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2012 New J. Phys. 14 113002
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Ultrafast anisotropic x-ray scattering in the condensed phase

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Received 9 March 2012
Published 6 November 2012
Online at http://www.njp.org/
doi:10.1088/1367-2630/14/11/113002

Abstract. The advent of x-ray free electron lasers offers new opportunities for x-ray scattering (XRS) studies of ultrafast molecular dynamics in liquids, which have so far been limited to the 100 ps resolution of synchrotrons. In particular, anisotropic XRS induced by photoselection, using a linearly polarized pump pulse, can enhance the contrast of the signal from excited molecules against the diffuse background and allows the probing of their vibrational and rotational dynamics. Here, we present a computational approach for calculating transient scattering intensities, based on molecular dynamics simulations. This is applied to the study of the excited state dynamics of molecular iodine dissolved in n-hexane. We report that at short times the transient XRS patterns reflect the evolving vibrational and rotational dynamics of I2, even when the disordered solvent environment is included. We then use these simulations to derive the anticipated signal-to-noise ratio for a large class of model diatomic systems in solution, indicating that an \( S/N \geq 1 \) will be possible from single-shot experiments in weakly scattering solvents.

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1. Introduction

The past decade has witnessed much progress in the study of the ultrafast structural dynamics using x-rays or electrons [1]. In the liquid phase, x-ray scattering (XRS) and x-ray absorption spectroscopy (XAS) have emerged as the methods of choice, at third generation sources of x-rays [2, 3]. However, synchrotron x-ray pulses have a temporal width of 50–100 ps and therefore only relatively long-lived transient structures can be probed. Femtosecond (fs) XAS of solutions has been demonstrated thanks to the slicing scheme at synchrotrons [4, 5]; however, the low fluxes of this scheme make fs XRS impossible. The advent of x-ray free electron lasers (X-FELs) offers new and exciting opportunities for fs XRS due to the ten orders of magnitude increase in flux per pulse, compared to the slicing scheme at synchrotrons. In particular, using a polarized pump laser pulse, one can induce anisotropy into the sample by preferably photo-exciting those molecules that have a favourable orientation of their transition dipole moment with respect to the electric field vector of the laser. This idea was first proposed by Bergsma et al [6], who calculated both the resulting isotropic and anisotropic scattering components separately and investigated their temporal evolution when applied to dissociating I\textsubscript{2} molecules in solution.

Advances in this domain brought about by X-FELs have led to growing interest in such experiments. Recently, Lorenz et al [7] calculated the expected anisotropic x-ray diffraction patterns for NaI in the gas phase, demonstrating a method for extracting the density distribution from such experiments. In a similar vein, Ho et al [8] and Debnarova et al [9] have performed computational studies, inducing the anisotropy of the sample by laser alignment. Experimentally, time-resolved anisotropic XRS using photoselection by a polarized pump laser pulse has recently been realized by Kim et al [10], who studied the anisotropic scattering from photo-excited myoglobin. In this case, the size of the system means that rotational diffusion is significantly slower than for small molecules, making it possible for the anisotropy to be detected over a few ns, with the 100 ps x-ray pulses from a synchrotron.

For investigating the ultrafast structural dynamics of molecular systems in solution by fs XRS, it is important to assess the feasibility of photoselection pump/X-FEL probe experiments. In this paper, we present a computational study of the fs XRS of photoselected molecular iodine dissolved in n-hexane. Our simulations show that the calculated transient XRS patterns reflect the evolving structure and rotational dynamics of I\textsubscript{2} even when the disordered solvent environment is included. These simulations are then used to estimate the anticipated signal-to-noise ratio (S/N) for a range of model diatomic systems in solution, showing that an S/N \(\geq 1\) will be possible from single-shot experiments in weakly scattering solvents.
2. Theory and computational details

