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Terahertz spectroscopy of solid serine and cysteine

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Abstract

Terahertz (THz) absorption spectra of the similarly structured amino acids L-serine and L-cysteine in the solid phase at 77 and 298 K are reported and compared to isolated molecule and solid-state infrared vibrational spectral calculations using empirical force field and density functional theory. These comparisons suggest that many higher frequency internal modes can readily be assigned but lowest frequency intermolecular and phonon modes can adequately be understood with more advanced solid-state theory using currently available potential functions.
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1. Introduction

Terahertz (THz, far-infrared) spectra exhibit absorptions that are characteristic of the three-dimensional arrangement and low frequency motions of the atoms in a molecule, but are also sensitive to the molecule's interaction with its environment. These low-frequency vibrations, typically between 0.5 and 6 THz (or 15–200 cm^{-1}) are dominated by non-covalent, intermolecular interactions such as electrostatic, Van der Waals, and hydrogen bonds. To explore the detailed contributions of hydrogen bonding in this region, we measured and modeled the THz spectra of two amino acids, serine and cysteine, which differ by only a single atom and have very similar molecular structures.

These two amino acids contribute significantly to the protein structure [1]. Cysteine is one of the most important amino acids since its thiol group forms disulfide linkages that play a major role in determining protein secondary structure. Serine is very similar to cysteine with the only difference being a hydroxyl group replaces the cysteine thiol group. Serine also plays an important role in protein structure determination since it readily forms two hydrogen bonds with other protein side groups. The essential nature of these amino acids was revealed in previous studies which investigated vibrational motions (not using THz) of these particular amino acids to identify protein secondary structures [2,3].

We have investigated the low-frequency vibrational motions of serine and cysteine in the solid-state by concentrating on the spectral region between 3 and 400 cm^{-1}, where crystal lattice vibrations and hydrogen bond bending modes occur. One finds that while the molecules are structurally very similar, they exhibit very different vibrational spectra and THz absorption frequencies. These differences are due primarily to the hydrogen bonding character of the thiol versus the hydroxyl groups within the crystalline lattice of these solid-state samples. The high frequency vibrational spectra of these molecules have been previously reported [4–7]. In fact, low-frequency infrared spectra of these and the other naturally occurring amino acid solids at 100 K have been published in a previous Letter [8], but our spectra exhibit slight frequency shifts and intensity variations when compared to that work. Additional low-frequency data is available in a recent inelastic neutron

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scattering study of L-serine [9]. In an effort to distinguish between internal vibrational modes of these species and external influences from the lattice, a set of anharmonic frequency and intensity calculations for the isolated species were conducted using gas phase density functional theory (DFT, commercially available GAUSSIAN03 software [10]), and related solid-state periodic boundary calculations using CHARMM [11] and CPMD [12] codes to compare to the experimental THz absorption spectra.

2. Experimental approach

Solid L-serine and L-cysteine (and analogous D-isomers) were obtained from Sigma–Aldrich, Inc. and ICN Biomedicals, Inc. [13] and re-crystallized from saturated aqueous solutions at room temperature. Pure serine and cysteine samples were maintained at 273 K in tightly sealed bottles until use to prevent decomposition or exposure to atmospheric water. Sample preparation and THz FTIR measurements were performed in a similar manner as in our earlier work performed on short-chain solid polypeptides [14]. Solid pellets of these samples were prepared by first mixing 10 mg of each amino acid with 100 mg of spectrophotometric grade high density polyethylene powder (Sigma–Aldrich, Inc.) and homogenizing the mixture in a mortar and pestle. This procedure ensured particle sizes sufficiently smaller than THz wavelengths to reduce baseline offsets at higher frequencies arising from non-resonant light scattering. Each sample was pressed as a pellet in a 13 mm diameter vacuum die at the lowest possible pressures (ca. 200 psi or 1.4×10^6 Pa) to minimize decomposition from pressure and transient heating. The 1.5 mm thick pellets have sufficient path length to eliminate etalon artifacts (3 cm^{-1} period) in the spectra. Sample pellets were mounted in an aluminum sample holder fixed in position with a Teflon securing ring for 298 K measurements. Pellets were also encapsulated in a brass fixture that adapts to the copper cold finger of a vacuum cryostat (Janis Research Company, Inc. model ST-100) [13] fitted with 3 mm thick high-density polyethylene windows for broadband 77 K far-infrared transmission studies.

