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Real-time detection of doorway states in the intramolecular vibrational energy redistribution of the OH/OD stretch vibration of phenol

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A picosecond time-resolved IR-UV pump–probe spectroscopic study was carried out for the intramolecular vibrational energy redistribution of the OH/OD stretching vibration of isolated phenol and its isotopomers in supersonic beams. The time evolution due to IVR showed a significant isotope effect; the OH stretch vibration showed a single exponential decay and its lifetime is greatly lengthened upon the deuterium substitution of the CH group. The OD stretch vibration exhibited prominent quantum beats. Especially, in phenol-d_1 (C_6H_5OD), the electronic transitions from the doorway states were clearly observed. They exhibited an out-of-phase quantum beat with respect to that of the OD stretch level and disappeared due to further IVR to the dense bath states. The transient spectra as well as the time evolution clearly evidenced the tier-model of the description of intramolecular vibrational energy redistribution. © *2004 American Institute of Physics.*

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The dynamics of the OH/OD stretching vibration has been studied for many decades in condensed phase.[1–3] The corresponding studies for isolated molecules, on the other hand, are still very few in spite of the fundamental importance. In general, the energy flow in isolated molecules, so called intramolecular vibrational energy redistribution (IVR), is described by a tier model; the energy put into the initial state flows into the sparse state(s), which is called ‘‘doorway state(s),’’ and the energy is further dissipated into the dense bath states.[4,5] A lot of efforts have been paid to evidence the doorway state and to characterize it by the use of frequency domain[5–7] or time domain spectroscopy,[8–10] and those works were successful in constructing the framework of the tier model. However, we have to say that the satisfactory characterization of the doorway state, such as the fulltime monitor of the time evolution of the population and its spectroscopic assignment, is still very few, especially for the OH stretch vibration in the electronic ground state (S_0).

In this work, we report the real-time observation of IVR of the OH/OD stretching vibration of phenol and its isotopomers in the S_0 state. Phenol is the simplest aromatic molecule having the OH group and its electronic, vibrational and the hydrogen-bonding structures have been studied by many researchers.[11–16] Very recently, we reported the first real-time measurement of the IVR of the OH stretch vibration for isolated phenol-d_0 (C_6H_5OH) and phenol-d_5 (C_6D_5OH) in supersonic beams.[17] We found a significant difference of the IVR lifetime between them. For more detailed understanding of the IVR mechanism, we extended our investigation to IVR of the OD stretch vibration of phenol-d_1 (C_6H_5OD) and phenol-d_6 (C_6D_5OD). Based on the observed results of the isotopomers, we propose the general mechanism controlling the IVR of the OH/OD stretch vibration.

We used picosecond IR-UV pump–probe spectroscopy [Fig. 1(a)];[18] an infrared (IR) picosecond pulse pumps the OH/OD stretching vibration of phenol in the supersonic beam and a ultraviolet (UV) pulse probes the population at the initial and redistributed levels by the 1+1 resonance enhanced multiphoton ionization (REMPI) via the S_1 state. The picosecond tunable UV pulse was obtained by doubling the frequency of the mode-locked Nd^{3+}:YAG laser pumped OPG/OPA output and that of IR pulse was obtained by another OPG/OPA system. The pulse width was obtained to be 12 ps. The generated ions were detected by a channeltron after passing through the time-of-flight tube.

Figure 1(b) shows the time profiles of the OH_1^0 band (upper traces) and the transition from the redistributed levels (lower traces) generated by IVR after the picosecond IR excitation of the OH stretch at 3657 cm^{-1} of phenol-d_0 (solid circles) and phenol-d_5 (open circles), where the transition of the redistributed levels appeared as the broad continuum at the lower frequency region of the (0,0) band.[17] In the figure, a good correlation is seen between the decay of the OH_1^0 band and the rise of the continuum in both molecules. The decay and the rise curves can be fitted by a single exponential parameter, and the IVR lifetimes (τ_{IVR}) are determined to be 14 ps for phenol-d_0, and 80 ps for phenol-d_5. It should be noted that in both molecules the time profiles of the broad continuum were independent of the monitoring UV wavelengths.

