

# Spatiotemporal reaction kinetics of an ultrafast photoreaction pathway visualized by time-resolved liquid x-ray diffraction

Kim *et al.* 10.1073/pnas.0601958103.

## Supporting Information Files in this Data Supplement:

Supporting Figure 6  
Supporting Figure 7  
Supporting Text

Supporting Figure 6 (/content/suppl/2006/06/02/0601958103.DC1/01958Fig6.pdf)

**Fig. 6.** Generation of difference diffraction data. (A) Scaled raw diffraction images at the time delay of  $-3$  ns and  $1$  ms together with the corresponding difference diffraction image. (B) 1D total scattering curves at  $-3$  ns and  $1$  ms and the difference curve with experimental error bars. These are radial integrations of the 2D images from A.

Supporting Figure 7 (/content/suppl/2006/06/02/0601958103.DC1/01958Fig7.pdf)

**Fig. 7.** Difference diffraction intensities  $DS(q)$  at selected time delays ( $-200$  ps,  $100$  ps, and  $1$  ms) from UV optical excitation ( $267$  nm) of HgI<sub>2</sub> in methanol solution (red) and pure methanol solution (black). In the pure methanol measurement, 4 repetitions were averaged, whereas 35 repetitions were averaged in the HgI<sub>2</sub> in methanol data.

## Supporting Text

**Experimental Methods and Materials.** The time-resolved diffraction data were collected on the beamline ID09B at the European Synchrotron Radiation Facility (ESRF). The adopted experimental setup was the typical optical pump and x-ray probe as described elsewhere (1). Femtosecond laser pulses (pump) from an amplified mode-locked Ti:Sapphire laser, synchronized to single pulses of x-rays, were frequency tripled to  $\lambda = 267$  nm. The laser pulse was temporally stretched by the passage through 30 cm of fused silica to lower the peak power of the laser pulse, thus preventing multiphoton excitation. The laser beam was focused to a diameter of  $100$   $\mu$ m, and the laser power was  $35$ – $40$  mJ at the sample with a pulse duration of  $2$  ps. The x-ray pulses (probe) were selected from the 16-bunch filling mode of the synchrotron ring by using a synchronized mechanical chopper. Quasi-monochromatic 100-ps-long x-ray pulses with  $5 \times 10^8$  photons per pulse were focused into a  $100 \times 60$  mm<sup>2</sup> spot at the sample. The spectrum of the x-rays was peaked at  $18.2$  keV and had a bandwidth of  $0.45$  keV. Diffraction data were collected with an area detector (MarCCD, Mar USA, Evanston, IL;  $2048 \times 2048$ ,  $64.3$ -mm effective pixel size) with a sample-to-detector distance of  $43$  mm. The temporal overlap of both pulses was measured by a fast photoconductor (GaAs detector) connected to a 6-GHz oscilloscope, and the delay was varied by means of electronic delay units to 5-ps precision. The jitter is much smaller than the x-ray pulse width and  $<5$  ps (rms).

A  $10$  mM solution of HgI<sub>2</sub> (Aldrich; 99.99%) dissolved in methanol (spectroscopic grade) was circulated through a high-pressure sapphire slit nozzle ( $0.3$ -mm slit size, Kyburz). This sapphire nozzle produced a thin and flat jet at the interaction region between laser and x-ray pulses. The jet speed was  $\gg 3$  m/s, and this condition provided a stable flow and replacement of the liquid between subsequent laser pulses at  $1$  kHz.



(/content/current)

Current Issue  
(/content/current)  
E-mail Alerts  
(/site/misc/PNASalerts.xhtml)  
Subscribe  
(/site/subscriptions/index.xhtml)  
RSS  
(/site/aboutpnas/rss.xhtml)

Published online before print June 13, 2006, doi:

10.1073/pnas.0601958103

PNAS (Proceedings of the National Academy of Sciences) June 20, 2006 vol. 103 no. 25 9410-9415

## Access

Abstract  
(/content/103/25/9410.abstract)

Full Text (HTML)  
(/content/103/25/9410.full)

Full Text (PDF)  
(/content/103/25/9410.full.pdf+html)

Full Text + SI (Combined PDF)  
(/content/103/25/9410.full.pdf+html?with-ds=yes)

