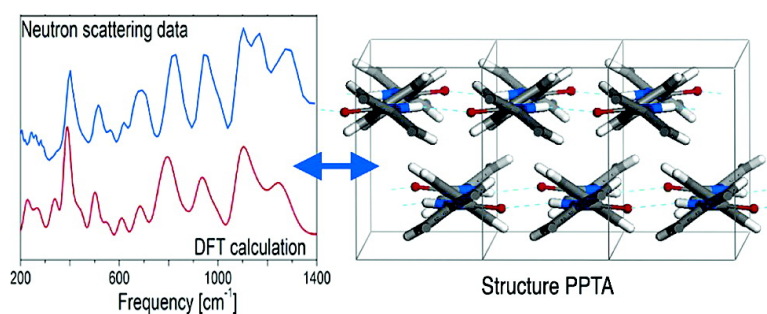


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Neutron Vibrational Spectroscopy Gives New Insights into the Structure of Poly(*p*-phenylene terephthalamide)

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Abstract: The vibrational spectra of benzanilide and poly(*p*-phenylene terephthalamide) have been measured using inelastic neutron scattering. These compounds have similar hydrogen-bond networks, which, for poly(*p*-phenylene terephthalamide), lead to two-dimensional hydrogen-bonded sheets in the crystal. Experimental spectra are compared with solid-state, quantum chemical calculations based on density functional theory (DFT). Such “parameter-free” calculations allow the structure–dynamics relation in this type of compound to be quantified, which is demonstrated here for benzanilide. In the case of poly(*p*-phenylene terephthalamide), vibrational spectroscopy and DFT calculations help resolve long-standing questions about the packing of hydrogen-bonded sheets in the solid state.

I. Introduction

In materials lacking long-range structural order, vibrational spectroscopy is a powerful method for obtaining structural information. Diffraction techniques rely on long-range order to give well-defined Bragg reflections, whereas the vibrational modes of molecules depend on the local intra- and intermolecular environment. Intermolecular interactions typically extend over distances of tens of angstroms, but the effective range of interactions that determine vibrational modes in organic compounds is more like 5–6 Å. The structure–dynamics relation can be established empirically as is the case for determining the presence of secondary structures such as β -sheets and helices in proteins from the optical, spectral profiles of the amide bands.^{1,2} Indeed the study of β -sheets has assumed greater importance over the past decade since highly aggregated β -sheets have been established as symptoms of amyloid and prion diseases. However, a higher level of structural information is potentially available if a quantitative link can be made between structure and vibrations via accurate interatomic potentials. In the case of polypeptides, first principles-based calculations of spectral profiles have been employed, although these have been limited to the amide bands.^{3,4}

One of the original uses of vibrational spectroscopy was precisely that of parametrizing interatomic interactions. Typically spectral frequencies rather than intensities were used for this purpose because, for optical spectroscopies (IR and Raman), spectral intensities have been difficult to determine, a knowledge of dipole moments and polarizability, respectively, being required. Although these quantities for optical spectroscopy can now be extracted from quantum chemical calculations, in inelastic neutron scattering (INS) spectral intensities are directly related to vibrational amplitudes via tabulated scattering cross-sections. The information content of INS spectra is more easily and reliably exploited.

The quantitative link between structure and dynamics depends on the accuracy of the interatomic potentials that are used to calculate either the vibrational density of states from molecular dynamics simulations or the normal modes from the dynamical matrix. For smaller systems (less than a few hundred atoms), the second approach entails fewer calculations and gives directly the vibrational modes, including their wavevector dependence (phonon dispersion). This approach has been exploited in recent years to study hydrogen-bonded molecular crystals, using “parameter-free”, solid-state, density functional theory (DFT)-based methods to determine the interatomic force constants.^{5–9}

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The purpose of this work is therefore two-fold: to extend recent experimental and computational work to hydrogen-bonded compounds more closely related to secondary structures in biological molecules and to investigate the solid-state structure-vibration relation in a crystalline polymer. Poly(*p*-phenylene terephthalamide) (PPTA) is a polymer which crystallizes in the form of hydrogen-bonded sheets, amide linkages in the polymer allowing hydrogen bonding between polymer chains to form 2D sheets. PPTA is a highly crystalline polymer that can be spun into fibers, which exhibit exceptional thermal and mechanical properties.¹⁰ It has numerous commercial applications and is sold under the trade names of Kevlar and Twaron. The fiber used in this work is estimated to have a crystallinity better than 90%, but the crystallites are small, ~ 50 Å in diameter perpendicular to the fiber axis,¹¹ limiting the long-range order and resulting in about 30% of the polymer chains being on the surface of crystallites. Thus, vibrational spectroscopy is an important tool for structure investigation. Uncertainty persists concerning the packing of hydrogen-bonded sheets in the crystal structure of PPTA, which is governed by weak intermolecular interactions. While the small crystallite size and partial crystallinity of PPTA degrade the quality of vibrational information, the fibrous nature of the sample allows additional information to be obtained by orienting it in the neutron beam and measuring the polarization of the vibrational modes directly.

