Melting and the Electronic Absorption of Benzene-Argon Clusters

Laurence E. Fried and Shaul Mukamel
Department of Chemistry, University of Rochester, Rochester, New York 14627

(Received 8 October 1990)

The coexistence of sharp and broad features in the electronic spectrum of a chromophore embedded in a rare-gas cluster has been interpreted as a signature of solid-liquid phase coexistence in the melting transition. We perform molecular-dynamics simulations of benzene-Ar$_N$ clusters which show that the observed spectral features are instead dominated by inhomogeneous broadening due to various cluster configurations.

PACS numbers: 64.60.−i, 33.10.−n, 33.70.−w, 36.40.+d

The nature of phase transitions in molecular and atomic clusters has been a subject of extensive experimental[1-5] and theoretical investigation.[6-11] Berry and co-workers[7-9] have proposed that it is possible for finite clusters to have separate melting and freezing temperatures. Between the melting and freezing temperatures is a coexistence regime, where segments of a trajectory at fixed energy show liquidlike or solidlike behavior. This picture has been confirmed by molecular-dynamics simulations of Ar clusters.[7] Phase coexistence depends on the presence of a potential minimum with low energy relative to other potential minima.[8]

In an important examination of temperature-dependent cluster spectra, Hahn and Whetten[2] have studied size-resolved benzene-Ar$_N$ clusters. They found that spectra with N between 18 and 25 showed both broad (FWHM$\approx$30 cm^{-1}) and sharp (FWHM$\approx$5 cm^{-1}) spectral features. The spectral features did not shift with temperature and the sharp features became dominant as the temperature was decreased. These observations were suggested to support the picture of phase coexistence with the sharp and broad features resulting from solidlike and liquidlike configurations, respectively.

Bösiger, Knochenmuss, and Leutwyler[1] have studied size-resolved carbazole-Ar$_N$ clusters, and found that the spectral shift and width of a cluster correlates well with Monte Carlo calculations of the inverse temperature at which an Ar atom can cross the carbazole plane. Even, Ben-Horin, and Jortner[3] have studied the electronic absorption spectrum of size-resolved dichloroanthracene-Kr$_N$ and dichloroanthracene-Ar$_N$ clusters. They found that the spectrum is sharp at $N=1$, but becomes broad and featureless at $N=11$. They interpret this behavior in terms of a wetting-nonwetting transition. Interestingly, at $N=17$, sharp spectral features once again appear. This change was assigned to a nonrigid 3D to rigid 3D transition.

Interpretations of these experiments assume a direct correlation between the width of spectral features and the amplitude of the underlying nuclear motion. In this Letter we test these interpretations by simulating the absorption spectrum of benzene-Ar$_N$ clusters. Our calculations show that the electronic absorption is dominated by inhomogeneous broadening resulting from multiple-cluster configurations. No clear correlation exists between the width of spectral features and the solid or liquid properties of the underlying nuclear motions; clusters that are solidlike can have both broad and sharp spectral features.

We consider a chromophore embedded in N solvent atoms. The Hamiltonian of the cluster is of the form

$$H=|a\rangle H_a(Q)\langle a|+|b\rangle[\omega_{ba}+H_b(Q)]\langle b|\,,$$

where a and b refer to the ground and excited electronic states of the cluster, respectively. Q is the collection of all nuclear coordinates. ω_{ba} is the absorption frequency of the isolated chromophore. The Hamiltonians H_a and H_b are given by the sum of kinetic energy and potential operators: $H_a=T+V_a(Q)$ and $H_b=T+V_b(Q)$.

Clusters at low temperatures often have many noninterconverting isomers of similar energy. This motivates writing the cluster absorption spectrum as a sum of spectra from each isomer. In practice, we calculate a fixed number of independent samples from the Boltzmann distribution: $I(\omega)=\sum_{\mathrm{samples}\,j}I_j(\omega)$. In the present molecular-dynamics calculation each sample represents an initial position and velocity for each atom. Initial positions were taken from a classical Monte Carlo annealing procedure, while initial velocities were chosen randomly from the thermal distribution. This procedure allows inhomogeneous broadening effects to be treated exactly.

