

Vibrational mode analysis of isomorphous hydrogen-bonded guanidinium sulfonates with inelastic neutron scattering and density-functional theory

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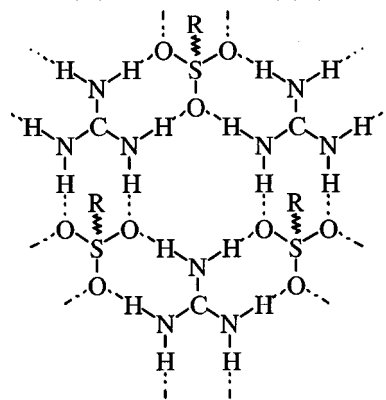
The inelastic neutron scattering spectra of a set of homologous lamellar molecular crystals containing two-dimensional hydrogen bonded sheets of guanidinium ions and sulfonate moieties of organomonosulfonates have been measured. The spectra were collected in the 35–105 meV range using a filter analyzer spectrometer and in the 0–35 meV energy range using a time-of-flight instrument. Parallel and perpendicular vibrational modes, associated with hydrogen displacements with respect to the hydrogen-bonded sheets, were analyzed between 35 and 105 meV by employing different scattering geometries. Comparison of the filter analyzer spectra of the isomorphous guanidinium salts of methanesulfonate, triflate and dithionate enabled assignment of specific modes while providing direct unambiguous measurement of the effect of the organic substituent on the strength of the (guanidinium)N–H···O–S(sulfonate) hydrogen bonds. Comparison of the time-of-flight spectra of the three compounds revealed that a mode observed at 7 meV corresponded to rotational motion of the methyl group. Density functional theory reproduced the experimental spectrum of guanidinium methanesulfonate, enabling assignment of the lattice vibrational modes. The scattering data compare well with a previously reported vibrational mode analysis of structurally homologous guanidinium nitrate. © 2001 American Institute of Physics. [DOI: 10.1063/1.1381530]

INTRODUCTION

Structures, interactions and dynamics associated with hydrogen-bonding in molecular systems, e.g., polypeptides,^{1,2} proteins,^{3,4} and molecular solids^{5,6} are commonly probed with optical spectroscopic methods which rely on electromagnetic radiation (i.e., infrared and Raman spectroscopies). The assignment of specific dynamic behavior to observed spectral signatures with these methods is, however, often complicated by symmetry-based selection rules and because the nature of the response is seldom entirely a function of molecular motions. For example, in an infrared or Raman measurement the total intensity of observed spectral peaks results from convolution of the atomic motions with the dipole moment and electronic polarizability of the molecules being probed. The theoretical description necessary to predict the electronic response of these measurements is rather complex, sometimes prohibiting comparisons of theoretical and experimental spectra. These limitations have made inelastic neutron scattering (INS) an attractive alternative for examining low-frequency vibrational modes in molecular materials. Neutrons have wavelengths comparable with interatomic distances and energies that are comparable to those associated with typical harmonic molecular motions, making them ideal for probing dynamic phenomena in solids. Furthermore, because neutrons interact primarily with nuclei

rather than electrons, the form of the interaction is relatively simple, often leading to rather straightforward comparison of experimental and theoretical data. When combined with the large incoherent scattering cross section of hydrogen, as compared with other nuclei, and the absence of symmetry-based selection rules, INS is ideally suited for studying low-frequency harmonic vibrations in hydrogen-bonded molecular materials.

Recently, one of our laboratories reported a series of crystalline guanidinium-organosulfonates with lamellar architectures based on two-dimensional quasi-hexagonal hydrogen bonded sheet consisting of topologically complementary guanidinium ions (G) and sulfonate (S) (Scheme 1).⁷