Optical spectroscopy techniques have been widely applied to PPTA in the past. IR spectra have been used to identify solid-state structures resulting from two different production techniques, and the vibrational modes were tentatively assigned based on atom-atom potentials.¹² Force field parameters were further refined (as described above) based on the structure of the hydrogen-bonded sheet and then used to investigate mechanical properties of fibers.¹³ Total energy calculations, based on empirical force fields, have been used to investigate the relative stability of two structures of PPTA,¹⁴ but the structure that will be shown here to be the most plausible was not studied. It will be demonstrated below that the energy differences between different solid-state structures are small and the precision of first principles calculations is required. The same precision is needed for accurate determination of vibrational spectra.

To validate the DFT-based methods used to establish the structure-dynamics relation for PPTA, we, like others,¹⁵ have also studied, as a model system, a highly crystalline powder of benzanilide, which is approximately the monomer of PPTA and also forms hydrogen-bonded chains in the crystal.

In the following section, we present in detail the structural information relevant to the samples in this work. In section III, computed and measured spectra are compared for the two compounds. The connection between structure and vibrations and the limitations of the approach adopted here are discussed in section IV. The conclusion and perspectives for vibrational spectroscopy in biomaterials are presented in section V.

Table 1. Structural Information for PPTA

| | Northolt ^{16,17} | Northolt-translated | Liu ¹⁹ | Pb |
|-------------------------------------|---------------------------|------------------------|---------------------|---------------------|
| <i>a</i> [Å] | 7.87 | 7.87 | 7.88 | 7.88 |
| <i>b</i> [Å] | 5.18 | 5.18 | 5.22 | 5.22 |
| <i>c</i> [Å] | 12.9 | 12.9 | 12.9 | 12.9 |
| α, β, γ (deg) | 90, 90, 90 | 90, 90, 90 | 90, 90, 90 | 90, 90, 90 |
| space group | <i>P11n</i> | <i>P11n</i> | <i>P1a1</i> | <i>Pb11</i> |
| chain location [x,y] | [0,0],[1/2,1/2] | [0,0],[1/2,1/2] | [1/4,1/4],[3/4,3/4] | [1/4,1/4],[3/4,3/4] |
| Z | 2 | 2 | 2 | 2 |
| glide plane symmetry operator | $x + 1/2, y + 1/2, -z$ | $x + 1/2, y + 1/2, -z$ | $x + 1/2, -y, z$ | $-x, y + 1/2, z$ |
| <i>c</i> translation between sheets | ~ 0.5 | ~ 0 | 0 | 0 |

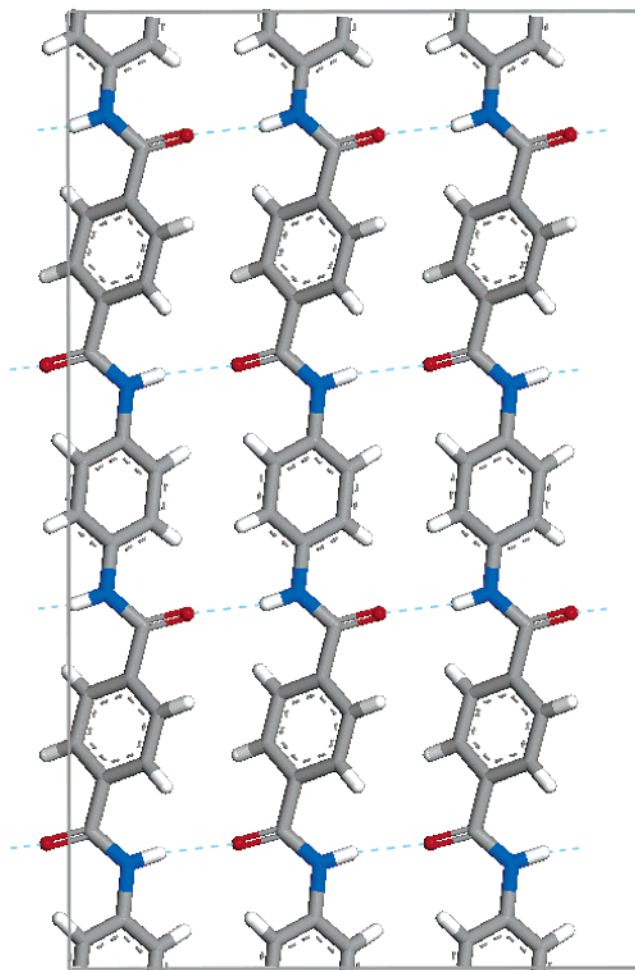


Figure 1. Two-dimensional hydrogen-bonded sheet structure common to all PPTA structures. The N-H \cdots O=C hydrogen bonds are shown by dashed lines.

