

Relaxation Processes of Molecules on a Solution Surface Studied by the Two-Color Pump–Probe Ionization Technique

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Received: November 10, 1998

A propanol (PrOH) solution of aniline (AN) was introduced into a vacuum chamber as a continuous liquid flow (liquid beam) and was irradiated with pump and probe laser beams having wavelengths of 266 and 500–600 nm, respectively. Ions produced by multiphoton absorption and ejected from the liquid beam surface were analyzed by a time-of-flight mass spectrometer. The mass spectra show that $\text{AN}^+(\text{PrOH})_n$ and $\text{H}^+(\text{PrOH})_n$ are produced. The $\text{AN}^+(\text{PrOH})_n$ and $\text{H}^+(\text{PrOH})_n$ intensities were measured as a function of the delay time between the pump and the probe lasers. The lifetime for relaxation of an excited aniline molecule on the liquid surface was obtained to be 7.8 ns from the dependence of the $\text{AN}^+(\text{PrOH})_n$ intensity on the delay time. In comparison with the lifetimes of an isolated aniline molecule in the gas phase and an aniline molecule in bulk solution, it is concluded that the aniline molecule does not strongly interact with its surrounding propanol molecules on the surface. Variation of the $\text{H}^+(\text{PrOH})_n$ intensity with the delay time indicates that H^+ produced by dissociative ionization of an aniline molecule is ejected with several propanol molecules as $\text{H}^+(\text{PrOH})_n$.

Introduction

A solute molecule on a solution surface is not completely solvated with its solvent molecules and is subjected to an asymmetric field so that the solvation structures and dynamics are very different from those inside the solution. The specificity of the solution surface, in turn, provides a unique opportunity to investigate how the solute molecule behaves under the asymmetric field built by the solvent molecules on the surface. Several spectroscopic techniques have been applied for the studies of surface molecules. For example, on the surface of a benzyl alcohol–formamide liquid mixture, benzyl alcohol is found to be enriched as expected from several macroscopic measurements such as surface tension.^{1–3} The kinetic energy distributions of electrons produced by photon and metastable atom impact, having different ionization depths, have revealed that benzyl alcohol tends to be segregated on the surface of a benzyl alcohol–formamide mixture even when they are homogeneously dissolved in the bulk.¹ A sudden change of the surface composition in a water–formamide mixture with a slight change of the bulk composition has been observed by photoelectron spectroscopy.² The change is attributed to a solvent–solvate transition.^{2,4} It has also been clarified in this study² that it takes 50–60 μs to reach an equilibrium value of the surface composition after changing the bulk composition. The latter information is related to the dynamical behavior of the solution surface in the long time regime and provided insight into the large-scale motion of the surface. Furthermore, the dynamics of the molecules on a liquid surface (molecular motion, chemical reaction, etc.) has been investigated by several methods. Scattering of atoms and molecules from a liquid surface has revealed a microscopic picture of how impinging atoms and molecules are accommodated in or rebounded from the sur-

face.^{5,6} The orientational relaxation time of rhodamine 6G on an aqueous solution surface has been observed to be 400–500 ps by second harmonic generation. This relaxation time is longer than the rotational relaxation time of 200 ps in the bulk. This finding is explained by a large frictional resistance exerted on the surface rather than on the bulk.⁷ Ion–molecule reactions induced by multiphoton excitation on various liquid surfaces have been investigated by using liquid-beam multiphoton ionization mass spectrometry.^{8–18}

In addition to the studies of the surface dynamics, it is important to obtain information on energy redistribution accompanied by the surface dynamic processes. A decay rate measurement of an excited surface molecule on a liquid surface is one of the most suitable means to gain an insight into the energy flow in relation to the local environment that surrounds the excited molecule. A system in which the energy redistribution depends sensitively on the local solvent structure should be suitable for investigation. For example, the electronic relaxation of an excited aniline molecule in an alcohol solution is considered to be shortened by the hydrogen bonding between aniline and alcohol molecules.¹⁹ A combination of pump–probe two-color photoionization with the liquid beam technique enables the measurement of the decay rate on the liquid surface. In addition to the usual merit of the liquid beam technique that ions produced in the vicinity of a liquid surface can be detected selectively by mass spectrometry, the time dependence of transient excited species on a liquid surface can be observed by introduction of the two-color photoionization.

