

New insight into experimental probes of cluster melting

John E. Adams and Richard M. Strat

Citation: *The Journal of Chemical Physics* **93**, 1358 (1990); doi: 10.1063/1.459146

View online: <http://dx.doi.org/10.1063/1.459146>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/93/2?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

Communication: New insight into electronic shells of metal clusters: Analogues of simple molecules
J. Chem. Phys. **138**, 141101 (2013); 10.1063/1.4801860

NEW EXPERIMENTAL CAPABILITIES AND THEORETICAL INSIGHTS OF HIGH PRESSURE COMPRESSION WAVES

AIP Conf. Proc. **955**, 1186 (2007); 10.1063/1.2832932

New insight in halo fragmentation

AIP Conf. Proc. **455**, 294 (1998); 10.1063/1.57222

New experimental setup for photoelectron spectroscopy on cluster anions

Rev. Sci. Instrum. **63**, 5661 (1992); 10.1063/1.1143397

Small clusters and fullerenes: New insights from abinitio molecular dynamics

AIP Conf. Proc. **258**, 190 (1992); 10.1063/1.42524



New insight into experimental probes of cluster melting

John E. Adams^{a)}

Department of Chemistry, University of Missouri-Columbia, Columbia, Missouri 65211

Richard M. Stratt

Department of Chemistry, Brown University, Providence, Rhode Island 02912

(Received 26 January 1990; accepted 22 March 1990)

Experiments are now appearing which attempt to probe melting in small clusters, a notable example of these being the recent studies of benzene-Ar_n clusters by Hahn and Whetten [Phys. Rev. Lett. **61**, 1190 (1988)]. We report a study of the dynamics of these same benzene-Ar_n clusters which seeks to clarify further the nature of "phase transitions" in small systems. The techniques used here, involving an instantaneous normal mode analysis based on the results of Monte Carlo calculations, have been shown previously to yield a picture of argon cluster melting which is more complete than the one which emerges from a mere enumeration of low-energy structures. Although the bare argon clusters are found to undergo dynamical transitions as the cluster temperature is increased, these transitions are inhibited by the presence of an embedded benzene molecule, which provides a template for ordering of the argon atoms. The calculations also suggest a possible explanation for the doubly peaked spectra observed in the experiments of Hahn and Whetten: the benzene may be found in two general types of bonding environments, either surrounded by or on surface of the Ar_n cluster. This occurrence is consistent with the finding of Bösiger, Knochenmuss, and Leutwyler [Phys. Rev. Lett. **62**, 3058 (1989)] that the solute-solvent interaction in clusters can be either wetting or nonwetting. We discuss how the evidence necessary to resolve such issues can be derived from an analysis of cluster dynamics.

I. INTRODUCTION

One of the primary motivations for the study of small clusters is the desire to bridge the conceptual gap separating the common descriptions of single molecules, or few-molecule systems, and bulk materials.¹⁻⁴ It is well known, for instance, that the fundamental macroscopic notions of melting and freezing are without a rigorous mathematical foundation in systems which are finite,⁵ and that even a definition of what constitutes a discrete thermodynamic phase in a microscopic system is lacking. Nonetheless, previous theoretical work in this area has produced a clear prediction that some sort of transition occurs between solidlike and liquidlike behavior in small clusters as the temperature (or energy) of the clusters is increased.^{4,6-9} While the characterization of this dynamical transition also has been the subject of experimental investigations,¹⁰⁻¹² the detection of an unambiguous signature of cluster melting has proved to date elusive. Perhaps much of the difficulty lies in the fact that most experimentalists really are not used to looking at intermediate-sized systems such as clusters. For example, conventional spectroscopic techniques are applied routinely only to two limiting types of systems, either those consisting of a very few atoms or those comprising on the order of 10²³ atoms. In the former case, the characteristic results are a series of individual narrow lines arising from discrete state-to-state energy transitions of a system which exists in a single (or at most a few) well-defined geometric configuration(s). From the positions of these lines, one then can extract a variety of

structural and bonding parameters (bond lengths and angles, force constants, and such), all of which are tied to a particular equilibrium arrangement of the atoms. Investigations of bulk systems, however, differ with respect to the degree of detail which may be obtained, since the interactions among the species necessarily lead to line broadening, either as a consequence of the distribution of local chemical environments (inhomogeneous broadening), or of the fluctuations of those environments on a time scale which is faster than or comparable with the fluctuations of the degree of freedom being probed (dephasing). An understanding of these macroscopic systems must derive from what is fundamentally an ensemble picture of the material, in which the dynamics of an individual atom or molecule is properly viewed as being perturbed via coupling to a bath that in some complicated manner reflects the motion of the other species in the system.

Clusters clearly represent an intermediate case for consideration, one which may or may not involve a reference to a small set of discrete structures.¹³ Furthermore, whether or not this referencing is even a useful concept may well depend on the temperature of the system, such that only at the very lowest temperatures is the cluster's structure confined to a region of small displacements about a minimum on the potential energy hypersurface. In general, one should expect to observe here a range of spectral line shapes, some of which are narrow and others broad, depending on the dynamics of the individual atoms or molecules within the cluster; even when the cluster is locked at low temperatures into a minimum-energy geometry, there will still be effects observed which are due to the inherent inhomogeneity of the chemical environment of the cluster. The fundamental property

^{a)} Current address (until July 1990): Department of Chemistry, Brown University, Providence, Rhode Island, 02912.

which distinguishes a cluster in the first place is a high dispersion, i.e., a large fraction of the constituent atoms are found in surface rather than interior binding sites.¹⁴ Just one example of such a species is the low-temperature Ar_{19} cluster, the structure of which is polyicosahedral (and about which more will be said below), where only two of the argon atoms are found in bulklike chemical environments. Systems such as these may in fact be better described in terms of phenomena normally associated with surfaces, such as surface diffusion, wetting, or even reconstruction, than simply in terms of bulk concepts such as melting or freezing. One therefore is struck immediately by the question of what is one looking at when one attempts to analyze cluster spectra. Certainly theory has an important role to play here in helping to understand the nature of the spectral results obtained for these novel systems.

In a recent paper,⁹ we presented a model for the melting transition in small argon clusters based on an analysis which is not tied intimately to either a microscopic or macroscopic point of view. The basis for this approach is a concentration not on an enumeration of low-energy structures, which has been the principal strategy employed in the prior studies of others,^{7,8} but rather on a description of the dynamics of the clusters as manifested in their distributions of vibrational frequencies. Note that the use of a dynamical instead of an equilibrium analysis neatly avoids the difficulties inherent in trying to extend the concept of sharp transitions between phases to systems containing only a few particles, since for these systems sharp dynamical (but not equilibrium) transitions are perfectly well defined. The vibrational frequency spectrum determined here refers to the set of instantaneous normal modes of the system, which may be defined without requiring that the system even be near one of its equilibrium geometries, and thus is valid in both a solidlike and a liquidlike dynamical regime.^{15,16} In addition, the methodology is applicable irrespective of the underlying statistical properties of the system and so can be implemented in both isothermal and isoergic situations. From this previous investigation,⁹ a picture of the transition has emerged comprising a series of isomerizations which preserve the short-range structures of the clusters, with the structures linked via these isomerizations sometimes being far from one of the local minima on the potential energy hypersurface. No evidence was found for the occurrence of jumps between exclusively rigid or fluid configurations characteristic of the "coexistence" behavior suggested by the calculations of Berry and co-workers.⁸ We also have warned against the potential for overlooking very valuable insight into cluster dynamics when pursuing a molecular dynamics (MD) study that relies solely on a periodic quenching of trajectories in order to probe cluster structures.

