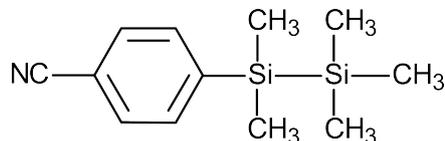


Report on my visit to TU Berlin

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From December 8th to 19th of 2014, I visited the laboratory of Prof. Otto Dopfer in Technische Universität Berlin as part of JSPS Core-to-Core Program. In this visit, the experimental purpose was the infrared spectroscopy of (*p*-cyanophenyl)pentamethyldisilane–water



1:1 cluster (CPDS–W, for short) in the cationic state by using infrared photodissociation (IRPD) technique. In addition, I participated in the Core-to-Core International Symposium held in the university. This is a brief report of my activities in Berlin.

1 Experiment

We tried to record the IR spectrum of $[\text{CPDS–W}]^+$ by using the IRPD experimental setup shown in Fig.1. The main part of the setup is a quadrupole–octopole–quadrupole tandem mass spectrometer coupled to electron impact (EI) ion source. In the beginning, CPDS was heated to 70°C and was expanded through a pulsed nozzle with its carrier gas (Ar), then cationic clusters $[\text{CPDS–W}_n]^+$ were generated by electron impact ionization. A specific cluster (in this case, $[\text{CPDS–W}]^+$) was mass-selected by passing through the first quadrupole mass filter. The desired cluster was introduced into an adjacent octopole ion guide, where infrared laser is irradiated to the cluster. When the infrared frequency is resonant to a vibrational excitation of the cluster, the evaporation of one or several water ligands is induced and some photofragments are generated. These fragments are then introduced into the second quadrupole mass filter. The signal intensity of a mass-selected fragment is measured by a Daly detector. Thus, by monitoring signal intensity of the fragment while scanning the infrared frequency, the infrared spectrum of the parent cationic cluster can be

recorded. In case of the $[\text{CPDS–W}]^+$ parent cluster, the infrared photofragment CPDS^+ is generated since only the water moiety is removed:



So, the second quadrupole was set to select CPDS^+ fragment and the ion signal is monitored. Before recording the IRPD spectrum, a collision-induced dissociation (CID) spectrum was recorded to confirm the composition of the fragments arising from clusters.

As the first step, we had to optimize the experimental condition by trial and error to make the photofragment signal more intense. In this setup, there are some experimental parameters which have a marked effects on the signal intensity (e.g. duration of the gas pulse (valve opening time), voltage of the electrodes in the mass spectrometer, and temperature of the sample). Especially, the anteroposterior position of the nozzle was found to be one of the critical parameters; a small change of the position often led to a drastic improvement of the fragment signal. After adjusting the parameters, the mass spectrum of EI source was recorded. As well as the desired cationic cluster (1:1), formation of a series of higher clus-

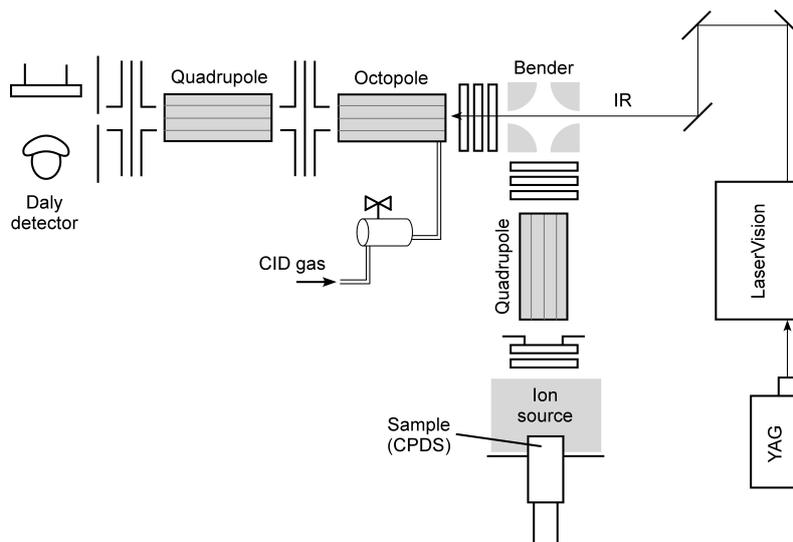


Fig.1 Experimental setup for IRPD spectroscopy.

ters was observed. The CID spectrum in the next step showed the peak assigned to CPDS^+ arising from the dissociation of $[\text{CPDS-W}]^+$, but it was weaker than the peak assigned to $[\text{CPDS-W}]^+$ from higher clusters; the experimental condition was not good enough to obtain the IRPD spectrum of $[\text{CPDS-W}]^+$. We tried to adjust the condition by changing some experimental parameters, but it did not improve drastically. Thus, we could not measure the IRPD spectrum during the stay.

