

Why Is Methylene a Ground State Triplet while Silylene Is a Ground State Singlet?[†]

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The singlet–triplet energy difference in CH₂ and SiH₂ was calculated at the CASSCF level of theory using large Gaussian basis sets that included f-type functions. The total energy was separated into nuclear repulsion and electronic energy, and the latter was further decomposed into the contributions coming from the two electrons highest in energy (the “frontier” electrons, denoted by “f”) and from all the other electrons (denoted by “c” for “core”). The contribution of the frontier electrons was further decomposed into the following terms: $E^{(0)}$, which is the sum of the kinetic energy and the attraction energy to the nucleus of the two frontier electrons and their repulsion energy from all other electrons, and $E_{ee}^{(0)}$, the repulsion energy between the two frontier electrons. The results are used to explain why CH₂ is a ground state triplet (lying ca. 10 kcal/mol lower in energy than the singlet) while SiH₂ is a ground state singlet (with the triplet lying ca. 20 kcal/mol higher in energy). The major conclusions are as follows: (1) In addition to the frontier electrons, the “core” electrons and the nuclear repulsion energy also affect the singlet–triplet gap. (2) About 60% of the singlet–triplet energy difference between CH₂ and SiH₂ of 29 kcal/mol may be attributed to the $E_{ee}^{(0)}$ term. (3) The remaining 40% of the energy difference can be interpreted as resulting from a balance between $E^{(0)}$, the energy of the “core” electrons ($E^{(c)}$), and the nuclear repulsion energy (E_{nuc}); these terms may be related to the HOMO–LUMO energy difference, which is often used in qualitative discussions of singlet–triplet energy gaps. A detailed discussion of the results is presented.

Introduction

There has been an upsurge of interest in the last two decades in organosilicon¹ and organogermanium² chemistry, interest which is still growing. Silylenes, R₂Si,³

and germynes, R₂Ge,⁴ are among the most important reactive intermediates in these fields, and their chemistry has therefore attracted considerable attention.^{3,4}

In all MH₂ species with six valence electrons the singlet state has two electrons in an orbital of σ -symmetry (a₁). In the triplet state this electron pair is unpaired and one electron resides in an orbital of π -symmetry (b₁). A major difference between silylene and germylene on one hand, and methylene—the iso-electronic lowest congener—on the other, is the multiplicity of their ground states. Methylene is a ground state triplet with the singlet lying 9.0 kcal/mol higher in energy,⁵ while both SiH₂^{3,6,7} and GeH₂⁴ are ground

[†] This paper is dedicated to Prof. Helmut Schwarz, a stimulating scientist and a wonderful human being, on the occasion of his 60th birthday.

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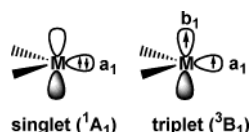
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state singlets, with the 3B_1 triplet state lying significantly higher in energy. This reversal in the multiplicity of the ground state on going from methylene to its heavier homologues has a marked effect on the chemistry of these species in comparison with the chemistry of methylenes.^{3,4}



The 1A_1 – 3B_1 energy difference (ΔE_{ST}) in SiH_2 was first estimated to be less than 14 kcal/mol,^{6a} but recent experiments have found higher values, either 21.0 or 18.0 kcal/mol.^{6b} Accurate calculations, carried out by Balasubramanian and McLean^{7a} using the same level of theory as used in highly accurate calculations done for methylene (a triple- ζ +d+f basis set and extensive MCSCF corrections for electron correlation), predicted a singlet–triplet splitting in SiH_2 of 21.0 kcal/mol.^{7a} More recent high-level calculations (at CASSCF SOCI^{7f–j} and SF OD (spin-flip approach)^{5f} predicted a singlet–triplet gap of 20 kcal/mol. Experimental determination of the 1A_1 – 3B_1 splitting in germylene is to the best of our knowledge not available, but high-level ab initio calculations similar to those used for silylene place it at ca. 23–24 kcal/mol.⁸ It is interesting that the 1A_1 – 3B_1 splitting calculated for SnH_2 is very similar, i.e., 23 kcal/mol.^{8b,h,9}

The quite surprising reversal in the ground state multiplicity on going from CH_2 to SiH_2 and GeH_2 was rationalized previously in terms of simple qualitative arguments based on the HOMO–LUMO gap,^{10–12} as follows.

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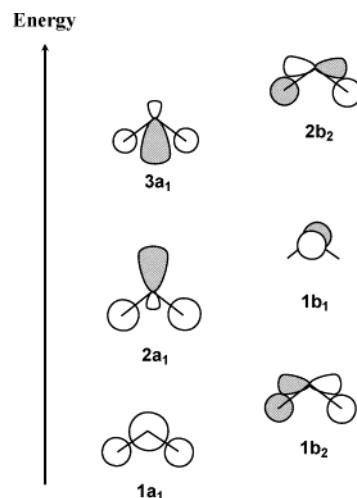


Figure 1. Schematic drawing of the molecular orbitals of MH_2 ($M = C, Si$) molecules.

