

Molecular Solvation in Atomic Clusters Studied by Means of Molecular Beam Infrared Spectroscopy

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Introduction

One of the primary aims of cluster science, i.e., the study of aggregates containing from a few to a few million atoms, is that of determining how large a chunk of matter must be before it can be called macroscopic. Naturally, any given property, such as structure, ionization potential, specific heat, conductivity, diffusion coefficient, etc., may reach its bulk limit at a different size, according to the sensitivity of that particular property to the proximity of a surface.

Some of the following examples may serve to illustrate the importance of studying clusters. For instance, while solvated chemical species (atoms, molecules, ions, and free radicals) are very common, the role of the solvation shell in a chemical reaction is far from understood. By building the solvation shell atom by atom or molecule by molecule, its influence on chemical reactivity can be clarified.¹ Moving from chemistry to physics, we find that the phenomenon of superfluidity in liquid helium is well-known, but is there a certain minimum number of helium atoms which are needed to observe it?^{2,3} In general, cluster studies have the potential to answer some of these questions and therefore to increase our fundamental understanding of the properties of matter.

With respect to the choice of a system, noble gas (NG) clusters have become prototypical systems because of their well-known interaction potentials, the ease with which they can be produced, and the availability of accurate information on their solid phases. Several experimental and theoretical studies involving NG clusters have been published in the last two decades. Theoretical efforts have revealed, among other features, the following features of NG clusters: (a) Argon clusters of sizes of up to a few tens of atoms may show coexisting solid- and liquid-phase behavior (Berry and co-workers⁴). (b) General criteria for solvation of guest species in NG solvents can be established (Amar,⁵ LeRoy⁶). (c) The evaporation rate of atoms and the temperature of a cluster produced

under various experimental conditions can be understood in terms of a simple model (Klots⁷). (d) The frequencies of the breathing vibrations (expansion and contraction) of clusters can be predicted (Ozaki et al.⁸). Finally, (e) several studies have focused on the cluster size at which the structural transition to the bulk phase takes place (see below).

Among the experimental work, electron diffraction^{9,10} (ED) has focused on properties such as cluster structure, temperature, and average size. For instance, it has shown that the temperature of NG clusters produced in a supersonic expansion is primarily a function of the molar energy of evaporation, being independent of the expansion conditions (for Ar⁹ it is 32 ± 2 K). Mass spectroscopy¹¹ used for size determination has identified the cluster sizes of maximum stability which have been said to occur at a "magic number" of monomers. The electronic energy levels of NG clusters of sizes from 10 to 10 000 have been studied by fluorescence excitation spectra, using synchrotron radiation.¹²

In this Account we discuss the progress made in our group measuring the IR spectra of guest molecules to probe the structure and properties of a host cluster. The basic methodology needed to obtain infrared spectra of molecular beams was introduced by Gough, Scoles, and co-workers more than a decade ago and was applied soon thereafter to the study of medium-large NG clusters seeded with infrared chromophores.¹³ The early work demonstrated that information about both the effects of the solvation on the guest molecule and the structural properties of the host cluster itself could be obtained as a function of the *average* cluster size, bridging the gap between molecular and bulk behavior. The existing vast literature on IR spectroscopy of molecules embedded in a NG matrix with which the data obtained for the clusters can be compared provides further motivation and support for this type of work.

A similar approach has been adopted by several other groups using electronic spectroscopy. Bösiger and

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Giacinto Scoles obtained his first degree in chemistry in 1959 at the University of Genoa, Italy, where in the next two years he studied and taught physics. From 1961 to 1964 he carried out research at the Kamerlingh Onnes Laboratorium of the University of Leiden in the Netherlands. In 1971 he moved to the University of Waterloo in Canada as a Professor of Physics and Chemistry. In 1987 he was named to the Donner Chair of Science at Princeton University. His fields of research are chemical physics, materials science, clusters, and surface science, mainly using molecular beams, laser spectroscopy, and X-ray scattering.

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Leutwyler¹⁴ employed the resonance two-photon ionization (R2PI) technique to measure the spectra of carbazole in argon clusters of up to 40 atoms. Changes in the band positions and the width of the features present in the spectra of the chromophore solvated by up to 8 argon atoms were interpreted as being caused by the surface melting of the argon atoms. Whetten and Hahn¹⁵ have employed the same technique with benzene as a chromophore to demonstrate a possible solid-liquid phase coexistence in argon cluster sizes between 16 and 22. Similarly, Jortner¹⁶ and co-workers performed both experimental and theoretical studies on the 9,10-dichloroanthracene molecule in association with Ar_n ($n = 1-34$) and Kr_n ($n = 1-18$). They identified several isomerization phenomena, including surface melting and wetting-nonwetting and rigid-nonrigid transitions. Also, Miller and co-workers¹⁷ have recorded the spectra of He, Ne, and Ar clusters containing the C_6F_6^+ ion and suggested possible mechanisms for cluster formation.

