

---

## General Discussion

---

**Prof. Hutson** introduced the discussion of Prof. Miller's, Prof. Vilesov's and Prof. Lehmann's papers: Helium clusters have emerged over the last 5 or 6 years as a gentle environment for cluster spectroscopy. They achieve and sustain very low temperatures: 0.38 K for pure helium-4 droplets and 0.15 K for helium-4 clusters contained within helium-3 droplets. The temperatures are sustained by evaporation: any process that deposits energy in the droplet simply causes helium atoms to boil off until the original temperature is restored. At these temperatures, helium-4 is superfluid and any molecules in the droplets can undergo nearly free rotation. The spectra of molecules in He droplets can often be rotationally resolved, and generally resemble those of the free molecule, though the rotational constants are reduced compared to the gas phase.

A major attraction of helium droplets is that they allow the production of novel species that do not exist (or are hard to make) in the gas phase. For example, alkali clusters tend to form in high-spin states in (or on) helium droplets, despite the fact that the low-spin states are lower in energy. This is exemplified here by the paper of Reho *et al.*, on triplet potassium dimer. In this case, formation of the low-energy singlet state releases so much energy that the droplet is destroyed. Accordingly, the droplets that survive are those that contain triplet dimers. Quartet alkali trimers have also been produced on the surface of droplets.<sup>1</sup>

Another type of novel species is exemplified by the work of Miller and coworkers, who have shown that HCN clusters form linear chains in helium droplets, even though rings tend to be favoured for unsolvated HCN clusters. In this case the reason is different: linear arrangements are favoured at large HCN–HCN distances, and the minimum-energy path from such a configuration leads to a linear complex at short distances. The role of the helium solvent in this case is to remove the energy released as the HCN molecules approach one another, so that the linear chain has insufficient energy to surmount the barrier that separates it from the stabler ring structures. Linear chains are thus kinetically favoured in droplets, even though rings are thermodynamically favoured.

A third advantage of helium clusters is exemplified in the paper by Grebenev *et al.*, who have studied clusters of the form  $(\text{OCS})(\text{H}_2)_n$  for  $n = 1-8$ . Helium droplets can pick up molecules one-by-one as they pass through a gas chamber. Because of this, it is much easier to make clusters of the form  $\text{AB}_n$ , with a range of values of  $n$ , in helium droplets than in the gas phase.

One of the remaining dynamical questions about superfluid helium droplets concerns the origin of the reduced rotational constants of molecules in droplets compared to the gas phase. In early work, this was interpreted in terms of a small number of helium atoms attached relatively rigidly to the central molecule and rotating with it. As discussed in the paper by Grebenev *et al.*, recent path-integral Monte Carlo calculations<sup>2</sup> have echoes of this explanation, because they identify a subset of non-superfluid helium atoms that cluster around the molecule. An alternative explanation has been offered by Callegari *et al.*,<sup>3</sup> in terms of hydrodynamic effects in the droplets. At first sight, these two explanations look as if they embody quite different physics. One issue that I hope will be explored in the Discussion here is whether the two explanations really are mutually exclusive, or whether they can be seen as different views of the same basic physics.

- 1 J. Higgins, W. E. Ernst, C. Callegari, J. Reho, K. K. Lehmann, G. Scoles and M. Gutowski, *Phys. Rev. Lett.*, 1996, **77**, 4532.
- 2 Y. Kwon and K. B. Whaley, *Phys. Rev. Lett.*, 1999, **83**, 4108; Y. Kwon, P. Huang, M. V. Patel, D. Blume and K. B. Whaley, *J. Chem. Phys.*, 2000, **113**, 6469.
- 3 C. Callegari, A. Conjusteau, I. Reinhard, K. K. Lehmann, G. Scoles and F. DaFolvo, *Phys. Rev. Lett.*, 1999, **83**, 5058.

**Dr Whitaker** asked: I am curious to know why molecular H<sub>2</sub> resides at the centre of a liquid helium droplet rather than on the surface since as we have heard from Prof. Miller the alkali metals, which have weak Van der Waals attractions with He atoms, reside on or close to the surface of He droplets. Now I don't know the depth of the H<sub>2</sub>-He well but I suspect that it is small. Is the H<sub>2</sub>-He Van der Waals potential known, and is it really the case that it is simply the depth of the Van der Waals well that determines where the impurity resides?

**Prof. Vilesov** responded: The H<sub>2</sub>-He Van der Waals potential has a well depth of  $\varepsilon = 9.54 \text{ cm}^{-1}$  at  $r_m = 3.39 \text{ \AA}$ ,<sup>1,2</sup> *i.e.* somewhat deeper than the He-He potential, having  $\varepsilon = 7.64 \text{ cm}^{-1}$  at  $r_m = 2.97 \text{ \AA}$ .<sup>3</sup> Thus a H<sub>2</sub> molecule can be expected to reside inside a helium droplet although it may be considerably delocalized. Definite evidence for an inside location follows from the variational diffusion Monte Carlo simulations,<sup>1,4</sup> which predict a significantly large negative chemical potential in helium. For the alkali metal atoms calculations<sup>5</sup> predict a positive chemical potential, which means that they can not penetrate to the inside. If an OCS molecule is already present in the droplet the H<sub>2</sub> molecule will be attracted to it and replace one of the He atoms in the OCS vicinity, as indicated by the noticeable spectral shift of the band origin of the OCS-H<sub>2</sub> (D<sub>2</sub>) complex compared to that of the bare OCS molecule in the droplet.

1 R. N. Barnett and K. B. Whaley, *J. Chem. Phys.*, 1992, **96**, 2953.

2 F. M. Tao, *J. Chem. Phys.*, 1994, **100**, 4946.

3 K. T. Tang, J. P. Toennies and C. L. Yiu, *Phys. Rev. Lett.*, 1995, **74**, 146.

4 M. A. McMahon, R. N. Barnett and K. B. Whaley, *Z. Phys. B*, 1994, **98**, 421.

5 F. Dalfovo, *Z. Phys. D*, 1994, **29**, 61.

**Prof. Howard** said: I am fascinated by the explanations of the effective moments of inertia of molecules like OCS when their quantised rotational motion is observed in small liquid helium droplets. To what extent do you think that the strength of the helium-molecule interaction potential influences the effective mass that must be ascribed to the helium atoms in the immediate solvent shell?

More fundamentally, what is the real meaning of the effective mass, especially if it can be larger than the actual mass, as in the case of the hydrogen molecules in the hydrogen complexes of OCS? Could it be that there is an increase in the size of the "immobile" helium solvent shell associated with the complexes compared to the monomer, *i.e.* more helium atoms are being "dragged round" when the complex rotates? In support of this interpretation, I notice that the effective masses of H<sub>2</sub> and D<sub>2</sub> differ by just 2 u, exactly the same as their true mass difference.

**Prof. Vilesov** responded: The strength and anisotropy of the helium-molecule interaction is definitely an important ingredient. We have found confirmation for this in a recent analysis of the rotational constants of glyoxal both in the ground and excited electronic states.<sup>1</sup> This also follows from the extensive studies of two-dimensional helium films on different solid substrates.<sup>2</sup> For example liquid helium does not wet Cs surfaces but does wet the surfaces of the lighter alkalis and all other substrates studied so far. Upon increase of the interaction several layers of helium solidify on strongly interacting substrates, such as graphite. In view of the microscopic nature of a molecule and the perfect smoothness of its "surface" it is reasonable to assume that the immobilization of the helium in its vicinity may not be complete and that the helium shell will only partially 'load' the rotating molecule. This idea is supported by microscopic calculations where evidence for a local non-superfluid density in the immediate vicinity of the molecule has been obtained.<sup>3</sup> For small rather compact molecules such as OCS and SF<sub>6</sub> this mechanism may well make a dominant contribution to the observed increase of the moments of inertia in helium. We expect that other contributions to the moments of inertia, such as from hydrodynamic backflow,<sup>4</sup> will become more important as the anisotropy of the rotating object becomes large relative to the range of the Van der Waals forces. Indeed for the spherical top SF<sub>6</sub> molecule, the hydrodynamic contribution of the superfluid has been shown to be negligibly small.<sup>3</sup> Therefore we tentatively assigned the observed moments of inertia of the OCS-H<sub>2</sub> complex to its much greater anisotropy as compared to that of the bare OCS molecule. Or in other words the incorporation of a H<sub>2</sub>

molecule disturbs the permutation symmetry of the ring of helium atoms in the first shell thereby enabling the ring atoms to rotate at the low temperature of the droplet. The observed difference in the effective moments of inertia of H<sub>2</sub> and D<sub>2</sub> in helium (*i.e.* 2 u) demonstrates that as expected from the identical interaction potentials this effect is essentially the same for both isotopes.

- 1 N. Pörtner, J. P. Toennies and A. F. Vilesov, in preparation.
- 2 J. Treiner, *J. Low Temp. Phys.*, 1993, **92**, 1.
- 3 Y. Kwon, P. Huang, M. V. Patel, D. Blume and K. B. Whaley, *J. Chem. Phys.*, 2000, **113**, 6469.
- 4 C. Callegari, A. Conjusteau, I. Reinhard, K. K. Lehmann, G. Scoles and F. Dalfovo, *Phys. Rev. Lett.*, 1999, **83**, 5058.

**Dr McKellar** said: We have recently observed infrared spectra of the Van der Waals complexes OCS–He and OCS–H<sub>2</sub> in the 2062 cm<sup>-1</sup> region of the  $\nu_1$  band of OCS.<sup>1</sup> These results are clearly relevant to the remarkable data shown by Prof. Vilesov for OCS–hydrogen clusters trapped in helium droplets, as reported in the present volume,<sup>2</sup> and elsewhere.<sup>3</sup>

The experimental set-up has been described previously. A tunable infrared diode laser operating in rapid scan mode probes a pulsed supersonic slit jet, with the laser beam passed through the jet region 182 times by means of a toroidal mirror system.<sup>4</sup> The spectrum is calibrated by simultaneously recording spectra of a temperature stabilized etalon and a standard reference gas (OCS in the present case). The expansion gas mixtures consisted of trace amounts (around 0.1%) of OCS in either helium or normal H<sub>2</sub> carrier, with backing pressures of about 4 atm.

