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High pressure, electronic structure and chemistry in solids

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High pressure is a powerful and effective tool for studying electronic behaviour. Solid state physicists have been making extensive and effective use of it for more than two decades but only recently has it become apparent that pressure studies have relevance in a variety of electronic problems of importance to chemists.

The basic effect of pressure is to increase overlap between adjacent electronic orbitals. Some of the consequences can best be described in terms of band theory in which more or less delocalized electrons are assumed to be distributed in bands of narrowly-spaced levels separated by energy gaps with no allowed electronic states. However, for most high pressure phenomena of interest to chemists, one is concerned primarily with more localized states.

One consequence of increased overlap is a broadening of energy bands with a reduction in the size of the forbidden gap between bands, and an increase in electron mobility. A second general consequence is the relative shift in energy of one type of orbital with respect to another. Since orbitals of different quantum number may differ in radial extent, or orbital shape (angular momentum) or in compressibility, this relative shift in energy is a common phenomenon. Such shifts and their consequences are considered in this article.

High pressure experiments can be divided into two classes—those involving hydrostatic pressure media (liquids or gases), over a pressure range of about 12 kilobars (1 kilobar = 10^8Pa = 987 atm); and those employing quasistatic media and extending to several hundred kilobars. The former will be mentioned only briefly.

In the 12 kilobar range, a significant number of solid-state physics experiments have been carried out. There has also been considerable chemical experimentation—although not primarily concerned with electronic structure. Many of Bridgman's early studies[1] *e.g.,* compressibility and viscosity measurements, are of interest to chemists. Probably the most extensive modern work of a physical chemical nature in fluids is that done by Franck and his coworkers at Karlsruhe, which included a variety of studies on physical properties:[2] his experiments in the supercritical region are of particular interest. There have also been several optical absorption studies,[3] studies of chemical kinetics[4,5] and, more recently, studies of molecular motion (translational, rotational *etc.*) by nuclear magnetic resonance relaxation.[6] These results have been helpful in testing and differentiating between theories of the liquid state, of reaction mechanisms, of solvent effects on spectra *etc.* Perhaps the most general point which has been established is the importance of experimentation *at constant density* for understanding processes in fluids.

Bridgman, working in the 1930s and 1940s, made pressure–volume and electrical resistance measurements on solids up to 70–100 kilobars pressure. In the past 15 years this range has been extended to several hundred kilobars. But more significant than the higher pressures, is the extension of types of measurements to those more directly applicable to studies of electronic behaviour. This article mainly refers to measurements of optical absorption and Mössbauer resonance. No details are given of high pressure techniques—for these the reader should consult references 7–9. Likewise, references to individual research papers are not given—for these the reader should consult references 9–11 which contain extensive citations to the original literature, both for pressure-induced shifts of energy levels and for electronic transitions.

Energy level shifts

The usual method of measuring differences of energy levels in insulators and solids is by optical absorption. As discussed below, it is important in interpreting and applying optical data to remember the restrictions on optical processes (Franck–Condon effect, selection rules *etc.*) relative to thermal processes. Shifts of electronic energy levels as observed optically are reviewed in some detail in references 9 and 11: five categories will be mentioned here.

Changes in the gap between the top of the valence band and the bottom of the conduction band (the absorption edge) with pressure are affected by two processes. Broadening of the bands tends to decrease the gap. The relative shifts in energy of the bands may augment or oppose this effect. In some cases decreases in gap of the order of an electron volt (1 eV/atom $\approx$ 23 kcal/gram-atom $\approx$ 8000 cm^{-1}) are observed for a pressure increase of 100–150 kilobars. These shifts may ultimately lead to band overlap and metallic behaviour.

Impurity centres in alkali halides and related ionic crystals have also been extensively studied. The most thoroughly investigated is the F centre—an electron trapped in a halide ion vacancy. With increasing pressure the volume of the hole decreases and the energy of excitation increases. One finds, in fact, that the simple 'particle in a box' analysis gives a reasonable first approximation to the energy change.

An electronic process of more direct interest to chemists is

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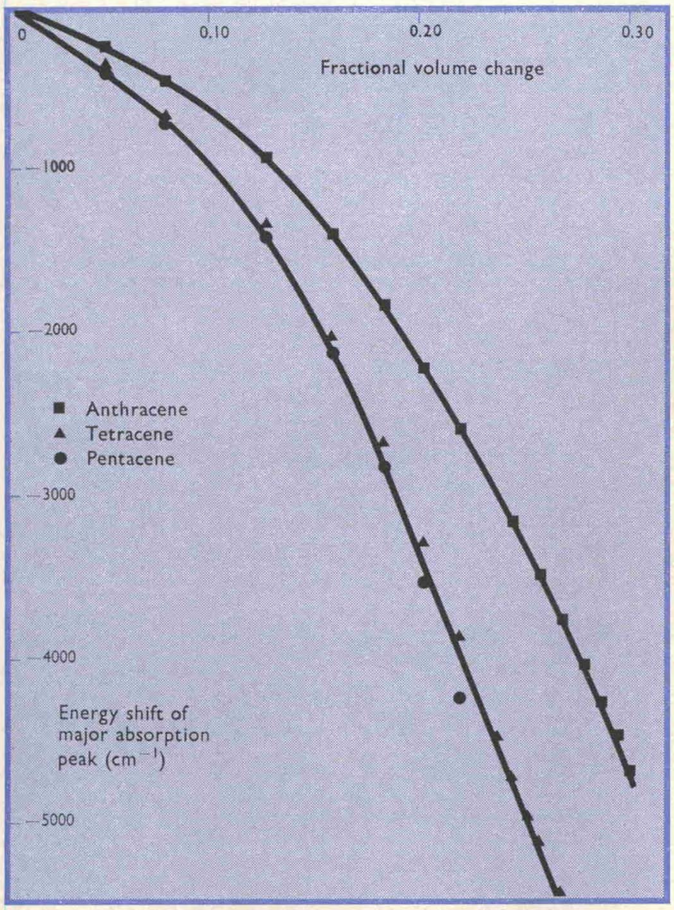


