Dissociation energetics of SiF systems of relevance to etching reactions

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The bond energies of the $^2\Pi$ and $^4\Sigma^-$ states of SiF, the $^1\Sigma^+$ state of SiF^+, the $^3\Sigma^-$ state of SiF^-, the $^1A_1$, $^3B_1$, and $^1B_1$ states of SiF_2, the $^2A_1$ state of SiF_2^+, and the ground states of SiH_3–F, SiF_3–F, SiH_3–SiH_3, and SiH_3–SiF_3 have been calculated using generalized valence bond and dissociation-consistent configuration interaction methods. Excellent bond energies are determined using only a relatively small number of configurations in the calculations. For example, the bond energy of the $^2\Pi$ state of SiF is calculated to be 5.45 eV, in excellent agreement with the experimental value of 5.62 eV. For the inversion bend of SiF_3 we predict that the transition state is a T-shaped configuration rather than one of D_{3h} symmetry. Of note for the etching of solid silicon by reaction with F atoms is that unsaturated Si species react readily with F atoms to form strong bonds and that the bonding of a F atom to a lone pair of electrons on a Si atom is an activated process.

I. INTRODUCTION

A particularly promising technology for constructing the structures in modern electronic devices is chemical etching of solid silicon by reaction with fluorine atoms.[1] It is presumed that species such as SiF_x ($x = 0,3$) initially form at the surface and in the solid, followed by the creation of SiF_4 molecules that desorb from the solid. Theoretical calculations by Seel and Bagus[2] suggest that F atoms can readily penetrate into the bulk. However, there is little information about the chemical mechanisms involved in the formation of the various SiF_x species. It is easy to envision that a F atom might readily attach to a silicon dangling bond,[3] but how does the product molecule SiF_4 form? There are formidable experimental difficulties in determining the reaction mechanisms, and hence it is valuable to use suitable theoretical approaches to obtain information about the various possible reaction paths. The difficulty there is that even with first principles calculations, conventional approaches to electronic structure are notoriously poor at predicting the relative energetics (e.g., dissociation and activation energies) of reaction processes. The main problem is that the changes in molecular geometry associated with bond rupture and formation lead to changes in electron correlation so that only fully correlated wave functions can be relied upon to predict reasonable bond and activation energies systematically.

Recently Bair and Goddard[4] have conceptualized a procedure based on generalized valence bond (GVB) wave functions that leads to compact configuration interaction (CI) wave functions which yield accurate bond energies. This dissociation-consistent configuration interaction (DC–CI) wave function includes the same level of electron correlation in the dissociated species, the bound molecule, and any possible transition states. The strategy behind GVB–DC–CI is to use the generalized valence bond wave function to define orbitals that change systematically with bond rupture and formation and to design the correlated wave function so as to be complete only for electron correlation involving orbitals that dramatically change their configuration with molecular rearrangement. This means full correlation for the orbital pair describing the bond being broken and partial correlation for the electrons in orbitals not directly involved in the bonding. With this approach various workers[4–6] have obtained excellent bond energies (good to ~3 kcal/mol) with relatively small calculations. The molecules SiF and SiF_2, especially the excited states, provide a challenge to the DC–CI procedure. In addition, these molecules exemplify possible ways a F atom can attach to a Si atom which is not fourfold coordinated. For example, the ground state of SiF is $^2\Pi$ which dissociates to F ($2p^5$;^2P) and Si ($3s^23p^2$;^3P). The bonding is straightforward in that the half-filled F $2p$ orbital bonds to one of the half-filled Si $3p$ orbitals. The excited state, $^4\Sigma^-$, has the same dissociation limit but the bonding configuration may be described using GVB terminology as having one of the Si $3s$ lobe orbitals bonded to the F $2p$ orbital.[7] In more conventional terminology the Si hybridizes to $3s^13p^3$ in forming the $^4\Sigma^-$ state and a *sp* hybrid forms the bond. In either language, the bonded and dissociated configurations are quite different.

In this study we have calibrated the DC–CI procedure by calculating the potential curves for SiF ($^2\Pi$ and $^4\Sigma^-$), SiF^+ ($^1\Sigma^+$), SiF^-($^3\Sigma^-$), SiF_2 ($^1A_1$, $^3B_1$, and $^1B_1$), and SiF_2^+ ($^2A_1$). For the ground state of SiF ($^2\Pi$) we predict a dissociation energy of 5.45 eV vs an experimental value of 5.62 eV. The CI for this state contained only 246 spatial configurations. For the most part the other diatomic and triatomic bond energies are calculated to a similar accuracy. In addition, we have examined the bond strengths of H_3Si–SiH_3, H_3Si–SiF_3, H_3Si–F, and F_3Si–F, molecules representative of the etching process.

We consider these SiF species to be the critical ones in

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the etching of solid silicon by fluorine radicals. The states considered here test calculational procedures for obtaining accurate potential curves for F atom bonding to Si dangling bonds and to configurations where the F atom bonds to a closed shell pair of electrons as in the case of a Si–Si bond in the solid state.

II. DESCRIPTION OF THE CALCULATION

The first step before starting any calculation is to understand the bonding in the species of interest. With a picture in mind of the molecular states of interest, the appropriate basis set, and the level of *ab initio* calculation are chosen. Each of these facets of the problem are discussed below.