II. Structural Information

The structure of PPTA was first determined by Northolt,^{16,17} an orthorhombic structure in the monoclinic space group *Pc* (*P11n*) being proposed. Details of the lattice are given in Table 1. Each polymer chain in the unit cell forms part of a 2D structure in which neighboring chains are connected at the amide linkages by hydrogen bonds (Figure 1). The hydrogen-bonded sheets are separated by ~ 4 Å (*a*/2). The relative alignment

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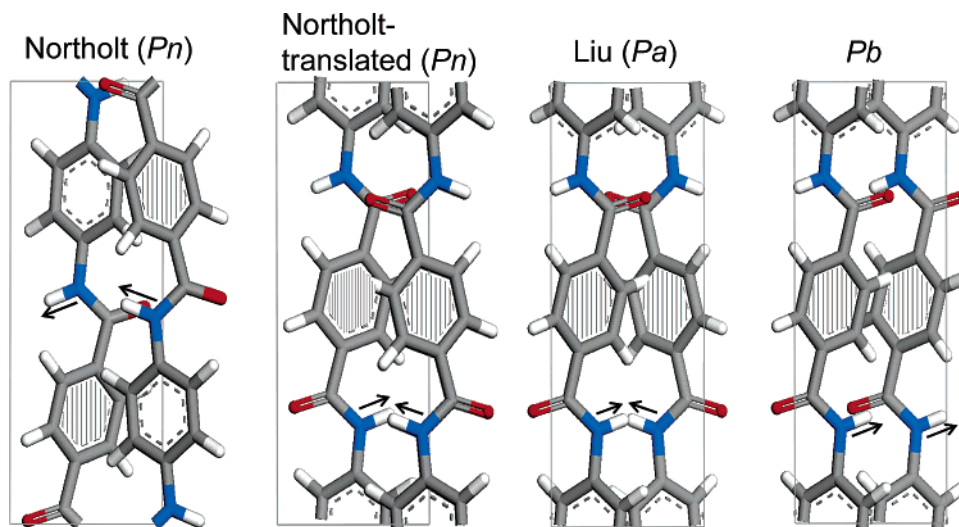


Figure 2. The principle PPTA structures studied in this paper. The two chains in the unit cell are shown, that is, one from each of the neighboring sheets. Terephthaloyl residues are shaded to show the alignment of the chains. Arrows on the N–H bonds indicate the orientations of the amide linkages. The Northolt and *Pb* structures have an approximately parallel alignment of amide linkages; the Northolt-translated and Liu structures have an antiparallel alignment. The packing of phenyl rings between sheets in all structures is of herringbone type, except in the Northolt-translated structure in which the phenyl groups are stacked with a similar, parallel orientation.

between sheets is characterized by the phenyl groups and the amide linkages. In the Northolt structure, terephthaloyl residues are offset by ~ 6.5 Å ($\sim c/2$); all amide linkages are oriented approximately along the *b*-axis, and these groups have a similar, parallel alignment in neighboring sheets. A similar structure but with higher symmetry ($P2_1/n$), which enforces the $c/2$ offset of equivalent phenyl groups, was proposed by Tadokoro and co-workers.¹⁸ Later, Liu and co-workers concluded from electron diffraction data from single crystals¹⁹ that the correct space group is *Pa*. In this structure, terephthaloyl residues are not offset, and the amide linkages have an antiparallel configuration along the *b*-axis between neighboring sheets. A structure similar to that of Liu can be obtained from the Northolt structure by introducing a ~ 6.5 Å relative translation of neighboring sheets along the polymer axis, the essential difference being that the Liu structure presents a herringbone packing of the phenyl rings, whereas the “Northolt-translated” structure has a parallel packing of the phenyl groups. Finally, a recent, neutron fiber diffraction experiment, in which the terephthaloyl residues were selectively deuterated, has confirmed the zero offset along *c* between equivalent residues in neighboring sheets.²⁰ From the initial analysis of the neutron diffraction data, a second structure in the same space group (*Pb*), in which the amide linkages have a parallel alignment between neighboring sheets, could not be ruled out. Figure 2 shows the four structures discussed above (Northolt, Northolt-translated, Liu (*Pa*), and *Pb*), and the relevant structural information is presented in Table 1. It should be noted that these four structures have a common hydrogen-bonded sheet structure, the packing of these sheets giving rise to the different, solid-state structures.

