

Vibrational Spectroscopy of Sulfur Hexafluoride Attached to Helium Clusters

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We have built an apparatus capable of attaching a molecule to a liquid-helium cluster and obtaining its infrared spectrum. Clusters made of a few thousand atoms and containing an SF₆ molecule show two absorptions located at 945.8 and 946.1 cm⁻¹ which indicate that the guest molecule is located near the surface of the cluster. If the cluster contains two SF₆ molecules, the spectrum obtained is that of a slightly perturbed SF₆ dimer.

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The study of atomic and molecular clusters has been, and continues to be, a fruitful area of research. The field has developed primarily as a method to study the physical properties of matter as a function of its size: from the molecular level to bulk behavior. The ease of producing rare-gas clusters, using supersonic free jets, and their simple, well-known interaction potentials has provided the impetus for a large number of theoretical and experimental investigations for these systems. In most atomic systems studied thus far, the clusters are solid. This is true for the rare-gas systems as well as ionic and metallic clusters. In fact, both theory and experiment have been successful in detecting structural transitions between different solid phases in atomic clusters [1,2]. Recently, however, there has been an increased interest in systems where the clusters are fluid or exhibit fluidlike behavior. It is well established that molecular clusters may exhibit fluidlike behavior [3]; however, experimental evidence of fluidity in atomic clusters is less convincing [4,5]. The most logical choice for a system which may exhibit fluidlike behavior is helium clusters [6]. Thus far, most of our knowledge on the energetics, and therefore the structure and dynamics, of clusters has been derived through the application of classical mechanics. However, because of helium's small mass and weak interatomic potential, a fully quantum-mechanical approach is required in this case. Therefore an additional motivation for investigating helium clusters is that by characterizing these systems, a better understanding of size-dependent properties of highly quantum systems may be possible.

Stingari and Treiner [7] investigated helium clusters using a density-functional approach and found that the ⁴He clusters are always bound, and to the contrary of ³He clusters, exhibit no shell effects. Cleveland, Landmann, and Barnett [8] carried out finite temperature studies of small helium droplets using quantum path-integral molecular dynamics and established that the density of helium droplets drops rather slowly at their surface. Furthermore, they found that a droplet containing 270 atoms has a core which exhibits properties similar to the bulk. Klein and Ceperley [9] used Monte Carlo path-integral simulations to investigate the behavior of the specific heat in helium clusters of variable sizes up to 128 atoms and observed a departure from the classical

value similar to what occurs in the bulk. They interpreted this deviation in the heat-capacity behavior as the onset of a superfluid phase. Rama Krishna and Whaley [10] investigated the microscopic excitations of helium clusters and found, in clusters composed of 240 atoms, an excitation spectrum in the clusters similar to that of bulk helium.

In spite of all the theoretical progress, there has been little overlap with experiment, especially on the question of superfluidity. While thermodynamic measurements of small helium bubbles (<110 Å) trapped in copper foil have shown that these systems can exhibit superfluid behavior [11], clusters formed in a free jet expansion offer several advantages over pseudobulk experiments. One advantage is the possibility to confine all three dimensions without applying a perturbing boundary (as in the case of copper foils). A second advantage is the ability to continuously vary the size of the aggregate from a few to 10⁸ atoms. Furthermore, techniques to investigate the microscopic properties of small aggregates have already been developed and have been applied to other noble-gas systems. For these reasons, beams of helium clusters have been the subject of a number of studies [12,13]. With the exception of one study, where Xe and Cs atoms were scattered from a neutral helium cluster beam [14], experiments with helium clusters have utilized mass spectrometric detection techniques relying on electron impact ionization of the clusters. This detection technique is likely to produce fragmentation of the cluster and consequently may alter the composition of the beam being studied. To avoid this problem, we have built an apparatus capable of attaching a weakly interacting probe molecule to the cluster and interrogating the system by means of a tunable infrared laser while the cluster is in its neutral state. With this instrument we have obtained and report here what we believe to be the first infrared spectrum of a molecule in contact with liquid helium (albeit in the form of a cluster). Optical spectra of alkali and alkaline earth atoms have recently been reported in bulk superfluid helium [15]. However, this type of experiment offers greater difficulties in the analysis and interpretation of the spectra because the guest-host interaction potentials of the electronic excited states are not as well understood as those in the ground state. For instance, the in-

teraction of SF₆ with helium is known to a reasonable degree of accuracy [16]. Furthermore, the rovibrational excitations are closer in energy to the internal excitations of the cluster and can therefore interact and probe them directly.

