Supporting Information

A Combined Experimental and Computational Study on the Reaction Dynamics of the D1-Silylidyne (SiD) - Silane (SiH_4) System

Zhenghai Yang,[a†] Bing-Jian Sun,[b†] Chao He,[a] Shane Goettl,[a] Yu-Ting Lin,[b] Agnes H. H. Chang,[b,*] Ralf I. Kaiser[a,*]

[a] *Department of Chemistry, University of Hawai'i at Manoa, Honolulu, Hawaii 96822, USA*

[b] *Department of Chemistry, National Dong Hwa University, Shoufeng, Hualien 974, Taiwan*

[*] Corresponding Authors:
Prof. Dr. Ralf I. Kaiser: ralfk@hawaii.edu
Prof. Dr. Agnes H. H. Chang: hhchang@mail.ndhu.edu.tw
[†]These authors contributed equally to this work.

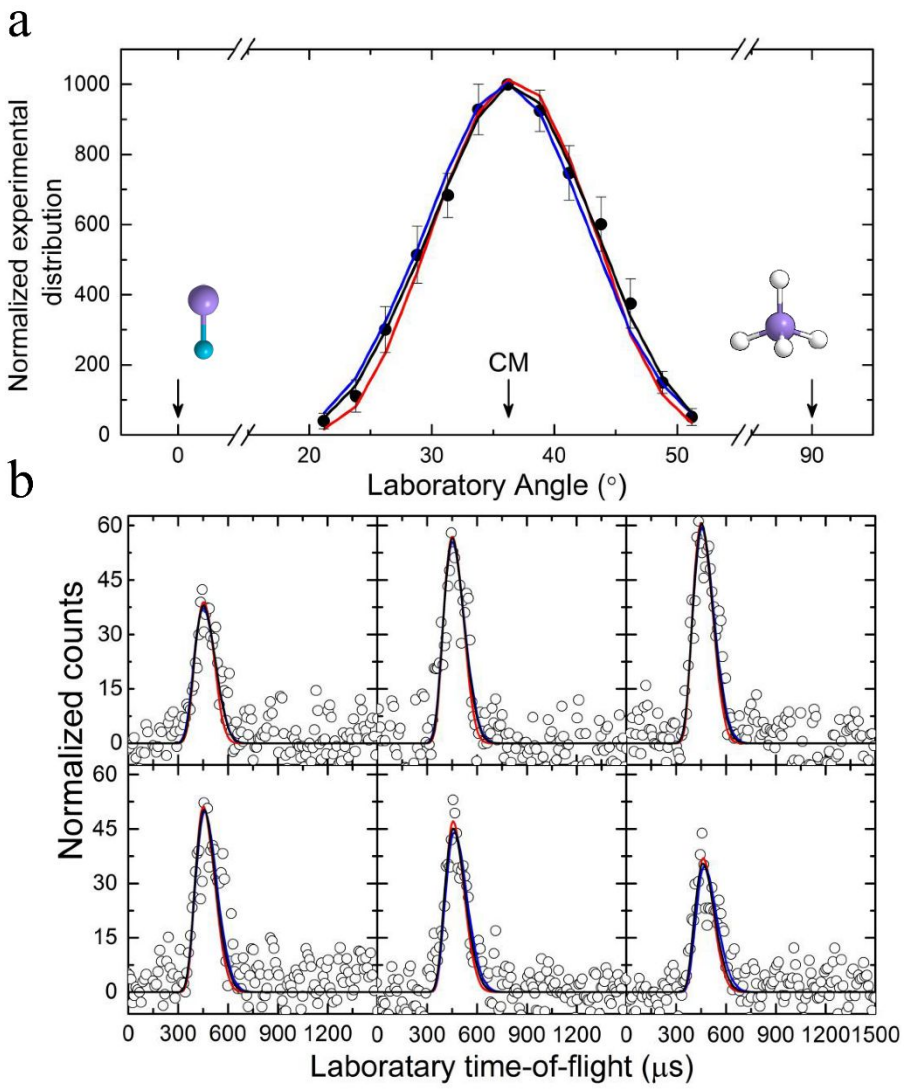


Figure S1. Laboratory angular distribution and the associated time-of-flight spectra. Laboratory angular distribution at mass-to-charge ratio (m/z) of m/z = 61 recorded in the reaction of the D1-silylidyne radical with silane (a) (^{28}SiD + ^{29}SiH$_4$ (red), ^{28}SiD + ^{30}SiH$_4$ (black) and ^{30}SiD + ^{28}SiH$_4$ (blue)), and the time-of-flight spectra recorded at distinct laboratory angles overlaid with the best fits (b). The solid circles with their error bars represent the normalized experimental distribution with ±1σ uncertainty; the open circles indicate the experimental data points of the time-of-flight spectra. Silicon, deuterium, and hydrogen are color coded in purple, light blue, and white, respectively.

