SUPPORTING INFORMATION

Filming the birth of molecules and accompanying solvent rearrangement.

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Experimental Procedure

The experiments were done on beamline ID09B at the European Synchrotron Radiation Facility in Grenoble. This beamline provides a quasi-monochromatic x-ray source with intense x-ray pulses. The detailed setup of the time-resolved x-ray liquidography experiment is described elsewhere ¹⁻⁷. Briefly, a typical pump-probe scheme with optical pump and x-ray probe pulses was adopted to initiate and monitor the chemical reaction of interest. The solutions were prepared by dissolving I₂ (Sigma-Aldrich, PN I8780, 99.2%) in CCl₄ (Sigma-Aldrich, PN 270652, 99.9%) or cyclohexane (Sigma-Aldrich, PN 676861, \geq 99%) at 25 mM or 20 mM

concentration, respectively, which were then circulated through a high-pressure slit nozzle (0.3 mm slit, Kyburz) to form a liquid jet. The nozzle provides a stable flow of liquid and its speed was adjusted to inject a fresh sample for every new x-ray pulse, maintaining the temperature of the liquid constant. A 1-kHz femtosecond laser was used to dissociate iodine and a chopper was used to reduce the x-ray frequency to 1 kHz. Photodissociation of I₂ was initiated by laser pulses at 530 nm (for I₂ in CCl₄) or 520 nm (for I₂ in cyclohexane) generated by a TOPAS OPA which was pumped by the 800 nm output from an amplified Ti:sapphire laser system. In order to prevent multi-photon excitation, the laser pulse was temporally stretched to ~0.5 ps by passing it through a fused silica rod. The laser pulse with the energy of 60 µJ per pulse was focused to a spot of ~205 µm diameter (220 µm for horizontal and 190 µm for vertical) at the sample, giving a fluence of 0.46 mJ/mm². Subsequently, a time-delayed x-ray pulse was used to probe the progress of the reaction. The experiment was performed in 16 bunch mode with 100 ps x-ray pulses. A single-harmonic undulator with a magnetic period of 17 mm provided an intense quasimonochromatic beam with a 3 % bandwidth around 18.15 keV with 5×10^8 photons per pulse. The scattering pattern was recorded by an integrating CCD detector with fast readout (FReLoN camera, 2048×2048 pixel, detection area $105 \times 105 \text{ mm}^2$, and readout to 16 bits in 0.5 s per image). The exposure time per image was about 2 s and 1200 images were taken per hour. The images were integrated azimuthally and were corrected for the polarization and space-angle effects.

Time-slicing

Scattering patterns containing a fingerprint of the iodine recombination were collected as a function of the pump-probe delay t from -174 ps to 426 ps, and -109 ps to 431 ps with a time step of 10 ps for CCl₄ and cyclohexane, respectively. This time step, which is much smaller than the usual ones used in previous experiments, was used to monitor the fast vibrational relaxation processes whose time scale is comparable to the full width at half maximum (fwhm) of the x-ray temporal profile (100 ps). The instrumental time resolution depends on the duration of the x-ray (100 ps) and laser (0.5 ps) pulses and their relative jitter (3 ps), and thus is governed by the x-ray pulse duration.

Data processing

The 2D scattering patterns recorded on the CCD detector were azimuthally integrated into one-dimensional intensity curves, S(q,t), as a function of momentum transfer q ($q = (4\pi/\lambda)\sin(\theta)$, where λ is the wavelength of the x-ray and the 2θ is the scattering angle) and time delay t between the laser and x-ray pulses. The curves were averaged and scaled to the total scattering, both elastic and inelastic, from non-excited solvent/solute background in the high qregion, where the scattering is insensitive to structural changes. After scaling the intensities, difference scattering curves $\Delta S(q,t)$ were generated by subtracting the reference data measured at -3 ns from the data at other time delays, as shown in Fig. S1 for I₂ in CCl₄, and in Fig. S20 for I₂ in cyclohexane. The correlated difference radial distribution function, $\Delta S[r,t]$, which is a measure of the radial electron density change as a function of interatomic distance r in real space, was obtained by sine-Fourier transforming the $q\Delta S(q,t)$ curves:

$$\Delta S[r,t] = \frac{1}{2\pi^2 r} \int_0^\infty \frac{q \Delta S(q,t)}{f_l^2} \sin(qr) e^{-q^2 \alpha} dq , \qquad (1)$$

where the constant α ($\alpha = 0.03$ Å²) is a damping term that accounts for the finite *q* range in the experiment (0.04 – 9.0 Å⁻¹) and *f*_I is the scattering factor of the iodine atom to sharpen the resulting peaks (sharpening term). The resultant $\Delta S[r,t]$ curves are shown in Fig. S2 and Fig. S21 for I₂ in CCl₄ and I₂ in cyclohexane, respectively.

Removal of the solvent contribution

In order to study the dynamics of the iodine recombination alone, the scattering from the pure CCl₄ (or pure cyclohexane) solvent was subtracted from the scattering of the solution. However, a complication arises when a chemical reaction takes place. The solvent changes temperature, giving rise to an unwanted thermal background in $\Delta S(q,t)$. A separate experiment was thus performed to evaluate this effect. Pure CCl₄ was irradiated with 0.1 ps laser pulses at the off-resonant wavelength of 390 nm to heat the solvent through multiphoton absorption without inducing any chemical change. Once the thermal response of the solvent is measured, it is subtracted from the solution signal by suitable scaling. The multiphoton excitation of pure solvent was made with 70 µJ pulses focused into Ø 150 µm; the signals $\Delta S[r,t]$ of the pure solvent were recorded at t = 200 ps and 1 µs for the constant volume and constant pressure

regimes respectively. The scale constant in the subtraction was determined by scaling the Fourier transforms $\Delta S[r,t]$ of the solution and the pure solvent to each other, at distances *r* much greater than the size of the I₂ molecule, here r > 6 Å, as shown in Fig. S3. Fig. S4 displays the $\Delta S[r,t]$ curves of the I₂ alone at various time delays after the solvent contribution was subtracted. In the case of pure cyclohexane, a near-IR (1725 nm) laser pulse was used to measure the thermal response. The pulse duration was 100 fs, and the energy was 60 µJ at the sample with the beam focused to Ø 100 µm. The signals were measured at two time delays at t = 200 ps and 1 µs. As in the case of CCl₄, the cyclohexane signal was subtracted from the I₂/cyclohexane signal after scaling at distances *r* greater than the size of the I₂ molecule as shown in Fig. S22.

Polychromatic correction

The x-ray pulse used in the experiment has a bandwidth of 3 % with a characteristic semi-Gaussian shape in the intensity vs energy (or wavelength) profile (Fig. S5a). This polychromaticity of the x-ray spectrum convolutes $\Delta S_{mono}(q)$, the function of interest, into the measured data:

$$\Delta S(2\theta) = \frac{\int \Delta S_{mono}(q) P(\lambda) d\lambda}{\int P(\lambda) d\lambda},$$
(2)

where $\Delta S(2\theta)$ is the observed signal as a function of the scattering angle (2 θ), $\Delta S_{mono}(q)$ is the scattering signal from monochromatic x-rays, and $P(\lambda)$ is the x-ray spectrum (Fig. S5a).

