The infrared absorption spectra in the out-of-plane bending ($\nu_2$) region of potassium nitrate were studied for three phases. Several types of sampled were used: nujol mulls, fused samples, and $^{14}$N-$^{15}$ isotopic mixtures. The existence of three of the reported polymorphic phases was confirmed by the spectra. The transitions between phase II and phase I and between phase III and phase II were followed spectroscopically. The effects of dipole-dipole interactions between nearest neighbors were observed.

The out-of-plane bending mode ($\nu_2$) and the antisymmetric stretching mode ($\nu_3$) were studied for nitrate ion in various alkali halide lattices. The two expected effects were observed. These effects were the narrowing of bands due to complete absence of coupling, and a lowering of absorption frequencies when the lattice constant of the host matrix was increased.
THE INFRARED SPECTRUM OF THE NITRATE ION
IN VARIOUS CRYSTALLINE ENVIRONMENTS

by

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A THESIS
submitted to
OREGON STATE UNIVERSITY

in partial fulfillment of
the requirements for the
degree of
MASTER OF SCIENCE

June 1965
APPROVED:

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Date thesis is presented August 14, 1964

Typed by Velia DeLeon
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THE INFRARED SPECTRUM OF THE NITRATE ION
IN VARIOUS CRYSTALLINE ENVIRONMENTS

INTRODUCTION

Potassium nitrate may exist in four polymorphic forms; phases I and II are stable at atmospheric pressure, phase III is metastable at atmospheric pressure and stable under high pressures, and phase IV occurs only at high pressures (2, p. 599-605). Phase II (Figure 1) is the stable, room temperature form. It is orthorhombic, isomorphous with aragonite, and has the space group $D_{2h}^{16}$ with four molecules per unit cell (6). At about $125^\circ$-$130^\circ$ C. (23), phase II transforms to phase I (Figure 2), a trigonal structure similar to that of calcite, with space group $D_{3d}^5$, one molecule per unit cell, and with the nitrate ions freely rotating (16). Khanna et al. (14) have recently shown that this X-ray structure is satisfied by a disordering of the nitrate orientation with respect to an $S_6$ symmetry operation rather than free rotation. Phase III (Figure 3) results from cooling phase I and appears only under completely dry conditions (15). Its region of stability, when it occurs, is generally considered to be approximately $124^\circ$ C. to approximately $110^\circ$ C. (22). KNO$_3$ III is trigonal, space group $C_{3v}^5$ with one molecule per unit cell. The nitrate ion is displaced 6 percent above (or below) the center of the cell (1). Below $110^\circ$, KNO$_3$ II is again the stable phase. KNO$_3$ IV, the high pressure phase, is orthorhombic with 18

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1The only apparent difference between the groups $D_{3d}^5$ and $C_{3v}^5$ is that in $C_{3v}^5$ the nitrates are fixed rather than disordered in orientation.
Figure 1. Aragonite unit cell, $D_{16}^6$. KNO₃ II is isomorphous.

Figure 2. Calcite structure, $D_{3d}$. KNO₃ I is similar.

Figure 3. Rhombohedral unit cell of KNO₃ III (21).
molecules per unit cell, and is similar to the normal KNO$_3$ structure (9).

KNO$_3$ III has been shown to be ferroelectric (22). The first studies of the ferroelectricity were with fused samples of the salt. The ferroelectricity is thought to arise from the displacement of the nitrate group from the center of the rhombohedral unit cell. The nitrate group is believed to make a "jumping" motion between a negative and a positive displacement along the c-axis when the external electric field is reversed. The group is also supposed to exhibit hindered rotation about the c-axis as well as the oscillation along the axis. Such motion would imply that the ferroelectricity of KNO$_3$ III is of the order-disorder type (21).

Kracek (15, p. 227, 233) cites examples of phase III existing, under certain conditions, below the 110$^\circ$ C. transition temperature and at atmospheric pressure. These findings were later substantiated by X-ray diffraction analysis. The lifetime of KNO$_3$ III at room temperature and atmospheric pressure may now be extended to several weeks (20).

