

Aspects of ^{57}Fe Mössbauer Spectroscopy

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I. Introduction

Ever since the discovery of recoilless nuclear gamma resonance by Rudolf Mössbauer in 1958, the technique, known as Mössbauer spectroscopy, has developed into a powerful tool to investigate the electronic structure of compounds with high resolution. The Mössbauer effect, which requires a nucleus with low-lying excited states, has been observed for 43 elements. The technique has been employed to study the electronic environment of Mössbauer-active atoms in metals and insulators by probing, for example, magnetism, electronic relaxation, chemical bonding, and redox reactions. By far the most utilized Mössbauer nucleus is ^{57}Fe , and for that reason this chapter will focus entirely on this isotope.

This chapter will focus on those aspects of Mössbauer spectroscopy that have played a decisive role in the characterization of iron-containing compounds in bioinorganic chemistry and metallobiochemistry. These aspects concern the

properties of paramagnetic centers as observed for mononuclear sites and exchange-coupled dinuclear clusters by electron paramagnetic resonance (EPR) and Mössbauer spectroscopy. Rather than describing and tabulating typical Mössbauer data of high-spin, intermediate-spin, or low-spin Fe(II), Fe(III), or Fe(IV) compounds, we will pick a high-spin ($S = \frac{5}{2}$) iron(III) site and describe typical spectra that have been observed for such a site. While Mössbauer spectroscopy can well stand on its own, its power is substantially increased when it is applied in combination with EPR. After discussing the connections between the two techniques and describing spectra of an Fe(III) site, we will couple an Fe(III) site ferromagnetically and antiferromagnetically to an Fe(II) site. Such spin-coupled pairs are presently under intensive study in many laboratories with bioinorganic and biochemical interests. While the choice of material, at first sight, may not seem to be entirely satisfactory to the reader, it is hoped that this chapter will facilitate access to a very active field of the current research literature.

It is important to know that the Mössbauer phenomenon rests on the fact that γ radiation (high-energy photons) can be emitted or absorbed without imparting recoil energy ($E_R = E_\gamma^2/2M = 1.95 \times 10^{-3}$ eV, where $E_\gamma = 14.4$ KeV and M is the mass of the ^{57}Fe nucleus). In a solid, most of the recoil energy is converted into lattice vibration energy. Mössbauer has shown, however, that there is a certain probability, described by the recoil-free fraction f , that γ emission and absorption take place without recoil. In order to observe the Mössbauer effect, the ^{57}Fe nucleus must be placed in a solid or frozen solution matrix. Among the many texts¹⁻⁴ that deal with the fundamentals of this technique, the book by Gülich et al.¹ is highly recommended.

II. Some Background on Basic Interactions

Iron-57 is a stable isotope with 2.2% natural abundance. In ^{57}Fe Mössbauer spectroscopy, we observe transitions between the nuclear ground state of ^{57}Fe (nuclear spin $I_g = \frac{1}{2}$; nuclear g factor, $g_g = 0.181$) and a nuclear excited state at 14.4 KeV ($I_e = \frac{3}{2}$, $g_e = -0.106$, nuclear quadrupole moment Q) (Fig. 1). For the bare nucleus, the nuclear ground and excited states would exhibit twofold and fourfold degeneracies, respectively, and only a single Mössbauer transition would be observed. If the nucleus is embedded in an electronic environment of symmetry lower than spherical, cubic, or tetrahedral, the degeneracy of the nuclear excited state is partially lifted by the quadrupole interaction between the nuclear quadrupole moment Q and the electric field gradient tensor V generated by the surrounding charges at the site of the ^{57}Fe nucleus. The electric field at the nucleus is the negative gradient of the potential, $V(x, y, z)$, and the electric field gradient (EFG) tensor is a 3×3 second-rank tensor, with element V_{ij} , formed by taking the spatial derivatives of the electric field. However, only five of the nine components are independent. Mixed derivatives, such as $\partial^2 V/\partial x \partial y = \partial^2 V/\partial y \partial x$, are the same, so the EFG tensor is symmetric. It can be shown that s electrons do not contribute to the EFG and, therefore, Laplace's equation evaluated at the nucleus requires that the EFG tensor is traceless, (i.e., $\sum V_{ii} = 0$). In an

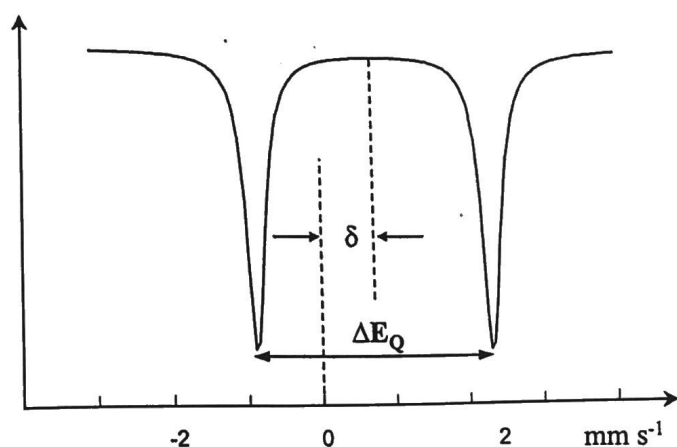
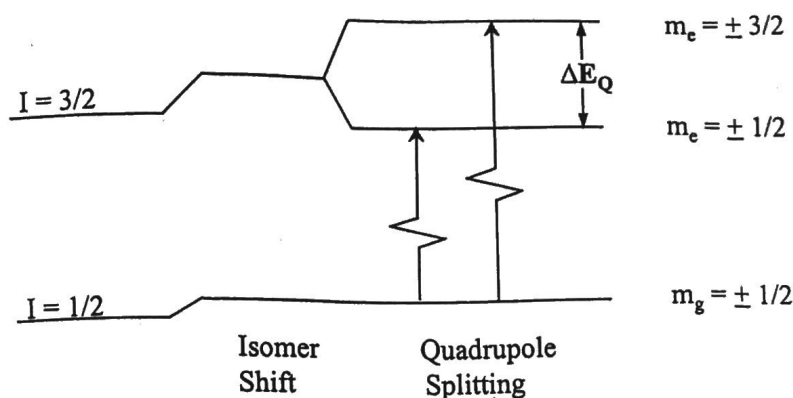


Figure 1
Quadrupole splitting of the ^{57}Fe excited state and shift of the nuclear states by the electric monopole interaction that gives rise to the isomer shift. Also shown is a typical Mössbauer spectrum for a sample containing randomly oriented molecules. In the absence of heterogeneities or relaxation effects the absorption lines have Lorentzian shape. The velocity scale is drawn relative to the centroid of Fe metal.

environment of spherical, octahedral, or tetrahedral symmetry we must have $V_{xx} = V_{yy} = V_{zz}$; thus $V_{ii} = 0$.

In the principal axis system of the EFG tensor, the off-diagonal elements vanish, and since the EFG tensor is traceless, only two independent components need to be specified. By convention, these parameters are V_{zz} and the asymmetry parameter η , defined by $\eta = (V_{xx} - V_{yy})/V_{zz}$. By choosing the coordinate system such that $|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|$, the asymmetry parameter can be restricted to $0 \leq \eta \leq 1$. The conventional Hamiltonian of the quadrupole interaction for the ^{57}Fe nuclear *excited* state is

$$\mathcal{H}_Q = \frac{eQV_{zz}}{12} [3I_z^2 - I(I+1) + \eta(I_x^2 - I_y^2)] \quad (1)$$

where e is the proton charge. One remark may be in order here. It is true that $\eta = 0$ for complexes with tetragonal or trigonal point symmetry. However, the

observation of $\eta = 0$ does not necessarily imply such a symmetry. For example, a d_{xy} orbital can be an eigenstate in rhombic symmetry; yet a d_{xy} orbital has a charge distribution with fourfold symmetry which yields $V_{xx} = V_{yy}$ and thus $\eta = 0$.

In the absence of magnetic interactions, $\mathcal{H}_Q$ splits the nuclear excited state into two degenerate doublets. For $\eta = 0$, these doublets are labeled by the magnetic quantum numbers $m_e = \pm \frac{3}{2}$ and $m_e = \pm \frac{1}{2}$; for $V_{zz} > 0$ the $m_e = \pm \frac{3}{2}$ levels have the higher energy. The two doublets are separated in energy by the quadrupole splitting

$$\Delta E_Q = \frac{eQV_{zz}}{2} \sqrt{1 + \eta^2/3} \quad (2)$$

Figure 1 shows the splitting of the nuclear excited state and the resulting Mössbauer spectrum, a quadrupole doublet, for a sample containing randomly oriented molecules such as found in polycrystalline samples or in frozen solution. For this case, the intensities of both lines are equal and the sign of ΔE_Q is thus undetermined. Although one should therefore write $|\Delta E_Q|$ in Eq. (2), it is customary to quote simply ΔE_Q . For diamagnetic (electronic spin $S = 0$) samples, the sign of ΔE_Q and η can be determined by studying the sample in strong applied magnetic fields. For compounds exhibiting magnetic effects, various methods can be used to determine the components of the EFG tensor; we will discuss one method below.

In Figure 1, we have indicated another quantity measured by Mössbauer spectroscopy. Electric monopole interactions between the nuclear charge distributions and the electrons at the nucleus cause a shift of the nuclear ground and excited states without affecting the splittings of the two multiplets. These interactions are described by the parameter δ , which measures the isomer shift. This parameter can be obtained directly from the centroid of the Mössbauer spectrum. Since both the Mössbauer source and the absorber experience an isomer shift, the experimental result depends on the nature of the radiation source used. Therefore, it is customary to quote δ relative to a standard. The standard most commonly used is Fe metal or sodium nitroprusside dihydrate, $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$, at 298 K.

The isomer shift is a measure of the s-electron density at the nucleus. This density can be influenced either by altering the s population of a valence shell or, via shielding effects, by increasing or decreasing electron density with p or d character. The parameter δ depends on the oxidation state, the spin state, the coordination environment and the degree of covalency, and thus this parameter conveys important structural and chemical information. If one deals with an iron compound of unknown structure and oxidation state, one can make use of correlation diagrams in which δ is plotted as a function of the oxidation and spin state.^{1,2} Unfortunately, among the common states only the high-spin ($S = 2$) iron(II) state has a unique range of δ values; the isomer shifts of other states overlap considerably. However, by taking into account quadrupole splittings and magnetic data, one can generally assign the spin and oxidation state with high

Table I
Values for ΔE_Q and δ for Some Compounds of Biological Interest^a

Oxidation State	Spin State	Ligand Set	$\Delta E_Q(\text{mm s}^{-1})$	$\delta(\text{mm s}^{-1})$
Fe(IV)	$S = 2$	Fe-(O,N) ^b	0.5–1.0	0.0–0.1
	$S = 1$	Hemes	1.0–2.0	0.0–0.1
		Fe-(O,N)	0.5–4.3	–0.20–0.10
Fe(III)	$S = \frac{5}{2}$	Hemes	0.5–1.5	0.35–0.45
		Fe-S	< 1.0	0.20–0.35
		Fe-(O,N)	0.5–1.5	0.40–0.60
	$S = \frac{3}{2}$	Hemes	3.0–3.6	0.30–0.40
	$S = \frac{1}{2}$	Hemes	1.5–2.5	0.15–0.25
		Fe-(O,N)	2.0–3.0	0.10–0.25
Fe(II)	$S = 2$	Hemes	1.5–3.0	0.85–1.0
		Fe-S	2.0–3.0	0.60–0.70
		Fe-(O,N)	2.0–3.2	1.1–1.3
	$S = 0$	Hemes	< 1.5	0.30–0.45
		Hemes	< 1.5	0.30–0.45

^aThe entries give *typical* numbers at 4.2 K. The isomer shifts are quoted relative to the centroid of Fe metal at 298 K, the standard most commonly used. Table I is by no means complete. The classes of compounds chosen are hemes, localized valence states of Fe with tetrahedral sulfur ligation (Fe-S), and hexacoordinate and pentacoordinate Fe sites with oxygen and/or nitrogen ligands [Fe-(O,N)].

^bOnly two examples; see Lee et al.²⁶ and Dong et al.²⁹

confidence. Table I lists typical values for ΔE_Q and δ for three classes of compounds important in bioinorganic chemistry and biochemistry, namely, hemes, iron-sulfur centers containing Fe sites in a distorted tetrahedral sulfur environment, and compounds with a hexa- or penta-coordinate N/O environment.

