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Electronic Supplementary Information

Radical abstraction vs. oxidative addition mechanisms for the activation of the S−H, O−H, and C−H bonds using early transition metal oxides

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MRCI calculations

We recently studied the electronic structure of the ground and several excited electronic states of ZrO^+ and NbO^+ [I. R. Ariyarathna and E. Miliordos, *Journal of Quantitative Spectroscopy and Radiative Transfer*, 2020, **255**, 107265]. In the present work, we considered their reaction with H_2O and H_2S for the $X^2\Delta$, $1^2\Sigma^+$, $1^2\Pi$, and $1^4\Pi$ states of ZrO^+ and $X^3\Sigma^-$, $1^1\Gamma$, $1^3\Delta$, $1^1\Sigma^+$, and $1^5\Sigma^-$ states for NbO^+. The wavefunction of the $1^4\Pi$ state of ZrO^+ and the $1^1\Gamma$, $1^1\Sigma^+$, and $1^5\Sigma^-$ states of NbO^+ bear two equivalent dominant electronic configurations, but the rest of the states are of single-reference character. The coordination of H_2X to the metals results in the elimination of one of the two dominant configurations in the former states. Generally, transition states and products are single reference.

All minima and transition states were optimized at the MRCI level of theory and they are depicted in Figures S2 and S3. The energy diagrams at the MRCI+Q//MRCI level (single point MRCI+Q energies at the MRCI optimized structures) are plotted in Figure S1. To assess our theoretical methods for the lowest state of each spin multiplicity, we compare the MRCI+Q and DFT/MN15 energetics. Overall, the trends are identical for both methods regarding the relative energetics of the reaction mechanisms. The two methods agree within ±15 kcal/mol except a few cases with differences that can approach 43 kcal/mol (see Table S18). This difference is considered reasonable based on the complexity of the wavefunction of the examined transition metal systems. Conclusively, qualitative results and valuable insights can be safely deduced with our DFT/MN15 results of the bigger systems, where the multi-reference character of the wavefunction quenches.

Table S1. MRCI/cc-pVDZ-PP(Zr) cc-pVDZ(H) aug-cc-pVDZ(O,S) optimal geometries (Cartesian coordinates in Å) of the reactants, transition states, and products of the $ZrO^+ + H_2S \rightarrow HS{-}Zr^+{-}OH$ reaction for the first five doublets (1^2A, 2^2A, 3^2A, 4^2A, 5^2A) and the first two quartet (1^4A, 2^4A).

	Reactants				Transition State [a]				Products			
1^2A	Zr	-0.2213530457	-0.6508217113	-0.1748902143	Zr	0.689613	-0.290703	0.000735	Zr	-0.4354319013	-0.3723800636	0.0000013531
	O	-0.7723232335	0.8211914811	0.5399759631	O	0.535572	1.481277	0.007804	O	-1.5134069558	1.1702231391	-0.0000026857
	S	2.5717090814	-0.2787726420	-0.2151464285	S	-1.823562	-0.082609	-0.080710	S	1.9119715810	0.2083832591	-0.0000048410
	H	2.4389585208	1.0281819224	0.1032796162	H	-0.757373	1.180166	-0.074571	H	-1.9892208779	2.0014665110	-0.0000054607
	H	2.9401749863	-0.6487375985	1.0306217382	H	-1.934740	-0.080533	1.274099	H	1.6767291540	1.5413131544	0.0000236343
2^2A	Zr	-0.2526605607	-0.6800605055	0.1936803775	N/A [b]				Zr	-0.4076572429	-0.1042916270	0.0453130413
	O	-0.7963804664	0.9617673213	0.0619308042					O	-1.8401281435	1.1516262847	-0.0893715798
	S	2.4782165311	-0.2237525125	-0.1814541252					S	2.0330783409	0.1532326196	0.0174768838
	H	2.4544474796	0.9927693373	0.4087932666					H	-2.3595891444	1.9561909199	-0.0787183955
	H	3.0763483655	-0.8482039545	0.8563273602					H	2.1335218679	1.2608736375	0.7855499097
3^2A	Zr	-0.2619686897	-0.4162798747	0.3684564765	N/A [b]				Zr	0.0253937900	0.1780488597	-0.9201778711
	O	-1.4066343526	0.8199193127	0.0028247279					O	0.2207806247	1.7671926955	0.1134585632
	S	2.6058964122	-0.3287171350	-0.1606210761					S	-0.2611724508	-2.1031402536	-0.2322867758
	H	2.8671553490	0.9748565542	0.0816867804					H	0.2762069018	2.2307359679	0.9511800587
	H	3.1527175908	-0.7787374055	0.9914937660					H	-0.2612088660	-2.0728372696	1.1178961563
4^2A	Zr	-0.0736681282	0.1696871521	0.0719699194	N/A [b]				N/A [b]			
	O	-2.0658692228	0.3192988174	0.2707243376								
	S	2.8076757299	0.0386189291	-0.2491800791								
	H	3.1955897931	0.8784977987	0.7384426436								
	H	3.0792835390	-1.0851078245	0.4542876849								
5^2A	N/A [b]				N/A [b]				N/A [b]			
1^4A	Zr	-0.4147590109	-0.3061189306	-0.7693761968	Zr	0.847549	-0.189534	0.002436	Zr	0.1351989878	-0.0533915096	0.3261321386
	O	-1.5084108005	0.6760291207	0.5810600683	O	-0.138631	1.472751	0.012938	O	0.4282424661	-0.1393684540	2.2012230710
	S	2.3090153166	0.1815962546	-0.4237182340	S	-1.823147	-0.317761	-0.075280	S	-0.2530944215	0.0467132357	-2.5628364566
	H	2.2305529826	1.4963443610	-0.1195945059	H	-1.510097	1.089328	-0.239499	H	0.5890043099	-0.1910175821	3.1428759680

	H 2.4627335119 -0.2264698056 0.8560298685	H -2.112462 -0.205797 1.243036	H 0.6833266116 -0.8677765673 -2.9228782861
2^4A	N/A [b]	N/A [b]	Zr 0.1389523276 -0.0526285275 0.3255915294 O 0.4285305097 -0.1385110407 2.2013191145 S -0.2553374590 0.0449162970 -2.5622999981 H 0.5870377987 -0.1918074001 3.1432537453 H 0.6834947769 -0.8668102060 -2.9233479562

[a] Optimized at DFT/MN15 using the same basis set.
[b] Geometry optimization calculations failed for these structures.

Table S2. Harmonic vibrational frequencies (cm^{-1}) of the optimal geometries given in Table S1.

	Reactants	**Transition States [b]**	**Products**
1^2A	85.5, 101.6, 211.2, 455.2, 515.1, 1001.4, 1221.7, 2753.9, 2768.4	1539.8i, 261.1, 269.0, 384.6, 449.2, 963.3, 1046.0, 1463.2, 2641.3	117.7, 130.4, 392.5, 400.6, 401.8, 452.6, 787.5, 2740.8, 3997.7
2^2A	81.9, 116.4, 228.2, 434.3, 653.5, 986.7, 1219.7, 2763.5, 2793.5	N/A [b]	84.2, 136.5, 383.2, 434.6, 443.8, 490.2, 764.7, 2751.6, 3997.6
3^2A	82.4, 94.8, 183.4, 421.2, 495.9, 996.7, 1218.7, 2748.4, 2766.3	N/A [b]	134.7, 387.2, 388.3, 488.7, 523.5, 575.1, 768.7, 2760.7, 3977.8
4^2A	7.9i, 34.5, 188.8, 426.2, 476.3, 659.1, 1211.7, 2739.2, 2754.3	N/A [b]	N/A [b]
5^2A	N/A [b]	N/A [b]	N/A [b]
1^4A	59.7, 69.1, 215.1, 446.5, 521.8, 664.6, 1217.4, 2749.6, 2764.8	1165.0i, 193.1, 308.2, 353.4, 489.3, 644.4, 1021.6, 1800.4, 2684.9	37.9, 39.9, 185.1, 456.0, 490.8, 496.9, 761.2, 2722.7, 4012.5
2^2A	N/A [b]		31.7, 43.3, 184.9, 454.8, 490.9, 497.8, 761.1, 2722.2, 4012.7

[a] Obtained at DFT/MN15; see Table S1.
[b] Unavailable due to technical issues; see Table S1.

Table S3. MRCI(+Q)/cc-pVTZ-PP(Zr) cc-pVTZ(H) aug-cc-pVTZ(O,S) electronic energies (a.u.) of optimal geometries of the fragments, reactants, transition states, and products of the $ZrO^+ + H_2S \rightarrow HS{-}Zr^+{-}OH$ reaction for the first five doublets (1^2A, 2^2A, 3^2A, 4^2A, 5^2A) and the first two quartets (1^4A, 2^4A).

State	Fragments [a]		Reactants		Transition States		Products	
	MRCI	MRCI+Q	MRCI	MRCI+Q	MRCI	MRCI+Q	MRCI	MRCI+Q
1^2A	-520.226037	-520.288207	-520.284898	-520.345326	-520.230991	-520.303657	-520.311609	-520.371615
2^2A	-520.226041	-520.288198	-520.284012	-520.344455	-520.229617 [d]	-520.301804 [d]	-520.305971	-520.364352
3^2A	-520.209652	-520.272802	-520.260005	-520.321561	-520.183332 [d]	-520.255969 [d]	-520.293545	-520.354301
4^2A	-520.139072	-520.204612	-520.154219	-520.208784	-520.092379 [d]	-520.164750 [d]	-520.187691 [f]	-520.246318 [f]
5^2A	-520.139072	-520.204612	-520.153818 [b]	-520.208447 [b]	-520.069622 [d]	-520.143456 [d]	-520.182145 [f]	-520.241150 [f]
1^4A	-520.111575	-520.166846	-520.161228	-520.216329	-520.137000	-520.196987	-520.228458	-520.282644
2^4A	-520.111575	-520.166846	-520.148846 [c]	-520.203507 [c]	-520.127750 [e]	-520.187519 [e]	-520.227617	-520.281992

[a] Single point energy calculations of ZrO^+ and H_2S separated by a distance of 1,000 Å.
[b] Single point energy using the 4^2A reactant structure.
[c] Single point energy using the 1^4A reactant structure.
[d] Single point energy using the 1^2A TS structure.
[e] Single point energy using the 1^4A TS structure.
[f] Single point energy using the 3^2A product structure.

Table S4. DFT/MN15/cc-pVTZ-PP(Zr) cc-pVTZ(H) aug-cc-pVTZ(O, S, Cl, N) optimal geometries (Cartesian coordinates in Å), harmonic vibrational frequencies (cm^{-1}, in brackets), and energies (total electronic energy, zero-point energy, free energy correction in a.u.) of the reactants, transition states, and products of the $ZrO^+ + H_2S \rightarrow [HS{-}Zr{-}OH]^+$ and $XZrO^+ + H_2S \rightarrow [XZr(OH)(SH)]^+$ reactions [X = Cl_2, $(NH_3)Cl_2$, $(NH_3)_2Cl_2$, $(NH_3)_3Cl_2$].

	Reactants	**Transition State**	**Products**
$ZrO^+ + H_2S$ (doublet)	Zr -0.685568 -0.307969 -0.000171 O -1.076663 1.341244 0.017167 S 1.992570 -0.000236 -0.055908 H 1.874370 1.273323 -0.451147 H 2.280517 0.319247 1.215166 (130.6, 144.3, 238.0, 395.5, 477.7, 1029.0, 1170.1, 2688.3, 2727.2) *-521.072095102, 0.020505, -0.010040*	Zr 0.686702 -0.289093 0.000786 O 0.537689 1.469854 0.006937 S -1.819113 -0.081035 -0.079571 H -0.744368 1.169110 -0.077114 H -1.919425 -0.067672 1.263298 (1567.2i, 251.7, 269.2, 382.1, 447.9, 966.5, 1049.4, 1479.0, 2652.5) *-521.040552999, 0.017083, -0.012272*	Zr -0.437492 -0.412500 0.000111 O -1.413196 1.140014 -0.000044 S 1.819411 0.239431 -0.000261 H -1.859277 1.996650 -0.000116 H 1.553932 1.552345 0.000189 (155.7, 170.3, 368.3, 427.2, 469.2, 476.1, 822.0, 2715.8, 3872.7) *-521.110909631, 0.021591, -0.008514*
$ZrO^+ + H_2S$ (quartet)	Zr -0.638698 -0.361562 -0.000001 O -1.249058 1.477933 0.000027 S 1.951531 0.049589 -0.000035 H 2.157665 0.923114 -0.992275 H 2.158230 0.922463 0.992647 (109.9, 151.6, 233.2, 408.2, 496.0, 698.7, 1180.7, 2716.8, 2723.0) *-520.953169645, 0.019861, -0.011548*	Zr 0.844764 -0.187479 0.002364 O -0.141253 1.458817 0.012447 S -1.816877 -0.315767 -0.074424 H -1.495238 1.082986 -0.235099 H -2.095264 -0.202101 1.231755 (1268.3i, 193.8, 305.5, 361.4, 489.1, 643.0, 1033.5, 1773.4, 2702.9) *-520.942839329, 0.017092, -0.013102*	Zr 0.613270 -0.399631 0.004075 O 1.054521 1.397473 0.001807 S -1.995032 0.140983 -0.085758 H 1.303352 2.328287 -0.012422 H -2.349817 0.221444 1.207097 (92.6, 234.8, 273.3, 417.0, 484.3, 495.9, 785.9, 2675.9, 3903.9) *-521.018352251, 0.021332, -0.009952*
$(Cl)_2ZrO^+ + H_2S$ (doublet)	Zr -0.239258 0.010865 0.261701 O -0.123331 -0.054580 2.190590 S 2.384153 -0.022233 -0.324121 H 2.675532 -1.257748 0.107060 H 2.315791 -0.369486 -1.616928 Cl -1.062922 -1.914663 -0.648861 Cl -0.853596 2.031428 -0.603901 (49.3, 61.4, 78.8, 88.4, 113.9, 126.0, 257.6, 428.8, 458.9, 489.8, 542.5, 691.2, 1171.1, 2708.4, 2718.8) *-1441.41831816, 0.022747, -0.015305*	Cl -1.899264 -1.508743 -0.205492 Cl -0.678993 2.221244 -0.088895 Zr -0.195768 -0.006783 0.023803 O 0.995567 -0.444892 1.494042 S 2.414765 -0.519022 -0.525711 H 2.253423 -0.734903 0.899984 H 2.806891 0.757212 -0.388481 (1266.0i, 26.5, 33.8, 93.8, 141.0, 199.5, 319.0, 336.0, 436.0, 472.2, 523.7, 642.4, 1026.9, 1716.0, 2701.6) *-1441.39925603, 0.019748, -0.017805*	Zr 0.186866 -0.175075 0.274484 O 0.227234 -0.215874 2.135649 S -1.414854 1.869056 -0.354981 H 0.339032 -0.317956 3.088538 H -2.318246 1.658129 0.616263 Cl 2.144014 0.347166 -0.799118 Cl -1.242580 -1.671584 -0.735567 (42.3, 53.7, 78.3, 97.1, 134.9, 135.9, 254.9, 383.6, 419.4, 463.0, 525.6, 538.1, 797.7, 2694.6, 3884.6) *-1441.48402545, 0.023929, -0.014245*
$(NH_3)(Cl)_2ZrO^+ + H_2S$ (doublet)	Cl -0.813986 -0.077614 2.096345 Cl -0.813986 -0.077614 -2.096345 Zr 0.102917 0.300090 0.000000 O 1.928203 0.981528 0.000000 S 0.828533 -2.371112 -0.000000 H 1.736035 -2.366827 0.982577 H 1.736035 -2.366827 -0.982577 N -0.813986 2.439583 0.000000 H -0.531372 2.977530 -0.820439 H -0.531372 2.977530 0.820439	Cl -0.892700 -1.911137 -1.014830 Cl -0.281180 2.073463 -0.983122 Zr -0.248046 0.017515 0.076486 O 0.785231 -0.160652 1.726845 S 2.498471 -0.344261 -0.007262 H 2.133107 -0.435456 1.390363 H 2.783193 0.962255 0.063486 N -2.042472 0.268974 1.500777 H -1.917669 1.074937 2.115990 H -2.143811 -0.546656 2.107725	Zr -0.244435 0.014471 0.240964 O -0.466303 0.292794 2.070446 S 2.118146 0.954162 -0.633171 H -0.661096 0.249120 3.013124 H 2.705125 0.873841 0.566967 Cl 1.387110 -1.701337 -0.081752 Cl -2.147161 -0.768152 -0.818406 N -0.909145 2.163605 -0.404059 H -1.887574 2.286653 -0.137160 H -0.872001 2.317110 -1.412442

