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

Electronic Supplementary Information

Ab initio investigation of the ground and excited states of $RuO^{+,0,-}$ and their reaction with water

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Table S1. Dominant electronic configurations for the lowest electronic states of RuO^+. $1\sigma^2$ (~$2s_O$) is implied for all states, and MOs are shown in Figure 2.

State	Coef.	2σ	3σ	4σ	$1\pi_x$	$2\pi_x$	$1\pi_y$	$2\pi_y$	$1\delta_{x^2-y^2}$	$1\delta_{xy}$
$X^2\Pi$	0.89	2	0	0	2	α	2	0	2	2
$1^4\Delta$	0.95	2	0	0	2	α	2	α	2	α
$1^6\Sigma^+$	0.94	2	α	0	2	α	2	α	α	α
$1^4\Phi$	0.66	2	α	0	2	0	2	α	2	α
	-0.66	2	α	0	2	α	2	0	α	2
$1^4\Pi$	0.66	2	α	0	2	0	2	α	2	α
	0.66	2	α	0	2	α	2	0	α	2
$1^2\Sigma^+$	0.89	2	α	0	2	0	2	0	2	2
$1^2\Gamma$	0.47	2	0	0	2	0	2	2	2	α
	-0.47	2	0	0	2	2	2	0	2	α
	0.47	2	0	0	2	β	2	α	α	2
	-0.47	2	0	0	2	α	2	β	α	2
$1^2\Delta$	0.67	2	0	0	2	α	2	α	2	β
	-0.34	2	0	0	2	β	2	α	2	α
	-0.34	2	0	0	2	α	2	β	2	α
	0.31	2	0	0	2	0	2	2	α	2
	0.31	2	0	0	2	2	2	0	α	2
$1^2\Sigma^-$	-0.46	2	0	0	2	0	2	2	2	α
	0.46	2	0	0	2	2	2	0	2	α
	0.46	2	0	0	2	β	2	α	α	2
	-0.46	2	0	0	2	α	2	β	α	2
$1^2\Sigma^+$	-0.46	2	0	0	2	β	2	α	2	α
	0.46	2	0	0	2	α	2	β	2	α
	-0.46	2	0	0	2	0	2	2	α	2
	0.46	2	0	0	2	2	2	0	α	2
$1^2\Phi$	-0.54	2	α	0	2	β	2	0	α	2
	0.54	2	α	0	2	0	2	β	2	α
	-0.31	2	β	0	2	0	2	α	2	α
	0.31	2	β	0	2	α	2	0	α	2
$2^2\Pi$	0.49	2	α	0	2	β	2	0	α	2
	0.49	2	α	0	2	0	2	β	2	α
	-0.42	2	β	0	2	0	2	α	2	α
	-0.42	2	β	0	2	α	2	0	α	2
$1^4\Sigma^+$	0.49	2	α	0	2	α	2	β	α	α
	0.49	2	α	0	2	β	2	α	α	α
$2^2\Delta$	0.51	2	2	0	2	0	2	0	2	α
	-0.45	2	0	0	2	0	2	2	2	α
	-0.45	2	0	0	2	2	2	0	2	α
$2^4\Delta$	0.64	2	α	0	2	0	2	2	α	α
	-0.64	2	α	0	2	2	2	0	α	α
$1^6\Phi$	0.68	2	α	0	α	α	2	α	2	α
	-0.68	2	α	0	2	α	α	α	α	2

Table S2. Spin-orbit energies for the lowest electronic states of RuO^+ at 1.70 Å at MRCI level.

State	Energy (Hartrees)	Energy difference (eV)
$^4\Delta_{7/2}$	-168.86142175	0.00
$^4\Delta_{5/2}$	-168.85922958	0.06
$^2\Pi_{1/2}$	-168.85816254	0.09
$^4\Delta_{3/2}$	-168.85735155	0.11
$^2\Pi_{3/2}$	-168.85138566	0.27
$^4\Delta_{1/2}$	-168.85126486	0.28
$^4\Pi_{5/2}$	-168.85017263	0.31
$^4\Pi_{3/2}$	-168.84641495	0.41
$^4\Phi_{9/2}$	-168.84634768	0.41
$^4\Phi_{7/2}$	-168.84450314	0.46
$^4\Pi_{1/2}$	-168.84352223	0.49
$^4\Phi_{5/2}$	-168.84274472	0.51
$^4\Phi_{3/2}$	-168.84108667	0.55
$^4\Pi_{1/2}$	-168.84002043	0.58
$^6\Sigma^+_{3/2}$	-168.83858745	0.62
$^6\Sigma^+_{5/2}$	-168.83849890	0.62
$^6\Sigma^+_{1/2}$	-168.83843296	0.63
$^2\Sigma^+_{1/2}$	-168.82918404	0.88

Table S3. Dominant electronic configurations for the lowest electronic states of RuO. $1\sigma^2$ (~$2s_O$) is implied for all states, and MOs are shown in Figure 2.

