Singlet–triplet energy gaps in fluorine-substituted methylenes and silylenes

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We report singlet and triplet state splittings (ΔE_{ST}) for fluorine-substituted *methylenes* and *silylenes* using dissociation-consistent configuration interaction (CI) (based on generalized valence bond wave functions). These relatively simple CI calculations emphasize *correlation consistency* between the singlet and triplet states. Values of ΔE_{ST} for CH_2, CF_2, SiH_2, and SiF_2 are in excellent agreement with available experimental results, and we expect the predictions for the other cases CHF (14.5) and SiHF (41.3) to be equally accurate. This result strongly suggests that the correct choice among the experimental values for ΔE_{ST} of CHF is 14.7 ± 0.2 kcal/mol.

I. INTRODUCTION

The structures, spectra, and reactivities of *methylenes* and *silylenes* have been of considerable experimental and theoretical interest.[1] The diverse chemical properties of *methylenes* and *silylenes* are strongly dependent upon the spin multiplicities of their low lying electronic states and the interstate energy gaps. Hence the energetics of these low lying electronic states are prerequisite to understanding the chemistry of *methylenes* and *silylenes*.

The parent molecule CH_2 has been studied extensively, and its singlet–triplet energy gap, ΔE_{ST} has been determined to be -8.998 ± 0.014 (T_0) kcal/mol, from experiment[2] and corroborated by theoretical calculations[3] (a negative value for ΔE_{ST} indicates a triplet ground state). However, there are only a few experimental data for the singlet–triplet energy gaps of the fluorine-substituted *methylenes* and *silylenes*.[4–7] Current knowledge about ΔE_{ST} for these systems is as follows.

From photoionization mass spectrometric studies of the SiH_2 radicals generated in the reaction of $F + SiH_4$, Berkowitz *et al.*[4] have reported a singlet–triplet energy gap in SiH_2 of either 21.0 ± 0.7 or 18.0 ± 0.7 kcal/mol. The two possible values arise from two possible assignments of either 9.15 or 9.02 eV, respectively, for the ionization potential (IP) of the singlet state SiH_2. Recent theoretical calculations by Bauschlicher *et al.*[3] suggest that values of 21.0 kcal/mol and 9.15 eV are the correct ΔE_{ST} and IP of SiH_2, respectively.

A value of 56.7 kcal/mol for $\Delta E_{ST}(CF_2)$ has been determined directly from observations of the $\tilde{a} \,^3B_1 \rightarrow \tilde{X} \,^1A_1$ phosphorescence transition of the triplet difluoromethylene produced in the reaction of oxygen atoms with tetrafluorethylene in the gas phase.[5]

A singlet–triplet splitting of 75.2 kcal/mol (or possibly 76.2 or 77.2) for SiF_2 has been assigned from the $\tilde{a} \,^3B_1 \rightarrow \tilde{X} \,^1A_1$ emission spectrum observed from a high frequency electrodeless discharge of flowing tetrafluorosilane.[6]

The most recent photoelectron spectroscopic studies of the halocarbene anions yield bounds for ΔE_{ST} of the halocarbenes.[7] These studies suggest that $\Delta E_{ST}(\text{CHF})$ is 14.7 ± 0.2, 11.4 ± 0.3, or 8.1 ± 0.4 kcal/mol (with 11.4 selected as most likely) and a lower bound on $\Delta E_{ST}(CF_2)$ is 50 ± 2 kcal/mol. No experimental observation exists for $\Delta E_{ST}(\text{SiHF})$.

Herein, we propose and apply a new level of CI that is correlation-consistent for both singlet and triplet states while retaining relative simplicity. Section II explains this dissociation-consistent configuration interaction (DCCI) method; Sec. III reports new results of ΔE_{ST} for CH_2, CHF, CF_2, SiH_2, SiHF, and SiF_2 obtained from the DCCI method. The convergence of the DCCI method with basis set in ΔE_{ST} of CH_2, SiH_2, and CHF is also included in Sec. III.

II. THEORETICAL METHODS

A. Basis sets

For the calculations of the singlet–triplet state splittings at various CI levels, we employed core double-ζ valence triple-ζ basis sets for carbon ($10s6p/5s3p$) (Refs. 8 and 9) and silicon ($11s7p/7s5p$) (Ref. 10) augmented with two sets of d polarization functions centered at 0.62 for carbon and 0.42 for silicon with an internal ratio of 2.3 [$\zeta^d(\text{C}) = 0.940$ and $0.409, \zeta^d(\text{Si}) = 0.637$ and 0.277]. In addition, one set of f functions was included, obtained by scaling the mean d exponents of 0.62 for carbon and 0.42 for silicon by 1.2 [$\zeta^f(\text{C}) = 0.893$ and $\zeta^f(\text{Si}) = 0.605$]. The s combination of d functions and p combination of f functions were excluded from all basis sets. Valence double-ζ basis sets[11] were used for hydrogen ($4s/2s$; scaled by 1.2 for hydrogen attached on carbon and unscaled for hydrogen attached on silicon) and fluorine ($9s5p/3s2p$), augmented with one set of p functions on hydrogen ($\zeta^p = 1.0$ and 0.6 for hydrogen attached on carbon and silicon, respectively) and one set of d functions on fluorine ($\zeta^d = 0.9$).

