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Electronic Transitions in Transition Metal Compounds at High Pressure

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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 $\hat{=}$ 23 kcal per g-atom $\hat{=}$ 8000 cm^{-1} = 8.0 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_{z^2} 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_{xz} 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.

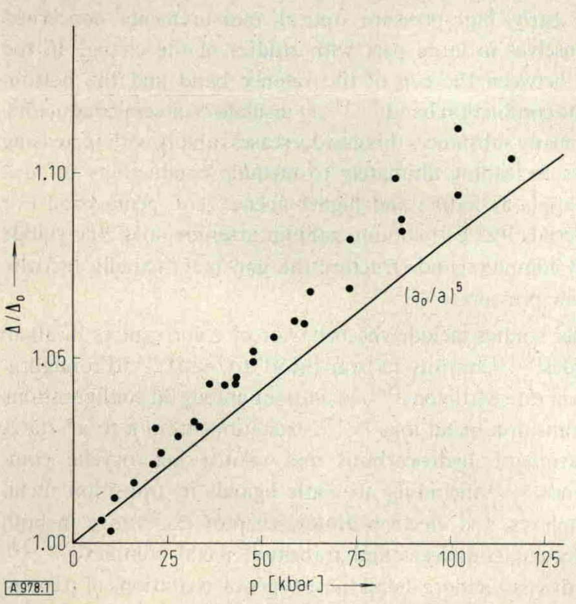

Fig. 1. NiO: Δ/Δ_0 and $\rho^{5/3}$ *vs* pressure (a = lattice constant).

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).

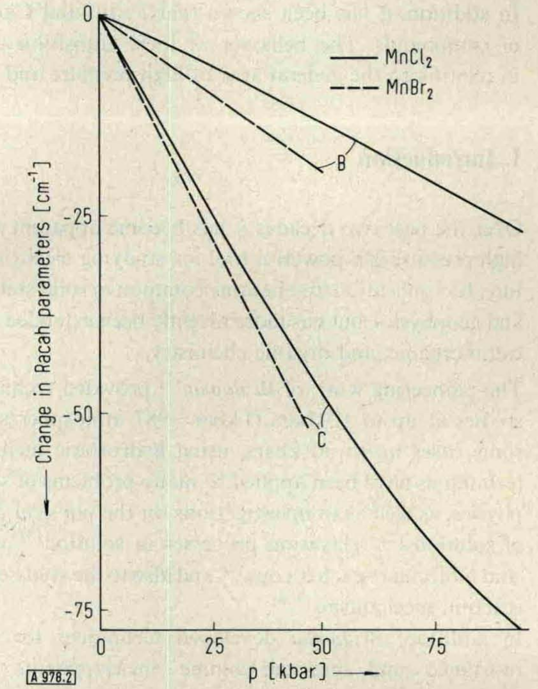

Fig. 2. Change in Racah parameters B and C with pressure for $MnCl_2$ and $MnBr_2$.

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

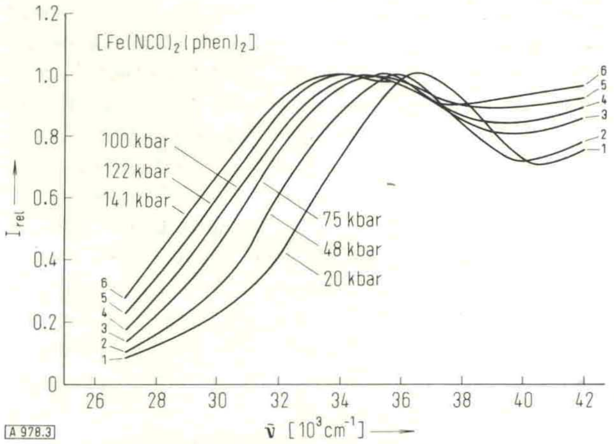

Fig. 3. 1,10-Phenanthroline: π-π^* excitation *vs* pressure.

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 *Jørgenson*[17] has assigned to ligand to metal (π-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].

