

Heavy mass effect on excited-state double-proton transfer in the 7-azaindole dimer by Cl substitution

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Abstract

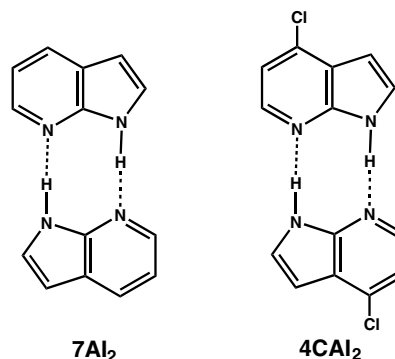
The measurement of the electronic spectra of jet-cooled 4-chloro-7-azaindole dimer (4CAI₂) revealed that the Cl substitution substantially suppresses the excited-state double-proton transfer (ESDPT). Quantum chemistry calculation at the CIS level suggested that the change in the intermolecular stretching mode, which promotes ESDPT, is important for the suppression of ESDPT.

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1. Introduction

The 7-azaindole dimer (7AI₂) has long been recognized as a prototype model system of the DNA base pairs [1]. Many experimental and theoretical studies have been carried out to investigate excited-state double-proton transfer (ESDPT) reaction dynamics in 7AI₂ in the condensed phase and in the gas phase [1–15]. Although the multi-dimensional character of proton tunneling is well recognized [14–16], one-dimensional picture has been still used to interpret the experimental results in the doubly hydrogen-bonded dimers, since one-dimensional model can qualitatively explain the experimental results and it is not easy to obtain multi-dimensional potential energy surfaces. The experimental results that show multi-dimensional nature of proton tunneling originating from the substitution are scarce in the hydrogen dimers, and a model system is anticipated. A good method to investigate the multi-dimensional nature of proton tunneling is the substitution of atom(s) or a functional group to the hydrogen atom of the chromophore.

We have demonstrated that the substitution of a heavy atom such as the Cl or Br atom provides electronic and/or the mass effects on intramolecular proton tunneling in tropolone and 9-hydroxyphenalenone [17,18]. In this communication, we report the ESDPT reaction in jet-cooled 4-chloro-7-azaindole dimer (4CAI₂) and its isotopomers, where the Cl atom is introduced into the pyridine ring of 7AI. The Cl atom acts as an electron-withdrawing group in the S₀ state, while it introduces a mass effect on the normal coordinates. Therefore, the substitution of Cl may provide the electronic and/or mass effects on ESDPT. The comparison of the result of 4CAI₂ with that of 7AI₂ in



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combination with quantum chemistry calculations may allow us to discuss the effect of the Cl substitution on the ESDPT reaction. It has been found that the substitution of the Cl atom into the 4-position of the hydrogen of 7AI substantially suppresses ESDPT in the S_1 state. The origin of the suppression of ESDPT has been discussed with the aid of theoretical calculations on the structure and the potential energies for the S_1 state.

2. Experimental

4CAI was synthesized according to the procedures described in the literatures [19,20] and purified by repeated recrystallization from dichloromethane solution ($^1\text{H NMR}$ (300 MHz, CDCl_3), δ (ppm) 6.608 (d, $J = 3.6$ Hz, 1H), 7.124 (d, $J = 5.1$ Hz, 1H), 7.414 (d, $J = 3.3$ Hz, 1H), 8.215 (d, $J = 5.4$ Hz, 1H), 11.748 (br, 1H, pyrrole NH)). Deuterated 4CAI₂ was directly generated by introducing a few drops of D₂O into the nozzle housing.

