MICHIGAN STATE UNIVERSITY

Contract N00014-68-A-0109-0003

NR 014 - 203

Technical Report No. 8 (33)

THE RAMAN SPECTRUM OF CRYSTALLINE LITHIUM NITRATE

by

R. E. Miller, R. R. Getty, K. L. Treuil, and G. E. Leroi

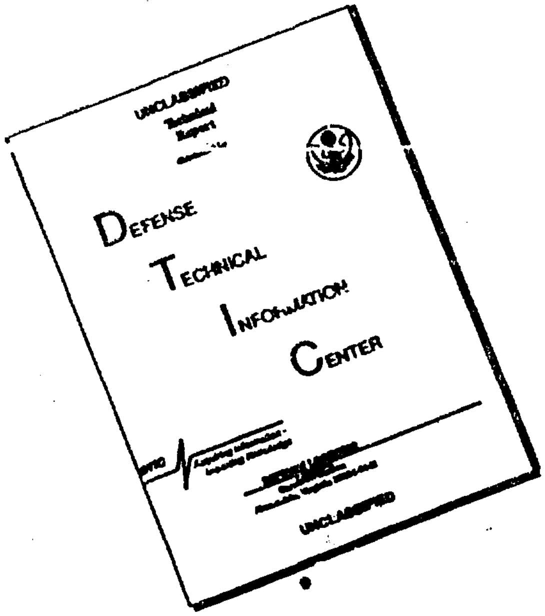
(Submitted for publication in the Journal of Chemical Physics)

Reproduction in whole or in part is permitted for any purpose of the United States Government. Distribution of this document is unlimited.

October, 1968

Reproduced by the
CLEARINGHOUSE
for Federal Scientific & Technical
Information Springfield Va 22151

20



UNCLASSIFIED

Technical Report

DEFENSE TECHNICAL INFORMATION CENTER

UNCLASSIFIED

THE RAMAN SPECTRUM OF CRYSTALLINE LITHIUM NITRATE

by

R. E. Miller, R. R. Getty, K. L. Treuil and G. E. Leroi

Department of Chemistry, Michigan State University, East Lansing, Michigan 48823

(Received October 1968)

ABSTRACT

Polarized Raman spectra of an anhydrous single crystal of $LiNO_3$ have been obtained under optimum experimental conditions. The internal vibrations of the nitrate ion are observed as follows: $\nu_4(E_g) = 735._4$, $\nu_1(A_{1g}) = 1071._0$ and $\nu_3(E_g) = 1384._6$ cm^{-1}; these frequencies are essentially independent of the cation in the host lattice. The two Raman-active (E_g) lattice modes have been located and assigned to primarily translational ($124._4$ cm^{-1}) and librational ($237._2$ cm^{-1}) motions. No indication of coupling between these vibrations is observed. The frequencies of the external vibrations relative to those of $NaNO_3$ demonstrate that they are dependent on the volume of the crystalline unit cell. Except for small intensity contributions in some orientations which are probably due to depolarization effects in the birefringent crystal, the polarizability activities of both the internal and external modes follow the expected symmetry selection rules.

INTRODUCTION

Raman scattering has been observed from $LiNO_3$ in the solid,[1] melt,[2] and solution,[3] and the results discussed by several authors.[1-5] However, there have been no reported attempts to conduct a polarization study of an anhydrous single crystal, or to locate the Raman-active external lattice frequencies of the solid. Lithium nitrate crystallizes in the calcite structure (D_{3d}^6 space group) with the nitrate ions occupying D_3 sites and the lithium ions S_6 sites.[6] Thus five Raman-active fundamental vibrations are expected.[7] Three are attributable to internal vibrations of the nitrate ion: $\nu_1(A_{1g})$, $\nu_3(E_g)$, and $\nu_4(E_g)$; the previous results for these vibrations in the various phases of $LiNO_3$ have been summarized by Bues.[2] The remaining Raman fundamentals are E_g external (lattice) oscillations. The normal modes of the lattice vibrations were depicted in our previous work on $NaNO_3$;[8] for convenience they are reproduced in Fig. 1. Although one of the vibrations is translational in character and the other librational, since they have the same symmetry mixing is allowed. It would be interesting to know whether the nature of the cation affects the degree of mixing, which was found to be undetectable for sodium nitrate.[8]

The Raman frequencies for NO_3^- internal modes in the solid, melt, and solution for a series of alkali nitrates have been compared by Bues,[2] who interpreted the small shifts in the symmetric stretching frequency ν_1 (less than 4%) according to a "free volume" model. Even smaller frequency differences were noted for ν_3 and ν_4, and it was argued that these motions should be less sensitive to the packing of the environment. However, it was also shown that the internal frequencies in $LiNO_3$ are quite dependent on the amount of water present and the physical state of the sample.[2,3] If the solid samples used in the early studies were not of the highest quality, for example because of the extremely hygroscopic nature of lithium nitrate, incorrect frequencies would have been observed for the crystal. This would significantly affect the hypothesis formulated to explain the small frequency shifts in the NO_3^- vibrations with change in cation.

