

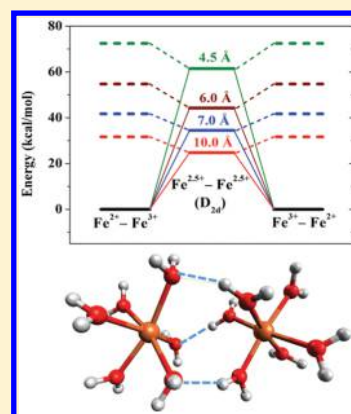
# Ground and Excited States of the $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ Clusters: Insight into the Electronic Structure of the $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ – $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ Complex

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## S Supporting Information

**ABSTRACT:** We report the ground and low-lying electronically excited states of the  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  and  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  clusters using multiconfiguration electronic structure theory. In particular, we have constructed the potential energy curves (PECs) with respect to the iron–oxygen distance when removing all water ligands at the same time from the cluster minima and established their correlation to the long-range dissociation channels. Due to the fact that both the second and third ionization potentials of iron are larger than the one for water, the ground-state products asymptotically correlate with dissociation channels that are repulsive in nature at large separations, as they contain at least one  $\text{H}_2\text{O}^+$  fragment and a singly positively charged metal center ( $\text{Fe}^+$ ). The most stable equilibrium structures emanate, via intersections and/or avoided crossings, from the channels consisting of the lowest electronic states of  $\text{Fe}^{2+}({}^5\text{D}, 3\text{d}^6)$  or  $\text{Fe}^{3+}({}^6\text{S}, 3\text{d}^5)$  and six neutral water molecules. Upon hydration, the ground state of  $\text{Fe}^{2+}(\text{H}_2\text{O})_6$  is a triply ( ${}^5\text{T}_g$ ) degenerate one, with the doubly ( ${}^5\text{E}_g$ ) degenerate state lying  $\sim 20$  kcal/mol higher in energy. Similarly, the  $\text{Fe}^{3+}(\text{H}_2\text{O})_6$  cluster has a ground state of  ${}^6\text{A}_g$  symmetry under  $T_h$  symmetry, which is well-separated from the first excited state. We also examine a multitude of electronically excited states of many possible spin multiplicities and report the optimized geometries for several selected states. The PECs of those states exhibit a high density of states. Focusing on the ground and the first few excited states of the  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  and  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  clusters, we studied their mutual interaction in the gas phase. We obtained the optimal geometries of the  $\text{Fe}^{2+}(\text{H}_2\text{O})_6$ – $\text{Fe}^{3+}(\text{H}_2\text{O})_6$  gas-phase complex for different Fe–Fe distances. For distances shorter than 6.0 Å, the water molecules in the respective first solvation shells located between the two metal centers were found to interact via weak hydrogen bonds. We examined a total of 10 electronic states for this complex, including those corresponding to the electron transfer (ET) from the ferrous to the ferric ion. The ET process is discussed and a possible path via a quasi-symmetric transition state is suggested.



## I. INTRODUCTION

The hydration of the  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  cations, either as isolated ions or as a  $\text{Fe}^{2+}$ – $\text{Fe}^{3+}$  pair, has attracted a lot of attention due to the fact that these ions constitute the archetypal system for describing the Marcus theory<sup>1–10</sup> for electron transfer (ET) in an aqueous solution with contributions from both the outer (effect of the solvent) as well as the inner<sup>11–13</sup> solvation shells of the two metal ions.

The importance of these cations has drawn a plethora of theoretical approaches aimed at describing the structural, dynamical, and spectral properties as well as the electronic structure of the solvated  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  cations. Curtiss et al.<sup>14</sup> constructed an iron–water interaction potential from calculations on the  $\text{Fe}^{2+}/\text{Fe}^{3+} + \text{H}_2\text{O}$  system. However, their simulations with the fitted potentials did not yield the correct coordination number, a fact that prompted them to conclude that many-body effects must be included. They subsequently obtained the correct coordination number by introducing an empirical iron–water potential. The latter potential was used by Guàrdia and Padro<sup>15</sup> to obtain the iron–water and iron–hydrogen radial distribution functions (RDFs) via molecular

dynamics (MD) simulations. Degréve and Quintale<sup>16</sup> focused on the second solvation shell of the two cations, reporting that it consists of 13 (for  $\text{Fe}^{2+}$ ) and 15 (for  $\text{Fe}^{3+}$ ) water molecules as a result of Monte Carlo (MC) calculations. The first quantum mechanical/molecular mechanical (QM/MM) calculations were reported by Remsungen and Rode,<sup>17–19</sup> relying on the Hartree–Fock (HF) theory for the QM part, which contained the metal and the first solvation shell, coupled to a two- plus three-body classical Stillinger–Rahman central force<sup>20</sup> modified by Heinzinger and co-workers<sup>21</sup> water potential (BJH-CF2) for the MM part. These authors reported that the first solvation shell of both ions consists of six water molecules, whereas an average of 12.4 and 13.4 water molecules constituted the second solvation shell of the aqueous  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  cations, respectively. Jarzecki et al. carried out density functional theory (DFT) calculations for the  $\text{Fe}^{2+}(\text{H}_2\text{O})_6$  and  $\text{Fe}^{3+}(\text{H}_2\text{O})_6$  clusters, describing the solvent through the polarizable continuum model (PCM).<sup>22</sup> A similar approach for the

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$[\text{Fe}(\text{OH})_n(\text{H}_2\text{O})_{6-n}]^{(2-n)+}$  systems was reported by Guimaraes et al.<sup>23</sup> The rigid SPC, SPC/E, and a newly constructed SPC-based flexible-water model (SPC + CCL) combined with effective cation–water classical potentials were employed by Amira et al.<sup>24</sup> to obtain the RDFs, self-diffusion coefficients, and O–H stretching spectra. The same authors later reported periodic Car–Parrinello plane wave DFT calculations using a box of 32 water molecules.<sup>25</sup> A larger box with 64 water molecules was subsequently used by Bogatko et al.<sup>26</sup> in conjunction with DFT-based MD simulations. Meanwhile, Li and Yang reported MD calculations using potentials obtained from the atom-bond electronegativity equalization method (ABEEM),<sup>27</sup> while Moin et al. applied the QM/MM based quantum mechanical charge field (QMCF) approach<sup>28</sup> in conjunction with MD simulations. Finally, Ye et al. reported new  $\text{Fe}^{2+}/\text{Fe}^{3+}$ –water potentials that reproduce their X-ray absorption spectra.<sup>29</sup> Recently, Semrouni et al. extended the AMOEBA classical force field to describe the interaction between the singlet, triplet, and quintet spin states of  $\text{Fe}^{2+}$  and a single water molecule based on MP2, CASPT2, and DFT calculations.<sup>30</sup>

Parallel to this effort, much progress has been made toward the estimation of the rate constant for the ET from  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  in an aqueous solution, based on the Marcus theory.<sup>6,9,10</sup> The local environment of the solvated cations is, in general, asymmetric, and there is a clear distinction (i.e., via the different Fe–O distances) between the  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  centers.<sup>31</sup> In an aqueous solution, those iron–oxygen distances,  $R(\text{Fe}–\text{O})$ , are experimentally 2.12(2) Å for  $\text{Fe}^{2+}$  and 2.01(2) Å for  $\text{Fe}^{3+}$ , as determined by neutron diffraction in heavy water ( $\text{D}_2\text{O}$ ) with six water molecules composing the first solvation shell of both ions.<sup>32,33</sup> However, the fluctuations of the solvent molecules can provide the appropriate conditions where the two metal centers,  $\text{Fe}^{2+}$ (left) and  $\text{Fe}^{3+}$ (right), are nearly symmetric (transition state), so an instantaneous ET can occur. The energy needed to access those metal–solvent configurations can be provided by an external stimulus, such as photoexcitation.<sup>34</sup> After that point, the system can relax back to  $\text{Fe}^{3+}$ (left) and  $\text{Fe}^{2+}$ (right), i.e., the charges on the metal centers are exchanged. More detailed and mathematically founded accounts for this process are given in refs 35–37. Through this mathematical formulation of the ET process, the following three factors have been assumed to determine the reaction rate constant: the reorganization energy, the crossover frequency through the transition state, and the transfer integral.<sup>38</sup>

Early experimental work suggested two different mechanisms for the ferrous–ferric exchange rate.<sup>39–43</sup> The first one does not involve any intermediate species (outer sphere mechanism), and the reaction rate is proportional to the concentrations of the  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  cations.<sup>43</sup> On the other hand, the ET can be facilitated by the exchange of some auxiliary ion such as the proton-coupled ET.<sup>40,44–46</sup> For instance, in the case of ice media, a water bridging mechanism has been proposed, allowing the ET to occur over very great distances.<sup>41</sup>

Theoretically, it has been rather accepted that the ET occurs at short  $R(\text{Fe}^{2+}–\text{Fe}^{3+})$  distances of approximately 5.5 Å.<sup>38,47–50</sup> Early theoretical work reported by Newton and co-workers in the early 1980s<sup>47,51–53</sup> proposed that the ET occurs at  $R < 6.9$  Å and most probably at  $R = 5.3$  Å.<sup>47</sup> These authors also studied the isotope effect (replacing H with D) and concluded that the exchange for D is twice as slow compared to H,<sup>54,55</sup> in agreement with experiment.<sup>56</sup> Kuharski et al. using an  $e^-–\text{Fe}^{3+}$

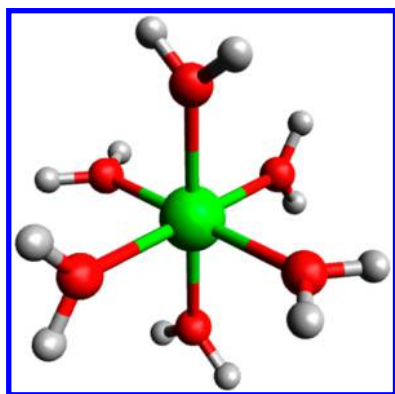
pseudopotential along with umbrella sampling suggested that the optimum distance is between 4.5 and 5.5 Å.<sup>48</sup> The activation energy of the ET process has been estimated to be about 20 kcal/mol. These authors stated that pushing the two positively charged ions from 6 to 4.5 Å is energetically costly. The molecular origin of the extra attraction needed by the two ions to come closer has been questioned earlier by Tembe et al.,<sup>47</sup> whereas Bader et al. extended their methodology<sup>48</sup> to consider the quantum effects due to the water fluctuations through the quantum MC technique.<sup>57</sup> They stressed the importance of the tunneling effect, and they confirmed the twice as large ET rate for H compared to D. Subsequently, Kumar and Tembe performed classical MD simulations while fixing the iron–iron distance at 5 Å.<sup>49</sup> The peaks of the reported  $\text{Fe}^{2+/3+}–\text{O}$  and  $\text{Fe}^{2+/3+}–\text{H}$  RDFs were found to be shifted by 0.2 Å compared to the single solvated ions. In addition, it was reported that the coordination shells remained intact. At the same time, Bader and Chandler produced MC trajectories and potential of mean force (PMF) curves with respect to the iron–iron distance.<sup>58</sup> The treatment of the long-range forces has been found to be of primary concern, namely, “...truncated long-ranged interactions can lead to substantial artifacts...”, suggesting that the use of the Ewald summation is more appropriate. Karlström and Malmqvist studied the gas-phase  $\text{Fe}^{2+}(\text{H}_2\text{O})_6–\text{Fe}^{3+}(\text{H}_2\text{O})_6$  interaction, assuming a specific arrangement of the water molecules.<sup>59</sup> Babu et al. studied the orientation of the water molecules lying in between the two ions, which were 5 Å apart, with the aid of MD simulations.<sup>60</sup> In 2004, Rustad et al. included the hydrolysis effect in their model, concluding that increasing the pH value causes the increase of the energy barrier of the ET process.<sup>50</sup> The recent work of Migliore et al.<sup>38</sup> acknowledges the complicated electronic structure of the  $[\text{Fe}^{2+}–\text{Fe}^{3+}]_{\text{aq}}$  system and thus fractional occupation numbers in conjunction with the DFT + U scheme were employed. These authors extracted geometric configurations from MD simulations, and they calculated the transfer integral using the first solvation shell molecules. We finally refer to the recent work by Menzelev et al.,<sup>61</sup> who examined the ET mechanism between a triply and a doubly charged metal using four different methodologies: ring polymer dynamics, semiclassical instanton theory, exact quantum dynamics, and the Marcus theory in a classical solvent.

Although there has been voluminous work on the solvated  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  cations, we are aware of only a couple of previous studies focused on the gas-phase water clusters of these ions. The first one analyzed the two-, three-, and four-body contributions to the interaction energy between  $\text{Fe}^{3+}$  and four, six, and eight water molecules at the HF level.<sup>62</sup> The second one was a systematic experimental investigation combined with theoretical results, focusing on the successive dehydration energies for the  $\text{Fe}^{3+}(\text{H}_2\text{O})_{n=1–6}$  species.<sup>63</sup> In the current study, we focus on the gas-phase structure, energetics, and, in particular detail, the electronic state manifold of the  $\text{Fe}^{2+}(\text{H}_2\text{O})_6$  and  $\text{Fe}^{3+}(\text{H}_2\text{O})_6$  clusters as well as their  $\text{Fe}^{2+}(\text{H}_2\text{O})_6–\text{Fe}^{3+}(\text{H}_2\text{O})_6$  gas-phase complex. Our results are aimed at providing the baseline benchmarks regarding the electronic structure aspects that need to be considered in order to establish a molecular level picture of the ET process in an aqueous solution, a problem that will be addressed in future simulation studies that will be based on the current findings. To our knowledge, the present study is the first systematic work examining the complicated manifold of electronic states of the gas-phase ferrous and ferric hexacoordinate water clusters.

