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K. Balasubramanian and A. D. McLean

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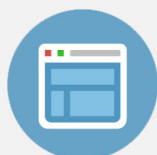
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# The singlet-triplet energy separation in silylene

K. Balasubramanian<sup>a)</sup>

Department of Chemistry, Arizona State University, Tempe, Arizona 85287

A. D. McLean

IBM Almaden Research Center, San Jose, California 95120-6099

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MCSCF calculations followed by large scale configuration interaction, comparable with the best done for isovalent methylene, give a singlet-triplet splitting in silylene of  $21.0 \pm 1$  kcal/mol. The singlet is the lower energy state. Structural parameters for the as yet unobserved triplet are  $r_e = 1.48 \pm 0.005$  Å and  $\theta_e = 118.5 \pm 1^\circ$ .

## INTRODUCTION

After many experimental and theoretical studies over more than 20 years,<sup>1</sup> an accurate value for the energy separation of the ground  $X^3B_1$  and excited  $\tilde{a}^1A_1$  lowest electronic states of the methylene radical,  $\text{CH}_2$ , has been obtained. The last word is a spectroscopic determination, reported in Ref. 1, that  $T_0 = 9.05 \pm 0.06$  kcal/mol and  $T_e = 8.56 \pm 0.09$  kcal/mol. However, the experimental path to this result,<sup>1</sup> going through values clustered in the 0–3 kcal/mol range, and 8–9 kcal/mol range, and one value of 19.5 kcal/mol,<sup>2</sup> has been much rockier than the computational one which, by 1982, had converged relatively smoothly to  $T_e = 9.8$  kcal/mol.<sup>3</sup> Until the spectroscopic work of Ref. 1, the most direct measurement was from the photoelectron spectrum of  $\text{CH}_2^-$ .<sup>2</sup> The value obtained was the 19.5 kcal/mol just referred to, making this result particularly disconcerting. However, a recent reinterpretation<sup>4</sup> of this spectrum, published concurrently with Ref. 1, gives  $T_0 = 9.3 \pm 0.6$  kcal/mol.

Because of the small size of the system, and fueled by the disarray in the ranks of experimentalists, computational chemists have generated wave functions for  $\text{CH}_2$  which approach the highest accuracy attained for any system; with large basis sets for orbital expansions, the wave functions are themselves expanded in the complete set of valence configurations plus all singly and doubly excited configurations that can be generated from the valence set in the given basis. Astonishingly, it was not until Werner and Reinsch's calculation,<sup>3</sup> that it was realized that  $f$  functions must be included in the basis for orbital expansions; doing so lowers the computed  $T_e$  by  $\sim 1$  kcal/mol. (This has been an almost universal deficiency in highly accurate work with Gaussian basis sets.)

In this paper we report calculations, at the same level of accuracy as the best done for methylene, on the isovalent radical silylene  $\text{SiH}_2$ . Relative to methylene, the lowest two states of silylene are reversed; the ground state is  $X^1A_1$  and the low lying excited triplet is  $\tilde{a}^3B_1$ , with dominant electron configurations  $\dots 4a_1^2 2b_2^2 5a_1^2$  and  $\dots 4a_1^2 2b_2^2 5a_1 2b_1$ , respectively. We also report calculations on the  $A^1B_1$  open shell singlet with the same  $\dots 4a_1^2 2b_2^2 5a_1 2b_1$  configuration as  $\tilde{a}^3B_1$ . (Orbitals  $4a_1$  and  $2b_2$  are the  $\text{SiH}$  bonds,  $5a_1$  is dominated by silicon  $3s$ , and  $2b_1$  is silicon  $3p$ .) This ordering ig-

nores the low lying "small angle"  $^3A_2$  and  $^1A_2$  states, discussed by Rice and Handy,<sup>5</sup> which are loose complexes of silicon  $^3P$  atom with a ground state hydrogen molecule.