We performed a decay measurement of an excited aniline molecule (AN) on the surface of a 1-propanol (PrOH) solution by using the method mentioned above. It is found that the lifetime of an aniline molecule in the S_1 state on the solution surface is comparable to the lifetime of an isolated aniline molecule in the S_1 state. This finding is related to the weak interaction between the aniline molecule and its surrounding propanol molecules on the surface. There exists a decay channel of the

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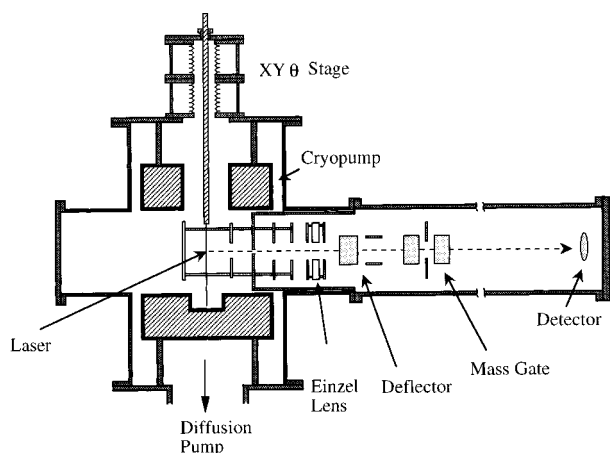


Figure 1. Schematic diagram of the liquid beam apparatus.

aniline molecule in the S_1 state, which correlates with the formation of $H^+(PrOH)_n$. The cluster ion, $H^+(PrOH)_n$, is considered to be formed via the S_1 and T_2 states of an aniline molecule.

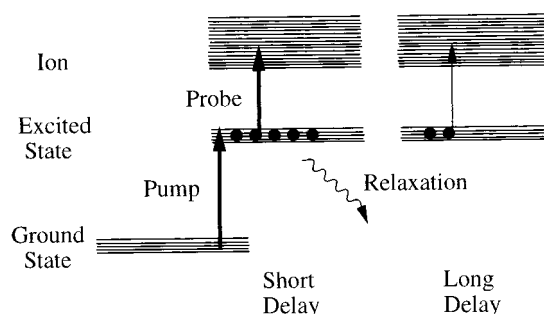
Experimental Section

Figure 1 shows a schematic diagram of the experimental apparatus used in the present study, which consists of a liquid beam source and a time-of-flight (TOF) mass spectrometer. A continuous laminar liquid flow (liquid beam) was introduced downward through an aperture with a diameter of $20\ \mu\text{m}$ into a vacuum chamber by applying a pressure of $\sim 20\ \text{atm}$ with a Shimadzu LC-6A pump. The flow rate was kept constant at $0.2\ \text{mL/min}$. Aniline and 1-propanol (Kanto Chemical Co., Inc.; G-grade) were used without further purification. The liquid beam was captured by a liquid N_2 trap (hatched areas in Figure 1) $10\ \text{cm}$ downstream from the aperture. The chamber was further evacuated down to 10^{-5} – 10^{-6} Torr by a $1200\ \text{L/s}$ diffusion pump. In this pressure range, the mean-free path of the molecules in the gas phase exceeds $1\ \text{m}$ so that molecules do not stagnate in the close vicinity of the solution surface. This feature is supported by the fact that electrons from a liquid surface have been observed after metastable-atom impact,²⁰ where the ionization probability of a molecule colliding with a metastable atom is almost unity. Evidently, there is no substantial gas layer on the liquid beam surface because the metastable atoms reach the surface without suffering collisional deactivation by molecules in the gas phase.

Traveling a distance of $1\ \text{mm}$ from the aperture, the liquid beam was crossed with two laser beams (pump and probe lasers) at the first acceleration region of the TOF mass spectrometer. A UV laser at $266\ \text{nm}$ was used as the pump laser, which is resonant with the S_0 – S_1 transition of an aniline molecule; the laser was provided by the fourth harmonic of a Quanta-ray GCR-3 Nd:YAG laser. The probe laser for ionization was provided by a Spectra-Physics MOPO optical parametric oscillator (500 – $600\ \text{nm}$). The pulse width of the lasers was $\sim 5\ \text{ns}$. The delay time between the pump and probe lasers was controlled by a Stanford Research Systems DG-535 digital delay pulse generator. The pump and the probe lasers were focused onto the liquid beam by a lens with a focal length of $400\ \text{mm}$. Throughout this study, the liquid beam was completely within the pump and probe laser spots. The method for measuring the lifetime of the S_1 state is depicted in Scheme 1.

