Gas-Phase Preparation of 1-Germavinylidene (H_2CGe; X^1A_1) – the Isovalent Counterpart of Vinylidene (H_2CC; X^1A_1) - via Non-Adiabatic Dynamics through the Elementary Reaction of Ground State Atomic Carbon (C; ^3P) with Germane (GeH_4; X^1A_1)

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EXPERIMENTAL AND COMPUTATIONAL

EXPERIMENTAL: The crossed molecular beam investigations of the reaction of atomic carbon (C; ^{3}P) with germane (GeH_4; X^1A_1; Air Liquide; 99.999%) was performed at the University of Hawaii.[1] The helium-seeded supersonic beam of ground state atomic carbon was prepared via ablation of a graphite rod at 266 nm, 30 Hz (Nd:YAG, 8-10 mJ pulse^{-1}).[2] The chopper wheel selects a section of the pulsed carbon beam characterized by the peak velocity v_p of 2560 ± 52 m s^{-1} and speed ratio S of 2.1 ± 0.3. The primary carbon beam crossed perpendicularly with a germane beam (v_p = 531 ± 5 m s^{-1}; S = 9.0 ± 0.7) leading to a center-of-mass (CM) angle of 53.3 ± 0.6° and a collision energy of 35.5 ± 1.2 kJ mol^{-1} (Table S2). The reactively scattered products were monitored via a rotatable detector at ultrahigh-vacuum conditions (8×10^{-12} Torr). In detail, the products were ionized (80 eV) and filtered (selected m/z) via a quadrupole mass spectrometer (QMS) operated in the time-of-flight (TOF) mode. The ions at the desired *m/z* traveled toward an aluminum coated stainless steel target biased at -22.5 kV, leading to a pulse of electron cascade. The electrons then impinged onto an organic scintillator yielding a photon pulse detected and filtered by a Burle photomultiplier tube and a discriminator (1.6 mV). Finally, a multichannel scaler was used to collect the TOF spectra at different angles between 17° and 65° with respect to the primary beam. These laboratory data were converted via forward-convolution to the CM frame yielding the CM translational energy ($P(E_T)$) and angular ($T(\theta)$) flux distributions, along with information of the reaction dynamics.[3] The fitting initially predicts the CM functions and the laboratory data (LAD, TOF) are then analyzed iteratively until leading to the best fits. The reactive differential cross section, $I(u, \theta) \sim P(u) \times T(\theta)$, which reports the products intensity (I) as a function of the CM angle θ and the velocity u, is the crucial output of the fitting and an image of the chemical reaction.[4]

5.2. COMPUTATIONAL:

The H and H_2 loss channels of the C−GeH_4 reaction on both adiabatic ground-state singlet and triplet potential energy surfaces are explored. The geometries of $CGeH_4$ intermediates, products, and transition states are optimized via the coupled cluster[5-7] CCSD/cc-pVTZ calculations, except for the transition states connecting ^{3}**i3** and ^{3}**p3**, ^{3}**i3** and ^{3}**p6**, and ^{1}**i2** and ^{1}**p5**, which are obtained by MP2/cc-pVTZ. The CCSD/cc-pVTZ（MP2/cc-pVTZ for the above mentioned species) zero-point energy corrected energies are refined to complete basis set limits[8]

(CCSD(T)/CBS), which are derived by extrapolating the CCSD(T)/cc-pVTZ, CCSD(T)/cc-pVDZ, and CCSD(T)/cc-pVQZ energies. The accuracy of these optimized energies is expected being within 8 kJ mol^{-1}.[9] The minimum energy crossing point between **^{3}i1** and **^{1}i1** is located using CPMCSCF/TZVPP calculation and its CCSD(T)/CBS energy is further obtained. MOLPRO[10] and GAUSSIAN16[11] programs are utilized in the surface-crossing and coupled cluster calculations, respectively.

The energy dependent RRKM (Rice−Ramsperger−Kassel−Marcus) rate constants[12] are estimated on singlet surface at collision energies of 0.0 and 35.5 ± 1.2 kJ mol^{-1}. The saddle-point approach[12,13] is employed to compute the number of states of transition states and the density of states of the intermediates with CCSD/cc-pVTZ (MP2/cc-pVTZ for **^{1}tsi2p5**) harmonic frequencies and CCSD(T)/CBS energies. All species are treated as a collection of harmonic oscillators. Finally, the product branching ratios are computed by solving the rate equations derived from *ab initio* reaction paths with with Runge-Kutta method.

