

Picosecond IR-UV pump-probe spectroscopic study on the intramolecular vibrational energy redistribution of NH₂ and CH stretching vibrations of jet-cooled aniline

Yuji Yamada, Jun-ichi Okano, and Naohiko Mikami

Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan

Takayuki Ebata^{a)}

Department of Chemistry, Graduate School of Science, Hiroshima University, Higashihiroshima 739-8526, Japan

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Intramolecular vibrational energy redistribution (IVR) of the NH₂ symmetric and asymmetric stretching vibrations of jet-cooled aniline has been investigated by picosecond time-resolved IR-UV pump-probe spectroscopy. A picosecond IR laser pulse excited the NH₂ symmetric or asymmetric stretching vibration of aniline in the electronic ground state and the subsequent time evolutions of the excited level as well as redistributed levels were observed by a picosecond UV pulse. The IVR lifetimes for symmetric and asymmetric stretches were obtained to be 18 and 34 ps, respectively. In addition, we obtained the direct evidence that IVR proceeds via two-step bath states; that is, the NH₂ stretch energy first flows into the doorway state and the energy is further dissipated into dense bath states. The rate constants of the second step were estimated to be comparable to or slower than those of the first step IVR. The relaxation behavior was compared with that of IVR of the OH stretching vibration of phenol [Y. Yamada, T. Ebata, M. Kayano, and M. Mikami *J. Chem. Phys.* **120**, 7400 (2004)]. We found that the second step IVR process of aniline is much slower than that of phenol, suggesting a large difference of the “doorway state ↔ the dense bath states” anharmonic coupling strength between the two molecules. We also observed IVR of the CH stretching vibrations, which showed much faster IVR behavior than that of the NH₂ stretches. The fast relaxation is described by the interference effect, which is caused by the coherent excitation of the quasistationary states.

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I. INTRODUCTION

The intramolecular vibrational energy redistribution (IVR) has been thought to be one of the most important dynamics of the vibrationally excited polyatomic molecules, because in most cases IVR is the first dynamical step prior to chemical reactions.^{1–3} Among many vibrations, IVR of the CH and the OH stretching vibrations has been extensively studied for many molecules, such as water,^{4–7} alcohol,^{8–12} acetylene derivatives,^{13–17} halogenated methane,^{18–23} aromatic molecules^{24–31} in the condensed phase as well as in the gas phase. Another important molecular vibration is the NH stretching vibration, which is one of the key vibrations to analyze the secondary structure of the biomolecules, such as polypeptide.³² Thus, it is important to study the vibrational dynamics of the NH stretch in connection with the structure. Up to now, however, there have been very few studies on the vibrational relaxation of the NH stretching vibration.^{33–37}

In this paper, we report a study on the IVR dynamics of the NH₂ stretching vibration of aniline in a supersonic beam by using a picosecond IR-UV pump-probe spectroscopy. Aniline is one of the most fundamental aromatic molecules having the NH₂ group, and its electronic and vibrational structures have been extensively studied by many

groups.^{38–52} Nakanaga and co-workers performed the detailed studies on the NH₂ stretching vibration of aniline and its hydrogen-bonded clusters in supersonic jets.^{53–57} Aniline is nonplanar in ground electronic state, in which the dihedral angle between the NH₂ amino group and aromatic ring is reported to be 37.5° by Lister *et al.*⁴⁹ and Sinclair and Pratt⁵⁰ or 42° by Quack and Stockburgen,⁴⁰ while in the first excited state, a near-planar structure is reported,^{40,51,52} so the S₁ ↔ S₀ electronic transition exhibits rich vibronic structures.^{38,43,47} Aniline has two NH₂ stretching modes: symmetric stretching vibration (ν_s) with the frequency of 3423 cm⁻¹ and asymmetric stretch (ν_a) with 3509 cm⁻¹,⁴⁵ and we are interested in the issue whether the NH₂ stretch vibrations show any mode dependence in their IVR rate constants.

The IVR of the NH₂ stretching vibrations in aniline can be compared with that of the OH stretch of phenol in order to obtain a general view of the IVR process of the XH stretch in aromatic molecules. Recently, we reported the real-time observation of IVR of the OH(OD) stretching vibration of isolated phenol and its isotopomers in supersonic jets.^{58,59} In those works, we investigated the pathway of the vibrational energy flow and found the following three results: Firstly, IVR of the OH stretch is described by two-step tier model,^{15–17,20} as shown in Fig. 1. Here the initially excited vibrational energy first flows into the doorway states,^{60,61} and the energy is further redistributed to dense base states. Sec-

^{a)}Electronic mail: tebata@hiroshima-u.ac.jp

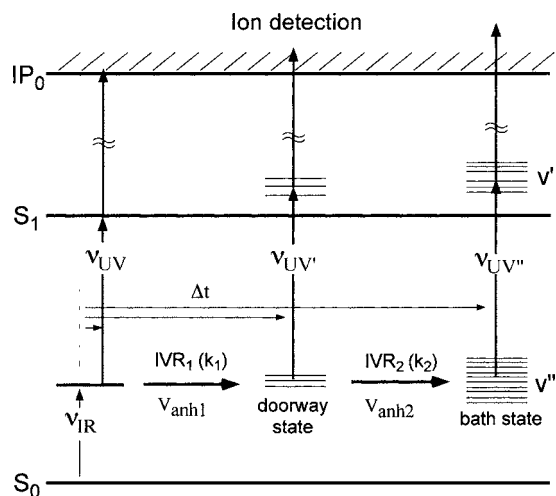


FIG. 1. Two-step tier model of IVR and the scheme of picosecond time-resolved IR-UV pump-probe spectroscopy. V_{anh1} and V_{anh2} indicate the anharmonic coupling matrix elements in each step and k_1 and k_2 are the rate constants.

only, the rate constant of the second step IVR (k_2) is much faster than the first step (k_1), so that the first IVR process is the rate-determining step. Finally, it is thought that the doorway states consist of the CH stretch modes because the deuterium substitution of the CH group significantly reduces the IVR rate constant of the first step. In this work, we examine whether the similar situation is held in the IVR of the NH_2 stretch vibrations of aniline. If it is the case, we can compare the rate constants of each step of IVR between the OH stretch of phenol and NH_2 stretches of aniline and find a similarity or a difference between them.

