

**FD 171: Toward Structural Femtosecond Chemical Dynamics: Imaging Chemistry in Space and Time**

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## Toward Structural Femtosecond Chemical Dynamics: Imaging Chemistry in Space and Time

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### ABSTRACT

We aim to observe a chemical reaction in real time using gas-phase x-ray diffraction. In our initial experiment at the Linac Coherent Light Source (LCLS), we investigated the model system 1,3-cyclohexadiene (CHD) at very low gas pressures. This reaction serves as a benchmark for numerous transformations in organic synthesis and natural product biology. Excitation of CHD by an ultraviolet optical pulse initiates an electrocyclic reaction that transforms the closed ring system into the open-chain structure of 1,3,5-hexatriene. We describe technical points of the experimental method and present first results. We also outline an approach to analyze the data involving nonlinear least-square optimization routines that match the experimental observations with predicted diffraction patterns calculated from trajectories for nonadiabatic vibronic wave packets.

## Introduction

The exploration of molecular reactions in the ultrafast time regime is an evolving focal point of scientists with diverse and unique interests including physics, material science, biology and chemistry. The common goal of those investigations is to observe the motions of molecules during chemical reactions. The phrase '*molecular movie*' is frequently invoked, suggesting that one day it may be possible to prepare a movie that depicts molecular motions with ultrafast (femtosecond) time resolution and structural resolution on atomic distance scales. New x-ray free-electron laser (FEL) facilities, such as the LCLS<sup>1</sup>, are bringing this dream closer to reality.

Conventional ultrafast methods apply spectroscopic techniques to study chemical dynamics: spectra are taken of the molecule at well-defined times after a pump pulse initiates a reaction. The problem is that, at its core, spectroscopy measures the energies and populations of states, and an inversion of a vibrational or electronic spectrum to yield a molecular structure is difficult for molecules larger than just a few atoms. All reacting molecules are inherently very energetic, so that a multitude of vibrational states are excited on complicated potential energy surfaces, making vibrational spectra difficult, or indeed impossible, to assign. Finally, many chemically interesting molecules have large densities of states which, coupled with broadening on account of the short lifetimes of reaction intermediates, make the spectra fundamentally unresolvable (the 'statistical limit' scenario). In what might be the best current spectroscopic approach, we have recently developed photoionization via Rydberg states as a tool to observe structural dynamics<sup>2,3,4,5</sup>. In this approach, the vibrational energy content of the molecule does not adversely affect the spectrum, clean spectra can be observed even for large systems, and for most reactions, lifetime broadening is insignificant so that well-resolved spectra result<sup>6</sup>. Yet, while capable and informative, that technique falls short in one important way: it is not yet possible to invert the spectrum to determine the molecular structure. Consequently, the method remains a fingerprint tool rather than a structure determination tool.

Diffraction experiments are fundamentally different from spectroscopic measurements. The molecular structure can be derived from a diffraction pattern by using a back transformation<sup>7,8</sup>, or through a statistical analysis using a cumulant expansion<sup>9</sup>. Diffraction patterns are advantageous also because they measure only the atomic positions, a much smaller parameter space than, for example, the vibrational spectrum of a hot molecule. In principle, the structural dynamics observed by diffraction gives access to the molecular geometry as a function of time, including the spatial distributions of functional groups, steric hindrances, or spatial electrostatic charge distributions.

To observe the dynamics of chemical reactions, gaseous systems are ideal: the background of solvent molecules in a solution can obscure the observation of the chemical reaction and the effects of the solvent complicate the molecular dynamics. Gas phase diffraction methods have traditionally been limited to electron scattering because the scattering cross sections for electrons are many orders of magnitude larger than those for x-rays. However, with the new FELs, the tables have turned: while the scattering cross sections are smaller, the number of photons in a single x-ray pulse is many orders of magnitude larger than the number of electrons in an ultrashort electron pulse.