Fig. 1. Variation of energy shift for the π–π^* transition with fractional volume change (ρ/ρ_0) for three aromatic hydrocarbons. The large decrease in energy with decreasing volume is nearly independent of the molecule.

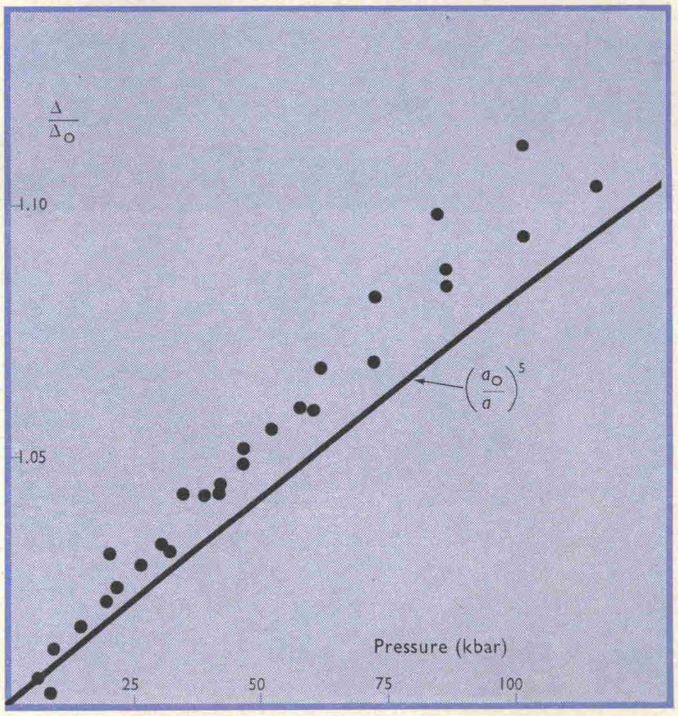
that involving the excitation of an electron from a bonding π orbital of an aromatic molecule to an empty antibonding state. The energy of these excitations is typically in the region 2–5 eV, being lower for longer conjugation paths. For simple benzenoid hydrocarbons the ground state is non-polar and relatively unreactive. The excited state is polar and may have greater self-complexing ability. As shown in *Fig. 1*, there is a large decrease in energy of the $\pi^* \leftarrow \pi$ transition with decreasing volume (the pressure range shown is about 60 kbar). The change is nearly independent of the molecule for these three, four, and five ring systems. However, since the one atmosphere energies are quite different (*e.g.* 2.1 eV for pentacene and 3.3 eV for anthracene) the fractional shifts differ significantly. This point will be important later.

A second type of excitation of chemical interest involves rearrangement of electrons among the partially-filled d orbitals of a transition metal ion in a molecule or a crystal lattice. The study of these transitions constitutes a major area of coordination chemistry. The five $3d$ orbitals of a free transition metal ion are degenerate. If the ion is incorporated into a molecule or a crystal lattice, the reduction in symmetry partially removes this degeneracy. In a situation of octahedral symmetry, one obtains a doublet of σ (E_g) symmetry located above a triplet of π (T_{2g}) symmetry by an amount which depends on the strength of the interaction between metal ion and ligands. It is characterized by the ligand field parameter Δ. (In molecular orbital language, the splitting is between strongly antibonding orbitals of σ (E_g) symmetry and the non-bonding or slightly antibonding π (T_{2g}) orbitals.) In the free ion, the electrons are arranged to give maximum multiplicity, according to Hund's first rule. This high-spin arrangement is retained in 'normal ionic' compounds, since the interelectronic repulsion involved in spin pairing is larger than the potential energy involved in occupying all the $3d$ orbitals. For these compounds $\Delta =$ 0.5–1.5 eV. The interelectronic repulsion is most conveniently expressed in terms of Racah parameters B and C. These can, in principle, be calculated for free atoms or ions, but, in molecules or crystals, are treated as empirically determined parameters.

When there is sufficiently strong interaction between metal and ligand, Δ may become so large that it more than compensates for the interelectronic repulsion involved in spin pairing, and then one obtains a low-spin configuration. Ligands which form low-spin complexes usually have low lying excited states which are empty and of the correct (π) symmetry to bond with the metal d_π orbitals. This donation of metal electrons into the ligand π orbitals, called back-donation, stabilizes the metal d_π orbitals and gives the large Δ. For systems of lower symmetry, such as phthalocyanine and metalloporphyrins, intermediate spin and mixed spin states are also possible.