The nuclear ground and excited states of the ^{57}Fe nucleus have magnetic moments that can interact with a magnetic field $\mathbf{B}$. This interaction is described by

$$\mathcal{H} = -\boldsymbol{\mu} \cdot \mathbf{B} = -g_n \beta_n \mathbf{B} \cdot \mathbf{I} \quad (3)$$

where g_n is the nuclear g factor and β_n is the nuclear magneton. In the absence of quadrupole interactions, the Hamiltonian in Eq. (3) splits the nuclear states into equally spaced levels of energy

$$E(m_I) = -g_n \beta_n B m_I \quad (4)$$

where m_I is the nuclear magnetic quantum number. Because $g_e/g_g < 0$, the sequence of m_I values is in reverse order for the excited state. Figure 2 shows schematically the splittings of the nuclear ground and excited states. The allowed γ transitions between the nuclear sublevels follow from the selection rules for

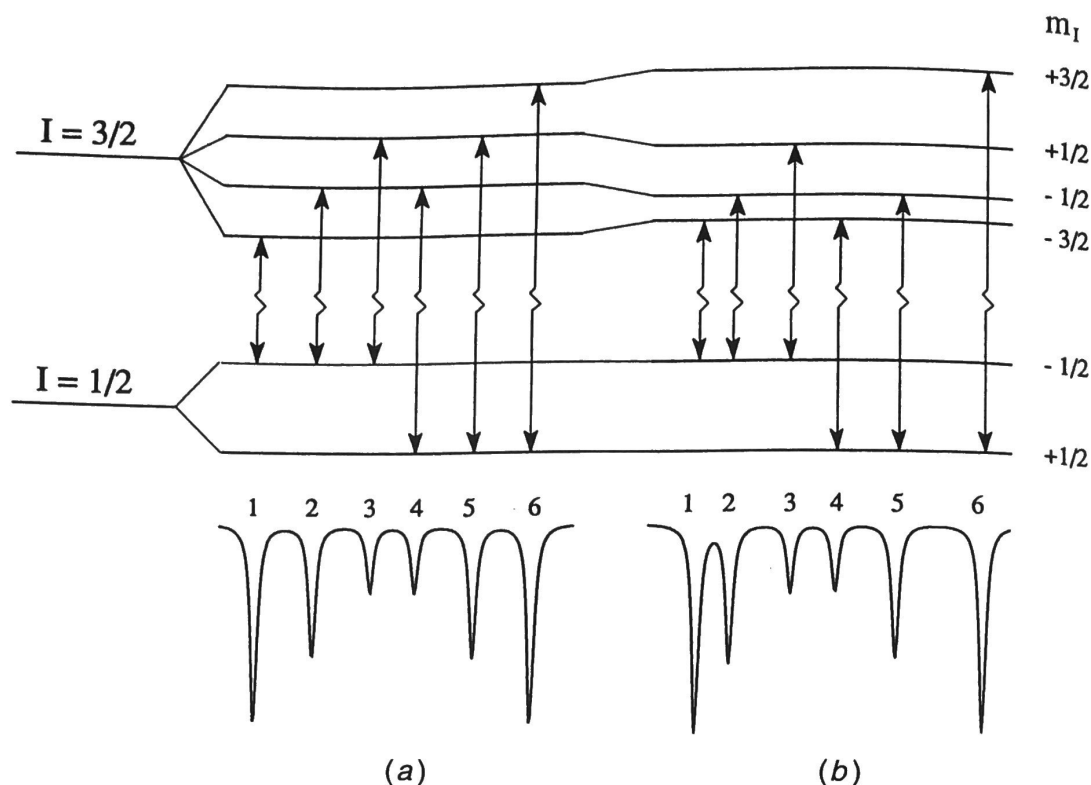


Figure 2

Magnetic hyperfine splittings of the nuclear ground state and the 14.4-keV level according to Eq. (4). The diagram drawn in (a) assumes $\Delta E_Q = 0$ while that of (b) is drawn for the case where a large magnetic interaction is perturbed by a quadrupole interaction with $eQV_{zz} > 0$ and $\eta = 0$. Note that the energy of the γ transition is 14,400 eV, whereas typical hyperfine splittings are about 3×10^{-7} eV. A typical line width is 1.5×10^{-8} eV.

magnetic dipole transitions: $\Delta I = 1$, $\Delta m_I = 0, \pm 1$. Note that the splitting of the six-line Mössbauer spectrum is a measure of the strength of the magnetic field at the nucleus. Note also that lines 1, 3, 4, and 6 derive from $|\Delta m_I| = 1$ transitions, while lines two and five result from $\Delta m_I = 0$ transitions.

In Eq. (3), the direction of the magnetic field defines the nuclear quantization axis. This field is generally not the applied field but an effective field B_{eff} , which we introduce below. If a γ quantum approaches the nucleus at an angle θ relative to the nuclear quantization axis, the angular dependence of the absorption probability is proportional to $\sin^2 \theta$ for $\Delta m_I = 0$ transitions and proportional to $(1 + \cos^2 \theta)$ for $\Delta m_I = \pm 1$ transitions. Thus, if we study a sample for which the effective magnetic field at the nucleus is *parallel* to the observed γ rays, we have $\theta = 0$ and the intensity of the $\Delta m_I = 0$ lines vanishes [Fig. 3(a)]. On the other hand, if the nuclear quantization axis is *perpendicular* to the observed γ rays, the intensity of the $\Delta m_I = 0$ lines is maximized [Fig. 3(b)]. Now, for paramagnetic systems it is frequently possible to orient B_{eff} by application of an external magnetic field of moderate strength (10 mT is generally sufficient). The degree of this

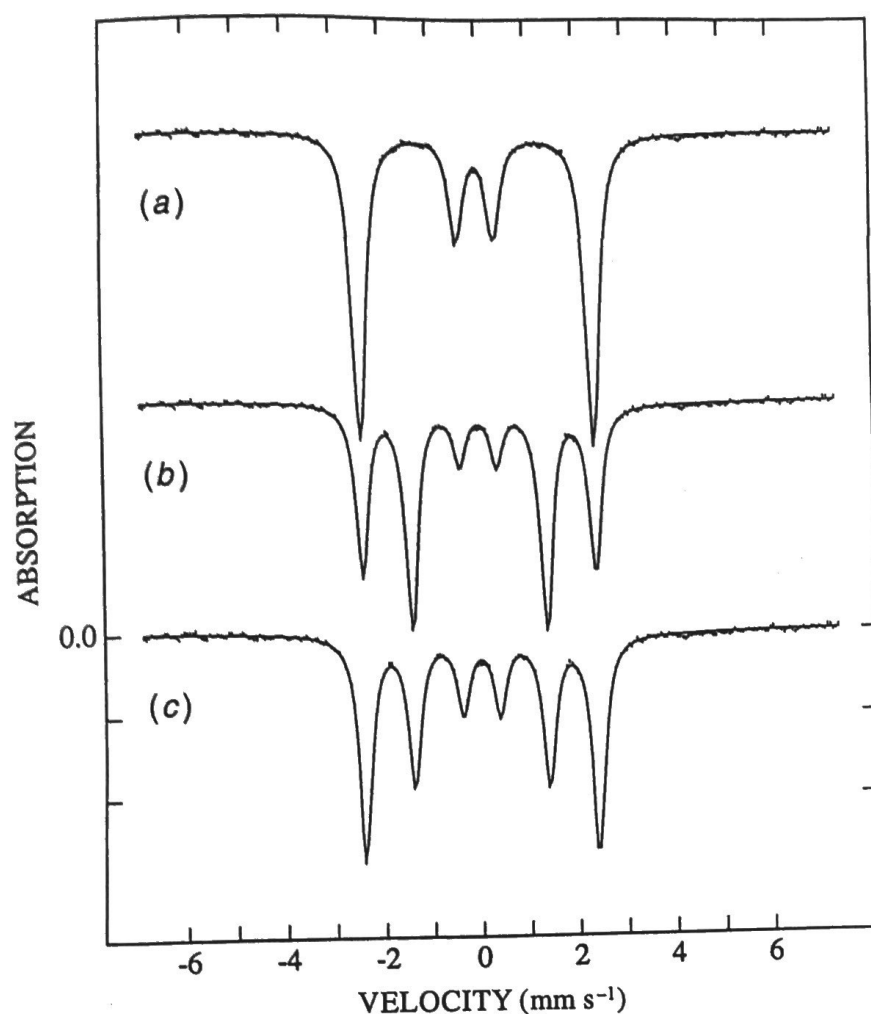


Figure 3

Illustration of Mössbauer spectra of an $S = \frac{1}{2}$ system with *isotropic* (a and b) and *uniaxial* (c) magnetic properties. It is assumed that the samples consist of a collection of randomly oriented molecules as occurs in frozen solution or polycrystalline powders. The spectra shown in (a) and (b) apply to the isotropic case, Eq. (6), with a weak magnetic field applied either parallel (a) or perpendicular (b) to the observed γ radiation. The spectrum in (c) illustrates the case $g_x = g_y = 0$ and $g_z \neq 0$; the intensities of the absorption lines are independent of the orientation of the (weak) applied field.

orientation depends on the properties of the electronic system, for example, on the electronic Zeeman term and the zero-field splitting (zfs). Since the properties of the latter interactions are sensitively probed by EPR, there must be a connection between the shapes of the Mössbauer and EPR spectra. This connection allows us to draw very powerful conclusions about the type and number of iron sites in a cluster of unknown structure. Moreover, it allows us to identify a paramagnetic species even if most of the iron in the sample belongs to other species or impurities. In the following section, we will elucidate these connections in a simplified but systematic way. For the remainder of this chapter, we will assume that the nuclear quantization axis is solely determined by B_{eff} . This is not strictly true because the nuclear quantization axis is determined by an interplay of magnetic

and quadrupole interactions. In many practical cases, however, the magnetic interactions dominate and we can safely ignore quadrupolar effects for the type of considerations we wish to develop here.

It is customary to describe the magnetic properties of the electronic ground manifold of a transition metal ion by a spin Hamiltonian. Let us consider an iron site, such as low-spin Fe(III), with electronic spin $S = \frac{1}{2}$. A suitable spin Hamiltonian for describing the EPR and Mössbauer spectra of such a system can be written as

$$\mathcal{H} = \beta \mathbf{S} \cdot \mathbf{g} \cdot \mathbf{B} + \mathbf{S} \cdot \mathbf{A} \cdot \mathbf{I} - g_n \beta_n \mathbf{B} \cdot \mathbf{I} + \mathcal{H}_Q \quad (5)$$

The first and the third terms describe the electronic and nuclear Zeeman interactions, respectively. The magnetic hyperfine interaction between the electronic system and the nucleus is described by the magnetic hyperfine tensor $\mathbf{A}$. This tensor contains spin-dipolar and orbital contributions as well as a contribution due to the polarization of the core electrons by unpaired electrons (Fermi contact term); $\mathbf{A}$ carries information about covalency and the orbital state of the unpaired d electrons. We start our considerations by assuming that $\mathbf{g}$ and $\mathbf{A}$ are *isotropic*, that is, $g_x = g_y = g_z = g$ and $A_x = A_y = A_z = A$, and discuss

$$\mathcal{H} = g\beta \mathbf{S} \cdot \mathbf{B} + \mathbf{A} \mathbf{S} \cdot \mathbf{I} - g_n \beta_n \mathbf{B} \cdot \mathbf{I} \quad (6)$$

For the following considerations, the quadrupole interactions are of little consequence and we therefore ignore this term. The A values of iron compounds are $|A| \leq 0.001 \text{ cm}^{-1}$, whereas $g\beta B = 0.3 \text{ cm}^{-1}$ for EPR at X band ($B \approx 0.33 \text{ T}$ at $g = 2$); the nuclear Zeeman term is more than four orders of magnitude smaller than the electronic Zeeman term. Thus, the electronic Zeeman term dominates and it follows that the quantization axis (the z axis) of $\mathbf{S}$ and the expectation values $\langle S \rangle = \langle \psi | S | \psi \rangle$ are solely determined by the electronic Zeeman interaction, even in applied fields as small as $H = 10 \text{ mT}$. For the system of Eq. (6) the electronic spin is quantized along $\mathbf{B}$ (the magnetic moment $\boldsymbol{\mu} = -g\beta \mathbf{S}$ precesses around the applied field) and $\langle S_z \rangle = M_S = \pm \frac{1}{2}$ and $\langle S_x \rangle = \langle S_y \rangle \approx 0$.

The first term in Eq. (6) depends only on the electronic variable $\mathbf{S}$, whereas the second term couples the electronic with the nuclear system. Since the electronic Zeeman interaction dominates, the $\mathbf{A} \mathbf{S} \cdot \mathbf{I}$ term has little influence in determining the expectation value of $\langle \mathbf{S} \rangle$. This fact allows us to replace the operator $\mathbf{S}$ in Eq. (6) by its expectation value $\langle \mathbf{S} \rangle$ to obtain a nuclear Hamiltonian for each sublevel of the electronic doublet

$$\mathcal{H}_n = \mathbf{A} \langle \mathbf{S} \rangle \cdot \mathbf{I} - g_n \beta_n \mathbf{B} \cdot \mathbf{I} \quad (7)$$

Although the electronic Zeeman term does not explicitly appear in Eq. (7), we have to keep in mind that it determines $\langle \mathbf{S} \rangle$. For the "spin-up" state, we take $\langle S_z \rangle = +\frac{1}{2}$, for the "spin-down" state $\langle S_z \rangle = -\frac{1}{2}$. Since $\langle S_x \rangle = \langle S_y \rangle \approx 0$, the magnetic hyperfine term is reduced to $A \langle S_z \rangle I_z$, that is, only the component of the magnetic hyperfine term along the electronic quantization axis matters. This is a general result from perturbation theory; the term $A(\mathbf{S}_x \mathbf{I}_x + \mathbf{S}_y \mathbf{I}_y)$ yields off-

diagonal elements that give second-order contributions of $A(A/g\beta B) \approx A/300$ to the energies for the conditions stated above. We can rewrite Eq. (7) as

$$\begin{aligned}\mathcal{H}_n &= -g_n\beta_n \left(\frac{-A\langle\mathbf{S}\rangle}{g_n\beta_n} + \mathbf{B} \right) \cdot \mathbf{I} \\ &= -g_n\beta_n (\mathbf{B}_{\text{int}} + \mathbf{B}) \cdot \mathbf{I} = -g_n\beta_n \mathbf{B}_{\text{eff}} \cdot \mathbf{I}\end{aligned}\quad (8)$$

where we have defined the internal magnetic field

$$\mathbf{B}_{\text{int}} = -A\langle\mathbf{S}\rangle/g_n\beta_n \quad (9)$$

Equation (8) connects the spin Hamiltonian [Eq. (6)] with Eq. (3); in a paramagnetic system it is $\mathbf{B}_{\text{eff}}$ that acts on the nuclear magnetic moment and causes the splitting of the nuclear levels. Iron compounds exhibit internal magnetic fields up to 60 T and for moderate applied fields ($B < 0.3$ T) the magnetic splitting of the Mössbauer spectrum is determined by $\mathbf{B}_{\text{int}}$.

Assume now that we have an iron site described by Eq. (6). If the sample is either polycrystalline or consists of molecules in frozen solution, the molecules are randomly oriented and spatially fixed. Since $\mathbf{B}_{\text{int}}$ is parallel to $\langle\mathbf{S}\rangle$ and thus parallel to the applied field $\mathbf{B}$, we can align the nuclear quantization axis of every molecule in the sample either parallel or perpendicular to the observed γ radiation by a suitable orientation of the applied field. If the field is applied parallel to the observed γ radiation, we have $\theta = 0$ for the entire population of molecules and a Mössbauer spectrum as shown in Figure 3(a) will result (angle θ has been defined above). Rotating the applied field by 90° will result in a spectrum as shown in Figure 3(b).

