VIBRATIONAL SELF-CONSISTENT FIELD CALCULATION AND TERAHERTZ SPECTRA OF VAL-ALA CLASS DIPEPTIDE NANOTUBES AND P-AAA IN CRYSTALLINE FORM.

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Harmonic and vibrational self-consistent field (VSCF) calculations implemented with the CHARMM22 program were conducted on the crystalline forms of paralle-alanyl-alanyl-alanine (p-AAA) and a series of dipeptide nanotube systems: l-alanyl-l-isoleucine (AI), l-isoleucyl-l-alanine (IA), l-alanyl-l-valine (AV) and l-valyl-l-alanine (VA). By utilizing periodic boundary conditions, the calculated spectra in the terahertz region (below 3 THz) were compared against the experimental terahertz spectra. We illustrate that the VSCF level of theory improved the calculations greatly as compared with harmonic level calculations. This work confirms that with VSCF implementation, the CHARMM 22 force field is sufficient and computational inexpensive to model terahertz spectroscopy of condensed and gas phase hydrogen-bonded systems. In addition, a normal mode analysis demonstrates the dynamical function of the dipeptide systems. In this case the hydrogen-bond torsions in the nanotube frames are important for the flexibility of the nanotube channel in order to accept guest molecules. Normal modes analysis also revealed a series of ”breathing” and ”deforming” motions which can open or deform the channels of the dipeptide systems to facilitate the entry of guest molecules. In particular, the lower frequency of the ”breathing” mode for AV with respect to other dipeptide systems may explain its exceptional stable behavior with flexible pores upon absorbance and removal of solvent molecules.