Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic supplementary information: Generation and structural characterization of Ge carbides GeC_n ($n = 4, 5, 6$) by laser ablation, broadband rotational spectroscopy, and quantum chemistry†

K. L. K. Lee,*,† S. Thorwirth,‡ M.-A. Martin-Drumel,¶ and M. C. McCarthy†

†*Harvard-Smithsonian Center for Astrophysics, 60 Garden Street, Cambridge, Massachusetts 02138, United States*

‡*I. Physikalisches Institut, Universität zu Köln, Zülpicher Straße 77, 50937 Köln, Germany*

¶*Institut des Sciences Moléculaires d'Orsay, CNRS, Univ paris Sud, Université Paris-Saclay, Orsay, France*

E-mail: kinlee@cfa.harvard.edu

Table S1: Measured Fourier-transform microwave cavity frequencies for the singlet species GeC_4 ($X\ ^1\Sigma$). Frequencies are given in MHz, and the difference between observed frequencies and those calculated with a linear molecule Hamiltonian ($o-c$) are given in kHz. Frequencies have a nominal 2 kHz uncertainty.

J'	J''	Frequency	Obs - Calc.
		$^{70}GeC_4$	
3	2	6218.4278	−0.7
4	3	8291.2352	0.5
5	4	10364.0375	−0.3
6	5	12436.8373	0.0
7	6	14509.6333	0.8
8	7	16582.4223	0.2
9	8	18655.2065	−0.1
		$^{72}GeC_4$	
3	2	6162.2583	0.7
4	3	8216.3395	0.3
5	4	10270.4195	0.3
6	5	12324.4944	0.3
7	6	14378.5653	−0.4
8	7	16432.6315	0.0
9	8	18486.6913	0.1
		$^{74}GeC_4$	
3	2	6108.8505	0.1
4	3	8145.1298	0.6
5	4	10181.4075	0.0
6	5	12217.6816	0.4
7	6	14253.9503	0.0
8	7	16290.2148	0.3
9	8	18326.4726	−0.2
		$^{76}GeC_4$	
4	3	8077.3476	0.2
5	4	10096.6792	0.3
6	5	12116.0062	−0.7
7	6	14135.3308	0.0
8	7	16154.6498	0.1

Table S2: Measured Fourier-transform microwave cavity frequencies for the singlet species GeC_6 ($X\ ^1\Sigma$). Frequencies are given in MHz, and the difference between observed frequencies and those calculated with a linear molecule Hamiltonian ($o-c$) are given in kHz. Frequencies have a nominal 2 kHz uncertainty.

J'	J''	Frequency	Obs - Calc.
		$^{70}GeC_6$	
10	9	8258.1270	0.7
11	10	9083.9352	−1
12	11	9909.7456	0.1
13	12	10735.5541	0.1
14	13	11561.3613	−0.1
15	14	12387.1682	0.1
		$^{72}GeC_6$	
9	8	7356.7530	7
10	9	8174.1673	4
11	10	8991.5818	−8
12	11	9808.9960	−3
13	12	10626.4071	15
14	13	11443.7570	−6
		$^{74}GeC_6$	
9	8	7284.6732	4
10	9	8094.0792	−0.6
11	10	8903.4854	−3
12	11	9712.8895	−5
13	12	10522.2945	0.3
14	13	11331.6956	9
15	14	12141.0626	−5
		$^{76}GeC_6$	
9	8	7215.8472	−0.1
10	9	8017.6043	−2
11	10	8819.3650	0.7
12	11	9621.1239	2
13	12	10422.8783	0
14	13	11224.6324	−2
15	14	12026.3895	0.4

Table S3: Measured Fourier-transform microwave cavity frequencies for the triplet species GeC_5 ($X\ ^3\Sigma$). Since the spin-spin interaction term is undetermined in our analysis, the quantum numbers presented below are those of a singlet linear molecule Hamiltonian (See Discussion). Frequencies are given in MHz, and the difference between observed frequencies and those calculated with a linear molecule Hamiltonian ($o - c$) are given in kHz.

