



GÖTEBORGS UNIVERSITET

Escape from the cage: Ultrafast structural dynamics of photodissociation reactions observed with X-ray solution scattering

Amke Nimmrich

Institutionen för kemi och molekylärbiologi
Naturvetenskapliga fakulteten

Akademisk avhandling för filosofie doktorsexamen i Naturvetenskap, inriktning kemi, som med tillstånd från Naturvetenskapliga fakulteten kommer att offentligt försvaras
Fredag den 20/01/2022 kl. 13 i Arvid Carlsson, Institutionen för kemi och molekylärbiologi, Medicinargatan, Göteborg.

ISBN: 978-91-8069-095-9



GÖTEBORGS UNIVERSITET

Abstract

The environment of a molecule is known to greatly impact the course of a reaction. Such an environment can, for instance, be the solvent in a solution phase reaction or the amino acid residues surrounding a chromophore in photoreceptor proteins. For a deeper understanding of the influence of the molecular environment, a structural insight into the underlying mechanisms is necessary.

In this work, time-resolved X-ray techniques are applied to directly observe the photoinduced structural dynamics of chromophores and their interaction with the environment. Solvent-solute interactions in the photodissociation reactions of triiodide and diiodomethane in solution were investigated using X-ray Solution Scattering (XSS). The studies give direct insight into the structural dynamics of the solute and the solvent cage. Further, we observe solvent-dependent branching ratios between geminate and non-geminate recombination. To investigate the solvent rearrangement during a reaction in more detail, both XSS experiments and molecular dynamics simulations on the photoionisation of aqueous iodide were performed. Comparison of experimental and simulated data reveal the ultrafast breaking of the initial solvent cage and formation of a new hydrogen bonding network. Finally, the light-induced structural dynamics in photoreceptor proteins were observed using both XSS and Serial Crystallography (SX). The results from SX studies on photolyases and phytochromes reveal how the amino acid residues around the chromophore move to accommodate the changes in structure and charge distribution on the chromophore.

This work presents the potential of time-resolved studies performed at X-ray Free Electron Lasers to gain direct insight into the structural dynamics of photo-initiated reactions and the complex interplay between chromophores and their environment.

Keywords:

Ultrafast X-ray science, X-ray Solution Scattering, X-ray Free Electron Lasers