

performed as a function of the energy  $E_{\sigma}$  associated with gauche states about  $\text{CH}_2\text{-CH}_2$  bonds. In the calculations it was assumed that the dipole moment of the ester group is 1.89 D and that it makes an angle of  $123^\circ$  with the direction of the  $\text{CH}_3\text{-CO}$  bond.<sup>21</sup> The results obtained, represented in Figure 8, indicate that  $\langle \mu^2 \rangle$  decreases as  $E_{\sigma}$  decreases; agreement between theory and experiment is found for values of  $E_{\sigma}$  close to  $-0.8$  kcal mol<sup>-1</sup>.

Calculations show that increasing  $E_{\sigma}$  from 0.1 to 1.5 kcal mol<sup>-1</sup> causes the value of  $\langle \mu^2 \rangle$  to change less than 5%. The change of the dipole moment of DDA with the fraction of gauche states about  $\text{CH}_2\text{-O}$  bonds of the ester residue is much more pronounced, as can be seen in Figure 8, where the variation of  $\langle \mu^2 \rangle$  with  $E_{\sigma}$ ,

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is represented. Here the dipole moment increases as the trans population about these bonds is stabilized. For  $E_{\sigma} < -0.8$  kcal mol<sup>-1</sup>, the theoretical values of  $\langle \mu^2 \rangle$  are less than the experimental results. In order to make the experimental results compatible with values of  $E_{\sigma} < -1$  kcal mol<sup>-1</sup>, it is necessary to postulate that the value of  $E_{\sigma}$  is somewhat greater than  $0.3\text{--}0.4$  kcal mol<sup>-1</sup>, the value commonly used for this quantity in the evaluation of the conformation-dependent properties of polyesters.

In conclusion, the critical analysis of the dipole moments of the model compounds used in this study suggests that gauche states about  $\text{CH}_2\text{-CH}_2$  bonds that give rise to first-order interactions between an oxygen atom of an ester group and an oxygen atom of an ether group are strongly favored over the alternative trans states; however, the experimental values are not reproduced for values of  $E_{\sigma}$  below  $-0.8$  kcal mol<sup>-1</sup>.

## An ab Initio Study of the Structures and Heats of Formation of $\text{SiH}_m\text{F}_n^+$ ( $m + n = 1\text{--}4$ )

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The equilibrium geometries of  $\text{SiH}_m\text{F}_n^+$  ( $m + n = 1\text{--}4$ ) were determined at the Hartree-Fock level by using the 3-21G and 6-31G\* basis sets. The structures of  $\text{SiH}$ ,  $\text{SiF}$ , and  $\text{SiH}_{2-n}\text{F}_n^+$  resemble the neutral molecules; the tricoordinate cations are planar, whereas the neutral radicals are pyramidal. The  $\text{SiH}_{4-n}\text{F}_n^+$  distort to form a complex between a silicon-containing cation and a neutral atom or diatom:  $\text{SiH}_2^+\text{-H}_2$ ,  $\text{SiHF}^+\text{-H}_2$  or  $\text{SiH}_2^+\text{-HF}$ ,  $\text{SiHF}^+\text{-HF}$ ,  $\text{SiF}_2^+\text{-HF}$ , and  $\text{SiF}_3^+\text{-F}$  are the lowest energy structures. Adiabatic ionization potentials and proton affinities were calculated at the MP4SDTQ/6-31G\*\* level. Heats of formation were computed by the bond additivity correction method and from the ionization potentials and proton affinities. The estimated heats of formations (298 K, ideal gas, thermal electron convention) are the average of the values obtained by the three different approaches:  $\text{SiH}^+$ ,  $273.6 \pm 4$ ;  $\text{SiF}^+$ ,  $154.1 \pm 4$ ;  $\text{SiH}_2^+$ ,  $276.7 \pm 4$ ;  $\text{SiHF}^+$ ,  $183.0 \pm 4$ ;  $\text{SiF}_2^+$ ,  $98.3 \pm 4$ ;  $\text{SiH}_3^+$ ,  $235.2 \pm 4$ ;  $\text{SiH}_2\text{F}^+$ ,  $141.5 \pm 4$ ;  $\text{SiHF}_2^+$ ,  $50.5 \pm 4$ ;  $\text{SiF}_3^+$ ,  $-30.5 \pm 4$ ;  $\text{SiH}_2\text{-H}_2^+$ ,  $266.1 \pm 4$ ;  $\text{SiH}_2\text{-HF}^+$ ,  $177.3 \pm 4$ ;  $\text{SiHF-HF}^+$ ,  $85.3 \pm 4$ ;  $\text{SiF}_2\text{-HF}^+$ ,  $-3.4 \pm 4$ ;  $\text{SiF}_3\text{-F}^+$ ,  $-31.3 \pm 4$  kcal/mol.

### Introduction

Interest in the thermochemistry and kinetics of small silicon compounds has grown rapidly in recent years, in part because of the importance of these compounds to semiconductor industry. The energetics of both neutral and charged species are fundamental to the understanding of processes such as chemical vapor deposition, glow discharge deposition, and plasma etching.

The thermochemistry of small, neutral and ionic silicon-containing compounds have been studied extensively both experimentally<sup>1-33</sup> and theoretically.<sup>34-50</sup> Vertical ionization potentials are available for a number of the  $\text{SiH}_n\text{F}_m$  species<sup>51,52</sup> but the data for adiabatic ionization potentials are more limited. Reliable experimental adiabatic ionization potentials are available for  $\text{SiH}_m$ ,<sup>2,3,5-20</sup> and some data are also available for  $\text{SiF}_n$ .<sup>4,21-33</sup> Pople and Curtiss<sup>34-37</sup> have carried out a systematic theoretical studies of a structures and energetics of  $\text{SiH}_n$  and  $\text{SiH}_n^+$  as well as the other second and third period hydrides and have obtained very good agreement with available experimental data. Good estimates of heats of formation have also been obtained for  $\text{SiH}_n$  and  $\text{SiH}_m\text{Cl}_n$  by Binkley and Melius using the BAC-4 approach.<sup>38</sup> Jahn-Teller distortion in  $\text{SiH}_4^+$  has been the subject of a number of studies.<sup>35,44-48</sup> The potential energy surfaces for  $\text{SiH}^+$ ,  $\text{SiF}^+$ , and  $\text{SiF}_2^+$  have also been calculated.<sup>39,41,42,49</sup>

In earlier work,<sup>39,40</sup> we have established a consistent and reliable set of heats of formation for the neutral  $\text{SiH}_m\text{F}_n$ , based on the experimental  $\Delta H_f^\circ$  for  $\text{SiH}_n$  and  $\text{SiF}_4$ , and high level ab initio calculations of isodesmic reactions.

