An x-ray probe of laser-aligned molecules

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We demonstrate a hard x-ray probe of laser-aligned small molecules. To align small molecules with optical lasers, high intensities at nonresonant wavelengths are necessary. We use 95 ps pulses focused to 40 μm from an 800 nm Ti:sapphire laser at a peak intensity of 10^{12} W/cm^2 to create an ensemble of aligned bromotrifluoromethane (CF_3Br) molecules. Linearly polarized, 120 ps x-ray pulses, focused to 10 μm, tuned to the Br 1s → σ^* pre-edge resonance at 13.476 keV, probe the ensemble of laser-aligned molecules. The demonstrated methodology has a variety of applications and can enable ultrafast imaging of laser-controlled molecular motions with Ångstrom-level resolution.

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Intense laser fields have greatly expanded our ability to control the behavior of isolated atoms and molecules. A nonresonant, linearly polarized laser field will align a molecule by interaction with the molecule’s anisotropic polarizability; the most polarizable axis within the molecule will align parallel to the laser polarization axis. Since the laser polarization direction is under simple control with a waveplate, so is the direction of the molecule’s most polarizable axis with respect to the laboratory frame. The polarizability interaction used to align molecules is identical to that used in optical trap studies of biomolecules, though the alignment aspect is not usually emphasized. Such experiments routinely use visible light probes and achieve nanometer-level resolution.

Here we demonstrate the use of 0.9 Å x-rays to probe a transient ensemble of laser-aligned molecules, thus, taking a step toward Ångstrom-level ultrafast imaging of molecular motions.

Laser control of molecular alignment enables control over x-ray processes. For instance, scattering from an ensemble of aligned molecules produces Bragg-like diffraction spots rather than the concentric rings observed in scattering from an isotropic gas. An important application is biomolecule structure determination with few x-ray processes. For CF_3Br, the Br 1s → σ^* pre-edge resonance is an excitation from the Br 1s orbital to an antibonding σ^* orbital containing substantial Br 4p_z character, where z refers to the C–Br axis. As a result of the molecular symmetry, x-ray absorption on the Br 1s → σ^* resonance occurs only when the x-ray polarization vector has a nonvanishing projection on the C–Br axis.

Two basic experiments demonstrate the x-ray probe of laser-aligned molecules. First, we show that resonant x-ray absorption changes reversibly in the presence of the laser field by measuring a laser/x-ray cross correlation. The ensemble is aligned only transiently and a theory including time dependence is required to describe the dynamics of molecular alignment. Second, we demonstrate control of x-ray absorption on the Br 1s → σ^* resonance by rotating the alignment of CF_3Br molecules with respect to the x-ray polarization axis. For each of these experiments, we compare with a theory developed to describe x-ray absorption of laser-aligned molecules.

Our experimental arrangement (Fig. 1) used microfocused x-rays to probe rotationally cooled CF_3Br in the presence of the linearly polarized aligning laser field. A λ/2 waveplate controlled ϑ_{LX}, the angle between the x-ray and laser polarization axes. Monochromatic, linearly polarized x-rays near 13.5 keV [bandwidth is 0.7 eV full width at half maximum (FWHM)] from an undulator source at Sector 7 of the Advanced Photon...
Source were focused to 10 µm (FWHM) and overlapped collinearly with the 40 µm (FWHM) aligning laser beam. Ti:sapphire oscillator pulses were stretched and amplified to produce alignment pulses (1.9 mJ, 95 ps FWHM) at a repetition rate of 1 kHz. The four dimensional overlap (temporal and spatial) was done with methods previously described.\textsuperscript{7} The signature of CF\textsubscript{3}Br x-ray absorption, Br K\textalpha~fluorescence at 11.9 keV, was viewed with Si drift detectors through molybdenum slits that limited the detection to the central 1.2 mm of the laser/x-ray overlap region. Spatial averaging over the crossing angle and viewed region yielded a peak laser intensity of \((0.85 \pm 0.09) \times 10^{12} \) W/cm\(^2\). CF\textsubscript{3}Br was rotationally cooled by expanding a mixture of 10% CF\textsubscript{3}Br/90% helium through pinhole nozzles of diameter \(d = 25\) or 50 µm at backing pressures up to \(P_0 = 9\) bar. The laser and x-ray beams intersected the supersonic expansion \(\sim 1\) mm downstream of the nozzle, where the number density of CF\textsubscript{3}Br was \(\sim 5 \times 10^{14} /\)cm\(^3\).

