Electronic Supplementary Information

Experimental set-up and procedures

Protonated naphthalene is produced in a pulsed, high-voltage electric discharge source coupled to a pulsed nozzle (General Valve) of 200 μ m diameter (Figs. S1 and S2). The discharge is produced 0.5 mm downstream from the nozzle between two electrodes, as described in previous studies.^{1,2} The gas mixture consists of 50% of He and 50% of H₂ seeded with naphthalene vapour (from Sigma-Aldrich used without any further purification), the protonated species being obtained only in presence of H₂. The typical backing pressure is about 2 bars while the pressure in the source chamber is 1×10^{-5} mbar.

The supersonic jet containing the ions produced in the discharge is collimated by a 5 mm diameter skimmer located 10 cm downstream from the nozzle orifice. The collimated ion beam is then passed into a second differentially pumped chamber where a reflectron time-of-flight mass spectrometer (RETOF) is set perpendicularly to the molecular beam axis, the pressure in the chamber being 2×10^{-6} mbar.

The cations produced in the source chamber are extracted into the reflectron time-of-flight mass spectrometer by applying pulsed voltages on the extraction and acceleration electrodes (\approx 2200 V and \approx 1800 V). A mass resolution of m/ Δ m>200 is achieved with a field free flight distance of 157 cm before the reflectron mirror, which is sufficient to separate the protonated species from the radical cation (see Fig. S1).

Laser induced photo-fragmentation of the ions is carried out just before the reflectron mirror using a 10 Hz, nanosecond OPO (optical parametric oscillator) laser (EUROSCAN). The BBO crystal (β -BaB₂O₄) of the OPO laser is pumped with the third harmonic (355 nm) of a Nd⁺³:YAG laser (Quantel YG981C) delivering a tunable wavelength between 413 and 670 nm with an output power in the range of 1 to 15 mJ. The laser is mildly focused to interact with the ion bunch in the interaction region located just before the reflectron mirror, the laser spot being typically 1 mm².

In the current experiment, the time-of-flight mass spectrometer is set to detect the neutral fragments on the microchannel plate (MCP) detector 1 (Fig. S2) located behind the reflectron mirror, while the ions (parent and fragments) are repelled by the voltages applied on the reflectron electrodes. The photo-fragmentation spectrum is recorded by monitoring the neutral fragments detected on the MCP as a function of laser wavelength.



Figure S1. Mass spectrum obtained with the discharge source coupled to a supersonic jet for a gas mixture of helium and hydrogen seeded with naphthalene vapor.



Figure S2: Scheme of the experimental set-up: the ions are formed in an electric discharge located just after the pulsed valve generating the supersonic expansion. The jet is skimmed; the parent ions are extracted and accelerated with pulsed voltages and enter a first field free region. They enter the interaction zone located just in front of the electrostatic reflector where they are photo-fragmented with the laser. The ions are selected by their arrival time in the interaction region. The interaction zone is held at a fixed potential so that the neutral fragments have a sufficient kinetic energy to be detected efficiently on detector 1 and differentiated from collision-induced fragments. The unfragmented parent ions as well as the fragment ions are reflected and may be detected after the second field free region on a second micro-channel plate detector 2.

Detector 1 receives all the neutral species produced from fragmentation of accelerated ions, which includes the fragments produced by the laser and those produced by collisions with the residual gas in the field free region. In order to discriminate between the photoproducts and the collisional background, the laser is interacting with the ions in a region held at a fixed potential of -2 kV where the parent ions gain a kinetic energy of \approx 4 keV. The interaction zone is short (2 cm) so that the number of neutral fragments produced by collisions in this region is very small and can be neglected. The neutral fragments produced from the photo-fragmentation process have the same velocity as their parent ions. The arrival time on detector 1 of the neutral fragments produced in the interaction region or in the field free region, is presented in Fig. S3. The narrow intense peak corresponds to the neutral particles produced in the interaction region from ions having a kinetic energy of ≈ 4 keV, whereas the weak broad peak around 31.5 µs corresponds to collisioninduced neutral fragments produced in the long field free region from ions having a kinetic energy of ≈ 2 keV. Hence, the neutral particles produced in the interaction region reach the detector at earlier times compared to those produced in the field free region. The kinetic energy of a parent ion changes due to a collision. This leads to a distribution in kinetic energy when fragmentation occurs, resulting in a velocity distribution for the neutral fragments which is reflected in the broadening of the signal observed on detector 1. The kinetic energy release in the fragmentation process is in the order of 1 eV in the center of mass frame, which is very small as compared to the kinetic energy of the parent in the laboratory frame (2 or 4 keV).