Figures Only  
(/content/103/25/9410.figures-only)

Supporting Information

**MOST READ**      **MOST CITED**

1. Evolutionary changes of multiple visual pigment genes in the complete genome of Pacific bluefin tuna  
(/cgi/content/short/110/27/11061?rss=1&source=mfr)
2. Ribonucleotide reduction is a cytosolic process in mammalian cells independently of DNA damage  
(/cgi/content/short/105/46/17801?rss=1&source=mfr)
3. HSP72 protects against obesity-induced insulin resistance  
(/cgi/content/short/105/5/1739?rss=1&source=mfr)
4. War, space, and the evolution of Old World complex societies  
(/cgi/content/short/110/41/16384?rss=1&source=mfr)
5. Restoring the sense of touch

The laser and x-ray pulses were overlapped in a quasi-parallel geometry with an angle of 10° to achieve optimal spatial overlap. Considering dimensions of laser and x-ray pulses and liquid jet size, it is estimated that <1% of the excited volume is out of the x-ray probed volume at the time delay of 1 ms.

with a prosthetic hand  
through a brain interface  
([cgi/content/short/1221113110v1?](http://cgi/content/short/1221113110v1?rs=1&ssource=mfr)  
[rs=1&ssource=mfr](http://cgi/content/short/1221113110v1?rs=1&ssource=mfr))

**50 Most-Read Articles »**  
([reports/most-read](#))

**Data Treatment and Analysis.** The diffraction images at –200 ps, 100 ps, 300 ps, 1 ns, 3 ns, 10 ns, 30 ns, 50 ns, 300 ns, and 1 ms time delays were recorded and interleaved by a measurement at –3 ns. The –200-ps time point was used to check the timing to high resolution. After radial integration of the 2D images to 1D curves, the curves were averaged and scaled to the total scattering, elastic and inelastic, from one solution unit-cell molecule in the region  $6.84 \text{ \AA} \leq q \leq 6.99 \text{ \AA}^{-1}$  where the scattering is insensitive to structural changes (isosbestic region for putative transitions). Difference–diffraction curves ( $DS(q, t)$  [ $q = (4\pi/\lambda)\sin(2\theta/2)$ , where  $\lambda$  is the wavelength of the x-rays and  $\theta$  is the scattering angle;  $t$  is the time delay]) were generated by subtracting the reference data at –3 ns from the data at any other time delay (2). Scaled total diffraction raw images at the time delay of –3 ns and 1 ms are shown in Fig. 6A together with the corresponding difference diffraction image. In the Fig. 6B, 1D total scattering curves at –3 ns and 1 ms and the difference curve are also shown with experimental error bars. Experimental error bars at all time delays and  $q$  values were obtained through several experimental repetitions, and the shapes and amplitudes of  $DS(q, t)$  curves are almost the same within experimental error bars (3). We multiply  $DS(q, t)$  by the scattering vector,  $q$ , to magnify the intensity at higher  $q$ . The corresponding difference radial distribution function (RDF),  $rDS(r, t)$ , which provides radial electron density changes as a function of interatomic distance  $r$ , was obtained by sine-Fourier transforming the  $qDS(q, t)$  curves:

$$r\Delta S(r, t) = \frac{1}{2\pi^2} \int_0^\infty q\Delta S(q, t) \sin(qr) \exp(-q^2 a) dq$$

. [S1a]

where the constant  $a$  ( $a = 0.03 \text{ \AA}^2$ ) is a damping constant.

A separate control experiment was performed by using 267-nm excitation of pure methanol to explore effects of signal contributions due to the solvent excitation. In Fig. 7, the difference diffraction curves from pure methanol (black curves) at selected time delays (100 ps and 1 ms) are shown together with those from measurements of Hgl<sub>2</sub> in methanol solution (red curves). In the pure methanol measurement, 4 repetitions were averaged, whereas 35 repetitions were averaged in the Hgl<sub>2</sub> in methanol data. It is clearly shown that the difference diffraction signal from pure solvents is negligible compared with that from Hgl<sub>2</sub> solutions.