State	Coef.	2σ	3σ	4σ	$1\pi_x$	$2\pi_x$	$1\pi_y$	$2\pi_y$	$1\delta_{x^2-y^2}$	$1\delta_{xy}$
$X^5\Delta$	0.95	2	α	0	2	α	2	α	2	α
$1^3\Pi$	0.80	2	α	0	2	α	2	0	2	2
$1^3\Delta$	0.79	2	β	0	2	α	2	α	2	α
	-0.41	2	α	0	2	β	2	α	2	α
	-0.41	2	α	0	2	α	2	β	2	α
$1^1\Sigma^+$	0.92	2	2	0	2	0	2	0	2	2
$1^1\Pi$	0.60	2	β	0	2	α	2	0	2	2
	-0.60	2	α	0	2	β	2	0	2	2
$1^3\Gamma$	0.56	2	α	0	2	α	2	β	2	α
	0.46	2	α	0	2	2	2	0	α	2
	-0.46	2	α	0	2	0	2	2	α	2
$1^3\Phi$	0.63	2	2	0	2	α	2	0	α	2
	0.63	2	2	0	2	0	2	α	2	α
$1^5\Sigma^+$	0.93	2	2	0	2	α	2	α	α	α
$1^3\Sigma^-$	0.50	2	α	0	2	α	2	β	α	2
	-0.43	2	α	0	2	0	2	2	2	α
	0.43	2	α	0	2	2	2	0	2	α
$2^3\Pi$	0.52	2	α	0	2	α	2	0	2	2
	0.51	2	2	0	2	0	2	α	2	α
	-0.51	2	2	0	2	α	2	0	α	2
$2^3\Sigma^-$	0.81	2	0	0	2	α	2	α	2	2
$1^3\Sigma^+$	-0.32	α	2	0	2	β	2	α	2	α
	0.56	α	2	0	2	α	2	β	2	α
	-0.45	α	α	0	2	0	2	2	2	2
	0.45	α	α	0	2	2	2	0	2	2
$2^3\Delta$	0.53	α	α	0	2	0	2	2	2	2
	0.53	α	α	0	2	2	2	0	2	2
$1^1\Delta$	0.49	2	α	0	2	β	2	β	α	2
	0.49	2	β	0	2	α	2	α	β	2

Table S4. Spin-orbit energies for the lowest electronic states of RuO at 1.70 Å at MRCI level.

State	Energy (Hartrees)	Energy difference (eV)
$^5\Delta_4$	-169.1554527	0.00
$^5\Delta_3$	-169.1535351	0.05
$^5\Delta_2$	-169.1518288	0.10
$^5\Delta_1$	-169.1499812	0.15
$^5\Delta_{0+}$	-169.1484284	0.19
$^5\Delta_{0-}$	-169.1484166	0.19
$^3\Pi_1$	-169.1293541	0.71
$^3\Pi_{0+}$	-169.1292645	0.71
$^3\Pi_{0-}$	-169.1288716	0.72
$^3\Pi_2$	-169.1288646	0.72
$^3\Delta_3$	-169.1216192	0.92
$^3\Delta_2$	-169.1173184	1.04
$^3\Delta_1$	-169.1151332	1.10
$^3\Gamma_5$	-169.1145857	1.11
$^3\Gamma_4$	-169.1126878	1.16
$^3\Phi_1$	-169.1097962	1.24
$^1\Pi_1$	-169.1094300	1.25
$^3\Gamma_3$	-169.1090370	1.26
$^3\Sigma^-_{0+}$	-169.1069723	1.32
$^3\Sigma^-_1$	-169.1066534	1.33
$^3\Phi_2$	-169.1064445	1.33
$^3\Phi_3$	-169.1056745	1.35
$^5\Sigma^+_2$	-169.1041079	1.40
$^5\Sigma^+_1$	-169.1034939	1.41
$^5\Sigma^+_{0+}$	-169.1033202	1.42

Table S5. MRCI optimal geometries (Cartesian coordinates in Å) of the reactants, transition state, and products of the RuO + H_2O → $Ru(OH)_2$ reaction for the first two quintets (1^5A, 2^5A), the first four triplet (1^3A, 2^3A, 3^3A, 4^3A), and the first singlet (1^1A) states.

