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Ge_2H_2: A Molecule with a Low-Lying Monobridged Equilibrium Geometry

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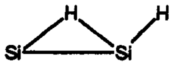
Abstract: Recent experimental and theoretical studies reporting remarkable monobridged structures for Si_2H_2, Al_2H_2, and Ga_2H_2 have motivated us to re-investigate the singlet potential energy surface of Ge_2H_2 using the self-consistent-field (SCF), single and double excitation configuration interaction (CISD), and single and double excitation coupled cluster (CCSD) methods in conjunction with a double-ζ plus polarization basis set (DZP). In addition to the dibridged (or butterfly) ground state and the low-lying vinylidene-like minimum reported earlier by Grev and DeLeeuw, our study predicts the existence of a monobridged isomer, which is characterized as a minimum by means of harmonic vibrational frequency analyses. Relative energies of the above structures were also predicted with use of the coupled cluster single, double, and (perturbative) triple excitation method (CCSD(T)), which employed a triple-ζ plus polarization basis set augmented with a set of f functions on the germanium atoms (TZP+f). Final energetic predictions suggest that the monobridged structure is the second most stable isomer of Ge_2H_2, lying 8.9 kcal mol^{-1} above the butterfly ground state and 2.1 kcal mol^{-1} below the branched (vinylidene-like) minimum.

Introduction

Among small molecules, one of the most interesting structural discoveries in recent years has been that of the monobridged equilibrium geometry of the Si_2H_2 molecule The existence of such a structure, which apparently has no precedent, was proposed in 1990 by Colegrove.[1] She predicted this structure to be a genuine equilibrium and to lie only 10.8 kcal/mol above the dibridged "butterfly" global minimum[2–4] of Si_2H_2.



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The spectacular success of the Lille group[4] in observing and analyzing the microwave spectrum of the butterfly global minimum of Si_2H_2 led them to attempt to synthesize other new Si_xH_y molecules. In cooperation with the Georgia theoretical group, Cordonnier, Bogey, Demuynck, and Destombes[5] were able to observe and analyze a total of 148 microwave features that were assigned to the monobridged Si_2D_2 and Si_2H_2 species **1**. The observed microwave lines are remarkably consistent with the theoretical predictions of Colegrove[1] and of Grev.[6] Grev has provided an incisive qualitative picture of the bonding in Si_2H_2 and related systems.

Given the very recent observation[5] of the peculiar monobridged structure **1** of Si_2H_2, an obvious question is whether comparably low-lying equilibrium geometries of other A_2H_2 molecules exist. It would certainly be surprising if the much studied[7] acetylene potential surface C_2H_2 revealed such a stationary point. The next sensible neutral example would be the germanium analogue Ge_2H_2. Therefore, we explore here a part of the Ge_2H_2 potential energy hypersurface not considered in previous theoretical work.[8]

Theoretical Methods

Several stationary points on the Ge_2H_2 potential energy surface were initially located by using SCF gradient techniques[9,10] in conjunction with a basis set designated double-ζ plus polarization (DZP). The DZP basis for germanium consists of the Dunning[11] 14s11p5d primitive set of Gaussian functions contracted to 7s5p2d[12] augmented by a set of six Cartesian d-like functions ($\alpha_d(\mathrm{Ge}) = 0.25$). For hydrogen we used the standard Huzinaga–Dunning–Hay[13–15] double-ζ basis set augmented by a set of p-like functions ($\alpha_p(\mathrm{H}) = 0.75$). The contraction scheme for this DZP basis is

$$\mathrm{Ge}[6112211/61211/411],\ \mathrm{H}[31/1]$$

For the evaluation of the relative energies of various structures we employed a basis set designated triple-ζ plus polarization plus f functions (TZP+f). For germanium, it consists of the above primitive set more loosely contracted to 10s8p2d and augmented with a set of d- and f-like polarization functions [$\alpha_d(\mathrm{Ge}) = 0.25$, $\alpha_f(\mathrm{Ge}) = 0.45$]. For hydrogen it is the standard Huzinaga–Dunning triple-ζ basis set augmented by a set of p-like functions ($\alpha_p(\mathrm{H}) = 0.75$). Thus the contraction scheme for this basis set is

$$\mathrm{Ge}[5111111111/41111111/411/1],\ \mathrm{H}[311/1]$$

DZP SCF quadratic force constants and harmonic vibrational frequencies were determined with the use of analytic energy second derivative methods.[16] Starting with the DZP SCF geometries and force constants, we then reoptimized the structures using first the configuration interaction

