

# Ultrafast and Photodissociation Dynamics of 1,2-Butadiene Studied by Photoelectron Spectroscopy

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**Abstract:** Ultrafast and photodissociation dynamics of a cumulated diene molecule, 1,2-butadiene, were investigated by time-resolved photoelectron spectroscopy using a high harmonic. In contrast with 1,3-butadiene, coherent oscillation by stimulated Raman process was observed prior to photodissociation.

**OCIS codes:** (320.7150) Ultrafast spectroscopy; (320.6500) Femtosecond phenomena

A conjugated polyene, consisting of alternating carbon-carbon double and single bonds, is one of the fundamental structures in the biological systems. In particular, the conjugation structures are often found in the light harvesting complex to transfer light energy to electrons. Therefore, it is interesting to investigate ultrafast relaxation of the excited states in the conjugated polyenes as a model system of the light harvesting complex. 1,3-butadiene has been investigated as the simplest conjugated polyene extensively. One of photochemical reactions in 1,3-butadiene, reported so far, is the isomerization to 1,2-butadiene before dissociation. Thus, in this work, we are interested in ultrafast and dissociation dynamics of 1,2-butadiene. Since 1,2-butadiene is a cumulative diene, the differences in the relaxation dynamics from that of 1,3-butadiene are also interesting issues.

To investigate the ultrafast and photodissociation dynamics, we employed time-resolved photoelectron spectroscopy (TRPES). PES probes the binding energies of molecular orbitals (MOs), depending on the chemical bonds inside a molecule. Hence, TRPES can detect the molecular rearrangement during the photo-physical and – chemical processes through the energy shifts and the appearance of new orbitals, which should be the advantage of TRPES over ionization spectroscopy observing only the photoproducts.

As a probe into MOs by TRPES, we used a single high harmonic selected by a time-delay compensated monochromator (TDCM) with the temporal duration preserved [1]. Since all harmonics are generated collinearly in high harmonic generation, it is necessary to select a single harmonic for PES. A TDCM separates the single harmonic order without the stretch of the pulse duration and the 19th harmonic (= 42 nm) of a Ti:sapphire (TiS) laser was selected in this work. The sample in gas phase was excited by the second harmonic of a TiS laser (= 400 nm) in the two-photon process. The time-resolved photoelectron spectra were recorded by a magnetic bottle photoelectron spectrometer by changing the optical delay between the pump and probe pulses.

Here, we would like to emphasize that the usage of a TDCM is advantageous over that of multilayer mirrors, selecting the harmonic order loosely, in that the observable spectral region is much wider than 10 eV. Because of this, we can gain insight into the structural changes by observing deeper MOs, which are inaccessible by visible and

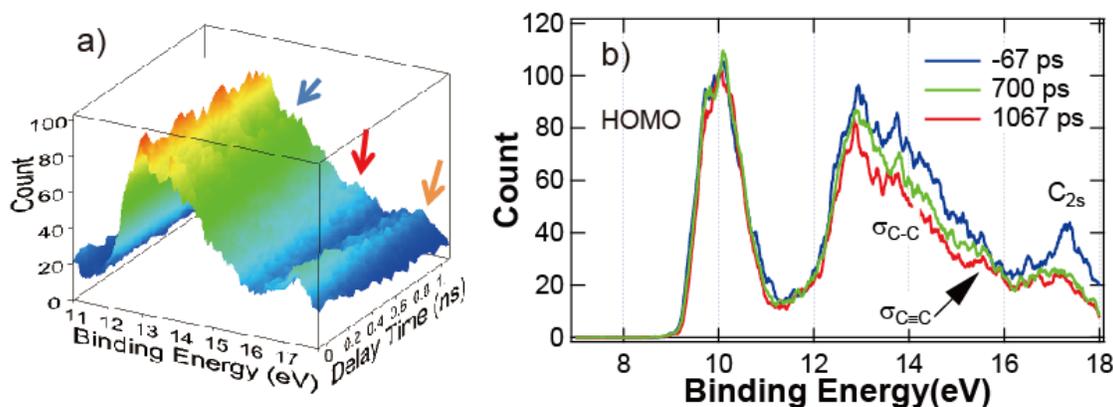
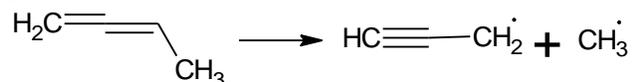


Fig. 1: a) Three-dimensional plot of photoelectron spectra in the picosecond region. b) Photoelectron spectra at -67, 700, and 1067 ps after pump. The characters of molecular orbitals are shown.

ultraviolet lights used so far.

