

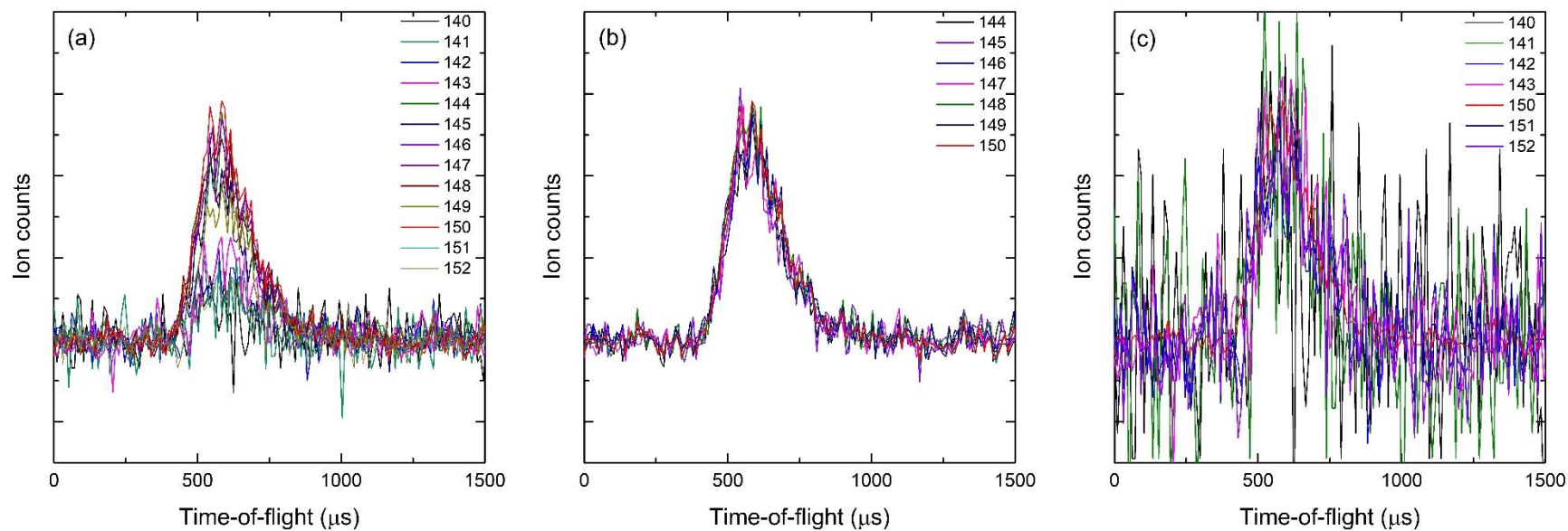


Figure S2. Time-of-flight spectra recorded at the CM angle from m/z 152 to 140 for the reaction of ground state atomic germanium (Ge; ^3P) with germane (GeH_4 ; $X^1\text{A}_1$). Panel a depicts raw TOF spectra, panels b and c the scaled TOF spectra, respectively.

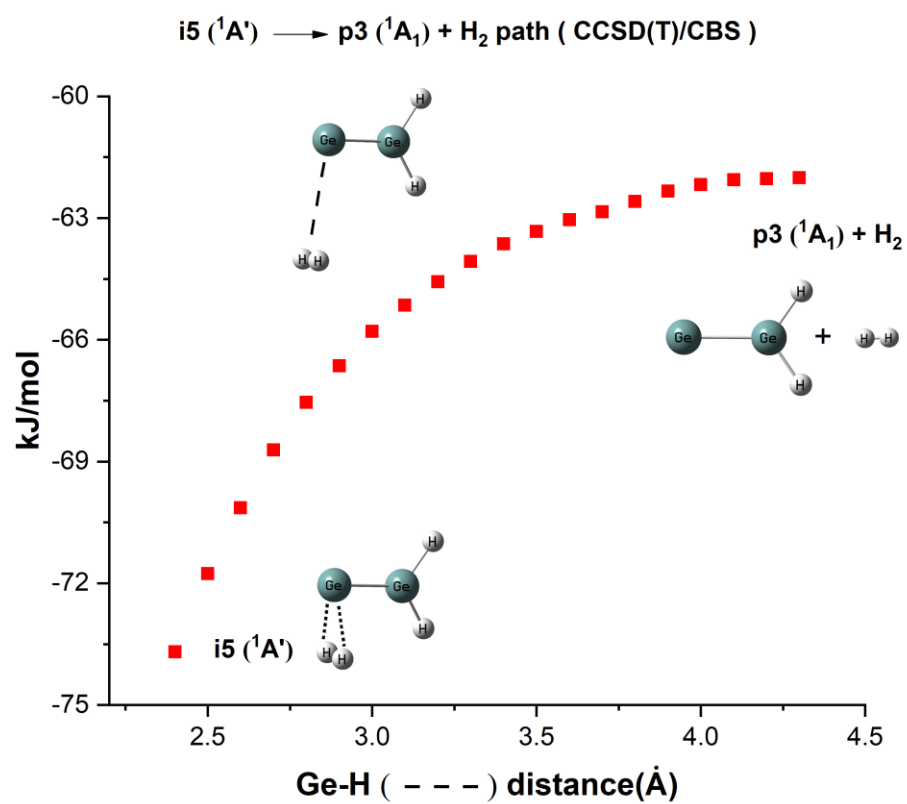


Figure S3. Reaction path of i5 to p3.

Table S1. Peak velocities (v_p) and speed ratios (S) of the germanium (Ge), and germane (GeH_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)
Ge	998 ± 12	5.6 ± 0.2		
GeH_4	529 ± 5	9.0 ± 0.7	24.3 ± 0.4	29.4 ± 0.4

Table S2. H_2 loss products from the reaction of ground state atomic germanium and germane considering the natural isotope abundances of germanium.

		$^{70}\text{GeH}_4$ (20.52%)	$^{72}\text{GeH}_4$ (27.45%)	$^{73}\text{GeH}_4$ (7.76%)	$^{74}\text{GeH}_4$ (36.7%)	$^{76}\text{GeH}_4$ (7.75%)
H_2 loss	^{70}Ge (20.52%)	$^{70}\text{Ge}^{70}\text{GeH}_2$ 142	$^{70}\text{Ge}^{72}\text{GeH}_2$ 144	$^{70}\text{Ge}^{73}\text{GeH}_2$ 145	$^{70}\text{Ge}^{74}\text{GeH}_2$ 146	$^{70}\text{Ge}^{76}\text{GeH}_2$ 148
	^{72}Ge (27.45%)	$^{72}\text{Ge}^{70}\text{GeH}_2$ 144	$^{72}\text{Ge}^{72}\text{GeH}_2$ 146	$^{72}\text{Ge}^{73}\text{GeH}_2$ 147	$^{72}\text{Ge}^{74}\text{GeH}_2$ 148	$^{72}\text{Ge}^{76}\text{GeH}_2$ 150
	^{73}Ge (7.76%)	$^{73}\text{Ge}^{70}\text{GeH}_2$ 145	$^{73}\text{Ge}^{72}\text{GeH}_2$ 147	$^{73}\text{Ge}^{73}\text{GeH}_2$ 148	$^{73}\text{Ge}^{74}\text{GeH}_2$ 149	$^{73}\text{Ge}^{76}\text{GeH}_2$ 151
	^{74}Ge (36.7%)	$^{74}\text{Ge}^{70}\text{GeH}_2$ 146	$^{74}\text{Ge}^{72}\text{GeH}_2$ 148	$^{74}\text{Ge}^{73}\text{GeH}_2$ 149	$^{74}\text{Ge}^{74}\text{GeH}_2$ 150	$^{74}\text{Ge}^{76}\text{GeH}_2$ 152
	^{76}Ge (7.75%)	$^{76}\text{Ge}^{70}\text{GeH}_2$ 148	$^{76}\text{Ge}^{72}\text{GeH}_2$ 150	$^{76}\text{Ge}^{73}\text{GeH}_2$ 151	$^{76}\text{Ge}^{74}\text{GeH}_2$ 152	$^{76}\text{Ge}^{76}\text{GeH}_2$ 154

Table S3. CCSD/cc-pVTZ optimized cartesian coordinates on the Ge₂H₄ adiabatic triplet and singlet ground state potential energy surface (¹i6, ¹tsi2i6 and ¹tsi6p2 are optimized at MP2/cc-pVTZ level).

