

Supporting information

Experimental setup

Entering the interferometer, the 800 nm (ω) beam is splitted in two parts by a beam splitter (BS). In the first arm, the beam is focused in a static cell filled with Ar. At this stage, odd harmonics of the fundamental frequency are generated and continue copropagating along with the remaining fundamental in rough vacuum. A set of two parallel Si wafers at Brewster angle for 800 nm serves to reduce the reflected energy of the fundamental. After that, a specially designed mirror reflects mainly the 5th harmonic (5ω) at 160 nm. In fact, a fraction of the 3rd harmonic is also reflected, but this problem is overcome in a manner that will be discussed later. Afterwards, the beam passes through a hole on the mirror H in Scheme 1.

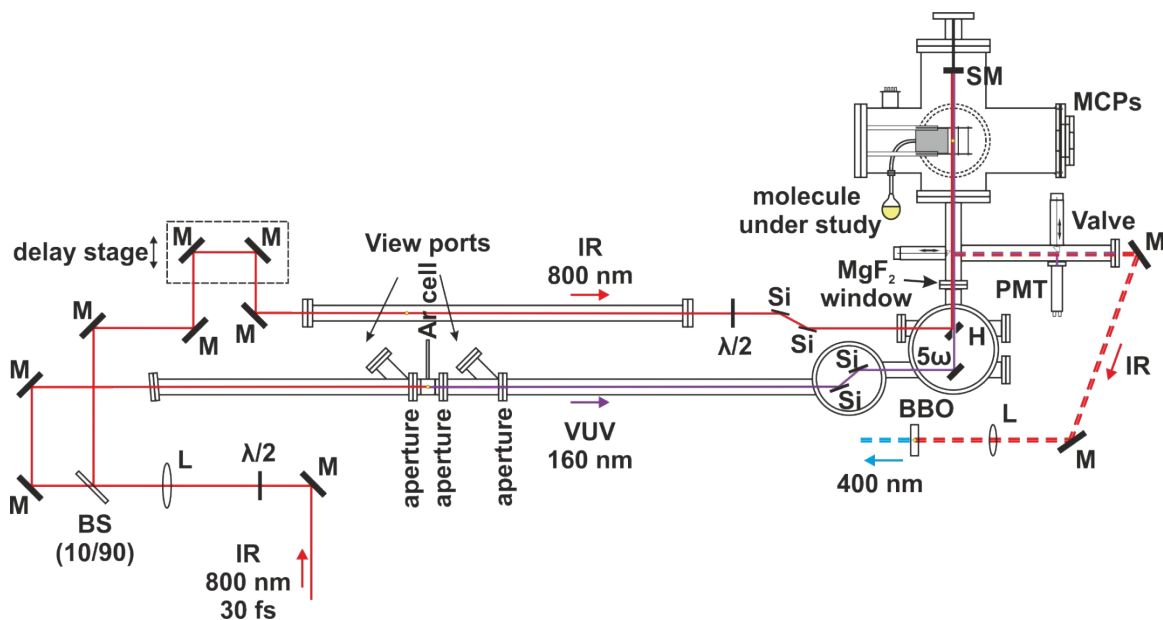
In the second arm of the interferometer propagates the fundamental beam. It enters a system of two mirrors on a PC controlled-moving stage, which changes its optical path in order to delay its pulse relatively to that of the other arm. It is then focused in vacuum so as to avoid the distortion of the pulse by nonlinear phenomena when focused in air. After passing through a set of two parallel Si wafers at Brewster angle that serves to control its intensity, it is reflected around the hole of the mirror H, thus having s-polarization and ring-like shape.

At this point, the two beams are recombined and propagate collinearly until they are reflected by a spherical mirror and focused on the gas-phase molecular sample (Scheme 1). The thus generated ions are then collected by the TOFMS.

In order to maintain a significantly lower pressure ($\sim 4 \times 10^{-7}$ mbar) in the TOFMS chamber, we isolated it using a 1 mm-thick MgF_2 window, which is transparent to the 5th harmonic. Thereby, we also achieved the temporal separation of the remaining 3rd harmonic component by the 5th one thanks to the different refractive index of MgF_2 at these wavelengths. More specifically, the 3rd harmonic pulse exits the window about 870 fs earlier than the 5th, lying thus out of our region of interest.

