Inelastic neutron scattering study of the proton dynamics in HNO₃ graphite intercalation compounds

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Abstract

Inelastic neutron scattering (INS) spectra of the α-form third stage of the graphite–nitric-acid intercalation compound G-HNO₃ (C₄₁HNO₃) at 20 K are presented for a powder sample and for aligned platelets of highly ordered pyrolytic31 5 3 graphite HOPG-HNO₃, with momentum transfer direction either parallel or perpendicular to the layer planes. The dynamics of the NO₃ entities are amenable to a slightly non-planar structure and tunnel splitting due to inversion is tentatively assigned at 100 cm⁻¹. The NO₃ mean-plane is tilted 35° 5° to the graphite layer. Proton dynamics are twofold. Bound protons form strong hydrogen bonds, canted at ~ 45° with respect to the layers, between NO₃ entities. In addition, a continuum of intensity is assigned to recoil of free protons.

1. Introduction

The graphite–nitric-acid compounds (G-HNO₃) obtained after intercalation of the pure nitric-acid vapour in graphite are good p-type conductors and can be regarded as ‘‘synthetic metals’’ [1–4]. With intercalation of nitrate ions and molecules of nitric acid the carbon hexagonal network behaves as a macroroation. At room temperature, these compounds have been characterised with X-ray and electron diffraction [5–10], ¹H, ²H and ¹³C NMR [11–14], quasi-elastic neutron scattering (QENS) [15] and inelastic neutron scattering (INS) [16].

The intercalated layers are ordered in regular sequences along the graphite c axis and the stage s is the number of graphite layers between two acid layers. Two forms of G-HNO₃ are known. The α-form is stable in sealed tubes at equilibrium with the HNO₃ vapour. It corresponds to the chemical composition C₄₁HNO₃, with stage s = 1,2,3 . . . . The interlayer distance d₁ is 7.80 Å. After exposure to ordinary atmosphere, the β-form (C₈₅HNO₃) is obtained without any stage variation whilst the interlayer distance decreases to d₂ = 6.55 Å [5]. At room temperature, the intercalated layers are disordered in a liquid-like state, modulated by the graphite lattice.

At low temperature, the situation is more complicated. For the α-form, positions of the molecules in the graphite lattice are not known precisely. It has
been speculated that the HNO$_3$ molecules are in the graphite sites. However, the closest simple commensurate structure $\sqrt{3} \times \sqrt{3}$ gives the chemical composition C$_{6s}$HNO$_3$, instead of C$_{5s}$HNO$_3$ derived from chemical analysis. Therefore, the material was tentatively represented with the $\sqrt{3} \times \sqrt{3}$ structure compressed by numerous domain walls [15]. However, the estimate of O atoms bonded to C atoms with $^{13}$C NMR [13,14] has provided further support to the stripe-like arrangement, not parallel to the basis vector of graphite, proposed from previous X-ray measurements [10]. The planes of the nitric-acid molecules should be tilted by $\sim 25^\circ$ to the $c$ axis [9,16]. For the $\beta$-form, the planes of the molecules are almost parallel to the graphite layers [17–21].

Despite numerous thorough studies, proton dynamics in G-HNO$_3$ are not yet fully understood [14]. Whereas the NMR and QENS techniques provide information on rather slow proton motions, the time scale of the vibrational spectroscopy techniques is necessary for a detailed view of proton dynamics (i.e., $10^{-12}$ to $10^{-15}$ s). Unfortunately, optical spectroscopies (infrared and Raman) have disadvantages for the study of proton dynamics in carbonaceous matrices. The opacity of the matrix and the lack of sensitivity to proton displacements preclude a clear characterisation of these dynamics. Most of these difficulties are overcome with the INS spectroscopy. Because the neutron scattering process is entirely attributable to nuclear interactions, each atom is characterised by the nuclear cross-section independent of chemical bonding. The intensity for any transition is simply related to the atomic displacements scaled by scattering cross-sections. The technique is particularly well adapted for proton dynamics in carbonaceous matrices, because the proton cross-section is about 10 times greater than that for carbon atoms.

Previous INS measurements [16] with the beryllium filter detector spectrometer IN1B (Institut Laue-Langevin, Grenoble, France) performed on the $\alpha$-form with $s = 2$ have been interpreted in terms of HNO$_3$ molecular entities interacting through rather weak hydrogen bonds ($r_{OH} \sim 3100$ cm$^{-1}$). Polarisation effects were claimed to confirm the orientation of the NO$_3$ planes, tilted to $\sim 25^\circ$ to the $c$ axis.

