Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

Electronic Structure of the dicationic first row transition metal oxides

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Table S1. Equilibrium bond length r_e (Å), equilibrium energy E_e (a.u.), harmonic vibrational frequency ω_e (cm^{-1}), anharmonicity $\omega_e x_e$ (cm^{-1}), and $\Delta G_{1/2}$ (cm^{-1}) for the ground electronic state of MO^{2+}, M = Ti – Cu, at MRCI / cc-pV*n*Z(M) aug-cc-pV*n*Z(O) and C-MRCI / cc-pwCV*n*Z(M) aug-cc-pV*n*Z(O) [$n = \infty$ signifies complete basis set or CBS limit].

n	r_e	$-E_e$	ω_e	$\omega_e x_e$	$\Delta G_{1/2}$	r_e	$-E_e$	ω_e	$\omega_e x_e$	$\Delta G_{1/2}$
	MRCI					**C-MRCI**				
					TiO^{2+} / $\tilde{X}\,^1\Sigma^+$					
3	1.558	922.874470	1050	3.7	1048	1.546	923.192919	1073	4.9	1064
4	1.556	922.894823	1054	3.3	1052	1.541	923.224779	1081	4.9	1073
5	1.554	922.901860	1057	3.2	1055	1.540	923.237170	1084	4.9	1076
∞	1.553	922.905776	1050	3.4	1049	1.539	923.245468	1078	4.8	1069
					VO^{2+} / $\tilde{X}\,^2\Delta$					
3	1.542	1017.317128	1014	6.0	1004	1.533	1017.658511	1029	5.8	1021
4	1.538	1017.338897	1022	5.5	1013	1.529	1017.694019	1034	5.2	1026
5	1.536	1017.346254	1026	5.4	1017	1.527	1017.707651	1038	5.2	1030
∞	1.535	1017.350196	1027	5.3	1019	1.526	1017.716724	1040	5.1	1032
					CrO^{2+} / $\tilde{X}\,^3\Sigma^-$					
3	1.541	1118.002155	947	13.2	919	1.535	1118.074084	948	13.3	920
4	1.529	1118.073063	966	13.3	940	1.535	1118.112704	965	13.4	939
5	1.529	1118.109357	972	13.2	947	1.527	1118.128122	971	13.3	946
∞	1.528	1118.150692	970	13.2	944	1.528	1118.138559	975	13.3	950
					MnO^{2+} / $\tilde{X}\,^4\Sigma^-$					
3	2.205	1224.201244	311	2.2	306	2.191	1224.567045	316	2.3	311
4	2.194	1224.223710	315	2.3	311	2.182	1224.607660	321	2.4	316
5	2.191	1224.230600	316	2.3	312	2.179	1224.623200	322	2.4	318
∞	2.187	1224.235232	315	1.9	312	2.172	1224.635534	322	1.8	319
					CoO^{2+} / $\tilde{X}\,^6\Phi$					
3	2.117	1455.809494	373	2.5	369	2.115	1456.198532	376	2.5	373
4	2.108	1455.842264	380	2.7	374	2.107	1456.250973	384	2.8	379
5	2.105	1455.854326	382	2.7	376	2.104	1456.272542	386	2.8	381
∞	2.110	1455.862149	382	2.6	377	2.103	1456.288614	386	2.6	381

					NiO^{2+} / $\tilde{X}\,^5\Delta$					
3	2.035	1581.306277	391	2.8	385	2.038	1581.700059	393	2.8	388
4	2.027	1581.344726	396	2.9	391	2.032	1581.759039	400	2.9	394
5	2.025	1581.359200	398	2.9	392	2.029	1581.783500	401	2.9	396
∞	2.023	1581.368956	399	2.8	393	2.027	1581.802144	402	2.8	396
					CuO^{2+} / $\tilde{X}\,^4\Sigma^-$					
3	1.954	1713.436267	408	2.4	403	1.961	1713.830091	409	2.5	404
4	1.946	1713.479521	414	2.4	409	1.953	1713.895522	415	2.5	410
5	1.945	1713.496299	415	2.4	410	1.951	1713.922793	416	2.5	411
∞	1.943	1713.507893	416	2.4	411	1.949	1713.943482	416	2.4	411

