图示

描述已自动生成

**Figure S1.** Potential energy surface for the reaction of the atomic germanium with germane. Germanium and hydrogen atoms are color coded in green and white, respectively.

图表, 直方图

描述已自动生成

**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 (GeH4; X1A1). Panel a depicts raw TOF spectra, panels b and c the scaled TOF spectra, respectively.

图表, 散点图

描述已自动生成

**Figure S3.** Reaction path of **i5** to **p3**.

**Table S1.** Peak velocities (vp) and speed ratios (S) of the germanium (Ge), and germane (GeH4) beams along with the corresponding collision energy (EC) and center-of-mass angle ().

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Beam | vp (m s-1) | S | Ec (kJ mol-1) | (deg) |
| Ge | 998 ± 12 | 5.6 ± 0.2 |  |  |
| GeH4 | 529 ± 5 | 9.0 ± 0.7 | 24.3 ± 0.4 | 29.4 ± 0.4 |

**Table S2.** H2 loss products from the reaction of ground state atomic germanium and germane considering the natural isotope abundances of germanium.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  |  | 70GeH4  (20.52%) | 72GeH4  (27.45%) | 73GeH4  (7.76%) | 74GeH4  (36.7%) | 76GeH4  (7.75%) |
| H2 loss | 70Ge  (20.52%) | 70Ge70GeH2  142 | 70Ge72GeH2  144 | 70Ge73GeH2  145 | 70Ge74GeH2  146 | 70Ge76GeH2  148 |
|  | 72Ge  (27.45%) | 72Ge70GeH2  144 | 72Ge72GeH2  146 | 72Ge73GeH2  147 | 72Ge74GeH2  148 | 72Ge76GeH2  150 |
|  | 73Ge  (7.76%) | 73Ge70GeH2  145 | 73Ge72GeH2  147 | 73Ge73GeH2  148 | 73Ge74GeH2  149 | 73Ge76GeH2  151 |
|  | 74Ge  (36.7%) | 74Ge70GeH2  146 | 74Ge72GeH2  148 | 74Ge73GeH2  149 | 74Ge74GeH2  150 | 74Ge76GeH2  152 |
|  | 76Ge  (7.75%) | 76Ge70GeH2  148 | 76Ge72GeH2  150 | 76Ge73GeH2  151 | 76Ge74GeH2  152 | 76Ge76GeH2  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** |
| *k1*  (i1i2) | 2.75×1012 | 2.78×1012 | 2.80×1012 | 2.85×1012 | 2.87×1012 | 2.90×1012 | 2.94×1012 |
| *k-1*  (i2i1) | 9.82×1012 | 9.85×1012 | 9.88×1012 | 9.94×1012 | 9.96×1012 | 9.99×1012 | 1.00×1013 |
| *k2*  (i1trans-i4) | 5.53×109 | 7.43×109 | 9.75×109 | 1.58×1010 | 1.91×1010 | 2.41×1010 | 3.48×1010 |
| *k-2*  (trans-i4i1) | 6.34×1011 | 8.05×1011 | 1.00×1012 | 1.47×1012 | 1.70×1012 | 2.04×1012 | 2.72×1012 |
| *k3*  (i2i3) | 3.50×1012 | 3.66×1012 | 3.83×1012 | 4.15×1012 | 4.29×1012 | 4.47×1012 | 4.79×1012 |
| *k-3*  (i3i2) | 2.83×1012 | 3.03×1012 | 3.23×1012 | 3.66×1012 | 3.84×1012 | 4.09×1012 | 4.53×1012 |
| *k4*  (i2i5) | 1.50×1010 | 1.93×1010 | 2.44×1010 | 3.72×1010 | 4.38×1010 | 5.37×1010 | 7.44×1010 |
| *k-4*  (i5i2) | 5.91×1011 | 6.34×1011 | 6.75×1011 | 7.55×1011 | 7.88×1011 | 8.30×1011 | 9.02×1011 |
| *k5*  (i2cis-i4) | 4.15×109 | 5.68×109 | 7.58×109 | 1.27×1010 | 1.54×1010 | 1.97×1010 | 2.90×1010 |
| *k-5*  (cis-i4i2) | 2.37×1011 | 3.05×1011 | 3.82×1011 | 5.68×1011 | 6.61×1011 | 7.97×1011 | 1.07×1012 |
| *k6*  (i2trans-i4) | 1.04×109 | 1.56×109 | 2.25×109 | 4.26×109 | 5.44×109 | 7.33×109 | 1.17×1010 |
| *k-6*  (trans-i4i2) | 3.33×1010 | 4.76×1010 | 6.55×1010 | 1.14×1011 | 1.40×1011 | 1.80×1011 | 2.67×1011 |
| *k7*  (i2i6) | 9.74×107 | 1.92×108 | 3.42×108 | 8.89×108 | 1.26×109 | 1.93×109 | 3.68×109 |
| *k-7*  (i6i2) | 2.95×1012 | 3.03×1012 | 3.08×1012 | 3.15×1012 | 3.18×1012 | 3.22×1012 | 3.27×1012 |
| *k8*  (trans-i4cis-i4) | 1.05×1012 | 1.18×1012 | 1.31×1012 | 1.60×1012 | 1.73×1012 | 1.90×1012 | 2.21×1012 |
| *k-8*  (cis-i4trans-i4) | 1.88×1012 | 2.07×1012 | 2.28×1012 | 2.69×1012 | 2.88×1012 | 3.12×1012 | 3.56×1012 |
| *k9*  (i2p1) | 1.49×108 | 2.84×108 | 4.96×108 | 1.26×109 | 1.77×109 | 2.68×109 | 5.05×109 |
| *k10*  (trans-i4p1) | 2.13×109 | 3.55×109 | 5.56×109 | 1.18×1010 | 1.56×1010 | 2.19×1010 | 3.67×1010 |
| *k11*  (cis-i4p1) | 2.28×109 | 4.07×109 | 6.68×109 | 1.52×1010 | 2.05×1010 | 2.94×1010 | 5.09×1010 |
| *k12*  (i5p2) | 3.32×1014 | 3.95×1014 | 4.60×1014 | 5.97×1014 | 6.58×1014 | 7.39×1014 | 8.85×1014 |
| *k13*  (i6p2) | 1.82×1012 | 2.28×1012 | 2.69×1012 | 3.41×1012 | 3.68×1012 | 4.00×1012 | 4.49×1012 |
| *k14*  (i5p3) | 1.69×1013 | 1.72×1013 | 1.75×1013 | 1.81×1013 | 1.83×1013 | 1.85×1013 | 1.90×1013 |

