

Motions of Molecules in Condensed Systems. IV. The InfraRed Spectra for Ammonium Nitrate and Thallous Nitrate

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Motions of Molecules in Condensed Systems. IV. The Infra-Red Spectra for Ammonium Nitrate and Thallous Nitrate

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The infra-red absorption spectra from 680 to 3600 cm^{-1} have been recorded for five crystalline modifications of NH_4NO_3 at 150°, 105°, 55°, 25°, and -40°; also the spectra from 680 to 1450 cm^{-1} of three modifications of TlNO_3 at 170°, 100°, and 25°. Fundamental frequencies of the nitrate ion were found for NH_4NO_3 at 715, 830, 1050, and 1350 cm^{-1} (those for TlNO_3 were found at approximately the same positions) and of the ammonium ion at 1430, 1760, 3100, 3200 cm^{-1} . The spectrum of each compound remains essentially the same with change of temperature, except that in NH_4NO_3 at 150° and 105° the band at 715 cm^{-1} is absent. It is notable that bands at 1050, 1760, and 3100 cm^{-1} , supposedly caused by symmetric vibrations, remain active in all crystal forms investigated.

INTRODUCTION

FOR some years it has been known that the character of the infra-red absorption spectrum of a compound depends largely upon the environment in which the molecules find themselves. Recently one of us¹ has advanced the thesis, subsequently verified² experimentally for the case of benzene, that (1) while the selection rules for the vapor are determined solely by the symmetry of the individual molecule; (2) for the liquid, in general, there are no strict selection rules; (3) the selection rules for the solid may be approximated by considering a single molecule and the symmetry of the potential field created by its neighbors. In passing from the liquid to the solid, it is expected that prohibitions may become operative, since in the latter the symmetry of the surroundings of a given molecule are more nearly space and time-fixed, than in the former.

It was thought of interest to extend experiments to include infra-red spectra of a single compound exhibiting several different crystal modifications. Presumably, with change in crystal structure, the change of potential field about any given molecule might alter the spectrum. Ammonium nitrate, capable of existing in five modi-

fications over a short temperature range at normal pressures, was chosen for this study.

In order to treat the problem in accordance with the stated principles, it is necessary to know beforehand the "site" symmetry of the molecules or ions in the crystal; that is, we must at least have knowledge of the space group and the number of molecules per unit cell for each of the five modifications of ammonium nitrate. Unfortunately, only two of the polymorphs have been sufficiently defined. These are NH_4NO_3 IV (orthorhombic) stable from about -18° to +32°C, having space group V_h^{13} ($P2_1/m2_1/m2/n$) and two molecules per unit cell,^{3,4} and NH_4NO_3 III (orthorhombic) stable from 32° to 84°C with space group V_h^{16} ($P2_1/n2_1/m2_1/a$) and four molecules per unit cell.³ The remaining modifications have been described as NH_4NO_3 I (cubic) stable from 125° to 169°C (melting point) with one molecule per unit cell; NH_4NO_3 II (tetragonal) assigned to space group D_{2d}^3 or C_{4v}^2 with two molecules per unit cell;⁵ and NH_4NO_3 V (hexagonal ?) with six molecules per unit cell.

During the course of our investigations the spectra of forms I and II were found to be irregular with respect to the nitrate ion. Lack of crystallographic knowledge prompted us to treat thallous nitrate as we had ammonium nitrate, since the former possesses a high temperature cubic modification (TlNO_3 α , space group un-

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¹ R. S. Halford, J. Chem. Phys. 14, 8 (1946). The same symmetry argument for crystals was first used, in another connection, by H. Bethe, Ann. d. Physik 3, 133 (1929).

² R. S. Halford and O. A. Schaeffer, J. Chem. Phys. 15, 141 (1946).

³ S. B. Hendricks, E. Posnjak, and F. C. Kracek, J. Am. Chem. Soc. 54, 2780 (1932).

⁴ C. D. West, J. Am. Chem. Soc. 54, 2256 (1932).

⁵ R. Tiemeyer, Zeits. f. Krist. 97, 386 (1937).

known) having cell dimensions⁶ almost those of NH₄NO₃ I. From these considerations we infer that the nitrate ions in the two compounds may exist in similar environments in the high temperature forms and could therefore give rise to correspondingly similar spectra. TlNO₃ exists in two other forms, thereby providing further possibilities of changes in spectra and of comparison with NH₄NO₃.

