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Calculations of the geometry and binding energy of aromatic dimers: Benzene, toluene, and toluene–benzene[a)]

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Calculations of the geometries and energies of the benzene, toluene, and toluene–benzene dimers using a combination of atom–atom and multipolar potentials are presented and discussed. An exponential-six atom–atom potential plus a molecular quadrupole–quadrupole interaction term gives the reported parallel displaced C_{2h} benzene dimer geometry. The excited state behavior of the benzene dimer can be qualitatively understood based on this calculation. The toluene–benzene dimer is well modeled by these terms in addition to a dipole–quadrupole interaction term. Both parallel displaced and perpendicular configurations are obtained in agreement with the experimental data. Using exponential-six dipole–dipole, quadrupole–quadrupole, and dipole–quadrupole interactions the toluene dimer can be satisfactorily modeled. The calculations generally suggest that excitation of parallel displaced dimers can lead to rearrangement (and possible excimer formation) in the excited state.

I. INTRODUCTION

One of the most important properties of a van der Waals (vdW) cluster is its geometry[1]: cluster geometry expresses not only the symmetry and steric properties of a system, but also its energtics. Such observables as spectral shifts and binding energy are sensitive to changes in the geometry of a cluster.[2] Since the equilibrium geometry of a cluster is the result of a delicate balance of a variety of intermolecular interactions, a knowledge of cluster geometry can lead to a better understanding of the relative sizes of the various contributions to the overall cluster interaction energy.

Computer modeling of the intermolecular energy of a vdW cluster has been shown to be a very useful contribution to the process of deducing cluster geometry from spectroscopic data.[3] Minimum energy configurations of the clusters of interest are obtained for a number of different intermolecular potentials. A geometry consistent with all spectroscopic observables is accepted as the sufficient one. In addition, this process suggests a form for the intermolecular interactions.

Spectroscopic data for aromatic dimers (benzene)$_2$, (toluene)$_2$, tol–ben are not always sufficient to determine the geometry of the dimers uniquely.[4] For example, a parallel-displaced (pd) dimer is suggested by the 2-color MS data for (ben)$_2$,[4] but less information is obtained from the spectra of (tol)$_2$ and tol–ben. The spectroscopic data, in addition, do not shed light on such questions as, why do dimers have certain geometries, why are some dimer red shifts large and others small, why do dimer excited state lifetimes differ from monomer lifetimes, or how can excimers[5] form upon excitation of ground state dimers. The computer modeling of aromatic dimers has enabled us to address these and a number of other questions discussed in this paper.

Recent reports from this laboratory have demonstrated the usefulness of potential energy calculations for benzene–solvent, toluene–solvent, and *n*-propyl benzene–solvent clusters.[3] An atom–atom exponential-six (exp-6)[6] form for the intermolecular potential provides reasonable geometries for the ben$(S)_x$, tol$(S)_x$, and *npb* $(S)_x$ $(x < 3)$ systems. However, the aromatic dimers are not well represented by an exp-6 form of the intermolecular potential: the predicted geometries are in general not consistent with the spectroscopic data. The approach taken by Williams to improve the intermolecular pair potential involves placing partial charges on the atoms.[6] Although reasonably successful, this approach is not ideal because some clearly incorrect low energy structures are obtained and the structures are quite sensitive to the size of the partial charges chosen. We have instead employed the exp-6 form supplemented by molecule–molecule multipolar terms such as quadrupole–quadrupole (V_{qq}), quadrupole–dipole (V_{dq}, V_{qd}), and dipole–dipole (V_{dd}) interactions as appropriate. While this procedure is subject to limitations as well, it at least has the advantage that experimental values of many of these moments are available in the literature. By exploring the relative importance of such terms and by estimating the magnitudes of the multipolar interactions in the excited state, dimer geometries and energetics can be elucidated.

This paper reports the results of computer modeling of (ben)$_2$, (tol)$_2$, and tol–ben. Spectroscopic data for these aromatic dimers demand the use of forms of the intermolecular potential more complicated than exp-6 atom–atom potentials. The choice of which extra terms to include is governed by symmetry and the observed data.

II. PROCEDURES

The computer modeling algorithm used to generate the aromatic dimer energy and geometry is similar to methods previously employed for solute–solvent clusters.[3] However, in this study five different expressions for the intermolecular energy are used (see Table I). The first involves only an exp-6 potential with parameters determined by Williams[6]: these terms are present in all other forms of the potential. The parameters are chosen to reproduce the heat of simulation of

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TABLE I. Potential energy expressions and parameters used to find minimum energy configurations of aromatic dimers.

