

energy of the lattice. Often the directions of shifts in the temperature dependence experiment may be opposite to each other, resulting in a cancellation, and a small overall shift. For example, the specific volume of  $\alpha$ -quartz shows only a 0.3% decrease from room to liquid-air temperatures (49), and this is smaller than the change occurring upon compression from ambient pressure to 4 kbar (50). Such pressure studies may provide useful information on the amount of anharmonicity existing in solids of this type. Further, it should be possible in some cases to obtain compressibility data in compressible solids from pressure-frequency measurements [see Eq. (1)]. Molecular lattices show similar pressure effects (42).

In addition to the spectral blue shifts, lattice vibrations will broaden and diminish in peak intensity. This appears to be characteristic of all types of vibrations. No quantitative studies have been made to determine the effect of pressure on the integrated intensities of these vibrations. This may prove to be very difficult, since results may not be reproducible because of the pressure gradient existing across the diamond anvil faces. The broadening effects may be connected in part with this pressure gradient, since Raman studies in a hydrostatic cell do not show this pressure broadening of lattice bands (42).

The blue shifts of ionic or molecular lattice modes may result from the contraction of the solid under pressure, causing interionic and intermolecular distances to shorten (2-5, 51). The large pressure effects on compressible lattices are related to the small repulsive forces present in the neighboring ions or molecules.

## 2. INTERNAL VIBRATIONS

Earlier work indicated that internal modes are affected by pressure, but in a much less dramatic way than the external modes. Frequency shifts are generally small in most cases, either in a blue or red direction. In hydrogen-bonded compounds, studies of the O-H stretching vibration indicated spectral red shifts (5, 52). Red shifts were also observed for  $\text{HgCl}_2$  and its dioxane complex by Mikawa *et al.* (53). In most of our pressure studies with internal modes, blue shifts have been observed.

The broadening of bands and decreased peak intensities also occur with pressure. In some cases the symmetrical stretching vibration ( $A_1$  species) is found to be particularly sensitive to pressure (43). This compares favorably with the findings of Nedungadi (54), who studied the temperature dependence of  $\alpha$ -quartz and found that the most sensitive vibration was an  $A_1$ -type mode. Pressure dependences of  $\alpha$ -quartz produced similar results with the  $A_1$  frequencies more sensitive than the E-type vibration (55). Again, it must be inferred that not all  $A_1$  vibrations are pressure sensitive, as  $A_1$  bending

vibrations and certain  $A_1$  stretching vibrations are not particularly affected at higher frequencies.

Other pressure effects have recently been demonstrated. The  $\nu_4(F)$  bending vibration in  $KMnO_4$ , which is already split into two bands at ambient conditions, proceeds to lose all of its degeneracy with pressure. Studies with ligand ring vibrations in the mid-infrared region have demonstrated that one can also obtain a doubling of vibrations with pressure (45). An attempt to explain these results, at least qualitatively, follows.

(a) *Sensitivity of  $\nu_1$  Stretching Vibration to Pressure.* The sensitivity of the  $\nu_1$  stretching vibration in various compounds (inorganic and coordination compounds) is especially interesting. By contrast, a symmetrical bending vibration of type  $A_1$  may not be particularly affected (Fig. 7 illustrates the sensitivity of the  $A_1$  species in the metal-chloride stretching region). The intensity of the symmetrical stretch has practically disappeared with pressure, while the asymmetric stretch, although diminished, is still readily observed.

This  $\nu_1$  vibration involves an expansion of molecular volume, and these "expansion vibrations" are particularly sensitive to pressure (43). In addition, the dipole moment change for the vibration apparently decreases and this causes a decrease in the intensity. The actual mechanism as to how this is accomplished is obviously unknown at present. Since the intermolecular distances are being diminished, it may be possible to change certain bond angles while the material is under external stress. If the bond angles increase and approach  $180^\circ$ , the dipole moment change for the vibration might approach zero. Carbon dioxide is a case in point, where the bond angle  $O-C-O$  is  $180^\circ$  and the  $\nu_1$  vibration is forbidden in the infrared spectrum. However, it is observed in the Raman measurements and it would be interesting to observe similar molecules in the Raman experiment with pressure. Water, with a bond angle of  $\sim 104^\circ$ , shows an infrared-active  $\nu_1$  vibration.

(b) *Splitting of Degenerate Vibrations.* The loss of the degeneracy of E or F type vibrations with pressure is possible. The case of  $KMnO_4$  has been mentioned. The sensitivity of the  $\nu_4$  vibration with pressure while the  $\nu_3$  vibration remains unaffected, even at higher pressures, is very interesting. This is not simply a lowering of symmetry of the molecule, for both F species would be expected to split. One would have to conceive of a symmetry in which only  $\nu_4$  splits, not  $\nu_3$ , and this is virtually impossible. The different behavior must be related to the energy of the vibration. The compound  $KMnO_4$  has two molecules per unit cell, and it is possible that the vibrations of one  $MnO_4$  group in the unit cell might couple with the other  $MnO_4$  group. This coupling phenomenon can cause the splitting of degenerate vibrations (Davydov splitting) (56), without a change in symmetry. It is generally believed that coupling occurs more readily in the low-frequency