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Infrared Depletion Spectroscopy Suggests Mode-Specific Vibrational Dynamics in the Hydrogen-Bonded Aniline−Diethyl Ether ($C_6H_5-NH_2\cdots OC_4H_{10}$) Complex

P. K. Chowdhury*

National Institute for Advanced Interdisciplinary Research, 1-1-4 Higashi, Tsukuba, Ibaraki 305, Japan

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The vibrational frequencies of the N−H stretching modes of aniline, after forming a strong H-bonded complex with diethyl ether (DEE), are measured with infrared depletion spectroscopy that uses cluster-size-selective REMPI time-of-flight mass spectrometry. Two strong absorption features observed at 3372 and 3478 cm^{-1} are assigned to the H-bonded and free N−H stretching vibrations of the 1:1 aniline−DEE complex. The spectral broadening observed for the free and H-bonded N−H stretching modes indicates mode-specific vibrational energy dynamics. While the narrow bandwidth ($\approx$3 cm^{-1}) of the N−H stretch at 3478 cm^{-1} incorporates all the common broadening mechanisms including IVR, the broader ($\approx$10 cm^{-1}) absorption feature at 3372 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 agree with the ab initio calculated (MP2/6-31G**) aniline−DEE structure in which one of the N−H bonds of aniline interacts with the oxygen atom of DEE through a hydrogen bond, giving a binding energy of 13 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 33292 cm^{-1}, giving a significant red shift of 737 cm^{-1} from that of the bare aniline. The vibrational bands 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 make 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.[30,31] 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 relatively small.

In weakly bound molecular complexes, the normal modes are divided between two distinct sets of vibrational modes: strongly bound, high-frequency intramolecular and weakly bound, low-frequency intermolecular modes. Intramolecular vibrational mode excitation that exceeds the binding energy of the complex is followed by energy flow to the intermolecular modes and causes vibrational predissociation of the complex. One interesting question is whether the energy flow is statistical in nature and follows RRKM behavior or nonstatistical, where mode-specific intramolecular vibrational motion must couple to the intermolecular coordinate followed by dissociation. A general prediction emerging out of the theoretical treatments[2,3] is that the most facile predissociation channel will be the one that leads to the fragments with the least translational energy. Some examples exist from molecular dimer vibrational predissociation studies. Dissociation of water dimer[4] leads to the formation of fragments that are strongly peaked in the forward direction, although significant excess energy is available. This implies that most of the excess energy is deposited into the internal rovibrational degrees of freedom and negligible amount of translational energy in the center of mass system. Hydrogen fluoride dimer exhibits mode-specific vibrational predissociation,[5,6] where two nonequivalent HF forms the structure. The two HF stretching modes, which couple with the intermolecular modes differently, have different predissociation lifetimes. The nitric oxide dimer has been studied by Casassa et al.[7] with a time-resolved technique and by Matsumoto et al.[8] with their high resolution infrared spectroscopy. Both sets of results are in excellent agreement. The lower energy mode is found to induce dissociation at a higher rate than the higher energy mode. This is unexpected in terms of purely statistical theories. Hence, the difference in decay rate indicates a mode-specific coupling in the vibrationally excited complex. The possibility of a direct nonadibatic transition from the initially excited vibrational state to a repulsive electronic surface has been suggested,[9,10] where the difference in the nonadiabatic energy gaps for the two modes could cause the observed mode specific lifetimes. Although various possible dissociation schemes were discussed[7,8] by the authors, it remained inconclusive of which mechanism dominates the predissociation.

Upon excitation of a vibrational stretching mode directly involved in H-bonding, energy may leak into the intermolecular dissociating mode undergoing a fast predissociation. To see whether there is such a mode specific vibrational coupling for a mode involved in a hydrogen bond (the promoter), we have chosen to study aniline−diethyl ether (DEE) complex. While 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

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* Address correspondence to Radiation Chemistry and Chemical Dynamics Division, Bhabha Atomic Research Center, Trombay, Mumbai 400085, India. E-mail: pkc@apsara.barc.ernet.in.

