Supplementary Material to "Oxidative properties of FeO2+: electronic structure and solvation effects".

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In the main article we propose a model for the reactivity of FeO^{2+} based on the relative energies of the LUMO of FeO^{2+} and the HOMOs of incoming molecules. The article is provided with simplified schematic orbital diagrams of the interactions of $[FeO(H_2O)_5]^{2+}$ with methane, methanol, and water. In this supplementary material, we give the complete orbital interaction diagrams for these interactions (Figure S2-S5) and tables with the mixings of all interacting orbitals (Table S1-S4).
For easy interpretation of the mixings, we depict in Figure S1 the orbitals of the substrate molecules. The orbitals of $[FeO(H_2O)_5]^{2+}$ are depicted in the main article (Figure 4).

In the orbital interaction diagrams (Figure S2-S5), the energy levels of the fragments in the geometry of the interacting complex plus the energy levels of the resulting molecular orbitals are given, showing the orbital mixing resulting from our fragment analysis. For the $[FeO(H_2O)_5]^{2+}$ fragment the levels of the *spin-restricted* orbitals are drawn, for technical reasons explained in the main article. For the incoming molecule the shift of the orbitals caused by the net charge of the complex is also depicted. In the middle two columns of the diagrams the levels of the resulting *unrestricted* molecular orbitals are drawn.

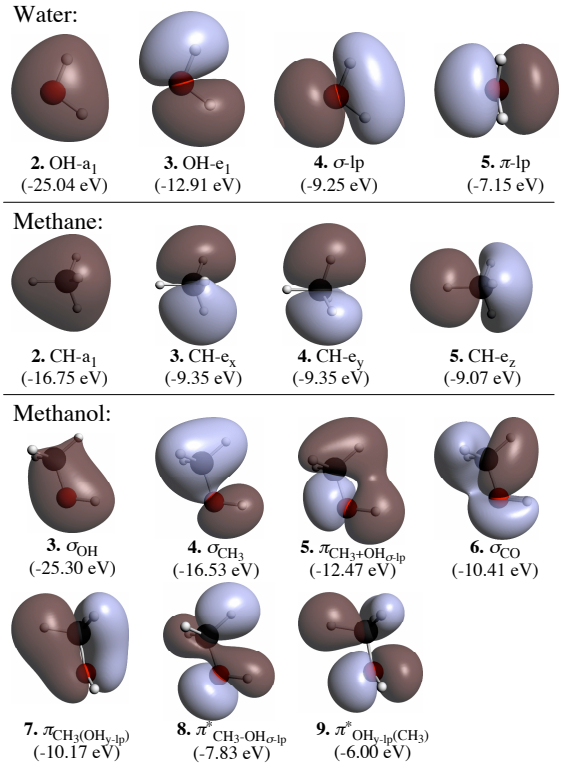

Figure S1. Occupied molecular orbitals of water, methane and methanol in the same configurations as in the optimized complexes with $[FeO(H_2O)_5]^{2+}$ (the methanol is taken from the CH-bonded complex). The 1s-orbitals of the O and C atoms are left out of the picture. Note that for different orbitals the molecules may be depicted in a different orientation.

For clarity, the energy levels mainly associated with the FeO^{2+} moiety itself are drawn in black; levels mainly associated with the water molecules of the first solvation shell (see also Table 2 of Ref. 16) are drawn in grey. Note that all grey levels are implicitly filled with electrons, though not depicted.
For the connecting lines different styles have been used: For levels that are not mixed between the two fragments the connecting lines are dashed grey. These levels are relatively unperturbed by the interaction with the other fragment. For occupied levels that are interacting (Pauli repulsion) the connecting lines are dashed black. Finally, for interactions of occupied orbitals with unoccupied orbitals, i.e. interactions that contribute to the bonding interaction, the connecting lines are solid black.