When nitrate ions are introduced as an impurity in another crystal lattice, perturbations due to nitrate-nitrate interactions are greatly reduced. The narrow bands of solid solutions are accounted for by absence of coupling between identical ions (7) (13) (17). In addition to noticeable narrowing of bands, solid solutions are characterized by shifts in fundamental frequencies; as the lattice parameter of the host matrix increases, the fundamental vibrations shift to lower frequency (3) (12) (13) (18).
This frequency shift may be explained in terms of the perturbing potential caused by the matrix ions. Various aspects of this perturbation have been studied for impurity ions in NaCl-type matrices (3) (13) (18). The observed frequency shifts may be accounted for by a change in force constant due to combinations of these effects: polarization of the matrix by induction such as dipole-induced dipole effects, dispersion effects, Coulombic effects, and short range repulsion effects between impurity ions and those of the host lattice. There seems to be disagreement as to which of these effects are small enough to be neglected, and which of these are the most important.
EXPERIMENTAL PROCEDURE

The nitrates used in this study were either analytical reagents containing the natural abundance ratio of isotopes, or were enriched in $^1^5\text{N}$ obtained as KNO$_3$ (95 percent $^1^5\text{N}$) from Isomet Corporation. Potassium nitrate containing the natural abundance ratio of isotopes (0.7 percent $^1^5\text{N}$) will be termed "shelf" KNO$_3$. Samples containing 24 percent and 50 percent $^1^5\text{N}$ were prepared from 95 percent KN$^{150}_3$ and appropriate amounts of "shelf" KNO$_3$. The mixture was dissolved in water and then evaporated to assure random $^1^5\text{N}$ distribution. The alkali halides used were spectrograde, with the exception of the NaBr which was analytical reagent.

The mull samples were prepared by grinding KNO$_3$ to fine powder with a mortar and pestle. The salt was then milled between two polished NaCl windows using 50 percent petroleum ether, 50 percent Nujol as emulsifying agent.

The fused samples (termed melt) were prepared by two methods. The first method was melting ground KNO$_3$ onto one or between two NaCl or KBr windows. The second method was spreading saturated KNO$_3$ solution on one window and allowing the water to evaporate. The second window was placed on top of the KNO$_3$ which was then melted. The second of these two methods produced samples with better transmission than the first; however, the use of the saturated solution resulted in exchange between sodium and potassium ions (when NaCl windows were used), forming Na$_2$NO$_3$ which complicated the spectra.
The solid solution samples were prepared by two methods and then compressed into pellets with a hydraulic press and an evacuable die. The first method used was freeze-drying\(^1\) nitrate-alkali halide solutions using about 0.001 gram nitrate per gram alkali halide. The second method was rapid precipitation of the salt mixture by adding chilled 100 percent ethanol to the saturated aqueous solution. Both these methods produced suitable solid solutions, but precipitation was used more extensively. In instances where samples were prepared from the same nitrate-alkali halide solutions by both freeze-drying and precipitation, absorption occurred at the same frequencies. Potassium nitrate was used in potassium halides, while sodium nitrate was used in sodium halides.

The equipment used for maintenance and control of high temperatures in the phase change studies was a "hot cell" adapted from a conventional low temperature cell (Figure 4), an oil immersion heater connected to a Variac, and a copper-constantan thermocouple with a Varian chart recorder. Pertinent parts of the cold cell labelled on the photograph are: (1) Sample (mull or melt) between NaCl or KBr plates held in a copper block, (2) NaCl windows, (3) insertion for oil bath, (4) opening for unit containing thermocouple leads, (5) joint for connection to diffusion pump.

