Supplementary Material (ESI) for PCCP

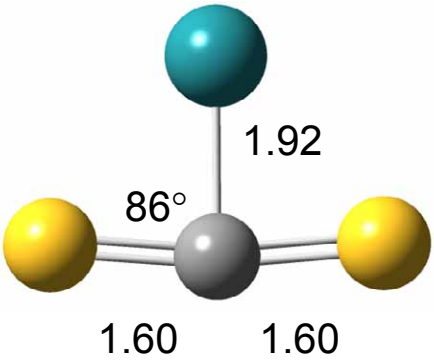
Supplementary Information for

Guided Ion Beam and Theoretical Studies of the Reaction of Ru^+ with CS_2 in the Gas-phase: Thermochemistry of RuC^+, RuS^+, and $RuCS^+$

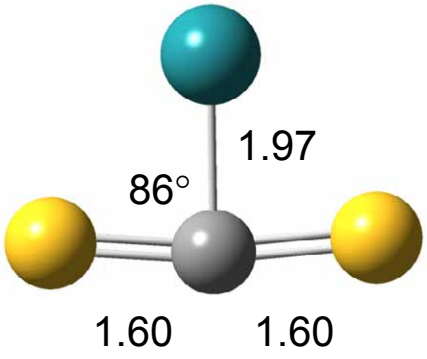
By P. B. Armentrout and Ilona Kretzschmar

Figure S1. Doublet spin intermediates, transition states, and products calculated at the B3LYP/Def2TZVPP level of theory in the order of the reaction coordinate diagram of Figure 1. Bond lengths are shown in Å. All species are planar. Atoms are color coded as ruthenium – blue, carbon – grey, and sulfur – yellow.

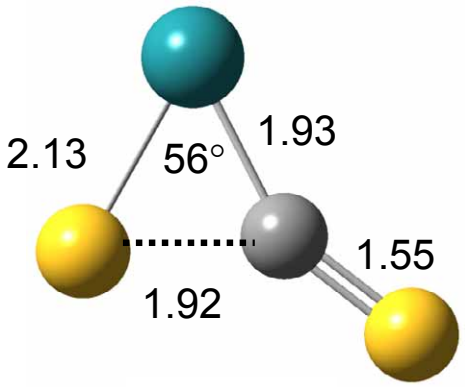
Figure S2. Reaction coordinate diagram for reaction of Ru^+ in quartet (blue line) , sextet (red line), and doublet (light green – A′, dark green – A″) states with CS_2 for dissociation of the $SRu^+(CS)$ intermediates into the products of reactions 1 – 3 along the path where the RuS bond is broken first. All energies are calculated at the CCSD(T)//B3LYP level including zero point energies. The large dot indicates a crossing point between the quartet and sextet surfaces.



