

Spin-exchange structures of S₂-state Mn-cluster in photosynthetic oxygen-evolving complex

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Spin-exchange structures of the S₂-state Mn-cluster in a photosynthetic oxygen evolution complex were numerically evaluated by diagonalizing the Heisenberg spin-exchange Hamiltonian. The calculation was performed by taking into account the magnetic properties of the S₂ multiline signal and the effective Mn hyperfine constants determined by simulating oriented multiline spectrum. The result indicates that only six types of spin-exchange structures are compatible with those of the S₂-state Mn-cluster.

Photosynthetic oxygen is evolved by a catalytic function of a tetranuclear Mn-cluster located on the donor side of photosystem II (PSII) protein complexes. The reaction involves five intermediate states labeled S_i (i = 0–4), and an S_n state advances to an S_{n+1} state by absorbing one photon by PSII,^{1,2)} where the cluster accumulates positive charges for water oxidation. However, the understanding of the mechanism of water oxidation is largely limited due to the lack of information on the cluster. The Mn-cluster reveals characteristic EPR signals in its S₀-, S₁-, S₂-states. Among them, a multiline signal (MLS) arising from the S₂-state Mn-cluster has been best characterized in terms of its magnetic properties. Recently, an anisotropic model for g-tensor and effective hyperfine coupling (hfc) tensors has been successfully applied to simulating the MLS in partially oriented PSII membranes.³⁾ Here, we numerically evaluated spin-exchange structures of the S₂-state Mn-cluster by taking into account the effective hfc tensors obtained by the simulation study.

Spin-exchange Hamiltonian is given by $\mathcal{H}_{\text{ex}} = \sum_{i < j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j$

where J_{ij} is the spin-exchange coupling constant. The spin-state vectors, $|\Phi_n(SM)\rangle$, for the S₂-state Mn-cluster is obtained by solving the Schrödinger equation:

$$\mathcal{H}_{\text{ex}} |\Phi_n(SM)\rangle = E_n(S) |\Phi_n(SM)\rangle, \quad (1)$$

$$|\Phi_n(SM)\rangle = \sum_{S_{12}, S_{14}} C_n(S_{12}, S_{34}, S) |S_1 S_2(S_{12}) S_3 S_4(S_{34}) SM\rangle, \quad (2)$$

$$|S_1 S_2(S_{12}) S_3 S_4(S_{34}) SM\rangle = \sum_{M_{ij}, M_i} C_{S_{12} M_{12} S_{34} M_{34}}^{SM} C_{S_1 M_1 S_2 M_2}^{S_{12} M_{12}} C_{S_3 M_3 S_4 M_4}^{S_{34} M_{34}} \prod_{i=1}^4 |S_i M_i\rangle, \quad (3)$$

where S and S_i are the magnitudes of total and i -th spins, $E_n(S)$ is the eigen value, $C_{\alpha\alpha\beta\beta}^{c\gamma}$ is the vector coupling coefficient, $|S_i M_i\rangle$ is the single-spin state vector. The effective (\mathbf{A}_i) and intrinsic (\mathbf{a}_i) hfc tensors of i -th Mn ion are related by the projection factor $P_i: \mathbf{A}_i = P_i \mathbf{a}_i$. The projection factor is given by the following equation: $P_i = \langle \Phi_0(SM) | \mathbf{S} \cdot \mathbf{S}_i | \Phi_0(SM) \rangle / \{S(S+1)\}$ (i = 1–4) where $|\Phi_0(SM)\rangle$ is the ground state vector. It is noted that P_i alters its value sensitively depending on the spin-exchange structure which is determined by bond-structure between Mn ions in the cluster.

