

Infrared transmission spectrum of nitrate-intercalated graphite

Morgan P. Conrad* and Herbert L. Strauss

Department of Chemistry, University of California, Berkeley, California 94720

(Received 25 June 1984)

Infrared transmission spectra of graphite, and of both normal and "lean" ("residual" or "B") graphite nitrate, are presented. These spectra allow determination of the intercalant species as HNO_3 . The nitrate plane is approximately perpendicular to the graphite planes in the normal compound and parallel in the lean compound. The out-of-plane infrared-active vibration of the graphite is observed to split by only 7 cm^{-1} upon forming the nitrate.

I. INTRODUCTION

Graphite intercalation compounds (GIC's) are formed when guest species penetrate the "gallery" between carbon layers, with consequent (and often large) crystal expansion along the c direction. Intercalating reagents vary, and include both powerful oxidizing and reducing agents. Most cause some charge transfer to the carbon π orbitals. The resultant compounds exhibit many fascinating properties—for example, near-metallic conductivities and high anisotropy—and have potential practical uses as electrochemical electrodes and catalysts. They also pose important fundamental questions, and have been the subject of many reviews and conferences.¹⁻⁷

The metallic nature of GIC's limits the usefulness of studies using long-wavelength radiation. For this reason, studies using hard x rays and extended x-ray-absorption fine structure (EXAFS) provide most of the known structural information. Unfortunately, the limitations of these techniques have caused much confusion, for example, over the crystal structure of graphite nitrate.⁸ Infrared transmission spectroscopy, which provides structural information complementary to that provided by the other methods, can resolve much of this confusion. We particularly note that transmission methods can probe the *interior* of the GIC and can determine the nature of the intercalant. Compared to most other GIC's, the nitrates are relatively nonreactive and stable,⁹ so they are a good choice for initial application of this new technique. We first briefly discuss the properties of GIC's most relevant to our studies, namely physical, vibrational, and electronic properties, and the crystal structures proposed for graphite nitrate, and then go on to present the transmission studies and our conclusions.

A. Electronic structure

The electronic structure of a single, ideal two-dimensional (2D) layer of graphite at 0 K is well known.¹⁰ The valence band is full and the conduction band empty, so our ideal system is a zero-band-gap semiconductor. In practice, the 3D structure causes some overlap of the two bands, and thermal motion excites some electrons, giving graphite semimetallic properties in the a - b plane. The weak c -axis bonding makes it an insulator in that direc-

tion. This anisotropy can be exploited by making infrared polarizers from chips thinned along the a axis.¹¹ The a - b layers serve as the wires in a wire polarizer, allowing only light polarized in the c direction to pass.

Both donor and acceptor intercalants shift the Fermi level E_F , vastly increasing the in-plane conductivity. Typical acceptor anions (NO_3^- , AsF_6^-) have closed shells and do not overlap with the carbon p_z orbitals, so the c -axis conductivity, already low, decreases. GIC's with these intercalants are even more anisotropic than pristine graphite and should form better polarizers, allowing more c -polarized light to pass. However, these compounds are also more fragile along the c axis, making them difficult to handle for the optical experiments.

By contrast, typical low-stage donor compounds exhibit large c -axis conductivity, even larger than that in the a - b plane. Little light of any polarization can pass. This behavior has been explained by postulating that the donor ion's empty s orbitals form a bond (or charge transfer) with the carbon p_z orbital.¹⁰ The simple 2D electronic model, which works well for most acceptor compounds, is a severe approximation here.

B. Vibrations

The vibrational modes of a single layer of graphite are shown in Fig. 1.^{12,13} The unit cell of the graphite crystal consists of four atoms with the two atoms shown in one layer and another two atoms in an adjacent layer. The normal modes of the full three-dimensional structure are listed in Table I. Each of the modes of the single-layer structure splits into two upon forming the three-dimensional structure. The splitting is due to the interlayer forces, and so is expected to be relatively small. The $E_{2g}^{(1)}$ and $B_{2g}^{(1)}$ modes involve motion of adjacent planes, and the $E_{2g}^{(1)}$ mode is seen in the Raman at about 50 cm^{-1} . The in-plane stretching or bending modes appear at 1584 cm^{-1} in the Raman ($E_{2g}^{(2)}$) and 1588 cm^{-1} in the infrared ($E_{1u}^{(2)}$). The other optically active mode is the $A_{2u}^{(2)}$ out-of-plane bending mode, and it has proven to be the most difficult to observe. However, it has been recently seen at 868 cm^{-1} , and this has allowed fitting to a fairly complete normal-mode calculation.^{13,14}

