tential barrier allows free rotation above 60°K in the potassium salts and above 150°K in the rubidium salt. In the sodium salts finally even at 300°K no free rotation is observed. At temperatures sufficiently below the ones mentioned the molecules perform librational (oscillatory) motions, and at intermediate temperatures the motion can be described with the classical picture of hindered rotation. The librational levels are split due to tunneling, and specific-heat measurements show that this tunnel splitting is in complete agreement with the theory. It was also found that the rotational and the tunneling states couple strongly to the phonons, whereas the librational states do not. The phonon-scattering cross sections have a Lorentzian resonance form. The phonon-molecule interaction is assumed to be through stress coupling which has been shown to be large from stress-induced alignment experiments.

In the KBr and KI host lattices an additional center-of-mass motion of the CN⁻ ions appears likely.

This type of motion had not been considered in the Pauling model. On the other hand a central instability should certainly be expected for cavities considerably larger than the impurity ion. We must therefore ask whether the Pauling model describes the general case of molecular degrees of freedom in solids, or whether the CN⁻ ion is an exception. It is the purpose of the following paper to answer this question.

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Rotational Degrees of Freedom of Molecules in Solids. II. The Nitrite Ion in Alkali Halides

V. NARAYANAMURTI,* W. D. SEWARD,† AND R. O. POHL Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York (Received 28 January 1966)

In continuation of the work described in the preceding paper we have studied a defect with three different principal axes of inertia, namely the NO₂⁻ ion. In KCl and KBr, the energy levels corresponding to free rotation, libration, and tunneling have been found. They have been analyzed in the same manner as in the preceding paper. Very different potential barriers for the three different axes of rotation have been found. Strong phonon scattering is again observed in connection with the states of free rotation and of tunneling. In NaCl the ion is frozen in even at room temperature and is only librating. In KI further evidence is found that the NO_2^- ion does occupy an off-center position. Consequently the molecule can perform not only rotational, but also translational motion, i.e., its potential is considerably more complex than the Pauling-Devonshire potential. Hence the KI:NO2 system seems to present the most general case of motion of molecules in solid solution. From the fine structure of the near infrared spectrum of KI:NO2 we have found all the impurity modes detected so far by different techniques, which shows that this type of spectroscopy is a very useful tool for the study of impurity modes. We suggest further that some of these impurity modes are librational motions.

I. INTRODUCTION

 \mathbf{I}^{N} the preceding article¹ we showed that infrared and thermal measurements combined gave a complete picture of the low-lying energy levels of the cyanide ion in various alkali halides. In the present paper we wish to report studies using NO₂⁻ ions, i.e., asymmetric tops. We shall see that the rotation-vibration fine structure is quite complex indeed, but with the knowledge gathered from the CN⁻ system we will be able to

interpret the measurements assuming rotational motions around the three principal axes of the NO_2^- ion plus translational center-of-mass motion of the ion in its cavity. The present paper,² therefore, can be regarded as a test for the model developed in the previous paper as well as an extension to the most general case of molecular motion in solids.

II. THE INFRARED RESULTS A. Spectra

The experimental techniques were the same as those described in I. Most of the crystals used have been

^{*} Present address: Department of Physics, Indian Institute of Technology, Bombay, India.

[†] Present address: Department of Physics, University of

¹ W. D. Seward and V. Narayanamurti, preceding paper, Phys. Rev. 148, 463 (1966). Hereafter referred to as I.

² Part of this work has been briefly presented previously. See V. Narayanamurti, Bull. Am. Phys. Soc. 9, 271 (1964).



FIG. 1. Schematic of the normal modes of the NO_2^- (top) and NO_3^- (bottom) molecules. For the NO_2^- the three principal axes of rotation and the direction of the permanent dipole moment are indicated.

described previously.^{3,4} In addition some crystals were prepared with isotopically enriched (98%) $\rm KN^{15}O_2$ using argon as protective atmosphere and with $\rm KNO_3$ using Ar or O₂.

Figure 1 shows the normal modes of the NO_2^- and NO_3^- ions.⁵ For the NO_2^- ion ν_1 is the symmetric stretching mode, ν_2 the bending mode, and ν_3 the antisymmetric stretching mode. For the NO_3^- ion ν_1 is the totally symmetric stretching mode, ν_2 the out-ofplane bending mode, ν_3 the antisymmetric stretching mode and ν_4 the in-plane bending mode. The vibrations ν_3 and ν_4 of the NO_3^- are each doubly degenerate. In solid solution the infrared active modes of both ions are easily identified in the absorption spectrum since their chemical shifts are small.⁶ The strongest absorption bands are found in the region of the ν_3 modes. Their shape at room temperature follows an exponential law

TABLE I. Room-temperature absorption in the stretching region of NO₂⁻ and NO₃⁻ in three potassium halides. Peak position and half-widths are given in wave numbers (cm⁻¹). σ is defined through the equation $N = \sigma \alpha$, where N is the concentration (in cm⁻³) and α is the peak absorption constant (in cm⁻¹).

| Impurity ion | Host | Peak position (cm ⁻¹) | Half-widths (cm ⁻¹) | σ^{a} (cm ⁻²) |
|-------------------|------------------|---|------------------------------------|--|
| NO_2^- | KCl KBr KI | 1287 1275 1257 | 16 20 24 | 1.7×10^{17} 2.9×10^{17} |
| NO_3^- | KCl KBr KI | 1395 1384 1372 | 5 5 5 | 3.5×10 ¹⁶ ь |

^a The chemical analyses for KCl were performed by the Schwartzkopf Microanalytical Laboratory, Woodside 77, New York, the KI was analyzed by the Analytical Facility of the Cornell Materials Science Center. ^b In this work assumed to be equal to the value determined for the same ion in KCl.

on both sides of the maximum. For NO_2^- this was measured over three orders of magnitude in absorption constant.⁷ Peak position, half-width and proportionality constant connecting peak height and concentration are listed in Table I.

In Fig. 2 these spectra ("stretching region") are shown at low temperatures. The broad bands break up into a large number of lines of different widths. In this as well as the following figures the distinction between the NO_2^- and NO_3^- lines was achieved by studying crystals with different NO_2^- : NO_3^- ratios and crystals with $N^{15}O_2^-$ and $N^{15}O_3^-$. For details of the isotope effect we refer to the Appendix. The peaks designated by arrows in Fig. 2 belong to the NO_3^- ion, *all* others to the NO_2^- ion.

At first sight the complexity of the low-temperature spectra seems discouraging. We shall see in Chapter III, however, that all these lines reflect on the degrees of freedom of the impurity ions and that they tie in

TABLE II. The frequencies of the $N^{14}O_3^-$ ion in KCl, KBr, KI at 15°K. The figures in brackets are for $N^{16}O_3^-$ where observed.

| | Frequencies in cm ^{-:} | ' in | |
|------------|---------------------------------|--------------|---------------------|
| KCl | KBr | KI | Assignment |
| 723 | 718 | ••• | V4 |
| 843 | 841 | 839(818) | ν_2 |
| 1064 | 1056 | ••• | ν_1 |
| 1398(1367) | 1386.5(1354) | 1373.5(1341) | ν_3 |
| 1442 | 1432 | 1425 (1423) | 224 |
| 1780 | 1768 | 1757 (1756) | $\nu_1 + \nu_4$ |
| 2110 | 2092 | 2079 (2046) | $\nu_{3} + \nu_{4}$ |
| 2445 | 2426 | 2409 (2377) | $\nu_1 + \nu_3$ |
| 2794 | 2768 | 2742 (2678) | 2 ₂₃ |

⁷ This band shape was independent of concentration and heat treatment: Crystals of KCl and KBr containing about 5×10^{18} cm⁻³ NO₂⁻ were heated in argon for 1 h at a temperature of approximately 20°K below the melting point and then rapidly cooled (within about 5 to 10 min) to room temperature. This had no effect on the ν_3 bands. In KBr+5×10¹⁹ cm⁻³ NO₂⁻, the half-width of the ν_3 band appeared to increase to 22 ± 2 cm⁻¹ which is, within experimental error, the same as the 20 cm⁻¹ value obtained for low concentration.

³ R. O. Pohl, Phys. Rev. Letters 8, 481 (1962).

⁴ R. O. Pohl, Z. Physik 176, 358 (1963).

