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Infrared-Absorption Spectra of Solid Solutions: The Rotatory Motions of Nitrate and Nitrite Ions in Alkali Halides

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The infrared absorption spectra of nitrite and nitrate ions as impurities in potassium chloride single crystals show a fine structure that must be attributed to rotational motions of these ions. Evidence is found for the existence of different groups of nitrite ions that occupy different lattice sites and that are characterized by a varying degree of rotational freedom. No such evidence is found for the nitrate ion for which a librational type of motion is described.

INTRODUCTION

THE infrared absorption spectra of nitrite and nitrate ions, both readily dissolvable in the alkali halides, show many remarkable features. Hitherto, combinations of the internal modes of the complex ion with the lattice vibrations of the host lattice and with the translatory movements of the complex ions,[1] and also satellite bands caused by the clustering of complex ions in the host lattice, have been described.[2] Nitrite ions as well as nitrate ions, however, also show a fine structure on the internal vibration bands that must have its origin in the rotatory movements of these ions. Analogous cases have been described for (a) the NH_3^+ ion[3] where the observed spectra have been qualitatively interpreted as arising from a rotatory motion more complex than just free rotation or just rotation around one axis, (b) the CN^- ion[4] that librates at low temperatures but attains an almost free rotation at higher temperatures and (c) the NCO^- ion[5] that just librates. Recently, the results have been published of an extensive investigation of the rotational fine structure in the infrared spectra of the nitrite and nitrate ions in the alkali halides.[6] However, our experimental data, as well as our conclusions about the origin of the fine structure in the spectra of these ions, deviate at some points from the results given in that publication. Therefore, we present here our experiments and indicate possible connections with existing theories.

EXPERIMENTAL

Single crystals of KCl containing nitrate and nitrate ions were prepared from the melt and samples cut, in thicknesses varying from 1 to 70 mm. The samples were cooled with liquid helium in a conduction cryostat.

The actual temperature of the sample in the light beam is probably close to 25°K. Spectra were recorded with a Perkin–Elmer 112G with a resolution of about 0.4 cm⁻¹.

Nitrite

The frequency regions of the three fundamentals of the nitrite ion are shown in Fig. 1. The ν_3 region shows a very strong absorption at 1286 cm⁻¹ with a remarkable fine structure mainly at the low-frequency side, about 20 lines with a spacing in the order of 1 cm⁻¹. The relative intensities of the lines in the observed fine structure do not seem to be concentration dependent. However, the very intense absorption of the band at 1286 cm⁻¹ does not allow a quantitative comparison of the intensity of this band with the intensity of the fine structure. At slightly higher temperatures the fine structure disappears; at 70°K there is just one broad band.

The regions of the ν_1 at 1320 cm⁻¹ and the ν_2 at 800 cm⁻¹ show less fine structure.

Nitrate

At concentrations of 0.2% a fine structure with about 10 lines within 30 cm⁻¹ is observed around the ν_3 fundamental of the nitrate ion in a KCl crystal (Fig. 2). This fine structure is not concentration dependent, but again, the strong absorption of the band at 1395 cm⁻¹ does not allow comparison of the intensity of this band with the intensity of the fine structure. Samples of this concentration do not allow any observations of fine structure of the other vibrational transitions since all the other fundamental and combination bands of the nitrate ion have an intensity of at most 0.04 times the intensity of the ν_3 band and the preparation and handling of the samples so far sets a limit to the thickness of such samples.

On the other hand, at higher concentrations when the ν_3 band becomes too broad to allow the observation of fine structure close to the band center, many other bands, notable the combination bands $\nu_1+\nu_3$ and $2\nu_3$, show two different types of fine structure. In the first place there is a concentration-dependent structure that is caused by clusters of nitrate ions.[2] This structure

[1] R. Metselaar and J. van der Elsken, Phys. Rev. Letters 16, 349 (1966).

[2] J. van der Elsken and S. G. Kroon, J. Chem. Phys. 41, 3451 (1964).