Infrared absorption spectra in the 0.1–12 THz range were obtained using two instruments: (1) a modified Nicolet Magna 550 Fourier transform infrared spectrometer (FTIR) using a silicon-coated broadband beam-splitter and DTGS room temperature detector fitted with a high density polyethylene window [13], and (2) a femtosecond pulsed apparatus utilizing 100 fs pulses at 800 nm to directly generate and detect the THz electric field and spectrum (via Fourier transform) using 0.5 mm thick ZnTe crystals. The dry-air purged, globar source FTIR has sufficient sensitivity to generate high quality spectra in the 1.2–12 THz range for both room temperature pellets and samples contained in the low-temperature dewar placed in its sample compartment. All measurements made using the FTIR (after ca. 1 h of sample compartment purging to eliminate water vapor interference) were obtained at 4 cm^{-1} spectral resolution and averaging 64 interferometric scans. Similarly, lower frequency measurements with the pulsed laser spectrometer (0.1–3.0 THz) were made with a time-delay step size to provide 3 cm^{-1} of spectral resolution. All pulsed spectra were obtained in a dry-nitrogen purged box and are the result of averaging 16 scans of the THz electric field.

In a standard fashion, spectra were converted to optical density (OD) units after ratioing raw sample transmission spectra (T_{sample}) to that of a pressed 100 mg polyethylene blank (T_{PE}) disk ($OD = -\log_{10}(T_{sample}/T_{PE})$ obtained under identical acquisition conditions. As expected, it was also found that there is no observable spectral difference between the L versus D rotary conformers of purified samples of these particular amino acids. Absorption band intensities were also found to obey Beer's law as the amount of amino acid is varied in several pellet samples of the same thickness and weight. This indicates the observed absorption features directly arise from the amino acid rather than pellet anomalies. Since the absolute THz absorption intensity is concentration dependent and difficult to quantify, the uncertainty in infrared optical densities (OD) was estimated to be less that 10% by comparing multiple spectra for the same molecule in different pellets (Type B uncertainty, $k = 1$).

3. Theoretical spectral calculations

In order to better understand the origin of the absorption features observed in our experimental spectra, a complementary series of calculations were performed to extract a picture of the intramolecular and intermolecular vibrational modes for these samples. Obtaining both accurate vibrational mode frequencies from properly minimized structures and extracting infrared intensities throughout the THz spectral region is crucial when comparing experimental observations to theory. Here, isolated gas phase calculations for the energy minimized structures (GAUSSIAN03) are directly compared to CHARMM and CPMD full solid-state calculations which describe the unit cell and crystal lattice vibrations using periodic boundary conditions derived from starting X-ray structures. Sample inhomogeneities that potentially yield varying spectral feature widths are not included in these models.

3.1. GAUSSIAN03

Isolated gas phase models of crystalline L-serine and L-cysteine using GAUSSIAN03 [10,13] with harmonic (L-cysteine only) and anharmonic frequency corrections for both species were performed using DFT and the B3LYP 6-31G* basis set.

3.2. CHARMM

The calculation of the terahertz vibrational spectrum of L-serine and L-cysteine was accomplished using the

CHARMM 22 empirical force field [11,13]. The method used is similar to the previous work of Gregurick et al. [15] for the calculation of the vibrational spectrum of small peptides and sugar molecules [16]. For both amino acids, the crystallographic coordinates were used as the starting structure for the calculations [17–22]. In order to represent the crystal environment of the experimental work, we constructed a pseudo crystal lattice comprised of single unit cells. The larger crystal was then reproduced by using periodic boundary conditions in all calculations. We first optimized the geometry of the crystals using a Adopted Newton Raphson method until the gradient change was less than 0.00001 kcal/mol. Then, using steepest descent method, we gently optimized the structure further to ensure an energy minimum, whereby all eigenvalues of the mass-weighted Hessian were positive (see Table 1).

