Supporting Information for

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

*Iakov A. Medvedkov,a Anatoliy A. Nikolayev,b Shane Goettl,a Zhenghai Yang,a Alexander M. Mebel, c\* Ralf I. Kaisera\**

a Department of Chemistry, University of Hawai‘i at Manoa, Honolulu, HI 96822, USA

b Samara National Research University, Samara 443086, Russia

c Department of Chemistry and Biochemistry, Florida International University, Miami, Florida 33199, USA

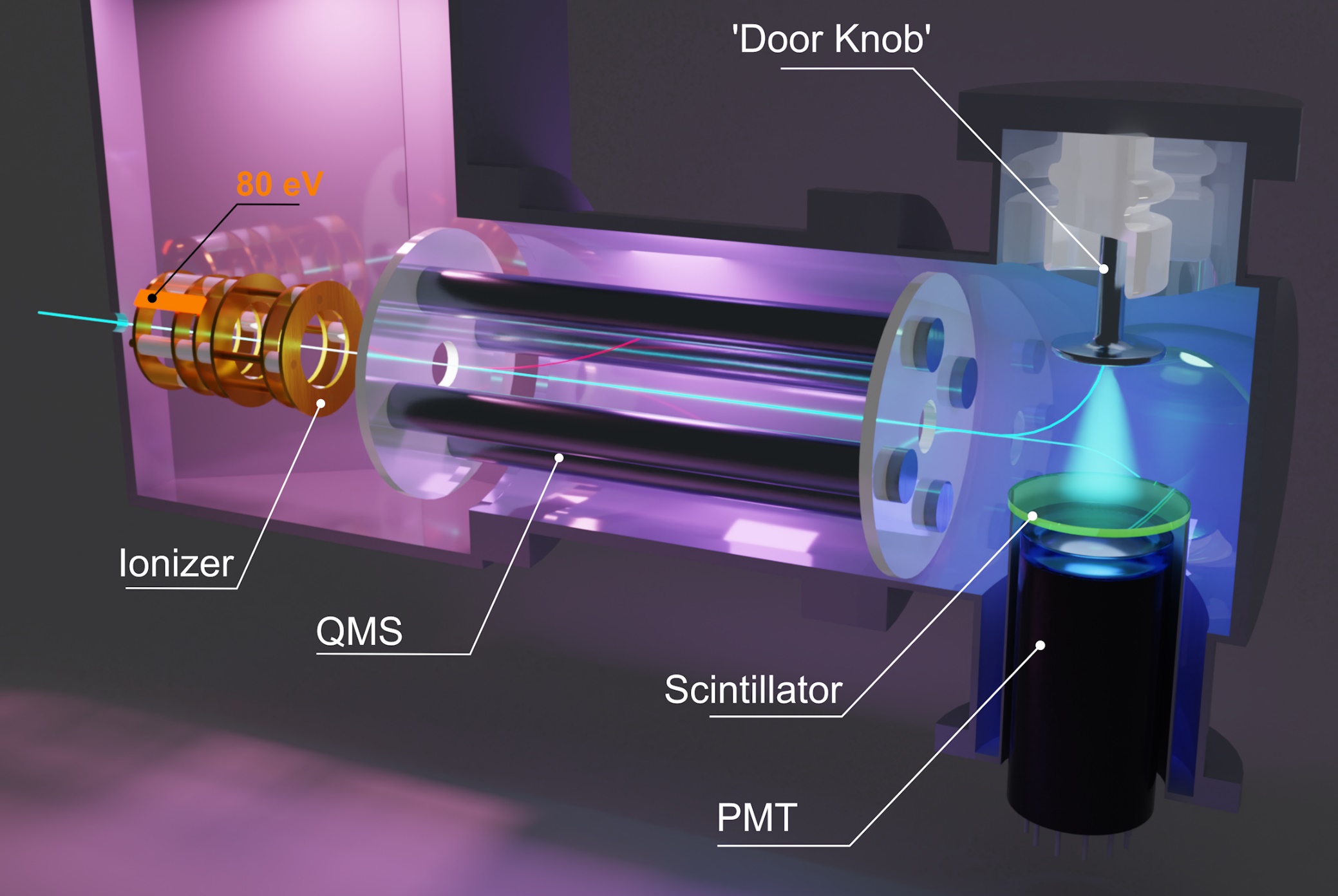
Corresponding to: ralfk@hawaii.edu; mebela@fiu.edu

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**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.

# **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; 3Pj) with oxygen (O2; X3Σg-).

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| --- | --- | --- | --- |
| Species,  bond lengths (angstroms) 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) | | | |
| 3Pj | Sn | Sn 0.000000 0.000000 0.000000 | - |
| D∞h  3Σg- | O2 | O 0.000000 0.000000 0.597984  O 0.000000 0.000000 -0.597984 | 1703 |
| 3P | O | O 0.000000 0.000000 0.000000 | - |
| C∞v  1Σ+ | 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) | | | |
| C2v  1A1 | ***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 |
| C2v  3B2  (for Cs 3A’  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 |
| Cs  3A”  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∞v  1Σ+ | ***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 |

|  |  |  |  |
| --- | --- | --- | --- |
| Cs  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 |
| C2v  3B2  (for Cs 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 |
| C2v  3B2  (for Cs 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∞h  1Σg+ | ***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) | | | |
| Cs  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. |
| Cs  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. |
| Cs  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 |
| Cs  3A’  alpha orbitals: 15A’+5A”  beta orbitals: 13A’+5A” | ***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 |
| C2v  3B2  (for Cs 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 |
| C2v  1A1 | ***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 |  |