

### General Discussion

Introducing his paper **Dr Sorokin** said: In our paper the photon mechanism shown in Fig. 4 was proposed to explain selective enhancement of the  $\lambda 5797$  and  $\lambda 6379$  DIB intensities. In this mechanism, coherent VUV Stokes-wave emission was assumed to occur on the transition B0-0P3. Although spectral evidence for such an emission band appears to be present in the low-resolution Copernicus VUV spectrum of  $\beta$  Ori A (see Fig. 11 of our paper), a prominent emission band peaking at the exact B0-0P3 wavelength (1115.9 Å) is not seen in the high-resolution Copernicus VUV spectrum of the same star that is shown in ref. 27. Therefore, it has become necessary for us to reexamine this situation and to try to find another mechanism capable of ‘feeding’ molecules to virtual quantum levels surrounding  $J' = 2$  of B0.

One such mechanism, shown in Fig. 1 here, appears to possess a number of conceptual advantages. In this new scheme, virtual quantum levels surrounding  $J' = 2$  of B0 are strongly fed from an excited vibrational level ( $J'' = 1$  of X2) by Ly- $\alpha$  photons trapped by elastic scattering in the cloud of our model. (The radiative strength of B0-2R1 is approximately fourteen times that of B0-0P3.) Molecules are driven from

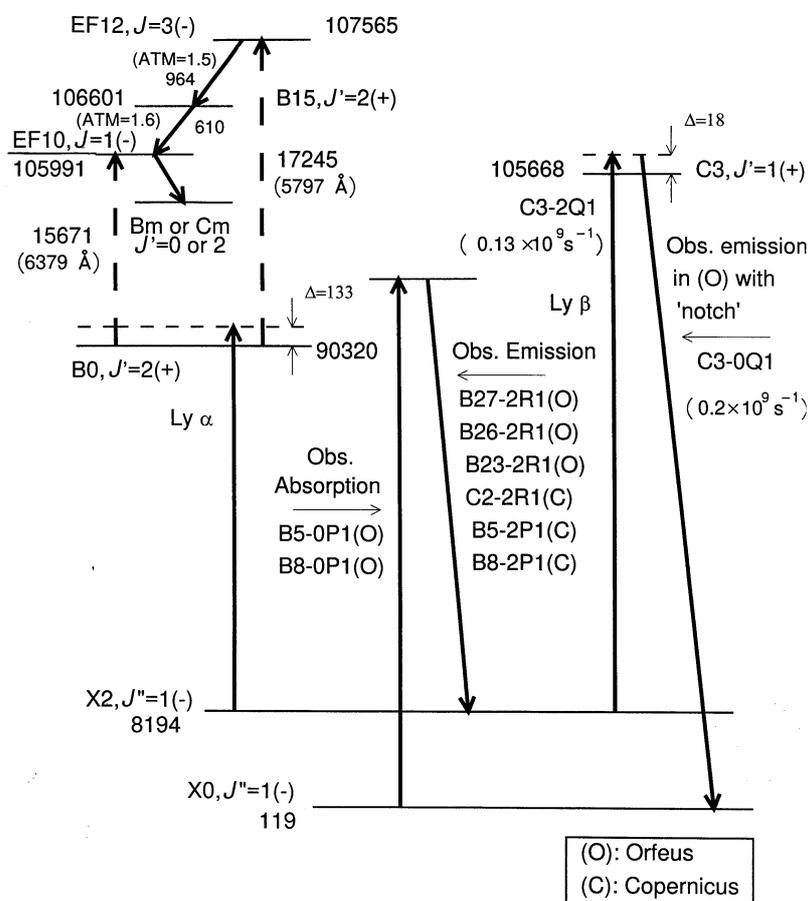


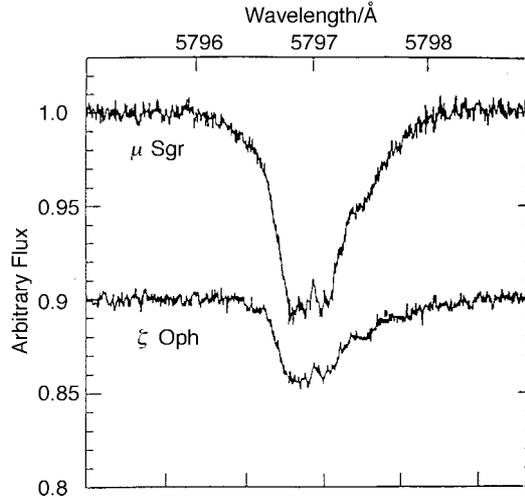
Fig. 1 New photon mechanism proposed for exciting virtual quantum levels around  $J' = 2$  of B0

$J'' = 1$  of X0 to  $J'' = 1$  of X2 as part of the four-wave mixing process shown on the right. Spectral evidence of the existence of components of this four-wave mixing process is indicated in the figure.

With this new scheme, one can also accurately account for the ‘notches’ that are observed on the  $\lambda 5797$  and  $\lambda 6379$  DIB profiles. Fig. 2 shows the very high resolution spectra of the  $\lambda 5797$  DIB profile that are presented in ref. 13. (Since the existence of the  $\lambda 5797$  ‘notch’ was first clearly revealed in this study, and since four of the six authors of this work hailed from Nottingham University, it seems appropriate that this spectral feature be designated ‘Nottingham Notch’!). The explanation for the notches in the scheme in Fig. 1 relies upon the fact that the narrow spectral portion of the Ly- $\alpha$  radiation that is exactly resonant with the ‘Doppler core’ of the B0-2R1 transition can, in principle, be directly absorbed in three-photon transitions originating from  $J'' = 1$  of X0 and terminating on  $J' = 2$  of B0. This would, in turn, leave less Ly- $\alpha$  radiation at these frequencies available for feeding virtual quantum levels of the  $J' = 2$ , B0 intermediate state in the inverse Raman absorption mixing processes proposed in the text as the sources of the  $\lambda 5797$  and  $\lambda 6379$  DIBs. A direct consequence of this diminished Ly- $\alpha$  flux resonant with the H<sub>2</sub> B0-2R1 Doppler core should be the appearance of notches in the spectral profiles of these DIBs. According to this scheme, the width of the ‘Nottingham Notch’ in any line-of-sight provides an accurate measurement of the H<sub>2</sub> Doppler width in the cloud in which the DIBs are actually produced.

The intrinsic profiles of most narrow DIBs that have been carefully studied are devoid of sharp spectral structure. An example is the very strong, narrow DIB at 7224 Å. We have very recently assigned this DIB to the inverse Raman process shown in Fig. 3. In Fig. 3, the *ca.* 10.75  $\mu\text{m}$  broadband IR radiation which ‘feeds’ virtual quantum levels around  $J' = 5$  of B11 is considered to be one of the two waves generated in a simultaneous two-photon emission process [EF7,  $J = 4$ ]  $\rightarrow$  [EF4,  $J = 4$ ]. Since the profile of this IR radiation should be spectrally smooth, the spectral profile of the 7224 Å inverse Raman absorption band should also be smooth, as is observed.<sup>1</sup>

Also shown in Fig. 3 is the same transition to which the strong DIB at 6284 Å was assigned in the text. However, the optical pathway shown in Fig. 3 feeding the quantum level EF4,  $J = 4$  seems more convincing to us than the one proposed in our paper (see



**Fig. 2**  $\lambda 5797$  DIB spectral profiles from ref. 13 of our paper (reproduced with kind permission from P. J. Sarre, J. R. Miles, T. H. Kerr, R. E. Hibbins, S. J. Fossey and W. B. Somerville, *Mon. Not. R. Astron. Soc.*, 1995, **277**, L41).

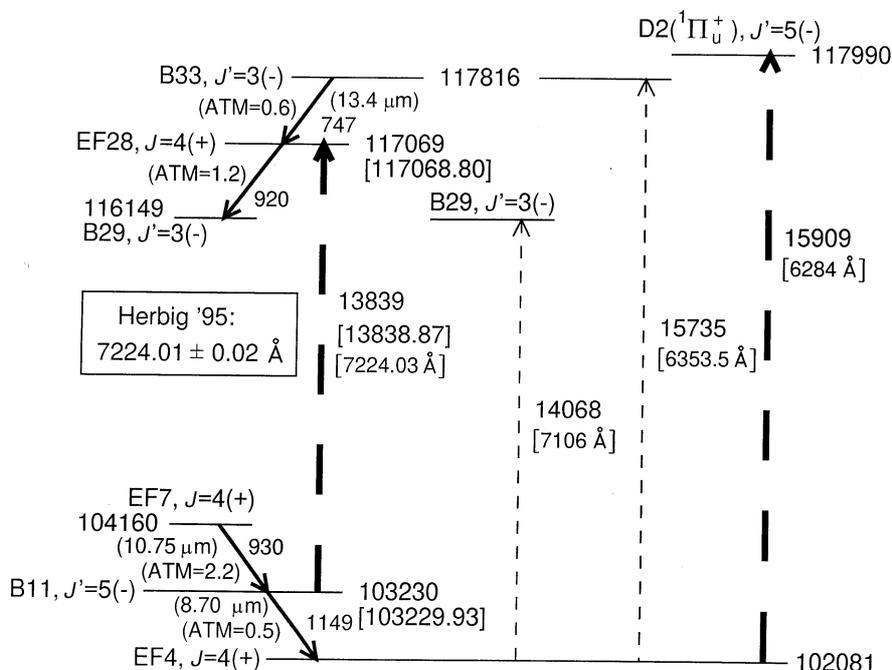


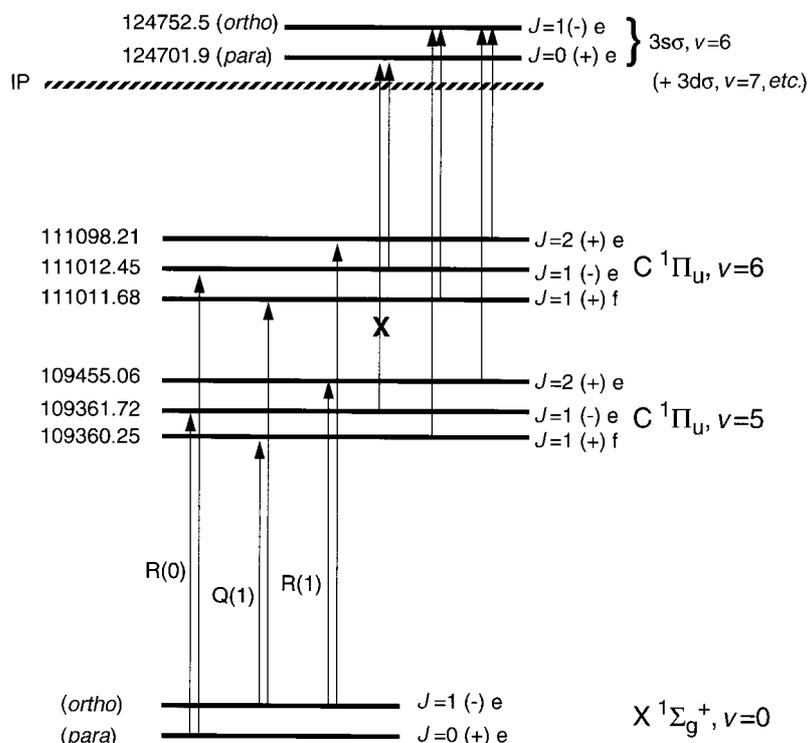
Fig. 3 Proposed assignment for λ7224 DIB

Fig. 23). Also shown in Fig. 3 are the transitions to which we have recently assigned two more DIBs. All four DIB assignments shown in Fig. 3 again illustrate a main theme that has evolved from our Faraday Discussion paper, namely, if a detectable inverse Raman absorption is to occur on a given H<sub>2</sub> inter-Rydberg transition, a ‘push-pull’ situation must prevail as a necessary condition. If the lower level of the transition happens to be a *gerade* quantum level, there must both be present a coherent light wave strongly populating this level and a broadband coherent light wave spectrally centered about a downward transition from the upper level. If the lower level is an *ungerade* quantum level, there must exist both a broadband coherent light wave ‘feeding’ virtual quantum levels surrounding this level as well as another coherent light wave actually originating from the upper level.

1 Herbig and Soderblom, *Astrophys. J.*, 1982, **252**, 610.

**Dr Ubachs** said: Following up on the laboratory observation of coincidences between pronounced inter-Rydberg transitions in H<sub>2</sub> with five diffuse interstellar bands, shown in Fig. 5 of our paper, we present some preliminary results from a multichannel quantum defect theory (MQDT) calculation performed with E. Reinhold, Ch. Jungen and S. C. Ross. As shown in the energy diagram of Fig. 4 here the five coincident resonances originate from the  $J = 1(f)$ ,  $J = 1(e)$  and  $J = 2(e)$  levels of the  $C^1\Pi_u$ ,  $v = 5$  and  $v = 6$  vibronic states, which couple *via* strong transitions in the XUV-domain to the lowest *para*- and *ortho*-levels in the  $X^1\Sigma_g^+$ ,  $v = 0$  electronic ground state of molecular hydrogen. Values for C-state energies are obtained from a high-resolution study of Reinhold *et al.*<sup>1</sup> As for the terminal levels of the two-photon absorption only one autoionizing level for both *para*- and *ortho*-hydrogen is involved (see Fig. 4).

In the MQDT calculations it is established that the level in *para*-hydrogen at 124 701.9 cm<sup>-1</sup> (above  $X^1\Sigma_g^+$ ,  $v = 0$ ,  $J = 0$ ) is a  $J = 0(e)$  level of (+) parity, while the

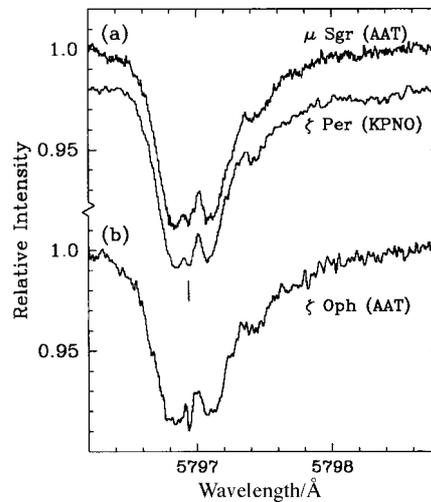


**Fig. 4** Energy level diagram, not to scale, pertaining to the five coincidences between observed inter-Rydberg transitions in  $H_2$  and DIBs. A sixth resonance originating in  $C^1\Pi_u, v=5, J=1(e)$  does not coincide with a documented DIB.

level in *ortho*-hydrogen at  $124752.5\text{ cm}^{-1}$  is a  $J=1(e)$  level of  $(-)$  parity. The terminal levels are Rydberg states, predominantly consisting of an  $X^2\Sigma_g^+, v=6$  core with a 3s Rydberg electron. Also some  $3d_s, v=7$  character is mixed in. The MQDT calculations confirm that for both *para*- and *ortho*-hydrogen there exists only one strong resonance in a frequency span of  $1000\text{ cm}^{-1}$ , namely the ones coinciding with the resonances observed in the double-resonance laser excitation study. The oscillator strength of transitions originating in  $C^1\Pi_u, v=6$  is found to be very high. These two conditions, strong and lone transitions from a specific state, are of importance for an explanatory model for the DIBs.

1 E. Reinhold, W. Hogervorst and W. Ubachs, *J. Mol. Spectrosc.*, 1996, **180**, 156.

**Prof. Sarre** said: We have just published<sup>1</sup> high-resolution and high signal-to-noise spectra of the  $\lambda 5797$  diffuse interstellar band, recorded along three lines of sight using the AAT and KPNO telescopes (see Fig. 5). This has revealed a considerable amount of structure, including clear evidence for a narrow absorption ‘spike’ near  $5796.9\text{ \AA}$ . The wavelength of the molecular hydrogen transition quoted by the authors is  $5796.96\text{ \AA}$  which is close to our reported rest wavelengths of  $5796.942$  and  $5796.945\text{ \AA}$  towards  $\mu\text{ Sgr}$  and  $\zeta\text{ Per}$ , which are deduced by reference to the K I line. Under the current proposal of molecular hydrogen as a carrier of diffuse bands, the entire  $\lambda 5797$  profile including its shape, width and fine structure arises from a single R(2) rovibronic line. My suggestion is that the problem is turned around and rather we should consider what is established and use this to predict the spectrum which would be expected for molecular hydrogen bathed in UV light to provide the initial excitation, with subsequent absorp-



**Fig. 5** Ultra-high-resolution spectra of  $\lambda 5797$  (a) toward  $\mu$  Sgr (AAT) and  $\zeta$  Per (KPNO) and (b) toward  $\zeta$  Oph (AAT). The vertical line indicates the position of the ‘spike’. Reproduced with permission from T. H. Kerr, R. E. Hibbins, S. J. Fossey, J. R. Miles and P. J. Sarre, *Astrophys. J.*, 1998, **495**, 941.

tion of visible photons. This predicted spectrum can then be sought through observations at high-sensitivity and high-resolution. It is conceivable that the sharp ‘spike’ might be due to  $H_2$  as this represents only a very small part of the  $\lambda 5797$  band, but at present it is hard to see how the rest of the observed band could arise from this transition in molecular hydrogen.

1 T. H. Kerr, R. E. Hibbins, S. J. Fossey, J. R. Miles and P. J. Sarre, *Astrophys J.*, 1998, **495**, 941.

**Dr Sorokin, Dr Glowina and Dr Ubachs** commented: After struggling to find a reasonable explanation for the ‘Nottingham Notch’, we learned that Prof. Sarre and colleagues have very recently reported new, refined measurements of the  $\lambda 5797$  DIB profile<sup>1</sup> which show the detailed spectral structure of this DIB to be rather different from that described in their previous study. The main ‘notch’ (feature *b* in Fig. 2 of their new study) is still present, but it appears shifted to slightly longer wavelengths (*ca.* 5797.0 Å) in the rest frame spectrum adopted in the new study. Immediately bordering the main notch on the high-frequency side, there now appears a remarkably sharp ‘spike’ of increased DIB absorption (feature 0 in Fig. 2 of their new study). There are also evident smaller notches (*i.e.* decreased DIB absorption) at *a* and *c*.