The polychromatic x-ray beam gives rise to a small shift and damping in the high-2 θ part of $\Delta S(2\theta)$. Consequently the Fourier transform slightly deviates from the corresponding monochromatic one, $\Delta S[r]$. The effect of the polychromatic beam on $\Delta S[r]$ is shown in Fig. S5b. To get accurate distance information, it is necessary to correct for the polychromaticity on $\Delta S[r]$. The polychromatic effect is applied to reciprocal-space data, $\Delta S(q)$, and $\Delta S[r]$ is affected as well. If the x-ray wavelength changes from λ_0 to λ' ($\lambda' = a\lambda_0$), the new scattering intensity ($\Delta S_{mono,\lambda'}(q')$) can be defined as $\Delta S_{mono,\lambda'}(q') = \Delta S_{mono,\lambda_0}(q)$, where q' is q/a.

If $P(\lambda)$ is normalized, Eq. (2) is simplified to

$$\Delta S(2\theta) = \int \Delta S_{mono,\lambda}(q) P(\lambda) d\lambda \,. \tag{3}$$

Eq. (3) can be converted to a discrete sum,

$$\Delta S(2\theta) = \sum_{\lambda} \Delta S_{mono,\lambda_i}(q) P(\lambda_i) .$$
(4)

The Fourier transform of polychromatic data $\Delta S(q)$ is as follows (ignoring the constant term):

$$r\Delta S[r] = \int_{0}^{q_{\text{max}}} q\Delta S(q) \sin(qr) dq$$

$$= \int_{0}^{q_{\text{max}}} q\Delta S(2\theta) \sin(qr) dq$$
(5)

Then, inserting Eq. (4) into Eq. (5) leads to

$$r\Delta S[r] = \int_{0}^{q_{\max}} q \sin(qr) dq \sum P(\lambda_i) \Delta S_{mono,\lambda_i}(q)$$

$$= \sum P(\lambda_i) \int_{0}^{q_{\max}} q \Delta S_{mono,\lambda_i}(q) \sin(qr) dq .$$

$$= \sum r\Delta S_{mono,\lambda_i}[r] P(\lambda_i)$$
(6)

This equation shows that the scattering data from polychromatic beam is still a weighted sum of monochromatic data in real-space.

Based on the relationship in *q*-space, $\Delta S_{mono,\lambda'}(q/a) = \Delta S_{mono,\lambda_0}(q)$ where *a* is the ratio between two wavelengths, the *r*-space relationship is found as follows:

$$r\Delta S_{mono,\lambda_0}[r] = \int_{0}^{q_{max}} q\Delta S_{mono,\lambda_0}(q)\sin(qr)dq$$

$$= \int_{0}^{q_{max}} q\Delta S_{mono,\lambda'}(q/a)\sin(qr)dq$$

$$= \int_{0}^{q_{max}} a'q'\Delta S_{mono,\lambda'}(q')\sin(aq'r)adq'$$

$$= a^2 \int_{0}^{q_{max}} q'\Delta S_{mono,\lambda'}(q')\sin(q'ar)dq'$$
(7)

Substituting *ar* for *r*' gives a new Fourier transform equation for $\Delta S_{\text{mono}, \lambda'}(r')$:

$$r\Delta S_{mono,\lambda_0}[r] = a^2 \int_{0}^{q_{max}} q' \Delta S_{mono,\lambda'}(q') \sin(q'r') dq'$$

$$= a^2 r' \Delta S_{mono,\lambda'}[r'] \qquad .$$
(8)
$$= a^3 r \Delta S_{mono,\lambda'}[ar]$$

By swapping the sides of and simplifying Eq. (8), the following equation is obtained:

$$r\Delta S_{mono,\lambda}[r] = \frac{1}{a^3} r\Delta S_{mono,\lambda_0}[r/a].$$
(9)

Finally, inserting Eq. (9) into Eq. (6) yields

$$r\Delta S_{poly}[r] = \sum_{\lambda} r\Delta S[r]_{mono,\lambda_i} P(\lambda_i)$$

= $\sum_{\lambda} \frac{1}{a_i^3} r\Delta S_{mono,\lambda_0}[r/a_i] P(\lambda_i)$. (10)

Therefore, the $\Delta S[r]$ from a monochromatic x-ray beam can be easily converted to the curves at many different x-ray wavelengths and construct $\Delta S[r]$ that can be obtained from a polychromatic x-ray beam by using Eq. (10). Conversely, $\Delta S[r]$ in monochromatic condition can be extracted from the polychromatic data by least-squares fitting. We start with a trail scattering curve and convolute it with the polychromatic spectrum. The comparison between polychromatic experimental data and the convoluted trial curve gives us, after least-square refinement, $\Delta S[r]$ under monochromatic conditions. The original experimental polychromatic $\Delta S[r]$ was used as the initial trial data. In practice, the trial data is divided into 50 intervals in r with a 5-order polynomial representing each interval. These intervals are connected smoothly using b-spline smoothing. The polychromatic correction is applied to this synthesized arbitrary data and then least-squares refinement against the experimental data gives theoretical $\Delta S[r]$ in monochromatic condition, which agrees with experimental data after polychromatic correction. The monochromatic $\Delta S[r,t]$ were obtained by the protocol shown in Fig. S5 and the results are shown in Fig. S6.

Experimental data, $r^2 \Delta S_{inst}[r]$ and the pair distribution function, $\rho(r)$

The radial distribution function, $\rho(r)$, is basically the same as $r^2S[r]$ from Eq. (1) except that the latter is modified by the damping term in the Fourier transform. The static scattering intensity is calculated from the pair distribution function $g_{ii}(r)$ as follows:

$$S(q) = \sum_{i} N_{i} f_{i}^{2}(q) + \sum_{i} \sum_{i \neq j} \frac{N_{i} N_{j}}{V} f_{i}(q) f_{j}(q) \int_{0}^{\infty} (g_{ij}(r) - 1) \frac{\sin(qr)}{qr} 4\pi r^{2} dr.$$
(11)

The first term in Eq. (11) is eliminated in the difference scattering because it does not depend on the molecular structure. Then, the difference intensity from the difference pair distribution function is

$$\Delta S(q) = \sum_{i} \sum_{i \neq j} \frac{N_i N_j}{V} f_i(q) f_j(q) \int_0^\infty \Delta g_{ij}(r) \frac{\sin(qr)}{qr} 4\pi r^2 dr \,. \tag{12}$$

For a I_2 molecule, Eq. (12) can be written as follows:

$$\Delta S(q) = \frac{N_{I_1} N_{I_2}}{V} f_I^2(q) \int_0^\infty \Delta g_{I_1 I_2}(r) \frac{\sin(qr)}{q} 4\pi r dr$$

$$q\Delta S(q) = 4\pi \frac{N_{I_1} N_{I_2}}{V} f_I^2(q) \int_0^\infty r \Delta g_{I_1 I_2}(r) \sin(qr) dr , \qquad (13)$$

$$q\Delta S(q) = 4\pi \frac{N_{I_1} N_{I_2}}{V} \int_0^\infty f_{I_1} \Delta g_{I_2}(r) \sin(qr) dr ,$$

$$\frac{q\Delta S(q)}{f_{I}^{2}(q)} = 4\pi \frac{N_{I_{1}}N_{I_{2}}}{V} \int_{0}^{\infty} r\Delta g_{I_{1}I_{2}}(r)\sin(qr)dr$$

Therefore, the inverse transform of $\frac{q\Delta S(q)}{f_I^2(q)}$ is

$$\frac{1}{2\pi^2 r} \int_0^\infty \frac{q\Delta S(q)}{f_I^2(q)} \sin(qr) dq = \frac{N_{I_1} N_{I_2}}{V} \Delta g_{I_1 I_2}(r) \,. \tag{14}$$

In Eq. (1), $\exp(-q^2\alpha)$ can be replaced to $\int_{-\infty}^{\infty} \sqrt{\frac{\pi}{\alpha}} \exp\left(-\frac{r'^2}{4\alpha}\right) \exp(iqr')dr'$, and then by using Eq.

