

2P149 Substituent effect on the excited-state double proton transfer of 7-azaindole dimer in gas phase

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The excited state double-proton transfer (ESDPT) in a model base pair, 7-azaindole dimer ($7AI_2$), has attracted much attention to its mechanism of reaction during a past decade. Recently, the ESDPT reactions in the substituted $7AI_2$ dimers have been extensively studied in the condensed phase, however the effect of the substitution on ESDPT has not been understood. The measurement of electronic spectrum in a supersonic free jet expansion provides information on vibronic-mode specific ESDPT. Previously, we have measured the fluorescence excitation (FE) spectrum of jet-cooled 3-methyl-7-azaindole dimer ($3MAI_2$) and showed that the methyl substitution has little effect on the ESDPT rate. Here we will report the electronic spectra of 4-chloro-7-azaindole dimer ($4CAI_2$) in a supersonic jet expansion to investigate the effect of Cl substitution on ESDPT. The Cl atom is an electron-withdrawing group and has a heavy mass. Therefore, the substitution of Cl may provide either electronic effect or mass effect on ESDPT. Spectroscopic measurement in the gas phase combined with quantum mechanical calculations may allow us to discuss the effect of Cl substitution on the ESDPT reaction.

Figure 1 displays the FE spectrum of $4CAI_2$ -*hh* near the origin. The vibronic pattern in the FE spectrum is similar to that of $7AI_2$ -*hh*, suggesting that $4CAI_2$ undergoes ESDPT. We noted that the bandwidths in the FE spectrum of $4CAI_2$ -*hh* are 2.0, 1.3, 3.0 and 5.0 cm^{-1} for the origin, intermolecular bending (β_1 , β_2), and stretching (σ) vibrations, which are significantly narrower than the corresponding bandwidths of 2.7, 3.0, 10.0 cm^{-1} for the origin, β , and σ of $7AI_2$ -*hh*, respectively. The reduced bandwidth indicates that ESDPT is suppressed in $4CAI_2$. Dual fluorescence has been detected in the dispersed fluorescence (DF) spectrum of $4CAI_2$ -*hh* excited to the origin (Figure 1). The observation of red-shifted tautomer fluorescence clearly evidences the occurrence of ESDPT in $4CAI_2$, whereas the observation of UV fluorescence of the normal dimer, that is absent in the DF spectrum of $7AI_2$ -*hh*, reveals that the ESDPT rate may be decreased in $4CAI_2$, in consistent with the narrower bandwidths in the FE spectrum.

We carried out ab initio and DFT calculations to obtain the geometries, binding energies, and the energy difference between the normal dimer and the transition state for 4CAI_2 and also 7AI_2 for comparison. The geometries of the two dimers in S_1 were obtained with CIS calculations. The results indicate that the geometries of the two normal dimers are very similar both in the S_0 and S_1 states, and the potential energy barriers are also similar between the two dimers, suggesting that the potential curve along the one-dimensional ESDPT coordinate does not change significantly upon the Cl substitution. However, the normal coordinates of β_2 and σ (Figure 2), are found to be substantially altered by the substitution of the Cl atom. The displacements of the NH stretching occur linearly along the $\text{NH}\cdots\text{N}$ bond in the σ mode of 7AI_2 and promote ESDPT. But the σ mode of 4CAI_2 involves the NH displacements similar to the β mode of 7AI_2 . Thus, the reduced ESDPT rate in 4CAI_2 is reasonably explained by the multidimensional nature of ESDPT; the motions of the heavy atoms couple with those of the NH stretching motions due to the introduction of the heavy Cl atom and change the ESDPT reaction path, which may be responsible for the reduced ESDPT rate in 4CAI_2 .

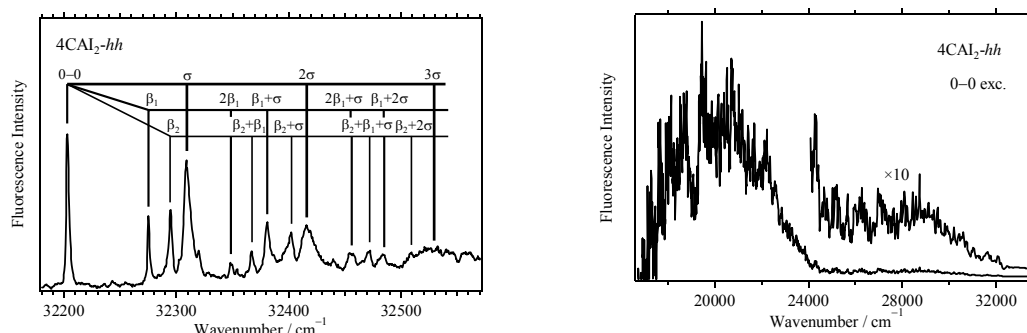


Figure 1 The FE (left) and DF (right) spectra of $4\text{CAI}_2\text{-hh}$

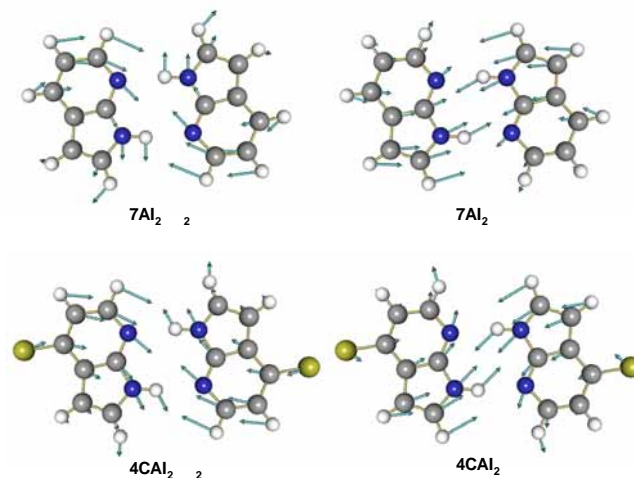


Figure 2 The normal coordinates of S_1 state of $7\text{AI}_2\text{-hh}$ and $4\text{CAI}_2\text{-hh}$