Supporting Information

Infrared Photodissociation Spectroscopy of $(Al_2O_3)_{2–5}FeO^+$: Influence of Fe-Substitution on Small Alumina Clusters

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1. Experimental vs. Simulated Spectra

1.1. *n* = 1

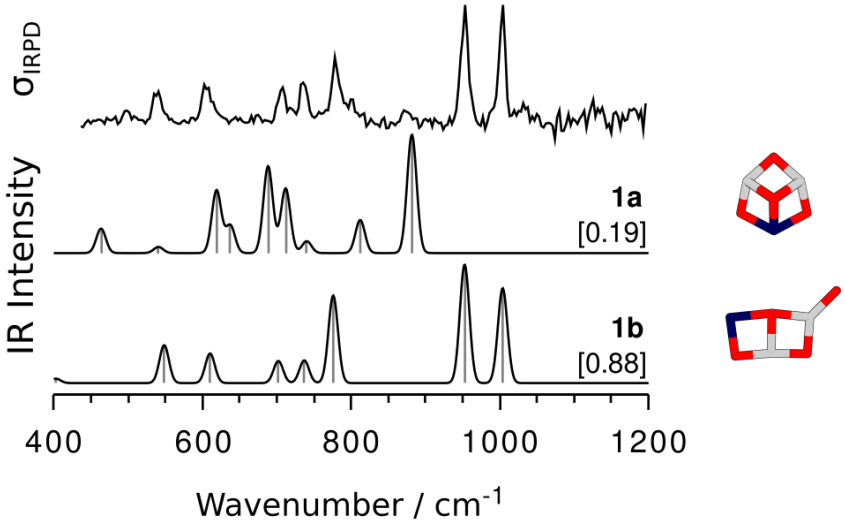

Figure S1. Experimental IRPD spectrum of He-tagged $Al_2FeO_4^+$ (top trace) compared with simulated IR spectra (lower traces) of the two lowest-energy isomers.[1] The calculated IR spectra, derived from TPSSh/def2-TZVP harmonic frequencies (scaled by 1.0175) and intensities, are plotted with sticks (gray) and a 15 cm^{-1} FWHM Gaussian line shape convolution. In square brackets the cosine similarity scores are given.

