

Ultrafast anisotropic X-ray scattering in the condensed phase

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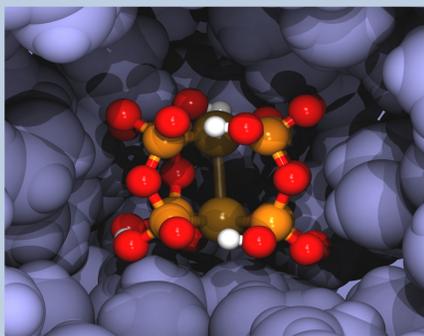
Problem

The advent of X-ray free electron lasers offers new opportunities for X-ray scattering studies of the ultrafast molecular dynamics in liquids, which was so far limited to the 100 ps resolution of synchrotrons. Photoselection induces anisotropy in the sample, which enhances the contrast of the signal from excited molecules against the diffuse background, while allowing probing of their vibrational and rotational dynamics. Here, we present a computational approach for calculating the transient scattering intensities of iodine in n-hexane, based on molecular dynamics simulations. We also derive, using realistic parameters the anticipated signal-to-noise ratio for a large class of diatomic elements in solution.

Basic Concept

The use of polarised pump laser pulses induces an anisotropy of the sample by preferably photoexciting those molecules that have a favourable orientation of their transition dipole moment with respect to the electric field vector of the laser [4]. Subtracting the unexcited sample pattern will therefore leave the contribution from the excited molecules, i.e. the anisotropic component and therefore were unable to fully characterise the signatures of vibrational and reorientational dynamics.

In the Future



Bimetallic complexes, such as $[\text{Pt}_2(\text{POP})_4]^{4-}$ ($\text{POP} = [\text{H}_2\text{P}_2\text{O}_5]^{2-}$) would be highly suited to fs XRS. This complex exhibits a rich wavepacket dynamics along the Pt-Pt bond, identical to that of a diatomic molecule [6].

This work is a first step in the investigation of fs XRS and further work to include solvent induced non-adiabatic processes and rotational diffusion is underway.

References

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Acknowledgements

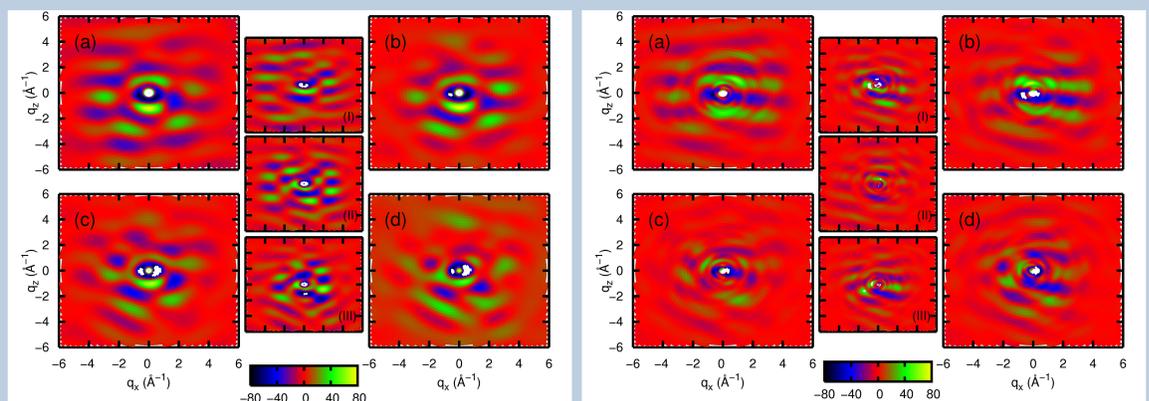
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The Transient Patterns and Signal to Noise Ratio

The calculation of anisotropic scattering signals is computationally expensive for liquid solutions where a large number of atoms must be considered. However anisotropy will only be introduced via the excited solute and a small region of the solvent in close proximity. Therefore, by solving exactly for the solute and a small region of the solvent around it, we can obtain realistic signals at much reduced computational expense:

$$\tilde{I}(\mathbf{q}) = \sum_h f_h^2(\mathbf{q}) + \sum_{j \neq h} f_h(\mathbf{q}) f_j(\mathbf{q}) \exp^{-i\mathbf{q}r_{hj}} + \sum_k N_k f_k^2(\mathbf{q}) + N_k N_l V \sum_{l \neq k} f_k(\mathbf{q}) f_l(\mathbf{q}) \int_{-\infty}^{\infty} (g_{kl}(r) - 1) \sin(\mathbf{q}r) \mathbf{q} r 4\pi r^2 dr \quad (1)$$

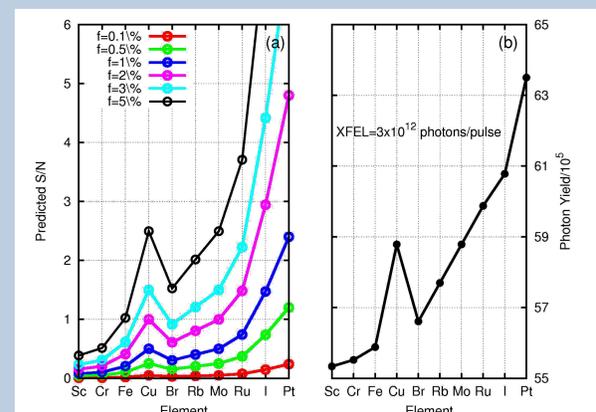
The intensity can be calculated from snapshots of molecular dynamics (MD) simulations of excited molecular systems. Below we plot the transient scattering patterns, with an without the solvent in the anisotropic region.



Given that these simulations concern only 3000 configurations, they hold the promise that single shot XRS of solutions can be envisioned at X-FELs. Therefore, we use realistic X-FEL parameters to predict a signal to noise ratio (S/N) for planning future experiments.

The derived S/N as a function of element and photolysis yield indicates that from a single shot X-ray diffraction experiment it would be possible to obtain a $S/N \geq 1$ for a photolysis yield of 3% from the elements heavier than iron. For the heaviest elements (ruthenium, iodine and platinum) the S/N can be greater than 3 and therefore one could expect a good experimental contrast.

We note that intensity fluctuations in the X-ray intensity would lead to a reduction in the signal to noise ratio. This could make single shot experiments for the lighter elements very difficult. In such cases accumulation could be used. This requires the accurate knowledge of the incoming X-ray intensity to account for shot to shot fluctuations. This can be measured to less than 0.5% as demonstrated in running experiments at the LCLS Facility (Stanford) and therefore we do not expect this to be a limiting factor.



Computational Details

The MD simulations were performed with the GROMACS molecular dynamics package [5]. The system is composed of one I_2 molecule and 106 hexane molecules within a box of 28 \AA^3 . It was propagated in the ground state for 20 ns, from which 3000 configurations from the last 5 ns were selected randomly and used.

100 out of the 3000 configurations were selected for the excited state dynamics according to the alignment of the transition dipole of I_2 with the electric field of the pump laser. These configurations were then propagated for 2 ps and snapshots from the photoselected simulations were taken at 100, 200, 300 and 400 fs. We assume an X-ray probe pulse at 8 keV with a 0.1% bandwidth and a temporal width of 10 fs.