Optical absorption peaks, generally in the visible or the near infrared part of the spectrum (the ligand field peaks), measure Δ, B and C. For most compounds Δ increases with pressure. *Figure 2* shows the change with pressure for Ni(II) in NiO. The solid line represents the prediction of a point charge model ($\Delta \sim R^{-5} \sim \rho^{5/3}$) where R is the metal ion–ligand distance and ρ the density. The point charge model is inadequate for calculating even the magnitude of Δ at one atmosphere and NiO is very far from being a purely ionic crystal, so the modest agreement shown may well be largely fortuitous. For the four or five hosts studied so far, Δ appears to increase slightly more rapidly than predicted from the simple model. The interelectronic repulsion parameters

Fig. 2. Variation of ligand field splitting (Δ/Δ_0) and of $(\rho/\rho_0)^{5/3}$ with pressure for Ni(II) in NiO. (a = lattice parameter).



decrease with increasing pressure by 5–15 per cent in 150 kilobars. This is associated with a delocalization of $3d$ orbitals and increased overlap with ligand orbitals whose electrons shield the metal $3d$ electrons from each other.

A third type of optical excitation of interest to chemists is that of charge transfer. One type of charge transfer occurs in electron donor–acceptor complexes of hydrocarbons (or heterocyclic bases) with acceptors such as iodine, tetracyanoethylene and chloranil. The properties of these complexes at one atmosphere have been studied at length.[12] The excitation involves transfer of an electron from an orbital largely on the donor to one largely on the acceptor. Many of these transitions exhibit a large shift to lower energy (red shift) with increasing pressure (a significant fraction of an eV in 150 kilobars), indicating an increased probability of occupation of an excited state with increasing orbital overlap. Another type of charge transfer occurs between ligand and metal in transition-metal complexes. In general these transitions also exhibit large red shifts with increasing pressure.

Electronic transitions

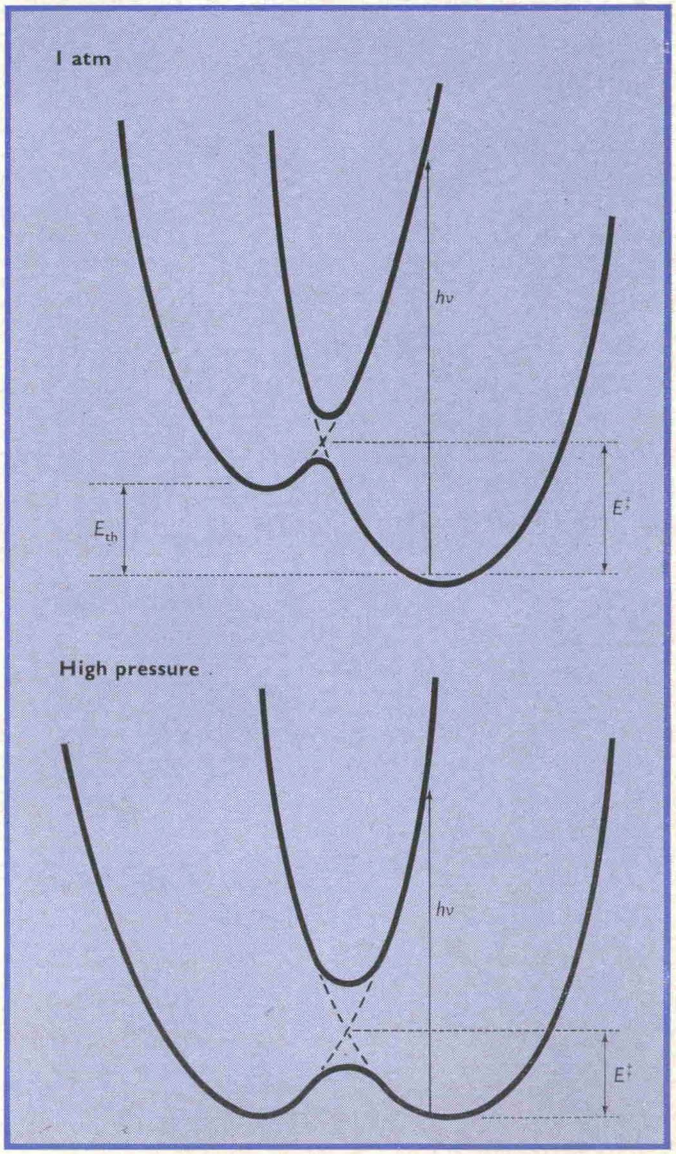
The discussion so far has demonstrated that, within the experimental pressure range presently available, there are very large changes in energy of one type of orbital with respect to another; this fact has an important consequence. Under many circumstances there are excited states which lie not too far in energy above the ground state. The relative shift may then be sufficient to provide a new state for the system or greatly to modify the character of the ground state by configuration interaction. This event is called an electronic transition. Such transitions may occur discontinuously at some fixed pressure or over a range of pressures, just as any change in physical properties may occur discontinuously below a critical point and continuously above, or as two components may exist in chemical equilibrium over a range of pressure or the reaction may run to completion at some pressure. Electronic transitions in metals and insulator–metal transitions have long been of interest to physicists; more recently it has been demonstrated that such transitions may also have unexpected and interesting chemical consequences.

