Plasmon assisted isomerisation in naphthalene and azulene

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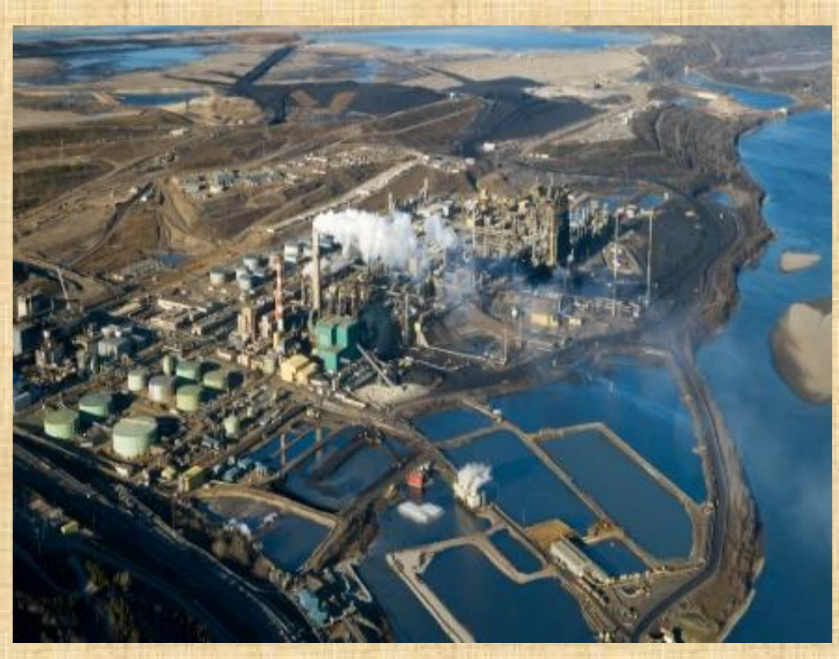
Motivation

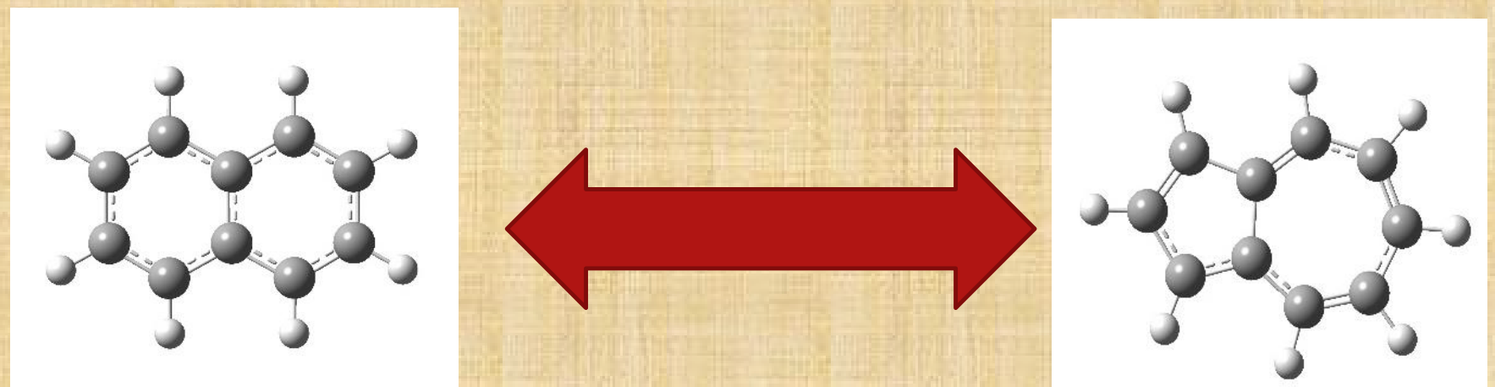
Two extremely bright stars illuminate a mist of PAHs in this Spitzer image (NASA/JPL-Caltech/2MASS/SSI/University of Wisconsin)



Terrestrial sources of PAHs: Industries and automobiles
http://blog.chemistry-matters.com

- Astrochemistry of ISM is a function of dissociative and isomerization processes in PAHs and their derivatives.
- Molecular dynamics of PAHs is a benchmark for several biologically important processes.
- 6 to 5 membered ring deformation is an important pathway of fullerene formation in ISM.
- Neutral elimination of PAH cations strongly depends on isomerisation.
- Azulene and Naphthalene are the simplest isomeric pairs with special attributes.
- Plasmon resonance as a dominant and constant energy loss mechanism in ion-PAH collision.

