

Why spin = 1, 2 species have no electron paramagnetic resonance signal under normal conditions: Possible detection by electron paramagnetic resonance at frequency close to D value?

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A universal EPR simulation program has been created by the author, which is based on the following spin Hamiltonian equation:

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

where D and E are the axial and rhombic zero-field splitting parameters, respectively. The program can be used for simulation of EPR spectra with half-integer electronic spin ($S = n/2$, $n = 3, 5, 7, 9$) systems. In this article, the integer spin ($S = n/2$, $n = 2, 4$) systems are also considered. The EPR simulation results show that when $D > \text{frequency}$, no EPR signal can be seen from EPR simulation; when $D \approx \text{frequency}$, whichever X/Q/W-band is used, the EPR signal can be seen on the basis of the simulated EPR results presented. © 1996 Elsevier Science Inc.

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INTRODUCTION

Electron paramagnetic resonance (EPR), also known as electron spin resonance (ESR) and electron magnetic reso-

nance (EMR), is widely used in different systems. In biological systems, there are many metal proteins with odd-spin species that can be detected by EPR; there are also EPR-“silent” species with even spin^{1,2} or diamagnetic species with spin equal to zero. The systems can be divided into two types: Kramers systems (Fe^{3+} , Fe^+ , and spin-coupled clusters with half-integer electronic spin, etc.) and non-Kramers systems (Fe^{2+} , Fe^{4+} , and clusters with integer or zero spin, etc.). The spin $S = 1, 2$ systems are non-Kramers systems. In this article, the EPR spectrum simulation program used is created on the basis of Refs. 1–8; this universal EPR spectrum simulation program, which is successful in simulation of EPR spectra with high odd-spin ($S = 3/2, 5/2, 7/2, 9/2$) systems,^{9–11} is also used for simulation of EPR spectra with even-spin ($S = 1, 2$) systems. When the D value is larger than the frequency, there is no transition between any pair of transitions, but when D is close to or lower than the frequency,¹² some transitions can be observed. Some simulated EPR spectra are presented and discussed in this article.

RESULTS

Table 1 presents a comparison of D values with microwave quantum $h\nu_0$ (or frequency), which gives the quantities in some of the units commonly employed. The author has simulated the EPR spectra of spin $S = 1$ under different conditions: If the X-band frequency is used (9.3 GHz), when $D > 0.4 \text{ cm}^{-1}$, no transition can be obtained from any transition ($1 \rightarrow 2, 1 \rightarrow 3, 2 \rightarrow 3$ for $S = 1$); when D is lower than 0.3 cm^{-1} , a strong transition between 1 and 2 occurs

Color Plates for this article are on pages 330–333.

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Table 1. Values of D and $h\nu$ in different units

Unit	D value	X-Band	$h\nu$ Q-Band	W-Band
GHz	30.0	9.3	35	95
cm^{-1}	1.0	0.31	1.17	3.17
K	1.44	0.44	1.68	4.56

(see Color Plate 1). The transition probability between 1 and 3 is stronger than the transition probability between 1 and 2 when $D = 0.2 \text{ cm}^{-1}$, $E/D = 0.0$ (see the right-hand side in Color Plate 1). From Color Plate 2, it can be seen that the signal or effective g value of either the $1 \rightarrow 2$ or $1 \rightarrow 3$ transition is sensitive to the D value when it is lower than the frequency (0.3 cm^{-1} for the X-band). At different E/D values ($E/D = 0.03, 0.06, 0.09, 0.1, 0.2, 0.3$), it can also be seen that different EPR signals appear with different strengths (see Color Plate 2).

The same results can also be seen from an EPR simulation of the spin $S = 2$ system. When $D > \text{frequency}$, no EPR signal can be seen in an EPR spectrum simulation. When the D value is lower (see Color Plate 3), high transition probabilities of $1 \rightarrow 2, 2 \rightarrow 3, 3 \rightarrow 4$ can be seen for $D = 0.2 \text{ cm}^{-1}$ and $E = 0.0$; the transition probability of $3 \rightarrow 4$ is relatively low, and other transition probabilities are almost

negligible. Color Plate 3 also shows how E/D values ($E/D = 0.05, 0.10, 0.20, 0.25, 0.30$) affect the signal or effective g value of transitions of $1 \rightarrow 2, 2 \rightarrow 3, 3 \rightarrow 4$, and $4 \rightarrow 5$.

The W-band and Q-band EPR simulations of spin $S = 1, 2$ systems are also presented here for $D = 1.0 \text{ cm}^{-1}$ and $E/D = 0.0$. Color Plate 4 shows the simulated EPR spectra of the spin $S = 1$ system and spin $S = 2$ system at the Q-band (see the left-hand side in Color Plate 4) and the W-band (see the right-hand side in Color Plate 4). EPR spectra at different E/D values can also be simulated (data not provided here).

One paper¹² shows that the triplet ($S = 1$) and quintet ($S = 2$) state for some high-spin organic molecules can be detected by EPR; these high-spin organic molecules have $|D|$ values less than 0.3 cm^{-1} (X-band frequency). On the basis of the given zero-field splitting parameters (D and E or E/D), the simulated EPR spectra are presented here (see Color Plate 5) for $S = 1$ with $|D| = 0.0507 \text{ cm}^{-1}$, $|E| = 0.0005 \text{ cm}^{-1}$ ($E/D \approx 0.01$) and $S = 2$ with $|D| = 0.0116 \text{ cm}^{-1}$, $|E| = 0.00215 \text{ cm}^{-1}$ ($E/D \approx 0.185$). The g value, frequency, and derivative width are shown in the captions to the Color Plate. By comparing Color Plate 5 with the experimental EPR spectra in Figure 1 of Ref 12, it can be seen that the signal positions match each other. Owing to the small $|D|$ value, other transitions occur with weak EPR signals known from EPR simulation of these transitions (see Figure 1).