However, a new view of the proton dynamics in carbonaceous systems has emerged from recent INS measurements with the TFXA and MARI spectrometers at the ISIS pulsed neutron source (Rutherford Appleton Laboratory, UK) performed on various coals [22–24] and carbon blacks [25]. Broad bands attributable to protons chemically bound to heavy atoms (C, O, N, ...) were observed on the top of a continuum of intensity which corresponds to the signal anticipated for recoil of free particles with a mass of 1 amu. Although the INS technique does not provide any information on the electrical charge of recoiling particles, these were tentatively regarded as free protonic entities not specifically bound to any atoms. These free entities could be of importance to modellling charge carriers in carbonaceous materials. Unfortunately, for technical reasons, this sort of continuum cannot be characterised with confidence with the IN1B spectrometer. Besides, free protons in solids cannot be characterised readily with other techniques like infrared, Raman or QENS.

In order to obtain more information on proton dynamics in G-HNO$_3$ compounds, we have carried out new INS measurements on the third stage of the $\alpha$-form at 20 K, with the TFXA spectrometer. A powder sample and oriented highly ordered pyrolytic graphite (HOPG-HNO$_3$) platelets, with graphite

---

\[ \text{C} \]

\[ \text{k}_0 \perp \]

\[ \text{k}_0 \parallel \]

Fig. 1. Schematic view of the scattering geometries for the (HOPG-HNO$_3$) sample. The incident wavevector $k_0$ is almost parallel to the momentum transfer direction.
Table 1

<table>
<thead>
<tr>
<th>Powder</th>
<th>HOPG</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>94vs</td>
<td>99s</td>
<td>Libration</td>
</tr>
<tr>
<td>100s</td>
<td></td>
<td>v₂ NO₃ 0⁺→0⁻</td>
</tr>
<tr>
<td>172wsh</td>
<td>--</td>
<td>Graphite lattice</td>
</tr>
<tr>
<td>295vw</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>475sh</td>
<td>--</td>
<td>v₂ NO₃ 0⁺→1⁺</td>
</tr>
<tr>
<td>620s</td>
<td>635vw</td>
<td>v₂ NO₃ 0⁺→1⁺</td>
</tr>
<tr>
<td>670s</td>
<td>680vw</td>
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<tr>
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<td>780vs</td>
<td>v₄ NO₃</td>
</tr>
<tr>
<td>940sh</td>
<td>930sh</td>
<td>v OH</td>
</tr>
<tr>
<td>1100w</td>
<td>1125w</td>
<td>v₁ NO₃</td>
</tr>
<tr>
<td>1270w</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>1420s</td>
<td>1420m</td>
<td>γ OH + v₃ NO₃</td>
</tr>
<tr>
<td>1655m</td>
<td>1660m</td>
<td>δ OH</td>
</tr>
</tbody>
</table>

$s$: strong; $m$: medium; $w$: weak; $v$: very; $sh$: shoulder. These symbols characterise the integrated intensities.

planes either parallel or perpendicular to the incident wavevector, were studied (Fig. 1). A new band assignment scheme is proposed (see Table 1). Possible inversion through tunnelling of non-planar NO₃ entities is emphasised. A continuum of intensity that may correspond to proton recoil is observed.

2. Experimental

2.1. Sample preparation

The G-HNO₃ compounds were obtained after equilibration with HNO₃ vapour in a ‘‘two bulbs tube’’. The chemical reaction can be written as:

$$6\text{HNO}_3 + 25\text{C} \rightarrow \text{C}_2\text{H}_3\text{NO}_3 + 4\text{HNO}_3 + \text{NO}_2 + \text{H}_2\text{O}. $$

In order to avoid wrapping of the HOPG sample, small amounts of HNO₃ vapour were intercalated slowly during several days. The formation of higher stages was controlled with X-ray diffraction. The HNO₃ vapour pressure was controlled via the temperature of the bulb containing the anhydrous nitric acid, between -20 and 20°C.

