

Supporting Information for

**A Crossed Molecular Beams and Computational Study on the Formation of  
the Astronomically Elusive Thiosilaformyl Radical (HSiS, X<sup>2</sup>A')**

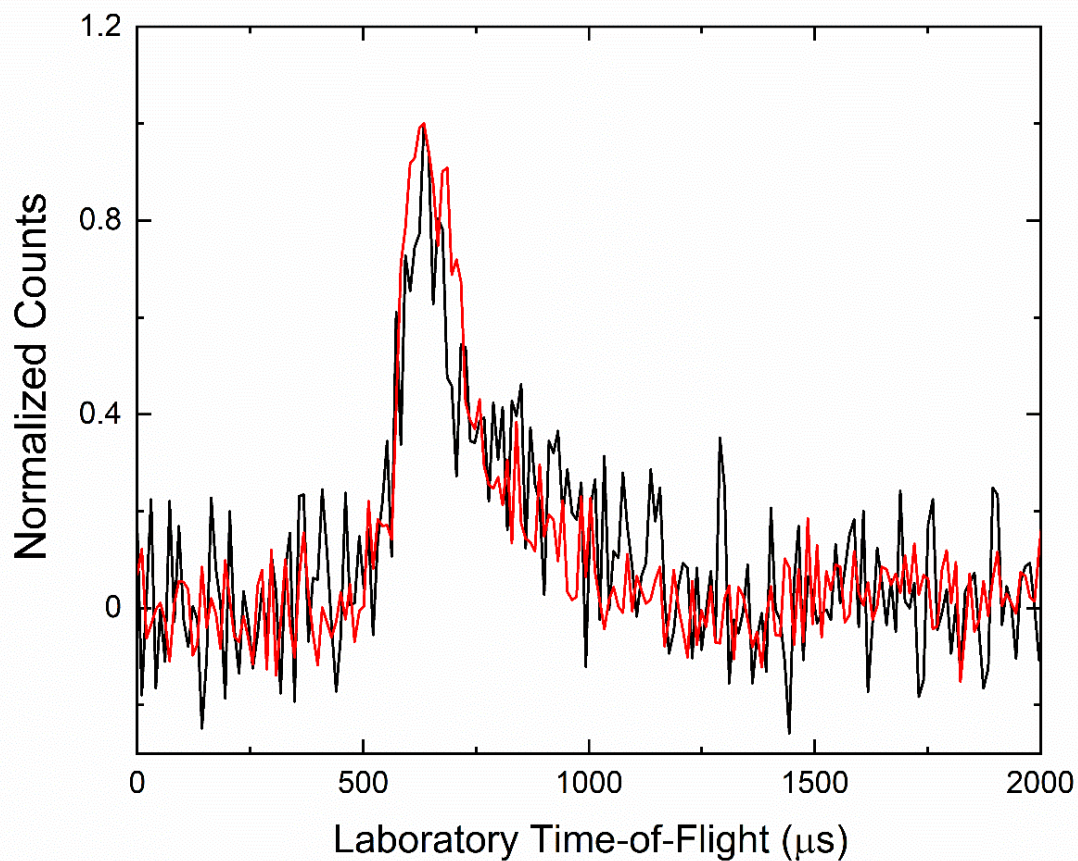
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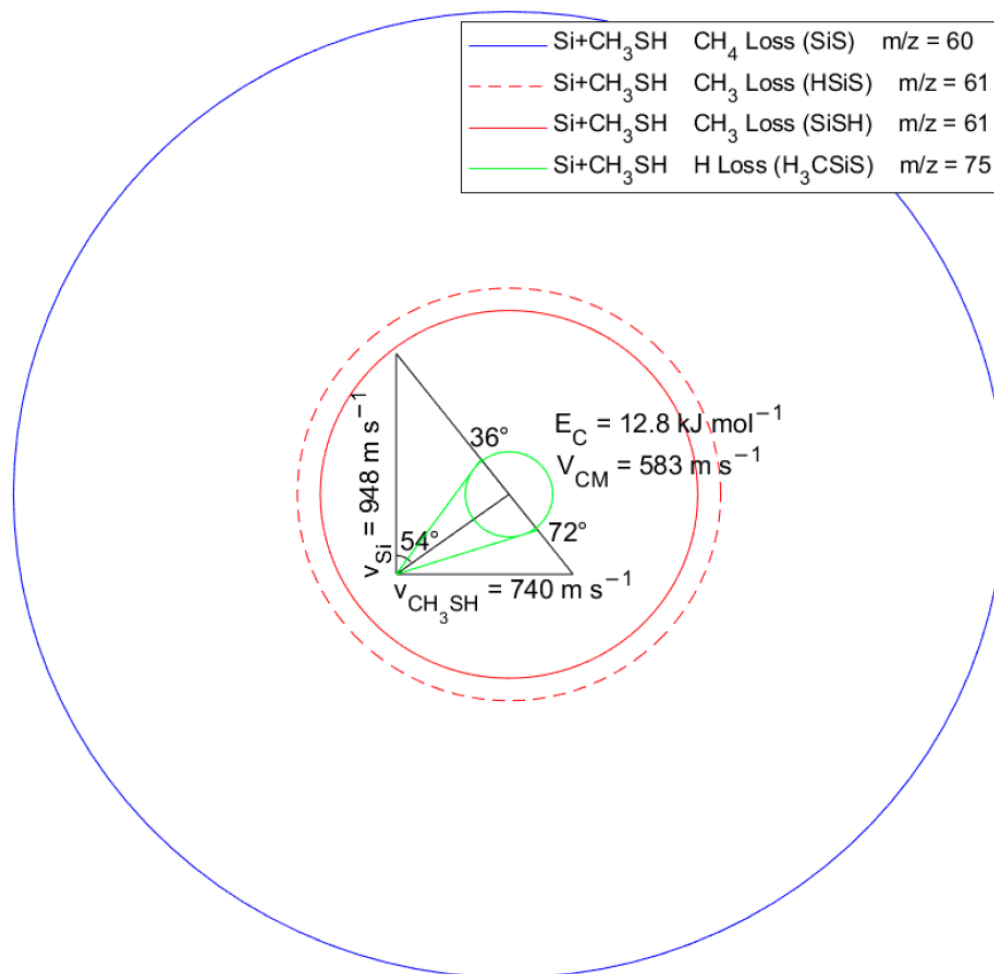
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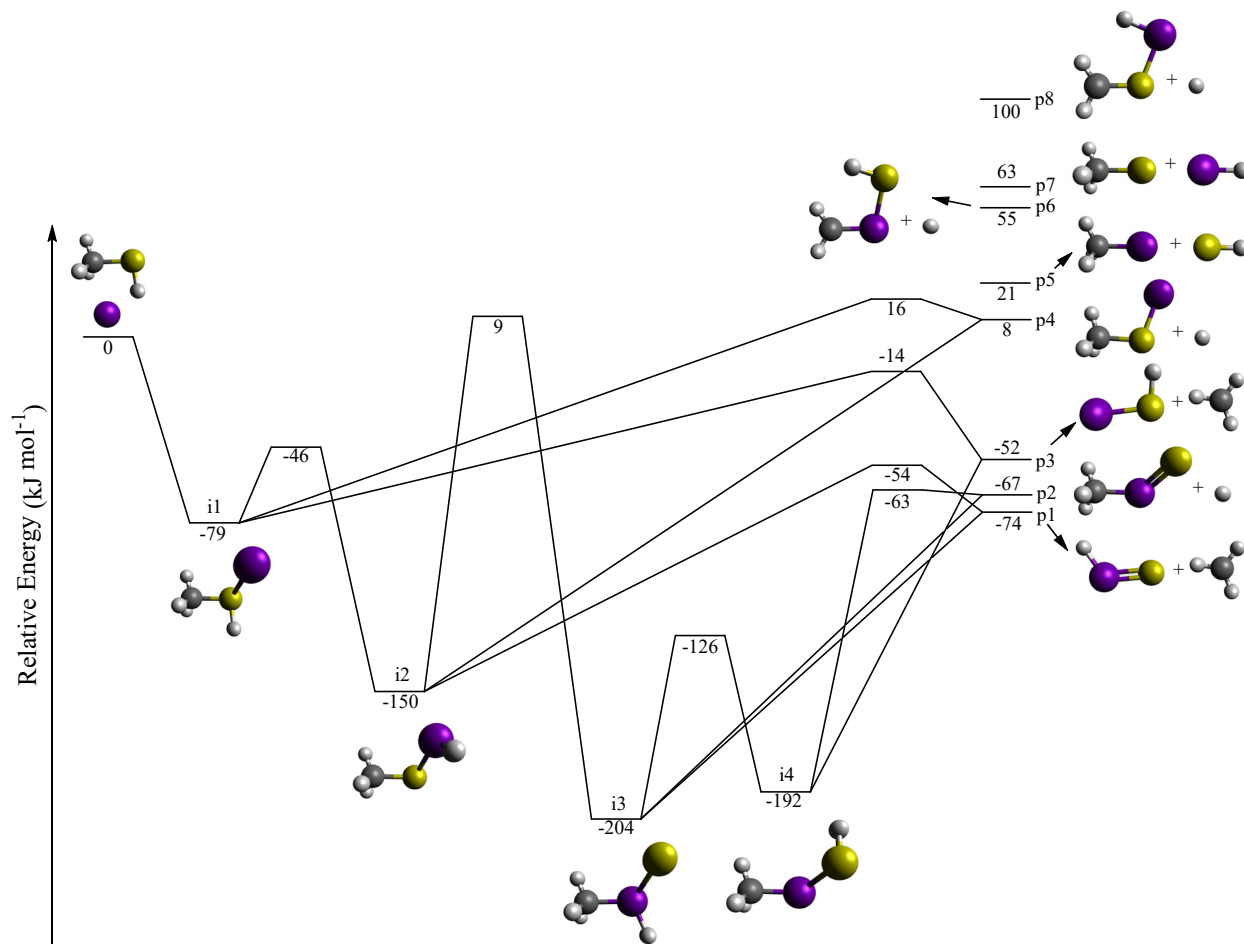
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**Figure S1.** Time-of-flight (TOF) spectra taken at the center-of-mass (CM) angle of  $54^\circ$  corresponding to  $m/z = 60$  (black) and  $m/z = 61$  (red) for the reaction of atomic silicon ( $\text{Si}(^3\text{P}_j)$ ) with thiomethanol ( $\text{CH}_3\text{SH}$ ).



