3 Molecular Dynamic Imaging Gourp

3-1 Outline

Introduction

Molecular dynamic imaging, which gives time-resolved images of precise atomic motion in condensed matter, will become a very important technique in the future application of next-generation synchrotron radiation sources. In order to develop the technique and a pilot facility for molecular dynamic imaging based on time-resolved X-ray diffraction and scattering, the Molecular Dynamic Imaging Group, which belongs to the Non-equilibrium dynamics project under the ERATO program of the Japan Science and Technology Agency (JST), started activity at KEK in autumn 2003. The project is financially supported by the Japanese Ministry of Education, Culture, Sports, Science and Technology (MEXT), and the project director is Prof. Shin-ya Koshihara, a professor of the department of chemistry and materials science of Tokyo Institute of Technology.

In November 2003, Prof. Koshihara was appointed by JST as director of the ERATO project, which will continue for 5 years with a total budget of 1.5 billion yen. The goal of the project is to reveal the physics of the ultrafast non-equilibrium dynamics in novel condensed matter samples which exhibit the so-called photo-induced phase transition. The project consists of (1) the structure analysis of non-equilibrium states based on picosecond-resolved X-ray diffraction/scattering using the single-bunch mode of the PF-Advanced Ring (AR), (2) the development of a new beamline AR-NW14 for X-ray diffraction/scattering measurement of photo-induced phase transition phenomena, (3) the synthesis of organic or inorganic crystals that show photo-induced phase transitions, (4) the characterization of the phase transition with conventional optical measurements, and (5) the feasibility study of new methods to realize dynamic imaging with femtosecond resolution using newly-developed sub-picosecond X-ray sources.

In addition to the research groups under the project, we collaborate with groups at several universities. For crystal preparation, we have links with Tokyo Institute of Technology for inorganic materials and Kyoto University for organic ones. We are planning to collaborate with a group at Osaka City University for preparations of photo-active protein crystals. Another collaborating group in Tokyo Institute of Technology is working on crystal characterization using optical methods. The final research group is based in KEK and uses the pulsed X-rays from PF-AR in single-bunch operation. The administrative section of the project is also located at KEK. Collaboration contracts with Rennes University in France and ALS in USA are on the way.

Members

In 2003, Dr. Shin-ichi Adachi was appointed as group leader of the Molecular Dynamic Imaging Group at KEK. In order to drive forward the structural studies on photo-induced phase transitions, researchers are needed from various fields including synchrotron radiation, lasers, solid state physics, crystallography and sample preparation. In the second year of the project, 2004, seven researchers have joined the project. Two of them, specializing in laser and X-ray spectroscopy measurements, are developing novel methods of time-resolved X-ray diffraction/scattering/spectroscopy at the existing AR-NW2 beamline, at PF-AR, and constructing a new beamline, AR-NW14, in conjunction with KEK staff. For the feasibility study of femtosecond X-ray sources, one researcher will join the ALS group for a few years. A Ph.D student has joined the project as a crystallographer in collaboration with Dr. Sawa's group at KEK. In autumn 2004, two master's course students will also join the project.

Office

A new office for the ERATO project was built with funds from KEK at the end of FY2003 (Fig. 1). The office is currently occupied only by the ERATO members: the ERATO researchers, a research manager, an administrative manager, and an administrative assistant. The project will be managed as "an independent mini institute" for 5 years at the project office for administration.

Figure 1
Near the PF-AR buildings, a new office was opened.

3-2 Research Subject

Photo-induced phase transitions

The primary scientific targets of the project are condensed matter systems which can be triggered reversibly by a laser pulse and include organic and inorganic materials, protein crystals, and liquids. In particular, photo-induced phase transitions (PIPT) in molecular charge-transfer crystals are one of the main candidates for our

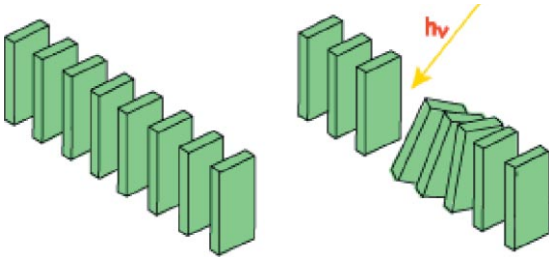

Figure 2
Schematic drawing of a photo-induced phase transition in a crystal. The structural relaxation of electronic excited state of a molecule causes a large-scale photo-induced phase transformation towards a new lattice, electronic order and physical properties, and is called a photo-domino effect.

