Electron spin resonance lineshifts in paramagnetic copper-amino acid complexes

Electron spin resonance lineshifts in paramagnetic copper–amino acid complexes

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Abstract. The angular variation of the gyromagnetic factor measured by electron spin resonance (ESR) in single crystals of several copper–amino acid complexes (CAC) does not follow the second-order tensorial dependence expected for spins 1/2. Fourth-order contributions with magnitudes of up to $\delta g = 0.01$ have been clearly distinguished from the ESR data. CAC have two copper positions per unit cell differing in the orientation of their anisotropic gyromagnetic tensors. The ESR spectra show a single, exchange collapsed line for both sites. Linewidth and magnetic susceptibility measurements indicate exchange interactions $0.2\,\text{K} > |J| > 0.6\,\text{K}$, and a low-dimensional magnetic behaviour which is supported by the structural information.

The observed anomalous contribution to the gyromagnetic factor is examined in terms of the theory of Kubo and Tomita, and we analyse three types of contributions to the shifts. One arises from the difference between the Zeeman interactions for the two sites, and is produced when the non-secular part of this term is modulated by the exchange interaction. The dipole–dipole interaction between copper ions gives rise to two additional contributions. One is due to the non-secular terms, while the other arises because of the low symmetry of CAC, and becomes important in magnetic low-dimensional systems. Only the secular part of this last term is studied, giving a contribution that depends on the orientation of the microwave field. Although the theoretical results obtained within the standard scheme give contributions with the right order of magnitude, the overall agreement with our experimental results is poor, suggesting that a more detailed analysis is required.

1. Introduction

Copper–amino acid complexes (CAC) form a large group of compounds whose magnetic properties have been extensively studied by magnetic susceptibility [1, 2] and electron spin resonance (ESR) [2–8] techniques in the last few years. The magnitudes of the exchange interactions $|J|$ are between 0.2 and 0.6 K, and in most cases they exhibit a low-dimensional behaviour in the spin dynamics. The ESR spectra consist of a single collective resonance, produced by the collapse of the resonances of the different copper species in the lattice, and of the hyperfine structure, due to the exchange. The linewidth of this resonance is strongly affected by exchange narrowing.

Most ESR studies performed in paramagnetic compounds analyse the linewidth and lineshapes, and their dependence on the direction of the applied magnetic field. Information about the exchange interactions and the spin dynamics can be extracted from the data [9–14]. Since the exchange interactions in CAC have values close to those of the Zeeman interactions in normal electron paramagnetic resonance (EPR)

experiments, one may expect that, besides producing changes in the linewidth, the position of the resonances could be noticeably modified by the exchange. The observed lineshifts may also give information about the exchange.

Measurements of absolute lineshifts are not common, being in general changes with external parameters (temperature, pressure, frequency, etc) [15–17]. The reason is simple; widths and shapes are absolute quantities, while shifts are related to a reference position, which is generally unknown.

In recent years we have studied several CAC using ESR. Most of them show an angular dependence of the position of the resonance, with an unexpected high-order angular contribution, easily separated from the normal second-order tensorial angular dependence. To the best of our knowledge, this type of behaviour has not been observed before. This contribution to the angular variation of the squared gyromagnetic factor proportional to fourth-order spherical harmonics is not expected for spins $1/2$, and is attributed to the collective nature of the resonance.

The observed lineshifts are analysed in terms of the theory of Kubo and Tomita [9] in its form extended to allow for low crystal symmetry effects [17].

Following standard methods and approximations we calculated the lineshifts produced by the contribution of different mechanisms. The results of these calculations are compared with experimental results in $Cu(L\text{-}Ala)_2$. They reproduce the order of magnitude of those observed, but the overall agreement with the data is poor. Several sources that may cause the observed discrepancies can be identified. Cross correlation between spins, which are usually neglected when considering the short-time regime, may be important. Also, the theory introduced by Richards [14] in order to analyse the linewidths in low-dimensional systems may have to be modified in order to account for low-symmetry effects that contribute to the lineshifts [18].

2. Experimental procedure and results

The copper–amino acid $Cu(AA)$ complexes we are dealing with crystallise in the $P2_1$ or $P2_1/c$ space groups, with two $Cu(AA)_2$ molecules per unit cell. There are two rotated copper sites A and B, differing by a $180°$ rotation around the $\hat{b}$ axis, plus a translation. Then, neglecting the hyperfine structure due to the copper nuclear spins, two ESR lines having anisotropic gyromagnetic factors and corresponding to the two spin-$1/2$ copper species should be observed. However, antiferromagnetic exchange interactions between copper neighbours having magnitudes $0.2\,\text{K} < |J| < 0.6\,\text{K}$ collapse to one of these two resonances and their hyperfine structure, and consequently the observed response of the spin system is a single collective resonance [3, 4, 6–8].