The experimental apparatus and procedures have been described previously [9–13]. Briefly, the vacuum chamber was evacuated with a 10 in. diffusion pump backed by an oil rotary pump. The sample mounted in the nozzle housing was heated to 90 °C to obtain enough vapor pressure to measure the electronic spectrum. 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 fluorescence excitation (FE) spectra were measured by using a frequency-doubled dye-laser (Lumonics HT-1000 and Lumonics HD-300) pumped by a XeCl excimer laser (Lambda Physik Compex 102). Only the visible emission was detected with a Toshiba Y-47 glass filter and a photomultiplier (Hamamatsu 1P28A). The dispersed fluorescence (DF) spectra were measured by using a monochromator (Spex 1704) equipped with a photomultiplier (Hamamatsu R955). The signal from the photomultiplier (Hamamatsu 1P28A) was fed into a digital oscilloscope (LeCroy 9310A), and the averaged signal was stored on a PC (NEC PC9801) for further analyses. The calibration of the detection sensitivity was carried out with a halogen lamp (USIO Inc. JPD-100-500CS) to obtain the corrected DF spectra. The intensities of the DF spectra were converted to the relative photon number.

3. Results and discussion

The FE spectrum of the undeuterated 4CAI₂-*hh* dimer near the electronic origin of the S_1 - S_0 transition is shown in Fig. 1, where a Toshiba Y-47 filter is used to detect only the red-shifted fluorescence ($\lambda > 420$ nm). The vibronic pattern in the FE spectrum of 4CAI₂-*hh* is similar to that of 7AI₂-*hh* [4]; the bandwidth remarkably depends on the vibronic state, revealing that the vibrational-mode selective ESDPT occurs. Prominent bands in Fig. 1 are assigned to the intermolecular bending (β_1 and β_2), the intermolecular stretching (σ) vibrations, and their overtones and combinations (Fig. 1 and Table 1) by analogy with the vibronic

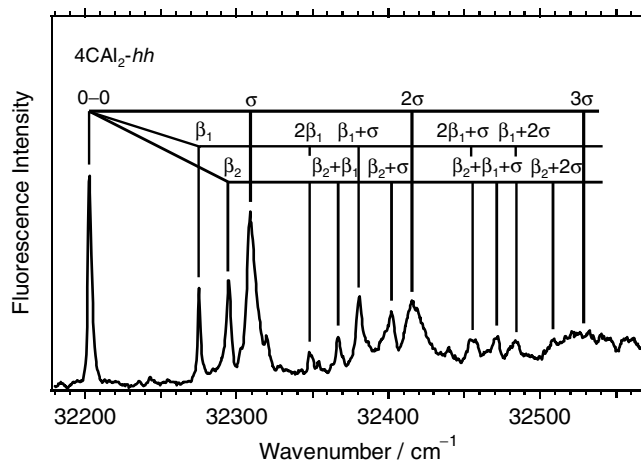


Fig. 1. FE spectrum of jet-cooled 4CAI₂-*hh* dimer measured with a Toshiba Y-47 glass filter to detect only the red-shifted visible fluorescence.

patterns in the spectra of 7AI₂ [4,9] together with the normal mode calculations. The three lowest frequency intermolecular vibrational modes in S_1 of 4CAI₂-*hh* are β_1 , β_2 , and σ , for which frequencies are calculated to be 53.3, 81.8, and 91.6 cm^{-1} , respectively, with CIS method. These modes may correspond to the vibrations at 72, 91, and 105 cm^{-1} in the FE spectrum.

The vibronic patterns in the FE spectra of deuterated isotopomers 4CAI₂-*hd* and 4CAI₂-*dd* are similar to that of undeuterated 4CAI₂-*hh* (Fig. 2), but the widths of the corresponding bands of the deuterated isotopomers are much narrower than the undeuterated dimer, implying that ESDPT proceeds via quantum mechanical tunneling. The assignments for the intermolecular vibrations are also compiled in Table 1.

The vibrational frequencies of the 4CAI₂ dimer, for example, 72, 91, and 105 cm^{-1} assigning to $1\beta_1$, $1\beta_2$, and 1σ of 4CAI₂-*hh* respectively, are slightly reduced as compared with the corresponding frequencies of 98 and 120 cm^{-1} for 1β and 1σ of 7AI₂-*hh* [4]. The decrease in the frequencies of 4CAI₂-*hh* may be mainly due to the mass effect.

