

Ultrafast Relaxation and Photodissociation Dynamics of 1,3-Butadiene Studied by Probing Molecular Orbitals

A. Makida,¹ T. Fujiwara,¹ Yu Harabuchi,² T. Taketsugu,² and T. Sekikawa^{1*}

¹Department of Applied Physics, Hokkaido University, Kita 13 Nishi 8, Kita-ku, Sapporo 060-8628, Japan

²Department of Chemistry, Hokkaido University, Kita 10 Nishi 8, Kita-ku, Sapporo 060-0810, Japan

*sekikawa@eng.hokudai.ac.jp

Abstract: Femtosecond relaxation and picosecond photodissociation dynamics of 1,3-butadiene were investigated by time-resolved photoelectron spectroscopy with high harmonics pulses, probing the deeper molecular orbitals which are sensitive to the molecular structure.

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

High harmonic pulses are promising for the investigation of ultrafast phenomena from the femtosecond to attosecond regions. In particular, the extreme ultraviolet (XUV) lights can access to deeper molecular orbitals (MOs) of molecules, characterizing the chemical bonds and the structures. Therefore, time-resolved photoelectron spectroscopy (TRPES) by high harmonics pulses provides us unique opportunities to observe the transient MOs produced by photoexcitation and we can gain insight into the electron dynamics during photo-physical and -chemical reactions.

We investigated the simplest conjugated diene, 1,3-butadiene, which is the fundamental unit of the polyene structure. It has been investigated both experimentally and theoretically to understand energy relaxation processes in polyene chromophores in photosynthesis reactions. In this work, we report the ultrafast recovery of valence electrons, the ultrafast energy redistribution, and structural changes in 1,3-butadiene upon photoexcitation revealed by TRPES.

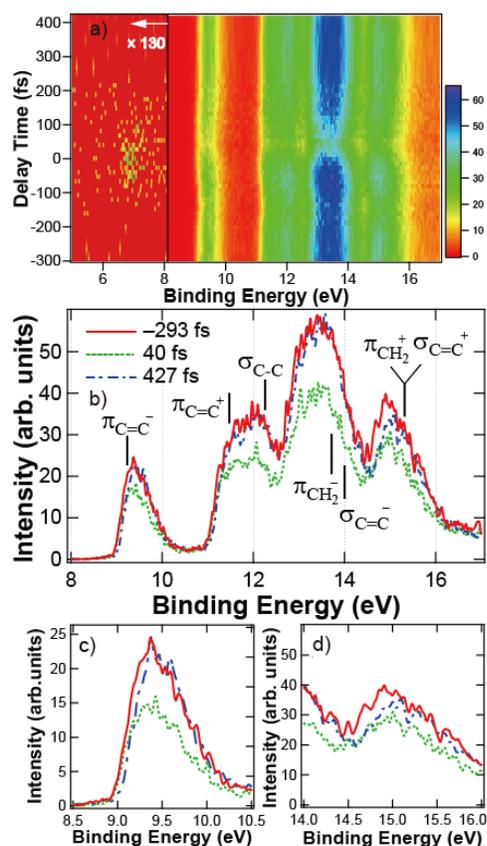


Fig. 1; (a) Photoelectron spectrogram of 1,3-butadiene. (b) Time-resolved photoelectron spectra of 1,3-butadiene at delay times of -293 (solid line), 40 (dotted line), and 427 fs (dashed-dotted line) and the assignment of the peaks. The lower panels are the magnified spectra between 8.5 and 10.5 eV (c) and between 14 and 16 eV (d).

We employed a time-delay compensated monochromator (TDCM) for TRPES to select a single harmonic order with the temporal duration preserved [1]. The spectral widths of attosecond pulses are too broad to probe the MOs of polyatomic molecules, where the energy separations are less than a few eV. Hence, it is necessary to limit the spectral width of high harmonics to observe several MOs separately. The sample in gas phase was excited by the second harmonic of a Ti:sapphire laser (= 400 nm) in the two-photon absorption to the 2^1A_g state. The 19th harmonic (= 42 nm) was selected for the probe pulses by the TDCM [1]. The time-resolved photoelectron spectra were recorded by a magnetic bottle photoelectron spectrometer by changing the optical delay between the pump and probe pulses.

Figures 1a and 1b show the photoelectron spectrogram and the photoelectron spectra at delay times of -270, 40, and 427 fs, respectively. The negative delay means that the pump pulse comes after the probe pulse. In Fig. 1a, the transient MO was observed around 7eV, of which lifetime was 47 fs. In Fig. 1b, at 40 fs, the number of the photoelectrons was reduced and then was almost recovered at 427 fs. The recovery time of the photoelectron number of the highest occupied MO (HOMO) was 53 fs.

To understand the experimental results and to elucidate the relaxation processes in 1,3-butadiene, the steepest decent path from the Franck-Condon region to the planar minimum in the 2^1A_g state, and the interpolated path from the planar minimum to the minimum energy CI (MECI) point between 2^1A_g and 1^1A_g states, were determined by the multi-state complete-active-space second-order

perturbation theory (MS-CASPT2) with cc-pVDZ basis sets, using MOLPRO2012.

