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Remarkable suppression of the excited-state double-proton transfer in the 7-azaindole dimer due to substitution of the dimethylamino group studied by electronic spectroscopy in the gas phase

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Abstract

The fluorescence excitation and dispersed fluorescence spectra of jet-cooled 4-dimethylamino-7-azaindole dimer are recorded to investigate the effect of a substitution of a dimethylamino group into the 4-position of the hydrogen atom of the 7-azaindole on the excited-state double proton transfer (ESDPT). The substitution of the dimethylamino group drastically suppresses the ESDPT reaction.
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1. Introduction

Recently, spectroscopic studies on the multiple-proton transfer reactions in the hydrogen-bonded clusters have been of considerable interests in the mechanism of the reaction and co-operative nature [1]. Dual hydrogen-bonded 7-azaindole dimer ($7AI_2$) is a prototype of the multiple-proton transfer reaction. The excited-state double-proton transfer (ESDPT) in $7AI_2$ has been extensively studied for a long time. Considerable efforts have been devoted to clarify the mechanism of the ESDPT dynamics in the gas phase as well as in the condensed phase [1–23]. Very recently, we obtained new experimental results on the excitonic interaction in the lowest excited electronic state and the mechanism of ESDPT by applying hole-burning [18,19], dispersed fluorescence (DF) [20], and picosecond time-resolved REMPI (resonance enhanced

multiphoton ionization) spectroscopy for jet-cooled $7AI_2$ and its isotopomers [21]. We have provided the final conclusion of the stepwise and concerted mechanism controversy and new features of ESDPT in dual hydrogen-bonded $7AI_2$-*hh* dimer [1]. Now, we can explore more detailed nature of ESDPT in $7AI_2$ and analogues.

The effects of substitution on the ESDPT reaction in $7AI_2$ have been extensively studied for 3-iodo- [24], 3-formyl- [25], 3-cyano- [26], 3-methyl- [27], and 4-dimethyl-amino-7-azaindole [28] dimers in crystal and in solution by Chou and co-workers. These studies provided useful data on the kinetics. However, vibronic-state resolved spectra have not been observed to obtain information about the ESDPT potential energy surfaces (PESs) except for the 3-methyl-7-azaindole dimer ($3MAI_2$) [29]. We reported the fluorescence excitation (FE) spectrum of jet-cooled ($3MAI_2$). We showed that the methyl substitution has little effect on the ESDPT reaction. In this study, we have investigated the ESDPT reaction in jet-cooled 4-dimethyl-amino-7-azaindole ($4DMAAI_2$) or 4-(dimethylamino)-1*H*-pyrrole[2,3-b]pyridine dimer, where the dimethylamino (DMA) group was introduced into the 4-position of the hydrogen atom of the pyridine ring. The electron-donating

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character of the dimethylamino (DMA) group is stronger than the methyl group, therefore a substantial change in the intermolecular hydrogen bonds and the ESDPT PESs can be expected. It is also well known that the DMA group acts as a strong electron-donating group that can open the intramolecular charge transfer (ICT) reaction channel in many electron donor–acceptor systems [30]. In the previous study in solution, 4DMAAI$_2$ was employed as a model compound to investigate the proton transfer coupled with charge transfer reaction [28]. The comparison of the results of 4DMAAI$_2$ with those of 7AI$_2$ studied previously allows us to discuss the effect of the DMA substitution on the intermolecular hydrogen bonds and the ESDPT reaction. We have observed a remarkable suppression of ESDPT induced by the substitution effect.
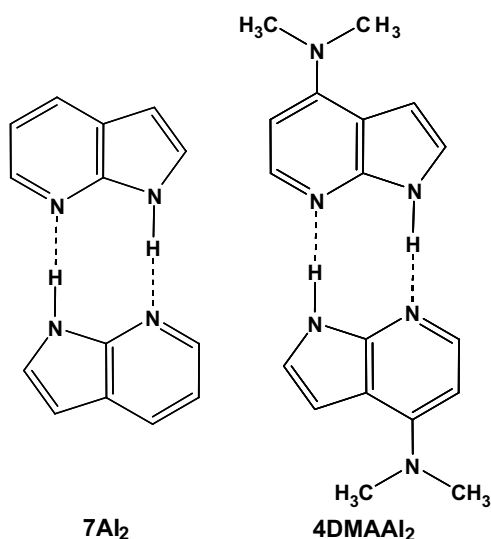
2. Experimental