In this work, we observed the photodissociation processes in the picosecond and ultrafast dynamics in the femtosecond region. Figure 1 shows a) the three-dimensional plot of the photoelectron spectra between 11 and 18 eV in the picosecond region and b) the spectra at -67, 700, and 1067 ps after pump. The characters of MOs are also presented in Fig. 1b, The electron counts of  $\sigma_{C-C}$  and  $C_{2s}$  bands, indicated by the blue and by the orange arrows in Fig. 1a, were found to decrease with delay time, although those from the highest occupied MO (HOMO) was almost constant. According to the ionization spectroscopy [2], 1,2-butadiene dissociates into methyl and methyl acetylene radicals as follows :



Therefore, the decrease in the  $\sigma_{C-C}$  band is attributable to the bond break and the formation of these two radicals. Our theoretical calculation predicts that the remaining methyl acetylene radical does not have any molecular orbitals around 14 eV and that the spectral shape of the  $C_{2s}$  band becomes broader, which is consistent with the experimental results. The time for photodissociation was 1 ns, estimated from the decay time of the  $C_{2s}$  band. When the dissociation takes place, the double bonds in the molecule transform into the triple bond in methyl acetylene radical, which is expected to appear in the photoelectron spectra. In fact, we observed a peak around 15.5 eV, appearing about after 0.8 ps indicated by the red arrow in Fig. 1a. Accordingly, our theoretical calculation predicts that the  $\sigma_{C\equiv C}$  band appear around 15 eV. Therefore, we assign this band to the  $\sigma_{C\equiv C}$  band in methyl acetylene radical formed upon photodissociation.

Figure 2a shows the three-dimensional plot of photoelectron spectra in the femtosecond region. The integrated electron numbers of the HOMO band and the transient structure observed around 7 eV were plotted as a function of delay time in Fig. 2b. The transient structure is the cross correlation between 400-nm photons and 19th harmonic and has a temporal duration of 90 fs. The intensity of the HOMO band oscillated with delay time in contrast with 1,3-butadiene, in which the depletion and the fast recovery with a time constant of 50 fs were observed [3]. Since the bands of all MOs oscillated in phase, the observed intensity oscillations were induced by stimulated Raman process in the ground state. In fact, Fourier transform of the oscillation of the HOMO band gives a frequency of  $195\text{ cm}^{-1}$ , corresponding to an in-plane carbon-skeleton bending vibration.

The different dynamics between 1,3- and 1,2-butadiene in the femtosecond region is attributable to the difference in the absorption coefficient at 200 nm. Since 1,2-butadiene is a cumulated diene, the energy stabilization due to the conjugation is much smaller than 1-3-butadiene. This leads to the shift of the absorption to higher photon energies. Hence, at 200 nm, 1,2-butadiene was less excited and the stimulated Raman process in the ground state contributed more to the observed processes in the femtosecond region. On the other hand, in the picosecond region, the dissociation of a small number of the excited molecules was observed.

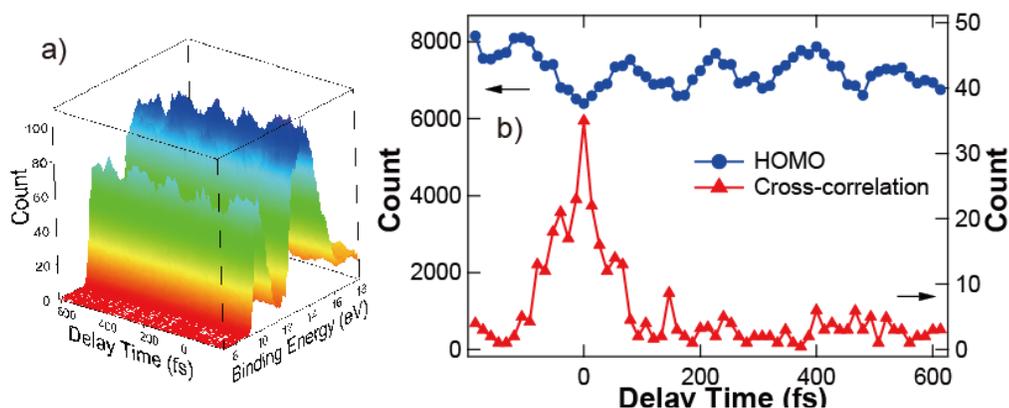


Fig. 2: a) Three-dimensional plot of photoelectron spectra in the femtosecond region. b) Time dependence of the integrated electron numbers of the HOMO band and the transient structure around 7 eV.

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