Figure 2 shows the predicted potential energy curve; In the Franck-Condon structure, the doubly-excited $\pi^2\pi^{*2}$ state (2^1A_g) is located slightly higher than the $\pi\pi^*$ state (1^1B_u). After the two-photon excitation to 2^1A_g , the molecule is relaxed rapidly to a region of the planar minimum energy structure, $(S_1)_{Cs-min}$, after passing through the conical intersection (CI) between S_2 and S_1 , $(S_2/S_1)_{CI}$. Around $(S_1)_{Cs-min}$, the potential energy surface shows a very flat nature as shown in Fig. 2. In the $\pi^2\pi^{*2}$ excitation, the C=C bond becomes weak and lengthens to 1.5 Å, which is almost equivalent to the C-C single bond. Then, the planarity and the inversion symmetry of the molecule are broken by the twist of one terminal C=C bond. There is no barrier from $(S_1)_{Cs-min}$ to $(S_1)_{C1-min}$, and from $(S_1)_{C1-min}$ to the CI between S_1 and S_0 , $(S_1/S_0)_{CI}$, indicating that the molecule easily goes back to the ground state through these key structures. At the MS-CASPT2 level, the binding energy for electron in the 2^1A_g state becomes smaller by 1.8 eV than in the 1^1A_g state, which decreases to 1.4 eV at the $(S_1)_{Cs-min}$ structure. The decrease in binding energy for electron due to photoexcitation is consistent with the experimentally observed value, 2.4 eV. Therefore, we attribute the observed excited state around 7 eV to the $(S_1)_{Cs-min}$ state. The 50-fs lifetime is due to the barrierless relaxation.

Figures 1c and 1d are magnified time-resolved spectra of Fig. 1b. The MOs observed around 15 eV were found to be still shifted at 427 fs, while the HOMO band was not. The twist of the CH_2 bond in the excited state stimulates the antisymmetric C=C vibration. The theoretical calculation predicts that only the binding energy of $\sigma_{C=C}$ is largely shifted by this vibrational mode than those of the other MOs. The spectral shift of $\sigma_{C=C}^+$ directly indicates the structural deformation even in the ground state after the relaxation. Probing deep MOs by high harmonic pulses enables us to detect the local deformation of the molecular structure sensitively.

1,3-butadiene has various dissociation pathways upon photoexcitation by ultraviolet light. By detecting photoproduct ions, we can suspect the dissociation processes. However, the dissociation processes are still under cover. TRPES provides us unique opportunities to gain insight into the processes even in the longer time ranges. Figure 3 shows the time-resolved photoelectron spectra in the picosecond regime. According to the previous work [2], the isomerization to 1,2-butadiene is the most probable relaxation pathway. Therefore, although the spectrum observed at 1.067 ns was still different from that of 1,2-butadiene, we suspect that the observed evolution of the spectrum is the isomerization process to 1,2-butadiene. In particular, the broadening of the MOs mainly consisting of $\sigma_{C=C}$ and σ_{CH} located between 14 and 18 eV suggests the recombination of the molecular bonds. TRPES is useful to observe the photochemical reactions.

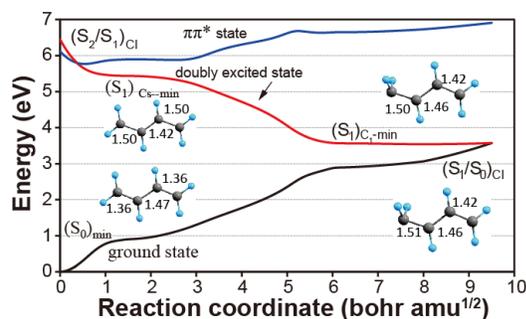


Fig. 2: Potential energy curve describing the relaxation processes in 1,3-butadiene along the reaction coordinate. The red, blue, and black lines are the curves for doubly excited state, $\pi\pi^*$ state, and the ground state, respectively. The insets are the molecular structures with bond length in Å at $(S_0)_{min}$, $(S_1/S_0)_{CI}$, $(S_1)_{Cs-min}$, and $(S_1)_{C1-min}$. The CI between S_2 and S_1 is indicated by $(S_2/S_1)_{CI}$.

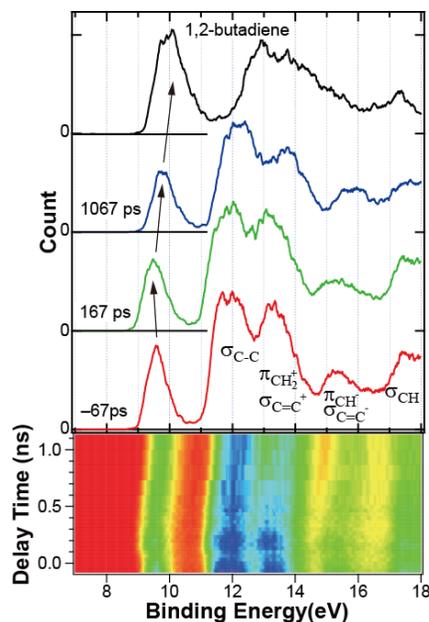


Fig. 2: Photoelectron spectrogram in the picosecond regime and the spectra of 1,3-butadiene at -67, 167, and 1067 ps after pump and 1,2-butadiene.

[1] H. Igarashi et al., Opt. Express **20**, 3725 (2012)

[2] J.C. Robinson, J. Am. Chem. Soc. **124**, 10211 (2002)