In the case of OCS–He, microwave spectra and a calculated intermolecular potential surface have been previously reported by Higgins and Klemperer,<sup>5</sup> following the observation of rotationally-resolved spectra of OCS in helium droplets.<sup>6,7</sup> A calculated potential surface with vibrational dependence has also been reported by Gianturco and Paesani.<sup>8</sup> Our results are entirely consistent with those of Higgins and Klemperer, but they extend to higher values of  $J$  (6 rather than 2). We observe relatively strong  $a$ -type transitions ( $\Delta K_a = 0$ ), as well as  $b$ -type transitions ( $\Delta K_a = \pm 1$ ) which are approximately 6 times weaker. The results can be fitted well using a conventional asymmetric rotor Hamiltonian, with parameters of the upper state (with  $\nu_1 = 1$ ) which are quite similar to those of the lower state ( $\nu_1 = 0$ ). The band origin is located at 2062.313 cm<sup>-1</sup>, which is only about 0.112 cm<sup>-1</sup> higher in wavenumber than that of the free OCS molecule. The OCS–He band origin is thus very close to that of OCS–Ne (2062.316 cm<sup>-1</sup>), as determined by Hayman *et al.*<sup>9</sup>

In the case of the free OCS–H<sub>2</sub> complex there are no previous published spectroscopic observations. However, we are aware of preliminary results by Yu *et al.*<sup>10</sup> involving three microwave pure rotational transitions of OCS–hydrogen which can be unambiguously assigned to the OCS–*ortho*H<sub>2</sub> species due to the presence of hyperfine structure. Our infrared spectrum is completely consistent with these microwave transitions,<sup>10</sup> and we therefore believe that we are also observing OCS–*ortho*H<sub>2</sub>. All our assigned lines are  $a$ -type transitions, with no evidence so far of  $b$ -type transitions. This suggests that the angle between the  $a$  inertial axis of the complex and the axis of the OCS moiety is smaller than in OCS–He, which is quite reasonable in view of the lightness of H<sub>2</sub>. As well, there is no evidence for transitions that might be due to the OCS–*para*H<sub>2</sub> species. This can be explained as a result of *ortho*H<sub>2</sub> being more strongly bound to OCS than is *para*H<sub>2</sub> and therefore “using up” the OCS in the gas mixture. There are a number of precedents for this sort of behaviour in supersonic jet experiments involving hydrogen, for example that of HF–H<sub>2</sub>.<sup>11</sup>

Preliminary molecular parameters from an asymmetric rotor fit to the current spectrum are listed in Table 1. The data set included approximately 40 infrared transitions with  $J$  values from 0 to 6, and  $K_a$  values of 0, 1 and 2, together with three microwave transitions ( $1_{01}-0_{00}$ ,  $2_{02}-1_{01}$  and  $2_{11}-1_{10}$ ).<sup>10</sup> Note that the uncertainties in the  $A$  rotational constant are larger than those for  $B$  and  $C$  due to the fact that only  $a$ -type transitions have been observed. The band origin of 2062.107 cm<sup>-1</sup> represents a small red shift of 0.094 cm<sup>-1</sup> with respect to the free OCS monomer.

In the near future, we hope to observe the OCS–*para*H<sub>2</sub> complex by using pure *para*H<sub>2</sub>, rather than normal H<sub>2</sub>, in our expansion gas mixture. It would also be very interesting to detect combination bands involving excited vibrational states of OCS–He<sup>5,8</sup> and OCS–H<sub>2</sub>, as well as  $b$ -type transitions of OCS–H<sub>2</sub>, but such observations may require a significant improvement in our experimental sensitivity.

**Table 1** Preliminary molecular parameters for OCS-*ortho*H<sub>2</sub> (in cm<sup>-1</sup>)

|            | Ground state,<br>$v_1 = 0$ | Excited state,<br>$v_1 = 1$ |
|------------|----------------------------|-----------------------------|
| $\nu_0$    |                            | 2062.1070(1) <sup>a</sup>   |
| $A$        | 0.7664(39)                 | 0.7649(39)                  |
| $B$        | 0.1891(1)                  | 0.1877(3)                   |
| $C$        | 0.1517(1)                  | 0.1513(3)                   |
| $A_K$      | $[0.144 \times 10^{-2}]^b$ | $0.170(3) \times 10^{-2}$   |
| $A_{JK}$   | $0.134(12) \times 10^{-3}$ | $0.128(18) \times 10^{-3}$  |
| $A_J$      | $-0.36(10) \times 10^{-5}$ | $-0.61(23) \times 10^{-5}$  |
| $\delta_K$ | $-0.01(6) \times 10^{-3}$  | $-0.16(13) \times 10^{-3}$  |
| $\delta_J$ | $-0.21(3) \times 10^{-5}$  | $-0.39(4) \times 10^{-5}$   |

<sup>a</sup> Uncertainties in parentheses correspond to  $1\sigma$  from the least squares fit expressed in units of the last quoted digit. <sup>b</sup> The ground state  $A_K$  value was fixed at this estimated value.

- 1 Jian Tang and A. R. W. McKellar, *J. Chem. Phys.*, 2001, in the press.
- 2 S. Grebnev, E. Lugovoi, B. Sartakov, J. P. Toennies and A. F. Vilesov, *Faraday Discuss.*, 2001, **118**, 19.
- 3 S. Grebnev, B. Sartakov, J. P. Toennies and A. F. Vilesov, *J. Chem. Phys.*, 2001, **114**, 617.
- 4 C. Xia, A. R. W. McKellar and Y. Xu, *J. Chem. Phys.*, 2000, **113**, 525.
- 5 K. Higgins and W. Klemperer, *J. Chem. Phys.*, 1999, **110**, 1383.
- 6 S. Grebnev, J. P. Toennies and A. F. Vilesov, *Science*, 1998, **279**, 2083.
- 7 S. Grebnev, M. Hartmann, M. Havenith, B. Sartakov, J. P. Toennies and A. F. Vilesov, *J. Chem. Phys.*, 2000, **112**, 4485.
- 8 F. A. Gianturco and F. Paesani, *J. Chem. Phys.*, 2000, **113**, 3011.
- 9 G. D. Hayman, J. Hodge, B. J. Howard, J. S. Muentner and T. R. Dyke, *J. Chem. Phys.*, 1987, **86**, 1670.
- 10 Z. Yu, K. Higgins and W. Klemperer, personal communication, 2001.
- 11 C. M. Lovejoy, D. D. Nelson and D. J. Nesbitt, *J. Chem. Phys.*, 1987, **87**, 5621.

**Prof. Vilesov** asked: Did you evaluate the effective structure of the OCS-*o*H<sub>2</sub> complex?

**Dr McKellar** replied: No, we plan to wait until we observe the other isotopes, OCS-D<sub>2</sub> and OCS-HD, before evaluating the structure of OCS-hydrogen.

**Prof. Nesbitt** said: It is rather remarkable that the series of OCS clusters with H<sub>2</sub>, HD and D<sub>2</sub> in helium droplets leads to a self-consistent analysis *via* Kraitchman's equations, since this analysis is exact only for rigid bodies and therefore usually most approximate for systems with large amplitude motion. Is there some physical reason why Kraitchman's analysis seems to work so well for these OCS-H<sub>2</sub> clusters and do you think this behavior is likely to be generally true for other cluster species as well?

**Prof. Vilesov** responded: As stated in our contributions to these Discussions the differences in the degree of delocalization of *p*-H<sub>2</sub>, HD and *o*-D<sub>2</sub> has been neglected. This approximation seems to be justified by the observed linear dependence of the moments of inertia on the isotope masses. It is further supported by the small <0.1 Å anharmonicity induced increase of the average distance calculated for the OCS-He free complex upon substitution of <sup>4</sup>He by <sup>3</sup>He.<sup>1</sup> Due to the roughly 4 times deeper potential well for OCS-H<sub>2</sub><sup>2</sup> the differences are expected to be even smaller upon substitution of H<sub>2</sub> by HD and HD by D<sub>2</sub>, and thus within the error bars of the obtained value of ⟨*R*⟩. Our analysis is also confirmed by the remarkably good agreement of the rotational constant *C* for the free OCS-H<sub>2</sub> complex predicted from our measurements in helium in ref. 3, with those obtained by McKellar from infrared spectra in seeded beams.<sup>4</sup> Note also that the difference in the delocalization between the isotopes may be smaller due to the interactions with the helium atoms of the environment, which corresponds to an increase in their effective masses. The fact that this treatment works well for such a light complex encourages us to hope that it may

work even better for heavier complexes or molecules, for which the above effects are expected to be even less important.

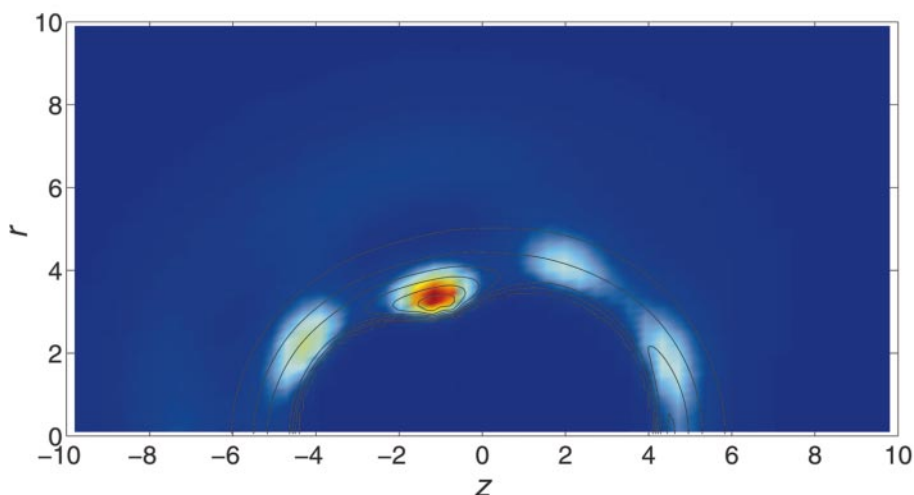
- 1 K. Higgins and W. Klemperer, *J. Chem. Phys.*, 1999, **110**, 1383.
- 2 K. Higgins, personal communication, 1999.
- 3 S. Grebenev, B. Sartakov, J. P. Toennies and A. F. Vilesov, *J. Chem. Phys.*, 2001, **114**, 617.
- 4 R. McKellar, see contribution to the present Discussion.

