



## Experiment Report Form

**The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.**

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

*<http://193.49.43.2:8080/smis/servlet/UserUtils?start>*

### ***Reports supporting requests for additional beam time***

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

### ***Reports on experiments relating to long term projects***

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

### ***Published papers***

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

### **Deadlines for submission of Experimental Reports**

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

### **Instructions for preparing your Report**

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



	<b>Experiment title:</b> The molecular structure of diiodoethyl radical	<b>Experiment number:</b> CH-1646
<b>Beamline:</b>	<b>Date of experiment:</b> from: 28/07/2004 to: 04/08/2004	<b>Date of report:</b> 23/09/2004
<b>Shifts:</b>	<b>Local contact(s):</b> Quingyu Kong	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants (* indicates experimentalists):</b> Maciej Lorenc (*), ESRF, Grenoble, France Hytcherl Ihee (*), Department of Chemistry and School of Molecular Science, KAIST, Deajeon, Republic of Korea Michael Wulff (*), ESRF, Grenoble, France		

## Report:

We have studied the elimination reaction of 1,2-diiodoethane ( $C_2H_4I_2$ ) molecule, which after photo-excitation with 267 nm photons gives a short-lived iodoethyl radical ( $CH_2ICH_2\bullet$ ) and iodine atom (I).

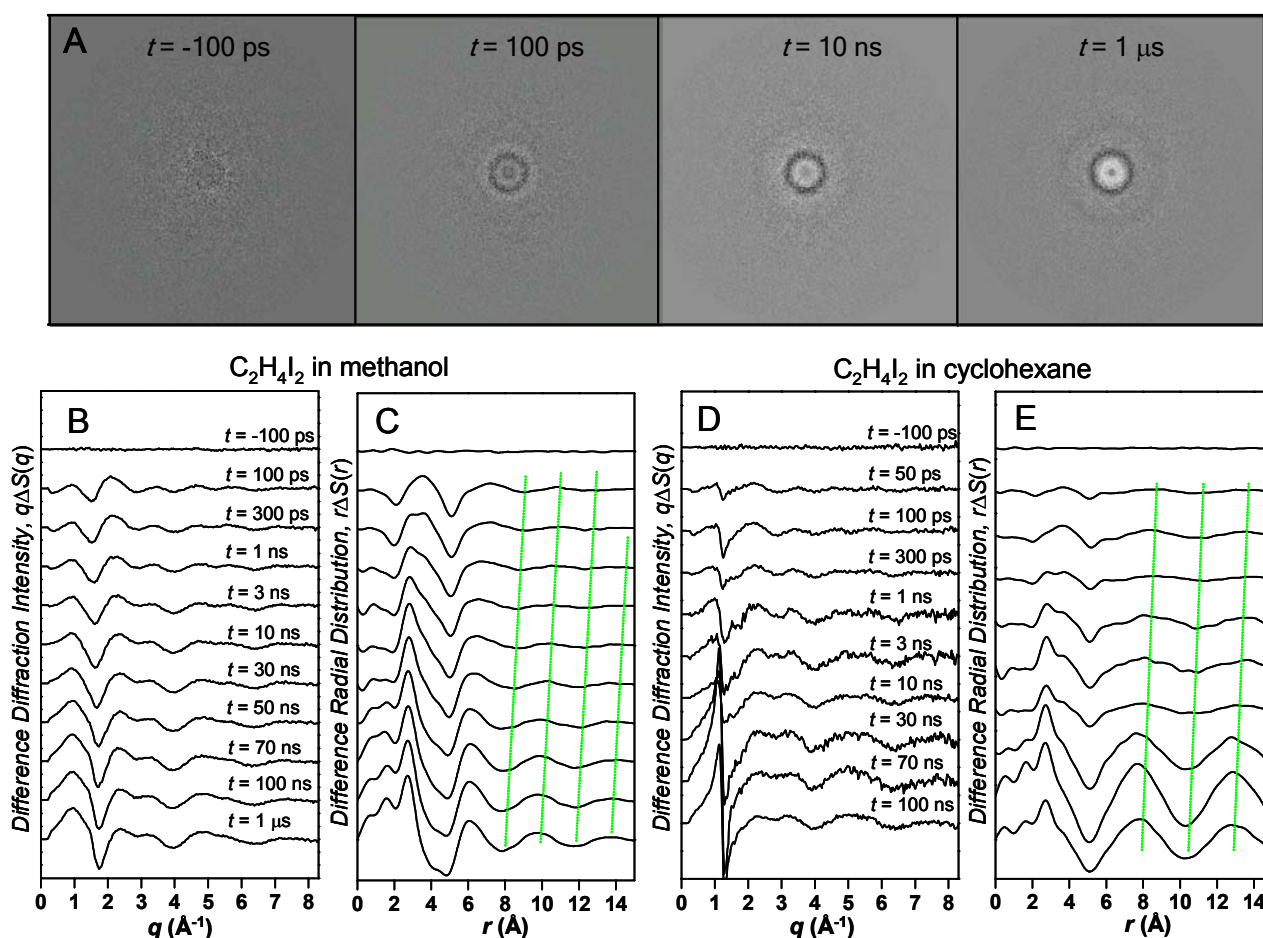
For this purpose we used a pump-probe diffractometer installed at ID09B. The photo-reaction was triggered by pulses delivered from a femtosecond CPA amplifier ( $\lambda=800\text{nm}$ ) and further converted to third harmonic (267nm,  $35\mu\text{J}/\text{pulse}$ , 1 kHz repetition rate). Before reaching the sample the pulses were stretched with silica prisms to the pulse-length of  $\sim 2\text{ps}$  in order to avoid multiphoton excitations. The reaction was probed with the white beam (0.45 keV bandwidth centred at 18.2 keV) produced by U17 undulator. The chromophore concentration of 60 mM was chosen to maximize the photo-products signal while keeping the inter-solute contributions negligible.

