Optical properties of a chromophore embedded in a raregas cluster: Cluster size dependence and the approach to bulk properties

John E. Adams and Richard M. Stratt

Optical properties of a chromophore embedded in a rare-gas cluster: Cluster size dependence and the approach to bulk properties

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

One of the most intriguing aspects of the behavior of small clusters is the extent to which their physical and chemical properties depend sensitively on the size of the clusters. But for clusters that are "large enough," surely their properties must approach those of the corresponding bulk systems. The property of special interest in the present work is the shift in the electronic absorption of a chromophore (benzene) deriving from interaction with nonpolar solvent atoms (Ar), a shift that can be calculated using a microscopic formalism described in this and in the preceding paper which is equally well suited to the study of cluster and condensed phase environments. We are able to identify the evolution of the collective character of the dielectric response of the solvent atoms as being the key feature of the optical properties of these clusters that determines the degree to which their behavior is bulklike. Furthermore, we can associate specific spectral features with particular classes of cluster geometries, and in doing so we derive support for our previous speculations concerning the evidence for the contribution of metastable, nonwetting cluster structures to the experimental spectra.

I. INTRODUCTION

Small clusters afford a unique opportunity for the examination of solvation phenomena, inasmuch as they in principle permit a correlation of observed properties with specific cluster structures. Accordingly, considerable effort to date has been expended in the study of size-specific cluster properties,[1–10] but experiments for the most part have as yet provided but partial answers. The internal temperatures of clusters produced in expansion jets still can only be bracketted at best, and so the question of what individual isomeric structural forms actually contribute to the observed properties is very much an open one. Theoretical investigations have clarified this situation substantially, however.[10–16] The exploration of stable cluster isomers and the energy barriers to their interconversions has become almost commonplace, certainly for those clusters for which empirical classical force fields have been devised but also to a certain extent for fully quantum mechanical systems.[17] There has been a lesser emphasis placed on associating these stable or metastable geometries with measured physical properties[12,18–21] (such work has taken somewhat of a backseat to considerations of the structural fluctuations usually termed "melting"), but more of those studies surely are in the offing.

Nonetheless, there has been a particularly unsettling aspect of extant work that has attracted a certain amount of attention and that has prompted the present investigation. While the unique chemical and physical properties of small clusters as distinct from those of the corresponding bulk phases were recognized immediately, quite reasonably it has been assumed that there must exist some range of cluster sizes over which the small cluster properties smoothly merge into those of the bulk. Estimates of just where this transition might occur have differed wildly; certainly the evidence suggests that this critical size differs for different physical properties.[1] As an extreme example we cite the change in the equilibrium geometry of argon clusters as they grow from icosahedral (calculated for small clusters) to fcc (observed in the bulk crystal) that was estimated to occur at about 750 Ar atoms in one study[22] but which subsequently was predicted to occur only for more than 8200 atoms![23] But our own special interest is in a situation where transitions from cluster to bulk behavior do not appear even for clusters that *a priori* seem large enough to yield bulk properties.

In 1991 Whetten and co-workers[24,25] reported a series of experiments in which the electronic spectra of chromophore-doped clusters were obtained by means of a (one-color) resonant two-photon ionization process. They found that the shift of the chromophore's absorption spectrum away from that of the neat gas-phase species apparently approaches a plateau value as the clusters became larger. Interestingly, though, this plateau value does not match the spectral shift of the chromophore measured in the corresponding liquid or in the analogous cryogenic matrix-isolation experiment, nor are these three values even close to one another! In the case of an Ar cluster doped with a benzene molecule, the apparent plateau value of roughly 35 cm^{-1} is only half of the dense-liquid result[26] and a mere quarter of the matrix value.[27,28] Clearly, if one desires to try to understand these experimental findings by carrying out modeling calculations, the model of spectral shifts that must be used is one that will be equally well suited to describing both clusters and condensed phases. Just such a model is proposed in the aforegoing companion article to this one [hereafter referred to as paper I (Ref. 29)]. It has the virtue of being fundamentally microscopic in nature and thus potentially sensitive to variations in

cluster structures while still incorporating the collective behavior that is the hallmark of condensed phase systems.[30]

Certainly we are not the only ones to devise microscopic models describing effects on the electronic spectrum of a chromophore deriving from dielectric interactions with its environment. As described in paper I,[29] there have been numerous attempts to model solute spectra,[31–33] although a truly microscopic quantitative model has proven elusive. In the case of clusters, the work of Fried and Mukamel[34] stands out, in that it can be implemented for specific classes of cluster structures (as long as isomerization does not occur too rapidly) and because it accommodates both inhomogeneous and homogeneous line broadening mechanisms.[35] One should not expect, however, this theory to be particularly successful in describing larger clusters that might have some bulklike properties due to its omission of many-body dielectric effects. As we shall show later in Secs. II and III, such effects indeed become significant as the size of the cluster increases and ultimately determine the nature of the approach of the cluster properties to those of the bulk. Therefore, the model described herein, which straightforwardly includes these effects, affords a fresh look at the evolution of cluster properties. In particular, it provides a framework for untangling the meaning of the surprising experimental results suggesting a lack of convergence of cluster properties to those of the bulk.[24]

II. MICROSCOPIC MODELING OF SOLUTE SPECTRAL SHIFTS

It would be inappropriate for us to reproduce the details of the derivation or implementation of our theoretical model that appear in paper I.[29] However, we will take this opportunity to remind the reader of the most significant features of that derivation, in particular those points that clarify the physical picture of the microscopic solvation process. In doing so we routinely will use the words "solute" and "solvent" to apply not only to species in bulk systems, but also to the chromophore and surrounding atoms, respectively, in cluster systems. Although in paper I we indicate extensions of our model to other situations, our specific focus here will be on describing the effect that a nonpolar solvent (argon) has on a strictly forbidden electronic transition, in particular the 6_0^1 vibronic transition in benzene.

A. Formalism

The fundamental description of the dielectric properties of our system is based on the assumption that solvent species having no permanent electrical moments themselves may be described as a collection of Drude oscillators, interacting with one another by means of induced-dipole–induced-dipole forces.[29,31,32,36] (Such a model has been shown to reproduce all the linear dielectric phenomena of the bulk phases.) Because these harmonically fluctuating point dipoles are in fact coupled, it makes sense though to view these solvent polarizations in terms of collective polarization fluctuations. We of course sacrifice

nothing by taking this viewpoint. If the interactions between oscillators are small, then the system will be effectively decoupled and the solvent species will behave independently; if, however, the interactions are indeed important, then we will recover the collective aspects of the solvent's dielectric response immediately.