2.2. TFXA spectrometer

The TFXA spectrometer at the ISIS pulsed neutron source (Rutherford Appleton Laboratory, Chilton, UK) is an inverted time-of-flight spectrometer with resolution $\Delta \omega/\omega \sim 3\%$ [26]. The detected spectra, normalised to the incident monitor, were converted by standard programs from counts per channel to the conventional scattering function $S(Q, \omega)$. The momentum transfer $Q$ is the vector difference between the incident and scattered wavevectors $|k_i| = 2\pi/\lambda_0$ and $|k_f| = 2\pi/\lambda_f$, where $\lambda_0$ and $\lambda_f$ are the incident and scattered wavelengths, respectively. The momentum and energy-transfer are correlated according to $h \omega \sim 16Q^2$, with $h \omega$ and $Q$ in cm⁻¹ and Å⁻¹ units, respectively. This corresponds to the maximum of intensity for harmonic oscillators with mass 1 amu.

Neutrons are collected at fixed scattering angle (135°) and the neutron momentum transfer vector has its principal component $(Q_y)$ along the incident
wavevector $k_0$. There is a small component $(Q_\perp)$ and the neutron momentum polarisation is:

$$R = \frac{|Q_\perp|^2}{E_0} \equiv \frac{E_0}{E_f}$$

$(E_0$ and $E_f$ (32 cm$^{-1}$) are the energies of the incident and scattered neutrons, respectively. At low energy transfer, $R$ is only moderate (~3 at 100 cm$^{-1}$). However, the polarisation improves rapidly, such that $R \sim 25$ at 800 cm$^{-1}$. For large energy transfer, any influence of $Q_\perp$ can be ignored.

The samples were sealed in silica cells. The spectrum of the empty cell was subtracted. The spectra were normalised with respect to the amount of sample in the beam.

### 3. Results and discussion

For the powder sample (Fig. 2A) broad bands at ~780, 1400 and 1650 cm$^{-1}$ due to the proton modes and narrow lines with much weaker integrated intensities at 630 and 1100 cm$^{-1}$ due to the NO$_3$ entities can be distinguished. Beneath these bands there is a continuum with virtually constant intensity over the whole energy transfer range.

The spectra of the oriented HOPG-HNO$_3$ sample with the incident wavevector $k_0$ either perpendicular or parallel to the graphite layers (Fig. 2B,C, respectively) reveal the orientations of the normal mode eigenvectors. Only three narrow lines at 100, 475 and 630 cm$^{-1}$ emerge clearly as vibrations mainly perpendicular to the layers. The weak band at ~1100 cm$^{-1}$ is well oriented parallel to the layers. These bands are assigned to the NO$_3$ entities. In addition, the complex band profile at ~780 cm$^{-1}$ for $k_{0\perp}$ (see Fig. 2C) is likely the superimposition of two different modes. Firstly, a broad component also observed for $k_{0\perp}$ (see Fig. 2B) corresponds to a proton mode. Secondly, a much weaker narrow line on the top of the broad proton mode, which is not observed for $k_{0\perp}$, is assigned to a vibrational mode of the NO$_3$ entities with the eigenvector nearly parallel to the layer.

The polarisation effects on the broad bands of the proton modes at ~780, 1400 and 1600 cm$^{-1}$ are rather weak. As a general trend, slightly more intensity is observed for $k_{0\parallel}$ than for $k_{0\perp}$. Even though the bands at ~780 and 1660 cm$^{-1}$ are more depressed for $k_{0\perp}$, compared to that at 1400 cm$^{-1}$, it is difficult to distinguish specific orientations for the proton modes.
The spectra presented in Fig. 2 resemble very much those previously published for the second stage analogue [16]. However, the TFXA spectrometer provides much better definition of the band profiles and more details below 500 cm\(^{-1}\) where no band was reported. In addition, the continuum of intensity was totally overlooked in the previous work.

Finally, the interpretation of the spectra is rather complex because we do not know exactly the structure of the G-HNO\(_3\) compound, the orientation of the HNO\(_3\) entities with respect to the graphite plane, the type of hydrogen bonding between these entities and the degree of disorder. Unfortunately, the band polarisations do not help very much to assessing precise assignments of the proton modes. In order to unravel the various contributions, the dynamics of the protons and NO\(_3\) entities are analysed separately.

3.1. NO\(_3\) entities

The incoherent cross-sections for the N and O atoms are virtually zero. However, for large energy and momentum transfer values, the coherent cross-section must be also considered. Then, the total cross-section for NO\(_3\) is \(\sim 24\) barns, compared to \(\sim 82\) barns for protons. For a harmonic mode at \(\sim 700\) cm\(^{-1}\), the intensity ratio \(I_H/I_{NO_3}\) is \(\sim 20\). The observed intensities suggest that there is no important mixing of the NO\(_3\) and proton dynamics. This is further supported by the very different bandwidths for the two dynamics and by the lack of correlation for polarisations of the proton and NO\(_3\) modes. However, the rather large intensity for the bands around 100 cm\(^{-1}\) suggests possible mixing of the dynamics in this frequency range and/or very anharmonic oscillations (see below).

