Supporting Information for

Thermochemical Studies of Re^+ Reactions with SO_2 using Guided Ion Beam Experiments and Theory

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References

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2. NIST Computational Chemistry Comparison and Benchmark Database, NIST Computational Chemistry Comparison and Benchmark Database, April 2018. Johnson III, R. D., http://cccbdb.nist.gov/ (accessed April 12, 2018).
3. Armentrout, P. B., The Bond Energy of ReO^+: Guided Ion-Beam and Theoretical Studies of the Reaction of Re^+ (^7S) with O_2. *J. Chem. Phys.* **2013,** *139*, 084305.

Table S1. Scaling factors for zero-point energies and frequencies in theoretical values.

	def2-TZVPPD	def2-QZVPPD	aug-cc-pVTZ	aug-cc-pVQZ	aug-cc-pV5Z
B3LYP	0.9885 [a]	0.9892 [b]	0.9896 [b]	0.9893 [b]	0.9893 [b]
BP86	1.0193 [a]	1.0192 [b]	1.0195 [b]	1.0192 [b]	1.0192 [b]
CCSD(T)	0.9868 [b]	0.9862 [b]	0.9868 [b]	0.9871 [b]	0.9871 [b]

[a] Taken directly from Ref. [1].

[b] Taken from similar levels in Ref. [1].

Table S2. Theoretical and experimental bond dissociation energies (eV), vibrational frequencies (cm^{-1}), rotational constants (cm^{-1}), and bond lengths (Å) of SO_2.

	Basis Set	B3LYP	BP86	CCSD(T)	Expt. [b]
D_0(OS-O)	def2-TZVPPD	5.26	5.85	5.29	5.66 ± 0.02
	def2-QZVPPD	5.31	5.89	5.50	
	aug-cc-pVTZ	4.95	5.56	5.07	
	aug-cc-pVQZ	5.14	5.73	5.39	
	aug-cc-pV5Z	5.31	5.88	5.58	
	CBS [a]			5.84	
D_0(S-O_2)	def2-TZVPPD	5.41	5.79	5.52	5.900 ± 0.004
	def2-QZVPPD	5.47	5.84	5.73	
	aug-cc-pVTZ	4.99	5.40	5.19	
	aug-cc-pVQZ	5.23	5.60	5.57	
	aug-cc-pV5Z	5.46	5.82	5.83	
	CBS [a]			6.15	
D_0(S-O)	def2-TZVPPD	5.40	6.00	5.06	5.36 ± 0.02
	def2-QZVPPD	5.43	6.01	5.22	
	aug-cc-pVTZ	5.28	5.88	5.00	
	aug-cc-pVQZ	5.37	5.95	5.20	
	aug-cc-pV5Z	5.43	6.02	5.31	
	CBS [a]			5.41	
Vibrational Frequency SO_2	def2-TZVPPD	513, 1163, 1360	498, 1127, 1326	507, 1159, 1371	518, 1151, 1362
	def2-QZVPPD	516, 1166, 1361	500, 1128, 1326	514, 1158, 1367	
	aug-cc-pVTZ	507, 1143, 1322	492, 1106, 1285	500, 1137, 1332	
	aug-cc-pVQZ	513, 1154, 1341	498, 1117, 1305	511, 1146, 1346	
	aug-cc-pV5Z	516, 1164, 1359	501, 1127, 1324	516, 1157, 1363	
Rotational Constant SO_2	def2-TZVPPD	1.989, 0.343, 0.292	1.945, 0.333, 0.284	1.989, 0.343, 0.292	2.027, 0.344, 0.294
	def2-QZVPPD	1.997, 0.344, 0.294	1.953, 0.334, 0.285	1.997, 0.344, 0.294	
	aug-cc-pVTZ	1.898, 0.340, 0.288	1.853, 0.330, 0.280	1.898, 0.340, 0.288	
	aug-cc-pVQZ	1.947, 0.343, 0.291	1.902, 0.333, 0.283	1.947, 0.343, 0.291	
	aug-cc-pV5Z	1.993, 0.344, 0.293	1.949, 0.334, 0.285	1.993, 0.344, 0.293	

Bond Length r(S-O), r(O-O)	def2-TZVPPD	1.438, 2.480	1.457, 2.516	1.438, 2.480	1.432
	def2-QZVPPD	1.435, 2.475	1.455, 2.511	1.435, 2.475	
	aug-cc-pVTZ	1.451, 2.491	1.472, 2.528	1.451, 2.491	
	aug-cc-pVQZ	1.442, 2.480	1.462, 2.517	1.442, 2.480	
	aug-cc-pV5Z	1.435, 2.475	1.455, 2.511	1.435, 2.475	

[a] Complete basis set limit obtained as discussed in the text. [b] Ref. [2].