	H -1.834760 2.422352 0.000000 (48.0, 69.7, 82.2, 91.4, 110.3, 114.2, 126.4, 138.3, 165.8, 218.9, 377.8, 399.9, 440.8, 458.5, 523.7, 614.5, 623.5, 675.8, 1181.2, 1294.7, 1610.7, 1612.6, 2730.3, 2741.8, 3452.1, 3556.7, 3557.4) *-1498.00769587, 0.061550, 0.020802*	H -2.937118 0.395347 1.024143 (1269i.1, 40.5, 52.6, 64.1, 80.8, 83.0, 93.9, 131.3, 170.3, 338.6, 359.5, 397.5, 409.7, 451.3, 498.8, 609.6, 622.0, 631.3, 1044.5, 1298.7, 1607.3, 1610.5, 1769.7, 2724.6, 3446.2, 3547.8, 3549.8) *-1498.00192562, 0.058399, 0.017478*	H -0.382069 2.921551 0.029221 (32.5, 91.8, 100.5, 110.3, 118.9, 140.4, 148.0, 167.5, 224.8, 274.4, 358.9, 387.6, 409.1,427.8, 469.8, 511.1, 607.0, 625.4, 792.0, 1291.4, 1611.3, 1616.9, 2724.6, 3453.5, 3551.7, 3566.4, 3900.8) *-1498.06629682, 0.063138, 0.023149*
$(NH_3)_2(Cl)_2ZrO^+ + H_2S$ (doublet)	Zr 0.000252 -0.426134 0.022641 O 0.001142 -2.361048 0.197970 S -0.001434 2.472261 -0.055280 H -0.995759 2.871988 -0.849764 H 0.994186 2.873386 -0.847432 Cl -2.342503 -0.093531 -0.005313 Cl 2.342660 -0.091105 -0.002905 N 0.002143 -0.532593 -2.323090 N -0.001869 -0.087483 2.345926 H -0.820934 -0.530462 2.763285 H -0.008480 0.887049 2.645233 H 0.822383 -0.519814 2.764210 H -0.822210 -1.039039 -2.647630 H 0.821156 -1.049427 -2.644808 H 0.008815 0.363237 -2.808151 (12.5, 40.3, 54.8, 71.5, 77.8, 98.2, 98.8, 105.5, 107.9, 134.5, 138.0, 167.6, 194.7, 312.4, 343.9, 373.1, 380.2, 397.5, 459.2, 578.3, 591.0, 596.6, 619.7, 671.1, 1180.1, 1266.8, 1272.2, 1611.4, 1613.4, 1615.2, 1616.4, 2750.5, 2766.5, 3457.9, 3460.0, 3564.1, 3564.8, 3570.5, 3577.2) *-1554.57643316, 0.099128, 0.052332*	Cl -0.222701 -2.080708 -0.950293 Cl -0.073537 2.145325 -0.824776 Zr -0.209059 -0.000307 0.122141 O 0.988489 -0.114683 1.688227 S 2.589044 -0.113020 -0.168791 H 2.310358 -0.300413 1.234702 H 2.778278 1.203985 -0.029761 N -1.523441 -0.038753 2.067394 H -1.160699 0.682720 2.692468 H -1.339325 -0.923715 2.542885 H -2.533549 0.076351 2.018977 N -2.435101 0.111702 -0.782750 H -2.284292 0.134286 -1.792691 H -2.965795 0.953504 -0.563627 H -3.029388 -0.697798 -0.610089 (1268.9i, 31.5, 46.8, 64.2, 96.8, 118.8, 137.6, 141.3, 150.7, 162.4, 174.1, 199.2, 309.0, 351.5, 362.1, 375.0, 392.4, 420.1, 537.8, 551.6, 573.3, 608.1, 622.4, 656.7, 1058.4, 1267.0, 1284.7, 1606.2, 1609.7, 1620.1, 1627.0, 1781.1, 2735.0, 3456.5, 3458.8, 3549.0, 3556.7, 3583.2, 3583.5) *-1554.56795802, 0.097643, 0.054780*	Zr -0.266125 -0.156701 0.218462 O -0.404915 -1.200286 1.787846 S 2.487589 -0.254714 0.417548 H -0.322925 -1.729226 2.586469 H 2.796065 -1.001554 -0.644754 Cl 0.957936 1.052451 -1.557707 Cl -2.452724 0.365177 -0.398042 N -0.260391 -2.017455 -1.212480 H 0.467504 -2.705548 -1.025761 H -0.156250 -1.717977 -2.182281 H -1.153805 -2.506180 -1.145437 N -0.038227 1.861389 1.391628 H -0.555814 1.869509 2.270025 H -0.415692 2.610618 0.810074 H 0.925544 2.118880 1.603319 (33.7, 56.5, 61.1, 79.2, 98.8, 108.5, 123.4, 126.8, 148.8, 156.8, 170.5, 187.5, 299.7, 321.2, 367.6, 377.3, 401.9, 432.7, 492.4, 537.9, 580.1, 596.9, 604.8, 611.9, 748.4, 1262.4, 1270.7, 1610.9, 1613.0, 1614.5, 1617.4, 2751.4, 3458.1, 3459.4, 3562.8, 3563.5, 3573.6, 3576.6, 3927.6) *-1554.63478226, 0.101575, 0.057489*
$(NH_3)_3(Cl)_2ZrO^+ + H_2S$ (doublet)	Zr 0.339156 0.001471 0.124988 Cl -0.231874 -1.822484 -1.328063 Cl 0.246129 1.924059 -1.281539 N 1.460801 1.482159 1.654317 N 1.121494 -1.659581 1.686971 H 2.096834 -1.735636 1.963134 H 0.861279 -2.548814 1.259861 H 0.562939 -1.569987 2.534106 H 0.679223 1.976042 2.086206 H 1.984254 2.180737 1.129152 H 2.055566 1.150756 2.409314 O -1.203805 0.109822 1.155568 N 2.653352 -0.329732 -0.781774 H 3.514976 -0.184598 -0.262173 H 2.670275 0.323379 -1.565609 H 2.698047 -1.262303 -1.189738	Zr 0.179578 0.000638 0.089580 Cl -0.063451 -1.980709 -1.205085 Cl -0.289905 1.959733 -1.192396 N 1.557864 -1.418315 1.468635 N 1.409129 1.595445 1.421981 H 0.771055 1.818339 2.186009 H 1.528549 2.451417 0.882152 H 2.306295 1.366384 1.842182 H 1.316283 -2.366012 1.177992 H 1.249121 -1.322486 2.434864 H 2.572907 -1.357045 1.458810 O -0.844465 -0.074839 1.781823 N 2.253553 0.089541 -1.158098 H 2.744420 -0.800912 -1.210349 H 2.937058 0.816785 -0.960311 H 1.908053 0.275006 -2.101093	Cl -0.490429 -2.167225 -0.717305 Cl 1.551169 1.536634 -0.727337 Zr -0.197779 0.046063 0.191619 O -0.158142 0.064829 2.100362 S 2.331404 -0.970224 0.367824 H -0.072122 -0.017611 3.052251 H 2.760589 -0.181721 1.358350 N -2.524907 -0.435467 0.594288 H -3.043000 -0.756707 -0.220610 H -3.099274 0.240626 1.092182 H -2.440764 -1.251967 1.200131 N -1.029403 0.541112 -2.044796 H -0.332005 0.074288 -2.626280 H -1.017245 1.519435 -2.325672 H -1.924160 0.140368 -2.317413 N -1.178962 2.232739 0.490281

	S -3.219696 0.242387 0.199311 H -3.578948 -0.532712 1.222569 H -2.856947 -0.789176 -0.573220 (6, 47, 51, 56, 74, 81, 85, 94, 107, 111, 128, 134, 151, 156, 189, 277, 281, 303, 338, 354, 369, 425, 473, 475, 480, 515, 564, 580, 597, 766, 1183, 1217, 1223, 1238, 1606, 1616, 1620, 1627, 1630, 1640, 2712, 2769, 3467, 3469, 3469, 3568, 3571, 3572, 3598, 3599, 3601) *-1611.13739367, 0.137347, 0.086643*	S -2.699267 -0.168216 0.201954 H -2.886015 1.152277 0.295700 H -2.223623 -0.279237 1.554541 (1248i, 43, 68, 77, 84, 91, 113, 124, 125, 135, 150, 155, 172, 184, 189, 296, 298, 320, 345, 353, 375, 380, 511, 519, 526, 535, 587, 606, 614, 627, 1060, 1228, 1237, 1257, 1603, 1609, 1620, 1625, 1630, 1641, 1821, 2740, 3464, 3465, 3466, 3564, 3569, 3571, 3595, 3595, 3596) *-1611.12948372, 0.135743, 0.090240*	H -0.505643 2.923027 0.159319 H -1.277509 2.373154 1.494217 H -2.074708 2.450877 0.061197 (44, 46, 84, 101, 109, 130, 133, 155, 159, 166, 178, 195, 198, 213, 221, 283, 287, 323, 335, 343, 363, 368, 393, 523, 526, 529, 547, 606, 617, 632, 715, 1221, 1249, 1266, 1600, 1607, 1610, 1624, 1628, 1638, 2736, 3465, 3467, 3471, 3565, 3573, 3576, 3596, 3597, 3600, 3953) *-1611.18490645, 0.140308, 0.094989*

Table S5. MRCI/cc-pVDZ-PP(Zr) cc-pVDZ(H) aug-cc-pVDZ(O) optimal geometries (Cartesian coordinates in Å) of the reactants, transition states, and products of the $ZrO^+ + H_2O \rightarrow Zr(OH)_2^+$ reaction for the first five doublets (1^2A, 2^2A, 3^2A, 4^2A, 5^2A) and the first two quartet (1^4A, 2^4A).

	Reactants				Transition State				Products			
1^2A	Zr	-0.0470340988	-0.7154691771	0.1806172035	Zr	0.5854332138	-0.0248913761	-0.2015824080	Zr	-0.0009914485	-0.0078951186	0.2046704547
	O	-0.6336052455	0.9173150507	0.0260757339	O	-0.3270959872	1.5521868093	-0.2571262774	O	0.2396656305	1.9254064975	0.2077941833
	O	2.1978183312	-0.1335438595	0.3384529064	O	-1.3385221025	-0.3861855795	0.4711309862	O	-0.2394472107	-1.9239816527	0.2041845587
	H	2.4050898720	0.8129038634	0.3232693349	H	-1.2626745876	0.8200852855	0.1885606615	H	0.3582197500	2.8784896880	0.2069274340
	H	3.0348974505	-0.6101644259	0.4154254960	H	-2.0670566076	-0.8812677080	0.9078879794	H	-0.3574467213	-2.8720194141	0.2064935007
2^2A	Zr	-0.0143812382	-0.4979971738	-0.2416950380	Zr	0.5836118398	-0.0051523682	-0.1658122455	Zr	-0.0009926016	-0.0078982247	0.2046403506
	O	-0.9924627049	0.7439593756	0.4941141768	O	-0.3487983847	1.5551290797	-0.2019554451	O	0.2396664643	1.9253855359	0.2078967223
	O	2.3279348460	-0.1438108708	0.1956278991	O	-1.4417328044	-0.4987078608	0.2885451723	O	-0.2394442502	-1.9239567112	0.2041284630
	H	2.8103623884	0.6288739309	-0.1235531648	H	-1.2144285200	0.8180840067	0.1629570680	H	0.3582151178	2.8784722873	0.2068661164
	H	2.8257130182	-0.4599838103	0.9593468016	H	-1.9885682017	-0.7894254263	1.0251363920	H	-0.3574447303	-2.8720028872	0.2065384791
3^2A	Zr	0.0360358201	-0.3411280125	-0.0298509745	Zr	0.6013850351	-0.0400814105	-0.1582643155	Zr	0.0022870383	-0.0016059878	-0.6020314148
	O	-1.3261522802	0.6625491973	0.2473629404	O	-0.3145613351	1.5665749600	-0.2156060172	O	0.2220245730	1.7722530310	0.0636554960
	O	2.3640345457	-0.0480474298	0.3058953029	O	-1.4469526876	-0.4081901105	0.3319942573	O	-0.2186743884	-1.7515372027	0.0986307619
	H	2.8075343114	0.7363062196	0.6573485163	H	-1.3058583191	0.7724931545	0.1749569303	H	0.3038091177	2.4512955220	0.7448509823
	H	3.0615593142	-0.6886851016	0.1054887214	H	-1.0653791324	-0.4086648857	1.4688102406	H	-0.3094463409	-2.4704053625	0.7249643060
4^2A	Zr	0.1436455304	0.1561063329	0.1903920097	N/A [b]				Zr	-0.0281778444	-0.1842589435	0.0898988883
	O	-1.8479166419	0.3141825094	0.1029013277					O	0.2763332593	2.2107405359	0.1346165113
	O	2.4966991785	-0.0204955297	0.3056236834					O	-0.2583865662	-2.0614184830	0.1617812193
	H	3.1259601263	0.6986109195	0.4534912256					H	0.4523204466	2.9207373941	0.7805557045
	H	3.0246235178	-0.8274093594	0.2338362600					H	-0.3687928216	-3.0090884234	0.2254625228
5^2A	Zr	0.1437831750	0.1560817530	0.1904041935	Zr	0.7611197349	-0.2237706884	-0.2035572001	Zr	-0.0195620310	-0.1900163900	0.1481774968
	O	-1.8471268521	0.3141559491	0.1029417450	O	-0.5036356619	1.5778297793	-0.3609237932	O	0.2756178625	2.2097577520	0.1330498560
	O	2.4964234955	-0.0205125879	0.3055903743	O	-1.2135207805	-0.2954363543	0.5469343102	O	-0.2590498849	-2.0673787693	0.1683563035
	H	3.1255714876	0.6987317765	0.4534903224	H	-1.3036126353	0.9770524343	0.2126793349	H	0.4511575621	2.9406889081	0.7551711568
	H	3.0243604051	-0.8274620179	0.2338178712	H	-1.3642204961	-0.3485387144	1.4681181697	H	-0.3748670349	-3.0163394206	0.1875600331
1^4A [a]	Zr	-0.2200301843	0.1268845678	-0.2355667575	Zr	0.573961	-0.064659	0.001667	Zr	0.1511943843	-0.0796031939	0.2218965085
	O	-2.1577697922	0.3393640813	0.2041272113	O	-0.966252	1.233550	0.033157	O	0.3871852436	-0.1080455295	2.0977201941
	O	2.1090583139	0.3896511332	-0.0104269090	O	-1.446346	-0.813035	-0.087618	O	0.0523812792	-0.2053109226	-2.2026210984
	H	2.6268398268	1.1529733802	-0.3001358876	H	-1.704966	0.378349	-0.303827	H	0.5411694570	-0.1574221657	3.0404700934
	H	2.7210338356	-0.1874921624	0.4664033428	H	-1.952681	-1.156088	0.672815	H	0.4507475898	-0.6544590656	-2.9729492628

2^4A	Zr	-0.2172062932	0.1273577759	-0.2338464641	N/A [b]	Zr	0.1537244546	-0.0753812976	0.2217616070
	O	-2.1564447452	0.3389617108	0.2034236049		O	0.3856926451	-0.1082783941	2.0976582086
	O	2.1069968864	0.3900453510	-0.0109082006		O	0.0497572354	-0.2078405570	-2.2024449640
	H	2.6268253999	1.1524772442	-0.3000812746		H	0.5414094044	-0.1591848333	3.0400374818
	H	2.7189607519	-0.1874610818	0.4658133345		H	0.4520942144	-0.6541557952	-2.9724958985

[a] The transition state is optimized at DFT/MN15 using the same basis set.
[b] Geometry optimization calculations failed for these structures.

Table S6. Harmonic vibrational frequencies (cm^{-1}) of the optimal geometries given in Table S5.

	Reactants	Transition States	Products
1^2A	119.0, 235.2, 382.8, 384.9, 555.1, 958.1, 1694.4, 3922.7, 3963.6	1856.0i, 437.7, 611.0, 703.2, 855.3, 932.9, 1087.8, 1951.0, 3656.0	49.9, 519.7, 529.4, 533.8, 580.8, 725.0, 768.6,3999.3,4029.3
2^2A	68.4, 77.2, 337.8, 401.8, 572.4, 864.0, 1721.2, 3948.5, 3950.6	1631.5i, 414.0, 549.0, 674.5, 845.0, 1002.8, 1182.9, 2007.7, 3940.0	49.8, 512.5, 529.5, 534.2, 581.2, 725.2, 768.6, 3999.3, 4029.3
3^2A	217.0, 264.2, 367.6, 436.2, 539.2, 1622.1, 1707.9, 3905.8, 3927.8	1530.9i, 469.8, 656.9, 827.7, 1058.1, 1169.5, 1537.7, 1686.2, 1829.9	169.3, 510.3, 534.4, 572.0, 590.6, 762.1, 796.2, 3948.8, 3996.6
4^2A	33.6, 47.1, 359.9, 407.2, 503.8, 693.7, 1705.6, 3892.1, 3916.1	N/A [b]	60.4, 94.0, 295.3, 370.6, 486.4, 491.6, 773.1, 3768.6, 4018.9
5^2A	26.4, 54.4, 360.2, 407.9, 504.3, 699.7, 1706.5, 3891.4, 3916.0	N/A [b]	97.4, 113.3, 292.8, 367.4, 487.9, 490.1, 773.0, 3769.8, 4019.0
1^4A [a]	18.2, 51.0, 363.6, 404.3, 502.0, 680.6, 1703.0, 3891.4, 3917.4	1813.6i, 282.7, 505.0, 557.2, 612.4, 650.7, 1127.0, 1855.1, 3784.0	56.5, 88.4, 282.3, 330.5, 483.3, 484.2, 777.5, 3769.3, 4015.1
2^2A	27.1, 30.4, 365.1, 402.7, 521.7, 680.0, 1706.4, 3892.3, 3915.1	N/A [b]	62.0, 102.8, 283.6, 331.7, 481.6, 486.3, 778.1, 3767.8, 4015.2

[a] The transition state is obtained at DFT/MN15; see Table S5.
[b] Unavailable due to technical issues; see Table S5.

Table S7. MRCI(+Q)/cc-pVTZ-PP(Zr) cc-pVTZ(H) aug-cc-pVTZ(O) electronic energies (a.u.) of optimal geometries of the fragments, reactants, transition states, and products of the $ZrO^+ + H_2O \rightarrow Zr(OH)_2^+$ reaction for the first five doublets (1^2A, 2^2A, 3^2A, 4^2A, 5^2A) and the first two quartets (1^4A, 2^4A).

State	Fragments [a]		Intermediate		Transition States		Products	
	MRCI	MRCI+Q	MRCI	MRCI+Q	MRCI	MRCI+Q	MRCI	MRCI+Q
1^2A	-197.634790	-197.691874	-197.700516	-197.756748	-197.655033	-197.714258	-197.733647	-197.787947
2^2A	-197.634629	-197.691554	-197.696813	-197.752303	-197.642968	-197.701006	-197.733658	-197.787966
3^2A	-197.618552	-197.676434	-197.675520	-197.734469	-197.562254	-197.622986	-197.709856	-197.769949
4^2A	-197.544412	-197.606380	-197.581322	-197.630002	-197.524073 [b]	-197.575686 [b]	-197.583847	-197.636545
5^2A	-197.539172	-197.602170	-197.581355	-197.630071	-197.516347	-197.571010	-197.583836	-197.636535
1^4A	-197.519973	-197.569085	-197.585800	-197.633099	-197.529436 [c]	-197.585893 [c]	-197.590023	-197.639035
2^4A	-197.520136	-197.569236	-197.585064	-197.632503	-197.500111 [c]	-197.551590 [c]	-197.590024	-197.639042

[a] Single point energy calculations of ZrO^+ and H_2O separated by a distance of 1,000 Å.

[b] Single point energy using the 5^2A TS structure.

[c] Single point energy using the 1^4A TS structure.

Table S8. DFT/MN15/cc-pVTZ-PP(Zr) cc-pVTZ(H) aug-cc-pVTZ(O, Cl, N) optimal geometries (Cartesian coordinates in Å), harmonic vibrational frequencies (cm^{-1}, in brackets), and energies (total electronic energy, zero-point energy, free energy correction in a.u.) of the reactants, transition state, and products of the $ZrO^+ + H_2O \rightarrow [HO{-}Zr{-}OH]^+$ and $XZrO^+ + H_2O \rightarrow [XZr(OH)_2]^+$ reactions [X = Cl_2, $(NH_3)Cl_2$, $(NH_3)_2Cl_2$, $(NH_3)_3Cl_2$].

