Theory of chemical bonds in metalloenzymes XX: magneto-structural correlations in the CaMn₄O₅ cluster in oxygen-evolving complex of photosystem II

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ABSTRACT
Magneto-structural correlations in oxygen-evolving complex (OEC) of photosystem II (PSII) have been elucidated on the basis of theoretical and computational results in combination with available electron paramagnetic resonance (EPR) experimental results, and extended x-ray absorption fine structure (EXAFS) and x-ray diffraction (XRD) results. To this end, the computational methods based on broken-symmetry (BS) UB3LYP solutions have been developed to elucidate magnetic interactions in the active manganese catalyst for water oxidation by sunlight. The effective exchange interactions \(J\) for the CaMn(III)Mn(IV)₃O₅(H₂O)₃Y(Y = H₂O or OH⁻) cluster (1) model of OEC of PSII have been calculated by the generalised approximate spin projection (GAP) method that eliminates the spin contamination errors of the BS UB3LYP solution. Full geometry optimisations followed by the zero-point energy (ZPE) correction have been performed for all the spin configurations of 1 to improve the \(J\) values that are compared with accumulated EPR in the \(S_1\) state of Kok cycle and magnetic susceptibility results of Christou model complex Ca₂Mn(IV)₃O₄ (2). Using the calculated \(J\) values, exact diagonalisation of the spin Hamiltonian matrix has been carried out to obtain excitation energies and spin densities of the ground and lower excited states of 1. The calculated excitation energies are consistent with the available experimental results. The calculated spin densities (projection factors) are also compatible with those of the EPR results. The calculated spin densities have been used to calculate the isotropic hyperfine (\(A_{iso}\)) constants of \(^{55}\)Mn ions revealed by the EPR experiments. Implications of the computational results are discussed in relation to the structural symmetry breaking (SSB) in the \(S_0\), \(S_2\) and \(S_3\) states, spin crossover phenomenon induced by the near-infrared excitation and the right- and left-handed scenarios for the O–O bond formation for water oxidation.

1. Introduction
Electron- and spin-correlation effects play important roles for theoretical insight of the nature of chemical bonds in metalloenzymes. Transition-metal clusters confined in protein fields have often been regarded as strong correlation electron systems (SCES), where the orbital, spin and charge degrees of freedom are variable, depending on environmental conditions. Structural deformations of proteins are responsible for active controls of such conditions. Mean field theories such as Hartree–Fock (HF) and Kohn–Sham (KS) density functional theory (DFT) have been a starting point for theoretical understanding of chemical bonds in SCES, where valence electrons are more or less localised to
avoid strong electron repulsions. The HF, KS-DFT and their hybrid models inevitably entail broken-symmetry (BS) pictures of the labile chemical bonds of metalloenzymes. Temperature-dependent paramagnetism has been regarded as an indication of appearance of local spins in SCES, providing several exchange-coupled models such as the Heisenberg, Kondo and Anderson models [1].

In this series of papers [2], we have examined the nature of chemical bonds in exchange-coupled open-shell systems on the basis of BS methods [1,3] followed by approximate spin-projection procedure for finite systems [4–6]. Three-centre, four-electron bonds in the exchange-coupled organic systems such as 1,3-diradicals exhibit the so-called triplet instability [1,3], providing BS orbitals obtained by the HOMO–LUMO mixing as illustrated in Figure 1(A). They are more or less localised on the left and right terminal atoms (∗R–O–R∗), respectively, being responsible for 1,3-diradical states with singlet and triplet spin configurations, where • denotes a local spin. The effective exchange integrals (J) in the spin Hamiltonian model are formally defined as 2J = 1E − 3E, where 3E denotes the total energy of the singlet (X = 1) or triplet (X = 3) state [7]. The same situation appears in the case of dπ − pπ − dπ bonds of the exchange-coupled transition-metal (M) oxides; (∗M–O–M∗) as shown in Figure 1(B) [4–6]. The HOMO–LUMO mixing of the dπ − pπ − dπ bonds affords the BS orbitals responsible for singlet (low spin) or triplet (high spin) metal–diradical state. Both orbital and spin degrees of freedom play crucial roles for exchange-coupled systems, providing iso-lobal and iso-spin analogies between organic (∗R–O–R∗) and inorganic (∗M–O–M∗) exchange-coupled systems as shown in Figure 1(C), where ↑ and ↓ denote the up-spin and down-spin, respectively.

The BS methods are applicable to multinuclear exchange-coupled systems. The HOMO–SOMO–LUMO mixing becomes necessary for equilateral triangle systems such as triangular H3 radical because of the near degeneracy among HOMO, and degenerated SOMO and LUMO in the BS approach [8], entailing an interesting spin state expressed by so-called triangular spin alignments as illustrated in Figure 2(A). Two-component spinors, namely general spin orbitals (GSO), are necessary for BS descriptions of such non-collinear spin structures [8,9]. Similarly the iso-lobal and iso-spin analogies indicate that triangle spin alignments are feasible for triangular manganese oxides Mn3O4 in Figure 2(C) and cubane-like CaMn3O4 cluster in Figure 2(F) [10]. Moreover, tetrahedral spin alignments are obtained for cubane-like structures such as the tetrahedral H4 cluster in Figure 2(B) [3,9,11]. Such non-collinear spin alignments are also feasible for Mn4O6 clusters with the cubane-like structure [12] and for Mn4O6 clusters with the adamantane-like structure as shown in Figure 2(D) and 2(E), respectively. Thus, magneto-structural correlations are important and interesting for elucidation of electronic and spin states of exchange-coupled cluster systems. The spin structures in Figure 2 are responsible for

Figure 1. (A) The HOMO–LUMO mixing for three-centre four-electron systems provides broken-symmetry (BS) molecular orbitals that are localised on the terminal atoms, respectively, in accord with 1,3-diradical character (∗R–X–R∗) and (B) the HOMO–LUMO mixing of exchange-coupled M–O–M systems (M = transition metal ions) with metal radical character (∗M–X–M∗) and (C) the BS orbitals indicate iso-lobal and iso-spin analogies between both systems.
The non-collinear spin structure for the equilateral $H_4$ radical (A), and the isolobal and isospin analogies are applicable to the triangular $Mn_3$ structures involved in the triangular $Mn_3O_4$ (C) and cubane-like $CaMn_3O_4$ (F) clusters. The tetrahedral spin structures for the tetrahedral $H_4$ radical (B), cubane-like $Mn_4O_4$ (D) cluster and adamantine-like $Mn_4O_6$ (E) cluster. The iso-lobal and iso-spin analogies are applicable for B, D and E.

In the past few decades, a number of electron paramagnetic resonance (EPR) experiments have been performed to elucidate the electronic structure and function of the catalytic site of water oxidation in the oxygen-evolving complex (OEC) of photosystem II (PSII) [13–56]. In the early 1980s, Dismukes and Siderer [25] first reported the EPR spectrum of the $S_2$ state of the Kok cycle for water oxidation. The EPR spectrum obtained was consistent with an exchange-coupled tetramer of $Mn$ ions. After this discovery [25], Brudvig et al. [26] proposed a cubane-like structure of the $Mn_4O_4$ complex in Figure 2(D) for OEC of PSII, which is reorganised into an adamantine-like $Mn_4O_6$ complex in Figure 2(E) after the insertion of molecular oxygen. Ferreira et al. [15] found that the London x-ray diffraction (XRD) structure consisted of cubane-like $CaMn_3O_4$ cluster in Figure 2(F) and an attached extra-$Mn$ ion: $CaMn_3O_4 + Mn (= CaMn_4O_4)$. Three $Mn$--$Mn$ distances in the $CaMn_3O_4$ cluster of the London structure [15] were almost equivalent, and therefore, our GSO DFT computations [10] indicated that the non-collinear spin structure was the ground state for the cluster as illustrated in Figure 2(F). On the other hand, the Berlin XRD structure [17] provided the isosceles triangle structure for the $Mn_3$ framework in OEC of PSII that was consistent with the extended x-ray absorption fine structure (EXAFS) structure with shorter $Mn$--$Mn$ distances (2.7 Å) and a longer $Mn$--$Mn$ distance (3.3 Å). This implies that the triangular spin alignment [10] in the London structure [15] is relaxed into an ordinary collinear spin structure [57–65] with the axial up(↑)–down(↓)–up(↑) spin alignment in the Berlin XRD structure [17].

Umema et al. [21] discovered the high-resolution XRD structure of the $CaMn_4O_5$ cluster in OEC of PSII at 1.9 Å resolution as illustrated in Figure 3. They have elucidated almost symmetrical structure of the catalytic site of water oxidation: the $CaMn(III)_2Mn(IV)_2O_5$ cluster in the $S_1$ state, where the $Mn(III)_{4(a)}$–$O_{(5)}$ and $Mn(III)_{1(d)}$–$O_{(5)}$ bond lengths are 2.5 and 2.6 Å, respectively, and $O_{(5)}$ is the bridge oxygen for the $Mn(III)_{4(a)}$–$O_{(5)}$–$Mn(III)_{1(d)}$ bond. The triangle $Mn_3$ structure of the cubane-like $CaMn_3O_4$ fragment in their distorted chair structure $CaMn_4O_3$ [21] exhibits the isosecile chair framework that is responsible for the collinear spin structure. The exchange-coupled four-manganese cluster affords one highest spin (HS) structure (A), four intermediate-spin (IS) structures (B, C, D, E) and three low-spin (LS) structures (F, G, H) as shown in Figure 4. The IS structure E was calculated to be the ground state [60–62] for the high-resolution XRD structure [21] in the $S_1$ state of the Kok cycle (see Figure S1) for water oxidation (substrate waters are shown in Figure S2) in Figure 3(A):

$$2H_2O + (4hn) \rightarrow O_2 + 4e^- + 4H^+$$ (1)

However, the computational result was in contradiction to the parallel polarisation EPR result [27] that was consistent with the paramagnetic spin...
Figure 3. Structural symmetry breaking in the $S_2$ state of oxygen-evolving complex of photosystem II: (A) almost symmetrical structure (central) revealed by the high-resolution XRD for the $S_1$ state ([21]), (B) broken-symmetry structure and (C) right (R)-opened structure and (D) left (L)-opened structure of the CaMn$_4$O$_5$ cluster of OEC. The notations $a$, $b$ and $c$ are used for $Y = O^{2-}$, $Y = OH^-$ and $Y = H_2O$, respectively.

$(S = 1)$ state of the $S_1$ state of OEC of PSII. Koulogliotis et al. [28] also performed the EPR studies of the $S_1$ state, concluding that the ground spin state of the $S_1$ resting state is diamagnetic, whereas the $S_1$ active state is paramagnetic. Yamauchi et al. [29] have also performed the parallel polarisation EPR studies of the $S_1$ state followed by the temperature variation experiment, elucidating that the signal at $g = 4.8$ originates from an excited state with triplet spin state $(S = 1)$ with separation from the diamagnetic ground state $(S = 0)$ of about 2.5 K (1.74 cm$^{-1}$). Thus, the temperature-dependent paramagnetism is familiar in the exchange-coupled Mn oxides in OEC of PSII (see Figure S1).

The above results indicated the necessity of refinements of the high-resolution XRD structure [21] by quantum mechanical (QM) calculations [64,65]. Therefore, full geometry optimisation followed by the vibrational analysis [23,65] was performed for each spin configuration of the model cluster in the $S_1$ state of OEC of PSII. The energy gaps among these configurations obtained by vertical, adiabatic and adiabatic plus zero-point energy (ZPE) correction procedures have been used for

Figure 4. Spin vector models for the eight spin configurations in the CaMn$_4$O$_5$ cluster of OEC. The eight broken-symmetry (BS) UB3LYP solutions are available in conformity with these spin vector models where each Mn ion has the local high-spin configuration. The six effective exchange integrals ($J$) for the Heisenberg spin Hamiltonian model are also determined by the generalised approximate spin projection (GAP) procedure using total energies and total spin angular momentums obtained by the BS UB3LYP calculations.
computation of the effective exchange integrals \( J \) in the spin Hamiltonian model [65]. The \( J \) values are calculated by (1) analytical method and (2) generalised approximate spin projection (GAP) method that eliminates the spin contamination errors of UB3LYP solutions. Using \( J \) values derived from these methods, exact diagonalisation of the spin Hamiltonian matrix was carried out to obtain exact QM energy spectrum and other physical observables such as spin densities of the ground and lower-excited states of the cluster. The exact diagonalisation results [65] for the right (R)-opened structure in the \( S_1 \) state in Figure 3(C) indicated the ground singlet state with the temperature excited triplet state \( (S = 1) \) that was consistent with the parallel polarisation EPR results [27–29].

The \( S_2 \) state of OEC of PSII exhibits two distinct classes of EPR signals [23,30–57]: (1) a \( ^{55}\text{Mn} (I = 5/2) \) hyperfine-resolved signal centred near \( g = 2 \) for the doublet state \( (S = 1/2) \) and (2) a broader signal without hyperfine structure centered near \( g = 4.1 \) for the \( S = 5/2 \) spin state. The full geometry optimisations of the \( \text{CaMn}_4\text{O}_5 \) cluster in the \( S_2 \) state have revealed that the R-opened structure, \( \text{Mn(IV)}_4\text{a}–\text{O(5)}–\text{Mn(III)}_1\text{d} \), of the \( \text{CaMn}_4\text{O}_5 \) cluster in Figure 3(C) is responsible for the multiline \( g = 2 \) doublet state \( (S = 1/2) \) spectra, whereas the left (L)-open structures, \( \text{Mn(III)}_4\text{a}–\text{O(5)}–\text{Mn(IV)}_1\text{d} \), of the \( \text{CaMn}_4\text{O}_5 \) cluster in Figure 3(D) are consistent with the \( g = 4.1 \) sextet spin state \( (S = 5/2) \) spectra [23,53–55,65]. Boussac et al. [36–38] have shown that the spin crossover between the \( R(S = 1/2) \) and \( L(S = 5/2) \) configurations has been induced by the near-infrared (NIR) light illumination. Previously, we have discussed briefly our BS computational results of the \( S_2 \) state that are consistent with the EPR results [23,65].

In this paper, we have performed the full geometry optimisation of each spin configuration of the \( S_2 \) state in Figure 4. The above three procedures developed by our group have been applied to elucidate the effective exchange integral \( (J) \) in the Heisenberg spin Hamiltonian. The exact diagonalisation of the spin Hamiltonian matrix has been carried out, yielding excitation energies and spin densities of the ground and lower-excited states of the cluster. The exact diagonalisation results of the spin Hamiltonian by the use of the \( J \) values obtained by the GAP procedure are found to be consistent with the EPR results for the \( S_2 \) state. Implications of the computational results are discussed in relation to (1) the necessity of the exact diagonalisation for computations of reliable energy levels, (2) magneto-structural correlations in the \( \text{CaMn}_4\text{O}_5 \) cluster of OEC of PSII, (3) structural symmetry breaking (SSB) in the \( S_1, S_2 \) and \( S_3 \) states, and (4) the R- and L-handed scenarios for the O–O bond formation for water oxidation. Implications of the computational results are also discussed in relation to the SSB in the labile \( \text{Mn}_n–\text{X}–\text{Mn}_d \) bond, spin crossover phenomenon induced by the NIR excitation, water-assisted proton-shuttle mechanism for the O–O bond formation for water oxidation.