quasi-hexagonal GS sheet

This quasi-hexagonal motif is unusually persistent, having

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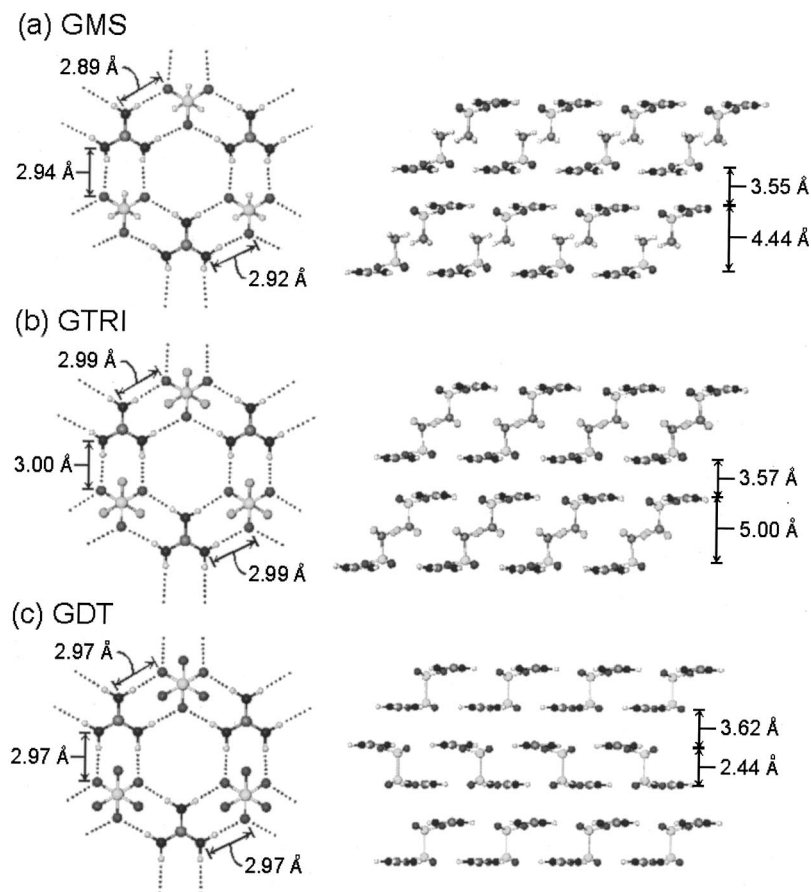


FIG. 1. Crystal structures of guanidinium methanesulfonate (**GMS**), guanidinium triflate (**GTRI**), and guanidinium dithionate (**GDT**) depicting the quasihexagonal hydrogen bonding (left) and bilayer stacking (right) observed in these materials. Note the incredible similarity in bond lengths and interlayer stacking distances throughout these structures.

been observed for numerous different organomonosulfonates⁸ and organodisulfonates (with various organic substituents), the latter affording a rich variety of inclusion compounds.⁹ This persistence has made possible the synthesis of numerous structurally isomorphous compounds with different *R* substituents but identical supramolecular hydrogen-bonding connectivity and lamellar architecture, providing a unique opportunity to measure the electronic effects of the substituents on lattice dynamics and hydrogen bonding in the absence of significantly different steric environments. As the energy landscape is similar throughout these materials, it is possible to rank hydrogen bond strength as a function of constituent electronegativity, a result that may have broad applicability in rationalizing observed hydrogen bonding patterns in both synthetic and natural materials.

Herein we describe a detailed analysis of the low-frequency vibrational modes observed in three relatively simple guanidinium organosulfonate compounds—guanidinium methanesulfonate (**GMS**, $[\text{C}(\text{NH}_2)_3]^+[\text{CH}_3\text{-SO}_3]^-$) and guanidinium triflate (**GTRI**, $[\text{C}(\text{NH}_2)_3]^+[\text{CF}_3\text{-SO}_3]^-$), which crystallize as isomorphous discrete bilayers, and guanidinium dithionate (**GDT**, $[\text{C}(\text{NH}_2)_3]_2^+[\text{SO}_3\text{-SO}_3]^{2-}$), a perfectly hexagonal bilayer structure in which opposing **GS** sheets are connected by covalent S–S bonds (Fig. 1). The sheet-like crystals of these materials were examined in different orientations in order to assign parallel and perpendicular vibrational modes associated with hydrogen displacements relative to the hydrogen-

bonded **GS** sheets. The INS spectrum of **GMS** calculated with density-functional theory (DFT) agreed reasonably with the experimentally determined spectrum, enabling assignment of the lattice vibrational modes in **GMS** and identification of the corresponding peaks in the **GTRI** and **GDT** spectra, as well as substantiating the reliability of DFT for analysis of molecular motions in hydrogen-bonded solids. Notably, the INS spectra of all three compounds were comparable to that previously reported for guanidinium nitrate [**GN**, $\text{C}(\text{NH}_2)_3^+\text{NO}_3^-$],¹⁰ which forms hydrogen-bonded sheets that are structurally homologous with the quasihexagonal **GS** sheets.^{11,12}