	Reactants	**Transition State**	**Products**
$ZrO^+ + H_2O$ (doublet)	Zr 0.316235 -0.320591 -0.000031 O 0.813699 1.298439 0.000079 O -1.812766 0.198137 0.000057 H -2.011992 1.149180 -0.000014 H -2.644874 -0.298134 0.000159 (155.4, 292.4, 405.1, 427.8, 557.4, 1040.1, 1600.1, 3765.5, 3858.2) *-198.184465583, 0.027570, -0.001273*	Zr 0.437851 -0.215448 -0.000001 O -0.156254 1.449339 0.000007 O -1.567509 -0.379762 0.000016 H -1.270862 0.823284 -0.000099 H -2.453056 -0.761961 -0.000045 (1817.1i, 319.8, 407.0, 616.5, 738.1, 962.8, 989.9, 1937.6, 3881.8) *-198.147850031, 0.022448, -0.005498*	Zr -0.000000 0.350497 -0.000026 O -1.520663 -0.698712 0.000101 O 1.520662 -0.698713 0.000002 H -2.161396 -1.420240 0.000188 H 2.161415 -1.420223 0.000042 (176.5, 435.5, 502.3, 515.9, 522.1, 800.8, 815.7, 3879.7, 3888.5) *-198.230895041, 0.026283, -0.002150*
$ZrO^+ + H_2O$ (Quartet)	Zr -0.246647 -0.377833 -0.000001 O -1.149249 1.340160 -0.000015 O 1.807542 0.382688 -0.000041 H 2.300200 0.665312 -0.787236 H 2.299334 0.665246 0.787724 (63.7, 307.3, 405.7, 467.4, 540.1, 696.0, 1608.2, 3753.7, 3834.5) *-198.058654975, 0.026601, -0.003712*	Zr 0.571984 -0.067099 0.001742 O -0.948750 1.230065 0.031820 O -1.453938 -0.803556 -0.088804 H -1.701115 0.391466 -0.295801 H -1.956749 -1.119582 0.681976 (1823.1i, 282.2, 502.1, 564.5, 603.1, 652.6, 1124.0, 1876.3, 3770.2) *-198.021359253, 0.021358, -0.007448*	Zr -0.271041 -0.408800 0.005503 O 1.918928 0.291480 -0.101550 O -0.741626 1.381022 -0.002350 H 2.437450 0.666694 0.644453 H -1.014236 2.305299 -0.033364 (69.2, 316.8, 337.3, 414.6, 478.8, 502.3, 782.8, 3669.9, 3896.9) *-198.061145047, 0.023849, -0.006601*
$(Cl)_2ZrO^+ + H_2O$ (doublet)	Zr 0.000009 0.137285 -0.131753 O 0.000385 0.997389 -1.862195 O -0.000569 1.939782 1.126374 H -0.001965 2.840943 0.762008 H 0.000515 2.002048 2.095767 Cl -1.944746 -0.995246 0.243924 Cl 1.944897 -0.994858 0.244247 (61.0, 70.5, 87.8, 98.9, 105.1, 163.4, 407.5, 421.1, 440.8, 477.6, 579.5, 691.6, 1615.8, 3752.0, 3830.1) *-1118.52945871, 0.029166, -0.007664*	Cl -1.930881 -1.099009 0.033825 Cl 1.930743 -1.099223 0.033842 Zr -0.000001 0.094121 -0.049839 O 0.000161 1.865718 -1.217863 O 0.000109 1.770757 1.086403 H 0.000165 2.275256 -0.037977 H 0.000066 2.238046 1.932875 (1484.6i, 49.0, 83.7, 93.9, 115.6, 349.3, 395.7, 465.4, 482.6, 556.2, 687.3, 723.8, 765.9, 1823.1, 3850.7) *-1118.49116531, 0.023789, -0.011580*	Zr -0.145306 0.278449 0.036858 O -0.393521 2.063717 -0.418841 O 1.008049 -0.069152 1.580227 H -0.583704 2.988254 -0.618513 H 1.661326 -0.151148 2.290792 Cl -2.020443 -1.033719 -0.101908 Cl 2.009760 -0.726962 -0.629721 (57.0, 77.3, 120.2, 145.4, 189.7, 214.2, 262.5, 398.4, 451.2, 500.6, 549.7, 635.8, 806.3, 3839.5, 3885.7) *-1118.54665309, 0.027642, -0.008299*
$(NH_3)(Cl)_2ZrO^+ + H_2O$ (doublet)	Zr -0.024949 -0.042560 0.199988 O -0.254102 -0.309841 2.129100 O 0.630968 -2.191901 0.146715 H 0.373413 -2.857945 0.801217 H 1.261581 -2.580727 -0.477027 Cl -1.967194 -0.251772 -1.024439 Cl 1.999350 0.470004 -0.827064 N -0.401561 2.231572 0.480672 H -0.410693 2.731133 -0.409462 H 0.318677 2.671867 1.054680	Cl 1.920109 -1.012558 -0.542489 Cl -1.918237 -1.016173 -0.541997 Zr -0.000088 0.127542 -0.032505 O -0.002153 2.020140 1.075409 O -0.002082 1.838092 -1.184043 H -0.002474 2.382063 -0.111004 H -0.003201 2.247573 -2.058194 N 0.001065 -0.577500 2.167087 H 0.001916 -1.595352 2.252157 H -0.815560 -0.236089 2.676735	Zr -0.128798 -0.064593 0.259542 O -0.486578 0.350501 2.044722 O 1.000215 -1.724943 0.197647 H -0.704466 0.427581 2.979381 H 1.675393 -2.412049 0.106611 Cl -2.051389 -0.561377 -0.927150 Cl 2.214282 0.148581 -0.636826 N -0.257997 2.149028 -0.447200 H 0.432514 2.760874 -0.011482 H -1.178575 2.528676 -0.220421

	H -1.295693 2.421064 0.935402 (49.1, 63.8, 82.9, 97.8, 111.8, 116.7, 130.2, 150.2, 237.8, 350.4, 357.5, 389.8, 403.9, 446.1, 545.1, 618.6, 620.0, 666.1, 1295.9, 1595.1, 1610.7, 1611.8, 3453.4, 3557.9, 3558.9, 3786.6, 3880.0) *-1175.11826557, 0.067862, 0.027992*	H 0.817459 -0.234774 2.676230 (1263.9i, 43.6, 86.5, 90.5, 107.8, 108.2, 111.9, 149.4, 314.0, 382.2, 406.6, 455.3, 460.7, 521.3, 594.1, 649.7, 657.0, 670.4, 781.4, 1303.5, 1608.0, 1609.1, 1829.3, 3448.1, 3550.3, 3553.0, 3869.5) *-1175.08963437, 0.062334, 0.023733*	H -0.145259 2.248484 -1.456716 (43.4, 95.3, 102.7, 111.1, 123.8, 133.9, 140.0, 157.4, 237.4, 298.7, 382.8, 388.2, 428.6, 462.0, 501.6, 590.4, 618.5, 637.5, 789.5, 1291.6, 1612.4, 1614.8, 3454.2, 3555.6, 3563.0, 3855.3, 3911.3) *-1175.13716898, 0.066296, 0.027084*
$(NH_3)_2(Cl)_2ZrO^+ + H_2O$ (doublet)	Zr -0.079069 -0.000476 0.135437 O -0.420673 0.046512 2.077563 O 0.366219 -2.193726 0.387866 H -0.034040 -2.757774 1.065434 H 0.731645 -2.738704 -0.324641 Cl -2.307406 -0.242865 -0.506081 Cl 1.484547 -0.165921 -1.667611 N -0.331153 2.287987 -0.254250 H -0.703687 2.411269 -1.196966 H 0.509065 2.861092 -0.198668 H -1.018032 2.687764 0.385931 N 1.943379 0.553266 1.333205 H 2.441156 -0.323778 1.485769 H 1.800068 0.975307 2.249347 H 2.575230 1.142182 0.792955 (56.0, 64.5, 70.0, 85.3, 95.5, 98.9, 116.6, 123.0, 139.2, 141.2, 196.4, 317.2, 342.0, 344.6, 373.4, 377.5, 394.5, 421.2, 529.8, 547.2, 582.5, 596.5, 615.2, 670.3, 1237.7, 1278.1, 1575.6, 1606.9, 1610.9, 1617.1, 1621.7, 3458.9, 3463.9, 3558.3, 3570.5, 3578.3, 358 6.2, 3785.1, 3884.8) *-1231.68466239, 0.106464, 0.063612*	Cl -2.149849 0.025283 -0.804451 Cl 2.150079 0.028219 -0.803839 Zr -0.000019 0.000161 0.128366 O -0.002569 1.156278 1.996441 O 0.001426 -1.095729 1.917943 H -0.000371 -0.005764 2.408584 H 0.002578 -1.936370 2.387547 N -0.001206 2.233501 -0.573579 H -0.000928 2.334554 -1.588138 H 0.819806 2.726199 -0.222965 H -0.823120 2.725030 -0.223442 N 0.001574 -2.184688 -0.738464 H 0.828342 -2.713682 -0.463682 H 0.001732 -2.157284 -1.758410 H -0.824609 -2.714742 -0.463957 (1165.6i, 1.2, 63.1, 97.6, 123.2, 137.4, 142.3, 148.3, 155.7, 173.8, 182.5, 252.1, 329.1, 369.0, 391.5, 414.6, 449.8, 511.3, 571.1, 571.3, 625.5, 634.3, 664.1, 688.4, 789.0, 1271.6, 1280.0, 1610.5, 1611.0, 1613.0, 1618.8, 1835.7, 3460.7, 3461.9, 3566.1, 3573.5, 3573.5, 3580.4, 3899.3) *-1231.66232867, 0.101247, 0.057059*	Zr 0.446825 -0.198106 -0.173530 O 1.603314 -1.627274 0.290935 O 0.788104 0.134487 -2.002097 H 2.164073 -2.405804 0.338207 H 0.925251 0.260740 -2.944399 Cl -1.865905 -1.140261 -0.192786 Cl -1.571228 1.471262 -0.028834 N 0.046719 -0.123564 2.231456 H 0.872390 -0.097185 2.825982 H -0.417610 -1.008598 2.436068 H -0.590136 0.609000 2.539884 N 1.751075 1.681463 0.344416 H 1.792802 2.249221 -0.501972 H 2.712673 1.448263 0.590479 H 1.382919 2.278566 1.082660 (39.6, 52.1, 80.6, 94.4, 105.0, 135.6, 140.8, 149.6, 170.0, 190.4, 212.3, 224.6, 297.7, 333.3, 356.1, 370.8, 411.1, 492.0, 504.5, 542.3, 558.7, 595.1, 611.6, 741.5, 755.7, 1245.3, 1260.3, 1609.8, 1617.6, 1624.1, 1630.7, 3467.7, 3469.3, 3570.8, 3570.9, 3583.5, 3592.8, 3936.2, 3942.0) *-1231.71207940, 0.105448, 0.063024*
$(NH_3)_3(Cl)_2ZrO^+ + H_2O$ (doublet)	Cl 2.186288 -0.528301 0.662203 Cl -1.672375 -1.426892 0.763934 Zr -0.022756 0.027574 -0.165317 O -0.497227 0.389688 -2.074516 O 0.611550 -1.739696 -1.430628 H 0.055413 -2.177575 -2.088952 H 1.365989 -2.292607 -1.182363 N 1.103162 2.140128 -0.443453 H 0.578350 3.011088 -0.416377 H 1.488387 2.072174 -1.385984 H 1.896645 2.227127 0.189194 N -0.184343 0.895934 2.075588 H 0.256019 0.146346 2.611211 H -1.139853 0.964167 2.420462 H 0.308048 1.750147 2.327251 N -1.900683 1.543670 -0.332901	Cl -2.058223 -0.805224 -0.763077 Cl 1.899451 -1.139387 -0.751571 Zr 0.014386 0.002224 0.115231 O 0.023648 0.221905 2.173867 O -0.221244 -1.735187 1.502034 H 0.088946 -0.920432 2.361990 H -1.128344 -2.062067 1.630365 N -1.313079 1.995955 0.405373 H -0.953975 2.914106 0.155442 H -1.539410 2.023477 1.399667 H -2.194173 1.865031 -0.090188 N 0.107523 0.938829 -2.103747 H -0.064024 0.106230 -2.669995 H 1.015142 1.291855 -2.400760 H -0.603165 1.613905 -2.377907 N 1.663187 1.704049 0.532014	Cl -1.981678 -1.200362 -0.368923 Cl 2.011549 -1.083848 -0.494489 Zr -0.012769 0.036524 0.140726 O 0.212835 0.869012 1.984192 O 0.071931 -1.297636 1.840368 H -0.151375 0.741378 2.869309 H 0.971012 -1.558901 2.117413 N -1.594014 1.846815 0.003068 H -1.858343 2.192170 -0.916750 H -1.328761 2.648246 0.572014 H -2.446015 1.459648 0.409816 N -0.104584 0.223737 -2.277241 H -0.013859 -0.758205 -2.542189 H 0.652044 0.711269 -2.752200 H -0.987396 0.535190 -2.677064 N 1.399207 1.952911 -0.266700

	H -2.709566 0.941034 -0.179449 H -1.981086 1.903038 -1.283974 H -1.986169 2.332338 0.303836 (38.2, 60.4, 73.3, 97.8, 104.5, 131.4, 141.0, 160.2, 166.1, 174.4, 186.7, 188.2, 204.0, 228.0, 270.7, 297.8, 305.3, 307.1, 313.4, 356.9, 372.0, 379.1, 523.9, 530.9, 539.9, 558.9, 594.6, 625.9, 636.5, 657.8, 1233.3, 1245.3, 1262.5, 1554.2, 1601.2, 1609.6, 1616.7, 1623.8, 1626.9, 1634.5, 3457.2, 3464.3, 3466.3, 3561.1, 3564.7, 3569.7, 3589.8, 3594.7, 3595.1, 3791.1, 3904.2) *-1288.24137434, 0.145327, 0.100697*	H 1.901466 2.364085 -0.204730 H 2.510997 1.166992 0.717993 H 1.467565 2.240667 1.375213 (1799.1i, 47.9, 72.6, 80.5, 86.5, 109.2, 140.2, 144.5, 156.1, 163.5, 165.6, 183.8, 193.9, 199.0, 279.3, 298.6, 302.7, 352.0, 365.1, 381.7, 481.8, 528.6, 533.6, 552.1, 579.0, 603.5, 620.1, 626.0, 636.4, 659.0, 1109.1, 1235.9, 1251.9, 1271.1, 1604.4, 1605.9, 1620.6, 1625.5, 1627.9, 1641.4, 1908.1, 3463.4, 3464.5, 3465.8, 3561.7, 3567.9, 3568.5, 3592.4, 3592.9, 3593.9, 3778.9) *-1288.21281567, 0.140551, 0.097010*	H 2.255654 1.622654 -0.709817 H 1.658430 2.284684 0.662280 H 1.069176 2.757240 -0.794225 (41.6, 70.4, 80.4, 89.2, 112.5, 145.1, 148.9, 155.8, 162.3, 169.8, 176.1, 195.5, 204.4, 277.5, 292.9, 302.6, 315.4, 356.5, 364.4, 376.6, 397.9, 451.9, 523.3, 531.0, 535.8, 566.9, 603.5, 617.3, 631.3, 633.6, 651.7, 1230.0, 1245.2, 1268.1, 1602.5, 1606.0, 1619.0, 1625.3, 1628.8, 1640.2, 3464.1, 3465.2, 3468.1, 3564.0, 3570.2, 3571.7, 3594.4, 3595.0, 3596.5, 3743.6, 3871.6) *-1288.23706860, 0.143870, 0.099859*
$(NH_3)_4(Cl)_2ZrO^+ + H_2O$ (doublet)	Cl 2.386856 -0.567652 0.219138 Cl -2.358160 -0.661298 0.148509 Zr 0.029226 0.065746 -0.109534 O 0.088166 0.707807 -2.011138 O -1.418869 2.023644 -0.200281 H -1.409532 2.320736 -1.123576 H -2.300227 1.631091 -0.061409 N 1.306626 2.116770 -0.122670 H 2.051661 2.090624 0.570300 H 0.814368 3.003666 -0.045344 H 1.771520 2.091690 -1.030202 N 0.076798 -1.965144 1.272296 H -0.848028 -2.316348 1.515080 H 0.609415 -1.814892 2.126881 H 0.584909 -2.700956 0.786252 N -0.191107 0.884881 2.132838 H -0.952449 0.392115 2.598235 H -0.443294 1.871501 2.129524 H 0.647071 0.781240 2.702312 N 0.012407 -1.740836 -1.656886 H -0.204777 -1.390028 -2.589631 H -0.694332 -2.437263 -1.428137 H 0.929388 -2.182171 -1.706623 (72.3, 80.2, 106.7, 110.3, 127.5, 141.4, 147.0, 154.7, 168.5, 177.2, 182.0, 191.2, 192.2, 206.9, 215.6, 233.7, 244.9, 265.2, 273.5, 295.6, 306.5, 314.3, 336.5, 349.3, 360.5, 494.7, 504.0, 531.5, 566.9, 586.0, 596.2, 606.6, 613.6, 652.8, 664.2, 675.4, 1213.2, 1218.2, 1229.5, 1238.5, 1598.0, 1601.2, 1609.1, 1610.7, 1613.7, 1625.6, 1630.8, 1634.8, 1641.4, 3455.2, 3464.5, 3465.3, 3466.4, 3566.1, 3574.1, 3578.4, 3585.3, 3586.9, 3591.0, 3591.6, 3598.9, 3694.7, 3820.1) *-1344.79039385, 0.185099, 0.139985*	Cl 2.342158 -0.637865 0.037371 Cl -2.390074 -0.641337 0.017877 Zr -0.038800 0.065268 -0.050588 O 0.007238 0.951846 -1.935009 O 1.137552 2.008556 -0.518262 H 2.054289 1.743342 -0.715837 H 0.520863 1.922567 -1.575248 N 0.551122 0.838846 2.126172 H 1.320801 0.266415 2.470582 H -0.164262 0.881284 2.849279 H 0.927222 1.779120 2.011578 N -0.092588 -1.917015 1.365840 H -0.585991 -2.649992 0.860299 H -0.628932 -1.788318 2.221742 H 0.834697 -2.263357 1.606871 N -1.376716 2.039665 0.335005 H -1.905410 2.119052 -0.533302 H -0.869050 2.912802 0.462947 H -2.074202 1.944659 1.069656 N 0.012641 -1.740680 -1.600084 H 0.386675 -1.339811 -2.459281 H -0.908331 -2.121967 -1.808619 H 0.638676 -2.498997 -1.338717 (1680.1i, 52.8, 79.7, 94.4, 117.0, 143.0, 155.1, 162.6, 171.6, 180.6, 188.8, 195.7, 196.4, 208.3, 220.0, 234.5, 240.5, 274.4, 282.9, 293.8, 310.3, 341.7, 350.1, 362.6, 468.1, 511.0, 521.8, 573.7, 591.9, 596.6, 603.3, 623.3, 637.6, 656.0, 664.2, 724.1, 1148.6, 1221.9, 1230.3, 1236.3, 1250.3, 1596.9, 1604.0, 1608.3, 1615.2, 1625.6, 1626.3, 1637.8, 1644.1, 1906.6, 3464.6, 3465.5, 3466.5, 3467.0, 3574.2, 3575.9, 3580.4, 3584.2, 3587.4, 3589.5, 3596.3, 3597.9, 3738.5) *-1344.76702855, 0.180587, 0.136294*	Cl 2.408260 -0.418353 0.048481 Cl -2.304540 -0.869557 0.035896 Zr -0.029283 0.090729 -0.062964 O -0.063378 0.943172 -1.944839 O 0.916741 2.055483 -0.400688 H 1.812146 1.892441 -0.751826 H -0.252140 1.801876 -2.343513 N 0.407424 0.835676 2.160497 H 1.272622 0.384867 2.457052 H -0.295327 0.683785 2.881157 H 0.604298 1.834678 2.127803 N 0.111303 -1.916126 1.335642 H -0.266983 -2.695252 0.801180 H -0.471453 -1.871677 2.169188 H 1.064640 -2.151507 1.606721 N -1.586397 1.892312 0.334871 H -2.203527 1.862205 -0.475103 H -1.163109 2.817242 0.374088 H -2.198376 1.763222 1.137332 N 0.201117 -1.700342 -1.615253 H 0.481145 -1.262669 -2.491785 H -0.670415 -2.200068 -1.781992 H 0.933499 -2.363685 -1.372240 (54.9, 88.4, 93.0, 114.2, 148.0, 153.8, 157.4, 177.9, 184.0, 189.7, 195.4, 201.6, 211.9, 225.7, 232.9, 242.8, 283.9, 284.6, 298.5, 309.5, 333.2, 344.1, 358.5, 365.2, 374.9, 497.7, 505.5, 521.7, 543.4, 591.5, 599.7, 612.8, 618.0, 629.0, 658.6, 671.1, 750.7, 1217.8, 1224.6, 1230.4, 1244.6, 1596.9, 1603.4, 1605.9, 1614.5, 1626.0, 1628.5, 1637.4, 1643.8, 3463.1, 3465.3, 3467.0, 3470.1, 3573.1, 3582.4, 3583.2, 3586.5, 3588.6, 3591.1, 3596.1, 3600.0, 3736.4, 3877.0) *-1344.78958805, 0.184253, 0.139787*

