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Motions of Molecules in Condensed Systems. VII. The Infra-Red Spectra for Single Crystals of Ammonium Nitrate and Thallous Nitrate in Polarized Radiation*

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Infra-red spectra in plane polarized light for properly oriented, thin sections from single crystals of NH_4NO_3 (IV), NH_4NO_3 (III), and TlNO_3 (γ) are described and interpreted. The selection of proper orientations for such work is indicated for crystals in general and potential difficulties with some types are noted.

Spectra for the first two crystals show (1) that absorptions by molecular modes of nitrate ion, and their combinations, are strongly polarized in directions predicted for these structures by the general theory of crystalline spectra; (2) that envelope structure resulting from combinations between molecular modes and lattice modes is present but not uniquely polarized, again in agreement with the general theory; (3) that absorptions by molecular modes of ammonium ion appear to be unpolarized,

indicating that these ions are disordered from rotation or other causes.

Spectra for the third substance are used to complete the determination of its crystal structure. One band in this substance has a remarkable envelope consisting of a strongly polarized central branch and, at room temperature, three pairs of symmetrically distributed, virtually unpolarized satellites. The satellites become more numerous at lower temperature (see accompanying article).

The spectra for the several substances suggest that optical branches of their lattice mode distributions are located between about 35 and perhaps 200 cm^{-1} .

INTRODUCTION

THE infra-red absorption spectrum for a single crystal, or other anisotropic specimen, in plane polarized radiation will depend upon the orientation of the specimen relative to both the plane of polarization and the direction of incidence of the light. It is convenient to recognize this situation by saying that the spectrum of the anisotropic substance is polarized.

The systematic study of polarized infra-red spectra offers promise of making significant contributions to the identification of crystal structures, molecular structures, and their respective modes of vibration. Such studies can serve also as a source of detailed information about crystalline and molecular dynamics, as a testing ground for general theories of crystalline and molecular spectra.

Pioneer investigations¹ of polarized infra-red spectra, stemming from the invention of a suitable polarizer by Pfund² in 1906, were severely hampered by difficulties with instrumentation, and by the lack of any fundamental theory of crystal spectra that might guide the detailed interpretation and thereby increase the value of these truly hard-won observations. As a result, the use of polarized infra-red radiation was, for the time being, almost abandoned.

Recent advances (1) in the field of general purpose infra-red instrumentation,³ (2) in the construction⁴ of convenient, efficient polarizers for infra-red radiations;

(3) in the development of a fundamental theory^{5,6} for interpretation of crystalline spectra, all may be expected to quicken interest in polarized spectra and to greatly enhance their value. At the present time the major obstacle to such work is the difficulty of obtaining suitable specimens, and even this one seems⁷ upon the verge of becoming relieved. A growing interest in the polarized spectra of crystals has indeed become evident,⁸ especially in England where a number of preliminary reports⁹ have appeared while our own work was in progress. An equally great interest is being shown¹⁰ also toward polarized spectra of plastics and natural or synthetic fibers, but results with these materials pose some problems of interpretation that will become apparent in the next section.

In the present article we shall describe in detail the methods and results of a study of polarized infra-red spectra for three crystalline nitrates: NH_4NO_3 (IV) and (III), TlNO_3 (γ). In the course of our discussions we shall have opportunities to illustrate the value of this and similar studies by indicating some of the variety of questions whose answers may be sought from polarized spectra. Specific questions that we touch upon here are (1) the general theory of crystalline spectra, (2) verification of the assignment of frequencies to molecular modes of vibration, in this case the ones for nitrate ion, (3) the degree of disorder, resulting from rotation or otherwise, of ammonium ions in two of the

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** University Fellow for the academic year 1948-49.

¹ R. E. Nyswander, *Phys. Rev.* **28**, 291 (1909). For reviews of other investigations see, C. Schaefer and F. Matossi, *Das Ultrarot Spektrum* (Julius Springer, Berlin, 1930), pp. 329-330; and J. Lecomte, *Le Spectre Infrarouge* (University of France Presses, Paris, 1928), pp. 177 f.

² A. H. Pfund, *Astrophys. J.* **24**, 19 (1906).

³ V. Z. Williams, *Rev. Sci. Inst.* **19**, 135 (1948).

⁴ R. Newman and R. S. Halford, *Rev. Sci. Inst.* **19**, 270 (1948).

⁵ Elliot, Ambrose, and Temple, *J. Opt. Soc. Am.* **38**, 212 (1948).

⁶ N. Wright, *J. Opt. Soc. Am.* **38**, 69 (1948).

⁵ H. Winston and R. S. Halford, *J. Chem. Phys.* **17**, 607 (1949).

⁶ D. F. Hornig, *J. Chem. Phys.* **16**, 1063 (1948).

⁷ Bauer, Cole, and Thompson, *Nature* **163**, 198 (1949).

⁸ W. E. Keller, Dissertation, Harvard University (1948).

⁹ J. Mann and H. W. Thompson, *Nature* **160**, 17 (1947), and *Proc. Roy. Soc.* **192A**, 489 (1948); D. A. Crooks, *Nature* **160**, 17 (1947); G. B. B. M. Sutherland and A. V. Jones, *Nature* **160**, 567 (1947); and others.

¹⁰ See for example, L. Glatt and J. W. Ellis, *J. Chem. Phys.* **15**, 880 (1947), **15**, 884 (1947), and **16**, 551 (1948); Ambrose, Elliot, and Temple, *J. Chem. Phys.* **16**, 877 (1948), *Nature* **163**, 859 (1949); and others.

crystals examined, (4) verification of the complete crystal structures for two of the substances and a partial determination of that for a third one, (5) evaluation of some properties of the distributions of frequencies among lattice modes in the several crystals. Although the discussion is organized, for convenience, around the observations, all of the foregoing questions will be found to have prominent places and to receive significant, if incomplete answers in it.

Before presenting our observations we shall discuss briefly some conditions governing their interpretations, conditions that have an important bearing upon the planning of the most significant experiments.

SELECTION OF ORIENTATIONS

The general theory of crystalline spectra, including polarized ones, has been thoroughly discussed elsewhere.^{5,6} It should suffice to say here that any fundamental mode of motion which is capable of absorbing radiation must be accompanied by an oscillating electric moment. This latter, because it is a vector quantity, will develop along a well-defined direction in the medium, a direction that is specified in the general theory, and will be incapable of absorbing radiation that is polarized in the plane perpendicular to that direction. This is the origin of polarized spectra, whose significances lie in the possibilities of identifying the characteristic direction associated with an absorption, correlating the latter with a mode of motion, and of interpreting these directions for different modes in terms of molecular and crystalline structures.

In order to realize the possibilities just noted we must first solve a crucial problem: the structurally significant directions are defined inside the absorbing medium whereas the plane of polarization of the radiation, and its direction of propagation, are easily identified only outside the medium. If we are to translate the latter directions, determined outside the medium, into knowledge of the former ones, defined inside the medium, we must, if possible, select orientations for our crystal such that plane polarized radiation may traverse it without suffering either refraction or change of polarization character (plane to elliptical, etc.). Otherwise, if plane polarized radiation is incident upon a plate of anisotropic crystal in an entirely arbitrary way, it will¹¹ suffer refractions not in accordance with any simple law and, furthermore, for a non-absorber at least, the electric vector of the light will be resolved along directions in the medium peculiar both to the directions of propagation of the light through the crystal and to the frequency of the light.

In certain special orientations, however, the requirements we must impose upon the behavior of the light inside the medium can[†] be met. These occur¹¹ for a

non-absorber when the light is incident normal to a plate, whose surface is parallel with a plane containing two principal axes of the dielectric ellipsoid of the crystal, and when the electric vector strikes parallel with one or the other of those principal axes. The orientation of the principal axes within the medium can depend, however, upon the frequency of the light. For an absorber we must¹¹ replace the real, dielectric tensor by the sum of it and an imaginary, conductivity tensor. Unless we can specify that the eigenvectors of these two tensors are parallel, which we sometimes can, the situation becomes highly involved. In the situations noted below where the two sets of eigenvectors are parallel, it is still necessary to say that the resolution of the electric vector of arbitrarily incident light takes place "along" two ellipses rather than definite directions. But, when the previously prescribed conditions of incidence are met, and the eigenvectors of the two tensors are parallel, the requirements we have had to place upon the light as it enters the medium will then be fulfilled. It is clear that severe difficulties may attend the interpretation of polarized spectra when they are obtained with crystal mosaics or partially oriented microcrystals.

As was noted above, the directions of the eigenvectors for the dielectric and conductivity ellipsoids can depend upon the frequency of the light. This circumstance may give rise to difficulties, especially if the two sets of eigenvectors depend differently upon the properties of the light, but also even when they change directions together. For example, suppose that the characteristic directions for monochromatic, visible light, normally incident, are determined with crossed Nicol prisms. It could happen, when we get into the region of infra-red absorption, that the principal axes would become rotated by some large undetermined angle from the positions observed with visible light. If the angle were near to 45° and infra-red spectra were observed with light polarized first along one, then along the other of the axes found in the visible light, these spectra would appear to be identical. In contrast, spectra properly obtained might show extreme differences.

For many forms of crystals, fortunately, the directions of the aforementioned, polarization axes are fixed by symmetry and become independent of the frequency of the light. In uniaxial crystals of the hexagonal, trigonal, and tetragonal systems, and for biaxial crystals of the orthorhombic system, all distinguishable polarization axes are symmetry fixed along crystallographic axes. Spectra observed along these axes will assume a fundamental significance, the ones for other conditions of incidence being representable as superpositions of them. For crystals of the regular system there are, of course, no polarized spectra.