A. The GVB model of bonding

In the ^3P ground state of Si, two electrons singly occupy two $3p$ orbitals and are triplet coupled. The $3s$ pair of electrons are correlated with the remaining $3p$ orbital leading to sp hybrid orbitals. If the F radical orbital is bonded to a singly occupied $3p$ orbital on the Si atom, the $^2\Pi$ ground state of SiF results.

The cation Si^+ (^2P) is similar to Si atom except that only one $3p$ orbital is singly occupied. Analogously, the GVB description of the molecular cation SiF^+ ($^1\Sigma^+$) is obtained by removing the electron from the singly occupied Si $3p$ orbital. In SiF^- the ground state ($^3\Sigma^-$) the bonding corresponds to the $p\ \sigma$ orbital of F^- donating electron density into the empty p orbital on Si. In this picture the Si $3s$ orbital cannot rehybridize with a Si $3p$ orbital, however, it is still described within the perfect pairing description using "in/out" correlation with a $3s$ antibonding orbital as the correlating orbital. For SiF_2 ($^1A_1$ ground state) we start with the ground $^2\Pi$ state of SiF and bond a F atom to the remaining singly occupied p orbital. All states described so far result from bonding the F radical orbital to a singly occupied Si $3p$ orbital.

Alternatively the F atom can be bonded to one of the lobe orbitals of Si leading to the $^4\Sigma^-$ state of SiF. For a bond to form the $3s$ singlet pair must partially uncouple at the cost of a large excitation energy ($\sim$4 eV in the isolated Si atom). Analogous to the quartet state, the $^3B_1$ and $^1B_1$ excited states of SiF_2 are formed by the F atom bonding to one of the $3s$ lobes of the $^2\Pi$ state of SiF. The $^2A_1$ state of SiF_2^+ also results from a F atom bonding to one of the $3s$ lobes of SiF^+.

Concerning the valence electron configuration of the F atom, in addition to the five $2p$ electrons, there is also a $2s$ lone pair of electrons. Full GVB calculations (in the perfect-pairing representation) of F atom in a molecular environment lead to mixing between the $2s$ and $2p$ lone pairs so that the final wave function has one partially covalent bond and three lone pairs that are roughly tetrahedral. However, if say for SiF, the orbitals are constrained to remain symmetry functions, these three lone pairs have σ, π_x, and π_y symmetry. In the CI calculations, this set of orbitals yields nearly the same energy as the tehrahedral ones, and in order to use an Abelian point group for the molecule we have chosen the σ, π_x, and π_{ly} description. The calculations on SiF presented here were performed with C_{2v} symmetry thus preventing the F atom from hybridizing into equivalent sp^3 lobes. The calculations on the SiF_2 were performed with C_s symmetry since one of the F atoms is allowed to dissociate from the SiF_2 molecule and because both Si–F bonds were described at the perfect pairing level. As a result, the lone pairs in the plane are each in approximately sp^2 hybrid orbitals.

The bonding in $H_3Si–SiH_3$, $H_3Si–SiF_3$, $H_3Si–F$, and $F_3Si–F$ is relatively straightforward compared to some of the cases described above. In all four molecules the bonds are formed from fragments with each having a singly occupied orbital participating in the bonding. These GVB calculations were performed in C_{3v} symmetry.

B. Basis sets

The Dunning[8] ($9s5p/3s2p$) valence double zeta (DZ) contraction of the Huzinaga[9] Gaussian basis set with an added set of d functions (without the s linear combination) with exponent 1.34 is used for the F atoms.[4] The exponents and contraction coefficients are given in Ref. 8. The unscaled Dunning ($4s/2s$) contraction of Gaussian orbitals was used for the H atom basis set.[10]

Ultimately for the larger systems it is computationally desirable to use effective potentials for the silicon atoms. Initially, however, an *ab initio* basis set was used for the atomic, and diatomic $^2\Pi$, $^1\Sigma^+$, and $^3\Sigma^-$ states. The *ab initio* valence double zeta plus polarization silicon basis[11] used in these calculations is given in Table I.[30]

A calibration of the effective core potential (EP) of Rappe' *et al.*[12] was made by calculating the $^2\Pi$ state bond energies at a few internuclear separations. As pointed out in the effective potential papers,[12,13] the EP becomes suspect for short internuclear separations where the core orbitals in the two atoms begin to overlap. For SiF with $R_e = 1.65$ Å, the *ab initio* basis yields a bond energy of 5.45 eV while the EP leads to a bond energy of 5.42 eV, in excellent agreement. At $R = 1.50$ Å the respective energies are 4.99 and 4.88 eV while at $R = 1.35$ Å the values are 3.06 and 2.87 eV. The error of 0.11 eV at 1.50 Å is acceptable for our purposes but use of effective potentials to determine the repulsive wall energetics may not be adequate. All calculations on SiF_2, the $^4\Sigma^-$ state of SiF, and the larger molecules were performed using the EP. The valence DZ + d basis for use with the EP is given in Ref. 12. As with the *ab initio* basis we include one set of d functions (without the s linear combination) with an exponent of 0.3247.

C. GVB calculations

The basis self-consistent field (SCF) procedure used in these studies is the generalized valence bond approach.[14] The GVB procedure corresponds to a multiconfiguration SCF (MCSCF) calculation in which each pair of valence electrons is described with two or more optimized orbitals. The GVB calculation thus includes the dominant correlation term for each valence electron pair. The terminology to denote the perfect pairing level of the GVB wave function is $GVB(n/m)PP$ where m is the number of orbitals used to correlate n electron pairs.

