Spectroscopic Observation of Phase Coexistence in SF_6-Ar_n Clusters for $n = 10-20$

Dieter Eichenauer and Robert J. Le Roy
Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Waterloo,
Waterloo, Ontario, Canada N2L 3G1

(Received 14 July 1986)

In infrared photodepletion spectroscopy of molecular beams of SF_6-Ar_n clusters, a shifting and broadening of the ν_3 band of SF_6 was observed by Gough, Knight, and Scoles for a narrow range of experimental conditions. A Monte Carlo simulation of those spectra based on an instantaneous dipole-induced dipole model reproduces them semiquantitatively and shows that such broadening can be caused by phase coexistence. However, cluster-size distribution effects make it unclear whether this is the source of the broadening observed in the existing data.

PACS numbers: 36.40.+d, 33.10.Gx

While phase transitions of small atomic or molecular clusters have been a subject of considerable interest since early in the century,[1] experimental measurements of such changes are still quite rare. The melting temperatures of metallic clusters with diameters as small as 20 Å have now been successfully studied by use of electron scattering techniques.[2] Moreover, for clusters containing only a small number of (under 100) atoms, a prediction of size-dependent and sharp but unequal freezing and melting temperatures was made,[3] and has been substantiated by the results of molecular dynamics calculations.[4] However, aside from an intriguing but somewhat speculative interpretation of the branching ratio for fragmentation within certain ion clusters,[5] no procedure for experimental detection of phase transitions or phase coexistence in clusters formed from fewer than several hundreds or thousands of atoms or molecules has yet been reported.[6] The object of the present paper is to demonstrate that the infrared spectra of small clusters may contain distinct features due to phase coexistence.

In recent experiments, Gough, Knight, and Scoles[7] used infrared photodepletion spectroscopy of molecular beams of SR_6-Ar_n clusters, for n ranging from 1 to a few hundred, to examine how the width and frequency shift of the ν_3 band of SR_6 depended on cluster size. Their results are summarized in Fig. 1(c). In that study, the key experimental parameter was the molecular-beam source pressure, but by extrapolation from other work, it was associated with an average cluster-size scale [top of Fig. 1(c)]. Those experiments showed that the band center shifted monotonically to the red with increasing cluster size (or source pressure), approaching the frequency associated with the matrix spectrum[8] in the high-pressure limit. In contrast, the linewidth did not change monotonically, but rather showed a distinct maximum in the middle of the range. At the time, this peak was attributed to the distribution of frequency shifts of the various sizes of clusters present in the beam.[7] However, the Monte Carlo simulation of these spectra described in the present paper indicates that this broadening is at least partly due to the coexistence of clusters with different types of structure, in the neighborhood of a phase transition.

Any calculation of the effect of the solvent (Ar) atoms on the ν_3 fundamental of an SF_6 molecule in a cluster involves two principal components: The frequency shift due to any particular cluster configuration must be determined, and the most probable structures must be identified and averaged over. In the present work, the shifting and splitting of the ν_3 line of SF_6 due to the Ar atoms was calculated by perturbation theory with use of an instantaneous dipole-induced dipole model, while the averaging over statistical ensembles of energetically allowed cluster configurations was performed by use of Monte Carlo methods.[9] Aspects of these methods are outlined below.

The shift (relative to the free gas value) of the vibrational frequency of an SF_6 molecule in a cluster occurs because the Ar neighbors perturb the ground and vibrationally excited states of the chromophore by different amounts. In the present work, the SF_6 molecule was treated as a three-dimensional harmonic oscillator and the shifts were calculated with use of degenerate perturbation theory (the ν_3 mode is triply degenerate), while neglecting rotational fine-structure effects. By first-order perturbation theory, the shift of a given SF_6 energy level due to a particular cluster structure is the expectation value (averaged over the SF_6 motions) of the total interaction potential

$$V(\{\mathbf{rR}_j\};Q_1,Q_2,Q_3)=\sum_j\left[V_j(\mathbf{R}_j;\{Q_i=0\})+\sum_{i=1}^{3}\frac{\partial V_j}{\partial Q_i}Q_i+\frac{1}{2}\sum_{i,k=1}^{3}\frac{\partial^2 V_j}{\partial Q_i\,\partial Q_k}Q_iQ_k+\cdots\right], \qquad (1)$$

where $V_j(\mathbf{R}_j)$ is the pair interaction between the SF_6 chromophore and the jth Ar atom, located at $\mathbf{R}_j$, and $\{Q_i, i=1-3\}$ are the (degenerate) normal-mode-displacement coordinates associated with the ν_3 band. Its lack of