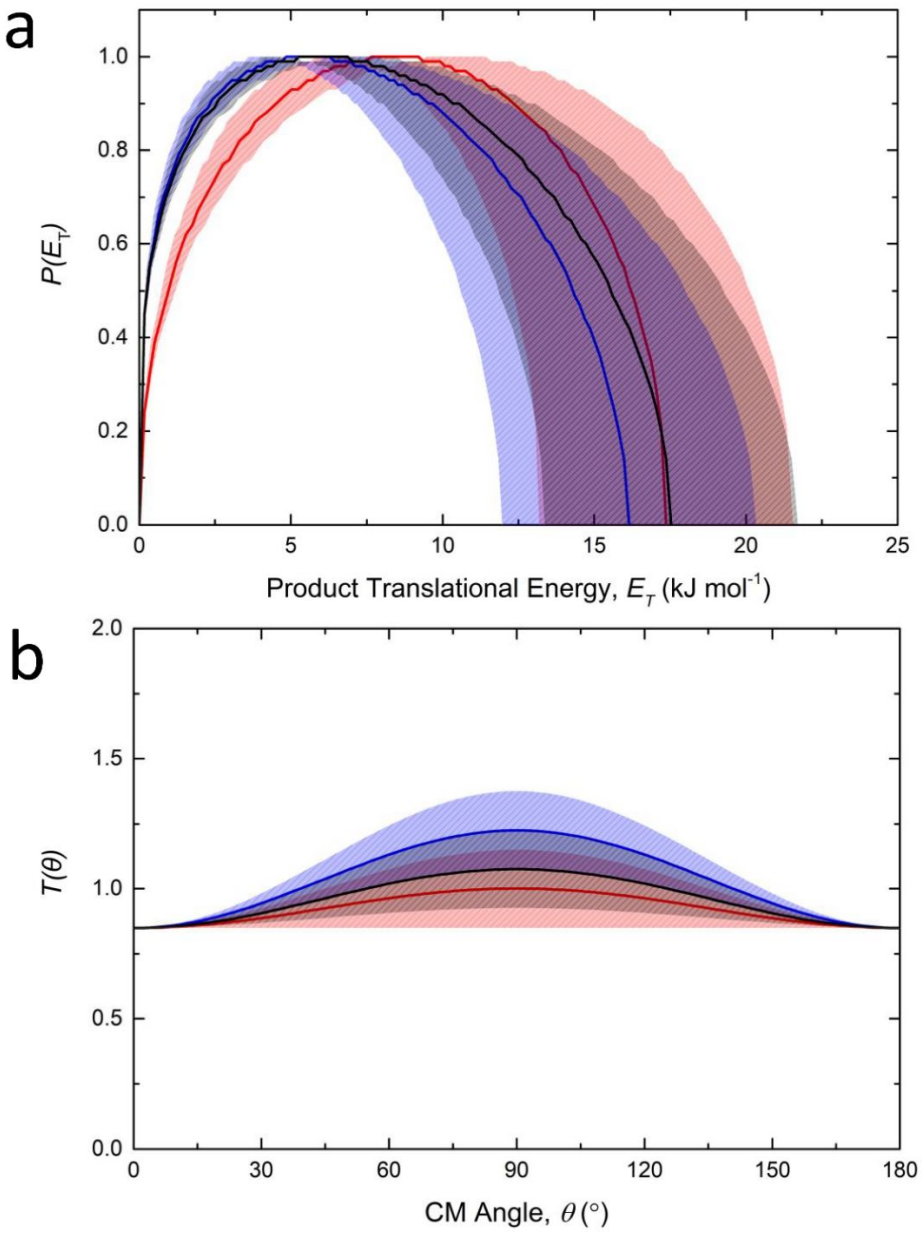


Figure S2. Center-of-Mass (CM) distributions. CM translational energy flux distribution (a), and CM angular flux distribution (b) in the reaction of D1-silylidyne radical with silane (a) (^{28}SiD + ^{29}SiH$_4$ (red), ^{28}SiD + ^{30}SiH$_4$ (black) and ^{30}SiD + ^{28}SiH$_4$ (blue)). Shaded areas indicate the error limits of the best fits accounting for the uncertainties of the laboratory angular distribution and TOF spectra. Silicon, deuterium, and hydrogen are color coded in purple, light blue, and white, respectively.

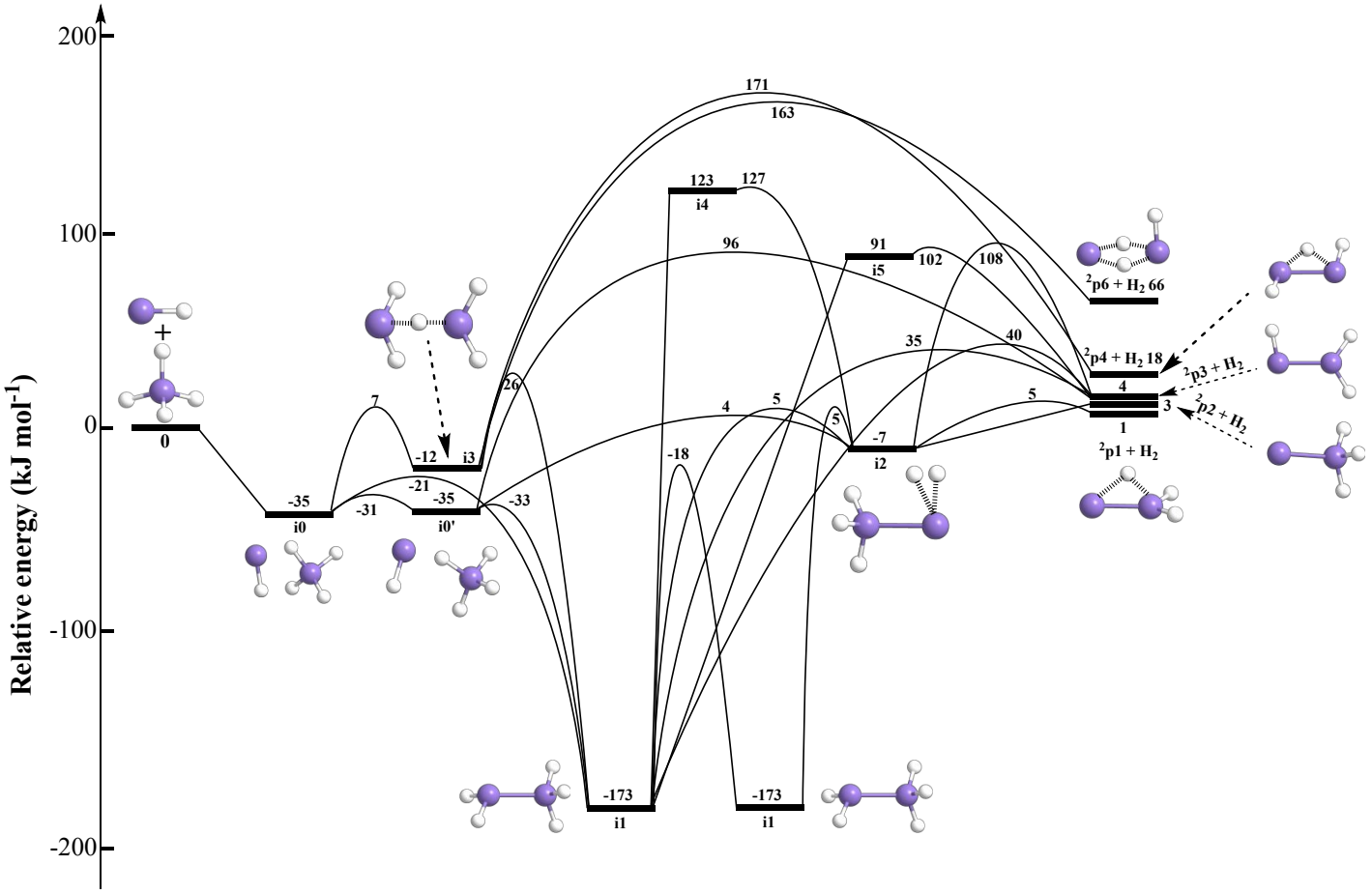


Figure S3. CCSD/cc-pVTZ//CCSD(T)/CBS potential energy surface of H_2 loss pathways for the reaction of the silylidyne radical with silane. Silicon and hydrogen are color coded in purple and white, respectively.

Table S1. Peak Velocity (v_p) and Speed Ratios (S) of the D1-Silylidyne (SiD) and Silane (SiH_4) Beams along with the Corresponding Collision Energy (E_C) and Center-of-Mass Angle Θ_{CM}.

beam	v_p (m s^{-1})	S	E_c (kJ mol^{-1})	Θ_{CM} (deg)
SiD	1206 ± 25	6.1 ± 1.1		
SiH_4	827 ± 20	10.1 ± 0.2	16.6 ± 0.5	36.2 ± 0.6

Table S2. H_2 and HD dissociation products from D1-silylidyne (SiD) plus silane (SiH_4) reaction considering isotopes of silicon.

		$^{28}SiH_4$ (92.2%)	$^{29}SiH_4$ (4.7%)	$^{30}SiH_4$ (3.1%)
H_2 loss	^{28}SiD (92.2%)	$^{28}Si_2H_2D$ 60	$^{28}Si^{29}SiH_2D$ 61	$^{28}Si^{30}SiH_2D$ 62
	^{29}SiD (4.7%)	$^{28}Si^{29}SiH_2D$ 61	$^{29}Si_2H_2D$ 62	$^{29}Si^{30}SiH_2D$ 63
	^{30}SiD (3.1%)	$^{28}Si^{30}SiH_2D$ 62	$^{29}Si^{30}SiH_2D$ 63	$^{30}Si_2H_2D$ 64
HD loss	^{28}SiD (92.2%)	$^{28}Si_2H_3$ 59	$^{28}Si^{29}SiH_3$ 60	$^{28}Si^{30}SiH_3$ 61
	^{29}SiD (4.7%)	$^{28}Si^{29}SiH_3$ 60	$^{29}Si_2H_3$ 61	$^{29}Si^{30}SiH_3$ 62
	^{30}SiD (3.1%)	$^{28}Si^{30}SiH_3$ 61	$^{29}Si^{30}SiH_3$ 62	$^{30}Si_2H_3$ 63

Table S3. H_2 dissociation products from silicon (Si) plus silane (SiH_4) reaction considering isotopes of silicon.

