



Fig. 16. Frequency of  $\nu_{\text{SnCl}_{3\text{asym}}}$  and  $\nu_{\text{SnCl}_{3\text{sym}}}$  in  $[\phi_4\text{As}][\text{SnCl}_3]$  as a function of pressure [203]. (Figure reproduced through the courtesy of the authors and the American Chemical Society, Washington, D.C.)

above). The use of low temperature has been suggested as a guide to band assignments in these complexes.

(d) *Metal-halide bridging vibrations.* Complexes of the type  $\text{CoL}_2\text{X}_2$ , where  $\text{L} = \text{py}$ , 4-Cl(py) or 4-Br(py) and  $\text{X} = \text{Cl}$  or Br are known to exist in polymeric and monomeric forms. The monomeric forms are tetrahedral and blue or green colored, and the polymeric forms are octahedral and lilac colored. The assignments for bridged cobalt-halide stretching vibration ( $\nu_b(\text{CoX})$ ) and terminal vibration ( $\nu_t(\text{CoX})$ ) in these complexes were made possible by pressure studies to 28 kbar [204]. The  $\nu_b(\text{CoX})$  vibrations manifested appreciable blue shifts as opposed to the  $\nu_t(\text{CoX})$  vibration. The  $\nu(\text{Co-N})$  shifts appear to be smaller, of the order of  $18 \text{ cm}^{-1}$ .

(e) *Complex compounds.* High pressure studies of some hexa-ammine complexes of Ni(II) and Co(II) have been made [205]. The pressure studies to 40 kbar for the Ni(II) complexes were different than low-temperature studies, and indicated a phase change and a lowering of symmetry being involved.

Complex halides like  $K_2PtCl_4$ ,  $K_2PdCl_4$ ,  $K_2PtCl_6$  and  $K_2PdCl_6$  have been studied at high pressure (ca. 33 kbar) [206]. In the  $K_2MCl_4$  complexes of  $D_{4h}^1$  symmetry [207] it was found that the  $E_u$  internal vibrations were more pressure sensitive than the  $A_{2u}$  internal vibration in the  $MCl_4^{2-}$  ions. The most pressure sensitive external mode was the translational lattice mode along the long axis  $a_0$ , while the mode along the short axis  $c_0$  was less pressure dependent. It was concluded that with an increase in pressure, contraction occurred along the  $a_0$  axis, while a contraction or even expansion occurred along the  $c_0$  axis. The X-ray work of Drickamer may lend some substantiation to these conclusions, as in the tetragonal solids  $MnO_2$  and  $SnO_2$  pressure contracts along the  $a_0$  axis while the  $c_0$  axis expands [172,173].

In the cubic crystals ( $O_h^5$ )  $K_2MCl_6$ , where  $M = Pt(II)$  or  $Pd(II)$ , differentiation between internal and external modes was less certain, although the lattice mode appeared to be slightly more pressure sensitive. A series of transition-metal hexahalides was also studied under pressure to 20 kbar, and Adams and Payne [208] concluded that the pressure sensitivity followed the order  $\nu_2 > \nu_4 > \nu_3$ . For  $M_2PtCl_6$ , where  $M = K, Rb, Cs, Tl$  or  $NH_4$ , the pressure sensitivity of the  $\nu(Pt-Cl)$  modes of vibrations decreased in the order  $A_{1g} > E_g > F_{1u}$  at pressures to 20 kbar [209].

Several complex cyanides have been investigated at high pressures up to 30 kbar, and the effects studied by IR spectroscopy [210]. The compounds examined were  $K_2[Zn(CN)_4]$ ,  $K_2[Cd(CN)_4]$ ,  $K_2[Hg(CN)_4]$ ,  $Zn(CN)_2$ ,  $Cd(CN)_2$  and  $Hg(CN)_2$ . Pressure effects were studied by examining the CN stretching region as well as the metal-CN stretching region ( $200-600\text{ cm}^{-1}$ ). For the  $M(CN)_4^{2-}$  tetrahedra it was found that the degeneracy of the  $F_2$  vibrations was removed with pressure. It was concluded that for  $M = Zn$  or  $Cd$  the symmetry had lowered to  $D_{2d}$ , while for  $M = Hg$  to  $D_2$  or  $C_{3v}$ . Lower symmetry resulted for  $Zn(CN)_2$ . However, an increase in symmetry took place for  $Hg(CN)_2$  and  $Cd(CN)_2$ .

A far IR study of salts of  $SeX_6^{2-}$ , where  $X = Cl$  or  $Br$  and  $TeX_6^{2-}$  where  $X = Cl, Br$  or  $I$  at pressures up to 40 kbar was made [211]. All bands were observed to show blue shifts with the  $\nu_4$  bending mode exhibiting the most dramatic effect. For some compounds which did not show  $\nu_4$ , the band appeared with increased pressure. In most cases which showed  $\nu_4$  at ambient pressures, the vibration eventually disappeared with increased pressure. The results were explained on the basis of an anion-cation bonding scheme, which allows a pressure-dependent delocalization of the inert-pair electrons throughout the lattice.

(f) *Miscellaneous*. In a Raman study of metal carbonyls the  $A_{1g}$   $\nu(CO)$  shifted  $12\text{ cm}^{-1}$  at 25 kbar in tungsten carbonyls, while the  $E_{1g}$  mode was substantially less sensitive [212].

## (2) Pressure effects on spin states

A number of changes of oxidation state and spin states caused by pressure