COMMENT ON A RECENT MODEL OF THE IRON COMPLEX IN SPINACH FERREDOXIN

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In this note we wish to point out some of the implications of the model of Gibson et al (1966) concerning the hyperfine splitting that would be produced by isotopic substitution of ^{57}Fe (with $I = \frac{1}{2}$) for ^{56}Fe and to discuss recent magnetic susceptibility data of spinach ferredoxin.

A hyperfine interaction of the usual type viz. $A\underline{S}.\underline{I}$, will produce an overall hyperfine splitting of $|A|$ for $I = \frac{1}{2}$. In the model scheme of Gibson et al (1966) a high spin ferric ion is coupled antiferromagnetically to a high spin ferrous ion to give a ground state with spin $\frac{1}{2}$. The hyperfine Hamiltonian for this system may be written

$$A_1\underline{S}_1\cdot\underline{I}_1 \quad + \quad A_2\underline{S}_2\cdot\underline{I}_2 \qquad (1)$$

where subscript 1 refers to the ferric ion and subscript 2 to the ferrous ion. If both the iron sites in this interacting pair are occupied by ^{57}Fe nuclei, one can show that the overall hyperfine splitting is (cf. equation 2 of reference 1).

$$\frac{7}{3}\,|A_1| \quad + \quad \frac{4}{3}\,|A_2| \qquad (2)$$

Assuming that $A_1 \sim A_2 \sim 10$ gauss, this will produce an overall splitting of ~ 37 gauss. For the case where not all the ^{56}Fe is replaced by ^{57}Fe an average must be taken over equation (2).

Shethna et al (1964) observed a hyperfine splitting of ~20 gauss when they substituted ^{57}Fe for ^{56}Fe in the non-haem iron protein from Azotobacter. This value is by no means inconsistent with the estimate above. An alternative explanation for the Azotobacter 20 gauss hyperfine splitting was put forward by Blumberg and Peisach (1965), who suggest that if a radical is bonded to an ion such as low spin Fe^{2+}, and the unpaired electron has some s character, then an unusually large hyperfine field can easily result. However, if such an effect were important, it would not necessarily be confined to transition metal ions, and it is doubtful whether such a general mechanism would not have been recognized earlier. A further criticism of the Blumberg-Peisach model is the difficulty the model encounters when trying to account for the experimentally observed g-shifts. For instance, one must make numerous arbitrary assumptions regarding overlap integrals, size and sign of exchange integrals, energy denominators, etc. Indeed, if one assumes that the radical - Fe^{2+} bond is a pure σ-bond, and that the Fe^{2+} ion is otherwise octahedrally coordinated, then a simple symmetry argument shows that only a g_z-shift can arise from the Blumberg-Peisach mechanism. Lastly, this model might be expected to predict absorption bands corresponding to excitation of an electron from a t_2 orbital on the Fe^{2+} to a radical orbital, or excitation of an electron from the radical to the Fe^{2+} e orbitals. We are not aware of any evidence for the existence of these bands.

We are greatly indebted to Dr. A. Ehrenberg of the Karolinska Institute, Stockholm, who has measured the magnetic susceptibility of a spinach ferredoxin sample prepared by the method of reference 1. The average of two room temperature measurements is $\chi_{ox} = 1015 \times 10^{-6}$ e.m.u. per iron atom and $\chi_{red} = 2285 \times 10^{-6}$ e.m.u. per iron atom (Ehrenberg, personal communication). Assuming the ground state only is occupied (and neglecting temperature-independent and orbital contributions), our model predicts $\chi_{ox} = 0$ (for $S = 0$), and $\chi_{red} = 625 \times 10^{-6}$ e.m.u. per iron atom (for $S = \frac{1}{2}$) for the oxidized and reduced states respectively. Since these values are lower than Ehrenberg's experimental numbers, it would appear that higher states ($S = 1,2$,etc. for the oxidized form; $S = 3/2,5/2$,etc. for the reduced form) might be partially occupied at room temperature. A good example of this type of behaviour is given by copper acetate (Bleaney & Bowers, 1952) where the ions are in interacting pairs. In this case the ground state has $S = 0$, the excited state $S = 1$, and the large exchange (about 300 cm^{-1}) produces an anomalously low susceptibility at room temperature. On this basis, exchange constants of between 200 and 400 cm^{-1} would account nicely for the susceptibilities of spinach ferredoxin at room temperature. It is not easy to see how the model of Blumberg & Peisach (1965), or that of Brintzinger et al (1966) (which predict simple Curie law behaviour with $S = \frac{1}{2}$; $\chi = C/T$) might explain the susceptibility data.

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