Supporting Information for

Experimental and theoretical study of the Sn – O bond formation between atomic tin and molecular oxygen

Iakov A. Medvedkov, [§] *Anatoliy A. Nikolayev,*[†] *Shane Goettl,*[§] *Zhenghai Yang,*[§] *Alexander M. Mebel,* [‡*] *Ralf I. Kaiser*[§*]

[§] Department of Chemistry, University of Hawai‘i at Manoa, Honolulu, HI 96822, USA

[†] Samara National Research University, Samara 443086, Russia

[‡] Department of Chemistry and Biochemistry, Florida International University, Miami, Florida 33199, USA

Corresponding to: ralfk@hawaii.edu; mebela@fiu.edu

Keywords: crossed molecular beams, intersystem crossing, reaction dynamics, tin

Contents

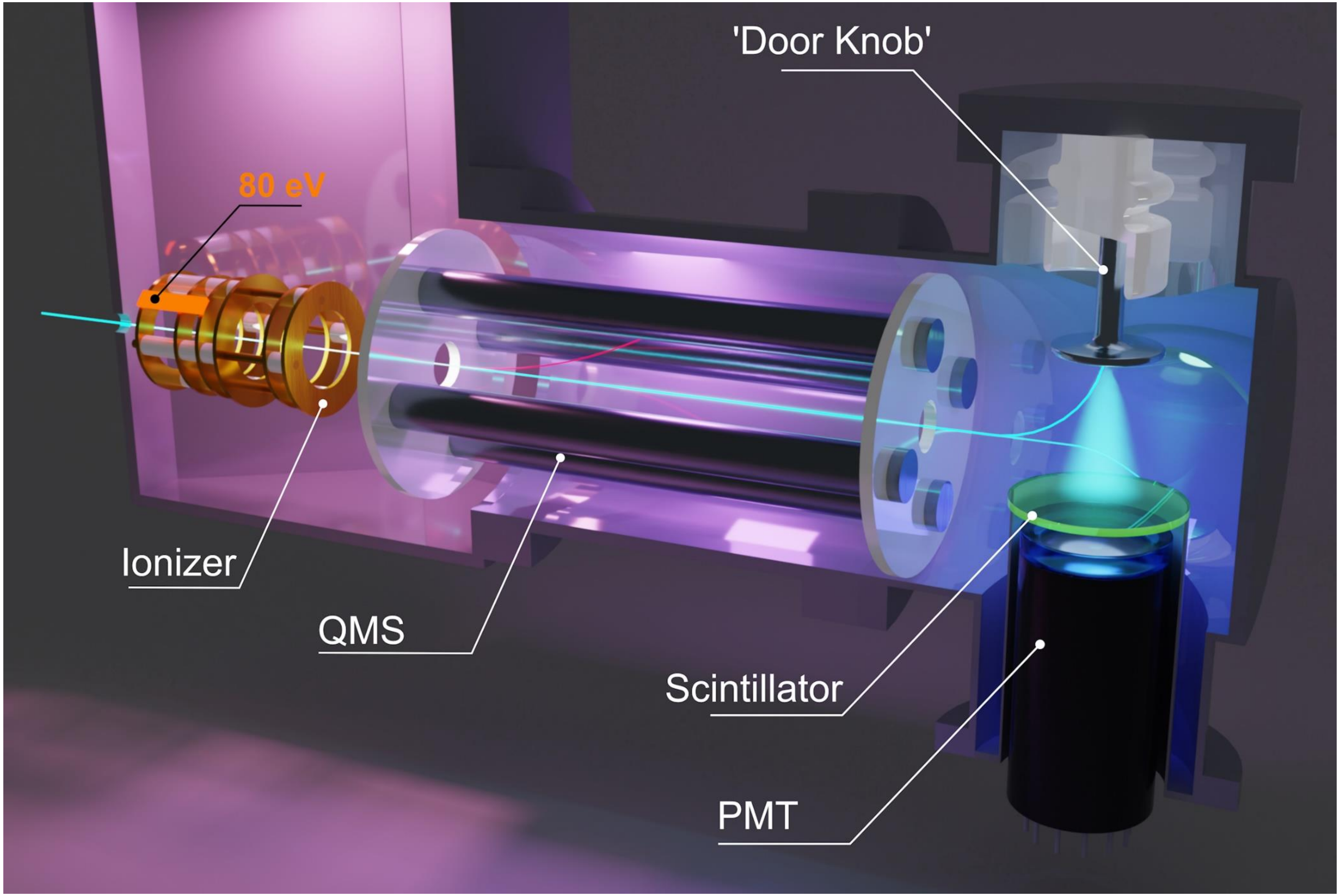


Figure S1. Schematic view of the 'Universal' detector. The reactively scattered products were ionized by electron ionization at 80eV (2mA) at the entrance of the detector, filtered according to *m/z* by the QMS (Extrel, QC 150; 1.2 MHz), and detected using a Daly-type particle ion counter.

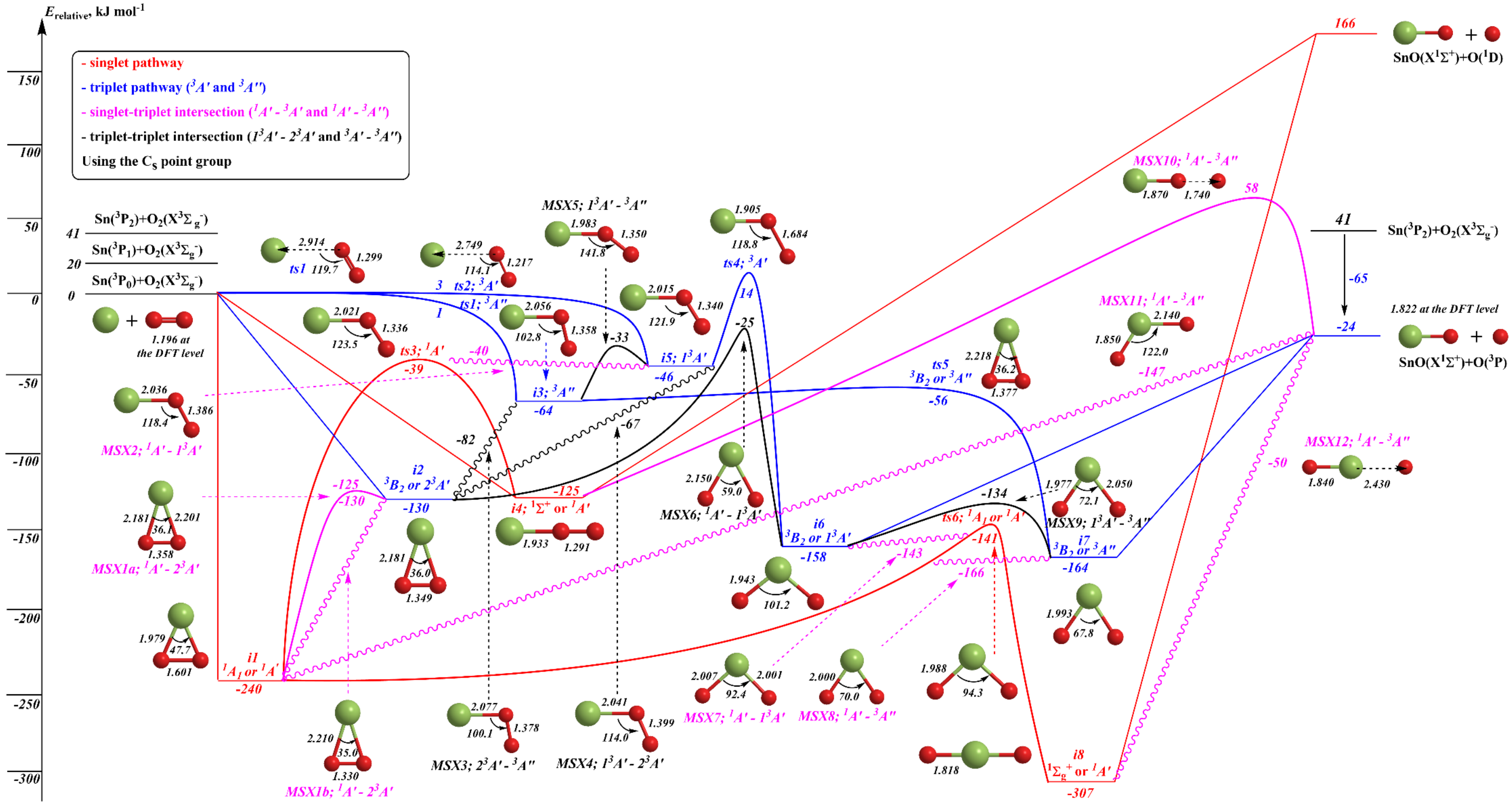
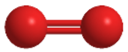
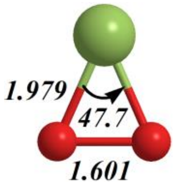
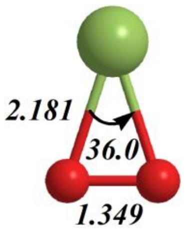
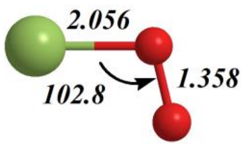
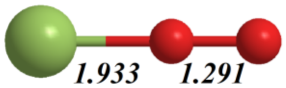


