

565a Computation of the Vibrational Spectra of Hydrogen-Bonded Aggregates in Solution Using Multiscale Modeling Approaches

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Fourier-transform infrared spectroscopy is a popular method for the experimental investigation of hydrogen-bonded aggregates, but linking spectral information to microscopic information on aggregate distribution over different sizes and architectures is an arduous task. Unfortunately, the long lifetimes and the size and architecture distributions that characterize these hydrogen-bonded aggregates make direct *ab initio* simulations unfeasible. Thus, multi-scale modeling approaches are used here to elucidate the vibrational spectra of 1-hexanol aggregates in dilute solutions in n-hexane. The computations consists of (i) large-scale Monte Carlo simulations to generate an ensemble of aggregate structures and of (ii) static electronic structure calculations with an implicit solvent model or Car-Parrinello molecular dynamics simulations to compute the vibrational spectra for selected aggregates. The computed spectra show that there is no simple relationship between peak shift and aggregate size nor architecture, but the effect of hydrogen-bond cooperativity is shown to differentiate polymer-like (cooperative) and dimer-like (non-cooperative) hydrogen bonds in the vibrational spectrum. Furthermore, it is shown that common molecular mechanics force fields greatly underestimate the vibrational peak shift due to hydrogen bonding.