Energy expressions	Terms[a]	Parameters[b]
I. Exp-6	$\frac{A_{ij}}{R_{ij}{}^{6}}+B_{ij}\exp[-C_{ij}R_{ij}]$	A_{ij}, B_{ij}, C_{ij} given in Ref. 6
II. Exp-6 + $\frac{qq}{R}$	$\frac{qq}{R}=\frac{q_iq_j}{R_{ij}}$	$q_c=-q_H=-0.153\,e$
III. Exp-6 + V_{qq}	$V_{qq}=\frac{3}{4}\frac{Q_aQ_b}{R_{ab}^{5}}[1-5(\mathbf{q}_a\cdot\mathbf{r}_{ab})^2-5(\mathbf{q}_b\cdot\mathbf{r}_{ab})^2$ $+2(\mathbf{q}_a\cdot\mathbf{q}_b)^2-16(\mathbf{q}_a\cdot\mathbf{q}_b)(\mathbf{q}_a\cdot\mathbf{r}_{ab})(\mathbf{q}_b\cdot\mathbf{r}_{ab})$ $+17(\mathbf{q}_a\cdot\mathbf{r}_{ab})^2(\mathbf{q}_b\cdot\mathbf{r}_{ab})^2]$	$Q_a=Q_b=5.6\times10^{-26}$ esu cm
IV. Exp-6 + V_{qq} + V_{dq}	$V_{dq}=\frac{3}{2}\frac{\mu_aQ_b}{R_{ab}^{4}}[(\boldsymbol{\mu}_a\cdot\mathbf{r}_{ab})+2(\boldsymbol{\mu}_a\cdot\mathbf{Q}_b)(\mathbf{Q}_b\cdot\mathbf{r}_{ab})$ $-5(\boldsymbol{\mu}_a\cdot\mathbf{r}_{ab})(\mathbf{Q}_b\cdot\mathbf{r}_{ab})^2]$	$\mu_a=0.38\,D$
V. Exp − 6 + V_{qq} + V_{dq}	$V_{qd}=V_{dq}$ with a and b interchanged	
+ V_{qd} + V_{dd}	$V_{dd}=-\frac{\mu_a\mu_b}{R_{ab}^{3}}[3(\boldsymbol{\mu}_a\cdot\mathbf{r}_{ab})(\boldsymbol{\mu}_b\cdot\mathbf{r}_{ab})-\boldsymbol{\mu}_a\cdot\boldsymbol{\mu}_b)]$	$\mu_b=\mu_a$

[a] Terms not written out explicitly for a particular potential are the same as those terms already presented in the previous potentials.

[b] Parameters not listed for a particular form of the potential are the same as those for the forms previously given.

the benzene crystal. Since the interactions in the crystal and the aromatic dimers are in general similar, such parameters should serve as a reasonable first approximation of the dimer interaction. The second energy expression is the improved potential of Williams[6] which places partial charges on the atoms. The remaining three expressions incorporate molecule–molecule terms appropriate for $(\text{ben})_2$, tol–ben, and $(\text{tol})_2$ as a replacement of the Coulomb part of the intermolecular potential. Expressions for V_{qq}, V_{dq}, and V_{dd} are derived from the text of Hirschfelder, Curtis, and Byrd[7] utilizing the quadrupole moment of benzene[8] and dipole moment of toluene.[9] The numerical values of the coefficient for the exp-6, V_{qq}, V_{dq}, and V_{dd} terms are the same in all expressions. The quadrupole moment of toluene is assumed to be the same as that of benzene. The geometry of benzene is that used by Williams,[6] and the geometry of toluene is taken from the crystal structure.[10] The center of the multipole moments of toluene is displaced from the center of the aromatic ring (0.464 Å) towards the methyl group at approximately the center of charge.[11]

In order to estimate the dimer spectral shifts and obtain some idea about excited state energetics and structure, excited state dimers are also modeled. The general approach employed involves changing the multipole moments of the molecule excited: the exp-6 parameters could not be readily varied in a systematic fashion. The excited state of toluene is modeled in two separate calculations: one calculation doubles both the dipole and quadrupole moments of toluene and the other increases the dipole moment by a factor of 8. This latter rather large change is suggested by a recent calculation.[12] The actual change in the moments of toluene most likely falls between these two limits.