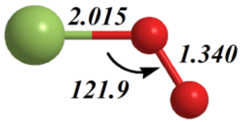
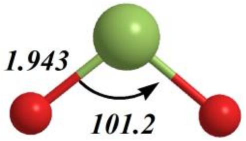
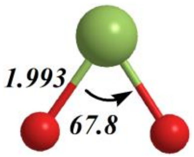
Figure S2. Potential energy surface (PES) of the reaction of atomic tin (Sn, ^3P_j) with oxygen (O_2, $X^3\Sigma_g^-$) with included bond distances (Å) and selected bond angles of each transition state, intermediate, or intersystem crossing. The italic numbers colored red, blue, black, and pink give the energies at the CASPT2(16,12)/aug-cc-pVQZ-(PP) (PP relates to Sn) level of theory with ZPE at the ωB97X-D/aug-cc-pVTZ-(PP) level of theory. The reaction energies of the products are calculated using CCSD(T)/CBS(aug-cc-pV(T+Q)Z-(PP)//ωB97X-D/aug-cc-pVTZ-(PP). The geometries of MSXs are either optimized at the CASSCF(16,12)/def2-TZVPPD level of theory, with their single-point energies recalculated at the CASPT2(16,12)/aug-cc-pVQZ-(PP) level of theory, or located using two-dimensional scans of the PES at the CASPT2(16,12)/aug-cc-pVQZ- (PP) level of theory. The energies are shown in kJ mol^{-1}. For structures with C_{2v}, $D_{\infty h}$, and $C_{\infty v}$ symmetry, electronic terms are given both for their highest point group and for C_s. The bond distances (Å) and selected bond angles of each molecule are also included. The tin atoms are colored green, and the oxygen atoms are colored red.

