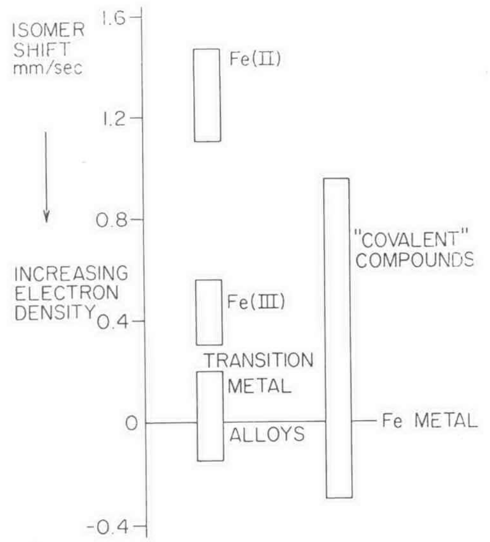

Figure 1. Ranges of isomer shift for iron.

(2–3 mm/sec). On the other hand, low-spin ferrous ion shows very small quadrupole splitting and low-spin ferric somewhat larger.

In our discussion we include two general topics: the effect of pressure on the isomer shift and the oxidation state of iron as a function of pressure, and two cases where Mössbauer resonance has revealed information on specific systems, ferrocene and α-Fe_2O_3.

Isomer Shifts

It should be understood that the interpretation of the effects of chemical environment and pressure on the isomer shift is an open question. We introduce it here in part to encourage more work, both experimental and theoretical, and we express opinions which are certainly subject to possible revision.

Figure 1 shows typical ranges of isomer shift for iron in various environments (by convention, the smaller the isomer shift, the larger the electron density). There are several salient features. Iron as a dilute solute in transition metals exhibits a modest range (0.4–0.5 mm/sec) of isomer shifts considering that the solvents have from one to nine 3d electrons. Evidentally the 3d electrons of iron are not totally integrated into the solvent 3d band. High-spin ferrous compounds lie in a relatively small range at very low electron density because of their nominal $3d^64s^0$ configuration. High-spin ferric systems lie at considerably higher electron density with a modest range of isomer shifts quite distinct from those of ferrous ions. The compounds covered include fluorides, chlorides, bromides, sulfates, phosphates, acetates, oxalates, citrates, thiocyanates, etc. Since the ferric ion is usually assumed to be more covalent than the ferrous, the small range of isomer shifts exhibited is of interest for the later discussion. The final classification in Figure 1, "covalent," is ambiguous, but there are certainly molecules such as ferrocene or the ferro- and ferricyanides which exhibit a high degree of electron sharing, and crystals like FeS_2, $FeSe_2$, $FeTe_2$, FeP, $FeAs_2$, etc., which have no easily describable valence. As one might expect, these materials show a large range of isomer shifts.

Ingalls[10] found empirically a linear correlation between the maximum of the 3d radial wave function squared and the 3s density at the nucleus using Hartree–Fock free ion wave functions. A variational calculation performed to determine the effect of change in shape of 3d orbitals, going from the free ion to the metal, on 3s density at the nucleus indicates that Ingalls' correlation is still valid for the band functions, some of which have large electron densities in the tail of the orbital. Thus, in the interpretation of the isomer shift in terms of covalency, one must consider that the isomer shift is not necessarily sensitive to electron density located between the iron ion and the ligand, a normal criterion for covalency, but only to the associated change of 3d density on the ion.

In Figure 2 are plotted the isomer shifts of several high-spin Fe(II) and Fe(III) compounds as a function of pressure.[9,11–13] Almost all "ionic" compounds studied fall within the limits shown. Several facts are evident. For all compounds there is an increase in electron density with increasing pressure. The ferrous compounds show slightly more change than the ferric, although there is no consistent difference in compressibility. The change for ferrous compounds is 10–12% of the over-all ferrous–ferric difference in 150 kbars—a nontrivial effect. The rate of change with pressure drops off more rapidly than $\Delta V/V$ for most ionic compounds. Figure 3 is a corresponding plot at double scale for relatively covalent compounds. Pyrites, ferrocene, and $K_4Fe(CN)_6$ all show large changes in isomer shift, although pyrite is quite incompressible[14] and the Fe–C bonds in ferrocene and ferrocyanide are surely not very compressible. The acetylacetonate is apparently rather covalent, although it is high spin. It exhibits a decrease in electron density at low pressure with a reversal at high pressure.

There are two factors which would change the electron density at the nucleus with compression: (1) changes in orbital occupation (these could be either transfer of electrons to or from the 4s levels, or transfer to, from, or among the 3d levels, changing the shielding of the 3s electrons); (2) distortion of the wave functions—either compression of the s electrons or the spreading of the 3d electrons mentioned earlier. The first factor undoubtedly is important in the case of the "covalent" compounds of Figure 3. We do not believe it is significant for the systems of Figure 2.

