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Excited-State Double-Proton Transfer in the 7-Azaindole Dimer in the Gas Phase. 3. Reaction Mechanism Studied by Picosecond Time-Resolved REMPI Spectroscopy

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The excited-state double-proton-transfer (ESDPT) reaction in the jet-cooled 7-azaindole dimer ($7AI_2$) has been investigated with picosecond time-resolved resonance-enhanced multiphoton ionization spectroscopy. The observed decay profiles of $7AI_2$ by exciting the origin and the intermolecular stretch fundamental in the S_1 state are well reproduced by single-exponential functions with time constants of 1.9 ± 0.9 ps and 860 ± 300 fs, respectively. This result provides clear evidence of the concerted mechanism of ESDPT in $7AI_2$.

The proton-transfer reaction is one of the most basic reactions and plays very important roles in physical, chemical, and biological systems.[1] There have been many spectroscopic and theoretical studies about the proton-transfer reactions. The excited-state double-proton-transfer (ESDPT) reactions in the doubly hydrogen-bonded systems have attracted a great deal of attention. The UV light may tautomerize the doubly hydrogen-bonded DNA base pairs that stabilize the double-stranded DNA helix, destroying the genetic information. Among the doubly hydrogen-bonded dimers that exhibit ESDPT, the 7-azaindole dimer ($7AI_2$) is one of the most extensively studied systems as an excellent model of the DNA base pairs.[2−16] Since the first observation of ESDPT in $7AI_2$ by Kasha et al.,[2] the mechanism of ESDPT in $7AI_2$ has been an important subject of the dynamics. Figure 1 shows the two mechanisms of the ESDPT reaction that have been discussed by several groups.[2,8,9,11−16] In the stepwise mechanism, single-proton transfer (SPT) occurs from the photoexcited normal form to the stable intermediate state, which has a zwitterionic structure. The intermediate-state dimer undergoes a second SPT to generate the tautomer. On the other hand, in the concerted mechanism, two protons transfer simultaneously and no stable intermediate state occurs.

Douhal et al. applied femtosecond pump−probe resonance-enhanced multiphoton ionization (REMPI) spectroscopy to investigate the mechanism of ESDPT in $7AI_2$.[8] They measured the decay profiles by changing the excess energies in the lowest excited electronic state. The decay profiles were well fitted with the biexponential functions. Two time constants obtained from the biexponential decay profiles were ascribed to the SPT reaction from the normal dimer to the stable intermediate and that from the intermediate to the tautomer. Fiebig et al. carried out the femtosecond fluorescence up-conversion and the transient absorption spectroscopy in the condensed phase.[13] Their observations were ascribed to the stepwise mechanism. Essentially, the same conclusion was derived from the femtosecond Coulomb explosion experiment in the gas phase.[12] On the other hand, Kasha et al. argued that ESDPT in $7AI_2$ proceeds via a concerted mechanism on the basis of the exciton theory.[2,15] In the condensed phase, Takeuchi and Tahara carried out femtosecond fluorescence up-conversion spectroscopy[11] and observed single-exponential decay profiles when the red edge of the absorption in $7AI_2$ was excited. They concluded that ESDPT in $7AI_2$ proceeds via a concerted mechanism. Thus, the mechanism of ESDPT has long been controversial.