We also used the following basis sets for carbon, silicon, hydrogen, and fluorine to examine the convergence of ΔE_{ST} of CH_2, CHF, and SiH_2 with basis set:

TABLE I. Geometries of fluorine substituted methylenes and silylenes. Experimental geometries (Ref. 19) are in parentheses.

Molecule	State	r(C,Si–H) (Å)	r(C,Si–F) (Å)	Angle (deg)
CH₂ [a]	$^1A_1$	1.113		101.8
	$^3B_1$	1.084		133.2
CHF [b]	$^1A'$	1.104	1.294	103.3
	$^3A''$	1.073	1.304	121.1
CF₂ [c]	$^1A_1$		1.291	104.7
	$^3B_1$		1.303	118.2
SiH₂ [d]	$^1A_1$	1.508(1.516)		92.4(92.1)
	$^3B_1$	1.471		118.2
SiHF [d]	$^1A'$	1.520	1.625	97.6
	$^3A''$	1.475	1.625	115.8
SiF₂ [d]	$^1A_1$		1.616(1.590)	100.9(100.8)
	$^3B_1$		1.617	115.8

[a] Reference 15.
[b] Reference 16.
[c] Reference 17.
[d] For silylenes the geometry was optimized at the MP2/6-31$G**$ calculational level/basis sets for the singlet state and UMP2/6-31$G**$ for the triplet state.

C($3s2p1d$) and Si($4s3p1d$): Valence double-ζ basis sets were used for carbon ($9s5p/3s2p$) (Ref. 11) and silicon ($11s7p/4s3p$) (Ref. 12) augmented with one set of d functions on carbon ($\zeta^d = 0.62$) and silicon ($\zeta^d = 0.42$).

C($6s4p2d1f$): To the C($5s3p2d1f$) basis described above was added one set of diffuse $s(\zeta^s = 0.046)$ and $p(\zeta^p = 0.033)$ functions.

C($7s4p3d2f$): The Huzinaga ($11s7p$) basis[13] for carbon was contracted to ($6s3p$) triple-ζ for both core and valence, but diffuse s and p functions ($\zeta^s = 0.0388$ and $\zeta^p = 0.0282$) were added.[14] Three sets of carbon d polarization functions were added, centered at 0.620 with an internal ratio of 2.5 (leading to exponents $\zeta^d = 1.550, 0.620,$ and 0.248). Two sets of carbon f functions were included, centered at the previous f exponent of 0.893 with an internal ratio of 2.5 ($\zeta^f = 1.412$ and 0.565).

H($3s2p$): The Huzinaga unscaled ($6s$) basis[9] was contracted to triple-ζ, with two sets of p functions centered at 1.0 with an internal ratio of 2.3 ($\zeta^p = 1.517$ and 0.659).

H($3s2p1d$): To the H($3s2p$) basis was added one set of d functions ($\zeta^d = 1.0$).

F($5s3p2d1f$): The Dunning core double-ζ valence triple-ζ contractions[8] of the Huzinaga ($10s6p$) basis[9] were used with two sets of d functions centered at 0.90 with an internal ratio of 2.3 ($\zeta^d = 1.365$ and 0.593). In addition, one set of f functions was included, obtained by scaling the mean d exponent of 0.90 by 1.2, yielding $\zeta^f = 1.296$.

B. Geometries

The geometries for *methylenes* in Table I were taken from the calculations of Harding and Goddard[15] (CH₂), Scuseria et al.[16] (CHF), and Bauschlicher et al.[17] (CF₂). The equilibrium geometries for the substituted *silylenes* were calculated at the MP2/6-31G$**$ level using the GAUSSIAN 86 program[18] and are listed in Table I with available experimental data.[19] For the singlet states of SiH₂ and SiF₂, the predicted bond angles are within 0.3° of the

experimental values, while the Si–H and Si–F bond distances are longer than the experimental values by 0.008 and 0.026 Å, respectively.

C. DCCI calculations

We have followed the philosophy of the CCCI methods previously described by Carter and Goddard.[20,21] This approach starts with the generalized valence bond wave function (GVB), in which the carbene lone pair and the two bond pairs are correlated, followed by a small CI based on the GVB orbitals.