Before discussing specific electronic transitions it is desirable to characterize them generally. They involve the thermal transition of an electron from one type of orbital to another. As discussed above, the energy differences between orbitals are usually measured by optical absorption, at least in non-metals. The energy involved in an optical process is usually quite different from that involved in a thermal process between the same two states. Thus, if we are to relate optical observations to electronic transitions some analysis is necessary.

Figure 3 shows a very simplified schematic configuration coordinate diagram. The vertical axis measures energy while the horizontal axis (the configuration coordinate) involves some relative displacement of the atoms, ions or molecules of the system (the system here is the solid not an individual molecule). The number of such coordinates equals the number of normal modes of the system. Optical excitations occur vertically on such a diagram as they are rapid compared with nuclear motions (the Franck–Condon principle). Thermal processes are not subject to this limitation. This is a basic difference—but other effects may be of comparable importance. One is configuration interaction, which results from partial relaxation of the Born–Oppenheimer condition for separability of electronic and nuclear coordinates. This relaxation is due to electron–lattice or spin–orbital coupling. In a solid of the complexity considered here, there is always an appropriate vibration to mix states of any symmetry. The effect of increasing configuration interaction is also illustrated in *Fig. 3.* Thirdly, optical processess are subject to parity selection rules, while, in the time scale of thermal processes, all selection rules are relaxed. Finally, the figure is oversimplified in that it shows only one coordinate. For a thermal process the coordinate conjugate to the pressure is the volume, but other coordinates may well be involved in the optical excitation.

Under these circumstances, to what degree can the two types of process be related? The effect of selection rules can usually be visualized directly. The effect of configuration interaction is difficult to generalize. However, an analysis has been presented based on the Franck–Condon effect. The one-dimensional analysis can be extended to include multiple coordinates. For a system consisting of two harmonic potential wells with force constants ω^2 and $(\omega')^2$ for the ground and excited states one can relate the thermal energy (E_{th}) to the absorption peak maximum ($h\nu_{\mathrm{max}}$) and the

Fig. 3. Schematic configuration coordinate diagram. The vertical axis measures energy. The horizontal axis involves some relative displacement in the system.



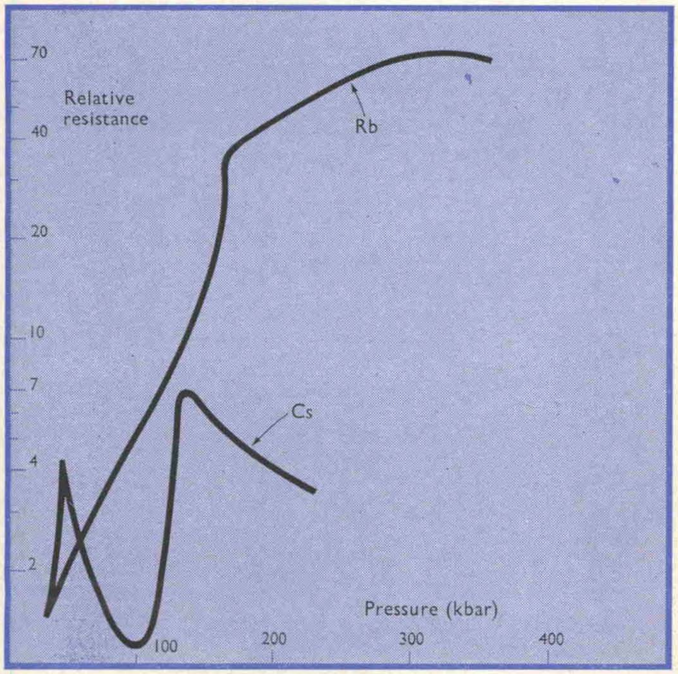
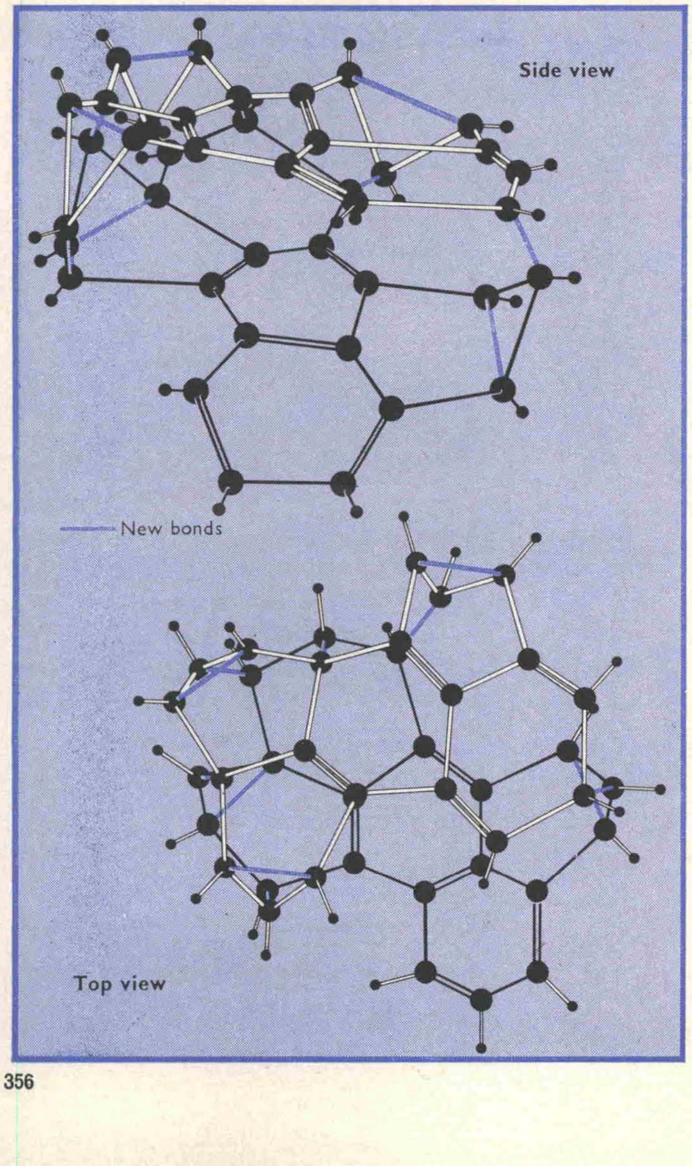