On the whole, the complementary experimental investigations have yielded only indirect evidence of cluster dynamical transitions. One unambiguous signature of such a transition would be temperature-dependent changes in the structure factor of the clusters as determined by electron diffraction,¹⁰ but to date experiments of this type have not yielded a conclusive result. Photoabsorption and photofragmentation studies of Ar_n^+ clusters have revealed a signifi-

cant increase in the photoabsorption cross section over a relatively narrow range of cluster sizes ($n = 15\text{--}20$),¹² but the authors of that work have not pursued the question of what this change signifies in terms of the detailed cluster dynamics. Other experimental approaches have involved doped rare gas clusters formed in seeded free-jet expansions, with the spectral perturbations of the dopant molecule resulting from van der Waals interactions with the rare gas atoms^{17,18} providing the clue to the clusters' structural changes. One of the most extensive bodies of work of this type is that of Bösiger and Leutwyler concerning mass-selected carbazole- Ar_n clusters.¹⁹⁻²¹ They have characterized the behavior of these clusters in terms of wetting and nonwetting structures,²⁰ the wetting clusters consisting of extended argon monolayers binding to both sides of the carbazole molecule, and the nonwetting clusters consisting of either an argon monolayer or a multilayer structure adsorbed on only one side of the carbazole. Their studies also attest to the benefit gained from a confluence of theory and experiment. Transitions among these various structural types as well as general features of surface melting have been identified on the basis of Monte Carlo (MC) calculations as providing the sources of the observed $S_1 - S_0$ electronic spectral peak widths and shifts. It is important to note though that the wetting-nonwetting transitions described by Bösiger and Leutwyler refer to alterations in the structure of the argon "solvent" relative to the carbazole "solute" and not to internal reorganization of the solvent atoms. Similar results have been suggested by MC and MD calculations carried out by LeRoy and co-workers on $\text{SF}_6\text{--Ar}_n$ clusters.²²

Of the experimental studies of cluster melting, surely one of the more interesting is the recent work of Hahn and Whetten,²³ who have used a measurement of the optical absorption line shape of a benzene dopant molecule in order to detect the rigid-fluid argon cluster transition. They have observed a splitting of the spectral line obtained from a resonant two-photon ionization of benzene in the region of 258 nm for a variety of argon cluster sizes in the range $n = 16\text{--}22$, with the sharper of the two resulting lines being attributed to benzene molecules which are found in rigid (solidlike) clusters and the broader one to benzene molecules which are found in fluid (liquidlike) environments. That these two binding environments are both detected under the conditions of the experiment is cited as direct evidence for the validity of the phase coexistence model proposed by Berry and co-workers.⁸ (For n values outside the range 16-22, only single peaks were observed. This result was assumed to imply the existence of only a single type of cluster geometry.) In an experiment such as this, in which the clusters are produced in a seeded free-jet expansion, it is very difficult to determine the internal temperature of the resulting clusters (assuming, of course, that it is even valid to assign a temperature in this case), and so it was hoped that the cluster size dependence of the results would yield the same sort of information that would be obtained if the temperature of a single, well-defined cluster were adjusted. (It is known from theoretical studies that the temperature at which the onset of melting in these small clusters occurs increases with an in-

crease in the number of cluster atoms.⁶⁻⁸)

Since the rigid-fluid cluster coexistence model seemingly confirmed by these experiments stands in contrast to the findings of our earlier work,⁹ we have decided to extend our analysis methods to the benzene-Ar_n system in order to determine whether or not we can develop a model which illuminates the experimental findings of Hahn and Whetten.²³ In addition, we are interested in understanding how the dynamics of the doped cluster differs, if it in fact does differ, from that of the neat cluster. Our focus here is, for the most part, on the benzene-Ar₁₉ cluster, inasmuch as it is one of those which displays the split ultraviolet spectral line shape, and its undoped analog Ar₁₉. In a theoretical study, we naturally are able to impose the temperature control which is so difficult to achieve experimentally and thus our calculations are reported for a range of temperatures for the single cluster rather than for a wide range of cluster sizes.

II. THEORETICAL BACKGROUND

A. Review of instantaneous normal modes

While for a rigid molecule a conventional normal mode analysis provides the apposite means for describing internal vibrations, a nonrigid system is more appropriately described in terms of its instantaneous normal modes. The formal details of the instantaneous normal mode method already are given in several places in the literature,^{9,15,16,24} and so we have opted to provide here only a précis of the technique. For an arbitrary system of N particles at a given instant of time, one characterizes the system by a $3N$ -dimensional coordinate vector \mathbf{R}_0 about which the potential may be expanded

$$V(\mathbf{R}) = V(\mathbf{R}_0) - \mathbf{F}(\mathbf{R}_0) \cdot (\mathbf{R} - \mathbf{R}_0) + \frac{1}{2}(\mathbf{R} - \mathbf{R}_0) \cdot \mathbf{d}(\mathbf{R}_0) \cdot (\mathbf{R} - \mathbf{R}_0), \quad (2.1)$$

where $\mathbf{F}(\mathbf{R}_0)$ is a $3N$ -dimensional vector representing the forces acting on the particles at $\mathbf{R} = \mathbf{R}_0$, and $\mathbf{d}(\mathbf{R}_0)$ is the Hessian matrix defined by

$$d_{j\mu, kv}(\mathbf{R}_0) = \left. \frac{\partial^2 V}{\partial r_{j\mu} \partial r_{kv}} \right|_{\mathbf{R} = \mathbf{R}_0},$$

where $r_{j\mu}$ ($j = 1, \dots, N; \mu = x, y, z$) is one of the atomic Cartesian coordinates (i.e., one of the components of \mathbf{R}). If \mathbf{R}_0 is a local minimum on the potential energy hypersurface [and hence $\mathbf{F}(\mathbf{R}_0)$ is identically zero], then the above expansion provides, of course, the usual way of defining the normal modes of the system; but in the case of an arbitrary \mathbf{R}_0 , the force vector in general will be nonvanishing. The potential expansion [Eq. (2.1)] nonetheless will converge if the magnitude of the vector $\mathbf{R} - \mathbf{R}_0$ is sufficiently small, i.e., if at time t the system is displaced only a small distance away from its configuration \mathbf{R}_0 at time $t = 0$. Conceptually, this convergence criterion signifies that we can obtain information about the exact short-time dynamics of our system from the instantaneous normal mode eigenvalues and eigenvectors that derive from a diagonalization of $\mathbf{d}(\mathbf{R}_0)$. (In our previous study of argon cluster dynamics, we ascertained a value for this time over which the above analysis should be valid of roughly 0.5 ps.)

Unlike the situation one finds in a conventional normal

mode analysis performed at a potential minimum,²⁵ some of the instantaneous normal mode frequencies may be imaginary if the system's configuration is near a potential barrier or saddle point, and thus these calculations suggest the extent to which the motion of the atoms is diffusive or fluidlike.²⁶ One may even use the frequency spectrum calculated here in order to extract estimates of the cluster atom self-diffusion constant via a short-time fit to an assumed form for the velocity autocorrelation function. The specific expression for D implemented in our earlier work⁹ is

$$D = (k_B T / m) \pi [2(c - 1)A_2]^{-1/2} \times \text{sech}\{(\pi/2)[(5 - c)/(c - 1)]^{1/2}\}, \quad (2.2)$$

where $c \equiv 6A_4/A_2^2$, and the quantities A_2 and A_4 are coefficients in a Taylor series expansion of the normalized autocorrelation function

$$A_2 = \frac{1}{2!}(3N)^{-1} \left\langle \sum_{\alpha=1}^{n_{\text{real}}} \omega_{\alpha}^2 - \sum_{\gamma=1}^{n_{\text{imag}}} \Omega_{\gamma}^2 \right\rangle, \\ A_4 = \frac{1}{4!}(3N)^{-1} \left\langle \sum_{\alpha=1}^{n_{\text{real}}} \omega_{\alpha}^4 + \sum_{\gamma=1}^{n_{\text{imag}}} \Omega_{\gamma}^4 \right\rangle,$$

the summations here being over the real and imaginary frequencies obtained for a given atomic configuration and the averaging being over an ensemble of configurations. (For convenience, the imaginary frequencies are written in terms of their magnitudes, $\Omega_{\gamma}^2 \equiv -\omega_{\gamma}^2$). While an estimation of D based on short-time dynamics is expected to be less satisfactory in the solidlike dynamical regime, characterized by long-time coherences, it nonetheless does predict the appearance of the discontinuity in the temperature dependence of D which signals the onset of liquidlike behavior.²⁶

Finally we note the expression for the Einstein frequency of the system

$$\omega_E = \left[(3N)^{-1} \left\langle \sum_{\alpha=1}^{n_{\text{real}}} \omega_{\alpha}^2 - \sum_{\gamma=1}^{n_{\text{imag}}} \Omega_{\gamma}^2 \right\rangle \right]^{1/2} = (2A_2)^{1/2}.$$

This particular quantity we have found in the past to be a useful probe of the dynamical transition in clusters, a result which is not surprising since $m\omega_E^2$ is just the average force constant for the system¹⁵ and thus reflects its overall "floppiness."

