

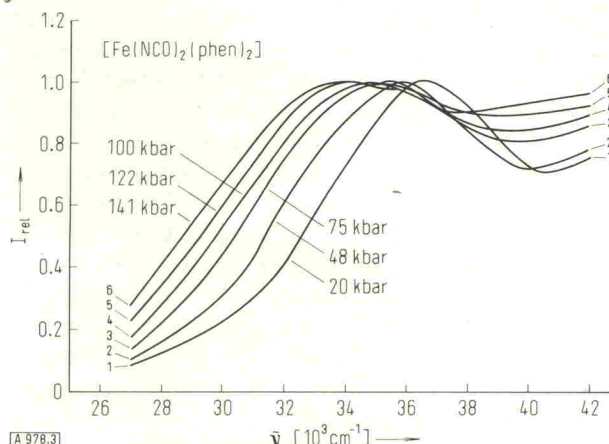


Fig. 3. 1,10-Phenanthroline: $\pi\text{-}\pi^*$ excitation vs pressure.

as ligands in some of the more interesting transition metal complexes.

2.3. Electron Donor-Acceptor Excitations

A wide variety of complexes exhibit relatively intense, broad optical absorption peaks which correspond to electron transfer between two entities of the complex. Molecular electron-donor acceptor complexes have been widely studied^[15, 16]. The excitations tend to shift strongly to lower energy with increasing pressure^[9, 11]. Similar excitations (ligand to metal or metal to ligand) are frequently observed in transition metal complexes. The halide complexes of the heavy metals (*e.g.* K_2OsBr_6) exhibit a pair of peaks at 16–17 kK and 21–22 kK which Jørgensen^[17] has assigned to ligand to metal ($\pi\text{-T}_{2g}$) electron transfer split by spin orbit coupling. As is shown in Figure 4, the center of the peak system shifts to lower energy by some 2.5 kK at 120 kbars, while the spin-orbit splitting increases by ~ 3.0 kK. A red shift of this magnitude is typical for this type of excitation. Tetrahedral cobalt complexes also exhibit increased spin-orbit splitting at high pressure^[10, 11].

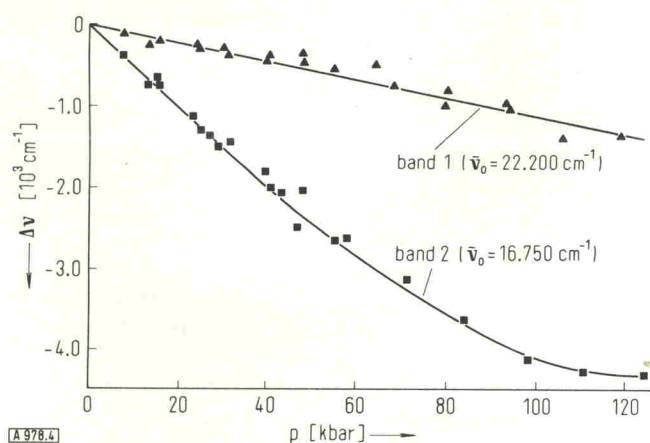


Fig. 4. Location of charge transfer peaks vs pressure (K_2OsBr_6).

3. Electronic Transitions

As indicated earlier, the relative shifts in energy levels discussed above can lead to a new ground state for a system, or a ground state whose properties are greatly modified by configuration

interaction. Let us first discuss some general characteristics of these electronic transitions, which may occur discontinuously at some definite pressure or over a range of pressures. They may be easily reversible, or may reverse with considerable hysteresis, or may result in a new stable compound. These characteristics are discussed in a detailed study^[9, 18] of which we can give only the barest essence here. The various transitions may to a greater or lesser degree be cooperative phenomena. When a site transforms there may be an electrical polarization and/or mechanical strain introduced, which may act either to inhibit or to accelerate the transformation of neighboring sites. The continuous or discontinuous nature of the transformation depends on the sign of the interaction and its magnitude relative to the thermal energy (kT). Hysteresis implies the locking-in of a transformation by interaction among transformed sites.

