Infrared Depletion Spectroscopy of the Hydrogen-Bonded Aniline−Diethylamine (C_6H_5-NH_2···NHC_4H_{10}) Complex Produced in Supersonic Jet

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The vibrational frequencies of the N−H stretching modes of aniline and diethylamine (DEA), after forming a strong H-bonded complex, are measured with infrared depletion spectroscopy that uses cluster-size-selective REMPI time-of-flight mass spectrometry. Three strong infrared absorption features observed at 3294, 3369, and 3473 cm^{-1} are assigned to the NH stretching vibration of DEA and H-bonded and free N−H stretching vibrations of aniline, respectively, in the 1:1 aniline−DEA complex. The spectral broadening observed for the free and H-bonded N−H stretching modes of aniline indicates mode-specific vibrational energy dynamics. Although the narrow bandwidth ($\approx$4 cm^{-1}) of the N−H stretch at 3473 cm^{-1} incorporates all of the common broadening mechanisms including intramolecular vibrational relaxation (IVR), the broader ($\approx$13 cm^{-1}) absorption feature at 3369 cm^{-1} suggests vibrational predissociation/IVR of the H-bonded complex, with a subpicosecond lifetime. The red-shifts of the N−H stretching vibrations of aniline and DEA agree with the ab initio calculated (MP2/6-31G**) aniline−DEA structure in which one of the N−H bonds of aniline interacts with the nitrogen atom of DEA through a hydrogen bond, giving a binding energy of 15.8 kJ mol^{-1} with due corrections for BSSE and zero-point energy. The electronic 0−0 band origin for the $S_1 \leftarrow S_0$ transition is observed at 32 916 cm^{-1}, giving a significant red-shift of 1113 cm^{-1} from that of the bare aniline. The vibrational progressions associated with the R2PI spectrum are assigned to the intermolecular modes of the complex.

1. Introduction

Hydrogen bonds formed between a proton donor molecule and a base (e.g., containing nitrogen or oxygen lone pair donors) are responsible for the existence of various stable H-bonded complexes in biological systems.[1] The partial charge-transfer nature of such bonds makes them exceptionally stable among neutral clusters, with binding energies of 8−24 kJ/mol.[1] When a molecule is involved in a hydrogen bond, its vibrational frequencies are red-shifted (or sometimes blue-shifted) from the isolated molecular values.[2,3] Among the high frequency stretches, the shifts are largest for those modes involving the hydrogen atom directly associated with the hydrogen bond. For the modes with hydrogen atoms not directly involved, the shift in vibrational frequency is expected to be relatively small. Such isolated clusters are considered as prototypes for the hydrogen bonding interactions of larger species in solution and in biological systems. It is of interest here to clarify the hydrogen bonding interactions involving the NH group in isolated clusters and its influence on vibrational modes, which is important for an understanding of the molecular structure in biological systems.

In earlier studies, we reported mode-specific vibrational dynamics in the aniline−triethylamine,[4] aniline−diethyl ether,[5] and aniline−tetrahydrofuran[6] complexes, where we have discussed in detail the question of vibrational predissociation and intramolecular vibrational relaxation (IVR) mechanisms responsible for broadening the hydrogen bonded mode. On excitation of a vibrational stretching mode directly involved in H-bonding, energy was found to leak into the intermolecular modes undergoing a fast predissociation/IVR. To extend such a study of mode specific vibrational coupling for a mode involved in a hydrogen bond, we have chosen to investigate aniline−diethylamine (DEA) complex. Although vibrational excitation of the free N−H stretching mode may give an upper limit of the spectral broadening due to all common mechanisms, including intramolecular vibrational energy redistribution (IVR), excitation of the bound N−H stretching mode has, in addition, a direct coupling mechanism of energy flow into the dissociating intermolecular mode. We report here experimental results, from an infrared depletion spectroscopic technique,[7] on the vibrational frequencies of the N−H stretching modes of the aniline−DEA complex. The one-color-resonant two-photon ionization (R2PI) spectrum of aniline−DEA was recorded to obtain the 0−0 band of the $S_1 \leftarrow S_0$ electronic transition at 32 916 cm^{-1}. The depletion of the two-photon ionization signal was measured as a function of infrared laser frequency. In the infrared depletion spectrum three strong features observed at 3294, 3369, and 3473 cm^{-1} are assigned to the NH stretch of DEA and H-bonded and free N−H stretching vibrations of aniline in the 1:1 aniline−DEA complex. The red-shift of the N−H stretching vibrations of aniline is used as a reference for the ab initio calculated aniline−DEA structure, where one of the N−H bonds of aniline interacts with the lone pair of the nitrogen atom of DEA through a hydrogen bond. Although the narrow bandwidth of the free N−H stretch at 3473 cm^{-1} sets an upper limit for the rate of IVR, the more intense, broader absorption band at 3369 cm^{-1} indicates a mode-specific vibrational predissociation and IVR of the H-bond in the ground-state complex.

