

where

$$\bar{M}\omega_0^2 = A - \frac{\frac{4}{3}\pi N s^2 e^2}{1 - \frac{4}{3}\pi N (\alpha_+ + \alpha_-)} \quad (1)$$

Here $\bar{M}$ is the reduced mass of the positive and negative ions, N is the number of ion pairs per unit volume, se is the effective ionic charge, and A is a force constant, which is given by $6R_0/K$ for a NaCl-type structure at zero pressure, where R_0 is the nearest-neighbor distance and K is the compressibility. At nonzero pressures, a second term involving pressure P is needed, and A is modified to $6R/K - 8RP$.

If the effective charge and the ionic polarizabilities can be regarded as constant, then the band center TO frequency can be calculated using experimental values of compressibility as the sole experimental parameter which varies as a function of pressure. Experimental results on the change of dielectric constant with pressure seem to indicate that changes in α_+ and α_- could effect the TO frequency by only 2 or 3%. The variation of effective charge se with pressure is considered later and is also found to be a relatively small effect. Since the TO at the band center is very close to the lowest optic-mode energy for NaI, the band center TO frequency can be taken as a good indicator of this energy. Using a very carefully drawn curve through Bridgman's³⁶ data for NaI, the compressibility (at 300°K) was obtained at various pressures and hence to TO frequency at these pressures calculated. These calculated TO values joined by a dotted line are also shown in Fig. 16, and it can be seen that the unusual shape of the in-gap external mode frequency versus pressure curve is to be found further emphasized in these calculated TO-versus-pressure curves. The reliability of the calculation is, of course, suspect, since it is so very sensitive to slight changes in slope of the $\Delta V/V$ -versus-pressure graph which is undoubtedly different at the lower temperature which should have been used if the data had been available. However, far from catching up to the optic band and then being restrained by it, the external-mode frequency appears qualitatively to follow the TO mode, although showing a rate of change less than that of the pure lattice mode.

PRESSURE DEPENDENCE OF SUPEROPTIC LOCALIZED MODES

As mentioned earlier, there always seems to be a feature in all the $\text{NCO}^- \nu_3 \pm \nu_{\text{ext}}$ spectra which corresponds to the top of the optic band of the pure lattice. It therefore seems fairly safe to assume that this feature moves under pressure in such a way as to monitor the top of the optic band. Unfortunately, from the point of view of utilizing this fact, calculated values of LO frequencies are unreliable when simple models are used. One can, however, approach this mode via the TO and

the LST³⁷ relationship $(\epsilon_0/\epsilon_\infty)^{1/2} = \nu_{\text{TO}}/\nu_{\text{LO}}$. Note that this expression was shown to hold at zero pressure by Woods *et al.*¹³ within the accuracy of the neutron-scattering data.

If the data of Gibbs and Jarman³⁸ and of Burstein and Smith³⁹ on the pressure dependence of ϵ_0 and ϵ_∞ of KBr are used, then the LO pressure dependence can be changed via the LST relationship to the TO pressure dependence. A rigid-ion model can then be used to evaluate the band center TO frequency and Szigeti's^{35,40} relationships used to explain any slight disparity between observed and calculated values. The most convenient expression to use is

$$\left(\frac{e^*}{e}\right)^2 = S^2 = \frac{9\bar{M}\omega_0^2(\epsilon_0 - \epsilon_\infty)}{4\pi N e^2(\epsilon_\infty + 2)^2}, \quad (2)$$

where the notation is the same as that used for Eq. (1). Since the dielectric-constant data are limited to zero-pressure values of the rates of change of ϵ_0 and ϵ_∞ with pressure, Eq. (2) was differentiated with respect to pressure and a value obtained for the rate of change of S with pressure. A value of $(\partial S/\partial p)_0 = -0.9 \times 10^{-3} \text{ kbar}^{-1}$ was obtained.

Both the size and the sign of the above result are of interest. The very small numerical value is to be expected, since the effective charge is found to vary very little over a wide range of different alkali halides,⁴⁰ and might therefore be predicted to change only slowly in a given alkali halide as a function of pressure. The negative sign of the pressure coefficient is consistent with Szigeti's⁴⁰ explanation of the significance of the effective charge. Since the effective charge is found to be less than the electronic-charge, Szigeti concludes that as an ion approaches its nearest neighbor, there is a reduction in the total electron density along the line of centers of the two ions. This indicates the dominance of repulsive forces in determining local distortions of the electron cloud. Under pressure the ions are forced closer together, the short-range repulsive term becomes still more dominant, and $(\partial S/\partial p)$ would be expected to be negative.

The small negative value obtained for $(\partial S/\partial p)_0$ does suggest that the starting assumption that the 167-cm⁻¹ band in the ν_{ext} spectrum was monitoring the LO frequency was reasonably justified, and it may therefore prove to be worthwhile using a more complex model for the alkali halide when assessing the significance of these shifts with pressure. However, as can be seen from Fig. 15, the 167-cm⁻¹ band moves very rapidly with pressure (and temperature; see Fig. 10), which is contrary to the predicted behavior of the LO band-center frequency.³⁰ It may be, therefore, that this

³⁷ R. H. Lyddane, R. G. Sachs, and E. Teller, Phys. Rev. **59**, 673 (1941).

³⁸ D. F. Gibbs and M. Jarman, Phil. Mag. **7**, 663 (1962).

³⁹ E. Burstein and P. L. Smith, Phys. Rev. **74**, 229 (1948).

⁴⁰ B. Szigeti, Proc. Roy. Soc. (London) **A204**, 51 (1950).