Formally the prescription for recasting the problem so as to identify the collective polarization structure is quite straightforward. The dielectric part of our initial solvent Hamiltonian describing N (harmonically fluctuating) point dipoles $\mathbf{q}_j$ located at $\mathbf{r}_j$ (the positions of the Ar atoms) and interacting via the point-dipole–point-dipole interaction tensor $T(\mathbf{r})$ may be written as

$$\hat{H}_v = \sum_{j=1}^{N} \hat{h}_v(\mathbf{q}_j) - \sum_{\substack{j,k \\ (j<k)}}^{N} \mathbf{q}_j \cdot T(\mathbf{r}_{jk}) \cdot \mathbf{q}_k, \qquad (2.1)$$

where $T(\mathbf{r}) \equiv (3\,\hat{r}\hat{r}-1)/r^3$, and $\hat{h}_v$ is a single-particle Hamiltonian, appropriate to an isolated harmonic oscillator of frequency ω_v. (For argon[26] this frequency, $\hbar\omega_v = 15.75$ eV, is just the ionization potential. The polarizability of an Ar atom, $\alpha_v = 1/m_v\,\omega_v^2 = 1.63$ Å^3, is used in determining effective Drude oscillator mass m_v which appears in the single-particle Hamiltonian.) But because this expression is in general a quadratic form, it may be diagonalized (*at a specific system configuration*) to yield $3N$ polarization modes[36] having frequencies ω_α. As a result $\hat{H}_v$ may be rewritten in a form that makes clear the collective nature of the polarization fluctuations,

$$\hat{H}_v = \sum_{\mathsf{v}} \sum_{\alpha=1}^{3N} \hbar\omega_\alpha(v_\alpha + 1/2) |\mathsf{v}\rangle\langle\mathsf{v}|, \qquad (2.2)$$

where the $|\mathsf{v}\rangle$ are the (harmonic oscillatorlike) quantum states of the $3N$ polarization modes, each of which is described by a quantum number $v_\alpha(=0,1,2,...)$.

But it is the Hamiltonian of the entire system, solvent plus solute, that we need to construct. If we assume the solute molecule to be characterized by a ground state $S_0(|0\rangle)$ and a first excited state $S_1(|1\rangle)$, then its contribution to the Hamiltonian in the absence of interactions with the solvent can be written compactly in terms of a 2×2 matrix

$$\hat{H}_u = \begin{pmatrix} 0 & 0 \\ 0 & \hbar\omega_u \end{pmatrix} \qquad (2.3)$$

with ω_u being the frequency of the $S_1 \leftarrow S_0$ transition.[32] (The relevant parameters describing an isolated benzene molecule[26] are a transition energy, $\hbar\omega_u = 4.7868$ eV, and a polarizability, $\alpha_u = 10.32$ Å^3.) Now, though, we also must account for the interaction of this solute with the solvent. Carrying our above treatment of the solvent one step further, we assume that the solute–solvent dielectric interactions are those due to the coupling of the solvent's polarization modes to the transition dipole moment of the solute via the same point-dipole–point-dipole forces mentioned previously. We mentioned above that our particular interest lies in modeling the 6_0^1 vibronic transition in benzene.

For a transition of this sort, which is strictly electronically forbidden, the appropriate coupling Hamiltonian[32] is

$$\hat{H}_{u/v} = -\sum_{j=1}^{N} \mathbf{q}_j \cdot T(\mathbf{r}_{0j}) \cdot \mathbf{d}(|0\rangle\langle 1| + |0\rangle\langle 1|)$$

with $\mathbf{r}_{0j}$ being the distance between the benzene's center of mass and the jth Ar atom, and $\mathbf{d}$ being the effective transition dipole of the benzene molecule (which we take to lie in the z direction). However, by introducing the collective polarization modes into this expression explicitly, we show in paper I (Ref. 29) that one may rewrite the above equation as

$$\hat{H}_{u/v} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} d \sum_{\alpha=1}^{3N} c_\alpha \hat{q}_\alpha, \tag{2.4}$$

where $\hat{q}_\alpha$ is the coordinate operator for the αth polarization mode, and the coupling constant c_α contains the information (because it depends directly upon the polarization mode eigenvector) about the degree to which an individual polarization mode couples to the chromophore's effective transition dipole (of magnitude d). More explicitly, the coupling constant takes the form

$$c_\alpha = \sum_{j,\mu} [U(\mathbf{R})]_{\alpha,j\mu} [T(\mathbf{r}_{0j})]_{\mu z}^{'},$$

involving the corresponding polarization mode eigenvectors $[U(\mathbf{R})]_\alpha$, just a column of the matrix that diagonalizes the solvent Hamiltonian [Eq. (2.1)] at a particular system configuration $\mathbf{R}$, and elements of the solvent–solute dielectric interaction tensor $T(\mathbf{r}_{0j})$, where $\mu = x, y, z$.

The total Hamiltonian is then just the combination of Eqs. (2.2)–(2.4), written here in a fashion that makes clear how it operates on the composite solute–solvent states of the system

$$\hat{H} = \begin{pmatrix} 0 & 0 \\ 0 & \hbar\omega_u \end{pmatrix} \sum_v |v\rangle\langle v| + \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \sum_v \sum_{\alpha=1}^{3N} \hbar\omega_\alpha$$

$$\times (v_\alpha + \tfrac{1}{2}) |v\rangle\langle v| + \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} d \sum_{\alpha=1}^{3N} c_\alpha \hat{q}_\alpha.$$

Solving for the energy states of this system actually is relatively simple at this point! We know that the coupling term [Eq. (2.4)] must make only a small contribution to those energies inasmuch as the observed spectral shifts of 10–100 cm^{-1} are but a small fraction of the electronic transition frequencies of the neat solvent or of the isolated solute. Hence a perturbative solution of the problem will be entirely adequate when carried to second order. [The polarization mode wave functions are just those of harmonic oscillators, so the matrix elements of the coordinate operators appearing in Eq. (2.4) will vanish when calculated between identical states. These are, of course, the very matrix elements that yield first-order energy corrections.] The final result is the solvent-induced spectral shift in terms of the polarization mode frequencies and corresponding coupling constants,
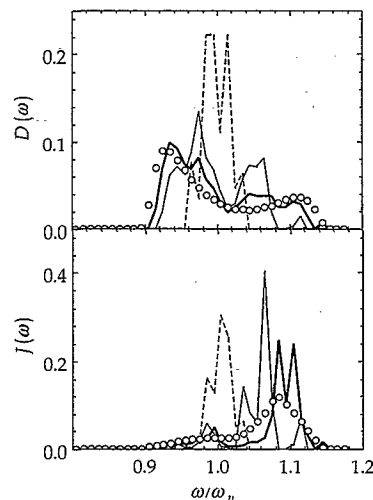

FIG. 1. Polarization mode densities of states $D(\omega)$ and spectra of couplings $J(\omega)$ for Bz(Ar)$_n$ clusters (10 K), with $n=3$ (dashed line), 19 (solid line), and 60 (thick line). For comparison purposes, the results for a benzene molecule dissolved in liquid Ar at $\rho = 0.0212$ atoms/Å^3 and a temperature of 120 K are also shown (open circles).

