

Lattice Sidebands of Vibrational Spectra and Their Pressure Dependence

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Vibrational spectra of solids which show the general form $\nu_{\text{int}} \pm \nu_{\text{ext}}$ are discussed, and the information that they contain about the lattice modes of the solid is considered. Small polyatomic impurity ions isolated in alkali halides are responsible for most of the spectra considered. The importance of torsional motion of the impurity ion is shown, and a directional selection of ν_{ext} controlled by the ν_{int} transition moment is suggested. The pressure dependence of some of these spectra, up to 50 kbar at 100°K, is presented and discussed in terms of the host-lattice dispersion curves. For instance, it is shown that there is no acoustic-to-optic energy gap in the high-pressure CsCl-type structures of KBr, KI, RbBr, and RbI. Some of the wider applications of this type of spectrum are also indicated.

INTRODUCTION

VIBRATIONAL spectra which have the general form $\nu_{\text{int}} \pm \nu_{\text{ext}}$ have been reported for several different systems, e.g., iodoform,¹ brucite,² polyatomic impurity ions in alkali halides,³⁻⁶ impurity molecules in solidified rare-gas matrices.⁷ ν_{int} is a frequency which

can be identified with a specific molecular group and which occurs at an energy only slightly displaced from that at which it would be found in an isolated molecule. ν_{ext} are frequencies associated with the movement of one molecule with respect to its neighbors, and represent a selection of the available energies of the lattice vibrations of the crystal at the point at which it is sampled. In iodoform, for example, if the C-H stretching frequency is used as ν_{int} and the radiation passed through the crystal such that its E vector is perpendicular to the C-H bonds, all of which align in the crystal, then the sharp C-H absorption is itself seen only very weakly (only seen at all because of convergence of the beam, crystal imperfections, etc.), and broad wings are seen extending between 20 and 50 cm^{-1} on each side. By cooling the crystal to liquid-helium temperature the low-energy wing can be completely suppressed. In principle, any strongly active band should show this kind of side structure, but the best examples are certainly those where complete longitudinal alignment of the ν_{int} transition moment renders it virtually non-absorbing and allows the usually broad $\pm \nu_{\text{ext}}$ bands to

¹ R. M. Hexter and H. Cheung, J. Chem. Phys. 24, 1187 (1956).

² R. M. Hexter, J. Opt. Soc. Am. 48, 770 (1958).

³ J. C. Decius, J. L. Jacobson, W. F. Sherman, and G. R. Wilkinson, J. Chem. Phys. 43, 2180 (1965).

⁴ R. Metselaar and J. van der Elksen, Phys. Rev. Letters 16, 349 (1966).

⁵ M. A. Cundill and W. F. Sherman, Phys. Rev. Letters 16, 570 (1966).

⁶ C. K. Chau, M. V. Klein, and B. Wedding, Phys. Rev. Letters 17, 521 (1966).

⁷ B. Vodar, in Fourth High-Pressure Research Meeting, Eindhoven, 1966 (unpublished). Although there are many references available in the published literature which give spectra of impurities isolated in rare-gas matrices [e.g., L. F. Keyser and G. W. Robinson, J. Chem. Phys. 44, 3225 (1966); D. E. Mann, N. Acquista, and D. White, *ibid.* 44, 3453 (1966)], there do not seem to be any examples which show a very strong Q branch accompanied by sum and difference binary combinations with the host crystal lattice vibrations. We understand, however, that this type of spectrum has been observed in Professor B. Vodar's laboratory, Bellevue, France.

be clearly seen right up to the center frequency, e.g., C-H bands of iodoform, O-H bands in $\text{Mg}(\text{OH})_2$, O-H bands in $\text{Ca}(\text{OH})_2$, and CO_3 bands in calcite have been used in this way in this laboratory.⁸ However, if a very strong band is exceptionally sharp, then only a little of the lowest-energy side structure is obscured by the main band. Very sharp, very strong bands can best be obtained by matrix isolation methods, and it is therefore not surprising that impurity molecules in rare-gas matrices, and impurity ions in alkali halides show good examples of $\nu_{\text{int}} \pm \nu_{\text{ext}}$ spectra.