These transitions involve the thermal transfer of an electron from one type of orbital to another or from one mixture of orbitals to another. Typically, however, we employ optical absorption to measure the shifts in relative energy of the orbitals which ultimately lead to the transition. The energies involved in optical and thermal transfers between the same electronic states differ for a number of reasons. Some of these are illustrated in Figure 5, which is a schematic configuration coordinate diagram. The horizontal axis represents some relative nuclear displacement of the system, while the vertical axis measures energy.

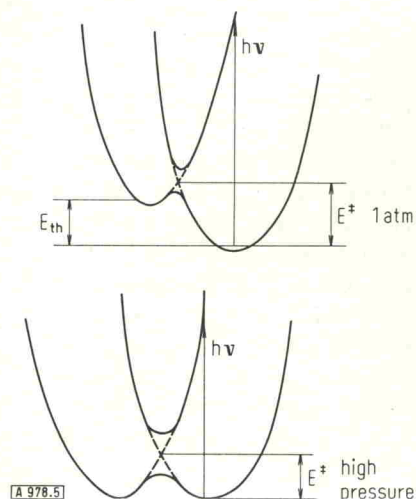


Fig. 5. Schematic configuration coordinate diagram.

Optical processes are represented vertically on such a diagram because they are rapid compared with nuclear displacements (the Franck-Condon principle). Thermal processes are sufficiently slow so that they can occur on a path of minimum energy requirement. This is a major difference, but there are others which can be of comparable magnitude. Configurational interaction, which involves mixing of electronic configurations by partial violation of the Born-Oppenheimer conditions through spin-orbit or other couplings is also illustrated in Figure 5. In solids of the complexity of most of those discussed here there is almost always a vibration suitable enough to mix configurations of any symmetry. A third factor, not illustrated here, is that of selection rules. Optical processes are subject to parity and spin selection rules, while in the time scale typical of thermal processes all selection rules are relaxed.

Finally, Figure 5 is greatly oversimplified in that only one configuration coordinate is illustrated. Actually, the total number of such coordinates equals the number of normal modes of the system. For a thermal process, the pressure selects the volume as its conjugate coordinate, but optical processes may involve other coordinates.

In view of these complications, to what degree can the observed optical shifts be related to the thermal transformations? An analysis has been presented^[9, 19] which relates the location of the optical peak ($\nu_{\max}$), its half-width ($\delta E_{1/2}$), and the force constants of the ground and excited state potential wells (ω and ω') to the thermal energy (E_{th}). At 25°C, if the energies are in eV, one obtains:

$$E_{\text{th}} = h\nu_{\max} - 3.6(\delta E_{1/2})^2 \left(\frac{\omega}{\omega'} \right)^2 \quad (1)$$

This result is based primarily on the Franck-Condon argument. It can be extended to include multiple configuration coordinates, but it is difficult to generalize the magnitude of the effect of configurational interaction. The analysis is approximate and the data to test it are crude; nevertheless, we shall see that useful results are obtained.

It is our purpose here to discuss primarily electronic transitions in transition metal complexes. It is, however, appropriate to outline briefly the other types of electronic transitions which have been observed to place the above in their proper context.

Over 20 years ago *Bridgman*^[20] discovered a cusp in electrical resistance and a volume discontinuity in cesium. *Sternheimer*^[21] showed that these are associated with a change from s to d character of the conduction band (i.e. a 6s→5d transition). About a decade ago a second maximum in the resistance of cesium was observed near 135 kbars. Recent work indicates that hybridization of the empty 4f and atomic 5p orbitals into the conduction band are both involved. Transitions which probably have a similar basis are observed in rubidium at 145 and 300 kbars. A transition in cerium metal near seven kilobars involves promotion of a 4f electron into the 5d shell, or into the conduction band. Resistance anomalies in other rare earth metals at higher pressures may be associated also with 4f→5d transitions. This is consistent with the shift to lower energies of the 4f→5d excitation in divalent rare earth salts which we mentioned earlier. Alkaline earth metals like calcium and strontium exhibit metal to semi-metal (or semiconductor) transitions because of changes in the band structure at high pressure.