For monoclinic crystals, one axis is symmetry fixed but the other two are unrestricted. There are no across the beam, the placement and small size of the specimen, all make for a good practical approximation to the ideal.

¹¹ M. Born, *Optik* (Julius Springer, Berlin, 1933).

[†] Met in theory but not strictly so in practice. The actual light is neither entirely parallel, nor perfectly polarized, nor all incident normal to the crystal face. However, the distribution of light

restrictions upon the axes of a triclinic crystal, and perhaps none upon the axes in some kinds of fibers, films, and other quasicrystalline materials. Particular pains will be required, when working with these latter kinds of substances to resolve the potential difficulties.

In the investigations that we shall now describe, all substances crystallize in the orthorhombic system. Their achromatic polarization axes were oriented in the light beam so as to satisfy all of the foregoing specifications.

EXPERIMENTAL PROCEDURES

The experimental program, in the case of each substance examined, consisted of the following steps: (1) the growing of suitable single crystals of the substance in question, (2) the locating of their axes by well-known techniques of optical or x-ray crystallography, (3) the producing of thin sections whose principal faces exhibited the desired crystallographic planes, (4) the obtaining of their spectra with radiation polarized successively along the several crystal axes. These steps will be described in appropriate detail in this section under the subheadings that follow.

Specimens

NH₄NO₃ (IV), stable from -16° to 32°C , was obtained by slow evaporation of an aqueous solution at 25°C in the form¹² of orthorhombic prisms, with (110) and ($\bar{1}10$) planes parallel to the principal faces, greatly elongated in the direction of the c axis. Preliminary observations with a petrographic microscope disclosed how the crystals should be cut in order to produce the desired thin sections, ones with principal faces parallel to the (100) and (010) planes. The usual mineralogical sectioning techniques were found to be unsuitable in our hands for these soft crystals. Instead, a crystal ($2\times 2\times 10$ mm) was (1) secured with pyroxilin mucilage, edge upward, into a long, shallow, right-angled V-groove in the face of a metal block, (2) polished down flush with the face of the block, (3) removed from the groove and attached, newly formed face down, on a glass flat, (4) polished down again parallel to the surface of the flat. Polishing was effected with absorbent cotton moistened with water, or with ethanol for finishing operations, as the abradant. Uniformity of thickness could be figured during finishing operations by observation of the polarization colors, seen with the aid of the petrographic microscope. The finished section, having a thickness in the range from 35 to 100 microns, uniform to within an estimated 5 microns through the useful region, was removed from the flat, washed exhaustively to remove mucilage, and dried. It was then attached to a suitably constructed mask, whose open area it covered completely, the mask being designed to facilitate mounting of the section immediately adjacent to the entrance slit of the spectrometer, long axis vertical.

¹² C. D. West, *J. Am. Chem. Soc.* **54**, 2256 (1932).

After it had been studied spectroscopically, the section was subjected to thorough crystallographic examination on the stage of the petrographic microscope, including refractive index measurements with polarized light, in order to establish beyond doubt its crystallographic orientation. Efforts to produce much thinner specimens, which would have been highly desirable for spectroscopic study, were unsuccessful with this technique because of severe fragmentation occurring at the edges of the section whenever its thickness was reduced much below 40 microns.

NH₄NO₃ (III), stable from 32° to 84°C , was obtained, by slow evaporation of a solution in methanol at 60°C , also in the form^{13,14} of orthorhombic prisms with (110) and ($\bar{1}10$) faces, greatly elongated in the direction of the c axis. All operations with these crystals, from beginning to end, were carried out while they were held at temperatures near 60°C , but otherwise the procedure resembled the one that has already been described. Essential innovations were the immediate transfer of a crystal from the mother solution into isoamyl acetate, in order to forestall the phase transition, induced by cooling that accompanied the rapid evaporation of methanol from the surface of the crystal, and, for the same reason, the use of water only during the operations of abrasion. Sections were prepared by working intermittently in a laboratory oven in which the crystals had been grown and the necessary apparatus, other than the microscope, were preheated. During microscopic observations the crystal was transferred to a hot stage, and during spectroscopic observations it was mounted in a small specially constructed oven that served to maintain its elevated temperature while the masked section rested immediately adjacent to the slit.

TiNO₃ (γ), stable below 75°C , was obtained, by slow evaporation of an aqueous solution at 55°C , as orthorhombic plates, not larger than $10\times 10\times 0.5$ mm, whose principal faces were subsequently identified as (010) planes. The fresh solution, prepared with Eimer and Amend Reagent Grade material, contained an appreciable amount of thallic salt which hydrolyzed immediately, forming a brown sludge. By heating the solution to boiling, and then filtering, this impurity was effectively removed. The resulting solution, if evaporated at room temperature, was prone to initiate dendritic growths but this habit was broken by proceeding to 55°C . Preliminary crystallographic examination of the plates was inconclusive and cursory, inasmuch as the optical constants of this substance are unknown and because the shapes of the plates were unfavorable anyhow for producing oblique sections having sufficient width to allow spectroscopic examination. Thin sections were prepared by securing the plates to glass flats and abrading them parallel to their principal faces with a

¹³ T. H. Goodwin and J. Whetstone, *J. Chem. Soc.* 1455 (1947).

¹⁴ Hendricks, Deming, and Jefferson, *Zeits. f. Krist.* **85**, 145 (1933).

felt buffing wheel, about 1 inch in diameter, powered by a small, motor driven hand tool of the kind used by hobbyists. The periphery of the wheel was continually moistened by holding a water saturated piece of cotton against it, about a quarter turn back from the point of contact with the crystal. By varying the amount of water, the speed of the wheel, and the pressure applied to the crystal, a rather delicate control could be exercised over the rate of abrasion. This technique, adopted because the crystals were hard, brittle, and poorly soluble in water, should be applicable to any fairly hard crystal, provided that a suitable solvent can be found, but was unsatisfactory for the soft NH_4NO_3 . Finished sections were mounted so as to have each of the two directions of extinction for polarized, visible light parallel in successive observations to the plane of vibration of the polarized infra-red beam. Different sections were observed to have similar spectra, their only differences being attributable to variations of thickness. Subsequently, a fragment was taken from the section whose spectra accompany this article and used to obtain x-ray photographs with the crystal rotating about either of the two directions of extinction contained in its principal face. These photographs yielded lattice spacings of 6.25 ± 0.1 and 3.99 ± 0.05 AU, rough because of imperfect alignment ($\pm 5^\circ$) between axes of extinction and rotation but satisfactory for purposes of comparison with the lattice parameters¹⁵ $a = 6.19$, $b = 12.27$, $c = 3.98$ AU, showing that the principal face was a (010) plane. While still attached to the camera mounting, these spacings were correlated with the axes of fast and slow extinction in the fragment, thus permitting their identification in the parent section and, in turn, labeling of the spectra. Once again, specimens much thinner than the ones used could not be obtained because of the onset of severe fragmentation. Moreover, because the original plates were rather thin, perpendicular sections prepared from them were correspondingly too narrow and yielded spectra of such poor quality that we have elected to omit the b spectrum from this report.

Spectra

Absorption spectra were obtained with a Perkin-Elmer Infra-red Spectrograph, Model 12B, equipped with the silver chloride polarizer described^{14a} by us previously, a Golay Detector with modified¹⁶ accessories permitting either single-beam or double-beam operation as desired, and a Brown Elektronik Recording Potentiometer. The crystal section, containing in every case two crystallographic axes at right angles in its principal face, was supported inside the entrance port of the monochromator immediately adjacent to the slit. It was arranged as well as possible so as to have the principal face parallel to the plane of the slit, with one

of its crystallographic axes vertical and the other axis horizontal, whereupon the third crystallographic axis would become aligned with the optic axis of the spectrometer. Specimens ranged in area from 0.5×4 mm on upward to 3×10 mm with average thicknesses in the range from 35 to 100 microns. With the radiation polarized either vertically or horizontally, a spectrum was obtained by the conventional method of single-beam spectroscopy; the blanks were obtained in each case under the same conditions of polarization, aperture, and slit schedule as used in the corresponding absorption runs. Dispersion was effected in the range from 700 to 1600 cm^{-1} with a rocksalt prism, from 1600 to 3400 cm^{-1} with a fluorite prism. The monochromator was calibrated against known absorption bands of ammonia, methane, carbon dioxide, and water vapor. Calibration was checked periodically.

Records for both blank and absorber were scrutinized thoroughly for evidences of interference fringes and suspect ones were discarded. Such fringes can originate either in the polarizer or in the specimen and occasionally are observed. Simple considerations show that fringes, if caused by interference between internally reflected and directly transmitted beams, will appear with wave number intervals $\Delta\nu = (2nd)^{-1}$ where d is the crystal thickness measured in cm and n is its refractive index. Moreover, the total amplitude of fluctuation about the mean intensity of the emergent beam may approach the fraction $2(n-1)^2/(n+1)^2$ of the beam. To illustrate the magnitude of this effect we may take $n = 2$ and $d = 0.01$, representative of either AgCl in a polarizer or TlNO_3 as a specimen, whereupon we find that fringes occur at intervals of 25 cm^{-1} with heights equal to 22 percent of the mean beam intensity. Such effects, if present and unrecognized, could obscure or distort the envelope structure appearing in our spectra, structure that may become of considerable interest. Fortunately, except for occasional instances, successive sheets of AgCl and their separations in the polarizer were sufficiently non-uniform, likewise our crudely cut specimens, so that the fringes did not appear. Irregularities of the order of 5 microns are probably sufficient to obliterate them.