Prior to photoexcitation, the XRS signal of a molecular system in solution exhibits a purely isotropic component, which can be described by the Debye scattering equation [11]. Upon excitation of the molecule with polarized light, an anisotropic component will be induced, because only those molecules whose transition dipole moment is favourably oriented with respect to the electric field vector of the pump pulse will be excited [12]. This photoselection scales as $\cos^2 \phi$, where $\phi$ is the angle between the transition dipole moment vector, which, in the present case, is parallel to the internuclear axis and the electric field vector. Throughout this work, we follow [18] and define the anisotropy as $A = 0.4 P_2(\cos \phi(t))$, where $P_2$ is the second order Legendre polynomial and therefore 0.4 is equivalent to perfect alignment.

Probing the sample by XRS, using an ultrashort x-ray pulse at a given time delay after the laser excitation, will yield an x-ray pattern containing fringes at early times due to the photoselected molecules. These will disappear as a function of time, because of rotational diffusion and the dissipation of energy to the solvent. However, overall, the pattern will be largely dominated by the scattering contribution of the unexcited (randomly orientated) molecules and the solvent, which will be similar to the pattern before $t = 0$. Consequently, subtracting the pattern at $t < 0$ from the scattering pattern of the excited sample will lead to a cancellation of the isotropic components, leaving only the contribution from the excited molecules.

In order to accurately describe the XRS intensity, one must consider every atom explicitly and, assuming that they are stationary under the temporal envelope of the probe pulse, calculate

$$\tilde{I}(q) = \sum_{N_{\text{config}}} \sum_h f_h^2(q) + \sum_{j \neq h} f_h(q) f_j(q) \exp(-iqr)_{hj},$$

where the total intensity is $I(q) = \int \tilde{I}(q) \int I^\ast(t) \, dt$, with $I^\ast(t)$ being the intensity of the incident x-ray pulse. The intensity ($\tilde{I}$) is calculated as a sum over all configurations ($N_{\text{config}}$) of a molecular dynamics (MD) simulation. The indices $h$ and $j$ run over all of the atoms and are separated by $r_{hj}$, $f$ is the atomic scattering factor (ASF), $q = 4\pi\sin\theta/\lambda$ is the magnitude of the scattering vector, $2\theta$ is the scattering angle, $\lambda$ is the wavelength of the x-ray photons, $j_l$ are spherical Bessel functions and $Y_{lm}$ are spherical harmonics.

This calculation 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, at least at early times and depending on the strength of the solute–solvent interaction. Therefore, by solving equation (1) for the solute and a small region of the solvent around it, we can obtain realistic signals at a much reduced computational expense. The rest of the signal arising from the isotropic solvent can be calculated using the Debye scattering equation [11]. We can then write the scattering intensity at a given time delay after the laser excitation, $t$. The intensity $\tilde{I}(q)$ is then given by

$$\tilde{I}(q) = \sum_{N_{\text{config}}} \sum_h f_h^2(q) + \sum_{j \neq h} f_h(q) f_j(q) \exp(-iqr)_{hj},$$

where $I(q)$ is the intensity of the incident x-ray pulse, $f_h$ is the atomic scattering factor (ASF), $q = 4\pi\sin\theta/\lambda$ is the magnitude of the scattering vector, $2\theta$ is the scattering angle, $\lambda$ is the wavelength of the x-ray photons, $j_l$ are spherical Bessel functions, $Y_{lm}$ are spherical harmonics, and $N_{\text{config}}$ is the number of configurations in the MD simulation.

