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Time-resolved reaction imaging by intense few-cycle laser pulses and laser high-order harmonics

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Abstract. We discuss two novel approaches to visualize ultrafast dynamics of polyatomic molecules using few-cycle intense laser pulses and the high-order harmonics in the soft X-ray region, respectively. First, we present the real-time Coulomb explosion imaging of recurrently migrating hydrogen in $\text{C}_2\text{D}_2\text{D}^+$. Secondly, we present a new experimental setup for the real-time inner-core excitation imaging, focusing on the generation and separation of the light source using the $59^{\text{th}}$ order harmonic pulses ($\sim$91 eV) and their characteristics.

1. Introduction
Understanding molecular dynamics in chemical reaction is one of the central subjects of chemistry. Among others, ultrafast laser spectroscopy has proved to be a powerful technique to unveil complex dynamics of large polyatomic molecules [1]. In its conventional pump-probe scheme, the evolution of the nuclear wavepacket in an excited electronic state created by the pump laser pulse is projected onto a reference electronic state by the time-delayed probe pulse. The pump-probe signal reflects the motion of the nuclear wave packet and thus can be converted to the changes in the instantaneous molecular structure when the potential surfaces of the excited and reference electronic states are well known. Here, we discuss two novel approaches to visualize directly how molecules change their structure in the course of reactions by using few cycle intense laser pulses and the high-order harmonics in the soft X-ray region with an unprecedented time resolution.

2. Real-time Coulomb explosion imaging of recurrently migrating hydrogen in $\text{C}_2\text{D}_2\text{D}^+$
Molecules exposed to intense laser fields ($\sim$1 PW/cm$^2$) promptly eject several electrons and undergo rapid bond breakings (called Coulomb explosion) on the repulsive Coulombic potential energy surface of the highly charged states. Since the momenta of the resultant fragment ions reflect sensitively the geometrical structure of the target molecule, the Coulomb explosion provides direct access to the
instantaneous structure in the course of reaction processes, as demonstrated for dissociating diatomic [2] and triatomic molecules [3].

Intramolecular hydrogen migration is important in various chemical processes as the large mobility of hydrogen often determines the main route of intra- and inter-molecular reactions [4]. Here we study the acetylene (DCCD) ↔ vinylidene (D2CC) isomerization of C2D2+ by the time-resolved Coulomb explosion imaging [5]. A pair of 9-fs intense laser pulses (0.13 PW/cm²) is used in a pump-probe scheme where the pump pulse doubly ionizes C2D2 and initiates the isomerization of acetylene dication via hydrogen migration and the time-delayed probe pulse induces the three-body Coulomb explosion from the triply charged states, C2D2+ → D⁺ + C⁺ + CD⁺. The momentum angle θ₁₂ between D⁺ and C⁺ fragments as a function of the pump-probe time delay Δt (figure 1) clearly shows that D atom in acetylene dication migrates recurrently [5]: One of the D atoms shifts from one carbon site to the other (D2CC) in 90 fs and then moves back to the original site (DCCD) by 280 fs.

3. Laser high-order harmonics for time-resolved inner-core excitation imaging

Laser high-order harmonics have novel features such as i) high photon energy up to several keV, ii) extremely short pulse duration in the sub-fs regime, iii) high-quality spatiotemporal coherence, iv) high photon flux comparable to synchrotron radiation and v) simple and precise synchronization with other laser light sources [6]. Because of these aspects, laser high-order harmonic pulses are of great interest as a potential light source for time-resolved spectroscopy of ultrafast dynamics that could not be elucidated in real time by conventional techniques.

Figure 2(a) shows the schematic of our new time-resolved reaction imaging system. It consists of a laser high-order harmonics source, a soft X-ray spectrograph, a beam line equipped with a time delay

**Figure 1** Angular distribution between momenta of D⁺ and C⁺ from the three-body Coulomb explosion, C2D2+ → D⁺ + C⁺ + CD⁺, as a function of the pump-probe time delay, showing the recurrently migrating D atom.

**Figure 2** (a) Schematic of time-resolved reaction imaging system by inner-core excitations. (b) Two-dimensional spectrum of laser high-order harmonics for 130 Torr of Ne. Side bands appearing below the 33rd order harmonic are due to the second order diffraction by the grating.
line as well as a pair of dielectric mirrors to select one of the harmonic orders, and an electron-ion coincidence imaging chamber.

3.1. Generation of laser high-order harmonics

Output from a Ti:sapphire laser system (~800 nm, ~30 fs, 1 kHz, 2 mJ/pulse) was focused with a plano-convex lens ($f = 600$ mm) into a cylindrical Ne cell placed in a high vacuum chamber. The spectral distribution and the divergence of the generated high-order harmonics were characterized by an XUV/soft X-ray spectrometer equipped with a flat-field imaging grating and a MCP/phosphor image intensifier. Figure 2(b) shows a two-dimensional spectrum of laser high-order harmonics at 130 Torr of Ne. The intensity of the fundamental pulse was set to $1 \text{ PW/cm}^2$ at the focus. The spectrum exhibits a flat intensity distribution (plateau) up to the 63rd order harmonic and a rapid decrease (cutoff) from the 65th order.

