Solvation and melting in large benzene(Ar) n clusters: Electronic spectral shifts and linewidths

John E. Adams and Richard M. Stratt

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Solvation and melting in large benzene·(Ar)$_n$ clusters: Electronic spectral shifts and linewidths

John E. Adams
Department of Chemistry, University of Missouri-Columbia, Columbia, Missouri 65211

Richard M. Stratt
Department of Chemistry, Brown University, Providence, Rhode Island 02912

Although there has been considerable interest in solvation processes in small atomic and molecular clusters, uncertainties in the interpretation of spectral probes have made the experimental elucidation of the solvation, and in particular how it relates to bulk solvation, problematical. We demonstrate here that, through the application of a microscopic formalism which has the novel feature of accounting for the collective dielectric response of a cluster, the reported spectra of large benzene·(Ar)$_n$ clusters can be readily understood. Specifically, we show that the apparent lack of convergence of the benzene's absorption spectrum to the corresponding bulk result derives from the dominance of nonwetting cluster structures for large n. Even observed peak multiplicities and individual linewidths may be understood within this formalism if the cluster structures upon which the calculations are based are generated in a nonequilibrium (rather than thermally equilibrated) simulation. Given this detailed understanding of the relationship between spectroscopy and structure, we also can clarify the experimental consequences of the so-called ''melting'' transition in benzene·(Ar)$_n$ clusters: The spectral signature of the melting is a change in the behavior of the linewidth of the absorption envelope which results from a subset, but not all, of the Ar atoms becoming fluid. This description of the melting behavior suggests an important refinement of the conventional picture of solid–fluid phase coexistence in clusters. © *1996 American Institute of Physics.* [S0021-9606(96)50829-9]

I. INTRODUCTION

Surely the nature of solvation is one of the most fundamental concepts in chemistry. It is only in recent years, however, with the development of techniques for the generation of small, size-selected atomic and molecular clusters, that more or less controlled probes of solvation have become possible. We now are able to examine ''differential'' solvation phenomena, i.e., the alteration of the chemical and physical properties of a solute atom (molecule) due to clustering with increasing numbers of solvent species.[1–11] This newfound capability gives us, in turn, a long sought-after probe of the microscopic details of cluster behavior, including the elusive phenomenon of cluster ''melting''.[9,12–16]

Because of these dual possibilities, this research area also has proved to be particularly fertile ground for collaboration between experimentalists and theorists. The sizes of the systems studied are such that they are often amenable to investigation both by high-resolution spectroscopic and scattering methods and also by sophisticated electronic structure and molecular dynamics (MD) or Monte Carlo (MC) techniques. The present work represents the final product of just such a synergism, having been stimulated directly by recent experimental results[6] that themselves stemmed from work suggested by the conclusions derived from previous theoretical analyses[17–19] of the problem.

The particular system of interest here, benzene clustered with varying numbers of Ar atoms, was brought to the attention of many through the work of Whetten and co-workers.[9,10,20] They performed one-color, two-photon ionizations of clusters containing as many as 40 Ar atoms, in doing so measuring the shift in the 6_0^1 transition frequency of benzene induced by the presence of the Ar ''solvent''. Most interesting (and, indeed, most puzzling) of their findings was that even though the observed spectral shift, as expected, reached a plateau value as the size of the cluster increased, this asymptotic value of the shift was quite different from the shift measured for the analogous bulk system.[10] A similar result also was obtained for benzene clustered with N$_2$ and for Al atoms clustered with Ar, but these workers were unable to decide among various possible structural explanations (dopant molecule binding in surface sites, in nonbulklike sites within the cluster, or in near-surface sites) for the observed behavior. Although this work was criticized in part by Schmidt *et al.*[4] the spectral shifts subsequently obtained for the smallest clusters (nine or fewer Ar atoms) using their two-color, resonant two-photon ionization (R2PI) scheme actually differed very little from those measured by the Whetten group. (The one-color excitation scheme leaves sufficient excess energy in the clusters that it is difficult to rule out the possibility of subsequent fragmentation. One thus runs a risk of being unable to associate a particular spectral peak with a cluster of well-defined size.[8])

In an early investigation of structural fluctuations in benzene·(Ar)$_n$,[17] we considered the possibility that one of the explanations indicated above, namely that clusters may be formed in which benzene is bound at a surface site of a neat Ar cluster, in fact did suggest a splitting of the spectral lines in accordance with the results reported by Hahn and

Whetten.[9,20] We were unable, however, to provide a *direct* correlation at that time between observed spectral shifts and microscopic cluster geometries. Later we returned to this problem, concentrating specifically on the convergence of the cluster spectral shift to that of the corresponding bulk system.[18] In that second paper we described the application of a formalism for calculating spectral shifts from representative system configurations that paid particular attention to the collective nature of dielectric effects on spectra.[21] We were able to show that indeed if one were to consider clusters larger than those studied by Whetten and co-workers[10] ($n > 40$), then one would begin to see the anticipated asymptotic approach to the bulk values. In a companion paper we also demonstrated that the formalism was reliable for calculating the bulk-system spectral shifts as well;[21] nothing was found to suggest that our methods were subject to failure as the size of the system was increased.

The publication of the results of our work had the happy effect of stimulating Knochenmuss, Ray, and Hess[6] to examine larger benzene·(Ar)$_n$ clusters, in particular those that we predicted to show the larger (red) spectral shifts characteristic of the bulk. Unexpectedly (at least in our view) that study did *not* uncover the anticipated asymptotic behavior with increasing cluster size, but rather lent support to the earlier work of Whetten's group.[10] Their finding of relatively narrow linewidths in the spectra of the larger clusters also tended to indicate that the discrepancy with our previous work was real, but it also hinted that the clusters being investigated experimentally were significantly different structurally than those deriving from our MC simulation. Of course, just such a situation would obtain if the empirical potential energy function used in our generation of cluster configurations were flawed, but then we would be at a loss to explain why our results appeared to be so accurate for both the small clusters *and* the bulk systems.

But the work described above certainly was not the only activity in the microsolvation field during the last half decade; a number of other studies have yielded results that pertain directly to the present investigation. One of the important considerations addressed below concerns the presence in the experimentally generated cluster jets of a variety of geometric isomers, including some characterized (in the language popularized by Leutwyler and co-workers[22]) as ''wetting'' and others that fall into the category of ''nonwetting''. Of that first group, fluorene·(Ar)$_2$ clusters[23] were shown to yield a UV spectrum consistent with a (1|1) structure, i.e., with Ar atoms bound symmetrically on opposite sides of the plane of the fluorene molecule, being the dominant species present. On the other hand, studies by Jortner and co-workers[24] have suggested that perylene·(Ar)$_n$ clusters ($6 < n \leq 22$) are predominantly nonwetting—the aromatic chromophore is bound in a surface site of the noble gas cluster—and that only those clusters larger than $n = 25$ exhibit a double-sided solvation structure. These same authors also reported a calculation of spectral line shapes[25] associated with particular cluster geometries using the semiclassical spectral density method,[26] noting that the observed linewidths derive principally from a zero-frequency diffusive mode rather than from finite-frequency nuclear motions. (It should be noted that while the spectral density formalism[26] permits the inclusion of both homogeneous and inhomogeneous line broadening mechanisms, it does not allow for collective polarization behavior as does ours.[18,21])

In work directly bearing on our system of interest, Guillaume *et al.*[7] reexamined benzene·(Ar)$_{20}$ clusters using a R2PI technique and identified three separate peaks that were associated with the totally wetting and partially wetting structures obtained in an MC simulation. What they did *not* report was the existence of totally nonwetting, i.e., one-sided, structures. They discarded the possibility that such structures might be correlated with one of the observed peaks on the basis of a one-side spectral additivity rule suggested by their previous small cluster results, which would predict that a net blue shift be associated with the larger nonwetting structures. Again, though, they did not consider the possibility that there might be a collective solvent dielectric response that evolves with increasing cluster size. Nonetheless, they did find the band assigned to totally wetting, interior-bound clusters to be the broadest feature present but not the one that is most red shifted. The most red shifted of the three peaks was instead associated with the *least-wetting* cluster geometries, those having benzene bound edgewise to the Ar cluster with roughly only 10 solvent atoms in the immediate vicinity of the chromophore. Also significant was their conclusion (based on their apparent ability to measure discrete, geometry-specific spectral lines) that what the Whetten group observed[9,20] could not reasonably be interpreted as rigid-fluid cluster coexistence.

