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Prof. K. Bowen (*Johns Hopkins University*) asked Dr Meiwes-Broer: How do the p.e. spectra of Cu_n^- and Ag_n^- compare?

Dr Meiwes-Broer replied: Although the atomic d orbitals have different binding energies Ag_n^- and Cu_n^- p.e. spectra nearly coincide in the spectral region we have investigated. Fig. 1 gives three examples for comparison. Both systems nearly coincide even in their bandwidths, with a slight shift (*ca.* 0.15 eV) of the copper p.e. spectra to lower binding energies. For larger n ($n \geqslant 10$) the p.e. thresholds of both systems are practically identical.
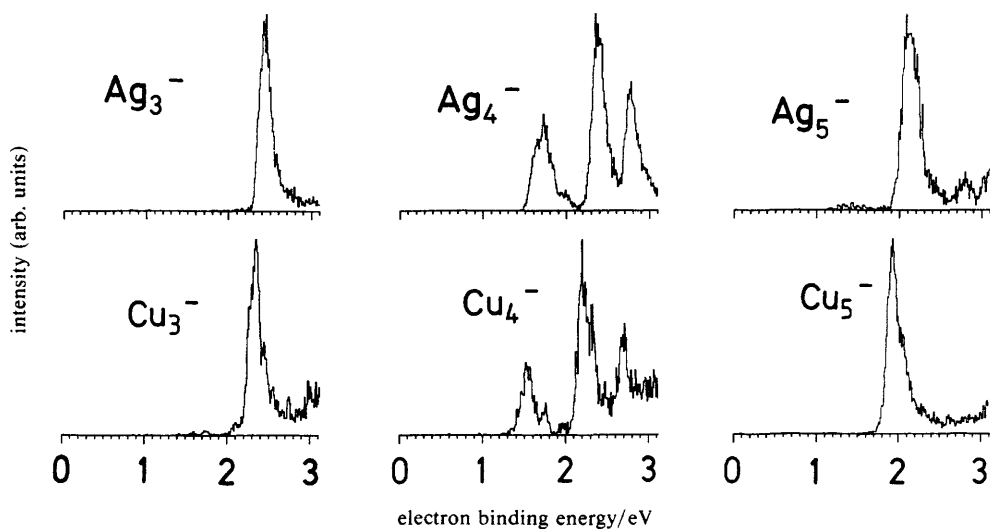

intensity (arb. units)

electron binding energy/eV

Fig. 1. P.e. spectra of Cu_n^- and Ag_n^-, $n = 3$–5, obtained with the experimental set-up described above.

Dr T. Softley (*Cambridge University*) also asked: Do you propose to use photo-detachment to produce neutral, mass-selected cluster beams?

Dr Meiwes-Broer replied: Photodetachment is suited to neutralize cluster anions. When the photon energy is chosen to be near the detachment threshold a neutral ground-state cluster may be formed.

For the production of intense, neutral, mass-selected cluster beams another technique might be of interest. A cluster anion beam undergoes mass-selection (*e.g.* by a Wien filter) and passes a gas cell filled with SF_6. We have shown recently that the resulting charge transfer proceeds with a cross-section substantially higher than that of collision-induced fragmentation.[1,2] Because of high neutralization cross-sections only a low gas load is necessary. With a gas cell length of, *e.g.* 10 cm and 300 dm³ s⁻¹ pumping rate the residual SF_6 pressure outside the cell can be kept below 5×10^{-7} mbar, for a degree of neutralization of *ca.* 50%. So far, however, we have not yet investigated whether the neutralized beam contains traces of (neutral) reaction products (cluster fluorides); the

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charged beam, on the other hand, contains (apart from the parent cluster anion) only SF_6^- and its fragments.