The spectrum of a particular sample was calculated using the semiclassical spectral density formalism,[12] which relates the spectrum to the fluctuations of the energy-gap function $U(Q)\equiv V_b(Q)-V_a(Q)-\langle V_b-V_a\rangle$. The normalized absorption line shape $I_j(\omega)$ is given by

$$I_j(\omega)=\pi^{-1}\mathrm{Re}\int_0^\infty dt\exp[-i(\omega-\omega_{ba}-\langle V_b-V_a\rangle)t-g(t)]\,, \tag{1}$$

where

$$g(t)=\int_0^t dt_1\int_0^{t_1}dt_2J(t_2) \tag{2}$$

and

$$J(t) \equiv \langle U(0) U(t) \rangle = \frac{\mathrm{Tr}[U \exp(iH_a t) U \exp(-iH_a t) \exp(-H_a/kT)]}{\mathrm{Tr}[\exp(-H_a/kT)]} . \tag{3}$$

The average energy gap $\langle V_b - V_a \rangle$ was calculated by a molecular-dynamics calculation. A semiclassical approximation which satisfies the fluctuation-dissipation relation was used to calculate $J(t)$. Introducing $J(\omega) = (1/2\pi) \int dt \exp(-i\omega t) J(t)$, we have

$$J(\omega) = [1 + \tanh(\omega/2kT)] J_C(\omega) , \tag{4}$$

where $J_C(\omega)$ is the classical power spectrum of $U(t)$ calculated along a trajectory. The semiclassical calculation of the absorption line shape is expected to become more accurate as the temperature is increased. In particular, at low temperatures our calculations may underestimate the degree of vibrational structure in the isomer absorption spectra. The portion of the spectrum due to inhomogeneous broadening, however, is expected to be less sensitive to quantum effects.

We took the benzene molecule to be rigid, thus neglecting high-frequency intramolecular vibrations. The ground-state potential consisted of a standard pairwise additive Lennard-Jones carbon-argon and hydrogen-argon parametrization that has been applied to other conjugated chromophore–rare-gas clusters.[13] Similarly, we used an empirical excited-state potential function. Since the first excited state of benzene has only modest charge separation, it was natural to take a Lennard-Jones form (thus neglecting charge-induced dipole interactions). We were able to approximately match the experimental spectral shifts by keeping the excited-state potential the same as the ground-state potential, except for the Ar-H σ and the Ar-C ϵ. The change in the Ar-H σ gives a repulsive contribution to $V_b - V_a$ in the neighborhood of the H atoms, while the Ar-C ϵ gives an attractive contribution in the neighborhood of the C atoms. We found that this balancing of attractive and repulsive interactions was necessary to approximate the experimental pattern of spectral shifts. The excited-state potential parameters used are $\sigma_{\text{Ar-H}} = 3.24$ Å and $\epsilon_{\text{Ar-C}} = 41.9\ \text{cm}^{-1}$, while the ground-state parameters are $\sigma_{\text{Ar-H}} = 3.21$ Å and $\epsilon_{\text{Ar-C}} = 40.4\ \text{cm}^{-1}$.

Initial conditions were generated by a staged classical Monte Carlo annealing procedure beginning at a temperature of 100 K. During the annealing, a confining sphere of radius 15 Å about benzene was imposed. Annealing runs of successively more Monte Carlo cycles were done until the internal energy was unchanged upon doubling the number of cycles. The number of cycles required to achieve equilibration varied greatly with N. 65000 cycles were sufficient to equilibrate $N=1$ clusters at 20 K. To equilibrate the $N=21$ clusters at 2.5 K took 500000 cycles. For each spectrum, 32 independent annealing runs were done. Subspectra corresponding to each run were generated by a 140-ps constant-energy molecular-dynamics simulation. We expect our calculation to be most accurate when isomer interconversion occurs many times over the length of the simulation, or when no interconversion occurs. At temperatures below the melting transition isomers do not interconvert on a 140-ps time scale. Above the melting transition, interconversion occurs frequently.

