

Addendum to Proposal LB01

Femtosecond Chemical Dynamics: Imaging Chemistry in Space and Time

Experimental Team

Name	Institute	Role in the experiment
Peter M. Weber	Brown University	Principal Investigator
Jerome Hastings	SLAC/LCLS	Scattering specialist
Michael Minitti	SLAC/LCLS	Spokesperson; Specialist in ultrafast experiments, laser technology, data collection and analysis
James Budarz	Brown University	Sample cell construction, data collection and analysis
Joseph Robinson	SLAC/LCLS	Laser technology & optical/x-ray cross-correlation
Daniel Ratner	SLAC/LCLS	Computational expert, data collection and analysis
Adam Kirrander	University of Edinburgh	Theoretical & computational specialist in time-resolved dynamics and spectroscopy, data analysis
Anatoli Ischenko	Moscow State University	Gas-phase scattering analysis, data analysis

Addendum

The referenced proposal builds on our past studies, L560, to explore the imaging of chemical dynamics with ultrafast time resolution and atomic scale molecular structure resolution. It makes the case that it will be possible to create a molecular movie that reveals just how the molecular structure changes, in real time, as the molecule undergoes a chemical reaction.

In the review of a prior submission of this proposal two questions were raised: first, the referees wished to learn about the outcome of the L560 experiments; and secondly, they wanted to see computer simulations that support the notion that varying the relative angles of the pump laser polarization and the x-ray polarization will shed light on the molecule from different sides and provide complementary information that can be used advantageously to better image the chemical reaction. This addendum provides this information.

Analysis of L560 results

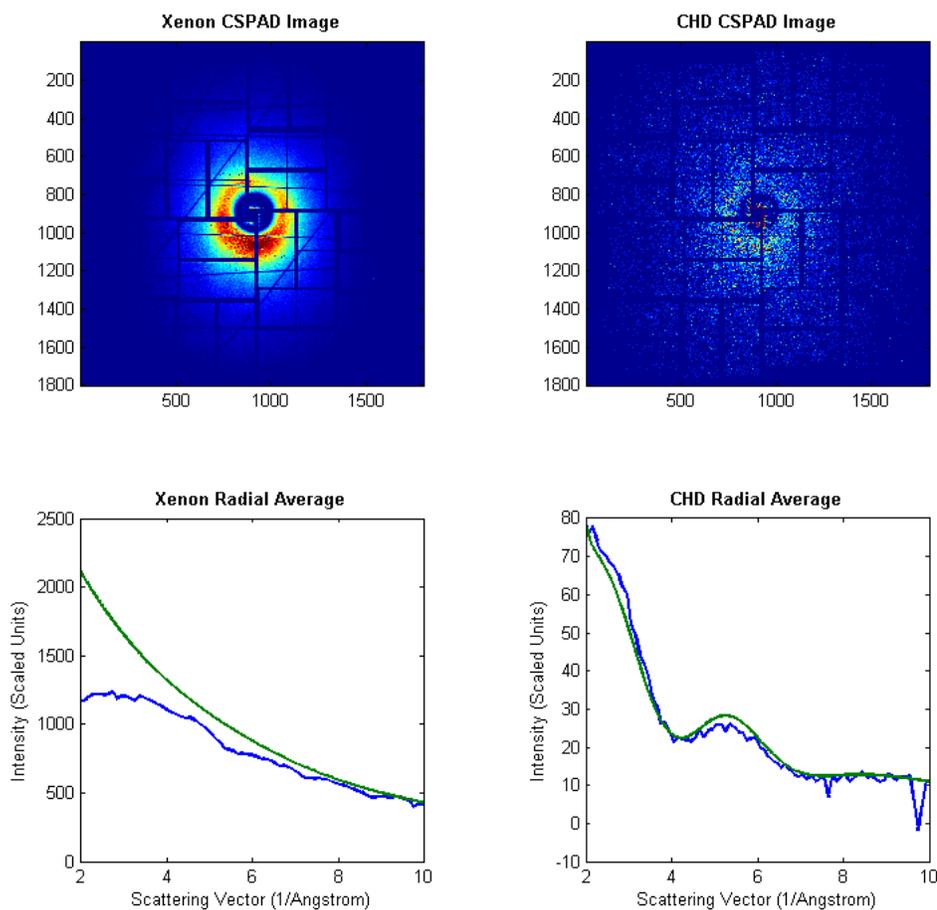
The ongoing analysis of the diffraction patterns from L560 (October 2012) has made much progress. The recovery of single-photon data from the diffraction pattern is fully functional, and all corrections have been made for the pedestal, the common mode, the pixel-specific gain, and the subtraction of background signal that is derived from vacuum images. We have implemented further corrections that take into consideration the spatial geometry of our apparatus, which results in an angle-dependent intensity instrument function correction. The latter is accomplished using data gathered from Xenon, which even in the gas phase provides a

large scattering signal and a correspondingly high signal-to-noise ratio. Additionally, the radial conversion of pixel position to scattering vector has been corrected using the exact, measured values of the pixel positions on the CSPAD. The result of this work, which to date has focused on a small subset of all the available data, is illustrated in Figure 1.

The left-hand-side of Figure 1 shows a diffraction image of Xenon, comprised of 6400 frames of data, top, and its associated radial distribution from 2\AA^{-1} to 10\AA^{-1} , bottom. The blue line is the experimental data while the green line is the theoretical diffraction curve. The two curves have been scaled by a factor to be on the same scale. It is apparent that the shape of the experimental curve is similar to, but somewhat different from the theoretical trace. This difference is because the path length of the x-rays in the sample cell depends on the scattering angle, a design feature of our cell that was carefully calculated to enable us to achieve a constant level of excitation of the molecules even though the laser beam is absorbed as it travels through the cell.