EXPERIMENT

Hexagonal plate-like crystals of the guanidinium organomonosulfonate salts were grown by slow evaporation from water or methanol solutions containing equimolar amounts of guanidine hydrochloride and the organosulfonate components. Guanidine hydrochloride [$\text{C}(\text{NH}_2)_3\text{Cl}$, 99%], methanesulfonic acid ($\text{CH}_3\text{SO}_3\text{H}$, 70% aqueous solution) and trifluoromethanesulfonic acid (triflic acid- $\text{CF}_3\text{SO}_3\text{H}$, 98%) were purchased from Aldrich. Sodium dithionate ($\text{Na}_2\text{S}_2\text{O}_6$, 98%) was obtained from TCI. All materials were used without further purification. The hexagonal plate morphology reflects the symmetry of the **GS** sheets with the large, flat face assigned to the (001) crystal plane, which is parallel to the hydrogen bonded layers.

Measurements were performed on samples containing ~3g of single crystals loaded in thin walled aluminum sample holders of rectangular geometry. The crystals were stacked to a thickness of ~0.4 cm on the large face of the sample holder (~12 cm²) such that their large faces were oriented parallel within the holder. The sample thickness was minimized to reduce secondary scattering of the neutrons, which may complicate interpretation of the collected spectra, while maintaining sufficient primary scattering intensity.

Because hydrogen has a much larger incoherent scattering cross section relative to all other nuclei the neutron scattering is almost exclusively due to interactions with the H atoms only. Because the scattering function $S(\mathbf{Q}, \omega)$ is dependent on both the scattering vector (\mathbf{Q}) and the phonon wave vector (\mathbf{q}) through the product $\mathbf{Q} \cdot \mathbf{e}_j^d(\mathbf{q})$, it is possible to use the experimental geometry (i.e., the direction of incident neutrons relative to the alignment of the oriented sample) to probe H motions in distinct crystallographic directions of oriented crystal samples. Thus, by aligning the (001) planes of **GS** crystals parallel to the surface of the aluminum sample holder it was possible to selectively probe scattering perpendicular (\mathbf{Q}_\perp) or parallel (\mathbf{Q}_\parallel) to the hydrogen bonded sheet plane. The spectra measured in these two geometries, therefore, reflect the contribution of molecular motions occurring normal to or within the hydrogen bonded layers. Further, alignment of the sample at a 45° incident angle allowed acquisition of INS spectra that were similar to that obtained for a randomly oriented powder sample (\mathbf{Q}).

INS spectra, which represent the intensity of scattered neutrons as a function of energy transfer, were recorded between 0 and 110 meV (0 and 880 cm⁻¹) using the filter analyzer spectrometer (FANS) BT-4 and the Fermi chopper time-of-flight (TOF) spectrometer on neutron guide NG-6 at the NIST Center for Neutron Research, USA. The FANS instrument was used to collect vibrational spectra in the \mathbf{Q}_\perp , \mathbf{Q}_\parallel , and \mathbf{Q} geometries over the 35–110 meV (~280–880 cm⁻¹) energy range. The TOF spectrometer was used for the 0–40 meV (~0–320 cm⁻¹) low-energy regime with the sample oriented 45° to the incident beam. Extensive details of the instrumental design of both spectrometers are available elsewhere.^{13,14} The spectra of the **GS** compounds were corrected for background scattering by subtracting the spectrum obtained from an empty sample holder.

Quantitative assignment of INS peaks observed for **GMS** to specific vibrational modes was achieved with a density-functional theory (DFT) calculation on a single unit cell constructed from the x-ray crystal structure. The *ab initio* geometry optimization and normal mode analysis were performed using the Dmol³ module contained in the software package Cerius². We employed the local density approximation, Perdew–Wang local correlation functionals, the 6-31-G** basis set and an atomic cut-off radius of 5.5 Å. In order to effectively replicate the experimental INS spectrum, the theoretical spectrum considers only the intensity contributed by the hydrogen motions, which are multiplied by the Debye–Waller factor and broadened in correspondence with the resolution of the instrument.

