

of the nearest-neighbor amplitude to that of the nitrogen nucleus is called α for the vibration responsible for the 183.6-cm^{-1} absorption and β for the 99.7-cm^{-1} band, then the following relationship can be derived: $(183.6/99.7)^2 = (1-\alpha)/(1-\beta)$. (All motion has been considered to be in a direction parallel to the plane in which the NCO^- oscillates.) Since both α and β must be small numbers ($-0.20 < \alpha < 0.20$ and $-0.42 < \beta < 0.42$) to stay within the observed degree of localization, then α can be seen to be a small negative number and β can be seen to be a small positive number.¹⁵ Thus, the three nearest neighbors must move with the nitrogen nucleus during the 99.7-cm^{-1} vibration and against it in the 183.6-cm^{-1} vibration. A similar result is obtained for the near neighbors to the oxygen nucleus for the other two bands, at 97.4 and 167.5 cm^{-1} .

The nature of the vibrations associated with the four bands can now be more fully described. The 97.4-cm^{-1} band is due to torsional oscillations of the NCO^- ion about an axis perpendicularly dividing the N-C bond, accompanied by an in-phase (acoustical) movement of the three potassium ion forming a ring round the oxygen nucleus of the NCO^- ion. The 99.7-cm^{-1} band corresponds to a large nitrogen amplitude acoustic torsional mode. The 167.5-cm^{-1} band is due to a large oxygen amplitude optical torsion and the 183.6-cm^{-1} band is due to a large nitrogen amplitude optical torsion.

Only the three nearest neighbors to the large amplitude nucleus of the NCO^- ion are being referred to when the terms "acoustic" and "optic" are used in the above description. Figure 5 shows schematically the four vibrations as described above. It is possible,

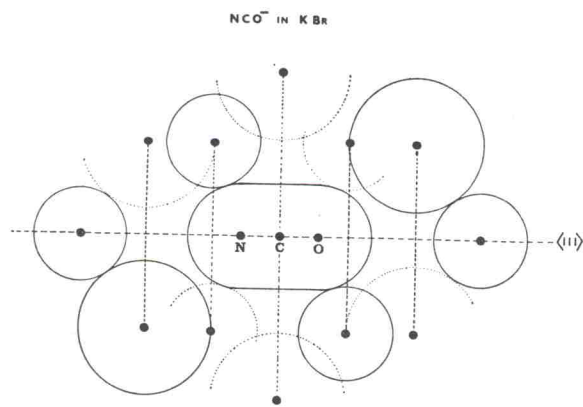


FIG. 4. Schematic presentation of the KBr environment surrounding an NCO^- present as a substitutional impurity with its axis orientated in a $\langle 111 \rangle$ direction is drawn to scale using Goldschmidt radii. The small circles represent K^+ ions, the large circles Br^- ions. Ions in the plane of the paper are presented as solid circles, ions out of this plane are shown dotted. Note particularly how the NCO^- is held between two rings of K^+ ions, each composed of one ion in the plane of the paper and two out of this plane.

¹⁵ α could only go positive if β were made greater than 0.705 , or β negative if α were taken more negative than -2.39 ; these two possibilities are outside the admissible range.

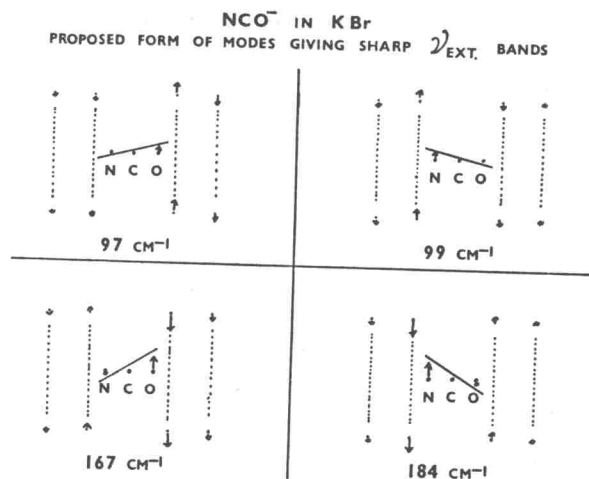


FIG. 5. Proposed form of the vibrations giving sharp bands in the external-mode spectrum of NCO^- isolated in KBr. The dotted lines represent the planes of nearest and next nearest neighbors illustrated in Fig. 4.