Anomalous polarization intensity ratios for the Raman bands of crystals with the calcite structure have been generally observed, and interpreted for $CaCO_3$[9] and $NaNO_3$[8] as being primarily due to depolarization of the incident and/or scattered light in the optically anisotropic crystals. Since the ratio of the molecular refractivity, a measure of birefrigence, is almost the same for sodium and lithium nitrates,[10] a careful polarization study of crystalline $LiNO_3$ should provide a test for this explanation.

Finally, in an interpretation of the infrared combination spectra of calcite and the alkali nitrates, Schroeder, Weir, and Lippincott[11] suggested that a torsional lattice vibration about the optic axis should exist with a fundamental frequency of 20-30 cm^{-1}. Although such a vibration should be Raman-inactive by symmetry, it was reported in early studies of calcite;[12,13] it was not observed in later investigations of $NaNO_3$[8] and $CaCO_3$.[9] Since measurements in the low frequency region were difficult due to scattered light and grating ghosts, it seemed worthwhile to confirm the absence of the torsional motion in the case of $LiNO_3$.

—— > In order to determine the external lattice vibration frequencies of $LiNO_3$ and to unambiguously establish the internal nitrate ion frequencies, as well as to study the effect of the alkali cation on these vibrations, the Raman spectrum of a large, anhydrous single crystal of lithium nitrate has been obtained. Using modern Raman instrumentation a complete polarization study has been made, and the available spectra region extended to within $10/cm^{-1}$ of the exciting radiation.

EXPERIMENTAL

The crystal used in this investigation was obtained from the Harshaw Chemical Company. Unfortunately, unlike $NaNO_3$, a clear, homogeneous single crystal of $LiNO_3$ can be grown only with some difficulty, and cannot be controllably cleaved. The sample received in our laboratory was a cube approximately 5mm on a side, polished to size from a larger ingot. The faces were mutually perpendicular within 1°, and the z-axis (optic axis) was normal to one of them. In order to facilitate orientation, the crystal was mounted in a W and W eucentric goniometer which had been placed in a small Plexiglass drybox. This ensured that the sample remained anhydrous; at no time was the crystal exposed to the room atmosphere.

The oriented single crystal was first irradiated using a Spectra-Physics Model 125 He-Ne laser emitting about 70 mW at 6328Å. The 90° scattered light was collected by appropriate optics, dispersed by a Spex Model 1400 double monochromator, and detected using a thermo-electrically cooled ITT FW-130 photomultiplier (S-20 response). The photomultiplier output signal was amplified with a Victoreen VTE-1 micro-microammeter, and displayed on a Moseley 7100B strip chart recorder.[14] The laser power was adequate to discern the general features and intensity patterns of the Raman spectrum. More detailed studies of each band were made using a Spectra-Physics Model 140 argon ion laser emitting about 600 mW at 4880Å and 700 mW at 5145Å as the excitation source.

In general, the spectra were obtained with the incident beam focused within the sample using a solid angle of less than 2°, and with the scattered light gathered using f/2 optics. Depending on the band being studied and the polarization conditions, spectral slit widths in the range 0.2 - 2 cm^{-1} were employed. The accuracy of the reported frequencies is within 0.5 cm^{-1}. All measurements were made at room temperature.

RESULTS AND DISCUSSION

As indicated in the third column of Table I, for a rhombohedral crystal with D_{3d} symmetry only four of the polarizability tensor derivatives are unique. According to the group theoretical analysis α_{xx} and α_{yy} are always related due to symmetry, as are α_{xz} and α_{yz}. Representative Raman spectra of crystalline $LiNO_3$ in the xx-, zz-, xy-, and xz-orientations are shown in Fig. 2. The polarization is specified by the commonly accepted notation[15] of the type x(yz)y, where the initial and final letters denote the direction of the incoming and observed light in the crystal coordinate system, and the letters in parenthesis indicate the polarization axes of the incident and scattered radiation. Thus in this example a measure of the α_{yz}-component of the polarizability tensor derivative would be obtained.

The observed frequencies, assignments, and relative intensities as a function of polarization are summarized in Table I. Theoretical considerations of the relative intensities have been developed by Bhagavantum[16] and Saksena.[17] Like the other crystals in its class, lithium nitrate is highly birefringent, and therefore anomalous depolarization effects, such as the presence of a given vibration in a polarized spectrum where it is theoretically forbidden, are to be expected. Fig. 2 shows that such small residual intensity is sometimes observed. This subject has been considered in the discussions of the Raman spectra of calcite[9] and sodium nitrate.[8] Furthermore, in the course of checking the polarized spectra using alternate incident and scattered light axes, it was observed that the relative intensities of the bands sometimes changed although the same tensor component was being observed. This effect is most striking for ν_1 in the α_{xy} polarization, which is shown in Fig. 3. Again the optical inhomogeneity of the $LiNO_3$ can account for this observation, as discussed in detail for the case of calcite by Porto, et al[9]

