



# Density functional theory calculation of $\mu$ -oxo and $\mu$ -hydroxo bridged iron(III) aqua dimer complexes in perfluorinated sulfonic acid ionomer membranes



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## ABSTRACT

Spectroscopic properties of diiron(III) decahydrates in iron(III) exchanged Nafion membranes were calculated by DFT method. Optimized geometries, quadrupole splitting constants in Mössbauer spectra, vibrational frequencies and electronic transition energies of  $\mu$ -oxo diiron(III) decahydrate calculated with range-separated hybrid functionals were in excellent agreement with the experimental values. Another doublet species observed in Mössbauer spectra was identified as  $\mu$ -hydroxo diiron(III) decahydrate, which has been hitherto assigned as a hydrogen peroxide bridged dimer. Changes in relative abundance of  $\mu$ -oxo and  $\mu$ -hydroxo complexes by protonation/deprotonation of the diiron(III) decahydrates were explained by relative abundance and stability of hydrated protons in iron(III) exchanged Nafion membranes.

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## 1. Introduction

Among various types of polymeric ion exchange membranes, perfluorinated sulfonic acid ionomer membranes such as Nafion<sup>®</sup> have been given special attention for its application to proton conducting membranes in fuel cells mainly due to their high proton conductivity and high durability under conditions where reactive species such as hydrogen peroxide or hydroxyl radical are generated that may lead to degradation of the membranes [1]. Various structural models have been proposed until recently and association of the hydrophilic sulfonic acid groups at the end of the side chains from the hydrophobic perfluorinated backbones has been postulated as a key to high proton conductivity at low water content and [1–3].

In the early period of the development of the membranes, metal cation exchanged membranes were employed to probe association of the acid sites through exchanged metal cations [4,5]. Iron cations have been the most extensively studied as they transform from monomer to polymer or precipitate which were presumed to be related to conformational changes of the acid sites as well as the backbones of the polymer membranes. Formation of dimeric Fe–O–Fe unit was identified in the infrared absorption spectra of the Nafion membrane exchanged with ferric ions [4].

One great advantage of the measurement of the membranes exchanged with ferrous or ferric ions is that <sup>57</sup>Fe Mössbauer spectroscopy can be applied to study local environment around the exchanged ferrous and ferric ions as well as their cluster formation. Heitner-Wirguin et al. identified two doublets with quadrupole splittings of 0.45 and 1.68 mm s<sup>-1</sup> in the Mössbauer spectra of the frozen Nafion membrane exchanged with ferric ions, which were assigned to small clusters and dimers, respectively. At very low temperature a sextuplet became dominant in the Mössbauer spectra, which was ascribed to magnetically-coupled large clusters [5]. Rodmacq et al. measured Mössbauer spectra of Nafion membranes exchanged with Fe<sup>2+</sup> and Fe<sup>3+</sup> ions [6–8]. While isolated Fe<sup>2+</sup> hydrate was the only species identified in the Fe<sup>2+</sup> exchanged Nafion membranes with different water content, a dimeric species was identified in the Fe<sup>3+</sup> Nafion membranes with quadrupole splittings of about 1.7 mm s<sup>-1</sup>, in addition to an isolated Fe<sup>3+</sup> species [7,8]. Although in the Mössbauer spectra another doublet with quadrupole splittings at around 0.4 mm s<sup>-1</sup> was identified, no definitive structure was given to this species. In the following paper of the same group they measured X-ray absorption spectra of the Fe<sup>3+</sup> Nafion membranes and from EXAFS analysis the dimeric species was shown to be  $\mu$ -oxo dimer [(H<sub>2</sub>O)<sub>5</sub>FeOFe(OH<sub>2</sub>)<sub>5</sub>]<sup>4+</sup> [9]. While this species was dominant in the dried Fe<sup>3+</sup> Nafion membrane giving doublet with quadrupole splittings of about 1.7 mm s<sup>-1</sup>, another doublet with the smaller splitting of about 0.5 mm s<sup>-1</sup> became more intense in the membrane after being

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boiled in hot water [9]. Precipitation of ferric ions occurred by immersion of the Fe<sup>3+</sup> Nafion membranes in aqueous solutions [10].