4-dimehylamino-7-azaindole (4DMAAI) was synthesized according to the procedures described in a literature [31] and purified by flash silica gel column chromatography (eluent: CH$_3$OH/CH$_2$Cl$_2$ = 1:5 (v:v), ^{1}H NMR (300 MHz, CDCl$_3$), δ (ppm) 3.237 (s, 6H), 6.187 (d, J = 5.7 Hz, 1 H), 6.639 (d, J = 3.6 Hz, 1 H), 7.119 (d, J = 3.9 Hz, 1 H), 8.031 (d, J = 5.7 Hz, 1 H), 11.156 (br, 1H, pyrrole NH)). Deuterated 4DMMAI$_2$ dimers were directly generated by introducing a few drops of D$_2$O into the nozzle housing and keeping several hours without operating the pulse valve for supersonic free jet expansion.

The experimental apparatus and procedures have been described elsewhere [18–20]. Briefly, the vacuum chamber was evacuated with a 10-in. diffusion pump backed by an oil rotary pump. The sample mounted on the nozzle housing was heated to 90–120 °C to obtain enough vapor pressure. The backing pressure was kept 2 atm using helium as a carrier gas. A pulsed valve (General Valve Series 9, 0.5 mm diam.) was operated at 10 Hz. The FE spectra were measured by using a frequency-doubled dye-laser (Lumonics HT-1000 and Lumonic Spectrum Master) pumped by a XeCl excimer laser (Lambda Physik Compex 102). The visible or UV emission from the 4DMAAI$_2$ dimer was detected with a photomultiplier (Hamamatsu 1P28A) through a Toshiba Y-43 or a UV-D33S glass filter, respectively. The dispersed fluorescence (DF) spectra were measured by using a monochromator (Spex 1704) equipped with a photomultiplier (Hamamatsu R955). The signal from the photomultiplier was fed into a digital oscilloscope (LeCroy 9310A), and the averaged signal was stored on a PC (NEC PC9801) for further analyses.

3. Results

The FE spectrum of jet-cooled 4DMAAI monomer recorded in the region of 34 050–34 250 cm^{-1} is shown in Fig. 1a. The strongest band at 34 068 cm^{-1} is assigned to the origin of the S$_1$–S$_0$ ($\pi\pi^*$) transition. The origin of 4DMAAI is red-shifted by 571 cm^{-1} with respect to the origin (34 639 cm^{-1}) of the 7AI monomer [6,7]. Two very weak low-frequency bands are detected at 34 106 (0−0+38) and 34 136 (0−0+67) cm^{-1}. These bands may be due to the methyl and/or the DMA torsional motions [32,33]. The spectrum in Fig. 1b was measured by introducing a few drops of D$_2$O into the nozzle housing. The vibronic pattern in Fig. 1b is more complicated than that in Fig. 1a due to the appearance of additional transitions of isotopomers near the origin of the 4DMAAI monomer. The three bands denoted A, B, and C at 34 072, 34 076, and 34 078 cm^{-1} are blue-shifted by 4, 8, and 10 cm^{-1}, respectively, from the origin of 4DMAAI. Relatively small (4–10 cm^{-1}) blue-shifts suggest that the species with the C–D bond(s) as well as the N–D bond are detected. Thus, bands A–C are assigned to the origins of the isotopomers of 4DMAAI.