Upon intercalation with FeCl_3 or K, two in-plane Ra-

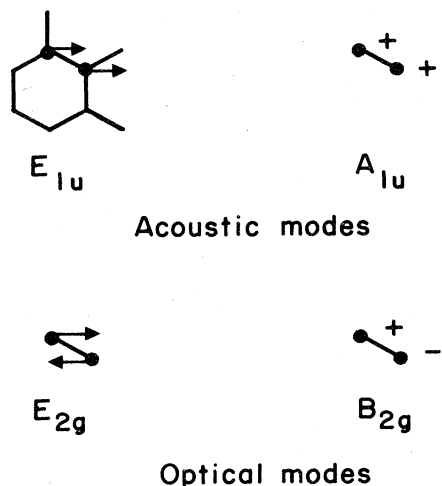


FIG. 1. Approximate normal modes for a single layer of graphite. The motions designated by + and - are out-of-plane.

man bands appear near the $E_{2g}^{(2)}$ stretching mode, one blue-shifted by only a few wave numbers from the band in pure graphite, the other around 20 cm^{-1} higher in frequency. The nearest-layer model, which considers only the two layers adjacent to any given layer, attributes these two bands to vibrations of "interior" layers (surrounded by other carbon layers) and "boundary" layers (with intercalant on one side), respectively. The model predicts that the relative intensity of the two bands should be proportional to the number of corresponding layers, and this is confirmed by experiment.¹² For example, stage-2 compounds show no "interior" line. Infrared reflectance studies, though harder to interpret, follow similar trends.¹⁵ Upon intercalation a new band also appears in the infrared, a few wave numbers lower than the pure graphite band, with an intensity proportional to the number of boundary layers.

In a few instances, the "guest" molecule modes have also been studied. The Raman bands of intercalated FeCl_3 lie within five wave numbers of those in the crystal,

TABLE I. Vibrations of graphite in D_{6h} symmetry. (ir denotes infrared; R denotes Raman.)

2D structure		3D structure
E_{2g}	in-plane	$E_{1u}^{(2)}$ (ir) (1584 cm^{-1})
		$E_{2g}^{(2)}$ (R) (1588 cm^{-1})
B_{2g}	out-of-plane	$B_{2g}^{(2)}, A_{2u}^{(2)}$ (ir) (868 cm^{-1})
A_{2u}	out-of-plane	$B_{2g}^{(1)}$ low-frequency vibration
		layer translation $A_{2u}^{(1)}$ acoustic mode
E_{1u}	in-plane layer translation	$E_{2g}^{(1)}$ (R) low-frequency vibration
		$E_{1u}^{(1)}$ acoustic mode

but are somewhat broader.¹² Raman lines observed in stage-1 graphite- H_2SO_4 are generally within several wave numbers of those found in $\text{S}_2\text{O}_7^{2-}$, which is proposed as the actual ionic species within the carbon layers.¹⁶ Solin¹⁷ has suggested that the FeCl_3 Raman spectra are resonance-enhanced, and that the lack of such enhancement explains the failure to observe molecular modes in GIC's intercalated with nitric acid, AsF_5 , SbCl_5 , and other molecules.

C. Graphite-nitrate crystal structures

Rudorff,¹⁸ who performed the first preparative and structural studies on salts of graphite and strong mineral acids (HNO_3 , H_2SO_4), found a typical formula of $\text{C}_{24}^+\text{NO}_3^-\text{HNO}_3$ with $x = 3$. He proposed a strange crystal structure where the nitrate ions form double planes between the graphite layers and leave a lot of empty space. This is illustrated in Fig. 2(a). The neutral molecules (which also appear in other graphite-acid salts) may serve as dielectric spacers between the anions, may aid in hydrogen bonding, or may be extraneous.³

A careful recheck of the x-ray data led Touzain⁸ to propose an alternate stoichiometry $\text{C}_{4.3n}\text{H}_x\text{NO}_3$ ($n = \text{stage}$, $x = \frac{5}{6}$), and a crystal structure with the nitrate ions perpendicular to the a - b plane. However, the available data is sparse enough to allow for other possibilities, such as the nitrate ions leaning at a slight angle. A further complication is the existence of another phase of graphite nitrate, alternately called "residual," "lean," or B .¹⁹ When "normal" graphite nitrate, which has a gallery spacing of 7.8 \AA , is either pumped on or allowed to sit in air for a few days, some intercalant desorbs and the gallery spacing drops to 6.55 \AA . There is little doubt that in these lean compounds the nitrate ions form single layers which are parallel to the graphite layers. These possibilities are all presented in Fig. 2.