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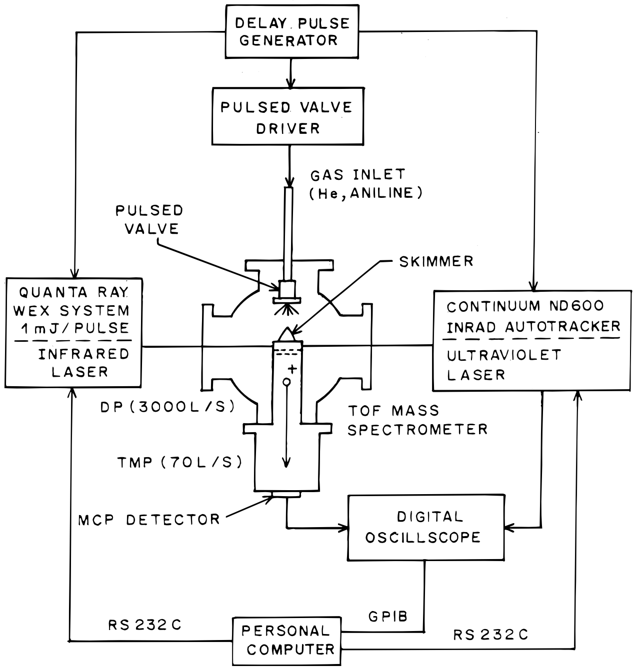

Figure 1. A schematic diagram of the apparatus used for REMPI and IR depletion spectrum.

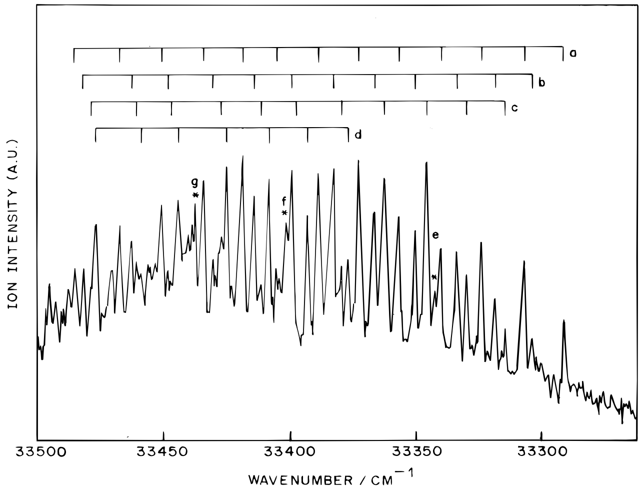

Figure 2. One color resonant two-photon ionization spectrum of the aniline−DEE complex detected by the ion signal at $m/z = 167$. The $S_1 \leftarrow S_0$ 0−0 transition is assigned at 33292 cm^{-1}, which is used to record the IR depletion spectrum. The R2PI spectrum shows a vibrational band progression of 16 cm^{-1} from the origin at 33292 cm^{-1} and three more progressions of the same frequency, shifted from the origin by 14, 23, and 86 cm^{-1}, which are marked as *a, b, c, d*, respectively.

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,[29] on the vibrational frequencies of the N−H stretching modes of the aniline−DEE complex. The one-color-resonant two-photon ionization (R2PI) spectrum of aniline−DEE was recorded to obtain the 0−0 band of the $S_1 \leftarrow S_0$ electronic transition at 33292 cm^{-1}. The depletion of the two-photon ionization signal was measured as a function of infrared laser frequency. In the infrared depletion spectrum two strong features observed at 3372 and 3478 cm^{-1} are assigned to the H-bonded and free N−H stretching vibrations of the 1:1 aniline−DEE complex. The red shift of the N−H stretching vibrations of aniline is used as a reference for the ab initio calculated aniline−DEE structure, where one of the N−H bonds of aniline interacts with the lone pair of the oxygen atom of DEE through a hydrogen bond. While the narrow bandwidth of the free N−H stretch at 3478 cm^{-1} sets an upper limit for the rate of IVR, the more intense, broader absorption band at 3372 cm^{-1} indicates a mode-specific vibrational predissociation and IVR of the H-bond in the ground-state complex.

2. Experimental Section

The experimental apparatus used for the study of infrared depletion spectroscopy of aniline−diethyl ether complex is shown in Figure 1. The details of the apparatus and of the measurement procedures have been previously reported.[11−14] Only salient features are given here. Aniline complexes were formed in the supersonic expansion of a mixture of aniline and diethyl ether (DEE) vapors by helium carrier gas at room temperature, with a stagnation pressure of 1.5 bar. The vapors of aniline and DEE were obtained by bubbling helium gas in their liquid mixture. Only a small amount (about 0.1%) of DEE 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−DEE 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 μJ/pulse in order to minimize the fragmentation of the aniline−DEE complexes by UV multiphoton absorption.