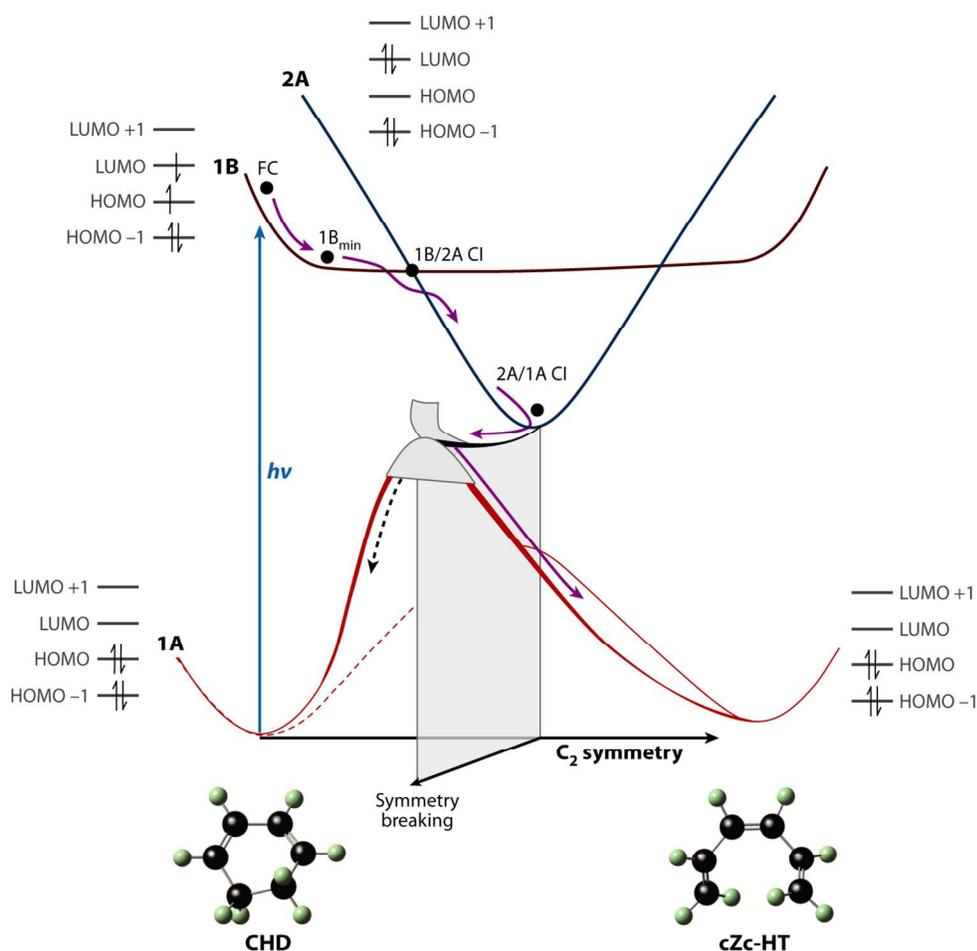


Figure 1. Ring-opening reaction of 1,3-cyclohexadiene (CHD). Upon excitation with a near UV pump photon (blue), the CHD molecule slides down the 1B surface, crosses to the 2A surface by avoiding a conical intersection that comes from above. Crossing to the ground state along a symmetry-breaking coordinate leads the molecule to the fully opened structure of hexatriene. (After Nenov et al.<sup>10</sup> reproduced with permission from Ref. 11).

We have focused our investigations on 1,3-cyclohexadiene (CHD), an important prototypical system that carries great relevance to synthetic organic chemistry and natural product synthesis<sup>12</sup>. For example, the synthesis of vitamin D involves a ring closing reaction that is the reverse of CHD's ring opening. Another advantage to using CHD to develop the ultrafast pump-probe x-ray diffraction method is that the photochemistry of CHD is quite well known, allowing us to calibrate our measurements against a large body of existing work.

We have recently reviewed our fairly extensive knowledge of CHD's photochemistry<sup>11</sup>. The picture shown in Fig. 1 is based on some 30 years of time-resolved studies: the optical pulse excites the molecule to the Franck-Condon region of the 1B state, from where the wave packet rapidly slides past a conical intersection and down the well of the 2A state. At that point (labeled 2A/1A CI in Figure 1), the conrotatory stereochemistry of the reaction is already decided. A symmetry-breaking displacement through the second conical

intersection brings the molecule back to the 1A ground state. In CHD, the geometry of the latter intersection causes the molecule to continue its downhill slide such that it ends up in the open structure, i.e. as 1,3,5-hexatriene. Cyclohexadiene is an attractive experimental system because it moves down this path in a ballistic fashion<sup>13</sup> and so 'structure' remains a well-defined and observable concept throughout the reaction.

The time scales of this reaction are such that the molecule crosses into the 2A surface within 55 fs and to the 1A surface after 84 fs<sup>14</sup>. Detailed calculations of the photochemical dynamics are challenging in a molecule the size of CHD, but from multiple computational studies, the nature of the surfaces is well established, and the motions of the wave packet have, at least in coordinate systems of reduced dimensionality, been carefully calculated (please see references in Ref. 11).

Yet there still remain unanswered questions and mysteries that the proposed studies aim to address. Specifically, as was pointed out by Deb and Weber<sup>11</sup>, the spectroscopic methods cannot affirm that they are, indeed, observing the dominant part of the wave packet: it might be that they show just a component that remains on the initially excited B state, while the dominant part of the wave packet undergoes the reaction through the 2A state. Clearly, a complementary view, such as that afforded by diffraction, is eminently desirable. In our experiments we aim to settle this question and to determine the molecular structures as the reaction proceeds.

### **Experimental setup, challenges and results**

The experimental concept is illustrated in Figure 2. The CHD molecules are isotropically distributed in the low-pressure gas. A linearly polarized ultraviolet laser pulse ( $\lambda=266-275$  nm, 65 fs, 4-18  $\mu$ J, 100  $\mu$ m FWHM focal spot) excites the CHD target molecule to the 1B state and thereby initiates the reaction. At a variable time delay from the optical pump, the x-ray pulse from LCLS (8.3 or 20.1 keV, 30-50 fs, 30  $\mu$ m FWHM focal spot) intersects the gas sample in a collinear geometry. Both the ultraviolet pump and LCLS probe pulses are aligned through a 250  $\mu$ m upstream alignment/differential-pumping aperture. X-rays scattered from CHD are projected onto a CSPAD detector<sup>15</sup>. Given the diffusion of the photo-generated 1,3,5-hexatriene through the 1,3-cyclohexadiene one is reasonably assured that fresh CHD molecules are observed by each pump and probe pulse pair. Even though molecules can be excited regardless of their rotational angle about the axis of the dipole moment, the pump pulse is expected to induce a limited alignment of the excited molecules along the laser polarization, with scattering of polarized x-rays into vertical and horizontal directions mapping different structural aspects of the molecules.