In this paper, the equilibrium geometries, harmonic frequencies, and energies of the  $\text{SiH}_m\text{F}_n$  cations are calculated by using ab initio

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TABLE I: Total Energies for  $\text{SiH}_n\text{F}_m^+$ <sup>a</sup>

molecule	3-21G		6-31G**					3-21G	
	HF	HF	HF	E <sub>2</sub>	E <sub>3</sub>	E <sub>4SDQ</sub>	E <sub>4T</sub>	ZPE	thermal
Si <sup>+</sup>	-287.062 11	-288.551 30	-288.551 30	-0.034 43	-0.011 42	-0.003 79	-0.000 29	0.0	0.9
SiH <sup>+</sup>	-287.630 41	-289.136 46	-289.138 17	-0.055 82	-0.015 08	-0.004 64	-0.000 52	3.2	1.5
SiF <sup>+</sup>	-386.042 65	-388.088 50	-388.088 50	-0.231 18	-0.003 33	-0.010 21	-0.006 31	1.5	1.5
SiH <sub>2</sub> <sup>+</sup>	-288.191 96	-289.709 83	-289.713 33	-0.058 65	-0.013 27	-0.003 33	-0.000 66	8.0	1.8
SiHF <sup>+</sup>	-386.564 63	-388.624 09	-388.625 88	-0.229 32	-0.002 87	-0.008 80	-0.005 59	5.6	1.9
SiF <sub>2</sub> <sup>+</sup>	-484.926 35	-487.530 40	-487.530 40	-0.398 99	0.007 63	-0.012 99	-0.010 34	3.5	2.1
SiH <sub>3</sub> <sup>+</sup>	-288.798 36	-290.328 91	-290.333 99	-0.079 70	-0.016 54	-0.003 62	-0.000 82	14.5	1.9
SiH <sub>2</sub> F <sup>+</sup>	-387.174 50	-389.244 02	-389.247 52	-0.249 28	-0.006 70	-0.008 51	-0.005 41	12.5	1.9
SiHF <sub>2</sub> <sup>+</sup>	-485.544 17	-488.157 03	-488.158 85	-0.418 55	0.002 66	-0.012 63	-0.009 92	9.5	2.2
SiF <sub>3</sub> <sup>+</sup>	-583.895 98	-587.056 19	-587.056 19	-0.586 52	0.011 38	-0.016 10	-0.014 23	6.2	2.6
SiH <sub>3</sub> <sup>+</sup> -H	-289.300 64	-290.831 66	-290.837 69	-0.081 78	-0.016 77	-0.003 67	-0.000 90	16.2	2.2
SiH <sub>2</sub> <sup>+</sup> -H <sub>2</sub>	-289.320 26	-290.843 01	-290.854 87	-0.090 30	-0.018 89	-0.004 30	-0.000 99	16.6	3.2
SiH <sub>2</sub> F <sup>+</sup> -H	-387.675 68	-389.745 39	-389.749 53	-0.250 14	-0.006 95	-0.008 41	-0.005 37	13.8	2.7
SiHF <sup>+</sup> -H <sub>2</sub>	-387.692 08	-389.753 67	-389.761 00	-0.256 40	-0.008 50	-0.009 90	-0.005 57	13.9	3.4
SiH <sub>3</sub> <sup>+</sup> -HF	-387.721 14	-389.760 63	-389.772 77	-0.249 90	-0.012 77	-0.006 56	-0.004 00	17.1	2.7
SiHF <sub>2</sub> <sup>+</sup> -H	-486.045 61	-488.658 38	-488.661 02	-0.419 23	0.002 33	-0.012 51	-0.009 81	10.7	3.1
SiF <sub>2</sub> <sup>+</sup> -H <sub>2</sub>	-486.055 83	-488.661 10	-488.664 20	-0.427 02	-0.001 53	-0.014 01	-0.010 29	12.4	3.3
SiHF <sup>+</sup> -HF	-486.099 40	-488.677 42	-488.687 77	-0.417 58	-0.003 47	-0.010 79	-0.008 27	14.5	2.8
SiF <sub>3</sub> <sup>+</sup> -H	-584.399 25	-587.560 51	-587.562 92	-0.587 81	0.010 73	-0.016 02	-0.014 03	7.4	3.4
SiF <sub>2</sub> <sup>+</sup> -HF	-584.473 15	-587.590 78	-587.599 55	-0.584 67	0.005 78	-0.014 40	-0.012 50	11.4	3.3
SiF <sub>4</sub> <sup>+</sup>	-682.773 41	-686.446 81	-686.446 81	-0.713 48	0.002 15	-0.017 23	-0.015 56 <sup>b</sup>	7.0	3.2

<sup>a</sup>Total energies in au, zero point energies, and thermal contributions in kcal/mol, 1 au = 627.51 kcal/mol. <sup>b</sup>Estimated by assuming E<sub>4T</sub> is the same as for the <sup>2</sup>A' state.

TABLE II: Optimized Geometries<sup>a</sup>

molecule	symmetry	parameter	HF/3-21G	HF/6-31G*
SiH <sup>+</sup>	C <sub>∞v</sub>	R(Si-H)	1.513	1.492
SiF <sup>+</sup>	C <sub>∞v</sub>	R(Si-F)	1.579	1.533
SiH <sub>2</sub> <sup>+</sup>	C <sub>2v</sub>	R(Si-H)	1.480	1.470
		∠(H-Si-H)	120.9	119.8
SiHF <sup>+</sup>	C <sub>s</sub>	R(Si-H)	1.495	1.482
		R(Si-F)	1.590	1.537
		∠(H-Si-F)	116.2	115.7
SiF <sub>2</sub> <sup>+</sup>	C <sub>2v</sub>	R(Si-F)	1.581	1.528
		∠(F-Si-F)	114.2	118.2
SiH <sub>3</sub> <sup>+</sup>	D <sub>3h</sub>	R(Si-H)	1.463	1.454
SiH <sub>2</sub> F <sup>+</sup>	C <sub>2v</sub>	R(Si-H)	1.453	1.449
		R(Si-F)	1.589	1.535
		∠(H-Si-F)	115.2	116.4
SiHF <sub>2</sub> <sup>+</sup>	C <sub>2v</sub>	R(Si-H)	1.443	1.442
		R(Si-F)	1.573	1.523
		∠(H-Si-F)	123.6	121.5
SiF <sub>3</sub> <sup>+</sup>	D <sub>3h</sub>	R(Si-F)	1.559	1.512
SiH <sub>n</sub> <sup>+</sup>	see Figure 1			
SiH <sub>3</sub> F <sup>+</sup>	see Figure 2			
SiH <sub>2</sub> F <sub>2</sub> <sup>+</sup>	see Figure 3			
SiHF <sub>3</sub> <sup>+</sup>	see Figure 4			
SiF <sub>4</sub> <sup>+</sup>	C <sub>s</sub> ( <sup>2</sup> A')	R(Si-F*)	2.006	2.006
		R(Si-F <sub>a</sub> )	1.563	1.520
		R(Si-F <sub>b</sub> )	1.562	1.519
		∠F <sub>a</sub> -Si-F <sub>b</sub>	118.8	118.5
		∠F*-Si-F <sub>a</sub>	92.9	92.9
		∠F*-Si-F <sub>b</sub>	96.6	97.1

<sup>a</sup>Bond lengths in angstroms, angles in degrees; longest bond is indicated with an asterisk.

