TRANSIENT IR ABSORPTION SPECTROSCOPY OF THE CHARGE-TRANSFER STATE OF (p-CYANOPHENYL)PENTAMETHYLDISILANE AND METHANOL CLUSTER

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

In the present study, we have concentrated to an OH stretching vibration of (p-cyanophenyl)pentamethyldisilane(CPDS)-MeOH 1:1 cluster. It is well-known that an OH stretching (ν_{OH}) frequency sensitively reflects the strength of the hydrogen bonding and the relative orientation to surrounding molecules around the OH group. Thus, it was expected that the ν_{OH} frequency of MeOH in the CPDS-MeOH cluster should reflect a change in its situation in the ICT process, that is, it should be a good indicator of the structural change in the ICT process.

We have succeeded in observing the ν_{OH} bands of the CT state as well as that of a locally excited (LE) $\pi\pi^*$ state. The ν_{OH} frequency of the CT state is much red-shifted compared to that of the S_0 and the LE states. The most outstanding result is that two distinct bands of OH stretching mode in the CT state appear in the spectrum. This indicates the existence of two local potential minima in the CT state. Time profiles of these bands indicated that the ICT process proceeds in two steps. The present result provides us with a new insight into the understanding of the ICT process.

[a] H. Ishikawa *et al*. *J. Am. Chem. Soc.* **124**, 6220 (2002).