Let us now consider the anisotropic case of Eq. (5). Since the product of a tensor with a vector gives another vector, we can write $\mathbf{g} \cdot \mathbf{B} = \mathbf{B}'$ to obtain the Zeeman term $\beta\mathbf{S} \cdot \mathbf{B}'$. Now, $\mathbf{B}'$ gives the quantization direction of the electronic spin, that is, the only nonvanishing component of $\langle\mathbf{S}\rangle$ is along $\mathbf{B}'$. Expressing the components of $\mathbf{B}$ in the principal axis frame of the $\mathbf{g}$ tensor we have

$$\begin{aligned}B_{x'} &= g_x B_x = g_x B \sin\beta \cos\alpha \\ B_{y'} &= g_y B_y = g_y B \sin\beta \sin\alpha \\ B_{z'} &= g_z B_z = g_z B \cos\beta\end{aligned}\quad (10)$$

where g_x, g_y , and g_z are the principal components of $\mathbf{g}$ and where α and β are polar angles. If the $\mathbf{g}$ tensor is anisotropic, $\mathbf{B}'$ is not parallel to $\mathbf{B}$, and thus $\mathbf{B}_{\text{int}} = -A \cdot \langle\mathbf{S}\rangle/g_n\beta_n$ is not parallel to the applied field. Therefore, the field dependence (parallel to the γ rays vs. perpendicular) of the Mössbauer spectrum is less pronounced as $\mathbf{g}$ becomes more anisotropic. Since the $\mathbf{g}$ values are determined by EPR, one can make reasonable predictions (usually by computer simulations) about the distribution of $\mathbf{B}_{\text{int}}$ and thus the shape of the Mössbauer spectrum once the result of an EPR study are known.

Let us now consider the case where one $\mathbf{g}$ value is very large compared to the

other two (e.g., $g_z \gg g_x, g_y$). This case of extreme anisotropy, called the *uniaxial* case, is frequently encountered. Examples are the low-spin Fe(III) highly anisotropic low-spin (HALS) complexes (see Chapter 3) and subdoublets of multiplets with $S \geq \frac{3}{2}$. As can be seen from Eq. (10), $B_x' \approx B_y' \approx 0$ and $B_z \neq 0$ for almost all orientations of the applied field relative to the molecular axes, that is, $\mathbf{B}$ is directed along the molecular z axis (the z axis of $\mathbf{g}$), and for moderate anisotropies of $\mathbf{A}$ the internal magnetic field, $\mathbf{B}_{\text{int}} = -\mathbf{A} \cdot \langle \mathbf{S} \rangle / g_n \beta_n$, will be directed along z as well. (If $\mathbf{A}$, on the other hand, is anisotropic such that $A_x \gg A_z$, the internal magnetic field will acquire a sizable x component if $\langle S_x \rangle \neq 0$. This anisotropy would cause the internal field to tilt away from the z axis.) If the internal magnetic field is locked along the molecular z axis, the intensities of the Mössbauer spectrum do not change when the applied field is changed from parallel to perpendicular. The six-line pattern, averaged over all molecular orientations, will have a 3:2:1:1:2:3 intensity pattern as shown in Figure 3(c). Aasa and Vännargard⁵ gave a very useful expression for the EPR transition probabilities observed in the "derivative" spectrum of samples with randomly oriented molecules. In the uniaxial case, the area under the peak at g_z is proportional to $g_x^2 + g_y^2$ and thus vanishingly small in the limit $g_x \approx g_y \approx 0$. In EPR jargon, such a system is called "EPR silent". Thus, a field-independent Mössbauer spectrum suggests an EPR silent state, and conversely, a field-dependent Mössbauer spectrum implies that an EPR signal must be observed. Next, we extend our discussion to a slightly more complicated case, namely, the high-spin ($S = \frac{5}{2}$) iron(III) ion.

III. Effective g -Values for High-Spin Fe(III)

For describing the magnetic properties of the electronic ground manifold of paramagnetic transition metal ions, it is customary to replace the true Hamiltonian by an effective Hamiltonian, which operates only on spin variables. The spin on which this so-called spin Hamiltonian operates is not necessarily the true spin; it may be an effective spin or a fictitious spin that obeys the same rules as the real spin.⁶ The spin Hamiltonian approach is extremely useful, because it allows one, without going into the messy details of fundamental calculations, to compare the results obtained by different techniques such as EPR, electron nuclear double resonance, magnetic circular dichroism (MCD), NMR, Mössbauer spectroscopy, and magnetic susceptibility. The spin Hamiltonian parameters such as the zfs parameters D and E , the g tensor and the A tensor of similar compounds fall into narrow ranges.

A suitable spin Hamiltonian for describing the EPR spectra of the high-spin ($S = \frac{5}{2}$) system can be written as

$$\mathcal{H}_e = D(S_z^2 - \frac{35}{12}) + E(S_x^2 - S_y^2) + g_0 \beta \mathbf{B} \cdot \mathbf{S} \quad (11)$$

where D and E are the axial and rhombic zfs parameters, respectively. (These parameters are the principal axis components of the traceless zfs tensor, $\mathbf{D}$). For the high-spin iron(III) ion $g_0 = 2.0$ is appropriate. For $B = 0$ the zfs term of

Eq. (11) partially removes the sixfold degeneracy of the spin sextet and three (Kramers) doublets result (see Fig. 11 of Chapter 3).

In order to describe the Mössbauer spectra of high-spin iron(III) complexes, Eq. (11) needs to be augmented by terms describing the hyperfine interactions

$$\mathcal{H}_{\text{hf}} = A_0 \mathbf{S} \cdot \mathbf{I} - g_n \beta \mathbf{B} \cdot \mathbf{I} + \mathcal{H}_Q \quad (12)$$

The orbital ground state of the iron(III) ion has a vanishingly small orbital angular momentum, and the magnetic hyperfine interaction is therefore dominated by the isotropic Fermi contact term. The majority of the high-spin iron(III) complexes of interest to the inorganic and bioinorganic chemist has D values larger than 0.5 cm^{-1} , ranging up to about 20 cm^{-1} for certain heme complexes. We can thus study Mössbauer spectra under conditions where $\beta B \ll |D|$, that is, under conditions where the three Kramers doublets are well separated in energy. It is customary in the EPR literature and useful for the consideration of the Mössbauer spectra to consider each doublet separately and describe its magnetic properties with an effective spin $S' = \frac{1}{2}$ Hamiltonian, as illustrated by the following example.

Consider Eq. (11) for $D > 0$ and $E = 0$ under the condition that $\beta B \ll D$. Without loss of generality we assume that the applied magnetic field is in the xz plane with polar angle β relative to the z axis of the zfs tensor. We then wish to solve

$$\mathcal{H} = D(\mathbf{S}_z^2 - \frac{35}{12}) + g_0 \beta B (\mathbf{S}_x \sin \beta + \mathbf{S}_z \cos \beta) + A_0 \mathbf{S} \cdot \mathbf{I} \quad (13)$$

For $B = 0$ the eigenstates of the electronic system are $|S = \frac{5}{2}, M_s\rangle$, which we order in such a way that the two levels that comprise a Kramers doublet stay together, that is, in the sequence $M_s = +\frac{5}{2}, -\frac{5}{2}, +\frac{3}{2}, -\frac{3}{2}, +\frac{1}{2}, -\frac{1}{2}$. In order to solve Eq. (13), we would have to diagonalize the 12×12 matrix $\{(2S+1)(2I_g+1) = 12\}$ involving the nuclear ground state and a 24×24 matrix involving the nuclear excited state. However, since $\beta B \ll D$ we can neglect off-diagonal elements of the Zeeman and magnetic hyperfine interactions that involve states belonging to different Kramers doublets. The 12×12 matrix is then in a block-diagonal form consisting of three 4×4 matrices that can be solved separately, each 4×4 matrix belonging to a specific Kramers doublet. With the nomenclature $|S = \frac{5}{2}, M_s\rangle |I_g = \frac{1}{2}, m_g\rangle \equiv |\phi_{M_s}\rangle |m_g\rangle$ and abbreviating $\Delta = \beta B/2$ we obtain for the matrix of the $M_s = \pm \frac{1}{2}$ ground doublet:

	$ \phi_{+1/2}\rangle +\frac{1}{2}\rangle$	$ \phi_{-1/2}\rangle +\frac{1}{2}\rangle$	$ \phi_{+1/2}\rangle -\frac{1}{2}\rangle$	$ \phi_{-1/2}\rangle -\frac{1}{2}\rangle$
$ \phi_{+1/2}\rangle +\frac{1}{2}\rangle$	$g_0 \Delta \cos \beta + A_0/4$	$3g_0 \Delta \sin \beta$	0	0
$ \phi_{-1/2}\rangle +\frac{1}{2}\rangle$	$3g_0 \Delta \sin \beta$	$-g_0 \Delta \cos \beta - A_0/4$	$3A_0/2$	0
$ \phi_{+1/2}\rangle -\frac{1}{2}\rangle$	0	$3A_0/2$	$-g_0 \Delta \cos \beta - A_0/4$	$3g_0 \Delta \sin \beta$
$ \phi_{-1/2}\rangle -\frac{1}{2}\rangle$	0	0	$3g_0 \Delta \sin \beta$	$g_0 \Delta \cos \beta + A_0/4$

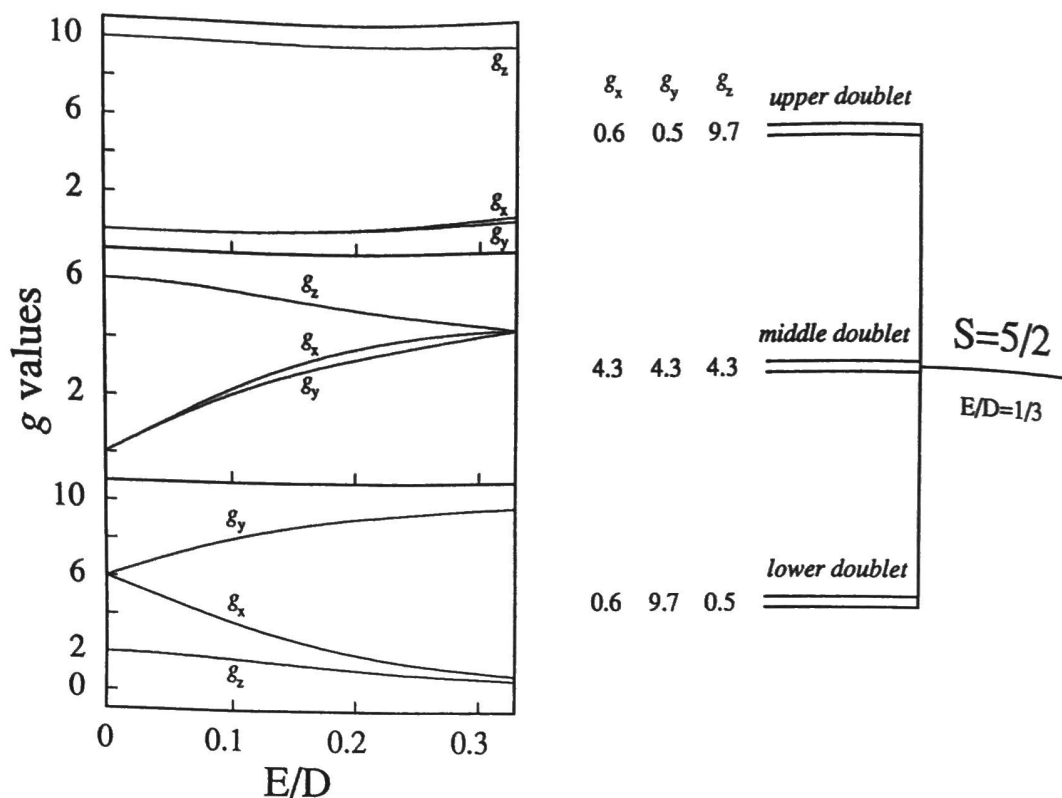


Figure 4

Effective g values for the three Kramers doublets of an $S = \frac{5}{2}$ spin multiplet plotted versus the rhombicity parameter E/D . It is assumed that $g_0 = 2$. The plot covers the whole range of g values. For $E/D > \frac{1}{3}$, one can relabel the coordinate axes and scale E/D back into the range $0 \leq E/D \leq \frac{1}{3}$. Also shown is an energy level diagram for the frequently occurring "rhombic" case $E/D = \frac{1}{3}$.

Of interest here are the factors 3 in the off-diagonal elements. They occur because $S_+|\phi_{-1/2}\rangle = \sqrt{S(S+1) + \frac{1}{4}}|\phi_{+1/2}\rangle = [2S+1]/2|\phi_{+1/2}\rangle = 3|\phi_{+1/2}\rangle$. Now, identical matrix elements are obtained for the $S' = \frac{1}{2}$ spin Hamiltonian

$$\mathcal{H} = \beta \mathbf{S}' \cdot \mathbf{g} \cdot \mathbf{B} + \mathbf{S}' \cdot \mathbf{A} \cdot \mathbf{I} \quad (14)$$

where $\mathbf{g}$ and $\mathbf{A}$ are tensors with principal axis values $g_x = g_y = 3g_0$, $g_z = g_0$ and $A_x = A_y = 3A_0$, $A_z = A_0$, and where $S' = \frac{1}{2}$ is an effective spin obeying the same rules as a real spin $S = \frac{1}{2}$. Thus for $g_0 = 2$, we can treat the ground doublet as a spin $\frac{1}{2}$ system with principal g values $g_x = g_y = 6$ and $g_z = 2$. Similarly, we obtain for the Kramers doublet at energy $2D$ the g values $g_x = g_y = 0$ and $g_z = 6$, and for the upper doublet $g_x = g_y = 0$ and $g_z = 10$.