In contrast, our infrared studies have primarily focused on the cluster size dependence of the following properties: (a) the onset of bulk structure,¹⁸ (b) the mobility of a chromophore deposited on the cluster surface, and (c) the complexation reaction of two molecular species¹⁹ either on the cluster surface or inside, depending on the ease of diffusion of one or the other species. A general advantage of dealing with the spectrum of species in their electronic ground states is that the interaction potential between the solute and the solvent is, in this case, well understood and can be modeled fairly accurately. Therefore the results can be gainfully combined with computer simulations and theoretical models to obtain a more complete understanding of the system under study.⁵

More recently, we have also recorded the IR spectrum of chromophores attached to highly quantum clusters, i.e., those of He, H_2 , and D_2 . In these systems, the mass of the atoms and the temperature of the cluster are so small that the zero-point energy of the system cannot be neglected and a full quantum treatment becomes necessary. Because of the existence of superfluidity in liquid ^4He below 2.1 K, clusters of this substance have received a fair amount of attention both theoretically^{20,21} and experimentally,^{22,23} with the ultimate goal of gaining an understanding of this phenomenon in systems of finite size. Theoretically it has been shown that clusters as small as 200 atoms exhibit superfluidity inasmuch as their excitation spectra²⁴ and heat capacity behavior

near the λ point²⁵ are similar to those of the bulk phase. Yet a convincing microscopic probe of superfluidity in these isolated finite-sized systems has not yet been found. Hydrogen clusters, instead, are of importance for both fundamental and applied reasons. In particular, small clusters of parahydrogen ($J = 0$) may also exhibit a superfluid phase.^{26,27} The applied interest in hydrogen clusters stems from the possibility that mixtures of molecular hydrogen and light metals may improve the thrust capabilities of rocket fuels. Consequently, the different phases of these mixtures must be investigated. Finally, since much of the quantum mechanical behavior is related to the zero-point energy of the system, deuterium clusters offer the unique opportunity to investigate the role of this quantity on the dynamical behavior of the system without changing the interaction potential.

It is only fair to underline, at the outset, a difficulty in our study that is shared by most other experimental methods for the study of clusters containing more than a few tens of atoms: we are referring to the fact that it has not been possible, so far, to measure, without distortion, the actual cluster size in beams produced by free jet expansions. For information on the *average* size of Ar, Kr, and Xe clusters, we have to rely on estimates obtained via measurements done by electron diffraction⁹ scaled to our experimental conditions by using the scaling laws developed by Hagena.²⁸ For He we have been able to devise a spectroscopic method which is described in ref 23.

After reviewing the experimental methods used, this Account will focus on the different aspects of the evolution to bulk-like properties studied by us with the help of molecular beam infrared spectroscopy. We will discuss first the transition from icosahedral to fcc structure that NG clusters undergo when their size exceeds a certain critical size, obtaining in the process also information on the mobility of the guest molecule in the cluster medium. Next we will show how a complexation reaction may occur when two similar or different molecules are picked up by the same cluster. Finally, our recent results on highly quantum clusters will be presented and a few directions for future work outlined.

The Experimental Apparatus

The clusters are produced in a supersonic free jet (Figure 1) by expanding the gas through a nozzle. For clusters of Ar, Kr, and Xe, the nozzle size was 50 μm (nozzle temperature, NT = 300 K), and for He, $\sim 2 \mu\text{m}$ (NT = 15 K), while for H_2 and D_2 , 10 μm (NT = 50 K) proved to be the best size. In the early part of the expansion, where the collisions are still numerous, the aggregates form, cooling successively mainly due to monomer evaporation. The center portion of the so-formed cluster beam is skimmed, entering the secondary chamber of a two-stage molecular beam machine.

The cluster beam can be seeded either by coexpanding a dilute mixture (typically one part in a few thousand) of the chromophore in the clustering gas or, alterna-

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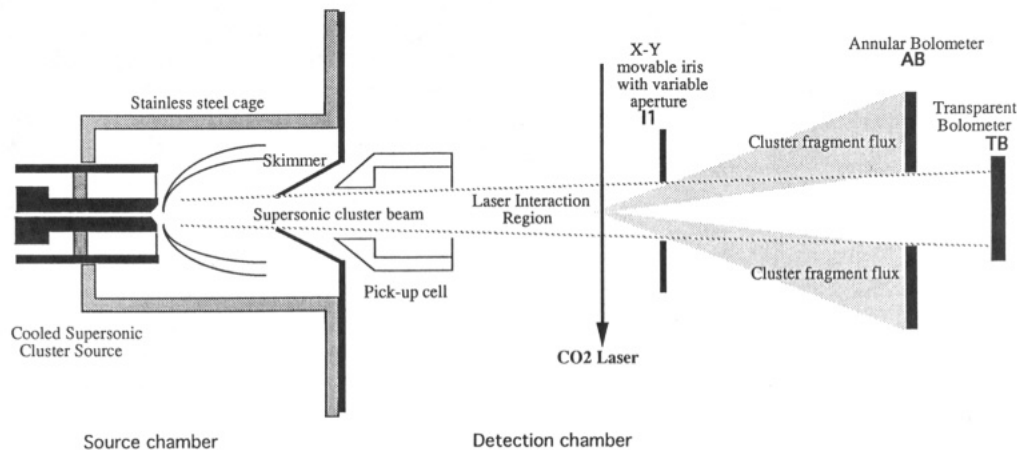


Figure 1. A schematic drawing of the experimental setup. The essential elements in the production of doped noble gas clusters and the detection scheme are shown here.

tively, by allowing the neat cluster beam to pass through a region (pick-up cell) in which the density of the chromophore is controlled. As the clusters travel through the cell, they collide with the chromophore molecules, causing one or more of these to attach. The energy released in this process is adsorbed by the cluster, which in turn can cool down again by evaporating a few atoms.

