

crease in that of the high pressure phase. With a reduction of the pressure, the frequencies of the CsCl phase do not coincide with those determined from increasing pressures (maximum experimental error $\pm 2 \text{ cm}^{-1}$). The low pressure phase does not reappear until 11 and 16 kbars for KBr and KCl respectively. Part of these discrepancies can be attributed to the sluggishness of the system and friction within the cell.

The vibrational frequency decreases at the transition pressure by about 10-12%. The ratio of TO frequency of the CsCl phase to that of the TO frequency in the NaCl phase should equal the square root of the coordination number of each phase; e.g., $\sqrt{6/8}$ or 0.87. The observed ratio for KBr is 0.88 and that of KCl is 0.92.

It has been found³¹ that the $k \sim 0$ TO frequency of the alkali halides of NaCl structure is proportional to $(a/\chi\mu)^{1/2}$, where a is the lattice constant and μ is the reduced mass per unit cell, and χ is the compressibility. The same is true for the CsCl structure. Figure 6 illustrates this. Thus, it may be possible to relate the frequency-pressure data to the structure of the ionic crystal.

Pressure studies with mixed ionic crystals are possible using the diamond cell technique and are now under way.

Certain molecular lattice modes were investigated by McDevitt, Witkowski and Fateley.⁹ The experiments are more difficult to perform, since a thicker sample is needed, and spacers must be used to accomplish this. Molecular lattice vibrations have been observed to also shift toward higher frequency with increasing pressure. It would be expected that their pressure dependencies would be greater than ionic lattice modes due to their greater compressibilities.

Coordination Compounds (Effect of Pressure on Molecular Vibrations)

Whereas certain ionic solids when submitted to pressures show shifts of the optical modes toward higher frequencies, internal modes in other compounds show very little pressure shifts. Nevertheless, certain intensity changes are possible under pressure. For example, a number of coordination complexes having two halides or nitrogens per metal atom would be expected to show an asymmetric and a symmetric stretching vibration. Wherever these two vibrations are resolved into two bands, pressure effects one mode more than another.³² Figures 7 and 8 illustrate the effect of pressure on the asymmetric and symmetric stretching vibrations of $[\phi_4\text{As}][\text{GeCl}_3]$ and $[\phi_4\text{As}][\text{SnCl}_3]$. The verification as to which is

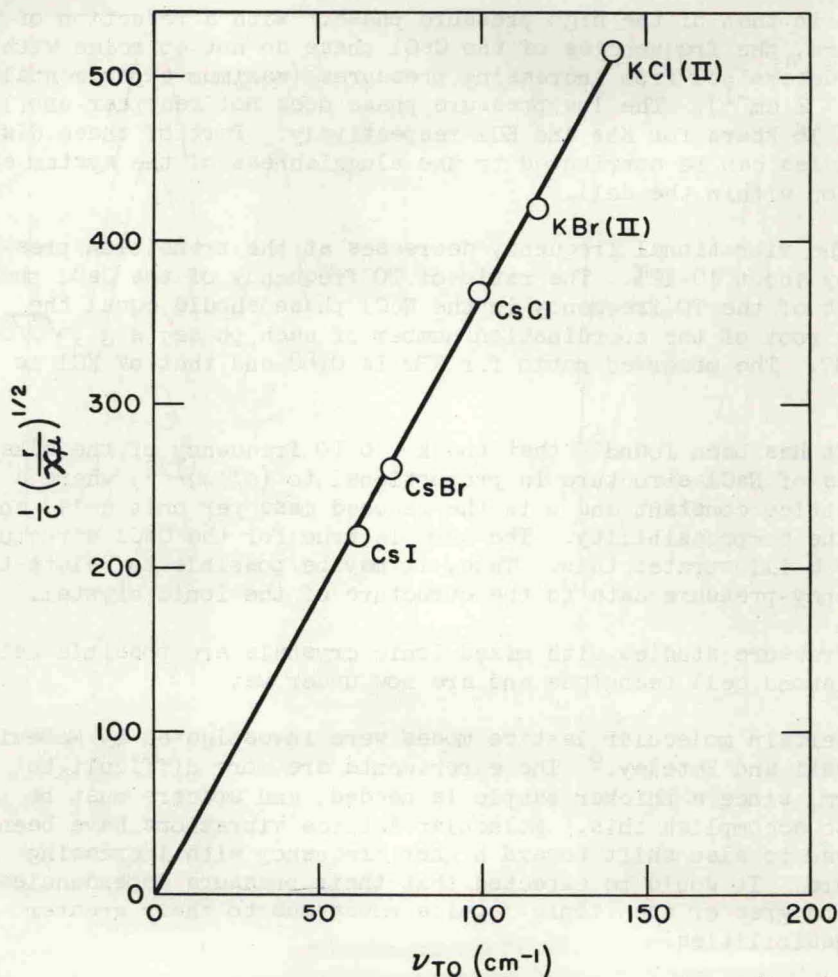


Fig. 6. Plot of TO Mode Frequency vs. $1/c \left(\frac{r}{\chi\mu} \right)^{1/2}$.

low frequency band splits into a doublet, and that the high frequency band decreases in intensity. Under pressure the degeneracy of the F vibration (ν_4) is completely removed. It is concluded that in the spectrum of KMnO_4 at ambient pressure the low frequency band is the E species and the high frequency band is the A_1 species. The results may be attributed to a further lowering of the symmetry of the solid under pressure to C_{2v} and illustrate that pressure can induce symmetry lowering. However, verification of this interpretation can only result when the F vibration (ν_3) is also studied under pressure. It is possible that not all solids will lend themselves to a lowering of the symmetry with the same ease, and one must consider the crystal packing involved for each solid.