	Reactants				Transition State				Products			
1^5A	Ru	0.1597804677	0.1623007048	0.1582543344	Ru	0.6254154857	0.0047848187	-0.1786618408	Ru	-0.0000000000	-0.0000000000	-0.0079837670
	O	-1.5320762648	0.2834936180	0.1594956641	O	-0.3663310005	1.5227326523	-0.0900564245	O	-0.0396575603	1.9203263554	-0.0079837670
	O	2.4443619857	0.0054447139	0.1420322867	O	-1.5545677686	-0.4783223626	0.1980892435	O	0.0396575603	-1.9203263554	-0.0079837670
	H	2.9802106979	0.6896882915	0.5287380877	H	-1.2399163461	0.7152313667	0.1118874754	H	0.4834729671	2.5003330149	0.5270106791
	H	2.8907348248	-0.8199324552	0.2977241337	H	-1.8745161242	-0.6844991220	1.0676124082	H	-0.4834729671	-2.5003330149	0.5270106791
2^5A	Ru	0.0807234607	0.1515772933	0.2369975398	Ru	0.5479568674	-0.0882491349	-0.0500685721	Ru	-0.0002633944	0.0424986808	0.0008489593
	O	-1.6013090692	0.2696490786	0.0533811726	O	-0.3802035230	1.4554802406	0.0032414712	O	-1.9181162259	-0.0074050560	0.0839236871
	O	2.3544547051	-0.0081669373	0.4672956361	O	-1.7108882071	-0.5760541217	-0.0536031028	O	1.9176073913	-0.0075865042	-0.0815292366
	H	2.8236577655	0.4750942340	1.1390244724	H	-1.3743475269	0.6597651950	0.0148002411	H	-2.5281622582	0.5122782842	-0.4200322790
	H	2.7881800032	-0.8498234952	0.3753917297	H	-2.3035066103	-0.8191781788	0.6793419626	H	2.5273644864	0.5193756714	0.4151688690
1^3A	Ru	0.3028008357	0.1584650854	-0.2512400199	Ru	0.4273108744	-0.1606414752	0.0002646837	Ru	-0.0000000000	-0.0000000000	-0.0061429588
	O	-1.1873792982	0.2382758057	0.4527066394	O	-0.3760781594	1.4447856828	0.0338348247	O	-0.0478326879	1.9013303154	-0.0061429588
	O	2.4821281599	0.0067805178	-0.1048069363	O	-1.6644454147	-0.4790217553	-0.1023756819	O	0.0478326879	-1.9013303154	-0.0061429588
	H	2.9771815994	0.7407945497	0.2425859822	H	-1.4623832462	0.6136870580	-0.0323718872	H	0.5831149289	2.4756954250	0.4054984193
	H	2.8735035439	-0.7921025112	0.2317648793	H	-2.0891240541	-0.7606865104	0.7055490607	H	-0.5831149289	-2.4756954250	0.4054984193
2^3A	Ru	0.3472419140	0.1414003459	0.0797003974	Ru	0.4444459332	-0.1551941346	0.0000135590	Ru	0.0000000000	-0.0000000000	-0.0000000000
	O	-1.3855820457	0.2625654282	0.2569668567	O	-0.3773581819	1.4418873187	0.0226831402	O	0.0000000000	-0.0560856158	1.9158183285
	O	2.5240771766	0.0021678386	-0.1422577948	O	-1.6729015147	-0.4748688472	-0.0963458378	O	0.0000000000	0.0560856158	-1.9158183285
	H	3.0257513241	0.7399420154	0.1944851508	H	-1.4552507295	0.6202702803	-0.0236378642	H	0.0000000000	0.6788383987	2.5125136639
	H	2.9367464718	-0.7938621806	0.1821159346	H	-2.1036555071	-0.7739716172	0.7021880028	H	0.0000000000	-0.6788383987	-2.5125136639
3^3A	Ru	0.0000000000	-0.0001543387	0.1138503939	Ru	0.4132513520	-0.1546456107	0.0051630660	Ru	0.0000000000	-0.0000000000	-0.0000000000
	O	0.0000000000	0.0007962603	1.7617039964	O	-0.4072649281	1.4221235297	0.0369615295	O	0.0000000000	-0.0562338192	1.9178097192
	O	-0.0000000000	-0.0014551164	-2.1410344929	O	-1.6903297569	-0.5045858908	-0.1139966089	O	0.0000000000	0.0562338192	-1.9178097192
	H	0.7704512071	0.0129671962	-2.6974814806	H	-1.4015776274	0.6625452224	-0.0421442247	H	0.0000000000	0.6818367394	2.5106820198
	H	-0.7704512071	0.0129671962	-2.6974814806	H	-2.0787990396	-0.7673142507	0.7189172380	H	0.0000000000	-0.6818367394	-2.5106820198
4^3A	Ru	0.2539392989	0.1541293658	-0.1534379511	Ru	0.4277131507	-0.1658767747	-0.0022851238	Ru	0.1501335000	-0.1830910660	0.0849376059
	O	-1.3611075848	0.2551610168	0.3620545358	O	-0.3918058138	1.4552295860	0.0432172583	O	0.2596118282	-0.0354343415	1.9832183314
	O	2.4809433501	0.0051851769	0.1668652004	O	-1.6768541756	-0.4923475793	-0.1084177875	O	0.2066317965	-0.1449339472	-1.8210294002
	H	3.0880022078	0.7337874922	0.1047096108	H	-1.4358672139	0.6163578363	-0.0408934535	H	-0.1953792346	-0.6173373713	2.5786556680
	H	2.9864575688	-0.7960496043	0.0908191488	H	-2.0879059475	-0.7552400684	0.7132801064	H	-0.2643909239	-0.7599415413	-2.3688314941
1^1A	Ru	0.3156197420	0.1426107944	0.4428148854	Ru	0.4889993499	-0.0434753815	-0.1042059419	Ru	-0.3276412162	-0.0596608404	0.0063160945
	O	-1.2474258266	0.2546471863	-0.0298245743	O	-0.3526301217	1.4866105925	-0.0840132031	O	0.0841708125	-0.1016958308	1.8188534191
	O	2.4945033819	0.0008369005	0.2767338972	O	-1.5089795412	-0.4480656964	0.1589031306	O	0.0454766914	0.1065676329	-1.8072837103
	H	2.9887805415	0.7448673433	-0.0523637068	H	-1.2928679804	0.7676084728	0.0896365859	H	0.2419441203	0.6695312227	2.3497936902
	H	2.8967575384	-0.7907487523	-0.0663499160	H	-1.7444377776	-0.6827505563	1.0485503699	H	0.4289064897	-0.5779133319	-2.3422630540

The grey highlighted TS are optimized at MRCI/cc-pVDZ-PP(Ru) cc-pVDZ(H) aug-cc-pVDZ(O). All other structures are optimized at MRCI/cc-pVTZ-PP(Ru) cc-pVTZ(H) aug-cc-pVTZ(O).

Table S6. Total energies (a.u.) of optimal geometries of the reactants, transition state, and products of the RuO + H_2O → $Ru(OH)_2$ reaction for the first two quintets (1^5A, 2^5A), the first four triplet (1^3A, 2^3A, 3^3A, 4^3A), and the first singlet (1^1A) states.

State	Total energy of RuO + H_2O reacting products (a.u.)					
	Intermediate		TS		Products	
	MRCI	MRCI+Q	MRCI	MRCI+Q	MRCI	MRCI+Q
1^5A	-245.380595	-245.481342	-245.336644	-245.434783	-245.444645	-245.533297
2^5A	-245.380567	-245.481273	-245.329243	-245.428893	-245.444698	-245.533234
1^3A	-245.351600	-245.458504	-245.333034	-245.436714	-245.403830	-245.494451
2^3A	-245.364523	-245.457565	-245.325976	-245.429525	-245.393832	-245.484247
3^3A	-245.346647	-245.454583	-245.323614	-245.427430	-245.393624	-245.483946
4^3A	-245.330938	-245.438278	-245.312765	-245.416998	-245.390701	-245.484407
1^1A	-245.329479	-245.438740	-245.317217	-245.422845	-245.389835	-245.484635

Table S7. Harmonic vibrational frequencies (cm^{-1}) of MRCI optimal geometries given in Table S5.