We have tried to think of suitable explanations for this newly revealed spectral structure based upon the scheme shown in Fig. 1. One possibility is that the trapped Ly- $\alpha$  continuum in the cloud has had small ‘bites’ taken out of it by impurity atoms present somewhere between the  $H_2$ -containing cloud and the bright illuminating star. Such ‘absorptions’ (*i.e.* elastic scatterings) would have to occur very close to the B0-2R1 frequency, 82 155.21  $\text{cm}^{-1}$  (1217.208 Å). A check of simple atoms such as O I, N I, C I, *etc.*, reveals no lines in this vicinity. None of the tabulated absorption lines of CO were also found to match. The fact that the Nottingham group observed almost identical spectral profiles for the  $\lambda 5797$  DIB in three different lines-of-sight (with the use of two widely separated telescopes), even with regard to the sharp features just mentioned, strongly argues against such an ‘impurity’ effect.

One might think generally that if the spectral structure is intrinsically due to molecular hydrogen, there necessarily would have to exist other  $H_2$  transitions located very



There is actually a severe intensity anomaly connected with the  $\lambda 6376$  assignment shown in Fig. 6 which is instructive to discuss. Despite the fact that the calculated radiative transition strength of B1-2P5 is twice that of B0-2R1, that its offset from the peak of the trapped Ly- $\alpha$  radiation spectrum is five times less, that the upper state for the inter-Rydberg transition to which the  $\lambda 6376$  DIB is assigned is the same as for the  $\lambda 5797$  DIB, and that the calculated ATM for the (EF12,  $J = 3$ )  $\leftrightarrow$  (B1,  $J' = 4$ ) transition is about six times greater than the calculated ATM for the (EF12,  $J = 3$ )  $\leftrightarrow$  (B0,  $J' = 2$ ) transition, the equivalent width of the  $\lambda 6376$  DIB is, as noted above, roughly five times less than that of the  $\lambda 5797$  DIB.

A possible explanation for this anomaly is provided by assuming that the coupling between the trapped Ly- $\alpha$  radiation and the transition B1-2P5 is strong enough so that the Ly- $\alpha$  radiation is able to excite a broadband SRS process from the X2,  $J'' = 5$  quantum level to some other X-state quantum level. This would lead to decreased absorption of *ca.* 6376 Å photons *via* the inverse Raman absorption process shown in Fig. 6, since a fraction of the Ly- $\alpha$  photons necessary for this process would be utilized in pumping the SRS process. In addition, the effect analyzed in ref. 19 of our paper, namely, the drastic reduction in two-photon absorption intensity that can occur in a three-level system when the intermediate state is radiatively coupled to a fourth state, might also play a role here.

At present, the only evidence we have of the quantum level (X2,  $J'' = 5$ ) being involved in an n-wave mixing process is the intense VUV emission band dominating the 1062–1080 Å spectral region in the high-resolution Copernicus  $\beta$  Ori A spectrum of ref. 27 in our paper. This band is the same band assigned as B9-2R1 in Fig. 12 and 14 of our paper. However, the high-resolution spectrum of ref. 27 definitely shows the peak occurring at 1078.25 Å, not at the wavelength (1078.40 Å) of B9-2R1. The only nearby H<sub>2</sub> transition is B10-2R5 at 1078.27 Å, and we have re-assigned the 1078.25 Å peak to this transition. Again, this illustrates the necessity for having extreme wavelength accuracy in seeking to interpret astrophysical data with the H<sub>2</sub> DIBs model. On the basis of ref. 27, we have already had to change many of the VUV emission band assignments made in our paper. However, although we seem to be continually proposing new excitation mechanisms for the DIBs, the actual assignments we have made of many narrow DIBs to H<sub>2</sub> inter-Rydberg transitions have not changed that much. To us, this is simply a reflection of the accuracy and precision with which astronomers have characterized the total DIB spectrum. It remains a remarkable template for evaluating astrophysical theories.

- 1 T. H. Kerr, R. E. Hibbins, S. J. Fossey, J. R. Miles and P. J. Sarre, *Astrophys. J.*, 1998, **495**, 941.
- 2 U. Fano, *Nuovo Cimento*, 1935, **12**, 156.

**Dr Schutte** said: Since ISO and IRTF, spectroscopy of the diffuse galactic emission in the mid-infrared region of the spectrum has become possible. These data show the well known specific UIR emission bands at 6.2, 7.7, 8.6 and 11.2  $\mu\text{m}$ , with no indication of additional features.<sup>1</sup> The UIR features have been identified with various vibrational modes of polycyclic aromatic hydrocarbons.<sup>2</sup> Where would the energy absorbed by H<sub>2</sub> and/or carbon-chains in the visual and possibly ultraviolet part of the spectrum be re-emitted? Would carbon chains show specific infrared features corresponding to the characteristic vibrational modes of the chain structure? Would the presence of the H<sub>2</sub>/carbon chain emission still be consistent with the ISO observations?

- 1 K. Mattila, D. Lemke, L. K. Haikala *et al.*, *Astron. Astrophys.*, 1996, **315**, L35; T. Onaka, I. Yamamuna, T. Tanabé, T. L. Roellig and L. Yuen, 1996, *Publ. Astron. Soc. Pac.*, 1996, **48**, L59.
- 2 A. Léger and J. L. Puget, *Astron. Astrophys.*, 1984, **137**, L5; L. J. Allamandola, A. G. G. M. Tielens and J. R. Barker, *Astrophys. J.*, 1985, **290**, L25.

**Prof. Maier** responded: The UIR features are the result of an overlap of IR transitions of many species. Carbon chains would contribute like other molecules to the IR

emission. Our study of the electronic spectrum of  $C_7^-$  in the visible, has concerned itself with merely one such chain, but numerous other, including hydrogen, nitrogen and oxygen containing derivatives would also contribute to IR emission.

**Prof. Thaddeus** said: I have only one comment to make on the wonderful work of Prof. Maier and his group: it is too good to be wrong. In the long literature on the interstellar diffuse bands, no identification has been made which is remotely as convincing as the assignment here of  $C_7^-$ .

Dr Schutte has asked where the energy absorbed by a DIB ends up—how is it rerradiated? It is rerradiated by the entire vibrational spectrum of a carbon chain, but mainly by the bond stretches, C—C, and C—H, and so blends into the fuzz of the UIR bands between 3 and 8  $\mu\text{m}$ .

**Dr Sorokin, Dr Glowonia and Dr Ubachs** commented: Our current  $H_2$  DIBs model does indeed predict coherent generation of broadband ( $10\text{--}100\text{ cm}^{-1}$  bandwidth) VUV and IR radiation at several frequencies. This generation is viewed as occurring in each of the (two-photon) steps comprised by the  $2n$ -wave mixing processes discussed in our paper. For example, the four-wave mixing process shown in Fig. 18 of our paper would predict generation of coherent IR light at *ca.* 6.2  $\mu\text{m}$  occurring as Stokes-wave emission in a broadband stimulated Raman scattering (SRS) process pumped by incoherent VUV light spectrally centered on the transition C4-0R0 at 929.5  $\text{\AA}$ . As explained at the beginning of our paper, one expects an enormous enhancement of the VUV photon density that is nearly resonant with C4-0R0 to result from the complete dominance of elastic (Rayleigh) scattering over inelastic scattering (*i.e.* ‘absorption’) in the cloud of our model. The wave mixing process shown in Fig. 18 also predicts generation of coherent broadband IR light in a band centered at *ca.* 8.4  $\mu\text{m}$  and generation of a similar bandwidth of coherent VUV light spectrally centered on the transition B13-0R0 at 954.4  $\text{\AA}$ . In the process shown in Fig. 18, absorption of a photon from the incoherent VUV pumping field and coherent emission of the three photons that are produced are to be visualized as occurring simultaneously, with total photon energy and total photon momentum being rigorously conserved in the overall process. The latter condition can be satisfied only if the four waves in Fig. 18 are co-propagating collinearly.

The scheme shown in Fig. 18 of our paper was suggested by the apparent presence of an  $H_2$  VUV emission peak at *ca.* 954.4  $\text{\AA}$  (see Fig. 19) and by the favorable calculated transition strengths shown in Fig. 18. A subsequent, more careful, examination of the spectrum shown in Fig. 19 revealed that the peak actually occurs at 954.47  $\text{\AA}$  and that it is apparently necessary to correct all wavelengths in this range by adding *ca.* 0.07  $\text{\AA}$ . This would position the peak at *ca.* 954.54  $\text{\AA}$  ( $104\,763\text{ cm}^{-1}$ )—about  $14\text{ cm}^{-1}$  less than the B13-0R0 frequency ( $104\,777\text{ cm}^{-1}$ ). The correct assignment of the emission peak here being considered could thus more likely be the transition D0-2R3 with frequency at  $104\,763\text{ cm}^{-1}$ . (The strong transition B25-2R3 is offset by only  $7\text{ cm}^{-1}$  from Ly- $\alpha$ , which would allow effective depopulation of X2,  $J'' = 3$ ). In this case, the scheme of Fig. 18 becomes irrelevant. This example illustrates once more the crucial need for obtaining astrophysical spectra that possess high signal-to-noise ratios, are taken at the maximum spectral resolutions that are technically available, and are precisely calibrated in terms of rest frame wavelengths. Of the archived VUV spectra analyzed in our paper, the high-resolution Copernicus VUV spectrum of  $\beta$  Ori A presented in ref. 27 turns out to be superior to all the others in these three respects. The one serious drawback of the archived Copernicus spectra we have examined is the fact that the detectors evidently ceased to respond at wavelengths shorter than *ca.* 1000  $\text{\AA}$ .

In the text of our original  $H_2$  DIBs paper<sup>1</sup> we went to extremes in ‘assigning’ most of the known UIR (UIB) emission bands as Stokes-waves in  $H_2$  SRS processes that *a priori* would be expected to have strong transition probabilities. However, in the ‘Note

Added in Manuscript' included in the same paper, we subsequently strongly cautioned the reader against accepting these assignments. At the present time, we simply must conservatively speculate that there is perhaps some component of the UIR emission band spectrum that is observed in some lines-of-sight that may be due either to H<sub>2</sub> SRS Stokes-wave generation or to parametric oscillation (the second two-photon step shown in the scheme of Fig. 18). Wavelengths of infrared emission bands that might plausibly be generated with the H<sub>2</sub> DIBs model can be seen in several of the other figures contained in our Faraday Discussion paper or in our earlier comment about our own paper. From Fig. 15 of our paper, one would predict broadband IR generation at 10.86  $\mu\text{m}$  and 3.47  $\mu\text{m}$ . From Fig. 21, IR generation at 8.45  $\mu\text{m}$  is predicted. From the scheme in Fig. 24, IR generation at 9.64  $\mu\text{m}$  seems most likely, although generation at 11.88  $\mu\text{m}$  is also predicted. From Fig. 3 earlier, IR generation at 13.4, 10.87, 10.75 and 8.70  $\mu\text{m}$  is likely. To try to find any real evidence of such broadband H<sub>2</sub> IR emissions, one might consider carefully probing lines-of-sight to unreddened bright, young stars.

1 P. P. Sorokin and J. H. Glowina, *Astrophys. J.*, 1996, **473**, 900.

**Dr Somerville** communicated: Astronomers are not irrationally prejudiced against the H<sub>2</sub> model for diffuse interstellar bands, but concerned about serious astrophysical implications of the model of which the authors seem not to be aware. One difficulty with a circumstellar model for the DIBs, pointed out before, is that DIB strengths are rather well correlated with the interstellar dust abundance, as measured by the reddening  $E(B - V)$ . Sorokin has responded to this, with an ingenuity that can only be admired, by arguing that because the DIB carrier is circumstellar so must the dust be, actually producing scattering of starlight that leads to DIB formation so that, as observed, DIB strength increases with the amount of dust.

The problem with this is that it is not only the diffuse bands that are correlated with  $E(B - V)$ , but so is everything else associated with what we call the diffuse interstellar medium along the line-of-sight, including atoms as well as other molecules. All the evidence indicates that the gas and dust are well mixed—not just correlations but for example the observed depletions of gas-phase atoms onto the dust grains. Properties of this gas are not consistent with it being bathed in a strong circumstellar ultraviolet flux. It is of low density, clumped into clouds, and must be distributed in space.

Several strong DIBs including  $\lambda 4428$ , 5797, 5780 and 6283 correlate well with the dust and cannot therefore be primarily of circumstellar origin. However, correlation studies have been carried out only for a relatively small number of the strongest features and the diffuse bands do not vary all together.<sup>1</sup> It is therefore not impossible that some of the weaker absorptions, observed so far in a few sightlines, may be produced only in circumstellar regions.

1 W. B. Somerville, in *The Diffuse Interstellar Bands*, ed. A. G. G. M. Tielens and T. P. Snow, Kluwer, Dordrecht, 1995, p. 83.

**Dr Sorokin, Dr Glowina and Dr Ubachs** communicated: In our H<sub>2</sub> nonlinear DIBs model, it appears no longer necessary to assume that the H<sub>2</sub>-containing cloud is circumstellar. If a thin 'planar' cloud containing at least *ca.*  $10^4 \text{ cm}^{-3}$  H<sub>2</sub> molecules and as many H atoms were located *ca.* 10 pc from an O- or B-type star, the enhancement in the near-resonant VUV photon density might well be high enough for sufficient SRS Stokes-wave gain to develop in some direction lying in the 'plane' of the cloud for coherent lightwave generation to occur, particularly if the cloud subtended a large solid angle about the star. Such a geometry is not totally unlike some of the models that were considered for the H<sub>2</sub>-containing cloud seen toward  $\zeta$  Oph, see for example ref. 1. In the line-of-sight to this star, velocity shift measurements show that it is possible to associate all of the observed absorption lines of known species with one (or more) of six different

velocity clouds. It thus would appear that towards  $\zeta$  Oph, at least, the interstellar gas can hardly be viewed as being 'well mixed'.

1 D. C. Morton, *Astrophys. J.*, 1975, **197**, 85.

**Prof. Krelowski** commented: It seems necessary to create good criteria for the identification of interstellar features. This task requires a close co-operation between experimentalists and observers. It is apparently impossible to compare astrophysical and matrix spectra as inside any possible wavelength inaccuracy caused by the matrix shift we observe up to several tens of unidentified features. It is interesting to observers whether they should expect similar profiles and/or intensity ratios of the features originating in one, even very complicated, molecule.

Concerning the proposed sequence of the  $C_7^-$  chain: the observed features do not obey the above-mentioned criteria: they barely match the wavelengths. Also the violet/blue features from the other electronic transition of  $C_7^-$  are not observed. This creates doubts concerning the proposed identification.

**Prof. Maier** responded: There seems to be a misunderstanding. We are not comparing astrophysical and matrix spectra. We present a gas-phase electronic spectrum of  $C_7^-$ , measured in the laboratory at rotational temperatures below 100 K (see Fig. 5 of our paper), and compare the band wavelengths with the DIB values given in the compilation of Jenniskens and Désert.<sup>1</sup> These wavelengths match very well as can be seen in Table 3 of the paper. The error limits given for the laboratory measurements ( $\pm 0.2$  nm) are deliberately conservative—the band maxima have been determined to  $\pm 0.05$  nm. The reason for this is stated in the paper—the band maxima will shift with temperature. The intensities in the gas-phase spectrum presented are not reliable because of saturation by the lasers (leading to band broadening). The absorption spectrum of  $C_7^-$  measured in a neon matrix gives a more realistic impression of the relative intensities.

$C_7^-$  does show another transition to the blue,  $B^2\Pi-X^2\Pi$ . The origin band is located at 493 nm in the gas-phase, but all the bands are much broader (2–3 nm) than for the  $A^2\Pi-X^2\Pi$  transition, due to intramolecular processes. These corresponding DIBs would be comparably broad and most of them happen to lie in regions where strong stellar or telluric lines are present; *i.e.* origin band near 493 nm,  $3_0^1$  near 480 nm,  $1_0^1$  near 448 nm.

1 P. Jenniskens and F.-X. Désert, *Astron. Astrophys. Suppl.*, 1994, **106**, 39.

**Dr Halasinski** communicated: The gas-phase experimental measurements reported by Prof. Maier for carbon chains represent an exciting step in the experimental approach to the DIB problem. The relatively small shift measured between the neon matrix and the gas-phase spectrum of  $C_7^-$  is very encouraging. It tends to support the recent consensus on carbon-bearing molecules and ions as carriers of the DIBs. We would like to add that, in addition to the proposed carriers discussed in this session, several PAH cations have been proposed as possible carriers for the DIBs, as has been amply discussed in the literature.<sup>1,2</sup> The comparisons in Table 1, made in neon matrices, do provide as good a match to several DIBs as those of the carbon chains in neon.<sup>3</sup> Thus, we wish to point out that, in view of the experimental results reported by Prof. Maier, gas-phase PAH cations are also expected to provide the same quality of match with some of the DIBs.

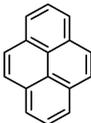
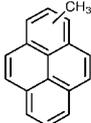
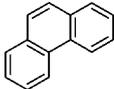
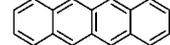
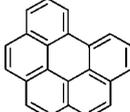
1 F. Salama, C. Joblin and L. J. Allamandola, *Planet. Space Sci.*, 1995, **43**, 1165.

2 F. Salama, E. L. O. Bakes, L. J. Allamandola and A. G. G. M. Tielens, *Astrophys. J.*, 1996, **458**, 621.

3 P. Freigovel, J. Fulara and J. P. Maier, *Astrophys. J.*, 1994, **431**, L151.

**Dr Krelowski** said: Large molecules are very likely to produce spectra with one strong and several much weaker features. This general picture may fit the observational

**Table 1** Comparison of DIBs with PAH cation bands PAHs isolated in neon matrices (reprinted from *Planetary Space Sci.*, 1995, **43**, 1165 with permission from Elsevier Science).