Atom	X	Y	Z	Atom	X	Y	Z
vdW				³i1			
H	-0.842383	-1.607566	1.258790	Ge	0.018176	-1.160167	0.000000
H	1.118017	-2.533274	0.000000	H	-0.680958	-1.702130	1.244177
H	0.759873	-0.139545	0.000000	H	1.474201	-1.607561	0.000000
H	-0.842383	-1.607566	-1.258790	Ge	0.018176	1.251849	0.000000
Ge	-0.003018	1.688050	0.000000	H	-1.275560	2.077981	0.000000
Ge	-0.003018	-1.504051	0.000000	H	-0.680958	-1.702130	-1.244177
³i3				³i4			
Ge	-1.203364	0.029129	-0.030968	H	0.615955	-1.869408	1.279816
H	-1.818087	-1.364244	-0.179017	H	-1.096594	0.047351	0.000000
H	-1.843182	0.737116	1.169978	H	1.053915	0.084772	0.000000
Ge	1.203365	-0.029126	-0.030968	H	0.615955	-1.869408	-1.279816
H	1.818100	1.364247	-0.178949	Ge	-0.018582	-1.314282	0.000000
H	1.843136	-0.737214	1.169943	Ge	-0.018582	1.426991	0.000000
i1-MSX				i1			
Ge	0.016463	-1.194498	0.000000	Ge	0.024138	-1.182455	0.000000
H	-0.677027	-1.751554	1.250671	H	-0.709195	-1.714780	1.235230
H	1.493419	-1.604776	-0.000001	H	1.428033	-1.788531	0.000000
Ge	-0.021534	1.279038	0.000002	Ge	0.024138	1.304934	0.000000
H	-1.261215	2.181184	-0.000003	H	-1.554477	1.298786	0.000000
H	-0.677029	-1.751551	-1.250671	H	-0.709195	-1.714780	-1.235230
i2				i3			
H	1.969414	-1.264440	0.183602	Ge	0.000000	1.129227	0.000000
H	0.164352	0.031136	1.319340	H	-0.515092	1.832128	1.252298
H	2.053423	1.214718	0.098327	H	-0.515092	1.832128	-1.252298

H	-1.167761	1.528381	0.031873	Ge	0.000000	-1.129227	0.000000
Ge	-1.230152	-0.046102	-0.014685	H	0.515092	-1.832128	-1.252298
Ge	1.135795	-0.001080	-0.036351	H	0.515092	-1.832128	1.252298
trans-i4				cis-i4			
H	0.000000	0.000000	1.066518	H	-1.060732	0.000000	-0.079197
H	0.000000	0.000000	-1.066518	H	1.060732	0.000000	-0.079197
H	-1.573034	1.280787	0.000000	H	0.000000	1.393799	1.524344
H	1.573034	-1.280787	0.000000	H	0.000000	-1.393799	1.524344
Ge	0.000000	-1.362604	0.000000	Ge	0.000000	-1.373730	-0.045161
Ge	0.000000	1.362604	0.000000	Ge	0.000000	1.373730	-0.045161
i5				i6			
H	1.146564	2.049919	0.000000	H	-1.634637	1.651045	0.106668
H	-1.347539	1.931837	0.000000	H	-1.645754	-0.351561	1.373338
H	1.959592	-0.808343	0.386731	H	-0.943045	1.633967	0.538123
H	1.959592	-0.808343	-0.386731	H	1.267085	1.428496	-0.528123
Ge	-0.058097	1.112976	0.000000	Ge	-1.166244	-0.094608	-0.070707
Ge	-0.058097	-1.186885	0.000000	Ge	1.258630	-0.041702	0.024144
³tsvdWi1				³tsi1i3			
H	-1.504173	-1.601488	0.000000	H	1.683573	1.141732	-0.917626
H	0.681176	-1.707308	1.264416	H	-1.862601	1.220425	0.621722
H	1.424427	0.620600	0.000000	H	-0.380225	-0.314852	1.334407
H	0.681176	-1.707308	-1.264416	H	1.598684	-1.382641	-0.438501
Ge	-0.020041	1.375304	0.000000	Ge	1.222730	0.020271	0.039829
Ge	-0.020041	-1.237944	0.000000	Ge	-1.255213	-0.041042	-0.058579
³tsi1p3				³tsi1transp4			
Ge	-1.305548	-0.076918	0.000683	H	-1.776088	1.107783	-0.831262
H	-0.091598	1.314795	-0.011410	H	-1.852230	-0.077649	1.328334
H	-1.134852	1.598308	-0.012641	H	-1.158189	1.598001	0.067573
Ge	1.226510	0.020675	-0.000441	H	2.032627	-1.001627	-0.754655

H	1.877776	-0.538233	1.263058	Ge	1.233380	0.050462	0.036940
H	1.877875	-0.575089	-1.246762	Ge	-1.147321	-0.101290	-0.031002
³tsi3p3				³tsi3transp4			
Ge	1.252232	-0.094366	0.023905	Ge	1.265230	-0.001249	0.057857
H	0.918539	1.320330	-0.850713	H	2.034448	-0.528560	-1.172029
H	1.655070	1.461238	0.180705	H	0.002148	1.258365	-0.402734
Ge	-1.223267	0.030398	-0.040161	Ge	-1.254259	-0.086185	-0.028548
H	-1.776426	-1.406115	-0.082378	H	-1.357816	0.628411	1.363325
H	-1.724055	0.671535	1.272592	H	-1.029870	1.439677	-0.726448
tsi1i2				tsi1transi4			
H	-2.047379	1.216071	-0.158459	H	-0.644864	-0.711252	1.246659
H	-1.979256	-1.274157	0.011263	H	-0.644864	-0.711252	-1.246659
H	-0.464038	0.094643	1.431531	H	1.538690	-1.238453	0.000000
H	1.200593	1.528950	0.030710	H	-1.560566	1.352911	0.000000
Ge	-1.138592	-0.001570	-0.025706	Ge	0.020494	1.346632	0.000000
Ge	1.241407	-0.047352	-0.015389	Ge	0.020494	-1.305756	0.000000
tsi1p3				tsi2i3			
Ge	-1.102606	-0.133014	0.000105	Ge	-1.138127	0.010183	-0.014367
H	-1.850150	1.215186	-0.003882	H	1.199488	1.399792	0.608697
H	-1.584517	-0.900177	1.234791	H	-2.212388	1.110734	0.108841
Ge	1.358386	0.069521	0.000099	H	0.625257	-0.823643	1.223686
H	-1.575180	-0.901483	-1.237714	H	-1.943478	-1.300246	-0.005190
H	-3.175112	2.618237	0.000266	Ge	1.210974	-0.022265	-0.046134
tsi2transi4				tsi2cisi4			
H	-1.850789	-1.333545	0.610762	H	0.707184	-0.710388	1.241127
H	0.086183	-0.837110	0.003061	H	-0.050677	1.003759	-0.019125
H	-0.995820	0.760199	1.271606	H	1.936977	1.245024	0.628355
H	0.899160	1.409112	-0.068641	H	-2.115145	1.337263	0.037685
Ge	1.497557	-0.030900	-0.001670	Ge	-1.351166	-0.055964	-0.005893