Ions ejected from the liquid beam were accelerated by a pulsed electric field in the first acceleration region of the TOF mass spectrometer, in the direction perpendicular to both the liquid and the laser beams. A delay time from the ionization to

SCHEME 1



the ion extraction was varied in the range of 0 – $5\ \mu\text{s}$ so as to improve the mass resolution. The ions were then steered and focused by a set of vertical and horizontal deflectors and an einzel lens. After traversing a 1-m field free region, the ions were detected by a Murata EMS-6081B Ceratron electron multiplier. Signals from the multiplier were amplified and processed by a Yokogawa DL 1200E transient digitizer based on a NEC 9801 microcomputer. The mass resolution, $m/\Delta m$, was found to be more than 85 at $m = 200$ in the present experimental conditions.

In the present study, the intensities of an aniline ion and its fragment ions were found to be much higher than those of the cluster ions of interest. In order to observe cluster ions in an effective manner, a mass gate was mounted in the field-free region of the TOF mass spectrometer to select the ions of interest. Rejecting the undesired ions, namely aniline ion and its fragment ions in the present study, improved the detector sensitivity. The mass gate consisted of two sets of horizontal deflectors which were mounted serially with a gap of $2\ \text{cm}$ between them. A metal grid electrically grounded was placed between the two deflectors. A pulsed electric field was applied to the mass gate so that only the ions having masses larger than that of an aniline ion were admitted.

Results

Figure 2 shows typical TOF mass spectra of ions produced from a $0.5\ \text{M}$ aniline solution in propanol. Panel a shows the mass spectrum of ions produced by irradiation of only the pump laser at $266\ \text{nm}$. A series of ion peaks ($m/z = 93, 153, 213, 273, \dots$, and $m/z = 61, 121, 181, \dots$) observed in the spectrum are assigned to $AN^+(PrOH)_n$ and $H^+(PrOH)_n$, respectively. These ions are produced by two-photon absorption of the pump laser. Panel b shows the mass spectrum of the ions when the probe laser at $500\ \text{nm}$ was introduced simultaneously with the pump laser. Although the mass spectral feature does not change significantly, the intensity of $AN^+(PrOH)_n$ increases by the addition of the probe laser: Note that no cluster ions were observed in the mass spectrum as long as the pump laser irradiates outside the liquid beam, even if the probe laser crosses the liquid beam or illuminates outside the liquid beam. The increment in the intensities of $AN^+(PrOH)_n$ and $H^+(PrOH)_n$ by the addition of the probe laser gives rise to the spectrum (the differential spectrum, panel c, obtained by subtracting a from b) of the ions produced only by the two-color two-photon pump–probe photoionization.

The total increment of the $X^+(PrOH)_n$ ($X = AN$ or H) intensity caused by addition of the probe laser to the pump laser, $\Delta I_X^{(\text{total})}$, is defined as

$$\Delta I_X^{(\text{total})} = \sum_n \Delta I_X^{(n)} \quad (1)$$

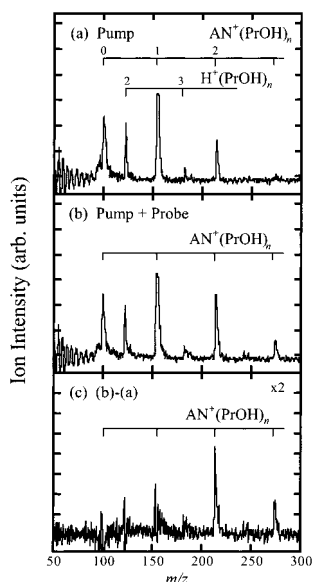


Figure 2. Mass spectrum of ions produced from a 0.5 M aniline solution of 1-propanol under the irradiation of the pump laser at 266 nm (a) and the pump and the probe laser at 500 nm (b). A subtracted spectrum (b-a) is exhibited in c. The two lasers illuminate the liquid beam simultaneously (delay time 0 ns). Solvated aniline cluster ions, $\text{AN}^+(\text{PrOH})_n$ ($m/z = 93, 153, 213, 273, \dots$), increase in intensity by addition of the probe laser, while the protonated propanol cluster ions, $\text{H}^+(\text{PrOH})_n$, scarcely change.