The type of lineshifts analysed in this paper have been observed by ESR studies in at least five copper–amino acid complexes. Here we will give a description of the general experimental findings using $Cu(L\text{-}Ala)_2$, the copper complex of the amino acid L-alanine, as an example, including an account of our actual theoretical understanding of the problem.

High-quality single-crystal samples of several CAC are easily grown from aqueous solutions [2–8]. The crystals are thin plates, which can be accurately oriented, and are well suited for ESR techniques. They were glued with the $\hat{a}' = \hat{b} \times \hat{c}$, $\hat{b}$ and $\hat{c}$ crystal axes parallel to the $\hat{x}$, $\hat{y}$ and $\hat{z}$ orthogonal axes of a sample holder. The sample holder was positioned inside of the microwave cavity so the magnetic field B could be rotated in the xy, zx, zy, yv and yw planes. The directions v and w are defined as $(-1/\sqrt{2}, 0,$
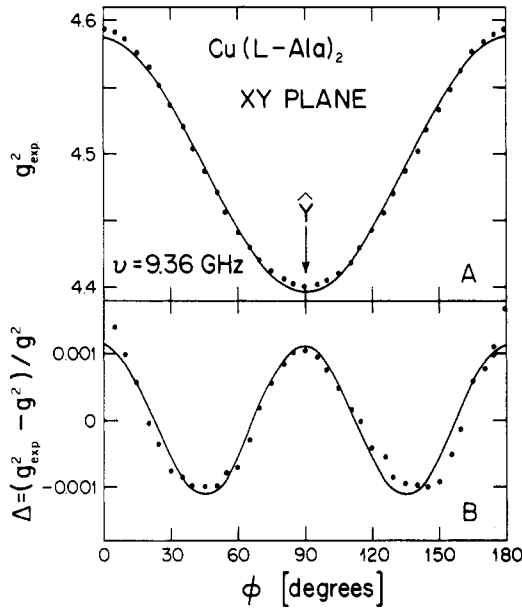
Figure 1. (A) Values of $(h\nu/\mu_0 B)^2$ measured at room temperature in the xy ($a'b$) plane of a single-crystal sample of Cu(L-Ala)$_2$, as a function of the equatorial angle ϕ. The full curve represents a least-squares fit to a gyromagnetic tensor (equation (1)) with components given in table 1. (B) Values of $\delta(\theta, \phi)$ obtained from the experimental data displayed in (A), using equation (2) and the components of the g^2 tensor of table 1.

$1/\sqrt{2}$) and $(1/\sqrt{2}, 0, 1/\sqrt{2})$, respectively, in the x, y, z system. The ESR data were taken with a standard spectrometer working at 9.3 GHz, at room temperature. The position of the observed resonance was measured as a function of the direction of $\boldsymbol{B}$ at 5° intervals in each of the five planes.

Figure 1A displays the squared gyromagnetic factor $g_{\exp}^2$ obtained for $\boldsymbol{B}$ in the xy plane, as a function of the equatorial angle ϕ, obtained in single crystals of Cu(L-Ala)$_2$. Similar results were obtained in the other four planes studied. In the planes xy, zy, yv and yw, the orientations of the axes were determined considering that the symmetry of the sample assures extrema of the angular variation of g^2 along the $\hat{y}$ axis. This symmetry does not allow one to determine the position of the axes in the zx plane, and in this case they were obtained from the g-values measured in the other planes.

In general, for a spin $1/2$, the observed angular variation of the squared gyromagnetic factor $g_{\exp}^2$ is fitted by a $g^2 = g \cdot g$ tensor projected on the direction of the magnetic field $\boldsymbol{B}$, using $g_{\exp}^2 = \hat{b} \cdot g \cdot g \cdot \hat{b}$, where

$$\hat{b} = \boldsymbol{B}/|\boldsymbol{B}| = (\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta).$$

For symmetry reasons in Cu(L-Ala)$_2$ one has $g_{xy}^2 = g_{zy}^2 = 0$ and the expected angular variation is

$$g_{\exp}^2(\theta, \phi) = g_{xx}^2 \sin^2\theta \cos^2\phi + g_{yy}^2 \sin^2\theta \sin^2\phi + g_{zz}^2 \cos^2\theta$$

$$+ 2g_{zx}^2 \sin\theta \cos\theta \cos\phi. \tag{1}$$

The full curve in figure 1A gives the best fit of the values of $g_{\exp}^2$ measured in the xy plane to this function. This and other similar fits in the remaining planes allowed us to determine the values of the components of the g^2 tensor given in table 1. However,

Table 1. Values of the components of the squared gyromagnetic tensor g^2 and the fourth-order coefficients A_{4m} defined in equation (2), obtained from the data in the planes xy, zy, yv, yw and zx.