Experimentally, the  $X^1A_1$  and  $A^1B_1$  states are well characterized.<sup>6</sup> In the ground state,  $r_0(\text{SiH}) = 1.516_3$  Å and  $\theta_0(\text{HSiH}) = 92.8^\circ$ ; in the  $^1B_1$  excited state,  $r_0(\text{SiH}) = 1.48_7$  Å and  $\theta_0(\text{HSiH}) = 123^\circ$  with a  $T_0 = 15\,533$   $\text{cm}^{-1}$  (44.4 kcal/mol). The only experimental information on the triplet comes from the photoelectron spectrum of  $\text{SiH}_2^-$  from which value of  $T_0 < 14$  kcal/mol is deduced.<sup>7</sup> Computationally, the best available wave functions<sup>8</sup> give  $T_e = 16.8$  kcal/mol for the  $\tilde{a}^3B_1$  state of silylene. These wave functions are expanded in a single-configuration SCF function plus all singly and doubly excited configurations relative to it for  $\tilde{a}^3B_1$ , and in the two configurations of a two-configuration SCF wave function plus the singly and doubly excited configuration space derived from them in the  $X^1A_1$  state; however, the basis for orbital expansion is only of double-zeta-plus polarization (DZP) quality. Combining this result with that of an earlier SCF calculation<sup>9</sup> (one-configuration for  $\tilde{a}^3B_1$  and two-configuration for  $X^1A_1$ ) where the orbital expansions were in a much larger basis, although still without  $f$  functions, Colvin *et al.*<sup>8</sup> were able to predict a  $T_e$  in the neighborhood of 20 kcal/mol. (In that earlier work, Meadows and Schaefer<sup>9</sup> had, by direct SCF computation, obtained  $T_e = 18.6$  kcal/mol but, influenced by the then chaotic situation with methylene, chose, as being more reliable, an indirect determination which combined the experimentally known  $X^1A_1$ – $A^1B_1$  separation with a computed  $\tilde{a}^3B_1$ – $A^1B_1$  separation. This indirect determination gave a singlet-triplet splitting of 10 kcal/mol in silylene. Their argument was that the single-configuration SCF separation of  $\tilde{a}^3B_1$  and  $A^1B_1$ , both with the same dominant open shell configuration, would be accurate because of equal correlation errors in both states. From what we know now, the argument is fallacious and, in fact, there is  $\sim 10$  kcal/mol more correlation energy in  $A^1B_1$  than in  $\tilde{a}^3B_1$ .) More recent computational information on the singlet-triplet splitting comes from Rice and Handy's<sup>5</sup> CASSCF calculations which, with a DZP quality basis, give 17.5 kcal/mol (0.759 eV). Equivalent calculations<sup>5</sup> on methylene gave 9.8 kcal/mol (experiment 8.56 kcal/mol); applying a 1.2 kcal/mol correction to silylene but with the opposite sign, because of the state reversal relative to methylene, would lead to a silylene singlet-triplet splitting of 18.7 kcal/mol.

<sup>a)</sup> Alfred P. Sloan Fellow. Camille and Henry Dreyfus Teacher-Scholar.

In summary, computational estimates are pointing to a singlet–triplet splitting near 20 kcal/mol in silylene while experiment indicates  $\leq 14$  kcal/mol. Our calculations, described below, confirm the theoretical estimate.

## CALCULATIONS

Our basis for orbital expansions starts from the Si(12s,9p/6s,5p) contracted Gaussian set of McLean and Chandler,<sup>10</sup> of triplet-zeta valence quality, and a H(5s/3s) set of comparable quality. From this, two polarized basis sets were derived. The first, referred to as the *f* basis, augments the silicon basis with two Gaussian six-component 3*d* functions (exponents 0.56, 0.14) and a ten-component 4*f* function (exponent 0.38). The hydrogen basis is augmented by 2*p*(0.75). The second referred to as the *d* basis and derived from the same starting unpolarized basis, has three sets of added 3*d* functions (exponents 0.99, 0.33, 0.11), and one diffuse set of 2*p* functions (exponent 0.03) on silicon, and a 2*p*(0.9) set on each hydrogen.

Three levels of wave function were computed for the  $X^1A_1$ ,  $\tilde{a}^3B_1$ , and  $A^1B_1$  states of silylene:

(1) MCSCF wave functions in the complete configuration space of the strongly occupied orbitals of the separated atoms—commonly referred to as CASSCF wave functions. The  $1s^2 2s^2 2p^6$  core of Si is not correlated; the configuration space is generated by distributing the remaining six electrons of SiH<sub>2</sub> in all possible ways into orbitals which, at large interatomic separation, span the space of Si 3*s* and 3*p* and H 1*s*; a space of five *a'* and one *a''* orbitals in the *C<sub>s</sub>* symmetry in which all calculations were done. These calculations are labeled CAS-*f* and CAS-*d* in the two polarized bases described above.

