

THE EFFECT OF PRESSURE ON THE ELECTRONIC STATES OF ORGANIC SOLIDS†

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ABSTRACT

The basic effect of pressure is to decrease intermolecular distance and to increase overlap between adjacent electronic orbitals. As a consequence, there is a relative shift in energy of one type of orbital with respect to another. These shifts are particularly large for π - π^* transitions in organic molecules and for excitations in electron donor-acceptor complexes. On many occasions there are unoccupied states of sufficiently low energy such that one may obtain a new ground state at high pressure or greatly modify the characteristics of the ground state by configuration interaction. It has been shown that one can relate this thermal process to the shift of energy levels as observed by optical absorption. A number of consequences of these electronic transitions are discussed, including pressure-induced reactivity of aromatic hydrocarbons and their complexes and piezochromism in photochromic materials. Finally, it is demonstrated that one can use the shift in energy of optical absorption and emission peaks and the change in half-width of those peaks to characterize in some detail electronic excitations in a wide variety of organic molecules in the solid state and in solution.

The basic effect of pressure is to reduce intermolecular distance and thus to increase overlap between adjacent electronic orbitals. As a result, there is generally a relative shift in energy of one type of orbital with respect to another. These shifts are especially large for π - π^* excitations in aromatic hydrocarbons and related compounds and for the relatively low lying excitations in electron donor-acceptor complexes corresponding to electron transfer from donor to acceptor (from the 'no bond' to the 'electron transferred' state in Mulliken's description).

Under many circumstances there exists a second electronic state not too high in energy above the ground state. The relative shift in energy may be sufficient to give a new ground state for the system, or greatly to modify its characteristics by configuration interaction (mixing of orbitals by spin-orbit or electron-lattice coupling). These transitions may occur discontinuously at a given pressure or over a range of pressures. They occur in a wide

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variety of materials with different consequences¹⁻³. Electronic transitions have been observed in alkali, alkaline earth and rare earth metals with changes in electrical resistance. Insulator-metal transitions have been observed in transition metal oxides, in rare earth chalcogenides, in silicon, germanium, and a variety of III-V compounds, in molecular crystals such as iodine as well as in some crystals of large aromatic molecules. The above types of transitions are of greatest interest to the physics community.

Electronic transitions have also been observed in a wide variety of transition metal compounds, especially those of iron. These involve changes in spin state and/or oxidation state of the transition metal ion^{1,2,4} and are of considerable importance in inorganic and physical chemistry as well as in geophysics.

In this paper we discuss electronic transitions in aromatic hydrocarbons and electron donor-acceptor complexes which result in enhanced chemical reactivity and in some new types of compounds, and pressure-induced transitions in photochromic bianthrone. Before taking up these specific materials we discuss some general characteristics of electronic transitions.

An electronic transition as defined above is a thermal process, i.e. it is the thermal energy of the electron which causes transfer from one orbital to another. On the other hand, the difference in energy between orbitals is normally measured by optical absorption. The thermal and optical paths differ in energy for several reasons. Two of these are illustrated in *Figure 1*. The horizontal axis is a configuration coordinate: some intermolecular (or intramolecular) displacement, such as the breathing vibration of the lattice. The vertical axis is energy. Optical excitations occur vertically (i.e. without molecular displacement) on such a diagram because they are rapid compared with molecular (or nuclear) motions, while the time scale of thermal transfer is such that a path of minimum energy may be involved. This is a major difference, but there are others of significance. In *Figure 1* the effects of configuration interaction are illustrated by the solid lines compared with the dotted line. As the lower figure indicates, an increase in configuration interaction can have different effects on the energies for the thermal and optical processes. In the third place, the optical processes are controlled by parity and other selection rules, while in the time scale of thermal processes all selection rules are relaxed. Finally, our diagram is oversimplified in that we show a single configuration coordinate, while the number of such coordinates equals the number of normal modes of the system. For thermal processes, pressure will primarily interact with a coordinate proportional

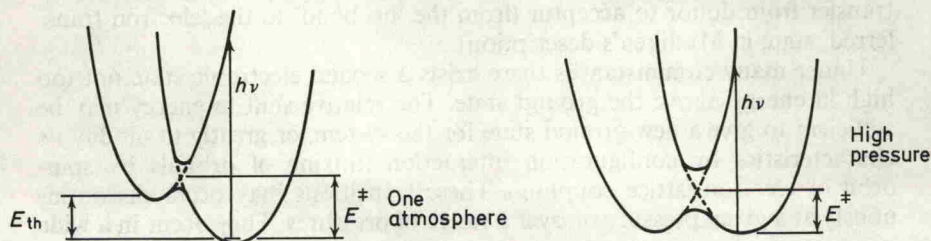


Figure 1. Schematic configuration coordinate diagram