Biochimica et Biophysica Acta 893 (1987) 365–371
Elsevier

BBA 42582

Angular-overlap analysis of the iron(II) site in [2Fe-2S] clusters

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(Received 20 February 1987)

Key words: Angular-overlap analysis; Ferredoxin; Fe-S cluster; *g*-Tensor variation

The angular-overlap model for $Fe(II)S_4$ centres is used to obtain structural information from the experimental data available for the $g_{av} \approx 1.96$ and $g_{av} \approx 1.91$ classes of [2Fe-2S] ferredoxin, showing that it is possible to translate the parameters obtained by Bertrand and Gayda in their non-additive ligand field model (Bertrand, P. and Gayda J.P. (1979 and 1980) Biochim. Biophys. Acta 579, 107–121 and 625, 337–342, respectively) into an additive one. The analysis of the e_λ ($\lambda = \sigma$ or π) parameters allowed us to conclude that the $Fe(II)S_4$ chromophores of the two types of [2Fe-2S] metallo-protein are similar to each other, being possible to reproduce nicely the different *g* tensors introducing only small variations in the angular and bonding parameters.

Introduction

Iron-sulfur proteins form a very important and widely occurring class of biological molecule, in which the active site can comprise one, 1-Fe, two, 2-Fe, three, 3-Fe, and four, 4-Fe, iron atoms [1,2]. Extensive studies with a great variety of experimental techniques [3–5] have shown that the iron atoms in these clusters are tetrahedrally coordinated to four sulfur atoms, can have oxidation state +2 and +3, and the electron-transfer process, which is one of the most relevant biological roles of these proteins, is accompanied by changes in the formal oxidation state of the iron atoms. Further, when more than one iron is present in the cluster, fairly strong exchange interactions are operative between the ions giving rise to interesting magnetic phenomena.

Several theoretical models have been used to characterize the iron clusters, ranging from ab-initio molecular orbital calculations [6] to crystal-field models [7–10]. It is particularly the latter which can be extremely useful in rationalizing a large number of experimental data, such as those which are available for the iron cluster. In fact, recently Bertrand and Gayda used a crystal-field approach to justify the variations of some physical parameters within the [2Fe-2S] reduced ferredoxin group [8]. The same model has subsequently been used for interpreting the spectral properties of selenium-substituted proteins [9], as well as of a second class of 2-Fe iron proteins [10]. They used a C_{2v} symmetry parameterization of the crystal field, and through these they interpreted the differences in the g and A values of a series of ferredoxins, using only the parameters α, which measures the admixture of z^2 and $x^2 - y^2$ orbitals due to the low symmetry of the system, and Δ_{xy}, the splitting of the two levels which span the E representation in T_d symmetry.

A crystal-field model like that used by Bertrand and Gayda is called non-additive [11,12] in the sense that it is constructed using only symmetry arguments and ignoring the contributions of the

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individual ligands. In this approach the parameters do not give any direct information on the individual bonding interactions, but reflect only the sum of the effects of the individual ligands, symmetry mediated. So, for instance, the parameter Δ_{xy} above only tells how far removed from tetrahedral symmetry is the system under investigation, but gives no information whether this is due to angular distortions or to differences in ligand field strength of the ligands.

Another possible approach is the additive one [11,12], in which the ligand field is constructed as a sum of contributions from each ligand. The advantage of this approach is that of providing parameters which reflect the nature of the bonding interaction of each ligand with the metal atom and the structural details of the complex under examination. The angular-overlap model is particularly well suited to this purpose, because it expresses the metal-ligand bonding interactions through parameters which reflect the σ and π bonding ability of the individual ligands.

The model has been found to give useful information on the electronic structure of simple transition metal complexes, and it has had also a limited application to metallo-enzymes and metallo-proteins [13].

We want here to develop the angular-overlap model for $Fe(II)S_4$ species, in order to verify if it is possible to obtain structural information from the set of experimental data available, and in particular to compare this model with the one previously used by Bertrand and Gayda (Bertrand and Gayda Model) [8].

