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Size-dependence of the electronic spectra of benzene·(N₂)_n clusters

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The evolution of the electronic spectral properties of benzene·(N₂)_n clusters to those of the corresponding bulk has been studied using a formalism that yields a direct correlation between cluster geometries and spectra. We show here that the calculated spectral shifts of the benzene chromophore as a function of cluster size are in good agreement with experimental values and that, as observed previously, the asymptotic limit of the shifts is considerably smaller in magnitude than the observed bulk values. An examination of the structures of these cryogenic clusters reveals a strong influence of quadrupolar interactions between dinitrogens, interactions that yield a degree of ordering not present in the ostensibly similar benzene·(Ar)_n clusters. These observations suggest a resolution of the problem posed by the apparent lack of asymptotic convergence to bulk spectral shifts, that at the higher temperatures associated with the bulk measurements, higher local dinitrogen densities become possible as the thermal energy exceeds the quadrupolar orientational ordering energy. These higher “solvent” densities would be expected to produce the larger spectral shifts seen in experiments. © 1998 American Institute of Physics. [S0021-9606(98)01039-3]

I. INTRODUCTION

Small neutral atomic and molecular clusters, because they may constitute viable models of the local solvation environments present in bulk fluids, have been the subject of numerous studies aimed at correlating physical and chemical properties with distinct cluster sizes and, in some cases, geometries.^{1–24} In principle these systems provide microscopic information about differential solvation, i.e., changes in “solute” properties deriving from the sequential addition of “solvent” species, that could not easily be extracted from the analogous measurements on the bulk materials.^{25,26} The limiting cases of these size-dependent cluster studies are, of course, these very same bulk phase measurements, and in fact it is the nature of the onset (or lack thereof) of bulklike properties in finite systems that has captured much of the attention.^{7,10,13–15,18} These systems are also ones to which theoretical approaches can contribute considerable insight. For example, previous work has revealed that quite different local environments, due to a cancellation of contributing factors, can produce nearly identical net shifts of the spectrum of a solvated chromophore.^{14,27}

Particularly dramatic examples of clusters whose properties do *not* appear to approach asymptotically the corresponding bulk properties with increasing cluster size were reported by Whetten and co-workers¹⁰ earlier in this decade. They found that in benzene·(Ar)_n, benzene·(N₂)_n, and Al·(Ar)_n, the position of the maximum in the chromophore’s absorption line (corresponding to the 6₀¹ vibronic transition in benzene^{4,5} and the 3*p*→4*s* transition in Al (Ref. 7) becomes independent of cluster size beyond about *n*=20 or so, but this asymptotic spectral shift is at most half of the value that would be expected for the chromophore when found in a bulklike solvation environment.^{26,28–30} In the case of benzene·(Ar)_n clusters, this peculiar state of affairs (elaborated in additional experiments by Knochenmuss *et al.*¹⁵) subse-

quently was shown to be less mysterious than initially thought, and in fact the results could be explained easily if the clusters were produced with a propensity for the benzene molecule to be bound at the surface of a neat argon cluster.^{14,18} These so-called “nonwetting” cluster structures^{6,11} need not correspond to global minimum-energy geometries, but rather need only display kinetic stability during the time interval between their production in an expansion jet and their spectral interrogation. The question of whether this explanation can be extended to other cluster systems for which investigators also have noted an apparent absence of convergence to bulk properties has spurred us to consider here the ostensibly similar system, benzene·(N₂)_n.

There have been investigations of benzene·(N₂)_n clusters in addition to the one by Whetten and co-workers,¹⁰ in particular a two-color time-of-flight mass spectrometry study of the smallest clusters (*n*≤8) by Bernstein and co-workers²⁸ and a Raman spectral study of the clustered N₂ molecules themselves by Felker and his collaborators.¹² In the first of these two works,³¹ a nearly linear dependence of the shift of the benzene’s 6₀¹ vibronic transition frequency on the number of bound N₂ molecules (when *n*=2–8) was found. The authors also suggested that their relatively small measured spectral shifts as compared with the bulk values reflected a lower local solvent density, that in a high-density bulk solvation environment dinitrogen atoms would be forced into relatively unfavorable interaction sites at the periphery of the aromatic ring that otherwise would remain unpopulated in either clusters or low-density fluids. A more detailed depiction of the clusters, however, derives from the work of Felker’s group.¹² They indicated that their measurements are consistent with a model in which the clusters have N₂ molecules bound directly above and below the benzene ring on the C₆ axis, at sites lying on circles above and below the ring plane and surrounding (more or less) the axially

bound molecules, at sites on the periphery of the aromatic ring, and at sites in a second solvation shell, these various sites being populated roughly in the order given here as the cluster size increases. Absent, though, is any definitive picture of the relative orientations of the dinitrogen molecules. Evidence for a distribution of geometric isomers also emerged from these experiments, but it is not clear whether such a distribution reflects an equilibrium ensemble or instead testifies to the presence of molecules in nascent metastable states.

