Time-Resolved Spectroscopy

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Remarkable Site Difference of Vibrational Energy Relaxation in Benzene Dimer: Picosecond Time-Resolved IR–UV Pump–Probe Spectroscopy**

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Benzene dimer (Bz_2) is one of the most fundamental molecular systems and shows intriguing properties attributed to aromatic–aromatic weak interactions. The structure of Bz_2 in the ground electronic state (S_0) has been extensively studied experimentally[1] and theoretically.[2] Several experimental studies on Bz_2, such as the molecular-beam electric deflection[1a,b] and Raman–UV double resonance[1h] and UV–UV hole-burning spectroscopy,[1g] strongly suggested that the two benzene (Bz) molecules are not symmetrically equivalent. Moreover, recent high-level ab initio calculations suggested that a floppy T-shaped structure is a global minimum, although there are several possible isomers in the nearly isoenergetic region.[2] The rotational constant obtained from the Fourier transform microwave spectrum agreed well with the predicted value for the T-shaped form.[1i]

An important subject closely related to the structure is the vibrational dynamics. In the T-shaped Bz_2, the two Bz molecules are in different symmetries; one is at the stem site, and the other is at the top site. Therefore, the rate constant as well as the process of vibrational energy relaxation of the two molecules will be different. In this sense, the study of a site-specified vibrational energy relaxation will provide us with a more detailed picture of the structure and vibrational dynamics of Bz_2. Several studies on the vibrational energy relaxation of Bz_2 have been reported.[3] Lee and co-workers estimated the lifetime of the CH stretching region to be approximately 3 ps based on the band-width measurement of the IR spectrum.[3c] Felker and co-workers suggested that the ν_2 (CH stretching, Wilson's numbering) level of the stem-site Bz relaxes faster than that of the top-site Bz, according to the difference in the band width of the Raman spectra.[1h] However, in both cases the measured band width was not that of a single rovibrational level. It is also not clear how the band width is related to the vibrational energy relaxation dynamics, such as intramolecular (intracluster) vibrational energy redistribution (IVR) and vibrational predissociation (VP). Moreover, there has been no report on the time-resolved spectroscopy for the site-specified Bz_2.

Herein we study the dynamics of the vibrational energy relaxation of the T-shaped Bz_2 in the CH stretching energy region using picosecond time-resolved IR–UV pump–probe spectroscopy. It is known that for the isolated Bz monomer with D_{6h} symmetry, the IR-active CH vibration (ν_{20}) with e_{1u} symmetry is anharmonically coupled with the $\nu_8+\nu_{19}$ and $\nu_1+\nu_6+\nu_{19}$ combination bands, forming a so-called Fermi triad. All the vibrational modes coupled with the CH stretching are in-plane modes with stretching or bending character. Their symmetries and frequencies in the isolated Bz molecule are as follow: ν_8 (e_{2g}) = 1600 cm^{-1}, ν_{19} (e_{1u}) = 1484 cm^{-1}, ν_1 (a_{1g}) = 993 cm^{-1}, and ν_6 (e_{2g}) = 608 cm^{-1}.[4] The Fermi triad appears at 3048, 3079, and 3101 cm^{-1} in the IR spectrum, and these levels were precisely investigated by Lee and co-workers using IR–UV double resonance spectroscopy.[4] They also investigated the CH stretching vibrational level for Bz_2 and suggested that the Fermi triad structure is very similar to that of the monomer, although the vibrational frequencies are slightly shifted from those of the monomer to 3047, 3078, and 3099 cm^{-1}.[3c] Each band contains the transitions of the Bz molecules at different sites. In addition, the Bz molecules at different sites have different symmetries. That is, the stem-site Bz has a C_{2v} symmetry, and the top-site Bz has a C_6 symmetry, assuming a nearly free rotational motion of the stem-site Bz along the C_6 axis of the top-site Bz.[2a]