To calculate an instrument function we divide the theoretical xenon pattern from the experimental one, and use that to correct the data of cyclohexadiene. The resulting diffraction

Figure 1.



image, using only 1000 frames of CHD, is shown on the top right of Figure 1. Because the analysis using the Xenon calibration corrects for all the instrumental details, the so-corrected experimental diffraction pattern of CHD, blue curve in the bottom right panel, is wonderfully close to the theoretical CHD trace, green curve in the bottom right panel.

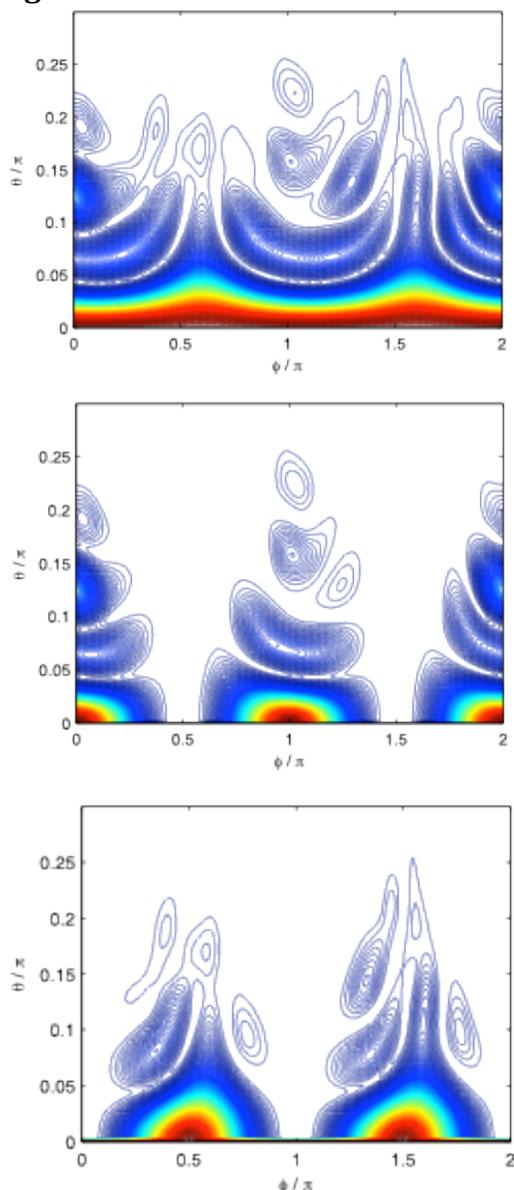
These results demonstrate clearly that we can measure high quality diffraction patterns of gaseous CHD with only 1000 shots. The signal to noise ratio (or better: modulation depth to noise) of that trace is about 10. Consequently, given that we have available for analysis several hundred thousands of shots, we should be well able to extract from this data set diffraction patterns with signal to noise ratios upward of 100. Given that our experiment excites 10% of the molecule to an excited state, this is easily sufficient to extract the pump probe signal. Work on the analysis of this large data set is continuing but will be complete (and the results published) before run 8. *From the discussion presented here, it is evident that the proposed experiments will work.*

Simulation of polarization dependent diffraction patterns

One important advantage of x-ray diffraction at LCLS compared to electron diffraction, which is conventionally used for gas phase systems, is that the x-rays are polarized. For isotropic samples, such as a gas where molecules are randomly oriented, this is of no consequence. In our experiments, however, the pump-laser excites preferentially those molecules that have their transition dipole moment aligned with the polarization of the laser radiation. The molecular excitation therefore induces an anisotropy, which persists longer than the duration of the chemical reaction we seek to study.

Figure 2 illustrates the effect, based on preliminary calculations by one of the members of our team (Kirrander). The three figures show the calculated diffraction pattern for our model CHD molecule, with a \cos^2 alignment by the excitation

Figure 2



pulse. The diffracted intensity is shown for the diffraction angles θ and ϕ on the Ewald sphere. The top figure illustrates the diffraction signal for an unpolarized x-ray beam; the result would be similar for an electron beam, except that electron diffraction is encumbered by the additional $1/s^4$ intensity scaling factor that poses significant additional demands on the signal to noise ratio.

The center and the bottom panels of Figure 2 show the scattering by a polarized x-ray pulse that is aligned parallel (center) or perpendicular (bottom) to the laser alignment pulse. Though the LCLS polarization is fixed, the same effect can be achieved by rotation of the polarization of the UV excitation pulse. For the molecules with an orientational distribution that aligns the molecular plane with the x-ray polarization, center, strong modulations in the direction of the polarization arise from interferences of the scattering wavelets originating at different atoms ($\phi = 0$ and π). When the molecules are oriented perpendicularly, bottom, the modulations are strongest at $\phi = \pi/2$ and $3\pi/2$.

The figures are for illustration purpose and assume that all of the molecules are excited by the laser, which of course in the experiment they are not. But by subtracting out the diffraction signal of the un-excited molecules, we should be able to recover images similar to those in Figure 2. It is quite apparent that by using the polarization of the x-ray and the laser beams to our advantage, additional information is obtained that will help us in analyzing the time-dependent molecular structures. *Thus, the computational simulations fully support the experimental plans outlined in our proposal.*