In order to calculate an accurate bond energy for a halogen-substituted double-bonded molecule, XYC=CZW, the DCCI prescription is to solve first for the GVB-PP (6/12) wave function in which the double bond and the four carbon–ligand bonds are correlated. In order to mimic the full GVB wave function in which various spin couplings (resonance structures) are included, we carry out a restricted CI (GVB-RCI) including all configurations having two electrons distributed among the two orbitals of each correlated pair. Since the orbitals of the double bond change dramatically as the bond is dissociated, we allow all quadruple excitations out of the double bond to obtain the wave function RCI*SDTQ($\sigma\pi$). This allows XYC=CZW to dissociate smoothly to the wave function RCI*SD($\sigma\pi$) on each carbene fragment, leading to a consistent description for dissociation of the double bond. Carter and Goddard have shown that to obtain accurate ΔE_{ST} for halogen-substituted carbenes, the GVB-RCI must allow resonance structures in which the π lone pair electrons in the CI can delocalize into the carbon $p\pi$ orbital.[20] This leads to the RCI*[ΠCI + SDTQ($\sigma\pi$)] wave function for XYC=CZW, which dissociates to RCI*[ΠCI + SD($\sigma\pi$)] on each carbene product, designated as the CCCI.[20] If calculated, self-consistently, these CCCI wave functions would lead to accurate bond energies. However, since the orbitals are calculated at the GVB-PP level, we should also include all single excitations from the GVB-RCI wave function (S_{val}) to mimic the effects of full self-consistency. This leads to RCI*[ΠCI + S_{val} + SDTQ($\sigma\pi$)] for XYC=CZW. This choice of the wave function for XYC=CZW ensures that as the double bond length in XYC=CZW is increased to $R = \infty$, the wave function changes smoothly to the RCI*[ΠCI + S_{val} + SD($\sigma\pi$)] wave function for the carbenes. Thus we refer to this as dissociation-consistent CI (DCCI). Since this DCCI wave function for XYC=CZW dissociates correlation-consistently to the corresponding DCCI wave functions for both ^{3}CXY + ^{3}CZW and ^{1}CXY + ^{1}CZW fragments, the present choice of the wave function for CXY is dissociation-consistent for both the singlet and triplet carbene fragments from the ethylene and describes both the singlet and triplet states correlation-consistently. This DCCI wave function leads to a description of the carbenes that differs from the CCCI description only by inclusion of all single excitations from the GVB-RCI wave function (S_{val}). We find that this inclusion of S_{val} is important to properly balance the relative stabilities of the singlet and triplet states.

TABLE II. Singlet–triplet splittings (ΔE_{ST}) for methylenes and silylenes.[a] The recommended theoretical values are DCCI. All quantities in units of kcal/mol.

Level	CH_2	CHF	CF_2	SiH_2	SiHF	SiF_2
HF	−24.9	−3.8	34.5	5.7	23.8	55.6
GVB(3/6)-PP	−6.9	13.1	49.8	21.4	39.3	69.5
RCI	−8.5	12.2	49.1	20.8	38.4	69.2
RCI*IICI	−8.5	15.1	53.7	20.8	38.8	69.9
RCI*[IICI + S_{val}]	−16.9	6.3	48.0	14.5	33.7	68.6
CCCI[b]	−5.1	19.9	60.3	26.7	45.6	78.1
DCCI[c,d]	−10.0	14.5	57.1	21.5	41.3	76.6
Experiment (T_e)[d]	−9.215[e]	14.6[f]	56.7[g]	20.7[h]	(40.9)[i]	76.2[j]
		11.3[f]		17.7[h]		75.2[j]
		8.0[f]				77.2[j]
Previous theory (T_e)[d]						
HF/GVB		9.2,[k] 8.1[l]	46.5,[k] 46.0[j]			
HF-SD		12.5[m]			37.7[n]	73.5,[n] 73.8[o]
HF-SD + D		13.2[m]				
MP4SDTQ		12.7[p]			37.7[p]	
CASSCF-SOCI + Q	−9.1[q]			20.4[q]		

[a] The following basis sets were used: CH_2 (C($7s4p2d1f$)/H($3s2p1d$)); CHF (C($5s3p2d1f$)/H($3s2p1d$)/ F($5s3p2d1f$)); CF_2 (C($5s3p2d1f$)/F($3s2p1d$)); SiH_2 (Si($7s5p2d1f$)/H($3s2p1d$)); SiHF (Si($7s5p2d1f$)/ H($2s1p$)/F($3s2p1d$)); SiF_2(Si($7s5p2d1f$)/F($3s2p1d$)).
[b] RCI*[IICI + SD($\sigma\pi$)].
[c] RCI*[IICI + S_{val} + SD($\sigma\pi$)].
[d] To obtain T_0 from T_e add 0.217 (CH_2), 0.3 (SiH_2), 0.1 (CHF and SiHF), and 0.0 kcal/mol (CF_2 and SiF_2).
[e] Reference 2.
[f] Reference 7.
[g] Reference 5.
[h] Reference 4.
[i] See text.
[j] See text (Ref. 6).
[k] Reference 17.
[l] Reference 24.
[m] Reference 16
[n] Reference 28.
[o] Reference 29.
[p] Reference 25.
[q] Reference 3.

III. RESULTS

The values for ΔE_{ST} of CH_2, CHF, CF_2, SiH_2, SiHF, and SiF_2 using the DCCI method are shown in Table II with available experimental data. Previous theoretical values for ΔE_{ST} of the fluorine-substituted *methylenes* and *silylenes* are available at various calculational levels and are listed in Table II. Table III summarizes the convergence of singlet–triplet state splittings of CH_2, CHF, and SiH_2 with basis set. Also included in Table III is the convergence of the singlet–triplet splitting of CHCl taken from our previous studies.[22] Figure 1 shows the discrepancy in ΔE_{ST} between available experimental results and the DCCI predictions as a function of the net charge on the carbon or silicon atom. The average net charge is evaluated from Mulliken total charges of the center atom in the singlet and triplet states listed in Table IV.

