2718 J. Phys. Chem. A **2005,** *109,* 2718−2721

Excited-State Double-Proton Transfer in the 7-Azaindole Dimer in the Gas Phase. 1. Evidence of Complete Localization in the Lowest Excited Electronic State of Asymmetric Isotopomers

Kenji Sakota and Hiroshi Sekiya*

Department of Chemistry, Faculty of Sciences, Kyushu University,
6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan

Received: September 17, 2004; In Final Form: December 27, 2004

The fluorescence excitation and UV−UV hole-burning spectra are measured for deuterated 7-azaindole dimers ($7AI_2$), $7AI_2$-(h_Nh_C)-(h_Nd_C), $7AI_2$-(d_Nh_C)-(h_Nd_C), $7AI_2$-(h_Nh_C)-(d_Nh_C), and $7AI_2$-(h_Nh_C)-(d_Nd_C), where *h* and *d* indicate the H and D atoms, respectively, and the subscripts *N* and *C* designate the imino N−H (or N−D) and C−H (or C−D) bonds at the 3-position. The transitions of the isotopomers have been consistently assigned. It has been found that the excitation is completely localized on one monomer unit in the lowest excited electronic state of asymmetrical $7AI_2$ dimers except for $7AI_2$-(d_Nh_C)-(h_Nd_C) in which the excitation is delocalized over the dimer. This indicates that the undeuterated $7AI_2$ dimer and its isotopomers that belong to the C_{2h} symmetry point group should be treated by the weak coupling limit of the exciton theory.

Introduction

The doubly hydrogen-bonded 7-azaindole dimer ($7AI_2$) is a prototypical system that exhibits the excited-state double-proton transfer (ESDPT) reaction.[1−20] The $7AI_2$ dimer has been regarded as a model system for the study of the photoinduced mutation in the DNA base-pairs. The investigation of the ESDPT reaction in $7AI_2$ may provide information about the mechanism of the mutation of DNA induced by UV radiation.

Recent studies of $7AI_2$ concentrated on the ESDPT mechanism; that is, ESDPT occurs sequentially via an intermediate state in the stepwise mechanism,[8,9,13,14,17] whereas two protons simultaneously transfer in the concerted mechanism.[12,18] We will discuss the mechanism of ESDPT in the successive paper (Part 2).[21] In the present study we focus on the geometry and the exciton resonance interaction in the electronic excited state of $7AI_2$. The geometry and potential energy surface of the electronic excited state of $7AI_2$ were calculated to investigate the mechanism of ESDPT.[22−24] Douhal et al. concluded that the excitation is localized on a monomer moiety and ESDPT proceeds via the stepwise mechanism.[22] However, Catalan et al. proposed that the excitation should be delocalized on $7AI_2$ and the ESDPT proceeds via the concerted mechanism.[23] These results indicate that the characterization of the initially excited state is crucial to clarify the mechanism of the ESDPT reaction in $7AI_2$.

To characterize the initially excited state of the normal dimer, we have measured the UV−UV hole-burning spectra of deuterated $7AI_2$ dimers $7AI_2$-(h_Nh_C)-(h_Nd_C), $7AI_2$-(d_Nh_C)-(h_Nd_C), $7AI_2$-(h_Nh_C)-(d_Nh_C), and $7AI_2$-(h_Nh_C)-(d_Nd_C). Throughout this paper, notations *h* and *d* indicate the H and D atoms, respectively, and the subscripts *N* and *C* discriminate the dimers containing the imino N−H (or N−D) bond and the C−H (or C−D) bond at the 3-position, respectively. The comparison of the hole-burning spectra of symmetrical and asymmetrical dimers enabled us to answer the question whether the lowest excited electronic state of $7AI_2$ should be treated by a strong coupling case or a weak coupling case of the exciton theory.[25−29]