II. EXPERIMENT AND RESULTS

A. Procedure

Highly ordered pyrolytic graphite²⁰ (HOPG) was mounted on a glass slide with crystal bond cement. The c

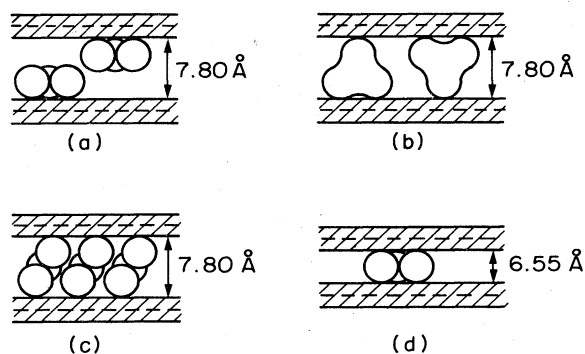
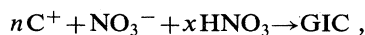
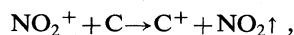
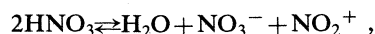


FIG. 2. Possible structures of graphite nitrate. Normal compound: (a) Rudorff's model (Ref. 18), (b) Touzain's model (Ref. 8), (c) tilt model, and (d) lean compound.

axis was placed parallel to the glass, and the specimen was ground on a standard grinding wheel.²¹ The glue was removed with acetone, yielding a fragile chip roughly $3 \text{ mm} \times 5 \text{ mm} \times 50 \mu\text{m}$, which was allowed to dry. Samples were placed between 1-in.-diam AgCl windows in a standard infrared cell, and an aluminum-foil shield was used to block light from going around the small sample. We used a Nicolet model 8000 vacuum Fourier-transform infrared spectrometer with a "globar" source and an extremely sensitive Infrared Associates liquid-nitrogen-cooled MCT-InSb sandwich detector which was often set to the low-frequency (MCT, mercury cadmium telluride, sensitive to light $< 1800 \text{ cm}^{-1}$) mode for increased sensitivity. Most sample spectra were run at one wave number resolution and extremely high gains (128 or more compared to one for the background). The aperture was increased by a factor of 10 for the sample spectra to further increase the signal. Inert silver chloride windows were used, and no reaction with the sample was observed. It was noticed that NaCl windows did react with the sample to form NaNO_3 .

Intercalation was achieved over the course of a few days in a closed two-chamber cell which held the chip in one side and Baker and Adamson red fuming nitric acid (specific gravity of 1.60) in the other. This gas-phase intercalation is gentle on the fragile sample, and yields a stage-2 compound when the chamber is continuously flushed with dry nitrogen.²² However, in our closed system, much water evolves, as is expected from the reaction mechanism,²³



which prevents the intercalation from reaching stage 2. Two types of samples were examined. One was fresh out of the reaction chamber, and presumably a "normal" intercalant. X-ray powder spectra, taken after the infrared spectra, revealed a predominantly stage-3 structure, but with some disorder. These samples then sat around for

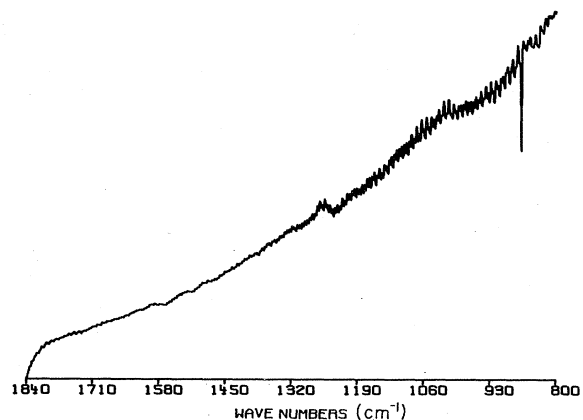


FIG. 3. Infrared transmission spectrum of a thin layer of pristine graphite; the transmission is polarized parallel to the c axis. The transmission scale has an arbitrary zero.

about 4 d, during which time HNO_3 desorbed and they changed to the "lean" form, as evidenced by the change in intensity of various spectral bands, which we will now discuss.