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Figure 1. (a) Potential energy curves for the ground (X) and excited (A, B and Π) states of molecular iodine (I\(_2\)). The purple line represents the excitation to the B state at 520 nm. (b) The radial distribution functions of I–C (red) and I–H (green) obtained from the equilibrium configurations of the classical MD simulations averaged over 5 ns. (c) Swarm of trajectories showing the time evolution of the I–I bond length following excitation to the B state, obtained from 100 initial configurations. (d) Time evolution of the anisotropy, \( A = 0.4 P_2(\cos \phi (t)) \), of the excited configurations. The inset is a zoom of the first 500 fs.

\[
\tilde{I}(q) = \sum_{1}^{N_{\text{config}}} \sum_{h} f_h^2(q) + \sum_{j \neq h} f_h(q) f_j(q) \exp(-iqr)_{h,j} + \sum_{k} N_k f_k^2(q) \\
+ \frac{1}{V} \sum_{l \neq k} N_k N_l f_k(q) f_l(q) \int_{-\infty}^{\infty} (g_{kl}(r) - 1) \sin(qr) q r^4 4\pi r^2 dr, \tag{3}
\]

where \( N_k \) and \( N_l \) are the number of atoms of type \( k \) and \( l \), respectively, \( g_{kl}(r) \) is the radial distribution function and \( V \) is the volume of the whole system. It is important to note that the fourth term in this equation corresponds to the isotropic component and will therefore cancel out when subtracting the \( t < 0 \) pattern from those at \( t > 0 \).

Equation (3) shows how the intensity can be calculated from snapshots of MD simulations of the excited molecular systems in solution. Our purpose in the present work is to translate into scattering patterns the structural (wavepacket) dynamics, occurring in a diatomic molecule. For this purpose we have chosen the well-characterized I\(_2\) molecule in solution. Its potential curves are shown in figure 1(a). Excitation into the bound B state gives rise to a rich wavepacket pattern that was first obtained by Zewail and co-workers [17] using fs optical spectroscopy in the gas.
They reported wavepacket oscillations with a period between 350 and 750 fs depending on the pump wavelength (620 and 520 nm, respectively) because of the anharmonicity of the potential. Apkarian and Schwentner [13] later characterized in detail the wavepacket dynamics in low-temperature cryogenic matrices, while Scherer et al [14] and Zadoyan et al [15] characterized them in solution and found that the wavepacket coherence time was significantly reduced compared to the gas phase due to solvent effects. Importantly, both studies in the condensed phase demonstrated the occurrence of a nonadiabatic curve crossing event from the B to the Π state. Given that this process only occurs once the wavepacket has reached the bottom of the B state potential, we will neglect it for the purpose of the present study.

The MD simulations were performed with the GROMACS MD package [19], the parameters for iodine were taken from [16] and for hexane from [6]. The system is composed of an I$_2$ molecule and 106 hexane molecules within a box of (28 Å)$^3$. It was propagated in the ground state for 20 ns, from which 3000 configurations from the last 5 ns were selected randomly and used as the equilibrium configurations for the scattering calculations. During this period the system was maintained at 300 K by the Nosé–Hoover thermostat in a canonical (NVT) ensemble.

Using a fs pump pulse of 520 nm with a spectral width of 10 nm, corresponding to a pulse width of 90 fs, we generate a wavepacket on the B state and obtain snapshots of the dynamics which are used to calculate the XRS patterns. The 520 nm pump pulse means that the system is excited near the asymptotic dissociation limit of the B state, where the wavepacket oscillations span the largest amplitude of internuclear distances. Within this model we do not consider effects related to the shape, phase and intensity of the optical pulse. 100 of the 3000 configurations were selected for the excited state dynamics (we therefore imposed a realistic photolysis yield of 3% [21]) according to the alignment of the transition dipole of I$_2$ with the electric field of the pump laser ($z$-polarized) defined by the polar angle $\phi$. The criterion for photoselection was $\cos^2 \phi \geq 0.8$, and the resulting anisotropy of the excited state configurations and their temporal evolution are shown in figure 1(d). These configurations were then propagated for 2 ps on the excited B state within a microcanonical (NVE) ensemble. Figure 1(c) shows the swarm of classical trajectories of the I–I bond distance as a function of time following photoexcitation. The first elongation, to 3.5 Å, is the largest, while for the following oscillations the elongation decreases as the system relaxes down the B potential.