**Figure S2.** Newton circles for the reaction of atomic silicon ( $\text{Si}(^3\text{P}_j)$ ) with thiomethanol ( $\text{CH}_3\text{SH}$ ) for the methane and methyl loss channels along with the atomic hydrogen emission pathway. Each Newton circle has a radius equal to the maximum CM recoil velocity of the heavy product.  $E_{\text{c}}$  and  $V_{\text{CM}}$  define the collision energy and velocity of the center of mass, respectively.



**Fig. S3:** Complete representation of the calculated products, intermediates, and transition states for the reaction between ground state atomic silicon and thiomethanol calculated at the CCSD(T)-F12/aug-cc-pV(T+d)Z//M06-2X/cc-pV(T+d)Z+ZPE(M06-2X/cc-pV(T+d)Z) level. Atoms are colored as follows: carbon (grey); silicon (purple); hydrogen (white); sulfur (yellow).

**Table S1.** Energy-dependent rate constants derived from RRKM calculations.

Reaction Pathway	Rate Constant ( $\text{s}^{-1}$ )
i1 $\rightarrow$ i2	$5.35267 \times 10^{11}$
i2 $\rightarrow$ i1	$2.41159 \times 10^9$
i1 $\rightarrow$ p3	$1.13573 \times 10^{10}$
i2 $\rightarrow$ p4	$1.08041 \times 10^{11}$

**Table S2.** Optimized Cartesian coordinates (Angstrom) and vibrational frequencies ( $\text{cm}^{-1}$ ) for all intermediates, transition states, reactants, and products involved in the reactions of atomic silicon ( $\text{Si}(^3\text{P}_j)$ ) with thiomethanol ( $\text{CH}_3\text{SH}$ ) at the M06-2X/cc-pV(T+d)Z level.

