H values observed in cometary ices were set in the Interstellar Medium. This conclusion receives additional support from the observation that D/H in H_2O was found to be the same in Hale Bopp, Hyakutake and Halley, despite the fact that Halley has approached the sun many more times than the other two comets, as Dr Thaddeus points out.

Prof. Irvine said: We don't really know the densities of cometary nuclei well, but some models suggest that they are quite porous. In this case, sublimation could lead to migration of volatiles inward and to some isotopic fractionation. However, the very large D/H fractionation seen from HCN certainly seems to indicate the presence of interstellar material.

Dr Ehrenfreund said: Large amounts of oxygen and nitrogen are apparently unaccounted for in the interstellar gas. New estimates of the oxygen budget, assuming the revised oxygen abundance for the local interstellar medium, show that about 35% of the total oxygen is incorporated in silicates and refractory material, up to 20% in CO gas, up to 10% in H_2O gas and a large fraction of oxygen may be present in oxygen-bearing ice species such as H_2O, CO, CO_2 and others. The remaining oxygen is either present in atomic or molecular form in the interstellar gas, though current observations indicate very little molecular oxygen in the interstellar gas. On the contrary, nitrogen is assumed to be dominantly present in molecular form in the interstellar gas. What do these interstellar measurements imply for the oxygen and nitrogen depletions in comets?

Prof. Owen responded: The current explanation of the nitrogen budget in the interstellar medium suggests that most ($\approx$ 70%) of the nitrogen is present as N_2. This suggestion is based on studies of HNN^+, which can be observed at radio frequencies, while N_2 cannot. We assume that nitrogen in the outer solar nebula was also dominated by N_2. Our laboratory experiments show that N_2 is not easily incorporated in ice forming at ≈ 50 K. Thus, we predict that N/Si in comets will be less than the solar value, which is exactly what the Halley observations by Giotto show. This picture is also supported by ground-based evaluations of $N_3^+ : CO^+$ in tails of two other comets. There is not yet any evidence for O_2 in comets, which is consistent with the low values Dr Ehrenfreund reports for the interstellar medium. O/Si is found to be solar in comets. The atomic oxygen in comets appears to come predominately from dissociation of H_2O. Nevertheless, continued searches for trace ($< 1\%$) amounts of O_2 in comets seems worthwhile.

Dr Crovisier responded: Molecular oxygen (O_2) cannot be observed spectroscopically in comets. A recent re-analysis of the measurements of comet Halley by the ion mass spectrometer (NMS) on Giotto yields an upper limit of 0.5% of O_2 relative to water.[1]

[1] A. Léger, M. Ollivier, K. Altwegg and N. J. Woolf, 1998, in preparation.

Prof. Thaddeus commented: The readily observed, interstellar ions HNN^+ and $HCO_2{}^+$ have long provided an indirect determination of the amount of the ratio invisible N_2 and CO_2. Both ions are made by the fast ion–molecule reaction, $H_3{}^+ + X \rightarrow XH_2 + H_2$. HNN^+ is found in many sources, HCO_2^+ in only one. From this it has been deduced that much of the interstellar N is in N_2, but little of the C is in CO_2.

Prof. van Dishoeck said: Indeed, both N_2H^+ and $HCOO^+$ are good tracers of N_2 and CO_2, as pointed out by Prof. Thaddeus and Prof. Herbst nearly two decades ago. The analysis of such data is still model dependent, however. For example, McGonagle *et al.*[1] and Womack *et al.*[2] use N_2H^+ 1–0 and 3–2 observations to derive that on average about 10% of the nitrogen is in the form of N_2 in dense clouds. On the other hand, van Dishoeck *et al.*[3] and de Boisanger *et al.*[4] obtained observations of higher excitation lines in smaller beams and find that for at least one region nearly 100% of the nitrogen is in the form of N_2. This difference between 10% and 100% is very important for accounting for the total nitrogen budget in interstellar clouds.

Note also that we have searched for $HCOO^+$ (sub)millimeter lines in some of the same clouds for which we have detected gas-phase CO_2, but have only obtained upper limits so far. Thus, the direct observation of gas-phase CO_2 by infrared absorption lines is a more sensitive method than the indirect search for the (sub)millimeter lines of $HCOO^+$, provided that an infrared source is present.

[1] McGonagle, W. M. Irvine, Y. C. Minh and L. M. Ziurys, *Astrophys. J.*, 1990, **359**, 121.
[2] M. Womack, L. M. Ziurys and S. Wyckoff, *Astrophys. J.*, 1992, **387**, 417.
[3] E. F. van Dishoeck, T. G. Phillips, J. Keene and G. A. Blake, *Astron. Astrophys.*, 1992, **261**, L13.
[4] C. de Boisanger, F. P. Helmich and E. F. van Dishoeck, *Astron. Astrophys.*, 1996, **310**, 315.

Dr Bernstein said: In her paper Dr Ehrenfreund estimated that in many clouds as much as 10% of the nitrogen could be in the form of N_2 and in at least one case (NGC 2264 IRS4) virtually all of the nitrogen may be in the form of N_2 (see also ref. 1). In light of this I thought that it would be appropriate to mention our latest work on the infrared spectra of N_2 containing interstellar ice analogues made for comparison to ISO spectra.

I remind you that being a symmetric diatomic molecule (having no dipole moment) gas phase N_2 is completely inactive in both the infrared and microwave and the N=N stretch at 2328.2 cm^{-1} (4.295 μm) is very weak even in solid state. For example, the intrinsic strength for this peak in pure N_2 is *ca.* 10^{-22} cm $(N_2)^{-1}$, or approximately one ten thousandth that of CO. This makes it difficult to establish the presence of N_2, even if it is an abundant molecule. In addition, this nitrogen feature falls within four wavenumbers of the asymmetric stretch of oxygen-18 CO_2 (a normal but minor isotopomer seen in the **ISO** spectra) and right on a photospheric CO line, so this is a really tough molecule to identify unambiguously.

There is hope, however. Our latest results demonstrate that the strength of the infrared N═N stretching feature near 2328 cm^{-1} (4.295 μm) is extremely sensitive to the composition of the ice. The intrinsic strength of this nitrogen feature is greatly enhanced when CO_2 is present, in some cases by factors of hundreds. The intensity of the nitrogen peak is also slightly enhanced in mixtures containing H_2O and NH_3, but essentially unaffected by the presence of CO, CH_4 or O_2. The implications of these results for the identification and quantification of N_2 are profound. This will make it much easier to detect the presence of molecular nitrogen, but more difficult to determine amounts. Quantitative measurements of N_2 based on its fundamental will require knowledge of the other constituents of the ice and appropriate laboratory data for comparison.

We have the laboratory data, so I would like to use this as an opportunity to encourage those that have **ISO** data in this region, especially towards field stars, where the cloud is quiescent, to look for this feature near 2328 cm^{-1} (4.295 μm) and if you see it let us know, we think that we can fit it and that it would make a very good piece of collaborative work.

1 J. Elsila, L. J. Allamandola and S. A. Sandford, *Astrophys. J.*, 1997, **479**, 818.

Dr Leach said: In your paper you state that it is reasonable to assume that some water in the Earth's interior emerged after the catastrophic formation of the moon, mixing with water of cometary origin to form the oceans. Is the emergence of the water from the Earth's interior due in some way to moon formation, or to some other catastrophic event?

Prof. Owen responded: The water that emerged from the Earth's interior after the formation of the moon probably came out gradually, by volcanism and other degassing processes associated with the action of plate tectonics. No catastrophic events are required.