

Time-resolved photoelectron imaging using ultrashort VUV pulses

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A photoexcited molecule is deactivated through a variety of photo-physical/chemical processes, and ultimately relaxes to the ground electronic state (S_0) or further undergoes chemical reactions in S_0 . Time-resolved photoelectron imaging (TRPEI) [1] enables full observation of these photoinduced dynamics, because photoionization can be induced from any part of the potential energy surfaces (PESs). However, observation of low-lying electronic excited states and S_0 requires probe pulses in the vacuum ultraviolet (VUV) region, and it has been difficult to generate intense ultrashort VUV laser pulses.

Following the generation of sub-20 fs deep UV (DUV) pulses at 4.7 and 6.3 eV by cascaded filamentation four-wave mixing (FWM) [2], we have succeeded in generating ultrashort DUV and VUV (7.8 and 9.3 eV) pulses simultaneously [3,4]. While this light source is simple and easily implemented (Fig. 1), it provides multiple colors with ultrashort time-duration (<20 fs) without any dispersion control (Fig. 2). Thus, it is an ideal light for TRPEI. In this talk, we present TRPEI using ultrashort VUV pulses to obtain a “global reaction map” of photoinduced dynamics of an isolated molecule.

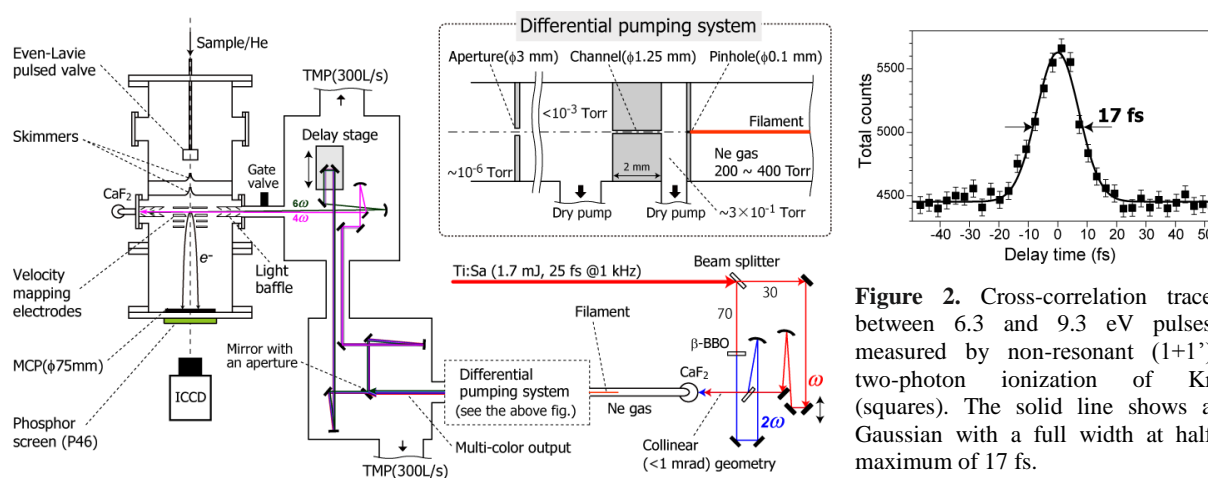


Figure 1. Schematic of the pump-probe photoelectron imaging system coupled with filamentation four-wave mixing light source.

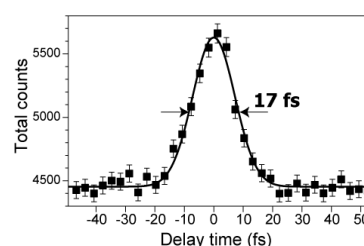


Figure 2. Cross-correlation trace between 6.3 and 9.3 eV pulses measured by non-resonant (1+1') two-photon ionization of Kr (squares). The solid line shows a Gaussian with a full width at half maximum of 17 fs.

The internal conversion (IC) from the $S_2(\pi\pi^*, {}^1B_{2u})$ state of pyrazine ($C_4H_4N_2$) to the $S_1(n\pi^*, {}^1B_{3u})$ state is one of the best-known examples for ultrafast IC via conical intersection (CI) in PESs [5]. Since the S_2 Franck-Condon region is very close to the $S_2(\pi\pi^*)/S_1(n\pi^*)$ CI, IC occurs on an extremely short time scale (<30 fs). Using the sub-20-fs DUV pulses at 4.7 and 6.3 eV, respectively employed as pump and probe pulses, we successfully observed the $S_2(\pi\pi^*) \rightarrow S_1(n\pi^*)$ IC through time-dependent photoelectron angular distributions (PADs) [6]. It should be noted that the $S_1(n\pi^*)$ state of pyrazine populated from $S_2(\pi\pi^*)$ is also short lived and it undergoes further dynamics, which have not been fully elucidated due to insufficient

