**Supporting Information for**

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

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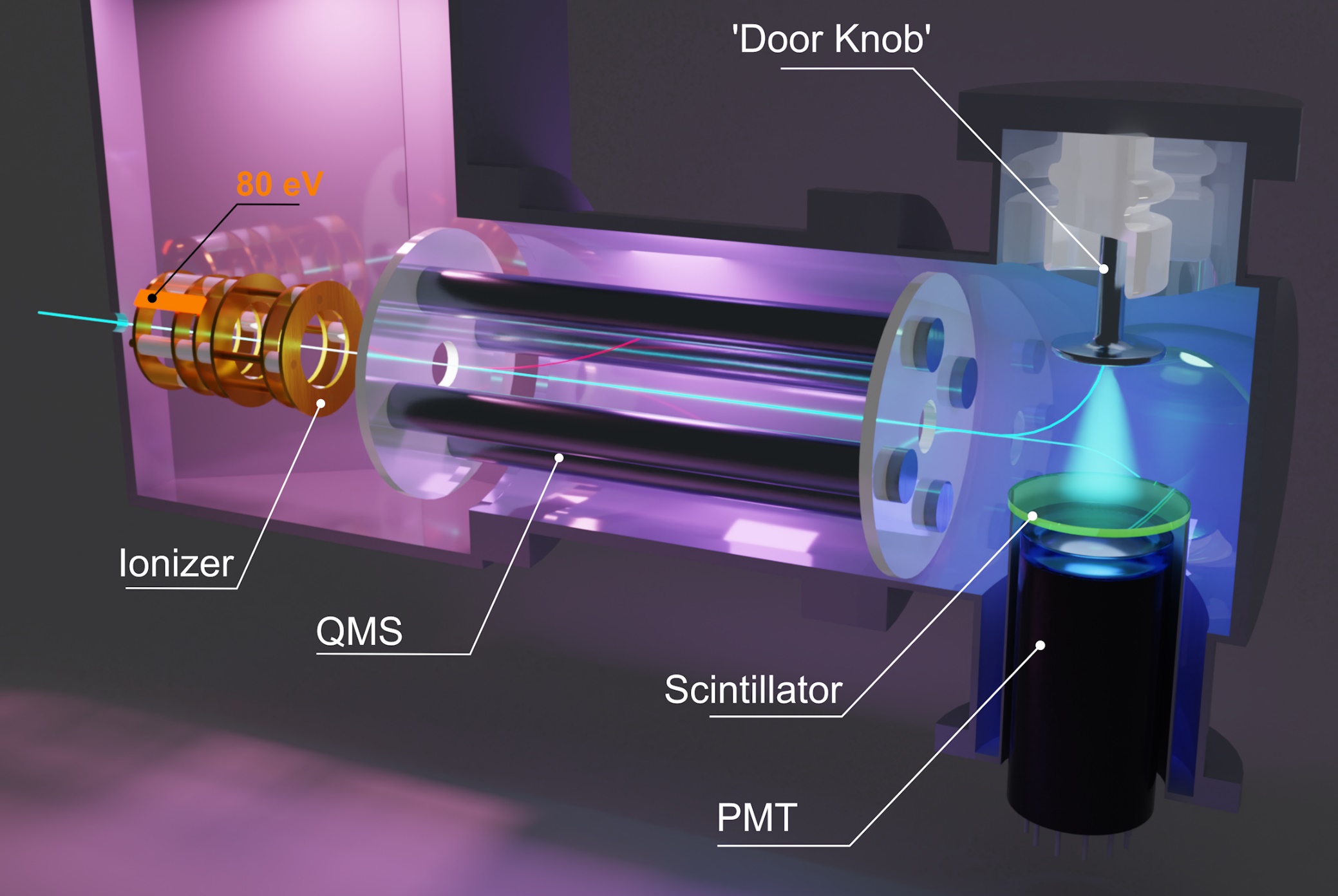
Keywords: crossed molecular beams, intersystem crossing, reaction dynamics, tin

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[**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-). 4](#_Toc179557733)



**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, 3Pj) with oxygen (O2, X3) 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 C2v, D∞h, and C∞v symmetry, electronic terms are given both for their highest point group and for Cs. 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; 3Pj) with oxygen (O2; X3Σg-).

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| --- | --- | --- | --- |
| 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) | | | |
| 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 |  |