[3] W. Vedder and D. F. Hornig, J. Chem. Phys. 35, 1560 (1961).

[4] (a) V. Narayanamurti, Phys. Rev. Letters 13, 693 (1965); (b) W. D. Seward and V. Narayanamurti, Phys. Rev. 148, 463 (1966).

[5] A. Maki and J. C. Decius, J. Chem. Phys. 31, 772 (1959).

[6] V. Narayanamurti, W. D. Seward, and R. O. Pohl, Phys. Rev. 148, 481 (1966).
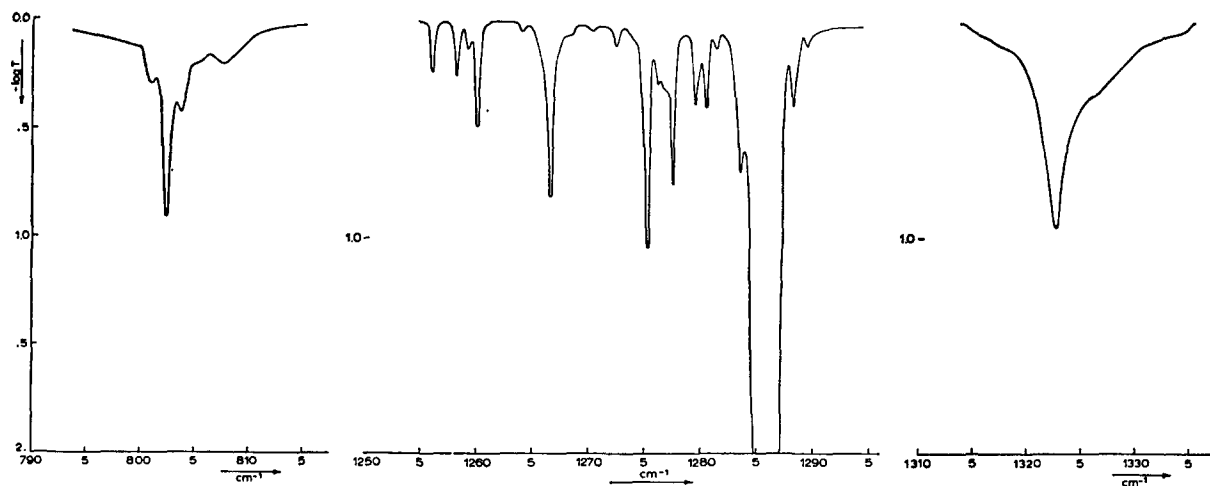
FIG. 1. The absorption spectrum of the NO_2^- ion in a KCl crystal at 25°K.

consists of one or two satellite lines within 6 cm^{-1} off the main peak. Secondly, there is in many cases a fine structure at greater distance, satellites on the low- as well as on the high-frequency side. The appearance of some of these satellites seems to be slightly temperature dependent; some do persist, however, at 77°K as well as at 25°K. A summary of the appearing sum and difference frequencies is given in Table I.