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

If we now make the conventional definition of the *spectrum of couplings*,[36,37]

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

we obtain, again for a single system spatial configuration,

$$\delta(h\nu) = -\frac{d^2}{\pi} \int d\omega \, J(\omega) \frac{2\omega_u}{\omega^2 - \omega_u^2}. \tag{2.5}$$

While obviously running the risk of getting ahead of ourselves in describing the methodology, we believe it useful here to give the reader a concrete illustration of the effects that we are discussing. In particular, we wish to underscore the importance of including collective polarization effects even when investigating clusters that represent quite different environments than the analogous bulk phases. In Fig. 1 we give results of a calculation of the polarization mode densities of states and spectra of couplings for Bz(Ar)$_n$ clusters (equilibrated at a temperature of 10 K) of sizes $n=3$, 19, and 60, and as a point of reference reproduce the results obtained for the highest density liquid considered in paper I (equilibrated at 120 K).[29] Only for the very smallest cluster are $D(\omega)$ and $J(\omega)$ even approximately peaked about $\omega = \omega_v$. Yet, if induced-dipole–induced-dipole interactions, and hence the collective character of the solvent response, were to be ignored entirely, both curves would be δ functions located at that point. Notice also that even for the small clusters one observes a separation of the polarization fluctuations into longitudinal and transverse modes,[36,38] with the longitudinal modes coupling far more effectively to the benzene's transition dipole. The largest cluster (specifically,

$n=60$) exhibits a polarization mode density of states that is strikingly similar to that of the liquid ($\rho=0.0212$ atoms/Å^3), but even so it is clear from the $J(\omega)$ plot that significant dielectric environment differences still exist between the two cases. We will have additional comments concerning the size evolution of the polarization modes in Sec. IV. Nonetheless, the limited results presented at this point do suggest that the consideration of collective dielectric effects may be an important aspect of understanding just how cluster spectral properties evolve to those of the bulk.

However, the shift predicted by Eq. (2.5), which will be to the red in the majority of systems of practical interest, is not the whole story. We cannot ignore the fact that there also will be a contribution to the total shift deriving from short-ranged repulsive interactions—the solvent species effectively confine the solute's electronic states and thereby shift their energies.[39] Since the S_1 state of the chromophore is characteristically more extended spatially than is S_0, a simple particle-in-a-box argument leads us to expect that these repulsions should contribute a blue component to the total spectral shift that to some extent counters the redshift from Eq. (2.5).

Although the modeling of repulsive effects from first principles is difficult, their short-ranged nature makes a simple phenomenological approach practical. As we showed in paper I,[29] good results can be obtained simply by taking a repulsion-induced shift of the form

$$\delta(h\nu)=b\sum_{j=1}^{z} r_{0j}^{-2}, \tag{2.6}$$

where b is a suitably chosen parameter. The summation over solvent species here is restricted, however, to the indices of those atoms that are the nearest neighbors of the chromophore. Practically, this restriction means that a spherical cutoff is introduced (taken here to be 5.4 Å) such that only the indices of those atoms whose centers lie within that sphere are included.

B. Implementation

To obtain a result that can be compared with experiment, the red (dielectric) and blue (repulsive) components of the total shift must now be averaged over a representative set of characteristic system configurations. These configurations were obtained via implementation of the Monte Carlo procedure detailed in paper I.[29] Data from calculations based on the configurations for $Bz(Ar)_3$, $Bz(Ar)_5$, and $Bz(Ar)_7$ then were used in fitting the two free parameters in our model, namely d (the magnitude of the 6_0^1 effective transition dipole moment) and b (the repulsive-force scaling parameter). Reiterating our findings, we note that values of $d=5.187$ D and $b=970.2$ cm^{-1} bohr^2 yield a good fit to the experimental data on these three clusters that was reported by Schmidt, Mons, and Le Calvé.[18]

The particular choice of cluster sizes employed in parameter fitting turns out to be of some importance. Of course, we are somewhat limited in the range of sizes that we can consider by the availability of high-quality, unam-
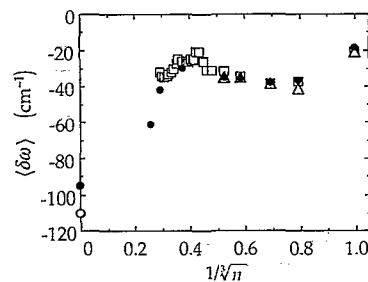

FIG. 2. Size dependence of the total spectral shifts for $Bz(Ar)_n$ clusters, including the shift for benzene isolated in a solid Ar matrix. The solid circles are the results of the present calculations, the open triangles are the experimental results from Ref. 18 (Schmidt, Mons, and Le Calvé), the open squares are selected experimental results taken from Ref. 24 (Li et al.), and the open circle is the experimental point for matrix-isolated benzene reported in Ref. 27 (Diamant, Hexter, and Schnepp).

biguous experimental data on these shifts. The study by Schmidt, Mons, and Le Calvé[18] does not extend to clusters larger than 9 Ar atoms, although this limitation really is not all that serious given our desire to use the smallest clusters possible. But on the other hand, parametrizations based on results from the very smallest clusters, consisting of 1 or 2 Ar atoms attached to benzene, are not likely to be transferable to the larger species. The reason for this imperfect transferability is simple. The low-temperature equilibrium structures of $Bz(Ar)_1$ and $Bz(Ar)_2$ consist of single Ar atoms bound along the C_6 axis above [and, in the case of $Bz(Ar)_2$, below] the plane of the benzene molecule. In these arrangements there is no Ar–Ar interaction of any significance, and thus a parametrization carried out using these configurations would not account for any of the subtle effects arising in response to the solvent atom interactions.

III. RESULTS

A. Cluster size dependence of spectral shifts

We begin the presentation of the results of our calculations by examining the general applicability of the approach. Ultimately, of course, the judgment of the validity of any theoretical method rests on its ability to reproduce the results obtained from carefully controlled experiments. A comparison of calculated total spectral shifts for $Bz(Ar)_n$ with the corresponding experimental shifts[18,24,25] is given in Fig. 2 for selected values of n between 1 and 60 as well as for benzene trapped in a cryogenic Ar matrix.[27,28] The particular choice for the abscissa of this plot deserves some mention. Some sort of reciprocal dependence on the number of Ar atoms must be used if the matrix limit (in principle, $n=\infty$) is to be shown in the same plot as the cluster results. However, since a simple plot of shift vs n^{-1} tends to compress the results for the larger cluster sizes, we have chosen to display an inverse cube root dependence.

Note first that at sizes where experimental shifts have been determined,[18,24,25,27,28] we achieve a very satisfactory fit between those values and the ones we have computed.

We are able to reproduce the increase (a doubling) of the shift towards the red in going from $n=1$ to 2 in accordance with the additivity rules[18,19,40] proposed for clusters of this sort. The second Ar adds to the face of the benzene molecule opposite to the binding site of the first Ar, and so the Ar atoms behave independently. We then observe the gradual decrease in the shift as the cluster grows beyond $n=2$ that has been seen in the experiments, although our excellent quantitative agreement with experiment here should not be overemphasized—these were in fact the cluster sizes ($n=3,5,7$) used in parametrizing our model. But far more significantly, our calculations predict a reversal of this trend, with the magnitude of the shift passing through a minimum, at intermediate cluster sizes. Note that the data of Whetten and co-workers[24,25] also clearly display this behavior.