$(NH_3)_5(Cl)_2ZrO^+ + H_2O$ (doublet)	Cl -1.877489 -1.693618 -0.601108 Cl -1.191390 2.110212 0.690970 Zr -0.151395 -0.032302 -0.050725 O 1.236150 -0.721480 -1.382377 O 3.627991 -0.360031 -0.094919 H 4.545730 -0.542241 -0.322123 H 3.053768 -0.662541 -0.822667 N 0.848130 -2.132171 0.681852 H 0.483073 -2.595574 1.509955 H 1.862187 -2.068154 0.767852 H 0.647839 -2.753908 -0.101061 N -1.213298 0.755910 -2.035149 H -1.061703 1.729808 -2.285780 H -2.214538 0.638976 -1.888778 H -0.957041 0.158776 -2.819737 N -1.305648 -0.493811 2.052755 H -2.250766 -0.221943 1.781942 H -1.068968 0.094181 2.849174 H -1.373363 -1.461138 2.360162 N 1.323683 1.705870 -0.996712 H 1.355857 1.669570 -2.012782 H 2.287961 1.599523 -0.682681 H 0.974886 2.621381 -0.716130 N 1.469753 0.549033 1.604765 H 1.374171 1.541302 1.815504 H 2.414883 0.368522 1.247279 H 1.381300 0.051730 2.487000 (36.7, 59.1, 93.3, 104.9, 120.8, 132.1, 133.6, 147.9, 152.4,170.8, 184.1, 189.9, 202.3, 203.8, 211.6, 226.7, 230.2, 242.8, 248.1, 258.6, 274.9, 283.4, 286.9, 300.1, 311.9, 335.6, 341.6, 347.0, 355.9, 394.2, 498.7, 506.4, 540.0, 565.0, 577.4, 591.3, 626.1, 636.8, 653.2, 655.1, 676.2, 702.6, 1195.4, 1228.9, 1232.8,1241.6, 1264.0, 1549.1, 1594.0, 1600.6, 1604.2, 1610.4, 1614.5, 1618.3, 1627.3, 1634.6, 1641.2, 1659.6, 3375.7, 3451.3, 3458.2, 3467.5, 3468.4, 3532.6, 3567.5, 3568.6, 3570.6, 3583.3, 3590.4, 3593.1, 3593.9, 3599.7, 3600.0, 3655.5, 3917.9) *-1401.33083936, 0.223991, 0.175842*	Cl 1.373052 2.008237 -0.663710 Cl 1.642487 -1.871097 0.439060 Zr 0.100694 0.015623 -0.021843 O -1.445838 0.640097 -1.319093 O -3.260702 0.105409 -0.103381 H -3.978366 -0.116703 -0.715690 H -2.402286 0.771316 -0.855386 N -1.156441 1.800328 1.078625 H -0.924029 2.120013 2.015255 H -2.158855 1.605960 1.055000 H -0.987344 2.584802 0.449665 N 1.004326 -0.463791 -2.173545 H 1.098282 -1.449379 -2.406787 H 1.938621 -0.059640 -2.204171 H 0.451428 0.007174 -2.888389 N 1.397843 0.601238 1.949326 H 2.342603 0.500817 1.578439 H 1.348524 -0.033601 2.743411 H 1.326879 1.560531 2.280628 N -1.107059 -1.928100 -0.858992 H -1.132093 -1.884089 -1.874304 H -2.080656 -1.862829 -0.564150 H -0.714184 -2.826655 -0.586041 N -1.207638 -0.944431 1.733875 H -0.978044 -1.929580 1.850654 H -2.185863 -0.857132 1.441631 H -1.121435 -0.508056 2.647789 (1481.7i, 65.7, 101.9, 110.2, 113.3, 116.6, 129.5, 134.1, 157.3, 161.2, 174.9, 182.9, 196.3, 200.8, 209.1, 220.8, 230.4, 234.5, 253.5, 271.3, 285.1, 289.9, 305.3, 313.6, 323.3, 344.1, 347.5, 354.4, 393.1, 437.2, 485.6, 521.2, 553.8, 558.4, 593.6, 603.8, 614.8, 626.6, 635.4, 661.2, 674.7, 702.0, 1108.4, 1195.6, 1219.0, 1231.7, 1243.2, 1264.4, 1594.9, 1596.2, 1603.8, 1610.8, 1616.4, 1622.5, 1630.4, 1636.9, 1643.3, 1663.6, 1886.4, 3407.2, 3444.6, 3459.4, 3465.4, 3467.8, 3547.8, 3552.4, 3571.1, 3577.7, 3582.6, 3591.2, 3597.5, 3598.5, 3599.4, 3603.0, 3822.6) *-1401.29643637, 0.219032, 0.172700*	Cl -1.768942 -0.852938 -1.198534 Cl 2.412651 -0.484149 -0.952055 Zr 0.168555 0.055246 0.136245 O -0.861922 -0.177353 1.796093 O -3.545860 -0.044828 0.665345 H -4.109847 -0.688777 0.199046 H -1.830177 -0.185952 1.829596 N -1.407269 1.924220 0.178974 H -1.347801 2.715586 -0.456471 H -1.453178 2.292070 1.126921 H -2.309026 1.466581 0.015729 N 0.340348 -2.326314 0.203924 H 1.221112 -2.700389 0.548707 H 0.230112 -2.669598 -0.748301 H -0.429358 -2.705518 0.751939 N 0.255609 1.119068 -2.074966 H 0.443365 0.304392 -2.658847 H 1.022155 1.761831 -2.263203 H -0.614965 1.519566 -2.416837 N 1.683773 -0.477044 1.987078 H 1.866173 0.269524 2.653017 H 2.578384 -0.858294 1.686325 H 1.162912 -1.177221 2.510471 N 1.434883 2.041801 0.639023 H 2.407532 1.760264 0.513769 H 1.320731 2.403035 1.583668 H 1.267450 2.818882 0.004950 (52.5, 78.3, 86.3, 107.7, 120.2, 131.6, 136.7, 142.7, 151.1, 159.1, 168.7, 182.6, 185.5, 198.8, 203.1, 205.2, 219.9, 226.7, 236.9, 243.5, 252.4, 274.9, 275.5, 280.0, 290.1, 309.8, 322.3, 335.6, 347.0, 423.8, 484.8, 519.9, 538.2, 571.5, 579.3, 598.2, 607.6, 611.2, 628.0, 645.5, 657.3, 674.2, 700.9, 1195.0, 1212.8, 1231.3, 1243.4, 1258.6, 1593.0, 1598.0, 1602.7, 1607.1, 1613.2, 1623.5, 1625.7, 1638.1, 1640.6, 1646.0, 3419.5, 3461.4, 3466.8, 3470.1, 3471.7, 3540.6, 3571.4, 3577.0, 3589.3, 3595.3, 3597.3, 3598.3, 3598.8, 3601.2, 3601.7, 3776.0, 3787.3) *-1401.31499165, 0.221479, 0.173215*

Table S9. MRCI/ cc-pVDZ-PP(Nb) cc-pVDZ(H) aug-cc-pVDZ(O,S) optimal geometries (Cartesian coordinates in Å) of the reactants, transition states, and products of the $NbO^+ + H_2S \rightarrow [HS{-}Nb{-}OH]^+$ reaction for the first three singlets (1^1A, 2^1A, 3^1A) and the first three triplets (1^3A, 2^3A, 3^3A).

	Reactants				Transition States				Products			
1^1A	Nb	0.5325567661	-0.3722759601	0.0003096869	Nb	0.6285221488	-0.1577295848	0.0043121959	Nb	0.3115461371	-0.1195300419	0.0000015261
	O	1.0602421696	1.2238390015	-0.0004031711	O	0.3419655320	1.5879114605	0.0444892713	O	1.5330512467	1.2683880773	0.0000014722
	S	-2.1020341103	-0.1105298716	0.0002055257	S	-1.8318532581	-0.2626476140	-0.1716820422	S	-2.0350591231	-0.0156908655	-0.0000024850
	H	-2.2973743632	0.7790585196	-0.9959372972	H	-0.8329081223	1.1964838610	-0.0406295144	H	1.7003226587	2.2141498819	0.0000016521
	H	-2.2975674624	0.7793033105	0.9960922557	H	-2.1882244952	-0.3120412198	1.1322840216	H	-2.1892139194	1.3288279482	-0.0000101655
2^1A	Nb	0.5194096900	-0.3197467094	0.0003114674	Nb	0.6177309638	-0.1610191390	-0.0024682116	Nb	0.2291144126	0.1231948378	0.0000006217
	O	1.1756375098	1.2243329908	-0.0004143877	O	0.3521749155	1.5832690793	0.0804991355	O	1.6419112218	1.3205861919	0.0000031121
	S	-2.1855039216	-0.1405274926	0.0002013215	S	-1.8262989502	-0.2635226742	-0.1590384340	S	-2.1373208505	-0.1193355109	-0.0000029576
	H	-2.3067838120	0.7675518473	-0.9939186037	H	-0.8578251254	1.1977987565	-0.0802390339	H	2.0903282695	2.1686015512	0.0000017763
	H	-2.3069364663	0.7677843638	0.9940872025	H	-2.1682799985	-0.3045491197	1.1300204762	H	-2.5033860534	1.1830979299	-0.0000105526
3^1A	Nb	0.5202277605	-0.1636799244	0.0002282747	Nb	0.6010830748	-0.1767754081	0.0895927942	Nb	0.1831418936	0.3031234570	-0.0000055778
	O	1.5477460193	1.1739517231	-0.0003727080	O	0.3603985869	1.5760093742	-0.0014269281	O	1.7141457075	1.3523606395	0.0000002320
	S	-2.2794914078	-0.1731159605	0.0002201086	S	-1.8723415610	-0.2008955407	-0.1937883395	S	-2.1494919196	-0.1633218729	-0.0000037365
	H	-2.4463115872	0.7309862762	-0.9917176369	H	-0.8608045233	1.2367071281	-0.0537985737	H	2.2894179722	2.1197276120	0.0000032672
	H	-2.4463477850	0.7312528856	0.9919089617	H	-2.1108337722	-0.3830686505	1.1281949792	H	-2.7165666537	1.0642551644	-0.0000021850
1^3A	Nb	0.5404235643	-0.2848369802	-0.1983257521	Nb	0.4946140875	0.0621794388	0.0213054509	Nb	-0.3221176963	-0.1232932549	0.4378361100
	O	1.0497177506	1.1864968037	0.4381243528	O	-0.0051252299	1.7447427239	-0.0324726453	O	-1.7801255366	0.9233980240	0.0559115254
	S	-2.1518239240	-0.1690067785	-0.3361893108	S	-1.9322757362	-0.2764449208	-0.2093017159	S	1.6592917725	0.5741423064	-0.5971681614
	H	-2.2454744921	1.0617163620	-0.8869293006	H	-1.1516678369	1.2939007535	-0.0235780542	H	-2.2501598199	1.6448603613	-0.3684466952
	H	-2.3810749752	0.2591927522	0.9253458635	H	-2.2745480101	-0.3634512104	1.1129881658	H	2.2111842804	1.2024185631	0.4718532212
2^3A	Nb	0.4689361201	0.4222005032	-0.5058857901	Nb	0.7377692956	-0.2665033405	0.0667854747	N/A [a]			
	O	1.8901301186	0.8236891560	0.3415140332	O	0.3171355409	1.5719213236	0.0133139778				
	S	-2.1777440507	-0.1682718727	0.1382010978	S	-1.8225839452	-0.1349080243	-0.1705615464				
	H	-2.8439579906	0.3407906815	-0.9243075921	H	-0.9901642420	1.2295572591	-0.0523032138				
	H	-2.4415411973	0.8809865318	0.9507452511	H	-2.1246548440	-0.3480903150	1.1115392399				
3^3A	Nb	0.5030264260	-0.0989354931	0.1943197422	Nb	0.7120100438	-0.2091041229	0.0362100393	Nb	-0.3616741068	-0.1586104278	-0.0000045176
	O	1.6339410944	1.1568803120	-0.0030132838	O	0.3129873636	1.5561669307	0.0293837920	O	-1.9045439846	0.8826582636	-0.0000405236
	S	-2.1937170571	-0.1135051503	-0.4196342526	S	-1.8197742512	-0.1767112824	-0.1823502322	S	1.9484554465	0.2003074424	0.0000304977
	H	-2.3485589375	1.2141327792	-0.6277237919	H	-0.9377453336	1.1950867357	-0.0358795772	H	-2.2985054673	1.7584494230	-0.0000847156
	H	-2.7829236023	-0.1050102886	0.7980774388	H	-2.1499760172	-0.3134613581	1.1214099104	H	2.1343411122	1.5387212989	0.0000852590

[a] Geometry optimization calculations failed for this structure.

Table S10. Harmonic vibrational frequencies (cm^{-1}) of the optimal geometries given in Table S9.

	Reactants	Transition States	Products
1^1A	85.1, 120.0, 230.7, 465.8, 568.3, 1033.6, 1236.8, 2764.3, 2776.2	1726.1i, 280.5, 409.2, 457.0, 647.3, 932.4, 1023.7, 1613.5, 2736.5	109.4, 247.5, 410.2, 453.2, 486.9, 523.7, 808.8, 2739.6, 3951.7
2^1A	45.8, 93.5, 228.5, 478.5, 535.8, 1041.8, 1219.8, 2751.0, 2764.9	1789.4i, 205.4, 283.4, 413.1, 498.2, 932.3, 1029.9, 1575.3, 2874.6	98.2, 131.6, 402.7, 403.2, 447.3, 474.2, 800.3, 2743.3, 3970.1
3^1A	37.3, 87.5, 212.3, 491.2, 519.5, 1009.5, 1214.8, 2747.9, 2762.0	1843.0i, 281.7, 282.9, 394.5, 520.8, 908.7, 1079.0, 1514.0, 2728.7	185.6, 205.9, 408.6, 436.4, 461.7, 522.3, 810.7, 2748.7, 3971.7
1^3A	60.4, 100.8, 232.3, 483.4, 537.0, 1031.2, 1221.5, 2753.2, 2766.9	1800.7i, 273.6, 403.0, 433.4, 630.6, 977.1, 1070.4, 1570.3, 2603.0	125.1, 176.2, 410.4, 464.0, 490.3, 526.0, 808.7, 2708.8, 3957.3
2^3A	82.3, 100.3, 211.6, 458.3, 521.4, 956.8, 1216.8, 2740.3, 2756.3	1592.2i, 131.9, 292.2, 406.2, 454.1, 675.1, 1170.9, 1433.4, 2880.2	-
3^3A	65.1, 87.6, 219.9, 473.1, 532.7, 955.4, 1216.6, 2743.9, 2758.8	1615.4i, 301.0, 361.7, 437.2, 576.8, 841.2, 1154.3, 1461.7, 2748.1	166.3, 302.1, 396.6, 502.1, 508.0, 639.1, 803.7, 2755.5, 3949.1

Table S11. MRCI(+Q)/cc-pVTZ-PP(Nb) cc-pVTZ(H) aug-cc-pVTZ(O,S) electronic energies (a.u.) of optimal geometries of the fragments, reactants, transition states, and products of the $NbO^+ + H_2S \rightarrow [HS{-}Nb{-}OH]^+$ reaction for the first three singlets (1^1A, 2^1A, 3^1A) and the first three triplets (1^3A, 2^3A, 3^3A).

State	Fragments [a]		Intermediate		TS		Products	
	MRCI	MRCI+Q	MRCI	MRCI+Q	MRCI	MRCI+Q	MRCI	MRCI+Q
1^1A	-530.033896	-530.099287	-530.091588	-530.159713	-530.019832	-530.096743	-530.088213	-530.155605
2^1A	-530.033789	-530.099095	-530.087944	-530.155477	-530.013375	-530.091162	-530.079884	-530.145326
3^1A	-530.030398	-530.097020	-530.078792	-530.146933	-530.000270	-530.078134	-530.081048	-530.145325
1^3A	-530.060853	-530.126131	-530.115254	-530.182418	-530.043880	-530.119788	-530.113260	-530.180685
2^3A	-530.032536	-530.097661	-530.080341	-530.145713	-530.023874	-530.090518	-530.102880 [b]	-530.169828 [b]
3^3A	-530.031965	-530.097154	-530.064042	-530.137288	-529.984466	-530.056883	-530.098702	-530.165182

[a] Single point energy calculations of NbO^+ and H_2S separated by a distance of 1,000 Å.
[b] Single point energy using the 3^3A product structure.

Table S12. DFT/MN15/cc-pVTZ-PP(Nb) cc-pVTZ(H) aug-cc-pVTZ(O, S, Cl, N) optimal geometries (Cartesian coordinates in Å), harmonic vibrational frequencies (cm^{-1}, in brackets), and energies (total electronic energy, zero-point energy, free energy correction in a.u.) of the reactants, transition states, and products of the $NbO^+ + H_2S \rightarrow [HS{-}Nb{-}OH]^+$ and $[XNbO]^+ + H_2S \rightarrow [XNb{-}OH..SH]^+$ reactions [X = Cl_3, $(NH_3)Cl_3$, $(NH_3)_2Cl_3$].