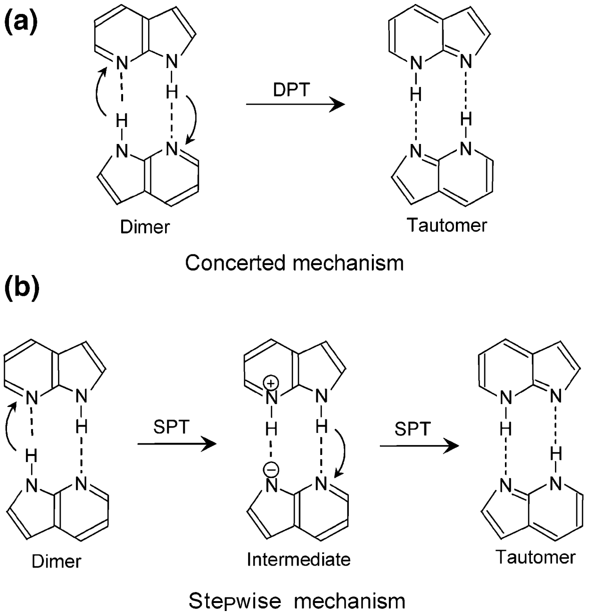

Figure 1. Two mechanisms of ESDPT in $7AI_2$: (a) the concerted mechanism; (b) the stepwise mechanism. SPT and DPT indicate single-proton transfer and double-proton transfer, respectively.

We measured the UV−UV hole-burning spectra of deuterated $7AI_2$ in the gas phase.[16a] The vibronic bands having different lifetimes were well separated in the UV−UV hole-burning spectra of deuterated $7AI_2$. We suggested that the biexponential decay profiles observed in the femtosecond spectroscopy in the

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gas phase are due to the simultaneous excitation of vibronic bands with different lifetimes, since the femtosecond laser pulse (∼150 fs) used by Douhal et al. cannot excite the single vibronic state. Very recently, we reported the dispersed fluorescence (DF) spectra of undeuterated and deuterated 7AI$_2$.[16e] The absence of the stable intermediate state was suggested from the analyses of the observed intensity ratios of the normal dimer fluorescence to the tautomer fluorescence, which excluded the stepwise mechanism. Thus, the vibronic-state-selected time-resolved study has been anticipated to solve the discrepancies in the mechanism of ESDPT in 7AI$_2$.

In this communication, we report picosecond time-resolved REMPI spectroscopy. It is crucial to use the picosecond laser pulse having enough time and frequency resolutions to investigate ESDPT in the single vibronic states, because 7AI$_2$ shows vibrational-mode-specific ESDPT.[6] We have found that the decay profiles of 7AI$_2$ are well reproduced by the single-exponential functions. The mechanism of ESDPT in 7AI$_2$ is discussed on the basis of the data obtained from the picosecond time-resolved experiment.

The experimental setup for picosecond time-resolved REMPI spectroscopy consists of a linear time-of-flight mass spectrometer and a picosecond laser system.[17,18] The linear time-of-flight mass spectrometer consists of differentially pumped two-vacuum chambers. The sample introduced in the stainless tube was heated to 373 K by a coiled heater and expanded into the vacuum chamber with He as a carrier gas. The backing pressure was 2−3 atm. The pulsed valve (General Valve, series 9, 0.8 mm diameter) was operated at 10 Hz, whose trigger pulse synchronized with the picosecond laser system (repetition rate 1 kHz) was divided by a homemade divider from 1 kHz to 10 Hz. The ion signal was detected by an MSP detector (El-Mul). A femtosecond Ti:sapphire laser (Spectra Physics, Tsunami) was pumped by a diode laser (Spectra Physics, Millennia). The output pulses from the Ti:sapphire laser were put into a picosecond regenerative amplifier (Quantronix, Titan) pumped by a Q-switched intracavity frequency-doubled Nd:YLF laser (Quantronix, 527DP-H). A half of the amplified output was frequency-doubled to excite an OPA (Light Conversion, TOPAS 4/400). The output from the OPA was frequency-doubled by a BBO crystal. The remainder of the amplified output was used to excite the other OPA system (Light Conversion, TOPAS 4/800). The output from the former OPA was used as the pump pulse, which excited jet-cooled 7AI$_2$ in the S$_1$ state, and that from the latter OPA was used as the probe pulse to ionize 7AI$_2$. The pump and probe pulses were superimposed by a dichroic mirror, focused by a lens with $f = 300$ mm, and coaxially introduced into the vacuum chamber. The cross-correlation trace between the pump and the probe pulses was obtained from the measurements of the photodissociation reaction in acetone. 7AI was purchased from TCI and was used without further purification.