The THz vibrational frequencies were obtained from the normal mode eigenvalues of the mass-weighted Hessian. The intensities of each normal mode were calculated from the dipole derivatives as given by the following formula:

$$I_i(v) = \left| \sum_{j=1}^{3N} \frac{\partial \mu_i}{\partial r_j} X_{ij} \right|^2, \quad (1)$$

where the sum is over all 3N coordinates, represented as r_j and the X_{ij}'s are the corresponding eigenvectors derived from the diagonalization of the mass-weighted Hessian. The dipole derivatives were calculated numerically from the displacement of the equilibrium structure along each normal mode direction. Eq. (1) yields only the height of the intensity, thus in our computed spectrum we represented each peak as a Gaussian function with a FWHM corresponding to 20 cm^{-1}. We note that our calculated spectra are strictly at the harmonic level. All calculations were performed on a UNIX-based silicon-graphics dual processor system taking about 15–30 min per simulation.

3.3. CPMD

We also preformed separate DFT calculations on the crystal structures of each amino acid using the program CPMD, version 3.9.2 [12]. For L-serine the calculations utilized the crystal structure coordinates [17–22]. However, to save a little CPU time, the L-cysteine amino acid calculations utilized the minimized structure output of CHARMM. For these calculations we created a super cell with four molecules per cell and then applied periodic boundary conditions to recreate a larger crystal lattice. The one-electron orbitals were expanded in a plane wave basis set with a kinetic energy cutoff of 80 Ry restricted to the Gamma point of the Brillouin zone. Medium soft norm-conserving pseudo potentials of Martins–Trouiller were used for all the elements [23]. The energy expectation values were computed in reciprocal space using the Kleinman–Bylander transformation [24].

In order to calculate the intensities of each normal mode, we allowed the system to propagate for a total time of 5 ps by applying ab initio molecular dynamics using 600 a.u. for the fictitious mass of the electron in the two systems studied. In these cases, we used a time step of 5 a.u (0.12 fs) and recorded positions and charges of each atom at every step. We calculated the total dipole moment at each step of the ab initio molecular dynamics using the Berry phase polarizability [25]. The IR intensities were computed from the auto correlation of the dipole magnitude followed by taking the Fourier transform [26]. Again, we have represented each peak as a Gaussian with a FWHM corresponding to 20 cm^{-1} which closely mimics the observed experimental widths. CPMD calculations were performed on a multi-node LINUX cluster using 4–8 nodes and took approximately 2–3 weeks for the optimization and frequency calculations. The molecular dynamics simulations used to extract dipole derivative intensities required several months of computation for each species.

Table 1
Experimentally observed vibrations of L-serine and L-cysteine[a]

L-Serine frequencies (cm^{-1})	L-Cysteine frequencies (cm^{-1})
363	381
295	302
255	226
150	206
114	172
98[a]	154
90[a]	97
85[a]	80[a]
74[a]	71[a]
67[a]	56[a]
	46[a]

Values reported are from the FTIR spectrometer unless otherwise noted.
[a] Frequencies observed with pulsed laser spectrometer.

4. Results and discussion

The experimental THz absorption spectra of L-serine and L-cysteine spanning 50–400 cm^{-1} obtained with the FTIR instrument are compared and shown in Fig. 1. These spectra were recorded at both room temperature and 77 K (as indicated). Lower and overlapping frequency THz spectra (3–100 cm^{-1}) obtained with the pulsed laser spectrometer are similarly shown in Fig. 2. A direct comparison between the spectra obtained for these solid amino acid systems emphasizes that several sample absorptions occur at different terahertz frequencies. In both cases, spectra recorded at 77 K exhibit sharper resolution features than those taken at room temperature (278 K), but these do not shift appreciably in frequency or change considerably in peak amplitude as a function of temperature.

It is clear that the hydrogen bonding character and strength of thiol versus hydroxyl groups is different noting, for example, that at standard temperature and pressure, H_2O exists as a liquid while H_2S is a gas. In addition, there is strong evidence from X-ray crystallographic [17–20] and neutron diffraction [21,22] data that the crystal structures of serine and cysteine are substantially different. These facts indicate that hydrogen bonding and other interactions