molecular orbital methods. The calculated adiabatic ionization potentials and proton affinities, as well as the bond additivity

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TABLE III: Calculated Harmonic Vibrational Frequencies<sup>a</sup>

molecule	frequencies
SiH <sup>+</sup>	2199 <sup>b</sup>
SiF <sup>+</sup>	1078
SiH <sub>2</sub> <sup>+</sup>	926, 2297, 2377
SiHF <sup>+</sup>	765, 1060, 2101
SiF <sub>2</sub> <sup>+</sup>	321, 966, 1136
SiH <sub>3</sub> <sup>+</sup>	893, <sup>c</sup> 972*, 2388, 2456*
SiH <sub>2</sub> F <sup>+</sup>	763, 843, 1012, 1093, 2470, 2539
SiHF <sub>2</sub> <sup>+</sup>	349, 633, 892, 1009, 1201, 2559
SiF <sub>3</sub> <sup>+</sup>	321*, 328, 867, 1251*
SiH <sub>3</sub> <sup>+</sup> -H	360*, 440, 889, 967*, 2387, 2453*
SiH <sub>2</sub> <sup>+</sup> -H <sub>2</sub>	11, 303, 381, 387, 485, 920, 2311, 2389, 4443
SiH <sub>2</sub> F <sup>+</sup> -H	192, 307, 390, 761, 847, 1007, 1087, 2475, 2541
SiHF <sup>+</sup> -H <sub>2</sub>	124, 194, 273, 336, 341, 773, 1054, 2153, 4487
SiH <sub>2</sub> <sup>+</sup> -HF	120, 389, 462, 647, 795, 925, 2359, 2417, 3832
SiHF <sub>2</sub> <sup>+</sup> -H	177, 218, 349, 390, 667, 894, 1003, 1195, 2571
SiF <sub>2</sub> <sup>+</sup> -H <sub>2</sub>	129, 168, 322, 372, 602, 631, 970, 1130, 4338
SiHF <sup>+</sup> -HF	211, 298, 487, 518, 680, 814, 1030, 2327, 3787
SiF <sub>3</sub> <sup>+</sup> -H	205*, 303, 323*, 494, 863, 1242*
SiF <sub>2</sub> <sup>+</sup> -HF	157, 254, 310, 333, 498, 559, 977, 1126, 3733
SiF <sub>4</sub> <sup>+</sup>	87, 156, 300, 326, 328, 409, 873, 1244, 1245

<sup>a</sup>In cm<sup>-1</sup>; doubly degenerate modes indicated with an asterisk. <sup>b</sup>Observed ω<sub>e</sub> = 2157 cm<sup>-1</sup>.<sup>14</sup> <sup>c</sup>Observed ω<sub>e</sub> = 820 cm<sup>-1</sup>.<sup>15</sup>

correction method<sup>38</sup> are used to estimate the heats of formation of SiH<sub>n</sub>F<sub>m</sub><sup>+</sup> (n + m = 1-4).

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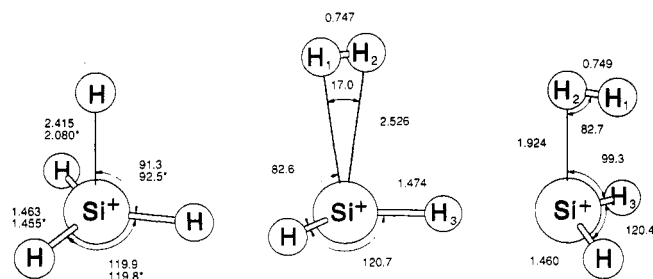
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**Figure 1.** Optimized geometries for  $\text{SiH}_3^+-\text{H}$  ( $C_{3v}$  symmetry),  $\text{SiH}_2^+-\text{H}_2$  (HF/3-21G optimized,  $C_2$  symmetry with  $\text{H}_2$  perpendicular to the symmetry plane), and  $\text{SiH}_2^+-\text{H}_2$  (HF/6-31G\* optimized,  $C_2$  with  $\text{H}_2$  in the symmetry plane,  $\angle\text{H}_1\text{H}_2\text{SiH}_3 = 61.5^\circ$ ).

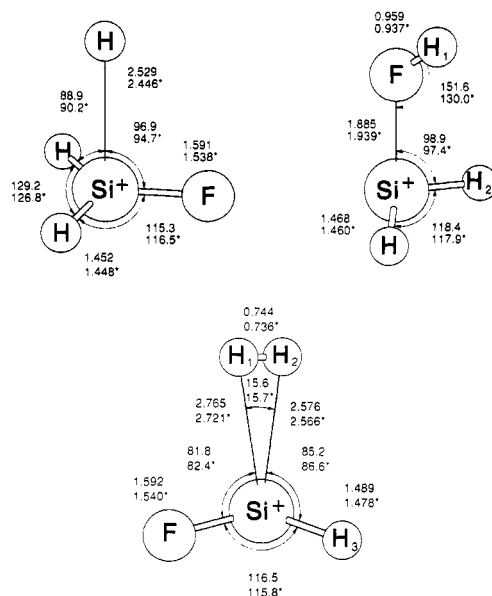
## Method

Ab initio molecular orbital calculations were performed with the GAUSSIAN 86 and 88 systems of programs,<sup>53</sup> using split valence and polarization basis sets (3-21G,<sup>54</sup> 6-31G\*, and 6-31G\*\*<sup>55</sup>). Geometries were fully optimized by using analytical gradient methods<sup>56</sup> at the Hartree-Fock level with the 3-21G and 6-31G\* basis sets. The vibrational frequencies, zero point energies, thermal corrections, and entropies were obtained from frequencies calculated analytically at the HF/3-21G level.<sup>57</sup> Electron correlation corrections were estimated by using fourth-order Møller-Plesset perturbation theory<sup>58</sup> with and without triple excitations (MP4SDTQ and MP4SDQ, frozen core). For selected systems, the MP $n$  calculations were spin projected<sup>59</sup> to test for the effects of spin contamination on the heats of reaction.

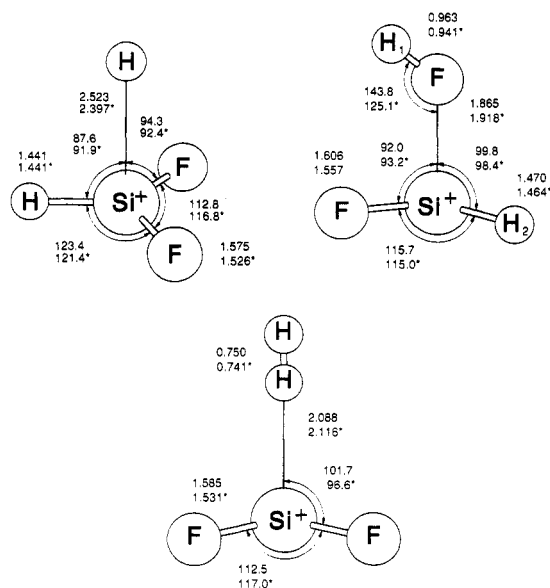
## Results and Discussion

The calculated total energies for  $\text{SiH}_n\text{F}_m^+$  ( $n + m = 1-4$ ) are listed in Table I; molecular geometries and vibrational frequencies are given in Tables II and III, respectively. The corresponding data for the neutral molecules have been published previously.<sup>39</sup> Relative energies and binding energies for the different isomers of  $\text{SiH}_{4-n}\text{F}_n^+$  are given in Table IV. The adiabatic ionization energies are summarized Table V and the calculated proton affinities are shown in Table VI. Ionization potentials, proton affinities, and the bond additivity method<sup>38</sup> are used in Table VII to estimate the heats of formation of  $\text{SiH}_n\text{F}_m^+$ .