(14) we have the following relations.

$$\Delta S[r] = \frac{1}{2\pi^2 r} \int_0^\infty \frac{q\Delta S(q)}{f_l^2(q)} \exp(-q^2 \alpha) \sin(qr) dq$$

$$= \frac{1}{2\pi^2 r} \int_0^\infty \frac{q\Delta S(q)}{f_l^2(q)} \int_{-\infty}^\infty \sqrt{\frac{\pi}{\alpha}} \exp\left(-\frac{r'^2}{4\alpha}\right) \exp(iqr') dr' \sin(qr) dq$$

$$= \frac{1}{4\pi^2 r} \int_{-\infty}^\infty \frac{q\Delta S(q)}{f_l^2(q)} \int_{-\infty}^\infty \sqrt{\frac{\pi}{\alpha}} \exp\left(-\frac{r'^2}{4\alpha}\right) \exp(iqr') dr' \exp(-iqr) dq$$

$$= \frac{1}{4\pi^2 r} \sqrt{\frac{\pi}{\alpha}} \int_{-\infty}^\infty \exp\left(-\frac{r'^2}{4\alpha}\right) \int_{-\infty}^\infty \frac{q\Delta S(q)}{f_l^2(q)} \exp(-iq(r-r')) dq dr'$$

$$= \frac{1}{2} \sqrt{\frac{\pi}{\alpha}} \int_{-\infty}^\infty \exp\left(-\frac{r'^2}{4\alpha}\right) \frac{N_{l_1} N_{l_2}}{V} \Delta g_{l_1 l_2}(r-r') dr'$$

$$= \frac{1}{2} \sqrt{\frac{\pi}{\alpha}} \frac{N_{l_1} N_{l_2}}{V} \int_{-\infty}^\infty \exp\left(-\frac{r'^2}{4\alpha}\right) \Delta g_{l_1 l_2}(r-r') dr'$$

$$\Delta S[r] = \sqrt{\frac{\pi}{\alpha}} \frac{N_{l_1} N_{l_2}}{2V} \Delta g_{l_1 l_2}(r) * \exp\left(-\frac{r^2}{4\alpha}\right)$$
(15)

where * stands for convolution.

Multiplying by r^2 on both sides of the last equation in Eq. (15) shows the relationship between $r^2\Delta S[r]$ and $\Delta \rho(r)$ for a I₂ molecule,

$$r^{2}\Delta S[r] = \sqrt{\frac{\pi}{\alpha}} \frac{N_{I_{1}}N_{I_{2}}}{2V} r^{2}\Delta g_{I_{1}I_{2}}(r) * \exp(-r^{2}/4\alpha)$$

$$= \sqrt{\frac{\pi}{\alpha}} \frac{N_{I_{1}}N_{I_{2}}}{2V} \Delta \rho(r) * \exp(-r^{2}/4\alpha)$$

$$r^{2}S[r] = r^{2}\Delta S[r] + \sqrt{\frac{\pi}{\alpha}} \frac{N_{I_{1}}N_{I_{2}}}{2V} \rho_{0}(r) * \exp(-r^{2}/4\alpha) .$$

$$= \sqrt{\frac{\pi}{\alpha}} \frac{N_{I_{1}}N_{I_{2}}}{2V} (\Delta \rho(r) + \rho_{0}(r)) * \exp(-r^{2}/4\alpha)$$

$$= \sqrt{\frac{\pi}{\alpha}} \frac{N_{I_{1}}N_{I_{2}}}{2V} \rho(r) * \exp(-r^{2}/4\alpha)$$
(16)

The damping factor, a Gaussian function, was convoluted and it broadens $r^2S[r]$ compared to $\rho(r)$. As a result, $\rho(r)$ shows two maxima close to the turning points of the X state whereas this feature is much less apparent in $r^2S[r]$ in Fig S18 (see also Fig. 3d). The loss of resolution in the x-ray data is due to the finite q range and the form factor effect, i.e. that x-rays probe atoms as "electron balls" unlike neutrons that probe the positions of the nuclei. Except the broadening by the damping term, the radial distribution, $\rho(r)$ is identical to $r^2S[r]$.

Deconvolution to retrieve $r^2 \Delta S_{inst}[r,t]$

In the present theory, the experimental signal $r^2 \Delta S[r,t]$ appears as a convolution integral

$$r^{2}\Delta S[r,t] = \int_{-\infty}^{\infty} d\tau I_{x-ray}(t-\tau)r^{2}\Delta S_{inst}[r,\tau], \qquad (17)$$

where $I_{x-ray}(t)$ is the x-ray intensity as a function of time, and $r^2\Delta S_{inst}[r,t]$ is the signal of the sample induced by an (hypothetical) ultrashort x-ray pulse (Fig. S7b). Thus, to extract $r^2\Delta S_{inst}[r,t]$ from the experimentally determined $r^2\Delta S[r,t]$, a deconvolution of the x-ray temporal profile is necessary. Various deconvolution algorithms exist, including the constrained iterative algorithm, inverse filter and the least-mean-squares algorithm⁸⁻¹⁰. We deconvoluted using the least-mean-squares technique⁸. For each r, $r^2\Delta S[r,t]$ is a function of t. This function $r^2\Delta S[r,t]$ is the convolution of $r^2\Delta S_{inst}[r,t]$ with the x-ray temporal profile $I_{x-ray}(t)$. The goal of deconvolution is to reconstruct $r^2\Delta S_{inst}[r,t]$ from $r^2\Delta S[r,t]$. To do so, a model function for $r^2\Delta S_{inst}[r,t]$ is expressed as a sum of three exponentials and the coefficients and the time constants of the exponentials were used as fitting parameters to minimize the discrepancy between the experimental $r^2\Delta S[r,t]$ and the model function convoluted with the x-ray temporal profile, as shown in Fig. S7. $I_{x-ray}(t)$ is approximated by four half-Gaussians which give a perfect fit to the the x-ray temporal profile measured by a streak camera. Note how the rising edge of the x-ray pulse (negative time) is slightly steeper that the falling edge.

Because the experimental data is convoluted in time, the least-mean-squares algorithm is applied to $r^2 \Delta S[r,t]$ for each r independently. For a given r_i , $r_i^2 \Delta S_{inst}[r_i,t]$ is calculated from the sum of three exponentials with 5 ps time steps. The least-squares fit between the experimental data $r_i^2 \Delta S[r_i,t]$ and $r_i^2 \Delta S_{inst}[r_i,t]$ convoluted with the x-ray temporal profile gives $r_i^2 \Delta S_{inst}[r_i,t]$ optimized for each r_i . In principle, any functional form can be used as a trial function for the deconvolution. The quality of the deconvolution can be checked by convoluting $r^2 \Delta S_{inst}[r,t]$ with the $I_{x-ray}(t)$ and then comparing it with $r^2 \Delta S[r,t]$. As shown in Fig. S8 and Fig. S23, they show a good agreement for both samples. The deconvoluted $r^2 \Delta S_{inst}[r, t]$ curves are shown in Fig. S9 (also in Fig. 2a) for I2 in CCl4 and in Fig. 2b for I2 in cyclohexane. Two effects slightly distort the features in the $r^2 \Delta S_{inst}[r,t]$ curves. First, although the equilibrium I-I distance in the X and A/A' state is 2.67 Å and 3.1 Å, respectively, the positions of the negative and positive peaks are slightly shifted from these values in the difference curves. This peak shift is due to a partial overlap of positive and negative peaks. Second, a limited q range of the experimental data causes artificial oscillation in the Fourier transformed data, $\Delta S_{inst}[r,t]$. Because of the r^2 factor, these oscillations are enhanced in the high r region (r > 3.5 Å) of $r^2 \Delta S_{inst}[r,t]$ and generates wiggles in an otherwise monotonous distribution as shown in Fig. 2a and 2b. This oscillation has a specific period $2\pi/q_{\text{max}}$, where q_{max} is the maximum q used in the Fourier transform. In our case, q_{max} is 9 Å $^{-1}$ and thus the period is ~0.7 Å.

