(rutile) [86]. Grüneisen parameters for each lattice mode were obtained. The B_{1g} phonon mode was found to have a negative pressure dependency. These results agree with earlier pressure measurements made to 40 kbar, which demonstrated a $d\nu/dp$ for this mode as -0.3 ± 0.1 cm^{-1} kbar^{-1} [196]. This mode softens as well with decreasing temperature, although only slightly. The unusual pressure dependency for this vibration may have important implications relative to pressure-induced phase transitions in rutile, as well as in other crystals with this structure.

(iii) Coordination compounds

Interest in solid coordination compounds has centered on the behavior of various vibrational transitions under high pressures. Considerable interest has also developed in changes occurring with pressure in spin states and in oxidation states, and to identify these changes with far IR spectroscopy. Perhaps of most significance are the structural transformations which pressure has induced. The latter effects have served to test the theoretical predictions of Pearson [197] and Bader [198] regarding stability of various geometrical configurations. It is also possible that these studies provide a foundation for anticipated ultra-high pressure measurements of minerals.

(1) High pressure effects on vibrational transitions

As more research involving high pressure effects accumulates with time, it has become clear that certain vibrations are more sensitive to pressure than others. For example, vibrations which involve expansion of molecular volume appear to be more sensitive to pressure. Attempts to quantify the behavior of vibrations with pressure may never be realized for the application of pressure to solids involves many factors, and screening these factors may be an impossible task. Such factors as packing effects, compressibilities, nature of bonds (ionic vs. covalent), crystal field stabilization energy, steric effects, electronic repulsions, electronic delocalization, and other effects all contribute toward pressure-sensitivity of various vibrations in a molecule.

Examples of pressure effects on vibrations in different molecules will be discussed in the following sections.

(a) Ligand vibration. Relatively little attention has been paid to the effects of pressure on ligand vibrational modes. In a study of pyrazine and its complexes up to 72 kbar several observations could be made [199]. (1) Ligand bonds showed blue shifts and were less sensitive than the bands of the complexes. (2) Some bands showed splitting. (3) Although the vibrations in the ligands and their metal complexes were not the same, the pyrazine spectrum under pressure showed similarities to spectra of the corresponding metal complexes. This may appear to indicate that metallic complexation involves a pressure effect. The splitting of bands can be accounted for in terms of a lower symmetry or involving factor-group splitting. A new study of dihalocy-

clohexanes in the far IR region has recently appeared [200]. Pressure dependencies of the Raman and IR spectra of α-, β-, γ- and δ-octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazine have been made [201].

(b) Metal sandwich compounds. In a study on the effects of pressure (to 35 kbar) on the IR active skeletal vibrations of metal sandwich compounds, it was found that the $\nu(\text{M—ring})_{\text{asym}}$ vibrations are more sensitive to pressure than the ring tilt mode [202]. Table 21 shows the pressure dependencies in these compounds.

(c) Metal—halogen stretching modes. In complexes displaying both asymmetric and symmetrical metal—halogen stretching vibrations it was demonstrated that pressure effects (to 50 kbar) on the symmetrical vibration are more effective [203]. Although only minor shifts are observed, the symmetrical mode shows large decreases in intensity. The compounds studied included the following: 1. norbornadienedichloroplatinum(II), $(C_7H_8)PtCl_2$; 2. 2,2′,2″-terpyridinedichlorozinc(II), (terpy)$ZnCl_2$; 3. bis(α-picoline)dichlorocobalt(II), $(C_6H_7N)_2CoCl_2$; 4. tetraphenylarsenic trichlorostannate(II) $[(C_6H_5)_4As]$-$[SnCl_3]$; 5. tetraphenylarsenic trichlorogermanate(II), $[(C_6H_5)_4As][GeCl_3]$; 6. norbornadienedibromoplatinum(II), $(C_7H_8)PtBr_2$; 7. 2,2′,2″-terpyridinebromozinc(II), (terpy)$ZnBr_2$; 8. bis(pyridine)dibromocobalt(II), $(C_5H_5)_2CoBr_2$; 9. bis(α-picoline)dibromocobalt(II), $(C_6H_7N)_2CoBr_2$.

Results with the bromides indicate that the metal—bromine stretching mode behaves similarly to the metal—chlorine mode under pressure. However, since the assignments for the ν_{MBr} vibration are less well known because of the close proximity of the metal—nitrogen stretching vibration, further studies are necessary. Figure 16 shows the low frequency $\nu\text{M—X}_{\text{asym}}$ and $\nu\text{M—X}_{\text{sym}}$ vibrations $[\phi_4As][SnCl_3]$ as a function of pressure.

Lever has reported in a series of papers [204a] that metal—ligand vibrations in coordination complexes upon cooling to 80 K, increase in frequency relative to the "pure" ligand vibrations. The cooling effects are very similar to those observed with the application of high pressure (Sections (1)(a) and (1)(c)

TABLE 21

Pressure effects on skeleton modes of metal sandwich compounds [202]

	Ring tilt (cm^{-1})		ν(M-ring) (cm^{-1})	
	Ambient pressure	35 kbar	Ambient pressure	35 kbar
$Fe(Cp)_2$	491	494	461	474
$Ru(Cp)_2$	447	476	381	390
$Mn(Cp)_2$	432	437	409	420
$Cr(C_6H_6)_2$	487	491	453	475