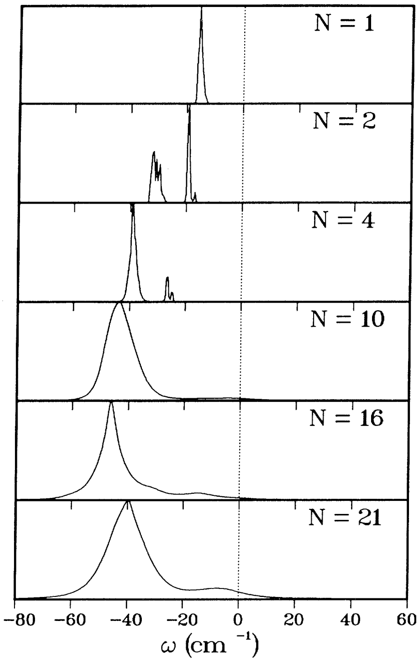

FIG. 1. Absorption spectrum of benzene-Ar$_N$ for various cluster sizes at 20 K. $\omega = 0$ corresponds to the absorption frequency of isolated benzene.

Figure 1 shows the resulting spectra for N values from 1 to 21 at $T = 20$ K. The experimental pattern of shifts is reproduced, with the $N=2$ shift nearly double that of the $N=1$ shift. We find that the structure in the $N=2$ spectrum is due to an inhomogeneous distribution of cluster isomers (some samples have both argon atoms on the same side of the benzene), rather than the previous assignment of van der Waals vibrations.[2] Also note that some spectra, such as $N=16$, appear to have relatively sharp (FWHM < 10 cm^{-1}) features on top of a broad background.

On the left-hand side of Fig. 2 we show the correlation between the Ar-Ar relative rms bond fluctuation

$$\delta \equiv 2 \sum_{i<j} (\langle r_{ij}^2 \rangle - \langle r_{ij} \rangle^2)^{1/2} / N(N-1) \langle r_{ij} \rangle$$

of a trajectory and the FWHM of its associated spectrum. Recall the Lindemann criterion: Solids generally have $\delta < 0.1$. Previous simulations on pure Ar clusters

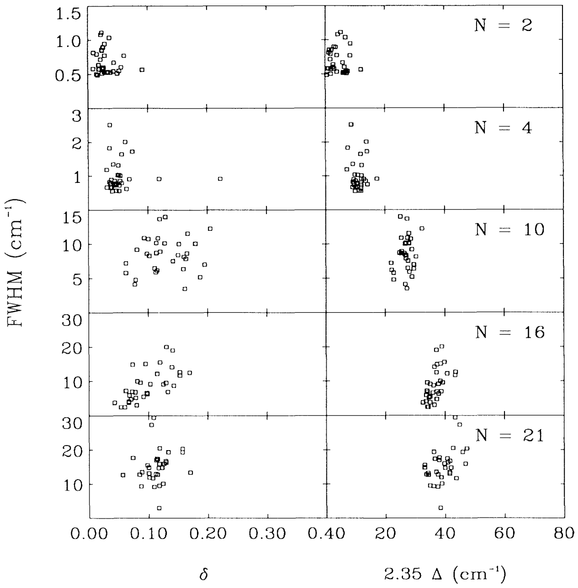

FIG. 2. Left-hand side: Correlation between the FWHM of the subspectra and the Ar-Ar rms bond fluctuation of the associated trajectory. Right-hand side: Correlation between the FWHM of the subspectra and the static approximation for the spectral width.

have borne out its empirical validity.[8] Based on this criterion, we characterize the system as making a transition from a solid at $N=2$ to a coexistence of solid and liquid forms at $N=4$, 10, 16, and 21. We use the term coexistence loosely, however, since there is no clear sign of a bimodal distribution of δ. Previously it was thought that broad spectral features came from fluid clusters, whereas narrow features came from solidlike clusters. This picture would suggest a bimodal distribution of FWHM and δ values, in contrast with the unimodal distributions seen in the present calculation. We also note that the correlation between δ and the FWHM is apparent, but not very strong. Relatively rigid clusters can have quite broad spectra. For instance, the broadest subspectrum for $N=10$ has a near-average value of δ.