TABLE I. Comparisons of the calculated spectroscopic constants with experimental values.

	D_e (eV)		R_e (Å)		ω_e (cm^{-1})		θ(°)	
	Calc.	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.	Expt.
SiF($^2\Pi$)	5.45	5.62[a]	1.67	1.6011[a]	733	857[a]		
SiF($^4\Sigma^-$)	2.12	1.92[a]	1.69	1.6046[a]	862	863[a]		
SiF$^+$($^1\Sigma^-$)	6.31	~6.5[b]	1.57		977			
SiF$^-$($^3\Sigma^-$)	3.24	~3.3[b]	1.79		556			
SiF$_2$($^1A_1$)	6.38	6.76[c]	1.64	1.59[d]			101	101[d]
SiF$_2$($^3B_1$)	3.09	3.50[e]	1.64				113	
SiF$_2$($^1B_1$)	0.15	1.29[e]	1.67	1.60[f]			117	116[f]
SiF$_2^+$ ($^2A_1$)	2.64	3.2[e]	1.56				119	

[a] K. P. Huber and G. Herzberg, *Constants of Diatomic Molecules* (Van Nostrand–Reinhold, New York, 1979). These values have been corrected for vibrational zero point energy.

[b] Estimate from P. A. G. O'Hare and A. C. Wahl, J. Chem. Phys. **55**, 666 (1971); P. A. G. O'Hare, J. Chem. Phys. **59**, 3842 (1973).

[c] Obtained from the data in Table VIII (Ref. 30).

[d] V. M. Rao, R. F. Curl, P. L. Timms, and J. L. Margrave, J. Chem. Phys. **43**, 2557 (1965).

[e] Estimated from the $^1A_1$ bond energy and the experimental excitation energies given in Table IV (Ref. 30).

[f] R. N. Dixon and M. Halle', J. Mol. Spectrosc. **36**, 192 (1970).

1. Atoms

The GVB wave functions for the both the ^3P and $^1D(3s^23p^2)$ states of Si atom are of the form GVB(1/2)*PP* where the 3*s* orbital pair of Hartree–Fock (HF) theory is described in terms of two lobe orbitals $(3s+\lambda\, 3p)$ and $(3s-\lambda\, 3p)$. For the $^5S(3s^13p^3)$ excited state all the valence electrons are in singly occupied orbitals and high spin coupled so that the GVB and HF descriptions are equivalent. For the F atom ($2s^22p^5$; ^2P) the GVB description leads to three correlated valence pairs and a singly occupied (radical) orbital, with a GVB(3/6)*PP* correlated wave function overall.

2. SiF

In addition to the correlation described above for the atomic fragments, the wave function of the molecular states of SiF also includes correlation of the new bond, thus the wave functions for all states except $^4\Sigma^-$ are GVB(5/10)*PP*. A description of the nature of the orbitals in the molecular and dissociated species is given in Sec. II A above. The $^2\Pi$ state of SiF dissociates to Si [$^3P-$GVB(1/2)*PP*] + F[$^2P-$GVB(3/6)*PP*]; the $^1\Sigma^+$ state of SiF$^+$ to Si$^+$ [$^2P-$GVB(1/2)*PP*] + F[$^2P-$GVB(3/6)*PP*]: and the $^3\Sigma^-$ state of SiF$^-$ to Si [$^3P-$GVB(1/2)*PP*] + F$^-$[$^1S-$GVB(4/8)*PP*]. In Sec. III the subtleties involved with calculating SiF$^-$ energies are discussed.

The $^4\Sigma^-$ state of SiF poses a special problem since the three sigma orbitals change spin coupling with distance. In the separated atom limit the triplet orbitals of Si are $3p_x$ and $3p_y$ so that the lobe pair, $(3s+\lambda\, 3p_z)$ and $(3s-\lambda\, 3p_z)$, is singlet coupled, while F has a singly occupied $2p_z$ orbital. However, near equilibrium, the $(3s+\lambda\, 3p_z)$ lobe orbital of Si pairs with the F radical orbital and the remaining singly occupied orbital is on the Si atom. In order to avoid bias in describing the three sigma orbitals we include all seven configurations of three electrons in three orbitals (a seven configuration MCSCF—also referred to as a CASSCF[15]) while simultaneously correlating the other four electron pairs at the GVB(4/8)*PP* level.[16] Thus the $^4\Sigma^-$ state is calculated at the GVB(4/8*PP* + 7 MCSCF) level.

3. SiF$_2$

For the $^1A_1$ state of SiF$_2$ we correlate the three lone pairs of one F atom, the two Si–F bond pairs and the Si 3*s* pair leading to a GVB(6/12)*PP* wave function. The $^3B_1$ and $^1B_1$ states of SiF$_2$ and the $^2A_1$ state of SiF$_2^+$ have the same characteristics as the diatomic $^4\Sigma^-$ state with three electrons whose spin coupling must be treated in a more general manner. Thus for each of these states the calculation is at the GVB(4/8*PP* + 7 MCSCF) level.