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

 

**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 + H2 | 1.67 | 2.40 | 3.23 | 5.13 | 6.02 | 7.26 | 9.45 |
| p2 + H2 | 93.58 | 93.55 | 93.25 | 92.11 | 91.47 | 90.52 | 88.70 |
| p3 + H2 | 4.75 | 4.06 | 3.52 | 2.76 | 2.50 | 2.22 | 1.85 |

**(b)**

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
|  | **0** | **5** | **10** | **20** | **24.3** | **30** | **40** |
| p1 + H2 (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 + H2 | 93.58 | 93.55 | 93.25 | 92.11 | 91.47 | 90.52 | 88.70 |
| p3 + H2 | 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**  **(-45 kJ/mol)** | **24.3**  **(-60 kJ/mol)** |
| *k15*  (p1p2) | 8.90×1011 | 1.67×1012 |
| *k-15*  (p2p1) | 7.64×1011 | 1.03×1012 |
| *k17*  (p2p3) | 7.43×1011 | 1.44×1012 |
| *k-17*  (p3p2) | 4.27×1012 | 7.03×1012 |

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

 

**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**  **(-45 kJ/mol)** | **24.3**  **(-60 kJ/mol)** |
| p1'' + H2 | 1.67 | 6.02 |
| p2'' + H2 | 0.24 | 1.43 |
| p3'' + H2 | 4.75 | 2.50 |
| p1' + H2 | 39.42 | 30.49 |
| p2' + H2 | 45.92 | 49.43 |
| p3' + H2 | 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)

