

Electronic Transitions in Transition Metal Compounds at High Pressure

By H. G. Drickamer^[*]

Very high pressure is becoming increasingly important for investigating electronic structure. The relative shift in energy of electronic orbitals which is commonly observed at high pressure can frequently lead to a new ground state for the system. These electronic transitions may result in changes in electrical, optical, or magnetic properties as well as changes in chemical reactivity. Electronic transitions in metals and insulator-metal transitions have been widely studied by physicists. Recently, it has been found that electronic transitions in aromatic hydrocarbons and their electron donor-acceptor complexes can induce chemical reactivity and lead to the formation of new classes of hydrocarbons.

Electronic transitions in transition metal complexes may lead to changes in spin state; both increase and decrease in multiplicity with increasing pressure have been observed. In addition, it has been shown that Fe(III) and Cu(II) reduce at high pressure in a variety of compounds. The behavior of these transition metal ions is described in some detail in relation to the general area of high pressure and electronic structure.

1. Introduction

Over the past two decades it has become apparent that very high pressure is a powerful tool for studying electronic structure. Its application first became common in solid state physics and geophysics, but has more recently been extended to physical, inorganic, and organic chemistry.

The pioneering work of *Bridgman*^[1] provided techniques for studies at up to 12 kbars (1 kbar = 987 atmospheres), and in some cases up to 30 kbars, using hydrostatic media. These techniques have been applied to many problems of solid state physics, as well as to investigations on the physical chemistry of solutions^[2], relaxation processes in solution^[3], electronic and molecular spectroscopy^[4], and also to the study of organic reaction mechanisms^[5, 6].

In addition, *Bridgman* developed techniques for electrical resistance and pressure-volume measurements utilizing quasihydrostatic media at 70 kbars or above. In the past fifteen years the static pressure range has been extended to several hundred kilobars. More important—measurements such as optical absorption and emission and Mössbauer resonance which are sensitive to electronic structure are now possible.

In this review we discuss studies of transition metal ions in this high pressure range. In order to place these investigations in their proper context a brief review of the general effects of pressure on electronic structure will first be given. The experimental techniques have been covered in detail elsewhere^[7-9] and will not be discussed here. There exist reviews^[9-13] with extensive references to the literature on high pressure and electronic structure. We list here primarily very recent references, or those not included in the above literature. In general we express energies in electron volts and optical peak locations in cm^{-1} or kilokaysers (one eV per atom $\approx 23 \text{ kcal per g-atom} \approx 8000 \text{ cm}^{-1} = 8.0 \text{ kK}$).

From our viewpoint the primary effect of compression is to increase overlap of adjacent electronic orbitals. A very

general consequence of this increased overlap is the relative shift in energy of one type of orbital with respect to another. Since orbitals of different quantum number differ in radial extent, or in orbital shape (angular momentum) or in compressibility, this *relative shift in energy* is not surprising. Under many circumstances there may be an excited state which lies not too far in energy above the ground state so that the pressure-induced shift may be sufficient to establish a new ground state for the system, or greatly to modify the characteristics of the ground state by change in configurational interaction. This event we call an electronic transition, which may occur discontinuously at a definite pressure or over a range of pressures, and may have a variety of physical and chemical consequences. We discuss first (Section 2) the kinds of shifts in orbital energy which have been observed, and second (Section 3), the variety of electronic transitions. In both cases strong emphasis is on events relevant to transition metal chemistry.

2. Shifts of Energy Levels

The early high-pressure optical measurements concerned themselves in large part with studies of the change in the gap between the top of the valence band and the bottom of the conduction band^[9-11], in insulators or semiconductors. For many substances this gap decreases rapidly with increasing pressure leading ultimately to metallic conductivity in such materials as iodine and higher acenes (*e.g.* pentacene). For materials like germanium, gallium arsenide, and zinc sulfide with complex band structure the gap may actually increase at low pressure.

Other studies include the behavior of color centers in alkali halides^[9, 11], transitions from the $4f^n$ to the $4f^{n-1}5d$ configuration in rare earth ions^[14], excitations among 3d configurations in transition metal ions^[9-13], excitations from π to π^* states in aromatic hydrocarbons and related heterocyclic compounds^[9, 11] including aromatic ligands in transition metal complexes, and electron donor-acceptor excitations in both molecular complexes and transition metal complexes^[9-13]. We discuss in more detail those types of excitations of particular interest to coordination chemistry.

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2.1. d-d Excitations

The interesting properties of transition metal ions center around the number and arrangement of electrons in the partially filled d shell. In the free ion the five orbitals are degenerate, and, in accordance with Hund's rule, the electrons are arranged to give maximum multiplicity in the ground state. Excited states with partially or completely paired spins lie higher in energy because of the increased interelectronic repulsion associated with spin pairing. The interelectronic repulsion is most conveniently expressed in terms of the Racah parameters B and C, which we take here to be empirically determined. When the ion is placed in a crystal lattice, or in a complex, the fivefold degeneracy is partially removed, as orbitals of different symmetry are affected differently by the nearest neighbor atoms or ions (the ligands). For instance, in an octahedral complex (six neighbors), the D_{22} and $d_{x^2-y^2}$ orbitals of $E_g(\sigma)$ symmetry are increased in energy relative to the d_{xy} , d_{yz} , and d_{zx} orbitals of $T_{2g}(\pi)$ symmetry. This splitting (Δ) is a measure of the field due to the ligands. In molecular orbital language the splitting is between the antibonding E_g orbitals and the essentially nonbonding T_{2g} orbitals.