1 W. Begemann, S. Dreihöfer, G. Ganteför, H. R. Siekmann, K. H. Meiwes-Broer and H. O. Lutz, in *Elemental and Molecular Clusters*, Springer Series on Materials Science (Springer-Verlag, Berlin, 1988).
2 W. Begemann, R. Hector, Y. Y. Liu, J. Tiggesbäumker, K. H. Meiwes-Broer and H. O. Lutz, *Z. Phys. D*, 1989, in press.

Prof. D. J. Nesbitt (*University of Colorado*) drew attention to Dr Stace's paper: Prof. Klemperer's question about the possibility of discrete line structure in the acetonitrile dimer spectrum that would not be manifest in a line-tunable, CO_2 laser photofragmentation spectrum is well taken. Indeed, as higher-resolution laser methods have been applied to the long-standing problem of ethylene dimers, sections of the spectra have now been shown to consist of instrumentally narrow, discrete peaks. I feel it is important to note that discrete line structure does not imply solely heterogenous effects (*e.g.* rotational and vibrational congestion, Doppler widths *etc.*), and in particular does not preclude the possibility of strong homogenous coupling (*e.g.* Coriolis, anharmonic *etc.*) between vibrational modes.

Dr A. J. Stace (*University of Sussex*) said: In reply to the comments made by Prof. Klemperer and Nesbitt, our objective has been to present a theoretical technique which might be applicable more to the analysis of spectra from large clusters rather than dimers. In view of the broad profiles predicted by the theory, we have not considered it necessary to undertake experimental measurements at a resolution greater than that provided by the CO_2 laser (1-2 cm^{-1}).

As the size of a cluster increases, it may be necessary to modify our view of the techniques used to analyse any spectroscopic data which we may obtain from such species. Consider, for example, the fact that existing spectroscopic data, from various sources,[1-3] point to benzene clusters having an internal temperature of the order of 200 K. Under such circumstances, the application of some of the techniques which have been presented at this meeting[4,5] to analyse the spectra of small van der Waals molecules, may not be appropriate. Indeed for very large clusters the type of structural information which we could expect to extract from a given experiment may be restricted to that of determining whether the clusters are either liquid-like or solid-like. Qualitative information of this nature is gradually becoming available for molecular clusters.[6]

At a theoretical level, Berry and co-workers[7] have provided evidence of liquid-like and solid-like behaviour in small argon clusters; whether or not the comparatively sharp transitions in phase they observe will also be present in molecular clusters remains to be seen. Evidence from our simulations on small acetonitrile clusters[8,9] points to sublimation preceding any evidence of liquid-like behaviour.

It is possible to identify a number of factors which will contribute to the width of the observed absorption profiles. Homogeneous contributions could include: (i) vibrational predissociation; (ii) dephasing, where the initial phase coherence between the transition dipole and the incident radiation slowly decays. Among the inhomogeneous contributions to the linewidth we should include (iii) isomers; (iv) size variations in the beam; (v) long-term changes in the local environment; (vi) a spread in overall rotational energy among clusters of the same size. If the timescales of (ii) and (v) are comparable then it may not be possible to separate homogeneous and inhomogeneous contributions to the linewidth.[10,11] The calculations presented in our paper[3] are concerned only with environmental contributions to the lineshape. However, more recent cluster simulations[9] have been directed towards estimating the homogeneous or dephasing contribution. In these calculations a lineshape, $I(\omega)$, has been calculated from the Fourier-transform of a correlation function of the unit vector **u**, which lies along the direction of the vibrational

transition moment.[12]

$$I(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \, \langle u(0) \cdot u(t) \rangle \exp(-i\omega t). \tag{1}$$

At a temperature of *ca.* 60 K and for $(CH_3CN)_4$, eqn (1) gives a homogeneous linewidth which is of the order of 1 cm^{-1}. Two factors influence the calculated value. First, the resolution we can achieve is limited by the length of physical time over which the correlation function is calculated. A simulation of the order of 10^{-11} s was necessary for the above result. Secondly, reorientation of the transition dipole is also influenced by overall rotation of the cluster. The coupling of this motion with that of molecular rotation within the cluster, can give $\langle u(0) \cdot u(t) \rangle$ quite a complicated shape.