In addition, we also investigate IVR of the aromatic CH stretching vibration of aniline. The aliphatic CH stretch of alcohol in the condensed phase is known to exhibit very rapid T_1 relaxation decay, and such a rapid process is explained by the strong interaction with the overtone of the CH bending modes.^{10–12} We will examine whether such a strong coupling also exists in aniline and will discuss the general mechanism of the CH vibrational relaxation by comparing with the similar experiments of phenol reported in the previous paper.

II. EXPERIMENT

A detailed description of the experimental setup of picosecond IR-UV pump-probe spectroscopy was given in our previous papers.^{58,62} Briefly, a fundamental output (1.064 μm) of a mode-locked picosecond Nd^{3+} : yttrium aluminum garnet (YAG) laser (Ekspra PL2143B) was split into two parts. The major part was frequency tripled and was introduced into an optical parametric generator/optical parametric amplifier (OPG/OPA) system (Ekspra PG401SH) to obtain a tunable UV light pulse. Typical bandwidth and output power of the UV light were 7 cm^{-1} and 50–100 μJ , respectively. The minor part of the 1.064 μm output was introduced into a pair of $LiNbO_3$ crystals to generate a tunable IR light pulse. The two crystals were separated by 1 m and were placed on rotational stages. They were synchronously rotated to generate a narrow-band IR pulse, and its

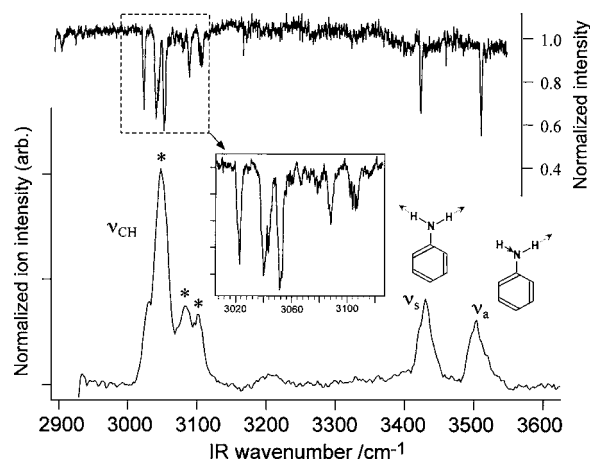


FIG. 2. IR spectra of aniline in a supersonic beam. The upper trace was obtained by IR-UV double-resonance spectroscopy with the use of the nano-second laser system. The inset shows the expanded spectrum in the CH stretch region. The lower trace is the ionization gain IR spectrum obtained with the picosecond laser system. The UV pulse was introduced at the delay time of 1.7 ns and its frequency was fixed at 33 370 cm^{-1} , corresponding to the transition from the redistributed levels. The asterisks indicate the positions tuned by the picosecond IR laser pulse.

bandwidth was achieved to 15 cm^{-1} with a typical output power of 50–100 μJ . CaF_2 , $ZnSe$, and Ge plates were used so that only the signal light at $\sim 3 \mu\text{m}$ was introduced into a vacuum chamber as the IR pulse. The temporal shapes of the UV laser pulse were determined by fitting the time profile of the cross correlation of the ammonia ionization in the molecular beam, which was well fitted by assuming a Gaussian shape for the pulses having 12 ps pulse width.⁶³ We assumed the same time profile for the IR pulse.

Jet-cooled aniline was generated by a supersonic expansion of aniline vapor seeded in He carrier gas (typically 3 atm) into vacuum through a pulsed nozzle (General valve) having a 0.8 mm aperture. The free jet was skimmed by a skimmer having a 0.8 mm diameter (Beam dynamics) located at 30 mm downstream of the nozzle. Aniline (99.0%) was purchased from Wako Chemicals Industry Ltd. and was purified by vacuum distillation before use.

The IR and UV lasers were introduced into a vacuum chamber in a counterpropagated manner and crossed the supersonic beam at 50 mm downstream of the skimmer. The vibrationally excited molecules in the supersonic beam were ionized by 1+1 resonance enhanced multiphoton ionization (REMPI) via S_1 , and the ions were repelled to the direction perpendicular to the plane of the molecular beam and the laser beams. The ions were then mass analyzed by a 50 cm time-of-flight tube and were detected by an electron multiplier (Murata Ceratron). The transient profiles of the pump-probe ion signals were observed by changing a delay time between UV and IR pulses by a computer-controlled optical delay line. The ion signals were integrated by a boxcar integrator (Par model 4400) connected with a microcomputer.