More recent studies by this group[8] have led to a revision of their thinking, though. They now suggest that careful spectroscopic measurements yield no support for the coexistence of cluster isomers. Rather, they believe that the extant spectra, characterized by multiple absorption peaks, in fact derive from ensembles comprising clusters of different sizes. Their analysis is still based, however, on the presumptions that solvent perturbations are exclusively near neighbor in character and that only minimum-energy cluster structures are found in their expansion beams.

Of course, any theoretical investigation of cluster structures and structural transitions, whether it be using MD or MC techniques, relies on the availability of an analytical potential energy function. Recently, Hobza and co-workers have proposed a nonempirical *ab initio* potential function[27] and have used that function in MD simulations designed not only to discover the global and local energy minimum structures (through energy quenching) but also to assess the relative populations of those stationary points.[28,29] Particular emphasis in these studies has been placed on clarifying the entropic contributions to the relative state populations. It was found, for example, that for small clusters the energetically *disfavored* wetting structures are entropically favored to the extent that they are more populated than the one-sided, nonwetting structures. At least in the case of benzene·(Ar)$_2$ clusters,[28] it was further noted that the relative state populations do not appear to be particularly sensitive to the choice of potential energy description; the conventional Lennard-

Jones choice yields results which do not differ significantly from those obtained using their own fit to *ab initio* data. Finally, but perhaps of most relevance to our work, these workers determined that the time scale for cluster isomerization or dissociation was on the order of a nanosecond or greater. This result immediately suggests that clusters formed in expansion jets very well might become trapped in configurations quite different from the minimum energy ones, and hence that the oft-made assumption that the clusters are thermally equilibrated indeed might be invalid.

In addition, there have been a few studies aimed at trying to understand the actual dynamics of cluster formation and cooling. These investigations have considered various $(C_6H_6)_n$ clusters [or $(C_6H_6)(C_6D_6)_{n-1}$ clusters], finding evidence for a transition between fluxional and rigid cluster structures as the clusters cool. Easter *et al.*[30] were able to identify a time scale for this process, reporting a value of 140 μs. While in their very recent MC study of these clusters Bartell and Dulles[16,31] did not determine a time scale for the transformation, they were able to say something about the temperature of clusters undergoing these structural changes. They found that rigid structures obtained by the time that the cluster temperature dropped to 140 K, with observable isomerization disappearing below 85 K.[16] Furthermore, they found evidence for evaporative cooling being the primary mechanism for the cooling of liquid-like clusters, in contrast to the conjecture of Easter *et al.*[30] that collisions with the He carrier gas were more likely to yield the observed cooling. (This difference in interpretation derives in part, though, from the two groups' differing estimates of cluster temperatures during the jet expansion.) Nonetheless, it is important to note that either mechanism is inherently *dynamical* in nature and that it is dangerous to presume thermal equilibration of individual clusters prior to being probed spectroscopically.

In the sections that follow, we report the results of a new set of calculations that demonstrate conclusively that the apparent lack of convergence of the 6_0^1 spectral shifts to bulk-phase values observed experimentally derives from cluster structures in which benzene is bound to the surface of an Ar cluster. In particular, we are able to show that such structures yield spectra displaying little or no dependence on cluster size and that the linewidths (as well as the positions) predicted for the spectral peaks are in agreement with the experimental values.[6] Additionally, we can confirm by means of an MD simulation that the multiple-peak structure seen in the observed spectra[6] of intermediate size clusters ($n = 20$–40) is the consequence of the fact that relatively few cluster isomers are "visited" by the system during the lifetime of these clusters in the expansion jet. Our simulations of wetting clusters, i.e., those in which the Ar atoms are bound to both faces of the benzene molecule, also predict an interesting dependence of the spectral linewidth on temperature. A change in this dependence is found to occur over the same temperature range for which we would expect to find structural fluctuations ("melting") in these clusters.

II. THEORY

Our arguments hinge on an ability to correlate discrete cluster structures with the electronic transition frequency of the chromophore or, more to the point, with the environment-induced shift of that transition frequency. To do so, we return to the formalism[18,19,21] used successfully in our previous modeling of the original Whetten group data,[9,10,20] the key feature of which is an ability to account for the *collective* dielectric response of the solvent atoms. Since the method already has been described in considerable detail[21] (as have the specifics of the potential energy description that we have adopted[32]), only an outline of it will be given here, one that stresses the link between the spectral shift and the instantaneous system configuration.

In this model the nonpolar but polarizable Ar atoms are taken to be interacting Drude oscillators[33,34] having isolated frequencies equal to the ionization frequency. For *each* configuration of this cluster, one now may renormalize the problem (the point-dipole–point-dipole interaction terms are quadratic functions of the oscillator displacement coordinates) and obtain a set of collective polarization modes. It is the coupling of these collective modes, which necessarily embody the geometry of the cluster as a whole, to the effective transition dipole of the benzene chromophore that then yields the cluster-geometry-dependent (red) shift of the molecule's transition frequency. Note that it is precisely at this point that the formalism transcends the nearest-neighbor analysis embodied in the spectral interpretation presented recently by Guillaume *et al.*[8]—we have demonstrated previously[18] that inclusion of the collective character of the dielectric response is absolutely critical in understanding the lack of precise spectral additivity with increasing cluster size. The explicit expression for this red shift, the result of the application of second-order perturbation theory, is just

$$\delta(h\nu)_{\text{dielectric}} = -d^2 \sum_{\alpha=1}^{3N} \frac{c_\alpha^2}{2m_v\omega_\alpha} \frac{2\omega_u}{\omega_\alpha^2 - \omega_u^2},$$

where d is the magnitude of the chromophore's effective transition dipole, ω_u is the transition frequency of the isolated solute molecule (for benzene, $\hbar\omega_u = 4.787$ eV; in contrast, the transition energy of an isolated Ar atom is taken to be its ionization energy, $\hbar\omega_v = 15.75$ eV[35]), ω_α is a collective polarization mode frequency obtained by diagonalizing a matrix of dipole–dipole interaction terms, m_v is an effective oscillator mass that may be calculated from the solvent's polarizability [$\alpha_v = (1/m_v\omega_v^2) = 1.64$ Å^3 for Ar[35]], and finally c_α is a constant that reflects the strength of the coupling of the αth polarization mode to the transition moment. It is sometimes convenient to go even further, though, and to recast this result in terms of the *spectrum of couplings*,[34,36] defined conventionally as

$$J(\omega) = \pi \sum_{\alpha=1}^{3N} c_\alpha^2 \delta(m_v\omega^2 - m_v\omega_\alpha^2), \qquad (2.1)$$

so that now

$$\delta(h\nu)_{\text{dielectric}} = -\frac{d^2}{\pi} \int d\omega\, J(\omega)\, \frac{2\omega_u}{\omega^2 - \omega_u^2}.$$

The explicit dependence of the spectral shift on the instantaneous system configuration is incorporated in these equations through the polarization fluctuation frequencies ω_α and the coupling constants c_α,

$$c_\alpha = \sum_{j,\mu} [\mathbf{U}(\mathbf{R})]_{\alpha,j\mu} [\mathbf{T}(\mathbf{r}_{0j})]_{\mu z}. \tag{2.2}$$

In this expression the vector $\mathbf{R}$ defines the cluster geometry, $\mathbf{r}_{0j}$ is the separation vector between the solute molecule (indexed by 0) and the jth solvent atom, $\mathbf{T}$ is the standard point-dipole–point-dipole interaction tensor, and $\mathbf{U}$ is the $3N \times 3N$ (orthogonal) matrix that accomplishes the renormalization of the Drude oscillator problem cited above. (The subscript μ here simply denotes a Cartesian component, i.e., $\mu = x,y,z$; for convenience the coordinate system has been chosen such that the effective transition dipole of the chromophore lies along the z axis.) The αth column of the matrix $\mathbf{U}$ is thus just the eigenvector of the corresponding polarization mode.

