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Group-theoretical selection rules and experimental determination of lattice modes in $NaNO_3$ via inelastic neutron scattering

S. F. Trevino* and H. Prask*

Feltman Research Laboratory, Picatinny Arsenal, Dover, New Jersey 07801
and Institute for Materials Research, National Bureau of Standards, Washington, D.C. 20234

R. C. Casella

Institute for Materials Research, National Bureau of Standards, Washington, D.C. 20234

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The general group-theoretical selection rules of Casella and Trevino for characterizing the harmonic vibrations of molecular crystals within the rigid-molecule model via inelastic neutron scattering are applied to $NaNO_3$. For a given reciprocal-lattice vector the experimental resonances are classified not only according to the irreducible representation to which the eigenmode belongs, but also as to whether the interaction proceeds via the translational or rotational character of the mode (or both). The structure functions (i.e., sums of structure factors) belonging to each representation at Γ and Z and along Λ in the Brillouin zone are calculated explicitly. The results of experimental measurements at Γ are presented and compared with theory. In particular, we conclude that the resonances at 120 and 175 cm^{-1} are both to be associated with A_{2g} modes of mixed translational-rotational character. At the (0, 0, 15) reciprocal-lattice point both are observed via their translational component and at (0, 2, 1) via their rotational part. These assignments differ from earlier ones made prior to development of the selection rules and moreover contradict the assignment of the 22-cm^{-1} mode to A_{2g} by Rao *et al.*, based upon their Raman measurements. A search was made for the 22-cm^{-1} mode at the (0, 2, 1) point, but none was found.

I. INTRODUCTION

In recent years, the study of phonon modes in molecular crystals by the technique of coherent inelastic neutron scattering has increased substantially. In these studies, a principal difficulty which must be overcome is that of associating the observed resonances with specific phonons. One method which has been employed is the rather laborious one of constructing a model for the lattice dynamics by postulating a force field. Using the model, one obtains the eigenvectors corresponding to the phonons for a given reduced wave vector and then calculates the structure factor. An alternate method developed by Elliott and Thorpe[1] uses group-theoretical techniques to calculate the structure function for modes belonging to a given irreducible representation of the group of the wave vector. The structure function is the sum of the structure factors for all modes belonging to a given irreducible representation. The technique treats the atoms in the primitive cell as individual particles. We have recently extended their work to apply to a class of models within which rigid molecular groups undergo translational vibrations of the center of mass and rotational vibrations about the center of mass.[2] The technique allows the separation of the structure function for modes belonging to a given irreducible representation into two additive terms F^T and F^R corresponding, respectively, to motions consisting of translations and motions consisting of rotations. This is not to say that a given phonon cannot consist of a combination of the two types of motion but rather that its observation via its translational character is governed by one structure function and its observation via its rotational character by another. The dependence of F^T and F^R on the reciprocal-lattice points used for the observation of the phonon is quite different so that it often happens that one or the other may be zero at a given reciprocal-lattice point. This enables an experimental determination of the degree to which a given phonon consists of a mixed mode. Moreover, knowledge of these selection rules as a function of reciprocal-lattice point aids greatly in choosing which lattice point to use in the measurements.

The purpose of the present work is to give a specific example of a set of selection rules for a molecular crystal and some experimental measurements for illustration.

In Sec. II we review, in broad outline, steps taken in the derivation of the selection rules. In particular, we present explicitly the expressions necessary for the calculation of the selection rules and discuss the significance of several factors. In Sec. III we give the details and results for the calculation of the selection rules for the crystal $NaNO_3$. In Sec. IV we present some experimental measurements with which to illustrate the application of these selection rules.

TABLE I. Positions of atoms and "molecules" in the unit cell of $NaNO_3$. X, Y, Z denote Cartesian coordinates ($c = 16.8290$ Å and $u = 1.241$ Å).