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | **3c1** | | | | **3i1** | | | |
| Normal modes | Frequency(cm-1) | | IR Inten | | Frequency(cm-1) | | IR Inten | |
| ν1 | 73.52 | | 0.1999 | | 99.63 | | 0.0108 | |
| ν2 | 103.53 | | 0.1027 | | 262.9 | | 2.6471 | |
| ν3 | 331.33 | | 35.4758 | | 413.7 | | 14.7667 | |
| ν4 | 800.54 | | 49.325 | | 495.72 | | 6.4466 | |
| ν5 | 818.14 | | 358.1966 | | 592.49 | | 13.818 | |
| ν6 | 884.47 | | 83.0634 | | 825.8 | | 299.8227 | |
| ν7 | 915.39 | | 22.5705 | | 904.28 | | 38.933 | |
| ν8 | 994.83 | | 56.8726 | | 909.18 | | 41.111 | |
| ν9 | 1961.43 | | 454.909 | | 2143.92 | | 111.1527 | |
| ν10 | 2245.01 | | 78.4748 | | 2205.26 | | 87.2642 | |
| ν11 | 2267.49 | | 47.5629 | | 2210.85 | | 96.4515 | |
| ν12 | 2276.17 | | 69.7227 | | 2233.91 | | 93.5736 | |
|  | **3i3** | | | | **3i4** | | | |
| Normal modes | Frequency(cm-1) | | IR Inten | | Frequency(cm-1) | | IR Inten | |
| ν1 | 191.07 | | 0.815 | | 219.17 | | 0.0558 | |
| ν2 | 270.83 | | 0.0064 | | 248.31 | | 0.0309 | |
| ν3 | 399.51 | | 13.7831 | | 405.05 | | 37.4538 | |
| ν4 | 440.83 | | 10.3483 | | 451.5 | | 1.4269 | |
| ν5 | 550.11 | | 40.8457 | | 469.17 | | 34.1758 | |
| ν6 | 576.01 | | 1.097 | | 704.51 | | 7.4243 | |
| ν7 | 850.21 | | 252.5386 | | 814.11 | | 84.6193 | |
| ν8 | 895.92 | | 20.1182 | | 1078.21 | | 70.557 | |
| ν9 | 2152.59 | | 170.8286 | | 1297.42 | | 166.0677 | |
| ν10 | 2157.67 | | 64.6261 | | 1517.52 | | 2.4977 | |
| ν11 | 2190.05 | | 29.9092 | | 1981.93 | | 151.6532 | |
| ν12 | 2193.87 | | 201.1334 | | 2044.15 | | 139.723 | |
|  | **MSX** | | | | **i1** | | | |
| Normal modes | Frequency(cm-1) | | IR Inten | | Frequency(cm-1) | | IR Inten | |
| ν1 | -492.58 | | 0.28 | | 96.27 | | 3.5275 | |
| ν2 | 250.23 | | 1.47 | | 242.52 | | 3.4276 | |
| ν3 | 321.92 | | 22.64 | | 353.72 | | 23.6363 | |
| ν4 | 339.08 | | 13.47 | | 387.16 | | 15.1643 | |
| ν5 | 552.88 | | 16.75 | | 663.17 | | 40.1148 | |
| ν6 | 862.89 | | 356.98 | | 815.19 | | 259.0599 | |
| ν7 | 934.25 | | 51.81 | | 904.01 | | 36.8478 | |
| ν8 | 952.37 | | 53.37 | | 916.27 | | 30.9037 | |
| ν9 | 2203.39 | | 132.78 | | 1991.57 | | 240.1421 | |
| ν10 | 2210.08 | | 154.15 | | 2175.87 | | 98.4278 | |
| ν11 | 2215.82 | | 139.67 | | 2186.05 | | 120.3072 | |
| ν12 | 2231.68 | | 147.78 | | 2202.4 | | 140.7084 | |
|  | **i2** | | | | **i3** | | | |
| Normal modes | Frequency(cm-1) | | IR Inten | | Frequency(cm-1) | | IR Inten | |
| ν1 | 285.36 | | 4.7443 | | 289.97 | | 0 | |
| ν2 | 352.24 | | 30.9175 | | 324.95 | | 14.9891 | |
| ν3 | 363.38 | | 6.1705 | | 413.07 | | 30.733 | |
| ν4 | 610.94 | | 6.2929 | | 455.63 | | 0 | |
| ν5 | 654.28 | | 19.4481 | | 503.7 | | 0.0912 | |
| ν6 | 823.51 | | 77.0408 | | 559.37 | | 0 | |
| ν7 | 902.4 | | 64.822 | | 882.87 | | 188.1866 | |
| ν8 | 929.03 | | 315.7046 | | 901.83 | | 0 | |
| ν9 | 1611.38 | | 137.2761 | | 2202.66 | | 160.5899 | |
| ν10 | 1998.34 | | 222.4699 | | 2203.71 | | 0 | |
| ν11 | 2189.46 | | 166.9608 | | 2216.24 | | 0 | |