	Reactants	**Transition States**	**Products**
1^5A	119.8, 140.5, 286.5, 341.8, 560.0, 973.4, 1703.7, 3985.7, 4080.2	1713.2i, 278.7, 445.9, 575.4, 681.8, 813.9, 1400.5, 1972.5, 4018.7	37.1, 107.9, 380.4, 617.4, 658.4, 749.4, 769.0, 4059.3, 4114.5
2^5A	22.9, 141.7, 282.4, 384.1, 514.6, 970.8, 1704.7, 3976.5, 4080.0	1912.5i, 217.2, 511.8, 754.3, 800.9, 894.8, 1436.7, 1707.5, 3709.3	55.7, 143.2, 170.7, 559.2, 596.5, 669.1, 685.7, 4078.8, 4095.7
1^3A	91.4 223.9, 312.8, 337.5, 525.4, 965.0, 1702.2, 3980.9, 4076.3	1020.7i, 387.0, 620.5, 727.5, 756.0, 827.9, 1526.2, 1973.5, 4014.3	125.8, 149.7, 170.5, 616.7, 627.0, 657.5, 685.0, 4069.6, 4073.1
2^3A	86.5, 135.9, 325.5, 376.3, 484.8, 749.0, 1678.3, 3948.7, 4043.7	1107.1i, 356.0, 570.3, 673.0, 743.2, 824.7, 1499.8, 1961.3, 4017.6	132.4, 187.1, 413.6, 494.9, 645.2, 719.7, 800.5, 4068.9, 4072.4
3^3A		1732.1i, 364.4, 605.9, 626.5, 724.7, 818.9, 1433.5, 1884.3, 4006.0	141.0, 182.7, 408.9, 476.4, 643.3, 713.6, 801.6, 4068.1, 4071.3
4^3A	161.4, 205.1, 224.1, 291.0, 444.8, 1347.8, 1702.3, 3991.3, 4083.9	1316.2i, 363.5, 608.3, 674.8, 734.1, 802.4, 1483.5, 1911.9, 4008.9	79.6, 206.8, 574.5, 595.3, 657.0, 741.1, 1316.2, 4038.5, 4052.6
1^1A	77.4, 207.7, 306.2, 339.4, 500.0, 1057.7, 1697.0, 3968.9, 4063.2	1624.5i, 450.6, 634.2, 668.2, 764.2, 876.1, 1459.8, 1944.9, 4034.1	88.7, 455.1, 542.6, 673.5, 687.9, 807.5, 844.0, 4021.8, 4025.6

Table S8. MRCI optimal geometries (Cartesian coordinates in Å) of the reactants, transition state, and products of the $RuO^+ + H_2O \rightarrow Ru(OH)_2^+$ reaction for the first four quartet (1^4A, 2^4A, 3^4A, 4^4A), the first two doublet (1^2A, 2^2A), and the first sextet (1^6A) states.