Fig. 2 displays the FE spectrum measured by detecting the red-shifted fluorescence in the visible region
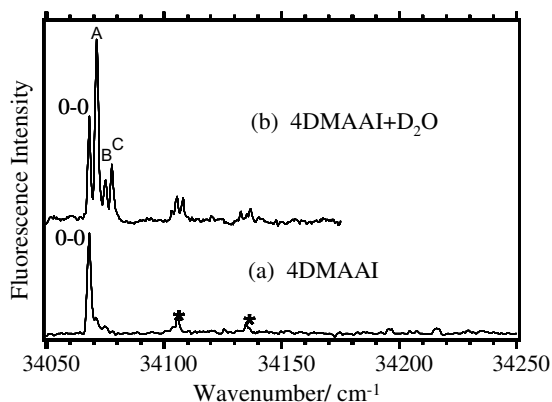

Fig. 1. The FE spectra of jet-cooled (a) undeuterated 4DMAAI and (b) deuterated 4DMAAI monomer. The 0–0 transition of 4DMAAI is detected at 34 068 cm^{-1}. The asterisks indicate low-frequency bands at +38 and +69 cm^{-1} above the 0–0 transition. Three bands, A, B, and C are the 0–0 transitions of the deuterated monomer.
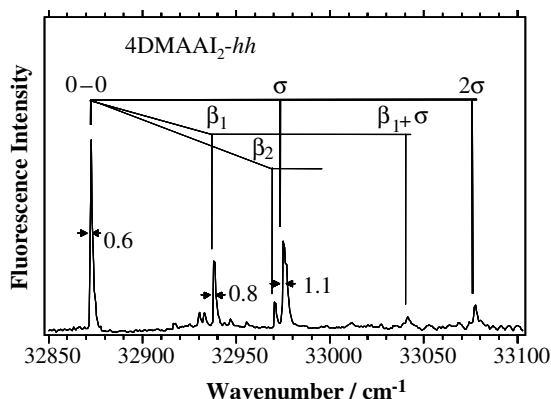
Fig. 2. The FE spectrum of 4DMAAI$_2$-hh measured by detecting fluorescence in the region (>400 nm). The assignments of the intermolecular vibrations and the bandwidths are indicated in the figure.

Fig. 3. The DF spectra of 4DMAAI$_2$-hh measured by exciting the origin at 32 873 cm^{-1} and the 1σ state at 32 975 cm^{-1}. The intensity of fluorescence is corrected against the sensitivity of the detection system.

($\lambda > 400$ nm). The vibronic pattern in Fig. 2 is very similar to those of 7AI$_2$-hh [7] and 3MAI$_2$-hh [29], where several bands due to the intermolecular vibrations are detected. The new system could be assigned to the $S_1 \leftarrow S_0(\pi\pi^*)$ transition of a planar 4DMAAI$_2$-hh dimer having a dual hydrogen-bonded structure. Prominent vibronic bands in Fig. 2 are assigned to the intermolecular bending (β_1 and β_2) and the intermolecular stretching (σ) vibrations and their overtones and combinations by density functional theory calculations at the B3LYP/6-31G** level [34]. Two weak vibronic bands at 57 and 60 cm^{-1} indicated with the asterisks in Fig. 2 may be due to the methyl and/or the DMA torsions [32,33], since such low-frequency modes other than the intermolecular vibrational modes have not been observed in the FE spectra of 7AI$_2$ [18,19] and 3MAI$_2$ [29]. The wavenumbers and the assignments for vibronic bands of 4DMAAI$_2$-hh are listed in Table 1 together with the bandwidths of vibronic bands.