Previously, we reported that the lowest excited state of $7AI_2$-(h_Nh_C)-(d_Nh_C) is localized on one of the monomer units.[18] However, it has not been whether the two excited states of $7AI_2$-(h_Nh_C)-(d_Nh_C) are partially localized or completely localized. When the excitation is completely localized, proton transfer and deuteron transfer may occur initially followed by photoexcitation of $7AI_2$-*h***d* and $7AI_2$-*hd**, respectively. Thus, the investigation of isotope-selective and electronic-state selective ESDPT reaction promises to obtain new information on the excite-state dynamics. We will report the dispersed fluorescence spectra of $7AI_2$ and deuterated $7AI_2$ dimers in the successive paper (Part II), where clear evidence for the occurrence of double-deuteron transfer or proton/deuteron transfer in $7AI_2$-(d_Nh_C)-(d_Nh_C) and $7AI_2$-(h_Nh_C)-(d_Nh_C) has been obtained.[21]

Experimental Procedures

The experimental apparatus used in this study has been described elsewhere.[18,30] Briefly, the fluorescence excitation (FE) spectrum was measured for jet-cooled samples using helium as a carrier gas. The sample mounted in the nozzle housing was heated to 80 °C. The backing pressure was 2 atm. The pulsed valve (General Valve Series 9, 0.5 mm diameter) was operated at 10 Hz. The FE spectra were measured by using a frequency-doubled dye-laser (Lumonics HD-300 and Lumonics HT-1000) pumped by a second harmonic of the Nd^{3+}:YAG laser (Spectra Physics GCR 230), and only visible emission was detected with a Toshiba Y45 glass filter. The UV−UV hole-burning spectra were measured by using a frequency-doubled dye-laser (Spectra Physics PDL-3 and Inrad Autotracker III) pumped by a second harmonic of the Nd^{3+}:YAG laser (Spectra Physics GCR 18) as a pump laser. 7AI was purchased from TCI and was used without purification. Deuterated $7AI_2$ were produced by introducing a few drops of D_2O into the nozzle housing.

---

* To whom correspondence should be addressed. E-mail: hsekiscc@mbox.nc.kyushu-u.ac.jp.

10.1021/jp045773e CCC: $30.25

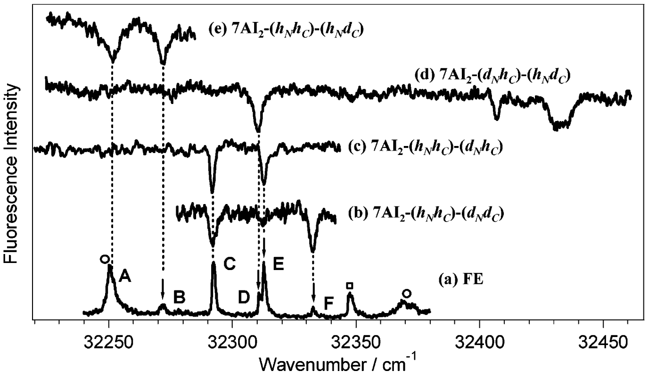

Figure 1. FE spectrum of the undeuterated and deuterated 7AI$_2$ dimers obtained by monitoring the visible emission (a) and the UV−UV hole-burning spectra obtained by probing fluorescence from bands (b) **F**, (c) **E**, (d) **D**, and (e) **B**, respectively. The bands due to 7AI$_2$-(h_Nh_C)-(h_Nh_C) and 7AI$_2$-(d_Nh_C)-(d_Nh_C) are marked with the open circles and the open square, respectively.