1.2. *n* = 2

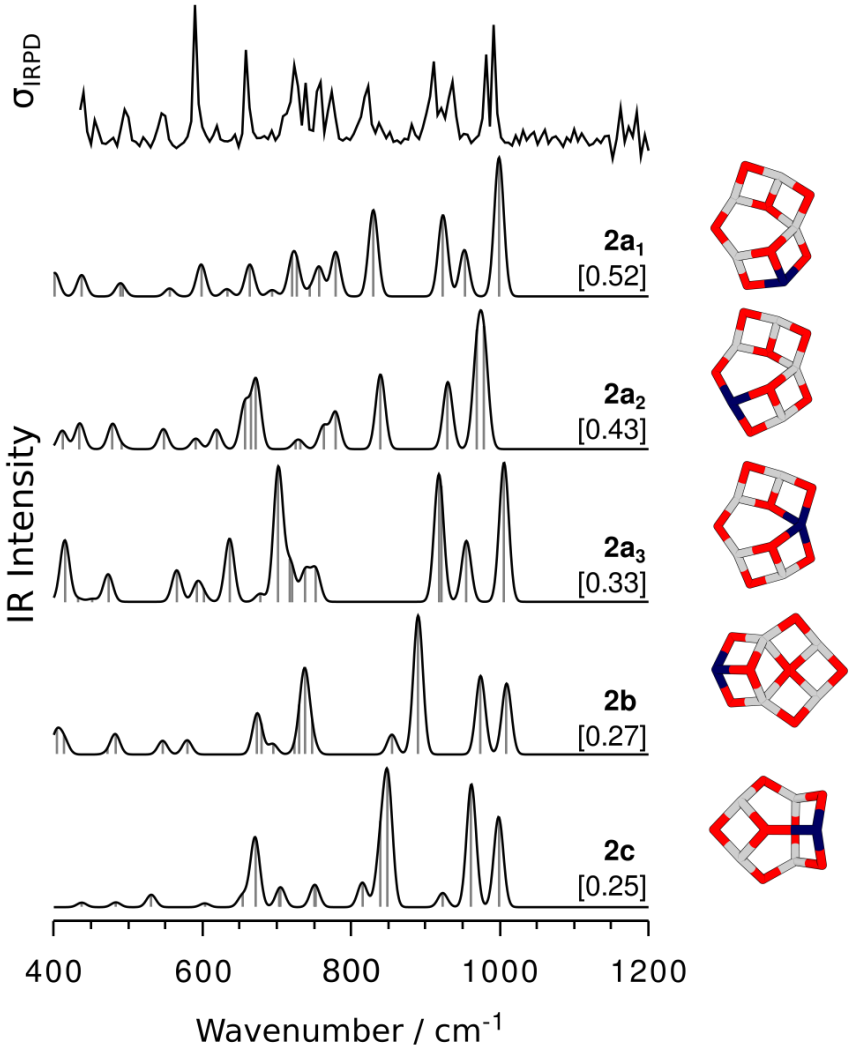

Figure S2. Experimental IRPD spectrum of He-tagged $Al_4FeO_7^+$ (top trace) compared with simulated IR spectra (lower traces) of calculated isomers. The calculated IR spectra, derived from TPSSh/def2-TZVP harmonic frequencies (scaled by 1.0175) and intensities, are plotted with sticks (gray) and a 15 cm^{-1} FWHM Gaussian line shape convolution. In square brackets the cosine similarity scores are given. See Tab. S1 for relative energies of the isomers.

