# Identification and consolidation of decay hierarchy of statistical fragmentation network in aromatic molecules and their fragments

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**Synopsis** The internal-energy-dependent fragmentation of a systematically connected series of aromatic molecules and their ionic fragments is investigated using complementary ionization and dissociation methods. Energy-correlated time-of-flight measurements establish precursor–product relationships and resolve fragmentation pathways as a function of internal energy, including the subsequent dissociation of reactive ionic fragments that are difficult to study as standalone species. Moreover, consolidation is provided with the help of low electron impact and collision induced dissociation measurements and DFT calculations.

The identification of individual polycyclic aromatic hydrocarbons (PAHs) in the interstellar medium (ISM) remains challenging, particularly because many symmetric PAHs possess no permanent electric dipole moment and are therefore not readily accessible through conventional rotational spectroscopy. Laboratory studies of their ionization and fragmentation under different energetic conditions are consequently important for understanding the chemical evolution of aromatic species in space. A systematically connected series of aromatic molecules is investigated, from benzene and toluene to naphthalene, 1- and 2-methylnaphthalene, ethylnaphthalene, indene, and indole. This molecular progression enables the effects of ring fusion, alkyl substitution, and heteroatom incorporation on internal-energy-dependent dissociation to be examined. The molecules are subjected to complementary energetic conditions using electron-impact ionization (EI), 266 nm multiphoton ionization (MPI), and, for selected species, proton-impact ionization at the LEIBF facility, IUAC. EI measurements are performed using a commercial quadrupole mass analyzer, while MPI measurements employ a high-resolution energy-correlated time-of-flight mass spectrometer equipped with an electrostatic parallel-plate analyzer (PPA) [1].

The PPA separates ions according to their kinetic energies, allowing prompt and delayed fragmentation products to be distinguished. Systematic variation of the PPA voltage establishes precursor–product relationships and resolves internal-energy-dependent dissociation pathways. Although conceptually related to tandem mass spectrometry (MS/MS), the energy-correlated approach provides far superior selectivity in the identification of decay hierarchy. The method is applied not only to conventional molecular ions but also to the ionic fragments generated from them. Coupling the ToF platform to a collision cell further enables collision-induced dissociation (CID) of selected ionic fragments, allowing their subsequent fragmentation pathways to be investigated, including whether they preferentially undergo H or $H_2$ loss or eliminate larger neutral hydrocarbon fragments.

Hence, a key aspect of this work is the investigation of ionic fragments that may be chemically reactive and difficult to study as standalone species. By generating these ions from well-characterized molecular precursors and combining experimental measurements with DFT calculations, their subsequent dissociation can be examined to understand how molecular structure and internal energy govern the competing fragmentation pathways.

## References

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