In the present work we seek to add to the understanding of these weakly bound clusters by employing a methodology that permits a prediction of the solute's spectral shift given an appropriate set of characteristic cluster geometries and hence yields a direct correlation between structure and spectroscopy. We will show that this approach predicts spectral shifts that are in good agreement with those reported by the Bernstein³¹ and Whetten¹⁰ groups. Furthermore, we confirm the observation that, as the clusters become larger, the asymptotic trend in these shifts is towards a value that is considerably smaller in magnitude than those found in studies of dense fluids or matrices, i.e., the result which piqued the initial interest of Whetten and co-workers. But beyond endorsing some of the conclusions emanating from the experimental work, we are able to address some of the structural details of these clusters that are not easily extracted from spectral measurements alone.

II. THEORY AND SIMULATIONS

The formalism adopted in the present work for calculating the electronic spectral shift of a chromophore (benzene) given a specific solvent cluster configuration is the same one that was used previously in studies of both benzene·(Ar)_n clusters and the analogous bulk solutions.^{14,18,27,32} In all these systems it is the collective dielectric response of the nonpolar (but polarizable) solvent species that dominates the spectroscopy and produces a shift of the absorption maximum to the red of the result obtained for an isolated benzene molecule. (One can easily show that for a symmetric solute molecule such as benzene, there is no additional spectral shift deriving from interactions with the quadrupole moments of the solvent molecules.) And again, since this shift is on the order of tens of cm⁻¹ while the transition frequency itself is on the order of tens of *thousands* of cm⁻¹, a perturbation theory approach to calculating the response is expected to be quite adequate. One of the lessons learned in the investigations of benzene·(Ar)_n clusters, though, is that one may not immediately equate the solute's spectral shift effected by the solvent's dielectric response with the experimentally observed shift. Consideration must also be given to the effect of short-range residual forces on the transition frequency. These repulsive forces tend to blue-shift the absorption spectrum thereby partially canceling the red shift deriving from the collective polarization of the solvent. The key equations²⁷ yielding these opposing shift contributions are

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

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

Here ω_u is the chromophore's transition frequency in the absence of a solvent, m_v is an effective oscillator mass determined from the solvent's polarizability, $\omega_{\alpha} = \omega_{\alpha}(\mathbf{R})$ is the frequency of the α th collective solvent polarization mode associated with the particular system geometry \mathbf{R} , $c_{\alpha} = c_{\alpha}(\mathbf{R})$ is the strength of the coupling between this mode and the chromophore's effective transition dipole, and $r_{0j} = |\mathbf{r}_0 - \mathbf{r}_j|$ is the distance between the center of mass of the chromophore (indexed by 0) and that of the j th solvent atom. (Only the z nearest-neighbor nitrogen atoms contribute to the short-range repulsive component. Note that the sum here is over *individual nitrogen atoms* rather than dinitrogen molecules.) The two remaining constants, d (the magnitude of the effective transition dipole moment of the chromophore) and b (a scaling constant for the repulsive forces), are treated as adjustable parameters²⁷ and are determined by fitting the calculated shifts to experimental results for small clusters, in particular to the $n=3, 5$, and 7 results reported by Bernstein and co-workers.³¹ The values determined by means of this procedure are $d=2.43$ D and $b=37.9$ cm⁻¹ a₀². Interestingly, an important difference between the benzene·(Ar)_n and the benzene·(N₂)_n systems emerges from this parametrization. To obtain the best fit to the experimental data, it was necessary to truncate the sum of contributions to the repulsive (blue) shift component at the interactions deriving from those (at most two) dinitrogen molecules bound directly above and below the benzene ring. In the next section we discuss some of the details of the cluster geometries, but let us simply state here that a direct inspection of the structures has indicated that this truncation is justified given the fashion in which the dinitrogen molecules arrange themselves relative to the ring *and* to one another.