Parts a and b of Figure 2 show the time profiles of the ion signal intensities of 7AI$_2$ following the excitation of the origin and the intermolecular stretch fundamental (1σ), respectively. It should be noted that the intermolecular stretching (1σ) and bending (1β) vibrations are observed at 120 and 98 cm^{-1} from the origin in the fluorescence excitation (FE) spectrum, respectively.[6b,16a] The separation of the two vibronic bands is 22 cm^{-1}. The lifetimes of the 1σ and 1β states must be very different, because the bandwidths of the two vibrations are determined to be 10 and 3 cm^{-1}, respectively. To determine the lifetimes of the two states, it is necessary to use the picosecond laser pulse which has enough energy resolution to excite the 1σ and 1β states separately. The time profiles in Figure 2a and b are well reproduced by the convolutions of the response functions shown in Figure 2c with biexponential decay profiles having the short and long time constants, respectively. In both profiles, the components of the time profiles with long lifetimes (>30 ps) were observed. The intensities of the decay components with the long lifetimes strongly depend on the experimental conditions such as the temperature of the nozzle and the timing between the pulsed nozzle and the laser pulse. In the FE spectrum, the broad background signals due to the UV emission are overlapping with sharp vibronic bands in the S$_1$−S$_0$ region of 7AI$_2$. The ESDPT reaction is inhibited in the higher clusters larger than the dimer, because no visible fluorescence arising from the tautomers of the higher clusters has been observed. This suggests that the lifetimes of the excited electronic states of higher clusters are much longer than that of the reactive 7AI$_2$ dimer. In addition, some vibronic bands were observed due to the nonreactive 7AI$_2$ dimer near the 1σ band of 7AI$_2$ in the FE spectrum.[6b] It was shown that the nonreactive 7AI$_2$ dimer contains a water molecule between the two 7AI monomer moieties in the S$_0$ and S$_1$ states, but the dissociation of the cluster in the D$_0$ state caused by REMPI produces the 7AI dimer ions; therefore, the nonreactive 7AI$_2$ dimer having long lifetimes may be detected on the same flight time as 7AI$_2$.[19] If the long-lifetime component essentially contributes to the ESDPT dynamics of 7AI$_2$, its decay profiles should not depend on the experimental conditions such as the temperature of the nozzle and the timing between the pulsed nozzle and the laser pulse. However, only the short-lifetime component in the decay profiles shown in Figure 2 is independent of the experimental conditions. Therefore, the long-lifetime component in Figure 2 has been assigned to the signals originating from the higher clusters larger than the dimer and/or the nonreactive 7AI$_2$ dimer. Thus, the two time profiles due to 7AI$_2$ are well reproduced with the single-exponential decays. The best-fitted time constants for the zero-point level and the 1σ state obtained from Figure 2a and b are 1.9 ± 0.9 ps and 860 ± 300 fs, respectively.

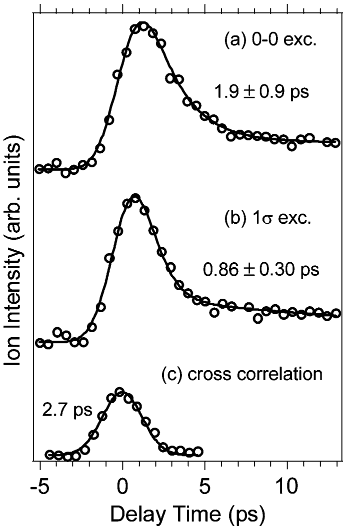

Figure 2. Decay profiles of 7AI$_2$ pumped at (a) the origin and (b) the intermolecular stretching band, respectively. The wavelength of the probe laser was fixed at 620 nm in parts a and b. The open circles are experimental data, while the solid curves are best-fitted curves obtained by biexponential functions. The cross-correlation trace is also indicated in part c. The instrumental time resolution given by the fwhm of the cross-correlation trace is 2.7 ps.