PAH <sup>+</sup>		$\lambda_{\text{peak}}/\text{nm}$	DIBs/nm
pyrene (C <sub>16</sub> H <sub>10</sub> <sup>+</sup> )		439.5 (443.0 in Ar)	442.9
1-methylpyrene (CH <sub>3</sub> -C <sub>16</sub> H <sub>9</sub> <sup>+</sup> ) 4-methylpyrene (CH <sub>3</sub> -C <sub>16</sub> H <sub>9</sub> <sup>+</sup> )		444.2 (457.7) 482.8 757.6	442.9  482.4 758.1
naphthalene (C <sub>10</sub> H <sub>8</sub> <sup>+</sup> )		674.2 652.0	674.1 652.0
phenanthrene (C <sub>14</sub> H <sub>10</sub> <sup>+</sup> )		898.3 856.8	857.2
tetracene (C <sub>18</sub> H <sub>12</sub> <sup>+</sup> )		864.7	864.8
benzo(ghi)perylene (C <sub>22</sub> H <sub>12</sub> <sup>+</sup> )		502.2 758.4 755.2 794.3	503.9 (?) 758.1; 758.6 755.8 (?); 756.2 793.5 (prob.)
coronene (C <sub>24</sub> H <sub>12</sub> <sup>+</sup> )		459.0 946.5	459.5 946.6

results as we observe about 20 strong DIBs accompanied by hundreds of very weak features. We managed (Galazutdimov, Fulara, Musaev and I) to extract a sequence of features (6614, 6520, 6150 and 5923); the first one is strong, the others very weak. Their intensity ratios and profiles are always the same. It may be the spectrum of one carbon chain.

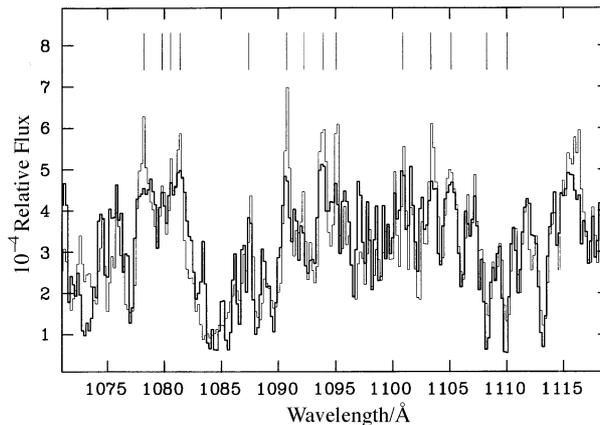
Concerning the H<sub>2</sub> hypothesis: (1) The 5797 and 6379 DIBs assumed to share the same ground level are of variable intensity ratio (HD 183143 vs. HD 41117); (2) DIBs are observed in spectra of F, G super-giants at high galactic latitudes.

**Dr Sorokin, Dr Glownia and Dr Ubachs** commented: On the basis of the  $H_2$  DIBs theory, an observed variable intensity ratio for the  $\lambda 5797$  and  $\lambda 6379$  DIBs might be explained in the following way (see Fig. 1 earlier). A variable intensity ratio would imply that the coherent lightwave emission step originating from (EF12,  $J = 3$ ) follows a path that is separate from the one by which (EF10,  $J = 1$ ) is populated. In the figure, for simplicity, we have shown these paths to be the same. In the ‘push–pull’ schemes for each of these DIBs, only the ‘push’ component is evidently the same!

**Dr Lynas-Gray** commented: Sorokin and Glownia<sup>1</sup> match the wavelengths of over 70 diffuse interstellar bands with those of inter-Rydberg transitions in  $H_2$ ; these are resonantly enhanced simultaneous two-photon absorption from an early-type star by  $H_2$  in a tenuous nearby cloud. Sorokin *et al.*<sup>2</sup> attempt to substantiate the Sorokin and Glownia model<sup>1</sup> by identifying ‘emission’ features in Copernicus and ORFEUS-1 ultraviolet spectra of early-type stars with both simulated Raman scattering (SRS) and four-wave parametric oscillations (FWPO) in  $H_2$ . Some of the identifications suggested by Sorokin *et al.*<sup>2</sup> in the reddened B5 Ia supergiant  $\eta$  CMa are indicated by vertical bars in Fig. 7 where part of the scaled Copernicus spectrum of  $\eta$  CMa is plotted as a thin line; from left to right the  $H_2$  SRS and FWPO features which Sorokin *et al.* advocate are B9-2R1, B9-2R2, B4-7P1, B9-2P2, B12-3P1, B8-2R1, B8-2R2, B8-2P2, B16-4P4, B8-2P4, B7-2R1, B7-2P1, B0-0R0 & B0-0R1 and B0-0P1.

Cassinelli *et al.*<sup>3</sup> make a detailed study of the B2 II giant  $\epsilon$  CMa; part of the Copernicus spectrum for this star is also shown in Fig. 7 as the heavy line; it can be seen that the SRS and FWPO features which Sorokin *et al.*<sup>2</sup> claim to identify in  $\eta$  CMa are also present in the spectrum of  $\epsilon$  CMa. At  $600 \text{ \AA}$ ,  $\epsilon$  CMa is the brightest star in the sky and Cassinelli *et al.*<sup>3</sup> establish a remarkably low neutral hydrogen column density of about  $1 \times 10^{18} \text{ cm}^{-2}$ . In the essential absence of neutral hydrogen it is unlikely that an  $H_2$  cloud could form in the vicinity of  $\epsilon$  CMa and the labeled features in the figure are consequently unlikely to be SRS and FWPO transitions in  $H_2$ ; because these also occur in  $\eta$  CMa, and other stars studied by Sorokin *et al.*,<sup>2</sup> their identifications must be in doubt. It is of course well established that line blanketing in the ultraviolet spectra of early-type stars means that only absorption features are observed; this is absolutely essential to any attempt to model the entire energy distribution, as Cassinelli *et al.*<sup>3</sup> discuss in the case of  $\epsilon$  CMa.

1 P. P. Sorokin and J. H. Glownia, *Astrophys. J.*, 1996, 473, 900.



**Fig. 7** Comparison of Copernicus spectra for  $\eta$  CMa (thin line) and  $\epsilon$  CMa (thick line) in  $1070 \text{ \AA} < \lambda < 1120 \text{ \AA}$ . Further details are given in the text above.

2 P. P. Sorokin, J. H. Glownia and W. Ubachs, *Faraday Discuss.*, 1998, **109**, 137.

3 J. P. Cassinelli, D. H. Cohen, J. J. MacFarlane, J. E. Drew, A. E. Lynas-Gray, M. G. Hoare, J. V. Vallergera, B. Y. Welsh, P. W. Vedder, I. Hubeny and T. Lanz, *Astrophys. J.*, 1995, **438**, 932.

**Dr Sorokin, Dr Glownia and Dr Ubachs** responded: Viewed together as a whole, the comments by Dr Lynas-Gray would appear to be very damaging to our H<sub>2</sub> DIBs model, which strongly relies upon the assumption that coherent oscillations produced in various wave mixing processes driven by broadband SRS transitions are occurring in H<sub>2</sub>-containing clouds near bright, young stars. In our reply, we consider the two main thrusts of his arguments separately.

We certainly agree with Dr Lynas-Gray that the EUVE spectroscopy measurements of the B2 II giant  $\epsilon$  CMa to which he refers in his comment (Cassinelli *et al.*) indicate a remarkably low H-atom column density of about  $1 \times 10^{18}$  cm<sup>2</sup> in the line-of-sight to this star, and that, consequently, it is unlikely that an H<sub>2</sub> cloud could form in the vicinity of this star. However, we differ with Dr Lynas-Gray's conclusion that the VUV 'emission bands' seen in a low-resolution Copernicus VUV spectrum of  $\epsilon$  CMa are exactly the same as those we assigned as emission bands coherently generated by SRS and FWPO processes in an H<sub>2</sub> cloud near the B5 Ia supergiant  $\eta$  CMa, one of the mid-/late-B supergiants considered in our Faraday Discussion paper. The evidence for Dr Lynas-Gray's conclusion is based upon a comparison of the low-resolution Copernicus VUV spectra of these two stars, which are shown superimposed in the Fig. 7. We refer now to this figure.

The vertical bar on the left hand side marks a very prominent 'emission band' seen in the four mid-/late-B supergiant spectra considered in our paper. However, as explained in our reply to the comment by Prof. Sarre, on the basis of the high-resolution Copernicus  $\beta$  Ori A spectrum shown in ref. 27, we now assign this band to the transition B10-2R5, rather than B9-2R1. From Fig. 7 shown by Dr Lynas-Gray, it is not at all apparent that at this wavelength there is any corresponding  $\epsilon$  CMa emission band rising significantly above the continuum level for that star. Interestingly enough, in neither the high-resolution Copernicus VUV spectrum of the B2 IV star  $\gamma$  Peg,<sup>1</sup> nor in the high-resolution Copernicus VUV spectrum of the B3 IV star  $\iota$  Herculis<sup>2</sup> is there likewise any sign of emission at 1078.27 Å rising significantly above the continuum level. In our paper, we focussed almost entirely on the VUV spectra of B-type supergiants, because these were the ones that most clearly seemed to show evidence of emission bands.

Corresponding to the position of the fourth vertical bar drawn in Fig. 7 is a somewhat less intense emission band that we now assign as D2-7P4 (1081.43 Å), rather than as B9-2P2 (1081.51 Å), since the band appears in the high-resolution Copernicus spectrum of  $\beta$  Ori A at 1081.45 Å. There appears to exist an emission band that slightly exceeds the continuum level at this wavelength in the  $\epsilon$  CMa spectrum shown in Dr Lynas-Gray's figure, but it appears to be much broader than the  $\eta$  CMa band. When one examines the high-resolution spectrum of  $\gamma$  Peg at *ca.* 1081.45 Å, one sees only a remarkably flat continuum emission, with almost no stellar or interstellar absorption lines. In  $\iota$  Her, there is likewise no emission above the continuum level at this wavelength. One should also be aware of the fact that very strong stellar absorptions definitely are seen in both  $\epsilon$  CMa and  $\eta$  CMa at *ca.* 1077.2 Å (S III), *ca.* 1084.0 Å (N II, partially interstellar), and *ca.* 1084.6 Å (N II, partially interstellar). These strong common absorptions have the effect of making the two superimposed spectra more similar in appearance.

The position of the sixth vertical bar in the figure marks one of the very strongest emission bands appearing at *ca.* 1090.84 Å in the high-resolution spectrum of  $\beta$  Ori A shown in ref. 27. We have re-assigned this band from B8-2R1 (1090.75 Å) to B20-5R3 (1090.84 Å). No especially prominent emission in excess of the continuum occurs here in the case of  $\epsilon$  CMa. In this wavelength region, the spectrum of  $\gamma$  Peg is even quieter,

showing only modest absorption lines on a relatively flat continuum. No emission above the continuum level is seen at this wavelength in  $\iota$  Her.

Similar comments apply to the coincidences marked by the other vertical bars. We conclude that the VUV spectrum of  $\epsilon$  CMa does not show the signature characteristics that we have interpreted in our paper as arising from  $H_2$  coherent emission. For reasons unknown to us, these characteristics seem only to be found in B-type supergiants and some B0 giants.

The figure included in Dr Lynas-Gray's comment does afford us an opportunity to make a correction to our paper. The spectra of both stars shown in this figure display very strong stellar absorption bands at *ca.* 1108.3 Å (Si II, Si III), *ca.* 1110.0 Å (Si III), and *ca.* 1113.2 Å (Si III). We have come to realize that these three bands are pervasive in the VUV spectra of B-type stars, and that two of them must undoubtedly mostly account for the absorptions labeled B0-OR0, B0-OR1, and B0-OP1, in Fig. 7 of our paper. The argument for non-linearity presented at the beginning of Section 4 of our paper had been based upon the deduction, made from a comparison of Fig. 7 and 8, that the observed absorption strengths of the B0-0 components, relative to those of B4-0, were much greater than they theoretically should be. By comparing the B4-0 components with those of B1-0 (Fig. 8), the argument for non-linearity can still probably be made, since there are no known stellar absorptions overlapping the latter, and the calculated B4-0 transition probabilities are roughly four times those of B1-0.

1 J. B. Rogerson, *Astrophys. J. Suppl. Ser.*, 1985, **57**, 751.

2 W. L. Upson and J. B. Rogerson, *Astrophys. J. Suppl. Ser.*, 1980, **42**, 175.

**Prof. Snow** said: I would like to suggest that we should hear nothing more about the hypothesis of DIB formation by non-linear radiative processes in molecular hydrogen until the following astronomical problems have been successfully addressed: (1) The DIBs do not exhibit dependence on stellar type; even late B stars have strong bands—this argues against any dependence on radiation field intensity. (2) DIBs correlate with distance and other IS parameters such as  $E_{B-V}$ , which argues against any circumstellar origin. (3) The DIBs tend to be weak, not enhanced, in regions with high FUV radiation fields, which argues against radiative processes in general. (4) The DIBs do not correlate well with  $H_2$ ; the correlation with atomic hydrogen is better—this argues against an origin related directly to molecular hydrogen. (5) The two-photon process is physically unrealistic: radiative relaxation of excited states of  $H_2$  is far more rapid (about  $10^{-9}$  s timescale) than the photon arrival time in any realistic environments (photon arrival times are *ca.* 1 per year in the diffuse ISM, a factor of *ca.*  $10^{16}$  too slow to support this model!)—this effectively rules out any two-photon process, even in circumstellar environments. (6) Copernicus observations show little or no  $H_2$  in excited states, yet there should be a large equilibrium population of excited  $H_2$  in the two-photon model. (7) The expected ultraviolet emission lines from circumstellar nebulae have not been observed—this argues strongly against the photon-trapping hypothesis that has been invoked to explain how the UV radiation field could be sufficiently intense to satisfy the requirements of this model. (8) DIBs have been detected in lines-of-sight toward cool stars (spectral types F and G; I refer here to a poster presented at this meeting by Drs Zacs and Schmidt). This is probably fatal to the entire hypothesis, because these lines-of-sight have virtually no UV photons available to excite  $H_2$ .

The suggestion that the DIBs might be formed by non-linear optical effects in molecular hydrogen has been an interesting and worthwhile contribution, but unfortunately further examination of the idea has found a number of very serious objections and inconsistencies, represented by the list above. It is now incumbent upon the authors of the hypothesis to withdraw from further promotion of the model unless and until they can provide realistic responses to this list of challenges.

**Dr Sorokin, Dr Glowina and Dr Ubachs** responded: As a scientist who has long been actively involved with both astronomical observations and laboratory experiments aimed at revealing the nature of the diffuse interstellar band (DIB) carriers, it is natural for Prof. Snow to demand that we try to provide some type of rational argument to show that the unusual non-linear lightwave mechanisms [*i.e.* broadband stimulated Raman scattering (SRS) and four-wave parametric oscillation (FWPO)] we invoke in our H<sub>2</sub> DIBs model could, in principle, occur in an astrophysical environment. Since Prof. Snow is here primarily concerned with there being orders-of-magnitude too little VUV pump light to drive the non-linear mechanisms at the (0.01–10 pc) cloud-to-star distances assumed in our model, we will begin our reply with a simple argument which we believe points the way out of this dilemma. We will then try to address some of Prof. Snow's specific questions.

Consider a thin spherical shell region bounded by two spheres with nearly equal radii that are centered about a bright star. (For the sake of definiteness, let us assume that the shell has a radius *ca.* 1 pc and a thickness *ca.* 0.01 pc.) Let  $\Delta\nu$  define a small bandwidth of VUV light centered around, let us say, the Ly- $\alpha$  resonance line of H atoms. Designate by  $S_{\Delta\nu}$  the total number of photons emitted by the star per second in the bandwidth  $\Delta\nu$ . We will calculate the steady state values of  $n(r)$ , the number of photons per cm<sup>3</sup> in the bandwidth  $\Delta\nu$  at a radius  $r$  lying within the shell for two separate cases: (a) an empty shell, and (b) a shell that is uniformly filled with H atoms at a density  $n_{\text{H}}$  per cm<sup>3</sup>.

In the first case, it is trivial to show that  $n_a(r) = S_{\Delta\nu}/4\pi r^2 c$ . For the second case, let us start by assuming a value for  $n_{\text{H}}$  of 10<sup>4</sup> per cm<sup>3</sup>. Since an atom in such a gas would collide with another one at an average rate of *ca.* 1 collision every two years, we assume this gas to be a collisionless medium. For VUV photons having frequencies that lie within  $\Delta\nu$ , one can entirely neglect inelastic scattering (*i.e.* 'absorption'). All scattering of these photons is elastic (*i.e.* resonance Rayleigh scattering). Therefore, the outward flow of such VUV photons through the thin spherical shell will be governed by Fick's first law of diffusion. At a distance  $r$  lying within the shell, one has:

$$-4\pi r^2 D \frac{dn}{dr} = S_{\Delta\nu} \quad (1)$$

where  $D$  is the diffusion coefficient, equal to  $(1/3)\eta c$ . Here  $\eta$  is the mean free path, equal to  $1/\sqrt{2}\sigma n_{\text{H}}$ . The quantity  $\sigma$  is the elastic scattering cross-section. For simplicity, we take it to be the maximum value it can have,  $\lambda^2/2\pi$ . It thus follows from eqn. (1) that, within the spherical shell,

$$n_b(r) = \frac{S_{\Delta\nu}}{4\pi r D} \quad (2)$$

For  $\lambda = 1216 \text{ \AA}$ , the mean free path  $\eta$  is *ca.*  $3 \times 10^6$  cm. Since the nearly resonant photon density enhancement is given by  $n_b(r)/n_a(r) = 3r/\eta$ , at  $r = 1$  pc, this ratio is *ca.*  $3 \times 10^{12}$ !

The biggest significance of eqn. (2) is probably the fact that the nearly resonant VUV photon density varies as  $1/r$ , not as  $1/r^2$ . This means that the Stokes-wave gain over a full great circle path in a spherical shell of H<sub>2</sub> gas would be independent of the radius of the shell. Thus, the thin H<sub>2</sub>-containing cloud of our model is really not required to be extremely close to the illuminating star. The total Stokes-wave gain existing in a path comprising a complete great circle in a thin gas-filled spherical shell of radius 10 pc would be the same as that existing in a great circle path in a shell with radius 1 pc, for example. It should be possible actually to calculate the gain for resonantly enhanced broadband IR or VUV Stokes-wave generation over a great circle for the case represent-

ed by eqn (2), but we have not done so yet. The methodology for performing such calculations was derived more than 20 years ago. (See, for example, ref. 1.)