Iron-sulfur clusters

In all the iron-sulfur clusters the iron atoms are tetrahedrally coordinated by four sulfur atoms [1]. In 1-Fe these are cysteinyl sulfurs, while in all the other clusters, two ligands are cysteinyl sulfurs and two are inorganic sulphide ions. In the natural and the synthetic models the symmetry of the FeS_n moieties is usually very low, but it seems possible to assume a C_{2v} symmetry in order to analyze the experimental spectral and magnetic properties. In the following we will refer the sites to a frame as shown in Fig. 1.

Both iron(III) and iron(II) species are in the high-spin form. High-spin iron(III) has a ground ^6S state, which yields an orbitally non-degenerate multiplet in any symmetry [14]. Spin orbit coupling with excited quartets can yield a zero-field splitting of the ground multiplet and cause some small deviations of the g factor from the free electron value. Typical values are generally considered [15] to have $2.010 < g_i < 2.035$ and the zero-field splitting parameters are typically of the order of 1–10 cm^{-1}. We will not try to analyze further the ligand field of the iron(III) species, because due to the nature of the ground state, it requires a rather subtle variation of the parameters. In a following section we will derive at some length the angular overlap model parameters of the iron(II) sites.

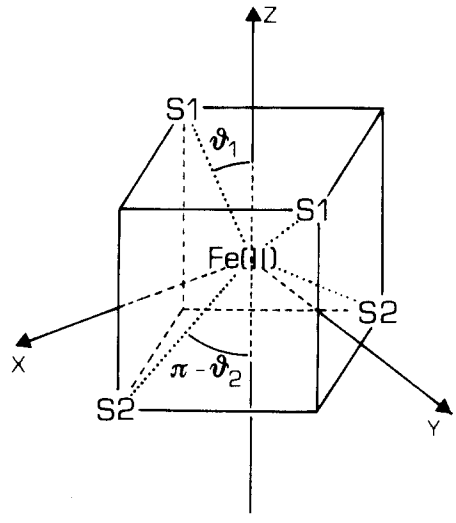

Fig. 1. Sketch of the iron(II) environment in [2Fe-2S] cluster. ϑ_1 and $\pi - \vartheta_2$ are the angles between the Fe(II)-S_i ($i = 1, 2$) directions and the z axis.

Angular-overlap model for $Fe(II)S_4$

The energies of the electronic levels of high-spin pseudotetrahedral $Fe(II)S_4$ centres can be conveniently expressed as a function of the angular overlap parameters for systems of C_{2v} symmetry using the reference frame of Fig. 1. In this symmetry the z^2 and the $x^2 - y^2$ orbitals are bases for the totally symmetric representation, while the other three orbitals span three different irreducible representations. The ground state of an iron(II) ion is

^{5}D [15]. The relative energies of the levels of this term in a ligand field can be expressed using the one-electron energies. The ground state corresponds to the lowest one-electron energy and the excited states are obtained similarly.

The angular-overlap model is a ligand field model which gives parametrically the energies of the partially filled d shell of transition-metal complexes through a first-order perturbation treatment using a basis of metal orbitals [16], without explicitly taking into account the ligand orbitals. The central assumption of the method is that for a ligand on the z axis the metal ligand interaction is diagonal and the energies of the d orbitals are given by three parameters, e_σ, $e_{\pi s}$, and $e_{\pi c}$ (σ, πs and πc correspond to the irreducible representations, and their components, of the $C_{\infty v}$ group). The energies of the d orbitals for a ligand in a general position can be obtained simply using a rotation matrix (the angular overlap matrix) relating the fixed reference frame to frame with the z' axis along the metal-ligand direction. The contributions of different ligands are assumed to be additive. The main advantage of using the angular-overlap model instead of the ligand-field model is that of using parameters which are related to the bonding interactions, σ and π, rather than to optimize spectral parameters such as Dq. The e_σ parameters are always positive, corresponding to an antibonding character of the metal d orbitals, while the e_π parameters can be either positive or negative, depending on whether the π metal-ligand interaction is bonding or antibonding. So, for instance, positive e_π has been calculated for oxygen ligands and negative e_π for phosphorus and cyanide [13].