The infrared absorption bands of the aniline−DEE 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 IR output was about 1 mJ/pulse at 3 μm and the 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−DEE complex, while the IR laser was scanned around the N−H stretching vibrational region around 3330−3510 cm^{-1}.

3. Results and Discussion

A. Electronic Excitation Spectrum. Figure 2 shows the one-color resonant two-photon ionization (R2PI) spectrum of aniline−DEE recorded at mass number 167. To our knowledge, there is no LIF or REMPI spectroscopic study on aniline−DEE

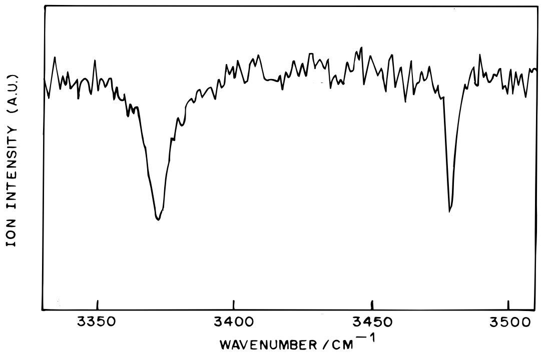

Figure 3. Infrared depletion spectrum of the aniline−DEE complex. The complex was ionized with a UV laser at 33292 cm^{-1}.

reported in the literature. The absorption system has its first band at 33292 cm^{-1}, which is red shifted by 737 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 16 cm^{-1} from the origin at 33292 cm^{-1} and three more progressions of the same frequency, shifted from the origin by 14, 23, and 86 cm^{-1}, which are marked in Figure 2 as *a, b, c,* and *d,* respectively. Assignment of the R2PI excitation spectral bands are made in comparison with the intermolecular modes of the ground-state complex calculated at the MP2 level of theory with 6-31G(d,p) basis set, which are shown in Table 1. The 737 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.

B. Infrared Depletion Spectrum. In Figure 3, the observed IR depletion spectrum of the aniline−DEE complex is shown in the region 3330−3510 cm^{-1}, with the UV laser fixed to the 0−0 transition at 33292 cm^{-1}. Here, two strong bands are observed at 3372 and 3478 cm^{-1}. By comparing NH_2 stretching vibrations of aniline monomer at 3422 and 3508 cm^{-1},[29] apparently, the frequency red shifts are obtained as 50 and 30 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 oxygen atom of DEE. 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 due to a decreased coupling between the two nondegenerate NH oscillators, the actual red shift for the hydrogen-bonded NH stretching mode is computed to be 80 cm^{-1}. Similar large red shifts are also observed by Felker et al. in the hydrogen-bonded phenol complexes.[28]

It is interesting to note that the integrated area of the lower frequency peak is about 2.5 times that of the higher frequency 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.[5] A factor of 8 was found to H-bonded methanol dimer,[15] 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[16]−37[17] 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 Gaussian 94 package.[18] As discussed in the next section, calculations on aniline−DEE 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 17 for the H-bonded stretch over the monomer value. Therefore, the observed absorption bands at 3372 and 3478 cm^{-1} are assigned to the H-bonded and free N−H stretching vibrations of the aniline−DEE complex system, respectively.

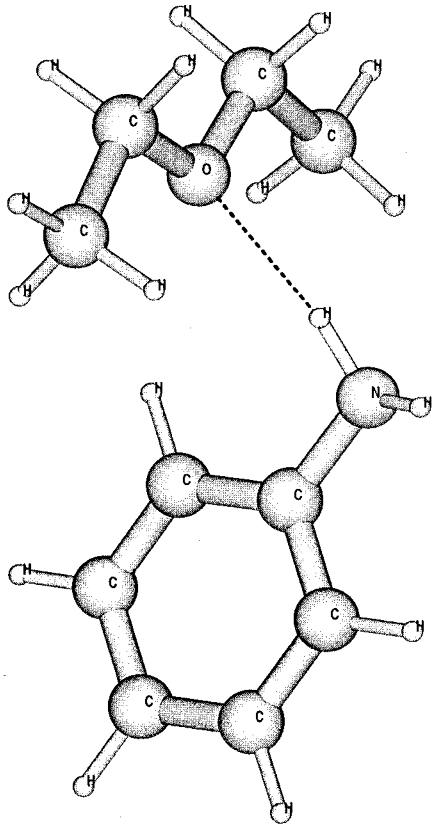

Figure 4. Geometry of the aniline−DEE complex fully optimized at the MP2/6-31G(d,p) level.