Ge	-1.439392	0.030942	-0.055105	Ge	1.336218	-0.033901	-0.053108
tsi2i5				tsi2i6			
H	-2.011741	1.227020	-0.026102	H	-1.478248	1.536027	0.279671
H	-1.996175	-1.200829	0.424508	H	-1.741799	-0.599081	1.246634
H	0.348276	1.286765	0.650328	H	-0.654109	1.350256	0.735050
H	0.954667	1.581145	-0.200647	H	1.248225	1.406412	-0.564492
Ge	-1.123877	-0.021586	-0.023914	Ge	-1.169750	-0.064248	-0.076066
Ge	1.208407	-0.068855	-0.002589	Ge	1.251810	-0.051178	0.023039
tsi2p1				tstransi4cisi4			
H	1.741447	-0.676930	1.224268	H	0.003619	0.046681	1.061183
H	0.579491	1.269823	0.804750	H	0.504377	-1.080800	-0.762563
H	1.464116	1.515725	0.340368	H	-1.512511	1.524268	0.010434
H	-1.295540	1.407541	-0.576333	H	0.686481	1.186579	-0.752873
Ge	-1.262841	-0.053798	0.021939	Ge	1.381920	-0.003002	0.017274
Ge	1.185044	-0.056082	-0.077971	Ge	-1.371981	-0.049396	-0.003405
tstransi4p1				tscisi4p1			
H	1.161966	1.607307	0.161770	H	1.252644	1.605883	0.092097
H	0.062924	0.005271	1.198078	H	0.094502	0.035053	1.229415
H	0.319297	1.295406	-0.389608	H	0.350127	1.329566	-0.361416
H	-1.149370	-1.536710	-0.135884	H	-1.518908	1.486064	0.143300
Ge	-1.282652	0.028226	-0.009361	Ge	-1.268926	-0.066726	-0.018593
Ge	1.270314	-0.071078	-0.016713	Ge	1.263352	-0.072542	-0.015888
tsi5p2				tsi6p2			
H	-0.863114	-1.499089	0.000473	Ge	-1.068746	-0.108680	-0.042164
H	1.768607	2.593819	-0.372542	H	-2.347743	-0.589704	0.634782
H	1.764535	2.594206	0.372813	H	-1.869023	1.627383	-0.190357
H	-2.587270	0.406573	-0.000063	Ge	1.219731	-0.022841	0.018563
Ge	1.104025	-0.197046	0.000008	H	0.939588	1.507898	-0.220124
Ge	-1.106611	0.069062	-0.000029	H	-1.554319	1.663103	0.530919

³p1				³p2			
H	0.316983	-0.001013	1.063833	H	1.548345	1.424435	0.411755
H	0.316983	-0.001013	-1.063833	H	0.018196	0.507024	-1.140779
Ge	-0.009906	1.345763	0.000000	Ge	1.210255	-0.058804	0.003812
Ge	-0.009906	-1.345699	0.000000	Ge	-1.259209	-0.001554	0.018970
³p3				trans-³p4			
Ge	0.000000	0.000000	1.256007	H	-1.518167	1.578907	0.000000
Ge	0.000000	0.000000	-1.127721	H	1.518167	-1.578907	0.000000
H	0.000000	1.227001	-2.052572	Ge	0.000000	-1.197474	0.000000
H	0.000000	-1.227001	-2.052572	Ge	0.000000	1.197474	0.000000
cis-³p4				p1			
Ge	0.043779	1.201425	0.000000	H	-1.026714	0.000000	0.764383
H	-1.265424	2.042820	0.000000	H	1.026714	0.000000	0.764383
Ge	0.043779	-1.231334	0.000000	Ge	0.000000	1.171039	-0.023887
H	-1.536418	-1.085725	0.000000	Ge	0.000000	-1.171039	-0.023887
p2				p3			
Ge	0.028725	1.070685	0.000000	Ge	0.000000	0.000000	1.205260
H	-0.517502	2.499626	0.000000	Ge	0.000000	0.000000	-1.083418
Ge	0.028725	-1.149836	0.000000	H	0.000000	-1.256087	-1.949482
H	-1.320904	0.033230	0.000000	H	0.000000	1.256087	-1.949482
p4				¹GeH₂			
H	-1.253722	1.982868	0.000000	Ge	0.000000	0.000000	0.064528
H	1.253722	-1.982868	0.000000	H	0.000000	1.133106	-1.032452
Ge	0.000000	-1.096430	0.000000	H	0.000000	-1.133106	-1.032452
Ge	0.000000	1.096430	0.000000				
tsp1p2				tsp1p4			
H	1.543938	1.332567	0.565380	Ge	-1.148466	0.056328	0.021895
H	-0.065263	0.693311	1.094493	H	-1.775083	-1.166066	0.700957
Ge	1.140027	-0.059314	0.004254	Ge	1.148444	-0.056310	0.021924
Ge	-1.186236	-0.003995	0.020789	H	1.775788	1.165486	0.701272

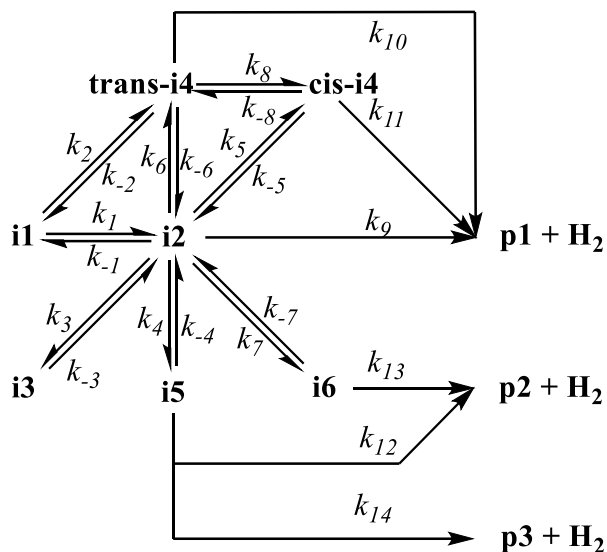
tsp2p3				tsp2p4			
Ge	0.019337	1.064100	0.000000	Ge	0.016089	1.075418	0.000000
H	0.286790	2.557897	0.000000	H	0.516855	2.525406	0.000000
Ge	0.019337	-1.167078	0.000000	Ge	0.016089	-1.124115	0.000000
H	-1.524329	0.737384	0.000000	H	-1.546554	-0.967098	0.000000
tsi5p3							
Ge	-1.181786	-0.118658	-0.000025				
H	1.998417	1.225037	0.000022				
H	1.974264	-1.277258	-0.001168				
H	-0.877586	2.180432	-0.379690				
H	-0.884646	2.181496	0.378786				
Ge	1.112709	-0.016020	0.000089				

Table S4. On singlet PES, the RRKM rate constants (s^{-1}) computed with CCSD/cc-pVTZ zero-point energy corrected CCSD(T)/CBS energies, and CCSD/cc-pVTZ harmonic frequencies at collision energies of 0.0, 5.0, 10.0, 20.0, 24.3, 30.0, and 40.0 kJ/mol.

	0	5	10	20	24.3	30	40
k_1 (i1 $\rightarrow$ i2)	2.75×10^{12}	2.78×10^{12}	2.80×10^{12}	2.85×10^{12}	2.87×10^{12}	2.90×10^{12}	2.94×10^{12}
k_{-1} (i2 $\rightarrow$ i1)	9.82×10^{12}	9.85×10^{12}	9.88×10^{12}	9.94×10^{12}	9.96×10^{12}	9.99×10^{12}	1.00×10^{13}
k_2 (i1 $\rightarrow$ trans-i4)	5.53×10^9	7.43×10^9	9.75×10^9	1.58×10^{10}	1.91×10^{10}	2.41×10^{10}	3.48×10^{10}
k_{-2} (trans-i4 $\rightarrow$ i1)	6.34×10^{11}	8.05×10^{11}	1.00×10^{12}	1.47×10^{12}	1.70×10^{12}	2.04×10^{12}	2.72×10^{12}
k_3 (i2 $\rightarrow$ i3)	3.50×10^{12}	3.66×10^{12}	3.83×10^{12}	4.15×10^{12}	4.29×10^{12}	4.47×10^{12}	4.79×10^{12}
k_{-3} (i3 $\rightarrow$ i2)	2.83×10^{12}	3.03×10^{12}	3.23×10^{12}	3.66×10^{12}	3.84×10^{12}	4.09×10^{12}	4.53×10^{12}
k_4 (i2 $\rightarrow$ i5)	1.50×10^{10}	1.93×10^{10}	2.44×10^{10}	3.72×10^{10}	4.38×10^{10}	5.37×10^{10}	7.44×10^{10}
k_{-4} (i5 $\rightarrow$ i2)	5.91×10^{11}	6.34×10^{11}	6.75×10^{11}	7.55×10^{11}	7.88×10^{11}	8.30×10^{11}	9.02×10^{11}
k_5 (i2 $\rightarrow$ cis-i4)	4.15×10^9	5.68×10^9	7.58×10^9	1.27×10^{10}	1.54×10^{10}	1.97×10^{10}	2.90×10^{10}
k_{-5} (cis-i4 $\rightarrow$ i2)	2.37×10^{11}	3.05×10^{11}	3.82×10^{11}	5.68×10^{11}	6.61×10^{11}	7.97×10^{11}	1.07×10^{12}
k_6 (i2 $\rightarrow$ trans-i4)	1.04×10^9	1.56×10^9	2.25×10^9	4.26×10^9	5.44×10^9	7.33×10^9	1.17×10^{10}
k_{-6} (trans-i4 $\rightarrow$ i2)	3.33×10^{10}	4.76×10^{10}	6.55×10^{10}	1.14×10^{11}	1.40×10^{11}	1.80×10^{11}	2.67×10^{11}
k_7 (i2 $\rightarrow$ i6)	9.74×10^7	1.92×10^8	3.42×10^8	8.89×10^8	1.26×10^9	1.93×10^9	3.68×10^9

