Structure, binding energy, and intermolecular modes for the aniline/ammonia van der Waals clusters

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Citation: The Journal of Chemical Physics **106**, 3029 (1997); doi: 10.1063/1.473048
View online: http://dx.doi.org/10.1063/1.473048
View Table of Contents: http://aip.scitation.org/toc/jcp/106/8
Published by the American Institute of Physics

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(Received 1 July 1996; accepted 15 November 1996)

Aniline(ammonia)$_n$, $n=1,2,3$, formed in a supersonic jet are investigated spectroscopically, using two-color mass resolved excitation spectroscopy (MRES), hole burning spectroscopy (HB), and by model potential energy calculations. The large shift in the cluster origin (ca. 875 cm^{-1} for $n=1$) with respect to the aniline bare molecule origin, and the extent (about 1500 cm^{-1} for the one-to-one cluster) of the aniline cluster spectra indicate strong interactions between the solute and solvent molecules in both S_0 and S_1 electronic states. A Lennard-Jones–Coulomb 6-12-1 potential is used to model the intermolecular interactions and predict minimum energy cluster geometries, binding energies, and van der Waals modes. Comparison between experimental results and calculations shows the importance of hydrogen bonding interactions for cluster properties. A minimum energy structure for the cluster is proposed based upon this comparison. © *1997 American Institute of Physics.* [S0021-9606(97)02807-9]

I. INTRODUCTION

The study of van der Waals (vdW) cluster formation in the gas phase can help in the understanding of the solvatation process, solution dynamics, and the nucleation and growth of small clusters. Previous work from our laboratory[1] has related the observed spectroscopic properties of vdW clusters with spectroscopic properties of cryogenic liquid solutions. The comparison between gas phase clusters and simple solutions has proved to be useful: it has shed some light on solute/solvent cage structure and dynamics.[1]

By employing gas phase supersonic expansions, molecules can be cooled to temperatures as low as 3 K. At these temperatures, long range weak forces (dipole–dipole, dipole–induced dipole) play an important role in the relative orientation of molecules and their ability to aggregate. Through mass detected spectroscopy one can select and study clusters of different stoichiometry. Using such techniques as dispersed emission (DE), hole burning (HB), and two-color mass resolved excitation (MRE) spectroscopy, one can determine the number of minimum energy conformations for each cluster stoichiometry, and estimate their geometries and binding energies.

In the past 10 years, a number of studies have been initiated whose aim has been to determine cluster structures. Cluster formation between aromatic molecules (aniline,[2] benzene,[3] toluene[4,5]) and small polar (NH_3, H_2O, CH_3OH) and nonpolar (He, Ar, CH_4,) solvents has been of particular interest because the systems serve as models for more complex ones of biological and large molecule interest. A principal difference between polar and nonpolar solvent clusters is the strength of the intramolecular interactions. Interactions between nonpolar solvents and a solute molecule are governed by induced dipole–induced dipole dispersive forces[6] and weak hydrogen bond formation.[7] These interactions yield small free molecule to cluster shifts of electronic transitions.[8] On the other hand, highly polar solvents can yield strong hydrogen bond formation and large permanent multipolar electrostatic interactions[9] that engender dramatic changes (within the limits of the vdW force scale) in the cluster electronic transition energy with respect to that of the bare molecule.[10] Large shifts in the cluster electronic transition origin are thereby produced.

In this paper we present a study of the aniline/ammonia cluster system for up to three ammonia molecules solvating the aniline molecule. This system is of particular interest because it suggests the possibility of three distinct limiting types of van der Waals bonding interactions, all of which are similar energetically (hundreds of cm^{-1}) for the these molecules. The possible interactions include: (1) the two hydrogen donor/acceptor arrangements of aniline and NH_3; (2) the hydrogen bonding interaction of NH_3 through its hydrogen atoms with the aromatic π-electron density of the aniline ring; and (3) a polar, multipole moment electrostatic interaction. These energetically similar interactions generate a number of possible minimum energy structures for aniline/NH_3 clusters and the possibility that several isomers will exist for each cluster size, aniline$(NH_3)_n$, $n=1, 2, 3,\ldots$. The sum of these interactions should lead to a strong van der Waals bond between the two molecules and, since the nitrogen atom attached to the aniline ring undergoes significant structural rearrangement upon $S_1 \leftarrow S_0$ excitation, one can anticipate large shifts in the transition energy for the aniline/NH_3 $S_1 \leftarrow S_0$ cluster absorption compared to that of the aniline bare molecule.

Our efforts in this work focus on the elucidation of the aniline$(NH_3)_1$ cluster structure, the cluster binding energies in both the ground and first excited electronic states, and cluster vdW mode energies in these states. For that purpose two different experimental techniques have been employed: two-color mass resolved excitation spectroscopy and hole burning spectroscopy. A comparison between experimental results (vdW modes and binding energies) and theoretical calculations based upon Lennard-Jones–Coulomb potentials

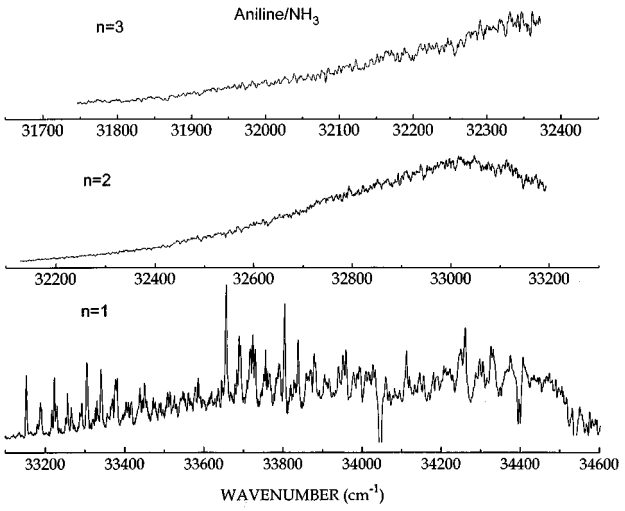

FIG. 1. One-color mass resolved spectrum of aniline$(NH_3)_1$, aniline$(NH_3)_2$, and aniline$(NH_3)_3$. The spectra are recorded using a 0.23% of NH_3 in He at a total backing pressure of 50 psi. The negative features ($\sim$34 031, $\sim$34 440, and 34 540 cm^{-1}) are due to detector overload at aniline bare molecule absorptions.

