SUPPORTING INFORMATION

Spinning Molecules, Spinning Spins: Modulation of an Electron Spin Exchange Interaction in a Highly Anisotropic Hyperfine Field

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1. Theory

To understand the effects of J modulation in the highly anisotropic hyperfine field of the copper-porphyrin dimer system, some basic equations are necessary. Simulation of biradicaloid steady-state EPR (SSEPR) spectra is accomplished by 1) selecting an appropriate spin Hamiltonian and basis set, 2) diagonalizing the Hamiltonian to obtain its eigenvalues, and 3) calculating the resonant EPR frequencies and transition probabilities from the energy differences for the allowed transitions using the standard selection rule: an allowed transition has a change in electron spin quantum number of ±1, and a change in nuclear spin quantum number of 0.¹

Eq 1 shows the spin Hamiltonian for a monoradical, which is the sum of the Zeeman and hyperfine interactions. Here $\beta_e$ is the Bohr magneton, $B_0$ is the applied external magnetic field, $g_1$ is the electron g-factor or chemical shift, $S_{1z}$ is electron spin along the axis of quantization forced by the applied magnetic field, along $z$, $a_i$ is the hyperfine coupling constant, and $I_{zi}$ is the nuclear spin projection along the applied field direction ($z$).

$$H = \beta_e \hbar^{-1} B_0 (g_1 S_{1z}) + \sum a_i S_{zi} I_{zi}$$ (1)
For a biradical species, the Hamiltonian is rewritten to account for the spin exchange interaction $(J_{\text{avg}})$ between the radical centers. This is the same spin Hamiltonian that used in the development of spin–correlated radical pair (SCRP) theory.\(^2\text{–}^4\)

\[
H = \beta \hbar^{-1} B_o(g_1 S_{1z} + g_2 S_{2z}) + \sum a_i S_{1z} I_{iz} + \sum a_i S_{2z} I_{iz} - J_{\text{avg}}(\frac{1}{2} + 2S_1 S_2) \tag{2}
\]

The Hamiltonian features the Zeeman and hyperfine terms for both sides of the biradical, in addition to the exchange interaction $J_{\text{avg}}$, which it is important to note here is written in the Dirac formalism, leading to a singlet–triplet energy gap of $-2J_{\text{avg}}$ and a singlet ground state when the value of $J_{\text{avg}}$ is negative.

The most appropriate basis set is a singlet state and three triplet states ($|S\rangle$ and $|T_+\rangle$, $|T_-\rangle$, and $|T_0\rangle$). The eigenfunctions and energies obtained after diagonalization are given below.

Each individual alignment of the nuclear spins of the system can be written as an independent four level system electron spin system, each with its own nuclear sub-state. In other words, the spin Hamiltonian can be symmetry factored to a set of 4 x 4 matrices that are easily diagonalized and the EPR spectrum is calculated for each set of 4 biradical transitions and then summed.

\[
|1\rangle = |T_+\rangle \tag{3}
\]
\[ \epsilon_1 = v_0 - J_{avg} + \sum (a_i m_i - a_j m_j)/2 \] (4)

\[ |2\rangle = \cos \theta |S\rangle + \sin \theta |T_0\rangle \] (5)

\[ \epsilon_2 = \Omega \] (6)

\[ |3\rangle = -\cos \theta |S\rangle + \sin \theta |T_0\rangle \] (7)

\[ \epsilon_3 = -\Omega \] (8)

\[ |4\rangle = |T_-\rangle \] (9)

\[ \epsilon_4 = -v_0 - J_{avg} - \sum (a_i m_i - a_j m_j)/2 \] (10)

Here \( v_0 \) is the center of the biradicaloid spectrum, defined rigorously as the average position defined by the two g–factors (eq 11). The terms \( m_i \) and \( m_j \) are the nuclear spin quantum numbers associated with a particular nucleus or set of equivalent nuclei.

\[ v_0 = \beta B_0(g_1 + g_2)/2 \] (11)

\[ \cos 2\theta = J_{avg}/\Omega \] (12)

\[ \sin 2\theta = q/\Omega \] (13)

\[ \Omega = \left( J_{avg}^2 + q^2 \right)^{1/2} \] (14)

\[ q = \left[ \beta B_0(g_1 - g_2) + \sum (a_i m_i - a_j m_j) \right]/2 \] (15)
The following new terms are defined: \( q \) is the Larmor precession frequency difference between radical centers, a result of the local magnetic field differences between spin centers, \( 2 \)

\( \Omega \) is the energy difference between the two new states (|2\rangle and |3\rangle) that arise from the mixing, due to \( q \), between |S\rangle and |T_0\rangle. We assume a high field limit that excludes mixing between |S\rangle and |T_+\rangle or T_. The allowed transition energies are given as:

\[
E_{21} = \nu_0 + \left(\frac{1}{2}\right)\sum (a_i m_i - a_j m_j) - J_{avg} + \Omega
\]

(16)

\[
E_{31} = \nu_0 + \left(\frac{1}{2}\right)\sum (a_i m_i - a_j m_j) - J_{avg} - \Omega
\]

(17)

\[
E_{42} = \nu_0 + \left(\frac{1}{2}\right)\sum (a_i m_i - a_j m_j) + J_{avg} - \Omega
\]

(18)

\[
E_{43} = \nu_0 + \left(\frac{1}{2}\right)\sum (a_i m_i - a_j m_j) + J_{avg} + \Omega
\]

(19)
Figure S1 contains an energy level diagram of these electronic states and allowed transitions. For the transition probabilities, there are two sets of equivalent probabilities:

\[ t_{p1} (1\rightarrow2, 2\rightarrow4) = (\cos(0.5 \times \arctan(q/J)))^2 \]  
\[ t_{p2} (1\rightarrow3, 3\rightarrow4) = (\sin(0.5 \times \arctan(q/J)))^2 \]  

The additional terms that describe the $J_{mod}$ theory have been presented in detail previously. Using the Redfield formalism, we treat the line shape as an effect of J modulation.
using perturbation theory to add $T_1$ and $T_2$ relaxation processes. Two simple equations result, expressed in terms from the spin Hamiltonian diagonalization procedure described above, which are easy to incorporate into the simulation program for EPR spectra of biradicals and biradicaloids.

$$T_1^{-1} = 4\langle V^2 \rangle \tau_e \left(q^2 / \omega^2\right)$$

$$T_2^{-1} = 2\langle V^2 \rangle \tau_e (1 \pm J / \omega)$$

The correlation times for the paddle-wheel motion of the porphyrin rings as a function of temperature were obtained from the Arrhenius equation:

$$k_r = A e^{-E_a/kT}$$

Where the terms have their usual meanings: $k_r$ is the rate constant for the motion, $A$ is a pre-exponential factor assumed to be $10^{10}$ s$^{-1}$, $k$ = Boltzmann's constant. The term $E_a$ is the activation energy for the rotational motion obtained from the slope of the plots of $J_{\text{mod}}$ vs. $1/T$, where $T$ is the absolute temperature. The correlation times reported in the paper are the inverse of $k_r$. 
2. Additional Simulations

**Figure S2**: Experimental and simulated spectra for PCu-PZn-PCu in toluene at 298K (~1 µM), in the same layout as Figure 4 in the main body of the paper.

**Figure S3**: Experimental and simulated spectra for PCu-PZn-PCu at 323K (~1 µM). In the center, simulations are presented with increasing values of $J_{\text{avg}}$ with fixed $J_{\text{mod}}$ and on the right with increasing values of $J_{\text{mod}}$ and fixed $J_{\text{avg}}$. The best fit spectrum in the center for both datasets.
3. References

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