

Report on visit to Technische Universität Berlin through the JSPS Core to Core Program

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As part of the JSPS (Japan Society for the Promotion of Science) Core-to-Core Program, I studied in the Prof. Otto Dopfer's group at the Technische Universität Berlin for two weeks, from December 7, 2014 up to December 20, 2014. This is a report of my stay.

The aim of this visit

I am investigating solvent reorientation of (p-cyanophenyl)pentamethyldisilane (CPDS, Fig.1) water 1:1 cluster (CPDS-W) induced by photoexcitation. An intramolecular charge transfer reaction (ICT), from the $\sigma_{\text{Si-Si}}$ bond to the phenyl ring, occurs in the excited state of CPDS, and charge distribution in CPDS changes significantly.

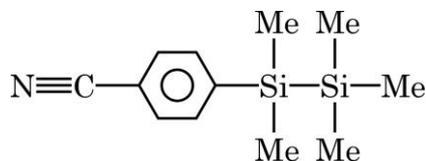


Fig. 1 Structure of CPDS.

Simultaneously with the ICT reaction, twisting of the pentamethyldisilanyl group takes place to inhibit a back reaction of transferred electron. In CPDS-W, reorientation of the water molecule following ICT, from side of the cyano group to above the phenyl ring, was reported. [1] Photo-ionization of CPDS, which removes an electron from the $\sigma_{\text{Si-Si}}$ bond, is also expected to induce large change in the charge distribution in CPDS. Thus, we expected migration of water molecular can be triggered but may be in a different manner from that in the excited state. Such ionization induce water migration reaction, however, has not been studied yet. Thus, we measured IR spectra of CPDS-W cluster cation generated by the photo-ionization to determine the hydration structure of this cluster cation.

Fig. 2 and Fig. 3 show experimental and theoretical IR spectra obtained in our laboratory and stable structures obtained by CAM-B3LYP/cc-pVTZ, respectively. Table 1 summarizes relative energies of these structures. In the experimental spectrum (Fig. 2(a)), there are two OH bands at 3267 cm^{-1} and 3639 cm^{-1} . They can be assigned to hydrogen bonded OH stretching and free OH stretching, respectively. In cationic state, hydrogen bond is expected not to be formed because of repulsion between positively charged hydrogens in the water molecule and CPDS cation. In fact, the calculation results (Fig. 2(b) and Fig. 3) did not predict such hydrogen bonded structure. They show only structures in which charge-dipole interaction dominates, instead. Experimental and theoretical results did not match because these charge-dipole type structures do not have hydrogen bonds and shows two free OH stretching vibrations, so called ν_1 and ν_3 . We think one of the reason of the this mismatch would be due to high excess energy of $[\text{CPDS-W}]^+$ generated

by the photoionization. In prof. Otto's laboratory, the most stable cluster cation can be generated by an EI source, and IR spectra of the cold cluster cation can be measured. In this visit, we aimed to measure IR spectra of cold CPDS-W cluster cation and to determine the structure.