Results and Discussion

A. FE and Hole-Burning Spectra. Figure 1a shows the FE spectrum of a mixture of undeuterated and deuterated 7AI$_2$ dimers near the 0−0 region of the transition from the electronic ground state to the lowest excited electronic state. The bands due to the introduction of D$_2$O are denoted with **A**−**F**. Bands **A**, **B**, **D**, and **F** have not been detected in the FE spectrum reported previously.[18] These bands were detected by the following procedures. A few drops of D$_2$O were introduced into the nozzle housing and the sample containing D$_2$O was kept in the nozzle housing for 2 days without operating the nozzle. In 2 days the pulse valve was operated for several hours to remove the D$_2$O and H$_2$O molecules. On the other hand, the FE spectrum in ref 18 was observed in several hours after the introduction of a few drops of D$_2$O. The deuteration may more easily occur in the N−H bond than in the C−H bonds owing to a larger pK_a value for the N−H bond. Thus, we assigned bands **A**, **B**, **D** and **F** to 7AI$_2$ dimers containing the C−D bond. It is known that the C−D deuteration preferentially occurs at the 3-position.[12b] The vibronic bands due to the dimers involving two C−D bonds in the monomer are not observed in the FE spectrum in Figure 1a.

Parts b−e of Figure 1 show the UV−UV hole-burning spectra near the 0−0 region obtained by probing fluorescence from the bands indicated by the arrows in Figure 1a. By comparing the vibronic patterns in Figure 1b−e we identified three pairs of transitions (**A**, **B**), (**C**, **E**), (**C**, **F**), where two transitions are overlapping in band **C**. In contrast with the spectra in Figure 1b,c,e only one band **D** is observed in Figure 1d near the 0−0 region. The predicted structures of deuterated dimers under our experimental conditions are illustrated in Figure 2.

Among the observed three pairs of bands, bands **C** and **E** in Figure 1c have been identified in the previous work. Bands **C** and **E** are due to the transitions from the ground state 7AI$_2$-(h_Nh_C)-(d_Nh_C) (7AI$_2$-*hd* in ref 18) to the zero-point levels of the two lowest excited electronic state of 7AI$_2$-(h_Nh_C)*-(d_Nh_C) (7AI$_2$-*h*d* in ref 18) and 7AI$_2$-(h_Nh_C)-(d_Nh_C)* (7AI$_2$-*hd** in ref 18), respectively.

In Figure 1c a fluorescence dip is detected at the same position as band **C** that has been assigned to the transition to 7AI$_2$-(h_Nh_C)*-(d_Nh_C). In Figure 1c a fluorescence dip is also observed at the same positions as band **C**, whereas the separation of **C** and **F** (41 cm^{-1}) is about twice that of **C** and **E** (21 cm^{-1}). We attributed two bands **C** and **F** to the 0−0 transitions from 7AI$_2$-(h_Nh_C)-(d_Nd_C) to the lowest excited electronic states of 7AI$_2$-(h_Nh_C)*-(d_Nd_C) and 7AI$_2$-(h_Nh_C)-(d_Nd_C)*, respectively. Thus, two electronic transitions to 7AI$_2$-(h_Nh_C)*-(d_Nh_C) and 7AI$_2$-(h_Nh_C)*-(d_Nd_C) are overlapping in band **C** observed in the FE spectrum because 7AI−(h_Nh_C) exists as a common monomer unit in 7AI$_2$-(h_Nh_C)*-(d_Nh_C) and 7AI$_2$-(h_Nh_C)*-(d_Nd_C). Band **F** is largely blue-shifted (41 cm^{-1}) from band **C**. This large blue-shift is due to the existence of a C−D bond as well as an N−D bond in the excited monomer unit.