	Reactants				Transition State				Products			
1^4A	Ru	0.1500735406	0.1602156348	0.1941391774	Ru	0.4567300323	-0.0482134207	-0.0961909985	Ru	-0.0019797675	0.0005203754	0.1371797952
	O	-1.4847276681	0.2834759158	0.1153230870	O	-0.3308802486	1.4786873267	-0.1008730909	O	-0.0223978534	1.8097061139	0.0899495880
	O	2.3802988460	-0.0123453925	0.3022890347	O	-1.4728695039	-0.4541577253	0.1777195534	O	0.0230642817	-1.8087064727	0.0938036086
	H	2.9978582937	0.6990780702	0.4606205934	H	-1.3011244705	0.8303818889	0.0809293941	H	0.4864119710	2.5725818012	0.3557404915
	H	2.8995086993	-0.8094293553	0.2138726141	H	-1.7617718803	-0.7267706385	1.0472860833	H	-0.4850986318	-2.5741018177	0.3533966480
2^4A	Ru	0.1498614531	0.1601218213	0.1941303829	Ru	0.4625067273	-0.0446422799	-0.1001005053	Ru	-0.0023797791	0.0006449307	0.1361641354
	O	-1.4849039792	0.2834998951	0.1153030811	O	-0.3112839397	1.5075914919	-0.1371938158	O	-0.0215119368	1.8100232396	0.0854338127
	O	2.3804190606	-0.0122573805	0.3023157200	O	-1.4831611116	-0.3962769782	0.2394011255	O	0.0220512978	-1.8087786194	0.0894807326
	H	2.9981266628	0.6990245679	0.4606227609	H	-1.2809366340	0.8414662468	0.0628540260	H	0.4856318507	2.5707131515	0.3607239687
	H	2.8995090136	-0.8093940078	0.2138726540	H	-1.7970411131	-0.8282110496	1.0439101110	H	-0.4837914326	-2.5726027024	0.3582674819
3^4A	Ru	0.2104091359	0.1544338068	0.1958925841	Ru	0.4684035675	-0.0485514668	-0.0787520035	Ru	0.0000000000	-0.0000000000	-0.3147827813
	O	-1.4279710871	0.2791354572	0.1188174532	O	-0.2979492166	1.5066039717	-0.2078747926	O	-0.0365676735	-1.4019955602	0.8238682012
	O	2.3438837940	-0.0084013312	0.3007567588	O	-1.4521240529	-0.3519877368	0.2177908047	O	0.0365676735	1.4019955602	0.8238682012
	H	2.9594735797	0.7072747790	0.4596975735	H	-1.3311459138	0.7650240732	0.1938743616	H	0.6071082029	-1.5123522074	1.5252290810
	H	2.8572172886	-0.8114477932	0.2110803217	H	-1.7971004554	-0.7911614104	0.9838325714	H	-0.6071082029	1.5123522074	1.5252290810
4^4A	Ru	0.2114230239	0.1577637855	0.1770976202	Ru	0.4878622195	-0.0561580166	-0.1147329201				
	O	-1.4282410551	0.2772030891	0.1300398923	O	-0.3189413921	1.5178296324	-0.1661100740				
	O	2.3440909581	-0.0085287115	0.2975408208	O	-1.3936860865	-0.3774761743	0.2422165240	No convergence. Used the same geometry from 3^4A to obtain the energy.			
	H	2.9580060326	0.7070079213	0.4630163617	H	-1.3449034601	0.7565551411	0.1542673490				
	H	2.8577327517	-0.8124512114	0.2185498116	H	-1.8402473519	-0.7608231516	0.9932300626				
1^2A	Ru	0.2140659629	0.1535778429	0.1928763798	Ru	0.4325606692	-0.1092533966	-0.0464368770	Ru	0.0007814266	-0.0008489912	-0.1735403733
	O	-1.5492207686	0.2892754525	0.1182233657	O	-0.2988578432	1.5493382193	-0.1754966050	O	-0.0695142254	1.7334475286	0.1216229898
	O	2.3828499834	-0.0117962762	0.2987293988	O	-1.4699475030	-0.4383291487	0.1872471607	O	0.0713412314	-1.7356071691	0.1198370481
	H	2.9980943437	0.7039826446	0.4474237573	H	-1.3377177756	0.8944912981	0.1062850383	H	0.4965207764	2.4197989336	0.4805516993
	H	2.8972221898	-0.8140447908	0.2289916049	H	-1.7359536184	-0.8163195410	1.0372722246	H	-0.4991292090	-2.4167903019	0.4815987674
2^2A	Ru	0.2133773721	0.1529126306	0.2016274902	Ru	0.4787506683	-0.0944034996	-0.0577355847	Ru	0.0014363744	-0.0322772463	-0.5240406763
	O	-1.5471534523	0.2889840678	0.1127683555	O	-0.3132716307	1.5013499414	-0.2201746684	O	-0.1755650997	1.6501204186	0.1452523439
	O	2.3820499124	-0.0112663875	0.3004104785	O	-1.4705514224	-0.3701399241	0.2523883662	O	0.1720798562	-1.6533549688	0.1453366922
	H	2.9988668037	0.7036966806	0.4467010694	H	-1.3293902860	0.9293732759	0.1346253173	H	0.5105855983	2.1298969705	0.6329462276
	H	2.8958710749	-0.8133321185	0.2247371130	H	-1.7754534003	-0.8862523626	0.9997675110	H	-0.5085367292	-2.0943851744	0.6305756179
1^6A	Ru	0.2204462185	0.1548714693	0.1931586192	Ru	0.7342920567	-0.3476735455	-0.1663128690	Ru	-0.0005979292	0.0001338717	-0.0230623355
	O	-1.5670136433	0.2877008883	0.1174502585	O	-0.0258147724	1.6043626866	-0.2904482579	O	0.2209794336	1.8210689842	0.0216265870
	O	2.3864445070	-0.0100793965	0.3011379337	O	-1.2640118170	-0.2212759617	0.2530828359	O	-0.2215313635	-1.8208280392	0.0220472330
	H	3.0056202203	0.7029501952	0.4506018626	H	-0.9933111871	0.9211836442	0.0824994892	H	0.3217551819	2.6354234757	0.5048686447
	H	2.8975144088	-0.8144482833	0.2238958327	H	-1.7460177961	-0.5869394301	1.0729277708	H	-0.3206053228	-2.6357982925	0.5045900021

All other structures are optimized at MRCI/cc-pVTZ-PP(Ru) cc-pVTZ(H) aug-cc-pVTZ(O).

Table S9. Harmonic vibrational frequencies (cm^{-1}) of MRCI optimal geometries given in Table S8

	Reactants	Transition States	Products
1^4A	89.5, 107.6, 344.2, 349.3, 572.9, 1147.6, 1735.4, 3931.7, 4007.5	1864.4i, 479.0, 602.6, 668.1, 890.8, 974.8, 1300.9, 1977.9, 3956.2	129.4, 161.5, 231.6, 558.4, 594.8, 822.6, 826.3, 3968.9, 3983.4
2^4A	72.8, 119.0, 340.7, 349.2, 573.8, 1147.9, 1736.0, 3931.9, 4007.7	1984.6i, 449.2, 559.2, 618.8, 830.4, 925.4, 1255.2, 1974.7, 3830.5	134.4, 157.6, 243.0, 553.8, 597.9, 822.2, 825.7, 3968.1, 3982.6
3^4A	18.7i, 154.8, 400.9, 434.8, 609.2, 1052.0, 1731.1, 3903.6, 3978.5	1297.2i, 443.1, 523.7, 710.7, 839.8, 973.7, 1349.7, 2163.7, 4067.2	279.8, 522.0, 530.0, 751.9, 879.1, 986.0, 2153.7, 3922.4, 3968.4
4^4A	55.1, 143.3, 400.4, 435.6, 608.9, 1053.9, 1730.9, 3904.4, 3979.3	1647.5i, 400.0, 496.2, 719.6, 775.4, 874.0, 1278.8, 2090.5, 3979.8	-
1^2A	107.7, 183.3, 349.6, 374.5, 622.6, 675.0, 1739.7, 3926.6, 4003.9	1891.8i, 464.6, 555.7, 672.4, 769.8, 944.7, 1326.1, 1797.0, 3799.1	92.8, 397.2, 524.9, 604.3, 690.7, 855.5, 865.9, 3902.1, 3918.6
2^2A	111.7, 184.2, 350.7, 375.2, 584.5, 675.2, 1740.9, 3926.7, 4003.5	1764.1i, 470.2, 554.9, 592.3, 732.3, 944.8, 1346.9, 1848.5, 3926.1	164.2, 589.7, 632.1, 795.8, 927.9, 999.4, 1106.5, 3905.5, 4194.0
1^6A	100.7, 165.3, 358.8, 379.4, 615.9, 635.7, 1735.3, 3919.0, 3995.5	1487.1i, 400.8, 513.7, 714.5, 971.8, 1030.7, 1274.6, 1871.3, 3175.6	91.8, 125.4, 194.4, 331.1, 412.2, 776.2, 841.9, 4006.5, 4020.3