4. H$_3$Si–SiH$_3$, H$_3$Si–SiF$_3$, H$_3$Si–F, and F$_3$Si–F

In all four molecules, correlation of the pair of electrons in the bond being broken is included. As for the SiF and SiF$_2$ molecules, the three lone pairs of the F atom being dissociated were correlated. The lone pairs on the F atoms not involved in the bond formation of interest were described at the Hartree–Fock level.

To minimize the number of geometrical parameters, unless otherwise noted we constrained all X–Si–Y angles where $\{X,Y\} = \{H,F\}$ to be tetrahedral. In addition, all Si-H bond lengths are fixed at 1.5 Å and the three secondary Si–F bonds lengths are assumed to be 1.65 Å. We also omitted the set of *d* functions on the three secondary F atoms. (A few calculations were performed with the *d* functions resulting in a 0.02–0.05 eV increase in bond strengths.) The H$_3$Si–SiX$_3$ molecules were assumed to be in a staggered configuration.

D. Dissociation-consistent configuration interaction (DC–CI)

Bair and Goddard[4] have developed a procedure for obtaining accurate bond energies using moderately correlated wave functions which include all electron correlation effects that are differential between the molecule and the fragments. This dissociation-consistent CI procedure involves starting with a GVB wave function in which the bond to be broken is correlated at the perfect-pairing level. In addition any other valence electron may also be correlated at the prefect-pairing level. The first level of DC–CI wave function is a GVB-restricted CI (GVB–RCI) where within each of the GVB

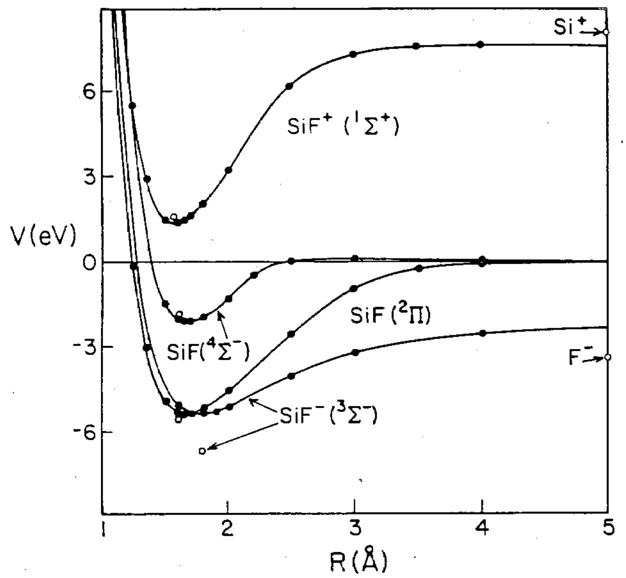


FIG. 1. Potential energy curves for SiF. The open circles denote the experimental values of D_e and R_e where known (Tables II and III). The experimental values of the IP of Si and EA of F are also given by open circles. All energy values are from the CI calculation and relative to Si (^3P) and F (^2P).

pairs we allow all three occupations [(20), (11), and (02)] of two electrons in two orbitals. For a GVB($n/2n$) wave function there are 3^n configurations in the GVB–RCI, assuming that none are eliminated by symmetry constraints. For our systems we must extend slightly the definition of GVB–RCI to also include the seven configurations of the MCSCF of the $^4\Sigma^-$-like states. Thus in these cases the GVB–RCI contains $3^n \times 7$ configurations. These GVB–RCI's are dissociation consistent, that is, the orbitals and configurations of the molecule change consistently to those of the separated fragments. Particularly important configurations for dissociation, such as simultaneous correlation between the bond pair and the F lone pairs and between the F lone pairs, are included.

The GVB–RCI does not, however, contain all of the important correlations that change upon dissociation. Also required are higher order excitations from the orbital of the bond that is being broken. Thus starting with the GVB–RCI wave function we also add all configurations that are single and double excitations from the bond pair being broken into all possible empty orbitals (i.e., full correlation of the electrons involved in bonding). Special treatment is again required for the seven MCSCF bonding states. For these cases we generate configurations that are single and double excitations from the three active orbitals for all seven spatial configurations into the entire unoccupied space.[17] Additional discussion concerning choosing dissociation-consistent configurations is given in Refs. 4–6.

III. RESULTS AND DISCUSSION

The results of our dissociation-consistent CI calculations for the fluorosilane systems are given below. Since our goal is to obtain useful dissociation energetics, we start with a comparison of our calculated energetics with experimental values. Other aspects, such as excitation energies and predicted molecular geometries, are discussed afterward.

A. Dissociation energetics

The calculated dissociation energies for the four diatomic states and four triatomic states along with the experimental values or estimates are given in Table I. The experimental bond energies have been obtained by using 0 K heats of formation and correcting for differences in zero point energies. When only heats of formation at 298 K are available, ideal gas heat capacities were used to determine the 0 K values. For diatomic molecules bond strengths at 0 K are readily available but still must be corrected for zero point energy. The relevant ΔH and vibrational frequency data is in Table VIII.[30] The overall agreement between the calculated and experimental values given in Table I is excellent. For example, for the $^2\Pi$ state, the calculated bond strength is 5.45 eV whereas the measured value is 5.62 eV. Of note is that this level of agreement was obtained with CI's that contained between 246 ($^2\Pi$ state of SiF) and 1416 ($^2A_1$ state of SiF_2^+) spatial configurations. This is in contrast to the recent trend to design CI calculations that contain thousands to millions of configurations.

