Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supplementary information for "Vibrational spectra of polyatomic molecules assisted by quantum thermal baths"

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In this supplementary material, we show an application of the QTB method for the linear IR absorption spectrum of a series of large polycyclic aromatic hydrocarbons (PAHs), in their ground vibrational state. The potential energy and dipole moment surfaces are obtained using the same tight-binding potential as used for naphthalene. Here we have chosen a set of four molecules larger than naphthalene and containing 4, 7, 10, and 19 aromatic cycles. The QTB and subsequent microcanonical simulations were performed under the same computational conditions as used for naphthalene. The IR spectrum is represented below in the same spectral regions already considered for naphthalene in the main text. More bands arise due to additional degrees of freedom and to lower molecular symmetries. The

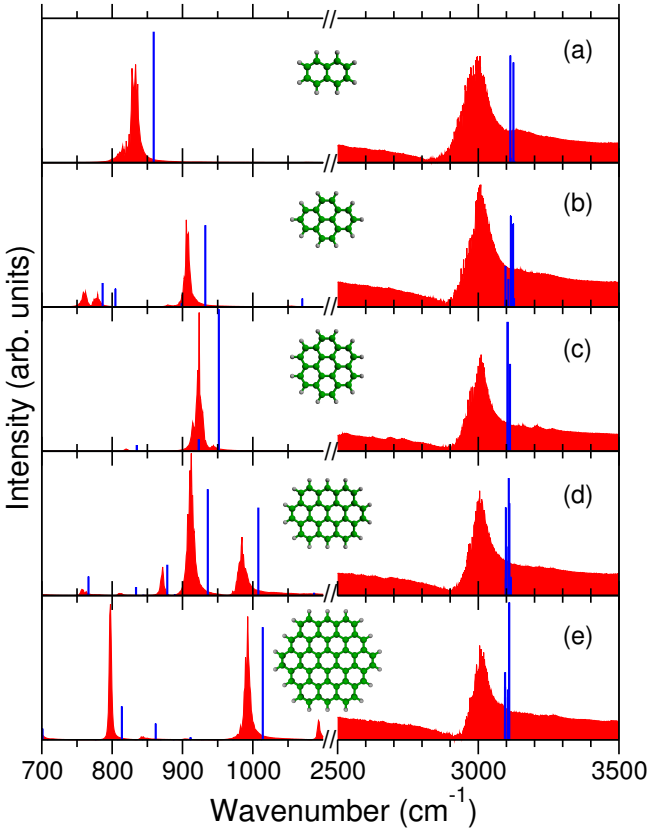

FIG. 1: Fundamental spectra at $T = 0$ of various polycyclic aromatic hydrocarbons obtained from microcanonical molecular dynamics initiated from quantum thermal baths (red lines). The static harmonic spectrum is indicated by blue vertical lines. (a) Naphthalene; (b) Pyrene; (c) Coronene; (d) Ovalene; (e) Circumcoronene.

C-H stretching band is again approximately redshifted by 100 cm^{-1} relative to the harmonic frequency, and acquires a width higher than 40 wavenumbers. The out-of-plane bending modes are also redshifted by a few percents with broadenings in the range 5–10 cm^{-1}. The shifting and broadening effect do not appear to vary significantly with the PAH size, albeit a minor decrease in both the position and width of the C-H stretching band can be discerned.