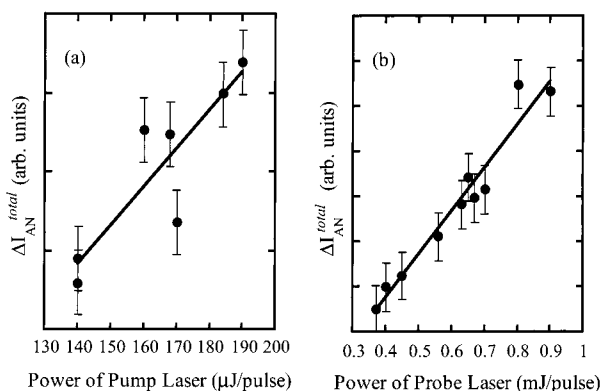


Figure 3. Intensity of $\text{AN}^+(\text{PrOH})_n$ ($n \geq 2$), plotted against the power of the laser. (a) Pump laser power dependence (probe laser power 0.8 mJ/pulse). (b) Probe laser power dependence (pump laser power 170 $\mu\text{J/pulse}$).

where $\Delta I_X^{(n)}$ stands for an increment of $\text{X}^+(\text{PrOH})_n$. The contributions of $\text{X}^+(\text{PrOH})_n$ with $n < 2$ for $\text{X} = \text{AN}$ and $n < 3$ for $\text{X} = \text{H}$ are excluded from the sum because these ions are not well separated from AN^+ due to insufficient mass resolution of the mass gate. This treatment is warranted because an ion, $\text{X}^+(\text{PrOH})_n$, with a different n was found to depend almost identically on the laser power and the delay time.

Panels a and b of Figure 3 represent $\Delta I_{\text{AN}}^{(\text{total})}$ plotted against the power of the pump and the probe lasers, respectively. The value, $\Delta I_{\text{AN}}^{(\text{total})}$, depends linearly on both the power of the pump and the probe lasers. It was also found that $\Delta I_{\text{H}}^{(\text{total})}$ depends linearly both on the power of the pump and the probe lasers.

Figure 4 shows $\Delta I_{\text{AN}}^{(\text{total})}$ as a function of the pump-probe delay time (0–35 ns). As the delay time increases, $\Delta I_{\text{AN}}^{(\text{total})}$ decreases exponentially, with the characteristic lifetime of 7.8 ± 0.8 ns, where the pulse widths of the two lasers are deconvoluted from the time profile of $\Delta I_{\text{AN}}^{(\text{total})}$. At negative delay times, $\Delta I_{\text{AN}}^{(\text{total})}$ decreased drastically and became half

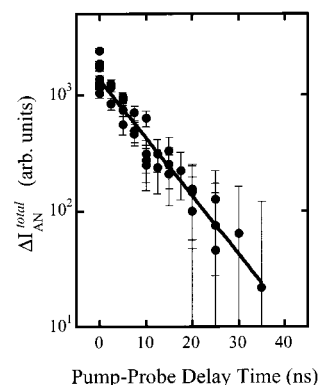


Figure 4. Total increase of the abundances of $\text{AN}^+(\text{PrOH})_n$ ($n \geq 2$), $\Delta I_{\text{AN}}^{(\text{total})}$, plotted against the pump-probe delay time (0–35 ns). The relaxation time of an excited aniline molecule on the solution surface is measured to be 7.8 ± 0.8 ns.

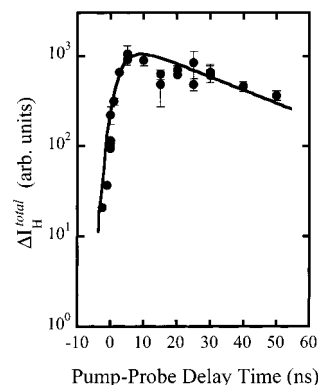


Figure 5. Increase of the abundances of all the $\text{H}^+(\text{PrOH})_n$ with $n \geq 3$, $\Delta I_{\text{H}}^{(\text{total})}$, plotted against the pump-probe delay time (0–50 ns). Note that $\Delta I_{\text{H}}^{(\text{total})}$ is negligibly small at delay time = 0 but shows a sharp increase within the first 5 ns of delay time.

within < 2 ns. This rapid decrease is consistent with the pulse width of the lasers. Similar measurements were performed for the 2 M and 0.25 M aniline solutions in propanol, and the lifetime was found to be the same within the experimental uncertainty.