In this article we shall describe the experimental methods and results of a study of the spectra of the five forms of ammonium nitrate and of the three forms of thallous nitrate.

EXPERIMENTAL AND RESULTS—NH₄NO₃

The requirements for the preparation of a solid sample for investigation in the infra-red include that the sample be transparent to infra-red radiations in the regions of non-absorption and that the sample not extensively scatter the radiation incident upon it. In the case of ammonium nitrate we found these requirements best met by preparing the sample in the following manner.

Analytical reagent NH₄NO₃ supplied by the Mallinckrodt Chemical Company was finely ground and spread in a thin layer upon a disk, 50 mm in diameter and 1 mm thick, of rolled silver chloride obtained from Harshaw Chemical Company. Then a similar disk of AgCl was placed on top of the NH₄NO₃ layer. This sandwich was placed upon a small aluminum plate and the whole heated by a cone heater to the melting point of NH₄NO₃. Once the entire layer was fused, another aluminum plate was laid upon the sandwich and on top of this a weight of about a kilogram, thereby squeezing out excess sample. The heater was removed and the specimen allowed to cool undisturbed. This last sequence of operations was carried out quickly since vaporized NH₄NO₃ slowly decomposes to water and nitrous oxide at the melting point of the salt. By varying the amount of salt and the weight placed upon the sandwich, the thickness of the sample could be roughly adjusted. An apparent drawback of this procedure was the indeterminacy of the exact thickness of the

specimen. However, for the investigation under discussion the main aim was a sample that would display the fundamental absorption bands. To this end, the above treatment was entirely satisfactory.

Since ammonium nitrate is highly volatile at the relatively high temperatures at which spectra were to be taken, it was desirable that the sample cell be closed from the atmosphere. The sandwich was held between cork insulators with an ordinary c-clamp, while a hot glass rod was applied to the rim of the AgCl disks, thus welding them together.

It was found that upon passing from one modification to another the sample became more opaque to infra-red radiations—it was by this evidence that we were assured a transition had occurred. Moreover, the sample would begin to scatter the shorter waves quite severely after several transitions. This was remedied by “rejuvenating” the salt layer: the sandwich was merely heated above the nitrate’s melting point and allowed to cool to the modification desired. This had to be done twice during the investigation.

Because polymorphic transitions in NH₄NO₃ are often delayed,⁷ in all cases, with the exception of modification V, the various crystal forms were obtained by maintaining the suitable temperature for at least twelve hours before recording the spectra. The low temperature form was pre-cooled for two hours.

The electric heating cell and the liquid nitrogen cooling apparatus employed for temperature control were those described by Carpenter,⁸ and Carpenter and Halford.⁹

An automatic recording prism spectrophotometer¹⁰ was used for measurements of the spectra. At all times a cell, made of two disks of AgCl treated exactly as those used in the sample, was used as a photometric standard. The spectra were recorded in the following order: (1) NH₄NO₃ IV at room temperature; (2) III at 55°C; (3) II at 105°C; (4) I at 150°C; (5) IV again at room

⁷ O. Lehmann, *Zeits. f. Kryst.* 1, 108 (1877).

⁸ G. B. Carpenter, thesis for the doctorate, Harvard University (1947).

⁹ G. B. Carpenter and R. S. Halford, *J. Chem. Phys.* 15, 99 (1947).

¹⁰ H. Gershinowitz and E. B. Wilson, Jr., *J. Chem. Phys.* 6, 197 (1938).

⁶ C. Finbak and O. Hassel, *Zeits. f. physik. Chemie* B35, 25 (1937).

temperature; (6) V at -40°C ; and (7) V at -65°C . Each spectrum was measured at least twice. In the region up to 1250 cm^{-1} a NaCl prism was used, while from 1250 to 3600 cm^{-1} a CaF_2 prism was employed.