But it has been recognized for several years that a purely dielectric theory such as the one outlined above does not adequately describe the entire perturbation of the solute's electronic states deriving from solvation.[37] One also needs to provide for the shifting of these states that arises from intrinsically quantum mechanical effects (exchange correlation and wave function orthogonality) as well as from any residual electrostatic effects that are not well represented by the simple truncated multipole expansion of the Coulombic forces that we have adopted. As noted previously,[18,21] we have found that these various effects, although in principle difficult to model due to their rather indirect definition as ''whatever is left'', actually are easily represented phenomenologically as a sum of short-range (and, of course, geometry-dependent) pair potentials. In particular, we have found that the (blue shifted) contribution of these repulsive effects can be written as

$$\delta(h\nu)_{\text{repulsive}} = b\sum_{j=1}^{z} (r_{0j})^{-2},$$

where the sum here is over the z solvent atoms that lie within a prescribed cutoff distance, and b is a parameter determined by fitting the results of our calculations to the spectroscopic shifts reported for small clusters ($n = 3, 5,$ and 7).

That the collective dielectric response of the solvent atoms as well as the repulsive contribution to the spectral shift depend sensitively on the cluster geometry implies, obviously, that a comparison with experiment entails averaging over an appropriate set of cluster configurations. But herein lies the potential problem. The set of configurations generated for this purpose must characterize the clusters actually present in expansion jets, but one cannot necessarily assume that these clusters are thermally equilibrated. They in fact may be ''frozen'' in local energy minima corresponding to geometries far from the structure of the global minimum.

(Note that only kinetic stability is required here; the fact that given sufficient time the structures might rearrange and reach the equilibrium geometry is irrelevant if that rearrangement time is long compared with the flight time through the apparatus.) Thus one must be cautious when drawing conclusions that depend on the association of experimental results with predictions derived for minimum-energy structures[7] or even for those structures that are found to be most populated at some particular temperature.[27–29]

And, of course, cluster structures can be fluxional on the time scale of the experiment if the internal energy of the cluster is sufficient for the surmounting of local potential energy barriers, with the probability of such a fluctuation being fixed as much by the distribution of local barrier heights as by the relative stabilities of the states that those barriers separate. It was with these considerations in mind that we previously investigated the structural fluctuations in benzene·(Ar)$_n$ clusters,[38] the study of which initially prompted the series of experiments by Whetten and co-workers[9,10,20] that eventually led to the present work. We adopted an instantaneous normal mode (INM) analysis approach to thinking about cluster fluidity, one first devised by Keyes and collaborators[39] as a means for characterizing diffusion in supercooled liquids, and demonstrated that this formalism permits the identification of the cluster melting regime and suggests a dynamical picture of this regime in terms of a series of cluster isomerizations, the rate of which increase as the cluster temperature is increased. In the present work we return to the INM formalism, which as input requires the same set of system configurations upon which our microscopic dielectric model is based. (Just as in a conventional normal mode analysis, an INM analysis involves an expansion of the potential energy about particular configurations, although now the expansion is about a series of instantaneous configurations rather than a stationary configuration.) The dynamics so obtained are used to demonstrate that the structural fluctuations associated with cluster melting are manifested in a change in the temperature dependence of the computed spectral linewidth. We refer the reader to the relevant publications to discover the details of the INM methodology.[37,38] The important point we are obliged to reemphasize here, though, is that the INM formalism too is microscopic in nature and can be implemented for any suitable set of cluster geometries.

III. MODELING SPECTRAL LINEWIDTHS

Since we can assign a spectral shift to a particular cluster geometry, we are able to determine the inhomogeneous broadening of the spectral line, i.e., to calculate the linewidth due to the distribution of local environments in the vicinity of the chromophore.[40] Practically, though, it is important to ask how many cluster configurations are required for the reliable prediction of a spectral width. To investigate this question, we have generated 3000 configurations of benzene·(Ar)$_{19}$ by a standard Metropolis Monte Carlo walk at 20 K. (The Metropolis MC technique used in determining these configurations was the same one used in previous
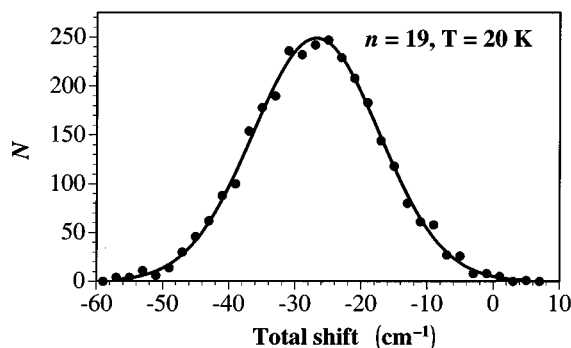
FIG. 1. Line shape of the 6^1_0 transition in benzene·(Ar)$_{19}$ at 20 K. The calculated points represent the number of configurations (N) from the total of 3000 that yield a total spectral shift within a 2 cm^{-1} interval centered about the frequency at which the point is plotted. The solid line is an appropriately normalized Gaussian fit to the calculated points.

FIG. 3. Calculated and observed spectral shifts for benzene·(Ar)$_n$ clusters at 20 K. The data sets plotted correspond to shifts calculated using wetting cluster structures (solid circles), shifts calculated using nonwetting structures (open symbols), and experimental shifts from Ref. 6 ($\times$). Calculated values of the FWHM of these spectral peaks are represented as error bars, with those corresponding to the wetting structures being shown with a darker line.

studies.[13,14,17–19] Initially the Ar atoms were distributed at random throughout a sphere with benzene at the center, with subsequent equilibrations being carried out at 5 K intervals as the temperature of the system was reduced to the desired temperature for the configurations.) The distribution of spectral shifts for this set of cluster geometries is shown in Fig. 1. The curve shown in this figure does not represent a smoothing of the calculated data but rather is a fit of a Gaussian function to the data by means of a Levenberg–Marquardt nonlinear least squares algorithm.[41] The Gaussian fit to this data is excellent—the reduced chi-squared is just 0.75, and the calculation of the moments of the distribution yield a mean and standard deviation of −26.84 and 9.61 cm^{-1}, respectively, for the actual data and −26.82 and 9.62 cm^{-1} for the fit Gaussian distribution—so we can be confident that the line shape will approach a Gaussian form as the number of configurations becomes large. Important for our purposes, though, is the observation that the moments of the calculated data converge quite rapidly to those of the limiting Gaussian distribution. In Fig. 2, we display the calculated moments (actually, the calculated peak center and the derived FWHM, which for a Gaussian line shape is simply related to the standard deviation of the distribution) as a function of the number of included configurations. On the basis of these results,
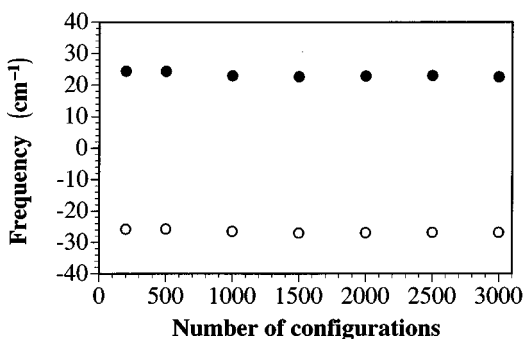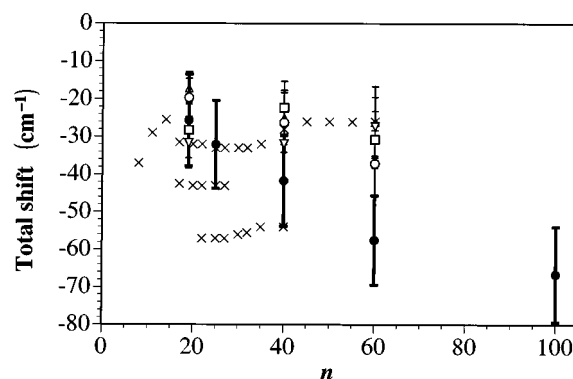
we feel quite justified in reporting spectral peak positions and widths derived from smaller sets of configurations, typically 200–500, than would be necessary for defining a smooth Gaussian line shape.

