Terahertz Vibrational Modes of the Rigid Crystal Phase of Succinonitrile

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ABSTRACT: Succinonitrile ($N \equiv C - CH_2 - CH_2 - C \equiv N$), an orientationally disordered molecular plastic crystal at room temperature, exhibits rich phase behavior including a solid-solid phase transition at 238 K. In cooling through this phase transition, the high-temperature rotational disorder of the plastic crystal phase is frozen out, forming a rigid crystal that is both spatially and orientationally ordered. Using temperature-dependent terahertz time-domain spectroscopy, we characterize the vibrational modes of this low-temperature crystalline phase for frequencies from 0.3 to 2.7 THz and temperatures ranging from 20 to 220 K. Vibrational modes are observed at 1.122 and 2.33 THz at 90 K. These modes are assigned by solid-state density functional theory simulations, corresponding respectively to the translation and rotation of the molecules along and about their crystallographic *c*-axis. In addition, we observe a suppression of the phonon modes as the concentration of dopants, in this case a lithium salt (LiTFSI), increases, indicating the importance of doping-induced disorder in these ionic conductors.



INTRODUCTION

The molecular plastic crystal succinonitrile (SN) has been the subject of several studies for its possible use as matrix for ionic conductors,^{1–3} forming a solid-state electrolyte for use in power sources similar to polymer-based electrolytes.⁴ While the static and low frequency (<1 GHz) permittivities of succinonitrile (both in its pure form and with various ionic dopants) have been characterized,^{5,6} there have been no studies of succinonitrile in the far-IR (THz) range, especially in its lowtemperature rigid crystal phase. In addition, there is some ambiguity in the crystal structure of rigid crystal phase succinonitrile, with contradictory results from different X-ray powder diffraction measurements.^{7,8} Terahertz spectroscopy is an effective tool for probing the characteristic low frequency lattice vibrational modes of molecular crystalline materials, such as explosives,^{9–12} pharmaceuticals,^{13–15} and narcotics.^{16–18} Comparison of the measured THz absorption peaks to resonances predicted using solid-state density functional theory (DFT) allows for the assignment of the measured resonances to specific lattice vibrational modes in the crystal. The assignment of the modes helps to improve semiempirical corrections for London dispersion forces, corrections that are necessary to increase the accuracy of structural DFT simulations.¹⁹ Here, THz time-domain spectroscopy (THz-TDS) is used to characterize the lattice phonon modes of rigid crystal phase succinonitrile from 0.3 to 2.7 THz. The measured modes are compared to solid-state DFT simulations using semiempirical corrections for London dispersion forces.

METHODS

The succinonitrile samples, obtained from Aldrich chemicals with >99% purity and used without further purification, are prepared by melting the plastic crystal above its 331 K solid-toliquid phase transition onto a thick (3 mm) high-resistivity Si wafer with a Teflon spacer. The spacer thicknesses, which determine the optical path length for the terahertz beam in the sample, are 250, 100, and 25 μ m. An identical wafer is then placed on top of the molten sample, effectively sandwiching it between the two thick HR Si wafers to ensure a constant sample thickness and to prevent the sample's evaporation under vacuum due to its relatively high vapor pressure. The sample is then cooled slowly back to room temperature in a dry-air environment. Using this method, a polycrystalline solid is formed between the two wafers. The entire sample is larger than the diffraction-limited spot size of the THz beam, but individual crystallites within the polycrystalline solid are significantly smaller. Thus, the measurements are considered to be an average over all crystal orientations.

The samples are placed inside a Cryo-Industries RC-102 cryostat, which is situated at the focal point of a traditional transmission geometry THz-TDS setup.²⁰ A voltage-biased GaAs photoconductive switch combined with ultrashort pulses (80 fs, 800 nm) from a Coherent Mira Ti:Sapphire oscillator

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are used for THz generation. Parabolic mirrors and high resistivity Si lenses are used for beam collimation and focusing. THz pulses are detected via electro-optic sampling using a ZnTe crystal and balanced photodetection. Inside the cryostat, the sample is held under vacuum ($<1 \times 10^{-4}$ mbar), while outside the THz beam path is purged with dry N₂ to eliminate water vapor absorption lines from the spectrum. The samples are then cooled slowly (<1.5 K/min) through succinonitrile's plastic crystal to rigid crystal phase transition in order to prevent quenching the sample into an orientationally disordered glassy crystal phase. Using the complex transmission function (the ratio of the Fourier transforms of the THz timedomain waveforms transmitted through the sample and reference), the index of refraction, $n(\nu)$, and absorption coefficients, $\alpha(\nu)$, at each different temperature are extracted numerically using the Newton-Raphson method.²¹ With these sample thicknesses, solving for $n(\nu)$ and $\alpha(\nu)$ numerically is necessary since the analytic solutions for both the thick and thin film approximations introduce significant error.