IONS IN ALKALI HALIDES

The ν_{ext} frequencies are such that they would occur directly in the far-infrared region of the spectrum, where alkali halides absorb very strongly; see, for example, the absorption of KI shown in Fig. 1. However, the absorption spectra associated with at least 12 different impurity ions isolated in KI have been recorded directly in the far infrared.^{9,10} In some, if not all, of these cases there is as much impurity activated absorption which has not been detected because of the very strong host-lattice absorption. When investigating the external motion of polyatomic ions isolated in alkali halides, there are several advantages to be gained from studying the binary combination of this motion with a suitable internal mode, rather than observing the fundamental absorption in the far infrared. Firstly, the entire range of external-mode energies is unobscured. Secondly, the external modes can be studied over a wide range of temperatures. Thirdly, the internal mode can be chosen to occur in a spectral region where subsidiary tech-

niques, in our case the use of high-pressure cells, are much more straightforward. Fourthly, features in $\nu_{\text{int}} \pm \nu_{\text{ext}}$ spectra are unambiguously associated with the ion responsible for ν_{int} , which makes it possible to obtain at least some of the relevant information from samples containing more than one impurity (i.e., NCO^- contained in CN^- - or NCS^- -doped crystals, NO_2^- contained in NO_3^- -doped crystals, etc.).

A disadvantage of using the binary combination spectra is that they are relatively weak, which is only partially compensated for by the increased sample thickness that can be used. Typically, doping concentrations of between 0.1 and 1.0% have been used, compared with the 0.01% which has usually been found to be sufficient for the direct observation of the external-mode absorption in the far infrared. Although concentrations as high as 1% can be expected, in some cases¹¹ to cause distortion of the spectra from that to be expected from a very dilute solution, none of our spectra was found to show any concentration dependence. The identification of genuine external-mode absorption from any other weak absorptions in the vicinity of the internal mode is greatly assisted by the temperature dependence of the difference band features.

There still remains the problem of the rules governing the intensity of the various features seen in direct absorption in the far infrared, and in binary combination with an internal mode in the near infrared. Even where there is insufficient symmetry to render inactive any of the modes in either region, the relative intensities of different modes as observed directly or in combination with ν_{int} may vary greatly. It is clearly advisable to investigate both regions if the external vibrations of the impurity are to be better understood.

Consider, for instance, a BO_2^- ion ($D_{\infty h}$) present as a substitutional impurity in a NaCl-type lattice (O_h) and oriented in a $\langle 111 \rangle$ direction. The local symmetry is D_{3d} and, as first pointed out to us by Decius,¹² out of the distinct rigid-body modes (T_z in A_{2u} , T_x and T_y in E_u , and R_x and R_y in E_g) only R_x and R_y can give infrared activity in binary combination with ν_3 (A_{2u}), and these are the modes which are inactive in the far infrared as fundamentals. There is also the possibility of infrared active binary combinations with the other two internal modes. Such combinations with ν_2 would have similar rules to those with ν_3 , but if the active combinations with ν_1 , the infrared inactive symmetric stretch, could be found, then they would show the translational modes in exactly the same form as the direct observations in the far infrared. Apart from the above rigid-body modes, there is the ability of the molecular impurity ion occupied lattice site to absorb energy, which for a pure lattice is associated with a propagating lattice mode. This can be justified by the same arguments as used for point impurities, but the charge distribution of a molecular impurity ion (dipole, or at least extended

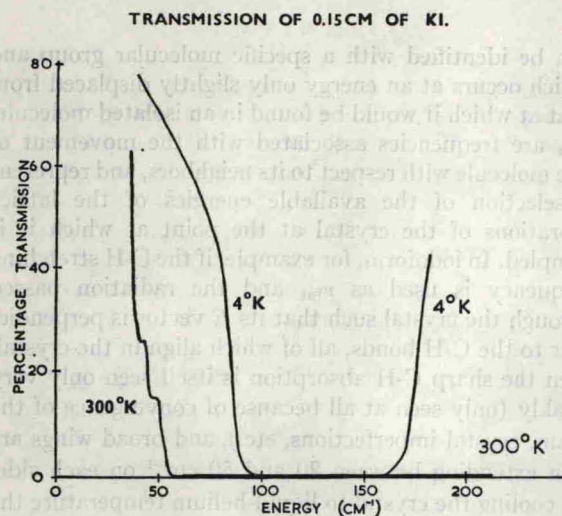


FIG. 1. Far-infrared transmission spectrum of a 1.5-mm-thick crystal of KI at room temperature and at 4°K.

⁸ See, e.g., Final Technical Reports on U. S. Army Contract Nos. DA-91-591-EUC-1308 (unpublished).

⁹ K. F. Renk, Phys. Letters 14, 281 (1965).

¹⁰ A. J. Sievers, A. A. Maradudin, and S. S. Jaswal, Phys. Rev. 138, A272 (1965).

¹¹ G. Benedek and G. F. Nardelli, Phys. Rev. 155, 1004 (1967).

¹² J. C. Decius (private communication).