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Probe of the NH Bond Strength in ^1L_a and ^1L_b States of 7-azaindole with IR-Dip Spectroscopy: Insights into the Electronic-State Dependence of the Multiple Proton/Hydrogen Transfers in Hydrogen-Bonded Clusters

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The difference in the NH bond strengths in the ^1L_a and ^1L_b state of 7-azaindole is examined with the fluorescence-detected IR-dip spectroscopy. It has been found that the NH stretch fundamental (3456 cm^{-1}) measured by probing the vibronic band at 280 cm^{-1} above the zero-point level of ^1L_b is remarkably red-shifted with respect to those (3483−3489 cm^{-1}) obtained by probing the other six vibronic bands in the 0−717 cm^{-1} region. The electronic state of the band at 280 cm^{-1} was assigned to a $S_1(L_b)/S_2(L_a)$ mixing state [Kang et al. *J. Chem. Phys.* 2005, *123*, 094306.]; the prominent red shift of the NH stretch fundamental indicates that the ^1L_a component significantly contributes to weaken the NH bond strength. This finding provides insight into electronic-state dependence of the proton/hydrogen-atom transfer reactions in the hydrogen-bonded 7-azaindole clusters.

The proton/hydrogen-atom (H-atom) transfer is one of the most basic chemical reactions. The complicated chemical and biological processes such as ion transport in aqueous solutions and proton transport via membrane-spanning proteins include the proton/H-atom transfer. The detailed understanding of the proton/H-atom transfer mechanism at the molecular scale might provide basic information to reveal the more complicated chemical and biological processes.[1,2]

The excited-state proton/H-atom transfer is ideal to investigate its dynamics in detail because the reaction can be easily triggered by UV or visible photon. The photoinduced solvent-assisted proton transfers in the hydrogen-bonded systems have attracted a great deal of attention in the gas phase as well as in the condensed phase.[3,4] Recently, we reported that 7-azaindole-[7AI]$(MeOH)_2$ shows the cluster-size and vibrational-mode specific excited-state triple-proton/H-atom transfer (ESTPT/HT) in the gas phase.[5,6] It was shown that the in-phase intermolecular stretching vibration enhances ESTPT/HT in 7AI$(MeOH)_2$ in the low internal energy region in S_1 (<600 cm^{-1}). In the high internal energy region in S_1 (>600 cm^{-1}), however, the vibrational-mode specificity observed in the low internal energy region disappears due to the intracluster vibrational energy redistribution.

The $\pi\sigma^*$ states play an important role in the dynamics of the electronic excited states of the heteroaromatic molecules and their hydrogen-bonded clusters, in which the H-atom transfer occurs via the surface-crossing between the $\pi\pi^*$ and $\pi\sigma^*$ potential energy surfaces, whereas the proton transfer occurs on the $\pi\pi^*$ potential energy surface.[3,7,8] H-atom transfers in the hydrogen-bonded clusters were experimentally confirmed by identifying the H-atom transferred products produced by the dissociative H-atom transfer.[9−11] However, it is difficult to identify whether the proton or H-atom transfer experimentally when the proton/H-atom transfer is not the dissociative reaction such as ESTPT/HT in 7AI$(MeOH)_2$. Tanner et al. reported that the cyclically hydrogen-bonded 7-hydroxyquinoline [7HQ]-$(NH_3)_3$ might show the excited-state H-atom transfer via the surface-crossing between the $\pi\pi^*$ and $\pi\sigma^*$ potential energy surfaces for the first time.[3] Very recently, however, Koizumi et al. reported that the $\pi\pi^*$ potential energy surfaces are stable as compared with the $\pi\sigma^*$ potential energy surfaces along the reaction paths for 7HQ$(NH_3)_3$ as well as for 7AI$(NH_3)_2$ on the basis of the CC2 calculations.[12] ESTPT in 7AI$(MeOH)_2$ might occur on the $\pi\pi^*$ potential energy surface, although it is difficult to conclude definitely whether ESTPT or ESTHT occurs on the basis of the experimental results. We point out that the reaction proceeds from the vertically excited $\pi\pi^*$ state of 7AI$(MeOH)_2$ in both ESTPT and ESTHT. Thus the investigation of the nature of the initially excited $\pi\pi^*$ state is important for understanding the reactivity of the other hydrogen-bonded 7AI clusters as well as 7AI$(MeOH)_2$.