This article is organized as follows. In Section II, we outline the computational methodology used; in section III, we report the potential energy curves (PECs) of six water molecules simultaneously approaching the metal center being  $\text{Fe}^{2+}$  (Section IIIa) or  $\text{Fe}^{3+}$  (Section IIIb), in a manner similar to that in our previous work for  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Al}^{3+}$ .<sup>64</sup> The approach of the two  $\text{Fe}^{2+}(\text{H}_2\text{O})_6$  and  $\text{Fe}^{3+}(\text{H}_2\text{O})_6$  clusters in the ground and excited electronic states forming the  $[\text{Fe}_2(\text{H}_2\text{O})_{12}]^{5+}$  complex is reported in Section IV. Finally, we recapitulate our findings in Section V.

## II. COMPUTATIONAL DETAILS

We constructed the PECs of six water molecules simultaneously approaching either the  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$  ions with the same iron–oxygen distances in an octahedral fashion. We selected the symmetric approach of all six water molecules simultaneously approaching the metal center in order to identify the asymptotic fragments that are responsible for the formation of the corresponding minima for each case. This helps to identify the nature and origin of the various stable configurations of the hydrated complexes in terms of their constituent fragments. There are certainly other interesting pathways on those multidimensional potential energy surfaces. However, the purpose of the present study is to identify the electronic states of the solvated  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions that are relevant to the electron transfer process, and this is the reason that the above reaction coordinate was selected at present. The arrangement and orientation of the water molecules are shown in Figure 1.



**Figure 1.** Tetrahedral-type arrangement ( $T_h$  point symmetry group) of the six water molecules (red and white spheres) around the ferrous or ferric metal center (green sphere).

The  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+/3+}$  clusters have  $T_h$  symmetry; however, our calculations were performed using the symmetry of its  $D_{2h}$  subgroup. For the purposes of the present study, the possible Jahn–Teller distortion of the  $T_h$  geometry has been ignored, since it is not going to affect the nature of the PECs.

We employed the correlation-consistent basis sets of triple- $\zeta$  quality, namely, the cc-pVTZ basis sets for iron<sup>65</sup> and hydrogen<sup>66</sup> and the aug-cc-pVTZ basis set for oxygen.<sup>67</sup> The PECs are constructed at the multiconfiguration self-consistent field (MCSCF) level. To enable the inclusion of the PECs emanating from both the ground-state adiabatic fragments, involving  $\text{H}_2\text{O}^+$  ( $\tilde{X}^2B_1$ ) and those from  $\text{Fe}^{2+/3+}$  and the neutral water molecules, we selected the active space arising from the 4s,3d atomic orbitals of iron and the 1b<sub>1</sub> molecular orbitals of two water molecules. The prohibitive number of the electronic states prevented the inclusion of the 1b<sub>1</sub> orbital of all six water molecules in the active space, thus resulting in a smaller number of electronic states. However, as will be discussed later, this does not affect either the energetics or the shape of the important PECs. The geometry of every water molecule was fixed with an O–H distance of 0.96 Å and HOH angle of 107.0°, which are average values for the optimized geometries of the  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  water clusters (vide infra).

Under  $D_{2h}$  symmetry, the active space consists of three  $a_g$ , one  $b_{1g}$ , two  $b_{2g}$ , one  $b_{3g}$  and one  $b_{3u}$  orbitals, thus distributing 9 (for  $\text{Fe}^{3+}$ )/10 (for  $\text{Fe}^{2+}$ ) electrons in 8 orbitals. The resulting number of configuration state functions (CSFs) for the  $\text{Fe}^{2+}(\text{H}_2\text{O})_6$  and  $\text{Fe}^{3+}(\text{H}_2\text{O})_6$  clusters in the various spins states and symmetries are given in Table 1. In order to examine several excited states, we relied on the state-averaged MCSCF (SA-MCSCF) technique. More specifically, we averaged each spin-multiplicity separately, i.e., 48 singlets, 32 triplets, 25 quintets, and 15 septets for  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  and 49 doublets, 37 quartets, 72 sextets, and 8 octets for  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ . At this level of theory, the ionization energy (IE) for gas-phase water is 11.2 eV (compared to the experimental value<sup>68</sup> of 12.62 eV), whereas the first three IEs for iron are 6.3, 15.1, and 28.4 eV (compared to the experimental values<sup>68</sup> of 7.90, 16.19, and 30.65 eV). To partially account for the missing nondynamical electron correlation, we applied the second-order multi-reference perturbation theory (MR-PT2), as implemented in MOLPRO (*rs2c* directive).<sup>69–71</sup> The MR-PT2 value for the IE of water is 12.7 eV, and that for the first three IEs of iron is 7.4, 15.8, and 30.1 eV, all of which are much closer to the experimental values. The inclusion of nondynamical correlation has an appreciable effect on the excited and the binding

**Table 1.** Number of Configuration State Functions (CSFs) in the MCSCF Calculations for the Various States of  $T_h$  Symmetry and Spin Multiplicities of the  $\text{Fe}^{2+}(\text{H}_2\text{O})_6$  and  $\text{Fe}^{3+}(\text{H}_2\text{O})_6$  Clusters

	$A_g$	$B_{3u}$	$B_{2u}$	$B_{1g}$	$B_{1u}$	$B_{2g}$	$B_{3g}$	$A_u$
$\text{Fe}^{2+}(\text{H}_2\text{O})_6$								
singlet ( $2S + 1 = 1$ )	198	128	120	160	122	168	160	120
triplet ( $2S + 1 = 3$ )	186	180	180	204	174	204	204	180
quintet ( $2S + 1 = 5$ )	46	59	65	45	56	39	45	65
septet ( $2S + 1 = 7$ )	2	7	5	1	4	3	1	5
$\text{Fe}^{3+}(\text{H}_2\text{O})_6$								
doublet ( $2S + 1 = 2$ )	330	278	264	310	272	324	310	264
quartet ( $2S + 1 = 4$ )	144	176	184	160	184	152	160	184
sextet ( $2S + 1 = 6$ )	21	39	36	15	36	18	15	36
octet ( $2S + 1 = 8$ )	n/a <sup>a</sup>	2	1	n/a <sup>a</sup>	3	1	n/a <sup>a</sup>	1

<sup>a</sup>No states were computed.



**Table 2.** Optimized Geometries (Distances in Å, Angles in Degrees), Excitation ( $T_e$ ), and Binding ( $D_e$ ) energies (kcal/mol) for Selected Electronic States of the  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  and  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  Clusters at the SS-MCSCF and MR-PT2 (in Parentheses) Levels of Theory under  $T_h$  Symmetry (see Figure 1)

state <sup>a</sup>	$R(\text{Fe}-\text{O})^b$	$R(\text{O}-\text{H})^b$	$\varphi(\text{HOH})^b$	$T_e^d$	$D_e^{c,d}$	$T_e^e$	$D_e^{c,e}$
$[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$							
$^5T_g$	2.199 (2.145)	0.946 (0.967)	107.0 (105.8)	0.0	204.5	0.0	227.1 (230.6)
$^5E_g$	2.255 (2.204)	0.947 (0.967)	106.6 (105.5)	10.6	193.9	19.3	207.8 (211.7)
$^3B_{3g}$	2.148	0.946	107.4	50.9	153.6	49.5	177.6
$^1A_g$	2.089	0.946	107.8	61.1	143.4	57.2	169.9
$^7A_g^f$	2.383	0.948	107.0	117.7	86.8	118.9	108.2
	2.073	0.956	108.2	120.0	84.5	132.5	94.6
$^5A_g$	2.070	0.955	108.4	130.7	73.8		
$[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$							
$^6A_g$	2.059 (2.032)	0.955 (0.975)	106.8 (106.0)	0.0	109.5	0.0	155.1 (158.3)
$^4B_{1g}$	2.011	0.954	107.4	76.6	32.8	60.3	94.8
$^2B_{2g}$	1.966	0.954	107.8	97.8	11.7	73.1	82.1
$^6A_u$	2.248	0.956	106.2	143.5	−34.0	100.7	54.4
$1^4A_u$	2.254	0.956	106.2	144.7	−35.3		
$^2A_u$	2.197	0.956	106.4	199.4	−89.9	149.7	5.4
$2^4A_u$	2.196	0.956	106.4	200.4	−91.0		
$^8B_{2g}$	2.490	0.957	106.0	254.4	−144.9		

<sup>a</sup>The lowest state of the singlet ( $^1X$ ), doublet ( $^2X$ ), triplet ( $^3X$ ), quartet ( $^4X$ ), sextet ( $^6X$ ), and octet ( $^8X$ ) manifolds was examined. Apart from the  $^5T_g$ ,  $^5E_g$ ,  $^5A_g$ ,  $^7A_g$ , and  $^6A_g$  states, which refer to the  $T_h$  symmetry, the rest of the electronic terms refer to the  $D_{2h}$  symmetry. <sup>b</sup>SS-MCSCF (MR-PT2) optimized geometries. <sup>c</sup> $D_e$  is computed with respect to the  $\text{Fe}^+(\text{^6D}) + \text{H}_2\text{O}^+(\text{^2X}_2\text{B}_1) + 5\text{H}_2\text{O}(\text{^1X}_1\text{A}_1)$  and the  $\text{Fe}^+(\text{^6D}) + 2\text{H}_2\text{O}^+(\text{^2X}_2\text{B}_1) + 4\text{H}_2\text{O}(\text{^1X}_1\text{A}_1)$  asymptotes. <sup>d</sup>SS-MCSCF values. <sup>e</sup>MR-PT2//SS-MCSCF (MR-PT2//CAS-PT2) values. <sup>f</sup>Two different minima were located on the same PEC.

energies (see below and Table 2), especially for the triply charged cluster. The reason is mainly attributed to the mismatch (by  $\sim 1.5$  eV or  $\sim 35$  kcal/mol) between the MCSCF and the experimental water ionization energies. Finally, we have fully optimized several electronic states at the state-specific MCSCF (SS-MCSCF) level of theory and performed MR-PT2 calculations at the SS-MCSCF geometries (MR-PT2//SS-MCSCF). All valence electrons of iron and water molecules were correlated at the MR-PT2 level. Additionally, for the lowest electronic states of both complexes [ $^5T_g$  and  $^5E_g$  states for  $\text{Fe}^{2+}(\text{H}_2\text{O})_6$  and the  $^6A_g$  state for  $\text{Fe}^{3+}(\text{H}_2\text{O})_6$ ], we also obtained MR-PT2 optimal structures. For these states, the six water molecules are clearly neutral, with their six  $1b_1$  molecular orbitals being practically doubly occupied. For this reason, all of them were kept closed at the SS-MCSCF calculations. Due to the inherent size-extensivity issues, the MR-PT2 binding energies were obtained via the supermolecule approach.

Concerning the  $\text{Fe}^{2+}(\text{H}_2\text{O})_6\text{--Fe}^{3+}(\text{H}_2\text{O})_6$  complex, we performed Hartree–Fock (HF) and MCSCF calculations using the cc-pVDZ (for Fe and H) and aug-cc-pVDZ (for O) basis sets.<sup>65–67</sup> The MCSCF active space for that complex consisted of the five 3d orbitals on each of the two iron centers (11 electrons in 10 orbitals), for a total of 10 CSFs for the high-spin states. All calculations were performed with the MOLPRO and Gaussian09 suite of electronic structure programs.<sup>72,73</sup>

### III. IRON–WATER INTERACTION

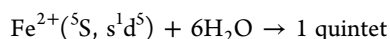
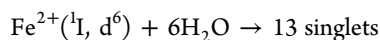
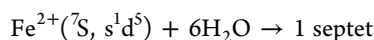
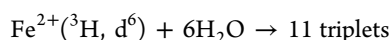
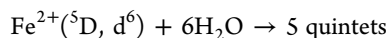
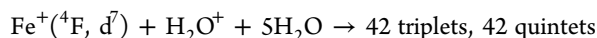
Recently, we have studied the interaction of the  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ , and  $\text{Al}^{3+}$  ions with up to six water molecules<sup>64</sup> with the water ligands approaching the metal centers along the same path as the one used in this study. We showed that the ground state hexa-aqua metal equilibrium structure originates from the

$\text{Mg}^{2+}/\text{Ca}^{2+}/\text{Al}^{3+} + n\text{H}_2\text{O}$  fragments and that these multivalent ions can be stabilized in an aqueous environment with respect to the water ionization channel only if the number of the water molecules in their first solvation shell is larger than a critical number  $n$ , which is 0, 1, and 4 for calcium, magnesium, and aluminum, respectively. We further obtained the different shapes of the PECs corresponding to the approach of different number of water molecules to the metal centers, which suggest that just the *ab initio* two-body metal–water interaction is not enough for simulating the solvation of the metal in bulk water, i.e., many-body effects<sup>14</sup> are quite important.

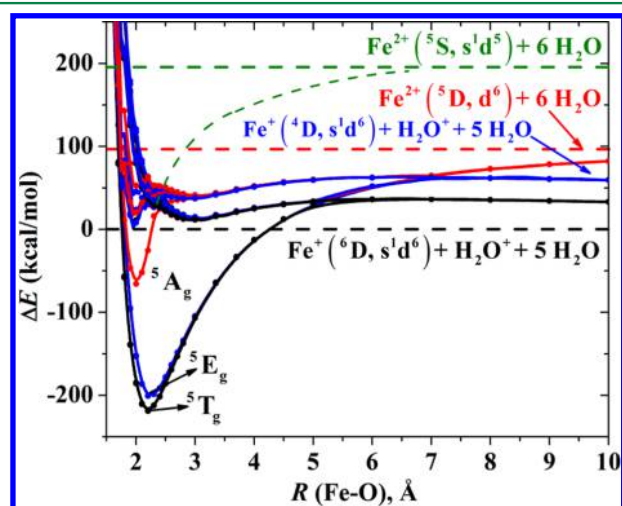
For the  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  case, an additional complexity is introduced arising from the electronic structure of a transition metal atom. The number of electronic states adiabatically correlated with the various states of all fragments increases dramatically, a fact that can cause convergence problems in the electronic structure calculations. The ground states of the  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions are  $^5D$  and  $^6S$ , with corresponding electronic configurations of  $3d^6$  and  $3d^5$ , respectively. In this study, our interest is limited to the states emanating from the  $^3H$ ,  $^7S$ ,  $^1I$ , and  $^5S$  states of  $\text{Fe}^{2+}$  and the  $^4G$  and  $^2I$  ones of  $\text{Fe}^{3+}$ . The cases of the  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions will be discussed in the Sections IIIa and IIIb.

