

Time-resolved photoelectron imaging using a femtosecond UV laser and a VUV free-electron laser

S. Y. Liu,^{1,2} Y. Ogi,^{1,*} T. Fuji,¹ K. Nishizawa,^{1,2} T. Horio,³ T. Mizuno,¹ H. Kohguchi,^{1,4} M. Nagasono,⁵ T. Togashi,^{5,6} K. Tono,⁵ M. Yabashi,⁵ Y. Senba,⁶ H. Ohashi,^{5,6} H. Kimura,^{5,6} T. Ishikawa,⁵ and T. Suzuki^{1,2,3,†}

¹*Chemical Dynamics Laboratory, RIKEN Advanced Science Institute, 2-1 Hirosawa, Wako 351-0198, Japan*

²*Department of Applied Chemistry, National Chiao Tung University, Hsinchu 30010, Taiwan*

³*Department of Chemistry, Graduate School of Science, Kyoto University, Kyoto 606-8502, Japan*

⁴*Department of Chemistry, School of Science, Hiroshima University, 1-3-1 Kagamiyama, Higashi-Hiroshima 739-8526, Japan*

⁵*RIKEN, XFEL Project Head Office, 1-1-1 Kouto, Sayo, 679-5148, Japan*

⁶*Japan Synchrotron Radiation Research Institute, 1-1-1 Kouto, Sayo, 679-5198, Japan*

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A time-resolved photoelectron imaging using a femtosecond ultraviolet (UV) laser and a vacuum UV free-electron laser is presented. Ultrafast internal conversion and intersystem crossing in pyrazine in a supersonic molecular beam were clearly observed in the time profiles of photoionization intensity and time-dependent photoelectron images.

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Time-resolved photoelectron imaging (TRPEI) allows unprecedented access to ultrafast electronic dynamics in photoexcited molecules [1]. However, ultraviolet (UV) and deep UV (DUV) photons generally employed for TRPEI often have insufficient energy to ionize molecules from low-lying excited states populated by electronic deactivation. For complete observation of ultrafast electronic dynamics and the subsequent photochemical reactions involving ground-state products, pump and probe experiments using a vacuum UV (VUV) or extreme UV (EUV) laser are necessary [2].

High-order harmonic generation in intense laser fields is becoming a useful tool for producing femtosecond or attosecond pulses in the VUV to soft-x-ray region [3–5]; however, a free-electron laser (FEL) provides much more intense pulses in this region [6–8]. Several pump-probe experiments, such as two-color above-threshold ionization of rare gases [9,10], have been reported using a femtosecond laser and an EUV FEL (Hamburg; FLASH) [9–13]. In contrast, although most previous studies deal with nonlinear optical processes of atoms using an FEL and a Ti:sapphire laser (800 nm) [9–13], it is very interesting to investigate the complex chemical dynamics of polyatomic molecules using an FEL and a tunable UV laser.

In this Rapid Communication, we present a TRPEI using a VUV FEL (SCSS: SPring-8 Compact SASE Source test accelerator; RIKEN Harima institute) [7] and a tunable UV femtosecond laser. One difficulty in the pump-probe experiment with short-wavelength probe light is that probe light ionizes the target molecules even in the absence of pump light, and this deteriorates the contrast of the two-color versus one-color signal. In this study, we avoid this difficulty using 161-nm VUV radiation as probe light, the energy of which does not exceed the ionization energy of the target molecule. The result clearly demonstrates a great potential of the UV

pump and VUV probe TRPEI of the ultrafast dynamics of molecules.