Molecule number	Atom number	Atom	X	Y	Z
1	1	Na	0	0	0
2	1	Na	0	0	$\frac{1}{2}c$
3	1	N	0	0	$\frac{1}{4}c$
3	2	O	$\frac{1}{2}\sqrt{3}u$	$-\frac{1}{2}u$	$\frac{1}{4}c$
3	3	O	0	u	$\frac{1}{4}c$
3	4	O	$-\frac{1}{2}\sqrt{3}u$	$-\frac{1}{2}u$	$\frac{1}{4}c$
4	1	N	0	0	$\frac{3}{4}c$
4	2	O	$-\frac{1}{2}\sqrt{3}u$	$\frac{1}{2}u$	$\frac{3}{4}c$
4	3	O	0	$-u$	$\frac{3}{4}c$
4	4	O	$\frac{1}{2}\sqrt{3}u$	$\frac{1}{2}u$	$\frac{3}{4}c$

II. SUMMARY OF THE THEORY

We briefly review here the development of the method by which the application of group-theoretical techniques leads to the formulation of selection rules for inelastic coherent neutron scattering by phonons.[2]

Our development is based upon the rigid-molecule model for the vibration of molecular crystals. The model assumes that, in the harmonic approximation, the motion of the molecules is described as translations of the centers of mass of the molecules plus rotations about the centers of mass. The model should be quite good for a large class of substances in which the internal vibrations are substantially higher in frequency than the external vibrations. Within the model, the displacement of individual atoms can be written as

$$\vec{u}(\vec{x}_{A,i}) = \vec{X}(\vec{x}_A) + \vec{\Theta}(\vec{x}_A) \times \vec{b}_{ni} \quad , \tag{1}$$

where $\vec{u}(\vec{x}_{A,i})$ is the displacement of the atom located at $\vec{x}_{A,i}$. A is a double index $(n, \vec{L})$ denoting molecule n in the unit cell $\vec{L}$ and i, the ith particle in the molecule. $\vec{X}(\vec{x}_A)$ is the displacement of the center of mass of the molecule at $\vec{x}_A$, $\vec{\Theta}(\vec{x}_A)$ is the rotation of the molecule at $\vec{x}_A$, and $\vec{b}_{ni}$ is the position of atom i in the molecule n with respect to the center of mass of the molecule. With respect to the coordinate system defined by the $\vec{X}$'s and $\vec{\Theta}$'s, one must construct a properly weighted system of coordinates for use in the description of the dynamics of the problem. Having solved this, the transformation properties of the coordinates approximate for the definition of the structure factor must be determined. Projection operators can then be constructed which will allow the calcula-

TABLE II. Symmetry operations of space group D_{3d}^6.

Seitz Notation	Matrix representation	Seitz Notation	Matrix representation
$\{E \mid 0\}$	$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$	$\{i \mid 0\}$	$\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$
$\{C_3^1 \mid 0\}$	$\begin{bmatrix} -\frac{1}{2} & -\frac{1}{2}\sqrt{3} & 0 \\ \frac{1}{2}\sqrt{3} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}$	$\{S_6^1 \mid 0\}$	$\begin{bmatrix} \frac{1}{2} & \frac{1}{2}\sqrt{3} & 0 \\ -\frac{1}{2}\sqrt{3} & \frac{1}{2} & 0 \\ 0 & 0 & -1 \end{bmatrix}$
$\{C_3^2 \mid 0\}$	$\begin{bmatrix} -\frac{1}{2} & \frac{1}{2}\sqrt{3} & 0 \\ -\frac{1}{2}\sqrt{3} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}$	$\{S_6^2 \mid 0\}$	$\begin{bmatrix} \frac{1}{2} & -\frac{1}{2}\sqrt{3} & 0 \\ \frac{1}{2}\sqrt{3} & \frac{1}{2} & 0 \\ 0 & 0 & -1 \end{bmatrix}$
$\{C_{2,1'} \mid v\}$	$\begin{bmatrix} -1 & 0 & 0 \\ 0 & +1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$	$\{\sigma_{v1} \mid v\}$	$\begin{bmatrix} +1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$
$\{C_{2,2'} \mid v\}$	$\begin{bmatrix} +\frac{1}{2} & -\frac{1}{2}\sqrt{3} & 0 \\ -\frac{1}{2}\sqrt{3} & -\frac{1}{2} & 0 \\ 0 & 0 & -1 \end{bmatrix}$	$\{\sigma_{v2} \mid v\}$	$\begin{bmatrix} -\frac{1}{2} & \frac{1}{2}\sqrt{3} & 0 \\ \frac{1}{2}\sqrt{3} & +\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}$
$\{C_{2,3'} \mid v\}$	$\begin{bmatrix} +\frac{1}{2} & \frac{1}{2}\sqrt{3} & 0 \\ \frac{1}{2}\sqrt{3} & -\frac{1}{2} & 0 \\ 0 & 0 & -1 \end{bmatrix}$	$\{\sigma_{v3} \mid v\}$	$\begin{bmatrix} -\frac{1}{2} & -\frac{1}{2}\sqrt{3} & 0 \\ -\frac{1}{2}\sqrt{3} & +\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}$

