Prediction of high-frequency electron paramagnetic resonance spectra of spin S = 3/2, 5/2 systems

Hanqing Wu

Department of Chemistry, University of Wisconsin-Milwaukee, Milwaukee, Wisconsin

By the use of the universal EPR simulation program created by the author, spin S = 3/2 and S = 5/2 systems are studied and their simulated EPR spectra at high frequencies (Q-band for 35 GHz and W-band for 95 GHz) are presented here. The mononuclear Fe^{3+} in rubredoxin, isolated from Pseudomonas oleovorans (which is an S = 5/2 system with D = 1.76 cm^{-1} and E/D = 0.28), is extensively studied by EPR spectrum simulation at the Q-band, W-band, and "Z"-band. The molybdenum- and iron-containing protein (MoFe protein), which has g values at g = 4.32, 3.65, and 2.01 (S = 3/2, D = 6.0 cm^{-1}, and E/D = 0.055) at the X-band, is also studied by EPR spectrum simulation at high frequencies. © 1997 by Elsevier Science Inc.

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INTRODUCTION

Electron spin resonance (ESR), also called electron paramagnetic resonance (EPR), gives valuable and detailed information about the structure and properties of paramagnetic systems in gaseous, liquid, and solid phase, i.e., for systems that have nonzero electron magnetic moments. Spectrometers for electron paramagnetic resonance (EPR) operating at about 9 GHz (X-band) are usual, but other frequencies are also available, both higher and lower. The main advantages of a higher frequency are increased resolution and reduction of second-order effects, but it is much more difficult to operate. The sweep-range is selected so as to cover the likely region of interest, and a marker with a known g value is often used as a reference. The EPR spectra

depend on the location of resonant fields, given via the Bohr frequency relation and the squared magnitudes of the transition dipoles—the matrix elements between the initial and final states of gβ times the spin component in the direction of the detection field, which is perpendicular to **B** in the usual experiment. The spin Hamiltonian equation is given by

$$H = \beta B \cdot g \cdot S + S \cdot D \cdot S + \text{(terms fourth-order in spin)}$$

Here **g** and **D** are symmetric tensors; **D** gives the fine structure. In this EPR spectrum simulation program, D and E have the following definitions:

$$S \cdot D \cdot S = D_x S_x^2 + D_y S_y^2 + D_z S_z^2$$
$$= D(S_z^2 - \tfrac{1}{3}S^2) + E(S_x^2 - S_y^2)$$
$$+ \tfrac{1}{3}S^2(D_x + D_y + D_z)$$

where $D = D_z - \tfrac{1}{2}(D_x + D_y)$, $E = \tfrac{1}{2}(D_x - D_y)$, and S^2 can be written as $S(S + 1)$. If taking the matrix **D** to be traceless, $D_x + D_y + D_z = 0$. So, the spin Hamiltonian equation can be written as

$$H = g\beta B \cdot S + D[S_z^2 - \tfrac{1}{3}S(S + 1)] + E(S_x^2 - S_y^2)$$

If both sides in the above equation are divided by the frequency υ_0, and $\lambda = E/D$, then the equation can be modified as

$$(H/\upsilon_0) = g\beta(B/\upsilon_0)S + (D/\upsilon_0)[S_z^2 - \tfrac{1}{3}S(S + 1)] + \lambda(D/\upsilon_0)(S_x^2 - S_y^2)$$

In this article, the EPR simulation program is created on the basis of Refs.[1-8]; some of the results are also presented elsewhere.[9,10] The simulated EPR spectra of S = 3/2, 5/2 at high frequency with different D and E/D values are presented and also discussed. Specific systems are also discussed.[11,12]

RESULTS

The author has simulated the EPR spectra of spin S = 3/2 and S = 5/2 systems with D = 1.0 cm^{-1}, 10.0 cm^{-1} and

Table 1. Adjusted D value at different frequencies

D value (in cm^{-1})			
X-band (9.3 GHz)	Q-band (35 GHz)	W-band (95 GHz)	"Z"-band (372 GHz)
>1.0	>3.8	>10	>40
0.4	1.5	4.1	16
0.3	1.1	3.1	12
0.2	0.75	2.0	8
0.1	0.38	1.0	4