The success of these intermolecular potential calculations is largely due to the separability of the interactions. It has been shown that spectral shift scales with polarizability[13] and dipole moment.[14] Since to a first approximation the exp-6 terms model the dispersion forces only, the multipolar terms can be added as appropriate without reoptimizing the exp-6 parameters.

The routine for minimizing the intermolecular energy of the dimers is the same as that described previously for clusters.[3] The energy for a particular configuration is calculated, then the ligand is moved a step in one of the six (three translational and three rotational) degrees of freedom and the energy is recalculated. If the resulting energy is lower, the step is repeated; if the energy is not lower the ligand is stepped back and another degree of freedom is explored. A minimum energy configuration can thus be achieved. Care must be taken to start the cluster in a number of sufficiently different configurations to ensure that all of the local minima in the potential surface (configuration space) are located. Atomic positions for all of the calculated geometries are available upon request. Only pertinent data for the geometries presented in figures are given in the text.

III. RESULTS AND DISCUSSION

A. Benzene

1. Spectroscopic data

The spectroscopic data for $(\text{ben})_2$ reveals much about the geometry of the dimer. A 0_0^0 transition is clearly evident for the dimer, whereas this transition is symmetry forbidden in the monomer. The dimer must, therefore, have less than C_3 symmetry. Since only one peak is observed in the origin region, only one type of benzene molecule in the dimer is present in appreciable amounts; both benzene molecules in the dimer must be spectroscopically equivalent [see the discussion below for $(\text{tol})_2$ and tol–ben]. A C_{2h} parallel-displaced (pd) geometry is consistent with the data.[4]

The observed spectral shift for $(\text{ben})_2$ is $-42\ \text{cm}^{-1}$. Comparison of this spectral shift with previous results allows a qualitative estimate of the relative displacement of the benzene molecules in the dimer. For clusters studied previously [ben$(S)_x$, tol$(S)_x$, *npb* $(S)_x$],[3] the spectal shift is found to be proportional to the polarizability of the solvent and the displacement of the solvent away from the center of the aromatic ring. The large polarizability of the benzene "solvent" implies that the relative displacement should be large (~ 2 Å) to produce such a relatively small (-42 cm^{-1}) spectral shift.

2. Computer modeling

The benzene dimer is modeled using three different forms for the intermolecular potential (labeled I, II, III in Table I). The exp-6 potential calculation predicts only one geometry for $(\text{ben})_2$ (see Fig. 1): the two molecules are centered over one another in a staggered configuration. This geometry of the dimer preserves the sixfold symmetry axis of benzene and consequently must be rejected.

The second expression used to calculate the geometry of $(\text{ben})_2$ contains a partial charge atom–atom term $(q_i q_j / R_{ij})$. The q_i's have been determined to fit the free energy of the benzene crystal[6] (see Table I). This expression predicts two stable geometries for $(\text{ben})_2$ (see Fig. 1); a "herring-bone" and a pd geometry. The two benzene molecules in the herring-bone configuration are physically distinguishable and this geometry is therefore rejected. The pd geometry is consistent with all spectroscopic data and has a binding energy within 15 cm^{-1} of that of the herring-bone configuration. Although this expression for the intermolecular energy predicts a configuration consistent with the $(\text{ben})_2$ spectroscopic data, it has at least two shortcomings. First, the lowest energy configuration generated by this calculation is not consistent with the $(\text{ben})_2$ spectrum. The herring-bone geometry should also be observed spectroscopically if this second calculation is valid. Second, the geometries predicted by calculations which include the $q_i q_j / R_{ij}$ term are very sensitive to the values chosen for q_i and q_j. Reducing the values of q_i and q_j to those which yield the correct molecular quadrupole moment eliminates the herring-bone configuration and greatly reduces the ring displacement in the pd configuration. A displacement this small would be expected to produce a spectral shift much larger than -42 cm^{-1}. On the other hand, increasing the q_i's can eventually generate a perpendicular configuration.