³⁶ P. W. Bridgman, Proc. Am. Acad. Arts Sci. **76**, 1 (1945).

feature has moved under pressure away from the special position that it occupied, at the very top edge of the optic band, at zero pressure. See also Fig. 11, which seems to indicate that the lower component of the "superoptic" doublet for NCO^- in KI moves with respect to the optic band when the crystal is compressed.

Bridgman's³⁶ data for KBr were also used with Eq. (1) to calculate TO frequencies for KBr similar to those described for NaI earlier. There was a very slight but possibly significant difference when the 167-cm^{-1} band's pressure dependence was compared, via the Szigeti relationships, with these calculations, rather than by the direct use of Eq. (2). This difference could be expressed as a very slight pressure dependence of Szigeti's⁴⁰ K^*/K value.

The absence of pressure-dependent dielectric-constant data for other alkali halides makes the above type of analysis impossible for the superoptic features of ions in other alkali halides. However, Figs. 13-15 show some of the shifts that we have observed for superoptic external-mode features for NCO^- in alkali halides. All the spectra shown in Fig. 7 to possess superoptic features have also been investigated and show the same general trends. Only in one case, NCO^- in CsI, has a noticeably nonlinear frequency shift rate with pressure been observed.

EFFECTS OF PRESSURE ON $\nu_{\text{C-H stretch}} \pm \nu_{\text{ext}}$ FOR CHI_3

All the pressure effects discussed above have been concerned with doped alkali halides, although, as was pointed out in the Introduction, the $\nu_{\text{int}} \pm \nu_{\text{ext}}$ type of spectrum is quite commonly found for a wide range of different systems. All such spectra could reasonably be investigated as a function of pressure, and information obtained about the respective crystal forces. As an example of a crystal containing binding forces very different from those of the alkali halides, we have investigated CHI_3 .

Figure 17 shows a zero-pressure spectrum of the C-H stretching region of an iodoform crystal looking along the direction containing the C-H bonds, and shows how the broad wings were observed to expand as the pressure was increased at 100°K . The spectrum deteriorated as the pressure was increased, presumably due to a progressively worsening alignment of the C-H bonds, but the wings were still fairly well defined up to 25 kbar, by which pressure both the upper and lower defining energies had increased by about 50%. This very rapid rise might be expected for molecular crystals with small initial binding forces.

CONCLUSIONS

A considerable amount of theoretical work has been published recently on the vibration of impurities within

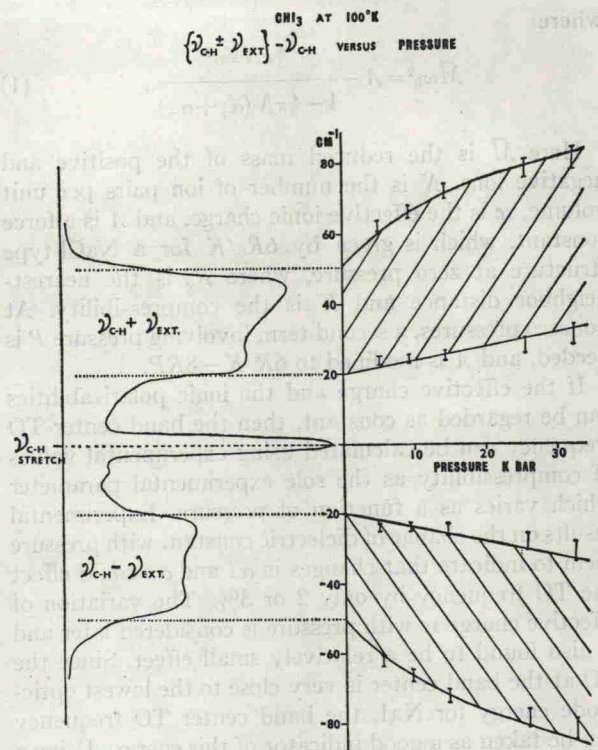


FIG. 17. Effect of pressure on the lattice sidebands on the C-H stretching vibration of iodoform at 100°K .

crystals (see, e.g., Refs. 11, 41-44), often with a good degree of agreement with experimental work on point defects. The extension of the theoretical work to include molecular impurities has been less convincing, however. Part of the purpose of this paper has been to underline two aspects of the molecular-impurity problem which seem to receive too little attention in the theoretical studies. These are (i) torsional motion of the impurity, and (ii) a directional selection of the modes which appear in strong binary combination with an essentially internal, vibrational (or electronic) transition of the impurity. The different ν_{ext} spectra shown by $\langle 111 \rangle$ -oriented NCO^- and $\langle 001 \rangle$ -oriented CN^- in the sodium and potassium halides show conclusively that these spectra cannot possibly be simply monitoring the total integrated density of states of the host lattice. Some conclusions about the host-lattice dispersion curves can be drawn, however, and these are summarized below.

External Modes within the Acoustic Band of the Host Lattice

Broad, poorly defined absorption has usually been found in the external-mode spectra at energies covered

⁴¹ A. A. Maradudin, *Solid State Phys.* **19**, 1 (1966).

⁴² P. G. Dawber and R. J. Elliott, *Proc. Roy. Soc. (London)* **A273**, 222 (1963).

⁴³ R. W. H. Stevenson, *Phonons* (Oliver and Boyd, Edinburgh, 1966).

⁴⁴ *Proceedings of the International Conference of Lattice Dynamics, Copenhagen, 1963*, edited by R. F. Wallis (Pergamon Press, Inc., New York, 1965).