The NO\(_3\) entities decoupled from the protons are amenable to either the \(D_{3h}\) (planar carbonate-like) or the \(C_{3v}\) (non-planar ammoniac-like) symmetry. In both cases, there are four modes, two of them being degenerate. For the planar structure, there is only one out-of-plane mode.

Within this scheme, the band at 630 cm\(^{-1}\), observed with large intensity for \(k_{\parallel}\), corresponds to the non-degenerate out-of-plane \(\nu_2\) mode. This is in accord with the assignment scheme \(\nu_2\) proposed in the previous INS work [16]. Furthermore, the band at 475 cm\(^{-1}\) with similar width and polarisation must be also assigned to \(\nu_2\). The other narrow bands at 1125, and 780 cm\(^{-1}\) with marked polarisation along \(k_{\parallel}\) are assigned to \(\nu_1\) and \(\nu_3\) (degenerate), respectively. The remaining degenerate \(\nu_3\) mode is probably partially hidden by the proton modes between 1400 and 1500 cm\(^{-1}\). There is some ambiguity for the band at 1125 cm\(^{-1}\) that was assigned previously to H\(_2\)O\(^+\) entity [16]. An alternative assignment to the very weak band at 1270 cm\(^{-1}\), not observed for the HOPG-HNO\(_3\) sample (Fig. 2), was preferred (see Table 1).

According to the assignment scheme proposed above, the NO\(_3\) entities are almost parallel to the graphite planes. For the bands at \(\sim 630\) cm\(^{-1}\) the estimated intensity ratio \(I_H/I_{NO_3}\) is compatible with a tilt angle \(\theta = 35 \pm 5^\circ\) between the NO\(_3\) mid-plane and the layers. This is at variance from the previous INS works on the second stage G-HNO\(_3\) [16] in which it was concluded that the NO\(_3\) planes are tilted to \(\sim 65^\circ\) to the layer plane (\(\sim 25^\circ\) to the \(c\) axis).

The splitting of the \(\nu_2\) mode is reminiscent of the inversion of the ammoniac molecule with non-planar \(C_{3v}\) symmetry. Polarisation and width of the band at \(\sim 100\) cm\(^{-1}\) are consistent with tunnel splitting. These dynamics can be represented with a nitrogen atom \((14\) amu) tunnelling through the plane of the three oxygen atoms \((48\) amu). For the effective oscillator mass of \(10.84\) amu, the double minimum potential consistent with the observed frequencies (Fig. 3) has a barrier height of \(\sim 900\) cm\(^{-1}\) and the minima are located at \(\sim \pm 0.07\) Å out of the mid-plane (this corresponds to a basal angle of \(\sim \pm 3^\circ\) for the pyramidal structure). This deviation from planarity is so tiny that the assignment scheme in terms of \(D_{3h}\) symmetry species remains quite pertinent, so long as bands below 500 cm\(^{-1}\) are ignored.

In the ground state, the wave functions associated to each minimum largely overlap one another and the two structures are almost indistinguishable. However, this potential gives larger amplitudes, and therefore, larger INS intensities, for the \(\nu_2\) modes than the harmonic vibrations of the planar structure.

3.2. Proton dynamics

Proton dynamics are characterised by three broad bands at \(\sim 780, 1400\) and 1650 cm\(^{-1}\) which corre-
Fig. 3. Double minimum potential for the inversion of the NO$_3$ entities:

$$V = 11818 x^2 + 970 \exp(-1014 x^2)$$

$V$ and $x$ are in cm$^{-1}$ and Å units, respectively. The oscillator mass is 10.84 amu. The minima are at $\pm 0.066$ Å and the barrier height is 907 cm$^{-1}$.

Spond to the three vibrational modes anticipated for protons involved in rather strong hydrogen bonds. Since there is virtually no visible band polarisation, the hydrogen bonds are likely canted to $\sim 45^\circ$ with respect to the layer direction, possibly with rather large disorder. According to the correlation between stretching frequencies and O···O distances [27], the hydrogen bonds length should be in between 2.46 and 2.56 Å, depending on the assignment of the stretching mode to the lowest or highest frequency.