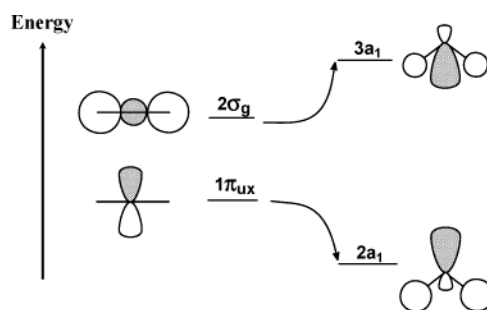


Figure 2. Energy change in the $1\pi_{ux}$ and $2\sigma_g$ orbitals of MH_2 ($M = C, Si$) on going from a linear to a bent geometry.

The HOMO–LUMO gap is larger in SiH_2 than in CH_2 . For SiH_2 the HOMO–LUMO gap (as calculated for the triplet states) is 52 kcal/mol, significantly larger than that for CH_2 (27 kcal/mol).^{10a} For SiH_2 the energy gained in forming a triplet configuration is not enough to compensate for the large HOMO–LUMO energy separation. Hence, SiH_2 favors the singlet configuration.^{10a} However, this factor alone cannot account quantitatively for the total observed effect.

Why is the HOMO–LUMO gap in SiH_2 (or GeH_2) larger than in CH_2 ? This can be understood in terms of the molecular orbitals of the MH_2 unit,¹¹ which are shown schematically in Figure 1.

The key point in dictating the energy gap between the $2a_1$ (HOMO) and the $1b_1$ (LUMO) orbitals is the degree of mixing between the occupied $2a_1$ orbital and the empty $3a_1$ orbital. The stronger the mixing between these orbitals, the lower the energy of the $2a_1$ orbital and the higher the $2a_1$ – $1b_1$ energy gap. The extent of mixing between the $2a_1$ and $3a_1$ MOs is determined by the energy gap between the unmixable MOs of linear MH_2 to which they are related, i.e., the $1\pi_{ux}$ and $2\sigma_g$ orbitals. As $1\pi_{ux}$ and $2\sigma_g$ become closer together, more mixing occurs between $2a_1$ and $3a_1$ and their separation increases, thus stabilizing the $2a_1$ orbital (Figure 2).

The relative energies of the $1\pi_{ux}$ and $2\sigma_g$ orbitals depend primarily on the electronegativity of M and the

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principal quantum number of the respective AO.^{11,12} A lower electronegativity of M and a higher principal quantum number increase the size of the AOs and lengthen the M–H bonds. This decreases the antibonding character of the $2\sigma_g$ orbital and thus lowers its energy. Since lower electronegativity of M also raises the energy of the $1\pi_{ux}$ orbital, the energy gap between these two MOs is reduced, causing greater mixing between the bent forms of the $2a_1$ and $3a_1$ orbitals. More effective mixing stabilizes the $2a_1$ orbital (it also destabilizes the $3a_1$ orbital, which however is empty). As the electronegativity of Ge and Si are lower than that of C (2.02, 1.74, and 2.50, respectively, on the Allred–Rochow scale¹³), there is more orbital mixing in SiH₂ (or GeH₂) than in CH₂ and the $2a_1$ – $3a_1$ energy gap is larger in the former two. Thus, due to the lower electronegativity of Si and Ge, the singlet state in SiH₂ and GeH₂ is stabilized compared to CH₂. The stronger $2a_1$ – $3a_1$ mixing and the resulting greater stabilization of the $2a_1$ orbital in SiH₂ and GeH₂ compared with CH₂ also accounts for the smaller HMM valence angles in the 1A_1 states of SiH₂ and GeH₂ of 91.5° and 90.8°, respectively, compared with that of CH₂ of 101.5° (B3LYP/6-311++G** values). Experimental values where available are similar.³

Another factor that influences the HOMO–LUMO gap is the polarity of the M–H bond. The C–H bonds in CH₂ are nearly nonpolar, but the Si–H bonds in SiH₂ are strongly polarized in the direction Si⁺–H[−] (the Allred–Rochow electronegativity of H is 2.20). The result is to make the HOMO–LUMO gap greater than it would be if the ligands and the silicon had similar electronegativity, and therefore this effect stabilizes the singlet state for SiH₂ (or GeH₂) relative to CH₂. In line with this argument, for (H₃Si)₂Si, where the bond polarity is small, the best calculated estimates for the singlet–triplet energy gap is 8–10 kcal/mol (depending on the computational level),¹⁴ significantly smaller than for SiH₂. Thus, this ligand-electronegativity effect could also contribute significantly to the difference between SiH₂ (or GeH₂) and CH₂.¹²

A somewhat different rationalization for the larger HOMO–LUMO gap in silylene and germylene relative to methylene is as follows: Silicon and germanium prefer to have nonbonding electrons in atomic orbitals with a higher percentage of s-character. For example, Pople, Apeloig, Schleyer, and co-workers calculated that in the 1A_1 state of MH₂ the lone pair is a hybrid orbital with 88.8% s-character in SiH₂ compared with only 51.6% s-character in CH₂.^{10b,15} This effect is associated with the difference in the expectation values for maximum radial density of the 3s and 3p orbitals for silicon (22%), which is much greater than the corresponding difference for the 2s and 2p orbitals of carbon (−0.2%).^{1c,16} The higher s-character in the $2a_1$ orbital of SiH₂ and GeH₂ compared to CH₂ suggests a relatively lower energy of this orbital and a higher HOMO–LUMO gap

in SiH₂ and GeH₂, as observed.¹² Likewise, the Ge–H and Si–H bonds will have higher p-character than the corresponding C–H bonds. The higher p-character in the M–H bonds in SiH₂ and GeH₂ than in CH₂ accounts for the smaller bond angles in SiH₂ and GeH₂.³

Another qualitative argument, which surprisingly has not been discussed before, is the electron–electron repulsion between the paired electrons in the $2a_1$ orbital of the singlet species. Because of the larger size of the lone pair orbital in SiH₂ and GeH₂ compared to CH₂, the electron–electron repulsion should be less in SiH₂ and GeH₂ than in CH₂, favoring the singlet state for the heavier elements.