It is known that the 7AI monomer has two close-lying lowest $\pi\pi^*$ electronic excited states ^1L_b (S_1) and ^1L_a (S_2).[13] On the basis of ab initio calculation, the ^1L_b state has a locally excited nature in the moiety of the six-membered ring, but ^1L_a has a charge transfer nature occurring from the five-membered to the six-membered ring.[14] The lowest electronic excited states of the hydrogen-bonded 7AI clusters such as the 7AI dimer ($7AI_2$) have been considered to be the ^1L_a state, because ^1L_a has a large dipole moment.[14,15] The measurements of the NH stretch fundamentals in the two electronic excited states ^1L_b and ^1L_a of 7AI provide useful information on the reactivity of the excited-state multiple proton/H-atom transfer (ESPT/HT) in the hydrogen-bonded 7AI clusters, because the red shifts of the NH stretch fundamentals in each electronic excited state with respect to that of S_0 reflect the change in the NH bond strengths, which is closely related to the determining factors of ESPT/HT such as

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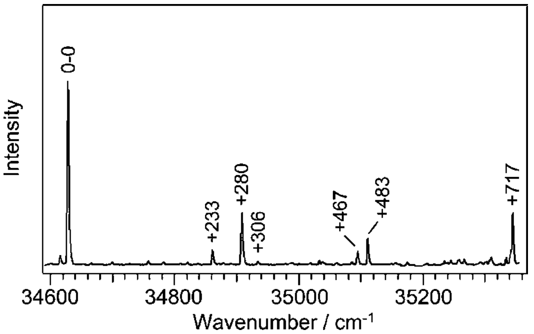

Figure 1. FE spectra of 7AI. The 0−0 transition of 7AI is observed at 34 628 cm^{-1}. The relative wavenumbers from the 0−0 transition of 7AI are indicated in the figure. The fluorescence intensities are corrected against the laser power.

the proton transfer distance and the potential energy barrier height along the reaction coordinate when 7AI forms the hydrogen-bonded clusters. In this Letter, we report the fluorescence-detected IR-dip (FDIR) spectra of 7AI in the electronic excited states. We will discuss the relation between the red shift of the NH stretch fundamentals in the excited states and the reactivity of ESPT/HT in the hydrogen-bonded 7AI clusters.

The experimental setup was described in detail elsewhere.[16] Briefly, 7AI was introduced in a stainless tube, heated to 353 K by a coiled heater and expanded into a vacuum chamber with Ne as a carrier gas. For the FDIR experiments, a frequency-doubled dye-laser (Sirah Cobra stretch) pumped by a second harmonic of the Nd^{3+}:YAG laser (Spectra Physics GCR 230) was operated at 10 Hz as the UV source, whereas an optical parametric converter (LaserVision) pumped by an injection-seeded Nd^{3+}:YAG laser (Continuum Powerlite Precision II 8000) was operated at 5 Hz as the IR source. The fluorescence signals generated by UV + IR pulses and UV pulse were averaged separately. The fluorescence signals due to the UV + IR pulses were divided by the fluorescence signals due to the UV pulse to eliminate long-term fluctuations of baselines.

The fluorescence excitation (FE) spectrum of supersonically jet-cooled 7AI was reported by Fuke et al. for the first time.[17] The vibronic bands observed in the FE spectrum of 7AI were assigned by comparing the dispersed fluorescence spectra obtained by exciting various vibronic bands with the simulated ones.[18] Figure 1 shows the FE spectrum of 7AI, which is essentially the same as that reported previously.[17]

Parts a and b of Figure 2 show the FDIR spectra (a) in the S_0 state and (b) in the S_1 state obtained by exciting the S_1−S_0 0−0 transition of 7AI. In Figure 2a, the fluorescence dip was observed at 3521 cm^{-1} in S_0, which was assigned to the NH stretch fundamental of 7AI.[19] In Figure 2b, the vibrational transition was observed at 3489 cm^{-1}, which is red-shifted by 32 cm^{-1} from the NH stretch fundamental of the S_0 state. In the region between 2800 and 3770 cm^{-1}, there is a strong vibrational transition at 3489 cm^{-1} in the S_1 state when the 0−0 band of 7AI is excited. Thus, we assigned the vibrational band at 3489 cm^{-1} in Figure 2b to the NH stretch fundamental of 7AI in the S_1 state. The observed red shift of the NH stretch fundamental in S_1 reflects the effect of the electronic excitation on the NH group; the NH bond strength becomes weaker in S_1 than in S_0 upon the π−π* electronic excitation. It is worthwhile to note that the NH stretch fundamental of indole in the S_1 state (3478 cm^{-1}) was red-shifted by 47 cm^{-1} from the corresponding one (3525 cm^{-1}) in the S_0 state.[20] The difference in the wavenumber of the NH stretch fundamentals between 7AI and indole in S_0 is smaller than that in S_1. Thus, the difference in the red shifts of the NH stretch fundamentals between 7AI and indole in S_1 is mainly due to a different charge distribution on the NH bond induced by the heteroaromatic N atom of 7AI upon the $\pi\,\pi$* electronic excitation.