Using the angular-overlap model to the case of interest here, assuming for the sake of simplicity $e_{\pi s} = e_{\pi c}$ i.e., cylindrical symmetry of the iron-sulfur bonds, the explicit expressions for the matrix elements of the d orbitals become:

$$E(z^2) = \tfrac{9}{2}(\cos^2\vartheta_1 - \tfrac{1}{3})^2 e_{\sigma 1} + 6\cos^2\vartheta_1 \sin^2\vartheta_1 e_{\pi 1} + \tfrac{9}{2}(\cos^2\vartheta_2 - \tfrac{1}{3})^2 e_{\sigma 2} + 6\cos^2\vartheta_2 e_{\pi 2} \quad (1a)$$

$$E(x^2 - y^2) = \tfrac{3}{2}\sin^4\vartheta_1 e_{\sigma 1} + 2\cos^2\vartheta_1 \sin^2\vartheta_1 e_{\pi 1} + \tfrac{3}{2}\sin^4\vartheta_2 e_{\sigma 2} + 2\cos^2\vartheta_2 \sin^2\vartheta_2 e_{\pi 2} \quad (1b)$$

$$E(x^2 - y^2, z^2) = \frac{3\sqrt{3}}{2}(\cos^2\vartheta_1 - \tfrac{1}{3})\sin^2\vartheta_1 e_{\sigma 1} - 2\sqrt{3}\cos^2\vartheta_1 \sin^2\vartheta_2 e_{\pi 1} - \frac{3\sqrt{3}}{2}(\cos^2\vartheta_2 - \tfrac{1}{3})\sin^2\vartheta_2 e_{\sigma 2} + 2\sqrt{3}\cos^2\vartheta_2 \sin^2\vartheta_1 e_{\pi 2} \quad (1c)$$

$$E(yz) = 2\cos^2\vartheta_1 e_{\pi 1} + 6\cos^2\vartheta_2 \sin^2\vartheta_2 e_{\sigma 2} + 2(2\cos^2\vartheta_2 - 1)^2 e_{\pi 2} \quad (1d)$$

$$E(xz) = 6\cos^2\vartheta_1 \sin^2\vartheta_1 e_{\sigma 1} + 2(2\cos^2\vartheta_1 - 1)^2 e_{\pi 1} + 2\cos^2\vartheta_2 e_{\pi 2} \quad (1e)$$

$$E(xy) = 2\sin^2\vartheta_1 e_{\pi 1} + 2\sin^2\vartheta_2 e_{\pi 2} \quad (1f)$$

where $E(z^2)$, $E(x^2-y^2)$ and $E(x^2-y^2, z^2)$ indicate the diagonal and off-diagonal elements of a 2×2 matrix, respectively, and ϑ_1 and $\pi - \vartheta_2$ are the angles between the metal-ligand directions and z axis, as shown in Fig. 1.

One parameter which is central to the interpretation of the EPR data is the admixture of z^2 and $x^2 - y^2$, determined by $E(x^2 - y^2, z^2)$. Expressing the appropriate linear combinations as $\cos\alpha\,|\,z^2\,| + \sin\alpha\,|\,x^2 - y^2\,|$ and $-\sin\alpha\,|\,z^2\,| + \cos\alpha\,|\,x^2 - y^2\,|$, respectively, α is given by:

$$\alpha = \tan^{-1}\left(\frac{2E(x^2 - y^2, z^2)}{E(z^2) - E(x^2 - y^2)}\right) \quad (2)$$

In the assumption of only moderate deviations from the tetrahedral angle, ϑ_t, it is essentially the difference in the e_π parameters for the two sets of sulfur atoms which makes α different from zero. Within this approximation it is also feasible to set $\vartheta_1 \approx \pi - \vartheta_2$, so that

$$\alpha = \tan^{-1}\left(\frac{-\sqrt{3}(e_{\pi 1} - e_{\pi 2})}{2(e_{\pi 1} + e_{\pi 2})}\right) \quad (3)$$

This parameter α is used by Gayda et al. in order to characterize the environment of 2Fe-2S ferredoxins [8]. They individuate two different types of ferredoxin, essentially on the basis of the g

values * [10]. The first type is that of classical ferredoxins, which have $g_{av} \approx 1.96$. Another class, which includes the ubiquitous Rieske protein, is characterized by more anisotropic EPR spectra with $g_{av} \approx 1.91$. They interpreted the experimental data available letting α to vary from $-5°$ to $-18°$ for the first set and from $-24°$ to $-30°$ for the second. Eqn. 3 shows that $(e_{\pi 1} - e_{\pi 2})/(e_{\pi 1} + e_{\pi 2})$ must vary from zero to approx. 0.4 for the former and from 0.5 to 0.67 for the latter.