ROTATORY MOVEMENTS OF THE NO_2^- ION

In view of what has been remarked about the concentration independence of the fine structure it might be assumed that the entire fine structure of the ν_3 band between 1255 and 1285 cm^{-1} arises from one species only—this with the exception of two lines due to the presence of different isotopes of N and O. The
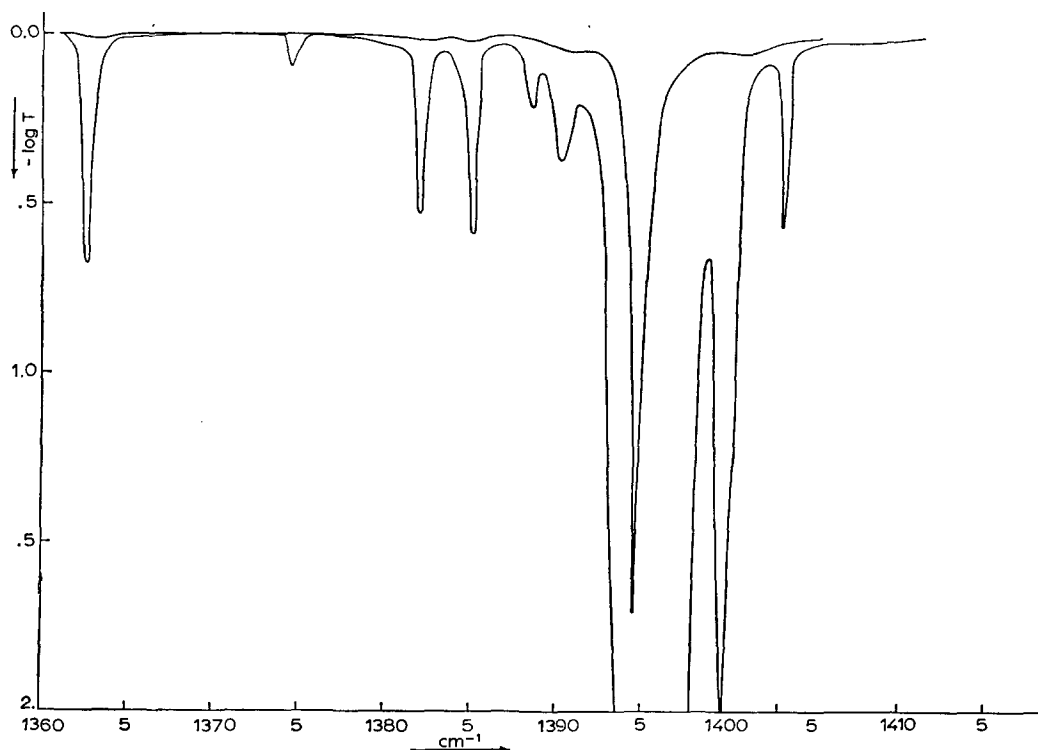

FIG. 2. The absorption spectrum of the NO_3^- ion in a KCl crystal at 25°K, two different crystal thicknesses.

TABLE I. The frequencies of the satellite lines relative to the main absorption band. NO_3^- ion in KCl.

Band	Temp	Observed satellite frequencies									
$2\nu_3$	25°		17	−23	28	37			83	108	128
$2\nu_3$	77°				28	38		53			
$\nu_1+\nu_3$	25°	−13	−18	−23	−29	−35					
$\nu_1+\nu_3$	77°	15		23	29		48	53			

natural abundance of ^{15}N is 0.36% and of ^{18}O, 0.20% The absorption of the $^{15}N^{16}O_2^-$ ion should be found[7] at about 1259 cm^{-1}. There are at least four peaks in the observed spectrum that lie close to this frequency. The $^{14}N^{16}O^{18}O^-$ ion, that should be present in a still smaller amount, should have an absorption peak at 1272 cm^{-1}. In the observed spectrum there is a small absorption feature at exactly this frequency that might very well have only 0.2% of the intensity of the peak at 1286 cm^{-1}.

The remaining fine structure as observed in the region of the ν_3 fundamental can not be caused by translatory combinations since these give rise to a spectrum of quite a different appearance.[1] Still, this structure must involve a great many closely spaced levels of which, according to the temperature dependence, a number can not be far from the ground state. A rotational type of movement of the ions must be the cause. But this leaves us with a number of possibilities, ranging from free rotation around three axes to a rotation around one or more axes with such a high hindering potential that the ion merely librates. Hindered rotations and librations are usually described in terms of cosine potentials $V=(V_0/2)(1-\cos n\alpha)$, where V_0 is the height of the potential hill separating the minima and n is the number of minima. However, in the case of a nitrite ion with symmetry C_{2v} on the site of a negative ion in an alkali halide, several cosine terms with different values of n and different values of V_0 would be needed to describe the potential for a rotation around one axis. The ν_3 vibration of the nitrite ion is of B_1 symmetry and has the transition moment parallel to the A axis of the molecule and therefore one might consider only rotations around the B and C axes as contributing to the structures of the ν_3 absorption band. But even this simplification leaves us with a potential expression with too many unknown parameters. Still, the complexity of the observed spectrum in the ν_3 region shows that it is in no way justifiable to make any further simplifications. The hindering potentials V_0 in the different terms may have values that all lie in the same order of magnitude.