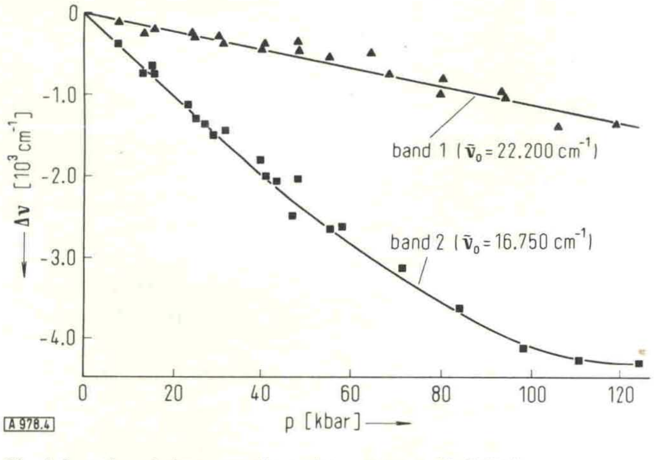

Fig. 4. Location of charge transfer peaks *vs* pressure (K_2OsBr_6).

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.

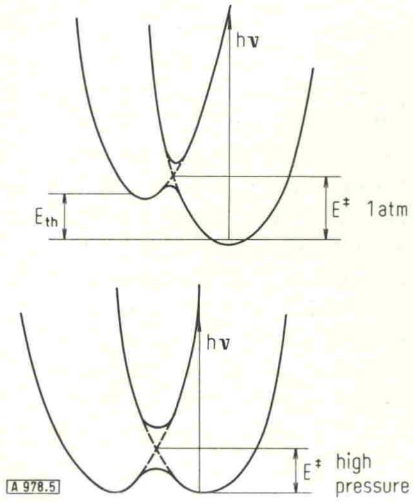

Fig. 5. Schematic configuration coordinate diagram.

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 (ν_{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:

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

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 semimetal (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 enlightning. 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 ($C_{20}H_{12}$) and pyrene ($C_{16}H_{10}$) 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 pertubation. 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

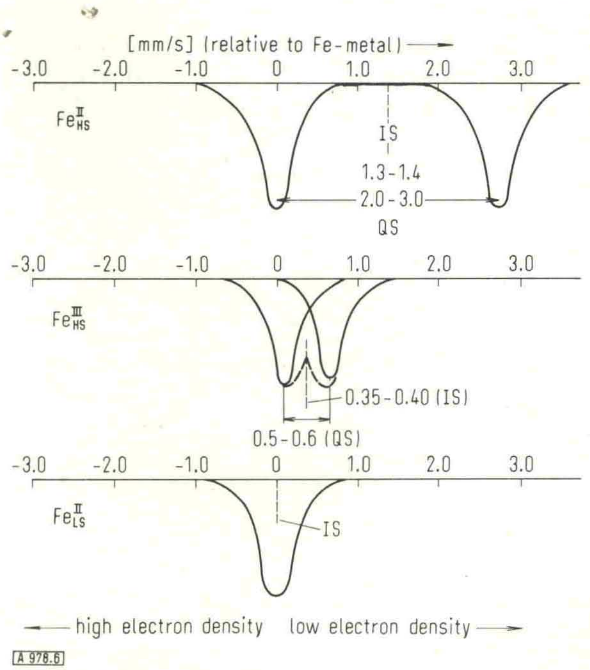

Fig. 6. Characteristic Mössbauer spectra.

has a smaller isomer shift, and, since the field of the 3d shell is spherical, only a small quadrupole splitting. The low-spin ferrous ion has a spherical electric field and thus a small quadrupole splitting. The low value of the isomer shift reflects the delocalization of the 3d electrons by "back donation" as discussed in Section 2.1, and the resultant high electron density at the nucleus. Our discussion will be largely limited to three transitions: 1. $\mathrm{Fe^{II}_{HS}}$ (high spin) → $\mathrm{Fe^{II}_{LS}}$ (low spin); 2. $\mathrm{Fe^{II}_{LS}}$ → $\mathrm{Fe^{II}_{HS}}$; 3. $\mathrm{Fe^{III}_{HS}}$ → $\mathrm{Fe^{II}_{HS}}$.

3.1.1. Spin Changes

We consider first the high-spin to low-spin transition. Since, as shown in Section 2.1, the ligand field increases with pressure, one might expect that at some pressure, Δ could become larger than the spin-pairing energy. One example is Fe(II) as a dilute substitutional impurity in MnS_2. In the isomorphous FeS_2 (pyrites), iron is low spin at all pressures. Since the lattice parameter of MnS_2 is distinctly larger than that of FeS_2 it is not surprising that iron in MnS_2 is high spin. One can think of the Fe(II) as being under a large negative pressure in MnS_2 relative to its situation in FeS_2. Figure 7 shows the Mössbauer spectra as a function of pressure. At low pressure (up to 40 kbars) one sees only the $\mathrm{Fe^{II}_{HS}}$ spectra. At 65 kbars the iron is over 50% converted to low spin. At 138 kbars the conversion is complete. The process is reversible with some hysteresis. This is, then, a transition from a paramagnetic to a diamagnetic ground state.