⁶ See, for instance, G. Herzberg, *Molecular Spectra and Molecular Structure* (D. Van Nostrand Publishing Co., Princeton, New Jersey, 1945), Vol. II.

⁶ These bands were first studied by I. Maslokowez, Z. Physik 51, 696 (1928). See also R. W. Pohl, *Optik und Atomphysik* (Springer-Verlag, Berlin, 1963), 11th ed., Sec. 141.



FIG. 2. Stretching region for NO_2^- and NO_3^- in KCl, KBr, and KI. Temperature and NO_2^- concentration as indicated on graphs. NO_3^- concentration: (a), (d), (g): 1.1×10^{17} cm⁻³; (b), (e): 2.5×10^{18} cm⁻³; (h): 1.3×10^{18} cm⁻³; (c), (f): 8.5×10^{17} cm⁻³; (i): 3.5×10^{17} cm⁻³, note that this is $N^{15}O_3^-$. Compare (i) with (f) and notice the isotope shifts to lower energy. See Appendix. The bands marked with an arrow belong to NO_3^- .

with a variety of other experimental results. We would like to precede this discussion with a brief description of the prominent features of these spectra. We begin with the simpler NO_3^- spectrum.

about 0.8 cm⁻¹ at 80°K (measured on the ν_3 band in KCl⁸). Satellites are observed between 3 and 4 cm⁻¹

The NO_3^- lines are temperature-insensitive between 2° and 80°K and approach a limiting linewidth of

⁸ Most of the runs were made with a resolution of 0.5 cm^{-1} over the entire wavelength range. Some selected portions of the spectrum were scanned with a higher resolution (0.25 cm⁻¹ to 0.3 cm⁻¹). These high-resolution measurements are identified in the text.



FIG. 3. Transmission spectra between 13°K and 80°K of the ν_2 bending mode of NO₂⁻ in KCl. Thickness 11.3 mm. N_{NO2}⁻ =1 \times 10¹⁹ cm⁻³.

away from the main band in KCl at 1398 cm⁻¹ (in KBr: 1386.5 cm⁻¹, spacing between 2.5 and 5 cm⁻¹; in KI: 1373.5 cm⁻¹, spacing between 3 and 4 cm⁻¹). The difference satellites appear to decrease in relative intensity at 2°K (by about a factor of 2 to 3 in KCl). In KI additional far off lines are observed as sum bands 72.5 cm^{-1} and 88.5 cm^{-1} away (at 1446 and 1462 cm⁻¹, respectively). This identification is completely confirmed by the isotopic shifts of the different modes for $KI+KN^{15}O_2$ [Fig. 2(i)]. These satellites will be of particular interest in the discussion. Further lines associated with the NO_3^- ion are listed in Table II. They are between 50 and 500 times weaker than the ν_3 lines. No satellites were observed with any of these bands. Since most of them are weak this is not surprising. However, the ν_2 band, which possesses sufficient intensity, did not show any structure even with crystals containing 1×10^{19} NO₃⁻ and about 12 mm thick. We conclude that any satellites of ν_2 must be at least 500 times weaker than the main band in all three host lattices.

In contrast to the NO_3^- bands the NO_2^- bands are strongly temperature-dependent. We start with KCl. All the lines between 1263 and 1314 cm⁻¹ in Figs. 2(a), (d) and (g) belong to ν_3 .⁹ The main peak at 1290 cm⁻¹ shows satellites at 2 and 15°K with a spacing of about 4 cm⁻¹. Their intensities are about 200 times weaker than the main line.¹⁰ All the other lines in Figs. 2(a), (d) and (g) belong to the symmetric stretching mode ν_1 of NO₂⁻ (besides the NO₃⁻ lines mentioned above). At 2.0°K the ν_1 band consists of an intense line at 1329 cm⁻¹ and weaker sum and difference satellites approximately 4 cm⁻¹ away from the central line.¹¹ In addition a broad sum band at 1349 cm⁻¹ is observed. As the temperature is increased all these satellites increase in intensity at the expense of the central line at 1329 cm⁻¹. In addition a poorly resolved difference satellite at about 1322 cm⁻¹ arises. By 80°K the entire ν_1 band is barely detectable due to overlap with the strong ν_3 fundamental.

The temperature dependence of the bending mode ν_2 of NO₂⁻ in KCl is shown in Figs. 3 and 4(a). The observed fine structure is almost identical to that seen with ν_1 above but is more clearly resolved. In addition, a weak transition at approximately 803 cm⁻¹ can be seen. At 15°K a new line arises at 797 cm⁻¹ and also a high-energy shoulder¹² at about 817 cm⁻¹ can be seen. By 30°K a near equalization of intensity of these lines is observed. At 80 and 295°K only a broad band with two maxima and a width of about 28 and 58 cm⁻¹, respectively, is seen. These maxima are peaked roughly at 796 and 811 cm⁻¹ at 80°K and at about 792±5 cm⁻¹ and 820±5 cm⁻¹ at 295°K. The spectra of the bending region resemble closely those obtained for CN⁻ (Ref. 1).

Figure 5 shows the absorption spectra for the combination mode¹³ $\nu_1 + \nu_3$ of NO₂⁻ in KCl at 15 and 295°K. This mode has a half-width of about 40 cm⁻¹ at 295°K and 10 cm⁻¹ at 80°K. At 15°K the spectrum consists of a line at 2592 cm⁻¹ with barely resolvable satellites

⁹ The conclusion that the 1314 cm⁻¹ line belongs to ν_3 was reached with the following argument: It does not belong to a molecule of different isotopic composition. It scales with the NO₂⁻ concentration. As a difference satellite of ν_1 it should be only barely detectable at 15°K and should vanish at 2°K. Instead it is almost temperature-independent.

¹⁰ The peak absorption coefficient of the main line was estimated by determining the room- and low-temperature absorption coefficient of a crystal containing 5×10^{17} NO₂⁻ and then assuming that the low-temperature absorption coefficients have the same ratio as that observed at room temperature. The same procedure was adopted for the ν_3 bands in the other host lattices to be discussed later.

 $^{^{11}}$ At 2°K there appeared to be a barely resolvable shoulder at 1327 cm⁻¹. This is probably real but has been smoothed out in the drawing.

¹² In the 2°K data with a thick crystal our scan stopped at 812 cm⁻¹ so that the intensity of the 818 cm⁻¹ line below 15°K is unknown. It is probably the same as the 1349 cm⁻¹ band observed in combination with ν_1 , the origins of which are discussed later.

 $^{^{13}\,\}rm This$ mode was studied only above $15\,^{\rm o}\rm K$ in all the host lattices.



FIG. 4. Bending region for NO_2^- in the three host lattices. Temperatures as indicated. The ν_2 mode of NO_3^- in KCl at 843 and at 839 cm⁻¹ in KI has been subtracted from the spectrum.

approximately 4, 8, and 12 cm⁻¹ away on the lowenergy side and a shoulder at about 2608 cm⁻¹ on the high-energy side. In addition a sharp line at 2565 cm⁻¹ is observed.

In KBr the spectrum is quite similar, as seen in Figs. 2, 4, and 5. We briefly point out the differences. In addition to the fine structure around the antisymmetric stretching mode ν_3 , which is more closely spaced than in KCl, a sum satellite approximately 1 cm⁻¹ from the main line (at 1276.5 cm⁻¹) and about four times weaker in intensity was clearly resolved at 1.6°K with a resolution of 0.25 cm⁻¹. It does not show on Fig. 2(h). In KCl no such satellite was seen. The fine structure around the symmetric stretching mode ν_1 (at 1319 cm⁻¹) is more closely spaced than in KCl, namely by ~ 1 cm⁻¹ (resolution 0.3 cm⁻¹) and is barely resolved. A similar fine structure is observed around the bending mode ν_2 (at 798.5 cm⁻¹) with spacings between 0.8 and 1.0 cm⁻¹. Instead of the broad high-energy band a group of well resolved lines is observed (at 808, 809.5, 811, and 815 cm⁻¹). Two maxima are clearly resolved at 80°K (at 798 and 811 cm⁻¹). At 300°K (not shown) the spectrum consists of one broad band peaked at 813 ± 3 cm⁻¹ with a half-width of 38 ± 2 cm⁻¹. The overtone vibration $\nu_1+\nu_3$ [Fig. 5(b)] narrows more than for KCl, namely from



FIG. 5. Absorption spectra in the overtone region. The sharp lines at 2445, 2426, and 2409 cm⁻¹ belong to the $(\nu_1 + \nu_2)$ mode of NO₃⁻ in KCl $(n=1.1\times10^{17} \text{ cm}^{-3})$, KBr $(n=2.5\times10^{18} \text{ cm}^{-3})$, and KI $(n=8.5\times10^{17} \text{ cm}^{-3})$, respectively. The line at 2742 cm⁻¹ in the KI host lattice is due to $2\nu_3$ of NO₃⁻. The rest of the absorption is caused by the $(\nu_1 + \nu_3)$ mode of NO₂⁻.

