1-1-7. Time-Resolved X-ray Measurements (Scattering and Spectroscopy)

Overview

By employing time-resolved (TR) X-ray measurements, photochemical reactions of molecules and complexes proceeding in solution after photoexcitation can be observed in situ with femtosecond-to-picosecond temporal resolution, taking advantage of the high structural sensitivity of X-rays. In particular, TR X-ray solution scattering (TR-XSS) has produced some of the most impactful results in recent XFEL science, because it allows the nuclear wavepacket motion and solvent rearrangement driven by photoinduced reactions to be followed directly in real space. Moreover, combining TR X-ray spectroscopy with the same pump–probe configuration now enables a unified description of electronic-state and structural changes in solution.

Current Status and Frontiers

1. Development of time-resolved X-ray solution scattering (TR-XSS)

Since the 2000s, TR-XSS has been established at synchrotron sources as a time-resolved technique for recording pump-induced structural changes in liquids as time series of difference scattering curves $\Delta S(q, t)$. With the advent of XFELs in the 2010s and the resulting extension of the accessible time regime into the femtosecond range, TR-XSS has advanced decisively as a tool for tracking photochemical reaction pathways. In TR-XSS measurements on the photoexcited trimeric complex $[Au(CN)_2]_3$ performed at XFEL facilities,[1] the delay range from −1 ps to +2 ps was scanned in 25 fs steps, and multivariate analysis of $\Delta S(q, t)$ enabled separation of the coherent nuclear vibrational components while the excited trimer evolved across multiple potential-energy surfaces to form an Au–Au bond (Fig. 1). The strengths of TR-XSS are: (i) it simultaneously captures solvent rearrangement as well as structural changes of the reacting solute, (ii) changes in bond distances and the identity of the bonds involved can be matched one-to-one with structural models, and (iii) component separation based on singular value decomposition has been established so that essentially identical difference-scattering curves can be reproduced across different facilities. Standardization on the analysis side has also progressed.[2] Therefore, the photochemical applications presented here can be quantitatively compared across different facilities and research groups.

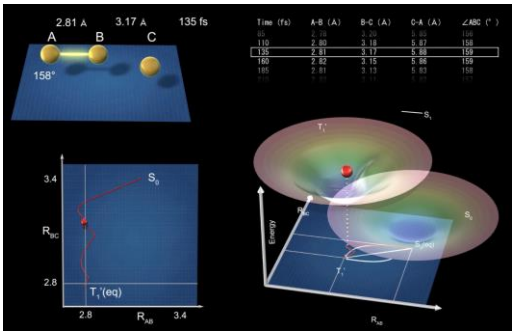

Figure 1. Visualization of the reaction pathway by TR-XSS.

2. Combination with time-resolved X-ray spectroscopy

The other major development is the simultaneous measurement of TR X-ray spectroscopy and TR-XSS, exemplified by the SACLA study on a Ru–Co complex (Fig.

2).[3] In this system, photoexcitation induces electron transfer from the Ru unit to the Co center via a bridging ligand; however, conventional optical techniques could not unambiguously determine the spin states or intermediate valence states involved in this process. By detecting the electronic state of Co through Co Kα time-resolved X-ray emission spectroscopy and, at the same time, monitoring solute and solvent structural changes by TR-XSS, the entire sequence—photoinduced charge transfer across the bridging ligand, subsequent spin crossover following charge transfer together with the accompanying local structural changes, and the final solvent rearrangement—was presented within a single, simultaneously acquired dataset. Such simultaneous "spectroscopy + scattering" TR X-ray measurements are complementary in nature: spectroscopy resolves changes in valence and spin states that are invisible to TR-XSS alone, whereas TR-XSS captures solute–solvent structural and configurational changes that cannot be accessed by spectroscopy alone. This approach is therefore expected to become a standard measurement scheme for XFEL-based studies of photochemical reactions.

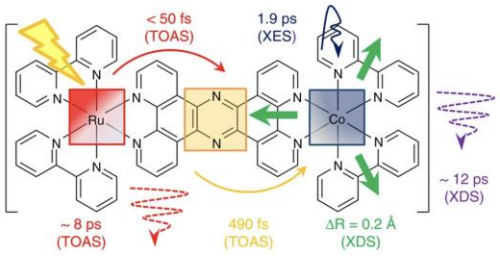

Figure 2. Simultaneous TR X-ray spectroscopy and TR-XSS measurement.

References

1. J. G. Kim, et al., *Nature*, **582**, 520–524 (2020).
2. S. E. Canton et al., *Nature Commun.*, **6**, 6359 (2015).
3. K. S. Kjær et al., *Phys. Chem. Chem. Phys.*, **15**, 15003–15016 (2013).
4. J. Duris et al., *Nature Photon.*, **14**, 30–36 (2020).

Future Perspectives and Directions

In the near future, the higher repetition rates of XFELs are expected to markedly improve statistical precision, thereby making molecular systems composed of light elements with inherently weak X-ray scattering intensities accessible targets. In addition, as techniques for generating sub-femtosecond X-ray pulses become established,[4] studies of electron–nuclear coupling dynamics immediately after photoexcitation are anticipated to become significantly more active.

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