Visualizing Chemical Reactions in Solution by Picosecond X-Ray Diffraction

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We present a time-resolved x-ray diffraction study to monitor the recombination of laser-dissociated iodine molecules dissolved in CCl_4. The change in structure of iodine is followed during the whole recombination process. The deexcitation of solute molecules produces a heating of the solvent and induces tiny changes in its structure. The variations in the distance between pairs of chlorine atoms in adjacent CCl_4 molecules are probed on the *m*Å length scale. However, the most striking outcome of the present work is the experimental determination of temporally varying atom-atom pair distribution functions. Variations of the mean density of the solution during thermal expansion are also followed in real time. One concludes that not only time-resolved optical spectroscopy but also time-resolved x-ray diffraction can be used to monitor atomic motions in liquids.

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Direct observation of temporally varying molecular structures during a chemical reaction represents a great challenge. Three major experimental techniques are available at the present time. The first is ultrafast optical spectroscopy. Photodissociation of gaseous ICN was "filmed" in real time by this method [1,2]; it was also applied to visualize the OH $\cdots$ O motions in liquid water [3,4]. The second is ultrafast electron diffraction. A transient structure of photoexcited 1,3-cyclohexadiene was recently reported [5,6]; this method, however, is difficult to use in condensed samples. The third method is ultrafast x-ray diffraction. Although this technique is still in an early stage of development, it has already provided a number of important results [7–15]. Recent studies of the structural dynamics of the myoglobin complex MbCO are particularly spectacular [11,12]. Here we describe a time-resolved x-ray diffraction study of the recombination of photodissociated I_2 in CCl_4. The main result of this research, realized with an unprecedented spatial and temporal resolution, is the detection of temporally varying atom-atom distribution functions at times longer than 100 ps. This is the best we were able to do to "film" atomic motions in liquids.

The photodissociation of an I_2 molecule generates a pair of nonbonded atoms. Two outcomes are then possible. The solvent can trap the atoms and force them to recombine in a process called geminate recombination. Alternatively, they may escape the solvent cage and recombine with other partners; this is nongeminate recombination. Considered as a prototype of a "simple" chemical reaction, this process has been extensively studied in the past. Quantum-chemical investigations have shown that I_2 possesses a large number of electronic states [16] (Fig. 1). The states X, A, A', and B are attractive; the others, including the low-lying state $^1\pi_u$, are repulsive. From the other side, careful laser spectroscopic [17–21] and computer simulation [22] studies have shown that three times govern spectral behavior: the time $\tau_\alpha = 0.18$ ns is associated with the relaxation of the hot I_2 along the X state potential; the time $\tau_\beta = 2.7$ ns is associated with the relaxation of the A/A' state populations; the time $\tau_\gamma \gg \tau_\alpha, \tau_\beta$ describes the nongeminate

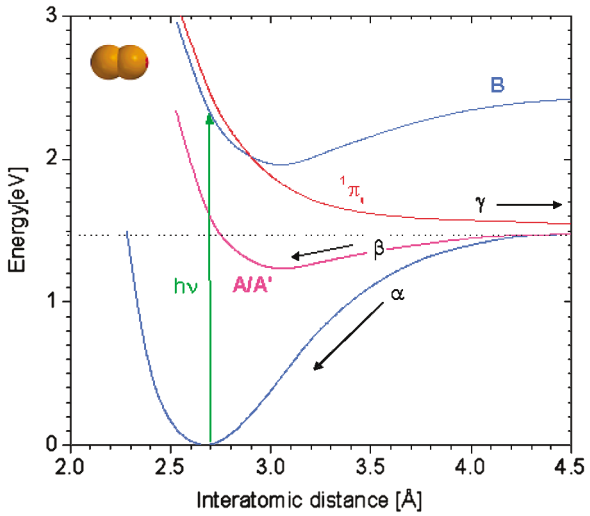

FIG. 1 (color). Low lying electronic energy surfaces of I_2: the states X, A/A', and B are attractive, whereas the state $^1\pi_u$ is repulsive. The processes α, β, and γ denote vibrational cooling along the X potential, geminate recombination through the states A/A', and nongeminate recombination, respectively.

recombination. In the absence of this information, the present study would hardly be practicable.