## 2. Theoretical and computational backgrounds

### 2.1. Structural symmetry breaking of the \( \text{CaMn}_4\text{O}_5 \) cluster

Past several years, the degree of SSB of the \( \text{Mn}_n–\text{X}–\text{Mn}_d \) bond \( (X = \text{O or OH}^-) \) in Figure 3 in the \( \text{CaMn}_4\text{O}_5 \) cluster of OEC of PSII has been under great debates (see supporting material SII.2). Our previous BS DFT computations [57–63] have revealed that the SSB via the Jahn–Teller (JT) effects of Mn(III) ions is a key concept for theoretical understanding of possible geometries of the labile Mn cluster, \( \text{CaMn(III)}_n\text{Mn(IV)}_2\text{O}_5\text{H}_2\text{O}_3 \) \( \text{Y}(Y = \text{H}_2\text{O or OH}^-) \) \( (1) \) for both \( S_1 (x = z = 2) \) and \( S_2 (x = 1 \) and \( z = 3) \) states, and have revealed three possible geometrical structures: R-opened \( (R; \text{Mn}_n–\text{X}–\ldots–\text{Mn}_d), \) central \( (C; \text{Mn}_n–\text{X}–\text{Mn}_d) \) and left-opened \( (\text{Mn}_n–\ldots–\text{X}–\text{Mn}_d) \) ones as illustrated in Figure 3(A), 3(C) and 3(D), respectively [23,24,62,63]. If the potential surface has a single-valley structure, the central structure \( (C) \) may become the true minimum. On the other hand, the R- and L-opened structures may become true local minima in the case of the double-well potential (see Figure S3). Previously, the SSB has been investigated by geometry optimisations based on the HS solution [23]. Moreover, the optimised HS geometry has been assumed for other spin configurations [23]. Therefore, in order to confirm previous magneto-structural correlations based on the vertical approximation [23,53,55], we here perform full geometry optimisations of all the spin configurations to elucidate energy levels and relative stabilities for the R-opened structures, \( S_{2\text{ac}}(R) \) and \( S_{2\text{ab}}(R) \), and left-opened structures, \( S_{2\text{ac}}(L) \) and \( S_{2\text{ab}}(L) \), of 1, where the notations ‘2’, ‘a’, ‘b’ and ‘c’ in \( S_{2XY} \) \( (X, Y \) in Figure 3 \) represent the \( S_2 \) state, \( Y = \text{O}^2\), \( Y = \text{OH}^- \) and \( Y = \text{H}_2\text{O}, \) respectively, and ‘L’ and ‘R’ represent the left-side- and right-side-opened structures in Figure 3, respectively. The \( X \) and \( Z \) in Figure 3 remain \( \text{O}^2 \) \( (=a) \) and \( \text{H}_2\text{O} \) in the \( S_2 \) state, respectively.

### 2.2. Damage-free X-ray free-electron laser (XFEL) structure

Very recently, Suga and their collaborators [66] performed the X-ray free-electron laser (XFEL) experiments of PSII and obtained a radiation damage-free XRD structure of the dark stable \( S_1 \) state of PSII by using the femtosecond X-ray pulses of XFEL provided by at the SPring-8 angstrom compact free-electron laser (SACLA) facility [66] and a huge number of highly isomorphous large
crystals. The new XFEL structure at 1.95 Å resolution [66] was found to be different from the R-opened structure [67] based on the assumption that the $O_{(5)}$ (= X) site ($S_{1ab(c)}$) in Figure 3 was the oxygen dianion [23,24]. Alternatively, the XFEL structure [66] was topologically similar to the high-resolution XRD structure [21] that was suggested to be X-ray damaged on the experimental and theoretical grounds [2,64]. The XFEL structure was theoretically reproduced on the assumption that the $O_{(5)}$ (= X) site was protonated, namely hydroxide anion ($S_{1hb(c)}$) [67,68]. This, in turn, implies that the Y site in Figure 3 may be hydroxyl anion (OH$^-$) (= b) or water molecule (H$_2$O) (= c). Thus, the XFEL results [66] raised a fundamental question, namely how to understand the geometrical structure of the CaMn$_4$O$_3$ cluster, indicating the necessity of re-examination of assumptions employed for several theoretical model structures of OEC of PSII, and also for re-examinations of the EXAFS structures reported previously.

2.3. Magneto-structural correlations

No XRD structure is reported for the $S_2$ state at present, though the high-resolution XRD result is available for the $S_1$ state [21]. Fortunately, a number of EPR experimental results are presented for the $S_2$ state [25–52], affording precise information to elucidate magneto-structural correlations in OEC. Moreover, accumulated biochemical results have suggested similarity between the $S_1$ and $S_2$ structures because of no proton release and one electron release in the $S_1$ to $S_2$ transition (Figure S1) [25–52], though the EPR results for the $S_1$ state [27–29] are limited. Figures S4A and S4B illustrate our strategy of elucidations of magneto-structural correlations in OEC of PSII based on theoretical and computational results in combination with available EPR experimental results, the high-resolution XRD [21] and XFEL [66] structures, together with EXAFS. EPR experimental results for the $S_2$ state have been analysed on the basis of spin Hamiltonian model [69–81]. The parameters such as effective exchange integrals ($J$) and spin density ($Q$) obtained by theoretical calculations are crucial for elucidation of magneto-structural correlations in the $S_2$ state based on available XRD and EPR results [1–81]. Therefore, both molecular structure determined by XRD [13–22] and magnetic structure obtained by EPR [25–52] would be self-consistently combined for theoretical elucidations of structural bases for water-splitting reaction in OEC of PSII. Moreover, reliable structural information for the $S_2$ state can be feedback to the $S_1$ and $S_3$ states [23,65].

The spin Hamiltonian models have been employed for theoretical analysis of the magnetic resonance and related experiments [25–56]. In order to elucidate magneto-structural correlations, we have developed the spin Hamiltonian model for four-site four spin systems [57–61]. Six effective exchange integrals ($J$) for the systems are determined by using the energy gaps among the eight spin configurations in Figure 4 obtained by the vertical, adiabatic and adiabatic, plus ZPE correction methods. Theoretical formulations and analytical expressions of the effective exchange integrals ($J$) for 1 in the $S_2$ state are also shown in supporting material SVIII. Derivations of spin Hamiltonian models and magnetic interaction parameters such as hyperfine constants [52,54–58] are also shown in supporting material SVI. Theoretical details of the reliability tests of BS DFT approach in relation to the density matrix renormalization group (DMRG) computational results [64] have been described in the supporting materials. The magnetic interaction parameters for the R- and L-opened structures of 1 have been evaluated for comparisons with accumulated EPR results [25–52] to confirm the magneto-structural correlations [23,65]. The computational methods and basis sets [82–85] are the same in previous papers, namely the use of G09 program [85] and our own subroutines for the BS computations [23,65] (see supporting information SIII). Scope and applicability of the QM model without protein environments in this paper are briefly discussed in supporting section SII.2.

3. Computational results

3.1. Optimised geometries of eight spin configurations

Previously, we have performed the full geometry optimisations of the R- and L-opened structures of the CaMn$_4$O$_3$ cluster by using the HS configuration [23]. The optimised geometry has been assumed for other spin configurations in Figure 4. However, reliability of this vertical approximation [23,53,57] is not examined yet for the CaMn$_4$O$_3$ cluster in the $S_2$ state of the Kok cycle. As a continuation of the previous work [23,65], we have performed the adiabatic and adiabatic + ZPE correction methods, respectively. The newly optimised geometrical parameters for $S_{2ac}(R), S_{2ab}(R), S_{2ac}(L), S_{2ab}(L)$, where $a = O^{2-}, b = OH^- \text{ and } c = H_2O$, are summarised in Tables S1A, S1B, S2A and S2B, respectively. For comparisons, the optimised geometrical parameters for the $S_1$ state are also summarised in Table S3.

As shown previously [23], there are two different geometrical structures relating to the SSB of the Mn$_{5-X-Mn_d}$ bond of the CaMn(IV)$_3$ Mn(III)O$_5$(H$_2$O)$_3$Y($Y = H_2O \text{ or } OH^-$) cluster (1) in the $S_2$ state as shown in Figure 3.
First of all, we have performed full geometry optimisations of the $S_2$ state structure ($S_{2ac}(R)$) of 1 in Figure 3 by using the UB3LYP energy gradient method. The supporting Table S1A summarises the optimised Mn–Mn and Ca–Mn distances for the eight spin configurations of $S_{2ac}(R)$. From the computational results in Table S1A, the geometrical parameters are almost the same among the eight different spin configurations, indicating no serious geometry change. Therefore, the average values for the eight spin configurations are also calculated to elucidate general trends for the geometrical parameters.

The average Mn–Mn distances optimised for $S_{2ac}(R)$ (X = a = $O^{2-}$, Y = b = $OH^-$) in Figure 3 indicated a general trend (rule Ib) [23,24]:

$$R(Mn_a - Mn_b) < R(Mn_b - Mn_c) \sim R(Mn_c - Mn_d)$$
$$< R(Mn_b - Mn_d) < R(Mn_a - Mn_d)$$  \hspace{1cm} (2)

This trend (Ib) revealed by full geometry optimisations of the eight spin configurations is common under the assumption that the O$_{(5)}$ site is the oxygen dianion. In fact, rule Ib is applicable to the proposed structures for the $S_1$ (or $S_2$) state by other theoretical groups [86–96], where the O$_{(5)}$ site is assumed to be the oxygen dianion (X = $O^{2-}$). The average Mn$_a$–Mn$_b$, Mn$_b$–Mn$_c$, Mn$_c$–Mn$_d$, Mn$_b$–Mn$_d$, and Mn$_a$–Mn$_d$ distances for $S_{2ac}(R)$ are 2.71, 2.76, 2.74, 3.39 and 5.08 Å, respectively. These values are consistent with the EXAFS results for the $S_2$ state [97–102]. The rule Ib is a general trend for the R-opened structure with O$_{(5)}$ = $O^{2-}$ (= a) even in the two-electron reduced ($S_{1ac}$) state [24]. On the other hand, the corresponding Mn–Mn distances by SP8 XRD [21] and XFEL [66] structures (in parentheses) in the $S_1$ state are 2.97(2.87), 2.89(2.70), 2.84(2.68), 3.29(3.20) and 5.00(4.93) Å, respectively, indicating the different tendencies from the rule Ib as follows:

$$R(Mn_b - Mn_c) \sim R(Mn_c - Mn_d) < R(Mn_a - Mn_b)$$
$$< R(Mn_b - Mn_d) < R(Mn_a - Mn_d)$$  \hspace{1cm} (3)

This trend referred to as the rule Ia was not altered for the damage-free XFEL structure (Mn–Mn distances are given in parentheses) in the $S_1$ state [66]. The rule Ia is applicable for the optimised structures where the O$_{(5)}$ site is assumed to be protonated, namely hydroxide anion (OH$^-$) [23,24]. Some of the Mn–Mn distances for the $S_1$ state by SP8 XRD [21] are a little longer than the corresponding calculated values. Possible origins of the elongations have already been discussed in our previous papers (see SII.4) [57–63]. The main conclusion is that the structure of the CaMn$_4$O$_5$ framework confined with protein matrix of PSII is reasonable even if the reductions of Mn ions were induced by X-ray radiation, indicating that the SP8 XRD [21] and SACLAXFEL [66] structures are reliable enough for initial trials of theoretical investigations of magneto-structural correlations in OEC of PSII.

We have performed full geometry optimisations of a deprotonated $S_2$ structure, $S_{2ab}(R)$ (X = a = $O^{2-}$, Y = b = $OH^-$), in Figure 3(C) for comparison with other theoretical computations [86–96]. Table S1B summarises the optimised Mn–Mn and Ca–Mn distances of the eight spin configurations of $S_{2ab}(R)$. The average Mn$_a$–Mn$_b$, Mn$_b$–Mn$_c$, Mn$_c$–Mn$_d$, Mn$_b$–Mn$_d$ and Mn$_a$–Mn$_d$ distances for $S_{2ab}(R)$ are 2.71(2.71), 2.78(2.76), 2.73(2.74), 3.40(3.39) and 4.94(5.08) Å, respectively, where the corresponding values for $S_{2ac}(R)$ are given in parentheses. The Mn$_a$–Mn$_d$ distance is a little shortened by the deprotonation of Y = H$_2$O to Y = $OH^-$, indicating the robust nature of the main skeleton revealed by the high-resolution XRD [21].

Recent discovery of the L-opened structure in the $S_2$ state [23,24,55] has been a remarkable contribution of theoretical investigations of OEC, showing the shift of the O$_{(5)}$ atom from the right to left side. The geometry optimisations of 1 by the high-spin UB3LYP solution [23] indeed elucidated two different L-opened structures: one is the intermediary L-opened structure $S_{2ay}(L)$ (Y = b, c) and the other is the fully L-opened structure $S_{2ay'}(L)$ (Y = b, c). In order to confirm this finding based on the HS solution [23], full geometry optimisations by using other seven spin configurations have been performed to confirm its reliability. Table 1 summarised the optimised geometrical parameters for the $S_{2ac'}(L)$ structure. The geometrical parameters are almost the same among the eight different spin configurations. Moreover, we have already pointed out the general trend, named rule Ic [23]:

$$R(Mn_a - Mn_b) \sim R(Mn_c - Mn_d) < R(Mn_b - Mn_d)$$
$$< R(Mn_a - Mn_b) < R(Mn_a - Mn_d)$$  \hspace{1cm} (4)

The optimised Mn–Mn distances for the eight-different-spin configurations (Table 1) are following the rule Ic, indicating that the rule Ic is independent on the spin configurations. The average Mn$_a$–Mn$_b$, Mn$_b$–Mn$_c$, Mn$_c$–Mn$_d$, Mn$_b$–Mn$_d$, and Mn$_a$–Mn$_d$ distances for $S_{2ac'}(L)$ are 3.19(2.71), 2.75(2.76), 2.71(2.74), 2.87(3.39) and 5.20(5.08) Å, respectively, where the corresponding values for $S_{2ac}(R)$ are given in parentheses. The Mn$_a$–Mn$_b$ and Mn$_b$–Mn$_d$ distances are elongated by 0.48 Å and are shortened by 0.52 Å, respectively, at the R- to L-transition. The general trend Ic is also observed for a deprotonated structure $S_{2ab'}(L)$ in accord with the L-opened structure [23,55,65] with the closed cubane skeleton.
Table S2A summarises the fully optimised geometrical parameters of the $S_{2ac}(L)$ in Figure 3(D). The geometrical parameters are almost the same for the eight different spin configurations. The average Mn–Mn distances optimised for $S_{2ac}(L)$ indicated the general trend (Ic). The Mn$_b$–Mn$_d$ distance becomes shorter than that of the Mn$_a$–Mn$_b$ distance in the L-type structure in accord with the rule Ic [23,24] because of the formation of closed cubane structure. The average Mn$_a$–Mn$_b$, Mn$_b$–Mn$_c$, Mn$_c$–Mn$_d$, Mn$_d$–Mn$_a$ and Mn$_a$–Mn$_d$ distances for $S_{2ac}(L)$ are 3.03, 2.75, 2.72, 2.84 and 4.75 Å, respectively. The Mn(IV)$_b$Mn(IV)$_c$, Mn(IV)$_d$ triangle in the cubane fragment of $S_{2ac}(L)$ is almost equilateral because no JT distortion of the Mn(III) ion as discussed previously [23], whereas it is obtuse in the XRD $S_1$ structure [21] because of the JT distortion of Mn(III)$_d$ [52]. The nearly equilateral triangle may have the HS ground state or the non-collinear LS configuration in Figure 2(C). Thus, general trends Ia–Ic concluded by using the HS solution [23] are not changed after the full geometry optimisations of all the spin configurations in Figure 4.