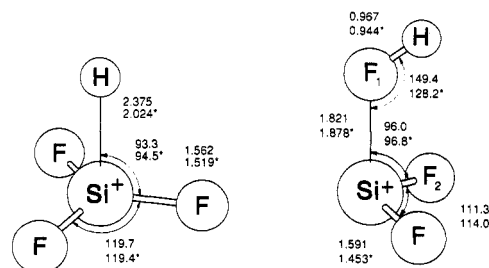
**Electronic Structure and Equilibrium Geometries.** A comparison of the optimized geometries for the cations (Table II) with their neutral counterparts (Table II of ref 39) reveals that the cations in general have shorter bonds. In  $\text{SiH}^+$  and  $\text{SiF}^+$ , the electron is removed from a  $p_x$  type orbital on the silicon and the effect on the geometry is primarily electrostatic. For  $\text{SiH}_2^+$ ,  $\text{SiHF}^+$ , and  $\text{SiF}_2^+$ , the electron is removed from the  $sp^2$  lone pair of the silylene; as expected by VSEPR theory, the bond angle at silicon increases significantly when the number of electrons in the lone pair is reduced. To form  $\text{SiH}_n\text{F}_{3-n}^+$  from the corresponding neutral silyl radicals, an electron is removed from the singly



**Figure 2.** Optimized geometries at HF/3-21G (no asterisk) and HF/6-31G\* (asterisk)  $\text{SiH}_2\text{F}^+-\text{H}$  ( $C_2$  symmetry),  $\text{SiH}_2^+-\text{HF}$  ( $C_2$  symmetry,  $\angle\text{H}_1\text{FSiH}_2 = 60.4^\circ, 59.7^\circ$ \*) and  $\text{SiHF}^+-\text{H}_2$  ( $C_1$  symmetry,  $\angle\text{H}_1\text{H}_2\text{SiH}_3 = 122.9^\circ, 119.2^\circ$ \*)).



**Figure 3.** Optimized geometries at HF/3-21G level (no asterisk) and HF/6-31G\* (asterisk):  $\text{SiHF}_2^+-\text{H}$  ( $C_2$  symmetry),  $\text{SiHF}^+-\text{HF}$  ( $C_1$  symmetry,  $\angle\text{H}_1\text{FSiH}_2 = 114.3^\circ, 114.6^\circ$ \*), and  $\text{SiF}_2^+-\text{H}_2$  ( $C_2$  symmetry,  $\angle\text{HHSi} = 180^\circ$ ).



**Figure 4.** Optimized geometries at HF/3-21G level (no asterisk) and the HF/6-31G\* (asterisk):  $\text{SiF}_3^+-\text{H}$  ( $C_{3v}$  symmetry) and  $\text{SiF}_2^+-\text{HF}$  ( $C_1$  symmetry,  $\angle\text{HF}_1\text{SiF}_2 = 56.5, 58.1^\circ$ \*)).

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occupied p orbital of the radical; consequently, the tricoordinated cations are planar with an empty  $p_x$  orbital on the silicon.

Formation of  $\text{SiH}_n\text{F}_{4-n}^+$  requires the removal of an electron from a bonding orbital, followed by rearrangement of the geometry to

TABLE IV: Relative Energies and Binding Energies for  $\text{SiH}_{4-n}\text{F}_n^+$ 

molecule	relative energy <sup>a,b</sup>					binding energy <sup>a,c</sup>				
	HF	MP2	MP3	MP4SDQ	MP4SDTQ	HF	MP2	MP3	MP4SDQ	MP4SDTQ
$\text{SiH}_3^+-\text{H}$	10.3	15.7	17.0	17.4	17.4	1.8	3.1	3.2	3.3	3.3
$\text{SiH}_2^+-\text{H}_2$	0.0	0.0	0.0	0.0	0.0	4.5	7.8	7.9	7.6	7.8
$\text{SiH}_2\text{F}^+-\text{H}$	11.3	11.1	14.8	13.6	12.8	1.0	1.6	1.7	1.7	1.7
$\text{SiHF}^+-\text{H}_2$	4.2	0.2	2.9	0.7	-0.3	0.7	1.2	1.3	1.1	1.1
$\text{SiH}_2^+-\text{HF}$	0.0	0.0	0.0	0.0	0.0	26.8	32.0	30.5	30.9	31.5
$\text{SiHF}_2^+-\text{H}$	12.9	11.9	15.5	14.5	13.5	1.3	1.7	1.9	1.8	1.8
$\text{SiF}_2^+\text{H}_2$	12.7	6.7	9.9	7.8	6.6	-0.7	0.4	0.7	0.5	0.5
$\text{SiHF}^+-\text{HF}$	0.0	0.0	0.0	0.0	0.0	28.5	31.8	31.1	30.6	30.9
$\text{SiF}_3^+-\text{H}$	19.1	17.1	20.2	19.2	18.2	4.1	4.9	5.3	5.3	5.2
$\text{SiF}_2^+-\text{HF}$	0.0	0.0	0.0	0.0	0.0	34.1	35.8	35.8	35.0	34.9
$\text{SiF}_3^+-\text{F}$	0.0	0.0	0.0	0.0	0.0	15.3	18.3	18.8	18.4	18.5

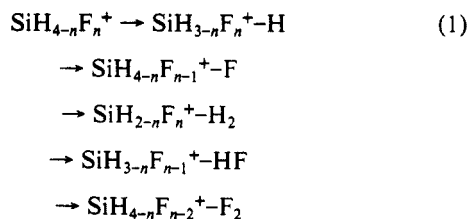
<sup>a</sup>In kcal/mol with the 6-31G\*\* basis set and including  $\Delta\text{ZPE}$  at the HF/3-21G level. <sup>b</sup>Relative to the most stable isomer of  $\text{SiH}_{4-n}\text{F}_n^+$ . <sup>c</sup> $\text{A}^+-\text{B} \rightarrow \text{A}^+ + \text{B}$ .