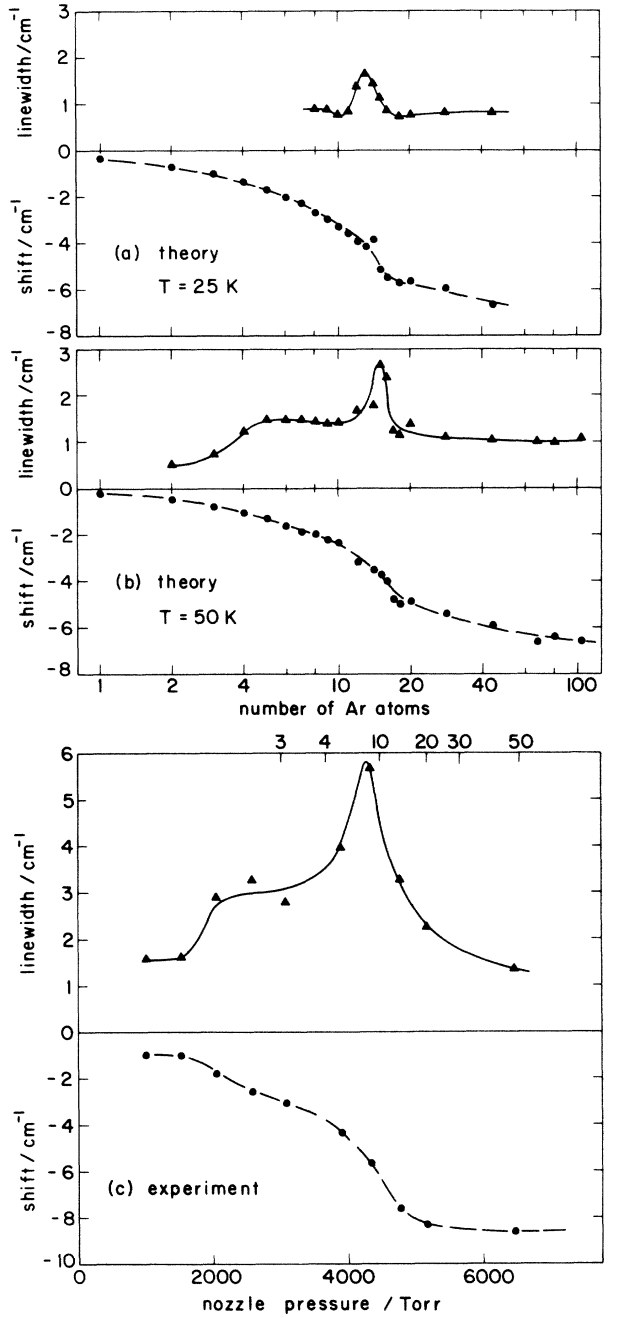

FIG. 1. Average frequency shift and width of the ν_3 transition of SF_6 in SF_6-Ar_n clusters, plotted vs the cluster size parameter n. (a),(b) Results generated from Monte Carlo simulations for the indicated temperatures. (c) Experimental results from Ref. 5.

dependence on $\{Q_i\}$ means that the first term in Eq. (1) will not affect transition frequencies, while neglect of SF_6 anharmonicity also makes this true for terms linear in Q_i. Thus, within this first-order approximation, it is the second derivatives of the Ar-SF_6 pair potential with respect to the ν_3 stretching coordinates $\{Q_i\}$ which give rise to the shifting and splitting of lines in the vibrational spectrum of SF_6-Ar_n clusters.