The principle of our experiment is as follows: One starts by exciting a dilute I_2/CCl_4 solution with a femtosecond optical pulse. That generates a mixture of the electronic states B and $^1\pi_u$, which mainly dissociate into ground state atoms. Hot iodine molecules I_2^* with a "bond length" $R_0 \approx 4$ Å are formed in less than 1 ps. They then transform into either $I_2^* \rightarrow 2I$ or $I_2^* \rightarrow I_2$; in the first case the atoms recombine nongeminately, and in the second geminately. The reaction products are monitored by a delayed x-ray probe pulse τ seconds later. Defined as the time-integrated energy flux $S(q, \tau)$ scattered in a solid angle in the presence of the pump minus the equivalent quantity in the absence of the pump, the diffracted signal $\Delta S(q, \tau)$ depends on two variables: the scattering wave vector $\mathbf{q}$ and the time delay τ.

The experimental setup is shown on Fig. 2. It comprises the pulsed synchrotron source, a chopper that selects single pulses of x rays from the synchrotron, a femtosecond laser, a capillary jet, and an integrating CCD detector [23,24]. To increase the intensity of the diffracted beam, an undulator formed by an array of 236 alternating magnets was placed inside the vacuum vessel of the synchrotron. In addition, the experiment used the polychromatic beam from the undulator, which gives rise to a gain in intensity of 450 as compared to a conventional monochromatized beam. The images were integrated azimuthally and were corrected for polarization and space-angle effects. Much attention was given to the reproducibility of the diffracted signals. These precautions are necessary, the difference signal $\Delta S(q, \tau)$ being only 10^{-2} to 10^{-4} of the solvent background.

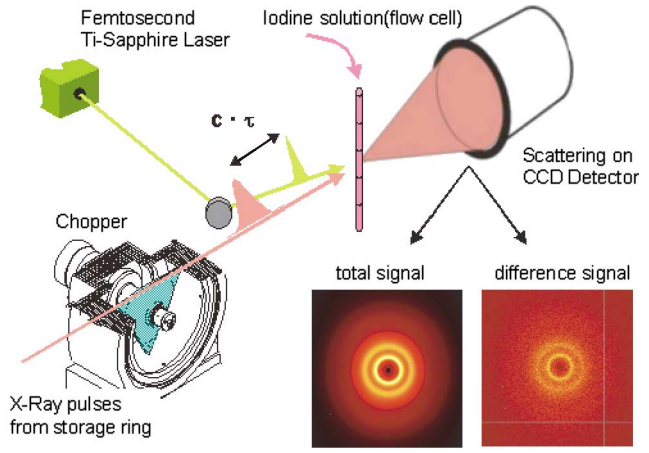

FIG. 2 (color). Experimental setup: the x-ray pulses are generated by an undulator. The spectrum is centered at 0.67 Å (18.5 keV) and its bandwidth width is $d\lambda/\lambda = 0.03$. The flux on the sample is 5×10^8 per pulse and the pulse length is 150 ps. The solution is excited by 150 fs laser pulses at 520 nm, populating the electronic states $^1\pi_u$ and B. The common laser/x-ray repetition frequency is 896.6 Hz and the exposure time 10 s per CCD frame.

The principle of our theoretical analysis is as follows: The theory underlying the present work is a statistical theory for time-resolved x-ray diffraction [25]. The electromagnetic fields are treated using Maxwellian electrodynamics and the molecular system is described by quantum mechanics. The theory takes a simpler form in the present case due to the time-scale separation of the ultrafast optical and relatively slow chemical processes. In spite of this simplification, some approximations are still necessary. Only the electronic degrees of freedom are considered quantum mechanically, whereas the others were assumed to be classical. Time-dependent quantities were all modeled using laser spectroscopic data [17–21], whereas static quantities were calculated by molecular dynamics simulations. None of these assumptions is believed to be restrictive.