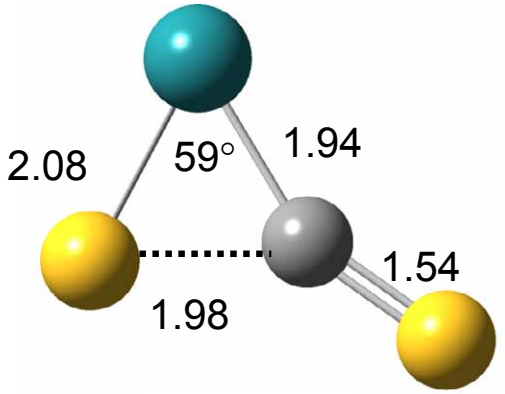
$Ru^{+}(SCS)\ ^{2}A_{2}$



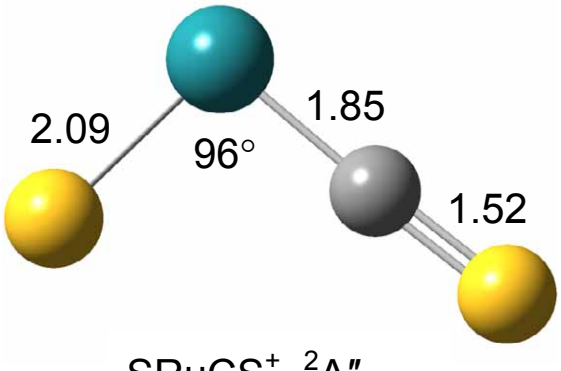
$Ru^{+}(SCS)\ ^{2}A_{1}$



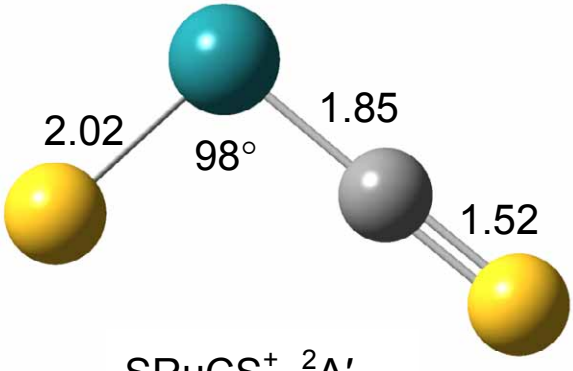
TS $^{2}A''$



TS $^{2}A'$

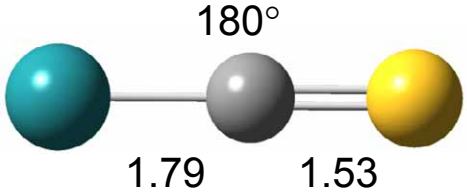


$SRuCS^{+}\ ^{2}A''$



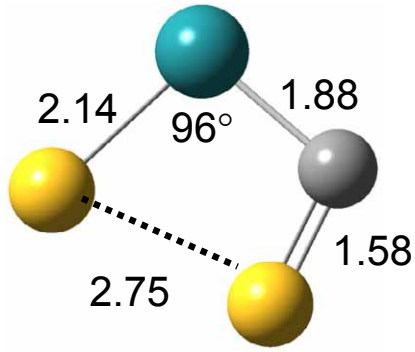
$SRuCS^{+}\ ^{2}A'$

$RuS^{+}\ ^{2}\Pi$

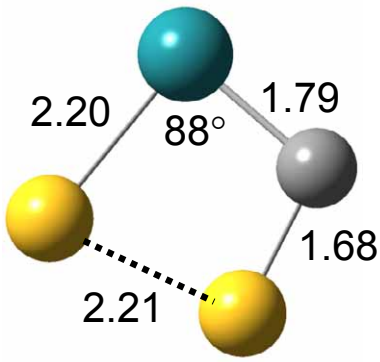


$Ru^{+}(CS)\ ^{2}\Delta$

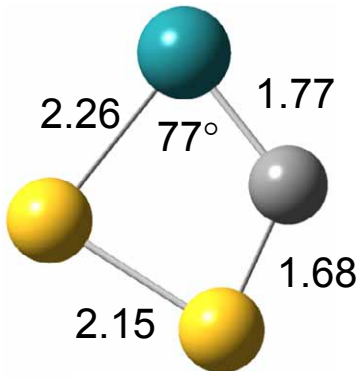