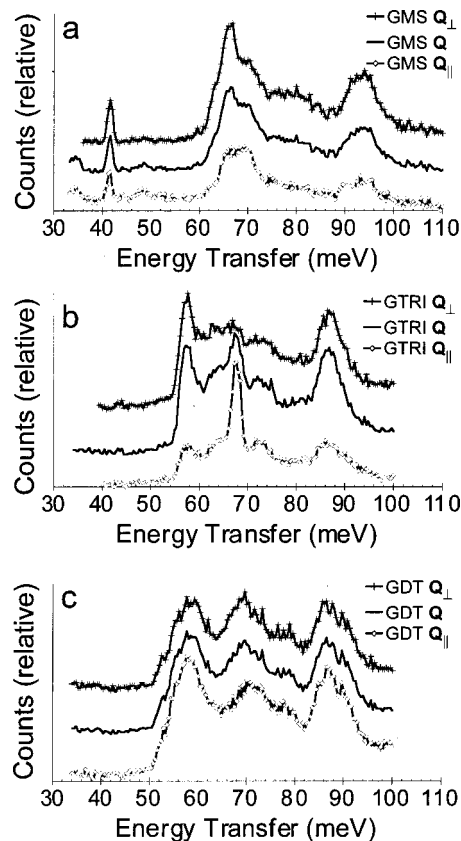


FIG. 2. Experimental INS spectra of (a) **GMS**, (b) **GTRI**, and (c) **GDT**, collected on the BT4 filter analyzer spectrometer. The samples were all collected at 20 K. The samples were preferentially oriented such that the incident neutron beam was 75°, 45°, or 15° off the plane of the hydrogen bonded sheets of the compounds, allowing one to selectively probe hydrogen dynamics occurring as molecular vibrations perpendicular (\mathbf{Q}_\perp), isotropic (\mathbf{Q}), and parallel (\mathbf{Q}_\parallel) to the two-dimensional **GS** layers.

RESULTS AND DISCUSSION

Inelastic neutron scattering spectra

The experimental INS spectra of **GMS**, **GTRI**, and **GDT** recorded at 20 K on the filter analyzer spectrometer (FANS) are shown in Fig. 2. Spectra were obtained with the incident neutron beam oriented 75°, 45°, 15° to the hydrogen bonded sheet for each sample, thus probing vibrational modes with displacements of H atoms perpendicular (\mathbf{Q}_\perp), isotropic (\mathbf{Q}) and parallel (\mathbf{Q}_\parallel) to the layers, respectively. The measured spectra revealed several distinct features as well as obvious orientational differences, which allowed qualitative assignment of the molecular motions associated with the vibrational modes.

The **GMS** spectra displayed a well-defined peak near 41 meV and broad peaks in the 62–74 and 88–96 meV ranges. In the \mathbf{Q}_\perp orientation a peak was observed near 66 meV that had a much greater relative intensity compared to the \mathbf{Q}_\parallel orientation. A similar trend was observed in the spectral band at 88–96 meV. This strong dependence on sample orientation with respect to the incident neutron beam suggests that these peaks correspond to hydrogen displacements that are principally orthogonal to the hydrogen bonded sheet. Furthermore, the intensity differences observed in the 62–74 meV spectral band as a function of scattering geometry re-

veals this feature to contain a convolution of overlapping peaks consisting of at least two vibrational modes in the crystal.

The INS spectra of **GTRI** reveal prominent peaks at 57, 67, and 85–90 meV, accompanied by less distinct features in the **Q** spectrum, including a shoulder at 64 meV and a small peak at 72–74 meV. The spectra for each orientation exhibit a difference in the relative intensity of the peaks at 57, 67, and 85–90 meV. The dependence of the scattering intensity on sample orientation enables assignment of the peaks at 57 and 85–90 meV to out-of-plane motions and the peak at 67 meV to a vibration occurring primarily within the plane of the **GS** sheet. Based on the trends in the orientation-dependent scattering intensity for both compounds, the **GTRI** peaks assigned to out-of-plane motion at 57 and 85–90 meV are most likely analogous to the **GMS** peaks observed at 66 and 88–96 meV, respectively. Furthermore, the in-plane motion at 67 meV may correspond to the peak shoulder observed in the INS spectrum of **GMS** at ~ 71 meV.

The Q_{\perp} and Q_{\parallel} spectra for **GDT** exhibit no significant differences. The broad features of **GDT** at 55–60, 67–74, and 85–90 meV occur at energies similar to the better resolved peaks observed for **GTRI**, suggesting analogous guanidinium ion vibrational modes in these two compounds occurring within similar energetic landscapes. The larger peak broadening observed in the **GDT** spectra relative to **GMS** and **GTRI** is attributed to increased dispersion interactions resulting from covalently connecting two adjacent hydrogen bonded sheets through the S–S bond of the dithionate anion, thus increasing long-range interactions between the vibrational modes.