The same authors showed also that the factors determining the splitting, Δ, of the xz and yz orbitals can be different from those determining an α value different from zero. Indeed within the same approximation above, our model predicts for the splitting:

$$\Delta = 2(4\cos^4\vartheta - 5\cos^2\theta + 1)(e_{\pi 1} - e_{\pi 2}) + 6\cos^2\vartheta \sin^2\vartheta (e_{\sigma 1} - e_{\sigma 2}) \quad (4)$$

The difference Δ depends not only on the π anisotropy, like α, but also on the σ anisotropy. For ϑ equal to the tetrahedral angle, ϑ_t, the coefficients for $(e_{\pi 1} - e_{\pi 2})$ and $(e_{\sigma 1} - e_{\sigma 2})$ are -0.45 and 1.33, respectively. Therefore the σ anisotropy can produce large effects on Δ, while it does not affect at all α, so it is possible to have small values of α even if the Δ splitting is large.

Another important parameter is the splitting Δ_{xy} of the E ground state of tetrahedral symmetry. In general it is assumed that the ground orbital is z^2, and the energy of the excited xy orbital can be expressed as:

$$\Delta_{xy} = (3\cos^2\vartheta - 1)\{2\sin^2\vartheta (e_{\pi 1} + e_{\pi 2}) + \tfrac{1}{2}(3\cos^2\vartheta - 1)(e_{\sigma 1} + e_{\sigma 2})\} \quad (5)$$

Since in the angular range of interest the coefficient of $(e_{\pi 1} + e_{\pi 2})$ is roughly 10-times larger than the coefficient of $(e_{\sigma 1} + e_{\sigma 2})$, it is the e_π values which largely determine the splitting. In the assumption of positive e_π, i.e., of an antibonding interaction between iron(II) and sulfur, the ground state is z^2 for $\vartheta > \vartheta_t$, while the reverse is true if e_π is negative.

Up to now we have made use of the approximation of small angular variations from the tetrahedral value. Without making use of this, the energy levels can be calculated using (1a–f). In Fig. 2a is shown the effect of varying $\vartheta = \vartheta_1 = \pi - \vartheta_2$ in the range 50°–90°. The quantitative data confirm that the sign of the splitting of the ground E level depends on ϑ. For $\vartheta < \vartheta_t$ the ground state is xy, while for $\vartheta > \vartheta_t$, z^2 goes to lower energy. For ϑ tending to 90° yz becomes the ground state. In Fig. 2b we report the effect of varying $\pi - \vartheta_2$, keeping $\vartheta_1 = 60°$: the overall pattern remains similar to that of Fig. 2a, but xy does not become the ground state even at $\pi - \vartheta_2 = 50°$. In Fig. 2c–f we show the effect of varying the bonding parameters $e_{\sigma 1}$, $e_{\pi 1}$, $e_{\sigma 2}$ and $e_{\pi 2}$ keeping the angular parameter fixed. $e_{\sigma i}$ $(i = 1, 2)$ but not affect Δ_{xy}, while they greatly vary Δ; on the other hand $e_{\pi i}$ $(i = 1, 2)$ affect Δ_{xy}, but they are practically not affecting Δ.

We used our model to reproduce the parameters used by Bertrand and Gayda, for the proteins and models characterized by $g_{av} \approx 1.96$, in order to refer their crystal-field parameters to geometrical and bonding properties of the individual ligands. Bertand and Gayda model fixed some of the parameters by taking advantage of electronic spectra and used the EPR and Mössbauer data to obtain the others [8]. In this way they used: $\Delta_{xz} = 6000\ cm^{-1}$; $\Delta_{yz} = 4000\ cm^{-1}$, and $\Delta_{xy} = 500\ cm^{-1}$ for α in the range $0°/-7°$, and $\Delta_{xy} = 2000\ cm^{-1}$ for $\alpha \approx -20°$.