Two important facts were obtained in the IVR of the OH stretch of phenol-d_0 and phenol-d_5. First, they exhibit a ‘‘statistical limit’’ like behavior[19] since the time profiles can be fitted by single exponential curves. Second, the lifetime of the OH stretch of phenol-d_5 is 5.7 times longer than that of

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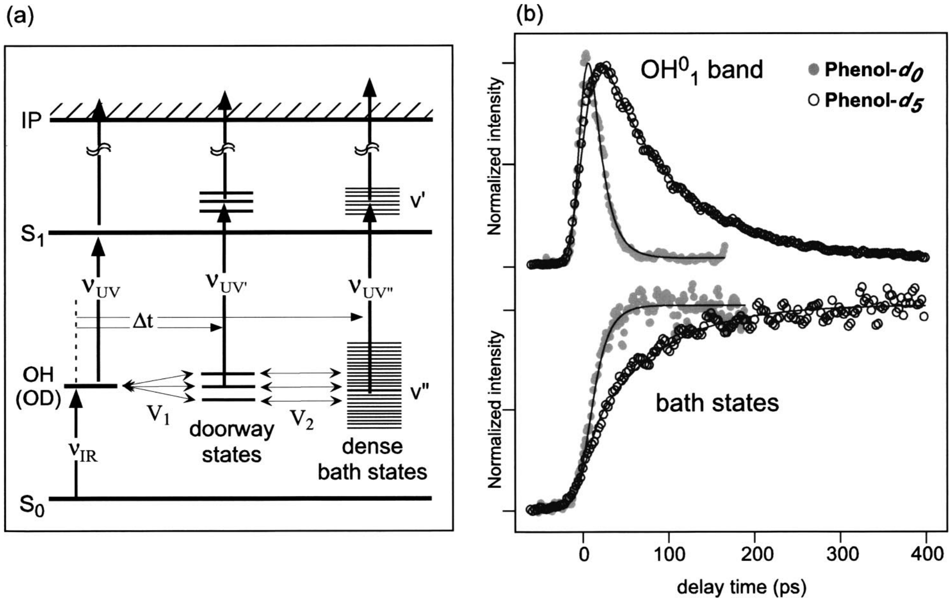

FIG. 1. (a) The tier-model diagram of IVR and the scheme of picosecond time resolved IR-UV pump–probe spectroscopy. (b) Upper traces: The time profile of the OH_1^0 band at 32 692 and 32 863 cm^{-1} for phenol-d_0 (solid circles) and phenol-d_5 (open circles), respectively. Lower traces: The time profile of the redistributed levels (bath states) monitored at 35 430 and 35 700 cm^{-1} for phenol-d_0 (solid circles) and phenol-d_5 (open circles), respectively.

phenol-d_0. A similar heavy atom effect was found in acetylenic CH stretch by Scoles and co-workers.[20] This heavy atom effect is opposite to the density of the bath states, since the calculated density of states (ρ) at the OH stretch energy for phenol-d_5 (350 states/cm^{-1}) is three times larger than that of phenol-d_0 (110 states/cm^{-1}).[21] Thus, it is concluded that the "OH stretch↔bath state" anharmonic coupling constant in phenol-d_0 is much larger than that of -d_5.

