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

Supplementary Information

CCSD(T)/cc-pwCVTZ-PP harmonic vibrational frequencies in cm^{-1} are reported for the neutral minimum structures.

Butterfly C_{2v}	**Monobridged** C_s	**Germylidene** C_{2v}	**Trans** C_{2h}
288 (a_1)	176 (a'')	225 (b_2)	213 (a_u)
810 (a_1)	320 (a')	299 (b_1)	228 (b_u)
1019 (a_2)	480 (a')	309 (a_1)	330 (a_g)
1094 (b_2)	1013 (a')	832 (a_1)	593 (a_g)
1433 (b_1)	1539 (a')	2123 (a_1)	2066 (a_g)
1515 (a_1)	2071 (a')	2147 (b_2)	2080 (b_u)

CCSD(T)/cc-pwCVTZ-PP harmonic vibrational frequencies in cm^{-1} are reported for the cationic minimum structures.

Butterfly C_{2v}	**Monobridged** C_s	**Germylidene** C_{2v}	**Trans** C_{2h}
196 (a_1)	151 (a'')	256 (a_1)	149 (a_u)
795 (a_1)	271 (a')	271 (b_2)	185 (b_u)
1026 (a_2)	471 (a')	384 (b_1)	272 (a_g)
1131 (b_2)	944 (a')	829 (a_1)	601 (a_g)
1405 (b_1)	1482 (a')	2158 (a_1)	2079 (a_g)
1511 (a_1)	2096 (a')	2196 (b_2)	2090 (b_u)

Vibration-Rotation constants of the neutral butterfly and monobridged Ge_2H_2 structures computed from CCSD(T)/cc-pwCVTZ-PP anharmonic vibrational frequencies

Geometry	**Rot Constant (cm^{-1})**	**Mode**	**Vib-Rot Constant (cm^{-1})**
Butterfly	$A = 5.0043$	a_1	-0.0287
		a_1	0.0825
		a_2	0.1864
		b_2	0.1648
		b_1	0.0142
		a_1	-0.0666
	$B = 0.0818$	a_1	0.0003
		a_1	0.0005
		a_2	0.0000
		b_2	-0.0001
		b_1	0.0004
		a_1	0.0002
	$C = 0.0815$	a_1	0.0003
		a_1	0.0004
		a_2	0.0000
		b_2	0.0000
		b_1	0.0003
		a_1	0.0001
Monobridged	$A = 7.8687$	a''	1.1260
		a'	-0.1678
		a'	-0.7313
		a'	0.0390
		a'	0.0300
		a'	0.0577
	$B = 0.0891$	a''	0.0004
		a'	0.0003
		a'	0.0000
		a'	-0.0001
		a'	0.0003
		a'	0.0001
	$C = 0.0881$	a''	0.0003
		a'	0.0003
		a'	0.0001
		a'	0.0000
		a'	0.0003
		a'	0.0002

Vibration-Rotation constants of the neutral germylidene and trans Ge_2H_2 structures computed from CCSD(T)/cc-pwCVTZ-PP anharmonic vibrational frequencies

Geometry	**Rot Constant (cm^{-1})**	**Mode**	**Vib-Rot Constant (cm^{-1})**
Germylidene	$A = 5.3594$	a''	0.3727
		a'	-0.4278
		a'	0.0000
		a'	-0.0555
		a'	0.0733
		a'	0.0480
	$B = 0.0837$	a''	-0.0003
		a'	0.0002
		a'	0.0003
		a'	0.0001
		a'	0.0001
		a'	0.0000
	$C = 0.0824$	a''	-0.0002
		a'	0.0001
		a'	0.0003
		a'	0.0000
		a'	0.0001
		a'	0.0001
Trans	$A = 5.4074$	a''	2.9035
		a'	-2.7428
		a'	0.0034
		a'	-0.1794
		a'	0.0979
		a'	0.1000
	$B = 0.0908$	a''	0.0029
		a'	-0.0011
		a'	0.0003
		a'	-0.0001
		a'	0.0002
		a'	0.0002
	$C = 0.0893$	a''	0.0015
		a'	0.0002
		a'	0.0003
		a'	0.0000
		a'	0.0002
		a'	0.0002

Vibration-Rotation constants of the cationic butterfly and monobridged $Ge_2H_2^+$ structures computed from CCSD(T)/cc-pwCVTZ-PP anharmonic vibrational frequencies

Geometry	**Rot Constant (cm^{-1})**	**Mode**	**Vib-Rot Constant (cm^{-1})**
Butterfly	$A = 5.2195$	a_1	-0.0568
		a_1	0.0488
		a_2	0.2251
		b_2	0.1858
		b_1	-0.0616
		a_1	-0.0642
	$B = 0.0757$	a_1	0.0004
		a_1	0.0010
		a_2	-0.0005
		b_2	-0.0004
		b_1	0.0007
		a_1	0.0002
	$C = 0.0753$	a_1	0.0004
		a_1	0.0010
		a_2	-0.0004
		b_2	-0.0003
		b_1	0.0007
		a_1	0.0002
Monobridged	$A = 7.7011$	a''	1.1624
		a'	-0.1684
		a'	-0.6804
		a'	0.0048
		a'	0.0041
		a'	0.0625
	$B = 0.0811$	a''	0.0003
		a'	0.0003
		a'	0.0000
		a'	-0.0001
		a'	0.0004
		a'	0.0002
	$C = 0.0802$	a''	0.0002
		a'	0.0004
		a'	0.0000
		a'	0.0000
		a'	0.0004
		a'	0.0002

Vibration-Rotation constants of the cationic germylidene and trans $Ge_2H_2^+$ structures computed from CCSD(T)/cc-pwCVTZ-PP anharmonic vibrational frequencies

Geometry	**Rot Constant (cm^{-1})**	**Mode**	**Vib-Rot Constant (cm^{-1})**
Germylidene	$A = 5.2112$	a''	-0.0029
		a'	0.1683
		a'	-0.02319
		a'	-0.0516
		a'	0.0714
		a'	0.0500
	$B = 0.0748$	a''	0.0003
		a'	-0.0002
		a'	0.0000
		a'	-0.0001
		a'	0.0001
		a'	0.0000
	$C = 0.0737$	a''	0.0003
		a'	-0.0002
		a'	0.0000
		a'	0.0000
		a'	0.0001
		a'	0.0000
Trans	$A = 5.1838$	a''	1.1809
		a'	-1.1477
		a'	0.0025
		a'	-0.1531
		a'	0.0797
		a'	0.0800
	$B = 0.0821$	a''	0.0019
		a'	-0.0003
		a'	0.0004
		a'	0.0000
		a'	0.0002
		a'	0.0002
	$C = 0.0808$	a''	0.0013
		a'	0.0003
		a'	0.0004
		a'	0.0000
		a'	0.0002
		a'	0.0002