Zeitschrift für Kristallographie, Bd. 126, S. 397—402 (1968)

# The crystal structures and infra-red spectra of barium and strontium nitrates

By **C. J. H. Schutte**

Chemistry Department, University of South Africa, Pretoria, South Africa

(Received September 14, 1967 and in revised form December 4, 1967)

## Auszug

Es wird gezeigt, daß die Elementarzellen (Faktorgruppen) analyse von Ultrarot- und Raman-Spektren der isomorphen wasserfreien Nitrate von Barium und Strontium besser ist als die Puntlagen-Methode (site-group method) und daß sie die vor kurzem von Birnstock vorgeschlagene nicht-zentrosymmetrische Raumgruppe $T^4$—$P2_1^x3$ stützt. Eine Anordnung der Kombinations- und der Überschwingungen von $Ba(NO_3)_2$ und $Sr(NO_3)_2$ wird unter Annahme der Birnstockschen Raumgruppe dargelegt.

## Abstract

It is shown that the unit-cell (factor group) analysis of the infra-red and Raman spectra of the isomorphous anhydrous nitrates of barium and strontium is superior to that of the site-group method and that it is also in favour of the non-centrosymmetric space group $T^4$—$P2_1^x3$ which was recently proposed by Birnstock. An analysis of the combination and overtone modes of $Ba(NO_3)_2$ and $Sr(NO_3)_2$ is also given in terms of the Birnstock space group.

## Introduction

The vibrations of the $NO_3^-$ ions in the lattices of barium nitrate and the isomorphous strontium nitrate[1,2] have been extensively studied and correlated with two theoretical approximations which

---

[1] K. Buys and C. J. H. Schutte, The infra-red spectra of the anhydrous nitrates of some alkali and alkaline earth metals. Spectrochim. Acta **18** (1962) 307—313.

[2] C. J. H. Schutte, The influence of coupling on the $NO_3^-$-vibrations in $Ba(NO_3)_2$ and $Sr(NO_3)_2$ with special reference to the overtone and combination bands. Z. physik. Chem. [Neue Folge] **39** (1963) 241—248.

describe the patterns of vibration of molecules and ions in condensed phases[3,4]. The site-group approach of HALFORD[3] is sufficient to describe the vibrational behaviour of the nitrate ion in the alkali nitrates[1,5]. In the isomorphous nitrates $Ba(NO_3)_2$ and $Sr(NO_3)_2$ with $Z = 4$, the inter-ionic coupling between equivalent $NO_3^-$-vibrations complicates the infra-red and Raman spectra so that the superior unit-cell method[4] was used by SCHUTTE[2] to explain the experimentally observed spectra.

## The Vegard space group

In a series of x-ray investigations VEGARD and others[6] decided that the most probable space group of barium nitrate and the other isomorphous nitrates is $T_h^6$—$P2_1^x3i$ with $Z = 4$, in spite of the fact that the crystal morphology shows that these crystals do not have centres of inversion. Preliminary neutron-diffraction studies by HAMILTON[7] and LUTZ[8] could not resolve this difficulty, although it was clear that there are discrepancies between the calculated and experimental intensities (which could not be removed even by allowing the $NO_3^-$ group to oscillate or librate[9]). This space group was thus used by SCHUTTE[2] to determine the coupling between the vibrations of the eight equivalent nitrate ions in the unit cells of these

---

[3] R. S. HALFORD, Motions of molecules in condensed systems: I. Selection rules, relative intensities and orientation effects for Raman and infra-red spectra. J. Chem. Physics **14** (1946) 8—17.

[4] D. F. HORNIG, The vibrational spectra of molecules and complex ions in crystals, I. General theory. J. chem. Physics **16** (1948) 1063—1076.

[5] K. BUIJS and C. J. H. SCHUTTE, The infra-red spectra and structures $Li_2CO_3$ and anhydrous $Na_2CO_3$. Spectrochim. Acta **17** (1961) 927—932. In this paper the site-group theory[3] is applied to $D_{3h}$ ions.

[6] For a complete bibliography, see: R. BIRNSTOCK, Erneute Strukturbestimmung von Bariumnitrat mit Neutronenbeugung, Z. Kristallogr. **124** (1967) 310—334, as well as Ref.[2]

[7] W. HAMILTON, A neutron crystallographic study of lead nitrate. Acta Crystallog. **10** (1957) 103—107.

[8] G. LUTZ, Strukturuntersuchung von $Ba(NO_3)_2$ mit Neutronenbeugung. Z. Kristallogr. **114** (1960) 232—244.

