Non-linear statistical physics
and Molecular Dynamics simulations
for the interpretation of Time-resolved X-ray diffraction

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We will present a theoretical study of time-resolved x-ray diffraction experiments on the recombinaison of photo-dissociated iodine in CCl_4. In recent experiments conducted at the ESRF (Grenoble), this process has been studied for times ranging from 100 ps to microseconds.

The non-linear response theory derivation of the signal measured in time-resolved x-ray experiments will first be presented. Dynamics at many different time-scales contribute to the time-resolved signal and we will focus our attention to the long time limit of this expression, times long with respect to the molecular vibrations (a few picoseconds). This will lead us to a natural phenomenological expression of the time-resolved x-ray signal which will be a function of the species present in the solution, plus a solvent response. This universal solvent response consists in the thermal heating due to the energy released by the chemical reaction which induces in turn a thermal expansion. The rate of this expansion is non uniform due to acoustic phenomena.

Molecular Dynamics simulations were then used to evaluate the x-ray form-factor of the different species in solution as well as the differential form-factor of the solvent, induced by thermal heating. This enabled us to reproduce the experimental time-resolved x-ray diffraction signals of the recombinaison of iodine in CCl_4. It will be shown that qualitatively and to a large extend quantitatively, the phenomenological expression for the signal based on reaction kinetics and hydrodynamics is valid already at early times (~100 ps) up to microseconds.

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