B. Computational method

For the most part, the methodology used in this study of Ar₁₉ and benzene-Ar₁₉ mirrors that employed previously, namely, that representative cluster configurations are generated at an assumed system temperature via a standard Metropolis Monte Carlo random walk.²⁷ (Only isothermal systems are considered in the present work.) These configurations ($\{\mathbf{R}_0\}$) are then the points about which the harmonic expansion of the potential is made as described above and at which the Hessian matrix is constructed and diagonalized. All the potential functions used here are pairwise-additive atom-atom potentials of the Lennard-Jones 6-12 type

$$V = \sum_{i>j} u(r_{ij}), \\ u(r_{ij}) = 4\epsilon [(\sigma/r_{ij})^{12} - (\sigma/r_{ij})^6].$$

The argon–argon potential parameters are the conventional ones given by Rahman²⁸ ($\epsilon = 1.67 \times 10^{-14}$ erg = 121 K, $\sigma = 3.4$ Å), while the argon–carbon and argon–hydrogen parameters are those suggested by Ondrechen, Berkovitch-Yellin, and Jortner,²⁹

$$\epsilon_{\text{Ar-C}} = 40.4 \text{ cm}^{-1} = 58.1 \text{ K}, \quad \sigma_{\text{Ar-C}} = 3.42 \text{ Å},$$

$$\epsilon_{\text{Ar-H}} = 45.0 \text{ cm}^{-1} = 64.7 \text{ K}, \quad \sigma_{\text{Ar-H}} = 3.21 \text{ Å}.$$

This is by far the most commonly used parametrization of an argon–aromatic molecule potential, primarily because it is known to give very good predictions for both the structures and the energetics of small van der Waals complexes formed between argon and various aromatic molecules.³⁰ We are obliged to caution, however, that these particular parameters, developed for complexes containing larger aromatic molecules and far fewer argon atoms than we are considering here, may provide a less satisfactory description of the bonding when the argon atoms lie on the periphery of the benzene ring. It is perhaps with this thought in mind that the most recent calculations of Leutwyler and co-workers^{19,20} have been carried out using a value for the Ar–H well depth which is only two-thirds of the one proposed by the Jortner group. (Somewhat different values of the other parameters are used as well.) We mention this fact in particular inasmuch as the relative magnitude of this interaction as compared with the values for Ar–C and Ar–Ar is explicitly cited by Bösiger, Knochenmuss, and Leutwyler²⁰ as being instrumental in producing the size-dependent transition between monolayer adsorption of argon to one face of the carbazole molecule and either monolayer adsorption on both faces or multilayer adsorption on a single face. In the present case, though, in which we are dealing with the interactions of roughly twice as many argon atoms with the far smaller benzene molecule, we do not feel that the results of the calculations are likely to be as sensitive as theirs might be to the exact value adopted for $\epsilon_{\text{Ar-H}}$.

Our particular interest in this work lies in the characterization of the dynamical effects on the argon cluster induced by the presence of the benzene molecule and not in a modeling per se of the benzene dynamics. Consequently, we have chosen to hold fixed the position, orientation, and geometry of the aromatic molecule throughout the MC calculations, with the C–C and C–H bond lengths taken to be 1.40 and 1.08 Å, respectively. Note that this complete neglect of the benzene motion means that the center-of-mass of our benzene–Ar_n system will be neither fixed nor freely translating and so this motion will be manifested as three small, but nonzero eigenfrequencies of the Hessian matrix. As in our previous isothermal simulations, we again have made no effort to project out the rotational motion of the clusters.

III. Ar₁₉ CLUSTERS

If we are to understand the effect on argon cluster dynamics arising from the introduction of a benzene molecule, it is crucial that we have a good grasp of the dynamics of the neat clusters. Instantaneous normal mode spectra calculated in the manner described in Sec. II from the results of 200 representative cluster configurations at each temperature are presented in Fig. 1. (As in our previous study,⁹ a thor-

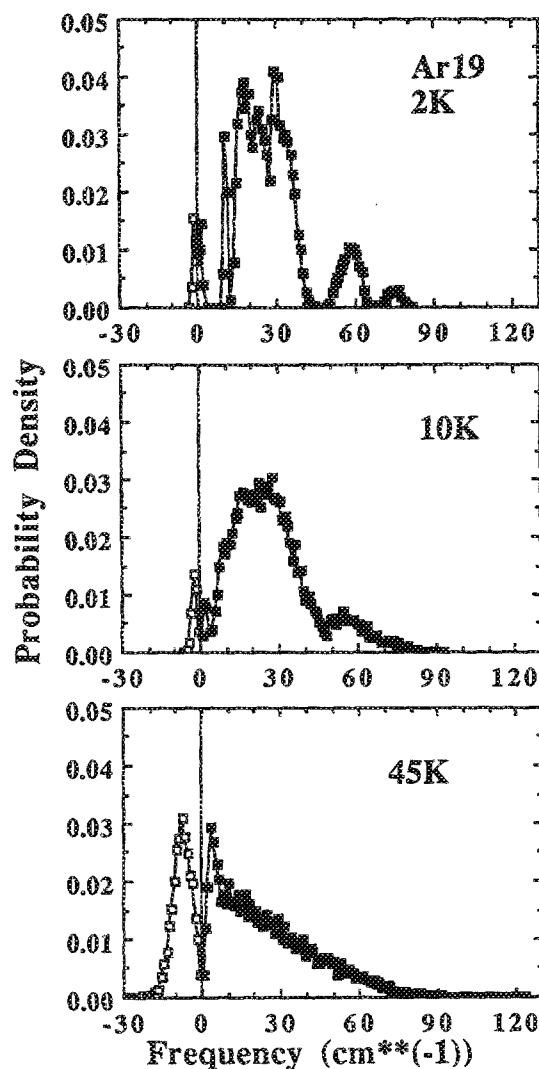


FIG. 1. Normalized frequency distributions calculated at three different temperatures for Ar₁₉. Imaginary frequencies are plotted on the negative frequency axis.

ough equilibration of the clusters is essential prior to the generation of these configurations. Throughout the work described here, on the order of 1×10^5 – 2×10^5 MC steps were required for this initial equilibration, with the representative configurations being obtained thereafter at intervals of 5×10^3 – 1×10^4 steps.) The most striking differences seen in these spectra are the overall loss of the discrete peak structure and the increase in the area of the imaginary-frequency peak which accompanies the increase in the equilibrium system temperature. Changes of this sort are quite consistent with our earlier model of the dynamical transitions in small argon clusters (similar trends were observed in the spectra of Ar₇ and Ar₁₃)⁹ consisting of a series of isomerizations which become possible as a consequence of the temperature-dependent softening of the vibrational modes. In order to make clearer the correlation of changes in the vibrational spectrum with alterations of the cluster's structure, we give in Figs. 2 and 3 representative depictions of the Ar₁₉ clusters in the low- and high-temperature dynamical limits. At very low temperatures (the structure in Fig. 2 was obtained from

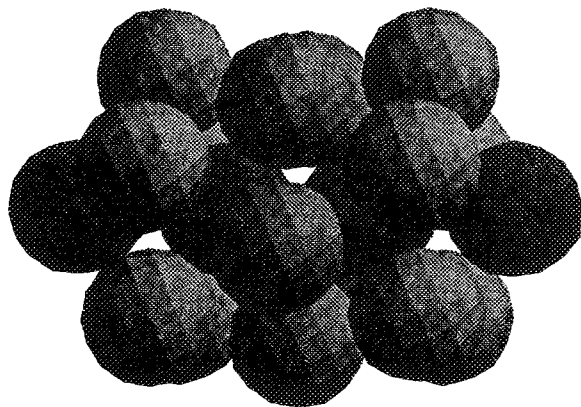


FIG. 2. A representative Ar_{19} cluster at 2 K. The fivefold symmetry axis lies horizontally in this drawing. In all the cluster drawings, the sphere sizes are based on standard van der Waals radius values.

a MC calculation at 2 K), we find that as expected the cluster geometry is that of a polyicosahedron (D_{5h} symmetry) consisting of three staggered five-membered rings separated by argon atoms which form part of the central linear core. These two argon atoms lying between the rings clearly can be seen to be the only atoms of the cluster which are located in binding sites roughly equivalent to those found in an argon crystal. When the temperature is increased through the region of the melting transition, the overall symmetry of the cluster is lost and an amorphous structure is obtained (Fig. 3, corresponding to 40 K, which is just below the highest temperature achievable without serious evaporation problems being encountered). We should mention, however, that even in the high-temperature regime, some clusters display local structure not unlike that which is observed at lower temperatures. These configurations tend to look as if they are intermediate between the structures depicted here, with one end of the cluster displaying the local fivefold symmetry (although somewhat distorted) and the other exhibiting no recognizable symmetry features.