One possible problem in describing a highly ionic bond such as in SiF is whether the ionic states of the individual fragments are properly treated. The main problem here is calculating the electron affinity of fluorine. At the GVB–RCI level and with the basis set described above, the calculated electron affinity of F is 2.21 eV whereas the experimental value is 3.42 eV.[18] By adding s and p diffuse functions[4] of exponents 0.112 and 0.076, respectively, the calculated electron affinity is 3.38 eV, a value in excellent agreement with the experimental value. Although the electron affinity increased by 1.16 eV, the effect of this "better" F atom basis on the bond strength of SiF ($^2\Pi$), however, is only 0.08 eV (1.8 kcal/mol). This improvement is in line with the 2 kcal/mol increase in bond strength due to diffuse functions found for HF.[4] Since ultimately we wish to examine larger reaction systems we have chosen not to include the diffuse functions in the remaining calculations.

One approach used by others to estimate ionic bond strengths is to perform a Hartree–Fock (HF) calculation; assume that the dissociation limits are the ionic fragments; and then adjust the bond strength by the experimental ionization energy and electron affinity of the fragments. Applying this procedure to SiF ($^2\Pi$) yields bond strengths of 6.36 eV if there are no diffuse functions on the F atom and 5.58 eV if diffuse functions are included. The diffuse functions are quite important for this correction to a HF calculation but not nearly as important for the GVB calculations. It should be pointed out that this correction to the HF values does not allow one to obtain a smooth potential curve for the dissociation process, rather it just helps estimate the bond strength.

The diatomic potential curves are shown in Fig. 1. The only state that exhibits any unusual character is the $^4\Sigma^-$ state of SiF where there is a barrier of 0.09 eV to attachment. This barrier arises because the Si 3s lobe pair must partially decouple their spins before one of the lobes can start bonding to the F atom. Such barriers tend to decrease as the description of electron correlation is improved. The calculated height therefore should be an upper bound to the actual value. It is important to note that the optimization of the spin

TABLE II. Energetics of the fluorosilane species. The upper set of numbers are in hartrees and the second set in eV. All bond angles are tetrahedral unless otherwise noted and the nonreacting Si–H bond lengths are 1.5 Å and the Si–F bond lengths are 1.65 Å. In all cases the EP has been used for silicon.

	GVB–*PP*	GVB–RCI	DC–CI	Number of GVB pairs	R_e (Å)[a]
F	− 99.414 57	− 99.450 74		3	
SiH_3	− 290.601 02			0	
$H_3Si–SiH_3$	− 581.303 80		− 581.316 81	1	2.38
$H_3Si–F$	− 390.210 52	− 390.279 87	− 390.285 30	4	1.65
$H_3Si–F$	− 390.182 63		− 390.188 85	1	(1.65)
SiF_3	− 587.415 26[b]			0	1.62
$H_3Si–SiF_3$	− 878.123 95	− 878.123 95	− 878.137 99	1	2.36
$F_3Si–F$	− 687.031 49	− 687.100 65	− 687.106 00	4	1.59

D_e values in eV

	GVB–*PP*	GVB–RCI	DC–CI	Expt.[c]	Number of GVB pairs
$H_3Si–SiH_3$	2.769		3.123	3.29	1
$H_3Si–F$	5.304	6.207	6.355	6.71	4
$H_3Si–F$	5.070		5.239		1
$H_3Si–SiF_3$	2.930	2.930	3.312		1
$F_3Si–F$	5.487	6.385	6.530	6.38[d] 7.08[d]	4

[a] Optimized at the DC–CI level except for the value in parenthesis.
[b] The optimized F–Si–F angle is 107.3°.
[c] Calculated from the information in Table VIII (Ref. 30).
[d] Using the two ΔH values of SiF_3 in Table VIII (Ref. 30).

coupling explicit in the MCSCF procedure[15] is essential in obtaining a smooth transition between small and large *R* regimes.

The only state where the calculated dissociation energy differs significantly from the experimental value is the $^1B_1$ state of SiF_2. Since the bonding here is similar to the $^4\Sigma^-$ state in that the spin coupling changes with distance, the energetics of the attachment of the F atom at the equilibrium bond angle of 117° (see Sec. III B below) were calculated. In this case there was a energy barrier at $R = 2.15$ Å with a height of 0.5 eV. If these calculated energetics are correct, then there should be predissociation of the $^1B_1$ state. However, the calculated bond strength is smaller than the experimental estimate and thus the calculated barrier is probably too large. Since the $^1B_1$ bond is not as strong as the $^4\Sigma^-$ one, we believe the barrier is real. We estimate that the value of 0.5 eV is an upper bound to the actual value.

The dissociation energetics for the four larger molecules are given in Table II. For disilane, Si_2H_6, the predicted bond strength at the DC–CI level is 3.1 eV. Horowitz and Goddard[6] found that by correlating the Si–H bonds and performing a DC–CI that the calculated bond strength increased to 3.3 eV, a value in exact agreement with the experimental value. Of note is that for disilane, most of the Si–Si bond strength can be predicted from merely correlating the bond pair of electrons involved in the dissociation process.