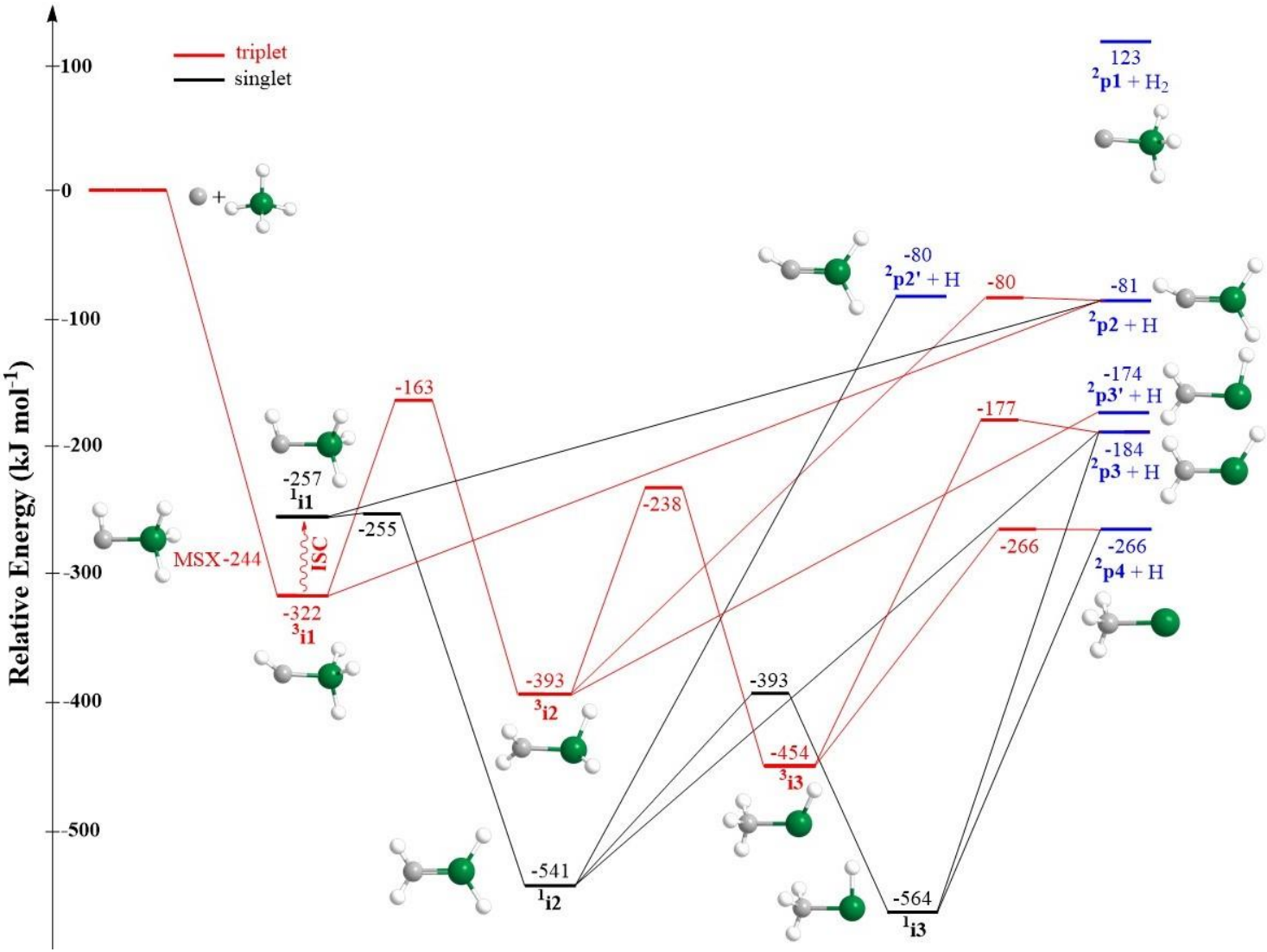


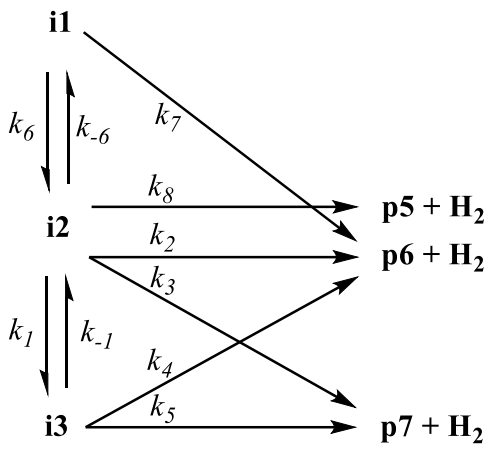
Figure S1. Triplet (red) and singlet (black) atomic hydrogen loss pathways of the C-GeH_4 reaction.

Table S1. (a) The RRKM rate constants (s^{-1}) computed using CCSD(T)/CBS energies with CCSD/cc-pVTZ zero-point energies, and CCSD/cc-pVTZ harmonic frequencies for molecular hydrogen loss channels of C + GeH_4 reaction on singlet potential energy surface at collision energies of 0.0 and 35.5 kJ/mol. **(b)** The reaction mechanism, rate equations, and branching ratios(%) of molecular hydrogen loss on singlet PES at collision energies of 0.0, and 35.5 kJ/mol. **(c) i2** and **i3** branching at collision energies of 0.0, and 35.5 kJ/mol. **(d)** The reaction mechanism, rate equations, and branching ratios ($\mathbf{p7_{i2}}$, $\mathbf{p7_{i3}}$) (%) on singlet PES at collision energies of 0.0, and 35.5 kJ/mol.