A. Internal Modes

The symmetric stretching vibration (ν_1) of the NO_3^- ion in crystalline $LiNO_3$ is observed at $1071._0$ cm^{-1}. This frequency is close to that observed[8] for $NaNO_3$ (ν_1 = 1068 cm^{-1}), but appreciably different from the value of 1086 cm^{-1} previously reported for solid $LiNO_3$,[1] which was used in the subsequent discussion of frequency trends among various alkali nitrates.[2-5] Detailed scans of the ν_1 region in the yy-polarization using the approximately 0.7 watt of power available in each of the argon ion laser lines at 4880 Å and 5145 Å showed the presence of a sharp band at 1050 ± 1 cm^{-1} with an intensity about 1/200 of the strong peak at 1071 cm^{-1}. The relative intensity suggests that the weak band at 1050 cm^{-1} is due to the ν_1 vibration of a nitrate ion containing one oxygen -18 atom.[18] Calculation of the isotopic frequency assuming a valence force field and a planar geometry for the XYZ_2 molecule[19] gives excellent agreement with the observed value, thus confirming this assignment.

The antisymmetric stretching vibration (ν_3) is located at $1384._6$ cm^{-1}, a value slightly lower than the previously reported[1] frequency of 1391 cm^{-1}, but essentially identical to ν_3 of the nitrate ion in $NaNO_3$, which is observed[8] at 1385 cm^{-1}. Careful examination of this spectral region using argon ion excitation revealed a weak band at 1354 cm^{-1}. Isotope shift calculations suggest the assignment of this band to ν_3 of $^{15}NO_3^-$ ions, present in 0.37% natural abundance.

The remaining internal fundamental, the in-plane bending motion, ν_4 is observed at $735._4$ cm^{-1}. This frequency is slightly higher than that listed by Bues[1] (728 cm^{-1}), and also higher than the value observed[8] for NaNO$_3$ (724 cm^{-1}). The frequency shift of 1-1/2% in this vibration upon change in cation, although the largest for the internal modes, confirms that the bonding in the nitrate ion is essentially unaffected by the packing in the crystal. None of the fundamentals show frequency shifts of sufficiently significant magnitude to be correlated with the available "free volume" in the various respective crystal lattices.

The depolarization behavior exhibited by the internal vibrations, shown in Fig. 2, closely follows expectation. For the E_g modes, ν_3 and ν_4, the group theoretical selection rules predict that the allowed polarizability components are $\alpha_{xx} = -\alpha_{yy} = \alpha_{xy}$ and $\alpha_{xz} = \alpha_{yz}$. However, it is expected that the intensity in the xz- and yz-spectra will be relatively weak,[17] since in the limit of an isolated nitrate ion (D_{3h} symmetry) the out-of-plane polarizability derivative components approach zero during the in-plane vibrations. The absence of ν_3 and ν_4 in the x(zy)z-spectrum of Fig. 2 demonstrates that there is little interionic coupling in the LiNO$_3$ lattice. It is satisfying to note that the intensities of these bands in the yy- and xy-spectra are indeed quite similar.

For the A_{1g} symmetric stretching vibration, ν_1, the only nonvanishing polarizability derivatives should be $\alpha_{xx} = \alpha_{yy}$ and α_{zz}. In addition, symmetry considerations suggest[17] that $\alpha_{yy}{}^2 > \alpha_{zz}{}^2$. The intensity ratio $(\alpha_{yy}{}^2/\alpha_{zz}{}^2)$ is approximately 10 for the 1071 cm^{-1} band of LiNO$_3$; the corresponding ratio is also 10 for NaNO$_3$,[8] and is about 5 for CaCO$_3$.[9]

The ν_1 band also appears weakly in the x(yx)y-spectrum of Fig. 2, and is barely discernible in the x(zy)z orientation; in both cases it should be absent. Furthermore, as shown in Fig. 3, the relative intensity of the 1071 cm^{-1} band in the xy-polarization is much higher when the crystal is rotated so that light either enters or is gathered along the crystallographic z-axis. This striking orientation dependence is clearly due to the particular properties of the $LiNO_3$ crystal, and not to an inherent breakdown of symmetry selection rules. Indeed, such behavior is expected for highly birefringent crystals, if either the incident or scattered light is convergent. This effect has been discussed in detail by Porto, Giordmaine, and Damen,[9] and is also observed in calcite[20] and sodium nitrate.[8] If the incident polarized light is not extremely well collimated and colinear with the intended crystalline axis interference between the ordinary and extraordinary components of other polarizations will contribute to the scattering. For example, in our z(yx)y spectrum depolarized z(xx)y light, where ν_1 is strongly allowed, would also be detected. Similarly, since the scattered radiation is collected over a finite solid angle, contributions from unwanted polarizations will also be measured. Thus depolarized scattering from x(yy)z will be contained in our x(yx)z-spectrum. The dependence of these effects on solid angle has been discussed by Porto, et al;[9] depolarization is important for divergence angles as small as 1°. In our experiments the half-angle of the focused incident light was about 0.5°, whereas the scattered radiation was collected over a cone with angle of approximately 16°. Thus the anomalous α_{xy} - intensity for ν_1 would be expected to be stronger in the x(yx)z-spectrum than in z(yx)y; this is borne out in Fig. 3. These interference effects are minimized in the x(yx)y geometry, since depolarization of the incident or scattered light gives rise to zx- or yz-polarizations, where the A_{1g} vibration is also forbidden. The weak appearance of ν_1 in the x(yx)y spectrum must therefore be attributed to crystalline imperfections or misalignment of the sample in the laser beam. Since the crystal orientation was adjusted to optimize the intensity expectations, it is likely that the unavoidable, natural imperfections in the $LiNO_3$ sample are responsible for most of the slight residual intensity

