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## Supplementary Information Photo-ionization Initiated Differential Ultrafast Charge Migration: Impact of Molecular Symmetries and Tautomeric Forms

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## Computed bond lengths and Molecular Orbitals

The geometry optimization for the keto and enol tautomers was done at PBE0/def2-TZVP level. The resulting bond lengths, together with known experimental results for keto  $\mathbf{U}$  are listed in  $\mathbf{ESI}^{\dagger}$  Table. S1. The computed bond length values for keto show good match with the experimental results [1].

bonds	keto (Ref. $[1]$ )	enol
C2-O7	1.2074(1.212)	1.3297
C4-O8	1.2096(1.212)	1.2112
C2-N3	1.372(1.391)	1.3427
C4-N3	1.3992(1.415)	1.4102
C2-N1	1.3823(1.395)	1.2919
C4-C5	1.4514(1.462)	1.440
C6-C5	1.3416(1.343)	1.3547
C6-N1	1.364(1.396)	1.3639

Table S1: Calculated bond lengths (in Å) for keto (experimental data [1]) and enol tautomers.

## Dynamics initiated by ionization of individual orbitals

Interesting charge migration dynamics after individual orbital ionization was observed for HOMO-4, HOMO-5, and HOMO-9 molecular orbitals of keto and HOMO-1, HOMO-4, HOMO-6 molecular orbitals of enol. These charge migration dynamics will be presented in detail in the following subsections.

#### Ionization of HOMO-4 of keto tautomer

The ionization of the HOMO-4 of the keto tautomer leads to a typical satellite structure, the specificity being that the satellite posses 1h configuration from both HOMO-4 and HOMO-5 (see Fig. 4(a) in main

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# **keto**



Figure S1: The 5 major orbitals from the a" (A, C) and a' (B, D) symmetry in the ionization spectra of keto (upper two panels) and enol (lower two panels) two symmetries are shown with isosurfaces of  $0.02 \text{ e/}\text{Å}^3$ .

text). As a result, the ionization of HOMO-4 will coherently populate two cationic states. This will lead to oscillation of residual charge with a period of  $t = \frac{2\pi}{\omega}$  with  $\omega = \frac{E_S - E_M}{\hbar}$ , where  $E_M$  is the ionization energy of the main state and  $E_S$  the one of the satellite. We observe at each quarter cycle an avoided crossing as shown in **ESI**<sup>†</sup> Fig. S2(a) where the two natural charge orbitals interchange their character between HOMO-4 and HOMO-5 (shown by change in colours along the curves for HOMO-4 and HOMO-5). Directly after the sudden ionization of HOMO-4 we see an increase in charge density on O7 (circled part on the molecular structure (shown in **ESI**<sup>†</sup> Fig. S2(a)). Then we observe the increase in hole occupancy on HOMO-5 and decrease on HOMO-4 leading to the increase of the charge density on N1 and its decrease on O7, respectively. At the crossing points (observed at 0.88 fs and 3.12 fs), we see both orbitals to contribute to charge density on O7 and N1. Whereas, the charge density on O7 and N1 originates mainly from HOMO-5 (at 2.26 fs) and HOMO-4 (at 4.15 fs).

#### Ionization of HOMO-5 of keto tautomer

From the ionization spectra presented in main text Fig. 4(a) we observe satellites structures populated by the ionization of HOMO-5 with a main state at 13.5 eV and satellite states at 14.43 eV and 15.39 eV. We see a significant contribution from 1h configuration of both HOMO-5 and HOMO-4 in the satellite at 13.5 eV. The dynamics resulting from the ionization of HOMO-5 is presented in **ESI**<sup>†</sup> Fig. S2(b). We see a prominent interchange of the molecular orbital character between HOMO-5 and HOMO-4 at the crossing points (observed at 0.82 fs and 3.65 fs). After the ionization, the hole density on O8 first increases and is then distributed on O7 and N1 as seen at 0.82 fs. To better understands the contribution of the involved molecular orbitals, we analysed the charge density at two other time steps, 3.39 fs (before the crossing at 3.65 fs) and 4.5 fs (after the crossing) where the contribution from HOMO-4 and HOMO-5 is high respectively. We found that at 3.39 fs the charge density contribution on O7 comes from HOMO-4, on N3 from LUMO, and on N1 and O8 from HOMO-5. Hence, due to correlation effects the charge density propagates with time from O8 to N1.