### Reagents

#### $\text{CH}_3\text{SH}$

C	-3.41176033	1.25439584	0.01449201
S	-1.60045278	1.28984702	0.02218826
H	-3.82207370	1.90858257	0.77812487
H	-3.78685069	0.24311264	0.14125393
H	-3.71781158	1.62130284	-0.96190315
H	-1.43594086	0.82071924	1.26236403

#### Frequencies

236.041  
732.010  
804.927  
977.459  
1101.351  
1361.538  
1481.980  
1494.617  
2741.296  
3089.114  
3176.547  
3177.949

### Products

#### $\text{CH}_3$

C	0.66410094	2.73329639	-0.00000000
H	1.51476645	2.07351351	0.00000000
H	0.81006140	3.79990077	0.00000000
H	-0.33263868	2.32650924	0.00000000

#### Frequencies

405.863  
1412.233

1412.371  
3144.143  
3323.125  
3323.298

### **HSiS**

S -3.5140755200 1.2168792500 0.0000000000  
Si -1.5816367900 1.4356775300 0.0000000000  
H -0.6953377100 0.2232032100 0.0000000000

### Frequencies

580.731  
724.768  
2077.406

### **HSSi**

Si -6.0232639300 -0.4069621600 -0.0000000000  
S -4.1160321200 0.4944951200 -0.0000000000  
H -3.3237240300 -0.5920630100 0.0000000000

### Frequencies

518.854  
675.323  
2651.064

### **CH<sub>3</sub>S**

C -3.4018590482 1.2522998432 0.0201163997  
S -1.6137606348 1.2888270144 0.0216427185  
H -3.8166823624 1.9128767148 0.7775576358  
H -3.7817406913 0.2403778458 0.1372127499  
H -3.7171155122 1.6208224788 -0.9593757732

### Frequencies

633.337  
743.794  
869.142  
1337.308  
1387.002  
1478.986

3053.926  
3129.352  
3153.624

### **CH<sub>3</sub>Si**

C -3.4070510575 1.2427420340 0.0450102109  
Si -1.5211101617 1.3041677327 -0.0129868177  
H -3.8689972994 1.9082363329 0.7758044799  
H -3.8345657120 0.2432227412 0.1380087186  
H -3.6994340183 1.6168350561 -0.9486828610

### Frequencies

502.819  
621.844  
693.285  
1242.984  
1363.488  
1444.282  
2996.870  
3086.121  
3124.474

### **SiH**

Si -1.4471899572 1.5322851907 0.1340533318  
H -0.7836439977 0.1846410261 -0.0654881498

### Frequencies

2060.131

### **SH**

S -4.0806275850 0.5482255800 0.1585125495  
H -3.3925807519 -0.5980317347 0.2394575334

### Frequencies

2727.726

### **H<sub>3</sub>CSiS**

Si -1.2922444017 2.3447081197 -0.9116030215



C	0.3530548631	2.5341783821	-0.0094074653
S	-3.0086234334	2.7190429318	-0.0681228236
H	0.3988512280	3.5383974752	0.4129005472
H	1.2045581107	2.3649898997	-0.6636071035
H	0.3712253429	1.8132848461	0.8093761265

#### Frequencies

28.456  
200.454  
601.640  
648.002  
746.390  
799.790  
1233.466  
1434.758  
1446.680  
3061.142  
3146.941  
3174.034

#### **H<sub>3</sub>CSSi**

C	-1.8311634692	0.2262129791	0.2401343951
Si	1.2847895101	0.7324340425	0.3716915006
H	-1.5104170895	0.1778200986	1.2776627094
H	-2.2712699269	-0.7213070719	-0.0593963275
S	-0.3974226854	0.5682218748	-0.8452514948
H	-2.5591441481	1.0228578845	0.1107956769

#### Frequencies

91.185  
216.923  
537.685  
690.499  
941.809  
974.020  
1339.821  
1471.766  
1480.365  
3078.111  
3175.993  
3176.393

#### **H<sub>2</sub>CSiSH**

Si	-1.0445620252	1.7530735297	-0.9807337388
C	0.2413969917	2.6328136230	0.0017374659
S	-2.7987231043	2.7995066603	-0.2966019905
H	0.0884899935	3.0436510667	0.9955430419
H	1.2783655866	2.6460468081	-0.3191422582
H	-2.2362652823	3.7285089322	0.4877366297