A. CH_2

The best estimate for the singlet–triplet splitting of CH_2 using the DCCI, is −9.99 kcal/mol, in reasonable agreement with experiment[2] $T_e = -9.215 \pm 0.014$ kcal/mol). [DCCI consists of 11 129/19 758 spa-

tial configurations/spin eigenfunctions for the singlet state and 8 120/23 344 for the triplet state with 75 basis functions (nb fs) and C_s symmetry.] We believe that the remaining discrepancy of 0.8 kcal in ΔE_{ST} is mainly due to incompleteness of the basis set. Using 120 nb fs in C_{2v} symmetry with the CASSCF-SOCI involving over 700 000 configuration state functions, Bauschlicher et al.[3] obtain −9.24 kcal/mol, in striking agreement with experiment.

As indicated in Table III, the singlet–triplet splitting of CH_2 decreases smoothly as the basis extended. It is evident that the extension of the carbon basis is more effective on minimizing the correlation error due to the basis set limitation than that of the hydrogen basis. For the HF wave function, the total change in ΔE_{ST} between the $VDZp$ basis (nb fs = 25) and the extended basis set (nb fs = 75) is 1.18 kcal/mol, while it is 3.52 kcal/mol for the GVB-RCI and 3.09 kcal/mol for the DCCI. For CASSCF-SOCI, the change in ΔE_{ST} is 2.73 kcal/mol between the C($4s2p1d$)/ H($2s1p$) basis[23] (nb fs = 26) and the C($5s4p3d2f1g$)/ H($4s3p2d$) basis[3] (nb fs = 120). This result indicates that the relatively simple DCCI wave function leads to correlation consistency between the singlet and triplet states, a

TABLE III. ΔE_{ST} (kcal/mol) of CH_2, CHF, SiH_2, and CHCl as a function of basis set.

Molecule	Basis set	HF	GVB-PP	GVB-RCI	DCCI [a]	CCCI [b]	Expt
CH_2	$C(3s2p1d)/H(2s1p)$	− 26.04	− 9.01	− 11.05	− 8.87	− 13.08	
	$C(5s3p2d1f)/H(2s1p)$	− 25.43	− 7.77	− 9.39	− 6.17	− 10.91	
	$C(5s3p2d1f)/H(3s2p1d)$	− 25.40	− 7.73	− 9.34	− 6.02	− 10.76	
	$C(6s4p2d1f)/H(2s1p)$	− 25.32	− 7.68	− 9.29	− 6.05	− 10.79	
	$C(7s4p3d2f)/H(3s2p)$	− 24.86	− 6.93	− 8.53	− 5.05	− 9.99	− 9.215 [c]
CHF	$C(3s2p1d)/H(2s1p)/F(3s2p1d)$	− 4.01	12.10	10.99	17.76	12.39	
	$C(5s3p2d1f)/H(2s1p)/F(3s2p1d)$	− 3.49	13.38	12.49	20.18	14.66	
	$C(5s3p2d1f)/H(3s2p1d)/F(3s2p1d)$	− 3.55	13.31	12.43	20.16	14.60	
	$C(5s3p2d1f)/H(3s2p1d)/F(5s3p2d1f)$	− 3.81	13.10	12.22	19.93	14.48	14.6 [d]
SiH_2	$Si(4s3p1d)/H(2s1p)$	5.34	20.18	19.40	23.93	18.74	
	$Si(7s5p2d1f)/H(2s1p)$	5.74	21.49	20.86	26.67	21.44	
	$Si(7s5p2d1f)/H(3s2p1d)$	5.67	21.44	20.81	26.69	21.46	20.7 [e]
CHCl [f]	$C(3s2p1d)/H(2s1p)/Cl(4s3p1d)$	− 12.61	3.28	1.94	7.94	2.89	
	$C(5s3p2d1f)/H(2s1p)/Cl(4s3p1d)$	− 11.89	4.61	3.53	10.32	5.10	
	$C(6s4p2d1f)/H(3s2p)/Cl(6s4p2d)$	− 11.47	4.99	3.90	10.65	5.47	
	$C(7s4p3d2f)/H(3s2p)/Cl(6s4p2d)$	− 11.27	5.38	4.34	11.28	5.95	6.3 [d]

[a] RCI*[ΠCI + SD($\sigma\pi$)].
[b] RCI*[ΠCI + S_{val} + SD($\sigma\pi$)].
[c] T_e (Ref. 2).
[d] T_e (Refs. 7 and 16).
[e] T_e (Refs. 3 and 4).
[f] Reference 22.

consistency we believe comparable to the much larger CASSCF-SOCI calculations.

B. CHF

Our best estimate for the singlet–triplet splitting of CHF using the DCCI with the extended basis set is 14.48
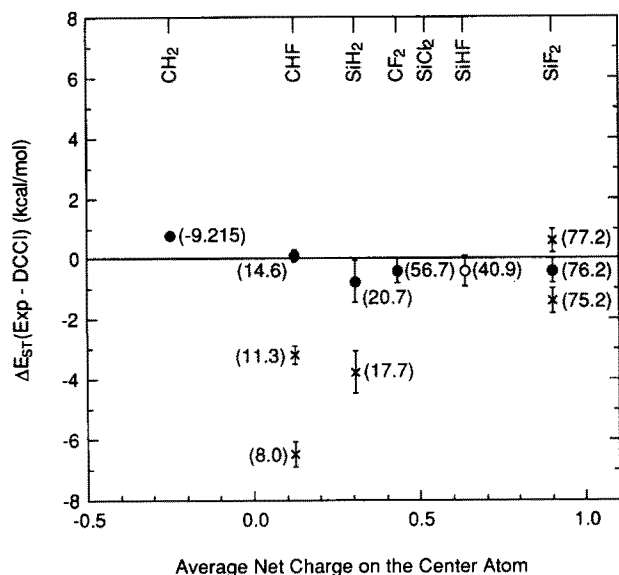