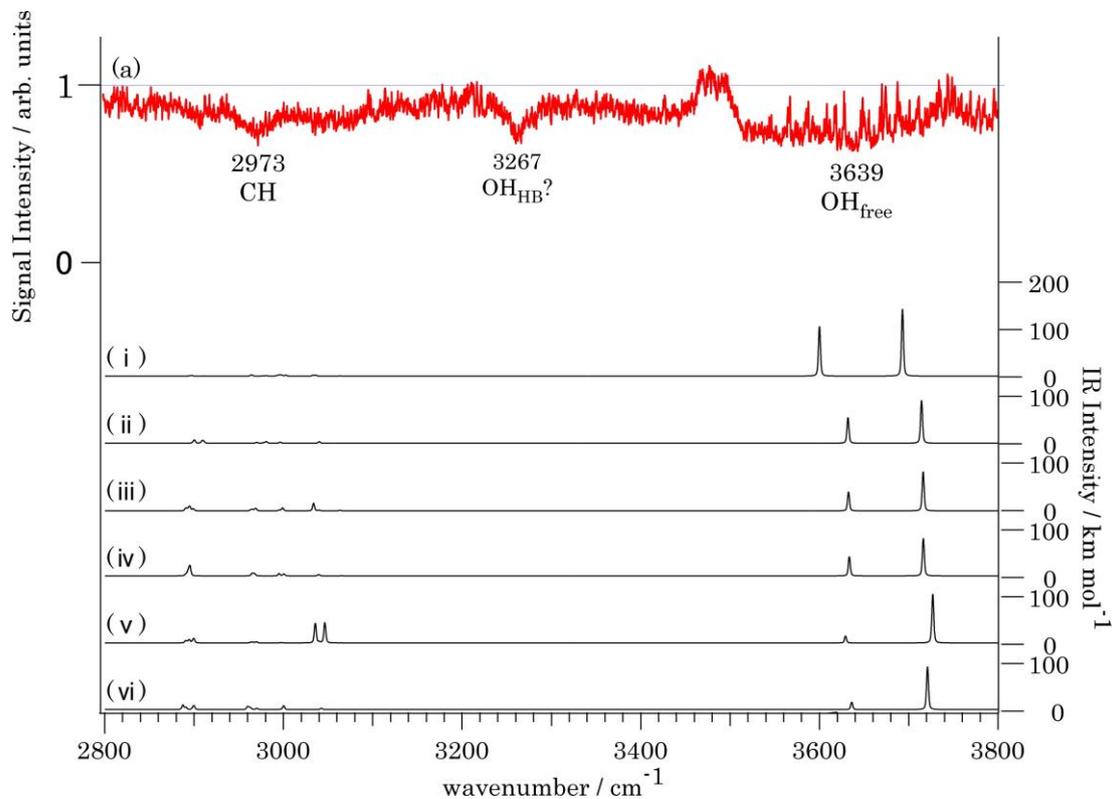


Fig. 2 IR-dip spectrum (a) and theoretical spectra (i)–(vi) of CPDS-W cluster cation.

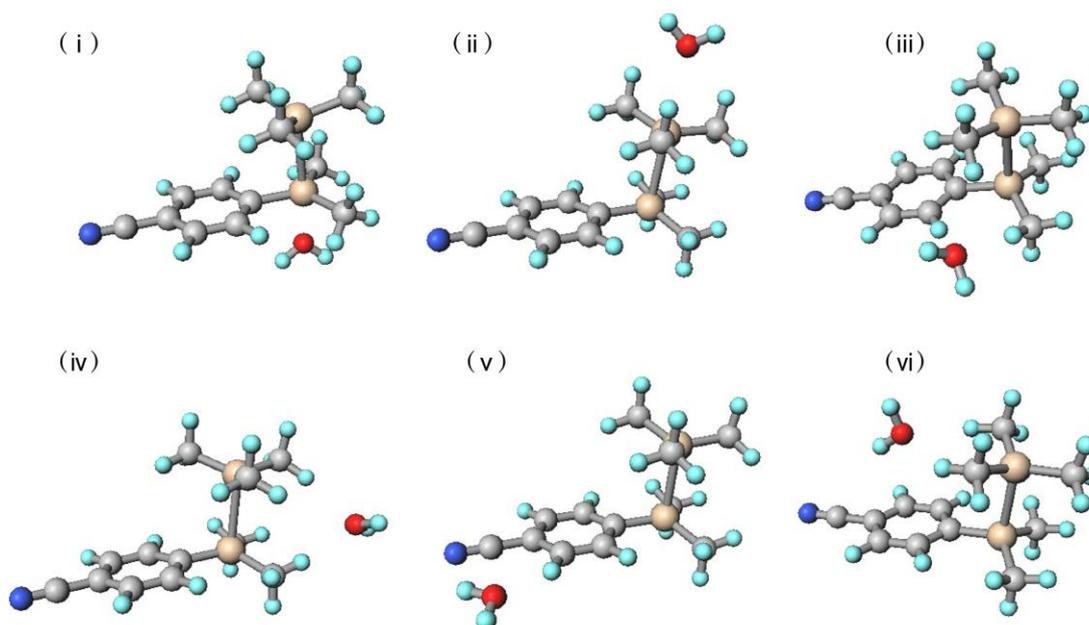


Fig. 3 Stable structure of CPDS-W cluster cation.