Double difference curves $r^2 \Delta \Delta S_{inst}[r,t]$

The $r^2 \Delta S_{inst}[r,t]$ monitors the evolution of iodine over two electronic surfaces X and A/A' simultaneously, which complicates the interpretation. The A/A' state has a rather long life time (2.7 ns or 1.2 ns for I₂ in CCl₄ as discussed below) compared with the investigated time range. In addition, a very small fraction of I₂ completely dissociates into atoms that do not return to I₂ in

the investigated time range. To clean up the contribution from these long-lived A/A' state and atomic iodine, double difference signals, $r^2 \Delta \Delta S_{inst}[r,t] = r^2 \Delta S_{inst}[r,t] - r^2 \Delta S_{inst}[r,t_{\infty}]$, were calculated (Fig. S10), where t_{∞} (426 ps was used in this case) is a time delay larger than the time scale of the vibrational relaxation in the X state. In addition, although the A/A' life time is long (1.2 ns; extracted from experiment data, details in next section), $r^2 \Delta \Delta S_{inst}[r,t]$ is still affected by the decay of A/A'. To remove this effect, theoretical $r^2 \Delta \Delta S_{inst}[r,t]$ curves corresponding to this A/A' decay were calculated (see the next section) and subtracted from $r^2 \Delta \Delta S_{inst}[r,t]$. The corrected $r^2 \Delta \Delta S_{inst}[r,t]$ curves are shown in Fig. S11. I₂ in cyclohexane shows faster population decay of A/A' than in CCl₄. The population decay of A/A' state is almost finished in 100 ps, making it hard to decouple the population decay of the A/A' state and the vibrational cooling. For this reason, the double difference curves were not calculated for I₂ in cyclohexane. Harris *et* al^{11} also reported that in cyclohexane a A/A' decay is ~71 ps, which is on the same time scale as the vibrational cooling.

The A/A' state lifetime measurement

To determine the lifetime of the A/A' state of I₂ in CCl₄ from the scattering data, two types of analysis were used. The first one is singular value decomposition (SVD) analysis on the scattering data $r^2\Delta S[r,t]$ at long time delays from 426 ps to 4 ns. SVD shows that there is only one major component. The first time-independent component (left singular vector) shown in Fig. 12a resembles the difference scattering signal of A/A'. Fig. S12b shows the first time-dependent component (right singular vector) and its exponential fitting gave 1.2 ± 0.1 ns lifetime. The second method to determine the lifetime of A/A' is to analyze the amplitude of the solvent contribution vs time. The solvent amplitude is directly related to the temperature change in the solvent, and the origin of the temperature change is the heat released from the solute to the solvent. Since the population relaxation from the A/A' state to the X state is an exothermic process, the temperature change of solvent is sensitive to this process. The solvent amplitude vs time and the exponential fit are shown in Fig. S12c. The exponential fit gives 1.2 ± 0.2 ns, which is identical to the value obtained from the SVD value. We note that this 1.2 ns life time of A/A' state is smaller than the 2.7 ns reported by spectroscopic studies^{1/1}.

Time-dependent pair distribution function $r^2S_{inst}[r,t]$

Finally, we compensate for the negative peak at ~2.67 Å, the I_2 hole from the depletion of the ground state and derive the time-dependent distance distribution $r^2 S_{inst}[r,t]$ for the bond formation in the X-state. Specifically $r^2 S_{inst}[r,t] = r^2 \Delta \Delta S_{inst}[r,t] + r^2 S_{I_2,X}[r]$, where $r^2 S_{I_2,X}[r]$ is the scattering curve of the ground state (X) of I₂. Since a damping term and a sharpening term were used in the Fourier transform as shown in Eq. (1), we first check the effect of these terms on the $r^2S[r]$ curves as shown in Fig. S13. It turns out that an intrinsic I-I distribution of ~0.2 Å do not have any significant effect on the $r^2S[r]$ compared with the case when a single I-I distance (i.e. a δ -function) was used. The only effect of a 0.2 Å dispersion in the ground state is that the height of $r^2S[r]$ is slightly reduced. The final effect of the size of an iodine atom (x-ray formfactor), damping and sharpening is a broadening of $r^2S[r]$ to ~0.6 Å (fwhm). A Gaussian function with a fwhm of 0.6 Å reproduces the peak shape satisfactorily, and thus we used a time-independent Gaussian function with ~0.6 Å fwhm to account for the contribution of the depleted ground state. By fitting the negative peak in $r^2 \Delta \Delta S_{inst}[r, 1 \text{ ps}]$, the Gaussian peak for the depleted ground state was scaled and added to $r^2 \Delta \Delta S_{inst}[r,t]$ at all time delays to construct $r^2 S_{inst}[r,t]$ as shown in Fig. S14. For I₂ in cyclohexane, rather than the double difference curves, $r^2 \Delta S_{inst}[r,t]$ was used to get $r^2 S_{inst}[r,t]$. The same Gaussian peak was added to $r^2 \Delta S_{inst}[r,t]$.

Dependence on the functional form used in the deconvolution procedure

So far we have described the case where a three-exponential function is used in the deconvolution process, but other functions (a two-exponential function, a four-exponential function and a stretched exponential function) were also used to check the dependence of the results on the functional form. As shown in Fig. S15, the $r^2 \Delta S_{inst}[r,t]$ curves obtained from using these four different functional forms yield almost identical deconvoluted curves, but those in the early time delays contain some noise. This noise reflects the poorer signal to noise ratio of the early delays. In this case, we have to choose the one that gives the lower chi-square value in the convoluted curves. In addition, the smoothness of the deconvoluted curves can guide us too.

curves. Actually if there is no noise at all or the noise is sufficiently low, then there is even less dependence on the choice of the functional forms.

Time-dependent average I-I distance as a function of time, $\langle r(t) \rangle$

The $r^2 S_{inst}[r,t]$ contains information about the time-dependent I-I distance distribution, and it was thus used to extract the dynamics of the vibrational relaxation processes. We calculated $\langle r(t) \rangle$, the average distance as a function of time (Fig. 3c) for I₂ in CCl₄, by using the data from 1.5 Å to 4.5 Å. A single exponential function does not provide a satisfactory fit to the experimental data and double exponential is necessary to attain a satisfactory fit with time constants, 16 ± 0.2 ps and 76 ± 2 ps with a relative ratio of about 2:1. Here the errors account for the fitting and do not account for any other experimental errors. Adding more exponentials does not improve the fit. For example, when three exponentials were used, the two of the time constants converge to an identical value, eventually reverting to the same result as with the case with the double exponentials. This result reveals that the vibrational cooling process in the X state occurs via a bi-exponential decay. We also tried a stretched exponential. This gives a slightly worse fit than the double exponential. The fit gives $\beta = 0.69 \pm 0.02$ and tau = 24 ± 1 ps. The mean relaxation time from the result of stretched exponential fit is 31 ps. Since the final $r^2 \Delta \Delta S_{inst}[r,t]$ curves depend on the widths of the added Gaussian function to compensate for the depleted ground state, we examined the effect of this Gaussian width on the final time constants. As shown in Fig. S16 and summarized in Table S1, the $\langle r(t) \rangle$ yields still the same bi-exponential decay profile with quite similar time constants. As mentioned earlier, whereas the previous spectroscopic study reported 2.7 ns for the lifetime of A/A', the analysis of our scattering data yields 1.2 ns. We also checked the effect of the lifetime values of A/A' on the final $\langle r(t) \rangle$ and the time constants for the vibrational cooling process. The final results do not show much dependence on the lifetime of A/A' as both values are much larger than the vibrational cooling times.