Douhal et al. observed the biexponential decay profiles of 7AI$_2$ in the S$_1$ state with the femtosecond pump−probe experiment under the jet-cooled conditions.[8] They assigned the fast and slow decays to the SPT reaction from the normal dimer to the intermediate and that from the intermediate to the tautomer, respectively. Thus, they concluded $7AI_2$ undergoes ESDPT by a stepwise mechanism. However, it is known that ESDPT in $7AI_2$ occurs in a highly vibrational-mode-specific fashion; the excitation of the intermolecular stretching vibration enhances ESDPT, but the intermolecular bending vibration suppresses ESDPT.[6] Therefore, the decay profiles of $7AI_2$ in the S_1 state should depend on the excited vibronic state. Actually, the decay time of the intermolecular stretching vibration is about twice faster than that of the zero-point level. This result is consistent with the promoting character of the intermolecular stretching vibration.

We carefully measured the FE spectrum of $7AI_2$ with the nanosecond laser pulse and obtained a bandwidth of the origin band of 2.7 cm^{-1}, providing a time constant of $\tau_{0-0} \approx 2$ ps. [16e] However, the time constants of $\tau \approx 650-660$ fs, which were obtained by femtosecond experiments for the nearly no excess energy in the S_1 state, were ascribed to SPT from the normal form to the intermediate state.[8,12] The time constants obtained from the femtosecond experiments are contradictory to the bandwidth of the origin band in the FE spectrum, because it should be much broader than 2.7 cm^{-1} if SPT really occurs on a time scale of 650−660 fs. In contrast, the time constant (1.9 ± 0.9 ps) obtained by the picosecond experiment is in good agreement with the bandwidth of the origin band. The time constants of $\tau \approx 650-660$ fs obtained from the femtosecond experiments in the gas phase agree with $\tau = 860 \pm 300$ fs within the experimental errors, which correspond to the decay of the 1σ state from the picosecond experiment. Thus, the comparison of the data from the femtosecond and picosecond experiments indicates that the biexponential decay profiles obtained by the femtosecond experiments may be due to simultaneous excitation of the origin and the 1σ state with different lifetimes. We should note that the relative contribution of the component with a time constant of $\tau \approx 650$ fs in ref 8 is very small when the excess energy is nearly zero. We infer that the origin band was dominantly excited by the femtosecond laser pulse when the frequency of the laser was tuned to the origin, but the 1σ state might be weakly excited by the blue-edge region of the laser profile in the femtosecond REMPI experiment, providing the biexponential decay profile.

The decay profiles of $7AI_2$ fitted with the single-exponential functions observed in this study indicate that no stable intermediate state exists in the ESDPT reaction, supporting the concerted mechanism of the ESDPT reaction. In addition, we showed that the H/D kinetic isotope effects measured by detecting the DF spectra of $7AI_2$ could not be well explained by the stepwise mechanism.[16e]

The final conclusion derived from a series of our frequency and time domain experiments is that the lowest excited electronic state of $7AI_2$ undergoes the ESDPT reaction by the concerted mechanism.

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References and Notes

(1) *Atom Tunneling Phenomena in Physics, Chemistry and Biology*; Miyazaki, T. Ed.; Springer: Berlin, 2004.

(2) (a) Taylor, C. A.; El-Bayoumi, M. A.; Kasha, M. *Proc. Natl. Acad. Sci. U.S.A.* **1969**, *63*, 253. (b) Ingham, K. C.; Abu-Elgheit, M.; El-Bayoumi, M. A. *J. Am. Chem. Soc.* **1971**, *93*, 5023. (c) Ingham, K. C.; El-Bayoumi, M. A. *J. Am. Chem. Soc.* **1974**, *96*, 1674. (d) El-Bayoumi, M. A.; Avouris, P.; Ware, W. R. *J. Chem. Phys.* **1975**, *62*, 2499.

(3) Hetherrington, W. M., III; Micheels, R. H.; Eisenthal, K. B. *Chem. Phys. Lett.* **1979**, *66*, 230.

(4) Bulska, H.; Grabowski, A.; Pakula, B.; Sepiol, J.; Waluk, J.; Wild, U. P. *J. Lumin.* **1984**, *29*, 65.