k_7 (i6 → i2)	2.95×10^{12}	3.03×10^{12}	3.08×10^{12}	3.15×10^{12}	3.18×10^{12}	3.22×10^{12}	3.27×10^{12}
k_8 (trans-i4 → cis-i4)	1.05×10^{12}	1.18×10^{12}	1.31×10^{12}	1.60×10^{12}	1.73×10^{12}	1.90×10^{12}	2.21×10^{12}
k_8 (cis-i4 → trans-i4)	1.88×10^{12}	2.07×10^{12}	2.28×10^{12}	2.69×10^{12}	2.88×10^{12}	3.12×10^{12}	3.56×10^{12}
k_9 (i2 → p1)	1.49×10^8	2.84×10^8	4.96×10^8	1.26×10^9	1.77×10^9	2.68×10^9	5.05×10^9
k_{10} (trans-i4 → p1)	2.13×10^9	3.55×10^9	5.56×10^9	1.18×10^{10}	1.56×10^{10}	2.19×10^{10}	3.67×10^{10}
k_{11} (cis-i4 → p1)	2.28×10^9	4.07×10^9	6.68×10^9	1.52×10^{10}	2.05×10^{10}	2.94×10^{10}	5.09×10^{10}
k_{12} (i5 → p2)	3.32×10^{14}	3.95×10^{14}	4.60×10^{14}	5.97×10^{14}	6.58×10^{14}	7.39×10^{14}	8.85×10^{14}
k_{13} (i6 → p2)	1.82×10^{12}	2.28×10^{12}	2.69×10^{12}	3.41×10^{12}	3.68×10^{12}	4.00×10^{12}	4.49×10^{12}
k_{14} (i5 → p3)	1.69×10^{13}	1.72×10^{13}	1.75×10^{13}	1.81×10^{13}	1.83×10^{13}	1.85×10^{13}	1.90×10^{13}

Table S5. The reaction mechanism and rate equations on singlet PES.



$$\frac{d[i1]}{dt} = k_{-1}[i2] + k_{-2}[transi4] - (k_1 + k_2)[i1]$$

$$\frac{d[i2]}{dt} = k_1[i1] + k_{-3}[i3] + k_{-4}[i5] + k_{-7}[i6] + k_{-5}[cisi4] + k_{-6}[transi4] - (k_{-1} + k_3 + k_4 + k_7 + k_9 + k_5 + k_6)[i2]$$

$$\frac{d[i3]}{dt} = k_3[i2] - k_{-3}[i3]$$

$$\frac{d[transi4]}{dt} = k_2[i1] + k_6[i2] + k_{-8}[cisi4] - (k_{-2} + k_{-6} + k_8 + k_{10})[transi4]$$

$$\frac{d[cisi4]}{dt} = k_5[i2] + k_8[transi4] - (k_{-5} + k_{-8} + k_{11})[cisi4]$$

$$\frac{d[i5]}{dt} = k_4[i2] - (k_{-4} + k_{12} + k_{14})[i5]$$

$$\frac{d[i6]}{dt} = k_7[i2] - (k_{-7} + k_{13})[i6]$$

$$\frac{d[p1 + H_2]}{dt} = k_9[i2] + k_{10}[transi4] + k_{11}[cisi4]$$

$$\frac{d[p2 + H_2]}{dt} = k_{12}[i5] + k_{13}[i6]$$

$$\frac{d[p3 + H_2]}{dt} = k_{14}[i5]$$

Table S6. Product branching ratios (%) for Ge + GeH₄ reaction at collision energies of 0.0, 5.0, 10.0, 20.0, 24.3, 30.0 and 40.0 kJ mol⁻¹: (a) all products, (b) p1+H₂ via different channels.

(a)

	0	5	10	20	24.3	30	40
p1 + H ₂	1.67	2.40	3.23	5.13	6.02	7.26	9.45
p2 + H ₂	93.58	93.55	93.25	92.11	91.47	90.52	88.70
p3 + H ₂	4.75	4.06	3.52	2.76	2.50	2.22	1.85

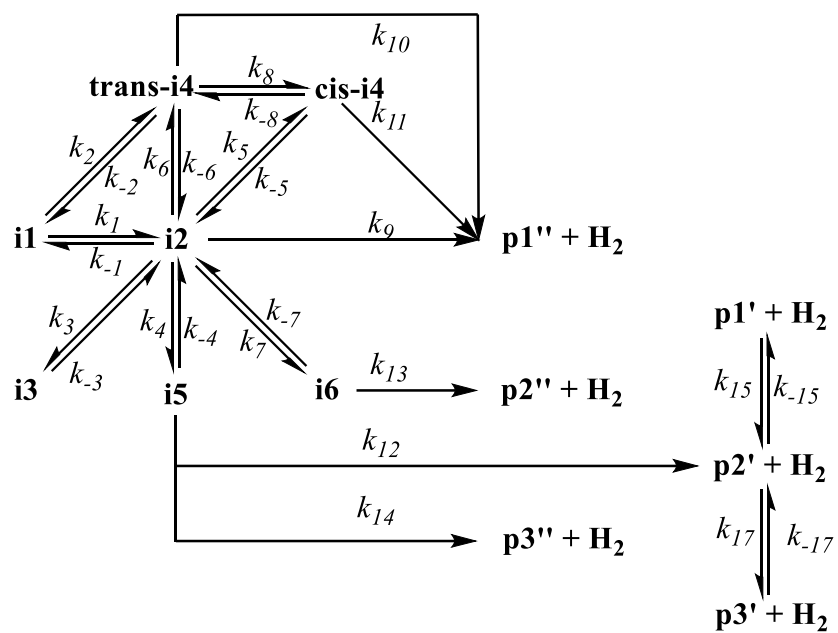
(b)

	0	5	10	20	24.3	30	40
p1 + H ₂ (i2)	0.98	1.43	1.96	3.18	3.74	4.54	5.98
(trans-i4)	0.43	0.58	0.75	1.11	1.28	1.50	1.87
(cis-i4)	0.26	0.38	0.52	0.85	1.00	1.22	1.60
p2 + H ₂	93.58	93.55	93.25	92.11	91.47	90.52	88.70
p3 + H ₂	4.75	4.06	3.52	2.76	2.50	2.22	1.85

Table S7. On singlet PES, the RRKM rate constants (s^{-1}) for secondary reactions of **p1**, **p2**, **p3** isomerization computed with CCSD/cc-pVTZ zero-point energy corrected CCSD(T)/CBS energies, and CCSD/cc-pVTZ harmonic frequencies at collision energies of 0.0, and 24.3 kJ/mol. The estimated translational and rotational energy of **p2** + H₂ along with vibrational energy of H₂, -45 and -60 kJ/mol, are subtracted from the available energy for **p2** isomerization at 0.0, and 24.3 kJ/mol collision energies, respectively.