Some progress also may be made in correlating discrete spectral features observed at the lowest temperatures with

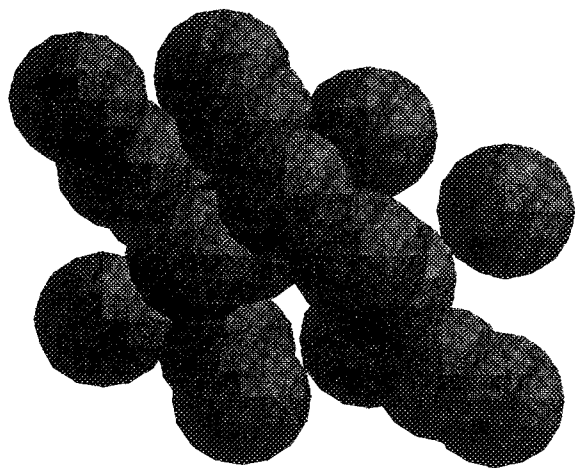


FIG. 3. A representative Ar_{19} cluster at 40 K.

particular atomic vibrational motions through an examination of the instantaneous normal mode eigenvectors. As one might anticipate for a system of 19 atoms at low temperatures, the majority of the eigenvectors describe highly delocalized motions, but the distinctive high-frequency peaks seen, e.g., in the 2 K spectrum appearing in Fig. 1, derive principally from the motions of the two argon atoms found in a bulklike environment. The highest-frequency motion, at roughly 75 cm^{-1} , can be traced to a symmetric stretching mode. (Selected representative instantaneous normal mode displacements are sketched in Fig. 4.) Unfortunately, this mode is not expected to be infrared active since it is of A_1' symmetry, but in principle it should be possible to observe the fundamental in an appropriate Raman experiment. Vibrations having frequencies that contribute to the second peak, which lies in the vicinity of 60 cm^{-1} , involve somewhat more participation of the atoms lying on the surface of the cluster, but again the two interior argon atoms are the ones that are displaced most, this time with a sizable component which is perpendicular to the fivefold symmetry axis. Although the analysis of the motion is more complex here due to the mixing of several nearly degenerate modes, the overall picture of the dynamics is still fairly clear. For example, the second mode diagrammed in Fig. 4 essentially consists of a planar vibration reminiscent of the bending mode of a nonlinear triatomic molecule. This vibration, which is of E_1' symmetry, would be expected to contribute to an infrared, but not a Raman spectrum, in contrast to the expectations for the highest-frequency vibration.³¹

In our previous work,⁹ we identified a number of quantities which are particularly useful in identifying a dynamical transition in small clusters. These temperature-dependent quantities have been calculated for the present 19-atom cluster and they reveal here that some sort of transition definitely occurs. The configurationally averaged values of the cluster potential energy, the percentage of the vibrational mode fre-

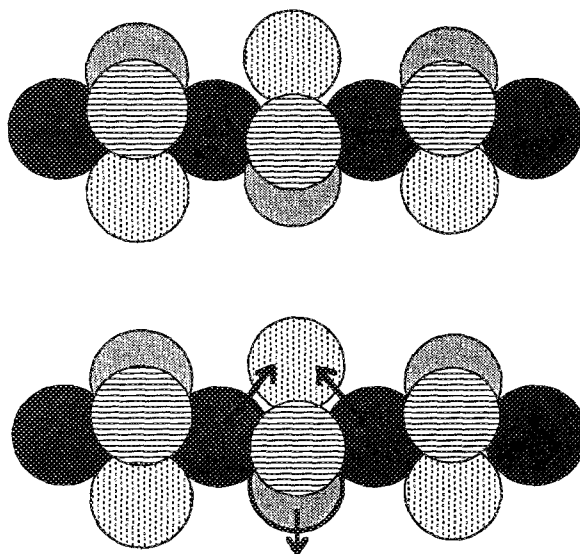


FIG. 4. A schematic of the two highest-frequency normal mode vibrations of Ar_{19} at 2 K. For clarity, the cluster has been elongated along the fivefold axis; the displacement arrows are meant to indicate direction only and thus are not drawn to scale.

quencies which are imaginary, and the Einstein frequency are plotted vs the equilibrium system temperature in Fig. 5, determined in each case using a total of 200 MC configurations. The signature of a transition clearly is seen in the discontinuity in the slopes of the curves which appears in the temperature range 32.5–35.0 K. As expected these slope changes occur at a higher temperature than one observes for the smaller clusters, e.g., the range observed for the onset of these transitions in the Ar_{13} clusters⁹ is 27.5–30 K. Also of interest is the change observed in the self-diffusion constant calculated via Eq. (2.2), the results of those calculations being displayed in Fig. 6. Again we find a discontinuity in the slope of the curve as the temperature is increased beyond about 32.5 K, the point at which the diffusion constant exceeds a value of $\approx 1 \times 10^5 \text{ cm}^2 \text{ s}^{-1}$; this result agrees very well with the behavior observed for the smaller argon clusters.⁹ Taken *in toto*, the four quantities mentioned here attest unmistakably to a transition that connects highly symmetric structures such as the one depicted in Fig. 2 with structures like the one in Fig. 3 having partial or complete loss of local

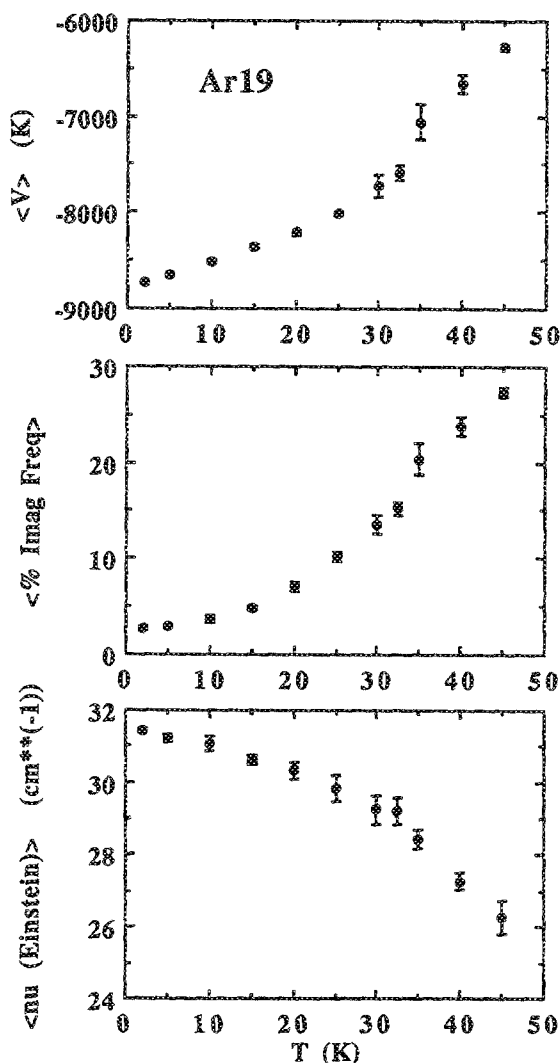


FIG. 5. The temperature dependence of various averaged properties of Ar_{19} clusters. The error bars indicate one standard deviation in the Monte Carlo calculation of the averages (Ref. 9).

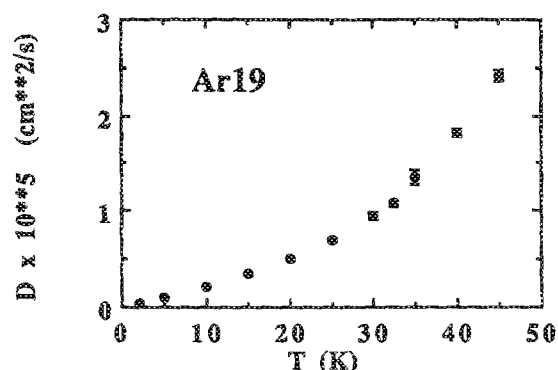


FIG. 6. Temperature dependence of the argon self-diffusion constant in Ar_{19} .

symmetry. Although this transition involves a gradual softening of the cluster's vibrational modes and a progressively greater probability that the cluster will be found with a geometry which is well removed from any of the underlying lowest-energy structures, the plots reveal the existence of a fairly narrow temperature range over which this change is accelerated. This range is expected to narrow further in larger clusters until it converges to the melting temperature observed in the bulk material.

