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Ultrafast fragmentation dynamics of polycyclic aromatic hydrocarbons after photoionization at 30.3 nm wavelength

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Polycyclic aromatic hydrocarbons (PAHs) are abundant in the interstellar medium, and understanding their fragmentation dynamics upon exposure to cosmic background radiation sheds light on key processes that affect the structure and evolution of galaxies [1,2]. Cosmic background radiation, i.e. the He II fluorescence line at 30.3nm wavelength, ionizes PAH molecules and triggers a range of competing processes, including dehydrogenation, fragmentation, and isomerization.

Here we present a laser pump-probe study of the gas-phase photophysics of the three PAHs phenanthrene ($C_{14}H_{10}$), fluorene ($C_{13}H_{10}$) and pyrene ($C_{16}H_{10}$), using XUV-pump IR-probe spectroscopy with mass spectrometric detection at the free-electron laser (FEL) FLASH [3]. The molecules are ionized by femtosecond FEL pulses at 30.3 nm wavelength and the fragmentation dynamics of the ionized PAHs are then probed by femtosecond NIR pulses at 800 nm. We have measured the delay-dependent yield of the various ionic fragments, comparing our data to a rate-equation model.

The main product channels arising from the ionization step are singly and doubly ionized parent molecules. In addition, triple ionization and loss of one or more acetylene moieties (C_2H_2) is observed. Pyrene is observed to exhibit a smaller degree of acetylene loss than phenanthrene and fluorene, in line with previous results from synchrotron experiments at this wavelength [4].

In the pump-probe experiments, we observed a rapid decline of the doubly and triply charged parent-ion yield within 100 fs, while the ion yield of small fragments increased on the same time scale. We attribute this behaviour to fragmentation of the parent ions in the IR laser pulse. A few ion channels show an additional transient feature of ~100 fs duration, when the pump probe pulses are temporally overlapped, i.e. the triple ionized parent ion. This is similar to the observation made by Marciniak et al. using longer pump wavelength [5], which was attributed to short lived states populated in the cation.

We have developed a kinetic model for PAH fragmentation based on rate equations describing the interaction of the molecule with the two laser pulses. The observed delay dependence in the experimental data is well reproduced using the known laser pulse durations and pulse energies and an estimated lifetime of the involved excited electronic state of the dication. To our knowledge this is the first estimation of the lifetime of excited states in doubly ionized PAHs.

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