Fig. 3 shows the DF spectra of 4DMAAI$_2$-hh measured by exciting the electronic origin band at 32 873 cm^{-1} and the 1σ band at 32 975 cm^{-1}. The DF spectra exhibit dual fluorescence in the visible region (390–550 nm) and the UV region (300–370 nm). The appearance of largely red-shifted visible fluorescence must be due to the formation

of the double-proton transferred tautomer, while the UV fluorescence arises from the S_1 state of the normal 4DMAAI$_2$-hh dimer. The intensity ratio of the fluorescence from the tautomer to the normal dimer prominently increases when the 1σ state is excited. Thus, it is clear that ESDPT occurs in 4DMAAI$_2$-hh and the excitation of 1σ promotes ESDPT.

We explored the H/D isotope effect on ESDPT by observing the FE spectra by separating the UV fluorescence from the visible fluorescence with glass filters. Fig. 4a, b show the FE spectra of a mixture or the undeuterated 4DMAAI$_2$-hh dimer and its isotopomers. The FE spectrum in Fig. 4a was obtained by detecting fluorescence only in the visible region ($\lambda > 400$ nm), whereas the spectrum in Fig. 4b was detected by monitoring the UV fluorescence ($\lambda \lesssim 400$ nm). Both the vibronic bands of undeuterated and deuterated species are detected in Fig. 4a. These bands have been ascribed to the $S_1 \leftarrow S_0(\pi\pi^*)$ transitions of the 4DMAAI$_2$-hh, 4DMAAI$_2$-hd, and 4DMAAI$_2$-dd dimers,

Table 1
Wavenumbers, bandwidths (FWHM) and assignments for vibronic bands in the FE spectra of 4DMAAI$_2$-hh and 7AI$_2$-hh dimers

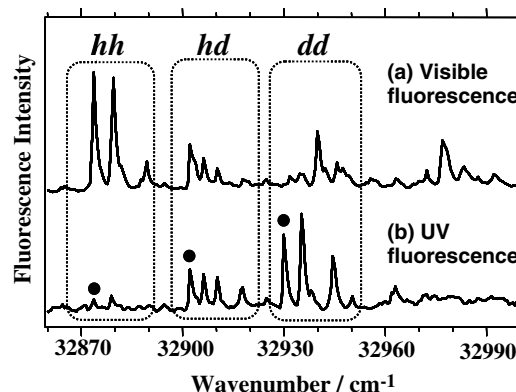| Species	$\Delta\nu$/cm^{-1}	FWHM /cm^{-1}	Assignment
4DMAAI$_2$-hh	0 (32 873)	0.6	origin
	65	0.8	β_1
	98		β_2
	102	1.1	σ
	168		$\beta_1 + \sigma$
	205		2σ
7AI$_2$-hh[a]	0 (32 252)	2.7	origin
	98	2.7	β
	120	10	σ

[a] Taken from Refs. [7,18].

Fig. 4. The FE spectra of deuterated 4DMAAI$_2$ dimer measured by detecting visible fluorescence (a) and UV fluorescence (b). In the figure hh, hd, and dd denote the regions of the origin bands of the isotopomers, where the N–H groups in 4DMAAI$_2$ are undeuterated, singly deuterated, and/or doubly deuterated. The closed circles and the asterisks indicate the origins of the hh, hd, and dd dimers without the C–D bonds and the vibronic bands of the undeuterated dimer, respectively.

where the notations *hd* and *dd* indicate the deuterated species where one of the NH proton and two NH protons are deuterated, respectively. The origins of the 4DMAAI$_2$-*hh*, 4DMAAI$_2$-*hd*, and 4DMAAI$_2$-*dd* dimers, for which no CH hydrogen is deuterated, are observed at 32 872, 32 903, and 32 930 cm^{-1}, respectively. The observation of additional transitions near the each origin band must be due to the formation of the *hh*, *hd*, and *dd* dimers, where the CH hydrogens are deuterated, since three origins were observed in Fig. 1 by the deuteration in addition to the origin of the undeuterated 4DMAAI monomer.