	0	24.3
	(-45 kJ/mol)	(-60 kJ/mol)
k_{15}		
(p1→p2)	8.90×10^{11}	1.67×10^{12}
k_{-15}		
(p2→p1)	7.64×10^{11}	1.03×10^{12}
k_{17}		
(p2→p3)	7.43×10^{11}	1.44×10^{12}
k_{-17}		
(p3→p2)	4.27×10^{12}	7.03×10^{12}

Table S8. The reaction mechanism and rate equations including secondary reactions of p2 isomerizations on singlet PES.



$$\begin{aligned}
\frac{d[i1]}{dt} &= k_{-1}[i2] + k_{-2}[transi4] - (k_1 + k_2)[i1] \\
\frac{d[i2]}{dt} &= k_1[i1] + k_{-3}[i3] + k_{-4}[i5] + k_{-7}[i6] + k_{-5}[i4'] + k_{-6}[transi4] - (k_{-1} + k_3 + k_4 \\
&\quad + k_7 + k_9 + k_5 + k_6)[i2] \\
\frac{d[i3]}{dt} &= k_3[i2] - k_{-3}[i3] \\
\frac{d[transi4]}{dt} &= k_2[i1] + k_6[i2] + k_{-8}[cisi4] - (k_{-2} + k_{-6} + k_8 + k_{10})[transi4] \\
\frac{d[cisi4]}{dt} &= k_5[i2] + k_8[transi4] - (k_{-5} + k_{-8} + k_{11})[cisi4] \\
\frac{d[i5]}{dt} &= k_4[i2] - (k_{-4} + k_{12} + k_{14})[i5] \\
\frac{d[i6]}{dt} &= k_7[i2] - (k_{-7} + k_{13})[i6] \\
\frac{d[p1'']}{dt} &= k_9[i2] + k_{10}[transi4] + k_{11}[cisi4] \\
\frac{d[p2'']}{dt} &= k_{13}[i6] \\
\frac{d[p3'']}{dt} &= k_{14}[i5] \\
\frac{d[p1']}{dt} &= k_{-15}[p2'] - k_{15}[p1'] \\
\frac{d[p2']}{dt} &= k_{12}[i5] + k_{15}[p1'] + k_{-17}[p3'] - (k_{-15} + k_{17})[p2'] \\
\frac{d[p3']}{dt} &= k_{17}[p2'] - k_{-17}[p3']
\end{aligned}$$

Table S9. Product branching ratios (%) for Ge + GeH₄ reaction including secondary reactions of p2 isomerizations at collision energies of 0.0, and 24.3 kJ mol⁻¹.

	0	24.3
	(-45 kJ/mol)	(-60 kJ/mol)
p1'' + H ₂	1.67	6.02
p2'' + H ₂	0.24	1.43
p3'' + H ₂	4.75	2.50
p1' + H ₂	39.42	30.49
p2' + H ₂	45.92	49.43
p3' + H ₂	7.99	10.13
p1 (p1' + p1'')	41.09	36.51
p2 (p2' + p2'')	46.17	50.86
p3 (p3' + p3'')	12.74	12.63

Table S10. Vibrational frequencies and infrared intensities on the Ge₂H₄ adiabatic triplet and singlet ground state potential energy surface. (¹i6, ¹tsi2i6 and ¹tsi6p2 are optimized at MP2/cc-pVTZ level)

³ c1			³ i1	
Normal modes	Frequency(cm ⁻¹)	IR Inten	Frequency(cm ⁻¹)	IR Inten
v1	73.52	0.1999	99.63	0.0108
v2	103.53	0.1027	262.9	2.6471
v3	331.33	35.4758	413.7	14.7667
v4	800.54	49.325	495.72	6.4466
v5	818.14	358.1966	592.49	13.818
v6	884.47	83.0634	825.8	299.8227
v7	915.39	22.5705	904.28	38.933
v8	994.83	56.8726	909.18	41.111
v9	1961.43	454.909	2143.92	111.1527
v10	2245.01	78.4748	2205.26	87.2642
v11	2267.49	47.5629	2210.85	96.4515
v12	2276.17	69.7227	2233.91	93.5736
³ i3			³ i4	
Normal modes	Frequency(cm ⁻¹)	IR Inten	Frequency(cm ⁻¹)	IR Inten
v1	191.07	0.815	219.17	0.0558
v2	270.83	0.0064	248.31	0.0309
v3	399.51	13.7831	405.05	37.4538
v4	440.83	10.3483	451.5	1.4269
v5	550.11	40.8457	469.17	34.1758
v6	576.01	1.097	704.51	7.4243
v7	850.21	252.5386	814.11	84.6193
v8	895.92	20.1182	1078.21	70.557
v9	2152.59	170.8286	1297.42	166.0677
v10	2157.67	64.6261	1517.52	2.4977
v11	2190.05	29.9092	1981.93	151.6532
v12	2193.87	201.1334	2044.15	139.723
MSX			i1	
Normal modes	Frequency(cm ⁻¹)	IR Inten	Frequency(cm ⁻¹)	IR Inten
v1	-492.58	0.28	96.27	3.5275

v2	250.23	1.47	242.52	3.4276
v3	321.92	22.64	353.72	23.6363
v4	339.08	13.47	387.16	15.1643
v5	552.88	16.75	663.17	40.1148
v6	862.89	356.98	815.19	259.0599
v7	934.25	51.81	904.01	36.8478
v8	952.37	53.37	916.27	30.9037
v9	2203.39	132.78	1991.57	240.1421
v10	2210.08	154.15	2175.87	98.4278
v11	2215.82	139.67	2186.05	120.3072
v12	2231.68	147.78	2202.4	140.7084
i2			i3	
Normal modes	Frequency(cm ⁻¹)	IR Inten	Frequency(cm ⁻¹)	IR Inten
v1	285.36	4.7443	289.97	0
v2	352.24	30.9175	324.95	14.9891
v3	363.38	6.1705	413.07	30.733
v4	610.94	6.2929	455.63	0
v5	654.28	19.4481	503.7	0.0912
v6	823.51	77.0408	559.37	0
v7	902.4	64.822	882.87	188.1866
v8	929.03	315.7046	901.83	0
v9	1611.38	137.2761	2202.66	160.5899
v10	1998.34	222.4699	2203.71	0
v11	2189.46	166.9608	2216.24	0
v12	2206.24	133.8602	2227.12	199.4993
trans-i4			cis-i4	
Normal modes	Frequency(cm ⁻¹)	IR Inten	Frequency(cm ⁻¹)	IR Inten
v1	237.8	0	236.37	0.3059
v2	270.3	1.2465	351.61	0.2694
v3	659.05	16.2848	598.82	0
v4	772.13	0	691.11	71.1302
v5	805.58	0	817.89	19.3112
v6	818.22	161.7812	851.45	28.1181
v7	1255.56	56.7769	1236.53	59.4887
v8	1349.07	0	1282.68	0
v9	1412.17	1299.149	1361.76	1585.864

v10	1563.44	0	1556.58	0.0558
v11	2001.63	0	2018.05	17.8684
v12	2019.35	493.0976	2042.51	438.9959
i5		i6		
Normal modes	Frequency(cm ⁻¹)	IR Inten	Frequency(cm ⁻¹)	IR Inten
v1	233.71	0.1342	167.35	14.3984
v2	295.63	7.9248	247.16	8.7533
v3	324.75	5.4208	300.85	3.861
v4	373.07	25.7082	403.09	11.4703
v5	377.1	1.4687	544.92	7.0916
v6	430.32	2.3658	661.98	23.947
v7	482.54	1.4052	674.17	9.5209
v8	877.88	80.7523	837.75	37.3408
v9	930.89	1.4716	1397.69	20.0555
v10	2190.85	95.5956	2033.55	233.051
v11	2210.98	97.4174	2145.52	149.5774
v12	3889.18	39.1952	3230.78	302.3669
³tsc1i1		³tsi1i3		
Normal modes	Frequency(cm ⁻¹)	IR Inten	Frequency(cm ⁻¹)	IR Inten
v1	-783.74	21.6824	-591.46	10.8647
v2	168.43	3.8734	214.55	12.0379
v3	228.68	0.1114	251.28	2.1541
v4	453.37	6.484	394.03	6.5059
v5	472.67	1.3242	536.79	51.4452
v6	800.18	262.7868	579.59	4.249
v7	885.89	43.9435	810.62	6.0524
v8	888.1	47.8031	846.29	91.4153
v9	1764.29	272.1746	1630.97	231.8283
v10	2196.85	59.437	2060.22	80.8718
v11	2240.58	63.4147	2061.35	165.2793
v12	2251.01	73.6654	2191.1	103.3873
³tsi1p3		³tsi1transp4		
Normal modes	Frequency(cm ⁻¹)	IR Inten	Frequency(cm ⁻¹)	IR Inten
v1	-1402.45	728.1866	-1350.71	568.9818
v2	193	0.1618	243.09	0.0248

