

molecular vibrations involving out-of-plane motions in ligands containing heterocyclic rings (e.g., pyrazine, dipyridyl etc.) are very sensitive to pressure.³⁴ Some in-plane motions are also sensitive. Thus, motions, generally involving large volume changes, may become pressure sensitive.

Although Lippincott et al.^{4,5} examined some inorganic compounds with pressure, no systematic studies have been made in the mid-infrared region and certainly none made in the low frequency region. A systematic basic study of inorganic compounds from 1600-100 cm^{-1} has been commenced. Preliminary results³⁵ with salts such as K_2SO_4 , K_2CrO_4 , KMnO_4 etc. in the ν_4 region (MO_2 deformation vibration) indicate some pressure sensitivity. For example, the ν_4 (a triply degenerate vibration) vibration in KMnO_4 at $\sim 400 \text{ cm}^{-1}$ is seen as a doublet at ambient pressure. The doublet is attributed to a lowered symmetry (probably to C_{3v}). In this symmetry the two vibrations are the A_1 and E species. Differentiation be-

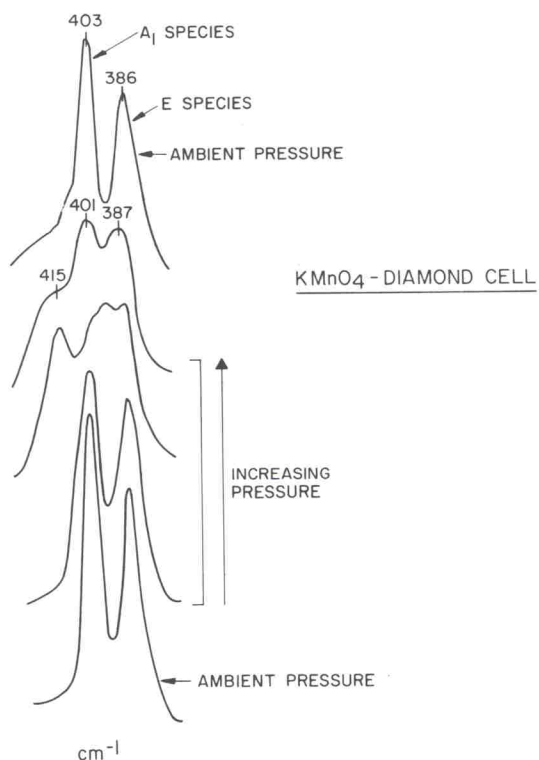


Fig. 9. Low Frequency Spectra of KMnO_4 with and without pressure.

tween the two species is normally difficult. Figure 9 illustrates the effect of pressure on the doublet. It is observed that the similarly effected. No noticeable shifts, or at the most, only slight shifts are observed. The direction of the slight shift may be either a blue or red shift. In hydrogen bonded compounds, studies of the OH stretching vibration has resulted in a red shift.^{5,27} Red shifts were also observed for HgCl_2 and its dioxane complex by Brasch and Jacobsen.³⁸ In most of our studies with internal modes, blue shifts have been observed. The attempts at converting a structural isomer to another having failed in the solid state, indicates that in the pressures used (up to 60 kbars) little effect on the interatomic distances or bond angles occur. However, the results do point to the fact that intermolecular distances are changed (e.g., distance between ions or molecules) under these pressures. It is conceivable that higher pressures are needed to successfully effect the interatomic distances. It should be mentioned, however, that pressure effects appear to be sufficiently large to cause changes in symmetry in a molecule.

The pressure effects on the ionic or molecular lattice modes may be accounted for by the contraction of the solid under pressure, placing ions or molecules closer to each other. Obviously, repulsive and attraction forces in the solid are involved. For internal modes which shift only slightly toward higher frequency the repulsive force must be greater. The shifts of out-of-plane and in-plane vibrations in ring compounds toward higher frequency under pressure, may be attributed to the more energy required to cause the vibration, since the molecules are in closer proximity to each other. Several reasons can be cited for the splitting of bands. The discussion concerns bands with no change in phase occurring with an increase in pressure. One involves the failure to resolve a band into two components at room temperature and ambient pressure. With high pressure this is possible because of the pressure shifts occurring, and one component being shifted a greater amount than the other. Another reason may be due to the removal of degeneracy in degenerate modes. Broadening of all bands occurs and this may be due, at least in part, to the pressure gradient existing in the diamond cell.

The changes in intensities that occur under pressure probably involves large changes in dipole moments for certain modes of vibration. It has been definitely established that other physical effects occurring simultaneously with the electromagnetic effect, can cause changes in the dipole moment for a particular vibration. For example, electrical effects cause dipole moment changes to be non-zero ($\frac{\partial \mu}{\partial Q} \neq 0$) and forbidden frequencies can occur. Pressure effects may cause similar changes, although tending toward $\frac{\partial \mu}{\partial Q} \rightarrow 0$. It has been observed that the A_1 species is particularly sensitive in this regard.