

# Time-resolved high-harmonic spectroscopy of ultrafast ring-opening of 1,3-cyclohexadiene

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**Abstract.** We report, to the best of our knowledge, the first time-resolved high-harmonic spectroscopy (TR-HHS) study of a chemical bond rearrangement. We investigate the transient change of the high-harmonic signal from 1,3-cyclohexadiene (CHD), which undergoes ring-opening and isomerizes to 1,3,5-hexatriene (HT) upon photoexcitation. By associating the variation in the harmonic yield to the changes in the electronic state and vibrational frequencies of the molecule due to isomerization, we find that the CHD excited via two-photon absorption of 3.1 eV photons isomerizes to HT, i.e., ring-opening occurs, around 400 fs after the excitation. The present results demonstrate that TR-HHS, which can track both electronic and nuclear dynamics, is a powerful tool for studying ultrafast photochemical reactions.

## 1 Introduction

High-harmonic generation (HHG) is a result of interactions between a freed electron and its parent ion, occurring under strong laser fields [1]. Since HHG contains information about the electron-ion interaction, one can retrieve the electronic state of the generating medium from the amplitudes and phases of the high-harmonic spectra. This technique is known as high-harmonic spectroscopy (HHS). On account of the strong nonlinearity of the ionization process in HHG, HHS of molecules can sensitively and selectively probe the highest occupied molecular orbitals (HOMOs), which are of prime importance for understanding chemical reactions.

HHS has been employed to study the ground-state electronic wavefunctions of gas-phase molecules [2]. Further, ultrafast molecular dynamics triggered by vibrational or electronic excitation have also been investigated via time-resolved HHS (TR-HHS) [3–6], where the high-harmonic signals are monitored as a function of the pump-probe delay. These experiments have shown that the HHG process is sensitive to both the valence electronic and the vibrational states of the molecules. Since chemical reactions result from the coupled dynamics of valence electrons and nuclei, the ability to simultaneously monitor the electronic and nuclear dynamics of molecules makes TR-HHS ideal for probing ultrafast chemical reactions.

However, the applications of TR-HHS were previously limited to photodissociation reactions of small molecules [5,6]. The TR-HHS of more complicated photoexcitation-

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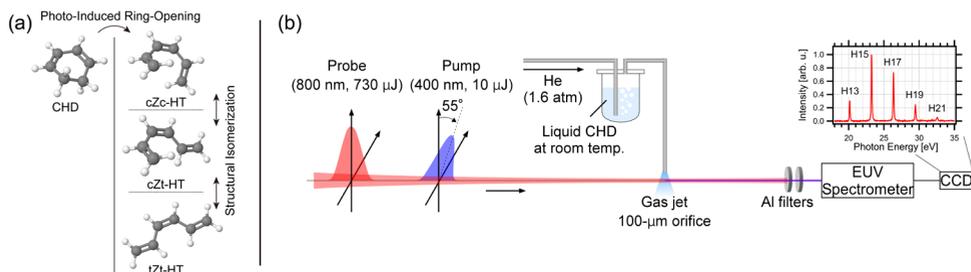
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induced reactions such as a concerted breakage and formation of bonds, i.e., a chemical bond rearrangement, remains a challenge. This limitation is caused by the difficulty in observing high-harmonic signals from photoreactive organic molecules because these molecules are in a condensed phase at room temperature [7].

In this study, we overcame this difficulty and demonstrated the TR-HHS of the ultrafast photo-isomerization dynamics of 1,3-cyclohexadiene (CHD),  $C_6H_8$ . CHD is a hydrocarbon ring molecule and exists in the liquid phase at room temperature. It undergoes ring-opening and isomerizes to 1,3,5-hexatriene (HT) upon photo excitation (Fig. 1a) [8,9].

## 2 Experiment

Figure 1(b) is a schematic diagram of our experiment. The second harmonic pulse (3.1 eV, 10  $\mu$ J, 74 fs) of a 1-kHz-repetition-rate Ti:sapphire chirped-pulse amplifier was used to excite an electron in CHD from the HOMO to the  $3p_x$ -Rydberg state via two-photon absorption (pump), and the fundamental pulse (1.55 eV, 730  $\mu$ J, 30 fs) was used to generate high harmonics from CHD (probe). We recorded the high-harmonic yields as a function of the pump-probe delay. The relative polarizations of the pump and probe pulses were set to the magic angle ( $54.7^\circ$ ) to eliminate the effect of nonresonant molecular alignment of CHD by the pump pulses. The intensities of the pump and probe pulses in the interaction region were estimated as 1.3 TW/cm<sup>2</sup> and 110 TW/cm<sup>2</sup>, respectively. Liquid CHD at room temperature flowed continuously through a 1-cm-long hollow glass fiber (inner diameter: 100  $\mu$ m) into a vacuum chamber using 1.6 atm He gas. We confirmed that harmonics from He were not observed upon introducing He alone into the system.