	Reactants	Transition State	Products
NbO^++H_2S (Singlet)	Nb 0.612615 -0.293785 -0.000006 O 1.130429 1.271947 -0.000284 S -1.852699 0.015281 0.000143 H -2.259096 0.812332 -0.993676 H -2.258379 0.812792 0.993894 (167.7, 218.9, 232.2, 442.0, 570.0, 1096.9, 1218.8, 2712.2, 2714.4) *-530.900066837, 0.021354, -0.007948*	Nb 0.616198 -0.304276 0.004625 O 0.717816 1.419921 0.000309 S -1.771735 -0.011671 -0.085616 H -0.536993 1.240820 -0.029368 H -2.121910 0.061836 1.207126 (1665.5i, 288.8, 409.6, 483.6, 620.1, 909.7, 1011.7, 1640.2, 2675.5) *-530.849358978, 0.018315, -0.009998*	Nb -0.369987 -0.348132 -0.000104 O -1.729641 0.855700 -0.000176 S 1.832234 0.253704 0.000351 H -2.021151 1.780011 0.000282 H 1.711995 1.588552 -0.000232 (109.8, 112.8, 431.7, 487.7, 497.4, 521.0, 819.6, 2701.5, 3816.6) *-530.917120968, 0.021638, -0.008101*
NbO^++H_2S (Triplet)	Nb 0.632664 -0.295848 -0.000031 O 1.117651 1.282195 0.000444 S -1.926505 0.004164 -0.000892 H -2.024938 0.910729 -0.981323 H -2.031399 0.894846 0.993296 (39.8, 142.0, 262.5, 427.7, 498.7, 1095.3, 1171.3, 2713.9, 2721.0) *-530.924868149, 0.020668, -0.011052*	Nb 0.622973 -0.300591 0.002406 O 0.685973 1.425495 0.004205 S -1.777500 -0.019008 -0.084125 H -0.575380 1.237458 -0.022431 H -2.014278 -0.013044 1.236148 (1686.5i, 285.3, 355.2, 413.5, 552.9, 951.0, 1010.0, 1599.6, 2690.9) *-530.877137812, 0.017903, -0.011562*	Nb 0.391567 -0.373737 0.000845 O 1.566223 0.984606 -0.014486 S -1.779018 0.331535 0.082339 H 1.909909 1.890364 0.000677 H -2.029645 0.251449 -1.236852 (144.7, 229.7, 424.4, 454.7, 465.8, 527.5, 851.0, 2660.3, 3827.9) *-530.936477130, 0.021838, -0.008386*
NbO^++H_2S (Quintet)	Nb 0.520539 -0.295828 0.003836 O 1.935213 0.975058 -0.025918 S -2.029937 0.164484 0.066541 H -2.363285 0.203159 -1.231364 H -1.981524 1.493585 0.216757 (83.6, 105.1, 256.1, 431.0, 513.2, 712.0, 1168.2, 2703.1, 2724.8) *-530.786028402, 0.019813, -0.012041*	Nb 0.774454 -0.193910 0.001885 O -0.101711 1.508846 0.013284 S -1.715498 -0.308326 -0.079515 H -1.505563 1.116157 -0.146035 H -1.985403 -0.303407 1.234733 (1092.7i, 281.9, 348.0, 376.5, 523.4, 667.4, 1044.3, 1825.2, 2695.3) *-530.781009724, 0.017683, -0.012407*	Nb 0.449254 -0.184269 0.000030 O 2.137396 0.440486 0.000045 S -2.265285 0.102519 -0.000096 H 2.960996 0.947173 0.000036 H -2.235011 1.443684 -0.000104 (63.3, 93.3, 217.2, 449.0, 511.0, 514.1, 833.2, 2702.7, 3850.7) *-530.855978723, 0.021038, -0.010877*
$(Cl)_3NbO^+$+H_2S (Doublet)	Nb -0.428155 -0.001082 0.007598 O 1.289132 -0.034955 0.253445 S 3.568154 -0.008423 0.030874 H 3.513989 -1.066799 0.847671 H 3.506200 0.879356 1.029946 Cl -1.020661 2.098733 -0.470201 Cl -1.411473 -0.698162 1.887866 Cl -0.913121 -1.362558 -1.694763 (26.5i, 36.0, 38.2, 112.8, 113.2, 118.7, 193.6, 223.6, 240.3, 435.0, 438.0, 482.1, 486.1, 487.2, 939.8, 1179.3, 2730.9, 2738.4) *-1911.45295757, 0.025044, -0.014374*	Nb -0.524306 0.000417 -0.061714 O 0.585485 0.004025 -1.373933 S 3.357355 0.082531 -0.510630 H 2.031370 0.030457 -1.089235 H 3.467213 -1.248000 -0.374944 Cl -1.752307 -1.861348 -0.156535 Cl -1.732103 1.875752 -0.125919 Cl 0.990081 -0.023361 1.644572 (185.8i, 36.4, 100.0, 106.0, 119.7, 145.2, 169.8, 212.3, 225.6, 384.6, 413.5, 465.7, 496.0, 696.0, 877.6, 1173.9, 1395.3, 2707.2) *-1911.44394803, 0.022155, -0.016378*	Nb 0.216130 0.031398 0.194281 O 0.067731 0.110048 1.987168 S -2.499773 0.132663 0.088241 H 0.133449 0.183747 2.949717 H -2.734489 -0.788154 1.032185 Cl 2.393343 -0.340639 -0.072184 Cl 0.039227 2.000640 -0.833470 Cl -0.479968 -1.876819 -0.815324 (47.5, 66.8, 125.2, 147.9, 158.5, 165.7, 191.0, 204.3, 242.1, 324.9, 348.8, 423.8, 460.9, 473.3, 533.4, 851.3, 2718.8, 3844.0) *-1911.46779436, 0.025807, -0.012985*
$(NH_3)(Cl)_3NbO^+$+H_2S	Nb -0.336289 0.005537 0.030198	Nb -0.450186 0.006563 -0.153673	Nb 0.463970 -0.004742 -0.000192

(Doublet)	O 1.394040 0.054583 0.294445 S 3.627002 -0.005045 -0.003778 H 3.612837 -0.741568 1.111426 H 3.601229 1.157140 0.655874 Cl -0.831206 2.169640 0.480759 Cl -0.899169 -1.540441 1.586216 Cl -0.300395 -0.643289 -2.143186 N -2.698185 -0.072296 -0.381036 H -2.969249 0.570638 -1.123309 H -3.232396 0.180254 0.448947 H -2.998518 -1.003826 -0.663316 (14.3, 23.8, 75.6, 81.2, 82.8, 150.1, 158.6, 161.7, 163.3, 212.4, 232.3, 266.2, 317.7, 405.1, 448.0, 450.4, 453.2, 505.1, 606.0, 607.2, 910.7, 1180.6, 1250.6, 1616.3, 1616.3, 2740.1, 2749.1, 3467.9, 3583.8, 3584.9) *-1968.01380803, 0.064052, 0.019717*	O 0.792151 0.068113 -1.356649 S 3.475690 0.108246 -0.384767 H 2.205088 0.090271 -1.099814 H 3.559742 -1.224685 -0.294688 Cl -1.593021 -1.855836 -0.681807 Cl -1.596291 1.907987 -0.510648 Cl 1.294327 -0.089253 1.461275 N -1.644050 -0.074574 1.916982 H -2.648178 -0.060418 1.738614 H -1.436989 0.718886 2.522034 H -1.447174 -0.917250 2.455098 (364.4i, 39.3, 52.2, 90.9, 133.6, 142.9, 148.6, 154.4, 181.1, 215.9, 236.3, 293.4, 304.2, 384.6, 407.8, 439.2, 465.9, 583.1, 597.3, 643.5, 911.6, 1185.9, 1262.5, 1312.5, 1615.6, 1616.8, 2729.1, 3463.2, 3572.6, 3579.4) *-1968.01043448, 0.060972, 0.019822*	O -1.326713 -0.042299 -0.001575 S -4.442617 0.070749 0.004104 H -2.331741 -0.038769 -0.001567 H -4.717824 -1.235035 -0.067200 Cl 0.830950 -1.525049 -1.613293 Cl 0.806467 -0.633079 2.129566 Cl 0.742779 2.164118 -0.516346 N 2.812442 0.054309 0.002346 H 3.184669 0.335665 -0.904307 H 3.214293 -0.856902 0.221305 H 3.172987 0.713845 0.691393 (24.1, 27.6, 85.0, 85.4, 91.7, 116.0, 174.6, 176.1, 182.2, 184.4, 216.0, 230.4, 309.5, 341.7, 419.0, 463.2, 463.7, 646.1, 647.5, 744.2, 843.8, 880.3, 1285.9, 1616.8, 1616.8, 2738.8, 3076.8, 3460.0, 3571.8, 3572.0) *-1968.03163820, 0.064453, 0.020526*
$(NH_3)_2(Cl)_3NbO^+ + H_2S$ (Doublet)	Nb -0.480791 0.002055 -0.175558 O 0.561491 0.012990 -1.519493 S 3.523070 0.086529 -0.547006 H 2.443856 0.054029 -1.365266 H 3.590029 -1.244578 -0.437135 Cl -1.044786 -2.241843 0.020607 Cl -1.048022 2.239430 0.054113 Cl 1.556873 -0.016974 1.262453 N -1.307777 -0.013905 2.123075 H -2.325264 -0.003740 2.175185 H -0.979775 0.802846 2.635259 H -0.996167 -0.845489 2.621314 N -2.371440 0.008721 -1.447497 H -2.392464 0.840992 -2.035814 H -3.231808 0.004565 -0.901469 H -2.391601 -0.815408 -2.047132 (25.1, 60.5, 71.1, 88.0, 96.8, 119.7, 131.5, 143.7, 169.4, 175.6, 185.8, 212.9, 230.2, 246.2, 258.8, 265.9, 311.8, 362.0, 402.2, 408.3, 413.1, 533.3, 553.9, 601.2, 648.0, 696.9, 998.8, 1188.3, 1235.4, 1278.4, 1609.6, 1610.9, 1617.2, 1617.3, 2500.9, 2740.1, 3463.5, 3468.8, 3578.3, 3578.8, 3581.1, 3591.4) *-2024.57949609, 0.102678, 0.057336*	Nb 0.429526 -0.001712 -0.131684 O -0.763907 -0.016825 -1.399792 S -3.445436 -0.088224 -0.555334 H -2.087924 -0.042008 -1.214927 H -3.520691 1.235714 -0.382909 Cl 1.055049 2.222563 -0.033910 Cl 1.069236 -2.217541 0.004017 Cl -1.432447 0.013602 1.401056 N 1.484624 0.018471 2.022389 H 2.503150 0.014710 1.986859 H 1.202727 -0.799159 2.560669 H 1.207708 0.847499 2.545499 N 2.136367 -0.008188 -1.671354 H 2.075252 -0.840114 -2.257268 H 3.065980 -0.004355 -1.253696 H 2.073267 0.815501 -2.268505 (792.3i, 34.9, 54.1, 76.0, 95.4, 116.7, 133.3, 145.9, 156.6, 190.9, 197.5, 209.6, 226.9, 231.5, 291.2, 332.4, 358.0, 384.9, 403.3, 413.8, 439.2, 493.5, 583.7, 629.1, 640.0, 694.8, 948.6, 1103.4, 1169.9, 1251.9, 1277.1, 1610.1, 1611.3, 1614.7, 1616.9, 2739.5, 3462.8, 3465.7, 3577.0, 3578.7, 3579.3, 3586.8) *-2024.57595862, 0.099617, 0.055771*	Nb 0.416056 0.000515 0.012830 O -1.380044 0.037346 -0.046730 S -4.528227 0.012009 -0.013655 H -2.377878 0.029852 -0.040629 H -4.683543 -0.001469 1.313395 Cl 0.811856 2.258206 -0.303609 Cl 0.705160 -2.240677 -0.480120 Cl 0.822264 -0.084716 2.234120 N 2.758444 -0.082660 -0.166896 N 0.505400 0.137122 -2.309351 H -0.314021 0.664710 -2.610042 H 0.481717 -0.772179 -2.768306 H 1.310569 0.656918 -2.653387 H 3.087987 -0.835887 0.436501 H 3.182770 0.784651 0.159790 H 3.131394 -0.277708 -1.093958 (22.3, 31.5, 60.8, 64.8, 78.1, 111.1, 112.6, 121.1, 136.3, 181.2, 191.3, 202.0, 214.9, 224.2, 234.8, 330.5, 341.4, 360.5, 401.9, 405.6, 432.2, 584.0, 646.2, 650.1, 671.1, 695.4, 825.9, 867.7, 1261.7, 1276.7, 1609.7, 1611.6, 1618.7, 1625.0, 2742.1, 3199.8, 3464.1, 3464.7, 3573.1, 3574.2, 3584.4, 3588.7) *-2024.59359361, 0.103415, 0.056282*

Table S13. MRCI/cc-pVDZ-PP(Nb) cc-pVDZ(H) aug-cc-pVDZ(O) optimal geometries (Cartesian coordinates in Å) of the reactants, transition states, and products of the $NbO^+ + H_2O \rightarrow Nb(OH)_2^+$ reaction for the first three singlets (1^1A, 2^1A, 3^1A) and the first three triplets (1^3A, 2^3A, 3^3A).

	Reactants				Transition State				Products			
1^1A	Nb	0.2920006556	-0.2459117977	0.0003536784	Nb	0.4645755532	-0.2712210726	-0.0070691884	Nb	-0.0018713769	-0.0005759759	0.0000014713
	O	1.2895619031	1.1069868810	-0.0001418951	O	0.0712980326	1.4644887038	-0.0676388087	O	-1.8676734572	0.0013617150	0.0000005931
	O	-1.8977780227	0.2830165241	-0.0002931718	O	-1.5945457499	-0.1778326251	0.0785488367	O	1.8671363551	0.0013184963	0.0000032153
	H	-2.3947374472	0.5776120177	-0.7690265797	H	-1.0288932378	1.0592197588	0.0268354144	H	-2.8243600524	0.0027174145	0.0000012527
	H	-2.3932240889	0.5776913750	0.7693749682	H	-2.1635471800	-0.3328608263	0.8356681237	H	2.8265695313	0.0030543500	-0.0000255323
2^1A	Nb	0.2982686207	-0.1543531902	-0.0003498039	Nb	0.4029850223	-0.3390389640	-0.0261100163	Nb	-0.0020804571	-0.0004890197	0.0000014362
	O	1.4538266280	1.0624218184	-0.0003982581	O	0.0024170484	1.4474580740	0.0690978844	O	-1.8686962517	0.0013360929	0.0000008334
	O	-1.9390874808	0.2959208065	0.0007176502	O	-1.6325113126	-0.1553688092	-0.1796038233	O	1.8684113033	0.0013025563	0.0000027286
	H	-2.4578048947	0.5475688460	-0.7695992837	H	-1.0623499392	1.0822313115	0.0017218912	H	-2.8251748699	0.0026977821	0.0000011554
	H	-2.4593798733	0.5478367192	0.7698966955	H	-2.4063098190	-0.5369826123	0.1352610640	H	2.8273412754	0.0030285883	-0.0000251535
3^1A	Nb	0.3057417296	0.1333683534	-0.2895118432	Nb	0.4995518518	-0.2890489403	-0.0996993137	Nb	-0.0020576801	-0.0005347191	0.0000011478
	O	1.7209665076	0.9019894519	0.2315480472	O	0.0154942926	1.4430020756	-0.0821336472	O	-1.8687143732	0.0013675983	0.0000006962
	O	-1.9920065212	0.3758175976	-0.0923150528	O	-1.5376938295	-0.1261008102	0.1445535881	O	1.8684139833	0.0013266464	0.0000033840
	H	-2.7153956593	-0.0838341924	-0.5299107466	H	-1.0282893477	1.0323012595	0.1343267294	H	-2.8251949823	0.0026904053	0.0000013026
	H	-2.4012097764	1.0427462786	0.4687904660	H	-2.1642268825	-0.4404387777	0.8015274551	H	2.8273540522	0.0030260691	-0.0000255306
1^3A	Nb	0.2871223830	-0.2324798900	0.0000737746	Nb	0.4423789308	-0.2537645816	0.0124801294	Nb	-0.0018758761	-0.0005131268	0.0000011404
	O	1.3108779149	1.1013126231	-0.0002626237	O	-0.0972534399	1.4475154516	0.0112421560	O	-1.8705615170	0.0013622416	0.0000006389
	O	-1.9028393609	0.2837537956	0.0001228992	O	-1.6108231805	-0.3187572360	-0.1106566014	O	1.8701120511	0.0013206219	0.0000033886
	H	-2.3997785047	0.5733331812	-0.7713979522	H	-1.1689156991	0.9466419603	-0.0372724930	H	-2.8268762469	0.0026850765	0.0000013595
	H	-2.3995594323	0.5734752900	0.7717309022	H	-2.2422516113	-0.5948095943	0.5575718091	H	2.8290025889	0.0030211868	-0.0000255275
2^3A	Nb	0.2414557407	0.1086698301	0.2743139617	Nb	0.5004600641	-0.2664568680	-0.0389554639	Nb	0.0398480925	-0.1961317627	0.3082897684
	O	1.6650215474	0.9199602981	-0.1766692090	O	-0.0751361915	1.4599293483	-0.1128780422	O	-1.7128088632	0.1121261135	-0.1943252929
	O	-1.9859591229	0.2986137005	-0.0038349934	O	-1.5133881281	-0.2442053741	0.1940072088	O	1.8269127357	0.0750397798	-0.1088123302
	H	-2.4265102030	0.9686370069	-0.5392654402	H	-1.2165083239	0.9237020820	0.0640256105	H	-2.4383422531	0.4471259332	-0.7250202015
	H	-2.6822400387	-0.2423186764	0.3874815336	H	-2.3722924204	-0.6461431883	0.3271656869	H	2.5541812647	0.4114474620	-0.6420862933
3^3A	Nb	0.2521412493	0.3794119061	-0.4482361348	Nb	0.4870154023	-0.2717897476	0.0127152699	Nb	0.0494723161	-0.2280620257	0.0009564423
	O	1.7123552412	0.7302215065	0.3479319649	O	-0.0919031730	1.4578103201	-0.0443608128	O	-1.7448943557	0.2268972050	-0.0009186513
	O	-1.9791065131	0.3886223830	-0.0392819203	O	-1.5896589732	-0.2670541222	-0.0407183975	O	1.8468414892	0.2366805852	-0.0010042725
	H	-2.6894649592	0.1632086263	-0.6511566017	H	-1.1912288724	0.9386395516	0.0059418235	H	-2.5370166298	0.7671106490	-0.0031626686
	H	-2.4001020182	0.6379305780	0.7910096919	H	-2.2910893837	-0.6307800019	0.4997871170	H	2.6120291903	0.8196060330	-0.0033712743

Table S14. Harmonic vibrational frequencies (cm^{-1}) of the optimal geometries given in Table S13.