Figure S1



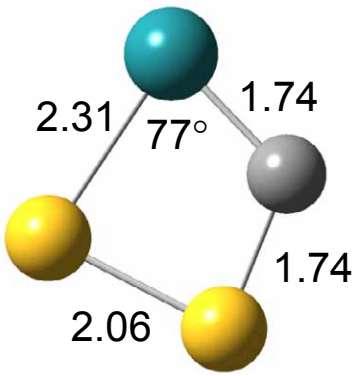
TS_{SS} $^2A''$



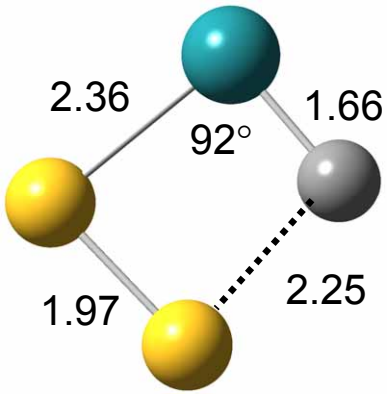
TS_{SS} $^2A'$



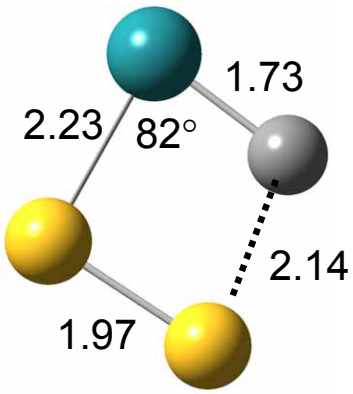
c-RuCSS $^2A''$



c-RuCSS $^2A'$

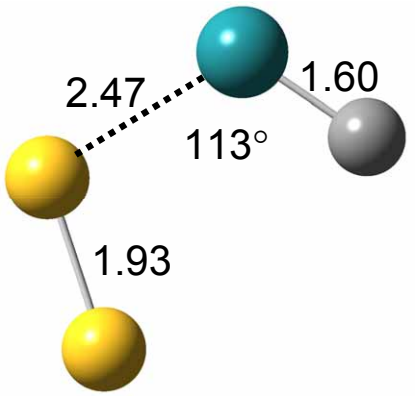


TS_{CS} $^2A''$

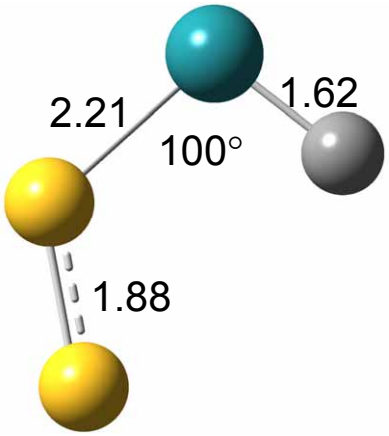


TS_{CS} $^2A'$

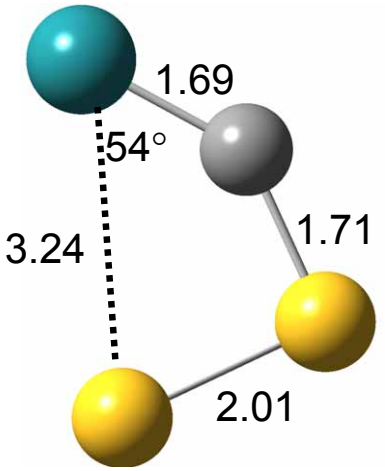
Figure S1



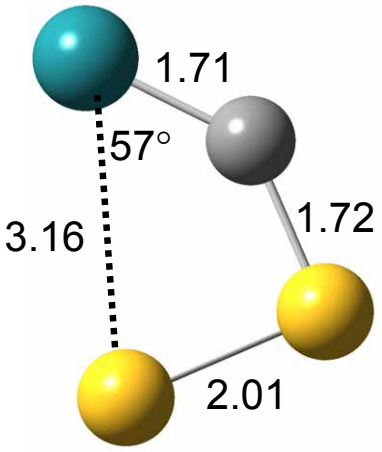
$CRu^{+}(SS)\ {}^{2}A''$