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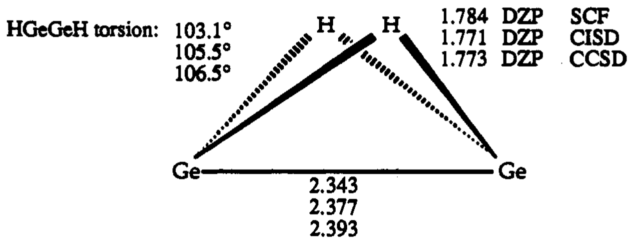

Figure 1. Theoretical equilibrium geometries for the global minimum closed-shell singlet, dibridged (C_{2v}) electronic ground state of Ge_2H_2. Bond distances are in angströms.

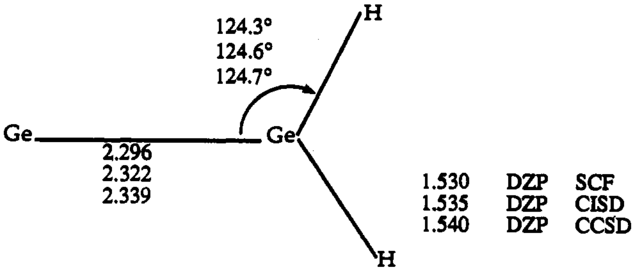

Figure 2. Theoretical geometries for the vinylidene-like closed-shell singlet state of Ge_2H_2. Bond distances are in angströms.

(CI) method[17] and then the coupled cluster (CC) method[18] in conjunction with the DZP basis set. Only the valence electrons have been correlated explicitly; the core-like SCF molecular orbitals (Ge 1s, 2s, 2p, 3s, 3p, 3d) and the virtual orbital counterparts (Ge $1s^*$, $2s^*$) were not included in the CI and CC procedures. Otherwise, all single and double excitations from the SCF reference wave function have been included (CISD, CCSD). The CISD energies have been corrected to approximately include the effects of unlinked quadruple excitations with use of the Davidson formula.[19] These corrected energies are denoted CISD+Q. For final energy predictions the effects of triple excitations were also included perturbatively with the use of CCSD(T) wave functions. We obtained CISD and CCSD harmonic vibrational frequencies by taking finite differences of analytic energy gradients.[20,21]

The choice of frozen and deleted molecular orbitals requires a bit more justification. First, the freezing of the germanium $3d^{10}$ orbital may seem a bit restrictive since this orbital is conclusively filled only two elements earlier with zinc. However, when one reaches Ge in the periodic table, the 3d orbital energy is −1.635 hartrees,[22] whereas the 4s orbital energy is −0.553 hartrees and the 4p orbital energy is −0.287 hartrees. Thus the energy gap $[\epsilon(4s) - \epsilon(3d)]$ is substantial, 1.081 hartrees or 29.4 eV. Concerning the virtual orbitals, a referee has questioned why only the $1s^*$ and $2s^*$ virtuals were deleted. The reason is that the other high-lying or core-like virtuals (especially $3s^*$, $3p^*$, and $3d^*$) tend to mix with the valence-like virtuals. That is, the distinction between core-like and valence-like virtuals becomes blurred. In such cases, the best strategy is to include all virtual orbitals which have some valence character.

Structures and Energies

Theoretical stationary point geometries are shown in Figures 1–3. Table I contains the predicted harmonic vibrational frequencies, infrared (IR) intensities, and normal mode assignments. The assignments were based on the potential energy distribution (PED) among the diagonal elements of the symmetrized force constant matrix on a percentage scale. Standard cotton coordinate systems[23] have been used, and whenever there is a choice of coordinate systems, the two germanium atoms have been chosen to lie on the y axis.

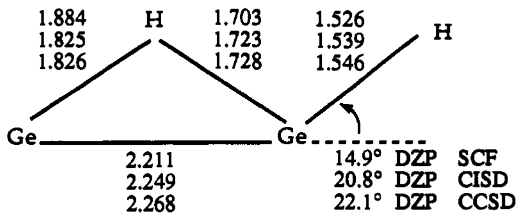

Figure 3. Theoretical geometries for the monobridged closed-shell singlet state of Ge_2H_2. Bond distances are in angströms.