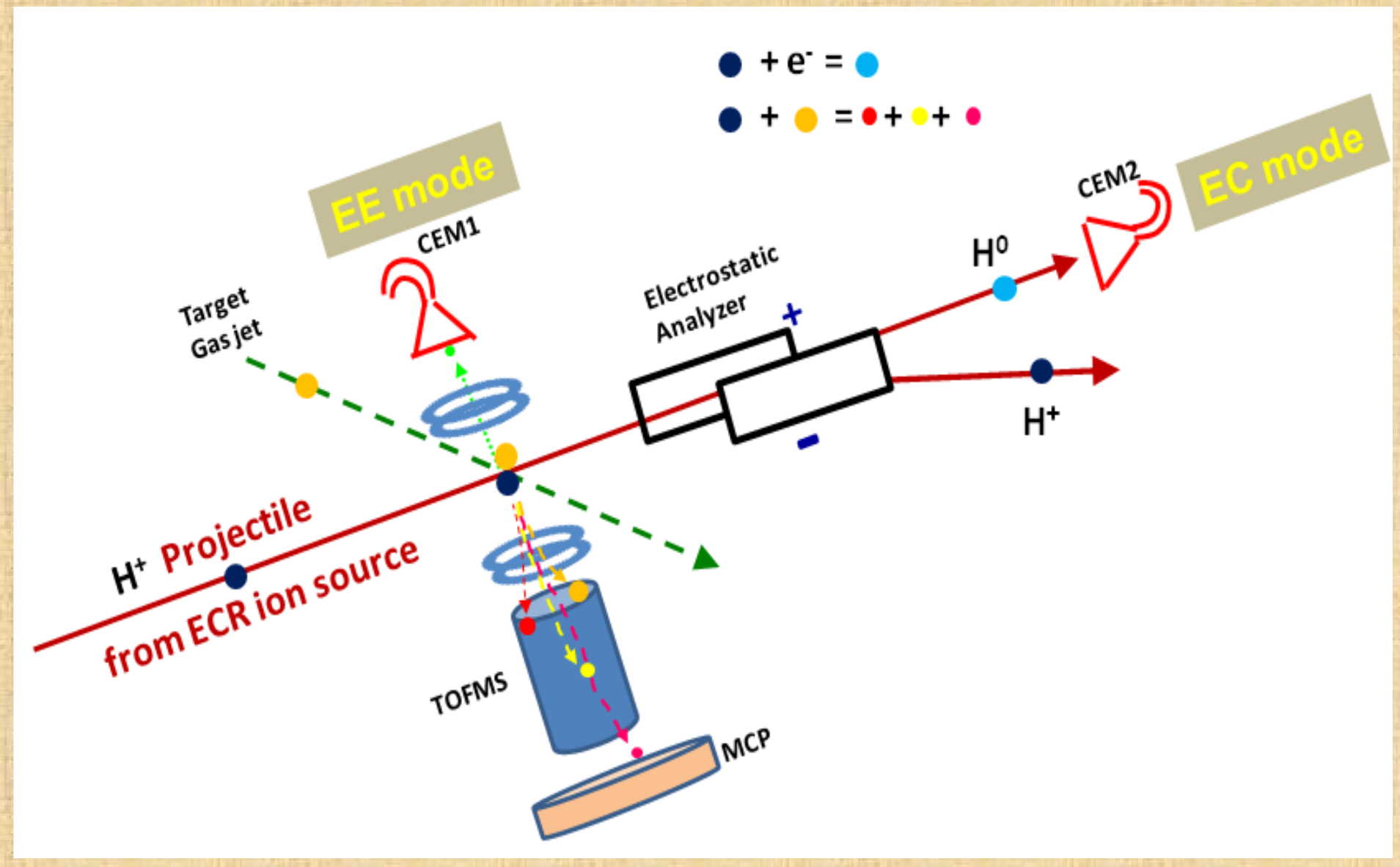
Isomerisation



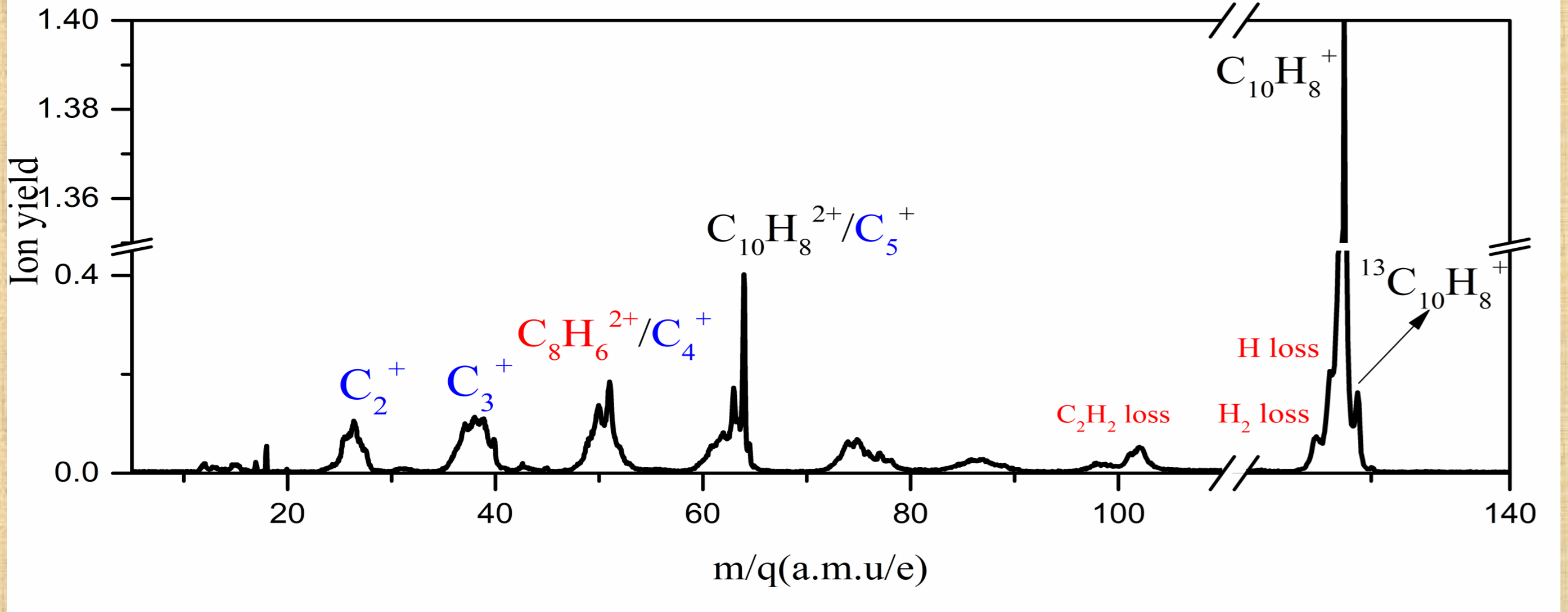
Naphthalene

Azulene

Experimental setup



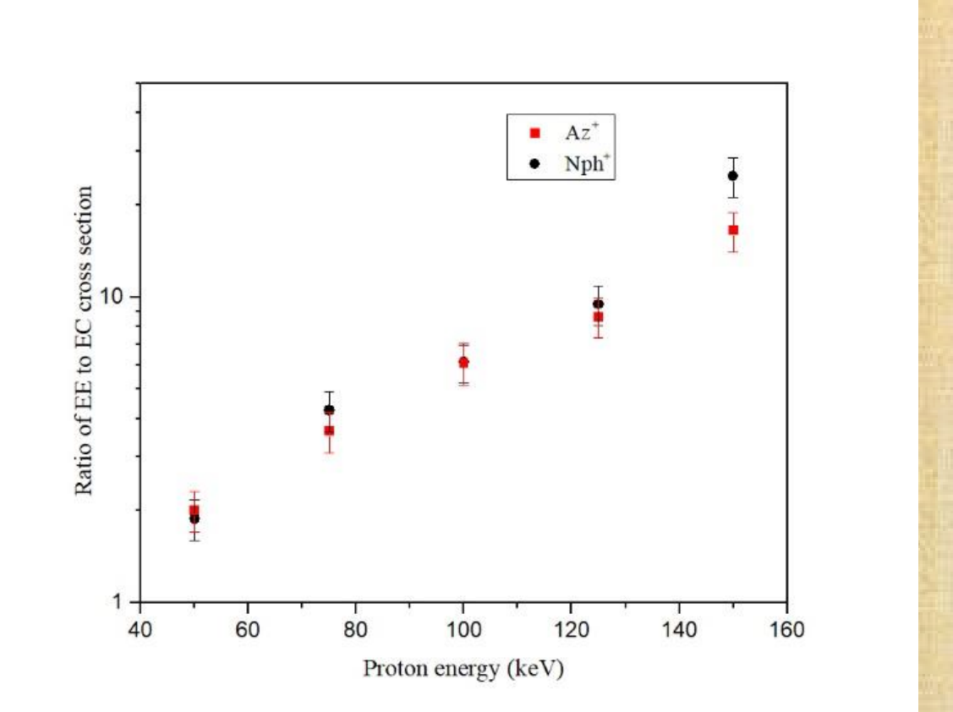
- Low Energy Ion Beam Facility, IUAC, New Delhi
- Energy of proton beam: 50 keV to 150keV (intermediate velocity).
- Target molecules:
  - Naphthalene ($C_{10}H_8$),
  - Azulene ($C_{10}H_8$),
  - Quinoline ($C_{10}H_7N$),
  - Iso-quinoline ($C_{10}H_8N$)
  - Fluorene ($C_{13}H_{10}$)
- Recoil ions were detected by a position sensitive MCP detector after extraction by a linear two field ToF mass spectrometer.
- Multi-hit coincidence measurement were done in both electron emission & electron capture mode.