	Reactants	Transition States	Products
1^1A	107.2, 208.0, 372.2, 416.6, 611.8, 1027.1, 1733.2, 3888.5, 3968.3	1828.6i, 391.5, 550.2, 639.3, 727.0, 912.5, 1198.1, 1905.2, 3948.4	12.6, 527.4, 528.5, 580.2, 581.5, 791.5, 820.8, 3970.4, 4009.7
2^1A	80.1, 122.4, 351.4, 378.9, 564.3, 1036.7, 1717.5, 3882.6, 3964.0	N/A [a]	71.2, 490.4, 491.3, 565.6, 566.3, 794.7, 812.0, 3978.4, 4013.4
3^1A	89.3, 129.7, 338.2, 378.8, 555.4, 999.5, 1721.0, 3877.0, 3959.2	1123.6i, 485.3, 567.5, 714.2, 881.3, 919.5, 1183.4, 1997.7, 3944.1	71.6, 490.0, 491.2, 566.1, 566.7, 794.8, 812.0, 3978.3, 4013.5
1^3A	102.6, 173.7, 365.1, 388.6, 575.8, 1029.6, 1715.4, 3880.2, 3962.8	1834.7i, 390.2, 551.6, 643.1, 692.0, 900.6, 1202.1, 1894.5, 3952.0	81.6, 486.4, 487.3, 564.9, 565.1, 792.5, 809.6, 3979.0, 4015.7
2^3A	102.7, 109.7, 371.9, 411.7, 565.1, 975.7, 1714.6, 3849.3, 3932.2	1765.3i, 423.2, 489.7, 664.6, 780.3, 853.4, 1166.1, 1968.2, 3985.5	118.4, 540.3, 563.58, 571.3, 609.0, 788.5, 831.9, 3922.8, 3968.1
3^3A	100.5, 199.0, 366.4, 386.0, 558.9, 974.7, 1712.7, 3855.5, 3938.9	1655.9i, 434.4, 521.8, 676.6, 719.4, 843.7, 1231.5, 1930.2, 3990.8	133.4, 562.1, 581.7, 583.3, 607.2, 789.6, 833.2, 3931.7, 3975.7

[a] Unavailable for technical issues.

Table S15. MRCI(+Q)/cc-pVTZ-PP(Nb) cc-pVTZ(H) aug-cc-pVTZ(O) electronic energies (a.u.) of optimal geometries of the fragments, reactants, transition states, and products of the $NbO^+ + H_2O \rightarrow Nb(OH)_2^+$ reaction for the first three singlets (1^1A, 2^1A, 3^1A) and the first three triplets (1^3A, 2^3A, 3^3A).

State	Fragments [a]		Intermediate		TS		Products	
	MRCI	MRCI+Q	MRCI	MRCI+Q	MRCI	MRCI+Q	MRCI	MRCI+Q
1^1A	-207.437395	-207.499651	-207.502974	-207.565476	-207.425659	-207.489299	-207.521206	-207.581457
2^1A	-207.437296	-207.499470	-207.500663	-207.562632	-207.418661	-207.481644	-207.522424	-207.579378
3^1A	-207.433886	-207.497404	-207.496433	-207.559123	-207.415976	-207.479527	-207.522387	-207.579348
1^3A	-207.463409	-207.525969	-207.528576	-207.590487	-207.455043	-207.517855	-207.548155	-207.605276
2^3A	-207.434255	-207.497028	-207.504313	-207.564763	-207.442919	-207.504740	-207.529095	-207.590082
3^3A	-207.434044	-207.496635	-207.503729	-207.564001	-207.435611	-207.497646	-207.528384	-207.589286

[a] Single point energy calculations of NbO^+ and H_2O separated by a distance of 1,000 Å.

Table S16. DFT/MN15/cc-pVTZ-PP(Nb) cc-pVTZ(H) aug-cc-pVTZ(O, Cl, N) optimal geometries (Cartesian coordinates in Å), harmonic vibrational frequencies (cm^{-1}, in brackets), and energies (total electronic energy, zero-point energy, free energy correction in a.u.) of the reactants, transition state, and products of the $NbO^+ + H_2O \rightarrow [HO{-}Nb{-}OH]^+$ and $XNbO^+ + H_2O \rightarrow [XNb(OH)_2]^+$ reactions [X = Cl_3, $(NH_3)Cl_3$, $(NH_3)_2Cl_3$, $(NH_3)_3Cl_3$].

	Reactants	Transition State	Products
NbO^++H_2O (Singlet)	Nb 0.257720 -0.300594 -0.000064 O 1.079532 1.128402 -0.000023 O -1.825224 0.267253 0.000284 H -2.300626 0.579331 -0.785567 H -2.300356 0.579800 0.786112 (158.4, 226.9, 416.4, 443.8, 594.1, 1102.4, 1621.5, 3766.1, 3845.1) *-208.008216768, 0.027736, -0.000504*	Nb 0.411943 -0.218715 0.002563 O -0.098175 1.439171 0.013430 O -1.582373 -0.348957 -0.089789 H -1.195077 0.909469 -0.029576 H -2.250219 -0.663850 0.535375 (1955.6i, 346.6, 514.2, 643.7, 675.7, 983.9, 1110.0, 1859.7, 3832.0) *-207.943680646, 0.022704, -0.004503*	Nb 0.000021 -0.000678 -0.000002 O -1.844953 0.001391 0.000014 O 1.844867 0.001403 0.000013 H -2.810691 0.002742 -0.000068 H 2.810535 0.002679 -0.000064 (16.2i, 545.7, 548.2, 611.1, 611.1, 808.2, 812.1, 3871.6, 3881.5) *-208.025800169, 0.026631, 0.005119*
NbO^++H_2O (Triplet)	Nb 0.256084 -0.299493 -0.000017 O 1.104120 1.116193 -0.000225 O -1.838586 0.271825 0.000264 H -2.311796 0.587418 -0.785136 H -2.311904 0.587657 0.785501 (149.1, 196.4, 406.6, 427.7, 568.7, 1098.6, 1616.3, 3774.5, 3853.5) *-208.026702160, 0.027546, -0.001880*	Nb 0.406197 -0.226317 0.002757 O -0.058703 1.444837 0.013056 O -1.597409 -0.328227 -0.093534 H -1.153427 0.940080 -0.036285 H -2.251766 -0.593953 0.567081 (1823.9i, 388.8, 516.6, 622.2, 669.1, 997.7, 1085.4, 1890.9, 3839.3) *-207.962660180, 0.022805, -0.005413*	Nb 0.000021 -0.000673 -0.000002 O -1.849196 0.001390 0.000017 O 1.849107 0.001398 0.000017 H -2.814546 0.002668 -0.000084 H 2.814388 0.002626 -0.000083 (36.5, 545.4, 548.1, 610.0, 610.0, 802.0, 807.2, 3876.6, 3886.3) *-208.049640696, 0.026705, 0.002434*
NbO^++H_2O (Quintet)	Nb 0.138887 -0.182889 0.002024 O 1.893525 0.530044 -0.006299 O -1.980631 0.278136 -0.002061 H -2.505757 0.481628 -0.793791 H -2.491760 0.551362 0.777683 (45.3i, 103.3, 403.1, 421.9, 532.0, 728.7, 1607.7, 3752.4, 3830.7) *-207.894124414, 0.025925, -0.003573*	Nb 0.549058 -0.069307 0.001519 O -0.908061 1.217530 0.029903 O -1.452200 -0.777210 -0.094753 H -1.721510 0.410719 -0.251409 H -1.907782 -1.091677 0.707927 (1822.6i, 402.5, 567.7, 607.0, 615.0, 699.2, 1129.6, 1906.9, 3747.9) *-207.854343480, 0.022043, -0.006779*	Nb -0.074486 -0.076590 0.000120 O -1.850391 0.176131 -0.000090 O 2.211443 0.076985 -0.000602 H -2.791778 0.397754 -0.001372 H 2.957299 0.717494 0.001980 (45.7i, 62.8, 282.7, 339.7, 524.6, 530.5, 848.3, 3680.8, 3852.2) *-207.904251059, 0.023059, -0.006332*
$(Cl)_3NbO^+$+H_2O (Doublet)	Nb -0.016725 0.000134 0.090801 O -0.218802 0.001042 1.924575 O 2.065577 0.013809 0.904562 H 2.506726 -0.778207 1.249761 H 2.489615 0.806147 1.269909 Cl 0.542088 1.935045 -0.867597 Cl -2.238472 -0.017703 0.035778 Cl 0.573748 -1.926297 -0.866747 (31.0, 89.7, 121.2, 121.8, 139.5, 175.1, 176.2, 205.2, 347.6, 370.6, 433.0, 458.7, 487.5, 608.9, 704.9, 1593.3, 3763.4, 3860.1) *-1588.52117022, 0.031183, -0.007227*	Nb 0.274925 -0.109809 -0.156017 O 0.871439 -0.620529 -1.716617 O 0.829616 -2.016182 0.059511 H 1.014110 -1.706581 -1.166866 H 0.608857 -2.828702 0.533354 Cl -1.520805 1.347640 -0.632892 Cl 1.760974 1.160421 0.887023 Cl -1.799188 -0.735639 0.939226 (1888.9i, 41.7, 112.0, 120.2, 137.7, 181.4, 215.2, 267.2, 351.6, 383.3, 456.7, 492.3, 681.9, 726.2, 978.5, 999.3, 1859.3, 3855.5) *-1588.48032957, 0.027019, -0.009796*	Nb -0.245710 -0.303060 0.119938 O -0.440774 -0.542803 1.886395 O -0.587414 -1.909380 -0.638226 H -0.674998 -0.862508 2.769672 H -0.563017 -2.729200 -1.151158 Cl -1.995709 0.871635 -0.614431 Cl 2.067778 -0.529138 -0.488042 Cl 1.077202 1.753658 0.130632 (28.5, 126.5, 149.2, 172.3, 194.8, 216.4, 250.9, 255.5, 307.6, 371.9, 391.8, 423.8, 449.6, 489.0, 836.8, 872.3, 3836.5, 3851.1) *-1588.54884161, 0.030128, -0.007233*
,			
$(NH_3)(Cl)_3NbO^+$+H_2O (Doublet)	Nb -0.082567 -0.000052 -0.094886 O 0.260341 0.000196 -1.850277	Cl 2.099759 -0.616065 0.565566 Cl -2.099856 -0.615735 0.565620	Nb 0.244107 -0.324551 -0.165852 O 0.576655 -2.042281 0.327809

	O -2.200260 -0.001652 -0.757006 H -2.628861 -0.798249 -1.104995 H -2.630040 0.794277 -1.105067 Cl -0.682276 2.117033 0.492454 Cl 2.223103 0.001492 -0.624951 Cl -0.679095 -2.117984 0.492601 N 0.903818 0.000811 1.982171 H 0.206565 0.000391 2.728333 H 1.489811 0.824870 2.116602 H 1.490983 -0.822387 2.116760 (63.2, 65.4, 150.4, 156.0, 164.8, 170.1, 190.9, 192.4, 213.3, 233.1, 297.5, 333.5, 362.0, 382.8, 397.1, 419.1, 446.4, 631.3, 662.0, 684.5, 767.8, 1291.8, 1579.9, 1609.3, 1611.6, 3450.8, 3558.8, 3569.6, 3770.4, 3873.5) *-1645.09757081, 0.071305, 0.031937*	Cl 0.000171 2.090018 -0.745614 N 0.000127 0.882838 2.025069 H 0.000298 0.184377 2.770376 H -0.823364 1.469528 2.162435 H 0.823535 1.469695 2.162216 O -0.000179 -2.057689 -0.583619 Nb -0.000012 -0.064486 -0.053638 H -0.000154 -1.568042 -1.718233 O -0.000071 -0.414124 -2.046234 H 0.000022 0.093323 -2.869000 (1456.8i, 73.9, 77.6, 118.7, 141.8, 157.2, 165.9, 173.2, 209.4, 219.4, 354.1, 410.6, 413.4, 425.2, 457.5, 472.4, 550.3, 673.8, 704.8, 721.6, 848.0, 942.7, 1305.7, 1609.1, 1611.9, 1873.5, 3448.4, 3555.3, 3564.9, 3846.4) *-1645.05926592, 0.066356, 0.027746*	O 0.147557 -0.451388 -1.970913 H 0.564454 -2.991295 0.502167 H -0.000963 -0.401284 -2.923858 Cl 2.216658 0.760211 0.052460 Cl -2.189860 -0.495753 0.153567 Cl -1.053524 1.807644 -0.194529 N 0.111680 0.119456 2.107199 H 0.154880 1.121561 2.289324 H 0.898071 -0.306336 2.597192 H -0.745952 -0.228628 2.534085 (68.8, 94.2, 124.0, 136.0, 164.9, 176.4, 184.3, 203.1, 223.5, 230.8, 246.5, 323.0, 347.0, 389.6, 410.5, 420.6, 447.7, 501.2, 655.8, 666.7, 820.6, 830.5, 1284.8, 1610.3, 1619.9, 3462.6, 3573.7, 3576.5, 3868.7, 3881.2) *-1645.12517118, 0.069582, 0.030291*
$(NH_3)_2(Cl)_3NbO^+ + H_2O$ (Doublet)	Nb -0.072681 0.001371 -0.146099 O 0.713793 -0.098041 -1.755822 O -1.450620 1.037588 -1.558093 H -1.086218 1.636854 -2.226106 H -2.349684 1.296205 -1.307760 Cl -2.212334 -0.745905 0.457589 Cl 0.175516 2.103052 0.739765 Cl 2.402805 -0.254781 -0.182861 N 0.404615 -0.512405 2.056884 H 0.588214 -1.487676 2.283426 H -0.383360 -0.209123 2.630144 H 1.219504 0.027120 2.347780 N 0.174078 -2.290640 -0.265544 H 1.156233 -2.564585 -0.279969 H -0.218739 -2.557119 -1.169318 H -0.324012 -2.833182 0.437411 (60.3, 78.3, 101.6, 129.8, 138.0, 166.9, 182.0, 191.4, 205.6, 209.9, 229.0, 232.7, 246.5, 296.4, 312.2, 336.4, 346.7, 387.4, 395.4, 397.4, 428.2, 627.1, 641.5, 665.1, 672.8, 702.6, 780.0, 1269.7, 1287.0, 1561.7, 1602.0, 1605.6, 1615.3, 1624.4, 3454.6, 3459.3, 3560.6, 3567.0, 3584.7, 3586.6, 3773.5, 3886.1) *-1701.65680694, 0.110717, 0.069076*	Cl 2.250442 -0.427979 0.057048 Cl -2.250303 -0.428698 0.057055 Cl -0.000390 2.295788 0.153924 N 0.000330 -2.087813 0.964520 H 0.000409 -2.762756 0.198991 H -0.831311 -2.272239 1.523231 H 0.832053 -2.271995 1.523189 O 0.000238 -1.521184 -1.590299 Nb 0.000003 -0.012639 -0.093075 H 0.000089 -0.525003 -2.318347 O -0.000085 0.618806 -2.019457 H -0.000209 1.481731 -2.454524 N -0.000036 0.386755 2.184649 H -0.816134 0.962918 2.393031 H 0.815833 0.963256 2.392992 H 0.000143 -0.396159 2.834902 (1304.4i, 41.6, 77.8, 104.7, 124.9, 146.7, 156.7, 166.6, 182.1, 229.2, 243.3, 249.8, 297.9, 325.1, 349.0, 369.3, 376.0, 409.3, 425.1, 452.4, 545.7, 660.3, 669.6, 707.5, 736.4, 741.1, 854.5, 873.4, 1270.6, 1302.2, 1598.6, 1606.2, 1616.6, 1643.3, 1899.7, 3454.4, 3458.4, 3561.1, 3562.6, 3584.2, 3585.9, 3846.4) *-1701.62180454, 0.105948, 0.064880*	Nb 0.144669 0.045065 -0.217106 O 1.174565 0.386908 -1.750662 O -1.266280 -0.177931 -1.649871 H 0.887701 0.240666 -2.662896 H -1.995404 0.432349 -1.854305 Cl -2.131618 -0.805041 0.366594 Cl -0.511301 2.200369 0.315995 Cl 0.991028 -2.073580 0.086622 N 0.118549 -0.142859 2.123919 H -0.333228 -1.024628 2.364753 H -0.423117 0.612213 2.544026 H 1.032141 -0.164007 2.571791 N 2.188024 0.850777 0.502190 H 2.547182 1.361114 -0.304601 H 2.850878 0.101167 0.698652 H 2.172281 1.496508 1.288842 (38.2, 79.0, 112.9, 119.9, 132.3, 141.8, 176.4, 195.3, 201.6, 210.5, 226.7, 263.0, 313.2, 338.1, 344.7, 397.0, 400.2, 403.2, 443.6, 477.2, 516.3, 601.9, 619.6, 637.7, 655.8, 695.3, 705.8, 738.9, 1265.7, 1281.7, 1600.0, 1610.2, 1623.3, 1635.3, 3458.9, 3461.1, 3568.3, 3570.8, 3586.6, 3589.8, 3785.1, 3842.9) *-1701.65545347, 0.109502, 0.067829*
$(NH_3)_3(Cl)_3NbO^+ + H_2O$ (Doublet)	Nb 0.030545 -0.073898 -0.112443 O -0.725302 -0.566529 -1.686171 O 1.408408 1.009340 -1.632795 H 1.917193 1.696381 -1.171499 H 0.852046 1.457054 -2.290846 Cl -2.466800 -0.438450 -0.192221	Nb 0.001937 -0.065686 -0.098899 O -1.365321 -1.528810 -0.666469 O -0.923588 0.220598 -1.967012 H -1.285672 1.078609 -2.223347 H -1.539582 -0.736010 -1.568566 Cl -2.256337 0.163408 0.738804	Nb 0.007589 -0.097834 -0.190334 O -0.597865 -0.099829 -1.967319 O 0.915614 1.640513 -1.001504 H 1.490460 2.108808 -0.369491 H -0.238405 0.401732 -2.712362 Cl -2.194174 -1.044176 0.017450