The weak and narrow band at 680 cm$^{-1}$ is most likely an “in-plane” mode of NO$_3$, but there is no obvious assignment within the $D_{6h}$ or $C_{3v}$ symmetry discussed above. This very weak band could be due to either some deviation from the ideal symmetry (possibly because of hydrogen bonding) or minor concentrations of additional species.

The assignment scheme presented in Table 1 is quite different from that proposed previously [16]. To assign the very weak band at 680 cm$^{-1}$ to the $\gamma_{OH}$ mode is obviously unacceptable. This mode corresponds to large amplitude for proton displacements and must be assigned to one of the most intense band of the spectrum.

For the ideal commensurate $\sqrt{3} \times \sqrt{3}$ structure, the shortest distances between NO$_3$ entities are 2.46 Å and hydrogen bonds canted to 45$^\circ$ should be $\sim 3.5$ Å long. The spectra are not amenable to so weak hydrogen bonds. We conclude that the NO$_3$ entities should adopt a zigzag structure schematically represented in Fig. 4. With O···O = (2.51 ± 0.05) Å the distances between the projections of the O atoms onto the layer planes or the $c$ axis are equal to (2.51 ± 0.05) cos(45$^\circ$) $\sim$ (1.77 ± 0.03) Å. Therefore, NO$_3$ entities canted to $\sim 35^\circ$ are located at $\sim \pm 0.5$ Å off the mean layer plane. The total size along the $c$ axis of $\sim 4.7$ Å is similar to the interlayer free space of $\sim 4.5$ Å (this is the interlayer distance, 7.80 Å, minus twice the C atom radius, 3.35 Å). However, preliminary neutron diffraction measurements on HOPG-DNO$_3$ suggest that the graphitic layers could be slightly curved around the intercalated.
molecules. The NO\textsubscript{3} positions do not match the graphite lattice sites. The incommensurate structure based on canted stripes [13,14] is more likely than the commensurate structure.

The \( \nu_{\text{OH}} \) frequency at 790 cm\(^{-1} \) may correspond to very short O\cdots O distances of \( \sim 2.4 \text{ Å} \), compatible with nearly symmetrical hydrogen bonds with protons siting near by the center of the O\cdots O lines. However, there is no evidence for any band splitting or proton tunnelling transition (above \( \sim 20 \text{ cm}^{-1} \)) supporting a symmetrical double minimum potential.

### 3.3. Free protonic entities

The continuum of intensity underneath the bands discussed above is attributed to the recoil of free particles with mass \( \sim 1 \text{ amu} \), by analogy to previous works [22–24,28–32]. This is the most straightforward evidence for mobile proton-like entities that are not chemically bound to any particular atom. In contrast to this, bound oscillators have a discrete energy spectrum. Since three modes are observed for bound protons, free entities are clearly different from the bound ones.

There is no visible cut-off at low frequency for the continuum intensity in Fig. 2. Apparently the recoiling particles are not bound to any local potential-well with dissociation threshold greater than \( \sim 20 \text{ cm}^{-1} \). Therefore, they can be regarded as a gas of free particles. The theoretical framework for the INS spectra of free particles is well-established [24,30,31]. Only guidelines necessary for further discussion of the data are presented. Free protons are represented as planar-waves with kinetic momentum distribution \( n_{\text{H}}(p_{\text{H}}) \) corresponding to that of an ideal gas at thermal equilibrium. At a very low temperature, free particles are virtually at rest with respect to the lattice referential that is still oscillating at zero-point energy with respect to a “fixed” laboratory-frame. These collective oscillations are represented as phonons with distribution of kinetic momentum

\[
n_{\text{L}}(p) = \left( \frac{2 \langle U_{\text{L}}^2 \rangle}{\pi} \right)^{1/2} \exp\left( -2 p^2 \langle U_{\text{L}}^2 \rangle \right),
\]

where \( \langle U_{\text{L}}^2 \rangle \) is the averaged mean-square amplitude of the lattice modes. All together, \( n_{\text{L}}(p) \) and \( n_{\text{H}}(p_{\text{H}}) \) form the total density-of-states which is probed by neutrons. For a given value of \( p_{\text{L}} \) the incoming wave-vector experienced by free protons is \( k_0 - p_{\text{L}} \) (\( k_0 \) is defined with respect to a “fixed” laboratory referential). The momentum effectively transferred to the free particles, \( Q_{\text{H}} = k_0 - p_{\text{L}} - k_f \), is different from that transferred to the sample: \( Q = k_0 - k_f \). The scattering-function is merely the convolution of the recoil spectrum with the kinetic-momentum distribution of the lattice modes

\[
S(Q, \omega) \propto \exp\left[ -2 \left( \frac{Q - \sqrt{2mE_r}}{h} \right)^2 \langle U_{\text{L}}^2 \rangle \right] \\
\times \delta(\hbar \omega - E_r).
\]

\( E_r \) is the recoil energy. The intensity at maximum is then largely independent of the energy-transfer value, in accord with the observation.

