Structural Dynamics in the Femtoseconds Domain: the 1,3-Cyclohexadiene Model System

Abstract

The ultrafast ring opening reaction of 1,3-cyclohexadiene (CHD, C₆H₈) is a prototypical electrocyclic reaction that serves as a model for numerous reactions in organic synthesis and natural products biology. While multiple investigations using pump-probe photoionization techniques have yielded a detailed understanding of the reaction, those measurements are all self-referential. Specifically, it is possible that they all capture the small part of the wave packet that remains in the initially excited 1B state, rather than the reacting component on the 2A surface.

We propose to use ultrafast x-ray pulses to derive a time resolved diffraction pattern of the ring opening reaction of CHD. The diffraction experiment is sensitive to the entire time-dependent electron density distribution, and thus images primarily the dominant component of the reacting wave packet. The experiment is designed to enforce or question our knowledge of the reaction of CHD, but more importantly, will open the x-ray diffraction methodology to the study of structural reaction dynamics of a wide variety of model systems.

Experimental team

<table>
<thead>
<tr>
<th>Name</th>
<th>Institute</th>
<th>Role in the experiment</th>
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<tbody>
<tr>
<td>Peter Weber</td>
<td>Brown University</td>
<td>Principal Investigator</td>
</tr>
<tr>
<td>James Budarz</td>
<td>Brown University</td>
<td>Data collection and analysis</td>
</tr>
<tr>
<td>Jerome Hastings</td>
<td>LCLS</td>
<td>Scattering specialist</td>
</tr>
<tr>
<td>Jan Feldkamp</td>
<td>LCLS</td>
<td>Scattering specialist, data collection, analysis</td>
</tr>
<tr>
<td>Michael Minitti</td>
<td>LCLS</td>
<td>Specialist in ultrafast gas phase experiments, laser technology</td>
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Scientific case

The investigation of molecular reactions with ultrafast time resolution is rapidly becoming a focal point of a community of scientists from backgrounds as diverse as chemistry, material science, physics and biology. The ultimate goal of those investigations is to observe the motions of molecules during chemical reactions, of biological systems while they perform their characteristic function, or of nanoscale objects while they fulfill their assigned tasks. The common objective is to watch these systems with ultrafast (femtosecond) time resolution, and simultaneously with a structural resolution on atomic distance scales. In short, we aspire to see movies of molecules in motion.

Conventional ultrafast methods use a spectroscopic approach to this problem: spectra are taken of the molecule at well-defined times after a pump pulse initiates a reaction. The problem with that approach is that all spectroscopic techniques primarily measure the energies and populations of energy levels. An inversion of a typical spectrum, for example a vibrational or electronic spectrum to yield a molecular structure is, for molecules larger than just a few atoms, virtually impossible: all reacting molecules are inherently very energetic, so that a multitude of
vibrational states are excited; potential energy surfaces are complex, so that spectra are difficult, indeed impossible, to assign; and broadening on account of the short lifetimes of reaction intermediates makes the spectra fundamentally unresolvable. In what might be the best current spectroscopic approach, we have recently developed photoionization via Rydberg states as a tool to observe structural dynamics. In this approach, the energy content of the molecules is of no consequence to the molecule, clean spectra can be observed even for large systems, and for most reactions, lifetime broadening is insignificant, resulting in well-resolved spectra. Yet while capable and productive, the technique lacks one important element: we cannot invert from the spectrum to the structure. Consequently, the method remains a fingerprint tool, rather than a structure determination tool.

Diffraction experiments are fundamentally different from spectroscopic measurements. A diffraction pattern is the Fourier transform of the molecular structure; to derive a structure from a pattern requires only a back transformation. Diffraction patterns are, at least in principle, advantageous also because fundamentally, only the molecular positions are measured, which is a much smaller parameter space than, for example, a vibrational spectrum of a hot molecule. Important also is that there is no Heisenberg uncertainty limit: atomic positions can be measured together with time, with impunity. In contrast, the spectral measurement of an energy level and its lifetime are constrained by $\Delta E \cdot \Delta t \geq \hbar/2$. Clearly, for studies at the frontiers of time, diffraction methods are favored. The aim of our research is therefore to perform ultrafast time-resolved x-ray diffraction measurements.