The details of the experimental apparatus will be provided in a future publication; however, a brief description will be provided here for completeness. The supersonic cluster beam is generated by expanding helium gas through a 10- μm nozzle into a vacuum chamber pumped by a 32000-l/s oil diffusion pump. The nozzle is cooled using a closed-cycle helium refrigerator and the temperature is stabilized by a temperature controller using a silicon diode sensor. The central portion of the expansion passes through a 390- μm skimmer into a high-vacuum chamber pumped by a baffled 5000-l/s oil diffusion pump. The beam subsequently passes through a stainless-steel scattering cell which contains a variable density of SF₆ molecules. In the cell, some of the clusters collide with the SF₆ molecules and are able to pick up one or two of these. The doped clusters are then interrogated by the modulated output of a line tunable cw infrared laser, which may or may not be in resonance with the infrared absorption of the system. In the case where a photon is absorbed, the SF₆ becomes vibrationally excited and subsequently relaxes into its ground state by releasing its energy into the cluster. The cluster releases this absorbed energy by evaporating a few atoms from its surface. The

resultant change in the energy content of the beam is measured using an on-axis semiconductor bolometer located downstream from the lasers, the resistance of which is monitored using a standard lock-in amplifier. The lasers utilized in this experiment were a line tunable N₂O and three line tunable isotopically substituted CO₂ (¹²C¹⁶O₂, ¹³C¹⁶O₂, and ¹²C¹⁸O₂) lasers. Combining these four lasers, an emission line is found approximately every 0.25 cm⁻¹ which then determines the spectral resolution. The lasers were made to cross the cluster beam at a carefully controlled point, so that after normalizing to constant photon flux, no scaling of the data was necessary. From one laser scan to another, the intensities could be reproduced within 5% with a signal to noise of approximately 100 for the strongest absorption.

Figure 1 below shows the absorption spectrum of the ν_3 mode of sulfur hexafluoride after attaching to a helium cluster. The two central absorptions located at 945.8 and 946.4 cm⁻¹, which increase linearly with the SF₆ pressure in the pickup cell, are assigned to a single isolated SF₆ molecule on the surface of a helium cluster; the outer two absorptions located at 932.9 and 954.7 cm⁻¹ are assigned to SF₆ complexing with itself on the cluster to form a dimer because their frequency separation is very near that of the SF₆ dimer in the gas phase [17] and because their intensity increases more than linearly with the pressure in the pickup cell. In this Letter we will only discuss in detail the two monomer absorptions and leave a