		$^{28}SiH_4$ (92.2%)	$^{29}SiH_4$ (4.7%)	$^{30}SiH_4$ (3.1%)
H_2 loss	^{28}Si (92.2%)	$^{28}Si_2H_2$ 58	$^{28}Si^{29}SiH_2$ 59	$^{28}Si^{30}SiH_2$ 60
	^{29}Si (4.7%)	$^{28}Si^{29}SiH_2$ 59	$^{29}Si_2H_2$ 60	$^{29}Si^{30}SiH_2$ 61
	^{30}Si (3.1%)	$^{28}Si^{30}SiH_2$ 60	$^{29}Si^{30}SiH_2$ 61	$^{30}Si_2H_2$ 62

Table S4. Cartesian coordinates of CCSD/cc-pVTZ optimized geometries of species including variational transition state tsi2p2 at 8.0, 10.0, 16.6 kJ/mol on the Si_2H_5 adiabatic doublet ground state potential energy surface (Figure S3).

	X	Y	Z		X	Y	Z
SiH				**SiH_4**			
Si	0.000000	0.000000	0.101782	Si	0.000000	0.000000	0.000000
H	0.000000	0.000000	-1.424947	H	0.855367	0.855367	0.855367
				H	-0.855367	-0.855367	0.855367
				H	-0.855367	0.855367	-0.855367
				H	0.855367	-0.855367	-0.855367
i0				**i0'**			
Si	-0.029424	-1.310446	0.000000	Si	-1.289849	-0.003659	-0.015803
H	0.760316	-1.468942	1.233049	H	-2.266255	0.420645	1.014382
H	-1.173513	-2.252046	0.000000	H	-1.244464	0.971960	-1.118151
H	0.760316	-1.468942	-1.233049	H	-1.576595	-1.378258	-0.465931
Si	-0.029424	1.619356	0.000000	Si	1.553004	-0.095615	-0.007132
H	1.291851	0.844079	0.000000	H	-0.005172	-0.046389	0.857487
H	-0.815109	0.021109	0.000000	H	1.408314	1.421874	0.033303
i1				**i2**			
Si	-0.034632	-1.125526	0.000000	Si	0.109862	-1.101993	0.000000
H	1.338087	-1.694606	0.000000	Si	0.109862	1.298032	0.000000
H	-0.745603	-1.610329	1.208567	H	1.556939	-1.451729	0.000000
H	-0.745603	-1.610329	-1.208567	H	-0.506204	-1.734376	1.198477
Si	-0.034632	1.215441	0.000000	H	-0.506204	-1.734376	-1.198477
H	0.561402	1.828226	-1.215120	H	-1.826055	1.477425	0.000000
H	0.561402	1.828226	1.215120	H	-1.794622	0.698508	0.000000
i3							

Si	0.019726	1.210680	0.000000				
H	-0.593458	1.836431	1.205918				
H	0.825943	-0.773917	-1.146580				
H	-0.593458	1.836431	-1.205918				
Si	0.019726	-1.353155	0.000000				
H	-1.017298	-0.130381	0.000000				
H	0.825943	-0.773917	1.14658				
tsi0i0'				**tsi0i1**			
Si	-1.346956	-0.003056	-0.011695	Si	-1.127854	-0.000130	-0.015789
H	-2.322445	-0.573494	0.944431	H	-1.625323	-0.000630	1.381351
H	-1.517401	1.454608	-0.132407	H	-1.647247	1.208325	-0.707554
H	-1.428429	-0.698369	-1.309300	H	-1.646484	-1.208058	-0.709179
Si	1.634592	-0.085269	-0.005612	Si	1.360608	0.000236	-0.074105
H	-0.023743	-0.340041	0.70259	H	0.832414	-1.219462	0.646935
H	1.265117	1.393839	0.036991	H	0.828091	1.218343	0.646964
tsi0'i1				**tsi0'i2**			
Si	1.122761	-0.001885	-0.021106	Si	1.118707	-0.016509	0.000110
H	1.789467	1.300206	0.213947	Si	-1.339263	-0.149814	-0.000024
H	-0.265252	0.621223	0.974266	H	1.432694	-1.465367	-0.007765
H	1.562313	-1.008296	0.966584	H	1.734046	0.598887	-1.202640
Si	-1.327917	-0.123112	-0.003187	H	1.732067	0.586265	1.210171
H	1.486585	-0.446232	-1.395657	H	-1.455343	1.434123	0.001869
H	-1.700922	1.283061	-0.419034	H	-0.355675	1.174619	-0.002827
tsi1i1				**tsi1i2**			
Si	-1.116565	-0.015663	-0.015789	Si	1.102888	-0.009815	-0.007032
H	-2.075835	-0.965852	-0.642304	H	1.586275	1.013992	-0.970128
H	0.000318	0.000779	1.326177	H	1.704227	0.258843	1.324070
H	-1.697346	1.324964	0.199106	H	1.602381	-1.342939	-0.440269

Si	1.11665	0.015745	-0.015371	Si	-1.297533	-0.171958	0.008109
H	2.075302	0.964473	-0.645176	H	-1.562186	1.344533	-0.299943
H	1.696378	-1.325517	0.198437	H	-0.605663	1.2704	0.371192
tsi2p2 (8.0 kJ/mol)				**tsi2p2 (10.0 kJ/mol)**			
Si	1.108929	0.009969	-0.000029	Si	-1.108826	0.007941	-0.000033
Si	-1.265452	-0.323740	-0.000033	Si	1.267914	-0.309233	-0.000032
H	1.659177	-1.377143	0.003325	H	-1.648928	-1.382703	0.002831
H	1.646341	0.706503	-1.200429	H	-1.650514	0.705358	1.198004
H	1.644982	0.711676	1.197975	H	-1.651726	0.701121	-1.199962
H	-1.744644	2.087633	-0.000011	H	1.73029	2.01863	0.000012
H	-1.014521	2.264123	-0.000003	H	0.993652	2.175678	0.000024
tsi2p2 (16.6 kJ/mol)				**tsi2p1**			
Si	-1.108792	0.004208	0.000020	Si	-1.094639	0.201533	0.002585
Si	1.273141	-0.280614	0.000013	Si	1.067637	-0.512524	-0.001853
H	-1.631372	-1.391975	-0.000969	H	-0.919852	-1.347138	-0.030168
H	-1.661238	0.692030	1.198875	H	-1.888946	0.522199	1.215181
H	-1.660889	0.693297	-1.198269	H	-1.8788	0.570388	-1.202961
H	1.701545	1.879621	0.000036	H	2.208142	2.464742	-0.081415
H	0.951061	1.996723	-0.000135	H	2.857485	2.143675	0.089111
p1				**p2**			
Si	-0.050727	-0.991730	0.000000	Si	1.030257	-0.000022	-0.006106
Si	-0.050727	1.261509	0.000000	H	1.654609	1.197105	-0.630697
H	1.266751	-0.063344	0.000000	H	1.378053	0.008961	1.446450
H	0.076804	-1.856780	1.202060	H	1.653791	-1.205330	-0.615634
H	0.076804	-1.85678	-1.20206	Si	-1.365004	-0.000031	-0.008188
p3				**p4**			
Si	-1.047469	-0.021690	0.060875	Si	0.000000	-1.131866	-0.055655
H	-1.878151	1.202909	-0.071150	H	-1.454579	1.460465	0.172334

H	-1.817188	-1.154077	-0.523397	H	1.454579	-1.460465	0.172334
Si	1.200441	0.111588	-0.042127	Si	0.000000	1.131866	-0.055655
H	1.553735	-1.307411	0.332073	H	0.000000	0.000000	1.213672
p5				**p6**			
Si	-1.108069	-0.123258	-0.057465	Si	0.045361	-1.254045	0.000000
H	-1.909793	1.134529	0.128795	H	0.100237	0.024439	1.037741
H	-0.052282	0.017044	1.217185	H	-1.470577	-1.210600	0.000000
Si	1.184824	-0.061011	-0.024332	Si	0.045361	1.337025	0.000000
H	0.8875	1.428194	-0.200822	H	0.100237	0.024439	-1.037741