However, we have extended our investigation to the consideration of larger clusters than those investigated by Whetten's group.[24,25] Whereas their results appear to stabilize at a constant value by $n=40$—this asymptotic behavior is more obvious in a direct plot of the shift vs n—ours continue to move farther towards the red until a limiting value is reached at roughly -95 cm^{-1} with the matrix simulation. This prediction for the solid solution is not perfect, falling slightly short of the -110 cm^{-1} experimental value,[27,28] but it actually is quite remarkable nonetheless. Remember that the simulation has been parametrized on the basis of data gleaned exclusively from quite small clusters. That those parameters and, indeed, the formalism itself can be extended to the solid state and yield a very respectable estimate of the shift is not insignificant. Certainly, we find no evidence for anomalous asymptotic behavior of the shifts; they do approach the condensed phase values as the clusters become larger, but even for 60 Ar atoms, the cluster dielectric environment is still considerably different than what one finds in the solid. We should add that it also differs from what is found in a liquid environment, a result that one can see by comparing the appropriate spectrum of coupling curves in the lower panel of Fig. 1.

To aid in understanding the nature of the evolution of the dielectric environment from that of the smallest clusters to those of the condensed phases, we plot the individual red and blue components of the benzene molecule's spectral shift as a function of cluster size in Fig. 3. This plot turns out to be particularly revealing in that it identifies the component that really determines the asymptotic shift behavior, namely the red (dielectric) one. We see in Fig. 3 that the blue component essentially has converged to its bulk value by $n=19$. Even though at $n=40$ the blueshift is a bit larger, this difference is quite small and appears to disappear by about $n=60$. In contrast, the red component of the shift is still well removed from its asymptote at $n=19$, and even at $n=60$ it falls short. Although we will discuss this point in more detail below, these results imply that it is the extent of the evolution of the collective polarization fluctuations that ultimately determines how bulk-like the spectral properties of the cluster are.

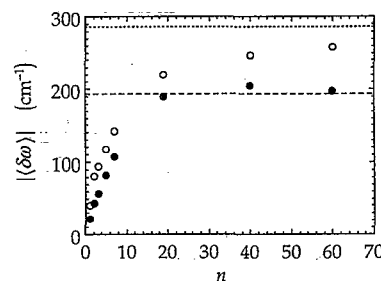Figure 4 reveals another facet of the behavior of the

FIG. 3. Convergence properties of the individual components of the spectral shift for Bz(Ar)$_n$. The solid circles are the blue (repulsive) component results, which converge to the bulk limit represented by the lower dashed line. The open circles are the absolute values of the red (dielectric) component results, which converge to the bulk limit represented by the upper dashed line.

spectral shift with increasing cluster size, in particular the changes occurring in the smaller clusters. These plots of the red and blue components vs the cube root of the number of Ar atoms are not only linear for $n \leqslant 19$ but also possessed of equal slopes. (R^2 values for the linear fits to each set of data are in excess of 0.99.) Clearly, then, in this cluster size range a common effect is responsible for the variation in the shifts of both components. The most plausible explanation for this phenomenon is that it simply reflects the physical packing of the Ar atoms about the benzene molecule. *Very roughly* the volume of the cluster will scale as n, so $(n)^{1/3}$ will be related to the cluster radius. The divergence of the behavior of the red- and blueshifts in the larger clusters might then be viewed as deriving from the saturation of nearest-neighbor binding sites in the case of the blue component, and from the growing importance of collective polarization fluctuations in the case of the redshift.

That the blueshift for the larger clusters is determined solely by solvent atom packing effects is made even clearer by the results shown in Fig. 5, where the average number of nearest neighbors has been divided out of the blue component. Note that the basic behavior here is the same that is seen in Fig. 3, i.e., the convergence to the matrix asymptote is accomplished by $n=19$, but now the deviation from the asymptotic value at $n=40$ is even less apparent. Actually, this deviation, which is greater than would be expected statistically, is likely the result of surface tension.
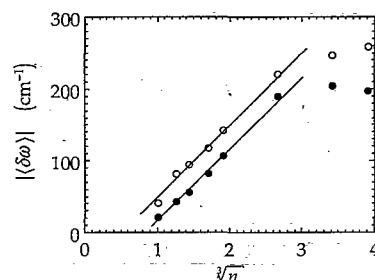

FIG. 4. The data of Fig. 3 replotted vs the cube root of the number of Ar atoms in the clusters. The solid lines represent the results of the linear fits to the small-cluster data described in the text.
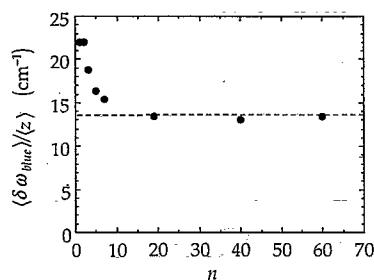
FIG. 5. Convergence to the corresponding bulk value (dashed line) of the ratio of the average blueshift to the average number of nearest-neighbor Ar atoms surrounding the benzene molecule.

For the intermediate-size clusters, minimizing their surface areas can lead to a slight compression of the Ar atoms near the benzene, although this effect will be damped out as the clusters continue to grow and the benzene molecule is located farther from the surface.

All our calculations so far are pointing to the development of collective solvent atom polarization effects as being the key to the approach of cluster spectral properties to those of the bulk phases. This conclusion also is supported by similar calculations carried out in the limit of negligible solvent–solvent dielectric interactions—the zero-bandwidth limit described in paper I.[29] Briefly, in this limit the calculation of the dielectric contribution to the spectral shift reduces just to a sum of two-body pair potentials—precisely the basic form adopted by Fried and Mukamel[34] in their work. Achieving the best results possible in this limit necessitates a reparametrization, though, with $d=5.463$ D and $b=1162$ cm^{-1} bohr^2 yielding the best fit to the small-cluster experimental data. A detailed comparison of the results obtainable using this model with those deriving from the finite-bandwidth theory that we are advocating is given in Table I, where we list not only the results from the clusters that we have examined but also values from the corresponding matrix case and from liquids of two different densities. (These densities lie at the extremes of the density range considered in paper I.[29]) Certainly the fit between calculated and experimental spectral shifts is equally good for the smallest clusters ($n \leqslant 7$), even though the individual red and blue components of those total shift can differ significantly. But by $n=19$ the collective character of the solvent atoms' polarization fluctuations have developed to the point that the zero-bandwidth approximation very seriously overestimates the dielectric stabilization afforded by the solvent. Of course, since the blue component essentially is converged to its asymptotic value for these larger clusters, the error involved in the use of this approximation is sufficiently great that this simple model has no quantitative predictive value.