Downstream from the pick-up cell, spectroscopy is performed on the doped cluster beam, by intersecting it with the modulated output of a line-tunable CO₂ laser beam. If the chromophore happens to resonate with the incoming photons, it absorbs a quantum from the laser, eventually relaxing into the cluster phonon modes. This excess energy released causes one or more atoms to evaporate and produces a signal which is measured by one of two bolometer detectors that are aligned with the molecular beam. The first, an annularly shaped Al₂O₃ disk with a small semiconductor temperature sensor attached to it (AB), can collect fragments released from the clusters, at the same time allowing the main part of the beam to pass through the center. The fragments impact heat onto the sensor, leading to a sharp resistance change that is detected using lock-in techniques. This bolometer was used to record the spectra of Ar, Kr, and Xe clusters. In contrast, a second bolometer (TB), directly on line with the molecular beam, detects the *loss* of fragments due to absorption of the photons and is used for the measurements on He, H₂, and D₂ clusters.

The signal is recorded for as many laser lines as we can produce in the absorption region of the chromophore by using three isotopes of CO₂ and one of N₂O as the lasing media. The resolution of the spectra is limited by the line tunability of the lasers, averaging about 0.3 cm⁻¹. These lasers have a relatively high power level, which is essential for our experiments. In the future, however, this technique may be combined with continuously tunable narrow band solid-state lasers of higher power, which may soon become commercially available.

Structural Transformation and Diffusion in Noble Gas Clusters

Spectra recorded by coexpanding a 0.025% mixture of SF₆ in Ar are shown in Figure 2a-d. The spectrum produced with a 100-psi nozzle expansion pressure

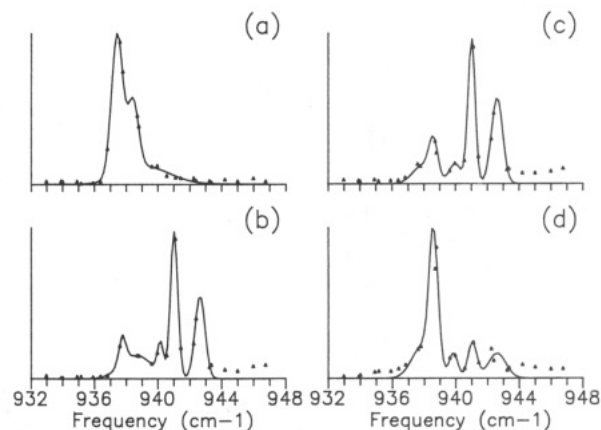


Figure 2. Spectra of SF₆ in argon clusters formed by coexpanding a 0.025% mixture of the chromophore at various stagnation pressures from a 50- μ m nozzle at a temperature of 300 K. The gas-phase absorption of the ν_3 mode of SF₆ is at 948.0 cm⁻¹. The average cluster size for each of the nozzle pressures is given in parentheses: (a) 100 psi ($\langle n \rangle = 60$ atoms); (b) 400 psi ($\langle n \rangle = 1000$ atoms); (c) 600 psi ($\langle n \rangle = 2200$ atoms); (d) 1200 psi ($\langle n \rangle = 9200$ atoms).

(average cluster size, $\langle n \rangle = 60$ atoms, Figure 2a) shows two absorptions at 937.5 and 938.4 cm⁻¹ that bracket a feature recorded at 937.9 cm⁻¹ in the spectrum of SF₆ in a bulk argon matrix. This absorption corresponds to the largest matrix red shift of the ν_3 mode of an SF₆ molecule caused by its interaction with an unannealed or moderately annealed (30 K) bulk argon matrix.²⁹ However, the cluster peak with the largest shift is definitely to the red of the matrix feature. This suggests that the argon atoms in the clusters formed at this pressure can pack around the chromophore more densely than in the bulk matrix. On increasing the average cluster size at a higher stagnation pressure of 200 psi ($\langle n \rangle = 270$ atoms) a dominant absorption peak at 937.9 cm⁻¹ emerges, which suggests that, in this size region, the matrix-like features of the SF₆/Ar cluster spectra are very close to those found in the *unannealed* bulk matrix. At this size the clusters are expected to have a Mackay icosahedral structure as predicted by electron diffraction results. Therefore, an unannealed matrix-like absorption is representative of an icosahedral-like site in a matrix. This absorption has,

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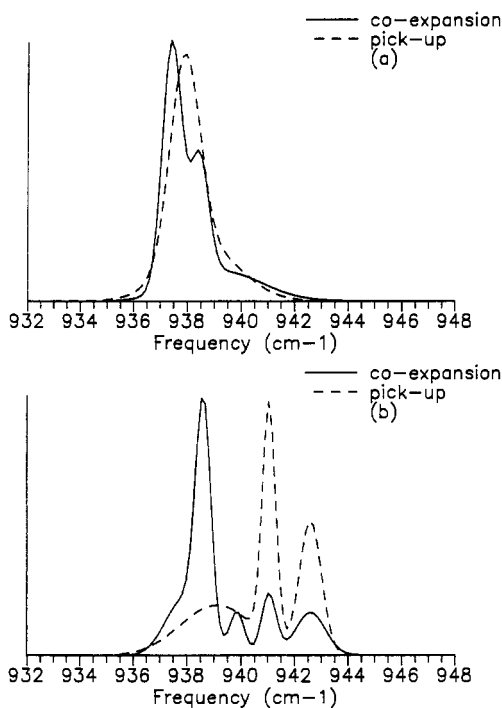


Figure 3. A comparison of the coexpansion and pick-up spectra at two different stagnation pressures. Here only the Gaussian curves fitted to the data points are plotted: (a) 100 psi ($\langle n \rangle = 60$ atoms); (b) 1200 psi ($\langle n \rangle = 9200$ atoms).

however, almost disappeared when the stagnation pressure reaches 400 psi.

