Time-resolved Coulomb Explosion Imaging of Ultrafast Fragmentation of CS_2 in Highly Charged States

Akitaka Matsuda[1], Eiji J. Takahashi[2], Akiyoshi Hishikawa[1]
[1]*Department of Chemistry, Graduate School of Science, Nagoya University, Nagoya, Aichi 464-8602, Japan*
[2]*Attosecond Science Research Team, RIKEN Center for Advanced Photonics, Wako, Saitama 352-0198, Japan*
amatsuda@chem.nagoya-u.ac.jp

Abstract: Time-resolved Coulomb explosion imaging of CS_2 in few-cycle intense laser fields revealed that the ultrafast fragmentation dynamics of CS_2 in highly charged states proceed in a different timescale depending on the charge state.
OCIS codes: 020.2649, 300.6500

1. Introduction

Recent advances in laser technology enabled us to utilize few-cycle intense laser fields (<10 fs, ~10^{15} W/cm^2) as a new probe for visualizing ultrafast structural deformation of molecules in course of chemical reaction. Molecules irradiated with few-cycle intense laser pulses promptly eject several electrons to form multiply charged ions, which subsequently undergo a rapid bond breaking process by strong Coulombic repulsion between the constituent atoms. The "Coulomb explosion" process provides a unique method to visualize the instantaneous structure of polyatomic molecules, because the momenta of the resultant fragment ions reflect sensitively the geometrical structure of the molecule at the time of the laser irradiation [1, 2].

However, for precise probing of the structural deformation of molecules, the effect of chemical bonding should be negligibly small compared to the Coulombic repulsion between the fragments so that the interactions between the fragment ions can be assumed to be purely Coulombic on the reconstruction of molecular structure. Here we study the ultrafast dynamics of fragmentation (explosion) of CS_2, $CS_2^{z+} \rightarrow S^{p+} + C^{q+} + S^{r+}$ ($z = p + q = r$), in few-cycle intense laser fields by monitoring the three-body Coulomb explosion from a highly charged state so that the relative contribution of chemical bonding becomes less significant [3].

2. Experiment

A pair of 9-fs intense laser pulses (4×10^{15} W/cm^2) is employed as the pump and probe pulses (Fig. 1(a)). The pump laser pulse removes electrons to produce highly charged CS_2^{z+} (z = 1-6). The structural deformation associated with the fragmentation (explosion) of the molecular ion was then probed by the second laser pulse introduced with a time delay Δt by monitoring the three-body Coulomb explosion of CS_2^{6+}, $CS_2^{6+} \rightarrow S^{2+} + C^{2+} + S^{2+}$. The linearly polarized Ti:sapphire laser pulse (9 fs, 800 nm, 1 kHz) was introduced into a high-precision Michelson-type interferometer to obtain the pump and probe laser pulses. The laser pulses were introduced into an ultra-high vacuum chamber and focused onto an effusive molecular beam of CS_2. The momenta of the fragment ions generated by the three-body Coulomb explosion were measuered by coincidence momentum imaging technique [4].

In order to discuss the non-Coulombic character of the potential energy surfaces, the molecular-frame momentum distribution is presented. The x-axis is defined as the direction bisecting the angle between the momenta of two sulfer ions, while the y-axis is in the direction perpendicular to the x-axis, in the plane spanned by the momenta of the three fragment ions. The total kinetic energy release E_{kin} is calculated from the measured momenta, $E_{\mathrm{kin}} = \Sigma|\boldsymbol{p}_i|^2/(2m_i)$, where $\boldsymbol{p}_i$ and m_i is the momentum and the mass of the i-th fragment ion.

3. Results and discussion

The molecular-frame momentum distribution for Coulomb explosion pathways (p, q, r) = (1, 1, 1), (1, 1, 2), (2, 1, 2), and (2, 2, 2) obtained with the probe pulse alone are shown in Fig. 1(b), together with that obtained by a classical simulation of the explosion on a Coulombic potential energy surface. A significant deviation between the experimental result and the simulation is observed for pathways (1, 1, 1) and (1, 1, 2), which reflect the non-Coulombic character of the potential energy surface. On the other hand, the momentum distribution is well reproduced by the simulation for pathways (2, 1, 2) and (2, 2, 2), indicating that the internuclear potential is well approximated by the Coulombic potential for highly charged states.

The time evolution of the kinetic energy distribution is presented in Fig. 1(c). At Δt = 30 fs, a clear shift of the peak position towards smaller energy is observed. Since the Coulomb repulsion energy is inversely proportional to the bond length, this indicates that the explosion proceeds within 30 fs after the irradiation of the pump pulse. This can be attributed to charge resonance enhanced ionization (CREI) [5] to CS_2^{6+} by the probe pulse, which explains

the enhancement of the ionization rate by the charge localization near a critical distance. As the time delay increases, the peak of the kinetic energy release distribution further shifts to lower energy side due to stretching of the C-S bonds.

At a longer time delay ($\Delta t \geq 160$ fs), several sub-peaks appear in the kinetic energy distribution. These peaks are associated with different Coulomb explosion pathways induced by the pump pulse, which can be assigned by using the asymptotic energies observed at a sufficiently long time delay [6]. At $\Delta t = 1280$ fs, two peaks are observed at ~51 eV and ~32 eV, which well agree with that observed for pathways (p, q, r) = (1, 2, 2), (2, 1, 2) and (1, 1, 2), respectively. The small shoulder observed at ~20 eV is identified as a contribution from pathway (1, 1, 1). It is also shown that the timescale in which the asymptotic energy is reached depends on the explosion pathway: ~300 fs for pathway (1, 2, 2) and (2, 1, 2) and ~1 ps for pathway (1, 1, 2). For pathway (1, 1, 1), it is inferred that the dissociation along this pathway is too slow to reach the asymptotic region at this time delay since the shoulder peak is observed at a slightly higher energy compared to that expected (14.4 eV).