An auxiliary external setup serves a dual purpose: to check the alignment and to coarsely adjust the temporal overlapping of the two pulses in the main setup. The two collinear IR beams (after turning off the Ar supply in the cell of the harmonics arm and

adjusting the polarization to s-type for both the beams) are steered out of the interferometer, using valves with Si-wafer mirrors, and are focused onto a barium boron oxide (BBO) crystal. A 400 nm flash can be observed when the two pulses overlap both temporally and spatially.



Scheme 1 Experimental setup of the VUV pump-IR probe technique. In the first arm of a Mach-Zehnder type interferometer odd harmonics of the fundamental frequency are generated. The 5th one (pump) is selected by the mirror 5 ω . In the other arm propagates the fundamental (probe) beam. They are recombined at H by a mirror with a hole. An auxiliary external setup serves to the alignment. The generated ions are collected by a TOF.

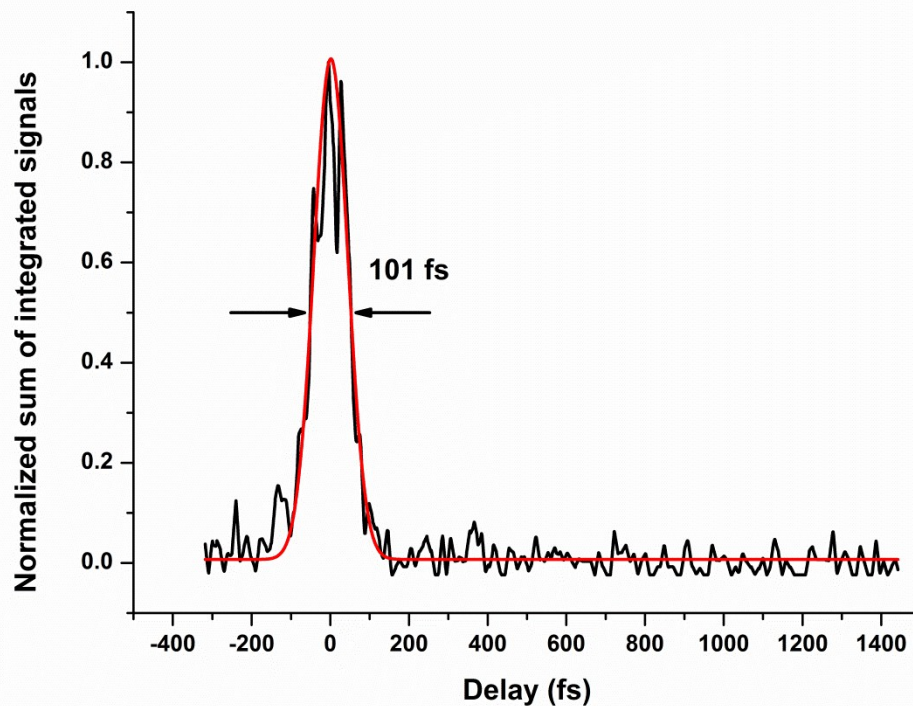
H₂O⁺ dynamics

In Scheme 2 the dynamics of the integral of the H₂O⁺ peak is plotted along with its fitting with the Gaussian function, as predicted by the theory for the cross-correlation of two Gaussian functions such as the pulses in our case. In fact, the normalized sum of six runs with a step of 10 fs is depicted. It reflects the cross-correlation between the pump and the 3rd or 4th power of the probe beam. The ionization potential of H₂O is 12.62 eV,²³ it needs thus one pump (7.75 eV) plus three or four probe (1.55 eV) photons in order to be ionized, depending on the bandwidth of both the beams, making though no significant

difference in the resulting dynamics. The Gaussian cross-correlation width $\gamma^{-1} = 101$ fs and the equation

$$\gamma^{-1} = \sqrt{l^{-1}\tau_{pr}^2 + \tau_{pu}^2} \quad (1)$$

with $l=3$ or 4 and $\tau_{pr}=30$ fs were used to derive the unknown τ_{pu} value, which was estimated at ~ 99 fs. Although it seems to be pretty large relatively to the expected (~ 10 fs), it is totally conceivable by considering the transmission of the 160 nm pump beam through the 1 mm thick MgF_2 window mentioned in the description of the experimental setup. The water ion dynamics was also used for the accurate determination of the zero-delay point, as it has been already mentioned in the experimental section.