For I₂ in cyclohexane, the change of $\langle r(t) \rangle$ agrees well with the single exponential function with a time constant of 55 ± 1 ps, instead of a double exponential that works for I₂ in CCl₄. Since both the population decay of A/A' state and the vibrational cooling are mapped in $\langle r(t) \rangle$, this single exponential decay behaviour of $\langle r(t) \rangle$ implies that both processes have similar

time constants and single-exponential decay profiles. This is consistent with the observation by Harris *et al*¹¹, who also reported that, in cyclohexane, the decay of A/A' state (~71 ps) is on the same time scale as the vibrational cooling process.

The deconvolution algorithm comparison: the least-mean-square method and the constrained iterative method

In addition to the least-mean-square deconvolution method, another deconvolution method was used to check the dependence of the deconvoluted signal on the deconvolution method. For this purpose, the constrained iterative method was applied to the same experimental data. Among various constrained iterative method, Jason's method⁸ was used because it introduces a boundary condition in the iteration so that it controls the solution to converge within physically meaningful region. In each iteration step, the following equation was used.

$$r^{2}\Delta S_{inst}^{k+1}[r,t] = r^{2}\Delta S_{inst}^{k}[r,t] + A\left(r^{2}\Delta S_{inst}^{k}[r,t]\right)\left\{r^{2}\Delta S_{EXP}[r,t] - \int d\tau I_{X-ray}(t-\tau)r^{2}\Delta S_{inst}^{k}[r,\tau]\right\}, (18)$$

where k and k+1 indicate iteration numbers, $A(r^2\Delta S_{inst}^k[r,t])$ is the function to provide a convergence factor based on the boundary condition defined by ±20 % from the initial guess values and is defined as follows:

$$A(r^{2}\Delta S_{inst}^{k}[r,t]) = \begin{cases} a \quad r^{2}\Delta S_{inst}^{k}[r,t] - 0.2 \times \left(\left|r^{2}\Delta S_{inst}^{0}[r,t]\right|\right) \le r^{2}\Delta S_{inst}^{k}[r,t] \\ \le r^{2}\Delta S_{inst}^{k}[r,t] + 0.2 \times \left(\left|r^{2}\Delta S_{inst}^{0}[r,t]\right|\right). \end{cases}$$
(19)
0 elsewhere.

One limitation of the iterative method is that the solution is strongly affected by noise. When the signal-to-noise ratio is not good enough, the experimental noise generates unphysical oscillations. The experimental noise causes a strange oscillation at late time delays (>100 ps). In the early time region (<100 ps), however, the deconvolutions using the constrained iterative method and the least-square-method give almost identical result within experimental errors as shown in Fig. S17.

Reliability test of the data analysis and estimation of spatial and temporal uncertainties

A series of data processing procedures were employed to extract the structural changes more clearly. To assess the reliability of the used procedures, we applied the exact same procedures to mock data and examined the uncertainties introduced by the procedures. This test confirmed that our procedures can extract reliable information.

The mock data $\Delta S(q,t)$ were calculated by Debye equation (Eq. (21)).

$$S(q,t) = \int_{r} f_{I}^{2}(q)\rho(r,t)\frac{\sin(qr)}{qr}dr$$
(21)

The difference radial distribution functions, $\Delta \rho(r,t)$, was calculated by using $\rho(r,t)$ from MD simulation (Fig. S18a) to mimic the vibrational relaxation process. The time scales of the MD simulation were doubled to make the relaxation rates roughly the same as that observed in the experimental data. Solvent heating signal was also added to the mock data to account for the effect of solvent heating. The random noise was generated by using a Gaussian distribution centered on the difference scattering intensity and a standard deviation proportional to q^{1.2} and the square of atomic form factor of iodine. The calculated mock data are shown in Fig. S24a and it has a similar noise level as the experimental data. This mock data of $\Delta S(q,t)$ were used to test the reliability of our procedures applied to the experimental data.

As was done for the experimental $\Delta S(q,t)$ curves, the mock $\Delta S(q,t)$ curves were converted to the difference radial distribution, $r^2 \Delta S[r,t]$, by Fourier transform in Eq. (1). The resulting $r^2 \Delta S[r,t]$ are shown in Fig. S24b. Then, solvent heating signal was subtracted from $r^2 \Delta S[r,t]$ by using the exact same procedure used for the real data. Fig. S24c shows the resulting $r^2 \Delta S[r,t]$ where the solvent heating signal was removed.

The deconvolution calculation of the mock data was done using the least-mean-square method by using the exact same target functional form (three exponentials) and x-ray temporal profile that were used in data analysis of the experimental data. In Fig. S25a, the deconvoluted $r^2\Delta S[r,t]$ curves are compared with the reference $r^2\Delta S[r,t]$ curves which were calculated from $\Delta \rho(r,t)$ by Eq. (16). The agreement is excellent.

Then, as was done in the real data analysis of the experimental data, a Gaussian distribution corresponding to the ground state was added to the deconvoluted $r^2\Delta S[r,t]$ to generate the radial distribution of iodine-iodine, $r^2S[r,t]$ (Fig. S25b). At this point, to quantitatively assess the errors introduced by our procedures, we checked the R values calculated by Eq. (22). The R values ranged from 0.12 to 0.16, indicating ~12–16% difference between the reference and the analyzed data. The peak positions of the analyzed data differ from those of the

reference data by less than 0.06 Å, which can be regarded as the maximum spatial uncertainty in our analysis.

$$R = \frac{\sum \left| r^2 S_{mock}[r,t] - r^2 S_{analyzed}[r,t] \right|}{\sum \left| r^2 S_{mock}[r,t] \right|}$$
(22)

As was done in the data analysis of the experimental data, $\langle r(t) \rangle$ was calculated for $r^2S[r,t]$ and compared with $\langle r(t) \rangle$ of the model used to generate the mock data as shown in Fig. S25c. As in experimental data, the temporal behavior of $\langle r(t) \rangle$ for the analyzed mock data is well described by a double exponential with lifetimes of 25 ps and 81 ps. The $\langle r(t) \rangle$ from the model data is also well fit by a double exponential with 23 ps and 91 ps. The time constants differ by less than 10 ps, which can be regarded as the temporal uncertainty for $\langle r(t) \rangle$. We also tested another set of mock data where a different set of noise with the same amplitude was used, and the spatial and temporal uncertainties were still ~0.06 Å and ~10 ps, respectively.