Typical mass spectrum of Naphthalene (Nph)

- Sharp peaks show intact single or multiply charged parent ion and neutral evaporation peaks whereas small fragment mass peaks are poorly resolved.
- Multiple H loss is observed with decreasing order of yield.
- Dication yield is accompanied by mostly $2H/H_2$ loss.
- Dication is followed by strong C_2H_2 loss with again mostly $2H/H_2$ loss.
- Azulene shows almost identical spectrum but with relatively larger fraction of C_2H_2 loss from mono cation.

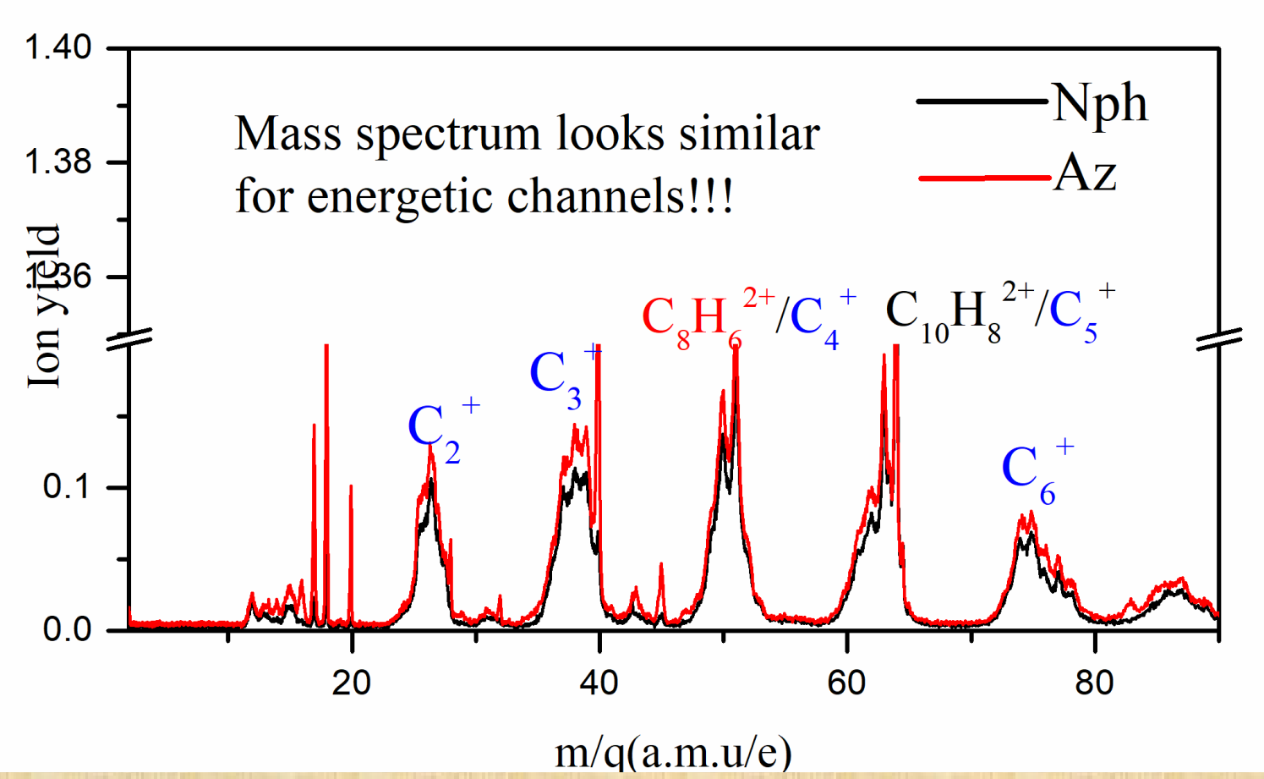
Electron emission & Electron capture cross sections of $C_{10}H_8$ isomers:

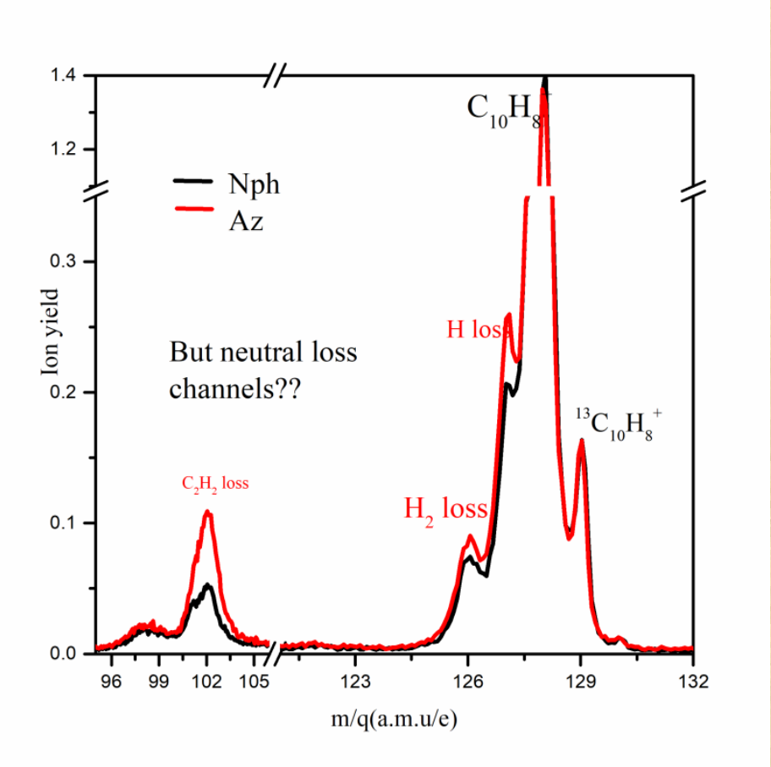


- ☐ Using correlated and coincidence measurements in EE, EC and CI mode detector efficiency could be obtained
- ☐ These efficiencies are then used to correct the individual peak yields.

