Fragmentation dynamics of exotic ionic species derived from the toluene cation under CID

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Synopsis This study covers the dissociation dynamics of toluene cations. Moreover, it extends beyond the ionization and dissociation of toluene to probe the subsequent fragmentation of the ionic species it produces. Energy-correlated time-of-flight measurements establish precursor–product correlations, revealing new fragmentation channels and reassessing previously proposed pathways of the toluene ion.

The fragmentation dynamics of the toluene molecular ion are examined as a function of internal energy using 266 nm multiphoton ionization (MPI) and energy-correlated time-of-flight mass spectrometry, complemented by electron-impact ionization (EI). Under MPI, H loss is observed as the intense primary fragmentation channel. Its pronounced abundance points to an alternative ionization pathway beyond the conventional sequential multiphoton ionization picture, while comparison with EI provides additional insight into the energy dependence of the fragmentation.

Energy-correlated time-of-flight measurements performed under this study establish precursor–product relationships for primary and secondary fragmentation channels, revealing losses of C_4H_3, C_4H_4, and C_4H_5 that are not readily resolved in conventional mass spectra. Several competing pathways are found to converge on the same $m/z = 51$ product ion, revealing multiple routes to its formation. Under collision-induced dissociation (CID), the formation of $m/z = 89$ is identified as H_2 loss from $m/z = 91$, rather than H loss from $m/z = 90$, demonstrating the ability to distinguish competing dissociation pathways and identify preferential H_2 elimination.

The combination of MPI and subsequent CID further enables the fragmentation behaviour of reactive ionic species produced from toluene to be probed as a function of internal energy, even when these species are not readily available as standalone ions. Together with density functional theory (DFT) calculations, the measurements provide an interconnected fragmentation network and identify previously unrecognized pathways. The resulting products include $C_7H_7^+$, $C_6H_5^+$, $C_5H_5^+$, $C_4H_4^+$, $C_4H_3^+$, $C_4H_2^+$, and $C_3H_3^+$. These reactive hydrocarbon ions are of astrochemical interest because ion–molecule reactions can promote the growth of larger hydrocarbon ions and polycyclic aromatic hydrocarbons (PAHs), contributing to the chemical complexity of planetary atmospheres and interstellar environments [1–3].

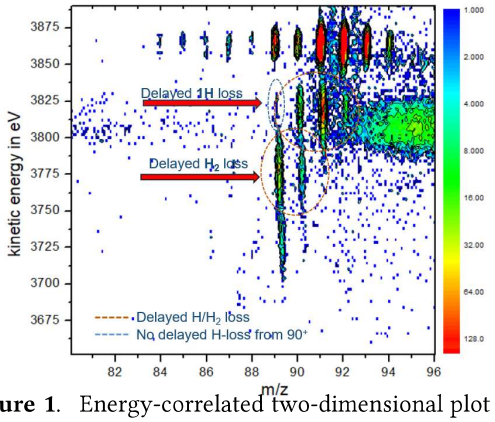

Figure 1. Energy-correlated two-dimensional plot of toluene in the $m/z = 94$–84 range, illustrating the progression of H- and H_2-loss fragmentation under MPI–CID.

References

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