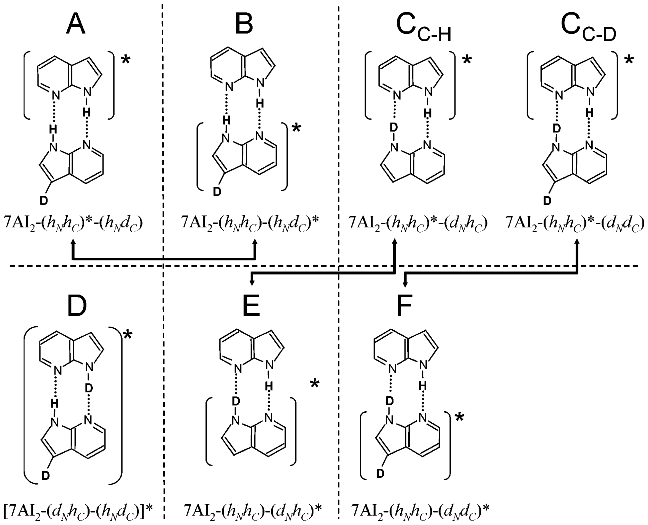

Figure 2. Vibronic bands (**A**−**F**) in Figure 1 are correlated to the excited-state structures. The asterisks indicate the electronically excited monomer units. Two structures (**A**, **B**), (**C**, **E**), and (**C**, **F**) linked by the arrows have a common structure in the electronic ground state. Only one structure exists for the excited state of **D**. Two dimers 7AI$_2$-(h_Nh_C)*-(d_Nh_C) and 7AI$_2$-(h_Nh_C)*-(d_Nd_C) provide band **C** in the FE spectrum. The structures of the two dimers are discriminated with notations $\mathbf{C}_{\mathrm{C-H}}$ and $\mathbf{C}_{\mathrm{C-D}}$.

In Figure 1d, band **D** is only slightly red-shifted from band **E** that is assigned to the transition to 7AI$_2$-(h_Nh_C)-(d_Nh_C)* (7AI$_2$-*hd**).[18] The vibronic structure in Figure 1d is similar to those of symmetrical isotopomers 7AI$_2$-(h_Nh_C)-(h_Nh_C) and 7AI$_2$-(d_Nh_C)-(d_Nh_C) (7AI$_2$-*hh* and 7AI$_2$-*dd* in ref 18) for which only one origin band appears in the electronic spectrum. Thus, the observation of a single origin band **D** suggests that the excitation is delocalized over the dimer. Thus, we have assigned band **D** to [7AI$_2$-(d_Nh_C)-(h_Nd_C)]*.

In Figure 1e, two bands separated by 21 cm^{-1} are observed. It should be noted that the lower wavenumber band **A** is observed at only slightly higher wavenumber (1 cm^{-1}) than that of the 0−0 band of the undeuterated 7AI$_2$-(h_Nh_C)-(h_Nh_C) (7AI$_2$-*hh*) dimer indicated by the open circle in the FE spectrum. The existence of a C−D bond in the electronic ground-state monomer moiety may provide a small blue-shift for **A** relative to the origin of the undeuterated dimer. Therefore, band **A** is assigned to the transition to 7AI$_2$-(h_Nh_C)*-(h_Nd_C), and band **B** to 7AI$_2$-(h_Nh_C)-(h_Nd_C)*. The bandwidths of **A** and **B** are very broad, in agreement with the existence of the two protons in the dimer. The C−D bond at the 3-position hardly changes the excitation energy when the deuterated monomer unit is not excited, because the C−D bond is located far from the dual hydrogen bonds.

Bands **A**−**F** observed in the FE and hole-burning spectra are correlated to the excited-state structures in Figure 2, where each pairs (**A**, **B**), (**C**, **E**) and (**C**, **F**) are connected by the arrows. The wavenumbers of bands **A**−**F** and assignment are also summarized in Table 1 to compare the isotopic shifts of the 0−0 transition. Hereafter, we discriminate the two transitions (and also structures 7AI$_2$-(h_Nh_C)*-(d_Nh_C) and 7AI$_2$-(h_Nh_C)*-