FIG. 1. The difference in singlet–triplet energy splitting between experiment and the DCCI predictions are plotted as a function of the average net charge on the center atom. The experimental results are indicated with a solid circle. In cases with several experimental values (depending on assignments) we show our selected value with a solid circle and other possible choices with a cross. For cases with no experiment we show our predicted experimental value with an open circle.

kcal/mol, which is close to an experimental estimate of 14.6 ± 0.2 kcal/mol (T_e)[7] as shown in Fig. 1. Murray et al.[7] reported three possible triplet excitation energies of 14.7 ± 0.2, 11.4 ± 0.3, and 8.1 ± 0.4 kcal/mol from the photoelectron spectroscopic studies of CHF$^-$ and suggested that 11.4 is the most likely (with 14.7 due to a hot band). The present calculational results strongly suggest that the actual singlet–triplet splitting of CHF is 14.7 ± 0.2 kcal/mol(T_0). [The DCCI with 87 nb fs consists of 15 020/26 972 spatial configurations/spin eigenfunctions for the singlet state and 10 943/36 787 for the triplet state.]

Previous theoretical results of 9.2 kcal/mol for ΔE_{ST} (CHF) were reported by Bauschlicher et al.[17] with simple wave functions [Hartree–Fock (HF) for the triplet and GVB (1/2) for the singlet] using double-ζ plus polarization (DZP) basis sets. Dixon[24] also examined ΔE_{ST} of CHF at the same level [with valence double-ζ plus polarization (VDZP) basis sets] yielding 8.1 kcal/mol. Luke et al.[25] calculated ΔE_{ST} of 12.7 kcal/mol for CHF at the MP4SDTQ (Moller–Plesset fourth-order perturbation theory) level using 6-31G* basis sets. The HF-SD calculations of CHF by Scuseria et al.[16] with the triple-ζ plus double polarization basis sets (67 nb fs) [involving 119 604 and 73 581 configurations for the singlet and triplet states] yielded ΔE_{ST} of 12.5 kcal/mol (13.2 kcal/mol after Davidson corrections). Although the HF-SD wave function has about ten times as many configurations as DCCI, the HF-SD result (even with Davidson corrections) is less accurate than the DCCI in pinpointing the correct experimental value between two possible choices of 14.7 and 11.4 kcal/mol. We believe that previous calculations have tended to underestimate ΔE_{ST} of singlet ground state of CHF due either to unbalanced levels of electron correla-

TABLE IV. Total charges, bond populations, and hybridizations for CXY and $SiXY$.[a]

Molecule	State	Total charges			Bond	Bond population on C and Si[b]	Hybridization on C, Si					
							Bonding orbital			Nonbonding σ orbital		
		C, Si	H	F	Bond		%s	%p	%d	%s	%p	%d
CH_2	$^1A_1$	6.21	0.89		C–H	1.06	18.9	79.0	1.9	61.8	37.9	0.2
CHF	$^1A'$	5.86	0.93	9.21	C–H	1.01	16.7	80.6	2.5	66.0	33.7	0.1
					C–F	0.52	17.1	76.5	4.8			
CF_2	$^1A_1$	5.60		9.20	C–F	0.53	17.6	75.6	5.4	68.8	30.7	0.3
SiH_2	$^1A_1$	13.63	1.18		Si–H	0.78	18.2	75.6	5.8	68.7	30.7	0.4
SiHF	$^1A'$	13.31	1.22	9.47	Si–H	0.73	19.7	72.2	7.5	71.9	27.0	0.1
					Si–F	0.34	20.3	60.1	15.4			
SiF_2	$^1A_1$	13.08		9.46	Si–F	0.34	21.8	57.0	16.7	76.3	22.4	1.4
CH_2	$^3B_1$	6.29	0.86		C–H	1.16	50.8	48.4	0.8	18.9	80.9	0.2
CHF	$^3A''$	5.89	0.87	9.25	C–H	1.18	59.8	39.3	1.0	34.0	65.0	0.9
					C–F	0.55	34.0	61.8	3.5			
CF_2	$^3B_1$	5.53		9.23	C–F	0.60	45.0	50.7	3.6	50.9	47.2	1.8
SiH_2	$^3B_1$	13.76	1.12		Si–H	0.91	51.4	45.2	3.4	36.1	62.1	1.9
SiHF	$^3A''$	13.42	1.12	9.47	Si–H	0.95	62.5	34.0	3.4	49.1	47.3	3.3
					Si–F	0.37	33.8	50.4	12.9			
SiF_2	$^3B_1$	13.12		9.44	Si–F	0.40	42.6	41.8	12.7	66.1	29.5	4.1

[a]Based on Mulliken populations with basis sets of $C(5s3p2d1f)$, $Si(7s5p2d1f)$, $H(2s1p)$, and $F(3s2p1d)$ (Ref. 32).
[b]Perfect covalent bonding would lead to a carbon– or silicon–ligand bond population of 1.00.

tion for both singlet and triplet states or to basis set limitations. The CCCI method[14] leads to ΔE_{ST} 5.4 kcal/mol larger than the DCCI value. This is due to the single excitations from the GVB-RCI wave function which are needed to correct for restrictions on the orbitals in the GVB-PP wave function. This restriction is most important for the triplet state because of the importance of several spin couplings.

