Utilizing tunable vacuum ultraviolet light and resonance enhanced multiphoton ionization for isomer specific detection of polycyclic aromatic hydrocarbons from astrophysical ice analogues

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More than 200 molecules have been detected in the interstellar medium (ISM), but no polycyclic aromatic hydrocarbons (PAHs)—organic molecules consisting of fused aromatic rings—have been observed spectroscopically in the gas phase of the ISM. PAHs have been proposed to be the parent for up to 20% of the interstellar carbon budget, and have been linked to the astrobiological evolution of the ISM as well as possible nucleation sites for carbonaceous interstellar grains. Although many attempts have been made to study complex ice mixtures there is still a lack of understanding of the chemical complexity from individual ice constituents such as acetylene. Acetylene has been detected in the ISM, but not within ice mantles. However, the gas-phase abundance of acetylene was only able to be accounted for by models when sublimation from icy grain mantles was included. Furthermore, the processing of methane ice, a known ISM ice constituent, results in the formation of acetylene as a product. Also, acetylene ice has been firmly identified as an ice on the surface of Titan. We will discuss the results of processing pure acetylene ices at 5 K with energetic electrons, simulating secondary electrons formed via penetration of galactic cosmic rays through ISM ices. The ices were monitored in-situ via Fourier transform infrared spectroscopy (FTIR) and during heating via mass spectrometry utilizing a quadrupole mass spectrometer with an electron impact ionization source as well as a reflectron time-of-flight mass spectrometer coupled to a tunable photoionization source (PI-ReTOF-MS) used to do single photon ionization (SPI) as well as resonance enhanced multiphoton ionization experiments (REMPI) allowing for a comprehensive analysis of the products formed in the acetylene ice. The FTIR analysis detected several small hydrocarbon products while the extremely sensitive SPI-ReTOF-MS analysis identified products with general formulae: $C_nH_{2n+2}$, $C_nH_{2n}$, $C_nH_{2n-2}$, $C_nH_{2n-4}$, $C_nH_{2n-6}$, $C_nH_{2n-8}$, $C_nH_{2n-10}$, $C_nH_{2n-12}$, $C_nH_{2n-14}$, and $C_nH_{2n-16}$. These SPI studies at 10.49 eV revealed ion signals that might belong to aromatic molecules like benzene ($C_6H_6$; m/z = 78), and PAHs like naphthalene ($C_{10}H_8$; m/z = 128) as well as phenanthrene or anthracene ($C_{14}H_{10}$; m/z = 178) subliming from the irradiated ice. However, to confidently determine which isomers these signals belonged to SPI cannot be used as not enough information is known about the other isomers’ ionization energies, and instead REMPI was exploited. These REMPI experiments were able to confirm several astrochemically interesting molecules and PAHs. With the proof that tunable photoionization is an extremely useful and important tool for furthering our understanding of astrochemistry a new instrument coupled to a synchrotron is currently being assembled (Hefei-Shanghai-Hawaii Center for Astrochemistry).

Figure 1: PI-ReTOF-MS data reporting the temperature dependent mass spectra from irradiated acetylene ice at a photoionization energy of 10.49 eV.