

ESRF

Experiment title:

Time-resolved study of high Z molecules in solution using pulsed anomalous scattering

Experiment

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SC248

Beamline:

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9

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Report:

This experiment is part of a long term project concerning time-resolved X-ray scattering applications for studying the photo dissociation process in high Z molecules in liquid solution. Such reactions are usually investigated with time-resolved laser spectroscopy [1]. These studies characterize the time evolution of the products after laser photolysis (product distribution, energy distribution among internal degrees of freedom) as well as the solvent reorganization and the energy partitioning between solute and solvent. The time-scales of such processes are in the ps range. With the perspective of accessing such time-scales by the use of a jitter-free streak camera, the aim of the project is to look at structural changes following photolysis by performing time-resolved X-ray Diffuse Scattering measurements. Such information can be accessed by optical measurements only with an indirect way.

The proposed study is to follow the photo dissociation of HgI_2 , I_3^- and I_2 in Methanol, systems which have been well characterized by ultra fast optical spectroscopy [2,3,4]. One problem is that HgI_2 is soluble in methanol only at the 20 mM level. The SC248 experiment was aimed to demonstrate the feasibility of a scattering experiment at these concentrations under static conditions, the technical facilities for the time-resolved part (phase locked chopper and fs laser) being not available at the moment.

We investigated the solution of HgI_2 in methanol at various concentrations. This system is expected to remain stable when not optically excited. We used the transmission geometry. The sample was set into the beam using the special closed-loop jet designed at the Laboratoire de Spectrometrie Physique of the University J. Fourier in Grenoble. This avoids the use of containers which contributes significantly to the scattered signal. "Fuji" image plates were employed as detectors. We work at $\lambda=0.442 \text{ \AA}$ in order to be able to collect the diffuse scattering pattern up to $q=11 \text{ \AA}^{-1}$. Fig. 1 shows the scattering intensities in e.u. vs. exchanged momentum q from the solvent and the solution at 40mM concentration. The difference signal clearly shows the interference pattern of a "gas like" distribution. Such a scattering pattern can be directly simulated by the Debye equation [5]. Fig.2 shows the difference signals at 10 and 40 mM concentration and the Debye equation with the literature values $r_{\text{Hg-I}}=2.6 \text{ \AA}$ and $r_{\text{I-I}}=5.1 \text{ \AA}$ [6]. The agreement is quite good if we consider that we are dealing with 4-16% of the total scattering pattern.

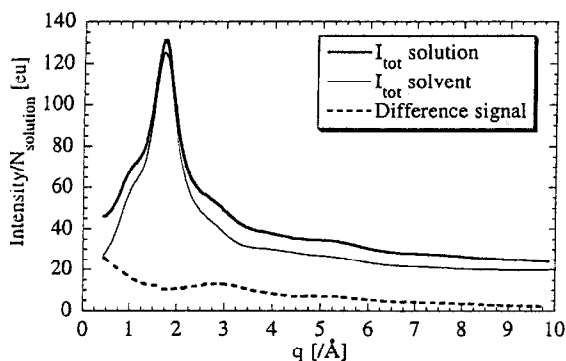


Fig. 1 - Scattered intensities for one molecule in e.u. from the 40 mM solution of HgI_2 in methanol and from the solvent. At the bottom the difference signal.

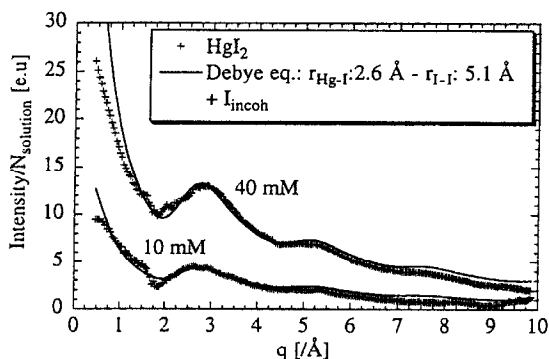


Fig. 2 - Difference signal in e.u. at 10 and 40 mM concentration and the simulated Debye pattern with $r_{\text{Hg-I}}=2.6 \text{ \AA}$ and $r_{\text{I-I}}=5.1 \text{ \AA}$.

The feasibility of a scattering experiment on solutions at the 10 mM concentration by using ESRF sources and area detectors is clearly demonstrated. It is possible to extract the "gas" signal from the HgI_2 solute in methanol at 10 and 40 mM concentration and apply the Debye equation for the non dissociated HgI_2 molecule with bond lengths derived from literature. We can estimate the distance within a 10% error, which is well below the expected bond length changes under photolysis.

Previous work on HgI_2 was performed at the 2 M concentration [6].

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