Table S10. Total energies (a.u.) of optimal geometries of the reactants, transition state, and products of the $RuO^+ + H_2O \rightarrow Ru(OH)_2^+$ reaction for the first four quartets (1^4A, 2^4A, 3^4A, 4^4A), the first two doublet (1^2A, 2^2A), and the first sextet (1^6A) states.

State	Total energy of $RuO^+ + H_2O$ reacting products (a.u.)					
	Intermediate		TS		Products	
	MRCI	MRCI+Q	MRCI	MRCI+Q	MRCI	MRCI+Q
1^4A	-245.110452	-245.208999	-245.053952	-245.154271	-245.101846	-245.191876
2^4A	-245.110370	-245.208921	-245.041200	-245.142492	-245.101758	-245.191783
3^4A	-245.098670	-245.201180	-245.030675	-245.133822	-245.096016	-245.191904
4^4A	-245.098315	-245.200911	-245.012842	-245.112806	-245.068340	-245.163550
1^2A	-245.074994	-245.160251	-245.039493	-245.130859	-245.098378	-245.193448
2^2A	-245.074782	-245.160289	-245.040073	-245.131031	-245.066715	-245.155556
1^6A	-245.103974	-245.187976	-245.039990	-245.118894	-245.116742	-245.201722

Table S11. MRCI optimal geometries (Cartesian coordinates in Å) of the reactants, transition state, and products of the $RuO^- + H_2O \rightarrow Ru(OH)_2^-$ reaction for the first two quartet (1^4A, 2^4A) and the first two doublet (1^2A, 2^2A) states.

	Reactants				Transition State				Products			
1^4A	Ru	-0.8857945363	1.0645114228	-0.3069587976	Ru	0.485839	-0.159057	-0.000326	Ru	0.0003370622	-0.0000982877	0.0005737372
	O	0.6245034977	0.2869708114	0.0299249010	O	-0.420263	1.394287	0.018152	O	-0.0819286493	1.9851694891	-0.0608584392
	H	0.0826828257	-2.6898045530	0.4135758395	O	-1.830459	-0.508984	-0.110660	O	0.0816979363	-1.9854162074	-0.0611852507
	H	0.9296416121	-1.4733449118	0.1607088731	H	-1.352388	0.697989	-0.044240	H	0.4946424357	2.3884116991	0.5756843853
	O	0.9926019258	-2.4421221186	0.2721474844	H	-2.018748	-0.781895	0.798662	H	-0.4947487849	-2.3880666929	0.5758556986
2^4A	Ru	-0.8726985663	1.0692807984	-0.3604450050					Ru	0.0003232048	-0.0001041286	-0.0003727837
	O	0.6248390029	0.2807316405	0.0056928271					O	-0.0828165854	1.9855231292	-0.0584966078
	H	0.0725591234	-2.6853670750	0.4271995979	Used the 1^4A geometry to do a single point calculation				O	0.0826018446	-1.9857834836	-0.0588343396
	H	0.9314212287	-1.4757313507	0.1845118385					H	0.4959554075	2.3918488030	0.5737995051
	O	0.9875145364	-2.4427033621	0.3124390422					H	-0.4960638714	-2.3914843200	0.5739743572
1^2A	O	0.0000000000	-0.0000000000	-3.4891347208	Ru	-0.1395744489	0.0001185510	-0.3838717944	Ru	0.0000000000	-0.0000000000	-0.0113729502
	H	0.0000000000	-0.7455490452	-2.8949850242	O	1.4679177158	-0.0082136424	0.4708909979	O	-0.0611910050	1.9198415151	0.0324467192
	H	0.0000000000	0.7455490452	-2.8949850242	O	-0.5615958556	0.0586721584	1.7350038604	O	0.0611910050	-1.9198415151	0.0324467192
	Ru	0.0000000000	-0.0000000000	0.2961388484	H	0.4413355644	0.0312186117	1.5825322270	H	0.8154630588	2.2867447398	0.0551659845
	O	0.0000000000	-0.0000000000	1.9831525594	H	-0.8320497102	-0.8440526368	1.8947859342	H	-0.8154630588	-2.2867447398	0.0551659845
2^2A	Used the 1^2A geometry to do a single point calculation				Used the 1^2A geometry to do a single point calculation				Used the 1^2A geometry to do a single point calculation			

The grey highlighted structures are optimized at MRCI/aug-cc-pVDZ-PP(Ru) cc-pVDZ(H) aug-cc-pVDZ(O). All other structures are optimized at MRCI/aug-cc-pVTZ-PP(Ru) cc-pVTZ(H) aug-cc-pVTZ(O). The green highlighted structure is optimized at DFT-MN15/ aug-cc-pVDZ-PP(Ru) cc-pVDZ(H) aug-cc-pVDZ(O).

Table S12. Total energies (a.u.) of optimal geometries of the reactants, transition state, and products of the $RuO^- + H_2O \rightarrow Ru(OH)_2^-$ reaction for the first two quartet (1^4A, 2^4A) and the first two doublet (1^2A, 2^2A) states.