Molecular Dynamics simulations

All the MD simulations were performed with periodic boundary conditions for a cubic box of 43.6 Å length consisting of one I₂ molecule embedded in 511 CCl₄ molecules. This setup corresponded to the density of CCl₄ at standard temperature and pressure (1.58 g/cm³). The classical equations of motion were integrated using the Gear predictor-corrector method with a time step of 1 fs, and the solvent molecules were kept rigid using quaternions ¹². Freezing the vibrational degrees of freedom of CCl₄ was in agreement with previous studies, which favoured the V-T energy transfer during the vibrational relaxation of I₂¹¹.

All interactions were assumed to be pairwise additive; for the intermolecular C-C, Cl-Cl, and C-Cl interactions, the OPLS parameters for Lennard-Jones 6-12 and Coulomb potentials were used ¹³. The I-C and I-Cl interactions were modeled by Lennard-Jones 6-12 potentials with parameters constructed using the usual Lorentz-Berthelot mixing rules, where $\varepsilon_{\rm I} = 240$ K and $\sigma_{\rm I} = 3.8$ Å were determined from a fit of parameters for I-Ne and I-Ar interactions ¹⁴. The cutoff distance for terminating the van der Waals dispersion forces was set to be half of the box length. The electronic ground state (X state) of I₂ was represented by a Morse potential V_X with the parameters $D_{\rm e} = 12547$ cm⁻¹, $\beta = 1.91$ Å⁻¹, and $r_{\rm eq} = 2.67$ Å^{-15,16}. The purely repulsive excited

state (Π state) was of the form $V_{\Pi}(\mathbf{r}) = \alpha (r/\text{\AA})^{-9.5}$ with $\alpha = 8.61 \times 10^7 \text{ cm}^{-1}$, and its dissociation limit was identical to that of the *X*-state ^{17,18}. The potentials are shown in Fig. 1.

The initial conditions for the photodissociation calculations were found by MD simulations performed in the canonical ensemble at T = 300 K using the Nose-Hoover thermostat ^{19,20}. For these equilibration runs, the initial center-of-mass coordinates of the molecules corresponded to the positions of the unit cells in the cubic simulation box, and the momentum components of each atom were chosen randomly from a distribution with a Gaussian weighting. This choice did not bias the ensemble sampling because position randomization was obtained from a 20-ps initial run, before all atomic positions and velocities were saved for every 10 ps (each set of atomic positions and velocities constituted the initial conditions for the photodissociation calculations). The I₂ molecule was kept rigid during the equilibration runs with a separation equal to the classical equilibrium distance r_{eq} .

The photodissociation trajectories were performed in the microcanonical ensemble to avoid non-collisional velocity scaling from the Nose-Hoover thermostat. A total of 272 initial conditions were used to run 200-ps photodissociation trajectories, where an instantaneous replacement of the X state by the Π state potential mimicked an optical laser excitation of I₂ from the X state to the Π state. Hence, at the first integration step, the total energy of the system increased by ~ 20000 cm⁻¹ (the energy difference between the two electronic states at the distance r_{eq} , see Fig. 1). In 32 trajectories the iodine atoms escaped the solvent cage and did not recombine within 200 ps. This corresponds to approximately 12 %, which match previous experimental results²¹.

In the classical treatment of the dynamics, any non-adiabatic transitions between the Π state and the X state, after laser excitation, could not occur. The non-adiabatic transition is an important quantum effect, especially in the asymptotic region of the two states, where the potentials are close enough to facilitate curve crossing ²². A simple surface hopping model was chosen in which an instantaneous deexcitation from the Π state to the X state occurred once the energy difference between the two states equaled $k_{\rm B}T \sim 208 \text{ cm}^{-1}$ ^{14,23}. This criterion for a non-adiabatic transition corresponded to a separation of ~5.2 Å between the iodine atoms, which was nearly always reached before the iodine atoms re-approached, now in the *X*-state, due to collisions with solvent molecules (in approximately 6 % of the trajectories the iodine atoms

oscillated twice or more before reaching a separation of ~ 5.2 Å). In order to maintain energy conservation "during" the transition, $k_{\rm B}T$ was added to the kinetic energy associated with the vibrational degree of freedom, while the direction of the corresponding momentum vector was conserved.

MD simulations allow us to compare the results of time-resolved X-ray liquidography and time-resolved spectroscopy. In Fig. S18a, the time evolution of the distribution function $\rho(r,t)$ of the I-I atomic pair obtained from the MD simulation is shown, with each function averaged over the vibrational period. The $\rho(r,t)$ curves can be converted to $r^2S_{inst}[r,t]$ for comparison with the experimental $r^2S_{inst}[r,t]$ curves. The $r^2S_{inst}[r,t]$ is basically the same as $\rho(r,t)$ except that the former is broadened by the convolution with Gaussian functions due to the damping term in the Fourier transform. It means that $r^2S_{inst}[r,t]$ can be obtained from $\rho(r,t)$ by using Eq. (16). As a result, the two maxima of $\rho(r,t)$ near the turning points of the potential energy surface of the X state are much less pronounced in the experimental $r^2S_{inst}[r,t]$ curves in Fig. S18a. The spread of $\rho(r,t)$ decreases with time as the ensemble of I₂ molecules relaxes towards the bottom of the potential well of the X state. In other words, as the vibrational energy decreases, so does the accessible range of r.

We obtained the time dependence of both the average energy $\langle E \rangle$ and the average I-I distance $\langle r \rangle$, as shown in Fig. S18b and S18c. The decay of $\langle E \rangle$ was fit by a bi-exponential, giving the relaxation times of $\tau_1^E = 9$ ps and $\tau_2^E = 71$ ps ($A_E = 6248$ cm⁻¹ and $B_E = 3824$ cm⁻¹). Especially, the decay described by the slower component is in good agreement with result from the spectroscopic study (indicated by green cross-bars), confirming that the cooling of I₂ in CCl₄ is well described by two relaxation components. The decay of the average I-I distance $\langle r \rangle$ was fit by a bi-exponential function with the relaxation times of $\tau_1^r = 3$ ps and $\tau_2^r = 44$ ps ($A_r = 1.22$ Å and $B_r = 0.22$ Å), in agreement with the bi-phasic decay behaviour observed in the experimental data. From the fittings of the $\langle E \rangle$ and $\langle r \rangle$ temporal profiles, we found that $\langle E \rangle$ and $\langle r \rangle$ exhibit bi-exponential decays different from each other and the amplitude ratio of the faster and slower components of the $\langle r \rangle$ decay is much larger than that of the $\langle E \rangle$ decay. This finding can be understood by considering the change in the accessible *r* range with respect to the change in energy *E*. When the energy decreases along the potential well, the accessible *r* range decreases more rapidly in the neighbourhood of the dissociation limit than in the lower-energy

range of the potential well because the slope of the potential energy versus *r* becomes steeper as the energy becomes lower from the dissociation limit (see Fig. 1). The relaxation times of $\langle r \rangle$, τ_1^r and τ_2^r , from the MD simulation are shorter than the experimental values (16 ps and 76 ps) and the amplitude ratio of the fast and slow components (11:2) from the simulation is larger than the experimental value (2:1). The quantitative difference between the distribution functions from the experiment and the simulation can be ascribed to the arbitrariness in the choice of the force field parameters, but the bi-phasic decay of the distribution functions is independent of this choice. We also note that the MD simulation neglects possible interference between the relaxation processes on the A/A' state and on the X state. However, due to relatively fast energy loss on the X state, such interference would only affect the relaxation on the X state at very early times (most likely resulting in slightly longer decay times).