Evaluation of spin-exchange structure

Firstly, spin exchange structures were given based on the following assumptions for the Mn cluster in the S₂ state: (1) one strong-antiferromagnetically coupled di-μ-oxo bridged Mn₁(III)-Mn₂(IV) dimer exists with a range of 230–300 cm⁻¹,^{4,5)} (2) at most three strong antiferromagnetic interactions and at least three weak exchange coupling with a value of –20–40 cm⁻¹,⁵⁾ (3) oxidation state of Mn(III, IV, IV, IV). Then, we selected exchange structures that meet the following magnetic properties of MLS: (1) the first excited spin manifold lies 35 ± 15 cm⁻¹ above the $S = 1/2$ ground one,⁶⁾ (2) the averaged effective hfc tensor is determined to be 3.70 × 10⁻³, 8.07 × 10⁻³ and 9.93 × 10⁻³ cm⁻¹ for the three Mn(IV) ions, and 8.56 × 10⁻³ cm⁻¹ for the Mn(III) ions, respectively.³⁾ It is notable that the effective hfc for a given spin structure lies in the range for Mn ion determined before (6.5 × 10⁻³–8.5 × 10⁻³ cm⁻¹).⁷⁾

Spin-exchange structures of Mn-cluster

Figure 1 shows the results of calculations presented by contour maps for six magnetic schemes, in which two of the five interactions ($J_{13}, J_{14}, J_{23}, J_{24}$ and J_{34}) are assumed to be strong and are plotted on the x- and y-axes. The magnetic structures compatible with those of the MLS as revealed by shaded region were found only when the first excited state was ascribed to the $S = 3/2$ one (Fig. 1A) and the $S = 1/2$ first excited state (Fig. 1B). These two states resulted in similar maps each other except for maps d and f . Maps a , c , d , e , and f (Fig. 1A) and the maps a , c , and e (Fig. 1B) have the shaded region only in the lower left corner. The shaded regions in maps b in Fig. 1A and map d in Fig. 1B spread obliquely within a relatively narrow area in the maps b but wider area in the map d . Figure 2 illustrates the possible exchange paths of the S₂-state multiline-cluster. Among the structures, structures A, C and D will be a better candidate for the S₂-state cluster because exchange couplings between 40 and 80 cm⁻¹ have not been reported in any Mn dimer complexes as far as we know. Figure 3I and 3II show the detailed coupling diagram for weak interactions in structures C and D. In the diagram for structure C, either $J_{23} = 0$ cm⁻¹ or $J_{24} = 0$ cm⁻¹ plane intercepts the shaded space, indicating that the Mn ions either between the positions 2 and 3, or 2 and 4 are not necessarily connected *via* bridge structure. On the other hand, the Mn ions between the positions 1 and 4 should be bridged by a weakly antiferromagnetic interaction. In the diagram for structure D, a $J_{14} = 0$ cm⁻¹ plane inter-