Since the **GMS** peak at 41 meV is not observed in either **GTRI** or **GDT**, it is likely that this vibrational mode corresponds to the motion of methyl hydrogens, absent in **GTRI** and **GDT**. These data also reveal a shift in the **GTRI** spectral peak at 57 meV to an energy ~ 9 meV less than the corresponding vibrational mode in the **GMS** data. This is attributed to the difference between the electron withdrawing capacity of the methyl group and the trifluoromethane group. The more electronegative $-\text{CF}_3$ group withdraws a greater amount of electron density from the sulfonate moiety. This reduces the strength of hydrogen bonding between the sulfonate and guanidinium ions, effectively reducing the basicity of the oxygen hydrogen bonding sites to the extent that the molecular motions of the amine hydrogens are shifted to lower energy in the **GTRI** sample. This is corroborated by a comparison of the N–H \cdots O bond lengths in **GMS** and **GTRI** determined by single crystal x-ray diffraction, which reveals that the average N–H \cdots O lengths, as measured by the distance between N and O atoms of a hydrogen bond, are 0.07 Å shorter in **GMS** than in **GTRI**. Notably, the INS spectra collected on **GMS** displays near identical peak trends with that of **GN** in the 35–110 meV range, with the peaks of **GMS** comparatively shifted to higher energy by roughly 3 meV. This is similarly revealed in the hydrogen bonds, which are on average 0.04 Å shorter in **GMS** than **GN**. From these results it is possible to rank the strength of the hydrogen bonding interactions between guanidinium and the anions in increasing order from $\text{CF}_3\text{--SO}_3^- < \text{NO}_3^- < \text{CH}_3\text{--SO}_3^-$.

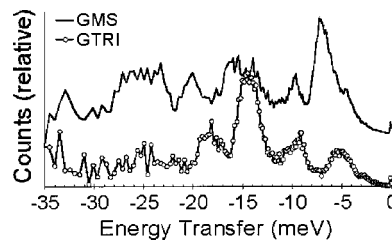


FIG. 3. Comparison of the low-energy experimental spectra for **GMS** and **GTRI** obtained using the TOF spectrometer.

Vibrational spectra for **GMS** and **GTRI** using the TOF spectrometer are depicted in Fig. 3. Though the **GTRI** data were shifted slightly downfield from **GMS** due to the electron withdrawing differences between the methyl and triflate substituents, the correlation between the spectra is clearly evident. The 7 meV peak observed in the **GMS** spectra has a relative intensity much greater than the corresponding **GTRI** peak at 6 meV. The relative intensity differences of these peaks, due to the large disparity in INS cross section of hydrogen and fluorine, permit their assignment to distinct motions of the methyl and trifluoromethane substituents, respectively. The remaining spectral peaks most likely correspond to the motion of guanidinium hydrogens, though comparison to the spectrum of **GN** over the same energy range reveal considerable differences.¹⁵ It should be noted that neither **GMS** nor **GTRI** exhibited any noticeable changes in their low energy spectra as a function of temperature.

Density-functional theory calculations

Figure 4 illustrates the comparison between the INS spectrum of **GMS** in the **Q** geometry from 35 to 110 meV with the spectrum calculated from a nonoriented DFT analysis performed on a single crystal unit cell with symmetrically constructed boundary conditions. The theoretical peaks were broadened in accordance with the resolution of the FANS instrument and scaling adjusted arbitrarily so as to most accurately reproduce the overall experimental data rather than the intensity of any specific peak. On the basis of the reasonable agreement between both the intensity and energies of the theoretical and experimental spectral peaks the specific molecular motions can be assigned to the vibrational peaks and bands in the experimental spectrum (Table I). A similar comparison was attempted using an *ab initio* calculation¹⁶ on

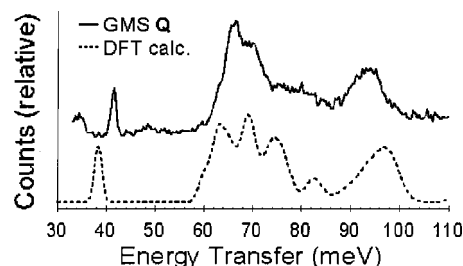


FIG. 4. Observed (solid line) and density-functional theory calculated (dotted line) INS spectra for **GMS** in the 35–100 meV energy range in the **Q** geometry (i.e., the incident neutron beam and the plane of the two-dimensional hydrogen bonded sheets are oriented at 45°).