2 Presentation in Lab Seminar

On December 11th, I made a short presentation (ca. 15 min.) in a lab seminar. In this presentation, I talked about the reconsideration of the reaction mechanism of ionization-induced water migration in acetanilide-water 1:1 cluster (AA-W).

A few years ago, Mr. Tanabe showed the result on real-time observation of the water migration from CO site to NH site of cationic acetanilide and its kinetic analysis based on the two reaction models. First model is the most simple 1-path model ($\text{FC}^+ \rightarrow \text{I}^+ \rightarrow \text{P}^+$), but experimental time profiles of the band were

not fitted successfully. Second model is a reaction including the back reaction path and IVR process. But available experimental data is not enough to determine all the kinetic parameters in the fitting model equations, because the reaction model is rather complicated.

Recently, a new reaction model to the water migration in AA-W was proposed according to MD simulation by Wohlgemuth *et al.* This new reaction model consists of two simultaneous paths; one is named fast-channel (direct path to the product), and the other is slow-channel (path to the product via some intermediate). Because this model includes less kinetic parameters than Tanabe's second model, more exact fitting analysis can be performed. To confirm whether this new model can reproduce our experimental time profiles, I tried the analysis based on the 2-path model.

In my presentation, I showed the comparison of the fitting curves obtained by my analysis and Tanabe's, and stated that the fit was clearly improved by employing the 2-path reaction model. And I also showed the obtained kinetic parameters; the time constant was ~ 1 ps for fast-channel, and ~ 8 ps for slow-

channel.

From the appearance of the obtained fitting curves, 2-path reaction model can be said more reasonable than models employed by Tanabe. Prof. Dopfer pointed out there were no decisive factors to conclude whether the 2-path reaction model is reasonable or not. I, however, think that this analysis is one of the best effort at this stage for approaching the reaction mechanism in terms of experimental observation.



Fig.2 A short presentation in lab seminar.

3 Core-to-Core International Symposium

On December 15th, I participated in *Core-to-Core International Symposium on Ionization-Induced Switching* held in TU Berlin. Participants were attended from the United Kingdom, Germany, France, and Japan. I was really pleased, because it was my first opportunity for attending the international symposium.

In the oral session, so many fascinating presentations were given. One of the interesting topics was the *ab initio* MD simulation about the ionization-induced water migration in acetanilide–water cluster, presented by M. Wohlgemuth at University of Würzburg. This topic is highly relevant to my recent work because our experimental time profiles are suc-

cessfully analyzed according to the reaction model based on the MD simulation (as mentioned above). The content of the presentation was a little bit difficult for me (since he mainly explained the theoretical background of applied *ab initio* MD), but a movie visualizing the migration process of the water molecule was straightforward.

In the poster session, I made a poster presentation, whose topic was the same as the presentation in the lab seminar. I had a good discussion with several participants about the result of analysis based on new reaction mechanism. After the symposium, I took part in a convivial meeting and enjoyed a dinner.

4 Life in Berlin

This was my first trip abroad, so every experience was interesting and meaningful for me. At first, I could not follow the experiment because I saw the IRPD experimental setup for the first time in Dopfer’s laboratory. But after a while, I gradually got to understand the procedure of the experiment. At lunch time, we went to “Mensa”, an eating place in the university. On December 17th, I took part in the Christmas party held in the university. There were many kinds of nice meals and we had a good time with the members of the laboratory.

5 Conclusion & Acknowledgment

In this visit, we tried to measure the IR spectrum of cationic cluster $[\text{CPDS-W}]^+$ by using IRPD technique at Dopfer’s laboratory, but the progress was not so good; more experiments will be required for getting clear results. The stay of two weeks in Berlin was a very good experience for me. I would like to express my gratitude to Prof. Otto Dopfer and the members of the laboratory, and special thanks for the financial help by JSPS Core-to-Core program.