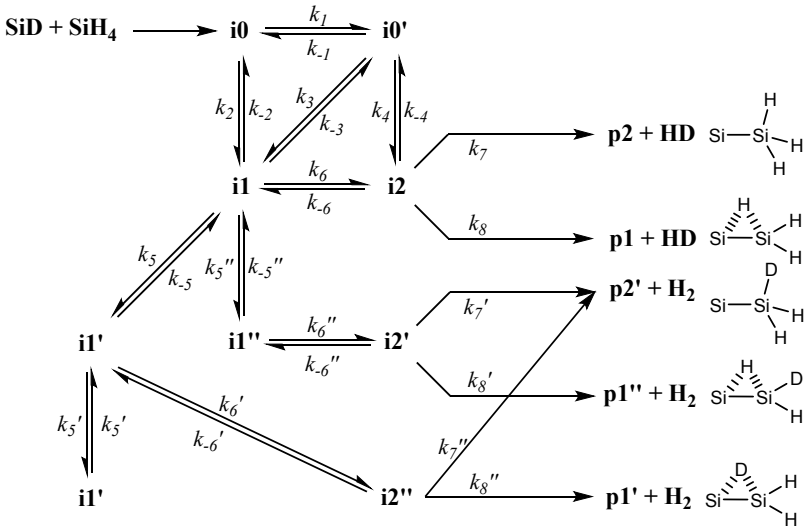
Table S5. The RRKM rate constants (s^{-1}) of SiD + SiH_4 reaction (Figure 3) computed with CCSD/cc-pVTZ//CCSD(T)/CBS energies, and CCSD/cc-pVTZ harmonic frequencies at collision energies of 8.0, 10.0, and 16.6 kJ/mol.

	8.0	**10.0**	**16.6**
k_1 (i0 → i0')	1.22×10^{12}	1.24×10^{12}	1.30×10^{12}
k_{-1} (i0' → i0)	2.23×10^{12}	2.26×10^{12}	2.36×10^{12}
k_2 (i0 → i1)	2.35×10^{11}	2.51×10^{11}	3.07×10^{11}
k_{-2} (i1 → i0)	2.54×10^{7}	3.16×10^{7}	6.06×10^{7}
k_3 (i0' → i1)	1.59×10^{12}	1.61×10^{12}	1.65×10^{12}
k_{-3} (i1 → i0')	9.41×10^{7}	1.10×10^{8}	1.80×10^{8}
k_4 (i0' → i2)	1.40×10^{9}	2.16×10^{9}	6.29×10^{9}
k_{-4} (i2 → i0')	8.04×10^{10}	1.01×10^{11}	1.68×10^{11}
k_5 (i1 → i1')	2.86×10^{7}	3.61×10^{7}	7.26×10^{7}
k_{-5} (i1' → i1)	1.43×10^{7}	1.80×10^{7}	3.63×10^{7}
k_5' (i1' → i1')	9.38×10^{6}	1.19×10^{7}	2.46×10^{7}
k_5'' (i1 → i1'')	1.47×10^{7}	1.85×10^{7}	3.70×10^{7}

k_{-5}'' (i1" → i1)	1.47×10^{7}	1.85×10^{7}	3.71×10^{7}
k_{6} (i1 → i2)	1.49×10^{5}	2.96×10^{5}	1.61×10^{6}
k_{-6} (i2 → i1)	1.45×10^{11}	2.02×10^{11}	3.96×10^{11}
k_{6}' (i1' → i2")	2.40×10^{5}	4.41×10^{5}	2.12×10^{6}
k_{-6}' (i2" → i1')	2.23×10^{11}	2.90×10^{11}	5.12×10^{11}
k_{6}'' (i1" → i2')	2.40×10^{5}	4.43×10^{5}	2.13×10^{6}
k_{-6}'' (i2' → i1")	2.23×10^{11}	2.90×10^{11}	5.15×10^{11}
k_{7} (i2 → p2)	9.34×10^{12}	1.09×10^{13}	1.33×10^{13}
k_{7}' (i2' → p2')	1.09×10^{13}	1.18×10^{13}	1.36×10^{13}
k_{7}'' (i2" → p2')	1.07×10^{13}	1.17×10^{13}	1.35×10^{13}
k_{8} (i2 → p1)	1.07×10^{12}	1.33×10^{12}	7.29×10^{12}
k_{8}' (i2' → p1")	1.15×10^{12}	2.25×10^{12}	9.10×10^{12}
k_{8}'' (i2" → p1')	6.20×10^{11}	1.35×10^{12}	6.28×10^{12}

Table S6. (a) The reaction mechanism derived from Figure 3, and (b) rate equations.

(a)



(b)

$$\frac{d[i0]}{dt} = k_{-1}[i0'] + k_{-2}[i1] - (k_1 + k_2)[i0]$$

$$\frac{d[i0']}{dt} = k_1[i0] + k_{-3}[i1] + k_{-4}[i2] - (k_{-1} + k_3 + k_4)[i0']$$

$$\frac{d[i1]}{dt} = k_2[i0] + k_3[i0'] + k_{-6}[i2] + k_{-5}[i1'] + k''_{-5}[i1''] - (k_{-2} + k_{-3} + k_5 + k''_5 + k_6)[i1]$$

$$\frac{d[i1']}{dt} = k_5[i1] + k'_{-6}[i2''] - (k_{-5} + k'_6)[i1']$$

$$\frac{d[i1'']}{dt} = k''_5[i1] + k''_{-6}[i2'] - (k''_{-5} + k''_6)[i1'']$$

$$\frac{d[i2]}{dt} = k_4[i0'] + k_6[i1] - (k_{-4} + k_{-6} + k_7 + k_8)[i2]$$

$$\frac{d[i2']}{dt} = k''_6[i1''] - (k''_{-6} + k'_7 + k'_8)[i2']$$

$$\frac{d[i2'']}{dt} = k'_6[i1'] - (k'_{-6} + k''_7 + k''_8)[i2'']$$

$$\frac{d[p2 + HD]}{dt} = k_7[i2]$$

$$\frac{d[p2' + H_2]}{dt} = k'_7[i2'] + k''_7[i2'']$$

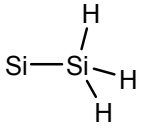
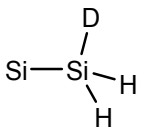
$$\frac{d[p1 + HD]}{dt} = k_8[i2]$$

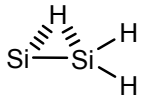
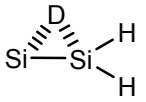
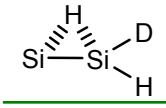
$$\frac{d[p1' + H_2]}{dt} = k''_8[i2'']$$

$$\frac{d[p1'' + H_2]}{dt} = k'_8[i2']$$

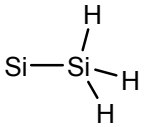
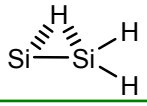
Table S7. Branching ratios (%) for SiD + SiH_4 reaction at collision energies of 8.0, 10.0, and 16.6 kJ/mol: (a) all products, (b) p1 and p2, (c) HD and H_2.