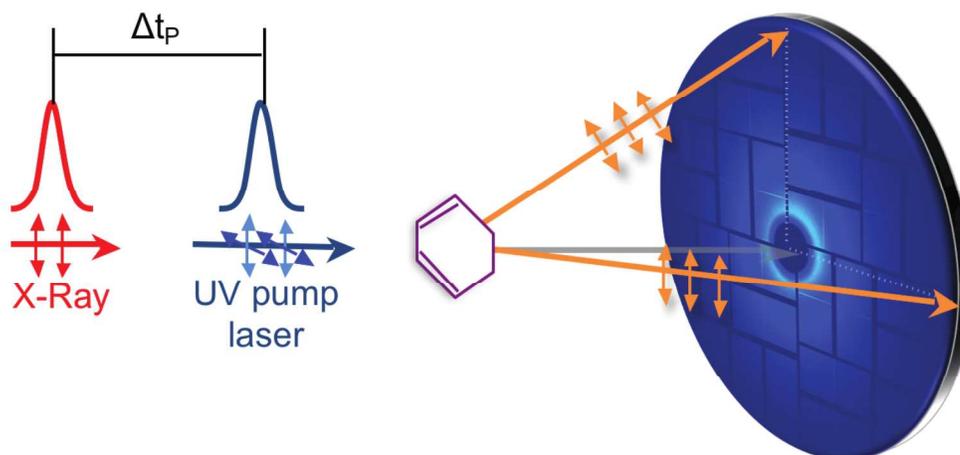


Figure 2. Schematic of the experiment. The target molecules are intercepted by a linearly polarized UV laser pulse (blue) and, after a fixed time delay ( $\Delta t_p$ ), by the polarized x-ray probe pulse (red). Absorption of the UV pump photon initiates the chemical reaction. The x-ray diffraction signal images the evolving reaction. Scattering of polarized x-rays into vertical and horizontal directions maps different structural aspects of the molecules that are partially aligned by the laser polarization. The diffraction pattern superimposed on the detector is from a dilute target of xenon gas recorded on the CSPAD.

For any diffraction experiment the structural resolution increases with the scattering vector,  $q$ , range measured. Given the wavelength of the LCLS fundamental at 8.3 keV (1.494 Å) and the third harmonic at 20.1 keV (0.617 Å), we positioned the CSPAD with an active area of 20 cm diameter at a 4 cm distance from the interaction region. This provides ranges of  $q = 1$  to 4.2 and 2 to 9 Å<sup>-1</sup>, respectively, for the two different x-ray energies.

The low density of the gas at pressures of only a few torr necessitates using a rather long interaction length of 13 mm. This requirement presents two challenges for the experiment. The first one is that the long interaction length reduces the achievable resolution in  $q$ -space because for any point on the detector, the different scattering points on the path of the x-rays through the gas span a range of scattering angles. To address this problem we positioned a beam block and inserted an aperture into the cell such that the low  $q$  regions of the detector only see the upstream part of the interaction path; the signal from downstream part of the interaction path is blocked by the beam block. Conversely, the high  $q$  regions of the detector only see the downstream part of the interaction path; signal from the upstream part is blocked by the aperture. With this approach, trajectory simulations show that the scattering signal can be measured with a resolution of about 0.2 Å<sup>-1</sup>, depending on the photon energy and the detector position. This approach enables use of a long interaction length while retaining an acceptable resolution, but requires consideration of the detector distance as a function of  $q$  during the analysis.

The second challenge arising from the long interaction length is in the absorption of the laser. CHD is a strong absorber, so that the UV laser is attenuated as it passes through the sample. This can be addressed by reducing the pressure of CHD and/or choosing a longer excitation laser wavelength. Additionally, we carefully designed the focal geometry such that the laser beam converges throughout the interaction region, reaching its focal point behind the observed region of the gas. At the centerline of the laser beam, where the x-ray

beam propagates, the increases as a result of the tighter focus is compensated by the decreases due absorption. We carefully balanced these two effects to maintain a reasonably uniform probability of excitation in the 10% range throughout the interaction length.

Given the complexity of the CSPAD and the intricate sample cell geometry, the scattering signal must be calibrated. To achieve this, we used xenon gas that provided a very large and uniform scattering signal. The comparison of the observed scattering intensity with the theoretically calculated signal provides an intensity correction factor that is applied to other gases to obtain a corrected scattering signal that can be compared to theory. Figure 3 shows the raw CHD signal on the CSPAD as well as the corrected radial diffraction signal for a 20.1 keV x-ray. The comparison to theory shows a satisfying agreement of the experimentally measured intensity with the theoretical pattern.