| ν12 | 2206.24 | | 133.8602 | | 2227.12 | | 199.4993 | |
|  | **trans-i4** | | | | **cis-i4** | | | |
| Normal modes | Frequency(cm-1) | | IR Inten | | Frequency(cm-1) | | IR Inten | |
| ν1 | 237.8 | | 0 | | 236.37 | | 0.3059 | |
| ν2 | 270.3 | | 1.2465 | | 351.61 | | 0.2694 | |
| ν3 | 659.05 | | 16.2848 | | 598.82 | | 0 | |
| ν4 | 772.13 | | 0 | | 691.11 | | 71.1302 | |
| ν5 | 805.58 | | 0 | | 817.89 | | 19.3112 | |
| ν6 | 818.22 | | 161.7812 | | 851.45 | | 28.1181 | |
| ν7 | 1255.56 | | 56.7769 | | 1236.53 | | 59.4887 | |
| ν8 | 1349.07 | | 0 | | 1282.68 | | 0 | |
| ν9 | 1412.17 | | 1299.149 | | 1361.76 | | 1585.864 | |
| ν10 | 1563.44 | | 0 | | 1556.58 | | 0.0558 | |
| ν11 | 2001.63 | | 0 | | 2018.05 | | 17.8684 | |
| ν12 | 2019.35 | | 493.0976 | | 2042.51 | | 438.9959 | |
|  | **i5** | | | | **i6** | | | |
| Normal modes | Frequency(cm-1) | | IR Inten | | Frequency(cm-1) | | IR Inten | |
| ν1 | 233.71 | | 0.1342 | | 167.35 | | 14.3984 | |
| ν2 | 295.63 | | 7.9248 | | 247.16 | | 8.7533 | |
| ν3 | 324.75 | | 5.4208 | | 300.85 | | 3.861 | |
| ν4 | 373.07 | | 25.7082 | | 403.09 | | 11.4703 | |
| ν5 | 377.1 | | 1.4687 | | 544.92 | | 7.0916 | |
| ν6 | 430.32 | | 2.3658 | | 661.98 | | 23.947 | |
| ν7 | 482.54 | | 1.4052 | | 674.17 | | 9.5209 | |
| ν8 | 877.88 | | 80.7523 | | 837.75 | | 37.3408 | |
| ν9 | 930.89 | | 1.4716 | | 1397.69 | | 20.0555 | |
| ν10 | 2190.85 | | 95.5956 | | 2033.55 | | 233.051 | |
| ν11 | 2210.98 | | 97.4174 | | 2145.52 | | 149.5774 | |
| ν12 | 3889.18 | | 39.1952 | | 3230.78 | | 302.3669 | |
|  | **3tsc1i1** | | | | **3tsi1i3** | | | |
| Normal modes | Frequency(cm-1) | | IR Inten | | Frequency(cm-1) | | IR Inten | |
| ν1 | -783.74 | | 21.6824 | | -591.46 | | 10.8647 | |
| ν2 | 168.43 | | 3.8734 | | 214.55 | | 12.0379 | |
| ν3 | 228.68 | | 0.1114 | | 251.28 | | 2.1541 | |
| ν4 | 453.37 | | 6.484 | | 394.03 | | 6.5059 | |
| ν5 | 472.67 | | 1.3242 | | 536.79 | | 51.4452 | |
| ν6 | 800.18 | | 262.7868 | | 579.59 | | 4.249 | |
| ν7 | 885.89 | | 43.9435 | | 810.62 | | 6.0524 | |
| ν8 | 888.1 | | 47.8031 | | 846.29 | | 91.4153 | |
| ν9 | 1764.29 | | 272.1746 | | 1630.97 | | 231.8283 | |
| ν10 | 2196.85 | | 59.437 | | 2060.22 | | 80.8718 | |
| ν11 | 2240.58 | | 63.4147 | | 2061.35 | | 165.2793 | |
| ν12 | 2251.01 | | 73.6654 | | 2191.1 | | 103.3873 | |
|  | **3tsi1p3** | | | | **3tsi1transp4** | | | |
| Normal modes | Frequency(cm-1) | | IR Inten | | Frequency(cm-1) | | IR Inten | |
| ν1 | -1402.45 | | 728.1866 | | -1350.71 | | 568.9818 | |
| ν2 | 193 | | 0.1618 | | 243.09 | | 0.0248 | |
| ν3 | 334.6 | | 5.4625 | | 270.08 | | 0.2478 | |
| ν4 | 341.26 | | 2.7841 | | 343.85 | | 3.6209 | |
| ν5 | 443.73 | | 3.3069 | | 467.66 | | 4.1087 | |
| ν6 | 794.29 | | 54.6558 | | 605.89 | | 4.46 | |
| ν7 | 810.53 | | 0.9149 | | 752.81 | | 21.2995 | |
| ν8 | 926.6 | | 58.603 | | 916.15 | | 118.7214 | |
| ν9 | 1306.22 | | 34.8205 | | 1607.99 | | 183.005 | |
| ν10 | 1753.57 | | 123.6864 | | 2025.91 | | 12.1893 | |
| ν11 | 2187.42 | | 88.0742 | | 2113.97 | | 127.1861 | |