**Mr Patel** said: In their Discussion contribution Grebenev *et al.* conclude from the absence of a Q-branch for  $n = 5$ , that five  $H_2$  molecules can form a symmetric ring around the waist of the OCS molecule. This confirms a recent prediction made by Kwon and Whaley based on their path integral calculations for clusters of  ${}^4He_N$  containing OCS and variable numbers of  $H_2$ , and described in our paper.<sup>1</sup> These calculations showed that  $n = 5$   $H_2$  molecules form a complete ring of density encircling the linear OCS molecule at the waist location of lowest potential energy, and that the helium density is excluded from this hydrogen ring region. Furthermore, the helium density that is removed from this ring is primarily redistributed further away from the molecule. This ring structure and displacement effect is illustrated in Fig. 1 and 2. Fig. 1 shows the helium density in  $OCS-{}^4He_{39}$ . Fig. 2 shows both the helium and hydrogen densities for the  $OCS(H_2)_5$  complex in the  ${}^4He_{39}$  cluster. We see that the region of the global potential minimum that was occupied by 6 helium atoms in Fig. 1 is now completely replaced by a ring of 5 hydrogen molecules. The potentials used in this study were obtained from ref. 2 (He–OCS) and ref. 3 ( $H_2$ –OCS).

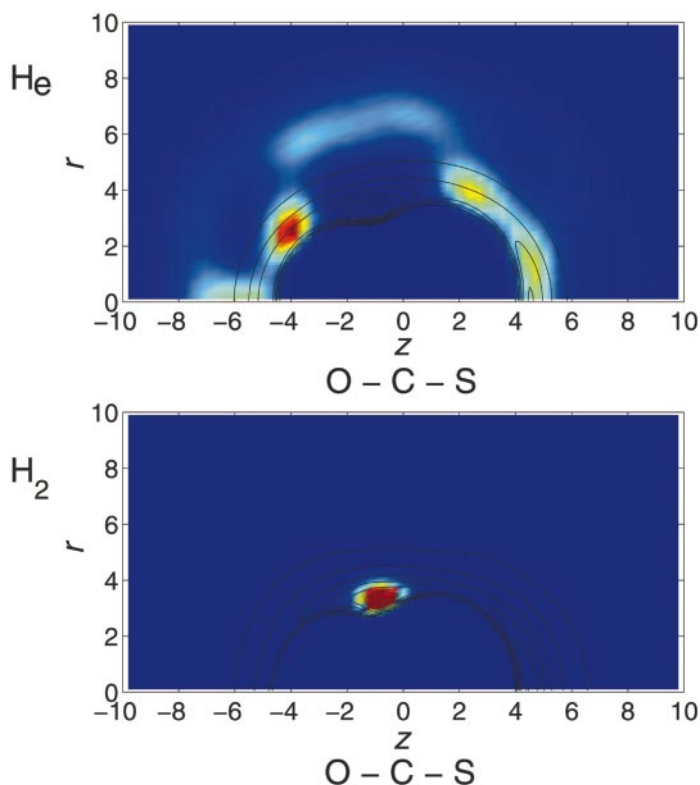
- 1 Y. Kwon, P. Huang, M. V. Patel, D. Blume and K. B. Whaley, *J. Chem. Phys.*, 2000, **113**, 6469; Y. Kwon and K. B. Whaley, *J. Chem. Phys.*, 2001, **115**, in press.
- 2 K. Higgins and W. Klemperer, *J. Chem. Phys.*, 2000, **110**, 1383.
- 3 K. Higgins and W. Klemperer, unpublished.

**Dr Wheeler** said: These calculations reproduce the experimental result for  $n = 5$   $p$ - $H_2$  molecules forming a ring around the waist of the OCS molecule, but do they reproduce the other experimental features, such as a symmetric ring for  $n = 6$   $p$ - $H_2$ , and the lack of symmetry for the  $n = 4$  and  $n = 7$  cases?

**Mr Patel** responded: Preliminary path integral results by Kwon and Whaley for  $n = 6$  show the presence of two low energy structures possessing the same symmetry with respect to the distribution of  $p$ - $H_2$  molecules relative to the OCS molecule.<sup>1</sup> One of these is a symmetric ring for  $n = 6$



**Fig. 1** Helium density in  $OCS-{}^4He_N$ ,  $N = 39$  ( $T = 0.3$  K). Red corresponds to high density, whereas blue indicates low density. Potential contours are drawn in increments of 10 K, with labeled distances in Å. A ring of six helium atoms occupies the region of the global potential minimum. Courtesy of Y. Kwon and K. B. Whaley.



**Fig. 2** Helium (top) and hydrogen (bottom) densities for  $\text{OCS}(\text{H}_2)_5$  in  ${}^4\text{He}_N$ ,  $N = 39$  ( $T = 0.6$  K). Red corresponds to high density, whereas blue indicates low density. The potential contours for He–OCS are shown on the top panel, those for  $\text{H}_2$ –OCS are shown on the bottom panel. Potential contours are drawn in increments of 10 K, with labeled distances in Å. Courtesy of Y. Kwon and K. B. Whaley.

$p$ - $\text{H}_2$  molecules in the OCS waist corresponding to the global potential minimum. The other has a symmetric ring of 5  $p$ - $\text{H}_2$  molecules at this position and the 6th  $p$ - $\text{H}_2$  molecule is located on the OCS axis beyond the S atom. Both of these structures would imply no Q-branch in the spectrum and hence are in agreement with the experimental observations for  $n = 6$ . More extensive calculations are required to determine the relative contributions of these different structures, as well as the sensitivity of these to details of the  $\text{H}_2$ –OCS, He–OCS and He– $\text{H}_2$  potential energy surfaces.

1 Y. Kwon and K. B. Whaley, in progress.

**Prof. Gerber** said: Can an effective mass, as arises in the hydrodynamic model for spectroscopy in liquid He, be extracted from path integral simulations (and used to test the model)?

**Mr Patel** responded: Kwon and Whaley’s path integral calculations provide continuous density distributions of helium and hydrogen around the OCS molecule. The distributions in Fig. 1 are calculated with all boson symmetry effects of  ${}^4\text{He}$  included, but as yet no exchange symmetry for  $\text{H}_2$ . In our Focus article,<sup>1</sup> we present helium densities for clusters containing  $\text{SF}_6$ , OCS and HCN, all calculated at  $T = 0.32$  K with full incorporation of boson permutation symmetry. The model of Grebenev *et al.* presented here for OCS in  ${}^4\text{He}$  clusters represents these continuous density distributions by a discrete set of point masses and then calculates the moments of inertia from this discrete distribution for comparison with the values extracted from the experimentally measured rotational constants at  $T = 0.38$  K. Effective masses appear as parameters in this model when the calculated moments of inertia are fit to the experimental values, given that the locations

of the discrete point masses are specified to approximate the microscopically calculated density distributions of ref. 1. There are therefore several obvious theoretical reasons why the fitted effective masses from this model differ from the true masses. Firstly, the true helium density which is of course continuous, is approximated in this model by a finite set of point masses. There are 19 of these in the model of Grebenev *et al.* while the path integral calculations show that the integrated density in the first solvation shell yields approximately 17 atoms.<sup>1</sup> Second, the model neglects exchange effects, as acknowledged by Grebenev *et al.* Since only the non-superfluid component of the <sup>4</sup>He in the first solvation shell actually behaves as if it is rigidly attached,<sup>1</sup> the density contributing to the moment of inertia is less than the true density. It is, however, not necessary to build such a discrete model requiring the introduction of effective masses, in order to relate the microscopic densities resulting from a path integral calculation to the experimentally measured moments of inertia. This can be done more directly with the two-fluid theory described in detail in ref. 1. In summary, the effective mass model of Grebenev *et al.* was constructed from the continuous density distribution derived from our path integral calculations, and therefore this already constitutes the calculation that you suggest.

1 Y. Kwon, P. Huang, M. V. Patel, D. Blume and K. B. Whaley, *J. Chem. Phys.*, 2000, **113**, 6469.

**Dr Garrett** asked: Do you include indistinguishability of the <sup>4</sup>He atoms in your path integral calculations and if so, how much effect does exchange of particles have on calculated properties? Do He atoms near the OCS molecule show less propensity to undergo exchange?

**Mr Patel** responded: The path integral calculations of Kwon and Whaley incorporate all boson symmetry effects. They allow detailed analysis of the contribution of boson permutation exchange symmetry to both the energetics and the cluster structure. As described in ref. 1 and 2, the length of permutation exchange paths contributing to the density at a given location can be used to obtain an estimate of the local superfluid density in an inhomogeneous helium fluid. Kwon and Whaley's analysis led in ref. 2 to the prediction of a local, molecular-interaction-induced non-superfluid density in the first solvation shell of helium around an embedded molecule. This non-superfluid density can be qualitatively attributed to the effect of the attractive molecular interaction in decreasing the propensity for neighbouring helium atoms to participate in exchange paths with more distant helium atoms. It is therefore correct to say that the helium atoms undergo reduced exchange in the immediate vicinity of the molecule. The molecule-induced non-superfluid density is to be distinguished from the bulk normal fluid density that was assigned by Landau to phonon and roton excitations. The molecule-induced non-superfluid density around the OCS molecule shows angular modulations that follow the potential contours, illustrated in Fig. 15 of ref. 1. As shown there, this local anisotropic structure in the non-superfluid density is very similar to that seen in the total and superfluid densities. A full analysis of the role of boson permutation exchange symmetry effects in <sup>4</sup>He clusters containing an embedded molecule, and the locally perturbing effect of the molecule on the helium superfluidity are given in ref. 1 and 2. Boson symmetry effects of hydrogen in clusters containing  $n > 1$  hydrogen molecules are currently under investigation.

1 Y. Kwon, P. Huang, M. V. Patel, D. Blume and K. B. Whaley, *J. Chem. Phys.*, 2000, **113**, 6469.

2 Y. Kwon and K. B. Whaley, *Phys. Rev. Lett.*, 1999, **83**, 3812.

**Dr Halberstadt** asked: Did you see in your calculation any evidence for He–He vibrations in the first solvent shell? These vibrations should be very low frequency, as deduced from the values obtained in He<sub>2</sub>Cl<sub>2</sub>,<sup>1</sup> hence they could play a role in the infrared spectra of molecules inside helium nanodroplets.

