

Terahertz Absorption Spectroscopy: A New Experimental Probe of Collective Vibrational Motions in Solvated Proteins

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Biological polymers are expected to exhibit functionally relevant, global and sub-global collective modes in the terahertz frequency range (*i.e.* picosecond timescale). In an effort to monitor these collective motions we have experimentally determined the absorption spectra of solvated bovine serum albumin (BSA) and hen egg white lysozyme (HEWL) from 0.3 to 3.72 THz ($10 - 124 \text{ cm}^{-1}$). The density of vibrational modes in the spectrum of solvated BSA increases monotonically over the observed frequency range. In contrast the terahertz spectrum of HEWL increases monotonically until leveling off above 2 THz, a discontinuity predicted by previously published normal mode and MD calculations. We see no evidence of distinct, strong features in the spectra of either protein, suggesting that no specific collective vibrations dominate either protein's spectrum of motions. Instead, in the regions of monotonic rise the shapes of the observed spectra closely resemble the ideal quadratic spectral density expected for a disordered ionic solid, indicating that the terahertz normal mode density of the solvated proteins may be modeled, to first order, as that of a three-dimensional elastic nanoparticle with an aperiodic charge distribution. Nevertheless, the observed frequency dependencies differ in detail from that of a disordered inorganic solid or the normal mode densities predicted for several smaller proteins. The techniques employed here and measurements have the potential to experimentally confront theoretical calculations on a frequency scale that is important for macromolecular motions in a biologically relevant water environment.