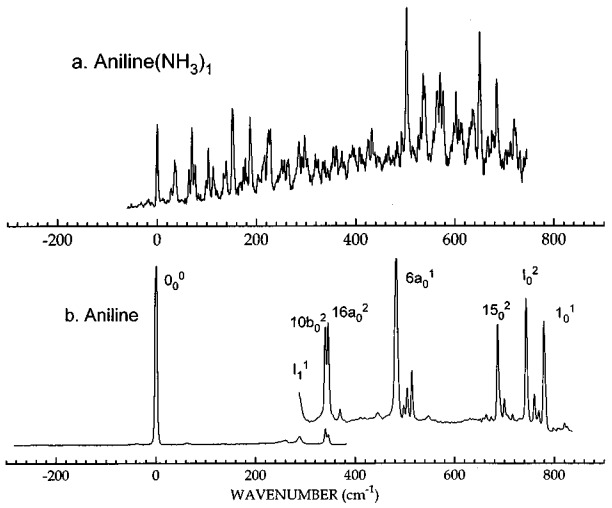

FIG. 2. Spectra of (a) aniline$(NH_3)_1$ and (b) aniline. The comparison between them allows one to assign the feature at 504 cm^{-1} in the cluster spectrum as the $6a^1$ vibration of the aniline S_1 molecule.

is presented, and minimum energy structures are proposed for the clusters observed.

II. EXPERIMENTAL PROCEDURE

The experimental apparatus has been described elsewhere.[1] Briefly the complexes are formed in a pulsed supersonic expansion inside a vacuum chamber containing a time of flight (TOF) mass spectrometer. The molecular beam is collimated through a skimmer that passes only the coldest part of the supersonic jet into the TOF ionization region. In one-color mass resolved excitation experiments, a Nd/YAG pumped dye laser system is used for promoting the clusters to an excited electronic state and ionizing them. In two-color mass resolved excitation experiments, a second Nd/YAG pumped dye laser system is used for ionizing the clusters. Detection is accomplished through a microchannel plate detector for ions with ca. 4.0 keV of kinetic energy. The signal from the detector is collected by a boxcar integrator and stored in a computer for further analysis.

Aniline is placed in an in-line trap directly behind the pulse valve. Solvent molecule typical concentrations are in the range $\sim$0.07 to 1% in a 50–150 psi total expansion gas backing pressure. The expansion gas for these studies is helium.

III. RESULTS

In Fig. 1 the one-color MRES of (a) aniline$(NH_3)_1$ (b) aniline$(NH_3)_2$ and (c) aniline$(NH_3)_3$ are shown. Only the cluster with one ammonia molecule presents resolvable structure, while the higher cluster spectra consist of a broad, structureless absorption commencing at ca. 1000 cm^{-1} to lower energy. The displacement of the cluster origins with respect to that of the bare molecule is large, as might be anticipated for strong interaction between the two polar molecules and significant change in the aniline electronic configuration upon $S_1 \leftarrow S_0$ excitation, especially about the α-nitrogen atom.[11] Even the aniline$(NH_3)_1$ spectrum presents a complex structure, not totally well solved in some of the regions. The displacement in the aniline$(NH_3)_2$ origin (about 1800 cm^{-1}) is larger than two times the displacement in the aniline$(NH_3)_1$ origin (about 875 cm^{-1}). On the other hand, the addition of a third solvent molecule produces a smaller per added molecule redshift (about 400 cm^{-1}) than for the 1:1 stoichiometry cluster, leading to a total 0_0^0 displacement of about 2200 cm^{-1}.

The aniline$(NH_3)_1$ spectrum has its origin redshifted 875 cm^{-1} from the aniline origin (34 032–33 157 cm^{-1}). The overall structure of this spectrum is quite complex. Features appearing as doublets and triplets can be found throughout the spectrum which continues for more than 1000 cm^{-1}. About 400 cm^{-1} from the origin the large number of peaks renders the spectrum difficult to follow. About 500 cm^{-1} from the origin another sequence of peaks appears, which extends for an additional 900 cm^{-1}. The extension of the whole spectrum (ca. 1500 cm^{-1}) serves as estimate of the excited state binding energy. Since the aniline$(NH_3)_1$ cluster has a redshift of 875 cm^{-1} with respect to the bare molecule, a first estimate of the binding energy for the ground state is ca. 625 cm^{-1}. The complex is much more tightly bound in the excited state than in the ground state. In Table I a list of the most intense features is given, together with some assignments. These assignments will be demonstrated and discussed extensively below.

A comparison between the aniline bare molecule spectrum and the aniline$(NH_3)_1$ spectrum is shown in Fig. 2 in order to aid in the understanding and assignment of this spectrum. The intense feature about 500 cm^{-1} from the origin in the aniline$(NH_3)_1$ spectrum coincides fairly well with the $6a^1$ vibration of the aniline bare molecule; we assign this peak as the $6a^1$ vibration of the complex. The van der Waals

TABLE I. Displacement in cm^{-1} with respect to the origin of the most intense features in the aniline$(NH_3)_1$ spectrum, together with a tentative assignment for some of the features (see the text for explanation): bend, stretch, rot refer to vdw mode approximate characteristics; h. b. refers to hot band (see Table II), a, b, c, d, e refer to peaks located in Fig. 7.

