LOST AND BOUND: UNDERSTANDING THE ELECTRON DETACHMENT PATHWAYS OF THE TETRACENYL ANION ISOMERS

COLE R SAGAN, ETIENNE GARAND, *Department of Chemistry, University of Wisconsin–Madison, Madison, WI, USA*.

Polycyclic aromatic hydrocarbons (PAH) are some of the most abundant complex molecules in the interstellar medium. In their anionic forms, these molecules can exist either as a radical anion or a singly deprotonated species. These deprotonated varieties have been proposed as key intermediates in the formation of much larger interstellar molecules such as C60. Previous work has used anion slow-electron velocity map imaging (SEVI) to study the naphthyl and anthracenyl anions and the corresponding neutral radical[a b]. Here, we extend this work to the larger tetracenyl anions and radical. For the 9-tetracenyl radical, we report an electron affinity value of 1.8457(5)eV which differs from the previously published result of 2.6(2)eV[c], but is more consistent with the values for the smaller deprotonated PAHs. We also report the first anion photoelectron spectra of 1 and 2-tetracenyl isomers, yielding electron affinity values of 1.623(2) and 1.547(2) eV, respectively. Interestingly, the ordering of electron affinities of these isomers differs from the anthracenyl radical. The most active vibrations in these spectra involve displacements near the deprotonation site. In order to explain high intensity of very low kinetic energy electrons in multiple SEVI images, we have acquired the action photoelectron spectra of the 9-tetracenyl radical. This spectrum reveals an anion excited state about 2000 cm^{-1}above the detachment threshold with peak widths that suggest lifetimes on the order of 4.5ps. The primary pathway to detachment from this anion excited state is via thermionic emission, in agreement with previously published results. Implications for possible detection in astrochemical data will be discussed.

---

[a] J. Am. Chem. Soc. 2015, 137, 4, 1420–1423

[b] PNAS February 16, 2016 113 (7) 1698-1705

[c] Phys. Chem. Chem. Phys., 2015,17, 32464-32471