IV. CLUSTER SPECTRA

A. Spectral shifts

We summarize our calculated spectral shifts and linewidths in Fig. 3, where one will also find the experimental peak positions reported by Knochenmuss, Ray, and Hess.[6] Note first the obvious result that our calculated peak positions (the filled circles) become increasingly red shifted towards the reported bulk values[35,42] as the number of Ar atoms increases in contrast to the trend shown by the experimental points. Although for the smaller clusters the calculated linewidths are such that they encompass the experimental points, such is not the case for the largest clusters; for $n = 60$ and greater, even the most uncritical observer would have to conclude that our results do not reproduce the experimental findings. We thus are led to suspect that the cluster configurations upon which our shifts are based do *not* represent the geometries actually found in the expansion jets. It is important that the reader recognize that the lack of correspondence between these calculated and measured peak positions does not, as has been intimated elsewhere,[6] necessarily indicate that there are fundamental errors in either the theoretical or experimental values. A nonequilibrium distribution of cluster structures in the jets also would yield this observed discrepancy.

That the experimental data display a plateau behavior for $n > 40$ suggests that the local environment of the benzene's bonding in these larger clusters is quite similar. Since the dielectric (red) component of the total spectral shift is relatively slow to converge with increasing number of Ar atoms when the chromophore is bound at an interior wetting site,[18] the most reasonable solution to our quandary is to consider nonwetting geometries, for which the added atoms would be

FIG. 2. Convergence of the total spectral shift (open circles) and FWHM (closed circles) for the 6^1_0 transition in benzene·(Ar)$_{19}$ at 20 K with increasing number of included configurations.

expected to be at a greater distance from the benzene molecule and thus to have little additional effect on the dielectric response. We therefore have generated configurations of benzene·(Ar)$_n$ in which benzene is bound to the surface of an Ar cluster. Initial conditions for the MC walks that yielded these configurations were determined by first equilibrating neat Ar$_n$ clusters at relatively high temperatures—temperatures high enough that the clusters were in the ''fluid'' regime—and then positioning those clusters immediately above one of the faces of the benzene ring, with the center of mass of the Ar cluster lying along the sixfold symmetry axis. These starting geometries were then immediately quenched to the lower temperature used in the configuration generation (20 K) and the preliminary equilibration steps were performed in the usual manner.[17] The configurations accumulated for spectral analysis were examined individually to make sure that they indeed described nonwetting cluster structures, i.e., that no Ar atoms had crossed the plane of the benzene ring. We do not expect, of course, that this scheme for generating cluster structures will sample all possible external benzene binding sites; any MC walk that would visit all such sites would be characterized by an energy high enough to overcome (eventually) the kinetic barriers to insertion of the chromophore into the cluster. To deal with this intrinsic limitation on our sampling efficiency, we instead have chosen a set of different initial starting geometries for the neat Ar cluster used in the scheme described above, and have generated independent sets of configurations based on these different starting geometries.

Our calculated spectral shifts for nonwetting clusters are shown in Fig. 3 as open symbols. For the smallest clusters considered ($n=19$) the total shifts calculated are comparable with the shift calculated for the fully equilibrated wetting geometries but display a large amount of scatter (15–20 cm^{-1}). Such a large degree of scatter is, of course, quite reasonable in these clusters, since there can be a wide range of surface binding environments in these species. Two examples of these sites are shown in Fig. 4, the first corresponding to binding at the ''side'' of the Ar cluster and the second to binding at a capping site (the cap atom is actually displaced as a consequence of the binding). In the large-cluster limiting case, though, the Ar cluster is expected to be essentially spherical and the number of unique surface binding sites for the benzene molecule should not vary significantly with cluster size. That the reported experimental shifts for $n=40-60$ fall within the range of the shifts calculated for these surface-bound species strongly suggests that a significant fraction of the clusters formed in the jets indeed are of this type, kinetically (but not thermodynamically) stable clusters in which the chromophore is bonded at the exterior of a neat Ar cluster. An example of just such a cluster (for $n=60$) is shown in Fig. 5.

Direct evidence for the assertion that the spectra of surface-bound benzene molecules should converge quite rapidly to a result that displays no further size dependence is seen in the plots shown in Fig. 6. There we compare the calculated spectrum of couplings [Eq. (2.1), with a 2 cm^{-1} frequency bin size] for $n=40$ (solid points) and $n=60$ clus-
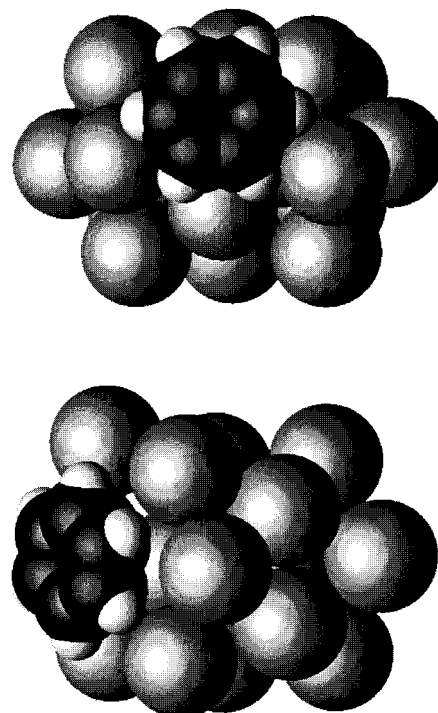

FIG. 4. Representative configurations of nonwetting benzene·(Ar)$_{19}$ clusters at 20 K, corresponding to binding of the aromatic at the side of the neat Ar cluster (upper drawing) and at a capping site (lower drawing).

ters (for clarity, only the lines connecting the latter set of calculated points are shown) determined using, in the top panel, fully equilibrated wetting structures and, in the bottom panel, one of the sets of kinetically stable nonwetting structures. Note that even for these relatively large clusters, $J(\omega)$ values associated with fully solvated benzene are not converged, the largest differences appearing at polarization mode frequencies for which coupling to the benzene's effective transition dipole moment is the greatest. (Comparison of these plots with ones published previously[21] pertaining to benzene dissolved in bulk liquid Ar also indicates that even the $n=60$ clusters do not reproduce the solvation environment of the analogous bulk.) In contrast, the nonwetting structures yield spectra of couplings that display only a negligible size dependence. But, of course this result is perfectly reasonable—far fewer Ar atoms are required to yield the asymptotic limit of the dielectric component of the shift if the interaction is only with one face of the chromophore. (Only the convergence of the dielectric contribution to the total shift needs to be considered here, since we have shown elsewhere that the repulsive component routinely saturates at a smaller number of solvent atoms.[18])