The Raman spectra shown in Figs. 2 and 3 were obtained with the He-Ne laser. The higher power Ar^+ laser was also used, and the spectra were again of excellent quality. The higher scattering intensity permitted narrower slits to be used, but no new fine structure was thus revealed. However, when slits comparable to those in the He-Ne experiments were employed, giving scattering due to the internal fundamentals far above the normal intensity scale, new, weak spectral features were observed. In addition to the isotopic bands mentioned above, several combination bands were observed. The peak located at 1675 ± 1 cm^{-1} is assigned to $2\nu_2$; thus the out-of-plane NO_3^- bend, ν_2, which is infrared-active only, should occur at about 840 cm^{-1}. Again, comparison to crystalline $NaNO_3$, where $2\nu_2$ is observed[21] at 1677 cm^{-1}, confirms that the internal vibrations of the nitrate ion are relatively insensitive to the change in cation. The bands observed at 1460 ± 2, 2115 ± 3 and 2134 ± 2 cm^{-1} are assigned as $2\nu_4$, $\nu_3 + \nu_4$, and $2\nu_1$, respectively. In each case the effects of anharmonicity are quite small. Another very weak band is found at 2159 ± 3 cm^{-1}, which cannot be readily assigned. It should be noted that even under the intense argon-ion excitation no evidence of Raman scattering due to combinations between nitrate ion internal modes and the external (lattice) vibrations could be observed.

B. Lattice Modes

The low frequency region of the Raman spectrum of crystalline $LiNO_3$ was investigated to within about 10 cm^{-1} of the exciting line. No evidence of the postulated low-frequency torsion around the optic axis was noted, even with the higher power exciting lines. Two lattice vibrations are observed (Figs. 2, 3) at $124._4$ cm^{-1} and $237._2$ cm^{-1}, and are attributed to the expected translational and librational normal modes, in analogy to sodium nitrate.[8] These assignments are supported by the depolarization ratios of the two bands, which are summarized in Table I. Both vibrations are of E_g symmetry, where the allowed polarizability components are $\alpha_{xx} = -\alpha_{yy} = \alpha_{xy}$ and $\alpha_{xz} = \alpha_{yz}$. However, as Saksena[17] has shown, the in-plane translation should have $\alpha_{xz} = \alpha_{yz} \approx 0$ and the out-of-plane libration should have $\alpha_{xx} = -\alpha_{yy} = \alpha_{xy} \approx 0$, if the coupling between the vibrations is small. This is precisely the behavior shown in Figure 2, where the 124 cm^{-1} band (translation) is absent in the x(zy)z-spectrum, and the intensity of the 237 cm^{-1} band (libration) is smallest in the x(yy)z-spectrum. The latter intensity is even slightly lower than in the x(zz)y-spectrum where E_g bands are not allowed by symmetry. The residual zz-scattering probably arises from the birefringence effects discussed above. In each polarization the $LiNO_3$ spectra are superior to those previously reported[8] for $NaNO_3$; since the crystals have similar birefringence, it is likely that crystal imperfections contribute most to the additional anomalous intensity in sodium nitrate. In neither crystal was evidence of mixing between the lattice modes apparent.

Unlike the internal fundamentals, the lattice frequencies are highly dependent upon the cation. The librational frequency is 1.9 times that of the translation in each case, but the $LiNO_3$ vibrations are a factor of 1.27 higher in frequency than the corresponding $NaNO_3$ bands. As Figure 1 shows, this cannot be attributed to the lighter mass of the lithium ion, since the cation is not involved in either Raman-active normal mode. However, it is quite reasonable that these relatively large-amplitude low-frequency nitrate ion vibrations will be dependent on the unit cell volume. Indeed, the volume of the $NaNO_3$ unit cell is approximately 30% larger than that of $LiNO_3$;[6] thus the external NO_3^- vibrations will be more highly hindered in the $LiNO_3$ lattice, and would be expected to exhibit higher frequencies.

SUMMARY

The polarized Raman spectrum of an anhydrous single crystal of $LiNO_3$ has been obtained under optimum experimental conditions. The Raman-active fundamental vibrations of the nitrate ion in the lattice have been established as follows: $\nu_4(E_g) = 735._4$, $\nu_1(A_{1g}) = 1071._0$ and $\nu_3(E_g) = 1384._6$ cm^{-1}. Several bands due to isotopic molecules and combinations of fundamentals were observed. The frequencies of the nitrate ion internal vibrations are essentially independent of the cation in the host lattice; thus there is no evidence to support the "free volume" theory for the frequency shifts advanced by Bues.[2] For some of the bands minor depolarization anomalies occur in the form of residual intensity in polarization orientations where Raman scattering is not expected according to symmetry. Although much of this intensity can be accounted for by the highly birefringent nature of the LiNO crystal, it is clear that crystalline imperfections may also contribute.