Figure 1 shows the absorption spectra in the range 680 to 3600 cm^{-1} of NH_4NO_3 in its five modifications. The regions of transparency have been corrected to read 100 percent by using a sliding correction factor in order to compensate for the small though increasing losses of radiation toward the short wave end of the spectra. The absorption bands have been corrected accordingly. The spectra at -40° and -65°C are virtually identical despite the fact that these temperatures straddle a reported lambda-point^{11,12} of NH_4NO_3 at about -60°C . Furthermore, the specimen gave the same spectrum at room temperature before and after it had been heated up to 150°C in the stages mentioned above.

It is altogether plausible that all the distinct fundamental frequencies of nitrate (four) and of ammonium (four) ions appear in the spectra. The fundamental absorption bands of the two ions are confined to separate frequency regions

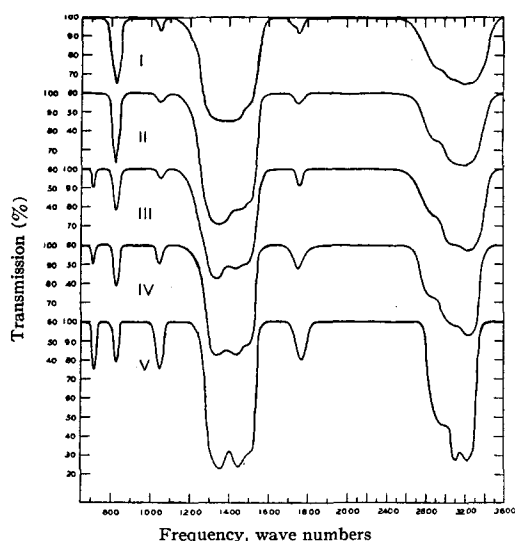


FIG. 1. Infra-red absorption spectra from 680 to 3600 cm^{-1} of five crystalline forms of NH_4NO_3 : I at 150°C ; II at 105°C ; III at 55°C ; IV at room temperature; V at -40°C . Measurements from 680 to 1250 cm^{-1} were made with a rock salt prism, from 1250 to 3600 cm^{-1} with a fluoride prism.

¹¹ J. L. Crenshaw, I. Ritter, *Zeits. f. physik. Chemie* **B16**, 148 (1932).

¹² R. Pohlman, *Zeits. f. Physik* **79**, 419 (1932).

and have been assigned¹³ elsewhere as shown in Table I, regarding nitrate ion as planar and ammonium ion as tetrahedral. Also listed is an overtone frequency.

Although the method of obtaining data does not lend itself to giving a quantitative picture of intensity changes in the five spectra, some qualitative information is readily presented. Most obvious is the disappearance in forms I and II of the band at 715 cm^{-1} . Another unusual feature displayed by the group of spectra is the comparative increase in intensity of the 830 cm^{-1} band, which contrasts with the losses of intensity at 715 , 1050 and 1760 cm^{-1} .

EXPERIMENTAL AND RESULTS— TlNO_3

Specimens of thallos nitrate of high purity were prepared by a method similar to that used

TABLE I. Assignment (13) of frequencies for ammonium and nitrate ions as found in NH_4NO_3 .

Ion	Frequency (cm^{-1})	Assignment
NO_3^-	715	Doubly degenerate bend in plane
NO_3^-	830	<i>N</i> in-and-out of plane
NO_3^-	1050	Symmetric stretch in plane
NO_3^-	1350	Doubly degenerate unsymmetric stretch in plane
NH_4^+	1430	Triply degenerate bend
NH_4^+	1760	Doubly degenerate totally symmetric bend
NH_4^+	3100	Totally symmetric stretch
NH_4^+	3200	Triply degenerate stretch
NH_4^+	2880	Overtone of 1430

for ammonium nitrate, but with the following variations. Melted TlNO_3 in contact with AgCl and oxygen of the air readily oxidizes to Tl_2O_3 ; to avoid this it was found sufficient to cool the melt soon after its formation as well as to keep the initial layer of powdered TlNO_3 compact so as to exclude as much air as possible from the sandwich filling. The cell was not sealed as before; but instead the sandwich was placed in a holder consisting of threaded male and female parts, both parts having equal apertures for traversal by the light beam. The rim of the sandwich was in this way held secure.