Based on the disilane results we attempted to predict the $H_3Si–F$ bond strength by only correlating the one bond pair of electrons. At the DC–CI level this results in a predicted $H_3Si–F$ bond strength of 5.2 eV whereas the experimental value is 6.7 eV. By also correlating the three lone pairs on the F atom and performing a DC–CI calculation using the GVB(4/8) wave function the bond strength increased to 6.4 eV. An additional ∼0.2 eV increase in bond strength was obtained by using the GVB–RCI set of configurations and performing MCSCF and corresponding DC–CI calculations. Calculations by Schlegel[19] predict a bond strength of 6.0 eV. In contrast to disilane, for a bond involving a F atom, correlation of the electron pairs on the F atom is crucial for obtaining the correct bond strength.

For the $H_3Si–SiF_3$ bond strength we calculate a value of 3.3 eV. Based on the disilane results, we estimate the actual value to be 0.1–0.2 eV larger. A bond strength of 6.5 eV is calculated for $F_3Si–F$ at the GVB(4/8)*PP* plus DC–CI level. The experimental values are 6.4 and 7.1 eV and Schlegel[19] has calculated a value of 6.8 eV. We estimate that a reasonable estimate of the true bond strength is ∼6.8–6.9 eV. That is, 6.5 eV plus ∼0.2 eV for a MCSCF wave function plus ∼0.1 eV for diffuse functions on the F atom. Replacing SiH_3 by SiF_3 tends to strengthen the neighboring Si–Si bond.

B. Molecular geometries

The calculated equilibrium distances for the diatomic and triatomic states, the ω_e values for the diatomic states and the equilibrium bond angles for the triatomic species are given in Table I. The calculated bond lengths of the larger molecules are given in Table II. As discussed in Secs. III C and III D, to describe the dissociation energetics of SiF_2 calculations of at least the GVB(6/12)*PP* or GVB(4/8*PP* + 7 MCSCF) level are required. To reduce the computer time necessary to determine the SiF_2 geometries, we chose not to correlate the F atom lone pairs of the F atom to be dissociated. The resulting calculations are GVB(3/6)*PP* for the $^1A_1$ state and GVB(1/2*PP* + 7 MCSCF) for the other three states plus corresponding CI's. The dissociation energetics

TABLE III. Excitation energies for the Si atom. The *ab initio* basis was used.

	^3P [a]	^1D [b]	^5S [b]
HF	− 288.4749	1.09[c]	2.39
GVB(1/2)	− 288.4880	1.09	2.75
GVB–SD[d]	− 288.5409	1.03	3.58[e]
Full[f]	− 288.5429	1.02	3.63
Expt.[g]	0.0 eV	0.78 eV	4.13 eV

[a] Term energy in hartrees.

[b] Excitation energies in eV.

[c] Approximately a 0.1 eV decrease in the ^1D excitation energy results from adding a set of *f* functions. The major improvement is in the HF orbitals of the ^1D state.

[d] Single and double excitations from the valence orbitals of the GVB wave function.

[e] There was a 0.0016 hartree lowering of the energy if the 2*p* electrons were included in the CI calculation.

[f] Full valence CI from the GVB wave function.

[g] W. C. Martin and R. Zalubas, J. Phys. Chem. Ref. Data 12, 323 (1983).

given in Table I are from the larger calculations described in Sec. II.

The calculated R_e values are consistently larger than the known experimental quantities by ~0.07 Å. We believe that this is due to the omission of dispersive configurations in the DC–CI, e.g., single and double excitations from all orbitals. These configurations should decrease the calculated R_e values. Other calculations on the SiF and SiF_2 molecules do a better job of predicting R_e[20–23] but do not attempt to predict D_e. Our calculated bond angles, θ, for the SiF_2 states are within 1° of the experimental values. The predicted ω_e values are in reasonable agreement with the experimental values.

The calculated R_e values for the larger molecules are given in Table II and as for the diatomic and triatomic molecules our values are 0.04–0.07 Å larger than the experimental values. Of note is that by substituting F atoms for H atoms that the Si–Si bond length decreases by 0.02–0.03 Å, a trend consistent with the increase in bond strength with F substitution for H.

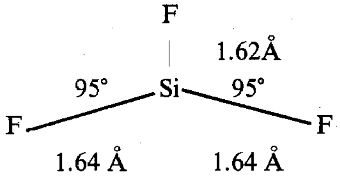
C. SiH_3 and SiF_3 inversions

We believe that the inversion or umbrella motion of $-SiF_3$ or $-SiH_3$ is a critical part of the etching reaction process. Of relevance to the calculations in progress on the etching reaction mechanism is the relative barriers for inversion of SiH_3 and SiF_3. The equilibrium geometry of these species has the three H atoms and the lone electron positioned in a near tetrahedral configuration. One possibility for transition state is a molecule of D_{3h} symmetry, i.e., a planar molecule with all bond angles equal. The lone electron in the transition state occupies a π-type orbital that is out of the plane of the molecule. This geometry is realized for SiH_3, however, for SiF_3 the transition state is not of D_{3h} symmetry, rather the molecule occupies a T-shaped planar geometry (C_{2v} symmetry).

For SiH_3, holding the SiH bond length constant at 1.5 Å, the predicted inversion barrier at the HF level is 0.46 eV, at the GVB(3/6)*PP* level is 0.37 eV and at the GVB–RCI level is 0.28 eV. A recently measured experimental value is 0.23 eV[24] and other calculations predict values between 0.19 and 0.25 eV.[25–27] Of note is that the transition state is a planar molecule with D_{3h} symmetry. As expected the radical orbital is out of the plane of the molecule. The main correlation effect in going from the GVB(3/6)*PP* to GVB–RCI wave functions is spin coupling with the radical orbital which would not be present if the SiH_3 moiety were bonded to another Si atom in the bulk.

