

mechanism for the pressure change gives a value of α which seems inconsistent with the data for metallic iron. At present the authors consider the change in shielding as probably the most important factor, but this is a tentative judgment, and considerable further study is needed.

It seems difficult to reconcile the narrow range of isomer shifts and the consistent change with pressure for both ferrous and ferric compounds with results of molecular orbital calculations using LCAO orbitals and a Mulliken population analysis. These indicate relatively small differences in electron distribution for ferrous and ferric ions with the same ligand, and, for the ferric ion in particular, a high covalency with the electron distribution strongly dependent on the ligand. These methods are probably particularly applicable to atoms with a relatively small number of electrons. It is also well known that one can get very satisfactory calculations of energies and of energy differences between states of a system using wave functions which are not a particularly accurate description of the true orbital. It may be that a linear combination of atomic orbitals using free ion wave functions is a rather inaccurate description of the wave function amplitude at the nucleus.

3. Covalent Compounds

Figure 12 exhibits the change in isomer shift with pressure for four compounds which show a high degree of electron sharing between ligand and metal. There is a very large change in isomer shift with pressure

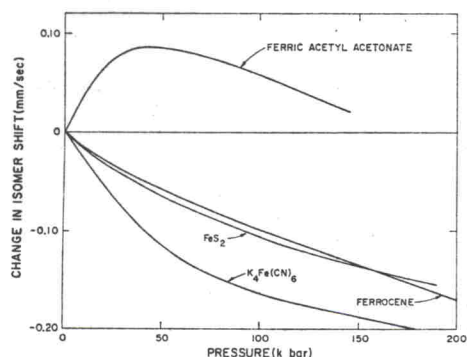


FIG. 12. Isomer shift versus pressure—"covalent" compounds.

for ferrocene, pyrites and potassium ferricyanide. This is not a compression effect, that is, it is not a result of especially high compressibility. The pyrites crystal is known to be relatively incompressible, and surely neither the ferrocene molecule nor the ferrocyanide molecular ion would show a large change in bond length with pressure. Also shown is ferric acetyl acetonate which actually exhibits a decrease in electron density with increasing pressure in the low pressure region with a reversal at higher pressures.

In these cases, in addition to changes in shielding and compression of the s wave functions, there must be significant change in orbital occupation with pressure. A calculation for ferrocene by Vaughan and Drickamer (1967a) indicates that at least one third of the change with pressure for that compound can be accounted for by changes in electron distribution among the orbitals. Each compound, however, requires an individual analysis so that no generalizations are possible.

B. QUADRUPOLE SPLITTING

As mentioned earlier, an electric field gradient at the nucleus can interact with nuclear states of spin equal to or greater than one, partially removing their degeneracy. The Mössbauer resonance is one of a variety of tools for investigating this effect. Here we shall discuss only briefly some high pressure results for a few compounds of iron. There are two possible sources of an electric field gradient at a transition metal nucleus. Firstly, the electrons in the partially filled $3d$ shell may exhibit less than spherical symmetry and, as mentioned earlier, this will be true, in general, for high spin ferrous or for low spin ferric compounds (see Fig. 4). Secondly, the ligands may exhibit less than cubic symmetry and thus impose an electric field gradient at the nucleus. Where the first effect is present it will dominate, since quadrupolar forces are short range and the effective radius of the $3d$ shell is much smaller than the average ligand-metal distance.

For preciseness, let us consider a high spin ferrous ion in an octahedral field. If the three t_{2g} levels are truly degenerate the orbital of the sixth electron will be spherically distributed and there will be no quadrupole splitting. As soon as the degeneracy is removed even by a very small splitting, the electron will not have an equal probability of being in the three t_{2g} states and a relatively large splitting results. Most high spin ferrous compounds exhibit a splitting of 2-3 mm/sec at room temperature. As one lowers the temperature one would expect the probability for occupation of the lowest level to increase by a Boltzmann factor and, in fact, the splitting does increase. If as the pressure