4. Conclusion

The ultrafast fragmentation of CS_2 in highly charged states was investigated by time-resolved Coulomb explosion imaging using few-cycle intense laser pulses. The explosion dynamics in different charge states (CS_2^{3+}, CS_2^{4+} and CS_2^{5+}) was simultaneously probed in real time showing that the explosion proceeds in different timescales depending on the charge state. By using a visible or ultraviolet ultrashort laser pulse as the pump along with the present technique, one can study ultrafast structural deformation during photochemical reactions of a variety of molecules to provide a deeper understanding of reaction processes.

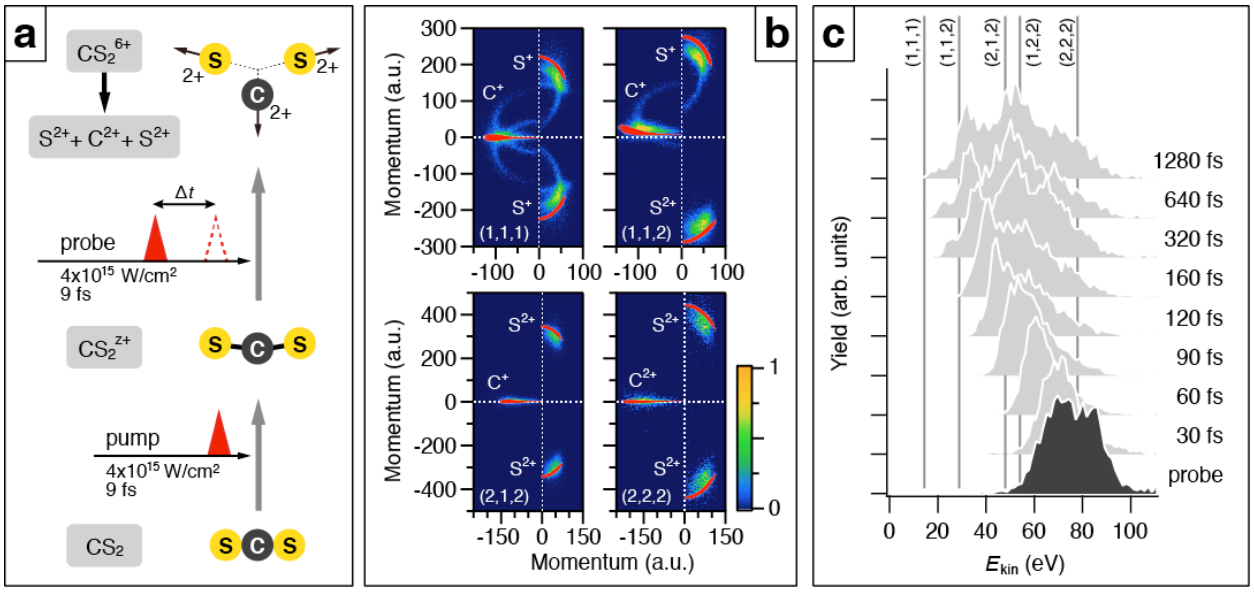

Fig. 1. (a) Scheme of pump-probe Coulomb explosion imaging employed in the present study. (b) Molecular-frame momentum distribution for Coulomb explosion pathways (p, q, r) = (1, 1, 1), (1, 1, 2), (2,1,2), and (2, 2, 2) observed with the probe pulse alone. The distribution in red indicates the results obtained by classical simulation. (c) Time evolution of the total kinetic energy release distribution. The vertical lines indicate peak kinetic energies for Coulomb explosion pathways observed with the pump pulse alone.

References

[1] A. Hishikawa, A. Matsuda, M. Fushitani, E. J. Takahashi, "Visualizing recurrently migrating hydrogen in acetylene dication by intense ultrashort laser pulses," Phys. Rev. Lett. **99**, 258302 (2007).

[2] A. Matsuda, M. Fushitani, E. J. Takahashi, A. Hishikawa, "Visualizing hydrogen atoms migrating in acetylene dication by time-resolved three-body and four-body Coulomb explosion imaging," Phys. Chem. Chem. Phys. **13**, 8697 (2011).

[3] A. Matsuda, E. J. Takahashi, A. Hishikawa, "Time-resolved laser Coulomb explosion imaging using few-cycle intense laser pulses: Application to exploding CS_2 in highly charged states," J. Electron Spectrosc. Relat. Phenom. doi:10.1016/j.elspec.2013.12.011.

[4] H. Hasegawa, A. Hishikawa, K. Yamanouchi, "Coincidence imaging of Coulomb explosion of CS_2 in intense laser fields," Chem. Phys. Lett. **349**, 57 (2001).

[5] I. Bocharova, R. Karimi, E. F. Penka, J. Brichta, P. Lassonde, X. Fu, J. Kieffer, A. D. Bandrauk, I. Litvinyuk, J. Sanderson, F. Légaré, "Charge Resonance Enhanced Ionization of CO_2 Probed by Laser Coulomb Explosion Imaging," Phys. Rev. Lett. **107**, 063201 (2011).

[6] A. Hishikawa, M. Ueyama, K. Yamanouchi, "Probing the ultrafast nuclear motion in CS_2^{2+} in intense laser fields," J. Chem. Phys. **122**, 151104 (2005).