TABLE I. Frequencies of the normal vibrational modes and their assignment for the FANS data and DFT calculations on **GMS** in the 35–100 meV energy range.

ν_{INS} (meV)	ν_{DFT} (meV)	Degeneracy	Guanidinium normal mode assignment	Description of motion
41.6	38.3	6	...	sym. methyl bending (both in and out-of-plane)
62–73	63.5	3	$\rho_t(e'')$	asym. NH ₂ twisting (out-of-plane)
	69.2	3	$\delta_s(e')$	sym. skeletal deformation of CN ₃ bonds (in-plane)
	74.2	2	$\rho_w(e'')$	asym. NH ₂ wagging motion (out-of-plane)
75–85	82.6	1	$\rho_w(a_2')$	sym. NH ₂ wagging motion (out-of-plane)
88–96	93.7	2	$\pi_s(e')$	sym. CN ₃ skeletal deformation (out-of-plane)
	97.4	3	$\rho_t(e')$	sym. NH ₂ twisting (out of plane)

an isolated guanidinium ion. This calculation, however, was unable to predict the experimental spectrum of **GMS** accurately as it did not account for hydrogen bonding interactions in the crystal.

The sharp experimental peak centered at ~ 41.6 meV in the **GMS** spectrum most closely corresponds to the calculated peak at a slightly lower energy of ~ 38.3 meV. As deduced from orientation studies described in the previous section, this peak can be assigned to rigid body bending of the methyl substituent on the organomonosulfonate. A small amount of skeletal deformation is observed in sulfonate portion of the anion, while the guanidinium ions do not substantially participate in any vibrations at this frequency. The peak results from multiple degenerate states of the molecular motions within the crystal lattice corresponding to bending motions wherein all of the methyl groups on two opposing sheets of a single bilayer are displaced either in the same or opposite direction. Due to the pseudo-three fold symmetry of the **GS** sheet (the actual point group symmetry of the **GMS** lattice is 2/m), both motions have three nearly equivalent vibrations—yielding an overall degeneracy of 6. This vibrational mode involves molecular motion with components both perpendicular and parallel to hydrogen bonded sheet and, therefore, is consistent with the lack of orientational differences observed in the INS peak at this frequency.

The theoretical signal calculated in the INS profile in the 60–75 meV range appears as three peaks that correspond to a broad band of overlapping vibrational modes. This compares favorably with the broad band in the experimental spectrum between 62 and 73 meV. The low energy peak of the calculated band, resulting from torsions of the guanidinium amine groups, occurs at ~ 63.5 meV. These motions occur with almost no deformation of the three C–N bonds of the guanidinium and only a slight deformation of the sulfonate moiety. The S–O bonds of the organosulfonate are deformed through the intermolecular hydrogen bonding forces by a push-pull type mechanism. As the torsions of the amine groups move the hydrogen involved in intermolecular bonding, the oxygen participating in the hydrogen bond compensates by moving in concert with the amine hydrogen, but at a much smaller intensity. Because this oxygen participates in N–H \cdots O bonds between two different guanidinium ions within the quasihexagonal motif, the motions are synchronously transmitted down each of the three nearly hydrogen bond directions of the **GS** sheet, yielding the threefold degeneracy of this molecular motion. Amine torsion motions

are almost entirely out-of-plane. It is possible, therefore, to assign the calculated peak at 63.5 meV to the experimental peak at ~ 66 meV, which was determined to be an out-of-plane motion by the larger intensity in the **Q_⊥** orientation.

The second peak of the three (69.2 meV) results from in-plane skeletal deformation of the three C–N bonds of the guanidinium ion, coupled with a NH₂ rocking deformation. Amine rocking induces a slight deformation of the sulfonate moiety, coupled to a small bending motion of the methyl group. Overall, this results in hydrogen motions that occur both perpendicular and parallel to the **GS** sheet. The threefold degeneracy of this motion is again a consequence of the internal threefold symmetry of the guanidinium ion itself and the **GS** hydrogen bonded sheet. This assignment is consistent with the qualitative assignment of a related peak at 68.9 meV observed in an INS study of **GN**.¹⁵ Although unambiguous assignment of this mode to a specific peak in the **GMS** experimental spectrum is difficult due to the low resolution of peaks within the 62–73 meV band, one may, by inspection, assign this motion directly to the in-plane peak observed strongly in the **Q_∥** of **GTRI** at 67 meV.

