Multiphoton ionization and dissociation of PAHs using ion-neutral coincidence spectrometer

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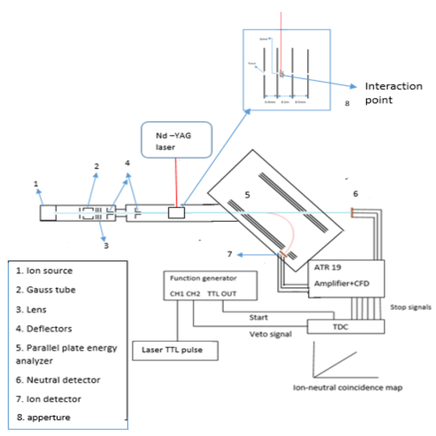
Multiphoton absorption and ionization of PAHs

- PAHs, their cation and clusters are important interstellar objects. They can absorb uv photons from stars and undergo radiative or dissociative relaxations
- Using resonant and nonresonant absorption of uv photons various electronic and vibrational state of neutral and ionized PAHs can be studied
- Multi photon absorption technique is state selective process, it is used to distinguish between isomers and isotopes of a given mixture of analyte

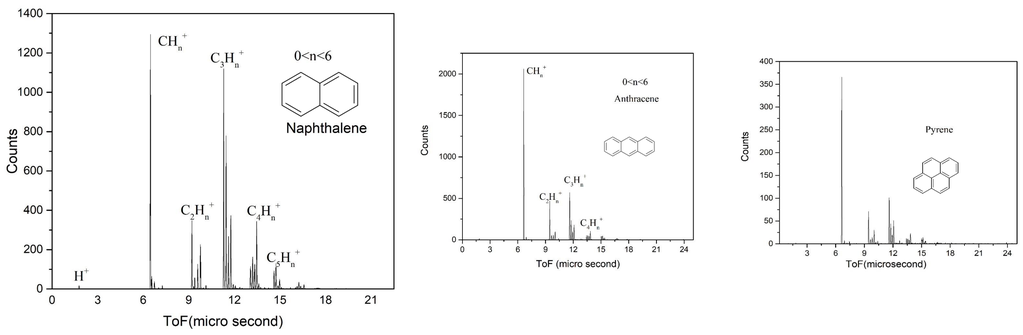
Two extremely bright stars illuminate a mist of PAHs in this Spitzer image

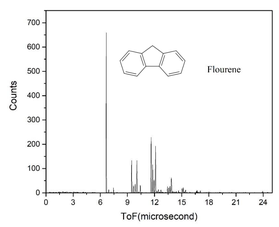
Experimental set up

- Radiation source (Nd:Yag laser), gas valve, interaction chamber, Mass and energy analysers are the main part of the set up
- Focussed laser light is allowed to interact with neutral molecules which are flooded in high vacuum
- Intact and fragment ions are mass analysed by ToF spectrometer
- Parallel plate energy analyser is included in the path of incoming particle so as to analyse the energy of ions
- Correlated detection of energy analysed fragment ion and its neutral counter part provides knowledge of various statistical evaporation channels of molecular ion.

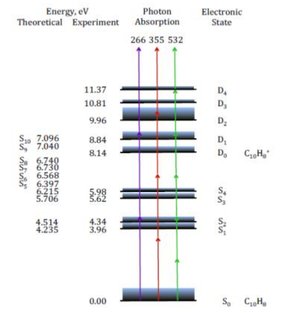


Dissociative ionization of PAHs by nonresonant absorption at 355nm





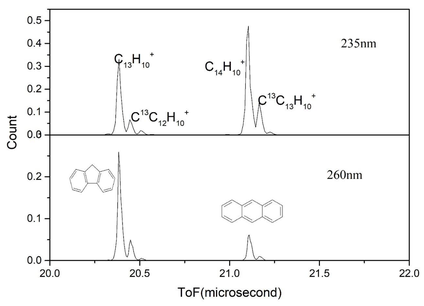
Experimental conditions:
Laser Intensity=$2x10^{10}$ W/cm^2
Energy/pulse=25mJ
Pulse width=5.5ns
Pressure=$2x10^{-7}$ mbar



Energies of excited states of nph

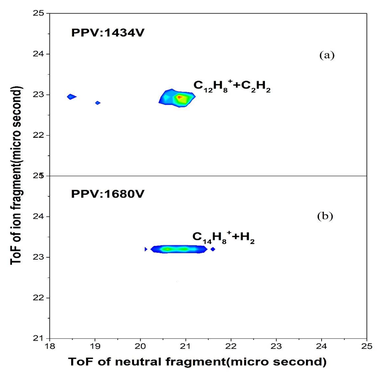
- CH_n^+,$C_2H_n^+$,$C_3H_n^+$ are the main fragment ions detected for all PAHs. Minor quantities of H^+ is also detected. But relative fragment yields are different for different molecules
- Laser intensities used in this experiment multiphoton absorption is the common process
- First, neutral PAH absorbs two 355nm (3.49eV) photons in sequence and access high vibrational level of electronic excited state S_4.
- This is a dissociative state and produce fragment ion. It further absorbs multiple photons and increase the ion current of smaller fragments like C^+
- . This type of fragmentation pattern is observed because of the higher laser intensity and the nonresonant absorption behaviour of PAH at 355nm

Resonant enhanced absorption and dissociation of PAHs at <270nm photons



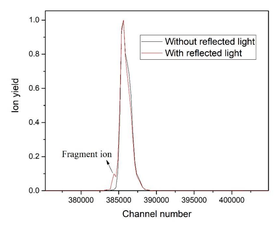
Experimental conditions:
Laser Intensity=$4x10^4$W/cm^2 (unfocussed beam)
Energy/pulse=15uJ
Pulse width=5.5ns
Pressure=$0.9x10^{-8}$ mbar

- At 235-270nm (5.3-4.6eV) PAH has resonant absorption
- Generally I.P of PAHs is ≈ 7-8eV,Neutral molecule can absorb two photons resonantly and ionize the molecule
- Formation of fragment ion is very sensitive to laser intensity, a small increment allows parent ion to absorb additional photons and dissociate
- Such dissociation channels is opened when focussed laser beam was used in the experiment.
- ToF of fragment ion was visible (which is fragmented in the acceleration region) in 1D ToF spectrum
- Delayed dissociation channels of anthracene ion (2Hand acetylene loss) are identified by analysing energy (mass) and ToF of fragment on.It is displayed in ion-neutral ToF spectra



Experimental conditions:
Laser Intensity=$2x10^8$W/cm^2 (unfocussed beam)
Energy/pulse=100uJ
Pulse width=5.5ns
Pressure=$0.9x10^{-8}$ mbar, wave length=235nm (focussed beam)
Compound:Anthracene

An attempt to activate the molecular ion using reflected laser pulse



- Reflected laser beam is used to heat the molecular ion further
- New fragmentation channels are opened
- More precise measurement of internal energy deposit of intact ion can be done using this method

References

[1]. Poveda et al J. Photochemistry and Photobiology A: Chemistry **215,** 140–146 (2010)
[2]. Van-Oanh et al J. Phys. Chem. A **110**, 5592-5598 (2006)