Benzanilide crystallizes in the monoclinic space group *Cc* ($Z = 4$).²¹ This structure (Figure 3) closely mimics that of Liu for PPTA in terms of hydrogen bonding, the relative orientations

of amide linkages, and the relative positions of phenyl groups, the main difference being the absence of polymeric chains due to the absence of a second amide linkage on the benzanilide molecule.

III. Vibrational Spectroscopy

III.1. Benzanilide. Figure 4 shows the experimental INS spectrum for the powder sample of benzanilide (measured on the TOSCA spectrometer at the ISIS facility, UK²²) and the calculated, gamma point, one-phonon spectrum. The spectral intensity is almost entirely due to incoherent scattering from hydrogen. The broad background intensity in the experimental spectrum is due mainly to multi-phonon excitations. In view of the fact that the calculated spectrum contains 312 modes (3 times the number of atoms in the unit cell), the agreement between these spectra is very good and serves to validate the use of solid-state DFT methods (as implemented in the VASP code^{23–27}) to determine molecular vibrations in this type of hydrogen-bonded solid, with only the crystal structure as input. The most apparent discrepancies between measurement and calculation relate to small errors in mode frequencies, which result in structured, calculated bands instead of intense peaks due to degenerate modes (e.g., at ~ 400 cm^{-1}) and vice versa (e.g., at ~ 900 cm^{-1}). With respect to the case of PPTA (to be discussed below), we draw attention to the out-of-plane N–H wagging vibrations, which are coupled to similar, out-of-plane vibrations of C–H bonds on the neighboring phenyl rings and are found in a family of nine modes between 667 and 710 cm^{-1} . The relatively high frequency of these modes is due to the hydrogen-bond network. The intense, calculated peak just below 700 cm^{-1} would therefore be expected to be broadened by dispersion due to the hydrogen-bond network.

In view of the accuracy of the gamma point calculation, the vibrational density of states was not calculated as this would

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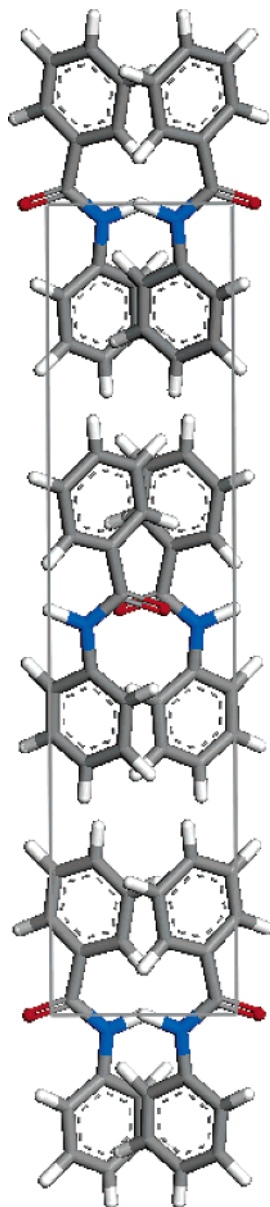


Figure 3. The crystal structure of benzanilide (ab plane), space group Cc , cell; $a = 24.34 \text{ \AA}$, $b = 5.33 \text{ \AA}$, $c = 8.01 \text{ \AA}$, $\beta = 107.2^\circ$.

have required computationally intensive calculations on a supercell composed of two unit cells ($a, 2b, c$, volume $\sim 1984 \text{ \AA}^3$), the VASP calculations scaling approximately with the cube of the number of atoms.

