

shift [Fig. 2(c)], which implies $\Delta n = 1.4 \times 10^{-5}$ since the filament was 3 cm long. This is consistent with the optical Kerr effect calculated in the filament which was 10 times brighter than the untrapped radiation of 16 MW/cm².

Most ruby-laser beams have intensities far above threshold for trapping in CS₂ and are sufficiently inhomogeneous to give the complex patterns which have been previously photographed.⁴ Figure 1(e) shows the development of many filaments from an apparently homogeneous beam about 1 mm in diameter and considerably above threshold power. Each trapped filament was in itself approximately cylindrical and was surrounded by a bright ring in this stage of development.

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IMPURITY-INDUCED NEAR-INFRARED SPECTRA AS A SOURCE OF INFORMATION ABOUT THE FREQUENCY DISTRIBUTIONS OF THE ALKALI HALIDES

R. Metselaar and J. van der Elsken

Laboratory for Physical Chemistry of the University of Amsterdam, Amsterdam, The Netherlands
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It has been recognized for some time now that bandwidths and band structures in the infrared spectrum of complex ions in the crystalline state cannot satisfactorily be explained by using the rules of factor-group analysis, nor by allowing for combinations with librational modes or optically active lattice fundamentals.^{1,2} In general, all normal vibrations and not just the $K=0$ modes may take part in combination modes. Hence the envelope shape of the band and its combinations depend on the shape of dispersion and frequency distribution curves. Selection rules may still favor some combinations and, therefore, the band shape does not have to resemble the distribution curve in all cases.

Complete experimental dispersion relations, however, are rarely available, which makes a comparison with the distribution function and a determination of the effect of selection rules unattainable.

With respect to the determination and calculation of the dispersion and frequency distribution curves, the alkali halides are among the most favorable cases. The lack of complex ions with readily observable vibrations in these crystals can be overcome by substitution of complex ions as impurities at lattice sites. Such ions may serve as detectors for the lattice modes of the alkali halide by giving combination bands of the internal vibration of the complex ion with the lattice modes of the host crystal.

The influence of the substitute on the lattice frequencies, if present in low concentrations, is negligible for nearly all phonons,³ so that the band structure due to these combinations will be related to the frequency distribution of the pure alkali halide lattice. The observed band structure may now be compared with the calculated distribution function of the crystal. However, a small number of phonon levels,

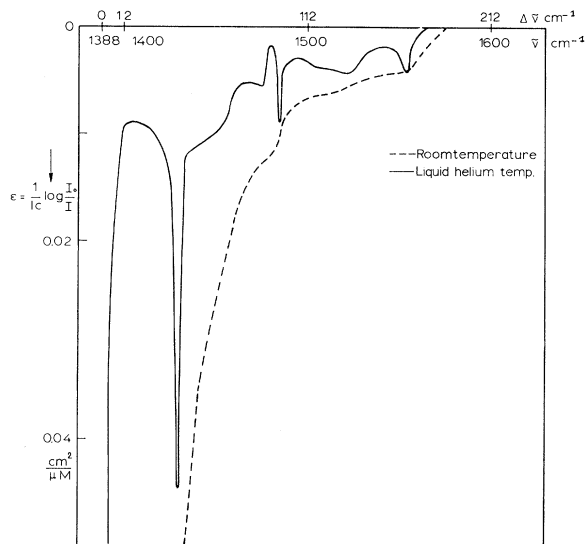


FIG. 1. The high-frequency side of the ν_3 infrared absorption band of the NO_3^- ion in KBr. $\Delta\tilde{\nu}$ counted from the peak frequency measured at low densities.

lying near the band edges, are strongly affected by the perturbation. These frequencies are related to localized vibrations of the impurity. In the factor-group approach they are the translational or rotational modes of the impurity. If these modes are situated in the gap between acoustical and optical branches or above the latter, they are called local modes; if they still lie in the band of lattice frequencies, they are called resonance modes. Due to the coupling with the in-band modes the bandwidth of a resonance mode will be greater than that of a local mode. The total number of these types of modes may vary strongly with the ratio of mass and force constants. According to a general rule, however, we can only expect local modes for impurities that have smaller mass than the substituted ion or are bonded with higher force constants.

It might be expected that these modes will appear as rather pronounced features in the combination band of the internal mode of the impurity ion and the lattice spectrum.

Further complications may arise with increasing concentrations of the impurity ions. It has been shown that the internal vibration frequencies of the impurity ion may shift when these ions cluster together.^{4,5} The existence of clusters of complex ions will therefore give rise to additional bands and band structures. It is to be expected that these clusters will also increase the disturbance of the lattice modes

with the effect of greater aberrations from the frequency distribution of the pure-host lattice.