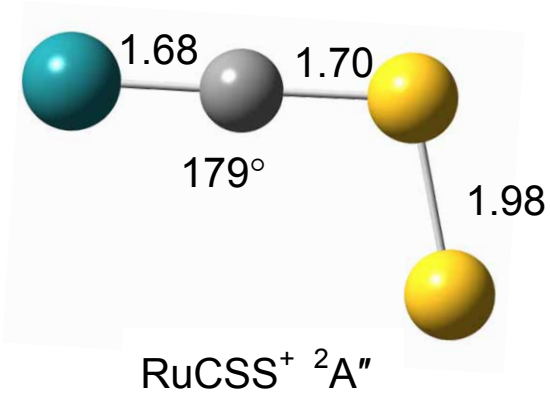
$CRu^{+}(SS)\ {}^{2}A'$



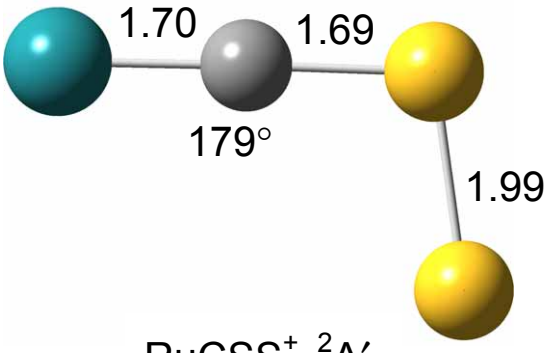
$TS_{RuS}\ {}^{2}A''$



$TS_{RuS}\ {}^{2}A'$



$RuCSS^{+}\ {}^{2}A''$



$RuCSS^{+}\ {}^{2}A'$

Figure S1

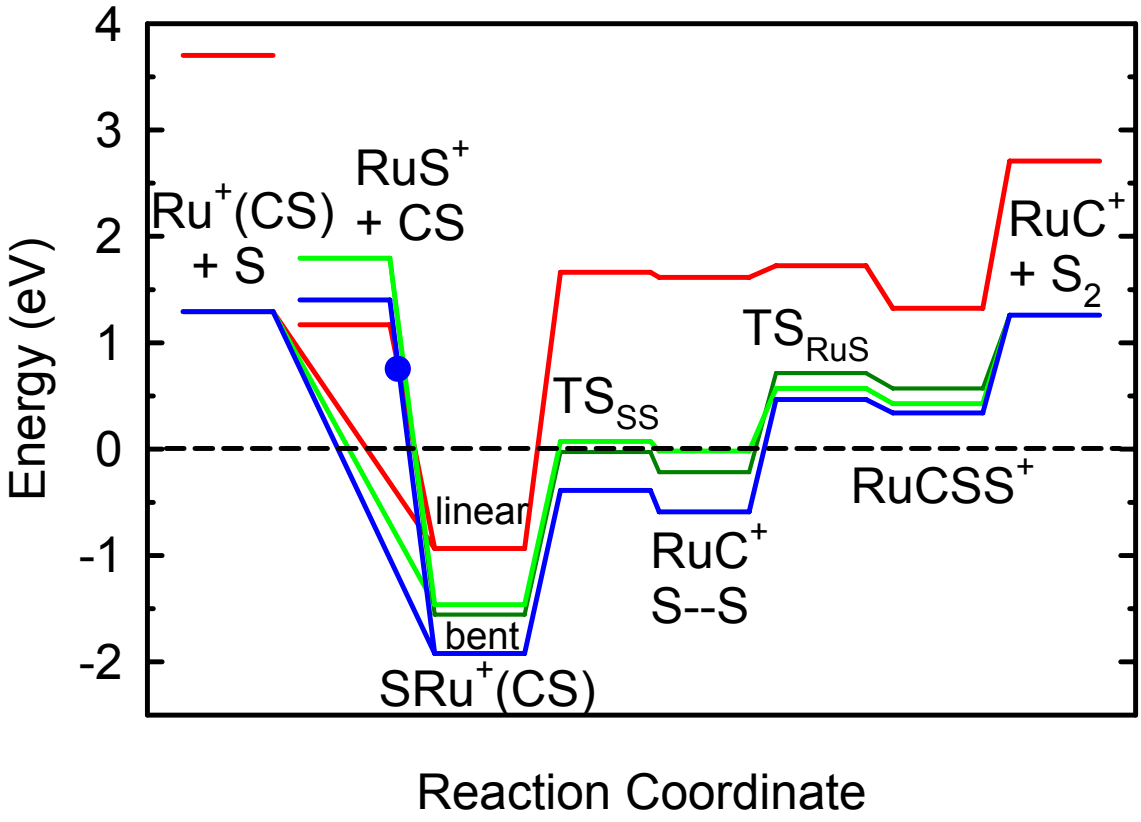


Figure S2

TABLE S1: Geometric Parameters, Vibrational Frequencies, and Relative Energies for Reactants, Products, Intermediates, and Transition States for Reaction of Ru^+ with CS_2[a]