Table S2B summarises the fully optimised geometrical parameters of $S_{2ab}(L)$ in Figure 1(D). The average Mn–Mn distances of the eight spin configurations optimised for $S_{2ab}(L)$ have also exhibited a general trend Ic [23], indicating the shorter Mn$_b$–Mn$_d$ distance than the Mn$_a$–Mn$_b$ distance. The average Mn$_a$–Mn$_b$, Mn$_b$–Mn$_c$, Mn$_c$–Mn$_d$, Mn$_d$–Mn$_a$ and Mn$_a$–Mn$_d$ distances for $S_{2ab}(L)$ are 2.97(3.03), 2.76(2.75), 2.70(2.72), 2.86(2.84) and 4.41(4.75) Å, respectively, where the corresponding values for $S_{2ac}(L)$ are given in parentheses. The Mn$_a$–Mn$_d$ distance is reduced by 0.3 Å with the deprotonation of $Y = H_2O$. The closed cubane skeleton (CaMn$_3$O$_4$) of $S_{2ac}(L)$ is similar to that of London structure for the $S_1$ state [15].

The optimised Ca–Mn distances obtained for the eight different spin configurations of the R-opened structure, $S_{2ac}(R)$, by UB3LYP are quite similar as shown in Table S1A. The average optimised Ca–Mn distances have elucidated a general tendency:

\[
R(Ca - Mn_c) < R(Ca - Mn_b) \sim R(Ca - Mn_d)
\]

\[
< R(Ca - Mn_a)
\]  

(5)

This relationship is the same as the distance rule IIa obtained by the high-spin solution [23]. The average Ca–Mn$_a$, Ca–Mn$_b$, Ca–Mn$_c$ and Ca–Mn$_d$ distances of $S_{2ac}(R)$ are 3.78(3.82), 3.47(3.55), 3.33(3.28) and 3.60(3.54), Å, respectively, where the corresponding Ca–Mn distances by the high-resolution XRD structure [21] are given in parentheses. The calculated Ca–Mn distances are consistent with the corresponding XRD values. The average optimised Ca–Mn distances for $S_{2ab}(R)$ also exhibit the trend Ila as shown in Table S1B.

The Ca–Mn distances for the L-opened structure, $S_{2ac}(L)$, are almost the same for all the spin configurations as shown in Table S2A. The average optimised Ca–Mn distances have provided the following relationship:

\[
R(Ca - Mn_c) \sim R(Ca - Mn_b) \sim R(Ca - Mn_d)
\]

\[
< R(Ca - Mn_a)
\]  

(6)

The above trend is the same as the distance rule IIb obtained by the high-spin solution [23]. The average Ca–Mn$_a$, Ca–Mn$_b$, Ca–Mn$_c$ and Ca–Mn$_d$ distances of $S_{2ac}(L)$ are 3.99, 3.39, 3.35 and 3.33 Å, respectively. The Ca–Mn(IV)$_b$, Ca–Mn(IV)$_c$ and Ca–Mn(IV)$_d$ distances are similar in accord with the undistorted cubane structure in the L-type structure without the JT distortion effect. The average optimised Ca–Mn distances for $S_{2ab}(R)$ also exhibit the same trend Iib as shown in Table S2B. However, the average Ca–Mn$_a$ distance is a little shortened by the deprotonation of $Y = H_2O$.

The average Ca–Mn$_a$, Ca–Mn$_b$, Ca–Mn$_c$ and Ca–Mn$_d$ distances for $S_{2ac}(L)$ are 4.27(3.99), 3.33(3.39), 3.40(3.35)
and 3.39(3.35) Å, respectively, where the corresponding values for $S_{2ac}(L)$ are given in parentheses. The Ca–Mn(IV)$_b$, Ca–Mn(IV)$_d$ and Ca–Mn(IV)$_d$ distances are quite similar between $S_{2ac}(L)$ and $S_{2ac}(L')$ responsible for the closed cubane formation. However, the Ca–Mn(IV)$_d$ distance for $S_{2ac}(L)$ is elongated by 0.3 Å as compared with that of $S_{2ac}(L)$ in accord with the elongation of the Mn(IV)$_a$–Mn(IV)$_d$ distance in the geometrical change from $S_{2ac}(L)$ to $S_{2ac}(L)$. Thus, the calculated Ca–Mn distances are variable, depending on variations of positions of Mn$_2$ ions.

The elongated Mn–O distances revealed by the high-resolution XRD structure [21] have been under debate among theoretical groups [86–96]. The optimised Mn$_{a}$–O$_{(5)}$ and Mn$_{d}$–O$_{(5)}$ distances were quite similar for the eight spin configurations of the R-opened structure, $S_{2ac}(R)$, as shown in Table S1A. In fact, the average Mn$_{a}$–O$_{(5)}$ and Mn$_{d}$–O$_{(5)}$ distances were 1.77 and 3.37 Å, in accord with the R-opened structure. The corresponding values are 1.79 and 3.20 Å, respectively, for $S_{2ab}(R)$ as shown in Table S1B. The Mn$_{d}$–O$_{(5)}$ distance is contracted by 0.2 Å by the depopulation of $Y = H_2O$ in Figure 3. The SSB parameters, defined by $[R(Mn_d–O_{(5)}) – R(Mn_a–O_{(5)})]/2$, are 0.80 and 0.71 Å, respectively. Thus, the R-opened structures are consistent with those of other groups [53,86,91] and our previous results [23,61,62].

The optimised Mn$_{a}$–O$_{(5)}$ and Mn$_{d}$–O$_{(5)}$ distances were almost the same for the eight spin configurations for the L-opened structure, $S_{2ac}(L)$: the situation was the same for $S_{2ab}(L)$. The average Mn$_{a}$–O$_{(5)}$ and Mn$_{d}$–O$_{(5)}$ distances for $S_{2ac}(L)$ were 2.89 and 1.85 Å, respectively, in accord with the L-opened structure in Figure 3(D). The corresponding values for $S_{2ab}(L)$ are 2.60 and 1.85 Å, respectively. Therefore, the Mn$_{a}$–O$_{(5)}$ distance is shortened by 0.3 Å by the depopulation of $Y = H_2O$ in Figure 3. On the other hand, the corresponding values for $S_{2ac}(L')$ were 3.40 and 1.85 Å, respectively. The Mn$_{a}$–O$_{(5)}$ distance is elongated by 0.5 Å in the transition from $S_{2ac}(L)$ to $S_{2ac}(L')$. Therefore, the SSB parameters for $S_{2ac}(L)$, $S_{2ab}(L)$ and $S_{2ac}(L')$ are 0.52, 0.38 and 0.78 Å, respectively.

The above computational results for the eight spin configurations support the use of the HS configuration for qualitative discussions of the optimised geometrical parameters [23,53,55]. However, it is noteworthy that subtle geometrical differences entail significant differences for magnetic interaction parameters as shown later. The almost symmetrical Mn(III)$_a$–O$_{(5)}$–Mn(III)$_d$ bond of the CaMn$_4$O$_5$ cluster revealed by the high-resolution XRD experiment in the $S_1$ state [21] in Figure 3(A) is collapsed into the R- and L-opened structures [23] as illustrated in Figure 3(C) and 3(D). The R-opened structures, $S_{2ac}(R)$ and $S_{2ab}(R)$, in the $S_2$ state are consistent with the mixed-valence (MV) configuration: Mn(IV)$_a$–O$_{(5)}$ …Mn(III)$_d$, where the JT effect for the Mn(III)$_a$ ion plays a significant role for the geometrical deformation [23]. On the other hand, the JT effect for the Mn(III)$_d$ ion affords the L-opened structure: Mn(III)$_a$ …O–Mn(IV)$_d$, in accord with the $S_{2ac}(L)$, $S_{2ab}(L)$ and $S_{2ac}(L')$ structures. The SSB [23,24] via the JT effect of Mn(III) is one of the most fundamental concepts for theoretical understanding of the nature of labile chemical bonds in the CaMn$_4$O$_5$ cluster of OEC revealed by the high-resolution XRD [21]. The R-opened structure discovered by previous computations [23,53,86,91] is only one of the BS structures of OEC. Present computational results for the $S_2$ state are consistent with existence of both R- and L-opened structures even in the $S_1$ and $S_3$ states [23] in conformity with the labile nature of the Mn$_a$–O–Mn$_d$ bond revealed by the BS DFT computations [57–61], though its main framework revealed by XRD [21] is robust in the $S_1$, $S_2$ and $S_3$ states.

### 3.2. Relative stabilities of the eight spin configurations

#### 3.2.1. Right-opened structure

In our early joint papers between theory and experiment [57–61], we have assumed the XRD structures [21] for eight spin configurations (Figure 4) to elucidate relative stabilities among them. We have shown that the HS configuration $(↑↑↑↑)$ ($1^4A$) based on the XRD structure in the ground state was contradicted to the available EPR results that indicate the LS ($S = 1/2$) ground state in the $S_2$ state [36–56]. We have examined several DFT functionals to reproduce the ground doublet state for the XRD structure [21] and found it was a difficult task as shown in S. Yamanaka et al. [60]. As a continuation work [23,24,60–63], we have performed full geometry optimisations of the eight spin configurations to elucidate the optimised geometries and relative energies among them. The vertical and adiabatic energy gaps, and adiabatic + ZPE values for OEC model at the B3LYP/BSI level, have been calculated, where the total energy of the HS ($1^4A$) configuration is used as the reference. Table S4A summarises the calculated energy differences for the R-opened structure $S_{2ac}(R)$. Figure 5 illustrates the energy gaps among the eight spin configurations of the species.

As shown in Figure 5, the relative energies of the eight spin configurations of $S_{2ac}(R)$ are variable, depending on the spin coupling modes and the optimised geometries. The energy gaps between the ground $(↑↑↑↑)$ and excited $(↑↓↓↓)$ spin configurations are only 0.51, 0.47 and 0.40 kcal/mol for $S_{2ac}(R)$, respectively, by the vertical, adiabatic and adiabatic + ZPE methods, where the corresponding values are 0.33, 0.34 and 0.26 kcal/mol.
for \( S_{2ab}(R) \) (see Table S4C). This means that the relative stability between the spin configurations \((\uparrow \downarrow \downarrow \uparrow)\) and \((\uparrow \uparrow \downarrow \downarrow)\) may be variable, depending on deprotonation of \( W2 \) (H\(_2\)O) and environmental effects such as pH and temperature.

The doublet spin configuration \((\uparrow \downarrow \downarrow \uparrow)\) (\( S_{\text{total}} = (3 - 3 + 3 + 4)/2 = 1/2 \)) is the ground state for the R-opened structure \( S_{2ac}(R) \) with the MV configuration: Ca(II)Mn(III)\(_b\)Mn(IV)\(_b\)Mn(IV)\(_c\)Mn(III)\(_d\). This trend is independent on the above computational procedures. The situation is not altered after the refinements by the UB3LYP calculations (Table S4B), where more flexible large basis sets (basis set II) have been used. This tendency is also true for \( S_{2ab}(R) \) generated by the deprotonation of \( Y = \text{H}_2\text{O} \) (Table S4C). The intermediate spin (\( S_{\text{total}} = (3 + 3 + 3 + 4)/2 = 5/2 \)) configuration \((\uparrow \uparrow \downarrow \downarrow)\) (\( S_{\text{total}} = (3 + 3 + 3 - 4)/2 = -1/2 \)) becomes the lowest excited configuration under the adiabatic and adiabatic + ZPE approximations (see Figure 5), indicating the necessity of full geometry optimisations. On the other hand, the doublet \((\uparrow \uparrow \downarrow \downarrow)\) (\( 2\text{G} \)) configuration becomes the first excited state for \( S_{2ab}(R) \) by all three computational methods (Figure S5 and Table S4C).

### 3.2.2. Left-opened structures

We have calculated the vertical, adiabatic and adiabatic + ZPE energy differences for the intermediately L-opened structure \( S_{2ac}(L) \) as shown in Table S4A. The HS configuration \((\uparrow \uparrow \uparrow \uparrow)\) \((14\text{A})\) \( S_{\text{total}} = (4 + 3 + 3 + 3)/2 = 13/2 \) is the ground state under the vertical approximation for \( S_{2ac}(L) \) with the MV configuration: Ca(II)Mn(III)\(_b\)Mn(IV)\(_b\)Mn(IV)\(_c\)Mn(IV)\(_d\). On the other hand, the intermediate spin (IS) \( S_{\text{total}} = (-4 + 3 + 3 + 3)/2 = 5/2 \) configuration \((\uparrow \uparrow \uparrow \uparrow)\) (\( 6\text{E} \)) becomes the ground configuration in the adiabatic and adiabatic + ZPE approximations. These tendencies are the same for \( S_{2ab}(L) \) (Table S4C). Full geometry optimisations are crucial for elucidations of the magneto-structural correlations. For the \( S_{2ac}(L) \) structure, the energy gaps between the IS (\( 6\text{E} \)) and HS (\( 14\text{A} \)) configurations are 0.59 and 0.51 kcal/mol for the adiabatic and adiabatic + ZPE approximations, respectively. The corresponding energy gaps are reduced to 0.16 and 0.26 kcal/mol for \( S_{2ab}(L) \), indicating significant effect of deprotonation of \( W2 \). Moreover, the HS (\( 14\text{A} \)) and doublet \((\uparrow \downarrow \uparrow \downarrow)\) (\( 2\text{H} \)) excited configurations for \( S_{2ac}(L) \) and \( S_{2ab}(L) \) are almost degenerated in energy under the adiabatic + ZPE approximation, indicating the necessity of the exact diagonalisation of the spin Hamiltonian model.