TABLE III. Comparison of the low-lying energy levels associated with $N^{14}O_2^-$ and $N^{14}O_3^-$ dissolved in KI as observed by different investigators. The distinction between NO_2^- and NO_3^- lines in Renk's work is tentatively made by us. The lowest rotational levels (in the cm⁻¹ range) observed in this work are omitted; see text. We also studied the satellites for N¹⁶O₂⁻. The narrow lines appeared to be shifted by ~ 0.5 cm⁻¹ to lower energies, as expected. The 53 cm⁻¹ line was more clearly resolved for N¹⁶O₂⁻. In fact, the spacing for N^{14} appeared to be ~47 cm⁻¹, barely resolved due to overlap with ν_1 (1308 cm⁻¹) which in turn appears slightly broader than ν_1 for $N^{16}O_2^{-1}$. In this table we therefore cite the $N^{16}O_2^{-1}$ satellite. An additional absorption in the spectrum of Timusk and Staude is found at 21.4 cm⁻¹. These authors have not commented on it, however. Sharp satellite lines, of unknown origin, were observed at \sim 20 cm⁻¹ and \sim 35 cm⁻¹ in combination with $\nu_1 + \nu_3$ in our IR spectrum. These are not observed with the fundamentals.

| Investigators | Ref. | $\mathrm{NO}_2^-, \lambda^{-1}$ in cm ⁻¹ | | | NO | 2⁻, λ⁻¹ i n c | cm ⁻¹ | | | |
|--------------------------------|----------|---|-------------|-------------------------|---|--|------------------|--------------|-------------------|--------------|
| Renk Timusk and Staude | 24 23 | | 65 63.5 | 71 70 | 79 | 136 | 206 | 73 | 78 not studied | 89 1 |
| Sievers and Lytle This work | 25 | 55 53∎ | 63.5 63ª | 71.2 71 ^b | 79.5 79 ^ь ; 80.5 ^ь | 137° | 206 ^b | 73.3 72.5 | 78.4 | 88.2 88.5 |

Broad lines.

• Narrow lines. • Broad, half-width at 15° K ~2.5 cm⁻¹; it may consist of more than one line.

50 cm⁻¹ at 295°K to 5 cm⁻¹ at 15°K. Only two high- and low-energy shoulders approximately 10 cm⁻¹ away from the main peak are seen at 15°K.

In KI, the ν_1 absorption (at 1308 cm⁻¹) is much narrower than in the other host lattices. Its half-width at 13°K is ~1.5 cm⁻¹. ν_3 [at 1253 cm⁻¹, see Fig. 2(f)] has satellites at 1300, 1318, 1324, 1332, 1333.5, 1390, and 1459 cm⁻¹ (see Table III). In addition to these highfrequency lines, closely spaced lines are observed at 1245 and 1248.5 cm^{-1} on the low-energy side, and at 1261 and 1265 cm⁻¹ on the high-energy side of ν_3 . At 1.6° K an additional sum satellite of ν_3 was observed at 1254.5 cm⁻¹ which was about 7 times weaker than the 1253 cm⁻¹ line. The bending mode ν_2 , like ν_1 , shows no fine structure [Fig. 4(c)]. The half-width at 10°K is ~ 1.5 cm⁻¹, at room temperature 20 cm⁻¹. The combination band $\nu_1 + \nu_3$ is peaked at ~2525 cm⁻¹ at room temperature with a half-width of \sim 74 cm⁻¹. The band is asymmetric and appears to possess a highenergy shoulder. This is resolved at 80°K where the spectrum consists of a strong doublet at 2533 and 2541, a weak shoulder at 2552, and a line at 2568 cm^{-1} [Fig. 5(c)]. A further narrowing of the absorption is observed at 15°K together with a slight change in relative intensities.14

Finally we describe the results obtained on NaCl: NO2. The IR spectrum of one boule (0.025 mole% NaNO₂ in melt) was measured between 15°K and room temperature. ν_1 (1346 cm⁻¹), ν_2 (836 cm⁻¹), and ν_3 (1304 cm^{-1}) showed no structure and had widths of $<1 cm^{-1}$ below 80°K. Between 1250 and 1280 cm⁻¹ a broad band containing many small peaks was found. It may result from NaNO₂ clusters since it was found that NaNO₂ precipitates in NaCl for concentrations above 1017 cm^{-3} . We conclude that isolated NO_2^- ions are frozen in NaCl and thus exhibit no rotational fine structure.

B. Electric-Field and Stress Effects

Electric-field-induced alignment of NO₂⁻⁻ in KCl and KBr was attempted at 2°K in a manner similar to that discussed in I. Fields up to 90 kV/cm along the [100] and $\lceil 110 \rceil$ crystal directions had no effect on the IR absorption. From our experimental sensitivity we conclude that any change in optical density of the $\mathrm{NO}_2^$ absorption bands was less than 5%. This is consistent with recent low-temperature ac dielectric measurements by Sack and Moriarty¹⁵ in which they found that the dipole moment of NO_2^- in KCl is 0.21 Debye and that the NO₂⁻ centers in KCl orient down to the lowest temperature of their measurement ($\sim 2^{\circ}$ K). From this a maximum polarization of 5% would have to be expected in our experiment.

We have also made preliminary measurements on the effect of uniaxial stress on the ν_1 and ν_3 vibrations of NO₂⁻ in KCl at 2°K using the experimental technique described in I. With [110] stresses of about 5.5 kg/mm^2 a complete alignment of the ions takes place. From a study of the directional dependence of the alignment we conclude that the equilibrium orientations of the NO_2^- dipole (it coincides with the C_2 axis of the molecule) are the (110) directions¹⁶ in the crystal. These measurements have not been performed for KBr and KI host lattices but in the ensuing it will be assumed that the C_2 axis of the NO₂⁻ molecule lies along the (110) directions in these host lattices as well.17

¹⁴ Verv weak lines (absorption coefficient 5×10^{-2} cm⁻¹ at 15° K for n_{NO_2} - 10^{19} cm⁻³) were observed at 2080 cm⁻¹ in KCl, 2063 cm⁻¹ in KBr, and 2045 cm⁻¹ in KI and are ascribed to $+\nu_3(NO_2^-)$. With KI+KN¹⁵O₂ this line was observed at 2014 cm⁻¹ as expected from isotopic shifts from the sum of the isotopic shifts of ν_2 and ν_3 .

¹⁵ H. S. Sack and C. M. Moriarty, Solid State Commun. 3, 93 (1965).

¹⁶ This is consistent with the C_{2v} symmetry of the NO₂⁻ molecule and also is electrostatically favored since in this orientation the negatively charged oxygen atoms of the molecule make their closest approach to the positively charged nearest-neighbor K⁺ ions.

¹⁷ C. Jaccard, Phys. Rev. 124, 60 (1961), previously found a (110) orientation from the symmetry of the g tensor of NO_2^- ' in KCl, KBr, and KI. The NO_2^{--} was formed after x irradiation of KNO₂ doped alkali halides. Thus the NO_2^{--} is probably not mobile.

III. DISCUSSION OF IR RESULTS

The observed frequency shifts with N^{15} enriched NO_2^- and NO_3^- in KI, the striking changes in the fine structure with host material and the fact that the observed structure is independent of concentration provides convincing evidence that the observed spectrum is due to isolated molecules. The strong temperature dependence of the spectra, similar to that observed for the CN^- in the potassium halides,¹ indicates that the NO_2^- can perform rotational motions in the crystal. We begin with the discussion of the details of the rotational motion of the NO_2^- molecule about its different principal axes of inertia. The NO_3^- ion will be discussed in Subsec. D of this section.