In most complexes the electrons are still arranged in a high spin configuration because the spin pairing repulsion is larger than the potential energy necessary to occupy the T_{2g} orbitals. If the ligand field Δ is sufficiently large the potential energy effect may more than compensate for the interelectronic repulsion, and a low spin configuration results. In low spin systems the ligands usually have low lying states of π symmetry which are empty and can bond with the metal d_π orbitals. This "back-donation" of metal electrons into ligand orbitals stabilizes the d_π orbitals and so gives the large value of Δ . Thus the 3d electrons tend to be delocalized in low spin complexes. Molecules of lower symmetry such as metalloporphyrins or phthalocyanines may exhibit intermediate spin or mixed spin states.

For high spin complexes the ligand field increases with increasing pressure. A simple point charge model would predict $\Delta \sim R^{-5} \sim \rho^{5/3}$, where R is the metal ion—ligand distance and ρ is the density. Figure 1 compares the measured values of Δ for NiO with the prediction (solid line) from density data.

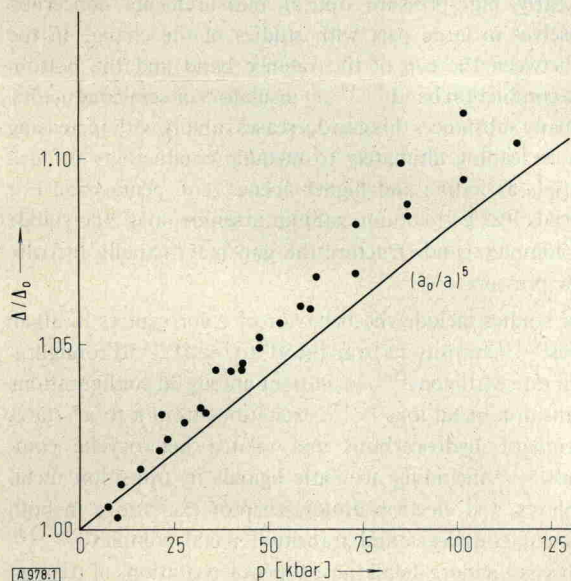


Fig. 1. NiO: Δ/Δ_0 and $\rho^{5/3}$ vs pressure (a = lattice constant).

The point charge model is inadequate to calculate Δ even approximately for any system, and NiO is far from an ionic crystal so the modest agreement shown may be in large part fortuitous. Measurements on several systems indicate that Δ generally increases somewhat more rapidly with density than the simple model predicts. Figure 2 shows the change in the Racah parameters with pressure for $MnCl_2$ and $MnBr_2$. The decrease shown is typical of most complexes. It is associated with a spreading of the 3d orbitals with pressure and increased shielding of 3d electrons from one another by ligand electrons. The spreading of the 3d orbitals is also reflected in the generally observed decrease of the isomer shift of Fe(II) and Fe(III) ions with pressure (decreased shielding of 3s electrons by 3d electrons) as observed in Mössbauer resonance studies (see Section 3.1).

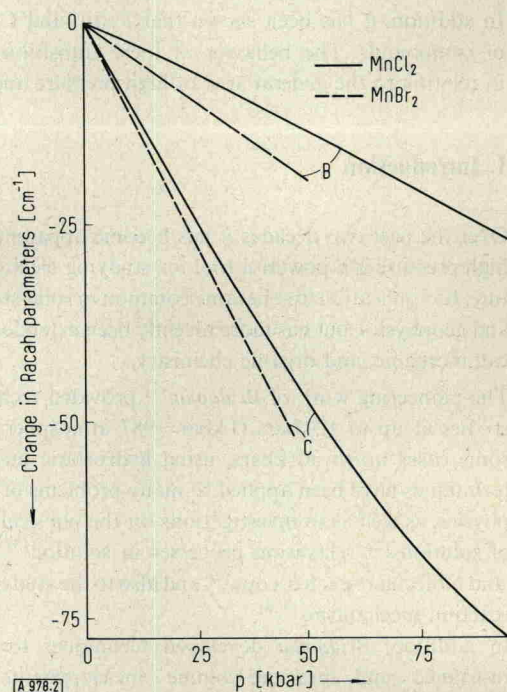


Fig. 2. Change in Racah parameters B and C with pressure for $MnCl_2$ and $MnBr_2$.

2.2. π - π^* Excitations

Aromatic hydrocarbons are characterized by conjugated π orbitals. In the ground state they are nonpolar and not very reactive, especially in solids. There are excited states (π^* states) which have nodes either at or between the carbons. These excited states generally have greater self-complexing ability, are more reactive, and probably involve stronger intermolecular forces than the ground state. The larger the aromatic molecule the smaller the energy of the π - π^* excitation and also the greater the self-complexing ability. These π - π^* excitations decrease in energy by 0.5–1.0 eV per 100 kbars. As discussed later, this implies a higher probability of mixing of π - π^* orbitals and of electron occupation of the π^* orbitals at high pressure.

Heterocyclic aromatic molecules also exhibit π - π^* excitations with very similar characteristics. In Figure 3 we illustrate the shift of a π - π^* excitation in 1,10-phenanthroline. Both the large red shift (to lower energy) and the broadening are typical. These heterocyclic molecules are frequently involved