Before we interpret the experimental data, we mention an unexpected finding. The diffracted signal $S(q) = S(q)_I + S(q)_S$ of an I_2/CCl_4 solution is a sum of two terms: $S(q)_I$ is associated with the iodine enclosed in its solvent cage and $S(q)_S$ is due to the solvent [26]. Given that only iodine molecules are excited, one would expect the solvent signal $S(q, \tau)_S$ to stay constant and therefore $\Delta S(q, \tau)_S$ to vanish. This is not the case: the energy released by excited iodine molecules heats the solvent and initiates its structural rearrangement and thermal expansion. The signature of this process is unexpectedly large since it integrates all CCl_4 molecules in the x-ray illuminated volume. The signal is comparable to that of iodine.

The q-resolved scans are first examined with τ kept constant (Fig. 3). We note that the information content depends on the q range. (i) In the high q range, $4.3 < q < 8.8$ Å^{-1}, the "naked" iodine structures are seen as they relax progressively towards the ground state. This statement is confirmed by the presence of oscillations similar to those expected from gas-phase iodine. Their temporal evolution agrees with the data from optical spectroscopy. (ii) By contrast, in the low q range $0.5 < q < 4.3$ Å^{-1}, the thermal expansion of CCl_4, heated by relaxing iodine molecules, is observed. To check this conjecture, the temperature and pressure changes $\Delta T(\tau)$ and $\Delta p(\tau)$ were calculated by solving linearized hydrodynamic equations for systems containing a heat source [27]. Moreover, the static diffraction signal $S(q)$ was determined by molecular dynamics simulations. The latter use 512 rigid CCl_4 molecules plus one I_2 molecule. We found a good agreement between theory and experiment which strongly supports the assumptions above.

The τ-resolved scans are studied next with a fixed q (Fig. 4). (i) When $q < 4.3$ Å^{-1}, the signal increases with time: the relaxing photoproducts revert to the ground state; the solvent takes up the excess energy and expands. We expect this behavior to be quite general: the cooling by the solvent generates necessarily thermal expansion. (ii) When $q = 4.3$ Å^{-1}, the τ-resolved signals decrease with time: $\Delta S(q, \tau)$ probes the relaxation of

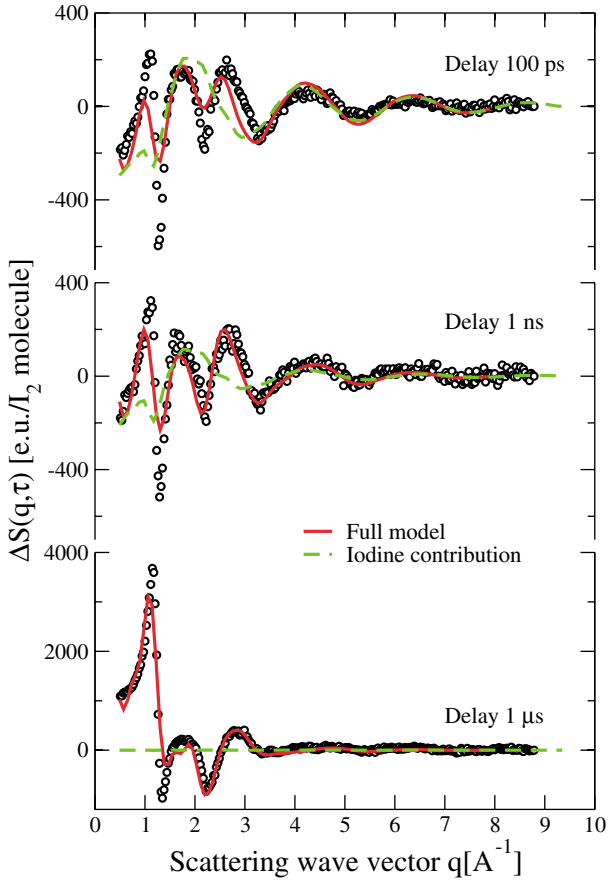

FIG. 3 (color). The q-resolved scans $\Delta S(q, \tau)$ for the time delays 100 ps, 1 ns, and 1 μs: The green curve shows the contribution from iodine in its cage and the red curve is the full model.