The laser arrival time is adjusted to select the parent ion. In Fig. S3, the red curve is the signal of neutral photo-fragments recorded when naphthalene ions (m/z 128) are selected while the blue spectrum corresponds to fragmentation of naphthaleneH⁺ ions (m/z 129), the difference in the laser time delay used to select either naphthalene⁺ or naphthaleneH⁺ being 130 ns. These signals have been recorded at λ =450 nm where both ions absorb, the naphthalene⁺ signal being much smaller than the naphthaleneH⁺ signal. The signal recorded at m/z 129 includes a contribution from the naphthalene⁺ isotope with one ¹³C atom, which is less than 10 % of the m/z 128 naphthalene⁺ signal and is thus very small (same order of magnitude as the noise).



S3: Time-of-flight spectra of the neutral fragments arriving on detector 1: in the red trace the laser delay is adjusted to dissociate the naphthalene⁺ ions, for the blue trace the delay is fixed to dissociate the naphthaleneH⁺ ions. The broad peak corresponds to collision-induced dissociations.

When the fragmentation spectrum is recorded, the fluctuation in the discharge source is taken into account by monitoring the collision-induced signal at the same time as the photo-induced signal. The signal from the MCP detectors is sent to the digitizing storage oscilloscope, which was interfaced to a PC.

The experimental method presented here is efficient to investigate the absorption spectra of ions using the photodissociation technique because it always produces a neutral fragment independently of the branching ratio. The major drawback is that there is no information on this branching ratio of the fragmentation process.

Another method that could have been used is depletion of the parent ion signal. The number of ions arriving at the correct mass in the interaction region is on the order of 10^4 , but since the ion cloud is quite diffuse, the laser will interact with only a small part of the ions (estimated as 1%).. The number of ions that will fragment is then much lower than the fluctuation of the parent ion signal, which can be as much as 20% due to the instability of the discharge. Under these conditions, the depletion of the parent ion signal is too weak to be detected.

Since our detection relies on the fragmentation of the molecule, the first band may correspond to the fragmentation threshold. If this were the case, one should observe a rather long fragmentation time for the first band and a strong dependence of the fragmentation time on the excess energy. The fragmentation time can be measured when a 1kV/cm electric field is applied in the interaction zone. In this case the kinetic energy of the parent ion is changing as it travels inside the interaction zone and the neural fragment keeps the parent ion velocity. When the photofragmentation is performed in the electric field configuration, a neutral issued from a very fast fragmentation (within the laser pulse) will appear at the time of the intense blue peak in figure S3 whereas if the fragmentation event occurs near the end of the interaction zone, the neutral fragment will have a lower velocity and will arrive at longer times on the detector, on the broad blue bump. As a result, if the fragmentation time is longer than 10 ns, the ensemble of neutrals emitted during the parent ion lifetime will give rise to a peak broadened towards longer time of flights. With this technique a resolution of 10 ns can be achieved.³ In the present case, we did not observe any broadening of the photo-fragment peak indicating that the neutrals are produced within10 ns for the first band, which seems to be too short for a fragmentation at threshold. Thus, the first band observed is not due to the fragmentation threshold and the photofragmentation spectrum cannot result from single photon absorption but is due to resonance enhanced multi-photon dissociation.

References

1. Jouvet, C.; Lardeux-Dedonder, C.; Martrenchard, S.; Solgadi, D., J. Chem. Phys. 1991, 94, 1759-1764.

2. Jouvet, C.; Lardeux-Dedonder, C.; Solgadi, D., Chem. Phys. Lett. 1989, 156, 569-572.

3. B. Lucas, M. Barat, J.A. Fayeton, C. Jouvet, P. Çarçabal, G. Gregoire Chem. Phys. 2008, 347, 324–330