In the proposed study we wish to employ the XPP hard x-ray endstation at LCLS which has all the necessary hardware to study the ultrafast ring-opening of 1,3-cyclohexadiene. This particular molecule is an important prototypical system that carries great relevance to synthetic organic chemistry and natural product synthesis. The study of its photochemistry, which has been rewarded by important Nobel prices, has also led to insights into the chemical workings of biological systems. For example, the synthesis of vitamin A involves a ring closing reaction that is the reverse of CHD’s ring opening. Finally, the photochemistry of CHD is very well known, allowing us calibrate our measurements against a large body of existing work. Yet even so, questions and mysteries remain that the proposed studies aim to uncover.

In a recent review we have assembled a fairly complete summary of the state of our knowledge of CHD’s
photochemistry. Based on some 30 years of time-resolved studies, the picture shown in figure 1 emerges: optical excitation lifts the molecule to the Franck-Condon region of the 1B state. The wave packet rapidly slides past a conical intersection and down the well of the 2A state. At this point, 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 1,3-cyclohexadiene, the geometry of the latter intersection is such that the molecule continues its downhill slide such that it ends up in the open structure, i.e. as 1,3,5-hexatriene.

Remarkable agreement has been reached about the time scales of this reaction: the molecule crosses into the 2A surface within 55 fs, and to the 1A surface after 84 fs. From multiple computational studies, the nature of the surfaces is well established. The motions of the wave packet have, at least in coordinate systems of reduced dimensionality, been carefully calculated. (Please see references in ref. x)

So, what is there to do? Here is the rub: all the experiments where those time scales have been measured used some form of photoionization as a probe. Each interpretation of experimental data rests on previous interpretations. If any of them is wrong, then all are wrong. And wrong they could be: as pointed out in our review article, an alternate explanation for the experiments could be that they capture only a small fraction of the wave packet, namely the part that remains on the 1B surface. Imagine that as the wave packet reaches the first conical intersection, it splits into two components: one that stays on 1B, and one that reacts down the 2A surface. If the experiments are more sensitive toward the 1B part of wave packet (which is, in fact, quite likely), then we are not really watching the reaction on 2A, but rather the small part left behind on 1B. While based on consistent data sets, the story described above would not be correct.

To affirm either the correctness of our understanding, or to uncover that we are wrong, an entirely different experiment is needed. We propose to use femtoseconds duration x-ray pulses to measure the time resolved structure of 1,3-cyclohexadiene as it evolves down its reaction path. A diffraction experiment ‘sees’ all molecules, regardless of the electronic state it is in. Consequently, this experiment will measure the reaction path of the largest part of the wave packet. If the time constants we observe agree with those measured previously using ionization then our current understanding is correct. But, there is the possibility that we will uncover very different dynamics, which would then reflect the true motion of this enigmatic system.

Several points are worth making.

1. From both the experiments and the computations it appears that the molecules move down the path in a ballistic fashion. This means that the molecule speeds down the energy surfaces so quickly that the wave packet has no time to diffuse. Consequently, ‘structure’ is a well-defined concept: at any time during its reaction, the molecule has a tightly focused wave packet and thus a measurable structure. The diffraction experiment should be well suited to measure this structure. A ballistic wave packet also implies that Debye-Waller type thermal broadening will not be an issue and that well modulated diffraction patterns ought to be measured.

2. Exciting the molecule with a (polarized) laser pulse introduces an alignment for those molecules participating in the reaction. Conversely, those molecules remaining in the ground state have a ‘hole’ in certain alignments. This affects not only the angular component of the diffraction pattern, but also the radial part. Since the ground state structure is well known, and the alignment is a well-defined function of the laser polarization, thorough modeling can be
performed. We have shown on the (non-reactive) example of tetrazine (C$_2$N$_2$H$_4$) how this is to be done.$^{xii}$

3. The x-ray diffraction pattern is the Fourier transform of the electron density distribution. In the independent atom approximation, one envisions electrons to be spherically distributed about atom centers. Refined models consider electron density distributions, which are affected by electronic excitation.$^{xiii}$ In the case of CHD, the electron density distribution changes upon electronic excitation, and again as the molecule crosses into the 2A well. While for some systems, the effect on the scattering factors could be sizable, in CHD the effect is expected to be small since only one (or two) out of 44 electrons are affected.