For the first limit, a significant fit could be obtained with the following parameters: $\vartheta_1 = \pi - \vartheta_2 = 57°$, $e_{\sigma 1} = 7200\ cm^{-1}$, $e_{\pi 1} = 2000\ cm^{-1}$, $e_{\sigma 2} = 5500\ cm^{-1}$, $e_{\pi 2} = 1500\ cm^{-1}$. The calculated values are $\Delta_{xz} = 6141\ cm^{-1}$, $\Delta_{yz} = 4144\ cm^{-1}$, $\Delta_{xy} = 500\ cm^{-1}$, and $\alpha = -4.2°$. By varying ϑ_1, or allowing ϑ_2 to be different from $\pi - \vartheta_1$, again reasonable fits could be obtained. These values cannot be compared with any corresponding values for simple compounds. But certainly appear to be rather reasonable, $e_{\sigma 2}$ being only slightly larger than the values used to describe the interaction of a cysteine sulfur with copper(II) in plastocyanine [13,17], and $e_{\pi 2}$ being just equal to the value used

* The experimental g values are those reported in Table I of Ref. 10. One point, corresponding to $g_2 - g_1 = 5.6 \cdot 10^{-2}$, has been corrected according to a personal communication from Dr. J.F. Gibson, Imperial College, London.