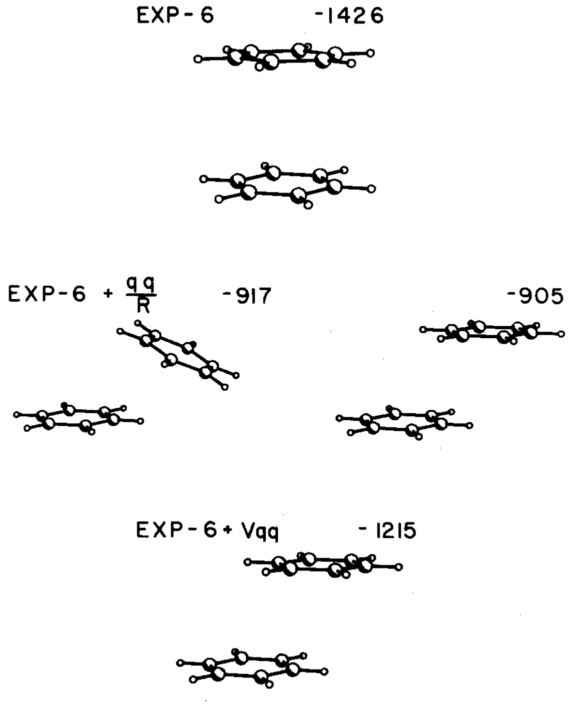

FIG. 1. Minimum energy configurations calculated for $(\text{ben})_2$ using three different expressions for the intermolecular potential (expressions I, II, and III in Table I). The total intermolecular potential energy (in cm^{-1}) for each of the calculated dimers is given in the figure. The exp-6 + V_{qq} geometry adequately models the ground state dimer while the exp-6 configuration models the equilibrium geometry of the excited state before excimer formation (see the text).

The third potential (Table I) employed in modeling this dimer consists of the exp-6 terms in addition to a molecular quadrupole–quadrupole interaction (V_{qq}). This interaction results in a geometry for the $(\text{ben})_2$ completely consistent with the spectroscopic data. The V_{qq} term in the potential incorporates the correct value for the benzene quadrupole moment and causes the two benzene molecules to be displaced in the X (C–H bond) direction by 2.3 Å (Fig. 1). A displacement this large is consistent with a -42 cm^{-1} spectral shift. The calculated geometry is pd and has C_{2h} symmetry. The two benzene molecules are indistinguishable, only one stable configuration is predicted, and the spectra are well modeled in all respects.

3. Excimer formation

Potential calculations for the benzene dimer shed some light on the formation of the suggested $(\text{ben})_2$ excimer.[5] Spectroscopic data point clearly to the formation of an excimer: the lifetime of all features in the spectrum falls from 100 ns in the isolated molecule to 40 ns while the fluorescence quantum yield falls significantly (probably a factor of 10^2).[5] The expected geometry for the excimer is D_{6h} or S_{12}, parallel undisplaced and closely spaced (< 3.5 Å ring separation).[5] The above calculations present a possible mechanism for the formation of the excimer from the pd ground state dimer. The calculations just described (potentials I and III, Table I) suggest that the displacement of the two benzene molecules in the benzene dimer is due essentially to the V_{qq} term. Excitation of benzene to the $^1B_{2u}$ state causes the molecular quadrupole moment to vanish and thus the V_{qq} term contribution to the binding energy is "zero" for the excited state benzene dimer. The dimer can then collapse to the parallel undisplaced configuration usually associated with excimer formation without a significant barrier.

The suggested dimer–excimer transition still presents somewhat of a puzzle: the excited state lifetime of the dimer is not consistent with the very low quantum yield for emission and the dimer absorption features are sharp (2.5 cm^{-1}) with large Franck–Condon overlap for the low lying vdW modes. Such spectral features are not characteristic of absorption to high lying levels of an excimer well. The present calculations may suggest a possible mechanism for this behavior. The pd ground state can undergo a transition to a pd excited state stabilized by small induced quadrupole moments in benzene. If this pd excited state lives for ~ 2 ps and then collapses to a parallel undisplaced configuration, the experimental data[5] can be rationalized.

B. Toluene–benzene

1. *Spectroscopic data*

The spectroscopic data[4] for tol–ben reveal two sets of peaks in the region of the toluene 0_0^0 transition (tol*–ben 0_0^0). One set of peaks has a small spectral red shift (< 25 cm^{-1}), a low intensity, and is composed of at least two separate origins. The other set of peaks in the tol*–ben 0_0^0 region has a large spectral shift (-250 cm^{-1}), only one obvious origin followed by a progression of vdW stretching and bending modes, and is about ten times more intense than the peaks with the small shift.

