

## Principal publication and authors

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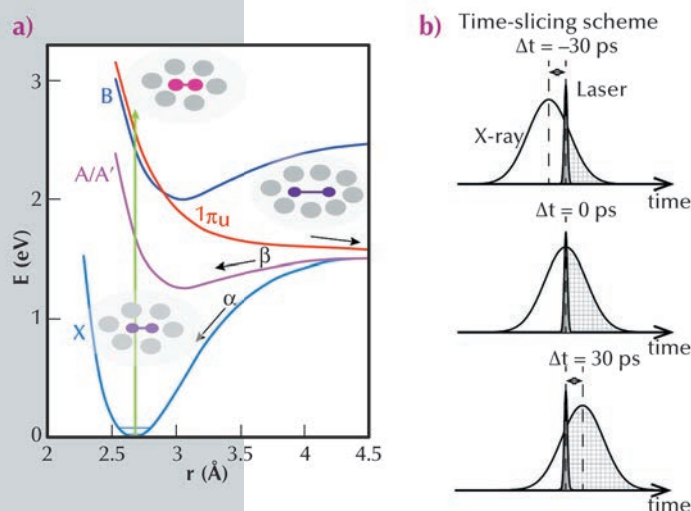
## FILMING THE BIRTH OF MOLECULES AND SOLVENT REARRANGEMENT

Solvent plays an important role in solution-phase chemical reactions by serving as an energy source to activate the reaction as well as a heat bath to stabilise the products. As a result, the properties of the solvent significantly affect the energy landscape, rates, and pathways of a reaction in solution. The interplay of solute and solvent molecules and its effect on the outcome of chemical reactions has been a topic of intense research in the field of reaction dynamics over several decades, and the kinetic and spectral signatures of the solvation process have been elucidated on femto- to picosecond time scales [1, 2]. It is still challenging experimentally to probe the bonds that are formed during a chemical reaction, especially the changes between solute and solvent accompanying the structural change of reacting solute molecules.

Geminate recombination of iodine atoms (Figure 89a) to form molecular  $I_2$  in solution after photodissociation is a good example of a prototype solution-phase reaction and has been investigated by spectroscopic studies and quantum chemistry [3]. However, the change in the molecular structure (*i.e.* bond length change) and the response of the surrounding solvent cage have never been directly observed. Time-resolved X-ray liquidography (solution scattering) is well suited for monitoring this solution-phase

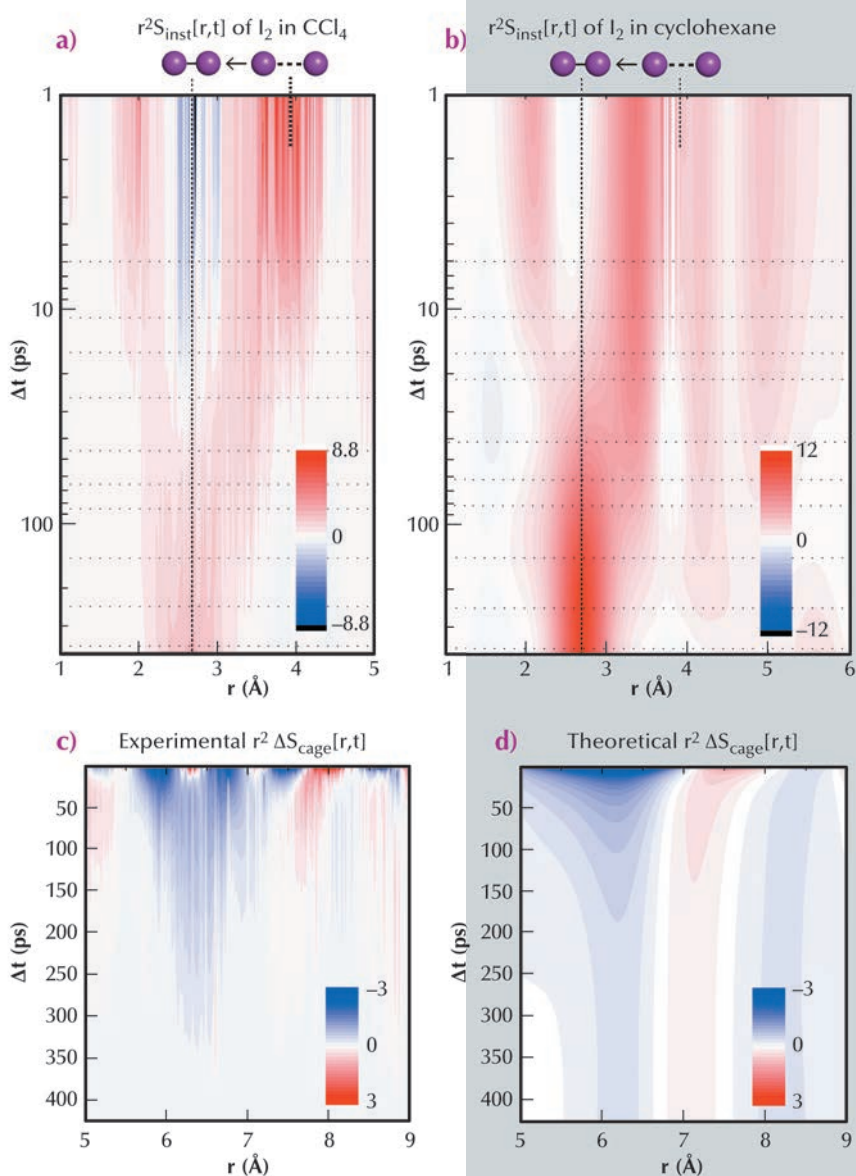
reaction because it directly probes the atom-atom distance distribution as a function of time. By using the time-slicing scheme where data are collected at earlier time delays and with finer time increments (down to 10 ps) than the X-ray pulse width ( $\sim 100$  ps) (Figure 89b) and the deconvolution data processing, we can extract the dynamics that occur faster than the X-ray pulse width and monitor the evolution of both the atom-atom distance distribution of iodine atoms in solvent and the solute-solvent distance distribution at the early stages of I-I bond formation within the solvation shell.