We obtain characteristic cluster geometries at a given temperature by means of routine Metropolis Monte Carlo techniques just as in our previously reported studies of benzene·(Ar)_n,^{14,27} the only addition to our procedure here being the specification of an orientation for each dinitrogen molecule.³³ (All intramolecular nitrogen-nitrogen atomic distances were held fixed at the experimental bond length of 0.1098 nm.³⁴) Dinitrogen-dinitrogen potential interactions were calculated using the five-site model proposed by Murthy *et al.*³⁵ (a combination of Lennard-Jones atom-atom potentials and pairwise interactions between charges distributed along the internuclear axes), which is parametrized to give the correct quadrupole moment of dinitrogen. Interactions between nitrogen atoms and the individual atoms of the benzene molecule were described by a sum of Lennard-Jones potential functions using the parameters suggested by Wanna and Bernstein.³⁶ All cluster results reported herein correspond to a temperature of 5 K.

III. RESULTS

A. Spectral shifts

We begin this discussion of the calculated spectral shifts with an examination of the size-dependence of a cluster's

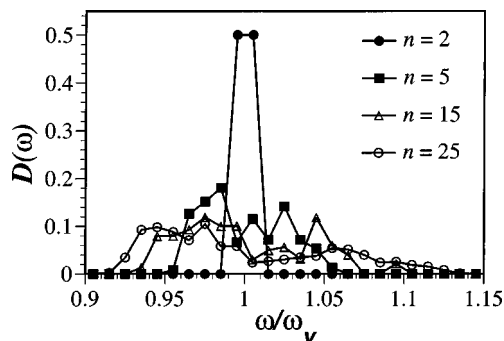


FIG. 1. Polarization mode densities of states $D(\omega)$ of benzene·(N₂)_n clusters, $T=5$ K.

dielectric response. In Fig. 1 are shown the plots of the collective polarization mode densities of states for four different cluster sizes, the abscissa being the mode frequency given as a fraction of the frequency appropriate to noninteracting solvent molecules. When $n=2$ the density of states does not really differ from what one would anticipate if each solvent molecule independently polarized the benzene molecule, i.e., a sharp peak at $\omega/\omega_v=1$, but for larger clusters the importance of collective solvent polarization becomes clear. For the largest clusters shown here ($n=25$), there is a clear division of the density of states into a high-frequency regime (studies of benzene·(Ar)_n indicate that these frequencies correspond to longitudinal modes²⁷) and a low-frequency regime (the transverse modes, of which there should be twice as many as there are longitudinal modes). But not all of these polarization modes couple efficiently to the effective transition dipole moment of the chromophore. If one instead examines a plot of the spectrum of couplings $J(\omega)$ (Fig. 2), which is defined as

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

and thus contains explicit information (expressed through the squares of the coupling coefficients) about the degree to which individual modes contribute to the dielectric response, it is easily seen that the high-frequency longitudinal modes dominate the dielectric contribution to the spectral shift even when just a few solvent molecules are present. Again, just as we found when benzene was clustered with argon,¹⁴ one

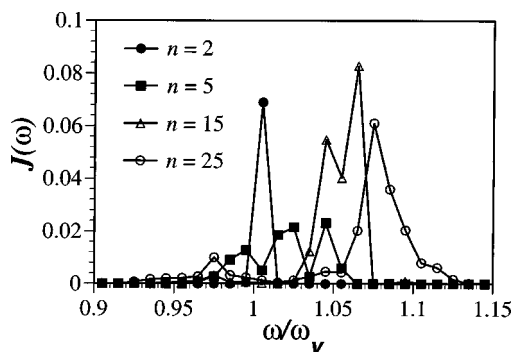


FIG. 2. Polarization mode spectra of couplings $J(\omega)$ of benzene·(N₂)_n clusters, $T=5$ K.

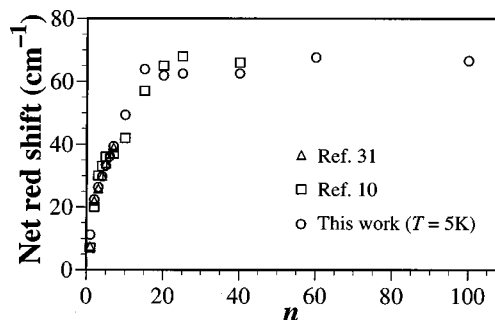


FIG. 3. Size-dependence of the total spectral shifts of benzene·(N₂)_n clusters, $T=5$ K. The circles denote the results of the present work, while the triangles and squares are the experimental results of Nowak *et al.* (Ref. 31) and Li *et al.* (Ref. 10), respectively.