III. RESULTS

A. IR spectra of aniline

Figure 2 shows the IR spectra of aniline in the 2900–3700- cm^{-1} region. Two types of spectra, which are

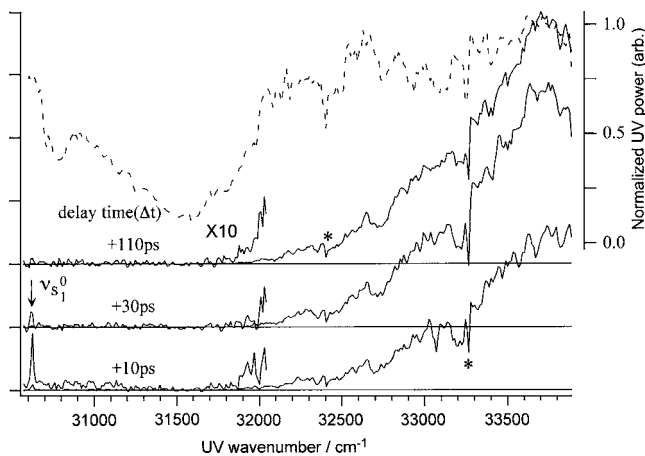


FIG. 3. Transient (1+1) REMPI spectra of aniline obtained at several delay times after pumping the NH_2 symmetric stretch (ν_s) vibration. The broken curve indicates the UV output power. The asterisks mean the position with very weak UV power output.

obtained by different methods, are shown. The upper trace shows the ionization-detected IR (IDIR) spectrum^{64–66} observed by the nanosecond laser system with a spectral resolution of 0.1 cm^{-1} . The lower trace is the ion-gain IR spectrum observed with the picosecond laser system. The UV laser pulse was introduced at the delay time of 1.7 ns after the IR pulse excitation, and the frequency (ν_{UV}) was fixed at $33\,370 \text{ cm}^{-1}$, which refers to the hot band ($\nu' - \nu''$) transitions from the levels (ν'') generated by the IVR of the IR-pumped vibrational level.

The spectral feature of the picosecond ion-gain IR spectra corresponds very well with the IDIR spectrum (upper) except for the low spectral resolution. In both spectra, many bands associated with the aromatic CH stretching vibrations appear in the $3000\text{--}3120 \text{ cm}^{-1}$ region, and the two bands at 3423 and 3509 cm^{-1} are assigned to be the NH_2 symmetric (ν_s) and asymmetric (ν_a) stretching vibrations, respectively. The inset of Fig. 2 shows an enlarged portion of the CH stretching region. Though five bands are mainly observed in this region, some of them are split and much weaker bands are also seen. The band split and the appearance of weak bands are attributed to the anharmonic interaction with overtone or combination bands, as Page *et al.* stated in the analysis of the complicated spectrum in the CH region of benzene.⁶⁷ On the other hand, only three peaks at 3047 , 3087 , and 3105 cm^{-1} are identified in the picosecond ion-gain IR spectrum, which is due to broad bandwidth of the IR laser. Thus, it is quite possible that several bands are simultaneously excited when the IR pump pulse is tuned to one of these main peaks. On the other hand, two NH_2 stretch bands are clearly separated in the lower spectrum, so that we can measure the intrinsic IVR process by pumping ν_s or ν_a , individually. In the following, we examine IVR for these vibrational modes by time-resolved spectroscopy.

B. IVR of the NH_2 symmetric stretching vibration

Figure 3 shows the transient (1+1) REMPI spectra of aniline observed at several delay times after exciting ν_s at 3423 cm^{-1} . All of the REMPI spectra are shown in the man-

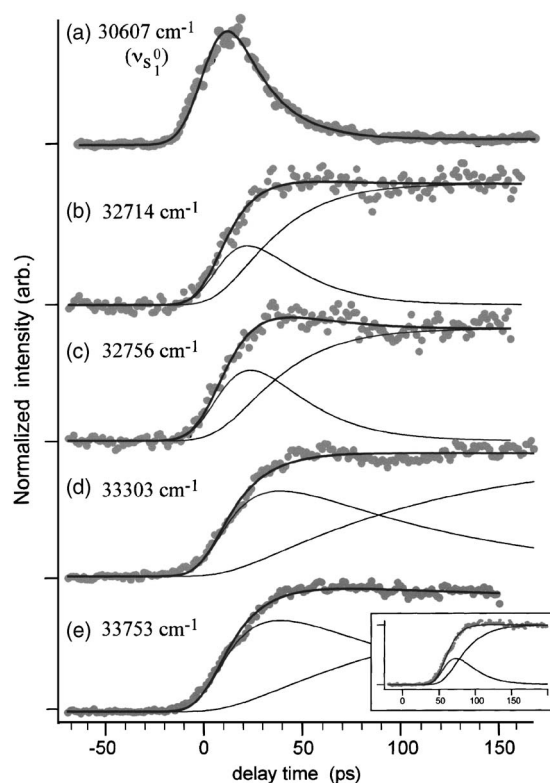


FIG. 4. Time profiles after pumping the NH_2 symmetric stretch (ν_s) vibration of aniline: (a) ν_{s1}^0 band ($30\,607 \text{ cm}^{-1}$), and redistributed levels with the probe frequencies of (b) $32\,714 \text{ cm}^{-1}$, (c) $32\,756 \text{ cm}^{-1}$, (d) $33\,303 \text{ cm}^{-1}$, and (e) $33\,753 \text{ cm}^{-1}$. The solid curves are convoluted ones with the best-fitted values in Table I, by using the two-step relaxation model. (e) The inset also shows the other convoluted curve with a set of parameters of $k_1=5.6 \times 10^{10} \text{ s}^{-1}$, $k_2=5.0 \times 10^{10} \text{ s}^{-1}$, and $A_0/B_0=1.31$ (see text).

ner that the REMPI spectrum measured without introducing the IR laser pulse is subtracted from the original spectra, representing that we can evaluate the amount of ion intensity enhanced by the IR pulse excitation. The intensities of the REMPI spectra below $32\,000 \text{ cm}^{-1}$ are multiplied by a factor of 10. The broken curve shown in the figure is the probe UV laser power as a function of UV frequency. Then, we see that the negative-going spikes marked with asterisks in the spectra are due to weak power output at particular UV frequencies in our laser system.