We now address some of the specific objections to the  $H_2$  DIBs model listed by Prof. Snow. (1) If the DIBs do not depend upon radiation field intensity, then why are virtually all of the stars listed in Table 3 of Herbig's pioneering study of diffuse interstellar bands<sup>2</sup> either O- or B-type stars? Of the 10 early A-stars listed by Herbig in this table, which are the only exceptions to the above statement, all happen to be supergiants. In exciting the various non-linear processes in our model the important quantity is the total amount of radiation emitted by the star in narrow wavelength regions in the VUV spanning the strongest ( $X \rightarrow B, C$ )  $H_2$  resonances and the Lyman lines of H atoms. Obviously, the amount of radiation emitted depends both upon a star's spectral type and upon its radius. An A0 supergiant has a surface emitting area that is about 30 times greater than that of a B0 V star, for example. (2) We are fully aware of the fact that DIB intensities in a given line-of-sight are strongly correlated with the amount of reddening (*i.e.*  $E_{B-V}$ ) observed in the same line-of-sight. In our paper, we propose an explanation for this fact based upon the  $H_2$  non-linear DIBs model. This explanation does not require the  $H_2$ -containing cloud of our model to be circumstellar. It only requires that there be dust present in the cloud. We do not fully understand Prof. Snow's statement that DIBs correlate with interstellar distance. To us, it would seem that a star that is viewed along a heavily reddened line-of-sight is not necessarily a very distant star. There may simply be present an intervening dust cloud. The B1 Ib halo star ( $d = 1.7$  kpc) HD 214080, discussed at length in our paper, is relatively distant from us, as far as standard DIB stars go, yet its line-of-sight is only slightly reddened ( $E_{B-V} = 0.07$ ). Comparatively weak DIBs are seen in this star.<sup>3</sup> (3) We are not knowledgeable enough about astronomical measurements of DIBs performed in specific lines-of-sight to comment with any real conviction on Prof. Snow's statement that DIBs tend to be weak, not enhanced, in regions of high VUV radiation fields. However, one might question the validity of this remark on the basis of one specific paper in which the environmental dependence of DIBs was studied.<sup>4</sup> In probing the strengths of two DIBs in various lines-of-sight in the Orion region, Ehrenfreund and Jenniskens did indeed find them to be absent or much weaker in lines-of-sight to H II regions, which are regions immediately adjacent to stars in which all of the hydrogen is ionized and in which, therefore, there should be no molecular hydrogen. However, in other lines-of-sight that probed various portions of the Orion Giant Molecular Cloud, they found that while in the lighter portions of the cloud the DIB intensities did increase with increasing reddening, in the darker portions of the cloud the DIB intensities decreased with increasing reddening. The scientists concluded that the determining factor for the decrease of DIB strength was the attenuated VUV field in dark clouds. (4) A universal correlation of DIB strength with atomic hydrogen is predicted by the version of the  $H_2$  DIBs model discussed in our paper. In Fig. 20, the secondary broadband SRS process involving the quantum level ( $B'1, J' = 1$ ) as resonant intermediate state is shown pumped by Ly- $\beta$  photons, the latter assumed to be present in the  $H_2$ -containing cloud at enormously enhanced densities *via* the mechanism of elastic scattering [*i.e.* the mechanism implied in the derivation of eqn. (1) and (2), above]. The Stokes-wave radiation generated in this process results in the appearance of the DIB at *ca.* 5780 Å through the inverse Raman absorption step pictured in Fig. 21. Likewise, Ly- $\alpha$  radiation is instrumental in producing the  $\lambda 5797$  and  $\lambda 6379$  DIBs in the scheme shown in Fig. 1 earlier.

With regard to the statement asserting that there is no correlation of DIB intensities with  $H_2$  column densities in various lines-of-sight, one should be somewhat cautious. Consider the ideal case of a thin spherical shell of hydrogen gas (both atomic and molecular) centered about a bright star that was assumed in the derivation of eqn. (1) and (2), above. This geometry should represent an ideal situation for generating strong DIB intensities, according to the non-linear model discussed in our paper (provided that

the shell also contains some dust). One pictures the light waves involved in the various coherent  $2n$ -wave mixing processes discussed propagating in great circles lying within the ‘plane’ of the thin  $H_2$ -containing cloud. One would expect to see strong Ly- $\alpha$  and Ly- $\beta$  ‘absorptions’ in the line-of-sight, because these radiations are truly absorbed in pumping various steps of the  $2n$ -wave mixing processes. For the same reason, one would also expect to see ‘absorptions’ around the stronger ( $X \rightarrow B, C$ )  $H_2$  absorption lines. But what about the weaker  $X \rightarrow B$  transitions, *e.g.* B0-OR0, B0-OR1, B0-OP1, B1-OR0, B1-OR1, B1-OP1, B2-OR0, B2-OR1, B2-OP1, ... *etc.*? In our model, SRS pumping would not likely occur on these transitions, so no non-linear absorptions would occur here. We have argued all along that linear inelastic scattering does not occur in our model. There is only linear elastic scattering. However, the spherical symmetry of the thin  $H_2$ -containing cloud here assumed implies that no attenuation of light should be evident in viewing these weaker  $X \rightarrow B$  transitions in the line-of-sight! If one were to estimate the  $H_2$  column density *via* only these weaker transitions, one would conclude that the  $H_2$  column density is zero.

In response to points (5) and (6), at the very basis of our  $H_2$  non-linear DIBs model is the fundamental assumption that excitation *via* single-photon transitions (*i.e.* inelastic scattering) does not occur at all. In this model, all the excitations occur to *gerade* state quantum levels in simultaneous two-photon steps. Our model does not involve direct one-photon absorptions originating from excited-state levels that need to be populated. The only vibrationally excited quantum levels of the X-state that are populated *via* two-photon transitions in the various  $2n$ -wave mixing processes we invoke are ones that can be depopulated by secondary SRS processes pumped by Ly- $\alpha$ , Ly- $\beta$ , Ly- $\gamma$ , ... *etc.*, radiation. Basically, the various  $2n$ -wave mixing processes act on the  $H_2$  molecules located in the very lowest energy quantum levels (*i.e.*  $J'' = 0$  and 1 of X0) in such a way that they remain in these same quantum levels. (7) The main thrust of Section 4 of our paper is that we feel evidence of VUV emission bands generated in  $2n$ -wave mixing processes exists in the VUV spectra of mid-/late-B supergiants. (8) At the Faraday Discussion meeting we did not actually see the poster paper presented by Drs Zacs and Schmidt. However, later in a private conversation with us at the meeting, Dr Ehrenfreund commented that the DIBs reside in the interstellar medium towards stars and that on 1 Kpc distance the effects of the circumstellar environment is often negligible. Only when the overall line-of-sight conditions and geometry towards the star are known can information on the excitation mechanism of the DIB carriers be obtained. To observe DIBs in cold stars is, however, very difficult due to strong stellar contamination, but apparently not impossible in very reddened targets.

- 1 V. S. Letokhov and V. P. Chebotayev, *Nonlinear Laser Spectroscopy*, Springer-Verlag, Berlin, Heidelberg, New York, 1977, ch. 5.
- 2 G. H. Herbig, *Astrophys. J.*, 1975, **196**, 129.
- 3 G. H. Herbig, *Astrophys. J.*, 1993, **407**, 142.
- 4 P. Ehrenfreund and P. Jenniskens in *The Diffuse Interstellar Bands*, ed. A. G. G. M. Tielens and T. P. Snow, Kluwer, Dordrecht, Boston, London, 1995.

**Dr Začs and Dr Schmidt** communicated: We have presented (on a poster) the results of our search for diffuse bands in the spectra of three post-AGB candidate stars (IRAS19244 + 1115, IRAS19114 + 0002, IRAS22272 + 5435) carried out in the frame of a more extensive study of the photospheric abundances of protoplanetary nebulae (PPN) candidates. DIBs in the spectrum of IRAS19114 + 0002 (=HD179821) have been identified. The optical spectrum of HD179821 (spectral type F5I, other authors give G5I) shows that it is a high-luminosity object and the presence of a detached cool dust shell suggest that it has experienced mass loss in the recent past. The observed spectrum (Fig. 8) [thick line; wavelengths corrected for the stellar heliocentric radial velocity (RV) of +88.4 km s<sup>-1</sup>] and synthetic (calculated) (thin line) spectrum of HD179821 around

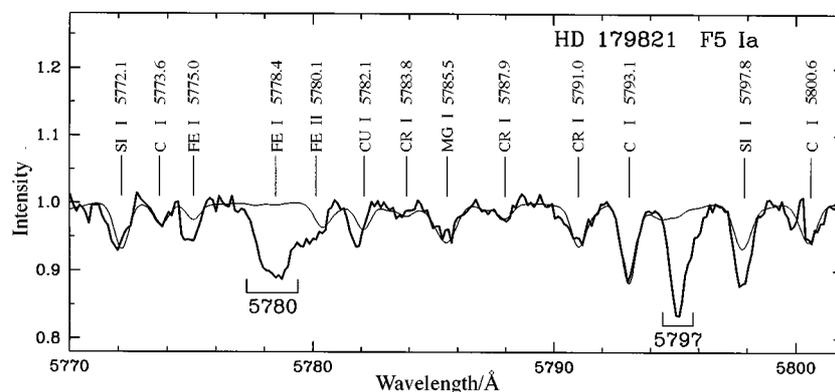


Fig. 8 Observed (—) and calculated (---) spectra of HD 179821 around DIBs at 5780 and 5797 Å

DIBs at 5780 equivalent widths (EW) = 230 mÅ and 5797 Å (160 mÅ) are shown. The synthetic spectrum was calculated in LTE using Kurucz's models and atmospheric parameters (and abundance) derived by Začs *et al.*<sup>2</sup> The presence of DIBs is evident. Note the strange profile of the DIB at 5780 Å if compared with the intrinsic profile of this DIB given by Krelowski and Schmidt.<sup>3</sup> Although there is a moderate contribution (15 mÅ) of the stellar Fe II absorption on the red wing the presence of the circumstellar component DCB (RV = +46 km s<sup>-1</sup>, EW ≈ 80 mÅ) is possible. Note that NaD lines consist of four absorption components with radial velocities (-11, +42, +64, +107) different from the mean photospheric velocity (+88.4 km s<sup>-1</sup>).

1 Kurucz, SAO CD-ROM no. 13, 1993.

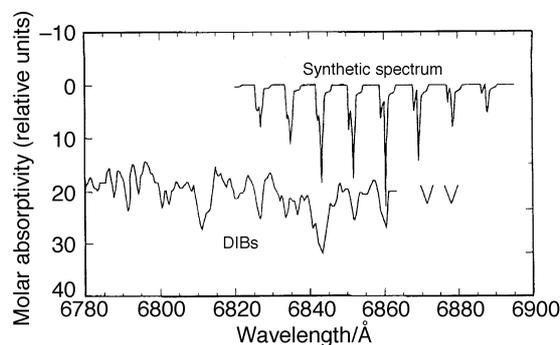
2 L. Začs, V. G. Klochkova, V. E. Panchuk and R. Spelmanis, *Mon. Not. R. Astron. Soc.*, 1996, **282**, 1171.

3 J. Krelowski and M. Schmidt, *Astrophys. J.*, 1997, **477**, 209.

**Dr Sorokin, Dr Glowina and Dr Ubachs** responded: We refer to the last item of our response to Prof. Snow's comments. From the actual comment (and Fig. 8) submitted by Drs Začs and Schmidt, it certainly would appear that the  $\lambda$ 5780 and  $\lambda$ 5797 DIBs are seen in the line-of-sight to HD 179821, an F5 Ia star.

**Prof. Glinski** commented: We have been studying the relatively regular Herbig DIB group near 6800 Å as it may be due to perpendicular, rovibronic bands of a molecule or ion of the form CH<sub>2</sub>X.<sup>1</sup> The regular spacing of about 18 cm<sup>-1</sup> and the intensity alternation is entirely consistent with the rotational constants and *ortho/para* ratio corresponding to the H—C—H moiety. We have been modelling the spectrum with various carbon chains as the X. In Fig. 9 we show one of our preliminary models of the perpendicular band group for H<sub>2</sub>C=C=C=CN, which could also be an ion (Schulz *et al.*<sup>2</sup>) We use the recently measured *B''* rotational constants for H<sub>2</sub>C<sub>5</sub> of McCarthy *et al.*<sup>3</sup> and the estimable *A''*, *A'*, and *B'* constants to synthesize the spectrum. We note that there is relatively little leeway for varying the *A* and *B* constants in these types of molecules because they are rather rigid. The required K-level temperature could present a problem unless the molecules were an ion. We are continuing to refine our models of these groups of bands along with their single, parallel band counterparts. These multiple bands will serve as a strong test of any spectroscopic fit.

Our result supports the idea that a family of carbon chain molecules may account for many of the weak DIBs in accord with the work of Prof. Maier's group. We would like to learn from Prof. Maier if the rotational temperature in the C<sub>7</sub><sup>-</sup> bands are sufficiently broad in order to fill in the DIB lines. The modelled width of the C<sub>7</sub><sup>-</sup> DIBs will



**Fig. 9** Synthetic rovibronic spectrum that was obtained using the following parameters:  $A'' = 9.40$ ,  $B'' = 0.070$ ,  $A' = 9.20$ , and  $B' = 0.068$ ;  $T_k = 600$  K,  $T_f = 300$  K. Absolute wavelength position of the synthetic spectrum is not definite. The Herbig spectrum is reproduced with kind permission from *Astrophys. J.*, 1988, **331**, 999. The two bands represented as arrowheads at the right are positioned where shown in the work of Herbig and Leka (*Astrophys. J.*, 1991, **382**, 193).

yield the rotational excitation temperature of that non-polar ion in those environments and that could be quite warm.

- 1 R. J. Glinski and J. A. Nuth, *Publ. Astron. Soc. Pac.*, 1995, **107**, 453.
- 2 S. A. Schulz, J. E. King and R. J. Glinski, in preparation.
- 3 M. C. McCarthy, M. J. Travers, A. Kovacs, C. A. Gottlieb and P. Thaddeus, *Astrophys. J. Suppl. Ser.*, 1997, **113**, 105.

**Prof. Maier** responded: The width of the bands in the electronic spectrum of  $C_7^-$  is very sensitive to the laser powers used in the two colour excitation/detachment approach because of saturation effects. The narrowest band-width we obtained for the origin band is 0.02 nm, which is less than the 0.1 nm FWHM of the 627.01 nm DIB. The rotational temperature in our gas-phase measurements is expected to be less than 100 K.

**Dr Ehrenfreund** commented: The development of DIB research in recent years indicates that most DIB carriers could be large carbon-bearing molecules which reside ubiquitously in the interstellar gas.<sup>1,2</sup> The first detection of substructures in the profile of several DIBs indicated the molecular nature of some DIB carriers<sup>3,4</sup> Foing and Ehrenfreund<sup>5</sup> observed two DIBs at 9577 and 9632 Å as first evidence for  $C_{60}^+$ , the largest molecule ever detected in space. A new reference target for DIB studies was recently detected, which shows the strongest DIBs ever measured and allows definition of the DIBs in several categories which respond in a totally different way to the local environment.<sup>6</sup> Cami *et al.*<sup>7</sup> completed a survey of DIB correlations over 4000 Å which showed that most of the DIB carriers are undergoing photo-ionization and that all measured DIBs do originate from different carriers. The spectra of PAH and fullerene cations, measured in a neon matrix, carbon chains measured in the gas phase and theoretical calculation of the non-linear  $H_2$ -DIB model have all shown striking coincidences with some diffuse bands. Another approach is to study the complete DIB spectrum in different interstellar and circumstellar regions and to relate the line-of-sight conditions directly to the formation/evolution and destruction properties of DIB carrier molecules. Additional observations of spectral molecular features such as CH,  $CH^+$ , CN (as well as atomic lines Ca I, Ca II, Na I) reveal variations of physical parameters of the interstellar environment and can constrain the chemistry, ionization balance, metallicity and electron density in the circumstellar and interstellar environment. Those observations show currently up to *ca.* 200 DIBs in dense and cold environments as well as in UV dominated regions. Their central wavelength is extremely constant. The band strength of the

strongest DIBs (such as the 5780 and 5797 Å DIBs, which are measured towards more than 200 sources) does not change more than a factor *ca.* 2. Even the high resolution profile of the 6613 Å DIB, which shows a characteristic triple peak displays only slight changes in different environments. The DIB strength varies with the total HI column density which results in a decline of DIB strength with depth in the cloud where the H<sub>2</sub> concentration rises. The so called ‘skin-effect’ can be explained by a concentration of DIB carriers in the surface layers of dense clouds.<sup>1</sup> The relative DIB strength  $W/E(B - V)$  seems to reflect an interplay between ionization and recombination and destruction of the DIB carrier molecules.

These recent observational results favour molecules such as PAH and fullerene cations as the most interesting DIB carrier molecules. PAH cations fulfil the criteria of abundance and stability and show in general only one strong band per molecule in the visible range. Salama *et al.*<sup>2</sup> have discussed the ‘one DIB–one PAH’ hypothesis, assuming that a limited number (150–200) of stable PAH cations can be responsible for the known DIB spectrum. Recent measurements of hydrogenated, dehydrogenated PAHs as well as PAH anions show that those species have a very different spectrum in the optical range compared to PAH cations. The complexity of visible absorption which would be created by the different transient forms of PAHs during their evolution, such as hydrogenated and dehydrogenated PAHs, dications or fragments is not manifested in the current DIB spectrum. There is a possibility that all those transient PAH states may be responsible for the very weak DIBs. The grouping of DIBs has recently been studied by Krelowski *et al.*<sup>8</sup> and indicated that certain combinations of strong and very weak DIBs close by, may be formed by the same carriers. The carbon chain hypothesis as well as the non-linear H<sub>2</sub>-DIB model show and predict a large number of DIBs. Due to the high density of known DIBs in the optical region there is a substantial risk of purely accidental coincidences. For such species a valid selection mechanism must be found which is compatible with interstellar line-of-sight conditions.