(a)

		8.0	**10.0**	**16.6**
	p2 + HD	22.0	22.6	17.8
	p2' + H_2	47.3	44.3	32.7

	p1 + HD	2.5	2.8	9.9
	p1' + H_2	2.7	5.0	15.1
	p1" + H_2	25.5	25.3	24.6

(b)

	p2	69.3	66.9	50.5
	p1	30.7	33.1	49.5

(c)

HD	24.5	25.4	27.6
H_2	75.5	74.6	72.4

Table S8. Cartesian coordinates of CCSD/cc-pVTZ optimized geometries for variational transition states, tsi2p2, tsi2'p2', tsi2''p2', at 8.0, 10.0, 16.6 kJ/mol, respectively, on the Si_2H_4D adiabatic doublet ground state potential energy surface (Figure 3).

tsi2p2

	X	Y	Z		X	Y	Z
8.0 kJ/mol				**10.0 kJ/mol**			
Si	1.109044	0.012489	0.000040	Si	1.108929	0.009969	-0.000029
Si	-1.262653	-0.338742	0.000016	Si	-1.265452	-0.323740	-0.000033

H	1.668110	-1.371520	0.000225	H	1.659177	-1.377143	0.003325
H	1.640732	0.714360	-1.199750	H	1.646341	0.706503	-1.200429
H	1.640834	0.715622	1.199014	H	1.644982	0.711676	1.197975
D	-1.761503	2.157209	-0.000121	D	-1.744644	2.087633	-0.000011
H	-1.037647	2.351867	-0.000149	H	-1.014521	2.264123	-0.000003
16.6 kJ/mol							
Si	-1.108792	0.004208	0.000020				
Si	1.273141	-0.280614	0.000013				
H	-1.631372	-1.391975	-0.000969				
H	-1.661238	0.692030	1.198875				
H	-1.660889	0.693297	-1.198269				
D	1.701545	1.879621	0.000036				
H	0.951061	1.996723	-0.000135				

tsi2'p2'

8.0 kJ/mol				**10.0 kJ/mol**			
Si	-1.108826	0.007941	-0.000033	Si	-1.108792	0.004208	0.000020
Si	1.267914	-0.309233	-0.000032	Si	1.273141	-0.280614	0.000013
H	-1.648928	-1.382703	0.002831	H	-1.631372	-1.391975	-0.000969
D	-1.650514	0.705358	1.198004	D	-1.661238	0.692030	1.198875
H	-1.651726	0.701121	-1.199962	H	-1.660889	0.693297	-1.198269
H	1.73029	2.01863	0.000012	H	1.701545	1.879621	0.000036
H	0.993652	2.175678	0.000024	H	0.951061	1.996723	-0.000135
16.6 kJ/mol							
Si	-1.108792	0.004208	0.000020				
Si	1.273141	-0.280614	0.000013				
H	-1.631372	-1.391975	-0.000969				
D	-1.661238	0.692030	1.198875				
H	-1.660889	0.693297	-1.198269				

H	1.701545	1.879621	0.000036	
H	0.951061	1.996723	-0.000135	

tsi2''p2'

8.0 kJ/mol				**10.0 kJ/mol**			
Si	-1.108826	0.007941	-0.000033	Si	-1.108792	0.004208	0.000020
Si	1.267914	-0.309233	-0.000032	Si	1.273141	-0.280614	0.000013
D	-1.648928	-1.382703	0.002831	D	-1.631372	-1.391975	-0.000969
H	-1.650514	0.705358	1.198004	H	-1.661238	0.692030	1.198875
H	-1.651726	0.701121	-1.199962	H	-1.660889	0.693297	-1.198269
H	1.73029	2.01863	0.000012	H	1.701545	1.879621	0.000036
H	0.993652	2.175678	0.000024	H	0.951061	1.996723	-0.000135
16.6 kJ/mol							
Si	-1.108792	0.004208	0.000020				
Si	1.273141	-0.280614	0.000013				
D	-1.631372	-1.391975	-0.000969				
H	-1.661238	0.692030	1.198875				
H	-1.660889	0.693297	-1.198269				
H	1.701545	1.879621	0.000036				
H	0.951061	1.996723	-0.000135				

Table S9. CCSD/cc-pVTZ optimized geometries on the adiabatic doublet ground state potential energy surface.

SiD				
Normal modes	Frequency(cm^{-1})	IR Inten	Frequency(cm^{-1})	IR Inten
v1	1470.54	132.2545		
	i0		**i0'**	
v1	50.35	0.3196	114.47	2.3379

ν2	137.8	2.4751	142.59	0.02
ν3	266.26	0.0294	183.79	0.1457
ν4	442.46	49.1723	452.38	6.9736
ν5	561.91	35.7289	558.37	29.5414
ν6	765.92	26.1616	825.85	61.9848
ν7	902.11	322.6288	885.85	406.3984
ν8	945.1	102.9553	940.56	52.7202
ν9	977.6	54.5933	965.73	54.9336
ν10	1261.45	66.7285	1209.18	126.238
ν11	1450.74	108.6922	1471.28	111.9561
ν12	1876.45	510.4743	1792.56	272.9188
ν13	2263.04	84.2919	2260.94	86.6077
ν14	2299.06	38.3101	2294.55	42.6057
ν15	2315.31	62.5922	2312.39	53.1184
	i1		**i1'**	
ν1	117.93	0.1386	124.92	0.1841
ν2	328.34	12.3164	344.72	13.2771
ν3	396.56	17.2463	405.09	18.5747
ν4	440.18	1.3516	441.96	1.55
ν5	572.65	12.7037	573.06	1.9622
ν6	609.78	2.2342	610.03	11.8918
ν7	820.43	192.3686	821.48	28.0032
ν8	913.16	198.4654	828.37	290.1689
ν9	959.93	52.661	932.87	97.695
ν10	966.35	42.0204	961.37	47.6476
ν11	1605.52	42.8107	1616.55	45.1397
ν12	2228.17	99.1917	2220.44	91.6457
ν13	2233.47	56.6037	2231.25	73.7087
ν14	2246.18	69.9016	2241.74	45.1481
ν15	2252.69	113.1191	2250.44	130.8216
	i1''		**i2**	
ν1	125.9	0.1164	113.37	0.4419

ν2	359.09	11.7532	179.28	0.9584
ν3	381.89	19.7764	279.58	1.127
ν4	439.42	0.5847	305.44	23.3033
ν5	557.16	31.1457	395.28	1.352
ν6	628.89	1.3269	474.03	16.0194
ν7	831.42	276.6797	512.86	8.3831
ν8	833.35	24.012	887.27	119.4113
ν9	941.63	98.9395	914.79	211.9651
ν10	950.1	21.3577	954.39	41.8087
ν11	1603.57	48.7449	971.05	45.4949
ν12	2221.39	87.15	2213.26	97.288
ν13	2241.22	27.8805	2215.99	111.8617
ν14	2245.52	59.4259	2221.92	100.3761
ν15	2253.89	159.4434	3290.63	11.6121
	i2'		**i2''**	
ν1	121.4	2.4362	120.63	2.3468
ν2	192.68	0.1195	193.81	0.0708
ν3	313.48	3.2231	300.04	5.6673
ν4	354.13	29.8456	341.05	19.5898
ν5	388.02	9.2689	399.98	4.852
ν6	410.96	8.4026	467.53	17.8237
ν7	515.86	8.3064	485.14	4.2859
ν8	824.11	90.7729	811.99	23.2852
ν9	834.8	170.9085	823.8	248.9727
ν10	947.29	66.223	962.91	90.7812
ν11	1040.82	9.6861	1038.57	7.0205
ν12	1592.75	58.2136	1596.03	50.806
ν13	2214.36	104.5157	2214.82	105.2858
ν14	2221.19	99.5607	2215.89	112.7879
ν15	3799.55	7.6289	3799.53	7.7978
	tsi0i0'		**tsi0i1**	
ν1	-134.9	0.3195	-1193.95	2000.9089