v3	334.6	5.4625	270.08	0.2478
v4	341.26	2.7841	343.85	3.6209
v5	443.73	3.3069	467.66	4.1087
v6	794.29	54.6558	605.89	4.46
v7	810.53	0.9149	752.81	21.2995
v8	926.6	58.603	916.15	118.7214
v9	1306.22	34.8205	1607.99	183.005
v10	1753.57	123.6864	2025.91	12.1893
v11	2187.42	88.0742	2113.97	127.1861
v12	2205.08	100.8506	2183.6	93.6441
³ tsi3p3			³ tsi3transp4	
Normal modes	Frequency(cm ⁻¹)	IR Inten	Frequency(cm ⁻¹)	IR Inten
v1	-1282.24	373.7738	-1309.37	861.0131
v2	76.71	0.1009	205.72	0.1069
v3	220.96	0.8026	312.86	2.8708
v4	326.25	3.5441	395.03	3.5772
v5	444.64	3.9998	625.97	1.3988
v6	558.18	26.465	722.28	40.8683
v7	741.35	34.0465	834.21	25.2703
v8	865.15	118.0397	950.48	46.8664
v9	1577.19	153.8602	1248.54	50.3075
v10	1848.48	51.0241	1659.08	90.7894
v11	2100.37	123.0481	2032.19	188.885
v12	2144.91	148.4104	2108.44	142.077
tsi1i2			tsi1transi4	
Normal modes	Frequency(cm ⁻¹)	IR Inten	Frequency(cm ⁻¹)	IR Inten
v1	-282.75	41.9396	-743.67	248.6808
v2	291.68	3.7258	103.31	6.0365
v3	370.41	8.1432	185.52	2.3624
v4	540.6	2.1826	436.53	1.4742
v5	652.2	26.5409	459.77	2.645
v6	796.88	224.9014	649.99	14.2348
v7	848.23	28.4651	845.44	55.1872
v8	903.5	75.6009	867.31	50.6548
v9	1835.32	104.6023	1981.22	273.1058
v10	1995.35	227.8083	2165.22	5.2040

v11	2207.98	142.1898	2178.07	47.7022
v12	2221.53	123.8547	2237.53	70.4064
tsi1p3			tsi2i3	
Normal modes	Frequency(cm ⁻¹)	IR Inten	Frequency(cm ⁻¹)	IR Inten
v1	-332.86	99.8001	-593.89	2.2741
v2	99.5	0.0748	267.98	2.0398
v3	124.12	0.556	300.8	5.5753
v4	241.91	24.8821	452.42	10.0942
v5	254.95	4.2298	614.67	5.2518
v6	418.6	13.3602	638.62	15.6223
v7	817.87	316.7675	876.7	76.709
v8	893.8	62.9431	937.61	198.8877
v9	912.11	29.8354	1829.74	110.9703
v10	2002.24	422.8273	2030.53	178.1774
v11	2178.25	91.8809	2135.07	202.2991
v12	2187.86	115.6326	2172.29	152.6731
tsi2transi4			tsi2cisi4	
Normal modes	Frequency(cm ⁻¹)	IR Inten	Frequency(cm ⁻¹)	IR Inten
v1	-485.72	26.8866	-529.52	3.2479
v2	120.19	5.3185	131	7.8968
v3	405.17	2.8555	393.2	7.055
v4	553.57	3.1732	543.4	3.1016
v5	650.72	4.3127	608.41	47.416
v6	766.54	84.0021	810.16	42.0856
v7	898.1	147.9299	893.15	227.5781
v8	1204.96	91.6571	1373.94	39.9266
v9	1860.65	604.2944	1661.66	337.253
v10	1965.03	193.0096	1908.11	111.1043
v11	2006.04	217.4132	1947.31	304.7144
v12	2085.65	173.1008	2017.72	269.3057
tsi2i5			tsi2i6	
Normal modes	Frequency(cm ⁻¹)	IR Inten	Frequency(cm ⁻¹)	IR Inten
v1	-1295.71	316.5997	-648.25	249.4191
v2	300.61	3.0475	204.73	8.3539
v3	350.38	14.0077	330.15	6.9163

v4	464.86	10.6951	454.28	15.0668
v5	487.99	12.3724	480.54	10.3735
v6	687.97	77.5117	718.81	45.9166
v7	845.86	6.3845	853.68	87.4717
v8	929.41	181.9666	938.68	67.5466
v9	1619.6	103.6871	1767.15	96.6983
v10	1759.24	112.2305	2000.95	212.2138
v11	2171.28	130.676	2034.92	305.234
v12	2186.96	125.7352	2175.35	146.7102
tsi2p1		tstransi4cisi4		
Normal modes	Frequency(cm^{-1})	IR Inten	Frequency(cm^{-1})	IR Inten
v1	-1149.82	461.79	-597.53	15.7664
v2	208.61	5.895	196.78	10.7285
v3	332.62	9.6234	582.23	12.9839
v4	425.24	10.6445	605.28	130.1714
v5	447.66	10.3086	689.3	13.7511
v6	709.88	44.4548	902.67	60.7683
v7	822.68	59.319	944.59	31.5823
v8	950.25	60.5075	1256.59	366.6139
v9	1728.24	169.2998	1430.75	73.1433
v10	1874.94	101.5367	1918.91	110.2969
v11	1985.17	244.2972	1978.41	152.3871
v12	2119.07	168.894	2005.15	302.5566
tstransi4p1		tscisi4p1		
Normal modes	Frequency(cm^{-1})	IR Inten	Frequency(cm^{-1})	IR Inten
v1	-1227.94	276.3292	-1177.18	439.6241
v2	236	0.4985	225.91	0.7889
v3	512.35	32.7636	549.88	7.8377
v4	622.29	8.6592	581.46	8.763
v5	731.68	6.0416	674.19	27.9223
v6	811.64	39.7917	801.04	52.7951
v7	957.54	20.7523	875.34	224.6189
v8	1118.61	364.9517	1014.04	248.0471
v9	1489.99	67.6018	1500.14	125.0714
v10	1741.29	89.0703	1718.17	55.3443
v11	1769.91	154.6512	1774.3	253.5251

v12	1990.2	246.67	1966.37	240.7512
tsi5p2			tsi6p2	
Normal modes	Frequency(cm ⁻¹)	IR Inten	Frequency(cm ⁻¹)	IR Inten
v1	-337.43	14.959	-140.52	24.7763
v2	23.11	0.0085	268.79	6.3634
v3	103.99	0.3486	286.9	5.5014
v4	176.84	1.8311	340.92	6.1503
v5	201.42	14.5326	483.16	0.3233
v6	222.29	11.6192	538.03	19.2947
v7	355.09	6.828	573.78	16.4562
v8	361.11	0.2708	789.95	8.8646
v9	784.34	54.0167	1176.9	7.1961
v10	1935.72	61.1949	2021.38	188.0934
v11	2219	87.8877	2216.87	113.557
v12	4365.99	4.8505	3651.6	179.602
³p1			³p2	
Normal modes	Frequency(cm ⁻¹)	IR Inten	Frequency(cm ⁻¹)	IR Inten
v1	125.41	4.1997	213.4	0.7333
v2	191.81	46.8226	389.02	2.7673
v3	434.8	0.2118	669.21	39.0096
v4	831.51	0.0021	1028.27	340.3396
v5	1323.18	62.7616	1383.41	115.704
v6	1573.34	0.0161	1985.36	258.0191
³p3			trans-³p4	
Normal modes	Frequency(cm ⁻¹)	IR Inten	Frequency(cm ⁻¹)	IR Inten
v1	272.86	1.6763	263.52	0
v2	279.59	5.6856	331.55	6.9855
v3	365.89	7.2002	426.19	10.115
v4	903.43	100.1509	663.39	0
v5	2150.26	134.1411	2031.06	0
v6	2161.55	136.2414	2037.46	423.4986
cis-³p4			p1	
Normal modes	Frequency(cm ⁻¹)	IR Inten	Frequency(cm ⁻¹)	IR Inten
v1	249.38	5.1925	306.59	0.3879