#### Frequencies

210.468  
262.133  
357.417  
484.335  
628.457  
678.220  
714.842  
778.981  
1403.638  
2712.465  
3121.218  
3213.255

#### **H<sub>2</sub>CSSiH**

S	-0.9567026038	1.9757610036	-0.9608665563
C	0.2829191708	2.6345584994	-0.0153133982
Si	-2.8773553868	2.7267400473	-0.3864600967
H	0.0655471300	3.3405076414	0.7707964359
H	1.2967443122	2.3282052985	-0.2208568881
H	-2.2824504625	3.5978281299	0.7012396535

#### Frequencies

254.375  
265.798  
374.468  
492.900  
549.573  
789.068  
818.251  
947.315  
1412.589  
2073.627  
3170.620  
3300.879

## Intermediates

### i1: H<sub>3</sub>C<sub>2</sub>SHSi

S	0.7535961169	-0.1476115477	-0.5173300205
C	-0.9562773727	0.1198347642	0.0329041416
H	-1.3128232823	0.9755020966	-0.5344925859
H	-0.9596138790	0.3617587404	1.0920844411
Si	1.9349681829	1.6840828295	0.3313963364
H	-1.5628324519	-0.7556180383	-0.1850482300
H	1.0196708961	-1.1677568348	0.3166149375

### Frequencies

159.376  
171.928  
291.118  
531.924  
700.609  
790.534  
977.839  
1086.982  
1349.374  
1466.167  
1473.789  
2646.142  
3081.432  
3184.048  
3186.853

### i2: H<sub>3</sub>C<sub>2</sub>SiH

C	-1.7971468245	0.1665999445	0.2578597815
Si	1.0906267164	1.2724759431	0.2543602640
H	-1.6161079716	-0.1763601524	1.2722259916
H	1.1548885191	2.6988159624	-0.1525096098
H	-2.5411101317	-0.4716157687	-0.2141035755
S	-0.2721496092	0.0210067579	-0.7395683877
H	-2.1487399884	1.1941330831	0.2648623859

### Frequencies

108.135  
198.960

294.803  
528.155  
631.713  
702.876  
966.094  
974.731  
1345.001  
1475.652  
1479.910  
2182.496  
3082.302  
3172.539  
3182.960

**i3: H<sub>3</sub>CSSiH**

C	-3.3827386431	2.6624157636	0.1516770214
Si	-1.5718081372	3.1137043610	0.3834937814
S	-0.3722024960	1.5751023630	-0.4828241569
H	-3.6118401673	1.7181076914	0.6427274332
H	-3.6188634230	2.5729736188	-0.9086696440
H	-4.0112174870	3.4377209013	0.5896835057
H	-1.2275596465	4.3439553010	-0.3760779407

Frequencies

136.780  
163.770  
488.990  
531.621  
599.910  
695.913  
789.148  
870.727  
1264.975  
1451.055  
1457.622  
2195.953  
3064.181  
3148.814  
3156.815

**i4: H<sub>3</sub>CSiHS**

Si	-1.2458788518	2.3231009761	-0.9781839766
C	0.3538990350	2.5314614087	0.0048513910

S	-3.0996226581	2.7404236958	-0.0325673291
H	-3.3744517095	1.5110983456	0.4304737402
H	0.4127997271	3.5397667691	0.4129170196
H	1.2047557930	2.3710300734	-0.6561591758
H	0.4008686644	1.8088187314	0.8186783307

#### Frequencies

93.421  
177.183  
272.428  
489.717  
687.808  
723.740  
785.220  
795.956  
1250.409  
1447.944  
1451.854  
2677.464  
3061.699  
3148.885  
3154.707

#### Transition states

##### i1 – i2

S	0.7481780063	-0.0822070340	-0.8525894498
C	-0.8492021348	0.1082606578	-0.0125276989
H	-1.3462752312	0.9896038306	-0.4089109885
H	-0.6724768830	0.2433247565	1.0530675469
Si	2.0423494127	1.5548214095	0.2135083332
H	-1.4506121282	-0.7801925322	-0.1864736118
H	1.6013989781	-0.1464216981	0.4181428489