The XRS patterns are calculated assuming an unpolarized x-ray probe pulse propagating perpendicular to the electric field of the pump pulse, at 8 keV with a 0.1% bandwidth and a temporal width of 10 fs. The scattering intensity was calculated using 20 Bessel functions ($j_l$ in equation (2)) in the anisotropic region of the system. This ensures convergence of this component of the diffraction pattern to less than 0.5%. Snapshots from the photoexcited state MD simulations were taken at 100, 200, 300 and 400 fs and added to 3000 randomly selected equilibrium configurations to calculate the scattering intensity using equation (3). The radial distribution function, shown in figure 1(b) was converged in all cases. The ASFs were assumed to be time-independent and the parameters were taken from the international tables for crystallography [20].

3. Results

Figure 2 shows the transient (excited minus unexcited) scattering patterns at 100, 200, 300 and 400 fs. In panels (a)–(d), we neglect the anisotropy of the solvent only including its contribution
Figure 2. The transient scattering patterns of photo-excited I$_2$ in n-hexane for time delays of 100, 200, 300 and 400 fs (descending order). The polarization of the pump laser pulse is along the $y$-axis in these plots. For panels (a)--(d) we have assumed that no anisotropy is induced in the solvent, while for panels (I)--(IV) we have assumed that anisotropy is induced in the first solvation shell and therefore the 54 closest carbon atoms are included in the explicit atomic description. The colour key is unitless, but the range shown corresponds to 3.5% of the total scattering signal. The white spots are regions of high signal.

in the Debye scattering part (fourth term) of equation (3), meaning that it cancels out in the transient signal. In panels (I)--(IV), the photo-induced anisotropy in the first solvation shell is considered and therefore we have included the 54 closest carbon atoms into the explicit atomic
Figure 3. The difference plots between the transient scattering patterns shown in figure 2. Panels (a)–(c) correspond to the differences between figures 2(a)–(d), respectively. Panels (I)–(III) correspond to the difference plots between figures 2(I) and (II), figures 2(II) and (III) and figures 2(III) and (IV), respectively. The colour key is unitless.

description. The hydrogen atoms are neglected due to their small scattering strength. At $t = 0$, the average bond length of the excited configurations is 2.66 Å, with a distribution between 2.58 and 2.75 Å (figure 1(c)) and an initial anisotropy (figure 1(d)) value of 0.38 (0.4 corresponds to perfect alignment).

According to figure 1(c), at 100 fs after excitation, the average bond length of the excited iodine is 2.70 Å with a distribution between 2.62 and 2.82 Å. The excited molecules form an anisotropic ensemble, and this is reflected in the fringe pattern of the transient scattering intensity that is visible in figure 2(a). This fringe pattern does not have a plane symmetry because our photoselected configurations at $t = 0$ are not totally symmetric around the axis of the laser polarization vector. The consequence of which is observed in the break-up of the fringes, most obvious at larger $q$, which arises due to the interferences of scattered rays from iodine molecules in slightly different orientations. After 200 fs the average bond length has increased to 3.00 Å with a distribution between 2.85 and 3.05 Å (figure 1(c)). This is reflected in a contraction of the fringes. To clarify these changes, figure 3(a) shows the difference between figures 2(a) and (b). We observe significant changes and in particular the presence of negative features corresponding to the position of positive intensities in figure 2(a), confirming the contraction of the fringes. In addition, figure 3(a) itself also shows a strong fringe pattern, indicating that the changes are dominated by the elongation of the I–I bond length and that there is only a small reduction of the anisotropy (0.38–0.36, figure 1(d)).

Figure 2(c), 300 fs after excitation, shows a further contraction of the fringes due to the increase in the average bond length, now 3.20 Å. This is again confirmed by the difference shown in figure 3(b). However, most noticeable in this case is the reduction of the fringe pattern due to a decreased anisotropy (0.36–0.32, figure 1(d)). In the next snapshot at 400 fs, the system is even more isotropic (anisotropy = 0.28, figure 1(d)) and this is clearly visible by the further
fading of the fringes. In this case, the difference between these two transient patterns, figure 3(c),
shows the weakest fringe pattern, indicating that although there is a further elongation of the I₂ bond length, the initial anisotropy is largely lost and dominates the difference between figures 2(c) and (d).