B. Linewidths

While the above analysis appears to provide a satisfactory explanation of the seemingly anomalous size dependence of the spectral shift observed for benzene·(Ar)$_n$ clusters[6,10] and in particular of the apparent failure of those shifts to display the expected convergence to corresponding
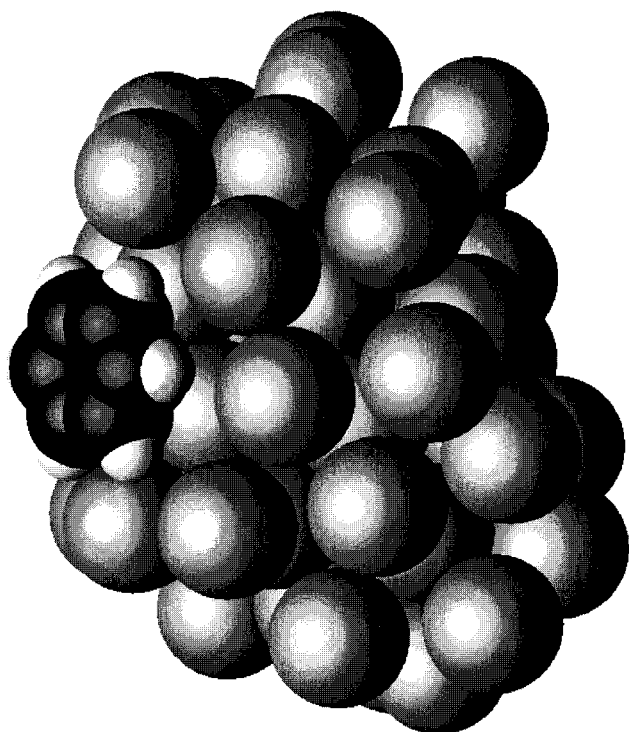
FIG. 5. Representative configuration of a nonwetting benzene·(Ar)$_{60}$ cluster at 20 K.

FIG. 6. Spectra of couplings for various large benzene·(Ar)$_n$ clusters. In both plots the solid circles correspond to $n = 40$ while the solid lines connect points corresponding to $n = 60$. Frequencies on the horizontal scale are given as fractions of the pure solvent frequency. The upper panel contains results calculated using sets of wetting configurations, while the lower panel contains the analogous results determined using nonwetting configurations.

bulk values,[35,42] there is as yet a troubling discrepancy between the theoretical predictions and the experimental results that must be addressed. By examining the plot shown in Fig. 3 it is easily seen that our calculations predict substantial inhomogeneous broadening of the benzene spectral peaks, with a typical FWHM value being on the order of 25–30 cm^{-1}. The experimental peaks displayed by Knochenmuss et al.[6] however, appear not to be broadened to that extent, but rather are characterized by widths that are roughly half of what we have calculated (i.e., in the range 10–15 cm^{-1} at most). Most obvious is the observation that for $n = 2 - 40$ clusters, the experiments indicate the presence of individual absorption maxima, the envelope of which is spanned by our single Gaussian peak of greater width. Is there a fundamental reason that our formalism does not resolve these individual peaks, or have we implemented that formalism in a way that obscures any substructure?

Missing from our analysis to this point, of course, is any direct reference to the actual *dynamics* of the clusters. While canonical MC calculations provide an efficient means for averaging over the thermally accessible spatial configurations of the system of interest, they necessarily ignore the possibility that a species of finite lifetime in fact may only access a very small number of those states. The very fact that the spectra of the largest clusters appear to be dominated by contributions from kinetically stable nonwetting structures testifies to the relatively slow rate of interconversion between structural types. Thus any conclusive comparison between theory and experiment also must include a comparison with the results derived from the application of a dynamical
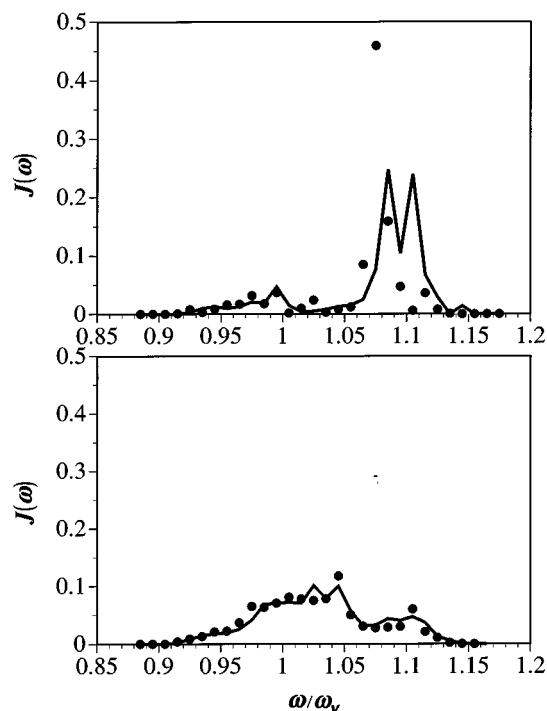
approach for those clusters that yield multiple peaks in the experimental spectra.

We have chosen to focus on $n = 25$ clusters, since these species are well within the size range for spectral substructure as reported by Knochenmuss et al.[6] Although in carrying out the analogous MC calculations it was sufficient to hold the benzene molecule fixed at the coordinate origin and only to consider the motion of the Ar atoms, such a procedure unacceptably biases an MD calculation. Consequently, we have carried out full MD calculations, the only constraint being that the benzene molecule was held internally rigid (through the familiar quaternion formalism[43]) throughout. Initial spatial coordinates for these trajectories were chosen from a set of equilibrated MC configurations at the desired temperature; initial velocities were chosen at random from the appropriate thermal distribution.[44] Trajectories were integrated using a leap-frog Verlet algorithm[45] with a time step of 0.002 ps, with configurations being stored every 100 ps following an initial 500 ps equilibration interval. (The overall translation and rotation of the cluster was removed following the equilibration period.[44] RMS energy fluctuations found in these trajectories were less than 0.03% of the total energy, while quaternion normalization was preserved to within 0.1%.)

We give the results of these calculations, carried out at two different temperatures, in Fig. 7. Each plot has been normalized such that the area under the curve is unity, and summarizes spectral shifts determined using the same for-
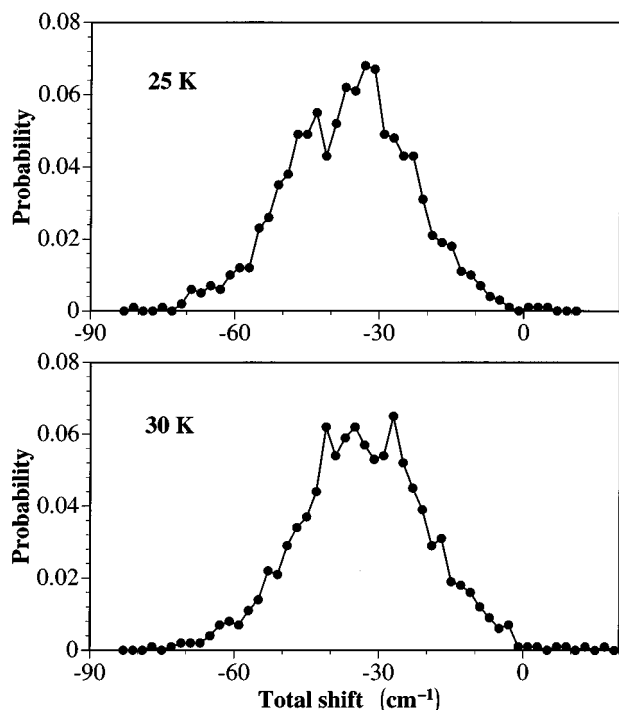
FIG. 7. Line shapes for benzene·(Ar)$_{25}$ determined using 1800 MD cluster configurations as described in the text. The points displayed represent the sum of contributions within a 2 cm^{-1} interval about the plotted frequencies; areas under the curves have been normalized to unity. The solid lines are meant to guide the eye only.