The final peak contributing to the broad band observed in the theoretical spectrum occurs at an energy transfer of ~ 74.2 meV. This peak corresponds to out-of-plane NH₂ wagging motions of two amine groups on the guanidinium. The remaining amine group and the CN₃ bonds of the guanidinium ion are rigid and relatively motionless in this mode. A doubly degenerate mode results from motions that occur with the two hydrogens of each amine group distorting to either the same or opposite sides of the molecular plane. The –NH₂ wagging motions in **GMS** are revealed to be much higher in energy compared to the 56–66 meV range reported for other solids having extensive amide hydrogen bonded structures.^{15,17} More than likely this difference arises as a result of the different hydrogen bonding motifs of the materials. This vibrational mode, along with the mode calculated at 69.2 meV, is responsible for the high energy portion of the experimental band at 62–73 meV.

A wagging motion of one NH₂ group is responsible for the peak observed at 82.6 meV in the calculated spectrum. This motion is accompanied by skeletal deformation of the CN₃ bonds, which allows the carbon atom of the guanidinium to be displaced to the same side of the mean molecular plane as the hydrogens of the amine. Skeletal deformation of the guanidinium causes this wagging motion to occur at an energy much higher than the aforementioned modes. At

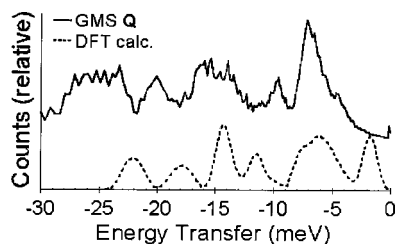


FIG. 5. Observed (solid line) and density-functional theory calculated (dotted line) INS spectra for **GMS** in the 0–35 meV energy range with an angle of 45° between the incident neutron beam and the plane of the two-dimensional hydrogen bonded sheets.

this frequency the features observed in the experimental spectrum are poorly resolved as a result of the FANS instrument resolution, noise in the background, possible multiphonon scattering and peak broadening due to dispersion interactions in the samples.

A broad, intense single peak in the DFT calculated spectra at 96.8 meV arises from two overlapping vibrational modes that become unresolved when broadened to the resolution of the FANS instrument. This peak comprises a CN_3 skeletal deformation and a complex NH_2 mode involving torsion and wagging motions centered at 93.7 and 97.4 meV, respectively. The overall peak at 96.8 is preferentially shifted towards the 97.4 meV torsion mode because it involves larger hydrogen displacements and, hence, a larger contribution to the INS intensity. Again, the out-of-plane skeletal deformation of the guanidinium C–N bonds is coupled with NH_2 rocking. At this frequency, however, the guanidinium motions are anchored to C–S bond stretching of the methanesulfonate molecules. Consequently, this peak is observed at a much higher energy compared with the previously mentioned skeletal deformation modes. The 97.4 meV mode represents a triply degenerate mode involving molecular motions of the guanidinium amine groups perpendicular to the hydrogen bonded sheet wherein one NH_2 group wags while the other two twist. When combined, these principally out-of-plane motions can be assigned to the broad envelope observed experimentally 88–96 meV range.

The INS spectrum of **GMS** collected on the FCS instrument is plotted with the results of the DFT calculation in the 0–30 meV energy transfer range in Fig. 5. The calculated INS spectrum was obtained by broadening the calculated modes obtained at different frequencies with the appropriate Debye–Waller factor and the resolution of the instrument. Simple inspection reveals that the experimental and theoretical spectra compare only modestly. This discrepancy between the experimental and calculated spectra can be attributed to the DFT calculation yielding only the vibrational modes in the center of the Brillouin zone, whereas all of the vibrations throughout the Brillouin zone are observed experimentally.

Although the intensity and energy transfer predicted by the calculations differ slightly from those observed experimentally, assignment of some of the vibrational modes is possible. The low energy molecular motions primarily consist of rigid body motions of the guanidinium and the methanesulfonate anions. For example, the calculated peak ob-

served at 1.8 meV corresponds to rigid body libration of the methanesulfonate molecule about the C–S bond. This motion produces deformation of the **GS** sheet by forcing the guanidinium ions to distort slightly in order to accommodate the steric size of the sulfonate oxygen atoms. Though no peaks are observed experimentally at this energy, this mode may be responsible for the shoulder at ~4 meV.