To summarise, the DIB spectrum follows rather simple rules and shows apart from a strong consistency in wavelength position and profile structure a strong dependence on the UV field. These important criteria have to be respected when searching for the carrier molecules.

1 G. H. Herbig, *Ann. Rev. Astron. Astrophys.*, 1995 **33**, 19.

2 F. Salama, E. L. O. Bakes, L. J. Allamandola and A. G. G. M. Tielens, *Astrophys. J.*, 1996, **458**, 621.

3 P. J. Sarre, J. R. Miles, T. H. Kerr, R. E. Hibbins, S. J. Fossey, W. B. Somerville, *Mon. Not. R. Astron. Soc.*, 1995, **277**, L41.

4 P. Ehrenfreund and B. H. Foing, *Astron. Astrophys.*, 1996, **307**, L25.

5 B. H. Foing and P. Ehrenfreund, *Astron. Astrophys.*, 1997, **317**, L59.

6 P. Ehrenfreund, J. Cami, E. Dartois and B. H. Foing, *Astron. Astrophys.*, 1997, **318**, L28.

7 J. Cami, P. Sonnentrucker, P. Ehrenfreund and B. H. Foing, *Astron. Astrophys.*, 1997, **326**, 822.

8 J. Krelowski, M. Schmidt and T. P. Snow, *Publ. Astron. Soc. Pac.*, 1997, **109**, 1135.

**Prof. Snow** commented: The 4430 Å diffuse band, once the principal subject of many DIBs studies, has been largely neglected in recent years. To date there have been no general studies of the 4430 Å DIB based on high-quality CCD spectra. This diffuse band is the strongest of all the DIBs and also the broadest, with the result that several stellar photospheric lines are superposed on it. Perhaps this has discouraged intensive studies of  $\lambda 4430$ , especially considering the fact that many DIBs in the red could be analyzed without confusion by stellar lines (an additional factor is the higher QE of CCD detectors in the red as compared with the blue).

We (Massey, Boyd and I) have undertaken a CCD-based survey of  $\lambda 4430$  in a number of highly reddened O stars, with the result that the band appears to be saturated in lines-of-sight with high extinction (the rate of growth of band strength with  $E_{B-V}$  levels off with increasing  $E_{B-V}$ ). This implies that  $\lambda 4430$  may be composed of many narrow, closely spaced individual lines which become saturated in high column-density

lines-of-sight. If so, this suggests that we should search for fine structure within the band, in less-reddened lines-of-sight where saturation will be less severe.

In June 1997, we carried out observations of the 4430 Å band using the ultra-high Resolution Facility (UHRF) on the Anglo-Australian Telescope, in lines-of-sight toward stars where fine structure had previously been detected in one or more of the longer-wavelength DIBs. At its resolving power of  $\lambda/\Delta\lambda$  *ca.*  $10^6$ , the UHRF provides coverage of about 2 Å at this wavelength (as compared with the DIB's FWHM of about 30 Å), so we chose several small 'windows' within the  $\lambda$ 4430 band, carefully selected to avoid contamination by stellar lines, and obtained high-resolution spectra in those windows.

The result is that no trace of fine structure within the 4430 Å band was detected. The high photometric quality of the data (signal-to-noise *ca.* 100) rules out significant fine structure at a level above *ca.* 1% of the local continuum. This result was uniform for the five lines-of-sight that were observed. We conclude that the 4430 Å DIB is either a smooth, continuous feature, or that its fine structure either has a scale length smaller than  $\Delta\lambda$  *ca.* 0.005 Å or else is broader than the *ca.* 2 Å bandpass that we observed (but in that case earlier searches for fine structure, such as the one by Herbig in 1966, would have revealed it).

It is not clear what this result implies for the identification of the  $\lambda$ 4430 carrier. A molecular origin is not ruled out, but it is now seen to be viable only if internal conversion completely eliminates fine structure or else the fine structure lines are so closely spaced as to appear smoothly blended to a part in  $10^6$  in wavelength. But on the other hand a dust impurity carrier, which would be expected to produce a smooth profile, may also be viable. In this latter connection, it is noteworthy that this particular DIB has not been scrutinized for signs of a solid-state carrier (*e.g.*, through searches for spectro-polarization structure) as have many of the longer-wavelength DIBs, and therefore a solid-state carrier has not been ruled out. It appears at least possible that the 4430 Å DIB has a different origin than the sharper features that appear at longer wavelengths.

**Prof. Bréchnac** commented: I think that there are two points that have not been well addressed yet in the discussion. The first one is the stability of the DIBs carriers, the second one is their abundance. As a matter of fact these two points may well be chemically connected in interstellar conditions. We heard about nice coincidences involving the photodetachment spectrum of  $C_7^-$  and the DIBs spectrum, and indeed there has been a large number of firm detections of chains in the interstellar medium. But, even when summing up the abundances of all of them, it does not count for much relative to the total abundance of cosmic carbon, in comparison to the amount estimated for PAHs through the flux emitted in the UIR bands. Similarly the PAHs are expected to offer a larger stability against the UV radiation field. These two arguments were at the basis of the proposition of PAH cations as DIBs carriers candidates.<sup>1</sup>

We have set up in my laboratory in Orsay an experiment devoted to the search for the electronic spectra of gas phase cold PAH cations in the visible. Making large quantities of cold cations in the gas phase in order to measure absorption directly is very difficult. The principle of the technique we used consists of inducing a fragmentation of the cation consecutive to the resonant absorption of laser photons, so that the change in the charge-to-mass ratio can be detected in a mass spectrometer. However, it is well known that because of their stability PAHs (neutrals as well as cations) need a fairly large excitation energy before they begin to fragment on a reasonable timescale. This usually requires several laser photons, which means high laser flux, and then a number of experimental difficulties associated to saturation effects, power broadening, non-resonant absorption and problems in controlling the number of photons involved in the process.

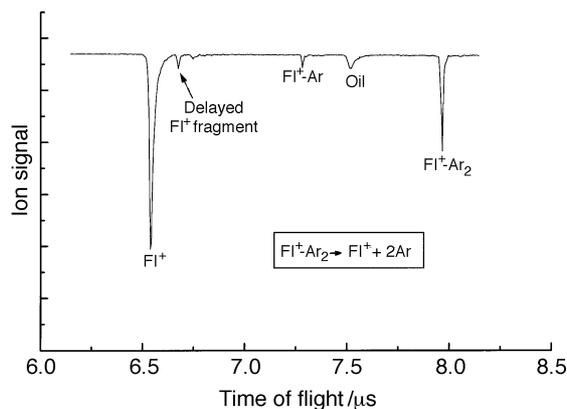
We have used a trick, consisting of attaching an argon atom to the PAH by forming van der Waals complexes in a molecular beam. This complex is photoionised by reso-

nant two-photon absorption in the near UV. Then the binding energy of the complex cation is so small (about  $500\text{ cm}^{-1}$ ) that it will fragment for every single photon absorbed. The use of two pulsed lasers of different colours in the ionisation step allows us to control exactly the total energy, and to produce complexes which are cold both rotationally and vibrationally.

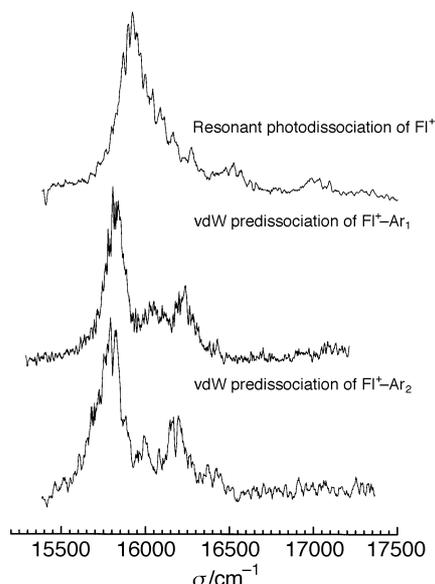
The technique has been tested first on a benzene derivative, the 4-fluorostyrene, and found to work. It was then applied to a larger aromatic hydrocarbon, the fluorene molecule  $\text{C}_{13}\text{H}_{10}$ . The time-of-flight spectrum shown in Fig. 10 illustrates how the technique works. The wavelength of the first UV photon has been tuned to optimise the formation of the fluorene<sup>+</sup>-Ar<sub>2</sub> ( $\text{Fl}^+\text{-Ar}_2$ ) complexes. Some signal can be seen at the mass of the  $\text{Fl}^+\text{-Ar}$  complex, and a larger peak at the mass of  $\text{Fl}^+$  since neutral fluorene is much more abundant but not formed efficiently. The pulsed visible laser inducing absorption by the cation is delayed with respect to the ionising lasers, so that the  $\text{Fl}^+$  fragment produced by ejection of the two argon atoms appears separated in time from the rest of the  $\text{Fl}^+$  ions.

The spectrum shown in the bottom trace of Fig. 11 has been obtained by monitoring the ion signal in the time window relative to this fragment while the laser wavelength is scanned. The middle trace is the spectrum obtained similarly after optimisation of the  $\text{Fl}^+\text{-Ar}$  signal. The recording of these spectra required a relatively small energy (of the order of a few microjoules per pulse) for the visible laser, since it corresponds to a single photon process. On the contrary the recording of the top trace, after optimisation of the  $\text{Fl}^+$  signal, and adjusting the time window on the channels associated to the main fragment of the free ion, *i.e.* the ion formed by the loss of a single H atom, required a laser energy about two orders of magnitude larger. As a consequence the spectrum looks broader and presents less structure.

It can be noted that the peak wavelength of this spectrum is found very close to  $6284\text{ \AA}$  which is the wavelength of one of the strongest DIBs. However, all of the three spectra appear to be several times broader than the interstellar band. This raises the question of the origin of the observed width. Although these results are still preliminary and should be confirmed, we believe that we deal with the spectra of vibrationally and rotationally cold cations. The order of magnitude of the laser energies used to fragment the van der Waals complexes does not seem sufficient to produce significant power broadening. Thus, we should be in the presence of a case of lifetime broadening, as a result of intramolecular dynamics effects. The fact that both argon atoms are ejected from the  $\text{Fl}^+\text{-Ar}_2$  is an indication that an ultrafast electronic internal conversion within the  $\text{Fl}^+$  moiety may have preceded the step of vibrational predissociation of the complex. If this



**Fig. 10** Time-of-flight spectrum showing the principle of the technique used to record the visible absorption spectra of cold PAH cations in the gas phase (see text)



**Fig. 11** Photodissociation spectra of the  $\text{FI}^+$  cation and its van der Waals complexes with one and two argon atoms

physical picture is correct, it rules out the  $\text{FI}^+$  cation from the possible candidates for the 6284 Å DIB carrier.

Some of you may object to the fact that the technique gives access to the spectra of the van der Waals complexes rather than of the PAHs cations, which is correct. But by using the van der Waals shift additivity rule, known to be obeyed by these aromatic clusters,<sup>2</sup> one can easily recover the spectrum of  $\text{PAH}^+$  from the spectra of  $\text{PAH}^+-\text{Ar}$  and  $\text{PAH}^+-\text{Ar}_2$ . In conclusion we hopefully believe that we are now in a position to produce electronic spectra for other gas phase PAH cations. This should help to progress in the testing of their suggestion as DIBs carriers.

1 A. Léger and L. d'Hendecourt, *Astron. Astrophys.*, 1985, **146**, 81; G. P. van der Zwet and L. J. Allamandola, *Astron. Astrophys.*, 1985, **146**, 76.

2 P. Hermine, P. Parneix, B. Coutant, F. G. Amar and Ph. Bréchnignac, *Z. für Phys. D*, 1992, **22**, 529.

**Prof. Thaddeus** commented: If the interstellar diffuse bands are carried by large molecules, and if some of these are unsymmetrical and polar, as seems likely, they will inevitably have low frequency radio lines. These potentially represent a new type of radio spectrum, probably best observed in absorption against intense galactic continuum sources like Cas A. The trouble is that these lines will be quite weak and undoubtedly very numerous—a thicket of lines. Probably the best instruments with which to search for them are the newly resurfaced Arecibo telescope working at 1–10 GHz and the 100 m GBT under construction by NRAO. There are plans to undertake such searches with these instruments.

In emission at slightly higher frequency ( $\approx 30$  GHz), these polar molecules may contribute to high latitude anisotropy in the cosmic microwave background claimed by radio astronomers, as Webster has pointed out.

**Ms Heyl** said: On the basis of large-scale coupled cluster calculations and comparison with experimental values for HCN,  $\text{HC}_3\text{N}$  and  $\text{HC}_5\text{N}$ , the ground-state dipole moments of  $\text{HC}_7\text{N}$  and  $\text{HC}_9\text{N}$  were established to be  $-4.82$  and  $-5.20$  D, with an

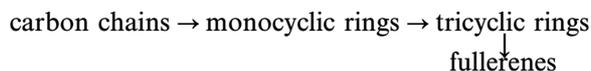
estimated uncertainty of *ca.* 0.02 D.<sup>1</sup> In a similar way,  $\mu_0$  (HC<sub>11</sub>N) is found to be  $-5.47$  D.<sup>2</sup> The  $\mu_0$  values of cyanopolyynes HC<sub>2n+1</sub>N up to  $n = 5$ , with experimental values<sup>3–5</sup> taken for species with  $n = 0, 1$  and  $2$ , are displayed graphically in Fig. 12. Pronounced non-linear behaviour is observed.

- 1 P. Botschwina and M. Horn, *J. Mol. Spectrosc.*, 1997, **185**, 191.
- 2 P. Botschwina, unpublished, cited in M. B. Bell, P. A. Feldmann, M. J. Travers, M. C. McCarthy, G. A. Gottlieb and P. Thaddeus, *Astrophys. J.*, 1997, **483**, L61.
- 3 Landoldt–Börnstein, *Molecular constants, Group II*, ed. G. Guelachvili, Springer, Berlin, vol. 20, sub. vol. B1, 1995.
- 4 R. L. DeLeon and J. S. Muentner, *J. Chem. Phys.*, 1984, **80**, 3892.
- 5 A. J. Alexander, H. W. Kroto and D. R. M. Walton, *J. Mol. Spectrosc.*, 1976, **62**, 175.

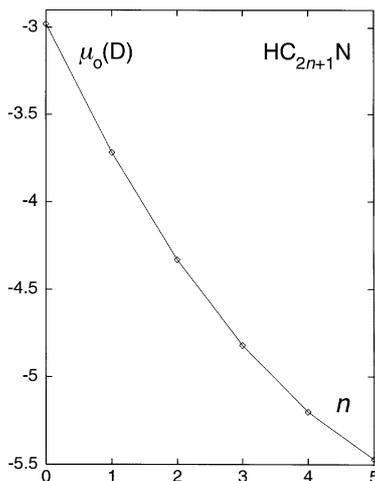
**Prof. Irvine** said: I would like to ask at what length long carbon chains will begin to form cyclic isomers, and whether that can be studied in the laboratory?

**Prof. Herbst** responded: Although the relative energies of linear and cyclic carbon chain molecules depend to some extent on whether one is referring to charged or neutral molecules and whether one is referring to bare carbon chains or to more complex entities, the general picture is as follows. For small molecules, both linear and cyclic isomers exist and can be relatively close in energy. The different isomers can be produced by different sequences of reactions. As one gets beyond 10 carbon atoms in size, the cyclic forms tend to become consistently lower in energy, although straight chain species have been studied in the laboratory, proving that kinetically controlled isomerization need not be rapid under all conditions. Experiments indicate, however, that isomerization of bare linear carbon chains to cyclic isomers eventually does occur for species with 10–20 carbon atoms.<sup>1</sup> In our theoretical treatment, we have estimated that spontaneous isomerization to cyclic molecules starts under interstellar conditions when the molecules contain somewhat more than 20 carbon atoms.<sup>2</sup>

We have shown that low temperature ion–molecule and neutral–neutral reactions operating in dense and diffuse clouds can produce the following classes of molecules:



PAHs, on the other hand, can only be formed at high temperatures, most probably in carbon rich circumstellar envelopes.



**Fig. 12** Values of  $\mu_0$  for cyanopolyynes HC<sub>2n+1</sub>N up to  $n = 5$ , with experimental values taken for species with  $n = 0, 1$  and  $2$

- 1 G. von Helden, N. G. Gotts and M. T. Bowers, *Nature (London)*, 1993, **363**, 60.  
 2 R. P. A. Bettens and E. Herbst, *Int. J. Mass Spectrom. Ion Proc.*, 1995, **149/150**, 321.

**Dr Takahashi** said: As a related work to radical ring-chain molecules in Prof. Thaddeus's paper, I would like to introduce an *ab initio* quantum chemical study on stable isomers of carbon chain molecules  $C_nH$  ( $n = 3-7$ ) by us.<sup>1</sup> We calculated most of all the stable isomers of  $C_nH$  molecules and found that there is a general tendency that the second most stable isomers have 3-member-ring structures for odd  $n$  while  $n$ -member-rings for even  $n$  (see Fig. 13).

The relative energies calculated at the QCISD/6-31G\*\* level are shown in Table 2. The ground electronic states of linear  $C_3H$ ,  $C_5H$ ,  $C_6H$ , and  $C_7H$  are  $^2\Pi$ . On the other hand, it is found that the difference between  $^2\Sigma$  and  $^2\Pi$  is very delicate for  $C_4H$ . The electronic states of 3-ring isomers of  $C_3H$ ,  $C_5H$ , and  $C_7H$  are  $^2B_2$ , while those of  $n$ -ring  $C_4H$  and  $C_6H$  are, respectively,  $^2B_1$  and  $^2A_1$ . As is now known,<sup>2-5</sup> the 3-ring isomer of  $C_3H$  is nearly as stable as or slightly more stable than the linear one. The 3-ring isomers of  $C_5H$  and  $C_7H$  are less stable than linear ones by only 4 and 15 kcal mol<sup>-1</sup>, respectively. The  $n$ -ring isomers of  $C_4H$  and  $C_6H$  are less stable by 23 and 15 kcal mol<sup>-1</sup>, respectively.