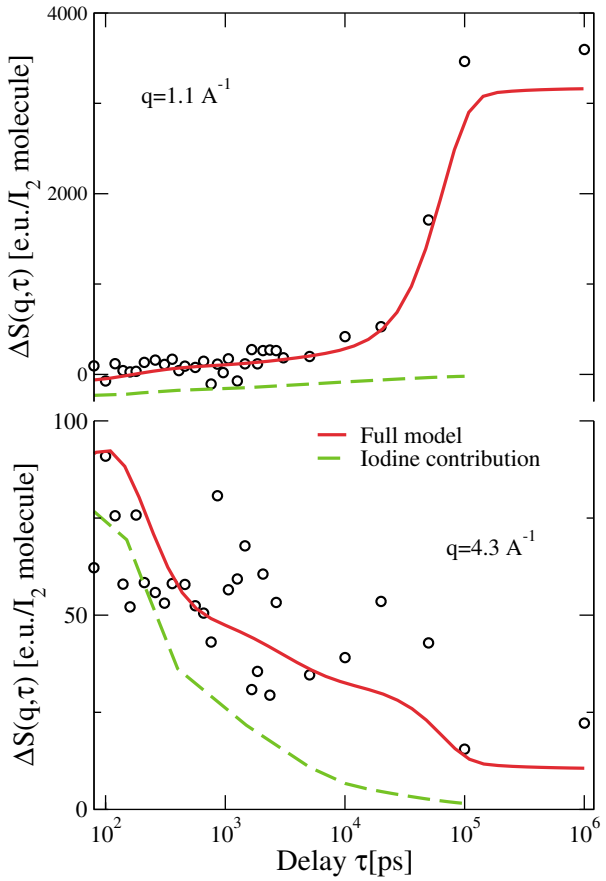

FIG. 4 (color). The τ-resolved scans $\Delta S(q, \tau)$ at $q = 1.1$ Å^{-1} and $q = 4.3$ Å^{-1}. The green curve shows the contribution from iodine in its cage and the red curve is the full model.

excited iodine molecules and the recombination of iodine atoms. The "asymmetry" in the time dependence of the signals is thus explained. It is interesting to note that only 14% of laser excited iodine molecules escape the solvent cage.

However, the most striking result is the experimental determination of the site-site distribution functions $g_{\mu\nu}(r, \tau)$. They measure the distribution of atomic pairs I-I, Cl-Cl, etc., in an I_2/CCl_4 solution as a function of time. In fact, introducing a properly normalized Fourier sine transform of $q\Delta S(q, \tau)$ gives

$$S[r,\tau] = \frac{1}{2\pi^2 r}\int_0^{+\infty} dq \left[\sum_{\mu\neq\nu} f_\mu(q) f_\nu(q)\right]^{-1} qS(q,\tau)\sin(qr)$$

$$= \text{const}\frac{1}{V(\tau)}\left\{\sum_{\mu\neq\nu} w_{\mu,\nu}[g_{\mu\nu}(r,\tau)-1]\right\}, \quad (1)$$

where the $w_{\mu\nu}$ are weighting coefficients, $V(\tau)$ is the volume of the system at time τ and $r > 0$. Defined in this way, $S[r, \tau]$ is proportional to a weighted superposition of site-site distribution functions. In turn, the difference $\Delta S[r, \tau] = S[r, \tau] - S[r]_{eq}$ describes the effect of the laser excitation. This function contains two terms: one expressing the variations in the pair distribution functions and the second expressing the volume change due to thermal expansion. The fact that the atomic form factors $f_\mu(q)$ are q dependent is not considered in the above equation. If it is, a small damping of the oscillations in $\Delta S[r, \tau]$ results; this effect was included in present calculations. The similarity between the above expression and the well-known Zernike-Prins formula for monoatomic liquids [26] is striking, but it exists only if the laser excitation and the reaction processes are well separated in time [25]. This limitation should be kept in mind.

