

# RAMAN SPECTRUM OF $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{NH}_3$ CRYSTAL; EFFECT OF CRYSTAL FIELD ON THE NITRATE ION

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## ABSTRACT

The Raman spectrum of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{NH}_3$  crystal is taken with the view of studying the effect of the crystal field on the inner vibrations of the  $\text{NO}_3$  group of which a peculiar behavior is suggested by X-ray analysis. One line is found at  $\sim 985 \text{ cm}^{-1}$ . This result and the splitting of the  $\nu_1 \sim 1050 \text{ cm}^{-1}$  line into a doublet in  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  and  $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  crystals observed by Ananthakrishnan are discussed from the viewpoint of the two-minimum problem similar to the  $\text{NH}_3$  molecule.

## INTRODUCTION

The Raman spectra of crystals containing the nitrate ion, such as  $\text{NaNO}_3$ ,  $\text{KNO}_3$ ,  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ , etc., have been studied by a number of investigations.<sup>1</sup> In almost all cases, the spectrum shows an intense line at ca.  $1050 \text{ cm}^{-1}$  due to the symmetric vibration  $\nu_1$  of the plane  $\text{NO}_3$  group and two weaker lines at ca.  $720$  and  $1450 \text{ cm}^{-1}$  due to the two double degenerate vibrations  $\nu_2$  and  $\nu_3$ . In a few cases, the latter two lines are split up into doublets. The explanation of this doubling is not certain. It does not seem to lie in the removal of the  $D_{3h}$  symmetry by crystal field alone, for the doubling is also found with solutions in some cases. Apart from these doublings, however, the spectra of the various nitrates differ comparatively little from one another in regard to the values of the frequencies.

(1) Cf. J. H. Hihben, *Raman Effect and Its Chemical Applications*, New York, (1939), p. 445 ff.

Except for the cases of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  and  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  in which the  $\nu_1$  line become a doublet with a separation of  $28$  and  $10^{-1}$  respectively as observed by Ananthakrishnan<sup>2</sup>, one may conclude that the effect of the crystal field on the inner vibrations of the  $\text{NO}_3$  ion is in general relatively small. The explanation of the doubling of  $\nu_1$  in the two crystals mentioned above is not so obvious; it may perhaps be connected with the effect of crystal field as discussed below.

The present study is an attempt to investigate the effect of crystal field on the  $\text{NO}_3$  ion in the  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{NH}_3$  crystal, a problem of special interest for the following reason: X-ray analysis of the crystal shows that the crystal is cubic, with the Ni atoms at the alternate corners of a cube (one octant of the unit cell) so as to form a regular tetrahedron; that  $6\text{NH}_3$  groups are attached to each Ni atom along the edges of the cube, and that the possible symmetry deduced from the X-ray pattern is not consistent with the  $\text{NO}_3$  group behaving normally in the cell<sup>3</sup>. Furthermore, the X-ray photograph shows that the reflections are weak and diffuse, indicating enormous amplitudes of heat motion. This inconsistency of the  $\text{NO}_3$  group with the symmetry of the crystal is thought by Yü to be due to the possibility of the planar  $\text{NO}_3$  group to oscillate among the four positions of equilibrium for the triangular  $\text{NO}_3$  in the tetrahedral field. These oscillations account at the same time for the "heat motions" mentioned above. Further study of the crystal at liquid air temperature reveals an increase in the intensity and sharpness of the reflections, indicating a great diminution of the "thermal motion", or, probably a freezing up of the  $\text{NO}_3$  in one of the 4 faces of a tetrahedron at the centre of the cube (hereafter referred to simply as the tetrahedron). If these explanations are correct it seems that the effect of the crystal field on the  $\text{NO}_3$  ion is considerable in this case and it would be of considerable interest to study the effect of the crystal field on the

(2) R. Ananthakrishnan, *Proc. Indian Acad. Sc. V A*, 447, (1937)  
 (3) S. H. Yü, *Nature* 141, 163 (1938).

$\text{NO}_2$  ion by means of the Raman effect. With this view the present study is undertaken.