The spectrum in the tol–ben* 6_0^1 region shows only one set of features. Presumably the lower overall intensity of the spectrum in this region precludes observation of the less shifted set of peaks. The geometry described as exhibiting a large spectral shift for the tol*–ben 0_0^0 region has a much smaller shift in the tol–ben* region (-40 cm^{-1}).

2. *Computer modeling*

The computer modeling of tol–ben using the exp-6 form for the potential energy predicts three stable geometries: two perpendicular ($\perp$) configurations and one pd configuration (see Fig. 2). The spectroscopic characteristics expected for the $\perp$ configurations are those of the less shifted set of features in the tol*–ben 0_0^0 region. The spectral shifts for the calculated $\perp$ geometries should be small, assuming the general relationship between spectral shift and overlap of the solvent with the aromatic system of the solute is valid. The prediction of more than one $\perp$ geometry is consistent with the observation of more than one origin in the less shifted set of features. Finally, the weak intensity expected for the less shifted peaks correlates well with the observed intensities: the $\perp$ geometries are less stable than the pd geometry (see Fig. 2).

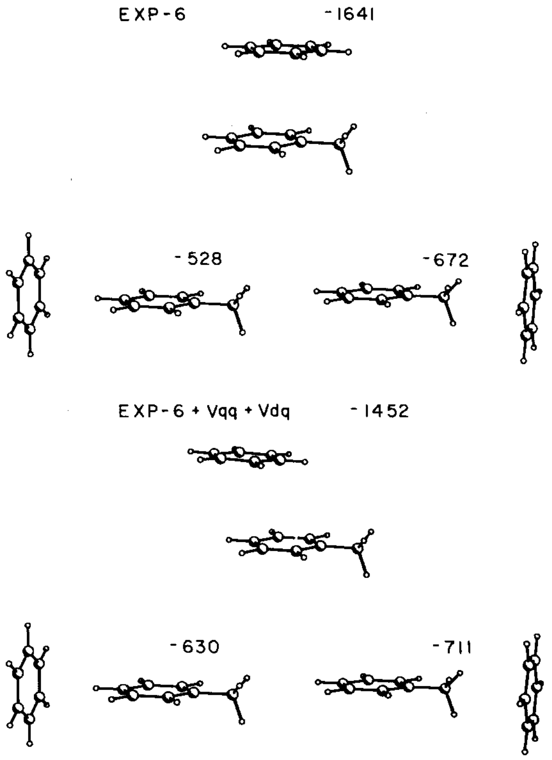

FIG. 2. Important minimum energy geometries for tol–ben calculated using two different intermolecular potentials (expressions I and IV in Table I). The exp-6 + $V_{\rm qq}$ + $V_{\rm dq}$ potential shows three ground state geometries assignable to features in the tol–ben spectrum. Excited state geometries are not shown. Intermolecular energies are given in cm^{-1}.

The tol–ben pd gometry calculated with the exp-6 potential (Fig. 2) is not entirely consistent with the observed spectrum. Although the large binding energy of the pd configuration serves as a rationalization for the high intensity of the features at -250 cm^{-1} from the toluene 0_0^0, the observed shifts of tol–ben transitions are not consistent with the pd geometry predicted by the exp-6 calculation. One would anticipate red shifts for the tol–ben* transitions of much more than 40 cm^{-1} and red shifts for tol*–ben much less than 250 cm^{-1}: in fact, expectations based on this potential form are for equal shifts for the excitation of either molecule in this geometry.

Additon of $V_{\rm qq}$ and $V_{\rm dq}$ terms to the exp-6 potential form (Table I, potential IV) provides calculated geometries consistent with the observed binding energies, spectral shifts, and intensities. The $\perp$ geometries generated by this improved potential are similar to those calculated with the exp-6 terms only. However, the pd configuration generated with potentials I and IV are quite different (Fig. 2). The greater displacement of the two molecules in the dimer obtained with the exp-6 + $V_{\rm qq}$ + $V_{\rm dq}$ reduces the π-system overlap between benzene and toluene such that the expected tol–ben* 6_0^1 red shift relative to benzene 6_0^1 is more like that found for the (ben)$_2$ 6_0^1.