A pulsed supersonic molecular beam of pyrazine ($C_4H_4N_2$) seeded in He was introduced into a photoionization chamber and crossed with a femtosecond UV laser pulse and a VUV FEL pulse (161 nm). The UV laser at 260 or 324 nm excited pyrazine to the first or second excited singlet state (S_1 or S_2), respectively, and the VUV laser ionizes molecules from the excited states. Electrons generated by ($1 + 1'$) resonance enhanced multiphoton ionization (REMPI) were accelerated along the molecular beam propagation axis and projected onto a position-sensitive detector comprising microchannel plates (MCPs), a phosphor screen, and a CCD camera. A permalloy shield installed in the photoionization chamber prevented penetration of the terrestrial magnetic field into the imaging spectrometer. Light baffles were used for the entrance and exit ports of the laser beams to reduce scattered light.

A femtosecond laser system comprises an oscillator, a regenerative amplifier, and an optical parametric amplifier (OPA). The laser system was operated at 1 kHz, and a pulse picker was used to gate a pulse train from the OPA. Although the gate width of our pulse picker was very long and allows two consecutive pulses separated by 1 ms to pass through each gate, background subtraction eliminated any influence from this additional pulse. The UV laser pulse was introduced into the vacuum chamber through an optical path length of about 10 m. The laser beam was focused with an axisymmetric lens placed in the air and reflected by an aluminum mirror inside the vacuum chamber toward the molecular beam. The timing of the laser pulse was synchronized to the 238-MHz master clock of the SCSS by feedback locking the cavity length of the Ti:sapphire oscillator. The time delay between the laser and VUV FEL pulses was varied electronically (with an expected accuracy in subpicoseconds) and the temporal overlapping of them is roughly observed by the high-speed photodiode.

The details of the SCSS have been described elsewhere [7]. The SCSS is normally operated at 51–61 nm with electron beam energy of 250 MeV; however, 161-nm radiation was generated for this experiment with a reduced energy of 160 MeV. The full power of VUV radiation was too strong

*ogi@riken.jp

†t-suzuki@riken.jp

TABLE I. Comparison of the anisotropy parameters in three-photon ionization of pyrazine. E_K is the photoelectron kinetic energy.

Excitation schemes	$3s(n^{-1})$ (50 700 cm^{-1})			$3pA(n^{-1})$ (55 000 cm^{-1})			$3pB(n^{-1})$ (56 800 cm^{-1})		
	E_K (meV)	β_2	β_4	E_K (meV)	β_2	β_4	E_K (meV)	β_2	β_4
$[1 + 2](324 + 330 \text{ nm})^a$	730	1	0.3	1260	0.6	-0.1	1470	0.6	0
$[2 + 1](330 \text{ nm})^a$	720	0.8	0	1280	0.4	0.2			
$[2 + 1](324 \text{ nm})^b$	820	1.30(9)	0.37(19)	1330	0.65(2)	-0.08(21)	1560	0.74(10)	0.01(30)

^aRef. [14].

^bThis work. Standard deviations in the last digits estimated by independent analysis of four quadrants of raw images are shown in parentheses.

for this measurement; thus, the intensity was attenuated to be less than 1 $\mu\text{J}/\text{pulse}$ with a gas filter using air as a medium. The beam size was controlled by slits. Finally, the VUV FEL beam was focused onto the molecular beam using a pair of elliptical and cylindrical mirrors. The repetition rate was 20 Hz. The crossing angle between the femtosecond laser and FEL beams was ca. 1 degree. The polarization of both the UV and VUV pulses was parallel to the face of the MCP detector. Owing to the characteristics of self-amplification of spontaneous emission (SASE), the spectrum of the SCSS fluctuated from pulse to pulse (for SCSS pulse characteristics, see [7]). The time-averaged spectrum of 161-nm radiation had an energy width (FWHM) of ca. 0.1 eV.

The photoelectron imaging spectrometer was calibrated against $(2 + 1)$ resonance-enhanced multiphoton ionization (REMPI) of pyrazine via the $3s$ and $3p$ Rydberg states [14]. Table I compares the photoelectron kinetic energy and anisotropy parameters β_2 and β_4 obtained for three different excitation schemes; these were used to ascertain the accuracies of the present measurements.