J'	J''	Frequency	Obs - Calc.
		$^{70}GeC_5$	
5	4	6174.8361	0
6	5	7409.8005	−0.5
7	6	8644.7656	0.7
8	7	9879.7259	−1
9	8	11114.6894	1
11	10	13584.6027	−1
12	11	14819.5603	1
13	12	16054.5107	−0.5
		$^{72}GeC_5$	
5	4	6114.7508	2
6	5	7337.6962	−0.6
7	6	8560.6432	−0.2
8	7	9783.5876	−1
9	8	11006.5338	1
10	9	12229.4745	−0.4
11	10	13452.4150	−0.3
12	11	14675.3542	0.4
		$^{74}GeC_6$	
5	4	6057.5281	1
6	5	7269.0304	0.1
7	6	8480.5338	0.1
8	7	9692.0333	−0.1
9	8	10903.5323	−0.6
11	10	13326.5268	0
12	11	14538.0183	−3
13	12	15749.5143	2
16	15	19383.9715	−0.1
17	16	20595.4548	0.7
18	17	21806.9326	0.4
		$^{76}GeC_6$	
6	5	7203.5661	1
7	6	8404.1562	0
8	7	9604.7490	2
9	8	10805.3352	−0.9
11	10	13206.5087	−2

Table S4: Equilibrium structures of GeC_4 (in Å).. $r_e^{\rm emp}$ refers to semi-experimental bond lengths.

Method	$r_{\rm Ge-C}$	$r_{\rm C-C}$	$r_{\rm C-C}$	$r_{\rm C-C}$
fc-CCSD(T)/cc-pVDZ	1.8076	1.2961	1.3225	1.3078
fc-CCSD(T)/cc-pVTZ	1.7977	1.2775	1.3069	1.2873
ae-CCSD(T)/cc-pwCVTZ	1.7770	1.2735	1.3030	1.2827
ae-CCSD(T)/cc-pwCVQZ	1.7757	1.2712	1.3015	1.2799
r_e^{emp}, fc-CCSD(T)/cc-pVTZ[a]	1.7757	1.2712[b]	1.3015[b]	1.2799[b]
r_e^{emp}, fc-CCSD(T)/cc-pVDZ[c]	1.7742	1.2712[b]	1.3015[b]	1.2799[b]

[a] Zero-point vibrational corrections for structural derivation calculated at the fc-CCSD(T)/cc-pVTZ level.

[b] Kept fixed at ae-CCSD(T)/cc-pwCVQZ value.

[c] Zero-point vibrational corrections for structural derivation calculated at the fc-CCSD(T)/cc-pVDZ level.

Table S5: Equilibrium structures of GeC_5 (in Å).. $r_e^{\rm emp}$ refers to semi-experimental bond lengths.

Method	$r_{\rm Ge-C}$	$r_{\rm C-C}$	$r_{\rm C-C}$	$r_{\rm C-C}$	$r_{\rm C-C}$
fc-UHF-CCSD(T)/cc-pVDZ	1.8432	1.2986	1.3079	1.3092	1.3201
fc-UHF-CCSD(T)/cc-pVTZ	1.8318	1.2818	1.2910	1.2928	1.3007
ae-UHF-CCSD(T)/cc-pwCVTZ	1.8095	1.2783	1.2871	1.2895	1.2959
ae-UHF-CCSD(T)/cc-pwCVQZ	1.8075	1.2765	1.2848	1.2879	1.2932
r_e^{emp}, fc-CCSD(T)/cc-pVDZ[a]	1.8104	1.2765[b]	1.2848[b]	1.2879[b]	1.2932[b]

[a] Zero-point vibrational corrections for structural derivation calculated at the fc-CCSD(T)/cc-pVDZ level.

[b] Kept fixed at ae-CCSD(T)/cc-pwCVQZ value.

Table S6: Equilibrium structures of GeC_6 (in Å).