B. Vibrational spectra

1. Graphite modes

The spectrum of pristine graphite, presented in Fig. 3, shows two features. The first feature arises since the penetration depth of radiation into a conducting solid is proportional to its wavelength and thus the transmittance is smaller at high frequencies. This gives the spectrum its overall shape. The other spectral feature is a sharp line at 867 cm^{-1} , which has a full width at half maximum (FWHM) of 0.7 wave numbers in our higher- (0.25 cm^{-1}) resolution studies. The frequency confirms the results of the earlier infrared reflectance spectra of the out-of-plane A_{2u} bending mode. However, our results are more direct since they need not be fitted using dispersion analysis to obtain the actual frequencies and bandwidths,¹² and are not due to a surface phenomenon. The in-plane modes have the wrong polarization (perpendicular to the c axis), and so do not appear.

Graphite nitrate has a less noticeable background frequency dependence, due to its lower c -axis conductivity (it also transmits more light than plain graphite), but still shows the sharp A_{2u} band at 867 cm^{-1} . In addition, another sharp (0.9 cm^{-1} FWHM) line appears at 873 cm^{-1} in the "normal" compound and at 872.5 cm^{-1} in the "lean" compound (Figs. 4 and 5). We attribute the new band to boundary-layer motions, and the nearest-neighbor model appears to work successfully. The small shift conflicts with lattice-dynamics results which factor the dynamic matrix into three submatrices,

$$\underline{D}_{\text{GIC}} = \begin{pmatrix} \underline{D}_{II} & \underline{D}_{GI} \\ \underline{D}_{GI}^+ & \underline{D}_{GG} \end{pmatrix},$$

containing graphite-graphite, graphite-intercalant, and intercalant-intercalant interactions. When \underline{D}_{GI} is chosen to give the observed Raman splitting of 20 cm^{-1} (the $E_{2g}^{(2)}$ mode discussed earlier), the predicted splitting of the A_{2u} band between interior and boundary layers is predicted to

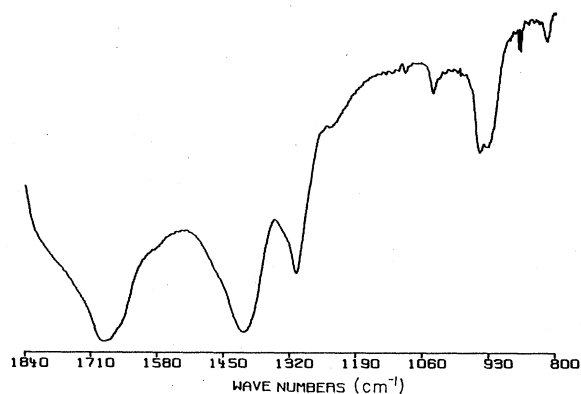


FIG. 4. Infrared transmission spectrum of "normal" graphite nitrate showing HNO_3 and graphite bands.

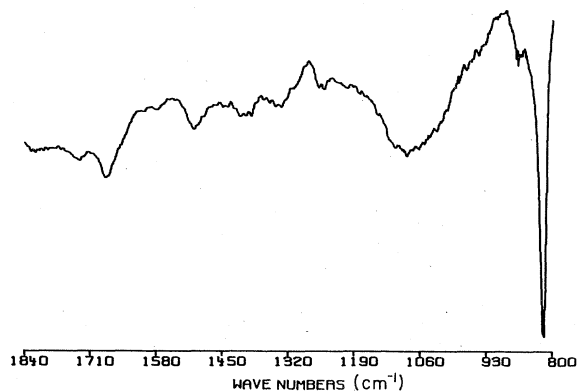


FIG. 5. Infrared transmission spectrum of "lean" graphite nitrate showing HNO_3 and graphite bands.

be roughly 100 cm^{-1} (Ref. 24) rather than the 6 cm^{-1} we observe.