We can generalize these ideas for $E \neq 0$ and generate plots of the effective g values as a function of E/D . Such a plot, introduced by Wickman,⁷ is shown in Figure 4. Similar plots can be generated for other multiplets. Such graphs are extremely useful for identifying the spin state by EPR studies. Note that because

of $S_+|S, -\frac{1}{2}\rangle = ((2S+1)/2)|S, +\frac{1}{2}\rangle$, we obtain $g_x = g_y = (2S+1)g_0/2$ for the $M = \pm \frac{1}{2}$ doublet for the axial case $E = 0$. (Thus, $g_x = g_y = 4.0$ implicates a spin $S = \frac{3}{2}$.) Note also that the following relations⁷ hold for each Kramers doublet,

$$A_x/g_x = A_y/g_y = A_z/g_z = A_0/g_0 \quad (15)$$

Before presenting specific examples, we wish to discuss briefly the effects of electronic spin relaxation on the Mössbauer spectra. Equation (9) shows that the internal field $\mathbf{B}_{\text{int}}$ is proportional to $\langle \mathbf{S} \rangle$. Thus, if the electronic spin fluctuates rapidly due to spin-lattice or spin-spin relaxation, the internal field will fluctuate. If this fluctuation is fast compared to the nuclear precession frequencies, which are of the order of 10 MHz, determined by $\mathbf{A}$ and $\mathcal{H}_Q$, the nucleus will sample an average field that can be computed by evaluating the thermal average $\langle \mathbf{S} \rangle_{\text{th}}$,

$$\langle S_i \rangle_{\text{th}} = \frac{\sum_n \langle S_i \rangle_n \exp(-\Delta E_n/kT)}{\sum_n \exp(-\Delta E_n/kT)} \quad (16)$$

where $i = x, y, z$ and where n sums over all thermally accessible states. If only one spin multiplet is thermally accessible, $\langle S_i \rangle_{\text{th}}$ is proportional to $g_i B_i S(S+1)/3kT$ for $kT \gg \Delta E_n$ and thus follows the temperature dependence of the magnetic susceptibility.

In the slow fluctuation limit, which prevails for most Fe(III) compounds for $T < 10$ K, $\langle \mathbf{S} \rangle$ is computed separately for each thermally populated level and thus each level contributes its own Mössbauer spectrum with an intensity according to the Boltzmann factor that determines the population of the level [Fig. 5(a-c)].

At intermediate fluctuation rates, the spectra are quite complex and difficult to analyze unless one knows some of the A values and quadrupolar parameters from studies at very low temperatures. In strong applied magnetic fields, $B > 5$ T, and at temperatures around $T = 1.5$ K, achieved by pumping on the liquid helium bath, one can usually work under conditions where only the lowest level is measurably populated. It follows from Eq. (16) that $\langle S_i \rangle_{\text{th}} = \langle \psi | S_i | \psi \rangle$, where $|\psi\rangle$ designates the ground state.

A. Example of a Mössbauer Spectrum for a High-Spin Iron(III) Center

Many well-analyzed Mössbauer spectra of high-spin iron(III) compounds have been published. Nevertheless, here we will discuss a fictitious compound, because this will allow us to adjust the parameters in such a way that we can see the crucial features of the Mössbauer spectra of high-spin Fe(III) in one example. Our compound of interest exhibits a weak EPR resonance at $g = 9.7$ and an intense derivation-type signal at $g = 4.3$. The diagram of Figure 4 (plus a bit familiarity with the shapes of EPR spectra, see Chapter 3) informs us that these resonances belong to an $S = \frac{5}{2}$ system with rhombicity $E/D = \frac{1}{3}$. Let us refer to the three Kramers doublets as the lower, middle ($g = 4.3$), and upper doublet (see Fig. 4).

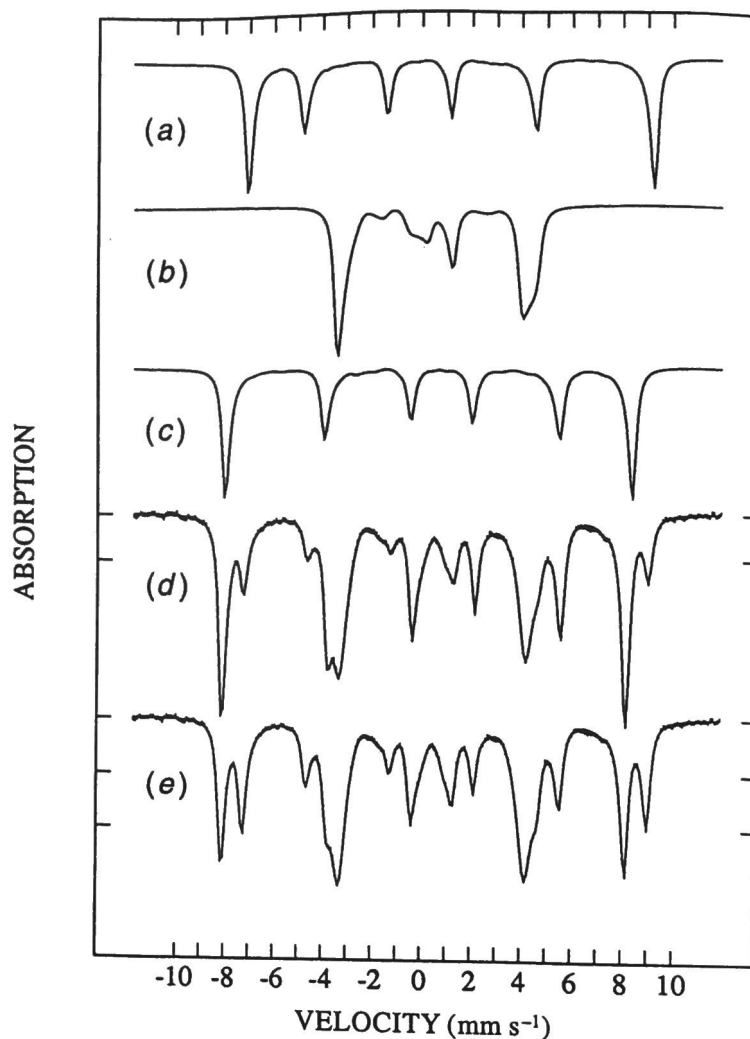


Figure 5

Mössbauer spectra of a high-spin iron(III) system with $E/D = \frac{1}{3}$. The “experimental” spectra shown in (d) and (e) were computed (and then endowed with random noise) with the following parameter set. $D = 0.5 \text{ cm}^{-1}$, $E/D = \frac{1}{3}$, $g_0 = 2.0$, $A_0 = -29 \text{ MHz}$, $\Delta E_Q = 1.0 \text{ mm s}^{-1}$, $\eta = 1$, and $\delta = 0.5 \text{ mm s}^{-1}$, parallel field of $H = 60 \text{ mT}$, $T = 4.2 \text{ K}$ for (d) and $T = 15 \text{ K}$ for (e). It is assumed that the electronic spin relaxation rate is slow so that each of the three Kramers doublets produces its own Mössbauer spectrum. The solid curves in A–C give the contributions of each doublet.

For $E/D = \frac{1}{3}$ the lower and upper doublets are uniaxial, whereas the middle doublet is magnetically isotropic. For $D > 0$ the lower doublet has an easy axis of magnetization along y ($g_y = 9.7$); the upper doublet, on the other hand, has the easy axis along z . Thus, for the ground doublet B_{int} will be directed along the molecular y axis (y is defined by the zfs). Because of relations (15), we expect the magnetic splittings of the Mössbauer spectra of the upper and lower doublets to be the same. The middle doublet should exhibit a splitting that is reduced by $4.3/9.7$ relative that of the ground doublet. Figures 5(d and e) show computer-generated spectra “measured” at $T = 4.2$ and 15 K , respectively. In order to make them look more like real data, we have added some random noise to the

baseline. The spectra in Figures 5(A–C) show the contributions of the lower doublet (c), of the middle doublet in parallel field (b), and of the upper doublet (a).

The Mössbauer spectra of the lower and upper doublets are readily identified by inspection of the data of Figure 5(d). At 4.2 K, the population of the upper doublet is significantly less than that of the ground doublet; the intensity ratio of the spectral components gives the Boltzmann factor and thus, with E/D known, the zfs parameter D . In our example, the spectra of the upper and lower doublets have the same magnetic hyperfine splittings. If one would observe that these splittings differ, and EPR would suggest that E/D is exactly $\frac{1}{3}$, the assumption of an isotropic magnetic hyperfine interaction, A_0 , would not be justified. Note that the internal magnetic field for the lower doublet depends on $\langle S_y \rangle A_0$, whereas that of the upper doublet depends on $\langle S_z \rangle A_0$. For $E/D = 1/3$, we have $|\langle S_z \rangle|_{\text{upper doublet}} = |\langle S_y \rangle|_{\text{lower doublet}} = 9.7/4$. Thus, if the magnetic hyperfine splittings differ, it follows that the magnetic hyperfine interaction in Eq. (13) is not isotropic and that $A_{0z} \neq A_{0y}$. Some spectra are so well defined that 2% differences between A_y and A_z are readily determined. Despite the identical magnetic splittings the lines of the spectra of the upper and lower Kramers doublets do not overlap. Rather, the outermost lines of the spectrum of the lower doublet are shifted to the left while those belonging to the upper doublet are shifted in the opposite direction. These shifts are caused by quadrupole interactions. For high-spin iron(III) compounds the magnetic interactions are generally much larger than the quadrupole splittings, and thus only the component of $\mathbf{V}$ along $\mathbf{B}_{\text{int}}$ matters. For our compound, the ground-state spectrum measures V_{yy} ; the shift pattern (see also Fig. 2) shows that $V_{yy} < 0$. From the spectrum of the upper doublet, we infer $V_{zz} > 0$. Closer inspection reveals that $eQV_{zz}/2 = -eQV_{yy}/2 = 0.86 \text{ mm s}^{-1}$. Since $\mathbf{V}$ is traceless, it follows that $V_{xx} = 0$ and thus $\Delta E_Q = 1.0 \text{ mm s}^{-1}$ and $\eta = 1$.^a

The magnitude of A_0 , but not its sign, can be determined from the magnetic splittings of the spectra of each of the three doublets. These splittings depends on $|B_{\text{eff}}|$. For the two levels of a Kramers doublet, $\langle S \rangle_{\text{spin up}} = -\langle S \rangle_{\text{spin down}}$, and thus both levels yield the same Mössbauer spectrum in weak applied fields. In strong fields, say for $B > 3.0 \text{ T}$, only the lowest level is appreciably populated at $T \leq 4.2 \text{ K}$, and since $\langle S_i \rangle < 0$ for the lowest level the sign of B_{int} , and thus the sign of A_0 , can be obtained by comparing $|B_{\text{eff}}| = |B_{\text{int}} + B|$ in strong and weak fields. Finally, by evaluating the centroid of the spectra of Figures 5(d and e) the isomer shift can be obtained. The spectra shown are plotted relative to the centroid of Fe metal, using $\delta = 0.5 \text{ mm s}^{-1}$.

We have also measured a spectrum of our fictitious compound at $T = 250 \text{ K}$. The spectrum consists of a quadrupole doublet (fast electronic spin relaxation!) with $\Delta E_Q = 1.0 \text{ mm s}^{-1}$. The observation that the same ΔE_Q is observed at $T = 4.2$ and 250 K is in accord with the electronic properties for high-spin iron(III) compounds. The quadrupole splitting would exhibit a temperature dependence if other *orbital* states become thermally populated. But the lowest

^aThe three Kramers doublets are sublevels of a spin multiplet. All six levels of the sextet belong to the same orbital state and thus the three doublets have the same EFG.

excited states of high-spin iron(III) compounds with weak ligand fields are spin quartets located at least 2000 cm^{-1} above the ground multiplet (1 cm^{-1} corresponds to 1.44 K in units of kT); thus the observed temperature-independent ΔE_Q .

The situation just described is frequently encountered in the literature; there are many iron(III) compounds, inorganic, bioinorganic, and biochemical that exhibit a $g = 4.3$ EPR signal. For further examples, we refer the reader to the literature: studies of the protein rubredoxin,⁸ the enzyme protocatechuate 3,4-dioxygenase,⁹ and an $\text{Fe(III)} \cdot \text{EDTA}$, EDTA-ethylenediaminetetraacetic acid, complex.¹⁰

Given the EPR information, an experienced graduate student with a good background in Mössbauer spectroscopy can analyze spectra such as those of Figure 4 in less than 1 h. Analyses, however, become challenging when one deals with clusters that contain three, four, six, or eight iron sites. We have struggled with such cases in our laboratory and our efforts have been facilitated by the knowledge of some of the principles discussed above.

IV. Exchange Coupled High-Spin Fe(II)–Fe(III) Complexes

A. Background

Two paramagnetic metal ions separated by intervening diamagnetic atoms, or group of atoms, can interact with each other. Although the fundamental interactions that give rise to this coupling involve the orbital coordinates of the electrons, strong restrictions are imposed on the spins of the two metal ions, because the wave functions must be antisymmetric with respect to the exchange of electrons. In the framework of a spin Hamiltonian, the interaction between the two metal sites, a and b , can be described by

$$\mathcal{H}_{\text{ex}} = J\mathbf{S}_a \cdot \mathbf{S}_b \quad (17)$$

where $\mathbf{S}_a$ and $\mathbf{S}_b$ are the spin operators of the two metal sites. The constant J measures the strength of the interaction. It conveys information about the nature of the bridging ligands and the geometry of the coordination environments of the metals. In many cases, the exchange interaction is much stronger than all other terms in the spin Hamiltonian and thus it is prudent to determine the energies and eigenstates of $\mathcal{H}_{\text{ex}}$ first. The exchange term has the same mathematical structure as the more familiar spin–orbit interaction for atoms, $\lambda\mathbf{L} \cdot \mathbf{S}$, and the problem is solved in the same way, namely, by solving Eq. (17) in the coupled representation obtained by combining the site spins $\mathbf{S}_a$ and $\mathbf{S}_b$ to a system spin $\mathbf{S}$, $\mathbf{S}_a + \mathbf{S}_b = \mathbf{S}$. Since $(\mathbf{S}_a + \mathbf{S}_b)^2 = \mathbf{S}_a^2 + \mathbf{S}_b^2 + 2\mathbf{S}_a \cdot \mathbf{S}_b = \mathbf{S}^2$ we write

$$\mathcal{H}_{\text{ex}} = (J/2)(\mathbf{S}^2 - \mathbf{S}_a^2 - \mathbf{S}_b^2) \quad (18)$$

which yields for the energies

$$E(S) = (J/2)[S(S+1) - S_a(S_a+1) - S_b(S_b+1)] \quad (19)$$

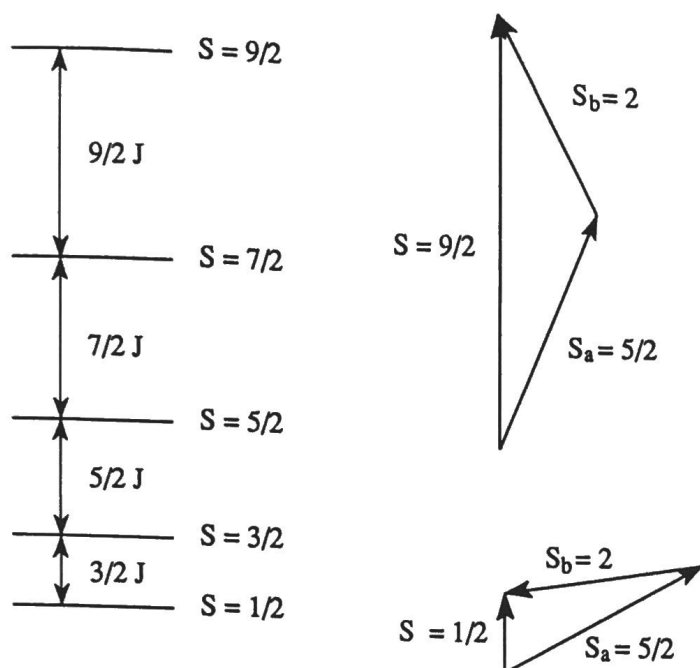


Figure 6

Spin ladder resulting from Eq. (19) for isotropic coupling of two spins $S_a = \frac{5}{2}$ and $S_b = 2$. Also shown are the arrangements of the spin vectors for the $S = \frac{1}{2}$ and $S = \frac{9}{2}$ system states.