As indicated in Table III, the values of ΔE_{ST} vary smoothly as the basis is extended. For the uncorrelated HF wave function, the total change in ΔE_{ST} between the $VDZp$ basis (nb fs = 35) and the extended basis set (nb fs = 87) is 0.20 kcal/mol, while it is 2.17 kcal/mol for the GVB-RCI and 2.09 kcal/mol for the DCCI. It is the extension of the carbon basis that is important (because the singlet–triplet splitting involves an electronic excitation between the nonbonding σ and π orbitals of the center carbon atom). The extension of hydrogen and/or fluorine basis exerts little influence on the singlet–triplet splitting of CHF.

C. CF_2

Using DCCI, the singlet–triplet splitting of CF_2 is 57.1 kcal/mol, in excellent agreement with the experimental result of 56.7±0.4 kcal/mol by Koda.[5]

Previous theoretical values for ΔE_{ST} (CF_2) are 46.5 kcal/mol by Bauschlicher et al.[17] at HF level for the triplet and GVB(1/2) level for the singlet using DZP basis sets and 46.0 kcal/mol by Dixon[24] at the same level with VDZP basis sets. The CCCI method[14] overestimates ΔE_{ST} by 3.6 kcal/mol compared with the DCCI.

D. SiH_2

The DCCI results in a singlet–triplet splitting for SiH_2 of 21.5 kcal/mol, which is close to an experimental esti-

mate of 20.7±0.7 kcal/mol (T_e)[3,4] as shown in Fig. 1. [This DCCI wave function with 74 nb fs has 10 148/17 966 spatial configurations/spin eigenfunctions for singlet and 7 373/21 229 for triplet with C_s symmetry.] The DCCI result is comparable to the value of 20.38 kcal/mol obtained from the big CASSCF-SOCI + Q with 124 nb fs by Bauschlicher et al.[3] [The SOCI expansions involve over 700 000 configuration state functions in C_{2v} symmetry.] An alternative experimental value of 17.7±0.7 kcal/mol (T_e)[3,4] is probably due to a vibrationally hot band in the photoionization mass spectrum of the SiH_2 radical generated in reactions of F + SiH_4. Recently, Johnson et al.[26] have observed the vibrationally hot SiH_3 radicals generated from the same reaction of F + SiH_4 in the multiphoton ionization mass spectrometric studies of the silyl radical. They suggested that the recommended IP of 8.01 eV for SiH_3 by Berkowitz et al.[4] is one vibrational quanta of the umbrella mode (v = 796 cm^{-1} = 0.1 eV) lower than the correct IP of 8.135 eV due to a vibrational hot band. The previously reported IP of 9.02 eV from photoionization studies of SiH_2 produced in the F + SiH_4 reaction also may be due to a vibrational hot band, a possibility also considered by Berkowitz et al.[4] Adopting their higher estimate of 9.15 eV for the experimental IP of SiH_2 leads to ΔE_{ST} of 21.0±0.7 kcal/mol (T_0) for SiH_2, which is in good agreement with the DCCI result and the previous prediction by Bauschlicher et al.[3]

As indicated in Table III, the values of ΔE_{ST} increase smoothly as the basis is extended. It is evident that the extension of the silicon basis is most important, while that of the hydrogen basis effects little on the singlet–triplet splitting of SiH_2. For the uncorrelated HF wave function, the total change in ΔE_{ST} between the $VDZp$ basis (nb fs = 29) and the extended basis set (nb fs = 74) is 0.33 kcal/mol, while it is 1.41 kcal/mol for the GVB-RCI

and 2.72 kcal/mol for the DCCI. For CASSCF-SOCI + Q, the change in ΔE_{ST} is 2.87 kcal/mol between the Si($5s3p1d$)/H($2s1p$) basis[27] (nb fs = 36) and the Si($6s5p3d2f1g$)/H($4s3p2d$) basis[3] (nb fs = 124).

E. SiF$_2$

The calculated singlet–triplet splitting of SiF$_2$ is 76.6 kcal/mol. [The DCCI involves 10 685/19 089 configurations/spin eigenfunctions for the singlet state and 7 199/28 879 for the triplet state with 74 nb fs and C_s symmetry.] The $\tilde{a}\ ^3B_1 \rightarrow \tilde{X}\ ^1A_1$ emission spectrum has been observed from a high frequency electrodeless discharge of flowing tetrafluorosilane.[6] The band origin at 26 310 cm^{-1} with long vibrational progressions involving the bending frequency of $\omega'' = 343$ cm^{-1} has been assigned from a Deslandres Table without a Franck–Condon analysis. Since the observed transition involves a large change (18.2°) in the bond angle from the triplet to singlet states, the observed long vibrational progressions are reasonable. However, it is quite possible that weak features due to the band origin may be unobserved. Therefore, the correct band origin would be 26 310 + 343n cm^{-1}, where $n = 0$, 1, or 2. Thus, in addition to the assigned value of $\Delta E_{ST} = 75.2$ kcal/mol, we must also consider 76.2 and 77.2 kcal/mol as possibilities. The present DCCI result suggests the actual singlet–triplet splitting of SiF$_2$ to be 76.2 kcal/mol as shown in Fig. 1.

