General Discussion

Prof. Howard introduced the discussion of Prof. Zwier's and Prof. Suhm's papers: Throughout this Discussion we have been concentrating on the importance of intermolecular interactions and how they influence the properties of clusters. Conversely we can use this same information, mainly from the spectroscopy of small clusters, to provide information on the nature of intermolecular forces.

Up to now we have mainly heard about studies of clusters containing small molecules, although perhaps with many of them in a single cluster. It is this fact that one can continue to study larger and larger clusters that allows us to assert (as also mentioned by Prof. Miller) that we are bridging the gap between individual molecules in the bulk condensed phases; this is often used to justify the funding of our research. The other great area of activity where intermolecular interactions play an important role is in biological systems. It is here that we need information from the studies of the interactions between large molecules to help us understand and provide models for the structures and other properties of biological systems. Most of these effects are driven by hydrogen bonds, often multiple H-bonds. Perhaps the simplest examples of such systems are the carboxylic acid dimers. In the papers presented by Prof. Zwier and Prof. Suhm we learnt about different methods of studying such species using a variety of infrared techniques.

Prof. van der Avoird commented: In the doubly hydrogen-bonded system one expects a concerted tunneling motion of the two protons involved in the hydrogen bonds between the two equivalent minima in the potential surface. Could some of the structure that you observe in the spectra of Figs. 1, 4 and 5 be caused by level splittings due to this tunneling motion?

Prof. Zwier replied: You are certainly correct that concerted H-atom tunneling is present in this system, and could in principle contribute to the spectral complexity. However, we think that this effect is not a major contributor to the observed complexity. Meerts' group[1] has recently resolved the tunneling splitting in the S_0–S_1 origin transition (1107 MHz). Our double resonance method does not resolve this tunneling splitting in the ultraviolet step, where we sit on the S_0–S_1 origin transition, and thus the IR spectra we record involve infrared excitations out of both tunneling levels. One might anticipate a larger tunneling splitting in the OH stretch vibrationally excited state; however, the b_u symmetry vibration is not along the reaction coordinate for tunneling, since it contracts one OH bond while stretching the other. In addition, neither the overall width nor complexity of the spectrum is changed much in going from OH/OH to OH/OD to OD/OD dimer.

1   K. Remmers, W. L. Meerts and I. Ozier, *J. Chem. Phys.*, 2000, **112**, 10890.

Miss Emmeluth, Dr Häber and **Prof. Suhm** responded: As pointed out by Prof. Zwier, the IR-active OH stretch coordinate is orthogonal to the tunneling mode and therefore the splitting may be relatively small despite an excitation energy close to or even exceeding the barrier for concerted hydrogen atom tunneling. Successive deuteration should reduce the splitting even further while conserving the symmetric double minimum character. In acetic acid, concerted internal rotation of the methyl groups is required to end up at an equivalent structure. Some of the spectral structure which we observe is reminiscent of tunneling patterns, in particular for CD_3COOD, but the change upon isotope substitution does not provide obvious support for such a simple interpretation. The same is true for Ar coating experiments, which might be expected to quench the tunneling. It should be mentioned that several dimer peaks in our spectra show a weak double-peak structure close to the spectral resolution (see Tables 4 and 5 of our paper), whose origin we have not yet assigned. Hole-burning experiments may shed some light on this issue. We

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would like to stress that to the best of our knowledge, there is not a single quantitative experimental tunneling splitting known in the electronic ground state of any carboxylic acid dimer.

Prof. Botschwina said: The apparently good performance of AM1 for N_2O clusters appears to be rather surprising and is certainly somewhat fortuitous. How well does that method perform for the transition dipole moments or the corresponding absolute IR intensities of the two stretching fundamentals of the monomer?

Dr Häber and **Prof. Suhm** replied: Indeed, the relatively good performance of AM1 predictions for the structure, energetics, and dynamics of N_2O clusters must be fortuitous. But as Table 1 shows, even monomer IR intensities are in reasonable agreement with experiment.[1] The performance of PM3, another semiempirical method, and also of Hartree–Fock predictions is significantly poorer. The MP2 level provides better absolute intensities for the v_{010} and v_{001} modes, but it inconsistently underestimates the v_{100} intensity by a factor of 4. Hybrid density functional methods perform best in terms of IR intensities, but they fail completely for cluster binding energies, as we have pointed out. On the other hand, the AM1 large cluster energetics is in remarkable agreement with the experimental bulk sublimation energy. This is confirmed by calculations of $(N_2O)_{135-177}$, whose energetics and dynamics we have recently evaluated in collaboration with Prof. Thiel's group in Mülheim.

1 R. H. Kagann, *J. Mol. Spectrosc.*, 1982, **95**, 2513.

Prof. Gerber asked: Was the AM1 method specially parameterized for the successful application to $(N_2O)_n$?

Dr Häber and **Prof. Suhm** replied: The N_2O monomer was one of many molecules used and tested in the original parameterization of the AM1 method, but the heat of formation is only moderately well described.[1] Certainly, the parameters were not adjusted to experimental data on N_2O clusters. We have used the standard N, O parameter set for AM1 as implemented in commercial quantum chemistry codes (Gaussian, MNDO97).

