Are the carriers of the UIR bands aromatic or aliphatic? Gas phase infrared spectroscopy of polycyclic aromatic hydrocarbons (PAHs) and of their monomethyl derivatives

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The unidentified infrared emission (UIE) features at 3.3, 6.2, 7.7, 8.6, and 11.3 μm are commonly attributed to polycyclic aromatic hydrocarbons (PAHs). Recently, however, Kwok & Zhang (Nature 2011, 479, 80) have ascribed these features to mixed aromatic–aliphatic organic nanoparticles (MAONs). Li and Draine (ApJL 2012, 760, L35) estimated the aliphatic fraction of the UIE carriers to be <15% based on the observed intensities of the 3.4 μm and 3.3 μm emission features by attributing them to aliphatic and aliphatic C–H stretching modes, respectively. This estimate assumed $A_{3.4}/A_{3.3} \approx 0.68$ based on a small set of aliphatic and aromatic compounds.

Here, we report the results of theoretical studies of the ratio $A_{3.4}/A_{3.3}$ to improve the estimate of the aliphatic fraction. We studied benzene, napththalene, anthracene, phenanthrene, pyrene, perylene, and coronene, and all isomers of their monomethyl derivatives with density functional theory (DFT) and second-order perturbation theory (MP2) and with various basis sets from 6-31G* to 6-311++G(3df,3dp). Direct comparisons are made to gas phase quantitative infrared spectra whenever possible. The theoretical level dependencies are discussed of the computed IR intensities, and especially of the ratio $A_{3.4}/A_{3.3}$, and methods for intensity scaling are described. The study suggests that the $A_{3.4}/A_{3.3}$ ratio is well over 1.5 and, hence, it is concluded that the UIE emitters are predominantly aromatic (>95%).