RESULTS AND INTERPRETATIONS

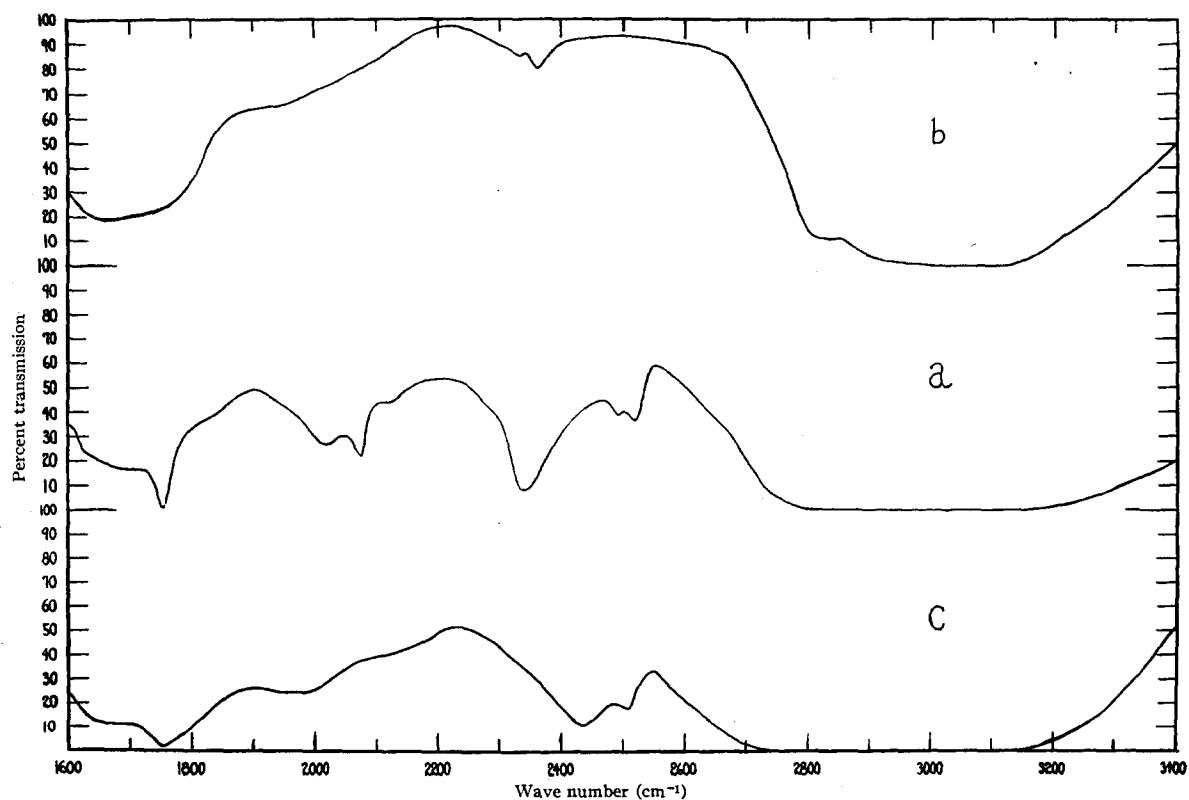
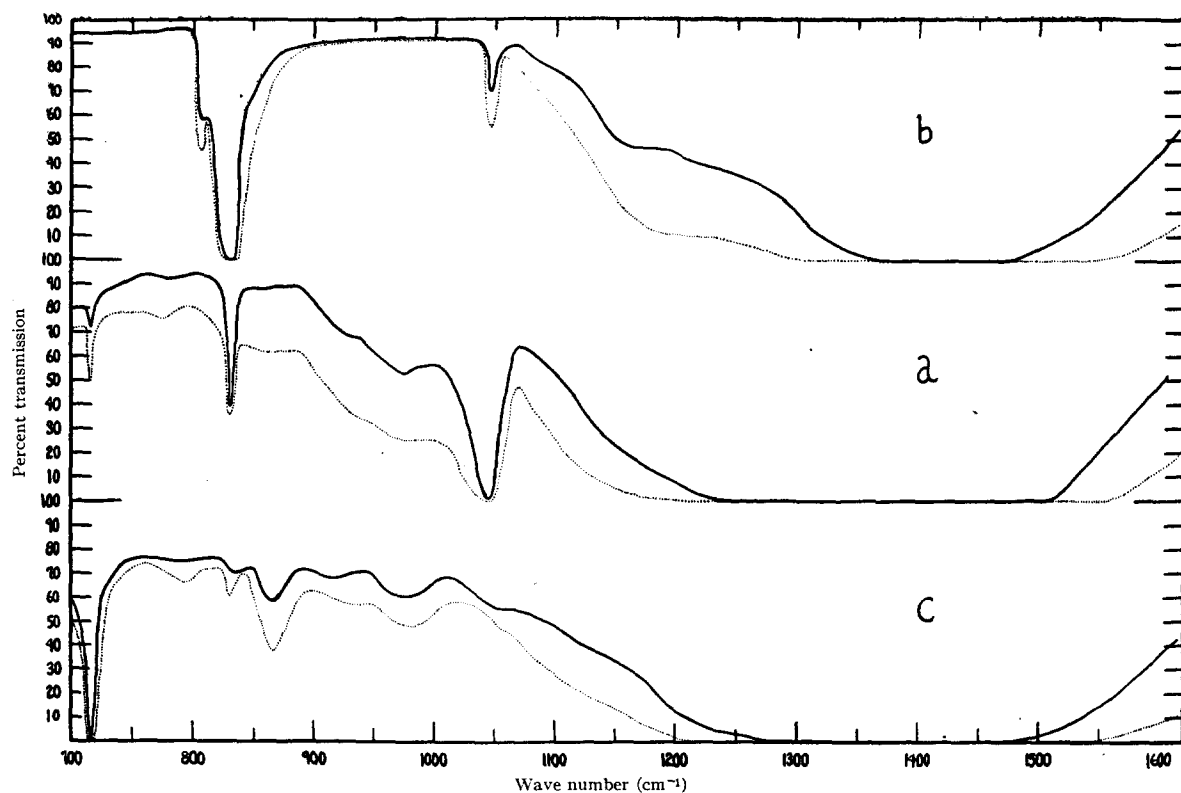
It is to be expected, inasmuch as intraionic forces in these crystals are more powerful than interionic ones, and it has been verified¹⁷ previously, that the nitrate and ammonium ions retain much of their dynamical individualities, that there are modes of vibration in these crystals which can be correlated with motions of the hypothetical, isolated ions. Accordingly, the description and interpretation of our present observations will be organized for each substance separately upon this basis.

The nitrate ion, known to be a centered equilateral

¹⁴ L. Rivoir and M. Abbad, *Anal. Fis. Quim.* **39**, 306 (1943).

¹⁶ A. Savitsky and R. S. Halford, *Rev. Sci. Inst.* **21**, 203 (1950).

¹⁷ W. Keller and R. S. Halford, *J. Chem. Phys.* **17**, 26 (1949).



FIGS. 1 and 2. Polarized spectra for single crystals of NH_4NO_3 (IV). Electric vector of the light beam is parallel to axis indicated. Dotted curve is for sample 80 microns thick, solid curve for sample 35 microns thick. Axes are identified in Fig. 3.

triangle having symmetry D_{3h} , would, if isolated, have^{17,18} four fundamental frequencies of vibration: ν_1 , near 1050, the totally symmetric stretching mode (forbidden in the infra-red spectrum for the isolated ion); ν_2 , near 830, the out-of-plane bending mode; ν_3 , near 1390, the doubly degenerate, predominantly stretching mode; ν_4 , near 715, the doubly degenerate, predominantly bending mode. This assignment of frequencies is the customary one and, as the polarized absorptions will be seen presently to be consistent with it, we do, in some measure, independently verify this assignment.

The ammonium ion, assumed to be a centered tetrahedron having symmetry T_d , would likewise, if isolated, have^{17,18} four fundamental frequencies: ν_1' , near 3033, the totally symmetric stretching mode; ν_2' , near 1685, the doubly degenerate bending mode; ν_3' , near 3134, the triply degenerate stretching mode; and ν_4' , near 1397, the triply degenerate bending mode (ν_1' and ν_2' would be forbidden to appear in the spectrum for the isolated ammonium ion). This assignment of frequencies, analogous to the well-established one for methane, is undoubtedly correct but we were unable, for reasons that will emerge during the discussion, to independently verify it.

It is to be expected also that the spectra obtained for the several different crystals may show marked differences in detail, depending upon the crystal structures. Selection rules governing absorption by the isolated ions, and strict degeneracies prevailing therein, will be relaxed^{5,6} or removed in ways that are peculiar to each crystal structure. In particular, transitory electric moments generated by the vibrations must develop along characteristic directions in a crystal and, depending upon its structure, may have components along only one or along several of the crystallographic axes. Thus, a mode having always the same molecular origin may appear completely polarized in the spectra for one crystal but not so in those for another. Moreover, it will be seen that the resolved bands appearing in our spectra have envelopes more or less rich in detail. These envelopes include many unresolved, composite absorptions, involving simultaneous changes in the molecular mode and various ones of the lattice modes, and thus assume appearances that are peculiar to the crystal structures. These matters will be considered, and interpreted wherever possible, during the course of the ensuing discussion.