(a)

	0.0	**35.5**
k_1 (i2 → i3)	1.08×10^{12}	1.29×10^{12}
k_{-1} (i3 → i2)	6.64×10^{11}	8.18×10^{11}
k_2 (i2 → p6)	3.87×10^{8}	1.52×10^{9}
k_3 (i2 → p7)	2.61×10^{11}	3.84×10^{11}
k_4 (i3 → p6)	9.95×10^{10}	1.90×10^{11}
k_5 (i3 → p7)	2.38×10^{11}	3.11×10^{11}
k_6 (i1 → i2)	7.75×10^{12}	7.83×10^{12}
k_{-6} (i2 → i1)	6.12×10^{10}	1.02×10^{11}
k_7 (i1 → p6)	1.64×10^{11}	3.82×10^{11}
k_8 (i2 → p5)	4.81×10^{10}	4.07×10^{11}

(b)



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

$$\frac{d[i2]}{dt} = k_6[i1] + k_{-1}[i3] - (k_1 + k_2 + k_3 + k_{-6} + k_8)[i2]$$

$$\frac{d[i3]}{dt} = k_1[i2] - (k_{-1} + k_4 + k_5)[i3]$$

$$\frac{d[p6]}{dt} = k_2[i2] + k_4[i3] + k_7[i1]$$

$$\frac{d[p7]}{dt} = k_3[i2] + k_5[i3]$$

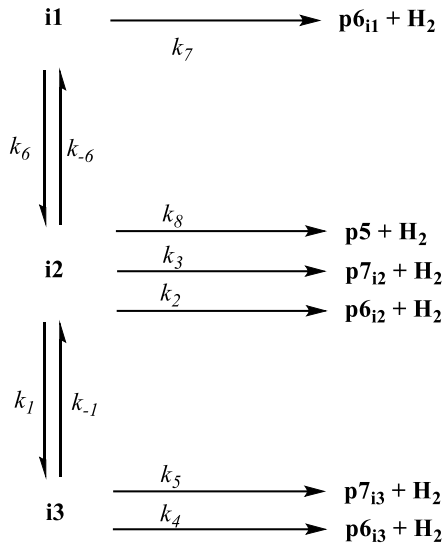
$$\frac{d[p5]}{dt} = k_8[i2]$$

	0.0	**35.5**
p6	17.89%	18.88%
p7	75.13%	50.97%
p5	6.98%	30.15%

(c)

			0.0	**35.5**
i2 → p7	$\frac{k_3}{k_1 + k_2 + k_3 + k_{-6} + k_8}$	=	18.03%	17.56%
i2 → i3	$\frac{k_1}{k_1 + k_2 + k_3 + k_{-6} + k_8}$	=	74.39%	59.06%
i3 → p7	$\frac{k_5}{k_{-1} + k_4 + k_5}$	=	23.78%	23.59%

(d)



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

$$\frac{d[i2]}{dt} = k_6[i1] + k_{-1}[i3] - (k_1 + k_2 + k_3 + k_{-6} + k_8)[i2]$$

$$\frac{d[i3]}{dt} = k_1[i2] - (k_{-1} + k_4 + k_5)[i3]$$

$$\frac{d[p6_{i2}]}{dt} = k_2[i2]$$

$$\frac{d[p6_{i3}]}{dt} = k_4[i3]$$

$$\frac{d[p6_{i1}]}{dt} = k_7[i1]$$

$$\frac{d[p7_{i2}]}{dt} = k_3[i2]$$

$$\frac{d[p7_{i3}]}{dt} = k_5[i3]$$

$$\frac{d[p5]}{dt} = k_8[i2]$$

	0.0	**35.5**
p6$_{i1}$	2.26%	5.00%
p6$_{i2}$	0.06%	0.11%
p6$_{i3}$	15.57%	13.76%
p7$_{i2}$	37.88%	28.44%
p7$_{i3}$	37.25%	22.53%
p5	6.98%	30.15%

Table S2. Peak velocities (v_p) and speed ratios (S) of the carbon (C), and Germane (GeH_4) reactants 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)
C	2560 ± 52	2.1 ± 0.3		
GeH_4	531 ± 5	9.0 ± 0.7	35.5 ± 1.2	53.3 ± 0.6

Table S3. CCSD/cc-pVTZ vibrational frequencies and infrared intensities on the $CGeH_4$ adiabatic triplet and singlet ground state potential energy surface. (*frequencies and infrared intensities by MP2/cc-pVTZ)

