

solid hydrogen, xenon. (4) Transformations in coordination compounds. The various types of transformations are listed in Table 24. It may be noted that some structural changes occur with an increase in coordination number, and others occur with no change.

(ii) Effects on vibrational transitions

Four types of pressure-sensitivity for molecular vibrations have been observed thus far in the course of pressure studies on various modes of vibrations: (1) a broadening and a decrease in peak intensity of vibrations; (2) the doubling of absorption bands; (3) the splitting of degenerate vibrations; (4) frequency shifts in bands. Some of these effects have been observed for both external and internal vibrations.

(1) External vibrations

The effects of pressure on external vibrations have been demonstrated. Both the longitudinal and transverse optical modes are seen to shift in compressible ionic solids. In all cases studied thusfar, the shift is in the direction of higher frequency in agreement with low-temperature shifts. However, the pressure shifts may be considerable when compared with the temperature shifts. It is known that the temperature dependence of the peak position and half-width of lattice vibrational modes consist of two contributions: (1) the purely volume-dependent contribution; and (2) the contribution from the various anharmonic (cubic and higher) terms in the potential 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 α -quartz shows only a 0.3% decrease from room to liquid-air temperatures [308], and this is smaller than the change occurring upon compression from ambient pressure to 4 kbar [309]. 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 eqn. (1)). Molecular lattices show similar pressure effects [79].

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 [79,159].

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 [48,167,310,311]. 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 [48,310]. Red shifts were also observed for HgCl_2 and its dioxane complex by Mikawa et al. [145]. 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 [203]. This compares favorably with the findings of Nedungadi [312], who studied the temperature dependence of α -quartz and found that the most sensitive vibration was an A_1 -type mode. Pressure dependencies of α -quartz produced similar results with the A_1 frequencies more sensitive than the E -type vibration [313]. 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-IR region have demonstrated that one can also obtain a doubling of vibrations with pressure [199]. An attempt to explain these results, at least qualitatively, follows.

(a) *Sensitivity of ν_1 stretching vibration to pressure.* The sensitivity of the ν_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. 16 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 less intense, is still readily observed.

This ν_1 vibration involves an expansion of molecular volume, and these "expansion vibrations" are particularly sensitive to pressure [203]. 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° , the dipole moment change for the vibration might approach zero. Carbon dioxide is a case in point, where the bond angle