One might expect the simple nearest-layer model to break down in stage-1 compounds, since in these the inter-layer interactions have been dramatically changed. Indeed, in stage-1 graphite fluoride²⁵ (Fig. 6) the out-of-plane vibrational band at 850 cm^{-1} is broad, in complete contrast to the present compounds, which have extremely narrow bands. Also, the in-plane vibration at 1584 cm^{-1} appears as a broad band, possibly due to the presence of a distribution of graphite-fluorine bonds (see Ref. 25 for a discussion of the x-ray structures).

2. Intercalant modes and assignments

A typical transmission spectrum of fresh, "normal" graphite nitrate (Fig. 4) has strong, broad bands at 1680, 1410, 1311, and 937 cm^{-1} wave numbers, and a weak band at 820 cm^{-1} . The intensity of this low-frequency band varied somewhat between different fresh samples, but was always small. In contrast, the lean samples (Fig.

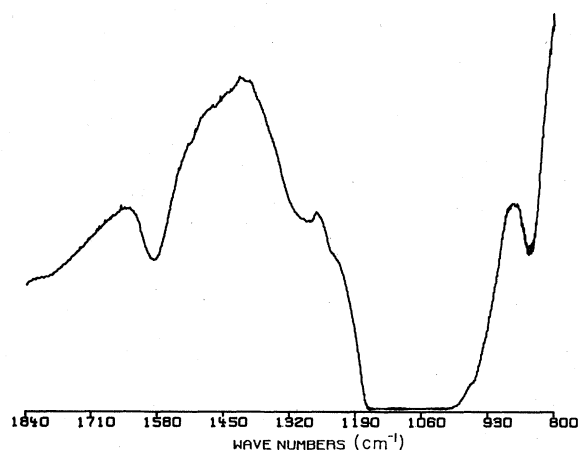


FIG. 6. Infrared transmission spectrum of stage-1 graphite fluoride. The very broad band at about 1100 cm^{-1} is the C-F stretch. Note the width of the 850-cm^{-1} graphite band compared to the narrow bands in Figs. 3-5.

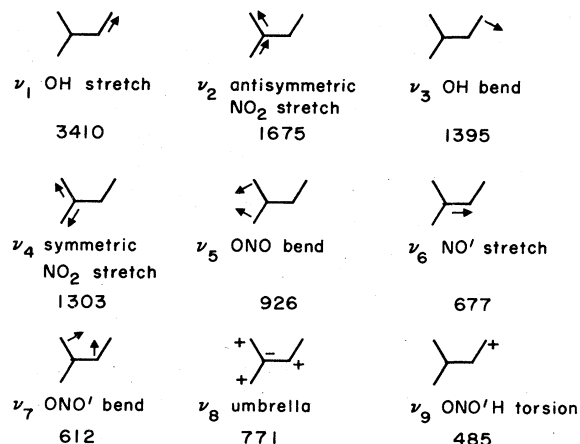


FIG. 7. Normal modes of HNO_3 . The diagrams show only the major motions of the atoms. The frequencies given are those observed in the liquid [Ref. 26(a)].

5) show only weak bands above 900 cm^{-1} , but do have an intense 820-cm^{-1} band. The frequencies, and those observed in nitric acid,^{26(a),26(b)} are summarized in Table II and Fig. 7. Remember that only vibrations polarized along the c axis should be observed.

Examination of Table II and Fig. 7 suggests that the observed 820-cm^{-1} band is due to the out-of-plane "umbrella" mode of the nitric acid, and that the higher-frequency bands are due to the various in-plane modes of the acid. The appearance of the 820-cm^{-1} band as the only intense band in the "lean" sample confirms the proposed crystal structure¹⁹ [Fig. 2(d)]. In this structure only the out-of-plane motions are polarized along the c axis, and thus are allowed in the transmission spectrum. The presence of the weak in-plane bands shows that either our lean samples still contain some normal graphite nitrate or our samples are not perfectly polarizing (possibly due to the disruption of the crystal structure by the grinding process).