Isomer 1		Isomer 2	
−32	x bend (h. b. a)		
−18	y bend (h. b. b)	−7.6	z rot (h. b. d)
0	Origin (33, 157)	0	Origin (33, 187)
11	x bend (h. b. c)	2.5	z rot (h. b. e)
63.6		63.6	
69.6		68.1	
76.7		78.1	
132.2			
138.7		138.8	
		142.8	
150.9	z stretch	152.4	z stretch
151.9			
202.8		215.5	
217.0		221.5	
224.0		229.6	
228.1			
285.6		283.6	
291.1		289.4	
296.7		298.7	
302.7			
354.2			
360.7		358.7	
372.4		373.4	
424.3			
426.3			
432.4			
		491.4	
503.5	$6a^1$	496.0	
		505.1	$6a^1$
536.6			
564.6		563.1	
570.1		568.1	
577.2		573.7	
		579.3	
629.5		632.2	
637.8		639.8	
650.9	$6a^1+z$ stretch		649.9 $6a^1+z$ stretch

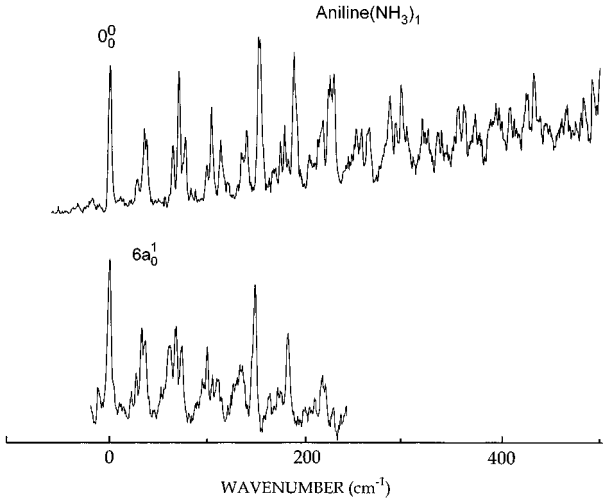

FIG. 3. Spectrum of aniline$(NH_3)_1$. The upper trace shows the spectrum around the origin while the lower trace shows the vdW modes built on the $6a^1$ vibration. Note the good correlation between both sets of vdW modes.

vibrations built on $6a^1$ seem similar to those found following the cluster origin. This suggestion is emphasized in Fig. 3, in which a portion of the aniline$(NH_3)_1$ spectrum is divided in two and placed so that the aniline$(NH_3)_1$ 0_0^0 and $6a_0^1$ regions of the spectrum are overlapped. A good correlation between the most intense features of both portions is observed.

No other features corresponding to bare molecule vibrations can be identified in the cluster spectrum. This is not surprising considering the number of intense van der Waals features present in the spectrum. This complexity also conceals hot bands and transitions from different cluster conformers.

A set of hole burning (HB) experiments is performed in order to address the issue of the number of conformers present in the expansion for the one-to-one cluster. With this technique one can group transitions in series that have their origin on the same conformer or vibrational level in the ground state. HB experiments show the existence of two main series of features each of which are specific to a distinct ground electronic state vibrational level. Figure 4 depicts the one-color spectra of the cluster together with the HB spectra recorded using (a) the feature at 33, 157 cm^{-1} and (b) the feature at 33, 187 cm^{-1} as the probe laser transition. As can be seen, all the intense features in the aniline$(NH_3)_1$ spectrum are uniquely present in either one or the other of the two HB traces. These two sets of features alternate in the composite one-color spectrum. One of these sets of features is associated with the ''cluster origin''; the other set can be due either to a hot band or another conformer.

Cluster conformers or isomers can be distinguished and identified through a double resonance experiment. If the two independent spectra identified through HB spectroscopy (Fig. 4) arise from two vibrational levels of the same cluster (i.e., are due to hot band and origin transitions), then $I \leftarrow S_1$ excitation for cluster ion creation will require exactly the same energy. If these two sets of features can be shown to arise from different $I \leftarrow S_1$ transition energies, then they are due to two distinct ground state clusters or conformers.

Ionization laser energy thresholds for (a) the bare molecule and (b) the aniline$(NH_3)_1$ cluster are shown in Fig. 5. As can be seen, aniline presents a well defined ionization threshold at about 28 140 cm^{-1} ($I \leftarrow S_1 0_0^0$). This gives a total threshold ionization energy of 62 170 cm^{-1} for aniline, compared to previous determinations employing the zero electron kinetic energy (ZEKE) technique[12] (62 271±2 cm^{-1}) and other ionization techniques[13] (62 208±10 cm^{-1}). This ionization threshold determination is influenced by the electric field generated at the time of flight mass spectrometer extraction plates (4000–3750 V) and is in reasonable agreement with the previously reported values.

The cluster ionization threshold has a long slope, extending for over 10^3 cm^{-1} [see Fig. 5(b)]. This threshold slope is probably due to a significant change in the cluster structure upon $I \leftarrow S_1$ excitation due to the strong solvation of the aniline cation by the polar ammonia molecule. The energy

difference between the cluster S_1 electronic state and the cluster ion is ca. 27 500 cm^{-1}. This leads to a total approximate ionization energy for the aniline$(NH_3)_1$ of 60 600±500 cm^{-1}.

To distinguish features associated with different possible cluster conformations, a series of spectra with ionization energy between 27 000 and 28 000 cm^{-1} can be obtained. Small changes in the intensity of different features are observed as a function of ionization laser energy and these systematic changes demonstrate the presence of different isomer features in the composite aniline$(NH_3)_1$ cluster spectrum. Two vibrational progressions (e.g., hot band features) for a single cluster structure would not show this behavior and can thus be eliminated as a cause of the many different cluster transitions.

