

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 ($\text{C}_{16}\text{H}_{10}$) and perylene ($\text{C}_{20}\text{H}_{12}$). 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

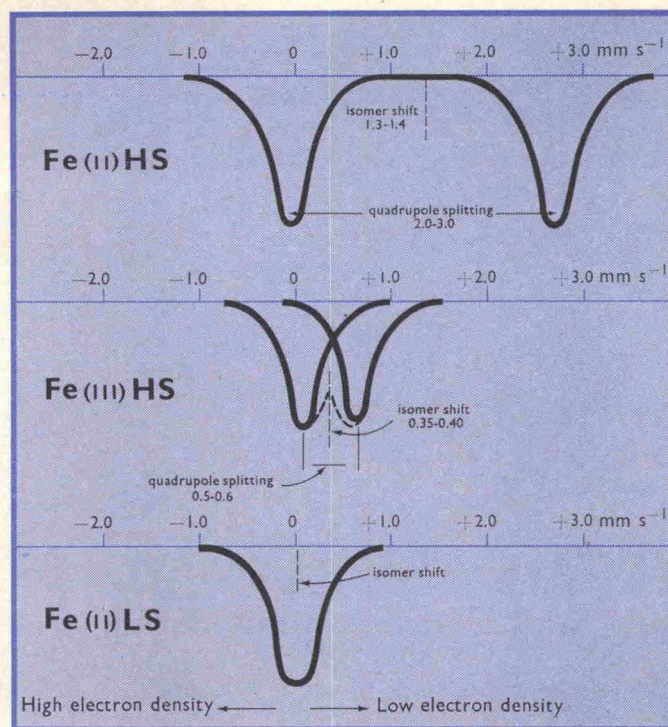


Fig. 6. (above) Characteristic Mössbauer spectra for three states of iron. (Velocities relative to Fe metal.)

Fig. 7. (below) Mössbauer spectra of $\text{Fe(phen)}_3\text{Cl}_2 \cdot 7\text{H}_2\text{O}$ at various pressures. Note the different ordinate scale for the two highest pressure spectra.