Furthermore, the -250 cm^{-1} spectral shift for the tol*–ben 0_0^0 can now be readily understood. The dipole moment (and presumably the quadrupole moment) of toluene is expected to increase upon excitation; perhaps by as much as a factor of 8.[12] This increase in multipole moment increases the binding energy of the complex, and therefore the spectral shift. The trends can be approximately modeled by increasing the multipole interaction terms until the desired change in intermolecular potential energy is achieved. Increasing the quadrupole and dipole moments of toluene by a factor of 2, or increasing the dipole moment by a factor of 8 produces an increase in the binding energy of 200 cm^{-1}. The equilibrium geometry of this model "excited state" complex is very similar to the ground state geometry and therefore is consistent with the large Franck–Condon overlap for the first few vibronic levels. Thus a modest increase in the quadrupole moment of toluene (benzene) and a reasonable increase in the dipole moment upon excitation would account for the large (-250 cm^{-1}) spectral shift for the tol*–ben 0_0^0 transition. The actual change in multipole moments upon excitation is probably within the limits expressed above (i.e., $Q'' < Q' < 2Q''$ and $D'' < D' < 8D''$).

Calculations of the tol–ben geometry using potential IV (Table I) yield an additional stable, nearly pd (10° from parallel) configuration in which the benzene is displaced 2.6 Å towards the methyl group of toluene. No spectroscopic features in the tol–ben spectrum can at present be assigned to this dimer geometry. Since the $V_{\rm dq}$ term is positive in this configuration, an excited state rearrangement to the more stable pd geometry discussed above could well occur. Absorption to this state (tol*–ben) would then be weak, broad, and blue shifted with respect to the tol 0_0^0; it could be buried in the region between the tol*–ben 0_0^0 and the tol–ben* 0_0^0. It is also possible that this configuration may undergo thermal rearrangement in the ground state to the more stable geometry depicted in Fig. 2, as the calculated barrier to rearrangement is estimated to be $\sim 50\ \mathrm{cm}^{-1}$.

3. Excimer formation

The lifetime data for the peaks in the tol–ben spectrum show that an excimer forms upon excitation of some of the tol–ben vibronic levels. The data are consistent with a barrier to excimer formation of approximately 900 cm^{-1}: roughly 900 cm^{-1} of toluene excess vibrational energy must be excited before appreciable excimer formation occurs.[4]

The formation of the tol–ben excimer upon excitation of benzene can be explained as before (see Sec. III A 3). The quadrupole moment of benzene vanishes in the ${}^1B_{2u}$ excited state and the V_{qq} and V_{dq} terms drop out of the intermolecular potential energy expression leaving only the exp-6 form (Table I). Without V_{qq} and V_{dq} terms, the minimum energy geometry is only slightly displaced and excimer formation should readily occur (Fig. 2).

On the other hand, both the spectroscopic data and the calculations (potential expression IV, Table I) indicate that the pd geometry of tol–ben changes very little at the tol*–ben 0_0^0 level. Therefore, the pd geometry of tol*–ben should feature the center of the benzene ring shifted about 2 Å from the center of the toluene aromatic ring. This displaced configuration is stabilized by the multipolar terms in the energy expression and a barrier to excimer formation is thereby quite reasonable. Conceivably, nearly 1000 cm^{-1} of excited state molecular vibrational energy could be required to transfer enough energy to the vdW modes to bring the benzene into a position favorable for excimer formation.

C. Toluene dimer

1. Spectroscopic data

Little is revealed about the geometry of the toluene dimer from its spectrum in the 0_0^0 region.[4] Two sets of absorption features can be identified. One set exhibits a small spectral shift ($-10\ \mathrm{cm}^{-1}$) and has relatively sharp features. The progression in the vdW stretch for this set of features shows a good Franck–Condon overlap near the dimer 0_0^0. The other set of peaks consists of a broad, structured background extending far to the red. Few assignments can be made in this region of the spectrum and several geometries are likely to contribute to the congestion.

2. Computer modeling

Computer calculations with potential V (Table I) yield a number of different geometries for the toluene dimer. pd, ⊥, and even nearly ⊥ geometries appear to be stable because of the interplay between the various orienting terms in the full potential. In addition, the nearly ⊥ configurations are highly dependent on the values of the multipolar moment parameters and may not actually be stable configurations. Below we will discuss only the more certain pd and ⊥ configurations of $(\mathrm{tol})_2$. Figure 3 contains the calculated geometries for the pd and ⊥ configurations.