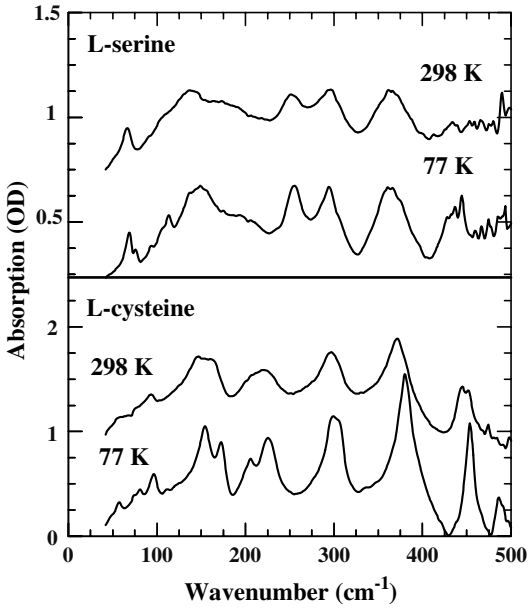

Fig. 1. Terahertz spectrum of L-serine (top panel) from 50 to 400 cm^{-1} at room temperature and 77 K. The upper, room temperature trace is offset by 0.5 OD units for clarity. Spectra of L-cysteine from 50 to 400 cm^{-1} at room temperature and 77 K (bottom panel) where the upper, room temperature trace is offset by 1.0 OD units for clarity.

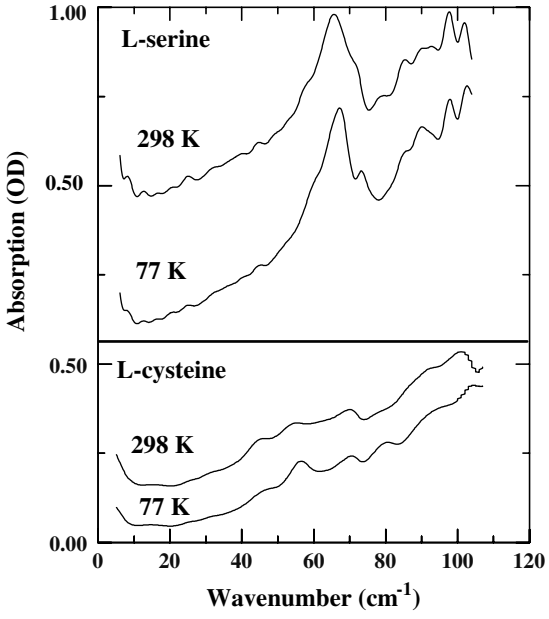

Fig. 2. Lower-frequency, terahertz spectra of L-serine (top panel) from 3 to 100 cm^{-1} at room temperature and 77 K. The upper, room temperature trace is offset by 0.4 OD units for clarity. Spectra of L-cysteine from 3 to 100 cm^{-1} at room temperature and 77 (bottom panel) where the upper, room temperature trace is offset by 0.1 OD units for clarity.

within the solid structures should give rise to varying numbers of phonon modes in the THz region, as well as frequency shifts of internal molecular modes resulting from the change of mass from oxygen to sulfur.

In an effort to explore whether these differences manifest themselves in the respective THz spectra, we first performed several gas phase isolated molecule harmonic and anharmonic DFT calculations [14] to determine if the mass change from S to O in similar structures for these species gives rise to frequency and absorption changes in the modeled spectra. The results of these calculations are in qualitative agreement with previous theoretical studies [27–32]. We emphasize that in ours and previous calculations, all solid-state interactions are omitted. As can be seen and compared in Fig. 3, the calculated spectra show similar higher frequency absorption structure and relative intensities as the experimental data. The similarity between the strong absorptions above 200 cm^{-1} for the calculated and experimental spectra (especially for the L-serine anharmonic calculation) strongly suggests that these absorptions arise from internal degrees of freedom of the molecule. There is also indication that one or more of the higher frequency modes shift to lower frequency as the atomic mass of the pendant OH versus SH group increases (e.g., the 250 cm^{-1} absorption for serine appears to occur at 225 cm^{-1} for cysteine). From these results, we suggest that the higher frequency THz spectrum provides evidence for effects largely due to the mass change of the molecular species. However, at frequencies <250 cm^{-1}, both the calculated harmonic and anharmonic isolated molecule vibrational spectra for L-cysteine do not correlate well with the measured spectrum. The anharmonic frequency calculation for L-serine appears to be better matched to the experimental result while for cysteine, intermolecular and lattice interactions omitted in the model may sufficiently perturb its structure to shift the absorption frequencies relative to the calculated free-molecular structure. Another