In this paper we attempt to pinpoint quantitatively, by using high-level correlated molecular orbital calculations, some of the factors that cause the striking differences in the ground state multiplicities of methylene and silylene. In this analysis the total energy is decomposed into nuclear repulsion energy and electronic energy, and the latter is further decomposed into the contributions coming from the two electrons highest in energy (the frontier electrons) and all the other electrons (“core” electrons).¹⁷ This kind of energy decomposition at a high computational level is rare¹⁸ and not only provides insight into the question of multiplicity in CH₂ and SiH₂ but may have wide implications for understanding chemical bonding generally.

Methods

The basis set employed for silicon in the SiH₂ calculations is the f-basis set of Balasubramanian and McLean.^{7a} This basis set is composed of a (12s9p/6s5p) contracted Gaussian set augmented with two Gaussian six-component 3d functions (exponents 0.56, 0.14) and a 10-component 4f function (exponent 0.38). For hydrogen a (5s/3s) basis set, augmented with a 2p function (exponent 0.75), was employed for both the SiH₂ and CH₂ calculations. The carbon basis set for the CH₂ calculations is composed of the (10s6p) primitive set of Huzinaga,¹⁹ contracted to (7s5p) and extended by the addition of two sets of d functions (exponents 1.3, 0.4) and a single f-type function (exponent 0.65).²⁰

Wave functions were computed for the lowest lying 1A_1 and 3B_1 states of silylene and methylene, and geometry optimizations were performed at the multiconfiguration SCF (MCSCF) level of theory using the above-mentioned basis sets.

The MCSCF wave functions were of the complete active space (CASSCF) type. The core electrons (1s²2s²2p⁶ for Si and

(16) (a) The expectation values of the maximum radial density of the *ns* and *np* orbitals are 1.220 and 1.217 Å for C (*n* = 2) and 1.79 and 2.18 Å for Si (*n* = 3). Desclaux, J. P. *At. Data Nucl. Data Tables* **1973**, 12, 311. (b) Kutzelnigg, W. *Angew. Chem., Int. Ed. Engl.* **1984**, 23, 272.

(17) We have chosen to decompose the total electronic energy to the energy of the two frontier electrons (denoted by the superscript “f”) and to the energy of all other electrons (referred to as “core” electrons, *E*^(c)) in order to test quantitatively the qualitative models (discussed in the Introduction) that attributed to the two frontier electrons a major role in the change in multiplicities on going from CH₂ to SiH₂. The energy of the “core” electrons includes of course the contribution of the electrons with a lower quantum number (i.e., the “real” core electrons; the 1s carbon electrons in CH₂ and the 1s, 2s, and 2p silicon electrons in SiH₂) as well as the lower lying four valence electrons that reside in orbitals $1a_1$ and $1b_2$ (Figure 1). Another possible decomposition is to separate the “real” core electrons from all valence electrons (i.e., in CH₂ to separate the contribution of 1s electrons from that of the four 2s and 2p carbon electrons), but this separation is, we believe, less informative than the one that we have used.

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(15) In the 3B_1 states the s-orbital contribution to the in-plane σ -type singly occupied MO of SiH₂ is 36.2% compared to only 20.8% in CH₂.^{10b}

1s² for C) were not correlated. The configuration spaces for calculations on SiH₂ and CH₂ were generated by distributing the remaining electrons (six for both SiH₂ and CH₂) in all possible ways into orbitals that, at large internuclear separation, are correlated into the H 1s and C 2s and 2p, and Si 3s and 3p atomic orbitals. The CASSCF calculations were carried out for both SiH₂ and CH₂, in a configuration space of the 1a₁, 1b₂, 2a₁, 1b₁, 3a₁, and 2b₂, orbitals in C_{2v} symmetry. The CASSCF wave functions included 51 configuration state functions (CSF) for the ³B₁ states of SiH₂ and CH₂, and 56 CSF were generated for the ¹A₁ states of both species. The MCSCF calculations were carried out using the GAMESS codes.²¹

Decomposition of the Electronic Energy. Molecular orbitals ψ_1 to ψ_a are doubly occupied in each case ($a = 3$ for CH₂, $a = 7$ for SiH₂). Let us denote the two highest molecular orbitals used in the calculations (the frontier orbitals) by ψ_b and ψ_c , respectively, where $b = a + 1$ and $c = a + 2$.