A comparison between a one-color spectrum (lower trace) and a two-color spectrum (upper trace) recorded with an ionization laser energy of 27 400 cm^{-1} is shown in Fig. 6. The relative intensities of some features undergo small changes as the ionization energy changes between ~33 700 and 27 400 cm^{-1}. These intensity differences are indicated with arrows in the figure. The intensity differences are small due to spectral overlaps and the broad nature of the cluster ionization threshold but are nonetheless quite obvious.

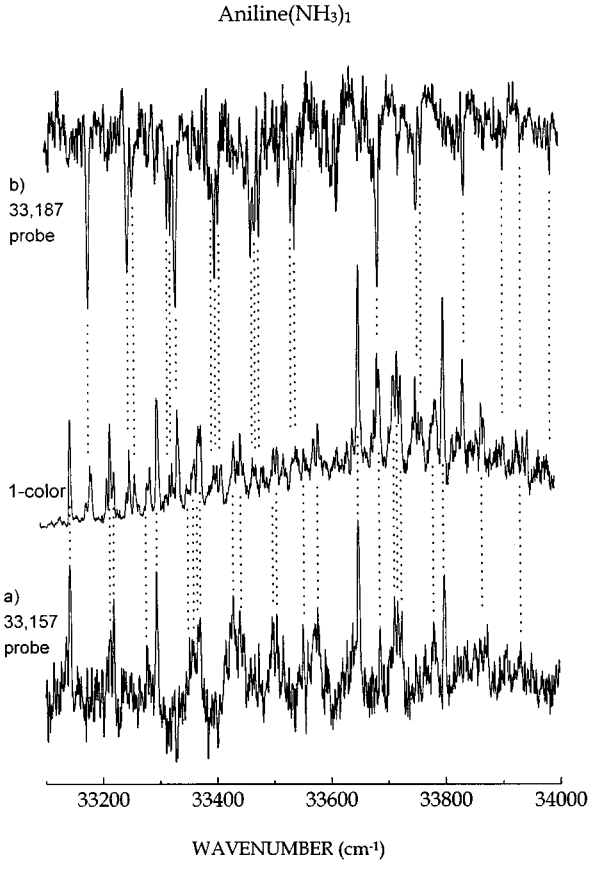

FIG. 4. Aniline$(NH_3)_1$ one-color MRES sandwiched between hole burning traces. All the intense features in the cluster spectrum are present in either one or the other of the two HB traces. Probe energies (cm^{-1}) are indicated for each HB spectrum. These probe features correspond to the cluster origin for the two observed distinct conformers of aniline$(NH_3)_1$.

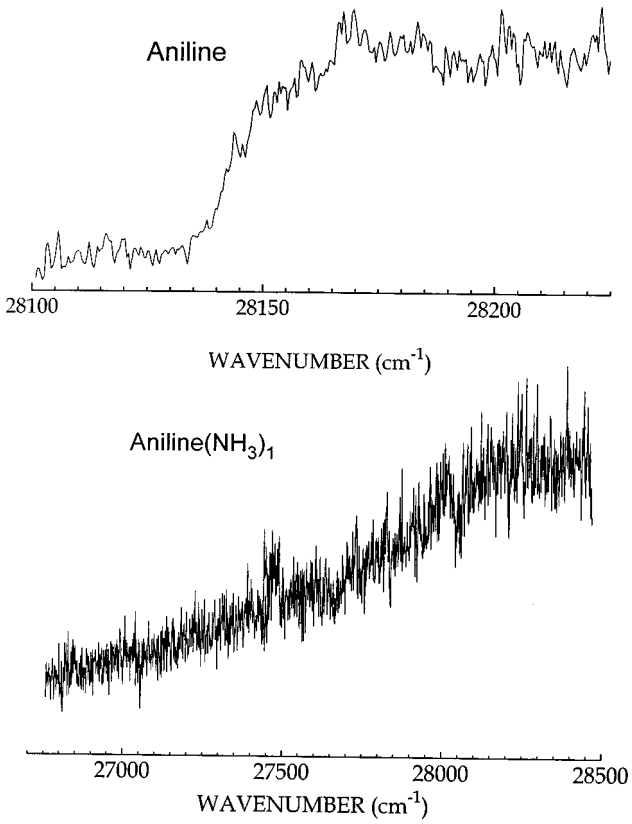

FIG. 5. Ionization laser energy thresholds for (a) aniline and (b) aniline(NH_3) following $S_1 \leftarrow S_0$ 0_0^0 excitation [34 031 cm^{-1} for aniline and 33 157 cm^{-1} for aniline$(NH_3)_1$].

A third set of experiments are carried out in order to provide further corroboration for a multiple isomer assignment of those aniline$(NH_3)_1$ features spectra at different relative temperatures and backing pressures are obtained for the cluster. Figure 7 depicts (a) a spectrum recorded using a backing pressure of <2 psi and selecting the hottest part of the molecular beam and (b) a spectrum recorded using a backing pressure of 130 psi, an expansion gas of 10% Ar/90% He and selecting the coldest part of the molecular beam. The differences in expansion conditions and choice of observation time should yield spectra reflecting a large temperature difference for the aniline$(NH_3)_1$ clusters formed.

