

FIG. 6. Pressure dependences of the $\text{KCl}_x\text{Br}_{1-x}$ system: in kilobars (\times) 13.9; (\bullet) 11.1; (\square) 8.3; ($+$) 5.5; (\circ) 2.8; (\triangle) ambient pressure. Experimental error, $\pm 1 \text{ cm}^{-1}$.

B. Coordination Compounds (Effect of Pressure on Molecular Vibrations)

Whereas certain compressible ionic solids show shifts of the optical modes toward higher frequencies when subjected to external pressure, internal modes in other compounds show very small 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 both an asymmetric and a symmetric stretching vibration. Whenever these two vibrations are resolved into two bands, pressure affects one mode more than another (43). Figure 7 illustrates the effect of pressure on the asymmetric and symmetric stretching vibrations of $[(\text{C}_6\text{H}_5)_4\text{As}][\text{GeCl}_3]$. Although both peaks diminish in intensity and broaden, it is observed that the symmetrical vibration (A_1 species) is most sensitive to pressure. It is important to be able to distinguish between these two modes in making correct far-infrared interpretations. This technique enables one to accomplish this with powdered or polycrystalline material. Previously, only in single-crystal-dichroism infrared measurements, single-crystal, or solution-Raman polarizability studies could this differentiation be made.

Attempts to induce structural changes in coordination compounds upon the application of pressure to the solids have all failed (44). Of course, only pressures of up to about 60 kbar have been used. At these pressures, only

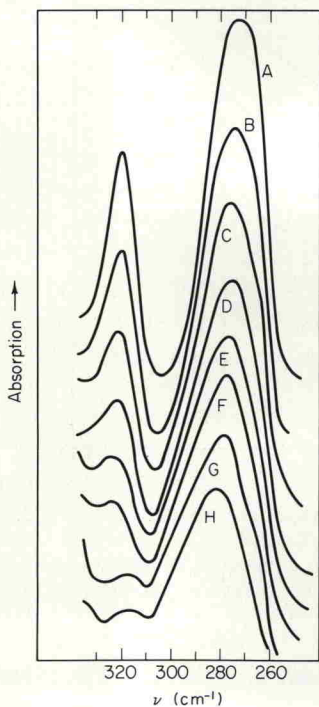


FIG. 7. Low-frequency spectra of $[(C_6H_5)_4As](GeCl_3)$ with and without pressure.

some color changes were observed, which were similar to those found for nickel dimethylglyoxime (23, 24). These involve spectral changes with pressure and can be observed under the microscope or in a visible spectrophotometer. These changes are not to be confused with any structural change (e.g., $T_d \rightarrow D_{4h}$). Thus, one is forced to conclude that it may be necessary to apply pressure in solution, where the added energy of solution may induce the transformation to occur. Such studies are now in progress (44).

C. Recent Developments

A basic study of the effects of pressure on free ligands as compared to the complexed ligands present in several metallic complexes was made recently (45). Some molecular vibrations involving volume expansions were found to be pressure sensitive and this sensitivity was found to be of three types: (1) a shift toward higher frequencies; (2) a drastic decrease in intensity and the disappearance of bands; and, (3) a doubling of some bands.

The behavior of ligands such as 2,2'-bipyridyl and pyrazine (1,4-diazine) under pressure appeared to simulate the effect of complexation of the ligands