The overall SF_6-Ar pair potential which governs the cluster structures may be thought of as a combination of a short-range electron overlap repulsion with attractive inverse power dispersion terms.[10] However, we found the effect of its stretching dependence to be dominated by the instantaneous dipole-induced dipole component of the dispersion interaction. [This makes our approach similar to a model used to describe line shifts in $(SF_6)_n$ clusters.[11]] In this approach, the instantaneous SF_6 dipole moment associated with a given normal-mode displacement Q_i,

$$\mu = (\partial\mu/\partial Q_i)Q_i, \tag{2}$$

gives rise to an electric dipole field $\mathbf{E}$ which induces a dipole moment $\alpha\mathbf{E}(\mathbf{R}_j)$ in the Ar atom located at $\mathbf{R}_j$, where α is the Ar atom polarizability. The resulting interaction energy expression is $\frac{1}{2}\alpha|\mathbf{E}(\mathbf{R}_j)|^2$. If we use the known value[12] of $\partial\mu/\partial Q_i = 226.1$ esu$\cdot$g$^{-1/2}$ for the ν_3 mode of SF_6 (corresponding to a transition dipole moment of 0.388 D[13]) and $\alpha(\text{Ar}) = 1.642$ Å^3,[14] the resulting expression for the shift of the ν_3 frequency due to an Ar atom a distance R away, for vibrational motion parallel to the SF_6-Ar axis, is

$$\Delta\nu_{\parallel} = -(5000\ \text{cm}^{-1}\ \text{Å}^6)/R^6. \tag{3}$$

Similarly, for the two ν_3 modes perpendicular to this axis, $\Delta\nu_{\perp} = \Delta\nu_{\parallel}/4$. At the distance $R = 4.2$ Å, corresponding to the minimum of the Ar-SF_6 pair potential,[10] the predicted shifts are $\Delta\nu_{\parallel} = -0.91$ cm^{-1} and $\Delta\nu_{\perp} = -0.23$ cm^{-1}.

A generalization of the above model which incorporated SF_6 stretching dependence into the other components of the pair potential changed the predictions by only ca. 20%. Relative to other uncertainties in the calculation, this does not represent an improvement sufficient to warrant our giving up the simplicity of the induced dipole model, and so the latter was the basis of the results reported below. This dominance of the induced dipole mechanism reflects the fact that both the transition dipole moment of the ν_3 mode of SF_6 and the Ar polarizability are relatively large. Note that the R^{-6} dependence in Eq. (3) makes the magnitude of the shifts very sensitive to the positions of the nearest-neighbor atoms surrounding the chromophore, which in turn makes the spectrum sensitive to structural changes in the cluster, such as those associated with phase transitions.

Our calculation of the most probable structures of the SF_6-Ar_n clusters started with the known Ar-SF_6 and Ar-Ar potentials, and neglected many-body interactions. For Ar-SF_6, an anisotropic potential-energy surface (with the SF_6 molecule treated as a rigid body) was obtained by Pack, Valentini, and Cross[10] from simultaneous fits to experimental scattering cross sections, viscosities, and virial coefficients. The Ar-Ar potential is even more well known, and the present work used the form recommended by Tang and Toennies.[15] Given this information, the total potential energy of any given cluster configuration may be obtained by a summing over of all distinct SF_6-Ar and Ar-Ar pairs.

As the particles involved are fairly heavy, the cluster structures should be accurately described by classical mechanics. With use of the standard Metropolis Monte Carlo algorithm,[9] statistical ensembles of 100000 SF_6-Ar_n configurations were generated according to the Boltzmann distribution for temperatures $T=25$ and 50 K and cluster sizes ranging from $n=1$ to 104. The infrared spectrum for each of these cases was then defined by a Boltzmann average of the line shifts associated with this ensemble. Test calculations in which the force-biased Monte Carlo algorithm[16,17] was used to generate 1000000 configurations were performed for a limited number of cases. They confirmed that the statistics obtained with the 100000 configuration runs correctly predicted the behavior of the infrared spectrum, even in the neighborhood of the phase transition.

