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, tetracyano-ethylene 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 ($h\nu_{max}$) and the

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