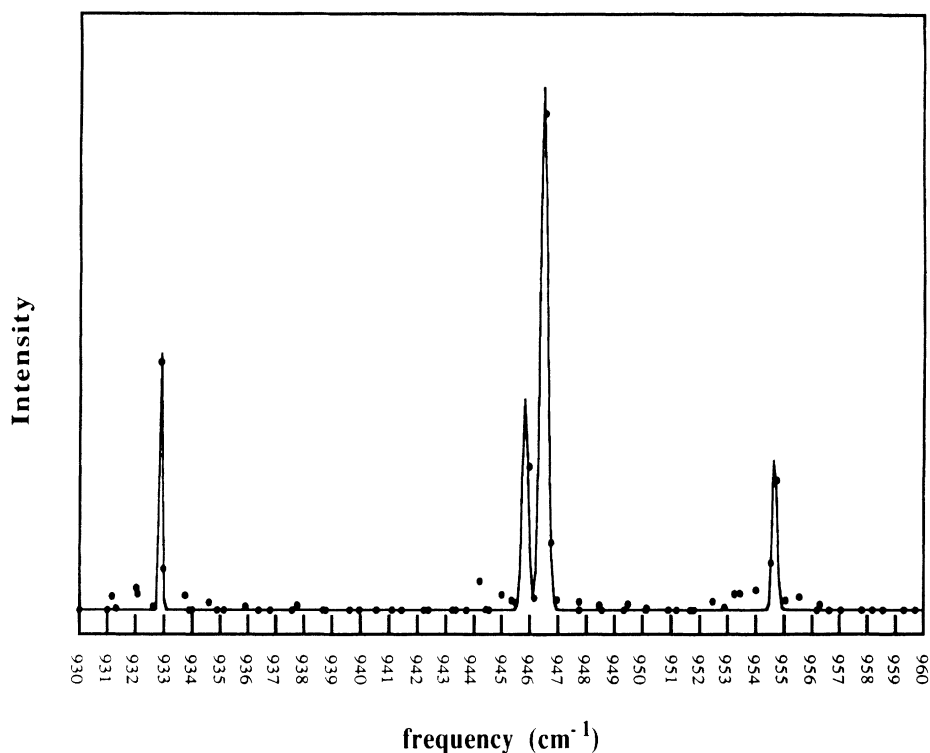


FIG. 1. The spectrum of SF₆ attached to a helium cluster produced in a 100-bar expansion from a 16-K nozzle. The darkened circles are the measured intensities and the solid line is a trace of Gaussians fitted to the data.

more thorough discussion of the dimer absorptions for a later publication. The assignments of the absorptions are based (see below) on the positions of the peaks relative to the gas-phase absorption in an analogous fashion as was done with the earlier studies carried out with SF₆ attached to other noble-gas clusters [2(b),18,19].

The ν_3 mode of SF₆ corresponds to the triply degenerate asymmetric oscillation of the fluorine cage around the sulfur atom and has a single gas-phase absorption at 948.0 cm⁻¹. If, however, the SF₆ is located near a perturbing surface, according to the instantaneous transition-dipole induced-dipole model [20], the degeneracy is lifted and a splitting in the energy levels occurs. As a consequence, the spectrum shows two absorptions with an intensity ratio of 1:2 for the modes which are, respectively, parallel and perpendicular to the surface normal (the perpendicular mode remains twofold degenerate). The magnitude of the shift is related to the polarizability and density of the perturbing surface, while the relative shifts of the two absorptions are related to the molecule's position with respect to the surface boundary. As the molecule approaches the surface from the vacuum side, the parallel mode will feel the effects of the surface more strongly than the perpendicular modes and therefore experience a larger redshift. The contrary happens for a molecule located just below the surface. For the case when the molecule is exactly in the center or at the surface of the cluster there would be no splitting since the degeneracy is restored. This instantaneous transition-dipole induced-dipole mechanism has been quantitatively developed and applied to the argon-SF₆ system with a good degree of success by Eichenauer and Le Roy [20]. Applying this simple model in the continuum limit to the spectrum of SF₆ attached to a helium cluster presented here, if the intensity ratio of the two absorptions is assumed to be correct, the conclusion is reached that the molecule is sitting outside, yet near, the surface of the cluster. However, the model underestimates the magnitude of the overall shift and the relative splitting between the two modes. Using a polarizability of 0.2 Å³ for the helium atom and the number density of bulk liquid helium as 2.2×10^{22} cm⁻³, the model predicts a surface shift of approximately 0.5 cm⁻¹ (with a splitting between the two modes of the order of 0.1 cm⁻¹) and a solvation shift of approximately 1.0 cm⁻¹. Treating helium as a fluid made of distinguishable particles, Chartrand and Le Roy have recently [21] calculated a shift of 1.43 cm⁻¹ for one layer (consisting of 27 atoms) and a 1.89-cm⁻¹ shift for two layers (a total of 98 atoms) of helium atoms around the SF₆ molecule. In the spectrum shown here, the overall shift is 1.5 cm⁻¹ with a splitting of 0.6 cm⁻¹.