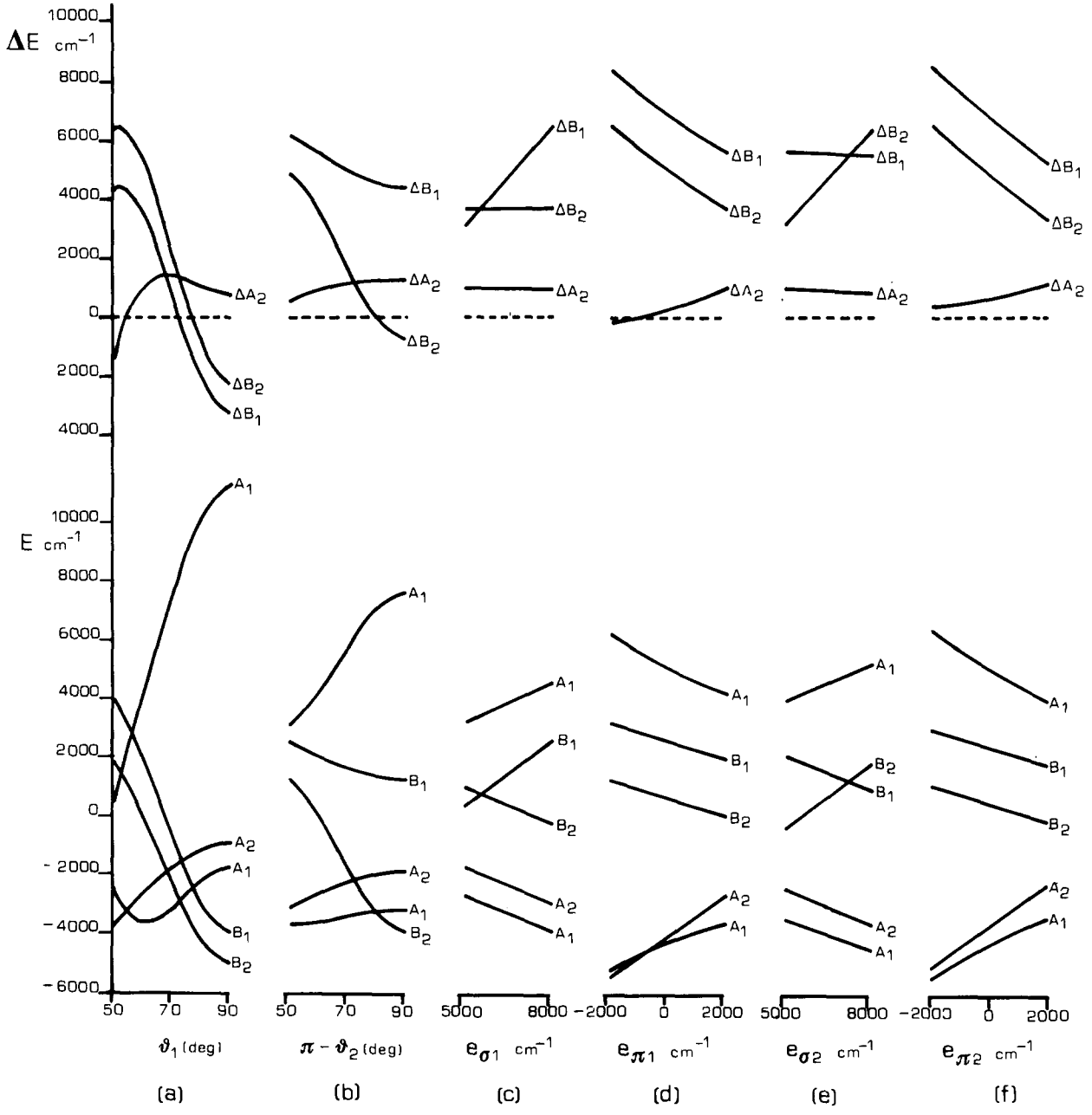

Fig. 2. Dependence of the calculated energy of the electronic levels for $Fe(II)S_4$ centre on angular-overlap model parameters. Using a C_{2v} symmetry the z^2 and $x^2 - y^2$ orbitals are bases for A_1 irreducible representation, while xy, xz and yz span the A_2, B_1 and B_2 irreducible representations, respectively. ΔX ($X = A_1$, A_2, B_1 or B_2) indicates the energy gaps between the $x^2 - y^2$, xy, xz and yz levels and the z^2 level: (a) the effect of varying $\vartheta_1 = \pi - \vartheta_2$ ($e_{\sigma 1} = 7200\ cm^{-1}$; $e_{\pi 1} = 2000\ cm^{-1}$; $e_{\sigma 2} = 5500\ cm^{-1}$; $e_{\pi 2} = 1500\ cm^{-1}$); (b) the effect of varying $\pi - \vartheta_2$ ($\vartheta_1 = 60°$; $e_{\sigma 1} = 7200\ cm^{-1}$; $e_{\pi 1} = 2000\ cm^{-1}$; $e_{\sigma 2} = 5500\ cm^{-1}$; $e_{\pi 2} = 1500\ cm^{-1}$); (c) the effect of varying $e_{\sigma 1}$ ($\vartheta_1 = \pi - \vartheta_2 = 60°$; $e_{\pi 1} = 2000\ cm^{-1}$; $e_{\sigma 2} = 5500\ cm^{-1}$; $e_{\pi 2} = 1500\ cm^{-1}$); (d) the effect of varying $e_{\pi 1}$ ($\vartheta_1 = \pi - \vartheta_2 = 60°$; $e_{\sigma 1} = 7200\ cm^{-1}$; $e_{\sigma 2} = 5500\ cm^{-1}$; $e_{\pi 2} = 1500\ cm^{-1}$); (e) the effect of varying $e_{\sigma 2}$ ($\vartheta_1 = \pi - \vartheta_2 = 60°$; $e_{\sigma 1} = 7200\ cm^{-1}$; $e_{\pi 1} = 2000\ cm^{-1}$; $e_{\pi 2} = 1500\ cm^{-1}$); (f) the effect of varying $e_{\pi 2}$ ($\vartheta_1 = \pi - \vartheta_2 = 60°$; $e_{\sigma 1} = 7200\ cm^{-1}$; $e_{\pi 1} = 2000\ cm^{-1}$; $e_{\sigma 2} = 5500\ cm^{-1}$).

for the π interaction. Therefore we identify the site 1 as the S^{2-}, and the site 2 as the cystein sulphur.