The previous HF-SD calculations on SiF$_2$ by Colvin et al.[28] with the double-ζ plus polarization basis sets (56 nb fs, 23 009 and 14 300 configurations for the singlet and triplet states) yielded 73.5 kcal/mol for ΔE_{ST}. Krogh-Jespersen[29] also reported ΔE_{ST}(SiF$_2$) of 73.8 kcal/mol from HF-SD/6-31G^* calculations. We conclude that these previous calculations underestimate ΔE_{ST} by 2 to 3 kcal/mol.

F. SiHF

The DCCI predicts a singlet–triplet splitting for SiHF of 41.3 kcal/mol. [With 64 nb fs, this leads to 7 739/13 653 spatial configuration/spin eigenfunctions for the singlet state and 5 297/19 001 for the triplet state.] The previous HF-SD calculations on SiHF by Colvin et al.[28] with double-ζ plus polarization basis set (45 nb fs) [involving 13 780 and 9 156 for configurations for the singlet and triplet states] resulted in ΔE_{ST} of 37.7 kcal/mol. The MP4-STDQ calculations using 6-31G^* basis sets by Luke et al.[25] yielded ΔE_{ST} of 37.7 kcal/mol. We believe that these levels of theory underestimate the ΔE_{ST} of SiHF by 3 to 4 kcal/mol.

Comparing our calculations on CHF, CF$_2$, and SiF$_2$, with experiment [theory (T_e): 14.5, 57.1, and 76.6 kcal/mol, experiment (T_e): 14.6±0.2, 56.7±0.4, and 76.2±0.4 kcal/mol], we estimate that the experimental value for SiHF is 40.9±0.5 kcal/mol as shown in Fig. 1.

IV. DISCUSSION

The agreement in ΔE_{ST} between DCCI and experiment is excellent; however, from Fig. 1 we see that the

DCCI method underestimates (by 1 kcal/mol) the ΔE_{ST} for CH$_2$ where the net charge on the center atom is negative, while it overestimates ΔE_{ST} by about 0.4 kcal/mol for CF$_2$ and SiF$_2$ where the net charge on the center atom is quite positive. This trend is probably due to the increased basis set error in describing the singlet state for negative carbons, and we expect that other systems would lead to a similar dependencies on charge. The DCCI result (14.5 kcal/mol) for the singlet–triplet splitting of CHF strongly suggests that the correct choice of experimental value is 14.7±0.2 kcal/mol and the DCCI result for ΔE_{ST} of SiF$_2$ (76.6 kcal/mol) suggests that the correct choice of experimental value for SiF$_2$ is 76.2 kcal/mol. We predict that ΔE_{ST} of SiHF is 40.9±0.5 kcal/mol, since the average net charge on silicon is more or less as positive as CF$_2$ and SiF$_2$ and the DCCI error of 0.4 kcal/mol is expected as CF$_2$ and SiF$_2$.

Substituting fluorine for hydrogen drastically stabilizes singlet state carbenes. Factors favoring singlet ground states by the fluorine substitution are (i) the donation of $p\pi$ lone pair electrons into an empty carbon or silicon $p\pi$ orbital of the singlet state and (ii) the increase of s character in the nonbonding σ orbital due to the electron-withdrawing substitution.[16,17,20,22,28,30,31] The contribution of the $p\pi$ lone pair donation to the stabilization of the singlet state may be estimated from the difference between ΔE_{ST} at the RCI and at the RCI*IICI shown in Table II (2.9 and 4.6 kcal/mol for CHF and CF$_2$; 0.4 and 0.7 kcal/mol for SiHF and SiF$_2$, respectively). The IICI contributions are greater for CHF and CF$_2$ than their silicon analogs because of the smaller C–F bond distance [r(C–F) $\cong$ 1.30 Å and r(Si–F) $\cong$ 1.62 Å; see Table I] and negative charge on the C. A quantitative indication of the s and p contributions is given by Mulliken population analysis.[32] Table IV summarizes the total charges on each atom, the bond populations on the center atom, and the hybridizations in various orbitals of the center atom. The s character in the bonding orbitals varies slightly with fluorine substitution for singlet state carbenes (from 18.9% s in CH$_2$ to 17.6% s in CF$_2$ and from 18.2% s in SiH$_2$ to 21.8% s in SiF$_2$) but decreases significantly for triplet states (from 50.8% s in CH$_2$ to 45.0% s in CF$_2$ and from 51.4% s in SiH$_2$ to 42.6% s in SiF$_2$). For singlet state carbenes, the s contributions in the nonbonding σ orbitals increase slightly ($\sim$7%) from CH$_2$ to CF$_2$ or SiH$_2$ to SiF$_2$. In contrast, fluorine substitution in triplet state carbenes greatly enhances s character in nonbonding σ orbitals (by $\sim$31%). This result indicates that the electron-withdrawing fluorine substitution induces an increase of s character in the nonbonding σ orbital of the center atom, stabilizing the σ orbital relative to the π orbital and thereby disfavoring the triplet state.