Comparison between the two spectra obtained for the cluster at widely different temperatures and shown in Fig. 7 demonstrates that two different sets of temperature dependent features are observed for the aniline$(NH_3)_1$ clusters. First, two sets of the features identified by HB and two-color mass detected spectroscopies also appear in these spectra as separate and distinct entities. The intensity of the features built on the high energy origin decrease as the sample temperature is lowered (backing pressure increased). This latter identified set of features also changes intensity in unison. A second set of features to the red of the cluster origin changes intensity dramatically and almost disappears as the cluster beam reaches its lowest temperature. These data demonstrate that the features built on the high energy cluster origin

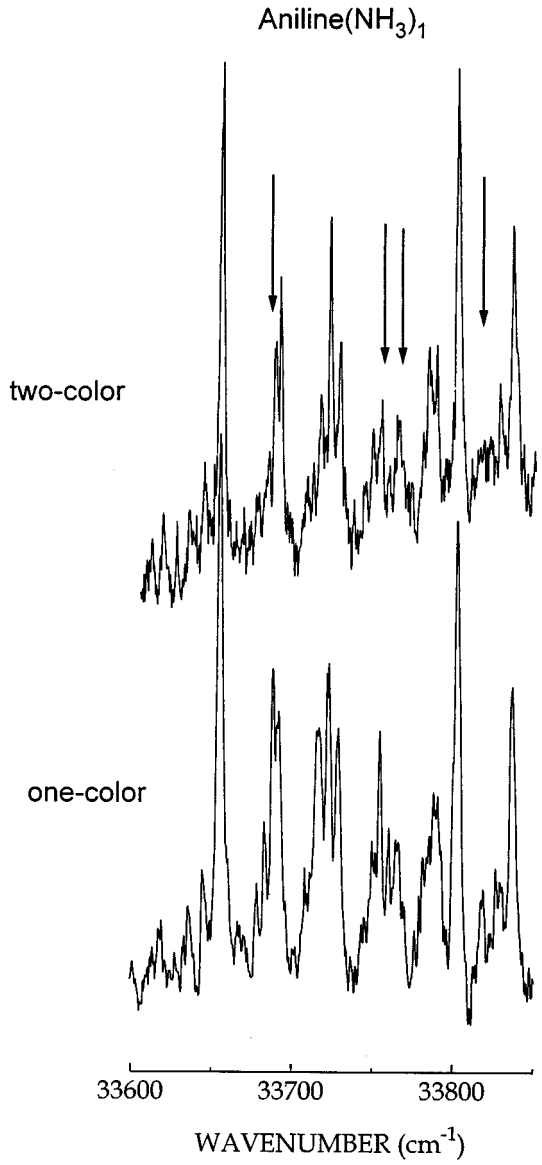

FIG. 6. Comparison between aniline$(NH_3)_1$ two-color spectrum recorded using an ionization energy of 27 400 cm^{-1} (upper trace) and the one-color spectrum. The arrows point to features that experience a significant change in intensity between the two spectra.

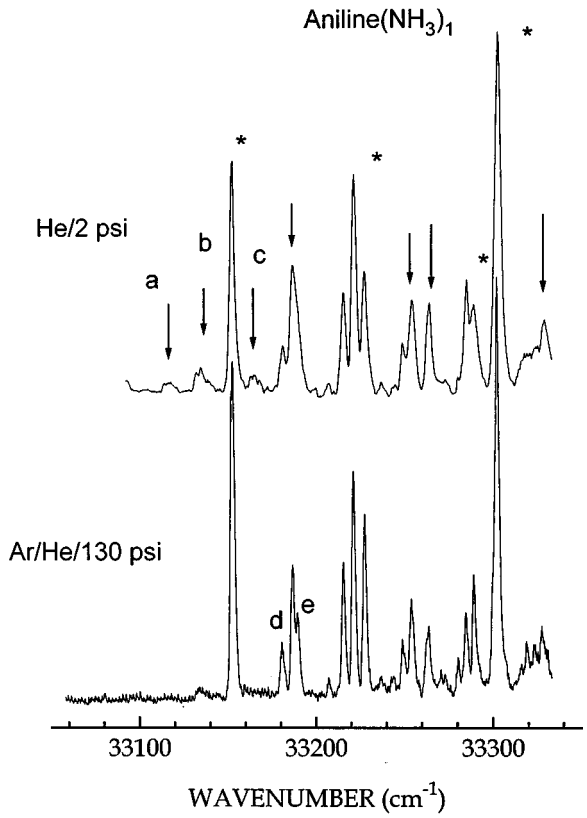

FIG. 7. Aniline$(NH_3)_1$ spectra recorded using a backing pressure of <2 psi of He (upper trace) and 130 psi He with 10% Ar (lower trace). The temperature difference between these samples allows one to detect hot bands (labeled a through e). The arrows point to all features that experience a change in intensity for the two sets of experimental conditions. The asterisks indicate features built on the lower energy origin.

(33 187 cm^{-1}—series 2), which are identified by HB, two-color ionization and temperature dependent spectroscopies as a unique set, are associated with a higher energy aniline$(NH_3)_1$ cluster isomer than are the features that are built on the lower origin at 33 157 cm^{-1} (series 1). Additionally, the separation between these two series of features does not correspond to any observable hot band feature that appears to the red of the cluster origin at 33 157 cm^{-1}. The true hot band features to the red of the 33 157 cm^{-1} of course are much more temperature sensitive than are the higher energy cluster isomer features identified as isomer 2 in Table I.

IV. STRUCTURE AND VAN DER WAALS CALCULATIONS

Two sets of calculations are performed in order to find the minimum energy structure and vdW vibrational modes for the aniline/NH_3 system. Calculational procedures described in previous publications[4,6,14] are employed. Briefly, in a first step a Lennard-Jones–Coulomb (6-12-1) potential is used to describe the interaction between solvent and solute molecules. The program generates an initial geometry using a Monte Carlo method by placing the solute molecule at the origin of the coordinate system and the solvent molecule(s) randomly around it within a certain ''box'' size. A conjugate gradient method[15] is then employed to minimize the cluster energy. The optimization ends with the reaching of a minimum energy structure. Repetition of the method for a large number of randomly chosen different initial configurations gives all the potential minima for the system, together with their statistical weight, energy and structure.