Figure 6 shows the energy levels for the fully L-opened structure: \( 2\text{ac}'(L) \) obtained by the vertical, adiabatic and adiabatic + ZPE procedures. From Figure 6, the IS configuration \((\downarrow \uparrow \uparrow \uparrow)\) (\( 6\text{E} \)) is the ground state [23] irrespective to the computational procedures, indicating the stabilisation of the IS (\( 6\text{E} \)) configuration for \( S_{2ac}'(L) \) consisted of the HS configuration \((\uparrow \uparrow \uparrow \uparrow)\) of the cubane fragment and down spin \((\downarrow)\) of the dangling Mn(III)\(_a\), namely (3 + 1) model [48] for the MV configuration: Ca(II)Mn(III)\(_b\)Mn(IV)\(_b\)Mn(IV)\(_c\)Mn(III)\(_d\). This trend is not altered by the UB3LYP computations by the use of the extended basis set II (see Table S4B) [23]. The doublet configuration \((\uparrow \downarrow \downarrow \uparrow)\) (\( 2\text{H} \)) is the lowest excited state for \( S_{2ac}'(L) \). The energy gaps between the ground sextet (\( 6\text{E} \)) and doublet excited (\( 2\text{H} \)) configurations are 0.78, 0.65 and 0.48 kcal/mol, for the vertical, adiabatic and adiabatic + ZPE computational procedures, respectively (Table S4A).

The energy differences between the ground states of \( S_{2ac}(R) \) and \( S_{2ac}'(L) \) are 0.50, 0.95 and 1.07 kcal/mol for the vertical, adiabatic and adiabatic + ZPE computational procedures, respectively (Table S4A). Therefore, the R-opened structure \( S_{2ac}(R) \) is more stable by about 1 kcal/mol than the L-opened structure \( S_{2ac}'(L) \) by the latter two methods. However, the energy differences between them become almost zero by the three methods with the basis set II as shown in Table S4B. On the other hand, the energy differences between the
3.3. Theoretical calculations of effective exchange integrals

3.3.1. Right-opened structures

The energy gaps shown in Figure 5 are mapped into spin Hamiltonian models (see supporting S.VIII) [57–63]. The analytical expressions of six effective exchange integrals (J) are first derived from total energies of the lower lying seven BS DFT solutions to explore variations of J values with contribution of the highest energy doublet spin configuration (2F) (↓↑↑↑↓). Using analytic computational formula (see Equation (S30)), the exchange integrals obtained for S_{2ac}(R) were calculated as −19.6, 3.49, 0.15, 16.7, −4.8 and −22.4 cm\(^{-1}\) for J_{ab}, J_{ac}, J_{bd}, J_{bc}, J_{cd}, respectively, under the assumption of the conventional vertical energy gap. The corresponding values obtained by the least square fitting [57,60,61] using the full eight spin configurations were −18.8, 2.72, −0.44, 15.9, −5.4 and −21.9 cm\(^{-1}\), respectively. The sign and magnitude of the J_{pq} values obtained by the analytical and fitting procedures under the classical spin vector model (see Figure 4) are quite similar. The J_{pq} values obtained by GAP procedure [57–63,65] were −18.8, 2.72, −0.44, 15.9, −5.4 and −21.9 cm\(^{-1}\), respectively. Therefore, the J_{pq} values obtained by the fitting [60,61] and GAP procedures [65] are almost the same under the vertical approximation without geometrical changes. The quantum spin corrections for the J_{pq} values by the GAP procedure are also small in the case of the CaMn\(_{4}\)O\(_{5}\) cluster in OEC, since the sizes of spins are 4/2 for Mn(III) and 3/2 for Mn(IV), respectively [62,63]. This is the reason why the BS DFT method provides reasonable J values for Mn clusters [62]. Table 2 summarises the J_{pq} values obtained for the R-opened structure S_{2ac}(R) by analytical, fitting, and GAP procedures based on the vertical energy gap.

Next, the effects of full geometry optimisations for J values are investigated. The adiabatic energy differences shown in Figure 5 are used to determine the J_{ab}, J_{ac}, J_{bd}, J_{bc}, J_{cd} and J_{cd} integrals for S_{2ac}(R) as shown in Table 2 (see also Table S5A). They are −23.9(−23.7), 1.94(1.84), −0.73(−0.87), 13.0(12.9), −0.73(−6.2) and

![Figure 6](https://example.com/fig6.png)

**Figure 6.** Energy levels of the eight different spin configurations of the left-opened structure S_{2ac}(L) (X = O\(^{2−}\) = a; Y = H\(_2\)O = c in Figure 3) of the CaMn\(_{4}\)O\(_{5}\) cluster obtained by the UBLYP calculations (BS set I) under three different procedures: (A) vertical approximation for which the full geometry optimised structure for the HS state is assumed for other seven configurations; (B) adiabatic approximation where full geometry optimisations of all the spin configurations are performed; (C) adiabatic + zero point energy (ZPE) corrections are performed. The S = 5/2 configuration (↓↑↑↑↑) was the ground state for S_{2ac}(L).

| J   | S_{2ac}(R)^{1a} | S_{2ac}(R)^{2a} | S_{2ac}(R)^{1b} | S_{2ac}(R)^{2b} | S_{2ac}(R)^{1c} | S_{2ac}(R)^{2c} |
|-----|----------------|----------------|----------------|----------------|----------------|----------------|
| J_{ab} | −19.6 (−20.4) | −18.8 (−20.1) | −23.9 (−23.1) | −23.7 (−23.3) | −26.1 (−26.8) | −25.8 (−26.4) |
| J_{ac} | 3.49 (3.11) | 2.72 (2.82) | 1.94 (5.44) | 1.84 (2.33) | 2.14 (9.12) | 1.94 (2.11) |
| J_{bc} | 0.15 (0.73) | −0.44 (0.51) | 0.73 (0.29) | 0.80 (0.44) | 0.73 (0.44) | 0.73 (0.15) |
| J_{bd} | 16.7 (14.2) | 15.9 (13.9) | 13.0 (12.8) | 12.9 (13.0) | 10.3 (10.9) | 10.1 (10.5) |
| J_{cd} | −4.80 (−0.58) | −5.38 (−0.80) | −0.73 (−1.60) | −6.20 (−1.46) | −0.44 (−1.46) | −6.40 (−1.75) |
| J_{cd} | −22.4 (−35.4) | −21.8 (−35.1) | −24.6 (−36.8) | −24.5 (−36.9) | −24.8 (−38.1) | −24.6 (−37.7) |

Table 2. The effective exchange integrals (cm\(^{-1}\)) of the Heisenberg spin Hamiltonian model for the right-opened structure S_{2ac}(R) in the S\(_2\) state of the Kok cycle for OEC of PSII (corresponding values for S_{2ac}(R) are given in parentheses).
−24.6(−24.5) cm⁻¹, respectively, by the analytical and GAP (the corresponding values are given in parentheses) procedures, indicating quite similar values except for $J_{bd}$. The discrepancy of $J_{bd}$ arises from the fact that the most unstable spin configuration (↓↓↑↑) (2F) with antiferromagnetic exchange interaction between Mn₈ and Mn₄ sites was neglected in the analytical derivation. This, in turn, indicates that $J_{bd}$ is sensitive to the energy level of 2F after full geometry optimisations. In fact, the Mn₈–Mn₄ distance in the CaMn₄O₅ cluster is just in the spin crossover region (3.2–3.4 Å) from antiferromagnetic (negative $J$) to ferromagnetic (positive $J$) interaction [4,60,80]. The same trends are also obtained for the $J_{pq}$ values based on the adiabatic + ZPE differences as shown in Table 2.

The situation is the same for the R-opened structure $S_{2ab}(R)$ (see parentheses in Table 2) [56]. The energy gaps obtained by three computational methods provide similar $J_{pq}$ values for $S_{2ab}(R)$. The $J_{ab}$, $J_{ac}$, $J_{bd}$, $J_{bc}$, $J_{cd}$ integrals obtained for $S_{2ab}(R)$ by GAP based on the adiabatic + ZPE gaps were −26.4(−25.8), 2.11(1.94), 0.15(−0.73), 10.5(10.1), −1.75(−6.40) and −37.7(−24.6) cm⁻¹, respectively, where the corresponding values for $S_{2ac}(R)$ are given in parentheses. The $J_{bd}$ and $J_{cd}$ values are sensitive to the deprotonation of $Y = H₂O$ coordinated to Mn₉a. Thus, four Mn ions are fully exchanged-coupled in OEC of PSII for water oxidation [45]. The $J_{bd}$ values reported in previous papers [53,75] are often positive (ferromagnetic) under the vertical approximation where the optimised Mn₈–Mn₄ distances by the HS solution are a little elongated.

The $J_{ab}$ and $J_{cd}$ values are negative in sign in accord with the antiferromagnetic (anti-parallel) spin alignment ($↑↓∥↑↓$) of the ground state of the R-opened structure, $S_{2ac}(R)$ and $S_{2ab}(R)$. On the other hand, the $J_{bc}$ value is positive in sign, in consistent with the ferromagnetic spin alignment between the b- and c-sites in these structures. Such qualitative tendencies are independent on the different energy levels obtained by three computational methods and ligands: $Y = H₂O$ or OH⁻ (see Figure S5).

3.3.2. Left-opened structures

As well as the analysis of the R-opened structures, we have performed the analysis of the fully L-opened structure $S_{2ac}'(L)$. The energy levels in Figure 6 are, therefore, mapped into the effective exchange integrals ($J_{pq}$) in the spin Hamiltonian model for $S_{2ac}'(L)$ as shown in Table 3 (see also Table SSC). By using the analytical expression in Equation (S33), the $J_{ab}$, $J_{ac}$, $J_{bd}$, $J_{bc}$ and $J_{cd}$ integrals based on the vertical energy levels were −28.1, 2.33, 1.02, 38.2, 5.05 and 36.7 cm⁻¹, respectively. On the other hand, by the least square fitting (spin-unprojected) procedure, they were −27.8(−27.7), 2.04(2.04), 0.73(0.73), 37.9(37.8), −5.44(−5.44) and 37.1(37.1) cm⁻¹, respectively, where the GAP values are given in parentheses. The sign and magnitude of the $J_{pq}$ values obtained by the analytical and fitting and GAP procedures are quite similar except for the $J_{bd}$ value. Thus the exchange coupling between Mn₈ and Mn₄ ions becomes negative in sign by including 2F (↓↓↑↑↑) configuration because the Mn₈–Mn₄ distance is just in the spin crossover region [60,81].

The adiabatic energy differences in Figure 6 were also transformed into the $J_{ab}$, $J_{ac}$, $J_{bd}$, $J_{bc}$ and $J_{cd}$ integrals for $S_{2ac}'(L)$: they were −41.6(−41.0), 2.18(1.82), 1.60(1.23), 36.9(33.0), −7.76(−8.25) and 35.1(34.6) cm⁻¹, respectively, by the analytical and GAP (values in parentheses) procedures. Furthermore, these procedures based on the adiabatic + ZPE energy differences revealed that they were −36.3(−35.7), 2.04(1.74), 1.31(1.01), 33.0(32.5), 9.90(−10.2) and 34.6(30.6) cm⁻¹, respectively. The analytical and GAP values are quite similar except for the $J_{bd}$ value that becomes negative in sign by including 2F (↓↓↑↑↑) configuration because of the same reason for the vertical case. Thus, the sign and magnitude of $J_{bd}$ are highly sensitive to the Mn₈–Mn₄ distance, indicating the necessity of full geometry optimisations of the eight spin configurations.

The $J_{pq}$ values obtained for the L-opened structure $S_{2ab}''(L)$ are summarised in the parentheses in Table 3. The energy gaps based on adiabatic and adiabatic + ZPE correction methods provide similar $J_{pq}$ values for $S_{2ab}''(L)$. The $J_{ab}$, $J_{ac}$, $J_{bd}$, $J_{bc}$, $J_{bd}$ and $J_{cd}$ integrals obtained for $S_{2ab}''(L)$ by the GAP method based on the adiabatic + ZPE

| $J$         | $S_{2ac}'(L)_{ab}$ | $S_{2ac}'(L)_{bc}$ | $S_{2ac}'(L)_{cd}$ | $S_{2ac}'(L)_{ac}$ | $S_{2ac}'(L)_{bd}$ | $S_{2ac}'(L)_{bc}$ |
|-------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|
| $J_{ab}$    | −28.1(−3.20)       | −27.7(−3.27)       | −41.6(−17.8)       | −41.0(−18.1)       | −36.3(−19.7)       | −35.7(−20.0)       |
| $J_{ac}$    | 2.33(0.00)         | 2.03(0.07)         | 2.18(0.36)         | 1.82(0.15)         | 2.04(0.15)         | 1.74(0.51)         |
| $J_{bd}$    | 1.02(20.7)         | 0.72(20.7)         | 1.60(13.1)         | 1.23(13.5)         | 1.31(11.9)         | 1.01(12.3)         |
| $J_{bc}$    | 38.2(32.8)         | 37.8(32.9)         | 36.9(31.1)         | 36.4(31.6)         | 33.0(28.0)         | 32.5(28.4)         |
| $J_{cd}$    | 5.05(1.36)         | −5.43(1.46)        | −7.76(6.60)        | −8.25(7.09)        | 9.90(5.26)         | −10.2(5.73)        |
| $J_{cd}$    | 36.7(20.3)         | 37.1(29.2)         | 35.1(28.0)         | 35.6(27.5)         | 34.6(23.5)         | 30.6(23.0)         |

Analytical, GAP, Vertical, Adiabatic, Adiabatic + ZPE.

Table 3. The effective exchange integrals (cm⁻¹) of the Heisenberg spin Hamiltonian model for the left-opened structure $S_{2ac}'(L)$ in the $S₂$ state of the Kok cycle for OEC of PSII (corresponding values for $S_{2ac}''(L)$ are given in parentheses).
energy level were \(-20.0(-35.7), \, 0.51(1.74), \, 12.3(1.01), \, 28.4(32.5), \, 5.73(-10.2)\), and \(23.0(30.6) \, \text{cm}^{-1}\) respectively, where the corresponding values for \(S^{2\text{ac}}(L)\) are given in parentheses. The \(J_{ab}\) value is negative in sign in accord with the antiferromagnetic (anti-parallel) spin alignment \((\downarrow\uparrow\uparrow\uparrow)\) of the ground state of the L-opened structure, \(S^{2\text{ac}}(L)\) and \(S^{2\text{ab}}(L)\). On the other hand, the \(J_{bc}\) and \(J_{cd}\) values are positive in sign, in consistent with the ferromagnetic spin alignment between the b- and c-sites and between the c- and d-sites in these structures. Such qualitative tendencies are independent on the three different energy levels and \(Y = \text{H}_2\text{O} \text{ or OH}^-\) (see Figure S5). Interestingly, the \(J_{bd}\) value for \(S^{2ab}(L)\) is positive in sign even though the \(\text{Mn}_b\text{-Mn}_d\) distance is short \((2.86 \, \text{Å})\), indicating that the \(\text{Mn}_b\text{-O-Mn}_d\) angle plays a significant role for ferromagnetic super-exchange interaction (near 90° of the \(\text{MnOMn}\) angle) [81].