The fact that such a large part of the total intensity is found in the one very intense absorption at 1286 cm^{-1} may be taken as an indication that the motion of the ion is a harmonic libration with high potential

barriers, but this is not in accordance with the great number of the other lines. Furthermore it would be inexplicable why most of the fine structure is found on the low-frequency side of this band.

We are left with only one limiting case to be tested quantitatively, free rotation of the ion around three axes. The nitrite ion is an almost symmetric-top molecule with rotational constants $A=4.22$ cm^{-1}, $B=0.45$ cm^{-1}, and $C=0.43$ cm^{-1}. Free rotation of such a molecule observed in combination with the vibrational transition of species B_1 gives rise according to the proper selection rules to a parallel band consisting of a strong central Q branch with P and R branches on both sides. At 4°K these P and R branches would only consist of a couple of lines within 5 cm^{-1} from the Q branch, at higher temperatures these branches might extend to greater distances from the Q branch but these would not give rise to a fine structure with separate peaks such as is found in the experimentally determined spectrum. However, if the symmetry of
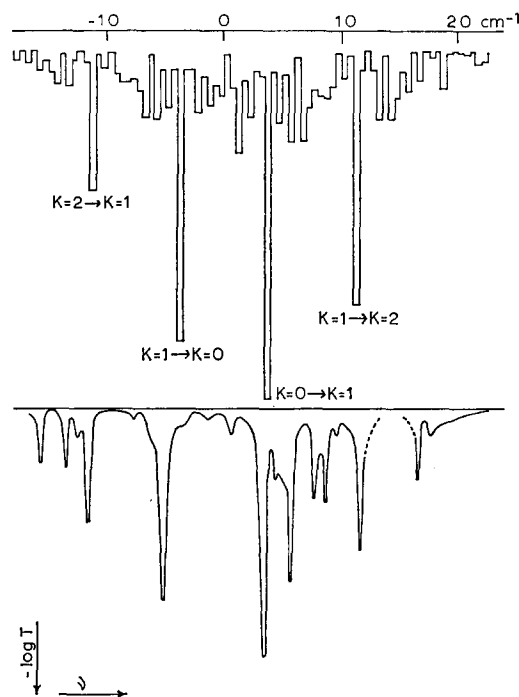

FIG. 3. The absorption spectrum of the NO_2^- ion in KCl, ν_3 region with the 1286 band subtracted, compared with the calculated spectrum for free rotation at 29°K.

[7] G. Herzberg, Molecular Spectra and Molecular Structure (D. Van Nostrand Co., Inc., New York, 1950), Vol. 2, p. 228.

the ion is lowered by an interaction with the lattice, the selection rules may be altered in such a way that a hybrid type band results. In such a band a series of equidistant lines with a spacing of $2(A-B) = 7.5$ cm^{-1} will be prominent. These $\Delta K = \pm 1$, $\Delta J = 0$ lines are clearly visible in the calculated perpendicular type band as shown in Fig. 3. There is a striking resemblance with a part of the observed spectrum, notably with the number and the positions of a series of strong lines grouped around a band center that must be situated at 1271 cm^{-1} to give the best fit. It seems justified to assume that at least a part of the ions occupy such positions in the lattice that the ions can perform a rotational motion being hindered by a potential that influences the symmetry of the ion sufficiently to alter the selction rules but does not affect the energy levels to an appreciable extent. Other positions that give less rotational freedom, might give rise to the remaining strong absorption band at 1286 cm^{-1}. This would explain why in the experimentally determined spectrum the fine structure is mainly found at the low-frequency side of the band at 1286 cm^{-1}. A 15-cm^{-1} difference of the band-center position for two different positions of the ion in the lattice is in accordance with reported band shifts for the nitrite ion in different alkali halide environments.[8]