1 M. J. S. Dewar, E. G. Zoebisch, E. F. Healy and J. J. P. Stewart, *J. Am. Chem. Soc.*, 1985, **107**, 3902.

Prof. Nesbitt asked: If the proposed model for IVR is based on bend–stretch coupling localized to the carboxylic acid ring, is there a simple reason why the spectra of the d_5 and d_0 dimer species are so different?

Prof. Zwier responded: You are right that one wouldn't anticipate that ring-deuteration would have such an effect. However, the point is that there is no pure OH bend normal mode in benzoic acid dimer. Instead, the OH bend is mixed with ring C–H bends and ring C=C stretches. The

Table 1 Calculated infrared intensities $\bar{A}$ (km mol^{-1}) (double harmonic approximation) of N_2O for various methods and the aug-cc-pVTZ basis set (where applicable) in comparison to experiment. Values in parentheses are relative intensities with respect to the v_{001} mode

| Method	$\bar{A}_{010}$	$\bar{A}_{100}$	$\bar{A}_{001}$
Exp.[a]	7(0.02)	55(0.16)	345
AM1	30(0.06)	129(0.23)	569
PM3	247(0.24)	176(0.18)	989
RHF	24(0.04)	193(0.34)	565
MP2	5(0.01)	14(0.04)	364
B3LYP	10(0.03)	71(0.18)	398
B3PW91	10(0.02)	66(0.17)	399

[a] Ref. 1

former vibrations are changed by ring deuteration, and play back into the model *via* changed normal modes with different degrees of OH bend character, and thus different degrees of mixing with the OH stretch. We are in the process of extending our model to all three dimers (d_0–d_0, d_5–d_5 and d_5–d_6), which should provide a more rigorous test of the model. We also hope to extend the model to other H-bonded dimers that we have studied, including oxindole dimer, pyridone dimer and the mixed 2-pyridone-2-hydroxypyridine dimer.

Miss Emmeluth, Dr Häber and Prof. Suhm also responded: Our most recent ragout-jet FTIR spectra of isotopically substituted acetic acid (Fig. 1 below) support the finding that subtle isotope substitution effects can give rise to dramatic spectral changes due to modified mode mixing. The center trace shows the OH stretching region of acetic acid dimer at 2 cm^{-1} resolution (see Fig. 15 in our paper for a higher resolution scan). Deuteration of the methyl protons (bottom trace) leads to substantial simplification of the absorption pattern, although the CH bonds are separated from the OH bonds by 3 atoms. The three most prominent absorption features of acetic acid dimer remain largely unshifted upon deuteration, whereas much of the remaining structure is lost. The spectrum of CD_3COOH dimer is dominated by a transition near 2940 cm^{-1}, which also exhibits a slight blue-shading characteristic for hydrogen-bonded OH-stretches (and residual hot band contributions). This indicates that the dominant coupling scenario involves two lower frequency combination bands which are in anharmonic resonance with the zero-order OH-stretch. Substitution of the carboxyl-carbon atom by ^{13}C (top trace) has the opposite effect of complicating the band pattern. At the same time, the most prominent absorptions move closer together, indicative of a somewhat weaker overall coupling strength in this slightly heavier frame.

These spectra illustrate quite pictorially how the complicated OH stretching band pattern observed in carboxylic acid dimers arises from a reasonably robust first-order coupling scenario, which is superimposed by additional, more subtle resonances and possibly also Franck–Condon transitions.

Prof. Howard said: You have provided a convincing model that explains the width of the spectral feature in the OH stretching region of benzoic acid dimer and provides almost quantitative agreement with the structure observed. However, even in your jet spectra the spectral features
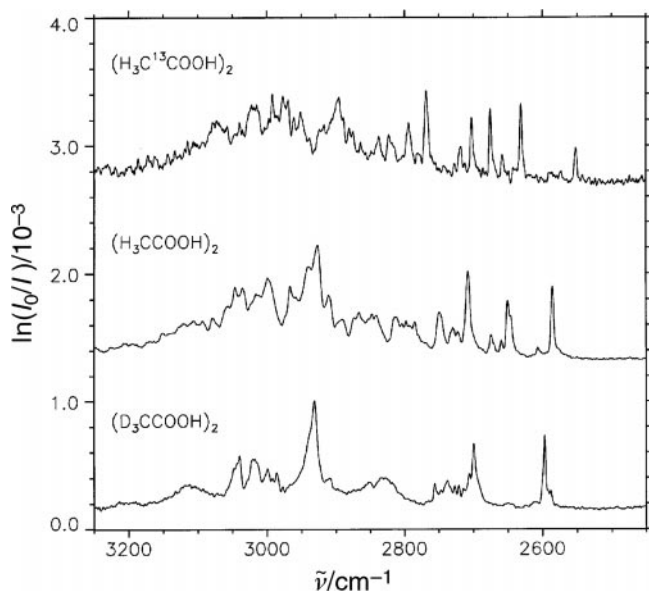
Fig. 1 Ragout-jet FTIR spectra of isotopic variants of acetic acid dimer in the OH stretching range recorded at 2 cm^{-1} resolution. The upper trace was obtained using less than 1 g of ^{13}C-labelled acetic acid in He, which lasted for 260 gas pulses of 0.14 s duration.

still display significant widths. Is this limited by the resolution of your techniques or is there something else going on? In other words, if you were to investigate the spectrum with MHz linewidth lasers, would one see rotationally resolved structure or do you think there would still be residual mechanisms for broadening.