Following conventional spectroscopic notation⁵ we label the three principal rotational inertias around the A, B, and C axes (see Fig. 1) as I_A , I_B , I_C , and the respective rotational constants¹ ($\tilde{B}=h/8\pi^2 c I_B$, where h=Planck's constant, and c=velocity of light) as \tilde{A} , \tilde{B} , and \tilde{C} . All rotational inertias are about axes passing through the center of mass of the molecule. They can be calculated from the known N-O bond length¹⁸ of 1.24 Å using an O-N-O bond angle of 118° as derived in the Appendix. From this one obtains $\tilde{A}=4.22$ cm⁻¹, $\tilde{B}=0.45$ cm⁻¹, and $\tilde{C}=0.43$ cm⁻¹.

The infrared vibration-rotation spectra arise from a changing dipole moment, $\partial \mu / \partial q_i$, where μ is the dipole moment which is a function of the normal coordinates q_i . The subscript *i* refers to the *i*th normal mode. The symmetric stretching and bending vibrations of the NO₂⁻ molecule have their $\partial \mu / \partial q_i$ lying along the *B* axis of the molecule. The antisymmetric ν_3 vibration has its $\partial \mu / \partial q_3$ lying along the *A* axis of the molecule.

Thus, in the first approximation, if one treats the rotations about the three axes of inertia independently, then the ν_1 and ν_2 vibrations will be sensitive to rotations about the *A* axis and not to rotations about the *B* axis since the $\partial \mu / \partial q_i$ for these two vibrations change during the *A* rotation. From similar arguments it can be seen that the ν_3 vibration will be sensitive to rotations about the *B* axis but not the *A* axis. All three vibrations will, however, be sensitive to rotations about the *C* axis. In the following we consider each host lattice in turn.

A. The KCl Host Lattice

From the fact that the bending and symmetric stretching vibrations exhibit an almost identical fine structure both in spacing and intensity while the ν_3 vibration shows only weak satellite lines it follows that the structure observed with ν_1 and ν_2 corresponds to rotations about the *A* axis of the molecule. Since the *B* axis of the NO₂⁻ molecule points along one of the $\langle 110 \rangle$ directions in the crystal a twofold rotation about the *A* axis provides an identical configuration for the



FIG. 6. KCl:NO₂. Rotational and librational fine structure of the ground and first excited vibrational states of the NO₂⁻ ion, for motion around the A axis. This fine structure was obtained as solutions to the Mathieu equation with $\tilde{V}_{0A}=2.8\tilde{A}=11.8~{\rm cm}^{-1}$, $\tilde{A}=4.22~{\rm cm}^{-1}$. The energy levels are given with respect to $\tilde{V}=0$ as multiples of the rotational constant \tilde{A} and also as energy differences (in cm⁻¹) with respect to the ground state K=0, L=0. The ground-state splitting (be_0-bo_1) gives the tunneling frequency.

molecule. We therefore determine the eigenvalues for the motion around the A axis using a two-well cosine potential. In doing this we follow Pauling as described in I, Sec. V, Subsec. A. The Schrödinger equation for this case is known as Mathieu's equation and can be solved exactly.¹⁹ It must be borne in mind, however, that this model assumes that the two potential wells are equivalent. In our case this is strictly true only for rotations about the axis joining the oxygen atoms $(\tilde{A} = 2.95 \text{ cm}^{-1})$. We believe, however, that the ion is rotating around its center of mass $(\tilde{A} = 4.22 \text{ cm}^{-1})$. The error introduced by using the Mathieu equation for this case is small.

For $\tilde{V}_{0A} = 0$ (the index A indicates the axis of rotation), the energy eigenvalues are the same as those of a 1-dimensional rotor whose energy eigenvalues go as $\tilde{A}K^2$ where the quantum number K takes the values 0, 1, 2, \cdots . For K > 0 each K level is twofold degenerate for such a rotor. For $\tilde{V}_{0A} \neq 0$ this degeneracy of the excited K levels is removed. An excellent fit to the line splittings observed with ν_1 and ν_2 can be obtained by choosing a value of $\tilde{V}_{0A} = 2.8\tilde{A} = 11.8$ cm⁻¹. The

¹⁸ G. B. Carpenter, Acta Cryst. 5, 132 (1962); 8, 852 (1955).

¹⁹ The solutions of the Mathieu equation together with the notation used here are given in: *Tables of the Mathieu Functions* (Columbia University Press, New York, 1951).

| TABLE IV. | Assignn | nent o | f tran | sitions a | ssociate | ed wit | h v1 | and | ν_2 |
|-----------|----------|--------|---------|-----------|----------|--------|------|-------|---------|
| vibration | s in the | KCl ł | iost la | ttice. Se | e also | Fig. 6 | and | text. | |

| Freque in cn | ncies | | Ob inte | served ensities | Calculated intensities |
|-----------------|---------|---------------------------|-------------|---------------------|---------------------------|
| v 1 | ν_2 | Assignment | 15°K | 2°K | 2°K |
| ~1322 | 797 | $P_{Q(2)}$ | 0.11 | <5×10 ⁻³ | 1.8×10 ⁻³ |
| 1325 | 801 | $P_{\rho(1)}$ | 0.65 | 0.2 | 0.21 |
| 1327ª | 803 | Q (Ò) | ~ 0.05 | ~ 0.040 | 0.05 |
| 1329 | 805 | Řam | 1.0 | 1.0 | 1.0 |
| 1332 | 809 | $R_{o(1)}$ | 0.61 | 0.16 | 0.19 |
| ~1349 | ~817 | $S_{Q(2)}$ and $S_{Q(1)}$ | ••• | ••• | ••• |

^{*} See Ref. 12.

successive even (L=0) and odd (L=1) solutions of the Mathieu equation for K=0, 1, 2 are shown in Fig. 6 for the vibrational ground and the first excited state. In the harmonic-librational approximation the levels be_0 and bo_1 would have the same energy and the state be_1 would represent the first excited librational state. This state lies very near the top of the barrier. The states bo_2 and be_2 have very nearly the same energy and represent the first rotational energy states.

The allowed transitions for the optical experiments are obtained from elementary dipole selection rules²⁰ which show that the strongest transitions correspond to $\Delta K=0, \pm 1; \Delta L=\pm 1. \Delta K=\pm 2; \Delta L=\pm 1$ are much weaker in intensity. The transitions $\Delta K = 0$, $\Delta L = 0$ are forbidden but may be allowed if the motion about one of the other axes of inertia is harmonic. This transition, the true Q branch $\lceil Q(0) \rceil$, is shown with a dashed line in the figure. The other allowed *Q* branches are labeled with a superscript P if they lie on the lowenergy side of Q(0) and with a superscript R or S if they lie on the high-energy side of Q(0). With a knowledge of selection rules and the fine structure observed with the ν_1 and ν_2 vibrations a direct correlation can be made with the calculated energy levels. This is shown in Table IV. The observed intensities refer to the fine structure observed with the ν_2 vibration [Figs. 3, 4(a)] because the spectrum was much more clearly resolved in this case but qualitatively at least, the lines associated with ν_1 show the same intensity behavior. From the calculated thermal populations at 2 and at 15°K, and from the measured intensities at 15°K one can compute the intensities at 2°K. These values are listed in the last column. They agree very well with the measured intensities. The intensities for the satellite at 817 $\rm cm^{-1}$ has not been quoted in the table since it was observed only as an imperfectly resolved shoulder. Its large breadth is due to its consisting of a group of lines $[S_{Q(2)} \text{ and } S_{Q(1)}]$. At about 30°K the levels be_0 , bo1, and be1 are equally populated, and the narrow lines disappear. By 80°K the maximum in the thermal population shifts to the K = 2 levels. This would predict Q transitions occurring at Q(0) + 20 cm⁻¹ and Q(0) - 10cm⁻¹, i.e., at 793 and 823 cm⁻¹ for the bending mode.