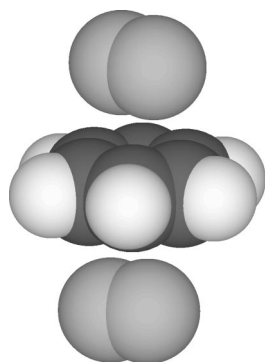
would miss part of the effect of solvation on the chromophore's absorption spectrum if the cooperative nature of that effect were ignored.

The calculated net spectral shifts are shown in Fig. 3 along with the extant experimental results.^{10,31} One sees there that the spectral shift increases monotonically towards the red with increasing cluster size until roughly 20 dinitrogen molecules have been added, at which point the shift becomes nearly independent of cluster size. Overall, the agreement between the calculations and the experimental results is quite good; not only do the calculations capture qualitatively the transition from a strong dependence on the number of solvent molecules to, at most, a very weak dependence, but the quantitative reproduction of the experimental measurements is also respectable. The calculations have been extended to larger cluster sizes than those studied in the experiments, making the plateau behavior even more pronounced.

Unlike the situation found for benzene·(Ar)_n,^{14,18} our calculated spectral shifts for benzene·(N₂)_n reproduce the large-cluster experimental results, not tending towards the dense-liquid results even for $n=100$. Thus the initial expectation that there would be little difference between benzene clustered with dinitrogen and benzene clustered with argon is not realized; carefully equilibrated large clusters were shown in the case of benzene·(Ar)_n to yield spectral properties very similar to those of the condensed-phase systems. The wetting vs nonwetting cluster geometry argument that served so well in the analysis of the argon case clearly is not the key to understanding the results here. Insight into the origin of this difference requires an examination of the cluster geometries themselves, which is described in the following section.

B. Cluster structures

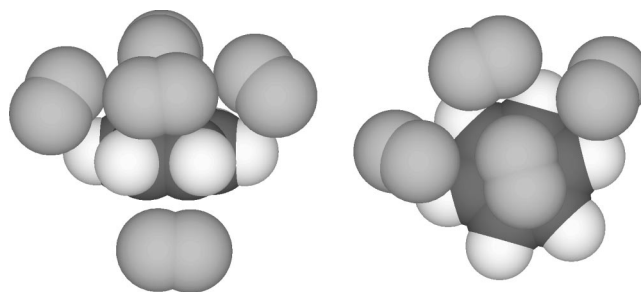
A real advantage of simulations is that one necessarily has a set of system structures that may be examined in an attempt to determine the origin of observed behavior. But before discussing the distribution of dinitrogen molecules around the benzene molecule, we should make a few observations about neat dinitrogen clusters and in particular about the structure of the dimer. The potential energy function of Murthy *et al.*³⁵ predicts the lowest-energy dimer structure to be T-shaped, i.e., the bond axis of one molecule bisects the

FIG. 4. Typical structure of a benzene·(N₂)₂ cluster at 5 K.

nitrogen-nitrogen bond of the other, a result which agrees with the structure proposed 25 years ago by Long *et al.*³⁷ and which reflects bonding that is strongly affected by quadrupolar interactions. In contrast, calculations by Berns and van der Avoird³⁸ suggest that the “cross” structure (the two dinitrogen bond axes lie in parallel planes, with one axis rotated 90° with respect to the other) is more stable by about 0.5 kJ/mol. (Both the empirical potential function³⁵ and the *ab initio* calculations³⁸ predict that the dimer bond distance is shorter in the cross structure than in the T-shaped structure by 0.05–0.06 nm.) The functional form parametrized using their results does not, on the other hand, give quite as good results for the lattice dynamics of solid N₂,³⁹ as does the one that we are using in the present study.³⁵ Nonetheless, both *do* predict that in a cryogenic cluster a dinitrogen molecule really is *not* equivalent to a rare gas atom, that an orientational dependence of the solvent-solvent interaction energy will yield a more structured solvation environment than one finds with noble-gas solvents.

