Supplementary Materials for

**Full Title: Non-Adiabatic Reaction Dynamics to Silicon Monosulfide (SiS) - A Key Molecular Building Block to Sulfur-Rich Interstellar Grains**

**Short Title: Gas Phase Synthesis of Silicon Monosulfide**

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**Experimental Section.** The crossed molecular beam experiments of ground state silicon atoms (Si; 3P) with deute­rium sulfide (D2S; X1A1) were performed in gas phase under single collision conditions exploi­ting a crossed molecular beam machine ([65](#_ENREF_65))[. Note that the reaction was](file:///D:\UHM\Si+H2S\Manuscript\ScienceAdvances\Revision_1\SISciAdv.docx#_ENREF_68) conducted with deute­rium sulfide, but not with hydrogen sulfide (≥ 99 %, Sigma-Aldrich) due to the presence of traces of dihydrogendisulfide in the hydrogen sulfide lecture bottle leading to non-reactive scattering signal at the prospective products of 61 amu (HSiS) and 60 amu (SiS). This problem was overcome by using deute­rium sulfide. A pulsed supersonic beam of neon-seeded ground state silicon atoms was produced via ablation of a rotating silicon rod at 266 nm (10 ± 1 mJ per pulse; 30 Hz). The ablated silicon atoms were entered into neon carrier gas (Ne; 99.999%; Specialty Gases) released from a pulsed piezoelectric valve operating at 60 Hz, a pulse width 80 µs, and a peak voltage -400 V. A four-slit chopper wheel rotating at 120 Hz selected a part of the pulsed beam defined by a peak velocity (vp) and speed ratio (S) of 984 ± 15 m s-1 and 5.9 ± 0.8, respectively. Laser induced fluorescence revealed that silicon atoms are in their electronic ground state (3P) ([77](#_ENREF_77))[. This section of the beam intersected perpendicularly an early section of a pulsed beam of deuterium sulfide (97 % D; Sigma-Aldrich) characterized by a peak velocity (v](file:///D:\\UHM\\Si+H2S\\Manuscript\\ScienceAdvances\\Revision_1\\SISciAdv.docx" \l "_ENREF_69" \t "Yang, 2017 #53)p) of 801 ± 21 ms-1 and a speed ratio (S) of 12.8 ± 0.8. The neutral reactive scattering products are ionized by electron impact at energy of 80 eV and 2 mA emission current; the ions are then extracted and mass filtered by a triply differentially pumped quadrupole mass filter operating in the TOF mode and detected by Daly-type ion counter; up to 2 × 105 TOF spectra were accumulated at each angle. The laboratory angular distributions were then obtained by integrating the TOF at each angle and normalized to the intensity of the TOF at the center-of-mass angle (CM). The reaction dynamics were extracted by converting the data from the laboratory frame to the CM reference frame exploiting a forward-convolution routine ([45](#_ENREF_45), [46](#_ENREF_46))  [providing the CM translational energy P(E](file:///D:\\UHM\\Si+H2S\\Manuscript\\ScienceAdvances\\Revision_1\\SISciAdv.docx" \l "_ENREF_56" \t "Weiss, 1986 #23)T) and angular T(θ) flux distribution for each channel. For barrierless reactions without threshold, a reactive cross-section with an ET-1/3 energy dependence; for reactions with a threshold (E0), a (1-E0/ET) energy dependence was utilized ([78](#_ENREF_78)) [. Branching ratios were calculated using the method of Krajnovich et al.](file:///D:\UHM\Si+H2S\Manuscript\ScienceAdvances\Revision_1\SISciAdv.docx#_ENREF_70)  ([79](#_ENREF_79)) [.](file:///D:\UHM\Si+H2S\Manuscript\ScienceAdvances\Revision_1\SISciAdv.docx#_ENREF_59)

C:\Users\Ralf I. Kaiser\Desktop\PES_SI.tif **Fig. S1.** Potential energy surface for the reactions of hydrogen sulfide (H2S) with atomic silicon (Si) at the MRCI-F12/cc-pVQZ-F12//CASSCF/aug-cc-pV(Q+d)Z level. Relative energies are given in units of kJ mol-1. Plain numbers are zero-point energies corrected for hydrogeneted reactants, whereas numbers in parentheses are for deuterated reactants. Colors of the atoms are defined as sulfur (yellow), silicon (blue), and hydrogen (gray). The cartesian coordinates and vibrational frequencies are compiled in the (Table S3).