After samples in which phase changes were to be studied were placed in the cell, the system was evacuated to approximately $10^{-3}$

\(^{1}\)A nearly saturated solution of the salt mixture was frozen in a dry ice-acetone bath. Water was sublimed from the frozen mixture by use of a vacuum pump and liquid nitrogen cold trap.
Figure 4. Cell used in phase change studies.
millimeters. A spectrum was taken at room temperature, and then the oil bath was slowly heated, usually at a rate of about 50 degrees per hour. The thermocouple junction was attached either to the copper block, or to the salt plates which contained the sample. The thermocouple and recorder had previously been calibrated with a retested thermometer, and temperatures given are accurate to ±2° C. After spectra of phase I were taken, the system was slowly cooled through the temperatures of phase III stability, and then more quickly cooled to room temperature. Spectra were taken during this cooling process, and in several cases the sample was left in the evacuated cell for a number of hours, with spectra taken at various intervals.

All spectra were recorded on a Beckman IR-7 spectrophotometer. The resolution was varied between 0.5 and 2.0 cm⁻¹.
RESULTS AND DISCUSSION

Potassium Nitrate

A free nitrate ion has four fundamental modes (8, p. 173-9), which are shown below in Table I.

Table I. The fundamental modes of the free nitrate ion.

<table>
<thead>
<tr>
<th>Mode</th>
<th>Frequency (cm(^{-1}))</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>(v_1)</td>
<td>1050 cm(^{-1})</td>
<td>symmetric stretch</td>
</tr>
<tr>
<td>(v_2)</td>
<td>830 cm(^{-1})</td>
<td>out-of-plane bend</td>
</tr>
<tr>
<td>(v_3)</td>
<td>1390 cm(^{-1})</td>
<td>antisymmetric stretch</td>
</tr>
<tr>
<td>(v_4)</td>
<td>720 cm(^{-1})</td>
<td>antisymmetric bend</td>
</tr>
</tbody>
</table>

Mull and melt samples of potassium nitrate proved too concentrated to accurately show the frequency of \(v_3\), and too dilute to show the modes \(v_1\) and \(v_4\). Because of this concentration problem, only \(v_2\) was studied for \(\text{KNO}_3\). Studies of \(v_1\) and \(v_4\) have, however, been done on a single crystal of \(\text{KNO}_3\) (14).

For mull and melt samples of shelf \(\text{KNO}_3\), \(v_2\) for phase II is at 826 cm\(^{-1}\). The mode for \(^{15}\text{N}\) exhibits a sharp peak at 811 cm\(^{-1}\). As the mull sample is slowly heated, transition to phase I occurs at 129.5 ± 2.0 °C. This was observed by setting the frequency at 826 cm\(^{-1}\) and watching the decrease in intensity of the isochochrome (Figure 5). The intensity decreased very slowly (and reversibly) until the transition temperature was obtained. At this temperature the intensity at 826 cm\(^{-1}\) decreased rapidly. Phase I absorbs at 834 cm\(^{-1}\). Shoulders at 811 and 825 cm\(^{-1}\), which slowly disappear with rising temperature, are indicative
Figure 5. Isochromate at 826 cm\(^{-1}\) of KNO₃ nujol mull at various temperatures.
of the slow transition. As the sample is cooled through the temperatures of phase III stability, no change in the spectrum of \( \nu_2 \) is observed. This is to be expected from the similarity in structure of phases I and III. There are no net differences in perturbation of the out-of-plane bending mode for the two phases (Figure 6).

As the temperature decreases below 110° C., no immediate change in the spectrum is noted. The peak at 83.4 \( \text{cm}^{-1} \) slowly disappears, however, concomitant with the growth of a peak at 826 \( \text{cm}^{-1} \) — the \( \nu_2 \) absorption of phase II. The transition to phase II is not complete even after several days if the sample remains in the evacuated cell. If air is admitted to the cell the transition is more rapid, especially if the NaCl windows are separated. A shoulder at 83.4 \( \text{cm}^{-1} \) is observable for as long as several weeks after phase II is again obtained.

Similar results were obtained for melt samples. When the initial room temperature spectra were recorded, a shoulder at 83.4 \( \text{cm}^{-1} \) was noted. This is to be expected, since the sample has necessarily passed through phase III. The transition to phase I was at 130 ± 2° C. Absorption for \( \nu_2 \) was 833.5 \( \text{cm}^{-1} \) with a gradually diminishing shoulder at 827 \( \text{cm}^{-1} \). Spectra taken while cooling the melt were essentially the same as for the mull samples, again with the partial phase III retention.