Let us now consider the transition from $\mathrm{Fe^{II}_{LS}}$ to $\mathrm{Fe^{II}_{HS}}$ with increasing pressure. We first look at the evidence for this somewhat surprising event. We consider complexes of iron with 1,10-phenanthroline. In tris complexes each of three phenanthrolines complexes through two nitrogens so that the Fe(II) is in an approximately octahedral field of six nitrogens. Because of back donation (see Section 2.1) to the ligands Δ is 2.0—2.5 eV and the iron is low spin. Figure 8 shows Mössbauer spectra as a function of pressure. At low pressure one observes only low spin iron. Above ~40 kbars a measurable amount of $\mathrm{Fe^{II}_{HS}}$ appears; and at 140 kbars there is about 30% conversion. Complexes involving substituted phenanthrolines may exhibit up to 60% conversion. The process is reversible, with hysteresis.

Complexes also form with two molecules of phenanthroline and two other ligands. These bis complexes are usually high spin at one atmosphere. At a modest pressure they convert partially or even completely to low spin, but above about 40—50 kbars the amount of high spin again increases[9, 29, 30].

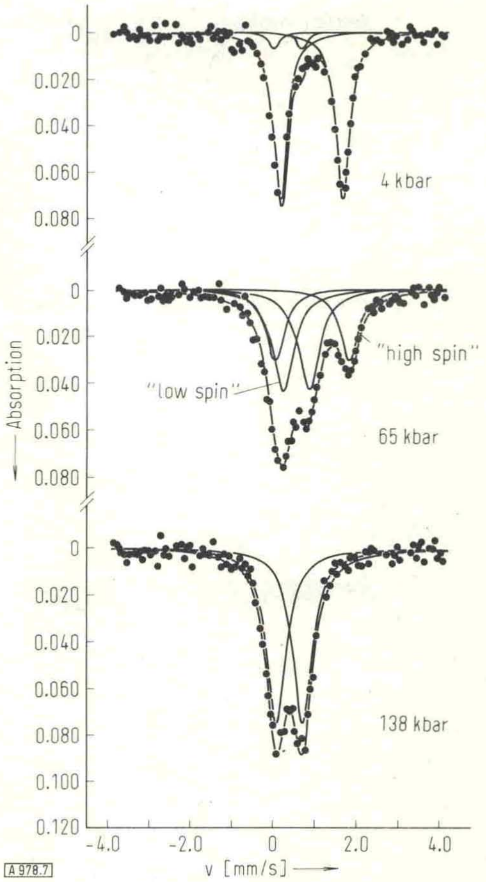

Fig. 7. Mössbauer spectra of Fe^{II} in MnS_2 at 4 kbar, 65 kbar, and 138 kbar.

The LS→HS transition seems paradoxical at first on both thermodynamic and electronic grounds. One must remember that it is the volume of the system *as a whole* which must decrease with increasing conversion at constant T and p. This volume decrease may involve changes in intermolecular forces as well as bond lengths. It is not, of course, necessary that any particular bond must shorten.

The back donation which provides the large ligand field depends on the availability of the ligand π^* orbitals. As already shown (Fig. 3), the π-π^* energy difference decreases rapidly with pressure. If there is significant mixing of the π and π^* orbitals they will become less available for back donation from the iron. In Table 1 a calculation for phenanthroline is given using Eq. (1). At one atmosphere the π orbital is stable by about 1.35 eV. Above 50 kbars the energy difference is such that there could be considerable thermal π-π^* transfer and hybridization inhibiting back donation. The calculation is very crude, but it illustrates that the hypothesis is feasible. This could be called an induced electronic transition, since a transformation on the ligand changes the bonding to the iron and thus its spin state.