 20 R. M. Hexter and D. A. Dows, J. Chem. Phys. 25, 504 (1956).

The higher K levels are all doubly degenerate for a simple 1-dimensional rotor and have significant but lower thermal populations than the K=2 levels at high temperatures. The successive Q transitions from these higher K levels are spaced $2\tilde{A} \sim 8 \text{ cm}^{-1}$ apart. Hence it is not surprising that the bending and symmetric stretching modes have such a large breadth at high temperatures.

The antisymmetric stretching vibration ν_3 is sensitive to rotations about the *B* axis and the weak sum and difference satellites spaced between 4 and 5 cm⁻¹ are probably due to harmonic librations about this axis.²¹ This axis is a twofold rotation axis. Again using a cosine potential function¹ one obtains from a librational frequency of 4.5 cm⁻¹ the barrier $\tilde{V}_{0B} \sim 11$ cm⁻¹. Since \tilde{V}_{0B} is much larger than \tilde{B} the motion of the molecule is extremely harmonic at low temperatures and it is not surprising that the Q(0) transition at 1290 cm⁻¹ dominates the absorption for this mode (the groundstate splitting for $\tilde{V}_{0B} \sim 23\tilde{B}$ is calculated to be 0.002 cm⁻¹).

The ν_3 sum satellite at 1314 cm⁻¹ may correspond to librations about the C axis²² with a frequency of ~ 24 cm^{-1} . Since the C axis is perpendicular to the plane of the molecule, this motion involves a simple planar oscillation of the molecule with the dipole axis (B axis) pointing along the 12(110) directions in the crystal. Since the molecules can be aligned along the (110)directions by uniaxial stress at low temperatures the barrier height for this motion must be less than 40 or 50 cm^{-1} if the reorientational motion is a thermally activated one. The tunneling probability for such motions has not been calculated since this requires a solution of the Schrödinger equation for a 12-minima potential. The tunneling splitting, however, must be less than about 0.5 cm⁻¹ since this was the limiting linewidth observed by us for all three modes of the NO₂⁻.

The weakly active combination mode $\nu_1 + \nu_3$ shows the same structure as ν_1 and ν_2 , though more poorly resolved. The line at 2565 cm⁻¹ is of unknown origin. The only other NO₂-lines not mentioned so far occurred on the low-energy side of ν_3 at 1263 cm⁻¹ and 1270 cm⁻¹. They are caused by naturally occurring N¹⁵ and O¹⁸, as discussed in the Appendix.

B. KI Host Lattice

We begin our discussion with the high energy satellites of ν_3 listed in Table III. Most of these bands have been observed previously in IR and uv spectro-

²¹ It is also conceivable that these satellites are caused by librations around the *C* axis whereby the same fine structure on ν_1 and ν_2 is not detectable because of the strong fine structure caused by rotation around the *A* axis. The reason why we prefer *B*-axis rotation will become apparent below in the discussion of KBr and KI.

²² Librations about this axis should be observable in principle with the ν_1 and ν_2 vibrations as well. However, the ν_1 and ν_2 fundamentals themselves are much weaker than the ν_3 band so that it is not surprising that this line was not observed in combination with ν_1 and ν_2 . scopic studies²³⁻²⁵ and have been attributed to resonant and local modes. According to this picture the NO₂⁻ ion should lead to three local modes, of symmetry A_1 , B_1 , and B_2 , in the gap between the acoustic and optic continuum in KI of which for unknown reasons only two had been observed in the infrared, namely at \sim 71 and at \sim 79 cm⁻¹. In the present experiments, three modes have indeed been observed, but from group-theoretical arguments only two modes are expected to couple to ν_3 . Recently Bilz et al.²⁶ have tried to explain the far IR results in KI: NO2 through local-mode absorption to which free rotations of the ions around the A axis were coupled. In order to fit their data they had to assume an O-N-O bond angle of 96° resulting in $\tilde{A} = 2.63$ cm⁻¹. From our isotopic studies we determined this angle to be 118°, or $\tilde{A} = 4.22$ cm⁻¹. This changes the spacing of their "ladders" considerably. Furthermore, we believe that several of the lines used in their "ladders" do not belong to the NO_2^- but rather to the NO_3^- ion (see caption to Table III).

As an alternative explanation of the nature of these modes we propose that at least some of them are caused by librational motions of the ions. The spectra connected with ν_1 and ν_2 each consist only of one very narrow structureless band whose width and shape is virtually temperature-independent below 80°K. We therefore conclude that the barrier heights \tilde{V}_{0A} and \tilde{V}_{0C} must be high. Librations about the C axis and possibly²⁷ the A axis should be observable with ν_3 . Following a procedure similar to that used during the discussion of the KCl data the barrier heights \tilde{V}_{0A} and \tilde{V}_{0C} can be obtained. For a twofold rotation about the A axis, using a librational frequency of 71 cm⁻¹ one obtains $\tilde{V}_{0A} = 290 \text{ cm}^{-1}$ [see Eq. (3) in Ref. 1]. Thus, the first three librational states (71, 137, 206 cm^{-1}) lie below the barrier. The selection rules for the librator²⁰ allow all three transitions.28 Similarly it follows from the assumption that the 79 cm^{-1} satellite is caused by librations around the C axis that the barrier for this motion is of order 100 cm⁻¹. These potential barriers

²³ T. Timusk and W. Staude, Phys. Rev. Letters 13, 373 (1964).

Note that the electronic transition appeared to couple only to the symmetric vibrations of the NO₂⁻, i.e., ν_1 and ν_2 . ²⁴ K. F. Renk, Phys. Letters 14, 281 (1965). ²⁵ A. J. Sievers and C. D. Lytle, Phys. Letters 14, 271 (1965); C. D. Lytle, M. Sc. thesis, Cornell University, MSC Report No. 390, 1965 (unpublished); C. D. Lytle and A. J. Sievers, Bull. Am. Phys. Scc. 10, 614 (1965).

Phys. Soc. 10, 616 (1965). ²⁶ H. Bilz, K. F. Renk, and K. H. Timmesfeld, Solid State Commun. 3, 223 (1965).

²⁷ This is possible if the transition involves a libration about the A axis plus a rotation about the B axis. This satellite would be expected to be weaker, and hence detectable only for strong absorption in the fundamental vibration.

 28 The second harmonic at 137 cm⁻¹ in our spectrum appears to be more intense than the 71 cm⁻¹ line. The reason for this may be that it is in sympathetic vibration with the longitudinal mode of pure KI which occurs at 139 cm⁻¹; E. Burstein in *Phonons and Phonon Interaction*, edited by Thor A. Bak (W. A. Benjamin, Inc., New York, 1964). This possibility was suggested to us by Professor A. J. Sievers. The same satellites are expected to appear with a cond. J. Sievers. with ν_1 and ν_2 . Their absence is explained with the lower absorption of these fundamentals.

are considerably higher than those found for $KCl:NO_2$. A similar conclusion was drawn by Sack and Moriarty¹⁵ from their low-temperature dielectric measurements. They found that the NO₂⁻ dipoles in KCl followed the field oscillations to the lowest temperature of their measurement ($\sim 2^{\circ}$ K), in agreement with our findings (tunnel splitting 2 cm⁻¹). In KI their measurements of the relaxation time as function of frequency yielded an approximate barrier height for the dipole reorientation of 0.014 eV (115 cm^{-1}). Furthermore, they found that the dipole moment in KCl: NO₂ was 0.21 Debye, close to the expected value for the NO_2^{-1} ions. In KI, however, they found a dipole moment of 1 Debye. As an explanation for these observations we had suggested¹⁵ that the center of mass of the NO_2^- may not coincide with the center of the cavity. For (110) orientation of the *B* axis, the above appears likely for the $NO_2^$ in the highly polarizable I⁻ cavity with the positively charged N atom making a very close approach to the next-nearest I⁻ ion. Such an environment would tend to increase the barriers for rotations about the A and C axes.²⁹ The separation of the negative charge of the NO_2^- from the effective positive charge of the cavity would cause the large dipole moment. Such a phenomenon has also been observed for monatomic impurities.30

The central absorption band associated with ν_3 has a larger half-width and shows a stronger temperature dependence than in KCl. Its satellites are more closely spaced (1.5 to 6 cm⁻¹) and have higher intensities. These features suggest that the barrier \tilde{V}_{0B} is low in KI. Since the shape of the potential for the off-center ion must be very complex we prefer to compare the splitting with that expected for free rotation around the B axis. For this the selection rule for transitions is $\Delta J = \pm 1$ where J is the rotational quantum number. Since the B axis coincides with the C_2 symmetry axis of the molecule and the oxygen atoms obey Bose statistics only the alternate J levels will be populated.³¹ Thus the successive transitions will be separated by $4\tilde{B} \sim 1.8$ cm^{-1} which is almost equal to the observed splitting of the doublet (1.5 cm⁻¹).³² Hence an almost free rotation seems to be a reasonable approximation to the motion around the B axis. We then explain the 80.5 cm⁻¹ satellite (see Table III) with a simultaneous excitation of a libration around the C axis and a free rotation around the B axis.