The geometrical structures of the closed cubane skeletons Ca(II)Mn(IV)\(_b\)Mn(IV)\(_c\) Mn(IV)\(_d\)O\(_4\) in \(S^{2\text{ac}}(L)\) and \(S^{2\text{ab}}(L)\) are quite similar to that of the HS \((\uparrow\uparrow\uparrow\uparrow)\) Ca(II)Mn(IV)\(_b\)Mn(IV)\(_c\)Mn(IV)\(_d\)O\(_3\) cluster (2) synthesised by Christou et al. [103]. Therefore, the antiferromagnetic spin coupling \((\downarrow)(\downarrow\uparrow\uparrow\uparrow)\) between the \(\text{Mn}(III)\)\(_a\) and cubane skeleton in \(S^{2\text{ac}}(L)\) and \(S^{2\text{ab}}(L)\) is reasonable. The \(J_{bc}, J_{bd}\) and \(J_{cd}\) integrals determined by the magnetic susceptibility experiments of 2 [103] are \(40.5(32.5), \, -9.2(-10.2)\) and \(40.5(30.6) \, \text{cm}^{-1}\), respectively, where the corresponding values for \(S^{2\text{ac}}(L)\) by the adiabatic + ZPE correction method are given in parentheses. The negative \(J_{bd}\) value observed for 2 is similar to that of \(S^{2\text{ac}}(L)\) with the cubane skeleton, indicating the importance of the optimisation of the \(\text{Mn}(IV)\)\(_b\text{-Mn}(IV)\)\(_d\) distance.

The \(J_{ab}, J_{bc}, J_{bd}\) and \(J_{cd}\) integrals reported by others [53] were \(-7.6(-20.0), \, 35.5(28.4), \, 13.0(5.73)\) and \(30.5(23.0) \, \text{cm}^{-1}\), respectively, where our corresponding values for \(S^{2\text{ab}}(L)\) are given in the parentheses. The \(J_{ab}, J_{ac}, J_{ad}\), \(J_{bc}, J_{bd}\) and \(J_{cd}\) integrals obtained for \(S^{2\text{ac}}(L)\) by using the least square fitting and GAP (values in parentheses) procedures are \(-7.57(-7.53), \, 1.89(1.89), \, 8.02(8.01), \, 40.0(40.0), \, -0.78(-0.78)\) and \(37.1(37.1) \, \text{cm}^{-1}\). Therefore, the \(J_{pq}\) values [53] are rather similar to those of the \(S^{2\text{ac}}(L)\) structure instead of \(S^{2\text{ac}}(L)\) except for the \(J_{bd}\) value. The \(J_{bd}\) value [53] is positive in sign in accord with the vertical approximation. Thus, \(J\) values are highly sensitive to small geometry changes, indicating sensitive fingerprint parameters for elucidations of magnetostructural correlations. The agreements between the calculated and observed \(J\) values for both R- and L-opened structures in the \(S_1\) state indicate that these optimised geometries starting from the XRD [21] and XFEL [66] structures are plausible for OEC of PSII, indicating, in turn, the reliability of the framework structure of XRD and XFEL because of the observed similarity between the \(S_1\) and \(S_2\) structures.

### 3.4. Energy levels by the exact diagonalisations

As shown in preceding computational results, electron- and spin-correlation effects in the CaMn\(_4\)O\(_5\) cluster in OEC of PSII are qualitatively grasped under the BS hybrid DFT approximations. Indeed, the energy gaps in Figure 5 provide qualitative picture for relative stabilities among spin configurations at the BS DFT followed by GAP procedure to eliminate spin contaminations. However, the GAP procedure is still insufficient because of lack of the configuration mixing of BS solutions. In this paper, the strong electron-correlation effects involved in the CaMn\(_4\)O\(_5\) cluster are mapped into the effective exchange interactions \((J)\) in the Heisenberg model. Therefore, the energy levels at the exact quantum mechanical level can be obtained by the exact diagonalisation of spin Hamiltonian model for further refinements of the BS DFT computations. The dimension of the spin Hamiltonian matrix becomes \(320 = 5 \times 4 \times 4 \times 4 \times 4\) where \(5(=2(4/2)+1)\) for Mn(III) and \(4(=2(3/2)+1)\) for Mn(IV) in the \(S_2\) state. Figure 7 illustrates the energy levels of the ground and lower excited states for the L-opened structure, \(S^{2\text{ac}}(R)\). The procedure of the exact diagonalisation of the spin Hamiltonian was described in Section SVII. The results show that the doublet state \((S = 1/2)\) is the ground state \(S^{2\text{ac}}(R)\) that is independent on the computational methods of \(J\) values. The spin densities of the ground doublet state exhibit the plus(+)–minus(–) topology in consistent with the LS \((S = 1/2)\) configuration \((\uparrow\downarrow\uparrow\uparrow)\) at the BS level computation (see Figure 5), indicating utility of the BS DFT approach as a first step to the CaMn\(_4\)O\(_5\) cluster in OEC of PSII. The energy gap between the ground doublet and lowest excited quartet states is over \(30 \, \text{cm}^{-1}\) for \(S^{2\text{ac}}(R)\). The corresponding experimental excitation energies are \(35\) [104], \(21.7\) [50], \(23.5\) [50] and \(26.5\) [52] \, \text{cm}^{-1}\), respectively, supporting the computational result based on the optimised geometry starting from the XRD structure [21]. The small energy gaps between the ground and excited states indicate thermal mixing of them at a room temperature: for example, \(300 \, K, kT = 208 \, \text{cm}^{-1}\).

Figure 8 illustrates the energy levels of the ground and lower excited states for \(S^{2\text{ac}}(L)\). The results show that the sextet state \((S = 5/2)\) is the ground state that is independent on the computational methods of \(J\) values. The spin densities of the ground sextet state exhibit the minus(–)–plus(+)–plus(+)–plus(+) topology in consistent with the IS \((S = 5/2)\) configuration \((\downarrow\uparrow\downarrow\uparrow)\) at the BS level computation (see Figure 6). The IS \((S = 9/2)\)
state is the lowest excited state, independent on the computational procedures of $J$. The energy gap between the IS $S = 5/2$ and $S = 9/2$ states is over 25 cm$^{-1}$. Furthermore, the energy gap between the $S = 5/2$ and $S = 7/2$ states is over 100 cm$^{-1}$ for $S_{2ac}'(L)$. Thus, the multiplet states ($S = 5/2$, 7/2 and 9/2) are nearly degenerated for the $S_{2ab}'(L)$ under the assumption $Y = OH^−$. Thus, the sign and magnitude of $J_{bd}$ play an important role for energy levels of these states, indicating discrimination between $H_2O$ and $OH^−$ at the W2(Y) site.

As well as the above discussions, the energy levels of $S_{2ab}(R)$ and $S_{2ab}'(L)$ were illustrated in Figures S5 and S6, and Figures S7 and S8, respectively. As for $S_{2ab}(R)$, the doublet state ($S = 1/2$) is the ground state, independent on the computational procedures of $J$ values (Figures S5 and S6). The spin densities for the ground doublet state also exhibit the plus(+)–minus(−)–plus(+) topology ($↑↓↓↑$) in Figure S5 (see also Figure 4). The energy gap between the ground doublet and lowest excited quartet states is over 20 cm$^{-1}$ for $S_{2ab}(R)$ in compatible with the experimental values [50,52,104].

The computational results indicate that the LS doublet ($S = 1/2$) configuration observed by EPR can be reproduced under both assumptions ($Y = H_2O$ and $OH^−$) in the R-opened structure.

As for $S_{2ab}'(L)$, the ground state is the highest spin at the vertical level of calculation (Figure S7). However, the sextet ($S = 5/2$) state is the ground state under the adiabatic and adiabatic + ZPE correction, indicating the importance of full geometry optimisation and the quantum correction. On the other hand, the septet ($S = 7/2$) becomes the ground state after the exact diagonalisation (see Figure S8). Moreover, the energy gap between the ground ($S = 7/2$) and the next excited intermediate ($S = 9/2$) states is smaller than 15 cm$^{-1}$ as shown in Figure S8. The multiplet states ($S = 5/2$, 7/2 and 9/2) are nearly degenerated for the $S_{2ab}'(L)$ under the assumption $Y = OH^−$. Thus, the sign and magnitude of $J_{bd}$ play an important role for energy levels of these states, indicating discrimination between $H_2O$ and $OH^−$ at the W2(Y) site. The calculated $S = 7/2$ spin state will be further discussed.
forelucidation of the excitation energies of the CaMn followed by the exact diagonalisation is useful enough for the Mn state has been detected [105, 106]. Judging from the porting materials SVI). The signals of the porting materials SVI). The signals of the porting materials SVI). The signals of the porting materials SVI). The signals of the porting materials SVI). The signals of the porting materials SVI). The signals of the porting materials SVI).

Table 4. The projection factors obtained by the $^{55}$Mn EPR experiments and spin densities obtained for the right-opened structure $S_{2ac}(R)(X = O^{2−} = a; Y = H_{2}O = c)$ by the exact diagonalisation of the spin Hamiltonian model consisting of the calculated $J$ values

| Methods       | Mn(IV)$_{a}$ | Mn(IV)$_{b}$ | Mn(IV)$_{c}$ | Mn(III)$_{d}$ | Ref |
|---------------|--------------|--------------|--------------|---------------|-----|
| Exp. I        | 1.27         | −1.00        | −0.99        | 1.70          | [43]|
| Exp. II       | 1.10         | −1.04        | −0.79        | 1.73          | [39]|
| Exp. III      | 1.12         | −0.95        | −0.90        | 1.73          | [50]|
| Exp. IV       | 1.34         | −1.11        | −1.02        | 1.89          | [52]|
| Vert.$^{a}$   | 1.42         | −0.99        | −0.86        | 1.44          | Anal.|
| Vert.$^{b}$   | 1.44         | −0.99        | −0.86        | 1.42          | GAP |
| Adia.$^{b}$   | 0.92         | −0.79        | −0.97        | 1.83          | Anal.|
| Adia.$^{c}$   | 1.34         | −0.98        | −0.89        | 1.53          | GAP |
| Adia.$^{d}$   | 0.67         | −0.60        | −0.99        | 1.92          | Anal.|
| Adia. + ZPE$^{e}$ | 1.27    | −0.96        | −0.90        | 1.58          | GAP |
| QM/MM$^{f}$   | 1.07         | −0.89        | −0.98        | 1.80          | GAP |
| DMRG$^{f}$    | 0.32         | −0.31        | −1.02        | 1.98          |     |

Vertical.$^{g}$ Adiabatic,$^{h}$ Adiabatic + ZPE.$^{i}$[24], $^{i}$[64], $^{i}$ references and computational procedures of $J$ (see text).

(see later) in relation to the ESR spectroscopy of the OEC after the irradiation of the NIR light, where the $S = 7/2$ state has been detected [105, 106]. Judging from all the computational results mentioned above, the BS approach followed by the exact diagonalisation is useful enough for elucidation of the excitation energies of the CaMn$_4$O$_5$ cluster in the S$_2$ state of OEC of PSII. The calculated excitation energies support the assumption of the main cluster skeleton revealed by XRD [21] for the S$_2$ state, though the XRD does not provide information on discrimination between H$_2$O and OH$^{-}$ at the Y-site.

3.5. Theoretical calculations of spin densities

Extensive$^{55}$Mn EPR measurements have been described by using the projection factors (spin densities) based on the observed hyperfine constants ($A_{iso}$) of the Mn ions (see Table S6) in the multiline $g = 2$ spectra for the doublet ground state of the CaMn$_4$O$_3$ cluster in OEC of PSII. The projection factors obtained by the experiments [40–56] are summarised in Table 4. The magnitude of the projection factors ($\rho$) for $S_{2ac}(R)$ indicates the following tendency:

$$\rho (\text{Mn}_b) \sim \rho (\text{Mn}_c) < \rho (\text{Mn}_d) < \rho (\text{Mn}_a) \quad (7)$$

According to the EPR results [52], the $\rho$ values are 1.34(0.99), −1.11(−0.82), −1.02(−0.75), and 1.89(1.39) for the Mn$_p$ ($p = a, b, c, d$) ions, respectively, where the $\rho$ values indicate the maximum (minimum) values (see supporting materials SVI). The signs of the $\rho$ values are consistent with the spin alignment ($\uparrow \downarrow \downarrow \uparrow$) for the ground state of the $S_{2ac}(R)$ structure. The $\rho$ values observed by others [39] are 1.10, −1.04, −0.79 and 1.73, respectively, for Mn(IV)$_a$, Mn(IV)$_b$, Mn(IV)$_c$, and Mn(III)$_d$, indicating the same trend in Equation (7).

Table 4 summarises the spin densities for the ground doublet state obtained by the exact diagonalisation of spin Hamiltonian models, which include effective exchange integrals ($J$) obtained by three different procedures [65]. The spin densities on Mn(IV)$_a$ and Mn(III)$_d$ are almost equivalent in contradiction to the experimental tendency when the $J_{pq}$ values are determined by using the vertical energy levels in Figure 5. The results are independent on the computational procedures of the $J_{pq}$ values. On the other hand, the spin density on Mn(III)$_d$ becomes the largest value for all the cases by using $J_{pq}$ values obtained by the adiabatic and adiabatic + ZPE energy levels. Moreover, the general trend in Equation (7) is reproduced by the analytical, fitting and GAP procedures by the use of adiabatic and adiabatic + ZPE energy levels. The full geometry optimisations for the eight spin configurations are not at all trivial for reproducing the general tendency for projection factors of the EPR experiments [25–52].

The spin densities ($Q$) for the Mn$_p$ ($p = a, b, c, d$) ions are 0.67(0.32), −0.60(−0.31), −0.90(1.02) and 1.58(1.97) for the analytical procedure based on the adiabatic + ZPE energy level, where the corresponding DMRG values [64] are given in parentheses. The DFT (GAP) and DMRG indicated the same the up–down–down–up spin alignment. Moreover, the spin density becomes the largest at the Mn$_d$ site by both methods in accord with the EPR results [39, 52]. The cut-off of the highest energy spin polarisation (SP) configuration $^2$E in the analytical procedure entails the reduction of SP. On the other hand, the spin densities ($Q$) for the Mn$_p$ ($p = a, b, c, d$) ions are 1.27, −0.96, −0.90 and 1.58 for the GAP procedure based on the adiabatic + ZPE energy level. The theoretical values are in good agreement with the corresponding experimental values by Britt et al. [43]: 1.27(1.12), −1.00(−0.95), −0.99 (−0.90) and 1.70(1.73), where the experimental values by Kulik et al. [52] are given in parentheses. Thus, both the experimental and theoretical values have supported the largest spin density on the Mn$_d$ ion for the multiline $g = 2$ spectra.