A sharp band shown at $30\,607 \text{ cm}^{-1}$ is assigned to ν_{s1}^0 band, that is, the transition from the NH_2 symmetric stretch level in S_0 to the zero-point level in S_1 . It rapidly decays with delay time due to IVR. No other vibronic transition from the $v=1$ of ν_s , such as, $\nu_{s1}^0 6_0^1$ and $\nu_{s1}^0 12_0^1$, was observed, which may be due to the weak intensity of the UV output in this region. In contrast to the decay of the ν_{s1}^0 band, a broad continuum starting from $32\,000 \text{ cm}^{-1}$ to higher-frequency region monotonically increases with the delay time. This continuum is assigned to the overlapped transitions from the redistributed levels generated by IVR of ν_s .³⁷ No sharp peak due to the transition from the particular vibrational level is identified in the broad continuum.⁵⁹

We then measured the time profiles of the ν_{s1}^0 band and the broad continuum at several UV frequencies, which are shown in Fig. 4. We first fitted the time profiles of the ν_{s1}^0

TABLE I. Obtained IVR rate constants ($\times 10^{10} \text{ s}^{-1}$) for the NH_2 symmetric (ν_s) and asymmetric (ν_a) stretching vibrations of aniline by the least-square fitting of the time profiles at the different monitoring UV frequencies.

Frequency (cm^{-1})	ν_s			ν_a		
	k_1	k_2^a	A_0/B_0	k_1	k_2^a	A_0/B_0
30 607	5.6 ^b
32 437	2.8	2.6	2.04
32 714	5.9	5.2	1.40	3.2	2.9	1.29
32 756	5.0	4.5	1.82
33 303	6.3	0.1	1.03	3.6	2.8	0.96
33 753	5.6	0.1	1.24	2.8	0.1	1.18

^aThere is a large uncertainty in the k_2 value. See text.^bThis value was obtained by the fitting of decay time profile of the ν_{s1}^0 band.

band and the broad continuum by using single exponential decay and rise functions with a time constant of τ_{IVR} , respectively,

$$I_{\text{NH}_2}(t) = I_0 \exp(-t/\tau_{\text{IVR}}) \quad (1a)$$

and

$$I_{\text{bath}}(t) = I_0 \{1 - \exp(-t/\tau_{\text{IVR}})\}, \quad (1b)$$

where I_0 means the initial population. These expressions mean that we assumed one-bath mode model for the IVR of the NH_2 stretch vibrations, and if this model is correct we will obtain the same lifetime τ_{IVR} for rise and decay curves. The IVR lifetime obtained by using a least-squares fitting and convolution with laser pulse width of 12 ps was $\tau_{\text{IVR}} = 18$ ps for the ν_{s1}^0 band, corresponding to the rate constant $k_{\text{IVR}} = 5.6 \times 10^{10} \text{ s}^{-1}$. On the other hand, those obtained from rise curves of the broad continuum gave different values at various UV frequencies (ν_{UV}); $\tau_{\text{IVR}} = 8$ ps at $\nu_{\text{UV}} = 32\,714 \text{ cm}^{-1}$, ≤ 5 ps at $\nu_{\text{UV}} = 32\,756 \text{ cm}^{-1}$, and 13 ps at $\nu_{\text{UV}} = 33\,303 \text{ cm}^{-1}$ and $\nu_{\text{UV}} = 33\,753 \text{ cm}^{-1}$. Thus, the lifetimes obtained from rise profiles are shorter than that from the decay of the ν_{s1}^0 band, and they depend on the monitoring UV frequencies. It should also be noted that the time profile monitored at $32\,756 \text{ cm}^{-1}$ reaches to maximum at the delay time of 50 ps and slightly decays to a constant value. All these results indicate that one-bath mode model cannot be used to the present system.

Thus, we use two-step tier model shown in Fig. 1 for the fitting of the observed time profiles. The time evolution of the populations on the $\nu_s[I_{\text{NH}_2}(t)]$ level, the doorway state [$I_{\text{doorway}}(t)$], and the bath states [$I_{\text{bath}}(t)$] are expressed as follows:

$$I_{\text{NH}_2}(t) = I_0 \exp(-k_1 t), \quad (2a)$$

$$I_{\text{doorway}}(t) = I_0 \frac{k_1}{k_1 - k_2} \{ \exp(-k_2 t) - \exp(-k_1 t) \}, \quad (2b)$$

and

$$I_{\text{bath}}(t) = I_0 \left[1 + \frac{k_2}{k_1 - k_2} \exp(-k_1 t) - \frac{k_1}{k_1 - k_2} \exp(-k_2 t) \right]. \quad (2c)$$