TABLE III. Character tables for the point groups of the wave vector $G_0^{\vec{q}}$.

Γ pt.

	E	$2C_3$	$3C_2$	i	$2S_6$	$3\sigma_v$	C_s
A_{1g}	1	1	1	1	1	1	0
A_{1u}	1	1	1	-1	-1	-1	1
A_{2g}	1	1	-1	1	1	-1	2
A_{2u}	1	1	-1	-1	-1	1	3
E_g	2	-1	0	2	-1	0	2
E_u	2	-1	0	-2	1	0	4

Λ line

	E	$3C_2$	σ_v	C_s
Λ_1	1	1	1	3
Λ_2	1	1	-1	3
Λ_3	2	-1	0	6

Z pt.

	E	$2C_3$	$3C_2$	i	S_6^1	S_6^2	$3\sigma_v$	C_s
Z_1	2	2	0	0	0	0	0	3
Z_2	2	-1	0	0	$-i\sqrt{3}$	$i\sqrt{3}$	0	3
Z_3	2	-1	0	0	$i\sqrt{3}$	$-i\sqrt{3}$	0	3

tion of the sum of the structure factors for modes belonging to a given irreducible representation. This sum consists of two terms;

$$F^{(r)}(\vec{k}) = F^{(r)}(\vec{k}\,|\,T) + F^{(r)}(\vec{k}\,|\,R) \quad , \tag{2}$$

where $F^{(r)}(\vec{k})$ is the structure function associated with irreducible representation r and momentum transfer $\vec{k}$ ($\vec{k} = \vec{K} + \vec{q}$, $\vec{K}$ being a reciprocal-lattice vector and $\vec{q}$ the reduced wave vector). $F^{(r)}(\vec{k}\,|\,T)$ is associated with translations of the molecular center of mass and $F^{(r)}(\vec{k}\,|\,R)$ is associated with rotation about the center of mass.[3] Having sketched the procedure for obtaining Eq. (2), we now omit all details (see Ref. 2) and simply present the expressions for $F^{(r)}(\vec{k}\,|\,T)$ and $F^{(r)}(\vec{k}\,|\,\vec{R})$ after defining further notation: α is the symmetry element (proper or improper rotation) in the group $G_0^{\vec{q}}$. ($G_0^{\vec{q}}$, of order h_0, is the point group associated with $G^{\vec{q}}$, the group of the wave vector $\vec{q}$.) $\vec{v}_\alpha$ is the fractional translation associated with α for nonsymorphic groups. $\chi_d^{(r)}(\alpha)$ is the character of irreducible representation r associated with element α of the point group of the wave vector. (r is of dimension l_r.) a_{ni} is the scattering length of the ith atom in the molecule n. $M(ni)$ represents the mass of the ith atom in molecule n. $\vec{\rho}_n$ is the vector to the center of mass of the nth molecule in the primitive cell. $\vec{b}_{ni}$ is the vector from the center of mass of the nth molecule to atom i in that molecule. $I_{\gamma\beta}(n)$ represents the moment-of-inertia tensor of the nth molecule with respect to a fixed Cartesian frame. We also define a rotation matrix $R_{\gamma\beta}(n)$, associated with molecule n, which diagonalizes $I_{\gamma\beta}$ and produces the principal moments of inertia $I(n, \lambda)$:

$$I(n,\lambda)\delta_{\lambda\omega} = R_{\beta\lambda}(n) I_{\beta\nu}(n) R_{\nu\omega}(ln) \quad . \tag{3}$$

Sums on repeated *subscripts*, e.g. β and ν in Eq. (3), are implied wherever they occur.

