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サブ 20fs 時間分解光電子イメージングによる二硫化炭素の励起状態ダイナミクスの研究

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Sub 20 fs photoelectron imaging of excited state dynamics of CS_2

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【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:

$$CS_2 + h\nu \rightarrow CS(X) + S(^1D, {}^3P).$$

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].

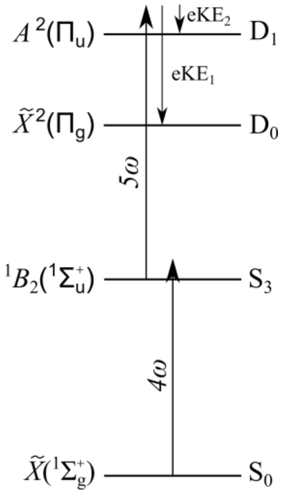

Fig. 1. CS_2 energy level diagram. The molecules are photoexcited using *4ω* pump pulse. Excited state dynamics are probed by ionizing the molecules with a delayed *5ω* laser pulse.

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 μm nozzle pulsed at 1 kHz. Fundamental (*ω*) 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 *4ω* (198 nm) laser pulse. The excited state dynamics is probed by ionizing the molecule with *5ω* (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 (*5ω*) probe photon has sufficient energy in order to ionize CS2 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].

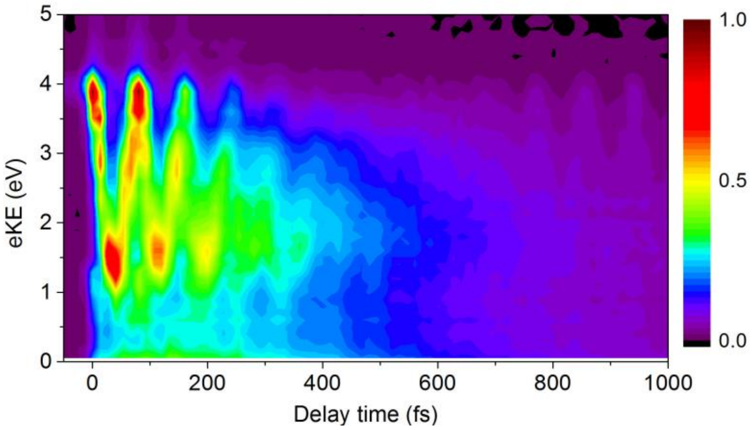

Fig. 2. Time-resolved photoelectron spectra of CS_2 obtained with a *4ω* pump and *5ω* probe laser pulses. The spectra were taken with a pump-probe delay step of 13 fs. The photoelectron energy is binned in 0.1 eV slices.

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

[1] R. J. Hemley et al., J. Chem. Phys. 79, 5219 (1983), [2] P. Farmanara, V. Stert and W. Radloff, J. Chem. Phys. 111 (12), 5338-5343 (1999). [3] T. Fuji, Y.-I. Suzuki, T. Horio, and T. Suzuki, Chem. Asian J. 6, 3028–3034 (2011), [4] P. Hockett, C. Bisgaard, O. Clarkin and A. Stolow, Nature Physics 7 (8), 612-615 (2011), [5] T. Suzuki, Molecules 19, 2410-2433 (2014), [6] T. Horio, R. Spesyvtsev, and T. Suzuki, Optics Express 21, 22423-22428 (2013), [7] T. Horio *et al.*, submitted (2014).