

FORMATION OF THE ACENAPHTYLENE CATION AS A COMMON C₂H₂-LOSS FRAGMENT IN DISSOCIATIVE IONIZATION OF THE PAH ISOMERS ANTHRACENE AND PHENANTHRENE

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Polycyclic aromatic hydrocarbons (PAHs) are thought to be a major constituent of astrophysical environments, being the carriers of the ubiquitous aromatic infrared bands (AIBs) observed in the spectra of galactic and extra-galactic sources that are irradiated by ultraviolet (UV) photons. Small (2-cycles) PAHs were unambiguously detected in the TMC-1 dark cloud, showing that PAH growth pathways exist even at low temperatures. The processing of PAHs by UV photons also leads to their fragmentation, which has been recognized in recent years as an alternative route to the generally accepted bottom-up chemical pathways for the formation of complex hydrocarbons in UV-rich interstellar regions. Here we consider the C₁₂H₈⁺ ion that is formed in our experiments from the dissociative ionization of anthracene and phenanthrene (C₁₄H₁₀) molecules. By employing infrared pre-dissociation (IRPD) spectroscopy in a cryogenic ion trap instrument coupled to the free-electron lasers at the FELIX Laboratory, we have recorded broadband and narrow line-width gas-phase IR spectra of the parent (C₁₄H₁₀⁺) and fragment (C₁₂H₈⁺) ions and also reference spectra of three low energy isomers of the latter. By comparing the experimental spectra to those obtained from quantum chemical calculations we have identified the dominant structure of the fragment ion to be the acenaphthylene cation for both isomeric precursors^a. Ab initio molecular dynamics simulations are presented to elucidate the fragmentation process. This result reinforces the dominant role of species containing a pentagonal ring in the photochemistry of small PAHs.

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