The structure factor associated with translation of the center of mass is defined in terms of a $\vec{k}$-dependent form factor $\bar{a}_n(\alpha^{-1}\vec{k})$ where

$$\bar{a}_n(\vec{k}) = \sum_i \left[a'_{ni}/M(n)\right] e^{-i\vec{k}\cdot\vec{b}_{ni}} \quad . \tag{4}$$

$M(n) = \sum_i M(ni)$ is the mass of molecule n and $a'_{ni} = a_{ni} \times$ (Debye-Waller factor). The rotational term in the structure factor contains a vector form factor $\vec{h}(n, \alpha^{-1}\vec{k})$, where

$$\vec{h}(n,\vec{k}) = \sum_i \mathrm{b}_{ni} \left[a'_{ni}/M(n)\right] e^{-i\mathrm{k}\cdot\mathrm{b}_{ni}} \quad . \tag{5}$$

We remark parenthetically that if we ignore the implicit $\vec{k}$ dependence of a'_{ni} introduced by the Debye-Waller factor, Eq. (5) can be written in the succinct form $\vec{h}(n,\vec{k}) = i\vec{\nabla}_k \bar{a}_n(\vec{k})$.[4] One can write both terms in Eq. (2) in the form

$$F^{(r)}(\vec{k}\,|\,\chi) = k_{\lambda_1} B_{\lambda_1\lambda_2}(\vec{k}, r\,|\,\chi) k_{\lambda_2}, \tag{6}$$

where χ takes the values T (translation) and R (rotation) and B can be expressed in terms of a matrix A as

$$B(\vec{k}, r\,|\,\chi) = \sum_n A(n, \vec{k}, r\,|\,\chi) A^\dagger(n, \vec{k}, r\,|\,\chi) \quad . \tag{7}$$

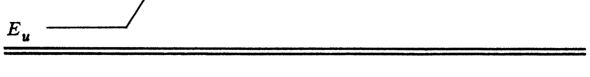
In the zone interior,

$$A_{\lambda\omega}(n, \vec{k}, r\,|\,T) = \frac{l_r}{h_0} \sum_\alpha \chi_d^{(r)*}(\alpha) \exp[-i\vec{K}\cdot(\alpha\vec{\rho}_n + \vec{v}_\alpha)] \times \bar{a}_n(\alpha^{-1}\vec{k})\alpha_{\lambda,\omega} \tag{8}$$

and

$$A_{\lambda\omega}(n, \vec{k}, r\,|\,R) = \frac{l_r}{h_0} \sum_\alpha \chi_d^{(r)*}(\alpha) \times \exp[-i\vec{K}\cdot(\alpha\vec{\rho}_n + \vec{v}_\alpha)] \times \alpha_{\lambda s}\epsilon_{stu} h_t(n, \alpha^{-1}\vec{k}) r_{u\omega}(n) \quad , \tag{9}$$

TABLE IV. Compatibility relations.