1.3. *n* = 3

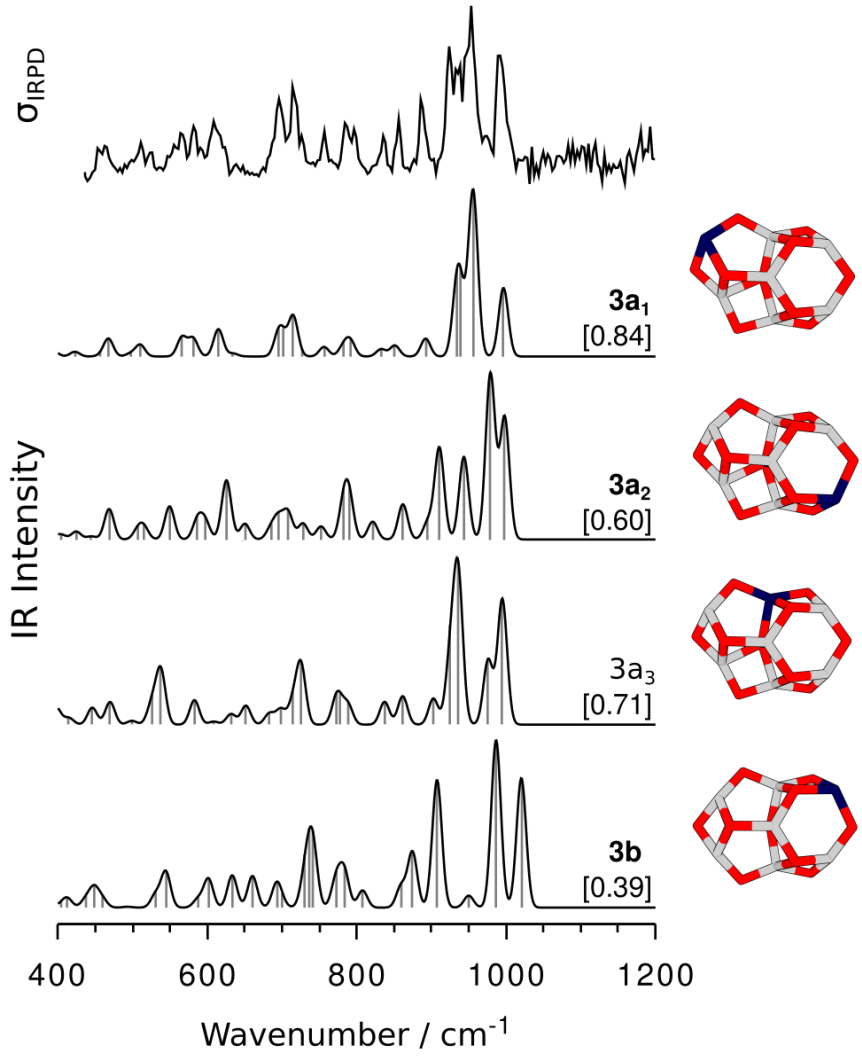

Figure S3. Experimental IRPD spectrum of He-tagged $Al_6FeO_{10}^+$ (top trace) compared with simulated IR spectra (lower traces) of calculated isomers. The calculated IR spectra, derived from TPSSh/def2-TZVP harmonic frequencies (scaled by 1.0175) and intensities, are plotted with sticks (gray) and a 15 cm^{-1} FWHM Gaussian line shape convolution. In square brackets the cosine similarity scores are given. See Tab. S1 for relative energies of the isomers.