Herein, we investigate the vibrational energy relaxation of Bz_2 to answer the three fundamental problems: 1) How fast are the IVR and VP in Bz_2? 2) Are there any site differences in the rate constants? 3) If so, how is the difference related to the structure? To accomplish the site-specific IR excitation, we use two isotope-substituted heterodimers: *h*(Stem)*d*(Top) and *d*(Stem)*h*(Top), where $h=C_6H_6$ and $d=C_6D_6$. Figure 1 shows the energy-level diagram of the T-shaped dimers and an excitation scheme. A picosecond IR pulse pumps the dimers to one of the CH stretching Fermi triads. For the *hd* dimer, the Fermi triad vibrational frequencies are reported to be 3045, 3077, and 3099 cm^{-1},[1k] and we chose the band at 3077 cm^{-1}. After a certain delay time (Δt), a UV pulse probes the population of vibrationally excited dimers *h**(Stem)*d*-(Top) and *d*(Stem)*h**(Top) by (1+1) resonance-enhanced multiphoton ionization (REMPI) through the S_1 state. The S_1–S_0 transition from the level at 3077 cm^{-1} occurs mostly by the $\Delta v_1=-1$ and $\Delta v_6=-1$ transitions, because the main character of this level is $\nu_1+\nu_6+\nu_{19}$.[4] The *h**(Stem) molecule exhibits a strong vibronic band, while *h**(Top) shows a weak

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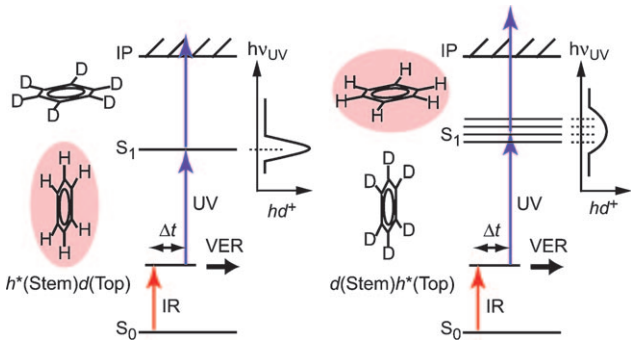

Figure 1. Energy-level diagram of benzene dimer isotopologues (*h*(Stem)*d*(Top) and *d*(Stem)*h*(Top)) and an excitation scheme. The dimers are vibrationally excited to the CH stretching region by a picosecond IR pulse, and the time evolution is probed by a picosecond UV pulse. The *h**(Stem) and *h**(Top) benzene components (an asterisk represents the vibrationally excited site) show different vibronic structures. Thus, the vibrationally excited dimers can be separately monitored by a tunable picosecond UV pulse. VER = vibrational energy relaxation.

progression on the higher frequency side of the band of *h**(Stem).[1c,g,h]

Figure 2 shows the mass-resolved transient (1 + 1) REMPI spectra at several delay times after the IR excitation

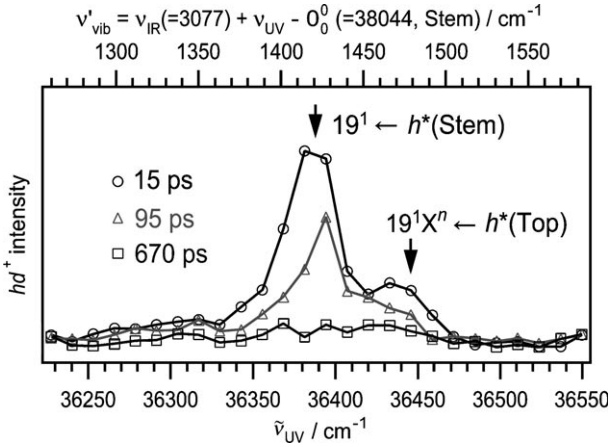

Figure 2. Transient (1 + 1) REMPI spectra at several delay times after the IR excitation of the band at 3077 cm^{-1}. In this case, the $[hd]^+$ mass channel is monitored. The spectra are shown as a function of ν_{UV} (UV frequency, lower axis) and ν'_{vib} (vibrational energy in $S_1 = \nu_{IR} + \nu_{UV} - 0_0^0$, upper axis).

of *hd* at 3077 cm^{-1} with the $[hd]^+$ mass channel being monitored. The spectra are shown as a function of ν_{UV} (UV frequency, lower axis) and ν'_{vib} (vibrational energy in $S_1 = \nu_{IR} + \nu_{UV} - 0_0^0$, upper axis). The spectrum at the delay time of 15 ps shows a strong peak at 36390 cm^{-1} and a weak one at 36440 cm^{-1}, and they decay with different time constants. In the present picosecond time-resolved study, the two Bz_2 isomers are simultaneously excited to the vibrational levels (*h**(Stem)*d*(Top) and *d*(Stem)*h**(Top)), as their vibrational levels are separated by only 1 cm^{-1}.[1k] Thus, the transitions of both *h**(Stem)*d*(Top) and *d*(Stem)*h**(Top) are overlapped in the REMPI spectrum. However, as described above, they exhibit different vibronic transitions; the stem-site Bz exhibits a strong vibronic band, while the top-site Bz shows a weak progression of 15 cm^{-1} interval in the higher frequency side of the strong band. Therefore, the bands at 36390 and 36440 cm^{-1} can be assigned to the transitions from *h**(Stem) and *h**(Top), respectively. Furthermore, as the frequency of mode 19 (ν'_{19}) of the isolated Bz in S_1 is 1405 cm^{-1}, and as the IR-excited bands mainly involve $\nu_1 + \nu_6 + \nu_{19}$ character,[4] the transitions at 36390 and 36440 cm^{-1} can be assigned to $19^1 \leftarrow h^*$(Stem) and $19^1X^n \leftarrow h^*$(Top) resonance transitions, respectively, where X represents an intermolecular vibration. A very weak, broad background in the 36250–36350 cm^{-1} region is due to larger clusters, which generate the $[hd]^+$ fragment ion after photoionization.[1c,d,f,5] As seen in Figure 2, the contribution of the larger clusters is very small under the present conditions.