2. Experimental Section

The apparatus and experimental procedures used for the study of infrared depletion spectroscopy of the aniline−diethylamine

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complex have been previously reported.[4−9] Only salient features are given here. Aniline complexes were formed in the supersonic expansion of a mixture of aniline and diethylamine (DEA) vapors by helium carrier gas at room temperature, with a stagnation pressure of 1.5 bar. The vapors of aniline and DEA were obtained by bubbling helium gas in their liquid mixture. Only a small amount (about 0.1%) of DEA was dissolved in liquid aniline. Finally, the gas mixture was injected into a vacuum chamber through a pulsed valve (General Valve, 0.8 mm diameter), which was operated at 10 Hz with a pulse duration time of 250 μs and then introduced into the ionization region of a time-of-flight mass spectrometer (TOF/MS) through a skimmer of 1 mm diameter. The skimmed beam intersected the frequency doubled dye-laser beam in the ion acceleration region of the TOF/MS. The positive ionized complexes were sampled by a high-voltage extraction pulse. The source chamber and the flight tube were differentially pumped by a 12 in. oil diffusion pump and a turbo-molecular pump, respectively. Under normal operating conditions, the pressure in the source chamber was 1×10^{-5} Torr.

The aniline−DEA complex was detected by the TOF/MS after one-color resonant two photon ionization (R2PI) via the S_1 state, with a UV laser around 300 nm, generated by the frequency doubling of the output of a dye laser (Continuum, ND6000). The pulse and bandwidths of the laser were 5 ns and 0.1 cm^{-1}, respectively. The energy of the UV laser beam was reduced to a few hundreds of μJ/pulse in order to minimize the fragmentation of the aniline−DEA complexes by UV multiphoton absorption.

The infrared absorption bands of the aniline−DEA complex were recorded as the depleted ion signal induced by predissociation of the complex in the ground state. The infrared light source was generated by difference frequency mixing of a dye laser with the fundamental of a Nd:YAG laser (Quanta Ray, Wex-1). The maximum IR output was about 1 mJ/pulse at 3500 cm^{-1}, which decreases linearly with the wavenumber, and the IR pulse duration was 6 ns. The bandwidth of the IR laser was less than 1 cm^{-1}. The infrared frequency was calibrated by monitoring the wavelength of the dye laser using a wavemeter (Burley, WA4500).

The sample beam was first irradiated with the IR laser and then probed with the UV laser pulse with a delay of 50 ns. The IR and UV beams were focused at the center of the ionization region of the TOF/MS using concave mirrors with a focal length of 35 cm. The frequency of the UV laser was fixed on a resonance line of the aniline−DEA complex, whereas the IR laser was scanned around the N−H stretching vibrational region around 3215−3515 cm^{-1}.

3. Results and Discussion

A. Electronic Excitation Spectrum. Figure 1shows the one-color resonant two-photon ionization (R2PI) spectrum of aniline−DEA recorded at mass number 166. To our knowledge, there is no LIF or REMPI spectroscopic study on aniline−DEA reported in the literature. The absorption system has its first band at 32916 cm^{-1}, which is red-shifted by 1113 cm^{-1} from the 0−0 band of free aniline. We assign this band to the 0−0 band of the $S_1 \leftarrow S_0$ transition of the complex electronic states. The R2PI spectrum shows a vibrational band progression of 21.5 cm^{-1} from the origin at 32916 cm^{-1} and another progression of the same frequency, shifted from the origin by 34 cm^{-1}, which are marked in Figure 1 as A and B, respectively. The 1113 cm^{-1} red-shift of the 0−0 band origin indicates a relatively large binding energy in the S_1 excited state, compared to the ground state (S_0) of the complex. The red-shifts of the 0−0 band origin observed earlier by us for the aniline−triethylamine,[4] aniline−diethyl ether,[5] and aniline−tetrahydrofuran[6] complexes are 876, 737, and 774 cm^{-1}, respectively.