1.4. *n* = 4

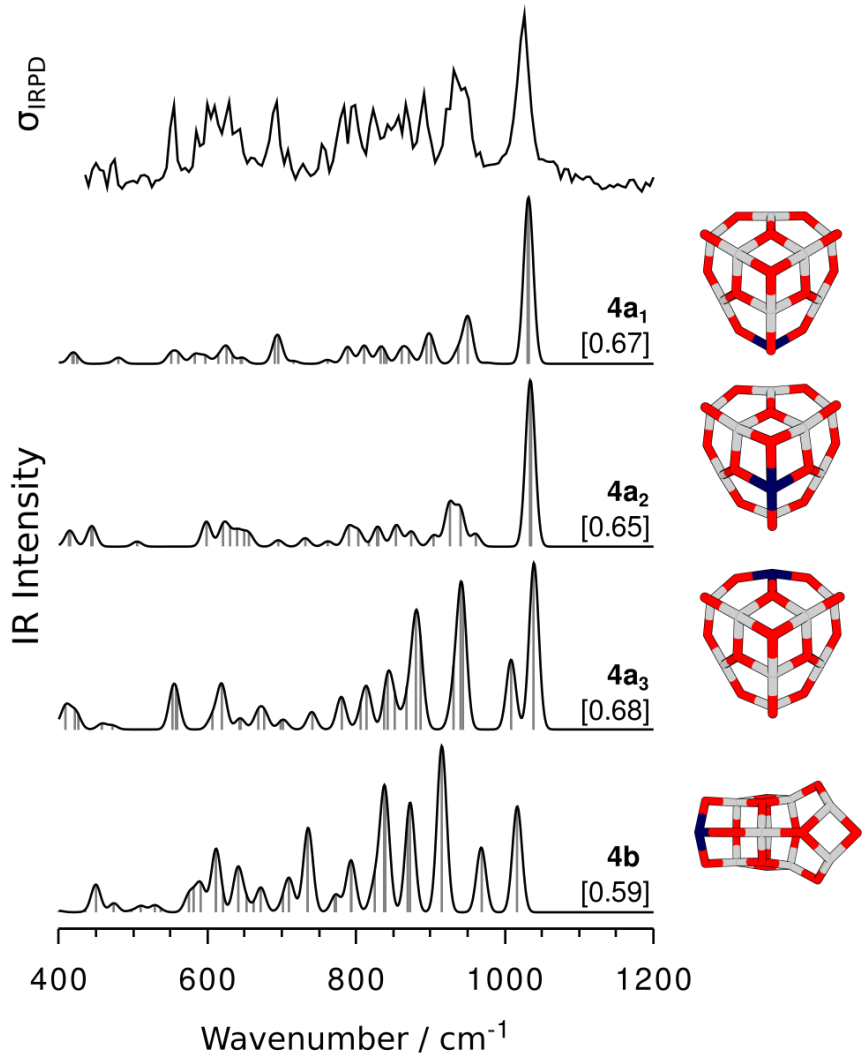

Figure S4. Experimental IRPD spectrum of He-tagged $Al_8FeO_{13}^+$ (top trace) compared with simulated IR spectra (lower traces) of all calculated isomers. The calculated IR spectra, derived from TPSSh/def2-TZVP harmonic frequencies (scaled by 1.0175) and intensities are plotted with sticks (gray) and a 15 cm^{-1} FWHM Gaussian line shape convolution. In square brackets the cosine similarity scores are given. See Tab. S1 for relative energies of the isomers.

1.5. *n* = 5

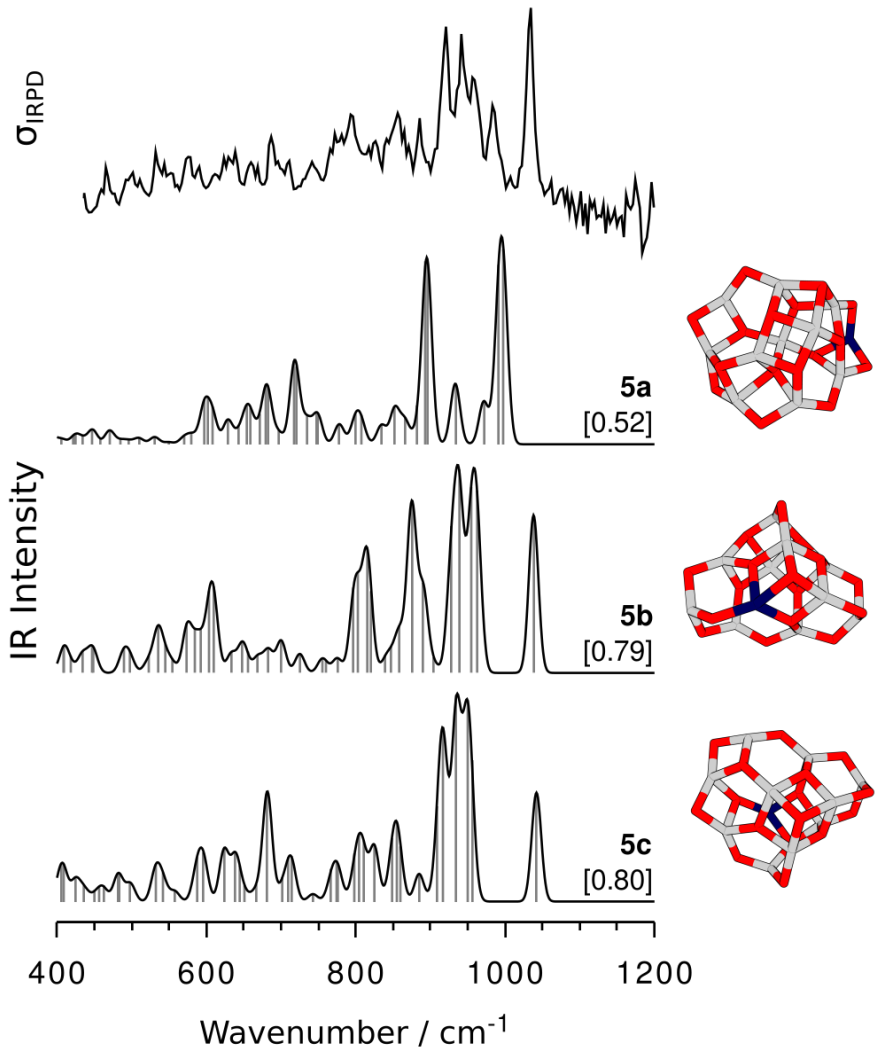

Figure S5. Experimental IRPD spectrum of He-tagged $Al_{10}FeO_{16}^{+}$ (top panel) compared with simulated IR spectra (lower traces) of calculated isomers. The calculated IR spectra, derived from TPSSh/def2-TZVP harmonic frequencies (scaled by 1.0175) and intensities, are plotted with sticks (gray) and a 15 cm^{-1} FWHM Gaussian line shape convolution. In square brackets the cosine similarity scores are given. See Tab. S1 for relative energies of the isomers.