species	state	*r*(Ru-S) Å	*r*(Ru-C) Å	*r*(C-S), Å *r*(S-S), Å	∠RuSC, ° ∠SRuC, ° ∠CSS, °	∠SCS, ° ∠RuCS, ° ∠RuSS, °	ν cm^{-1}	E_{rel}[b] eV
$Ru^+ + CS_2$	^4F			1.553 (2)[c]		180.0 [d]	408 (2), 678, 1561	0.000 (0.000)
$Ru^+(SCS)$	$^4B_1$	2.554 (2)	2.020	1.594 (2)[c]	52.3 (2) [d]	178.2 [d]	104, 200, 493, 533, 629, 1356	-1.932 (-1.902)
	$^2A_1$	2.440 (2)	1.966	1.595 (2)[c]	53.5 (2) [d]	171.7 [d]	237, 245, 385, 476, 675, 1380	-1.473 (-1.441)
	$^2A_2$	2.408 (2)	1.923	1.598 (2)[c]	52.8 (2) [d]	171.5 [d]	195, 237, 259, 487, 688, 1375	-1.244 (-1.258)
	$^2A_1$	2.518 (2)	1.992	1.596 (2)[c]	52.3 (2) [d]	176.8 [d]	162, 201, 356, 525, 540, 1368	-1.205 (-1.178)
	$^2B_2$	2.670 (2)	2.141	1.580 (2)[c]	72.6 [d]	179.1 [d]	57, 157, 382, 422, 631, 1425	-0.348 (-0.551)
	$^6A'_a$	2.366 (2)	2.084	1.690 (2)[c]	59.1 (2) [d]	136.3 [d]	212, 242, 316, 357, 668, 977	0.073 (0.007)
	$^6A'_b$	2.467	2.099	1.607 [c] 1.684 [c]	57.1 [d]	133.4 [d]	119, 213, 259, 333, 674, 1021	0.731 (0.162)
	$^4B_2$	2.989 (2)	1.983	1.647 (2)[c]	38.4 (2) [d]	139.0 [d]	-79, 16, 177, 459, 763, 834	0.767 (0.559)
$SRuCS^+$ (TS)	$^4A''$	2.126	1.932	1.539,[c] 2.001 [c]	55.7, [d] 58.9 [e]	137.0,[d] 157.6 [e]	-338, 195, 314, 391, 503, 1303	-1.304 (-1.311)
	$^2A''$	2.129	1.931	1.546,[c] 1.925 [c]	56.6, [d] 56.4 [e]	138.0, [d] 155.0 [e]	-312, 184, 321, 396, 503, 1276	-0.632 (-0.839)
	$^2A'$	2.078	1.936	1.540,[c] 1.981 [c]	56.9, [d] 59.0 [e]	139.8, [d] 156.1 [e]	-357, 193, 304, 388, 512, 1289	-0.571 (-0.643)
	^6A	2.228	2.111	1.543,[c] 2.127 [c]	57.9, [d] 58.6 [e]	117.9, [d] 178.7 [e]	-407, 141, 158, 234, 380, 1221	0.636 (0.535)

