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Ultrafast Diffraction Imaging of the Electrocyclic Ring-Opening Reaction of 1,3-Cyclohexadiene

Ray C. Dudek and Peter M. Weber*

Department of Chemistry, Brown University, Providence, Rhode Island 02912

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Changes in electron diffraction patterns are observed on ultrashort time scales upon irradiation of 1,3-cyclohexadiene with femtosecond laser pulses. 1,3- Cyclohexadiene is known to experience a ring opening reaction to hexatriene upon excitation to the $^1B_2$ electronic state. Internal conversion brings the molecule to a saddle point, from where one pathway leads back to cyclohexadiene, while another path generates 1,3,5-hexatriene in one of its isomeric forms. Structural observations are made at picosecond time delays using an ultrashort electron pulse that is diffracted off the nascent product molecules. The diffraction images illustrate that structural observations of prototypical organic reactions can be made in real time, opening a new methodology to study chemical reaction dynamics.

Molecular spectroscopy with femtosecond or picosecond time resolution has become tremendously successful in exploring energy relaxation processes and chemical reactions in real time. It is now possible to obtain spectra of molecules just as they cross a transition state during a chemical reaction.[1] Such spectroscopic studies have led to enormous insights about the flow of energy within and between molecules, allowing detailed inferences about the mechanisms of the reactions.

Nonetheless, time-resolved spectroscopy is burdened by fundamental constraints. Most mechanistic chemistry is based on structural models, whereas spectroscopy reveals energy levels. Synthetic chemists describe reactions as transformations of molecular structures, with reaction channels that are determined by spatial distributions of functional groups, steric hindrances, or spatial electrostatic charge distributions. In contrast, spectroscopy can measure only energy levels and populations of molecules in energy levels. Thus, time-resolved spectroscopy, however useful, shows only the time dependence of energy level populations.

Energy levels and structures are of course connected via potential energy surfaces and quantum mechanics. However, this link is conceptually difficult, and tremendous computational resources must applied to understand even simple chemical reactions from a quantum mechanical perspective. It therefore has been a long-standing goal of experimental physical chemists to observe time-dependent structures of molecules during chemical reactions. Such structural observations carry the promise of a much more direct connection to mechanistic organic chemistry. We report here the investigation of a prototypical organic reaction by time-resolved electron diffraction.

The concept of probing time dependent molecular structures by diffraction has been well documented.[2] Provided one succeeds in generating short bursts of electrons or X-rays, both electron diffraction[3−37] and X-ray diffraction[38−49] can be adapted to the time domain. Indeed, developments of the recent past have shown that it is possible to generate pulses of even subpicosecond duration of both X-rays[49−51] and electrons.[29]

In time-domain diffraction experiments a short laser pulse initiates a change in a molecular structure. The electron or X-ray pulse arrives with a small time delay at the sample, from which it is diffracted. The diffraction pattern reveals the molecular

structure at the time when the electron or X-ray pulse interacts with the sample. By adjusting the delay time between the laser pulse that induces the structural change and the pulse that probes the structure, one may obtain stroboscopic snapshots showing the structural rearrangements of the molecular sample as a function of time. The time resolution of such experiments is largely limited by the duration of the electron or X-ray pulse.

One of the main obstacles of pump−probe diffraction experiments arises from the fact that not only molecules that are excited by the laser but also molecules that remain in the ground state contribute to the diffraction patterns. Even in conventional electron diffraction, the molecular contributions to the diffraction pattern are only a small fraction of the total signal. In pump−probe diffraction experiments, the additional scattering from unexcited molecules makes this fraction even smaller. Moreover, it is generally important to keep the pump pulse energy small so as to minimize multiphoton processes that could ionize the molecule or trigger competing reactions. Thus, the effect that the exciting laser pulse has on the overall diffraction pattern is by necessity small, so that measurements of pump−probe diffraction patterns pose a tremendous challenge to the signal-to-noise ratio of an experiment.