The reason for this poor correlation is that the spectrum is not directly sensitive to the amplitude of the ground-state motion. A better indicator of the spectral FWHM is the fluctuation of the energy gap along a trajectory. On the right-hand side of Fig. 2 we show the correlation between $\Delta \equiv \sqrt{J(t=0)}$ and the FWHM of the associated subspectrum. For very slow nuclear motions the absorption spectrum becomes inhomogeneously broadened with FWHM equal to 2.35Δ. Any deviations from this linear relation are due to cluster dynamics. 2.35Δ becomes more nearly equal to the FWHM as N is increased. This is because as spectral features become broader, nuclear motion becomes less relevant and the static solvent approximation becomes more applicable. Nevertheless, the FWHM never becomes close to 2.35Δ. This means that the absorption spectrum consists of an inhomogeneous distribution of homogeneous isomer spectra. Also note that 2.35Δ is always an overestimate of the FWHM. This is an example of motional narrowing.

Next we consider how spectral features change with temperature. In Fig. 3 we show the 32 subspectra, the total spectrum, and the correlation between the FWHM and δ for a cluster with 21 Ar atoms at varying temperatures. At 2.5 K the spectrum consists of two sharp lines. Each sharp line corresponds to a different isomer type; the total spectrum reflects an inhomogeneous distribution of cluster configurations. The δ values are extremely small, and the maximum FWHM of a subspectrum is 5 cm^{-1}.

When the temperature is increased to 10 K, the total spectrum appears to be made up of a relatively sharp feature on top of a broad background. This is highly reminiscent of Hahn and Whetten's experimental results. The magnitude of δ, however, is far below what would be expected for a liquid. *Even solidlike clusters can have spectra that consist of sharp and broad spectral features.* This is consistent with the observations of Bösiger and Leutwyler,[1] who found that carbazole-Ar$_N$ clusters were characterized by small δ values at the estimated experimental temperatures. Note that the apparent broad background at 10 K is caused by an inhomogeneous superposition of narrower subspectra with different shifts. Adams and Stratt[11] have conjectured that the double-peaked absorption spectra may be due to configurations with benzene on the surface of the cluster. We find no such configurations in the thermal ensemble. Instead, we find that the spectrum is due to different isomers with the benzene inside the cluster.

Hahn and Whetten[2] found that when they changed preparation conditions of the clusters (thus changing their temperature by an unmeasured amount), sharp spectral features did not shift. They argue that this is supportive of a phase coexistence model. Spectral features can shift even when the underlying motion is solidlike. We find a substantial spectral shift as the temperature is varied from 2.5 to 30 K. Also, our spectral changes are quite dramatic when compared to the experimental results. This suggests that the experimental changes in temperature are small compared to the temperature changes we consider.

At $T=30$ K, sharp features broaden. The δ values indicate that the motion is liquidlike, and the various subspectra have become more similar than at 10 K. Large-amplitude motions and rearrangements of the Ar atoms are apparent in the trajectories.

Our simulations indicate that the common assumption that broad spectral features come from liquidlike motions does not necessarily hold for rare-gas clusters. Cluster vibrations and inhomogeneous broadening can

