Rigid-Fluid Transition in Specific-Size Argon Clusters

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Larger argon atomic clusters undergo a size-specific transition from rigid to fluid forms as the cluster temperature is varied. The observed nature of this phase change, detected by measurement of the spectral line shape of a benzene dopant molecule, favors the phase-coexistence model of the cluster melting transition.

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The fate of the solid-liquid transition in finite material systems has been a subject of sustained interest throughout much of this century.[1] While the lowering of the melting point in particles as small as 25 Å in diameter can evidently be accounted for in terms of Pawlow's thermodynamic argument,[2] the absence of universal scaling relations for the bulk first-order transition has led to a hodgepodge of phenomenological models with uncertain microscopic foundations.[3] Early molecular-dynamics simulations revealed a smoothed transition in the equilibrium properties of clusters of up to 10^3 molecules.[4] But Berry, Jellinek, and Natanson have argued on rather general quantum statistical grounds for *distinct* melting and freezing temperatures separated by a *sharply* bounded coexistence region.[5] Recent simulations of specific-size clusters are said to be consistent with this theory.[6]

A promising means of investigating the rigid-fluid transition is to observe the behavior of molecular spectroscopic line shapes of size-selected (or mass-selected) clusters in a supercooled molecular beam.[7] For such an experiment carried out on a N-molecule cluster, the Berry, Jellinek, and Natanson theory's predictions are as follows: Below a certain temperature $T_f^{(N)}$, all clusters are rigid, and a solid-type line shape and shift are observable. Above a somewhat higher temperature $T_m^{(N)}$, all are fluid, with a corresponding simple line shape and shift. Between these temperatures, some clusters are fluid and some rigid at any one instant. Coexistence implies a superposition of the two line shapes, with the relative abundances of the two forms given by the area under the lines. By the observation of a size series of M_N clusters *at the same temperature,* only a few sizes should be found in the coexistence region, with larger clusters tending to be rigid and smaller tending to be fluid.

While neat (single component) molecular clusters should exhibit the closest correspondence to the systems studied in simulations, exciton effects dominate the sharp spectral transitions of these systems.[8] Instead, one can dope an impurity molecule into an otherwise homogeneous cluster and observe how the spectrally isolated line evolves with size and temperature. In Fig. 1 typical results are presented for the sharp ultraviolet line of some size-resolved Ar_N clusters doped with a single benzene molecule (C_6D_6). These clusters are formed in a pulsed free-jet expansion of a benzene-Ar-He mixture (ratio 1:5000:30000) through a conically diverging nozzle. The jet and cluster temperatures are controlled by variation of the He content at fixed total pressure (8–10 atm). The beam composition is independently determined by a quadrupole mass spectrometer with electron impact ionization; besides He it consists primarily of argon atoms and neat Ar_N clusters, with a small fraction of benzene Ar_N clusters (N to 100). Optical spectra are recorded by resonant two-photon ionization in benzene's ultraviolet spectral region,[9] with a frequency-doubled pulsed dye laser. Cluster ions are separated by a time-of-flight mass spectrometer (acceleration time $\approx 0.2N^{1/2}$ μs) so that optical spectra of many size-selected argon clusters are simultaneously recorded.

As shown in Fig. 1 for one set of preparation conditions, the argon cluster spectra in the narrow region around the dopant resonance are highly sensitive to N, the number of argon atoms in the cluster. For $N<6$

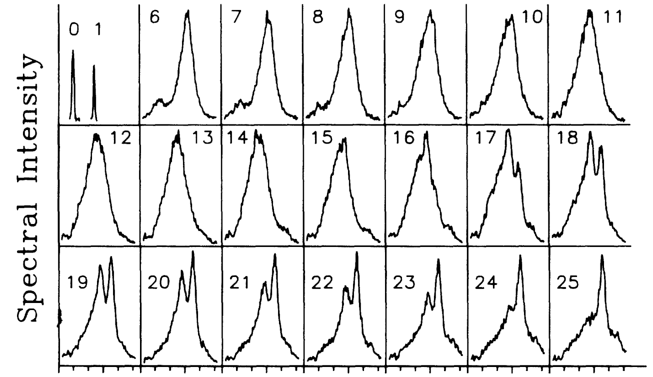

FIG. 1. Optical absorption spectra of benzene-doped argon atomic clusters, $C_6D_6\cdot\mathrm{Ar}_N$, detected by photoionization time-of-flight mass spectrometry, in the region of the 6_0^1 transition of the isolated benzene molecule (indicated at upper left, $N=0$). The clusters are synthesized in a 9-atm, 15:85 Ar-He jet.