Method	r_{Ge-C}	r_{C-C}	r_{C-C}	r_{C-C}	r_{C-C}	r_{C-C}
fc-CCSD(T)/cc-pVDZ	1.8145	1.2972	1.3139	1.2863	1.3207	1.3093
fc-CCSD(T)/cc-pVTZ	1.8043	1.2789	1.2985	1.2679	1.3048	1.2892
ae-CCSD(T)/cc-pwCVTZ	1.7832	1.2751	1.2946	1.2645	1.3012	1.2844
ae-CCSD(T)/cc-pwCVQZ	1.7818	1.2728	1.2929	1.2620	1.2997	1.2816
r_e^{emp}, fc-CCSD(T)/cc-pVDZ	1.7820	1.2728[b]	1.2929[b]	1.2620[b]	1.2997[b]	1.2816[b]

[a] Zero-point vibrational corrections for structural derivation calculated at the fc-CCSD(T)/cc-pVDZ level.

[b] Kept fixed at ae-CCSD(T)/cc-pwCVQZ value.

Table S7: Rotational and centrifugal distortion parameters and zero-point vibrational corrections ΔB_0 of GeC_4, GeC_5, and GeC_6 (in Å). In the case of GeC_4, the two determinations of $B_{0,theo}$ are given based on different *ab initio* force fields.

Species	$B^a_{0,meas}$	$B^b_{0,theo}$	$B^c_{e,theo}$	$D_0 \times 10^{-6}$	ΔB^d_0
$^{70}GeC_4$	1036.4053(2)	1036.406	1033.862	30.50(133)	-2.544^e
$^{72}GeC_4$	1027.0435(2)	1027.047	1024.524	31.44(133)	-2.523^e
$^{74}GeC_4$	1018.1423(1)	1018.148	1015.645	30.16(133)	-2.503^e
$^{76}GeC_4$	1009.6690(2)	1009.678	1007.194	29.30(223)	-2.484^e
$^{70}GeC_4$	1036.4053(2)	1035.718	1033.862	30.50(133)	−1.856
$^{72}GeC_4$	1027.0435(2)	1026.365	1024.524	31.44(133)	−1.841
$^{74}GeC_4$	1018.1423(1)	1017.473	1015.645	30.16(133)	−1.828
$^{76}GeC_4$	1009.6690(2)	1009.009	1007.194	29.30(223)	−1.815
$^{70}GeC_5$	619.02366(4)	619.630	619.330	8.332(101)	−0.300
$^{72}GeC_5$	612.98821(4)	613.596	613.298	7.691(135)	−0.298
$^{74}GeC_5$	607.23788(6)	607.850	607.553	7.64(33)	−0.297
$^{76}GeC_5$	600.46651(4)	602.372	602.077	6.65^f	−0.295
$^{70}GeC_6$	412.90688(3)	412.926	412.320	2.83(38)	−0.606
$^{72}GeC_6$	408.70900(1)	408.730	408.129	3.04(33)	−0.601
$^{74}GeC_6$	404.70546(1)	404.727	404.132	6.39(33)	−0.595
$^{76}GeC_6$	400.88084(1)	400.904	400.314	2.68(33)	−0.590

[a] Uncertainties in parentheses are 1σ in the units of the last significant digit. The complete set of spectroscopic constants, derived from the measurements in Tables SXX-YY, is given in Tables S2 and S4.

[b] Calculated as $B_0 = B_e - \Delta B_0$.

[c] Calculated at the ae-CCSD(T)/cc-pwCVQZ level of theory.

[d] Calculated at the fc-CCSD(T)/cc-pVDZ level of theory, unless noted otherwise.

[e] Calculated at the fc-CCSD(T)/cc-pVTZ level of theory.

[f] Remained fixed in the fits.