III.2. PPTA. Ten INS spectra of PPTA were measured on the IN1 spectrometer (at the ILL, France²⁸) at a temperature of 10 K, as a function of fiber orientation with respect to the incident beam (approximately the momentum transfer vector \mathbf{Q}) ranging from parallel to perpendicular. These spectra were corrected for the effective, illuminated area of the sample and summed to give the upper spectrum in Figure 5 (curve e). Modes above 1400 cm^{-1} could not be measured due to the lack of hot neutrons on IN1 at the time of the experiment. The rising background is due, in part, to multi-phonon excitations and an orientation-dependent background signal. A couple of these measurements were repeated on the higher resolution, TOSCA instrument, but this did not result in significantly more detailed

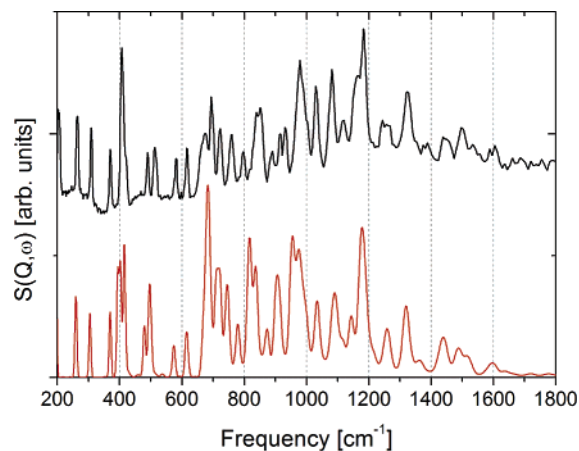


Figure 4. The INS spectrum of benzanilide measured on TOSCA (top) and calculated for the gamma point using VASP and CLIMAX (bottom).

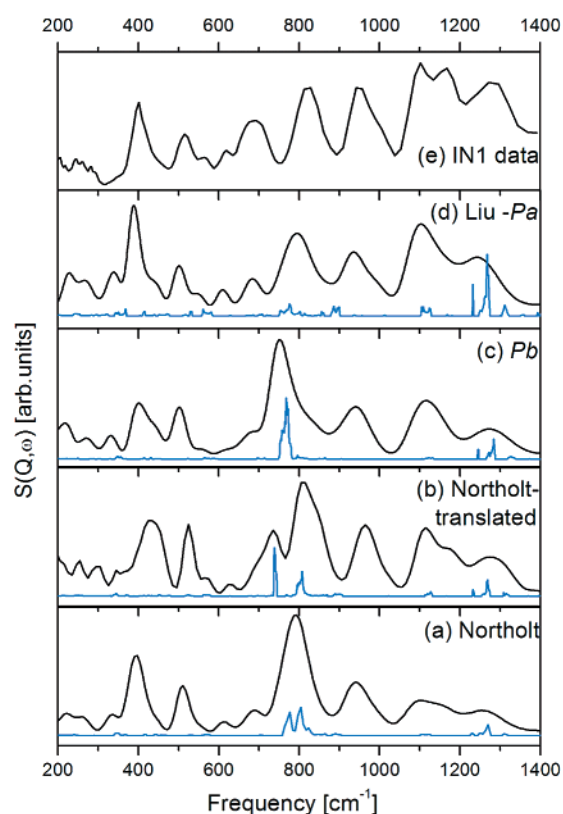


Figure 5. The measured INS spectrum of PPTA, summed over fiber orientations ranging from parallel to the momentum transfer \mathbf{Q} vector to perpendicular (top, e). Calculated INS spectra for the same, average fiber and instrument configuration are shown in the lower four panels. The smooth curves are the result of convolution of the calculated total scattering function with the frequency-dependent, instrument resolution function. The unconvoluted, partial scattering function for the amide hydrogen is also shown in each panel.

spectra, effective resolution being limited by the crystallite size and partial crystallinity of the sample.

In view of the smaller size of the unit cell, the vibrational density of states, rather than the gamma point modes, was calculated for the four PPTA structures shown in Table 1 and Figure 2 from supercells of dimension $8 \text{ \AA} \times 10 \text{ \AA} \times 12 \text{ \AA}$, composed of two unit cells. The bottom panel (a) in Figure 5 shows the calculated, summed spectrum for the original Northolt structure. The total scattering function has been convoluted with

(28) <http://www.ill.fr/YellowBook/IN1/>.

the frequency-dependent, instrument resolution function to give the smooth curve. The lower curve in the panel is the partial scattering function (not convoluted) due to the hydrogen atom in the amide linkage, showing the contribution of this atom to the spectrum. Despite the lower resolution of the PPTA spectra, the agreement between calculation and experiment is much worse than in the case of benzanilide. In particular, the triplet of peaks (690, 830, 950 cm^{-1}) in the intermediate frequency range in the experimental spectrum is not well-reproduced. The strong peak at 790 cm^{-1} in the calculated spectrum has a dominant contribution from pure, N–H out-of-plane, wagging modes.