In this study, we measured the dynamics of geminate recombination and vibrational relaxation of  $I_2$  in two different solvents,  $CCl_4$  and cyclohexane, in real time using picosecond X-ray liquidography at beamline ID09TR. The birth and vibrational relaxation of  $I_2$  molecules and the associated rearrangement of solvent molecules are mapped out in the form of temporally varying interatomic distance distribution. The atom-atom distance distribution clearly shows the time-dependent progression of the I-I distance (Figure 90a,b). The relaxation of elongated iodine distribution is followed by bi-exponentials, which is well in agreement with previous spectroscopic observations [4] and our molecular



**Fig. 89:** a) Potential energy surface of  $I_2$  in  $CCl_4$ . The processes  $\alpha$  and  $\beta$  represent the geminate recombination of two I atoms in the X and A/A' states, respectively. The process  $\gamma$  represents nongeminate recombination through the solvent. b) Schematic of the time-slicing experiment. At a negative time delay (for example  $-30$  ps), the X-ray pulse arrives (effectively) earlier than the laser pulse, but the X-ray pulse, which is much longer in time than the laser pulse, is still present after the interaction with the laser-illuminated sample. At time zero, half of the X-ray pulse probes the laser-illuminated sample.

dynamics (MD) simulation. Also iodine atoms can be separated by larger distances in cyclohexane than in  $\text{CCl}_4$  and the vibrational relaxation of a newly born “hot”  $\text{I}_2$  molecule occurs faster in  $\text{CCl}_4$  than in cyclohexane. In addition to the structural progression of the solute molecule, the concomitant swelling and shrinking of the solute-solvent cage were also clearly observed. The atom-atom distribution change that appeared above  $5 \text{ \AA}$  is well reproduced by the MD simulation, which indicates the solvation dynamics of newly formed iodine molecules in the course of a vibrational cooling process (Figure 90c,d).



**Fig. 90:** a) Time-dependent I-I distance distribution functions ( $r^2 S_{inst}[r,t]$ ) corresponding to  $\text{I}_2$  in  $\text{CCl}_4$ . b) The  $r^2 S_{inst}[r,t]$  of  $\text{I}_2$  in cyclohexane. c) The experimental  $r^2 \Delta S_{cage}[r,t]$  curves at large  $r$  values: time-dependent solute-solvent distance distribution functions. d) Theoretical  $r^2 \Delta S_{cage}[r,t]$  based on the experimental data from (a) and MD simulation.

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