TlNO_3 freezes at 206°C to form a clear mass of cubic crystals (form α); at 145°C the salt undergoes a transition to a trigonal form (β);

¹³ G. Herzberg, *Infra-red and Raman Spectra*, Vol. II (D. Van Nostrand Company, Inc., New York, 1945), p. 167, 178.

and at 75°C it passes into an orthorhombic form (γ) stable down to very low temperatures. Of these modifications only the latter has been well defined crystallographically: possible space groups are given as D_2^2 ($P222_1$) and D_2^3 ($P2_12_12$) the latter being most probable, with four molecules per unit cell.¹⁴ Upon passing from one form to another, TlNO₃ crystals do not fracture¹⁵ into microcrystals as do those of NH₄NO₃,³ so that the occurrence of a transition was not immediately obvious. Also, the sample never required rejuvenation. Absorption measurements were made in the following order: (1) γ -form at room temperature; (2) β -form at 100°C; (3) α -form at 170°C; and (4) γ -form at room temperature again. Each of the absorption regions was measured at least in duplicate. The same electrical heating cell as mentioned above was employed for temperature control.

Figure 2 depicts the spectra of the three forms of TlNO₃ in the fundamental region from 680 to 1450 cm⁻¹. For this work the NaCl prism only was used. (680 cm⁻¹ seemed to be the lower useful limit for work with the NaCl prism on TlNO₃; in this region the KBr prism has poor resolving power. Hence the band at 715 cm⁻¹ is covered as well as can be done on our instrument.) The data as presented appears uncorrected for any effect of light-scattering that might be operative.

The presence of all the nitrate fundamentals in all the modifications is evident, but the envelopes of the bands near 700 and 1050 cm⁻¹ are quite different from the corresponding absorptions in the ammonium compound. Aside from the effect of temperature in broadening out the absorption envelopes, very little can be said concerning the changes in intensity of the various components of the spectra.

DISCUSSION

In view of the wide variety of environments in which the respective ions exist in NH₄NO₃ and TlNO₃, it is indeed singular that the spectra of the different modifications are so similar. Group theoretical considerations show that only the totally symmetric vibration of NO₃⁻ (1050

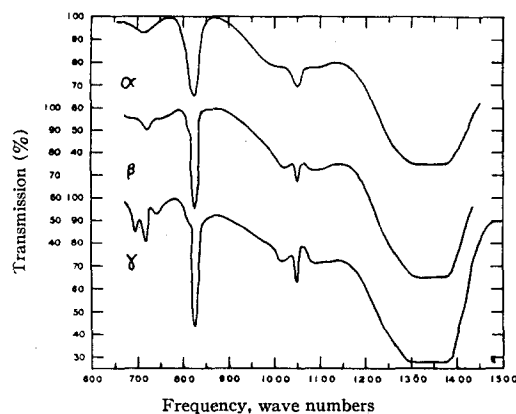


FIG. 2. Infra-red absorption spectra from 680 to 1450 cm⁻¹ of three crystalline forms of TlNO₃: α at 170°C; β at 100°C; and γ at room temperature. All measurements were made with a rock salt prism.

cm⁻¹) and symmetric stretch and bend of NH₄⁺ (3100 and 1760 cm⁻¹ respectively) would be expected to become infra-red inactive if the ions were either in no potential field or in a very symmetrical one. Yet it is evident that these frequencies remain active in all the polymorphs investigated. It may be mentioned that in the two cases for which space-group information is complete (NH₄NO₃ IV and III) the proposed criteria for selection rules are in agreement with the results.

Finbak and Hassel⁶ have shown by x-ray diffraction powder-diagrams that NH₄NO₃ I has a cubic structure, $a_0 = 4.39\text{\AA}$ at 150°C and that TlNO₃ also is cubic, $a_0 = 4.31\text{\AA}$ at 170°C. Pauling¹⁶ lists the crystal radii of NH₄⁺ and Tl⁺ as 1.48Å and 1.44Å, respectively. In the light of this information, structural considerations do not readily explain the apparent failure of these two crystals to give similar spectra (i.e., in NH₄NO₃ the absorption at 715 cm⁻¹ is missing).