State	Total energy of $RuO^- + H_2O$ reacting products (a.u.)					
	Intermediate		TS		Products	
	MRCI	MRCI+Q	MRCI	MRCI+Q	MRCI	MRCI+Q
1^4A	-245.424785	-245.530067	-245.382325	-245.485853	-245.498484	-245.593741
2^4A	-245.424744	-245.530022	-245.380955	-245.484964	-245.498367	-245.593536
1^2A	-245.410662	-245.499918	-245.372464	-245.476123	-245.457301	-245.556542
2^2A	-245.410309	-245.499555	-245.360603	-245.466479	-245.448781	-245.549738

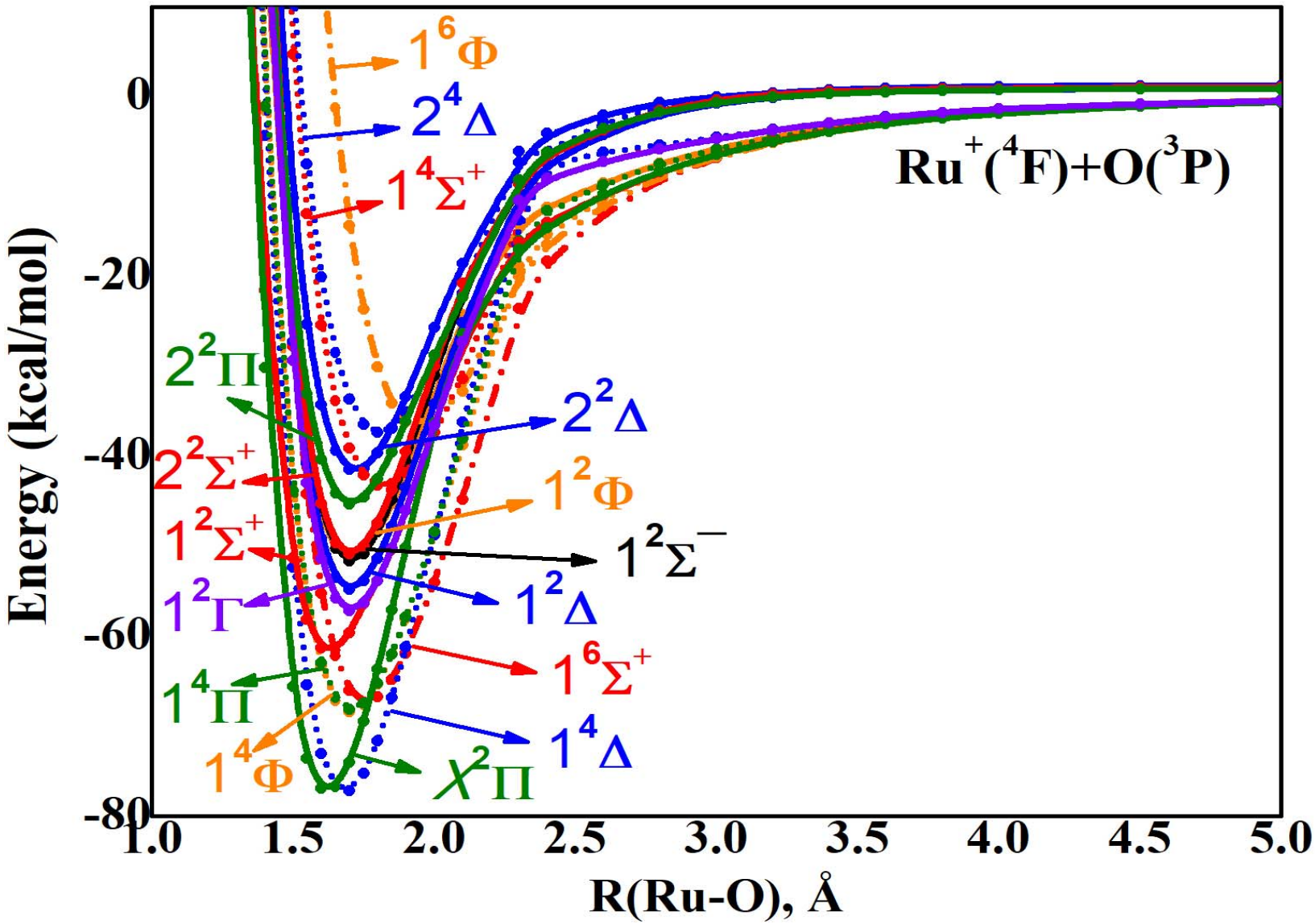

Figure S1. Potential energy curves of RuO^+ as a function of the Ru-O distance at the MRCI level of theory.

