

*Time-resolved study of the photo-dissociation and recombination of Hgl<sub>2</sub> and I<sub>3</sub><sup>-</sup> in solution by picosecond x-ray diffraction*

The aim of this proposal was to study, by time resolved diffraction, the structure of laser excited Hgl<sub>2</sub> dissolved in liquid methanol and determine the rate of recombination. The experiment was done in a pump & probe fashion: UV pulses from the frequency tripled Ti: Sapphire laser were used to dissociate Hgl<sub>2</sub> into Hgl and a free iodine atom according to the scheme:



The polychromatic beam from the single-harmonic undulator U20 was used; it has a fundamental of 17 keV and produces  $1 \times 10^8$  ph/pulse. The effect of the laser excitation was evaluated from the difference between diffraction spectra with and without laser. The time resolution of the experiment was 100 ps and about 20 time delays between 50 ps to 5 us were collected. The diffraction spectra for time delays of 100 ps and 1 us are shown below:

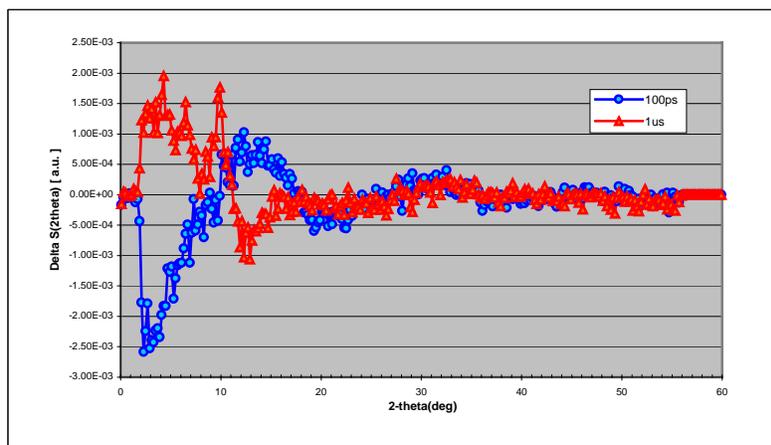


Fig. 1 Difference spectra from excited Hgl<sub>2</sub>\* in methanol. The 100 ps curve is consistent with the formation of the Hgl radical. The 1 us curve, by contrast, is ascribed to thermal expansion of methanol.

The analysis has revealed a striking point: the difference curves can be put on absolute scale by scaling the difference curves to the liquid background from pure methanol. In doing so, we observe that about 0.4 % of the initial 20 mM concentration Hgl<sub>2</sub> molecules are dissociated. By contrast, from the amplitude of the 1 us time-point, we infer that only 0.4% of Hgl<sub>2</sub> molecules are excited at 100 ps, whereas the amplitude of the thermal expansion, as inferred from the 1 us time-point, tells us that 22.0% of the molecules must have been excited. We interpret that as an indication that a large fraction of the excited Hgl<sub>2</sub>\* molecules recombine directly, while being cooled by the solvent.