	^{3}i1		^{3}i2	
Normal modes	Frequency(cm^{-1})	IR Inten	Frequency(cm^{-1})	IR Inten
ν1	124.21	25.9259	99.63	0
ν2	476.12	4.931	536.07	11.5361
ν3	597.15	40.7507	590.21	6.9978
ν4	637.69	53.0301	800.37	8.5798
ν5	696.26	55.4492	859.04	43.3575
ν6	881.76	126.261	1266.52	3.336
ν7	910.3	39.1571	1473.07	4.251
ν8	913.9	38.0044	1474.33	5.1253
ν9	2211.17	119.9298	2144.26	92.3977
ν10	2214.17	88.2178	3067.3	8.8443
ν11	2240.3	92.2643	3156.39	1.4012
ν12	3251.52	0.4501	3166.71	3.5235
	^{3}i3		MSX	
ν1	302	1.123	104.68	36.43
ν2	515.87	8.3109	510.52	510.52
ν3	554.67	17.0698	598.3	45.54
ν4	612.42	67.1689	616.87	14.37
ν5	656.41	24.9568	866.99	24.4
ν6	778.23	44.944	905.96	100
ν7	887.06	68.8417	937.76	28.1
ν8	1406.58	2.1669	945.82	18.38
ν9	2158.7	83.2691	2284.66	90.24
ν10	2175.11	157.9042	2289.87	68.53
ν11	3147.42	6.7593	2309.45	30.55
ν12	3253.34	0.9913	3357.8	12.5
	^{1}i1		^{1}i2	
ν1	234.14	52.1033	373.15	11.1132
ν2	372.25	35.3822	468.24	12.811
ν3	544.41	45.6344	730.05	0
ν4	622.58	8.5122	767.65	40.041
ν5	831.27	109.0657	815.47	47.0054
ν6	875.24	44.9663	856.02	16.2447

ν7	901.61	15.2357	889.46	22.1965
ν8	923.09	60.6815	1417.58	2.1496
ν9	2186.04	50.477	2264.54	30.4345
ν10	2199.98	129.9817	2274.15	91.8965
ν11	2242.06	92.4194	3178.41	0.9434
ν12	2985.19	42.2965	3277.47	0.1122
	^{1}i3		^{3}tsi1i2	
ν1	155.99	0.1569	-1726.16	495.0536
ν2	569.78	41.913	344.57	21.6419
ν3	582.01	3.3972	522.68	38.39
ν4	614.6	12.9922	565.55	9.0039
ν5	907.42	53.7164	613.79	26.2498
ν6	1261.16	7.6032	676.14	29.512
ν7	1456.43	2.8258	810.41	6.0238
ν8	1470.73	7.5069	841.68	56.8662
ν9	1972.97	352.9344	1864.73	14.9923
ν10	3036.73	5.8567	2185.26	73.0163
ν11	3106.2	15.6503	2240.44	93.8215
ν12	3153.8	12.2097	3209.96	0.0405
	^{3}tsi1p5		^{3}tsi1p6	
ν1	-1382.15	580.3693	-1398.34	623.334
ν2	339.61	19.9786	299.08	16.7235
ν3	512.6	7.0981	473.89	6.1365
ν4	551.06	1.0687	549.69	10.9423
ν5	642.23	103.2131	684.31	14.0507
ν6	767.18	5.6472	725.28	33.581
ν7	917.14	174.24	738.09	29.046
ν8	973.01	4.2982	965.21	26.1528
ν9	1476.89	10.6395	1488.18	311.9976
ν10	1932.6	337.6127	2107.57	6.5546
ν11	2146.31	191.8961	2227.03	66.7277
ν12	2154.04	156.9282	3226.5	3.7986
	^{3}tsi2i3		^{3}tsi2p2	
ν1	-1872.17	524.9885	-335.64	48.8931
ν2	234.62	5.2528	144.46	0.0575
ν3	514.46	61.7924	217.49	2.4299