**IIIa.  $\text{Fe}^{2+}$ –Water Interaction.** The first IE of iron ( $\text{IE}_1 = 7.90$  eV) is smaller than that of the water molecule (12.62 eV), whereas its second IE ( $\text{IE}_2 = 16.19$  eV) is larger.<sup>68</sup> Therefore,  $\text{Fe}^{2+}$  contains enough energy to ionize one water molecule and the ground-state dissociation channel of the  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  cluster is  $\text{Fe}^+(\text{^6D}, s^1d^6) + \text{H}_2\text{O}^+ + 5\text{H}_2\text{O}$ . On the other hand, the  $\text{Fe}^{2+} + 6\text{H}_2\text{O}$  asymptote lies [ $\text{IE}_2(\text{Fe}) - \text{IE}(\text{H}_2\text{O})$ ] 3.57 eV or  $\sim 96.5$  kcal/mol above the lowest dissociation channel. In between these two channels, there exists a large number of other channels involving excited states

(valence or Rydberg) of all species ( $\text{Fe}^+$ ,  $\text{Fe}^{2+}$ ,  $\text{H}_2\text{O}$ , and  $\text{H}_2\text{O}^+$ ). The MCSCF active space used in this study allowed for the consideration of the channels related to  $\text{Fe}^+$  ( $^6\text{D}$ ,  $s^1d^6$ ;  $^4\text{D}$ ,  $s^1d^6$ ) and  $\text{Fe}^{2+}$  ( $^5\text{D}$ ,  $^3\text{H}$ ,  $^7\text{S}$ ,  $^1\text{I}$ ,  $^5\text{S}$ ). The first excited state of  $\text{Fe}^+$  is the  $^4\text{F}(d^7)$  state lying lower than the  $^4\text{D}(s^1d^6)$ . However, our SA-MCSCF failed to converge to the fragments involving  $\text{Fe}^+(^4\text{F}, d^7)$  at large distances, converging to the  $\text{Fe}^+(^4\text{D}, s^1d^6)$  state instead. The issues arising from this behavior will be discussed later. The channels of interest at large separations along with the spin multiplicity of the producing states are



Because of the inclusion of the  $1b_1$  orbital of just two water molecules (necessary to be able to describe the  $\text{Fe}^+ + \text{H}_2\text{O}^+ + \text{H}_2\text{O}^+$  channel), the above number of states is smaller in our calculations (see below). We begin our discussion with the PECs of the quintet states shown in Figure 2. The ground-state



**Figure 2.** Potential energy curves of the quintet electronic states of  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ . Different colors correspond to different adiabatic fragments. The dashed green line traces the expected diabatic curve for the  $^5\text{A}_g$  state.

fragments,  $\text{Fe}^+(^6\text{D}, s^1d^6) + \text{H}_2\text{O}^+ + 5\text{H}_2\text{O}$ , give rise to 10 PECs colored in black, all of which are repulsive for distances larger than 5 Å. The reason is the Coulombic repulsion between  $\text{Fe}^+$  and the approaching  $\text{H}_2\text{O}^+$  ions that varies as  $1/R(\text{Fe}-\text{O})$  at long separations. Under  $D_{2h}$  symmetry, these 10 states belong to the following irreducible representations:  $\text{A}_g$ ,  $\text{A}_w$ ,  $\text{B}_{1g}$ ,  $\text{B}_{2g}$  (two states),  $\text{B}_{3g}$ ,  $\text{B}_{1w}$ ,  $\text{B}_{2w}$  and  $\text{B}_{3u}$  (two states). For instance, at 10 Å, the Coulombic repulsion amounts to 33.2 kcal/mol, which is precisely the energy of all 10 states (with respect to the

asymptote) at this  $R(\text{Fe}-\text{O})$  separation (cf. Figure 2). However, for shorter distances, the charge-dipole interaction starts playing an important role. The charge-dipole interaction decays at infinity as  $1/[R(\text{Fe}-\text{O})]^2$ , and, as such, it is weaker than the Coulombic repulsion at long range. The additive effect, though, of five water dipoles attracted by the  $\text{Fe}^+$  cation core overwhelms the  $\text{Fe}^+-\text{H}_2\text{O}^+$  repulsion for  $R(\text{Fe}-\text{O}) \leq 5$  Å and creates 10 shallow local minima at  $R(\text{Fe}-\text{O}) \sim 3$  Å lying  $\sim 10$  kcal/mol above the adiabatic fragments. These minima, although thermodynamically unstable, can be kinetically stable. Note that at a distance of  $\sim 5$  Å another effect comes into play. The PECs of the five quintet states ( $2^5\text{A}_g$ ,  $^5\text{B}_{1g}$ ,  $^5\text{B}_{2g}$ ,  $^5\text{B}_{3g}$ ) stemming from the  $\text{Fe}^{2+}(^5\text{D}, d^6) + 6\text{H}_2\text{O}$  asymptote cross four of the aforementioned 10 states having the same symmetry (see below).

The next adiabatic channel corresponds to the  $\text{Fe}^+(^4\text{D}, s^1d^6) + \text{H}_2\text{O}^+ + 5\text{H}_2\text{O}$  asymptote. In this case, one of the electrons of iron undergoes a spin flip ( $^6\text{D} \rightarrow ^4\text{D}$ ) and therefore the spatial symmetries of the resulting 10 electronic states are identical with the ground-state fragments, viz.,  $\text{Fe}^+(^6\text{D}, s^1d^6) + \text{H}_2\text{O}^+ + 5\text{H}_2\text{O}$ . Due to the same nature of interactions, the PECs of those states are parallel to the ones for the previous 10 states, and they also have a shallow minimum at  $\sim 3$  Å lying  $\sim 40$  kcal/mol above the asymptote. At shorter distances ( $R \leq 2.5$  Å), we observe some avoided crossings due to PECs coming from some excited states of  $\text{Fe}^{2+}$  combined with six neutral water molecules. The new incoming PECs lead to several local minima, only one of which is thermodynamically stable with a binding energy relative to the ground state fragments of about 65 kcal/mol at the SA-MCSCF level. This state is of  $^5\text{A}_g$  symmetry and seems to be the only one state coming from the  $\text{Fe}^{2+}(^5\text{S}, s^1d^5) + 6\text{H}_2\text{O}$  asymptote. In Figure 2, we show the expected (not calculated for technical reasons) diabatic curve connecting the equilibrium structure of  $^5\text{A}_g$  symmetry with the  $\text{Fe}^{2+}(^5\text{S}) + 6\text{H}_2\text{O}$  asymptote (dashed green curve). Note, finally, that the fifth state of the  $\text{Fe}^{2+}(^5\text{D}, d^6) + 6\text{H}_2\text{O}$  channel (the second  $^5\text{A}_g$  state), which does not cross any of the  $\text{Fe}^+(^6\text{D}, s^1d^6) + \text{H}_2\text{O}^+ + 5\text{H}_2\text{O}$  state manifold, does cross with the only state of  $^5\text{A}_g$  symmetry coming from the  $\text{Fe}^+(^4\text{D}, s^1d^6) + \text{H}_2\text{O}^+ + 5\text{H}_2\text{O}$  asymptote. Recall that the  $\text{Fe}^+(^4\text{F}, d^7) + \text{H}_2\text{O}^+ + 5\text{H}_2\text{O}$  asymptote lies lower than  $\text{Fe}^+(^4\text{D}, s^1d^6) + \text{H}_2\text{O}^+ + 5\text{H}_2\text{O}$  one and therefore the PECs dissociating to  $\text{Fe}^+(^4\text{F})$  are missing, but they should have the same shape as those arising from  $\text{Fe}^+(^6\text{D})$ .

The last adiabatic channel shown in Figure 2 correlates with the  $\text{Fe}^{2+}(^5\text{D}, d^6) + 6\text{H}_2\text{O}$  fragments. The PECs of this channel cross the PECs of the two lowest adiabatic channels and create the most stable structures at  $\sim 2.2$  Å and about  $-200$  kcal/mol. In this case, the Coulombic repulsion vanishes while the charge-dipole interaction is enhanced since now iron is doubly charged. Considering only the electrostatic interactions and the  $\text{IE}_2 = \text{IE}(\text{Fe}^+ \rightarrow \text{Fe}^{2+})$  and  $\text{IE}_w = \text{IE}(\text{H}_2\text{O} \rightarrow \text{H}_2\text{O}^+)$  ionization energies, we can estimate the distance  $R^*$  for which the PECs from the first and third adiabatic channels under consideration cross by<sup>64</sup>

$$\text{IE}_2 - \text{IE}_w - 6 \frac{2 \cdot \mu}{(R^*)^2} = \frac{1 \cdot 1}{R^*} - 5 \frac{1 \cdot \mu}{(R^*)^2} \quad (1)$$

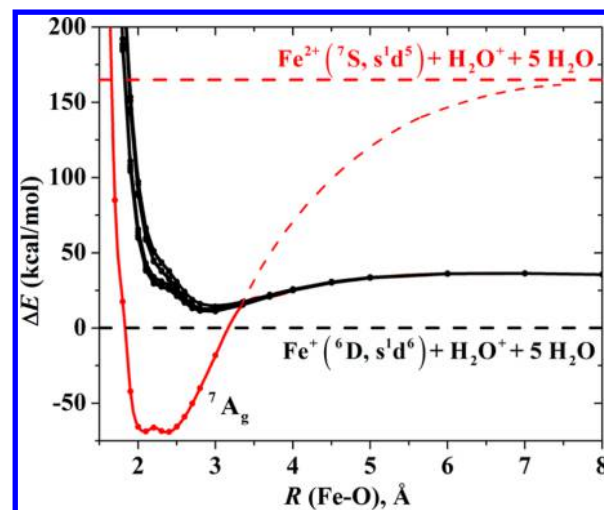
where  $\mu$  is the dipole moment of the water molecule. The last term of the left-hand side is the  $\text{Fe}^{2+}-\text{H}_2\text{O}$  attraction, whereas the two terms of the right-hand side describe the  $\text{Fe}^+-\text{H}_2\text{O}^+$  and  $\text{Fe}^+-\text{H}_2\text{O}$  interactions. Using the values of  $\text{IE}_2 = 15.1$  eV,  $\text{IE}_w = 11.2$  eV, and  $\mu = 1.79$  D (obtained at the SS-MCSCF

level), we obtain  $R^* = 5.5 \text{ \AA}$ , which is in good agreement with the SA-MCSCF value of  $5 \text{ \AA}$  from Figure 2. To estimate the crossing distance between the PECs of the second and third channels, we have to subtract the  $\text{Fe}^+(\text{}^6\text{D} \rightarrow \text{}^4\text{D})$  excitation energy (1.1 eV at the SS-MCSCF level) in the left-hand side of the above equation. This yields  $R^* = 7.1 \text{ \AA}$ , as compared to  $R^* = 7 \text{ \AA}$  from Figure 2.

The  $\text{}^5\text{D}(\text{}^6\text{d})$  electronic term of  $\text{Fe}^{2+}$  consists of five  $M_L = 0, \pm 1, \pm 2$  components, which are degenerate in energy. The six neutral closed-shell water molecules (approaching  $\text{Fe}^{2+}$  as in Figure 1) break the spherical symmetry of the single ion, resulting in an overall  $T_h$  point group symmetry. Under  $T_h$  symmetry, the five states are grouped in a triply ( $\text{}^5\text{T}_g$ ) and one doubly ( $\text{}^5\text{E}_g$ ) degenerate energy levels. As a result, the PECs coming from the  $\text{Fe}^{2+}(\text{}^5\text{D}, \text{}^6\text{d}) + 6\text{H}_2\text{O}$  asymptote crossing the PECs of the two lowest adiabatic channels and creating the most stable structures at  $\sim 2.2 \text{ \AA}$  and  $-200 \text{ kcal/mol}$  are all degenerate at long distances (quasi-spherical symmetry) but split into two groups at equilibrium.