TABLE 1: Wavenumbers of the 0−0 Transitions and the Isotopomers in the FE Spectrum[a]

bands	$\tilde{\nu}$/ cm^{-1}	isotopomer[b]
A	32252	7AI$_2$-(h_Nh_C)*-(h_Nd_C)
B	32273	7AI$_2$-(h_Nh_C)-(h_Nd_C)*
C$_{\mathrm{C-H}}$	32293	7AI$_2$-(h_Nh_C)*-(d_Nh_C)
C$_{\mathrm{C-D}}$	32293	7AI$_2$-(h_Nh_C)*-(d_Nd_C)
D	32311	[7AI$_2$-(d_Nh_C)-(h_Nd_C)]*
E	32314	7AI$_2$-(h_Nh_C)-(d_Nh_C)*
F	32334	7AI$_2$-(h_Nh_C)-(d_Nd_C)*

[a] The 0−0 band of undeuterated 7AI$_2$ is observed at 32251 cm^{-1}. [b] The asterisks indicate the electronically excited units in the dimer.

(d_Nd_C)) in Figure 2 that provide band **C** with notations **C**$_{\mathrm{C-H}}$ and **C**$_{\mathrm{C-D}}$, where C−H and C−D indicate the existence of the C−H or C−D bond at the 3-position, respectively.

B. Strong Coupling Case or Weak Coupling Case. Previously, we reported that the lowest excited electronic state of 7AI$_2$-(h_Nh_C)-(d_Nh_C) (7AI$_2$-*hd*) is localized on one monomer unit. However, there is an ambiguity whether the excitation is partially localized or completely localized. The comparison of the spectra of various isotopomers may provide information on the degree of localization by deuteration.

In symmetrical 7AI$_2$ dimers such as 7AI$_2$-(h_Nh_C)-(h_Nh_C) and 7AI$_2$-(d_Nh_C)-(d_Nh_C) (7AI$_2$-*hh* and 7AI$_2$-*dd* in ref 18), the electronic excited states are described by the exciton theory.[1a,25−33] Two cases, the strong coupling case and the weak coupling case, have been classified to elucidate the excited electronic state of various dimers. In the strong coupling case where the resonance integral is large, the ground-state and excited-state vibronic wave functions, $\Psi_{G,\upsilon w}$ and $\Psi_{\pm,\upsilon w}$, are expressed as

$$\Psi_{G,\upsilon w} = \phi_a\phi_b\chi_\upsilon(Q_a)\chi_w(Q_b) \tag{1}$$

$$\Psi_{\pm,\upsilon w} = \frac{1}{\sqrt{2}}[\phi'_a\phi_b \pm \phi_a\phi'_b]\chi'_\upsilon(Q_a)\chi'_w(Q_b) \tag{2}$$

where ϕ_i and ϕ'_i are the ground-state and excited-state electronic wave functions of the two monomers, respectively, and $\chi_\upsilon(Q_i)$ and $\chi'_w(Q_i)$ are the ground-state and excited-state vibrational wave functions with the vibrational quantum number υ and w, respectively, with subscripts a and b distinguishing between the two monomer units. Equation 2 indicates that the *electronic wave functions* are delocalized over the dimer due to the exciton resonance interaction, and the vibrational wave functions in the excited states are described by new excitonic electronic states. In the case of strong coupling case, the ground-state and excited-state electronic wave functions may not change for asymmetrically deuterated 7AI$_2$ dimers such as 7AI$_2$-(h_Nh_C)-(h_Nd_C), 7AI$_2$-(h_Nh_C)-(d_Nh_C), and 7AI$_2$-(h_Nh_C)-(d_Nd_C), because the deuteration should not change the electronic wave functions. Therefore, the excited-state electronic wave functions must be delocalized even for the asymmetrically deuterated 7AI$_2$ dimers. However, the experimental results clearly indicate that the 7AI$_2$ dimers do not belong to the strong coupling case.