TABLE V: Adiabatic Ionization Energies<sup>a</sup>

reaction	3-21G	6-31G*	6-31G**					$\Delta$	thermal	experimental
	HF	HF	HF	MP2	MP3	MP4SDQ	MP4SDTQ			
$\text{SiH} \rightarrow \text{SiH}^+$	184.8	183.8	183.7	182.4	182.1	182.1	182.2	182.2	1.3	$183.6 \pm 1.5$ , <sup>16c</sup> $182.4 \pm 0.2$ , <sup>2</sup> $183.8 \pm 1.5$ <sup>14d</sup>
$\text{SiF} \rightarrow \text{SiF}^+$	175.0	171.5	171.5	166.7	167.7	167.1	166.3	166.3	1.3	$173.9 \pm 4$ , <sup>4</sup> $168$ , <sup>21</sup> $173 \pm 9$ , <sup>22</sup> $170.6 \pm 2.3$ <sup>31</sup>
$\text{SiH}_2 \rightarrow \text{SiH}_2^+$	222.8	222.5	219.3	213.0	212.4	212.6	212.8	209.0	1.5	$211 \pm 5$ , <sup>2</sup> $205.7 \pm 1.6$ <sup>3</sup>
$\text{SiHF} \rightarrow \text{SiHF}^+$	237.8	233.2	230.2	222.5	222.9	222.3	222.0	218.6	1.5	
$\text{SiF}_2 \rightarrow \text{SiF}_2^+$	273.78	262.6	259.7	252.0	253.2	252.4	251.9	248.4	1.5	$248.6 \pm 11$ <sup>26</sup>
$\text{SiH}_3 \rightarrow \text{SiH}_3^+$	188.6	186.7	186.3	187.6	188.1	188.6	188.7	185.4	1.5	$184.7 \pm 0.5$ , <sup>2</sup> $187.0 \pm 1.6$ , <sup>3</sup> $187.7 \pm 0.2$ <sup>15</sup>
$\text{SiH}_2\text{F} \rightarrow \text{SiH}_2\text{F}^+$	190.1	187.7	187.4	185.2	186.6	186.3	185.7	184.0	1.5	
$\text{SiHF}_2 \rightarrow \text{SiHF}_2^+$	203.1	196.8	196.7	191.9	193.9	193.2	192.1	190.5	1.5	
$\text{SiF}_3 \rightarrow \text{SiF}_3^+$	228.9	216.4	216.4	209.6	212.1	211.1	209.7	206.7	1.5	$207.5 \pm 6$ , <sup>23e</sup> $216.8 \pm 5$ , <sup>27</sup> $221 \pm 14$ , <sup>33</sup> $230 \pm 5$ <sup>4</sup>
$\text{SiH}_4 \rightarrow \text{SiH}_3^+-\text{H}$	277.1	282.9	279.8	276.2	275.2	275.0	275.1	271.1	2.1	
$\text{SiH}_4 \rightarrow \text{SiH}_2^+-\text{H}_2$	265.3	276.2	269.5	260.6	258.2	257.6	257.7	254.6	2.8	$253.7 \pm 0.5$ <sup>2</sup>
$\text{SiH}_3\text{F} \rightarrow \text{SiH}_2\text{F}^+-\text{H}$	284.5	288.7	286.0	279.2	279.3	278.2	277.7	275.0	2.2	
$\text{SiH}_3\text{F} \rightarrow \text{SiHF}^+-\text{H}_2$	274.3	283.6	279.0	268.2	267.3	265.3	264.7	260.9	3.0	
$\text{SiH}_3\text{F} \rightarrow \text{SiH}_2^+-\text{HF}$	259.2	282.4	274.7	268.0	264.5	264.6	264.9	260.3	2.3	
$\text{SiH}_2\text{F}_2 \rightarrow \text{SiHF}_2^+-\text{H}$	302.2	300.9	298.3	288.8	289.8	288.3	287.2	282.3	2.3	
$\text{SiH}_2\text{F}_2 \rightarrow \text{SiF}_2^+-\text{H}_2$	297.5	300.9	298.0	283.6	284.1	281.6	280.3	276.2	2.6	
$\text{SiH}_2\text{F}_2 \rightarrow \text{SiHF}^+-\text{HF}$	272.3	292.8	285.4	276.9	274.2	273.8	273.7	268.8	2.1	
$\text{SiHF}_3 \rightarrow \text{SiF}_3^+-\text{H}$	332.9	322.4	319.0	307.3	308.8	306.9	305.4	299.9	2.3	
$\text{SiHF}_3 \rightarrow \text{SiF}_2^+-\text{HF}$	290.5	307.4	300.0	290.2	288.6	287.7	287.2	281.6	2.2	
$\text{SiF}_4 \rightarrow \text{SiF}_4^+$	350.1	354.1	351.3	363.2	355.1	354.0	353.7	351.2	1.6	$350$ <sup>27</sup>

<sup>a</sup>In kcal/mol, computed by using eqs 2 and 3 of the text (zero point energy included) and without thermal corrections. <sup>b</sup>Using the best theoretical estimates of the neutrals and the ions from Table VII. <sup>c</sup>Using  $\Delta H_f^\circ[\text{SiH}]$  from ref 2. <sup>d</sup>Using  $\Delta H_f^\circ[\text{SiH}]$  from ref 2. <sup>e</sup>Using  $\Delta H_f^\circ[\text{SiF}_3]$  from ref 8.

maximize the bonding via the remaining electrons. Several possibilities can be considered:



The geometries of some of the more stable complexes are shown in Figures 1-4; their relative energies and binding energies are given in Table IV. Since Si-H bonds are more easily ionized than Si-F bonds,  $\text{SiH}_{3-n}\text{F}_{n-1}^+-\text{H}$  will be lower in energy than  $\text{SiH}_{4-n}\text{F}_{n-1}^+-\text{F}$ . These structures are characterized by a long Si-H bond (or Si-F bond in the case of  $\text{SiF}_4^+$ ) and a nearly planar  $\text{SiH}_{3-n}\text{F}_{n-1}^+$  group (Figures 1-4). As has already been demonstrated for  $\text{SiH}_4^+$ ,<sup>44-48</sup> this bonding arrangement is not the lowest in energy. Except for  $\text{SiF}_4^+$ , a complex between a silylene cation and a diatomic is lower in energy. Because of the low bond energy of  $\text{F}_2$ , the  $\text{SiH}_{4-n}\text{F}_{n-2}^+-\text{F}_2$  structures are much less stable than the remaining structures. Complexes involving  $\text{H}_2$  and HF, i.e.,  $\text{SiH}_{2-n}\text{F}_n^+-\text{H}_2$  and  $\text{SiH}_{3-n}\text{F}_{n-1}^+-\text{HF}$ , should be similar in energy based on Si-H, Si-F,  $\text{H}_2$ , and HF bond energies. However,

examination of their structures indicates that  $\text{SiH}_{2-n}\text{F}_n^+-\text{H}_2$  complexes have long Si-H<sub>2</sub> distances and weak interactions between the  $\text{H}_2$  and the silylene cations (Figures 1-4 and Table IV). The  $\text{SiH}_{3-n}\text{F}_{n-1}^+-\text{HF}$  complexes have comparatively short Si-F distances because of a strong interaction between the fluorine lone pair and the empty  $p_\pi$  orbital on silicon. For the monofluorosilane cation,  $\text{SiHF}^+-\text{H}_2$  and  $\text{SiH}_2^+-\text{HF}$  are equal in energy, but for the difluorosilane cation, the HF complex is ca. 7 kcal/mol more stable.