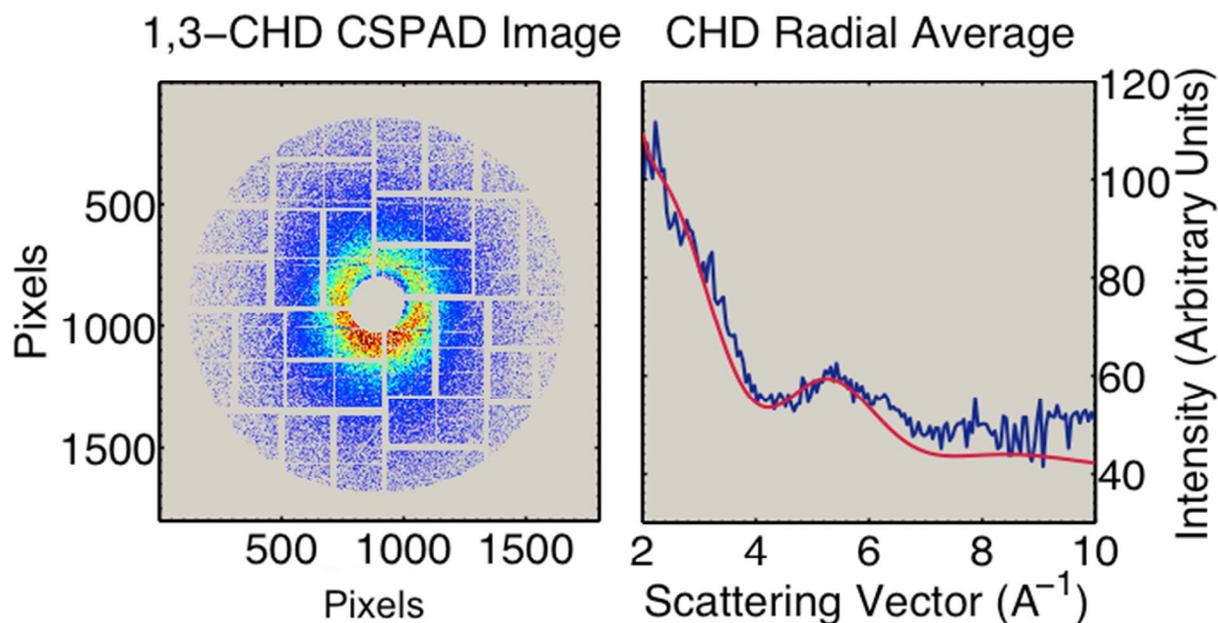


Figure 3. Experimental results for scattering from 1,3-cyclohexadiene. Left: A composite of 1000 frames reveal the signal as observed on the CSPAD detector. Right: After scaling using a separately measured pattern of xenon gas, the radial diffraction pattern of CHD is recovered. The green line shows a theoretical pattern of CHD. In this experiment, the x-ray photon energy was 20.1 keV.

Observation of pump-probe diffraction patterns places high demands on the signal to noise ratio of a measurement. First, it is important not to excite the target molecules too strongly because invariably, multi-photon absorption would lead to the preparation of the molecules on excited states higher than the target 1B, or cause ionization. This would make impossible an interpretation of the data in terms of chemical dynamics on specific potential energy surfaces. As a rule, therefore, we aim to excite no more than 10% of the target molecules to an excited state.

The diffraction pattern of a reacting molecule is not very different from that of a molecule in the ground state. In the example of the reaction of CHD to hexatriene, most carbon-carbon distances retain a distance typical of a conjugated double bond, while the carbon-

hydrogen distances change little and contribute less to the overall diffraction signal. The atom-atom distances across the ring change substantially, but their overall contribution to the signal is comparatively small because their separation is large. Between the small excitation probability and the small change in the molecular diffraction pattern, it is expected that the observed diffraction signal changes will be on the order of 1% of the overall signal as a function of  $q$ . Such a small change was beyond the reach of the experimental setup and signal shown in Fig. 3. However, only 1,000 shots were summed to provide that pattern and that it was taken with the third harmonic x-ray pulse, which has  $\sim 100$  times fewer photons per pulse compared with the x-ray fundamental.

In a repeat experiment, using the x-ray fundamental, it was possible to attain signal-to-noise ratios that captured extremely clear pump-probe signals. Figure 4 shows preliminary scattering signals at delay times of -2 ps and +2 ps, respectively. The difference signal, also shown in Fig. 4, is plotted as a percentage of the total signal as a function of the scattering vector. It is evident that the level of noise is on the level of 0.1%, which is expected to be adequate to perform time-resolved pump-probe experiments.