4. Discussion

The vibronic pattern in the FE spectrum of 4DMAAI$_2$-*hh* is similar to those of 7AI$_2$-*hh* and 3MAI$_2$-*hh* [18–20,29]. The observation of the tautomer fluorescence in the DF spectrum unambiguously shows the occurrence of the ESDPT reaction leading the tautomer. We observed the remarkable narrowing of the bandwidths of the intermolecular vibrational bands in the FE spectrum of 4DMAAI$_2$-*hh*. The drastic decrease in the bandwidths in the FE spectrum indicates that the ESDPT reaction is suppressed in 4DMAAI$_2$-*hh*. The ESDPT rate for 4DMAAI$_2$-*hh* has not been directly determined in the present study, but the comparison of the bandwidths in the FE spectrum of 4DMAAI$_2$-*hh* together with the ESDPT times of 7AI$_2$-*hh* [21] allows us to predict the relative ESDPT rate for 4DMAAI$_2$-*hh*. The bandwidth of the 1σ state of 4DMAAI$_2$-*hh* (1.1 cm^{-1}) is about one order different from the corresponding bandwidth (10 cm^{-1}) of 7AI$_2$-*hh* [7]. In the previous study of 7AI$_2$-*hh* we determined the ESDPT time for the 1σ state to be 0.86 ± 0.3 ps [21]. The ESDPT time for the 1σ state of 4DMAAI$_2$-*hh* is estimated to be $\sim$9 ps.

The DMA group is a strong electron-donating group, therefore the substitution of the DMA group may provide substantial electronic effect on the intermolecular double N–H $\cdots$ N hydrogen bonds. It should be noted that the red-shift of 1195 cm^{-1} for 4DMAAI$_2$-*hh* is about a half that of the corresponding red-shift of 2387 cm^{-1} for 7AI$_2$-*hh* [21]. This observation suggests that the double hydrogen-bond strength is substantially weakened in the S$_1$ state by the DMA substitution in 4DMAAI$_2$-*hh*. In a simple one-dimensional model, the barrier height and the tunneling distance increase when the hydrogen-bond is weakened. Therefore, the smaller red-shift for 4DMAAI$_2$-*hh* is consistent with the reduction of the ESDPT rate.

The H/D kinetic isotope effect (KIE) on ESDPT was extensively investigated for 7AI$_2$. The ESDPT reaction rate was remarkably reduced by the deuteration of the NH hydrogen(s). The ratios of the reaction rates were determined to be $k(hd)/k(hh) = 1/60$ and $k(dd)/k(hh) = 1/710$ [20]. It is clear from Fig. 4 that the first deuteration of NH decreases the intensity of the visible fluorescence and the second deuteration of NH further reduces the intensity of the visible fluorescence. The H/D isotope effect on the

vibronic pattern in Fig. 4 suggests that the trend of KIE in 4DMAAI$_2$ is similar to that in 7AI$_2$ [20]. The results obtained from this study provide insights into the ESDPT reaction in dual hydrogen-bonded dimers with rather weak hydrogen-bond strength.

In summary, the electronic spectra of jet-cooled 4DMAAI$_2$-*hh* dimer and its isotopomers have been measured to investigate the effect of the DMA substitution on the ESDPT reaction. The bandwidth of the intermolecular stretching vibration (1σ) of 4DMAAI$_2$-*hh* (1.1 cm^{-1}) is almost one order narrower than the corresponding bandwidth of 7AI$_2$-*hh* (10 cm^{-1}). The spectral red-shift (1195 cm^{-1}) in the FE spectrum of 4DMAAI$_2$-*hh* induced by dimerization is found to be only half of the corresponding shift (2387 cm^{-1}) of 7AI$_2$, suggesting that dual hydrogen bond in S$_1$ is weakened as compared with that of 7AI$_2$-*hh*.

The charge transfer (CT) emission was observed from 4DMMAI$_2$ in the polar solution, while it was absent in the nonpolar solution. In the isolated jet-cooled conditions no CT emission has been observed. The PES of the CT state may be located substantially higher than that of the S$_1(\pi\pi^*)$ state.

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