NH_4NO_3 (IV)

The spectra, designated as a , b , and c to denote the crystallographic axis along which the light was polarized, are shown for this crystal in Figs. 1 and 2 supplemented by Table I wherein we have tabulated the

TABLE I. Frequencies (cm^{-1}) observed for NH_4NO_3 (IV).

a	b	c	Assignment ^a
715	—	715	ν_4
780	—	—	—50
—	—	792	—38
—	807	—	$\nu_2(\text{N}^{15}\text{O}_3)?$
830	830	830	ν_2
865	—	865	+35
—	—	915	—131
~930	—	—	~—116
975	—	975	—70
1046	1046	1046	ν_1
—	~1095	—	~+50
—	—	~1125	~+80
—	~1170	—	~+125
—	—	~1180	~+135
1250 to 1550	1370 to 1470	1280 to 1470	$\nu_3, \nu_4', 2\nu_4$
1700	1700	1700	ν_2'
1750	—	1750	$\nu_1 + \nu_4$
2016	~1900	~2000	
2074	to	2060	$2\nu_1, \nu_4 + \nu_3, \nu_2 + \nu_3, 3\nu_4$
2130	~2200	to	
—	2330	2200	$2\nu_2 + \nu_4$
2330	2360	—	
—	—	2434	$2\nu_4 + \nu_1$
2490	—	2508	$\nu_1 + \nu_2 + \nu_4$
2520	—	—	
—	2830	—	$2\nu_1 + \nu_2$
2800 to 3160	3000 to 3140	2740 to 3140	$\nu_1', \nu_3', \nu_2' + \nu_4', 3\nu_1$

^a Unprimed, boldface symbols denote fundamental modes of nitrate ion, primed ones those for ammonium ion. Positive numbers show spacing from nearest fundamental of lower frequency, negative numbers show spacing from nearest fundamental of higher frequency. Absolute values of these numbers are thought to be indicative of groups of frequencies for optical branches in lattice mode distribution.

locations for all components of absorption that appear to have been resolved.

The crystal structure,^{12,19} space group V_h^{13} with two molecules per unit cell, site²⁰ groups C_{2v} for both kinds

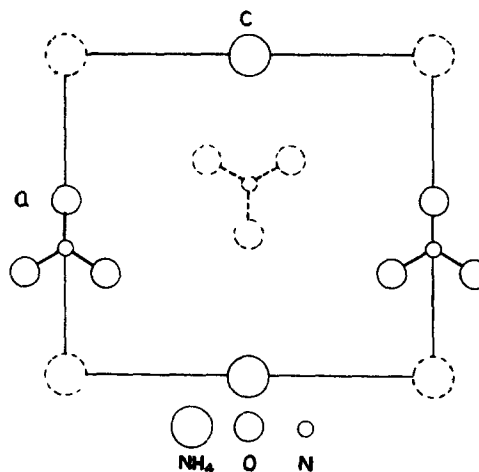


FIG. 3. Unit cell of NH_4NO_3 (IV) projected onto (010) plane. Full lines depict atoms or ammonium ions whose centers are in upper and lower faces of unit cell, broken lines depict ones that are halfway between. Sites for both kinds of ions have symmetries C_{2v} , with C_2 axes along a , symmetry planes parallel with (010) and (001). Axes are labeled according to West (reference 12).

¹⁸ G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945), pp. 167, 178.

¹⁹ Hendricks, Posnjak, and Kracek, *J. Am. Chem. Soc.* **54**, 2780 (1932).

²⁰ R. S. Halford, *J. Chem. Phys.* **14**, 8 (1946).

TABLE II. Binary combinations involving lattice modes, allowed in spectra for NH_4NO_3 (IV).^a

<i>a</i>	<i>b</i>	<i>c</i>
$\nu_{1g} \pm t_{au}$ $\nu_{1u} \pm t_{ag}$	$\nu_{1g} \pm t_{bu}, R_{cu}$ $\nu_{1u} \pm t_{bg}, R_{cg}$	$\nu_{1g} \pm t_{cu}, R_{bu}$ $\nu_{1u} \pm t_{cg}, R_{bg}$
$\nu_{2g} \pm t_{bu}, R_{cu}$ $\nu_{2u} \pm t_{bg}, R_{cg}$	$\nu_{2g} \pm t_{au}$ $\nu_{2u} \pm t_{ag}$	$\nu_{2g} \pm R_{au}$ $\nu_{2u} \pm R_{ag}$
$\nu_{3ag} \pm t_{au}$ $\nu_{3au} \pm t_{ag}$	$\nu_{3ag} \pm t_{bu}, R_{cu}$ $\nu_{3au} \pm t_{bg}, R_{cg}$	$\nu_{3ag} \pm t_{cu}, R_{bu}$ $\nu_{3au} \pm t_{cg}, R_{bg}$
$\nu_{3cg} \pm t_{cu}, R_{bu}$ $\nu_{3cu} \pm t_{cg}, R_{bg}$	$\nu_{3cg} \pm R_{au}$ $\nu_{3cu} \pm R_{ag}$	$\nu_{3cg} \pm t_{au}$ $\nu_{3cu} \pm t_{ag}$
ν_4 is like ν_3		

^a Boldface symbol identifies fundamental mode allowed in that spectrum without combination.

of ions, is depicted in Fig. 3. The crystallographic information is subject to the reservation that it describes the arrangement of heavier atoms only, the positions of the hydrogen atoms being unknown. The spectra furnish evidence, to be reviewed presently, that the hydrogen atoms are disoriented with respect to the elements of symmetry at the sites C_{2v} .

The selection rules for nitrate ion under the site group C_{2v} show^{5, 6, 20} that all modes are permitted to absorb, with ν_1 polarized along *a*, ν_2 polarized along *b*, ν_3 , and ν_4 each split into two components polarized along *a* and *c*, respectively. Lattice modes of translatory origin t_a , t_b , and t_c will be active and polarized along *a*, *b*, and *c*, respectively, while lattice modes of rotatory origin R_a , R_b , and R_c will involve librations about *a*, *b*, and *c*, respectively, with R_a inactive, R_b polarized along *c* and R_c polarized along *b*. The physical basis for these selection rules becomes apparent upon inspection of Fig. 3. The lattice modes, which can be correlated with motions of the free ion by inspection of Fig. 3, will have frequencies too low to appear as fundamentals in the range covered by our observations but could conceivably become the source of envelope structure by entering into combinations with molecular modes. Under the factor group, each of the foregoing modes gives rise⁶ to two, symmetric or antisymmetric under the crystallographic inversion, respectively. These will be distinguished henceforth, when necessary, by appending the subscripts *g* and *u* to the symbols defined previously. The binary combinations between molecular modes and lattice modes allowed under the factor group, a conceivable basis for interpreting envelope structure, are presented in Table II.

$\nu_1(1046)$ appears strongly in the *a* spectrum where it is allowed. It appears also, but more weakly, in the *b* spectrum where it is forbidden except in combinations. We believe that this should be attributed tentatively to the crudity of our sectioning technique, that the section being observed was not accurately a (100) plane but was tilted sufficiently to admit an appreciable

component of *a*. It is possible, of course, that the band results from combinations between the molecular mode and an acoustical branch of the lattice spectrum.

$\nu_2(830)$ appears strongly in the *b* spectrum where it is allowed, to a lesser extent in the *a* spectrum and very weakly in the *c* spectrum. Its appearance in the *a* spectrum we attribute again to inaccuracy of sectioning. Its appearance in the *c* spectrum might be caused by incomplete polarization and lack of parallelism in the incident light, but then we should expect to find a residual of similar strength for ν_1 in *c* where none is observed. It appears probable therefore that the weak component of ν_2 in the *c* spectrum arises from its combinations with lattice modes.

The weak satellite at 807 appears also in the spectra for NH_4NO_3 (III) and TlNO_3 and it is found²² to be intensified, if anything, at low temperatures, showing that it is not a difference band involving ν_2 . A frequency 808 is predicted¹⁸ for ν_2 in the isotopic molecule wherein N^{15} replaces N^{14} . The ratio of extinctions was determined with powdered specimens of TlNO_3 , whose thickness could be adjusted to afford such a measurement, to be 1/150 which stands in some agreement with the known²¹ isotopic abundance ratio of 1/350. Nevertheless, and although we shall have no other suggestion to offer, we are somewhat hesitant about accepting this interpretation for the satellite because the intensities of it and the main band are inverted,²² perhaps as an unrelated coincidence, in the spectrum of $\text{Pb}(\text{NO}_3)_2$.

$\nu_3(1390?)^{17, 18}$ may appear in the *a* and *c* spectra but is forbidden to appear in the *b* spectrum. This band remains unresolved from the neighboring overtone $2\nu_4$ and the ammonium ion fundamental ν_4' at 1397, all of which produce together the intense, broad absorption occurring in our spectra. We are probably observing the disappearance of ν_3 from the *b* spectrum in the form of a narrowing of the region of intense absorption, especially on the low frequency side. The complicating absorption by ammonium ion involves a triply degenerate mode and, accordingly, is most likely unpolarized, while the overtone $2\nu_4$ would be more likely to affect the high, rather than the low frequency side of the absorption. In addition, it would require but little inaccuracy of sectioning, already suggested in connection with ν_1 and ν_2 , to cause an appreciably broad residual of a highly absorptive ν_3 to appear in the *b* spectrum.

$\nu_4(715)$ may appear in both the *a* and the *c* spectra but should be absent from the *b* spectrum as is seen to be the case. It is surprising, perhaps, that there should be such a disparity in the intensities of the two allowed components of a degenerate mode when their frequencies are so nearly alike. Moreover, this is the mode

²¹ D. Yost and H. Russell, *Systematic Inorganic Chemistry* (Prentice-Hall, Inc., New York, 1944), p. 4.

