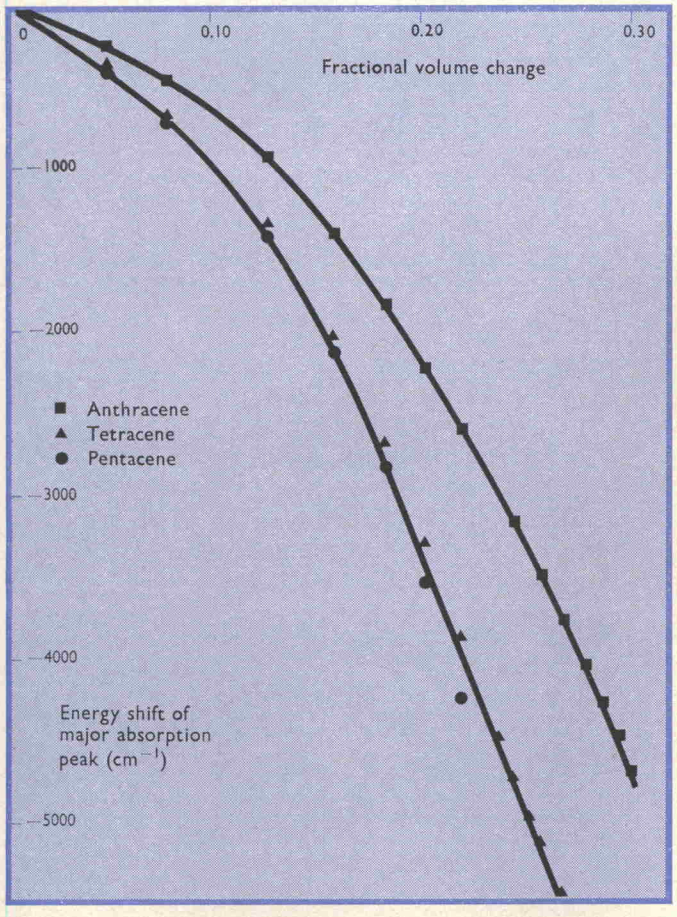

Fig. 1. Variation of energy shift for the π–π^* transition with fractional volume change (ρ/ρ_0) for three aromatic hydrocarbons. The large decrease in energy with decreasing volume is nearly independent of the molecule.

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 3*d* 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 3*d* orbitals. For these compounds Δ = 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).