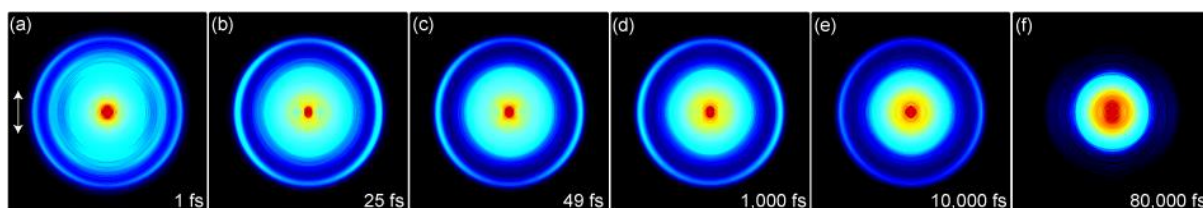


Figure 3. Photoelectron scattering distributions obtained at (a) 1, (b) 25, (c) 49, (d) 1,000, (e) 10,000, and (f) 80,000 fs. The directions of the polarization vectors of the 3ω and 6ω pulses are parallel to each other and vertical in the plane of the figure.

probe photon energy. Here we present full observation of the cascaded radiationless transitions from the $S_2(\pi\pi^*)$ pyrazine by TRPEI using the VUV probe pulses at 9.3 eV [7].

We excited jet-cooled pyrazine molecules into the $S_2(\pi\pi^*)$ state with 4.7-eV DUV pulses and probed subsequent electronic dephasing processes by single-photon ionization using 9.3-eV VUV pulses. Figures 3(a) – (c) present representative snapshots of the photoelectron scattering distributions observed at short time delays. The images observed at 1 and 25 fs are noticeably different, which manifests that the ultrafast $S_2(\pi\pi^*) \rightarrow S_1(n\pi^*)$ IC occurs on this ultrafast time scale. Figures 3(d) – (f) present representative snapshots of the photoelectron scattering distributions observed at long time delays. As seen in the figures, while the intensity of the outer ring, assigned as $D_0(n^{-1}) \leftarrow S_1(n\pi^*)$ photoionization signal, diminishes with the time delay, the inner part signals do not exhibit a noticeable decay within this time scale, indicating that long-lived state(s) are populated from $S_1(n\pi^*)$.

We extracted time-dependent photoelectron spectra from the observed images and performed global fitting analysis to the spectra, which has revealed that the vibrationally-hot $S_1(n\pi^*)$ state further decays into S_0 and $T_1(n\pi^*)$ with a time constant of 14.8 ps. In this talk, we also demonstrate that the configuration interaction of the $S_2(\pi\pi^*)$ electronic wave function can be explored by ultrafast VUV photoionization (Figure 4). New experimental results on ultrafast electrocyclic ring-opening reaction are also presented.

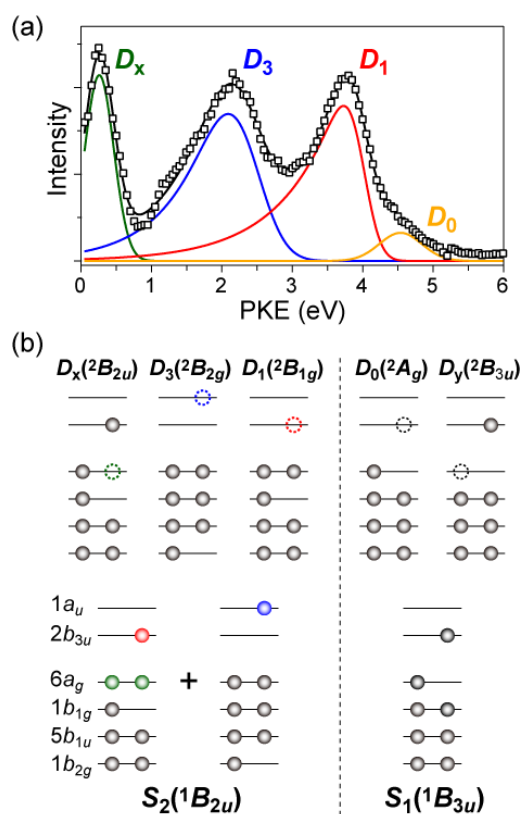


Figure 4. (a) Photoelectron spectrum of $S_2(\pi\pi^*)$. (b) The leading configurations for S_1 , S_2 , D_0 , D_1 , D_3 , D_x , and D_y .

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【References】

- [1] T. Suzuki, *Annu. Rev. Phys. Chem.* **57**, 555 (2006).
- [2] T. Fuji, T. Horio, and T. Suzuki, *Opt. Lett.* **32**, 2481 (2007).
- [3] T. Horio, R. Spesyvtsev, T. Suzuki, *Opt. Express* **21**, 22423 (2013).
- [4] T. Horio, R. Spesyvtsev, T. Suzuki, *Opt. Lett.* **39**, 6021 (2014).
- [5] W. Domcke et al., *Conical Intersections*, Vol. 15 of Adv. Ser. Phys. Chem.; World Scientific: Singapore, 2004.
- [6] T. Horio, T. Fuji, Y.-I. Suzuki, and T. Suzuki, *J. Am. Chem. Soc.* **131**, 10392 (2009).
- [7] T. Horio et al., *J. Chem. Phys.* **145**, 044306 (2016).