1 M. I. Hernández, N. Halberstadt, W. D. Sands and K. C. Janda, *J. Chem. Phys.*, 2000, **113**, 7252.

**Mr Patel** responded: In this study, Kwon and Whaley<sup>1,2</sup> did not look at specific He–He vibrations; however, they are, of course, implicitly included in the thermal averages (at  $T = 0.38$  K) used to obtain their results. You raise an interesting general question regarding excited states. It is indeed possible to make explicit studies of the excited states of helium clusters containing embedded molecules, both the collective excitations and the local excitations deriving from the molecular

excitation. Several quantum Monte Carlo based methods are available for this. Chin and Krotscheck have used variational Monte Carlo to analyze the effect of an embedded molecule on the phonon–roton spectrum of collective excitations of  $^4\text{He}$  clusters.<sup>3</sup> This requires use of accurate trial functions, which is a topic with a considerable history in the theory of helium clusters (see ref. 4). Local excitations have been the focus of recent work in our group. We have employed the projection operator imaginary time spectral evolution approach to calculate rotational excitations of diatomic molecules in  $^4\text{He}$  clusters.<sup>5,6</sup> The early version of this was restricted to small numbers of  $^4\text{He}$  atoms, but recent improvements to the spectral evolution approach have allowed calculations of excitations in clusters with up to  $N = 25$ .<sup>7</sup> This approach, which is free of any nodal constraints, is now being applied to study of the local vibrational excitations of helium in the first solvation shell around aromatic molecules.<sup>8</sup> We have also employed an importance-sampled rigid body diffusion Monte Carlo algorithm within the fixed node approximation to study rotational excitations of  $\text{SF}_6$  and  $\text{HCN}$ .<sup>9,10</sup> Additional rotational energy level studies for  $\text{OCS}$  are now underway.<sup>11</sup> All three of these Monte Carlo methods (variational, spectral evolution without nodal constraints, and fixed node diffusion) could be applied to the study of He–He excitations in the first solvation shell and beyond. Other quantum Monte Carlo studies of local excitations include the calculation of molecular vibrational shifts by correlated sampling of two vibrationally adiabatic potential surfaces.<sup>12</sup>

- 1 Y. Kwon, P. Huang, M. V. Patel, D. Blume and K. B. Whaley, *J. Chem. Phys.*, 2000, **113**, 6469.
- 2 Y. Kwon and K. B. Whaley, *Phys. Rev. Lett.*, 1999, **83**, 3812.
- 3 S. A. Chin and E. Krotscheck, *Phys. Rev. B*, 1995, **52**, 10405.
- 4 K. B. Whaley, *Adv. Mol. Vib. Collision Dyn.*, 1998, **3**, 397.
- 5 D. Blume, M. Mladenovic, M. Lewerenz and K. B. Whaley, *J. Chem. Phys.*, 1999, **110**, 5789.
- 6 A. Viel and K. B. Whaley, *J. Chem. Phys.*, 2001, **115**, in press.
- 7 P. Huang, A. Viel and K. B. Whaley, *Recent Advances in Quantum Monte Carlo Methods—Part II*, World Scientific Press, in press.
- 8 P. Huang and K. B. Whaley, in preparation.
- 9 E. Lee, D. Farrelly and K. B. Whaley, *Phys. Rev. Lett.*, 1999, **83**, 3812.
- 10 A. Viel, M. V. Patel, P. Niyaz and K. B. Whaley, *Comput. Phys. Commun.*, 2001.
- 11 F. Paesani, F. Gianturco and K. B. Whaley, in preparation.
- 12 D. Blume, M. Lewerenz, G. Huisken and Kaloudis, *J. Chem. Phys.*, 1996, **105**, 8666.

**Prof. Lehmann** said: I would like to take exception to the closing comments in the paper by Vilesov and coworkers that their results would appear to be inconsistent with the expectations based upon the hydrodynamic model put forward by my coworkers and myself.<sup>1</sup> The qualitative changes in rotational constants with hydrogen solvation that Vilesov and coworkers observed in helium are certainly consistent with the directions expected from the quantum hydrodynamic model. In this model, gradients of the density in the direction of rotational motion are the source terms for the hydrodynamic flow of the helium many body ground state density in the time dependent field of the rotating molecule. In particular, the increase moment of inertia produced by the substitution of a He atom by a ‘hole’, which is clearly inconsistent with a rotating ‘doughnut’ model, is naturally explained in the hydrodynamic model. The only qualitative observation of this paper that the hydrodynamic model does not provide a natural explanation for, is the apparent nearly linear increase of moment of inertia with added *para*- $\text{H}_2$  molecules. However, the details of the three-dimensional hydrodynamic flow are complex and quantitative changes cannot be predicted without a quantitative calculation, which could easily be done once 3D helium solvation densities around  $\text{OCS}-(\text{H}_2)_n$  are available. The alternative model that the authors claim their results support is based upon a local estimator for the super and normal fluid densities.<sup>2</sup> This estimator has highly unphysical properties, such as not obeying the proper tensor symmetries of the response of the helium.<sup>3</sup> Furthermore, the moment of inertia is calculated from this density by making a questionable assumption of rigid rotation of the nonsuperfluid part of the density.<sup>2,3</sup> More relevant to the current discussion, in the cases that have been published, the local non-superfluid density was found to be highly anisotropic in the first solvation shell.<sup>2</sup> Thus, there appears to be even less reason than the hydrodynamic model to believe that this model would predict the near linear increase of moment of inertia observed in the experiment. Short of detailed microscopic calculations, the present results do not appear to offer any evidence that supports two fluid model of Kwon and Whaley over the quantum hydrodynamic model as is claimed without

support in the conclusions of the paper. I would like to ask the authors of this paper what observations they could have made which would have led them to claim that the quantum hydrodynamic model was to be preferred?

- 1 C. Callegari, A. Conjusteau, I. Reinhard, K. K. Lehmann, G. Scoles and F. Dalfovo, *Phys. Rev. Lett.*, 1999, **83**, 5058; C. Callegari, A. Conjusteau, I. Reinhard, K. K. Lehmann, G. Scoles and F. Dalfovo, *Phys. Rev. Lett.*, 2000, **84**, 1848.
- 2 Y. Kwon and K. B. Whaley, *Phys. Rev. Lett.*, 1999, **83**, 3812.
- 3 Y. Kwon, P. Huang, M. V. Patel, D. Blume and K. B. Whaley, *J. Chem. Phys.*, 2000, **113**, 6469.

**Prof. Vilesov** responded: First of all we would like to reply to the comment made by Prof. Lehmann that “the increase moment of inertia produced by the substitution of a He atom by a ‘hole’ is clearly inconsistent with a rotating ‘doughnut’ model” is not correct. Rather the moments of inertia obtained by extrapolating the data for OCS–D<sub>2</sub>, –HD and –H<sub>2</sub> to zero mass (*i.e.* doughnut with a hole) are in reasonable agreement with those calculated for a free complex consisting of an OCS molecule with the five attached He atoms in the remaining ring (*i.e.* with one atom missing from a six membered ring). Certainly the doughnut model is not perfect in all respects. Some of its limitations have been assessed in our Discussion contribution and are further examined in a forthcoming article.<sup>1</sup>

In response to Prof. Lehmann’s other comment we feel that, as I have already mentioned in response to Prof. Howard’s question both contributions to the moment of inertia can be expected to be present and we see no particular reason to consider only one of them as Prof. Lehmann does in the hydrodynamics model. Indeed, in a very recent paper Prof. Lehmann<sup>2</sup> himself considered a two-dimensional model for rotations in helium, which includes a molecule in a ring of six helium atoms. There he estimated the effect of increasing the strength of the interaction on the conversion of the hindered rotor states of a molecule into the rigid rotation of both the molecule and the ring. As expected for a finite system there is no sharp transition and the coupling sets in gradually. Taking into account all the reservations in making a classical interpretation of a quantum mechanical effect in our opinion the partial drag on the ring exerted by the molecule comes closest to the concept of a nonsuperfluid fraction contribution, rather than to the hydrodynamic effect.

On the atomic length scale of about or less than the distance between the helium atoms and in the presence of Van der Waals interaction an application of the continuum hydrodynamic equations seems highly suspect. As the length scales become much larger than the interatomic distances the hydrodynamic description will clearly become valid. Thus it will be interesting to study the interplay between these two effects with increasing size of the rotating object. This was indeed one of the main motivations of the present work. Recently we have extended the interpretation to spectra of OCS–(*o*-D<sub>2</sub>)<sub>*n*</sub> clusters, for *n* = 1–16, which include the completion of the first shell of molecules around the OCS chromophore. The analysis extends the linear dependence of  $I_{\text{tot}} = I_A + I_B + I_C$  on *n*, shown for *n* = 1–8 in Fig. 8 of our contribution, up to *n* = 16. It is difficult for us to explain this striking trend in terms of the hydrodynamical model for which we would have expected a gradual saturation of  $I_{\text{tot}}$  upon the completion of the first layer. Although we are fully aware of the empirical nature of our new shell model, which may very well be an over-simplification of the actual physical phenomena, it does provide us with a simple means to classify the moments of inertia and direction of the transition moments consistent with the experimental observations. Since this model already nicely accounts for the observations we did not feel it to be appropriate to include additional variables, which would have made it less unambiguous. Of course we agree with Lehmann and co-workers that it would be very instructive to compare our results with calculations based on the hydrodynamical equations. If the hydrodynamical model could explain the new data, this would definitely provide an intriguing turn in the present discussion.

- 1 S. Grebenev, B. Sartakov, J. P. Toennies and A. F. Vilesov, unpublished results.
- 2 K. Lehmann, *J. Chem. Phys.*, 2001, **114**, 4643.

**Prof. Polanyi** said: This comment comes from a dihard reaction dynamicist. For people in our line of business the virtue of a cluster or complex is that it provides a favourable starting point for chemical reaction. If the complex is irradiated with light or low-energy electrons, reaction can be induced between the loosely-held reagents in a preferred initial-state geometry.

A problem with this approach (nonetheless successfully employed in the laboratories of Soep, Visticot, and colleagues, as well as by Wittig, Neumark and our laboratory) is that the constituents of the complex collide with thermal energies in the course of its formation, and may well react in that collision. A solution employed up to the present is to use constituents that, due, for example, to the endoergicity of the reaction, do not react until triggered by radiation. This is, however, a considerable restriction.

The “gentler environment” of the surface of, say, a helium droplet, offers a more general solution to this problem. It should, for example, be possible to bring atomic Na to within complexing distance of XH (where X = Cl, Br or I) without substantial reaction, relying on the low energy-barrier to exoergic reaction to keep Na and XH apart in  $\text{Na} \cdots \text{XH}$ .

This approach could open the way not only to the study of radiation induced reaction in highly-reactive complexes, but also in weakly-bound non-reactive complexes such as  $\text{Li} \cdots \text{H}_2$  which are of fundamental interest since they are related to the prototypical reaction  $\text{H} + \text{H}_2$ .

**Prof. Miller** responded: The idea of using helium droplets to form novel Li–HX species is being actively pursued in our laboratory, as well as others. There is a potential problem here, however, given that Li is on the outside of the cluster, while the molecule is solvated. It is still not clear if the helium droplets will be able to keep the two separated, or if the molecule will pull the atom into the droplet or the atom pull the molecule out.

