Energy selective time of flight mass spectrometer to study low energy dissociation channels of PAHs

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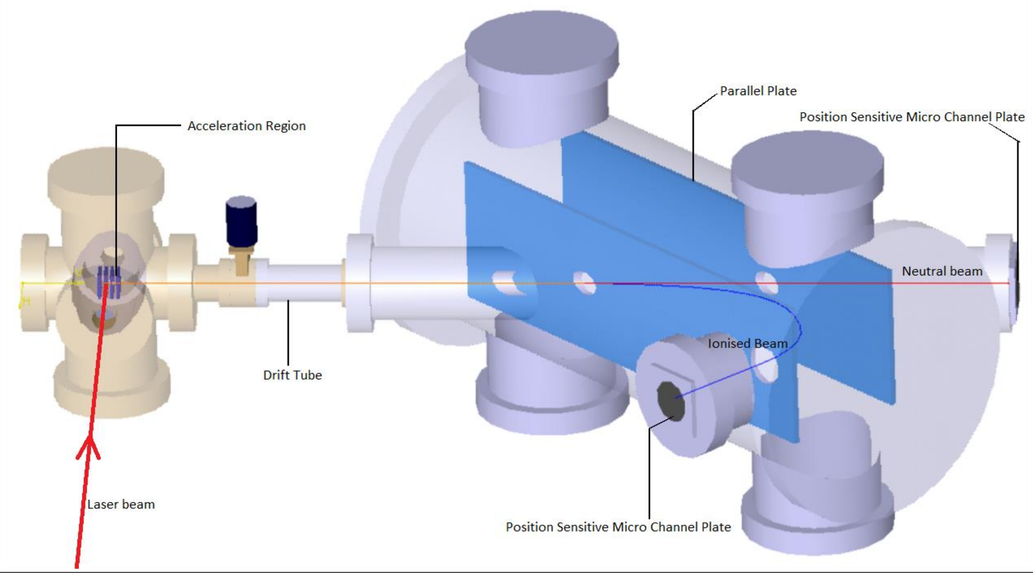
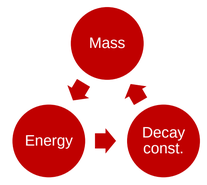
Experimental Setup



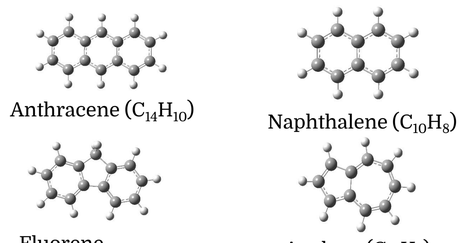


- The experimental setup has an interaction chamber where absorption of photons by PAHs molecule occurs.
- Interaction chamber has four biased electrode plates that extract and accelerate the fragments into drift tube.
- Ion beam pass through parallel plate energy analyzer for energy analysis of fragment ions, it also allows undeflected neutral beam to pass through it and get detected by an alternate position sensitive detector kept downstream.

Specification

- Energy correlated time of flight measurement allows the unimolecular dissociation mechanism to be studied for tens of microseconds.
- The time window available with this instrument is very special for Polycyclic aromatic Hydrocarbons (PAHs). Neutral decay channels can be probed with much less internal energy than conventional studies.
- ToF mass analysers are sufficient to predict reaction kinematics of smaller molecules, but for larger molecules mass cum energy analysis predicts dissociation pathways more accurately.
- Spectrometer is equipped with an alternate position sensitive detector. It can detect neutral products in coincidence with residual ion. It offers possibility to do multidimensional analysis of complex dissociation channels of larger molecules such as PAHs and biomolecules.

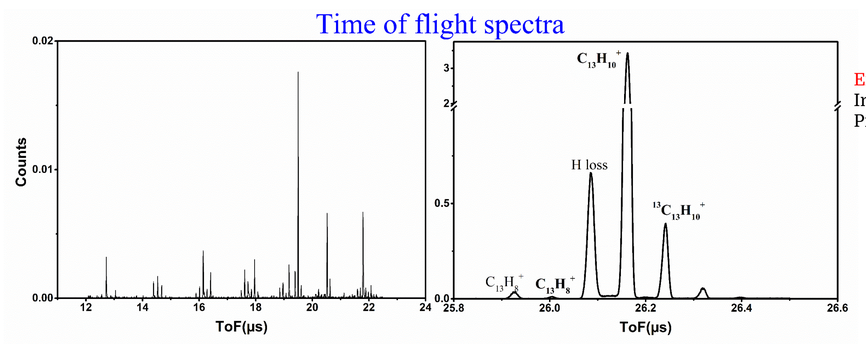
Target molecules



Why Fluorene?