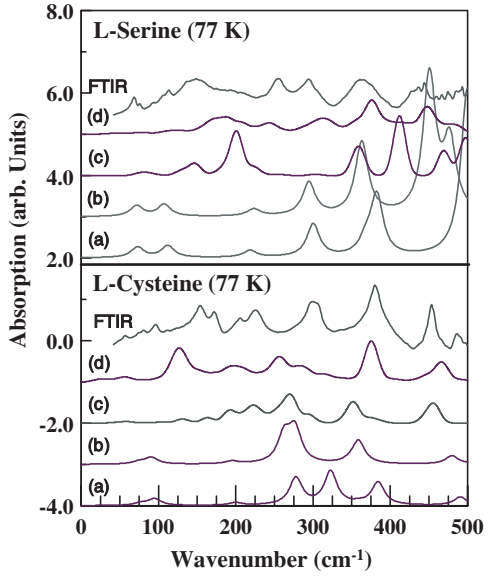

Fig. 3. Comparison of the experimental 77 K absorption spectra (FTIR) and calculated gas phase spectral models of crystalline L-serine and L-cysteine using GAUSSIAN03 [17] with (a) harmonic and (b) anharmonic frequency corrections for both species applying DFT with the B3LYP 6-31G* basis set. Results for solid-state periodic boundary calculations using (c) CHARMM and (d) CPMD are included (see Section 4).

possibility is that available molecular potentials for SH-containing species are not adequately refined to model crystalline vibronic motions that occur in the low frequency THz spectral range. Further comparisons between experiment and theory are clearly indicated to better understand the origin of the different features obtained from the experimental spectra.

We must emphasize that in general, relatively straightforward isolated molecular modeling using DFT approaches cannot provide clear insight into the details of the spectral structure observed below about 200 cm^{-1} where phonon and crystal lattice mode absorptions are expected to contribute. DFT methods have been successfully applied to crystalline samples where no strong intermolecular interactions or hydrogen-bonding exists (e.g., azobenzenes, dicyanobenzenes). It is still possible, however, to examine the predicted isolated molecule atomic motions associated with the lowest energy calculated modes from DFT theory. The corresponding modes for both L-serine and L-cysteine, shown in Fig. 4, encompass motion of all the atoms in each structure. One may be convinced that there is absorption intensity in the respective experimental spectra arising from these internal motions (sharp structure near 80 and 100 cm^{-1} in Fig. 3) but the lack of calculated intensity and higher density of absorption features between 100 and 250 cm^{-1} indicates the simpler model is insufficient to fully compare theory to experiment.

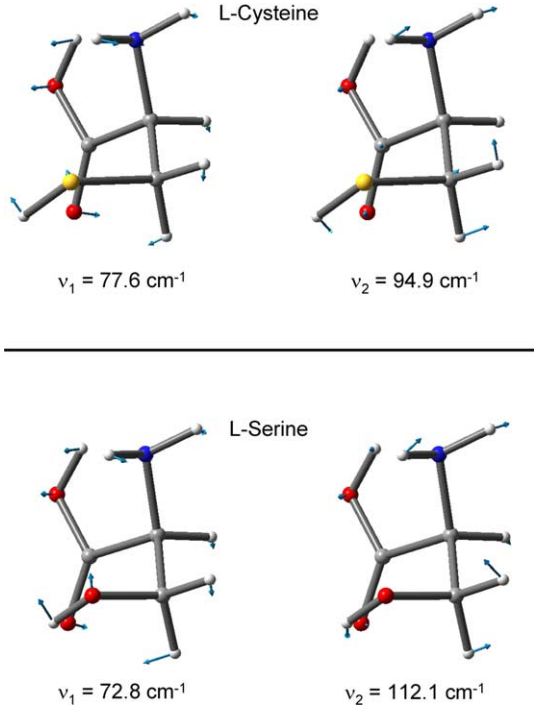

Fig. 4. Harmonic displacement vectors for the two lowest internal normal modes of vibration of L-serine and L-cysteine as predicted by DFT (B3LYP/6-31G*) theory. These equilibrium structures represent the lowest energy atomic coordinates calculated from theory. Atomic color code: gray (carbon), white (hydrogen), blue (nitrogen), red (oxygen) and yellow (sulfur). (For interpretation of the references in colour in this figure legend, the reader is referred to the Web version of this article.)

