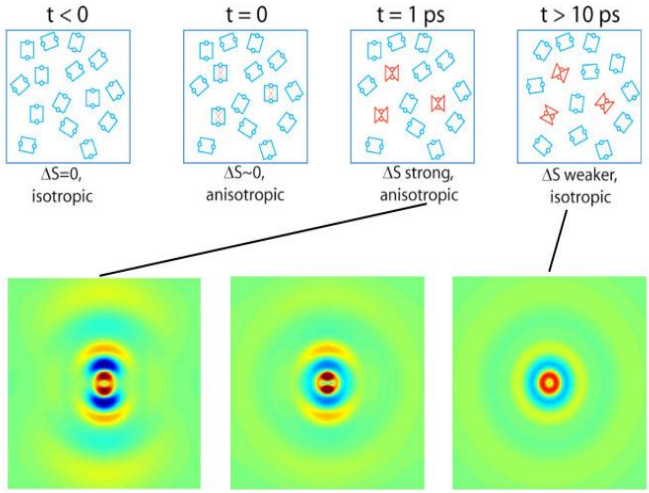
Tracking the structural effects of photo excitation of molecular systems

Martin Nielsen
Technical University of Denmark

Every photochemical reaction starts with an electronically excited state and ends with a ground state molecule. The pathway taken by the atomic nuclei, while molecules undergo such reactions, and is a fundamental question in chemistry, and a host of systems have been studied by laser spectroscopy down to the femtosecond time scale. However, while spectroscopic methods provide detailed information on the energy levels involved, direct structural information is in general not available. In the last few years, this gap of information has been bridged by X-ray scattering experiments on time scales down to picoseconds. Initially this has been made for crystalline systems with their inherent amplification of the scattered intensity and recently also for liquid systems, the natural environment for most chemical reactions.

On the 100 ps time scale, we have recently been able to determine key structural parameters directly for the highly reactive excited state of the square-planar platinum compound PtPOP (Pt2(P2O4H2)4(4–)) in aqueous solution [1]. Furthermore we were able to obtain the first direct structural fingerprint of a bimolecular reaction between the excited state PtPOP and Tl+ and Ag+ ions in solution [2, 3].



On the sub-picosecond time scale, hard and intense X-ray sources allow a detailed look at how energy introducedinto the electronic degrees of freedom in molecular systems can lead to pronounced structural reorganisation. Wepresent ideas for experiments involving binuclear metal complexes, where excitation of an electronic transition with well-defined energy and transition dipole moment leads to coherent intramolecular motion and significant orientational ordering of a sub-ensemble of an initially disordered molecular population. Ultrafast time-resolved X-ray scattering allows the direct tracking of the structural changes and orientational ordering/disordering through careful analysis of the strongly asymmetric scattering patterns on the very shortest time scales. Preliminary optical measurements are presented, allowing us to establish limits on the necessary time resolution.

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[2] Kristoffer Haldrup, Morten Christensen, Marco Cammarata, Qingyu Kong, Michael Wulff, Simon O. Mariager, Klaus Bechgaard, Robert Feidenhans'l, Niels Harrit, Martin M. Nielsen, Structural Tracking of a Bimolecular Reaction in Solution by Time-Resolved X-ray Scattering, Angew. Chem. Int. Edit., **48**, 4180- 4184 (2009)

[3] Morten Christensen, Kristoffer Haldrup, Kasper S. Kjær, Marco Cammarata, Michael Wulff, Klaus Bechgaard, Høgni Weihe, Niels H. Harrit, and Martin M. Nielsen, Structure of a Short-lived Excited State Trinuclear Ag-Pt-Pt Complex in Aqueous Solution by Time Resolved X-ray Scattering, Phys Chem ChemPhys, **12**, 6921-6923 (2010)