Table S7A summarises the spin densities ($Q$) calculated for the R-opened structure $S_{2ac}(R)$. The $Q$ values are 1.22(1.16), −0.94(−0.91), −0.89(−0.91) and 1.60(1.66) for the Mn$_p$ ($p = a, b, c, d$) ions, respectively, by the GAP procedure based on the vertical energy gap, where the corresponding GAP values by the adiabatic energy levels are given in parentheses. Similarly, the $Q$ values by GAP based on the adiabatic + ZPE gap are obtained as 0.98(0.30), −0.81(−0.31), −0.93(−1.02) and 1.76(1.98) for the Mn$_p$ ($p = a, b, c, d$) ions, respectively, where the corresponding values by DMRG are given in parentheses. The DMRG calculations have underestimated the spin
densities at Mn_a and Mn_b sites. On the other hand, all the theoretical values for S_{2ac}(L) by BS DFT are compatible with the general trend in Equation (7). This, in turn, implies that discrimination between H_2O and OH^- at the Y-site only by the observed projection factors by EPR is still difficult. The ESEEM [48] and ENDOR [56] results were consistent with Y = H_2O and OH^-, respectively.

The spin densities (Q) of the Mn ions for S_{2ac}(L) were also obtained by the exact diagonalisations as the same as above. The results are summarised in Table 5. The results show that the magnitude of the spin densities Q indicates the following tendency:

\[ Q(Mn_b) < Q(Mn_a) \sim Q(Mn_c) < Q(Mn_d). \] (8)

Based on the vertical energy levels, the spin densities Q for the Mn_p (p = a, b, c, d) ions are -1.32, 1.07, 1.32 and 1.40 by the analytical procedure, and -1.25, 0.97, 1.32 and 1.42 for the GAP procedure, respectively. The signs of the spin projections are consistent with the spin alignment (\( \downarrow \uparrow \uparrow \uparrow \)) for the ground state of the S_{2ac}(L) structure. Based on the adiabatic + ZPE energy levels in Figure 8, the corresponding spin densities Q for S_{2ac}(L) are -1.30, 1.02, 1.35 and 1.40 by the analytical procedure, and -1.02, 0.72, 1.30 and 1.47 for the GAP procedure. The topology of the Q values is also consistent with the spin alignment (\( \downarrow \uparrow \uparrow \uparrow \)) (see also Table S7B). Thus, the experimental projection factors for the S_2 state of OEC of PSII by EPR [48] are correctly reproduced by spin densities (or projection factors) obtained for the CaMn_3O_5 cluster by the exact diagonalisation of the spin Hamiltonian matrices consisting of the calculated J values. This means that the R- and L-opened structures in Figure 3 are plausible models for the S_2 state, supporting the main framework by the high-resolution XRD structure [21] used for starting trials for geometry optimisations of the S_1 and S_2 states.

### Table 5. The spin densities obtained for the left-opened structure S_{2ac}(L) (X = O^{2-} = a; Y = H_2O = c) in the S_2 state by the exact diagonalisation of the spin Hamiltonian model consisting of the calculated J values

| Methods | Mn(II)_a | Mn(IV)_b | Mn(IV)_c | Mn(IV)_d | Ref. |
|---------|----------|-----------|-----------|-----------|------|
| Vert.^a | -1.32    | 1.07      | 1.32      | 1.40      | Anal.|
| Vert.^b | -1.25    | 0.97      | 1.32      | 1.42      | GAP  |
| Adia.^b | -1.10    | 0.80      | 1.30      | 1.45      | Anal.|
| Adia. | -1.10    | 0.80      | 1.30      | 1.45      | GAP  |
| Adia. + ZPE^c | -1.30 | 1.02      | 1.35      | 1.40      | Anal.|
| Adia. + ZPE^d | -1.02 | 0.72      | 1.30      | 1.47      | GAP  |
| QM/MM^d | -1.08    | 0.92      | 1.06      | 1.12      | GAP  |

Vertical, ^a Adiabatic, ^b Adiabatic + ZPE [24], ^c computational procedures of J (see text).

### 3.6. Comparison between the calculated and experimental hyperfine constants

Extensive CW-EPR and pulsed-ENDOR measurements [40–56] have revealed the hyperfine constants of the ^55Mn ions in the multiline g = 2 spectra for the doublet ground state of the OEC of PSII. Britt et al. [43–48] have reported the hyperfine constants (\( A_{iso} \)) obtained on the assumption of the high-oxidation-state scenario for the S_2 state; Mn(IV)_{3}Mn(III). The observed \( A_{iso} \) values for the Mn_{2} (Z = A, B, C, D) ions are, respectively, -245, 217, -297 and 200 MHz, where the notations of Mn ions are given in the original paper of Britt et al. [41–46]. According to the recent EPR studies by Cox et al. [52], the \( A_{iso} \) values for the Mn_{a(1)}, Mn_{b(2)}, Mn_{c(3)} and Mn_{d(4)} are -242 (-251), 208(203), 191(173) and -312 (-332) MHz, respectively, where the corresponding values for the Sr-substituted cluster, SrMn_{4}O_{5}, were given in parentheses. Boussac et al. [39] have also presented the similar \( A_{iso} \) values. However, the notations and assignments of Mn ions are different between the experimental groups [39,48,52]. Therefore, we have re-assigned the Mn ions on the basis of the sign and magnitude of the spin densities obtained by the exact diagonalisation of the spin Hamiltonian matrices consisting of J by GAP. Table 6 summarises the isotropic hyperfine constants \( A_{iso} \) obtained by the average of the observed \( A_{xx}, A_{yy} \) and \( A_{zz} \) components (details are given in supporting material SVI).

The results show that the magnitude of the hyperfine components for the multiline g = 2 spectra for the doublet ground state of the OEC of PSII indicates the following tendency:

\[ A_{iso}(Mn(IV)_b) \sim A_{iso}(Mn(IV)_c) < A_{iso}(Mn(IV)_a) < A_{iso}(Mn(III)_d) \] (9)

The corresponding \( A_{iso} \) values by Britt et al. [43–48] are -245, 217, 200 and -297 MHz for the Mn_{a(1)}, Mn_{b(2)}, Mn_{c(3)} and Mn_{d(4)} ions, respectively. The signs of the re-assigned \( A_{iso} \) values in Table 6 are consistent with the spin alignment (\( \uparrow \downarrow \downarrow \downarrow \)) for the ground state of the S_{2ac}(R) structure. Thus, the sign and magnitude of the experimental \( A_{iso} \) values by the three groups [39,48,52] are consistent within error bars, indicating that the observed \( A_{iso} \) value at the Mn(III)_d site is the largest among the four Mn sites.

The calculated spin densities (Q) for the R-opened structure, S_{2ac}(R) or S_{2ab}(R), are consistent with the sign and magnitude of the hyperfine constants for the S_2 multiline spectra. Therefore, we have calculated the \( A_{iso} \) values by scaling the calculated spin densities by using a simple relationship: \( A_{iso} = -aQ \), where the scaling constant a
is taken to be 208 MHz (see supporting material in Equation (S23)). The $A_{iso}$ values obtained for the Mn$_a$, Mn$_b$, Mn$_c$, and Mn$_d$ ions by this scaling procedure are, respectively, $-295(-300)$, $206(206)$, $179(179)$ and $-300(-295)$ by the exact diagonalisations using the $J_{pq}$ values obtained by the analytical and GAP (values in parentheses) procedures based on the vertical energy levels in Figure 3. The $A_{iso}$ values for Mn$_d(4)$ and Mn$_d(1)$ by both methods are similar in contradiction to the experiments [48], indicating that the $A_{iso}$ values are sensitive to subtle geometry changes.

The corresponding $A_{iso}$ values become, respectively, $-191, 164, 202$ and $-381$ MHz by using the $J_{pq}$ values obtained by the analytical procedure based on the adiabatic energy levels in Figure 6 (see Tables S4A and 5). The magnitude of the $A_{iso}$ value on the Mn$_d(1)$ by these computations becomes larger than that of Mn$_d(4)$, indicating the tendency concluded by the EPR experiments [39,43–48,52]. The calculated $A_{iso}$ value for Mn$_d(1)$ is consistent with the observed values (about 400 MHz) for the Mn(III) ion in model complexes [69]. This indicates that full geometry optimisations of each spin configuration are desirable for improvements of subtle energy differences for the eight spin configurations. The same tendency is obtained by all other computations examined later. For example, the corresponding $A_{iso}$ values are, respectively, $-279, 204, 185$ and $-318$ by the GAP procedure based on the same adiabatic energy level.

The addition of the ZPE correction to adiabatic energy level has also been examined. The $A_{iso}$ values for the Mn$_a$, Mn$_b$, Mn$_c$ and Mn$_d$ ions are, respectively, $-139(-66.6), 125(64.5), 206(212)$ and $-339(-421)$ by using the $J_{pq}$ values obtained by the analytical procedure based on the adiabatic + ZPE energy level in Figure 5, where the corresponding DMRG values by our scaling procedure are given in parentheses. The ratio $A_{iso}(\text{Mn}_d)/A_{iso}(\text{Mn}_a)$ are calculated to be 2.43 and 6.32 by the analytical and DMRG methods, respectively, in contradiction to the experimental value, 1.24–1.32. The $A_{iso}$ values for the Mn$_a$, Mn$_b$, Mn$_c$ and Mn$_d$ ions are, respectively, $-264(-251), 200(208), 187(191)$ and $-329(-312)$ by the GAP procedure, where the corresponding experimental values are given in parentheses [40]. The ratio $A_{iso}(\text{Mn}_d)/A_{iso}(\text{Mn}_a)$ becomes 1.25 in accord with the experimental value 1.24 [40]. Thus, the computational results are consistent with the available experimental values for the multiline $g = 2$ EPR spectra, indicating that the $A_{iso}$ value on the Mn(III)$_d$ ion is the largest among those of four Mn ions of the CaMn$_4$O$_5$ cluster of OEC of PSII [39,43–48,52].

Table S8A summarises the hyperfine components ($A_{iso}$) for the R-opened structure $S_{2ab}(\text{R})$. The $A_{iso}$ values for the Mn$_a$, Mn$_b$, Mn$_c$ and Mn$_d$ ions are, respectively, $-254(-241), 196(189), 185(189)$ and $-333(-345)$ MHz by using the $J_{pq}$ values obtained by the GAP procedure based on the vertical and adiabatic (values in parentheses) energy gaps in Table S4C. The experimental trend in Equation (9) is reproduced for $S_{2ab}(\text{R})$ even by the vertical energy gap. The corresponding $A_{iso}$ values are, respectively, $-204(-251), 168(208), 193(191)$ and $-366(-312)$ by GAP based on the adiabatic energy gaps, indicating the experimental trend: the experimental values are given in parentheses [52]. Therefore, the ratio $A_{iso}(\text{Mn}_d)/A_{iso}(\text{Mn}_a)$ is 1.79(1.24) [40]. The computational results for the $S_{2ab}(\text{R})$ structure are also consistent with the accumulated EPR experiments [39,43–48,52]. This means that the $A_{iso}$ values are not conclusive for discrimination between H$_2$O and OH$^-$ at the Y-site, indicating the necessity of the ENDOR experiment [56].

The CW EPR $g = 4.1$ spectra is too broad to determine the hyperfine constants for the sextet ($S = 5/2$) ground state of the OEC of PSII. However, the ammonia-treated

**Table 6.** Isotropic hyperfine parameters ($A_{iso}$) of the Mn ions in the multiline $g = 2$ doublet state obtained for the EPR experiments and the calculated $A_{iso}$ values obtained for $S_{2ab}(\text{R})$ ($X = \text{O}^2-, Y = \text{H}_2\text{O} = c$) by the exact diagonalisation of the spin Hamiltonian model involving the calculated $J_{pq}$ values.

| Methods | Mn(IV)$_a$ | Mn(IV)$_b$ | Mn(IV)$_c$ | Mn(III)$_d$ | Ref |
|---------|------------|------------|------------|-------------|-----|
| Exp. I  | $-244$     | 217        | 200        | $-297$      | [43]|
| Exp. II | $-255$     | 238        | 191        | $-324$      | [39]|
| Exp. III| $-248$     | 205        | 193        | $-298$      | [50]|
| Exp. IV | $-251(-243)$ | 208(203)   | 191(173)   | $-312(-332)$ | [53]|
| Vert. $^a$ | $-295$     | 206        | 179        | $-300$      | Anal |
| Vert. $^b$ | $-300(-254)$ | 206(196)   | 179(185)   | $-295(-333)$ | GAP |
| Adia.$^b$ | $-191$     | 164        | 202        | $-381$      | Anal |
| Adia.$^b +$ ZPE$^c$ | $-279(-241)$ | 204(189)   | 185(189)   | $-318(-345)$ | GAP |
| Adia.$^b +$ ZPE$^c$ | $-139$     | 125        | 206        | $-399$      | Anal |
| Adia.$^b +$ ZPE$^c$ | $-264(-204)$ | 200(168)   | 187(193)   | $-329(-366)$ | GAP |
| QM/MM$^d$ | $-223$     | 185        | 204        | $-374$      | GAP |
| DMRG$^e$ | $-66.6(-66.6)$ | 64.5(64.5) | 212(212)   | $-412(-412)$ | |

Vertical,$^a$Adiabatic,$^b$Adiabatic + ZPE,$^c$[24],$^d$[64],$^e$computational procedures of J (see text),$^f$values of Sr-substituted system are given in parentheses.
sample exhibited the weak hyperfine lines for the g = 4.1 spectra. The simulations of the line by Britt et al. [43–48] have shown that the A_{iso} values for the Mn_{a}, Mn_{b}, Mn_{c} and Mn_{d} ions are, respectively, 117, −238, −259 and −327 MHz as shown in Table S8B. Previous [23] and present computational results indicate that the L-opened structure, S_{2ac}′(L), is responsible for this broadband. We have calculated the A_{iso} values for the S_{2ac}′(L) structure by using the same procedures for the S_{2ac}(R) structure. The calculated values are summarised in Table S8B. The A_{iso} values for the Mn_{a}, Mn_{b}, Mn_{c} and Mn_{d} ions by the S = 5/2 (S = 3/2) model are, respectively, 297(218), −271(−200), −334(−247) and −354(−262) by the exact diagonalisations using the J_{pq} values obtained by the analytical procedure based on the vertical energy levels in Figure 6. The tendency for the absolute A_{iso} values indicates that the A_{iso} value of the Mn_{d} ion is the largest. The relationship is applicable for all other parameter sets examined here. The calculated A_{iso} values are consistent with the observed values by Britt et al. [43–48] except for the small observed A_{iso} value for the Mn_{c} ion. This discrepancy, in turn, suggests that the ammonia may be ligated to the Mn(III)_{a} ion of the L-opened structure (see Figure S3) in the ammonia-treated sample with the g = 4.1 spectra exhibiting no oxygen evolution.