In the corresponding tables (Table S1-S4) mixing percentages of the orbitals are given. In these tables, the orbitals that contribute to the bonding interaction (interactions of the HOMOs of the incoming molecules with the LUMO of $[FeO(H_2O)_5]^{2+}$) are presented in bold. For each interacting orbital (through Pauli repulsion or charge transfer), percentages are given for the contribution of $[FeO(H_2O)_5]^{2+}$ orbitals and of orbitals of the incoming molecule. Values labeled "empty" represent relative contributions from empty fragment orbitals. Note that added to an orbital name, the label "empty" means that the molecular orbital is empty.
For the precise interpretation of the FeO^{2+} orbital contributions to the molecular orbitals, we performed an additional fragment analysis in which the $[FeO(H_2O)_5]^{2+}$ fragment was partitioned into a FeO^{2+} and 5 water fragments. This was done because there is substantial spurious mixing of the $[FeO(H_2O)_5]^{2+}$-orbitals during complexation, caused by changing first-shell water contributions. In the fourth and fifth columns of the tables the resulting contributions of FeO^{2+} orbitals and of water orbitals are given. Note that occasional mixing of the 2σ and the $3\sigma^*$ orbitals is an effect of the axial water ligand and is not caused by the interaction with the incoming molecule.

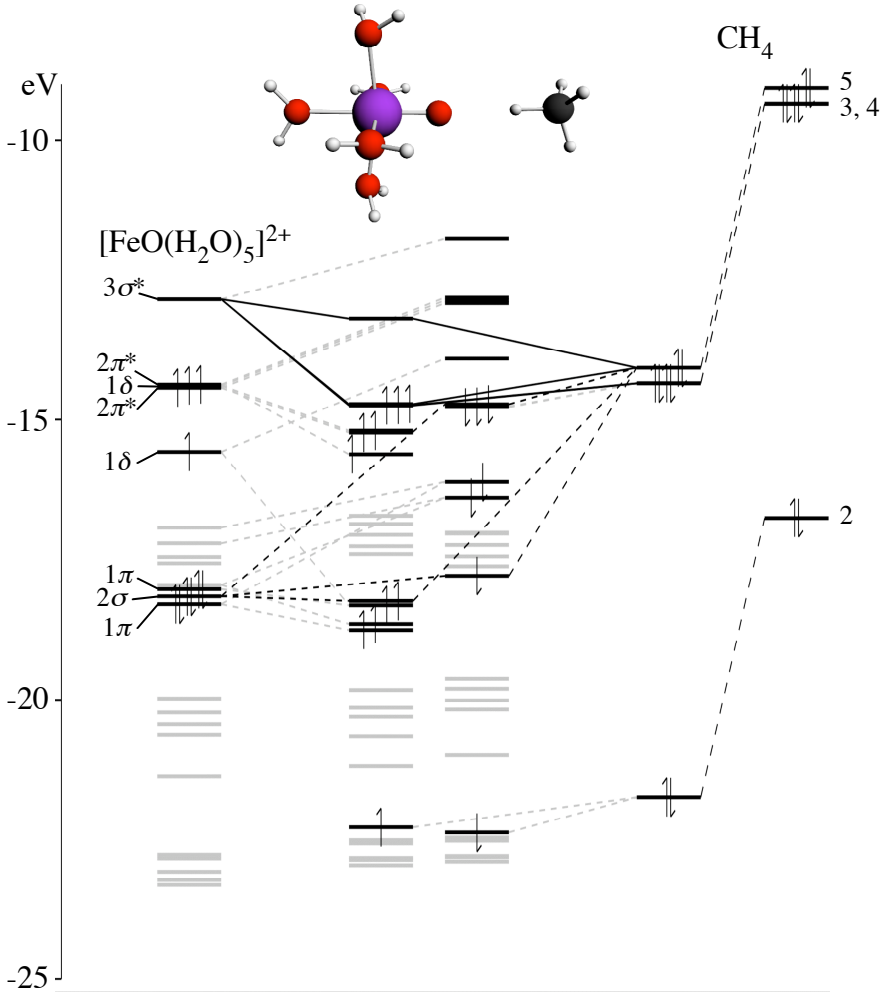

Figure S2. Orbital interaction diagram for the interaction of $[FeO(H_2O)_5]^{2+}$ with methane.

