

JSPS Core-to-Core Program
-Strategic Research Networks-
Research Report

(別表6)

Project No.	22003
Research Theme	Photoionisation-induced switch in aromatic molecule-solvent recognition
Duration of Project	April 1, 2012 – March 31, 2015 (36 months)
Core Institution in Japan	Tokyo Institute of Technology

Implementing Organizations

Country	Japan
Core Institution	Tokyo Institute of Technology
Co-Chair (name and title)	Masaaki Fujii, Professor
Number of Cooperating Institutions	4
Cooperating Institutions	Yokohama City University Tokyo Metropolitan University Kyusyu University Hiroshima University

Country	Germany
Core Institution	TU Berlin
Co-Chair (name and title)	Otto Dopfer, Professor
Number of Cooperating Institutions	1
Cooperating Institutions	University of Düsseldorf
Matching Fund	1) Photoionisation-induced switch in aromatic molecule – solvent recognition (DO 729/4) 2) Electronic structure of protonated aromatic molecules (DO 729/3) 3) Geometric and electronic structure of silicon-containing aggregates (DO 729/5) 4) Reactivity and Structure of isolated and solvated flavin ions under cryogenic temperatures in a 22-pole ion trap (DO 729/6)

Country	England
Core Institution	The University of Manchester
Co-Chair (name and title)	Klaus Müller-Dethlefs, Professor
Number of Cooperating Institutions	2
Cooperating Institutions	The University of York The University of Oxford
Matching Fund	1) The University of Manchester 2) Engineering and Physical Sciences Research Council (EPSRC)

Country	France
Core Institution	Université Paris Sud
Co-Chair (name and title)	Christophe JOUVET, Professor
Number of Cooperating Institutions	1
Cooperating Institutions	Université d'Aix-Marseille
Matching Fund	1) French National Research Agency (ANR) 2) National Center for Scientific Research (CNRS)

Result of Program Implementation

(別表6)

After the shift to "Strategic Research Networks" program, we have started the collaborative researches on four following themes.

(Germany) Structural analysis of ionic cluster studied by EI-IR spectroscopy.

(UK) Structural analysis of neutral and ionic cluster studied by ZEKE photoelectron spectroscopy.

(France) Mechanism of molecular switching of protonated ionic cluster studied by electrospray ionization method.

(Japan) Analysis of photoionization dynamics studied by photoionization-IR spectroscopy.

Many young scientists and students have gone to Germany, UK and France and carried out joint experiments.

We organized the international symposium: Core-to-Core International Symposium on Ionization Induced Switching on March 15th, 2013 at Université d'Aix-Marseille that is the cooperating institution in France. Many scientists (oral: 16, poster: 7) presented the latest advances in aromatic-solvent interactions including photoionization-induced switching.

We also encouraged young scientists/students to make an English presentation at international conferences such as 67th International Symposium on Molecular Spectroscopy and Gordon Research Conference on Gaseous Ions, Structures, Energetics & Reactions.

Achievements in FY2012 (Self Review)

It is very important to understand the aromatic-solvent interactions between molecules such as van der Waals forces and vibronic interactions based on hydrogen bonds, because the understanding interactions between molecules can solve higher order structure of biologically relevant molecule such as peptide, protein and DNA.

This year we started to investigate the IR spectroscopic and quantum chemical characterization of not only the photoionization-induced molecular switching but also aromatic molecule-solvent hydrogen bond network systems, through the formation of EU-Japan collaborative research network.

As a result, the bonding-site switching of a solvent molecule was observed in acetanilide-H₂O (1:1), acetanilide-methanol (1:1), and 4-aminobenzonitrile-H₂O (1:1) clusters.

In the case of acetanilide-H₂O (1:1) cluster, for example, the H₂O is hydrogen-bonded to the CO site of the peptide bond in the neutral state. After the photoionization, the H₂O is released from CO binding site and eventually trapped at the NH site of the same peptide bond within only 5 picoseconds. These results are very important as a first step toward the direct measurement of solvent dynamics around proteins.

Future Plan (Measures toward Achieving Research Objectives)

In a collaborative effort, a variety of spectroscopic techniques, such as photoionization-IR spectroscopy (Japan), EI-IR spectroscopy (Germany), ZEKE photoelectron spectroscopy (UK), and electrospray ionization method (France) with quantum chemical calculations, shall be applied to some types of neutral and ionic aromatic molecule-solvent interaction systems in order to understand the effects of ionization on the intermolecular potential energy surface. The joint application of spectroscopic techniques is required to obtain a full understanding of photoionisation-induced switching in the aromatic molecule-solvent recognition involving the dynamical processes.

The aromatic molecule-solvent interaction systems are also related to the biophysical interactions in the biologically relevant molecules such as peptides, proteins and DNA. Biological molecules include simple benzene derivatives, like phenol (residue of tyrosine), catechol and tyramine (aromatic core of neurotransmitters), the amino acid phenylglycine, and the aromatic amides formanilide and phenylamide (mimicking peptide bonds in proteins). The ligands involve rare-gas atoms and water molecules, which represent nonpolar (hydrophobic) and polar (hydrophilic) solvent molecules. However, for example, the picosecond experiments in Japan are quite challenging and cannot be carried out for all species listed. Therefore, the initial focus will be on the simple systems. Later, we will concentrate on the more complex species, with the selection strongly depending on the success of generating the species, and the feedback from theory and the experimental results of the other groups.