In the weak coupling case[25−29] the excited-state vibronic wave functions $\Psi_{\pm,\upsilon w}$ are expressed as

$$\Psi_{\pm,\upsilon w} = C_1\phi'_a\phi_b\chi'_\upsilon(Q_a)\chi_w(Q_b) \pm C_2\phi_a\phi'_b\chi_w(Q_a)\chi'_\upsilon(Q_b) \tag{3}$$

When complete resonance occurs, $C_1 = C_2 = 1/\sqrt{2}$, whereas $C_1 \approx 1$ and $C_2 \approx 0$, or $C_1 \approx 0$ and $C_2 \approx 1$ for the completely localized case. Equation 3 indicates that the excitonic vibronic states should be described by the exciton interaction between the localized *vibronic* states in the weak coupling case.

Symmetric dimers 7AI$_2$-(h_Nh_C)-(h_Nh_C) and 7AI$_2$-(d_Nh_C)-(d_Nh_C) have two degenerated locally excited vibronic states: 7AI$_2$-(h_Nh_C)*-(h_Nh_C) and 7AI$_2$-(h_Nh_C)-(h_Nh_C)* for 7AI$_2$-(h_Nh_C)-(h_Nh_C), and 7AI$_2$-(d_Nh_C)*-(d_Nh_C) and 7AI$_2$-(d_Nh_C)-(d_Nh_C)* for 7AI$_2$-(d_Nh_C)-(d_Nh_C), respectively. The exciton resonance interaction splits the degenerated locally excited vibronic states into two delocalized excited vibronic states in the weak coupling case. The transition from the electronic ground state to the lower delocalized excited vibronic state is electric-dipole allowed. In this case, the vibronic energies of the two zeroth-order states (i.e., the locally excited vibronic states) are the same (*a complete resonance case*). The observation of a single origin in the electronic transition to [7AI$_2$-(d_Nh_C)-(h_Nd_C)]* (**D** in Figure 2) suggests that the excited state of 7AI$_2$-(d_Nh_C)-(h_Nd_C) may be *nearly complete resonance case*. In the *complete resonance case*, the energies of vibronic states of two monomer units in the dimer should be equivalent. In 7AI$_2$-(d_Nh_C)-(h_Nd_C), one monomer moiety contains an N−D bond and the other one contains a C−D bond. The two locally excited states of 7AI$_2$-(d_Nh_C)*-(h_Nd_C) and 7AI$_2$-(d_Nh_C)-(h_Nd_C)* may be accidentally degenerate or nearly degenerate; therefore these two locally excited states split into two excitonic states as in the cases of 7AI$_2$-(h_Nh_C)-(h_Nh_C) and 7AI$_2$-(d_Nh_C)-(d_Nh_C).

In asymmetrical dimers, for example, in 7AI$_2$-(h_Nh_C)*-(d_Nh_C) (**C**$_{\mathrm{C-H}}$) the vibronic energies of the two zeroth-order states should be different owing to the difference in the zero point energies depending on the excited monomer unit. Therefore, the lowest excited vibronic state of 7AI$_2$-(h_Nh_C)*-(d_Nh_C) (**C**$_{\mathrm{C-H}}$) may be either a *near resonance case* or a *complete localization case*. It should be noted that the transition to 7AI$_2$-(h_Nh_C)*-(d_Nh_C) (**C**$_{\mathrm{C-H}}$) is detected at the same position as 7AI$_2$-(h_Nh_C)*-(d_Nd_C) (**C**$_{\mathrm{C-D}}$**)**. If the observation of 7AI$_2$-(h_Nh_C)*-(d_Nh_C) (**C**$_{\mathrm{C-H}}$) and 7AI$_2$-(h_Nh_C)*-(d_Nd_C) (**C**$_{\mathrm{C-D}}$) is due to the near resonance interaction, the transition energies should be different between 7AI$_2$-(h_Nh_C)*-(d_Nh_C) and 7AI$_2$-(h_Nh_C)*-(d_Nd_C). Since the energies of the two locally excited vibronic states, i.e., 7AI$_2$-(h_Nh_C)*-(d_Nh_C) and 7AI$_2$-(h_Nh_C)-(d_Nh_C)* for 7AI$_2$-(h_Nh_C)-(d_Nh_C), or 7AI$_2$-(h_Nh_C)*-(d_Nd_C) and 7AI$_2$-(h_Nh_C)-(d_Nd_C)* for 7AI$_2$-(h_Nh_C)-(d_Nd_C), are different, the degree of the exciton interaction should be different. Therefore, the experimental results indicate that the excitation is completely localized on one of the two monomer moieties in 7AI$_2$-(h_Nh_C)*-(d_Nh_C) (**C**$_{\mathrm{C-H}}$) and 7AI$_2$-(h_Nh_C)*-(d_Nd_C) (**C**$_{\mathrm{C-D}}$).