Systems studied to date have been carefully selected to maximize any observable signal. In condensed phases, relaxation dynamics of crystal lattice structures[47] and the propagation of strain waves[49] have been observed by time-resolved X-ray scattering. In the gas phase, pump−probe electron diffraction has been applied to observe the photodissociation of a heavy atom from small molecules.[25,29] Heavy atoms help the diffraction experiments because their atomic scattering factors are large, resulting in large scattering signals.

The success of those experiments points to the tremendous potential of pump−probe diffraction techniques in exploring chemical reaction dynamics. However, given the experimental constraints, the molecular systems have been chosen for experimental feasibility, rather than interest in an inherently important chemical reaction. The application of pump−probe diffraction to important chemical reactions therefore remains an outstanding challenge.

In our laboratory, we have developed a pump−probe diffractometer with improved performance. This instrument allows us to investigate time-resolved structural dynamics of common organic substances, without the need of heavy atom substitutions. We applied this instrument to study the ring-opening reaction of 1,3-cyclohexadiene (CHD) to form hexatriene (HT), a prototypical electrocyclic reaction that features prominently in organic chemistry. Our experiments demonstrate that pump−probe diffraction experiments can successfully explore a large class of photochemical reactions, opening up new venues for mechanistic studies of chemical reaction dynamics.

The time domain electron diffractometer is based on a regeneratively amplified, femtosecond pulsed, titanium−sapphire laser. A second harmonic of this laser output, at 398 nm, is used to generate a pulsed electron beam by photoemission of electrons from a copper photocathode. The new and unique feature of this instrument is that it operates at a repetition rate of 50 kHz, which is 10 to 1000 times higher than the repetition rates of most regeneratively amplified laser systems. The advantage of the pump−probe electron diffraction experiment is that moderately high time-averaged electron beam currents can be maintained, as are needed for diffraction studies, while keeping the number of electrons per pulse small. Small numbers of electrons per pulse are required in order to minimize space−charge interactions between electrons within a pulse. Typical

electron currents at the intersection with the molecular sample are 20 pA. The average pulse therefore contains 2500 electrons. As has been shown by Williamson et al.,[29] this electron count borders the onset of space−charge effects that cause spatial and temporal broadening of the electron pulses.

In the experiment, 1,3-cyclohexadiene at a pressure of 80 Torr bleeds into the vacuum system through a 50 μm pinhole. The gas is intersected by both the pulsed electron beam and a pump laser beam. The pump laser beam is derived from the same laser that generates the electron beam. For the pump light we use the third harmonic output at 265 nm, which typically has pulse durations of 200 fs and pulse energies of 300 nJ. Both the electron beam and the pump laser beam are focused to spot sizes of about 30 μm. At the focus, the peak laser intensity is estimated to be about 2×10^{11} W/cm^2. We expect one-photon absorption processes to dominate, even though two-photon ionization and absorptions to superexcited molecular states[52] may occur. The time delay between the electron and the laser pulses is adjusted by a variable delay line. The diffraction pattern is projected on a scintillator and imaged with a lens system onto a 512 × 512 pixel, liquid nitrogen cooled CCD chip. Exposure times of 2 min produce high-quality diffraction images.

The intensity of the electron diffraction signal as a function of the absolute value of the momentum transfer vector s is often described as a sum of an atomic scattering term, $I_a(s)$, and a molecular scattering term, $I_m(s)$:[53]

$$I(s) = I_a(s) + I_m(s) \tag{1}$$

It is the molecular term that contains the structural information, because it consists of a sum of terms containing Bessel functions: one from each atom−atom distance. In traditional diffraction experiments, an empirical, rapidly decaying function, chosen to approximate $I_a(s)$, is subtracted from the total signal $I(s)$ to reveal the oscillatory ring structure, $I_m(s)$. Upon Fourier transformation, one obtains the distances between atoms. This procedure is somewhat open to ambiguity, as the empirical function for $I_a(s)$ is chosen to produce good structures, rather than structures obtained independently from the experiment.