²² See R. Newman and R. S. Halford, *J. Chem. Phys.* **18**, 1291 (1950).

that has been found¹⁷ to disappear anomalously from the spectra for NH_4NO_3 (II) and (I). In spite of these seeming aberrations, which might be attributed to an erroneous assignment, we feel that the behavior of this band in the several nitrates we have examined is consistent with its assignment to a degenerate mode, that the behavior in question must be more or less accidental. Although this motion is permitted to absorb in the isolated ion, it is not necessary that it should do so. Indeed, it is possible to construct normal coordinates for the degenerate bending mode such that it would generate little or no transitory electric moment. Then, the capacity of this mode to absorb when it occurs in a crystal would be largely an acquired characteristic, sensitive to details of the environment, anisotropic along with the latter. We know²³ from experience that the environment can induce an appreciable absorption intensity without much alteration of frequency. At any rate, the behavior of this absorption is strictly correct as regards its disappearance from the b spectrum, a characteristic that marks it unequivocally as an in-plane motion.

The nitrate ion fundamentals, in summary, appear to have been correctly assigned by previous investigators and to behave in accord with selection rules characteristic of their environment in NH_4NO_3 (IV). Uncertainties regarding the positions of hydrogen atoms in this crystal do not materially effect these conclusions.

The selection rules for ammonium ion will depend upon the unknown positions taken by the hydrogen atoms. If these are distributed with a pair in each of the reflection planes at the site C_{2v} , so as to be consistent with the space symmetry found for the heavier atoms, all modes will be permitted²⁰ to absorb, with ν_1' polarized along a , ν_2' split into two components, one inactive and one polarized along a , ν_3' and ν_4' each split into three components, polarized along a , b , and c , respectively. If, instead, the ammonium ion is now rotated around b so that the ac plane remains the only one of symmetry, ν_1' will acquire a component along c , ν_2' along both b and c . If, to the contrary, it were rotated only about c , ν_1' would acquire a component this time along b , ν_2' again along both b and c . If the ion is rotated about both axes b and c together, or about a alone, all modes are permitted to have components along all axes. Thus, the polarization of the absorptions attributable to ν_1' and ν_2' furnishes us with a clue to the positions of the hydrogen atoms in this crystal. Unfortunately, none of these highly absorptive vibrations were resolved at all distinctly in the polarized spectra, our conclusions must be entertained with some reservations.

$\nu_1'(3033?)$ ^{17,18} is proximate to, and unresolved from ν_3' and several bands attributable to nitrate ion, which latter may be seen clearly in our spectra for TiNO_3 .

²³ O. A. Shaeffer and R. S. Halford, J. Chem. Phys. 14, 141 (1946).

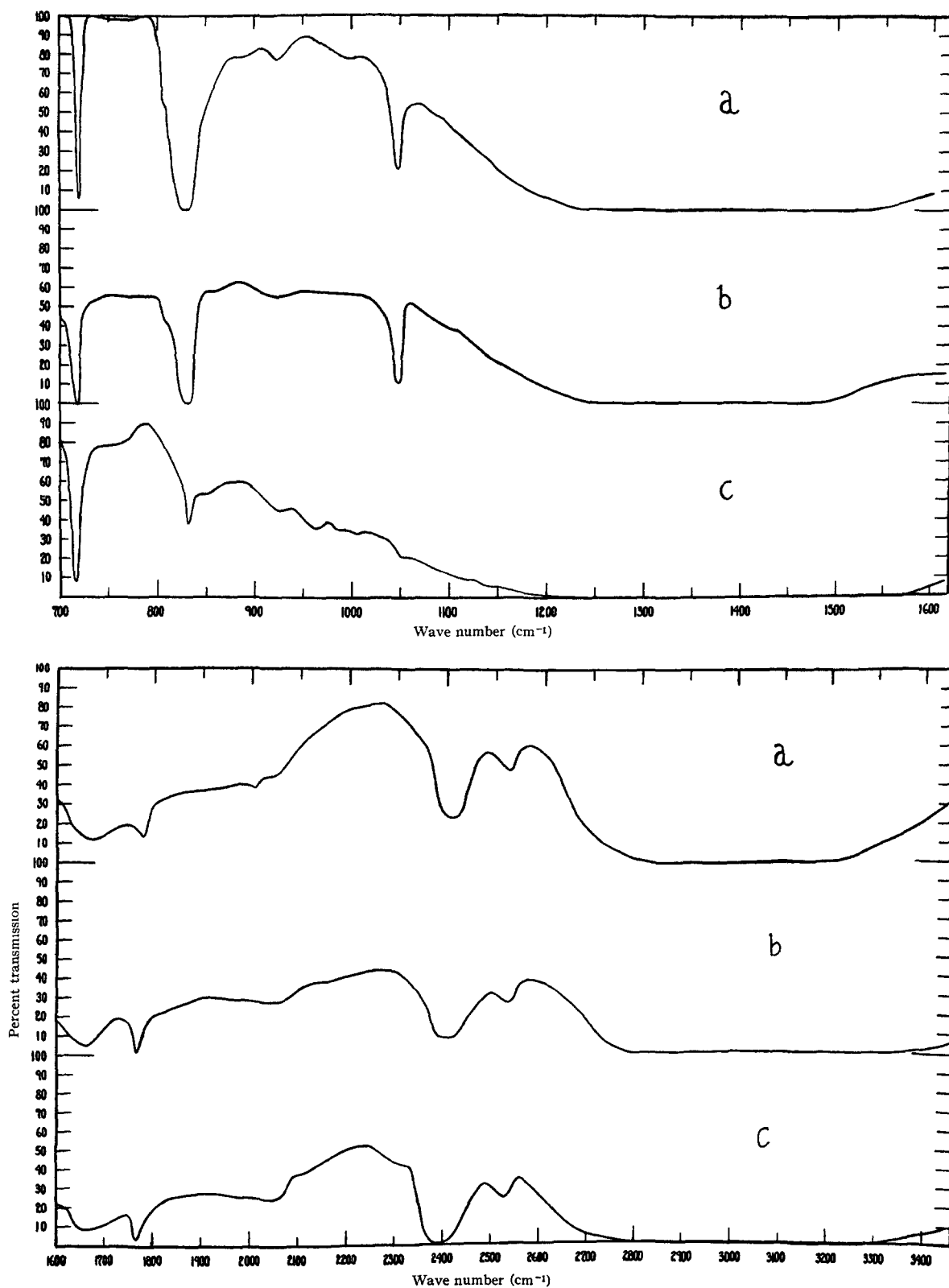
TABLE III. Frequencies (cm^{-1}) observed for NH_4NO_3 (III).

a	b	c	Assignment ^a
—	—	716	ν_4
720	720	—	ν_4
—	—	750	$-80, +30?$
808	808	—	$\nu_2(\text{N}^{18}\text{O}_3)?$
830	830	830	ν_2
—	—	~ 850	$\sim +20$
—	855	—	$+25$
880	—	—	$+50$
925	925	—	$-122, +95?$
—	—	927	$-120, +97?$
—	—	964	-84
—	—	988	-60
995	—	—	-48
—	—	1005	-43
1048	1048	1048	ν_1
~ 1100	~ 1100	—	$+52$
—	—	~ 1120	$\sim +72$
1140	—	~ 1140	$\sim +92$
1240 to 1530	1250 to 1480	1230 to 1580	$\nu_3, \nu_4', 2\nu_4$
1660	1660	1660	ν_2'
1766	1766	1766	$\nu_1 + \nu_4$
2005	2052	2052	$2\nu_1, \nu_4 + \nu_3, \nu_2 + \nu_3$
2055	—	2100	
—	2160	—	$3\nu_4$
—	—	2390	$2\nu_4 + \nu_1$
2405	2405	—	$\nu_1 + \nu_2 + \nu_4$
2530	2530	2530	
2840 to 3200	2800 to 3320	2800 to 3300	$\nu_1', \nu_3', \nu_2' + \nu_4', 3\nu_1$
			$2\nu_1 + \nu_2$

^a See Table I.

Observations, not shown here, with extremely thin, sublimed films of NH_4NO_3 showed the bands clearly resolved, with ν_1' but slightly less intense than ν_3' , the latter having about the same intensity as ν_2 at 830. Basing our judgment upon the knowledge gained from these observations and upon the course of the envelope as it rises at higher frequencies, we are of the opinion that a disappearance of ν_1' from the b or c spectrum, especially the former, should have been discernible in the region from 2900 to 3000. We see, however, that absorption remains intense in this region, even in the b spectrum where the total range of absorption has become markedly narrower, a circumstance that is entirely attributable to loss of the contributions from nitrate ion. Indeed, the appearance of the b spectrum is rather suggestive of the presence of two, highly absorptive bands with envelope structure beginning to be partly resolved in the lower lying one. Nevertheless, we are not justified in reaching any conclusions beyond the cautious one that ν_1' could have been, and more probably was present in all three spectra although this last is by no means certain.

$\nu_2'(1685)$ is seen to be a broad region of incomplete absorption in all cases, with a sharp band at 1750 superimposed upon it in the a and c spectra. The sharp band has both the proper frequency and the proper polarization for the combination of nitrate ion frequencies $\nu_1 + \nu_3$; moreover, a similar, polarized band appears in the TiNO_3 spectra, confirming this assignment. The residual, surely attributable to ammonium ion by virtue of its absence from the spectra of TiNO_3 ,



FIGS. 4 and 5. Polarized spectra for single crystals of NH_4NO_3 (III). Electric vector of the light beam is parallel to axis indicated. *a* and *c* spectra are from a sample about 75 microns thick, *b* spectrum from a sample about 40 microns thick. Axes are identified in Fig. 6.

presumably ν_2' , exhibits no appreciable polarization, contrary to the behavior expected of ammonium ions oriented so as to preserve the site symmetry C_{2v} . At the same time, the appearance of this absorption seems odd, its unusual width for incomplete absorption suggesting the presence of a complex of unresolved bands, possibly connected with the circumstances of disorientation. The alternative to this interpretation would assign the unpolarized residual to a combination of ν_4' or ν_2' with lattice modes, which, because of the triply degenerate origin of ν_4' , and for other reasons,⁵ would not be expected to be polarized. In view of the great intensities of absorption by the other ammonium ion fundamentals, including the here allowed but sometimes forbidden ν_1' , we think it unlikely that ν_2' would fail to appear in our spectra.