ν4	539.2	3.7126	327.97	16.8624
ν5	684.04	17.8873	371.61	12.6949
ν6	772.46	30.3745	575.03	45.2612
ν7	970.44	7.705	645.72	42.5057
ν8	1363.69	0.8617	867.81	50.9284
ν9	1804.51	29.1618	913.12	8.2815
ν10	2138.17	68.8177	2232.29	58.4666
ν11	3155.61	0.1265	2269.1	56.7865
ν12	3274.07	0.1089	3308.47	6.3713
	^{3}tsi2p6		^{3}tsi2p7	
ν1	-1664.1	208.1201	-1358.65	388.199
ν2	445.75	8.7259	233.45	3.1384
ν3	502.83	3.6479	460.33	2.8392
ν4	587.02	31.7228	523.07	50.4399
ν5	719.19	68.9148	594.58	9.719
ν6	747.65	32.6751	643.98	3.8247
ν7	824.17	13.2652	823.26	13.5618
ν8	1054.3	28.5408	1375.14	15.0391
ν9	1664.79	9.9288	1427.88	197.3868
ν10	1727.44	93.5841	1805.68	25.9906
ν11	2027.7	234.31	3136.85	6.3456
ν12	3187.26	7.3441	3246.18	2.3258
	^{3}tsi3p3*		^{3}tsi3p4	
ν1	-65.41	3.4015	-52.35	0.018
ν2	101.96	0.7511	18.17	0.1677
ν3	116.76	0.0575	46.6	0.0074
ν4	522.54	5.2003	530.25	19.2849
ν5	598.37	49.2626	602.61	17.926
ν6	739.4	51.9742	611.26	12.8553
ν7	801.51	43.9526	1254.27	6.4689
ν8	830.32	48.2019	1401.4	4.837
ν9	1387.46	0.2734	1466	13.1583
ν10	2183.32	51.9323	3016.35	6.3562
ν11	3196.48	4.3883	3100.51	15.4899
ν12	3316.2	1.6976	3133.76	5.823
	^{3}tsi3p6*		^{3}tsi3p7	
ν1	-2855.22	14764.35	-1605.97	211.5467

ν2	305.18	125.2055	504.74	16.5305
ν3	492.61	9.9342	583.69	0.1947
ν4	523.21	36.2229	632.18	19.2414
ν5	589.81	65.1766	638.37	2.5435
ν6	623.75	27.4237	778.73	106.0655
ν7	751.18	31.3	1053.07	2.3926
ν8	1247.18	134.6517	1394.48	4.6988
ν9	1338.28	51.848	1662.82	5.0384
ν10	2081.6	159.6289	1766.43	110.6462
ν11	3218.87	4.4796	3118.43	14.1566
ν12	3745.96	608.3767	3215.55	2.3677
	^{1}tsi1i2		^{1}tsi1p5	
ν1	-472.5	70.9459	-1961.74	1677.347
ν2	505.38	39.4814	133.51	5.8514
ν3	685.59	13.7482	490.41	19.7814
ν4	724.94	37.3373	646.86	40.1186
ν5	770.1	82.1122	753.9	7.484
ν6	838.78	21.4634	786.27	73.3849
ν7	892.8	5.2101	869.92	115.1364
ν8	922.47	83.1902	901.02	68.359
ν9	2008.88	43.3775	1502.64	1303.305
ν10	2199.17	134.9934	1822.38	14.35
ν11	2259.32	81.7415	2188.65	114.8984
ν12	2987.42	36.3467	2228.43	81.4211
	^{1}tsi1p6		^{1}tsi2i3	
ν1	-1554.14	1235.769	-1159.76	209.0432
ν2	60.57	0.2364	548.39	5.4261
ν3	347.1	24.0299	705.74	3.1334
ν4	700.87	17.6333	746.15	39.8504
ν5	751.8	8.7679	848.08	35.4612
ν6	818.34	2.3244	932.52	63.6616
ν7	879.64	3	989.35	80.7802
ν8	903.39	94.0555	1442.57	2.4554
ν9	1756.8	0.3589	1865.35	15.4635
ν10	1830.69	166.9097	2089.62	218.8945
ν11	2309.98	33.6348	3111.28	11.944
ν12	3039.05	20.2398	3209.38	2.1422

	^{1}tsi2p5*		^{1}tsi2p6	
ν1	-31.89	3.4005	-1510.68	729.1094
ν2	9.87	1.258	255.2	4.268
ν3	113.64	0.6669	519.26	66.7632
ν4	249.24	40.8076	613.2	1.7753
ν5	251.55	0.0011	773.14	43.1923
ν6	286.86	9.6713	805.12	9.511
ν7	372.02	1.7847	877.49	75.4993
ν8	778.72	39.4162	1016.88	1.3272
ν9	831.02	18.976	1769.78	150.0343
ν10	2276.51	19.9174	1849.31	48.5706
ν11	2307.5	44.579	2195.74	94.8142
ν12	4494.94	11.8452	3017.79	26.9009
	^{1}tsi2p7		^{1}tsi3p6	
ν1	-1212.3	332.3145	-893.9	362.7156
ν2	198.17	84.5545	286.53	18.2196
ν3	489.68	22.0967	367.08	3.4994
ν4	734.08	18.6099	437.63	99.0903
ν5	769.85	48.262	531.96	1.4197
ν6	806.53	20.8575	572.67	18.6046
ν7	898.95	56.0987	798.48	0.0313
ν8	1442.86	1.7688	819.02	6.8567
ν9	1566.64	251.2365	1118.12	18.2714
ν10	2070.09	22.6097	2086.05	141.591
ν11	3142.68	5.4826	3272.72	4.0539
ν12	3245.15	0.4304	3898.82	30.4772
	^{1}tsi3p7			
ν1	-1696.47	259.8812		
ν2	626.6	9.9009		
ν3	698.57	33.0677		
ν4	784.48	91.7883		
ν5	869.76	22.6192		
ν6	991.13	83.1738		
ν7	1141.84	25.542		
ν8	1448.04	2.6518		
ν9	1732.7	169.4531		
ν10	1823.8	7.6828		