It should be noted that these doublet species have also been identified in aqueous solutions. As for the  $\mu$ -oxo dimer bridged dimer complex, Knudsen et al. assigned the doublet with  $|\Delta E_Q| = 1.67 \text{ mm s}^{-1}$  in frozen aqueous solutions of Fe(ClO<sub>4</sub>)<sub>3</sub> to a  $\mu$ -oxo bridged dimer based on its quadrupole splitting which is very close to the value of  $\mu$ -oxo bridged binuclear iron(III) complex [(Fe heedta)<sub>2</sub>O]<sup>2-</sup> (heedta<sup>3-</sup> = *N*-(2-hydroxyethyl)-ethylenediamine-*N,N,N'*-triacetic acid) with  $|\Delta E_Q| = 1.66 \text{ mm s}^{-1}$ . They also measured infrared spectra of aqueous solutions of ferric perchlorate and nitrate and identified a band at 870 cm<sup>-1</sup>, which is assigned to the Fe–O–Fe antisymmetric stretching mode of the  $\mu$ -oxo bridged dimer [11]. Junk et al. have successfully isolated crystals of  $\mu$ -oxo bridged dimers from iron(III) solutions by addition of crown ethers and subsequent evaporation and their structures were determined by X-ray crystallography [12,13]. Very recently, Zhu et al. identified formation of a  $\mu$ -oxo bridged dimer in concentrated aqueous solutions of ferric nitrate from the Fe K-edge EXAFS data, whose frozen samples showed the doublet with  $|\Delta E_Q| = 1.65 \text{ mm s}^{-1}$  [14].

On the other hand, although a  $\mu$ -hydroxo bridged dimer Fe<sub>2</sub>OH<sup>5+</sup> has been proposed to assign the doublet with smaller quadrupole couplings observed in the Mössbauer spectra, Meagher proposed a hydrogen oxide (H<sub>3</sub>O<sub>2</sub><sup>-</sup>) bridged Fe<sup>3+</sup> species, based on a very simple point charge model estimation of the quadrupole coupling constant [15]. This assignment was supported by Kiwi et al. who attributed an absorption band in an UV absorption spectrum at  $\lambda_{\text{max}} = 334 \text{ nm}$  to this species [16]. However, no EXAFS analysis consistent with this geometry having fairly large Fe–Fe distance has ever been reported, while the  $\mu$ -hydroxo bridged species was refuted as it was inconsistent with the EXAFS data [15].

Based on the existence of the  $\mu$ -oxo bridged binuclear iron(III) complex in the Nafion membranes as well as concentrated aqueous solutions [11–14], it seems very plausible to assume formation of  $\mu$ -hydroxy bridged complex by protonation of the  $\mu$ -oxo bridged complex. In fact, Armstrong et al. suggested reversible protonation of  $\mu$ -oxo bridged iron(III) binuclear complex, ( $\mu$ -oxo)bis( $\mu$ -acetato)bis(tri-1-pyrazolylborato)diiron(III), [(HBpz<sub>3</sub>)FeO(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>Fe(HBpz<sub>3</sub>)], by synthesis of its protonated form, i.e., ( $\mu$ -hydroxo)bis( $\mu$ -acetato)bis(tri-1-pyrazolylborato)diiron(III), [(HBpz<sub>3</sub>)Fe(OH)(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>Fe(HBpz<sub>3</sub>)], and structural determination by X-ray crystallography [17]. The most significant difference in the properties of the  $\mu$ -oxo and the  $\mu$ -hydroxo complexes was found in their magnetic properties: their magnetic coupling constants determined from magnetic susceptibility data were  $J = -121$  and  $-17 \text{ cm}^{-1}$ , respectively. Another  $\mu$ -hydroxo bridged iron(III) dimer, {[(salten)Fe]<sub>2</sub>(OH)[B(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>](CH<sub>3</sub>CN)<sub>x</sub>(H<sub>2</sub>O)<sub>y</sub> [H<sub>2</sub>salten = 4-azaheptane-1,7-bis(salicylideneiminato)] was studied by Jullien et al. [18]. Its  $J$  value was  $42 \text{ cm}^{-1}$  and showed a doublet in Mössbauer spectra with quadrupole splitting of  $|\Delta E_Q| = 0.97 \text{ mm s}^{-1}$ . These values are quantitatively reproduced by DFT calculation to be  $J = 46 \text{ cm}^{-1}$  and  $\Delta E_Q = -1.09 \text{ mm s}^{-1}$ . Although its  $\mu$ -oxo bridged analogue has not been synthesized, their calculated magnetic coupling and quadrupole splitting constants are calculated to be  $J = 203 \text{ cm}^{-1}$  and  $\Delta E_Q = -1.22 \text{ mm s}^{-1}$ , which are significantly larger than the corresponding values of the  $\mu$ -hydroxo bridged complex.