IV. BENZENE- Ar_{19}

We now turn to the primary focus of this work, namely, benzene- Ar_{19} . The MC calculations on this system were begun from a rather arbitrary configuration representing the insertion of the aromatic ring into a polyicosahedral argon cluster. An example of the instantaneous normal mode spectrum obtained after appropriate equilibration of the cluster is given in Fig. 7, superimposed upon a trace of the spectrum deriving from the neat argon cluster. Note that these two curves differ significantly over the entire frequency range, with the high-frequency secondary maximum disappearing altogether upon inclusion of the aromatic molecule. Clearly the benzene is inducing a nonnegligible perturbation of the argon dynamics (recall that only the motion of the argon atoms contributes to the spectral features calculated in the present study) and thus from the very beginning we are

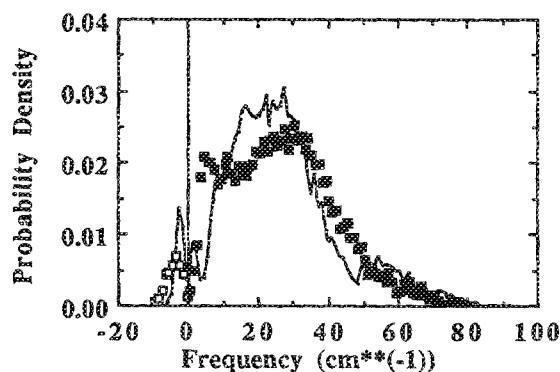


FIG. 7. Normalized argon frequency distribution calculated at 10 K for benzene- Ar_{19} (interior binding site). The calculated points are superimposed here on a trace of the analogous result for Ar_{19} .

made skeptical of claims that the aromatic molecule represents an innocuous probe of cluster melting.

To determine more directly the effect of the presence of a benzene molecule on argon cluster melting dynamics, we have calculated several averaged quantities from the 200 MC configurations generated at each given temperature. In contrast to what we observed in the absence of the aromatic species (Fig. 5), we find now that the temperature dependence of the average potential energy, of the average percentage of vibrational modes that have imaginary frequencies, and of the average Einstein frequency for the cluster is essentially devoid of the dramatic changes which provide a sure indication of a melting transition (see Fig. 8). The trends here instead reflect a more gradual evolution of the dynamics, one which is not accompanied by a sudden loss of cluster symmetry over a relatively narrow temperature range. This same effect is seen in the calculated values of the argon self-diffusion constant which are plotted in Fig. 9. In particular, notice that we no longer find the obvious upturn in the data when D attains a value of $1 \times 10^5 \text{ cm}^2 \text{ s}^{-1}$ that characterizes the melting of the neat argon clusters.

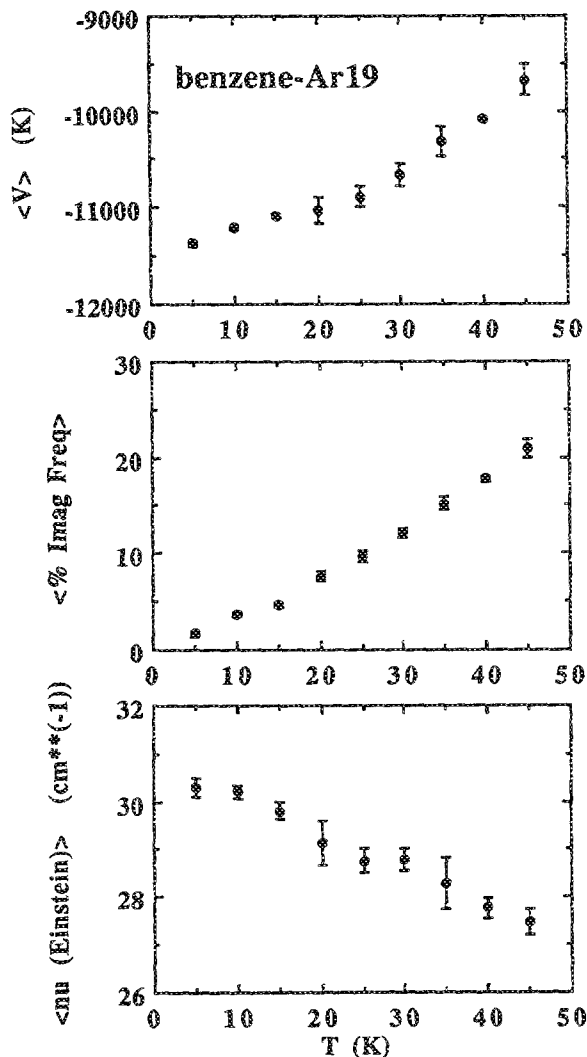


FIG. 8. Averaged quantities as in Fig. 5, but for benzene-Ar₁₉ (interior binding site).

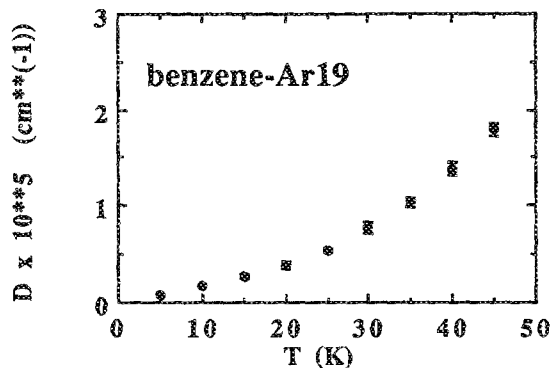


FIG. 9. Temperature dependence of the argon self-diffusion constant in benzene-Ar₁₉ (interior binding site).

Inasmuch as the above results point to a fundamental alteration of the argon cluster dynamics when a benzene molecule is introduced, a direct examination of some of the individual cluster configurations is clearly desirable. One of these configurations, obtained at 10 K, is shown in Fig. 10. In this particular depiction, it is very easy to see that the fivefold symmetry found in the Ar₁₉ clusters at this temperature has been lost, being replaced by the sixfold symmetry characteristic of crystalline argon. The benzene molecule here is providing a template for the ordering of the argon atoms; since the energy difference between the polyicosahedral and close-packed structures of argon clusters is known to be relatively small,³² it is not surprising that the interactions with the benzene molecule are sufficient to shift the relative energies in favor of the bulklike geometry. (For a single argon atom forming a van der Waals complex with benzene, the interaction energy calculated for the lowest-

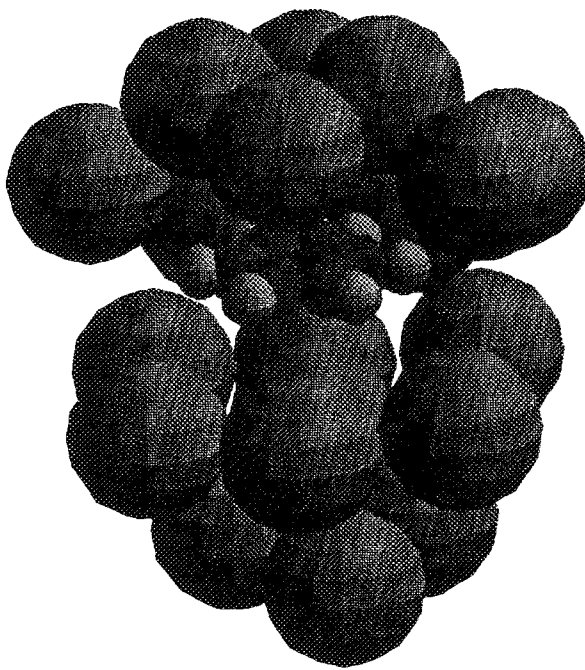


FIG. 10. A representative benzene-Ar₁₉ cluster at 10 K (interior binding site).

energy configuration²⁹ is 564 K, which is about four-and-one-half times larger than the Ar_2 well depth. The key effect here is simply that the aromatic species provides a plane surface against which the rare gas atoms can close pack. It is less likely that the peculiar sixfold symmetry of the benzene is being enforced on the argon layers, inasmuch as argon atoms are relatively large compared to a benzene molecule.) We find the appearance of an argon bilayer on one side of the cluster to be quite normal at this low temperature, with the consequence being that there are few argon atoms found in (or very near) the plane of the aromatic ring.

A rather different cluster configurations is found when the MC equilibration is performed at 40 K. The representative structure shown in Fig. 11 does not exhibit the argon layering found at lower temperatures, but rather reflects a spreading of the argon atoms and a more complete envelopment of the benzene molecule. However, the sixfold local symmetry of argon atoms adjacent to the aromatic ring is maintained even at an energy at which the neat argon cluster would be essentially amorphous. So the central result of our examination is simply this: because benzene induces a local structuring of the argon which for the most part survives increases in the cluster temperature, the benzene- Ar_{10} clusters do not undergo the sort of melting (disordering) transition which is characteristic of their pure argon analogs. Certainly the high-temperature clusters are less rigid than are the low-temperature ones, particularly insofar as the motions of the atoms on the periphery of the aromatic ring are concerned, but still the interactions leading to the retention of local symmetry on either side of the ring effectively forestall liquefaction.