	$^4A'$	2.327	1.995	1.557,[c] 2.011[c]	54.2,[d] 54.8[e]	125.4,[d] 163.6[e]	-379, 156, 261, 306, 350, 1174	1.070 (1.008)
$SRu^+(CS)$	$^4A''$	2.083	1.862	1.516[c]	95.1[e]	176.9[e]	102, 295, 345, 416, 503, 1406	-1.921 (-1.939)
	$^2A''$	2.090	1.848	1.518[c]	95.8[e]	177.7[e]	104, 298, 349, 422, 488, 1402	-1.642 *-1.555*
	$^2A'$	2.015	1.853	1.518[c]	97.5[e]	179.3[e]	106, 249, 302, 402, 559, 1397	-1.450 (-1.462)
	$^6\Sigma^+$	2.196	2.093	1.506[c]	180.0[e]	180.0[e]	69 (2), 252, 290 (2), 379, 1412	-0.934 (-0.769)
	$^6A'$ CP1	2.170	2.116	1.506[c]	156[e]	173[e]	-34, 190, 252, 268, 406, 1404	-0.792 (-0.649)
	$^4A''$ CP1	2.091	2.140	1.504[c]	163[e]	178[e]	-107, 84, 158, 257, 433, 1416	-0.641 (-0.646)
	$^4A'$	2.105	2.033	1.511[c]	126.4[e]	167.9[e]	45, 236, 240, 290, 408, 1370	-0.547 (-0.593)
	$^4\Phi$ ($^4A''$)	2.102	2.184	1.502[c]	180.0[e]	180.0[e]	-126, 27, 155, 234, 240, 417, 1429	-0.589 (-0.559)
	$^4\Delta$	2.122	2.100	1.509[c]	180.0[e]	180.0[e]	93(2), 239, 433, 1075 (2), 1390	-0.198 (-0.276)
	$^2\Delta$	2.028	2.189	1.504[c]	180.0[e]	180.0[e]	-161, -105, 151, 195, 229, 554, 1415	-0.208 (0.206)
	$^4A''$ CP2	2.056	3.262	1.509[c]	155[e]	178[e]	-82, -68, 24, 153, 457, 1390	0.412 (0.485)
TS_{SS}	$^4A''$	2.191	1.804	1.599[c] 2.463[f]	76.1[e]	129.5[e]	-336, 228, 304, 392, 652, 1009	-0.387 (-0.345)
	$^2A''$	2.136	1.878	1.584,[c] 2.748[f]	96.0[e]	104.8[e]	-200, -55, 205, 430, 556, 1011	-0.027 (0.280)
	$^2A'$	2.196	1.786	1.683[c] 2.208[f]	88.4[e]	104.1[e]	-193, 113, 261, 370, 659, 764	0.074 (0.093)

	^{6}A	2.262	1.890	1.692,[c] 2.239[f]	79.3[e]	105.0[e]	-373, 175, 268, 305, 608, 755	1.663 (1.677)
c-RuCSS$^+$	^{4}A″	2.280	1.780	1.674[c] 2.139[f]	77.7[e]	115.5[e]	212, 224, 309, 407, 721, 848	-0.590 (-0.502)
	^{2}A″	2.256	1.772	1.679[c] 2.146[f]	76.8[e]	117.3[e]	228, 254, 303, 405, 730, 842	-0.216 (-0.161)
	^{2}A′	2.307	1.738	1.742[c] 2.062[f]	77.4[e]	114.3[e]	208, 226, 229, 450, 674, 877	-0.017 (0.051)
	^{6}A	2.302	1.872	1.754[c] 2.098[f]	78.2[e]	105.3[e]	113, 221, 259, 427, 548, 727	1.615 (1.668)
	^{6}A″	2.331	1.862	1.774[c] 2.067[f]	77.6[e]	110.2[e]	-97, 182, 247, 477, 621, 741	1.703 (1.685)
TS_{CS}	^{2}A′	2.229	1.727	2.144[c] 1.967[f]	82.4[e] 79.5[g]	104.4[e] 93.8[g]	-352, 190, 277, 330, 581, 798	0.124 (0.368)
	^{4}A″	2.396	1.646	2.417[c] 1.968[f]	94.6[e] 86.2[g]	93.1[e] 86.2[g]	-269, 89, 208, 266, 598, 971	0.211 (0.250)
	^{2}A″	2.360	1.660	2.254[c] 1.975[f]	92.3[e] 87.8[g]	84.4[e] 95.5[g]	-370, -10, 214, 284, 585, 949	0.374 (0.418)
	^{6}A′	2.550	1.763	2.228[c] 2.017[f]	103.8[e] 107.7[g]	80.3[e] 68.2[g]	-355, 130, 137, 227, 555, 770	1.953 (2.115)
CRu^+(SS)	^{4}A′	2.455 (2)	1.614	1.978[f]	112.6 (2)[e]	66.3 (2)[g]	134, 183, 225, 239, 615, 1101	-0.367 (-0.307)
	^{2}A′	2.214	1.618	1.882[f]	100.3[e]	121.4[g]	118, 127, 270, 308, 701, 1079	-0.013 (-0.099)
	^{4}A″	2.467	1.602	1.928[f]	113.2[e]	104.9[g]	-14, 78, 149, 232, 649, 1131	0.012 (0.036)
	^{2}A″$_a$	2.337	1.603	1.906[f]	105.9[e]	120.0[g]	-37, 100, 219, 245, 671, 1127	0.122 (-0.003)
	^{2}A	2.268	1.614	1.891[f]	101.6[e]	119.4[g]	96, 120, 214, 264, 696, 1091	0.148 (0.123)
	^{2}A″$_b$	2.468	1.603	1.929[f]	113.1[e]	104.5[g]	14, 78, 151, 231, 644, 1128	0.294 (0.243)