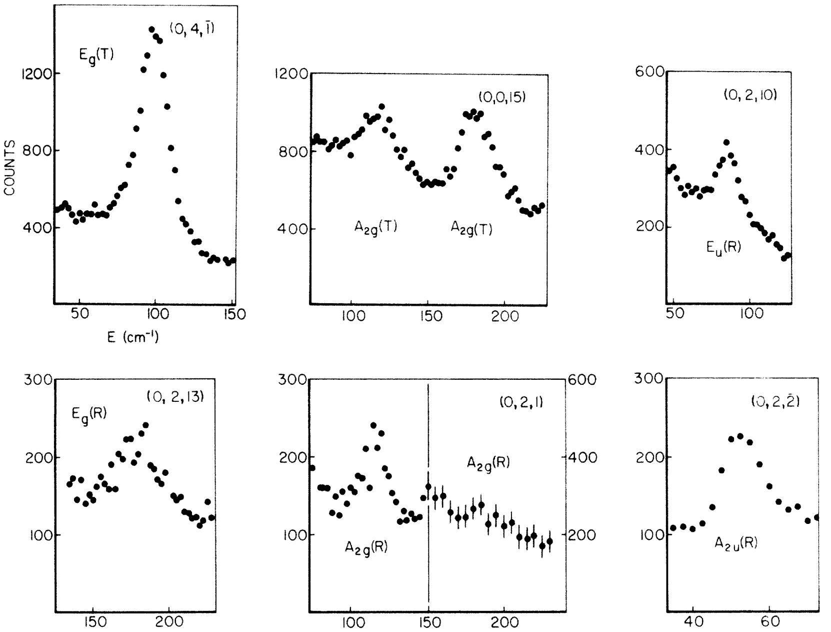


FIG. 1. Single-phonon resonances. Experimental counts vs E, the neutron-energy transfer to the lattice. Graphs are labeled by the reciprocal-lattice point associated with the momentum transfer and individual peaks by the theoretically assigned group representation. Error bars (statistical only) are omitted from all data except those associated with the (doubtful) $A_{2g}(R)$ resonance at 175 cm^{-1}. The curves are not (relatively) normalized.

where ϵ_{stu} is the Levi-Civita symbol and

$$r_{u\omega}(n)=\left(\frac{M(n)}{I(n\omega)}\right)^{1/2} R_{u\omega}(n) \quad . \tag{10}$$

At the zone boundary the character $\chi_d^{(r)}(\alpha)$ is to be replaced with a quantity involving the multiplier representation, $\tau^{(r)}$. That is,

$$\chi_d^{(r)}(\alpha)\rightarrow\chi_\tau^{(r)}\exp[i\vec{K}(\vec{q},\alpha)\cdot\vec{\rho}_n], \tag{11}$$

where

$$\vec{K}(\vec{q},\alpha)=\alpha^{-1}\vec{q}-\vec{q} \quad . \tag{12}$$

The characters $\chi_\tau^{(r)}(\alpha)$ for the multiplier representations have been tabulated by several sources.[5]

We have now written all the expressions required for the calculation of the structure factor.

III. SELECTION RULES FOR NaNO$_3$

Sodium nitrate crystallizes in the rhombohedral system. It belongs to space group D_{3d}^6 ($R\bar{3}c$) with two formula units of NaNO$_3$ per unit cell. The lattice can also be described by a pseudohexagonal structure. In what follows we will use the pseudohexagonal lattice notation to describe the reciprocal lattice. The sodium and nitrogen atoms lie on the unique threefold axis and the three oxygen atoms of each nitrate group are arranged symmetrically about the nitrogen atoms in planes normal to the threefold axis. Each oxygen atom lies on a twofold axis. Successive nitrate groups are rotated 60° relative to one another. The unique threefold axis is chosen as the hexagonal c axis. A complete classification of the lattice modes according to symmetry has been published previously.[6] Table I gives the atomic positions in Cartesian coordinates. The vectors reciprocal to the hexagonal direct lattice have Cartesian components,

$$\vec{h}^*=(a^*,0,0) \quad ,$$
$$\vec{k}^*=(\tfrac{1}{2}a^*,\tfrac{3}{2}a^*,0) \quad ,$$
$$\vec{l}^*=(0,0,c^*) \quad . \tag{13}$$

TABLE V. Neutron inelastic scattering selection rules. Values are given for the structure function $F^{(r)}(\vec{k}\,|\,\chi)$ where $\chi=T$ (translation) or R (rotation).