The basis sets convergence for DCCI is shown in Fig. 2 as a function of an average net charge on the center atom. Data for CHCl are taken from our previous studies on the singlet–triplet energy gaps in chlorine substituted methylenes and silylenes.[22] The values of ΔE_{ST} converge to the experimental limit as the basis sets for the center atoms are extended from valence double-*zeta* plus polarization basis
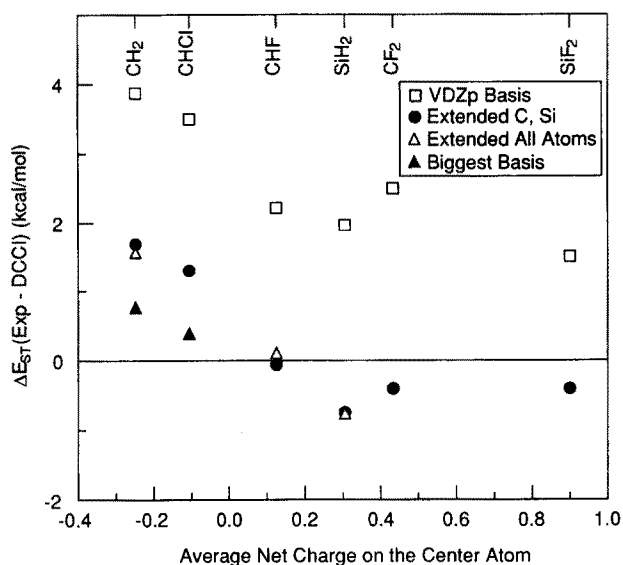
FIG. 2. Convergence of DCCI with basis. Results are plotted as a function of the net charge on the center atom. The discrepancy between experimental results and DCCI predictions are shown. Open squares indicate results using the simplest basis, valence double-*zeta* plus polarization functions on C($3s2p1d$), Si($4s3p1d$), H($2s1p$), F($3s2p1d$), and Cl($4s3p1d$). Solid circles indicate results with extended carbon and silicon basis sets: C($5s3p2d1f$) and Si($7s5p2d1f$). Open triangles indicate further extensions of the hydrogen and fluorine basis sets to H($3s2p1d$) and F($5s3p2d1f$). The most complete basis sets are indicated by solid triangles where we use C($7s4p3d2f$), H($3s2p$), and Cl($6s4p2d$).

to the larger bases. However, basis extensions for hydrogen or fluorine in CH_2, CHF, and SiH_2 have little influence on ΔE_{ST}. This importance of basis extension of the center atom is plausible since the process of interest involves electronic excitation between the nonbonding σ and π orbitals of the center atom. Thus, to obtain accurate values in ΔE_{ST} for CF_2, SiHF, and SiF_2, it is sufficient to use valence double-ζ plus polarization bases for hydrogen and fluorine along with extended basis sets for carbon and silicon. The very slow convergence of ΔE_{ST} with respect to central atom basis for CH_2 and CHCl compared with the rapid convergence in CHF and SiH_2 is attributed to the electronegative carbons in CH_2 and CHCl (see Fig. 2), which require additional diffuse basis functions for a proper description of the singlet state.

V. SUMMARY

Ab initio GVB-DCCI calculations have been used to estimate the singlet–triplet splittings for fluorine substituted *methylenes* and *silylenes*. The relatively simple DCCI wave functions (emphasizing correlation consistency in the double bond breaking processes) shows correlation consistency for the singlet and triplet states of methylenes. For the current basis sets, all systems yield results accurate to 0.4 to 0.8 kcal/mol. Indeed, the accuracy changes smoothly with net charge on the central atom, allowing accurate extrapolations. The uncertainty related to the present choice of the bond distances and bond angles is estimated to be about 0.1 kcal/mol in total energy and at most 0.2 kcal/mol in energy gap.[33]

ACKNOWLEDGMENT

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[33] The uncertainty related to the present choice of the geometry is estimated from the valence force field expression of the potential energy,

$\Delta E_{ST} = \frac{1}{2} f_{rr} \delta r_1^2 + \frac{1}{2} f_{rr} \delta r_2^2 + f_{rr} \delta r_1 \delta r_2 + \frac{1}{2} f_{\theta\theta} \delta\theta^2 + f_{r\theta} \delta r_1 \delta\theta + f_{r\theta} \delta r_2 \delta\theta$. For example, deviations of $\delta r_1 = \delta r_2 = 0.01$ Å and $\delta\theta = 1°$ yield uncertainties in total energy of 0.12, 0.05, and 0.06 kcal/mol for CH_2 ($^3B_1$), SiH_2 ($^1A_1$), and SiH_2 ($^3B_1$), respectively, using the previ-ously reported force constants [see P. R. Bunker, P. Jensen, W. P. Kraemer, and R. Beardsworth, J. Chem. Phys. **85**, 3724 (1986) for CH_2 ($^3B_1$) and W. D. Allen and H. F. Schaefer III, Chem. Phys. **108**, 243 (1986) for SiH_2].