In the spectral range of Figure 5, the amide linkage hydrogen atom also contributes intensity at $\sim 1250 \text{ cm}^{-1}$ through N–H in-plane wagging modes. Beyond this spectral window, the calculations predict low intensity bands at $\sim 1600 \text{ cm}^{-1}$ due to C=O stretching modes and at 3200 and 3400 cm^{-1} due to C–H and N–H stretching modes, respectively. Such a high N–H stretching frequency indicates that the hydrogen bond is weak, the optimized Northolt structure giving a N–H bond length of 1.04 Å, a N \cdots O distance of 2.98 Å, and a N–H \cdots O angle of 165°.

Because the principal result from the recent neutron diffraction experiment was that equivalent phenyl rings should not be offset along the direction of the polymer chains between neighboring sheets, the “Northolt-translated” structure (described above) was investigated. The calculated spectrum (Figure 5, panel b) is in better agreement with the measured spectrum, the amide group hydrogen atom contribution being split between the peaks at 740 and 810 cm^{-1} .

Calculations were performed on the *Pb* structure that was considered to be compatible with the initial inspection of the fiber diffraction data. The spectrum (Figure 5, panel c) strongly resembles that of the Northolt structure (panel a), again pure N–H wagging modes making a significant contribution to the most intense peak (at 755 cm^{-1}). The common feature of the *Pb* and Northolt (*Pn*) structures is the parallel configuration of amide linkages between sheets.

Finally, calculations on the Liu (*Pa*) structure, which is compatible with the fibre diffraction data, give the spectrum shown in Figure 5, panel d. This spectrum is in best agreement with the experimental data. Virtually all calculated peaks are close to the measured peak positions, and variations from peak to peak, in intensity and profile, are well-reproduced. In contrast to the other structures, especially Northolt and *Pb*, the N–H wagging modes make a relatively weak contribution to the spectrum because they are strongly mixed with the out-of-plane C–H wagging modes. Like the Northolt-translated structure, the amide linkages have an antiparallel alignment. The difference between the two structures concerns the packing of the phenyl groups, which participate in many vibrations and therefore lead to small differences throughout the spectrum.

The spectra presented in Figure 5 have all been summed over a range of fiber orientations with respect to \mathbf{Q} . Information about the polarization of the vibrational modes, and further validation of the calculation, can be sought from the orientation dependence of the spectral intensities, because modes give the strongest intensity when \mathbf{Q} is parallel to the principal direction of atomic displacements. Figure 6 shows the measured spectra and those calculated for the Liu structure; the fiber axis is parallel to \mathbf{Q}

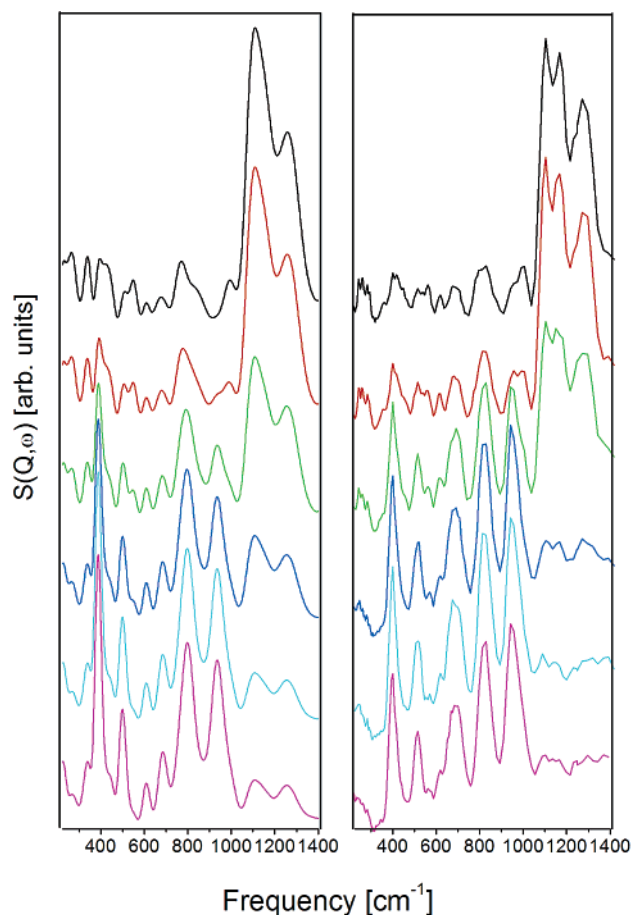


Figure 6. Comparison of measured (left) and calculated (right) INS vibrational spectra of PPTA for fiber orientations varying from parallel to the momentum transfer vector \mathbf{Q} (top) to perpendicular (bottom).

in the top spectrum and perpendicular in the bottom spectrum. The measured and calculated variations in intensity with fiber orientation match well. Most modes in the range from 200 to 1000 cm^{-1} are polarized perpendicular to the fiber axis, like the out-of-plane N–H wagging modes. Only the band at 1100 to 1300 cm^{-1} has a significant longitudinal polarization, these higher frequency modes involving wagging of the C–H bonds in the planes of the phenyl groups and wagging of the N–H bonds in the planes of the amide linkages. The decay in intensity of these modes is smoother in the experimental spectra than in the calculated spectra because the detector on IN1 covers a 15° 2θ scattering angle around 90°, whereas the calculation is performed for a single scattering angle of 90°.