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2 R. K. Heenan, E. J. Valente and L. S. Bartell, *J. Chem. Phys.*, 1983, **78**, 243.
3 A. J. Stace, D. M. Bernard, J. J. Crooks and K. L. Reid, *Mol. Phys.*, 1987, **60**, 671.
4 D. J. Nesbitt and C. M. Lovejoy, *Faraday Discuss. Chem. Soc.*, 1988, **86**, 13.
5 R. W. Randle, T. R. Dyke and B. J. Howard, *Faraday Discuss. Chem. Soc.*, 1988, **86**, 21.
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7 See, for example, J. Jellinek, T. L. Beck and R. S. Berry, *J. Chem. Phys.*, 1986, **84**, 2783.
8 A. S. Al-Mubarak, G. Del Mistro, P. G. Lethbridge, N. Y. Abdul-Sattar and A. J. Stace, *Faraday Discuss. Chem. Soc.*, 1988, **86**, 209.
9 G. Del Mistro and A. J. Stace, unpublished work.
10 K. S. Schweizer and D. Chandler, *J. Chem. Phys.*, 1982, **76**, 2296.
11 R. M. Lynden-Bell, personal communication.
12 R. G. Gordon, *Adv. Mag. Reson.*, 1968, **3**, 1.

Prof. E. Knözinger also questioned Dr Stace: (1) Your i.r. absorption profile comprises contributions of different species. How do you compare this profile with the calculated band contour, which exhibits a width of *ca.* 10 cm^{-1}?

(2) Do you have any data related to the stability of the different acetonitrile clusters? We have invested considerable efforts in characterising such species in the gas phase, in cryogenic matrices and in the pure gas-phase-deposited solid. We have, however, found only the antiparallel dimer ('head-to-tail') which appears to be particularly stable.

Dr Stace replied: With regard to the comments made by Prof. Knözinger: (1) A typical absorption profile measured in our experiment will contain contributions from all those neutral clusters which when ionized, fragment to the ion being monitored. The only aspect we can be certain of is that the neutral clusters are larger than the ion. However, experience gained from studying the fragmentation patterns of ion clusters,[1] suggests that in systems where the clusters are held together by comparatively strong intermolecular forces, ionization results in a cluster losing just two or three molecules. Hence the size range which contributes to a given absorption profile can be quite narrow.

Beyond $(CH_3CN)_3H^+$ the widths of the experimental absorption profiles appear to be independent of cluster size.[2] Therefore, we can assume that those factors which contribute to the shape of a profile will be similar for all sizes of cluster. This assumption is confirmed by the calculations; in the range $(CH_3CN)_4$–$(CH_3CN)_{10}$ the calculated widths (f.w.h.m.) at a given temperature are all very similar.[2] Two features of the calculations appear to have a strong influence on the width of an absorption profile: (1) the temperature of the cluster and (2) the magnitudes of the cubic anharmonicities, ϕ_{kkl}. Westlund and Lynden-Bell[3] give two sets of values for ϕ_{kkl}, one empirical the other *ab initio*. Use of the latter shifts $(\nu_{max} - \omega_0)$ to 8 cm^{-1} at 27 K and increases the f.w.h.m. from 6 to 10 cm^{-1}.

(2) The confidence we can place in our calculated structures and their relative stabilities is restricted by the quality of the potential-energy surface. Within that bound,

it is found that the most stable clusters are those of an even size, which adopt antiparallel or 'head-to-tail' configurations of the type given in fig. 3(I) of our paper.[4] Of particular interest are the high-temperature (150 K) simulations of odd-sized clusters.[2] There appears to be a sequence of events which involves the making and breaking of molecular pairs, with a single unpaired molecule moving around on the surface of the cluster until it finds a suitable partner. That pattern is then repeated by the molecule which has been displaced.

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