$(g^2)_{xx} = 4.5903 \pm 0.0003$	$A_{40} = (-0.076 \pm 0.035) \times 10^{-3}$
$(g^2)_{yy} = 4.3954 \pm 0.0003$	$A_{41} = (0.98 \pm 0.07) \times 10^{-3}$
$(g^2)_{zz} = 4.4801 \pm 0.0003$	$A_{42} = (-0.27 \pm 0.04) \times 10^{-3}$
$(g^2)_{zx} = -0.3319 \pm 0.0003$	$A_{43} = (-0.193 \pm 0.005) \times 10^{-3}$
	$A_{44} = (1.47 \pm 0.07) \times 10^{-3}$

systematic differences between the values of g^2_{exp} and those obtained with the tensor g^2 were observed, and are amplified in figure 1B, where we plot

$$\delta(\theta, \phi) = (g^2_{exp} - \hat{b} \cdot g \cdot g \cdot \hat{b})/\hat{b} \cdot g \cdot g \cdot \hat{b}$$

for $\hat{b}$ in the xy plane. These values of $\delta(\theta, \phi)$ have a well defined angular variation with a 90° periodicity observed in the five measured planes, and show that, besides the second-order tensorial angular dependence of g^2_{exp} given by equation (1), angular components of fourth (and higher) order in a spherical harmonics expansion should be added to equation (1) to improve the agreement with the experiments. The crystal symmetry allows only for the following five angular functions of fourth order [19]:

$$C_{40}(\theta, \phi) = (1/8)(35 \cos^4\theta - 30 \cos^2\theta + 3)$$

$$C_{41}(\theta, \phi) = (\sqrt{10}/4)(7 \cos^3\theta - 3 \cos\theta) \sin\theta \cos\phi$$

$$C_{42}(\theta, \phi) = (\sqrt{5}/4)(7 \cos^2\theta - 1) \sin^2\theta \cos 2\phi$$

$$C_{43}(\theta, \phi) = (\sqrt{70}/4) \sin^3\theta \cos\theta \cos 3\phi$$

$$C_{44}(\theta, \phi) = (\sqrt{35}/8) \sin^4\theta \cos 4\phi.$$

Since the isotropic and second-order angular dependences of g^2_{exp} are eliminated in the definition of $\delta(\theta, \phi)$, we propose

$$\delta(\theta, \phi) = (g^2_{exp} - \hat{b} \cdot g \cdot g \cdot \hat{b})/\hat{b} \cdot g \cdot g \cdot \hat{b} = \sum_m A_{4m} C_{4m}(\theta, \phi) \qquad (2)$$

and obtained the values of the coefficients A_{4m} given in table 1 from least-squares fits of equation (2) to the experimental data in the five planes. The full curve in figure 1B is obtained with these values. The angular variation of the lineshifts is one of the characteristic features that allow one to determine the coefficients A_{4m} in equation (2).

The experimental data also show smaller contributions to $g^2_{exp}(\theta, \phi)$ with periodicity of 60°, which could be fitted to sixth-order angular functions. The analysis of these contributions will not be considered here.

3. The magnetic Hamiltonian and the shifts of the ESR lines

In attempting to analyse the experimental results we describe the magnetic interactions in a single-crystal sample of CAC. They contain electronic $S = \frac{1}{2}$ spins coupled to their nuclear spins, interacting through exchange and dipole–dipole couplings, in the presence of an externally applied magnetic field B. In each unit cell i there are two species A and

B of electronic spins, S_{iA} and S_{iB}, at R_{iA} and R_{iB}, related by a screw axis operation and having anisotropic gyromagnetic tensors g_A and g_B. The Hamiltonian of the system is

$$H = H_Z + H_{ex} + H_{dd} + H_{hyp}. \tag{3}$$

In equation (3), the first term is the Zeeman interaction,

$$H_Z = -B \cdot M = \mu_0 B \cdot \sum_{i=1}^{N} (g_A \cdot S_{iA} + g_B \cdot S_{iB}) \tag{4}$$

where μ_0 is the Bohr magneton. The second,

$$H_{ex} = \tfrac{1}{2} \sum_{i\alpha,j\beta} J_{i\alpha,j\beta} S_{i\alpha} \cdot S_{j\beta} \tag{5}$$

with α, β = A, B, is the exchange interaction. The third,

$$H_{dd} = \tfrac{1}{2} \sum_{i\alpha,j\beta} S_{i\alpha} \cdot D(i\alpha, j\beta) \cdot S_{j\beta} \tag{6}$$

with

$$D(i\alpha, j\beta) = \mu_0^2 [g_\alpha \cdot g_\beta - 3g_\alpha \cdot \hat{R}_{i\alpha,j\beta})(\hat{R}_{ia,j\beta} \cdot g_\beta]/R_{i\alpha,j\beta}^3 \tag{7}$$

is the dipolar interaction betwen spin pairs. In equation (7), $R_{ia,j\beta} = R_{i\alpha} - R_{j\beta}$, and $\hat{R} = R/|R|$. The last contribution,

