

Report of 7th Core-to-Core International Symposium on “Ionization Induced Switching”

The amphitheatre Chimie, Université d'Aix Marseille, St. Charles, Marseille, France, 15th Mar.
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Mitsuhiko Miyazaki (Tokyo Institute of Technology)

The 7th symposium of the Core to Core program was held at Université d'Aix Marseille on 15th Mar. 2013. The symposium intended to discuss recent progress of switch in intermolecular interactions and to give a chance for young students to present their research topics in English. This time we had 38 participants, the maximum on the series of the symposiums so far, because the collaboration network has been expanded since last year. Detailed program of the symposium can be seen in another web page (<http://www.res.titech.ac.jp/~kiso/CoreToCore/seminar-info-03.html>).

After an opening remark by prof. Christophe Juvet in Univ. d'Aix Marseille who was the host of this time symposium, prof. Otto Dopfer from TU Berlin first presented an overview of current stage of the photoionization induced intermolecular interaction switching featuring particular cases of “rare gas” and “water” solvents. The story started with the history of collaboration with prof. Masaaki Fujii and other persons who join the symposium and the Core-to-Core program. He suggested next direction of experimental work such as extension of targets to much larger clusters and peptides, improvement of state selectivity and/or challenge of new probe methods e.g. electronic spectroscopy. Such things are actually important because introduction of new techniques has a possibility of providing new clue to clarify the switching mechanism.

The second speaker was a theoretician: prof. Roland Mitric from Freie University Berlin with whom we have just started collaboration since last year, and this was the first time to invite him to Core-to-Core symposium. His profession is *ab initio* MD simulation, and we have asked him to calculate the dynamics of water isomerization observed in acetanilide–water cluster. His results based on a DFT interaction potential (calculated by “on the fly” manner) shows two isomerization paths, one of which called “fast path” connected between the C=O and N-H sites via an in-plane path around the CH₃ group and the other called “slow path” via an out-of-plane on the peptide bond. The probability of which path is selected by the water molecule is about 7:3 depending on the initial structure and velocity of the water molecule on the cationic state that are randomly sampled assuming a distribution prepared based on a temperature e.g. 100K. Along the fast path, the water molecule reaches the N-H site ~3 ps, on the other hand, it walks around on the peptide bond for a while in the slow path and takes more than 5 ps to arrive the N-H site. In some of the trajectories, the water molecule fluctuates around the global minimum because of the excess energy and in effect temporally leaves the N-H site. Such multiple isomerization paths are more than our first kinetic treatment of the experimental results where a single path was assumed despite a partial back reaction was

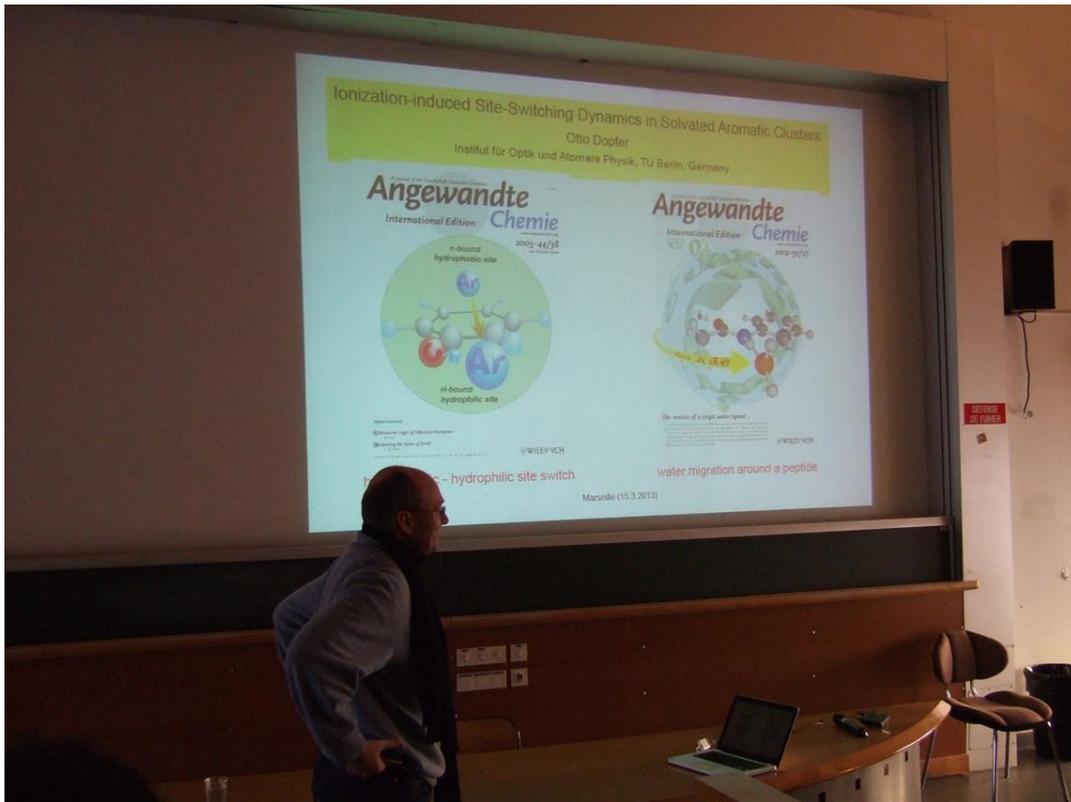
incorporated. The overall (average of 50 trajectories) time evolution, however, shows similar behavior our first analysis; it takes ~1 ps to break the hydrogen bond and to leave from the C=O site, takes ~4 ps to reach the N-H site, and then dissipates the excess energy via IVR. He also simulated TRIR spectra by evaluating dipole functions along selected vibrational motions and cross-correlation of the laser pulses. These results looked to reproduce well the experimental observations and to match with our first analysis. Anyway, further kinetic analysis based on the two paths model and making the consistency with the MD simulation and also with the excess energy dependence of the reaction are necessary to shed light on the water dynamics. His simulation is worth to shows us a molecular image that cannot be obtained only by vibrational spectroscopy. Much higher levels of calculation, both of the functional and the basis set, and much longer simulation time are desired, though of course such a simulation takes quite long time (He said even at the present level of calculation a month is necessary to finish a trajectory. He also said a wave packet treatment is not available for this system at this moment due to the complexity though he prefers that way similar to Masaaki.). Much sophistication is needed from both the experimental and theoretical aspects.