The allowed values of S are restricted to $|S_a - S_b| \leq S \leq |S_a + S_b|$. For fixed values of S_a and S_b , we obtain a spin ladder with a level spacing according to the Landé interval rule. For $J > 0$ the ground state has the minimum allowed S and the coupling is called antiferromagnetic; for ferromagnetic coupling ($J < 0$) the level scheme is reversed. Figure 6 shows a level diagram resulting from antiferromagnetic coupling of two spins $S_a = \frac{5}{2}$ and $S_b = 2$, appropriate for a high-spin iron(III) and high-spin iron(II) ion, respectively. Also shown are the arrangements of the spin vectors for the $S = \frac{1}{2}$ and $S = \frac{9}{2}$ system states. A spin Hamiltonian for describing the Mössbauer spectra of such a dinuclear pair of ions can be written as

$$\mathcal{H} = JS_a \cdot S_b + \mathcal{H}_e(a) + \mathcal{H}_e(b) + \mathcal{H}_{hf}(a) + \mathcal{H}_{hf}(b) \quad (20)$$

with

$$\mathcal{H}_e(i) = S_i \cdot D_i \cdot S_i + \beta S_i \cdot g_i \cdot B \quad (20a)$$

and

$$\mathcal{H}_{hf}(i) = S_i \cdot A_i \cdot I_i - g_n \beta_n B \cdot I_i + \mathcal{H}_Q(i) \quad (20b)$$

where $i = a, b$. For arbitrary J , this spin Hamiltonian is immensely complex. Considering that Eqs. (20) contain eight tensors, the situation seems rather hopeless. However, under certain circumstances the complexity is reduced con-

siderably. First, $\mathbf{g}$ and $\mathbf{A}$ of the high-spin iron(III) ion are isotropic. Second, for strong antiferromagnetic coupling ($J \gg zfs$) we need to consider only the $S = \frac{1}{2}$ manifold. We will discuss this particular case in some detail.

If $\mathcal{H}_{ex}$ is large compared to all other interactions in Eq. (20), we can treat $\mathcal{H}_e(i)$ and $\mathcal{H}_{hf}(i)$ as perturbations, that is, we evaluate their matrix elements within the coupled representation, $|S, M_s\rangle$, ignoring elements connecting different multiplets S . By using the celebrated Wigner-Eckart theorem, we can obtain for the $S = \frac{1}{2}$ manifold a spin Hamiltonian for which the individual spin operators $\mathbf{S}_a$ and $\mathbf{S}_b$ of Eqs. (20) have been replaced by $\mathbf{S}$. The reader will find a detailed account in the book by Bencini and Gatteschi.¹¹ In short, the following steps are involved. First, since the zfs are described by (spherical) tensors of second rank, their matrix elements vanish within the $S = \frac{1}{2}$ manifold. Second, the matrix elements of the electronic Zeeman interactions can be cast into a different form by using

$$\langle S = \frac{1}{2}, M_s | \mathbf{S}_a | S = \frac{1}{2}, M_s' \rangle = \frac{7}{3} \langle S = \frac{1}{2}, M_s | \mathbf{S} | S = \frac{1}{2}, M_s' \rangle$$

and

$$\langle S = \frac{1}{2}, M_s | \mathbf{S}_b | S = \frac{1}{2}, M_s' \rangle = -\frac{4}{3} \langle S = \frac{1}{2}, M_s | \mathbf{S} | S = \frac{1}{2}, M_s' \rangle$$

Thus, we can replace, for calculations within the $S = \frac{1}{2}$ manifold, the electronic Zeeman terms of Eq. (20a) $\beta \mathbf{S}_a \cdot \mathbf{g}_a \cdot \mathbf{B} + \beta \mathbf{S}_b \cdot \mathbf{g}_b \cdot \mathbf{B}$ with

$$\beta \mathbf{S} \cdot \left(\frac{7}{3} \mathbf{g}_a - \frac{4}{3} \mathbf{g}_b \right) \cdot \mathbf{B} = \beta \mathbf{S} \cdot \mathbf{g} \cdot \mathbf{B} \quad (21)$$

where

$$\mathbf{g} = \frac{7}{3} \mathbf{g}_a - \frac{4}{3} \mathbf{g}_b$$

In frozen solution or polycrystalline samples, the principal components of $\mathbf{g}$ are determined from EPR experiments. The same equivalence factors $\frac{7}{3}$ and $-\frac{4}{3}$ come into play when $\mathbf{S}_a$ and $\mathbf{S}_b$ of the magnetic hyperfine tensors are replaced by $\mathbf{S}$ (In the semiclassical vector coupling model these factors arise when $\mathbf{S}_a$ and $\mathbf{S}_b$ are projected onto the direction of the system spin $\mathbf{S}$). Thus, in the spin $S = \frac{1}{2}$ manifold, the spin Hamiltonian of the coupled pair takes the form

$$\begin{aligned} \mathcal{H} = & \beta \mathbf{S} \cdot \mathbf{g} \cdot \mathbf{B} + [\mathbf{S} \cdot \mathbf{A}_a^c \cdot \mathbf{I}_a - g_n \beta_n \mathbf{B} \cdot \mathbf{I}_a + \mathcal{H}_Q(a)] \\ & + [\mathbf{S} \cdot \mathbf{A}_b^c \cdot \mathbf{I}_b - g_n \beta_n \mathbf{B} \cdot \mathbf{I}_b + \mathcal{H}_Q(b)] \end{aligned} \quad (22)$$

where we have replaced the $\mathbf{A}$ tensors of the uncoupled representation by those of the coupled system.

$$\mathbf{A}_a^c = \frac{7}{3} \mathbf{A}_a \quad \text{and} \quad \mathbf{A}_b^c = -\frac{4}{3} \mathbf{A}_b \quad (23)$$

Viewing Eq. (22) from a standpoint of the Mössbauer nuclei at sites a and b ,

we see that the spectrum of each site is described by

$$\mathcal{H}(i) = \beta \mathbf{S} \cdot \mathbf{g} \cdot \mathbf{B} + \mathbf{S} \cdot \mathbf{A}_i^c \cdot \mathbf{I}_i - g_n \beta_n \mathbf{B} \cdot \mathbf{I}_i + \mathcal{H}_Q(i) \quad (24)$$

Thus *both* iron sites share the same Zeeman term, and *one* spin thus determines the distribution of *two* internal magnetic fields.

B. Example of Antiferromagnetic Coupling: Fe_2S_2 Clusters

As an example of a spin coupled $\text{Fe(II)}\text{--Fe(III)}$ cluster, we will discuss some studies of a protein that contains an iron–sulfur cluster with an Fe_2S_2 core. This type of cluster has been studied intensively with a variety of spectroscopic techniques. These studies have established that the cluster contains two iron sites bridged by two sulfide ligands, and that each iron is coordinated additionally to two thiolate ligands provided by cysteine residues. The spectroscopic studies have also suggested that each iron is surrounded by a tetrahedral arrangement of ligands. These ideas were confirmed by subsequent X-ray crystallographic studies.¹²

Figures 7–9 show Mössbauer spectra of MMO reductase, a 40-kDa component protein of the methane monooxygenase (MMO) complex of *Methylosinus trichosporium*.¹³ Next, we discuss a few features of these spectra,¹⁴ emphasizing

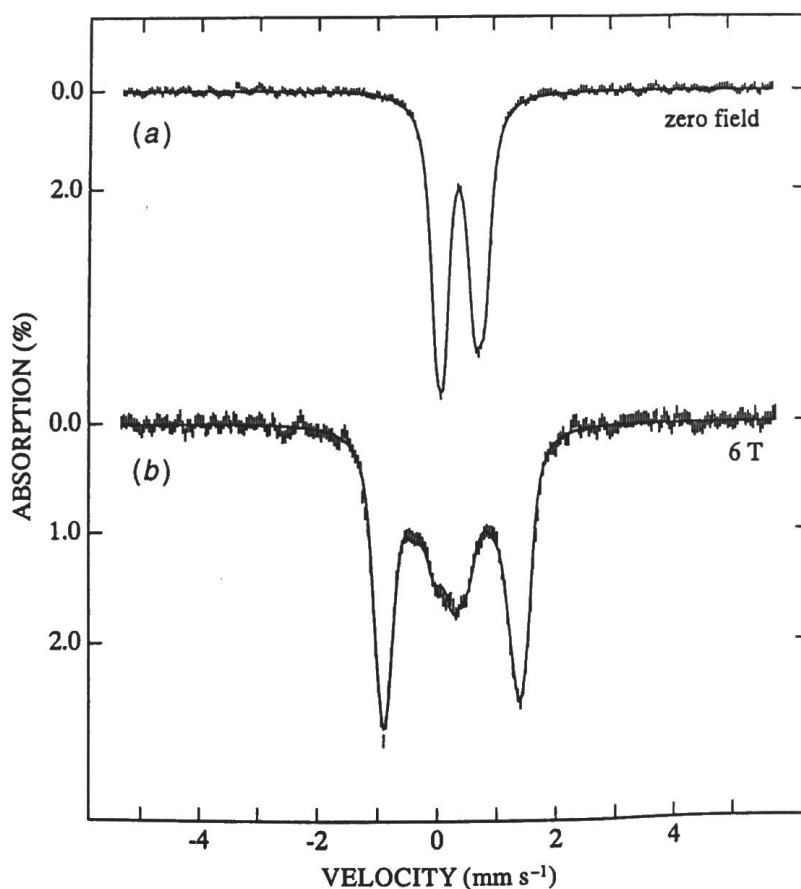


Figure 7

Mössbauer spectra of oxidized $[\text{Fe}^{\text{III}}\text{--Fe}^{\text{III}}]$ MMO reductase recorded at 4.2 K in zero field (a) and in a parallel field of 6.0 T (b). Solid lines are theoretical curves calculated with the assumption that $S = 0$. The shape of the 6.0 T spectrum indicates that $\Delta E_Q > 0$ for both sites of the cluster. [Adapted from Fox et al.¹⁴]

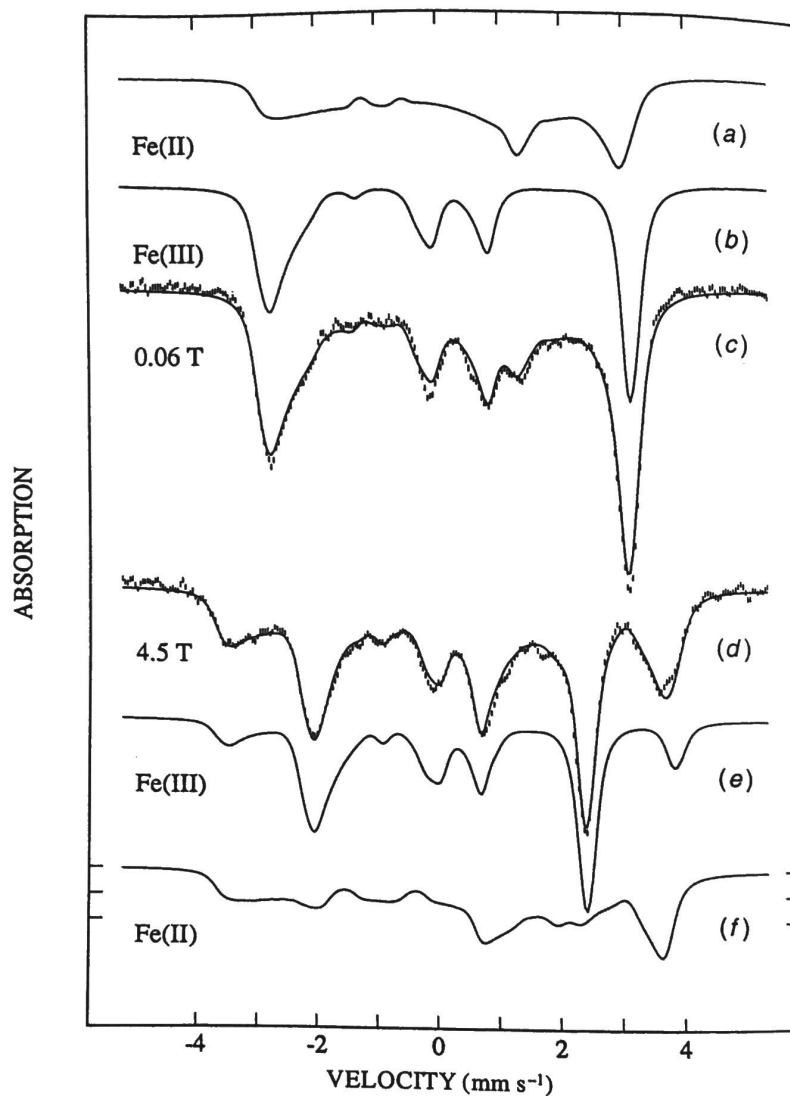


Figure 8

Mössbauer spectra of *reduced* $[\text{Fe}^{\text{II}}\text{--Fe}^{\text{III}}]$ MMO reductase recorded at 4.2 K in parallel field of 50 mT (c) and 4.5 T (d). The solid lines are theoretical spectra generated from Eq. (22) with the following parameters. The Fe(III) site: A_a^c (MHz) = $(-53, -49, -43)$, $\Delta E_Q = +0.59 \text{ mm s}^{-1}$, $\eta = 0$, $\delta = 0.31 \text{ mm s}^{-1}$. The Fe(II) site: A_b^c (MHz) = $(+14, +15, +37)$, $\Delta E_Q = -3.01 \text{ mm s}^{-1}$, $\eta = 0.9$, $\delta = 0.65 \text{ mm s}^{-1}$. The curves in (a, b, e, and f) show the spectra of the two sites separately. [Adapted from inconsistent Fox et al.¹⁴]