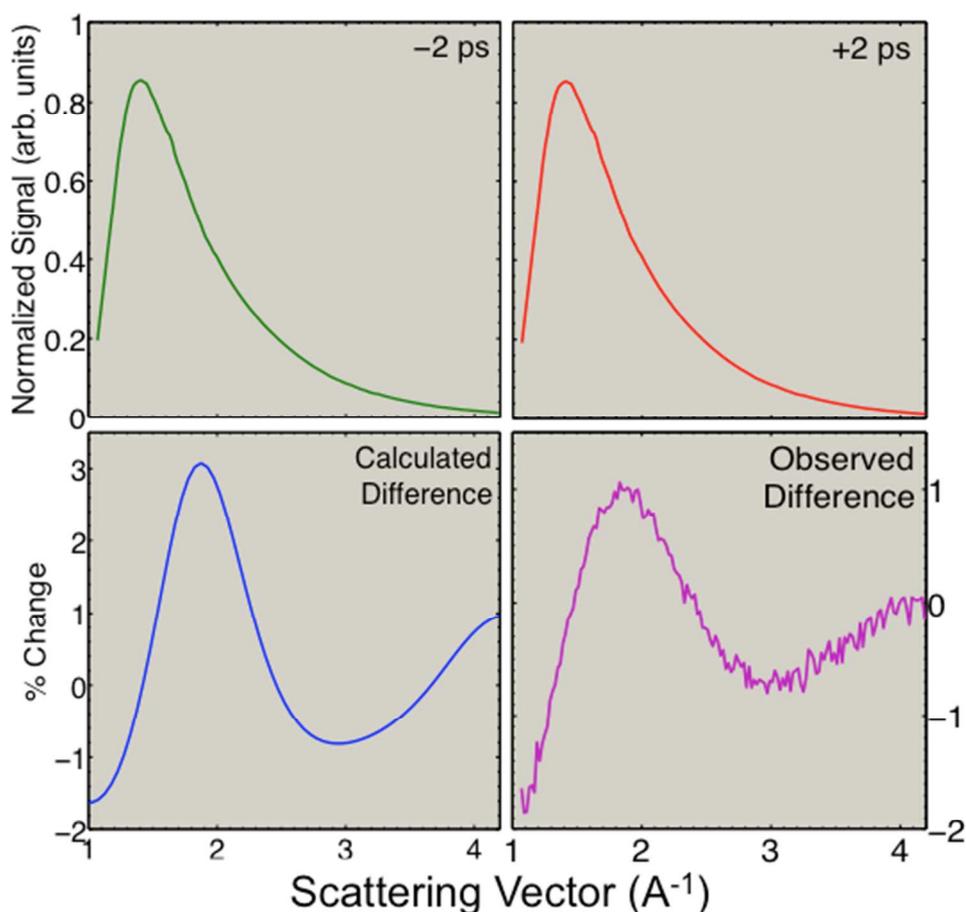


Figure 4. Preliminary CHD data showing the experimental diffraction signals with the laser pump pulse after the x-ray probe pulse (-2 ps), top left, the laser pump pulse ahead of the x-ray probe pulse (+2 ps), top right. The calculated difference signal at +100 fs pump-probe delay is displayed in the lower left while the experimentally observed difference signal at +2 ps is in the lower right. The difference signals are plotted as a percentage of the signals at each value of the scattering vector.

It is well known the ring opening reaction of CHD occurs on timescales far less than 100 fs and could result in several, non-equilibrium structures at this calculated small pump-probe delay time.<sup>11,14</sup> However, even with this, the non-equilibrium pattern calculated at short pump-probe delay time is in remarkable agreement to the observed equilibrium structure at long pump-probe timescales, showing the ultrafast progression of the electrocyclic ring-opening reaction in CHD.

### Theory and data analysis

The experimental, time-independent, x-ray scattering data shown in Fig. 3 is reasonably reproduced by a simple elastic x-ray scattering model with the observed signal proportional to the molecular form-factor  $f^0(\mathbf{q})$ ,

$$f^0(\mathbf{q}) = \langle \Psi_0 | \sum_{j=1}^N e^{i\mathbf{q}\cdot\mathbf{r}_j} | \Psi_0 \rangle = \int \rho_0^{(N)}(\mathbf{r}) e^{i\mathbf{q}\cdot\mathbf{r}} d\mathbf{r}, \quad (1)$$

where the momentum transfer vector,  $\mathbf{q} = \mathbf{k}_0 - \mathbf{k}$ , is defined as the difference between the incident and the scattered wave vectors, with  $|\mathbf{k}| = |\mathbf{k}_0|$  for elastic scattering, and where  $\Psi_0$  is the electronic wave function and  $\rho_0^{(N)}(\mathbf{r})$  the corresponding  $N$ -electron density. We therefore base our initial, zeroth-order, analysis of anticipated time-dependent ‘laser on’ – ‘laser off’ data,  $I_{exp}(t) = I_{UV}(t) - I_{noUV}(t)$ , on time-dependent form-factors,  $f^0(\mathbf{q}, t)$ , where the time-dependence mainly relates to changes in molecular geometry. Predictions of these geometry changes can be made on the basis of *ab initio* trajectories. Since the structural dynamics is underdetermined given the data available, the trajectories provide sufficient prior information to infer a parsimonious model.