### EXPERIMENTAL

The  $\text{Ni}(\text{NO}_2)_2 \cdot 6\text{NH}_3$  crystals are prepared by adding concentrate  $\text{NH}_3$  solution to a saturated solution of  $\text{Ni}(\text{NO}_2)_2$  in water and grown to approximately 1—2 mm in linear dimensions. As the only available Hg arc is straight one (a General Electric UV arc with oxide coated filament electrodes and operated on a.c.), two arrangements are finally adopted to get as much radiation onto the crystals as possible from the arc. In one arrangement the Raman "tube" is made by cementing rightangled prisms on microscope slides as shown in Fig. 1. The arc is run at 3.5 amperes (rated at 4 amperes) and is cooled by an electric fan so as to reduce the rather strong continuous background. This cooling reduces the intensities of the mercury lines at the same time and brings out the lines of the "red spectrum" of the argon for starting the arc. The radiation is filtered by a 5 mm thickness of a concentrated solution of iodine in  $\text{CCl}_4$  to clear the region to the long wavelength side of 4047Å. This filter is cooled by a water cell which is placed as close to the arc as practicable. In another arrangement, A Raman tube of the conventional type, of 1 cm inner diameter, is surrounded by a jacket containing a 5 mm thickness of saturated solution of iodine in  $\text{CCl}_4$ . The tube and the arc are placed parallel to each other at the focal lines of a cylindrical aluminium elliptical reflector. The scattered radiations are filtered by a cell of  $\text{NaNO}_2$  solution and are focussed on the slit of a three-prism Steinheil spectrograph having a relative aperture of 1:10 and a dispersion of about 10 Å per mm at 4358Å. Exposures of 100, 150, 200 hours, with a slit width of 0.10 mm, are made Kodak portrait film and Ilford selenochrome portrait plate (which are the only photographic material available here). As no source of direct current is available for operating an iron arc, the argon lines of the Hg arc itself are taken as standards for wave-length measurements. On four separate dates, only one line at ca.  $985\text{ cm}^{-1}$  excited by 4047Å is found. This line is shown to be absent in the spectrum of the Hg arc by control exposures,

and is hence believed to be a genuine Raman line. Attempts to excite the spectrum with 4358 Å by employing a moderately concentrated solution of iodine in  $\text{CCl}_4$  as filter have not been successful.

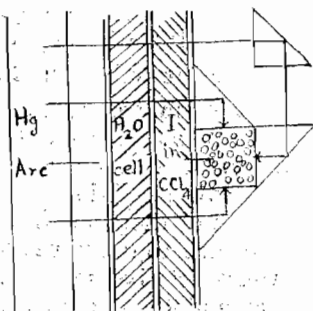


Fig. 1

#### DISCUSSION

The result is rather unsatisfactory in that only one line is found while a complete spectrum is necessary for a discussion of the problem. But as the arc and the spectrograph are rather inefficient affairs, longer exposures of the order of a few hundred hours will not yield additional information concerning the weaker lines that have not come out after 200 hours of exposure. Since better equipment probably will remain unavailable for a long time to come on account of the war conditions, it is thought justified to report this preliminary result and a discussion based on it.

From X-ray studies, it seems that in  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{NH}_3$ , any two positions of equilibrium of the  $\text{NO}_2$  ion in the cube (corresponding to any two faces of the tetrahedron) are separated by a potential barrier whose height is of the order of  $kT \sim 200 \text{ cm}^{-1}$  since the oscillations from one to another of these faces are frozen at liquid air temperature. Now two situations may arise: (A) If the effect of the crystal field on the N atom is very small so that the tetrahedral field is felt mostly by the O atoms, the  $\text{NO}_2$  will remain a plane structure which either

swings among the four positions of minimum energy corresponding to the 4 faces of the tetrahedron, or remains in one of them, according as the potential barrier separating two of them is less or greater than  $kT$ . In either case the inner vibrations of  $\text{NO}_3$  will show comparatively little change compared with the free ion. In Fig. 2a are shown schematically the potential functions for the symmetrical vibration  $\nu_1(s)$  and the antisymmetric vibration  $\nu_3(a)$  of a free  $\text{NO}_3$  ion. Here  $r$  denotes the N—O distance,  $r_0$  the equilibrium value of  $r$  in the planar  $\text{NO}_3$ , and  $x$  the displacement of the N atom from the plane of the O atoms. If the crystal field on the N atom is small, its effect will be to superpose a shallow potential trough on the curve  $V(x)$  at a distance  $h_0$  on both sides of the plane of the O atoms, where  $h_0$  is the distance from the centre to the faces of the tetrahedron. This corresponds to a very weak relative minimum in the energy when the N atom is at the centre and the O atoms are at the corners of the tetrahedron. The crystal field also brings about a slight change in the potential  $V(r)$ . As a result, the frequency  $\nu_1$  may undergo a small shift from the value  $\sim 1050 \text{ cm}^{-1}$  while  $\nu_3$  remains inactive in the Raman effect. This situation is indicated in Fig. 2b.