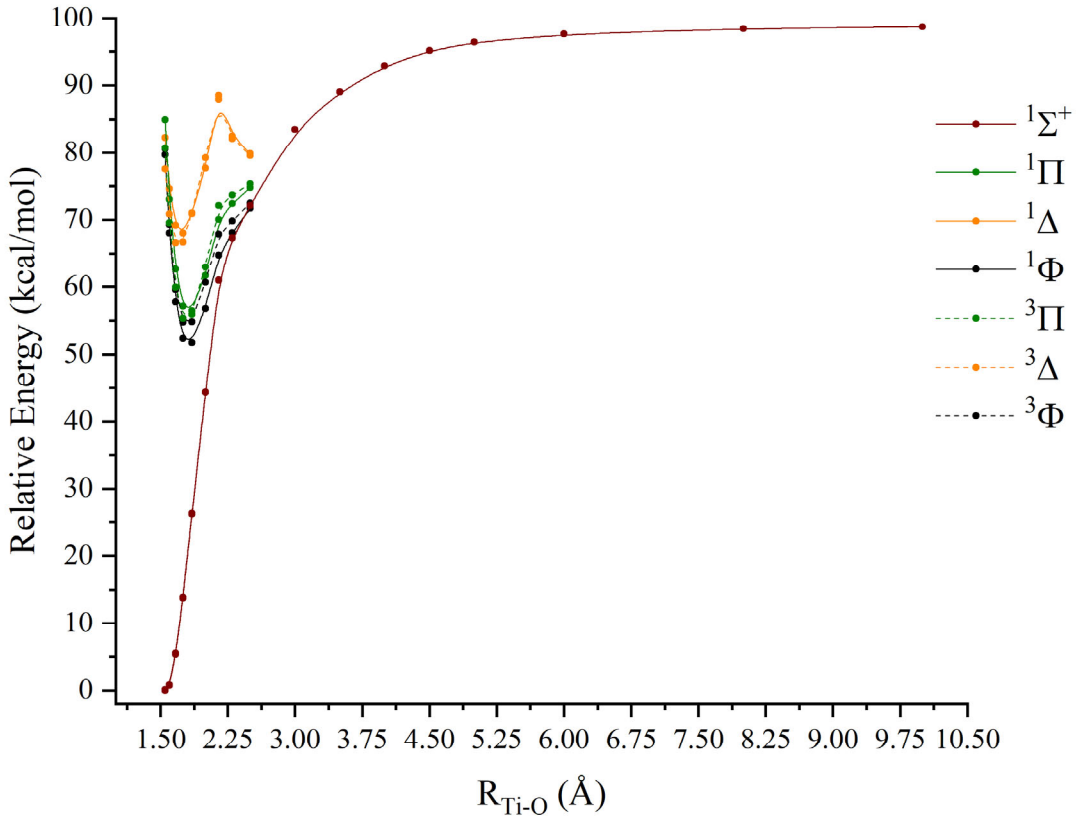

Figure S1. CASSCF PECs for the ground electronic state of FeO^{2+} from equilibrium to complete dissociation. PECs for the lowest lying excited electronic states are also shown in the avoided crossing region.