Mull samples of 50 percent and 24 percent \(^{15}\)KNO\(_3\) were studied to determine the \(^{15}\)K isotopic shift. The results for each of these compositions were similar, except of course in intensities, so only the 50 percent \(^{15}\)K spectra will be discussed. Phase II has bands at 806, 811, 829, 832 and 837 \( \text{cm}^{-1} \). Phase I absorbs at 812 and 834 \( \text{cm}^{-1} \). On
Figure 6. Infrared absorption spectrum of KNO$_3$

nujol mull in $\nu_2$ region at three temperatures.
dotted line— room temperature
solid line— approximately 125$^\circ$ C.
broken line— approximately 120$^\circ$ C.
cooling to room temperature, the frequencies gradually drop to 811.5 and 833.5 cm\(^{-1}\), then shoulders appear where phase II absorbs, and finally the phase II spectrum appears again (Figure 7).

The frequencies of the \( \nu_2 \) absorption of KNO\(_3\) I satisfy the Redlich-Teller product rule.\(^1\) The KNO\(_3\) II spectrum with its five maxima, is in obvious disagreement with the product rule. This spectrum may be divided into two approximate regions: 806 and 811 cm\(^{-1}\) for \( N^{15} \), and 829, 832 and 837 cm\(^{-1}\) for \( N^{14} \). The difference between the spectra of phases I and II is directly related to the nearest neighbor nitrate distances in the two structures as discussed by Decius (5). In phase II, nearest neighbor nitrates are close enough and have an angular distribution\(^2\) such that coupling (the dipole-dipole interaction between nearest neighbors) is an important consideration (Figure 1). In the rhombohedral phases, coupling is expected to be much smaller than in the orthorhombic phase, because of the nearest neighbor distance and the less favorable angular distribution\(^3\) (Figure 2).

One effect of the coupling is to lower the frequency of the out-of-plane bending mode as is readily observed in the "shelf" KNO\(_3\)

\[
\frac{1}{\nu_2(N^{14}O_3)} = \frac{m_{N^{14}} m_{N^{14}O_3}}{m_{N^{14}O_3}} = 1.0268 \\
\nu_2(N^{15}O_3) \approx \frac{m_{N^{15}}}{m_{N^{15}O_3}} \\
(812) (1.0268) = 834 \quad (8, \ p. \ 293)
\]

\(^2\)The nearest neighbor nitrates are directly above one another.

\(^3\)The effective nearest neighbors are coplanar.
Figure 7. Infrared absorption spectrum of potassium nitrate containing $50\%$ $\text{K}^{15}\text{O}_3$ in the $\nu_2$ region.
samples where phase I absorbs at 834 cm\(^{-1}\) and phase II at 826 cm\(^{-1}\). The other effect of this dipole-dipole interaction is to produce the intensity asymmetry and the fine structure as shown in the 50 percent \(^{15}\)N\(^{15}\)KNO\(_3\) II spectrum (Figure 7). When the coupling constant becomes smaller, as in phases I and III, then all the frequencies of one isotope are coincident (5).

**Nitrate Ion in Solid Solution**

By making very dilute solid solutions of NO\(_3^-\) in various alkali halide lattices, it was possible to observe the frequencies of both \(\nu_2\) and \(\nu_3\) (Figure 8). These frequencies are listed in Table II, according to the particular alkali halide in which nitrate was dissolved, with values reported by (A) Ketelaar, Haas and Van der Elskens (11) and (B) Frevel (7) in parentheses. The same samples were used to obtain both \(\nu_2\) and \(\nu_3\) for a particular alkali halide. The molar ratios used were:

- \(\text{NaNO}_3 = 1.8\times10^{-3}\)
- \(\text{KNO}_3 = 1.1\times10^{-3}\)
- \(\text{KNO}_3 = 1.6\times10^{-3}\)
- \(\text{KNO}_3 = 1.5\times10^{-3}\)

Table II. Absorption frequencies for the nitrate ion in solid solution.