We expect that the second most stable isomers, especially, of  $C_5H$  and  $C_7H$  might be detectable in interstellar clouds. We have calculated rotational constants, dipole moments, IR spectra, *etc.* for them, which would be useful for their detection.

- 1 J. Takahashi and A. Murakami, in preparation.  
 2 J. Takahashi and K. Yamashita, *J. Chem. Phys.*, 1996, **104**, 6613.  
 3 C. Ochsenfeld, R. I. Kaiser, A. G. Suits, Y. T. Lee and M. Head-Gordon, *J. Chem. Phys.*, 1997, **106**, 4141.  
 4 S. Ikuta, *J. Chem. Phys.*, 1997, **106**, 4536.  
 5 K. Aoki, K. Hashimoto and S. Ikuta, *Astrophys. J.*, submitted, 1997.

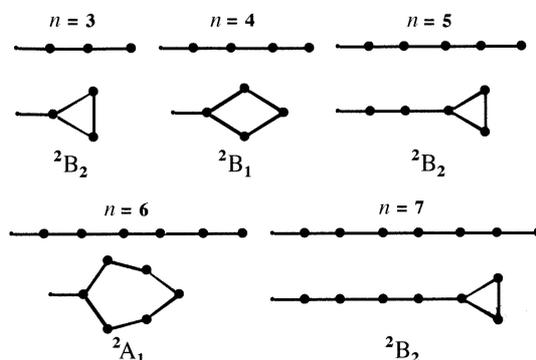


Fig. 13 Stable isomers of  $C_nH$  molecules

**Table 2** Relative energies of  $C_nH$  ( $n=3-7$ ) isomers calculated by *ab initio* molecular orbital method at the QCISD/6-31g\*\* level (kcal mol<sup>-1</sup>)

	$C_3H$	$C_4H$	$C_5H$	$C_6H$	$C_7H$
linear $^2\Pi$	0	0	0	0	0
linear $^2\Sigma$	—	+0.3	—	+2.9	—
3-ring	-0.6	+40	+3.7	+30	+15
$n$ -ring	—	+23	+55	+15	—

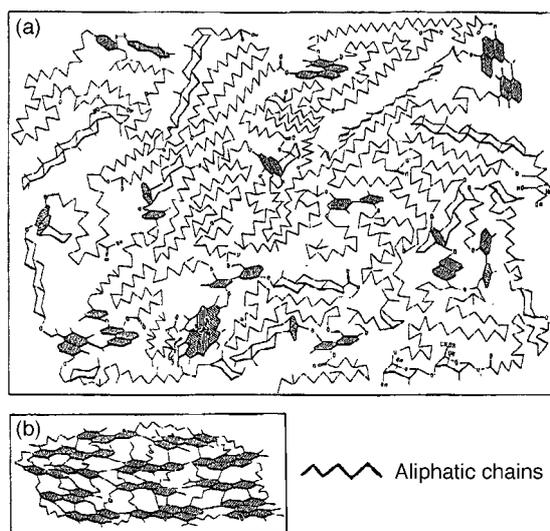
**Prof. Papoular** said: I wish someone would come up here to talk about free-flying PAHs and give us such a convincing proof of their existence in space as Prof. Thaddeus did for long carbon chains! Regarding the formation of the latter, theorists seem to have a hard time synthesizing molecules larger than three or four atoms using exclusively gas-phase molecular reactions. On the other hand, the number of long carbon chains identified in space is increasing steadily, and the largest size observed is already 19 atoms. How is this paradox to be resolved?

Noting that these chains are of the unsaturated carbon type (alternating single and triple bonds, or successive C=C double bonds), I propose that they are, essentially extracts from kerogen-type interstellar grains. This is justified as follows. The SiC emission feature at 11.3  $\mu\text{m}$  bears witness to the formation of carbonaceous grains around C-rich stars on the Red Giant Branch. Later in their evolution (on the Asymptotic Giant Branch) when their mass loss increases and their circumstellar shell becomes thicker this feature is replaced by near-IR features in extinction: the ice feature near  $3300\text{ cm}^{-1}$  and the aliphatic C—H feature around  $2900\text{ cm}^{-1}$  ( $3.4\text{ }\mu\text{m}$ ). The latter becomes prominent towards the Galactic Center<sup>1</sup> which is known to harbour many of these stars.

The  $3.4\text{ }\mu\text{m}$  feature is also exhibited by meteorites, where it is assigned to a notable, kerogen-like, carbonaceous component.<sup>2</sup> Kerogen is an earthly mineral associated with oil beds and similar to the less evolved coals.<sup>3</sup> Geologists describe it schematically as in Fig. 14: it is made up of a few benzenic ring clusters, a number of isolated rings, all with attached hydrogen and oxygen atoms or functional groups (mainly aliphatic C—H,  $\text{CH}_2$ ,  $\text{CH}_3$ , responsible for the  $3.4\text{ }\mu\text{m}$  band) and embedded in a matrix of long, undulating, aliphatic (unsaturated) chains, exactly like the molecules identified by Thaddeus *et al.* in their paper.

It is very tempting to imagine that, in their journey in the harsh interstellar medium, kerogenic grains from the stars are eroded into the observed long chains on the one hand, and on the other hand, into ring clusters which ultimately form the polycrystalline graphite responsible for the UV extinction bump at  $217\text{ nm}$ .<sup>4</sup>

1 S. A. Sandford, Y. J. Pendleton and L. J. Allamandola, *Astrophys. J.*, 1995, **440**, 697.



**Fig. 14** Chemical models of a type 1 kerogen (reproduced with kind permission from Behar and Vandenbroncke, *Rev. Inst. Francais Pétrole*, 1986, **41**); (a) early stage of evolution, (b) later stage (ageing in mild temperatures helps expel the aliphatic chains)

- 2 J. F. Kerridge, in *Carbon in the Galaxy*, ed. J. C. Tarter, S. Chang and D. J. De Frees, NASA Conference Publication 3061, 1990, p. 3.
- 3 See *Kerogen*, ed B. Durand, Editions Technip, Paris, 1980.
- 4 R. Papoular, O. Guillois, I. Nenner, J. M. Perrin, C. Reynaud and J-P. Sivan, *Planetary Space Sci.*, 1995, **43**, 1987.

**Prof. Thaddeus** opened the discussion of Dr Ohishi's paper: Do you think better sources than TMC-1 of large molecules can be found, either in Taurus or elsewhere in the Galaxy? It would be peculiar if this somewhat obscure cloud core turned out to be the best in the entire system.

**Dr Ohishi** responded: It is a difficult question to answer. If I knew a better source than TMC-1, I would have observed it already. Even in the Taurus region, there are several cores with high carbon chain abundances. Generally speaking, there is, of course, a possibility that better sources exist between the Galactic Center and us. Therefore it is important to survey such sources.

**Dr Webster** commented: John Maier's suggested identification of four diffuse interstellar bands,  $C_7^-$ , is unusual in that it is an anion. A polar carbon chain anion would show up in Dr Ohishi's centimetre-wave survey of TMC-1 as an unidentified line, so the number of anionic species could be estimated or limited by the number of unidentified lines. Is that number large or small?

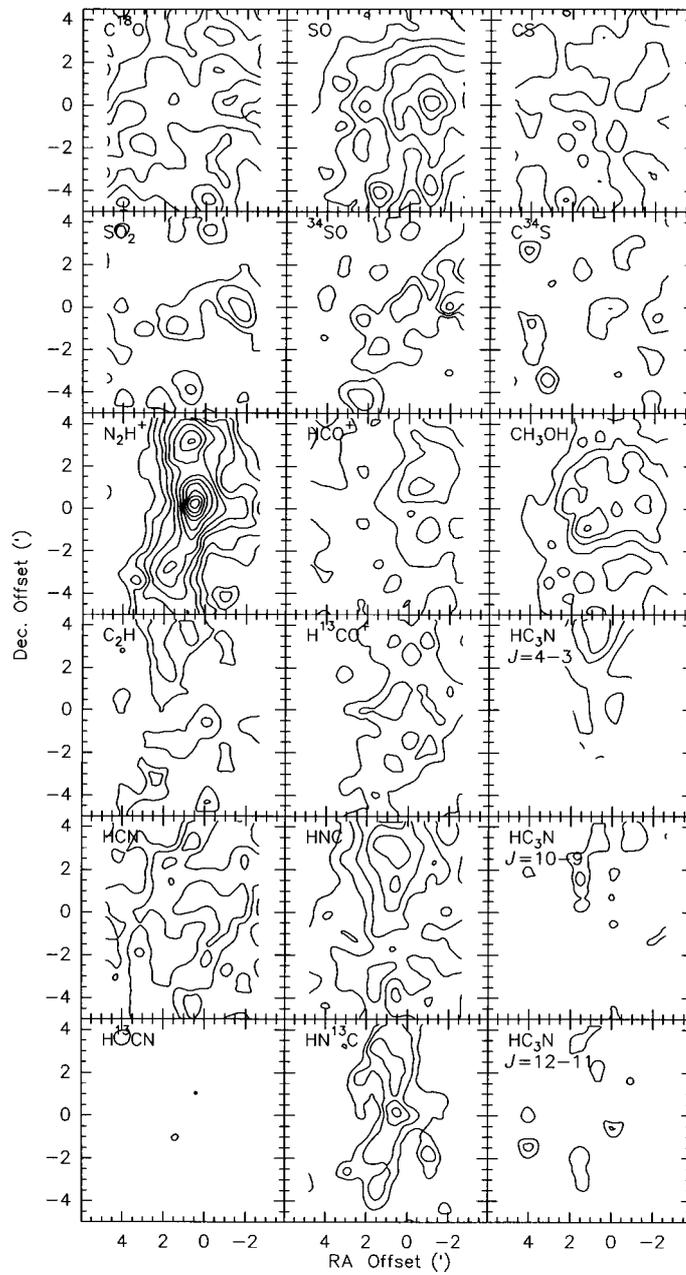
**Dr Ohishi** responded: At present we have only one confirmed unidentified line in our data. This line was observed three times to check its reliability. We have about 10 lines with less reliability and about 200 lines whose intensities are 2–3  $\sigma$  (noise fluctuation) levels. I don't deny the possibility that new species could be found from these unidentified lines.

**Prof. Irvine** commented: It is perhaps useful to point out that, in addition to the source-to-source abundance variations mentioned by Dr Ohishi, there are definitely abundance gradients within specific interstellar clouds of which chemical modelers should be aware. One study of such variations in TMC-1 has been recently published by Pratap *et al.*<sup>1</sup> An example for another cold dark cloud is shown in Fig. 15 where the emission maps for the cloud L134N are given. Although these intensity distributions have not yet been converted to abundance distributions, it seems clear that there must be gradients in, for example, the relative abundances of  $N_2H^+$  and SO.

- 1 P. Pratap, J. E. Dickens, R. L. Snell, R. P. Miralles, E. A. Bergin, W. M. Irvine and F. P. Schloerb, *Astrophys. J.*, 1997, **486**, 862; J. E. Dickens, W. M. Irvine, R. L. Snell, E. A. Bergin, F. P. Schloerb, P. Pratap and M. P. Miralles, in preparation; J. E. Dickens, PhD Thesis, University of Massachusetts, 1998.

**Dr Palumbo** asked: Carbon-chain molecules have been detected both in the molecular cloud TMC-1 and in the circumstellar shell of the nearby carbon star IRC + 10216. Do you think that the formation mechanism of these molecules in these different environments is the same?

**Prof. Herbst** responded: Current generations of gas-phase chemical models, such as ours and those of the UMIST group, are capable of reproducing most if not all observed abundances in the molecular cloud TMC-1 (ref. 1) and in the circumstellar shell of the carbon star IRC + 10216.<sup>2</sup> Although these models both contain ion–molecule and neutral–neutral reactions, the role of neutral–neutral reactions in the syntheses of complex molecules does seem to be more important in the circumstellar shell than in the molecular cloud. In addition, photochemistry is far more important in the circumstellar model. In TMC-1, which is thought to be oxygen-rich, inclusion of unstudied neutral–

L134N – (0,0) at  $15^{\text{h}}51^{\text{m}}30^{\text{s}}$ ;  $-02^{\circ}43'31''$ 

**Fig. 15** Maps of the intensity of molecular transitions of the indicated molecular species over an extended region of the dark cloud L134N, observed in the 3 mm band at the Five College Radio Astronomy Observatory of the University of Massachusetts (J. E. Dickens, W. M. Irvine, R. L. Snell, E. A. Bergin, F. P. Schloerb, P. Pratap and M. P. Miralles, in preparation; J. E. Dickens, PhD Thesis, University of Massachusetts, 1998.)

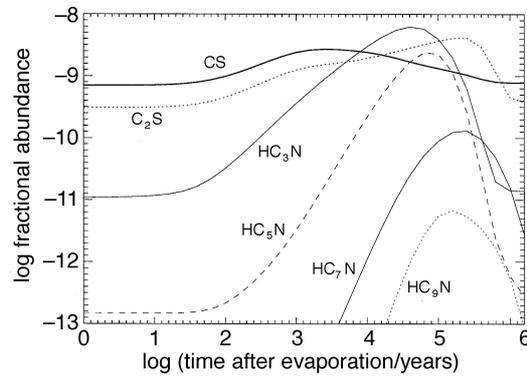
neutral reactions involving atomic oxygen actually worsens agreement with observation.<sup>1,3</sup>

- 1 R. Terzieva and E. Herbst, *Astrophys. J.*, 1998, **501**, 207.
- 2 T. J. Millar and E. Herbst, *Astron. Astrophys.*, 1994, **288**, 561.
- 3 R. P. A. Bettens, H-H. Lee and E. Herbst, *Astrophys. J.*, 1995, **443**, 664.

**Mr Markwick** commented: Recently we (Markwick *et al.*<sup>1</sup>) have been investigating the chemical effects on a model of TMC-1 of injecting some carbon-bearing species into the gas phase which would result from the evaporation of grain ice mantles. This evaporation could be triggered by an MHD Alfvén wave of the kind argued for by Charnley and Butner<sup>2</sup> propagating down the ridge away from the IRAS source located towards the northwest.

Briefly, the cloud model is run to steady state ( $10^8$  yr) and then small quantities of  $\text{CH}_4$ ,  $\text{C}_2\text{H}_2$  and  $\text{C}_2\text{H}_4$  are injected to simulate the ice mantle evaporation. The clock is reset and the model run for a further  $10^6$  yr. The results for some species are shown in Fig. 16.

The main aim was to see whether this evaporation process could produce the chemical gradients observed along the TMC-1 ridge,<sup>3</sup> and we found that it could. To calculate abundance gradients along the ridge, the time ordinate has to be converted to distance along the ridge, so a speed of  $2 \text{ km s}^{-1}$  is assumed for the wave. The zero time at the cyanopolyynes (CP) peak is arbitrary (we don't know when the wave passed) and so it was chosen to be the point at which the cyanopolyynes species peak after injection ( $\approx 3 \times 10^5$  yr).



**Fig. 16** Variation of fractional abundances of cyanopolyynes species, CS and CCS with time after the evaporation of grain ice mantles

**Table 3** Observed fractional abundance of cyanopolyynes species at the CP peak, together with the two peak values in the model. 'Peak 1' is before mantle evaporation and 'Peak 2' after.  
[ $a(b) = a \times 10^b$ ]

	observed	peak 1	peak 2
$\text{HC}_3\text{N}$	8.0(-08)	9.1(-11)	6.2(-09)
$\text{HC}_5\text{N}$	6.0(-09)	1.3(-11)	2.4(-09)
$\text{HC}_7\text{N}$	1.0(-09)	5.4(-13)	1.3(-10)
$\text{HC}_9\text{N}$	7.0(-10)	4.1(-15)	6.7(-12)

The data presented here by Ohishi and Kaifu means that we can compare the abundances at the CP peak point in our model with observed values. There are two points of interest: (1) The evaporation of ice mantles boosts the abundances of cyanopolyne species by orders of magnitude (Table 3), suggesting that this process could be important for their formation in the quantities observed. (2) The ‘unusual’ result of CCS being more abundant than CS at the CP peak can be obtained, as seen in Fig. 16. In the model, CCS is more abundant than CS between  $1.6 \times 10^1$  and  $7.9 \times 10^5$  yr after evaporation, consistent with the adoption of  $3 \times 10^5$  yr for the time at the CP peak.

1 A. J. Markwick, T. J. Millar and S. B. Charnley, in preparation.

2 S. B. Charnley and H. Butner, 1995, in *Circumstellar Matter*, ed. G. D. Watt, Kluwer, Dordrecht, 1995, p. 443.

3 P. Pratap, J. E. Dickens, R. L. Snell, M. P. Miralles, E. A. Bergin, W. M. Irvine and F. P. Schloerb, *Astrophys. J.*, 1997, **486**, 862.

**Dr Ohishi** responded: This is an interesting and important comment on the chemistry occurring in dark cloud cores. As we have noted in the text the abundance of CS was calculated by using a single transition ( $J = 1-0$ ), the value quoted in the paper may contain a large uncertainty. Therefore we plan to improve the CS abundance toward the cyanopolyne peak of TMC-1 in the near future. When a more reliable value has been obtained, and it has been verified that CS is less abundant than CCS, your theoretical work gives a great impact on the interstellar chemistry that evaporation of molecules from grain mantles is also occurring even in dark clouds, as is the case for hot cores.

**Miss Chastaing, Mr L. James, Dr Sims and Prof. Smith** opened the discussion of Dr Kaiser’s paper: You have presented an exciting study of the dynamics of C-atom reactions with small hydrocarbons, studied in a crossed molecular beam apparatus at collision energies down to approximately  $8 \text{ kJ mol}^{-1}$ . In your presentation, you referred to the importance of possible small exit and entrance channel barriers in such reactions to the chemistry of dense interstellar clouds. However, the average collision energy at the low temperatures prevailing in dense clouds is two orders-of-magnitude less than the lowest energy you were able to reach. Small barriers which may be influential in determining rate coefficients and product branching ratios at these temperatures (10–50 K) would be very unlikely to be inferred from your higher energy studies. Is there any way that you could extend these interesting studies to lower collision energies of more relevance to the chemistry of dense clouds?