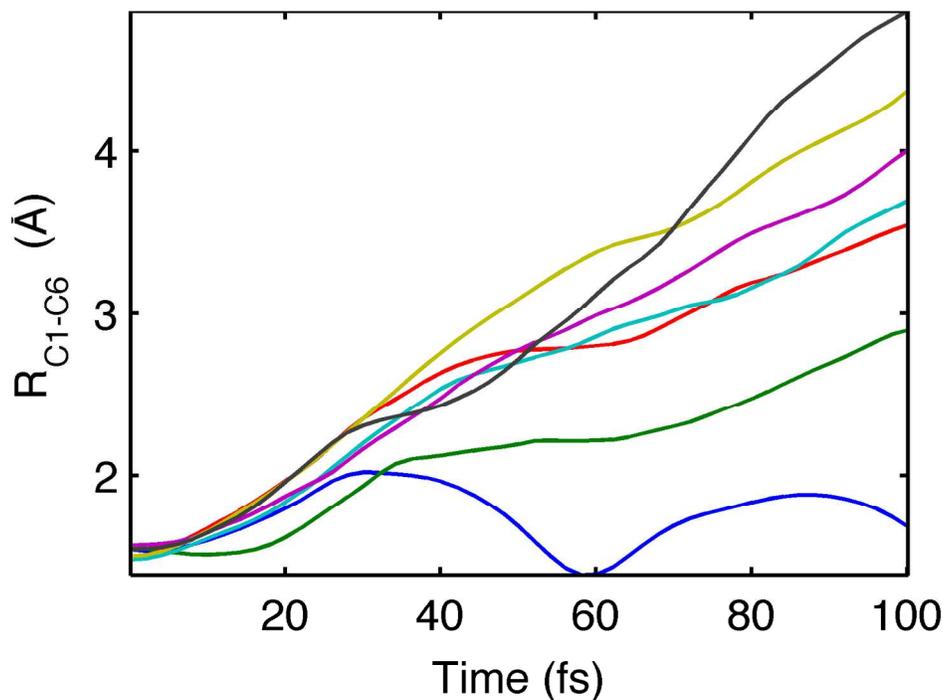


Figure 5. End-to-end (C1-C6) distances as a function of time for the CHD molecules in the Ehrenfest trajectories. Most trajectories lead to ring opening, but one of the trajectories shown returns to the ring-closed CHD structure.

We begin the discussion with the time-dependent trajectories. The photo-induced dynamics of CHD is simulated using *ab initio* Ehrenfest trajectories<sup>16</sup>. Each trajectory corresponds to a nonadiabatic wave packet,

$$|\Psi(\mathbf{R}, \mathbf{r}, t)\rangle = \left[ \sum_i a^{(i)}(t) |\phi^{(i)}(\mathbf{r}; \mathbf{R})\rangle \right] |\chi(\mathbf{R}, t)\rangle, \quad (2)$$

where  $a^{(i)}(t)$  are the complex Ehrenfest amplitudes that give the amplitude of the vibrational wave packet on each electronic state  $i$ , with  $|\phi^{(i)}(\mathbf{r}; \mathbf{R})\rangle$  the corresponding electronic wave function, and  $|\chi(\mathbf{R}, t)\rangle$  the vibrational coherent-state wave packet that propagates on the electronic potential energy surfaces,

$$|\chi(\mathbf{R}, t)\rangle = \left( \frac{\gamma}{\pi} \right)^{M/4} \exp \left( -\frac{\gamma}{2} (\mathbf{R} - \bar{\mathbf{Q}}(t))^2 + \frac{i}{\hbar} \bar{\mathbf{P}}(t) (\mathbf{R} - \bar{\mathbf{Q}}(t)) + \frac{i}{2\hbar} \bar{\mathbf{P}}(t) \bar{\mathbf{Q}}(t) \right), \quad (3)$$

where  $M = 3N_{at}$  in Cartesian coordinates with  $N_{at}$  the number of atoms. The Ehrenfest trajectory, given by phase-space coordinates  $(\bar{\mathbf{P}}(t), \bar{\mathbf{Q}}(t))$ , is generated by Hamilton's equations via semiclassical propagation on the quantum averaged molecular Hamiltonian. The amplitudes  $a^{(i)}$  are calculated from coupled differential equations with the nonadiabatic coupling vectors  $\delta^{(ij)} = \langle \phi^{(i)} | \nabla | \phi^{(j)} \rangle$ . The electronic structure calculations are performed using the *ab initio* package MOLPRO<sup>17</sup>, which supplies the adiabatic electronic states and the nonadiabatic couplings using 3SA-CAS(6,4)-SCF/cc-pVDZ level of theory. An important point is that these calculations are made *on-the-fly* for each trajectory, eschewing the cumbersome task of calculating global potential energy surfaces. A set of calculated Ehrenfest trajectories with initial conditions sampled in the Franck-Condon region are shown in Fig. 5, in terms of the end-to-end (C1-C6) distance in CHD as a function of time for each trajectory. The time-dependent electron density for each trajectory that is required by Eq. (1) can be calculated as

$$\rho^{(N)}(\mathbf{r}, t) = \int \left[ \sum_i |a^{(i)}|^2 \rho_i^{(N)}(\mathbf{r}, \mathbf{R}) \right] |\chi(\mathbf{R})|^2 d\mathbf{R}, \quad (4)$$

where, to first approximation, the density cross-terms between different configurations have been ignored. An even simpler approximation uses atomic form-factors at the nuclear coordinates  $\bar{\mathbf{Q}}(t)$  for each trajectory to calculate the scattering signal.

