

Fig. 7. Low Frequency Spectra of $(\phi_4\text{As})(\text{GeCl}_3)$ with and without Pressure.

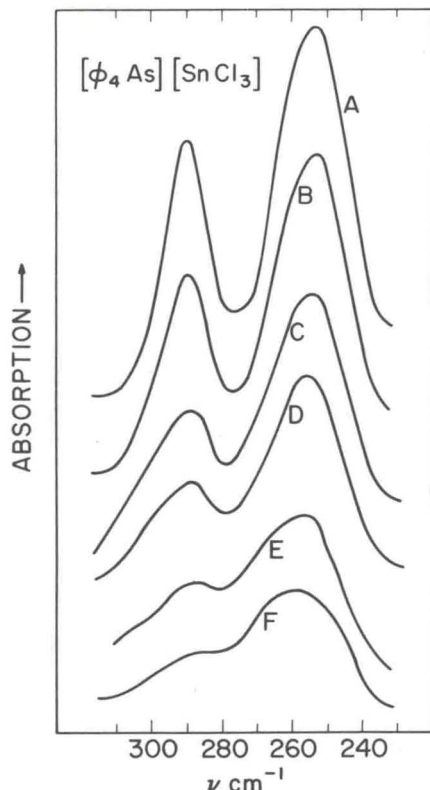


Fig. 8. Low Frequency Spectra of $(\phi_4\text{As})(\text{SnCl}_3)$ with and without Pressure.

The pressure gradient existing in the multiple anvil diamond cell has already been discussed. In an attempt to eliminate as much of the gradient as possible, experiments with molybdenum steel gaskets were made. It has been our experience that applying pressure on a solid with a gasket does not give hydrostatic pressures. However, using a gasket with the solid (HgI), and adding a drop of Nujol and then applying pressure gave what appeared under the microscope to be a single pressure.²⁶ Similar results were obtained recently by Davies¹⁸ with nickel dimethylglyoxime with other organic solvents. Further studies are now under way in our laboratory with other solids and other liquids. The use of a liquid under these conditions, with a freezing point at a known pressure can also give a pressure calibration point besides a hydrostatic pressure.

Discussion

It has been demonstrated that in compressible ionic solids lattice vibrations are pressure sensitive to frequency shift. In all cases studied thus far, 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. Apparently molecular lattices, generally speaking, show similar pressure effects. It may be possible in some cases to obtain compressibility data in compressible solids from pressure-frequency measurements (see Equation 1). On the other hand, internal modes which consist of motions involving changes in interatomic distances are not the symmetric mode and which is the antisymmetric mode was made by Raman polarizability data in solution. It is observed that although both peaks diminish in intensity and broaden, the symmetrical vibration (A_1 species) is the most sensitive to pressure. It is important to be able to distinguish between these two modes in making correct far infrared interpretations. The technique is able to do this on powdered or polycrystalline material. Heretofore, only single crystal-dichroism infrared measurements, single crystal or solution-Raman polarizability studies would make this differentiation.

Attempts to induce structural changes in coordination compounds upon the application of pressure to the solids have all failed.³³ Of course, only pressures to about 60 kbars have been used. At these pressures only color changes were observed, similar to those found for nickel dimethylglyoxime.¹⁷⁻¹⁸ These spectral changes with pressure can be observed under the microscope or in a visible spectrophotometer. These changes are not to be confused with any structural changes (e.g., $Td \rightarrow D_{4h}$ etc). It becomes apparent that to determine if any structural changes occur, one should go to solution studies. Such studies are now being initiated.

Newer Developments

Our interest in coordination compounds has motivated us to make a basic study of effects of pressure on the uncomplexed ligands as compared to those in the complexes. Although only preliminary results are available at this time, it appears that some