In Table 2, we list our SS-MCSCF optimized geometries of the lowest  $\text{}^5\text{T}_g$ ,  $\text{}^5\text{E}_g$ , and  $\text{}^5\text{A}_g$  states. The splitting between the  $\text{}^5\text{T}_g$  and  $\text{}^5\text{E}_g$  states is 10.6 kcal/mol at the SS-MCSCF level of theory and 19.3 kcal/mol at the MR-PT2 level of theory, whereas the  $\text{}^5\text{A}_g$  state lies 130.7 kcal/mol higher than the ground  $\text{}^5\text{T}_g$  state at the SS-MCSCF level of theory. Recall that the *in situ* electronic structure of iron in the  $\text{}^5\text{T}_g$  and  $\text{}^5\text{E}_g$  states is  $\text{Fe}^{2+}(\text{}^5\text{D}, \text{}^6\text{d})$ , whereas in the  $\text{}^5\text{A}_g$  state, one of the 3d electrons moves to the 4s orbital, and all six lone electrons are coupled into a quintet spin state ( $\text{}^5\text{S}, \text{}^1\text{s}^1\text{d}^5$ ). Markedly, the SA-MCSCF energy difference between the  $\text{Fe}^{2+}(\text{}^5\text{D}, \text{}^6\text{d})$  and  $\text{Fe}^{2+}(\text{}^5\text{S}, \text{}^1\text{s}^1\text{d}^5)$  states is 133.0 kcal/mol, quite close to the energy difference between the weighted-average of the ( $\text{}^5\text{T}_g$ ,  $\text{}^5\text{E}_g$ ) and  $\text{}^5\text{A}_g$  states, viz.,  $\Delta E = 130.7 - (3 \times 0.0 + 2 \times 10.6)/5 = 126.5 \text{ kcal/mol}$ . Unfortunately, we could not obtain the MR-PT2 energy for the  $\text{}^5\text{A}_g$  state, but we expect that its excitation energy should be closer to the  $\text{Fe}^{2+}(\text{}^5\text{D}, \text{}^6\text{d}) \rightarrow \text{Fe}^{2+}(\text{}^5\text{S}, \text{}^1\text{s}^1\text{d}^5)$  MR-PT2 excitation energy of 92.2 kcal/mol. According to Table 2, the geometry of the water molecules in all three states is insensitive to the local electronic structure of iron, as opposed to the iron–oxygen distances, which vary from 2.070  $\text{\AA}$  ( $\text{}^5\text{A}_g$ ) to 2.255  $\text{\AA}$  ( $\text{}^5\text{E}_g$ ) at the SS-MCSCF level. The optimal iron–oxygen distance for the  $\text{}^5\text{T}_g$  and  $\text{}^5\text{E}_g$  states at the MR-PT2 level decreases by approximately 0.05  $\text{\AA}$ , whereas the OH bond length of water increases by 0.02  $\text{\AA}$  and its angle contracts by about  $1^\circ$ . The binding energy lowering as the result of the MR-PT2 optimization is 3.5 and 3.9 kcal/mol for the  $\text{}^5\text{T}_g$  and  $\text{}^5\text{E}_g$  states, respectively.

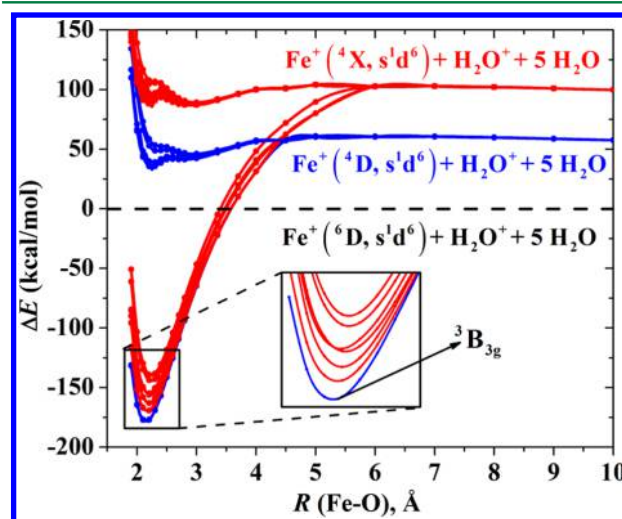
We next discuss the septet electronic states. Among those, we studied only the ones dissociating to the ground-state fragments. Their PECs, shown in Figure 3, are repulsive for distances longer than 6  $\text{\AA}$  (like the previous case of the quintet states) because of the  $\text{Fe}^+-\text{H}_2\text{O}^+$  Coulombic repulsion. At shorter distances, the  $\text{Fe}^+-5\text{H}_2\text{O}$  (charge–dipole) attraction takes over, and a minimum is formed for nine out of the 10 states currently examined. Their equilibrium Fe–O distance is at 2.8  $\text{\AA}$ , and the bonding picture is best described by a  $\text{Fe}^+(\text{}^1\text{s}^1\text{d}^6)$  core and a positively charged cluster of six water molecules around it, with the whole system kept together by the charge–dipole interaction. One electronic state of  $\text{}^7\text{A}_g$  symmetry undergoes a crossing from a higher excited state at  $\sim 3.3 \text{ \AA}$ . At equilibrium, this state bears the same electronic structure with the  $\text{}^5\text{A}_g$  state examined earlier and thus correlates with the  $\text{Fe}^{2+}(\text{}^7\text{S}, \text{}^1\text{s}^1\text{d}^5) + 6\text{H}_2\text{O}$  asymptote. In Figure 3, we



**Figure 3.** Potential energy curves of the septet electronic states of  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ . All curves dissociate to  $\text{Fe}^+(\text{}^6\text{D}) + \text{H}_2\text{O}^+ + 5\text{H}_2\text{O}$ . The dashed red line traces the expected diabatic curve for the lowest  $\text{}^7\text{A}_g$  state.

show, in a manner similar to the one in Figure 2, the expected diabatic curve connecting the  $\text{}^7\text{A}_g$  equilibrium structure with the  $\text{Fe}^{2+}(\text{}^7\text{S}) + 6\text{H}_2\text{O}$  fragments (dashed red curve). Using the electrostatic arguments discussed earlier, we predict (using eq 1) the crossing to occur at  $\sim 3.8 \text{ \AA}$ , in relatively good agreement with the value obtained from Figure 3. It is noteworthy that our PEC features two local minima with different Fe–O distance (Table 2) and the same electronic structure.

The first adiabatic channel giving rise to triplet electronic states is the first excited one, viz.,  $\text{Fe}^+(\text{}^4\text{F}, \text{}^1\text{d}^7) + \text{H}_2\text{O}^+ + 5\text{H}_2\text{O}$ . As mentioned earlier, due to technical difficulties, the first adiabatic channel of Figure 4 is  $\text{Fe}^+(\text{}^4\text{D}, \text{}^1\text{s}^1\text{d}^6) + \text{H}_2\text{O}^+ + 5\text{H}_2\text{O}$ . According to the SA-MCSCF wave function, the second asymptotic pathway of Figure 4 also correlates with a  $\text{Fe}^+(\text{}^1\text{s}^1\text{d}^6)$  state lying  $\sim 40 \text{ kcal/mol}$  higher than  $\text{Fe}^+(\text{}^4\text{D})$ . However, we are unable to identify the electronic term, since there are three different candidate states, viz.,  $\text{}^4\text{P}(\text{}^1\text{s}^1\text{d}^6)$ ,  $\text{}^4\text{H}(\text{}^1\text{s}^1\text{d}^6)$ , and  $\text{}^4\text{F}(\text{}^1\text{s}^1\text{d}^6)$ , within  $2000 \text{ cm}^{-1}$  of each other lying  $\sim 35 \text{ kcal/mol}$  higher than

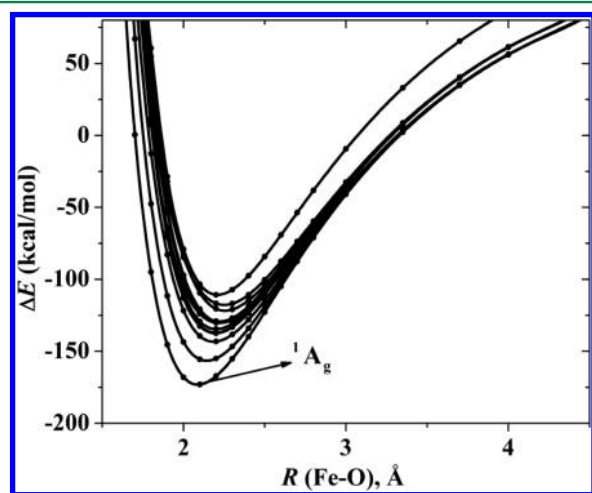


**Figure 4.** Potential energy curves of the triplet electronic states of  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ . The  $\text{Fe}^+(\text{}^4\text{X})$  state can be one of the  $\text{}^4\text{P}$ ,  $\text{}^4\text{H}$ , or  $\text{}^4\text{F}$  states of  $\text{Fe}^+$ . Different colors correspond to different adiabatic fragments.



the  $^4D(s^1d^6)$  state. Both channels of Figure 4 are initially repulsive, but again some shallow minima appear at distances of around 3 Å and energies of  $\sim 40$  and  $\sim 70$  kcal/mol above the asymptote. There is also a second group of local minima at 2.2–2.3 Å due to some incoming PECs from higher energy fragments. However, the only bound energy minima in Figure 4 are those located at distances 2.2–2.3 Å and energies from  $-180$  to  $-130$  kcal/mol. These 16 PECs belong to the  $^3A_g$ ,  $^3B_{1g}$ ,  $^3B_{2g}$ , and  $^3B_{3g}$  irreducible representations (four states each). Five of them dissociate to the first channel, and the rest, to the second one. However, all of them bear a  $d^6$  character, i.e., the 4s orbital is practically unoccupied. As a result, only six electrons are localized on the iron, and this lends credence that the picture of these 16 states is rather a  $Fe^{2+}(d^6)$  ion surrounded by six neutral water molecules. Further examination of the wave function leads us to ascribe those states to  $Fe^{2+}(^3H)$ . In Table 2, we included only the optimized geometry of the lowest ( $^3B_{3g}$ ) within the manifold of triplet states. The geometry of the water molecules remains the same as that in the previously discussed states, and the Fe–O distance is 2.148 Å.

We finally turn to the singlet states. Unfortunately, we could not converge the long-range part of the PECs shown in Figure



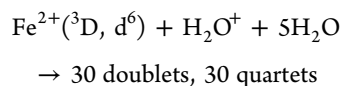
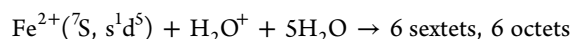
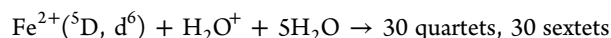
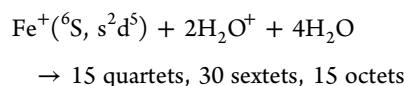
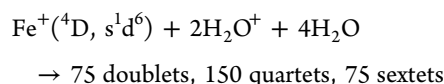
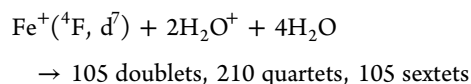
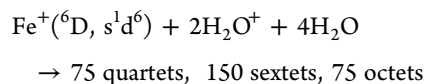
**Figure 5.** Potential energy curves of the singlet electronic states of  $[Fe(H_2O)_6]^{2+}$ .

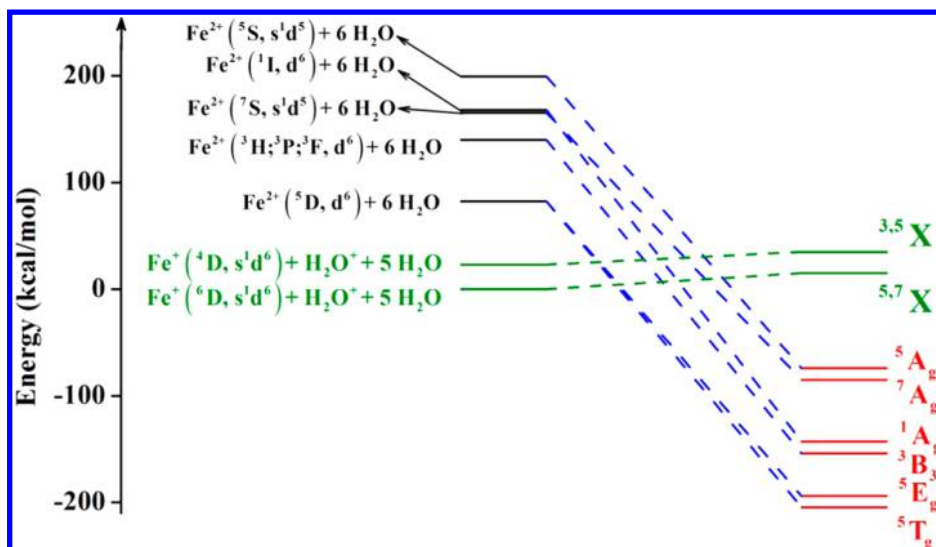
5. We constructed the PECs of 21 electronic states (six  $^1A_g$ , six  $^1B_{1g}$ , three  $^1B_{2g}$ , and six  $^1B_{3g}$ ) with equilibrium distances between 2.1 and 2.2 Å. The lowest one ( $^1A_g$ ) has been optimized at the SS-MCSCF level and lies 61.1 (57.2) kcal/mol at the SS-MCSCF (MRPT2) higher than the ground state (Table 2). The electronic structure of these states resembles the one of the triplet states with iron being populated by six d-electrons ( $Fe^{2+}$ ) and surrounded by six neutral water molecules. The first singlet state of  $Fe^{2+}$  is the  $^1I$  state lying  $\sim 30\,000\text{ cm}^{-1}$  above the ground  $^5D$  state.<sup>74</sup>

In Figure 6, we summarize the pathways forming the lowest electronic states of the  $[Fe(H_2O)_6]^{2+}$  cluster. The channels pertaining to the  $Fe^+ + H_2O^+ + 5H_2O$  fragments are creating several shallow minima of rather unstable character. However, the energetically excited  $Fe^{2+} + 6H_2O$  fragments create more stable equilibrium structures. Since the  $Fe^{2+}$ – $H_2O$  interaction is expected to be roughly independent of the *in situ* electronic nature of  $Fe^{2+}$ , the resulting states of the  $Fe^{2+}(H_2O)_6$  cluster

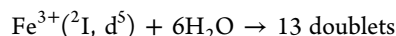
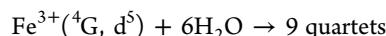
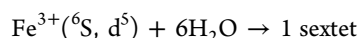
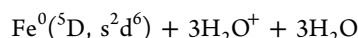
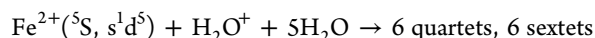
follow approximately the same energy order as the one in  $Fe^{2+}$ . Therefore, the  $^5E_g$  and  $^5T_g$  states coming from the  $Fe^{2+}(^5D)$  are the most stable ones, with the  $^3B_{3g}$  and  $^1A_g$  states coming from the metal's  $^3(H, P, F)$  and  $^1I$  states, and finally the  $^7S$  ones coming from the  $^7S$  states are the higher-lying ones. Note that only the most stable singlet and triplet states are shown and that several others (not shown) lie just above these levels, forming a dense manifold. This may be the reason that Hofstetter and Armentrout<sup>63</sup> failed to converge a DFT or MP2 calculation for a triplet state of  $[Fe(H_2O)_4]^{2+}$ , as only multi-reference calculations can cope with a system with such a complicated electronic structure manifold. Our SS-MCSCF computed binding energy for  $Fe^{2+}(H_2O)_6 \rightarrow Fe^{2+} + 6H_2O$  is 297.7 kcal/mol, a value that is in surprisingly good agreement with the MP2/6-311+G(2d,2p)//B3LYP/6-311+G(d,p) zero-point energy and counterpoise-corrected value of 294.3 kcal/mol reported by Hofstetter and Armentrout.<sup>63</sup> We obtained our 294.3 kcal/mol value by adding all of the  $Fe^{2+}(H_2O)_n \rightarrow Fe^{2+}(H_2O)_{n-1} + H_2O$  dehydration energies with  $n = 1$ –6 reported in Table 3 of ref 63. Finally, the  $^5X$  and  $^3X$  states correspond to the shallow minima of Figures 2–4, lying above the ground-state fragments.