Outputs from Least-Squares Fits to Frequency Data

GeC_4

Table S8: Truncated fit output for $^{70}GeC_4$

```
                                   EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG. CALC.FREQ. -  DIFF. - WT.
    1:   3  2                        6218.42780    6218.42857   -0.00077    0.00200   0.00081
    2:   4  3                        8291.23520    8291.23468    0.00052    0.00200   0.00095
    3:   5  4                       10364.03750   10364.03786   -0.00036    0.00200   0.00099
    4:   6  5                       12436.83730   12436.83738   -0.00008    0.00200   0.00093
    5:   7  6                       14509.63330   14509.63250    0.00080    0.00200   0.00086
    6:   8  7                       16582.42230   16582.42251   -0.00021    0.00200   0.00104
    7:   9  8                       18655.20650   18655.20666   -0.00016    0.00200   0.00166
NORMALIZED DIAGONAL:
    1   1.00000E+00    2   3.79034E-01
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                          NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1          100          B      1036.405310(158)         0.000000
   2          200          D         -0.03050(133)E-03     -0.00000E-03
 MICROWAVE AVG =       -0.000036 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.000493 MHz, IR RMS =        0.00000
 END OF ITERATION  2 OLD, NEW RMS ERROR=        0.24641         0.24641
```

Table S9: Truncated fit output for $^{72}GeC_4$

```
                                   EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG. CALC.FREQ. -  DIFF. - WT.
    1:   3  2                        6162.25830    6162.25754    0.00076    0.00200   0.00081
    2:   4  3                        8216.33950    8216.33986   -0.00036    0.00200   0.00095
    3:   5  4                       10270.41950   10270.41917    0.00033    0.00200   0.00099
    4:   6  5                       12324.49440   12324.49470   -0.00030    0.00200   0.00093
    5:   7  6                       14378.56530   14378.56571   -0.00041    0.00200   0.00086
    6:   8  7                       16432.63150   16432.63143    0.00007    0.00200   0.00104
    7:   9  8                       18486.69130   18486.69112    0.00018    0.00200   0.00166
NORMALIZED DIAGONAL:
    1   1.00000E+00    2   3.79034E-01
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                          NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1          100          B      1027.043489(158)        -0.000000
   2          200          D         -0.03144(133)E-03      0.00000E-03
 MICROWAVE AVG =        0.000039 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.000399 MHz, IR RMS =        0.00000
 END OF ITERATION  2 OLD, NEW RMS ERROR=        0.19974         0.19974
```

Table S10: Truncated fit output for $^{74}GeC_4$

```
                                  EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG. CALC.FREQ. -  DIFF. - WT.
    1:   3  2                            6108.85050    6108.85034    0.00016    0.00200   0.00081
    2:   4  3                            8145.12980    8145.13041   -0.00061    0.00200   0.00095
    3:   5  4                           10181.40750   10181.40759   -0.00009    0.00200   0.00099
    4:   6  5                           12217.68160   12217.68114    0.00046    0.00200   0.00093
    5:   7  6                           14253.95030   14253.95036   -0.00006    0.00200   0.00086
    6:   8  7                           16290.21480   16290.21450    0.00030    0.00200   0.00104
    7:   9  8                           18326.47260   18326.47286   -0.00026    0.00200   0.00166
NORMALIZED DIAGONAL:
    1   1.00000E+00    2   3.79034E-01
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                          NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1          100          B      1018.142267(158)         0.000000
   2          200          D         -0.03016(133)E-03     -0.00000E-03
 MICROWAVE AVG =       -0.000015 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.000333 MHz, IR RMS =        0.00000
 END OF ITERATION  2 OLD, NEW RMS ERROR=        0.16636         0.16636
```

Table S11: Truncated fit output for $^{76}GeC_4$

```
                                  EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG. CALC.FREQ. -  DIFF. - WT.
    1:   4  3                            8077.34760    8077.34732    0.00028    0.00200   0.00121
    2:   5  4                           10096.67920   10096.67888    0.00032    0.00200   0.00117
    3:   6  5                           12116.00620   12116.00692   -0.00072    0.00200   0.00101
    4:   7  6                           14135.33080   14135.33074    0.00006    0.00200   0.00104
    5:   8  7                           16154.64980   16154.64965    0.00015    0.00200   0.00175
NORMALIZED DIAGONAL:
    1   1.00000E+00    2   3.35360E-01
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                          NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1          100          B      1009.669353(216)        -0.000000
   2          200          D         -0.02930(223)E-03      0.00000E-03
 MICROWAVE AVG =        0.000017 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.000381 MHz, IR RMS =        0.00000
 END OF ITERATION  2 OLD, NEW RMS ERROR=        0.19065         0.19065
```