The results of our Monte Carlo simulation are shown in Fig. 1(a), where the average shift and the full width at half maximum of the red-shifted peak are plotted versus the cluster size parameter n. For $T=25$ K [Fig. 1(a)], the linewidths for clusters with $n<8$ are not shown because additional structure due to a splitting of the shifted ν_3 line in this region makes the assignment of a width difficult. A continuum estimate of the influence of Ar atoms lying more than 10 Å away from the SF_6 suggests that our calculated shifts for $n=100$ clusters are within 0.2–0.3 cm^{-1} of the fully converged values for infinitely large model systems.

It is immediately clear that at both temperatures, the qualitative behavior of the calculated shifts and linewidths is remarkably similar to that of the experimental results. Since the simulations were performed for a single cluster size at a time, the peak in the calculated bandwidth at around $n=13$–15 *cannot* be due to the cluster-size-distribution effects proposed as the reason for the analogous peak in the experimental results [see Fig. 1(c)].[7] Rather, various features of the simulations show that in the simulated spectra, this line broadening is due to the coexistence of two phases.

The simplest justification for the above conclusion is provided by the presence of two distinct but strongly overlapping peaks in the simulated spectra for $n=10$–20. The peak shifted farthest to the red becomes dominant for the larger clusters, while the one with the smaller shift is the only one present at small n. The fact that these two peaks have roughly comparable intensities in the middle of this region causes the line broadening seen in the upper portions of Figs. 1(a) and 1(b). Moreover, in a plot of the average potential energy per Ar atom versus $\log(n)$, observation of a slight change of slope in the region $n=10$–20 provides further evidence of the occurrence of a phase change.

Our association of these two spectral peaks with different phases is confirmed by an examination of the correlation between the frequency shift and aspects of the cluster structure during the Monte Carlo "walk" through configuration space. It appears that the larger red shifts are typically associated with clusters in which the SF_6 is totally surrounded by Ar atoms, while the other peak arises from structures in which the chromophore lies at the surface of the Ar cluster. In the Monte Carlo walk, the system typically retains one or the other of these structures for a considerable number of steps, but hops back and forth from one to the other with only a small fraction of the accessible configurations being associated with intermediate structures. This behavior is strikingly similar to the kind of hopping between the liquid and solid phases seen in molecular dynamics simulations of clusters of pure Ar_{13} at temperatures similar to those considered here.[4]

In previous simulations of pure Ar clusters,[3,4] it was clearly demonstrated that solid and liquid phases coexist simultaneously at the temperatures of interest here. By analogy, it seems reasonable to identify the two phases observed in the present study as liquid and solid. Evidence supporting this conclusion is provided by the nature of the calculated Ar-Ar radial distribution functions which show a more pronounced shell structure in the "surrounded chromophore" phase which predominates at large n. Simulations of the temperature dependence of the spectra and structure of SF_6-Ar_{15} clusters further strengthen this assignment. In particular, the broad peak observed at around $T=50$ K becomes narrower and shifts farther to the red as the temperature is decreased, while it also becomes narrower, but shifts back toward the free SF_6 transition frequency as the temperature is raised. This accords well with the idea that the surrounded-chromophore large-shift phase is solid while the surface-chromophore smaller-shift phase is a liquid.

The good qualitative agreement between experiment and theory seen in Fig. 1 attests to the validity of the instantaneous dipole-induced dipole mechanism used here. The fact that this agreement is not more quantitative should not be surprising. First of all, we must remember that the experimentalists' cluster-size scale [top of Fig. 1(c)] is only a rough estimate, and that their cluster-size distributions are not known and may be rather broad. As a result, the maximum in the curve of observed linewidths versus pressure cannot be assigned to a unique n value, and it is not clear how the broadening due to the experimental cluster-size distribution compares to that due to the phase coexistence. As both mechanisms yield local maxima in the linewidth versus pressure curve, it is difficult to discern which has a dominant effect on the existing data. Moreover, the internal temperature of the clusters in the beam experiments is not accurately known, although it has been estimated to lie in the range 25–50 K.[18]