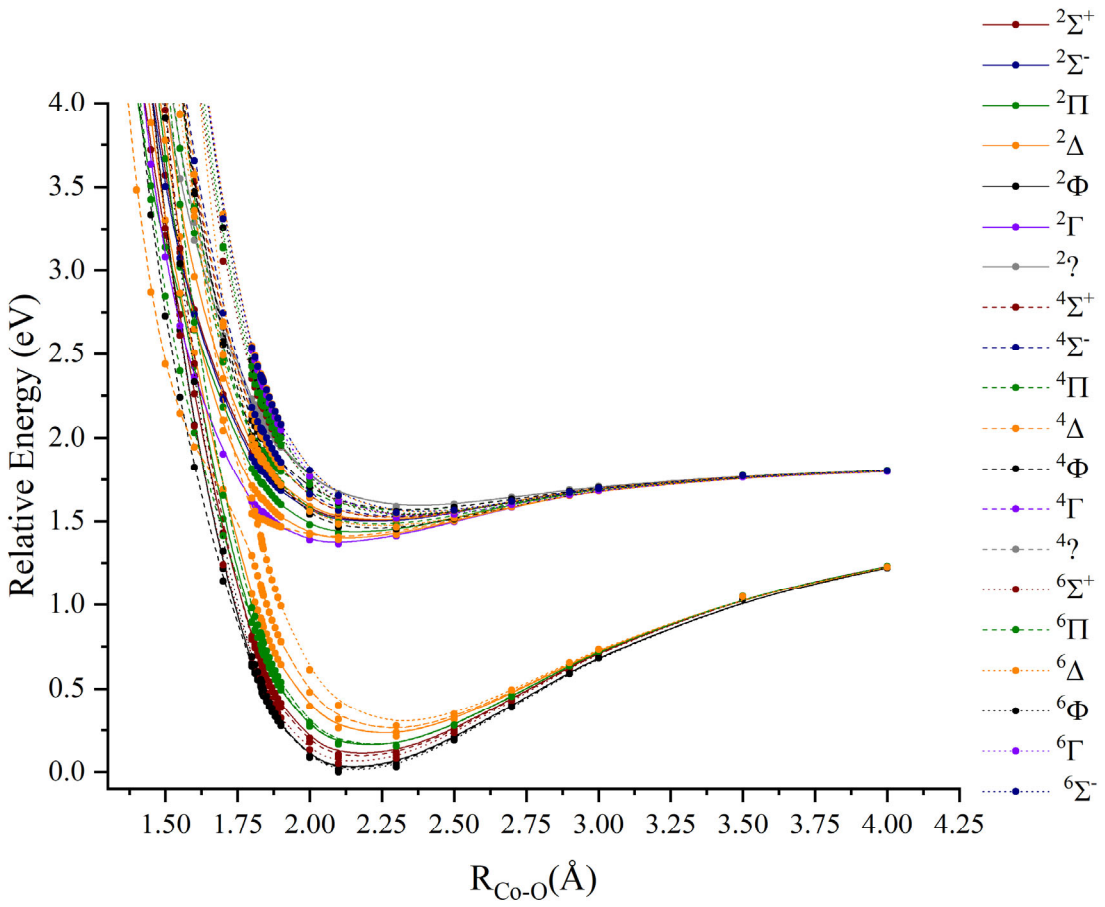

Figure S2. CASSCF PECs for numerous excited electronic states of CoO^{2+}.