It should be noted that the bandwidths of the origin and 1σ of 4CAI₂-*hh*, are determined to be 2.0 and 5.0 cm^{-1} , is narrower than the corresponding ones of 7AI₂-*hh* (2.7 and 10 cm^{-1}) [4,9,12]. The bandwidth of the 2σ state of 4CAI₂-*hh* is 10.0 cm^{-1} , while the corresponding bandwidth of 7AI₂-*hh* is 30 cm^{-1} [4]. The bandwidths of 1σ in 4CAI₂-*h*d* and 4CAI₂-*hd** are 1.8 cm^{-1} . These values are also much narrower than the corresponding values of 4.1 and 2.4 cm^{-1} of 7AI₂-*h*d* and 7AI₂-*hd**. The prominent narrowing in the bandwidths indicates that the ESDPT reaction is suppressed in 4CAI₂-*hh*. The ESDPT rate for the excitation of the 1σ state in S_1 of 4CAI₂-*hh* is estimated to be roughly a half that of 7AI₂-*hh*, for which the ESDPT rate has been determined to be $(0.86 \pm 0.3 \text{ ps})^{-1}$ [13]. The excitation of the 2σ state of 4CAI₂-*hh* enhances ESDPT, however, the increase of the ESDPT rate is not prominent as compared with that of 7AI₂-*hh*. The bandwidth of the 1β state is

Table 1
Wavenumbers, bandwidths and assignments for vibronic bands in FE spectra of 4CAI_2^a

Species	$\Delta\nu/\text{cm}^{-1}$	Bandwidth/ cm^{-1}	Assignments
$4\text{CAI}_2\text{-}hh$	0 (32202)	2.1	Origin
	72	1.2	β_1
	91	3.3	β_2
	105	5.1	σ
	144		$2\beta_1$
	163	6.4	$\beta_1 + \beta_2$
	177	7.3	$\beta_1 + \sigma$
	198		$\beta_2 + \sigma$
	211	18.4	2σ
	235		$2\beta_1 + \beta_2$
249		$2\beta_1 + \sigma$	
$4\text{CAI}_2\text{-}h^*d$	0 (32242)	1.6	Origin
	70		β_1
	90		β_2
	106	1.8	σ
	176		$\beta_1 + \sigma$
	196		$\beta_2 + \sigma$
	213	2.5	2σ
	247		$2\beta_1$
	303		$\beta_2 + 2\sigma$
	318		3σ
$4\text{CAI}_2\text{-}hd^*$	0 (32261)	1.3	Origin
	70		β_1
	91		β_2
	108	1.8	σ
	179		$\beta_1 + \sigma$
	199		$\beta_2 + \sigma$
	215	2.5	2σ
	280		$\beta_1 + 2\sigma$
	303		$\beta_2 + 2\sigma$
	318		3σ
$4\text{CAI}_2\text{-}dd$	0 (32293)	1.5	Origin
	71	1.5	β_1
	91	1.5	β_2
	108	1.5	σ
	179	1.5	$\beta_1 + \sigma$
	200	1.5	$\beta_2 + \sigma$
	217	1.7	2σ
	284		$2\beta_1$
	307		$\beta_2 + 2\sigma$
	324	2.5	3σ

^a $\Delta\nu$ is the relative shift from the electronic origin band. The number in the parentheses is the wavenumber of the electronic origin. Bandwidth is full width at half maximum (FWHM).

1.2 cm^{-1} ; the ESDPT rate for the excitation of 1β may slightly decrease the ESDPT rate.

Two transition systems are observed in the FE spectrum of $4\text{CAI}_2\text{-}hd$. By analogy with the FE spectrum of $7\text{AI}_2\text{-}hd$. The two systems are assigned to the transitions from S_0 of $7\text{AI}_2\text{-}hd$ to S_1 of $4\text{CAI}_2\text{-}h^*d$ and $4\text{CAI}_2\text{-}hd^*$, where one of the monomer moiety is excited. The separation of the two origins is 19 cm^{-1} , which is similar to the corresponding value of 21 cm^{-1} [9]. The S_1 state of the normal dimer of 7AI_2 has been classified as the weak coupling case of the exciton theory [15], and the excitonic splitting of the zero-point level was estimated to be $2\sim 3\text{ cm}^{-1}$ [21]. A similar value of the difference in the zero-point energies in the