**IIb.  $Fe^{3+}$ –Water Interaction.** The second and third IEs of iron ( $IE_2 = 16.19$  and  $IE_3 = 30.65\text{ eV}$ )<sup>68</sup> are sufficient to induce the ionization of up to three water molecules. Consequently, the ground-state fragments of the  $[Fe(H_2O)_6]^{3+}$  cluster are  $Fe^+(^6D) + 2H_2O^+ + 4H_2O$ . The  $Fe^{3+} + 6H_2O$  fragments lie  $[IE_2(Fe) + IE_3(Fe) - 2IE(H_2O)]$  21.60 eV or  $\sim 498$  kcal/mol higher. We have also considered the  $Fe^{2+} + H_2O^+ + 5H_2O$  channel, which lies  $[IE_2(Fe) - IE(H_2O)]$  3.57 eV or  $\sim 82$  kcal/mol higher. Compared to the  $[Fe(H_2O)_6]^{2+}$  cluster, the Coulombic repulsion is now larger and the  $Fe^+(^6D) + 2H_2O^+ + 4H_2O$  asymptotes are expected to be rather dissociative in nature. The states coming from the  $Fe^{2+} + H_2O^+ + 5H_2O$  asymptote may be associated with some shallow minima, if the  $Fe^{2+}$ – $5H_2O$  attraction outweighs the  $Fe^{2+} - H_2O^+$  repulsion. Finally, simple chemical intuition arguments suggest that the  $Fe^{3+} + 6H_2O$  pathway is going to give rise to the most stable  $Fe^{3+}(H_2O)_6$  structures. Consequently, we are interested in the following asymptotic pathways:





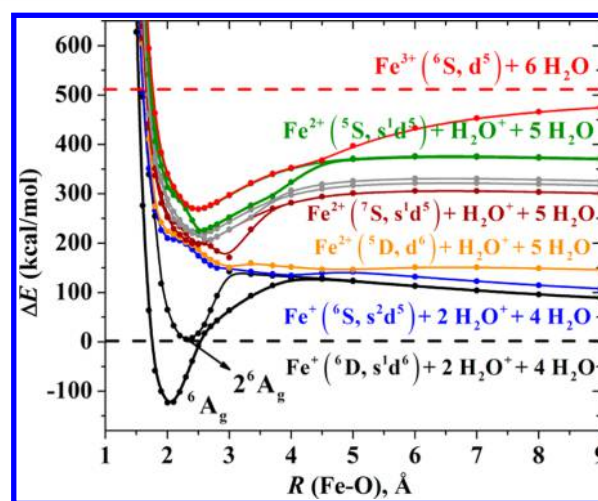
**Figure 6.** Energy level diagram at the SS-MCSCF level of theory of the electronic states of  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  correlating the equilibrium structure of the lowest electronic state of each spin multiplicity manifold with the corresponding asymptotic fragments.



In principle, the construction of all iron–water PECs necessitates the inclusion of several dozens of states in a SA-CASSCF calculation. However, since the active space contains the  $1b_1$  orbital of just two water molecules, the above numbers must be divided by 15 in the  $\text{Fe}^+ + 2(\text{H}_2\text{O}^+)$  cases because we used only one out of the  $\binom{6}{4} = 6!/4!2! = 15$  ways to allow the two positive charges among the six water molecules. Similarly, for the  $\text{Fe}^{2+} + \text{H}_2\text{O}^+$  cases, one must divide by 3.

We would like to mention that there are additional channels correlating to  $\text{Fe}^0$  between the first  $\text{Fe}^0({}^5\text{D}, s^2d^6)$  and the first  $\text{Fe}^{3+}({}^6\text{S}, d^5)$  asymptotic products. Note that the number of electronic states coming from the  $\text{Fe}^0 + 3\text{H}_2\text{O}^+ + 3\text{H}_2\text{O}$  asymptote is prohibitive. Therefore, the active space chosen in this study does not allow the inclusion of PECs involving three or more water cations. Additional SA-MCSCF calculations with a larger active space that includes the molecular orbitals of two additional water fragments showed that they are all repulsive, probably due to the Coulombic repulsion as the three charged fragments approach the metal center and the absence of a strong attractive force between the neutral iron and the remaining neutral water molecules.

Assuming that the  $\text{Fe}^{3+} + 6\text{H}_2\text{O}$  fragments will produce the most stable structure, we expect that the ground state will have  ${}^6\text{A}_g$  symmetry (under both  $D_{2h}$  and  $T_h$ ) correlating with the  $\text{Fe}^{3+}({}^6\text{S}, d^5) + 6\text{H}_2\text{O}$  asymptote. Therefore, we first present the PECs for all the  ${}^6\text{A}_g$  states obtained at the SA-CASSCF level but averaging only the  ${}^6\text{A}_g$  states, i.e., not including the sextets of any other irreducible representation (Figure 7). The  ${}^6\text{A}_g$  states are generated (in energy order) by  $\text{Fe}^+({}^6\text{D})$ ,  $\text{Fe}^+({}^6\text{S})$ ,



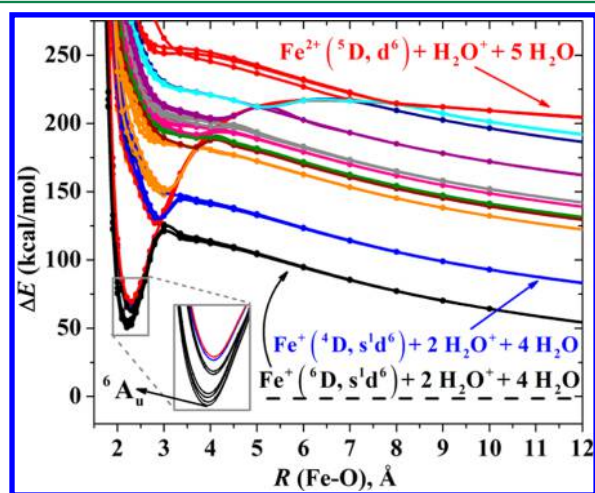
**Figure 7.** Potential energy curves of the  ${}^6\text{A}_g$  electronic states of  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ . Different colors correspond to different adiabatic fragments.

$\text{Fe}^{2+}({}^5\text{D})$ ,  $\text{Fe}^{2+}({}^7\text{S})$ ,  $\text{Fe}^{2+}({}^5\text{S})$ ,  $\text{Fe}^{3+}({}^6\text{S})$ , and two more states of  $\text{Fe}^{2+}({}^s1d^5)$  character (indicated by gray color in Figure 7), combined with the appropriate number of neutral and cationic water molecules. All  $\text{Fe}^+ + 2\text{H}_2\text{O}^+ + 4\text{H}_2\text{O}$  channels lead to pure repulsive interactions, whereas the  $\text{Fe}^{2+} + \text{H}_2\text{O}^+ + 5\text{H}_2\text{O}$  channels, although repulsive for iron–oxygen distances longer than 5 Å, produce quite stable minima for shorter distances. For instance, the minimum located at 2.3 Å with energy of almost 0 kcal/mol comes from  $\text{Fe}^{2+}({}^5\text{D}) + \text{H}_2\text{O}^+ + 5\text{H}_2\text{O}$  asymptote (running into three different avoided crossings) and is stabilized by  $\sim 150$  kcal/mol with respect to the barrier at 5 Å ( $2^6\text{A}_g$  state). This is due to the  $\text{Fe}^{2+}$ –water dipole attraction, which is stronger than the corresponding  $\text{Fe}^+$ –water dipole attraction present in the  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  cluster. As a result, a ferrous ion core and a positive charge that is delocalized among the six water ligands is representative of the aforementioned minimum. The  $\text{Fe}^{3+} + 6\text{H}_2\text{O}$  channel features an even stronger ferric ion–water dipole attraction. This fact, combined with the absence of any Coulombic repulsion, makes the corresponding PEC bound with respect to the ground-state products,  $\text{Fe}^+({}^6\text{D})$



+ 2H<sub>2</sub>O<sup>+</sup> + 4H<sub>2</sub>O, by ~120 kcal/mol. Notably, the overall binding energy between Fe<sup>3+</sup> and the six water ligands is ~625 kcal/mol (Figure 7). Therefore, the Fe<sup>3+</sup> + 6H<sub>2</sub>O PEC crosses all lower-lying PECs. The same PECs for Al<sup>3+</sup> reported earlier<sup>64</sup> exhibited the same characteristics, but the crossing between the Al<sup>3+</sup> + 6H<sub>2</sub>O channel and the lower PECs in Al<sup>3+</sup> is less profound than that for the Fe<sup>3+</sup> case since, in the case of aluminum, the gap between these two states in the avoided crossing region is much larger.

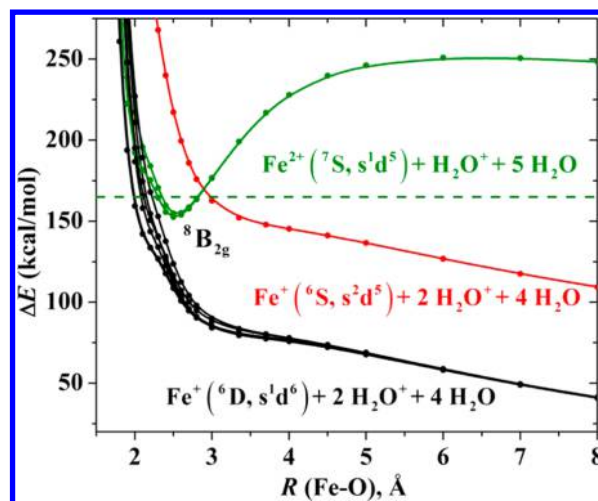
The PECs of the rest of the sextets are depicted in Figure 8. The general shape of these PECs can be now rationalized using



**Figure 8.** Potential energy curves of the sextet (excluding the <sup>6</sup>A<sub>g</sub>) electronic states of [Fe(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup>. Different colors correspond to different adiabatic fragments.

similar arguments: all PECs are connected with different states of Fe<sup>+</sup> apart from the green PECs, which correlate with Fe<sup>2+</sup>(<sup>5</sup>D). In accordance to the earlier discussion, the former PECs are purely repulsive, whereas the latter ones create several stable minima that are almost degenerate with each other. These minima (<sup>6</sup>X) have the same equilibrium distance with the 2<sup>6</sup>A<sub>g</sub> state (see above), but they lie as much as 50 kcal/mol higher in energy (compare Figures 7 and 8). However, when performing a SA-MCSCF calculation including all eight irreducible representations, both the <sup>6</sup>X and 2<sup>6</sup>A<sub>g</sub> minima are nearly isoenergetic, as expected from the fact that they correlate with the same asymptotic fragments and as a result are subjected to the same electrostatic effects. As a consequence, the difference in their energies shown in Figures 7 and 8 is an artifact that is due to the shortcomings of the SA-MCSCF methodology when different numbers of electronic states are included in the averaging. To demonstrate this effect, we report the optimal geometries and their energies for the ground <sup>6</sup>A<sub>g</sub> state and the lowest non-<sup>6</sup>A<sub>g</sub> state (<sup>6</sup>A<sub>u</sub>) at the SS-MCSCF level (Table 2).

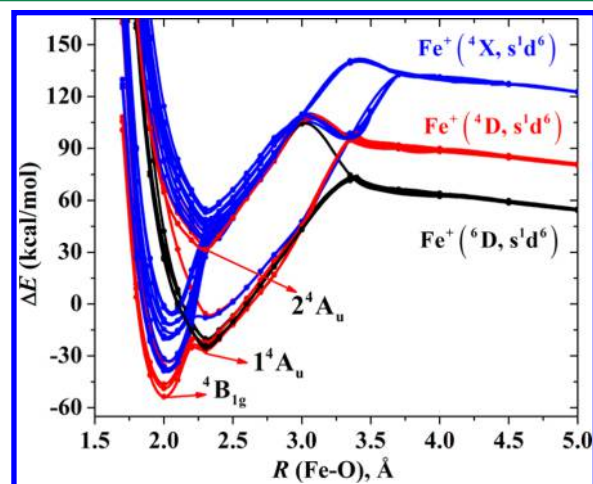
We next consider the octet states. Their PECs are shown in Figure 9, and they follow the same rules as the sextet states. The only channels providing octet spin multiplicity are Fe<sup>+</sup>(<sup>6</sup>D) + 2H<sub>2</sub>O<sup>+</sup> + 4H<sub>2</sub>O (six states), Fe<sup>+</sup>(<sup>6</sup>S) + 2H<sub>2</sub>O<sup>+</sup> + 4H<sub>2</sub>O (one state) and Fe<sup>2+</sup>(<sup>7</sup>S) + H<sub>2</sub>O<sup>+</sup> + 5H<sub>2</sub>O (two states). We did not locate any octet state coming from some electronic state of Fe<sup>3+</sup> + 6H<sub>2</sub>O in the energy range of our interest. The reason is that the water molecules are closed-shell systems and the ferric ion accommodates only five lone valence electrons. In harmony with the behavior of the sextet states, the lowest seven PECs are



**Figure 9.** Potential energy curves of the octet electronic states of [Fe(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup>. Different colors correspond to different adiabatic fragments.

repulsive, whereas the two highest ones are initially repulsive, turning to a binding potential energy well for shorter distances. In reality, the minimum of the latter PECs is lower than the adiabatic fragments by ~15 kcal/mol. The energy of the <sup>8</sup>B<sub>2g</sub> state is also listed in Table 2.