The large difference of the "OH stretch↔bath states" anharmonic coupling constant is hard to be explained by simple Fermi's Golden rule with a uniform reduction of the coupling constant in phenol-d_5 than that of phenol-d_0, because it is very unlikely that all the levels in the bath states have a uniform coupling constant. Rather, the result can be understood by that some specific levels (doorway states) in the bath states are strongly coupled to the OH stretch in phenol-d_0 and they are removed in phenol-d_5. Thus, the IVR of the OH stretch can be described by the two-step tier model as shown in Fig. 1(a). Here, the decay lifetime of the OH stretch is determined by the "OH stretch↔doorway states" coupling strength, which differs significantly between phenol-d_0 and -d_5. As to the doorway states, we could not obtain their direct evidence, since we did not identify any transitions due to them, and the time profiles of the broad continuum were the same at different wavelengths. However, we think the failure of finding the doorway states can be explained by that in these molecules the "doorway state→dense bath states" IVR rate, k_2, is much faster than that of "OH stretch→doorway states" IVR, k_1. If it is the case, the population of the doorway states becomes too small to be detected, and the decay time constant of the OH stretch and the time constant of the rise of the dense state become equal as was observed experimentally. The large reduction of $k_1(=\tau_{IVR}^{-1})$ by the deuterium substitution of the CH group suggests that the doorway states include the vibrational modes involving the CH stretch or bend.

The frequency of the OD stretching vibration is 2701 cm^{-1}, so the density of states will be considerably reduced for this vibration. Actually, the estimated density of states[21] are ρ=15 and 43 states/cm^{-1} for phenol-d_1 and -d_6, respectively. Figure 2 shows the transient UV spectra of phenol-d_1 observed after the IR pump of the OD stretch vibration. Both the sharp vibronic bands from $v''_{OD}=1$ and broad continuum at higher frequency region are seen. In addition, we find

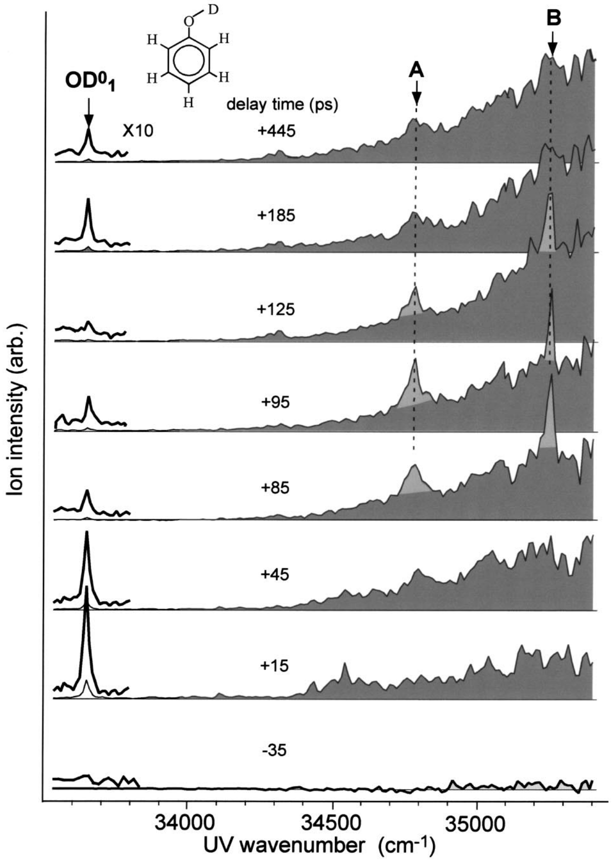

FIG. 2. The transient UV spectra observed at several delay times after exciting the OD stretching vibration of phenol-d_1.