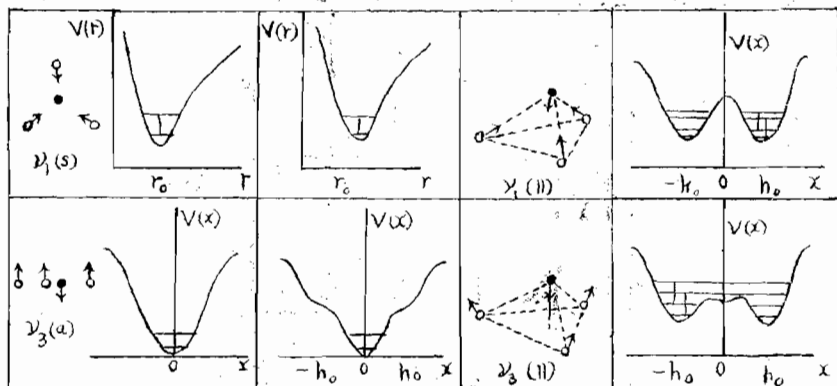


Fig. 2a. Free  $\text{NO}_3$  ion. Fig. 2b. Crystal field on N atom very weak. Fig. 2c. Crystal field on N atom very strong. Vertical lines indicate allowed Raman transitions.

(B) On the other hand, if the effect of the crystal field on the N atom is comparable with the inner potential field of  $\text{NO}_3$ , then, on account of the tetrahedral symmetry, the position of lowest energy of the N atom will be at the centre, while that of the plane of the O atoms will be in one of the faces of the tetrahedron. This superposition of the crystal field on the inner field of  $\text{NO}_3$  distorts the  $\text{NO}_3$  into a pyramidal structure, and the oscillation of the plane of the O atoms between two faces of the tetrahedron is equivalent to the passage of the N atom from one vertex through the base to the opposite side of the pyramid, in so far as motions in the  $\text{NO}_3$  group are concerned. This immediately reminds us of the situation in the case of the  $\text{NH}_3$  molecule where the resonance effect between the two identical potential valleys for the N atom on both sides of the plane of the H atoms gives rise to a doubling of the energy levels for the parallel vibrations and hence a doubling of the parallel infrared absorption bands and the related Raman lines.<sup>2</sup> In Fig. 2c we indicate schematically the potential curves for the two parallel vibrations of the pyramidal  $\text{NO}_3$ , into which the curves in Fig. 2b pass on enhancing the crystal field on the N atom. For the vibration  $\nu_1$  (1f) which is essentially a vibration of the plane of the O atoms past the N atom, the potential curve can be obtained by lowering the two minima at  $h_0$  and  $-h_0$  in Fig. 2b such that the height of the barrier becomes of the order of  $kT$  for  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{NH}_3$ . The frequencies of the two parallel vibrations will naturally be very different from  $\nu_1$  and  $\nu_2$  of the free  $\text{NO}_3$ . For  $\nu_1$  (1f) for which the potential hill is high, one may expect a doubling of the vibrational levels and hence a doubling of the Raman lines. For  $\nu_2$  (1f) for which the potential hill is low, the splitting of the level will be large so that the transition from the lowest level to the next one having a symmetrical wave function, while allowed, may not be easily observed in the Raman effect on account of its being a harmonic and hence of its low intensity.

Dr. Wu, T. Y., *Vibrational Spectra and Structure of Polyatomic Molecules*, National University of Peking Press, Prentice-Hall, New York, (1939), pp 76-80, 193-5.

Let us now consider the  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{NH}_3$  in the light of these considerations. That one Raman line at  $985\text{ cm}^{-1}$  is observed in the neighborhood of the value  $1050\text{ cm}^{-1}$  for the free  $\text{NO}_3$  ion may be taken to indicate that while the crystal field is considerable compared with other crystals containing the  $\text{NO}_3$  ion in view of the great shift of  $\sim 65\text{ cm}^{-1}$ , the situation is likely one which is depicted in Fig. 2b. The absence of doubling of the Raman line corresponding to  $\nu_1$  shows that the crystal field on the N atom is not great enough compared with the inner potential of  $\text{NO}_3$  to distort it into the situation represented by (B) above. The non-appearance of the two other frequencies due to the degenerate vibrations of  $\text{NO}_3$  may be due simply to their weak intensity and the inefficiency of the arc and the spectrograph employed in this work. Their detection by better experimental outfit will be of interest.

Consider now the doubling of the  $\nu_1$  frequency of  $\text{NO}_3$  in the case of the  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  and  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  crystals as observed by Ananthakrishnan<sup>7</sup>. It is possible that the doubling may be due to the effect of crystal field as pictured under (B) and Fig. 2c above, if the doublets in each case are known definitely not to be due to such causes as the presence of two crystal forms having different numbers of molecules of water of crystallization. An X-ray study of these crystals would be very desirable in throwing light on this question.

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