Table S3. Theoretical calculations at various levels of theory for ReS^+.

State	Level	Basis Set	r(M-S) (Å)	E (E_h)	ω_e (cm^{-1}) [a]	D_0 (eV)	D_0 (eV) [b] incl S.O.
$^5\Pi$	B3LYP	def2-TZVPPD	2.087	-476.175726	505	3.52	3.67
		def2-QZVPPD	2.085	-476.190019	506	3.53	3.69
		aug-cc-pVTZ	2.086	-476.481417	505	3.51	3.67
		aug-cc-pVQZ	2.082	-476.486110	508	3.54	3.70
		aug-cc-pV5Z	2.079	-476.490347	510	3.57	3.73
	BP86	def2-TZVPPD	2.083	-476.300468	545	4.11	4.27
		def2-QZVPPD	2.082	-476.315115	545	4.13	4.29
		aug-cc-pVTZ	2.082	-476.601522	545	4.09	4.25
		aug-cc-pVQZ	2.078	-476.606435	546	4.13	4.28
		aug-cc-pV5Z	2.076	-476.611406	548	4.16	4.32
	CCSD(T)	def2-TZVPPD	2.087	-475.386981	514	3.02	3.18
		def2-QZVPPD	2.085	-475.470883	509	3.17	3.33
		aug-cc-pVTZ	2.086	-475.730400	511	3.04	3.19
		aug-cc-pVQZ	2.082	-475.809426	509	3.23	3.38
		aug-cc-pV5Z	2.069	-475.849155	525	3.31	3.47
		CBS [c]		-475.891214	525	3.42	3.58

Table S3. Theoretical calculations at various levels of theory for ReS^+ (Cont.).

State	Level	Basis Set	r(M-S) (Å)	E (E_h)	ω_e (cm^{-1}) [a]	E_{rel} (eV)	E_{rel} (eV) [b] incl S.O.
$^3\Sigma^-$	B3LYP	def2-TZVPPD	2.010	-476.162277	587	*0.37*	*0.52*
		def2-QZVPPD	2.009	-476.176582	587	*0.37*	*0.52*
		aug-cc-pVTZ	2.009	-476.467816	589	*0.37*	*0.53*
		aug-cc-pVQZ	2.005	-476.472922	590	*0.36*	*0.52*
		aug-cc-pV5Z	2.003	-476.477356	592	*0.35*	*0.51*
	BP86	def2-TZVPPD	2.012	-476.285501	612	*0.41*	*0.57*
		def2-QZVPPD	2.011	-476.299999	612	*0.41*	*0.57*
		aug-cc-pVTZ	2.011	-476.586164	614	*0.42*	*0.58*
		aug-cc-pVQZ	2.008	-476.591380	614	*0.41*	*0.57*
		aug-cc-pV5Z	2.006	-476.596503	615	*0.41*	*0.56*
	CCSD(T)	def2-TZVPPD	2.010	-475.369848	592	*0.47*	*0.62*
		def2-QZVPPD	2.009	-475.455045	590	*0.43*	*0.59*
		aug-cc-pVTZ	2.009	-475.714403	594	*0.44*	*0.59*
		aug-cc-pVQZ	2.005	-475.794645	594	*0.40*	*0.56*
		aug-cc-pV5Z	2.013	-475.834726	577	*0.39*	*0.55*
		CBS [c]		-475.877636	577	*0.37*	*0.53*

Table S3. Theoretical calculations at various levels of theory for ReS^+ (Cont.).