$\nu_3'(3134?)^{17,18}$ has been considered previously in our discussion of ν_1' . Its triply degenerate origin makes it of little interest in the present study.

$\nu_4'(1397?)^{17,18}$ appears, unresolved from the neighboring ν_3 , in all three spectra. Again, its triply degenerate origin detracts from its interest.

Disorientation of ammonium ions seems to be indicated by our observations, although not conclusively. Taking all things into consideration, the probable behavior of ν_1' , the definitely unpolarized nature of what is probably ν_2' , and the marked contrast between these observations and the pronounced polarizations observed with the numerous bands attributable to nitrate ion, the conclusion is somewhat forcefully indicated. It is confirmed, to be sure, by other sorts of observations.²⁴

Overtone and combinations involving internal modes of nitrate ion give rise to a number of sharp, polarized bands in the region from 1600 to 3400, in addition to ones that may not have been resolved. The assignments listed in Table I were chosen so as to give the correct polarization behavior and a frequency reasonably close to the one observed. We have ignored the possibilities for combinations involving one molecular mode from nitrate ion, one from ammonium ion, inasmuch as all bands in question have counterparts in the spectrum of TiNO_3 . In a few instances we have included alternative assignments that give a superior fit to the observed frequency but are not entirely in accord with the observed polarization.

Combinations of lattice modes with internal modes of nitrate ion are presumed to be the source of weaker, but clearly discernable components, not otherwise explicable, falling in the region below 1200. Reference to the tabulation given earlier for fine structure components allowed under the factor group selection rules shows that a large number of these may be expected. One would suppose, for the lower lying lattice frequencies at least, that any additive combination would

be accompanied by a subtractive one, the two having approximately equal intensities and being symmetrically disposed about the fundamental. However, if a number of these satellites are present, not well resolved, and if additive combinations with one molecular mode are superimposed upon subtractive ones with another, individual components may become badly obscured and symmetry of envelopes may be destroyed. This possibly may account for our inability to find any correlation between the fine structure components observed and the ones predicted. On the other hand, factor group selection rules for combinations are known⁶ to be woefully incomplete with vastly many more being allowed under the complete space group selection rules. Probably, then, our hope of finding such a correlation represents little more than mere wishful thinking. For the present we have merely indicated in Table I the molecular mode from which each such component seems to us to be derived. This element of identification is based mainly upon an expectation of symmetrical envelopes, realized as we shall see with TiNO_3 . Low temperature spectra²² also have been consulted, but these are of dubious significance with NH_4NO_3 where a phase transition intervenes.

NH_4NO_3 (III)

The spectra, again designated as *a*, *b*, and *c* with unchanged significance, are shown for this crystal in Figs. 4 and 5 supplemented by Table III.

The crystal structure,^{13,14,19} space group V_h^{16} with four molecules per unit cell, site groups C_s for both

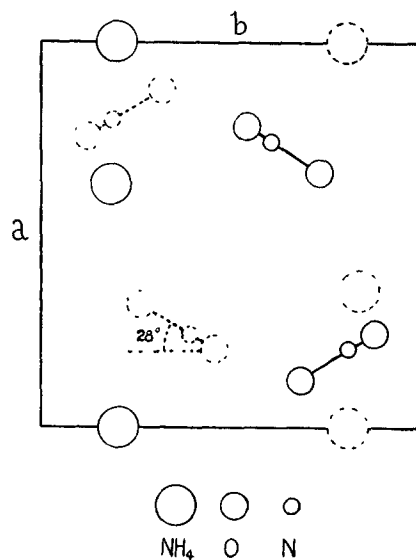


FIG. 6. Unit cell of NH_4NO_3 (III). Full lines depict ions centered in upper and lower faces of unit cell, broken lines depict ones centered halfway between. Both kinds of ions occupy sites with symmetries C_s , with planes of symmetry parallel to (001). The ammonium ions have been displaced slightly from their actual positions in the planes of symmetry for sake of clarity. Axes are labeled according to reference 14 (see footnote to text).

²⁴ J. L. Crenshaw and I. Ritter, *Zeits. f. physik. Chemie* **B16**, 143 (1932). G. E. Pake and H. S. Gutowsky, *J. Chem. Phys.* **16**, 1164 (1948).

kinds of ions, is shown[‡] in Fig. 6. The crystallographic information is again subject to the reservation noted previously for NH_4NO_3 (IV).

The selection rules for nitrate ion under the site group C_s show that all modes are permitted to absorb, with ν_1 and ν_2 polarized along a and b , ν_3 and ν_4 each split into two components, one polarized along both a and b , the other polarized along c . The analysis for lattice modes will be omitted in consequence of its demonstrated unsuitability for interpretation of the previous case.

$\nu_1(1048)$ is forbidden to appear in the c spectrum and is not observed there. Intensities for the a and b spectra should be in the ratio of one to three, respectively, as can be deduced from the disposition of nitrate ion planes depicted in Fig. 6. Inasmuch as the two spectra were obtained with sections of unequal thickness, direct verification of this prediction is impossible. Using the measured thicknesses and amounts of absorption at the band center, assuming an exponential law for absorption, one obtains for the ratio of extinction coefficients the result $1/2.8$. Considering the crudity of the calculation, this may be a fortuitous check.

$\nu_2(830)$ is forbidden to appear in the c spectrum

where, however, a weak residual is observed. We interpret this, as we did the corresponding band in the c spectrum for NH_4NO_3 (IV), to be the result of combination between ν_2 and low lying lattice modes, a proposal that seems in accord with the diffuse background accompanying this band. For the allowed components appearing in the a and b spectra, the expected apportionment of intensities seems to hold qualitatively, that is, $a > b$. The completeness of the absorptions precludes any attempt to examine the quantitative check by the means used for ν_1 .

The weak satellite at 808 appears less well resolved than formerly, its frequency becoming correspondingly more uncertain. Once again it has the proper location and something like the proper intensity for assignment to the isotopic ion.

$\nu_3(1390?)^{17,18}$ is again completely obscured by neighboring bands. Expected to appear in all three spectra, it seems this time to do so. At least, the b spectrum stands in contrast with the corresponding one for the previous substance where a marked narrowing of absorption was seen to occur.

$\nu_4(720, 716)$ is allowed in all three spectra and appears in all of them. In gratifying agreement with

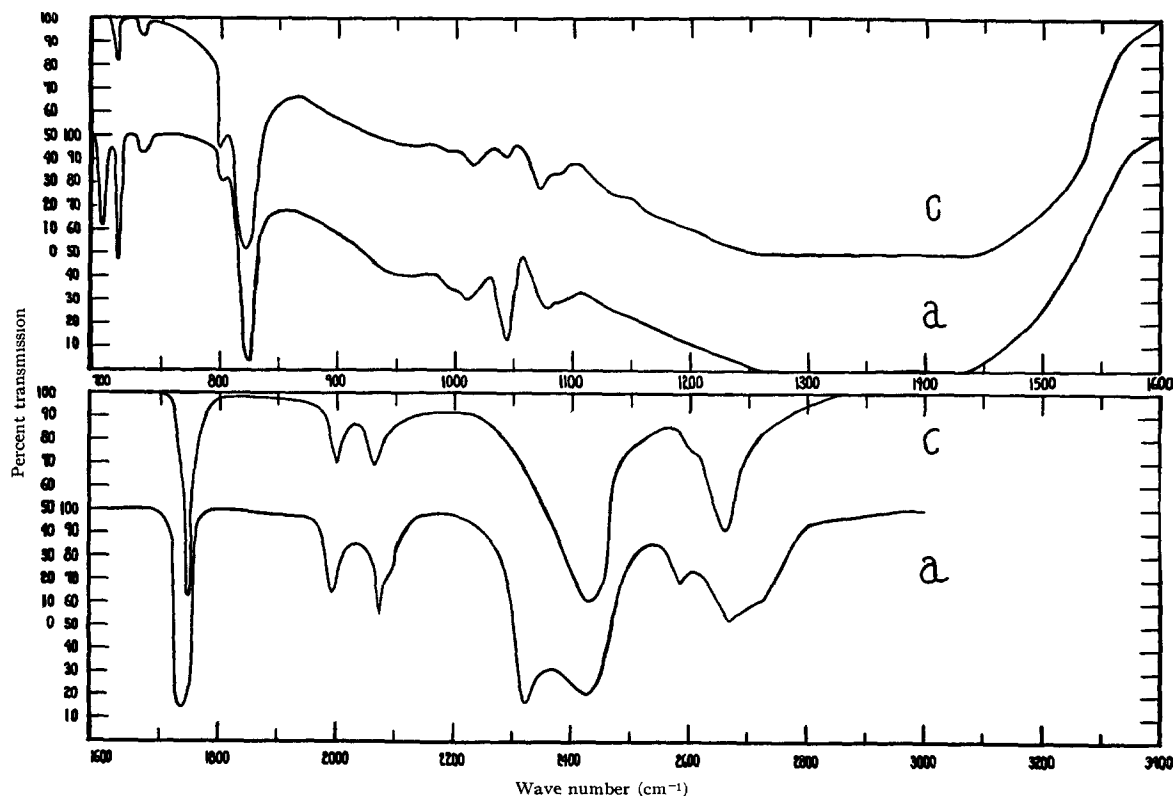


FIG. 7. Polarized spectra for single crystal of TlNO_3 (γ). Electric vector of the light beam is parallel to axis indicated, sample about 60 microns thick. Axes are labeled according to reference 15.