Prof. Zwier answered: I suspect that one would see individual rotational transitions that would not be broadened by any mechanism beyond lifetime, Doppler, or saturation broadening. The infrared excitation is below the dissociation threshold for the cluster, so broadening by this mechanism is not energetically possible, although one could imagine that breaking a single H-bond in the dimer might be possible. Even without any H-bond breaking mechanism, I would expect that vibrational state mixing will be so great that one would observe a "sea" of transitions that would be uninterpretable at this high resolution. Of course, scanning the full 550 cm^{-1} would also be a particular challenge at 1 MHz resolution!

Prof. Dagdigian said: I would like to ask how much the relative intensities in your recorded vibrational spectra in the ground electronic states could differ from those in the corresponding absorption spectra? Strictly speaking, your spectra are action spectra, which depend upon differences in the electronic spectra from the ground *vs.* vibrationally excited levels. In your paper, you do compare the vibrational spectra from the ground and S_1 electronic states.

Prof. Zwier replied: You are right that the magnitude of the infrared depletion signal would be affected if the vibrationally-excited species had a significant absorption at the wavelength being monitored in the ultraviolet. In fact, if one could detect the ultraviolet absorption spectrum of the vibrationally-excited species, such absorptions could be used as a background-free means of taking the infrared spectrum, which would be preferable over a depletion signal in some circumstances. However, for most clusters that we have studied, when we search for gain signals in the ultraviolet spectrum, we can't detect any. This is because the vibrationally-excited species has a very broad ultraviolet absorption, as a "hot" dimer. This very broad absorption contains a negligible component at the wavelength where we monitor the cold dimer in its zero-point vibrational level. In such circumstances, the fluorescence-dip infrared spectrum is essentially equivalent to an infrared absorption spectrum. A greater concern for us than the issue you have raised is simply saturation effects. Such saturation effects are always a concern in a depletion scheme in which the infrared absorption must remove a significant fraction of the population in order to be observed with good signal-to-noise ratio.

Prof. Gellene commented: Your anharmonic treatment considers only cubic force constants which mix normal modes in second order. Can you comment on the possible importance of quartic force constants which can mix normal modes in first order?

Prof. Zwier responded: Following the lead of previous work on strongly H-bonded dimers (refs. 5–13 in the paper), we are focusing attention on OH stretch–OH bend and OH stretch–intermolecular stretch coupling as two of the largest couplings present, because they represent strong, near-resonant Fermi resonances. Cubic terms in the potential are required to mix the $|v_3 = 1, v_4 = 0, v_5 = 0\rangle$ b_u symmetry OH stretch fundamental with the $|v_3 = 0, v_4 = 1, v_5 = 1\rangle$ b_u symmetry bending combination band, since this is a three-quantum change. Similarly, the $|v_3 = 1, v_1 = 1\rangle$ combination band involves a three-quantum change in mixing with $|v_3 = 1, v_1 = 0\rangle$. So quartic terms in the potential won't mix these particular levels. However, there are other levels that could be mixed *via* quartic terms in the potential. What we have shown is that the stretch–bend cubic term is capable of producing the over-all breadth and qualitative sub-structure of the observed OH stretch absorption. Clearly, there will also be second- and third-tier couplings that will also contribute to the sub-structure. Later refinements, in principle, could include such terms.

Prof. Saykally commented: We have measured low resolution vibrational spectra of several nucleotide bases, base clusters and complexes of these with water with IR cavity ringdown spectroscopy. Uracil, thymine and adenine were vaporized and supersonically expanded in a heated pulsed slit jet, described in connection with our published study of arginine.[1] Very large red-shifts

observed may indicate the presence of unusually stable clusters, such as 6-membered rings of uracil.

1   C. J. Chapo, J. B. Paul, R. A. Provencal, K. Roth and R. J. Saykally, *J. Am. Chem. Soc.*, 1998, **120**, 12956.

Prof. Nesbitt commented: One of the powerful aspects of direct absorption methods is that you can easily estimate the density of species from the measured absorbances, path lengths, *etc.* What density of jet cooled uracil species have you been able to achieve?

Prof. Saykally answered: We estimate densities of about 10^{11} cm^{-3}, by comparisons with similar spectra of other systems.[1]

1   M. R. Viant, R. S. Fellers, R. P. McLaughlin and R. J. Saykally, *J. Chem. Phys.*, 1995, **103**, 9502.

Prof. Miller asked: Given the high resolution of the cavity-ring-down method using your laser system, why are the N–H stretches not resolved?