research (Fig. 2). The remarkable feature of PIPT is its cooperativity, that is, the structural relaxation of the electronic excited state of a molecule causes a large-scale photo-induced phase transformation towards on new lattice, electronic order and physical properties. Time-resolved X-ray diffraction enables direct access to the dynamics of electronic, atomic and molecular motion in such systems. A preliminary experiment on an organic charge transfer complex crystal was successful using a combination of 100 picosecond synchrotron pulses and femtosecond laser pulses at the ESRF [1]. Since the X-ray and laser pulses must be synchronized by 1:1 during the pump-probe X-ray diffraction experiment, the repetition rate of the X-ray pulses from the synchrotron ring must be reduced to 1 kHz by using a high-speed chopper (X-ray pulse selector). Thus, single-bunch operation (i.e., relatively low repetition rate operation) of synchrotrons is crucial in enabling the use of an X-ray pulse selector for pump-probe diffraction experiments with synchrotron X-rays. PF-AR is the only facility in the world where the normal operation mode is single bunched, and this is why the Molecular Dynamic Imaging Group is based at KEK.

Future research targets

In addition to organic charge transfer complex crystals, we are planning to apply the picosecond-resolved pump-probe X-ray diffraction/scattering/spectroscopy methods to novel systems such as strongly correlated electron systems of organic and inorganic materials, photo-active protein crystals, and photo-active molecules in solution. In order to apply picosecond-resolved pump-probe X-ray diffraction to biological systems, we have started feasible studies on photoactive protein crystals for structural analysis of photo-induced intermediate states. For studies of samples in solution, X-ray scattering and spectroscopy will be the most powerful tools, and such methodological developments are also underway.

3-3 Beamline Development

AR-NW2 beamline

At the end of May 2004, a laser hutch (Fig. 3) was completed near the experimental hutch (Fig. 4) of AR-NW2. An X-ray pulse selector, a Ti:sapphire femtosecond laser (wavelength 800 nm, average output power 800 mW, repetition rate 1 kHz) and a nanosecond Nd:YVO laser (wavelength 532 nm, output power 50 mW) were installed. Another pulsed light source, a femtosecond fiber laser (508 MHz repetition, 1500 nm) will be purchased at the end of 2004. This equipment allows us to perform various types of pump-probe experiments using femtosecond or nanosecnod lasers at different wavelengths. Until the completion of the new beamline at AR-NW14, this beamline will be our main workhorse.

AR-NW14 beamline

A new beamline for time-resolved X-ray diffraction/scattering experiments is currently in the planning stage. Eventually we will move the laser system currently located at AR-NW2 to this new beamline. The installation of the beamline is expected to be completed by the end of summer 2005. More detailed plans for AR-NW14 are described elsewhere in this volume (see, pp 66).

Reference

[1] E. Collet, M.-H.L.-Cailleau, M.B.-L. Cointe, H. Cailleau, M. Wulff, T. Luty, S. Koshihara, M. Meyer, L. Toupet, P. Rabiller and S. Techert, *Science*, **300** (2003) 612.

Figure 3
The green box is an experimental hutch and the black box is a laser hutch. The hutches are connected by a black pipe for transport of the laser beam.

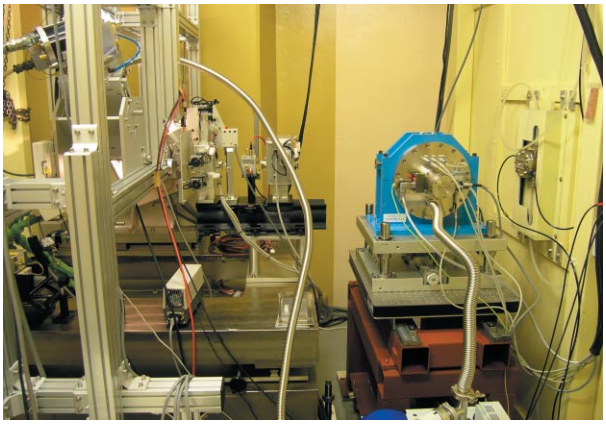

Figure 4
In the experimental hutch, the repetition rate of X-ray pulses is reduced by a mechanical chopper (X-ray pulse selector) (blue) from 794 kHz to 945 Hz to match to the repetition rate of the laser.