| ν12 | 2205.08 | | 100.8506 | | 2183.6 | | 93.6441 | |
|  | **3tsi3p3** | | | | **3tsi3transp4** | | | |
| Normal modes | Frequency(cm-1) | | IR Inten | | Frequency(cm-1) | | IR Inten | |
| ν1 | -1282.24 | | 373.7738 | | -1309.37 | | 861.0131 | |
| ν2 | 76.71 | | 0.1009 | | 205.72 | | 0.1069 | |
| ν3 | 220.96 | | 0.8026 | | 312.86 | | 2.8708 | |
| ν4 | 326.25 | | 3.5441 | | 395.03 | | 3.5772 | |
| ν5 | 444.64 | | 3.9998 | | 625.97 | | 1.3988 | |
| ν6 | 558.18 | | 26.465 | | 722.28 | | 40.8683 | |
| ν7 | 741.35 | | 34.0465 | | 834.21 | | 25.2703 | |
| ν8 | 865.15 | | 118.0397 | | 950.48 | | 46.8664 | |
| ν9 | 1577.19 | | 153.8602 | | 1248.54 | | 50.3075 | |
| ν10 | 1848.48 | | 51.0241 | | 1659.08 | | 90.7894 | |
| ν11 | 2100.37 | | 123.0481 | | 2032.19 | | 188.885 | |
| ν12 | 2144.91 | | 148.4104 | | 2108.44 | | 142.077 | |
|  | **tsi1i2** | | | | **tsi1transi4** | | | |
| Normal modes | Frequency(cm-1) | | IR Inten | | Frequency(cm-1) | | IR Inten | |
| ν1 | -282.75 | | 41.9396 | | -743.67 | | 248.6808 | |
| ν2 | 291.68 | | 3.7258 | | 103.31 | | 6.0365 | |
| ν3 | 370.41 | | 8.1432 | | 185.52 | | 2.3624 | |
| ν4 | 540.6 | | 2.1826 | | 436.53 | | 1.4742 | |
| ν5 | 652.2 | | 26.5409 | | 459.77 | | 2.645 | |
| ν6 | 796.88 | | 224.9014 | | 649.99 | | 14.2348 | |
| ν7 | 848.23 | | 28.4651 | | 845.44 | | 55.1872 | |
| ν8 | 903.5 | | 75.6009 | | 867.31 | | 50.6548 | |
| ν9 | 1835.32 | | 104.6023 | | 1981.22 | | 273.1058 | |
| ν10 | 1995.35 | | 227.8083 | | 2165.22 | | 5.2040 | |
| ν11 | 2207.98 | | 142.1898 | | 2178.07 | | 47.7022 | |
| ν12 | 2221.53 | | 123.8547 | | 2237.53 | | 70.4064 | |
|  | **tsi1p3** | | | | **tsi2i3** | | | |
| Normal modes | Frequency(cm-1) | | IR Inten | | Frequency(cm-1) | | IR Inten | |
| ν1 | -332.86 | | 99.8001 | | -593.89 | | 2.2741 | |
| ν2 | 99.5 | | 0.0748 | | 267.98 | | 2.0398 | |
| ν3 | 124.12 | | 0.556 | | 300.8 | | 5.5753 | |
| ν4 | 241.91 | | 24.8821 | | 452.42 | | 10.0942 | |
| ν5 | 254.95 | | 4.2298 | | 614.67 | | 5.2518 | |
| ν6 | 418.6 | | 13.3602 | | 638.62 | | 15.6223 | |
| ν7 | 817.87 | | 316.7675 | | 876.7 | | 76.709 | |
| ν8 | 893.8 | | 62.9431 | | 937.61 | | 198.8877 | |
| ν9 | 912.11 | | 29.8354 | | 1829.74 | | 110.9703 | |
| ν10 | 2002.24 | | 422.8273 | | 2030.53 | | 178.1774 | |
| ν11 | 2178.25 | | 91.8809 | | 2135.07 | | 202.2991 | |
| ν12 | 2187.86 | | 115.6326 | | 2172.29 | | 152.6731 | |
|  | **tsi2transi4** | | | | **tsi2cisi4** | | | |
| Normal modes | Frequency(cm-1) | | IR Inten | | Frequency(cm-1) | | IR Inten | |
| ν1 | -485.72 | | 26.8866 | | -529.52 | | 3.2479 | |
| ν2 | 120.19 | | 5.3185 | | 131 | | 7.8968 | |
| ν3 | 405.17 | | 2.8555 | | 393.2 | | 7.055 | |
| ν4 | 553.57 | | 3.1732 | | 543.4 | | 3.1016 | |
| ν5 | 650.72 | | 4.3127 | | 608.41 | | 47.416 | |
| ν6 | 766.54 | | 84.0021 | | 810.16 | | 42.0856 | |
| ν7 | 898.1 | | 147.9299 | | 893.15 | | 227.5781 | |
| ν8 | 1204.96 | | 91.6571 | | 1373.94 | | 39.9266 | |
| ν9 | 1860.65 | | 604.2944 | | 1661.66 | | 337.253 | |