- ☐ σ_{EE}/σ_{EC} is measured to be same for target isomers as well as for a range of proton energies
- ☐ For ion-PAH collision electron emission (EE) cross section is weakly dependent on the projectile speed and electron capture (EC) cress section shows a rapid decrease
- ☐ it is highly unlikely that two different molecules have same ratios of absolute cross sections unless their respective absolute values are equal.
- ☐ Collisional excitation in the intermediate velocity regime(1.41-2.41 a.u) of proton is related to electron density distribution, which will be similar in molecules
- ☐ Single ionization for naphthalene is known to be dominated by plasmon resonance hence we show that it is application to azulene as well

Similarities & differences in the mass spectra of $C_{10}H_8$ isomers ⇨ Isomerisation



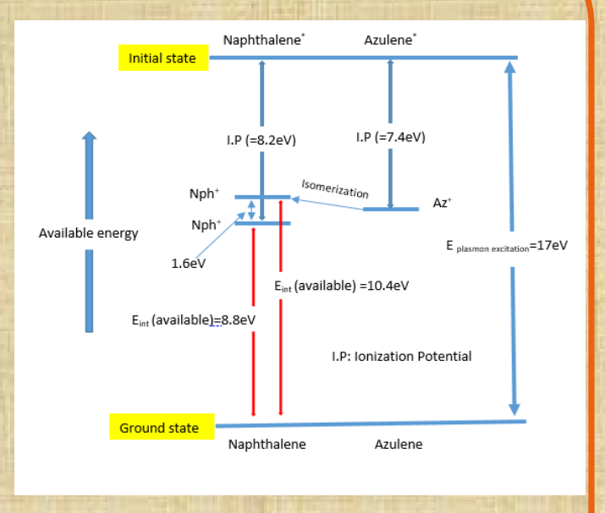


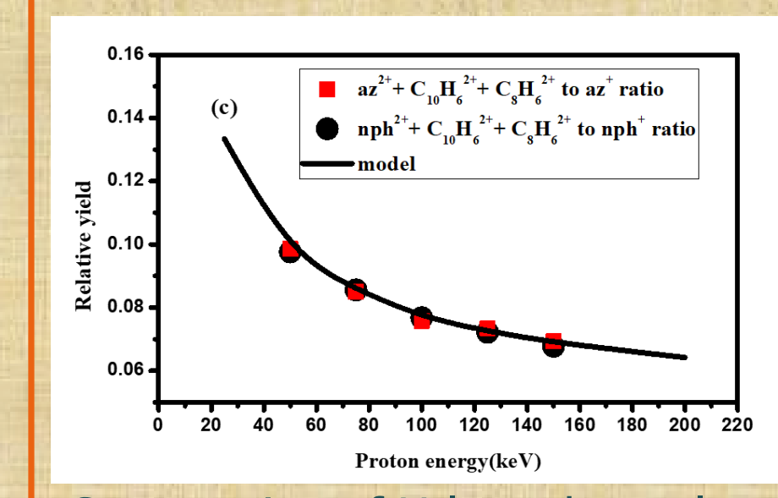
Results & discussions

- ☐ Smaller fragments produced via energetic reactions can come from equilibrium mixture of possible parent ions.
- ☐ For low energy reactions, isomerisation between cationic az and nph is a steady state reaction, which favours one direction.
- ☐ For a fixed energy excitation process (plasmon resonance at 16-17eV), $k(az^+) > k(Nph^+)$.
- ☐ As per Dykov's et al calculation, Az^+ isomerises to Nph^+ prior to dissociation.
- ☐ Internal energy of Nph^+ produced from Az^+ would have enhanced by isomerization and resulted a fast decay, it is conspicuous from the mass spectrum $E_{int}(az^+)-E_{int}(nph^+) = E_{iso} + IP_{nph} - IP_{Az} = 1.6eV$

Energy diagram: plasmon resonance and isomerization

- ☐ For Nph^+ ion formed after plasmon excitation, the internal energy can be calculated by considering the plasmon energy - adiabatic IP.
- ☐ For Nph^+ ion formed after isomerisation of Az^+, the internal energy can be calculated by considering the plasmon energy - adiabatic IP + isomerisation energy.