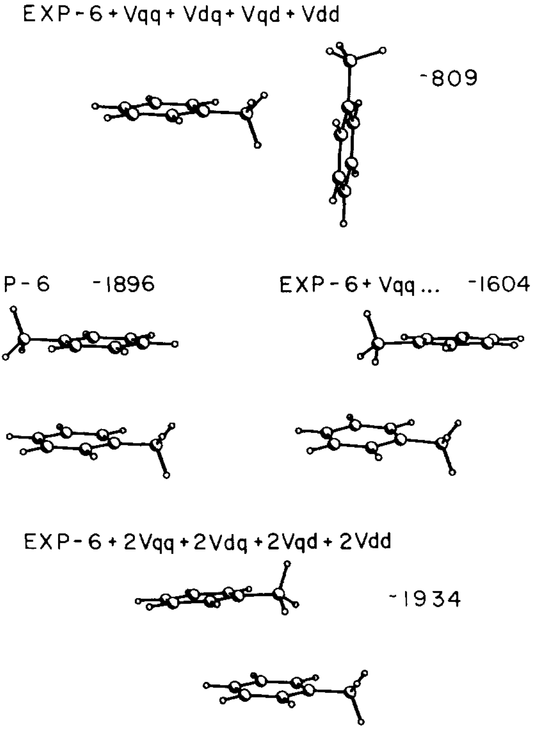

FIG. 3. Representative minimum energy geometries of $(\mathrm{tol})_2$. Serveral ⊥ and nearly ⊥ configurations are found: pictured are the geometries for which spectroscopic features are discernable. The pd configuration undergoes substantial change in geometry upon excitation. The excited state is modeled here by doubling the V_{qq}, V_{dq}, V_{qd}, and V_{dd} terms. Intermolecular energies are given in cm^{-1}.

The ⊥ configuration displayed in Fig. 3 is stable for reasonable values of the molecular moments. The two toluene molecules are distinguishable in the ⊥ configuration and should give different spectral shifts: the horizontal (Fig. 3) toluene would be expected to yield the smaller spectral shift. Consequently, the sharp features in the $(\mathrm{tol})_2$ 0_0^0 spectrum are assigned to excitation of the horizontal (Fig. 3.) toluene in the ⊥ configuration. Excitation of the vertical toluene should lead to features with larger spectral shifts, presumably obscured by the broad, more red-shifted features mentioned above.

The ground state pd geometry predicted by the exp-6 potential is very different from that predicted by the full potential (exp-6 $+ V_{\mathrm{qq}} + V_{\mathrm{dq}} + V_{\mathrm{qd}} + V_{\mathrm{dd}}$), as shown in Fig. 3. The geometry calculated with this full potential is very sensitive to the assumed value of the quadrupole moment of toluene. Clearly, the spectral shift associated with the pd geometry is larger than that of the ⊥ geometry. Doubling of the toluene dipole moment causes substantial reorientation of the toluene dimer: doubling the quadrupole moment has little effect on this geometry. Increasing the dipole moment of toluene by a factor of 8 produces a qualitatively similar geometry. This calculated dramatic change in equilibrium configuration upon excitation, and concomitant increase in binding energy, can serve to rationalize the diffuse nature of the more red shifted features in the $(\mathrm{tol})_2$ spectrum. The ground state dimer may have a maximum Franck–Condon overlap with a dense, high energy portion of the vdW vibrational manifold of the excited state: a broad, relatively unstructured spectrum can thus be generated.

3. Excimer formation

The lifetime data for some of the toluene dimer 0_0^0 features suggest excimer formation. The sharp features shifted by $-10\ \text{cm}^{-1}$ from the toluene 0_0^0 do not show lifetime shortening, but the broad more red shifted features do. The computer modeling of the toluene dimer geometry is consistent with this observation: excimer formation is most likely to occur for a pd rather than a ⊥ geometry. The calculations further indicate that a barrier to excimer formation might occur. If absorption is to high energy vdW modes (as discussed previously), the excess vdW energy could lead to excimer formation despite the barrier.

IV. CONCLUSIONS

An atom–atom exp-6 potential is not adequate for the computer modeling of the aromatic dimers $(\text{ben})_2$, $(\text{tol})_2$, and tol–ben. The addition of a quadrupole–quadrupole interaction term (V_{qq}) for the modeling of $(\text{ben})_2$ results in a pd geometry consistent with the spectroscopic data. The magnitude of the spectral shift ($-45\ \text{cm}^{-1}$) is consistent with the predicted displacement of the two rings. Moreover, since the displacement of benzene in the dimer is due to the V_{qq} term and the quadrupole moment vanishes in the excited state, the $(\text{ben})_2$ upon excitation moves to an undisplaced parallel geometry which allows excimer formation.