Table II summarizes the relative energies as well as the total energies of the global minimum dibridged butterfly structure. Table III lists the largest CI coefficients for each wave function and the corresponding electron configurations. These results show that the single-configuration Hartree–Fock approach is qualitatively reasonable for all three isomers. The fact that the C_0 values (0.938, 0.935, and 0.936) are nearly the same further suggests that single-configuration-based correlated methods (such as CISD and CCSD) should do a reasonable job in describing the relative energies of the three isomers. For brevity in this discussion, only results obtained with the DZP CCSD method will be reported explicitly, except relative energies, which are TZP+f CCSD(T) results including DZP CCSD harmonic vibrational energy corrections (see final column of Table II).

The structures corresponding to the butterfly (Figure 1) and vinylidene (Figure 2) isomers are qualitatively similar to those reported earlier by Grev and Deleeuw.[8] Previous experience would suggest that the true equilibrium geometries should lie intermediate between our DZP CISD and DZP CCSD predictions.

The monobridged structure (Figure 3) is, of course, the principal focus of this research. The theoretical predictions for this peculiar isomer are similar to those for Si_2H_2. For example, monobridged Ge_2H_2 is actually predicted to be a transition state at the DZP SCF level, precisely as was found[1] for Si_2H_2. At the DZP SCF level the monobridged structure is a transition state, with its imaginary vibrational frequency being the terminal out-of-plane bend. This appears to confirm that the monobridged structure at the DZP SCF level of theory is a transition state for the degenerate rearrangement of the butterfly global minimum. For both molecules, the introduction of electron correlation at the DZP CISD level is seen to properly describe the monobridged structure as a genuine minimum.

One of the most critical structural features of the monobridged geometry is the angle between the terminal Ge–H bond and the extension of the Ge–Ge bond. This angle is seen in Figure 3 to be 20.8° at the DZP CISD level of theory. The analogous DZP CISD prediction for the monobridged structure of Si_2H_2 is very similar, namely 20.0°. From Grev's work[6] on Si_2H_2 using much higher levels of theory, a final value of 18.9° is found for this critical angle in monobridged Si_2H_2.

Another interesting feature of the monobridged Ge_2H_2 structure is the difference between the two bridging Ge–H distances. This difference is 0.181 Å with the DZP SCF method, 0.102 Å with the DZP CISD method, and 0.098 Å with the DZP CCSD method. Colegrove's analogous results[1] for monobridged Si_2H_2 are Δr = 0.119 (DZP SCF) and 0.082 Å (DZP CISD). At the highest level of theory considered to date for Si_2H_2 {TZ2P+f CCSD(T)], Grev[6] predicts the monobridged Δr to be 0.083 Å. Thus, for Ge_2H_2 the ultimate difference between bridging Ge–H distances should be about 0.1 Å, or roughly 0.02 Å more than is the case for monobridged Si_2H_2.

Finally, we compare the predicted Ge–Ge bond distances for the butterfly (2.377 Å), monobridged (2.249 Å), and vinylidene-like (2.322 Å) structures. The bond distances cited are the DZP CISD values, which are expected to be closest to the (unknown) experimental values. As was the case for the valence isoelectronic

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Table I. Harmonic Vibrational Frequencies (cm^{-1}) for Ge_2H_2 Structures with Infrared Intensities in Parentheses (km/mol)

isomer		description	DZP SCF	DZP CISD	DZP CCSD
vinylidene	b_2	Ge–H antisym str	2241 (99)	2192 (83)	2158 (78)
	a_1	Ge–H sym str	2235 (83)	2180 (73)	2144 (72)
	a_1	H–Ge–Ge sym bend	909 (65)	860 (73)	843 (75)
	b_1	oop bend	385 (4)	332 (4)	304 (4)
	a_1	Ge–Ge str	337 (2)	318 (4)	305 (5)
	b_2	H–Ge–H in-plane wag	304 (29)	260 (21)	252 (19)
monobridged	a'	terminal H–Ge str	2231 (102)	2143 (122)	2095 (122)
	a'	bridging H sym str	1612 (132)	1560 (105)	1532 (95)
	a'	bridging H antisym str	865 (96)	962 (150)	964 (145)
	a'	H–Ge–H bend	395 (23)	465 (7)	462 (5)
	a'	Ge–Ge str	309 (17)	328 (7)	314 (6)
	a''	terminal H oop bend	43i (68)	123 (43)	114 (38)
dibridged	a_1	Ge–H sym str	1537 (24)	1534 (12)	1520 (10)
	b_1	Ge–H antisym str	1456 (72)	1446 (51)	1424 (48)
	b_2	Ge–H str	957 (525)	1054 (469)	1056 (443)
	a_2	Ge–H str	736 (0)	931 (0)	947 (0)
	a_1	torsion (butterfly)	925 (62)	863 (42)	838 (38)
	a_1	Ge–Ge str	331 (0)	304 (0)	291 (0)