Figure 5 shows $\Delta I_{\text{H}}^{(\text{total})}$ as a function of the pump-probe delay time (0–50 ns). As shown in Figure 2, only a trace amount of $\Delta I_{\text{H}}^{(\text{total})}$ is observed when the pump and the probe lasers concurrently irradiate the liquid beam. As the delay time increases, $\Delta I_{\text{H}}^{(\text{total})}$ increases sharply up to 5 ns and then decreases.

Discussion

Ionization of Aniline Molecules on the Solution Surface.

When aniline molecules in a propanol solution are irradiated with the 266 nm laser, the aniline molecule is excited by absorption of one photon and then ionized by absorption of another photon. A photoelectron generated in the liquid beam has a fate of being (1) captured by a neutral molecule as a negative ion, (2) delocalized in the solution as a solvated electron, (3) neutralized at a certain site via geminate recombination, or (4) liberated as a free electron in the gas phase. As the mean-free path of the electron is shorter than ~ 1 nm,^{20,21} only electrons generated as deep as 1 nm from the liquid surface can escape into vacuum. Therefore, only a surface region (at most, several nanometers deep) becomes positively charged due to the electron depletion. When the repulsive Coulomb energy exceeds the solvation energy of the ion concerned, the ion is ejected from the surface (Coulomb ejection model).^{9,11}

During excitation by the pump pulse, many aniline molecules are excited without being ionized. In the pump–probe configuration, the probe laser photon ionizes a portion of the excited aniline molecules. As a result, the abundance of the ions in the liquid beam increases, and hence, the intensities of the cluster ions ejected in the gas phase also increase. Therefore, the increment of the $X^+(\text{PrOH})_n$ intensity is attributed to the two-color pump–probe two photon ionization.

In the Coulomb ejection scheme above the ejection threshold, the abundance of the ions ejected into vacuum, N_{ejec} , is expressed as

$$N_{\text{ejec}} = N_{\text{liq}} - N_{\text{re}} \quad (2)$$

where N_{liq} is the abundance of the ions initially produced in the liquid and N_{re} is the abundance of the ions remaining inside the liquid after the Coulomb ejection. Our previous experiment on single-color two-photon ionization has shown that N_{re} is independent of the laser power.¹⁷ The ion intensity ($I_{\text{ejec,pump}}$, see panel a of Figure 2) observed under the irradiation of the pump laser alone is given by

$$I_{\text{ejec,pump}} = cN_{\text{ejec}} = c(aP_{\text{pump}}^2 - N_{\text{re}}) \quad (3)$$

where P_{pump} represents the power of the pump laser, a is the pump-only ionization cross section, and c is a constant depending on the collection efficiency and the velocity of the ions. The ions are produced by two-photon absorption of the pump laser (“pump–pump ionization”) under the condition of the pump laser alone.¹¹ Similarly, the ion intensity ($I_{\text{ejec,all}}$, see panel b of Figure 2) observed under the irradiation of both the pump and the probe lasers is given by

$$I_{\text{ejec,all}} = c(aP_{\text{pump}}^2 + bP_{\text{pump}}P_{\text{probe}} - N_{\text{re}}) \quad (4)$$

where P_{probe} represents the power of the probe laser and b is the pump–probe ionization cross section. The increment in ion intensity by introduction of the probe laser over the pump laser ($I_{\text{ejec,pump+probe}}$, corresponding to Figure 2, panel c) is expressed simply by subtracting eq 3 from eq 4; that is,

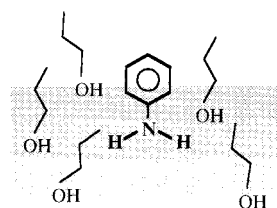
$$I_{\text{ejec,pump+probe}} = cbP_{\text{pump}}P_{\text{probe}} \quad (5)$$

It follows that the effect of Coulomb ejection does not appear explicitly (no threshold in the laser powers for the ion production). The arguments given so far lead us to conclude that the linear dependence of $\Delta I_{\text{AN}}^{(\text{total})}$ arises from the ionization by absorption of one photon of the pump laser and another photon of the probe laser (“pump–probe ionization”). The non-zero intercept, which appears when the probe laser power is weak (see Figure 3b), may be caused by the experimental condition and the effect of the probe laser on Coulomb ejection. On the other hand, when the pump laser power is weak, a non-zero intercept must appear since the laser power becomes below the ejection threshold (see Figure 3a).