Figure 1(a) shows a time profile of the pyrazine ion observed by $(1 + 1')$ REMPI with 260-nm pump and 161-nm probe pulses. Here, 260 nm is resonant with the $S_2 \leftarrow S_0$ transition of pyrazine. According to the VUV spectrum of pyrazine reported by Walker and Palmer [15], 161 nm is also resonant with a transition to a higher electronic state. Therefore, one-color two-photon ionization signals were observed using either pump or probe pulses; the one-color signal, which is a factor of 3–4 smaller than the two-color signal, is already subtracted in Fig. 1(a). The ion signal clearly diminishes with time. Least-squares fitting of this time profile, with a single exponential decay assumed, yielded a lifetime of ca. 20 ps. Previously, we performed TRPEI with 264-nm pump and 198-nm probe and found that the S_2 state dephases to S_1 in ca. 23 fs [16] and that the S_1 state decays subsequently in ca. 22 ps [17,18]. The lifetime observed in the present study agrees well with the reported values. The lifetime of these highly vibrationally excited S_1 molecules are determined by internal conversion (IC) to the S_0 state [19].

Figure 1(b) shows an example of a photoelectron image observed at the delay time of about 5 ps. The background photoelectron signals due to the one-color ionization induced by the pump and probe laser pulses were subtracted from the observed image. The photoelectron image corresponds to a 2D projection of the 3D photoelectron velocity distribution, and a slice through the 3D distribution is calculated by an inverse Abel transform. The photoelectron kinetic energy distribution (PKED) and photoelectron angular distribution (PAD) are

obtained by integrating the angular part and the radial part of the 2D slice, respectively. The PAD extracted from Fig. 1(b) is analyzed with least-squares fitting of the following standard formula:

$$I(\theta) = \frac{\sigma}{4\pi} [1 + \beta_2 P_2(\cos \theta) + \beta_4 P_4(\cos \theta)], \quad (1)$$

where P_n is the n th order Legendre polynomial and θ is the angle between the photoelectron velocity and the linear polarization of the laser. The least-squares fitting provides $\beta_2 = -0.15 \pm 0.05$ and $\beta_4 = -0.03 \pm 0.10$. The low anisotropy is typical for valence excited states of molecules.

The PKED observed in the present experiment [blue curve in Fig. 2(a)] shows the clear advantage of using VUV radiation over 198-nm DUV light [red curve in Fig. 2(a)] [16] as

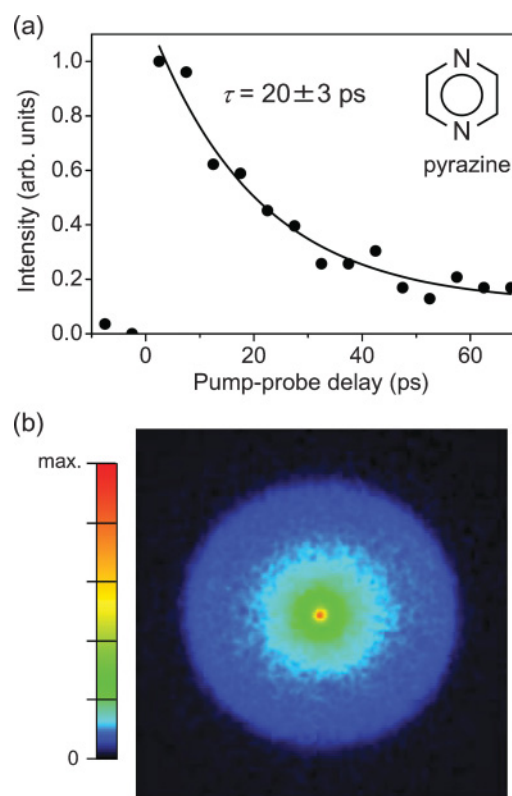


FIG. 1. (Color online) $(1 + 1')$ REMPI signal with 260-nm pump and 161-nm probe light. (a) Time profile of the pyrazine ion signal and least-squares fit of a single exponential decay curve. (b) Observed photoelectron image at the delay time of about 5 ps. A one-color background signal was already subtracted from the image.

