

quadrupole) and the transition moment of ν_{int} define directions within the crystal, in contrast to the point impurity system. Thus, although all modes will in general be allowed, in the sense that they are not forbidden by any selection rules, it is to be expected that the relative intensities with which they appear, both directly and in binary combination with ν_{int} (vibrational, or electronic), will vary considerably, just as the intensities of the various allowed internal modes are found to vary considerably.

$\nu_{\text{int}} \pm \nu_{\text{ext}}$ spectra for a variety of ions in up to 12 different alkali halides will now be presented. The type of impurity ion motion to be associated with specific features in ν_{ext} will be considered, as will the relevance of impurity-ion axis orientation, and an indication will be given of the information which can be obtained from the pressure dependence of these spectra.

NCO⁻ IN KBr

Figure 2 shows the $\nu_3 \pm \nu_{\text{ext}}$ spectrum for NCO⁻ isolated in KBr compared with the dispersion curves of the lattice vibrations of KBr at 90°K obtained from neutron-scattering experiments.¹³ This was the first impurity ion spectrum of this kind which we investigated (see Ref. 3), and the four relatively sharp lines to be seen in ν_{ext} make it an attractive spectrum with which to work. Dispersion curves have been used in

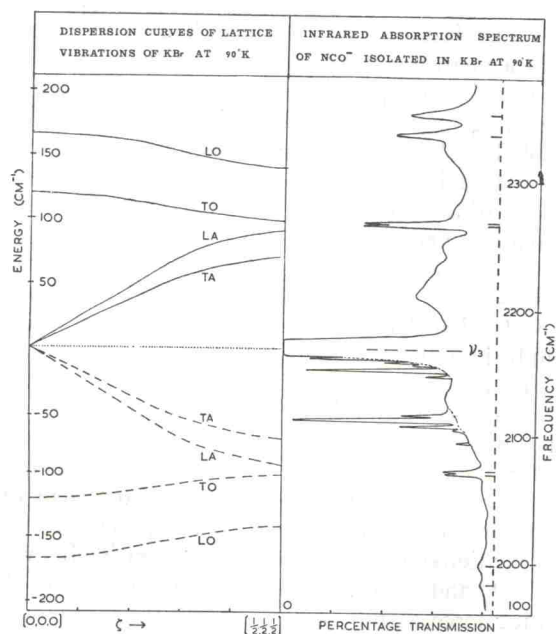


FIG. 2. Absorption spectrum of NCO⁻ isolated in KBr, showing the external-mode vibrations in sum and difference combination with ν_3 compared with the $\langle 111 \rangle$ dispersion curves of the lattice vibrations of pure KBr. The sharp, dotted-under features to the low-energy side of the main ν_3 absorption line are due to small traces of the various isotopic species of NCO⁻ as they occur in natural abundance. (See Ref. 3.)

¹³ A. D. B. Woods, B. N. Brockhouse, R. A. Cowley, and W. Cochran, Phys. Rev. 131, 1025 (1963).

LOCAL MODE FREQUENCIES AT 100°K OF NCO⁻ ISOLATED IN KBr

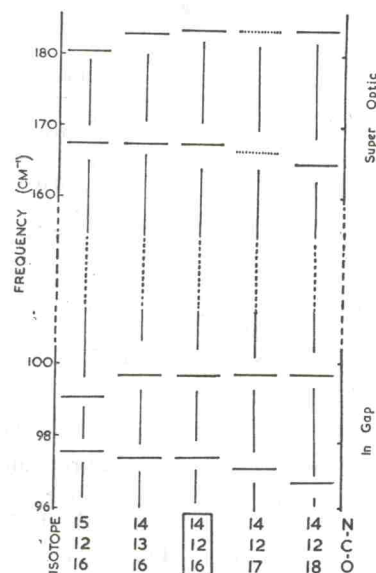


FIG. 3. External local-mode frequencies found in combination with ν_3 (NCO⁻) isolated in KBr for the various isotopic species.

Fig. 2, because it is believed that this type of presentation shows most clearly the interrelation of the ν_{ext} spectra with the host-lattice properties. It is not intended to suggest that preferential combination takes place with lattice vibrations which propagate in any particular direction, or even that the radiant energy is directly transformed into propagating modes, although it is quickly dissipated via such modes.

In Ref. 3, the C¹²-to-C¹³ shift in the four sharp bands shown in ν_{ext} (see Fig. 2) was found to be very small. Since for a completely localized translational mode this shift would be just over 1 cm⁻¹ for lines at 97.4 and 99.7 cm⁻¹ and about 2 cm⁻¹ for bands at 167.5 and 183.6 cm⁻¹, it was suggested that these bands did not represent highly localized vibrations. However, our trial calculations on the motion of polyatomic impurities suggest that in this case, and in many others, torsional oscillations are likely to produce the highest-energy (and therefore most clearly resolved) localized modes.

In this type of motion, the isotopic mass of the center nucleus is relatively unimportant, and for this reason we decided to investigate the effects of the other isotopic substitutions that were possible with the NCO⁻ ion.

Figure 3 shows schematically the sharp external-mode frequency data collected for the isotopically different species of NCO⁻ ions isolated in KBr.

Although very high purity isotopically enriched samples are available, the data presented in Fig. 3 refer to samples which contain only partial enrichment. This allowed the separation of peaks to be measured for two different species in the same sample, at the same

TABLE I. Isotopic frequency shifts (in cm^{-1}) of sharp external-mode features found in combination with $\nu_3(\text{NCO}^-)$ isolated in KBr. The observed values are compared with values calculated on the assumption of pure torsional modes within an infinitely massive containing well, about two axes perpendicular to the ion axis, one bisecting the N-C bond and the other bisecting the C-O bond. Figures in brackets represent $\text{calc}\Delta\nu/\text{scaling factor}$.