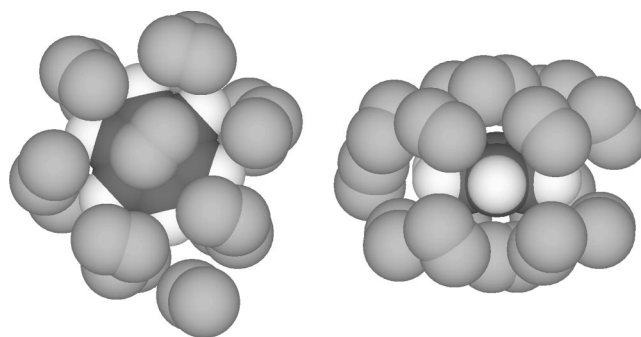
A typical benzene·(N₂)₂ structure ($T=5$ K) is shown in Fig. 4. One clearly sees the preference for occupation first of the binding sites directly above and below the aromatic ring. As noted by Nowak *et al.*,³¹ these sites are interesting due to the fact that there is only a negligible barrier to rotation of the molecule in a plane parallel to the aromatic ring. A structure such as the one shown here is in complete accord with the Raman results of Felker’s group,¹² which suggest that the first two dinitrogen molecules occupy sites that remain occupied as the clusters become larger and that are associated with the most red-shifted Raman line.

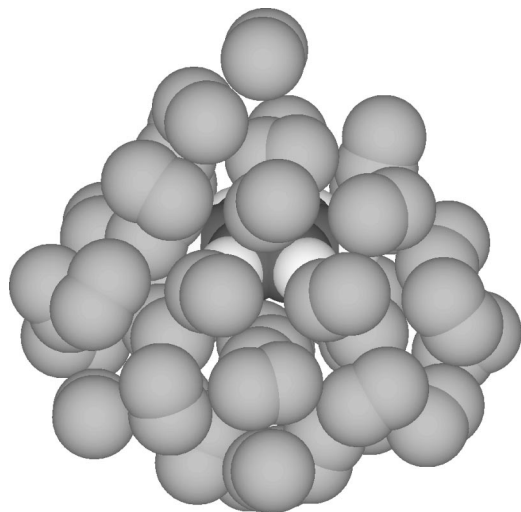
The first evidence of the importance of the orientational dependence of the N₂-N₂ intermolecular forces appears when more than two dinitrogen molecules are present. As an example consider the structure of a typical benzene·(N₂)₅ cluster, which is shown in Fig. 5. (In order to show more clearly the relative orientations of the dinitrogen molecules, we give two views of the same cluster configuration.) Again one finds that the central binding sites above and below the ring are occupied, but the thing to note in these structures is the way in which the other three dinitrogen molecules are distributed. As suggested by Felker and co-workers,¹² they are bound in sites such that their centers of mass lie on a ring above (or, equivalently, below) the benzene, but the individual atoms themselves do not all lie in the plane of that

FIG. 5. Two views of a typical benzene·(N₂)₅ cluster at 5 K.

ring. Recall that our potential function favors a T-shaped dinitrogen-dinitrogen structure; if some of the atoms move out of the plane of the binding sites, they can arrange themselves so as to maximize their mutual quadrupolar attractions. This same orientational preference is seen in all the larger clusters. In Fig. 6 are shown two views of an $n=15$ cluster, in which now all the sites immediately above and below the aromatic ring are occupied (14 dinitrogen molecules fill those sites) and an additional solvent molecule is seen to bridge these two rings of binding sites. (In the left-most view this extra dinitrogen is the one at the bottom of the figure, while in the right-most view, it is seen to lie in the gap at the left-hand-side of the structure.) By doing so, it occupies a binding site lying in the plane of the benzene ring. This disposition is a result anticipated both by Felker and co-workers¹² and also by Nowak *et al.*,³¹ who predicted that increases in local density would eventually lead to dinitrogen molecules being located at peripheral ring sites. (Here, however, the interaction of those molecules is not repulsive as was previously suggested.³¹)