The construction of the PECs of the quartet states has proven to be a harder task owing to the fact that almost every Fe<sup>+</sup> or Fe<sup>2+</sup> pathway results in some quartet states. This, in turn, requires the inclusion of a large number of states in the SA-MCSCF procedure. All PECs shown in Figure 10 dissociate to

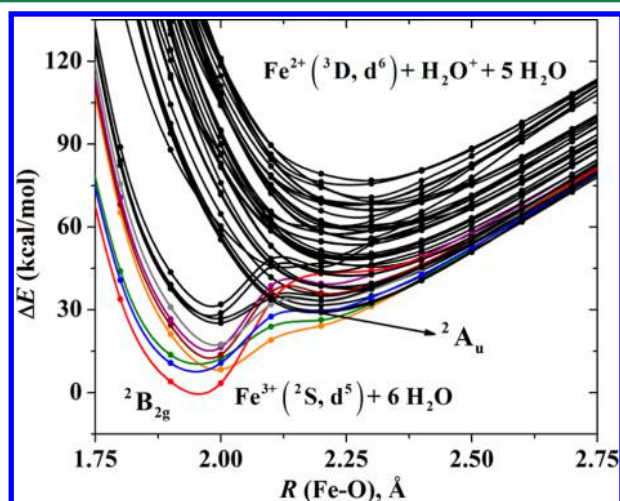


**Figure 10.** Potential energy curves of the quartet electronic states of [Fe(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup>. The <sup>4</sup>X state can be one of the <sup>4</sup>P, <sup>4</sup>H, or <sup>4</sup>F states of Fe<sup>+</sup>. Different colors correspond to the different Fe<sup>+</sup> + 2H<sub>2</sub>O<sup>+</sup> + 4H<sub>2</sub>O adiabatic fragments. Only the electronic state of Fe<sup>+</sup> is shown.

Fe<sup>+</sup> fragments. Although we were not able to construct the higher-lying PECs coming from the Fe<sup>2+</sup> + H<sub>2</sub>O<sup>+</sup> + 5H<sub>2</sub>O or the Fe<sup>3+</sup> + 6H<sub>2</sub>O asymptotic limits, we can assign the different set of minima to those channels based on the analysis of the wave function at the equilibrium distances. The lowest group of minima (totally 16) at ~2 Å and in the energy range from -60 to 0 kcal/mol correspond to a Fe<sup>3+</sup>(d<sup>5</sup>) core with six neutral water molecules around it. Besides, since the water molecules do not affect the overall spin multiplicity, the Fe<sup>3+</sup> core must be

in a quartet state. The first three excited states of  $\text{Fe}^{3+}$  ( $^4\text{G}$ ,  $^4\text{P}$ ,  $^4\text{D}$ ) are indeed quartet states of  $d^5$  character, experimentally lying from 91 to 112 kcal/mol higher than the ground  $^6\text{S}$  state.<sup>74</sup> Unfortunately, at present, we cannot provide a definitive assignment of the  $\text{Fe}^{3+}$  state generating the aforementioned minima. The lowest of these states ( $^4\text{B}_{1g}$ ) is located 76.6 (60.3) kcal/mol higher than the  $^6\text{A}_g$  ground state at the SS-MCSCF (MR-PT2) level (Table 2). The other two groups of states with equilibrium distances at  $\sim 2.25$  Å and energies from  $-60$  to  $0$  and  $30$  to  $60$  kcal/mol seem to be of a  $\text{Fe}^{2+}(\text{d}^6)\cdots(\text{H}_2\text{O})_6^+$  nature. The lowest among the first manifold of states ( $1^4\text{A}_u$ ) lies just 1.2 kcal/mol higher than the  $^6\text{A}_u$  state discussed earlier and is therefore attributed to the same channel, viz.,  $\text{Fe}^{2+}(\text{d}^6) + \text{H}_2\text{O}^+ + 5\text{H}_2\text{O}$ . The lowest state in the second manifold ( $2^4\text{A}_u$ ) is 55.7 kcal/mol (SS-MCSCF) higher than  $1^4\text{A}_u$  (Table 2), which matches favorably with the excitation energies of  $59 \pm 3.5$  kcal/mol<sup>74</sup> from  $\text{Fe}^{2+}(\text{d}^6)$  to either the  $\text{Fe}^{2+}(\text{d}^5)$  or the  $\text{Fe}^{2+}(\text{d}^5)$  and  $\text{Fe}^{2+}(\text{d}^5)$  states.

Lastly, we discuss the doublet states. The high density of states restricted us to construct PECs for iron–oxygen distances between 1.75 and 2.75 Å (Figure 11). Here, we

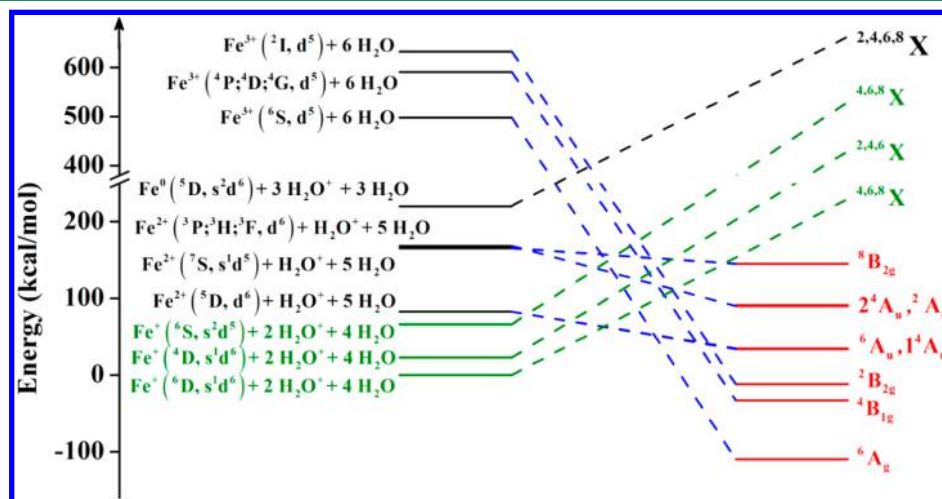


**Figure 11.** Potential energy curves of the doublet electronic states of  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ .

again have two different groups of minima with iron–water distances of 2 and 2.25 Å, with the first one corresponding to  $\text{Fe}^{3+}(\text{d}^5)\cdots(\text{H}_2\text{O})_6$  and the second one,  $\text{Fe}^{2+}(\text{d}^6)\cdots(\text{H}_2\text{O})_6^+$ . The lowest  $\text{Fe}^{3+}$  doublet state is  $^2\text{I}$  ( $d^5$ ) and could be responsible for producing the first manifold of minima. Many different triplet states of  $\text{Fe}^{2+}$  combined with the  $S = 1/2$  of a  $\text{H}_2\text{O}^+$  ion can generate the second group of minima. Probably the first three excited states of  $\text{Fe}^{2+}$  ( $^3\text{P}$ ,  $^3\text{H}$ , and  $^3\text{F}$ ) are the ones that contribute the most. Table 2 lists the SS-MCSCF and MR-PT2 results for the lowest states of the two different groups of minima ( $^2\text{B}_{2g}$  and  $^2\text{A}_u$ ).

We collect the energy levels of the several asymptotic limits and the lowest state of the different minima groups of each spin multiplicity in Figure 12. For the case of  $\text{Fe}^{3+}(\text{H}_2\text{O})_6$ , the picture is evidently more complicated than the one for  $\text{Fe}^{2+}(\text{H}_2\text{O})_6$ , previously presented in Figure 6. For  $\text{Fe}^{3+}(\text{H}_2\text{O})_6$ , there exist more crossings between the PECs correlating with the three kinds of asymptotic fragments corresponding to  $\text{Fe}^+$ ,  $\text{Fe}^{2+}$ , and  $\text{Fe}^{3+}$ . The larger the charge on the iron core is, the more bound the resulting  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  minima are. The  $\text{Fe}^+$  channels produce repulsive PECs (green lines), the  $\text{Fe}^{2+}$  channels yield slightly stable minima, and the  $\text{Fe}^{3+}$  channels yield the lowest electronic states, although their asymptotic energy  $[\text{Fe}^{3+}(\text{H}_2\text{O})_6 \rightarrow \text{Fe}^{3+} + 6\text{H}_2\text{O}]$  is as high as  $\sim 500$  kcal/mol at the SA-MCSCF level. The corresponding SS-MCSCF energy is 600.8 kcal/mol, illustrating the large ( $\sim 100$  kcal/mol) effect of the averaging of so many states in the relative energetics. However, at the MR-PT2 level, this energy difference is 531 kcal/mol, a value that is close to the SA-MCSCF result. Interestingly, the energy ordering of the different states of the  $\text{Fe}^{3+}$ –water clusters asymptotically correlating with the  $\text{Fe}^{3+}$  channel retain the energy ordering of the atomic states of the bare  $\text{Fe}^{3+}$  cation.

A final comment regarding the  $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$  ionization energy is due. The gas-phase value, i.e., when the two ions are stripped of water molecules, is 30.1 eV at the MR-PT2 level. However, the  $\text{Fe}^{2+}(\text{H}_2\text{O})_6 \rightarrow \text{Fe}^{3+}(\text{H}_2\text{O})_6$  energy difference is just 16.0 eV, about half of that for the bare ions. The reason is that the  $\text{Fe}^{3+}(\text{H}_2\text{O})_6$  cluster is stabilized more than the  $\text{Fe}^{2+}(\text{H}_2\text{O})_6$  one, mainly due to the stronger charge–dipole attraction.



**Figure 12.** Energy level diagram at the SS-MCSCF level of theory of the electronic states of  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  correlating the equilibrium structure of the lowest electronic state of each spin multiplicity manifold with the corresponding asymptotic fragments.

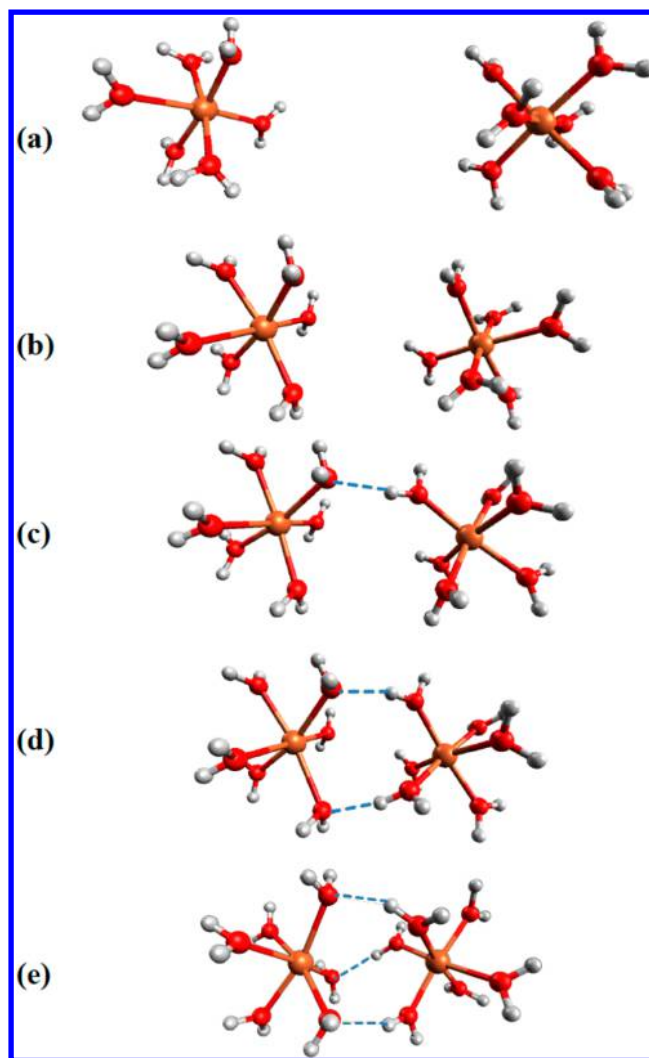


#### IV. $\text{Fe}^{2+}(\text{H}_2\text{O})_6\text{--Fe}^{3+}(\text{H}_2\text{O})_6$ INTERACTION

In this section, we study the gas-phase interaction between the two iron–water clusters examined so far. This is aimed at providing initial insights into the ET process (outer sphere mechanism) by examining the zero-order picture rendered by the interaction of the two moieties in the gas phase. The effect of the most important solvent fluctuations that are crucial in facilitating this process<sup>31</sup> will be accounted for in a future publication. What we are after at this point is establishing the correlation between the various complicated manifolds of the electronic states of the two fragments and identify the most important ones that will be included, together with the effect of the solvent, in subsequent studies aimed at providing a molecular level mechanism of the ET process in solution. According to the results presented earlier in Section III, the ground state of the  $\text{Fe}^{3+}(\text{H}_2\text{O})_6$  cluster is a single electronic state ( ${}^6\text{A}_g$ ) that is well-separated from the first excited state. However, the case of  $\text{Fe}^{2+}(\text{H}_2\text{O})_6$  is more complicated, since two degenerate states ( ${}^5\text{T}_g$  and  ${}^5\text{E}_g$ ) under  $T_h$  symmetry or five quintet states under no symmetry prevail. In the case of  $\text{Fe}^{2+}$  solvated in bulk water, the local structure around the ferrous ion is distorted, and, for this reason (i.e., the lack of even local symmetry within the first coordination shell), all of the five electronic components should, in principle, be considered. However, only the lowest component has been so far considered in previous *ab initio* molecular dynamics simulations. In addition, classical molecular mechanics simulations cannot take this effect into account since they are not able (by construction) to describe any electronic degrees of freedom.