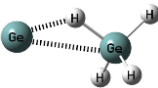
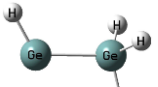
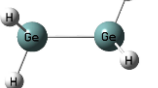
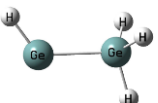
v2	324.38	2.1312	846.2	37.7283
v3	387.04	4.2089	1020.51	0
v4	584.03	22.0511	1110.65	458.1158
v5	1949.39	205.1258	1486.36	35.8855
v6	2048.53	194.5562	1561.91	10.0911
p2		p3		
Normal modes	Frequency(cm ⁻¹)	IR Inten	Frequency(cm ⁻¹)	IR Inten
v1	146.13	41.8162	251.73	21.284
v2	336.3	6.7852	322.04	4.645
v3	472.67	4.5376	326.43	5.3091
v4	1019.09	139.6876	850.76	64.0203
v5	1593.93	84.0702	2188.89	70.3001
v6	2161.98	119.8511	2210.9	82.8437
p4		¹GeH₂		
Normal modes	Frequency(cm ⁻¹)	IR Inten	Frequency(cm ⁻¹)	IR Inten
v1	233.41	35.8088	954.73	72.999
v2	260.48	45.3567	1998.59	277.8718
v3	341.39	0	2008.99	344.5842
v4	584.98	0		
v5	2144.91	0		
v6	2154.82	174.8482		
¹tsp1p2		¹tsp1p4		
Normal modes	Frequency(cm ⁻¹)	IR Inten	Frequency(cm ⁻¹)	IR Inten
v1	-254.57	52.2092	-262.26	0.2532
v2	310	0.5686	148.33	53.8314
v3	728.66	32.4165	345.71	0.0001
v4	972.58	138.7537	548.06	1.8569
v5	1489.82	91.6642	2076.17	29.4407
v6	2053	124.4454	2082.17	212.5136
¹tsp2p3		¹tsp2p4		
Normal modes	Frequency(cm ⁻¹)	IR Inten	Frequency(cm ⁻¹)	IR Inten
v1	-331	6.6966	-404.41	17.4665

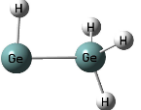
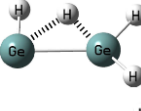
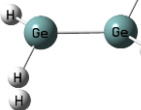
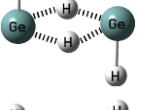
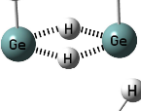
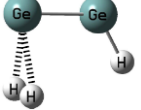
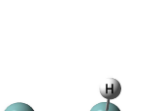
v2	207.3	20.0179	348.63	0.0047
v3	353.33	6.8136	351.2	17.7096
v4	781.8	49.4719	598.11	16.7517
v5	1970.3	55.3648	2021.7	84.4179
v6	2225.74	82.1813	2164.35	153.1724

Table S11. Reaction path of **i5** to **p3**.

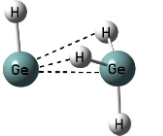
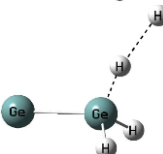
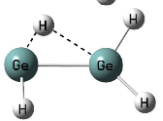
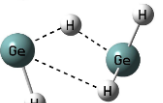
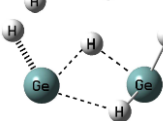
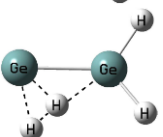
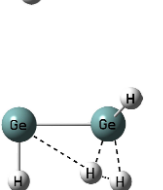
tsi5p3	
Å	kJ/mol
2.4	-73.7
2.5	-71.8
2.6	-70.1
2.7	-68.7
2.8	-67.5
2.9	-66.6
3	-65.8
3.1	-65.1
3.2	-64.6
3.3	-64.1
3.4	-63.6
3.5	-63.3
3.6	-63.0
3.7	-62.8
3.8	-62.6
3.9	-62.3
4	-62.2
4.1	-62.1
4.2	-62.0
4.3	-62.0

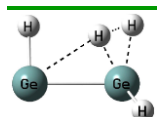
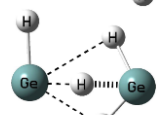
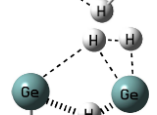
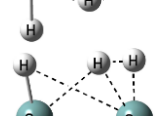
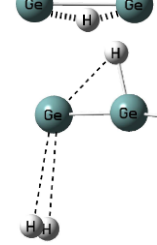
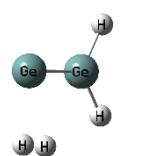
Table S12. Structures and energies of species participating on the adiabatic triplet and singlet ground state potential energy surfaces for Ge + GeH₄ reaction. Energies are determined at the CCSD(T)/CBS//CCSD/cc-pVTZ level of theory with CCSD/cc-pVTZ ZPE corrections.

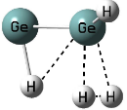
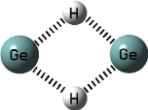
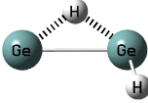
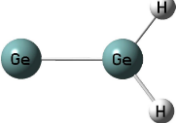
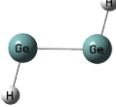
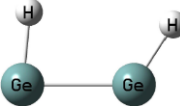
	CCSD/ cc-pVTZ + E _{zpc} ^a	E _{zpc} ^b	CCSD(T)/ pVDZ	cc- CCSD(T)/ pVTZ	cc- CCSD(T)/ pVQZ	cc- CCSD(T)/ CBS	E ^c (kJ/mol)
Ge(³P)	-2075.493248	0.000000	-2075.364439	-2075.499140	-2075.560244	-2075.596899	
GeH₄(T_d, ¹A₁)	-2077.936132	0.030660	-2077.809373	-2077.974911	-2078.043434	-2078.084036	
Ge + GeH₄	-4153.429380	0.030660	-4153.173812	-4153.474051	-4153.603678	-4153.680935	0
 ³c1(C_s, ³A'')	-4153.437119	0.031147	-4153.178924	-4153.484204	-4153.615062	-4153.692977	-30
 ³i1(C_s, ³A'')	-4153.456487	0.030294	-4153.194943	-4153.503258	-4153.636619	-4153.716123	-93
 ³i3(C₁, ³A)	-4153.452250	0.029317	-4153.189178	-4153.498040	-4153.631658	-4153.711316	-83
 ³i4(C_s, ³A'')	-4153.412118	0.027304	-4153.149686	-4153.458879	-4153.591187	-4153.669946	20
 i1-MSX^d		0.030316	-4153.194851	-4153.502286	-4153.635283	-4153.714571	-89

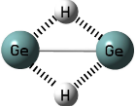
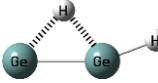
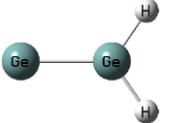
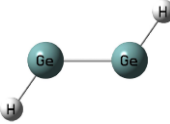
	i1(Cs, ¹A')	-4153.482624	0.029466	-4153.220136	-4153.529627	-4153.663837	-4153.743874	-168
	i2(C1, ¹A)	-4153.477250	0.029449	-4153.215485	-4153.526519	-4153.661044	-4153.741240	-162
	i3(C_{2h}, ¹A_g)	-4153.484295	0.030029	-4153.223979	-4153.535794	-4153.670424	-4153.750663	-185
	trans-i4(C_{2h}, ¹A_g)	-4153.464707	0.029991	-4153.205260	-4153.514484	-4153.647280	-4153.726369	-121
	cis-i4 (C_{2v}, ¹A₁)	-4153.461711	0.029720	-4153.202116	-4153.511133	-4153.643776	-4153.722768	-112
	i5(Cs, ¹A')	-4153.442485	0.028743	-4153.183211	-4153.493173	-4153.627495	-4153.707591	-75
	i6(C1, ¹A)^e	-4153.389807	0.028807	-4153.161192	-4153.471652	-4153.606010	-4153.686113	-18