At 400 psi (Figure 2b), two additional peaks located at 941.1 and 942.6 cm^{-1} become resolved, which are due to the chromophore residing at the surface of the cluster. The identity of these features is established by comparing the spectra obtained by coexpansion with those from the pick-up technique, since in the latter, the surface peaks are greatly enhanced.

At 600-psi ($\langle n \rangle = 2200$ atoms) nozzle pressure (Figure 2c), a different peak is resolved at 938.6 cm^{-1} . This peak gains prominence at a still higher pressure of 800 psi and becomes the dominant peak at 1200 psi (Figure 3d). We believe that the appearance of this peak is important for several reasons. Swanson and Jones²⁹ have reported that a doublet at 938.6 and 938.45 cm^{-1} caused by a splitting of the ν_3 mode of SF_6 dominates the spectrum in a well-annealed argon matrix. This doublet can be used as an infrared signature for bulk-solid argon. Therefore, it is natural to conclude that the appearance of the peak at 938.6 cm^{-1} , first observed in clusters produced at a stagnation pressure of 600 psi, signifies the point at which the transition to the bulk fcc solid argon structure occurs. Computer simulations³⁰⁻³² and electron diffraction data^{9,10} have shown that, for smaller cluster sizes, icosahedral configurations are more stable than the fcc structure which occurs at larger sizes. The icosahedral clusters are, locally, more densely packed than the fcc solid. Assuming that the increase in density also occurs for the smaller clusters containing SF_6 , this could explain the larger red shift found at smaller sizes.

The above assignments made on the basis of coexpansion spectra are further supported by contrasting them with those from pick-up. At lower pressures (100 psi), the differences in the spectra produced by the two techniques are minor (Figure 3a) and similar features are seen. Apparently, diffusion of SF_6 from the surface to the interior of the neat argon clusters occurs up to a pressure of about 400 psi, which may indicate that at the cluster's temperature, which is believed to be about 32 K, the system can rearrange within the time scale of our experiment (approximately 100 μs). At higher pressures (600–1200 psi), the matrix peak at 938.6 cm^{-1} is completely absent in the pick-up spectra. Figure 3b superimposes the spectra at 1200 psi obtained from the two techniques to highlight this difference. Due to the presence of bulk-like solid argon clusters, the chromophore deposited by the pick-up method is unable to diffuse and is forced to stay on the surface, giving rise to the dominant surface doublet. We note that the icosahedral configuration, while more tightly packed around the SF_6 , is bound to be more rich in defects and, therefore, is more likely to allow for diffusion than the more periodic bulk-like fcc structures. The diffusion is observed in argon clusters till they attain an average size of about 700 atoms (stagnation pressure of 300 psi), while our data on krypton shows a diffusion till an average size of about 300 atoms. Swanson and Jones recorded no signs of diffusion of the chromophore in an argon matrix, even at a temperature of 42 K. Since the clusters produced in the molecular beam are at an even lower temperature, it is reasonable to expect that diffusion is quite slow in these finite-size systems that have attained a bulk solid character.

The two resolved surface peaks at 941.1 and 942.6 cm^{-1} in both the pick-up and the coexpansion spectra are due to a splitting of the triply degenerate ν_3 mode caused by the site asymmetry. Eichenauer and LeRoy³³ have calculated the magnitude of such a splitting for SF_6 interacting with a bulk argon surface modeled as a polarizable continuum with the same density as the solid. For SF_6 more than half embedded in the cluster surface, their model predicts that the two ν_3 modes which are perpendicular to the normal to the cluster surface experience a greater shift than the parallel mode, and the difference in their shift may be of the order of 1.5 cm^{-1} , consistent with our results.

The relative intensities of the unannealed (icosahedral) and the annealed (fcc) peaks are plotted as a function of cluster size in Figure 4. It is seen that the icosahedral peak, starting from a relatively high value at lower sizes, decreases in intensity till a size of about 1800 atoms, at which point it remains more or less constant. By contrast, the fcc peak, starting at a lower value, increases rapidly at a size of about 1800 atoms. Hence, at this point, where the two peaks cross over in dominating the spectrum, we place the point of structural transition. Several spectra of SF_6 were also recorded in krypton clusters and were found to behave quite similarly to argon (see Figure 4).