Fig. 4. (above) Change in relative resistance with pressure for rubidium and caesium at 296 K.

Fig. 5. (below) Structure of the perylene dimer formed at high pressure.



peak half width ($\delta E_{\frac{1}{2}}$) as follows:

$$E_{\mathrm{th}} = h\nu_{\mathrm{max}} - \frac{1}{RT\,16\ln 2}(\delta E_{\frac{1}{2}})^2\left(\tfrac{\omega}{\omega'}\right)^2 \qquad 1$$

We shall see later that this equation gives reasonable qualitative predictions in a few cases where it has been applied.

Transitions in metals and insulator–metal transitions

These are the areas of most activity in physics. Resistivity can be defined as

$$r = \frac{1}{n\mu e}$$

where n is the number of carriers, μ their mobility and e their charge. Conduction in a metal is mobility limited. To the extent that mobility is limited by scattering due to lattice vibrations, we expect resistivity to increase with increasing temperature as vibrations are enhanced, and to decrease with increasing pressure, which inhibits vibrational amplitude. The expected temperature effect is observed, and, in simple metals like copper, the resistivity decreases by perhaps 20–40 per cent in several hundred kilobars. The conductivity ($1/r$) of insulators and semiconductors is controlled by the number of carriers, which, for simple cases, is:

$$n = n_0 \exp\left(\frac{-E_g}{2kT}\right)$$

where E_g is the gap between valence and conduction bands. E_g is a function of pressure. Since it generally decreases, a rapid decrease in resistivity with pressure is usually observed.

Electronic transitions were first discovered in metals. Nearly 25 years ago Bridgman found a cusp in the resistance of caesium near 40 kilobars (*see Fig. 4*). Sternheimer attributed this to donation of an electron from the 6*s* to the 5*d* band, *i.e.* a change in character of the conduction band. His analysis, while approximate, appears basically correct. In the last decade, a second maximum near 135 kilobars has been observed. Recent calculations indicate that there are two causes—a lowering in energy and broadening of the empty 4*f* band until it overlaps the conduction band, combined with hybridization of atomic 5*p* orbitals into the conduction band. One might say that with increasing pressure one goes from alkali to transition to rare-earth metal. The resistance of rubidium is also shown in *Fig. 4*. The sharp rise near 140 kilobars is the 5*s*→4*d* transition and the maximum near 300 kilobars may involve hybridization of 4*p* electrons into the conduction band. A number of rare earths exhibit unusual electrical behaviour which may in some cases involve transfer of an electron from 4*f* to the 5*d* band or to the conduction band. Electronic transitions of a somewhat different type are observed in calcium, strontium and ytterbium.

Insulator–metal transitions can occur in a number of ways. In molecular crystals, like iodine and a few aromatic hydrocarbons, it appears to happen by broadening and shift of the valence and conduction bands with no apparent structural discontinuity. In Si, Ge and their III–V analogues, it occurs discontinuously with a change to the white tin structure or its diatomic analogue. In some transition-metal oxides it occurs discontinuously by a mechanism very close to the electron–electron correlation proposed by Mott. McWhan and his associates at Bell Laboratories have done particularly effective studies on mixed V_2O_3–Cr_2O_3 crystals. Jayaraman, also at Bell Laboratories, has shown that divalent samarium chalcogenides become metallic at high pressure either discontinuously or over a range of pressure by transfer of an electron from Sm(II) to the conduction band.

Transitions with chemical consequences

Earlier, it was shown that the energy of the $\pi^* \leftarrow \pi$ transition in aromatic hydrocarbons decreases rapidly with increasing pressure. For materials like anthracene with a large initial transition energy there is a rapid decrease in resistance with pressure but nothing unusual happens. For pentacene, however, at pressures above 200 kilobars at room temperature, the resistance tends to drift upward with time, and the behaviour is irreversible. The recovered material, which is reddish-brown in contrast to the bluish-black pentacene, is very insoluble and so difficult to characterize. From the visible and infrared spectra it appears that a polymer is formed. Apparently the excited state is shifted sufficiently with pressure for it to be thermally occupied by π electrons. This state is polar so the intermolecular forces are stronger; it also has greater self-complexing tendencies and is more reactive than ordinary pentacene so the polymer is formed.