The excitation energies are different between 7AI$_2$-(h_Nh_C)-(d_Nh_C)* (**E**) and 7AI$_2$-(h_Nh_C)-(d_Nd_C)* (**F**), because the locally excited monomer moiety does not contain a C−D bond in 7AI$_2$-(h_Nh_C)-(d_Nh_C)* (**E**), but it exists in 7AI$_2$-(h_Nh_C)-(d_Nd_C)* (**F**). Thus, we conclude that the excitation is completely localized in the lowest excited states of 7AI$_2$-(h_Nh_C)-(d_Nh_C) and 7AI$_2$-(h_Nh_C)-(d_Nd_C). Similarly, the excitation is completely localized in 7AI$_2$-(h_Nh_C)*-(h_Nd_C) (**A**) and 7AI$_2$-(h_Nh_C)-(h_Nd_C)* (**B**). These findings unambiguously indicate that the lowest excited electronic state of 7AI$_2$ should be treated by a weak coupling case.

The exciton resonance interaction in the lowest excited electronic state of 7AI$_2$ had been treated by a strong coupling case.[5,23] Kanamaru proposed that the lowest excited state of 7AI$_2$ should be treated by a weak coupling case[29] on the basis of similar vibronic structures in one-photon and two-photon absorption spectra in gas pahse.[5] However, no other experimental evidence has been reported. The measurement of the electronic spectra of 7AI$_2$ isotopomers unambiguously shows that the lowest excited electronic state of 7AI$_2$ can be treated by the weak coupling case of the exciton theory. Very recently, we observed the FE spectrum of 3-methyl-7-azaindole (3MAI) dimer and its isotopomers.[34] The observed spectra of the deuterated $3MAI_2$ dimers are very similar to those of the deuterated $7AI_2$ dimers. This observation strongly suggests that the resonance interaction in the lowest excited electronic state of $3MAI_2$ belongs to a weak coupling case.

Conclusion

We have measured the UV−UV hole-burning spectra of various $7AI_2$ isotopomers. In $7AI_2$-(h_Nh_C)-(d_Nh_C) and $7AI_2$-(h_Nh_C)-(d_Nd_C), the lower vibronic bands were observed at the same wavenumber although the higher ones at the different wavenumbers separated by 20 cm^{-1}. This observation is consistently explained by taking into account the localized excited states for the asymmetrically deuterated $7AI_2$ dimers. The complete localization of the excitation in the asymmetric $7AI_2$ dimers indicate that the symmetric isotopomers such as $7AI_2$-(h_Nh_C)-(h_Nh_C) and $7AI_2$-(d_Nh_C)-(d_Nh_C) should be treated by a weak coupling case of the exciton theory. Present study indicates that the photoexcitation of the completely localized states of deuterated dimers is possible. The investigation of the isotope-selective and electronic-state selective ESDPT reaction may be very useful to investigate the mechanism of the ESDPT reaction. We will report the experimental results on the H/D kinetic isotope effects on ESDPT in the successive paper (Part II).

Acknowledgment. This work was supported in part by the Grant-in-Aid for Scientific Research No. 15250015 from the Japanese Ministry of Education, Science, Sports and Culture.

References and Notes

(1) (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.

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

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

(4) (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.