GeC_5

Table S12: Truncated fit output for $^{70}GeC_5$

```
                                  EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG. CALC.FREQ. -  DIFF. - WT.
    1:   5  4                          6174.83610    6174.83601    0.00009    0.00050   0.00021
    2:   6  5                          7409.80050    7409.80102   -0.00052    0.00050   0.00022
    3:   7  6                          8644.76560    8644.76482    0.00078    0.00050   0.00023
    4:   8  7                          9879.72590    9879.72723   -0.00133    0.00050   0.00022
    5:   9  8                         11114.68940   11114.68803    0.00137    0.00050   0.00021
    6:  11 10                         13584.60270   13584.60404   -0.00134    0.00050   0.00021
    7:  12 11                         14819.56030   14819.55885    0.00145    0.00050   0.00027
    8:  13 12                         16054.51070   16054.51125   -0.00055    0.00050   0.00038
NORMALIZED DIAGONAL:
    1   1.00000E+00    2   3.79287E-01
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                           NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1           100          B      617.4840181(251)       -0.0000000
   2           200         -D          -8.332(101)E-06        0.000E-06
 MICROWAVE AVG =       -0.000006 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.001045 MHz, IR RMS =        0.00000
 END OF ITERATION  2 OLD, NEW RMS ERROR=        2.08936         2.08936
```

Table S13: Truncated fit output for $^{72}GeC_5$

```
                                  EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG. CALC.FREQ. -  DIFF. - WT.
    1:   5  4                          6114.75080    6114.74902    0.00178    0.00050   0.00022
    2:   6  5                          7337.69620    7337.69680   -0.00060    0.00050   0.00023
    3:   7  6                          8560.64320    8560.64347   -0.00027    0.00050   0.00023
    4:   8  7                          9783.58760    9783.58884   -0.00124    0.00050   0.00022
    5:   9  8                         11006.53380   11006.53274    0.00106    0.00050   0.00020
    6:  10  9                         12229.47450   12229.47497   -0.00047    0.00050   0.00020
    7:  11 10                         13452.41500   13452.41537   -0.00037    0.00050   0.00026
    8:  12 11                         14675.35420   14675.35373    0.00047    0.00050   0.00039
NORMALIZED DIAGONAL:
    1   1.00000E+00    2   3.56507E-01
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                           NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1           100          B      611.4752870(282)        0.0000000
   2           200         -D          -7.691(135)E-06       -0.000E-06
 MICROWAVE AVG =        0.000046 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.000924 MHz, IR RMS =        0.00000
 END OF ITERATION  2 OLD, NEW RMS ERROR=        1.84817         1.84817
```

Table S14: Truncated fit output for $^{74}GeC_5$

```
                                  EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG. CALC.FREQ. -  DIFF. - WT.
    1:   5  4                           6057.52810    6057.52686    0.00124    0.00500   0.00140
    2:   6  5                           7269.03040    7269.03021    0.00019    0.00500   0.00160
    3:   7  6                           8480.53380    8480.53247    0.00133    0.00500   0.00176
    4:   8  7                           9692.03330    9692.03343   -0.00013    0.00500   0.00188
    5:   9  8                          10903.53230   10903.53293   -0.00063    0.00500   0.00195
    6:  11 10                          13326.52680   13326.52680    0.00000    0.00500   0.00194
    7:  12 11                          14538.01830   14538.02080   -0.00250    0.00500   0.00188
    8:  13 12                          15749.51430   15749.51259    0.00171    0.00500   0.00182
    9:  16 15                          19383.97150   19383.97293   -0.00143    0.00500   0.00222
   10:  17 16                          20595.45480   20595.45409    0.00071    0.00500   0.00274
   11:  18 17                          21806.93260   21806.93212    0.00048    0.00500   0.00347
NORMALIZED DIAGONAL:
    1   1.00000E+00    2   4.09462E-01
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                           NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1          100          B       605.753068(155)        -0.000000
   2          200         -D            -7.64( 33)E-06         0.00E-06
 MICROWAVE AVG =        0.000088 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.001195 MHz, IR RMS =        0.00000
 END OF ITERATION  2 OLD, NEW RMS ERROR=        0.23907         0.23907
```