The introduction of new ultrafast sources such as the one at LCLS have advanced the field of ultrafast molecular dynamics to a pivotal point. With the work on CHD we aim to show the superiority of diffraction methods over most spectroscopic techniques. Our team is well suited for this task as we have performed many of the leading time resolved molecular beam studies of CHD’s reaction dynamics, and because we have extensive experience with diffraction measurements$^{xiv,xv}$ and theory.$^{xvi,xvii,xviii}$ By combining the proposed x-ray studies with the laser ionization studies at Brown we will be uniquely positioned to evaluate their relative merits. It is our hypothesis that the x-ray results will be superior – but that needs to be proven. Yet if shown correct, then the door is open to study many other model reactions. Organic chemistry has myriad such reactions in store, and their study will provide a thorough understanding of the foundations of chemistry.

In summary, while many experiments draw an amazingly consistent picture of the electrocyclic ring opening of 1,3-cyclohexadiene, they are self-referential. (We feel we can say that, because to some extend, these are our own measurements). Specifically, we do not know if the ionization experiments probe the dominant part of the wave packet, or some small fraction that is left on the 1B surface. By applying the complementary diffraction methodology to the CHD system, we will be able to obtain a complete picture of the structural dynamics of this important model reaction.

**Experimental Procedure**

The first question is: can single shot x-ray patterns be collected from a gas phase sample. To answer this question, we scale the single shot electron diffraction experiment on CHD.$^{xv}$ In the table below we compare incident beam flux, molecular density, detector efficiency and cross section for both photons and electrons. Also listed is the ratio between photons and electrons for each quantity.

<table>
<thead>
<tr>
<th></th>
<th>Photons</th>
<th>Electrons</th>
<th>Ratio (photons/electrons)</th>
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</thead>
<tbody>
<tr>
<td><strong>Particles/pulse</strong></td>
<td>3x10$^9$ *</td>
<td>1x10$^3$</td>
<td>3x10$^6$</td>
</tr>
<tr>
<td><strong>Molecular density</strong></td>
<td>2x10$^{10}$ mol/cm$^3$</td>
<td>2x10$^{16}$ mol/cm$^3$</td>
<td>1x10$^4$</td>
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<tr>
<td><strong>Detector efficiency</strong></td>
<td>0.25</td>
<td>1</td>
<td>0.25</td>
</tr>
<tr>
<td><strong>Cross section</strong></td>
<td>1</td>
<td>1x10$^7$</td>
<td>1x10$^{-7}$</td>
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* The experiment is designed to cover the same range of momentum transfer as used in the electron diffraction experiment, $\sim$10Å$^{-1}$. This requires an x-ray photon energy of 19.7 keV which is obtained from the 3rd harmonic of 6.57 keV.
The flux listed above is based on 2 mJ in the fundamental and 1% of the 3rd harmonic. The ratio of the photon based experiment is then the product of the ratios from the table above, which is 75. The sample is enclosed in an Al₂O₃ tube and its absorption is accounted for in the above calculated values. Thus the x-ray photon experiment should easily be capable of measuring single shot diffraction patterns.

The figure below shows a schematic of the experiment. Note, the CS-PAD detector has a central hole to permit the incident beam to pass and can be placed such that a scattering angle of 60 degrees can be measured.

The sample container is a single crystal Al₂O₃ tube with a nominal diameter of 2 mm and 0.375 mm walls. This has a transmission of 5x10⁻⁸ for the x-ray fundamental and 0.5 for the 3rd harmonic that will be used for the scattering experiment. It is also transparent to the tripled Ti:saph pump laser beam. The laser beam will be focused to 100 microns and the x-ray beam to less than 20 microns to ensure that the x-ray probes the maximum number of excited molecules. We request 5 shifts for the experiment. This will permit sufficient time for set-up including alignment of the x-ray beam obtaining spatial and temporal overlap and data collection as a function of delay, gas pressure and laser fluence.

References


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