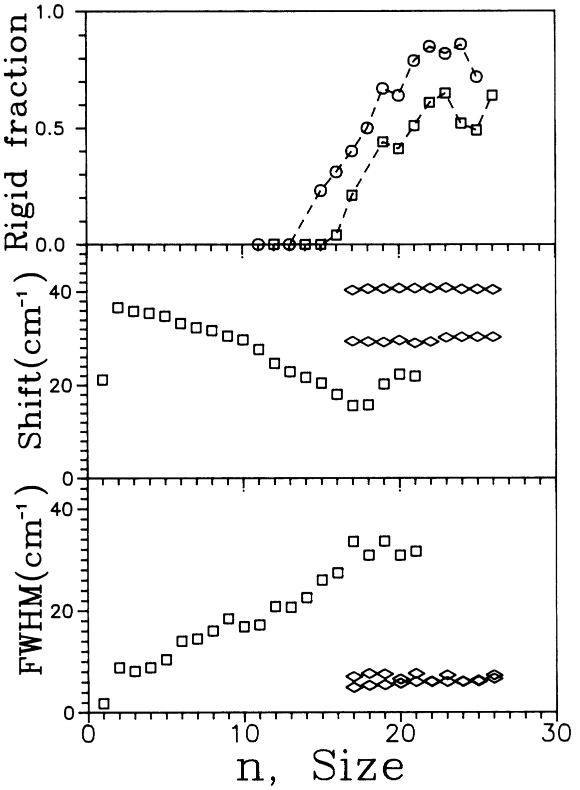

FIG. 2. Properties of argon clusters as a function of size, $N=1-16$. Lower panel: Width (FWHM) of the spectral lines. Squares correspond to the broad (fluid) peak, lozenges to the two sharp (rigid) peaks of Fig. 1. Center panel: Shifts to lower energy of the spectral line-shape maxima from that of isolated benzene. Upper panel: Fraction of the integrated line shape associated with the sharp bands (rigid clusters), for two temperature conditions (circles, neat Ar; squares, 8:92 Ar-He). Beyond $N=21$ only a lower bound is given.

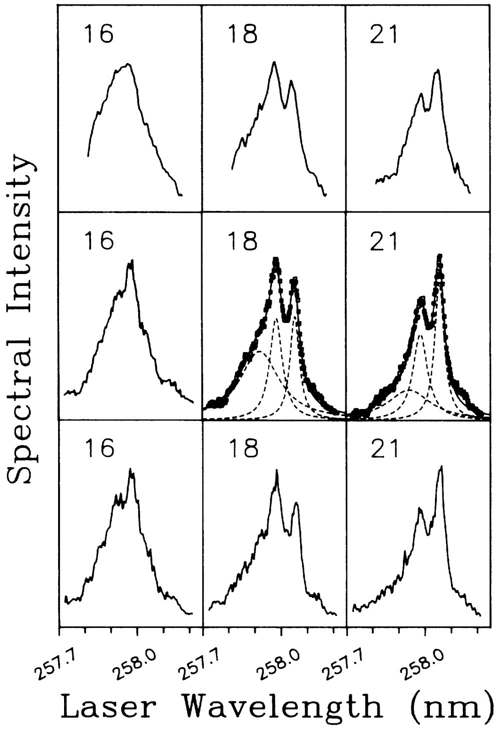

FIG. 3. Effect of temperature on the $N=16$, 18, and 21 cluster spectra. Upper, center, and lower frames are from 100%, 15%, and 8% Ar jets, respectively. Fits to discrete experimental points (center) indicate the procedure of decomposing line shapes into broad and sharp Lorentzian functions. Fine structure in lower frames is reproducible and size specific.

there are highly distinctive patterns indicating that these spectra should be explained in terms of the modes of a quantum few-body system. Depending on cooling conditions, an abrupt change occurs in the $N=15-19$ region, with a sharp doublet ($\simeq 5$ cm^{-1} FWHM), appearing on the broad main band ($\simeq 30$ cm^{-1}). Figure 2 presents the line widths and shifts observed as a function of N. The relative intensity of these peaks continues to increase with N, until the lower-frequency one is dominant. It is proposed that the broad band at small sizes be associated with fluid clusters, the sharp bands at large sizes with rigid clusters, and the region $N=16-22$ with clusters coexisting in the two states.[10] For comparison, the same resonance's width (FWHM) for benzene doped in solid Ar or N_2 at 20 K is 6-11 cm^{-1}, while for benzene in liquid N_2 near the freezing point (75 K) it is 50 cm^{-1}.

Accordingly, a change in the cluster temperature is found to significantly alter the appearance of the spectra in the coexistence region. Figure 3 presents spectra in the $N=16-21$ region for several seed ratios (Ar:He of 0.08-1.0); as this ratio increases one can observe the weakening ("melting") of the sharp spectral features at the expense of the broad ones. Over a wide range of seed ratios, one always finds spectral changes indicative of a transition or coexistence strongly dependent on the cluster's energy content. Actual cluster temperatures could be determined by the relative intensity of dopant vibrational hot bands, but under these conditions they are too weak. Instead, an estimated highest temperature is calculated with the principle that clusters synthesized in a neat expansion (no He) will cool by evaporation. Our equating the time of neutral flight ($\simeq 5\times 10^{-4}$s) and the mean evaporation time [computed by the Rice, Ramberger, and Kassel (RRK) expression[11]] yields a stability condition for each cluster size in terms of its total energy content. The corresponding temperature decreases gradually from 34 to 26 K as N varies from 10 to 30 atoms. These temperatures are in the range of melting and freezing temperatures found in simulations of Ar_N clusters ($N=13-100$); for example, simulated Ar_{19} exhibits coexistence in the 26-37-K range.[6]