The black and red curves in Figure 3 show the time profiles of the pump–probe signals obtained by fixing the UV

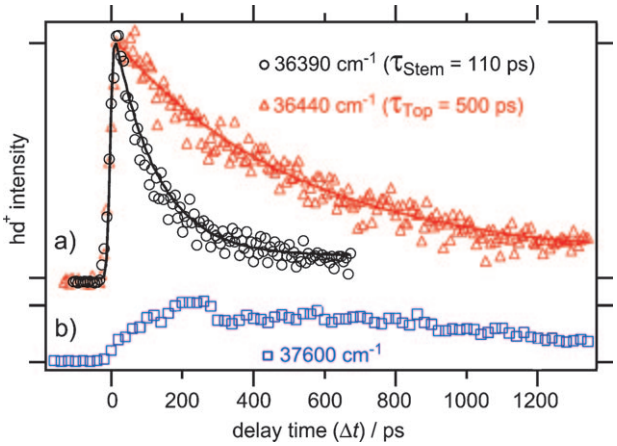

Figure 3. Picosecond IR–UV pump–probe signals of the vibronic bands at 36390 cm^{-1} (black) and 36440 cm^{-1} (red) and the broad band at 37600 cm^{-1} (blue) after the IR excitation of the band at 3077 cm^{-1}.

frequencies to the bands at 36390 and 36440 cm^{-1}, respectively. This is the first real-time observation of the site-specified vibrational energy relaxation of Bz_2. It is clear that the intensity of the band at 36390 cm^{-1} (black curve) decays much faster than that of the band at 36440 cm^{-1} (red curve). The decay curves can be fitted by the single exponential decay function given in Equation (1):

$$I(t) = I_0 \exp(-\Delta t/\tau), \quad (1)$$

convoluted with the 12 ps widths of the laser pulses. Note that in Figure 3 the two curves do not completely reach zero at long delay times because of unavoidable fragmentation from the larger clusters after ionization. Therefore, we fitted the decay curves by including the nonzero baseline as a step function. Finally, we obtained the decay lifetimes $\tau_{Stem} = 110$ ps ($k_{Stem} = 9.0 \times 10^9\ s^{-1}$) and $\tau_{Top} = 500$ ps ($k_{Top} = 2.0 \times 10^9\ s^{-1}$) for *h**(Stem)*d*(Top) and *d*(Stem)*h**(Top), respectively. Thus, the lifetime of the stem-site Bz is 4.5 times

shorter than that of the top-site Bz, despite the fact that their vibrational frequencies differ by only 1 cm^{-1}. It was reported that the isolated Bz molecule does not show vibrational energy relaxation in this energy region,[4,8a] which may be because of its high symmetry (D_{6h}). In the dimer, on the other hand, the two Bz molecules are in environments of lower symmetry; the stem- and top-site benzene molecules have C_{2v} and C_6 symmetry, respectively. The lowering of the symmetry may cause the vibrational energy relaxation in the T-shaped Bz_2. Moreover, the present study indicates that the initial-level↔dark-state coupling strength of the stem-site Bz is 4.5 larger than that of the top-site Bz. The larger coupling of the stem-site Bz is partly explainable by the nature of the CH stretching mode and the structure of Bz_2. In the stem-site Bz, the CH stretching motion is parallel to the intermolecular stretching motion, hence an efficient CH↔intermolecular-modes coupling may occur through the CH···π interaction. In the top-site Bz, on the other hand, the coupling of the CH stretching motion with the intermolecular modes is negligibly small. A theoretical treatment is strongly encouraged to support this hypothesis.