Prof. Saykally replied: I believe that the data that you are referring to were actually taken in "low resolution" mode with *ca.* 0.5 cm^{-1} resolution.

Prof. Müller-Dethlefs commented: The shallowness of the potential wells of different isomers or local minima on the potential energy surface, and the barriers between local minima and the global minimum are of considerable interest. For instance, for the resorcinol···water and resorcinol···CO rotational isomers, we have found a striking difference in this respect. In the
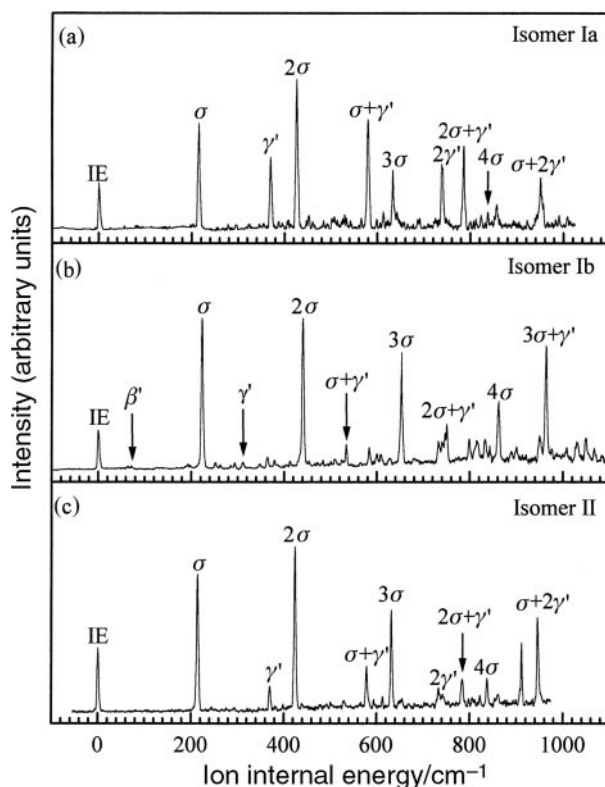
Fig. 2   ZEKE spectra recorded *via* the S_1O^0 origin transitions of isomers Ia, Ib and II of resorcinol···water. Intermolecular vibrational mode assignments are included on the figure. Reproduced with permission from ref. 1.

resorcinol· · ·water system, all three isomer structures predicted by *ab initio* computations are observed in the REMPI spectrum, and can be further characterized using ZEKE spectroscopy (Fig. 2).[1] In fact, the ZEKE spectra of all three isomers look very similar to that of phenol· · ·water.[2] For resorcinol· · ·CO, the *ab initio* calculation still predicts three isomers with similar structures to the three resorcinol· · ·water isomers, however, only two isomers are seen in the REMPI experiment.[3] For isomer I, the ZEKE spectrum (Fig. 3a) looks completely different compared to that of isomer II (Fig. 3b). For isomer I, one observes a long progression in a low frequency vibration β' = in-plane bend), indicating that the CO molecule is moving between the two OH groups and isomers 1a and 1b are probably connected by a rather low barrier. The *ab initio* results (Fig. 4) should be interpreted in this context.

1   W. D. Geppert, C. E. H. Dessent, S. Ullrich and K. Müller-Dethlefs, *J. Phys. Chem. A*, 1999, **103**, 7186.
2   O. Dopfer, G. Reiser, K. Müller-Dethlefs, E. W. Schlag and S. Colson, *J. Chem. Phys.*, 1994, **101**, 974.
3   W. D. Geppert, C. E. H. Dessent and K. Müller-Dethlefs, *J. Phys. Chem. A*, 1999, **103**, 9687.

Prof. Neumark commented: Devlin *et al.*[1] have measured infrared spectra of water nanoclusters with up to 64 000 molecules and interpreted them to indicate that the hydrogen-bonding network is different in the exterior *vs.* interior layers of the clusters. Their method of producing the clusters is quite different from yours. Can you perform measurements of water clusters in this size range on your instrument, and if so do you observed similar results?