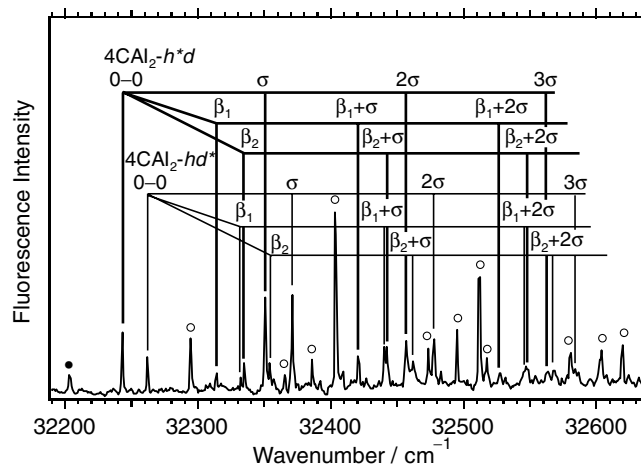


Fig. 2. FE spectrum of $4\text{CAI}_2\text{-}hd$ measured with a Toshiba Y-47 glass filter. The solid and open circles indicate the bands of $4\text{CAI}_2\text{-}hh$ and $4\text{CAI}_2\text{-}dd$, respectively.

h^*d and hd^* dimers reflects that the strength in the excitonic interaction in $4\text{CAI}_2\text{-}hh$ is similar to that in $7\text{AI}_2\text{-}hh$.

Fig. 3 displays the DF spectrum of $4\text{CAI}_2\text{-}hh$ measured by exciting the electronic origin bands at 32203 cm^{-1} , where the fluorescence intensity is corrected for the sensitivity of the optical system and converted to the relative photon number. The UV and visible dual fluorescence is clearly observed in Fig. 3. The largely red-shifted visible fluorescence must be due to the double-proton transferred tautomer. The weak fluorescence in the UV region arises from $4\text{CAI}_2\text{-}hh$. It should be noted that the UV fluorescence from the $7\text{AI}_2\text{-}hh$ is absent in a supersonic jet condition, although it appears in the deuterated dimers [12], in agreement with the finding that the ESDPT reaction is suppressed in 4CAI_2 from the narrower bandwidths in the FE spectra than those of the 7AI_2 dimer.

It is clear that ESDPT is suppressed by the Cl substitution. However, it is difficult to obtain further information of the ESDPT potential from experiment. Therefore, we investigated the origin of the suppression of ESDPT with the aid of quantum chemical calculations. The full geometry optimizations were carried out by HF calculation for

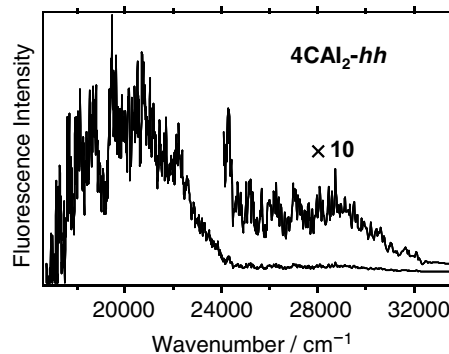


Fig. 3. DF spectrum of $4\text{CAI}_2\text{-}hh$ by exciting the origin. The intensity of fluorescence is corrected against the sensitivity of the detection system and converted to relative photon number.

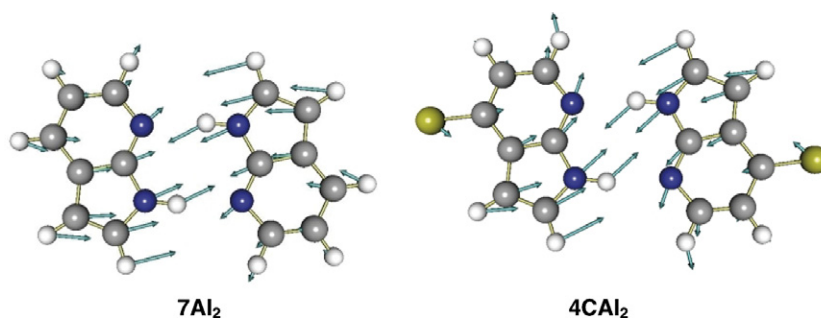


Fig. 4. The σ modes of 7Al_2 - hh and 4CAI_2 - hh in the S_1 state, where the displacements of the atoms are shown by the arrows.