Table 1 Calculated relative and binding energies of CPDS–W cluster cation

Structure	(i)	(ii)	(iii)	(iv)	(v)	(vi)
$\Delta E / \text{kJ mol}^{-1}$	0	2.67	5.92	8.02	10	10.9
Binding energy / kJ mol^{-1}	39.6					

Experiment

Fig. 4 shows setup of the EI-IR experiment. First, the neutral molecules were ionized before skimmer by electro-impact. By collisions of the cationic molecules with water molecule and Ar gas, cluster cations were generated. The cluster cation passed the first quadrupole mass filter (QP1) to select a single mass species. Next, the cluster cations were bent at

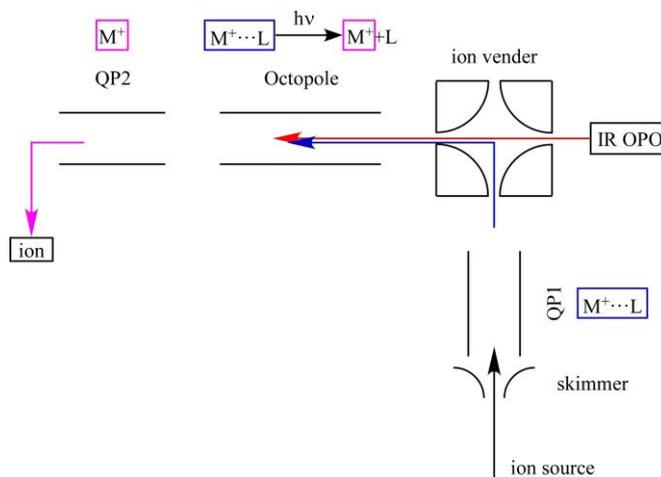


Fig. 4 Experimental setup.

right angle by an ion vander and were introduced into an octopole ion guide, where IR laser was irradiated to the cations. When vibrational excitation of the cluster cation occurs, they dissociate into some fragment ions. These ions were selected by a second quadrupole mass filter (QP2) and detected by a Daly detector. By monitoring the fragment intensity as a function of IR wavelength, the IR photo dissociation (IRPD) spectrum of the cation was obtained.

Results and discussion

Fig. 5(a) shows the IRPD spectrum monitored at the $[\text{CPDS-W}]^+ \rightarrow \text{CPDS}^+$ fragment mass channel. Two weak humps at $\sim 3620 \text{ cm}^{-1}$ and $\sim 3690 \text{ cm}^{-1}$ may be assigned to free OH bands. They look to match symmetric and antisymmetric OH stretching of the water molecule. Taking into account the theoretical relative energies of obtained structures, it is expected that CPDS–W cluster cation has structure (i). The quality of the IRPD spectrum, however, is not enough to firmly confirm this assignment. Thus, I think the IRPD spectrum of the CPDS–W cluster cation must be measured again. This is future work.