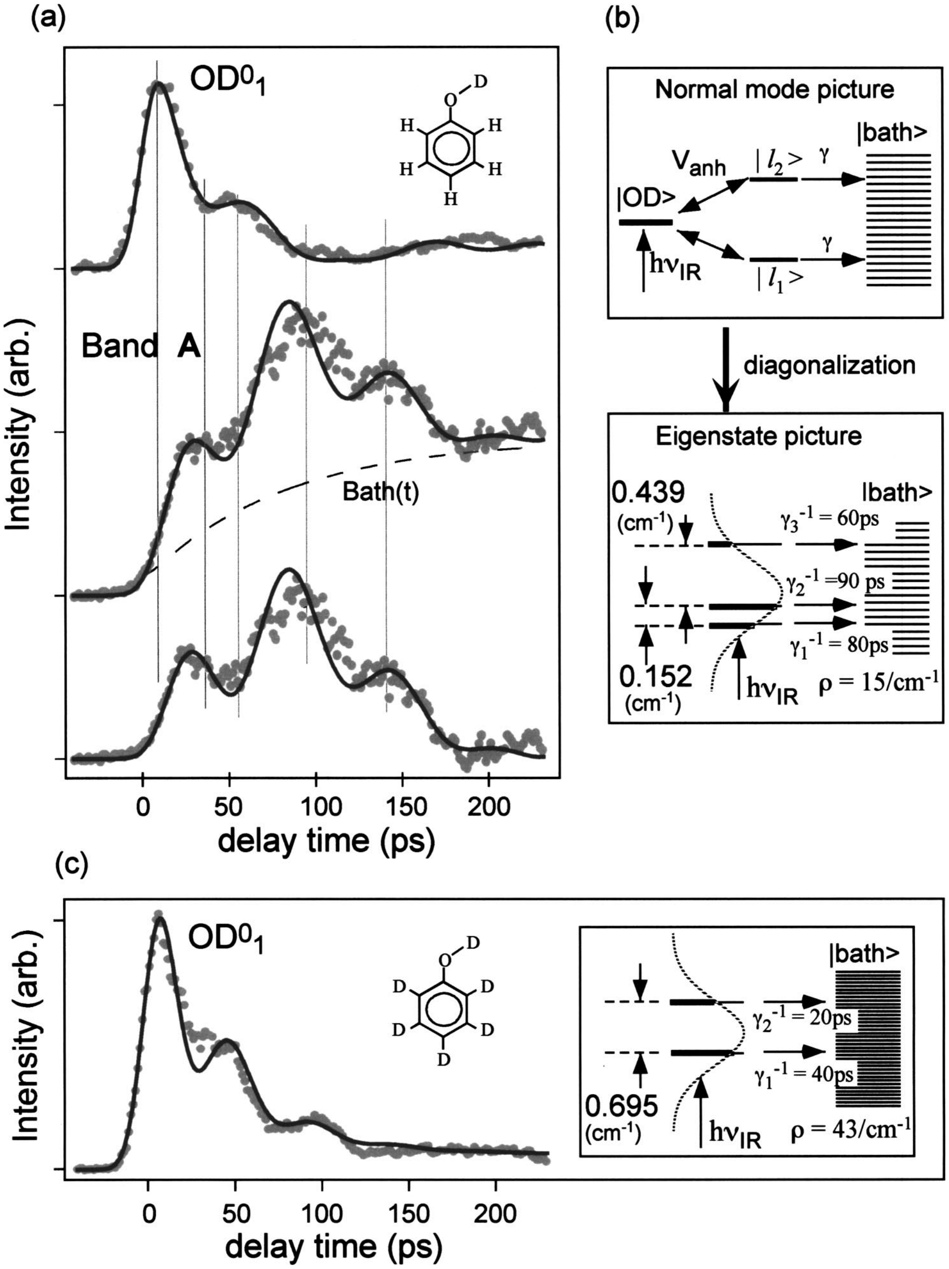

FIG. 3. (a) The time profiles of OD_1^0 and band A of phenol-d_1. Lower trace is that of band A with the subtraction of the rise function due to dense bath states. The solid curves are the calculated time evolution of the OD level and the doorway state. (b) The coupling scheme for IVR of the OD stretch of phenol-d_1. Upper trace: The $|\mathrm{OD}\rangle$ state is coupled with the doorway states, $|l_1\rangle$ and $|l_2\rangle$, via $\mathrm{V}_{\mathrm{anh}}$ and the later states are further coupled with the bath states, $|\mathrm{bath}\rangle$, in the statistical limit (decay rate γ_1). Lower trace: The diagonalized picture forming three quasistationary states. (c) The time evolution of the OD_1^0 band (33 817 cm^{-1}) of phenol-d_6. the solid curve is simulated one based on the model shown in the right (see text).

several new features. First, the OD_1^0 band does not decay monotonously. Second, two sharp vibronic bands, marked by A and B, are seen at 34 784 and 35 254 cm^{-1}, and their time evolutions are different from those of OD_1^0 and the broad continuum.