$$H_{hyp} = \sum_{i\alpha} S_{i\alpha} \cdot A_\alpha \cdot I_{i\alpha} \tag{8}$$

is the hyperfine interaction between the electronic spins $S_{i\alpha}$ and the nuclear spins $I_{i\alpha}$.
The total spin of the system is

$$S = \sum_{i=1}^{N} (S_{iA} + S_{iB}). \tag{9a}$$

Defining,

$$T = \sum_{i=1}^{N} (S_{iA} - S_{iB}) \tag{9b}$$

$$g = (g_A + g_B)/2 \tag{10a}$$

and

$$G = (g_A - g_B)/2 \tag{10b}$$

we can write the Zeeman interaction in equation (4) as

$$H_Z = H_{Z0} + H_Z'$$

where

$$H_{Z0} = \mu_0 S \cdot g \cdot B \tag{11a}$$

is the main contribution to H_Z, and

$$H_Z' = \mu_0 T \cdot G \cdot B \tag{11b}$$

is the 'residual Zeeman interaction'. Since H_{Z0} of equation (11a) is proportional to S of equation (9a), it is true that

$$[H_{Z0}, H_{ex}] = 0. \tag{12}$$

The full Hamiltonian of equation (3) can be written as

$$H = H_0 + H'$$

where

$$H_0 = H_{Z0} + H_{ex} \tag{13}$$

and

$$H' = H_Z' + H_{dd} + H_{hyp}. \tag{14}$$

We choose $\hat{z} = g \cdot \hat{b}/g$, with $\hat{b} = B/|B|$ and $g = |g \cdot \hat{b}|$. With this election $H_{Z0} = g\mu_0 B S_Z$ and H_{ex} of equation (5) are diagonal.

Typically in CAC, H_{Z0} and H_{ex} have similar magnitudes (0.3–1.0 K), while the components of H' are smaller contributions (0.01–0.10 K). Because of equation (12), the spectrum consists of a single 'exchange collapsed' line due to H_0 of equation (13). Since $[H', H_0] = 0$, H' of equation (14) shifts and broadens this resonance, and may be treated using perturbation theory when $H' < H_{ex}$ and $H' < H_{Z0}$.

In a magnetic resonance experiment the RF power absorbed by the sample is given by the imaginary part of the dynamic magnetic susceptibility $\chi''(\omega)$ which at high temperatures T ($\hbar\omega \ll kT$) can be written as

$$\chi''(\omega) = \frac{\omega V}{2kT} \int_{-\infty}^{\infty} \langle M_h(t) M_h \rangle e^{-i\omega t} \, dt \tag{15}$$

where $M_h = M \cdot \hat{h}$ is the component of the magnetic moment operator along the direction $\hat{h} = H_1/|H_1|$ of the RF field and V is the volume of the sample. The time dependence of M_h is produced by the full Hamiltonian H of equation (3):

$$M_h(t) = \exp(iHt/\hbar)M_h \exp(-iHt/\hbar).$$

The angular brackets in equation (15) indicate thermal averages defined as $\langle Op(t) \, Op \rangle = \text{Tr}(\rho \, Op(t) \, Op)$. The theory of Kubo and Tomita (KT) provides a method to calculate the ESR spectrum using equation (15). It gives

$$\chi''(\omega - \omega_0) = \frac{\omega V}{2kT} \langle M_+ M_- \rangle \int_{-\infty}^{\infty} \Phi(t) \exp[-i(\omega - \omega_0)t] \, dt$$

where $\omega_0 = g\mu_0 H/\hbar$ is the Larmor frequency, and the relaxation function $\Phi(t)$ is defined as

$$\Phi(t) = \exp\left(-\int_0^t K(t, t') \, dt'\right). \tag{16}$$

The function $K(t, t')$ was calculated by KT up to second order in H', and was extended

by Natsume *et al* in order to allow for contributions arising in low-symmetry magnetic systems [16, 17]. Defining

$$H'(t) = \exp(-iH_0 t/\hbar)H' \exp(iH_0 t/\hbar)$$

one obtains

$$K(t, t') = K^{HS}(t, t') + K^{LS}(t') \tag{17}$$

where

$$K^{HS}(t, t') = \frac{(t - t')}{\hbar^2 \langle S_+ S_- \rangle} \langle [H'(t'), S_+][S_-, H'] \rangle \tag{18}$$

will be called the 'high-symmetry' (HS) term. The 'low-symmetry' (LS) contribution $K^{LS}(t')$ is

$$K^{LS}(t') = \frac{-i}{2\hbar^2 \omega_0 \langle S_+ S_- \rangle} \{ b_-^2 \langle [H'(t'), S_+][S_+, H'] \rangle + b_+^2 \langle [H'(t'), S_-][S_-, H'] \rangle$$

$$\times \exp(-2i\omega_0 t') \} \tag{19}$$

with

$$b_\pm^2 = -(\hat{h} \cdot g \cdot e_\pm)^2 / |\hat{h} \cdot g \cdot e_+|^2 = 2(\hat{h} \cdot g \cdot e_\pm)^2 / |\hat{h} \cdot g \cdot g \cdot \hat{h}|. \tag{20}$$