**Adiabatic Ionization Energies.** Calculated ionization energies in Table V were obtained by combining the computed relative ionization energy ( $\Delta H_f$  at 0 K) with the experimental ionization energy of Si (187.98 kcal/mol<sup>52</sup>):

$$\begin{aligned} \text{SiH}_m\text{F}_n + \text{Si}^+ &\rightarrow \text{SiH}_m\text{F}_n^+ + \text{Si} \\ \text{IP}(\text{SiH}_m\text{F}_n) &= \text{IP}(\text{Si}) + \Delta H_f \end{aligned} \quad (2)$$

In this manner, basis set deficiencies cancel to a large extent. If the neutral molecule is open shell ( $\text{SiX}$  and  $\text{SiH}_{3-n}\text{F}_n$ ), eq 2 is isogyric; i.e., the number of unpaired electrons is unchanged. For closed-shell systems, the appropriate isogyric reaction can be obtained by adding  $2\text{H} \rightarrow \text{H}_2$  to eq 2<sup>35,36</sup>

$$\begin{aligned} \text{SiH}_m\text{F}_n + \text{Si}^+ + 2\text{H} &\rightarrow \text{SiH}_m\text{F}_n^+ + \text{Si} + \text{H}_2 \\ \text{IP}(\text{SiH}_m\text{F}_n) &= \text{IP}(\text{Si}) + D_0(\text{H}_2) + \Delta H_f \end{aligned} \quad (3)$$

TABLE VI: Proton Affinities<sup>a</sup>

reaction	3-21G		6-31G*		6-31G**				thermal
	HF	HF	HF	MP2	MP3	MP4SDQ	MP4SDTQ		
Si + H <sup>+</sup> → SiH <sup>+</sup>	182.7	184.8	184.7	195.0	198.1	199.5	199.6	0.3	
SiH + H <sup>+</sup> → SiH <sub>2</sub> <sup>+</sup>	179.9	179.9	179.9	179.9	179.9	179.3	179.9	0.7	
SiF + H <sup>+</sup> → SiHF <sup>+</sup>	165.7	169.3	169.2	169.7	169.2	169.8	170.1	0.7	
SiH <sub>2</sub> + H <sup>+</sup> → SiH <sub>3</sub> <sup>+</sup>	196.5	196.4	196.5	196.4	196.5	196.4	196.3	0.8	
SiHF + H <sup>+</sup> → SiHF <sub>2</sub> <sup>+</sup>	183.3	185.8	185.8	186.5	185.9	186.2	186.4	0.8	
SiF <sub>2</sub> + H <sup>+</sup> → SiHF <sub>2</sub> <sup>+</sup>	153.0	161.5	161.4	161.8	161.1	161.7	162.0	0.8	
SiH <sub>3</sub> + H <sup>+</sup> → SiH <sub>3</sub> <sup>+</sup> -H	142.1	136.0	135.7	132.6	133.0	133.5	133.4	0.3	
SiH <sub>3</sub> + H <sup>+</sup> → SiH <sub>2</sub> <sup>+</sup> -H <sub>2</sub>	153.9	142.6	146.0	148.2	150.0	150.9	150.8	-0.4	
SiH <sub>2</sub> F + H <sup>+</sup> → SiH <sub>2</sub> F <sup>+</sup> -H	140.2	134.4	133.8	133.5	133.1	134.2	134.7	0.1	
SiH <sub>2</sub> F + H <sup>+</sup> → SiH <sub>2</sub> <sup>+</sup> -HF	165.5	140.6	145.1	144.7	147.9	147.8	147.5	0.1	
SiH <sub>2</sub> F + H <sup>+</sup> → SiHF <sup>+</sup> -H <sub>2</sub>	150.4	139.4	140.9	144.5	145.1	147.1	147.7	-0.6	
SiHF <sub>2</sub> + H <sup>+</sup> → SiHF <sub>2</sub> <sup>+</sup> -H	127.6	125.4	124.8	126.9	125.9	127.4	128.4	0.0	
SiHF <sub>2</sub> + H <sup>+</sup> → SiF <sub>2</sub> <sup>+</sup> -H <sub>2</sub>	132.3	125.4	125.1	132.1	131.6	134.0	135.3	-0.2	
SiHF <sub>2</sub> + H <sup>+</sup> → SiHF <sup>+</sup> -HF	157.5	133.5	137.8	138.8	141.5	141.9	141.9	0.3	
SiF <sub>3</sub> + H <sup>+</sup> → SiF <sub>3</sub> <sup>+</sup> -H	102.9	107.7	107.9	112.4	111.2	113.0	114.3	0.0	
SiF <sub>3</sub> + H <sup>+</sup> → SiF <sub>2</sub> <sup>+</sup> -HF	145.3	122.7	127.0	129.5	131.3	132.1	132.5	0.2	

<sup>a</sup>In kcal/mol with ZPE, without thermal corrections.

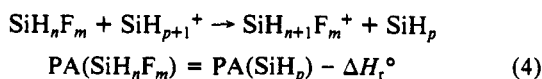
TABLE VII: Theoretical Heats of Formation

molecule	cation <sup>c</sup>								S(298) theoretical
	neutral			theoretical ΔH <sub>f</sub> <sup>o</sup> (298)				ΔH <sub>f</sub> <sup>o</sup> (298) experimental	
	ΔH <sub>f</sub> <sup>o</sup> (298)	IP <sup>b</sup>	PA <sup>b</sup>	BAC	using IP	using PA	best est		
Si	107.5 ± 2	189.9	200.5					297.1 ± 1.0 <sup>51</sup>	
SiH	89.9 ± 2	183.6	181.2	273.0	273.5	274.3	273.6	272.0 ± 1.2, <sup>2</sup> 274.7 ± 0.7, <sup>14</sup> 274.3 ± 1.5 <sup>16</sup>	45
SiF	-14.2 ± 2	167.6	171.4	154.8	153.4		154.1	170.4 ± 2.2 <sup>4</sup>	51
SiH <sub>2</sub>	65.7 ± 2	214.3	197.7	274.1	280.0	275.9	276.7	276.6 ± 6, <sup>2</sup> 276.1 ± 1.7 <sup>3</sup>	51
SiHF	-37.8 ± 2	223.5	187.8	181.6	185.7	181.6	183.0		58
SiF <sub>2</sub>	-153.0 ± 2	253.4	163.4	96.2	100.4		98.3	109 ± 2 <sup>4</sup>	64
SiH <sub>3</sub>	47.7 ± 2	190.2	151.0	232.4	237.9	235.2	235.2	232.4 ± 1.4, <sup>2</sup> 234.2 ± 2, <sup>15</sup> 237.1 ± 2 <sup>3</sup>	52
SiH <sub>2</sub> F	-44.9 ± 2	187.2	148.2	140.6	142.3	141.6	141.5		57
SiHF <sub>2</sub>	-142.6 ± 2	193.6	142.8	49.8	51.0	50.8	50.5		62
SiF <sub>3</sub>	-240.7 ± 2	211.2	133.3	-31.4	-29.5		-30.5	-31.4 ± 2, <sup>23</sup> -26.7 ± 4.5 <sup>4</sup>	65
SiH <sub>4</sub>	8.2 ± 0.5	260.5		265.6	268.7	263.9	266.1	264.2 ± 0.8 <sup>2</sup>	57
SiH <sub>3</sub> F	-85.8 ± 2	267.2		176.3	181.4	174.1	177.3		65
SiH <sub>2</sub> F <sub>2</sub>	-186.3 ± 2	275.8		84.5	89.5	81.8	85.3		70
SiHF <sub>3</sub>	-288.2 ± 2	289.4		-4.7	1.2	-6.8	-3.4		75
SiF <sub>4</sub>	-386.0 ± 0.2	355.3		-31.7	-30.9		-31.3	-35.9 <sup>27</sup>	75