Figures 2(I)–(IV) show the transient scattering patterns, taking into account the anisotropy of the solvent around the solute. Comparison of figures 2(a) and (I) shows that all the major features of the iodine scattering remain; however, they are not as intense because of the destructive interference between the iodine–iodine and iodine–hexane scattering components, which is the only additional term in the calculation. In figure 2(II), the contraction of the diffraction peaks, due to bond elongation, is again visible, in agreement with the previous case of the isotropic solvent. This is confirmed by figure 3(I), which shows a similar, albeit weaker, difference pattern to figure 3(a).

The largest difference can be seen in figures 2(III) and (IV), 300 and 400 fs, respectively. In figure 2(III), the scattering intensity is greatly reduced. Comparison of figures 2(c) and (III) shows that the position and shape of the transient scattering features are similar and therefore the loss of intensity is due to the increasing importance of the solute–solvent scattering terms. In figure 2(IV), the intensity appears slightly increased in comparison with figure 2(III) and we also observe more differences in comparison with figure 2(d). This is pronounced when one compares the corresponding difference plots (figures 3(c) and (III)). These differences arise because the I₂ bond length is now 3.35 Å; leading to a decrease in the iodine–iodine scattering component, but also an increase in the iodine–solvent scattering terms, which have become increasingly dominant as seen by the effect on the transient scattering pattern after 400 fs.

Given that these simulations concern only 3000 configurations for an excitation yield of 3%, they hold the promise that single-shot XRS of solutions can be envisioned at X-FELs. In order to assess the feasibility of such experiments, we estimate the anticipated S/N using realistic X-FEL parameters. We also calculate the scattering intensity, using the previous MD configurations for different transition metals in diatomic form including the solute–solute, solute–solvent and solvent–solvent terms described in equation 3. Although they are model systems, these diatomics do occur in a large class of binuclear metal complexes, at equilibrium bond distances close to that of iodine. In calculating the photon yields and S/N, we assume a zero noise detector and only take into account the Poisson noise calculated as \( n / \sqrt{N} \), where \( n \) is the transient signal intensity and \( N \) is the total signal of the excited system. To calculate the scattering intensity in photons, we use

\[
I(q, \Omega) = N_e \sin^2 \theta \Omega r_e^2 \tilde{I}(q) \int I^x(t) \, dt,
\]

where \( N_e \) is the number of ensembles \((7 \times 10^{12})\) within a pulse of focal spot radius 40 µm. The solid angle, \( \Omega \), for a detector pixel with dimensions 0.4 mm² is \( 6.4 \times 10^{-5} \) sr when placed 50 mm from the sample and at an angle of 0° with the incident x-ray pulse. \( r_e \) is the classical electron radius and \( I^x \) is the incident x-ray pulse intensity, \( 5 \times 10^{12} \) photons per pulse [25].

The derived S/N as a function of element and photolysis yield is shown in figure 4(a). It indicates that from a single-shot x-ray diffraction experiment, it would be possible to obtain an S/N \( \geq 1 \) for a photolysis yield of \( \sim 3\% \) from the elements heavier than iron. The enhanced S/N peak for copper is due to the resonance of the X-FEL energy with that of the copper K-edge, giving rise to anomalous scattering. For the heaviest elements, namely ruthenium, iodine and platinum, the S/N can be greater than 3 and therefore one could expect a good experimental
Figure 4. (a) The predicted signal-to-noise ratio for a range of photo-excited diatomic molecules as a function of the photolysis yield. The transient scattering intensity for each system is calculated using exactly the same configurations as for the iodine dynamics, assuming a completely isotropic solvent. (b) Predicted photon yield as a function of atomic weight for a typical scattering intensity around $q_x = q_z = \pm 2\text{Å}^{-1}$.