The total energies of the molecules are first separated into the nuclear repulsion and electronic energy components. The electronic energies of the singlet ($E_{\text{el}}^{(1)}$) and the triplet ($E_{\text{el}}^{(3)}$) states are decomposed as shown in eqs 1 and 2, respectively,¹⁷ where the left-hand superscripts s and t denote the singlet and triplet states, respectively:

$$E_{\text{el}}^{(1)} = E^{(c)} + {}^s E_1^{(f)} + {}^s E_{\text{ee}}^{(f)} + {}^s E_{\text{ee}}^{(fc)} \quad (1)$$

$$E_{\text{el}}^{(3)} = E^{(c)} + {}^t E_1^{(f)} + {}^t E_{\text{ee}}^{(f)} + {}^t E_{\text{ee}}^{(fc)} \quad (2)$$

where

$$E^{(c)} = \sum_{i=1}^a (2h_{ii} + \gamma_{ii}) + 2 \sum_{i < j}^{a-1} (2\gamma_{ij} - \delta_{ij}) \quad (3)$$

$${}^s E_1^{(f)} = 2h_{bb}; \quad {}^t E_1^{(f)} = h_{bb} + h_{cc} \quad (4)$$

$${}^s E_{\text{ee}}^{(f)} = \gamma_{bb}; \quad {}^t E_{\text{ee}}^{(f)} = \gamma_{bc} - \delta_{bc} \quad (5)$$

$${}^s E_{\text{ee}}^{(fc)} = 2 \sum_{i=1}^a (2\gamma_{ib} - \delta_{ib}) \quad (6)$$

$${}^t E_{\text{ee}}^{(fc)} = \sum_{i=1}^a [2(\gamma_{ib} + \gamma_{ic}) - (\delta_{ib} + \delta_{ic})] \quad (7)$$

$$E^{(f)} = E_1^{(f)} + E_{\text{ee}}^{(fc)} \quad (8)$$

$$\gamma_{ij} = (ii|jj) \text{ and } \delta_{ij} = (ij|ji) \quad (9)$$

where

$$(ij|kl) = \int \int \psi_i(1)\psi_j(1)(1/r_{12})\psi_k(2)\psi_l(2)d\mathbf{v}_1d\mathbf{v}_2 \quad (10)$$

The meaning of the different terms is as follows: $E^{(c)}$ describes the electronic energy contributions in the one-determinant approximation of the doubly occupied orbitals from 1 to a (referred to as “core”, hence the superscript (c)). This expression is common to the singlet and triplet electronic energies. The terms $E_1^{(f)}$, $E_{\text{ee}}^{(f)}$, and $E_{\text{ee}}^{(fc)}$ are different for the singlets and triplets, and they are denoted by superscripts s and t, respectively. The superscript (f) refers to the “frontier” electrons, i.e., the two electrons in the highest molecular orbitals, Ψ_b in the singlet state and Ψ_b and Ψ_c in the triplet state. $E_1^{(f)}$ gives the contribution from the kinetic energy and

Table 1. Optimized Geometries^a of CH₂ and SiH₂ at the CASSCF Level^{b,c}

	parameter	¹ A ₁	³ B ₁
CH ₂	r^d	1.126 (1.115)	1.090 (1.083)
	θ^e	101.06 (101.42)	131.32 (133.06)
SiH ₂	r^d	1.539 (1.515)	1.498 (1.477)
	θ^e	94.25 (92.52)	117.97 (118.49)

^a Distances in Å, angles in deg. ^b At MCSCF, see text for a definition of the basis set and the CASSCF procedure. ^c The values in parentheses are optimized at CCSD/6-311++G(d,f). ^d $r = r(\text{M}-\text{H})$. ^e $\theta = \angle \text{H}-\text{M}-\text{H}$.

Table 2. Energy Data (Hartrees) at the CASSCF Level for CH₂ and SiH₂

	state	nuclear (E_{nuc})	electronic (E_{el})	total (E_{tot})
CH ₂	¹ A ₁	5.94259	−44.89715	−38.95455
	³ B ₁	6.08671	−45.05837	−38.97166
SiH ₂	¹ A ₁	9.86371	−299.94154	−290.07783
	³ B ₁	10.09775	−300.14654	−290.04880

nuclear attraction of the two electrons in the highest molecular orbitals. $E_{\text{ee}}^{(f)}$ is the two-electron repulsion contribution (hence the subscript (ee)) between the two “frontier” electrons (both in Ψ_b in the singlet and in Ψ_b and Ψ_c in the triplet), and $E_{\text{ee}}^{(fc)}$ gives the electron repulsion contribution between the electrons found in the two highest orbitals (Ψ_b and Ψ_c) and between those in all other doubly occupied orbitals (Ψ_i , $i = 1, \dots, a$). In eqs 3–7, h_{ij} is the diagonal matrix element of the one-electron Hamiltonian (kinetic energy and nuclear attraction) over the molecular orbitals i ; the terms γ_{ij} and δ_{ij} are defined in eqs 9 and 10.