These results provide us with spectroscopic evidence for a structural transformation in NG clusters at a certain critical size. The only other experimental evidence comes from the electron diffraction data of Torchet and co-workers at Orsay,⁹ and those of Lee

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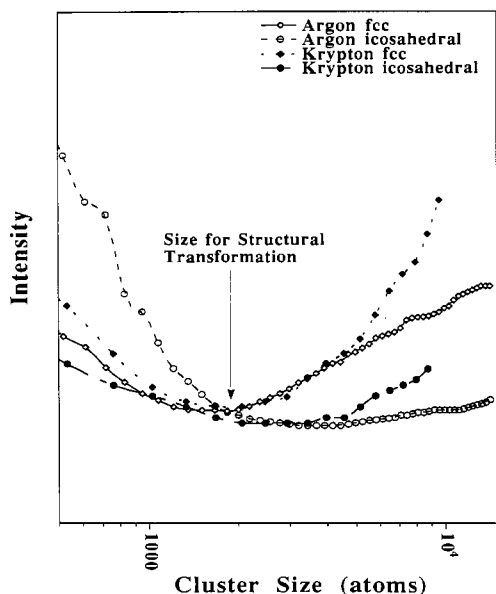


Figure 4. The intensities of the peaks characteristic of icosahedral and fcc-like clusters are plotted for both argon and krypton as a function of the cluster size (number of atoms). The intensities for both argon and krypton were normalized individually to their highest value.

and Stein.¹⁰ Torchet has reported an average cluster size of 600 for the transformation to fcc, with an estimated size distribution lying between 450 and 750. Since the clusters with fcc structure correspond to the largest clusters in their distribution, they report a size of 750 atoms for the transformation. Lee and Stein¹⁰ report a size of 1500 argon atoms for the transition. The electron diffraction results are, however, sensitive to structural defects, as their analysis assumes monocrystalline clusters, and this gives our data an added degree of relevance. However, it must be added that, in our observations, the SF₆ could stabilize the icosahedral structures up to larger cluster sizes, and in our case, the transition point to the fcc structure could be higher than that measured for neat noble gas clusters.

Precise calculations on the structural transition have been done independently by Northby³⁰ et al. and van de Waal,³¹ who found the critical size to be at 14 shells or 10 179 atoms. However, on using a more realistic interaction energy, Northby et al. found that the fcc structure had a lower energy at 13 complete shells (8217 atoms). Similarly, Raoult and co-workers³⁴ have calculated the transition point from an icosahedral to fcc structure between 1600 and 2400 atoms. In these calculations, the transition point depends on the cluster surface structure and the potential that is used, underlining the difficulties for a precise solution of this problem. Several other authors have also performed somewhat less comprehensive theoretical studies on this subject, with Lee and Stein¹⁰ reporting a crossover point at 3000 atoms, while Andersen³² found it to be at about 5000.

Complexation of Molecular Species in Clusters

It is, of course, possible to embed a molecule inside a cluster using the coexpansion method and subsequently pick up another molecule on the surface and

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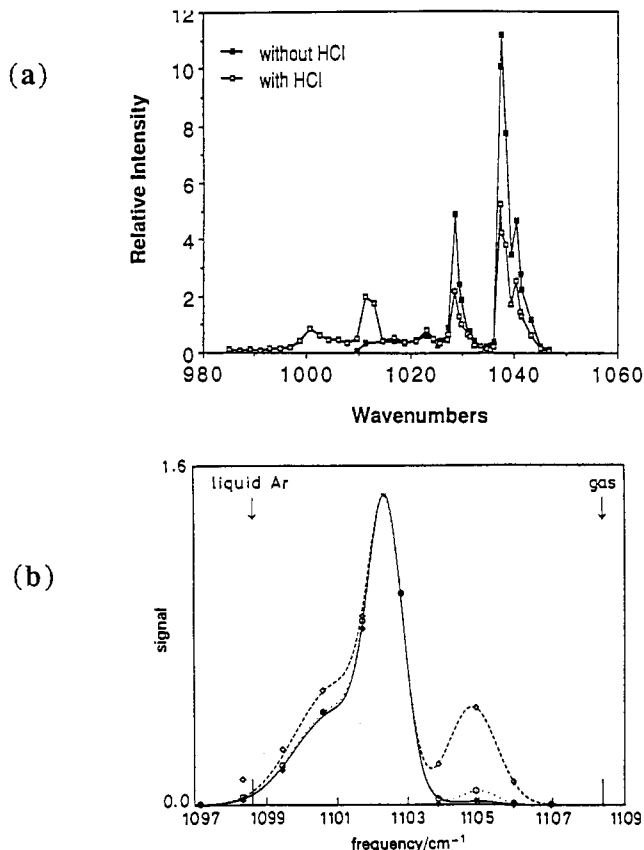


Figure 5. (a) Spectra of a 0.1% CH₃F/Ar mixture expanded at a 100-psi expansion pressure with HCl (open squares) and without HCl (filled squares). Reprinted with permission from ref 19a. Copyright 1988 Springer. (b) Superimposed pick-up spectra of CF₃Cl/Ar measured using a stagnation pressure of 400 psi and pick-up fluxes of 1.5×10^{-5} , 4.5×10^{-5} , and 1.0×10^{-4} Torr. Reprinted with permission from ref 19b. Copyright 1990 Royal Society of Chemistry. These spectra were recorded using a 30- μ m nozzle.

spectroscopically monitor the complexation reaction between the two. Complexation naturally requires that the surface species diffuses inside. Alternatively, it is possible to sequentially pick up two species which may form a complex on the cluster surface. We have seen examples of both cases. Figure 5a shows two spectra of CH₃F in argon clusters of about 60 atoms.^{19a} The first was recorded by coexpanding a 0.1% mixture of the chromophore in argon, producing two peaks from the solvated monomer (1040 cm⁻¹) and dimer (1030 cm⁻¹) which were identified by comparison with bulk matrix spectra. Next, HCl molecules are deposited on the surface of the clusters and diffuse inside to form a complex with the CH₃F. This leads to a decrease in the monomer intensity, while at the same time giving rise to an additional peak at 1013 cm⁻¹ which is due to the complex. These data demonstrate that it is possible to study a reaction occurring between a single pair of molecules in a "reactor" made by a few tens of atoms.