Scheme 2 Normalized sum of the normalized integrated signal of H_2O^+ of six scans (black line). The Gaussian fitting (red line) is also depicted. The FWHM is 101 fs.

Fitting model

The rate equation model described briefly below has been originally developed by W. Fuß and coworkers (see ref. 25 for more details) and is used for the derivation of the decay times and the corresponding ionization probabilities.

Considering the case that no branching to different pathways exists, the excited state population of the molecule flows from one location to another on a single potential energy surface (PES) or from location to location on different coupled PESs through radiationless transitions (Scheme 3). Each location L_i is characterized by a time constant τ_i , which corresponds to an exponential decay and reflects its lifetime. After the pump beam has excited the molecules to their Franck-Condon region, the probe beam arrives delayed by Δt , meets them at a location L_i and induces the generation of parent (P^+) and/or fragment ($[P-\dots]^+$) ions with relative probabilities (cross-sections) $s_i^{P^+}$ and $s_i^{[P-\dots]^+}$ respectively.

More specifically, the equations describing the temporal evolution of the two Gaussian pulses are

$$I_{pu}(t) = I_{pu}^0 \exp\left[-\left(t / \tau_{pu}\right)^2\right]$$
$$I_{pr}(t) = I_{pr}^0 \exp\left[-\left(t / \tau_{pr}\right)^2\right]$$

for the pump and the probe pulse respectively, assuming a Gaussian profile for both of them. τ_{pr} and τ_{pu} are the corresponding Gaussian widths.

The transition rate from the ground state to the first excited location by the pump beam is $W_{pu} = s_{pu} I_{pu} / \hbar \omega_{pu}$, where s_{pu} is the cross-section for the absorption of one pump photon, while the transition rate for ionization by the probe beam is $W_{pr} = s I_{pr} / \hbar \omega_{pr}$, where s is the ionization cross-section (that depends on the location i and the absorption order l).

The rate equations describing the population evolution on the different locations, for example in the case where two locations are involved and ionization occurs only from the second one, can be written as follows:

$$\frac{dn_g}{dt} = 0 \Rightarrow n_g = N \quad (2)$$

$$\frac{dn_1}{dt} = W_{pu}(t)n_g - k_1n_1 \quad (3)$$

$$\frac{dn_2}{dt} = k_1n_1 - k_2n_2 \quad (4)$$

$$\frac{dn_{ion}}{dt} = W_{pr}(t - \Delta t)n_2 \quad (5),$$

where $k_n = \tau_n^{-1}$ is the decay rate for L_n .

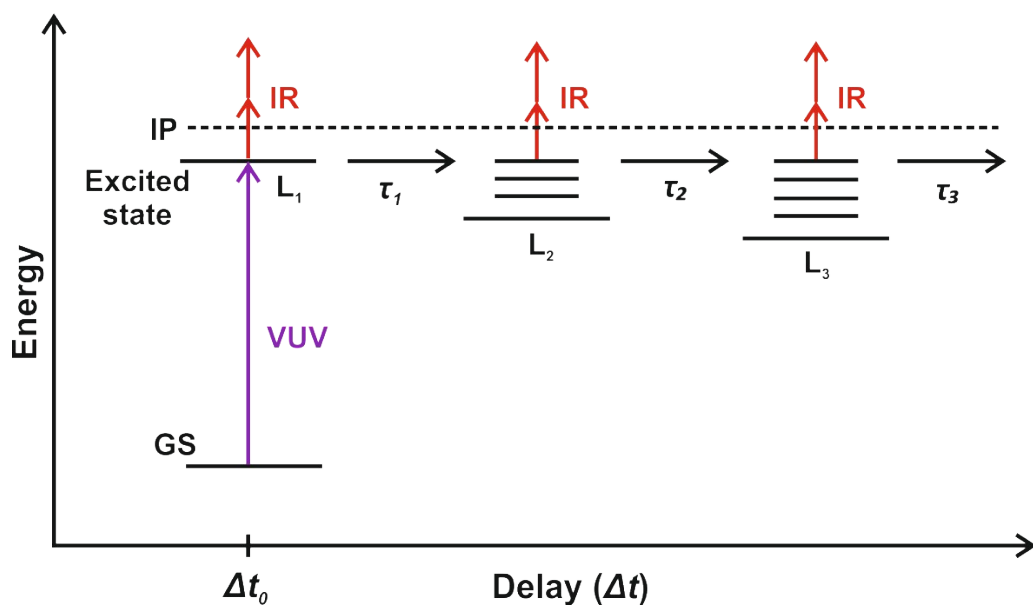
In fact, because of the statistical nature of the experiment, the signal of each single ion contains contributions from both locations L_1 and L_2 , that depend on the delay Δt and the relative probabilities s_i , and not only from L_2 (equation (5)). As a consequence, it can be shown that the ion signal is simulated by a sum of exponentials convoluted with the instrumental function, that is the cross-correlation function between the pump pulse and the l -th power of the probe pulse, which takes the form