We can attempt to assign the in-plane modes using two different models for the normal structure. One views the interior as being predominantly composed of NO_3^- ions with protons in random positions. (This is closest to the various x-ray structures proposed, which tend to ignore the invisible protons.) As already noted, the 820-cm^{-1} band is then the "umbrella" mode, which occurs at 838 cm^{-1} in the sodium salt.²⁷ However, the other lines are hard to assign. The 937-cm^{-1} band does not correlate well with any nitrate modes. The NO_3^- degenerate (E) ν_3 stretch, which occurs around 1350 cm^{-1} in the sodium salt, could split under the strongly anisotropic environment into the two bands observed at 1311 and 1410 cm^{-1} , but even then only the component polarized along the c axis should be observed. The 1680-cm^{-1} band would have to be assigned to a hydrogen bending motion of some type and the $\nu_4\text{ NO}_3^-$ band (at about 724 cm^{-1} in the crystal) would remain unobserved.

A better model views the intercalant as HNO_3 molecules. Although some are missing their protons (the exact percentage of nitrate anions is subject to debate, but always well under half), we assume that the protons are

TABLE II. Graphite nitrate assignments.

Observed frequency (cm ⁻¹)	Band	Frequency in liquid HNO ₃ ^a (cm ⁻¹)	Comments
Intercalant modes			
820	ν_8	771	"umbrella" mode, 838 cm ⁻¹ in NaNO ₃
937	ν_5	926	
~1050	$\nu_2(\text{H}_3\text{O}^+)$	1100	H ₃ O ⁺ "umbrella" ^b
1311	ν_4	1303	1350 cm ⁻¹ in NaNO ₃ (<i>E</i> mode)
1410	ν_3	1395	OH bend
1680	ν_2	1675	
Graphitic modes			
868			interior layers <i>A</i> _{2<i>u</i>}
872.5			boundary layers ("lean" GIC)
873			boundary layers ("normal" GIC)

^aReference 26(a).

^bReference 28.

shared, and so treat all the intercalant as the neutral form. Again, the 820-cm⁻¹ band can be assigned to an out-of-plane NO bend, this time ν_8 , which shifts up from 770 cm⁻¹ (see Table II). The 937-cm⁻¹ band is the in-plane NO₂ band ν_5 , the 1311-cm⁻¹ band the symmetric NO₂ stretch ν_4 , and the 1680-cm⁻¹ band the antisymmetric stretch ν_2 . In this model the O-H bend, ν_3 , is assigned to the 1410-cm⁻¹ line. The nitric acid model is thus satisfactory (Table II), and the frequencies observed in the GIC's lie between those observed in liquid and solid nitric acid.^{26(a)} All of these in-plane bands are intense in the "normal" GIC's, and weak in the "lean" GIC's.

Two other weak bands appear. The "lean" spectrum has a band at 1550 cm⁻¹ which we cannot assign. Both samples have a weak feature around 1050 cm⁻¹ wave numbers. This band appears in wet nitric acid, and has been attributed to the ν_2 symmetric bend ("umbrella") of H₃O⁺.^{26(a),28} Water is generated during the reaction, so it is certainly possible that some H₃O⁺ is present in the "normal" GIC galleries. In order to fit into the "lean" compound, the pyramidal hydronium ion would have to lie parallel to the *a-b* planes and be squashed flat, in which case this mode would have the correct symmetry (parallel to the *c* axis) to be seen. Since the inversion barrier of H₃O⁺ is estimated to be less than 1 kcal/mol,²⁹ it seems possible to squeeze the H₃O⁺ into the graphite galleries.

Spectra of graphite prepared with DNO₃ all were identical to those above. Either the deuterium exchanges with hydrogen too quickly, so that most of the observed bands are due to HNO₃, or there is no observable isotope shift. In any case, this prevents us from assigning the hydrogen modes with complete certainty. The assignments we have made are summarized in Table II.

C. Implications for crystal structure

The fresh "normal" compound shows only a weak HNO₃ "umbrella" mode, and this is strong evidence

against Rudorff's model, for which this absorption should be strong, as in the "lean" compound. The strong in-plane absorptions can be explained only if the nitrates, instead of lying flat, "sit up" roughly perpendicular to the graphite layers. If the angle were exactly 90°, the "umbrella" mode should not appear at all. There are three possible explanations for the occurrence of this weak absorption: either our samples are not perfect polarizers, there is some lean component present, or the nitrates are tilted.

The strong in-plane lines are almost absent from the "lean" samples (the samples do polarize the light better than 90%), so it seems that the degree of polarization is sufficiently good that the first possibility cannot fully explain the results. The disorder evident in the x-ray data, and the fact that the samples are exposed to air for many minutes during transfer to the sample cell, and then exposed to the windows (and some air) for hours while the spectrum is taken, suggests the second possibility. It is even possible that in our samples, during the transition to a lean compound, there coexist three nitrate orientations: parallel, perpendicular, and in between.