The second case of complexation, occurring between two surface species that do not diffuse inside the cluster, is shown in Figure 5b. These spectra are due to CF₃Cl picked up by argon clusters of about 600 atoms^{19b} and show two well-resolved peaks at 1102.2 and 1105 cm⁻¹. The first absorption is due to a CF₃Cl monomer, and the second arises from the formation of a dimer on the surface of the cluster. This is demonstrated by showing that the first peak's intensity grows linearly with the

density of the pick-up gas, while the second peak increases quadratically with that quantity, being the consequence of independent pick-up of two monomers. The two monomers move on the cluster's surface till they meet to form a dimer. This occurs in the time period between pick-up and laser crossing, which is a few tens of microseconds.

Solvation Effects in Simple Systems

The discussion in the last two sections shows that it is possible to identify whether the chromophore interacting with a noble gas cluster is solvated by the medium or prefers to remain on the surface. In these experiments, the clusters are formed from a relatively high temperature, which helps the annealing process, letting these systems adopt the most stable structure. If similar spectra are recorded for a number of solute-solvent combinations at different cluster sizes, can a model be found that predicts a general criterion for determining if a particular molecule may or may not be solvated in a given solvent? Can this criterion be based on the relative solute-solvent interaction energy and size? An attempt to find such a model has been made recently by Amar and Perera.⁵ In their model, they have tried to predict the solvation behavior of different chromophores in various solvents (clusters). Both the solute-solute and the solvent-solute interactions are described in terms of spherical Lennard-Jones (L-J) potential. Using such an interaction between the solute and a 54-atom cluster, they performed molecular dynamics calculations which predicted the average number of solvent atoms surrounding the solute. A diagram (see Figure 6) representing the average number of solvent neighbors was presented as a function of $\epsilon_i(\epsilon_{AB}/\epsilon_{AA})$ and $\sigma_i(\sigma_{AB}/\sigma_{AA})$. Here A and B represent the solvent and the chromophore (solute), respectively; $\sigma_{AB} = (\sigma_A + \sigma_B)/2$; $\epsilon_{AB} = (\epsilon_A \epsilon_B)^{1/2}$, and ϵ and σ are the L-J interaction parameters. In the plot, the number of solvent atoms around a molecule are expressed as the ratio of the average number of nearest neighbors to the maximum possible number ($\langle NN \rangle / NN_{max}$).

We have spectroscopically determined the solvation of several molecules in NG clusters: SF₆, CH₃F, SiF₄, CF₃Cl, CF₃I, and HCl in Ar,³⁵ and SF₆ in Kr and Xe. Briefly, in the small cluster sizes at which the simulations of Amar and Perera were performed, the results may be stated as follows: SF₆ is solvated in Ar and Kr but not Xe; SiF₄ is not solvated in Ar; CH₃F and HCl are solvated in Ar; and CF₃Cl and CF₃I are partially solvated in Ar. Is this data consistent with the model described above? The coordinates of the systems measured by us are shown on the plot (Figure 6) published by Amar and Perera.⁵ Taking into account that a high value of $\langle NN \rangle / NN_{max}$ indicates solvation, it is seen that there is excellent agreement between the theory and experiment, showing the predictive abilities of the simulations. In the case of CF₃Cl and CF₃I, which are partially solvated, an intermediate value of $\langle NN \rangle / NN_{max}$ is seen.

Similar work done by LeRoy⁶ and co-workers to predict the solvation effects using an anisotropic solute-