$$Sig(\Delta t) = \sum_n a_n \times e^{-k_n \Delta t} \times \left(1 + erf \left[\frac{1}{\sqrt{2}} \left(\Delta t \gamma - \frac{k_n}{2\gamma} \right) \right] \right) \quad (6),$$

where $a_n = \sum_{i \geq n} \beta_i \times s_i$, i and n correspond to the different locations through which the molecule decays, $\gamma^{-1} = \sqrt{l^{-1}\tau_{pr}^2 + \tau_{pu}^2}$ is the cross-correlation between the two beams and l is the number of probe-photons needed to generate the ion of interest.

Only the fragment ions generated during the acceleration time of the TOFMS can be distinguished in the mass spectrum. In general, the parent ion has enough time to dissociate in the acceleration region (~ 500 ns). Another possible process that could give detectable fragment ions is the dissociation of the neutral (excited) molecule followed by ionization (by the probe beam) of the neutral fragments. In the time delay region investigated in the present work, such a process is the H-elimination, which is known to occur in a few tens of femtoseconds.

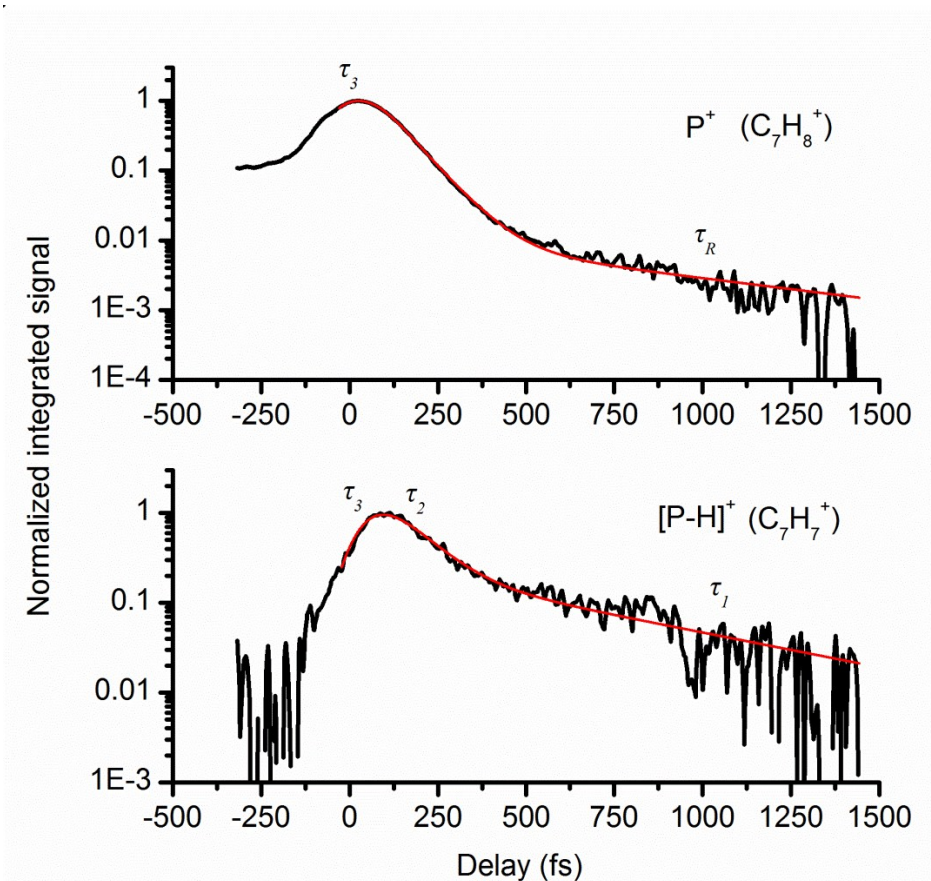
The pump-probe technique elucidates thus the time behavior of the excited neutral molecule, i.e. before its interaction with the probe beam. Many information concerning possible internal conversions and intersystem crossings, conical intersections and isomerizations can be derived.