2. Relative Energies

Table S1. Relative stabilities of low-energy isomers for the compositions $(Al_2O_3)_nFeO^+$ and $(Al_2O_3)_nAlO^+$ with n = 1–5. For the assigned isomers also relative energies of intermediate and low-spin configurations are given (S is the theoretical total spin quantum number and $\langle S^2 \rangle = S(S+1)$ is the calculated expectation value of the $\hat{S}^2$ operator). All pure aluminium oxide clusters are in the singlet spin state (S = 0). The used basis set for all calculations is def2-TZVP; the zero point vibrational energy contribution is always included; all energies are in kJ mol^{-1}.

			$(Al_2O_3)_nFeO^+$			$(Al_2O_3)_nAlO^+$[a]	
Iso	***S***	**$\langle S^2 \rangle$**[b]	**TPSSh**	**B3LYP**	**PBE0**	**TPSSh**	**B3LYP**
1a[c]	5/2	8.76	-47	-12	-22	0	0
1b[c]	5/2	8.77	0	0	0	132	112
	3/2	4.76	-1	12	12		
	1/2	2.37	76	110	113		
2a$_1$	5/2	8.76	0	0	0	0	0
	3/2	3.79	18	35	47		
	1/2	1.51	75	105	131		
2a$_2$	5/2	8.76	52	49	48		
2a$_3$	5/2	8.76	95	89	87		
2b	5/2	8.76	5	---	8	---	---
2c	5/2	8.76	31	28	31	10	11
3a$_1$	5/2	8.76	0	0	0	0	5
	3/2	3.82	65	62	90		
	1/2	1.35	87	117	142		
3a$_2$	5/2	8.76	23	23	21		
3a$_3$	5/2	8.76	59	57	57		
3b	5/2	8.76	24	19	21	0	0
4a$_1$	5/2	8.76	0	0	0	0	0
	3/2	3.79	29	53	68		
	1/2	1.86	98	133	156		
4a$_2$	5/2	8.76	13	14	13		
4a$_3$	5/2	8.76	20	22	19		
4b	5/2	8.76	49	110	67	74	134
5a	5/2	8.76	0	24	4	91	83
5b	5/2	8.76	10	0	0	0	0
	3/2	3.82	52	73	91		
	1/2	1.71	119	135	162		
5c	5/2	8.76	16	11	13	32	37

[a] Recalculated based on structures from Ref. [2]; all systems are closed-shell (S = 0); results for **5a$_{Al}$**, **5b$_{Al}$** and **5c$_{Al}$** are new in this study.

[b] Calculated for TPSSh/def2-TZVP.

[c] Taken from Ref. [1].

3. Band Positions

Table S2: Experimental band positions (in cm^{-1}) from the IRPD spectra of He-tagged $(Al_2O_3)_nFeO^+$ (n = 2–5), shown in Figure 1 of the main text.

n	**Bands**		
	Region (iii)	**Region (ii)**	**Region (i)**
2	455, 495, 549, 593	659, 724, 739, 755, 775, 825	914, 938, 983, 993
3	452, 465, 511, 564, 582	608, 696, 714, 757, 784, 796, 835, 856, 886	924, 938, 953, 992
4	475, 555, 585	600, 629, 693, 754, 784, 799, 823, 842, 857, 867, 891	931(b), 1026
5	465, 502, 532, 579	639, 687, 741, 796, 856, 886	921, 941, 959, 983, 1034