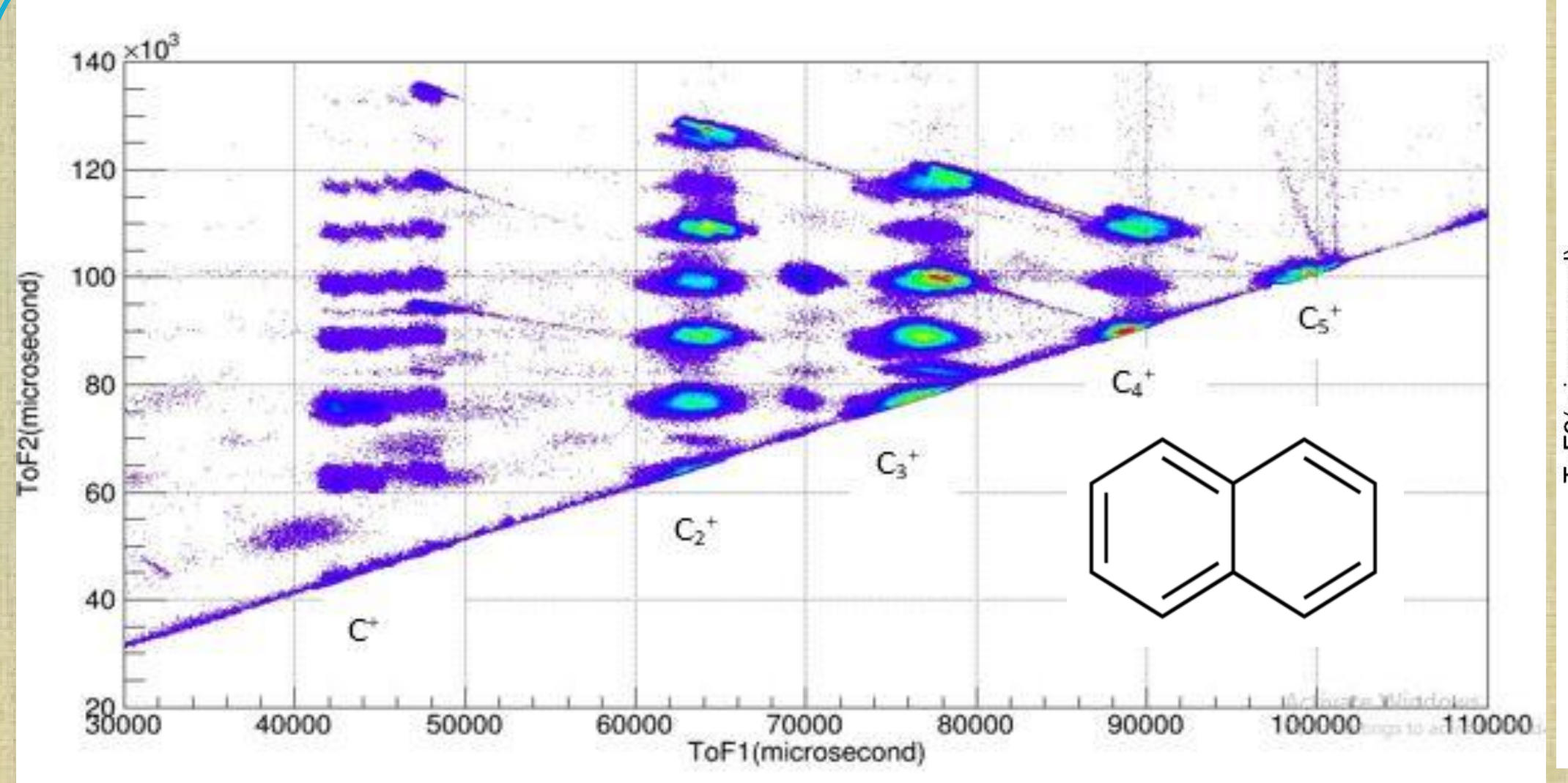


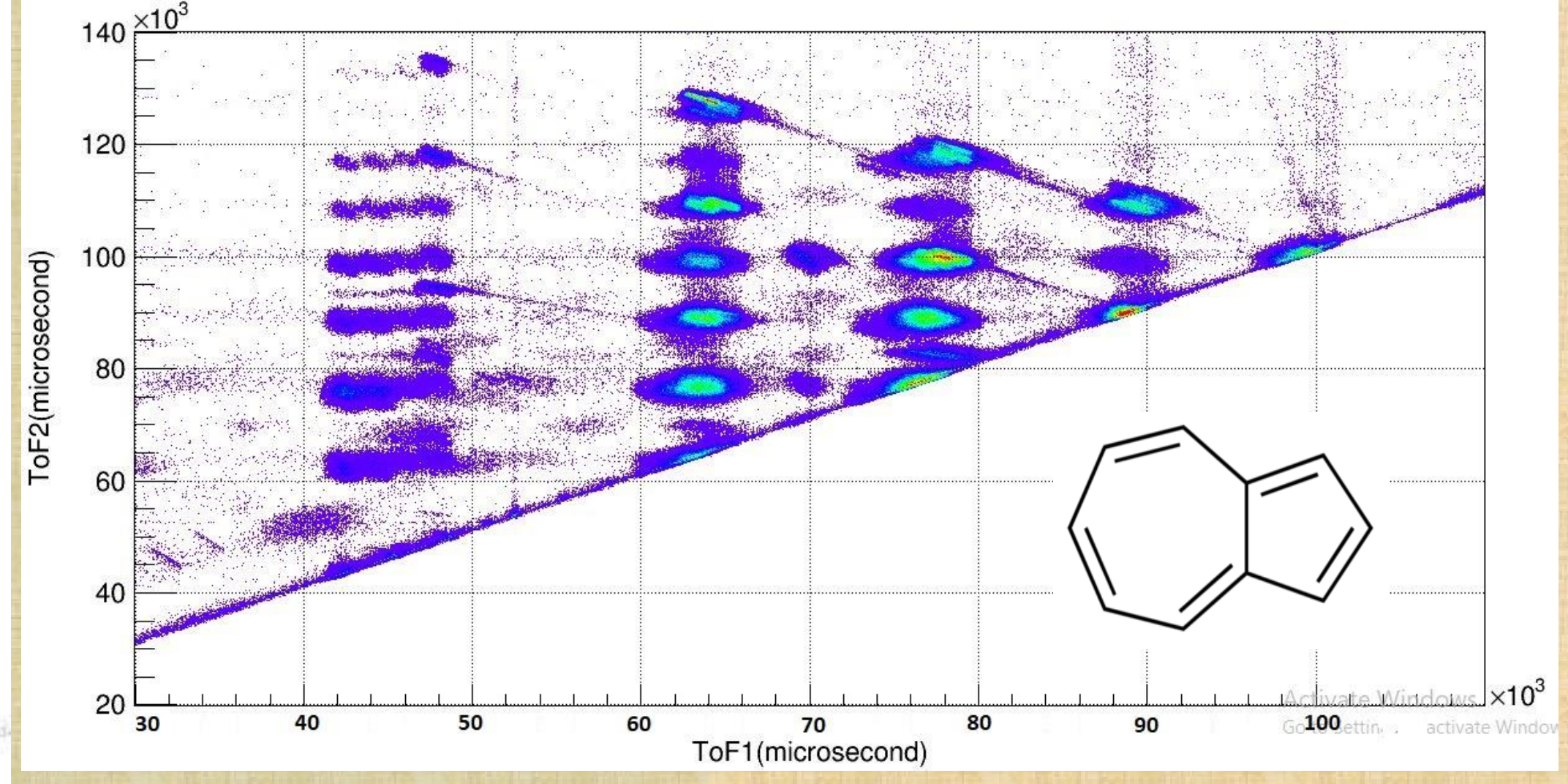


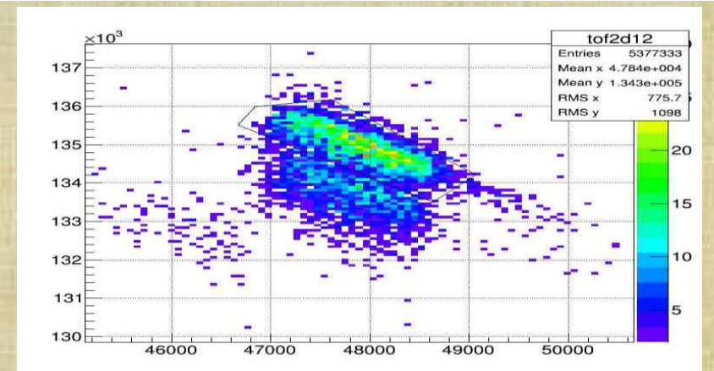
- ☐ Even the dication formation was observed to be sourced from double plasmon excitation.
- ☐ The relative cross sections of dication formation were well matched with double plasmon excitation model.