	Cl -0.550583 2.206222 -0.004048 Cl 2.094703 0.117270 1.131029 N -0.303779 -2.156078 0.795729 H -0.477501 -2.816649 0.039103 H -1.145432 -2.170834 1.368985 H 0.481885 -2.492361 1.351963 N 1.542626 -1.579779 -1.101454 H 2.191003 -0.989138 -1.619359 H 1.084818 -2.190655 -1.776838 H 2.106278 -2.129031 -0.455840 N -0.644063 0.288871 2.095220 H -0.151614 1.138321 2.370342 H -0.410284 -0.418452 2.789328 H -1.643519 0.485858 2.139182 (79.1, 104.6, 117.3, 134.0, 146.3, 152.1, 157.4, 186.6, 199.2, 210.0, 223.5, 236.9, 247.1, 249.6, 253.6, 263.7, 288.5, 309.4, 326.0, 341.0, 369.6, 380.5, 393.6, 401.4, 618.1, 626.3, 638.7, 668.6, 670.3, 687.2, 702.0, 717.6, 763.8, 1245.1, 1262.4, 1277.3, 1569.8, 1585.8, 1597.5, 1604.0, 1617.2, 1632.9, 1647.3, 3454.9, 3458.0, 3459.1, 3569.4, 3575.7, 3578.8, 3581.4, 3583.4, 3591.4, 3746.8, 3839.0) *-1758.19943094, 0.151136, 0.108443*	Cl 0.408177 2.177799 -0.596813 Cl 2.336116 -0.235276 0.486175 N 0.039799 -1.787637 1.428201 H 0.210304 -2.654939 0.921188 H -0.887923 -1.883850 1.842487 H 0.750132 -1.716370 2.154244 N 1.012426 -1.416036 -1.638133 H 1.617027 -0.790553 -2.174215 H 0.350211 -1.837884 -2.288821 H 1.620256 -2.132408 -1.245066 N 0.165858 0.986317 1.957838 H 1.121166 1.323537 2.076604 H -0.091548 0.434442 2.774035 H -0.454351 1.794919 1.939968 (1345.1i, 35.2, 113.1, 119.1, 146.2, 153.5, 176.3, 195.1, 217.6, 232.6, 234.8, 238.2, 257.2, 262.8, 280.0, 295.6, 310.8, 335.6, 340.4, 367.6, 400.8, 407.0, 470.1, 501.3, 523.9, 632.1, 680.7, 696.3, 724.8, 728.1, 749.5, 764.5, 810.3, 1251.3, 1264.0, 1286.4, 1298.3, 1590.2, 1594.5, 1599.9, 1604.6, 1617.4, 1622.4, 1828.1, 3446.2, 3453.4, 3454.1, 3556.0, 3568.6, 3571.5, 3582.2, 3585.5, 3587.8, 3853.7) *-1758.16982784, 0.147209, 0.105300*	Cl -0.988502 2.137031 0.143697 Cl 2.009377 0.193359 1.197000 N 0.334141 -2.281446 0.415305 H 0.139268 -2.899738 -0.372825 H -0.366542 -2.524253 1.115083 H 1.261985 -2.486030 0.784851 N 1.799081 -0.893649 -1.429195 H 2.173505 -0.057884 -1.879043 H 1.523785 -1.539061 -2.168225 H 2.562897 -1.289881 -0.884232 N -0.610972 0.022370 2.098989 H -0.190696 0.854294 2.510540 H -0.293977 -0.761990 2.665976 H -1.625069 0.083153 2.179828 (67.9, 74.9, 110.4, 149.2, 177.0, 179.4, 191.3, 204.7, 223.5, 231.9, 236.2, 252.2, 263.6, 269.4, 276.8, 293.5, 323.6, 340.6, 347.7, 377.3, 382.3, 398.0, 449.6, 485.8, 562.9, 599.1, 633.8, 660.9, 673.5, 691.9, 710.4, 724.7, 753.5, 815.6, 1253.4, 1264.7, 1280.7, 1583.3, 1599.2, 1603.9, 1609.3, 1627.0, 1643.4, 3448.5, 3451.1, 3456.0, 3559.6, 3563.6, 3576.6, 3579.6, 3581.7, 3586.2, 3751.1, 3835.3) *-1758.18348596, 0.150331, 0.108250*
$(NH_3)_4(Cl)_3NbO^+ + H_2O$ (Doublet)	Nb -0.256986 0.011341 -0.016187 O 0.799646 0.129561 -1.456378 Cl -2.041930 -1.251059 -1.063655 Cl 1.078229 2.209635 -0.474691 Cl 1.344709 -0.077786 1.751232 N -1.383323 -1.289279 1.721209 H -1.496232 -2.241029 1.378871 H -2.331511 -0.972999 1.916219 H -0.859830 -1.318278 2.595023 N 0.647972 -2.073545 -0.197442 H 1.641818 -1.916570 -0.441340 H 0.208652 -2.605476 -0.946564 H 0.635988 -2.629305 0.654208 N -1.624504 1.482034 -1.209641 H -1.408618 2.470504 -1.094924 H -2.624984 1.321574 -1.113594 H -1.385482 1.238233 -2.170986 N -1.164939 1.524067 1.528795 H -2.176378 1.638361 1.561939 H -0.749959 2.434185 1.328832 H -0.835250 1.261130 2.456604	Nb -0.183934 -0.009436 -0.079133 O 0.809523 -0.427990 -1.490045 Cl 2.396077 -0.406790 0.899670 Cl -1.836987 -1.325931 -1.211726 Cl -1.746505 1.744101 -0.440379 N 0.119295 1.001900 2.010999 H 1.036970 1.435613 2.093864 H 0.038492 0.353084 2.790508 H -0.599038 1.716482 2.126032 N 1.042026 1.936637 -0.459846 H 0.848567 2.151035 -1.437832 H 2.049512 1.796867 -0.366436 H 0.751230 2.756678 0.067725 N 0.063462 -2.098271 0.828117 H -0.822799 -2.599517 0.824601 H 0.508298 -2.164652 1.741446 H 0.679308 -2.575390 0.168984 N -2.158589 -0.442190 1.592032 H -2.132477 -0.977731 2.458020 H -2.783102 -0.928391 0.948426 H -2.617591 0.443509 1.795750	Nb -0.162739 -0.024713 -0.035507 O 0.727870 -0.678382 -1.532597 Cl 2.080582 -0.366075 1.066455 Cl -1.982435 -1.245898 -1.044973 Cl -1.722989 1.738671 -0.482706 N 0.123432 1.483615 1.771376 H 0.992710 1.997786 1.647958 H 0.232807 1.010017 2.665730 H -0.644831 2.151590 1.828810 N 1.070159 1.760232 -0.834982 H 0.844307 1.793894 -1.828953 H 2.076793 1.602600 -0.748471 H 0.818560 2.672861 -0.462202 N 0.069319 -2.261872 0.618842 H -0.797993 -2.789849 0.542939 H 0.524240 -2.434876 1.512346 H 0.689769 -2.617273 -0.107472 N -1.708291 -0.466739 1.741122 H -1.390305 -0.682236 2.684047 H -2.295637 -1.232562 1.413975 H -2.325801 0.343845 1.787479

	O 3.285366 -1.337543 -1.013907 H 4.211396 -1.495492 -0.804842 H 3.223119 -0.462330 -1.413013 (43.6, 60.0, 70.9, 108.9, 109.2, 127.3, 129.9, 151.5, 162.2, 172.6, 173.6, 193.7, 196.7, 203.5, 210.7, 216.9, 231.5, 241.5, 243.5, 262.1, 275.8, 288.2, 300.2, 320.4, 327.2, 346.4, 360.4, 373.0, 398.3, 411.8, 547.3, 594.7, 625.5, 642.3, 693.5, 707.9, 732.2, 768.1, 808.5, 1225.5, 1246.2, 1270.3, 1318.8, 1578.4, 1580.5, 1596.3, 1601.5, 1612.2, 1621.6, 1624.7, 1645.4, 1649.9, 3244.0, 3453.3, 3460.4, 3461.2, 3514.9, 3563.3, 3571.1, 3582.6, 3583.8, 3588.7, 3593.5, 3597.6, 3850.6, 3961.1) *-1814.73726218, 0.187787, 0.139816*	H 1.947933 -0.277561 -1.527969 O 3.138945 0.048765 -1.279521 H 3.770916 -0.689328 -1.289855 (921.5i, 42.7, 71.7, 100.5, 111.3, 115.8, 145.8, 150.2, 163.6, 177.2, 184.2, 210.0, 218.4, 232.9, 245.0, 251.4, 263.6, 271.0, 279.3, 291.7, 303.9, 318.2, 326.4, 335.8, 358.5, 386.4, 400.4, 518.7, 538.9, 549.7, 592.9, 605.9, 662.4, 669.8, 694.9, 706.4, 721.9, 781.0, 934.0, 1215.4, 1243.8, 1265.9, 1271.0, 1276.5, 1399.5, 1578.6, 1595.9, 1598.8, 1610.2, 1617.3, 1623.8, 1632.9, 1653.2, 3445.2, 3449.1, 3459.7, 3460.0, 3559.6, 3559.6, 3569.5, 3577.8, 3585.0, 3586.1, 3589.3, 3592.1, 3802.8) *-1814.70455229, 0.183965, 0.138412*	H 1.690164 -0.574631 -1.694365 O 3.383407 -0.002198 -1.236154 H 4.107294 -0.543819 -0.869719 (46.5, 70.9, 93.6, 104.4, 123.3, 145.4, 164.2, 166.7, 193.6, 197.7, 212.3, 219.2, 230.2, 233.0, 252.0, 253.9, 265.8, 273.4, 284.6, 296.3, 311.0, 322.5, 324.3, 346.8, 350.7, 374.6, 380.0, 388.9, 430.6, 582.5, 594.3, 660.6, 670.6, 698.4, 701.6, 723.4, 726.8, 735.4, 761.3, 820.8, 1236.6, 1252.5, 1265.2, 1282.4, 1573.6, 1589.6, 1601.4, 1607.3, 1621.0, 1623.7, 1644.8, 1658.0, 3431.3, 3452.5, 3458.7, 3461.0, 3540.9, 3552.4, 3560.8, 3578.1, 3582.8, 3583.8, 3586.0, 3588.0, 3596.2, 3767.3) *-1814.71067601, 0.187785, 0.141951*

Table S17. DFT/MN15/cc-pVTZ-PP(Zr) cc-pVTZ(H) aug-cc-pVTZ(C, O) optimal geometries (Cartesian coordinates in Å), harmonic vibrational frequencies (cm^{-1}, in brackets), and energies (total electronic energy, zero-point energy, free energy correction in a.u.) of the reactants, transition state, and products of the $ZrO^+ + CH_4 \rightarrow [HO{-}Zr{-}CH_3]^+$ reaction.

Spin	Reactants	Transition state	Products
Doublet	Zr 0.313623 -0.317005 0.000001 O 1.017121 1.220129 -0.000002 C -2.051909 0.279529 0.000007 H -3.031558 0.750204 -0.000089 H -2.220738 -0.802598 0.000201 H -1.559081 0.646995 -0.924168 H -1.559062 0.647376 0.924004 (115.3, 162.1, 275.7, 335.3, 488.5, 1041.8, 1272.0, 1312.2, 1341.7, 1518.7, 1527.7, 2863.5, 2963.4, 3090.2, 3181.8) *-162.231281875, 0.048958, 0.019273*	Zr 0.000000 0.496544 0.000000 O 1.372554 -0.623504 0.000000 C -1.146778 -1.428915 0.000000 H -0.943749 -2.500027 0.000000 H -1.752809 -1.221492 0.894249 H 0.349602 -1.357210 0.000000 H -1.752809 -1.221492 -0.894249 (1647.9i, 132.2, 288.0, 306.6, 527.7, 740.5, 975.6, 1106.4, 1223.2, 1396.9, 1397.6, 1939.4, 2986.1, 3046.7, 3142.3) *-162.177905131, 0.043762, 0.014795*	Zr 0.097754 -0.401935 -0.000236 O 1.340680 0.948044 0.000080 C -1.732550 0.688410 -0.001628 H 1.928147 1.714011 -0.000608 H -2.582345 -0.004014 -0.041087 H -1.785304 1.369593 -0.855754 H -1.800811 1.282986 0.916016 (21.1i, 164.1, 299.9, 422.4, 485.1, 487.7, 553.5, 821.2, 1160.5, 1363.2, 1375.1, 3010.9, 3094.2, 3110.2, 3878.9) *-162.238160324, 0.046080, 0.017176*
Quartet	Zr -0.211521 -0.322968 -0.000006 O -1.626427 1.006764 0.000033 C 2.131685 0.476004 0.000087 H 3.134069 0.895708 -0.000955 H 2.049508 -0.115960 -0.925409 H 2.051013 -0.115544 0.925871 H 1.447574 1.344398 -0.000055 (34.2, 140.5, 258.8, 285.5, 395.8, 691.6, 1251.8, 1317.5, 1327.4, 1492.7, 1525.0, 2907.6, 3019.4, 3043.7, 3182.3) *-162.102223499, 0.047554, 0.015848*	Zr -0.603854 -0.173638 0.000354 O 0.423931 1.405499 -0.001707 C 2.088645 -0.466035 0.008595 H 2.850275 -0.248895 -0.733416 H 2.440447 -0.583156 1.026296 H 1.468704 0.635449 0.005790 H 1.471398 -1.305674 -0.350737 (1467.8i, 91.0, 174.9, 366.7, 437.3, 666.6, 757.2, 1005.3, 1239.2, 1335.0, 1387.0, 1429.2, 2975.0, 3159.8, 3252.5) *-162.087587982, 0.041637, 0.011255*	Zr 0.257951 -0.416496 0.000042 O 1.005768 1.272413 -0.000041 C -2.165825 0.471536 -0.000027 H 1.411195 2.146386 0.000152 H -2.629143 -0.508649 -0.017154 H -2.068715 1.019492 -0.926954 H -2.082583 0.994077 0.942757 (53.0i, 96.1, 234.6, 283.5, 302.0, 417.2, 472.6, 795.3, 906.7, 1372.8, 1389.2, 3100.9, 3264.3, 3292.4, 3905.2) *-162.157946464, 0.045182, 0.014501*

Table S18. Energy comparison between MRCI+Q and DFT/MN15 for the $MO^+ + H_2X$ reactions. The aug-cc-pVTZ-PP basis set is used for metals, cc-pVTZ for H, and aug-cc-pVTZ for O and S. R, IC, TS, and P stands for the corresponding reactants ($MO^+ + H_2X$), interacting complex ($[H_2X...MO]^+$), transition state, and products $[HX-M-OH]^+$, respectively.

Spin Multiplicity	Species	MRCI+Q	MN15	Difference
$ZrO^+ + H_2O$				
Doublet	R	0.00	0.00	0.00
	IC	-40.71	-47.52	6.81
	TS	-14.05	-24.55	10.50
	P	-60.29	-76.66	16.37
Quartet	R	77.05	85.19	-8.14
	IC	36.88	31.42	5.46
	TS	66.50	54.83	11.67
	P	33.16	29.86	3.30
$ZrO^+ + H_2S$				
Doublet	R	0.00	0.00	0.00
	IC	-35.84	-36.37	0.53
	TS	-9.69	-16.58	6.89
	P	-74.97	-60.73	-14.24
Quartet	R	76.16	85.19	-9.03
	IC	45.10	38.26	6.84
	TS	57.24	44.74	12.50
	P	-19.14	-2.65	-16.49
$NbO^+ + H_2O$				
Singlet	R	16.51	15.57	0.94
	IC	-24.79	-34.09	9.30
	TS	23.01	6.40	16.61
	P	-33.50	-45.13	11.63

Triplet	R	0.00	0.00	0.00
	IC	-40.49	-45.69	5.20
	TS	5.09	-5.51	10.60
	P	-49.77	-60.09	10.32
Quintet	R	102.69	87.41	15.28
	IC	80.29	37.50	42.79
	TS	84.90	62.46	22.44
	P	39.87	31.15	8.72
$NbO^+ + H_2S$				
Singlet	R	16.84	15.57	1.27
	IC	-21.07	-25.59	4.52
	TS	18.44	6.23	12.21
	P	-18.50	-36.29	17.79
Triplet	R	0.00	0.00	0.00
	IC	-35.32	-41.15	5.83
	TS	3.98	-11.20	15.18
	P	-34.23	-48.44	14.21
Quintet	R	96.07	87.41	8.66
	IC	55.51	45.97	9.54
	TS	63.41	49.12	14.29
	P	11.48	2.08	9.40

Table S19. Relative ZPE-corrected (ΔE_{ZPE}) and free (ΔG) energies of all intermediate and transition state structures for the reaction of H_2S and H_2O with bare and ligated ZrO^+ and NbO^+ units. [Zr]/[Nb] denotes the metal-ligands combination, and A represents an ammonia molecule. The radical high-spin state is listed for the bare units. Compare to Table 1 of the manuscript.

Species	**[Zr]/[Nb] compound**									
	ΔE_{ZPE}					**ΔG**				
	Zr	**Cl_2Zr**	**Cl_2ZrA**	**Cl_2ZrA_2**	**Cl_2ZrA_3**	**Zr**	**Cl_2Zr**	**Cl_2ZrA**	**Cl_2ZrA_2**	**Cl_2ZrA_3**
$[Zr]O^+ + H_2S$	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
$(H_2S)[Zr]O^+$	-45.2	-40.0	-26.1	-16.2	-16.2	-37.3	-30.8	-16.6	-7.8	-6.8
TS	-40.5	-29.9	-24.5	-11.8	-12.2	-31.8	-20.4	-15.0	-0.9	0.4
$HS[Zr]OH^+$	-85.2	-80.5	-61.9	-51.3	-44.1	-77.2	-71.3	-51.9	-41.2	-31.4
	Nb	**Cl_3Nb**	**Cl_3NbA**	**Cl_3NbA_2**		**Nb**	**Cl_3Nb**	**Cl_3NbA**	**Cl_3NbA_2**	
$[Nb]O^+ + H_2S$	0.0	0.0	0.0	0.0		0.0	0.0	0.0	0.0	
$(H_2S)[Nb]O^+$	-39.7	-51.1	-35.3	-31.4		-31.9	-41.0	-26.6	-22.0	
TS	-37.9	-47.2	-35.1	-31.1		-29.0	-36.6	-24.5	-20.8	
$HS[Nb]OH^+$	-82.9	-59.9	-46.2	-39.8		-75.1	-49.5	-37.3	-31.5	
	Zr	**Cl_2Zr**	**Cl_2ZrA**	**Cl_2ZrA_2**	**Cl_2ZrA_3**	**Zr**	**Cl_2Zr**	**Cl_2ZrA**	**Cl_2ZrA_2**	**Cl_2ZrA_3**
$[Zr]O^+ + H_2O$	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
$(H_2O)[Zr]O^+$	-51.7	-50.2	-36.1	-24.0	-20.9	-44.6	-41.8	-27.5	-14.7	-9.3
TS	-31.6	-29.5	-21.6	-13.2	-6.0	-23.6	-20.2	-12.2	-4.8	6.3
$HO[Zr]OH^+$	-55.0	-61.9	-48.9	-41.8	-19.1	-48.0	-53.0	-40.0	-32.3	-7.2
	Nb	**Cl_3Nb**	**Cl_3NbA**	**Cl_3NbA_2**		**Nb**	**Cl_3Nb**	**Cl_3NbA**	**Cl_3NbA_2**	
$[Nb]O^+ + H_2O$	0.0	0.0	0.0	0.0		0.0	0.0	0.0	0.0	
$(H_2O)[Nb]O^+$	-48.2	-34.5	-27.8	-19.3		-40.5	-25.4	-17.6	-9.3	
TS	-25.7	-11.5	-6.8	-0.4		-17.5	-1.4	3.8	10.1	
$HO[Nb]OH^+$	-56.4	-52.5	-46.2	-19.2		-48.6	-42.8	-36.0	-9.2	

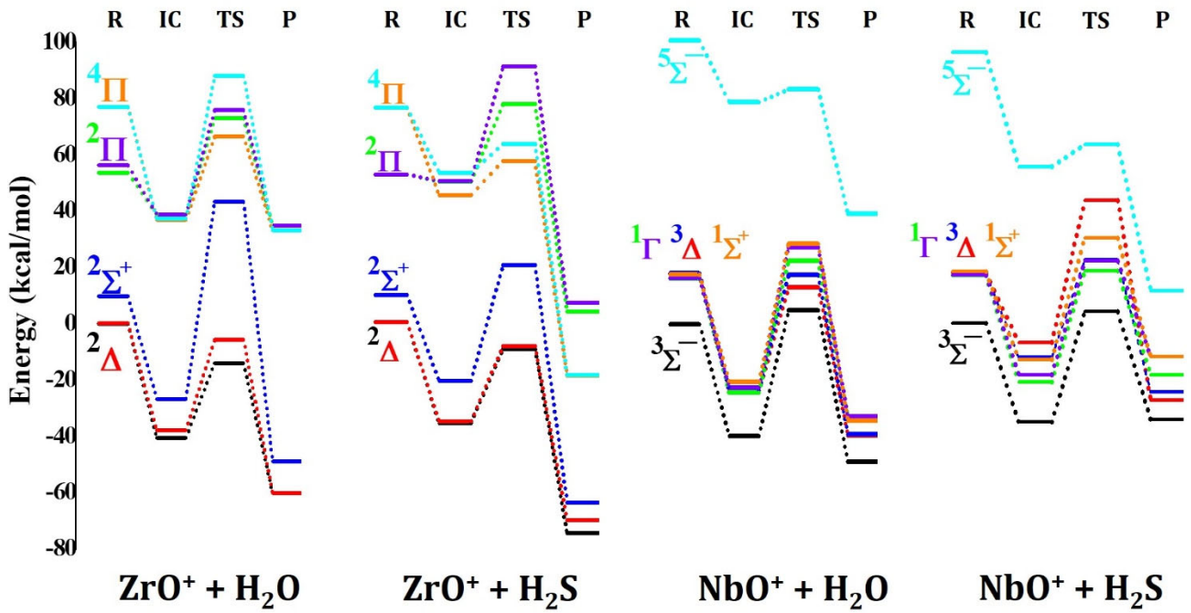

Figure S1. MRCI+Q//MRCI energy landscape of $MO^+ + H_2X \longrightarrow [HX-M-OH]^+$ (M = Zr, Nb and X = O, S) reactions. R, IC, TS, and P stands for the corresponding reactants ($MO^+ + H_2X$), interacting complex ($[H_2X...MO]^+$), transition states, and products $[HX-M-OH]^+$, respectively.