In conclusion we state that an unambiguous assignment of the fine structure observed in KI is not possible

²⁹ In the determination of \tilde{V}_{0A} and \tilde{V}_{0C} we did not consider the off-center position of the ion. Hence they must be taken with a grain of salt.

⁸⁰ G. Lombardo and R. O. Pohl, Phys. Rev. Letters 15, 291 (1965).

³¹ Reference 5, p. 462.

³² We exclude the possibility that the ν_3 satellites belong to a motion around the C axis on the grounds that ν_1 and ν_2 do not show the doublet structure. The same doublet structure of μ_3 was observed with crystals doped with KN¹⁵O₂. Therefore we do not believe that it is caused by some impurities.



FIG. 7. Same as Fig. 6, but for KBr: NO₂. Here $\tilde{V}_{0A} = 5\tilde{A} = 21 \text{ cm}^{-1}$.

with the experimental information available. This fine structure may be caused by rotations of the NO_2^- ion around its *B* axis and by librations around its *A* and *C* axes and also by resonant and local modes. The understanding of these states gets further complicated by the fact that the center of mass of the ion is not located at the center of the iodine cavity.

C. KBr Host Lattice

The NO₂⁻ ion in KBr shows hindered rotational motion which is similar in some respects to that observed in KCl and in other respects to that observed in KI. Again the ν_1 and ν_2 modes show similar structures with the only difference that the ν_2 structure is more clearly resolved. Most of this structure can be interpreted with a motion of the molecule about its A axis.

Figure 7 shows the K=0, 1, 2 energy eigenvalues of the Mathieu equation for a value of $\tilde{V}_{0A} = 5\tilde{A} \sim 21 \text{ cm}^{-1}$. With such a choice of \tilde{V}_{0A} the ground state is split by about 1 cm⁻¹ in agreement with our experiments. The first excited state (be_1) lies about 10 cm⁻¹ above the state bo_1 . Thus at low temperatures (below 15°K) the only levels possessing a significant thermal population are be_0 and bo_1 . In the figure the allowed transitions from these states are shown with solid lines while the forbidden ones are shown with dashed lines. Similar to the KCl case these forbidden transitions appear to be weakly active as can be seen from the assignment given in Table V. At higher temperatures the excited levels be_1 , bo_2 , and be_2 acquire a significant thermal population. The strongest transition from be_1 is to bo_2

TABLE V. Assignment of transitions associated with ν_1 and ν_2 vibrations. KBr host lattice. The last four ν_2 satellites (808–815 cm⁻¹) are the well resolved ones in Fig. 4(b). See also Fig. 7 and text.

| Observed fr in cr | | |
|----------------------|---------|-----------------------|
| ν_1 | ν_2 | Assignment |
| | 795.0 | |
| 1316.5 | 796.5 | $P_{Q(1)}$ |
| 1318.0 | 797.5 | O(0) |
| 1319.0 | 798.5 | $\tilde{R}_{\rho(0)}$ |
| 1320.0 | 800.0 | • (-) |
| 1321.5 | 801.0 | |
| | 802.5 | |
| 1330 | 808.0 | $R_{\rho(1)}$ |
| to | 809.5 | <i>O</i> *(0) |
| 1337 | 811.0 | Ŏ*(1) |
| | 815.0 | $S_{Q(2)}; S_{Q(1)}$ |

and is separated from Q(0) by about 10 cm⁻¹. Similar transitions from bo_2 to be_3 and be_3 to bo_3 are separated from Q(0) by 16 to 20 cm⁻¹. As these transitions increase in intensity due to thermal population the closely spaced transitions arising from the ground state decrease in intensity [see Fig. 4(b) for ν_2 absorption at 80°K].

From the assignment given in Table V it can be seen that more transitions are observed than are predicted by the solutions of the Mathieu equation. Since $\tilde{C} \sim 0.42 \text{ cm}^{-1}$, it is possible that a few of the closely spaced lines are due to motions about the *C* axis of the molecule. This assignment is not unambiguous, because, in combination with ν_3 , a weak sum satellite is observed 30 cm⁻¹ away (at 1306 cm⁻¹) from the fundamental which could be due to librations about the *C* axis. Such a choice puts the librational frequency about the *C* axis at a value in between that observed in KCl and KI (i.e., between 24 and 79 cm⁻¹).

Finally, the ν_3 fundamental shows a satellite structure very similar to that observed in KI. Therefore we explain it too with an almost free rotation about the *B* axis. The splitting of the central doublet is now 1 cm⁻¹ instead of 1.5 cm⁻¹ in KI. From this a barrier height \tilde{V}_{0B} , using a twofold potential, is estimated to be 1 to 2 cm⁻¹. As in KI, this analysis is based on the doublet of the ν_3 main band. The rest of the fine structure is not well understood, in particular because the difference satellites do not seem to decrease in intensity with decreasing temperature.

We infer from the resemblance of the KBr spectrum to that of KI that an off-center position of the NO_2^{-1} ion is probable. Hence a more detailed description of the energy levels and the potential barrier heights does not seem warranted.

D. The Nitrate Ion

This ion shows a very similar spectrum in all three host lattices. The ν_3 vibration has closely spaced sum and difference satellites 4.5 cm⁻¹ apart in KCl, 2.5 cm^{1–} apart in KBr and 3.5 cm⁻¹ apart in KI. The strong temperature dependence of the intensities of these satellites indicates that they are to be associated with the equally spaced energy levels of a librating oscillator. Since no satellites were observed with the out-of-plane bending vibration ν_2 , the libration must occur about the C_3 symmetry axis of the molecule. Such a planar oscillation of the molecule would give rise to a change in $\partial \mu / \partial q_3$ but not $\partial \mu / \partial q_2$. Using N-O bond distance³³ of 1.2 Å, a value of 0.24 cm⁻¹ is obtained for the rotational constant, \tilde{A} , about the C_3 axis. From this it follows that at low temperatures the librations are very harmonic since the observed frequencies are 10 to 20 times larger than \tilde{A} . The potential well is certainly very deep since the librational satellites persist up to temperatures of about 150°K. Using a frequency of 4.5 cm^{-1} for the librational frequency and a threefold cosine potential one obtains a value of 9 cm⁻¹ for \tilde{V}_{0A} , i.e., $\tilde{V}_{0A} \sim 36\tilde{A}$ so that the potential barrier is high and the Q(0) branch always dominates the IR absorption. However, the persistance of the librational satellites at higher temperatures and the narrowness of the ν_3 vibration at all temperatures indicates that the actual height of the potential well is at least 10 times that calculated above.

Finally, the NO₃⁻ ion in KI showed two high frequancy lines, about 72.5 cm⁻¹ and 88.5 cm⁻¹ away from ν_3 . These lines, similar to those observed with NO₂⁻, lie in the gap and could be due to librations about other axes of inertia or translational local modes.³⁴ Since the NO₃⁻ ion has symmetry D_{3h} , two translational modes of symmetry A_2'' and E' are allowed. Both modes can coupled strongly to the phonons. In the following we shall see if the same holds for the NO₂⁻ ion.