This is demonstrated by the fact that $NaNO_3$, which has about the same birefringence, exhibited stronger anomalous depolarization[8] than $LiNO_3$. The predicted[9] sensitivity of the interference effects due to birefringence to the orientation of the crystalline sample is quite striking in the present example.

The Raman-active lattice modes of $LiNO_3$ have been obtained, and assigned to primarily translational ($124._4$ cm^{-1}) and librational ($237._2$ cm^{-1}) vibrations, respectively. No indication of coupling between these E_g vibrations is observed. There is no evidence of an additional low-frequency torsional lattice mode. The frequencies of the external vibrations of the nitrate ion do depend strongly on the host lattices. Although the ratio of the libration/translation frequency is about the same in $LiNO_3$ as in $NaNO_3$, the values of the frequencies themselves are about 30% higher. A shift in this direction is quite reasonable in light of the significantly smaller unit cell volume of $LiNO_3$.

ACKNOWLEDGMENTS

Partial support from the U. S. Office of Naval Research is gratefully acknowledged.

References

1. V. N. Thatte and A. S. Ganesan, Indian J. Physic. 8, 341(1934).
2. W. Bues, Z. Physik Chem., Neue Folge, 10, 1(1957).
3. J. P. Mathieu and H. Lounsbury, Discuss. Faraday Soc. 9, 196(1950).
4. O. Theimer, Monatsh. Chem. 81, 424(1950).
5. K. W. F. Kohlrausch, Raman-Spektren (Eucken-Wolff, Hand-und Jahrbuch der chem. Physik Bd. 9VI, Liepzig 1943).
6. R. W. G. Wyckoff, The Structure of Crystals, (Chemical Catalog Company, Inc. New York, 1931) 2nd Ed.
7. S. Bhagavantam and T. Venkatarayudu, Proc. Ind. Acad. Sci. A9, 224(1939).
8. D. L. Rousseau, R. E. Miller, and G. E. Leroi, J. Chem. Phys. 48, 3409(1968).
9. S. P. S. Porto, J. A. Giordmaine, and T. C. Damen, Phys. Rev. 147, 608(1966).
10. The Handbook of Chemistry and Physics, (The Chemical Rubber Co., Cleveland, Ohio, 1967) 35th Ed. Recent editions contain a misprint for $Si^{18}O_2$.
11. R. A. Schroeder, C. E. Weir, and E. R. Lippincott, J. Res. Natl. Bur. Stds. 66A, 407(1962).
12. J. H. Hibben, Raman Effect and its Chemical Applications (Reinhold Publ. Co., New York, 1939) p. 422.
13. D. Krishnamurti, Proc. Ind. Acad. Sci. 46A, 183(1957).
14. R. E. Miller, K. L. Treuil, R. R. Getty, and G. E. Leroi, Technical Report No. 4(29), "Redesign and Construction of a Laser Raman Spectrophotometer," May, 1968, DDC Accession No. 669797.
15. T. C. Damen, S. P. S. Porto, and S. B. Tell, Phys. Rev. 142, 570(1966).
16. S. Bhagavantam, Proc. Ind. Acad. Sci. A13, 543(1941).
17. B. D. Saksena, Proc. Ind. Acad. Sci. A11, 229(1940).
18. The natural abundance of ^{18}O is 0.204%.
19. G. Herzberg, Infrared and Raman Spectra of Polyatomic Molecules (D. Van Nostrand Co., Inc., Princeton, N. J., 1945).
20. See references cited in reference 9.
21. T. M. K. Nedungadi, Proc. Ind. Acad. Sci. A8, 397(1938).

TABLE I. **Raman frequency shifts and relative magnitudes of polarizability derivatives for crystalline $LiNO_3$.**