The above observations, of course, immediately present us with a dilemma, in that they suggest that the "phase transition" apparently responsible for the benzene spectral features observed by Hahn and Whetten²³ in fact does not occur. How do we then understand the significance of their reported peak structure?³³ Presumably the absorption line splitting must reflect different perturbations of the benzene transition dipole and hence different benzene chemical envi-

ronments, but what is the nature of these environments if they cannot be classified simply as solidlike or liquidlike? A clue to the resolution of this problem may be found in the work of several groups, in particular those of Leutwyler,¹⁹⁻²¹ LeRoy,²² and Scoles.¹⁷ These workers have related observed shifts in electronic or vibrational spectral lines to the existence of two general types of molecule-rare gas cluster structures, specifically those representing solvated probe molecules (wherein the rare gas atoms effectively surround the probe species) and those consisting of the probe molecule bound to the surface of a rare gas cluster. Our MC calculations begun from a solvated benzene structure have not produced configurations in which the argon atoms are segregated to one side of the aromatic ring, a result suggesting that in this system solvation leads to energy lowering. However, one in general is not guaranteed that clusters produced in free-jet expansions achieve their minimum-energy configurations on the time scale of the experiments and so it is necessary to consider structures which might be kinetically although not thermodynamically stable.

We employed several initial geometries in an investigation of these prospective metastable states in which the benzene molecule is exterior to the 19-atom argon cluster. Examples of these are a structure in which one of the capping atoms of the polyicosahedral cluster is centered above the aromatic ring and another in which one of the atoms of the central five-atom ring of this same cluster is instead the one which is located exactly over the benzene ring. If the MC walk is carried out at an elevated temperature, say 30 K, then eventually the system is found in the region of configuration space describing solvated structures (after 5×10^5 – 1×10^6 steps). On the other hand, 2.2×10^6 steps are insufficient for stepping the system away from this same local potential minimum when the temperature is decreased to 10 K. This result suggests that it is reasonable to pursue further the notion of there being "inside" and "outside" benzene binding sites which actually might be responsible for the data obtained by Hahn and Whetten.²³

An example of one such outside binding geometry is shown in Fig. 12, obtained at 10 K after 2.2×10^6 steps of a MC calculation that began with benzene bound to an Ar_{19} capping atom. Although most of the argon cluster retains the symmetry expected for the neat cluster at this temperature, there is a distortion of the atoms on the end of the cluster nearest the benzene which brings four argon atoms into close proximity to the aromatic ring. Only slightly higher in energy, though, is a second sort of configuration involving less distortion wherein the benzene molecule binds in what would be analogous to a threefold surface site formed by the capping argon atom and two atoms of the immediately adjacent five-membered ring. The frequency spectrum obtained in this particular calculation is shown in Fig. 13. Note in particular the relatively small differences between the spectra of the benzene-doped and neat clusters and the persistence of the peak at high frequencies corresponding to argon found in bulklike bonding sites. We by no means claim to have discovered all the ways in which benzene can bind to the surface of these clusters, but it appears certain that there are a large number of such binding geometries, all of which

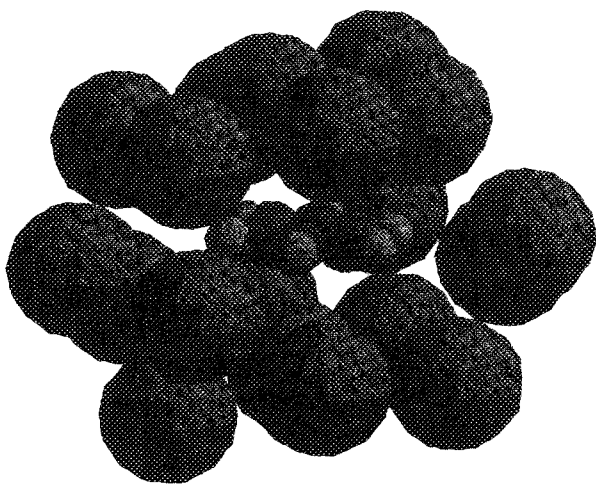


FIG. 11. A representative benzene- Ar_{10} cluster at 40 K (interior binding site).

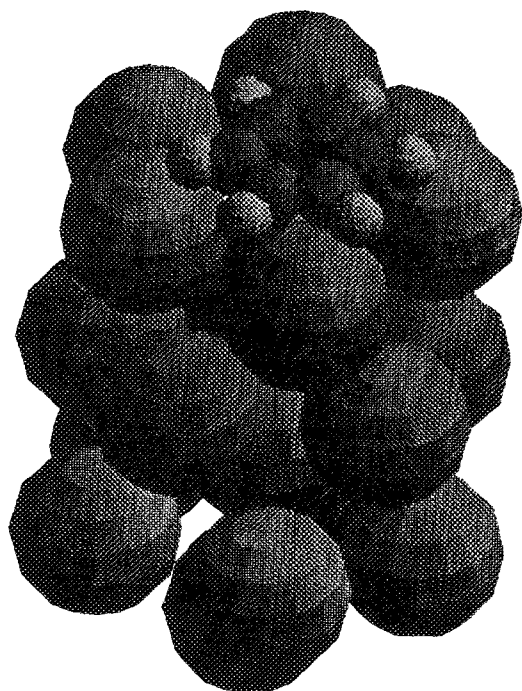


FIG. 12. A representative benzene-Ar₁₉ cluster at 10 K (exterior binding site).

are relatively close in energy as compared with the interior binding site. Diffusion of the benzene over the surface of the argon cluster, probably in concert with small local cluster geometry changes, may be relatively facile, but we have not explored this possibility further.

But is the presence of two qualitatively different bonding environments sufficient to produce the experimentally observed splitting and broadening of the benzene absorption spectrum? To estimate what the effect of the argon cluster arrangement might be, we have calculated values of the benzene-Ar₁₉ interaction potential energy (which is equal to the total potential energy minus the Ar-Ar contributions) for the various configurations generated in this study. A simple sketch of the distributions of these energies, corresponding to one interior and two exterior binding environments, is given in Fig. 14 for a temperature of 10 K. The interior binding arrangement is associated with the lower-energy peak, as

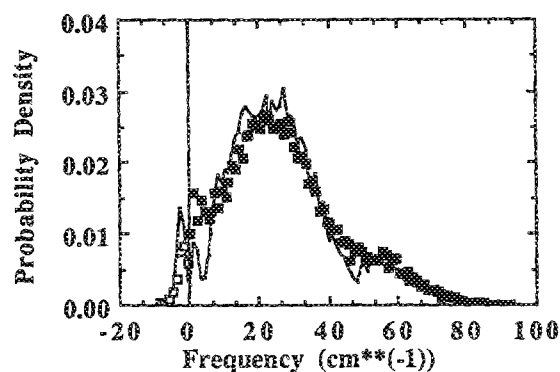


FIG. 13. Normalized argon frequency distribution as in Fig. 7, but for benzene in an exterior binding site.

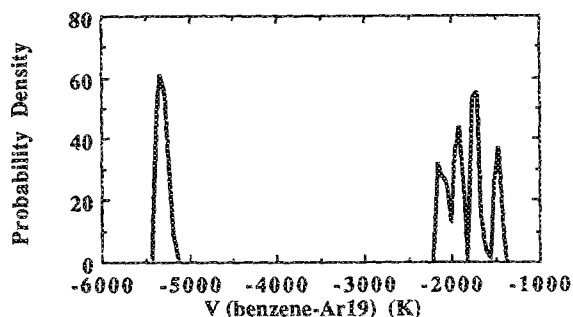


FIG. 14. Distributions of potential interactions between benzene and the argon atoms for different benzene binding sites. (The units on the vertical axis here are arbitrary.) The peak on the left corresponds to an interior site, while the peaks on the right correspond to various external sites.

one would expect given the behavior of the high-temperature MC walk, while each of the exterior arrangements yields two peaks at higher energies. The high-energy features seen here in the distributions of potential energies simply reflect the fact that at these temperatures the benzene molecule is still able to sample a couple of slightly different binding sites on the surface of the argon cluster. Since we think that there actually are more nearly degenerate exterior binding geometries than those we have considered so far, we expect the complete distribution of energies to exhibit a broad peak centered in the vicinity of -2000 K, i.e., shifted by roughly 3000 K to higher energies relative to the interior peak, and having a width of at least 1000 K. This shift in binding energy constitutes about 30% of the total system potential $\langle V \rangle$. The total energies themselves actually differ only by about 10% though ($\langle V \rangle = 11\,000$ K for an interior site and $\langle V \rangle = 10\,000$ K for an exterior site), since the change in the benzene binding energy is largely offset as a result of the rearrangement of the argon atoms. We also estimate that the minimum width of the less-shifted peak represents about 10% of the total perturbing potential, so that overall our prediction of the ratio of peak width to peak splitting is quite consistent with the experimental observations. (For benzene-Ar₁₉, Hahn and Whetten²³ find the peak splitting to be roughly one-third the magnitude of the overall peak shift and the width of the less-shifted peak to be about one-third of the splitting. We must emphasize that our analysis here does not represent a direct modeling of the spectroscopy. Therefore the differences in benzene-Ar₁₉ interactions described above cannot be equated with the experimental peak shifts, although one would hope that they do reflect the differential effect on the benzene molecule's transition dipole moment arising from different arrangements of the nearby argon atoms. At best, it is the ratios of the peak splittings or widths to the total peak shift which may be estimated by the consideration of just the individual potential contributions.)

