THZ SPECTROSCOPY AND DFT MODELING OF INTERMOLECULAR VIBRATIONS IN HYDROPHOBIC AMINO ACIDS

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Vibrations that involve intermolecular displacements occur in molecular crystals at frequencies in the 0.5-5 THz range ($\sim$15-165 cm^{-1}), and these motions are direct indicators of the interaction potential between the molecules. The intermolecular potential energy surface of crystalline hydrophobic amino acids is inherently interesting simply because of the wide variety of forces (electrostatic, dipole-dipole, hydrogen-bonding, van der Waals) that are present. Furthermore, an understanding of these particular interactions is immediately relevant to important topics like protein conformation and pharmaceutical polymorphism.

We measured the low-frequency absorption spectra of several polycrystalline hydrophobic amino acids using THz time-domain spectroscopy, and in addition we carried out DFT calculations using periodic boundary conditions and an exchange-correlation functional that accounts for van der Waals dispersion forces. We chose to investigate a series of similar amino acids with closely analogous unit cells (leucine, isoleucine, and *allo*-isoleucine, in racemic or pseudo-racemic mixtures). This allows us to consider trends in the vibrational spectra as a function of small changes in molecular arrangement and/or crystal geometry. In this way, we gain confidence that peak assignments are not based on serendipitous similarities between calculated and observed features.