The experimental and calculated functions $\Delta S[r, \tau]$ are shown in Fig. 5 for time delays τ of 200 ps, 1 ns, and 1 μs. The first minimum at 2.7 Å appearing at early times indicates the depletion of the X state of molecular iodine from laser-induced excitation. A fraction of excited molecules then reach the A/A' and higher electronic states, and a maximum appears at 3.2 Å. The energy transferred from the solute molecules to the solvent gives rise to structural rearrangements of the latter. The minima at 3.9 and 6.2 Å are due to the variations of the Cl-Cl distances; the atomic pairs I-C, I-Cl, and C-Cl are not seen as the coefficients $w_{I\text{-}C}$, $w_{I\text{-}Cl}$, and $w_{C\text{-}Cl}$ are too

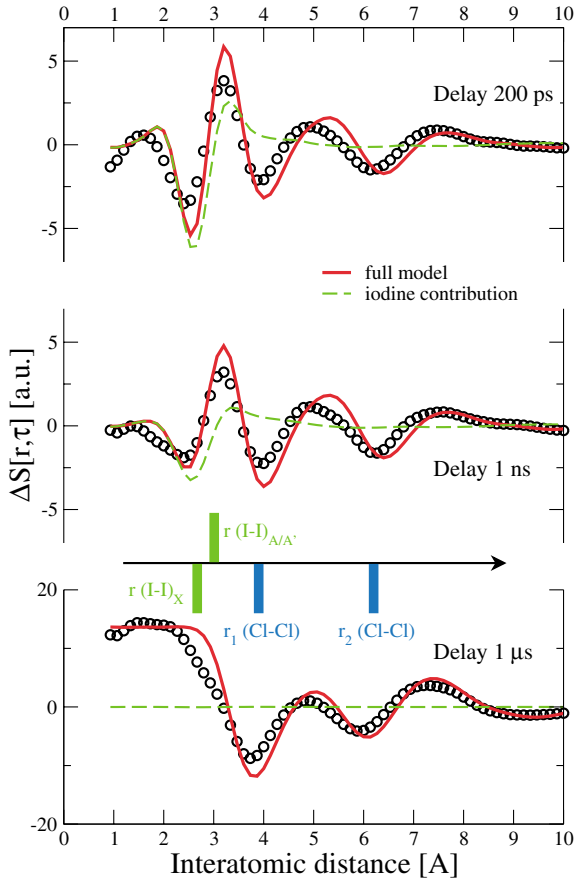

FIG. 5 (color). The change in the atom-atom pair distribution $\Delta S[r, \tau]$ for $\tau = 200$ ps, 1 ns, and 1 μs. The green bars indicate the bond lengths of iodine in the X and the A/A' state. The blue bars show the positions of the first two intermolecular peaks in the partial distribution function $g_{\mathrm{Cl\text{-}Cl}}$. These Cl atoms are located in the first solvation shell of CCl_4.

small. If τ is much larger than τ_γ, the iodine molecules all deexcite, and the signal reduces to that of heated CCl_4 alone. A strong increase of $\Delta S[r, \tau]$ observed at small r's is due to a decrease in the mass density ρ of CCl_4. In turn, the features observed at large r's reflect the variations in the intermolecular Cl $\cdots$ Cl distances upon heating. Transient effects just described are by no means an artifact of laser heating; they result intrinsically from the recombination of hot iodine molecules and atoms. One concludes that a hundred years after Röntgen's fundamental discovery, real-time x-ray monitoring of atomic motions has become possible.

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