- Fluorene has several astrophysical interests as a test molecule because it is one of the smallest molecule containing a pentagonal ring.
- For this molecule central carbon site is weakly bonded to two out-of-plane hydrogen atoms. Thus, one of these two C-H bonding can be broken easily.
- Dissociation barrier of H loss channel is calculated to be 2.62eV (low value). Therefore an efficient and fast dehydrogenation channel for fluorene cation is expected within the time window available to the spectrometer as a test case.

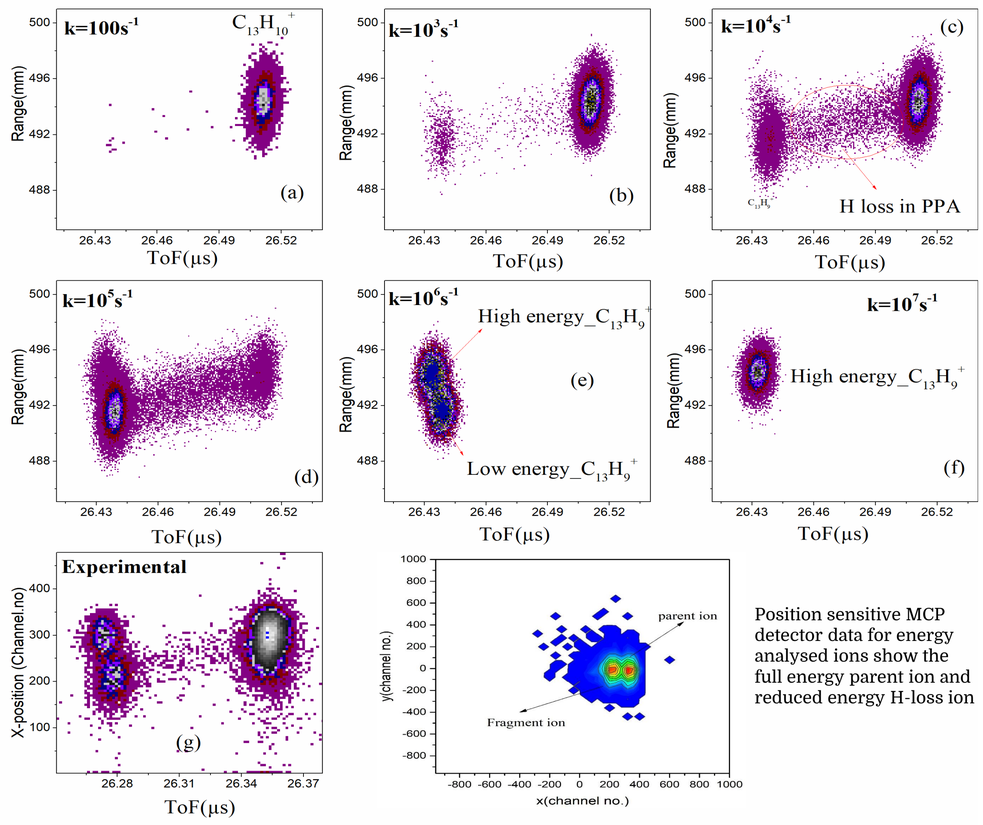
Time of flight spectra



Experimental conditions:
Intensity: 8.0×10^8 W/cm^2
Pressure: 9.0×10^{-8} mbar

Time of flight (ToF) spectra recorded for fluorene ($C_{13}H_{10}$) at of an average pulse energy of 20 μJ and photon energy of 4.71eV (corresponding wavelength, λ=263nm).

ToF-Range spectrum simulated for various decay rates

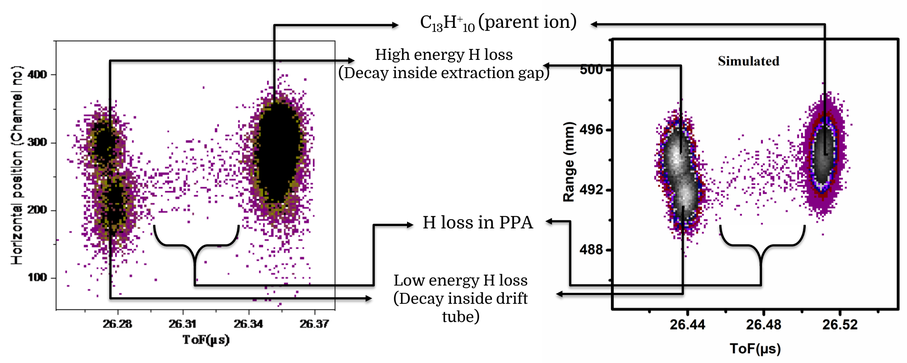


Position sensitive MCP detector data for energy analysed ions show the full energy parent ion and reduced energy H-loss ion