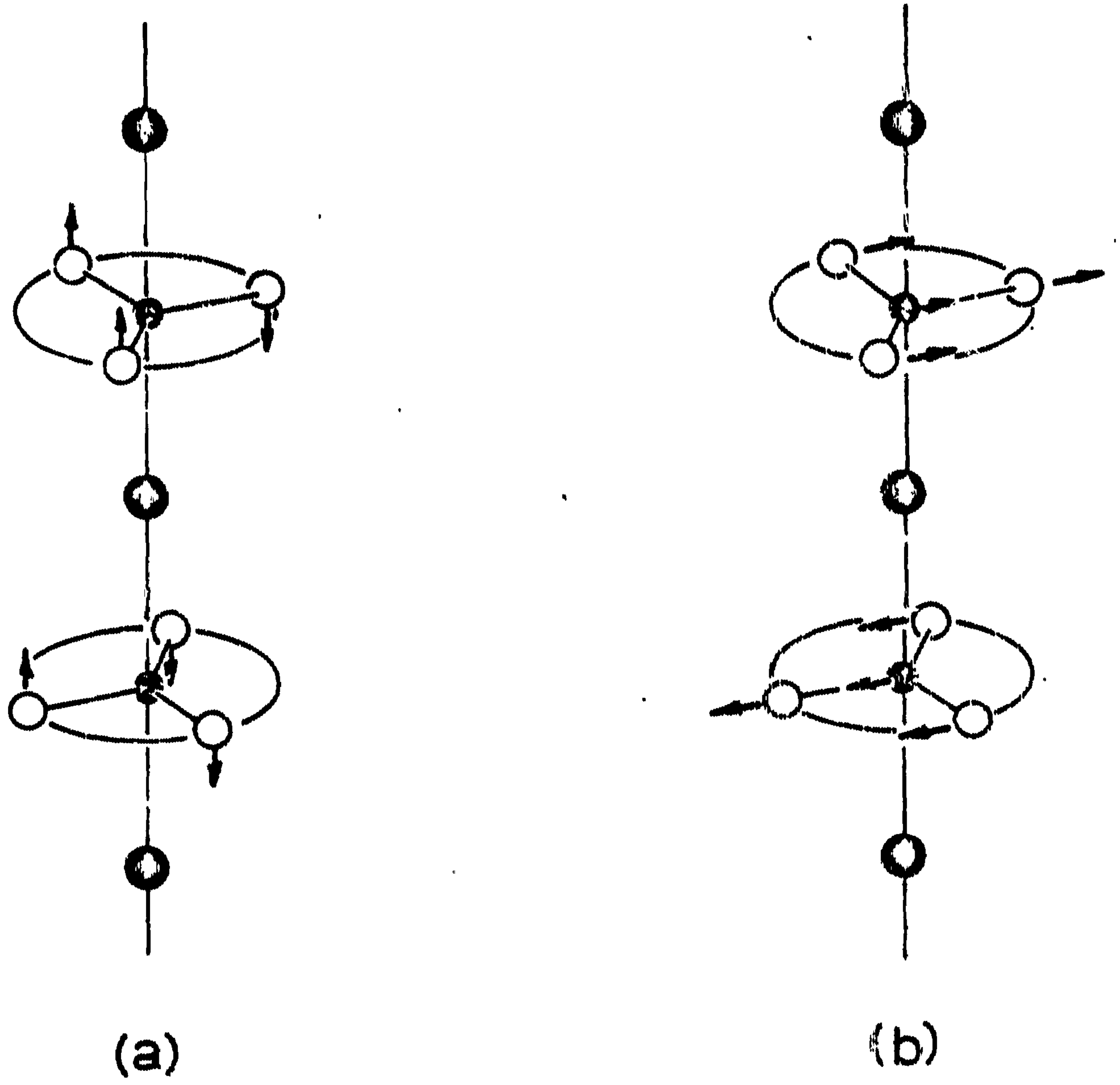
Symmetry Character	Frequency Shift (cm^{-1})	Allowed Polarizability Changes	Expected Relative Magnitude	Observations
$A_{1g}(\nu_1)$	1071.0	$\alpha_{xx} = \alpha_{yy}, \alpha_{zz}$	$\alpha_{xx}^2 > \alpha_{zz}^2$	$\alpha_{xx}^2 \approx 10\alpha_{zz}^2$
$E_g(\nu_3)$	1384.6	$\alpha_{xx} = -\alpha_{yy} = \alpha_{xy}$	$\alpha_{xx}^2 >> \alpha_{xz}^2$	$\alpha_{xz}^2 \approx 0$
$E_g(\nu_4)$	735.4	$\alpha_{xz} = \alpha_{yz}$		$\alpha_{xx}^2 >> \alpha_{xz}^2$
E_g(Lib)	237.2	$\alpha_{xx} = -\alpha_{yy} = \alpha_{xy}$	$\alpha_{xz}^2 >> \alpha_{xx}^2$	$\alpha_{xz}^2 \approx 40\alpha_{xx}^2$
		$\alpha_{xy} = \alpha_{yz}$	$\alpha_{xx}^2 = \alpha_{yy}^2 = \alpha_{xy}^2 = 0$	$\alpha_{xz}^2 \approx 40\alpha_{zz}^2$
E_g(Trans)	124.4	$\alpha_{xx} = -\alpha_{yy} = \alpha_{xy}$	$\alpha_{xx}^2 >> \alpha_{xz}^2$	$\alpha_{xz}^2 \approx 0$
		$\alpha_{xz} = \alpha_{yz}$	$\alpha_{xz}^2 = \alpha_{xy}^2 = 0$	$\alpha_{xx}^2 >> \alpha_{xz}^2$ $\alpha_{xx}^2 \approx \alpha_{xy}^2$