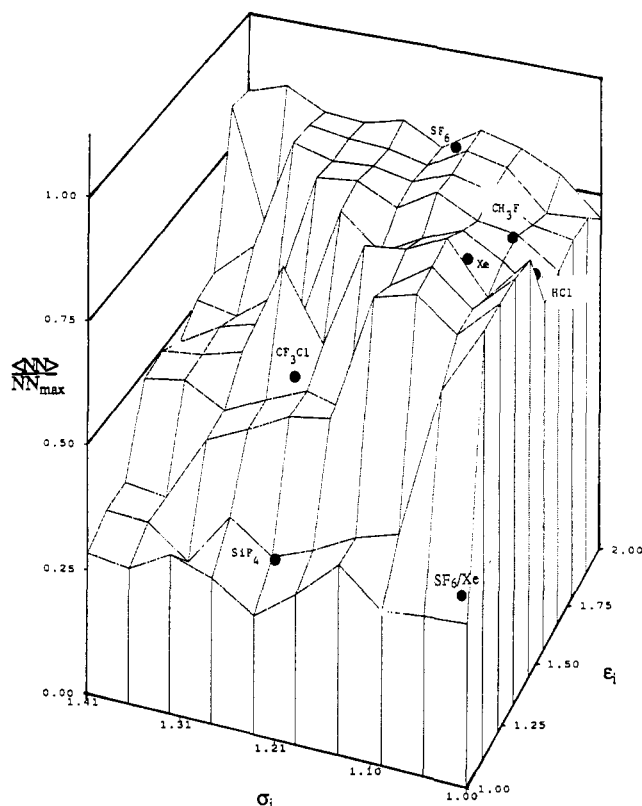


Figure 6. Three-dimensional plot of the calculated number of nearest neighbors (NN_i) divided by the maximum number of nearest neighbors vs reduced ϵ and σ values for impurity-Ar₅₄ clusters. Note the appearance of a cliff marking the transition zone between surface behavior (low $\langle NN_i \rangle$) and matrix behavior (high $\langle NN_i \rangle$). The positions of ϵ_i and σ_i for some of the molecules are marked. Reprinted with permission from ref 35. Copyright 1990 American Institute of Physics.

solvent potential is consistent in most of its conclusions with the above results.

All of the simulations have been performed for relatively small cluster sizes, and their reliability for larger clusters remains to be seen. However, the predictability of solvation effects within such a simple model for small clusters is very encouraging and allows us to be somewhat optimistic vis-à-vis the whole field of solution chemistry.

Study of Quantum Clusters

All the work described so far can be placed in the framework of classical mechanics and concerns mostly solid clusters. To extend this type of study to liquid crystals and to investigate the importance of quantum mechanical effects, the logical system to choose is of course helium.

To begin investigating the properties of ⁴He clusters, excitation spectra (Figure 7a) of the ν_3 vibration of (SF₆)_{n=1,2} using the pick-up technique were recorded. The SF₆ monomer shows two features located at 945.8 and 946.1 cm⁻¹ with the weaker absorption located on the red side of the spectrum. This spectral pattern is characteristic of a molecule residing near the surface of the cluster. More specifically, the doublet splitting has its origin in the partial removal of the 3-fold degeneracy of the ν_3 vibration. When the SF₆ is exposed to a perturbing surface, the vibrational mode which is parallel to the surface normal will experience a different

(35) Gu, X. J.; Levandier, D. J.; Zhang, B.; Scoles, G.; Zhang, D. J. *Chem. Phys.* 1990, 93, 4898.

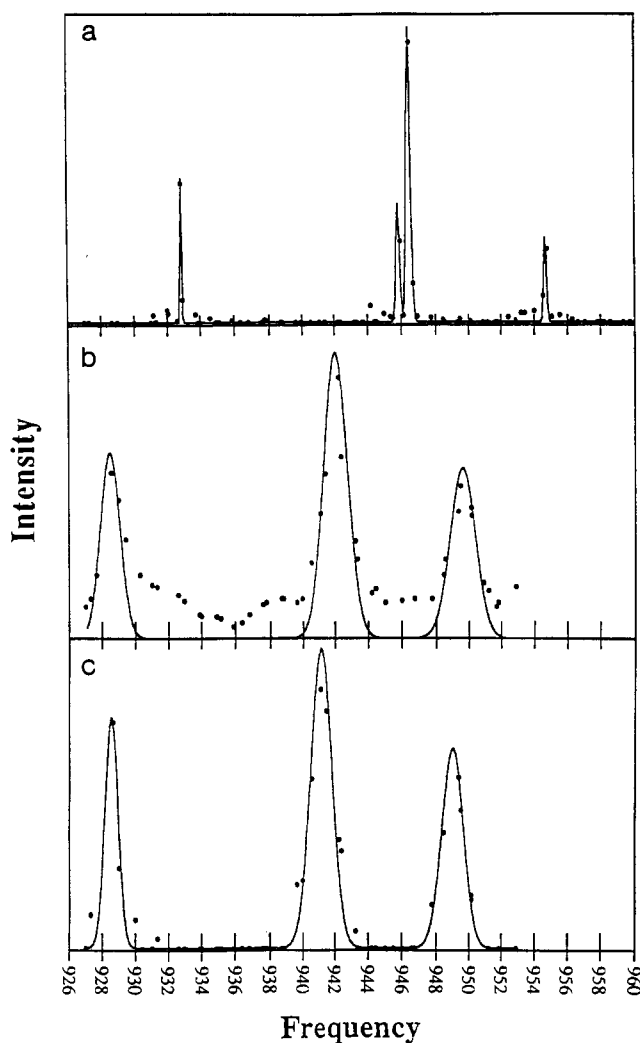


Figure 7. The spectrum of SF_6 attached to clusters of (a) He at 1500-psi nozzle pressure, 15 K, and a nozzle size of $2 \mu\text{m}$; (b) H_2 at 450-psi nozzle pressure, 60 K, and a nozzle size of $10 \mu\text{m}$; and (c) D_2 at 450-psi nozzle pressure, 60 K, and a nozzle size of $10 \mu\text{m}$. The darkened circles are the measured intensities, and the solid line is a trace of Gaussian curves fitted to the data.

perturbation than the 2-fold-degenerate mode which is perpendicular to it. Consequently, the two absorptions will shift by unequal amounts. The intensity of the two modes will be unequal because of the degeneracy which remains in the perpendicular mode.