A related electronic transition with chemical consequences occurs in certain donor–acceptor complexes. Consider, for example, the catacondensed aromatic molecules pyrene ($C_{16}H_{10}$) and perylene ($C_{20}H_{12}$). Their $\pi^* \leftarrow \pi$ transitions are in the region 3–3.5 eV and so the pure hydrocarbons do not react at the highest available pressures. They form electron donor–acceptor complexes of definite stoichiometry with iodine. These have relatively low lying excited states corresponding to electron transfer from the hydrocarbon to iodine, which shift to lower energy with pressure. At high pressure these complexes react irreversibly. The iodine

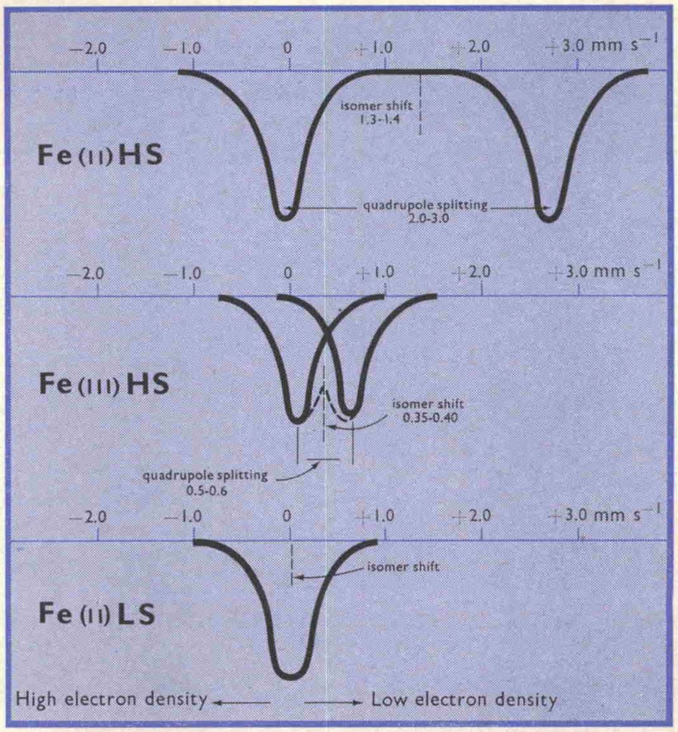


Fig. 6. (above) Characteristic Mössbauer spectra for three states of iron. (Velocities relative to Fe metal.)

Fig. 7. (below) Mössbauer spectra of $Fe(phen)_3Cl_2\ 7H_2O$ at various pressures. Note the different ordinate scale for the two highest pressure spectra.