In equation (20) the directions $e_\pm$ are related to the $\hat{x}$ and $\hat{y}$ axes used to define H_0 and H' by

$$e_\pm = \mp(\hat{x} \pm i\hat{y})/\sqrt{2}.$$

However, the $\hat{x}$ and $\hat{y}$ axes do not need to be defined explicitly, and only $\hat{z}$ is important, as expected.

$K^{LS}(t')$ of equation (19) does not depend on t and gives a non-zero contribution only when the symmetry of the spin distribution is low. It is important to remark that while $K^{HS}(t, t')$ of equation (18) depends only on the direction $\hat{b}$ of the applied static field, $K^{LS}(t')$ depends also on the direction $\hat{h}$ of the RF field H_1.

To calculate $K(t, t')$ of equations (17)–(19) we analyse the contributions to H' arising from operators linear (H_{hf} and H'_Z of equations (11b) and (8)) and bilinear (H_{dd} of equations (6) and (7)) in spin variables.

There are two sources of time dependence in the HS contributions. One is produced by H_{ex} and appears through the spin correlation functions. The other affects the non-secular terms H' (those not commuting with H_{Z0}) which are harmonically modulated at the Larmor frequency ω_0. Secular contributions to $K^{HS}(t, t')$ are real, and the non-secular are complex. Therefore, the secular contributions broaden, while the non-secular broaden and shift the resonance [12, 14]. Since we want to analyse resonance shifts, we will only deal with the non-secular HS contributions. Similarly, due to the imaginary factor i in equation (19), we will retain only the secular part of the LS term [17]. It can be proved that the contributions of H'_Z and H_{hf} and the non-secular parts of H_{dd} to $K^{LS}(t')$ of equation (19) are small compared with the non-secular HS terms, and can be neglected.

As explained previously, the resonance line was found to be shifted with reference to the position predicted by an effective gyromagnetic tensor. This shift was described by the function $\delta(\theta, \phi)$, which was fitted to fourth-order tesseral harmonics, as given by equation (2).

From the contributions to the shifts of the HS terms described previously, those giving rise to angular terms of fourth order involve only the non-secular parts of the residual Zeeman and the dipole–dipole interactions. It can be easily shown that H_{hf} does not introduce this kind of contribution. The secular part of the dipole–dipole interaction contributes through the LS term. In order to calculate these contributions explicitly it is necessary to propose a time dependence for the spin correlation functions. The main difficulty appears when describing the long-time behaviour of these functions. They are acceptedly regulated by spin diffusion, and consequently depend strongly on the magnetic dimensionality of the sample [14]. In the case of non-secular HS contributions the presence of $\exp(iq\omega_0 t)$ factors, rapidly fluctuating with the Larmor frequency, average to zero any slowly decaying behaviour, and only the short-time parts of the correlation functions become important. If we assume that in this range only self-correlations dominate the effects of the dipole–dipole interaction, the fourth-order contribution to the HS terms can be written as

$$K_{HS}(t, t')|_{4th} = (t - t')\left(Z_1(\hat{b})|_{4th} f_T(t') \exp(-i\omega_0 t) + \sum_{q \neq 0} M_q(\hat{b})|_{4th} \right.$$

$$\left. \times \exp(iq\omega_0 t)[f_S(t')]^2 \right) \tag{21}$$

where

$$f_T(t) = 2\langle T_Z^{ex}(t)T_Z\rangle/\langle S_+ S_-\rangle$$

and

$$f_S(t) = \langle S_{i\alpha Z}(t)S_{i\alpha Z}\rangle/\langle S_{i\alpha Z}^2\rangle$$

are time correlation functions associated with the residual Zeeman interaction and with a single spin, respectively. Also,

$$Z_1(\hat{b}) = \omega_0^2[\hat{b} \cdot \mathbf{G} \cdot \mathbf{G} \cdot \hat{b} - (\hat{b} \cdot \mathbf{g} \cdot \mathbf{G} \cdot \hat{b})^2/g^2]/2g^2$$

is the second moment of the residual Zeeman interaction. The $M_q(\hat{b})$ in equation (21) are the tensorial components of the second moment of the dipole–dipole interaction given by [20]:

$$M_q(b) = \frac{S(S + 1)}{24\hbar^2}(-1)^q[6 - q(q + 1)]\sum_{\alpha, j\beta} T_{-q}^2(0\alpha, j\beta)T_q^2(0\alpha, j\beta)$$

where

$$T_q^k(i\alpha, j\beta) = \frac{(2k + 1)^{1/2}}{2}\sum_{u, u'}\begin{pmatrix} 1 & 1 & k \\ u & u' & q \end{pmatrix} e_{-u} \cdot [D(i\alpha, j\beta) + (-1)^k D(j\beta, i\alpha)] \cdot e_{-u}.$$