A variety of insulator-metal transitions have been observed. In molecular crystals like iodine or pentacene the energy gap decreases continuously with pressure, and metallic conductivity appears, with no apparent discontinuity in resistance or structure. Silicon, germanium, and related compounds undergo a first order change in structure which transforms them to metals like tin. Some semiconducting oxides undergo a discontinuous transition without structure change to a metallic state. The work of *McWhan et al.*^[22-24] on these compounds has been especially enlightening. In particular these authors have demonstrated the parallelism between change of chemical composition and increase of pressure. *Jayaraman*^[25, 26] has shown that samarium chalcogenides transform from semiconductor to metal by promotion of an electron from the 4f orbitals to the conduction band.

Transitions with chemical consequences have been observed in certain aromatic hydrocarbons and their electron donor-acceptor complexes. We have indicated earlier that the π - π^* excitations of these hydrocarbons as well as the D-A excitations of the complexes decrease rapidly in energy with increasing pressure. If the excited state at one atmosphere is not too high in energy, it may be occupied at high pressure with consequent changes in intermolecular interactions including reactivity. It has been observed that pentacene forms a new type of polymer at high pressure^[9, 27]. The complexes of perylene ($\text{C}_{20}\text{H}_{12}$) and pyrene ($\text{C}_{16}\text{H}_{10}$) with iodine also react^[9, 28]. In this case, the iodine does not enter into the product although its presence is necessary to bring the hydrocarbon into a reactive configuration. The product structures have been rather completely elucidated. Perylene forms a new type of layered dimer, while pyrene forms a similar tetramer. These types of reactive electronic transitions may have important implications for solid state organic chemistry.

3.1. Transition Metal Complexes

With this background, we now consider changes of spin state and oxidation state of transition metal complexes. Most of our observations concern complexes of iron. Iron is of interest not only in chemistry and physics but also in biology and geophysics. Further, in addition to optical absorption, we have available Mössbauer resonance spectroscopy to sharpen our identification of the states involved.

We offer only a very brief outline of the principles of Mössbauer resonance here. Under certain circumstances, the energy of a gamma ray emitted by ^{57}Fe in the solid state is a measure of the separation of nuclear energy levels. This separation is perturbed by electronic wave functions. From the measured perturbations information can be inferred about the electronic structure—very much as in the employment of nuclear magnetic resonance. For this study there are two useful types of perturbation. Electronic wave functions which overlap the nucleus (s electrons) affect the energy difference between the ground and excited state (the isomer shift). From our viewpoint, changes in the isomer shift reflect changes in shielding of 3s electrons by 3d electrons. This depends on the number of 3d electrons (oxidation state) and the radial extent and shape of the 3d orbitals (covalency). An electric field gradient at the iron nucleus partially removes the degeneracy of the excited state and gives two peaks in the spectrum instead of one. The electric field gradient may arise from the arrangement of the ligands (a long range, small effect) or from the partially filled 3d shell (a short range, large effect). Because of these perturbations ^{57}Fe in one chemical state is not in resonance with ^{57}Fe in a different state. By moving a radioactive source with respect to an absorber we utilize the Doppler velocity to bring about resonance, and express the perturbation energies in terms of this resonant velocity.

We are concerned here primarily with transformations involving three states; high-spin ferrous, high-spin ferric, and low-spin ferrous. Figure 6 exhibits typical spectra for these states. The high-spin ferrous ion exhibits a large positive isomer shift (IS) (low electron density) because of the six 3d electrons shielding the 3s electrons, and a large quadrupole splitting (QS) because the field of the 3d electrons is not spherically symmetric. The high-spin ferric ions with five 3d electrons