Reciprocal-lattice point			Γ point $q=(0,0,0)$										Λ line $q=(0,0,\mu)$						Z point $q=(0,0,\frac{3}{2}c^*)$					
			A_{1u}		A_{2g}		A_{2u}		E_g		E_u		Λ_1		Λ_2		Λ_3		Z_1		Z_2		Z_3	
			T	R	T	R	T	R	T	R	T	R	T	R	T	R	T	R	T	R	T	R	T	R
0	0	12	0	0	0	0	61	0	0	0	0	0	68	0	0	0	0	0	77	0	0	0	0	0
0	0	15	4	0	91	0	0	0	0	0	0	0	0	0	103	0	0	0	115	0	0	0	0	0
0	2	−2	0	0	0	0	0	6	0	0	2	1	0	6	0	0	2	0	0	3	1	0	1	0
0	2	1	0	0	0	6	0	0	0	0	1	0	0	0	0	6	2	1	1	3	1	1	1	1
0	2	13	3	0	1	6	0	0	0	33	1	0	0	0	5	6	2	37	16	7	2	24	2	14
0	4	−1	0	0	0	0	0	0	94	0	4	0	0	0	0	0	98	0	8	0	44	0	44	0
0	4	2	0	0	0	0	2	0	0	0	98	0	3	0	0	0	98	0	12	0	44	0	44	0
0	2	10	0	0	0	0	3	6	0	0	1	12	3	6	0	0	2	37	10	6	1	9	1	15

Along the c^* axis, the Brillouin-zone boundary occurs at

$$(0, 0, \tfrac{3}{2}c^*) \quad .$$

Table II gives the symmetry elements and fractional translations in the notation of Seitz and the corresponding Cartesian matrix representation. The fractional translation, in Cartesian coordinates, is

$$\vec{v} = (0, 0, \tfrac{1}{2}c) \quad . \tag{14}$$

Three high-symmetry values of $\vec{q}$ will be analyzed here, viz.,

$$q_1 = (0, 0, 0) \,, \quad \Gamma \text{ point}; \quad .$$
$$q_2 = (0, 0, \mu), \quad \Lambda \text{ line};$$
$$q_3 = (0, 0, \tfrac{3}{2}c^*) \,, \quad Z \text{ point}.$$

The character tables and modes breakdown are given in Table III. Table IV gives the compatibility relations for the points $\Gamma \rightarrow \Lambda \rightarrow Z$.

In Table III, if various symmetry elements belong to the same class, the generic symbol is used to label the class. Thus in all three groups, the character corresponding to the element labeled C_2 refers to the three elements $C_{2,1'}$, $C_{2,2'}$, and $C_{2,3'}$ and similarly for the other symmetry elements. Note that in the case of the Z point, the two S_6 elements do not belong to the same class and are thus listed separately in the character table.

In Table V we present values for the structure functions $F^{(r)}(k \mid \chi)$ for $\chi = T$ and R. Only a few reciprocal-lattice points were used in the present example but these suffice to illustrate the use of the selection rules. Thus, the translational modes of A_{2u} symmetry at Γ can be unambiguously measured at the (0, 0, 12) lattice point. Not all cases are as clear as the above, however. Note, for example, the selection rules corresponding to the point (0, 2, 13) and (0, 2, 1) which must be used in concert to distinguish between the E_g rotation, which should appear at (0, 2, 13) but not at (0, 2, 1), and the A_{2g} rotation, which should appear in both measurements. In general the selection rules are sufficiently varied such that the use of at most three reciprocal-lattice points is required for the assignment of a given mode to a symmetry species.

IV. EXPERIMENTAL RESULTS

The measurements presented here were made on a standard triple-axis spectrometer mounted on the 10-MW research reactor at the National Bureau of Standards. The single crystal of $NaNO_3$ had a volume of approximately 16 cm^3 and was grown by slowly lowering the temperature of a seeded saturated aqueous solution. Only phonons at the Γ point ($\vec{k} \simeq 0$) will be presented here. Figure 1 presents six scans which are used to identify most of the Γ-point phonons. Thus, the (0, 4, − 1) and (0, 2, 13) reciprocal-lattice points are used to verify the assignment of Rousseau *et al.*[7] of the E_g modes, viz., $E_g(T) \simeq 100$ cm^{-1} and $E_g(R) \simeq 175$ cm^{-1}.[8]