We collected time-resolved data for the following time-delays: -3ns, -100ps, 50ps, 100ps, 300ps, 1ns, 3ns, 10ns, 30ns, 50ns, 70ns, 100ns, 300ns, 1  $\mu\text{s}$ , 3 $\mu\text{s}$ . The data point at -3ns served as a reference point. To recover from the diffraction signal the changes due to photo-excitation, difference signal ( $\Delta S$ ) was generated by subtracting the reference data at -3ns from the data at each time-point. For  $C_2H_4I_2$  in polar methanol, we extracted laser-induced signal to high precision through numerous repetitions. We also obtained preliminary data for  $C_2H_4I_2$  in non-polar cyclohexane. The figure below shows the difference signal as a function of time delays in both methanol and cyclohexane. The  $\Delta S(q)$  was multiplied by  $q$  and its sine-Fourier transform,  $\Delta S(r)$ , was multiplied by  $r$  to magnify the intensity at high  $q$  and  $r$ , respectively. Inspecting the figure, one can see that difference patterns at low  $q$  are markedly different in methanol and cyclohexane, whereas at high  $q$  they are nearly identical, i.e. independent of the solvent.

In the real space, the negative peak near 5 Å is due to the depletion of the I...I internuclear distance in  $C_2H_4I_2$ . This feature would be common for all reaction channels

potentially taking place. However, the peaks between 1 Å and 3 Å are sensitive to the position of the I atom relative to the two carbon centres. It is expected from the theory that the bridged structure will give only one peak in this region while the classical anti structure will give two peaks. Looking at the measured 100ps curves on figures C and E, it is clear that we have observed the bridged radical in both solvents. Another, unexpected, feature emerges with time. On the nanosecond time scale a new peak appears at 2.7 Å. This feature corresponds to the I-I distance of the nascent I<sub>2</sub> molecule. This process seems to be solvent independent too.

We also note that the low  $q$  data contains information about the structural change in the solvent. The peaks and valleys above 6 Å in figures C and E contain important information about the response of the solvent cage to the solute excitation, and of the bulk solvent to the energy released by relaxing solutes. To fully explore solvent dynamics, apparent temporal evolution of peaks and valleys at long distances ( $r > 6$  Å), molecular dynamics (MD) simulations will be necessary.



**Figure:** Time-resolved diffraction signal as a function of time delays for  $C_2H_4I_2$  in methanol (A, B, C) and cyclohexane (D, E). (A) Raw difference images for selected time delays ( $t = -100$  ps,  $100$  ps,  $10$  ns, and  $1$   $\mu$ s). (B) Difference diffraction intensities,  $q\Delta S(q)$ , excited minus non-excited, for  $C_2H_4I_2$  dissolved in methanol. (C) Difference radial density functions,  $r\Delta S(r)$  for  $C_2H_4I_2$  in methanol. (D) Difference intensities,  $q\Delta S(q)$  for  $C_2H_4I_2$  in cyclohexane. (E) Difference radial density functions,  $r\Delta S(r)$  for  $C_2H_4I_2$  in cyclohexane. The dashed lines in C and E are drawn to show the trend in the positions of the peaks and valleys as a function of time.