In the remaining morning session, new systems that are interested with respect to interaction switches were introduced by several researchers such as tryptamine–water and –nitrogen, phenylethanol–water, and ortho-methoxy-para-coumaric acid–W etc. taking a coffee break. These systems will be the next targets of time resolved spectroscopy to trace their dynamics in real time.

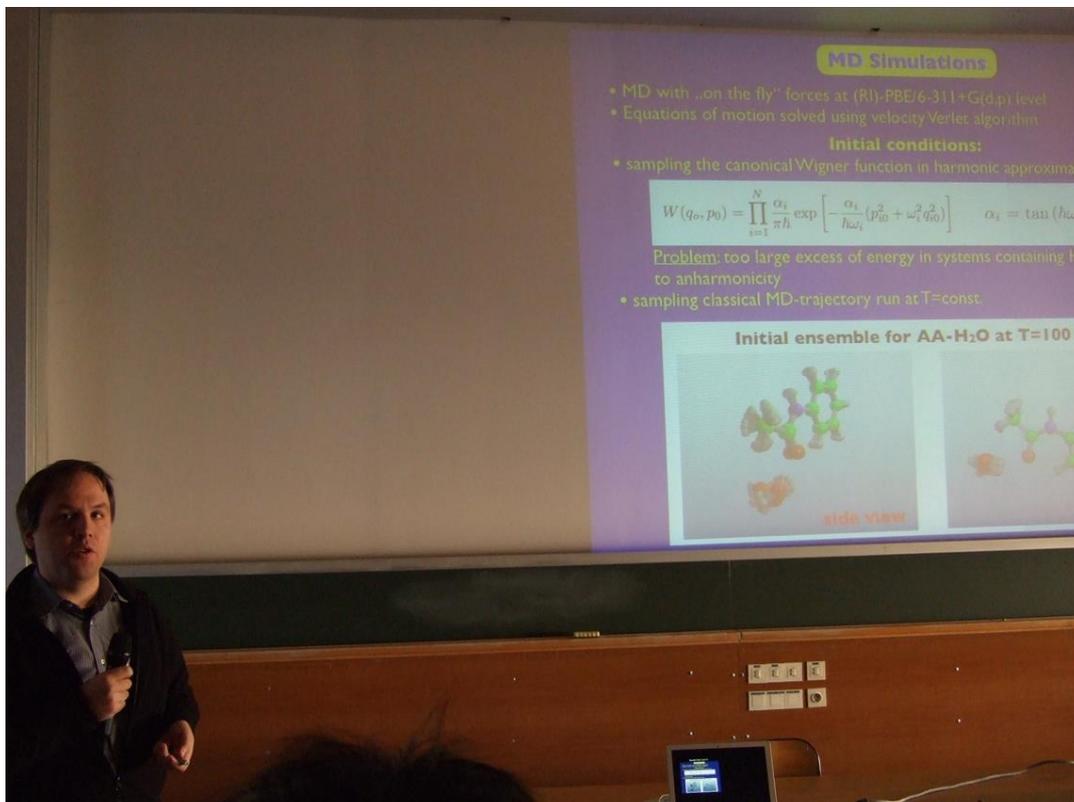
During lunch time we had a poster session. Having lunch box, we had good interactions among the attendees. Such a close friendship will help future progress of scientific activity.