The tol–ben dimer can be modeled by the addition of V_{qq} and V_{dq} terms to the basic exp-6 potential form. The ⊥ geometries computed within this format should produce features consistent in shift and intensity with the tol*–ben 0_0^0 features near the tol 0_0^0 transition. The large spectral shift of the other set of tol*–ben 0_0^0 features can be associated with a pd geometry. The large change in binding energy upon excitation in the pd configuration is explained by a significant increase of the molecular dipole moment and a moderate increase in the quadrupole moment of toluene in the excited state. The large relative displacement of the two rings in this dimer even in the excited state may give rise to the observed barrier to excimer formation. Excitation of benzene in the pd geometry of tol–ben causes the V_{qq} and V_{dq} potential terms to vanish.

The $(\text{tol})_2$ spectrum is qualitatively consistent with the geometries predicted by the calculations if V_{qq}, V_{dq}, and V_{dd} terms are added to the intermolecular potential. The two toluene molecules are distinguishable in the ⊥ $(\text{tol})_2$ geometry. Excitation of the horizontal toluene (Fig. 3) in the ⊥ geometry produces the less red shifted features in the 0_0^0 spectrum. The broad, more red shifted features can be associated with other ⊥ forms and the pd configuration. In the pd configuration the increase in the toluene dipole moment upon excitation may cause significant reorientations of the molecules. The absorption spectrum of the pd $(\text{tol})_2$ may then be broad because the Franck–Condon maximum for the transition occurs for a dense manifold of higher energy excited state vdW modes. Excimer formation is expected for the pd but not the ⊥ geometry.

The interplay of model calculations and spectroscopy has proven essential to the understanding of aromatic dimers. Without the calculations the spectroscopic results are quite puzzling. The major test of the calculations, of course, is that they are consistent with the experimental observations. Taken together, the calculations and the data reveal a good deal about the investigated dimers.

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[1] See for example: (a) D. H. Levy, Adv. Chem. Phys. **47**, Part 1, 323 (1981); (b) M. Schauer, K. Law, and E. R. Bernstein, J. Chem. Phys. **81**, 49 (1984).

[2] (a) M. J. Ondrechen, Z. Berkovitch-Yellin, and J. Jortner, J. Am. Chem. Soc. **103**, 6586 (1981); (b) A. Amirav, U. Even, J. Jortner, and B. Dick, Mol. Phys. **49**, 899 (1983).

[3] (a) M. Schauer and E. R. Bernstein, J. Chem. Phys. **82**, 726 (1985); (b) M. Schauer, K. Law, and E. R. Bernstein, *ibid.* **82**, 736 (1985); (c) K. Law and E. R. Bernstein, *ibid.* (in press).

[4] K. Law, M. Schauer, and E. R. Bernstein, J. Chem. Phys. **81**, 4871 (1984).

[5] (a) P. R. R. Langridge-Smith, D. V. Brumbaugh, C. A. Haynam, and D. H. Levy, J. Phys. Chem. **85**, 3742 (1981); (b) J. B. Hopkins, D. E. Powers, and R. E. Smalley, *ibid.* **85**, 3739 (1981).

[6] D. E. Williams, Acta. Crystallogr. Sect. A **32**, 715 (1980).

[7] J. O. Hirshfelder, C. F. Curtis, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York), 1954.

[8] R. L. Shoemaker and W. H. Flygare, J. Chem. Phys. **51**, 2988 (1969).

[9] A. L. McClellan, *Tables of Experimental Dipole Moments* (Rahara Enterprises, San Francisco, 1974).

[10] R. Seip, G. Schultz, I. Hargittai, and Z. G. Szabo, Z. Naturforsch. Teil A **32**, 1178 (1977).

[11] W. C. Ermler and R. S. Mulliken, J. Am. Chem. Soc. **100**, 1647 (1978).

[12] L. S. Prabhumirashi, D. K. Narayana Kutty, and A. S. Bhide, Spectrochim. Acta Part A **39**, 663 (1983).

[13] S. Leutwyler, U. Even, and J. Jortner, J. Chem. Phys. **79**, 5769 (1983).

[14] P. D. Dao, S. Morgan, and A. W. Castleman, Jr., Chem. Phys. Lett. **111**, 38 (1984).