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# ELECTRONIC STRUCTURE, ELECTRONIC TRANSITIONS, AND THE HIGH PRESSURE CHEMISTRY AND PHYSICS OF SOLIDS

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## INTRODUCTION

The basic effect of high pressure is to increase the overlap between electronic orbitals on adjacent atoms or molecules. There are a number of consequences of this increased overlap. Perhaps the simplest is the broadening of allowed energy bands and the resulting increase in electron mobility. This is a major factor in the "red shift" (shift to lower energy) of the absorption edge observed as a function of pressure in many crystals. It may ultimately lead to an overlap between the valence and conduction band, and thus to metallic conductivity as observed, for instance, in iodine (1).

In the second order, one observes a relative shift of one orbital energy with respect to another. Since orbitals of different quantum number may differ in radial extent, orbital angular momentum (orbital shape), or diffuseness or compressibility, these relative shifts are rather common. In terms of the band picture of solids, one may observe a shift of the center of gravity of one band with respect to another which can either augment or counteract the broadening effect mentioned above.

High pressure experiments measuring the shifts of various parts of the conduction band with respect to the valence band have been instrumental in understanding the structure of the conduction band and the nature of the deformation potential in silicon, germanium, and the III-V and II-VI semiconductors (1, 2). In the alkali, alkaline earth, and rare earth metals, the relative shifts of various parts of the conduction band can lead to drastically different electronic behavior, as discussed below.

Of more direct interest to chemists generally are the relative shifts of orbital energies involving more localized electrons. We mention three classes of such transitions. The  $\pi$ - $\pi^*$  transitions in aromatic hydrocarbons and related materials generally shift rather strongly to lower energy with increasing pressure. Shifts of  $\frac{1}{3}$ -1 eV in 100 kbar are not uncommon (1, 3). This implies a higher dipole moment in the excited state, i.e. a greater charge separation with increasing pressure. To the extent that the decrease in the relative energy of

the  $\pi^*$  levels vis à vis the  $\pi$  levels indicates a greater occupation of the excited state at high pressure, the implication is that the volume of the system as a whole decreases with increased occupation of the  $\pi^*$  orbitals. We make use of this fact later. Offen (4-12) has made extensive studies of the effect of pressure to 30 kbar on  $\pi$ - $\pi^*$  and  $n$ - $\pi^*$  transitions and on fluorescence in aromatic molecules in the solid state and as dilute solutes dissolved in plastics.

A second type of localized electronic transition of interest here is the internal rearrangement of the  $3d$  electrons of transition metal ions. In a field of octahedral symmetry the  $3d$  orbitals split into a higher energy doublet of  $\sigma$  symmetry ( $e_g$ ) and a lower energy triplet of  $\pi$  symmetry ( $t_{2g}$ ). In molecular orbital language, the  $e_g$  orbitals are strongly antibonding, while the  $t_{2g}$  orbitals are nonbonding or slightly antibonding. The occupation of these orbitals depends on the magnitude of the splitting compared with the energy involved in pairing spins. Optical transitions measure the magnitude of the ligand field ( $\Delta$ ) and of the Racah (interelectronic repulsion) parameters  $B$  and  $C$ . For high spin systems the ligand field increases with pressure, approximately as  $R^{-5}$  where  $R$  is the ligand-metal distance (13, 14). The Racah parameters decrease by 5-10% in 100 kbar. Qualitatively similar observations have been made for symmetries other than octahedral. These parameters have been very little studied as a function of pressure for low spin systems. There are, however, indications that for some such systems  $\Delta$  may decrease with pressure and  $B$  may increase (15).

There is a third type of transition where a relative shift with pressure has been observed. This excitation involves the transfer of charge from one type of entity to another. Molecular electron donor-acceptor complexes have been widely studied both experimentally and theoretically (16). A variety of these complexes have been observed as a function of pressure (17). The energy of the donor-acceptor transition decreases with pressure, as indicated by the red shift of the optical absorption peak. There is also a decrease in electrical resistance (18).

Coordination compounds of transition metals also may exhibit charge transfer spectra. The transfer may be from the predominantly ligand  $\pi$  orbitals to the metal nonbonding  $3d$  orbitals, or from the metal orbitals to the empty ligand  $\pi^*$  orbitals. The available data indicate that both metal-to-ligand and ligand-to-metal charge transfer peaks usually shift to lower energy with increasing pressure (19), with few exceptions (20). The fact that both transitions shift to the red reflects the large decrease in the  $\pi$ - $\pi^*$  energy with increasing pressure.

There is a third consequence of increased orbital overlap. For a wide variety of systems there exists an excited state which lies not too high in energy above the ground state. The relative displacement of orbitals with pressure may be sufficient to establish a new ground state for the system or to modify drastically the properties of the ground state by configuration interaction as shown schematically in Figure 1. We call this type of event an electronic transition. It may occur at some definite pressure at a given tempera-