TRANSIENT IR ABSORPTION SPECTROSCOPY OF THE CHARGE-TRANSFER STATE OF (*p*-CYANOPHENYL)PENTAMETHYLDISILANE AND ITS CLUSTERS

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We have been investigating the intramolecular charge-transfer (ICT) process of jet-cooled phenyldisilanes by laser spectroscopic methods.[b] In order to make a detailed discussion on the ICT process, it is necessary to determine an equilibrium structure of the CT state. Since a profile of the CT emission is broad and structureless, it is difficult to extract information about the structure from it. Thus, we have carried out a transient IR spectroscopy on the CT state to obtain structural information of the CT state.

In the previous paper [c], we have reported the transient IR spectroscopy in the OH and CH stretching region of (*p*-cyanophenyl)pentamethyldisilane(CPDS) and its clusters. The IR spectrum of the CH stretching vibration of the CT state was analyzed by the theoretical calculation and the equilibrium structure of the ICT state was determined. In addition, the IR spectrum of the ICT state of CPDS-methanol clusters in the OH stretch region indicated the existence of the intermediate CT^* state in the CT reaction.

In the present study, we have carried out a transient IR spectroscopy of the CT state of CPDS-water cluster in the CN stretch region to obtain detailed information about the intermediate CT^* state. The frequency of the CN stretch mode (ν_{CN}) of the S_0 state was found to be 2238 cm^{-1}. The ν_{CN} of the CT^* and the CT states are 2161 and 2155 cm^{-1}, respectively. This rather small low-frequency shift of the ν_{CN} of the CT^* state compared with that of the S_0 state should be a clue to reveal the character of the CT^* state. The character of the CT^* state will be discussed in the paper.

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