Since in no sample is the "umbrella" mode entirely absent, nitrate tilt remains a strong possibility. Recent x-ray studies on carefully prepared samples suggest that the nitrate plane lies along, but may be rotationally disordered about, the graphite *c* axis.³⁰ A tilt of the plane away from the *c* axis cannot be ruled out and we cannot discriminate between this "nitrate tilt" explanation and the "some lean compound present" explanation for our spectra.

Some samples were cooled below the reported 2D order-disorder (sometimes termed "ordered-liquid") transition at -20°C,³¹ but gave identical infrared spectra. One interesting result was obtained when, in attempting to prepare DNO₃ samples, the graphite was reacted with a mixture of nitric and sulfuric acid. An additional broad band appeared at 1100 cm⁻¹, near the frequency observed in crystalline K₂SO₄ for the ν_3 in-plane stretching vibration.³² This indicates that intercalated sulfate ions do not

lie parallel to the carbon layers. As in graphite nitrate, the "guest" molecule's frequencies do not shift much upon intercalation. Since $\text{S}_2\text{O}_7^{2-}$ also has a strong band at 1100 cm^{-1} ,¹⁶ it is also possible that it is $\text{S}_2\text{O}_7^{2-}$ that is the sulfate species present.

III. SUMMARY AND CONCLUSION

We have shown that it is possible to take infrared transmission spectra of both pristine graphite and graphite nitrate. The spectra show only bands that are polarized along the *c* axis of the graphite, and so provide a measure of the orientation of the intercalant in the graphite. We have examined both the "normal" and "lean" forms of graphite nitrate. Surprisingly, both the graphite and nitrate bands are shifted only slightly upon intercalation and remain sharp. The graphite modes can be satisfactorily explained by a nearest-layer model. The nitrate bands correspond to nitric acid. Since the frequencies are hardly shifted, we conclude that there are no strong "valence" interactions between the nitric acid and the graphite.

Different nitrate bands are strong in the "normal" and "lean" compounds. The bands show that the nitrate planes are perpendicular to the graphite planes for the "normal" compound and parallel for the "lean" compound. The possibility of a tilt of the nitrite away from exactly perpendicular is discussed.

The A_{2u} graphite mode moves only slightly upon forming the GIC and the 7-cm^{-1} splitting between the interior and boundary-layer modes is much less than predicted by recent theory. No effect on the infrared spectrum is observed upon cooling through the phase transition at -20°C .

ACKNOWLEDGMENTS

We are indebted to Professor Neil Bartlett and Dr. Tom Mallouk, who helped us with the preparation of the GIC's and took the x-ray spectra, and who provided invaluable discussion on the nature of the GIC's. Professor Roy Clarke of Physics Department of the University of Michigan sent us a copy of Dr. Homma's Ph.D. dissertation (Ref. 30). We thank the National Science Foundation for support.

*Present address: Becton Dickinson Monoclonal Center, 2375 Garcia Avenue, Mountain View, CA 94043.

¹M. S. Dresselhaus, *Physics Today* **37**(3), 60 (1984).

²John E. Fischer and Thomas E. Thompson, *Physics Today* **31**(7), 36 (1978).

³H. Selig and L. W. Ebert, *Adv. Inorg. Chem. Radio.* **23**, 281 (1980).

⁴Proceedings of the Franco-American Conference on Intercalation Compounds of Graphite, edited by F. L. Vogel and A. Herold [*Mater. Sci. Eng.* **31** (1977)].

⁵Proceedings of the International Conference on Layered Materials and Intercalates, Nijmegen, The Netherlands, 1979 [*Physica (Utrecht)* **99B** (1980)].

⁶S. A. Solin, *Adv. Chem. Phys.* **49**, 455 (1982).

⁷N. Bartlett and B. W. McQuillan, in *Intercalation Chemistry*, edited by M. S. Whittingham and A. J. Jacobson (Academic, New York, 1982), p. 19.

⁸P. Touzain, *Synth. Met.* **1**, 3 (1979); R. Moreh and O. Shalal *Solid State Commun.* **43**, 529 (1982). These authors present data for the "normal" compound using nuclear resonance scattering of γ rays and show that the nitrate planes are oriented at $82^\circ \pm 8^\circ$ with respect to the graphite planes.

