

features were all visible in the $\nu_{\text{int}}-\nu_{\text{ext}}$ spectra, thus allowing us to be fairly sure about the features, if any, which are obscured by the NCO^- bands. Since the spectra for the potassium halides only began to show their true shape below 20°K, no such assistance from $\nu_{\text{int}}-\nu_{\text{ext}}$ features is available for them.

Points of interest about these spectra may be listed as follows: (a) There are no strong sharp features in the chloride spectra. (b) There are no strong superoptic features in any of the spectra. (c) The smallest separation feature is only about $12\frac{1}{2} \text{ cm}^{-1}$ above the main band for all three potassium halides, whereas it is seen at 27, 38, and 54 cm^{-1} , respectively, in sodium iodide, bromide, and chloride.

The lightness of the impurity is seen not to be a dominant factor in determining the presence either of sharp features or strong superoptic structure in the ν_{ext} spectra. Although the canide ion is lighter than the chloride ion which it replaces and the translational restoring forces are quite comparable to those acting on a host-lattice ion it is known^{17,19} that the rotational restoring force is very small, particularly in the potassium halides. The absence of any in-the-gap or superoptic features which could be considered as directly analogous to the structure observed in the cyanate spectra appears to be consistent with the proposed torsional origin of the cyanate bands and the known tendency of the cyanide to perform hindered rotation in these alkali halides.

If the nature of the acoustic- and optic-torsional modes proposed for NCO^- is considered as a function of steadily decreasing torsional restoring force, then the acoustic torsion can be seen to go over into hindered rotation at a sufficiently low restoring couple. The fate of the optic-type mode is less obvious, but for still moderate restoring couple in the sodium halides, for example, it seems reasonable that such an oscillation could drop in frequency sufficient to find itself in the optic to acoustic gap. This may be the origin of some of the in-gap features observed for sodium bromide and iodide, but the possibility that they are essentially translational modes of the ion cannot be ruled out, especially in view of the extra in-gap structure shown by the spectra of NCO^- in these lattices.

Several further points which apply to individual spectra of Fig. 8 are worth mentioning.

In NaCl considerable absorption of a broad, but peaked, nature can be seen to extend well into the optic-band region, and this is to be contrasted with the NCO^- spectrum. The dominant factor here may well be the relative lightness of the CN^- ion.

Sharp in-gap structure is found for CN^- in NaBr at about the same separation as that observed for NCO^- and again suggests a wide gap at energies higher than those calculated by Karo and Hardy.²⁴ These in-gap bands were quite sharp at 90°K, at which temperature they could also be seen in $\nu(\text{CN}^-)-\nu_{\text{ext}}$. Contrasted with this, however, is the band at $\nu(\text{CN}^-)+154 \text{ cm}^{-1}$, which

was still quite broad at 90°K, had sharpened somewhat by 25°K, but only attained the prominence shown in Fig. 8 below about 10°K. This band is discussed later in the section concerned with temperature effects.

Although the NCO^- band in NaI has always obscured $\nu(\text{CN}^-)+93 \text{ cm}^{-1}$ and several cm^{-1} on each side of this value, the band at this energy has been dotted-in, in Fig. 8, because it has been recorded repeatedly in $\nu(\text{CN}^-)-\nu_{\text{ext}}$ at 90°K and frozen out at lower temperatures. By 7°K, its energy would probably have increased slightly, and it is interesting to compare this with the similar band observed directly in the far infrared by Lytle and Sievers.²⁵

Evidence for a sharp line at $\nu(\text{CN}^-)+82 \text{ cm}^{-1}$ in KI is to be found in the spectrum shown in Fig. 8 and this may also be compared with the far-infrared work of Lytle and Sievers.²⁵

The absorption, if any, shown by these $\nu(\text{CN}^-)\pm\nu_{\text{ext}}$ spectra in-the-gap is particularly useful information, and it is most unfortunate that so much of this has been obscured by $\nu_3(\text{NCO}^-)$ absorption. Our crystal-growing facilities are therefore being considerably extended to enable us to grow larger, more carefully controlled crystals with which to continue this investigation.

ν_{ext} SPECTRA FOUND IN COMBINATION WITH $\nu_3(\text{BO}_2^-)$, $\nu_3(\text{N}_3^-)$, AND $\nu_3(\text{NCS}^-)$

Other ions which may profitably be compared with NCO^- are NCS^- , BO_2^- , and N_3^- . BO_2^- and N_3^- , because of their similarity with NCO^- in size, nuclear masses, internal force constants, etc., can be considered as limited extensions of the progression of NCO^- isotopic species discussed in detail earlier. Although these ions cannot be so easily incorporated into the alkali halides in the relatively high dopings used for the NCO^- samples, the spectra so far obtained have been strong enough to show two points of interest. (i) The in-gap and superoptic doublets which have been shown to be characteristic of the NCO^- spectra have always been replaced by single lines in the BO_2^- and N_3^- spectra. (ii) Within the limits set by the reduced absorption intensity, no broad features have been identified in these spectra. These two points should be considered together with the introductory comments on the type of motion expected to combine with ν_3 of these ions under the prevailing D_{3d} selection rules. Added weight is then given to the proposal that the sharp features in these spectra, and in the spectra combined with $\nu_3(\text{NCO}^-)$, represent essentially torsional motion of these ions, and this suggests that translational impurity motion should be associated with the broader features in these cases.