In obtaining equation (21) the four-spin correlation functions have been decoupled into products of two-spin correlation functions. Only self-correlations were subsequently retained. This approximation affects only the functional part of the dipolar interaction. Although we are neglecting cross correlations in this case, it is necessary to stress that in the short-time regime some of these functions involving nearest neighbours may be of importance. Note that no approximations are involved in equation (21) in obtaining the contribution proportional to $f_T(t)$.
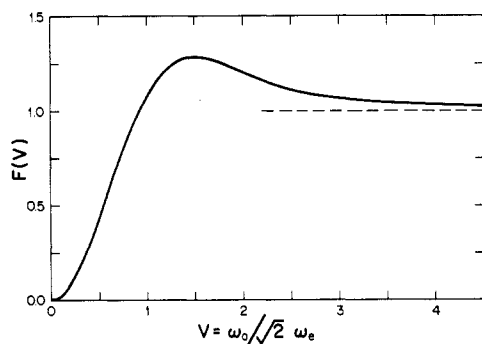
Figure 2. Function $F(V)$ defined in equation (23) displayed as a function of V. Values obtained from [21].

We assume a Gaussian decay for the correlation function [10]

$$f_r(t) = \exp(-\omega_r^2 t^2/2)$$

where ω_r can be either ω_T or ω_S (in general $\omega_T \neq \omega_S$). Then, we can perform the time integral involved in equation (16), and extend to ∞ the upper limit of the integral. In that case the only relevant contribution to $\Phi(t)$ is that containing t, since that containing t' adds only a t-independent phase factor to the integral. It is easy to show that under these circumstances

$$\delta_{HS}(\theta, \phi) = -\left((\hat{\boldsymbol{b}} \cdot \boldsymbol{g} \cdot \boldsymbol{G} \cdot \hat{\boldsymbol{b}})^2/2g^4|_{4\text{th}}\, F(V_1^T) \right.$$

$$\left. + \sum_m \mathsf{b}_m C_{4m}(\hat{\boldsymbol{b}})\,[F(V_1^S) - F(V_2^S)/4] \right) \tag{22}$$

where [21]

$$F(V_q^r) = \mathrm{Im} \int_0^\infty \exp(-\omega_r^2 t^2/2 + iq\omega_0 t)\,\mathrm{d}t = 2V_q^r \exp[-(V_q^r)^2] \int_0^{V_q^r} \exp(t^2)\,\mathrm{d}t \tag{23}$$

with

$$F(V_q^r) = F(V_{-q}^r).$$

We have used

$$V_q^T = q\omega_0/\sqrt{2}\omega_T \qquad \text{and} \qquad V_q^S = q\omega_0/\sqrt{2}\omega_S$$

and

$$b_m = (9g^4\mu_0^4/35\omega_0^2) \sum_{\alpha, j\beta} (1/R_{0\alpha,j\beta}^6)\, C_{4m}(\hat{\boldsymbol{R}}_{0\alpha,j\beta}).$$

The function $F(V)$ is plotted in figure 2 as a function of V for $0 < V < 2$. For larger values of V, $F(V) = 1$. This function has a maximum at $V \simeq 1.5$, and tends to zero for $V \to 0$. Thus, for large exchange frequencies the shift $\delta(\theta, \phi)$ will vanish. It is worth while stressing that our theory is valid as long as the exchange is large enough to collapse the structures of the lines, i.e. when $\omega_{ex} > H'/\hbar$. From the experimental point of view the model we have just described depends only on two unknowns, $F(V_1^T)$ and $(F(V_1^S) - F(V_2^S)/4$. The angular functions giving the contributions to the second moments $Z_1(\hat{\boldsymbol{b}})$ and $M_q(\hat{\boldsymbol{b}})$ of the residual Zeeman and dipole–dipole interactions can be easily calculated using ESR results ($\boldsymbol{g}$ and $\boldsymbol{G}$ tensors) and crystallographic data.