The x-ray absorption spectrum of CF\textsubscript{3}Br shown in Fig. 2 was obtained by collecting Br K\textalpha~fluorescence as a function of the incident x-ray energy. The Br 1s \(\rightarrow \sigma^*\) resonance at 13.476 keV is the prominent feature below the Br K-edge energy. The resonance was fit to a Lorentzian with \(\Gamma = 2.6\) eV and the Br K-edge plus Rydberg excitations were fit to an arctangent function.\textsuperscript{14} The arctangent function contributes a 10% background under the Br 1s \(\rightarrow \sigma^*\) resonance.

In the first experiment, we measured a laser/x-ray cross-correlation signal by tuning the x-ray energy to the Br 1s \(\rightarrow \sigma^*\) resonance and varying the laser/x-ray time delay \(\tau\). Figure 3(a) shows the cross-correlation signal, defined by the ratio of parallel \((\vartheta_{\text{LX}} = 0^\circ)\) to perpendicular \((\vartheta_{\text{LX}} = 90^\circ)\) x-ray absorption, as a function of laser/x-ray delay. The ratio was formed after subtracting the 10% background discussed above. The alignment evolves adiabatically—following the laser pulse envelope.

A Gaussian fit to the cross correlation signal yields a FWHM of 150 ± 14 ps and amplitude of 1.22 ± 0.03. We calculated for comparison with experiment the absorption cross sections for (1) parallel laser and x-ray polarizations, (2) perpendicular laser and x-ray polarizations, and (3) a laser-free thermal ensemble.\textsuperscript{15} In these calculations, the only adjustable parameters are the rotational temperature and the pulse length of the x-rays. The relevant molecular parameters, e.g., rotational constants, calculated by theory are in agreement with measured values. Comparison of the cross-correlation signal with theory yields an x-ray pulse length of 122 ± 18 ps, consistent with expectations.

The usual criterion for adiabatic molecular response is \(\tau_{\text{pulse}} \gg \tau_{\text{rot}}\), where \(\tau_{\text{pulse}}\) is the laser pulse duration and \(\tau_{\text{rot}}\) is the rotational period of the molecule.\textsuperscript{2} A 20 K thermal ensemble of CF\textsubscript{3}Br has an average rotational period of 28 ps, much less than our 95 ps laser pulse duration, thus, fulfilling the adiabatic criterion (the ground state rotational period of CF\textsubscript{3}Br is 235 ps for rotation about an axis perpendicular to the C–Br axis).\textsuperscript{15} The commonly used measure of molecular alignment is \((\cos^2 \theta)\), where \(\theta\) is the angle between the laser polarization and the molecular axis. For our experimental parameters, we calculated that the evolution of \((\cos^2 \theta)\) follows the laser pulse envelope, as shown in Fig. 3(b).

After optimizing temporal overlap at \(\tau = 0\), we demonstrated control of resonant x-ray absorption by varying the angle between the laser and x-ray polarizations, \(\vartheta_{\text{LX}}\) (Fig. 4). The quantity plotted on the ordinate is the ratio of the Br K\textalpha~fluorescence signal from the aligned sample (laser on) to the isotropic sample (laser off). A maximum occurs for the parallel configuration \(\vartheta_{\text{LX}} = 0^\circ\) and a minimum for the perpendicular configuration \(\vartheta_{\text{LX}} = 90^\circ\). This confirms the symmetry of the \(\sigma^*\) resonance with respect to the C–Br axis. To compare with experiment, we calculated the \(\vartheta_{\text{LX}}\) dependence of the laser-on/laser-off ratio at \(\tau = 0\), as shown in Fig. 4, where good agreement is found for a rotational temperature \(T_{\text{rot}} = 24 \pm 2\) K and x-ray pulse duration of 122 ps, determined from the cross-correlation measurement.

Significant improvement in the degree of alignment can be achieved with lower rotational temperature or higher...
edge resonances. These techniques have been used for molecules adsorbed on surfaces\textsuperscript{20} but they can now be extended generally to isolated molecules in the gas phase. They are more general than angle-resolved photoion yield spectroscopic methods\textsuperscript{21} which rely on ion dissociation and the axial recoil approximation. In addition, x-rays are ideal probes of laser-aligned molecules in the solution phase, where Coulomb explosion imaging techniques typically used in gas phase experiments\textsuperscript{22,23} are not applicable. An x-ray probe is also free from the complications of strong-field probes arising from complex ionization pathways.\textsuperscript{24} There also is an opportunity to use x-rays as a probe of laser-controlled rotations to achieve a better understanding of solvent dynamics.\textsuperscript{25} The penetrating power of x-rays in low-Z solvents, combined with the localized core-level absorption on the solute molecule, are both significant assets. The advent of tunable, polarized 1 ps x-rays at the Advanced Photon Source\textsuperscript{26} will enable tracking rotational dynamics in condensed phases as well as impulsively aligned molecules in the gas phase.