Even in this model, $I_{\text{NH}_2}(t)$ decays exponentially and k_1 has already been obtained to be $5.6 \times 10^{10} \text{ s}^{-1}$. The observation of the decay of the NH_2 stretch level plays an important part in this analysis, since it directly gives the k_1 value. For k_2 , we can obtain its value if we can distinguish the transitions of the doorway state from that of the dense bath states by fitting the time profiles with Eqs. (2b) and (2c). As mentioned above, however, we could not observe any sharp bands assignable to the transitions from the doorway state and the rise profiles of the broad continuum depend on different UV frequencies. This UV frequency dependence of the time profile strongly indicates that the broad continuum consists of both components of $I_{\text{doorway}}(t)$ and $I_{\text{bath}}(t)$, whose ratio is different at various transition frequencies. Then, its time profile can be fitted by the following equation:

$$\begin{aligned} I_{\text{continuum}}(t) &= A_0 I_{\text{doorway}}(t) + B_0 I_{\text{bath}}(t) \\ &= A_0 I_0 \frac{k_1}{k_1 - k_2} \{ \exp(-k_2 t) - \exp(-k_1 t) \} \\ &\quad + B_0 I_0 \left[1 + \frac{k_2}{k_1 - k_2} \exp(-k_1 t) \right. \\ &\quad \left. - \frac{k_1}{k_1 - k_2} \exp(-k_2 t) \right], \quad (3) \end{aligned}$$

where A_0 and B_0 are the coefficient of each component. We simulated the rise-time profiles to reproduce the observed ones by least-square fitting by changing three parameters of k_1 , k_2 and, A_0/B_0 ratio in Eq. (3).

In Fig. 4, the time profiles of the doorway state and bath state components convoluted by the two-step tier model are shown by the thin solid curves and total time profiles are shown as thick solid curves. The k_1 , k_2 , and A_0/B_0 ratio values obtained by least-square fitting for each curves different from this procedure for several monitoring UV frequencies are listed in Table I. The rate constants of the first step obtained from the rise-time profiles of broad continuum are $k_1 = 5.6(\pm 0.6) \times 10^{10} \text{ s}^{-1}$, which is in good agreement with that obtained from the decay curve of the ν_{s1}^0 band. For k_2 , on

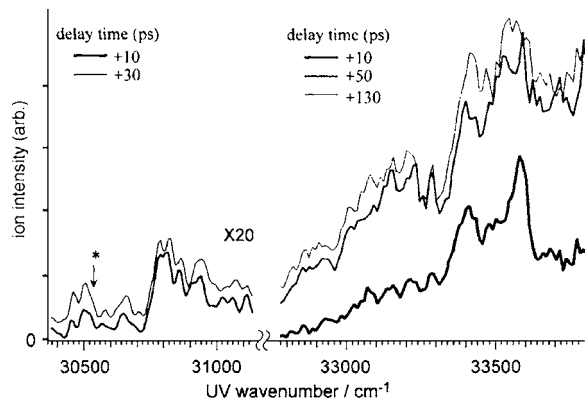


FIG. 5. Transient 1+1 REMPI spectra of aniline obtained at several delay times after pumping the NH_2 asymmetric stretch (ν_a) vibration. The asterisk indicates the expected position of the ν_{a1}^0 band.

the other hand, its value is scattered in a wide range, as seen in Table I. For example, the k_2 values obtained at the monitoring frequencies of 32 714 and 32 756 cm^{-1} are 5.2 and $4.5 \times 10^{10} \text{ s}^{-1}$, while those at 33 303 and 33 753 cm^{-1} are $0.1 \times 10^{10} \text{ s}^{-1}$, giving a difference by a factor of 50. This large difference is not a meaningful one but is attributed to the uncertainty to determine k_2 by this fitting procedure. This is explained as follows: k_1 is accurately determined from the rise curve at the delay time shorter than 40 ps, where the component of $I_{\text{doorway}}(t)$ mainly composes its profile. On the other hand, k_2 is determined by curve fitting at a longer delay time, where the ion intensity approaches to a constant value, and the superposition of the decay profile of $I_{\text{doorway}}(t)$ and the rise profile of $I_{\text{bath}}(t)$ can easily reproduce the longer delay time profile by various combinations of A_0/B_0 and k_2 . A typical example is seen in Fig. 4(e). The solid curve in Fig. 4(e) was simulated by using $k_1 = 5.6 \times 10^{10} \text{ s}^{-1}$, $k_2 = 0.1 \times 10^{10} \text{ s}^{-1}$, and $A_0/B_0 = 1.24$, while the curve in the inset was obtained with $k_1 = 5.6 \times 10^{10} \text{ s}^{-1}$, $k_2 = 5.0 \times 10^{10} \text{ s}^{-1}$, and $A_0/B_0 = 1.31$. As seen in the figures, both the calculated curves reproduce well the observed time profile, leading to an uncertainty for k_2 value. Though we could not give an accurate k_2 , we estimated $k_2 = (0.1-5) \times 10^{10} \text{ s}^{-1}$, that is, k_2 is comparable to or smaller than k_1 . This situation largely differs from the IVR rate constants of the OH stretching vibration of phenol, which will be discussed later.

C. IVR of the NH_2 asymmetric stretching vibration

Similar experiment was performed for the NH_2 asymmetric stretching vibration (ν_a) at 3509 cm^{-1} . Figure 5 shows the transient (1+1) REMPI spectra measured at several delay times after the excitation of ν_a , where the intensities below 31 100 cm^{-1} are multiplied by a factor of 20. The spectral feature is similar to that of the ν_s excitation, except for no appearance of the ν_{a1}^0 band, whose expected position (30 521 cm^{-1}) is indicated with an asterisk. The missing ν_{a1}^0 band due to this transition is symmetry forbidden.