The above model provides a straightforward explanation for the lack of polarisation effects for the continuum of intensity. Within the harmonic approx-
imination, $\langle U_2^2 \rangle$ in Eqs. (2) and (3) is proportional to $\langle \Sigma, \mu, \nu \rangle^{-1}$, where $\mu$, $\nu$, and $\omega$ are the effective masses and frequencies for the lattice modes. Because the C, O and N atoms are heavy, the averaged mean-square amplitude is largely dominated by the bound protons. Since there is virtually no polarisation effect for the proton bands, the mean-square amplitude for bound protons ($\langle u_0^2 \rangle \sim 1.5 \times 10^{-2} \AA^2$) is almost the same for $k_{||}$ and $k_{\perp}$ and give no visible polarisation for the continuum intensity.

In principle, $Q$ profiles for recoiling and bound protons are different. However, they are very similar in shape and their widths are almost the same ($\sim 1.18 \langle u_0^2 \rangle^{-1/2}$ and $1.15 \langle u_0^2 \rangle^{-1/2}$) for free and bound protons, respectively. Therefore, the intensities measured with the TFXA spectrometer for the bands and for the continuum are proportional to the amount of bound and free protons with similar scaling factors. In addition, in the case of isotropic recoil, the intensity of the continuum includes contributions from the three degrees of freedom, whilst each band corresponds to a single mode. A rough estimate of the relative intensities integrated from 250 to 2000 cm$^{-1}$ for proton bands and for the underlying continuum gives $\sim 3:1$ for the ratio of bound to free protons. Although this is in line with previous estimates for free protons in some coals [22,23], this ratio is subjected to large uncertainties. Nevertheless, it transpires that the amount of free protonic entities is too large to be due to defects or grain boundaries in graphite. Instead of a regular network of hydrogen bonds extending over large domains, the G-HNO compound must be regarded as a mixture of free protonic entities and hydrogen bonded oligomeric entities with an average number of about four NO entities bound by $\sim 3$ hydrogen bonds $\langle NO_3 \cdots H \cdots NO_3 \cdots H \cdots NO_3 \cdots H \cdots NO_3 \cdots \rangle$.

Since INS does not provide any information on the effective electric-charge of the recoiling entities, it is not possible to distinguish between $H^+$, $H^0$ and $H^-$, or any intermediate entity. $H^-$ like entities are the less probable for stability and steric hindrance reasons. $H^+$ or $H^0$ entities are both consistent with the p-type conduction of the G-HNO$_3$ compounds. $H^0$ entities withdrawing electrons from graphite might increase the p-type conduction whilst $H^+$ entities should give rise to proton conduction.

4. Conclusions

The INS spectra of the third stage $\alpha$-form G-HNO$_3$ compound at 20 K obtained with excellent resolution and background definition shed a new light onto dynamics and structure. Powdered and oriented HOPG intercalated compounds yield a straightforward assignment scheme. The dynamics of NO$_3$ entities on the one hand and those of protons, on the other, are largely independent.

The spectra of the NO$_3$ entities are amenable to a slightly non-planar structure with $C_{3v}$ symmetry. The tunnel splitting due to inversion of the pyramid is observed and the double minimum potential is determined. The NO$_3$ entities are tilted to $35 \pm 5^\circ$ to the layer direction.

Proton dynamics can be represented with free and bound entities. About 25% of the protons are free. Bound protons form quite strong hydrogen bonds within oligomer-like entities $\langle NO_3 \cdots H \cdots NO_3 \cdots H \cdots NO_3 \cdots H \cdots NO_3 \cdots \rangle$. Hydrogen bonds are canting at $\sim 45^\circ$ to the layer. The local structure can be represented with zigzag chains between the graphitic layers that do not match the graphite lattice. Models based on the commensurate $\sqrt{3} \times \sqrt{3}$ structure are unlikely. The stripe model is more probable.

The observation of free protonic entities opens new prospects. Further understanding of the mechanism that determines the degree of electron transfer between graphite and protons could be of importance to the tailoring of G-HNO$_3$ materials.

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References