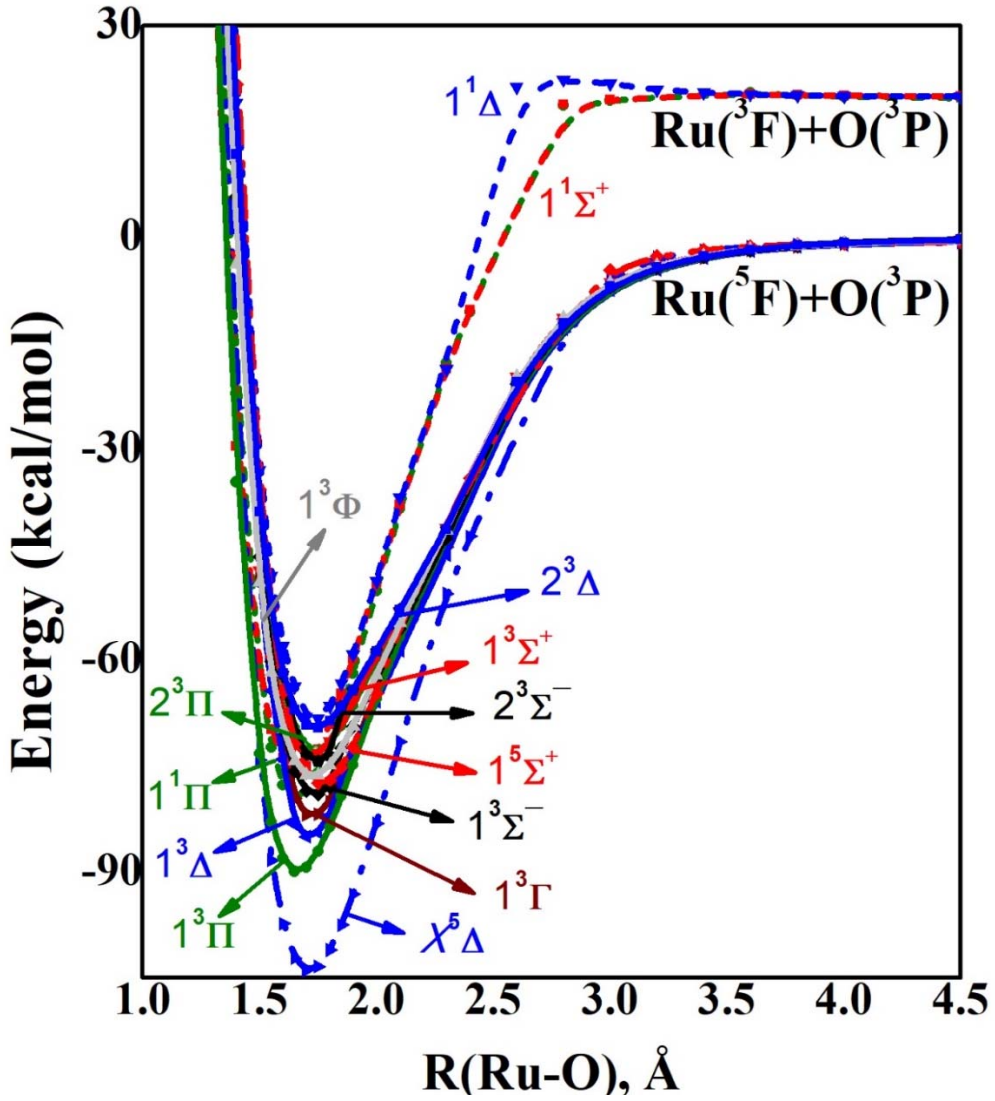

Figure S2. Potential energy curves of RuO as a function of the Ru-O distance at the MRCI level of theory.

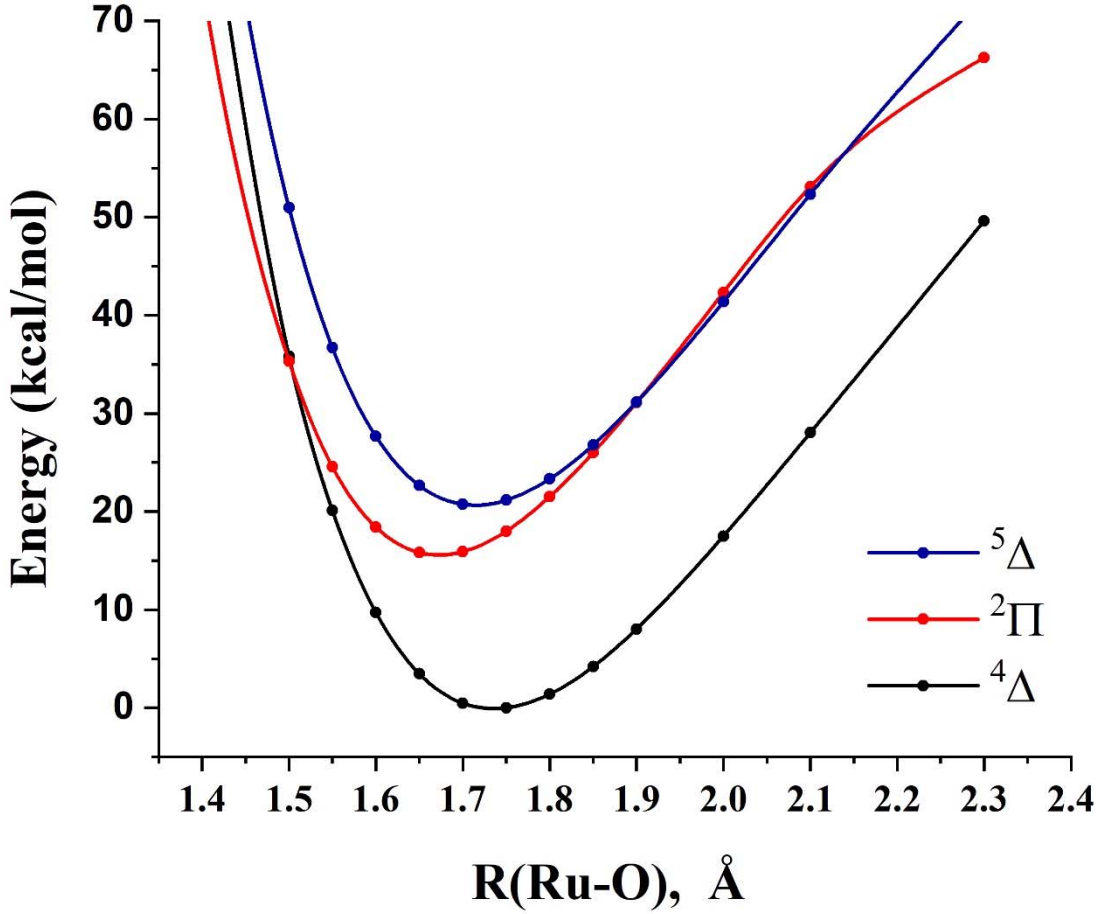

Figure S3. Potential energy curves of RuO^- as a function of the Ru-O distance at the MRCI level of theory.