The time profiles of the ion intensities at different UV frequencies are shown in Fig. 6. Similar to the case of ν_s , the rise profiles of the broad continuum are different at the different UV frequencies. Thus, the curve-fitting analysis was carried out by the similar method described in ν_s . The k_1

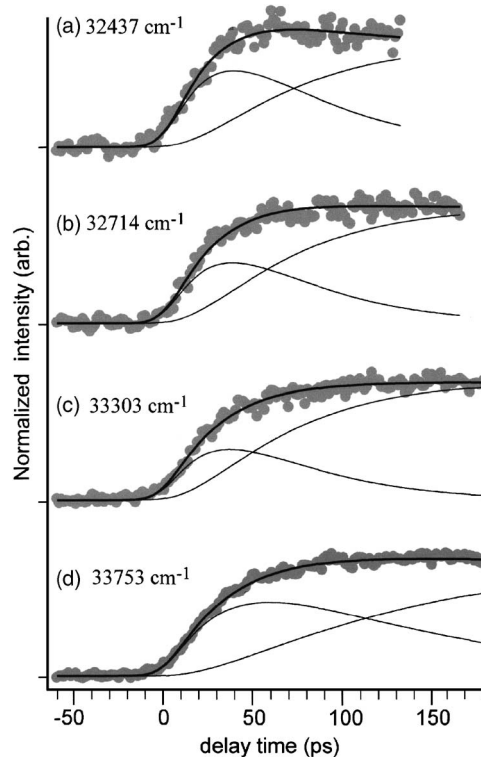


FIG. 6. Time profiles of the IVR redistributed levels after exciting the NH_2 asymmetric stretching vibration (ν_a) of aniline with the probe frequencies of (a) 32 437, (b) 32 714, (c) 33 303, and (d) 33 753 cm^{-1} . The solid curves are the convoluted ones by using the set of values in Table I.

value was unambiguously determined to be $2.9 (\pm 0.6) \times 10^{10} \text{ s}^{-1}$, corresponding to the lifetime of about 34 ps, while k_2 was estimated to be $(0.1-2) \times 10^{10} \text{ s}^{-1}$. The solid curves in Fig. 6 are obtained by the convolution with rate constants and A_0/B_0 ratio listed in Table I.

D. IVR of the CH stretching vibrations

As shown in Fig. 2, five intense peaks are identified in the IDIR spectrum (upper portion), which may have the main character of the CH stretching vibrations. However, some of them are split or their width are broader compared to other bands. This clearly indicates that the CH stretch levels are coupled with overtones or combination bands by anharmonic resonance. Furthermore, the corresponding IR spectrum in the picosecond ion-gain spectrum (lower of Fig. 2) exhibits broader feature. Thus, several bands will be coherently excited when the picosecond IR pulse is tuned to each peak.

Figure 7 shows the time profiles of the pump-probe ion intensities versus delay time after the IR excitation of the CH band at 3047, 3087, and 3105 cm^{-1} , respectively, which are marked with asterisks in Fig. 2. In these measurements, the probe frequencies were fixed to 33 754 cm^{-1} , which refers to the broad continuum due to the transitions from dense bath states ($\nu' - \nu''$ transitions). It should be noted that time profiles were independent of the monitoring UV frequencies, so that we used Eq. (1b) to obtain the IVR lifetimes. The obtained lifetimes were equal to or shorter than 5 ps for the bands at 3047 and 3087 cm^{-1} and 10 ps for the band at 3105 cm^{-1} . Thus, all the IVR lifetimes for the CH stretch

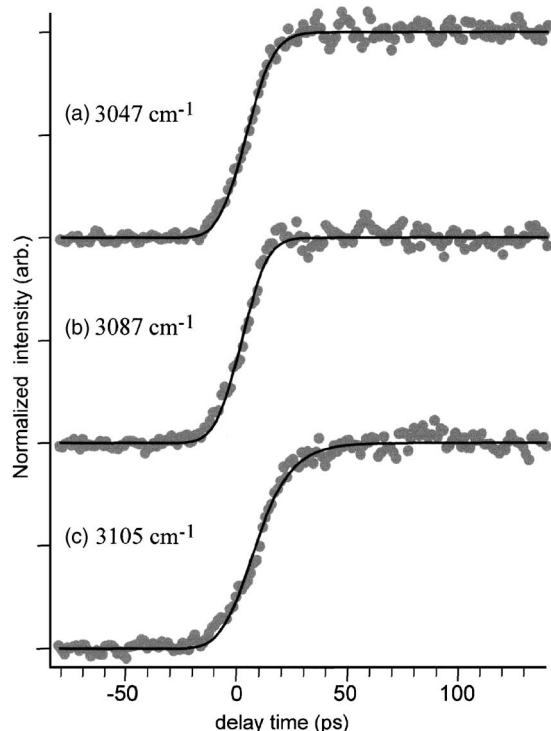


FIG. 7. Time profiles of broad continuum appeared after the IR excitation of the CH stretching vibration at (a) 3047, (b) 3087, and (c) 3105 cm^{-1} , respectively. In all measurements, the UV probe frequency was fixed to 33 754 cm^{-1} . The solid curves are the convoluted ones by using a single exponential rise function with the time constants of (a) 5, (b) 5, and (c) 10 ps, respectively. See text.

vibrations are much shorter than those of the NH_2 stretching vibrations. We tried to measure the CH stretch levels by observing the CH_1^0 band. However, we could not observe the CH_1^0 band in transient UV spectra, which may be due to the small Franck-Condon factor.