Furthermore, you mentioned the possibility of inferring rate coefficients for these reactions by estimating absolute cross sections. However, not only is the estimation of absolute cross sections notoriously difficult,<sup>1</sup> but their subsequent conversion to rate coefficients introduces further unknowns. Are you able to address these concerns in order to provide absolute rate coefficients for interstellar chemistry?

1 See for example G. Scoles, *Atomic and Molecular Beam Methods*, ed. G. Scoles, D. E. Bassi, U. Buck and D. Lainé, Oxford University Press, New York and Oxford, 1988, vol. 1, p. 4.

**Dr Kaiser** responded: Since our crossed beams machine has two sources fixed at  $90^\circ$ , it is extremely difficult to go to collision energies less than  $8 \text{ kJ mol}^{-1}$ . If we push it to the lower limit we might go down to about  $4 \text{ kJ mol}^{-1}$ . But that’s it. As stated, small barriers might influence the reactions at lower energies such as present in cold, molecular clouds, but we cannot investigate these low energy processes with our machine. I agree that the branching ratio to, *e.g.*  $1\text{-C}_3\text{H}$  vs.  $\text{c-C}_3\text{H}$ , depends strongly on the collision energy and that it is tricky to extrapolate branching ratios from our studies, but the prime directive of our experiments is to investigate the chemical dynamics, reaction products, and the potential energy surface of these reactions. Both experiments and high level *ab initio* calculations can then be combined to get information on possible branch-

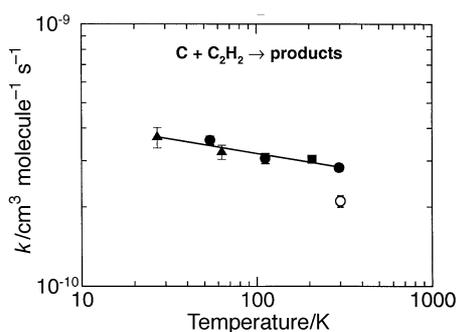
ing ratios relevant to cold molecular clouds. However, based on the chemical dynamics, the reaction products investigated over a wide range in our crossed beam experiments should be present in the ISM as well, if small entrance barriers are absent. Currently, the group of Prof. Head-Gordon at UC Berkeley is extending the *ab initio* studies of the reaction  $C + C_2H_2 \rightarrow C_3H + H$  to  $C_3HD + C \rightarrow C_3H/C_3D + D/H$  including transition state calculations. Hence these calculations should give the final answer if there are any small entrance/exit barriers and the influence on the reaction pathway. Regarding the cross sections, of course it is extremely difficult, but it is feasible. It's only a question of time, but sooner or later it will work. If the absolute reactive cross sections are known, we can convert them to collision energy dependent rate constants  $k(E)$ . We cannot give temperature dependent rate constants. Even an approximation would be too shaky.

**Miss Chastaing, Mr James, Dr Sims and Prof. Smith** commented: Kaiser *et al.*<sup>1</sup> have in their article highlighted the importance of C-atom reactions with neutral co-reagents, especially unsaturated hydrocarbons, in interstellar chemistry. Husain and co-workers have measured the rate coefficients of a wide range of such reactions at room temperature, and, in collaboration with Clary, have related these to a simple electrostatic capture model.<sup>2</sup> We have very recently performed measurements of the rate coefficients of  $C(^3P_J)$  with  $C_2H_2$ ,  $C_2H_4$  and  $O_2$  at temperatures from 295 K down to 27 K within the ultracold environment of the Birmingham CRESU apparatus,<sup>3</sup> using a chemiluminescent marker technique resembling, in principle, that described by us in our study of  $C_2H$  reactions reported in this Discussion.<sup>3</sup>  $C(^3P_J)$  atoms were produced by the 193 nm excimer laser photolysis of carbon suboxide,  $C_3O_2$ ,<sup>4</sup> and detected by adding a constant excess of  $NO_2$  to the gas flow and observing the chemiluminescence resulting from the reaction

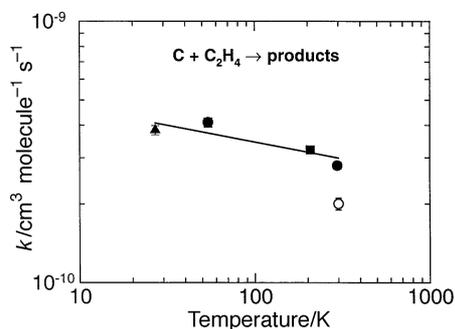


Some proportion of the NO is formed in the  $B^2\Pi$  electronically excited state,<sup>5</sup> and observation of the NO  $\beta(B^2\Pi-X^2\Pi; v' = 0 \rightarrow v'' = 8)$  emission *via* an interference filter centred at 320 nm (10 nm FWHM) gave a signal proportional to the C-atom concentration.

Our preliminary results for the reactions of C atoms with  $C_2H_2$ ,  $C_2H_4$  and  $O_2$  at temperatures between 295 and 27 K are shown in Fig. 17–19, and the results of non-linear least-squares fitting to a rate coefficient expression of the form  $k = A (T/298 \text{ K})^n$  are given in the figure captions. It should be emphasised that these are approximate expressions (estimated confidence  $\pm 20\%$ ) which should only be used in the measured



**Fig. 17** Rate coefficients  $k$  for the reaction of C with  $C_2H_2$  plotted on a log-log scale against temperature. The filled symbols show the results of this work: ●, denotes Ar carrier gas; ■,  $N_2$ ; and ▲, He. The room temperature result of Naider and Husain<sup>6</sup> is shown as ○, while — shows the fitted expression  $k = 2.84 \times 10^{-10} (T/298 \text{ K})^{-0.11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .



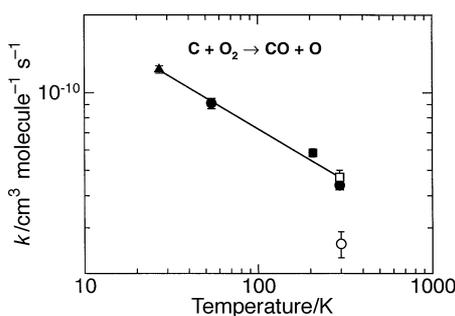
**Fig. 18** Rate coefficients  $k$  for the reaction of C with  $C_2H_4$  plotted on a log–log scale against temperature. The filled symbols show the results of this work: ●, denotes Ar carrier gas; ■,  $N_2$ ; and ▲ He. The room temperature result of Naider and Husain<sup>6</sup> is shown as ○, while — shows the fitted expression  $k = 3.00 \times 10^{-10} (T/298 \text{ K})^{-0.13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

temperature range, 27–295 K. We note that, while our room temperature rate coefficients are somewhat higher than those measured by Husain and co-workers<sup>6,7</sup> (by ca. 30–40%), in the case of  $C + O_2$  we are in near exact agreement with the recent, laser-based determination of this rate coefficient by Becker *et al.*<sup>8</sup>

We plan on making measurements at lower temperatures and with a wider range of reaction partners in the very near future, as well as further measurements using a complementary technique involving direct detection of C atoms by vacuum ultraviolet laser-induced fluorescence.

- 1 R. I. Kaiser, C. Ochsenfeld, D. Stranges, M. Head-Gordon and Y. T. Lee, *Faraday Discuss.*, 1998, **109**, 183.
- 2 See D. C. Clary, N. Haider, D. Husain and M. Kabir, *Astrophys. J.*, 1994, **422**, 416, and references contained therein.
- 3 D. Chastaing, P. L. James, I. R. Sims and I. W. M. Smith, *Faraday Discuss.*, 1998, **109**, 000.
- 4 D. J. Anderson and R. N. Rosenfeld, *J. Chem. Phys.*, 1991, **94**, 7857.
- 5 G. Dorthe, J. Caille, S. Burdenski, P. Caubet, M. Costes and G. Nouchi, *J. Chem. Phys.*, 1985, **82**, 2313.
- 6 N. Naider and D. Husain, *J. Photochem. Photobiol. A: Chem.*, 1993, **70**, 119.
- 7 D. Husain and A. N. Young, *J. Chem. Soc., Faraday Trans. 2*, 1975, **71**, 525.
- 8 K. H. Becker, K. J. Brockmann and P. Wiesen, *J. Chem. Soc., Faraday Trans. 2*, 1988, **84**, 455.

**Prof. Clary** commented: The elegant molecular beam experiments of Kaiser and co-workers have quite high initial collision energies which are much higher than those



**Fig. 19** Rate coefficients  $k$  for the reaction of C with  $O_2$  plotted on a log–log scale against temperature. The filled symbols show the results of this work: ●, denotes Ar carrier gas; ■,  $N_2$ ; and ▲ He. The room temperature result of Husain and Young<sup>7</sup> is shown as ○, and that of Becker *et al.* as □, while — shows the fitted expression  $k = 4.68 \times 10^{-11} (T/298 \text{ K})^{-0.40} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

expected for interstellar clouds. The *ab initio* calculations for some of their reactions give some products that are almost equal in energy to that of the reactants (*e.g.*  $C + C_2H_2 \rightarrow \text{linear} - C_3H + H$ ). If there was a small exit channel barrier in the potential surface for producing these particular products then they might not be produced efficiently in the conditions of the interstellar medium. What are the prospects for Dr Kaiser, and his colleagues who do electronic structure calculations, for studying this point in more detail?

**Dr Kaiser** responded: Currently, Prof. Head-Gordon's group at UC Berkeley is extending the *ab initio* studies of the reaction  $C + C_2H_2 \rightarrow C_3H + H$  and  $C_3HD + C \rightarrow C_3H/C_3D + D/H$  including transition state calculations. These investigations should resolve the question of whether there are any entrance/exit transition states.

**Prof. Clary** said: The interesting experimental results of Prof. Smith on  $C_2H$  reactions and Dr Sims on C atom reactions provide an excellent test of simple predictions we made<sup>1</sup> on the temperature dependence of rate constants for C atom reactions with alkenes and alkynes. A simple capture theory predicted that the reaction rate constant was proportional to  $N^{1/3}T^{1/6}$ , where  $N$  is the number of carbon atoms in the organic molecule. Systematic experiments undertaken by Husain and co-workers showed the predicted  $N$  dependence to work well.<sup>1</sup> The new experiments by Smith and Sims and co-workers give a very weak temperature dependence for the reaction rate constants at lower temperatures and this also fits in quite well with the prediction from simple capture theory.

<sup>1</sup> D. C. Clary, N. Haider, D. Husain and M. Kabir, *Astrophys. J.*, 1994, **422**, 416.

**Prof. Herbst** said: The temperature dependence of radical–neutral reactions depends both on long-range and short-range forces. For  $CN + C_2H_2$  and  $C_2H + C_2H_2$ , simple capture calculations yield a  $T^{1/6}$  dependence for the rate coefficient, in disagreement with the measured inverse temperature dependence for temperatures above 50 K. A phase space calculation for  $CN + C_2H_2$  using a small exit channel barrier reproduces the experimental temperature dependence.<sup>1</sup>

<sup>1</sup> D. E. Woon and E. Herbst, *Astrophys. J.*, 1997, **477**, 204.

**Prof. Smith** said: I should like to respond to two comments made by Prof. Herbst. My first remark relates to the term 'capture' or 'capture theory'. I believe that two points are now generally agreed in regard to the factors which control the rate coefficients of neutral–neutral reactions proceeding over potential energy surfaces without barriers. First, the rates are always determined by 'capture'; that is by the magnitude of the reactive flux through some crucial region of the attractive potential between the reagents. However, it is generally not sufficient to consider only the attractive potential in the limit of long-range which is determined by the dispersion forces and by interaction of non-symmetric charge distributions on the reagents. Capture theories based on such potentials generally provide an upper limit to the rate of capture which is approached only at very low temperatures. At higher temperatures, the transition state region moves to smaller separations and the magnitude of the reactive flux, or capture falls. It is such effects which cause the rate coefficients of many of the neutral–neutral reactions that have been measured down to *ca.* 20 K to fall with increasing temperature. Therefore, the principal difference between different theoretical estimates is in the potential which is used.

My second comment relates to what might be termed the 'wish list' of reactions for which it would be desirable to have low temperature rate coefficients. It would certainly be very worthwhile if astrochemical modellers advise experimental and theoretical physical chemists about which processes have particularly strong influences on observed

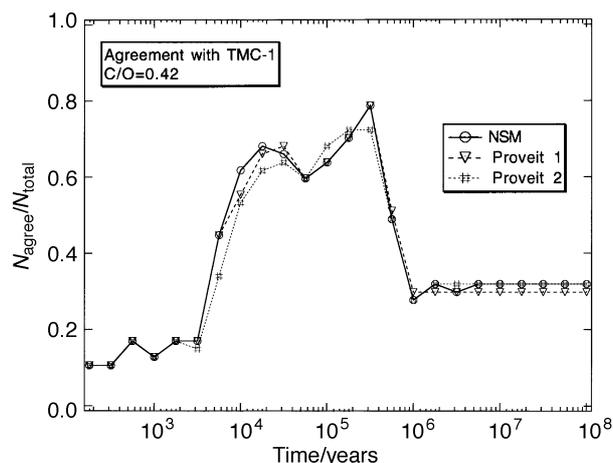
abundances in particular astronomical regions, so that they can be studied particularly intensively. However, it has to be realised that there is little prospect of some reactions being studied experimentally by techniques that are currently available. It is for this reason, that the combined efforts of experimentalists and theoreticians are so important. Finally, in this respect I wonder if it would be useful to attempt to set up a body of experts to review data for astronomical modelling along the lines that has been adopted so successfully for atmospheric chemistry.

**Miss Terzieva** (with **Prof. Herbst**) commented: Starting with our New Standard Model<sup>1</sup> we introduced a number of neutral-neutral reactions studied at temperatures below 25 K, or close analogs to such reactions, including the reactions just described by Prof. Smith. I will refer to this model as Proveit 1 (see Table 4). In a second model called

**Table 4** Modifications to neutral-neutral rates and models

updates to the NSM:	ref. <sup>a</sup>
Proveit 1	
$\text{CN} + \text{C}_n\text{H}_2 \rightarrow \text{HC}_{n+1}\text{N} + \text{H}$ $n = 2, 4, 6 \text{ and } 8$	2
$\text{CN} + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_3 + \text{HCN}$	2
$\text{CN} + \text{C}_2\text{H}_4 \rightarrow \text{C}_3\text{H}_3\text{N} + \text{H}$	2
$\text{C}_2\text{H} + \text{C}_m\text{H}_2 \rightarrow \text{C}_{m+2}\text{H}_2 + \text{H}$ $m = 2, 3, \dots 7$	3
$\text{C}_2\text{H} + \text{O}_2 \rightarrow \text{CH} + \text{CO}_2$	3
$\text{C}_2\text{H} + \text{O}_2 \rightarrow \text{H} + \text{CO} + \text{CO}$	3
$\text{C}_2\text{H} + \text{O}_2 \rightarrow \text{HCO} + \text{CO}$	3
$\text{CN} + \text{O}_2 \rightarrow \text{O} + \text{OCN}$	4
$\text{CH} + \text{H}_2 \rightarrow \text{CH}_3$	5
reaction deleted: $\text{CN} + \text{O}_2 \rightarrow \text{CO} + \text{NO}$	
Proveit 2	
$\text{C} + \text{C}_p\text{H}_2 \rightarrow \text{C}_{p+1}\text{H} + \text{H}$ $p = 2, 3, \dots 8$	5

<sup>a</sup> Full references are given with the comment.



**Fig. 20** Molecular production efficiency  $N_{\text{agree}}/N_{\text{total}}$ , where  $N_{\text{agree}}$  is the number of species with calculated abundances within one order of magnitude of the observed abundances, and  $N_{\text{total}}$  is the total number of species detected in TMC-1, is plotted *vs.* time for the three models discussed.

Proveit 2 we also included the reaction between C and C<sub>2</sub>H<sub>2</sub> and analogs and adopted the room temperature rate constant, not knowing about the study that Dr Sims just described.

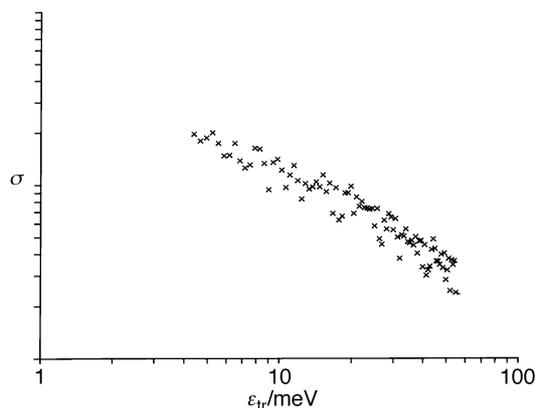
From Fig. 20 one can see that the addition of reaction classes, well studied at low temperature (Proveit 1) maintains the level of agreement with the observations in TMC-1. The introduction of reaction classes which have not been studied at low temperatures and the extrapolations people make are critical for the models. So the negative conclusions concerning models with rapid neutral–neutral reactions may be overly harsh.

- 1 R. P. A. Bettens, H-H. Lee and E. Herbst, *Astrophys. J.*, 1995, **443**, 664.
- 2 I. R. Sims, J-L. Queffelec, D. Travers, B. R. Rowe, L. B. Herbert, J. Karthaeuser and I. W. M. Smith, *Chem. Phys. Lett.*, 1993, **211**, 461.
- 3 D. Chastaing, P. L. James, I. R. Sims and I. W. M. Smith, *Faraday Discuss.*, 1998, **109**, 165.
- 4 B. R. Rowe, A. Canosa and I. R. Sims, *J. Chem. Soc., Faraday Trans*, 1993, **89**, 2193
- 5 R. A. Brownsword, I. R. Sims, I. W. M. Smith, D. W. A. Stewart, A. Canosa and B. R. Rowe, *Astrophys. J.*, 1997, **485**, 195.
- 6 N. Haider and D. Husain, *J. Photochem. Photobiol. A*, 1993, **70**, 119.