Table S15: Truncated fit output for $^{76}GeC_5$

```
                                  EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG. CALC.FREQ. -  DIFF. - WT.
    1:   6  5                           7203.56610    7203.56461    0.00149    0.00050   0.00016
    2:   7  6                           8404.15620    8404.15629   -0.00009    0.00050   0.00019
    3:   8  7                           9604.74900    9604.74685    0.00215    0.00050   0.00021
    4:   9  8                          10805.33520   10805.33614   -0.00094    0.00050   0.00024
    5:  11 10                          13206.50870   13206.51025   -0.00155    0.00050   0.00029
NORMALIZED DIAGONAL:
    1   1.00000E+00    2   1.00000E+00
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                           NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1          100          B      600.2975296(133)       -0.0000000
   2          200         -D     -6.650000000(  0)E-06 -0.000000000E-06
 MICROWAVE AVG =        0.000212 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.001422 MHz, IR RMS =        0.00000
 END OF ITERATION  2 OLD, NEW RMS ERROR=        2.84412         2.84412
```

GeC_6

Table S16: Truncated fit output for $^{70}GeC_6$

```
                                      EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG. CALC.FREQ. -  DIFF. - WT.
    1:  10  9                          8258.12700    8258.12622    0.00078    0.00200   0.00126
    2:  11 10                          9083.93520    9083.93622   -0.00102    0.00200   0.00110
    3:  12 11                          9909.74560    9909.74548    0.00012    0.00200   0.00092
    4:  13 12                         10735.55410   10735.55392    0.00018    0.00200   0.00084
    5:  14 13                         11561.36130   11561.36147   -0.00017    0.00200   0.00106
    6:  15 14                         12387.16820   12387.16808    0.00012    0.00200   0.00159
NORMALIZED DIAGONAL:
    1   1.00000E+00    2   2.39384E-01
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                          NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1           100          B       412.906877(135)         0.000000
   2           200          D            -2.83( 38)E-06        -0.00E-06
 MICROWAVE AVG =        0.000005 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.000540 MHz, IR RMS =        0.00000
 END OF ITERATION  2 OLD, NEW RMS ERROR=        0.26996         0.26996
```

Table S17: Truncated fit output for $^{72}GeC_6$

```
                                    EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG. CALC.FREQ. -  DIFF. - WT.
    1:   9  8                          7356.75300    7356.75316   -0.00016    0.00200   0.00113
    2:  10  9                          8174.16730    8174.16787   -0.00057    0.00200   0.00105
    3:  11 10                          8991.58180    8991.58185   -0.00005    0.00200   0.00092
    4:  12 11                          9808.99600    9808.99503    0.00097    0.00200   0.00081
    5:  13 12                         10626.40710   10626.40734   -0.00024    0.00200   0.00081
    6:  14 13                         11443.81920   11443.81869    0.00051    0.00200   0.00106
    7:  15 14                         12261.22850   12261.22903   -0.00053    0.00200   0.00153
NORMALIZED DIAGONAL:
    1   1.00000E+00    2   2.76178E-01
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                          NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1           100          B       408.709001(112)         0.000000
   2           200          D            -3.04( 33)E-06        -0.00E-06
 MICROWAVE AVG =       -0.000010 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.000519 MHz, IR RMS =        0.00000
 END OF ITERATION  2 OLD, NEW RMS ERROR=        0.25956         0.25956
```