ν2	120.91	0.0768	216.05	0.0443
ν3	206.8	0.2678	313.3	4.0544
ν4	418.6	29.0043	348.09	0.5407
ν5	534.61	13.2633	430.02	21.2554
ν6	841.94	111.4235	524.36	8.3577
ν7	897.74	349.3196	775.99	62.1338
ν8	946.44	63.2645	887.04	431.3387
ν9	964.05	53.6906	962.33	44.7918
ν10	1148.47	80.5604	966.32	48.9854
ν11	1472.27	107.3436	1483.03	18.9401
ν12	1865.78	394.4175	2068.91	49.561
ν13	2269.21	75.0715	2220.37	127.7676
ν14	2296.6	42.3195	2234.97	108.0514
ν15	2315.23	55.2254	2247.48	121.4099
	tsi0'i1		**tsi0i2**	
ν1	-420.25	36.6227	-892.79	182.7828
ν2	185.57	0.287	140.12	0.8063
ν3	311.68	4.3	288.22	0.0055
ν4	404.42	12.2746	342.94	0.7881
ν5	595.75	24.0637	561	12.3988
ν6	720.83	36.6197	583.94	16.9115
ν7	883.28	67.0115	692.63	52.8532
ν8	911.45	271.4984	920.62	353.2908
ν9	945.41	66.21	961.06	38.9986
ν10	994.76	118.7829	969.37	39.0784
ν11	1507.67	80.63	1257.11	84.21
ν12	1686.47	256.2818	1893.14	87.3723
ν13	2191.63	71.3183	2235.53	90.7051
ν14	2252.7	91.5919	2240.41	98.6252
ν15	2285.39	71.1628	2248.98	72.7935
	tsi1i1'		**tsi1'i1'**	
ν1	-1519.45	956.3057	-1139.79	574.0676
ν2	239.47	6.9916	255.67	8.595

ν3	365.72	7.4159	406.38	0.285
ν4	392.08	1.9764	431.08	12.581
ν5	503.46	1.795	528.51	0.6738
ν6	520.12	3.283	535.58	0.4355
ν7	570.28	5.0501	620.59	5.7451
ν8	826.93	157.4124	781.5	66.3318
ν9	919.6	68.8153	917.3	206.2429
ν10	1028.61	31.3051	919.52	1.6248
ν11	1499.12	82.0697	1095.39	60.2653
ν12	1580.32	75.6239	2188.44	20.7195
ν13	2190.85	135.8578	2192.51	255.6427
ν14	2279.23	10.0459	2280.14	6.1754
ν15	2284.28	113.4394	2285.32	117.0892
	tsi1'i1''		**tsi1i2**	
ν1	-1533.2	1011.9435	-1099.82	171.8586
ν2	234.08	5.6309	58.61	2.4104
ν3	364.55	1.8264	212.85	1.7324
ν4	398.33	9.8644	404.04	10.3162
ν5	499.55	3.051	407.31	8.8649
ν6	530.9	0.2111	565.62	13.7742
ν7	615.57	8.9955	674.06	22.8715
ν8	789.92	104.2742	918.05	332.443
ν9	909.92	138.0253	951.86	54.2501
ν10	1010.87	28.6195	988.77	61.0669
ν11	1501.76	89.6349	1392.2	26.7007
ν12	1639.69	33.9364	1708.64	159.2876
ν13	2189.39	33.1231	2217.92	94.3781
ν14	2194.5	237.7274	2228.85	84.8304
ν15	2282.77	62.2511	2236.66	103.569
	tsi1'i2''		**tsi1''i2'**	
ν1	-1259.06	214.6089	-1258.81	213.4564
ν2	70.32	3.017	70.02	2.9926
ν3	212.92	2.3109	205.9	2.4463

ν4	387.93	3.5824	391.25	9.9677
ν5	441.3	13.8845	409.29	1.7195
ν6	493.7	15.1578	561.94	15.0048
ν7	743.59	23.1507	720.95	120.9769
ν8	841.86	153.2208	808	21.8471
ν9	865.43	163.8726	861.6	161.6474
ν10	945.21	58.2571	985.84	101.8451
ν11	1595.08	49.4735	1602.71	46.4084
ν12	1708.07	164.0666	1707.57	161.8459
ν13	1935.15	53.9487	1935.36	51.0552
ν14	2227.95	83.855	2219.27	98.6111
ν15	2236.14	104.2843	2234.96	100.3764
	tsi2p2 (collision energies=8.0kJ/mol)		**tsi2p2 (collision energies=10.0kJ/mol)**	
ν1	77.16	0.0216	82.49	0.0117
ν2	112.6	0.0019	120.71	0.0171
ν3	152.85	2.107	170.26	3.0004
ν4	266.13	1.0635	288.13	1.1071
ν5	359.36	13.8707	365.54	11.8103
ν6	449.95	13.8135	456.02	17.3404
ν7	453.68	17.3652	457.02	13.7622
ν8	894.61	286.0934	895.74	290.1502
ν9	942.62	39.2513	943.95	39.5285
ν10	971.45	52.6919	971.6	51.8109
ν11	2197.75	83.967	2199.92	84.9035
ν12	2217.82	106.6304	2217.61	106.8643
ν13	2218.39	108.1789	2217.99	108.7087
ν14	3570.26	8.4836	3562.75	8.7921
ν15				
	tsi2p2 (collision energies=16.6kJ/mol)		**tsi2'p2' (collision energies=8.0kJ/mol)**	
ν1	101.09	0.031	97.61	0.1576
ν2	153.27	0.2119	126.99	0.0234

ν3	230.34	7.3223	217.29	6.314
ν4	381.54	4.6625	362.32	7.0582
ν5	396.46	2.0735	378.26	12.8154
ν6	462.66	17.0154	426.19	4.5263
ν7	490.11	11.8228	469.89	14.6029
ν8	899.55	303.8431	814.31	112.7262
ν9	948.36	40.4694	835.2	140.4988
ν10	971.58	48.7591	939.61	60.8387
ν11	2207.3	86.724	1593.92	57.2742
ν12	2216.63	110.5356	2202.59	89.5617
ν13	2217.24	108.046	2217.41	109.4411
ν14	3439.73	4.867	4122.85	13.8114
ν15				

	tsi2'p2' (collision energies=10.0kJ/mol)		**tsi2'p2' (collision energies=16.6kJ/mol)**	
ν1	112.48	0.586	112.48	0.586
ν2	157.2	0.0289	157.2	0.0289
ν3	262.07	10.888	262.07	10.888
ν4	379.32	10.7539	379.32	10.7539
ν5	382.67	5.5935	382.67	5.5935
ν6	461.06	8.9905	461.06	8.9905
ν7	573.12	7.6538	573.12	7.6538
ν8	818.86	109.7336	818.86	109.7336
ν9	835.17	146.3985	835.17	146.3985
ν10	942.34	63.4072	942.34	63.4072
ν11	1593.21	57.7032	1593.21	57.7032
ν12	2208.07	90.7551	2208.07	90.7551
ν13	2216.84	110.3948	2216.84	110.3948
ν14	3994.87	9.4586	3994.87	9.4586
ν15				

	tsi2''p2' (collision energies=8.0kJ/mol)		**tsi2''p2' (collision energies=10.0kJ/mol)**	
ν1	96.8	0.1493	111.68	0.5645
ν2	126.82	0.017	157.24	0.02