Figure 6 (a) shows a simulated '*experimental*' difference signal,  $I_{exp}(q, t)$ , as a function of time  $t$  and  $q$ , assuming rotational averaging. The calculated Ehrenfest trajectories  $\{I_{th}^{(i)}(q, t)\}$  are used to fit the experiment with the target function,

$$F(\mathbf{w}) = \left| \sum_{i=1}^{N_{traj}} w_i I_{th}^{(i)} - I_{exp} \right|^2, \quad (5)$$

where  $w_i$  are the weights to be optimized. In practice, it is often better to fit percentage changes in the signal rather than absolute intensities. The weights are calculated using a multi-start nonlinear least-square optimization routine using a trust-region-reflection algorithm with a finite-difference gradient. A best-fit theoretical signal,  $I_{opt}(q, t) = \sum w_i I_{th}^{(i)}$  is shown in Fig. 6 (b). The trajectories in Fig. 5 have been assigned different weights, and, in this instance, the synthetic data is best reproduced by the trajectory that ends with the largest C1-C6 distance at  $t=100$  fs, which receives more than 86% of the weight.

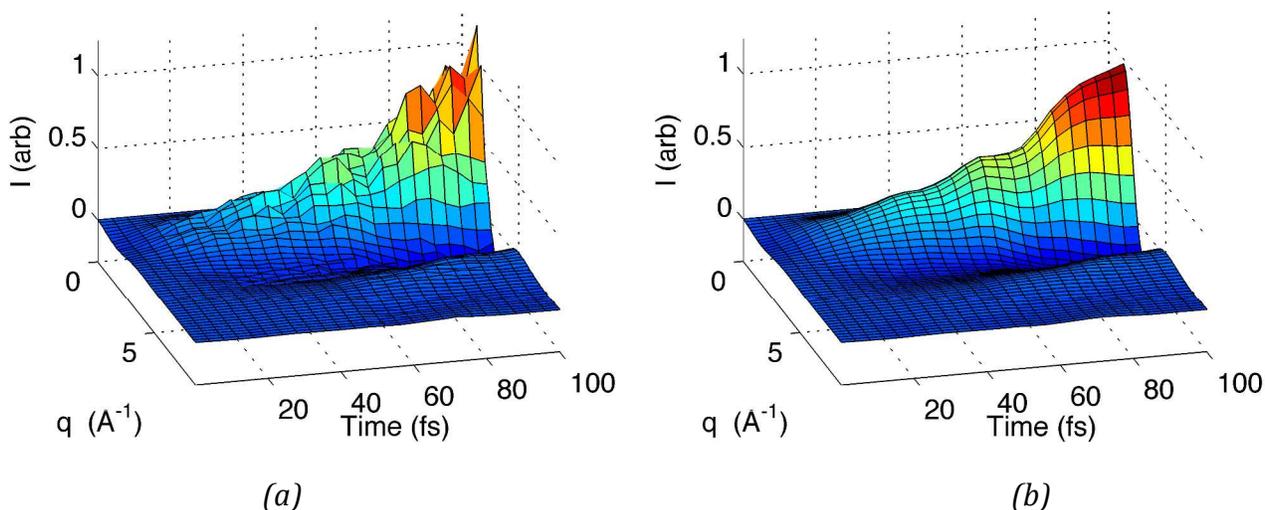


Figure 6. The intensity of the “laser on” – “laser off” difference signal,  $I_{UV} - I_{noUV}$ , shown as a function of time (fs) and  $q$  ( $\text{\AA}^{-1}$ ). a) The simulated experimental signal,  $I_{exp}(q,t)$ , b) The optimized signal from the Ehrenfest trajectories,  $I_{opt}(q,t)$ .

A simple check on the capability of the experimental data to order structures in a sensible time-sequence can be devised by matching the experimental signal to a small number of scattering responses,  $\{I_i(\mathbf{q})\}$ , each representing a molecular structure commensurate with the ring-opening reaction of CHD. The measured signal can be expressed as the weighted sum,  $I(\mathbf{q}, t) = \sum_i I_i(\mathbf{q}) p_i(t)$ , where  $p_i(t)$  is the population of species  $i$  at pump-probe delay time  $t$ . Our goal is to infer  $\mathbf{p}(t)$  from experiment for some small but representative set of  $\{I_i(\mathbf{q})\}$  to confirm that the species follow the same sequence as observed in the Ehrenfest trajectories. In our present example, shown in Fig. 7, the weights for three structures, corresponding to an early ring-closed structure, an intermediate structure, and a final ring-open structure, appear in correct order following optimization against the simulated,  $I_{exp}(q, t)$ , signal.