In pump−probe diffraction experiments, we take the difference between a diffraction−pattern with the pump laser on and a diffraction pattern with the pump laser off. To the extent that the atomic scattering factors do not change upon electronic excitation, an assumption that we discuss below, the difference pattern is free of any contribution from the atomic scattering factors. Similarly, atom−atom distances that do not change during the course of the reaction lead to identical contributions to $I_m(s)$ and therefore subtract out when taking the difference between pump-laser-on and pump-laser-off patterns. Thus, the difference patterns selectively show those diffraction rings that arise from a photoinduced change in the molecular structure.

Two effects contribute to changes in the molecular scattering observed in the difference patterns. First, one observes new atom−atom distances that are generated by the structural rearrangement. This is the component of the signal that can be analyzed to give the time dependent structural dynamics. Second, one observes the depletion of atom−atom distances from reactant molecules that are eliminated by the photochemical reaction. This contribution is superimposed with the first, and the pump−probe diffraction experiment will always show both. To account for this effect, the structure of the reactant molecule either must be known or analyzed as part of the experiment.
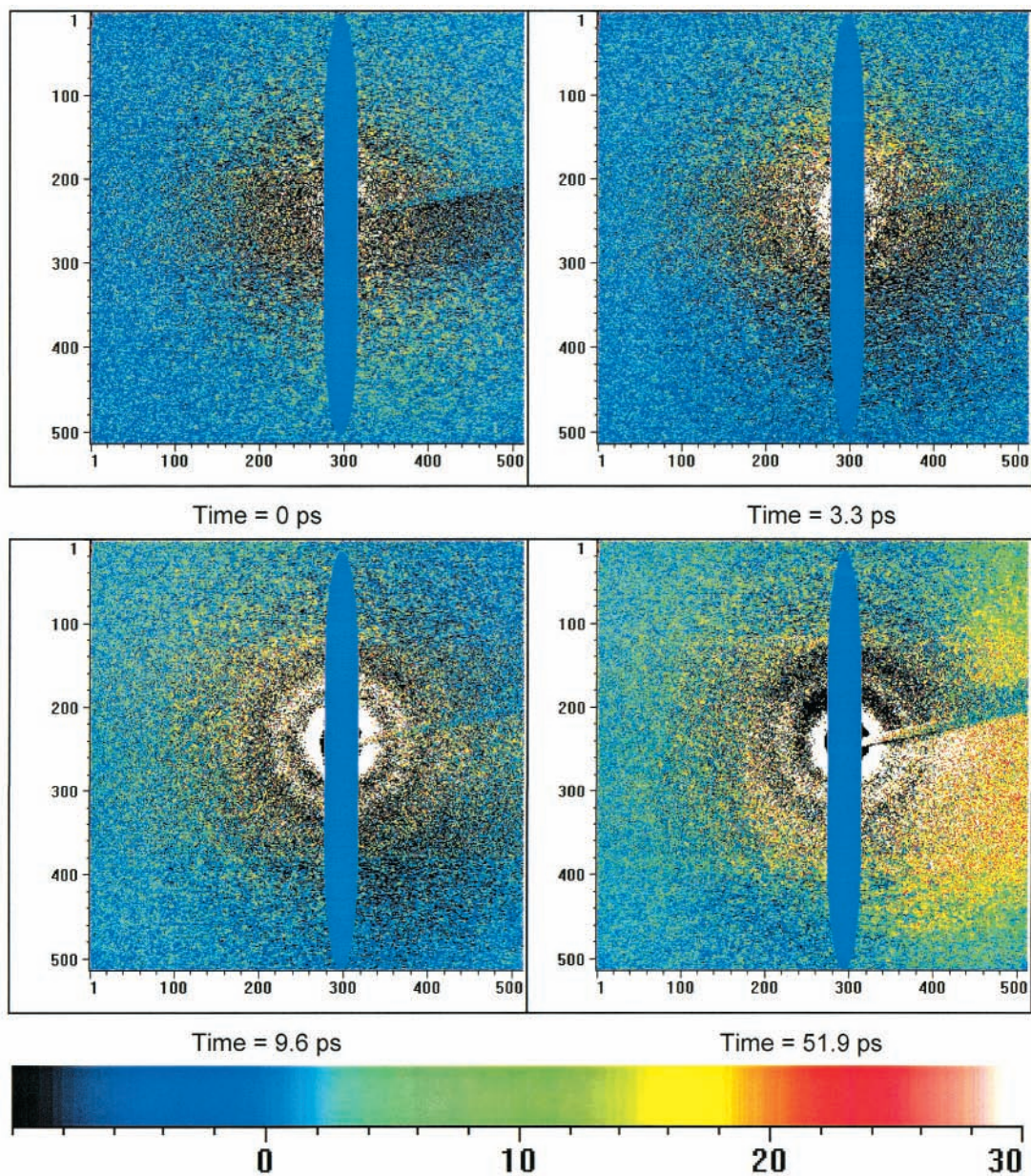
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Figure 1. Time sequence of electron diffraction difference images (pump laser on minus pump laser off). The intensity of the difference signal is given by the color scale at the bottom of the figure.