**Prof. Lester** commented: Prof. Polanyi suggested that exothermic reactions might be studied in He clusters. To follow this comment, I would like to add that He clusters are not necessarily needed. In our recent work (this Discussion), we have stabilized OH radicals with  $\text{H}_2/\text{D}_2$ ,  $\text{CH}_4$  and CO, all of which are exothermic reactions, in binary complexes:  $\text{OH}-\text{H}_2/\text{D}_2$ ,  $\text{CH}_4-\text{OH}$  and  $\text{OH}-\text{CO}$ .

**Prof. Gerber** asked: Is there anything anomalous in the slow vibrational relaxation of HF (and other diatomics) in superfluid He, or is this similar to the corresponding behaviour in rare-gas solids?

**Prof. Miller** responded: I would say that the anomaly is really in the way diatomic molecules interact with cryogenic liquids, in general, compared to polyatomic molecules. Since there is only a single vibrational mode in diatomics, the vibrational energy gaps are large, making vibrational relaxation slow. Similar behaviour has been observed previously by Ewing and Calaway for CO in cryogenic liquids, such as argon and nitrogen.<sup>1</sup>

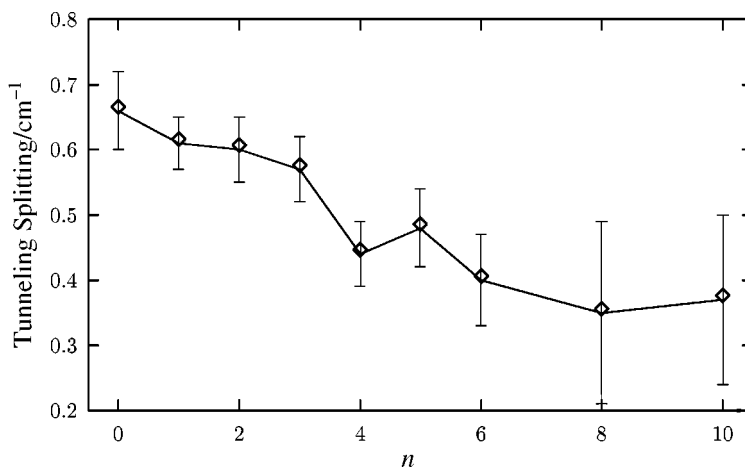
1 W. F. Calaway and G. E. Ewing, *J. Chem. Phys.*, 1975, **63**, 2842.

**Prof. Bačić** said: We<sup>1</sup> have performed diffusion quantum Monte Carlo (DMC) calculations of the ground state interchange tunneling splitting of HF dimer in  $\text{He}_n$  clusters, for  $n$  ranging from 1 to 10. The potential energy surfaces of the clusters were constructed in a pairwise-additive fashion, from highly accurate pair potentials for  $(\text{HF})_2$ ,  $\text{He}-\text{HF}$  and  $\text{He}-\text{He}$ . As shown in Fig. 3 the tunneling splitting decreases rather monotonically with the size of the  $\text{He}_n$  cluster, from 0.66  $\text{cm}^{-1}$  for the isolated  $(\text{HF})_2$  to 0.37  $\text{cm}^{-1}$  for  $n = 10$ . Interestingly, the tunneling splitting changes little from  $n = 6$  to  $n = 10$ . Our DMC calculated tunneling splitting for  $n = 6-10$  of about 0.4  $\text{cm}^{-1}$  is in excellent agreement with that measured for HF dimer in helium droplets,<sup>2</sup> whose average size was estimated to be 2100 He atoms.

1 A. Sarsa, Z. Bačić, J. W. Moskowitz and K. E. Schmidt, in preparation.

2 K. Nauta and R. E. Miller, *J. Chem. Phys.*, 2000, **113**, 10158.

**Prof. Hutson** commented: The model you have described is very interesting. I am particularly intrigued that you can reproduce most of the changes in tunneling frequency without including the effect that I expected to be dominant, and which I mentioned to Prof. Miller when I first heard him describe his HF dimer results. This is the non-additive induction term in the potential: HF dimer is highly polar at its equilibrium geometry, but non-polar at the transition state for tunneling, where the two HF molecules are antiparallel. Polarisation of the solvating He atoms would



**Fig. 3** The ground state tunneling splitting of HF dimer in  $\text{He}_n$  clusters, from DMC calculations.

thus be expected to stabilise the equilibrium geometry with respect to the transition state, and decrease the tunneling splitting.

Your potential surface is pairwise additive. The individual He–HF potentials implicitly include induction, but the pairwise sum of them does not take account of interference effects between the electric fields due to the two HF molecules. The real induction depends on the square of the vector sum of the fields at the He atoms, rather than the sum of the squares.

I believe that Prof. Miller has made some estimates of the magnitude of this effect in HF dimer, and perhaps he could comment on them here.

**Prof. Miller** responded: We have not used pairwise additive potentials in the calculation. In fact, the helium is treated as a continuum in our model. The dipole moment function of the dimer is just the vector sum of the monomer dipoles along the tunneling path. There is certainly an induction term that is lacking in this picture, however a much more important factor is the size of the cavity in which the HF is inserted. All we can really say is that we get reasonable changes in the barrier height using reasonable cavity sizes. The model certainly is not capable of differentiating between dipole moment functions with and without induction. There is obvious need for a more sophisticated, potential energy surface based, calculation of the type you suggest.

**Prof. Suhm** said: Prof. Bačić, you have presented diffusion Monte Carlo results for tunneling splittings in HF dimer solvated by a number of helium atoms. Did you apply a fixed node which is antisymmetric with respect to HF exchange for the excited state? As pointed out previously,<sup>1</sup> the choice of such a fixed node is somewhat ambiguous in higher than four-dimensional space and therefore it only provides an upper bound to the excited state energy. In the present case of a weak coupling of the tunneling motion to the HF stretching and helium modes, it is however likely that this upper bound is quite tight.

1 M. Quack and M. A. Suhm, *Chem. Phys. Lett.*, 1991, **183**, 187.

**Prof. Bačić** responded: Yes, the tunneling splittings were calculated using the fixed-node approximation. In addition, we assumed that the symmetry of the nodal surface is the same as in free HF dimer *i.e.*, unaffected by the He atoms. The HF monomers were treated as rigid in the DMC calculations. However, as you pointed out, the coupling between the high-frequency HF stretching vibrations and the low-frequency tunneling motion (and other intermolecular vibrations) is weak, and the rigid-monomer approximation should have a very small effect on the calculated tunneling splittings. This is certainly the case for free HF dimer, where the tunneling splittings from our 4D and 6D calculations<sup>1</sup> on the SQSBDE PES<sup>2</sup> differ by less than 10%. Moreover, since here we are interested in how the interchange tunneling splitting changes with increasing number of He atoms, the effect of the HF stretch is expected to be even smaller.

- 1 D. H. Zhang, Q. Wu, J. Z. H. Zhang, M. von Dike and Z. Bačić, *J. Chem. Phys.*, 1995, **102**, 2315.
- 2 M. Quack and M. A. Suhm, *J. Chem. Phys.*, 1991, **95**, 28.

**Prof. Lehmann** said: In addition to the changes in barrier height already discussed at this meeting by Profs. Miller and Bačić, I would like to point out that there is an additional physical mechanism that should contribute to the reduction in tunneling splittings that have been observed in liquid helium. If we consider an HF dimer molecule localized in either of the two equivalent minima, we expect the helium atoms to develop an asymmetric solvation structure. If the HF dimer donor–acceptor tunneling occurs without change in the helium density, then the system will not find itself in an isoenergetic configuration. If the change in this solvent reorganization energy exceeds the tunneling energy separation, one would expect a sizable suppression of the tunneling rate. One can view the suppression as reflecting a solvation Frank–Condon factor between the relaxed and frozen helium many body wavefunctions. Equivalently, one could consider the effect as arising from an enhanced effective mass for the tunneling motion, reflecting the kinetic energy required to undergo the helium solvent reorganization. I have worked out how one could use quantum hydrodynamics<sup>1</sup> to estimate the angular dependent effective mass of this changing solvation density, but currently lack the helium density as a function of the tunneling coordinate, which is the required input for such a calculation. I hope that Prof. Bačić and his coworkers will be able to provide the densities for such a calculation.

- 1 C. Callegari, A. Conjusteau, I. Reinhard, K. K. Lehmann, G. Scoles and F. Dalfovo, *Phys. Rev. Lett.*, 1999, **83**, 5058; C. Callegari, A. Conjusteau, I. Reinhard, K. K. Lehmann, G. Scoles and F. Dalfovo, *Phys. Rev. Lett.*, 2000, **84**, 1848.

**Prof. Bačić** responded: I am well aware of your very nice work with Scoles and co-workers. We will try to provide the helium densities needed for your model calculations.

**Prof. McCoy** asked: What factors determine when clusters retain their gas phase structures, as seen in (HF)<sub>2</sub> in He droplets, and when they form linear chains, as in (HCN)<sub>n</sub>?

**Prof. Miller** responded: Let me begin by saying that we do not yet have all the answers to this question. My feeling is that one can understand these differences by considering the relative heights of the barriers between local minima and the ease with which molecules can tunnel. Therefore, heavy rotors will be more difficult to reorient than light ones. Thus the HF clusters formed in helium tend to be the same ones seen in the gas phase, while for HCN and other ‘heavy’ systems, the tendency is to become trapped in local minima. An issue we do not yet fully understand is the role of the helium solvation interactions in changing the energy landscape from that of the gas phase cluster.

**Dr Harvey** said: Can Prof. Miller comment on the large difference between the C–H stretching spectra of HCN·Mg<sub>3</sub> and HCN·Mg<sub>4</sub>? The fourth Mg atom sits in the “second layer” of a cluster model of surface bound HCN. Also, is experimental data available for reference on the surface species?

**Prof. Miller** replied: As I mentioned in my talk, the implication here is that the interactions are highly non-additive. This system is not acting like a collection of argon atoms. Magnesium is highly polarizable and *ab initio* calculations indicate that the metal cluster itself undergoes considerable bond length changes with cluster size. As the Mg–Mg distance decreases with increasing cluster size, the HCN can get closer and interact more strongly. Here again, further theoretical work is needed to fully understand these effects. It is important to note, however, that the frequency shift observed for the Mg<sub>4</sub> system is much larger than we typically see for “free” C–H stretches.

**Prof. Polanyi**, commented: Prof. Miller spoke of the growing interest in free-radical clusters, such as XHY’ where X and Y are halogens. Reaction dynamicists share that interest since free-radicals ABC’ constitute the transition-state in atomic reactions A’ + BC → AB + C’.

