ELECTRONIC SPECTROSCOPY OF HYDROGENATED CARBON CLUSTER ISOMERS

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Highly unsaturated $C_x H_y^+$ clusters are important in combustion and the chemistry of interstellar space. However, interrogating carbonaceous molecules containing more than 10 carbon atoms is complicated by the coexistence of different isomers possessing unique spectroscopic properties. To disentangle this complexity, we have developed an apparatus that allows formation and selection of a particular $C_x H_u^+$ isomer population by ion mobility and mass to charge ratio. The selected ions are then incarcerated in a cryogenically cooled ion trap and subjected to tunable radiation. Resonant excitation of an electronic transition leads to cluster fragmentation, which when monitored as a function of wavelength yields an action spectrum. We have also measured electronic spectra for a variety of $C_x H_y^+$ ions, which are formed by photoionizing and photodissociating PAHs in the ion source. The $C_x H_y^+$ clusters can be linear or cyclic, but can be selected by their ion mobility arrival time and mass to charge ratio. Pyrene photoproducts include $C_{2n+1}H_3^+$ and $C_{2n+1}H^+$ clusters. The $C_{2n+1}H_3^+$ clusters are mostly linear isomers with characteristic vibronic progressions of low frequency modes (see

Figure). $C_{2n+1}H^+$ clusters are shown to exist as linear and cyclic isomers that have distinct electronic spectra. These results provide clues on how different $C_xH_y^+$ cluster isomers form, dissociate, and isomerise in interstellar space, and provide spectroscopic fingerprints to aid their astronomical detection.