**Fig. S2.** Structures of minima-on-the-seam-of-crossings (MSXs).



**Fig. S3.** Computed geometries of the exit transition states leading to the formation of SiS (p1) plus molecular deuterium from intermediates cis-**S2** (left) and **S3** (right).

**Table S1.** Peak velocities (vp) and speed ratios (*S*) of ground state atomic silicon (Si(3P)) and deuterium sulfide (D2S; X1A1) beams along with the collision energy (*E*C) and center-of-mass angle (ΘCM).

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| beam | v*p* (m s-1) | *S* | *EC* (kJ mol-1) | ΘCM (deg) |
| Si(3P) | 984 ± 15 | 5.9 ± 0.8 |  |  |
| D2S (X1A1) | 801 ± 21 | 12.8 ± 0.8 | 12.7 ± 0.4 | 46.3 ± 0.8 |

**Table S2.** D and D2 loss product mass combinations of silicon and sulfur isotopes from the reaction of ground state atomic silicon and deuterium sulfide. Isotope abundance given in the parenthesis.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Si + D2S** | | D232S (94.93%)  36 | D233S (0.76%)  37 | D234S (4.29%)  38 |
| D Loss | 28Si (92.23%)  28 | 28Si32SD  62 | 28Si33SD  63 | 28Si34SD  64 |
| 29Si (4.68%)  29 | 29Si32SD  63 | 29Si33SD  64 | 29Si34SD  65 |
| 30Si (3.09%)  30 | 30Si32SD  64 | 30Si33SD  65 | 30Si34SD  66 |
| D2 Loss | 28Si (92.23%)  28 | 28Si32S  60 | 28Si33S  61 | 28Si34S  62 |
| 29Si (4.68%)  29 | 29Si32S  61 | 29Si33S  62 | 29Si34S  63 |
| 30Si (3.09%)  30 | 30Si32S  62 | 30Si33S  63 | 30Si34S  64 |

**Table S3.** Optimized Cartesian Coordinates (Å) and Vibrational Frequencies (cm-1) of the reactants, products, transition states, and MSX on the singlet and triplet potential energy surfaces.