A tempting approach to the formation of XHY’ (rather than bringing the constituents X’ + HY together) would be to photolyze a precursor such as HX···HY, causing it to emit an H-atom. One

could use Karl Welge's very sensitive Rydberg-atom method<sup>1</sup> to measure H-atom time-of-flight a metre away. The translational-energy distribution of the H will have the vibrational-energy spacing in the XHY' residue imprinted on it, providing low-resolution vibrational spectra.

We have, in fact, done something on these lines, studying the charge-transfer photodissociation of (HCl)<sub>2</sub> adsorbed on sodium 'dots' (mostly single atoms) at a surface. The recoiling H(g) gave evidence of the asymmetric stretch vibration in the XHX', left at the surface. Interestingly, vibrational levels with vibrational energies up to ~1 eV could be observed.<sup>2</sup>

- 1 I. Schnieder, K. Seekamp-Rahn, F. Liedeker, H. Steuwe and K. H. Welge, *Faraday Discuss. Chem. Soc.*, 1991, **91**, 259.
- 2 J. B. Giorgi, T. G. Lee, F. Y. Naumkin, J. C. Polanyi, S. A. Raspopov and J. Wang, *Faraday Discuss.*, 2000, **117**, 85.

**Prof. Miller** responded: A measurement of the hydrogen atom kinetic energy distribution, resulting from photodissociation of a molecule solvated in helium, would certainly be of great interest. It would provide detailed information about how the atom escapes from the helium droplet. It is quite likely that experiments of this type will be forthcoming.

**Dr Mestdagh**† commented: Our group in Saclay has somehow accidentally done an experiment that is conceptually close to that proposed by Prof. Polanyi. We tried to do a cluster isolated chemical reaction by depositing the Ba/SF<sub>6</sub> reactant pair at the surface of a large argon cluster.<sup>1,2</sup> We were very surprised not to observe any reaction although the Ba + SF<sub>6</sub> → BaF + SF<sub>5</sub> reaction is believed to proceed through a harpoon mechanism and is very exothermic. The reason for this is a small barrier in the entrance channel of the reaction which cannot be passed over at the cluster temperature (30 K), but was unsuspected in standard beam experiments at 0.1 or 0.2 eV collision energy. The origin of the barrier is due to the short crossing distance between the covalent curve correlating to the reactants and the ion-pair curve correlating to the products. The ionization energy decreases substantially when going from Ba to Ba<sub>2</sub>, Ba<sub>3</sub> and larger barium clusters. Correlatively, the crossing distance increases and the barrier to reaction drops. The beauty in this work was to show that when three or more barium atoms are deposited on the cluster, then the energy barrier is low enough for the reaction to be turned on.

- 1 C. Gée, M. A. Gaveau, O. Sublemontier, J. M. Mestdagh and J. P. Visticot, *J. Chem. Phys.*, 1997, **107**, 4194.
- 2 J. M. Mestdagh, M. A. Gaveau, C. Gée, O. Sublemontier and J. P. Visticot, *Int. Rev. Phys. Chem.*, 1997, **16**, 215.

**Dr Whitaker** asked: In a photodissociation experiment, provided that the kinetic energy of the photofragments was high enough so that the droplet was dispersive, *i.e.* above the roton energy, the fragments should be caged and eventually recombine. Would they do so as a singlet or triplet?

**Prof. Lehmann** responded: The answer to this interesting question has yet to be established experimentally, so I will restrict my answer to my current expectations based upon general principles. In a finite helium droplet, there should be perfect caging of the dissociation products, at least as long as the kinetic energy release is not enough to allow ejection of the products from the droplet. If the fragments separate sufficiently that orbital overlap becomes negligible, then I would expect the spins of the products to become uncorrelated, which should lead to more probable recombination on potential surfaces of higher spin multiplicity. For example, we have recently obtained the depletion spectrum of NO<sub>2</sub>, solvated in helium, in a spectral region that extends through the gas phase threshold for dissociation into NO(<sup>2</sup>Π) + O(<sup>3</sup>P).<sup>1</sup> By a simple vector model argument, one would expect the two spin vectors of the products to precess on timescales dictated by their spin-orbit splittings, that is ~100 fs in both cases. The timescale for motion of the fragment molecules in the droplets, once they thermalize, is expected to be three orders of magnitude longer,<sup>2</sup> so recombination should be much slower than spin precession, at least if one of the products has unquenched orbital angular momentum. Statistically, if the spins are uncorrelated,

---

† Also M. A. Gaveau and J. P. Visticot, CEA/DRECAM, France.

they will combine on the metastable quartet surfaces twice as often as on the doublet surfaces that leads to ground state molecules. Our detection method, beam depletion, gives a measure of the energy released into the helium droplet. As a result, if the quartet states are long-lived, one expects to observe a rapid drop of the He depletion signal above the  $\text{NO}_2$  dissociation threshold. Instead, an almost flat depletion spectrum was observed for up to several hundred  $\text{cm}^{-1}$  above the gas phase dissociation threshold. This result can be rationalized if one assumes that, unlike the case of the high spin states of the alkali dimers and trimers previously investigated in helium droplets, the lifetime(s), due to intersystem crossing, of the quartet state(s) formed is(are) much shorter than the flight time from laser interaction to He detector ( $\sim 100 \mu\text{s}$  in this experiment).

In summary, I would expect that in many cases of dissociation to radical products, the spin projections of the dissociation products will become randomized before recombination, with the result that the products will approach each other on different spin surfaces with a statistical distribution, which will favor higher spin states. The helium 'heat bath' will initially quench the system on the energy surface on which the fragments approach. However, intersystem crossing, analogous to that we reported for the excited state of  $\text{K}_2$  in our paper, could lead to relaxation to the lower spin states. Clearly, what is needed are time resolved pump-probe experiments that could catch a spectral signature of a transient high spin species and determine the lifetime for any high spin states that might be formed.

- 1 A. Conjusteau, C. Callegari, K. Lehmann and G. Scoles, unpublished.
- 2 K. K. Lehmann, *Mol. Phys.*, 1999, **82**, 645.

**Dr Mestdagh** asked: What could be the mechanism by which the helium cluster drops the u-g symmetry of the  $\text{K}_2$  molecules? Is it due to an asymmetric solvation with  $\text{K}_2$  away from the centre of the helium droplet?

**Prof. Lehmann** responded: Spectroscopic evidence strongly indicates that all the alkali species, including  $\text{K}_2$ , reside on the surface of the helium droplets. The minimum energy configuration would be expected to have the molecule with its molecular axis parallel to the helium surface, which would preserve the reflection symmetry in the plane perpendicular to the molecular axis, though the inversion symmetry implied by the g-u label would be lost. The remaining plane of symmetry would prevent mixing of the  $\Pi_g$  and  $\Pi_u$  states by the static field of the helium atoms. However, turning the molecular axis normal to the He surface, as would occur in free rotation, would remove the instantaneous symmetry plane perpendicular to the molecular axis and allow mixing of  $\Pi_g$  and  $\Pi_u$  states, but rotational averaging will restore this symmetry.

Even if the  $\text{K}_2$  molecule were in a symmetric environment, its relaxation could lead to formation of phonons with a node at the molecule. This would lead to decay that would violate the g-u selection rule of the isolated molecule. Another way to put this is to consider that while the total ground state wavefunction for the  $\text{He}_n$  may be symmetric about the  $\text{K}_2$  molecule, it is made up of the superposition of amplitudes of configurations that mostly do not have any symmetry. Interactions lead to an entanglement of the  $\text{K}_2$  and helium coordinates, which allows a spontaneous symmetry breaking if one looks only at the  $\text{K}_2$  reduced density matrix.

**Dr Bunker** said: The levels of  $^3\Pi_g$  and  $^1\Pi_u$  states can be mixed by the hyperfine hamiltonian (as can the levels of  $^3\Pi_g$  and  $^1\Sigma_u^+$  states) but the timescale may not be appropriate here.

**Prof. Neumark** asked: Since K atoms and  $\text{K}_2$  molecules are very weakly bound to the surface of He droplets (I believe you said the binding energy was only  $7 \text{ cm}^{-1}$  for a K atom), how can you tell whether the  $\text{K}_2$  emission in your experiments is from surface-bound or free  $\text{K}_2$ ?

**Prof. Lehmann** responded: The binding of a ground state K atom to the helium droplet is more like  $15 \text{ cm}^{-1}$ , but still quite weak. There are three signatures that suggest quantitative desorption of the excited electronic states of the alkali atoms and oligomers. Firstly, the spectra are detected with good signal to noise ratio *via* depletion of the alkali flux, measured with a surface ionization detector.<sup>1</sup> This makes sense if the alkalis desorb and leave the beam, but much smaller signals would be expected if the alkalis stay attached to the droplets which are moving towards the detector. It could be argued, however, that this desorption takes place following excited state

emission. Second, in dispersed emission we have not observed any evidence of the ‘phonon wings’ that are quite evident in the excitation spectra from species on the droplets surface.<sup>2</sup> Lastly, we have measured radiative lifetimes and found that they agree with those measured in the gas phase. If the species remained on the surface, one would expect some change in lifetime. For example, consider the case of Mg, which is fully solvated and does not undergo quenching in helium. The radiative lifetime of the excited <sup>1</sup>P Mg atom is about 20% longer in the helium droplet than in the gas phase.<sup>3</sup> This increase in lifetime, we have calculated, is largely due to the effect of induced dipole moments in the asymmetric helium solvation around the excited atom.

- 1 C. Callegari, J. Higgins, F. Stienkemeier and G. Scoles, *J. Phys. Chem. A*, 1998, **102**, 95.
- 2 J. Higgins, C. Callegari, J. Rheo, W. Ernst and G. Scoles, *J. Phys. Chem. A*, 1998, **102**, 4952; J. Higgins, C. Callegari, J. Rheo, F. Stienkemeier, W. E. Ernst, K. K. Lehmann and G. Scoles, *Science*, 1996, **273**, 629.
- 3 J. Reho, U. Merker, M. R. Radcliff, K. K. Lehmann and G. Scoles, *J. Chem. Phys.*, 2000, **112**, 8409.

**Prof. Vilesov** commented: From my previous work on N<sub>2</sub> molecule I know that transitions between the gerade and ungerade states are readily induced by collisions with He atoms. Similar observations have been done in solid rare gas matrix. Therefore the energy transfer from <sup>3</sup>Π<sub>g</sub> state may involve an intermediate <sup>3</sup>Π<sub>u</sub> state, from which the transition to the emitting <sup>1</sup>Π<sub>u</sub> and <sup>1</sup>Σ<sub>u</sub><sup>+</sup> states may be induced by spin-orbit interaction.