The data in Table I also permit an important comparison between the cluster results and those deriving from the liquid simulations that provided the focus for the aforegoing paper.[29] One finds, for example, that the total shifts predicted for $n=40$ and $\rho=0.008\,48$ atoms/Å^3 are statistically identical, while those for $n=60$ and $\rho=0.0212$

atoms/Å^3 differ only slightly. Do these similarities imply something about the structure of the liquid, that perhaps the ordering in the liquid state is similar to that found in these clusters? No support for this interpretation is to be found in a comparison of the component red- and blue-shifts. A lack of agreement in those values in fact indicates that the liquid and cluster environments are quite different. For a given total shift, both the dielectric stabilization of the chromophore and the repulsive interactions in the clusters are greater than they are in the liquid examples, results which reflect the fact that the local solvent atom density in the cold clusters is far greater than in the warm liquid. We cite this comparison in order to make an important point: One must be very cautious in drawing conclusions concerning system structure on the basis of total spectral shifts alone. In many cases either more direct probes of local geometry will be required, or the measurements must be augmented by extensive simulations if useful structural information is to be extracted.

B. Bz(Ar)$_{19}$: Isomer-dependent spectral shifts

In an earlier study[12] we discussed a number of issues involved in the interpretation of spectral shifts measured for Bz(Ar)$_{19}$ clusters. A cluster of this size turns out to be particularly interesting because it appears to lie at the border between the regimes of small cluster and what might be termed "asymptotically bulk" behavior. In this latter regime, the clusters are sufficiently large that their spectral properties depart from the simple scaling laws obeyed by the smaller clusters (see Fig. 4) and begin to approach those exhibited by the analogous bulk systems. A cluster of this size also possesses a multitude of metastable isomeric forms, many of which might contribute to the observed spectroscopy if their lifetimes in an expansion jet are sufficiently long. The question here goes beyond just an identification of the lowest energy structure or structures; there is no guarantee that all the nascent clusters find their way into low-energy geometries, particularly if they cool so rapidly that they never have the opportunity to sample the available configuration space. The microscopic formalism described in this work and in paper I (Ref. 29) is particularly well suited to the study of the influence of these metastable isomers on cluster spectroscopy. The spectral consequence of any particular type of isomeric structure can be assessed quickly and easily, thereby yielding evidence for the existence or nonexistence of that particular species in the cluster jet.

Hahn and Whetten[25] have reported that for Bz(Ar)$_n$ clusters with n equal roughly to 19, there are two different sorts of peaks seen in the (one-color) resonant two-photon ionization spectra that they obtain. First, there is a pair of relatively narrow peaks shifted to the red of the isolated benzene absorption line by about 30 and 40 cm^{-1}, respectively, which they attribute to two isomeric forms of the cluster, both of which are rigid. Second, however, there is a quite broad peak shifted by only 20 cm^{-1} to the red, the intensity of which appears to be rather sensitive to cluster size. This peak they assigned to a cluster in which benzene

TABLE I. Comparison of spectral shifts determined using zero-bandwidth and finite-bandwidth models. Asterisks indicate clusters used for fitting the free parameters in the theory.

n	$\langle \delta\omega \rangle_{red}$ (cm^{-1})		$\langle \delta\omega \rangle_{blue}$ (cm^{-1})		$\langle \delta\omega \rangle$ (cm^{-1})		
	ZBW[a]	FBW[b]	ZBW	FBW	ZBW	FBW	Expt.
1	44.7 (0.9)[d]	40.3 (0.8)	26.3 (0.2)	22.0 (0.1)	−18.4 (0.9)	−18.3 (0.6)	−21[c] (1)
2	90.3 (0.4)	80.8 (0.4)	52.8 (0.1)	44.1 (0.1)	−37.5 (0.4)	−36.7 (0.3)	−41[c] (1)
3*	105.9 (3.6)	94.4 (3.6)	67.9 (0.2)	56.7 (0.2)	−38.0 (3.6)	−37.7 (3.4)	−38[c] (1)
5*	133.1 (1.7)	117.6 (1.5)	98.2 (0.3)	82.0 (0.3)	−34.9 (1.7)	−35.6 (1.3)	−35[c] (1)
7*	163.0 (2.4)	141.5 (1.6)	128.0 (1.4)	106.9 (1.2)	−35.0 (2.8)	−34.6 (1.0)	−35[c] (1)
19	286.7 (0.6)	219.8 (0.4)	228.1 (0.6)	190.5 (0.5)	−58.6 (0.8)	−29.4 (0.2)	−26[e] (1)
40	329.6 (0.8)	246.7 (0.6)	245.1 (0.8)	204.7 (0.7)	−84.5 (1.1)	−42.0 (0.6)	−32[e] (1)
60	357.7 (2.3)	257.6 (1.6)	235.3 (1.7)	196.5 (1.5)	−122.4 (2.9)	−61.1 (1.5)	
$\rho = 0.008\,48$[f] (liquid)	152 (4)	125 (3)	101 (4)	84 (4)	−51 (6)	−41 (2)	−37[g]
$\rho = 0.0212$ (liquid)	285 (5)	216 (4)	179 (4)	149 (3)	−106 (6)	−67 (3)	−62[g]
solid (matrix)	381 (3)	288 (2)	231 (2)	193 (2)	−150 (4)	−95 (1)	−110[h]

[a]Results calculated using the zero-bandwidth model as defined in paper I (Ref. 29).
[b]Results calculated using the model described in Sec. II A, which allows for collective solvent polarization modes (finite-bandwidth model).
[c]Reference 18.
[d]The number in parentheses is the standard deviation obtained by averaging the results from 5 sets of 40 instantaneous system configurations [5 sets of 100 configurations in the case of Bz(Ar)$_{19}$].
[e]Reference 24.
[f]Liquid densities are given in units of atoms/Å^3.
[g]Reference 26.
[h]Reference 27.

is found in a fluidlike environment, and consequently suggested that they are observing the coexistence of rigid and fluid cluster structures predicted by Berry and co-workers[41] in their studies of the "melting" transition in these small systems. We, on the other hand, offered an alternate interpretation of these experimental results after performing a simulation of the structural fluctuations in Bz(Ar)$_{19}$ and finding little change in the local ordering of the Ar atoms about the benzene molecule as the system temperature was raised.[12] We suggested that the clusters present in the jet in fact may not have been well equilibrated and that the broad background peak could instead derive from spectral transitions in clusters where benzene was bound to a surface site on an Ar cluster. Such structures would then be (metastable) examples of the nonwetting chromophore–rare-gas structures proposed by Leutwyler and collaborators[8,10] and subsequently used by Schmidt, Mons, and Le Calvé [18,21] in explaining their careful measurements of the spectra of small benzene–argon clusters.