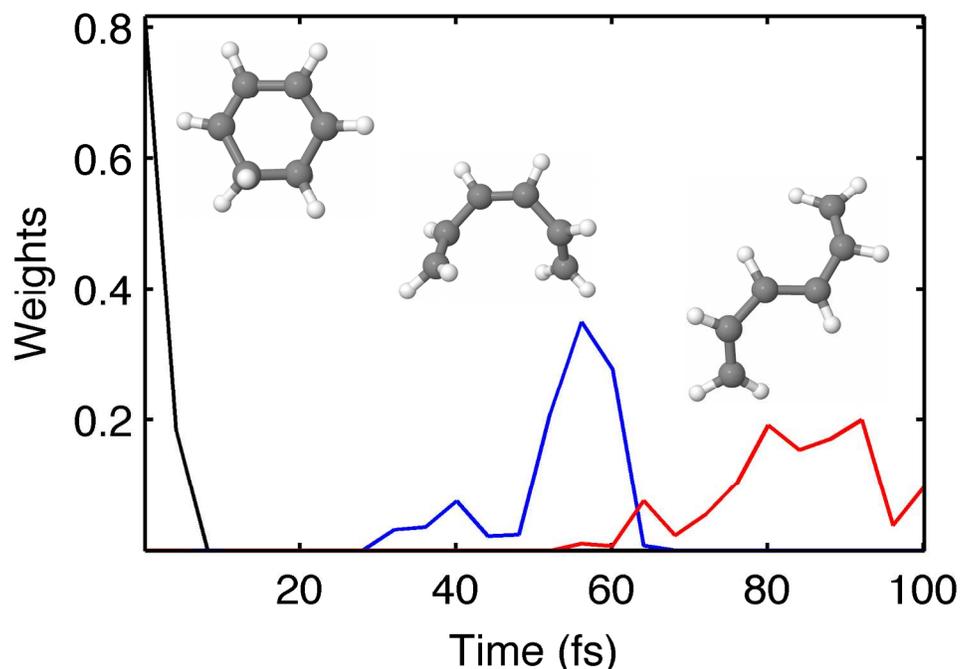


Figure 7. The weight as a function of time for three dominant structures when fitted against the simulated data shown in Fig. 6a.

## Conclusions

Time-resolved pump-probe diffraction experiments are important for the study of chemical reaction dynamics because they promise to provide uniquely useful views of the time-dependent molecular structures and because they yield a view of chemical dynamics that is complementary to traditional spectroscopic methods. Our investigations on 1,3-cyclohexadiene have proven the feasibility of the experiment when high intensity ultrafast pulsed x-ray sources such as LCLS are used. The experiment places high demands on the stability of the experiment and the data acquisition to recover the small changes in the diffraction patterns. Yet with a sufficiently careful setup, those demands can be met. Moreover, it is possible to compute the time dependent diffraction pattern of a wave packet that evolves on an excited electronic surface. Consideration of the electron density of the electronically excited molecule and the time-evolving vibrational wave packet should provide benchmarks against which to compare the experiment.

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## References

- <sup>1</sup> C. Bostedt *et al.*, Ultra-fast and ultra-intense x-ray sciences: first results from the Linac Coherent Light Source free-electron laser, *Journal of Physics B: Atomic, Molecular and Optical Physics* **46**, 164003 (2013).
- <sup>2</sup> J. L. Gosselin and P.M. Weber, *J. Phys. Chem. A*, **109**, pp 4899 – 4904 (2005).
- <sup>3</sup> M.P. Minitti and P.M. Weber, *Phys. Rev. Lett.*, **98**, 253004 (2007).
- <sup>4</sup> S. Deb, B. Bayes, M.P. Minitti and P.M. Weber, *A. J. Phys. Chem. A*, **115**, 1804 (2011).
- <sup>5</sup> S. Deb, M.P. Minitti, and P.M. Weber, *The Journal of Chemical Physics* **135**, 044319 (2011).
- <sup>6</sup> M.P. Minitti, J.D. Cardoza and P.M. Weber, *J. Phys. Chem. A*, **110**, 10212-10218 (2006).
- <sup>7</sup> L. S. Bartell, in *Stereochemical Applications of Gas-Phase Electron Diffraction*, edited by I. Hargittai and M. Hargittai, Verlag Chemie, New York, 1988, pp. 55–84.
- <sup>8</sup> R. A. Bonham, M. Fink, *High Energy Electron Scattering*, Van Nostrand Reinhold, New York, 1974.
- <sup>9</sup> Ischenko A.A., Schäfer L., Ewbank J.D., *J. Mol. Structure*, **376**, 157-171 (1996).
- <sup>10</sup> A. Nenov, P. Kölle, M. A. Robb, R. deVivie-Riedle, Beyond the van der Lugt/Oosterhoff model: when the conical intersection seam and the S<sub>1</sub> minimum energy path do not cross. *J. Org. Chem.* **75**, 123–129 (2010).
- <sup>11</sup> S. Deb and P. M. Weber, *Annu. Rev. Phys. Chem.* **62**:19–39 (2011).
- <sup>12</sup> Woodward R.B., Hoffmann R. 1970. *The Conservation of Orbital Symmetry* Weinheim: Verlag Chemie 177pp.
- <sup>13</sup> M. Garavelli, C.S. Page, P. Celani, M. Olivucci, W.E. Schmid, S.A. Trushin and W. Fuss, *J. Phys. Chem* **105**:4458 – 4469 (2001).
- <sup>14</sup> N. Kuthirummal, F. M. Rudakov, C. Evans, and P. M. Weber, *Spectroscopy and femtosecond dynamics of the ring-opening reaction of 1,3-cyclohexadiene*. *J. Chem. Phys.* **125**, 133307 (2006).
- <sup>15</sup> Hugh T. Philipp, Marianne Hromalik, Mark Tate, Lucas Koerner, Sol M. Gruner. *Pixel array detector for x-ray free electron laser experiments*. *Nucl. Instr. Meth. Phys Res. A.* **649**, 67-69 (2011).
- <sup>16</sup> K Saita, D. Shalashilin, *J. Chem. Phys.*, **137**, 22A506 (2012)
- <sup>17</sup> H.-J. Werner, P.J. Knowles, G. Knizia, F.R. Manby, M. Schütz, et al., MOLPRO V.2012.1, a package of *ab initio* programs.