Comparison of the experimental and theoretical radial distribution functions

As the I-I distance changes in the low r region (1 - 5 Å), the experimental data also show changes in the interatomic distance at r values larger than 5 Å. To examine the origin of these changes, a series of MD simulations were performed using MOLDY²⁴ while varying the I-I distance from 2.3 to 4.2 Å (with an interval of 0.1 Å). One I_2 molecule and 256 CCl₄ molecules were used in the MD simulations. The simulation was done with a canonical ensemble and the temperature was set to be 300 K by a Nose-Hoover thermostat. The Lennard-Jones potential was used and its parameters are summarized in Table S2. The pair distributions, g(r), for I-Cl and I-C atomic pairs were extracted from MD simulations (Fig. S19a and S19b) and transformed to S(q)by Eq. (11). Then, $r^2S[r]$ is obtained by the Fourier transform with a damping term and a sharpening function as shown in Fig. S19c. The difference between $r^2S[r]$ curves of the elongated I₂ molecule (with an I-I distance of 2.3 - 4.2 Å) and the ground-state I₂ molecule (with the I-I distance of 2.65 Å) gives a contour map of theoretical difference cage term, $r^2 \Delta S_{cage}[r]$. Figure S19d shows $r^2 \Delta S_{cage}[r]$ as a function of I-I distance in the solute I₂ molecule. The $r^2 \Delta S_{cage}[r]$ at large r values obtained from the MD simulation clearly shows a peak shift with the change of the I-I distance. With the decrease of the I-I distance towards the equilibrium distance in the ground state, the negative peak at around 6 Å becomes narrower, and the positive peak between 7 and 8 Å shifts to 7 Å.

The theoretical cage term was calculated by a linear combination (Eq. (20)) of the I-I distribution based on the experimental interatomic distance distribution contour map in Fig. 3A and the MD simulation result in Fig. S19d. For example, at a given *t* and *r*, the theoretical cage terms, $r^2 \Delta S_{\text{cage}}[r]$, were calculated as the sum of interatomic distributions at various I-I distances (*r*_i) from the MD simulations, $r^2 S_{\text{MDi}}[r]$, weighted by the experimental radial distribution curves, $r^2 S_{\text{EXP}}[r_{i},t]$, at corresponding r_i 's:

$$r^{2}\Delta S_{cage}[r,t] = \sum_{r_{l-l}} r^{2}\Delta S_{MD_{i}}[r] \times r^{2}S_{\exp}[r_{i},t]$$

$$\tag{20}$$

Fig. 5b shows the change of the theoretical solute-solvent distance distribution (i.e. cage term) as a function of time based on the experimental I-I distribution of the solute molecules.



Fig. S1. Difference scattering curves $\Delta S(q,t)$ for I₂ in CCl₄ recorded with 100 picosecond x-ray pulses. The curves show the change in scattering induced by a 0.5 ps laser pulse at 530 nm. Note the weak signal at negative delays due to the laser-truncated x-ray pulse. These signals comprise three states of iodine, their associated solvent cages plus solvent heating from recombining iodine atoms.



Fig. S2. Difference radial distribution function $\Delta S[r,t]$ for I₂ in CCl₄ obtained from the Fourier transform of $\Delta S(q,t)$. For interatomic distances *r* above 6 Å, the signal is approaching that from the (pure) heated solvent. Eliminating the solvent term is essential for precise estimates of the solute dynamics. At early times, only a fraction of the x-ray pulse probes the laser-triggered event, which explains why the difference signal is small at negative times. The red dotted curves include the correction for this partial temporal overlap by (roughly) normalizing the curves with respect to the number of x-ray photons that probe the excited molecules (erf function). After 50 ps the red and black curves coincide for the 100 ps x-ray pulse.



Fig. S3. Typical difference scattering curves for solute and solvent contributions. (a) The signals $\Delta S[r, 426 \text{ ps}]$ from the I₂/CCl₄ solution (black curve) and that from thermally excited pure CCl₄ (red curve). (b) The signal $\Delta S[r, 426 \text{ ps}]$ of I₂ alone obtained from subtracting the solvent contribution from the total signal. Note the negative peak from the depletion of I₂ in the ground (X) state and the positive peak corresponding to the A/A' state.



Fig. S4. $\Delta S[r, t]$ curves of I₂ molecules alone after the correction from solvent heating as shown in Fig. S3 (I₂ in CCl₄). Again at early times, only a fraction of the x-ray pulse probes the lasertriggered molecules and thus the difference signal is small. The red dotted curves correct for this partial temporal overlap (erf function). Note how the depth of the I₂ hole at 2.6 Ang decreases with time from the reformation of I₂ in the ground state.



Fig. S5. A scheme to correct for the asymmetric x-ray spectrum of the U17 undulator, the correction for the polychromatic x-rays inherent in pink beam experiments. (a)The x-ray pulse used in the experiment has a 3 % bandwidth with a characteristic half-Gaussian shape in energy. (b) The polychromaticity of the x-ray spectrum shifts the r-scale in the Fourier transformed data (red curve). The black curve is a monochromatic trial function which, after convolution with the U17 spectrum, gives the observed curve in blue.



Fig. S6. $\Delta S[r,t]$ curves for I₂ in CCl₄ polychromatically corrected as shown in Fig. S5. The red dotted curves include the correction for the partial overlap of the laser illumination and x-ray pulse at early times by normalizing the curves with respect to the the number of x-ray photons influenced by laser illumination.



Fig. S7. Deconvolution concept. The x-ray temporal pulse width is larger or comparable to the time scale of the process of interest. The dynamic features are thus blurred in the experimental data due to the convolution of the sample signal with the temporal profile of the x-ray pulse. (a) Experimental data $r^2\Delta S[r,t]$ in r space for various time delays. The red line indicates the position of r = 3.1 Å. (b) Upper figure is $r^2\Delta S[r,t]$ versus time at r = 3.1 Å. The sample signal is constructed using the deconvolution procedure. For each r value, $r^2\Delta S[r, t]$ changes as a function of t. This function $r^2\Delta S[r, t]$ is the result of the convolution of the sample signal $r^2\Delta S_{inst}[r, t]$ with the x-ray temporal profile $I_{x-ray}(t)$. The goal is to reconstruct $r^2\Delta S_{inst}[r, t]$. $r^2\Delta S_{inst}[r, t]$ is expressed as a sum of three exponentials and the pre-exponential factors and the time constants were used as least-squares fitting parameters to minimize the discrepancy between the convoluted curve and the experimental $r^2\Delta S[r, t]$.



Fig. S8. Experimental data $r^2 \Delta S[r, t]$ for I₂ in CCl₄ (black) and the convolution (red) of the optimized $r^2 \Delta S_{inst}[r,t]$ with the $I_{x-ray}(t)$. The good agreement between black and red curves assures that the deconvolution was successfully done.



Fig. S9. Deconvoluted $r^2 \Delta S_{inst}[r, t]$ for I₂ in CCl₄. Note the broad positive intensity at early times.



Fig. S10. $r^2 \Delta \Delta S_{inst}[r,t]$ for I₂ in CCl₄ obtained by subtracting $r^2 \Delta S_{inst}[r,426 \text{ ps}]$ from $r^2 \Delta S_{inst}[r,t]$ to remove the contribution from the A/A' state and dissociated iodine atoms remaining at 426 ps.



Fig. S11. $r^2 \Delta \Delta S_{inst}[r,t]$ for I₂ in CCl₄ obtained by subtracting the contribution from the population decay of A/A' (1.2 ns).