We attempted also to fit the second set of values of Bertrand and Gayda. A significant fit could be obtained with the following parameters: $\vartheta_1 = \pi - \vartheta_2 = 57°$, $e_{\sigma 1} = 7200$ cm^{-1}, $e_{\pi 1} = 4000$ cm^{-1}, $e_{\sigma 2} = 4800$ cm^{-1}, $e_{\pi 2} = 500$ cm^{-1}, yielding $\Delta_{xz} = 6088$ cm^{-1}, $\Delta_{yz} = 4002$ cm^{-1}, $\Delta_{xy} = 1785$ cm^{-1}, $\alpha = -23°$.

Comparing this fit with that for the first set of parameters we see that no large adjustment is required for the e_σ parameters, but the largest differences are required for the e_π parameters. This of course could be predicted on the basis of the simplified model, since the two sets differ essentially for Δ_{xy} and α, which are largely determined by the e_π values.

We fitted the second set of values also for different ϑ angles. For instance for $\vartheta_1 = \pi - \vartheta_2 = 61°$ we found $e_{\sigma 1} = 8000$ cm^{-1}, $e_{\pi 1} = 4000$ cm^{-1}, $e_{\sigma 2} = 6500$ cm^{-1}, $e_{\pi 2} = 500$ cm^{-1} yielding $\Delta_{xz} = 6270$ cm^{-1}, $\Delta_{yz} = 4331$ cm^{-1}, $\Delta_{xy} = 2044$ cm^{-1}, $\alpha = -14.6°$. This shows that increasing the angle ϑ required larger e_π values to obtain comparable fits.

2Fe-2S species with $g_{av} \approx 1.91$

When applying the Bertrand and Gayda model to 2Fe-2S species with $g_{av} \approx 1.91$, Bertrand et al. [10] introduced significant variations as compared to the $g_{av} \approx 1.96$ case. In fact, on the basis of Mössbauer data for *Thermus thermophilus* [18], solutions were searched for α values close to $-30°$, and the assignment of the g values was completely changed, assuming that the largest experimental value, $g \approx 2.02$, corresponds to g_y, while it was attributed to g_z for the other class of proteins. The final result was that in order to fit the data the energies of the yz and xz excited states had to be largely changed, the former decreasing to 1900 cm^{-1} and the latter increasing to 15000 cm^{-1}.

As an alternative Bertrand et al. [10] consider acceptable also solutions for $\alpha \approx 90°$, in which case the ground state is $x^2 - y^2$. However, the two cases with $\alpha = 30°$ and $\alpha = 90°$ are actually similar, the former corresponding to a ground $z^2 - x^2$, i.e., an orbital similar to $x^2 - y^2$, but with lobes along the z and x axes. Therefore the two solutions are not different, but rather they correspond to a mere relabelling of the axes.

We attempted some fits in this assumption, but we could not find any reasonable range of parameters which could reproduce the reported energy level pattern. In particular, as is apparent from Fig. 2, in the range of values of the parameters which are compatible with a ground A_1 state, corresponding to a linear combination of z^2 and $x^2 - y^2$, the highest energy state is also A_1, and there is no way of pushing B_1 as high in energy as 15000 cm^{-1} from the ground state, unless the relative energies of all the other parameters are pushed to unacceptable high values.

We tried to fit the data, with an assignment which is parallel to that of the first class, i.e., setting $g_1 = g_x$, $g_2 = g_y$, $g_3 = g_z$ (with $g_1 < g_2 < g_3$). The results are given in Fig. 3. The fit is satisfactory for $\Delta_{xz} = 4300$ cm^{-1}; $\Delta_{yz} = 2300$ cm^{-1}; $\Delta_{xy} = 1000$ cm^{-1} and α in the range $-20°/+3°$. The fit is not fully satisfactory for g_3, which is expected to vary much more than experimentally observed. However, since the g_z value is the most sensitive to variation in Δ_{xy}, it is possible that Δ_{xy} varies slightly in the series as it