The wave functions for the ¹A₁ and ³B₁ states of methylene and silylene were decomposed into the energy terms described by eqs 1–7 above. The ³B₁ state of these species is reasonably well characterized by a single configuration, (core)1a₁²1b₂²2a₁¹1b₁¹ (only the valence ns and np electrons of C ($n = 2$) and Si ($n = 3$), along with the 1s electrons of H, are shown). A complete description of the ¹A₁ state of both species required two configurations: the dominant one, (core)1a₁²1b₂²2a₁², and a less important configuration, (core)1a₁²1b₂²1b₁². The energy decomposition was performed for the single configuration in the ³B₁ wave function and for both configurations for the ¹A₁ wave functions. Cross-products between the two singlet configurations were not evaluated. For the ¹A₁ state, we have used only the contribution of the dominant (core)1a₁²1b₂²2a₁² configuration in the calculation of singlet–triplet energy differences of the various energy decomposition components. The integrals in the atomic basis set were transformed over the appropriate set of CASSCF natural orbitals at the optimized CASSCF geometry.

Results and Discussion

The calculated optimized geometries of the singlet and triplet states of SiH₂ and CH₂ are given in Table 1. The results of the CASSCF energy calculations are shown in Table 2, decomposition into the various energy terms is given in Table 3, and the singlet–triplet energy differences (ΔE_{ST}) are summarized in Table 4.

The singlet–triplet energy differences are calculated to be −10.8 and 18.2 kcal/mol for CH₂ and SiH₂, respectively. These values compare favorably both to previously calculated values (at similar levels of theory) of −8.7 to −9.0⁵ and 20–21.0^{7a,f-k} kcal/mol, respectively, and to the experimental values.^{5,6}

Let us proceed now to discuss the contribution of each of the above-mentioned energy components, i.e., E_{nuc} , E_{el} , $E^{(c)}$, $E^{(f)} = E_1^{(f)} + E_{\text{ee}}^{(fc)}$, and $E_{\text{ee}}^{(f)}$, to the total energies of the singlet and triplet states of the MH₂

(21) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S. J.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347.

Table 3. Energy Decomposition Data (Hartrees) for the 1A_1 and 3B_1 States of CH_2 and SiH_2

	state	coeff ^a	config ^b	$E^{(c)}$	$E^{(f)}$	$E_{ee}^{(f)}$
CH_2	1A_1	0.9661	$1a_1^2 1b_2^2 2a_1^2$	-43.33338	-2.11872	0.61857
	3B_1	-0.1808	$1a_1^2 1b_2^2 1b_1^2$	-43.33338	-1.68930	0.62667
SiH_2	1A_1	0.9865	$1a_1^2 1b_2^2 2a_1 1b_1$	-43.68699	-1.79406	0.46246
	3B_1	-0.1886	$1a_1^2 1b_2^2 1b_1^2$	-298.7430	-1.56776	0.42189
	3B_1	0.9865	$1a_1^2 1b_2^2 2a_1 1b_1$	-299.1123	-1.29651	0.29372

^a Expansion coefficient in the CASSCF wave function. ^b Only the valence electrons (C: $2s^2 2p^2$; Si: $3s^2 3p^2$; H: $1s$) are shown.

(M = C, Si) molecules and to their singlet–triplet energy differences. The singlet–triplet energy differences (ΔE_{ST}) of the total energy and of each of these decomposition terms (listed in Table 4) are depicted schematically in Figure 3.

A. Nuclear Repulsion Energy (E_{nuc}). This component of the total energy is always more positive (i.e., more destabilizing) for the species having a triplet multiplicity. Thus, the nuclear repulsion energy term favors the singlet state for both CH_2 and SiH_2 (Table 4 and Figure 3). This trend is caused by the fact that the M–H bonds are shorter in the triplet states than in the corresponding singlet states; that is, $r(H-C) = 1.126$ vs 1.090 Å, $r(H-Si) = 1.539$ vs 1.498 Å in the singlets and triplets, respectively. The wider H–M–H bond angles in the triplets than in the singlets (i.e., H–C–H = 131.32° vs 101.06° , H–Si–H = 117.97° vs 94.25° , respectively) decrease the hydrogen–hydrogen nuclear repulsion in the triplets, but this effect is apparently much smaller than the increase of the M–H repulsion caused by the shortening of this bond.¹⁸

The difference in the nuclear repulsion energies (ΔE_{nuc}) between the singlets and the triplets favoring the singlets is larger for SiH_2 than for CH_2 , i.e., 146.9 and 90.4 kcal/mol, respectively, consistent with the fact that the change in the M–H bond length between the singlet to the triplet is larger in SiH_2 . The larger positive value of ΔE_{nuc} for SiH_2 than for CH_2 indicates that for this component of the total energy the singlet state for SiH_2 is more favored than for CH_2 , by ca. 56 kcal/mol.

B. Electronic Energy (E_{el}). We will first discuss the contribution of the total electronic energy E_{el} and then the contribution of each of its corresponding components, $E^{(c)}$, $E^{(f)}$, and $E_{ee}^{(f)}$. $E^{(c)}$ is the contribution to the total electronic energy (kinetic energy + nuclear–electron attraction energy + electron–electron repulsion energy) of all electrons except the two highest in energy (the “core” electrons). This expression is the same for the singlet and the triplet electronic energies. $E^{(f)}$ and $E_{ee}^{(f)}$ are energy terms that are both associated with the two highest energy electrons (the “frontier” electrons), and they are therefore different for the singlets and for the triplets. $E^{(f)}$ is the sum of the kinetic energy and