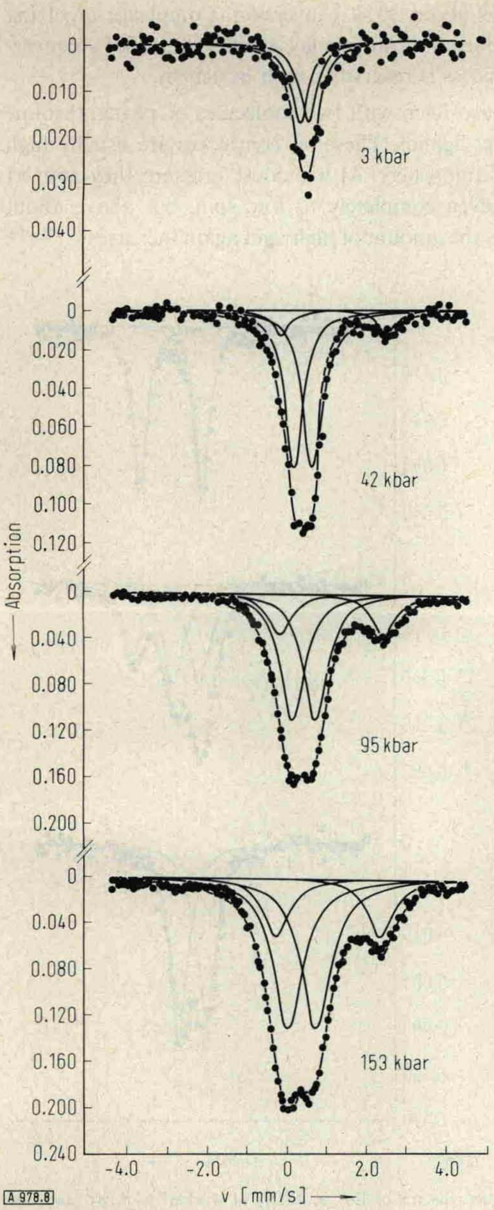

Fig. 8. Mössbauer spectra of Fe^{II} in $Fe(phen)_3Cl_2 \cdot 7H_2O$ at various pressures.

Table 1. Comparison of the energies associated with thermal and optical excitation: π-π* transition in 1,10-phenanthroline.

p (kbar)	$h\nu_{max}$ [eV]	$\delta E_{1/2}$ [eV]	E_{th} [eV]
0	4.6	0.95	+1.35
50	4.45	1.05	+0.45
100	4.30	1.14	−0.40
150	4.20	1.20	−0.98

One would expect that, at any pressure, the amount of low spin present for a series of related compounds would depend on the size of the ligand field. Δ is difficult to measure directly for these complexes, but it has been shown[31] that there is a good correlation between the Fe^{II}_{LS} isomer shift and Δ; the smaller the isomer shift (*i. e.* the larger the back donation) the larger is Δ. Figure 9 shows the relative amounts of Fe^{II}_{HS} and Fe^{II}_{LS} at 100 kbars for a series of substituted phenanthrolines. It can be seen that the correlation with the isomer shift of Fe^{II}_{LS} is, indeed, very good.

An increase in spin multiplicity with pressure has also been observed in other iron compounds. The ferrocyanides are low spin compounds with relatively large ligand fields. At room temperature they remain low spin to 200 kbars, at least. However, at 100 °C and 150 kbars $Cu_2Fe(CN)_6$ exhibits 65% high spin ferrous ion and $Ni_2Fe(CN)_6 \sim 18$—20%. $Zn_2Fe(CN)_6$, which is isomorphous, shows no conversion. Neither do the sodium nor potassium salts with slightly different structure. At 150 °C and 150 kbars the zinc salt shows ~25% conversion and the sodium and potassium salts only small traces thereof. Apparently cation electrons also interact with the ligand orbitals in these compounds.

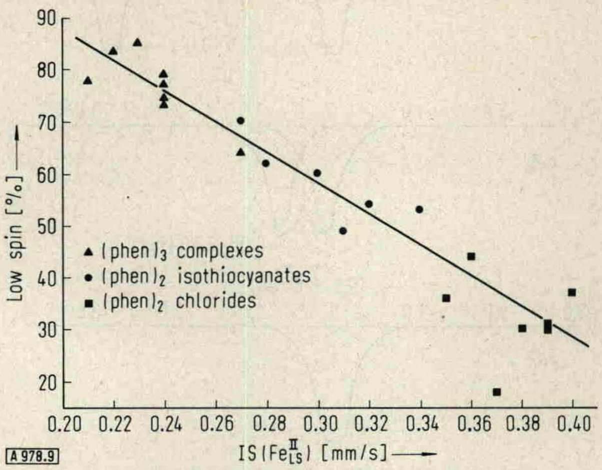

Fig. 9. Percent low spin Fe^{II} *vs* Fe^{II}_{LS} isomer shift in phenanthroline complexes.