NCS^- could be considered as a distant extension of the progression of NCO^- isotopic species, but here the extreme asymmetry of the ion might be expected to

²⁵ C. D. Lytle and A. J. Sievers, Bull. Am. Phys. Soc. 10, 616 (1965).

change the nature of the doublets and also to increase the relative intensity of translational-type modes in binary combination with ν_3 . Note that the infrared activity of the various internal modes of an impurity ion gives an indication of the probable degree of selection operating in combinations of internal with external modes; e.g., for NCO^- , $2\nu_3$ is unobservably weak [even in the strongest samples so far used, where ν_3 of double isotopic species such as $(\text{N}^{15}\text{CO}^{18})^-$ in natural abundance of about 0.0007% can be easily seen], ν_1 is about 30 times weaker than ν_3 , $\nu_3 + \nu_2$ is very weak, etc. This pattern shows a clear tendency towards the D symmetry rules, by which this slightly asymmetric ion cannot really be governed. The $2\nu_3$ for NCS^- is, however, clearly visible even in samples which contain only moderate dopings.

The increased size of this ion does, however, limit its use, for although it can be introduced in low concentrations into all the various alkali-halide crystals such that its internal modes can be easily recorded,²⁶ it is difficult to obtain sufficient concentration to observe the much weaker $\nu_{\text{int}} \pm \nu_{\text{ext}}$ spectra. Thus only in the four iodides have we obtained good external-mode features in

combination with ν_3 of this ion. Figure 9 shows the four spectra for sample temperatures of about 40°K. This lower temperature was required to bring the spectra to a degree of sharpness comparable with that shown by the NCO^- spectra at 100°K. As with our heavily doped cyanide crystals, these spectra also show the $\nu_3(\text{NCO}^-)$ absorption, which is again at an unfortunate spacing from the $\nu_3(\text{NCS}^-)$. However, these spectra are all sufficiently sharp at 100°K for the $\nu_{\text{int}} - \nu_{\text{ext}}$ spectra to show unambiguously what features are being obscured, and these have been "dotted-in" in Fig. 9.

The sodium-, rubidium-, and cesium-iodide spectra show a shifting of the emphasis from the sharp doublets towards the low-energy broad feature when compared with the corresponding NCO^- spectra (Fig. 7). For NCS^- in both potassium and cesium iodide, the spectra look qualitatively quite different from the equivalent NCO^- spectra. We suggest the possibility that in these two crystals the different impurities align in different orientations. There is good evidence to support this in the case of CsI , for in all the cesium halides different internal-mode frequencies can be obtained by varying the conditions under which the doped crystals are

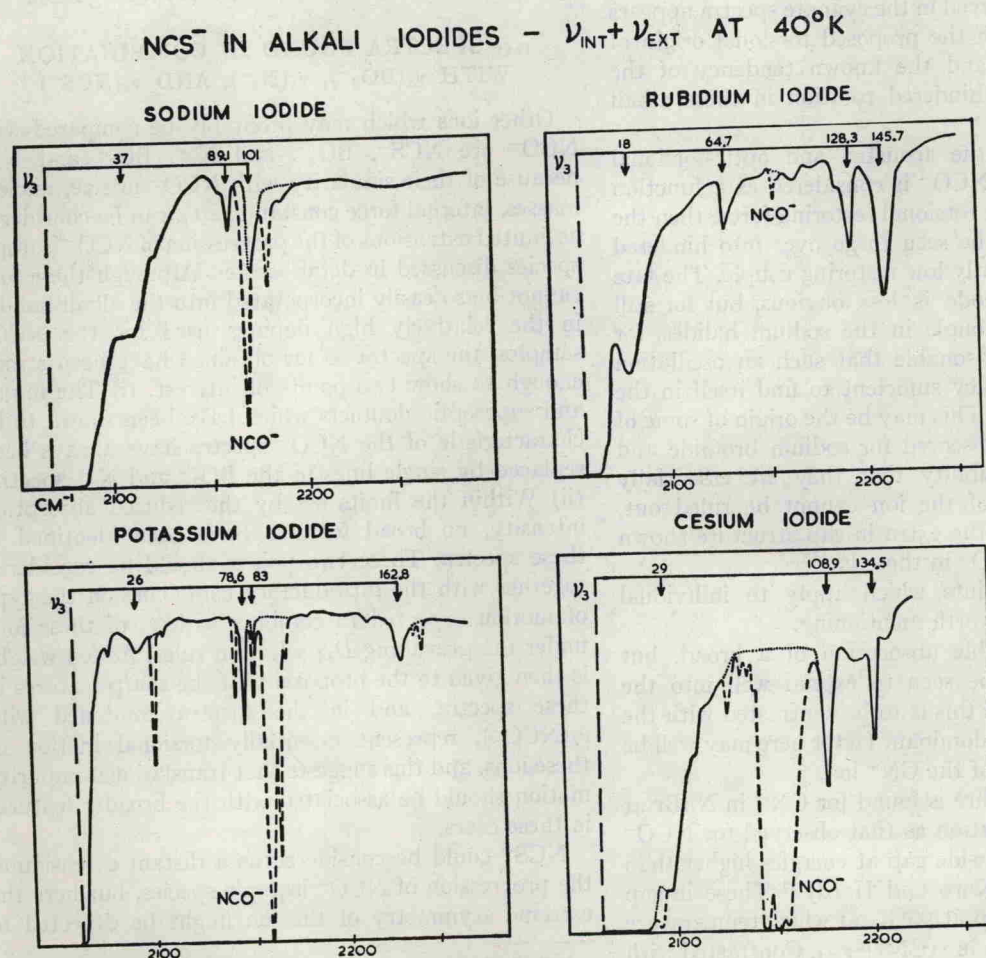


Fig. 9. $\nu_3 + \nu_{\text{ext}}$ spectra at 40°K for NCS^- isolated in alkali iodides. Features due to NCO^- are shown dashed.

²⁶ M. A. Cundill and W. F. Sherman (to be published).