There are two basically different theoretical approaches to the isomer shift, both attempts to evaluate

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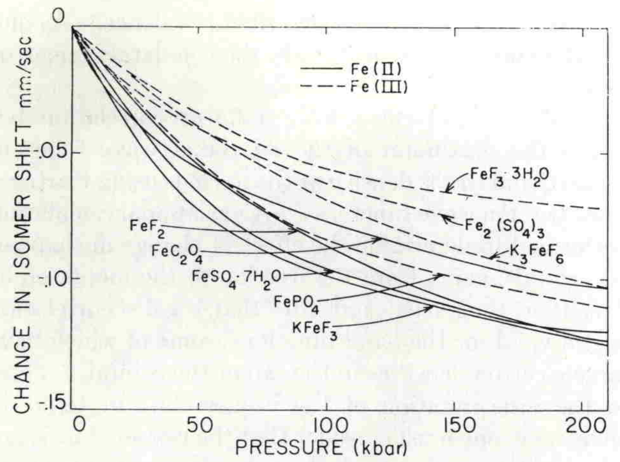

Figure 2. Change of isomer shift *vs.* pressure diagram for "ionic" compounds.

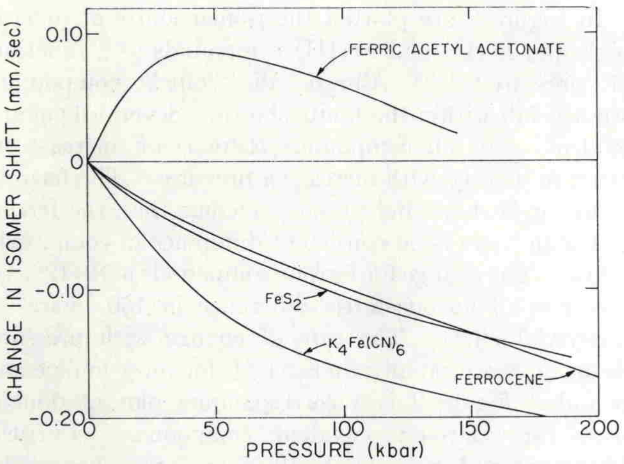

Figure 3. Change of isomer shift *vs.* pressure diagram for "covalent" compounds.

α (or $\Delta R/R$). Walker, *et al.*,[15] have assumed that the configurations of Fe(II) and Fe(III) are $3d^64s^0$ and $3d^54s^0$ and have used the difference in measured isomer shift (~0.9 mm/sec) as a scaling factor. On this argument, one would explain the effect of pressure entirely by reduced shielding because the 3d orbitals have spread out, as discussed earlier. This explanation was used by Champion, *et al.*[11] On the other hand, Simanek and Sroubec[16] assume that compression of the wave functions is the major factor in the pressure effect and use the pressure data to evaluate α, obtaining a number about one-fourth the magnitude of that derived by Walker, *et al.* Gol'danski[17] and Danon[18] arrive at values similar to that of Simanek and Sroubec on more intuitive grounds. Simanek and Sroubec would assign the difference between Fe(II) and Fe(III) isomer shifts entirely to fractional occupation of the 4s level in the latter case.

Insofar as we can estimate, neither effect is insignificant. There are several factors which make us believe that the change in shielding is more important. (1) Both the range of atmospheric isomer shifts and the range of changes with pressure are quite small. These include ligands with many different propensities for electron sharing. If occupation of the 4s levels were an important factor, one would expect a large spread in isomer shifts. In fact, it is difficult to reconcile the small spread of isomer shifts observed with the results of molecular orbital (LCAO) calculations which indicate a high covalency for Fe(III) which varies widely with the ligand. Apparently this type of wave function is adequate for calculating energy differences observed optically, but is a poor approximation to the amplitude of the ground state as seen at the nucleus. As mentioned earlier, changes in the tail of the wave function are not necessarily reflected in the shape of the inner part. (2) The change in isomer shift with pressure does not correlate with the compressibilities, as would be expected from compression of the s electronic wave functions, but ferrous materials do tend to show a somewhat larger shift than the ferric materials, which would be expected if the dominant mechanism were changing of the 3d shielding. (3) Band calculations for iron[19] indicate that with decreasing interatomic distance the energy of the 3d part of the conduction band lowers in energy *vis-à-vis* the 4s part. Measurements of the change of isomer shift with pressure[3,20-22] combined with the analysis of Ingalls[10] are more consistent with a large negative value of α as predicted by Walker, *et al.*, than with the smaller magnitude calculated by Simanek and Sroubec. One can relate this to the dominant role of changing 3d shielding. We wish to emphasize, however, that the change of isomer shift with environment is still an open question, and an interesting one.

The Oxidation State of Iron

As discussed in the previous sections, the Mössbauer spectra of high-spin Fe(II) and Fe(III) are entirely different as regards both isomer shift and quadrupole splitting, so that it is easy to estimate the relative amount of one oxidation state in the presence of the other from computer-fit areas. Although the difference in spectra for low-spin states is less spectacular, the calculation is still possible. One of the most interesting results of high-pressure studies is the observation that ferric ion reduces to the ferrous state with pressure, and this is reversible, with some hysteresis.[9,11-13] Typical spectra appear in ref 9 and 11. A greater or lesser degree of conversion has been observed in $FeCl_3$, $FeBr_3$, $KFeCl_4$, Li_3FeF_6, $FePO_4$, $Fe_2(SO_4)_3$, $Fe(NCS)_3$, Fe-

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