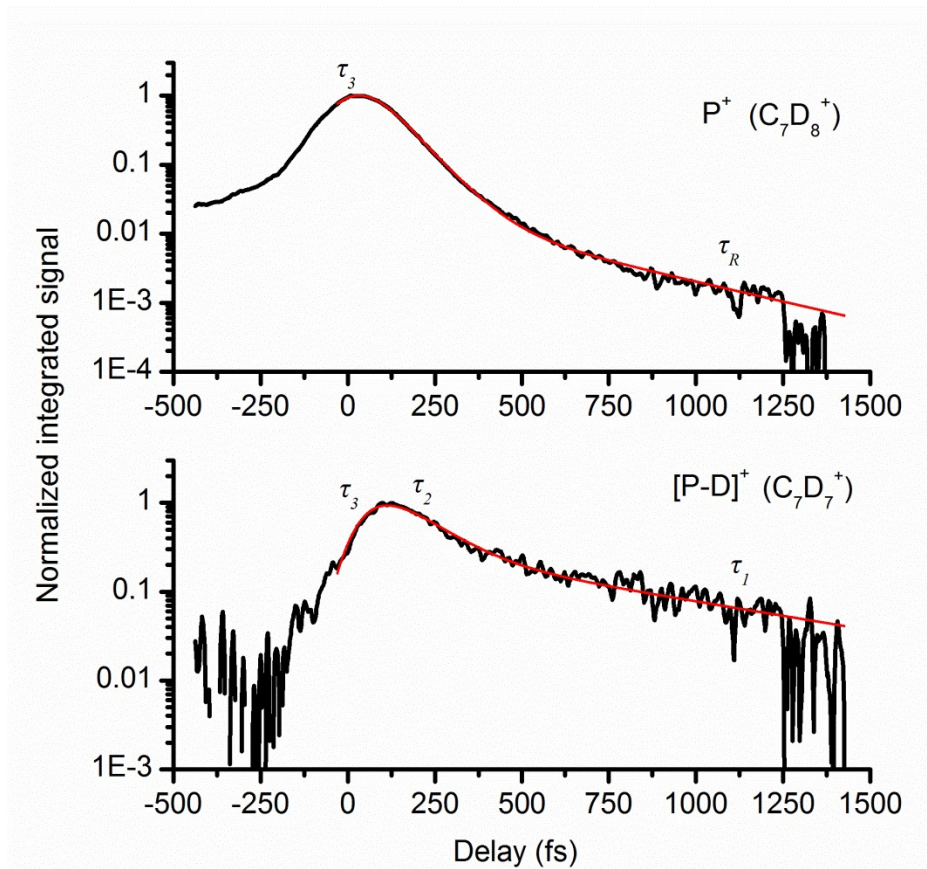
Scheme 3 VUV pump-IR probe scheme. One VUV photon excites the molecule from the ground state (GS) to an excited state. The molecule returns to its GS through several locations L_1 , L_2 , L_3 etc. (on the same or on different PESs). A couple of IR photons delayed by Δt lead to ionization and/or fragmentation.