#### Frequencies

623.663 i  
113.981  
182.596  
409.484  
679.399  
717.074  
974.354

982.807  
1348.403  
1465.433  
1471.919  
1484.081  
3074.159  
3165.467  
3179.486

**i2 – i4**

C	-1.5301634034	-0.0552895284	0.1285954464
Si	0.4902640488	0.1658458420	-1.0038804565
S	0.4293183823	-0.3786115151	1.0086322597
H	-1.7958080293	0.9942789921	0.1373633933
H	-1.9530861682	-0.5639735863	0.9868776101
H	-1.8758576940	-0.5600036796	-0.7703438002
H	0.2012321238	-0.8413371546	-2.0560213327

Frequencies

1153.918 i  
152.351  
359.306  
395.345  
582.590  
650.456  
780.006  
819.176  
1242.002  
1439.121  
1481.042  
2172.933  
3089.882  
3168.599  
3221.493

**i3 – i4**

Si	-0.5242511057	0.0746288215	-0.4976388744
C	0.6087369755	0.0071929366	-2.0042215073
S	0.2827566741	0.0215922105	1.4399347849
H	-0.2481535695	-1.1916203276	0.5579910894
H	1.0341165470	0.9930479366	-2.1904494097
H	0.0460899998	-0.3045415080	-2.8826754995
H	1.4132532842	-0.7029903520	-1.8188214101

Frequencies

1208.268 i  
103.067  
181.806  
443.086  
537.088  
698.386  
776.514  
787.555  
1248.775  
1445.029  
1452.001  
1674.260  
3064.349  
3151.854  
3162.567

**il – p3**

C	-0.7194774720	0.0267300161	2.2910587295
H	-1.4761812181	-0.7324624505	2.1639155760
H	0.0736284538	-0.1903587240	2.9921544956
H	-1.0432497535	1.0542980628	2.2151031599
S	0.4742360782	-0.2377614662	0.1966917599
H	1.1973049861	0.8172951249	0.6078055140
Si	-0.4122244745	0.5119183768	-1.5954806648

Frequencies

394.822 i  
75.918  
95.622  
419.633  
460.670  
537.167  
583.356  
693.979  
895.558  
1422.864  
1428.581  
2651.294  
3116.926  
3280.378  
3286.219

**i2 – p1**

C	0.6523314477	-0.0111790027	-2.4168348591
Si	0.1285160059	0.1084339313	1.4128391872
H	-0.1111659228	-0.3531614760	-3.0965671594
H	1.0680026049	-0.7146165498	2.2376055716
H	1.5053219784	-0.6454547594	-2.2407367647
S	-0.6689207316	-0.6085433644	-0.2293891769
H	0.7526867975	1.0488562510	-2.2522248587

## Frequencies

257.689 i  
46.325  
103.239  
297.489  
423.840  
439.544  
633.878  
675.983  
759.672  
1420.035  
1421.084  
2110.037  
3137.621  
3309.675  
3313.448

**i1 – p4**

C	-0.8514941561	0.0057960073	1.6196638831
H	-0.4884599523	0.5996148041	2.4551046565
H	-1.7071132737	0.4906773293	1.1566936162
H	-1.1225604185	-0.9889408194	1.9622120958
S	0.5072723247	-0.1526533034	0.4052042039
H	1.5385644267	1.4823897055	1.4598152027
Si	-0.2779194008	0.3602617665	-1.4713452883

## Frequencies

458.001 i  
76.782  
185.691  
218.219  
336.252



522.070  
691.170  
950.418  
978.393  
1340.534  
1472.017  
1477.165  
3078.206  
3175.065  
3180.812

### **i3 – p2**

Si	-0.5429894632	-0.0155967501	-0.4888451895
C	0.5194410958	-0.0170592525	-2.0445820662
S	0.2068322020	0.1225332353	1.3113741480
H	0.2881308659	-2.0150159796	2.3472828756
H	1.1873447863	0.8438089250	-2.0115142810
H	-0.0801524271	0.0100821807	-2.9510387368
H	1.1229344874	-0.9262028526	-2.0344329433

### Frequencies

389.096 i  
33.377  
110.409  
177.238  
204.162  
603.703  
662.319  
745.716  
799.239  
1236.102  
1435.082  
1446.453  
3061.168  
3147.114  
3173.541