The band near 715 cm⁻¹ is comparatively quite sensitive to the environment in which the nitrate ion finds itself. In two of the five modifications of NH₄NO₃ this band seems to be absent altogether, while it becomes noticeably less intense as one progresses toward higher temperatures through either the remaining three modifications of this substance or the three modifications of TlNO₃. Moreover, loss of intensity is accompanied by small but definite shifts of the band

¹⁴ L. Rivoir and M. Abbad, *Anales fis. quim.* **39**, 306 (1943).

¹⁵ G. Tammann and W. Boehme, *Zeits. f. allgem. anorg. Chemie* **223**, 365 (1935).

¹⁶ L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1939), p. 350.

toward lower frequencies. These changes are not paralleled in our observations by any of the other bands, although ones at 1050 and 1760 cm^{-1} do become less intense at higher temperatures.

The behavior of this band at 715 cm^{-1} is of the sort that might be expected¹ if it originates with a molecular mode whose capacity for absorption results solely from perturbations produced by the environment, one that could not contribute to the infra-red spectrum of the isolated molecule. The only fundamental mode that is forbidden to contribute to the infra-red spectrum of the isolated nitrate ion is the totally symmetric one. On the basis of strong evidence from the Raman effect¹⁷ in inorganic nitrates, this mode is assigned the frequency 1050 cm^{-1} : the Raman line at this frequency is intense, sharp, and strongly polarized, all features characteristic of a completely symmetric vibration. The Raman line for nitrate ion at 715 cm^{-1} , on the other hand, is not polarized and has for some

compounds been resolved into a doublet,¹⁸ indicating that the mode may be doubly degenerate. It is interesting to note that light scattering experiments with single crystals of KNO_3 (isomorphous with NH_4NO_3 IV) at different temperatures¹⁹ show that the 715 cm^{-1} line shifts to lower frequency with increasing temperature, in accord with the infra-red behavior of this vibration. Considering this data and that of earlier workers on the infra-red spectra of nitrates,²⁰ we cannot seek the explanation for the strange disappearance of the NH_4NO_3 band at 715 cm^{-1} in a mere shuffling of the assignment of nitrate ion frequencies. We are of the opinion, however, that a proper understanding of this anomaly will require some knowledge of the lattice modes and their combinations with the molecular modes. This question is being investigated currently with a more powerful spectrometer, using single crystals in polarized light, and, accordingly, additional comment will not be offered at this time.

¹⁷ See, for example: P. Grassmann, *Zeits. f. Physik* **77**, 616 (1932); P. A. Moses, *Proc. Ind. Acad. Sci.* **10A**, 71 (1939); T. M. K. Nedungadi, *Proc. Ind. Acad. Sci.* **14A**, 242 (1941).

¹⁸ P. Grassmann, see reference 17.

¹⁹ T. M. K. Nedungadi, see reference 17.

²⁰ See, for example: C. Shaefer and C. Bormuth, *Zeits. f. Physik* **67**, 508 (1930); D. Williams and L. Decherd, *J. Am. Chem. Soc.* **61**, 1382 (1939).

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The Vibration-Rotation Mechanics of the Allene Molecule.

Part I. Classical Vibration Problem

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Symmetry coordinates are set up from the standpoint of group theory for describing the normal modes of oscillation of the allene molecular model in such a manner that maximum factorization of the secular determinant is accomplished. The cubic and quartic portions of the anharmonic potential function are derived, and the components of vibrational angular momentum are set down. The complete valence-type potential function is discussed. Explicit relations are derived between the force constants occurring in the secular determinant and the physical valence force constants.

I. INTRODUCTION

THE infra-red and Raman spectra of the allene molecule, C_3H_4 , have been studied experimentally by several observers.¹ The non-

degenerate normal modes of vibration have been investigated by Thompson and Linnett² and by

(1932); L. G. Bonner and R. Hofstadter, *Phys. Rev.* **52**, 249 (1937); E. H. Eyster, *J. Chem. Phys.* **6**, 580 (1938); J. W. Linnett and W. H. Avery, *J. Chem. Phys.* **6**, 686 (1938).

² H. W. Thompson and J. W. Linnett, *J. Chem. Soc. London*, p. 1384 (1937).

¹ M. Bourguet and L. Piaux, *Bull. Soc. Chim.* **51**, 1041 (1932); H. Kopfer and A. Pongratz, *Wien. Ber.* **141**, 840