The second set of calculations uses the output of the first program and gives all the vdW vibrational modes for the system and their displacement coordinates in a graphical form.[4] The program generates a normal coordinate analysis of the cluster by employing the FG matrix method of Wilson *et al.*[16] Assuming that intramolecular vibrations are uncoupled from the low-frequency intermolecular modes, this calculation will generate all the intermolecular vibrations and their eigenvectors.

Calculations of this nature, based on empirical potentials energy functions that are well parametrized and thoroughly

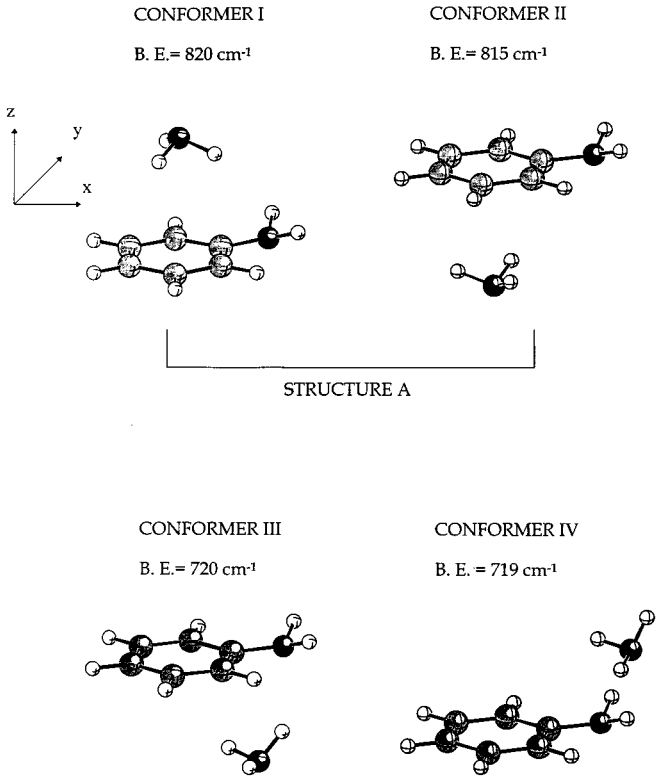

FIG. 8. The four minimum energy structures found for aniline$(NH_3)_1$, together with their binding energies.

tested for crystal structure and thermodynamics, have a long and useful history[17] and in general are found to be quite reasonable[18] for condensed phase, cluster, and scattering problems.[19] At the present time, these calculations give results that qualitatively (and often quantitatively) agree with experiments for clusters[20] and are more reliable than an *ab initio* approach. We trust that as computer software and hardware advance over the next 10 years or so *ab initio* results will become more reliable.

The calculations for aniline$(NH_3)_1$ give four different minimum energy structures (see Fig. 8). Two of them, the most stable ones, have the NH_3 molecule close to the ring, with its hydrogen atoms pointing toward the ring and apparently ''hydrogen bonding'' to the π system of aniline. The principal interaction between the two molecules (ca. 600 cm^{-1}) is of a dispersion nature. The NH_3 C_3 axis is close to the ring center, but does not pass through it. The only difference between conformations I and II is the relative position of the ammonia molecule respect to the hydrogens of the aniline NH_2 group. In the most stable conformation the NH_3 and the NH_2 hydrogen atoms are in the same side of the ring. An energy difference of ca. 8 cm^{-1} between these two conformations (I and II) is found. Calculations for other aniline/solvent clusters[21] show this to be a typical structure for such systems and for many other solvent/molecule aromatic clusters, as well.[22] For example, the same conformations have been calculated for aniline$(He)_1$ and aniline$(CH_4)_1$ clusters. While these two structures are predicted to have a distinct binding energy difference, they have not been distinguished experimentally.[1(b)] Most likely the electronic transitions of the two structures are too close in energy for the available experimental resolution. The distinction between the two conformers in $\pi\pi^*$ excited electronic state should even be smaller, as the aniline molecule becomes nearly planar with a much higher barrier to inversion in this state.[23] Therefore, hereafter we will refer to conformers I and II as only one Structure A.

On the other hand, in spite of similar binding energies for conformers III and IV of Fig. 8, large differences in their apparent structure are quite obvious. In conformer III, the NH_3 molecule and the NH_2 hydrogen atoms of aniline are on opposite sides of the ring; in conformer IV the NH_3 molecule and the NH_2 hydrogen atoms are in the same side of the aromatic ring. Even though these structures seem to suggest that the NH_3/aniline interaction is quite different for each of them, the main interaction for these cluster isomers seems to be that of strong NH_3–NH_2 interaction. Structure III suggests the hydrogen bonding is of the type $H_2NH\cdots NH_2C_6H_5$, while conformer IV structure suggests $H_3N\cdots HNHC_6H_5$ hydrogen bonding. In both structures the two other ammonia hydrogen atoms apparently bond to the π-electron density of the aromatic ring. The aniline NH_2 moiety mostly acts as a proton donor in conformer IV and as a proton acceptor in conformer III. Apparently the $H_2NH\cdots NH_2C_6H_5$ and $H_3N\cdots HNHC_6H_5$ bonding are of similar energies, as are the other $HNH_2\cdots\pi$-system interactions.

If we assume that the experimental excited state cluster binding energy for aniline$(NH_3)_1$ is roughly ca. 1500 cm^{-1} (see Fig. 1) and that the bare molecule to cluster shift is ca. 875 cm^{-1}, then the ground state binding energy is roughly 625 cm^{-1}. This is to be compared to the two calculated ground state cluster binding energies for Structure A and the other two conformers of 820 and 720 cm^{-1}, respectively. The calculations seem actually to be quite reasonable, even for this relatively complicated cluster interaction system.