1   J. P. Devlin, J. Sadlej and V. Buch, *J. Phys. Chem. A*, 2001, **105**, 974.
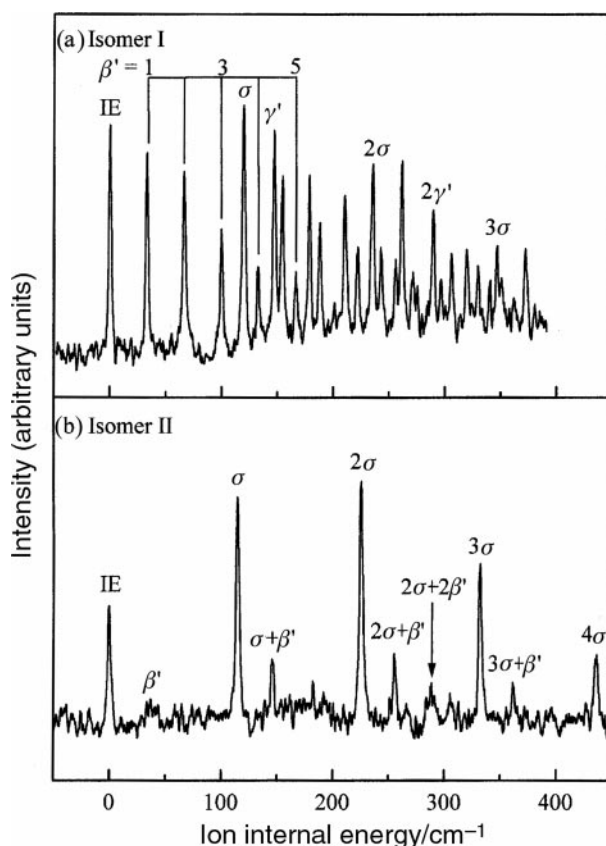
Fig. 3 ZEKE spectra recorded *via* the S_1O^0 origin transitions of isomers I and II of resorcinol· · ·CO. Intermolecular vibrational modes assignments are included on the figure. Reproduced with permission from ref. 3.
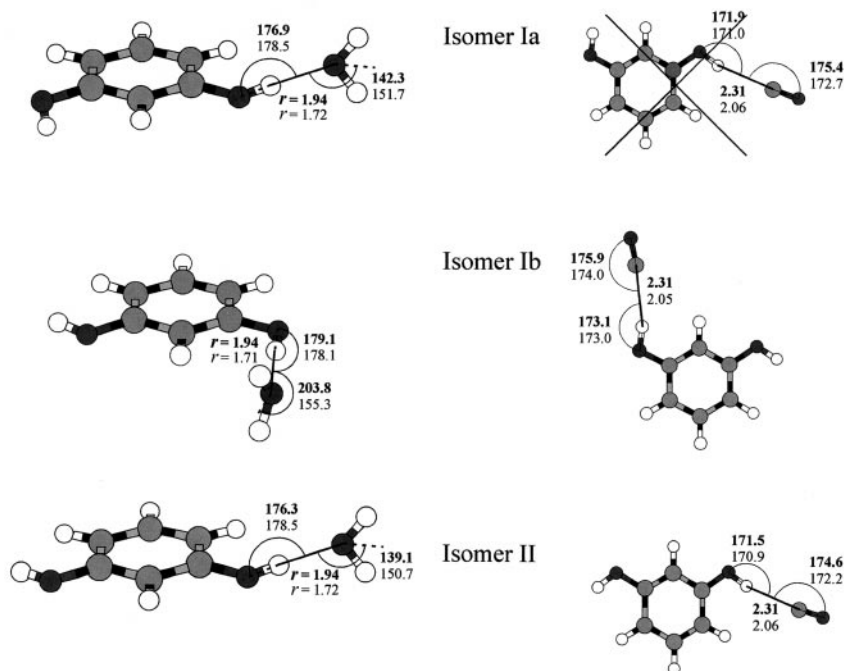
Fig. 4 *Ab initio* geometric structures of the S_0 state rotational isomers of resorcinol $\cdots$ water and resorcinol $\cdots$ CO, obtained at the B3LYP/cc-pVDZ and MP2/6-31G* levels of theory, respectively.[1,3]

Prof. Suhm and **Dr Häber** answered: The method used by Devlin is based on diffusive trapping at liquid nitrogen temperatures. With this technique, one can generate clusters ranging from several μm down to several nm in diameter. There is a related collisional flow cooling technique[1,2] which we use in our group to generate clusters in this size range.[3] For such collisional cooling techniques, the major challenge is to produce clusters in the sub- and low nm range. This can be achieved at cryogenic temperatures closer to that of liquid He, due to larger supersaturation ratios.[4] For supersonic jet techniques such as the ragout-jet method, high stagnation pressures and constrained expansions (Laval nozzles) help to increase the cluster size beyond 1 nm. In this regime of large clusters, ragout-jet FTIR provides high-quality panoramic IR-spectra in a single gas pulse, *i.e.* in a fraction of a second, whereas cavity ring-down methods using highly reflective mirrors may suffer from additional noise due to the fast ring-down times. In the case of N_2O, we have succeeded in bridging the gap in cluster size between the two techniques.[3,4] In the field of intermediate and large water clusters, other groups have been active. Collisional cooling experiments with about 20 m optical pathlength have been extended to even smaller cluster sizes,[2] whereas large size-selected water clusters in supersonic jets are currently studied in Prof. Buck's group, who may want to comment on this topic of exterior *vs.* interior layers in ice particles.

1 S. Bauerecker, F. Taucher, C. Weitkamp, W. Michaelis and H. K. Cammenga, *J. Mol. Struct.*, 1995, **348**, 237.
2 S. Bauerecker, M. Taraschewski, C. Weitkamp and H. K. Cammenga, *Rev. Sci. Instrum.*, 2001, in press.
3 T. Häber, M. K. Kunzmann and M. A. Suhm, *Proceedings of Bunsentagung*, Würzburg, 2000.
4 M. K. Kunzmann, R. Signorell, M. Taraschewski and S. Bauerecker, *Phys. Chem. Chem. Phys.*, 2001, **3**, in press.