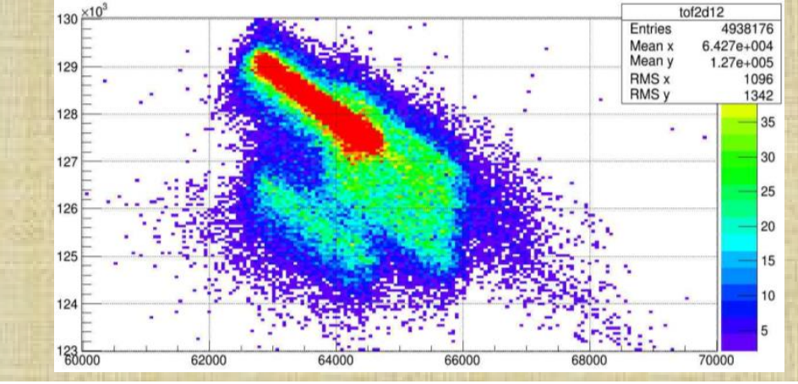
Suppression of H-loss channel seen in dication could also be addressed by double plasmon excitation. At the internal energy available of ≈13eV, the main evaporation pathway is $2H/H_2$ loss channel. Whereas H loss dominates at lower internal energies (7-8 eV).

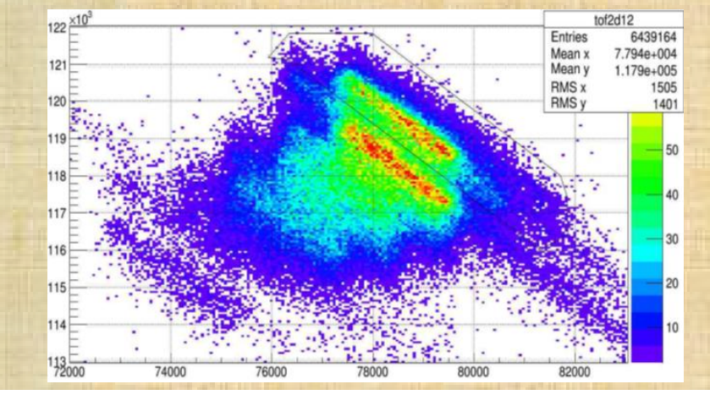
Ion-ion coincidence channels & KER values