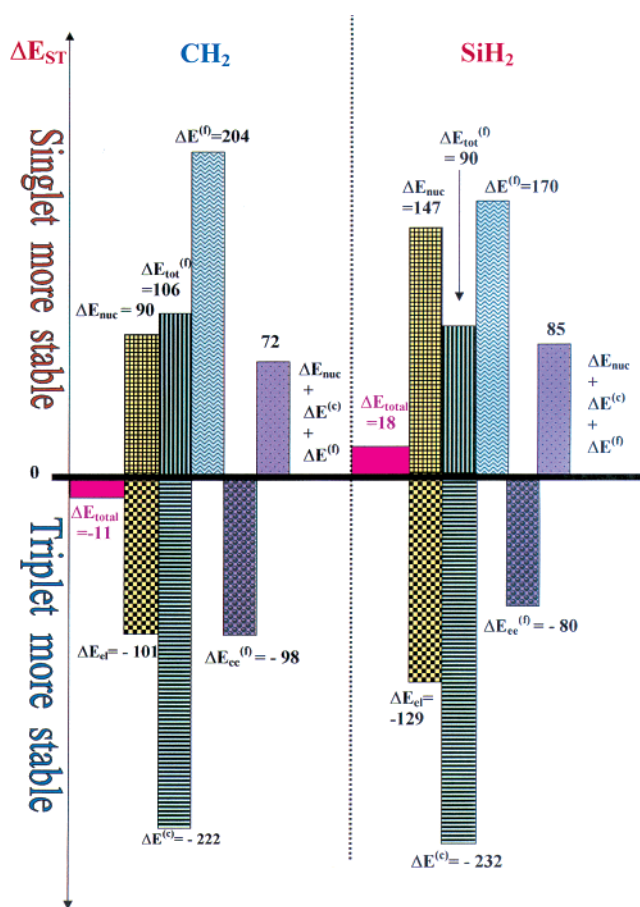


Figure 3. Schematic drawing of the singlet–triplet energy differences (kcal/mol) for CH_2 and SiH_2 , calculated for each of the energy decomposition terms: E_{nuc} , E_{el} , $E^{(c)}$, $E^{(f)}$, and $E_{ee}^{(f)}$. ΔE_{total} is the singlet–triplet energy gap and $\Delta E_{el} = \Delta E_{total} - \Delta E_{nuc}$, both calculated using the full CASSCF wave function.²² All other energy terms were calculated using the dominant configuration of the singlet and triplet CASSCF wave functions; $\Delta E_{tot}^{(f)} = \Delta E^{(f)} + \Delta E_{ee}^{(f)}$.

electron–nuclear attraction energy of the two frontier electrons ($E_1^{(f)}$), plus the repulsion energy between these electrons and all other electrons (i.e., the “core” electrons, $E_{ee}^{(fc)}$); $E_{ee}^{(f)}$ measures the electronic repulsion between the two frontier electrons.

Table 2 and Figure 3 show that the total electronic energy, E_{el} , of the MH_2 species is always more negative (i.e., more stabilizing) for the species with triplet multiplicity. Thus, in contrast to the nuclear repulsion energy which favors the singlet states, the electronic energy favors the triplet species. This trend can again be attributed to the shorter M–H bonds in the triplets than in the singlets and to the fact that the repulsion between the two electrons that occupy the same orbital in the singlet is relieved in the triplet (see also below).

Table 4. Singlet–Triplet Energy Differences (ΔE , kcal/mol)^a for the Individual Energy Decomposition Terms^b

	ΔE_{total}	ΔE_{nuc}	ΔE_{el}^c	$\Delta E^{(c)}$	$\Delta E^{(f)}$	$\Delta E_{ee}^{(f)}$	$\Delta E_{tot}^{(f)d}$	$\Delta E_{el}(dec)^e$
SiH_2	18.2	146.9	-128.6	-231.8	170.2	-80.4	89.8	-142.0
CH_2	-10.8	90.4	-101.2	-221.9	203.7	-98.0	105.7	-116.2
$\Delta \Delta E(SiH_2-CH_2)^f$	29.0	56.5	-27.4	-9.9	-33.5	17.6	-15.9	-25.8

^a A negative value indicates that the singlet is less stable than the triplet. ^b The energy differences of the decomposition terms, $\Delta E^{(c)}$, $\Delta E^{(f)}$, $\Delta E_{ee}^{(f)}$, $\Delta E_{tot}^{(f)}$, and $\Delta E_{el}(dec)$, were calculated using only the dominant configuration of the CASSCF wave function. ^c $\Delta E_{el} = \Delta E_{total} - \Delta E_{nuc}$, calculated using the full CASSCF wave function, see ref 22. ^d $\Delta E_{tot}^{(f)} = \Delta E^{(f)} + \Delta E_{ee}^{(f)}$. ^e $\Delta E_{el}(dec)$ is the sum of the electronic decomposition terms $\Delta E^{(c)} + \Delta E_{tot}^{(f)}$, see ref 22. ^f A positive sign indicates that the silylene favors the singlet state more than CH_2 .

The singlet–triplet electronic energy difference ΔE_{el} is more negative for SiH_2 than for CH_2 (−129 and −101 kcal/mol, respectively²²), indicating that E_{el} favors the triplet for SiH_2 more than for CH_2 .

Let us now discuss the individual decomposition terms.