| ν10 | 1965.03 | | 193.0096 | | 1908.11 | | 111.1043 | |
| ν11 | 2006.04 | | 217.4132 | | 1947.31 | | 304.7144 | |
| ν12 | 2085.65 | | 173.1008 | | 2017.72 | | 269.3057 | |
|  | **tsi2i5** | | | | **tsi2i6** | | | |
| Normal modes | Frequency(cm-1) | | IR Inten | | Frequency(cm-1) | | IR Inten | |
| ν1 | -1295.71 | | 316.5997 | | -648.25 | | 249.4191 | |
| ν2 | 300.61 | | 3.0475 | | 204.73 | | 8.3539 | |
| ν3 | 350.38 | | 14.0077 | | 330.15 | | 6.9163 | |
| ν4 | 464.86 | | 10.6951 | | 454.28 | | 15.0668 | |
| ν5 | 487.99 | | 12.3724 | | 480.54 | | 10.3735 | |
| ν6 | 687.97 | | 77.5117 | | 718.81 | | 45.9166 | |
| ν7 | 845.86 | | 6.3845 | | 853.68 | | 87.4717 | |
| ν8 | 929.41 | | 181.9666 | | 938.68 | | 67.5466 | |
| ν9 | 1619.6 | | 103.6871 | | 1767.15 | | 96.6983 | |
| ν10 | 1759.24 | | 112.2305 | | 2000.95 | | 212.2138 | |
| ν11 | 2171.28 | | 130.676 | | 2034.92 | | 305.234 | |
| ν12 | 2186.96 | | 125.7352 | | 2175.35 | | 146.7102 | |
|  | **tsi2p1** | | | | **tstransi4cisi4** | | | |
| Normal modes | Frequency(cm-1) | | IR Inten | | Frequency(cm-1) | | IR Inten | |
| ν1 | -1149.82 | | 461.79 | | -597.53 | | 15.7664 | |
| ν2 | 208.61 | | 5.895 | | 196.78 | | 10.7285 | |
| ν3 | 332.62 | | 9.6234 | | 582.23 | | 12.9839 | |
| ν4 | 425.24 | | 10.6445 | | 605.28 | | 130.1714 | |
| ν5 | 447.66 | | 10.3086 | | 689.3 | | 13.7511 | |
| ν6 | 709.88 | | 44.4548 | | 902.67 | | 60.7683 | |
| ν7 | 822.68 | | 59.319 | | 944.59 | | 31.5823 | |
| ν8 | 950.25 | | 60.5075 | | 1256.59 | | 366.6139 | |
| ν9 | 1728.24 | | 169.2998 | | 1430.75 | | 73.1433 | |
| ν10 | 1874.94 | | 101.5367 | | 1918.91 | | 110.2969 | |
| ν11 | 1985.17 | | 244.2972 | | 1978.41 | | 152.3871 | |
| ν12 | 2119.07 | | 168.894 | | 2005.15 | | 302.5566 | |
|  | **tstransi4p1** | | | | **tscisi4p1** | | | |
| Normal modes | Frequency(cm-1) | | IR Inten | | Frequency(cm-1) | | IR Inten | |
| ν1 | -1227.94 | | 276.3292 | | -1177.18 | | 439.6241 | |
| ν2 | 236 | | 0.4985 | | 225.91 | | 0.7889 | |
| ν3 | 512.35 | | 32.7636 | | 549.88 | | 7.8377 | |
| ν4 | 622.29 | | 8.6592 | | 581.46 | | 8.763 | |
| ν5 | 731.68 | | 6.0416 | | 674.19 | | 27.9223 | |
| ν6 | 811.64 | | 39.7917 | | 801.04 | | 52.7951 | |
| ν7 | 957.54 | | 20.7523 | | 875.34 | | 224.6189 | |
| ν8 | 1118.61 | | 364.9517 | | 1014.04 | | 248.0471 | |
| ν9 | 1489.99 | | 67.6018 | | 1500.14 | | 125.0714 | |
| ν10 | 1741.29 | | 89.0703 | | 1718.17 | | 55.3443 | |
| ν11 | 1769.91 | | 154.6512 | | 1774.3 | | 253.5251 | |
| ν12 | 1990.2 | | 246.67 | | 1966.37 | | 240.7512 | |
|  | **tsi5p2** | | | | **tsi6p2** | | | |
| Normal modes | Frequency(cm-1) | | IR Inten | | Frequency(cm-1) | | IR Inten | |
| ν1 | -337.43 | | 14.959 | | -140.52 | | 24.7763 | |
| ν2 | 23.11 | | 0.0085 | | 268.79 | | 6.3634 | |
| ν3 | 103.99 | | 0.3486 | | 286.9 | | 5.5014 | |
| ν4 | 176.84 | | 1.8311 | | 340.92 | | 6.1503 | |
| ν5 | 201.42 | | 14.5326 | | 483.16 | | 0.3233 | |
| ν6 | 222.29 | | 11.6192 | | 538.03 | | 19.2947 | |
