Sub 20 fs photoelectron imaging of excited state dynamics of CS$_2$
(Kyoto Univ.) OSpesvytsev Roman, Horio Takuya, Takufumi Kobayashi and Suzuki Toshinori

【Introduction】
Ultrafast photodynamics of carbon disulfide (CS$_2$) has been used as a benchmark system for study of photodissociation of triatomic molecules. CS$_2$ has a strong single photo-absorption band in the UV region from 210 to 190 nm. Upon absorption of a single UV photon, CS$_2$ is promoted to the $S_3(^1B_2)$ electronically excited state, populating both symmetric stretching ($v_1 = 392$ cm$^{-1}$) and bending ($v_2 = 426$ cm$^{-1}$) vibrational modes of the molecule [1]. The $S_3$ electronic state has bent equilibrium geometry with the barrier to the linearity estimated to be 3400 cm$^{-1}$ above the $S_3$ origin (46248.7 cm$^{-1}$). After photoexcitation the molecule dissociates into a CS radical in its electronic ground state and a sulfur atom in singlet or triplet states:

\[
\text{CS}_2 + h\nu \rightarrow \text{CS}(X) + S(^1D, ^3P).
\]

The lifetime of the initially excited $^1B_2$ electronic state depends on the excitation energy and varies between 620 fs and 180 fs [2]. Previous time-resolved measurements, however, employed UV probe pulses which have insufficient energy to ionize CS$_2$ away from the Frank-Condon region [3,4].

In this work, we present time-resolved photoelectron imaging (TRPEI) of gas phase CS$_2$ with sub-20 fs VUV probe pulses. TRPEI technique has been shown to be a powerful tool for studying excited state dynamics of small molecules [5]. TRPEI is sensitive to both nuclear and electronic changes in molecules. Recently we develop vacuum ultraviolet (VUV) laser source [6,7] which extended our TRPEI to high energy probe photons. VUV probe pulses are able to ionize $^1B_2$ state of CS$_2$ away from the initial excitation point, significantly extending our electron kinetic energy (eKE) observation window.

【Experiments】
Details of the experimental setup are described in references [6,7]. Briefly, carbon disulfide is seeded in helium and introduced into the vacuum under a stagnation pressure of 0.5 MPa through a 250 $\mu$m nozzle pulsed at 1 kHz. Fundamental ($\omega$) of the 1 kHz multipath amplifier is used for generation of pump and probe laser pulses. CS$_2$ molecules are promoted to the $S_3(^1B_2)$ electronically excited state...
using $4\omega$ (198 nm) laser pulse. The excited state dynamics is probed by ionizing the molecule with $5\omega$ (159 nm) laser pulse. The cross-correlation between the pump and the probe laser pulses is 17 fs. Figure 1 shows CS$_2$ energy level diagram and pump-probe scheme used in this experiment. The eKE and angular distributions are measured using a velocity map imaging spectrometer. Photoelectron spectra were collected with the pump-probe delay step of 13 fs. Pump only and probe only background signals are subtracted from each image.

【Results&Discussion】

VUV ($5\omega$) probe photon has sufficient energy in order to ionize CS$_2$ molecule to first two cation states, D$_0$ and D$_1$ (see Figure 1). Ionization to D$_0$ cation state produces photoelectrons with a maximum eKE of 4 eV, while ionization to D$_1$ produces maximum eKE of 1.3 eV. The total photoelectron signal decays with a single exponential lifetime of 400 fs lifetime in a good agreement with previous time-resolved experiments [2,3,4]. In contrast, the time-energy map (Figure 2) shows a clear wavepacket motion on the $^1B_2$ state of CS$_2$. Initially excited CS$_2$ has a linear geometry in the Frank-Condon region, producing high energy photoelectrons (eKE = 4 eV) upon ionization. After about 40 fs, the wavepacket approaches an outer turning point when CS$_2$ is bent and stretched, producing photoelectrons with eKE = 1.5 eV. The energy difference between two turning points is determined as 2.5 eV which is larger than previously thought [3].

![Fig. 2. Time-resolved photoelectron spectra of CS$_2$ obtained with a $4\omega$ pump and $5\omega$ probe laser pulses. The spectra were taken with a pump-probe delay step of 13 fs. The photoelectron energy is binned in 0.1 eV slices.](image-url)

The power spectrum of the time-resolved map provides us with two main frequencies of 391 cm$^{-1}$ and 426 cm$^{-1}$, which can be unambiguously assigned to the symmetric stretching and bending vibrations of CS$_2$. In addition, a modulation of the photoelectron signal with a 500 fs is observed. This modulation corresponds to the beating frequency 34 cm$^{-1}$ between the symmetric stretching and bending vibrations.

References