$E^{(c)}$ has a large absolute value compared to $E^{(f)}$ and $E_{\text{ee}}^{(f)}$ (Table 3), because it includes interactions involving more electrons. However the *differences* in the $E^{(c)}$ term between the singlets and triplets, $\Delta E^{(c)}$, in CH_2 and SiH_2 are quite similar, −222 kcal/mol for CH_2 and −232 kcal/mol for SiH_2 (Table 4 and Figure 3), favoring the silylene triplet over the methylene triplet by 10 kcal/mol.

$E^{(f)}$ favors the singlets for both species, but the difference is greater for CH_2 than for SiH_2 by about 33 kcal/mol (Table 4 and Figure 3).

Of the electronic energy terms, the most easily interpreted is $E_{\text{ee}}^{(f)}$, describing the repulsion between the two frontier electrons. This term behaves as expected from simple qualitative arguments based on Hund's rule. Thus $E_{\text{ee}}^{(f)}$ is larger in the singlets where both electrons reside in the same orbital than in the triplet configuration where they occupy different orbitals. The preference for the triplet state becomes smaller on moving down the periodic table, because, for example, in Si the two electrons are placed in more diffuse orbitals than in C, and in the singlet state the repulsion between the two electrons is therefore smaller than for C.^{16b}

The results of our energy decomposition calculations show that several common assumptions concerning chemical bonding are not fully justified. First, the ground state multiplicities of CH_2 and SiH_2 are not explained by changes associated with the frontier electrons alone. Actually, the sum of all energy terms involving the frontier electrons, $\Delta E_{\text{tot}}^{(f)}$, acts in the direction *opposite to experiment*, favoring the singlet state of CH_2 over the singlet state of SiH_2 by 16 kcal/mol. Nor can the multiplicity of CH_2 and SiH_2 be understood from the changes of the energies of all electrons, frontier and “core” together. Thus, *the total electronic energies, ΔE_{el} , operate counter to experiment* by yet a larger amount than $\Delta E_{\text{tot}}^{(f)}$, favoring the triplet state of SiH_2 over the triplet of CH_2 by 27 kcal/mol. To understand the triplet and singlet preference of CH_2 and SiH_2 , the differences in *the nuclear repulsion energies*—ignored in most qualitative treatments of bonding—*must also be taken into account*.^{18,23}

(22) These values correspond to $\Delta E_{\text{el}} = \Delta E_{\text{total}} - \Delta E_{\text{nuc}}$ and were calculated using the full CASSCF wave function. Note, that $\Delta E_{\text{el}}(\text{dec})$ calculated from the sum of the electronic decomposition components, i.e., $\Delta E^{(c)} + \Delta E_{\text{tot}}^{(f)}$, are somewhat different, i.e., −142 and −116 kcal/mol for SiH_2 and CH_2 , respectively, underestimating the stability of the singlet states of SiH_2 and CH_2 by a similar amount of 13 and 15 kcal/mol, respectively. This relative destabilization in the decomposition type calculations of the singlet species may result from the fact that in the calculation of the singlets we have included only the dominant (core) $1a_1^2 1b_2^2 2a_1^2$ configuration and have neglected the contributions of the minor configurations and of the cross terms that contribute to the CI stabilization. In contrast, the decomposition terms of the triplet 3B_1 states are well characterized by a single configuration, and therefore the corresponding decomposition terms are calculated accurately. Note, however, that $\Delta \Delta E_{\text{el}}(\text{dec})(\text{SiH}_2 - \text{CH}_2) = -26$ kcal/mol and $\Delta \Delta E_{\text{tot}}(\text{dec})(\text{SiH}_2 - \text{CH}_2) = 31$ kcal/mol, calculated from the decomposition terms, are very similar to those calculated using the full CASSCF wave function, from ΔE_{total} and $\Delta E_{\text{el}} = \Delta E_{\text{total}} - \Delta E_{\text{nuc}}$, i.e., −28 and 29 kcal/mol, respectively (Table 4, Figure 3), making our analysis valid despite the differences in the individual values of $\Delta E_{\text{total}}(\text{dec})$ and $\Delta E_{\text{el}}(\text{dec})$ vs ΔE_{total} and ΔE_{el} , respectively.

Now let us proceed to analyze how the energy terms that have been computed contribute to the difference between the ground state multiplicities of SiH_2 and CH_2 ($\Delta \Delta E_{\text{ST}}$). In doing this, it is important to realize that the 29 kcal/mol energy difference that makes their properties so diverse represents a small difference between very large numbers. As a result, several different interpretations are possible, depending on which terms are emphasized.