**Prof. Lehmann** said: Prof. Vilesov is correct that there are precedents for the collisional transfer from g to u electronic states of molecules. This suggests that we should not have been surprised by our observation of relaxation of the excited state of K<sub>2</sub> on a timescale of ~10 ps. However, I would like to point out that the K<sub>2</sub> <sup>3</sup>Σ<sub>u</sub> initial state of our experiment also could be expected to relax to the ground <sup>1</sup>Σ<sub>g</sub> state by the same general type of mechanism. The energy separations of the states involved in both the observed and these other possible relaxation pathways are of similar magnitude. However, we know that this <sup>3</sup>Σ<sub>u</sub> state survives for hundreds of microseconds (the flight time between when it is formed and when it is probed), at least 10<sup>7</sup> times longer than the relaxation time we infer for the <sup>3</sup>Π<sub>g</sub> state. Likely, the very large difference in decay time for the two electronic states of K<sub>2</sub> arises, at least in part, from the atomic spin-orbit interactions in the 4s + 4p configurations that dominate the <sup>3</sup>Π<sub>g</sub> state, which are absent in the 4s + 4s configuration that dominates the <sup>3</sup>Σ<sub>u</sub> state. At present, I do not know a reliable way to predict which excited states of solutes in or on helium have very long lifetimes and which ones are rapidly quenched. Obviously, we would like to be able to make such predictions since the quenching lifetime helps determines the photochemistry that takes place in this novel solvent.

**Prof. Gerber** asked: Does the hydrodynamic model assume a classical-like fluid?

**Prof. Lehmann** responded: The hydrodynamic treatment is a well defined approximation to the quantum problem that does not assume a classical-like fluid. It has been known since the dawn of quantum theory<sup>1,2</sup> that quantum dynamics can be exactly formulated as a set of coupled equations for real, single valued amplitude and phase functions in configuration space, and that the phase functions satisfy the equation of continuity of an ideal fluid. The quantum hydrodynamic theory makes the approximation of adiabatic following, which is expressed mathematically by the statement that the instantaneous many body density is equal to that of the helium many body ground state around a static potential created by the solute-helium interaction. Given that the natural excitation energy for the helium is expected to be on the order of 5 K, such an adiabatic separation of the helium and solute motions is expected to be a good approximation for all but the lightest rotors. For the case where a single helium is present, or if one makes a Hartree type approximation to the helium many body wavefunction (as in helium density functional theory), the hydrodynamic approach can be shown to provide the first order, in the angular velocity, perturbation correction to the ground state wavefunction.<sup>3</sup> More generally, one can make a Feynman-type *ansatz* that the many body helium wavefunction can be written in the form:

$$\psi(\mathbf{r}) = u(\mathbf{r}) \exp \left[ -\frac{im}{\hbar} \sum_k \phi(r_k) \right]$$

where  $r_k$  are the coordinates of the  $k$ th helium atom in the frame rigidly moving with the solute, and  $u(\mathbf{r})$  is the ground state many body wavefunction for the helium in the field of the solute, and  $m$  is the mass of a helium atom. Variational minimization of the energy with respect to the single particle phase function,  $\phi$ , gives the classical equation of continuity for the velocity potential (where the irrotational fluid flow is given by  $v = -\nabla\phi$ ).<sup>3</sup>

$$\nabla \cdot (\rho \nabla \phi) = \nabla \rho \cdot \left( \frac{\partial \mathbf{r}}{\partial t} \right)_R$$

Here,  $\rho$  is the one body density and  $R$  is a fixed point in the laboratory frame. Calculation of the kinetic energy with this velocity field gives an increased kinetic energy (proportional to the rotational angular velocity,  $\omega$ ), which can be equated with  $(1/2) I_h \omega^2$ , where  $I_h$  is the contribution of the helium motion to the moment of inertia of the system.

$$I_h = \omega^{-2} m \int \rho(r) |\phi|^2 dr$$

Further, when  $\phi$  is the solution to the equation of continuity, it can be shown that the total angular momentum of the helium implied by the assumed wavefunction is equal to  $I_h \omega$ . Given an estimate of the anisotropic helium density around a solute,  $\rho$ , one can numerically solve the equation of continuity for  $\phi$  (which is proportional to  $\omega$ ) and thus determine  $I_h$ . In the limit that the adiabatic approximation holds (*i.e.* that the  $\omega$  dependence of  $\rho(r)$  can be neglected), it can be shown that  $I_h$  defined by the above quantum hydrodynamic approach is a rigorous lower bound on the effective moment of inertia produced by helium motion, consistent with the Kelvin minimum energy principle of classical hydrodynamics. It has already been demonstrated that this approach predicts  $I_h$  values in excellent agreement with those determined from experiment for a number of symmetric top molecules, except for the very lightest rotors, where the adiabatic following assumption can be called into question.<sup>4</sup>

1 E. Madelung, *Z. Phys.* 1926, **40**, 332.

2 L. De Broglie, *Compt. Rend.*, 1926, **183**, 447.

3 K. K. Lehmann and C. Callegari, unpublished work.

4 C. Callegari, A. Conjusteau, I. Reinhard, K. K. Lehmann, G. Scoles and F. Dalfovo, *Phys. Rev. Lett.*, 1999, **83**, 5058; C. Callegari, A. Conjusteau, I. Reinhard, K. K. Lehmann, G. Scoles and F. Dalfovo, *Phys. Rev. Lett.*, 2000, **84**, 1848.

**Mr Patel** commented: Prof. Lehmann's statement that both models rely on the assumption of adiabatic following is misleading. The DMC-based calculations do not *a priori* make this assumption and can, in fact, be used to evaluate the degree of adiabatic following (see ref. 1 and 2).

The two-fluid analysis of the moments of inertia presented in our paper<sup>1</sup> analyzes separately the contributions of both non-superfluid and superfluid densities under the assumption of adiabatic following. The notion of adiabatic following of helium with the molecular rotation was introduced in an earlier paper from our group.<sup>3</sup> We have since made extensive studies investigating the validity of assuming adiabatic following.

First, we showed in ref. 1 from simple classical energetic considerations that for heavy molecules, such as SF<sub>6</sub> and OCS, the local non-superfluid can adiabatically follow the molecular rotation, but that for lighter molecules, such as HCN, the local non-superfluid will not adiabatically follow.

Second, we have completed a series of detailed diffusion Monte Carlo calculations quantifying and comparing the extent of adiabatic following for this same trio of molecules.<sup>2,3</sup> These calculations compare the angular anisotropy of the total helium density in the molecular frame in terms of whether or not the molecular rotation is incorporated into the calculations. These microscopic quantum calculations demonstrate that there is essentially no adiabatic following for the light HCN molecule, and that there is some limited, incomplete adiabatic following for the heavier molecules, SF<sub>6</sub> and OCS.

In our full two-fluid analysis, described in detail in ref. 1, we conclude from these results that while adiabatic following can be justified for the local non-superfluid component around heavier molecules, it does not hold for the local superfluid component. Furthermore, the explicit hydro-

dynamic calculations for SF<sub>6</sub> summarized there show that for this octahedral molecule, the hydrodynamic contribution to the moment of inertia is negligible, regardless of the extent of adiabatic following by the superfluid, and regardless of whether total or superfluid entities are input into the hydrodynamic calculations. This is in contradistinction to the conclusions arrived at for linear and rod-like molecules in ref. 4. In ref. 1 we concluded that, in general, any significant hydrodynamic contribution from the superfluid would necessarily be accompanied by generation of angular momentum in the superfluid, and that this is inconsistent with angular momentum constraints derived from explicit quantum energy level calculations for the rotating molecule. The assumption of complete adiabatic following by the superfluid underlies this relation between hydrodynamic moment of inertia increment and angular momentum generation.

1 Y. Kwon, P. Huang, M. V. Patel, D. Blume and K. B. Whaley, *J. Chem. Phys.*, 2000, **113**, 6469.

2 E. Lee, D. Farrelly and K. B. Whaley, *Phys. Rev. Lett.*, 1999, **83**, 3812.

3 M. V. Patel, A. Viel, F. Paesani and K. B. Whaley, in preparation.

4 C. Callegari *et al.*, *Phys. Rev. Lett.*, 1999, **83**, 5058.

**Prof. Lehmann** responded and in part communicated: My comments about the assumption of adiabatic following were directed at the path integral Monte Carlo (PIMC) based ‘two fluid’ model of Kwon and Whaley,<sup>1</sup> which does explicitly make this assumption, as this is the method referred to by Grebenev *et al.*<sup>2</sup> The comment by Mr Patel refers instead to the fixed frame, diffusion Monte Carlo (FFDMC) method introduced by Lee, Farrelly and Whaley,<sup>3</sup> which I had not discussed. It is agreed that this later method can in principle be used to test for the accuracy of the adiabatic following assumption. However it must be recognized that the FFDMC method makes a fixed node approximation, and that the form of the nodes used are justified by physical arguments closely related to those used to justify the adiabatic following assumption. A recent model calculation<sup>4</sup> has demonstrated that the adiabatic following and fixed node approximations break down under similar conditions.

The simple consideration introduced by the Whaley group<sup>3</sup> to evaluate adiabatic following can be questioned since it is based upon the localization of a single He atom in the helium–solute potential. Simple model calculations<sup>4</sup> have demonstrated that exchange symmetry of a ring of *N* helium atoms dramatically raises the potential anisotropy required to ‘localize’ the heliums.

In contrast with the calculations reported by Mr Patel that are reported to find ‘that there is essentially no adiabatic following for the light HCN molecule’, experimental evidence<sup>5</sup> has conclusively demonstrated that HCN and DCN are in the intermediate situation with partial following of the helium. Physically, if there was essentially no adiabatic following of the helium, then the rotational constant of the HCN would be expected to be essentially identical to that of the gas phase, which is not the case.

The calculations reported by Kwon *et al.*<sup>6</sup> that find a negligible hydrodynamic contribution to the moment of inertia for SF<sub>6</sub> are based upon their calculated ‘non-superfluid density’. We independently did similar calculations and found a similar result. However, if we used an estimate of the total helium density around the molecule, which is what is used in the quantum hydrodynamic calculations for linear and rod-like molecules,<sup>7</sup> we find a hydrodynamic contribution<sup>8</sup> that is greater than 50% of the experimentally determined value.<sup>9</sup> This later calculation used only the lowest few tensor components calculated from published cuts of the potential.<sup>10</sup> We have not been granted access to the full three-dimensional helium density around SF<sub>6</sub>; the hydrodynamic calculations could be repeated with a more accurate density.