Calculations for the aniline$(NH_3)_2$ system find up to 34 minimum energy conformations. This serves to explain the broad absorption found for the spectrum of this cluster. The energy stabilization for the most stable conformation is 1808 cm^{-1}, higher than two times the binding energy for aniline$(NH_3)_1$ cluster, pointing to a large interaction between the two NH_3 solvent molecules that leads to an increase in the cluster total binding energy. The redshift for the aniline$(NH_3)_2$ cluster transition is also larger than two times the one for aniline$(NH_3)_1$; however, the lack of a well defined origin for this spectrum prevents an estimate of the cluster ground state binding energy.

The vdW mode calculation gives very similar energies for the two most stable conformers (Structure A) as shown in Table II. The lowest energy mode corresponds to NH_3 rotating about the cluster z axis. The potential energy barrier for this motion is very low (about 2 cm^{-1}), smaller than the mode zero point energy, so the vibration becomes a real rotation and its ''harmonic frequency'' is not valid. The cal-

TABLE II. Calculated vibrational energy (cm^{-1}) for the four minimum energy aniline$(NH_3)_1$ structures, together with the experimental values found and the nature of the mode. (B. E.=binding energy). Each structure generates six calculated zero energy modes to better than ± 0.1 cm^{-1} in accord with the requirements of Ref. 4. The strong asymmetry of conformer IV vibrations makes difficult a simple description of the modes: α refers to a yz rotation+xyz displacement; β refers to a xy rotation+xyz displacement, γ refers to a xz rotation+xyz displacement; δ refers to a yz rotation+xyz displacement.

Structure										
I B. E: 823 Mode			II B. E: 815 Mode			III B. E: 720 Mode			IV B. E: 719 Mode	
Calc.	Exp.		Calc.	Exp.		Calc.	Exp.		Calc.	
15	z rot		15	z rot		11	z rot+y *trans*	8[c]	14	α
22	x bend	18[a]	24	x bend	18	19	x bend		46	x bend
33	y bend	32	32	y bend	32	34	z rot		56	xz rot
102	z stret	[b]	102	z stret		103	z stret	[d]	90	β
150	y rot		151	y rot		112	x rot		122	γ
160	x rot		157	x rot		204	y rot		174	δ

[a]S_1 state: 30 cm^{-1}.
[b]S_1 state: 150 cm^{-1}.
[c]S_1 state: 10 cm^{-1}.
[d]S_1 state: 151 cm^{-1}.

culated energy of this internal rotation is an artifact of the harmonic approximation.

The vibrations of conformer III are similar to those of Structure A isomers, especially with regard to the four higher energy modes. Conformer IV is very different from the others with regard to the van der Waals modes, as shown in Table II. Aside from the z-axis rotation for the Structure A conformer, the other modes of these isomers are reasonably well represented for at least the harmonic fundamentals; that is, the potential surface has high barriers for the other cluster degrees of freedom, even for large amplitude translational motion.[21]

Note that these calculations for the van der Waals stretching mode are typically quite good and often predict the mode energy to $\pm 10\%$ even when the calculation is for the ground electronic state and the observation is for the S_1 state of the aromatic ring.

V. DISCUSSION

A. The van der Waals interaction

The results show that the aniline$(NH_3)_1$ cluster is more tightly bond in the excited than in the ground state. This is in agreement with theoretical considerations. In the Structure A, the principal interaction between the two molecules is the dispersion interaction. This interaction will be stronger in the excited state, as the π system of aniline will be more delocalized and thus more polarizable. Hydrogen bonding between the NH_3 hydrogens and the aniline π system serves as a geometry controlling influence on the final structure, but is considerably weaker than the dispersion component of the intermolecular interaction.

For conformers III and IV, a major component of the interaction is hydrogen bonding between aniline (the NH_2 moiety) and NH_3 molecule. For conformer III, a delocalization of the π system and the lone pair of the aniline N atom also increases the binding energy.

B. Structure identification and van der Waals modes

HB spectroscopy, hot band studies, and two-color MRES results show that the aniline$(NH_3)_1$ spectrum consist of two distinct sets of transitions which can be associated with two cluster isomers. One of these progressions should be due to the most stable conformer (Structure A) and the other should be due to either conformer III or IV. The ground state binding energy for these latter two conformations is very similar so in principle their $S_1 \leftarrow S_0$ spectral shifts could also be quite similar. At present only two conformers of the aniline$(NH_3)_1$ can be identified in the spectrum. We have searched for another transition for this cluster in the region 31 700 to 34 600 cm^{-1} and have not found any reproducible features other than those shown in Fig. 1.

We next try to match the two isomer spectra of aniline$(NH_3)_1$ with Structure A, and conformers III and IV. The separation between origins, about 30 cm^{-1}, does not give any clue to this correspondence, because the position of the two progressions depends on both the ground and excited state binding energies. The analysis of the hot bands in the spectrum, however, can be of some help in this identification.

The two hot bands to the red of the cluster spectrum origin (features a and b in Fig. 7) can give an estimate of the energy of the lower two ground electronic state vdW vibra-

tional modes. The hot bands fall at ~ -18 and -32 cm^{-1} with respect to lower energy 0_0^0 transition for the isomers.

Considering the calculated cluster isomer modes that might correspond to the -18 and -32 cm^{-1} hot bands observed we need to ignore the 15 cm^{-1} mode of Structure A but should consider all the other modes for the conformers. For conformers III and IV, all modes are true vibrations, at least for the fundamentals, as the barriers to internal NH_3 rotation and translations are high (ca. 100 cm^{-1}). Consequently one can compare the 18 cm^{-1} hot band with the following modes: 22 cm^{-1} of Structure A; 19 cm^{-1} of conformer III; and 14 cm^{-1} of conformer IV. If feature b (-18 cm^{-1}) is assigned to the 19 cm^{-1} mode of conformer III one should find another mode at -11 cm^{-1} (see Table II—not observed). If the conformer IV 14 cm^{-1} mode is assigned as the -18 cm^{-1} feature, other observed modes are unassignable (e.g., -32 cm^{-1}). On the other hand, Structure A seems to fit well to the observed hot bands with 22 and 33 cm^{-1} modes corresponding to observed -18 and -32 cm^{-1} hot bands. We thus concluded that the lower energy origin and vibronic structures built on it correspond to the spectrum of Structure A isomers of aniline$(NH_3)_1$.