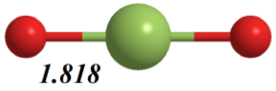
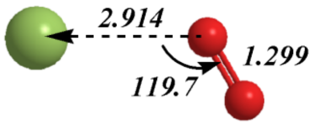
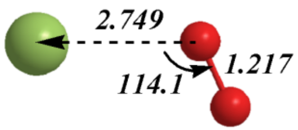
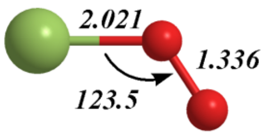
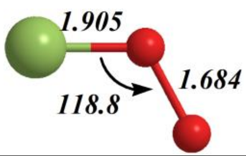
Table S1. Optimized Cartesian coordinates (in angstroms) and vibrational frequencies (in cm^{-1}) for all intermediates, transition states, minima-on-the-seam-of-crossings (MSX), reactants, and products involved in the reactions of the atomic tin (Sn; $^{3}P_{j}$) with oxygen (O_2; $X^{3}\Sigma_{g}^{-}$).

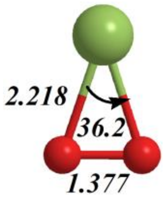
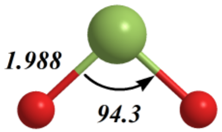
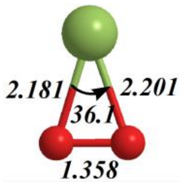
Species, bond lengths (Å) and bond angles (°), point group, electronic state	Label	Cartesian coordinates (Å)	vibrational frequencies (cm^{-1})
Reactants and products ωB97X-D/aug-cc-pVTZ (for O) & aug-cc-pVTZ-PP (for Sn)			
 $^{3}P_{j}$	Sn	Sn 0.000000 0.000000 0.000000	-
 *1.196* $D_{\infty h}$ $^{3}\Sigma_{g}^{-}$	O_2	O 0.000000 0.000000 0.597984 O 0.000000 0.000000 -0.597984	1703
 ^{3}P	O	O 0.000000 0.000000 0.000000	-
 *1.822* $C_{\infty v}$ $^{1}\Sigma^{+}$	SnO	Sn 0.000000 0.000000 0.251357 O 0.000000 0.000000 -1.570983	892

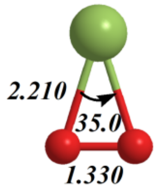
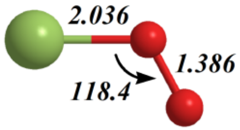
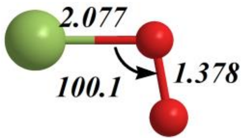
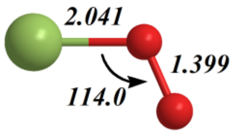
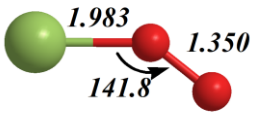
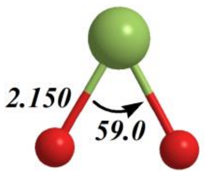
Intermediates Geometries: CASPT2(16,12)/aug-cc-pVQZ (for O) & aug-cc-pVQZ-PP (for Sn) Frequencies: ωB97X-D/aug-cc-pVTZ (for O) & aug-cc-pVTZ-PP (for Sn)

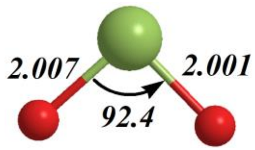
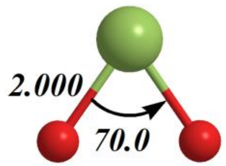
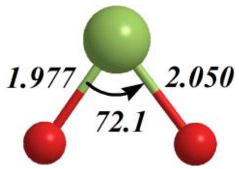
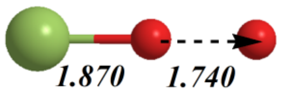
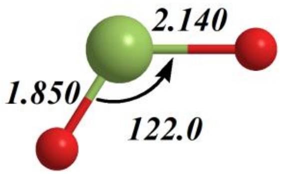
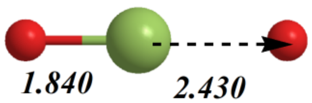
 C_{2v} $^{1}A_{1}$	***i1***	O 0.7993001955 -1.0082972776 0.0000000000 Sn 0.0029142337 0.8031705674 0.0000000000 O -0.8012144292 -1.0048732899 0.0000000000	544 548 870
 C_{2v} $^{3}B_{2}$ (for C_s $^{3}A'$ alpha orbitals: 14A’+6A” beta orbitals: 14A’+4A”)	***i2***	O 0.6747492868 -1.1665110555 0.0000000000 Sn 0.0003269865 0.9080281073 0.0000000000 O -0.6740762733 -1.1665170518 0.0000000000	382 403 1255
 C_s $^{3}A''$ alpha orbitals: 15A’+5A” beta orbitals: 14A’+4A”	***i3***	O 0.5811594308 -2.1128987816 0.0000000000 O -0.5949375100 -1.4340154336 0.0000000000 Sn 0.0137780792 0.5297252152 0.0000000000	169 503 1196
 $C_{\infty v}$ $^{1}\Sigma^{+}$	***i4***	Sn 0.6478785415 0.0008905207 0.0000000000 O -1.2855047078 0.0002734865 0.0000000000 O -2.5760888338 -0.0001640072 0.0000000000	96 142 374 1244