The inversion of SiF_3 is not nearly so straightforward. Assuming the transition state to be of D_{3h} symmetry results in a barrier of 2.17 eV at the HF level, a value much greater than for SiH_3. The critical difference is that the electron affinity of F is larger than of H, thus SiF_3 is better described as $Si^{3+}(F^-)_3$. This hypothetical planar transition state has the radical electron on the Si^{3+} in a 3*s*-like orbital. There is consequently a larger repulsion due to spatial proximity between this lone electron and the three bonding pairs, and thus a large barrier. The barrier for the π-type radical orbital is ~1.2 eV higher than for the 3*s* orbital.

The inversion transition state of SiF_3 turns out to be nearly T-shaped, with the geometry as shown below.



For the HF wave function the inversion barrier is 1.56 eV, still much larger than the inverstion barrier of SiH_3. In the T-shaped configuration the radical orbital is a *sp* hybrid in the molecular plane. The absolute energy (at the HF level) of this transition state is − 587.354 22 hartrees. The predicted equilibrium geometry and energy are given in Table II.

As the SiF bonds in SiF_3 are ionic, one would expect the Hartree–Fock description to be reasonable for the energetics. A GVB–(12/24)*PP* description of the orbitals at the equilibrium tetrahedral geometry shows that one of the four sp^3 hybridized lobes on each F atom is oriented toward the Si atom, i.e., along the bond. For the transition state, however, two lone pairs of electrons on each F atom appear to form a "banana" bond arrangement around the Si atom.

D. Excitation energies

Although our CI calculation has not been designed to calculate excitation energies, it is worthwhile to compare our values to the experimental ones and those obtained in other calculations. These excitation energies are given in Tables III, IV, and V for the states of Si, SiF, and SiF_2, respectively. The SiF_2 values are also compared to those determined in other electronic structure calculations.

The calculated energies for the ^3P, ^1D, and ^5S states of atomic silicon at the HF, GVB(1/2)*PP*, singles and the doubles CI, and full valence CI levels are given in Table III. The first discrepancy is that the calculated ^3P to ^1D excitation energy (1.02 eV) is too large as compared to the experimental value of 0.78 eV. A 0.1 eV decrease in the excitation energy was achieved by adding a set of *f* functions which interacted strongly with the ^1D HF orbitals. This overly high triplet to singlet energy is also observed in the $^{1,3}B_1$ states of SiF_2 calculated by us ($\Delta E = 2.94$ eV whereas the experimental

TABLE IV. Adiabatic excitation energies ($^2\Pi$ to $^4\Sigma^-$), ionization potentials, and electron affinities of the diatomic states. There are no corrections for the vibrational zero point energies as the ω_e values are almost equal in all the states.

	Energy (eV)		
	Calc.	Expt.	Difference
SiF(ΔE)	3.33	3.70[a]	-0.37
Si(IP)	7.68	8.151[b]	-0.47
SiF(IP)	6.82	7.26[b,c]	-0.44
F(EA)	-2.21	-3.42[d]	1.21
SiF(EA)	0.03	-1.1[e]	1.13

[a] K. P. Huber and G. Herzberg, *Constants of Diatomic Molecules* (Van Nostrand–Reinhold, New York, 1979).

[b] *Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions* (NSRDS-NBS 26), edited by J. L. Franklin *et al.*, (U. S. Department of Commerce, National Bureau of Standards, Washington, D. C., 1979), pp. 162–4.

[c] T. R. Hayes, R. C. Wetzel, F. A. Baiocchi, and R. S. Freund, J. Vac. Sci. Technol., presented at the 32nd National Symposium of the American Vacuum Society.

[d] H. Hotop and W. C. Lineberger, J. Phys. Chem. Ref. Data **4**, 539 (1975).

[e] Estimate from P. A. G. O'Hare and A. C. Wahl, J. Chem. Phys. **55**, 666 (1971); P. A. G. O'Hare, J. Chem. Phys. **59**, 3842 (1973).

value is 2.21 eV—from Table V) and Colvin *et al.*[20] and the same states of SiH_2 calculated by others.[6] The reason for this deficiency is not understood at this time.

On the other hand, even with a full valence CI, the ^3P to ^5S excitation energy is ~0.5 eV smaller than the experimental value. Again we are at a loss to explain the difference. However, in determining the SiF $^2\Pi$ to $^4\Sigma^-$ excitation energy a value which is 0.4 eV smaller than experiment is calculated (Table IV). This analogy does not hold true for the triatomic molecule as the calculated $^1A_1$ to $^3B_1$ energy of 3.29 eV (Table V) is within 0.03 eV of the experimental value, 3.26 eV. All of the calculations reproduce well the $^3B_1$ to $^1B_1$ excitation energy. (Carter and Goddard[28] have given an extensive discussion of the proper choice of configurations so that $^1A_1$ and $^3B_1$-like states are calculated at the same level of electron correlation.)