#### Ionization of HOMO-9 of keto tautomer

The ionization of HOMO-9 leads to population of several states due to the presence of a complex satellite structure (see Fig. 4(a) in main text). After the ionization, we observe that hole density is created on N1, O7, and N3. The 2h1p state is dominated by two different configurations; one with holes in HOMO-9 and HOMO-5 and an excited electron to LUMO, and another one with holes in HOMO-9 and HOMO-4 and a particle in LUMO+1. The charge migration dynamics is presented **ESI**<sup>†</sup> Fig. S2(c). The initially created hole density on N1 decreases at the first crossing point and at 1.88 fs we observe an increased hole density on O7, O8, and N3 with an electron density on C2. Therefore, we observe here a prominent charge migration from O7, N3 and N1 to O7, O8 and C2.

#### Ionization of HOMO-1 of enol tautomer

Ionization of HOMO-1 leads to the population of a main state at 10.02 eV and a relaxation satellite at 16.0 eV (see Fig. 4(d) in main text). The principal 2h1p configuration of the relaxation satellite is holes in HOMO and HOMO-1 and a particle in LUMO. In this case the initially created hole stays nearly constant, but an excitation-deexcitation dynamics is triggered between HOMO and LUMO (see **ESI**<sup>†</sup> Fig. S2(d)). Immediately after the ionization, at 0.04 fs, the charge density is mainly localized on the oxygen atom O8. We observe small oscillations of the charge density between O8, and N3 and C5. The charge density on O8 and N3 is more pronounced than on C5 and is thus observed clearly through density plots (with an iso-value of 0.03 charge/Å<sup>3</sup>).

#### Ionization of HOMO-4 of enol tautomer

The ionization of HOMO-4 leads to a complex satellites structure with in particular hole mixing character with HOMO-2 for states at 10.99 eV and 12.01 eV (see Fig. 4(c) in main text). The ionization of HOMO-4 creates hole density on O7, O8, and N1 (see **ESI**<sup> $\dagger$ </sup> Fig. S2(e)). After 0.76 fs, about 40% of the initial charge



Figure S2: Time evolution of the leading occupation number  $\tilde{n}_p(t)$  (see Eq. 4 in main text)) after ionization of a molecular orbital of uracil tautomer. Snapshots of the charge density are also shown. The colours of the circles around the charge distribution on the molecular structures show the corresponding molecular orbitals contributing to the charge density at each position. (a) HOMO-4, (b) HOMO-5, (c) HOMO-9 of keto tautomer (iso-value 0.01 e/Å<sup>3</sup>, hole density in green and electron density in orange) and (d) HOMO-1, (e) HOMO-4, (f) HOMO-6 of enol tautomer of uracil (with an iso-value of 0.03 charge/Å<sup>3</sup>).

is redistributed between HOMO-4 and HOMO-2 orbitals, accompanied by an additional excitation of a fraction of an electron (0.28) to LUMO. After 0.76 fs, we observe an avoided crossing and the character of the corresponding natural charge orbitals is interchanged, i.e. HOMO-4 continues to lose occupation (the hole gets filled) and HOMO-2 to gain occupation (the hole continues to open). This process lasts until 2.17 fs, when more than 88% of initial hole charge has migrated to HOMO-2. This exchange of charge density keeps repeating with a period of about 4.4 fs. Looking at the charge density plots, at the 0.76 fs and 3.06 fs crossing points, we see that the hole density is mainly on O7, O8, and N1 with some electron density on O7. The excess electron density is due to the increase in occupation number of LUMO resulting from the accompanying excitation. At the peak of the process (at 2.17 fs), the positive charge is mainly on O8. Therefore, the process observed after ionization of HOMO-4 is a charge migration from O7 and N1 to O8.

#### Ionization of HOMO-6 of enol tautomer

The ionization of HOMO-6 leads to a complex satellite structure with a main state at 13.74 eV and satellite states at 13.99 eV, 15.72 eV and 17.1 eV. The cationic states at 13.99 eV and 15.72 eV show a small 1h contribution from HOMO-4 (see Fig. 4(c) in main text). The evolution of the main hole occupation numbers after ionization of HOMO-6 of enol is shown in **ESI**<sup>†</sup> Fig. S2(f). Immediately after the ionization of HOMO-6, hole density is localized on O7 and O8. As time proceeds, the hole migrates to HOMO-4 which results in formation of a hole density on N1. The process is accompanied by excitation for an electron to LUMO. The overall process represents oscillations of hole density between O8 and O7, as well as oscillations of charge density on O8 and N3, where hole density on O8 and electron density on N3 increase and decrease periodically.