starting with the diagrams of Fig. 5, to calculate amplitude envelope functions which decay exponentially with distance from the large amplitude NCO^- nucleus such that the vibrations depicted have about the observed delocalization factors, while satisfying the requirements of no-net translation and zero-net angular momentum. A small percentage of the motion of some of the ions is required to be nonparallel to the plane in which the NCO^- ion oscillates.

Several points mentioned earlier are illustrated in the diagrams of Fig. 5. Firstly, the degree of delocalization of the acoustic-type modes was found to be greater than their corresponding optic-type modes (factors of 7 and 4 compared with $2\frac{1}{2}$ and $1\frac{1}{2}$; see Table I). The requirement of stationary c.m. could ideally be satisfied by the nearest neighbors alone for the optic-type modes, whereas in the acoustic-type modes at least the next nearest neighbors are required. It soon becomes apparent when making calculations on the models illustrated in Fig. 5, that the optic-type modes for this system are inevitably going to be more highly localized than the corresponding acoustic modes.

Secondly, the fact that all four sharp features in the ν_{ext} spectrum, shown in Fig. 2, are being attributed to localized torsional modes is seen to be quite reasonable. A calculation of the somewhat similar modes involving translation of the NCO^- ion results in appreciably lower frequencies. Essentially, this is because the whole NCO^- mass vibrates against the environment in the translational modes, whereas effectively only one end is concerned in the torsional case. Thus it is to be expected that modes involving torsion of this impurity ion will find it easiest to rise in frequency, sufficiently to come clear of the corresponding lattice band and appear as sharp localized absorptions.

This pattern of localized acoustic- and optic-type torsional modes which we have justified above for the

case of NCO^- in KBr we believe to be a general feature of many polyatomic impurity ion in alkali-halide ν_{ext} spectra.

The proposed torsional nature of these modes would explain why when N_3^- or BO_2^- is used in KBr as the source of ν_{int} , only one in-the-gap and one superoptic mode is seen. (See Refs. 3 and 5.) In these cases, as was mentioned earlier, it is the torsional modes (R_x, R_y) that are expected to be active in combination with ν_3 .¹⁶

If NO_2^- or NO_3^- (see Refs. 4, 5, and 9) or any other nonlinear ion is used, an increased number of lines becomes possible in terms of torsional motion about different axes.

Since the torsional motion of the ions seemed likely to be playing an important part in at least some of the sharper features in the ν_{ext} spectra of polyatomic impurity ions in alkali halides, it was decided that the ν_{ext} spectra for ions suspected of hindered rotation¹⁷⁻¹⁹ should be further investigated. Reference 5 contains some of our earlier data on ν_{ext} for CN^- in the sodium halides, where ν_{int} was sharp enough at 90°K for the ν_{ext} features to be seen virtually undistorted. In the sodium halides, the barriers to rotation of the CN^- ion are quite large,^{17,19} and it is the corresponding spectra for this ion in the potassium, rubidium, or cesium halides where it is able to rotate relatively freely that are interesting in the present context. For CN^- isolated in these halides, however, it is necessary to work at temperatures of 15°K or below if ν_{int} is to be reduced to a useably sharp line. At temperatures below 15°K the difference part of the spectrum ($\nu_{\text{int}} - \nu_{\text{ext}}$) is almost completely suppressed, which is unfortunate from the point of view of checking the identification of features in the $\nu_{\text{int}} + \nu_{\text{ext}}$ region. However, bands due to other impurities which might be found in the relevant region are unlikely to show the marked temperature dependence below 25°K that is expected of the spectra of interest. In all our heavily cyanide-doped crystals, there was at least a small amount of cyanate impurity also. Although $\nu_3(\text{NCO}^-)$ is usually a very sharp band, its presence in these spectra is unfortunate in that it appears in the various alkali halides at 90–100 cm^{-1} above the fundamental cyanide band, which is a region of considerable interest in many of the ν_{ext} spectra.