<sup>a</sup>Heats of formation in kcal/mol, entropies in cal/(deg mol); neutral heats of formation taken from refs 40, 5, and 9. <sup>b</sup>Adiabatic IP and PA with thermal corrections to 298 K. <sup>c</sup>Thermal electron convention (i.e., ΔH<sub>f</sub><sup>o</sup>(298) = 0 for the electron); for the ion convention, subtract 1.48 kcal/mol from the values listed; (BAC: bond additivity correction method, eq 13; using IP: eq 7; using PA: eq 8. ΔH<sub>f</sub><sup>o</sup>(H<sup>+</sup>) = 365.23 kcal/mol at 0 K and 367.2 kcal/mol at 298 K.

(D<sub>0</sub>(H<sub>2</sub>) = 103.26 kcal/mol). Isogyric reactions are relatively insensitive to spin contamination problems. Test calculations on SiH<sub>n</sub><sup>+</sup> indicate that projection to remove spin contamination<sup>59</sup> changes the ionization potentials calculated by eqs 2 and 3 by ±0.2 kcal/mol or less. Compared with the high-level calculations of Pople and Curtiss,<sup>35-37</sup> the average error in the ionization potentials for SiH<sub>n</sub><sup>+</sup> (eqs 2 and 3 without spin projection) is ±1.8 kcal/mol. Where reliable experimental data are available, the average error in the calculated adiabatic ionization energies is ±3 kcal/mol. As shown in Figure 5, progressive substitution of hydrogen by fluorine generally causes the ionization potential to increase (SiH → SiF and SiH<sub>3</sub> → SiH<sub>2</sub>F being the only exceptions).

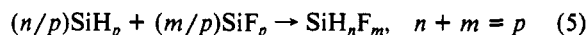
**Proton Affinities.** The data in Table I can also be used to calculate proton affinities, as listed in Table VI. Similar to the ionization energies, the proton affinities are calculated relative to a silicon containing standard:



Since there is good agreement between theory<sup>35-37</sup> and experiment<sup>2,3</sup> on the proton affinity of SiH, PA(SiH) = 179.9 kcal/mol is used as the standard. Except for PA(Si), eq 4 is isogyric and should not be affected significantly by spin contamination. Spin projection changes the PA's of SiH<sub>n</sub>, calculated via eq 4 by less than ±0.3 kcal/mol. The average error in the PA(SiH<sub>n</sub>) is ±2 kcal/mol compared to either experimental values derived from the ΔH<sub>f</sub><sup>o</sup><sup>2,3</sup> or the high-level calculations of Pople and Curtiss.<sup>35-37</sup>

Other than for SiH<sub>n</sub>, there are very few direct experimental determinations of proton affinities of SiH<sub>n</sub>F<sub>m</sub><sup>52</sup> available for comparison with the theoretical values. Fluorine substitution generally lowers the proton affinity, as expected from the electron-withdrawing nature of fluorine.

**Heats of Formation.** In our earlier papers<sup>39,40</sup> a consistent set of heats of formation for the neutral SiH<sub>n</sub>F<sub>m</sub> was obtained by combining experimental ΔH<sub>f</sub><sup>o</sup> for SiH<sub>n</sub> and SiF<sub>n</sub> with theoretically calculated ΔH<sub>r</sub> for the isodesmic reactions

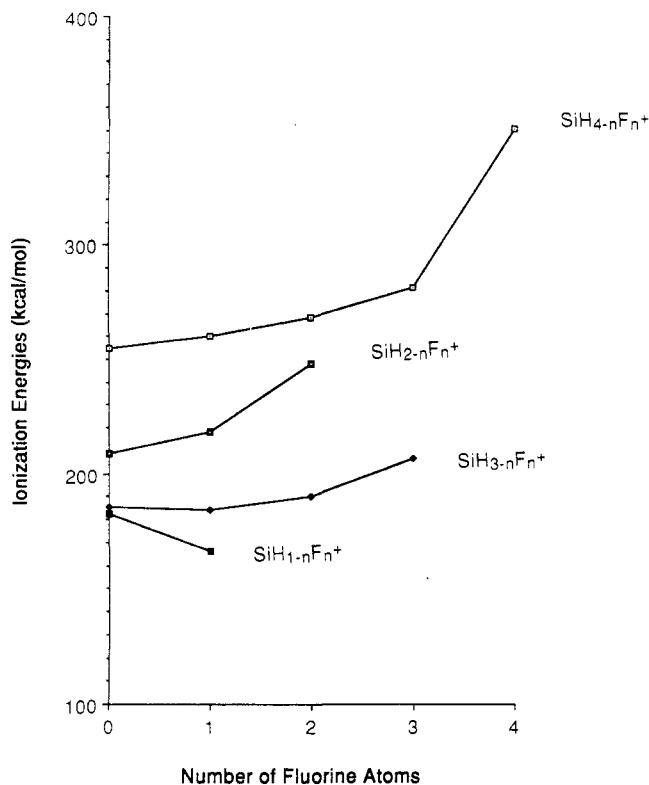


and related thermodynamic cycles. Table VII lists our best estimates of the heats of formation of the neutral SiH<sub>n</sub>F<sub>m</sub>.<sup>40</sup> A similar set of isodesmic reactions could be used to estimate the heats of formation of the SiH<sub>n</sub>F<sub>m</sub> cations; however, the ΔH<sub>f</sub><sup>o</sup> for SiF<sub>n</sub><sup>+</sup> are not sufficiently well established (equivalently, the adiabatic ionization potentials for SiF<sub>n</sub> are not firmly established). Three different and independent methods have been used to estimate the heats of formation of the SiH<sub>n</sub>F<sub>m</sub><sup>+</sup>.

The direct approach for obtaining the ΔH<sub>f</sub><sup>o</sup>(SiH<sub>n</sub>F<sub>m</sub><sup>+</sup>) is simply to add the theoretical adiabatic ionization potentials to the ΔH<sub>f</sub><sup>o</sup> of the neutral SiH<sub>n</sub>F<sub>m</sub>



Another method for computing the heats of formation applicable to all but the perfluoro members of the SiH<sub>n</sub>F<sub>m</sub><sup>+</sup> is to

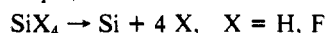


**Figure 5.** Calculated adiabatic ionization energy as a function of fluorine substitution.

combine the calculated proton affinities with the  $\Delta H_f^\circ$  of the neutral  $\text{SiH}_{n-1}\text{F}_m$ .

