

referring the results to isothermal equations of state derived from shock-wave experiments.

The piston-cylinder type cells have been calibrated by measuring bismuth and barium transition pressures or the resistance changes with pressure of various metals (e.g., manganese, lead, iron, barium, calcium and rubidium) [33]. In some cases, pressure transducers are used to measure the pressures [136]. Alternatively, the NDMG or ruby methods, crystals showing phase changes, or a change in the index of refraction may be used. For reviews on pressure calibration see refs. 17 and 137.

#### D. CHOICE OF OPTICAL REGIONS TO USE AS A PROBE

The optical region one chooses for pressure studies depends on the particular application. For ionic or pseudo-ionic crystals the far IR region (FIR) is the most useful, since all of the lattice modes occur in this region. For organic compounds the "fingerprint" (mid-IR) region is the most useful. For coordination compounds of the  $MX_n$  type, where X = halogen, pseudo-halogen or inorganic anion, the low frequency region is useful as the metal-X vibrations are located there. However, the visible region should be examined conjunctively to monitor the "d-d" transitions. For coordination compounds involving organic ligands (of the type  $ML_nX_m$  where L = organic ligand) the FIR may offer some complications since the organic ligands' strong absorptions could mask the M-X or M-L vibrations. In that case, the visible region may be used. If L = CO or en, one can resort to the mid-IR region using sapphire windows ( $\nu_{CO}$  in 5  $\mu\text{m}$  range), since diamond has absorption in this region. If L = NO one may use the mid-IR region likewise, but in this case one must use diamond windows ( $\nu_{NO}$  in the range 6-6.5  $\mu\text{m}$ ), since sapphire shows absorption in this region. For heavy element complexes such as the actinide or lanthanide complexes, the FIR is perhaps the most useful, as "f-f" transitions appear to be less pressure-sensitive than "d-d" transitions [138]. Whenever possible, it would be better to use several optical probes to study a particular pressure change.

#### E. VIBRATIONAL STUDIES AT HIGH PRESSURES

The opportunity to subject a molecule to an external perturbation such as pressure and measure the resultant changes by spectroscopic techniques, affords the scientist an additional mechanism whereby he can study physical and/or chemical changes. Vibrational spectroscopy becomes a viable method of studying these changes, for in most cases the space group is changed and this is reflected by changes in the vibrational selection rules.

The area of vibrational spectroscopy of molecules subjected to pressure was long neglected [139]. The reasons for the neglect were probably experimental since it was easier to cool or heat a material, and these non-ambient temperature experiments did not require microtechniques in IR or Raman that are



required with pressure measurements. The strides that the matrix isolation technique has made in the past 10 years attests to this. However, the advent of the DAC in 1959 [48] generated the notion that vibrational spectroscopic techniques used conjunctively with pressure were possible. This paper is planned to present a review of the accomplishments of the past 20 or so years, since Weir and co-workers constructed the DAC [48]. In most cases the review will concern itself with results obtained with the DAC.

### (i) Inorganic compounds

Primary motivations in studying solid inorganic systems have been based on studying pressure effects on various polymorphs, those stable under ambient conditions and those achieved only under high pressures. In this way phase diagrams, previously unknown, can be constructed or adjusted. In cases where no X-ray is known (e.g., phases obtainable only at elevated conditions of temperature and pressure) some inference may be obtained on the nature of the space group involved from the spectroscopic results. In certain instances interest has been based on obtaining order-disorder information existing in the various phases of a material (for example, electrical conducting phases). Comparisons of intra- and intermolecular forces, the latter being pressure sensitive, are also of interest. Of interest are hydrogen bonded systems where pressure shows effects which can be observed by studying the vibrational spectra.

#### (1) Mercuric halides

Adams and Appleby [140] have investigated the halides of Hg(II) under high pressure. The three phases (I, II and IV), of  $\text{HgCl}_2$  have been subjected to pressures up to 30 kbar. Results are shown in Table 8. The Raman and IR spectra of phases I and IV were found to be similar, and it was concluded that a second-order transition characterized by molecular orientation with retention of the space group was involved. Phase II was found to be entirely different and to approximate a  $T_h^6$  structure with  $z = 4$ , based on the spectroscopic results. Phases I and IV possess a  $D_{2h}^{16}$  space group with  $z = 4$ .

All four phases of  $\text{HgBr}_2$  (I, II, III and IV) were investigated by Raman and IR techniques to 50 kbar [141]. Phases I and II were considered to have similar structures. Phase III appears to possess a  $C_{2h}$  space group, and phase IV probably has a  $\text{CdI}_2$  structure. These conclusions were reached, based on the spectroscopic results obtained. Table 9 tabulates the Raman frequencies at various pressures.

Early superficial Raman experiments with  $\text{HgI}_2$  have been made [59,60]. In a more thorough study the high temperature ( $127^\circ\text{C}$ ) phase and the high pressure phase (ca. 13 kbar) of  $\text{HgI}_2$  were compared, using Raman and far IR data [142]. The red, ambient temperature,  $\text{HgI}_2$  has a  $P4_2/nmc$  ( $D_{4h}^{15}$ ) space group,  $z = 2$ , with 4 iodine atoms around the mercury atom [143]. At  $127^\circ\text{C}$  it turns yellow and this phase has a  $Cmc2_1$  space group with  $z = 4$  [144]. At