Table II. Relative Energies (kcal/mol) of Stationary Point Structures for the Ge_2H_2 System, Corrected with Zero-Point Vibrational Energies in the Final Column

	SCF		CISD[a]		CCSD		CCSD(T)	
isomer	DZP	TZP+f[c]	DZP	TZP+f[c]	DZP	TZP+f[c]	TZP+f[d]	+ZPVE[e]
vinylidene	4.3	5.6	9.2 9.3	10.6 10.7	9.0	10.4	11.1	11.0
monobridged	13.4	13.7	11.6 10.4	12.0 10.9	10.6	11.0	9.8	8.9
butterfly[b]	0.0	0.0	0.0 0.0	0.0 0.0	0.0	0.0	0.0	0.0

[a] The lower number in the CISD boxes is the Davidson corrected energy difference. [b] Total energies (au) for the dibridged structure are as follows—DZP SCF, –4151.592681; TZP+f[c] SCF, –4151.782305; DZP CISD, –4151.783933; DZP CISD+Q, –4151.806522; TZP+f[c] CISD, –4151.991863; TZP+f[c] CISD+Q, –4152.016976; DZP CCSD, –4151.802324; TZP+f[c] CCSD, –4152.012199; TZP+f[d] CCSD(T), –4152.024124; +ZPVE,[e] –4152.010282. [c] At the DZP optimized geometry obtained with the corresponding level of theory. [d] At the DZP CCSD optimized geometry. [e] TZP+f[d] CCSD(T) including DZP CCSD harmonic zero-point vibrational energy correction.

Table III. Coefficients Greater than 0.05 in the TZP+f CISD Wave Functions for the Different Ge_2H_2 Structures

isomer	coefficient	configuration
dibridged	0.938	(core) $11a_1^2 12a_1^2 13a_1^2 5b_1^2 11b_2^2$
	–0.051	$13a_1^2 \rightarrow 12b_2^2$
monobridged	0.935	(core) $21a'^2 22a'^2 23a'^2 24a'^2 9a''^2$
	–0.102	$9a''^2 \rightarrow 10a''^2$
	–0.055	$24a'^2 \rightarrow 25a'^2$
	–0.054	$24a'9a'' \rightarrow 25a'10a''$
vinylidene	0.936	(core) $15a_1^2 16a_1^2 17a_1^2 7b_1^2 7b_2^2$
	–0.118	$7b_1^2 \rightarrow 8b_1^2$

Si_2H_2 system, the central Ge–Ge bond distance is shortest for the monobridged structure. The reader is referred to our recent paper[6] on Si_2H_2 for a further discussion of the bonding in these closely related systems.

The relative energies of Table II show that the vinylidene-like structure of Ge_2H_2 is the second lowest-lying isomer at the SCF level of theory. However, correlation effects tend to destabilize the vinylidene structure while stabilizing the monobridged structure compared to the global minimum butterfly. Thus, as was the case with the Si_2H_2 energetics,[1,6] the Ge_2H_2 monobridged structure eventually becomes the second lowest-lying isomer of Ge_2H_2. At the ZPVE-corrected TZP+f CCSD(T) level of theory, the monobridged and vinylidene Ge_2H_2 structures are predicted to lie at 8.9 and 11.0 kcal/mol, respectively, above the butterfly global minimum.

Concluding Remarks

The recent experimental discovery[5] of the peculiar monobridged isomer **1** of Si_2H_2 has raised the question whether other such species might be synthesized. The answer presented here for Ge_2H_2 is an unqualified "yes". For both Ge_2H_2 and Si_2H_2, the unexpected monobridged structure is energetically the second lowest-lying isomer, predicted to lie less than 9 kcal/mol above the butterfly global minimum.

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