One also observes an increase in spin state with pressure in some substituted ferrous phthalocyanines[9, 32]. This planar molecule involves four pyrrole rings bridged by nitrogens with the iron in a site of D_{4h} symmetry. The iron is in an intermediate spin state. When pyridines or picolines are coordinated axially to the iron a low spin Fe(II) (S=O) state results, primarily because of back donation to the nitrogens on the axial ligands. At high pressure a partial conversion of low spin to intermediate spin iron is observed as the back donation is reduced.

3.1.2. Reduction of Fe(III) and Cu(II)

The third electronic transition of interest here is the reduction of Fe^{III}_{HS} to Fe^{II}_{HS} with pressure. Recent studies on Cu(II) are also discussed briefly. Once again Mössbauer spectra are presented as primary evidence. In Figure 10 we show an Fe(III) spectrum at low pressure, the continuing increase in the amount of Fe^{II}_{HS} with pressure, and the reversibility (with hysteresis) upon release of pressure. The reduction takes place by transfer of a ligand electron (probably from a nonbonding orbital) to the metal 3d orbital. The electron and the hole on the ligand probably remain closely associated. There should be a definite relationship between the amount of reduction (*i. e.* the fraction of ferric sites still present) and the area under a ligand-metal charge transfer peak in the optical spectrum. Figure 11 exhibits such a relationship for two hydroxamate-iron complexes (AHA = acetohydroxamic acid, SHA = salicylhydroxamic acid) and a protein (FA = ferrichrome A) which complexes to Fe(III) through three hydroxamate groups. The solid line shows the conversion obtained from Mössbauer measurements while the points represent relative area under the optical absorption peak. The agreement is good.

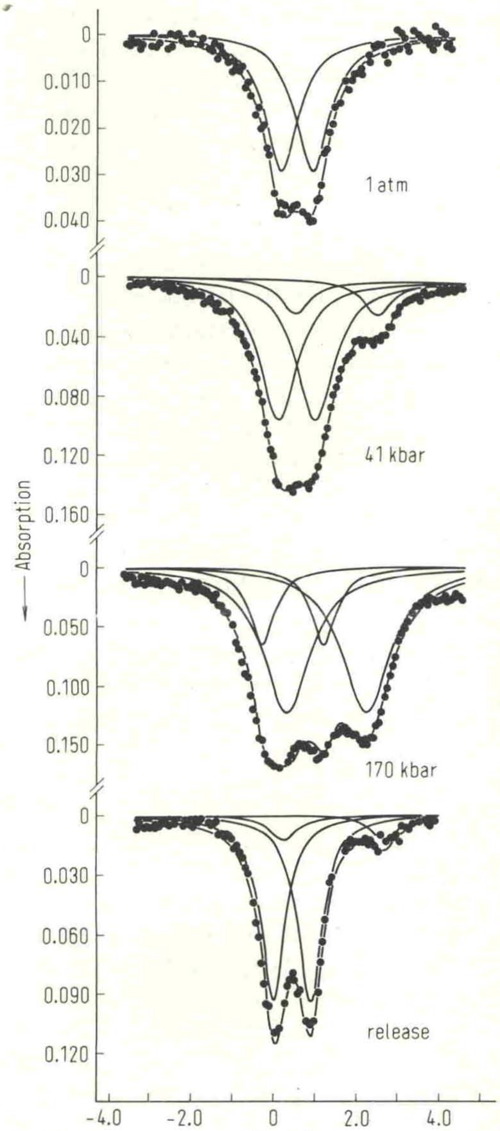

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Fig. 10. Mössbauer spectra of tris(2,4-pentanedionato)iron(III) at various pressures.