The isotropic hyperfine constants (A_{iso}) have been regarded as very sensitive fingerprint parameters for magneto-structural correlations for the CaMn_{4}O_{5} cluster of OEC of PSII [25–48]. The calculated A_{iso} values for the R- and L-opened structures are consistent with the magnetic interaction parameters revealed by accumulated EPR and related experiments in the S_{2} state [25–52]. This means that the main geometric structures by the high-resolution XRD [21] and XFEL [66] in the S_{2} state are reliable enough for refinements of the S_{1} and S_{2} structures by eliminating the experimental errors with full geometry optimisations that are applicable for the eight spin configurations in Figure 4.

4. Discussions and concluding remark

4.1. Comparison with the EXAFS structure

Since the reports of XRD with 1.9 Å high resolution [21], the structural studies on OEC of PSII have dramatically advanced. However, at present, the reported OEC structure is only in the static S_{1} state, not in the S_{2} state, where detailed magnetic structural work has been reported. EXAFS results have provided essential distance information for both S_{1} and S_{2} states. The EXAFS results [97–102] showed that the Mn_{a}–Mn_{b}, Mn_{b}–Mn_{c}, Mn_{c}–Mn_{d} and Mn_{b}–Mn_{d} distances for the S_{1} state are 2.71(2.74), 2.79(2.74), 2.71(2.74) and 3.28(3.30) Å, respectively, where the corresponding values for the S_{2} state are given in parentheses. The Mn–Mn distances by EXAFS [97] become homogeneous after the S_{1}–S_{2} transition. The calculated Mn_{a}–Mn_{b}, Mn_{b}–Mn_{c}, Mn_{c}–Mn_{d} and Mn_{b}–Mn_{d} distances for S_{1ac}(R) are 2.71, 2.78, 2.73 and 3.40, respectively. Present results for the S_{1} state by the QM Model I [23,65] are consistent with the S_{1} results by EXAFS [97].

The latest EXAFS results by Berkeley group [97] elucidated that there are two Mn–Mn distances with 2.7 Å and one Mn–Mn distance with 2.8 Å in OEC of PSII. Previous S_{1} results, 2.70(2.75), 2.80(2.80), 2.80(2.80) and 3.38(3.38) Å, for S_{1ac}(R) by QM(Model II)/MM model [24] are rather close to the S_{0} results by EXAFS [97], where the corresponding QM/MM values combined with EXAFS by Luber et al. [90] are also given in parentheses. These results indicated one shorter (2.7 Å) and two longer (2.8 Å) Mn–Mn distances (see Table S3) in contradiction to the EXAFS results [97]. Situations were the same for the QM computations by other groups [53,89].

The above results indicated that more realistic QM models are crucial for the reproduction of the EXAFS results [97–102] (see Table S3). The Mn_{a}–Mn_{b}, Mn_{b}–Mn_{c}, Mn_{c}–Mn_{d}, Mn_{b}–Mn_{d} and Mn_{a}–Mn_{d} distances for S_{1ac}(R)(Y = H_{2}O) in the S_{1} state by the large QM(Model V)/MM calculations [107] were 2.70(2.71), 2.78(2.79), 2.73(2.71), 3.30(3.29) and 4.90 Å, respectively, where the corresponding values by EXAFS [97] are given in parentheses. Thus, the QM/MM results [107] are consistent with those of EXAFS. On the other hand, the corresponding Mn–Mn distances for S_{lab}(R)(Y = OH{^{-}}) by the large-scale QM/MM [107] (EXAFS values in parentheses) were 2.78(2.71), 2.79(2.79), 2.73(2.71), 3.22(3.28) and 4.84 Å, respectively, indicating one shorter (2.7 Å) and two longer (2.8 Å) Mn–Mn distances in contradiction to the EXAFS results [97].

The corresponding values for the S_{2} state were 2.73(2.74), 2.76(2.74), 2.75(2.74), 3.34(3.30) and 4.95 Å, respectively. The calculated average value of the Mn_{a}–Mn_{b}, Mn_{b}–Mn_{c} and Mn_{c}–Mn_{d} distances was 2.75 Å in accord with the EXAFS value (2.74 Å). Thus, the calculated Mn–Mn distances for the S_{1} and S_{2} states are compatible with the EXAFS results [97–102] when the realistic QM model has been employed for the QM/MM computations [107]. The long Mn_{b}–Mn_{d} distances (3.3 Å) by both theory (BS DFT) and experiments (EXAFS [97], XRD [21] and XFEL [66]) are consistent with the open cubane structure in the R-opened structure in Figure 3 in contradiction to the closed cubane structure [15]. Thus, the present and previous BS DFT computations [43,55,61,62] have revealed plausible magneto-structural correlations in the R-opened structure of the S_{2} state based on the XRD structure for the S_{1} state [21].
Refinements of the present \( J_{pq} \) and \( A_{iso} \) values by QM/MM calculations will be published elsewhere.

Previous [23] and present computational results indicate that three short Mn–Mn distances of the L-opened structures, \( S_{2ac}(L) \), \( S_{2ab}(L) \), \( S_{2ac}^\prime(L) \) and \( S_{2ab}^\prime(L) \), are heterogeneous, splitting into one long (>3.0 Å), two short (2.70–2.75 Å) and intermediate (2.85 Å) groups. The long Mn\(_{0a}–Mn_4\) (3.3 Å) distance in the open cubane structure is shortened to about 2.85 Å to form the closed cubane skeleton. Therefore, one of the L-opened structures in the \( S_1 \) state is rather similar to that of the \( S_3 \) state [23].

The \( Mn_1–Mn_2, Mn_0–Mn_4, Mn_2–Mn_4 \) and \( Mn_0–Mn_4 \) distances for \( S_{2ac}^\prime(L) \) are 3.19(3.20), 2.75(2.74), 2.71(2.72) and 2.87(2.81) Å, where the corresponding calculated values for the \( S_3 \) state [23,65] are given in parentheses. The geometrical parameters for the B-model for \( S_3 \) state by EXAFS are 2.82, 2.72, 2.72 and 2.82 Å, respectively [97]. Therefore, the B-model [97] is rather similar to the \( S_{2ac}^\prime(L) \) structure (see also Section 4.4 below). The closed cubane structure is characteristic for the L-opened structure by BS DFT and EXAFS [97–102].

Previous DFT calculations [23,57–63] showed that the valence states of the Mn ions in the \( S_0 \) and \( S_1 \) states are the \( Mn(III)_aMn(III)_bMn(IV)_cMn(III)_d \) and \( Mn(III)_aMn(IV)_bMn(IV)_cMn(III)_d \) configurations, respectively, in the high-oxidation-state scenario. The \( Mn_0 \) ion is oxidised in the \( S_0–S_1 \) transition. There are two possibilities of oxidation of Mn ion in the \( S_1–S_2 \) transition, namely \( Mn(III)_a \) or \( Mn(III)_d \). The latter oxidation provides the L-opened structures, \( S_{2ac}(L) \), \( S_{2ab}(L) \), \( S_{2ac}^\prime(L) \) and \( S_{2ab}^\prime(L) \), with the closed cubane structure. Recently, Christou et al. [103] have synthesised the complex model, \( Ca_2Mn(IV)_3O_4 \) (2), for which the \( Mn_0–Mn_4, Mn_2–Mn_4 \) and \( Mn_0–Mn_4 \) distances are 2.76(2.75), 2.73(2.71) and 2.86(2.87) Å, respectively, where the corresponding values for \( S_{2ac}^\prime(L) \) are given in parentheses. The geometrical parameters for Christou complex [103] and \( S_{2ac}^\prime(L) \) are well consistent with the closed cubane structure without the JT distortion.

4.2. Magneto-structural correlations in OEC

In the past decade, we have investigated magneto-structural correlations in OEC as illustrated in Figure 9. In our early papers [5,6,10,12,57–63,65,80,108], we have elucidated possible spin and charge configurations of Mn oxide clusters and the CaMn\(_{11}O_{12} \) cluster in OEC under the assumption of \( O(3) = O^{2−} \) and \( Y = H_2O \), assuming the XRD structure at 1.9 Å resolution [21]: a and c in \( S_{1ac} \) (i = 0, 1, 2) denote \( O^{2−} \) and \( H_2O \), respectively. The \( MnO_4 \) [12], CaMn\(_{11}O_{12} \) [10] and CaMn\(_{4}O_4 \) [80,108] clusters were precursors for OEC of PSII. The doublet ground state \( S = 1/2 \) in the \( S_{0bc} \) state with the XRD structure was resulted in accord with the EPR experiment. On the other hand, the IS (\( S = 3 \)) and HS (\( S = 13/2 \)) configurations were predicted in the \( S_{1ac} \) and \( S_{2ac} \) states, respectively, under the assumed XRD geometry [21] in contradiction to the available experimental results, indicating the necessity of refinements of the XRD structure [62,63]. The optimised R-opened structure \( S_{1ac}(R) \) [65] exhibited the thermally excited triplet state that was detected by the parallel EPR spectroscopy [27–29]. On the other hand, the optimised structure \( S_{1bb}(C_R) \) with \( X = O(5) = OH^{−} \) and \( Y = OH^{−} \) (b denotes \( OH^{−} \)) provided large (>25 cm\(^{-1} \)) triplet excitation energy, indicating the EPR silent state at 4.8 K in accord with the EPR experiments in polar conditions [27–29,65]. The optimised \( S_{1ac}(R) \) and \( S_{1bb}(C_R) \) structures [67,68] were found to be compatible with the EXAFS [97] and XFEL [66] structures, respectively (see Section 4.1).

Full geometry optimisations in the \( S_0 \) state were performed to elucidate possible structures in the one-electron reduction state, providing the \( S_{0bc}(R) \) and \( S_{0bc}(C_R) \) structures as shown in Figure 9 [23,62]. Therefore, the degree of contamination of \( S_{0bc}(C_R) \) in the XFEL structure \((C_R) \) in the \( S_1 \) state [66] remains as one of the many unsolved problems [67,68]. On the other hand, the R- and L-opened geometrical isomers were obtained by the geometry optimisations of the \( S_{2ac}(R) \) (or \( S_{2ab}(R) \)) and \( S_{2ac}(L) \) (or \( S_{2ab}(L) \)) structures in the \( S_0 \) state generated in the one-electron oxidation of the \( S_3 \) state [23,62]. The spin structures of these isomers were thoroughly investigated in this paper. The proton release becomes necessary for transition from \( S_{1ac}(R) \) or \( S_{1bb}(C_R) \) to \( S_{2ab}(R) \) or \( S_{2bb}(L) \). However, the proton release from OEC was found to be very small in this step, indicating the necessity of proton trapping by amino acid residues such as Asp61, Glu65 and Glu312 [62,63,107]. The geometrical and spin structures of the \( S_{2ab}(R) \) and \( S_{2ab}(L) \) isomers were also examined previously [65]. The \( S = 3 \) ground state with the (\( ↓↑↑↑ \)) spin structure was the ground state for \( S_{2ab}(L) \), whereas \( S = 3 \) with the (\( ↑↓↓↑ \)) spin structure and \( S = 0 \) with the (\( ↑↑↓↑ \)) spin correlation were nearly degenerated for \( S_{3ab}(R) \) [23,65]. This means that the relative stability between them may be variable, depending on environmental effects, indicating the necessity of detailed experimental and theoretical investigations.

4.3. Spin crossover phenomena induced by the NIR irradiation

In cyanobacterial PSII, the \( g = 4.1 \) EPR signal has not been reported [25–56]. Biochemical procedures leading to the formation of this signal in plant PSII do not yield the detectable \( g = 4.1 \) signal in cyanobacteria. Boussac
et al. [36–39,105,106] have detected a third signal at \( g = 10 \) and \( g = 6 \) optimally formed by IR illumination of the \( S = 1/2 \) ground state. This signal converges to the \( g = 4.1 \) state in the case of plant PSII, whereas it decays directly to the \( S = 1/2 \) multline signal in cyanobacteria PSII. Therefore, they have concluded that the \( g = 4.1 \) state in cyanobacteria, should it exist, is unstable and cannot be trapped by the EPR signal. The present computational results may provide a possible explanation of the absence of the \( g = 4.1 \) signal in cyanobacteria.

The energy difference between the R-opened \( S = 1/2 \) and the L-opened \( S = 5/2 \) configurations is not so large in present QM model calculations as shown in Tables S4A and S4B. However, previous QM/MM computations [24,107] using the protein matrix of the high-resolution XRD structure for *Thermosynechococcus (T.) vulcanus* [21] have revealed the greater stability (over 10 kcal/mol) of the \( S = 1/2 \) R-opened structure than the \( S = 5/2 \) L-opened structure. The projection factors and isotropic hyperfine constants obtained for the R-opened structure by the QM/MM method are consistent with the available experiments as shown in Tables 4 and 5. The situation is the same for the L-opened structure as shown in Tables 6 and S8C. Therefore, the large energy difference between the R- and L-opened structures is responsible for the absence of the \( g = 4.1 \) EPR signal for cyanobacteria.

We have also shown that the intervalence transition (IVT) between Mn(III) and Mn(IV) in the mixed valence Mn complexes is often thermally impossible because of tight ligand fields [63]. The present computational results provide a possible energy diagram for the spin crossover phenomenon induced by the IR illumination of OEC of PSII as illustrated in Figure 10 [36–39,105,106].

The vertical IVT from Mn(III)\(_\text{a}\) to Mn(IV)\(_\text{a}\) in the doublet (\( \uparrow \downarrow \uparrow \uparrow \)) ground state of the R-opened structure affords the doublet (\( \uparrow \downarrow \uparrow \uparrow \) (\( S = 1/2 \)) excited state: it is noteworthy that the up-spin transfer (spin delocalisation) is feasible between parallel spin alignments [63].
Figure 10. Schematic illustration of the infrared (IR) light (820 nm)-induced spin crossover phenomena accompanied with the oxygen atom (O(5)) shift of the CaMn₃O₅ cluster in the S₂ state of OEC of PSII. The vertical intervalence transition (IVT) (up-spin transfer) from Mn(III)d to Mn(IV)a in the doublet (↑↓↓↑) ground state of the right (R)-opened structure affords the doublet (↑↓↓↑) (S = 1/2) excited state which relays into the excited octet (↑↑↑↓) (S = 7/2) state without significant geometry change. The oxygen atom (O(5)) shift from the left (Mnₐ) to right (Mn₇) side occurs because of change of the mixed-valence configuration. The intermediate spin states with S = 4/2 and S = 7/2 are nearly degenerated in energy in the case of the left (L)-opened structure with Y = OH⁻. The L-opened structure with S = 5/2 collapses into the most stable R-opened structure with S = 1/2.