Table S1. Orbital mixings for the interaction of $[FeO(H_2O)_5]^{2+}$ with methane.

Orbital	Energy (eV)	% $[FeO(H_2O)_5]^{2+}$ character	interacting FeO^{2+} orbitals	% first shell water orbitals	% CH_4 character	CH_4 orbitals
49 α (empty)	**-13.19**	**89 % (86 % empty)**	**3σ* (72 %)**	**16 %**	**11 %**	**5 (11 %)**
48 α	**-14.72**	**12 % (9 % empty)**	**3σ* (6 %) 2σ (2 %)**	**4 %**	**88 %**	**5 (66 %) 3 (21 %) 4 (1 %)**
47 α	**-14.74**	**3 % (2 % empty)**	**3σ* (1 %)**	**1 %**	**97 %**	**4 (63 %) 3 (23 %) 5 (11 %)**
46 α	**-14.75**	**2 % (1 % empty)**	**3σ* (1 %)**	**1 %**	**98 %**	**3 (54 %) 4 (34 %) 5 (9 %)**
37 α	-18.25	98 % (0 % empty)	2σ (64 %)	34 %	2 %	5 (2 %)
44 β	-14.72	7 % (1% empty)	2σ (6 %)	0 %	93 %	5 (92 %) 3 (1 %)
34 β	-17.79	95 % (1 % empty)	2σ (76 %) 3σ* (5 %)	14 %	5 %	5 (5 %)