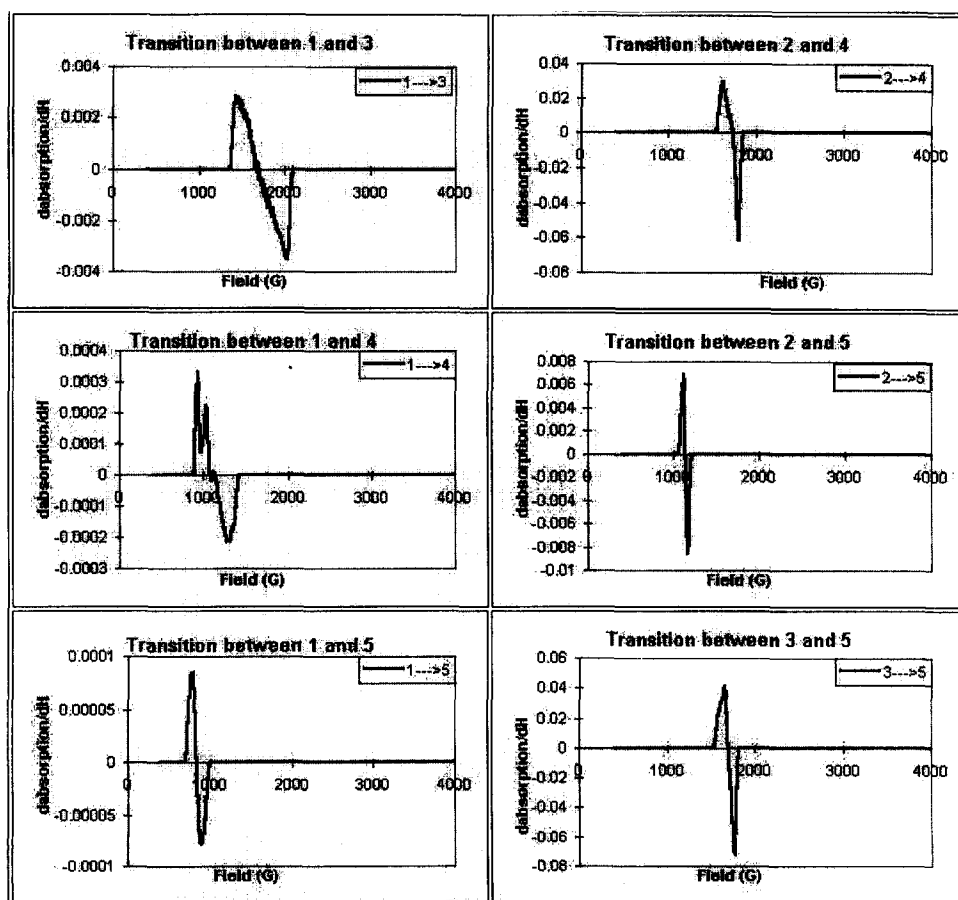


Figure 1. Transitions among $1 \leftrightarrow 3, 1 \leftrightarrow 4, 1 \leftrightarrow 5, 2 \leftrightarrow 4, 2 \leftrightarrow 5$, and $3 \leftrightarrow 5$ for $S = 2$ with $|D| = 0.0116 \text{ cm}^{-1}$, $|E| = 0.00215 \text{ cm}^{-1}$ (same condition as in Color Plate 5 for $S = 2$ system).

DISCUSSION

As an example of the high-spin ferrous state ($S = 2$), for symmetries lower than trigonal or tetragonal the fivefold degeneracy of the spin quintet is totally removed by the zero-field splitting term (D , E is nonzero). The metal proteins studied so far exhibit fine-structure splitting in the range from 10 to 50 cm^{-1} (it is reported that $D = 8.0 \text{ cm}^{-1}$ for ferrous rebredoxin, which has spin $S = 2$); that is why there is no EPR signal for the spin $S = 2$ systems under "normal" conditions ($D \gg \text{frequency}$). From Table 1, it can be seen that even with the use of the Q-band or W-band of a spectrometer, it is still difficult to detect the EPR signal from spin $S = 2$ species in proteins. The highest frequency at which the EPR spectrum of $S = 5/2$ methemoglobin has been measured is 372 GHz,^{8,13} which corresponds to 12.4 cm^{-1} ; this means part of the spin $S = 2$ species of proteins or others might be detected by EPR at as high a frequency as 372 GHz (the author calls it the "Z" band frequency). The EPR spectrum simulation at this frequency or above can be done easily by the program of the author, created on the basis of another paper, because high frequency EPR spectra of spin $S = 1, 2$ systems with known zero-field splitting parameters can also be predicted by two methods proposed in Ref. 11.

CONCLUSION

1. When $D > \text{frequency}$, no transitions can occur for spin $S = 1, 2$ systems and no EPR signal can be observed. Normally, the species with spin $S = 1, 2$ systems have D values larger than the frequency, and so the spin $S = 1, 2$ species have no EPR signal and are "silent."
2. When $D \approx \text{frequency}$ (by using high frequency at the Q- or W-band), spin $S = 1, 2$ systems are never silent again and different transitions can be obtained by EPR spectrum simulation. Different D and E/D values also affect the position and relative strength of the signal.

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