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Molecular structural dynamics in solution probed by ultrafast pump-probe X-ray liquidography (solution scattering)

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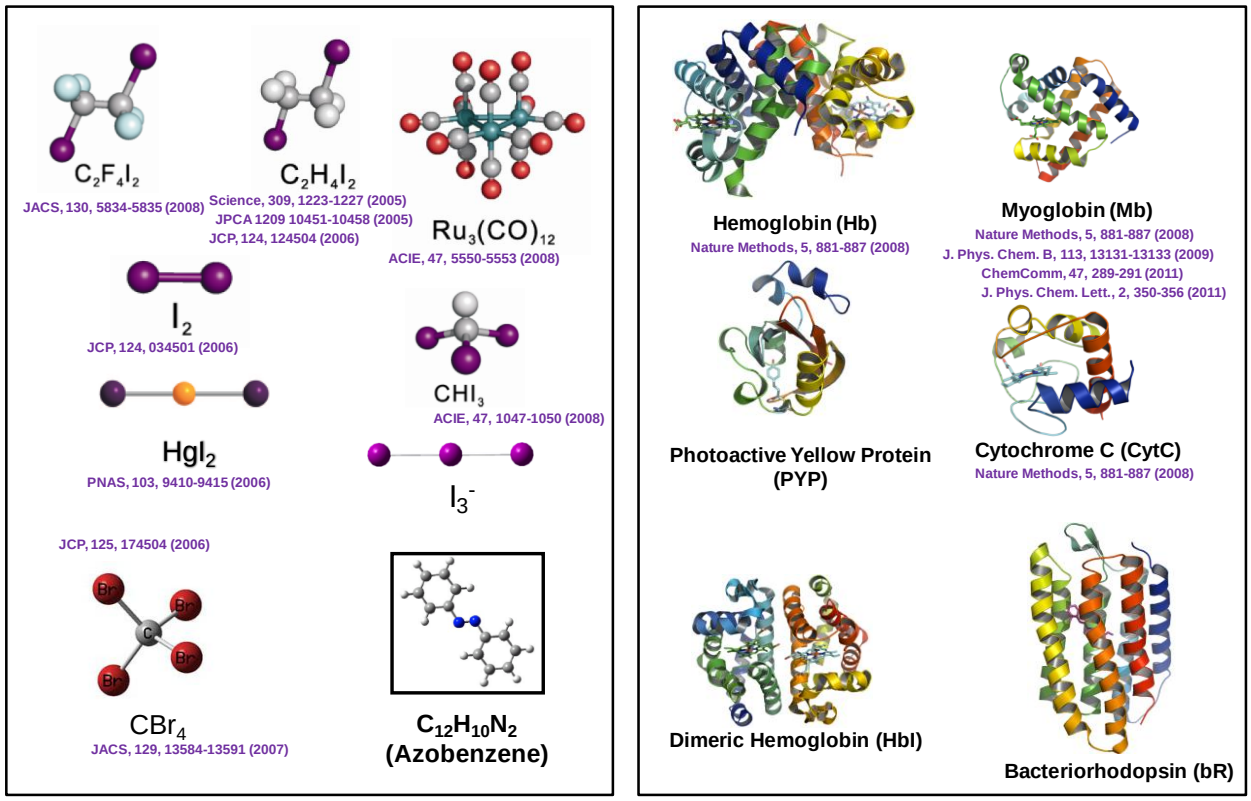
[Introduction] Solution-phase reactions are complex due to the interactions between solutes and solvents. Tracking time-dependent processes in such reactions is often accomplished by time-resolved spectroscopy. However, detailed structural information such as bond lengths and angles of reaction intermediates is not directly accessible because spectroscopic signals utilizing light in the range from ultraviolet to infrared are generally not a direct function of the molecular structure. In addition, a spectroscopic signal can be sensitive to only a particular species, leaving the possibility that optically silent intermediates escape detection. These shortcomings have been overcome by the advent of time-resolved X-ray solution scattering (TRXSS), which is also called time-resolved X-ray liquidography (TRXL) [1-10]. The principle, experimental technique, data analysis, and applications of TRXL will be described. Using ultrashort optical pulses to trigger a reaction in solution and detecting time-resolved X-ray diffraction signals to interrogate the molecular structural changes, TRXL can provide direct structural information generally difficult to extract from ultrafast optical spectroscopy such as the temporal progression of bond lengths and angles of all molecular species including short-lived intermediates over a wide range of times, from picoseconds to milliseconds. TRXSS elegantly complements ultrafast optical spectroscopy because diffraction signals are sensitive to all chemical species simultaneously and the diffraction signal from each chemical species can be quantitatively calculated from its three-dimensional atomic coordinates and compared with experimental TRXL data.

[Results] Application examples include spatiotemporal kinetics and structural dynamics of a halomethane, a triatomic molecule, haloethanes, an organometallic catalyst and proteins. In particular, we succeeded in tracking protein's structural changes in solution using TRXL. TRXL permitted us to investigate the tertiary/quaternary conformational change of human hemoglobin in nearly physiological conditions triggered by laser induced ligand photolysis. Data on optically induced tertiary relaxations of myoglobin and refolding of cytochrome c are also reported to illustrate the wide applicability of the technique. By providing insights into the structural dynamics of proteins functioning in their natural environment, TRXSS complements and extends results obtained with time-resolved spectroscopy and X-ray crystallography.

Various molecules studied by ultrafast X-ray liquidography (solution scattering)



[References]

1 Ihee, H. Visualizing Solution-Phase Reaction Dynamics with Time-Resolved X-ray Liquidography. *Acc. Chem. Res.* **42**, 356-366 (2009).

2 Lee, J. H. *et al.* Capturing transient structures in the elimination reaction of haloalkane in solution by transient X-ray diffraction. *J. Am. Chem. Soc.* **130**, 5834-5835 (2008).

3 Cammarata, M. *et al.* Tracking the structural dynamics of proteins in solution using time-resolved wide-angle X-ray scattering. *Nat. Methods* **5**, 881-886 (2008).

4 Ihee, H. *et al.* Ultrafast X-ray diffraction of transient molecular structures in solution. *Science* **309**, 1223-1227 (2005).

5 Ihee, H., Wulff, M., Kim, J. & Adachi, S. Ultrafast X-ray scattering: structural dynamics from diatomic to protein molecules. *Int. Rev. Phys. Chem.* **29**, 453-520 (2010).

6 Ihee, H. *et al.* Ultrafast x-ray diffraction of transient molecular structures in solution. *Science* **309**, 1223-1227 (2005).

7 Ahn, S., Kim, K. H., Kim, Y., Kim, J. & Ihee, H. Protein Tertiary Structural Changes Visualized by Time-Resolved X-ray Solution Scattering. *J. Phys. Chem. B* **113**, 13131-13133 (2009).

8 Kim, K. H. *et al.* Direct observation of myoglobin structural dynamics from 100 picoseconds to 1 microsecond with picosecond X-ray solution scattering. *Chem. Commun.* **47**, 289-291 (2011).

9 Kim, J. *et al.* Anisotropic Picosecond X-ray Solution Scattering from Photoselectively Aligned Protein Molecules. *J. Phys. Chem. Lett.* **2**, 350-356 (2011).

10 Kim, J., Kim, K. H., Lee, J. H. & Ihee, H. Ultrafast X-ray diffraction in liquid, solution and gas: present status and future prospects. *Acta Cryst. A* **66**, 270-280 (2010).