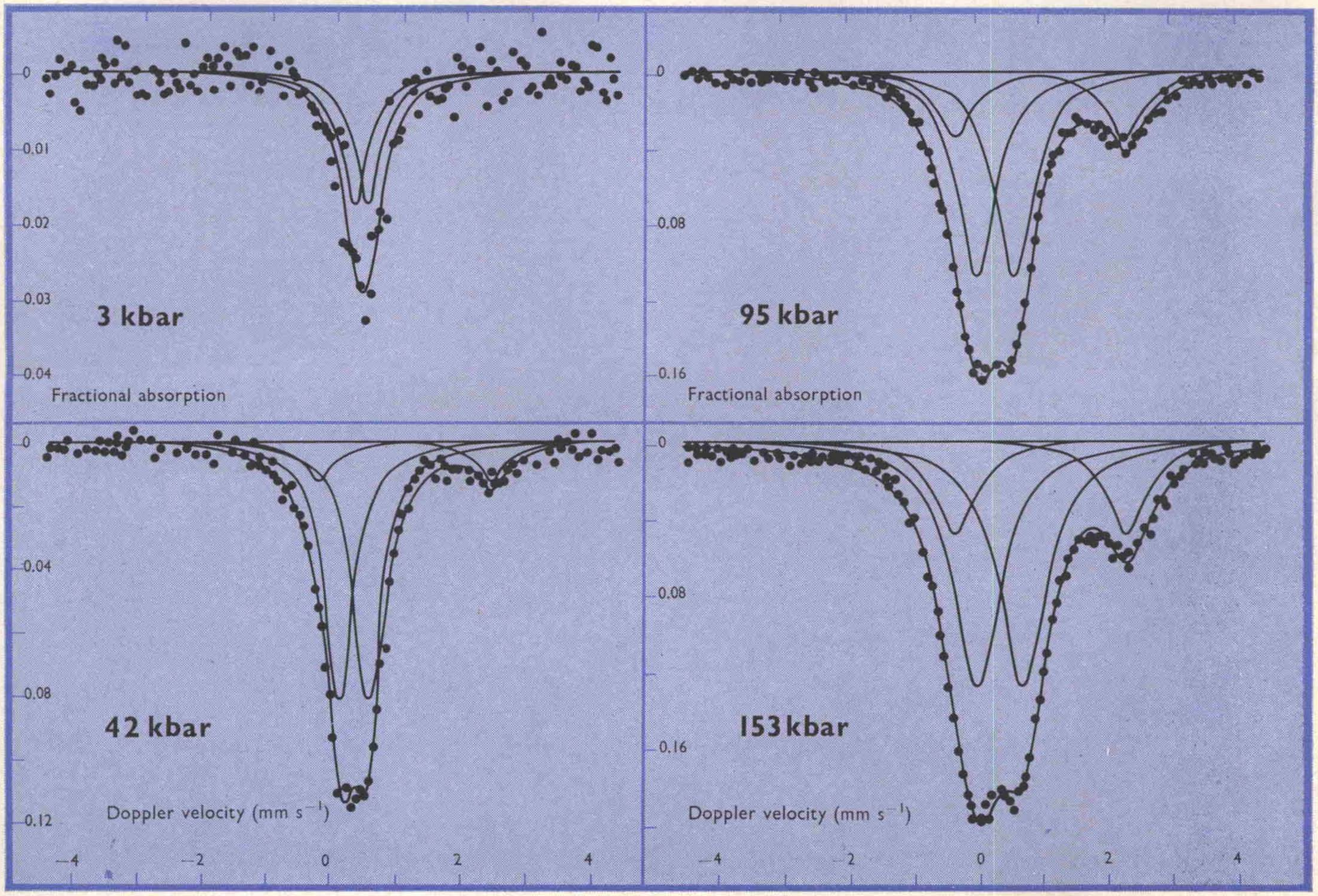


Table 1. Comparison of the energy (in eV) associated with thermal and optical excitations of the π–π^* transition in phenanthroline.

P(kbar)	$h\nu_{max}$	$\delta E_{\frac{1}{2}}$	E_{th}
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

can be completely removed from the recovered material. Its function is to provide a new ground state at high pressure to put the hydrocarbon into a reactive configuration, but it does not enter into the product. The hydrocarbons formed are soluble and can be fractionated by chromatography and characterized by nmr and by optical and mass spectroscopy. The major product from the perylene complex is a cage-like dimer of a type not previously seen. Its structure is shown in *Fig. 5*. The major product from pyrene is a tetramer of analogous structure. By establishing complexes of appropriate geometry and electronic structure it may be possible to develop a series of products and a new solid state chemistry of organic compounds.

Three electronic transitions which have been observed in the chemistry of iron compounds are Fe(II)HS → Fe(II)LS, Fe(II)LS → Fe(II)HS, and Fe(III)HS → Fe(II)HS. In addition to optical absorption measurements, one can utilize Mössbauer resonance to identify the states of iron. The latter is similar to nmr in that one measures the energy of a nuclear transition which is perturbed by electronic wave functions to infer information about the electronic structure. The perturbations take the form of changes in the energy of the transition (isomer shift) and of the splitting of the excited state (quadrupole splitting). To bring about resonance between a source and absorber in different chemical environments one is moved with respect to the other. The velocities necessary for resonance are correlated with energy perturbations characteristic of the various states. *Figure 6* shows typical Mössbauer spectra for the high-spin ferrous, high-spin ferric and low-spin ferrous states.

The high-spin to low-spin conversion is easiest to understand. We know that the ligand field Δ increases with pressure. If it becomes greater than the spin pairing energy a low-spin compound will result. One example is Fe(II) as a dilute substitutional impurity in MnS_2 which is isomorphous with FeS_2 (pyrites). In FeS_2 iron is low spin, while in MnS_2 it is high spin. This is not surprising since the lattice parameter of the latter is significantly larger than that of the former so that one can think of the Fe(II) as being under a negative pressure, relative to its situation in pyrites. At about 40 kilobars pressure some low spin appears in the spectrum; by 140 kilobars it is completely converted. The process is reversible with some hysteresis.

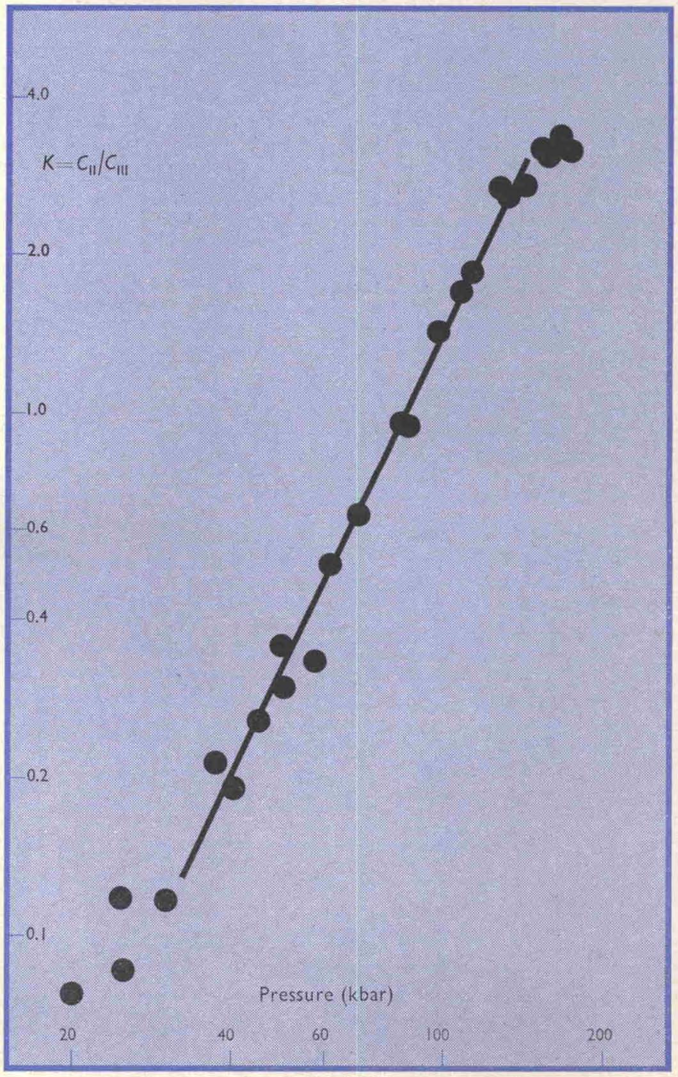
Table 2. Optical v. thermal excitation for ligand–metal charge transfer in ferric hydroxamates and ferrichrome A [for 10 per cent reduction of Fe(III)].