ν3	213.32	6.496	252.57	10.1595
ν4	325.34	4.8688	353.14	2.3746
ν5	420.61	4.1638	441.41	2.6814
ν6	453.16	18.2113	457.14	18.2102
ν7	461.62	6.202	571.91	4.5875
ν8	803.13	22.6021	806.04	22.8507
ν9	814.78	222.6202	817.53	231.2769
ν10	965.03	93.3694	964.52	92.5557
ν11	1583.5	49.512	1587.79	49.959
ν12	2216.37	103.8243	2215.46	104.4847
ν13	2217.57	110.0526	2216.54	111.3889
ν14	4122.84	13.7225	3994.86	9.3468
ν15				

	tsi2''p2' (collision energies=16.6kJ/mol)		**tsi2p1**	
ν1	111.68	0.5645	-278.19	55.4418
ν2	157.24	0.02	63.58	0.0071
ν3	252.57	10.1595	84.17	0.3312
ν4	353.14	2.3746	93.05	0.8757
ν5	441.41	2.6814	104.24	1.1679
ν6	457.14	18.2102	226.04	1.0138
ν7	571.91	4.5875	428.03	11.5975
ν8	806.04	22.8507	491.6	9.0586
ν9	817.53	231.2769	835.89	26.9749
ν10	964.52	92.5557	866.48	185.4093
ν11	1587.79	49.959	962.86	131.3713
ν12	2215.46	104.4847	1889.75	73.6718
ν13	2216.54	111.3889	2230.97	123.3635
ν14	3994.86	9.3468	2239.03	98.438
ν15			3798.67	1.648

	tsi2''p1'		**tsi2'p1''**	
ν1	-229.26	33.4046	-266.94	52.5573

ν2	73.31	0.0227	72.92	0.0382
ν3	88.9	0.9174	90.65	0.9563
ν4	101.03	0.0243	101.08	0.0169
ν5	116.96	0.7164	118.7	0.8223
ν6	257.21	1.5054	257.21	1.654
ν7	426.01	11.2387	355.27	9.5612
ν8	489.53	9.25	483.5	13.4743
ν9	705.21	17.5815	748.01	50.5784
ν10	771.43	102.7476	834.94	212.9134
ν11	961.19	142.0253	865.9	29.913
ν12	1358.23	45.6365	1606.82	55.8116
ν13	2230.7	120.2326	1890.17	78.4012
ν14	2239.03	98.5602	2235.09	112.3277
ν15	4385.7	2.3651	4385.71	2.3482
	p1		**p2**	
ν1	414.25	28.6421	328.57	24.0625
ν2	420.33	8.4455	391.91	9.821
ν3	493.56	18.0563	425.7	13.2065
ν4	744.28	15.7684	889.97	273.5098
ν5	950.12	30.9735	931.84	46.0093
ν6	986.8	381.5553	970.65	58.8817
ν7	1683.26	104.7685	2191.61	74.3026
ν8	2221.26	140.6656	2220.4	107.7723
ν9	2229.58	103.3607	2222.11	106.4032
	p3		**p4**	
ν1	327.7	9.0471	326.55	22.7253
ν2	403.75	14.8923	455.54	0.9063
ν3	450.93	10.3565	660.4	7.0436
ν4	481.93	2.4203	732.77	0.0536
ν5	630.55	6.6723	749.45	31.1766
ν6	968.69	96.8136	1134.26	135.0814
ν7	2114.05	126.0511	1511.24	82.2665
ν8	2214.4	92.9007	2116.25	2.749

ν9	2242.07	96.2428	2122.52	314.1377
	p5		**p6**	
ν1	384.07	9.3704	184.54	1.3323
ν2	412.31	5.652	393.21	0.9596
ν3	564.69	3.2292	777.87	5.9723
ν4	654.22	53.3221	824.34	74.2013
ν5	891.78	29.8301	1322.32	22.9041
ν6	1009.92	226.0309	1469.97	1022.7297
ν7	1534.52	86.505	1471.26	0.8822
ν8	2026.71	117.9133	1681.53	67.3518
ν9	2128.84	171.8728	2078.47	159.78

Table S10. CCSD/cc-pVTZ//CCSD(T)/CBS energies on the adiabatic doublet ground state potential energy surface.

	CCSD/ cc-pVTZ + E_{zpc} [a]	E_{zpc} [b]	CCSD(T)/ cc-pVDZ	CCSD(T)/ cc-pVTZ	CCSD(T)/ cc-pVQZ	CCSD(T)/ CBS	E[c] (kJ/mol)
SiH ($C_{\infty v}$, $^2\Pi$)	-289.538875	0.004656	-289.520106	-289.546538	-289.553670	-289.557575	

SiH_4 (T_d, $^1A_1$)	-291.401964	0.031561	-291.392685	-291.437349	-291.450714	-291.458201	
SiH ($^2\Pi$) + SiH_4 ($^1A_1$)	-580.940839	0.036217	-580.912791	-580.983886	-581.004383	-581.015776	0
i0 (C_s, $^2A''$)	-580.948731	0.039462	-580.921299	-580.997772	-581.020043	-581.032449	-35
i0' (C_1, ^2A)	-580.948198	0.039198	-580.920259	-580.997036	-581.019440	-581.031925	-35
i1 (C_s, $^2A'$)	-580.999786	0.040063	-580.971028	-581.048853	-581.072321	-581.085490	-173
i2 (C_s, $^2A'$)	-580.937638	0.038128	-580.908133	-580.986320	-581.008240	-581.020348	-7
i3 (C_s, $^2A'$)	-580.936099	0.038523	-580.908365	-580.987071	-581.009938	-581.022669	-12
H_2	-1.162291	0.010045	-1.163446	-1.172337	-1.173796	-1.174474	
^{2}p1 (C_s, $^2A''$)	-579.772434	0.023108	-579.738278	-579.806779	-579.826676	-579.837754	
^{2}p2 (C_1, ^2A)	-579.774915	0.024087	-579.741721	-579.807905	-579.827220	-579.837984	
^{2}p3 (C_1, ^2A)	-579.768677	0.022404	-579.737146	-579.804748	-579.824780	-579.835980	
^{2}p4 (C_2,^2A)	-579.764713	0.022346	-579.731158	-579.799712	-579.819624	-579.830709	
^{2}p5 (C_1, ^2A)	-579.753562	0.021887	-579.719210	-579.787725	-579.807446	-579.818404	
^{2}p6 (C_s, $^2A'$)	-579.749178	0.023245	-579.717346	-579.783990	-579.802754	-579.813129	
p1 + H_2	-580.934725	0.033153	-580.901724	-580.979116	-581.000473	-581.012227	1
p2 + H_2	-580.937206	0.034132	-580.905167	-580.980241	-581.001016	-581.012457	3
p3 + H_2	-580.930968	0.032449	-580.900592	-580.977085	-580.998577	-581.010454	4
p4 + H_2	-580.927004	0.032391	-580.894604	-580.972049	-580.993420	-581.005183	18
p5+ H_2	-580.915853	0.031932	-580.882656	-580.960061	-580.981242	-580.992877	49
p6 + H_2	-580.911469	0.033290	-580.880792	-580.956326	-580.976550	-580.987603	66
tsi0i0'	-580.947619	0.038856	-580.919752	-580.995809	-581.017982	-581.030336	-31
tsi0i1	-580.939865	0.037524	-580.910699	-580.989231	-581.012316	-581.025201	-21
tsi0'i1	-580.945057	0.038025	-580.914158	-580.993996	-581.017168	-581.0300661	-33
tsi0'i2	-580.929719	0.036435	-580.899157	-580.978855	-581.001790	-581.014533	4
tsi1i1	-580.936476	0.036670	-580.903316	-580.985123	-581.009542	-581.023215	-18
tsi1i2	-580.929148	0.035730	-580.897713	-580.977614	-581.000654	-581.013461	5
tsi2p2[d]	-580.938499	0.035753	-580.907541	-580.983763	-581.005071	-581.016833	-4
	-580.938635	0.035912	-580.907695	-580.984153	-581.005517	-581.017310	-5
	-580.938917	0.036217	-580.908017	-580.985021	-581.006529	-581.018400	-7
tsi2p1	-580.933661	0.034128	-580.901672	-580.978479	-580.999915	-581.011743	5

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[a] CCSD/cc-pVTZ energy with zero-point energy correction in hartree.

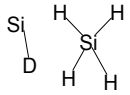
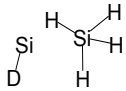
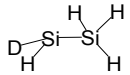
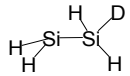
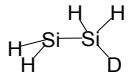
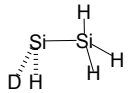
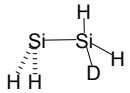
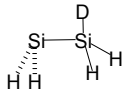
[b] zero-point energy by CCSD/cc-pVTZ in hartree.