For complexes having weak antiferromagnetic coupling with  $J \sim 10 \text{ cm}^{-1}$ , the diamagnetic ground state is populated close to 100% only at very low temperature and at the paramagnetic excited states are populated at higher temperature which results in a broad and asymmetric doublet in Mössbauer spectra [11]. The doublet with the smaller quadrupole splitting observed in the Mössbauer spectra of the iron(III) exchanged Nafion membranes show such asymmetric and broad features and consistent with its assignment to a  $\mu$ -hydroxo bridged dimer. These results

strongly support that two doublets with two different quadrupole coupling constants observed in the Mössbauer spectra are  $\mu$ -oxo and  $\mu$ -hydroxo bridged binuclear iron(III) complexes. However, while the assignment of the doublet with the larger  $|\Delta E_Q|$  to the  $\mu$ -oxo bridged dimer has been also substantiated by the EXAFS data analysis [9,14], observation of the asymmetric doublets with smaller quadrupole splittings in the Mössbauer spectra is the only experimental clue to support formation of the  $\mu$ -hydroxo bridged dimer.

In this study we report results of DFT calculation of monoxy and monohydroxy bridged complexes to confirm that the two doublets in the Mössbauer spectra can be assigned to these two species based on the calculated quadrupole splitting and magnetic coupling constants. As shown by Julien et al. and other recent studies, these values can be quantitatively reproduced by DFT calculation with popular hybrid DFT functionals and basis sets [18]. In addition to such hybrid exchange–correlation functionals with constant mixing factors of the exact exchange, a hybrid exchange correlation functional with distance dependent mixing factors is also employed as this type of functionals give slightly better calculated values of the electric field gradients from which quadrupole splitting constants are obtained [19]. It is also expected that the functional give more accurate values of the electronic excitation energies which are known to be underestimated by the typical hybrid functionals with constant mixing factors.

## 2. Computational method

All the calculations were performed by using the Gaussian09 (Rev.C.01) program [20]. Hybrid DFT calculations were performed by using three different functionals: Becke's three parameter hybrid exchange functional with the correlation functional of Lee, Yang and Parr, denoted as B3LYP [21], and PBE gradient corrected exchange correlation functional with exact exchange, denoted as PBE0 [22], are two hybrid functionals with constant mixing factors of exact exchange employed in this study as the most popular ones. A range separated hybrid functional with the PBE exchange–correlation functional denoted as LC- $\omega$ PBE [23–25] is also used as this type of the functional give good results for excited states as well as open shell systems. Ahlrich's triple zeta basis sets with polarization functions denoted as TZVP are used throughout this study [26]. Solvation effect was taken into account by polarizable continuum model [27].

As the first step of calculations of binuclear iron(III) complexes, geometries of the high symmetry state ( $S = 5$ ) were optimized. Then singlet state wavefunctions ( $S = 0$ ) were prepared with fragment molecular orbitals of the two iron(III) pentaqua complexes ( $S = 5/2$ ) and a bridging moiety ( $S = 0$ ) by assuming antiferromagnetic coupling. Then geometries of the singlet state binuclear complexes were optimized and they found to be very close to those of the high spin state ( $S = 5$ ). Hessians at the optimized geometries were analytically calculated and infrared absorption spectra were simulated with calculated frequencies and absorption intensities of the normal modes under harmonic approximation. Electronic excitation energies and oscillator strengths were calculated by TDDFT. Quadrupole splitting constants in Mössbauer spectra were calculated from electric field gradients at nuclei according to the equation by Schwerdtfeger et al. [28].

$$\Delta = \frac{Q}{0.09893} V_{zz} \left( 1 + \frac{\eta^2}{3} \right)^{1/2} \quad (1)$$

where  $Q$  is quadrupole moment of <sup>57</sup>Fe ( $I = 3/2$ ), which was assumed to be  $0.16 \text{ b}$  ( $1 \text{ barn} = 10^{-28} \text{ m}^2$ ),  $V_{zz}$  is the largest component of the electric field tensor (a.u.),  $\eta$  is anisotropy parameter,

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