The simulations in this work were performed using the CRYSTAL09 software package²² utilizing the B3LYP²³ density functional in combination with the atom-centered Gaussiantype pob-TZVP²⁴ basis set. The total energy convergence criteria were $\Delta E < 10^{-8}$ hartree for geometry optimizations and ΔE < 10⁻¹⁰ hartree for frequency calculations. All structural optimizations were performed without limits on atomic positions or unit cell dimensions, other than those imposed by space group symmetry, and were begun using starting structures obtained by experimental X-ray diffraction measurements. The radial and angular distributions for DFT integration were defined by a pruned (75,974) grid. Truncation tolerances for Coulomb and Hartree-Fock (HF) exchange integrals were defined as 10^{-8} , 10^{-8} , 10^{-8} , 10^{-8} , and 10^{-16} hartree (TOLINTEG command).^{22,25} A shrinking factor of 6 (64 kpoints in the irreducible Brillouin zone) was determined after sampling and monitoring of the total energy convergence as a function of k-point count in reciprocal space according to the Pack-Monkhorst method.²⁶ Normal-mode frequencies and infrared intensities were then calculated for the optimized structures. The frequency of each normal mode was calculated within the harmonic approximation by numerical differentiation of the analytical gradient of the potential energy with respect to atomic position.²⁵ The infrared intensities for each normal mode were calculated from the dipole moment derivatives $(d\mu/$ dQ) determined using the Berry phase technique of calculating Born charges as polarization differences between equilibrium and distorted geometries.^{22,27} Mode descriptions and assignments were made by visual inspection of the atomic displacements for each normal mode.

The explicit consideration of weak noncovalent interactions in molecular solids can be a significant factor in achieving valid simulations of crystalline structure and dynamics. London-type dispersion force corrections are important augmentations to include in solid-state DFT investigations since these forces are generally underestimated in commonly used density functionals but play an integral role in solid-state characteristics. The solidstate DFT approach used in this study has been supplemented with corrections for London-type dispersion forces, using a semiempirical method proposed by Grimme²⁸ and then later modified for the CRYSTAL program by Civalleri et al.²⁹ A global scaling factor (s6 value) of 0.43 was used in all simulations and was determined through comparison of the calculated unit cell parameters (*a*, *b*, *c*, α , β , γ , and volume) to the experimental 90 K X-ray diffraction data previously reported. 7

RESULTS AND DISCUSSION

Plotted in Figure 1 are the measured time domain waveforms, indices of refraction, and absorption coefficients for the two



Figure 1. (a) Time-domain waveforms of an empty cell reference (gray), SN in its plastic crystal phase at 294 K (red line) and in its rigid crystal phase at 90 K (black line) for the 100 μ m sample. (b) The indices of refraction (black) and absorption coefficients (red) at 294 K (dashed lines) and 90 K (solid lines) for the 100 μ m sample. The DFT predicted vibrational modes at 1.266 and 1.7105 THz are plotted as the gray vertical lines.

different solid phases of succinonitrile at 294 and 90 K for the 100 μ m thick sample. Succinonitrile's two solid phases have fundamentally different structures. Above its solid-solid phase transition at T = 238 K, succinonitrile's orientationally disordered yet spatially ordered plastic crystal (PC) phase has a bcc structure. The orientational disorder arises from the rotation of its central carbon-carbon bond, allowing for gauche-trans isomerization dynamics, while the molecules are spatially fixed in its crystalline lattice. Below T = 238 K, the orientationally ordered rigid crystal (RC) phase of succinonitrile has a monoclinic unit cell with primarily gauche conforming isomers.^{7,8} Not surprisingly, the THz spectra for the two separate phases are fundamentally different as well. In the PC phase, the behavior of its THz spectrum can be attributed to a Debye-like molecular reorientational process.³⁰ In the RC phase, this reorientational process is completely suppressed, leaving a relatively dispersionless spectrum with the exception of two Lorentzian-like absorption peaks centered near 1.122 and 2.33 THz at 90 K. A sample thickness of 100 μ m results in the best balance between the available dynamic range and the material's optical density, allowing for the observation of *both* phonon modes in the same spectra.