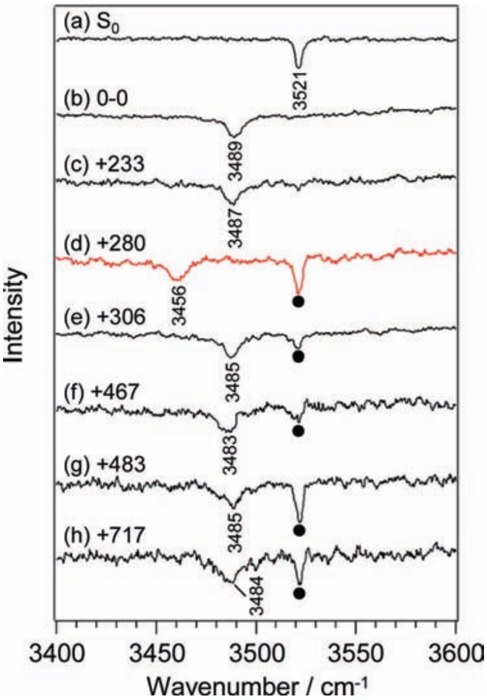

Figure 2. Overview of FDIR spectra of the 7AI monomer (a) in the S_0 state and (b)−(h) in the electronic excited states. The FDIR spectra were focused on the region of the NH stretch fundamentals. The wavenumbers of the excited vibronic bands from the 0−0 band are shown in the figure. The filled circles indicate the dips corresponding to the NH stretch fundamentals in the S_0 state.

Parts b−h of Figure 2 show the FDIR spectra in the excited state obtained by exciting the vibronic bands at +233, +280, +306, +467, +483, and +717 cm^{-1} above the origin band of 7AI. In Figure 2c,e−h, the fluorescence dips are detected within a few wavenumbers as compared with the value of 3489 cm^{-1} obtained by exciting the 0−0 band (Figure 2b). In Figure 2d, however, the fluorescence dip is observed at 3456 cm^{-1}, which is explicitly red-shifted by 33 cm^{-1} with respect to the frequency obtained by exciting the 0−0 band (Figure 2b). It should be noted that no fluorescence dip is detected around 3489 cm^{-1} in Figure 2d, where the NH stretch fundamental is observed by exciting the 0−0 transition. We assign the vibrational band at 3456 cm^{-1} in Figure 2d to the NH stretch fundamental of 7AI.

The two lowest-excited electronic $\pi\pi$* states ^1L_b and ^1L_a exist in 7AI. Kang et al. revealed that the transition moment direction of the +280 cm^{-1} band from the S_1−S_0 origin band is largely rotated as compared with the corresponding one of the origin band by measuring the rotationally resolved electronic spectra.[21] They pointed out the possibility that the difference in the direction of the transition moment between the origin and +280 cm^{-1} band is due to different nature of the electronic state; the origin band belongs to the ^1L_b state but the +280 cm^{-1} band may arise from a S_1/S_2 ($^1L_b/^1L_a$) mixing. Very recently, it was shown that the lowest electronic excited states of 7AI and $7AI(H_2O)_{1,2}$ are ^1L_b and ^1L_a, respectively, by measuring the rotationally resolved electronic spectra and quantum chemical calculations.[22−24] The ^1L_a state has a larger dipole moment than the ^1L_b state, because the ^1L_a state has a character of the charge transfer occurring from the five-membered ring to the six-membered ring. Thus, the lowest electronic excited state is reversed in $7AI(H_2O)_{1,2}$ by bonding of H_2O molecule(s) to 7AI probably due to the large dipole−dipole interaction in the ^1L_a state. This result suggests that the ^1L_b and ^1L_a states are close enough to reverse their energy due to the intermolecular interaction with water molecule(s). A high-level quantum chemical calculation at the CASPT2 level of theory predicts that the energy gap between ^1L_b and ^1L_a in 7AI is only 0.07 eV.[14] On the basis of the results mentioned above, we conclude that the red shift of the NH stretch fundamental observed in Figure 2d (+280 cm^{-1}) from the corresponding one observed in Figure 2b (0−0 band) is due to the $^1L_b/^1L_a$ mixing in the +280 cm^{-1} vibronic band. An alternative assignment for the +280 cm^{-1} band is the origin of the ^1L_a-S_0 transition.[21] However, it is difficult to conclude whether the +280 cm^{-1} band is the $^1L_a/^1L_b$ mixing band or the ^1L_a-S_0 origin at the present stage. The FDIR spectra of the indole monomer were measured by exciting four vibronic bands, 479, 736, 988, and 1414 cm^{-1} above the origin. These bands have ^1L_b and/or ^1L_a characters.[20] The NH stretch fundamentals in the FDIR spectra were detected at the positions within a few wavenumbers. However, in the present study we clearly show the effect of the mixing of ^1L_a with ^1L_b on the shift of the NH stretch fundamental of 7AI that is an analogue of indole. No prominent vibronic band was observed around +280 cm^{-1} in the resonance-enhanced two-photon ionization (RE2PI) spectrum of $7AI(MeOH)_2$.[5,6] As is the case of $7AI(H_2O)_{1,2}$, the lowest electronic excited state of $7AI(MeOH)_2$ may be the ^1L_a state. Therefore, the vibronic pattern observed in the RE2PI spectrum of $7AI(MeOH)_2$ is different from that of 7AI.