| ν7 | 355.09 | | 6.828 | | 573.78 | | 16.4562 | |
| ν8 | 361.11 | | 0.2708 | | 789.95 | | 8.8646 | |
| ν9 | 784.34 | | 54.0167 | | 1176.9 | | 7.1961 | |
| ν10 | 1935.72 | | 61.1949 | | 2021.38 | | 188.0934 | |
| ν11 | 2219 | | 87.8877 | | 2216.87 | | 113.557 | |
| ν12 | 4365.99 | | 4.8505 | | 3651.6 | | 179.602 | |
|  | **3p1** | | | | **3p2** | | | |
| Normal modes | Frequency(cm-1) | | IR Inten | | Frequency(cm-1) | | IR Inten | |
| ν1 | 125.41 | | 4.1997 | | 213.4 | | 0.7333 | |
| ν2 | 191.81 | | 46.8226 | | 389.02 | | 2.7673 | |
| ν3 | 434.8 | | 0.2118 | | 669.21 | | 39.0096 | |
| ν4 | 831.51 | | 0.0021 | | 1028.27 | | 340.3396 | |
| ν5 | 1323.18 | | 62.7616 | | 1383.41 | | 115.704 | |
| ν6 | 1573.34 | | 0.0161 | | 1985.36 | | 258.0191 | |
|  | **3p3** | | | | **trans-3p4** | | | |
| Normal modes | Frequency(cm-1) | | IR Inten | | Frequency(cm-1) | | IR Inten | |
| ν1 | 272.86 | | 1.6763 | | 263.52 | | 0 | |
| ν2 | 279.59 | | 5.6856 | | 331.55 | | 6.9855 | |
| ν3 | 365.89 | | 7.2002 | | 426.19 | | 10.115 | |
| ν4 | 903.43 | | 100.1509 | | 663.39 | | 0 | |
| ν5 | 2150.26 | | 134.1411 | | 2031.06 | | 0 | |
| ν6 | 2161.55 | | 136.2414 | | 2037.46 | | 423.4986 | |
|  | **cis-3p4** | | | | **p1** | | | |
| Normal modes | Frequency(cm-1) | | IR Inten | | Frequency(cm-1) | | IR Inten | |
| ν1 | 249.38 | | 5.1925 | | 306.59 | | 0.3879 | |
| ν2 | 324.38 | | 2.1312 | | 846.2 | | 37.7283 | |
| ν3 | 387.04 | | 4.2089 | | 1020.51 | | 0 | |
| ν4 | 584.03 | | 22.0511 | | 1110.65 | | 458.1158 | |
| ν5 | 1949.39 | | 205.1258 | | 1486.36 | | 35.8855 | |
| ν6 | 2048.53 | | 194.5562 | | 1561.91 | | 10.0911 | |
|  | **p2** | | | | **p3** | | | |
| Normal modes | Frequency(cm-1) | | IR Inten | | Frequency(cm-1) | | IR Inten | |
| ν1 | 146.13 | | 41.8162 | | 251.73 | | 21.284 | |
| ν2 | 336.3 | | 6.7852 | | 322.04 | | 4.645 | |
| ν3 | 472.67 | | 4.5376 | | 326.43 | | 5.3091 | |
| ν4 | 1019.09 | | 139.6876 | | 850.76 | | 64.0203 | |
| ν5 | 1593.93 | | 84.0702 | | 2188.89 | | 70.3001 | |
| ν6 | 2161.98 | | 119.8511 | | 2210.9 | | 82.8437 | |
|  | **p4** | | | | **1GeH2** | | | |
| Normal modes | Frequency(cm-1) | | IR Inten | | Frequency(cm-1) | | IR Inten | |
| ν1 | 233.41 | | 35.8088 | | 954.73 | | 72.999 | |
| ν2 | 260.48 | | 45.3567 | | 1998.59 | | 277.8718 | |
| ν3 | 341.39 | | 0 | | 2008.99 | | 344.5842 | |
| ν4 | 584.98 | | 0 | |  | |  | |
| ν5 | 2144.91 | | 0 | |  | |  | |
| ν6 | 2154.82 | | 174.8482 | |  | |  | |
|  | | **1tsp1p2** | | | | **1tsp1p4** | | | |
| Normal modes | | Frequency(cm-1) | | IR Inten | | Frequency(cm-1) | | IR Inten | |
| ν1 | | -254.57 | | 52.2092 | | -262.26 | | 0.2532 | |
| ν2 | | 310 | | 0.5686 | | 148.33 | | 53.8314 | |
| ν3 | | 728.66 | | 32.4165 | | 345.71 | | 0.0001 | |
| ν4 | | 972.58 | | 138.7537 | | 548.06 | | 1.8569 | |
| ν5 | | 1489.82 | | 91.6642 | | 2076.17 | | 29.4407 | |
| ν6 | | 2053 | | 124.4454 | | 2082.17 | | 212.5136 | |
|  | | **1tsp2p3** | | | | **1tsp2p4** | | | |
| Normal modes | | Frequency(cm-1) | | IR Inten | | Frequency(cm-1) | | IR Inten | |