In Figure 2, absorption spectra of the low temperature RC phase are plotted for temperatures ranging from 90 to 210 K



Figure 2. Several $\alpha(\nu)$ spectra showing a redshift in peak frequency and broadening as the temperature increases (100 μ m sample). Each spectrum is offset by 60 cm⁻¹. The small features between the two dominant modes are not repeatable and are assumed to be spectral noise.

for the 100 μ m thick sample. We observe a significant red-shift in the center frequencies of both phonon modes as the temperature increases, an indication that both modes are soft, with anharmonic vibrational potentials. In addition, there is a continuous background absorption that increases approximately as a power of ν . Interestingly, the background absorption spectra resemble the spectra of amorphous, disordered materials like glass, for which the power law functionality of their absorption spectra can be used as a metric for disorder.³¹ In this case the background absorption and index can be fitted to the function $n(\nu)\alpha(\nu) = K(h\nu)^{\beta}$, where K and β are parameters, which are on the order of $10^5 - 10^7 \text{ eV}^{-2} \text{ cm}^{-1}$ and 2, respectively, for disordered materials such as polycrystalline quartz or amorphous silica in the THz range.³² This absorption dependence can be attributed to disorder-induced coupling of the radiation to Debye-like acoustic vibrational modes since their density of states exhibit an ω^2 dependence. Ignoring the absorption peaks, succinonitrile's absorption background does exhibit the same approximate dependence with $\beta = 2.03 \pm 0.03$ and $K = 9 \pm 5 \times 10^6 \text{ eV}^{-2} \text{ cm}^{-1}$. Further analysis of this continuous absorption background is hindered by the limited spectral bandwidth and the IR-active phonon absorption resonances. Nevertheless, the functionality of the measured background absorption may indicate the presence of amorphous, disordered regions in the samples. The smaller structures between the two phonon modes, which become more apparent at higher temperatures, are not repeatable spectral features between different samples and are most likely additional spectral noise caused by the polycrystalline nature of the samples and amorphous background scattering.

Figure 3 illustrates the relative temperature shift of each of the phonon modes' center frequencies, ν_c . As *T* increases, both center frequencies shift monotonically to lower frequencies; this confirms they are soft lattice phonon modes and their vibrational potentials are not harmonic. Interestingly, the higher frequency mode red-shifts at a slightly faster rate compared to its low frequency counterpart, indicating it has a greater vibrational anharmonicity compared to the lower frequency



Figure 3. $\Delta \nu_c$ vs *T* for both phonon modes relative to their lowest measured temperature ν_c and the corresponding linear fits to their average values. Adjacent to the fit lines are their slopes $(d\nu_c/dT)$.

mode. In addition, there is significantly higher scatter in the 2.33 THz phonon modes' measured ν_c between different sample path lengths and different cooling/heating trials. This scatter in the measured values of ν_c between samples also increases as T approaches the material's solid–solid phase transition temperature.

Given the interest in using this material as a solid host for an electrolyte through ionic doping, it is important to characterize the effect of doping on the crystal structure. Figure 4



Figure 4. Absorption spectra of pure and LiTFSI-doped SN with varying concentrations at 90 K, offset for clarity. Alternatively, in mole percentages (n/n%) the concentrations are 0.5 M = 3.9%, 0.35 M = 2.7%, 0.2 M = 1.6%, and 0.1 M = 0.8%. Each sample is 250 μ m thick. Inset: The infrared line intensities of the 1.1 THz vibrational mode vs LiTFSI concentration.

demonstrates the effects of an ionic impurity, in this case lithium-bis(trifluoromethanesulfonyl)imide (LiTFSI),¹ on the low temperature absorption spectrum of succinonitrile at 90 K. The Li salt is solvated at 0.1 M (0.8% (n/n)), 0.2 M (1.6% (n/n)), 0.35 M (2.7% (n/n)), and 0.5 M (3.9% (n/n)) concentrations into molten SN in a dry N₂ environment and then prepared in the same fashion as the pure SN samples with spacer thicknesses of 250 μ m. As the concentration of the lithium salt increases, the intensity of the 1.12 THz phonon