4. Structures and Spin Densities

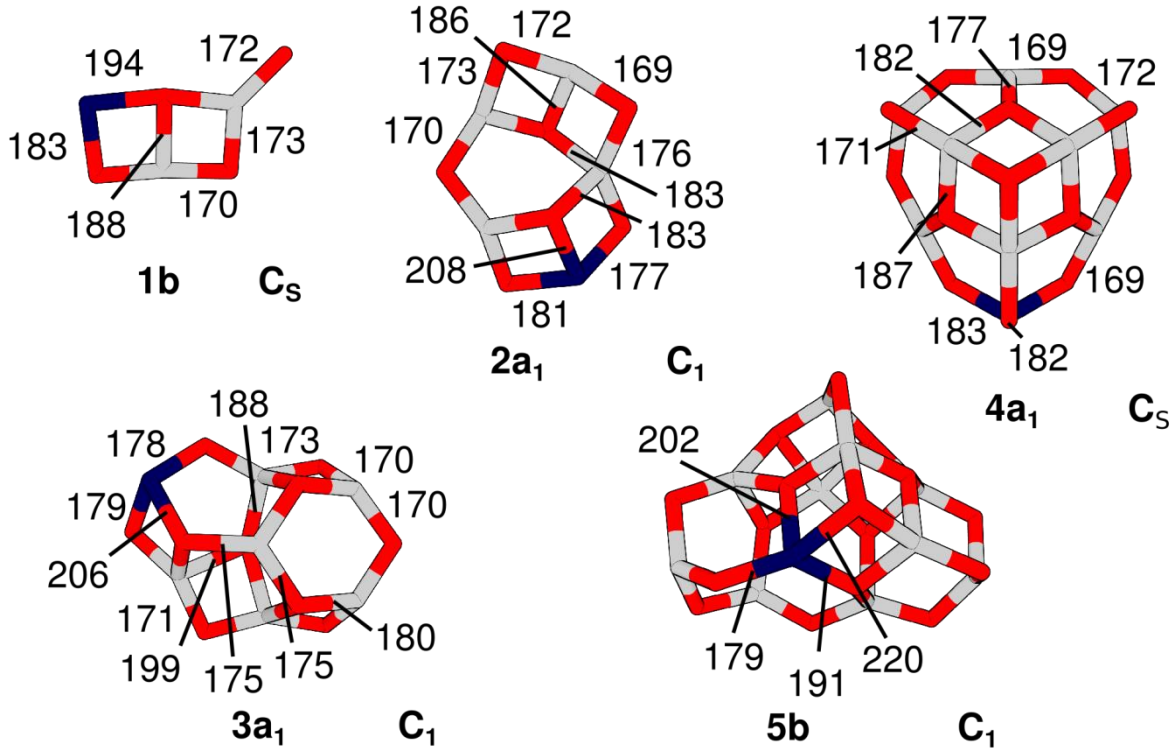

Figure S6. TPSSh/def2-TZVP minimum-energy structures (gray: aluminium, dark blue: iron, red: oxygen) of low-energy isomers that are found to contribute to the IRPD spectra of $(Al_2O_3)_n(FeO)^+$ (n = 1–5). Bond lengths are given in Angrstøm.