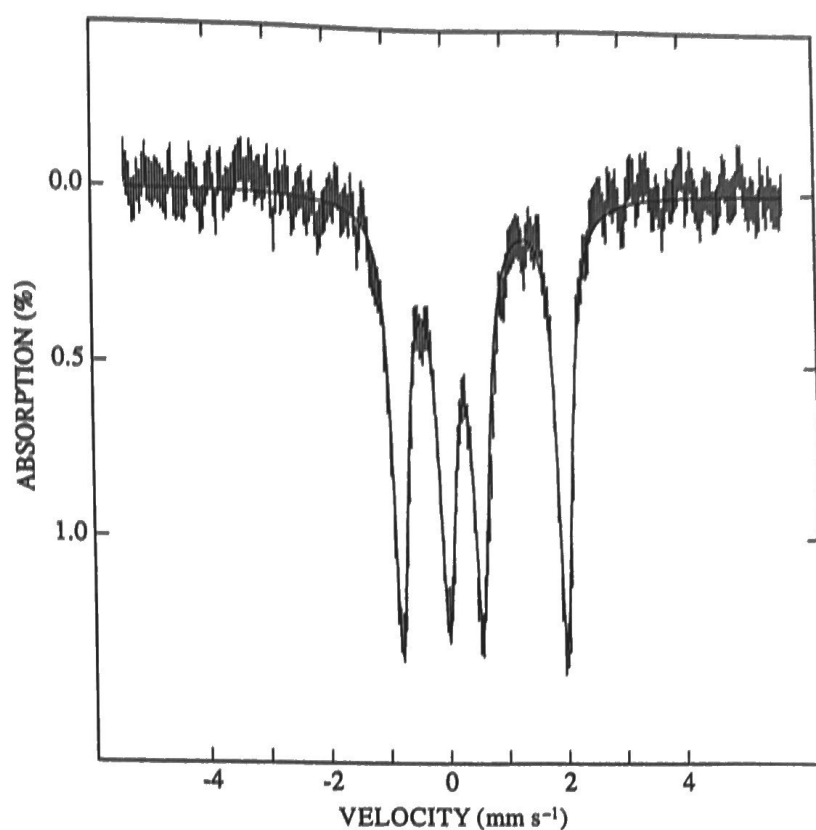


Figure 9

Mössbauer spectra of reduced MMO reductase recorded at $T = 200$ K in zero magnetic field. The theoretical curve is the result of least-squares fitting two quadrupole doublets to the data. The two innermost lines belong to the Fe(III) site. [Adapted from Fox et al.¹⁴]

the utility of Mössbauer spectroscopy for the elucidation of the electronic structure of clusters in general.

1. The Fe_2S_2 cluster of MMO reductase can exist in two oxidation states. Two Mössbauer spectra, recorded at $T = 4.2$ K, of the *oxidized* $\text{Fe}^{\text{III}}\text{--Fe}^{\text{III}}$ protein are shown in Figure 7. The spectrum of Figure 7(a), recorded in zero magnetic field, consists of a superposition of two very similar quadrupole doublets with $\Delta E_Q(\text{site 1}) = 0.81 \text{ mm s}^{-1}$, $\delta(1) = 0.29 \text{ mm s}^{-1}$, and $\Delta E_Q(2) = 0.51 \text{ mm s}^{-1}$, $\delta(2) = 0.25 \text{ mm s}^{-1}$. Figure 7(b) shows a spectrum recorded in a parallel applied field of $B = 6.0$ T; the solid line is a theoretical curve generated by computer simulation under the assumption that the cluster is *diamagnetic*. Recall that $B_{\text{int}} = 0$ for a diamagnetic ($S = 0$) compound. The observed magnetic splittings are entirely attributable to the *applied* field. The values for ΔE_Q and δ are typical for high-spin iron(III) with tetrahedral sulfur coordination. High-spin iron(III) is, however, not diamagnetic. The observed diamagnetism can be explained by assuming antiferromagnetic coupling of two $S = \frac{5}{2}$ spins to a resultant dimer spin $S = 0$.
2. Full reduction of the cluster is achieved by a one-electron reduction. In the *oxidized* form, the cluster is EPR silent. Electron paramagnetic resonance

studies of the *reduced* $\text{Fe}^{\text{II}}\text{--Fe}^{\text{III}}$ sample reveal a system with $S = \frac{1}{2}$ and g values at $g_x = 1.86$, $g_y = 1.94$, and $g_z = 2.06$. Integration of an EPR signal allows one to determine the spin concentration of the sample; the sample discussed here yielded 1.06 ± 0.1 spins per 2 Fe.

3. Consider the 4.2 K Mössbauer spectrum of the *reduced* protein, shown in Figure 8(c), and compare the spectrum with that of Figure 7(a). It is quite apparent that all the iron of the reduced sample belongs to species exhibiting magnetic hyperfine structure. Thus, the addition of *one* electron has transformed *both* iron atoms from a non-Kramers system (complex with an even number of electrons; $S = \text{integer or zero}$) to a Kramers system (complex with an odd number of electrons; $S = \text{half-integer}$). One conclusion is inescapable: The electron that entered the protein upon reduction must be shared by both iron sites, that is, the two sites must be covalently linked.
4. The Mössbauer spectrum of the reduced reductase of Figure 9 was recorded at $T = 200$ K under conditions where the electronic spin relaxes fast on the Mössbauer time scale. The spectrum consists of two nested quadrupole doublets. The inner doublet has $\Delta E_Q(a) = 0.58 \text{ mm s}^{-1}$ and $\delta(a) = 0.26 \text{ mm s}^{-1}$, whereas the outer doublet has $\Delta E_Q(b) = 2.80 \text{ mm s}^{-1}$ and $\delta(b) = 0.57 \text{ mm s}^{-1}$ (isomer shifts are temperature dependent because of the so-called second-order Doppler shift¹; for comparison with the shifts of the oxidized protein we use the shifts observed at 4.2 K, $\delta(a) = 0.31 \text{ mm s}^{-1}$ and $\delta(b) = 0.65 \text{ mm s}^{-1}$). The parameters of site (b) are typical of those reported for high-spin Fe(II) in a tetrahedral environment of sulfur ligands. The parameters of site (a), on the other hand, are still those of a high-spin iron(III) site. Thus, the reduced cluster consists of a localized Fe(III) and a localized Fe(II) site.
5. From the preceding discussion, it appears plausible that the reduced Fe_2S_2 clusters consists of an antiferromagnetically coupled pair of Fe(II) and Fe(III) ions. Thus, we would anticipate that the 4.2 K Mössbauer spectra need to be evaluated with Eq. (22). Note that the coupling model predicts a sign reversal for the A tensor of the iron(II) site [see Eq. (23)]. It is well established from Mössbauer studies of mononuclear iron(III) and iron(II) compounds with tetrahedral sulfur coordination that the components of the A tensors are negative. Equation (23) predicts the negative components for A_a^c and *positive* components for A_b^c .

A comparison of the features of the spectra of Figure 8(c and d) confirms this prediction. The essential arguments for determining the sign of the A tensors are as follows. In an applied field of 4.5 T, the Zeeman splitting of the $S = \frac{1}{2}$ doublet is such that at $T = 4.2$ K 81% of the molecules are in the spin-down state for which $\langle S_z \rangle = -\frac{1}{2}$. By measuring the sign of B_{int} the sign of A tensor components can be determined [see Eq. (9)]. As discussed above, the magnetic splitting of a Mössbauer spectrum is determined by $|B_{\text{eff}}| = |B_{\text{int}} + B|$. Thus, depending on the sign of B_{int} the magnetic splitting will either increase or decrease as the applied field is increased. A comparison of the spectra shown in Figure 8(c and d) shows

that one site has $B_{\text{int}} > 0$, while the other site has $B_{\text{int}} < 0$ (cf. also the theoretical spectra for both sites). Which spectrum belongs to the iron(III) site? This question is answered by computer simulations that show that unacceptable fits result if the iron(III) site has $B_{\text{int}} > 0$ [recall that the iron(III) site has a distinctively smaller ΔE_Q and is in this respect quite different from the iron(II) site].

It turns out that the A tensor of the iron(III) site is slightly anisotropic. [In part, this is so because J is not infinitely large and Eq. (22) is therefore only approximately correct.¹⁴] If we take the average of the x , y , and z components, $A_a^c(\text{av}) = -48.3$ MHz we obtain with Eq. (23) $A_a = -20.7$ MHz. This value is in excellent agreement with the value reported for the single Fe(III) site of rubredoxin, $A = -20$ MHz, which has tetrahedral sulfur coordination.⁸

6. Much more can be learned from the parameter set listed in the caption of Figure 8. For instance, consideration of the ligand fields in conjunction with the coupling model explains why g_x and g_y are less than 2; the spin coupling model originally proposed by Gibson et al.¹⁵ has been exceedingly successful. For further details on the pioneering work on the Mössbauer spectra of Fe_2S_2 clusters, the reader is referred to the literature.^{16,17} The lessons learned from the studies of Fe_2S_2 clusters have been successfully applied to gain an understanding of the electronic structure of the oxo- and hydroxo-bridged dinuclear clusters of nonheme diiron proteins, such as MMO hydroxylase.¹⁴ The EPR and Mössbauer spectra of these proteins are a bit more complex than those of the Fe_2S_2 clusters, primarily because their J values are substantially smaller. Because the level spacings between the multiplets of the spin coupled system are smaller for iron-oxo proteins, the zfs terms of Eq. (20a) can effectively mix the excited $S = \frac{3}{2}$ multiplet with the $S = \frac{1}{2}$ ground doublet. Consequently, Eqs. (21) and (23) need to be modified by terms that depend on J and the zfs parameters.^{14,18,19} This dependence allows one to determine J from an analysis of the EPR and Mössbauer spectra of the ground state. Debrunner and co-workers¹⁸ published a pioneering study of the enzyme purple acid phosphatase.

C. Example of Ferromagnetic Coupling

In this section, we consider briefly the Mössbauer spectra of a ferromagnetically coupled $\text{Fe}^{\text{II}}\text{--Fe}^{\text{III}}$ complex. Starting again from Eq. (20), now for $J < 0$, and still using $\beta H \ll |zfs|$, we obtain a ground multiplet with $S = \frac{9}{2}$. Since $S > \frac{1}{2}$, the zfs terms of Eq. (20a) need to be considered. By using the same methods as described above (see also Bencini and Gatteschi¹¹), we obtain an effective spin Hamiltonian for the $S = \frac{9}{2}$ multiplet

$$\mathcal{H} = \mathcal{H}_e + \mathcal{H}_{\text{hf}} \quad (25)$$

with

$$\mathcal{H}_e = \mathbf{S} \cdot \mathbf{D} \cdot \mathbf{S} + \beta \mathbf{S} \cdot \mathbf{g} \cdot \mathbf{B} \quad (25a)$$

$$\mathcal{H}_{\text{hf}} = [\mathbf{S} \cdot \mathbf{A}_a^c \cdot \mathbf{I}_a - g_n \beta_n \mathcal{H} \cdot \mathbf{I}_a + \mathcal{H}_Q(a)] \\ + [\mathbf{S} \cdot \mathbf{A}_b^c \cdot \mathbf{I}_b - g_n \beta_n \mathcal{H} \cdot \mathbf{I}_b + \mathcal{H}_Q(b)] \quad (25b)$$

$$\mathbf{g} = \frac{5}{9} \mathbf{g}_a + \frac{4}{9} \mathbf{g}_b, \quad (25c)$$

$$\mathbf{D} = \frac{5}{18} \mathbf{D}_a + \frac{3}{18} \mathbf{D}_b \quad (25d)$$

$$\mathbf{A}_a^c = \frac{5}{9} \mathbf{A}_a \quad \text{and} \quad \mathbf{A}_b^c = \frac{4}{9} \mathbf{A}_b \quad (25e)$$

Note that no sign reversal occurs when the A tensor of the iron(II) site, $\mathbf{A}_b$, is referred to the coupled system. For $\beta B \ll |D|$ we can proceed as for the $S = \frac{5}{2}$ multiplet discussed above and consider each Kramers doublet separately.

As an example, we consider the Mössbauer spectra of a dinuclear complex with the trianionic dinucleating ligand salmp [bis(salicylideneamino)-2-methylphenolate(3-)], $(\text{Et}_4\text{N})[\text{Fe}_2(\text{salmp})_2]^{2-}$; the structure of the compound is indicated in Figure 10. From these spectra we can draw the following conclusions.

