

TABLE II. Sharp features and lowest-energy broad bands in ν_{ext} spectra of impurity ions in alkali halides. (See Table I, Ref. 5 for values obtained with other ions.) Energies quoted in cm^{-1} . Sharp features above and below the lowest optic-mode frequency of the host lattice are separated by a colon.

	Sharp features			Lowest-energy broad bands		
	NCO ⁻ at 100°K	NCS ⁻ at 40°K	CN ⁻ at 7°K	NCO ⁻ at 100°K	NCS ⁻ at 40°K	CN ⁻ at 7°K
NaCl	a	b	a	86	b	54
NaBr	117, 123, 127:a	b	110, 123:(156)	52	b	38
NaI	91, 105:a	89, 101:a	93:a	35	37	27
KCl	a	b	a	52	b	13.5
KBr	97, 100:168, 184	b	a	41	b	12
KI	78, 82:(133), 152	79, 83:163	83:a	31	26	12.5
RbCl	a	b	b	36	b	b
RbBr	a:141, 154	a:144, 184	b	31	24	b
RbI	a:115, 134	a:128, 148	b	24	18	b
CsCl	a	b	b	37	b	b
CsBr	a:119, 138	b	b	37	b	b
CsI	a:(81), 107	a:109, 135	b	40	29	b

^a No features observable in spectra.
^b Spectra not yet investigated.

made to fit low-temperature neutron-scattering results for NaI,¹³ KBr,¹³ and KI,²³ and the others from the calculations of Karo and Hardy²⁴).

Several general trends can be seen to exist in these spectra: (a) No sharp ν_{ext} features are shown by the four chloride spectra. (b) In the bromides and iodides, the observed sharp features appear in the sodium salts only in-the-gap; in the potassium salts both in-the-gap and superoptic; and in the rubidium and caesium salts predominantly superoptic. (c) There is a tendency for the sharp features to occur as doublets, though the two components do not always seem to be of equal intensity. (d) The separation of the in-the-gap doublet seems to vary directly with the size of the gap. (e) The three cesium halides do not show the strong broad lowest-separation band which is to be seen in the other spectra. (f) Apart from the case of NaCl, which appears to show only the broad absorption at acoustic-band energies, all the spectra show a relatively strong feature at the extreme high-energy end of the optic band. This takes the form of the lower-energy component of the super-optic doublet in those cases where this doublet is clearly resolved. In those cases that show no superoptic structure it takes the form of the highest energy maximum in the ν_{ext} spectrum, and in the cases of KI and CsI, lower-temperature spectra and high-pressure spectra (see below) suggest that this is still the low-energy component of the superoptic doublet which has just failed to rise clear of the optic-band modes in these two cases at zero pressure.

The fact that the chlorides show no sharp features will be returned to in the later discussion of the ν_{ext} spectra shown by the cyanide ion, which is the only ion that we have so far used in this investigation which is lighter than the chloride ion.

The presence of in-the-gap modes in combination

with $\nu_3(\text{NCO}^-)$ in the bromides and iodides seems to depend simply on whether or not a gap exists in the integrated density of states for the particular alkali halide. Thus we would feel justified in suggesting that there was no gap in RbBr, RbI, CsBr, or CsI, and that the calculations of Karo and Hardy²⁴ have put the gap in NaBr noticeably too low. For a superoptic mode to exist, the motion must be highly localized, and it therefore seems reasonable to suggest that the absence of these modes in NaBr and NaI is primarily due to the relative lightness of the nearest-neighbor sodium ions. These ions, being incapable of playing their part in such a vibration without having relatively large amplitudes, inevitably involve further ions, delocalize the motion, and thus hold down the frequency to within the optic band.

Following our assignment of the sharp bands in ν_{ext} for NCO⁻ in KBr as acoustic- and optic-torsional modes about two axes, which perpendicularly cut the N-C and C-O bonds, we would expect to see this general pattern repeated for NCO⁻ in other lattices. Many of the spectra are seen to show evidence of similar in-gap and superoptic doublet structure, where it can reasonably be expected (i.e., in-gap if a gap exists, and superoptic if nearest neighbors are sufficiently massive). The two components of any given doublet of the described torsional origin would be expected to be similar in intensity. However, this does not always appear to be the case. The superoptic doublets in KI and CsI have been considered above. An extra component is to be seen in-the-gap in NaBr, and most of the imbalance between the components in-the-gap in NaI appears to be due to an underlying absorption presumably of similar origin to that of the extra band observed in NaBr. Thus, if the presence of extra in-gap or superoptic structure of an unspecified origin is accepted, then it does seem that the pattern of acoustic and optical-torsional-type doublets can be followed through these spectra.

²³ G. Dolling, R. A. Cowley, C. Schittenhelm, and I. M. Thorson, Phys. Rev. 147, 577 (1966).

²⁴ A. M. Karo and J. R. Hardy, Phys. Rev. 129, 2024 (1963).

The in-the-gap doublets, having grown out of the acoustic band, appear to have retained sufficient of their acoustic nature to find it very difficult to move up to an energy associated with optic-mode vibrations. Thus in KBr the in-gap doublet, having climbed clear of the acoustic band, finds itself almost immediately opposed and cramped into a very narrow energy band just below the optic modes. This results in the close spaced doublet observed in this case, which if the optic bands had started higher, might well have appeared as a much wider spaced doublet as is observed in KI and more particularly NaI.