Hence it is imperative that measurements should be carried out with very dilute solid solutions and, therefore, since crystal sizes are experimentally limited, with ions that possess an extremely active internal vibration. The nitrate ion with its ν_3 (E') fundamental at 1388 cm^{-1} , readily soluble in the alkali halides, is very suitable for this purpose.

Spectra were taken of solid solutions of nitrate ions in KCl, KBr, KI, NaCl, NaBr, and NaI grown from the melt. The nitrate concentrations were chosen well below the range where cluster formation would be of any importance (concentration $\approx 10^{18}\text{ cm}^{-3}$). The absence of any concentration dependence was shown by comparing samples with widely varying concentrations and thicknesses (up to 80 mm) but equal optical density. The temperature dependence is strong in the temperature range between 300 and 90°K; further lowering of the temperature to liquid-helium temperature does not have much effect.

In Fig. 1 we have shown the structure on the high-frequency side of the ν_3 vibration of nitrate in KBr. All sharp features as well as the band structure are present at 80°K. At the low-frequency side possible structure is obscured by the presence of nitrite ion absorption. Apart from the strong band at about 1430 cm^{-1} , which is the overtone $2\nu_4$, we can interpret the structure in terms of the frequency distribution of the alkali halides.

After subtraction of the absorption due to the ν_3 and $2\nu_4$ (band shapes estimated from low-concentration spectra), we are left with the spectra shown in Fig. 2. If we ascribe the sharp bands, marked with an asterisk, to local or resonance modes, the resulting bands give us an experimental frequency distribution curve. In the same figure we have compared these with the best available calculated curves.⁶

Finally in Fig. 3 we have given the curve for KBr after subtraction of the localized modes. We see that there is a very close resemblance between this curve and the two calculated curves which are based on two different models.^{6,7} For the others the agreement is satisfactory, though it is not always easy to subtract the local modes. From Fig. 2 we see that in NaCl and KCl no local modes appear, which is in accordance with the fact that in these cases the mass ratio is smaller than one.

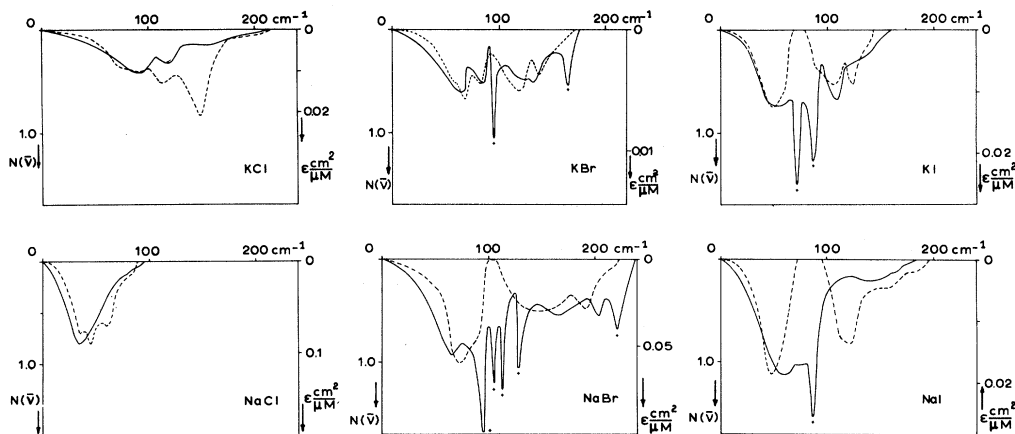


FIG. 2. Estimated contribution of lattice combinations to the ν_3 infrared absorption band of the NO_3^- ion in the alkali halides (solid line), compared with calculated frequency distributions⁶ (broken line). Localized modes marked with an asterisk.

Apparently there are no selection rules which forbid special phonon combinations with the ν_3 . This is in accordance with a full space-group analysis. The observation that there is not much change in the spectrum from liquid-

helium temperature up to about 80-90°K probably means that only binary combinations $\nu_3 + \nu_1$ play a role.

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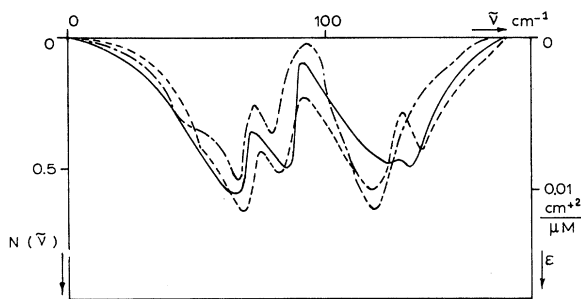


FIG. 3. The frequency distribution of KBr deduced from the measured combination band (solid curve), compared with calculated curves by Karo and Hardy⁶ (dashed curve) and Cowley *et al.*⁷ (dash-dot curve).

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