The oxygen atom (O(5)) shift from the left (Mnₐ) to right (Mn₇) side is induced by change of the MV configuration from Ca(II)Mn(IV)ₐMn(IV)ₐMn(IV)ₐMn(III)ₐ to Ca(II)Mn(III)ₐMn(IV)ₐMn(IV)ₐMn(IV)ₐ. The oxygen atom shift (O(5)) is induced by the IVT as illustrated in Figure 10. The newly formed S = 7/2 state with the L-opened structure may be assigned as the S = 7/2 state of the L-opened structure with Y = OH⁻. Indeed, the SSB parameters were 0.47 and 0.77, respectively, showing the different degrees of the SSB. The Mnₐ–O(5) bond length for S₂ac(L) (W = H₂O in Figure S3) was shorter than 3.3 Å, indicating no possibility of insertion of small molecules such as H₂O, NH₃, F⁻, etc. The Mnₐ–O(5) bond length for S₂ac(L) was longer than 3.3 Å, indicating vacancy for the insertion of such small molecules.

4.4. One g2 and two g4 S2 structures

The DFT calculations revealed one R-opened S₂ structure with the g2 (S = 1/2) spin state detected by EPR. The R-opened S₃(R) structure with S = 3 (or 0) optimised by DFT was similar to that of the S₂ac(R) g2 state. Indeed, the SSB parameters were 0.66 and 0.79 (0.80) for S₂ac(R) and S₃ac(R) (S₂ab(R), respectively, indicating the structural similarity among them [23]. On the other hand, two L-opened S₂ structures with the same g4 (S = 5/2) spin state were revealed by the BS DFT calculations [23,55]. The SSB parameters for S₂ac(L) and S₂ac(L) were 0.47 and 0.77, respectively, showing the different degrees of the SSB. The Mnₐ–O(5) bond length for S₂ac(L) was shorter than 3.0 Å, indicating no possibility of insertion of small molecules such as H₂O, NH₃, F⁻, etc. The Mnₐ–O(5) bond length for S₂ab(L) was longer than 3.3 Å, indicating vacancy for the insertion of such small molecules. Indeed, the SSB parameter was 0.77 for water-inserted S₂ac(L) (W = H₂O in Figure S3). Similarly, the SSB parameters were 0.83 and 0.89, respectively, for the L-opened S₃ structure, S₃ab(L), and water-inserted S₃ac(L) (W = OH⁻ in Figure 3). Judging from the SSB parameters, S₂ab(L), S₃ab(L) and water-inserted S₃ac(L) exhibited structural similarity.
The different behaviours of the Berkeley EXAFS spectra for the $S_1$ and $S_2$ states in the Kok cycle of OEC of PSII [97–102] are consistent with the geometrical change from $S_{2ab}(R)$ (or $S_{2ab}(L)$) to $S_{3ab}(L)$ (or water-inserted $S_{3ab}(L)$) in the $S_2\rightarrow S_1$ transition. In fact, the $\text{Mn}_a\text{–Mn}_b$, $\text{Mn}_b\text{–Mn}_c$, $\text{Mn}_a\text{–Mn}_d$, $\text{Mn}_b\text{–Mn}_d$ and $\text{Mn}_a\text{–Mn}_d$ distances for the $S_3$ state at high resolution (2.5 Å) will provide clear-cut evidence for three-dimensional discrimination between $S_3(R)$ with $R(\text{Mn}_a\text{–Mn}_b) = 2.7 \text{ Å}$ and $S_2(L)$ with $R(\text{Mn}_a\text{–Mn}_b) = 3.4 \text{ Å}$.

4.5. Right- and left-handed scenario for water oxidation

The $R$- and $L$-opened structures revealed by the BS DFT calculations [23,55] open $R$- and $L$-handed scenarios for the $O$–$O$ bond formations of water oxidation in OEC of PSII. In fact, full geometry optimisations have revealed that water molecule can be inserted into the coordination-unsaturated Mn(III)$_3$ site in the R-opened structure, whereas it is inserted into the Mn(III)$_3$ site in the L-opened structure generated by the oxygen (O$_{5(1)}$ shift) as shown in Figure S3 [23]. Past several years, Siegbahn [86–89] has theoretically investigated several radical-coupling pathways (for example, O$_{2(3)}$–O$_{4(5)}$ coupling [58]) for the water splitting reaction, proposing several $R$-handed transition structures for water oxidations. Our computational results have shown that the L-handed scenario presented by several groups [9,57–63,108,110–116] in the past decades still remains as a possible route for water oxidation. We have located a transition state for the $O$–$O$ bond formation in the L-handed scenario based on the small QM model (QM Model I in our notation) [59]. However, as shown in our recent paper [24], valine185 in front of the O$_{5(1)}$ site may play significant role(s) [117] for controlling relative stability between the $R$- and $L$-type transition structures: they are supposed to be highly dependent on structures of protein matrix employed for QM/MM modelling [24] of OEC of PSII [21] (see also Figure 12).

4.6. Spin Hamiltonian model for radical coupling reactions

Historically transition-metal oxo bonds had been formally regarded as $\text{M}(m + 2)\text{O}^{2-}$, $(m = 1–3)$ indicating the nucleophilic reactivity of oxygen dianions. Therefore, it was so surprising that in the early 1980s, the high-valent $(m = 2, 3)$ transition metal oxo species (M = Fe, Mn, etc.) were found to exhibit the radical and/or electrophilic reactivity as demonstrated in the case of epoxidation reactions of double bonds and hydrogen abstraction reactions from $\text{H}$–$\text{C}$ bonds of alkanes, etc. In the early 1980s, we have examined the HOMO–LUMO mixing of the $\sigma$–$\pi$ bonds of transition metal oxo $(\text{M} = \text{O})$ species [4,6], showing the metal diradical character (•$\text{M}$–$\text{O}$•) that can be grasped by spin Hamiltonian models [118]. In this series of papers [79,108], we have examined the scope and applicability of the BS approaches to the species. Developments of our theoretical approaches to the manganese-oxo $\text{Mn} = \text{O}$ (•$\text{M}$–$\text{O}$•) species were summarised previously [80].

Spin Hamiltonian models examined in this paper have been used for theoretical modelling of radical reactions [118]. The radical abstraction reaction with linear tri-centre system was characterised as exchange-allowed because of smooth bond interchange of covalent bonds. On the other hand, the radical insertion reaction through the triangle geometry in Figure 2(A) is exchange-forbidden because of the necessity of sudden switching of exchange couplings [118]. The radical reaction through planar four-centre transition structure was regarded as exchange-allowed [119] because of no curve crossing, whereas the radical reaction through the perpendicular $(D_{2d})$ transition structure in Figure 2(B) was characterised as exchange-forbidden because of the curve crossing between different spin structures [119]. Thus, the effective exchange interactions $(J)$ were useful for prediction of allowed or forbidden radical coupling modes, providing spin-correlation diagrams for radical reactions [120]. The spin Hamiltonian models [118–120] were applied for the derivation of selection rules of radical-coupling reactions in native and artificial water-oxidation catalysts [108]. They were successfully applied to the Tanaka-type Ru catalyst for water oxidation [121,122]. The spin-correlation diagrams were already presented in our previous papers [6,57–63,80,108] for pictorial understanding of variations of exchange coupling modes in the water oxidation.

As an example [108], Figure 11 illustrates the spin-correlation diagrams for water oxidation (see Equation (1)) in a $\text{CaMn}_2\text{O}_5$ model complex that has been proposed before discovery of the high-resolution XRD structure [21] (see Figure 6 in Part XV [108] of this series of
Figure 11. Spin correlation diagrams for the water-oxidation reaction (see Equation (1)) in oxygen-evolving complex (OEC) of photosystem II (PSII) that has been assumed to have the CaMn$_3$O$_5$ core [108] instead of the CaMn$_4$O$_5$ core of the London structure [15] before the discovery of the high-resolution XRD structure [21] since the O$_{(4)}$ site was crucial for maintaining the high-valent Mn$_a$ = O species. The intermediate spin (↓↑↑↑) ($S = 5/2$) configuration was also assumed for the initial stage of the O–O bond formation in accord with the magneto-structural correlations [23,65]. The local singlet diradical (LSD) configuration is crucial for the exchange-allowed O–O radical coupling (RC) reaction. After the O–O bond formation, spin inversion is necessary for generation of triplet molecular oxygen via local triplet diradical (LTD) configuration.

4.7. Proton shuttle mechanism for water oxidation in OEC

In radical coupling mechanisms in Figure 11, the Ca ion and hydrogen-bonding networks for the CaMn$_4$O$_5$ cluster (see Figure S2) play no significant role for the O–O bond formations. Our previous QM/MM computations [24,107] have revealed the channel structures for proton transfer and water inlet for water oxidation in Equation (1) in OEC of PSII. Previously [23], we have proposed a water-assisted proton-shuttle mechanism for the water oxidation based on (1) the Lewis acid character of the Ca(II) ion, (2) proton-accepting (base) ability of the O$_{(5)}$ site and (3) four hole-doped states of the CaMn$_4$O$_5$ cluster, indicating stabilisation of a newly formed Mn(IV) = O(•Mn(III)–O•) bond with hydrogen bonding of W3 on Ca(II) in the $S_3$ state as illustrated in Figure 12; the latter state corresponds to the ((3444) with (↓↑↑↑) + O•(↑)) structure [98]. After photoinduced one-electron oxidation in the $S_4$ state, the following reactivity scenarios are feasible: (A) radical coupling mechanism where the radical character (•Mn(IV)–O•) of the high-valent Mn(V) = O bond may play an important role for oxygen activation, and the generated oxygen radical site may couple with a hydroxyl radical (•OH) formed with electron transfer from hydroxyl anion to a high-valent Mn site of the CaMn$_4$O$_5$ cluster, or (B) acid–base mechanism where the electrophilic character of the high-valent Mn(V) = O bond may play an important role for the nucleophilic attack of hydroxyl anion generated by the proton transfer from W3 on the Ca(II) ion to the O$_{(5)}$ site. The elongation
Figure 12. A water-assisted proton-shuttle mechanism for the water oxidation based on (1) the Lewis acid character of the Ca(II) ion, (2) proton-accepting (base) ability of the O(5) site and (3) four hole-doped states of the CaMn$_4$O$_5$ cluster, indicating stabilization of a newly formed Mn(IV) = O (Mn(III)–O) bond with hydrogen bonding of W3 on Ca(II) in the S$_2$ state; the latter state corresponds to the (3444) with (↓↑↑↑↑) + O*(↑) structure [98]. After photoinduced one-electron oxidation in the S$_5$ state, following reactivity scenarios are feasible: (A) radical coupling mechanism where the radical character (Mn(IV)–O) of the high-valent Mn(V) = O bond may play an important role or (B) acid–base mechanism where the electrophilic character of the high-valent Mn(V) = O bond play an important role for the nucleophilic attack of hydroxyl anion generated by the proton transfer from W3 on the Ca(II) ion to the O(5) site. The superposed state of the above two extremes (A) and (B) may also be feasible, providing a chameleonic mechanism (C) [23,80] where the weight of the structure (B) may be variable with the environmental conditions.

5. Conclusion remarks

As a continuation of previous theoretical studies on the S$_1$ and S$_3$ states [65], we have elucidated magneto-structural correlations in the S$_2$ state of OEC of PSII. Theoretical discovery [23,55] of the L-opened structure in the S$_2$ state of OEC of PSII based on the BS UB3LYP computations has opened a new structural basis for lucid understandings of accumulated EPR and related experimental results [25–53] because previous theoretical computations have provided only the R-opened structure [86–94]. The optimised geometrical parameters for the CaMn$_4$O$_5$ cluster model in the S$_2$ state are consistent with the available EXAFS results of OEC of PSII [97–102], though the high-resolution S$_2$ XRD structures are not available yet. Recently, Kern et al. [123] presented the XFEL structure...
for the $S_2$ state, but the resolution was not sufficient for elucidation of subtle geometry change in the $S_1$–$S_2$ transition. The full geometry optimisations have elucidated three different rules (Ia–Ic) for the Mn–Mn distances in the cluster. The calculated magnetic interaction parameters by BS DFT have concluded that the R- and L-opened structures [23,55] in the $S_2$ state are assigned, respectively, as the $g = 2.1$ multiline doublet ($S = 1/2$) and $g = 4.1$ sextet ($S = 5/2$) states observed by the EPR spectroscopies [25–56]. The spin crossover phenomenon from the R($S = 1/2$) to L($S = 5/2$) state induced by the infrared light illumination [36–39] in cyanobacteria PSII is also explained based on the computational results for the model clusters with and without deprotonation of water molecule coordinated to the Mn$_4$ ion. Thus, the SSB in the labile Mn–O–Mn bond [57–63] of the CaMn$_4$O$_5$ cluster in Figure 3 is one of the basic features for the active site of water oxidation in the high-resolution XRD structure [21] of OEC of PSII. The discovery of the L-opened structures in the $S_2$ state [23,55] supported our previous left-handed scenarios [23,58,108,124] for the O–O bond formation in water oxidation in Equation (1) (see Figures 11 and 12).

The energy gaps among the eight spin configurations have been calculated by the vertical, adiabatic and adiabatic + ZPE correction methods based on the geometry optimisations by the BS UB3LYP computations. These energy gaps have been mapped into the effective exchange integrals ($J$) in the spin Hamiltonian model by the GAP procedure eliminating spin contamination errors of the BS approximation [65]. The exact diagonalisation of the spin Hamiltonian model consisting of the $J$ values has been performed to obtain the excitation energies and spin densities (projection factors) which are utilised for elucidation of the magneto-structural correlations in OEC of PSII. The full geometry optimisations of the eight spin configurations have been necessary for the reproduction of the EPR experimental results [25–52]. The calculated spin densities ($Q$) on the Mn ions are mapped into the isotropic hyperfine constant ($A_{iso}$) of the $^{55}$Mn$_{4}(4)$ site by using a scaling factor: $A_{iso} = -aQ$ ($a = 208$ MHz). This simple and practical procedure has supported the magneto-structural correlations [23]. The present theoretical computations of magnetic interaction parameters for the CaMn$_4$O$_5$ cluster have provided reasonable explanations of the EPR [25–56] and EXAFS results in the $S_2$ state of OEC of PSII [97–102]. Spin Hamiltonian models examined have been applied for the derivation of spin-correlation diagrams of water-oxidation processes in OEC of PSII [57–63].

In conclusion, theoretical computations based on QM models [57–63] for OEC of PSII are crucial for unification of available geometrical, electronic and spin-state information obtained by XRD, XFEL, EXAFS, EPR and optical results for the active site (the CaMn$_4$O$_5$ cluster) of OEC (see Figures S4A and S4B). The BS DFT computations of the cluster models in the $S_1$, $S_2$ and $S_3$ states of OEC [23,24,57–63] have revealed that the CaMn$_4$O$_5$ cluster in OEC of PSII can be regarded as a typical SCES, where the orbital, spin and charge degrees of freedom play important roles for theoretical description of labile Mn–O bonds confined with proteins. In this regard, the mean-field hybrid DFT approach is regarded as a first theoretical step to elucidate the mechanisms of water oxidation in OEC of PSII. Mapping of the BS DFT results to the spin Hamiltonian models followed by the exact diagonalisation provided the energy levels and projection factors that are responsible for the EPR and optical spectroscopies. Post-DFT approaches are crucial for confirmation and refinement of the hybrid DFT results and spin Hamiltonian models.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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