Table S18: Truncated fit output for $^{74}GeC_6$

```
                                    EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG. CALC.FREQ. -  DIFF. - WT.
    1:   9  8                            7284.67320    7284.67956   -0.00636    0.00200   0.00113
    2:  10  9                            8094.07920    8094.08354   -0.00434    0.00200   0.00105
    3:  11 10                            8903.48540    8903.48600   -0.00060    0.00200   0.00092
    4:  12 11                            9712.88950    9712.88676    0.00274    0.00200   0.00081
    5:  13 12                           10522.29450   10522.28568    0.00882    0.00200   0.00081
    6:  14 13                           11331.69560   11331.68262    0.01298    0.00200   0.00106
    7:  15 14                           12141.06260   12141.07740   -0.01480    0.00200   0.00153
NORMALIZED DIAGONAL:
    1   1.00000E+00    2   2.76178E-01
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                             NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1           100          B       404.705455(112)        -0.000000
   2           200          D            -6.39( 33)E-06         0.00E-06
 MICROWAVE AVG =       -0.000223 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.008722 MHz, IR RMS =        0.00000
 END OF ITERATION  2 OLD, NEW RMS ERROR=        4.36109         4.36109
```

Table S19: Truncated fit output for $^{76}GeC_6$

```
                                    EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG. CALC.FREQ. -  DIFF. - WT.
    1:   9  8                            7215.84720    7215.84732   -0.00012    0.00200   0.00113
    2:  10  9                            8017.60430    8017.60609   -0.00179    0.00200   0.00105
    3:  11 10                            8819.36500    8819.36422    0.00078    0.00200   0.00092
    4:  12 11                            9621.12390    9621.12164    0.00226    0.00200   0.00081
    5:  13 12                           10422.87830   10422.87829    0.00001    0.00200   0.00081
    6:  14 13                           11224.63240   11224.63411   -0.00171    0.00200   0.00106
    7:  15 14                           12026.38950   12026.38902    0.00048    0.00200   0.00153
NORMALIZED DIAGONAL:
    1   1.00000E+00    2   2.76178E-01
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                             NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1           200          D            -2.68( 33)E-06        -0.00E-06
   2           100          B       400.880841(112)         0.000000
 MICROWAVE AVG =       -0.000014 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.001313 MHz, IR RMS =        0.00000
 END OF ITERATION  2 OLD, NEW RMS ERROR=        0.65634         0.65634
```

Table S20: Internal coordinates of CH_3GeH_3, optimized at the ae-CCSD(T)/cc-pwCVQZ level of theory, in Å and degrees.

```
H
C 1 r1
GE 2 r2 1 a1
H 3 r3 2 a2 1 d180
H 2 r1 3 a1 1 d120
H 2 r1 3 a1 5 d120
H 3 r3 2 a2 4 d120
H 3 r3 2 a2 7 d120

r1   =         1.0879
r2   =         1.9454
a1   =       110.3295
r3   =         1.5271
a2   =       110.3410
d180 =       180.0000
d120 =       120.0000
```

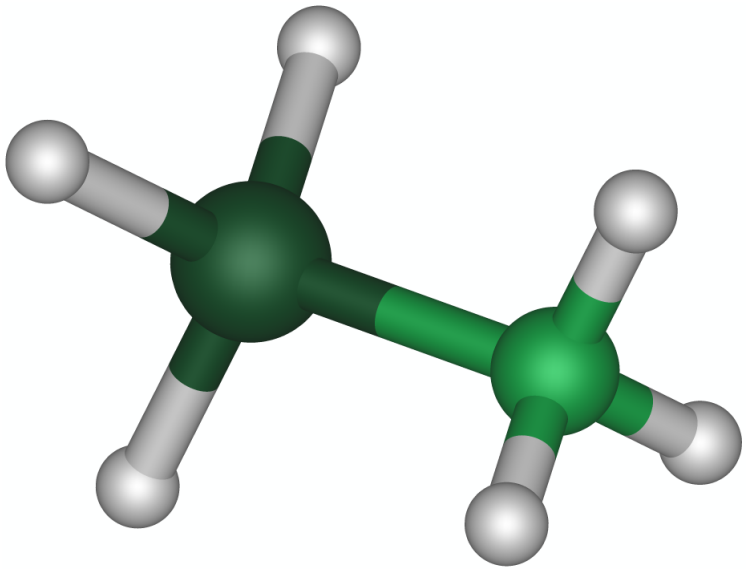

Figure S1: Molecular structure of methyl germane, CH_3GeH_3.