**Density Functional Theory (DFT) Calculation.** Structural information on the conformation of the solute molecules and their presumed photoproducts was calculated by DFT. All calculations were carried out by B3PW91 (4) DFT as implemented in the GAUSSIAN03 program package (5). In the DFT calculations, the Becke's three-parameter exchange functional (4) was used in conjunction with the Perdew and Wang's correlation functional (6) (PW91). Because Hg is a heavy element, we used the Stuttgart Relativistic Large Core (RLC) Effective Core Potential (ECP) (7) for the Hg atom to include relativistic effects. The all-electron basis set (8) with added  $d$  and  $f$  polarization functions and  $s$  and  $p$  diffuse functions was used for the I atom. The calculated bond distance of I<sub>2</sub> with this basis set is in perfect agreement with the experimental I<sub>2</sub> distance (9, 10). To describe the solvent effects, the Polarizable-Continuum Model (PCM) was used. Especially, we used the Integral Equation Formulation PCM (IEFPCM) method (11), which is a modified version of PCM. The structures were fully optimized in the solvent, and subsequent harmonic vibrational frequencies were calculated for the optimized structures.

**Molecular Dynamics (MD) Simulations.** The intermolecular correlations of the solute and photoproducts with the solvent was obtained by MD simulation using the program MOLDY (12). The so-called H1 methanol model (13) was used. For the MD simulation of the diffraction from the solute in its solvation cage, we used 1 solute (Hgl<sub>2</sub>, Hgl, Hgl-I(isomer), I, I<sub>2</sub>) surrounded by 512 methanol molecules in a cubic box of »25 Å. The structures of solute molecules and the charges on each atom were obtained from DFT calculations and kept constant during the simulation. All simulations were performed at ambient temperature (300 K) with a density of 0.790 g/cm<sup>3</sup>. The system was equilibrated at 300 K over 200 ps at constant temperature via coupling to a Nose–Hoover thermostat (14). The time step was 0.5 fs; the simulations were performed in the NVT ensemble, and the trajectories were followed up to 1 ns. The scattered intensity from each molecular configuration was calculated from the atom–atom distribution functions  $gab(r)$  by using our own programs and tabulated atomic form factors.

1. Wulff, M., Plech, A., Eybert, L., Randler, R., Schotte, F. & Anfinrud, P. A. (2003) *Faraday Discuss.* **122**, 13–26.

2. Plech, A., Wulff, M., Bratos, S., Mirloup, F., Vuilleumier, R., Schotte, F. & Anfinrud, P. A. (2004) *Phys. Rev. Lett* **92**, 125505.

3. Ihee, H., Lorenc, M., Kim, T. K., Kong, Q. Y., Cammarata, M., Lee, J. H., Bratos, S. & Wulff, M. (2005) *Science* **309**, 1223–1227.

4. Becke, A. D. (1993) *J. Chem. Phys.* **98**, 5648–5652.

5. Frisch, M. J., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Robb, M. A., Cheeseman, J. R., Montgomery, J. A. J., Vreven, T., Kudin, K. N., Burant, J. C., *et al.* (2003) GAUSSIAN03 (Gaussian, Pittsburgh), Revision A.1.
6. Perdew, J. P. (1991) *Electronic Structure of Solids* (Akademie, Berlin).
7. Kuechle, W., Dolg, M., Stoll, H. & Preuss, H. (1991) *Mol. Phys.* **74**, 1245–1250.
8. Glukhovtsev, M. N. & Pross, A. (1995) *J. Chem. Phys.* **103**, 1878–1885.
9. Kong, Q. Y., Kim, J., Lorenc, M., Kim, T. K., Ihee, H. & Wulff, M. (2005) *J. Phys. Chem. A* **109**, 10451–10458.
10. Plech, A., Randler, R., Wulff, M., Mirloup, F. & Vuilleumier, R. (2003) *J. Phys. Condens. Mat.* **15**, S137–S143.
11. Cancès, E., Mennucci, B. & Tomasi, J. (1997) *J. Chem. Phys.* **107**, 3032–3041.
12. Refson, K. (2000) *Comp. Phys. Comm.* **126**, 310–329.
13. Haughney, M., Ferrario, M. & McDonald, I. R. (1987) *J. Phys. Chem.* **91**, 4934–4940.
14. Hoover, W. (1985) *Phys. Rev. A* **31**, 1695–1697.