It is shown [7] that the phase mismatch between the fundamental and high-order harmonics pulses is mainly caused by (i) a phase shift due to absorption of soft X-ray pulses, (ii) dispersion of IR pulses by a nonlinear medium, and (iii) a phase delay of fundamental pulses around the focus (Gouy phase shift). Here, we change the density of a nonlinear medium to minimize the total phase mismatch. Figure 3 shows the intensity and divergence for the 59th order harmonic as a function of Ne gas pressure, $P_{\text{Ne}}$, between 50 and 180 Torr. As $P_{\text{Ne}}$ increases, the intensity reaches its maximum while the divergence exhibits the minimum value of 1.1 mrad around $P_{\text{Ne}} = 130$ Torr, indicating that the phase mismatch is minimized at this pressure. The photon flux is evaluated to be $3.4 \times 10^9$ photons/s by using a photodiode for soft X-rays under the phase matching condition.

3.2. Beam line

A set of coaxial mirrors is placed in the beam line to independently reflect the fundamental and high-order harmonic pulses; the outer mirror is coated with silver to reflect the fundamental pulse, while a Mo/Si multilayer mirror is adopted as the inner mirror to selectively reflect the 59th order harmonic. The latter is mounted on a piezo transducer stage to control the time delay between the fundamental and 59th order harmonic pulses. Both pulses are focused on a sample beam in a coincidence chamber by a concave Mo/Si multilayer mirror ($f = 650$ mm).

The reflectance of the Mo/Si multilayer mirrors was measured as a function of photon energy at BL8B1 of UVSOR synchrotron radiation facility at IMS. While the reflectance is constant at the peak (~60 %), the peak position shifts to higher energies as the incident angle increases. At the incident angle of 5 degrees, the reflectance peak and the full width at half maximum (FWHM) of a single

![Figure 3](image-url)

**Figure 3** Ne pressure dependence of the intensity (triangle) and divergence (circle) of the 59th order harmonic. The dotted curves are shown to guide to the eye.

![Figure 4](image-url)

**Figure 4** (a) Photoelectron spectrum of Xe 4d inner-core states by exciting with the 59th order harmonic ($h\nu = 92.5$ eV) from the beam line. (b) High resolution Auger electron spectrum ($h\nu = 110$ eV) from ref. [8].
3.3. Photoelectron spectrum of Xe 4d inner-core states

The 59th order harmonic pulse from the beam line was used to ionize Xe from the 4d inner-core states. Figure 4(a) shows a photoelectron spectrum of Xe measured by a magnetic bottle photoelectron spectrometer [9]. The broad doublet observed around 24 eV in figure 4(a) are assigned to the associated Auger electrons (see figure 4(b)). From the binding energies of the 4d spin-orbit states (4d_{5/2}: 67.5 eV, 4d_{3/2}: 69.5 eV), photon energy of the 59th order harmonic pulse used was determined to be 92.5 eV. It should be noted that doublet peaks from the 4d states associated with neighboring orders (i.e. 57th and 61st) of harmonics are not observed, which clearly demonstrates that the Mo/Si mirror pair selectively reflects the 59th order harmonic to produce a single isolated pulse in the time domain.

The linewidths of the 4d photoelectron peaks are much broader than those of Auger electron peaks because the former widths reflect the spectral bandwidth of the 59th order harmonic while the latter ones are determined by the lifetimes of the 4d hole states. From the FWHM of the 4d_{5/2} peak, 1.1 eV, in figure 4(a), the pulse duration of the 59th order harmonic is estimated to be 1.8 fs in the Fourier-transform limit. A broader spectrum with the FWHM of 2.1 eV corresponding to 0.87 fs in the Fourier transform limit has been obtained by few-cycle intense laser pulses (12 fs, 1.1 mJ, ~800 nm). Characterization of the temporal profile of the harmonic pulse is in progress.

4. Summary

Two novel approaches to visualize ultrafast dynamics of polyatomic molecules are presented. First, we discussed the real-time Coulomb explosion imaging of ultrafast hydrogen migration process in C_2D_2^+ by using intense few-cycle laser pulses (<10 fs, ~1 PW/cm^2, ~800 nm). The temporal evolution of the momenta of the fragment ions produced by the three-body explosion, C_2D_2^+ → D^+ + C^+ + CD, shows that the migration proceeds recurrently in competition with the molecular dissociation. Secondly, we presented a real-time inner-core excitation imaging system constructed at IMS, focusing on the generation and separation of the light source using the 59th order harmonic pulses (~91 eV) and their characteristics.

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