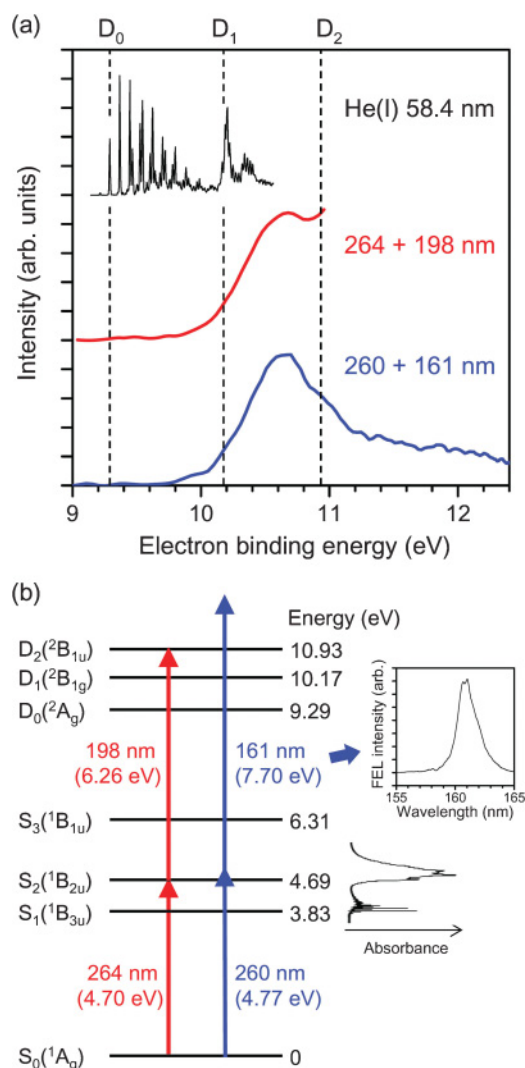


FIG. 2. (Color online) (a) Photoelectron kinetic energy distribution in He(I) photoelectron spectroscopy of the ground-state pyrazine (black) [20], 264-nm UV pump and 198-nm DUV probe experiment (red) [16] and 260-nm UV pump and 161-nm VUV probe (blue) (this experiment). (b) Schematic energy diagram of ionization process. UV absorption spectrum of pyrazine vapor at room temperature and time-averaged spectrum of VUV FEL are shown as insets.

a probe light. In the latter, the observed distribution was truncated at the electron binding energy (EBE) of 10.96 eV, owing to insufficient photon energy [see Fig. 2(b)]. In contrast, 161-nm radiation, with 1.5 eV higher probe photon energy, allows observation of the entire Franck-Condon envelope. Also shown in the figure is the He(I) photoelectron spectrum of jet-cooled pyrazine adopted from Oku *et al.* [20]. The 260-nm excitation prepares an S_2 vibronic state, which rapidly dephases, within 23 fs [16], to isoenergetic S_1 vibronic states under the collision-free condition. Therefore, ionization was observed from the S_1 manifold after $S_2 \rightarrow S_1$ IC in the present study. The difference of the electronic energies of S_2 and S_1 , 0.86 eV, is transformed into the vibrational energy in S_1 upon IC, which is approximately conserved upon ionization. The actual shift of EBE, ca. 1.2 eV, is even larger than 0.86 eV, because the S_1 and D_0 potentials are not identical.