The infrared laser was found to show the depletion of the ion signal due to the aniline−DEE 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−DEE complex is smaller than the energy of one IR photon. The widths of the peaks in the complex spectrum are about 3 and 10 cm^{-1} (fwhm), respectively. The former has been occasionally found by us earlier[13] and is attributed to the participation of rotational transitions. Since 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 E) in eq 1 to be about 0.5 ps.

$$\tau = (2\pi\Delta \mathrm{v})^{-1} \tag{1}$$

This difference might seem surprising if we consider only the energetics of this system since the two modes are only separated by 106 cm^{-1} out of 3400 cm^{-1}. However, if one considers the structure shown in Figure 4 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. A similar example occurs in the infrared photodissociation of $NO-C_2H_4$ (υ_7) study of King and Stephenson using a nanosecond IR pump−UV probe technique.[19] The lifetime estimated from the width of the $NO-C_2H_4(\upsilon_7)$ photodissociation

TABLE 1: Comparison of the Experimental Vibrational Frequencies of the S_1 State of Aniline−DEE Complex and the Calculated Ground State Frequencies (cm^{-1}) from Normal Mode Analysis at the MP2/6-31G(d,p) Level

exptl (in reference to Figure 2) (relative to 33292 cm^{-1})	calculated frequency	assignment[a,27]
14 (*b*)	19	ρ_1
16 (*a*)	21	β_1
23 (*c*)	41	τ
52 (*e*)	52	β_2
86 (*d*)	89	ρ_2
111 (*f*)	128	σ
147 (*g*)	169	$\sigma + \tau$

[a] For nomenclature, see: Schutz, M. ; Burgi,Th.; Leutwyler, S. *J. Chem. Phys.* **1993**, *98*, 3763.

TABLE 2: Vibrational Frequencies (cm^{-1}) and Infrared Absorption Intensities (km mol^{-1}) of the N−H Stretching Bands of the Aniline−DEE, Aniline−TEA,[a] and Aniline Monomer[b]

mode	frequency observed	calcd[c]	intensity calcd
aniline−DEE			
free NH stretch	3478	3498	70
H-bonded NH stretch	3372	3388	175
aniline−TEA			
free NH stretch	3466	3474	39
H-bonded NH stretch	3328	3256	447
aniline monomer			
NH_2 asymmetric stretch	3508	3520	11
NH_2 symmetric stretch	3422	3411	10

[a] Reference 11. [b] Reference 13. [c] Calculated using MP2/6-31G** basis. The calculated frequencies were scaled with a factor of 0.9421 to reproduce the aniline monomer values.

spectrum was 0.7 ps. 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−DEE complex using the GAUSSIAN-94 program.[18] 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 criterion 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 oxygen of the DEE, with a calculated binding energy of 13 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.[20]

Figures 4 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 oxygen atom of DEE forming a nearly collinear bond N−H···O (∠NHO = 173°) with an intermolecular distance H···O of 2.04 Å. The hydrogen-bonded N−H bond length in the aniline−DEE complex increased to 1.0141 Å from 1.0103 Å of aniline. As expected, the complex shows a strong red shift in the electronic spectrum and in the IR depletion spectrum due to 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−DEE.

Our calculated binding energy of 13 kJ/mol for the aniline−DEE is found to be lower than that of the aniline-triethylamine (17 kJ/mol).[11] 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 2. 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 2, the calculation reproduces the experimental results on the frequency and IR absorption intensity fairly well.

D. Vibrational Predissociation Dynamics. The separate and distinct processes of intramolecular vibrational redistribution (IVR) and vibrational predissociation (VP) are related to the general phenomenon of radiationless transition and 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.[2] 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. Further, the width of this broadening is a measure of the strength of these couplings and of the time scale of the vibrational energy flow.