contrast. In particular, bimetallic complexes, such as $[\text{Pt}_2(\text{POP})_4]^4^-$ (POP = $[\text{H}_2\text{P}_2\text{O}_5]^2^-$) and $[\text{Ir}_2(\text{dimen})_4]^{2^+}$ (dimen = 1,8-diisocynano-p-menthane), would be highly suited for fs XRS experiments. Indeed, ideal in the context of this paper is the fact that these complexes exhibit a rich wavepacket dynamics identical to a diatomic molecule along the Pt–Pt [22] and Ir–Ir bonds [23], respectively. In addition, for $[\text{Pt}_2(\text{POP})_4]^4^-$, XRS studies with 100 ps time resolution have already been carried out [24].

Figure 4(b) shows the photon yield for a typical scattering intensity around $q_x = q_z = \pm 2\text{Å}^{-1}$. This is representative of the region of importance in the transient spectrum. The situation will be worse at large $q$, due to the lower intensity of the scattering signal, while at smaller $q$, the larger scattering intensity would likely lead to saturation of the detector. The simulation shows that one could expect a photon count per pixel in this region of $\approx 60 \times 10^5$ photons, of which 90% comes from the solvent. Therefore for such signals, in which the transient pattern is small, a careful choice of the detection is important. The suitability of detection methods also depends on the count rate and quantum efficiency. For the former, the spacing between the pulses at the planned SwissFEL will be 10 ms and therefore a count rate dynamic range of approximately $>100$ Hz is required. For the latter, in the energy range between 8 and 12 keV, detectors with a quantum efficiency of between 0.8 and 1 have been developed [26, 27].

Another possible source of noise in such experiments arises from the well-documented fluctuations in the x-ray intensity at FELs. At the LCLS Facility (Stanford) the typical x-ray intensity fluctuations are $<10\%$ [28] and using the previous calculations this would lead to a reduction in the S/N of between 5 and 7%. This could render single-shot experiments for the lighter elements very difficult and in such cases, accumulation should be used. The
latter requires accurate knowledge of the incoming x-ray intensity to account for shot-to-shot fluctuations. Therefore, taking into account that the changes in the excited x-ray pattern are of the order of \( \leq 3\% \), depending on the atomic species and photolysis yield, one requires a careful measurement of the shot-to-shot intensity to at least 0.5\%, to minimize the effect on the S/N.

4. Conclusions

We have presented an efficient method for calculating the anisotropic XRS from photo-excited molecules in solution. Applying it to molecular I\(_2\) dissolved in n-hexane, we have derived scattering patterns and described how they may be used to provide structural details. Our simulations show that using photoselection pump/X-FEL probe experiments, it will be possible to obtain detailed information about the structural dynamics of molecules in solution.

Using these simulations, we have also estimated the S/N for a range of transition metals in diatomic form, indicating that an S/N \( \geq 1 \) will be possible from single-shot experiments in weakly scattering solvents. This work is a first step in the investigation of fs XRS of molecular systems and further work to include solvent-induced nonadiabatic processes and rotational diffusion is under way.

Finally, in light of these results, future efforts should focus on schemes to extract the structural information from the experimental data in this regime, for which the scattering patterns will be highly complex. It is well established that for isotropic systems, the structure may be extracted from the Fourier transform of the diffraction pattern, which in the case of liquids can be expressed in terms of a radial distribution function [29]. However, in the present case, due to the anisotropy, it would be necessary to fit the experimental data using a model of the molecular structure and its environment. This will require the development of new analysis tools which consider each atom in the model explicitly and thus presents a significant theoretical challenge.

Acknowledgments

The authors thank Dr Bruce Patterson (PSI, Villigen) for useful discussions and Professor Ursula Rothlisberger (EPFL) for computational resources. This work was partly funded by the National Centre of Competence in Research (NCCR) MUST network.

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