Prof. Buck also replied: In fact, we recently measured the OH-stretch spectra of water clusters $(H_2O)_n$ in the size range from $\langle n \rangle = 16$ to 2400.[1] The clusters were generated in an adiabatic expansion and the size distribution was measured by doping them with one Na atom with subsequent detection by nearly fragmentation free single photon ionisation. The spectra were taken by detecting the fragments which leave the cluster after the infrared excitation. We found a

maximum of the intensity of hexamer fragments in the size range of $<n> = 65$ which gradually decreases with increasing cluster size. We interpret the appearance of these fragments as indication of an amorphous surface structure which loses its influence with increasing cluster size at the expense of a crystalline core. These are preliminary results which have to be confirmed by further experiments and calculations. But, in principle, these results are in line with the model developed by Devlin *et al.* for water clusters in this size range which consists of a crystalline core and subsurface and an amorphous surface which gradually decreases for larger clusters.[2]

1 P. Andersson, C. Steinbach and U. Buck, unpublished results.
2 J. P. Devlin, C. Joyce and V. Buch, *J. Phys. Chem. A*, 2000, **104**, 1974.

Prof. Miller asked: I was wondering if either speaker has looked at the effects of solvation of these dimers in argon clusters on the anharmonic coupling, in an effort to probe the effects of a solvent?

Prof. Zwier responded: No, we haven't considered this to date.

Miss Emmeluth, Dr Häber and **Prof. Suhm** responded: We have looked at Ar coating effects in acetic acid dimers and its isotopomers and we find a range of phenomena associated with the solvation. The shifting into resonance of a reasonably local C=O stretch perturber has already been described in our paper (Fig. 14). Also, some of the smaller absorptions which we attribute to structural isomers disappear upon Ar coating. Any systematic change of the highly congested OH/OD stretching spectrum upon Ar coating would be most helpful in the analysis of the energy redistribution dynamics. In Figs. 15 and 16 of our paper, one can see a general broadening of most peaks and a weakening or even disappearance of some others. However, the changes are not very systematic and typically rather subtle. In the case of singly deuterated acetic acid (Fig. 16), the persistence of the band doublets upon Ar coating provides some evidence against a tunneling splitting interpretation. This leaves anharmonic coupling as a more likely cause for most of the band structure. It will be interesting to systematically correlate the Ar solvation changes in the ν_{C-O}, δ_{O-H} and $\nu_{C=O}$ fundamentals with the changes in the OH stretching range, where combination bands of these fundamentals contribute. Our ragout-jet FTIR approach provides access to both spectral ranges. To give an example of such a correlation, we consider the lowest and strongest peak of the C–O stretch/O–H bend manifold for acetic acid, a doublet at 1306 and 1308 cm^{-1}, which is shifted 2–3 cm^{-1} to lower wavenumber upon Ar-coating (Tables 4 and 5 of our paper). The A_g counterpart of this vibration is expected about 10 cm^{-1} lower in wavenumber. The B_u–A_g combination band would therefore be expected near 2605 cm^{-1} for the free dimer and roughly 4–6 cm^{-1} lower for the Ar-coated one (assuming that the B_u and A_g states are affected similarly by the matrix). In the spectrum, there is a strong band near 2585 cm^{-1} which upon Ar solvation shifts to lower wavenumber by 5–7 cm^{-1} (Fig. 15 in our paper). The global -20 cm^{-1} wavenumber difference between predicted and observed band positions can easily be rationalized by coupling to the zero order bright state (OH stretch near 2900 cm^{-1}), from which it gains intensity. Although these consistent matrix shifts provide no rigorous proof for the combination band assignment, they lend significant additional support to it.

Prof. Lineberger asked: What will be required, experimentally and theoretically to achieve the next major advances?

Prof. Zwier answered: From an experimental stand-point, our particular experiment could benefit from further advances in solid-state materials that would provide high-power, tunable infrared well down into the 'fingerprint region' of the infrared. One of the significant advantages of Prof. Suhm's method is that it has no such wavelength restrictions. However, we are restricted to the hydride stretch region from 2000 cm^{-1} up by the long-wavelength cut-off of the KTA crystal we use to generate the infrared radiation.

Theoretically, we need to test the simple theoretical model by applying it to the set of deuterated isotopomers, and to a wider range of strongly H-bonded complexes, among them perhaps the beautiful spectra of acetic acid dimer from the Suhm group would be good candidates for modeling *via* reduced-dimension models like we are using.

I'm sure there are other incisive experiments and theory waiting to be done. Perhaps others in the audience have some in mind! Some examples might be: lasers further into infrared, *e.g.*, direct probe of bending fundamentals; femtosecond experiments?