(2) First order wave functions expanded in the zeroth order MCSCF configuration space (six electrons in all possible ways in the five *a'* and one *a''* MCSCF orbitals determined in CAS-*f* and CAS-*d*), plus the first order space (five electrons in all possible ways in the six active MCSCF orbitals, and one electron in the MCSCF virtual space—the orthogonal complement of the MCSCF orbital space in either the *f* or the *d* basis). These wave functions are labeled FOCI-*f* and FOCI-*d*.

(3) Second order wave functions expanded in the configuration space of FOCI-*d* and FOCI-*f*, plus the second order space (four electrons in all possible ways in the six active MCSCF orbitals and two electrons in the MCSCF virtual space); they are labeled SOCI-*f* and SOCI-*d*.

We have made an empirical correction to the second order results which estimates the effect of higher order unlinked cluster configurations. It is patterned on the Davidson correction for a single reference configuration.<sup>11</sup> The corrected second order energy  $E[\text{SOCI}(\text{D})]$  is given by

$$E[\text{SOCI}(\text{D})] = E(\text{SOCI})$$

$$- \left( 1 - \sum_I C_I^2 \right) [E_{\text{ref}} - E(\text{SOCI})],$$

where *I* runs over the zeroth order configuration space, *C<sub>I</sub>* are the expansion coefficients in the SOCI wave function of the zeroth order functions, and  $E_{\text{ref}}$  is the energy of a wave function derived from the second order wave function by

setting the expansion coefficients of all first and second order terms to zero and then renormalizing.

Table I shows the dimensions of the configuration spaces for our wave function expansions. All calculations were done with the IBM San Jose ALCHEMY II programs.<sup>12</sup>

## RESULTS AND DISCUSSION

Table II contains our results. For CAS and FOCI wave functions, we report equilibrium geometries and adiabatic energy separations. At the SOCI level we report only results with the *f* basis. SOCI-*f* total energies are  $\sim 1$  kcal/mol lower than SOCI-*d*, and the SOCI-*f* basis has the superior composition. A commonly seen trend of too long CAS and FOCI bond lengths corrected to near experimental values by SOCI is observed.

We note that the Davidson correction makes gratifyingly small changes in our SOCI  $T_e$  values—as is expected for these extended CI expansions. Our best computed results for  $T_e(X^1A_1 - \tilde{a}^3B_1)$  is the SOCI-*f* result of 19.6 kcal/mol; the unchanged prediction after applying a Davidson-type correction indicates that this value is near the complete CI results in our chosen orbital basis. McLean has done comparable methylene calculations (unpublished) which give an adiabatic singlet–triplet splitting  $\sim 1.5$  kcal/mol more than the true one, close to that observed by other workers and reviewed in our Introduction. These calculations are missing  $\sim 1.5$  kcal/mol more correlation energy in the closed shell singlet than in the open shell triplet due to the finite size of the orbital basis. A similar effect in our silylene calculations, noting the reversal of the state ordering, would increase  $T_e$  by a  $\sim 1.5$  kcal to 21.1 kcal/mol. Werner and Reinsch<sup>3</sup> have calculated a core-valence correlation effect in CH<sub>2</sub> which increases the singlet–triplet  $T_e$  by 0.2 kcal/mol. The effect may be considerably bigger in SiH<sub>2</sub> and, again, in the opposite direction. The effect of *f* functions in the orbital basis on the value of  $T_e$  is smaller ( $\sim 0.2$  kcal/mol) in silylene than in methylene ( $\sim 1$  kcal/mol).<sup>3</sup>

We have no reliable information on the value of the zero point correction to the silylene singlet–triplet  $T_e$ . Comparison with methylene shows why this correction must be determined with considerable care. Analysis of the methylene spectra<sup>1</sup> shows that the singlet state contains 0.5 kcal/mol more zero point energy than the triplet, while computed estimates run from 1 kcal/mol more to 0.5 kcal/mol less.<sup>3</sup> In silylene, based on harmonic frequencies, Colvin *et al.*<sup>8</sup> indi-

TABLE I. Dimension of configuration spaces for SiH<sub>2</sub> wave function expansions.<sup>a</sup>

	$X^1A_1$	$\tilde{a}^3B_1$	$A^1B_1$
CAS- <i>f</i> , CAS- <i>d</i>	100	99	75
FOCI- <i>f</i>	4 900	6 531	4 515
FOCI- <i>d</i>	4 805	6 382	4 400
SOCI- <i>f</i>	109 190	162 721	103 505
SOCI- <i>d</i>	104 800	155 142	98 550

<sup>a</sup> The *f* basis is (12s9p2d 1f/6s5p2d 1f) for Si. The *d* basis is (12s10p3d/6s6p3d) for Si. Both basis sets are (5s1p/3s1p) for each H. Configuration count is for *C<sub>s</sub>* symmetry.