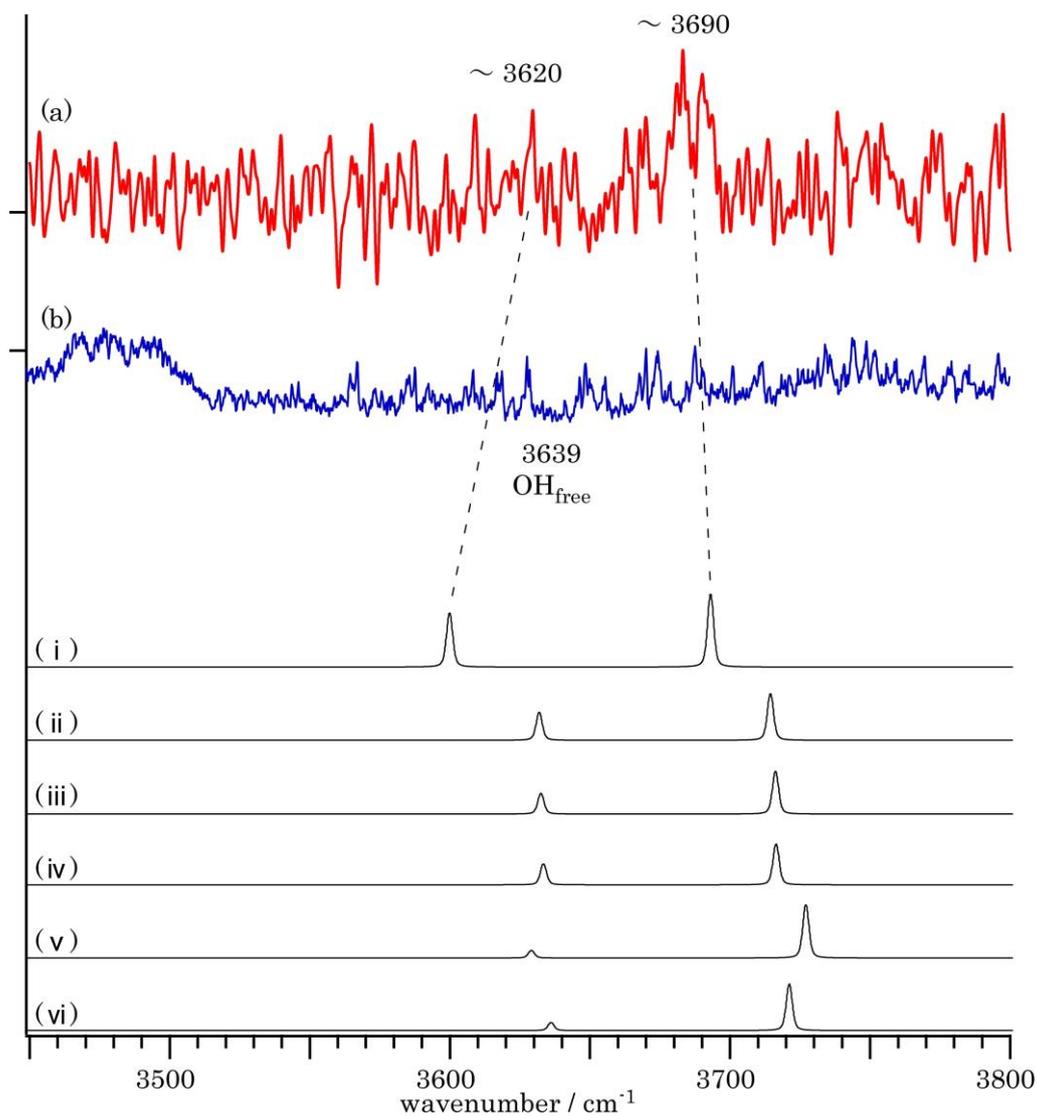


Fig. 5 IRPD spectrum (a), IR-dip spectrum (b), and calculated spectra ((i)-(vi)) of CPDS-W cluster cation.

Conclusion and acknowledgement

I measured the IRPD spectrum of the CPDS-W cluster cation. But the result we obtained cannot be satisfied. So if possible, it had better be re-measured in TU berlin.

Finally, I would like to express my appreciation to prof. Otto Dopfer who gave me wonderful opportunity. And I would like to express my appreciation to prof. Masaaki Fujii, Dr. Shun-ichi Ishiuchi and all members in the Otto's laboratory.

Reference

[1] H. Ishikawa et al., *Phys. Chem. Chem. Phys.* **9**, 117 (2007).