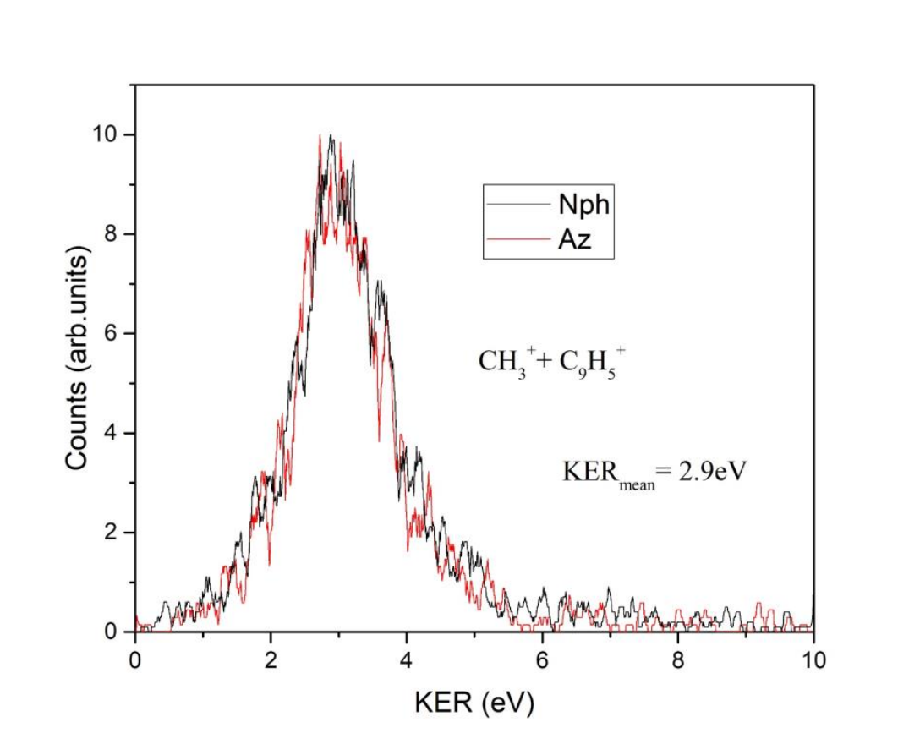


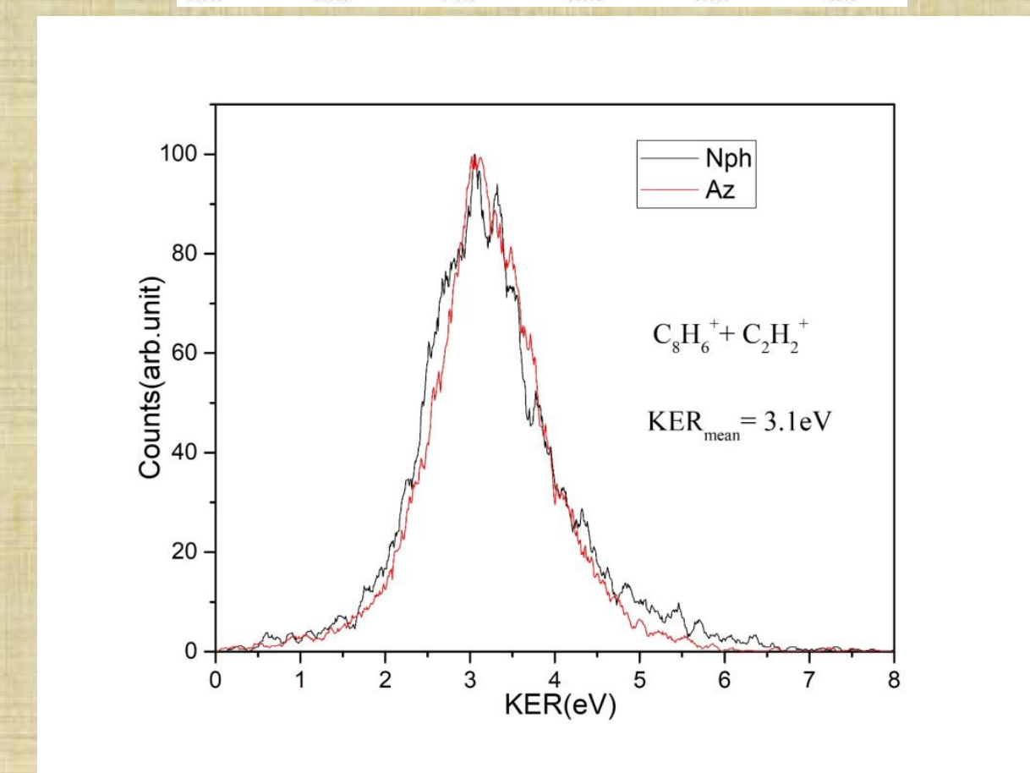


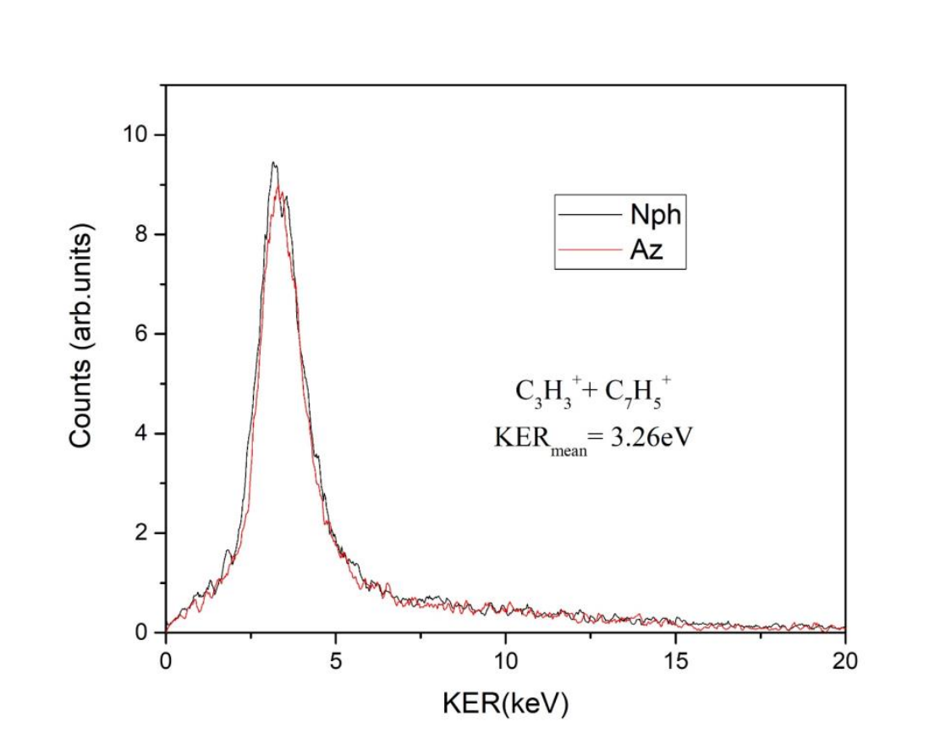


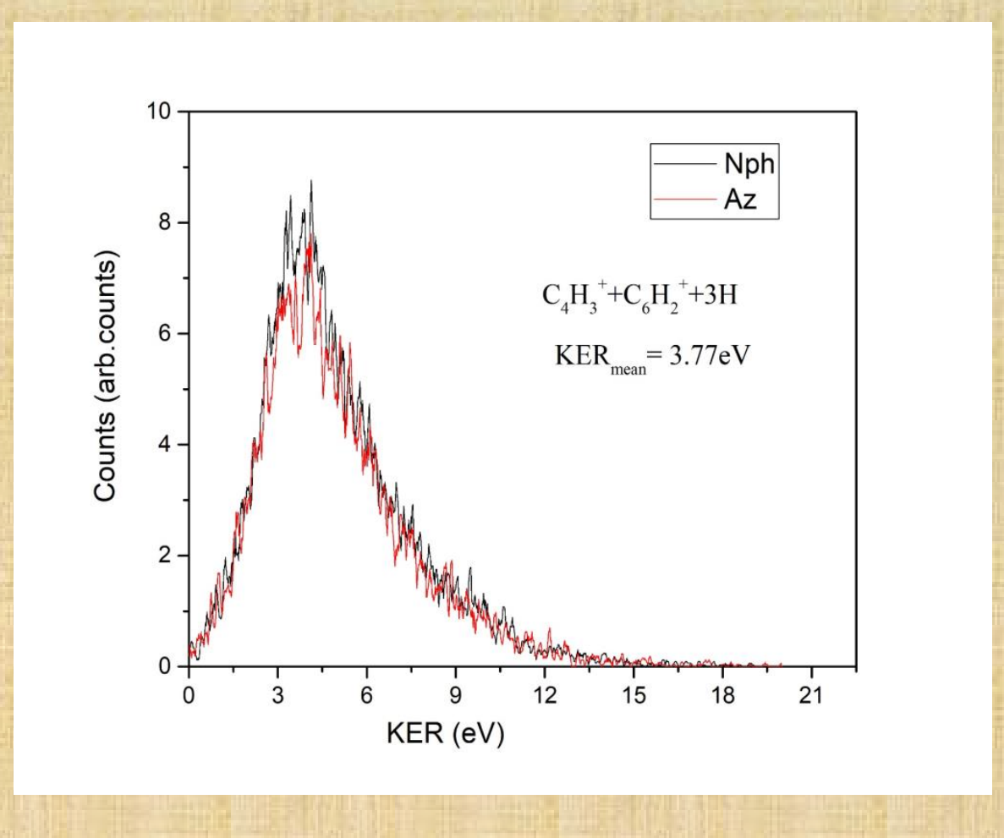












- **A remarkable similarity is observed between KER spectra of azulene and naphthalene.**
- **It indicates both molecules have same dication precursors in double product reactions.**
- **KER is measured upto 3.26eV for carbon conserving channels.**