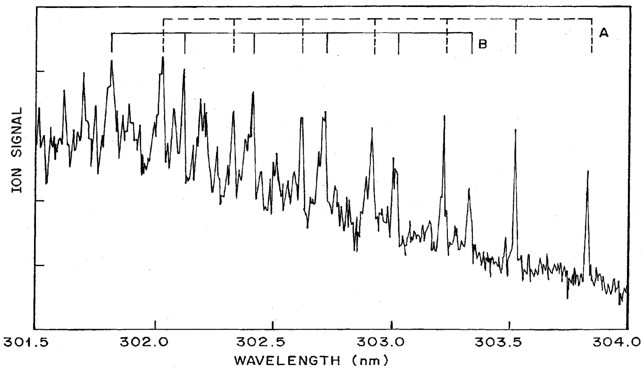

Figure 1. One color resonant two-photon ionization (R2PI) spectrum of the aniline−DEA complex detected by the ion signal at $m/z = 166$. The first band observed at 32 916 cm^{-1} has been assigned to the $S_1 \leftarrow S_0$ 0−0 transition of the complex. The R2PI spectrum shows a vibrational progression of 21.5 cm^{-1} from the origin at 32 916 cm^{-1} and one more progression of the same frequency, shifted from the origin by 34 cm^{-1}, which are marked as A and B, respectively.

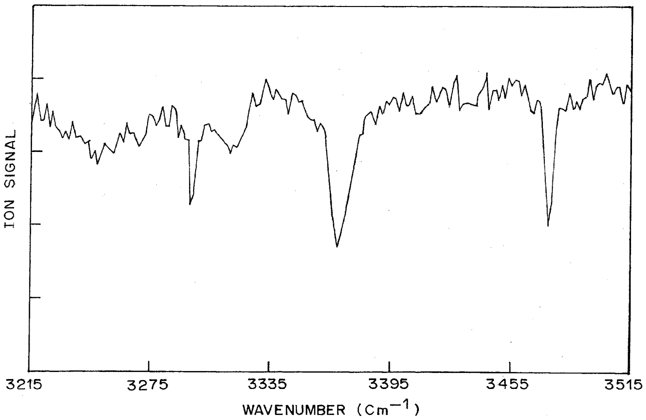

Figure 2. Infrared depletion spectrum of the aniline−DEA complex. The complex was ionized with a UV laser at 32 916 cm^{-1}.

B. Infrared Depletion Spectrum. In Figure 2, the observed IR depletion spectrum of the aniline−DEA complex is shown in the region 3215−3515 cm^{-1}, with the UV laser fixed to the 0−0 transition at 32 916 cm^{-1}. Here, three strong bands are observed at 3294, 3369, and 3473 cm^{-1}. The IR depletion spectrum of the aniline−DEA complex in the 3215−3515 cm^{-1} region was repeated with the UV laser fixed to other strong UV transitions. The spectra obtained was found to be similar to that of at the 0−0 transition at 32 916 cm^{-1}. This suggests that the IR depletion spectral bands observed are due to only one isomer of the aniline−DEA complex. By comparing the NH stretch of DEA[10] at 3334 cm^{-1}, and NH_2-stretching vibrations of aniline[7] monomer at 3422 and 3508 cm^{-1}, apparently, the frequency red-shifts are obtained as 40, 53, and 35 cm^{-1}, respectively. The frequency red-shifts may be understood on the basis of a hydrogen bond formation by one of the NH bonds of aniline with the nitrogen atom of DEA. The coupling of the local degenerate NH modes of aniline results in symmetric and antisymmetric normal modes at 3422 and 3508 cm^{-1}. When the molecule interacts via hydrogen bonding, the degeneracy is broken. Considering that the red-shift of the higher frequency band occurs because of a decreased coupling between the two nondegenerate NH oscillators, the actual red-shift for the hydrogen-bonded NH stretching mode is computed to be

88 cm^{-1}. This compares well with the actual red-shifts of the hydrogen-bonded NH stretching mode for the aniline−triethylamine,[4] aniline−diethyl ether,[5] and aniline−tetrahydrofuran[6] complexes observed by us to be 136, 80, and 81 cm^{-1}, respectively. Similar large red-shifts are also observed by Felker et al. in the hydrogen-bonded phenol complexes.[11] The 40 cm^{-1} red-shift of the NH stretching vibration with the DEA moiety of aniline−DEA complex is comparable to our earlier observation[8] of the 35 cm^{-1} red-shift with the pyrrole moiety of the aniline−pyrrole complex.