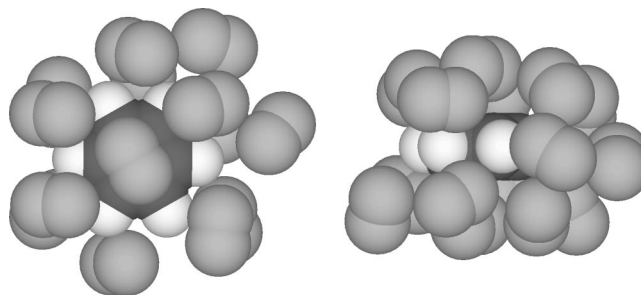
In the $n=15$ clusters, one is approaching the point at which the first solvation shell becomes completely filled. Looking back at the spectral shifts given in Fig. 3, it now becomes easier to divine the origin of the plateau behavior, the onset of which appears in the range $n=15$ –20. It is in this range that additional dinitrogen solvent molecules can no longer be accommodated in the first solvation shell of the solute but instead must bind at more distant sites where they have a relatively negligible effect on the spectroscopy. This result is quite similar to what we have observed in simulations of benzene dissolved in supercritical argon.³² In that system irrespective of the long-range correlations characteristic of a bulk supercritical fluid in the near-critical regime,

FIG. 6. Two views of a typical benzene·(N₂)₁₅ cluster at 5 K.

FIG. 7. Typical structure of a benzene·(N₂)₄₀ cluster at 5 K.

the spectroscopy of the infinitely dilute solute is strongly dominated by the dielectric response of only those atoms lying in the first solvation shell, the disposition of which is determined by short-ranged potential interactions. A somewhat different behavior, however, was seen in studies of cryogenic benzene-argon clusters. In those systems, although the repulsive (blue) contribution to the benzene's spectral shift saturates at the filling of the first solvation shell, the dielectric (red) contribution continues to increase in magnitude as the second shell fills. We believe that two influences may be of importance here, the first of which involves the local solvent density. Because the interactions between dinitrogen molecules include an orientational dependence not present in the interactions between noble gas atoms, the relative arrangement of dinitrogens around the benzene molecule is such that these molecules are experiencing less than optimal interactions with one another. This effective weakening of the dinitrogen-dinitrogen interactions leads to less dense packing of the solvent species in the immediate vicinity of the solute molecule than might be expected otherwise, and as a result the molecules in more distant shells are too far away to have any appreciable effect on the spectroscopy. In the case of benzene in supercritical argon, reduced local density relative to the cryogenic clusters is clearly responsible for the relative independence of the spectral shift on all but the first solvation shell.

A second consideration, however, is suggested by the structure of the $n=40$ cluster shown in Fig. 7, in which we see a benzene molecule enveloped by dinitrogen in an asymmetric fashion. Although solvent molecules are bound to both faces of the aromatic ring, they do not form neat, concentric solvation shells. Instead, we find a net accumulation of solvent molecules on one side of the ring. It comes as no surprise when addition of solvent to this sort of cluster structure yields no appreciable change in the benzene's spectral shift—the appropriate analogy here is to the loss of a dependence of the spectral shift on cluster size seen in nonwetting benzene·(Ar)_{*n*} clusters.^{14,18} The further addition of solvent molecules simply has no effect on the local solvation environment of the benzene molecule.

FIG. 8. Two views of a typical benzene·(N₂)₁₅ cluster at 40 K.

It is fair to ask, though, whether the $T=5$ K cluster structures on the basis of which these conclusions are drawn do in fact have a direct relevance to the clusters produced in experiments. In particular, experimental cluster temperatures are often imprecisely characterized, assuming of course that their internal energies are distributed such that temperature is a relevant variable. We therefore have generated additional cluster structures consistent with a temperature of 40 K. An example of such a structure for $n=15$ is shown in Fig. 8, with two views being given in order to make the comparison easier with the structure found in Fig. 6. Certainly the higher temperature structure is less well ordered, but the difference is not especially dramatic. Some of the orientational preference has been lost and a few of the dinitrogen molecules have moved into the plane of the benzene molecule. The six-fold symmetry with which the dinitrogens are disposed on the benzene's face—the symmetry is most obvious in the left-most view—is nonetheless largely preserved when the temperature is raised.

However, these modest structural changes are reflected in a significant change in the spectral shift of the clusters. The average shift of -64 cm^{-1} calculated for the 5 K configurations is 30% greater in magnitude than is the value of -49 cm^{-1} obtained at 40 K. Since solvent molecules lying in the plane of the aromatic solute contribute less to the dielectric shift component than do those situated with their centers of mass lying in rings immediately above and below the benzene, the disordering that accompanies a temperature increase yields a net reduction in the solvent-induced spectral perturbation.