We constructed the PECs of several low-lying electronic states of the  $\text{Fe}^{2+}(\text{H}_2\text{O})_6\text{--Fe}^{3+}(\text{H}_2\text{O})_6$  complex as a function of the iron–iron distance. For each such distance we optimized all of the remaining 107 geometric parameters for the ground ( $\tilde{\text{X}}^{10}\text{A}$ ) state at the HF level, and we subsequently obtained (at the SA-MCSCF level of theory) the energies at those geometries for the following 10 states that are related to the ET process: the first five states are the ones coming from the  ${}^5\text{T}_g$  and  ${}^5\text{E}_g$  states of the  $\text{Fe}^{2+}(\text{H}_2\text{O})_6$  and the  ${}^6\text{A}_g$  state of the  $\text{Fe}^{3+}(\text{H}_2\text{O})_6$  clusters, and the remaining five states correspond to the electronically excited ones for the  $\text{Fe}^{3+}(\text{H}_2\text{O})_6$  (left)– $\text{Fe}^{2+}(\text{H}_2\text{O})_6$  (right) complex at the optimized geometry of the  $\text{Fe}^{2+}(\text{H}_2\text{O})_6$  (left)– $\text{Fe}^{3+}(\text{H}_2\text{O})_6$  (right) complex.

The HF optimized geometries for the five iron–iron distances of 10, 7, 6, 5, and 4.5 Å are depicted in Figure 13, and their Cartesian coordinates are given in the Supporting Information. At 10 Å, the two clusters practically retain their individual tetrahedral ( $T_h$ ) arrangement, with average Fe–O distances of  $2.22 \pm 0.03$  (Fe<sup>2+</sup>) and  $2.06 \pm 0.01$  Å (Fe<sup>3+</sup>). Note that the two prisms are oriented relative to one another so that three water molecules of each prism face the other ones, in agreement with the solution phase results of Babu et al.<sup>60</sup> At  $R(\text{Fe–Fe}) = 7$  Å, the electric field of the  $\text{Fe}^{3+}(\text{H}_2\text{O})_6$  fragment is strong enough to change the orientation of the three water molecules of the  $\text{Fe}^{2+}(\text{H}_2\text{O})_6$  fragment that are in close proximity to it. In contrast, the three waters of the  $\text{Fe}^{3+}(\text{H}_2\text{O})_6$  fragment are not appreciably affected by the field of the  $\text{Fe}^{2+}(\text{H}_2\text{O})_6$  fragment. The average iron–oxygen distances are only slightly elongated for Fe<sup>2+</sup> ( $2.23 \pm 0.02$  Å) compared to their values at  $R(\text{Fe–Fe}) = 10$  Å, where the ones for Fe<sup>3+</sup> remain practically unchanged. Moving closer to  $R(\text{Fe–Fe}) = 6.0$  Å, an interesting structural effect emerges. One of the three water molecules of the  $\text{Fe}^{3+}(\text{H}_2\text{O})_6$  fragment that is positioned



**Figure 13.** Optimized geometries of the  $\text{Fe}^{2+}(\text{H}_2\text{O})_6\text{--Fe}^{3+}(\text{H}_2\text{O})_6$  complex in its ground electronic state ( $\tilde{\text{X}}^{10}\text{A}$ ) at  $\text{Fe}^{2+}\text{--Fe}^{3+}$  distances of (a) 10 Å, (b) 7 Å, (c) 6 Å, (d) 5 Å, and (e) 4.5 Å. The left-hand side corresponds to the  $\text{Fe}^{2+}$  core, and the right-hand side, the  $\text{Fe}^{3+}$  core.

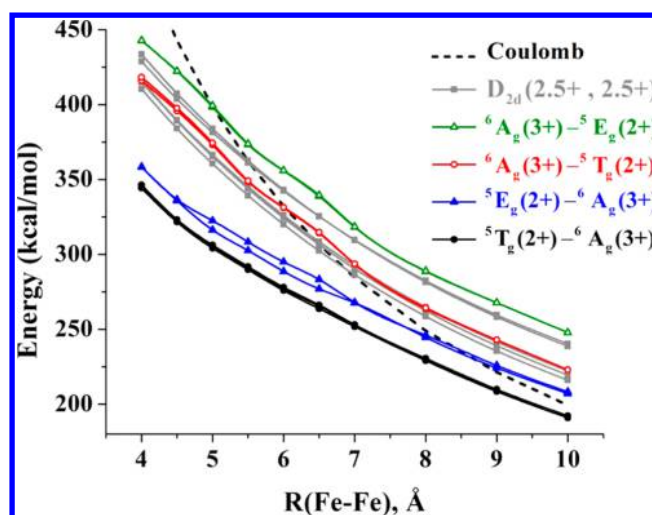
in between the two metal centers (water “A”) approaches a water molecule attached to the  $\text{Fe}^{2+}(\text{H}_2\text{O})_6$  fragment while at the same time it is tilted toward the  $\text{Fe}^{3+}(\text{H}_2\text{O})_6$  fragment (water “B”) in such a way to create a hydrogen bond (Figure 13c). At this distance, all  $\text{Fe}^{3+}$ –oxygen bond lengths are elongated ranging from 2.06 to 2.08 Å except from  $\text{Fe}^{3+}\text{--O}_A$ , which is 2.04 Å. The  $\text{Fe}^{2+}$ –oxygen bond lengths range from 2.17 to 2.25 Å except for  $\text{Fe}^{2+}\text{--O}_B$ , which is much longer (2.42 Å). It seems that water B is trying to detach from  $\text{Fe}^{2+}(\text{H}_2\text{O})_6$  due to the field it experiences from  $\text{Fe}^{3+}(\text{H}_2\text{O})_6$  through its participation in the hydrogen bond. Pushing the two iron centers closer together, the number of hydrogen bonds between the water molecules in the two fragments increases to two at  $R(\text{Fe–Fe}) = 5.0$  Å and finally to three at  $R(\text{Fe–Fe}) = 4.5$  Å, producing the exotic structure shown in Figure 13e. The results of previous simulations suggest these gas-phase structural features are perhaps elusive in an aqueous environment, since all of the first solvation-shell water molecules prefer to make hydrogen bonds with the water molecules in the second solvation shell. Our own preliminary simulations suggest that the two hydrogen-bonded water molecules bridging the ferrous–ferric fragments break their H-bonds



(found to be formed at the gas phase) and create another one sharing a third water molecule from the second solvation shell. It remains to be seen whether the microscopic picture rendered from the existing molecular dynamics simulations (which do not take into account the rich manifold of low-lying electronic states as well as the ability of the charge on the metal center to change in classical force fields) is preserved in future QM/MM simulations in which the QM part properly accounts for these states as well as the second solvation shell of the iron centers or there exists evidence of the mechanism suggested by the gas-phase interaction between the two hydrated fragments.

It is intuitive to investigate the strength of the water–water interaction between the hydrogen-bonded water molecules in the complex and how it changes as a function of the Fe–Fe distance. At the level of theory used for the  $\text{Fe}^{2+}(\text{H}_2\text{O})_6$ – $\text{Fe}^{3+}(\text{H}_2\text{O})_6$  complex, the water dimer optimum O–O separation is 3.031 Å, and its binding energy is –4.01 kcal/mol (compared to 2.904/2.912 Å and –4.98/–4.99 kcal/mol at the MP2/CCSD(T) complete basis set level).<sup>75,76</sup> At the gas-phase water dimer optimum geometry, the dihedral angle  $\delta = [\text{H}_d-(\text{O}_d\text{O}_a\text{M})]$  between the water donor free hydrogen atom  $\text{H}_d$  and the bisector M of the acceptor molecule is 180° (staggered configuration), whereas the OH···O hydrogen-bond angle amounts<sup>64,75</sup> to 171.6/172.1°. At  $R(\text{Fe}–\text{Fe}) = 6$  Å, the corresponding O–O distance is 2.923 Å, and the interaction –2.76 kcal/mol for the only hydrogen-bonded pair of water molecules, whereas the dihedral angle is 61.1°, i.e., it is now closer to the eclipsed configuration ( $\delta = 0$ ), and there is little change in the OH···O hydrogen-bond angle (168.7°). The energy difference between the staggered and eclipsed conformations amounts to 0.9 kcal/mol for the gas-phase water dimer.<sup>77</sup> At  $R(\text{Fe}–\text{Fe}) = 5$  Å, the two pairs of hydrogen-bonded water molecules have O–O distances of 2.816 and 2.877 Å, corresponding interaction energies of –2.44 and –1.85 kcal/mol, dihedral angles of 51.3 and 43.8°, and hydrogen-bond angles of 166.8 and 163.5°, respectively. Finally, at  $R(\text{Fe}–\text{Fe}) = 4.5$  Å, the three pairs of hydrogen-bonded water molecules have corresponding O–O distances of 2.812, 2.839, and 2.840 Å, interaction energies of –1.60, –1.57, and –1.60 kcal/mol, dihedral angles of 45.7, 49.1, and 46.8°, and hydrogen-bond angles of 155.3, 152.7, and 153.5°. Therefore, as the Fe–Fe distance becomes shorter, there is more strain in the hydrogen-bonding interaction between the water molecules of the two hydration shells of the metal centers because of the steric interactions that arise in conjunction with their strong interaction with the charged ion cores to which they belong. This strain is manifested by the shortening of the O–O distances and the simultaneous transition from the near-staggered to the near-eclipsed mutual orientation and the decrease of the hydrogen-bond angle from its near-linear value. All above effects contribute to the decrease in the water–water interaction energy by more than 50% from the ideal value in the gas-phase water dimer.

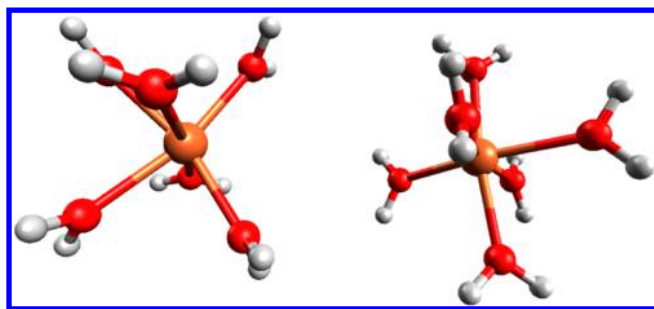
The energy of several excited states of the  $\text{Fe}^{2+}(\text{H}_2\text{O})_6$ – $\text{Fe}^{3+}(\text{H}_2\text{O})_6$  complex (<sup>10</sup>A state) as a function of  $R(\text{Fe}–\text{Fe})$  is shown in Figure 14. The three lower-energy solid black PECs correspond to the  $\text{Fe}^{2+}(\text{H}_2\text{O})_6$  (<sup>5</sup>T<sub>g</sub>, left) and  $\text{Fe}^{3+}(\text{H}_2\text{O})_6$  (<sup>6</sup>A<sub>g</sub>, right) fragments, which bear a triple degeneracy for large iron–iron separations. This degeneracy is practically retained even for short distances. In energy order, the next pathway (blue curves) are the  $\text{Fe}^{2+}(\text{H}_2\text{O})_6$  (<sup>5</sup>E<sub>g</sub>, left) and  $\text{Fe}^{3+}(\text{H}_2\text{O})_6$  (<sup>6</sup>A<sub>g</sub>, right) doubly degenerate fragments, i.e., the first excited state of the  $\text{Fe}^{2+}(\text{H}_2\text{O})_6$  (<sup>5</sup>T<sub>g</sub>, left) and the ground state of  $\text{Fe}^{3+}(\text{H}_2\text{O})_6$



**Figure 14.** Potential energy curves of the  $\text{Fe}^{2+}(\text{H}_2\text{O})_6$ – $\text{Fe}^{3+}(\text{H}_2\text{O})_6$  interaction as a function of the Fe–Fe distance. See text for details.

(<sup>6</sup>A<sub>g</sub>, right). The two blue curves are also degenerate at long distances, but they split for Fe–Fe distances between 5.0 and 6.5 Å. The next excited-state PECs (red curves) trace the states formed by the  $\text{Fe}^{3+}(\text{H}_2\text{O})_6$  (<sup>6</sup>A<sub>g</sub>, left) and the  $\text{Fe}^{2+}(\text{H}_2\text{O})_6$  (<sup>5</sup>T<sub>g</sub>, right) fragments, i.e., the states at the ground-state geometries (black curves) where the ET has occurred or in other words the  $\text{Fe}^{3+}(\text{H}_2\text{O})_6$  (<sup>6</sup>A<sub>g</sub>, left) state at the  $\text{Fe}^{2+}(\text{H}_2\text{O})_6$  (<sup>5</sup>T<sub>g</sub>, left) geometry and vice versa. These states lie higher in energy because of the Fe–O mismatch in the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  fragments (i.e., the Fe–O distances in the  $\text{Fe}^{2+}(\text{H}_2\text{O})_6$  fragment are the ones in the  $\text{Fe}^{3+}(\text{H}_2\text{O})_6$  fragment and vice versa). Finally, we also examined the PECs of the  $\text{Fe}^{3+}(\text{H}_2\text{O})_6$  (<sup>6</sup>A<sub>g</sub>, left)– $\text{Fe}^{2+}(\text{H}_2\text{O})_6$  (<sup>5</sup>E<sub>g</sub>, right) pair at the ground-state  $\text{Fe}^{2+}(\text{H}_2\text{O})_6$  (<sup>5</sup>T<sub>g</sub>, left)– $\text{Fe}^{3+}(\text{H}_2\text{O})_6$  (<sup>6</sup>A<sub>g</sub>, right) optimal geometries (green curves); these can be considered as the excited state of the red curves for the right  $\text{Fe}^{2+}(\text{H}_2\text{O})_6$  fragment. The PEC corresponding to the Coulombic interaction between the bare  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions is also shown with a black dashed line. The Coulomb PEC coincides with the ground-state PEC (black solid line) for large distances, but it deviates appreciably as the two clusters approach each other, mainly due to the fact that the individual fragments experience screened charges at shorter Fe–Fe distances (the stabilization due to the formation of hydrogen bonds is negligible on that scale, and it is also offset by the deformation energy of the first solvation shells due to the interaction).