One would expect that, for a series of related compounds, the conversion would correlate with the electron donor abilities of the ligands. One such study involves the chelates of β-diketones shown in Table 2[9, 33]. At one atmosphere one can measure relative donor character of the ligands by such parameters as the acid dissociation constant, the Hammett σ, the appearance potential from mass spectroscopy, or the half wave potential from polarography. These measurements cannot be obtained on the solid under pressure. However, they correlate well with the ferric isomer shift; a lower isomer shift corresponds to better donor ability. With increasing pressure, the ligand nonbonding orbitals approach the metal 3d orbitals in energy, so the reduction, in general, increases with pressure. This tendency will be augmented in those systems where the isomer shift decreases (relative electron donor ability increases) with pressure, and diminished where the isomer shift increases (relative donor ability decreases). Figure 12 shows the change of conversion between 60 and 160 kbars for the series of compounds of Table 2, plotted against the change of isomer shift in this pressure range. The expected relationship applies very well.

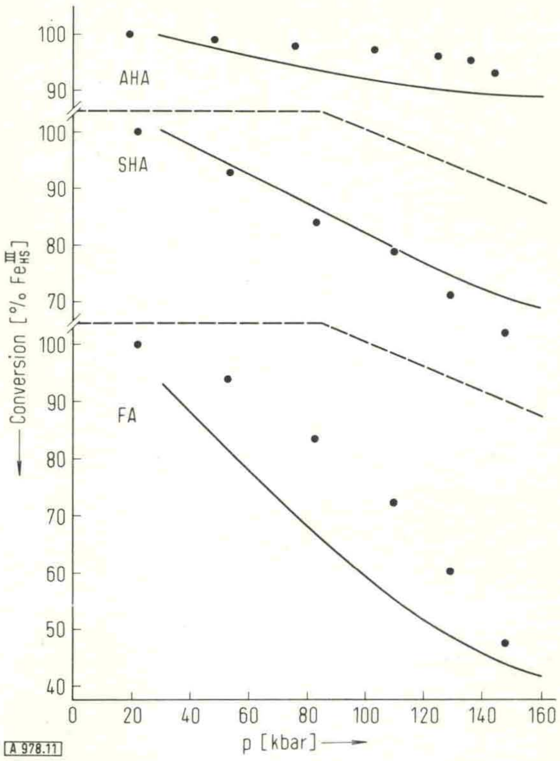

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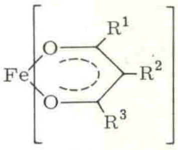
Fig. 11. Comparison of conversion of Fe^{III} to Fe^{II}—from optical (●) and Mössbauer data (—).

Table 2. Tris(β-diketonato)iron(III) complexes.



Ligand	R^1	R^2	R^3
(1)	CH_3	H	CH_3
(2)	C_6H_5	H	C_6H_5
(3)	$C(CH_3)_3$	H	$C(CH_3)_3$
(4)	C_6H_5	H	CH_3
(5)	CF_3	H	CH_3
(6)	CF_3	H	2-Furyl
(7)	CF_3	H	2-Thienyl
(8)	CF_3	H	C_6H_5
(9)	CH_3	CH_3	CH_3
(10)	CH_3	C_6H_5	CH_3
(11)	CH_3	NO_2	CH_3
(12)	CH_3	C_2H_5	CH_3

We can also use Eq. (1) to relate the location and half-width of the charge transfer peak to the reduction of Fe(III). In Table 3 there are shown, for three ferric hydroxamates and the related protein ferrichrome A, the pressure at which 10% reduction occurs, the location and half-width of the charge transfer peak, and the resultant value of E_{th} (assuming $\omega = \omega'$). It can be seen, as one would expect, that within the accuracy of the data and of the analysis $E_{th} \approx 0$.

A recent study[34] on complexes of Cu(II) with organic ligands shows that reduction occurs for these compounds also at high pressure. Cu(II) has nine 3d electrons and Cu(I) has ten. Because of the filled 3d shell, Cu(I) has no d-d excitations. As illustrated in Fig. 13 for $Cu(dtc)_2$ (dtc = diethyldithiocarbamate) the conversion is demonstrated by a decrease in integrated intensity of the Cu(II)-ligand charge transfer peak (b)

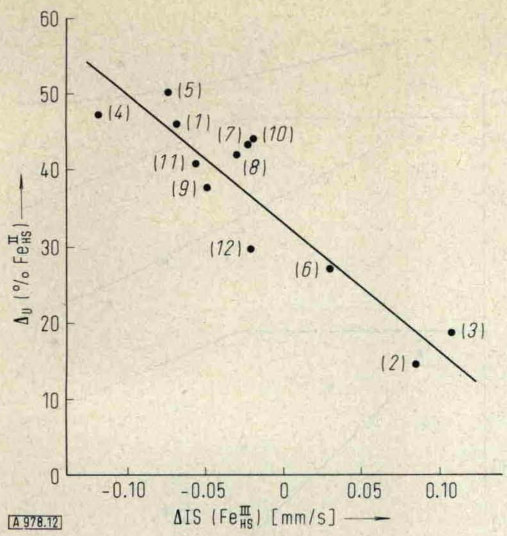


Fig. 12. Change in conversion of Fe^{III} to Fe^{II} *vs* change in isomeric shift between 60—160 kbar.