State	Level	Basis Set	r(M-S) (Å)	E (E_h)	ω_e (cm^{-1}) [a]	E_{rel} (eV)	E_{rel} (eV) [b] incl S.O.
$^3\Delta$	B3LYP	def2-TZVPPD	2.014	-476.154834	602	*0.57*	*0.41*
		def2-QZVPPD	2.013	-476.169204	601	*0.57*	*0.41*
		aug-cc-pVTZ	2.013	-476.459749	603	*0.59*	*0.43*
		aug-cc-pVQZ	2.009	-476.464963	604	*0.58*	*0.42*
		aug-cc-pV5Z	2.007	-476.469408	606	*0.57*	*0.41*
	BP86	def2-TZVPPD	2.018	-476.280343	616	*0.55*	*0.39*
		def2-QZVPPD	2.017	-476.294960	615	*0.55*	*0.39*
		aug-cc-pVTZ	2.017	-476.580563	617	*0.57*	*0.41*
		aug-cc-pVQZ	2.014	-476.585919	617	*0.56*	*0.40*
		aug-cc-pV5Z	2.012	-476.591087	618	*0.55*	*0.40*
	CCSD(T)	def2-TZVPPD	2.014	-475.359860	597	*0.74*	*0.58*
		def2-QZVPPD	2.013	-475.445125	593	*0.70*	*0.54*
		aug-cc-pVTZ	2.013	-475.702781	597	*0.75*	*0.59*
		aug-cc-pVQZ	2.009	-475.784662	597	*0.67*	*0.52*
		aug-cc-pV5Z	2.007	-475.825732	596	*0.64*	*0.48*
		CBS [c]		-475.867933	596	*0.63*	*0.48*

[a] Vibrational frequency scaled by factors indicated in Table S1. [b] Bond dissociation energy (roman) or relative energy to ground state (italic). [c] Complete basis set limit obtained as discussed in the text.

Table S4. Various states of $ReSO_2^+$ calculated at the B3LYP/def2-TZVPPD level of theory

State	Species	r(Re-S) (Å)	r(Re-O) (Å)	r(Re-O) (Å)	r(S-O) (Å)	r(S-O) (Å)	∠OReS (°)	∠SReO (°)	∠OReSO (°)	ω_e (cm^{-1}) [a]	E (E_h)	E_{rel} (eV) [b]	E_{rel} (kJ/mol) [b]
	Re^+ (^7S) + SO_2 ($^1A_1$)				1.438	1.438				513, 1163, 1360	-626.632496	0.00	0.0
	Re^+ (^5D) + SO_2 ($^1A_1$)				1.438	1.438				513, 1163, 1360	-626.554407	2.12	205.0
	Re^+ (^3H) + SO_2 ($^1A_1$)				1.438	1.438				513, 1163, 1360	-626.523466	2.97	286.3
$^7A'$	Re^+OSO $^71'$	3.824	2.466	4.285	1.469	1.426	10.4	19.2	180.0	52, 103, 148, 513, 1109, 1336	-626.659134	-0.72	-69.9
^7A	^{7}TS1′/1	3.030	1.889	2.961	1.688	1.475	30.1	28.5	152.8	-83, 125, 400, 536, 606, 1125	-626.646218	-0.37	-36.0
$^7A''$	Re^+O_2S ^{71}	2.891	1.915	2.540	1.667	1.499	33.4	31.2	180.0	106, 126, 399, 640, 657, 1067	-626.646979	-0.39	-38.0
$^7A''$	^{7}TS1/2	2.638	1.784	3.124	2.362	1.481	61.0	28.2	180.0	-211, 64, 95, 252, 784, 1083	-626.590400	1.15	110.5
^7A	ORe^+SO ^{72}	2.611	1.695	3.388	4.181	1.484	151.6	24.5	83.1	76, 105, 156, 198, 989, 1095	-626.628486	0.11	10.5
$^7A''$	^{7}TS1/3	3.424	1.717	2.839	2.576	1.482	46.9	25.2	180.0	-190, 74, 90, 235, 847, 1123	-626.618506	0.38	36.7
^7A	ORe^+OS ^{73}	3.532	1.695	2.175	4.948	1.509	139.7	13.7	121.2	70, 112, 126, 290, 999, 1109	-626.658471	-0.71	-68.2
^7A	^{7}TS3/4	2.786	1.668	1.889	4.140	2.805	135.2	70.8	125.9	-138, 123, 137, 197, 576, 1026	-626.582994	1.35	130.0