Considering the contributions arising from $K_{LS}(t)$, even in the simple case of an isotropic g-factor we are faced with the time dependence of the correlation functions. However, it is the long-time behaviour of these functions that is important in this case, where we consider secular contributions. We follow closely the formulation given by Richards [14], who assumes that after a characteristic time τ_c the correlation functions are governed by spin diffusion. In this case the dominant contribution comes from the $q = 0$ modes in the first Brillouin zone and we arrive at

$$\delta_{LS}(\theta, \phi) = (9g^4 \mu_0^4/16\omega_0^2) \left(\sum_{\alpha,j\beta} \frac{1}{R^3_{0\alpha,j\beta}} [1 - 3(\hat{z} \cdot \hat{R}_{0\alpha,j\beta})^2] \right)$$

$$\times \left(\sum_{\alpha,j\beta} \frac{1}{R^3_{0\alpha,j\beta}} [1 - (\hat{z} \cdot \hat{R}_{0\alpha,j\beta})^2 - 2(\hat{h} \cdot \hat{R}_{0\alpha,j\beta})^2] \right) \Big|_{4\text{th}} F_{LS}(t) \tag{24}$$

where

$$F_{LS}(t) = (1/t) \int_{\tau_c}^{t} \mathrm{d}t' \left(\frac{1}{\Omega_{BZ}} \int_{BZ} \exp(-Dq^2 t') \,\mathrm{d}q \right)$$

with D as the diffusion constant. The magnetic dimensionality d enters through the integral over the magnetic Brillouin zone, as in Richards' theory. We will treat $F_{LS}(t)$ as an adjustable parameter, and examine the angular variation of $\delta(\theta, \phi)$ given by equations (21) and (22).

Although there is a dependence on the direction of the microwave field, the fourth-order contribution to Φ_{LS} does not arise from these terms in each of the planes analysed in the experiments. This is because in our experiments $\hat{h}$ is always fixed, and perpendicular to the plane where $\hat{b}$ is varied. Thus the fourth-order angular variation within each plane comes from the first factor within curly brackets, and the first two terms of the second factor.

We give in table 2 the results for the angular contributions to the A_{4m} corresponding to each of the mechanisms considered. The tensors g and G, defined in equations (10a) and (10b), needed to calculate $Z_1(\hat{b})$ were obtained from the values of the components of g^2 given in table 2. We assume that g is a symmetric tensor and that g_A and g_B have axial symmetry. This last assumption allows us to obtain the values of the components xy and zy of g_A and g_B, and then the tensor G (see [3–5]). The crystallographic data [22] for Cu(L-Ala)$_2$ were used to calculate $M_q(\hat{b})$. The results of table 2 must be combined with their corresponding $F(V)$ and F_{LS} factors in order to obtain the theoretical appropriate A_{4m}.

Table 2. Values of the contributions to the angular factors from each of the mechanisms considered in the text.

m	Residual Zeeman, $A_{4m}/F(V_\uparrow^1)$	HS dipole–dipole, $A_{4m}/[F(V_s^1) - F(V_s^2)/4]$	LS dipole–dipole, A_{4m}/F_{LS}
0	0.208×10^{-3}	-0.645×10^{-3}	0.627×10^{-2}
1	-0.299×10^{-3}	-0.348×10^{-5}	-0.679×10^{-4}
2	0.357×10^{-3}	0.211×10^{-3}	-0.811×10^{-2}
3	-0.790×10^{-3}	0.362×10^{-5}	0.470×10^{-4}
4	0.661×10^{-3}	-0.997×10^{-3}	0.785×10^{-2}

4. Discussion and conclusions

In order to obtain the predictions of the model for the parameters A_{4m}, we should first estimate values for the coefficients $F_Z = F(V_T^1)$, $F_D = [F(V_S^1) - F(V_S^2)/4]$ and F_{LS}. The values of F_Z and F_D may be obtained from figure 2 in terms of the ratios between the microwave frequency ω_0 and the exchange frequencies ω_T and ω_S, respectively. They should be between 0 and a number of the order of 1, and always positive. Considering the results for Cu(L-Ala)$_2$ reported in [1], both F_Z and F_D should be close to 1. In the case of the LS contribution we have closely followed the procedure given by Richards in dealing with contributions to the linewidths arising from the secular parts of the HS terms. This makes $F_{LS}(t)$ a time-dependent factor accompanying the angular variation of δ_{LS}, which in turn also results in a function of time. Since we are interested in the description of the central portion of the resonance, $F_{LS}(t)$ should be evaluated for $t \sim 1/\delta\omega$, where $\delta\omega$ is the linewidth. This assumes that F_{LS} is a slowly varying function in this region of t, and can be taken as a parameter to be obtained from the experiments. This approach was adopted in describing the LS contribution.

The values of the different contributions to the A_{4m} were obtained from the F coefficients estimated as described above, and the results given in table 2. We obtain the same order of magnitude as the experimental value given in table 1. However, it is not possible to obtain an overall agreement with all the parameters with any unique set of values for the F coefficients. In the case of A_{41} it is not even possible to get the sign of the experimental value.

The sources for the discrepancies between theoretical and experimental results may be of various kinds. Since we have analysed all the contributions to the interaction Hamiltonian H' of equation (14), the discrepancy should arise from some of the approximations made during the calculations.

One strong possibility for the failure is the assumptions adopted to select either the short- or the long-time behaviour of the correlation functions.