In their paper, Hahn and Whetten²³ explicitly discount the possibility that differences in the perturbation of the benzene transition dipole derive from the existence of interior and exterior binding geometries on the basis of an argument concerning the correlation between peak shifts and widths. They assert, quite correctly, that if benzene were to bind to the surface of an argon cluster, then the shift of the absorp-

tion line would be less than that seen when the benzene is solvated. However, they also assume that the line corresponding to externally bound benzene would be relatively sharp, when in fact their experiments indicate that the broader of the two observed peaks is the one which is shifted the least. Our results suggest that this less-shifted peak actually is the envelope of several peaks arising due to the slightly different energies of the various surface binding sites. Even though the individual peaks here indeed may be fairly narrow, the energy differences are such that the width of the envelope can exceed the width of the more-shifted peak (corresponding to configurations in which benzene is surrounded by argon atoms). Thus we conclude that the experimental findings are in no way inconsistent with the model developed here on the basis of MC simulations and in fact can be adequately explained by the consequences of this model.

There remains a final point concerning the interconversion of the two general cluster structural forms which deserves comment. If the metastable surface-bound benzene- Ar_{19} clusters decay very rapidly to lower-energy solvated forms, then irrespective of the nascent cluster geometry, only interior-bonded benzene should be observed. Clearly the MC calculations heretofore reported cannot provide the sort of kinetic data required for evaluation of the lifetimes here, so standard MD calculations³⁴ were performed. In these calculations, particular surface-bonded configurations generated in the MC walks were used in defining the initial position vectors, while conjugate momentum vectors were selected at random from the appropriate thermal distribution. Integration of Hamilton's equations of motion for the argon atoms then proceeded (Adams-Moulton fifth-order predictor, sixth-order corrector with a Runge-Kutta-Gill starting algorithm and a step size of 0.01 ps) until either an argon atom passed through the plane of the benzene ring or the maximum trajectory time of 1 ns was exceeded. The results of these calculations are quite simply stated: no rearrangement of the argon atoms involving the passage of one or more of the atoms to the other side of the benzene molecule occurred on the 1 ns time scale which we could access via trajectory methods. This behavior persisted even when the cluster temperature was increased to 30 K, a temperature at which the outside-inside isomerization was observed in MC calculations. We therefore believe that the clusters having an externally bound benzene molecule may indeed be sufficiently stable that at least some fraction of them could survive and account for one of the observed spectral peaks, although in our simulations we are unable to access the microsecond time scale corresponding to flight times in the experimental apparatus.

Interestingly, it is here, in the consideration of the kinetics of the conversion from surface-bound to solvated benzene, where the notion of cluster melting transitions actually may be of some relevance. We have found, e.g., that in the benzene- Ar_{13} system far fewer MC steps are required at 30 K in order for the benzene molecule to find its way inside the cluster. This effect very likely derives from the relative fluidity of Ar_{13} clusters relative to their 19-atom counterparts at this temperature. So while it is not the liquefaction of the argon layers surrounding a benzene molecule which is ulti-

mately responsible for observed spectral shifts, it may be true that liquefaction of the neat argon cluster is a prerequisite for the solvation of the benzene which in turn does yield the distinctive spectral signatures.

V. CONCLUDING REMARKS

In this study, we have examined the dynamics of benzene- Ar_{19} clusters in order to understand the origin of the peak structure observed in spectroscopic measurements of Hahn and Whetten²³ on this system. While the initial explanation offered for the phenomenology rested on a coexistence of solidlike and liquidlike argon structures, our instantaneous normal mode analysis, coupled with a direct look at the typical cluster configurations, has revealed that the benzene molecule actually retards this melting transition by providing a template for ordering of the argon atoms. The explanation of the spectral results suggested by these investigations instead is based on the existence of two general types of cluster structures, one in which benzene is bound to the surface of the argon cluster and one in which benzene is enveloped by the argon atoms. Although the solvated structures have a lower energy than do the surface-bound structures, the latter metastable structures may well be kinetically stable on a time scale accessed by the experiments.

On the whole we feel that the language advocated by Bösigger, Knochenmuss, and Leutwyler²⁰ provides a very useful means for describing the dynamics in these aromatic-rare gas clusters. Their emphasis is not on cluster melting transitions, or in fact on any transitions occurring within the rare gas layers, but rather on transitions which lead to changes in the relative orientation of the rare gas clusters with respect to the organic "substrate." These orientations have been characterized as either wetting or nonwetting depending on whether the binding of the rare gas atoms is to both sides or to only one side of the aromatic ring(s). Essentially these are the two classes of structures which, we submit, are responsible for the observed spectroscopy of benzene- Ar_{19} clusters. It also seems that these ideas provide a unifying theme for understanding a number of different cluster experiments and not just those involving incorporated aromatic molecules, which suggest that clusters having probe molecules attached to their surfaces have different properties than those with solvated probe molecules. Certainly one cannot ignore these effects when attempting to investigate transitions within the structure of the solvent species, inasmuch as the two binding environments are so different chemically. Practically, these doped clusters constitute a class of systems that one can investigate with the hope of determining the origins not only of bulk material behavior, but also of the unique properties of solid (and perhaps even liquid) surfaces. The difficulties inherent in the interpretation of experiments on clusters such as these should not deter workers from attempting their study, for useful information surely can be extracted. For example, in aromatic-rare gas clusters having larger numbers of rare gas atoms, it is very likely that some sort of melting transition within the cluster accompanies the nonwetting-wetting transition, so that probing directly one of the transitions per-

mits one to infer something about the other.

Before closing we should note a question which remains unresolved as a result of this inquiry, that being why there might be two types of clusters existing in the jet at the point at which Hahn and Whetten²³ do their spectroscopy. It may be the case that the clusters are for the most part formed with the benzene bound in a surface site and the nonwetting-wetting transition occurs on a time scale (> 1 ns) such that some of the clusters convert to the lower-energy forms prior to spectroscopic study. On the other hand, the jet initially may contain a mixture of both structural types as a result of variations in cluster nucleation processes or of the condensation of smaller clusters. Further investigations will be required in order to resolve these remaining questions, but the present work clearly indicates that understanding the spectroscopy of clusters requires a convergence of traditionally different viewpoints, since these measurements have the potential of providing a window into the microscopic analogs of both surface and bulk behavior.

ACKNOWLEDGMENTS

We wish to thank Peter Weber and Robert Whetten for helpful discussions concerning experimental measurements on clusters and Margaret Doll for her assistance with the computer graphics. JEA acknowledges the donors of the Petroleum Research Fund, as administered by the American Chemical Society, for partial support of this work, and the Research Council of the University of Missouri-Columbia for the research leave which has made this collaborative project possible. RMS acknowledges the support of the National Science Foundation under grant CHE-8815163.