Table 3. Optical and thermal excitation: Ligand-metal charge transfer in ferric hydroxamates and ferrichrome A (10% reduction of Fe(III)).

Ligand	p [kbar]	$h\nu_{max}$ [eV]	$\delta E_{1/2}$ [eV]	E_{th} [eV]
AHA	125	2.80	0.90	0.11
BHA	105	2.70	0.875	−0.06
SHA	70	2.54	0.84	−0.02
FA	37	2.65	0.835	+0.11

and growth of a new peak (c) at lower energy—in a region typical for cuprous charge transfer peaks. Furthermore, the d-d excitation [peak (a)] near 16 kK also decreases in intensity as one would expect.

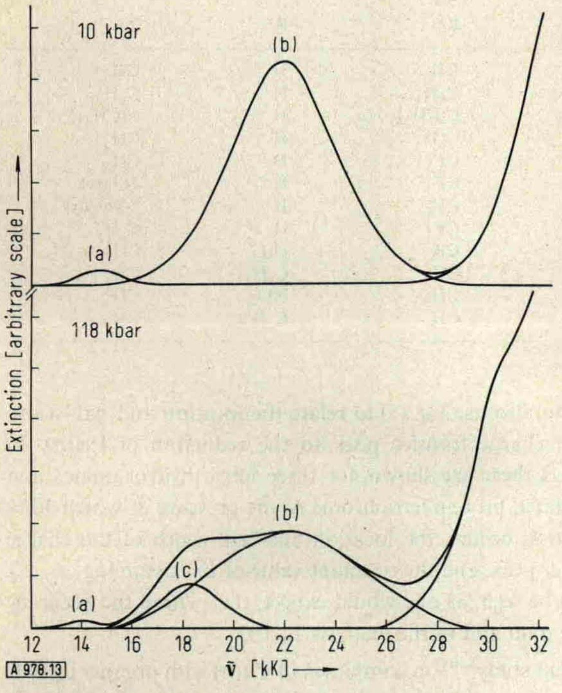


Fig. 13. Optical spectrum of $Cu(dtc)_2$ at various pressures.

The ferric porphyrins have been widely studied as prototypes for hemoglobin, although the applicability is limited by the fact that iron in hemoglobin is apparently in the ferrous state. Porphyrin is a planar molecule with four pyrrole rings connected by methine groups. There are various substituents on the periphery of the pyrroles. In hemin and hematin there is respectively, one Cl^- or one OH^- coordinated axially to the iron which is some 0.5 Å out of the plane of the ring and is high spin. The high spin state would be very improbable with the iron in the plane. In imidazole protoheme two imidazoles are coordinated axially to the iron which is in the plane of the ring and is low spin. Of course, it is something of an oversimplification to speak of definite spin states and oxidation states for iron where the bonding is so complex.

With pressure the ferric ion reduces in all three compounds[9]. At relatively high pressure the ferrous ion produced appears to be in an intermediate spin state in all three cases. For the imidazole protoheme the increase in spin multiplicity is caused by decreased back donation to the imidazoles. For the hemin and hematin the decrease in spin state is apparently associated with the effect of pressure in forcing the iron back into the molecular plane. The large increase in the ferric quadrupole splitting which is observed is consistent with this interpretation.

These reductions illustrate an electronic transition resulting from the shift of energy levels of one member of a complex (the ligand) with respect to those of the other member (the metal).

4. Summary

We have shown that pressure has a very significant effect on the relative energy of electronic orbitals. In a wide variety of circumstances the relative change in energy is sufficient to establish a new, or a greatly modified ground state. These electronic transitions occur in a wide variety of materials; here we have emphasized changes in the coordination chemistry of transition metal ions. It is hoped that this brief outline will amply demonstrate the power of pressure as a tool for investigating electronic structure.

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