the S_0 state and CIS calculation for the S_1 state, respectively, by using a GAUSSIAN 2003 program package [22]. The basis sets used for atoms which construct the intermolecular hydrogen bonds $\text{N}-\text{H}\cdots\text{N}$ were the 6-31++G(d, p) level, while the 6-31G(d, p) level basis sets were used for the other atoms. The binding energies (BE) in the S_0 state was obtained at B3LYP/6-31+G(d, p) level with the corrections of the zero-point energy (ZPE) and the basis set superposition error (BSSE). The normal coordinate calculations of intermolecular modes are also carried out for the S_1 state.

The geometrical parameters in the stable structures are very similar between 4CAI_2 - hh and 7Al_2 - hh in the S_0 state. The ZPE and BSSE corrected binding energy for the 4CAI_2 - hh normal dimer in the S_0 state is calculated to be $12.20 \text{ kcal mol}^{-1}$, which is very similar to a value of $12.12 \text{ kcal mol}^{-1}$ for 7Al_2 - hh , suggesting that the Cl substitution does not significantly influence the intermolecular hydrogen-bonding interactions in the S_0 state.

The geometrical parameters in the S_1 state of the 4CAI_2 - hh normal dimer are calculated and compared with those of 7Al_2 - hh . The average $\text{N}\cdots\text{H}$ distance and the $\angle\text{N}-\text{H}\cdots\text{N}$ angle are 2.045 \AA and 172.1° , respectively, for 4CAI_2 - hh , while the corresponding values for 7Al_2 - hh are 2.043 \AA and 172.5° , respectively. Thus, the substitution of the Cl atom does not significantly change the geometry around the intermolecular hydrogen bonds. The potential barrier heights for ESDPT are calculated to be 15.7 and $15.5 \text{ kcal mol}^{-1}$ for 4CAI_2 and 7Al_2 , respectively, while the relative energies of the tautomer to the normal dimer are calculated to be -2.5 and $-3.9 \text{ kcal mol}^{-1}$ for 4CAI_2 and 7Al_2 , respectively. Thus, the Cl substitution slightly increases the potential barrier, while the energy difference between the normal dimer and the tautomer decreases. These changes may contribute to the suppression of ESDPT, however, the calculated changes in the potential energies seems to be too small to explain the substantial suppression of ESDPT.

The investigation of the intramolecular proton tunneling in substituted tropolone and 9-hydroxyphenalenone molecules showed that the heavy atom substitution changes the normal coordinates and influences the tunneling splitting [16–18]. Since the σ mode plays a crucial role in ESDPT of 7Al_2 - hh , we calculated the σ mode in the S_1 state of 4CAI_2 - hh and compared with that of 7Al_2 - hh (Fig. 4). It

is clear that the displacements of the atoms in the σ mode of 4CAI_2 - hh are substantially different from those in the σ mode of 7Al_2 - hh . The displacements of the atoms in the $\text{N}-\text{H}\cdots\text{N}$ moiety occur linearly along the $\text{N}-\text{H}\cdots\text{N}$ bond in the σ mode of 7Al_2 . The two monomer units approach each other due to the motions of the symmetric stretching, which may reduce the tunneling distance and the barrier height. Therefore, the excitation of 1σ of 7Al_2 promotes ESDPT [4,12,23]. However, the directions of the displacements of the four nitrogen atoms and the two NH hydrogen atoms, which participate in the intermolecular hydrogen bond, substantially deviate from the direction of the hydrogen bond. Therefore, the excitation of 1σ of 4CAI_2 - hh cannot effectively couple with the ESDPT coordinates as compared with the case of 7Al_2 - hh , which may be responsible for the suppression of ESDPT by the Cl substitution. It is clear that the change in the σ mode of 4CAI_2 arise from the heavy mass effect of the Cl atom.