The time evolutions of OD_1^0, and band A are shown in Fig. 3(a). Both OD_1^0 and band A show prominent quantum beats. Interestingly, band A exhibits out-of-phase quantum beat with respect to OD_1^0 and reaches to a constant value at longer delay time. The time profile of band B, which is not shown here, was the same with that of band A, so we concluded that the bands A and B are the vibronic bands originating from the same level in S_0. Their assignment will be discussed later. The time evolution of bands A and B is really the behavior of the doorway state in the two-step tier model. The picosecond IR pulse coherently excites the strongly coupled states in the OD stretch region, producing the nonstationary states. The nonstationary states evolve in the oscillatory manner, and dissipate into the dense bath states. The theory of the time evolution of the coherently excited states was discussed in detail by several people,[22,23] and its schemes is shown in Fig. 3(b). In this model, the OD stretch level is coupled with the several doorway states, which are coupled further with dense bath states in "pseudo" statistical limit. We found that the quantum beat in Fig. 3(a) is composed of the oscillations with three different frequencies, which means that the OD stretch vibration is coupled with two doorway states. By using the formulation given in Ref. 22, the quasistationary states are expressed as

$$|n\rangle=\alpha_n|\mathrm{OD}\rangle+\sum_{m=1}^{2}\beta_n^{l_m}|l_m\rangle. \tag{1}$$

Here, $|\mathrm{OD}\rangle$ and $|l_m\rangle$ denote the OH stretch and the doorway states in the zeroth order, respectively, and α_n and $\beta_n^{l_m}$ are the coefficients. The time evolution of the coherently excited quasistationary states[24] is expresses as

$$|\varphi(t)\rangle=\sum_{n=1}^{3}\alpha_n|n\rangle e^{-i(\epsilon_n/\hbar)t}. \tag{2}$$

In Eq. (2), $\epsilon_n=E_n-(i/2)\gamma_n$, where E_n is the energy of the stationary state and γ_n is its width. The time profiles of OD stretch, one of the doorway states, and the dense bath states are given by

$$|\langle \mathrm{OD}|\varphi(t)\rangle|^2=\sum_{n=1}^{3}|\alpha_n|^4 e^{-(\gamma_n/\hbar)t}+2\sum_{n\neq m}|\alpha_n|^2|\alpha_m|^2 \times\cos\left(\frac{E_{nm}}{\hbar}t\right)e^{-[(\gamma_n+\gamma_m)/2\hbar]t}, \tag{3a}$$

$$|\langle l_1|\varphi(t)\rangle|^2=\sum_{n=1}^{3}|\alpha_n|^2|\beta_n^{l_1}|^2 e^{-(\gamma_n/\hbar)t} +2\sum_{n\neq m}\alpha_n\alpha_m\beta_n^{l_1}\beta_m^{l_1}\cos\left(\frac{E_{nm}}{\hbar}t\right) \times e^{-[(\gamma_n+\gamma_m)/2\hbar]t}, \tag{3b}$$

$$\mathrm{Bath}(t)=1-\sum_{n=1}^{3}|\alpha_n|^2 e^{-(\gamma_n/\hbar)t}, \tag{3c}$$