Monte Carlo simulation carried out for probabilistic decay of $C_{13}H_{10}^+$

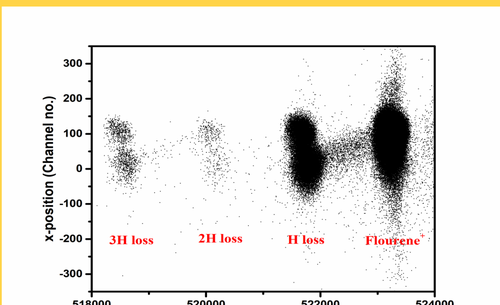
- Since the output from the instrument is very complex & multidimensional, it was very necessary to perform a detailed simulation including probabilistic decay behavior at varying decay constants.
- ToF versus range spectrum is reproduced in the simulation for present electrical and mechanical configurations of the spectrometer.
- In 2D diagram H loss channel has two peaks along energy axis, which corresponds to a decay in microsecond timescales (k= 10^6 s^{-1}). The tail connecting low energy H loss peak and parent peak represents long time decay (k= 10^4-10^5 s^{-1}) and a single high energy H loss peak in the correlation diagram represents very fast decay rate of the order of 10^7 s^{-1}
- Decay constant can be predicted by analysing ToF-Range spectrum of parent /fragment ions, numerical value of the decay constant can be obtained by overlapping 1D energy spectrum of experimental and simulated H loss peaks.

Comparison of experimental & simulated results



Experimental spectrum is measured for fluorene ionization & dehydrogenation channels at 263nm with an average pulse energy of 20 μJ. Fluorene parent ion is produced by 2-photon process, which can have very slow decay rate and its H loss channel is produced by 3-photon process with very fast decay rate. Experimental spectrum is reproduced in the simulation for two extreme H loss decay rates, $k_{parent}=10^3$ s^{-1} and $k_{Hloss}=10^6$ s^{-1}

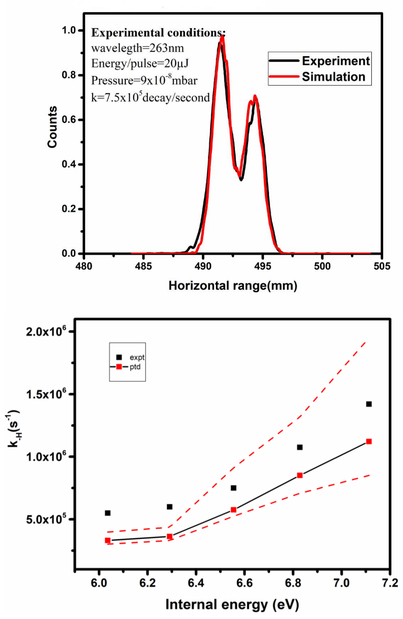
Dehydrogenation series of fluorene cation



- Typical 2D plot measured for H loss series of fluorene parent ion for an excitation wavelength of 268nm.
- 3H loss is seen to be stronger than 2H loss.
- In contrast to H loss decay, multiple H emission rate is seen to be very sensitive to wavelength.
- Prompt vs delayed as well as sequential vs. concerted decay channels can be observed effectively.

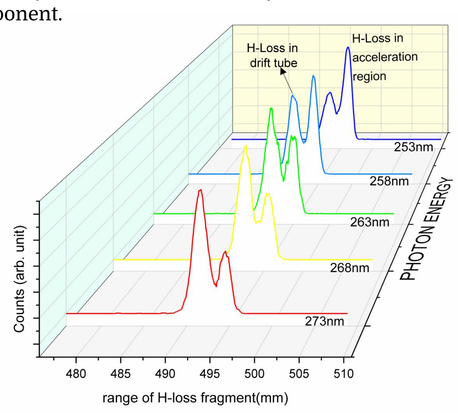
Decay measurement as a function of photon energies

Comparison of experimental and simulated KE spectrum of H loss peak



H loss mass peak evolution for a range of photon energies

The dominant source of H-loss was demonstrated to be 3-photon process. This lead to a variable internal energy to be left in the cation produced after photo excitation. As the photon energy was increased a systematic shift of H-loss yield was observed from slow to fast component.



Decay constants measured for a range of excitation wavelengths 253-273nm.This measurement is compared with previously known rate-energy curve, which is calculated by photothermodissociation model, the dashed lines indicates uncertainties connected to the bivariate error contours of the E_0 and k_0 parameters.

References

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