To our best of knowledge, the present result is the first observation of the heavy mass effect on the intermolecular modes in the doubly hydrogen-bonded system that undergoes ESDPT. Thus, the suppression of the ESDPT in 4CAI_2 can be explained by the multidimensional nature of proton tunneling; the motions of heavy nuclei efficiently couples with the NH stretching motions that may change the ESDPT reaction path on a multidimensional potential energy surface.

In summary, the ESDPT reaction in 4CAI_2 - hh has been found to be substantially suppressed. The Cl substitution influences both the σ mode and the ESDPT potential of 7Al_2 . The former effect is the mass effect, while the latter one is the electronic effect. Both effects may contribute to the suppression of ESDPT. In this work we pointed out the importance of the mass effect on ESDPT for the first time. In other words, the multi-dimensional nature in the ESDPT reaction is revealed by the heavy atom substitution.

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References

- [1] C.A. Taylor, M.A. El-Bayoumi, M. Kasha, Proc. Natl. Acad. Sci. USA 63 (1969) 253.
- [2] K.C. Ingham, M. Abu-Elgheit, M.A. El-Bayoumi, J. Am. Chem. Soc. 93 (1971) 5023.
- [3] K.C. Ingham, M.A. El-Bayoumi, J. Am. Chem. Soc. 96 (1974) 1674.
- [4] K. Fuke, K. Kaya, J. Phys. Chem. 93 (1989) 614.
- [5] A. Douhal, S.K. Kim, A.H. Zewail, Nature 378 (1995) 260.
- [6] S. Takeuchi, T. Tahara, J. Phys. Chem. A 102 (1998) 7740.
- [7] D.E. Folmer, L. Poth, E.S. Wisniewski, A.W. Castleman Jr., Proc. Natl. Acad. Sci. USA 96 (1999) 12980.
- [8] J. Catalan, P. Perez, J.C. del Valle, J.L.G. de Paz, M. Kasha, Proc. Natl. Acad. Sci. USA 101 (2004) 419.
- [9] K. Sakota, A. Hara, H. Sekiya, Phys. Chem. Chem. Phys. 6 (2004) 32.
- [10] A. Hara et al., J. Phys. Chem. A 108 (2004) 10789.
- [11] K. Sakota, H. Sekiya, J. Phys. Chem. A 109 (2005) 2718.
- [12] K. Sakota, H. Sekiya, J. Phys. Chem. A 109 (2005) 2722.
- [13] K. Sakota, C. Okabe, N. Nishi, H. Sekiya, J. Phys. Chem. A 109 (2005) 5245.
- [14] H. Sekiya, K. Sakota, Bull. Chem. Soc. Jpn. 79 (2006) 373.
- [15] N. Kanamaru, J. Mol. Spectrosc. 225 (2004) 55.
- [16] H. Sekiya, in: T. Miyazaki (Ed.), Atom Tunneling Phenomena in Physics, Chemistry and Biology, Springer, Berlin, 2004, p. 201.
- [17] T. Tsuji, H. Sekiya, Y. Nishimura, R. Mori, A. Mori, H. Takeshita, J. Chem. Phys. 97 (1992) 6032.
- [18] K. Nishi, H. Sekiya, H. Hamabe, Y. Nishimura, T. Mochida, T. Sugawara, Chem. Phys. Lett. 257 (1996) 499.
- [19] B.A.J. Clark, J. Parrick, J. Chem. Soc. Perkin Trans. 1 (1974) 2270.
- [20] S.W. Schneller, J.K. Luo, J. Org. Chem. 45 (1980) 4045.
- [21] K. Sakota, H. Sekiya, unpublished results.
- [22] M.J. Frish et al., GAUSSIAN03, Revision B.03. Gaussian, Inc., Pittsburgh, PA, (2003).
- [23] N. Sato, S. Iwata, J. Chem. Phys. 89 (1988) 2932.