|  |  |  |
| --- | --- | --- |
| Species | Vibrational Frequencies  (cm-1) | Cartesian Coordinates (Å)  Atom X Y Z |
| H2S | 1198.66  2649.17  2673.60 | S 0.000000 -0.000000 -0.054937  H 0.000000 0.980451 0.873707  H 0.000000 -0.980451 0.873707 |
| T1:H2SSi | 180.99  452.65  456.47  1195.18  2623.98  2642.47 | S -0.000000 -0.057984 1.143524  H 0.983506 0.816017 1.464236  H -0.983516 0.816007 1.464236  Si -0.000000 0.005839 -1.415638 |
| T2: HSSiH-T | 356.19  523.32  629.64  712.77  2324.36  2649.52 | S -0.017379 -0.042315 -1.003641  H -1.202415 0.140549 1.871912  H 0.117356 1.276157 -1.202526  Si 0.058780 -0.002538 1.121647 |
| T3:SSiH2 | 526.65  546.81  779.02  983.76  2315.08  2332.64 | Si 0.000013 -0.415804 1.128159  H 1.215114 0.161026 1.738861  H -1.215074 0.161026 1.738887  S -0.000008 0.093786 -0.946350 |
| TS-diss-T1-HSSi+H | 1241.64i  280.81  468.18  550.99  722.52  2553.70 | S -0.063268 -0.051584 -0.956192  H -0.248702 1.264111 -1.243756  H 1.496326 0.136322 -2.112130  Si 0.027446 0.008625 1.211943 |
| TS-diss-T2-SSiH+H | 1160.07i  293.08  369.05  670.50  696.85  2245.18 | S -0.084482 0.011817 -0.923990  Si 0.033259 -0.058072 1.052597  H -0.057254 1.158677 1.902668  H 1.817687 0.083575 -1.842725 |
| TS-diss-T2-SiS+H2 | 1576.14i  409.61  650.42  858.49  1656.42  1898.54 | S -0.034198 -0.277604 -1.195345  H 0.030896 1.657612 0.666896  H 0.010530 1.293253 -0.246914  Si 0.003231 0.054909 0.946863 |
| TS-iso-T1-T2 | 764.49i  349.98  533.83  790.94  1458.44  2594.07 | S -0.033970 -0.042377 -1.085872  H -0.995963 0.645453 0.120600  H 0.574657 1.150514 -1.292633  Si 0.019234 -0.010937 1.317689 |
| TS-iso-T2-T3 | 1367.75i  561.52  652.40  680.25  1713.17  2295.52 | Si 0.089515 -0.429029 1.096976  H 1.192570 0.168324 1.880465  H -0.798269 0.729392 0.363414  S -0.063646 -0.018946 -0.962976 |
| S1: H2SSi | 237.01  447.66  592.03  1328.08  2170.30  2378.53 | S -0.154062 0.004596 0.971997  H 0.265997 -1.004536 1.797108  H 0.269769 0.997112 1.825832  Si 0.052595 -0.007143 -1.160358 |
| Trans-S2: (HSSiH) | 526.81  604.66  684.12  954.11  2191.62  2669.86 | S 0.075031 0.191007 -1.262024  H -1.532691 -0.016944 0.873414  H 1.338415 0.639985 -1.307538  Si -0.115595 0.490031 0.842247 |
| Cis-S2: (HSSiH) | 502.68  507.86  696.89  863.10  2188.78  2591.10 | S 0.000005 -0.040326 -1.004445  H 0.000139 1.438803 1.347005  H -0.000157 1.284931 -1.229789  Si -0.000006 -0.051717 1.142382 |
| S3: SSiH2 | 676.08  716.44  742.74  1108.26  2369.51  2375.63 | Si -0.000001 -0.000001 0.972899  H 1.196893 0.000017 1.826892  H -1.196846 0.000017 1.826928  S -0.000000 0.000000 -0.967161 |
| TS-diss-S1-SiSH+H | 867.31i  151.61  431.08  553.68  865.07  2539.96 | S 0.007998 -0.037728 0.908483  H 1.178415 0.366882 1.442400  H -0.988090 0.421180 2.484369  Si -0.015961 0.014785 -1.177971 |
| TS-diss-cisS2-SiS+H2 | 1623.18i  595.96  987.12  1012.77  1593.39  1761.39 | S -0.032598 -0.232483 -1.143046  H 0.031563 1.693082 0.660862  H 0.009419 1.255357 -0.273546  Si 0.002075 0.012213 0.927230 |
| TS-isom-S1-cisS2 | 1077.46i  232.48  590.27  1275.32  1929.94  2284.54 | S 0.010733 -0.060461 1.064112  H 0.702898 0.972366 0.386708  H -0.673559 0.984744 1.651843  Si -0.013305 -0.001219 -1.287859 |
| TS-isom-cisS2-transS2 | 665.95i  405.95  625.92  692.29  2346.37  2539.95 | S 0.249499 -0.142744 -1.332041  H -1.422203 0.642659 0.801443  H 0.787729 1.101897 -1.306465  Si -0.051067 0.140840 0.896848 |
| TS-isom-transS2-S3 | 1663.18i  548.54  579.71  786.17  1784.87  2224.48 | Si 0.116033 0.446121 1.102345  H 1.280799 -0.224639 0.256350  H -0.940142 -0.277625 1.871131  S -0.101890 0.027183 -0.934486 |
| TS-S3-SiS+H2 | 1342.25i  512.68  539.05  678.02  1143.88  2305.40 | Si         0.000000        0.103972        0.984152 H          0.000000       -1.614781        1.503071 H          0.000000       -0.507192        2.338307 S          0.000000       -0.024369       -0.982915 |
| SiS (singlet) | 733.92 | S 0.000000 0.000000 -0.908295  Si 0.000000 0.000000 1.036832 |
| SiS (triplet) | 488.72 | S 0.000000 0.000000 -1.021078  Si 0.000000 0.000000 1.165575 |
| SSiH | 690.09  701.86  2199.56 | Si 0.000000 -0.059692 -1.011007  S 0.000000 0.016031 0.944641  H 0.000000 1.153351 -1.875656 |
| HSSi | 502.92  622.25  2559.67 | S 0.003305 0.176352 -1.019021  H -0.029846 -1.129548 -1.347360  Si -0.001829 -0.075434 1.089941 |
| H2 | 4285.17 | H 0.000000 0.000000 -0.377382  H 0.000000 0.000000 0.377382 |
| MSX1 | 2573.91  1440.46  774.33  578.73  283.65 | S -0.005107 -0.049059 -1.084659  H -1.049825 0.654129 0.173867  H 0.596803 1.146190 -1.308290  Si 0.022088 -0.008608 1.278866 |
| MSX2 | 2669.15  1803.68  812.94  660.83  564.82 | S -0.013581 -0.044940 -0.995519  H -1.043264 -0.025168 2.073599  H -0.043435 1.275840 -1.229478  Si 0.054503 0.006416 1.106105 |
| MSX3 | 2130.73  1792.85  1072.02  754.85  277.53 | Si -0.067398 -0.038147 -1.107977  H 0.559253 1.010089 -2.000754  H 1.377742 -0.461322 -0.653008  S -0.001854 0.016165 1.054052 |