It is interesting to note that the integrated area of the lower frequency 3369 cm^{-1} peak is about 2.5 times that of the higher frequency 3473 cm^{-1} peak. This is in accord with the previous observations associated with hydrogen bond formation. In $(HF)_2$ absorption measurements, the H-bonded HF band was found to be 2−3 times more intense than the free HF band.[12] A factor of 8 was found to the H-bonded methanol dimer,[13] where, in addition to that, an enhanced intensity of 12 times over the monomer value was observed for the proton donor O−H stretch. A much greater enhancement factor of 32[14] to 37[15] over the monomer value is reported for acetic acid H-bonded dimer. Our experimentally observed band intensity ratio agrees with the ab initio calculation using the Gaussian 94 package.[16] As discussed in the next section, calculations on aniline−DEA have resulted in the red-shifted absorption bands for the H-bonded and free N−H stretching modes with an intensity ratio of 2.5 and an enhancement factor of 18 for the H-bonded stretch over the monomer value. Therefore, the observed absorption bands at 3369 and 3473 cm^{-1} are assigned to the H-bonded and free N−H stretching vibrations of the aniline−DEA complex system, respectively.

The infrared laser was found to show the depletion of the ion signal due to the aniline−DEA complex to about 90%. This may be attributed to the vibrational predissociation and/or IVR of the complex, suggesting that the binding energy of the aniline−DEA complex is smaller than the energy of one IR photon. The widths of the peaks in the complex spectrum are about 4 and 13 cm^{-1} (fwhm), respectively. The former has been occasionally found by us earlier[9] and is attributed to the participation of rotational transitions. Because the lifetime of the complex could not be resolved with our limited time resolution of 10 ns, an upper limit of 10 ns can be assumed for this mode. However, the latter much broader and stronger signal suggests predissociation and/or fast IVR. The predissociation/IVR lifetime has been calculated using homogeneous line width (see section D) in eq 1 to be about 0.5 ps

$$\tau = (2\pi\Delta\nu)^{-1} \qquad (1)$$

This difference might seem surprising if we consider only the energetics of this system because the two modes are only separated by 104 cm^{-1} out of 3400 cm^{-1}. However, if one considers the structure shown in Figure 3 and the possible vibrational displacements for the two modes, this difference in lifetimes becomes clearer. A large-amplitude motion of the bonded hydrogen may lead to dissociation more rapidly than the vibration of the nonbonded hydrogen, which is much more decoupled. Therefore, it appears from our results that the process of vibrational predissociation is mode-selective and that the coupling is much more effective for a mode involved in the H bond, the promotor, than for the free one, the spectator.

C. Ab Initio Calculations. We performed ab initio calculations to investigate the geometry and vibrational frequencies of the aniline-DEA complex using the Gaussian 94 program.[16] Energy optimization (full) was done at the MP2 level with the 6-31G(d,p) basis set. The SCF convergence criterion was 10^{-8} hartree; the convergence criteria for the structural gradient optimization were 1.5×10^{-5} hartree/bohr and 1.5×10^{-5} hartree/deg, respectively. The vibrational frequencies were obtained by performing a normal-mode analysis on the optimized geometries using numerical gradients of the energy. The most stable structure found corresponds to a hydrogen-bonded geometry, i.e., one amino hydrogen of the aniline pointing to the nitrogen of the DEA, with a calculated binding energy of 15.8 kJ mol^{-1}, after corrections for basis set superposition error (BSSE) and zero-point energy (ZPE). The BSSE corrections were made using Boys and Bernardi full counterpoise method.[17]

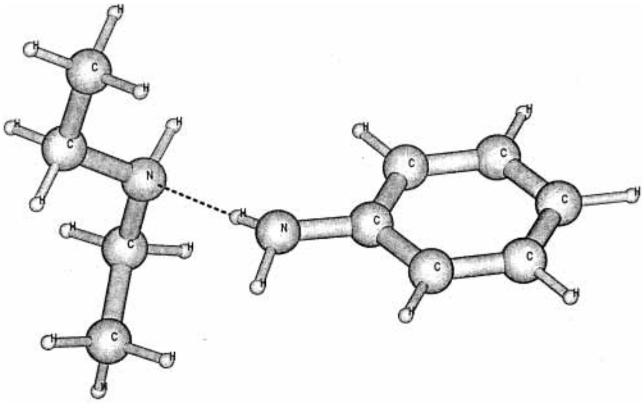

Figure 3. Geometry of the aniline−DEA complex fully optimized at the MP2/6-31G(d,p) level.