E/D = 0.00, 0.10, 0.33 for both the X-band and the Q-band (see Color Plates 1–3, and finds that when D > frequency (D = 1 cm^{-1} at the X-band, D = 10 cm^{-1} at both the X-band and Q-band), the simulated EPR spectra are similar to each other, that is, only 1 → 2, 3 → 4 (and 5 → 6) transitions can be observed; when D ≈ frequency (D = 1 cm^{-1} at the Q-band), additional transitions can be observed. Thus the spectra of spin S = 3/2 and S = 5/2 systems with D = 1 cm^{-1} at the Q-band are different from those under D > frequency conditions. The curves for some transitions in the simulated spectra for Q-band appear rippled because the steps for theta and phi (equaling 2°) are larger and the derivative width is small for Q-band EPR simulation (the author set the derivative width as 100 MHz for both the X-band and the Q-band); Q-band and W-band EPR simulation with larger derivative widths (1 000 and 3 000 MHz) for S = 3/2 and S = 5/2 systems can also be obtained (the graphs are not shown here). The author provides two methods with which to predict high-frequency EPR spectrum simulation for S = 3/2 and S = 5/2 systems: one is to simulate directly the Q-band, W-band, and even "Z"-band EPR spectra by increasing the derivative width and field step by a factor that is the ratio of high frequency to 9.3 GHz (the X-band); the other method is to use an adjusted D value (which is the real D value reduced by the factor mentioned above) and simulate the EPR spectrum at the X-band. The author has found the second method is much more convenient, thus, most of the Color Plates shown are derived using that method.

Direct high-frequency EPR spectrum simulation can be done if both D and E/D values are given. Here are two systems: one specific system is the mononuclear Fe^{3+} in rubredoxin, which is isolated from *Pseudomonas oleovorans* and has an S = 5/2 system with D = 1.76 cm^{-1} and E/D = 0.28; the other specific system is the molybdenum- and iron-containing protein (MoFe protein), which has g values at g = 4.32, 3.65, and 2.01 (S = 3/2, D = 6.0 cm^{-1},

and E/D = 0.055). Color Plate 4 shows the simulated EPR spectra of two systems at the W-band with two different derivative widths.

From the modified spin Hamiltonian equation, the authors can predict a high-frequency EPR spectrum at a convenient band (like the X-band) by adjusting the D parameter. It is clear that a small D value at low frequency and a large D value at high frequency can obtain the same value of the ratio, which is the D value over frequency [for example, D/frequency = (F*D)/(F*frequency)]. Table 1 lists the adjusted D values at Q-, W-, and "Z"-bands (high frequencies) corresponding to the D values at X-band (low frequency), and we can predict high-frequency EPR spectra at Q-, W-, and "Z"-bands by simulation EPR spectra at the X-band by the use of adjusted D values.

Both systems mentioned above easily obtain their simulated EPR spectra at the X-band (by using a derivative width of 300 MHz); to predict their high-frequency EPR spectra, the author can easily decrease the D value by a certain factor, depending on the band chosen for prediction. Table 2 gives the adjusted D values at different bands. The deduction factors (F) are also calculated, which can also be used for expanding the *x* axis by multiplication of this factor if the relevant band EPR spectrum needs to be plotted.

The author can predict that: for an S = 3/2 system with D = 6.0 cm^{-1} and E/D = 0.055, the predicted EPR spectra at the Q-band and W-band are the same as that at the X-band, but the predicted EPR spectrum at the "Z"-band is totally different from that at the X-band. Not only do additional transitions appear, but the signal positions for the transition between 1 and 2 are also shifted (see Color Plate 5, left side). For S = 5/2 system with D = 1.76 cm^{-1} and E/D = 0.28, the predicted EPR spectrum at the Q-band is almost the same as that at the X-band, but the predicted EPR spectra at the W- and "Z"-bands are totally different from that at the X-band; not only do additional transitions appear, but also the signal positions for transition between 3 and 4 are shifted (see Color Plate 5, right side). By comparing Color Plate 4 and Color Plate 5, the author can know that both methods can produce the same results known from the W-band EPR spectra simulation in both systems.

CONCLUSION

1. When D > frequency, the simulated EPR spectra are the same: Only 1 → 2, 3 → 4, (5 → 6) transitions can occur for spin S = 3/2 (S = 5/2) systems. When D ≈ frequency (by using high frequency at the Q- or W-band), other transitions like 2 → 3 (4 → 5) for spin S = 3/2 (S = 5/2) can be obtained by EPR spectrum simulation.

Table 2. Reduced D value and its reduction factor (F) at different bands

	D value (in cm^{-1})			
Spin system	X-band	Q-band	W-band	"Z"-band
S = 5/2, E/D = 0.28	1.76	0.47	0.17	0.044
S = 3/2, E/D = 0.055	6.0	1.59	0.59	0.15
Reduction factor	9.3/9.3 = 1.00	35/9.3 = 3.76	95/9.3 = 10.2	372/9.3 = 40.0

Different D and E/D values also affect the position and relative strength of the signal.

2. The simulated EPR spectrum from direct simulation of EPR spectrum at high frequency is same as that from indirect simulation of EPR spectrum at the X-band by the use of an adjusted D value. By the latter method, any EPR spectrum at high frequency can be easily predicted.

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