CN⁻ IN KBr

Figure 6 shows the spectrum obtained from a 1-cm-long crystal of KBr at about 7°K, which was nominally

¹⁶ However, the four sharp NCO^- bands must all be doubly degenerate and the two N_3^- bands would each be fourfold degenerate. Thus they cannot simply represent the rigid-body modes, but must include six degrees of freedom "borrowed" from the lattice modes.

¹⁷ W. D. Seward and V. Narayanamurti, Phys. Rev. 148, 463 (1966).

¹⁸ V. Narayanamurti, W. D. Seward, and R. O. Pohl, Phys. Rev. 148, 481 (1966).

¹⁹ G. R. Field and W. F. Sherman, J. Chem. Phys. 47, 2378 (1967).

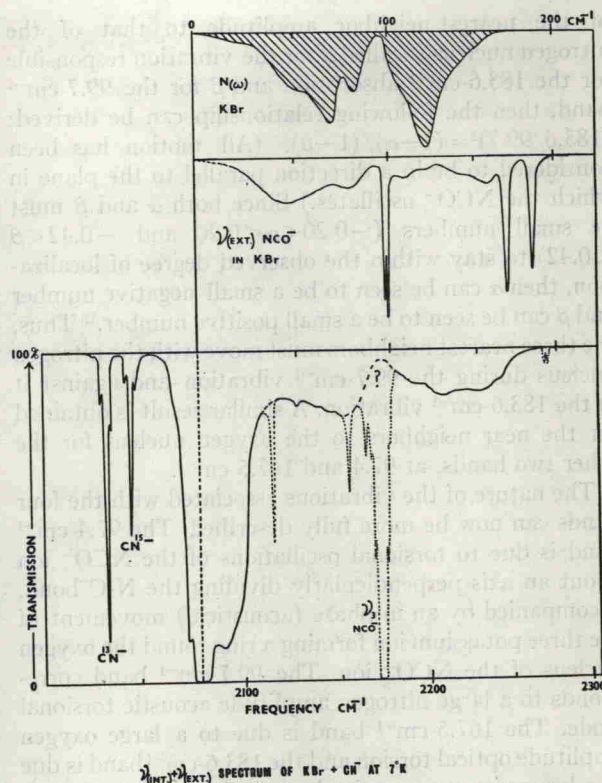


Fig. 6. 7°K absorption spectrum of CN^- -doped KBr. The external modes seen in combination with the C-N stretching mode (2078 cm^{-1}) of the $(\text{C}^{12}\text{N}^{14})^-$ species are compared with the similar spectrum for NCO^- in KBr and the integrated density of states for KBr (see Ref. 13). Features due to NCO^- in the CN^- -doped crystal have been shown dotted.

doped with 0.8% CN^- . In this, the most heavily doped crystal that we used, almost 10% of the cyanide is estimated to have converted to cyanate.

The strong band at 2078 cm^{-1} is due to the stretching vibration of the $(\text{C}^{12}\text{N}^{14})^-$ ion. Its strength can be gauged from the intensity of the less abundant isotopic species [i.e., it is approximately 90 times stronger than the $(\text{C}^{13}\text{N}^{14})^-$ band]. The external-mode bands of interest in this figure are those seen in combination with the 2078- cm^{-1} C-N stretching mode, and for comparison, the density of states of pure KBr¹³ and the external modes found in combination with $\nu_3(\text{NCO}^-)$ isolated in KBr have been drawn to the same scale, starting vertically above the 2078- cm^{-1} line. Concentration-dependent satellites (see Ref. 3), which can be clearly seen on the low abundant isotopic species of the cyanide ion, are absorbing effectively 100% on the 2078- cm^{-1} band and giving it an unnatural width. The greater transition probability¹⁹ of the $\nu_3(\text{NCO}^-)$ results in a peak absorbance ratio of only about 3:1 in favor of the CN^- bands in spite of the estimated 10:1 ratio in numbers.

First, consider the unobscured optic and superoptic regions of Fig. 6, where it can be seen that there are no sharp features in this spectrum. The acoustic to optic