In summary, photo-ionization of individual orbitals of both the tautomers show different behaviour with different patters and timescales. We observe, clear charge oscillation between N1 and C2, with period of 1.88 fs on ionization of HOMO-9 of keto, and, relatively stronger and faster beating between N1, C2 and O7 with period of 0.98 fs on ionization of HOMO-6 of enol tautomer. This shows the enol leads to stronger correlation effects and fast charge migration compared to keto.

#### Schematics of the proposed experimental setup

Several pioneering experiments have been performed to address charge dynamics [2, 3, 4], yet given the complexity of the process it is difficult to extract all information at once. To study the electron dynamics during the first few femtoseconds after the ionization, we propose to use the experimental schematics shown in **ESI**<sup>†</sup> Fig S3. The three major steps envisaged are: (i) alignment of the molecules using non-ionizing NIR pulse with duration of ~100 fs, (ii) ionization of the molecule with an *as* XUV-pump pulse, and (iii) tracing the charge migration dynamics in the ion using a second XUV-probe pulse by measuring its absorption as a function of the pump-probe delay.

Impulsive alignment of the molecule can be achieved using long pulse (for example THz or NIR pulse) [5]. Note that controlling the alignment of large molecules is certainly challenging. However, the topic of aligning asymmetric-top molecules in 3D in a field-free environment is developing fast. For the molecule under consideration, 3D alignment can be achieved either through picosecond pulse shaping [6] or by using multipulse techniques. In either case, following the metric for 3D alignment [7] a typical alignment of  $\langle \cos^2(\delta) \rangle \sim 0.8$  can be expected, as TDSE simulations on Uracil have shown (see figure 3.16 in ref. [8]). This will be sufficient for a potential experiment, in which the subsequent charge dynamics signatures will be captured in the Recoil-ion and electron momentum with COLTRIMS [9].

After alignment of molecules, the ionization of the valence molecular orbitals (MO) can by be performed with a linearly polarized attosecond XUV pulse. In such a way, we will be able to selectively address the orbitals belonging to a' or a" symmetries. We can further extract the contribution of different MOs with the help of COLTRIMS techniques [10]. The photoelectron emission direction is related to the shape of the MO which is ionized, and thus angular resolved photoelectron-photoion coincidence map may allow to identify the dominant MOs bearing the initial hole.

The hole migration triggered after the ionization of  $\mathbf{U}$  can be captured with the help of attosecond transient absorption spectroscopy (ATAS). A delayed second *as* XUV-pulse can probe the charge dynamics, by driving resonant transitions in the ion which will depend on the momentary charge distribution in the



Figure S3: Schematics for the proposed experimental setup with (a) showing the direction of the molecular jet, pulse propagation and detectors. (b) The experiment is executed in two independent steps: (i) The molecular gas jet with molecules entering the interaction chamber are aligned with a long NIR alignment pulse. The aligned molecules are ionized with *as* XUV-pump pulse and the resulting photoelectrons and ions are detected by the COLTRIMS to identify the orbitals involved in photo-ionization. (ii) A delayed *as* XUV-probe pulse interacts with the target and captures the temporal evolution of the charge migration. The later is observed with ATAS where the XUV pulse after reflection from grating is captured by an XUV photon-detector (assembled with a micro-channel plate (MCP) and phosphor screen or XUV CCD). The alignment NIR-pulse is blocked by a filter placed between the gas target and the grating. (c) Shows the time delay between the three pulses (alignment, XUV-pump and the XUV-probe) when entering the interaction chamber.

molecule. In such a way, at each time delay, the absorption/transmission spectrogram will take snapshot of the actual electron distribution in the molecule. The transmitted XUV pulse can be detected with an XUV spectrometer (grating, micro-channel plate (MCP) and phosphor screen or XUV CCD), as shown in **ESI**<sup>†</sup> Fig. S3.

The proposed experiment is technically very challenging. The state-of-the-art HHG-driven as XUV beamlines are yet to overcome the bottlenecks of implementing XUV-pump–XUV-probe experiments. However, there are a few research facilities, like ELI-ALPS, that hold the prospects to host such experiments in the near future. Furthermore, the proposed experiment relies on aligned molecules which in combination with ATAS has some limitations. As temperature of the molecules have a large impact on the degree of molecular alignment, one usually uses supersonic jets for preparing the sample, which however have relatively low density of molecules. ATAS, on the other side, relies on high density samples for achieving a good signal to noise ration. We will, therefore, probably need to make a compromise between the degree of alignment and the molecular beam density, such that we still get a good alignment, and thus selectivity, and perform ATAS [11]. This can be solved by performing the COLTRIMS measurement first with a lower density gas jet, then after switching off the sensitive electronics one can increase the pressure which makes absorption of the XUV measureable.

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