[‡] It should be noted that references 13 and 14 differ, as far as the present work is concerned, in the assignment of the a and b periods relative to the angles of the NO_3 planes. The labeling of the spectra (Figs. 4, 5) and the crystal diagram (Fig. 6) is in accordance with reference 14. In as much as both sets of authors are in agreement as to the relation of the angles of the nitrate planes and the directions appropriate to the principal refractive indices, it would perhaps have been better to have labeled the spectra and diagram α , β , and γ , the measured quantities, rather than a , b , and c as was done.

expectations, the same frequency 720 appears in both *a* and *b* spectra with a qualitatively correct apportionment of intensities ($b > a$) while a new frequency 716 appears in the *c* spectrum. This difference in frequencies is well beyond experimental precision in this region. Moreover, we should note that the anomaly of intensities encountered with NH_4NO_3 (IV) no longer confronts us, tending to confirm some of the views expressed there.

The nitrate ion fundamentals, in summary, absorb in a manner that seems to dispel all doubt concerning the correctness of their previous identifications, one that is in good accord with selection rules characteristic of their environment in this crystal.

The ammonium ion fundamentals will not be discussed again here, inasmuch as the bands show no polarization and the remarks offered for the previous case will hold as well for this one.

Combinations among molecular modes and between molecular modes and lattice modes will not be treated separately for this case. In general, all remarks made for the previous case will apply here as well. Assignments appear in Table III.

TlNO_3 (γ)

This substance will be treated as an example to show how polarized spectra might be used in conjunction with the established methods of x-ray crystallography to identify a crystal structure when it is difficult to obtain by the latter method alone. The example is a valid one because the orientations of the nitrate ions in this crystal must be deduced from features of the x-ray diffraction that are overshadowed by the preponderant scattering from the heavy thallous ions. To this end, we shall depart from the previous order of presentation to describe first the spectra, next the selection rules that might be indicated by them, and last the implications of this information toward the crystal structure.

The spectra, only two of them because of our failure to produce sections capable of exhibiting satisfactorily the third one, are shown in Fig. 7 and Table IV, wherein they have been designated as *a* and *c* according to our previously explained conventions.

$\nu_1(1044)$ appears prominently in the *a* spectrum, probably[¶] likewise along *b*, and just perceptibly along *c*. The remarkable envelope structure accompanying this band will be treated in another paragraph dealing with combinations between molecular modes and lattice modes.

$\nu_2(824)$ appears in both the *a* and *c* spectra, but broadens asymmetrically upon passing from *a* to *c*. That is, it appears as though another absorption were

[¶] Although we were unable to produce sections that would be altogether satisfactory for observations at longer wave-lengths, we conducted observations with a small fragment having the proper orientation and obtained what we believe was a partial *b* spectrum containing this and other principal bands. See Table V.

TABLE IV. Frequencies (cm^{-1}) observed for TlNO_3 (γ).

<i>a</i>	<i>c</i>	Assignment*
700	—	ν_4
713	713	ν_4
735	735	+35
800	800	$\nu_2(\text{N}^{18}\text{O}_3)?$
824	822	ν_2
—	960	—84
965	—	—79
—	~988	~-56
~1000	—	~-44
1010	—	—34
—	1015	—29
1044	1044	ν_1
—	1072	+28
1078	—	+34
~1085	~1085	~+41
—	~1130	~+86
—	~1180	~+136
1260 to 1430	1260 to 1440	$\nu_3, 2\nu_4$
1736	—	$\nu_1 + \nu_4$
—	1750	—
1994	—	—
—	2000	—
—	2064	$2\nu_1, \nu_3 + \nu_4, 3\nu_4$
2074	—	—
~2080	—	—
2320	—	$2\nu_2 + \nu_4$
2430	2430	$\nu_1 + \nu_3$
2584	—	—
—	2610	$\nu_1 + \nu_2 + \nu_4$
2670	2660	$2\nu_2 + \nu_1$
~2720	—	—

* See Table I

added in the *c* spectrum at a slightly lower frequency than the one appearing along *a*. Occasionally, under conditions of best resolution, a small shoulder appeared at about 821. The effect was never great enough, however, relative to noise, to establish its reality. The spectra of powdered specimens at low temperatures showed²² the band sharpened and shifted slightly toward higher frequency but did not produce any resolution into two bands. Whatever be the case, a multiplicity of frequencies, a number not exceeding the population of the unit cell, is permissible^{5,6} for a fundamental under the complete space group selection rules. It is significant, though, that this band appears prominently in both *a* and *c* spectra.

The weak satellite, now at 800, has shifted frequency parallel with ν_2 , behaving properly for an isotopic shift. We remark again, however, that the appearance of this pair in²² $\text{Pb}(\text{NO}_3)_2$ casts some doubt upon this assignment.

$\nu_3(1390?)$,^{17,18} although no longer complicated by the absorption in ammonium ion, remains concealed in a broad region of complete absorption. It is probably obscured in part by the overtone $2\nu_4$ and, although the fundamental would be expected to behave like ν_4 , no significant changes in the envelope were detected. The study of this fundamental and the possible Fermi resonances between components of it and the degenerate overtone must await the preparation of much thinner sections.

$\nu_4(696, 700, 713)$ is involved in absorptions at these places, at 735, and probably at lower frequencies as well. The band at 700 appears in the a spectrum only, the one at 713 in both spectra but is noticeably weaker along c , the one at 735 in both spectra with about the same intensity. The bands at 700 and 713 are sharp, whereas the one at 735 is comparatively broad. Upon the basis of their strengths and sharpness we assign the bands at 700 and 713 to the now separate components of the originally degenerate mode ν_4 . The band at 735 we believe to be a combination of one component of ν_4 with some branch of the lattice spectrum and we prefer to attribute it to the component at 700, rather than 713, because the former is polarized like ν_1 , the latter more like ν_2 , and ν_1 is evidently prone to enter into such combinations. This would place the difference combination at 665 where it would be masked by an atmospheric absorption and thus account for our lack of success when searching for this companion at lower frequencies. Observations²² with a powder specimen at low temperature served to eliminate the possibility that 735 is a difference frequency involving any of the other fundamentals and disclosed, at the same time, that the situation is rather more complicated than it thus far appears. In the powder spectra at room temperature the band noted here at 700 appears instead at 697, noticeably broadened, while 713 and 735 appear unchanged. When the powder is cooled with liquid air, the band at 735 is unaffected, the one at 713 is sharpened and shifted upward to 714, while the third band becomes²² resolved into two components at 696 and 700, respectively. The latter is evidently the one we have seen in our polarized spectra whereas the former, since we have not found it along either a or c , must be virtually completely polarized along b . This multiplicity of frequencies arising out of ν_4 is, as we remarked before, evidence for a plural number of molecules per unit cell. We are unable at this time, however, to better clarify the situation that we have been describing.

Combinations and overtones involving molecular modes of nitrate ion give rise to a number of bands, more or less sharp, falling at higher frequencies, and, in several instances, appearing to be virtually excluded from the spectrum as seen along c . Assignments, based upon gaining agreement with frequencies and tending to be confirmed by polarization properties observed in the other crystals, are included in Table IV.

Combinations between molecular modes and lattice modes produce the truly remarkable envelope structure observed in the vicinity of ν_1 . As can be seen in Fig. 7, and spectacularly so in the original records, three pairs of branches, whose members are distributed symmetrically above and below another central one, were more or less well resolved. When examined in

detail it is found that (1) the most immediate satellites move from 1015 and 1072 in the c spectrum to 1010 and 1078 in the a spectrum, changing thus from ± 28 to ± 34 , (2) the proximate shoulders at 1000 and 1085 appear to become intensified upon passing from c to a , as does the broad, outermost satellite at 960 and probably also its companion at 1145. While these effects may denote the presence of some polarized components contributing to the fine structure, we must bear in mind that the first two could be caused in some part, if not altogether, by the introduction of the strongly polarized central branch which is absent from c but appears along a . We are left to conclude that the resolved components of the fine structure are not strikingly polarized, a conclusion that is in accord⁸ with the general theory and bespeaks against any attempt at this time to identify the resolved increments with particular branches of the lattice mode distribution. Especially striking is the sharp contrast between the behavior of the central branch and that of the satellites. It is possible, of course, that the small shift of spacing described above results from the substitution, in the combinations, of lattice modes polarized along a for ones polarized along c but, if so, the case needs to be more convincingly demonstrated. The complexity of these satellites, as well as the correctness of identifying them with combinations, is indicated by the low temperature spectra.²²

Selection rules appear to be operating in this crystal although, from the standpoint of strict logic, we cannot be absolutely certain that crystallographic symmetry is their cause. The evidence for selection rules is summarized in Table V, where we show the presence or absence of each fundamental absorption by + or - respectively, and in the untabulated behaviors of several combinations at higher frequencies. When assembling this evidence we have ignored small residuals such as the trace of ν_1 that remains along c . The significance of these empirical selection rules is discussed below.

