Semi-Empirical Methods for Vibrational Spectroscopy

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Polycyclic aromatic hydrocarbons (PAHs) have been hypothesized as the carriers of the unidentified infrared bands since the early 1980s. These bands are a set of ubiquitous infrared spectral features found in virtually all kinds of astronomical environments. Their ubiquity makes them very appealing targets for investigation since any insight into their spectra can shed light on chemical and physical conditions in the environments where they are observed in space. However, their tendency to aggregate into soot makes them very difficult to isolate experimentally, and their great size makes them impossible to study with high-level theoretical methods such as coupled cluster theory. As such, previous theoretical work has turned to harmonic frequencies that are then scaled to approximate fundamental frequencies. Custom semi-empirical methods in which the parameters are optimized to reproduce higher-level theoretical results offer an alternative that is even faster than density functional theory, while also representing a substantial increase in accuracy. This work presents the first set of such parameters, optimized for computing anharmonic vibrational spectra of PAH and PAH-like molecules.