**Table S4:** Source data from Tercero et al([28](#_ENREF_28))

|  |  |  |  |
| --- | --- | --- | --- |
|  | OHC | OPl | O15 |
| T(K) | 225 | 125 | 200 |
| n(H2) (cm-3) | 5 ×107 | 106 | 5 ×106 |
| Source diam (arcsec) | 10 | 30 | 10 |
| Source diam (cm) | 6×1016 | 1.8×1017 | 6×1016 |
| N(SiS) (cm-2) | (3.0±0.7)×1014 | (3.5±0.8)×1014 | (7.0±1.7)×1014 |
| N(H2) (cm-2) | 4.2×1023 | 2.1 ×1023 | 1023 |
| f(SiS) | (7.1±1.7)×10-10 | (1.7±0.4)×10-9 | (7.0±1.7)×10-9 |

Fractional abundances are difficult to determine for such small, dense sources because of approximatons made about optical depth of observed emission lines, source size, density, and excitation temperature. As an example, the Orion Plateau source was also observed in SiS by Ziurys([80](#_ENREF_80)) in the 5-4 and 6-5 transitions with a relatively large beam, 58 and 49 arcsec, larger than the source size, 30 arcsec. In this paper she derived N(SiS) = (2.8-3.9)×1015 cm-2 and adopted N(H2) = 1024 cm-2 (although she noted that its value could be anywhere form (5-50)×1023 cm-2) to find f(SiS) = (2.8-3.9)×10-9. In this analysis she adopted a rotational temperature of 230K, higher than that currently thought (125K). Ziurys ([81](#_ENREF_81))reobserved these two transitions with a different telescope and added the 15-14 transition to them. In this paper, she used a rotational temperature of 100K and derived N(SiS) = 4×1015 cm-2 for a 10 arcsec source and 1.4×1014 cm-2 for a 27 arcsec source, closer to the actual size of the plateau.

**Table S5**: Initial fractional abundances, f(X), of species relative to H2

|  |  |  |  |
| --- | --- | --- | --- |
| Species | Abundance | Species | Abundance |
| He | 1 ×10-1 | CH3OH | 1 ×10-6 |
| H2O | 2 ×10-4 | N2 | 4 ×10-7 |
| CO | 1 ×10-4 | SiH4 | 2 ×10-7 |
| NH3 | 2 ×10-5 | OCS | 1 ×10-7 |
| H2S | 2 ×10-6 | CH4 | 1 ×10-7 |