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

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

(7) Chen, Y.; Rich, R. L.; Gai, F.; Petrich, J. W. *J. Phys. Chem.* **1993**, *97*, 1770.

(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) Nakajima, A.; Hirano, M.; Hasumi, R.; Kaya, K.; Watanabe, H.; Carter, C. C.; Williamson, J. M.; Miller, T. A. *J. Phys. Chem. A* **1997**, *101*, 392.

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

(12) (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.

(13) (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.

(14) Chachisvilis, M.; Fiebig, T.; Douhal, A.; Zewail, A. H. *J. Phys. Chem. A* **1998**, *102*, 669.

(15) Mente S.; Maroncelli, M. *J. Phys. Chem. A* **1998**, *102*, 3860.

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

(17) 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.

(18) Sakota, K.; Hara, A.; Sekiya, H. *Phys. Chem. Chem. Phys.* **2004**, *6*, 32.

(19) 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.

(20) Sekiya, H. Atom Tunneling and Molecular Structure in *Atom Tunneling Phenomena in Physics, Chemistry and Biology*; Miyazaki, T., Ed.; Springer: Berlin, 2004.

(21) Sakota, K.; Sekiya, H. *J. Phys. Chem. A* **2005**, *109*, 2722.

(22) (a) Douhal, A.; Moreno, M.; Lluch, J. M. *Chem. Phys. Lett*. **2000**, *324*, 75. (b) Douhal, A.; Moreno, M.; Lluch, J. M. *Chem. Phys. Lett*. **2000**, *324*, 81. (c) Moreno, M.; Douhal, A.; Lluch, J. M.; Castano, O.; Frutos, L. M. *J. Phys. Chem. A* **2001**, *105*, 3887.

(23) (a) Catalan, J.; Del. Valle, J. C.; Kasha, M. *Proc. Natl. Acad. Sci. U.S.A.* **1999**, *96*, 8338. (b) Catalan, J.; Del Valle, J. C.; Kasha, M. *Chem. Phys. Lett*. **2000**, *318*, 629. (c) Del Valle, J. C.; Kasha, M.; Catalan, J. *Int. J. Quantum Chem*. **2000**, *77*, 118.

(24) Serrano-Andres, L.; Merchan, M.; Carlos Borin, A.; Stalring, J. *Int. J. Quantum Chem.* **2001**, *84*, 181.

(25) Fulton, R. L.; Gouterman, M. *J. Chem. Phys.* **1961**, *35*, 1059.

(26) Fulton, R. L.; Gouterman, M. *J. Chem. Phys*. **1964**, *41*, 2284.

(27) McRae, E. G.; Siebrand, W. *J. Chem. Phys*. **1964**, *41*, 905.

(28) Förster, T. Delocalized excitation and excitation transfer. In *Modern quantum chemistry*; Sinanoglu, O., Ed.; Academic Press: New York, 1965; Vol. III.

(29) Kanamaru, N. *J. Mol. Spectrosc.* **2004**, *225*, 55, and references therein.

(30) Sakota, K.; Nishi, K.; Ohashi, K.; Sekiya, H. *Chem. Phys. Lett*. **2000**, *322*, 407.

(31) Held, A.; Pratt, A. *J. Chem. Phys.* **1992**, *96*, 4869.

(32) Muller, A.; Talbot, F.; Leutwyler, S. *J. Chem. Phys.* **2002**, *116*, 2836.

(33) Southern, C. A.; Levy, D. H.; Stearns, J. A.; Florio, G. M.; Longarte, A.; Zwier, T. S. *J. Phys. Chem. A* **2004**, *108*, 4599.

(34) Hara, A.; Yusuke, K.; Sakota, K.; Miyoshi, R.; Inokuchi, Y.; Ohashi, K.; Kubo, K.; Yamamoto, E.; Mori, A.; Nishi, N.; Sekiya, H. *J. Phys. Chem. A* **2004**, *108*, 10789.