- ¹ M. R. Hoare, *Adv. Chem. Phys.* **40**, 49 (1979).
- ² *The Physics and Chemistry of Small Clusters*, edited by P. Jena, B. K. Rao, and S. Khanna (Plenum, New York, 1987).
- ³ *Large Finite Systems*, edited by J. Jortner, A. Pullman, and B. Pullman (Reidel, Dordrecht, 1987).
- ⁴ R. S. Berry, T. L. Beck, H. L. Davis, and J. Jellinek, *Adv. Chem. Phys.* **70**, 74 (1988).
- ⁵ C. J. Thompson, *Mathematical Statistical Mechanics* (Macmillan, New York, 1972), p. 79.
- ⁶ See, e.g., C. L. Briant and J. J. Burton, *J. Chem. Phys.* **63**, 2045 (1975); J. B. Kaelberer and R. D. Etters, *ibid.* **66**, 3233 (1977); R. D. Etters and J. B. Kaelberer, *ibid.* **66**, 5112 (1977); E. Blaisten-Barojas, in *Elemental and Molecular Clusters*, edited by G. Benedek, T. P. Martin, and G. Pacchioni (Springer, Berlin, 1988), p. 106; M. Bixon and J. Jortner, *J. Chem. Phys.* **91**, 1631 (1989); T. L. Beck and T. L. Marchioro II, *ibid.* (submitted).
- ⁷ J. D. Honeycutt and H. C. Andersen, *J. Phys. Chem.* **91**, 4950 (1987).
- ⁸ G. Natanson, F. Amar, and R. S. Berry, *J. Chem. Phys.* **78**, 399 (1983); R. S. Berry, J. Jellinek, and G. Natanson, *Phys. Rev. A* **30**, 919 (1984); J. Jellinek, T. L. Beck, and R. S. Berry, *J. Chem. Phys.* **84**, 2783 (1986); F. G. Amar and R. S. Berry, *ibid.* **85**, 5943 (1986); H. L. Davis, J. Jellinek, and R. S. Berry, *ibid.* **86**, 6456 (1987); T. L. Beck, J. Jellinek, and R. S. Berry, *ibid.* **87**, 545 (1987); T. L. Beck and R. S. Berry, *ibid.* **88**, 3910 (1988); T. L. Beck, D. M. Leitner, and R. S. Berry, *ibid.* **89**, 1681 (1988).
- ⁹ J. E. Adams and R. M. Stratt, *J. Chem. Phys.* **93**, 1332 (1990).
- ¹⁰ See, e.g., J. Farges, M. F. de Feraudy, B. Raoult, and G. Torchet, *J. Chem. Phys.* **78**, 5067 (1983); **84**, 3491 (1986).
- ¹¹ E. J. Valente and L. S. Bartell, *J. Chem. Phys.* **80**, 1451 (1984); 1458 (1984); L. S. Bartell and Y. Z. Barshad, *J. Phys. Chem.* **91**, 2890 (1987); L. S. Bartell, L. Harsanyi, and E. J. Valente, *NATO ASI Ser., Ser. B* **158**, 37 (1987); R. Nowak, J. A. Menapace, and E. R. Bernstein, *J. Chem. Phys.* **89**, 1309 (1988); M. L. Alexander, N. E. Levinger, M. A. Johnson, D. Ray, and W. C. Lineberger, *ibid.* **88**, 6200 (1988); R. Beck and J. W. Nibler, *Chem. Phys. Lett.* **148**, 271 (1988).
- ¹² N. E. Levinger, D. Ray, M. L. Alexander, and W. C. Lineberger, *J. Chem. Phys.* **89**, 5654 (1988).
- ¹³ The concept of inherent structures in a liquid is developed in F. H. Stillinger and T. A. Weber, *Kinam* **3**, 159 (1981); *Phys. Rev. A* **25**, 978 (1982); **28**, 2408 (1983).
- ¹⁴ A. Brenner, in *Metal Clusters*, edited by M. Moskovits (Wiley, New York, 1986), p. 249.
- ¹⁵ For the most recent applications to liquid systems, see G. Seeley and T. Keyes, in *Spectral Line Shapes*, edited by J. Szudy (Ossolineum, Wroclaw, Poland, 1989), Vol. 5, p. 649; *J. Chem. Phys.* **91**, 5581 (1989); B.-C. Xu and R. M. Stratt, *ibid.* **92**, 1923 (1990).
- ¹⁶ R. A. LaViolette and F. H. Stillinger, *J. Chem. Phys.* **83**, 4079 (1985); R. O. Rosenberg, D. Thirumalai, and R. D. Mountain, *J. Phys. Condensed Matter* **1**, 2109 (1989).
- ¹⁷ T. E. Gough, D. G. Knight, and G. Scoles, *Chem. Phys. Lett.* **97**, 155 (1983).
- ¹⁸ D. H. Levy, *Adv. Chem. Phys.* **47**, 323 (1981); C. A. Haynam, D. V. Brumbaugh, and D. H. Levy, *J. Chem. Phys.* **80**, 2256 (1984); A. Avirav, U. Even, and J. Jortner, *ibid.* **75**, 2489 (1981); *J. Phys. Chem.* **86**, 3345 (1982).
- ¹⁹ J. Bösigler and S. Leutwyler, *Phys. Rev. Lett.* **59**, 1895 (1987); S. Leutwyler and J. Bösigler, *Z. Phys. Chem. NF* **154**, 31 (1987); in *Large Finite Systems*, edited by J. Jortner, A. Pullman, and B. Pullman (Reidel, Dordrecht, 1987), p. 153.
- ²⁰ J. Bösigler, R. Knochenmuss, and S. Leutwyler, *Phys. Rev. Lett.* **62**, 3058 (1989).
- ²¹ S. Leutwyler and J. Bösigler, *Faraday Discuss. Chem. Soc.* (in press); *Chem. Rev.* **90**, 489 (1990); *J. Chem. Phys.* **92**, 4686 (1990).
- ²² D. Eichenauer and R. J. LeRoy, *Phys. Rev. Lett.* **57**, 2920 (1986); *J. Chem. Phys.* **88**, 2898 (1988); R. J. LeRoy, J. C. Shelley, and D. Eichenauer, in *Large Finite Systems*, edited by J. Jortner, A. Pullman, and B. Pullman (Reidel, Dordrecht, 1987), p. 165; J. C. Shelley, R. J. LeRoy, and F. G. Amar, *Chem. Phys. Lett.* **152**, 14 (1988).
- ²³ M. Y. Hahn and R. L. Whetten, *Phys. Rev. Lett.* **61**, 1190 (1988).
- ²⁴ W. H. Miller, W. L. Hase, and C. L. Darling, *J. Chem. Phys.* **91**, 2863 (1989).
- ²⁵ E. B. Wilson, J. C. Decius, and P. C. Cross, *Molecular Vibrations* (Dover, New York, 1955), pp. 14–17; M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University, Oxford, 1954), pp. 173–175.
- ²⁶ An alternate formulation of the self-diffusion constant, one which provides a more uniform treatment of the solid and liquid dynamical regimes, has been suggested very recently by B. Madan, T. Keyes, and G. Seeley, *J. Chem. Phys.* (submitted). We have explored the application of this methodology to clusters and have confirmed that in the instantaneous normal mode method, the imaginary frequencies contain sufficient information for the quantitative prediction of diffusion constants; J. E. Adams and R. M. Stratt, *J. Chem. Phys.* (in press).
- ²⁷ N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. H. Teller, and E. Teller, *J. Chem. Phys.* **21**, 1087 (1953); M. Kalos and P. A. Whitlock, *Monte Carlo Methods* (Wiley-Interscience, New York, 1986).
- ²⁸ A. Rahman, *Phys. Rev. A* **136**, 405 (1964).
- ²⁹ M. J. Ondrechen, Z. Berkovitch-Yellin, and J. Jortner, *J. Am. Chem. Soc.* **103**, 6586 (1981).
- ³⁰ See, e.g., S. Leutwyler, A. Schmelzer, and R. Meyer, *J. Chem. Phys.* **79**, 4385 (1983); S. Leutwyler, *ibid.* **81**, 5480 (1984).
- ³¹ One should keep in mind that densities of states such as those depicted in Fig. 1 do not correspond to the results of any spectroscopic measurements. In particular, the formalism does not incorporate information about transition dipole matrix elements and hence cannot embody spectroscopic selection rules. The question of the survival of selection rules at higher temperatures, where the clusters display an increasing degree of disorder, is itself an interesting point, but not one which we are able to address in the present calculations.
- ³² For a recent investigation of the transitions between these structures, see J. Xie, J. A. Northby, D. L. Freeman, and J. D. Doll, *J. Chem. Phys.* **91**, 612 (1989).
- ³³ As pointed out in Ref. 20, there are potential difficulties in the assignment of spectral features to clusters having particular numbers of argon atoms due to the possibility of fragmentation. We do not believe, however, that uncertainties in these assignments detract from the fact that peak shifts and splittings have been observed.
- ³⁴ See, e.g., L. M. Raff and D. L. Thompson, in *Theory of Chemical Reaction Dynamics*, edited by M. Baer (CRC, Boca Raton, Fla., 1985, Vol. 3); D. G. Truhlar and J. T. Muckerman, in *Atom-Molecule Collision Theory*, edited by R. B. Bernstein (Plenum, New York, 1979), p. 505.