IV. THERMAL CONDUCTIVITY

In I we concluded that the tunneling and the rotational states of the CN⁻ ion in solid solution are coupled strongly to the phonons. In the following we shall see if the same holds for the NO_2^- ion. Figure 8 shows the thermal conductivity data of KCl:NO₂. They are an extension of work reported earlier³ in which a defect scattering rate τ_{def}^{-1} $=ND\omega_0^2\omega^2(\omega_0^2-\omega^2)^{-2}$ was shown to qualitatively fit the depression in the thermal conductivity of the doped crystals. More careful fits to the experimental data are the solid lines in Fig. 8 calculated with the above equation using $\omega_0 = 3.8 \times 10^{12} \text{ sec}^{-1}$ (20 cm⁻¹) and $D=3.3\times10^{-10}$ sec⁻¹ cm³. N is an effective concentration adjusted to fit each curve. The scaling of Nwith the spectroscopically determined concentration is shown in Fig. 9. The agreement of the computed curves with the data in Fig. 8 is good above 2°K. Below 2°K appears to be evidence for another resonance at



FIG. 8. Thermal conductivity of KCl:NO₂. NO₂⁻ concentrations: (A) undoped; (B) 9×10^{16} cm⁻³; (C) 4×10^{17} cm⁻³; (D) 1.6×10^{18} cm⁻³; (E) 4×10^{18} cm⁻³; (F) 4×10^{19} cm⁻³. NO₃⁻ concentration: (A) and (B): not detectable; (C) 1.3×10^{16} cm⁻³; (D) 1.2×10^{18} cm⁻³; (E) 4.5×10^{17} cm⁻³; (F) unknown. Curves are machine fits.

 $\omega_1 < 1.5 \times 10^{11} \text{ sec}^{-1} (<0.8 \text{ cm}^{-1}).^{35}$ We attribute the high-frequency resonance to scattering by states of free rotation. From the infrared studies these were determined to begin around 12 cm⁻¹ (*A* axis), 11 cm⁻¹ (*B* axis), and 40 cm⁻¹ (*C* axis). We believe that the resonance frequency of 20 cm⁻¹ seen in the thermal conductivity represents some average of these three energies. From our experience it appears impossible to resolve two resonance frequencies separated by less than a factor of 3 except through a flattening of the "dip" which is indeed noticed in Fig. 8. The suspected resonance at <0.8 cm⁻¹ may be caused by tunneling about the *C* axis estimated to be <0.5 cm⁻¹ from the IR data. Tunneling around the *A* axis might also be involved (2 cm⁻¹).

The thermal conductivity of KBr:NO₂ is shown in Fig. 10. In previous work⁴ it was shown that the data above 1.5°K could be described with a scattering rate $\tau_{def}^{-1} = NA\omega$ where $A = 8 \times 10^{-23}$ cm³ and N is the NO₂⁻ concentration. This rate leads to a T^2 dependence of the thermal conductivity. The rapid recovery of the thermal conductivity below 1°K observed in the present work indicates that the scattering cross section for

 $^{^{33}}$ R. L. Sass, R. Vidale, and J. Donahue, Acta Cryst. 10, 567 (1957). 34 The other fundamentals of $\rm NO_3^-$ are much weaker. Therefore

³⁴ The other fundamentals of NO₃⁻ are much weaker. Therefore we cannot expect to see any of these relatively weak satellites with them.

³⁵ From the apparent depression at T < 0.3°K we conclude that the resonance energy must be less than 0.8 cm⁻¹. See I, Ref. 72, for the dominant phonon frequency argument.



FIG. 9. Comparison of effective NO_2^- concentrations as determined from best fit to thermal-conductivity data (Fig. 8) with spectroscopically determined NO_2^- concentrations. Straight line has slope of one.

 $\omega < 6 \times 10^{11} \text{ sec}^{-1}$ (~2 cm⁻¹) decreases rapidly. We suggest that such scattering could result from a series of closely spaced rotational levels with a splitting of $1-2 \text{ cm}^{-1}$ as should be found for a very low barrier around the *B* or *C* axis (for which the rotational constants are small). In the discussion of the IR data we suspected such a low barrier for the *B* axis. Thus the thermal conductivity results lend support to that assumption. The peculiar frequency dependence of the scattering cross section ($\propto \omega$) could presumably be explained as a sum of a number of resonances, but probably a continuum treatment would be more appropriate. Note also that the ground state splitting for motion about the *A*-axis was found to be 1.1 cm⁻¹ (Fig. 7).

Figure 11 shows the thermal conductivity of KI: NO₂. The conductivity of the doped crystal is uniformly lower at low temperatures and shows no structure. The scattering is about 25 times weaker here than for NO₂in KCl and the defect scattering rate is approximately frequency-independent. The phonon scattering above the conductivity maximum seems to be stronger than in KCl and KBr. We explain the low-temperature phonon scattering with excitation of the molecules over the low barrier which in this case is for rotation around the B axis. Motions about this axis do not involve a change in the orientation of the electrical dipole of the NO_2^{-} ion. We speculate that the weaker scattering may be an indication that the phonon-defect coupling is through the electrical dipole moment μ rather than through the stress dipole. The phonon scattering at high temperatures $(T>20^{\circ}K)$ is consistent with the high barriers for rotations around the A and C axes deduced from the IR spectra. It was observed by Baumann,³⁶ however, that KI containing monatomic Cl⁻ ions has a thermal conductivity similar to that observed in KI:NO₂. Hence the phonon scattering may also be caused by impurity modes not involving a rotation of the NO_2^- ion.

Next, let us consider a possible phonon scattering by librational states. In previous work⁴ it had been noted that the NO_3^- ions had no noticeable influence on the thermal conductivity in KBr. From the present work we know that the barrier to rotation is very high for this defect. Hence the only energy levels comparable in energy to the energy of the phonons carrying the heat in our experiments (energies between 1 and 100 cm⁻¹) are those of libration. So we conclude again that the librational states are relatively weakly coupled to the phonons.

So far we have been able to correlate the phonon scattering with the tunneling or rotational states of the molecular dopings. This is not possible for NaCl doped with NaNO₂. One sample, doped with 0.025 mole% in the melt, and containing *ca.* 2×10^{16} cm⁻³ isolated NO₂⁻ ions, was measured between 2° and 0.3°K. Below 2°K, $K=4\times10^{-3}$ T³ W cm⁻¹ deg⁻⁴, with a rapid recovery toward that of pure NaCl below 0.5°K. Two other samples, doped with 0.04 and 0.1 mole % and containing 1×10^{17} and 1.3×10^{18} cm⁻³ NO₂⁻ ions as determined spectroscopically at room



FIG. 10. Thermal conductivity of KBr:NO₂. NO₂⁻ concentrations: (A) undoped; (B) 3.5×10^{17} cm⁻³ (circles) and 4×10^{17} cm⁻³ (triagles); (C) 5.3×10^{18} cm⁻³; (D) 5.7×10^{19} cm⁻³. NO₃⁻ concentrations: (B) 10^{16} cm⁻³ (circles) and 2×10^{17} cm⁻³ (triangles); (C) 1.5×10^{18} cm⁻³; (D) 1.1×10^{19} cm⁻³.

³⁶ F. Baumann (to be published). See also C. T. Walker and R. O. Pohl, Phys. Rev. 131, 1433 (1963), and C. W. McCombie and J. Slater, Proc. Phys. Soc. (London), 84, 499 (1964), also for earlier references.

temperature, showed identical conductivities. The curve was very similar to those obtained previously by Klein³⁷ on NaCl doped with about the same mole ratios of NaOH, NaOD, and Na₂O₂, with an indentation in the conductivity curve at about 5°K and a conductivity proportional to T^3 above and below.

From the IR work it appeared that the NO_2^{-} ions in NaCl are frozen in at low temperatures. Hence we do not expect any phonon scattering through rotational motions of the ion. We ascribe, therefore, the strong scattering at low temperatures to what appeared in the IR as NaNO₂ clusters, or to some decomposition products of the dopings, as suggested previously by Klein.

Finally the influence of an electric field on the thermal conductivity of KCl:NO₂ was studied, Fig. 12. In spite of the complexity of the energy levels of the NO₂⁻ ion as borne out by infrared and thermalconductivity results the field effect is just what one would expect if a resonance frequency were shifted upward by the electric field. At high temperatures the resistivity increases whereas at low temperatures it decreases. The dotted line in Fig. 12 was computed using an initial resonance angular frequency of 3.0×10^{11} sec⁻¹ and a shifted frequency of 3.6×10^{11} sec⁻¹. With the experimental data available a more precise fit of the data is not warranted. One might speculate, however,



FIG. 11. Thermal conductivity of KI:NO₂. (A) undoped; (B) 10¹⁹ cm⁻³ NO₂⁻; NO₃⁻: unknown.