The first vibrational hot band to the blue of the origin (feature c in Fig. 7) must originate at the same vibrational level as feature b. This gives us a value for the lowest vibrational mode frequency in the excited state of $\sim$30 cm^{-1}. This value is larger than that for the ground state. If the cluster is more tightly bound in the upper electronic state, the corresponding vibrational energies of the excited state should be larger than those in the ground state.

Looking at the origin (33 187 cm^{-1}) of the second series of transitions (see Figs. 4 and 7 and Table I), one can to find a similar structure as described above, but with different intensities: a main band with two less intense bands, one to the blue and one to the red. The feature at ca. 2 cm^{-1} to the blue of this origin (e) could possibly be the origin of the conformer IV. But based on its position and temperature dependence, it is most likely a hot band associated with the second conformer origin.

If these two features (d and e) of Fig. 7 and Table I) are hot bands, the one to the red is related to a vibration of ca. 8 cm^{-1}. This vibration should correspond with a conformer III vibration at the calculated ground state value of 11 cm^{-1} (see Table II). This assignment helps to identify the second conformer features, built on the 33 187 cm^{-1} 0_0^0, as the spectrum of the III structure.

The small vibrational energy for the z-rotation mode of conformer III also explains the large intensity of the *d* and *e* hot bands compared with their origin. At a temperature of 10 K the population ratio of the 8 cm^{-1} mode to the zero point level in the ground state, would be $\sim$0.57. The feature to the blue will then be a hot band transition that starts in the same vibrational vdW mode as the feature (d), giving a vibrational frequency of $\sim$10 cm^{-1} for that mode in the excited state. The upper electronic state vibration would be then, as for the Structure A conformers, higher in energy than the corresponding mode in the lower electronic state. The second series of features is again indicated as the spectrum of the conformer III. We tentatively conclude then that no features are found related to conformer IV.

The totally symmetric z-stretch van der Waals mode [ca. 100 cm^{-1} for ground state aniline$(NH_3)_1$ cluster] is typically a prominent feature in van der Waals mode spectra.[24] As we have shown above, the vibrational frequencies of the excited electronic state are larger than those of the ground electronic state (30 cm^{-1} compared to 18 cm^{-1} for the least energetic vibration of Structure A). If the symmetric stretch energy is scaled by 30/18 we find that an intense feature should be found at about 165 cm^{-1} in the excited state. An excited state van der Waals strong feature at 151 cm^{-1} from the origin that can be assigned as the S_1 z-stretch mode of cluster Structure A.

The same arguments can be employed with regard to the spectra of isomer 2 (see Table I). The stretching mode for the conformer III ground state is ca. 103 cm^{-1}, so the transition corresponding with this vibration must be a strong feature to high energy of the progression origin at roughly 0_0^0+150 cm^{-1}. A feature at this energy matches the description. This assignment reinforces the assignment of the isomer 2 features to conformer III.

It is not possible to assign more transitions within the isomer 2 features due to the large number of features in the spectrum. Most of them appear as doublets and triplets, probably due to combinations and overtones of different van der Waals modes.

The large number of features in the spectrum suggests the occurrence of a large change in cluster structure and potential energy surface upon excitation from the electronic ground state to the excited electronic state. The Franck–Condon factors do not favor only the 0_0^0 transition but rather a wide range of transitions. The result is long progressions with features of similar intensity. This change in the cluster geometry can be observed in the transition from the electronic excited state to the ionic ground state as well. The ionization threshold is then a long gradual slope instead a sharp onset as found for the aniline molecule.

VI. CONCLUSIONS

An investigation of the aniline/ammonia cluster system is presented. Four different minimum energy conformations are calculated for the aniline$(NH_3)_1$ cluster. Two of these conformers (I and II) are so similar that one cannot distinguish between them experimentally. Experimentally only two different sets of transitions are observed for this cluster system so one of the structures, we suggest conformer IV in Fig. 8, apparently does not appear in the spectrum.

The most stable two conformers (I and II) have the NH_3 molecule close to the aromatic ring, with the hydrogen atoms of the NH_3 molecule pointing toward the ring. The principal interaction between the aniline and the ammonia in this structure is dispersion. In the other two conformations, the NH_3 molecule is placed close to the NH_2 group of aniline. This group acts as proton donor in one of the conformers (IV) and as proton acceptor in the other (III): conformer III is

the one assigned to the higher energy set of features (isomer 2).

The clusters are more tightly bound in the upper electronic state than in the ground state, due to a delocalization of the electron cloud in the upper state. The vibrational frequencies for the upper electronic state are also larger than those for the ground electronic state. The inclusion of another solvent molecule in the cluster increases the cluster binding energy by more than a factor of 2, due to an interaction between solvent molecules, as well as that between solvent and solute molecules. This additional binding energy is reflected in the spectral shift for the aniline$(NH_3)_2$ clusters. The aniline$(NH_3)_3$ clusters have a higher binding energy than the aniline$(NH_3)_{1,2}$ clusters but this does not result in an expected spectral shift of ca. 900 cm^{-1}/NH_3 solvent molecule. As NH_3 molecules are added to the cluster at further distances from the site of the transition (aniline nitrogen and ring π and π^* orbitals), their effect on the cluster transition energy decreases on a per solvent molecule basis.

ACKNOWLEDGMENTS

One of us (J.A.F.) thanks the Basque Government for a postdoctoral fellowship. We also thank the U.S. ARO and U.S. NSF for support of these studies.

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