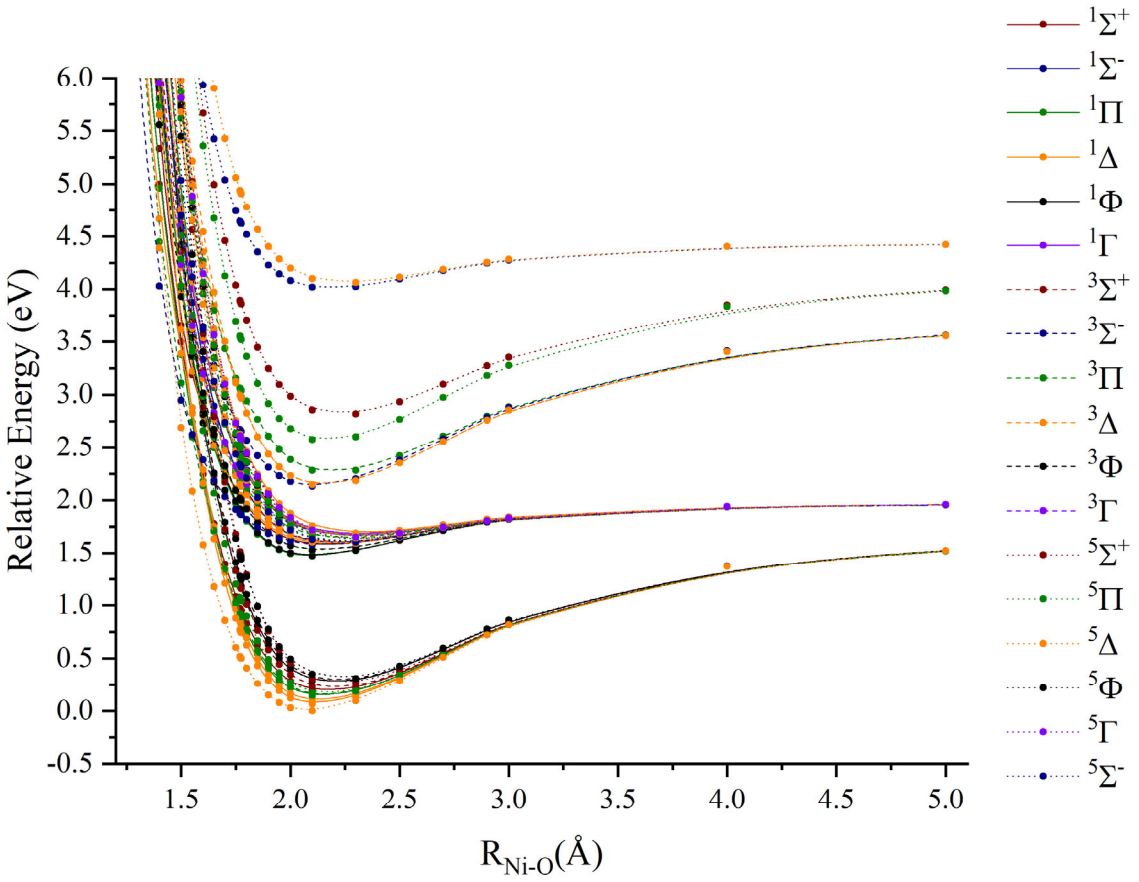

Figure S3. CASSCF PECs for numerous excited electronic states of NiO^{2+}.

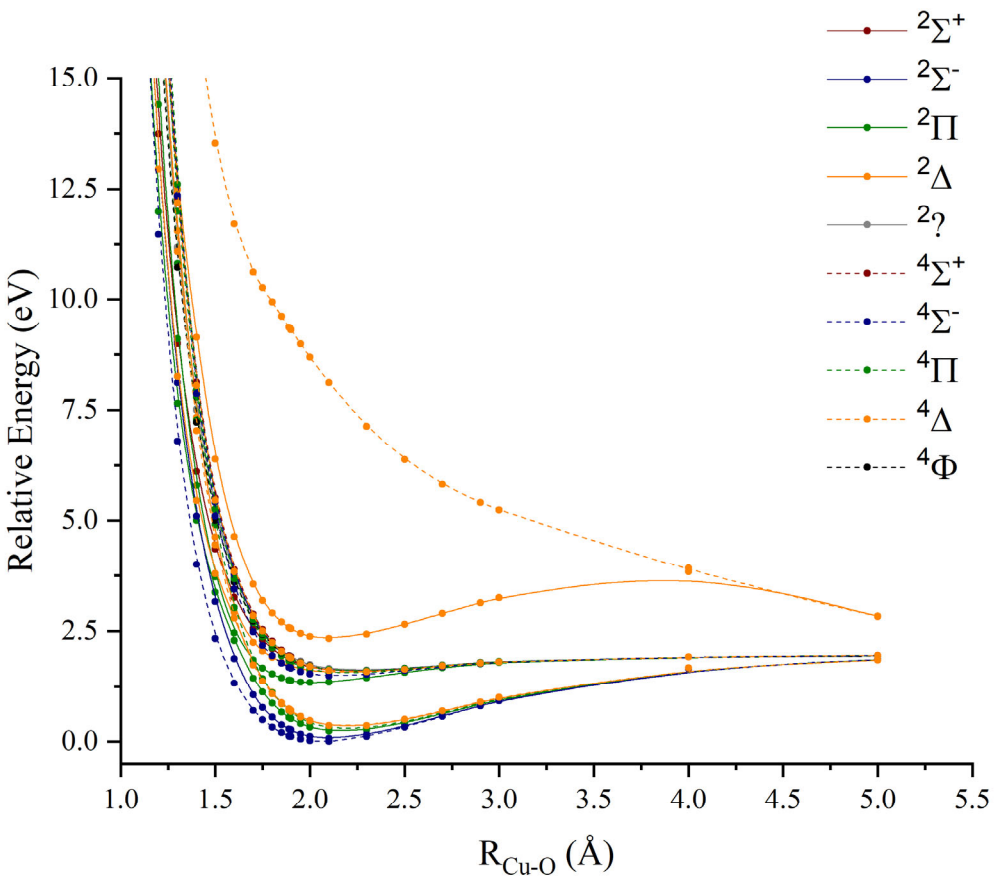

Figure S4. CASSCF PECs for numerous excited electronic states of CuO^{2+}.