After lunch break, recent researches carried out in French research groups were introduced. Their studies mainly utilize IR spectroscopy but the targets range wide areas of chemistry. Prof. Anne Zenacker-Rentin presented IR spectroscopic analysis of conformations of Cinchona Alkaloids, quinine and quinidine that are a pair of pseudo enantiomers, kind of diastereomer. Change in stereo configuration was probed as a difference in the shifts of hydrogen bonded O-H stretching vibrations. Prof. Pierre Çarçabal introduced a spectroscopic study on oligosaccharides isolated in supersonic jets. Oligosaccharides, especially pentasaccharides are very important as modifiers of peptides that adjust biological functions of peptides finely. The pentasuger systems, however, are so big that they are quit challenging themes from both aspects of experiment and theory. The obtained spectra were very broad and it is not easy to extract information from these spectra at this moment. New concept to extract meaning of isolated sugars is desired to make further development.

Young graduated students and post-doctoral researchers gave their respective research themes in the remaining session. The discussion time was not long enough due to limitation of schedule, even so, we believe such a fundamental effort is necessary particularly for Japanese students to skill up their international scientific communications, and is one of the main themes of the Core-to-Core program.



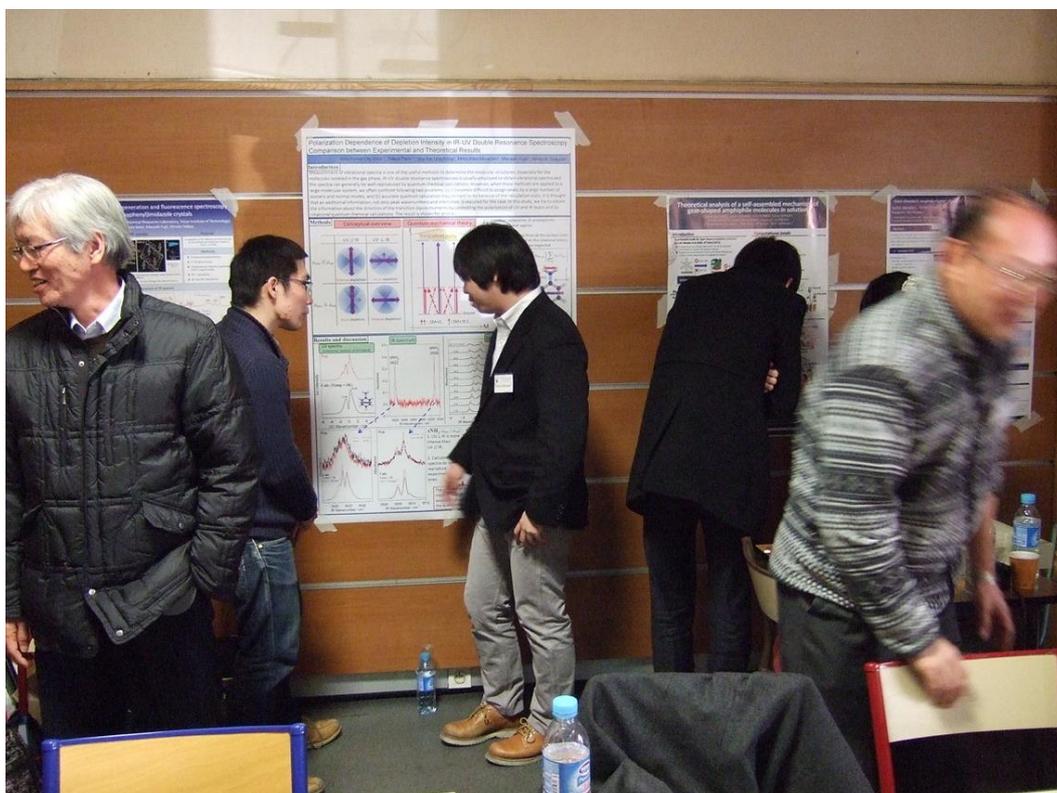
Prof. Otto Dopfer, an overview of interaction switching.



Prof. Roland Mitric, analysis of water dynamics by *ab initio* MD simulation.



Discussion at the lunch time, prof. O. Dopfer and Dr. K. Sakota.



Discussion in the poster session.



Group photo in front of the seminar house after the meeting.