(5) (a) Tokumura, K.; Watanabe, Y.; Itoh, M. *Chem. Phys. Lett.* **1984**, *111*, 379. (b) Tokumura, K.; Watanabe, Y.; Udagawa, M.; Itoh, M. *J. Am. Chem. Soc.* **1987**, *109*, 1346.

(6) (a) Fuke, K.; Yoshiuchi, H.; Kaya, K. *J. Phys. Chem.* **1984**, *88*, 5840. (b) Fuke, K.; Kaya, K. *J. Phys. Chem.* **1989**, *93*, 614.

(7) Share, P.; Pereira, M.; Sarisky, M.; Repinec, S.; Hochstrasser, R. M. *J. Lumin.* **1991**, *48/49*, 204.

(8) Douhal, A.; Kim, S. K.; Zewail, A. H. *Nature* **1995**, *378*, 260.

(9) Douhal, A.; Guallar, V.; Moreno, M.; Lluch, J. M. *Chem. Phys. Lett.* **1996**, *256*, 370.

(10) Lopez-Martens, R.; Long, P.; Sogaldi, D.; Soep, B.; Syage, J.; Millie, P. *Chem. Phys. Lett.* **1997**, *273*, 219.

(11) (a) Takeuchi, S.; Tahara, T. *Chem. Phys. Lett.* **1997**, *277*, 340. (b) Takeuchi, S.; Tahara, T. *J. Phys. Chem. A* **1998**, *102*, 7740. (c) Takeuchi, S.; Tahara, T. *Chem. Phys. Lett.* **2001**, *347*, 108.

(12) (a) Folmer, D. E.; Poth, L.; Wisniewski, E. S.; Castleman, A. W., Jr. *Chem. Phys. Lett.* **1998**, *287*, 1. (b) Folmer, D. E.; Wisniewski, E. S.; Castleman, A. W., Jr. *Chem. Phys. Lett.* **2000**, *318*, 637.

(13) (a) Chachisvilis, M.; Fiebig, T.; Douhal, A.; Zewail, A. H. *J. Phys. Chem. A* **1998**, *102*, 669. (b) Fiebig, T.; Chachisvilis, M.; Manger, M.; Zewail, A. H.; Douhal, A.; Garcia-Ochoa, I.; de La Hoz Ayuso, A. *J. Phys. Chem. A* **1999**, *103*, 7419.

(14) Guallar, V.; Batista, V.; Miller, W. H. *J. Chem. Phys.* **1999**, *110*, 9922.

(15) (a) Catalan, J.; Kasha, M. *J. Phys. Chem. A* **2000**, *104*, 10812. (b) Catalan, J.; Perez, P.; del Valle, J. C.; de Paz, J. L. G.; Kasha, M. *Proc. Natl. Acad. Sci. U.S.A.* **2004**, *101*, 419.

(16) (a) Sakota, K.; Hara, A.; Sekiya, H. *Phys. Chem. Chem. Phys.* **2004**, *6*, 32. (b) Hara, A.; Komoto, Y.; Sakota, K.; Miyoshi, R.; Inokuchi, K.; Ohashi, K.; Yamamoto, E.; Mori. A.; Nishi, N.; Sekiya, H. *J. Phys. Chem. A* **2004**, *108*, 10789. (c) Komoto, Y.; Sakota, K.; Sekiya, H. *Chem. Phys. Lett.* **2005**, *406*, 15. (d) Sakota, K.; Sekiya, H. *J. Phys. Chem. A* **2005**, *109*, 2718. (e) Sakota, K.; Sekiya, H. *J. Phys. Chem. A* **2005**, *109*, 2722.

(17) Nakabayashi, K.; Kamo, S.; Sakuragi, H.; Nishi, N. *J. Phys. Chem. A* **2001**, *105*, 8605.

(18) Okabe, C.; Nakabayashi, K.; Nishi, N.; Sekiya, H. *J. Chem. Phys.* **2004**, *121*, 9436.

(19) Yokoyama, F.; Watanabe, H.; Omi, T.; Ishiuchi, S.; Fujii, M. *J. Phys. Chem. A* **2001**, *105*, 9366.