Theoretical model calculations[2,3] have predicted vibrational predissociative lifetimes that have varied from picoseconds to minutes. A general prediction emerging out of the theoretical treatments[2,3] is that the most facile predissociation channel will be the one that leads to the fragments with the least translational energy. Using the widely accepted momentum gap relation,[2] the lifetime (τ) of the aniline−DEE complex has been evaluated using eq 2,

$$\tau^{-1} \approx 10^{12} \exp[-\pi^2(2\mu_v \Delta E)^{1/2}/ah] \qquad (2)$$

where μ_v = reduced mass of the complex, ΔE = vibrational energy in excess of binding energy of the complex, and a = fitting parameter. The value of a may be estimated by fitting a Morse potential, $D_e\{1 - e^{-a(r-re)}\}^2$, to experimentally determined intermolecular potential surface. Its value is typically between 1 and 2×10^8 cm^{-1}. For a short-lifetime calculation, an uncertainty in a is found to be not important. Assuming that none of the residual energy in the vibrational predissociation process is retained in rotation or vibration of the fragments, one obtains an upper limit for the lifetime. Using $a = 1.5 \times 10^8$ cm^{-1}, one estimates τ to be more than minutes. Although the model appears to be successful on I_2-rare gas predissociation,[21] a difference of 10 orders of magnitude has been found in the case of $N_2O^*-N_2O$.[22,3] It has been argued that efficient V−V/R relaxation channels open up reducing the momentum gap, to account for the short lifetimes observed. In the case of vibrational predissociation of C_2H_4···Ne complex, a detailed close coupling calculation of Hutson et al.[23] revealed such a V−V channel incorporating a low-lying vibrational mode of ethylene. Since aniline has a large number of low-frequency vibrational modes, it seems likely that an efficient V−V

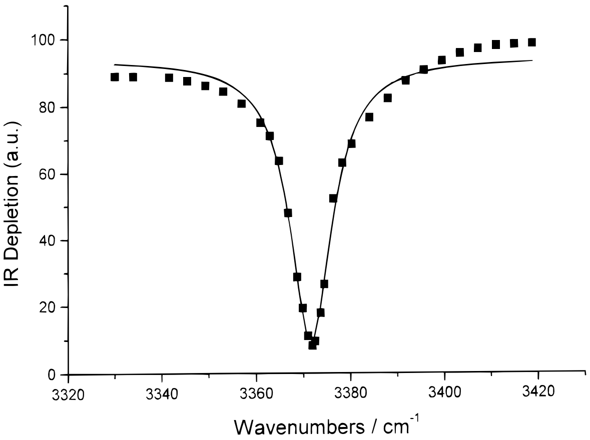

Figure 5. Lorentzian fit on the smoothened data of the IR depletion spectral band at 3372 cm^{-1}.

coupling between the bound N−H stretching mode and an internal aniline mode takes away the excess energy.

E. Possibility of Mode Specificity. The large spectral broadening observed by us in the infrared depletion spectrum of the ground state of aniline−DEE complex may be due to rotational−vibrational structure as well as the homogeneous broadening by IVR and predissociation. The band structure of a hydrogen-bonded absorption system is described as a progression of combination bands, with eq 3

$$\nu^{\mathrm{obs}} = \nu^{\mathrm{intra}} + m\nu^{\mathrm{inter}},\ m = 0, 1, 2 \qquad (3)$$

where ν^{intra} is the fundamental frequency of the hydrogen-bonded intramolecular H−N stretching motion, ν^{inter} is a frequency of the intermolecular $Et_2O\cdots H{-}N<$ hydrogen bond, and ν^{obs} is the frequency of the observed band. The decrease of ν^{intra} is due to a weakening of the intramolecular bond on complex formation. The progression of 16 cm^{-1} observed by us in the REMPI detected electronic spectrum may be assumed as the ν^{inter} of the intermolecular $Et_2O\cdots H{-}N<$ hydrogen bond. There are six H-bond vibrational modes. However, no such intermode-structure could be observed in the infrared depletion spectrum of aniline−DEE. Inhomogeneous 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 3372 cm^{-1} is due to homogeneous broadening. The spectral feature fits well with a Lorentzian profile (Figure 5), giving a spectral line width of 10.6 cm^{-1}. The conclusion 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. While an output of about 250 μJ/pulse 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 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.