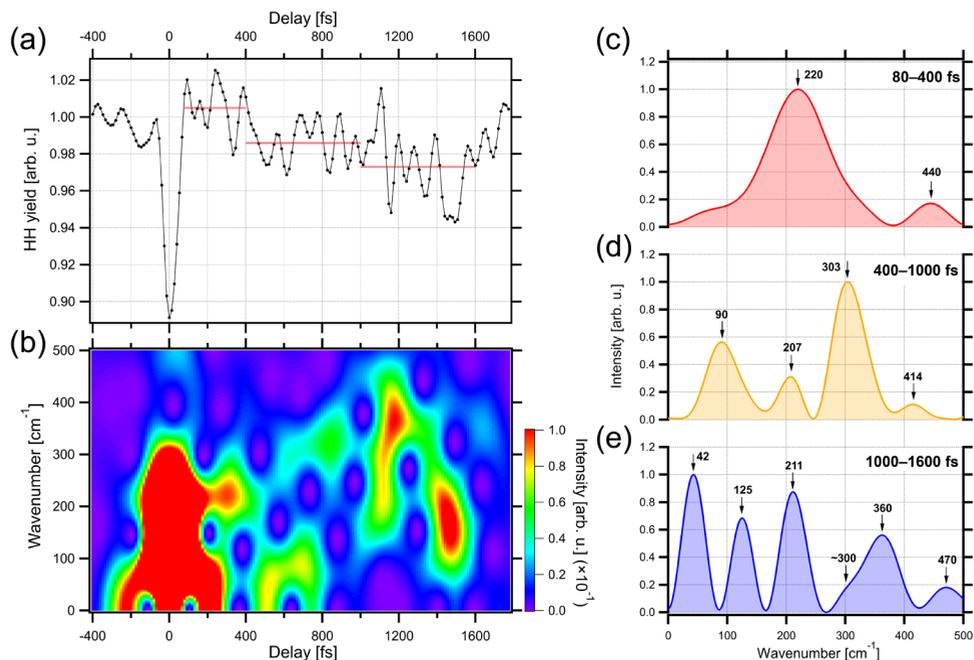


**Fig. 1.** (a) Three-dimensional representations of 1,3-cyclohexadiene (CHD) and its isomers. (b) Schematic of the experimental setup. Inset shows the observed harmonic spectrum.

## 3 Results and discussion

Figure 2(a) shows the experimentally observed yield of the 19th harmonic. Figure 2(b) shows its spectrogram obtained by short-time Fourier transform with a 250 fs Gaussian window. By comparing Figs. 2(a) and 2(b), we noticed that both the harmonic yield and its spectrogram changed at around 400 and 1000 fs. Hence, we concluded that the molecule was isomerized at around these delays. To observe more clearly the changes in the modulation frequency due to the isomerizations, we obtained colored curves (Fig. 2c-e) by Fourier transforming the data points in the corresponding delay ranges, i.e., 80–400 fs (Fig. 2c), 400–1000 fs (Fig. 2d), and 1000–1600 fs (Fig. 2e).

Next, we tried to identify the isomers by associating the experimentally observed vibrational frequencies with the theoretically calculated vibrational modes of the isomers (the calculation results are not shown to conserve space). By comparing the experimentally obtained spectra (Fig. 2c-e) with the theoretically calculated vibrational modes of the isomers, we confirmed that the peak positions in Figs. 2(c), 2(d), and 2 (e) correspond with the vibrational modes of CHD, cZc-HT, and cZt-HT, respectively. Therefore, we concluded that the isomerization from CHD to cZc-HT, i.e., the ring-opening, occurs at around 400 fs after the excitation. Then, the structural isomerization from cZc-HT to cZt-HT occurs at around 1000 fs.



**Fig. 2.** (a) Experimentally observed yield of the 19th harmonic. The horizontal red lines show the average values of the data points (black dots) within the range of the length of each red line. (b) Short-time Fourier spectra of the transient harmonic yield [black dots in (a)]. (c)–(e) Experimentally extracted modulation frequencies of the 19th harmonic yield. The colored curves were obtained by Fourier transforming the data points in the following delay ranges: (c) 80–400 fs, (d) 400–1000 fs, and (e) 1000–1600 fs. The black arrows depict the peak positions (in cm<sup>-1</sup>) of the spectra.

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