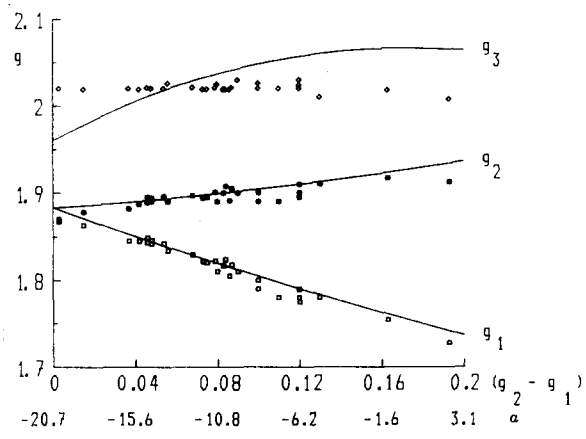

Fig. 3. Experimental g values measured in [2Fe-2S] $g_{av} \approx 1.91$ species, versus $(g_2 - g_1)$ (with $g_1 < g_2 < g_3$). The theoretical curve are calculated with the reported formulae (Eqns. 2 and 3 in Ref. 8) setting $\lambda = -80$ cm^{-1}; $\Delta_{xz} = 4300$ cm^{-1}, $\Delta_{yz} = 2300$ cm^{-1} and $\Delta_{xy} = 1000$ cm^{-1}; $g_{Fe(III)1} = 2.015$, $g_{Fe(III)2} = 2.034$ and $g_{Fe(III)3} = 2.030$ (Eqn. 3 in Ref. 8). (□) g_1; (*) g_2 and (◇) g_3 experimental values [19].

was suggested for the first class of compounds.

A typical fit with the angular-overlap model parameters with α close to $-6°$ yields: for $\vartheta_1 = \pi - \vartheta_2 = 64°$, $e_{\sigma 1} = 6650\ cm^{-1}$, $e_{\pi 1} = 1700\ cm^{-1}$, $e_{\sigma 2} = 4700\ cm^{-1}$, $e_{\pi 2} = 1150\ cm^{-1}$ yielding $\Delta_{xz} = 4343\ cm^{-1}$, $\Delta_{yz} = 2321\ cm^{-1}$, $\Delta_{xy} = 1023\ cm^{-1}$, $\alpha = -5.7°$; or for $\vartheta_1 = \pi - \vartheta_2 = 60°$, $e_{\sigma 1} = 5850\ cm^{-1}$, $e_{\pi 1} = 1950\ cm^{-1}$, $e_{\sigma 2} = 4100\ cm^{-1}$, $e_{\pi 2} = 1350\ cm^{-1}$ yielding $\Delta_{xz} = 4290\ cm^{-1}$, $\Delta_{yz} = 2298\ cm^{-1}$, $\Delta_{xy} = 1008\ cm^{-1}$, $\alpha = -6.8°$ showing that, using the same type of assignment for the two classes of proteins, passing from class I to class II a decrease of the bonding parameters is obtained.

However, it must be noticed that these values do not fit the Mössbauer data for *T. thermophilus,* which, as stated above, requires either $\alpha = -30°$ or $-90°$. Therefore it seems that more data are needed on class II before a clear indication of the pattern of the energy levels emerges.

Conclusions

We have shown that it is possible to translate the Bertand and Gayda model aprameters into an additive ligand field model, although the calculated sets of parameters are not totally interely consistent. Indeed the required variations of the e_π parameters on passing from set 1 to set 2 of the $g_{av} \approx 1.96$ class is perhaps too large. Further, while both $e_{\sigma 2}$ and $e_{\pi 2}$ decrease, indicating a lengthening of the Fe-S(2) bond, $e_{\sigma 1}$ remains substantially stable, while $e_{\pi 1}$ increases sharply. However, without going too much into detail the analysis above shows that: (i) the $Fe(II)S_4$ chromophores are tetrahedrally compressed; and (ii) the passage from one scheme to another of the series requires only modifications which can be both angular and bonding. However, as previously observed, the variations need not to be too large and they seem to indicate that in systems with larger g anisotropy the S^{2-} parameters are larger and the S^{cys} parameters smaller than in systems with smaller g anisotropy.

In order to understand fully the details one should have some more independent information, since the number of angular-overlap parameters is too large to allow the meaningful determination of all of them.

Acknowledgment

Thanks are due to Dr. J.P. Gayda (Laboratoire d'Electronique des Milieux Condensés, Université de Provence, Marseille, France) for helpful discussion.

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