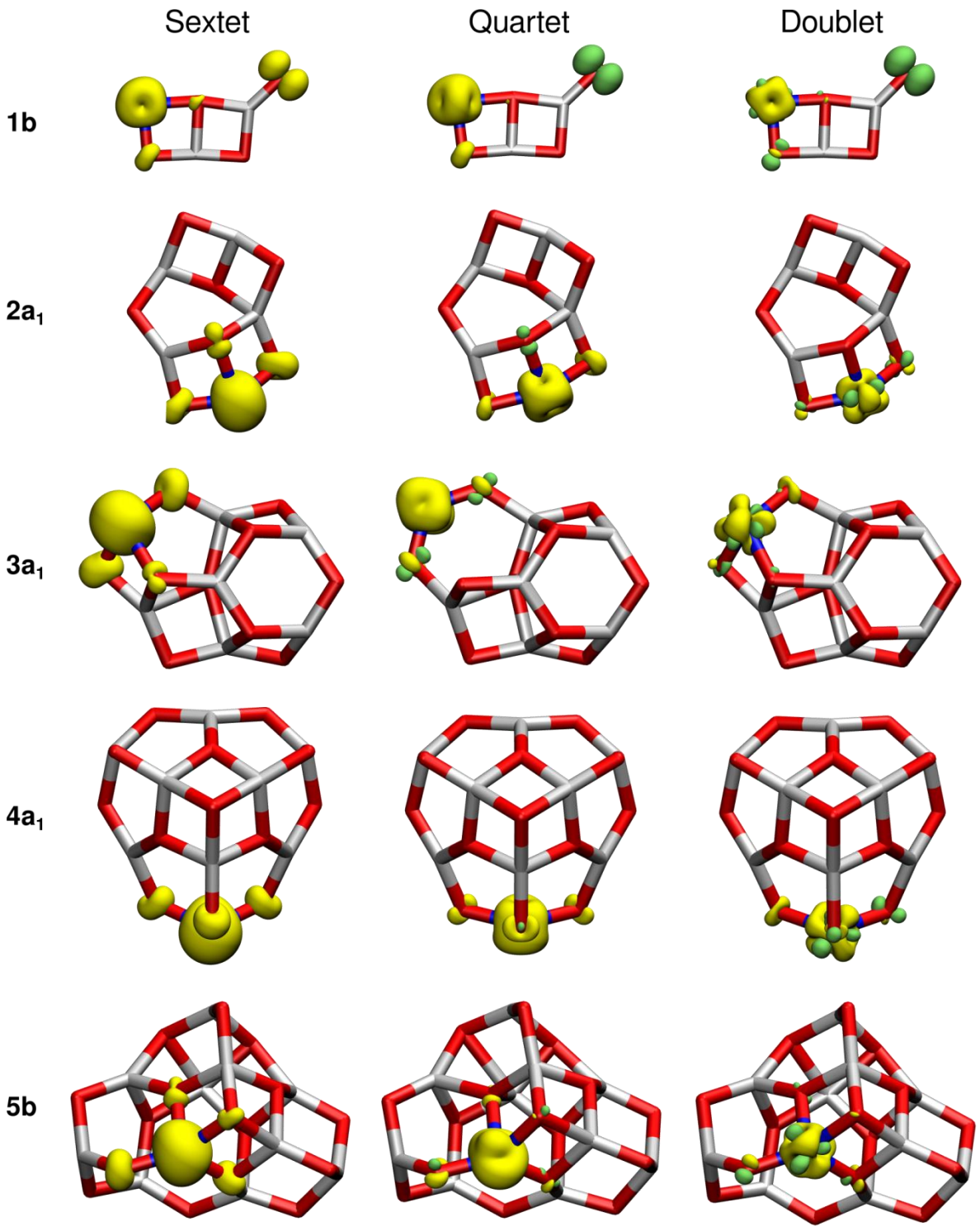

Figure S7. TPSSh/def2-TZVP spin densities (yellow: α-electron excess, green: β-electron excess) of the assigned minimum-energy structures (gray: aluminium, dark blue: iron, red: oxygen) of $(Al_2O_3)_n(FeO)^+$ (n = 1–5) in three different spin multiplicities.

5. References

1. Müller, F.; Stückrath, J. B.; Bischoff, F. A.; Gagliardi, L.; Sauer, J.; Debnath, S.; Jorewitz, M.; Asmis, K. R., Valence and Structure Isomerism of Al2FeO4+: Synergy of Spectroscopy and Quantum Chemistry. *J. Am. Chem. Soc.* **2020,** *142* (42), 18050-18059.
2. Santambrogio, G.; Janssens, E.; Li, S.; Siebert, T.; Meijer, G.; Asmis, K. R.; Döbler, J.; Sierka, M.; Sauer, J., Identification of Conical Structures in Small Aluminum Oxide Clusters: Infrared Spectroscopy of (Al2O3)1−4(AlO)+. *J. Am. Chem. Soc.* **2008,** *130* (45), 15143-15149.