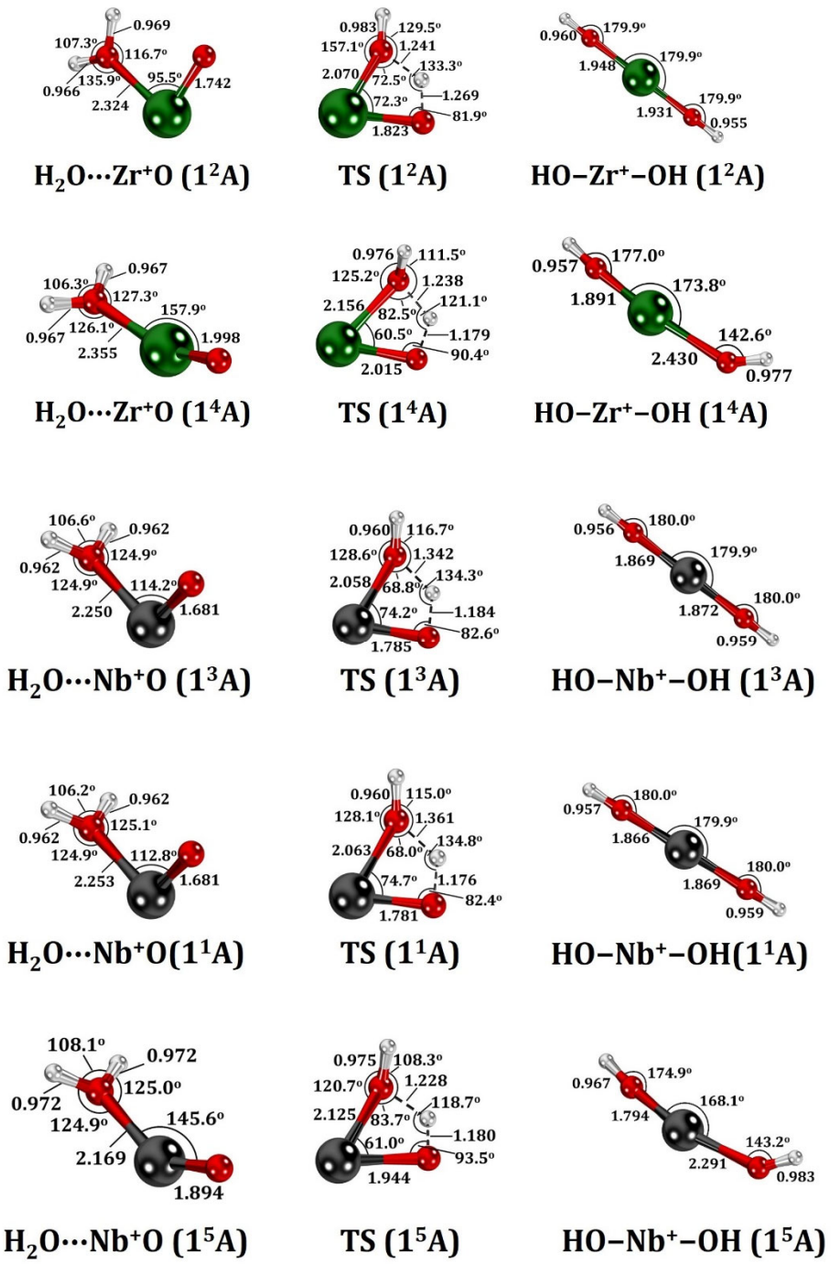

Figure S2. MRCI optimized structures for the ground and excited states for the $ZrO^+ + H_2O$ and $NbO^+ + H_2O$ reactions.

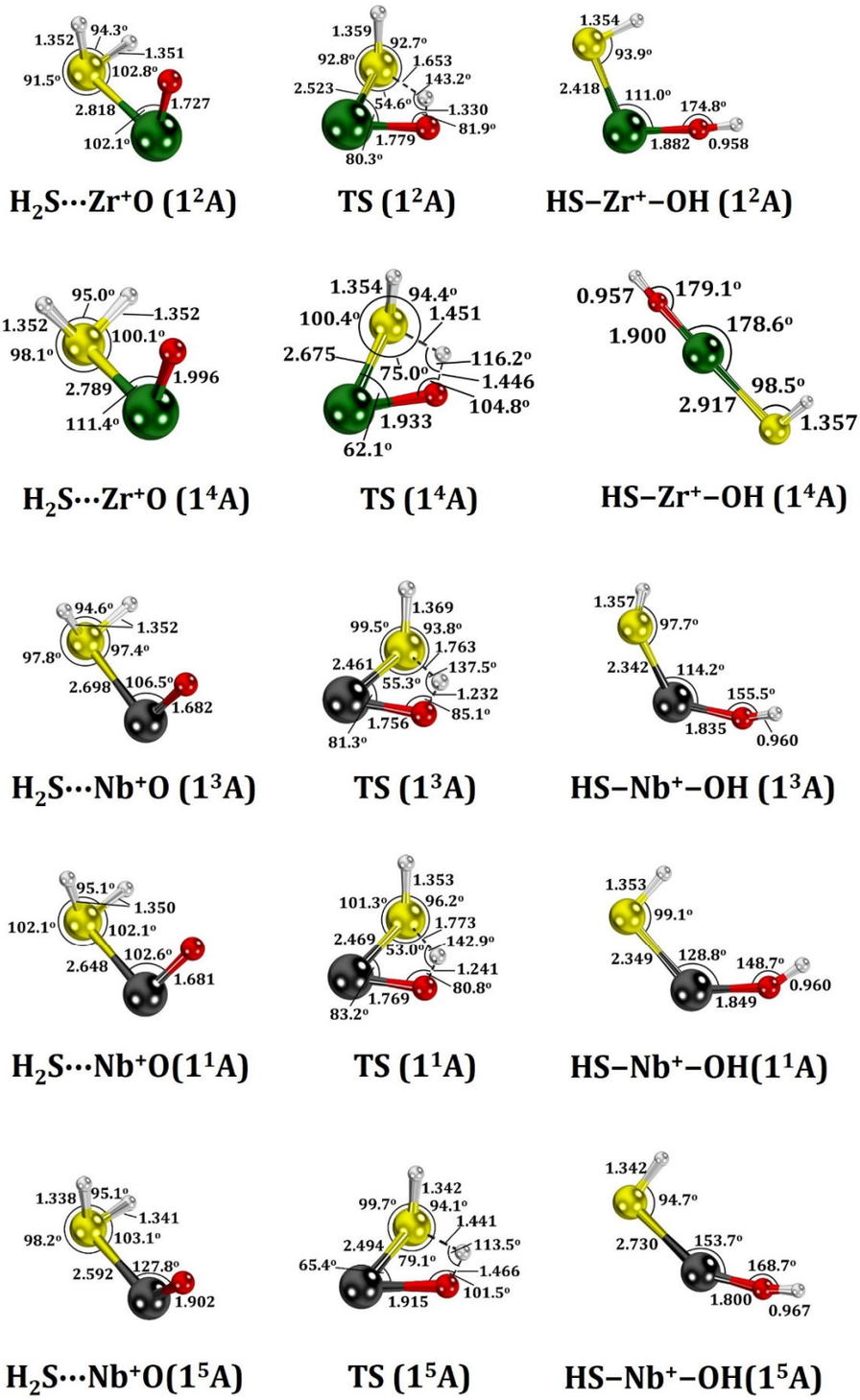

Figure S3. MRCI optimized structures for the ground and excited states for the $ZrO^+ + H_2S$ and $NbO^+ + H_2S$ reactions.

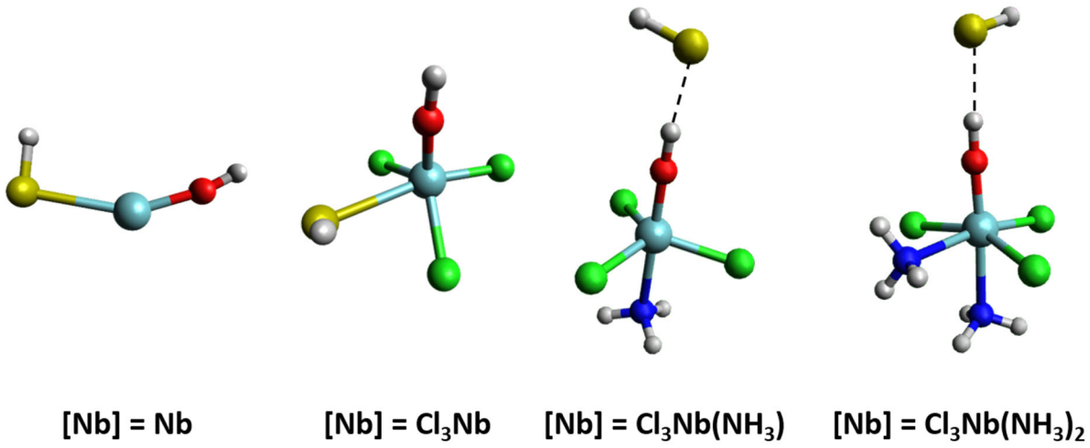

Figure S4. DFT/MN15 optimized structures for the ground state of the HS[Nb]OH products.

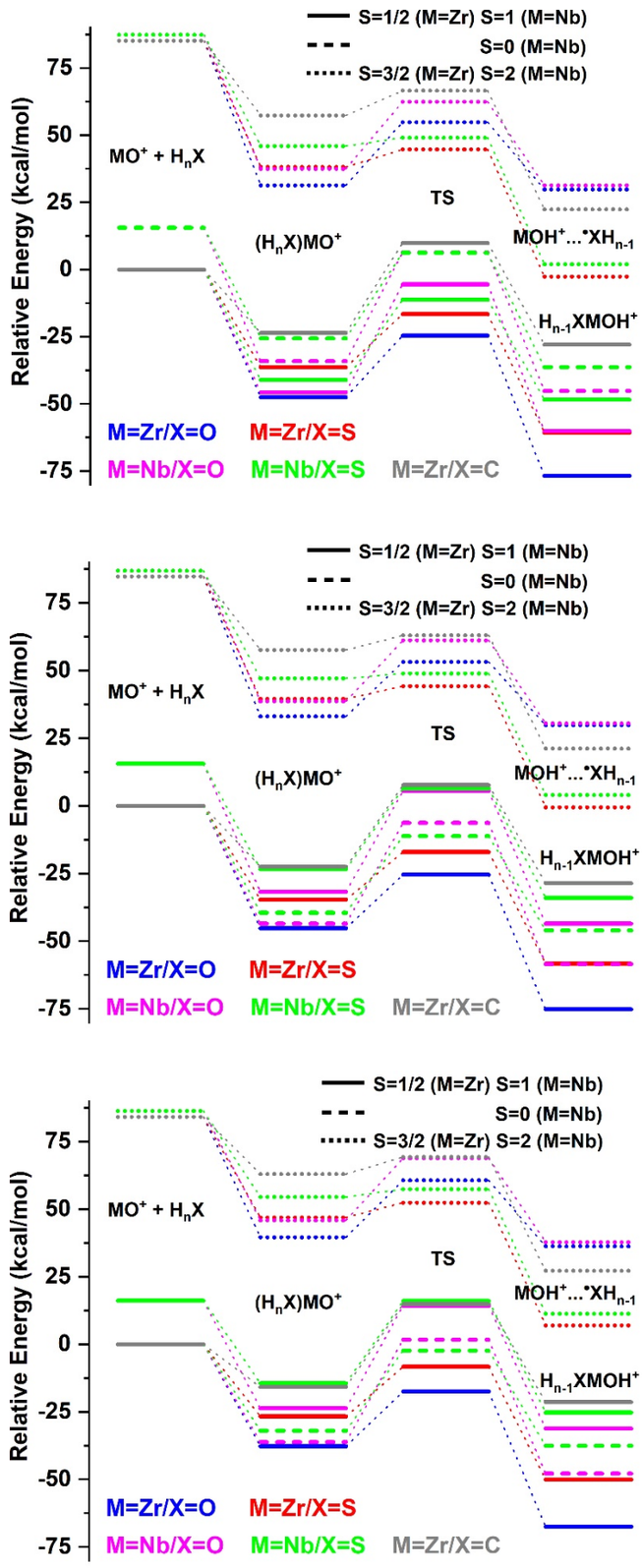

Figure S5. Energy diagrams (top: total energy; middle: ZPE-corrected energy; bottom: free energy at room temperature and 1 atm pressure) for the $ZrO^+/NbO^+ + H_2O/H_2S/CH_4$ reactions (n=2 except for X=C where n=4). The zero of the energy scale is set to the energy of the ground state fragments (compare to Figure 1 of the manuscript).

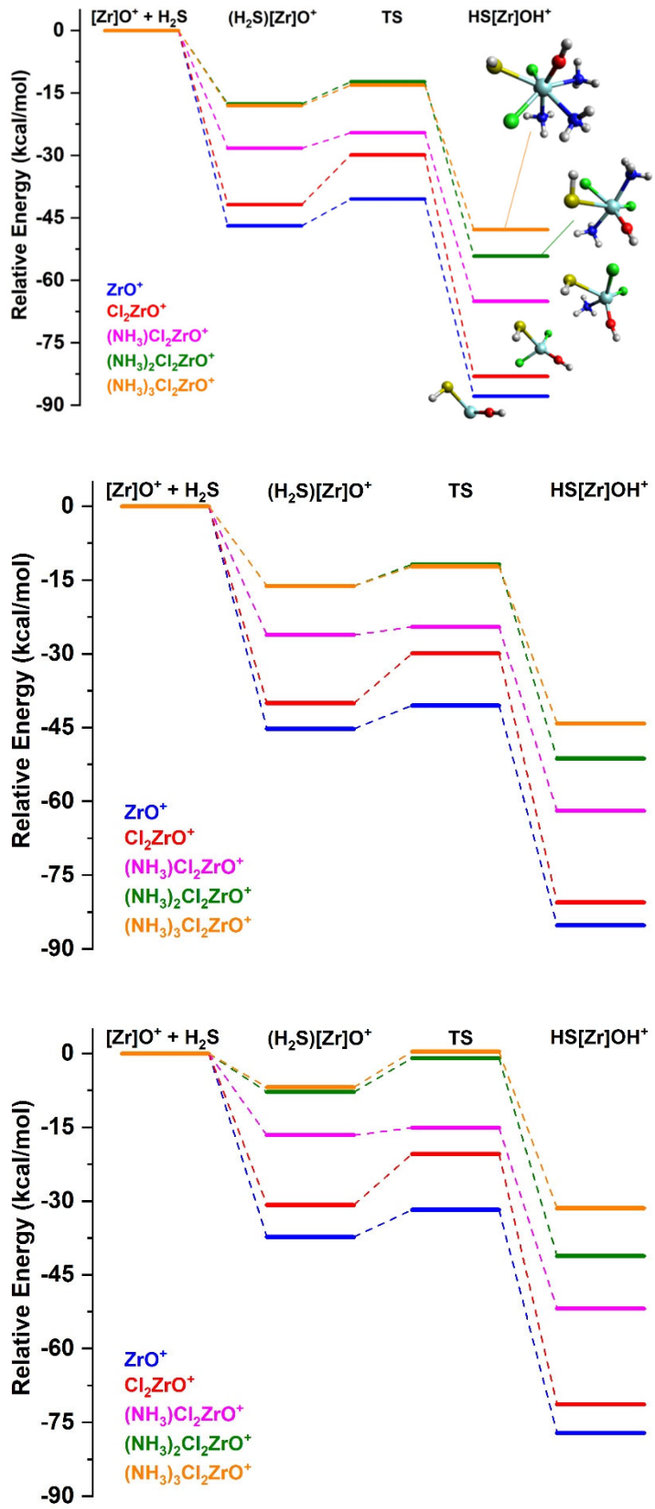

Figure S6. Energy diagrams (top: total energy; middle: ZPE-corrected energy; bottom: free energy at room temperature and 1 atm pressure) for the reaction of $[Zr]O^{\bullet+}$ (S=3/2 for ZrO and S=1/2 otherwise) with H_2S, where [Zr] represents the transition metal complex $(NH_3)_mCl_nZr$ (m,n = 0,0 ; 0,2; 1,2; 2,2; 3,2); compare to Figure 4 of the manuscript.