Most of the available experimental data on IVR and VP are interpreted in terms of two models treating them as "parallel" or "serial" processes. The model by Beswick−Jortner[2] considers dissociation to be a process which occurs in parallel with IVR. One quantum energy change in the chromophore's vibrational mode which is larger than the binding energy of the complex, flows to the vdW modes. A direct coupling between the chromophore's vibrational states of the bound complex and the plane wave states of a dissociated complex leads to dissociation in one-half of the vibrational period. This results in IVR/VP occurring directly into the "dissociation continuum". Serial IVR cum VP processes incorporating Rice−Ramsperger−Kassel−Marcus (RRKM) reaction rate theory has been used to interpret experimental results on large clusters where the chromophore is an aromatic molecule.[32] Nimlos et al.[24] studied aniline clusters with Ar and methane, where an initial vibronic excitation put vibrational energy into the chromophore phase-space region. The IVR process was considered to be restricted to vdW modes only. Chromophore vibrational energy transfer to vdW modes leads to a rapid IVR where VP is the RRKM rate constant depending only upon the amount of energy in vdW modes. Knee et al.[25] measured the predissociation rates of the phenol−benzene complex by a picosecond pump−probe technique, upon exciting ring-type vibrational modes of the S_1 state of phenol. The measured rates correspond to RRKM dissociation rates calculated, however, with the exclusion of benzene vibrational modes. It was argued to be unlikely that an amount of energy necessary to excite the relatively high frequency modes of the benzene moiety would transfer efficiently across the weak vdW bond. Recent studies[26] on "benchmark" hydrogen bonded cluster systems such as $(HF)_2$ and its $(DF)_2$ isotopomers provide predissociation rates as a function of both intra- and intermolecular excitation. The high-resolution line shape analysis demonstrated that the vibrational predissociation broadening is a mode specific behavior, controlled predominantly by intramolecular excitation, and is only modestly affected by intermolecular excitation. Excitation of the bound intramolecular stretching mode gives rise to predissociation that is 20−50-fold faster than that resulting from excitation of the free stretching mode. While in $(HF)_2$ the intermolecular vdW stretching mode and geared bending modes are strongly mixed, in $(DF)_2$ they are decoupled exibiting some intermolecular mode specific effects. While the "geared bend" combined with bound stretch excitation increases the predissociation rate by 40% over the stretch excitation alone, a slight decrease of about 25% in the predissociation rate observed with "van der Waals" stretch excitation. It appears therefore that the direct coupling between the intramolecular mode and dissociating continuum is responsible for the observed mode specificity, rather than IVR.

In this study on the aniline−DEE complex, observation of a much higher predissociation rate for the lower energy mode (ν_{bound}) than the higher energy (ν_{free}) mode, suggests mode-specific behavior. The geometry of the complex during its dissociation may be far removed from the equilibrium configuration of the separated products. Thus, many low-frequency vibrational motions are expected to be excited in the complex fragments left in these extended orientations. It seems possible that no energy appears in translational degrees of freedom of the products and a modified energy gap relation or parallel model calculation reproduces the observed rates corresponding to the broadened infrared depletion spectrum.

4. Conclusions

Aniline−DEE 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 33292 cm^{-1}, giving a significant red shift of 737 cm^{-1} from that of the bare aniline. All the vibrational bands associated with the R2PI spectrum are assigned to intermolecular modes of the complex. The N−H vibrational stretching modes of aniline, upon forming a strong H-bonded complex with diethyl ether (DEE), give rise to two strong IR absorption features, $\nu_{\mathrm{H-bonded}}$ at 3372 and ν_{free} at 3478 cm^{-1}, respectively. While the sharp band at 3478 cm^{-1} has showed an apparent red shift of 30 cm^{-1} due to a reduced coupling between nondegenerate NH modes, the band at 3372 cm^{-1} is homogeneously broadened by 10.6 cm^{-1} as well as red shifted by 80 cm^{-1}. The red shifts agree with our ab initio calculated aniline−DEE structure, where one of the N−H bonds of aniline interacts with the lone pair of the oxygen atom of DEE through hydrogen bond, giving a binding energy of 13 kJ mol^{-1}. While the narrow bandwidth of the free N−H stretch at 3478 cm^{-1} may have an upper bound of the experimentally limited lifetime, the 10.6 cm^{-1} homogeneously broadened absorption feature at 3372 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−DEE indicate a strong coupling with the intermolecular modes and a rapid energy flow.

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