Fig. S12. a) 1^{st} LSV (left singular vector) from SVD of the data for I_2 in CCl₄ at late time delays and the singular values (inset). b) 1^{st} RSV (right singular vector) and the single exponential fit with 1.2 ± 0.1 ns lifetime. c) Solvent contribution as a function of time and its exponential fit. The lifetime is fitted as 1.2 ± 0.2 ns.



Fig. S13. The effect of the damping and sharpening terms on $r^2S[r]$. (a) Calculated difference scattering intensities of a I₂ molecule when it has only one distance of 2.67 Å without any dispersion (i.e. a δ -function) (black) and when the intrinsic distribution of I-I distance with 0.2 Å FWHM Gaussian distribution is considered (red). Upper curves are $\Delta S(q)$ and lower curves are $q\Delta S(q)$. (b) Fourier transformation of (a). The two curves are quite similar, indicating that the effect of the intrinsic I-I distance distribution is negligible compared to the size of an iodine atom seen by x-rays. (c) Comparison of the FT curves in (b) and a Gaussian peak with 0.6 Å FWHM (blue), indicating that the FT curve is well represented by a Gaussian function with 0.6 Å FWHM. (d) Comparison of the FT curves and Gaussian distribution with 0.2 Å FWHM (blue).



Fig. S14. $r^2 S_{inst}[r,t]$ for I₂ in CCl₄ with the negative peak at 2.67 Å eliminated by adding a Gaussian.



Fig. S15. Deconvoluted $r^2 \Delta S_{inst}[r, t]$ for I₂ in CCl₄ from various functions: two exponentials (magenta), three exponentials (red), four exponentials (black) and a stretched exponential (blue). (a) All time delays from 1 ps to 426 ps. (b) Enlarged for early time delays up to 76 ps.



Fig. S16. The effect of the width of the Gaussian peak on the average I-I distance change for I₂ in CCl₄. (a) $r^2S_{inst}[r,t]$ in case of adding a normal Gaussian peak. (b) $r^2S_{inst}[r,t]$ in case of adding a wider Gaussian peak than in (a). (c) $r^2S_{inst}[r,t]$ in case of adding a narrower Gaussian peak than in (a). (d) $\langle r(t) \rangle$ corresponding to (a). (e) $\langle r(t) \rangle$ corresponding to (b). (f) $\langle r(t) \rangle$ corresponding to (c).



Fig. S17. Comparison of the deconvoluted signals for I_2 in CCl_4 by two different deconvolution methods: the least-mean-square method (black) and the constrained iterative method (red).



Fig. S18. Molecular dynamics simulation of the vibrational cooling process of I₂ in CCl₄. (a) Time evolution of the distribution function $\rho(r,t)$ of the I-I atomic pair obtained by MD simulation (black, dashed line). The I-I distance distribution function $r^2S[r,t]$ converted from $\rho(r,t)$ (blue, solid line) are plotted together for comparison. The potential energy curve corresponding to the X state is also shown (red, dashed line). (b) The density $\gamma(E,t)$ of the S37

vibrational energy as a function of time. Fit of the average energy $\langle E \rangle$ (blue, solid line) to a biexponential function, $f(t) = A_E \exp(-t/\tau^E) + B_E \exp(-t/\tau_2^E) + 222 \text{ cm}^{-1}$ (red, dashed line), gives the relaxation times $\tau_1^E = 9$ ps and $\tau_2^E = 71$ ps. The average vibrational energy of I₂ at T = 300 K is 222 cm⁻¹, as indicated by the cyan, dash-dotted line. The simulated results agree with the experimental data from Harris *et al* ²⁵ (green crossbar). Note that the relaxation is not completed within 200 ps. (c) Time dependence of the radial distribution function $r^2S[r,t]$. Fit of the average distance $\langle r \rangle$ (blue, solid line) to a bi-exponential function, $g(t) = A_r \exp(-t/\tau^2) + B_r \exp(-t/\tau_2^r) +$ 2.67 Å (red, dashed line), gives the relaxation times $\tau^r = 3$ ps and $\tau_2^r = 44$ ps. The equilibrium distance (green, dash-dotted line) is also shown.



Fig. S19. MD simulation results. (a) The pair distribution function between the C atom in the solvent and the I atom. The blue curve and red curve are for I-I distance at 4.0 Å and 3.1 Å, and the black curve is for an I-I distance of 2.65 Å. (b) The pair distribution function between Cl atoms in solvent and I atom. The blue curve and red curve are for I-I distance at 4.0 Å and 3.1 Å, and black curve is for I-I distance at 2.65 Å. (c) $r^2_{cage}S[r]$ is converted from g(r)–1 calculated from MD simulation. (d) $r^2\Delta S_{cage}[r]$ obtained by subtracting $r^2S_{cage}[r]$ of I₂ in the ground-state configuration from $r^2\Delta S_{cage}[r]$ at other distances. With the decrease of I-I distance towards the equilibrium distance in the ground state, the width of negative peak at around 6 Å is narrowed, and positive peak between 7 and 8 Å is shifted to 7 Å.



Fig. S20. Difference scattering curves $\Delta S(q,t)$ for I₂ in cyclohexane.



Fig. S21. Difference radial distribution function $\Delta S[r,t]$ for I₂ in cyclohexane.



Fig. S22. $\Delta S[r, t]$ curves of pure I₂ obtained by subtraction of the solvent contribution for I₂ in cycohexane.



Fig. S23. Experimental data $r^2 \Delta S[r, t]$ for I₂ in cyclohexane (black) and the convolution (red) of the optimized $r^2 \Delta S_{inst}[r,t]$ with the $I_{x-ray}(t)$. The good agreement between black and red curves assures that the deconvolution was successfully done.



Fig. S24. The generation of mock data. (a) Mock $\Delta S(q,t)$ calculated by Eq. (21) from model $\rho(r,t)$. (b) Fourier transform of the mock data, $r^2 \Delta S[r,t]$. (c) Solvent heating signals were removed from b).



Fig. S25. Analysis of mock data by deconvolution and other subsequent procedures used for the real experimental data. (a) The $r^2\Delta S[r,t]$ for the reference data directly converted from the model $\Delta \rho(r,t)$ (black) and the analyzed mock data after deconvolution (red). (b) Radial distribution function $r^2S[r,t]$ curves for the reference data (black) and the analyzed mock data (red). (c) <r(t)> for the reference data (black circle) and analyzed mock data (red square). Both <r(t)> can be fit well by double exponentials with lifetimes of 23 ps and 91 ps for the reference (black line) and 25 ps and 81 ps for analyzed mock data (red line), respectively.

	Functions	Offset (Å)	k ₁ (ps)	k ₂ (ps)	β
а	double	2.66 ± 0.002	15.8 ± 0.2	76.0 ± 1.5	
	stretched	2.67 ± 0.004	24.1 ± 0.8		0.69 ± 0.02
b	double	2.66 ± 0.001	13.5 ± 0.1	70.0 ± 0.1	
	stretched	2.67 ± 0.003	20.3 ± 0.7		0.65 ± 0.02
c	double	2.66 ± 0.003	19.7 ± 0.6	85.6 ± 6.0	
	stretched	2.67 ± 0.004	29.7 ± 0.9		0.75 ± 0.03

Table. S1. Fitting results of the bond length relaxation for I_2 in CCl₄ in Fig. S16.

Table. S2. Lennard-Jones parameters for $I_2 \mbox{ and } CCl_4.$

	σ (Å)	ε (kJ/mol)
I-I	4.10	2.0
I-C	3.95	0.6
I-Cl	3.79	1.4
C-C	3.80	0.2
C-Cl	3.64	0.5
Cl-Cl	3.47	1.13

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