[9] The librational frequencies for the $NO_3^-$ groups in single crystals of $Ba(NO_3)_2$, $Pb(NO_3)_2$ and $Sr(NO_3)_2$ were determined to be ca. 17 $cm^{-1}$ in each case, see R. A. SCHROEDER, C. E. WEIR and E. R. LIPPINCOTT, Lattice frequencies and rotational barriers for inorganic carbonates and nitrates from low temperature infra-red spectroscopy, J. Res. Nat. Bur. Standards (USA) **66** A (1962) 407—434.

nitrates. This coupling scheme relies heavily upon the centre of inversion which mutually excludes the coincidence of the infra-red and Raman spectra but allows an adequate explanation of the observed spectra so that a consistent assignment for the fundamentals could be made. In this analysis a few discrepancies remained, e.g. the presence of the centre of inversion dictated the assignment of nearly coincident infra-red and Raman frequencies to different modes, e.g. $\nu_{11}$ (1048 $cm^{-1}$ Raman) and $\nu_{14}$ (1046 $cm^{-1}$ infra-red).

## The Birnstock space group

In a recent neutron-diffraction analysis Birnstock[6], after an extensive series of experiments, came to the conclusion that there is no centre of inversion in these crystals and that the relevant space group is definitely $T^4$—$P\,2_1^x3$ with $Z = 4$. There are two non-interacting sets of four nitrate groups in the unit cell, each being perturbed by a different crystalline potential field having the symmetry $C_3$—3. In view of the very faint occurrence of the *hkl* lines which are forbidden by the reflection conditions of the space group $T_h^6$—$P\,2_1^x3\,i$, it can be concluded that the fields of symmetry $C_3$ which act upon the different sets of four nitrate groups must be of *comparable strength*, i.e. that they would perturb the vibrations of the two sets to the same extent. This means that the infra-red and Raman spectra of these two sets will be coincident and that the vibrational modes of the unit cell can be treated as if there are only $Z = 2$ molecules present; there is no vibrational interaction between non-equivalent sets of group in the same unit cell.

The site group $C_3$ does not allow the lifting of the $E$ degeneracy of the $\nu_3$ and $\nu_4$ modes as observed in the Raman spectra[1,2,10,11], showing the approximate nature of the site-group method.

If the unit cell is treated as a whole, the *four* equivalent $NO_3^-$ ions couple as shown in Table 1, using standard group-theory

---

[10] L. Couture and J. P. Mathieu, Experimental study of several cubic crystals. Compt. rend. **225** (1947) 1140—2. — J.-P. Mathieu, The anisotropy of the Raman effects in cubic crystals. J. Physique Radium **9** (1948) 83. — L. Couture, Vibrational spectra of single ionic crystals. Ann. Physique [12] **2** (1947) 5—94. — L. Couture and J.-P. Mathieu, Raman effect in cubic crystals. Ann. Physique [12] **3** (1948) 521—49.

[11] The weak band which occurs on the low-frequency side of the $\nu_2$-band of all flat $XO_3^-$ ions is due to the $N^{15}O_3^-$ species, and not to a lattice mode as assigned by Ref.[1].

methods[4,12]. The assignment of the fundamental modes given in Table 1 is more satisfactory than those given earlier[1,2,10,11] because the apparent anomaly between the Raman and infra-red spectra and the splitting of the $E$ modes under the perturbing potential of symmetry $C_3$ are adequately resolved.

Table 1. *The fundamental vibrations under $T^4$ unit cell*

| Vibrational mode and symmetry under site group $C_3$ | Vibrational mode and symmetry under unit-cell group $T^4$—$P2_1^x3$ | $Ba(NO_3)_2$ | | $Sr(NO_3)_2$ | |
|---|---|---|---|---|---|
| | | IR[1,2] | R[10,11] | IR[1,2] | R[10,11] |
| $\nu_1$ A | $\nu_{11}$ A R | 1046 $cm^{-1}$ | 1048 $cm^{-1}$ | 1055 $cm^{-1}$ | 1055 $cm^{-1}$ |
| | $\nu_{12}$ F R,IR | | | | |
| $\nu_2$ A | $\nu_{21}$ A R | 818 | (817)* | 817 | (812)* |
| | $\nu_{22}$ F R,IR | | | | |
| $\nu_3$ E | $\nu_{31}$ E R | — | 703 | — | 715 |
| | $\nu_{32}$ F R,IR | 729 | 731 | 741 | 736 |
| | $\nu_{33}$ F R,IR | | | | |
| $\nu_4$ E | $\nu_{41}$ E R | — | 1387 | — | 1403 |
| | $\nu_{42}$ F R,IR | 1354 | 1357 | 1364 | 1369 |
| | $\nu_{43}$ F R,IR | | | | |

* Computed frequency from $2\nu_{21}$ or $2\nu_2$ which occurs at 1635 $cm^{-1}$ in $Ba(NO_3)_2$ and at 1624 $cm^{-1}$ in $Sr(NO_3)_2$.