^{7}A	S$Re^{+}O_2$ ^{7}4	2.514	1.670	1.966	3.689	2.734	122.4	74.1	120.6	131, 156, 186, 237, 522, 1015	-626.584502	1.31	126.0
^{5}A	Re^{+}OSO ^{5}1′	2.495	1.899	3.314	1.651	1.438	41.4	23.7	101.1	125, 266, 395, 555, 738, 1253	-626.659504	-0.74	-70.9
^{5}A	^{5}TS1′/3	2.311	1.808	1.960	2.111	1.623	60.2	43.7	129.0	-519, 203, 281, 460, 784, 799	-626.620643	0.32	31.1
^{5}A	ORe^{+}OS ^{5}3	2.427	1.665	2.015	3.787	1.598	134.6	40.9	111.0	139, 183, 309, 477, 883, 1046	-626.703759	-1.94	-187.1
^{5}A	^{5}TS3/4	2.428	1.678	1.787	3.526	2.136	117.2	58.6	125.4	-415, 79, 246, 332, 813, 1033	-626.660721	-0.77	-74.1
^{5}B$_2$	S$Re^{+}O_2$ ^{5}4	2.611	1.684	1.684	3.748	3.748	119.9	120.0	180.0	77, 78, 215, 322, 972, 1050	-626.690774	-1.59	-153.0
^{3}A	Re^{+}OSO ^{3}1′	2.423	1.776	3.273	1.809	1.434	48.1	23.7	99.7	168, 287, 309, 403, 829, 1277	-626.620066	0.34	32.6
^{3}A	^{3}TS1′/1	2.258	1.938	2.526	1.631	1.491	44.9	35.8	115.3	-235, 336, 386, 477, 788, 1058	-626.619496	0.35	34.1
^{3}A″	$Re^{+}O_2$S ^{3}1	2.219	2.000	2.000	1.593	1.592	44.0	44.0	121.0	324, 386, 434, 481, 831, 849	-626.635034	-0.07	-6.7
^{3}A	^{3}TS1/3	2.309	1.814	1.958	1.931	1.588	54.3	42.7	124.1	-361, 334, 390, 492, 785, 860	-626.627245	0.14	13.8
^{3}A	ORe^{+}OS ^{3}3	2.290	1.670	1.958	3.581	1.619	128.8	43.9	112.9	123, 193, 338, 480, 853, 1044	-626.716886	-2.30	-221.6
^{3}A	^{3}TS3/4	2.296	1.669	1.742	3.460	2.056	120.8	59.3	105.0	-672, 166, 246, 388, 871, 1045	-626.689886	-1.56	-150.7
^{3}A″	S$Re^{+}O_2$ ^{3}4	2.237	1.677	1.677	3.267	3.269	112.4	112.5	131.4	150, 167, 302, 436, 999, 1054	-626.753620	-3.30	-318.0
ReO^{+} ($^{5}\Pi$) [c] + SO ($^{3}\Sigma^{-}$)			1.679			1.489				1015 (ReO^{+}) 1145 (SO)	-626.601301	0.69	66.7

$OReS^+$ ($^5A''$) + O (^3P)	2.260	1.663				126.6		161, 398, 1038	-626.528780	2.81	271.4
$ReOS^+$ ($^5A'$) + O (^3P)	2.232	1.889		1.688		47.5		393, 548, 790	-626.502969	3.51	339.1
ReO^+ ($^3\Delta$) [c] + SO ($^3\Sigma^-$)		1.613			1.489			1157 (ReO^+) 1145 (SO)	-626.600099	0.57	54.6
ReO_2^+ ($^3B_1$) [c] + S (^3P)		1.669	1.669					348, 994, 1074	-626.617104	0.39	38.1
$OReS^+$ ($^3A''$) + O (^3P)	2.077	1.667				111.1		276, 560, 1027	-626.576606	1.51	145.8
ReS^+ ($^5\Pi$) + O_2 ($^3\Sigma^-$)	2.087							505 (ReO^+) 1618 (O_2)	-626.562822	1.74	167.7
ReS^+ ($^5\Pi$) + 2O (^3P)	2.087							505	-626.369683	6.97	672.9

[a] Vibrational frequencies scaled by 0.9885, Table S1.

[b] Energy relative to the ground reactant state: Re^+ ($^7S_3$) + SO_2 ($^1A_1$).

[c] Ref. [3]