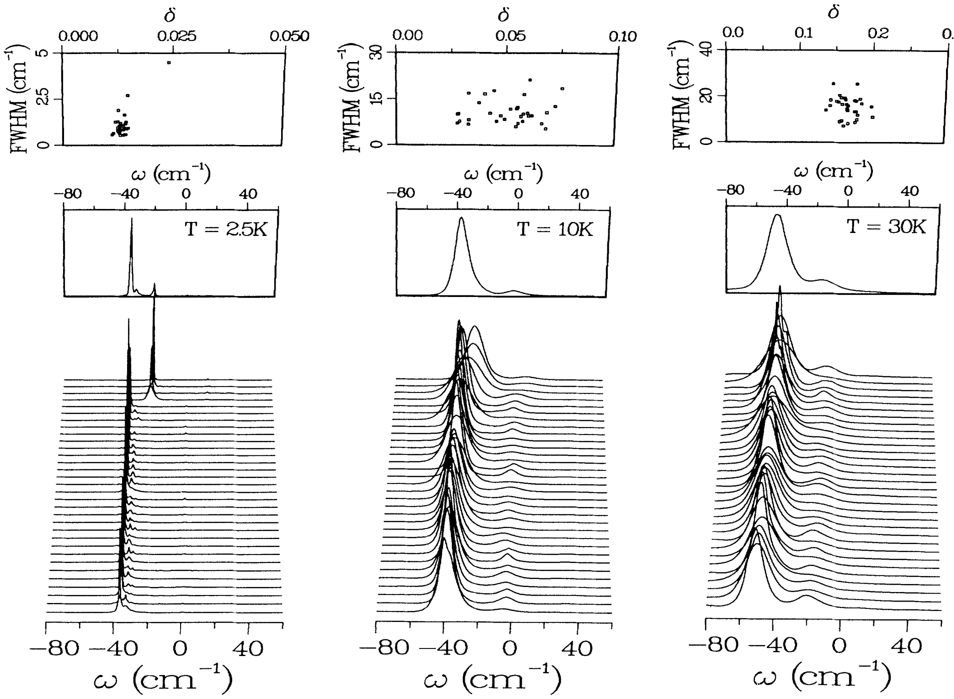

FIG. 3. Spectra at various temperatures for $N=21$. Bottom: 32 calculated subspectra. Middle: Total spectrum, which is the sum of the subspectra. Top: Correlation between the FWHM of a subspectrum and the associated Ar-Ar rms bond fluctuation δ.

cause spectral lines with widths that are consistent with experimental observation. Nonlinear spectroscopies such as hole burning should afford more direct experimental probes of phase transitions (and related properties such as diffusion and isomerization) in clusters, since they allow inhomogeneous broadening to be selectively eliminated. Knochenmuss and Leutwyler[14] have conducted a hole-burning study of carbazole-Ar clusters in which spectral holes had different lifetimes in broad and narrow absorption features. It is also clear that further simulations will be an important guide in the interpretation of cluster spectra. We believe that the computational method presented here will prove to be a powerful tool in the analysis of phase transitions in finite systems and cluster spectra.

The support of the National Science Foundation, the Air Force Office of Scientific Research, and the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. We also thank Cray Research, Inc., for providing a grant of computer time through the NSF Center for Photoinduced Charge Transfer. L.E.F. acknowledges the support of a NSF Postdoctoral Fellowship in Chemistry.

---

[1] J. Bösiger and S. Leutwyler, Phys. Rev. Lett. **59**, 1895 (1987); J. Bösiger, R. Knochenmuss, and S. Leutwyler, Phys. Rev. Lett. **62**, 3058 (1989).

[2] M. Hahn and R. Whetten, Phys. Rev. Lett. **61**, 1190 (1988); M. Hahn, Doctoral Dissertation, University of California at Los Angeles, 1989 (unpublished).

[3] U. Even, N. Ben-Horin, and J. Jortner, Phys. Rev. Lett. **62**, 140 (1989); Chem. Phys. Lett. **156**, 138 (1989).

[4] G. Rajagopal, R. Barnett, A. Nitzan, U. Landman, E. Honea, P. Labastie, M. L. Homer, and R. L. Whetten, Phys. Rev. Lett. **64**, 2933 (1990).

[5] M. Mons, J. Le Calvé, F. Piuzzi, and I. Dimicoli, J. Chem. Phys. **92**, 2155 (1990); M. Schmidt, M. Mons, and J. Le Calvé, Chem. Phys. Lett. **177**, 371 (1991).

[6] F. H. Stillinger and T. A. Weber, J. Chem. Phys. **81**, 5095 (1984).

[7] F. G. Amar and R. Berry, J. Chem. Phys. **85**, 5943 (1986).

[8] J. Jellinek, T. L. Beck, and R. S. Berry, J. Chem. Phys. **84**, 2783 (1986); T. L. Beck and R. S. Berry, J. Chem. Phys. **88**, 3910 (1988).

[9] D. J. Wales and R. S. Berry, J. Chem. Phys. **92**, 4283 (1990).

[10] T. Beck, J. Doll, and D. Freeman, J. Chem. Phys. **90**, 5651 (1989).

[11] J. E. Adams and R. M. Stratt, J. Chem. Phys. **93**, 1358 (1990).

[12] R. Islampour and S. Mukamel, Chem. Phys. Lett. **107**, 2391 (1984); J. Chem. Phys. **80**, 5487 (1984).

[13] M. Ondrechen, Z. Berkovitch-Yell, and J. Jortner, J. Am. Chem. Soc. **103**, 6586 (1981).

[14] R. Knochenmuss and S. Leutwyler, J. Chem. Phys. **92**, 4686 (1990).