Miss Emmeluth, Dr Häber and **Prof. Suhm** also replied: We agree that on the experimental side, the two techniques presented in this session already provide nicely complementary and powerful approaches to the intricate dynamics of carboxylic acid dimers. This is particularly true if the techniques are applied to a range of isotopically and chemically substituted derivatives and involve a sufficiently broad spectral window. Vapor pressure is currently a limiting factor in the ragout-jet technique, because the nozzle is not heatable. One could compare the two techniques explicitly by studying mixed aromatic–aliphatic dimers.[1] For the ragout-jet FTIR method, it will be interesting, but also challenging, to extend the spectral range deep into the far infrared with useful signal-to-noise ratio. In this context and also with respect to concerted tunneling and other symmetric vibrations, non-resonant Raman spectroscopy can provide complementary information, but the issue of sensitivity will be even more challenging. The probing of dimers in the threshold region for single hydrogen bond cleavage is crucial for an understanding of the dissociation process. We have summarized the available evidence for singly hydrogen-bonded dimers obtained using different techniques and we are also exploring chemical blocking of one hydrogen bond in mixed acid–ester dimers. Recent results of an interesting kinetic approach towards carboxylic acid dimer isomerism have been obtained by Quack *et al.*[2]

In our opinion, major advances now have to come from theory. The elegant and efficient model treatment by Zwier *et al.* very convincingly shows the importance of extensive anharmonic resonances and it will be interesting to apply it to acetic acid and its isotopomers. This perturbational model will now have to be verified and refined by more extensive multidimensional variational treatments. The required number of electronic structure calculations is large, but feasible. Our isotopomer spectra suggest that the coarse-grained coupling pattern will be reasonably robust with respect to the quality of the electronic structure approach, whereas the fine details will probably not be within reach in the near future. The nuclear configuration subspace relevant for the OH stretching dynamics is sizeable. It certainly involves the two OH stretches, the two C=O stretches, and a C–O stretch/COH bend/CH bend manifold of isotope- and species-dependent size, *i.e.* around 8 dimensions or more. By concentrating first on isotopomers with simple COH bend spectra such as $(CD_3COOH)_2$ and by exploiting the dimer symmetry as well as other simplifications, the essential dynamics should be tractable. Some efforts along these lines are currently under way in Göttingen, in cooperation with Dr Luckhaus.

1 P. Imhof, W. Roth, Ch. Janzen, D. Spangenberg and K. Kleinermanns, *Chem. Phys.*, 1999, **242**, 141; P. Imhof, W. Roth, Ch. Janzen, D. Spangenberg and K. Kleinermanns, *Chem. Phys.*, 1999, **242**, 153.
2 J. Blumberger, T.-K. Ha, J. Paff, M. Quack and G. Seyfang, *Time resolved FTIR Detection of IR-multiphoton Initiated Dissociation of Formic Acid Dimer: Evidence for a Dimer with a Single Strong Hydrogen Bond*, XII Symposium on Atomic and Surface Physics and related topics, Trento University, 2000, pp. 1–4.

Prof. Howard said: We have discussed the complexity of the spectral features in the carboxyl OH stretch region of carboxylic acid dimers. Presumably this is all due to the large density of background states at about the same energy as the first excited OH stretching state. However this problem is going to increase as one increases the size of the interacting molecules. Do you think there is going to be any real chance of understanding all the structure in the spectra of complexes of similar or larger size?

Prof. Zwier replied: I think the simple answer is 'no'; that is, I don't think that, in molecules the size of benzoic acid dimer, it will be possible to understand every detail of the structure in the spectra. Instead, the experiment is being tested against a simple physical model that we hope can provide a qualitative or semi-quantitative understanding of the sub-structure, say at the 80% level. For instance, we were surprised to find that it was the stretch–bend coupling, rather than the OH stretch–intermolecular stretch coupling, that provides most of the breadth and sub-structure in the case of benzoic acid dimer. If such a physical understanding were possible for a wide range of strongly H-bonded dimers, I would find this a cause for celebration, even though it offers only a partial account of the full complexity in the spectra.

Prof. Gerber asked: Can methods such as 2D IR that are being used for complex condensed-phase systems, be applied also for these clusters?

Prof. Zwier responded: It certainly would be intriguing to apply such methods, since they do provide a means for picking apart a spectrum in terms of the mode coupling present. (For example, see refs. 1 and 2). In seeking to apply such methods to a gas-phase, jet-cooled sample, sensitivity may be an issue, but perhaps this is not insurmountable.

It is worth pointing out that the double resonance scheme of fluorescence-dip infrared spectroscopy that we use is capable of recording infrared spectra of single conformations of flexible biomolecules, which is one of the goals of the 2D IR methods, as I understand it.

1   W. Zhao and J. C. Wright, *J. Am. Chem. Soc.*, 1999, **121**, 10994.
2   P. Hamm, M. Lim and R. M. Hochstrasser, *J. Phys. Chem. B*, 1998, **102**, 6123.

Prof. Miller commented: For theoretical work to be helpful on these systems it is essential that the spectra be free of hot bands. Could the authors comment on this for their respective methods.

Prof. Zwier replied: This is one distinct advantage of the fluorescence-dip infrared method over many other methods, including the ragout method of Suhm and coworkers. As a double resonance scheme, it assures that the infrared spectrum is exclusively from the zero-point level that is monitored by the LIF transition. In the present case, this includes transitions from both tunneling levels, as mentioned earlier in the discussion.