The generality of these observations has been verified in a number of ways. The same phase-coexistence region can be observed with laser fluences of 0.2-4 mJ/cm^2 or other benzene spectral lines (e.g., the 1^16^1 level at 900-cm^{-1} higher energy), although ion-fragmentation effects are then found to be greater for the smaller clusters. Exciting through the 6^1 level, as in Figs. 1 and 3, is known[12] to leave the ion predominantly in states of less than 700-cm^{-1} excess energy, and calculations indicate that one or at most two Ar atoms will evaporate during the mass measurement process. However, the highly specific and detailed differences in the spectra for each value of N (see Fig. 3, for example) argue against any role for fragmentation for $N > 10$.

The features described correspond very closely to what one expects of the cluster rigid-fluid transition, based on its recent theoretical description.[5,6] In particular, Fig. 3 illustrates how the line shapes for clusters in the coexistence region decompose into rigid (sharp) and fluid (broad) contributions, with the derived widths and peak shifts reported in Fig. 2. The superimposed line shapes favor the coexistence theory's assertion that a cluster is either rigid for fluid (for periods of time sufficiently long to define spectral quantities), spending negligible time in jumps between the two states. These observations reject the earlier assertion[4] of a *smoothed* or rounded transition which would be signified by a gradually changing (width and shift) single line shape, in clear contrast to Figs. 2 and 3 which show approximately invariant shifts and widths, while only the relative amplitudes change with temperature.

From the spectral decomposition we have derived the fraction of the N clusters that are rigid under various conditions; this quantity is also plotted in Fig. 2 and may be compared to equilibrium constants found in simulations.[6] From this diagram and the temperature estimates, one concludes that for $N < 16$ both T_m and T_f are probably less than 30 K, for $16 < N < 20$ T_m and T_f bracket this temperature, while for $20 < N < 26$, both exceed it. It is of interest to determine whether all larger argon clusters ($N > 27$) are frozen under the same conditions or if $T_m^{(N)}$ and $T_f^{(N)}$ have an oscillating or fluctuation behavior as a function of N. Our preliminary results indicate the latter, with clusters in the $N = 28$–30 region again completely melted (broad lines) and the $N > 30$ peak again sharp but further shifted to the red. Such an observation is consistent with structural shell packing, while the evolution of the sharp peak shift is necessary if the benzene$\cdot$Ar$_N$ excitation is to converge (as $N \rightarrow \infty$) to the known spectral shift ($-112\ \mathrm{cm}^{-1}$) of the bulk solid system.[10]

Despite these correspondences, several potential problems remain, including those associated with the inherent inhomogeneity of a dopant-solvent cluster. For example, the spectral observations could be accounted for by the proposition that the cluster expels benzene to its surface at a sufficiently large size, giving rise to the narrower line observed. However, the greater shift (relative to vacuum) observed for the sharp lines contradicts this (Fig. 2). Simulations with realistic model potentials could be used to examine such arguments, but quantum-dynamical simulations of the spectral changes accompanying the transition are also desirable.[13] Another difficulty arises because clusters in the laser interaction region are under collision-free conditions, and hence exist in a range of fixed-energy states. One might argue that the sharp lines correspond to a few very cold clusters, or that the cluster temperature is more strongly size dependent than indicated above. But then the observed transition would be sharper still were one to observe monoenergetic clusters.

Earlier experimental evidence for cluster phase transitions includes electron diffraction patterns from jet experiments that had been interpreted in terms of crystalline and fluid or amorphous behavior.[14] Stace[15] invoked a size-dependent melting transition to account for sudden change in branching ratio for an intracluster chemical reaction. Eichenauer and LeRoy[16] explained an earlier experiment[17] on SF$_6$-Ar$_N$ vibrational line shapes in terms of such a transition. The much larger magnitude of electronic solvent shifts and the line shape and linewidth changes (associated with phase transformations) should be noted. In all these experiments the cluster size was not directly determined. Recently, Bösiger and Leutwyler demonstrated that abrupt changes in the electronic absorption line shape of carbazole, a large planar molecule, solvated by up to eight argon atoms, are caused by surface melting of the argon atoms.[18] It is possible that this transition is the two-dimensional analog of the one described here.

In conclusion, spectroscopic experiments on size-selected argon atomic clusters doped with a single molecule have revealed a size-dependent rigid-fluid transition. The observation of phase coexistence offers particularly striking support for the quantum statistical theory of cluster melting. It additionally demonstrates that experiments on atomic and molecular clusters should include a determination of the phase under the actual experimental conditions used. We are extending these observations to a number of related systems, which will be the subject of later reports.

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