

that $\pi-\pi^*$ energy differences decrease rapidly with increasing pressure. These ligands also exhibit large red shifts for their $\pi-\pi^*$ 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 $\pi-\pi^*$ 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_{II}/C_{III} , where C_{II} and C_{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 (~ 10 per cent) conversion, E_{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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