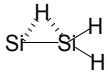
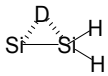
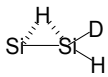
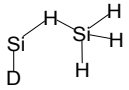
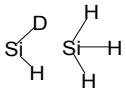
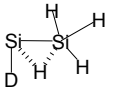
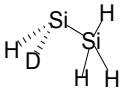
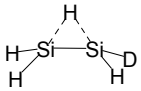
[c] relative energy by CCSD(T)/CBS with CCSD/cc-pVTZ zero-point energy correction.

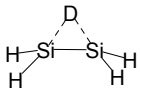
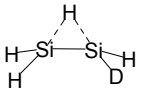
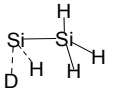
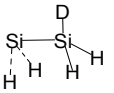
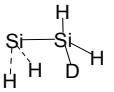
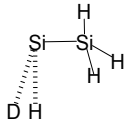
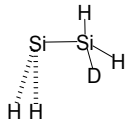
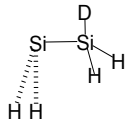
[d] the variational transition states found at collision energies, 8.0, 10.0, and 16.6 kJ/mol, respectively.

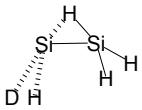
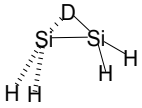
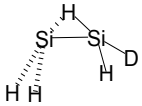
Table S11. CCSD/cc-pVTZ//CCSD(T)/CBS energies on the adiabatic doublet ground state potential energy surface of SiD + SiH_4.

	CCSD/ cc-pVTZ + E_{zpc} [a]	E_{zpc} [b]	CCSD(T)/ cc-pVDZ	CCSD(T)/ cc-pVTZ	CCSD(T)/ cc-pVQZ	CCSD(T)/ CBS	E[c] (kJ/mol)

	SiD($^2\Pi$)	-289.540181	0.003350	-289.520106	-289.546538	-289.553670	-289.557575	
	SiH_4($^1A_1$)	-291.401964	0.031561	-291.392685	-291.437349	-291.450714	-291.458201	
	SiD + SiH_4	-580.942145	0.034911	-580.912791	-580.983886	-581.004383	-581.015776	0
	**i0**	-580.950568	0.037625	-580.921299	-580.997772	-581.020043	-581.032449	-37
	**i0'**	-580.950010	0.037386	-580.920259	-580.997036	-581.019440	-581.031925	-36
	**i1**	-581.001823	0.038026	-580.971028	-581.048853	-581.072321	-581.0854896	-175
	**i1'**	-581.002021	0.037827	-580.971028	-581.048853	-581.072321	-581.0854896	-175
	**i1''**	-581.001998	0.03785	-580.971028	-581.048853	-581.072321	-581.0854896	-175
	**i2**	-580.939476	0.036289	-580.908133	-580.9863198	-581.008240	-581.020348	-8
	**i2'**	-580.939836	0.035930	-580.908133	-580.9863198	-581.008240	-581.020348	-9
	**i2''**	-580.939835	0.035931	-580.908133	-580.9863198	-581.008240	-581.020348	-9
	HD	-1.163636	0.008701	-1.163446	-1.172337	-1.173796	-1.174474	
	H_2	-1.162291	0.010045	-1.163446	-1.172337	-1.173796	-1.174474	
	**^{2}p2(C_1, ^{2}A)**	-579.774915	0.024087	-579.741721	-579.807905	-579.827220	-579.837984	

	**^{2}p2'(C_1, ^{2}A)**	-579.777011	0.021991	-579.741721	-579.807905	-579.827220	-579.837984	
	**^{2}p1(C_s, ^{2}A")**	-579.772434	0.023108	-579.738278	-579.806779	-579.826676	-579.837754	
	**^{2}p1'(C_s, ^{2}A")**	-579.774307	0.021236	-579.738278	-579.806779	-579.826676	-579.837754	
	**^{2}p1''(C_s, ^{2}A")**	-579.774535	0.021007	-579.738278	-579.806779	-579.826676	-579.837754	
	p2 + HD	-580.938551	0.032788	-580.905167	-580.980241	-581.001016	-581.012457	3
	p2' + H_2	-580.939302	0.032036	-580.905167	-580.980241	-581.001016	-581.012457	1
	p1 + HD	-580.936070	0.031809	-580.901724	-580.979116	-581.000473	-581.012227	1
	p1' + H_2	-580.936598	0.031281	-580.901724	-580.979116	-581.000473	-581.012227	0
	p1'' + H_2	-580.936826	0.031052	-580.901724	-580.979116	-581.000473	-581.012227	-1
	**tsi0i0'**	-580.949343	0.037131	-580.919752	-580.995809	-581.017982	-581.030336	-32
	**tsi0i1**	-580.941672	0.035717	-580.910699	-580.989231	-581.012316	-581.025201	-23
	**tsi0'i1**	-580.946913	0.03617	-580.914158	-580.993996	-581.017168	-581.0300661	-34
	**tsi0'i2**	-580.931424	0.034730	-580.899157	-580.978855	-581.001790	-581.014533	3
	**tsi1i1'**	-580.938518	0.034628	-580.903316	-580.985123	-581.009542	-581.023215	-20

	**tsi1'i1'**	-580.937976	0.035170	-580.903316	-580.985123	-581.009542	-581.023215	-19
	**tsi1'i1''**	-580.938605	0.034541	-580.903316	-580.985123	-581.009542	-581.023215	-21
	**tsi1i2**	-580.930785	0.034094	-580.897713	-580.977614	-581.000654	-581.013461	4
	**tsi1'i2''**	-580.931379	0.033500	-580.897713	-580.977614	-581.000654	-581.013461	2
	**tsi1'i2'**	-580.931356	0.033522	-580.897713	-580.977614	-581.000654	-581.013461	2
	**tsi2p2[d] (8.0)**	-580.940050	0.033910	-580.907388	-580.983399	-581.004657	-581.016393	-4
	(10.0)	-580.940195	0.034058	-580.907541	-580.983763	-581.005071	-581.016833	-5
	(16.6)	-580.940697	0.034436	-580.908017	-580.985021	-581.006529	-581.018400	-8
	**tsi2'p2' [d] (8.0)**	-580.940819	0.033727	-580.907695	-580.984153	-581.005517	-581.017310	-7
	(10.0)	-580.941104	0.034030	-580.908017	-580.985021	-581.006529	-581.018400	-9
	(16.6)	-580.941104	0.034030	-580.908017	-580.985021	-581.006529	-581.018400	-9
	**tsi2''p2' [d] (8.0)**	-580.940782	0.033765	-580.907695	-580.984153	-581.005517	-581.017310	-7
	(10.0)	-580.941080	0.034054	-580.908017	-580.985021	-581.006529	-581.018400	-9
	(16.6)	-580.941080	0.034054	-580.908017	-580.985021	-581.006529	-581.018400	-9

	**tsi2p1**	-580.935178	0.03261	-580.901672	-580.978479	-580.999915	-581.011743	5
	**tsi2''p1'**	-580.935428	0.03236	-580.901672	-580.978479	-580.999915	-581.011743	4
	**tsi2'p1''**	-580.935789	0.031999	-580.901672	-580.978479	-580.999915	-581.011743	3

[a] CCSD/cc-pVTZ energy with zero-point energy correction in hartree.

[b] zero-point energy by CCSD/cc-pVTZ in hartree.

[c] relative energy by CCSD(T)/CBS with CCSD/cc-pVTZ zero-point energy correction.

[d] the variational transition states found at collision energies, 8.0, 10.0, and 16.6 kJ/mol, respectively