Unfortunately, the location of the SF_6 on the surface of the cluster runs contrary to the predictions based on calculations.^{36,37} In both of these calculations, the SF_6 is found inside the cluster. A possible rationalization of the discrepancy between the experiment and the calculations can be obtained if the angular momentum acquired by the system during the doping process is considered. When the SF_6 collides with the cluster it has, on average, a nonzero impact parameter. As a result, the system gains angular momentum. If some of the angular momentum remains with the SF_6 and does not couple entirely into the rotation of the cluster as a whole or is not entirely dissipated by the evaporation of helium atoms, the molecule will experience a centrifugal force and will be pushed toward the surface of the cluster. This scenario is entirely consistent with

the fact that, below a critical velocity, an impurity can no longer create excitations in superfluid helium. Theoretical investigations are presently underway to include cluster rotation in the molecular dynamics simulation of the cluster structure and spectrum.

As indicated above, the excitation spectrum of $(\text{SF}_6)_2$ was also measured. The spectrum shows two absorptions located at 932.9 and 954.7 cm^{-1} that are respectively assigned to the parallel and perpendicular vibrational modes of the dimer. As for the monomer, the parallel mode is red-shifted 1.5 cm^{-1} from the gas-phase value. However, the absorption of the perpendicular vibration is only shifted by about 0.3 cm^{-1} . On the basis of the behavior of the monomer, the dimer can also be assumed to be on the surface of the cluster. Plotting the intensity of the monomer and dimer absorptions as a function of the SF_6 density in the pickup cell, one sees that the former grows linearly while the latter increases quadratically. Taking the ratio between the two probabilities, an absolute probability for SF_6 pick-up is measured which provides us with a reasonably good estimate of the average cluster size (found to be $\sim 40 \text{ \AA}$ in diameter).

The excitation spectra of $(\text{SF}_6)_{n=1,2}$ were also recorded in hydrogen³⁸ and deuterium clusters, where, in contrast to helium, the impurities were found to be solvated. For hydrogen (Figure 7b), the monomer shows a single absorption at 942.0 cm^{-1} and two dimer modes at 928.6 and 949.6 cm^{-1} . The single absorption of the monomer is indicative of a fully solvated SF_6 since the 3-fold degeneracy of the energy levels is regained. The spectrum in deuterium (Figure 7c) is very similar to that in hydrogen and exhibits absorptions at 941.1 , 928.6 , and 949.0 cm^{-1} with the same assignments as reported for hydrogen. Since the intermolecular potential and the polarizability of hydrogen and deuterium are essentially identical, the 0.9-cm^{-1} increase in the red shift of the monomer absorption in deuterium reflects the lowering of the zero-point energy in this system. In other words, because of the large deuterium mass, the zero-point energy of this molecule in both the crystal field and the force field generated by SF_6 is lower. This produces a larger molecular and, therefore, polarizability density around the SF_6 which, in turn, produces a larger dipole-induced shift.

Possible Directions for Future Work

Higher resolution IR spectroscopy, with the resolution of the rotational or librational structure in the vibrational spectrum of the probe molecule, could be useful in the determination of the cluster temperature. For this purpose, probes such as HF and HCl are accessible by a color center laser and have been well studied in noble gas matrices, both experimentally³⁹ and theoretically.⁴⁰ The lower power level of the color center lasers and the lower transition probabilities for these molecules as compared to SF_6 will require the application of multipass devices, which, however, are well within the range of possible improvements.

(38) Goyal, S.; Robinson, G. N.; Schutt, D. L.; Scoles, G. *Chem. Phys. Lett.* 1992, 196, 123.

(39) Mason, M. G.; Von Holle, W. G.; Robinson, D. W. *J. Chem. Phys.* 1971, 54, 3491.

(40) (a) Friedman, H.; Kimel, S. *J. Chem. Phys.* 1967, 47, 3589. (b) Flygare, W. H. *J. Chem. Phys.* 1963, 39, 2263.

(36) R. Barnett and K. B. Whaley, private communication.

(37) D. Chartrand and R. J. Le Roy, private communication.

The technique of optothermal bolometric detection may also be carried into other spectral regimes such as the electronic spectroscopy of metals and ions solvated in or residing on the surface of noble gas clusters. For example, attempts are underway in our laboratory to measure the mobility of lithium atoms in H_2 clusters. This system is important for applied reasons, given the role of solid and liquid H_2 as fuel for space and high altitude propulsion devices.

Molecular spectroscopy in highly quantum clusters has, in our opinion, many exciting prospects. The investigation of SF_6 in 3He clusters may be used to investigate whether or not the behavior of SF_6 in 4He clusters is a result of superfluidity since 3He will not become a superfluid at the terminal temperature of the cluster. Also, attaching ions to 4He clusters with the pick-up technique offers the opportunity to investigate

their behavior in a superfluid medium under restricted geometries. Ion cyclotron resonance spectroscopy may be applied in this case.

The helium clusters are, in several respects, a unique medium to perform spectroscopy. With an estimated temperature of less than 0.5 K, they can be used as a medium to perform spectroscopy on molecules, complexes, and free radicals that need these extreme temperatures to be understood. Free radicals, in particular, may be produced in a pick-up cell in which a microwave discharge is sustained. In a certain sense this method could carry the advantages of matrix isolation studies a step further as the interaction with the He cluster would be minimal (due to low polarizability), allowing an easier interpretation of the spectra, at the same time stabilizing and isolating short-lived or unstable species.