respectively, with $\gamma_n=(1-|\alpha_n|^2)\gamma$. The coefficients (α_n), energy spacing (E_{nm}), and width (γ) were determined by fitting the time profile of Eq. (3a) to the observed one of the OD_1^0 band. In the calculation, we assumed that γ are equal for the two doorway states and that of OD stretch is negligibly small. The latter assumption is reasonable because the coupling between the high frequency OD stretch and the dense bath states consisted of large quantum number of low frequency vibrations is thought to be very weak. The obtained coefficients and width are $\alpha_1=0.152$, $\alpha_2=0.663$, $\alpha_3=0.424$, and $\gamma=(50\ \mathrm{ps})^{-1}$. The energy spacing and γ_n are shown in Fig. 3(b). The coefficients $(\beta_n^{l_1})$ were obtained by fitting the time profile of Eq. 3(b) to the observed one of band A, and they were $\beta_1^{l_1}=0.784$, $\beta_2^{l_1}=-0.465$, and $\beta_3^{l_1}=-0.411$. Lower trace of Fig. 3(a) is the time profile of band A after subtracting the part of dense bath state overlapped. The good agreement between the observed and the calculated time profiles (solid curves) for the OD_1^0 and band A shows the validity of the model.

We also observed a quantum beat in the IVR of the OD stretch of phenol-d_6 [Fig. 3(c)]. In this case, the OD_1^0 band exhibits a single frequency beat, so we conclude only one state is coupled with the OD stretch. The convoluted curve is also shown in Fig. 3(c), and the energy levels are shown in the inset. The obtained values are $\alpha_1=0.806$, $\alpha_2=0.592$, and $\gamma=(15\ \mathrm{ps})^{-1}$. In the case of phenol-$d_6$, we could not observe any sharp transitions from the doorway state.

As shown above, the time evolution of the IVR process is quite different for different isotopomers. However, all the time behaviors can be described by use of the two-step tier model [Fig. 1(a)]. First, in phenol-d_0 and -d_5, the "doorway states" are thought to be extremely broadened due to the strong "doorway states↔bath states" coupling, V_2. The OH stretch level is coupled with this "broadened doorway states" via the weaker coupling V_1, resulting in a Lorentzian-like spectral shape with its width corresponding to the decay time constant of the OH_1^0 band. In phenol-d_1, on the other hand, the energy widths of the doorway states are much narrower and they do not overlap with each other. The reason of the narrower width is probably due to lower density of bath states. Thus, the picosecond IR pulse coherently excites the three states formed by the coupling (V_1), causing the quantum beat. By selecting the electronic transitions, i.e., OD_1^0 or band A, we can probe the time evolution of the initial or the doorway state. This situation is also the same in phenol-d_6, except for larger γ than that of phenol-d_1.

Another aspect of this work is that one of the doorway states can be determined from the spectroscopic assignment for the bands A and B. The assignment was carried out by using the reported vibrational frequencies in S_0 and S_1.[14,15] For band A, the energy of the level in S_1 of this transition is 1140 cm^{-1}. Since the anharmonicity due to the combination or overtone is not known, we examined possible combination levels within the range of 10 cm^{-1}. There were five candidates within the first overtone and the combination levels with total quantum number of two, and ten within the second overtone and the combination levels with total quantum number of three. We also examined the possible combination levels in S_0 having A' symmetry and the frequency of 2701 cm^{-1} within the range of 10 cm^{-1}. Finally, we examined the possible pair between S_0 and S_1, which is thought to exhibit intense vibronic band, and found that band A can be uniquely assigned as $1_1^0 6a_1^0 12_1^1 18b_1^1$. As to band B, we proposed that both bands A and B are the transitions originating from the same doorway state in S_0. This is supported by that the frequency difference (470 cm^{-1}) of the two transitions, is equal to the frequency of mode $6a$ in S_1. So, the band B is assigned as $1_1^0 6a_1^1 12_1^1 18b_1^1$. Very interestingly, the doorway sate has the Franck–Condon active modes, such as 1, $6a$ and 12, and that is the reason why we could observe those bands.[13] At this moment, it is not clear why one of the doorway states is constructed with those vibrational modes and theoretical support is strongly demanded.

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