**Dr Costes and Prof. Naulin** said: Laboratory studies of neutral–neutral atom-exchange reactions ( $A + BC \rightarrow AB + C$ ) are essential for the comprehension of interstellar chemistry. In this context, the contributions of the CRESU apparatus at Rennes<sup>1</sup> and Birmingham<sup>2</sup> are particularly relevant. Kaiser *et al.*<sup>3</sup> have also demonstrated the benefits that are gained by crossed beam experiments which yield detection of reaction products in single collision conditions. However, as noted by these authors themselves, the coldest known interstellar clouds have kinetic energy of reactant molecules that can be as low as 0.08 kJ mol<sup>-1</sup>, which is considerably lower than the collision energies obtainable in their own experiments.

We recently designed in Bordeaux a crossed beam machine especially fitted to approach such very low collision energies. This new apparatus, which employs laser-induced fluorescence detection, has common features with the experiment of Kaiser *et al.*<sup>3</sup> It thus has two differentially pumped, pulsed, supersonic beam sources and also uses laser ablation to generate beams of refractory species such as carbon atoms. A large range of velocities ( $v_A = 740\text{--}3000\text{ ms}^{-1}$ ) with good velocity resolution ( $\Delta v_A/v_A = 0.08\text{--}0.13$ ) is obtainable for the A atom beam. A more restricted range ( $v_{BC} = 700\text{--}1400\text{ ms}^{-1}$ ,  $\Delta v_{BC}/v_{BC} = 0.10\text{--}0.20$ ) is obtainable for the BC molecular beam, but the whole molecular beam source assembly is rotatable under vacuum with respect to the atom beam. Collisions at beam intersection angles varying between 22.5 and 90°, with a higher limit that can be extended to 145° in some favourable cases, are achieved. As a result, an exceptionally large range of relative translational energies,  $\epsilon_{tr}$ , is accessible with the machine, including those relevant to the conditions of the interstellar medium.

The machine has been first tested with the  $Al(^2P_J) + O_2(X^3\Sigma_g^-) \rightarrow AlO(X^2\Sigma^+) + O(^3P_J)$  reaction.<sup>4</sup> Experiments performed with Al beams of the same velocity distribution, but with different populations of spin–orbit states (obtained with a different carrier gas), have revealed substantial differences in the Al spin–orbit reactivity. Hence  $Al(^2P_{3/2})$  reacts six times less than the ground-state  $Al(^2P_{1/2})$  at the lowest collision energy sampled (6.8 meV). The difference in reactivity reduces when increasing collision energy and cancels at the highest energies (200–250 meV). Such an experiment demonstrates the importance that spin–orbit effects could have under conditions relevant to the interstellar chemistry. The translational energy dependence of the reaction cross section was also determined for the ground  $^2P_{1/2}$  state. It could be fitted between 6 and 200 meV by a dependency in  $(\epsilon_{tr})^{-0.82}$ . Averaging over a Maxwell distribution of velocities yields a temperature dependance of the rate coefficient in  $T^{-0.32}$ , in very good agreement with recent CRESU experiments at Rennes.<sup>5</sup>

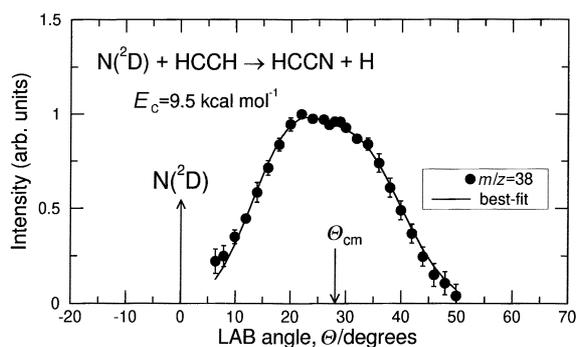


**Fig. 21** Log-log plot of the detailed reactive cross section (in arbitrary units) of the  $C + NO \rightarrow CN + O$  reaction for  $CN(X^2\Sigma^+, v'' = 2, J'' = 18)$  vs. relative translational energy

A quick run was also performed very recently on the  $C(^3P_J) + NO(X^2\Pi_r) \rightarrow CN(X^2\Sigma^+) + O(^3P_J)$  reaction. Carbon atoms were detected by a two photon laser-induced fluorescence scheme at 280 nm and CN radicals were probed by LIF on the  $(B^2\Sigma^+ \leftarrow X^2\Sigma^+)$   $\Delta v = -2$  sequence around 460 nm. Fig. 21, which plots the dependence of the detailed reaction cross section for  $CN(X^2\Sigma^+, v'' = 2, J'' = 18)$  between 4.4 and 56 meV, demonstrates that this is another neutral-neutral reaction without an energy barrier.

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**Prof. Casavecchia** and co-workers<sup>†</sup> commented: In relation to the interesting work of Kaiser *et al.* on combined crossed molecular beams and *ab initio* investigation of carbon-bearing molecules in the interstellar medium *via* neutral-neutral reactions, we would like to report on similar studies on the formation of nitrogen-bearing molecules *via* neutral-neutral reactions. In our laboratory during the last few years we have been investigating in crossed molecular beams a series of reactions of potential relevance in astrochemistry, such as those of oxygen atoms with  $H_2S$  and  $H_2$  and those of OH radicals with  $H_2$  and  $CO$ .<sup>1</sup> Very recently we have been investigating reactions of nitro-

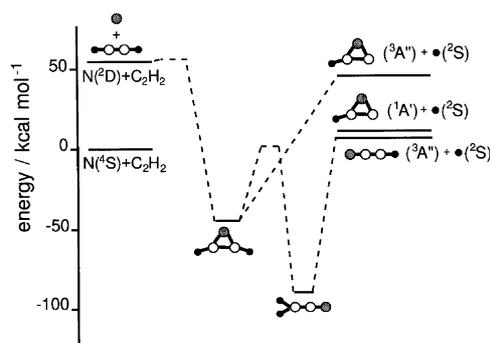


**Fig. 22** Laboratory angular distribution of the HCCN product (detected at  $m/z = 38$ ) from the  $N(^2D) + C_2H_2$  reaction at a collision energy ( $E_c$ ) of  $9.5 \text{ kcal mol}^{-1}$

gen atoms in the electronically excited  $^2\text{D}$  state,  $\text{N}(^2\text{D})$ , with some simple unsaturated hydrocarbons as possible one-step neutral processes for the formation of nitriles in the atmosphere of Titan. We have carried out product angular and velocity distribution measurements under single-collision conditions in crossed beam experiments<sup>2</sup> with mass spectrometric detection using supersonic beams of N atoms generated by radio-frequency discharge<sup>3</sup> in high pressure  $\text{N}_2$ -rare gas mixtures [a magnetic analysis<sup>4</sup> by a Stern–Gerlach magnet has given the following electronic state beam composition:  $\text{N}(^4\text{S})$  72%,  $\text{N}(^2\text{D})$  21%,  $\text{N}(^2\text{P})$  7%]. These are the first successful reactive scattering experiments involving atomic nitrogen. From product angular (see Fig. 22) and velocity distribution measurements at different collision energies we conclude that HCCN (cyanomethylene) formation is the major reaction pathway and arises from the reaction of  $\text{C}_2\text{H}_2$  with  $\text{N}(^2\text{D})$  [the reaction of  $\text{N}(^4\text{S})$  with  $\text{C}_2\text{H}_2$ , as well as that with  $\text{C}_2\text{H}_4$ , is nearly thermoneutral and has high activation energy,<sup>5</sup> while the possible reactions of  $\text{N}(^2\text{P})$  are expected to be slow on the basis of simple adiabatic electronic energy correlation diagrams]. The reaction is found to proceed *via* formation of a long-lived complex at low collision energy ( $3.1 \text{ kcal mol}^{-1}$ ) and *via* an osculating complex (*i.e.*, a complex whose lifetime is comparable to its rotational period) at higher collision energy ( $9.5 \text{ kcal mol}^{-1}$ ).<sup>2</sup>

Very recently, Takayanagi and co-workers<sup>6</sup> have carried out high quality electronic structure calculations on the geometry and energy of the possible reaction intermediates and products of the  $\text{N}(^2\text{D}) + \text{C}_2\text{H}_2$  reaction. Their work shows that  $\text{N}(^2\text{D})$  attacks the two C atoms of acetylene forming a cyclic intermediate which can lead to the very stable  $\text{CH}_2\text{CN}$  intermediate radical complex by (1,2) H-shift and ring opening, or to a somewhat less stable linear  $\text{HNCCH}$  intermediate by simple ring opening. With the support of these calculations we conclude that HCCN formation proceeds through the cyanomethyl ( $\text{H}_2\text{CCN}$ ) complex intermediate (see Fig. 23).<sup>2</sup> The internally hot  $\text{H}_2\text{CCN}$  radical will then dissociate under single collision conditions to  $\text{HCCN} + \text{H}$  by C–H bond cleavage. The HCCN radical is found to be highly internally excited. Although formation of the cyclic-HCCN isomer cannot be ruled out, theoretical calculations indicate that cyclic triplet HCCN (more stable than the singlet form by about  $40 \text{ kcal mol}^{-1}$ )<sup>6,7</sup> does not correlate adiabatically with  $\text{N}(^2\text{D}) + \text{C}_2\text{H}_2$ .<sup>2,6</sup> This suggests that formation of cyclic HCCN does not occur readily in the reaction  $\text{N}(^2\text{D}) + \text{C}_2\text{H}_2$ . Interesting similarities as well as differences are noted with respect to the results obtained by Kaiser *et al.*<sup>8</sup> for the similar reaction  $\text{C}(^3\text{P}) + \text{C}_2\text{H}_2$ .

Our results strongly support the hypothesis made about ten years ago by Yung<sup>9</sup> about the origin and role of HCCN radicals to explain the Voyager observations on Titan and suggest that the  $\text{N}(^2\text{D}) + \text{C}_2\text{H}_2$  reaction may well be the first step in the



**Fig. 23** Schematic energy level and correlation diagram for the  $\text{N}(^2\text{D}) + \text{C}_2\text{H}_2 \rightarrow \text{HCCN} + \text{H}$  reaction (based on theoretical calculations by Takayanagi and co-workers<sup>2,6,10</sup>)

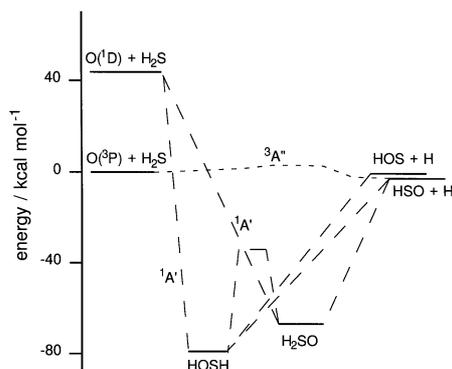
formation of nitriles and should be included in chemical reaction networks modeling of the Titan atmosphere.

The H-displacement pathway has also been observed in the study of the  $\text{N}(^2\text{D}) + \text{C}_2\text{H}_4$  reaction, leading presumably to  $\text{CH}_3\text{CN}$  (acetonitrile) formation, a species also detected in Titan's atmosphere. Studies such as these are expected to play an important role in understanding data of the Cassini probe, a spacecraft with the scope of analyzing Titan's atmosphere within the Huygens–Cassini mission.

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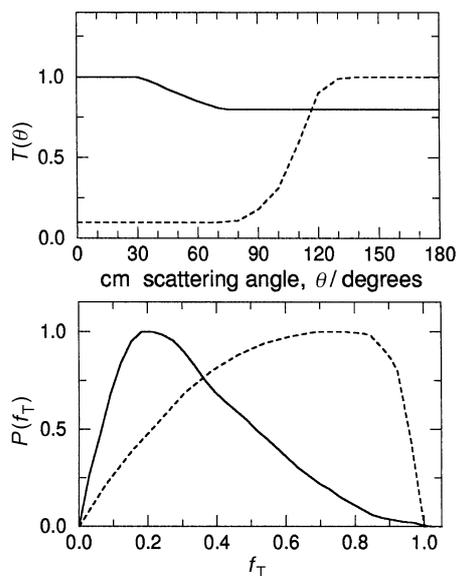
† M. Alagia, N. Balucani, L. Cartechini and G. G. Volpi.

**Prof. Casavecchia** and co-workers† communicated: In relation to the paper presented by Kaiser *et al.* and, specifically, to the study of the reaction  $\text{C}(^3\text{P}) + \text{H}_2\text{S} \rightarrow \text{HCS} + \text{H}$ , we would like to introduce the results we obtained by using the same experimental technique (crossed molecular beams with mass spectrometric detection) on the closely related reaction  $\text{O}(^3\text{P}) + \text{H}_2\text{S} \rightarrow \text{HSO} + \text{H}$ , which may also be of astrophysical relevance. In spite of the strong similarity between the two reacting atoms,  $\text{C}(^3\text{P})$  and  $\text{O}(^3\text{P})$ —both having two unpaired 2p electrons but with the noteworthy difference that  $\text{C}(^3\text{P})$  has an empty p orbital while  $\text{O}(^3\text{P})$  has a fully occupied p orbital—a comparison between the results by Kaiser *et al.* and our results points to different behaviours of the two reacting systems. According to Kaiser's suggestion, the reaction  $\text{C}(^3\text{P}) + \text{H}_2\text{S} \rightarrow \text{HCS} + \text{H}$  occurs by addition of  $\text{C}(^3\text{P})$  to  $\text{H}_2\text{S}$  to form triplet 2,2-dihydrothiocarbonyl; owing to the small gap between the singlet and the triplet states of both 2,2-dihydrothiocarbonyl and thiohydroxycarbene, the occurrence of intersystem crossing (ISC) before and/or after H-migration is called into play to account for the experimental finding of the HCS isomer product.<sup>1</sup> An argument in favour of ISC is the presence of a



**Fig. 24** Schematic energy level and correlation diagram for the  $\text{O}(^3\text{P}, ^1\text{D}) + \text{H}_2\text{S}$  reaction relative to the hydrogen atom displacement channel

sulfur atom, whose relatively large atomic weight may make the spin conservation rule less rigid. Interestingly, our results on the dynamics of  $O(^3P) + H_2S$  may be interpreted without invoking the occurrence of ISC to the singlet surface. Indeed, we studied the reaction dynamics of both the ground,  $^3P$ , and the first electronically excited,  $^1D$ , states of atomic oxygen under the same experimental conditions and for different values of the initial collision energy; this has permitted us to compare directly the dynamical behavior of the two electronic states.<sup>2-5</sup> These studies were made possible by the capability of generating, by high-pressure and high-power radio-frequency discharge, continuous supersonic beams of atomic oxygen containing in addition to  $O(^3P)$  also a small percentage of  $O(^1D)$ .<sup>6,7</sup> Fig. 24 depicts the energy level and correlation diagram for the triplet and singlet reaction leading to H-displacement. It should be noted that the triplet reaction can only lead to formation of the HSO isomer following addition of oxygen to the sulfur atom, while the singlet reaction can lead to both HSO and HOS isomers following  $O(^1D)$  insertion into the HS bond or  $O(^1D)$  addition to the sulfur (the more exoergic, by about  $3.5 \text{ kcal mol}^{-1}$ ,<sup>8</sup> HSO + H channel is expected to be favored). In Fig. 25 the center-of-mass (cm) functions derived from measurements of angular and velocity distributions of the HSO(HOS) product at a collision energy of  $8.15 \text{ kcal mol}^{-1}$  are shown. Notable differences between the cm functions for the reactions of the two states are present: (1) the angular distribution for  $O(^1D) + H_2S$  is almost symmetric with respect to  $\theta = 90^\circ$  with a slight preference for forward ( $\theta = 0^\circ$ ) scattering, while that for  $O(^3P) + H_2S$  is strongly anisotropic with the backward direction ( $\theta = 180^\circ$ ) favored; (2) the translational energy distribution for  $O(^1D) + H_2S$  peaks at a value which corresponds to  $\approx 20\%$  of the total available energy, while that for  $O(^3P) + H_2S$  peaks at a value close to  $\approx 80\%$ . Similar results have been found in a wide range of collision energies (up to  $12 \text{ kcal mol}^{-1}$ ) and have been interpreted in terms of two different reaction mechanisms.<sup>3,5</sup> The reaction of  $O(^1D)$  proceeds through the formation of a complex whose average lifetime is longer than (at  $E_c = 3.4\text{--}4.8 \text{ kcal mol}^{-1}$ ) or a fraction



**Fig. 25** Upper: Center-of-mass HSO product angular distributions from the  $O(^1D)$  (—) and  $O(^3P)$  (---) reaction with  $H_2S$  at a collision energy of  $8.15 \text{ kcal mol}^{-1}$ . Lower: Product translational energy distributions for the same reactions, plotted vs. the fraction of energy in translation.

(at  $E_c = 6.7\text{--}12 \text{ kcal mol}^{-1}$ ) of the complex rotational period; the complex can either be the thioperoxide, HOSH, formed following the  $O(^1D)$  insertion into one of the H—S bonds, or the sulfoxide,  $H_2SO$ , which can be formed after isomerization of the thioperoxide or directly by addition of the oxygen atom to sulfur (see Fig. 24). On the contrary, the reaction of  $O(^3P)$  with  $H_2S$  follows a direct rebound mechanism on the triplet surface with a strong energy release in relative motion of the two moieties.

In conclusion, the dynamics followed by the triplet and singlet reactions are remarkably different, implying no evidence of ISC between the surfaces of the two electronic states. If fact, if a nonadiabatic transition occurred on the entrance channel from the triplet to the singlet potential energy surface (PES), the dynamics of HSO (HOS) formation from  $O(^3P)$  would reflect the influence of the deep well characterizing the singlet intermediate, but the experimental results do not indicate this. The different behavior of the  $C(^3P) + H_2S$  and  $O(^3P) + H_2S$  reactions can be attributed to the significant differences in the corresponding PES and, particularly, to the fact that no stable triplet intermediate exists for  $O(^3P) + H_2S$  as pointed out by detailed theoretical calculations.<sup>8</sup>

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