One must therefore be cautious in excluding the possibility that SF₆ may be solvated by the helium clusters. For example, a splitting also occurs in the ν_3 mode of SF₆ inside a rare-gas matrix such as argon or krypton. This splitting is a consequence of the inhomogeneous environment felt by the impurity as a result of the site asym-

metry present in the lattice of the rare-gas matrices. The splitting in the cases of argon, krypton, and xenon is 0.15, 0.20, and 0.25 cm⁻¹, respectively. Since the splitting is proportional to the polarizability of the matrix atoms, it is reasonable to expect that, if it is present in helium (in spite of the fluid nature of this medium), its value should be below our spectral resolution. On the other hand, preliminary calculations conducted by Barnett and Whaley [22], using a quantum Monte Carlo method, indicate that small clusters of helium do indeed solvate the SF₆. Using a spherically symmetric potential, they carried out calculations at zero temperature for the He-SF₆, He₂₀-SF₆, and He₁₁₁-SF₆ systems. In each case they found that the SF₆ was solvated by the helium cluster. The values of the spectral shifts calculated by these authors were about 0.5 cm⁻¹, which is smaller but of the order of what we found experimentally. However, because of the angular momentum acquired by the cluster as a consequence of the pickup process (estimated to be of the order of $1000h/2\pi$), even if the SF₆ solvates, it is likely to be centrifugated towards the cluster's surface [23]. Since our resolution is limited and therefore the peak intensities are not sufficiently well known and since exact calculations for such large clusters are quite difficult, the question of the precise position of the molecule (just inside or just outside) will have to be the subject of further investigations.

Considering now the spectrum as a whole, several features are worth noting. Unlike previous studies of SF₆ solvated by rare-gas clusters [2(b),19], varying the source pressure from 20 to 175 bars and the temperature from 12 to 20 K (and, therefore, likely the cluster size) had little effect on the spectrum only affecting the absolute intensities of the absorptions. Keeping the temperature of the nozzle and the partial pressure of SF₆ in the cell constant, an increase in stagnation pressure (thereby increasing the average cluster size) only results in an increase in the dimer to monomer ratio. This can be easily understood in terms of the pickup process where a larger cluster has a higher probability of colliding with more than one SF₆ molecule and consequently more dimers are able to form. Keeping everything else constant, lowering the temperature of the nozzle increases the intensity of all four absorptions equally. The highest temperature at which a spectrum could be obtained using a stagnation pressure of 100 bars was 20 K. As the temperature of the nozzle was lowered, the intensity of the absorptions increased by a factor of roughly 2 for every 2° decrease in temperature. This phenomenon was previously observed by Scheidemann, Toennies, and Northby [24] in the capture of neon by helium clusters. However, that paper reported a maximum in the capture probability for neon at a nozzle temperature of 16 K and a stagnation pressure of 80 bars. As the nozzle temperature was lowered below 16 K, the detected neon signal decreased. We see no evidence of a drop in signal intensity below 16 K, rather we see a monotonic increase. An explanation for this may be

found in the different detection schemes. In the experiment presented here, we are sensitive to the absolute number of SF₆ molecules captured by the clusters. Provided the evaporation of cluster fragments is not significantly altered as the cluster size increases (we have seen no evidence of this in any of our previous experiments), an increase in signal intensity correlates to a larger number of SF₆ molecules being captured by the clusters. In contrast, the experiments of Scheidemann, Toennies, and Northby are sensitive to the ionization efficiencies of the neon containing clusters. As the cluster size increases, the probability of having an ionized fragment containing a neon atom may not be constant, which could, therefore, explain the observed signal trend.

The spectrum reported in this paper represents only a first step towards a deeper understanding of the nature of closed-shell quantum clusters but may be useful in stimulating more theoretical activity in this area. As soon as higher-power *continuously tunable* infrared lasers become available, experiments of the type reported here may provide the first direct probing of the microscopic nature of helium clusters.

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