IV. DISCUSSION

From the obtained results, it is concluded that IVR of the NH_2 stretch vibrations proceeds via two types of states, doorway and dense bath states, and the rate constants in each step are summarized as follows:

- (1) $\nu_s(3423 \text{ cm}^{-1})$: $k_1 = 5.6 \times 10^{10} \text{ s}^{-1}$, and $k_2 = (0.1-5) \times 10^{10} \text{ s}^{-1}$, and
- (2) $\nu_a(3509 \text{ cm}^{-1})$: $k_1 = 2.9 \times 10^{10} \text{ s}^{-1}$, and $k_2 = (0.1-2) \times 10^{10} \text{ s}^{-1}$.

Two important issues are raised from the obtained results. First is that the IVR rate constant of the first step of ν_s is about two times larger than that of ν_a in spite of that the former vibrational energy is 86 cm^{-1} lower than the latter. Second is that the first IVR step, “ NH_2 stretch \rightarrow doorway state,” is comparable to or faster than the second one of “doorway state \rightarrow bath state” in both vibrations. Hereafter, we will discuss the IVR mechanism based on the two findings.

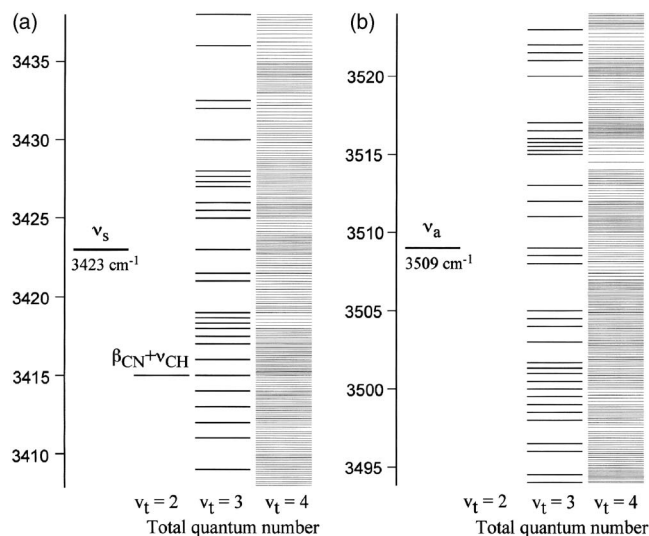


FIG. 8. (a) and (b) Calculated vibrational levels within 30 cm^{-1} of the NH_2 symmetric and asymmetric stretch levels, respectively, as a function of total quantum number (v_t) up to $v_t=4$. $\beta_{\text{CN}} + \nu_{\text{CH}}$ means the combination band of the CN bending and the CH stretching mode.

A. Mode dependence of IVR of the NH_2 vibration

To describe that k_1 of ν_s is larger than that of ν_a , we examined possible candidates of the doorway state(s). The vibrational frequencies of aniline have been reported by several groups.³⁹⁻⁴⁵ By using those data, we listed vibrational levels lying close to the NH_2 stretching vibrations by direct counting method under the symmetry restriction in which only the levels belonging to the same symmetric species can be coupled to each mode. In aniline, ν_s and ν_a belong to a' and a'' species, respectively, and the calculated density of states are 185 and 257 states/ cm^{-1} , respectively. Thus, the higher density of states at ν_a than that at ν_s is opposite to the difference of the observed k_1 values.

Figure 8 shows the calculated vibrational levels as a function of total quantum number (v_t) of vibrational combination levels. In the figure, the vibrational levels up to the total quantum number of four are shown within the frequency range of $\pm 15 \text{ cm}^{-1}$ for each vibration. These levels could be the possible doorway states, because the anharmonic coupling matrix element decreases remarkably with the coupling order, so that the levels consisting of the small total quantum number can be coupled strongly.^{18,68} When the total quantum number exceeds four, the density of states becomes very large, suggesting that they would be the dense bath states. In Fig. 8, we see that the ($\beta_{\text{CN}} + \nu_{\text{CH}}$) combination level lies close to ν_s , where β_{CN} and ν_{CH} are the CN bending and the CH stretch modes, respectively. On the other hand, such a level which can be coupled with the lowest order is not seen for ν_a in the examined energy region. Though it is not clear how accurate the reported frequencies of these vibrations as well as the combination anharmonicity, this combination mode may couple strongly to the NH_2 stretch mode, since the CN bend is spatially close to the NH_2 group. In addition, the possibility that the doorway state involves the CH stretch mode is supported by our previous work on phenol, where we found a drastic decrease of the

IVR rate constant of the OH stretch vibration upon the D atom substitution of the CH group. In Sec. IV B, we will investigate the doorway state in more detail.

B. Comparison of the IVR of the NH₂ stretch with other system and characterization of doorway state

Another interesting issue is the comparison of the IVR feature of the NH₂ stretching vibration with that of other X–H stretching vibration of aromatic molecules. Up to now, there is very small number of experiments for IVR of the X–H stretching vibration under the isolated condition.^{8,24,25} To the best of our knowledge, only the available one may be the IVR of OH stretching vibration of phenol.⁵⁸ In phenol, the IVR rate constant for the first step was $k_1 = 7.1 \times 10^{10} \text{ s}^{-1}$ and it was concluded that k_2 is much larger than k_1 . By the comparison of the present results with those of phenol, we first see that k_1 of the OH stretch of phenol is slightly larger than that of NH₂ stretch of aniline. This suggests that the anharmonic coupling strength between the initial state and doorway state is not so different between the two systems. Second, a large difference is seen in the rate constants of the second step of IVR, that is, k_2 . In phenol, we reported that the second IVR step is much faster than the first IVR step, that is, $k_2 \gg k_1$, while in aniline, k_2 is estimated to be comparable to or smaller than k_1 . This is a very surprising result since k_1 is not so different between aniline and phenol. The calculated total density of states at the OH stretch vibration (with the *a'* symmetry) is 133 cm^{-1} in phenol. Since this value is not so different from those of NH₂ stretch vibrations as described above, we consider that this difference is attributed to much larger “the doorway state ↔ dense bath state” anharmonic coupling matrix element in phenol.