References

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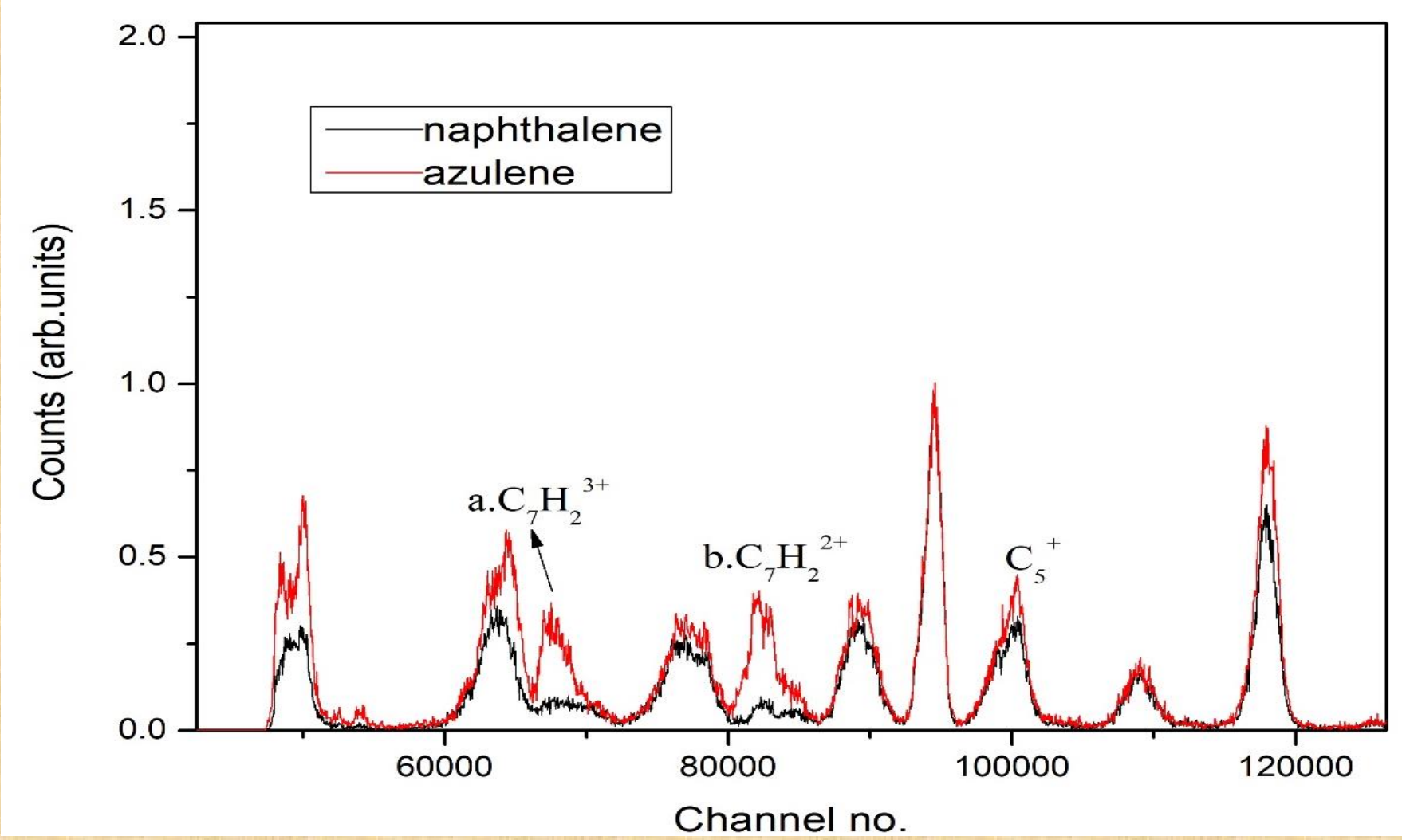
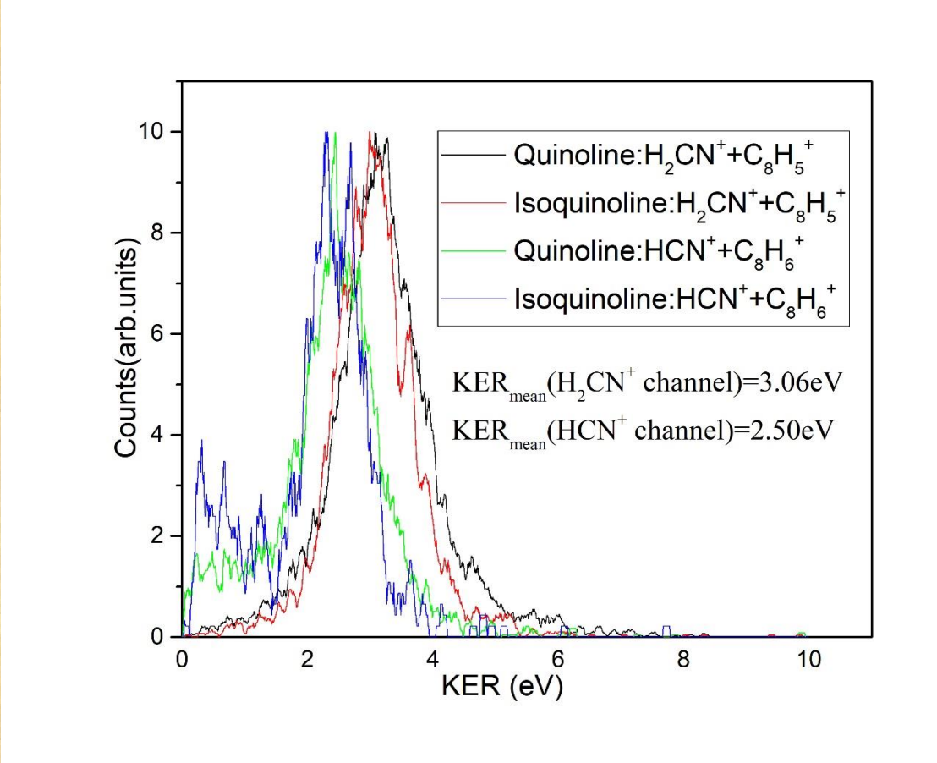
CH_3^+ emission channels of azulene and naphthalene



- ☐ Fragments a and b as indicated in the figure, is specific to azulene. Quadruply and triply charged products from azulene eliminate CH_3^+ and become stable in microsecond time scale



- ○ Identical KER spectra is obtained for quinoline and isoquinoline for the two binary channels.
- ○ Unlike other channels, HCN^+ emission has low KER component.
- ○ KER distribution of H_2CN^+ channel and $C_2H_2^+$ emission channel of $C_{10}H_8^{2+}$ are found to be identical.

KER spectra for PAH and PANH isomers for their binary fission channels

- ○ A remarkable similarity is observed between ion-ion correlation spectra of isomeric PAHs & PANHs.
- ○ Distribution of KER in the binary fission channels of isomeric PAHs and PANHs are measured to be identical.
- ○ Identical KER spectra is obtained for quinoline and isoquinoline for the two binary channels.

Results & discussions

- ○ KER is measured upto 3.26eV for carbon conserving channels.
- ○ In contrast to naphthalene certain triply and quadruply charged azulene ion have higher propensity to decay via CH_3^+ elimination.
- ○ Emission of H_2CN^+ from PANH dication is observed as one of the strongest channels among binary fission, corresponding molecule (amidogen) is a newly detected interstellar molecule.

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