The factor-group approach predicts that the $\nu_3$ and $\nu_4$ vibrational degeneracy should be lifted in such a way that each mode gives rise to an $E$ mode which is active in the Raman effect and to two separate $F$ modes which are active in both infra-red and Raman. The $E$—$F$ splitting is observed in the Raman spectrum. The $F$—$F$ splitting, however, is not observed in both the Raman and infra-red spectra.

The $F$—$F$ splitting of the $\nu_3$ and $\nu_4$ bands in the infra-red spectra of these salts may be obscured by the broadness of these bands, i.e. the spectrometer traces the *envelope* of the two equally intense bands and does not resolve the splitting. The same argument applies for

---

[12] E. B. WILSON, JR., J. C. DECIUS and P. C. CROSS, Molecular vibration. McGraw-Hill Publishing Company Ltd., London, 1955. —F. MATOSSI, Gruppentheorie der Eigenschwingungen von Punktsystemen. Springer-Verlag, Berlin, 1961.

the Raman spectra of these compounds. Another factor which contributes to the broadness of the bands is the other group of four nitrate ions in the unit cell which absorbs at nearly the same frequencies. These splittings will probably be resolved if the sample is cooled down to very low temperatures if complicating phase changes do not occur simultaneously.

Table 2. *A comparison of the calculated infra-red overtones and combination bands for* $Ba(NO_3)_2$ *and* $Sr(NO_3)_2$ *with the observed spectra of Ref.*[2]

| Vibrational mode | $Ba(NO_3)_2$ | | $Sr(NO_3)_2$ | |
|---|---|---|---|---|
| | calc. | found | calc. | found |
| $\nu_{31}^2$ | 1406 $cm^{-1}$ | 1412 $cm^{-1}$ | 1430 $cm^{-1}$ | 1403 $cm^{-1}$ |
| $\nu_{31} + \nu_{32}$ | 1434 | 1413 | 1456 | 1441 |
| $\nu_{32}^2$ | 1458 | 1462 | 1482 | 1477 |
| $\nu_{12} + \nu_{32}$ | 1775 | 1780<br>1783 | 1791 | 1789<br>1794 |
| $\nu_{12} + \nu_{22}$ | 1866 | 1873 | 1872 | 1867 |
| $\nu_{31} + \nu_{41}$ | 2090 | 2080 | 2118 | 2100 |
| $\nu_{12}^2$ | 2094 | 2106 | 2110 | 2130 |
| $2\nu_{32} + \nu_{31}$ | 2135 | 2146 | 2171 | 2171 |
| $\nu_{22} + \nu_{41}$ | 2175 | 2182 | 2186 | 2200 |
| $\nu_{12} + \nu_{42}$ | 2400 | 2400 | 2419 | 2426 |
| $\nu_{12} + \nu_{41}$ | 2433 | 2423 | 2458 | 2445 |
| $\nu_{12} + \nu_{31}^2$ | 2452 | 2468 | 2485 | 2490 |
| $\nu_{12} + \nu_{32}^2$ | 2500 | 2503 | 2537 | 2520 |
| $\nu_{41} + \nu_{42}$ | 2741 | 2742 | 2767 | 2770 |
| $\nu_{41} + \nu_{32} + \nu_{31}$ | 2789 | 2775 | 2825 | 2810 |
| $\nu_{42} + \nu_{32}^2$ | 2816 | 2814 | 2836 | 2833 |
| | — | 2850* | — | — |
| | — | 3120 | — | ca 3150 |
| | | 3427 | — | 3460 |

* shoulder

The assignment of the overtone and combination bands is shown in Table 2; the agreement is good and the anharmonicity small[13]. The symmetry of each level can be easily determined using the methods of group theory[12].

---

[13] The effect of anharmonicity is usually to make overtone and combination frequencies appear at lower frequencies than expected. It is to be noted that the apparent positive anharmonicities of some of the bands in Table 2 are caused by the uncertainty in the positions of these overtone and combination bands—they are very very much weaker than the strong fundamentals, and hence difficult to detect (see References[1,2] for the relative intensities).

## Conclusion

The infra-red and Raman evidence is also in favour of the new $T^4$—$P2_1^x3$ unit cell recently proposed by BIRNSTOCK for the isomorphous salts $Ca(NO_3)_2$, $Ba(NO_3)_2$, $Sr(NO_3)_2$ and $Pb(NO_3)_2$. The vibrational analysis of the unit cell clearly shows that the splitting of the $E$ mode of the $C_3$ ion (i.e. a $D_{3h}$ ion occupying a $C_3$-crystalline site) is caused by the coupling between the vibrations of the four identical $NO_3^-$ ions per set, giving rise to the factor group $E$—$2F$ splitting observed in practice. The splitting caused by the vibrational coupling is not enough to lift the $2F$ accidental degeneracy in the $\nu_3$ and $\nu_4$ modes nor that the $A$—$F$ degeneracy of $\nu_1$.