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Probing Ultrafast Photoinduced Structural Dynamics in Molecular Solutions using Angular X-ray Cross-Correlation Analysis

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Understanding photoinduced chemical reactions at the electronic, atomic and molecular scales and on relevant timescales is critical for controlling reaction pathways, rates and efficiency. This fundamental knowledge is essential for applications such as catalysis, photoswitching, and light-harvesting. X-ray free-electron lasers (XFELs) produce intense and ultrashort x-ray pulses, allowing to probe chemical processes experimentally with high spatial and temporal resolution. Here we apply femtosecond XFEL pulses to track ultrafast optically excited dynamics of a model photocatalyst $Ir_2(dimen)_4]^{2+}$ (dimen=1,8-diisocyano-p-menthane) in solution [1].

Time-resolved x-ray solution scattering (TRXSS) with an XFEL directly probes the time-dependent structure of a solution through the atomic pair distribution function (PDF). While this established approach simplifies the interpretation of experimental scattering data, the one-dimensional shape of the PDF in solutions limits the structural information that can be extracted. Here we employ an alternative approach to analyze TRXSS measurements based on the application of angular cross-correlation functions (CCFs) [1,2], which was originally proposed to facilitate biological structure determination from solution x-ray scattering [3-5].

We perform a model-assisted analysis of correlations in scattered x-rays, which allows us to elucidate various aspects of photoinduced changes in photoexcited molecular ensembles [1]. We unambiguously identify that in our experiment the photoinduced transition dipole moments in $[Ir_2(dimen)_4]^{2+}$ molecules are oriented perpendicular to the Ir–Ir bond. The analysis also shows that the ground state conformer of $[Ir_2(dimen)_4]^{2+}$ with a larger Ir–Ir distance is mostly responsible for the formation of the excited state. We also reveal that the ensemble of solute molecules can be characterized with a substantial structural heterogeneity due to solvent influence.

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