FIG. 8. Comparison between the temperature dependence of the FWHM for benzene·(Ar)$_{19}$ clusters (open circles) and the behavior of the Ar atom diffusion constant as determined from an INM analysis (closed circles). The error bars shown correspond to one standard deviation in the calculated diffusion constants; error bars that are not shown are smaller than the size of the plotting symbols. The arrows indicate the vertical scale appropriate to each of the data sets.

malism as before, but now based on 1800 individual dynamically accessible configurations (200 configurations from each of 9 independent trajectories). In the top panel, the line shape determined at 25 K is plotted, and there one sees that even though the overall absorption envelope is roughly Gaussian in form, definite substructure is revealed. Notably, a distinct gap is found in the line shape at roughly −40 cm^{-1}. It should be mentioned that this feature is maintained as the number of included configurations is increased, so we do not believe it to be an artifact of the calculation. Also, the two peaks that emerge from the overall line shape occur at, roughly, 35 and 45 cm^{-1}, in quite reasonable agreement with the spectral structure reported by Knochenmuss et al.[6] These results tend to support the contention by that group that the structure observed in the spectra of $n = 20$–40 clusters indeed derives from the existence of distinct isomers and, in addition, suggest that the clusters formed in their experiments can be characterized by a temperature near the one we are considering here, namely 25 K. But of particular practical importance here is the finding that the discrepancies in numbers of absorption peaks and in the widths of those peaks found when comparing the calculated and experimental results in this system stem from a neglect of explicit cluster dynamical effects.

Our calculations furthermore reveal the line shape to have exactly the sort of temperature dependence seen in the experiments (Figs. 3 and 5 from Ref. 6). The plot appearing in the lower panel of Fig. 7 shows that as the clusters are warmed, the spectral intensity shifts towards the red, reflect-
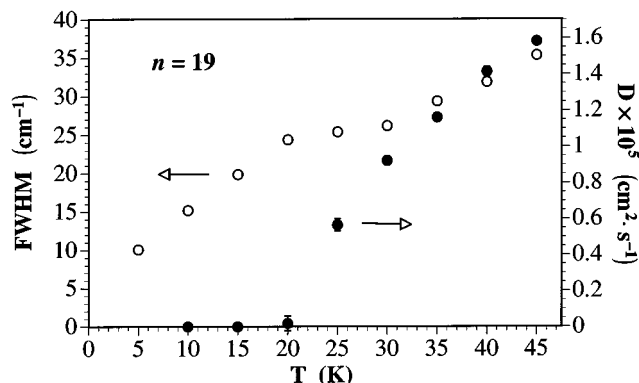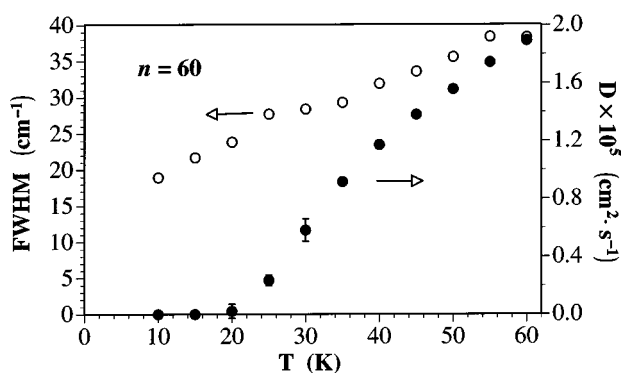
ing a change in the distribution of states visited by the cluster as the average energy increases. The gross features of this result also are reflected in the spectral parameters derived from calculations based on MC configurations—at 25 K the spectral shift and FWHM are −32.1 and 23.5 cm^{-1}, respectively, while at 30 K the corresponding values are −33.7 and 32.1 cm^{-1}—but those features alone clearly are not the whole story. Although in examining the temperature effect on the line shape it certainly would be preferable to consider a wider temperature range than the one considered here, we necessarily are limited by the range of energies over which the clusters are stable (that is, the trajectory time must be short compared with the average time between evaporation events) yet sufficiently fluxional that a range of coordinate states can be accessed. But even a 5 K range is large enough to demonstrate that a significant change in the line shape with changing expansion conditions should be expected.

V. SPECTRAL LINEWIDTHS AND "MELTING"

In previous work,[18] we showed that the calculated spectral shift of benzene embedded in an Ar cluster is only a weak function of temperature, since the component dielectric and repulsive contributions to the shift tend to vary in parallel. Yet it seems that there ought to be some spectral manifestation of the structural fluctuations loosely termed melting. The obvious candidate is the linewidth of the absorption envelope, since the extent of inhomogeneous broadening surely depends on the number of accessible isomeric forms at the given temperature. In Fig. 8, we plot the FWHM of the spectral peak as a function of temperature for benzene·(Ar)$_{19}$, revealing the distinct break in the curve that occurs over the range 20–30 K. To make the connection between this break and evidence of structural fluctuations, we also plot on the same temperature scale Ar diffusion constants as given by an INM analysis based on the same cluster configurations as the spectral analysis. The correspondence between these two graphs really is quite striking—the in-

FIG. 9. As in Fig. 8, but for benzene·(Ar)$_{60}$.

FIG. 10. Temperature dependence of projected and unprojected diffusion constants for Ar atoms in benzene·(Ar)$_{19}$. The squares are the diffusion constants from the complete set of Ar atoms (already reported in Fig. 8), while the circles and triangles denote the diffusion constants corresponding to just the nearest-neighbor and non-nearest-neighbor Ar atoms, respectively. The error bars shown for these quantities are as in Fig. 8. The horizontal error bar above the center of the figure demarcates the temperature interval over which a spectroscopic signature of melting is observed (Fig. 8).

crease in the diffusion constant that we earlier identified as defining the structural transition region occurs exactly over the same temperature range as does the change of slope of the FWHM. And this result is not unique to the $n = 19$ clusters! The analogous results for $n = 60$ clusters are shown in Fig. 9, in which the transition region has broadened to the 20–40 K range although the basic trends remain unaltered. How does one understand this behavior of the linewidth, then, in terms of the fluctuations known (or proposed) to occur as the cluster moves from a rigid, solidlike structural regime to one which is fluid?

To answer this question, we require further clarification of the exact nature of the melting transition. In previous studies, we noted that a direct examination of cluster configurations revealed no significant change in the appearance of the local benzene–Ar binding environment with increasing temperature, but can we say more? The diffusion constant calculations described above do not distinguish *per se* between subsets of Ar atoms that might behave quite differently. A straightforward modification of the INM formalism permits such a distinction, however. As reported elsewhere,[46] one needs only to partition the total INM density of states by projecting out the contributions from a selected subset of the total number of atoms. Specifically, the averages involving INM frequencies must be weighted by a projector of the form

$$P_\alpha^A = \sum_{j=1}^{N_A} \sum_{\mu=x,y,z} [U_{j\mu,\alpha}]^2,$$

where N_A ($\leq N$) defines that specific subset and $\mathbf{U}$ is a $3N \times 3N$ orthogonal matrix [*not* the same matrix that appears in Eq. (2.2)], the columns of which are the INM eigenvectors. For our purposes the useful mode partitioning isolates the contributions to the INMs from the nearest-neighbor Ar atoms, defined here as those lying within the radial cutoff distance used in the calculation of the repulsive contributions to the total spectral shift (namely, for $r \leq 5.4$ Å), from those of the non-nearest-neighbor atoms.