In this subsection we want to test our hypothesis concerning the nature of the Bz(Ar)$_n$ spectra by associating specific cluster geometries with observed absorption frequencies.[42] However, before we examine the spectral contributions associated with particular metastable structures, it is useful to return to the question of what happens to the spectrum of Bz(Ar)$_{19}$ when the temperature of the cluster is raised. In Fig. 6 we give the breakdown of the components of the average total shift (for equilibrated clusters) as a function of temperature from 5 K, where the clusters certainly are rigid, to 45 K, where evaporation of Ar atoms from the clusters begins to become important. The absolute values of both components decrease monotonically over that temperature range, with the rate of decrease becoming larger beyond about 30 K. Note, however, that the curves run roughly parallel to one another, so no great effect on the total shift is expected. Indeed, such a result is just what we find in Fig. 7, where we give the temperature dependence of the total spectral shift. The changes seen in these two figures can be explained simply by positing that with
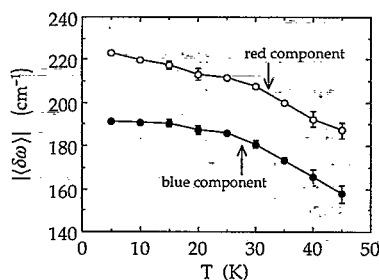
FIG. 6. Absolute values of the individual red and blue components of the total spectral shift for Bz(Ar)$_{19}$ as a function of equilibrium cluster temperature. The lines shown merely connect the calculated points and are meant to guide the eye only.

FIG. 8. Simulated absorption spectra of Bz(Ar)$_{19}$ corresponding to three different temperatures: 10 K (dashed line), 20 K (solid line), and 40 K (thick line).

the increase in temperature comes an expansion of the cluster. This expansion, the existence of which is supported by the fact that the average number of Ar nearest neighbors decreases from 14.1 to 12.1 over this temperature range, would tend to decrease both the dielectric and repulsive contributions to the total shift, but would do so equally and thus not radically alter the total shift. Significantly, the relative insensitivity of the total shift to a change in temperature lends credence to our proposition that changes in the shift of the benzene's absorption frequency does not yield any evidence for a rigid-to-fluid structural transition *per se*.[12]

Our calculations do say something about the *broadening* of the spectral line as a function of temperature. A simulated absorption spectrum can be obtained by determining total shifts at each of several characteristic system configurations and histogramming the results as a function of frequency. (Of course, we really cannot claim to be simulating experimental line shapes here, since we certainly are not doing justice to the vibrational effects on the absorption. Consideration of the entire vibrational envelope would be required for a more realistic modeling of the problem.) Examples of these histograms, determined using a bin width of 2 cm^{-1} and normalized to unit area, are given in Fig. 8. One clearly sees a diminution of the intensity of the peak as the temperature is increased, as well as an increase in the peak width full width at half maximum (FWHM) from roughly 10 to about 25 cm^{-1}. This degree of broadening is in fairly good agreement with what is reported by Fried and Mukamel[34] in their simulation of the
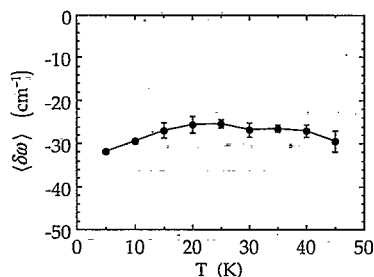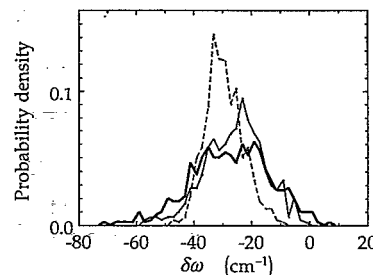
absorption line shapes for the $n = 16$ and 21 systems even though our formalism only takes into account inhomogeneous line broadening mechanisms. (Theirs accounts for both inhomogeneous and homogeneous contributions. We also should note that given our use of only 500 cluster configurations at each temperature, we do not attribute any significance to the local structure seen in the histograms.)

An exhaustive survey of all the isomeric forms of Bz(Ar)$_{19}$ that potentially could be present in an expansion jet is impractical at this point; too little is known about the expansion conditions for us to have much confidence in any criterion for assessing the likelihood of any particular cluster's presence. We can examine, however, the spectral contributions of a few selected clusters having special geometries, especially those with benzene bound in a surface site of an Ar cluster that we have suggested might be responsible for the broad background peak seen in Hahn and Whetten's experiments.[25] Configurations for these clusters cannot be prepared in the usual way, namely via a process of simulated annealing starting from equilibrated high-temperature species, because we are not attempting to access global potential minima but rather only local minima. Therefore, we begin the generation of these configurations by assuming a particular initial geometry and equilibrating at low temperature (10 K). Such a procedure will fail, of course, to locate all of the possible metastable surface binding sites on the Ar cluster, so we must be content to generate configurations starting from different initial geometries and to investigate this very limited set of possible structures that might be obtained if the clusters cool very rapidly in the jet.

(It should be mentioned that Fried and Mukamel,[34] in their study of the spectroscopy of these clusters, dismissed the possibility that surface-bound structures might contribute to the observed spectra on the grounds that they were able to observe the movement of Ar atoms from one face of the benzene ring to the other. We believe, however, that one should be very cautious in ruling out such structures altogether based on the Fried and Mukamel work, because those calculations were carried out using annealed system structures. Metastable geometries, which may well be present under actual expansion conditions, are not likely to appear in a simulation unless a special attempt is made to locate them. In fact, conventional annealing procedures are

FIG. 7. Calculated total spectral shift for Bz(Ar)$_{19}$ as a function of equilibrium cluster temperature. The lines shown are as in Fig. 6.

TABLE II. Details of calculations on selected nonwetting Bz(Ar)$_{19}$ structures.

Configuration set	$\langle z \rangle^a$	$\langle \delta\omega \rangle_{red}$ (cm^{-1})	$\langle \delta\omega \rangle_{blue}$ (cm^{-1})	$\langle \delta\omega \rangle$ (cm^{-1})
1	7.00	110.9	93.2	−17.1
	(0.01)^b	(0.9)	(0.2)	(0.7)
2	4.50	96.6	64.8	−31.7
	(0.06)	(1.2)	(0.9)	(0.8)
3	3.42	80.6	52.4	−28.3
	(0.38)	(3.9)	(4.1)	(3.5)
4	5.54	95.7	76.0	−19.7
	(0.87)	(9.3)	(10.1)	(1.0)

^{a}Average number of (nearest-neighbor) Ar atoms in contact with the benzene molecule.
^{b}Standard deviation as defined in Table I.

TABLE III. Calculations involving small Bz(Ar)$_n$ isomers.

n	Isomer	$\langle \delta\omega \rangle_{red}$ (cm^{-1})	$\langle \delta\omega \rangle_{blue}$ (cm^{-1})	$\langle \delta\omega \rangle$ (cm^{-1})
3	(2|1)^a	94.4	56.7	−37.7
		(3.6)^b	(0.2)	(0.3)
	(3|0)	67.7	48.2	−19.5
		(1.3)	(0.3)	(1.0)
5	(3|2)	117.6	82.0	−35.6
		(1.5)	(0.3)	(1.3)
	(4|1)	117.5	81.9	−35.6
		(1.0)	(0.2)	(0.9)
	(5|0)	90.8	71.1	−19.7
		(0.6)	(0.2)	(0.5)
	(4+1$_2$|0)	79.0	59.2	−19.8
		(1.1)	(0.5)	(0.9)

^{a}Isomer geometry designated using the notation convention of Ref. 5.
^{b}Standard deviation as defined in Table I.

designed so as to reduce the chance that the system remains trapped in these structures long enough for them to be readily identified.)