At this moment, we again argue the character of the doorway state. We proposed that the doorway state involves the CH stretching mode in both systems. If it is the case, the difference of k_2 can be attributed to the difference of the “CH stretch ↔ bath state” coupling matrix element since the total density of states is not so different between them. This difference can be seen in the IR spectra in the CH stretching region.^{29,67} If the CH vibration is not coupled with the bath states, only five bands, corresponding to the number of the CH oscillators, will appear in this region for both molecules. However, in phenol, more than 20 bands appeared in this region,⁵⁸ which is much larger than that of aniline, indicating a stronger “CH stretch ↔ dense bath state” coupling of phenol than aniline. Thus, the smaller k_2 of aniline can be described by the weaker CH stretch ↔ dense bath state coupling strength. It is very interesting to note such a large difference of the CH stretch ↔ bath state coupling strength between phenol and aniline in spite of the fact that the phenyl ring structure is common in both molecules. For the further investigation on the role of the CH stretch vibration as the doorway state of the IVR of the NH₂ stretch of aniline, a deuterium isotope substitution of the phenyl CH group will be essential, which will be the future work.

C. IVR mechanism of the CH stretching vibrations and the effect of anharmonic resonance

As shown above, the CH stretching vibrations exhibit much faster IVR than the NH₂ stretching vibrations though the CH stretching frequencies are lower by 300 cm^{-1} than those of NH₂. This behavior is very similar to that observed in phenol and the detailed discussion is given in the previous paper.⁵⁸ Here, we briefly describe the mechanism by using the same argument with that of phenol.

As we discussed in the IR spectrum of the CH stretch bands in Fig. 2, it is strongly suggested that several bands are overlapped in each peaks, because most of them are split or show broad features. The picosecond IR pulse will coherently excite them and the time evolution of such the coherently excited quasistationary states exhibits an interference. The multiplication of this interference and the intrinsic decay of each level due to IVR, i.e., the population decays of the individual CH stretch levels into the bath states, results in the apparent fast IVR time profile. Many studies on the time evolutions of quasistationary states^{69–71} suggest that the number of bands, their intensities, and the energy interval between individual peaks are the important factors for the time evolution. For example, a large number of quasistationary states provides a fast decay lifetime, as explained by the different relaxation case between statistical limit and intermediate case.⁷² On the other hand, as the modulation frequency, which is proportional to the energy interval, becomes higher the rise of modulation component becomes steeper, resulting in the fast rise of the observed time profile. In our previous work, we successfully reproduced the very fast decay time profile of CH₁⁰ band as well as the rise profile of broad continuum, whose apparent lifetimes were as short as 5 ps.⁵⁸ A similar analysis can be applied to the present case, though it is not clear how many levels are coherently excited and how large are their energy intervals.

The description is supported by the different IVR lifetimes at different excitation frequencies. The time constant of the rise curves is less than 5 ps for the IR excitation frequencies at 3047 and 3087 cm^{-1} , while 10 ps at 3105 cm^{-1} . The difference can be explained by the difference of the number of the coherently excited bands within the IR bandwidth or the small energy intervals between them. As seen in the IR spectrum (upper of Fig. 2), the band at 3105 cm^{-1} is relatively isolated compared to other bands and consists of several bands with very small interval. Thus, the lifetime shortening due to the interference effect is small in this band.

V. CONCLUSIONS

In this article, picosecond time-resolved IR-UV pump-probe spectroscopy has revealed the IVR mechanism of the NH₂ and CH stretching vibrations of jet-cooled aniline in *S*₀. It was found that the IVR of the NH₂ stretch vibrations proceeds through the two types of bath states, doorway and dense bath states. The rate constant for the first step was determined to be 5.6×10^{10} and $2.9 \times 10^{10} \text{ s}^{-1}$ for the symmetric and the asymmetric NH₂ vibrations, respectively. The rate constants of the second step were estimated to be comparable to or smaller than the first step.

The faster IVR of the symmetric NH₂ than that of asymmetric was described by the existence of the doorway state which can be coupled to the symmetric NH₂ with the lowest order of perturbation. Furthermore, by the comparison of the present results with that of phenol, we found a large difference of the rate constants of the second step between them. The difference was explained by that the doorway state consists of the CH stretching vibrational mode in both cases but the coupling between the CH stretch and the bath states is quite different between them. The CH stretch vibrations exhibited shorter IVR lifetimes than those of the NH₂ stretches although their vibrational frequencies are 300 cm⁻¹ lower than those of the NH₂ stretches. The fast IVR of the CH stretches was explained by the interference effect due to the coherent excitation of several bands by a picosecond IR pulse and their intrinsic population decay due to IVR.

Finally, we compared the present results with those of phenol. We found that IVR of the X–H stretch (X=O and N) proceeds via the two types of bath modes in both molecules. The rate constant of the first step, that is, from the X–H stretch to the doorway state, is not so different between them, while there is a larger difference in the second step, that is, from the doorway state to the dense bath states. The difference of the rate constant in the second step was described by the difference of “the CH stretch ↔ bath state” coupling strength.

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