Diffusion constants calculated for the two subsets of Ar atoms thus defined in benzene·(Ar)$_{19}$ clusters are given in Fig. 10 along with those appropriate to the entire cluster. It is immediately evident that those atoms lying more distant

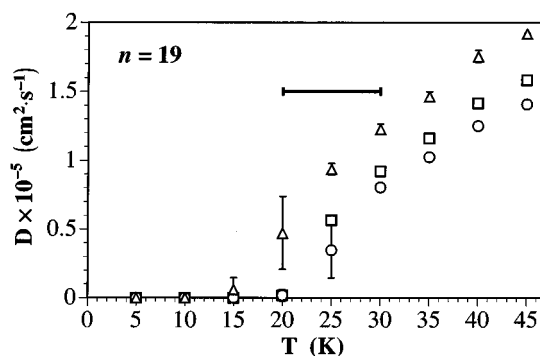from the benzene molecule, which include those bound at the periphery of the ring, are the first to exhibit fluidlike behavior as the temperature is increased through the melting regime. Furthermore, they generally are more mobile at all temperatures beyond the melting threshold. One also finds that the nearest-neighbor projected diffusion constants are much more similar in magnitude to the unprojected ones than are the non-nearest-neighbor projected values. This result, though, merely reflects the fact that in relatively small clusters such as these a large fraction of the atoms lie immediately on either face of the benzene ring. It should be noted that atom exchange between the nearest neighbor and more distant atom subsets is not precluded in our analysis, so a contribution to the diffusion constants of both subsets of atoms may derive from that motion in the high-temperature regime.

Returning to the consideration of the spectral linewidth's temperature dependence, we now may deduce more readily the nature of the atomic dynamics that yields the observed behavior. In the low-temperature regime, prior to the onset of significant Ar atom motion, one finds a (more or less) linearly increasing linewidth, indicative of the increasing amplitude of the motion of the benzene molecule within the relatively rigid first solvation shell. This motion, as well as the increasing magnitude of the vibrational displacements of the Ar atoms, yields an inhomogeneity in the local bonding environment that is translated into the observed line broadening. This basic picture changes, however, when isomerizations within the Ar shells become energetically possible. But the interactions between Ar and benzene are sufficiently great that throughout this regime and beyond, the Ar atoms in immediate contact with the chromophore (above and below the plane of the ring) tend to adhere and to move with it. The transition from solidlike to fluidlike cluster structures is thus more limited than has been generally thought; the truly fluidlike dynamics is exhibited only by the atoms in the second solvation shell (or, for larger clusters, in yet more distant

shells) or by Ar atoms bound at the ring periphery. Note that the slope of the FWHM versus T line is less subsequent to the melting region (i.e., above the ''freezing'' temperature) than it is prior to that region, a result which itself suggests that more distant interactions are responsible for the increasing inhomogeneity at the highest temperatures. (These less well bound atoms also are the ones that would be expected to evaporate first from the cluster as the temperature is increased further.)

Yet another way of looking at this transition recalls the picture of cluster melting proposed by Berry and co-workers,[47] who have described the finite melting range as a regime of phase coexistence. Viewed appropriately, that model is in fact relevant to our findings. At the melting threshold temperature, a small fraction of the ensemble of clusters will be characterized by fluid-like structures, at least with respect to the arrangement of the non-nearest-neighbor atoms. This fraction then increases as the temperature is raised until, when the freezing point is finally reached, all the clusters exhibit such structures. One consequently could estimate the fractional populations of rigid and fluidlike cluster geometries at a particular temperature just by noting the relative difference between that temperature and the observed melting and freezing temperatures. But we want to emphasize that the above interpretation of a phase coexistence model does *not* imply that all Ar atoms need be disordered at high temperatures. A decoupling of the motion of the non-nearest-neighbor atoms from that of the nearest-neighbor atoms as a result of cluster melting is in fact quite sufficient for there to be a linewidth bimodality such as we observe in Figs. 8 and 9.

Our interpretation of the nature of phase coexistence in these clusters also is consistent with an experimental study of Guillaume *et al.*[7] to which we alluded in the Introduction. They concluded that the time scale for isomer interconversion in benzene·(Ar)$_{20}$ clusters could not be reconciled with a picture of rigid-fluid phase coexistence in *individual* clusters. We concur with this analysis. That some clusters in the ensemble may be disordered (fluidlike) while others are quite ordered certainly need not imply phase coexistence in any particular isolated cluster.[48] In fairness, we should note, however, that our agreement with a number of their other conclusions in this as well as their more recent work[8] is not complete. In systems away from equilibrium, a definitive determination of just which structures contribute to the spectroscopy certainly is not, in our opinion, as clear-cut as they suggest; there is no *a priori* reason that only minimum-energy structures should be populated, and indeed we suggest otherwise.

Ultimately, the above linewidth analysis suggests another way of approaching the study of cluster structural fluctuations that could prove useful in clarifying the more typical analysis based on peak positions. Unfortunately, selecting cluster temperatures or even ascertaining cluster temperatures (assuming, of course, that they are characterized by a single temperature at all) is a vexing experimental problem. Turning this problem around, though, we would suggest that a study of absorption linewidths as a function of expansion

conditions (including nozzle temperature) at least might yield information that would help bracket the cluster temperature more accurately than is now possible.

VI. SUMMARY

In this paper, we have described a calculation of the absorption spectra of large benzene·(Ar)$_n$ clusters that resolves the apparent discrepancy between the anticipated behavior of the spectra with increasing number of Ar atoms and the experimental results of Knochenmuss *et al.*[6] and leads to the assignment of the relatively small spectral shifts seen experimentally to nonwetting cluster isomers. On detailed inspection, the prior lack of agreement between experiments and theoretical predictions is seen to derive from the differences in the clusters being studied. Theoretical work usually is based on the assumption that a set of well-equilibrated cluster structures is available for analysis, since such clusters are the easiest to simulate. (Their stability makes the appropriate configuration averaging relatively straightforward and accurate.) And, of course, when one develops a model to aid in the interpretation of the experiments, the natural inclination is to think in terms of well-characterized, minimum-energy clusters. The evidence gathered in the present work, however, suggests that kinetically stable, but by no means thermodynamically stable, cluster states may be populated quite significantly and in fact may provide the dominant contribution to the observed spectra.

In fact, it now appears clear that a one-to-one correspondence between experimental and theoretical spectra is only obtainable when actual cluster dynamics is incorporated explicitly into the modeling. The time scale for significant isomerization of these clusters can be long compared with the time between cluster creation and observation, so that only a small set of the energetically accessible cluster geometries contribute to the observed spectrum. The envelope of the absorption is nonetheless given quite reliably by a purely statistical model. One therefore needs to ask exactly what sort of comparison is desired when designing a simulation of cluster systems.

Our calculations also have clarified substantially the character of the melting transition in benzene–Ar clusters, having shown that not all solvent atoms need participate equally in the dynamical changes that accompany this transition. Nearest-neighbor atoms are notably less mobile than are the more distant ones, and they do not contribute appreciably to the onset of atomic self-diffusion at the melting temperature. These conclusions stem directly from our identification of a spectral signature of the transition, a bimodality in the temperature dependence of the width of the absorption envelope, that can be correlated with unambiguous measures of atomic mobility. In finding this spectral signature, we believe we have obtained the elusive relationship between cluster spectroscopy and melting that was sought by Whetten and co-workers[9,10,20] in their original investigations. Interestingly, though, it is not (as many have assumed) a change in the position or the multiplicity of spectral peaks

that signals the onset of melting, but rather the temperature dependence of the width of the absorption envelope that provides the ultimate clue.

ACKNOWLEDGMENTS

[1] See, for example, S. Leutwyler and J. Bösiger, Chem. Rev. **90**, 489 (1990); E. R. Bernstein, in *Studies in Physical and Theoretical Chemistry*, edited by E. R. Bernstein (Elsevier, Amsterdam, 1990), Vol. 68, p. 551; J. Jortner, Z. Phys. D **24**, 247 (1992), and the references cited therein.