NO$_3^-$ ION

At least part of the fine structure in the region of the ν_3 fundamental between 1360 and 1410 cm^{-1} must be caused by the rotatory movement of the NO$_3^-$ ion just as in the case of the NO$_2^-$ ion. An exception is the band at 1362 cm^{-1} that is caused by the ^{15}N^{16}O$_3^-$ ion. Furthermore, since the ν_3 vibration of the NO$_3^-$ ion is of species E', this mode may split under local symmetry groups lower than C_{3v}. But in view of the spectrum measured at low optical density (Fig. 2), it is not likely that this is actually causing any contribution to the structure. So the remainder of the fine structure must be of rotatory origin. The general appearance of the spectrum of the nitrate ion is, however, quite different from that of the nitrite ion. Much more of the total intensity is found in the main peak and the number of fine structure lines is considerably smaller. In addition there are the satellite lines that appear at distances up to a 100 cm^{-1} off the main peaks of the less intense combination bands like $2\nu_3$ and $\nu_1 + \nu_3$ that must be explained.

Of all the possible explanations for the fine structure in the vibration spectrum those based on a free rotation around one or more axes can be ruled out. The nitrate ion is a symmetric-top molecule with a rotational constant for rotation around the top axis $A = 0.24$ cm^{-1} and the other rotational constants $B = 0.48$ cm^{-1}. Free rotation of such a molecule in combination with a

transition between the ground state and a degenerate vibrational level like the ν_3 would give rise to a perpendicular band type with a spacing between the different Q branches in the order of 0 to 1 cm^{-1} depending on the values of the vibrational angular momentum. One can not expect to resolve these branches as different lines. The resulting spectrum at 25°K would consist of one strong central maximum formed by the Q branch with weak maxima on both sides due to the P and R branches, respectively. Although the interaction with the crystal field may have consequences for the symmetry of the distinct levels, depending on the exact site and orientation of the nitrate ion in the lattice, the over-all appearance of the absorption band will still be the same as long as the interaction is weak and does not influence the energy of the levels too much. Stronger interaction with the crystal field might ultimately result in a free rotation only around the top axis of the disk-shaped ion. This would give rise to a Gaussian-shaped band. at 25°K this band would have a half-width of about 10 cm^{-1}.

It is seen that neither of the models, free rotation nor free rotation around one axis, can account for separate maxima at 4 to 10 cm^{-1} from the main peak. A more complete model in which the nitrate ion rotates in a hindering potential field that can be developed into a series of cosine terms has the disadvantages as put forward in the consideration of the possibilities for the nitrite ion. However, in the case of the nitrate ion the potential function may be approximated by one simple cosine term for a hindered rotation around only the threefold axis. The rotation around the other axes may very well be hindered by a potential with much steeper and higher potential hills and in that case a separate consideration of the motion of the ion around the threefold axis is justifiable. If we assume a potential of the form $V(\alpha) = (V_0/2)(1-\cos 3\alpha)$, the energy levels, characterized by the quantum numbers K and L, can be found.[9,10] The transitions from the ground state to the vibrationally excited state, will now be governed by the selection rules $\Delta K = 0$, ± 1 and $\Delta L = \pm 1$. A series of lines results, of which the relative intensities are determined by the population of the levels of the initial states. The frequencies of the lines depend on the height of the barrier V_0. A choice in the order of 10 cm^{-1} will give rise to two prominent lines within 10 cm^{-1} from the band center together with an increasing number of additional lines that, with increasing temperature, makes the bandform rapidly approach the Gaussian shape of the free plane-rotor bands.