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mode decreases and is effectively suppressed for concentrations higher than 0.1 M. In addition, the absorption background increases when succinonitrile is doped with a Li salt, especially at higher frequencies. On the basis of these two factors, we conclude that the presence of an ionic dopant strongly affects the long-range order of succinonitrile's rigid crystal structure. Interestingly, the background absorptions do not exhibit any dependence on the concentration of the dopant, with $\beta \approx 2$ for all concentrations and erratically varying Ks. In this case many more measurements are necessary to determine if there is a statistically relevant trend in these parameters. The modes' linewidths, which theoretically could be a metric for residual disorder in the sample due to inhomogeneous broadening, do not increase with dopant concentration. Therefore, their origin is dominated by other effects. Because of the path lengths of the doped samples and the increased background absorption at higher frequencies, the THz signal was too strongly attenuated to observe the 2.33 THz mode in doped samples.

Since there are only two strongly absorbing modes in both the measured and predicted spectra, the two experimentally observed modes can be unambiguously assigned to the two modes predicted by the DFT calculations (1.2660 and 1.7105 THz). The low frequency mode corresponds to a correlated translation of the succinonitrile molecules along the crystallographic *c*-axis. There is a 13% error between the predicted ν_c of this vibrational mode and the measured value. The measured infrared intensity of the low frequency mode is 9.91 \pm 1 km/ mol at 90 K, while the predicted intensity is 1.13 km/mol. The higher frequency mode corresponds to a rigid correlated rotation of the succinonitrile molecules about the c-axis. For this mode, there is a 26.5% error in the predicted ν_{ci} a predicted intensity of 64.48 km/mol, and a measured intensity of 83 ± 50 km/mol. For only the higher frequency mode, there is a large disparity in the measured intensities between samples of different path length, which can not be attributed exclusively to error in the measured sample thickness. Figure 5 illustrates the relative motion of the molecules in a unit cell for both vibrational modes.

CONCLUSIONS

The THz vibrational modes of rigid crystal phase succinonitrile have been measured using THz-TDS and compared with the vibrational modes predicted using solid-state DFT simulations. The simulations, combined with the repeatability and continuous temperature dependence of the measured vibrational frequencies, supports the conclusion that there is only one stable low-temperature polymorph of succinonitrile, i.e., the 90 K structure as determined by Whitfield et al.⁷ The larger magnitude $d\nu_c/dT$ for the high frequency rotational mode suggests it has a greater vibrational anharmonicity compared to the low frequency translational mode, which may explain the higher error in its predicted frequency since, for this work, harmonic-limit simulations are used. For both modes the DFT simulations underestimate the measured mode intensities; however, the simulations correctly predict the greater line strength of the high frequency rotational mode. Interestingly, the higher frequency rotational mode is much more sensitive to the temperature and sample consistency, with an overall higher error in the measured center frequency compared to the translational mode. Additionally, this mode also has a high error in the measured intensities between different sample path lengths. Since this mode is rotational, we speculate that the errors in frequency and intensity may partly be due to the



Figure 5. Unit cell of SN with the relative motion of the molecules for the low frequency translational (\sim 1.266 THz, top) and the higher frequency rotational phonon mode (\sim 1.7105 THz, bottom).

presence of rotationally disordered glassy crystal regions in the samples; regions that also contribute to the $\beta \approx 2$ dependence of the background absorption. The randomly oriented molecules of these disordered regions could contribute to the large variance in the center frequencies and intensities that are observed for only the higher frequency rotational mode. Since these regions are still spatially ordered, the lower frequency translational mode is much less affected. However, it is challenging to confirm this assertion using these data since the higher frequency mode lies near the upper limit of the measurable spectral bandwidth, where the signal-to-noise is lowest. Even so, despite the varying disorder of the polycrystalline samples and succinonitrile's ambiguously defined low temperature crystalline structure, the DFT simulations and the THz-TDS measurements agree well within the constraints of the experimental and theoretical methods used.

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Notes

The authors declare no competing financial interest.

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