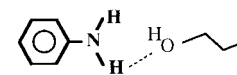
The ionization potential (IP) of an isolated aniline molecule is known to be 7.7 eV, while the IP of an aniline molecule on the liquid surface is determined to be lower by 1.4 eV according to our previous experiment.¹⁸ Therefore, an aniline molecule in the gas phase cannot be ionized by the two-color pump–probe ionization, because the photon energy (7.2 eV) is less than the IP of the aniline molecule in the gas phase. Actually, AN^+ and $\text{AN}^+(\text{PrOH})_n$ do not increase when the probe laser irradiates outside the liquid beam. On the other hand, an aniline molecule in bulk aqueous solution is reported to be ionized by

CHART 1

Liquid Surface



Bulk Liquid

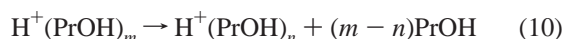
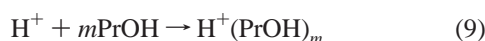
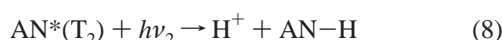
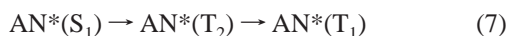


a lower photon energy inside the solution²² than on the surface, since the solute is completely solvated by the surrounding molecules inside the solution, whereas it is incompletely solvated on the surface. In addition, the electrons in the solution are stabilized by ~ 1 eV,²³ while the electrons in the vicinity of the surface are more readily ejected into vacuum.

Relaxation of Excited Aniline Molecules on Solution Surface. It has been reported that the lifetime of the S_1 state of an aniline molecule in an alcohol solution is 3.1 ns and is much shorter than the lifetime of 7.5 ns in the gas phase.²⁴ The lifetime is shortened because the amino group of the aniline molecule is hydrogen-bonded to the hydroxy group of its neighboring alcohol molecule. The increase in the electron density on the N atom of the aniline molecule enhances the intersystem crossing rate.¹⁹ If this scheme is also applicable to the aniline molecule on the surface, its long lifetime of 7.8 ± 0.8 ns (see Figure 4) implies that the hydrogen bonding between the surface aniline molecule and alcohol molecules is significantly weaker than that in solution. This weak hydrogen bonding might result from a specific arrangement of the solute and solvent molecules on the surface. For example, surface alcohol molecules have been shown to be oriented with its hydroxy group pointing into the liquid.²⁵ If the aniline molecule is also oriented with its NH_2 end pointing inward, the interaction between the NH_2 and OH groups is considered to be minimized because steric hindrance of the benzene ring prevents the alcohol molecule from approaching the aniline molecule (see Chart 1).

Formation of Protonated Propanol Cluster Ions. The linear laser-power dependence of $\Delta I_{\text{H}}^{(\text{total})}$ both on the pump and probe laser powers indicates that one pump photon and one probe photon are involved in the production of $\text{H}^+(\text{PrOH})_n$. As the sum of the energy of one pump photon and one probe photon (less than 7.2 eV) is insufficient to ionize a propanol molecule in the vicinity of the liquid surface (9.72 eV),²⁶ the formation of $\text{H}^+(\text{PrOH})_n$ should proceed via an excited aniline molecule and/or an aniline ion. Our previous study¹¹ shows that $\text{H}^+(\text{PrOH})_n$ is produced from an aniline–propanol solution by single-color two-photon excitation at 272 nm (9.1 eV). In this case, proton transfer from the aniline ion to a neighboring propanol molecule precedes the production of $\text{H}^+(\text{PrOH})_n$, as the proton affinity of $(\text{PrOH})_{m \geq 3}$ exceeds the dissociation energy of AN^+ into $\text{AN}-\text{H}$ and H^+ , where $\text{AN}-\text{H}$ is a dehydrogenated aniline radical. In the present measurement, even though the intensity of $\text{AN}^+(\text{PrOH})_n$ increases considerably by additional irradiation of the probe laser with no pump–probe delay time, only a slight increase of $\text{H}^+(\text{PrOH})_n$ intensity is observed as shown in Figure 5. Namely, AN^+ is not likely to be involved in the formation of $\text{H}^+(\text{PrOH})_n$. Therefore, an alternative mechanism must account for the formation of $\text{H}^+(\text{PrOH})_n$ in the photon energy range studied. Since $\Delta I_{\text{H}}^{(\text{total})}$ increases with a rise time comparable with the characteristic time of the intersystem crossing of the aniline molecule in alcohol, the intersystem crossing of the