⁹P. C. Eklund, D. S. Smith, and V. R. K. Murthy [*Synth. Met.* **3**, 111 (1981)] and V. R. K. Murthy, D. S. Smith, and P. C. Eklund [*Mater. Sci. Eng.* **45**, 77 (1980)] point out that the SbCl_3 GIC's are also quite stable in air and suitable for diverse physical measurements.

¹⁰J. E. Fischer, *Physica (Utrecht)* **99B**, 383 (1980).

¹¹G. Rupprecht, D. M. Ginsberg, and J. D. Leslie, *J. Opt. Soc. Am.* **52**, 665 (1962).

¹²S. A. Solin, *Physica (Utrecht)* **99B**, 443 (1980).

¹³R. J. Nemanich, G. Lucovsky, and S. A. Solin, *Solid State Commun.* **23**, 117 (1977).

¹⁴M. Maeda, Y. Kuramoto, and C. Horie, *J. Phys. Soc. Jpn.* **47**, 337 (1979).

¹⁵C. Underhill, S. Y. Leung, G. Dresselhaus, and M. S. Dresselhaus, *Solid State Commun.* **29**, 769 (1979).

¹⁶B. Iskander and P. Vast, *J. Raman Spectrosc.* **11**, 247 (1981) (French).

¹⁷S. A. Solin, *J. Phys. (Paris Colloq.)* C6-283 (1981).

¹⁸W. Rudorff, *Z. Phys. Chem. B* **45**, 42 (1939).

¹⁹H. Fuzellier, J. Melin, and A. Hérold, *Mater. Sci. Eng.* **31**, 91 (1977).

²⁰Professor Neil Bartlett provided the raw graphite. They obtained the graphite from the National Aeronautics and Space Administration and Arthur Moore of Union Carbide.

²¹Unlike most cements, crystal bond cement is applied by melting it at 120°C , mounting the sample, and letting it cool. The sample preparation was planned and performed by Peter Daugherty and Timothy Teague of the Thin Section Laboratory, Geology Department, University of California, Berkeley.

²²A. R. Ubbelohde, *Proc. R. Soc. London, Ser. A* **304**, 25 (1968).

²³W. C. Forsman, F. L. Vogel, D. E. Carl, and J. Hoffman, *Carbon* **16**, 269 (1978).

²⁴S. Y. Leung, G. Dresselhaus, and M. S. Dresselhaus, *Synth. Met.* **2**, 89 (1980); *Physica (Utrecht)* **105B**, 375 (1981); R. Al-Jishi and G. Dresselhaus, *Mater. Res. Soc. Symp. Proc.* **20**, 301 (1983).

²⁵T. Mallouk, B. L. Hawkins, M. P. Conrad, K. Zilm, G. E. Maciel, and N. Bartlett, *Philos. Trans. R. Soc. London* (to be published); T. Mallouk and N. Bartlett, *J. Chem. Soc. Chem. Commun.* **1983**, 103.

²⁶(a) G. E. McGraw, D. L. Bernitt, and I. C. Hisatsune, *J. Chem. Phys.* **42**, 237 (1965); (b) D. E. Bethell and N. Shepard, *J. Chim. Phys.* **50**, C72 (1953). These authors present some unassigned spectra which look much like ours.

²⁷J. C. Decius and R. M. Hexter, *Molecular Vibrations in Crystals* (McGraw-Hill, New York, 1977).

²⁸C. C. Ferriso and D. F. Hornig, *J. Chem. Phys.* **23**, 1464 (1955).

²⁹P. W. Payne and L. C. Allen, *Applications of Electronic Structure Theory*, edited by H. F. Schaefer (Plenum, New York, 1977), p. 29. For comparison, the experimental inversion barrier for ammonia is 5.8 kcal/mol.

³⁰H. Homma, Ph.D. dissertation, University of Michigan, 1984. The thesis results do not rule out the possibility of nitrate tilt

[R. Clarke (private communication)].

³¹A. R. Ubbelohde, Proc. R. Soc. London, Ser. A **309**, 297 (1969).

³²F. Meserole, J. C. Decius, and R. E. Carlson, Spectrochim. Acta **30A**, 2197 (1974).