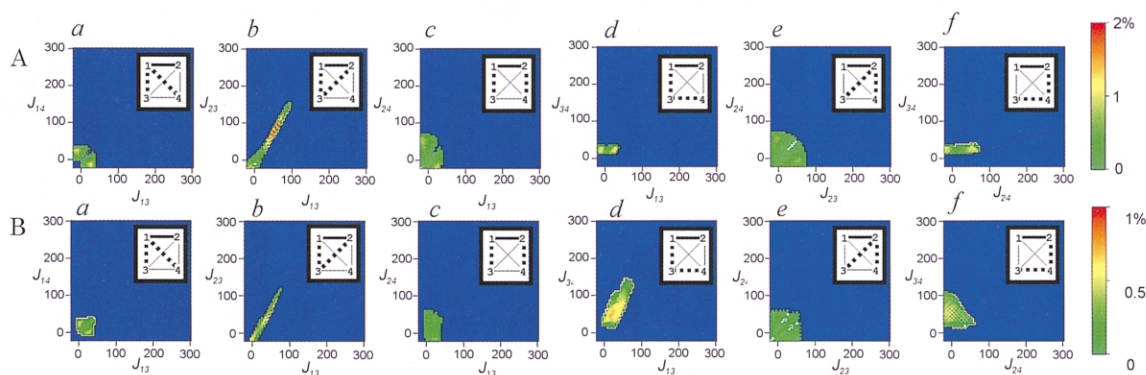


Fig. 1. Contour maps for magnetic interaction sets compatible with the S_2 -state Mn-cluster. A: the first excited state of $S=3/2$, B: the first excited state of $S=1/2$. The bar indicates the number of compatible interaction sets as expressed in % relative of the total calculation sets (32955 per $5 \text{ cm}^{-1} \times 5 \text{ cm}^{-1}$ lattice). The blue-colored region indicates no compatible interaction sets.

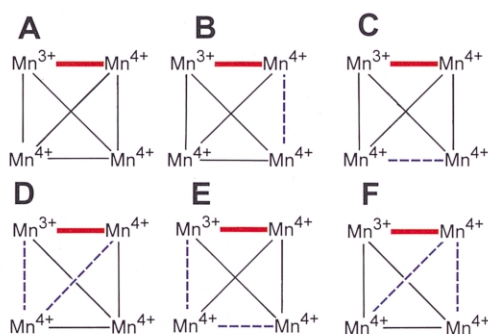


Fig. 2. The exchange paths in the Mn-cluster compatible with the S_2 -state Multiline-cluster. Red-colored bold, blue-colored bold-dashed and thin lines represent strong ($230 \text{ cm}^{-1} \leq J \leq 300 \text{ cm}^{-1}$), intermediately strong ($40 \text{ cm}^{-1} < J < 170 \text{ cm}^{-1}$) and weak ($-20 \text{ cm}^{-1} \leq J \leq 40 \text{ cm}^{-1}$) couplings, respectively.

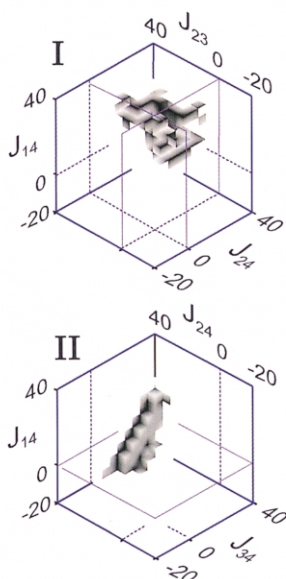


Fig. 3. Three dimensional diagram for the weak magnetic interactions of structure C (Map I) and structure D (Map II).

cepts the shaded space, while $J_{24} = 0 \text{ cm}^{-1}$ and $J_{34} = 0 \text{ cm}^{-1}$ planes do not intercept the shaded space. The results indicate that the Mn ions between position 1 and 4 are not necessary connected chemically, and that the Mn ions between positions 2 and 4, and between 3 and 4 should be bridged by a weakly antiferromagnetic interaction. With respect to the structure A, no characteristic feature was detected in weak interactions except for that J_{34} is always weakly antiferromagnetic.

The dimer structure of di- μ -oxo bridged Mn proposed by Berkley group⁷⁾ is the most authorized model of the Mn-cluster in OEC. The magnetic structure C in Fig. 2 is compatible with this model, and provides detailed magnetic properties that should be sufficed in this model: (1) the spin of the first excited state for the S_2 -state multiline-cluster is $S = 1/2$, (2) the plane of di- μ -oxo $\text{Mn}_3(\text{IV})$ - $\text{Mn}_4(\text{IV})$ dimer unit bends to have an intermediate strength exchange coupling ($< 150 \text{ cm}^{-1}$), (3) the Mn ions between the positions 1 and 4, and between the positions 1 and 3 should be connected *via* bridge structure with a weakly antiferromagnetic interaction.

The information on magnetic interactions obtained in this study provides principal prerequisites for evaluating any structural models of the Mn-cluster, although the assignment of the chemical identity of the bridge structure may be relatively imprecise due to shortage of basic knowledge of the magnetic properties of the model Mn complexes.

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