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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 l_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 (~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 I₂ in different solvents, CCl_4 and two cyclohexane, in real time using picosecond X-ray liquidography at beamline ID09TR. The birth and vibrational relaxation of I₂ 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 CCl₄. The processes α and β represent the geminate recombination of two I atoms in the X and A/A' states, respectively. The process γ represents nongeminate recombination through the solvent. b) Schematic of the timeslicing 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 pulse and thus scattered off the laser-illuminated sample. At time zero, half of the X-ray pulse probes the laserilluminated sample.

dynamics (MD) simulation. Also iodine atoms can be separated by larger distances in cyclohexane than in CCl_{μ} and the vibrational relaxation of a newly born "hot" I_2 molecule occurs faster in CCl₄ than in cyclohexane. In addition to the structural progression of the solute molecule, the concomitant swelling and shrinking of the solutesolvent cage were also clearly observed. The atom-atom distribution change that appeared above 5 Å 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 $(r^2S_{inst}[r,t])$ corresponding to I₂ in CCI₄. b) The $r^2S_{inst}[r,t]$ of I₂ in cyclohexane. c) The experimental $r^2\Delta S_{inst}[r,t]$ curves at large r values: time-dependent solute-solvent distance distribution functions. d) Theoretical $r^2\Delta S_{inst}[r,t]$ based on the experimental data from (a) and MD simulation.





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