The broad lowest-energy ν_{ext} absorption which becomes increasingly evident as one goes from sodium to potassium to rubidium halides is not to be seen at all in the cesium halides, although a much sharper, weaker absorption, at higher energies, is found within the acoustic continuum. There is the obvious difference in structure between the cesium halides (CsCl type) and the other nine halides (NaCl type) to be considered, and also the orientation of the NCO^- ion within this structure.

Calculations of the energy of the system, as a function of NCO^- axis orientation within CsCl-type structures, suggest either a $\langle 001 \rangle$ or a $\langle 110 \rangle$ direction as the lowest-energy configuration, and rule out a $\langle 111 \rangle$ orientation. Since $\langle 110 \rangle$ would result in a splitting of ν_2 which is not observed, it seems fairly certain that the ion lies in a $\langle 001 \rangle$ direction. Although the resultant C_{4v} symmetry

does not result in any rigid selection rules, it is worth considering the D_{4h} rules to see what trends to expect in the relative intensities of different types of absorption, as in the earlier discussion of $C_{3v}\text{NCO}^-$ and $D_{3h}\text{N}_3^-$ for the NaCl structure. As for the previously considered case, it is R_x and R_y which give the only active binary combinations with ν_3 , so there is no guide here as to the absence of the broad low-energy band in the CsCl structures. It may be that here again there is evidence of a directional property which cannot be adequately described by simple selection rules. These points will be considered again later when the NaCl to CsCl-type pressure induced phase changes are discussed.

The persistent appearance of a feature at the extreme high-energy limit of the optic band suggests that for some reason this feature is held located close to this point in the dispersion curves. This is used later when the pressure dependence of some of these spectra is used to obtain information about the pressure dependence of the host-lattice vibrations.

$\nu(\text{CN}^-) \pm \nu_{\text{ext}}$ SPECTRA FOR VARIOUS ALKALI HALIDES

Figure 8 shows the spectra recorded at 7°K for CN^- isolated the chlorides, bromides, and iodides of sodium and potassium. For the sodium halides these spectra have not changed radically in lowering the temperature from 90°K, and at this higher temperature the stronger

$\nu_{(\text{INT.})} + \nu_{(\text{EXT.})}$ SPECTRA OF CN^- DOPED ALKALI HALIDE CRYSTALS AT 7°K

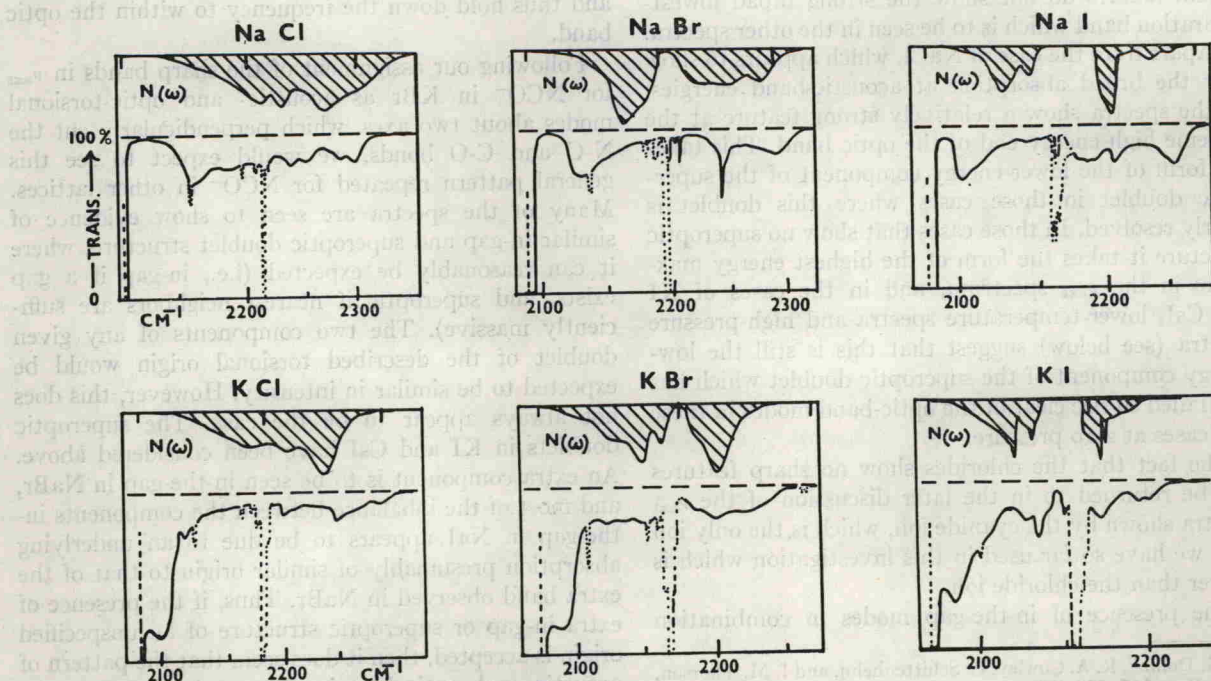


FIG. 8. $\nu_{\text{int}} + \nu_{\text{ext}}$ spectra at 7°K for CN^- isolated in various alkali halides, compared with the integrated density of states for the pure crystals (see Refs. 13, 23, and 24).