IV. Discussion

The origin of the variations in the spectra of Figure 5 in terms of intra- or inter-sheet interactions can be considered in terms of the structural characteristics of the different systems. The hydrogen-bond geometry, described above for the Northolt structure, is common to all systems. The polymer chain structure is characterized by the torsion angle between the amide linkage and the phenyl group and the bond angles ($\angle \text{C}_{\text{phenyl}}\text{NC}_{\text{amide}}$ and $\angle \text{C}_{\text{phenyl}}\text{C}_{\text{amide}}\text{N}$) within the amide linkage. To within 1°, the Northolt, *Pb*, and Liu structures have the same characteristic angles of 150°, 124°, and 114°; thus they have the same hydrogen-bonded sheet structure. The parallel packing of the phenyl groups in the Northolt-translated structure, as opposed

to herringbone for the other structures, results in a torsion angle of 159° , the other angles being unchanged. In terms of the packing of amide linkages between hydrogen-bonded sheets, the Northolt and *Pb* systems with a parallel alignment present a similar structure in which the two nitrogen–nitrogen distances between a amide linkage and the two nearest groups in a neighboring sheet are almost identical (~ 4.7 Å). In the case of antiparallel packing of amide linkages in the Northolt-translated and Liu systems, these two distances are different (4.3 and 5.0 Å). The Northolt and *Pb* systems therefore present almost identical 2D sheet structures and packing of phenyl groups and amide linkages between sheets, and the spectra of vibrations are similar. The Liu system has a similar sheet structure but a different packing of amide linkages, and the spectrum differs considerably from the Northolt and *Pb* spectra. Finally the Northolt-translated structure has a different sheet structure in terms of the phenyl-amide torsion but the same packing of amide linkages as in the Liu system, and the spectrum resembles that of the Liu structure. Clearly the spectra of vibrations are most sensitive to the inter-sheet interactions and, to a lesser extent, the modification of the sheet structure (phenyl-amide torsion) by these interactions.

The VASP/DFT method can also be used to investigate the relative stability of the four structures. By comparing the total energies of the optimized structures in the same experimentally determined unit cell, the Northolt, Liu, and *Pb* structures, which all exhibit herringbone packing of the phenyl groups between neighboring sheets, are found to have similar stabilities (within 1 kcal/mol). The “Northolt-translated” structure, with its parallel packing of phenyl groups, is more than 20 kcal/mol less stable than the other three structures. Therefore, these calculations clearly exclude the parallel packing of phenyl groups in the solid state, but the effect of the relative orientation of amide linkages between sheets (parallel for Northolt and *Pb* structures, antiparallel for Northolt-translated and Liu (*Pa*) structures) is more subtle. Assigning reasonable partial charges to the four atoms in each of these three amide groups ($q(\text{O}) = -0.60$ e, $q(\text{C}) = 0.45$ e, $q(\text{N}) = -0.49$ e, $q(\text{H}) = 0.28$ e) and calculating the van der Waals (parameters from the Universal Force Field²⁹) and Coulomb contributions to the total energy show that Coulomb interactions favor, by a few kcal/mol, the packing of amide linkages found in the antiparallel case. However, this simple analysis of the inter-sheet packing of amide linkages depends on the partial charges and VDW parametrization. While the packing of phenyl groups can be determined from the energies of the equilibrium structures, the packing of the amide groups gives much smaller energy differences, and the role of vibrational spectroscopy coupled with DFT calculations in clarifying this structural issue is therefore crucial.

The structural information used as input to the phonon calculations was obtained at room temperature, whereas the INS spectra were measured at 10 K. Using the spectra to identify the correct structure therefore depends on there being no major structural changes in cooling from room temperature to 10 K. That the calculation spectra based on the Liu structure are in good agreement with the measured spectra suggests that this structure is stable down to low temperatures.