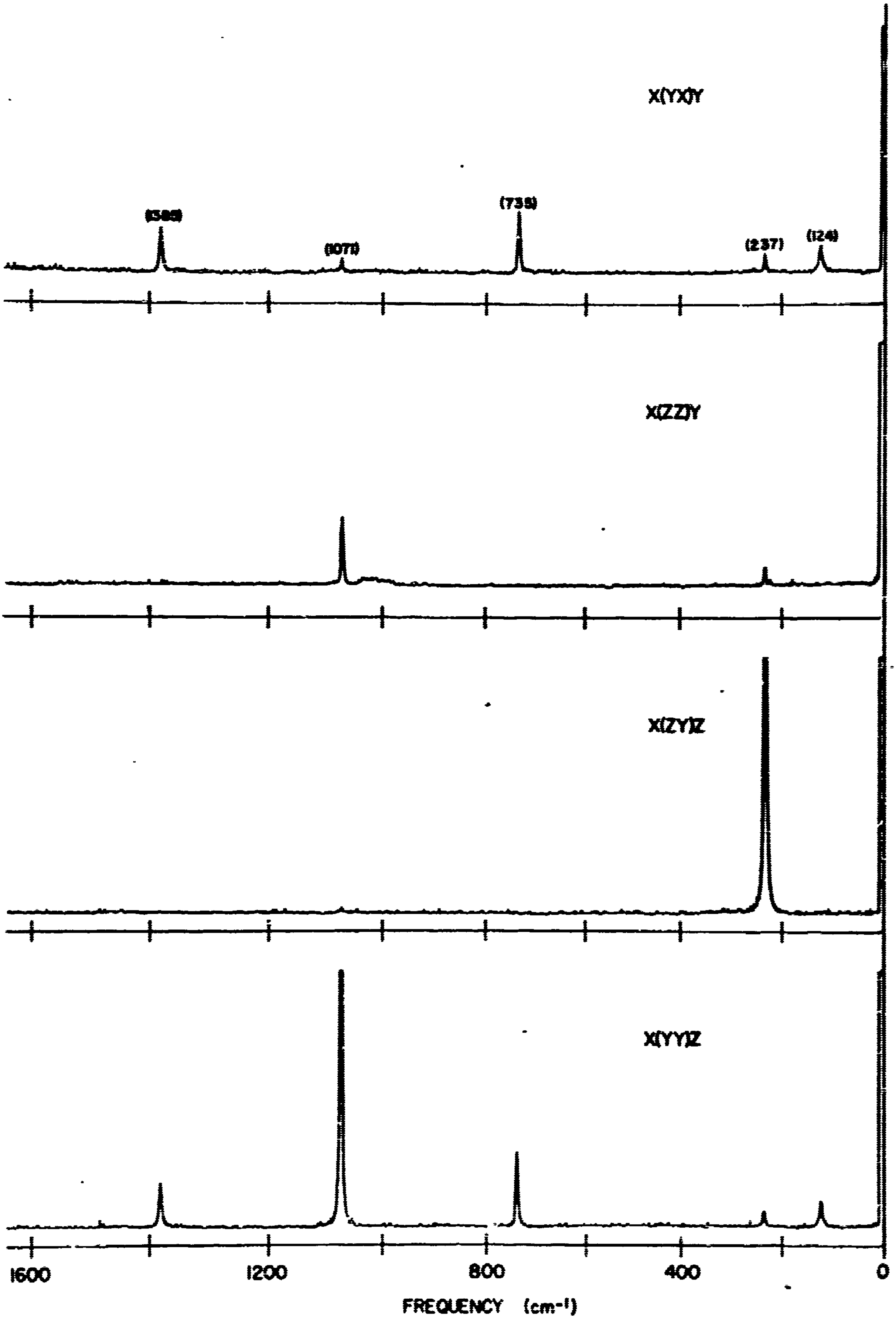
Figure Captions

Fig. 1. The Raman-active lattice modes of crystalline $LiNO_3$. a. Libration. b. Translation.

Fig. 2. Raman Spectra of $LiNO_3$ in the four unique polarization orientations.

Fig. 3. The Raman spectrum of $LiNO_3$ in the xy-polarization as a function of crystal orientation.


(a)
(b)


X(YX)Y
(1385)
(1071)
(735)
(237)
(124)
X(ZZ)Y
X(ZY)Z
X(YY)Z
1600
1200
800
400
0
FREQUENCY (cm-1)

Unclassified
Security Classification

DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY *(Corporate author)* Michigan State University Department of Chemistry	**2a. REPORT SECURITY CLASSIFICATION** Unclassified **2b. GROUP** ---------

3. REPORT TITLE

THE RAMAN SPECTRUM OF CRYSTALLINE LITHIUM NITRATE

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*

Technical Report

5. AUTHOR(S) *(Last name, first name, initial)*

Miller, R. E., Getty, R. R., Treuil, K. L., Leroi, G. E.