Figures 3 shows the ab initio fully optimized structure of the complex. The structure clearly shows that one of the two protons of $-NH_2$ directly interacts with the nitrogen atom of DEA forming a nearly collinear bond N−H···N (∠NHN = 175°) with an intermolecular distance H···N of 2.06 Å. The three bond lengths involved in the NH_2 group, $N-H_{bonded}$, $N-H_{free}$, and N−C, are 1.020, 1.010, and 1.399 Å for the aniline−DEA, which may be compared to our earlier calculated values of 1.021, 1.011, and 1.399 Å for the aniline−triethylamine (TEA) complex[4] and 1.010, 1.010, and 1.405 Å for the aniline monomer, respectively. As expected, the complex shows a strong red-shift in the electronic spectrum and in the IR depletion spectrum because of a stronger intermolecular interaction in the excited states. The electronic shift is due to a relatively stronger H-bonded S_1 state than the S_0. The vibrational red-shift is due to a relatively stronger H bond in the vibrationally excited state than in the ground state of aniline−DEA.

Our calculated binding energy of 15.8 kJ/mol for the aniline−DEA is found to be lower than that of the aniline−triethylamine (17 kJ/mol).[4] The vibrational frequencies of the complex which were calculated using the same level of theory (i.e., MP2/6-31G** basis set) are given in Table 1. The calculated frequencies in the table were corrected using a frequency factor of 0.9421, which was determined by fitting the calculated vibrational frequencies of free aniline to the experimentally observed values. As seen in Table 1, the calculation reproduces the experimental results on the frequency and IR absorption intensity fairly well.

D. Possibility of Mode Specificity. The separate and distinct processes of intramolecular vibrational redistribution (IVR) and vibrational predissociation (VP) are related to the general phenomenon of radiationless transition and Rice−Ramsperger−Kassel−Marcus (RRKM) unimolecular rate theory. In a vibrationally excited complex, the intramolecular vibrational-mode energies in the subunits typically are much higher than the dissociation limit of the complex. Hence, the excited vibrational states are metastable with respect to vibrational predissociation.[18]

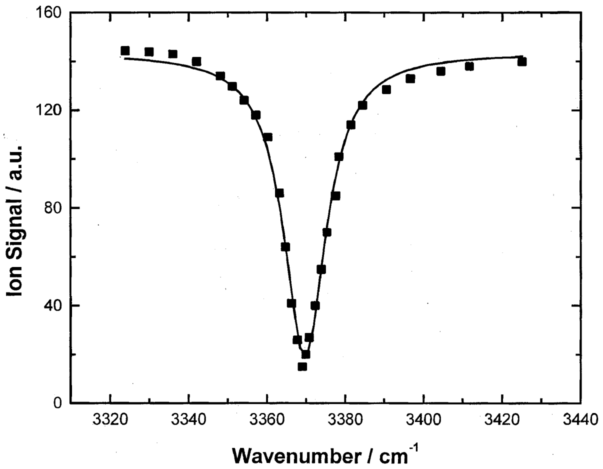

Figure 4. Lorentzian fit on the smoothened data of the IR depletion spectral band at 3369 cm^{-1}.

TABLE 1: Vibrational Frequencies (cm^{-1}) and Infrared Absorption Intensities ($km\ mol^{-1}$) of the N−H Stretching Bands of the Aniline−DEA, Aniline−TEA,[a] and Aniline Monomer[b]

mode	frequency obs.	calc.[c]	intensity calc
	Aniline−DEA		
free NH str.	3473	3471	70
H-bonded NH str.	3369	3355	181
free NH str.(DEA)	3294	3305	4
	Aniline−TEA		
free NH str.	3466	3474	39
H-bonded NH str.	3328	3256	447
	Aniline Monomer		
NH_2 asym. str.	3508	3520	11
NH_2 sym. str.	3422	3411	10

[a] Reference 4. [b] Reference 9. [c] Calculated using MP2/6-31G** basis. The calculated frequencies were scaled with a factor of 0.9421 to reproduce the aniline monomer values.

