

INFRARED SPECTROSCOPY OF THE CATIONIC –H FRAGMENTS OF METHYL-PAHS

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Cationic benzylum and tropylium are two competitive isomers formed by dissociative ionization of methylbenzene (toluene). Infrared predissociation (IRPD) spectroscopy of ions tagged with Ne has been established as a powerful tool in disentangling these cationic species^a. Methylated polycyclic aromatic hydrocarbons (PAHs) are expected to be abundant in space and their dissociative ionization could lead to the formation of both the benzylum- (XCH_2^+) and tropylium-like (XC_7^+) cations, which are expected to be the two lowest-energy isomers and whose isomerization process might impact their chemical evolution in photodissociation regions (PDRs). Here, we consider three methyl-PAHs as precursors, namely 1-methylpyrene, 2-methylnaphthalene, and 2-methylanthracene. Their cationic –H fragments, $C_{17}H_{11}^+$, $C_{11}H_9^+$, and $C_{15}H_{11}^+$, were probed at the Free Electron Laser for Infrared eXperiments (FELIX) Laboratory using IRPD spectroscopy at the FE-Lion cryogenic ion trap beamline. Their strongest vibrational band is located at about $6.2 \mu\text{m}$ revealing the predominance of the XCH_2^+ isomers^b. Isomer abundance measurements and spectral comparison to computed anharmonic IR spectra show that only this isomer is present for $C_{17}H_{11}^+$, whereas at least two isomers are present with a large abundance for the acene-derived species. Clear spectral evidence for the XC_7^+ isomer is found in the $C_{11}H_9^+$ case consistent with a relative abundance of 30 %. These results demonstrate the important role of steric hindrance in the formation of XC_7^+ and reveal the potential of XCH_2^+ to account for the aromatic IR emission band (AIB) observed at $6.2 \mu\text{m}$ in astrophysical environments, e.g. the planetary nebula NGC 7027 and the PDR at the Orion Bar.

^aJusko et al., *ChemPhysChem* 19 (2018) 3182

^bWenzel et al., *J. Mol. Spectros.* 385 (2022) 111620