Of course, Prof. Suhm's method has advantages that counter-balance this, including its experimental simplicity, wide frequency range, and excellent signal-to-noise. The two methods are nicely complementary to one another.

Miss Emmeluth, Dr Häber and **Prof. Suhm** answered: In the case of the ragout-jet experiment, we only have indirect evidence for the absence of major hot band transitions in the spectra. The near invariance of the spectra with respect to stagnation pressure, expansion gas, and nozzle distance supports this view. Obviously, for systems of this size and floppiness, there will always be some vibrational hot band intensity even at a vibrational temperature as low as the rotational temperature, but most of this will fall within the homogeneous or rotationally inhomogeneous width of the cold bands. We estimate that less than 10% of the spectral structure is explicitly due to residual hot bands, excluding possible tunneling contributions, but including contributions from non-symmetric structural isomers which are discussed in our paper. On the other hand, we find a surprising degree of spectral invariance even for stagnation pressures and acid concentrations well above the values where dimer formation is expected to dominate. This suggests that clusters consisting of stacks of dimers may have very similar vibrational spectra in the mid-infrared.

Prof. Nesbitt asked: Does your IVR analysis model suggest interesting time domain dynamics experiments to be performed by using ultrafast pump–probe methods to watch the flow of initial OH stretch vibrational excitation into the carboxylic acid dimer ring?

Prof. Zwier replied: Most definitely. Of course, the over-all breadth of the OH stretch band (550 cm^{-1}) suggests a 10 fs timescale for the stretch–bend coupling. As you well know, if one could make the assignments of the sub-structure in the frequency domain, then this would tell us what to expect in a time-domain experiment.

Miss Emmeluth, Dr Häber and **Prof. Suhm** also replied: In fact, coherent IR excitation of acetic acid dimers in solution has recently been achieved[1] using ps pump–probe spectroscopy. Very rapid (sub-ps) energy flow into the hydrogen-bonded ring modes followed by further redistribution processes on a 4–15 ps timescale was extracted from the experimental data. This interpretation is consistent with the coupling scenario extracted from the cold frequency domain spectra in the two papers of this session.

1   G. Seifert, T. Patzlaff and H. Graener, *Chem. Phys. Lett.*, 2001, **333**, 248.

Prof. Lehmann commented: I would like to propose to Prof. Zwier and his coworkers that they consider experiments where they compare the double resonance signals for parallel *vs.* perpendicular relative orientation of the polarizations of their two lasers. Even despite rotational averaging, sizable differences in double resonance intensities are expected, as can be found in the literature on polarization spectroscopy. As one example, Steve Coy and I made extensive use of these polarization effects in making rotational assignment of the highly perturbed overtone spectrum of NH_3.[1] In the present case, the only requirement is that spectral resolution of the pump and probe lasers be high enough to spectrally resolve the branches in the spectra, not the individual rotational lines. This arises from the fact that polarization signals of opposite signs are expected when either is switched from P or R branch to Q branch. Averaged over the entire rotational band, the polarization dependence will give information on the relative orientation of the transition moments of the two excitations involved in the double resonance experiment, which could assist in assignments.

1   K. K. Lehmann and S. L. Coy, *J. Chem. Soc., Faraday Trans. 2*, 1988, **84**(9), 1389.

Prof. Zwier answered: This is an intriguing possibility, which we haven't pursued to date. If it would allow us to determine vibrational assignments for the levels mixed with the OH stretch, this would be a significant break-through in analysis of the spectra. However, in its present configuration, neither our infrared (0.25 cm^{-1}) nor ultraviolet (~ 0.3 cm^{-1}) lasers are capable of resolving even P, Q and R branches in benzoic acid dimer, so higher resolution sources would certainly be required for such experiments. I would guess that the extent of vibrational state mixing is so great that polarization effects may be washed out or difficult to interpret, but it is certainly an experiment worth pursuing.

Dr Meuwly commented: The pronounced stability of organic, hydrogen-bound dimers which make spectroscopic investigations such as the ones carried out by Zwier and coworkers possible has recently also been found in computational studies. Using the density functional based DFTB-SCC (density functional tight bind method with self consistent charges)[1] in conjunction with classical molecular dynamics simulations to investigate the dynamics in 2-pyridine-2-hydroxy-pyridone we found a characteristic stability of the dimers even at temperatures of 400 K. These calculations are carried out at constant total energy. Another system where this stability plays a crucial role is $N_2H_7^+$. Simulations conducted in a similar manner as described above aiming at the investigation of proton transfer between the two ammonia molecules gave perfect stability of the system up to energies equivalent to a temperature of 600 K.[2]

1   M. Elstner, D. Porezag, G. Jungnickel, J. Elsner, M. Haugk, T. Frauenheim, S. Suhai and G. Seifert, *Phys. Rev. B*, 1998, **58**, 7260.
2   M. Meuwly and M. Karplus, results presented at the Poster Session for this Faraday Discussions (see List of Posters).