1. At $T = 100$ K we observe two quadrupole doublets with a 1 : 1 intensity ratio (data not shown). Doublet (a) has parameters typical of high-spin iron(III) in an octahedral environment of N, O ligands, with $\Delta E_Q(a) = 0.98 \text{ mm s}^{-1}$ and $\delta(a) = 0.60 \text{ mm s}^{-1}$. Doublet (b), with $\Delta E_Q(b) = 2.29 \text{ mm s}^{-1}$ and $\delta(b) = 1.13 \text{ mm s}^{-1}$, reflects a high-spin iron(II) site.
2. Figure 11 shows a Mössbauer spectrum recorded at $T = 1.5$ K (for $3 \text{ K} \leq T \leq 50 \text{ K}$ the spectra are poorly resolved due to relaxation effects.) The intensities of this exceptionally well-resolved spectrum are the same whether the 50-mT field is applied parallel or perpendicular to the observed γ radiation. As discussed above, this situation implies that the electronic ground state is a Kramers doublet with uniaxial magnetic

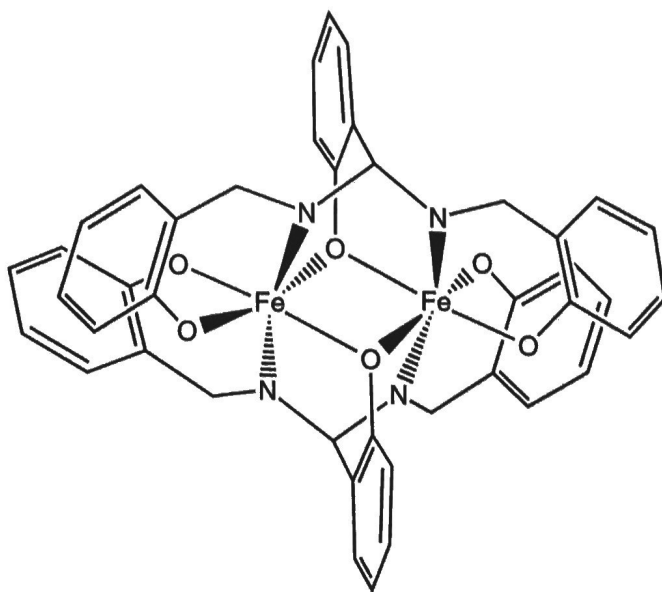


Figure 10
Schematic structure of $[\text{Fe}_2(\text{salmp})_2]^{2-}$.

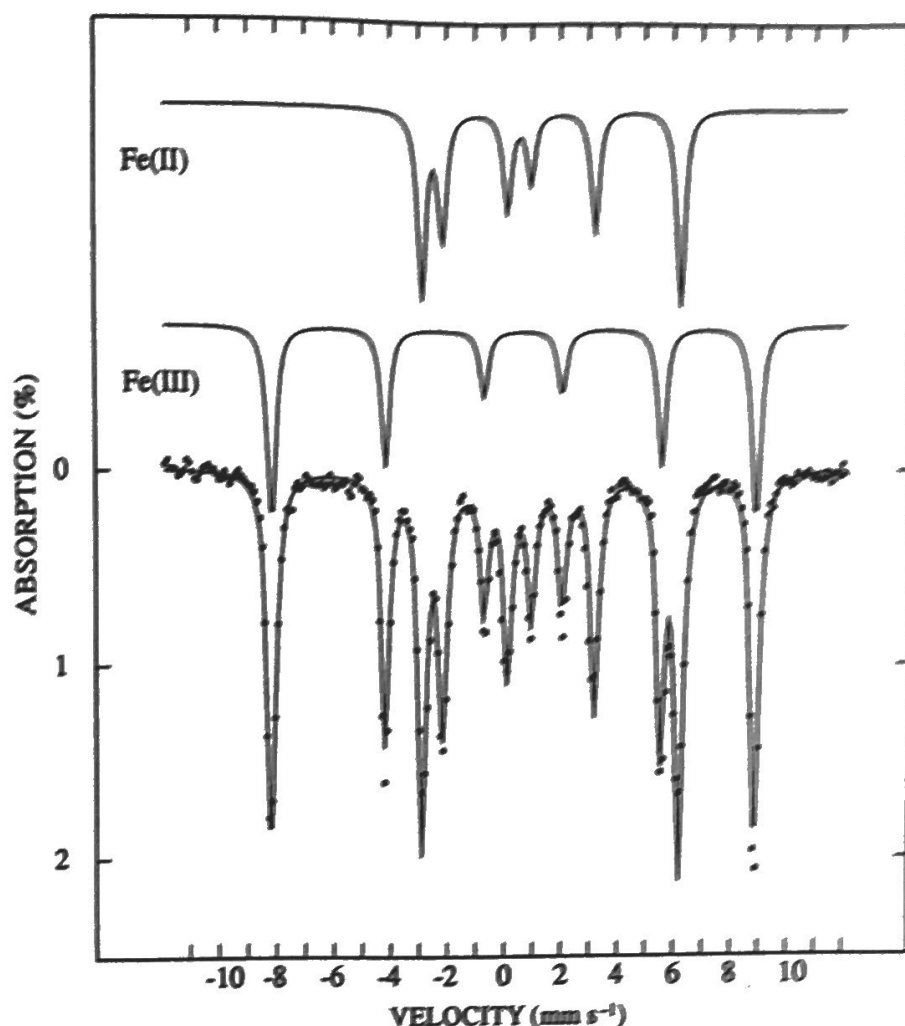


Figure 11

Mössbauer spectrum of polycrystalline $(\text{Et}_4\text{N})[\text{Fe}_2(\text{salmp})_2]$ recorded at 1.5 K. The spectrum results from the lowest Kramers doublet of an $S = \frac{9}{2}$ multiplet. The theoretical curves were generated from Eq. (25); the parameters used are given in Surerus et al.²¹ [Adapted from Surerus et al.²¹]

properties. For a pair of high-spin iron(III) and iron(II) ions, the $S = \frac{1}{2}$ system state cannot have an uniaxial (or highly anisotropic) g tensor. The g tensor of the high-spin Fe(III) is nearly isotropic, $g_0 = 2.0$, and the g values of high-spin Fe(II) are slightly above $g = 2$, with anisotropies smaller than 15%; the system g tensor, computed with Eq. (21), therefore cannot be uniaxial. Thus, we can conclude from the 1.5 K spectrum that the ground multiplet must be the $S = \frac{9}{2}$ manifold that results from ferromagnetic coupling. This conclusion is in accord with magnetic susceptibility studies²¹ and subsequent EPR studies, which confirm that the ground multiplet has $S = \frac{9}{2}$. Resonances were observed for the first and second excited-state Kramers doublet of an $S = \frac{9}{2}$ system with $D \approx 2.5 \text{ cm}^{-1}$ and $E/D \approx 0.25$. These parameters produce a ground Kramers doublet with $g_x \approx g_z \approx 0$ and $g_y \approx 17.5$. For $D \approx 2.5 \text{ cm}^{-1}$ and $E/D = 0.25$ the first excited Kramers doublet is at energy 14.9 cm^{-1} and thus not populated at the temperature the spectrum of Figure 10 was recorded.

3. With the known values for ΔE_Q and δ and the knowledge that B_{int} has to be along the y direction for both iron sites (they share the same electronic system), it is relatively straightforward to decompose the experimental spectrum of Figure 10 into an iron(III) and an iron(II) subspectrum. This decomposition yields for the iron(III) site $A_a^c = -16.1$ MHz, and using Eq. (25e) we obtain $A_a = -29$ MHz, which is typical for such a site. Since high-spin iron(II) A tensors are in general quite anisotropic and only the y component of B_{int} is measured here, a comparison with A tensors of high-spin iron(II) sites is not meaningful.

D. Double Exchange, a Coupling Mechanism in Delocalized Mixed-Valence Systems

In the two preceding examples, we have discussed dinuclear clusters with *localized* Fe(III) and Fe(II) sites. Valence localization was evident by the observation of *two* quadrupole doublets with values for ΔE_Q and δ typical for high-spin Fe(III) and Fe(II) sites. In a fully *delocalized* system, one would observe only one quadrupole doublet with values for ΔE_Q and δ , which are averages between those observed for localized sites. Formally, the two sites are in the $Fe^{2.5+}$ oxidation state. Recently, it has been shown that for *delocalized* systems the Heisenberg-Dirac-Van Vleck (HDVV) Hamiltonian $\mathcal{H}_{ex} = JS_a \cdot S_b$ needs to be augmented by a term that takes the delocalization into account. The new term, referred to as double exchange or spin-dependent delocalization, produces splittings that are linear in the system spin S , in contrast to the HDVV term, which yields the characteristic $S(S+1)$ dependence. For a dinuclear cluster with valence delocalization, one has to replace Eq. (19) with

$$E(S) = (J/2)[S(S+1) - S_a(S_a+1) - S_b(S_b+1)] \pm B(S + \frac{1}{2}) \quad (26)$$

where B measures the strength of the double exchange. For sufficiently large B , the ground state can thus have $S = \frac{9}{2}$ even if the HDVV coupling is *antiferromagnetic* ($J > 0$). Thus, without information from a Mössbauer study, one could easily mistake the situation for HDVV ferromagnetism ($J > 0$). Girerd and co-workers have introduced a spin Hamiltonian with a novel transfer operator that produces the correct energies of Eq. (26), and that can describe double exchange in more complicated system²²; Münck et al.²³ provides a relatively elementary account. To date, only one dinuclear complex exhibiting double exchange has been well characterized; Wieghardt and co-workers²⁴ synthesized an $Fe^{II}-Fe^{III}$ complex, which has an $S = \frac{9}{2}$ ground state and yields identical Mössbauer spectra for both sites. Inclusion of double exchange is also important for the description of the magnetic properties of clusters with Fe_3S_4 and Fe_4S_4 cores. The interested reader will find an illuminating discussion about the interplay of Heisenberg exchange, double exchange, and vibronic interactions in an article by Blondin et al.²⁵

E. An Example for Combined EPR and Mössbauer Studies

Much attention in metalloprotein research and in bioinorganic chemistry is being devoted to the elucidation of the structure and function of diiron proteins, a class that includes the enzymes methane monooxygenase, ribonucleotide reductase, and the purple acid phosphatases as well as the oxygen carrier hemerythrin.¹³ For our discussion, it is of interest that an iron(IV) intermediate has been proposed for the catalytic cycle of methane monooxygenase; Mössbauer studies have shown that this oxidation level is indeed attained.²⁶ The active sites of diiron proteins contain oxo (or hydroxo)-bridged dinuclear clusters, and much effort is under way to synthesize appropriate structural and functional models.

Que and co-workers²⁷⁻²⁹ characterized a number of formally $\text{Fe}^{\text{III}}\text{-Fe}^{\text{IV}}$ intermediates having the formulation $[\text{Fe}_2(\text{O})_2\text{L}_2]^{3+}$ derived from the reactions of (μ -oxo)-diiron(III) complexes $[\text{Fe}^{\text{III}}_2\text{O}(\text{L})_2\text{OH}(\text{H}_2\text{O})](\text{ClO}_4)_3$ with H_2O_2 (Fig. 12). For $\text{L} = \text{TPA}$, 5-Me₃-TPA, 5-Et₃-TPA [$\text{TPA} = \text{tris}(\text{pyridyl-2-methyl})\text{-amine}$], the intermediates have an $\text{Fe}_2(\mu\text{-O})_2$ core based on extended X-ray absorption fine structure (EXAFS), resonance Raman, and electrospray ionization

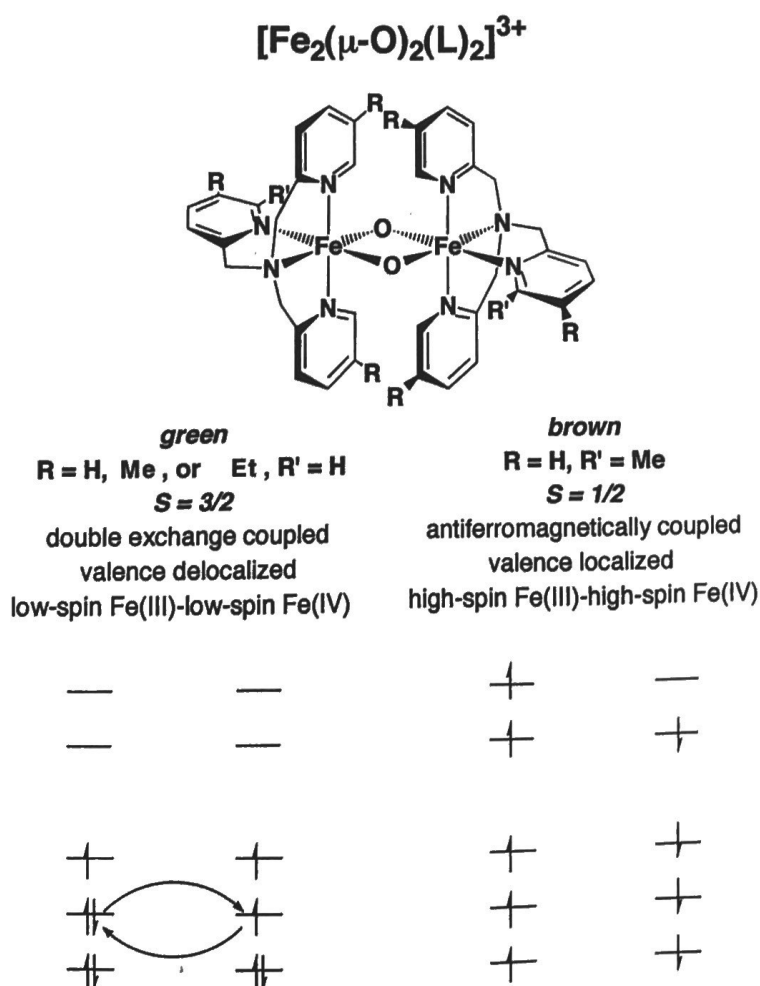


Figure 12

Proposed structures and spin coupling schemes for $[\text{Fe}_2\text{O}_2\text{L}_2]^{3+}$ complexes.

mass spectral data.^{27,28} The presence of the 5-alkyl substituents does not significantly affect the electronic properties of this core. The introduction of a 6-methyl substituent, that is, 6-Me-TPA, affords an intermediate with a similar formulation on the basis of its electrospray ionization mass spectrum but with dramatically different electronic structure.²⁹ Mössbauer spectroscopy has played a key role in elucidating the nature of these novel Fe^{III}–Fe^{IV} species.

For L = TPA, 5-Me₃-TPA, 5-Et₃-TPA, treatment of the diiron(III) starting material [Fe^{III}₂O(L)₂OH(H₂O)](ClO₄)₃ with H₂O₂ in MeCN affords a green (λ_{max} 614 nm) metastable intermediate at –40 °C. It exhibits a well-resolved EPR spectrum with g values at $g_x = 3.90$, $g_y = 4.45$, and $g_z = 2.01$. From our discussion of effective g values of Kramers doublets, we recognize these g values as those belonging to the $M = \pm \frac{1}{2}$ doublet of a system with $S = \frac{3}{2}$. The temperature dependence of the EPR spectra revealed that the $M = \pm \frac{1}{2}$ doublet is the ground state (i.e., $D > 0$) and that the $M = \pm \frac{3}{2}$ doublet is at least 40 cm^{–1} above the ground state. Thus, at 4.2 K only the $M = \pm \frac{1}{2}$ doublet is populated.