Finally, our work demonstrates column densities of aligned molecules that are sufficient for coherent diffraction imaging. We already have achieved an aligned molecule density of $\sim 5 \times 10^{14}$/cm$^3$, corresponding to $4 \times 10^5$ molecules within the laser/x-ray overlap volume. With this density, we estimate that less than 6 min is required to acquire a coherent diffraction image for the prototypical Br$_2$ with a total of $10^8$ events, assuming an elastic scattering cross section of 1.6 kb (obtained by summing the contributions of the individual atoms), $10^8$ x-rays/pulse/(10$\mu$m)$^2$ at a repetition rate of 1 kHz. At a 10% seeding fraction, the coexpanded He would provide only a $\sim 2\%$ background and dimer formation is expected to be $< 1\%$. Thus, this demonstration can be considered a first step toward Angstrom-level x-ray imaging of uncrystallized molecules.

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1 K. Yamanouchi, Science 295, 1659 (2001).
2 H. Stapelfeldt and T. Seideman, Rev. Mod. Phys. 75, 543 (2003).
3 B. Friedrich and D. Herschbach, Phys. Rev. Lett. 74, 4623 (1995).
4 A. Ashkin, Phys. Rev. Lett. 24, 156 (1970).
5 A. Ashkin, Appl. Phys. Lett 19, 283 (1971).
6 K. C. Neuman and S. M. Block, Rev. Sci. Instrum. 75, 2787 (2004).
7 R. Neutze, R. Wouts, D. van der Spoel, E. Weckert, and J. Hajdu, Nature 406, 752 (2000).
8 H. N. Chapman, A. Barty, M. J. Bogan, S. Boutet,
M. Frank, S. P. Hau-Riege, S. Marchesini, B. W. Woods, S. Bajt, W. Benner, R. A. London, E. Plönjes, M. Kuhlmann, R. Treusch, S. Düsterer, T. Tschentscher, J. R. Schneider, E. Spiller, T. Möller, C. Bostedt, M. Hoener, D. A. Shapiro, K. O. Hodgson, D. van der Spoel, F. Burmeister, M. Bergh, C. Caleman, G. Huldt, M. M. Seibert, F. R. N. C. Maia, R. W. Lee, A. Szöke, N. Timneanu, and J. Hajdu, Nat. Phys. 2, 839 (2006).

9 J. C. H. Spence and R. B. Doak, Phys. Rev. Lett. 92, 198102 (2004).

10 J. Stöhr, NEXAFS Spectroscopy (Springer, New York, 1996).

11 R. Torres, R. de Nalda, and J. P. Marangos, Phys. Rev. A 72, 023420 (2005).

12 C. Buth and R. Santra, Phys. Rev. A 77, 013413 (2008).

13 L. Young, D. A. Arms, E. M. Dufresne, R. W. Dunford, D. L. Ederer, C. Höhr, E. P. Kanter, B. Krässig, E. C. Landahl, E. R. Peterson, J. Rudati, R. Santra, and S. H. Southworth, Phys. Rev. Lett. 97, 083601 (2006).

14 B. K. Agrawal, X-ray Spectroscopy (Springer, Berlin Heidelberg, 1991).

15 A. P. Cox, G. Duxbury, J. A. Hardy, and Y. Kawashima, J. Chem. Soc., Faraday Trans. 2 76, 339 (1980).

16 V. Kumarappan, C. Z. Bisgaard, S. S. Viftrup, L. Holmegaard, and H. Stapelfeldt, J. Chem. Phys. 125, 194309 (2006).

17 J. Adachi, N. Kosugi, and A. Yagishita, J. Phys. B. 38, R127 (2005).

18 D. Pavičić, K. F. Lee, D. M. Raymer, P. B. Corkum, and D. M. Villeneuve, Phys. Rev. Lett. 98, 243001 (2007).

19 S. Ramakrishna and T. Seideman, Phys. Rev. Lett. 95, 113001 (2005).

20 M. Borland, Phys. Rev. ST Accel. Beams 8, 074001 (2005).