 C_s $^3A'$ alpha orbitals: 15A’+5A” beta orbitals: 13A’+5A”	***i5***	Sn -0.1144524295 0.5111143186 0.0000000000 O 0.8478744899 -1.2587750740 0.0000000000 O 0.1868047724 -2.4246432448 0.0000000000	203 470 1181
 C_{2v} $^3B_2$ (for C_s $^3A'$ alpha orbitals: 15A’+5A” beta orbitals: 13A’+5A”)	***i6***	O 0.9712464518 -1.5009340633 0.0000000000 Sn -0.2618478470 0.0000000000 0.0000000000 O 0.9712464518 1.5009340633 0.0000000000	178 546 584
 C_{2v} $^3B_2$ (for C_s $^3A''$ alpha orbitals: 15A’+5A” beta orbitals: 14A’+4A”)	***i7***	O 1.1002553867 -1.1713071143 0.0000000000 Sn 0.0204542785 0.5033234051 0.0000000000 O -1.1207096652 -1.1301122907 0.0000000000	125 517 590

 $D_{\infty h}$ $^1\Sigma_g^+$	***i8***	O 1.8184171239 0.0008375013 0.0000000000 Sn 0.0003333470 0.0003348168 0.0000000000 O -1.8177504710 -0.0001723181 0.0000000000	166 166 800 908
Transition states Geometries: CASPT2(16,12)/aug-cc-pVQZ (for O) & aug-cc-pVQZ-PP (for Sn) Frequencies: ωB97X-D/aug-cc-pVTZ (for O) & aug-cc-pVTZ-PP (for Sn)			
 C_s $^3A''$	***ts1*** ***(R – i3)***	Sn 0.0153936136 -0.6925109794 0.0000000000 O -0.5252575870 2.1709211914 0.0000000000 O 0.4110615548 2.9664044678 0.0000000000	Frequencies were not computed because this structure optimizes only at the CASPT2(16,12) level of theory where frequency computations proved to be unfeasible.
 C_s $^3A'$	***ts2*** ***(R – i5)***	Sn -0.0155674663 -0.6472306238 0.0000000000 O -0.4345841985 2.7581882431 0.0000000000 O 0.5500699402 2.0432294810 0.0000000000	Frequencies were not computed because this structure optimizes only at the CASPT2(16,12) level of theory where frequency computations proved to be unfeasible.
 C_s $^1A'$	***ts3*** ***(i1 – i4)***	Sn -0.0047097720 0.6306450697 0.0000000000 O 0.4598695758 -1.3361318363 0.0000000000 O -0.4551598038 -2.3101332334 0.0000000000	-154 371 1226
	***ts4*** ***(i5 – i6)***	O 0.5734054056 -2.4534788241 0.0000000000 O -0.5806837936 -1.2275633844 0.0000000000 Sn 0.0072783880 0.5844652084 0.0000000000	-1038 161 628