In the case of the residual Zeeman interaction, no approximations have been made on the correlation functions except a Gaussian form in the short-time regime. This may introduce only small errors in the values of $F(V_T^1)$. It is worth mentioning that in the zx plane the residual Zeeman interaction does not give any contribution for symmetry reasons. In this plane the angular variation of the fourth-order shift of equation (2) is given by

$$\delta(\theta) = (\sqrt{35}/64)(\sqrt{35}\, A_{40} - 2\sqrt{7}\, A_{42} + A_{44}) \cos 4\theta$$
$$+ (\sqrt{70}/32)(\sqrt{7}\, A_{41} - A_{43}) \sin 4\theta$$

where θ is the azimuthal angle. This vanishes identically if only the residual Zeeman contribution of table 2 is considered. Then, in the zx plane only the dipole–dipole interaction contributes to the (HS and LS) shifts. No agreement is obtained, however, even in this simple situation. Thus we can trace back a source of disagreement in the assumptions involved when considering H_{dd}. In this case the coupling scheme of the four-spin correlations plus a specific selection of the correlation functions alter the angular dependence of the angular factors. One of the sources for the disagreement could be associated with the neglect of cross correlations between neighbouring spins in the short-time regime for HS contributions. These cross correlations can strongly change the angular functions, particularly when summed over several near neighbours. This is because non-secular contributions involve time integrals, which are modulated at the

Larmor frequency (or its second harmonic). The cross correlation function is zero at $t = 0$, and has a maximum at a time near to that required for a spin excitation in one spin to reach the neighbouring spin [18]. If the width of this maximum is similar to one cycle of the Larmor frequency, there will be a non-zero contribution to the time integral. This problem is not important when analysing linewidths where non-secular contributions are small, or less important than the secular ones.

Another source for the discrepancies may be a poor description of the correlation function in the diffusion regime, involved in the LS contributions. This is particularly important in the cases of the parameters A_{40}, A_{42} and A_{44}, where the contributions of the LS terms are large.

More experimental data on the lineshifts is needed to guide the calculations. For example, detailed lineshift measurements at different microwave frequencies may be helpful in order to clarify the role of the different contributions, using their known frequency dependence. Also, a more elaborate theoretical analysis of the correlation functions is needed.

As a conclusion, it is important to remark that copper–amino acid complexes are interesting systems showing several features of unexpected behaviour not observed before in other paramagnets.

References

[1] Calvo R, Novak M A, Oseroff S B and Symko O G 1987 *Japan. J. Appl. Phys.* **26** S3 861
[2] Newman P R, Imes J L and Cowen J A 1976 *Phys. Rev.* B **13** 4093
[3] Calvo R and Mesa M A 1983 *Phys. Rev.* B **28** 1244
[4] Calvo R, Mesa M A, Oliva G, Zukerman-Schpector J, Nascimento O R, Tovar M and Arce R 1984 *J. Chem. Phys.* **81** 4584
[5] Calvo R, Isern H and Mesa M A 1985 *Chem. Phys.* **100** 89
[6] Gennaro A M, Levstein P R, Steren C A and Calvo R 1987 *Chem. Phys.* **111** 431
[7] Levstein P R, Steren C A, Gennaro A M and Calvo R 1988 *Chem. Phys.* **120** 449
[8] Steren C A, Gennaro A M, Levstein P R and Calvo R 1990 *J. Phys.: Condens. Matter* at press
[9] Kubo R and Tomita K 1954 *J. Phys. Soc. Japan.* **9** 888
[10] Anderson P W 1954 *J. Phys. Soc. Japan.* **9** 316
[11] Abragam A 1961 *The Principles of Nuclear Magnetism* (Oxford: Oxford University Press)
[12] Pake G E 1962 *Paramagnetic Resonance* (New York: Benjamin)
[13] Atherton N M 1973 *Electron Spin Resonance, Theory and Applications* (New York: Wiley)
[14] Richards P M 1975 *Local Properties at Phase Transitions* (Bologna: Editrice Compositori) p 539
[15] Svare I and Seidel G 1964 *Phys. Rev.* **134** A172
[16] Nagata K and Tazuke Y 1972 *J. Phys. Soc. Japan* **32** 337
[17] Natsume Y, Sasagawa F, Toyoda M and Yamada I 1980 *J. Phys. Soc. Japan* **48** 50
[18] Levstein P R, Pastawski H M and Calvo R *J. Phys.: Condens. Matter* submitted
[19] Prather J L 1961 *National Bureau of Standards Monograph* 19, Washington
[20] Passeggi M C G and Calvo R 1989 *J. Magn. Reson.* **81** 382
[21] Abramowitz M and Stegun I A 1970 *Handbook of Mathematical Functions* (New York: Dover)
[22] Dijkstra A 1966 *Acta Crystallogr.* **20** 588