TABLE II. Structures and energies for silylene.<sup>a</sup>

		$X^1A_1$	$\bar{a}^3B_1$	$A^1B_1$
CAS- <i>f</i>	$r_e$	1.542	1.501	1.514
	$\theta_e$	94.5	118.4	120.4
	Energy <sup>b</sup>	-290.077 972	18.2	45.6
CAS- <i>d</i>	$r_e$	1.536	1.497	1.510
	$\theta_e$	94.3	118.1	121.0
	Energy <sup>b</sup>	-290.077 589	17.9	45.8
FOCI- <i>f</i>	$r_e$	1.542	1.511	1.515
	$\theta_e$	92.9	118.7	122.6
	Energy <sup>b</sup>	-290.102 199	17.4	43.8
FOCI- <i>d</i>	$r_e$	1.541	1.507	1.514
	$\theta_e$	92.0	117.9	122.1
	Energy <sup>b</sup>	-290.100 917	17.2	44.7
SOCl- <i>f</i>	$r_e$	1.520	1.484	1.493
	$\theta_e$	92.7	118.4	122.3
	Energy <sup>b</sup>	-290.159 62 <sup>c</sup>	19.6	44.5
SOCl- <i>f</i> (D)	$r_e$	1.519	1.484	1.493
	$\theta_e$	92.5	118.5	122.7
	Energy <sup>b</sup>	-290.163 76 <sup>c</sup>	19.6	44.2
Experiment <sup>c</sup>	$r_0$	1.516 <sub>3</sub>		1.48 <sub>7</sub>
	$\theta_0$	92.8		123
	$T_0$			44.4
	Recommended		1.48 ± 0.005	
	$r_e$		118.5 ± 1	
	$\theta_e$			
	$T_e$		21.0 ± 1	

<sup>a</sup> Distances in Å, angles in deg, total energies in hartree, relative energies in kcal/mol.

<sup>b</sup> For  $X^1A_1$ , the total energy, in hartree. For  $\bar{a}^3B_1$  and  $A^1B_1$  the energy  $T_e$  relative to  $X^1A_1$ , in kcal/mol.

<sup>c</sup> Reference 6.

cate that there is 0.3 kcal/mol more zero point energy in the triplet than in the singlet, but a more accurate vibrational analysis is probably called for.

Comparison of the equilibrium structures of CH<sub>2</sub> and of SiH<sub>2</sub> shows that the bond angles are ~10° smaller in SiH<sub>2</sub>; in the  $^1A_1$  state CH<sub>2</sub> has 102.4°, SiH<sub>2</sub> 92.8°; in the  $^3B_1$  state CH<sub>2</sub> has 130°, SiH<sub>2</sub> 118°. This is a clear indication of more hybridization in CH<sub>2</sub> than in SiH<sub>2</sub>, which in turn means that the strongly occupied valence  $a_1$  orbital on the heavy atom has

more  $p$  character in CH<sub>2</sub> than in SiH<sub>2</sub>. This means that, in CH<sub>2</sub>, the  $a_1$  and  $b_1$  orbitals, singly occupied in the triplet state, come closer in energy than the corresponding orbitals in SiH<sub>2</sub>, as Meadows and Schaefer<sup>9</sup> observed. In methylene, the exchange stabilization arising from the parallel spins of electrons in the  $a_1$  and  $b_1$  orbitals leads to a lower energy than pairing two electrons in the lower  $a_1$  orbital. In silylene it does not.

## CONCLUSION

From second order calculations in an extended basis, consideration of the size of a Davidson-type correction for neglected unlinked cluster terms, and the differences between computation and experiment in isovalent methylene, we predict that the  $\bar{a}^3B_1$  state of silylene has an equilibrium geometry  $r_e = 1.48 \pm 0.005$  Å,  $\theta_e = 118.5 \pm 1^\circ$ , and  $T_e = 21.0 \pm 1$  kcal/mol.

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