C_s $^3A'$ alpha orbitals: 15A’+5A” beta orbitals: 13A’+5A”			
 C_{2v} $^3B_2$ (for C_s $^3A''$ alpha orbitals: 15A’+5A” beta orbitals: 14A’+4A”)	***ts5*** ***(i3 – i7)***	O -0.7496784919 -1.6174647373 0.0000000000 Sn 0.0606699029 0.4474931208 0.0000000000 O 0.6259130359 -1.6892947984 0.0000000000	-1473 115 673
 C_{2v} $^1A_1$	***ts6*** ***(i1 – i8)***	O 1.4580517843 -1.1579023883 0.0000000000 Sn 0.0002350814 0.1941967182 0.0000000000 O -1.4582868657 -1.1571417540 0.0000000000	-223 538 609
Intersystem crossings CASSCF(16,12)/def2-TZVPPD (with effective core potentials) for MSX 1a, 2, 3, 4, 5, 7, and 9 CASPT2(16,12)/aug-cc-pVQZ (for O) & aug-cc-pVQZ-PP (for Sn) PES scan for MSX 1b, 6, 8, 10, 11, and 12			
	***MSX1a*** ***(i1 – i2)***	Sn -0.4424075765 0.0010764936 0.0000000000 O 1.6287295160 -0.6831150802 0.0000000000 O 1.6532282607 0.6751292166 0.0000000000	

	***MSX1b*** ***(i1 – i2)***	O 0.746114 -1.037237 0.010374 Sn 0.018682 1.049759 0.000289 O -0.583081 -1.076760 -0.008405	
	***MSX2*** ***(i1 – i5)***	Sn -0.5179106073 0.0265308448 0.0000000000 O 1.4246785727 -0.5819568026 0.0000000000 O 2.4173911287 0.3851402989 0.0000000000	
	***MSX3*** ***(i2 – i3)***	Sn 0.0241617272 -0.4879916339 0.0000000000 O -0.6855963820 1.4644865511 0.0000000000 O 0.5063549479 2.1556321423 0.0000000000	
	***MSX4*** ***(i2 – i5)***	Sn 0.0272822549 -0.5115296570 0.000000000 O -0.6174788219 1.4252050809 0.0000000000 O 0.4150880548 2.3695281583 0.0000000000	
	***MSX5*** ***(i3 – i5)***	Sn 0.0193985138 -0.5406100813 0.0000000000 O -0.3758181818 1.4023955023 0.0000000000 O 0.2319121852 2.6080680492 0.0000000000	
	***MSX6*** ***(i2 – i6)***	O 0.886543 -0.773140 0.042042 Sn -1.009571 0.239578 0.000000 O 0.835525 1.343316 0.000000	

	***MSX7 (i1 – i6)***	O 1.0813498558 -1.4575587687 0.0000000000 Sn -0.2944472688 0.0030410264 0.0000000000 O 1.1029787021 1.4349992089 0.0000000000	
	***MSX8 (i1 – i7)***	O 1.435165 -0.527011 0.032357 Sn 0.046781 0.912271 0.001080 O -0.830625 -0.884898 -0.020456	
	***MSX9 (i6 – i7)***	O 1.1419611764 -1.2768537685 0.0000000000 Sn -0.3446169587 0.0266702341 0.0000000000 O 1.4145463696 1.0790032190 0.0000000000	
	***MSX10 (i4 – P)***	Sn 1.611984 0.000527 0.000000 O -0.258040 -0.000070 0.000000 O -1.998072 -0.000659 0.000000	
	***MSX11 (i1 – P)***	O 0.948057 -1.058228 0.021021 Sn -0.939243 -0.050218 -0.020826 O -1.074056 1.765230 -0.350377	
	***MSX12 (i8 – P)***	O 1.818084 0.000505 0.000000 Sn -0.021941 -0.000004 0.000000 O -2.451970 -0.000682 0.000000	