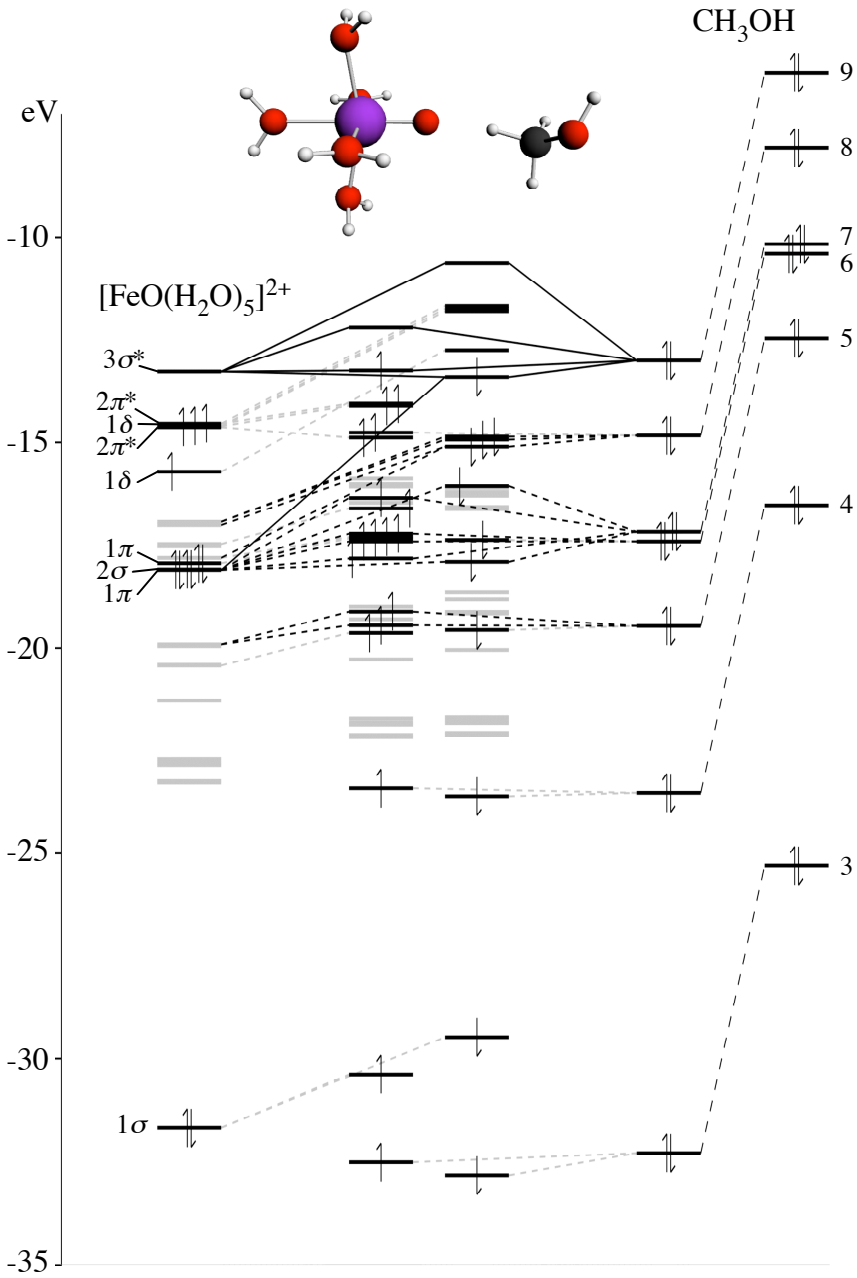

Figure S3. Orbital interaction diagram for the interaction of $[FeO(H_2O)_5]^{2+}$ with methanol interacting via its C–H bond.

Table S2. Orbital mixings for the interaction of $[FeO(H_2O)_5]^{2+}$ with methanol interacting via its C–H bond.

orbital	Energy (eV)	% $[FeO(H_2O)_5]^{2+}$ character	interacting FeO^{2+} orbitals	% first shell water orbitals	% CH_3OH character	CH_3OH orbitals
53 α (empty)	**-12.20**	**55 % (50 % empty)**	**3σ* (45 %) 2σ (2 %)**	**9 %**	**45 %**	**9 (43 %) 7 (2 %)**
52 α	**-13.25**	**47 % (46 % empty)**	**3σ* (35 %)**	**12 %**	**53 %**	**9 (53 %)**
44 α	-16.35	48 % (3 % empty)	2σ (32 %)	16 %	52 %	7 (48 %) 9 (2 %) 6 (1 %)
41 α	-17.22	7 % (0 % empty)	1π (4 %) 2σ (1%)	2 %	93 %	6 (85 %) 7 (8 %) 8 (1 %)
38 α	-17.41	96 % (0 % empty)	1π (71 %)	25 %	4 %	6 (3 %) 7 (1 %)
37 α	-17.82	55 % (0 % empty)	2σ (29 %)	26 %	45 %	7 (35 %) 6 (8 %) 5 (2 %)
35 α	-19.11	91 % (0 % empty)	2σ (21 %)	70 %	9 %	5 (7 %) 7 (1 %)
33 α	-19.45	12 % (0 % empty)	2σ (4 %)	8 %	88 %	5 (87 %)
53 β (empty)	**-10.63**	**98 % (97 % empty)**	**3σ* (80 %)**	**18 %**	**2 %**	**9 (1 %)**
48 β	**-13.41**	**10 % (1 % empty)**	**2σ (8 %)**	**2 %**	**90 %**	**9 (88 %) 7 (2 %)**
47 β	-14.86	38 % (0 % empty)	1π (31 %)	7 %	62 %	8 (60 %) 6 (1 %)
46 β	-14.93	64 % (0% empty)	1π (50 %)	14 %	36 %	8 (36 %)
45 β	-15.10	97 % (0 % empty)	1π (83 %)	14 %	3 %	8 (3 %)
44 β	-16.06	70 % (0 % empty)	2σ (55 %)	14 %	30 %	7 (19 %) 9 (9 %) 6 (2 %)
37 β	-17.91	28 % (1 % empty)	2σ (16 %) 3σ* (3 %)	6 %	72 %	7 (64 %) 6 (6 %) 5 (2 %)