The crystal structure of this substance will now be discussed from the standpoint of ascertaining, insofar as possible from our spectra, the orientations of the nitrate ions. For this purpose we shall find it convenient to make use of the knowledge¹⁵ that the crystal is orthorhombic with four molecules per unit cell, and illuminating to carry the argument as far as possible without resorting to any other crystallographic information.

Orthorhombic space groups include the classes C_{2v}^n , V^n , V_h^n . The maximum symmetry that is common²⁰ to any of these and to the molecular group D_{3h} is C_{2v} . Accordingly, C_{2v} and its subgroups C_2 and C_s are the only possible non-trivial site groups for nitrate ion. Referring to Table V and recalling the selection rules for nitrate ion under the group C_{2v} , described in connection with NH_4NO_3 (IV), we see that the rotation axis, if it exists, cannot lie along c . Furthermore that,

|| Although not shown in Fig. 7, the region below 680 was searched as well as possible with the rocksalt prism, handicapped as we were by the light losses attending use of the polarizer and the inferior aperture presented by the crystal.

if the ions do occupy sites having symmetry C_{2v} , the axis at some of them must lie along a (ν_1 is in a), at others along b (ν_2 is in a). Moreover, for either of the two axial orientations, the plane of the molecule might lie in either of two crystallographic planes, yielding four possible arrangements in all, and the entirety of Table V cannot be accounted for unless at least three of these possibilities are invoked. These three possibilities are all non-equivalent under the operations of any orthorhombic space group. The class V_h^n is now ruled out, because it would demand²⁰ two equivalent sites of each kind, a total of six in all, exceeding the known population of the unit cell. The classes C_{2v}^n and V^n are likewise impossible; the former because we would require rotation axes along both a and b , the latter because it lacks planes of symmetry. Thus, we have shown that the site group cannot, under any likely circumstances, have the symmetry C_{2v} .

If we suppose instead that the site group is C_s , and recall that ν_1 must develop its transitory electric moment entirely in the plane of symmetry, we find that the only possibility for this plane is the one of a and b . Again, however, in order to account for all of Table V we must arrange the plane of the molecule sometimes parallel with a and b , sometimes perpendicular to them, to produce arrangements that are non-equivalent. Space groups of class V_h^n are now ruled out, on ground of population, and those of class V^n , because they contain no plane of symmetry. Space groups of class C_{2v}^n are possible wherein the nitrate ions occupy non-equivalent sites as described above, but in this case are restricted to ones having not more than one glide plane, ones whose rotational element lies along a or b but never along c .

If we suppose next that the site group is C_2 , and compare the observed occurrences of ν_1 and ν_2 with ones permitted by the appropriate selection rules, we find it necessary to invoke sites with the C_2 axis sometimes along a , sometimes along b , but never along c . Because these sites are non-equivalent, space groups of class V_h^n are eliminated on ground of population, while ones of class C_{2v}^n are eliminated because they do not contain the required, two, rotation axes. Space groups of class V^n are possible wherein the nitrate ions occupy non-equivalent sites C_2 described above, provided that they contain not more than one screw axis which, if it exists, must have the direction of c .

In both of the foregoing instances, where we have been able to find acceptable arrangements of nitrate ions at sites with non-trivial symmetry, we have had to invoke duplicate, non-equivalent²⁰ sets of sites. Although there is no clearly stated principle in our knowledge that forbids such occurrences they are nevertheless quite rare, and when they are observed there is usually some recognizable reason whereas none seems evident in this substance. We would, accordingly, regard both of these possibilities for site groups as highly unlikely and expect to find the nitrate ions in

TABLE V. Observed behaviors of fundamentals.

	a	$b^a(?)$	c
ν_1 1044	+	+	—
ν_2 824	+	+	+
ν_3 $\left\{ \begin{array}{l} 696 \\ 700 \end{array} \right\}$	+	+	—
715	+	+	+

^a See footnote ¶ under discussion of ν_1 .

general positions, ones having the trivial symmetry C_1 , an expectation that can be tested objectively by examination of the systematic x-ray extinctions.

If we suppose finally that the nitrate ions are in general positions, space groups of class V_h^n are eliminated immediately on ground of population, classes V^n and C_{2v}^n remain acceptable without restriction upon their symmetry elements. We must, however, explain the apparent exclusions to be found in Table V. For this latter purpose it is instructive to compare the acceptable, if unlikely arrangements we have described in the preceding paragraphs. The sites of kind C_s , whose common plane of symmetry is required to be the one of a and b , will have always one molecular C_2 axis in that plane. These sites will effect the exclusions of ν_1 and one component of ν_4 from the spectrum along c , independent of the direction given to the molecular C_2 axis in that plane. On the other hand, sites of kind C_2 , whose axes are required to lie along both a and b , will effect the same exclusions, independent of the amount of rotation of the molecular plane around those axes. At each kind of site the selection rule is preserved during an operation that would destroy the symmetry of the other kind of site, an operation that in either case would do so without removing the molecular axis from the plane of a and b . This latter restriction upon the directions taken by molecular C_2 axes, rather than the existence of any actual symmetry at the site, is evidently a sufficient and more likely cause for the observed selection rules.

Summarizing our conclusions concerning the crystal structure: when the crystal is viewed along its c axis (1) the nitrate ions each will be seen to have one of their molecular C_2 axes lying in a plane that contains only a and b , (2) these axes in the different nitrate ions will be pointing in four directions, necessarily intermediate between a and b , that are equivalent under the operations of the orthorhombic space group, (3) the molecular planes will appear tilted, by equivalent rotations about these molecular C_2 axes only. The four directions for molecular C_2 axes must have equal absolute values for their corresponding direction cosines. These values could be estimated by comparing the intensities for ν_1 along a and b , respectively, if the latter spectrum were available. The angles of tilt given to the molecular planes must correspond in a similar way, and these can be estimated by comparing the intensities for ν_2 , or for the persistent component of ν_4 , along a

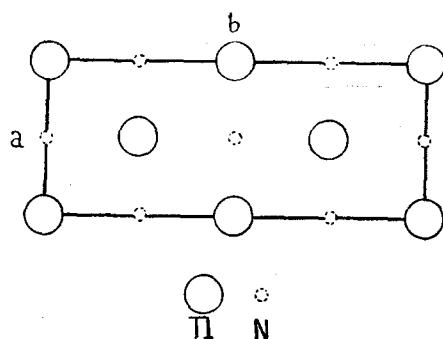


FIG. 8. Unit cell of TiNO_3 (γ) showing occupied sites according to Rivoir and Abbad. Full lines depict thallous ions in upper and lower faces, broken lines depict nitrogen atoms in plane exactly halfway between. Positions of oxygen atoms, which determine both space symmetry of lattice and point symmetries of sites, are described in accompanying text.

and c . The former, although too intense for satisfactory measurement, suggests by its widths an angle in the neighborhood of $\pm 30^\circ$; the latter an angle near $\pm 22^\circ$.

Employing the conventional methods for structure determination, Rivoir and Abbad¹⁵ obtained the lattice of occupied sites which we show in Fig. 8. It will be seen that this partial lattice, into which the oxygen atoms have yet to be introduced, is tetragonal, with completely equivalent axes a and b , that the sites assigned to nitrate ions have in this incomplete lattice a higher kind of symmetry than will the finished nitrate ion itself. Thus, when the nitrate ions are completed by addition of their oxygen atoms, the symmetry of their sites, and of the complete lattice, will be lowered thereby to an extent depending solely upon the orientations given to these ions. In this way a variety of space groups, with corresponding site symmetries, could be generated. Rivoir and Abbad attacked the problem of determining the complete structure upon the basis of how best to accommodate the dimensions of nitrate ions, as determined in other crystals, into the spaces available in the readily ascertained partial lattice of thallous ions. They concluded that the space group is either V^2 or V^3 , more probably the latter. In the structure selected finally by them the nitrate ions meet our specifications in all respects save one. They show the

molecular C_2 axes all aligned with a , the molecular planes tilted by rotation about this direction. We hold to our conclusion that these axes must have directions intermediate between a and b , for otherwise ν_2 would not be seen along a . Moreover, since these two directions are equivalent before introducing oxygen atoms, it would seem remarkable if these atoms should show any preference between them. From this point of view it appears probable that the four axial directions would be exactly midway between a and b , along the lines of closest approach for nitrate ions. This would be compatible with our incomplete spectroscopic information.

Lattice Frequencies

On the basis of the observations made, it is felt that certain tentative conclusions may be drawn as to the range of frequencies of the low lying lattice modes. If the various assignments of the fine structure as combinations of lattice and internal modes are correct, then it would appear that optical branch lattice frequencies in these crystals have a lower limit at about $35\text{--}50\text{ cm}^{-1}$ and range upward to perhaps between $100\text{--}200\text{ cm}^{-1}$. It is, for the moment, impossible to determine whether a band is a result of a simple transition, wherein the quantum number of the associated lattice mode changes by one, or whether it results from more complicated transitions involving overtones of lattice frequencies or combinations of them.

It is interesting to note that the Raman spectrum of single crystals of NaNO_3 showed²⁶ anti-Stokes lines at 100 and 185 cm^{-1} , which are presumably caused by excited lattice modes. Other Raman investigations on ionic single crystals have shown similar magnitudes for the frequencies of the lattice modes. Again, of course, it is not known whether the observed lines are simple transitions.

Perhaps when microwave or other techniques are suitably perfected for work in the 100 cm^{-1} range, they will yield sufficient information on lattice frequencies to make data, such as have been obtained here, somewhat more intelligible.

²⁶ Shaefer, Matossi, and Adelhold, *Physik. Zeits.* **30**, 581 (1929).