Vibrational spectroscopy gives clear structural information despite disorder in the sample, arising from the imperfect crystallinity and the small fiber diameter, which limits spectral

resolution. The sample-limited resolution is illustrated by the fact that the higher resolution TOSCA spectrometer did not give better-resolved spectra than IN1. The phonon calculations on PPTA show weak dispersion, the width of the spectral contributions of the amide linkage hydrogen atom being smaller than 20 cm^{-1} (see, for example, the amide group hydrogen-bond intensity at 800 cm^{-1} in Figure 5, panel b). This hydrogen atom participates in the hydrogen-bond network, and its modes could be expected to show dispersion, but the length of the hydrogen bond (the N–H \cdots O distance is 2.98 Å) and the high N–H stretch frequency (~ 3400 cm^{-1}) indicate a weak hydrogen bond, which is consistent with the lack of significant dispersion. The $\sim 30\%$ of polymer chains on the outer surface of the fibers have vibrations modified by the molecular environment, but the remaining 70% of chains therefore have well-defined vibrations that are typical of the bulk material. If the coupling between molecules, indicated by more pronounced dispersion, were stronger, the effect of the surface would propagate further into the bulk and reduce the bulk signal. In this context, the total vibrational spectrum has been compared with calculations performed on perfect, infinite crystals.

In a periodic model, surfaces can be modeled by removing some of the molecules, leaving a slab with an upper and a lower surface. Large models are therefore required to separate the two surfaces both via the vacuum and via the bulk. The calculations should be repeated for different molecular planes at the surface. Because good agreement has been obtained between calculations performed on the bulk material and measurements on fibers, it is expected that, in the case of PPTA, the effect of the fiber surfaces is mainly to broaden a fraction ($\sim 30\%$) of the bulk signal. Separating the crystalline and amorphous contributions quantitatively is therefore difficult. However, quantifying different crystalline contributions in a sample would be possible, with a precision dependent on there being distinct spectral features associated with each component.

V. Conclusion

The calculations on benzanilide demonstrate how well solid-state DFT methods describe intra- and intermolecular interactions. Applying the same method to PPTA gives clear evidence for an antiparallel configuration of amide linkages in neighboring hydrogen-bonded sheets. The calculations presented here are therefore in agreement with the *Pa* structure determined by Liu¹⁹ and the new neutron diffraction data.²⁰ It is the accurate calculation of the weak inter-sheet interactions, in the presence of stronger intra-sheet interactions, that enables the structures to be distinguished. The N–H wagging mode is the principle probe of the inter-sheet packing because the hydrogen atom can have a large amplitude motion (when this mode is pure), giving an intense peak.

In DFT-based calculations, the total energy is not determined from a pairwise sum of interatomic interactions, so the contributions from different structural units cannot be determined by “tuning” empirical atom–atom potentials. It is only by repeating the phonon calculations on a set of structures that the key structural feature probed by the vibrations, the relative orientation of the amide linkages in neighboring hydrogen-bonded sheets, can be identified. While total energy calculations can

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exclude the Northolt-translated structure due to its parallel packing of phenyl groups, the different packing of amide groups gives much smaller energy differences and the vibrational spectroscopy therefore provides uniquely clear information.

Because INS intensities can be calculated reliably from a given structure and its vibrational modes, the validity of the structure can be established even when the spectral resolution is limited and individual modes are not resolved. Thus, by using a fully converged, first principles method that allows the whole spectral profile (peak positions, intensities, and shapes) to be calculated, a direct link is established between the structure and dynamics of these model amide compounds. In view of the small shifts of vibrational modes that change the overall spectral profile, any parametrized description of the interatomic interactions could not be relied upon to obtain such precise structural information.

As computing power continues to grow and with the development of more efficient computational codes, the methods used here will be extended to more complex systems of biological and technological interest. Intra-sheet modes in β -sheet compounds could be investigated, as has been done elsewhere,^{3,4} but avoiding the transfer of parameters from ab

initio calculations to empirical potentials. Assemblies of amino acids or nucleic acids in their natural aqueous environment, such as collagen, small globular proteins, and DNA, are also coming within the scope of these methods. The partially crystalline nature of such systems results in a relatively high level of spectral information, justifying the use of computationally intensive, first principles methods. However, due to the presence of noncrystalline water, a molecular dynamics approach, in which a range of conformational states of the system is explored and the vibrational spectrum is calculated from the velocity auto-correlation function, may be preferred to the structure-specific, dynamical matrix approach employed here. As the work presented here demonstrates, interest need not be limited to particular vibrational bands; the whole spectral profile and its information content can be investigated. By calculating charge tensors, the calculation of spectral profiles can also be extended from INS spectra to the more commonly measured IR spectra.

Supporting Information Available: Sample details, inelastic neutron scattering, and numerical simulations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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