The two resonances observed at the (0, 0, 15) reciprocal-lattice point must be assigned either to $A_{1u}(T)$ or $A_{2g}(T)$. If both are present, then, from the relative size of the structure functions and the relative size of the observed resonances, we must assign the lower-energy mode (120 cm^{-1}) as $A_{1u}(T)$ and the higher mode (175 cm^{-1}) as the $A_{2g}(T)$. However, the observation of a mode at 120 cm^{-1} at the (0, 2, 1) point where only $A_{2g}(R)$ contributes raises another possibility.[8] Either the $A_{1u}(T)$ and $A_{2g}(R)$ modes are accidentially degenerate at the Γ point or the 120 cm^{-1} mode is an A_{2g} mode of mixed translation-rotation character and the $A_{1u}(T)$ mode is unobserved. In order to resolve this question, this mode was measured across the zone to the zone boundary along the c direction using both the (0, 0, 15) and (0, 2, 1) reciprocal-lattice points. The behavior of the branch with $\vec{k}$ was identical in both cases. Thus, either the modes are accidentally degenerate across the zone or it is the same mode. We prefer the interpretation that it is the same mode. Thus, the two modes observed at the (0, 0, 15) point are both A_{2g} with the higher-energy mode having the larger translational component and the lower-energy mode the larger rotational component. We would expect to see a very weak resonance at 175 cm^{-1} using the (0, 2, 1) reciprocal-lattice point due to the small rotational component of this mode. In fact, a very weak band has been found by careful measurements with various monochromator and analyzer combinations. The above assignment of the A_{2g} modes constitutes a revision of an earlier assignment[9] [120 cm^{-1} : $A_{1u}(T)$; 175 cm^{-1} : $A_{2g}(T)$] which was made prior to the development of the present selection rules which allow the identification of those reciprocal-lattice points for which the translational or rotational character of a given mode may be observed. In addition, the observation of the $A_{2g}(R)$ phonon at 120 cm^{-1} contradicts the assignment by Rao *et al.*[10] of this mode to 22 cm^{-1}. A careful search was conducted for a 22 cm^{-1} mode using the (0, 2, 1) point but none was found. We remark that *a priori* there exists the possibility that resonances observed at the (0, 2, 1) point are due to a Bragg-scattering event followed by inelastic scattering, thus leading to erroneous assignments. This possibility was eliminated by employing several different incident energies in the measurement.

The TO modes of rotational character belonging to the E_u and A_{2u} symmetry species are shown in the last two spectra.

V. CONCLUSION

In conclusion, the selection rules derived in Ref. 2 have proved to be very useful in analyzing the data from complex crystals, such as sodium nitrate, as illustrated here by explicit calculation and comparison with the experimental results presented.

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*Guest scientists at the National Bureau of Standards, Washington, D. C. 20234.

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[2] R. C. Casella and S. F. Trevino, Phys. Rev. B 6, 4533 (1972).

[3] The notation used here is different from that in Ref. 2 in that here T and R denote translational and rotational motion, respectively, whereas in Ref. 2 they were denoted by R and θ, respectively. Here, as in Ref. 2, we set $\hbar = 1$.

[4] This abbreviated form is given in Eq. (3) of Ref. 2 and throughout that paper. There and also here we in fact set the Debye-Waller factor equal to unity in carrying out explicit calculations. A thorough study of the renormalization effects introduced by higher-order many-phonon processes within the present context is presently underway and will be reported elsewhere. In Ref. 2 we also used the abbreviation $\bar{a}_{ni} = [\alpha'_{ni}/M(n)]$.

[5] O. V. Kovalev, *Irreducible Representations of Space Groups* (Gordon and Breach, New York, 1965); S. C. Miller and W. F. Love, *Tables of Irreducible Representations of Space Groups and Corepresentations of Magnetic Space Groups* (Pruett, Boulder, Colo., 1967). A word of caution regarding the use of the multiplier representations may be worthwhile. Note that the representations $\tau(\alpha)$ at $\vec{q}$ and at $\vec{q}+\vec{K}$ are not identical. Rather, $\tau(\alpha \mid \vec{q}+\vec{K}) = \exp(i\vec{K}\cdot\vec{v}_\alpha)\tau(\alpha \mid \vec{q})$, a result which follows directly from Eq. (6) of Ref. 2. (Here $\vec{K}$ connects any two zone faces.)

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