There are three black, two blue, three red, and two green PECs, for a total of 10 states shown in Figure 14. When  $D_{2d}$  symmetry is imposed, the resulting 10 states, indicated by the gray curves in Figure 14, are collected in two groups of six and four states, respectively. The optimal arrangement for  $R(\text{Fe}–\text{Fe}) = 6.0$  Å under  $D_{2d}$  symmetry is shown in Figure 15. The importance of this specific configuration lies on the fact that its symmetry operations (identity, one  $S_4$  pseudorotation axis, three  $C_2$  rotation axes, and two mirror planes) render the two iron centers equivalent. Therefore, the +5 positive charge of the complex is shared equally between the two iron centers (+2.5e each). As a result, the three PECs corresponding to  $\text{Fe}^{2+}(\text{H}_2\text{O})_6$  (<sup>5</sup>T<sub>g</sub>)– $\text{Fe}^{3+}(\text{H}_2\text{O})_6$  (<sup>6</sup>A<sub>g</sub>) (black lines) and the three PECs corresponding to  $\text{Fe}^{3+}(\text{H}_2\text{O})_6$  (<sup>6</sup>A<sub>g</sub>)– $\text{Fe}^{2+}(\text{H}_2\text{O})_6$  (<sup>5</sup>T<sub>g</sub>) fragments (red lines) are now nearly degenerate, comprising the group of six lower gray PECs. Similarly, the  $\text{Fe}^{2+}(\text{H}_2\text{O})_6$  (<sup>5</sup>E<sub>g</sub>)–

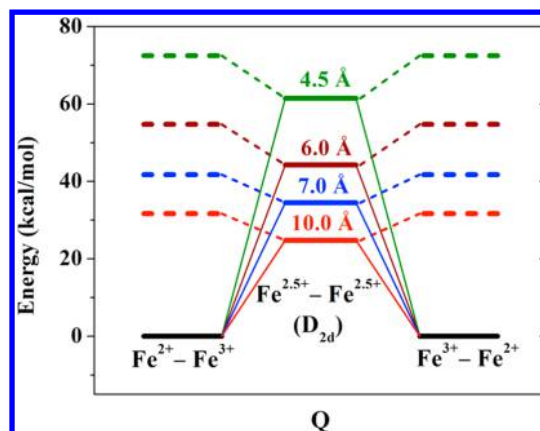


**Figure 15.** Optimized geometry of the  $\text{Fe}^{2.5+}(\text{H}_2\text{O})_6\text{--Fe}^{2.5+}(\text{H}_2\text{O})_6$  complex under  $D_{2d}$  symmetry for  $R(\text{Fe--Fe}) = 6.0 \text{ \AA}$ . The charge of  $+2.5e$  on each metal center is due to the symmetry.

$\text{Fe}^{3+}(\text{H}_2\text{O})_6$  ( ${}^6\text{A}_g$ ) (blue lines) and  $\text{Fe}^{3+}(\text{H}_2\text{O})_6$  ( ${}^6\text{A}_g$ )– $\text{Fe}^{2+}(\text{H}_2\text{O})_6$  ( ${}^5\text{T}_g$ ) (green lines) PECs compose the group of four higher lying gray PECs. Another symmetry operation that could result in the two metal centers being equivalent is the  $C_s$  point group with a mirror plane in the middle of the metal centers. However, in this case, there are always two water molecules in between the two iron centers that are mirror images of each other that have to come in close proximity when the  $R(\text{Fe--Fe})$  distance decreases. As a result, the path under  $C_s$  is a rather a high-energy one since it does not allow for the possibility of forming a hydrogen bond between the water ligands of the two fragments that come in close proximity. Besides, the conformation under near- $D_{2d}$  symmetry is more likely to occur in bulk water; observe, for instance, the resemblance of the  $\text{Fe}^{2+}(\text{H}_2\text{O})_6\text{--Fe}^{3+}(\text{H}_2\text{O})_6$  relative arrangement in Figure 15 with those reported in earlier molecular dynamics simulations.

For a system of two (indistinguishable) iron atoms and a total positive charge of  $+5$ , quantum mechanics commands that the total charge will be equally shared between the two metal centers. The addition of a single water molecule breaks the degeneracy of the system forming a  $\text{Fe}^{3+}(\text{H}_2\text{O})\text{--Fe}^{2+}$  arrangement due to the larger binding energy of the water ligand to  $\text{Fe}^{3+}$  compared to  $\text{Fe}^{2+}$ . A  $\text{Fe}^{2.5+}\text{--}(\text{H}_2\text{O})\text{--Fe}^{2.5+}$  symmetric structure with one water molecule equally shared between the two metal centers lies higher in energy. Therefore, by adding at least one water molecule, the system is trapped to the  $\text{Fe}^{3+}(\text{H}_2\text{O})_n\text{--Fe}^{2+}(\text{H}_2\text{O})_m$  configuration. For the present case with 12 water molecules, the most favorable structure is  $\text{Fe}^{3+}(\text{H}_2\text{O})_6$  (left)– $\text{Fe}^{2+}(\text{H}_2\text{O})_6$  (right), which is equivalent to  $\text{Fe}^{2+}(\text{H}_2\text{O})_6$  (left)– $\text{Fe}^{3+}(\text{H}_2\text{O})_6$  (right). The transition from the former to the latter and vice versa (or else the transfer of an electron from one iron center to the other) must occur via a transition state at which the geometric structure around the two iron atoms forms an equivalent (or nearly equivalent) environment for the electron to resonate between the two metal centers. Although at this point we cannot make a definitive statement, the near- $D_{2d}$  structure could be considered as a plausible scenario for such a transition state.

The energy diagrams along one possible path tracing the ET process from  $\text{Fe}^{2+}(\text{H}_2\text{O})_6$  (left)– $\text{Fe}^{3+}(\text{H}_2\text{O})_6$  (right) to  $\text{Fe}^{3+}(\text{H}_2\text{O})_6$  (left)– $\text{Fe}^{2+}(\text{H}_2\text{O})_6$  (right) in the  $[\text{Fe}_2(\text{H}_2\text{O})_{12}]^{5+}$  complex via the  $\text{Fe}^{2.5+}(\text{H}_2\text{O})_6\text{--Fe}^{2.5+}(\text{H}_2\text{O})_6$   $D_{2d}$  configuration are shown in Figure 16 for several fixed Fe–Fe distances. The  $x$  axis corresponds to a one-dimensional (yet to be determined) collective variable  $Q$  that is appropriate for describing the electron transfer process. The solid lines of different colors represent the ground electronic state (the lowest solid black



**Figure 16.** Energy diagram along one possible  $\text{Fe}^{2+}(\text{H}_2\text{O})_6$  (left)– $\text{Fe}^{3+}(\text{H}_2\text{O})_6$  (right) to  $\text{Fe}^{3+}(\text{H}_2\text{O})_6$  (left)– $\text{Fe}^{2+}(\text{H}_2\text{O})_6$  (right) conversion pathway ( $Q$ ) going through the  $D_{2d}$  configuration for different Fe–Fe distances (4.5, 6.0, 7.0, and 10.0 Å). The solid/dashed curves trace the ground/excited state; see text for details.

line of Figure 14), whereas the dashed lines represent the sixth (or fifth excited) electronic state (the lowest red line of Figure 14). In other words, the solid curves in Figure 16 correspond to the ground state of the  $\text{Fe}^{2+}(\text{H}_2\text{O})_6$  (left)– $\text{Fe}^{3+}(\text{H}_2\text{O})_6$  (right) or equivalently the  $\text{Fe}^{3+}(\text{H}_2\text{O})_6$  (left)– $\text{Fe}^{2+}(\text{H}_2\text{O})_6$  (right) optimal geometries, whereas the dashed lines trace their excited states at the same geometries but with the charge interchanged between the two iron centers. The two families of energy levels become the same at the  $D_{2d}$  geometry. Notice that the barrier is larger for shorter Fe–Fe distances, whereas it converges (assuming a  $1/R$  dependence) to the value of 24.5 kcal/mol at long distances. Naturally, the relative energies depend upon the basis set and the energy correlation treatment as well as including the effect of the solvent.

## V. SUMMARY

We report the PECs for the ground and the low-lying excited electronic states describing the simultaneous removal of all six water ligands from the minima of the  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  and  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  clusters using high levels of electronic structure theory. The lowest-lying electronic states do originate from the atomic states of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  combined with those for six water molecules, therefore confirming the  $\text{Fe}^{2+}(\text{H}_2\text{O})_6$  and  $\text{Fe}^{3+}(\text{H}_2\text{O})_6$  configurations, in agreement with chemical intuition. The ground state of  $\text{Fe}^{2+}(\text{H}_2\text{O})_6$  originates from  $\text{Fe}^{2+}({}^5\text{D}; 3\text{d}^6)$ , and the five degenerate components of  $\text{Fe}^{2+}$  split into one triply ( ${}^5\text{T}_g$ ) and one doubly ( ${}^5\text{E}_g$ ) degenerate state under the overall  $T_h$  symmetry of the cluster. Likewise, the  $\text{Fe}^{3+}({}^6\text{S}; 3\text{d}^5)$  state correlates with the  ${}^6\text{A}_g$  ground state of  $\text{Fe}^{3+}(\text{H}_2\text{O})_6$ . The examination of the various PECs revealed the existence of local minima, lying higher in energy, where a  $\text{Fe}^+$  or  $\text{Fe}^{2+}$  core is surrounded by a positively charged hexa-water cluster, viz.,  $\text{Fe}^+(\text{H}_2\text{O})_6^+$  and  $\text{Fe}^{2+}(\text{H}_2\text{O})_6^+$ . Because of the large orbital and spin angular momenta of the underlying atomic states of  $\text{Fe}^+$ ,  $\text{Fe}^{2+}$ , and  $\text{Fe}^{3+}$ , the energy spectrum of the  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  and  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  clusters is characterized by a high density of states, many of which nearly form an energy band in some regions.

We have furthermore made an attempt to investigate the interaction between the gas-phase  $\text{Fe}^{2+}(\text{H}_2\text{O})_6$  and  $\text{Fe}^{3+}(\text{H}_2\text{O})_6$  clusters, aiming at providing a molecular level picture of the ET process in the gas phase, as an initial insight and the stepping

stone for future molecular dynamics QM/MM simulations in the bulk phase. The construction of the minimum energy paths as a function of  $R(\text{Fe}-\text{Fe})$  for the ground and several excited states of the  $\text{Fe}^{2+}(\text{H}_2\text{O})_6-\text{Fe}^{3+}(\text{H}_2\text{O})_6$  complex suggested the initial formation of one hydrogen bond between the water molecules of the two hydration spheres at  $R(\text{Fe}-\text{Fe}) = 6.0 \text{ \AA}$ , followed by a subsequent formation of two and three hydrogen bonds at 5.0 and 4.5  $\text{\AA}$ , respectively. The strong interaction of the water molecules participating in the hydrogen bonds with the metal cores induces steric effects manifested by the shorter O–O separations, the deviation of the hydrogen-bond angles from linearity, and the almost eclipsed intermolecular arrangements that all result in reduced strengths (by  $\sim 60\%$ ) of the corresponding water–water interactions. For all examined  $R(\text{Fe}-\text{Fe})$  distances in the range 4.0–10.0  $\text{\AA}$ , the ground state is trapped in a  $\text{Fe}^{2+}(\text{H}_2\text{O})_6-\text{Fe}^{3+}(\text{H}_2\text{O})_6$  arrangement, with the  $\text{Fe}^{3+}-\text{O}$  distances being, in general, shorter than the  $\text{Fe}^{2+}-\text{O}$  ones. In order for the ET to occur between the two fragments, there must be a transition state that creates almost the same local structure for both irons. One possible path for this process is via a  $D_{2d}$  arrangement that facilitates the equal sharing (+2.5e) between the two metal centers. In other words, the geometry of at least the first solvation shell and the electron ET is coupled. It remains to be seen whether this still remains a plausible route when the effect of the solvent that breaks the overall symmetry is taken into account and whether in that case a near- $D_{2d}$  arrangement still emerges as a viable mechanism for facilitating the ET.

Our results suggest that classical molecular dynamics simulations with force fields that keep the charges on the two irons fixed at 2+ and 3+ add external constraints that, in our opinion, cannot effectively account for the ET process. On the other hand, the electron–particle pseudopotentials previously suggested in the literature<sup>48,61</sup> or a full quantum mechanical treatment of at least the first solvation shell (still lacking) constitute more appropriate strategies to attack the problem. These issues will be addressed in forthcoming studies.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

Table S1 lists the SS-MCSCF and MRPT2 absolute energies for the states listed in Table 2. Tables S2 and S3 contain the potential energy curves for the  $\text{Fe}^{2+}(\text{H}_2\text{O})_6$  and  $\text{Fe}^{2+}(\text{H}_2\text{O})_6$  species, respectively. Table S4 lists the Cartesian coordinates of the optimal geometries for the  $\text{Fe}^{2+}(\text{H}_2\text{O})_6-\text{Fe}^{2+}(\text{H}_2\text{O})_6$  complex for different Fe–Fe distances. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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## Notes

The authors declare no competing financial interest.

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