Time-resolved signals in logarithmic scale

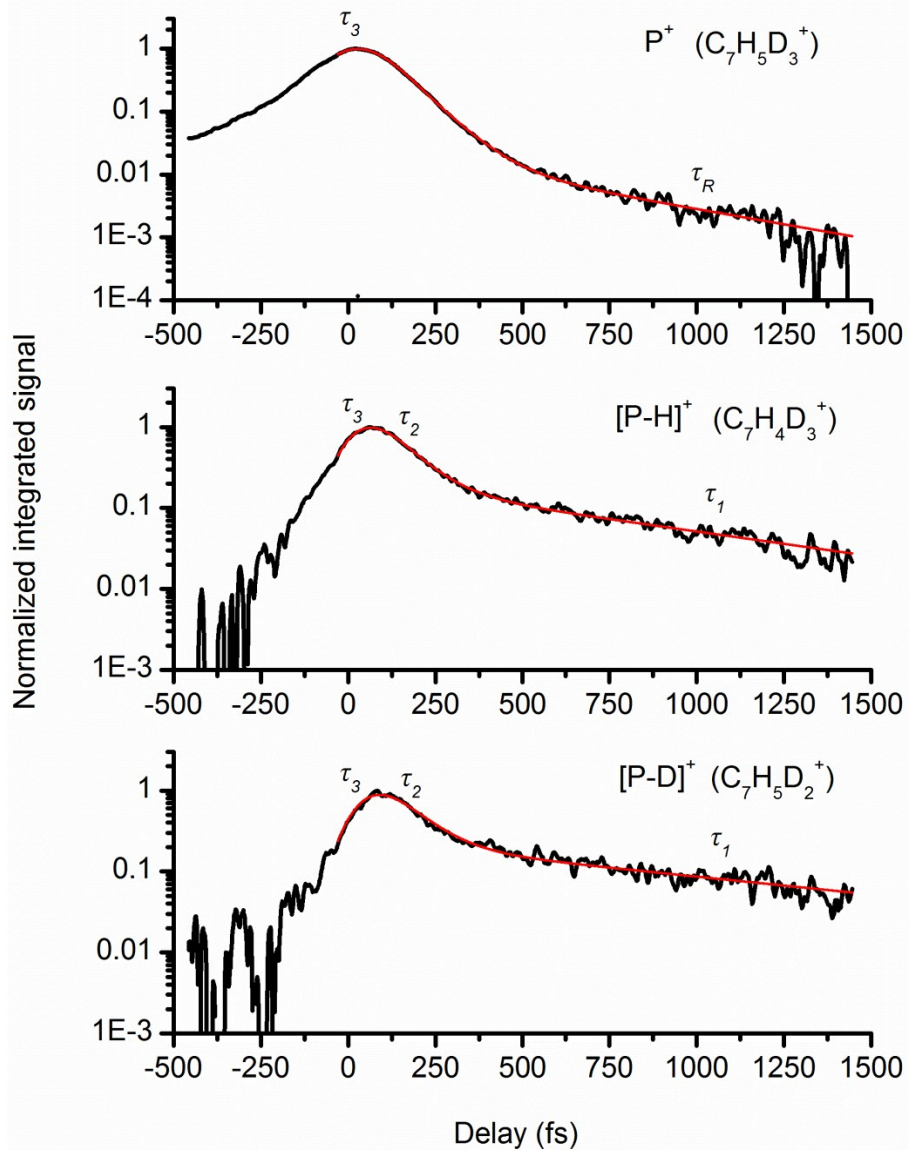
In the following three schemes the time-resolved signals of the parent and the fragment ions for toluene-h₈, toluene-d₈ and toluene- α,α,α -d₃ respectively are depicted in logarithmic scale. The slow processes (long times) appear as straight lines, while for short times the time constants are actually extracted by deconvolution of the part near the maximum using the known (by the H₂O⁺ signal) instrumental function. The equation (6) includes all these processes.



Scheme 4 Time-resolved P^+ and $[P-H]^+$ signal for toluene-h₈ (black lines) together with the fitted with eq. (6) curve (red lines). The lifetimes found are also noted near the corresponding curve part.



Scheme 5 Time-resolved P^+ and $[P-D]^+$ signal for toluene- d_8 (black lines) together with the fitted with eq. (6) curve (red lines). The lifetimes found are also noted near the corresponding curve part.



Scheme 6 Time-resolved P^+ , $[P-H]^+$ and $[P-D]^+$ signal for toluene- α,α,α - d_3 (black lines) together with the fitted with eq. (6) curve (red lines). The lifetimes found are also noted near the corresponding curve part.