Figure 1 shows several snapshots out of a time sequence of difference patterns of 1,3-cyclohexadiene, taken at different delay times between the pump laser and the electron pulse that probes the molecular structure. In this sequence, time zero is set to the first panel. Each image represents the difference between an image with the pump laser on and one with the pump laser off. As can be seen, when the timing of the pulses is such that the electron pulse hits the sample simultaneously or just before the laser pulse, the difference shows no signal (0 ps panel). However, when the timing of the pump laser pulse is adjusted to arrive before the electron pulse (panels labeled as 3.3, 9.6, and 51.9 ps), the electron pulse interacts with molecules that were pumped to the excited state. Molecules in those frames participate in the electrocyclic ring opening reaction. The resulting change in the atom−atom distances gives rise to distinct rings in the pump−probe diffraction images taken at longer delay times. It is important to emphasize that only the changes in the atom−atom distances are seen in the difference patterns. More diffraction rings are visible in the individual images, arising from all of the interatomic distances

present in the molecule; however, most of those rings subtract out when taking difference patterns.

The intensity of the total diffraction signal is very large at small diffraction angles but falls off very rapidly. As a result, the central part of the image saturates the CCD detector. This part is blocked off in the diffraction patterns displayed here. In some of the frames, the shadow of a small needle that acts as a Faraday cup to block the electron beam is apparent. Some electrons can scatter off that needle, giving rise to an elevated background, for example in the 51.9 ps panel at the lower right side.

The signal at small diffraction angles in the individual images is on the order of 20 000 counts per pixel. Taking the difference between the pump laser on and pump laser off images removes almost that entire signal, revealing the difference pattern with oscillations on a scale of tens of counts. The noise from the individual images is also in that range. As a result, the noise at small diffraction angles is large compared to the intensity of the oscillatory ring structures. This gives rise to a granular, black and white appearance of the central regions of the difference
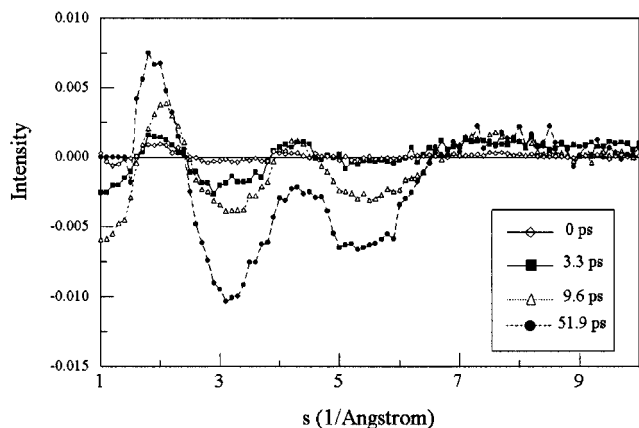
Figure 2. Radial averages of electron diffraction difference images divided by the ground state (pump laser off) diffraction signal.

images. However, most of that noise is removed when taking averages over pixels at the same distance from the central electron beam. Figure 2 shows the radial averages of the patterns in Figure 1. Plotted is the intensity of the difference pattern, divided by the intensity of the diffraction pattern of CHD without pump laser, as a function of the absolute value of the scattering vector, s. In generating this plot, we eliminated the regions of the image where the detector was saturated. The modulations from atom−atom distances that change in the course of the photochemical reaction are clearly visible, and can be measured with good signal-to-noise ratio.

