CATION FAR INFRARED VIBRATIONAL SPECTROSCOPY OF POLYCYCLIC AROMATIC HYDROCARBONS

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The far infrared (FIR) region is crucial for spectroscopic investigations because of the existence of skeletal modes of moderately sized molecules. However, our knowledge of FIR modes is significantly lacking, largely due to the limited availability of light sources and detectors in this spectral region. The technique pulsed field ionization zero kinetic energy electron spectroscopy (PFI-ZEKE) is ideal for studies of FIR spectroscopy. This is because the low internal energy of the cation associated with the skeletal modes is particularly beneficial for the stability of the corresponding Rydberg states. In this work, we report our effort in studies of FIR spectroscopy of cationic polycyclic aromatic hydrocarbons (PAH). Using laser desorption, we can vaporize the non-volatile PAH for gas phase spectroscopy. To ensure the particle density and therefore the critical ion density in prolonging the lifetime of Rydberg electrons, we have used a chamber-in-a-chamber design and significantly shortened the distance between the desorption region and the detection region. From our studies of catacondensed PAHs, we have observed the emergence of the flexible waving modes with the increasing length of the molecular ribbon. Pericondensed PAHs, on the other hand, have shown significant out of plane IR active transitions. The planarity of the molecular frame is therefore a question of debate. The FIR modes are also interesting for another reason: they are also telltales of the precision of modern computational packages. The combination of experimental and theoretical studies will help with the identification of the chemical composition of the interstellar medium. This effort therefore directly serves the missions of the Spitzer Space Observatory and more importantly, the missions of the Herschel Space Observatory.