Another important issue remains: What dynamics can the observed decay be attributed to? Since the binding energy of Bz_2 is reported to be 500–800 cm^{-1},[6] and the input energy of 3077 cm^{-1} is much larger than the binding energy, the vibrationally excited Bz_2 finally dissociates. Two dissociation pathways must be considered [Eqs. (2a) and (2b)]:

$$hd_{\text{inital}} \xrightarrow{\text{IVR}} hd_{\text{bath}} \xrightarrow{\text{VP}} h + d \quad (2a)$$

$$hd_{\text{inital}} \xrightarrow{\text{VP}} h + d \quad (2b)$$

In Equation (2a), the dimer sequentially predissociates through IVR, while in Equation (2b) the dimer directly predissociates from the initial level. One way to answer the above question is to observe the electronic transitions from the redistributed levels (hd_{bath}). Actually, we observed a broad transition at approximately 37 600 cm^{-1}, which is assignable to the hot band transitions from the bath modes (the UV spectrum is not shown here). The blue curve in Figure 3 shows the IR–UV pump–probe time profile obtained by fixing the UV frequency to 37 600 cm^{-1}. The intensity of the broad transition reaches its maximum at $\Delta t = 200$–300 ps and decays on the time scale of approximately 1 ns. The time required to reach the maximum, $\Delta t = 200$–300 ps, is close to the time scale of the disappearance of the stem-site Bz signal, meaning that the rise corresponds to IVR, and the decay with the long time scale is attributed to VP. Thus, we can say that at least Equation (2a) occurs. At present, however, we cannot conclude that the sequential process in Equation (2a) is the only one that occurs. Zewail and co-workers investigated the vibrational energy relaxation processes in detail for the van der Waals complexes of stilbene with helium, neon, and argon in S_1 by picosecond time-resolved photofragment spectroscopy. They concluded that IVR precedes VP and that the complexes dissociate through the sequential process.[7] A similar sequential process was also reported for the dissociation from the excited OH stretching vibration of hydrogen-bonded clusters of phenol.[8c] For further confirmation, the detection of the Bz fragment and its time profile measurement are necessary, and these issues are to be addressed in future work. We also performed the experiments for the other bands forming the Fermi triad (3045 and 3099 cm^{-1}) and found that they show very similar relaxation rate constants. This result is understandable because this Fermi triad is composed of the same set of the vibrations.

In conclusion, we investigated the site-specified vibrational energy relaxation of the benzene dimer by picosecond time-resolved IR–UV pump–probe spectroscopy. By using isotopologues, the IR excitation of the site-specified benzene components and time-resolved probe of the vibrational energy relaxation have become possible for the first time. It was found that the CH stretching vibrational level of the stem-site benzene relaxes 4.5 times faster than that of the top-site benzene, although their vibrational energies differ by only 1 cm^{-1}. The result indicates the importance of the CH···π interaction not only to the structure of aromatic systems but also to their vibrational energy relaxation dynamics, which will trigger numerous theoretical investigations. The studies of the vibrational energy relaxation of the homodimer (*hh*) and that starting from the CD stretching vibration of *hd* and *dd* dimers are now in progress.

Experimental Section

The experimental setup for the picosecond time-resolved IR–UV pump–probe spectroscopy is an upgraded version of that described previously.[8] Briefly, a tunable picosecond IR pulse is obtained by difference frequency generation (DFG) between the signal and the idler output of an optical parametric generation/optical parametric amplifier (OPG/OPA) system (Ekspra PG401/DFG2-10P) pumped by a mode-locked picosecond Nd:YAG laser (Ekspra PL2143S). A tunable picosecond UV pulse is obtained by second harmonic generation (SHG) of the output of an OPG/OPA system (Ekspra PG401SH) pumped by the same Nd:YAG laser. The spectral resolutions of the IR and UV beams are 5 cm^{-1}, and the time resolution of the two pulses is 12 ps. The delay time between IR and UV pulses is changed by an optical delay line. For generating *hd* heterodimers, a gaseous mixture of *h* and *d* (50:50(v/v)) diluted with helium carrier gas at a total pressure of 3 bar is expanded into vacuum by a pulsed valve (General valve, Series 9). The molecular beam is obtained by skimming the center of the expansion. To reduce the formation of the clusters larger than dimers, the container of the sample is maintained at −20 °C, and the width and timing of the pulse valve are carefully controlled. The IR and UV laser beams cross the molecular beam, and the photoionized benzene clusters are mass-analyzed by a time-of-flight mass spectrometer and detected by a channeltron (Burle 4900).

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