The above finding allows for discussing the electronic-state dependence of the ESPT/HT reactions in hydrogen-bonded clusters of 7AI with water and alcohols. The initial state of ESPT/HT in the hydrogen-bonded 7AI clusters has been considered to be ^1L_a, because ^1L_a, which has a large dipole moment originating from charge-transfer character, may be preferentially stabilized due to the dipole−dipole interaction with the solvent molecules as compared with ^1L_b. It has been emphasized that the strong H-bonding interaction of ^1L_a may enhance the ESPT/HT rates for the 7AI clusters, because the potential barrier height along the ESPT/HT coordinate should be lowered by shortening the hydrogen-bond length. The red shift of the NH stretch fundamental in the $^1L_b/^1L_a$ mixing band (Figure 2d) reveals another important point to understand the reactivity of ESPT/HT in the hydrogen-bonded 7AI clusters. On the basis of the experimental results, the component of the ^1L_a state weakens the NH bond strength of 7AI in the $^1L_b/^1L_a$ mixing band. Thus, the NH bond is weaker in the ^1L_a state than in the ^1L_b state. This implies that the potential energy curve along the NH bond length in ^1L_a is shallower than in ^1L_b, which reduces the potential energy barrier height in ^1L_a along the ESPT/HT coordinate when 7AI forms the hydrogen-bonded clusters because the NH bond strength in ^1L_a is weaker than that in ^1L_b. In addition, the acidity of the NH bond is larger for ^1L_a than for ^1L_b because the NH bond is weaker in ^1L_a than in ^1L_b. Therefore, the ^1L_a state has a potential to form stronger intermolecular hydrogen bond(s) than ^1L_b. The reduction of the potential energy barrier for ESPT/HT may promote the reaction. This idea reasonably explains the observation of ESPT/HT in the ^1L_a state of $7AI_2$, $7AI(MeOH)_2$, and $7AI(EtOH)_2$ in the gas phase. To the best of our knowledge, we are first to show the difference in the NH bond strength between ^1L_a and ^1L_b. This information is very important to understand the electronic-state dependence of ESPT/HT in the hydrogen-bonded 7AI clusters.

In summary, we have measured the FDIR spectra of 7AI in the electronic excited states. The $^1L_b/^1L_a$ (S_1/S_2) mixing band observed at +280 cm^{-1} shows the red shift of the NH stretch fundamental as compared with the corresponding ones obtained by exciting the other vibronic bands that have the ^1L_b character. Thus the component of ^1L_a weakens the NH bond. This observation indicates that the potential energy curve along the NH bond length in ^1L_a is shallower than in ^1L_b, which reduces the potential barrier height along the ESPT/HT coordinate in ^1L_a when 7AI forms the hydrogen-bonded clusters. In addition, the strength of the intermolecular hydrogen bond between the NH group and the solvent molecule may be stronger in ^1L_a than in ^1L_b, leading to lower potential barrier height for the ESPT/HT reactions. This idea reasonably explains the observations of ESPT/HT in $7AI_2$, $7AI(MeOH)_2$, and $7AI(EtOH)_2$ in the ^1L_a states.

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