 37 M. V. Klein, Phys. Rev. 122, 1393 (1961). In this connection it is worth emphasizing that our crystals were doped with previously vacuum dried reagent grade NaNO₂ using alumina or quartz crucibles. Klein had used graphite crucibles. Apart from this our crystal preparation was the same as that reported by Klein.



FIG. 12. Influence of a dc electric field on the thermal conductivity. Plotted is $\Delta R/R$, the increase in thermal resistivity when the field is turned on, divided by the zero-field resistivity. Open and closed circles: KCl with $4.1 \times 10^{18} \text{ NO}_2^-$ and $4.5 \times 10^{17} \text{ cm}^ \text{NO}_5^-$ for 15 and 20 kV cm⁻¹, respectively. Squares: KBr $+5.3 \times 10^{18} \text{ NO}_2^-$ cm⁻³ and $1.5 \times 10^{18} \text{ NO}_5^-$ cm⁻³ for 20 kV cm⁻¹. For zero-field resistivity see Fig. 8, curve (E) and Fig. 10, curve (C), respectively. The dashed curve was computed (ω_0 : 1.6 cm⁻¹, $\omega_0 + \Delta$: 1.9 cm⁻¹) and is intended only to show the qualitative behavior of the $\Delta R/R$ curves. Details in text. The computed curve has a minimum of -45% at 0.4°K.

that the tunneling frequency as predicted from thermal conductivity and infrared data $(0.5-0.8 \text{ cm}^{-1})$ when shifted by about 20% would fit the above data better. Further work on this is in progress.

SUMMARY AND CONCLUSIONS

Through measurements of the fine structure observed with the infrared active normal modes of NO₂and NO3⁻ ions substituted into alkali halide lattices combined with measurements of the thermal conductivity a detailed picture of the degrees of freedom for molecular motion has been obtained. It has been shown that the molecule can rotate about each one of the three principal axes of inertia. In the equilibrium orientation the permanent dipole moment points in the $\langle 110 \rangle$ direction. Unlike the case of the CN⁻ discussed in I, the barrier hindering rotation depends strongly on the cavity size. Similar to the case of the CN⁻ it was found that the rotational and tunneling states couple to the phonons. In KBr the phonon scattering cross section is not given by a resonance expression as in KCl. Instead it is proportional to the phonon frequency. We suspect that this is due to the large number of rotational levels available in this host lattice, each of which scatters phonons with a resonance scattering cross section, but with a different resonant frequency. The NO3⁻ ion appears to be frozen in all host lattices even at room temperature. Here only librational motion is found, and no phonon scattering is observed. From our studies of molecular systems, therefore, the weak coupling of phonons to librational states appears to be a general property of molecules in alkali halides.

In KI a rich fine structure is found with a spacing between 50 and 80 cm⁻¹. These energies are found to be identical with those found in direct optical excitation in the far IR as well as in vibronic absorption. Hence near infrared spectroscopy appears to be a useful tool for the study of impurity modes connected with defects. This study has led us to a new model for the nature of the impurity modes. We propose that some of the gap modes are high-frequency librations.

The results of our studies of the rotational degrees of freedom of molecules in solids in this and the preceding paper can be summarized as follows: Pauling's model describes the rotational degrees of freedom of molecules in solid solution very well, in particular in the alkali chlorides, and to a somewhat lesser degree also in the bromides. In the iodides, particularly in the system KI:NO₂, the motion is more complex, and we conclude that in addition to the rotational motion a translational motion of the ion, similar to that found recently in KCl:Li, is observed. Another way of expressing this is that the Pauling potential has a considerably more complicated structure for KI:NO₂ with a larger number of not necessarily equivalent wells. The beginning of this is already noticed in KBr. More work will be required to determine these potentials accurately. It must be kept in mind, though, that in the more highly polarizable host lattices the assumption of a rigid potential becomes questionable. In addition to translational and rotational motion of the impurity molecule a rearrangement of the nearestneighbor ions must be expected. Such a rearrangement is presently under study, using monatomic impurities in alkali bromides and iodides.

APPENDIX

The isotopic shift of molecular normal-mode frefrequencies plays an important role in the assignment of infrared absorption lines. In this investigation we have made extensive use of this technique by comparing crystals containing the normal N¹⁴O¹⁶₂ and N¹⁴O¹⁶₃ ions with crystals containing isotopically enriched $\rm N^{15}O^{16}{}_2^{-}$ and $\rm N^{15}O^{16}{}_3^{-}$ ions. The error in our frequency determination was less than 1 cm⁻¹. The observed shifts are given in Table VI. For a comparison with the theory the O-N-O bond angle, 2α , was calculated by means of the formula⁵

$$\frac{\nu_{3}^{(i)}}{\nu_{3}} = \frac{m_{\rm N}m_{\rm O}}{m_{\rm N}^{(i)}m_{\rm O}} \frac{m_{\rm N}^{(i)} + 2m_{\rm O}\sin^{2}\alpha}{m_{\rm N} + 2m_{\rm O}\sin^{2}\alpha}$$

where the superscript (i) stands for the isotopic molecule and m_N and m_O are the masses of the nitrogen

TABLE VI. Experimentally observed isotopic shifts of the NO_2^- vibrations, compared to the $N^{4}O^{16}_2^-$ ions. Heavier molecules have lower frequencies. For a listing of the isotopic shifts in NO₃⁻ we refer to Table II.

| Mode | Isotopic shift experiment |
|--|--|
| $\begin{array}{c} \nu_1(\mathrm{N^{16}O^{16}g^-}) \\ \nu_2(\mathrm{N^{16}O^{16}g^-}) \\ \nu_3(\mathrm{N^{15}O^{16}g^-}) \\ \nu_1 + \nu_3(\mathrm{N^{16}O^{16}g^-}) \\ \nu_3(\mathrm{N^{14}O^{16}O^{18}-}) \end{array}$ | $\begin{array}{cccc} 23 & \mathrm{cm}^{-1} \\ 4.5 & \mathrm{cm}^{-1} \\ 26 & \mathrm{cm}^{-1} \\ 48-49 & \mathrm{cm}^{-1} \\ 17-20 & \mathrm{cm}^{-1} \end{array}$ |

and oxygen atoms, respectively. Using the experimentally observed values of 1227 cm⁻¹ for N¹⁵ and 1253 cm⁻¹ for N¹⁴ for the ν_3 vibration in KI, we find $2\alpha = 118^{\circ} \pm 2^{\circ}$, in excellent agreement with the bond angles obtained previously by Carpenter¹⁸ for the NO₂⁻ in NaNO₂ from x-ray diffraction measurements and by Sidman³⁸ and Price et al.,³⁹ from studies of the isotopic shift of the ν_3 vibration of NO₂⁻ in pure NaNO₂ and in alkali-halide pressed pellets. The isotopic shift for ν_1 and ν_2 is given by the formula⁴⁰

$$\frac{\Delta \nu_1}{\nu_1} + \frac{\Delta \nu_2}{\nu_2} = -\frac{m_{\rm O}(m_{\rm N}{}^{(i)} - m_{\rm N})}{m_{\rm N}{}^{(i)}(2m_{\rm O} + m_{\rm N})} = -0.02319.$$

The observed shifts of -4.5 and -23 cm⁻¹ for KI yield

$$(\Delta \nu_1 / \nu_1) + (\Delta \nu_2 / \nu_2) = -0.0227$$

Thus the agreement between theory and experiment is excellent.

The isotope effect due to N¹⁵ was also observed in KBr and KCl. The natural abundance of N^{15} is 0.36%and the weak lines observed at 1250 cm^{-1} in KBr and 1263 cm⁻¹ in KCl are the ν_3 lines due to this isotope. The calculated bond angle is found to be the same in all three host lattices.

Finally the lines at 1270 cm^{-1} in KCl, 1258 cm^{-1} in KBr and 1236 cm⁻¹ in KI are probably due to (NO¹⁶O¹⁸)⁻⁻ which has a natural abundance of 0.2%. The agreement between theory and experiment is, however, not as good for these O¹⁸ lines. According to theory the shift should be about 14 cm⁻¹ while the observed shifts are between 17 and 20 cm⁻¹. In order to conclusively decide the origin of these lines it would be necessary to grow crystals with enriched O¹⁸.

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