Disordering of higher-temperature clusters is also evident in a comparison of the typical $n=40$ cluster shown in Fig. 7 with the one obtained in a 40 K simulation that is shown in Fig. 9. The most dramatic changes observed, however, do not involve the dinitrogen molecules in closest proximity to the solute to the degree that the more distant solvent species are affected. This observation is consistent with our previous finding that the “melting” transition in large benzene-argon clusters is not characterized by appreciable disruption of the innermost solvation shell but rather by a loss of structural rigidity in the outer solvent layers.¹⁸ The shift of the spectrum is less here in warming from 5 K to 40 K, the lower-temperature shift being -63 cm^{-1} and the higher-temperature one being -55 cm^{-1} , with this change (which is only half of that seen in the $n=15$ case) attribut-

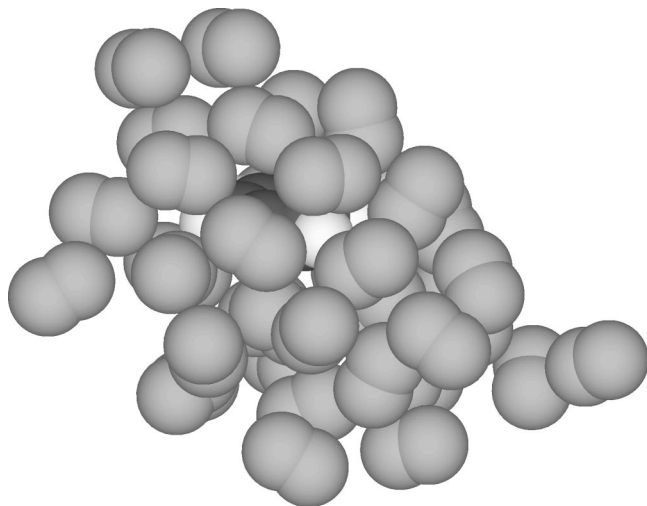


FIG. 9. Typical structure of a benzene·(N₂)₄₀ cluster at 40 K.

able principally to a net expansion of the cluster and hence a decrease in the local solvent density.

IV. SUMMARY

In the present work we have performed simulations yielding characteristic structures of benzene·(N₂)_n clusters from which geometry-dependent shifts of the 6₀¹ vibronic transition of benzene have been calculated. The calculated shifts are in good agreement with the experimental results for these systems, reproducing not only the sharply increasing magnitude of the shift for clusters containing fewer than 15–20 dinitrogen molecules but also the loss of that size-dependence in the larger clusters. In accordance with the observations of Whetten and co-workers,¹⁰ these asymptotic shift values do not approach those of benzene dissolved in a dense fluid but rather are only about half as large. The benzene-dinitrogen clusters thus differ from the deceptively similar benzene-argon clusters in that the lack of convergence of the chromophore's spectral shift to the bulk values with increasing cluster size cannot be explained by a preference for formation of nonwetting cluster structures under the conditions of the experiments.

So why does one find this peculiar size dependence when the solvent is dinitrogen? An examination of individual cryogenic cluster structures suggests that the dinitrogens in the immediate vicinity of the benzene molecule are hindered in their packing by the orientational dependence of their interaction forces. The suggestion offered by Nowak *et al.*,³¹ that at higher liquid densities the solvent molecules are forced into binding geometries that would not be favored at lower densities, contains an important basic truth. At the higher temperatures associated with the liquid studies, the translational energy of the dinitrogen molecules would be sufficient to overcome the interactions that produce structure in the cryogenic clusters. With these forces overcome, the molecules are then able to achieve higher densities than would otherwise be possible in the clusters, thereby yielding a local solvation environment that further shifts the benzene's spectrum to the red. As hinted in our discussion of the

dinitrogen-dinitrogen potential energy function, there may be many more relative orientations that are possible, including some involving closer approach of the centers of mass of the molecules, once there is sufficient thermal energy to overcome the quadrupolar orientation-dependent forces. A closer approach of dinitrogens to one another might also lead to second-solvation-shell dinitrogen molecules being near enough to the benzene to have a significant effect on the spectroscopy. Clearly, simulations of the analogous bulk system, benzene dissolved in liquid nitrogen, will be required in order to test this hypothesis. An extension of this work to systems involving molecules such as CO₂ is also of interest, since these species would be similar but characterized by a different relative orientation of the solvent molecules.

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