The results of these calculations are indicated in Table II. The four sets of configurations here (each consisting of 200 unique, nonwetting configurations), representing a range of cluster geometries that might exit under the appropriate conditions, indicate that such structures are likely to contribute a fairly broad feature to the observed spectra, since the total shifts may vary greatly. Certainly there is evidence for absorption at frequencies that are red-shifted by about 20 cm^{-1}, which is the center of the background peak reported by Hahn and Whetten,[25] but also larger shifts are possible, to the extent that these nonwetting structures can contribute to the peak arising from the fully equilibrated clusters having an embedded benzene molecule. Note, in particular, how significant the variations are in the average number of nearest neighbors about the benzene. The value of $\langle z \rangle$ calculated for set 1 suggests that in these configurations, the binding to one face of the benzene molecule is essentially saturated, since for the embedded-benzene clusters a value of about 14 is typical. The smaller $\langle z \rangle$ values would be expected for benzene bound in a site on the "cap" of a relatively undistorted, polyicosahedral Ar$_{19}$ cluster, but it is interesting to find that even for these species the resulting shift in the benzene's absorption can be considerable.

It also is useful to examine some isomers of the small benzene–Ar clusters to which particular spectral features have been attributed by Schmidt, Mons, and Le Calvé.[18,21] The results of these calculations are summarized in Table III. Notice first that there is a sizable difference between the shifts predicted for the Bz(Ar)$_3$ wetting (2\|1) and nonwetting (3\|0) isomers.[43] As expected, this difference is not easily explained just on the basis of physical packing arguments (the repulsive contributions to the total shifts are nearly the same in the two cases), but it can be understood in terms of the differences between the local dielectric environments. With three Ar atoms in close contact on one side of the benzene molecule, it becomes difficult to achieve a favorable mutual orientation of their instanta-

neous induced dipole moments that also yields the maximum dielectric stabilization of the benzene's transition dipole. Consequently, a compromise orientation is adopted, one that yields a lesser redshift contribution to the spectral shift. We note that Schmidt, Mons, and Le Calvé[18] have assigned a (3\|0) isomer designation to the peak shifted by 14 cm^{-1} to the red in their experiments, with this assignment being quite consistent with our findings.

Our observation that it is difficult to achieve the maximum dielectric stabilization of a chromophore when the cluster structure is of the nonwetting type also applies to the Bz(Ar)$_5$ results. We also find no change in the spectroscopy in going from the (3\|2) isomer to the (4\|1) moiety, a result which is in accord with the previously proposed assignment of both structures to the principal absorption peak seen in the experiments.[18] A less satisfactory agreement between our work and the experiments, however, is seen in the assignment by Schmidt, Mons, and Le Calvé[18] of the peak at −9 cm^{-1} to a nonwetting (5\|0) structure. We find it noteworthy that both of our nonwetting structures, whether they be two dimensional (5\|0) or three dimensional (4+1$_2$\|0), yield the same net spectral shifts, even though the individual component shifts do differ somewhat.

IV. SUMMARY

We have described here a truly microscopic model that provides a powerful framework within which to examine the evolution of cluster spectral properties with cluster size and the approach of cluster properties to those of the corresponding bulk phases. Actually, in retrospect it seems fairly obvious that this asymptotically bulk behavior can be usefully modeled only by adopting a formalism that itself is applicable to the bulk systems, and thus provides for proper handling of collective dielectric effects. Perhaps it is somewhat surprising that these effects become significant even for clusters having as few as 19 Ar atoms, but for the

larger clusters that might be expected to display convergent behavior, one should anticipate that their influence will be substantial.

A fairly clear picture is emerging from our study of both clusters and condensed phases of the general progression of spectral properties from those of the smallest clusters to those of the cryogenic matrix. Initially, the addition of solvent atoms to a small cluster produces a gradual diminution of the magnitude of the net (red) spectral shift of the chromophore as the increased contribution of repulsive force effects more than compensates for any development of many-body dielectric effects. However, the repulsive contribution quickly reaches an asymptotic value as the nearest-neighbor solvent atom binding sites at the chromophore becomes saturated, and the trend is reversed. Now the continued evolution of the collective character of the solvent dielectric effects arising from an increase in the spatial extent of the polarization modes becomes the dominant contribution to the predicted shift, and the clusters begin to look more and more like the bulk. In a sense, we can summarize this behavior by stating that we in fact observe nothing that could be described as a unique small cluster property except that in those systems the collective dielectric effects, which are so important in condensed phases, are imperfectly developed.

In addition we have reaffirmed our position that one must be very cautious in attributing changes in spectral shifts with temperature to the sort of melting transition predicted for the neat solvent clusters.[12] The very presence of the chromophore is likely to so influence the local structure of the nearest-neighbor solvent atoms, that a rearrangement of the more distantly bound atoms may occur with little or no effect on the observed spectrum. Unexplained peaks in the absorption spectra of clusters of certain sizes may instead be due to the presence of unequilibrated, metastable species having structures that might be quite different from the equilibrated ones. (One should keep in mind, though, that since it is impossible to rule out the possibility that cluster fragmentation products are present in Hahn and Whetten's experiments,[25] absorption by smaller clusters also might provide an explanation for these peaks. Certainly the fact that the shift that we predict for $n=40$ is larger than the experimental observation tends to support the speculation that the sizes of the larger clusters may be ill-defined.) In particular, our calculations indicate that the broad background absorption measured by Hahn and Whetten for $Bz(Ar)_{19}$ and similar clusters may indeed derive from metastable structures such as those characterized by a benzene molecule that is bound to an argon cluster in a surface site. The uncertainty concerning the identities of all the species present in an expansion jet and the nascent internal states of those species still is great enough that the presence of surface-bound chromophores cannot be disregarded.

Interestingly, structures of this type have been proposed by Troxler and Leutwyler[8] to explain why the spectral shifts of naphthalene–Ar_n clusters do not appear to converge to the value that is observed in the solid matrix. They suggest that these nonwetting structures actually are

highly probable even when n is large (on the order of 30). It would not be surprising, then, for these larger clusters to display shifts different from those of the analogous bulk species. While these findings would appear to provide important supporting evidence for our suggestions concerning benzene–argon clusters, our own work in fact suggests an alternative explanation. We think it just as likely for the collective dielectric effects described herein to be the source of the lack of convergence. Even for clusters as large as those studied by Troxler and Leutwyler,[8] the polarization mode spectra may be incompletely developed and the resulting dielectric environments may be quite different from the bulk situation.

A very recent ionization-loss stimulated Raman study by Felker and co-workers[44] has yielded, however, a somewhat different picture of the physical origins of the extra peaks, one that deserves mention here. They have interpreted their experiments to suggest that the spectroscopically important differences between isomeric structures really lie in the numbers of Ar atoms bound in the plane of the benzene molecule rather than in whether they constitute wetting or nonwetting structures. We caution, however, that theirs is a very different sort of experiment than the one we are attempting to model here. It also is not clear at present that the interpretation of the Raman experiment is completely unambiguous, and that an alternative explanation is necessarily precluded.