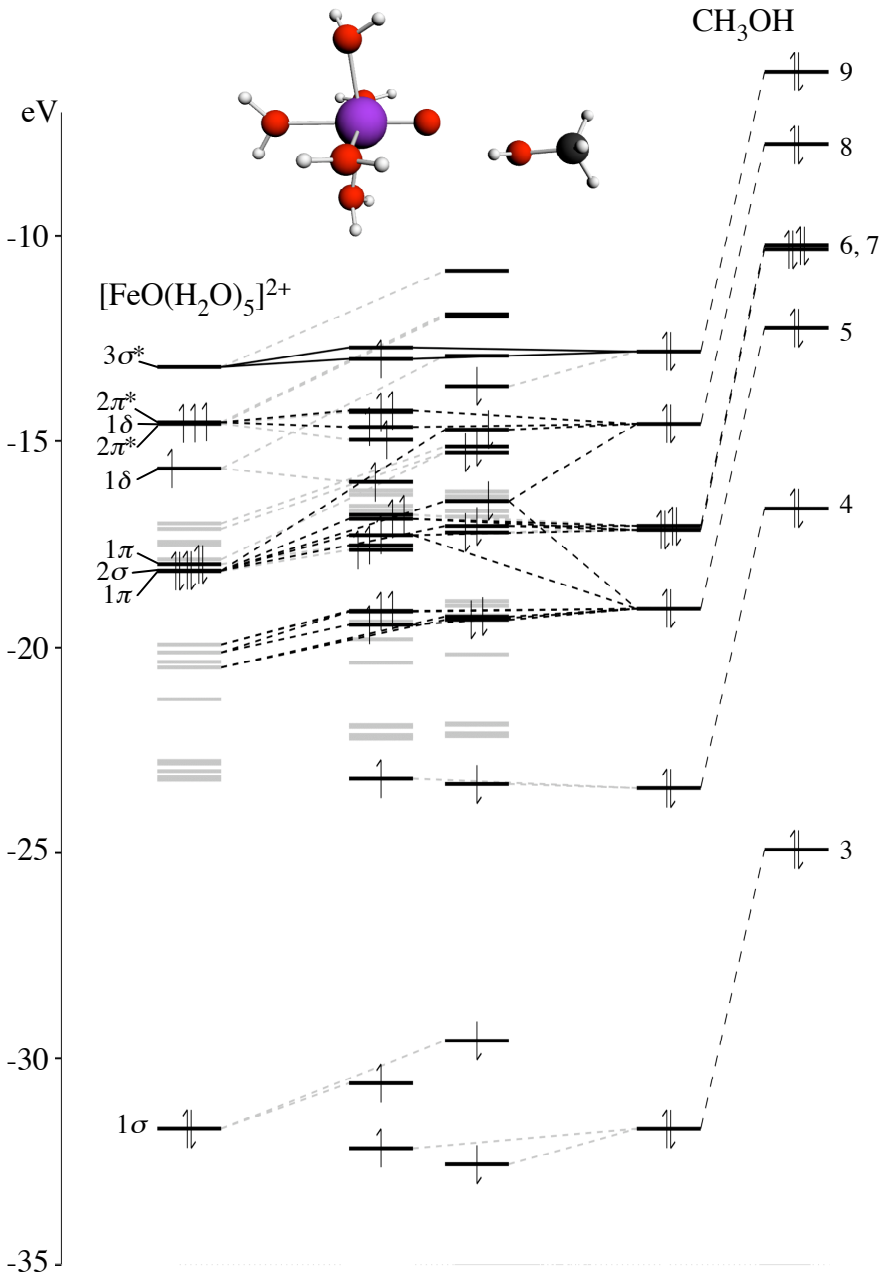

Figure S4. Orbital interaction diagram for the interaction of $[FeO(H_2O)_5]^{2+}$ with methanol interacting via its O–H bond.