First, the singlet–triplet energy difference caused by the nuclear repulsion energy, ΔE_{nuc} , favoring the singlet states can be compared with the total electronic energy, ΔE_{el} , which favors the triplet states. The balance between these two terms determines whether the ground state is a singlet or a triplet. For CH_2 , ΔE_{el} is larger (and of opposite sign) than ΔE_{nuc} , leading to a triplet ground state. For SiH_2 the absolute value of ΔE_{nuc} is larger than ΔE_{el} , and consequently the ground state for this species is a singlet (Table 4, Figure 3).²⁴

Let us consider now the effects on the multiplicity of the terms that contribute to ΔE_{el} , the quantity that the various qualitative arguments, such as those presented in the Introduction, attempt to analyze. First we separate ΔE_{el} into two terms: $\Delta E^{(c)}$, traced to the contribution of the “core” electrons, and $\Delta E_{\text{tot}}^{(f)}$, which describes the total contribution of the two frontier electrons. The contribution of the “core” electrons is generally ignored in qualitative electronic arguments because common chemical intuition argues that the contribution of the “core” electrons on ΔE_{ST} should be zero or tiny. Surprisingly we find that the “core” electrons contribute quite significantly ($\Delta \Delta E^{(c)}(\text{SiH}_2 - \text{CH}_2) = -10$ kcal/mol), although their effect is smaller than that of the frontier electrons ($\Delta \Delta E_{\text{tot}}^{(f)}(\text{SiH}_2 - \text{CH}_2) = -16$ kcal/mol). Moreover, as pointed out above, both terms act so as to favor a triplet state for the silylene over a triplet state for the carbene, contrary to the trend in the total singlet–triplet energy difference, ΔE_{tot} , and in the corresponding $\Delta \Delta E_{\text{ST}}$.

What is the role of the frontier electrons, which are the only ones that were considered in previous discussions (see Introduction)? To analyze this, we factor out the electron–electron repulsion between these two electrons. The remaining part is $\Delta E^{(f)}$, which is positive for both CH_2 and SiH_2 , but it is larger for CH_2 by 33 kcal/mol, favoring a singlet state for CH_2 over SiH_2 (Table 4, Figure 3). Thus, also the $\Delta E^{(f)}$ term acts in contradiction to the trend of the ground state multiplicities of these species.

The *only* electronic term that acts in the right direction, i.e., favors the singlet state of SiH_2 over that of CH_2 , is $\Delta E_{\text{ee}}^{(f)}$. This term favors the triplet state over

(23) It is generally assumed that small changes in the nuclear positions will be reflected in the electronic energy in such a way that one can neglect the changes in the nuclear energy and analyze only the changes in the electronic energy.

(24) The effect of the change in the geometry on going from the triplet to the singlet cannot explain the multiplicity difference. Thus, similar results are obtained even if the geometries of the species are kept unchanged on changing the multiplicity (i.e., a vertical transition). Thus, when calculating the triplet using the optimized geometry of the singlet, ΔE_{ST} is 25 and −0.4 kcal/mol for SiH_2 and CH_2 , respectively, and when the singlets are kept in the triplet geometries, ΔE_{ST} are 9.9 and −22.6 kcal/mol for SiH_2 and CH_2 , respectively. Thus $\Delta \Delta E_{\text{ST}}$ values for the “frozen” geometries, of 25.4 and 32.5 kcal/mol, respectively, remain nearly the same as $\Delta \Delta E_{\text{ST}}$ of 29 kcal/mol obtained for the fully optimized species.

the singlet state by 98 kcal/mol for CH₂ but by only 80 kcal/mol for SiH₂. Thus of the total difference of 31 kcal/mol (calculated from the sum of $\Delta\Delta E(\text{SiH}_2-\text{CH}_2)$ of the decomposition terms²²), 18 kcal/mol could be attributed to this term. The remaining 13 kcal/mol could then be traced to the sum of ΔE_{nuc} , $\Delta E^{(c)}$, and $\Delta E^{(f)}$ (see Figure 3).²⁵

Conclusion

Energy decomposition of the CASSCF computations for CH₂ and SiH₂ shows that many factors are involved in determining their multiplicity. One of the major surprises of this study is that the total electronic energies run counter to experiment (or to the total calculated energies) and that *nuclear repulsion energies—ignored in most qualitative treatments—must be taken into account in order to understand the different multiplicities of CH₂ and SiH₂*. However, of the 31²² kcal/mol energy difference in the singlet–triplet splitting between these species, which we wish to understand, about 60% may be attributed to the difference in electron–electron repulsion between the two frontier electrons. This term is relaxed on going from the singlet state, where the electrons occupy the same orbital, to the triplet, where each electron occupies a separate orbital, and as expected from qualitative considerations, this relaxation is greater for CH₂ than for SiH₂.

The remaining 40% of the energy difference could be assigned mainly to a complex balance of the terms which express attraction to the nucleus of the two frontier electrons, their kinetic energy, and the repulsion of these electrons from all other electrons as well as the energy of the “core” electrons and the nuclear repulsion

energy. This result is a very interesting new insight, as it expresses the importance of new factors not considered previously and it indicates their complex nature. Furthermore, not all these terms are related to the frontier electrons, which are the only electrons referred to in qualitative discussions. All of these terms may be associated (although in a complex way not explored by us) with changes in the HOMO–LUMO gap and in s and p orbital occupancy, as described in the Introduction.

In closing, the following philosophical comment might be in order. The analysis above demonstrates again the vast complexity of the chemical bond. Detailed analysis of fundamental electronic terms can lead to important insights, but it also makes our qualitative models more nebulous and more difficult to apply. It seems that in the near future chemists will still have to find a delicate balance between using qualitative and incomplete models to guide their chemical intuition and their attempts to carry out quantitative calculations of fundamental bonding questions. Eventually, we can hope that quantitative considerations of the kind carried out in this paper will lead to better models and a more detailed understanding of the chemical bond.

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