ν11	3119.8	8.5624		
ν12	3202.4	1.9684		
	^{3}p5		^{3}p6	
ν1	501.05	31.8649	500.67	13.8663
ν2	518.25	18.6728	547.19	8.4518
ν3	677.06	24.2556	678.92	57.9753
ν4	880.18	50.2583	774.15	38.2768
ν5	2179.1	36.0183	1990.79	276.9228
ν6	2193.29	128.5912	3173.31	7.8577
	^{3}p7		^{2}p1	
ν1	633.62	18.2556	372.75	45.133
ν2	635.15	59.917	444.31	25.5105
ν3	657.68	2.2789	600.97	4.3587
ν4	1419.7	0.7047	821.01	130.2169
ν5	3103.96	14.1689	882.51	35.0869
ν6	3194.3	3.2542	908.66	40.9159
			2197.64	42.3763
			2215.64	119.7048
			2216.9	83.4914
	^{2}p2		^{2}p2'	
ν1	339.06	24.1922	106.23	16.8251
ν2	405.16	32.8193	403.24	14.1547
ν3	579.11	48.6265	583.8	54.4387
ν4	616.52	25.9864	649.65	23.923
ν5	881.7	67.7842	853.7	29.7685
ν6	965.55	37.1042	915.89	5.39
ν7	2230.75	60.0314	2241.2	52.2228
ν8	2270.43	55.4766	2283.89	48.4694
ν9	3306.43	6.4657	3317.45	4.2731
	^{2}p3		^{2}p3'	
ν1	377.26	14.756	408.38	19.3047
ν2	515.59	5.7414	552	0.6601
ν3	738.14	36.0671	566.98	6.7401
ν4	798.21	33.8456	701.68	53.5985
ν5	839.13	7.9366	826.92	57.4531
ν6	1384.63	0.705	1411.6	2.035

ν7	2127.97	73.5697	2001.01	247.4857
ν8	3161.06	0.5235	3121.18	10.1642
ν9	3276.58	0.1438	3217.3	3.4105
	^{2}p4		^{1}p5	
ν1	530.11	19.173	302.36	47.0035
ν2	580.87	3.0342	347.03	2.7122
ν3	605.66	29.0681	791.03	32.4704
ν4	1254.28	6.3159	828.02	11.1502
ν5	1394.11	5.9068	2230.8	18.7304
ν6	1466.14	13.0056	2255.33	51.3247
ν7	3018.08	6.3699		
ν8	3101.17	15.5802		
ν9	3131.95	5.0227		
	^{1}p6		^{1}p7	
ν1	402.62	54.2712	380.03	2.2889
ν2	578.71	81.3053	703.57	106.2787
ν3	740.11	69.1266	808.74	15.4959
ν4	968.08	3.4538	1365.6	10.6486
ν5	2233.23	29.2732	3122.91	0.3734
ν6	3295.78	2.8212	3209.66	1.9542

Table S4. CCSD/cc-pVTZ optimized cartesian coordinates on the $CGeH_4$ adiabatic triplet and singlet ground state potential energy surface. (*geometries optimized by MP2/cc-pVTZ)