Compound	Pressure	$h\nu_{max}$	$\delta E_{\frac{1}{2}}$	E_{th}
Tris(acetohydroxamoto) iron(III)	125	2.80	0.90	−0.11
Tris(benzohydroxamato) iron(III)	105	2.70	0.875	−0.06
Tris(salicyclohydroxamato) iron(III)	70	2.54	0.84	−0.02
Ferrichrome A	37	2.65	0.835	+0.11

Turn now to the inverse transformation, *i.e.* low-spin ferrous to high-spin ferrous, with increasing pressure. First, what is the evidence for this somewhat surprising transformation? *Figure* 7 shows Mössbauer spectra for a trisphenanthroline ferrous complex as a function of pressure. At one atmosphere, it has a typical low-spin spectrum. By 42 kilobars, there is a measurable amount of high-spin material and by 153 kilobars there is perhaps 30 per cent conversion. Some substituted phenanthrolines may give as high as 60 per cent high-spin at high pressure. Significant low-spin to high-spin conversions have been observed in heavy metal ferrocyanides at high pressure and temperatures above 110 °C, and phthalocyanine complexed with pyridine exhibits a low-spin to intermediate-spin transition at high pressure.

At first this transformation seems paradoxical on both thermodynamic and electronic grounds. From the thermodynamic viewpoint one must remember that it is the volume of the *system as a whole* which must decrease with increasing conversion. Changes in both bond length and intermolecular distance may be involved, so not every bond need shorten. All of the complexes which exhibit this phenomenon are extensively backbonded. Backbonding requires low lying *available* π^* orbitals on the ligands. It was shown earlier

Fig. 8. Plot of ln K *against ln* P *for the reduction of ferric acetylacetonate.* K *is the ratio of the fractions of ferrous and ferric ion.*



that π–π^* energy differences decrease rapidly with increasing pressure. These ligands also exhibit large red shifts for their π–π^* transitions. We postulate that at high pressure the π^* orbitals are significantly occupied by *ligand* π electrons and are thus less available for back donation from the metal.

One may question the feasibility of the thermal π–π^* transfer. Table 1 shows the result of applying equation 1 to phenanthroline. With increasing pressure the $\pi^* \leftarrow \pi$ peak shifts to lower energy and broadens. At one atmosphere the π orbital is thermally stable by about 1.3 eV. Above 50 kilobars, it appears that the π^* orbital becomes the stable one. Both the measurements and the analysis are crude; nevertheless they demonstrate that the hypothesis used to explain the spin transformation is not unreasonable.

The third electronic transition of iron—the reduction of ferric iron with pressure—has been observed in a wide variety of compounds, but most of the early data must be regarded as only qualitative because of experimental difficulties. More recent studies on a series of β-diketonates and ferric hydroxamates provide more quantitative information. If an equilibrium constant is defined as $C_{\rm II}/C_{\rm III}$, where $C_{\rm II}$ and $C_{\rm III}$ are the fractions of ferrous and ferric ion, a plot of $\ln K$ *vs* $\ln P$ is frequently linear over a considerable range of pressure and conversion, as demonstrated in *Fig. 8*.

The reduction process generally involves transfer of an electron from a ligand non-bonding orbital to the metal d_π orbital. This gives a ferrous ion and a hole on a ligand. The hole is probably usually closely localized near the iron. One might expect this process to be reflected in the behaviour of the ligand–metal charge-transfer peaks. Indeed the area under these peaks decreases with increasing pressure in a manner closely paralleling the conversions obtained from Mössbauer measurements. Using equation 1, one can calculate the relative stability of the ligand π and metal d_π orbitals if the appropriate charge-transfer peaks are available. Table 2 shows the results of such a calculation for a series of ferric hydroxamates. At one atmosphere the ligand π orbital is stable by an eV or so. Yet, at the pressure where one first obtains measurable ($\sim$10 per cent) conversion, $E_{\rm th}$ is approximately zero. Again, although the analysis and data are crude they demonstrate the feasibility of the hypothesis. In addition, the study of the β-diketonates has shown that the reduction correlates well with the electron donor properties of the ligand. In materials like ferric porphyrins and prussian blue more complicated changes, apparently involving both change of oxidation state and spin state, are observed.

Summary

In this article, I have tried to outline some of the effects of pressure on electronic behaviour, and I hope I have left certain clear impressions: that pressure has a profound effect on electronic energy levels; that under many circumstances the relative shifts of these levels can lead to a new, or a greatly modified, ground state; and that these new ground states have interesting chemical as well as physical properties. I hope I have made a convincing case for expanded use of pressure as a tool for chemists in studying electronic structure.

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