6. REPORT DATE October 1968	**7a. TOTAL NO. OF PAGES** 19	**7b. NO. OF REFS** 21

8a. CONTRACT OR GRANT NO. N00014-68-A-0109-0003 **b. PROJECT NO.** NR 014-203 **c.** **d.**	**9a. ORIGINATOR'S REPORT NUMBER(S)** Technical Report No. 8(33) **9b. OTHER REPORT NO(S)** *(Any other numbers that may be assigned this report)* ------------

10. AVAILABILITY/LIMITATION NOTICES

Distribution of this document is unlimited

11. SUPPLEMENTARY NOTES -------------	**12. SPONSORING MILITARY ACTIVITY** Office of Naval Research Physics Branch, Code 421

13. ABSTRACT

Polarized Raman spectra of an anhydrous single crystal of $LiNO_3$ ~~have-been~~ obtained under optimum experimental conditions. The internal vibrations of the nitrate ion ~~are~~ observed as follows: $\nu_4(E_g) = 735._4$, $\nu_1(A_{1g}) = 1071._0$ and $\nu_3(E_g) = 1384._6$ cm^{-1}; these frequencies are essentially independent of the cation in the host lattice. The two Raman-active (E_g) lattice modes have been located and assigned to primarily translational ($124._4$ cm^{-1}) and librational ($237._2$ cm^{-1}) motions. No indication of coupling between these vibrations is observed. The frequencies of the external vibrations relative to those of $NaNO_3$ demonstrate that they are dependent on the volume of the crystalline unit cell. Except for small intensity contributions in some orientations which are probably due to depolarization effects in the birefringent crystal, the polarizability activities of both the internal and external modes follow the expected symmetry selection rules.

DD FORM 1 JAN 64 1473

Unclassified
Security Classification

14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Raman Spectra Crystalline $LiNO_3$ Lattice Vibrations						

INSTRUCTIONS

1. ORIGINATING ACTIVITY: Enter the name and address of the contractor, subcontractor, grantee, Department of Defense activity or other organization *(corporate author)* issuing the report.

2a. REPORT SECURITY CLASSIFICATION: Enter the overall security classification of the report. Indicate whether "Restricted Data" is included. Marking is to be in accordance with appropriate security regulations.

2b. GROUP: Automatic downgrading is specified in DoD Directive 5200.10 and Armed Forces Industrial Manual. Enter the group number. Also, when applicable, show that optional markings have been used for Group 3 and Group 4 as authorized.

3. REPORT TITLE: Enter the complete report title in all capital letters. Titles in all cases should be unclassified. If a meaningful title cannot be selected without classification, show title classification in all capitals in parenthesis immediately following the title.

4. DESCRIPTIVE NOTES: If appropriate, enter the type of report, e.g., interim, progress, summary, annual, or final. Give the inclusive dates when a specific reporting period is covered.

5. AUTHOR(S): Enter the name(s) of author(s) as shown on or in the report. Enter last name, first name, middle initial. If military, show rank and branch of service. The name of the principal author is an absolute minimum requirement.

6. REPORT DATE: Enter the date of the report as day, month, year; or month, year. If more than one date appears on the report, use date of publication.

7a. TOTAL NUMBER OF PAGES: The total page count should follow normal pagination procedures, i.e., enter the number of pages containing information.

7b. NUMBER OF REFERENCES: Enter the total number of references cited in the report.

8a. CONTRACT OR GRANT NUMBER: If appropriate, enter the applicable number of the contract or grant under which the report was written.

8b, 8c, & 8d. PROJECT NUMBER: Enter the appropriate military department identification, such as project number, subproject number, system numbers, task number, etc.

9a. ORIGINATOR'S REPORT NUMBER(S): Enter the official report number by which the document will be identified and controlled by the originating activity. This number must be unique to this report.

9b. OTHER REPORT NUMBER(S): If the report has been assigned any other report numbers *(either by the originator or by the sponsor)*, also enter this number(s).

10. AVAILABILITY/LIMITATION NOTICES: Enter any limitations on further dissemination of the report, other than those imposed by security classification, using standard statements such as:

(1) "Qualified requesters may obtain copies of this report from DDC."

(2) "Foreign announcement and dissemination of this report by DDC is not authorized."

(3) "U. S. Government agencies may obtain copies of this report directly from DDC. Other qualified DDC users shall request through
_______________ ."

(4) "U. S. military agencies may obtain copies of this report directly from DDC. Other qualified users shall request through
_______________ ."

(5) "All distribution of this report is controlled. Qualified DDC users shall request through
_______________ ."

If the report has been furnished to the Office of Technical Services, Department of Commerce, for sale to the public, indicate this fact and enter the price, if known.

11. SUPPLEMENTARY NOTES: Use for additional explanatory notes.

12. SPONSORING MILITARY ACTIVITY: Enter the name of the departmental project office or laboratory sponsoring *(paying for)* the research and development. Include address.

13. ABSTRACT: Enter an abstract giving a brief and factual summary of the document indicative of the report, even though it may also appear elsewhere in the body of the technical report. If additional space is required, a continuation sheet shall be attached.

It is highly desirable that the abstract of classified reports be unclassified. Each paragraph of the abstract shall end with an indication of the military security classification of the information in the paragraph, represented as *(TS), (S), (C), or (U)*.

There is no limitation on the length of the abstract. However, the suggested length is from 150 to 225 words.

14. KEY WORDS: Key words are technically meaningful terms or short phrases that characterize a report and may be used as index entries for cataloging the report. Key words must be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical context. The assignment of links, roles, and weights is optional.