	³tsc1i1(Cs, ³A'')	-4153.421985	0.028135	-4153.159237	-4153.467377	-4153.600802	-4153.680354	-5
	³tsi1i3(C1, ³A)	-4153.406596	0.026374	-4153.142401	-4153.451654	-4153.585706	-4153.665644	29
	³tsi1p3(C1, ³A)	-4153.398080	0.025735	-4153.134913	-4153.444223	-4153.577681	-4153.657215	49
	³tsi1transp4(C1, ³A)	-4153.379948	0.026270	-4153.116953	-4153.426461	-4153.560200	-4153.639917	96
	³tsi3p3(C1, ³A)	-4153.388917	0.024842	-4153.124259	-4153.433621	-4153.567339	-4153.647047	74
	³tsi3transp4(C1, ³A)	-4153.388064	0.025276	-4153.125796	-4153.434365	-4153.567836	-4153.647405	74
	tsi1i2(C1, ¹A)	-4153.477324	0.028850	-4153.214679	-4153.525283	-4153.659930	-4153.740223	-160

	tsi1transi4(Cs, ¹A')	-4153.433242	0.027588	-4153.171923	-4153.482230	-4153.616969	-4153.697336	-51
	tsi1p3(C1, ¹A)	-4153.352236	0.023081	-4153.126315	-4153.434651	-4153.569220	-4153.649541	63
	tsi2i3(C1, ¹A)	-4153.463698	0.027922	-4153.201197	-4153.512541	-4153.647215	-4153.727501	-129
	tsi2transi4(C1, ¹A)	-4153.431398	0.028515	-4153.169901	-4153.479751	-4153.612237	-4153.691094	-32
	tsi2cisi4(C1, ¹A)	-4153.433546	0.027994	-4153.172058	-4153.482189	-4153.615541	-4153.694974	-44
	tsi2i5(C1, ¹A)	-4153.433200	0.026892	-4153.171723	-4153.483893	-4153.618535	-4153.698770	-57
	tsi2i6(C1, ¹A)^e	-4153.390586	0.027245	-4153.157419	-4153.469049	-4153.603735	-4153.684019	-17

	tsi2p1(C1, ¹A)	-4153.420720	0.026437	-4153.158000	-4153.469088	-4153.603680	-4153.683919	-19
	tstransi4cisi4(C1, ¹A)	-4153.444924	0.028501	-4153.184466	-4153.493937	-4153.627410	-4153.706948	-74
	tstransi4p1(C1, ¹A)	-4153.419955	0.027296	-4153.159033	-4153.470508	-4153.604904	-4153.684997	-19
	tscisi4p1(C1, ¹A)	-4153.418417	0.026611	-4153.156887	-4153.468324	-4153.602818	-4153.682979	-16
	tsi5p2(C1, ¹A)	-4153.435933	0.024488	-4153.173753	-4153.483265	-4153.616385	-4153.695684	-55
	tsi5p3(C1, ¹A)	-4153.443316	0.027190	-4153.182826	-4153.491970	-4153.625938	-4153.705823	-74

	tsi6p2(C1, ¹A)^e	-4153.388633	0.028131	-4153.158039	-4153.469206	-4153.603466	-4153.683478	-13
	H₂(¹Σ_g⁺, D_{∞h})	-1.162291	0.010045	-1.163446	-1.172337	-1.173796	-1.174474	
	³p1(Cs, ³A^{''})	-4152.233031	0.010206	-4151.967967	-4152.265001	-4152.394332	-4152.471501	
	³p2(C1, ³A)	-4152.251180	0.012914	-4151.987350	-4152.282676	-4152.412663	-4152.490335	
	³p3(C_{2v}, ³A₂)	-4152.266611	0.013973	-4152.001992	-4152.297912	-4152.428304	-4152.506230	
	trans-³p4 (C_{2h}, ³A_u)	-4152.262689	0.013107	-4151.999431	-4152.294891	-4152.425334	-4152.503312	
	cis-³p4 (Cs, ³A^{''})	-4152.253013	0.012627	-4151.988538	-4152.283765	-4152.414048	-4152.491924	

	p1(C_{2v}, ¹A₁)	-4152.294212	0.014426	-4152.030373	-4152.330677	-4152.461839	-4152.540134	
	p2(C_s, ¹A')	-4152.279228	0.013054	-4152.015621	-4152.316326	-4152.447427	-4152.525666	
	p3(C_{2v}, ¹A₁)	-4152.278622	0.014012	-4152.014786	-4152.313319	-4152.444725	-4152.523246	
	p4(C_{2h}, ¹A_g)	-4152.265416	0.013031	-4152.004680	-4152.304071	-4152.435299	-4152.513669	
	GeH₂(C_{2v}, ¹A₁)	-2076.705952	0.011305	-2076.573686	-2076.724902	-2076.790174	-2076.829075	
	³p1 + H₂	-4153.395322	0.020251	-4153.131413	-4153.437338	-4153.568128	-4153.645975	64
	³p2 + H₂	-4153.413471	0.022959	-4153.150796	-4153.455013	-4153.586459	-4153.664809	22
	³p3 + H₂	-4153.428902	0.024018	-4153.165438	-4153.470249	-4153.602100	-4153.680704	-17
	trans-³p4 + H₂	-4153.424980	0.023152	-4153.162877	-4153.467228	-4153.599130	-4153.677786	-11
	cis-³p4 + H₂	-4153.415304	0.022672	-4153.151984	-4153.456102	-4153.587844	-4153.666398	17
	p1 + H₂	-4153.456503	0.024471	-4153.193819	-4153.503014	-4153.635635	-4153.714608	-105
	p2 + H₂	-4153.441519	0.023099	-4153.179067	-4153.488663	-4153.621223	-4153.700140	-70
	p3 + H₂	-4153.440913	0.024057	-4153.178232	-4153.485656	-4153.618521	-4153.697720	-61

p4 + H₂	-4153.427707	0.023076	-4153.168126	-4153.476408	-4153.609095	-4153.688143	-39
GeH₂+ GeH₂	-4153.411904	0.022610	-4153.147372	-4153.449805	-4153.580348	-4153.658150	39

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

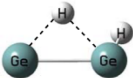
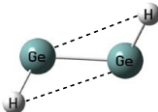
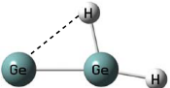
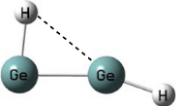
^b zero-point energy by CCSD/cc-pVTZ in hartree.

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

^d geometry optimized by CPMSCF(4,4)/TZVPP with MOLPRO 2015 program package.

^e geometries optimized by MP2/cc-pVTZ.

Table S13. Structures and energies of species participating on the adiabatic triplet and singlet ground state potential energy surfaces for Ge + GeH₄ reaction. Energies are determined at the CCSD(T)/CBS//CCSD/cc-pVTZ level of theory with CCSD/cc-pVTZ ZPE corrections.

	CCSD/ cc-pVTZ + E _{zpc} ^a	E _{zpc} ^b	CCSD(T)/ pVDZ	cc- CCSD(T)/ pVTZ	cc- CCSD(T)/ pVQZ	cc- CCSD(T)/ CBS	E ^c (kJ/mol)
Ge(³P)	-2075.493248	0.000000	-2075.364439	-2075.499140	-2075.560244	-2075.596899	
GeH₄(T_d, ¹A₁)	-2077.936132	0.030660	-2077.809373	-2077.974911	-2078.043434	-2078.084036	
Ge + GeH₄	-4153.429380	0.030660	-4153.173812	-4153.474051	-4153.603678	-4153.680935	0
 ¹tsp1p2(C_i, ¹A)	-4152.276043	0.012653	-4152.011344	-4152.310443	-4152.441793	-4152.520256	
 ¹tsp1p4(C_i, ¹A)	-4152.263520	0.011848	-4151.999418	-4152.297417	-4152.428666	-4152.507100	
 ¹tsp2p3(C_s, ¹A')	-4152.273815	0.012618	-4152.009126	-4152.308782	-4152.440045	-4152.518430	
 ¹tsp2p4(C_s, ¹A')^d	-4152.238826	0.012493	-4151.997527	-4152.297755	-4152.429084	-4152.507495	
¹tsp1p2 + H₂	-4153.438334	0.022698	-4153.174790	-4153.482780	-4153.615589	-4153.694730	-57
¹tsp1p4 + H₂	-4153.425811	0.021893	-4153.162864	-4153.469754	-4153.602462	-4153.681574	-25
¹tsp2p3 + H₂	-4153.436106	0.022663	-4153.172572	-4153.481119	-4153.613841	-4153.692904	-52

¹tsp2p4 + H₂	-4153.401117	0.022538	-4153.160973	-4153.470092	-4153.602880	-4153.681969	-24
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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 geometries optimized by MP2/cc-pVTZ.