Atom	X	Y	Z	Atom	X	Y	Z
^{3}i1				**^{3}i2**			
Ge	-0.302187	-0.005125	-0.000019	Ge	-0.032997	-0.366661	0.000000
H	-0.872703	1.385280	-0.244846	H	0.655824	-0.932027	1.248337
H	-0.796630	-0.526747	1.347240	H	0.655824	-0.932027	-1.248337
H	-0.767193	-0.950574	-1.105759	C	-0.032997	1.555718	0.000000
C	1.595972	0.113674	-0.000180	H	0.887514	2.127301	0.000000
H	2.530682	-0.425990	0.005053	H	-0.945280	2.135611	0.000000
^{3}i3				**MSX**			
C	-0.031474	1.535964	0.000000	Ge	-0.304876	0.001885	-0.002766
H	-1.057490	1.896320	0.000000	H	-0.992450	-1.254794	-0.548937
H	0.474958	1.905863	0.889469	H	-0.974580	1.247106	-0.610355
H	0.474958	1.905863	-0.889469	H	-0.429919	0.045942	1.538558
Ge	-0.031474	-0.429377	0.000000	C	1.708787	-0.170229	-0.041194
H	1.303599	-1.183778	0.000000	H	1.900268	0.922784	-0.043581
^{1}i1				**^{1}i2**			
Ge	-0.300195	0.004110	-0.002310	Ge	0.000000	0.000000	0.326159
H	-0.959060	-1.252548	-0.553193	H	0.000000	1.280538	1.135857
H	-0.891607	1.237624	-0.685989	H	0.000000	-1.280538	1.135857
H	-0.555476	0.094544	1.506015	C	0.000000	0.000000	-1.447023
C	1.658380	-0.177362	-0.028883	H	0.000000	-0.919832	-2.013329
H	2.062103	0.853016	-0.019604	H	0.000000	0.919832	-2.013329
^{1}i3				**^{3}tsi1i2**			
Ge	-0.039634	-0.449607	0.000000	Ge	0.338433	-0.007148	0.030651
H	1.539090	-0.556991	0.000000	H	0.976784	1.276126	-0.469328
C	-0.039634	1.532283	0.000000	H	0.902855	-1.296254	-0.556480
H	-1.041122	1.956132	0.000000	C	-1.569367	0.095626	-0.212543
H	0.504056	1.897292	0.875365	H	-2.462075	-0.387294	0.168656
H	0.504056	1.897292	-0.875365	H	-0.831216	0.062402	1.151568
^{3}tsi1p5				**^{3}tsi1p6**			
Ge	-0.279618	-0.058058	-0.000195	Ge	0.289093	-0.078644	-0.064009
H	-1.189374	0.060629	-1.235519	H	1.001165	-0.715538	1.122447
H	-1.187163	0.049997	1.237677	H	0.999864	1.276760	-0.399942
C	1.679992	-0.201923	-0.000628	C	-1.573566	0.102241	0.171264
H	0.225988	1.723633	0.004523	H	-2.464378	-0.081876	-0.413804

H	1.018370	1.235141	0.003328	H	0.653766	1.423828	0.711993
^{3}tsi2i3				**^{3}tsi2p2**			
C	1.516390	0.079341	-0.118520	H	1.106138	0.438416	-1.229754
H	0.696201	-0.176076	1.217707	C	-1.395370	-0.270173	-0.099995
H	2.130816	-0.789423	-0.304722	H	-2.288537	-0.737249	0.273917
H	2.000316	0.970089	0.260139	H	-2.630587	1.782341	0.098989
Ge	-0.395117	-0.051934	-0.008202	H	1.028532	0.303785	1.327362
H	-1.281944	1.181246	-0.199546	Ge	0.348646	-0.005196	0.004045
^{3}tsi2p6				**^{3}tsi2p7**			
C	1.579410	-0.097917	0.162212	Ge	-0.374569	-0.101405	-0.014100
H	2.435106	-0.361022	-0.451106	C	1.545276	0.082307	0.011732
Ge	-0.380711	-0.070614	-0.047962	H	2.057321	0.511697	-0.842489
H	-0.668041	0.345047	1.435335	H	2.166779	-0.461134	0.710996
H	0.057050	1.634316	-0.374209	H	-0.510682	1.362967	0.873913
H	0.882184	1.228803	-0.048517	H	-0.998877	1.337599	-0.361617
^{3}tsi3p3*				**^{3}tsi3p4**			
C	-1.284751	-0.360221	0.113446	C	1.513121	0.307698	0.000828
H	-1.757967	-0.287943	1.082544	H	2.066553	-0.637469	-0.069980
H	-3.233591	1.738714	-0.249380	H	1.799305	0.914196	-0.858329
H	-1.890599	-0.698397	-0.710647	H	1.829954	0.799820	0.920208
Ge	0.415734	0.028495	-0.059582	Ge	-0.402447	-0.211853	0.000073
H	1.287156	0.497106	1.103431	H	-1.896245	3.856567	0.000788
^{3}tsi3p6*				**^{3}tsi3p7**			
H	-2.250279	-0.996445	-0.204276	C	1.571140	-0.085652	-0.000044
H	-2.074898	0.960021	0.089894	H	2.144198	-0.220591	-0.911752
H	-2.341318	-0.597672	-0.883974	H	2.143382	-0.222336	0.911911
H	0.910262	-0.962787	1.049812	Ge	-0.450904	-0.062046	-0.000030
Ge	0.442420	0.024806	-0.057162	H	-0.069273	1.693223	0.000508
C	-1.400199	0.133848	0.296287	H	0.783791	1.249072	0.000548
^{1}tsi1i2				**^{1}tsi1p5**			
Ge	0.299042	-0.004078	-0.008623	Ge	-0.259207	-0.063900	0.001164
H	1.119548	1.260194	-0.192153	H	-0.953740	-0.143095	-1.351967
C	-1.592849	0.176999	-0.100856	H	-1.210701	-0.186469	1.188061
H	-1.972870	-0.861649	-0.053155	C	1.678569	-0.129850	0.017501
H	1.117604	-1.253786	-0.329685	H	-0.268981	1.788163	0.034406
H	-0.276538	-0.076249	1.456064	H	0.656625	1.365312	-0.012767
^{1}tsi1p6				**^{1}tsi2i3**			
Ge	0.251255	-0.053650	0.005887	Ge	0.395416	-0.033650	-0.039825