On the computational side, the uncertainties in the simulations for the larger clusters are fairly high, especially for n values near the phase transition, and so calculations that use significantly more than 100000 configurations will be required to define this behavior more precisely. Moreover, the dipole-induced dipole model used for the calculation of the line shifts is only a first approximation, in that it is only first order, and that it neglects contributions to the frequency shift from the stretching dependence of the potential repulsion and other parts of the interaction potential. The dipole model itself could be improved by our taking into account the screening of the electric dipole field by the atoms close to the molecule, and the delocalization of the induced dipoles due to the finite size of the Ar atoms. The effect of some of these improvements will be examined in future studies of this phenomenon; however, they will not affect the basic conclusions reported here.

In conclusion, the present simulations have shown that the dipole-induced dipole mechanism, together with a Monte Carlo thermal averaging procedure, provide a semiquantitative explanation of the shifting of the ν_3 band of SF_6 in SF_6-Ar_n clusters. These simulations also clearly indicate that a phase coexistence occurs for these clusters and that it has a distinctive spectroscopic signature, namely, a significant broadening of the spectral peak for a relatively narrow range of cluster sizes. However, in spite of the qualitative similarity between the linewidth curves for the experimental and simulated spectra seen in Fig. 1, uncertainty regarding the experimental cluster-size distribution makes it impossible to associate unambiguously the peak in the existing experimental curve with this phenomenon. Moreover, from the present study alone, the question of whether one or the other of these phases is solid or liquid may not be answered rigorously; molecular dynamics studies to resolve this question are now under way.

We would like to thank Dr. M. Mengel, Professor G. Scoles, and Professor T. E. Gough for numerous helpful discussions, and we are pleased to acknowledge the practical advice of Professor S. Goldman and Ms. H. Gordon regarding the performance of Monte Carlo calculations. We are also pleased to thank Professor R. S. Berry for his comments on the manuscript.

---

[1] P. Pawlow, Z. Phys. Chem. **65**, 1 (1909).

[2] Ph. Buffat and J-P. Borel, Phys. Rev. A **13**, 2287 (1976).

[3] R. S. Berry, J. Jellinek, and G. Natanson, Chem. Phys. Lett. **107**, 227 (1984), and Phys. Rev. A **30**, 919 (1984).

[4] J. Jellinek, T. L. Beck, and R. S. Berry, J. Chem. Phys. **84**, 2783 (1986).

[5] A. Stace, Chem. Phys. Lett. **99**, 470 (1983).

[6] J. Jortner, Ber. Bunsen Ges. Phys. Chem. **88**, 188 (1984).

[7] T. E. Gough, D. G. Knight, and G. Scoles, Chem. Phys. Lett. **97**, 155 (1983).

[8] B. L. Swanson and L. H. Jones, J. Chem. Phys. **74**, 3205 (1981).

[9] N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. H. Teller, and E. Teller, J. Chem. Phys. **21**, 1087 (1953).

[10] R. T. Pack, J. J. Valentini, and J. B. Cross, J. Chem. Phys. **77**, 5486 (1982).

[11] J. Geraedts, S. Stolte, and J. Reuss, Z. Phys. A **304**, 167 (1982).

[12] P. N. Schatz and D. F. Hornig, J. Chem. Phys. **21**, 1516 (1953).

[13] K. Fox and W. B. Person, J. Chem. Phys. **64**, 5218 (1976).

[14] R. R. Teachout and R. T. Pack, At. Data **3**, 195 (1971).

[15] K. T. Tang and J. P. Toennies, J. Chem. Phys. **80**, 3726 (1984).

[16] M. Rao, C. Pangali, and B. J. Berne, Mol. Phys. **37**, 1773 (1979).

[17] S. Singh and S. Goldman, J. Comput. Phys. **62**, 464 (1986).

[18] J. Farges, M. F. De Feraudy, B. Raoult, and G. Torchet, J. Chem. Phys. **78**, 5067 (1983).