The quantum hydrodynamic approach does not involve any artificial partition of the local ground state density into ‘superfluid’ and ‘non-superfluid’ components,<sup>1</sup> something that Feynman explicitly warned against as being unphysical.<sup>11</sup> The inertial response of the helium is a second rank tensor, yet the algorithm used in ref. 1 and ref. 6 to define the ‘superfluid’ density yields a scalar and thus violates a fundamental physical characteristic of the quantity it claims to represent. The generation of angular momentum in the helium is not in conflict with any explicit quantum energy level calculations published to date despite the unsubstantiated published claim to the contrary.<sup>6</sup>

1 Y. Kwon and K. B. Whaley, *Phys. Rev. Lett.*, 1999, **83**, 4108.

2 S. Grebenev, E. Lugovoi, B. G. Sartakov, J. P. Toennies and A. F. Vilesov, *Faraday Discuss.*, 2001, **118**, 19.

- 3 E. Lee, D. Farrelly and K. B. Whaley, *Phys. Rev. Lett.*, 1999, **83**, 3812.
- 4 K. K. Lehmann, *J. Chem. Phys.*, 2001, **114**, 4643.
- 5 A. Conjusteau, C. Callegari, I. Reinhard, K. K. Lehmann and G. Scoles, *J. Chem. Phys.*, 2000, **113**, 4840.
- 6 Y. Kwon, P. Huang, M. V. Patel, D. Blume and K. B. Whaley, *J. Chem. Phys.*, 2000, **113**, 6469.
- 7 C. Callegari, A. Conjusteau, I. Reinhard, K. K. Lehmann, G. Scoles and F. Dalfovo, *Phys. Rev. Lett.*, 1999, **83**, 5058; C. Callegari, A. Conjusteau, I. Reinhard, K. K. Lehmann, G. Scoles and F. Dalfovo, *Phys. Rev. Lett.*, 2000, **84**, 1848.
- 8 K. K. Lehmann and C. Callegari, unpublished work.
- 9 M. Hartmann, R. E. Miller, J. P. Toennies and A. F. Vilesov, *Phys. Rev. Lett.*, 1995, 1566.
- 10 R. N. Barnett and K. B. Whaley, *J. Chem. Phys.*, 1993, **99**, 9730.
- 11 R. P. Feynman, *Statistical Mechanics: A Set of Lectures*, Addison-Wesley, Reading, Massachusetts, 1990.

**Mr Patel**‡ communicated: The above communication contains several factual errors and misconceptions that must be clarified. First, it should be noted that FFDMC does not necessarily imply use of the fixed node approximation for obtaining excited states. Rigid body DMC<sup>1</sup> (including FFDMC) calculations can be made without the use of the fixed node approximation. OCS and HCN, for example, have recently been studied by RBDMC using POITSE to obtain the rotational excitations free of nodal constraints.<sup>2,3</sup> Also, it should be emphasized that the more realistic RBDMC calculations contain many more degrees of freedom and interaction details than are included in the simple model calculation<sup>4</sup> referred to above. The inaccuracy of the fixed node reported in ref. 4 reflects merely the imposition of incorrect nodal surfaces. It is agreed that a complete evaluation of adiabatic following requires consideration of more than one helium atom. The recent calculations<sup>5</sup> alluded to in my previous response are in no way limited to a single He atom and, in fact, included systems up to  $N = 20$ . Furthermore, as described explicitly in ref. 5, the hydrodynamic calculations for SF<sub>6</sub> were actually made using both total helium density and superfluid density as input. A negligible hydrodynamic contribution to the molecular moment of inertia was found in both cases, *i.e.*, regardless of whether total or superfluid density was employed.

Rotational dynamics of HCN are studied in several forthcoming articles.<sup>1,2,6</sup> As shown there, lack of, or limited, adiabatic following does not necessarily imply a gas-phase rotational constant, when other quantum dynamical factors are involved.<sup>2</sup>

- 1 A. Viel, M. V. Patel, P. Niyaz and K. B. Whaley, 2001, *Comput. Phys. Commun.*, in press.
- 2 A. Viel and K. B. Whaley, *J. Chem. Phys.*, 2001, **115**, in press.
- 3 F. Paesani, A. Viel, F. Gianturco and K. B. Whaley, to be published.
- 4 K. K. Lehmann, *J. Chem. Phys.*, 2001, **114**, 4643.
- 5 Y. Kwon, P. Huang, M. V. Patel, D. Blume and K. B. Whaley, *J. Chem. Phys.*, 2000, **113**, 6469.
- 6 M. V. Patel, A. Viel, F. Paesani and K. B. Whaley, in preparation.

**Prof. Lehmann** communicated: My above comment about the use of a fixed node approximation refers to an assumption made in the published work to which Patel and I referred.<sup>1</sup> The fixed nodes used in my DMC calculation on the simple model<sup>2</sup> resemble those used in ref. 1; this calculation was done to provide a direct test of the accuracy of this node choice in a case where comparison with exact results was possible. The claim of an experimental demonstration of partial adiabatic following for the case of HCN and DCN<sup>3</sup> was based upon the observed increase in the helium contribution to the moment of inertia upon isotopic substitution.

- 1 E. Lee, D. Farrelly and K. B. Whaley, *Phys. Rev. Lett.*, 1999, **83**, 3812.
- 2 K. K. Lehmann, *J. Chem. Phys.*, 2001, **114**, 4643.
- 3 A. Conjusteau, C. Callegari, I. Reinhard, K. K. Lehmann and G. Scoles, *J. Chem. Phys.*, 2000, **113**, 4840.

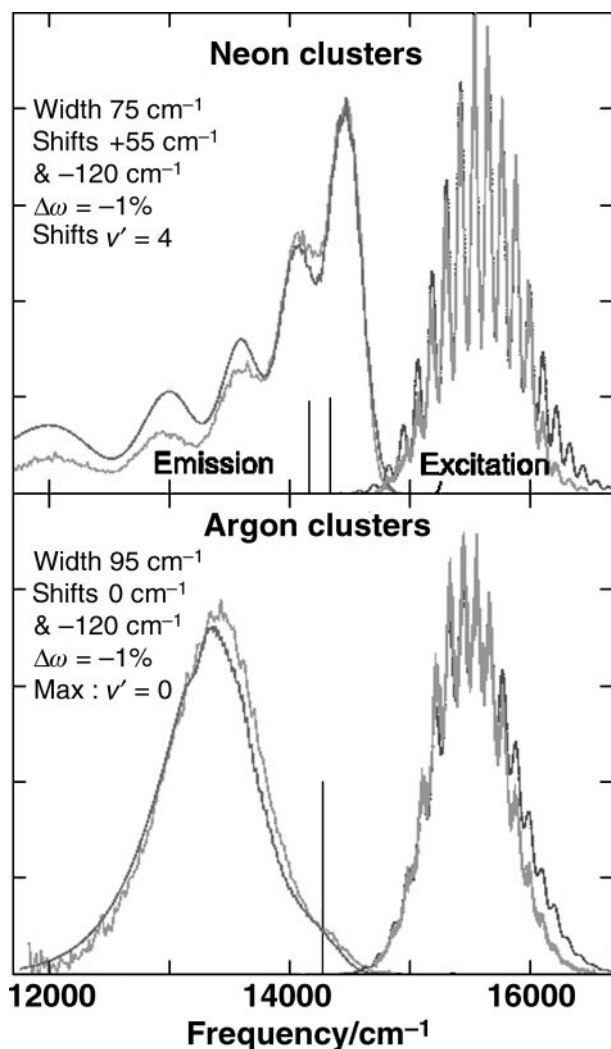
[To avoid publication delays, the exchange of communicated comments was terminated at this point by the Editor.]

**Dr Mestdagh**§ said: Let me report some recent work by our group in Saclay that is in connection with the paper presented by Prof. Lehmann. It concerns the dynamics of electronically excited Ca<sub>2</sub> molecules at the surface of a large argon or neon cluster.

---

‡ Also K. B. Whaley, University of California, USA.

§ Also P. R. Fournier, M. A. Gaveau and J. P. Visticot, CEA/DRECAM, France.



**Fig. 4** Excitation and emission spectra of the  $\text{Ca}_2$  molecule either on neon or argon cluster. The emission spectra are taken with the excitation laser tuned to the maximum of the excitation efficiency. The grey curves show the experimental results and the black curves are spectra simulation using the parameters indicated at the left of each panel.

The experiment is performed using our well established CICR technique.<sup>1</sup> In the present case, two calcium atoms are bound together as a  $\text{Ca}_2$  molecule at the surface of a cluster formed of several thousands of either neon or argon atoms.

The results are shown in Fig. 4. The excitation spectrum  $\text{Ca}_2(\text{X} \rightarrow \text{A})$  is nearly the same in both the neon and argon experiment. The only difference is a small blue shift of  $55 \text{ cm}^{-1}$  in the neon experiment that is not to be discussed here. The important observation in the figure is the very different emission spectrum  $\text{Ca}_2(\text{X} \leftarrow \text{A})$  which reveals important differences in the excited state dynamics whether the A state of  $\text{Ca}_2$  is excited either on a neon or on an argon cluster. The  $\text{Ca}_2(\text{X} \leftarrow \text{A})$  emission in the neon experiment comes essentially from the  $v = 4$  vibrational level whereas emission from  $v = 0$  dominates in the argon experiment. A tentative explanation can be

found in the cooling mechanism of the vibrational excitation of  $\text{Ca}_2$ . In the argon experiment, because of the 1 : 1 mass ratio between Ca and Ar, one vibrating Ca atom can be stopped in one collision with argon. As a result,  $\text{Ca}_2$  ( $A, v \neq 0$ ) can be cooled down to  $v = 0$  in one collision. The picture is different with neon which is twice as light as argon. We consider that the vibrational cooling by neon is almost completely inefficient. Importantly, the  $\text{Ca}_2$  ( $A$ ) potential is crossed by a repulsive curve correlating to  $\text{Ca}(4s4p^3P) + \text{Ca}$  slightly above the  $v = 4$  vibrational level. By the way, all the higher vibrational levels of  $\text{Ca}_2$  ( $A$ ) are predissociated to  $\text{Ca}(4s4p^3P) + \text{Ca}$ , and the only emitting levels are those that have been cooled by neon below  $v = 4$ . Nevertheless, because of the inefficient cooling by neon, the population of the  $v = 4$  level still dominates over those of levels  $v = 0, 1, 2, 3$ .

- 1 J. M. Mestdagh, M. A. Gaveau, C. Gée, O. Sublemontier and J. P. Visticot, *Int. Rev. Phys. Chem.*, 1997, **16**, 215.