$(\nu_{\text{int}} + \nu_{\text{ext}}) - \nu_{\text{int}}$ $\text{N}^{14}\text{C}^{12}\text{O}^{16}$	97.4 cm^{-1}	99.7 cm^{-1}	167.5 cm^{-1}	183.6 cm^{-1}	
$\Delta\nu(14,12,16)-(15,12,16)$	-0.2 0.2(0.03)	0.6 2.5(0.62)	~ 0 0.5(0.2)	3 4 (3.0)	obs. calc.
$\Delta\nu(14,12,16)-(14,13,16)$	0 0.2(0.03)	0 0.2(0.05)	~ 0 0.4(0.16)	0.4 0.4(0.3)	obs. calc.
$\Delta\nu(14,12,16)-(14,12,17)$	0.3 2.5(0.34)	~ 0 0.3(0.07)	~ 1.5 4 (1.6)	~ 0 0.5(0.37)	obs. calc.
$\Delta\nu(14,12,16)-(14,12,18)$	0.7 5 (0.71)	~ 0 0.6(0.15)	3 8 (3.2)	~ 0 1 (0.7)	obs. calc.
Estimated reliability of observed frequency shifts	± 0.15	± 0.15	± 0.3	± 0.3	
Scaling (delocalization) factor	~ 7	~ 4	$\sim 2\frac{1}{2}$	$\sim 1\frac{1}{2}$	

temperature on the same spectrum. A spectral resolution of better than 1 cm^{-1} was used with a precision of about $\pm 0.1 \text{ cm}^{-1}$, but we only feel justified in quoting values for centers of the broader, superoptic bands to an accuracy of about $\pm 0.2 \text{ cm}^{-1}$. This means that with the possible exception of the $97.4\text{--}97.6\text{-cm}^{-1}$ shift for N^{15} substitution, the frequency changes shown in Fig. 3 are all unambiguously established. The samples used were about 1 cm along the radiation path and about 6 mm by 4 mm in cross section. They were grown from the melt with total NCO^- doping of about 0.8% anion replacement, and were apparently completely homogeneous.

If the features referred to in Fig. 3 are described as a sharp in-the-gap doublet, and a broader superoptic doublet, then it can be seen that oxygen substitution effects only the lower component of each doublet, while nitrogen substitution effects primarily the upper components, and carbon substitution has very little effect on any of these bands. There would appear to be only one plausible expansion of these shifts. The motion of the NCO^- ion is predominantly torsional in all four cases. The 97.4-cm^{-1} and 167.5-cm^{-1} bands involve large oxygen movement and small carbon and nitrogen movement, and thus represent torsion about an axis cutting the NCO^- ion somewhere along the C-N bond. The 99.7-cm^{-1} and 183.6-cm^{-1} bands involve large nitrogen movement and therefore represent torsion about an axis cutting the C-O bond. It remains to distinguish between the in-the-gap modes and the superoptic modes in terms of the part played by the environment.

What information is available about the part played by the environment? Consider first the magnitude of the observed frequency shifts compared with the values obtained from the simplest possible calculation of such shifts. Table I shows this comparison. The assumptions made in the calculation are: (i) The NCO^- ion is treated as rigid; (ii) the N-C spacing is taken equal to the C-O spacing within the NCO^- ion; (iii) the 97.4-cm^{-1} and 167.5-cm^{-1} bands result from torsional motion about an axis which perpendicularly bisects the C-N bond; (iv) the

99.7-cm^{-1} and 183.6-cm^{-1} bands represent torsional motion about an axis which perpendicularly bisects the C-O bond; (v) the motion takes place within an infinitely massive containing potential well. (This ignores the fact that these could not all be normal vibrations of such an oversimplified system.¹⁴)

The general form of the table of calculated values can be seen to result immediately from the fact that the sensitivity to mass change of a given oscillation is nine times greater for the nucleus farthest from its torsional axis than it is for either of the other two. These calculated shifts are all inevitably too large, but if a scaling factor is associated with each absorption band, then agreement between calculated and observed shifts (within the experimental errors) is easily obtained. The scaling factors required are included at the foot of Table I, and indicate the extent of the environmental participation in the motion. Thus for the 97.4-cm^{-1} band $6/7$ of the energy is associated with motion of the environment and only $1/7$ with motion of the NCO^- ion, whereas for the 183.6-cm^{-1} band only $\frac{1}{4}$ of the energy is associated with the environment and $\frac{3}{4}$ with the NCO^- ion. This scaling, or delocalization, factor would be infinite for a completely delocalized mode and unity for a completely localized mode.

These delocalization factors show that the superoptic modes are more localized than the in-the-gap modes, and for both doublets the higher-energy component (large nitrogen amplitude) is more localized than the lower-energy component (large oxygen amplitude).

Calculations on the force constants operating between the NCO^- and its neighbors show that the bulk of the restoring force acting on an NCO^- rotated out of its $\langle 111 \rangle$ equilibrium orientation comes from the two rings of three nearest neighbors between which it can be regarded as being held (see Fig. 4). If only the nearest-neighbor restoring force is considered, and the ratio

¹⁴ A fairly simple system which would be capable of all these modes is obtained if each of the three NCO^- nuclei is surrounded by a ring (of neighboring ions moving together), when out of the 27 deg of freedom, eight (four double degenerate modes) involve large torsional motion of the NCO^- .