The objective of a comprehensive analysis of the pump−probe diffraction patterns is to elucidate the products of the reaction, the branching ratios between reaction channels, and the time scales for individual dynamical processes. Such a full analysis of the pump−probe diffraction patterns is a complicated task, as there are many factors that deserve careful consideration. In the following we will outline the issues that need to be addressed, while reserving the complete analysis of the presented data for a later publication.

(1) The analysis of the diffraction patterns must consider at least four distinct product structures. In the condensed phase, three different hexatriene structures have been observed on the time scale of our experiment.[54,55] The three isomeric forms arise from rotations about carbon−carbon axes: the cis, cis form; the cis, trans form; and the trans, trans form. In addition, cyclohexadiene generated in a back-reaction must be considered a separate product, because of its high vibrational energy content. The diffraction patterns of the four structures are quite similar, because many intermolecular distances are the same.[56] Careful analysis of the data and accurate models of the intermediate hexatriene structures are needed to fully examine the kinetics involved in the ring opening process.

(2) The pump laser excites the molecule with a photon energy of about 4.7 eV. During the relaxation to the ground-state surface, electronic energy is converted to vibrational energy. The amount of vibrational energy of a product molecule depends on its enthalpy as compared to the enthalpy of the cyclohexadiene in its ground state. For those molecules that undergo a back reaction to cyclohexadiene, the vibrational energy is 4.7 eV. For the hexatriene products, the vibrational energy is 4.7 eV minus the reaction enthalpy.

Vibrational excitation may have a profound impact on molecular diffraction patterns.[53] Assuming that the energy is evenly distributed over all vibrations, Pullen et al. estimate the vibrational temperature to be 2270 K for CHD, and 2025 K for the hexatrienes, for excitation at 270 nm.[55] In simulating the

diffraction images of the product molecules, this vibrational excitation must be included. Standard models can be applied for that purpose,[53] even though one questions if within the picosecond time scale of our observation that the energy is indeed completely distributed over all vibrational modes.

(3) The independent atom model is often invoked in analyzing traditional electron diffraction patterns.[53] This model assumes that a molecule is a collection of atoms, each with a scattering factor identical to that of an unbound atom. Electron delocalization due to chemical bonding is neglected. The number of bonding electrons in typical molecules is small compared to the total number of electrons, so that the independent atom model is fairly successful in describing diffraction patterns. However, bonding effects have been observed in traditional diffraction experiments,[57] and theoretical studies suggest that electronic excitation may significantly alter the scattering factors.[35] In our difference diffraction patterns, we observe oscillations that are very small compared to the overall diffraction intensity. Thus, it seems possible that a change in the chemical bonds during the electrocyclic reaction affects the electronic scattering factor of the molecule. This concern is exacerbated by the realization that any effect arising from the electronic scattering factors would be most prominent at the small diffraction angles where we observe the pump−probe signal.

A full discussion of these complicating factors will be the subject of a more detailed publication. As a preliminary observation we note that, once the rings in the pump−probe diffraction image appear, there seem to be few changes in the periodicity of the oscillatory ring structure. This may indicate that whatever structures are generated shortly after the internal conversion from the excited electronic surface, they are not continuing to evolve on a picosecond time scale. In solution, Reid et al.[54] and Pullen et al.[54] observed conversion between the hexatriene isomers on a picosecond time scale. No such sequential processes are immediately apparent in our diffraction patterns taken with gas-phase molecules.

In summary, we have shown that a newly constructed pump−probe electron diffractometer based on a high repetition rate, amplified laser system is capable of observing structural dynamics in prototypical organic reactions. We demonstrate the performance of the instrument on the electrocyclic ring opening reaction of 1,3- cyclohexadiene. The analysis of the data involves a careful consideration of a number of factors, which have been delineated in this initial report.

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