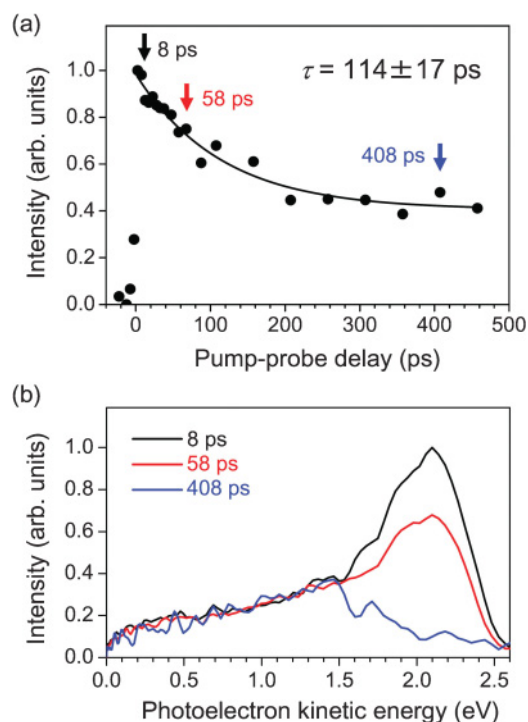


FIG. 3. (Color online) (1 + 1') REMPI with 324-nm pump and 161-nm probe. (a) Time profile of pyrazine ion signal and least-squares fit of a single exponential decay curve. (b) Photoelectron kinetic energy distribution obtained by angular integration of the inverse Abel transforms of the time-resolved photoelectron images.

The S_1 state is expected to have an electronic configuration of (n, π^*) , whereas the D_0 and D_1 states are of n^{-1} and π^{-1} . Therefore, the frozen-core approximation predicts that ionization from S_1 predominantly occurs to D_0 . However, such a prediction is often invalid, as configuration interactions may mix different electronic states, and electron reorganization may occur upon ionization, allowing ionization into cation states that cannot be reached within the frozen-core approximation. This question was not answered by the previous laser-based experiment with a 198-nm probe pulse [16], as the photon energy was insufficient to cover the D_1 continuum region in ionization from vibrationally excited S_1 molecules. The present experiment clearly indicates that the D_1 - S_1 transition is minor, if present.

Figure 3(a) shows the time profile of the pyrazine ion in the 324-nm pump and 161-nm probe experiment. The ion signal exhibits an initial decay, due to S_1 - T_1 intersystem crossing (ISC), and a plateau at later times: From the least-squares fitting of the decay curve, we estimate the lifetime of S_1 state as 114 ps, which is consistent with the previous reports [21–23]. On the basis of previous studies, it has been concluded that the S_1 state dephases exclusively to T_1 . We anticipated that ionization would occur with the same efficiency from S_1 and T_1 and that the ion intensity does not decay for the probe light of 161 nm. However, the observed decay of photoionization intensity suggests that ionization from S_1 is more efficient than that from T_1 at 161 nm. The PKEDs determined from the images observed at different delay times are presented in Fig. 3(b). By taking into account the energy resolution of

our imaging spectrometer, and the broad bandwidth (0.1 eV) of the SCSS, the energy resolution of PKED is estimated to be 0.2–0.3 eV. Accordingly, no distinct vibrational structure is discernible. However, ISC from S_1 is clearly visible as the decay of the high-kinetic-energy component.

Although we did not measure the cross-correlation between the UV and VUV pulses, the rising edge of the observed time profiles indicates that the time-averaged cross-correlation including jitters and drifts is smaller than 5 ps over our signal accumulation time (several hours). This proves that the tunable UV and SCSS synchronization system is ready to explore the picosecond dynamics of complex polyatomic molecules.

This study demonstrates that picosecond TRPEI experiments of photoinduced chemical dynamics are possible with

a SASE FEL and a tunable UV femtosecond laser. An experiment using 60-nm radiation is feasible, although the technical difficulty increases owing to the smaller contrast between the one-color and two-color signals. The time resolution can be improved by recording the signal and pulse timing on a shot-to-shot basis and sorting the data after the measurement [12,13]. By seeding a coherent laser radiation into the SCSS [24], FEL radiation will be more stable in both lasing wavelength and timing, which will allow us to carry out femtosecond time-resolved measurements in a straightforward manner.

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