<table>
<thead>
<tr>
<th>(\nu_2 (\text{cm}^{-1}))</th>
<th>(\nu_3 (\text{cm}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>K</td>
</tr>
<tr>
<td>Cl</td>
<td>--</td>
</tr>
<tr>
<td>Br</td>
<td>836</td>
</tr>
<tr>
<td>I</td>
<td>--</td>
</tr>
</tbody>
</table>
Figure 8. Infrared spectra of $v_2$ (above) and $v_3$ (right) regions of NO$_3^-$ in various alkali halide lattices. The maximum absorption frequencies are listed in Table II. Some of the curves have been vertically displaced for clarity.
These values may be compared with those obtained from Nujol mulls: 826 and 1380 cm\(^{-1}\) for \(\text{KNO}_3\), and 836 and 1358 cm\(^{-1}\) for \(\text{NaNO}_3\) (19). The agreement between values obtained in this study and values previously reported is very good. A definite problem exists, however, and that is the adherence of only the \(v_3\) potassium halide series with the apparent trend for most reported solid solution frequencies -- the larger the lattice constant, the lower the frequency.

A possible explanation for the deviation of \(v_2\) frequencies from the expected order is that for the out-of-plane bending mode the dipole derivative, \(\frac{d\mu}{dQ}\), is much smaller than that for the degenerate stretching mode, \(v_3\). The shift in frequency contributed by dipole-induced dipole interactions is directly proportional to \(\frac{d\mu^2}{dQ}\). It is therefore possible that the theoretical frequency shifts are so slight that they are incorporated in the experimental error.\(^1\)

However, recent work by G. R. Wilkinson (24) shows that the \(v_2\) potassium halide series does indeed follow the expected frequency

\[
\frac{1}{\omega_0} \Delta \frac{\omega}{\omega_0} = \left[ \frac{-\left(\epsilon - 1\right)}{2\epsilon + 1} \right] \left[ \frac{1}{3} \right] \left[ \frac{1}{\omega_0^2} \right] \left[ \frac{1}{a} \right] \left[ \frac{\delta \mu}{\delta Q} \right]^2 \left[ \frac{1}{h^2 c^2 \omega_0^2} \right]
\]

where \(\epsilon\) is the dielectric constant, \(\omega_0\) is the gas phase frequency and \(a\) is the spherical cavity radius (18).
shifts, indicating an error for the KCl value listed in Table II. A summary of Dr. Wilkinson's study of NO$_3^-$ in alkali halides, including rubidium halides, is shown in Table III. Each of the series demonstrates frequency shifts consistent with previously reported trends.

Table III. Absorption frequencies for the nitrate ion in solid solution (24).

<table>
<thead>
<tr>
<th></th>
<th>$v_2(\text{cm}^{-1})$</th>
<th>$v_3(\text{cm}^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Na</td>
<td>K</td>
</tr>
<tr>
<td>Cl</td>
<td>851.5</td>
<td>842.5</td>
</tr>
<tr>
<td>Br</td>
<td>846.5</td>
<td>841.2</td>
</tr>
<tr>
<td>I</td>
<td>841.1</td>
<td>838.8</td>
</tr>
</tbody>
</table>
CONCLUSIONS

1. The infrared spectra show that the transition KNO$_3$ II to KNO$_3$ I is slow. The transition from phase III to phase II may be prolonged indefinitely.

2. The absorption frequencies of the out-of-plane bending modes for the three phases of KNO$_3$ are relatively predictable on the basis of structure. The rhombohedral phases are expected to show no coupling, while the orthorhombic phase should show a high degree of coupling. The results of this coupling were observed.

3. The shifts in fundamental frequencies for $\nu_2$ and $\nu_3$ of NO$_3^-$ in alkali halide matrices are consistent with previously reported solid solutions. As the lattice constant increases, the vibrational frequencies decrease.


