Imaging the ring opening reaction of 1,3-cyclohexadiene with MeV ultrafast electron diffraction

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Abstract. We resolve the structural dynamics of the ultrafast photoinduced ring opening reaction of 1,3-cyclohexadiene in space and time employing megaelectronvolt gas phase ultrafast electron diffraction. We, furthermore, observe coherent large amplitude motions of the photoproduct.

1 Introduction

The ultrafast photoinduced ring opening reaction of 1,3-cyclohexadiene (CHD) is a model for a whole class of electrocyclic reactions with biological importance, for instance as a key step of vitamin D production in human skin [1,2]. Therefore, it has received a lot of research interest [2,3]. Except for a recent ultrafast x-ray scattering study [4], experimental knowledge about the reaction in the gas phase comes from valence electron spectroscopy, which is directly sensitive to transient changes in the electronic structure e.g. internal conversion through conical intersections [3,5,6]. It is, however, only indirectly sensitive to the nuclear wavepacket dynamics involved in this reaction. Direct access to the nuclear wavepacket dynamics can in principle be achieved by time-resolved x-ray or electron diffraction. However, temporal and/or spatial resolution has been insufficient so far to capture ultrafast reaction dynamics with spatial resolution down to atomic distances. Here, we present a study of the structural dynamics during the CHD ring opening reaction in the gas phase with an unprecedented combination of sub-Å spatial and fs temporal resolution using the MeV ultrafast electron diffraction facility at SLAC National Accelerator Laboratory [7].

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2 Experiment

The details of the experimental setup are described elsewhere [7]. In short, 3.7 MeV electron pulses with 180 Hz repetition rate were created by directing the third harmonic of a Ti:Sapph laser system onto the photocathode of an electron gun and subsequent acceleration of the ejected electrons in an RF cavity. The electron pulses were temporally and spatially overlapped with another portion of the Ti:Sapph third harmonic in the experimental chamber. The sample was introduced into the interaction region using a pulsed nozzle. Diffracted electrons were detected at 4 m distance from the interaction region using a combination of a phosphor screen and a camera. The instrument response function is estimated to be 160 fs.

3 Results and Discussion

Figure 1 shows an atomic pair distribution function (PDF) from real-space transformation of radially averaged static diffraction signals (blue). It exhibits two maxima associated with C-C bond distances and additional carbon-carbon distances across the CHD ring, respectively (see inset of Fig. 1).

Fig. 1. Static pair distribution function (PDF) of 1,3-cyclohexadiene (CHD, blue). The two maxima in the PDF can be associated with carbon-carbon distances as color-coded in the inset and marked by arrows. A representative difference PDF (ΔPDF) 0.7 ps after photoexcitation (green) shows negative contributions at the peak positions of the static PDF due to ground state population loss. It exhibits positive amplitudes from the photoexcited population, in a distance range, where CHD has negligible contributions. Comparison with carbon-carbon distances in two isomers of the photoproduct 1,3,5-hexatriene (inset) shows good agreement.
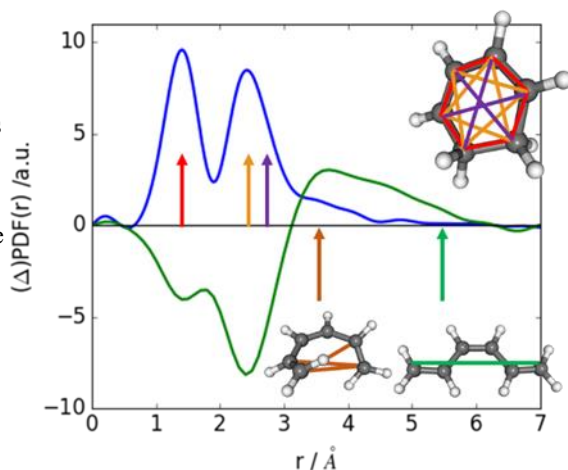
Photoabsorption transfers part of the CHD population to an excited state. The difference PDF (ΔPDF, PDF after time zero minus PDF before time zero) in Fig. 1 (green) 0.7 ps after photoexcitation shows negative amplitudes at the positions of the static PDF due to the loss of ground state population. In addition, it exhibits positive amplitudes between 3 Å and 6 Å, which stem from the photoexcited population. The range is outside the C-C distances of CHD. Comparison with C-C distances of two isomers of the photoproduct 1,3,5-hexatriene (HT) shows good agreement. The broad amplitude distribution suggests a high level of vibrational excitation due to redistribution of large amounts of the absorbed photon energy.

The ΔPDFs around time zero show, apart from an overall amplitude increase due to the finite instrument response function, two sets of time-dependent changes in their shape. These must be due to the underlying ring opening dynamics. The two negative peaks from ground state population loss initially exhibit similar intensity. At the latest delay, the peak at 2.4 Å shows approximately twice the amplitude of the peak at 1.4 Å. Furthermore, the positive signature first peaks at 3.4 Å. At later delays, the signature develops a second peak at 4.5 Å.

Both effects can be associated with the nuclear wavepacket dynamics during the ring opening: Directly after photoexcitation, the positive contribution from the photoexcited

population to the ΔPDF and the negative contribution from the ground state population loss cancel each other out, since the nuclei have not moved yet.

During the ring opening, the positive PDF amplitudes associated with the breaking C-C bond must move from 1.4 Å into the range beyond 3 Å. Likewise, amplitudes connected to part of the C-C distances across the CHD ring (2.4 Å) move to larger distances. The negative PDF contribution from ground state population loss, however, remains static. Thus, the negative PDF amplitudes from ground state population loss at 1.4 Å become exposed earlier than the negative amplitudes at 2.4 Å. This is, what we observe in the changes of the relative negative amplitude. After ring opening, the molecules arrive on the HT ground state potential energy surface, with substantial amounts of vibrational energy. The nuclear wavepacket broadens considerably, which is visible in the time-dependent broadening of the positive contributions in Fig.1. In addition to the immediate ring opening dynamics, we find evidence for coherent large amplitude motion of the HT carbon chains in the investigated time window of 0.7 ps.

We compare our experimental findings with multi-reference excited state trajectory simulations, which we extend by simulations in the ground state on density functional theory level to cover the experimentally investigated 0.7 ps time window. Except for slight disagreements in time scales, Simulated ΔPDFs are in excellent agreement with our experimental data. They support both our interpretation of the experimental data about both the ring opening dynamics and the following large amplitude motion on the sub-ps timescale.

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