Coupling between strongly bound, high-frequency intramolecular modes and dissociating low-frequency intermolecular modes may promote vibrational energy redistribution within the complex. Thereby, vibrational predissociation occurs via direct or indirect coupling of the initially excited mode with the intermolecular stretch. Because of such vibrational couplings, a mixing of the zeroth-order excited state with the continuum distributes the oscillator strength for the transition over a continuous range of nearby frequencies, resulting in line broadening. Furthermore, the width of this broadening is a measure of the strength of these couplings and of the time scale of the vibrational energy flow. Becuase aniline has a large number of low-frequency vibrational modes, it seems likely that an efficient V−V coupling between the bound N−H stretching mode and an internal aniline mode takes away the excess energy.

The large spectral broadening observed by us in the infrared depletion spectrum of the ground state of the aniline−DEA complex may be due to a rotational−vibrational structure as well as the homogeneous broadening by IVR and predissociation. There are six H-bond vibrational modes. However, no rotational−vibrational fine structure could be observed in the infrared depletion spectrum of aniline−DEA. The nhomogeneous contribution due to rotational excitation may not be significant if the vibrationally excited state has a shorter lifetime, compared to a rotational period of the large complex.

The above factors indicate that the broad structureless band at 3369 cm^{-1} is due to homogeneous broadening. The spectral feature fits well with a Lorentzian profile (Figure 4), giving a spectral line width of 13 cm^{-1}. That the homogeneous contribution to the line width is dominant comes from the observation that more than 90% of the complexes are dissociated by the laser. Although an output of about 250 μJ/pulse by the IR laser around 3369 cm^{-1} gives negligible power broadening, the laser line width is much smaller (about 0.5 cm^{-1}) than the spectral bandwidth found. The maximum fraction of the molecules that can be dissociated by the laser is given by the ratio of the homogeneous line width to that of the overall width of the spectrum. Whether the homogeneous broadening is due to vibrational predissociation or an IVR process could not be answered explicitly from this frequency domain measurement. In this study on the aniline−DEA complex, observation of a much higher predissociation/IVR rate for the lower energy mode (ν_{bound}) than the higher energy (ν_{free}) mode suggests mode-specific behavior.

4. Conclusions

The aniline−DEA complex is investigated using one color resonant two-photon ionization spectroscopy in combination with infrared depletion spectroscopy. The electronic 0−0 band origin for the $S_1 \leftarrow S_0$ transition is observed at 32 916 cm^{-1}, giving a significant red shift of 1113 cm^{-1} from that of the bare aniline. Two vibrational progressions associated with the R2PI spectrum are assigned to intermolecular modes of the complex. The N−H vibrational stretching modes of DEA and aniline, on forming a H-bonded complex, give rise to three strong IR absorption features, ν_{free} at 3294 cm^{-1}, $\nu_{\mathrm{H-bonded}}$ at 3369, and ν_{free} at 3473 cm^{-1}. This shows a red-shift of 40 cm^{-1} with the NH stretch of DEA moiety in the complex. Although the sharp band at 3473 cm^{-1} has showed an apparent red shift of 35 cm^{-1} due to a reduced coupling between nondegenerate NH stretching modes in aniline, the band at 3369 cm^{-1} is homogeneously broadened by 13 cm^{-1} as well as red-shifted by 88 cm^{-1}. The red shifts agree with our ab initio calculated aniline−DEA structure, where one of the N−H bonds of aniline interacts with the lone pair of the nitrogen atom of DEA through a hydrogen bond, giving a binding energy of 15.8 kJ mol^{-1}. Although the narrow bandwidth of the free N−H stretch at 3473 cm^{-1} may have an upper-bound of the experimentally limited lifetime, the 13 cm^{-1} homogeneously broadened absorption feature at 3369 cm^{-1} suggests vibrational predissociation and/or IVR of the H bond in the ground-state complex, with a subpicosecond lifetime. A large intensity enhancement, homogeneous broadening and red shift in the infrared spectrum for the H-bonded N−H stretching mode in aniline−DEA indicate a strong coupling with the intermolecular modes and a rapid energy flow.

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