Supporting information

Experimental setup

The experiments have been performed on a quadrupole ion trap coupled to the Free Electron Laser for InfraRed eXperiments (FELIX) beamline with a time-of-flight mass analyzer that has been described previously.[1] The instrument has recently been extensively modified and will be described in some detail in this section.

The quadrupole ion trap (R.M. Jordan Co, Inc.)[2] consists of a torroidal ring electrode with an inner radius of 1 cm that is capped with two hyperbolically shaped electrodes. A 1 MHz radio-frequency (RF) signal with a voltage ranging from 0–4000 V top-top and referenced to ground is supplied to the ring electrode. The trap assembly is mounted in a vacuum chamber that is kept at a pressure of 1×10^{-7} mbar by means of a 170 $\mathrm{l \cdot s^{-1}}$ turbo pump. A flow of helium is typically supplied to the vacuum chamber with a precision dosing valve, raising the pressure in the ion trap chamber to 2×10^{-5} mbar to confine the ions to the center of the trap, which enhances the overlap of the ion cloud with the FELIX IR beam.

Naphthalene (Fluka, $\geq$98%) has been used without further purification. The sample is introduced by allowing vapor to enter the the vacuum chamber effusively. Ions are generated in the center of the ion trap by 2-photon UV ionization. To facilitate this, two holes are drilled in the ring electrode through which a 3.5 mJ pulse from a MPB PSX-100 ArF excimer laser enters and exits. The laser is focused in the center of the trap using a f =25 cm MgF_2 lens that is positioned outside the vacuum chamber. Alternatively, ions can be generated by an electron impact (EI) source that is located at the repeller side of the ion trap assembly. The ions formed by EI are gated into the trap through a hole in one of the endcap electrodes.

The endcaps are referenced to ground when the ions are trapped and voltages of +800 and -800 V are supplied to the repeller and extractor endcaps, respectively, to

eject the ions. The ions are ejected through a hole in the extractor endcap, after which they are accelerated by a grid that is set to -2375 V. Directly after the grid the ions enter a 50 cm long flight-tube. The ion trap and flight tube assembly are separated by a 4 mm hole through which the ions pass, to ensure good differential pumping of the two chambers. An inner tube(liner) that is electrically isolated from the outer tube is mounted in the flight tube and is biased at the same voltage as the extraction grid to ensure a field free region in the flight tube. The flight tube is pumped by a separate 210 $\mathrm{l{\cdot}s^{-1}}$ turbo pump and the pressure in the detection chamber is typically $\leq 1 \times 10^{-7}$ mbar while operating the ion trap. The ions are collected on a Jordan Z-gap microchannel plate MCP detector of which the first grid is also biased to the liner and grid voltage of -2375 V to terminate the field free region. This layout allows to operate the ion trap at a bias of 0 V, while efficiently detecting ions. The mass resolution of the setup is determined to be better than $m/\Delta m$=250. The ion signal that is recorded on the MCP is digitized in a Acquiris U1070A 200 MS/s digitizer card with 12 bit A/D converter resolution.

The repeller endcap is connected to an in-house designed microprocessor controlled High Voltage (HV) relay switch box that allows for a fail safe switching between the +HV pulse that is used for ejection of trapped ions and an RF Stored Waveform Inverse Fourier Transform (SWIFT) signal [3] that is used to filter the trapped ions by mass. The SWIFT pulses are computed in a LabVIEW routine as described by Doroshenko and Cotter [4] and are generated by a Rhode & Schwarz model AM300 arbitrary wave generator (AWG). Typical swift pulses comprise 262144 datapoints of 14 bit resolution that are output at a sample rate of 3 Ms/s, resulting in an excitation pulse of 87 ms duration.

Infrared spectra are recorded by means of InfraRed MultiPhoton Dissociation (IRMPD). To this end, the cloud of mass selected ions is irradiated with the high-power tunable mid-IR radiation from the free electron laser FELIX. [5] The laser beam is

tightly focused in the center of the ion trap, through an additional pair of holes drilled in the ring electrode. A double pass configuration facilitated by two concave mirrors increases the photon flux seen by the ions. The FELIX pulse energy in the trap is typically $\sim$40 mJ with a pulse duration of 8 μs. FELIX is operated at a repetition rate of 10 Hz and two pulses are typically used to dissociate the isolated ions in the trap. Spectra are recorded by tuning the wavelength from 5.5–16 μm while recording the IR induced fragmentation yield. A small part of the IR radiation is guided into a grating spectrometer that is used to monitor the laser wavelength as the scan proceeds. A power scan is recorded before and after the measurement of each individual spectrum and is used for a linear power correction of the recorded dissociation signal.

Computational methods

Electronic structure optimizations of the reaction products have been performed at the B3LYP/6-311+G(d,p) level of theory. A harmonic frequency analysis is performed and the resulting frequencies are scaled by a factor 0.9679 to compensate for anhamonicities.[6] The theoretical spectra are then convoluted with 30 cm^{-1} Full Width at Half Maximum (FWHM) Gaussian line shapes to facilitate comparison with experimentally recorded spectra.

References

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