| ν1 | | -331 | | 6.6966 | | -404.41 | | 17.4665 | |
| ν2 | | 207.3 | | 20.0179 | | 348.63 | | 0.0047 | |
| ν3 | | 353.33 | | 6.8136 | | 351.2 | | 17.7096 | |
| ν4 | | 781.8 | | 49.4719 | | 598.11 | | 16.7517 | |
| ν5 | | 1970.3 | | 55.3648 | | 2021.7 | | 84.4179 | |
| ν6 | | 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 + Ezpc a | Ezpc b | CCSD(T)/ cc-pVDZ | CCSD(T)/ cc-pVTZ | CCSD(T)/ cc-pVQZ | CCSD(T)/ CBS | Ec  (kJ/mol) |
|  | **Ge(3P)** | -2075.493248 | 0.000000 | -2075.364439 | -2075.499140 | -2075.560244 | -2075.596899 |  |
|  | **GeH4(Td, 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(Cs, 3A'')** | -4153.437119 | 0.031147 | -4153.178924 | -4153.484204 | -4153.615062 | -4153.692977 | -30 |
|  | **3i1(Cs, 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(Cs, 3A'')** | -4153.412118 | 0.027304 | -4153.149686 | -4153.458879 | -4153.591187 | -4153.669946 | 20 |
|  | **i1-MSXd** |  | 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(C2h, 1Ag)** | -4153.484295 | 0.030029 | -4153.223979 | -4153.535794 | -4153.670424 | -4153.750663 | -185 |
|  | **trans-i4(C2h, 1Ag)** | -4153.464707 | 0.029991 | -4153.205260 | -4153.514484 | -4153.647280 | -4153.726369 | -121 |
|  | **cis-i4 (C2v, 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 |
| 图示  描述已自动生成 | **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(1Σg+, 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(C2v, 3A2)** | -4152.266611 | 0.013973 | -4152.001992 | -4152.297912 | -4152.428304 | -4152.506230 |  |
|  | **trans-3p4 (C2h, 3Au)** | -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(C2v, 1A1)** | -4152.294212 | 0.014426 | -4152.030373 | -4152.330677 | -4152.461839 | -4152.540134 |  |
|  | **p2(Cs, 1A')** | -4152.279228 | 0.013054 | -4152.015621 | -4152.316326 | -4152.447427 | -4152.525666 |  |
|  | **p3(C2v, 1A1)** | -4152.278622 | 0.014012 | -4152.014786 | -4152.313319 | -4152.444725 | -4152.523246 |  |
|  | **p4(C2h, 1Ag)** | -4152.265416 | 0.013031 | -4152.004680 | -4152.304071 | -4152.435299 | -4152.513669 |  |
| 图片包含 游戏机, 钟表, 画  描述已自动生成 | **GeH2(C2v, 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 CPMCSCF(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 + Ezpc a | Ezpc b | CCSD(T)/ cc-pVDZ | CCSD(T)/ cc-pVTZ | CCSD(T)/ cc-pVQZ | CCSD(T)/ CBS | Ec  (kJ/mol) |
|  | **Ge(3P)** | -2075.493248 | 0.000000 | -2075.364439 | -2075.499140 | -2075.560244 | -2075.596899 |  |
|  | **GeH4(Td, 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 |
| 图示  描述已自动生成 | **1tsp1p2(C1, 1A)** | -4152.276043 | 0.012653 | -4152.011344 | -4152.310443 | -4152.441793 | -4152.520256 |  |
|  | **1tsp1p4(C1, 1A)** | -4152.263520 | 0.011848 | -4151.999418 | -4152.297417 | -4152.428666 | -4152.507100 |  |
|  | **1tsp2p3(Cs, 1A')** | -4152.273815 | 0.012618 | -4152.009126 | -4152.308782 | -4152.440045 | -4152.518430 |  |
|  | **1tsp2p4(Cs, 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 |

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.