Table S3. Orbital mixings for the interaction of $[FeO(H_2O)_5]^{2+}$ with methanol interacting via its O–H bond.

orbital	Energy (eV)	% $[FeO(H_2O)_5]^{2+}$ character	interacting FeO^{2+} orbitals	% first shell water orbitals	% CH_3OH character	CH_3OH orbitals
53 α (empty)	**-12.72**	**57 % (55 % empty)**	**3σ* (47 %)**	**10 %**	**43 %**	**9 (42 %)**
52 α	**-13.00**	**42 % (42 % empty)**	**3σ* (33 %)**	**9 %**	**58 %**	**9 (57 %)** **6 (1 %)**
51 α	-14.26	92 % (0 % empty)	$2\pi^*$ (87 %)	5 %	8 %	8 (7 %)
49 α	-14.66	10 % (1 % empty)	$2\pi^*$ (8 %)	2 %	90 %	8 (87 %) 7 (2 %) 6 (1 %)
41 α	-16.87	7 % (0 % empty)	2σ (4 %)	3 %	93 %	7 (58 %) 6 (32 %) 8 (3 %)
40 α	-17.27	87 % (1 % empty)	2σ (65 %)	23 %	13 %	6 (7 %) 5 (5 %) 7 (1 %)
36 α	-19.10	62 % (0 % empty)	–	62 %	38 %	5 (37 %)
35 α	-19.12	58 % (0 % empty)	–	58 %	42 %	5 (42 %)
33 α	-19.45	88 % (0 % empty)	2σ (21 %)	67 %	12 %	5 (12 %)
47 β	-14.72	6 % (0 % empty)	1π (3 %) 2σ (2 %)	1 %	94 %	8 (90 %) 7 (3 %) 6 (1 %)
41 β	-16.44	95 % (0 % empty)	2σ (41 %)	55 %	5 %	5 (2 %) 6 (2 %) 8 (1 %)
38 β	-17.05	3 % (0 % empty)	2σ (2 %)	1 %	97 %	7 (66 %) 6 (26 %) 8 (3 %) 5 (1 %)
33 β	-19.24	43 % (0 % empty)	–	43 %	57 %	5 (57 %)
32 β	-19.32	65 % (0 % empty)	2σ (5 %)	60 %	35 %	5 (35 %)