The broad, intense peak observed experimentally at 7 meV appears in the calculated spectra as a convoluted peak consisting of a vibrational mode with a degeneracy of four. The calculated peak is shifted ~1 meV downfield and has a relative intensity approximately two-thirds of the experimental peak. Rigid body methanesulfonate pendulumlike librations involving the sulfonates shifting out of the **GS** sheet contribute to the observation of this peak. In this mode the guanidinium ions experience a slight deformation about the three C–N bonds. Assignment of the experimental peak at 7 meV to motions primarily involving the methyl hydrogens is supported by the low intensity of the corresponding peak in the spectrum of **GTRI**.

The next major features in the calculated spectrum are the two peaks in the 11–17 meV range. Major contributions to this peak are modes calculated at 11.6 and 14.6 meV. At a frequency of 11.6 meV the methanesulfonate molecules twist about their C–S bond such that the methyl and sulfonate groups rotate in opposite directions. Twisting of the methanesulfonate deforms the bonds of the guanidinium ions by pushing two of the nitrogen atoms to one side of the mean molecular plane and the remaining nitrogen to the other. Rigid body bending of the guanidinium out of the **GS** sheet coupled with rotation of the methanesulfonate about the C–S bond occurs at 14.6 meV. In this vibrational mode the CH_3 and SO_3 groups rotate in the same direction and have a nearly degenerate mode at 14.4 meV in which the groups rotate in opposite directions. The predicted mode at 11.6 meV has an obvious experimental counterpart at 10 meV and the calculated modes at 14.4 and 14.6 can most likely be assigned to the experimental band in the 13–18 meV range. Calculated peaks at 17.9 and 22.0 meV appear to have analogs in the experimental spectrum, however, the two potential corresponding peaks are shifted to higher energy by ~2 meV.

Overall, the DFT calculated spectrum for **GMS** reproduces the experimental data collected with the FANS and TOF instruments quite well. In the higher energy range both the intensities and energy transfer of the calculated spectrum allow confident assignment of distinct vibrational modes within the crystal lattice. Quantitative assignment of all the INS peaks using the theoretical calculations is additionally supported by comparison with the results obtained for samples in the \mathbf{Q}_\perp and \mathbf{Q}_\parallel orientations. Unfortunately, comparison of the DFT calculated and experimental TOF spectra is not as straightforward. It is still possible, however, to assign the experimental peaks with reasonable certainty. The discrepancy arises from the shift in energy between some of the calculated and experimental vibrational modes, indicative of a limitation in the calculations in the 0–35 meV range. Overcoming limitations in peak assignment requires both improving the quality of the experimental data and the accuracy

of the computational techniques. Increasing the data quality may be accomplished by analyzing larger samples with longer counting times and/or employing an instrument with an inherently lower resolution limit. Inaccurate prediction of the energy and intensity of vibrational modes is fundamentally limited by the available computational theories. It may be possible to more accurately reproduce the experimental spectrum of **GMS** using available methods by starting with a larger supercell model of the crystal structure. This entails, however, a drastic increase in the time and cost of the computations.

CONCLUSIONS

The results of this study demonstrate the usefulness of the INS technique for obtaining information about frequency and polarization of vibrational modes in oriented samples of materials with structures reliant upon the formation of quasi-hexagonal hydrogen bonded **GS** sheets. A DFT calculation performed with a suitable representation of the crystal structure with symmetry generated boundary conditions enabled assignment of the vibrational character of nearly every peak observed in the INS spectra of **GMS** collected with FANS and TOF spectroscopic instruments. Experimental peak assignments have been rationalized from both the intensity and energy of calculated peaks in the theoretical spectrum, and qualitative phenomena discerned through isotopic substitution effects and orientation differences of our samples. The success of the DFT calculation, coupled with the inability of an *ab initio* calculation to describe accurately the molecular motions in **GMS** based a single, isolated molecule, demonstrates the necessity of including the long-range intermolecular interactions when analyzing the dynamic behavior of hydrogen bonded materials. The overall shift of the INS peaks to lower energies upon substitution of the methyl groups in **GMS** with the more electron withdrawing group of **GTRI** demonstrates that INS is also a sensitive probe of hydrogen bond strength in crystalline materials, particularly when structural contributions can be minimized by the existence of isostructural crystal environments. We anticipate that further advances will make INS an even more reliable tool for elu-

cidating substituent effects in other hydrogen bonded materials, including other molecular solids, polypeptides, and proteins.

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