[2] C. Guillaume, J. Le Calvé, I. Dimicoli, and M. Mons, J. Phys. Chem. **98**, 13443 (1994).

[3] V. A. Venturo, P. M. Maxton, and P. M. Felker, Chem. Phys. Lett. **198**, 628 (1992).

[4] M. Schmidt, M. Mons, and J. Le Calvé, Chem. Phys. Lett. **177**, 371 (1991).

[5] M. Schmidt, J. Le Calvé, and M. Mons, J. Chem. Phys. **98**, 6102 (1993).

[6] R. Knochenmuss, D. Ray, and W. P. Hess, J. Phys. Chem. **100**, 44 (1994).

[7] C. Guillaume, M. Mons, J. Le Calvé, and I. Dimicoli, J. Phys. Chem. **97**, 5193 (1993).

[8] C. Guillaume, J. Le Calvé, I. Dimicoli, and M. Mons, J. Chim. Phys. Phys.-Chim. Biol. **92**, 334 (1995).

[9] M. Y. Hahn and R. L. Whetten, Phys. Rev. Lett. **61**, 1190 (1988).

[10] X. Li, M. Y. Hahn, M. S. El-Shall, and R. L. Whetten, J. Phys. Chem. **95**, 8524 (1991).

[11] R. Nowak, J. A. Menapace, and E. R. Bernstein, J. Chem. Phys. **89**, 1309 (1988).

[12] R. S. Berry, T. L. Beck, H. L. Davis, and J. Jellinek, Adv. Chem. Phys. **70**, 74 (1988).

[13] J. E. Adams and R. M. Stratt, J. Chem. Phys. **93**, 1332 (1990).

[14] J. E. Adams and R. M. Stratt, J. Chem. Phys. **93**, 1632 (1990).

[15] N. Ben-Horin, U. Even, and J. Jortner, Chem. Phys. Lett. **188**, 73 (1992).

[16] L. S. Bartell and F. J. Dulles, J. Phys. Chem. **99**, 17107 (1995).

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

[18] J. E. Adams and R. M. Stratt, J. Chem. Phys. **99**, 789 (1993).

[19] J. E. Adams and R. M. Stratt, Z. Phys. D **26**, S323 (1993).

[20] M. Y. Hahn, Ph.D. thesis, University of California, Los Angeles, 1989.

[21] R. M. Stratt and J. E. Adams, J. Chem. Phys. **99**, 775 (1993).

[22] See, for example, J. Bösiger, R. Knochenmuss, and S. Leutwyler, Phys. Rev. Lett. **62**, 3058 (1989); S. Leutwyler and J. Bösiger, Chem. Rev. **90**, 489 (1990); T. Troxler and S. Leutwyler, J. Chem. Phys. **95**, 4010 (1991).

[23] R. Sussman, U. Zitt, and H. J. Neusser, J. Chem. Phys. **101**, 9257 (1994).

[24] D. Bahatt, A. Heidenreich, N. Ben-Horin, U. Even, and J. Jortner, J. Chem. Phys. **100**, 6290 (1994).

[25] A. Heidenreich, D. Bahatt, N. Ben-Horin, U. Even, and J. Jortner, J. Chem. Phys. **100**, 6300 (1994).

[26] L. E. Fried and S. Mukamel, Phys. Rev. Lett. **66**, 2340 (1991); J. Chem. Phys. **96**, 116 (1992); Adv. Chem. Phys. **84**, 435 (1993).

[27] O. Bludsky, V. Spirko, V. Hrouda, and P. Hobza, Chem. Phys. Lett. **196**, 410 (1992).

[28] J. Vacek, K. Konvicka, and P. Hobza, Chem. Phys. Lett. **220**, 85 (1994).

[29] J. Vacek and P. Hobza, J. Phys. Chem. **98**, 11034 (1994); **99**, 17088 (1995).

[30] D. C. Easter, A. P. Baranavski, and M. Hawley, Chem. Phys. Lett. **206**, 329 (1993).

[31] F. J. Dulles and L. S. Bartell, J. Phys. Chem. **99**, 17100 (1995).

[32] M. J. Ondrechen, Z. Berkovitch-Yellin, and J. Jortner, J. Am. Chem. Soc. **103**, 6586 (1981); A. Rahman, Phys. Rev. A **136**, 405 (1964).

[33] See, for example, D. Chandler, K. S. Schweizer, and P. G. Wolynes, Phys. Rev. Lett. **49**, 1100 (1982); R. F. Loring, J. Chem. Phys. **92**, 1598 (1990); J. Phys. Chem. **94**, 513 (1990); Y.-C. Chen, J. Lebowitz, and P. Nielaba, J. Chem. Phys. **91**, 340 (1989).

[34] Z. Chen and R. M. Stratt, J. Chem. Phys. **95**, 2669 (1991).

[35] R. Nowak and E. R. Bernstein, J. Chem. Phys. **87**, 2457 (1987).

[36] See, for example, A. O. Caldeira and A. J. Leggett, Ann. Phys. (N.Y.) **149**, 374 (1983).

[37] V. Dobrosavljevic, C. W. Henebry, and R. M. Stratt, J. Chem. Phys. **88**, 5781 (1988); **91**, 2470 (1989).

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

[39] G. Seeley and T. Keyes, in *Spectral Line Shapes*, edited by J. Szudy (Ossolineum, Wroclaw, Poland, 1989), Vol. 5, p. 649; G. Seeley and T. Keyes, J. Chem. Phys. **91**, 5581 (1989); B. Madan, T. Keyes, and G. Seeley, *ibid.* **92**, 7565 (1990); **94**, 6762 (1991); G. Seeley, T. Keyes, and B. Madan, *ibid.* **95**, 3847 (1991).

[40] We recognize, of course, that inhomogeneous broadening is not the only potential mechanism for line broadening in clusters. For a discussion of approaches that also permit inclusion of homogeneous effects such as motional narrowing (but not the collective character of the dielectric response), see Ref. 26.

[41] W. H. Press, S. A. Teukolsky, W. T. Vetterling, and B. P. Flannery, *Numerical Recipes in* FORTRAN: *The Art of Scientific Computing*, 2nd ed. (Cambridge University Press, Cambridge, 1992), pp. 678–683.

[42] Y. Diamant, R. M. Hexter, and O. Schnepp, J. Mol. Spectrosc. **18**, 158 (1965); R. B. Merrithew, G. V. Marusak, and C. E. Blount, *ibid.* **25**, 269 (1968); T. J. Barton, I. N. Douglas, and R. Grinter, Mol. Phys. **30**, 1677 (1975).

[43] M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Clarendon, Oxford, 1989), pp. 88–89.

[44] J. E. Adams, J. Chem. Phys. **92**, 1849 (1990).

[45] Reference 43, pp. 78–82, 89–90.

[46] M. Buchner, B. M. Ladanyi, and R. M. Stratt, J. Chem. Phys. **97**, 8522 (1992).

[47] R. S. Berry, T. L. Beck, H. L. Davis, and J. Jellinek, Adv. Chem. Phys. **70**, 74 (1988), and the references cited therein; R. S. Berry and D. J. Wales, Phys. Rev. Lett. **63**, 1156 (1989). For more recent work in this area, see J. P. K. Doye and D. J. Wales, J. Chem. Phys. **102**, 9673 (1995).

[48] In an ergodic macroscopic system there is no real difference between the behavior of different members of an ensemble and the behavior seen in any one member. Given a reasonable time interval, even a single ensemble member will evolve so as to sample virtually the entire ensemble. However, in a small system studied over microscopic times, these two concepts can in principle and, we suggest, in practice, be quite distinct.