H	1.332618	-1.098749	-0.069421	H	0.733339	1.385212	0.489462
H	0.979513	1.288460	-0.591228	C	-1.477652	0.071545	-0.043285
C	-1.577453	-0.115488	-0.010827	H	-2.028262	-0.854549	-0.178848
H	-1.919358	0.931895	0.011007	H	-2.123079	0.938491	0.085286
H	1.031789	1.288131	0.526224	H	-0.369407	-0.821623	1.138218
^{1}tsi2p5*				**^{1}tsi2p6**			
Ge	-0.434581	0.057185	0.000074	Ge	-0.315699	-0.050670	-0.068697
H	-0.701459	1.542795	-0.002110	H	-1.104151	-0.552238	1.142281
C	1.278738	-0.616333	-0.001096	C	1.550402	-0.225063	0.123514
H	4.561852	0.836534	0.001593	H	2.026360	0.632866	-0.381260
H	4.009354	0.346127	0.001496	H	-0.505727	1.595941	0.085626
H	-1.635589	-0.857393	0.003246	H	0.383470	1.295236	0.610580
^{1}tsi2p7				**^{1}tsi3p6**			
Ge	-0.359256	-0.093991	0.019364	Ge	0.450047	-0.024632	-0.000044
C	1.484709	0.054666	-0.096585	H	0.534822	1.524705	-0.001080
H	2.030336	0.943819	0.188940	C	-1.321968	-0.293725	0.000341
H	2.052118	-0.862920	0.025713	H	-2.138371	-0.999186	-0.001507
H	-0.303131	1.557246	0.386240	H	-2.426007	1.010879	0.388133
H	-1.191387	1.041584	-0.641030	H	-2.440130	1.014173	-0.386175
^{1}tsi3p7							
Ge	-0.421118	-0.057220	-0.006873				
C	1.458930	-0.100864	-0.027696				
H	-0.085382	1.628563	-0.042595				
H	1.961700	-1.010337	0.289420				
H	2.153013	0.666530	-0.354811				
H	0.692874	1.151466	0.494089				
^{3}p5				**^{3}p6**			
Ge	-0.241628	0.000000	-0.039971	C	0.020722	1.556442	0.000000
H	-0.960920	-1.254840	0.460540	H	0.757503	2.355678	0.000000
H	-0.960908	1.254848	0.460537	Ge	0.020722	-0.349225	0.000000
C	1.608986	-0.000001	0.059666	H	-1.544943	-0.519131	0.000000
^{3}p7				**^{2}p1**			
C	0.000000	0.000000	-1.529411	Ge	0.255681	-0.000010	-0.001433
H	0.000000	0.907107	-2.128668	H	0.851080	-1.251578	-0.639669
H	0.000000	-0.907107	-2.128668	H	0.553367	0.007380	1.499070
Ge	0.000000	0.000000	0.419806	H	0.851100	1.245296	-0.651797
				C	-1.739558	-0.000127	-0.026956

^{2}p2				^{2}p2'			
Ge	-0.286770	0.004971	0.020367	Ge	0.284275	0.004876	-0.003712
H	-1.022753	1.310810	-0.228728	H	1.125550	-1.250074	0.029799
H	-1.108362	-1.251805	-0.171961	H	1.033044	1.323851	0.041476
C	1.477200	-0.091640	-0.064795	C	-1.468574	-0.096810	0.012563
H	2.444547	0.331767	0.137720	H	-2.443967	0.351055	-0.027859
^{2}p3				^{2}p3'			
C	0.032514	-1.425433	0.000000	Ge	0.389546	-0.053544	0.013073
H	0.940340	-2.008484	0.000000	H	0.700545	1.447910	-0.327397
H	-0.906619	-1.964546	0.000000	C	-1.500742	0.035678	-0.043219
Ge	0.032514	0.354873	0.000000	H	-2.128130	-0.833905	-0.207426
H	-1.269258	1.169702	0.000000	H	-2.033442	0.885331	0.375812
^{2}p4				^{1}p5			
C	1.520879	0.000000	-0.010994	Ge	0.000000	0.000000	0.235904
H	1.952894	-0.891422	-0.465574	H	0.000000	1.287742	1.037675
H	1.814155	0.000512	1.046364	H	0.000000	-1.287742	1.037675
H	1.953201	0.890824	-0.466488	C	0.000000	0.000000	-1.604046
Ge	-0.463923	0.000003	-0.001510				
^{1}p6				^{1}p7			
Ge	0.014818	-0.298469	0.000000	Ge	0.000000	0.000000	0.387754
H	-1.173227	-1.239179	0.000000	C	0.000000	0.000000	-1.403309
C	0.014818	1.413206	0.000000	H	0.000000	0.911467	-1.994135
H	0.610134	2.310958	0.000000	H	0.000000	-0.911467	-1.994135

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