S_1 state almost certainly must play an important role in the initial stage of the $H^+(PrOH)_n$ formation. The photodissociation by the probe laser of $AN^+(PrOH)_n$ generated by the pump–pump ionization to form $H^+(PrOH)_n$ is unlikely, since the $AN^+(PrOH)_n$ intensity does not decrease by the probe–laser irradiation. It is highly likely that the T_2 state is produced by the intersystem crossing, since the T_2 state is located slightly lower in energy than the S_1 state.²⁷ The T_2 state thus formed is considered to be involved in proton donation after its further excitation by a probe laser pulse. The involvement of the T_2 state is consistent with the energetics since the energy of the pump and the probe photons exceeds the ionization energy of an aniline molecule via the T_2 state. The gradual decrease in signal for pump–probe delay times longer than ~ 10 ns is likely to result from the T_2 – T_1 decay. Therefore, the following scheme is conceivable:



where $h\nu_1$ and $h\nu_2$ represent the photon energies of the pump and probe lasers, respectively. Processes 6–10 proceed in the solution. An aniline molecule in the solution is excited to the S_1 state ($AN^*(S_1)$) by absorption of one photon of the pump laser (process 6), and is converted to the T_2 state ($AN^*(T_2)$) by intersystem crossing (process 7). The excited molecule, $AN^*(T_2)$, is dissociatively ionized and releases a proton after absorbing one more photon of the probe laser (process 8). The proton, H^+ , is expelled from the surface as a nascent cluster ion, $H^+(PrOH)_n$ (process 9), which decays by unimolecular dissociation (process 10).

According to a simple kinetics, the population of $AN^*(T_2)$, $D(t)$, at time t , measured after excitation with the pump laser, is expressed as

$$D(t) = \frac{\tau_2}{\tau_1 - \tau_2} (e^{-t/\tau_1} - e^{-t/\tau_2}) D_0 \quad (11)$$

where τ_1 and τ_2 are the characteristic times for the S_1 – T_2 intersystem crossing and the T_2 decay, respectively, and D_0 is the initial abundance of $AN^*(S_1)$. In this scheme, $\Delta I_H^{(total)}$ should be proportional to the population of $AN^*(T_2)$, $D(t)$ (process 8), so that the time dependence of $\Delta I_H^{(total)}$ is proportional to $D(t)$. The time dependence of $\Delta I_H^{(total)}$ was fit with the rate equation given by eq 11, where τ_1 is fixed at 7.8 ns using the surface intersystem crossing rate obtained in this study and τ_2 is the variable parameter. The best fit gives τ_2 of 30 ns with τ_1 of 7.8 ns (see Figure 5). The characteristic time, τ_2 , seems to be related to the T_2 – T_1 internal conversion, although it is much larger than the prediction of the Kasha rule.

Conclusion

The relaxation processes of an aniline molecule on and in the close vicinity of the surface of an aniline–propanol solution was studied by liquid beam photoionization mass spectrometry combined with a two-color pump–probe method. Cluster ions, $AN^+(PrOH)_n$ and $H^+(PrOH)_n$, were found to be produced. Analysis of $AN^+(PrOH)_n$ gives the relaxation time of 7.8 ns

for a surface aniline molecule in the S_1 state. The comparable relaxation rate with that for an isolated aniline molecule in the S_1 state leads us to conclude that the hydrogen bonding between aniline and propanol molecules is weakened on the surface, probably because of their specific orientation. In the production of $H^+(PrOH)_n$, formation of the T_2 state of an aniline molecule on and/or in the close vicinity of the solution surface is considered to precede the formation of the proton. The proton thus produced is ejected with several accompanying alcohol molecules. The characteristic decay time of the T_2 state was estimated.

Acknowledgment. This work was conducted under the special program of cluster studies of the Genesis Research Institute, Inc., and the NEDO International Joint Research Program.

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