More refined modeling, using recently improved pseudo-potentials and DFT codes to calculate mode frequencies and intensities arising from crystal lattice periodicity and intermolecular interactions were therefore employed to gain confidence in low frequency THz spectral mode assignments. Results from rigorous and computationally intensive solid-state modeling studies using both CHARMM and CPMD codes described above are also included in Fig. 3 for comparison to experiment. In both cases, these theories use vastly different approaches (empirical potential functions versus DFT with molecular dynamics) but were run using the same starting crystallographic structures. The models do not include anharmonic, overtone or combination mode corrections and assume the lattice is at 0 K although temperature effects are included somewhat by broadening the line spectrum to the desired temperature. One readily finds that the CHARMM results for both systems reasonably agree with the frequency positions and intensities obtained from experiment. While there are minor shifts for features >300 cm^{-1}, they again agree very well with the Gaussian free-molecule results indicating they arise predominantly from internal molecular motions. The appearance of new features and closely corresponding absorption frequencies and intensities in the region below 250 cm^{-1} signifies that intermolecular interactions (hydrogen-bonding, IR-active phonon modes) are contributing to the spectral density. It is most striking that the two experimental doublet features centered near 160 and 205 cm^{-1} are very nicely reproduced in position and intensity by this modeling approach. It should again be emphasized that once an appropriate structural minimization was obtained that yields no negative eigenvalues for each species, these spectral calculations converged quickly (<30 min) for modeling the THz experiments.

Application of CPMD code to the same starting structures resulted in the simulations also depicted in Fig. 3. Again, the higher frequency intramolecular modes with larger intensities are simulated as well as the Gaussian and CHARMM approaches for both species. The serine result is remarkably similar to the experimental spectrum agreeing well in intensity and feature breadth throughout the < 250 cm^{-1} region. While the simulations yield significantly different-looking spectra (as expected and observed in experiments), there are clear inconsistent deviations between intensities and feature positions for the cysteine simulation in this same region (e.g., the doublet features are absent and an intense absorption at 125 cm^{-1} is not experimentally observed). The CPMD structure optimization and frequency calculations are exceedingly time consuming, but give reasonable results compared to experiments. While it is encouraging that employing the molecular dynamics charge-dipole Berry phase code with Fourier transform [21,25] yields reasonable infrared spectral intensities (n.b. this is the first known application of this approach for complex solid-state systems), the extremely long computation time required and somewhat poor

agreement for cysteine makes this approach less desirable than employing CHARMM at this time.

5. Conclusions

The low frequency THz vibrational spectra of solid serine and cysteine amino acids have been experimentally obtained and studied theoretically in detail. These molecules differ only by a single atom but the low frequency spectra exhibit very different absorption features. Spectral differences can be attributed to changes of the internal atomic masses and hydrogen-bonding character of the O–H versus S–H groups within the solid phase unit cell. These differences give rise to different intermolecular interactions and therefore the lowest frequencies reflect the different lattice vibrations resulting from the change in H-bonding strength between O–H and S–H. Similar strongly absorbing modes observed at higher frequencies (above 250 cm^{-1}) are attributed to internal molecular vibrational degrees of freedom. This conclusion was reached by comparing the experimental spectra to ab initio GAUSSIAN03 DFT calculations that yield close correspondence to the observed absorption frequencies. More rigorous and complete solid-state DFT and ab initio calculations with periodic boundary conditions for these systems were also performed to take hydrogen-bonding and intermolecular interactions within the crystal lattice into account and better model the experimental spectra in the THz frequency range. These novel results indicate that when applying solid-state modeling approaches that rigorously incorporate all intermolecular interactions, exceptionally good agreement with experiment ensues. Correspondance between a close fit theoretical spectrum and an experimentally obtained spectrum suggests that a more refined physical picture of the intermolecular and intramolecular motions is attained. At present, application of CHARMM force fields and methods appear to be adequate and computationally inexpensive (compared to CPMD) for these model complex hydrogen-bonded biosystems. We plan to further compare the theoretical results to other codes (e.g., VASP, AbInit) which also utilize periodic boundary conditions to model mode frequencies and estimate THz absorption intensities [33]. Improvements to include anharmonic effects are also underway [13,14,34] and the software suite will be applied to THz studies of carbohydrates and related peptide systems. Results from these and related studies (on trialanine systems) [35] will be reported and compared to the spectra of this work in a subsequent publication.

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