The Mössbauer spectra of the green intermediate recorded at $T = 140$ and 4.2 K are shown in Figure 13. The spectra are dominated by two unresolved quadrupole doublets with $\Delta E_Q(1) = 1.57 \text{ mm s}^{-1}$ and $\Delta E_Q(2) = 1.03 \text{ mm s}^{-1}$ and $\delta(1) = \delta(2) = 0.42 \text{ mm s}^{-1}$ at 140 K, which arise from the starting diiron(III) complex; note the major doublet in Figure 13(a) (experimental spectrum minus the contribution of the doublet outlined by the solid line). The starting material is diamagnetic, as expected for an antiferromagnetically coupled pair of high-spin iron(III) sites. Except for a shoulder on the left, the spectrum of the green intermediate is hidden under the major doublet in Fig. 13(b), because the species of interest has small magnetic hyperfine interactions. Since the green intermediate is EPR active, it should have a magnetic component in the $T = 4.2 \text{ K}$ spectrum, whose shape we can describe very well by using the correlations between EPR and Mössbauer spectroscopy as described below.

Consider a diamagnetic compound exhibiting a quadrupole doublet at 4.2 K. Application of a weak field of 50 mT will not cause any measurable changes in the spectrum; the nuclear Zeeman interaction is too small for $B = 50 \text{ mT}$. Assume that we measure the spectrum in parallel as well as in perpendicular field. The difference spectrum will yield a flat baseline. Contrast this situation with that of a *paramagnetic EPR active* compound. Assume that we obtain spectra similar to those of Figure 3(a and b). Subtracting the perpendicular spectrum from that obtained in parallel field will produce a difference spectrum for which the $\Delta m_I = 0$ lines point upward. Thus, if we have a sample containing an EPR active and a diamagnetic (or integer spin paramagnetic) species, we can cancel the contribution of the latter by taking the difference spectrum. The difference spectrum shown in Figure 13(c) is the contribution of the desired EPR active green intermediate. By computer simulations, one can fit the difference spectrum and determine the magnetic hyperfine interactions, the quadrupole splittings, and the isomer shift. The solid lines in Figure 13(b and c) show the results of such calculations. By matching the simulated spectrum to the left shoulder of the spectrum of Figure 13(b), we infer that 30% of the total Fe in the sample belongs to the green intermediate. Most interestingly, the computer simulations showed

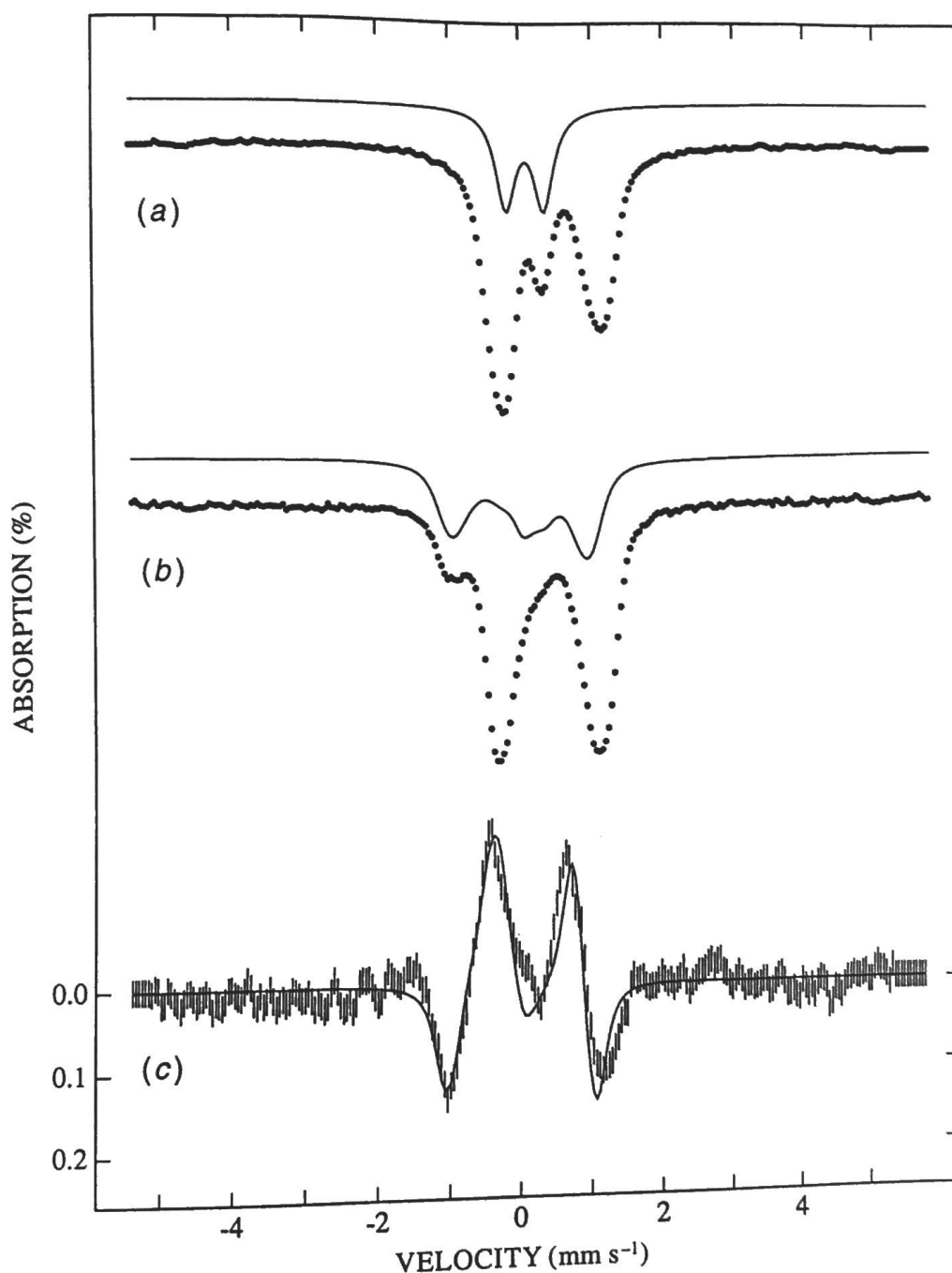


Figure 13

Mössbauer spectra obtained to characterize the green intermediate $[\text{Fe}_2\text{O}_2(\text{TPA})_2]^{3+}$ generated by reacting $[\text{Fe}_2\text{O}(\text{TPA})_2(\text{OH})(\text{H}_2\text{O})(\text{ClO}_4)_3]$ at -40°C in acetonitrile with H_2O_2 . The spectra were obtained at $T = 140\text{ K}$ in zero field (a) and at $T = 4.2\text{ K}$ in a 0.15 T parallel field (b). The difference spectrum shown in (c) was obtained by subtracting a spectrum obtained in 60 mT perpendicular field from the corresponding parallel field spectrum. The solid lines are theoretical curves computed with an $S = \frac{3}{2}$ spin Hamiltonian. [Adapted from Leising et al.²⁷]

that the paramagnetic species consists of only one spectral component, that is, if the $S = \frac{3}{2}$ system represents a diiron center, both iron sites are equivalent.

At 140 K, the electronic spin of the $S = \frac{3}{2}$ species relaxes fast on the time scale of Mössbauer spectroscopy, and the magnetic spectrum observed at 4.2 K collapses into one quadrupole doublet. This doublet again accounts for 30% of the iron in the sample and, when correlated with its EPR signal intensity, corresponds to about 1 spin/2 Fe for the $S = \frac{3}{2}$ species. The Mössbauer parameters for the doublet are $\Delta E_Q = 0.53 \text{ mm s}^{-1}$ and $\delta = 0.07 \text{ mm s}^{-1}$. The decrease in the isomer shift from 0.42 mm s^{-1} indicates that the diiron center has been oxidized in the intermediate, in agreement with the formal $\text{Fe}^{\text{III}}\text{--Fe}^{\text{IV}}$ state deduced from the mass spectral data. However, the fact that the iron sites are equivalent in this species implies a valence delocalized description. The system spin $S = \frac{3}{2}$ is proposed to result from parallel spin alignment of low-spin ($S_1 = \frac{1}{2}$) $\text{Fe}(\text{III})$ and low-spin ($S_2 = 1$) $\text{Fe}(\text{IV})$ sites, likely coupled via a double exchange mechanism (Fig. 12).^{28,30}

The electronic description that is emerging for the green intermediate is corroborated by more recent data obtained on a related "brown intermediate". The brown intermediate $[\text{Fe}_2(\text{O})_2(6\text{-Me-TPA})_2]^{3+}$ is generated by the reaction of H_2O_2 with the corresponding (μ -oxo)diiron(III) 6-Me-TPA complex.²⁹ It exhibits a brown color ($\lambda_{\text{max}} = 350 \text{ nm}$) and an isotropic EPR signal at $g = 2.0$. This signal broadens when either ^{57}Fe or ^{17}O is introduced into the intermediate, showing that the resonance originates not from a radical but from the Fe_2O_2 core. Figure 14 shows a Mössbauer spectrum of the brown intermediate recorded at 1.5 K in the presence of a 2.5 T applied field. Analysis of this spectrum is straightforward. The central part of the spectrum is a quadrupole doublet (53% of the total Fe) with parameters identical to that of the diiron(III) starting material. The remainder (47%) is a paramagnetic component that corresponds to the $S = \frac{1}{2}$ species. Correlation of the Mössbauer and EPR intensities gives a spin concentration of 1 spin per 2Fe for the $S = \frac{1}{2}$ species.

The Mössbauer spectrum of the brown intermediate consists of two subspectra of equal intensity. By studying the sample in parallel and transverse applied fields, it was possible to prove that these two subspectra belong to the $S = \frac{1}{2}$ spin system. One subspectrum, labeled $\text{Fe}(\text{III})$ in Figure 14, has parameters typical of a high-spin ($S_1 = \frac{5}{2}$) $\text{Fe}(\text{III})$ site; for example, its isomer shift, $\delta = 0.48 \text{ mm s}^{-1}$, is identical to that observed for the two sites of the diiron(III) starting material. The second site has $\delta = 0.08 \text{ mm s}^{-1}$, which implies that one of the iron sites is oxidized to the $\text{Fe}(\text{IV})$ state.³¹ By taking into account that the intermediate has a system spin $S = \frac{1}{2}$ and that one of the iron sites is high-spin $\text{Fe}(\text{III})$, it follows that the second site must be high-spin ($S_2 = 2$) $\text{Fe}(\text{IV})$. One can use Eqs. (21) and (23) to analyze the properties of the brown intermediate, since an octahedral high-spin d^4 electronic configuration is complementary to a tetrahedral high-spin d^6 configuration. Such an analysis shows that the electronic structure of the brown intermediate is appropriately described as an antiferromagnetically coupled diiron center with localized high-spin $\text{Fe}(\text{III})$ and $\text{Fe}(\text{IV})$ sites.

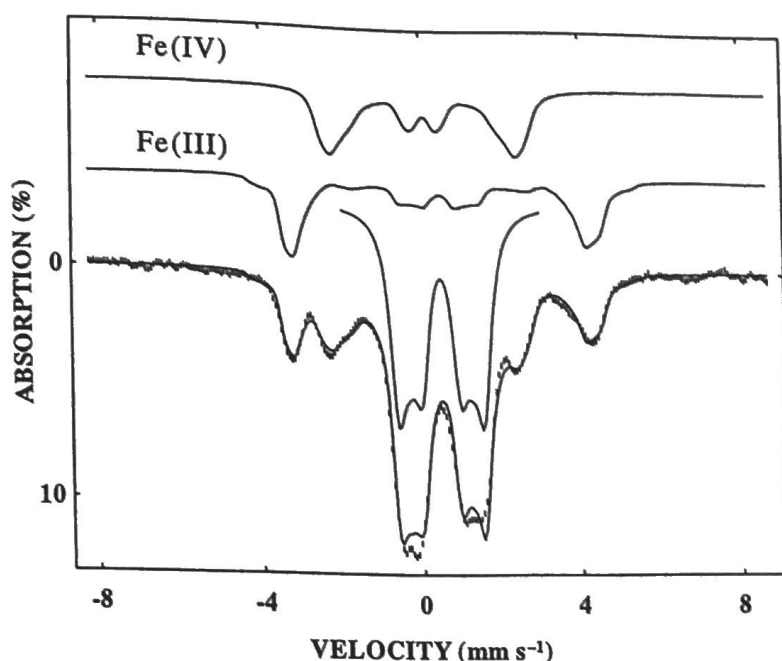


Figure 14

Mössbauer spectrum of the brown intermediate $[\text{Fe}_2\text{O}_2(6\text{-Me-TPA})_2]^{3+}$ recorded at 1.5 K in a parallel applied field of 2.5 T. The solid lines drawn above the data are theoretical curves describing the Fe(III) site and the Fe(IV) site, as well as a remnant (53%) of the diiron(III) starting material. The solid line drawn through the data is the sum of the three theoretical curves. [Adapted from Dong et al.²⁹]

The differing electronic properties of the green and brown intermediates can be understood by considering the effects of the 6-methyl substituent. Based on a comparison of structures of Fe(III) TPA and 6-Me-TPA complexes, introducing the 6-methyl substituent imposes steric constraints that discourages formation of the shorter metal–ligand bonds required by a low-spin configuration. Thus a low-spin configuration for an Fe(TPA) center would likely be converted to a high-spin configuration for the corresponding Fe(6-Me-TPA). For the green intermediate, the low-spin configurations of the individual iron sites give rise to the $S = \frac{3}{2}$ system spin via double exchange, while for the brown intermediate, the high-spin configurations of the individual iron sites give rise to the $S = \frac{1}{2}$ system spin via antiferromagnetic exchange (Fig. 12). These insights into electronic structure could only be obtained by a judicious application of Mössbauer principles in combination with EPR analysis.

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