The spectrum calculated in this way can with no single choice of V_0 be brought in complete agreement

[8] J. A. A. Ketelaar, C. J. H. Schutte, and B. L. Schram, Spectrochim. Acta 13, 336 (1959).

[9] H. Eyring, J. Walter, and G. E. Kimball, *Quantum Chemistry* (John Wiley & Sons, Inc., New York, 1965).
[10] E. Jahnke, F. Emde, H. Lösch, *Tables of Higher Functions* (B. G. Teubner, Stuttgart, Germany, 1960).

with the actual spectrum; it is clear that a more complete knowledge of the hindering potential is needed. Nevertheless, it can be said that the general appearance of the fine structure within 10 cm^{-1} from the main peak is in qualitative agreement with the model of a libration around the A axis with the height of the potential barrier in the order of 10 cm^{-1}. Now, this leaves the satellite lines at a greater distance (up to 128 cm^{-1}) to be explained. The higher levels of the librator are given by $E = AK^2 \pm 2AK\zeta$ but since the vibrational angular momentum ζ of the ν_3 mode is not known, we can only estimate the energies of the resulting rotational levels. The augmentation of the spacing between these levels is such that transitions with $\Delta K = \pm 1$ might give rise to a series of almost equidistant lines of which the observed satellites might be the representatives. This explanation, however, demands the population of very high levels and since even the highest satellites have been observed at 25°K, we may conclude that these satellites do not arise from any rotatory motion around the A axis unless there would be a complete lack of equilibration between rotation and translation temperatures. Another explanation might be that these high-frequency satellites have their origin in a libration around the B axis of the ion. With a barrier of 170 cm^{-1}, $n = 2$, and $B = 0.48$ cm^{-1}, we calculated librational levels with 18-cm^{-1} spacing. Thus, the satellite lines at 18, 35, 54, 108, and 128 cm^{-1} could satisfactorily be explained as librational transitions L, $2L$, $3L$, $6L$, and $7L$, respectively. This leaves the possibility that the lower satellites, including those at 15, 23, and 29^{-1}, are associated with the movement around the A axis as well and only a more complete treatment of the hindering potential would give us the levels and transitions in this frequency region.

Meanwhile, the conclusion from the foregoing that the height of the barrier for rotation around the A axis is 10 cm^{-1} and for rotation around the B axis 170 cm^{-1} can be compared with the values found by Schroder, Weir, and Lippincott for a series of different nitrates.[11] These authors found satellite bands with the nitrate fundamentals and concluded that barriers, varying in height for the different nitrates between 160 and 200 cm^{-1}, hindered the rotation around the

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[11] R. A. Schroeder, C. E. Weir, and E. R. Lippincott, J. Chem. Phys. 36, 2803 (1962).

A axis. The question arises why the potential field hindering the rotation around the A axis of the nitrate ion would be so different for the ion in, for instance, a cubic nitrate crystal or for the ion in a cubic KCl host lattice. It might be that the satellites that are round in the spectra of the different nitrates, do also arise from the libration around the B axis and that the rotatory movement of the ion around the A axis just broadens the lines.

CONCLUSIONS

From the experimental data presented here it follows that the nitrite—as well as the nitrate ion—performs some rotational movement when these ions are present as impurities in alkali halide lattices. It follows also that some complications prevent at present a more quantitative evaluation of the perturbing potentials and the perturbed energy levels. It is very likely that the nitrite ion and possibly also the nitrate ion may occupy more than one position in the lattice leaving the ion more or less rotational freedom. Since the way of preparation of the samples may have great influence on the number and properties of the lattice defects, it is not surprising that our experimental results deviate at some points markedly from the results published by Narayanamurti, Seward, and Pohl. Beside the possibility that some differences are due to a difference in used resolving power, we have to count with the possibility that the relative number of different defects may vary and that this variation may also have a great influence on the relaxation time and hence on the temperature. A lack of temperature equilibrium may in turn have great consequences for the appearance of the spectra.

A study of the influence of these factors is in progress.