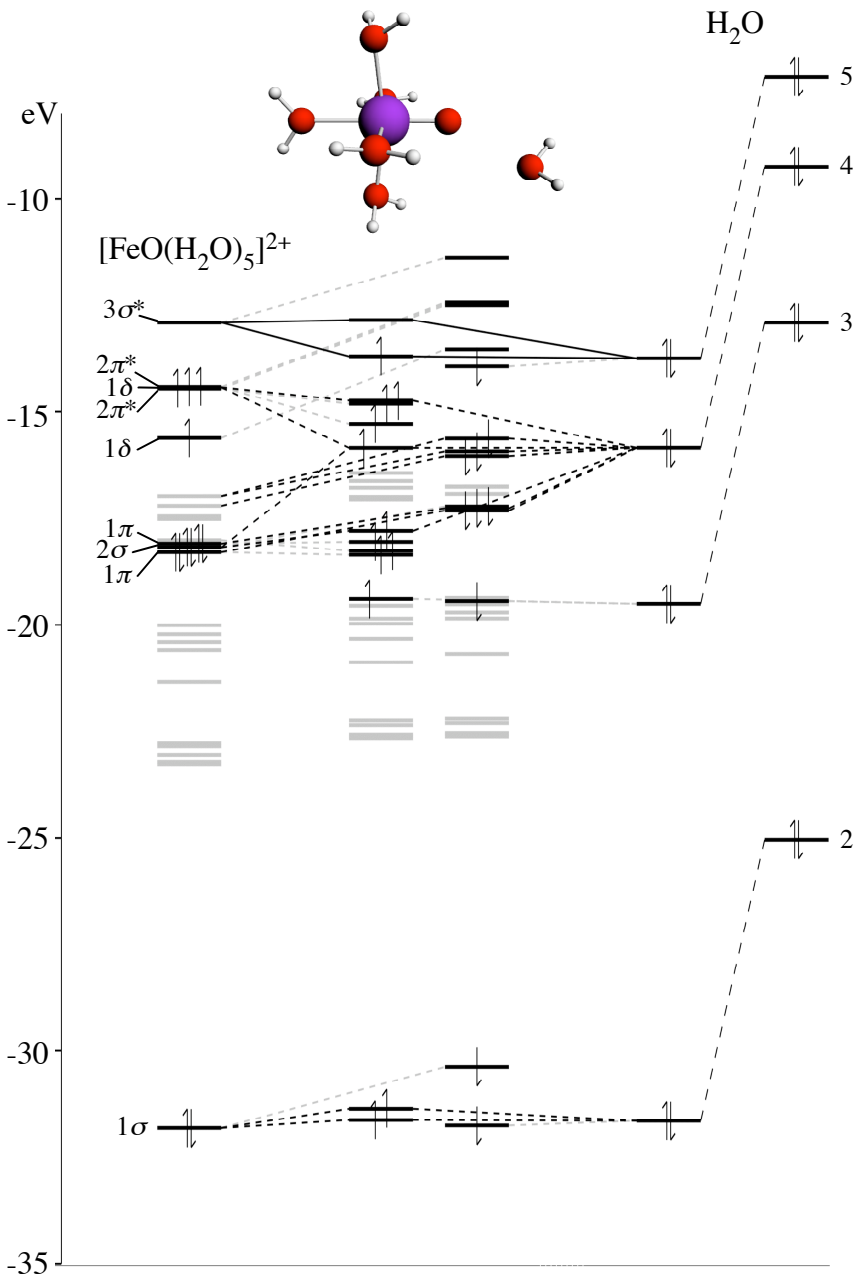

Figure S5. Orbital interaction diagram for the interaction of $[FeO(H_2O)_5]^{2+}$ with water.

Table S4. Orbital mixings for the interaction of $[FeO(H_2O)_5]^{2+}$ with water.

orbital	Energy (eV)	% $[FeO(H_2O)_5]^{2+}$ character	interacting FeO^{2+} orbitals	% first shell water orbitals	% H_2O character	H_2O orbitals
49 α (empty)	**-12.85**	**87 % (85 % empty)**	**3σ* (71 %)**	**16 %**	**13 %**	**5 (13 %)**
48 α	**-13.70**	**15 % (14 % empty)**	**3σ* (10 %)**	**5 %**	**85 %**	**5 (85 %)**
47 α	-14.74	94% (0 % empty)	2π* (90 %)	4 %	6 %	4 (5 %) 5 (1 %)
44 α	-15.85	8 % (1 % empty)	2π* (5 %)	3 %	92 %	4 (92 %)
38 α	-17.80	98 % (1 % empty)	2σ (72 %)	26 %	2 %	4 (2 %) 5 (1 %)
23 α	-31.36	90 % (0 % empty)	1σ (89 %)	0 %	10 %	2 (10 %)
22 α	-31.62	10 % (0 % empty)	1σ (10 %)	0 %	90 %	2 (90 %)
43 β	-15.63	61 % (0 % empty)	1π (46 %) 2σ (1 %)	13 %	39 %	4 (39 %)
42 β	-15.93	61 % (0 % empty)	1π (39 %) 2σ (3 %)	19 %	39 %	4 (39 %)
41 β	-16.04	84 % (0 % empty)	1π (64 %) 2σ (1 %)	19 %	16 %	4 (16 %)
36 β	-17.26	97 % (1 % empty)	2σ (24 %) 1π (6 %)	67 %	3 %	4 (3 %)
35 β	-17.32	98 % (1 % empty)	2σ (15 %) 1π (7 %)	76 %	2 %	4 (2 %)