The calculated ionization potentials of both Si and SiF are too small by ~0.45 eV and the calculated electron affinities of F and SiF are both too small by ~1.2 eV (Table IV) as diffuse functions were not included in these calculations (see Sec. III A). Basis set deficiencies in describing the atomic ions carry over to the molecular ions. It is thus surprising that the calculated ionization potential of SiF_2 is within 0.04 eV of the experimental value. Since the errors in describing the ionic states shown in Fig. 1 are consistent for the entire range of R values, to obtain realistic potential curves with respect to the SiF $^2\Pi$ state it is feasible to shift the curves at $R = \infty$ to the experimental values of the Si ionization potential and F electron affinity.

E. Negative ion state

The negative ion state, SiF^-, displayed conceptual subtleties that caused problems in determining the dissociation energetics. In the separated atom limit, a F^- ion is formed. Conceptually there is the problem of whether to describe it as having four equivalent sp^3 hybridized lobes or as having symmetry orbitals ($2s$, $2p_x$, $2p_y$, and $2p_z$). Both descriptions give a spherically symmetric F^- ion. At the GVB(4/8)*PP* level of calculation, the lobe configuration is lower in energy by ~10 mhartree. However, at the GVB–RCI level the symmetry orbital configuration is lowest by about 10 mhartree. This reversal of energetics is basically independent of basis set.[29] The sp and sp^2 hybridization schemes give energies that are in line with the above discussed limits. For the SiF^- molecule, since we have carried out the calculations in C_{2v} symmetry, the question is do we describe the asymptotic limit of F^- as symmetry lobes or as sp hybridized? Near equilibrium, of course, the sp hybridization is appropriate because the Si atom distorts the electron distribution from a totally spherical one. We repeated a few of the GVB calculations with a full CI within the F s and p_z space. The other three pairs of electrons were left at the GVB(3/6)*PP* level. This was a 152 configuration MCSCF. The results of these calculations are shown in Table V.[30] This new calculation allowed the F $2s$ and $2p_z$ electrons complete freedom in choosing either symmetry or hybridized orbitals.

All of the effort to correctly describe F^- is probably for naught as F^- is a closed shell system and the Si–F^- interaction is electrostatic in nature, precisely the two regimes where low level SCF calculations should be adequate in describing the interaction. As shown in Table V,[30] the bond energies from the GVB(5/10), DC–CI, and the MCSCF calculations are essentially equivalent.

IV. CONCLUSIONS

A systematic scheme of dissociation-consistent configuration interaction wave functions for calculating bond strengths in silicon–fluoride systems relevant to the etching process has been presented. That is, configurations for a CI have been chosen that change systematically as bonds are broken or formed. For the diatomic states SiF ($^2\Pi$ and $^4\Sigma^-$), SiF^+ ($^1\Sigma^+$), and SiF^- ($^3\Sigma^-$) we predict dissociation energies to within 10% of the experimental values. For the triatomic states of SiF_2 ($^1A_1$ and $^3B_1$) and SiF_2^+ ($^2A_1$) the predicted energies for the dissociation to SiF and F are with-

TABLE V. Energetics (in eV) of the SiF_2 molecules. The absolute energies in hartree plus 487 hartree for the $^1A_1$, $^3B_1$, $^1B_1$, and $^2A_1$ states at equilibrium and with one F atom a distance of 6 Å from the silicon atom are given in order in the following pairs of numbers: $(-1.0781, -0.8436)$; $(-0.9753, -0.8617)$; $(-0.8673, -0.8617)$; $(-0.6987, -0.6015)$.

	Energy relative to the $^1A_1$ energy			
State	This work	Colvin[a]	Wirsam[b]	Experiment
$^3B_1$	3.29	3.19	3.21	3.26[c]
$^1B_1$	6.23	5.94	5.92	5.47[d]
$^2A_1$	10.82			10.78[e]

[a] M. E. Colvin, R. E. Grev, H. F. Schaefer III, and J. Bicerano, Chem. Phys. Lett. **99**, 399 (1983).

[b] B. Wirsam, Chem. Phys. Lett. **22**, 360 (1973).

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in 15% of the estimated experimental values. For the inversion bend of SiF_3 we predict that the transition state is a T-shaped configuration rather than one of D_{3h} symmetry. Of importance to the etching process, we have found that a F atom can readily bond to an unsaturated Si atom and that the bonding of a F atom to a closed shell of electrons is an activated process.

The major advantage of the DC–CI scheme presented here is that the bond energies can be calculated with relatively modest-sized CI calculations. The longest CI ($^3B_1$ state) took about 3 h of VAX 11/780 time. Thus it is feasible and reliable to examine a number of reaction pathways for the etching of silicon by fluorine.

Supplementary materials: Supplementary materials available with this paper include the eight tables of Appendix A. These consist of the Si *ab initio* basis set and the dissociation energy values for the four diatomic SiF states. Also included are the potential curves near equilibrium for SiH_3–SiH_3, SiH_3–SiF_3, SiF_3–F, and SiH_3–F and the potential curves for the inversion of SiH_3. The data values for determining bond energies are given in the final table. (See Ref. 30.)

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[30] See AIP document no. PAPS JCPSA-87-1307-9 for 9 pages of Appendix A. Order by PAPS number and journal reference from American Institute of Physics, Physics Auxiliary Publication Service, 335 East 45th Street, New York, NY 10017. The price is $1.50 for each microfiche (98 pages) or $5.00 for photocopies of up to 30 pages, and $0.15 for each additional page over 30 pages. Airmail additional. Make checks payable to the American Institute of Physics.