	$^6A'$	2.492	1.697	1.957 [f]	128.7 [e]	61.9 [e]	78, 101, 149,	1.700
					89.5 [g]	79.9 [g]	216, 641, 913	(1.803)
TS_{RuS}	$^4A''$	3.301	1.712	1.706 [c]	53.6 [e]	143.7 [e]	-117, 216, 273,	0.466
				1.995 [f]	91.9 [g]	70.8 [g]	499, 563, 978	(0.283)
	$^2A'$	3.165	1.706	1.725 [c]	56.6 [e]	140.1 [e]	-119, 193, 262,	0.570
				2.006 [f]	89.9 [g]	73.3 [g]	496, 568, 1006	(0.405)
	$^2A''$	3.245	1.691	1.706 [c]	54.4 [e]	143.5 [e]	-119, 224, 272,	0.715
				2.005 [f]	90.6 [g]	71.5 [g]	491, 565, 1058	(0.624)
	^6A	2.539	1.830	1.775 [c]	72.7 [e]	112.9 [e]	-695, 126, 129,	1.725
				2.024 [f]	88.3 [g]	81.5 [g]	508, 603, 657	(1.710)
$RuCSS^+$	$^4A''$		1.708	1.689 [c]	102.4 [g]	179.8 [e]	72, 228, 316,	0.340
				1.978 [f]			422, 534, 1029	(0.115)
	$^2A'$		1.700	1.695 [c]	99.7 [g]	179.2 [e]	74, 242, 314,	0.427
				1.995 [f]			417, 517, 1072	(0.202)
	$^2A''$		1.684	1.697 [c]	103.1 [g]	179.3 [e]	76, 235, 322,	0.570
				1.980 [f]			432, 528, 1071	(0.418)
	$^6A'$		1.851	1.616 [c]	110.0 [g]	166.0 [e]	55, 253, 309,	1.324
				2.041 [f]			378, 384, 1090	(1.140)
RuS^+	$^6\Sigma^+$ +	2.121					466	1.169
+ CS	$^1\Sigma^+$			1.532 [c]			+ 1311	(1.377)
$RuCS^+$	$^4\Sigma^-$ +		1.878	1.517 [c]		180.0 [e]	270 (2), 377,	1.293
+ S	^3P						1417	(1.425)
RuC^+	$^2\Delta$ +		1.590				1156	1.260
+ S_2	$^3\Sigma^-$			1.904 [f]			+ 715	(1.290)

[a] All geometrical parameters are calculated at the B3LYP/Def2TZVPP level of theory. [b] Relative energies calculated at CCSD(T)/Def2TZVPP//B3LYP/Def2TZVPP (B3LYP/Def2TZVPP) levels of theory, corrected for zero point energies. Absolute calculated energies for the ground state $Ru^+ + CS_2$ asymptote are 927.832727 (929.112010) E_h, including zero point energies. [c] r(C-S). [d] ∠RuSC and ∠SCS. [e] ∠SRuC and ∠RuCS. [f] r(S-S). [g] ∠CSS and ∠RuSS.