ACKNOWLEDGMENTS

[1] For a recent review of several manifestations of size-dependent phenomena, see J. Jortner, Z. Phys. D **24**, 247 (1992), and the references cited therein.

[2] S. Leutwyler and J. Bösiger, Chem. Rev. **90**, 489 (1990).

[3] S. Leutwyler and J. Jortner, J. Phys. Chem. **91**, 5558 (1987).

[4] U. Even, A. Amirav, S. Leutwyler, M. J. Ondrechen, Z. Berkovitch-Yellin, and J. Jortner, Faraday Discuss. Chem. Soc. **73**, 153 (1982).

[5] N. Ben-Horin, U. Even, and J. Jortner, J. Chem. Phys. **97**, 5988 (1992); N. Ben-Horin, D. Bahatt, U. Even, and J. Jortner, *ibid.* **97**, 6011 (1992).

[6] N. Ben-Horin, U. Even, J. Jortner, and S. Leutwyler, J. Chem. Phys. **97**, 5296 (1992).

[7] A. W. Castleman, Jr. and R. G. Keesee, Annu. Rev. Phys. Chem. **37**, 525 (1986).

[8] T. Troxler and S. Leutwyler, J. Chem. Phys. **95**, 4010 (1991).

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

[10] J. Bösiger, R. Knochenmuss, and S. Leutwyler, Phys. Rev. Lett. **62**, 3058 (1989).

[11] D. Eichenauer and R. J. LeRoy, Phys. Rev. Lett. **57**, 2920 (1986); R. J. LeRoy, J. C. Shelley, and D. Eichenauer, in *Large Finite Systems*, edited by J. Jortner, B. Pullman, and A. Pullman (Reidel, Dordrecht, 1987), p. 165; D. Eichenauer and R. J. LeRoy, J. Chem. Phys. **88**, 2898 (1988); J. C. Shelley, R. J. LeRoy, and F. G. Amar, Chem. Phys. Lett. **159**, 14 (1988); M. A. Kmetic and R. J. LeRoy, J. Chem. Phys. **95**, 6271 (1991).

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

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

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

[15] S. Leutwyler, A. Schmelzer, and R. Meyer, J. Chem. Phys. **79**, 4385 (1983).

[16] J. Bösiger, R. Bombach, and S. Leutwyler, J. Chem. Phys. **94**, 5098 (1991).

[17] See, for example, S. W. Rick, D. L. Lynch, and J. D. Doll, J. Chem. Phys. **95**, 3506 (1991); S. W. Rick, D. L. Leitner, J. D. Doll, D. L. Freeman, and D. D. Frantz, ibid. **95**, 6658 (1991).

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

[19] M. Schmidt, M. Mons, J. Le Calvé, P. Millié, and C. Cossart-Magos, Chem. Phys. Lett. **183**, 69 (1991).

[20] W. Scherzer, H. L. Selzle, and E. W. Schlag, Chem. Phys. Lett. **195**, 11 (1992).

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

[22] J. Farges, M. F. de Feraudy, B. Raoult, and G. Torchet, J. Chem. Phys. **78**, 5067 (1983); **84**, 3491 (1986).

[23] J. Xie, J. A. Northby, D. L. Freeman, and J. D. Doll, J. Chem. Phys. **91**, 612 (1989).

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

[25] A preliminary report of the work on Bz(Ar)$_n$ is given in M. Y. Hahn and R. L. Whetten, Phys. Rev. Lett. **61**, 1190 (1988). See also M. Y. Hahn, Ph.D. thesis, University of California, Los Angeles, 1989.

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

[27] Y. Diamant, R. M. Hexter, and O. Schnepp, J. Mol. Spectrosc. **18**, 158 (1965). The analysis of these experiments is complicated, however, by the apparent presence of multiple solute binding environments.

[28] T. J. Barton, I. N. Douglas, and R. Grinter, Mol. Phys. **30**, 1677 (1975); R. B. Merrithew, G. V. Marusak, and C. E. Blount, J. Mol. Spectrosc. **25**, 269 (1968).

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

[30] A preliminary report of this work is given in J. E. Adams and R. M. Stratt, Z. Phys. D (in press).

[31] D. Chandler, K. S. Schweizer, and P. G. Wolynes, Phys. Rev. Lett. **49**, 1100 (1982); K. S. Schweizer and D. Chandler, J. Chem. Phys. **78**, 4118 (1983); R. F. Loring, ibid. **92**, 1598 (1990); J. Phys. Chem. **94**, 513 (1990); N. Shemetulskis and R. F. Loring, J. Chem. Phys. **95**, 4756 (1991); B. M. Ladanyi, N. Shemetulskis, and R. F. Loring, ibid. **96**, 8637 (1992).

[32] Y.-C. Chen, J. Lebowitz, and P. Nielaba, J. Chem. Phys. **91**, 340 (1989).

[33] A recent example of a more "traditional" cavity model of cluster dielectric effects is given in J. Gersten and A. Nitzan, J. Chem. Phys. **95**, 686 (1991). We believe that the good results obtained using a continuum dielectric model in that work will not be universal, though, and that a truly microscopic model must be adopted if clusters are to be described accurately. For example, Gersten and Nitzan's formalism appears to suggest that the dielectric component of the spectral shift should converge as the inverse of the cluster volume. Such a results is not corroborated by our calculations, however.

[34] L. E. Fried and S. Mukamel, Phys. Rev. Lett. **66**, 2340 (1991); J. Chem. Phys. **96**, 116 (1992); Adv. Chem. Phys. (in press).

[35] For recent applications of the method of Ref. 34 to other systems, see T. Troxler and S. Leutwyler, J. Chem. Phys. (in press); P. Parneix, F. G. Amar, and Ph. Bréchignac, Z. Phys. D (in press); A. Heidenreich and J. Jortner, ibid. (in press).

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

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

[38] B. Cichocki and B. U. Felderhof, J. Chem. Phys. **90**, 4960 (1989); **92**, 6104 (1990).

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

[40] Additivity rules also have been validated using more complex solvent species. See, for example, M. Schauer and E. R. Bernstein, J. Chem. Phys. **82**, 726 (1985); R. Nowak, J. A. Menapace, and E. R. Bernstein, ibid. **89**, 1309 (1988).

[41] See, for example, R. S. Berry, T. L. Beck, H. L. Davis, and J. Jellinek, Adv. Chem. Phys. **70**, 74 (1988), and the references cited therein.

[42] A related experimental study, involving aniline rather than benzene, was recently reported by S. Douin, P. Hermine, P. Parneix, and P. Bréchignac, J. Chem. Phys. **97**, 2160 (1992).

[43] There appears to be no generally agreed upon notation for designating specific isomer geometries. We have adopted the convention used in Ref. 5.

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