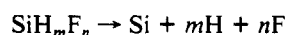
$$\Delta H_f^\circ(\text{SiH}_n\text{F}_m^+) = \Delta H_f^\circ(\text{SiH}_{n-1}\text{F}_m) - \text{PA}(\text{SiH}_{n-1}\text{F}_m) + \Delta H_f^\circ(\text{H}^+) \quad (8)$$

The third method uses the bond additivity correction (BAC) approach of Binkley and Melius.<sup>38</sup> The heat of formation of a compound is calculated from theoretical the heat of atomization and the experimental heat of formation of the atoms. Depending on the level of theory, the dissociation energy of each bond is in error to some degree and must be corrected by some amount. If these corrections are assumed to be additive, the bond additivity corrections (BAC) can be computed from a few reference compounds. For example,



$$\text{BAC}(\text{Si-X}) = \frac{1}{4}(\text{experimental } \Delta H_f - \text{calculated } \Delta H_f) \quad (9)$$

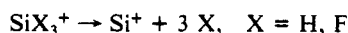
The heat of formation  $\text{SiH}_n\text{F}_m$  can then be calculated in the following manner:



$$\Delta H_f^\circ = \text{calculated } \Delta H_f^\circ + m\text{BAC}(\text{SiH}) + n\text{BAC}(\text{SiF})$$

$$\Delta H_f^\circ(\text{SiH}_n\text{F}_m) = \Delta H_f^\circ(\text{Si}) + m\Delta H_f^\circ(\text{H}) + n\Delta H_f^\circ(\text{F}) - \Delta H_f^\circ \quad (10)$$

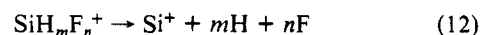
This approach yields  $\text{BAC}(\text{SiH}) = 4.69$  kcal/mol and  $\text{BAC}(\text{SiF}) = 9.53$  kcal/mol (MP4/6-31G\*\* at 298 K), resulting in an average error of  $\pm 3$  kcal/mol in the heats of formation of the neutral  $\text{SiH}_n\text{F}_m$ . The BAC for the SiX bonds in the cations can be different than in the neutrals. Since the structure of  $\text{SiH}_4^+$  and  $\text{SiF}_4^+$  are better represented as  $\text{SiH}_2^+-\text{H}_2$  and  $\text{SiF}_3^+-\text{F}$ , respectively, the BAC are calculated from the tricoordinated cations.



$$\text{BAC}(\text{Si-X}^+) = \frac{1}{3}(\text{experimental } \Delta H_f - \text{calculated } \Delta H_f) \quad (11)$$

At the MP4SDTQ/6-31G\*\* level (with  $\Delta\text{ZPE}$  and thermal corrections to 298 K computed at the HF/3-21G level),  $\text{BAC}(\text{SiH}^+) = 6.49$  kcal/mol and  $\text{BAC}(\text{SiF}^+) = 11.54$  kcal/mol, based on  $\Delta H_f^\circ_{298}(\text{SiH}_3^+) = 232.4$  kcal/mol (ref 2) and  $\Delta H_f^\circ_{298}(\text{SiF}_3^+) =$

$= -31.36$  kcal/mol.<sup>27,37</sup> The heat of formation  $\text{SiH}_n\text{F}_m^+$  can then be calculated in the following manner:



$$\Delta H_f^\circ = \text{calculated } \Delta H_f^\circ + m\text{BAC}(\text{SiH}^+) + n\text{BAC}(\text{SiF}^+)$$

$$\Delta H_f^\circ(\text{SiH}_n\text{F}_m^+) = \Delta H_f^\circ(\text{Si}^+) + m\Delta H_f^\circ(\text{H}) + n\Delta H_f^\circ(\text{F}) - \Delta H_f^\circ$$

For  $\text{SiH}_{4-n}\text{F}_n^+$ , the equations are suitably modified to take account of the fact that the structures are loosely bound complexes, e.g.,  $\text{SiH}_{3-n}\text{F}_n^+-\text{H}$ ,  $\text{SiH}_{2-n}\text{F}_n^+-\text{H}_2$ ,  $\text{SiH}_{3-n}\text{F}_{n-1}^+-\text{HF}$  or  $\text{SiF}_3^+-\text{F}$ .

The final estimates of the heats of formation are the average of the three approaches. The average difference between the best estimate and the three different approaches is  $\pm 2.4$  kcal/mol, suggesting a degree of internally consistency. Compared to both the experimental heats of formation and the high-level calculations by Pople and Curtiss,<sup>35-37</sup> the present estimates of  $\Delta H_f^\circ_{298}$  for  $\text{SiH}_n^+$  differ by  $\pm 2$  kcal/mol or less. Residual errors due to basis set effects and electron correlation may be somewhat larger for the fluorine containing compounds, suggesting error bars of perhaps  $\pm 4$  kcal/mol.

The consistency of the calculated  $\Delta H_f^\circ$  for  $\text{SiF}_n$  and  $\text{SiF}_n^+$  given in Table VII can be tested by comparing directly with experiment. The observed thresholds for the following reactions have been used by various authors to estimate the experimental heats of formation of  $\text{SiF}_n$  and  $\text{SiF}_n^+$ <sup>4,21,23,27,28,33</sup>

	exptl, calcd
$\text{Si}^+ + \text{SiF}_4 \rightarrow \text{SiF}^+ + \text{SiF}_3$	0.10 eV, 0.11 eV (13)
$\text{Si}^+ + \text{SiF}_4 \rightarrow \text{SiF}_3^+ + \text{SiF}$	2.48 eV, 1.93 eV (14)
$\text{Si}^+ + \text{SiF}_4 \rightarrow \text{SiF}_2^+ + \text{SiF}_2$	2.35 eV, 1.49 eV (15)
$\text{Si}^+ + \text{SiF}_4 \rightarrow \text{SiF}_2^+ + \text{SiF} + \text{F}$	ca. 8 eV, 8.33 eV (16)
$\text{SiF}^+ + \text{SiF}_4 \rightarrow \text{SiF}_3^+ + \text{SiF}_2$	ca. 4 eV, 2.11 eV (17)
$\text{SiF}_4 \rightarrow \text{SiF}_3^+ + \text{F} + \text{e}^-$	16.20 eV, 16.25 eV (18)

The calculated  $\Delta H_f$  for reaction 13 is in good agreement with the threshold obtained by Weber and Armentrout.<sup>4</sup> For reactions 14 and 15 the experimental thresholds<sup>4</sup> are higher than the calculated heats of reaction, indicating an activation energy of ca. 0.5 and 0.9 eV, respectively, for the reverse reaction. Considering the electronic and geometric rearrangements involved, such activation energies are sensible. The onset of reaction 16 is difficult to determine accurately from the cross-section data,<sup>4</sup> but agreement between theory and experiment is reasonable. Reaction 17 has a threshold "in the neighborhood of 4 eV";<sup>28</sup> the calculated heat of reaction is ca. 2 eV lower, suggesting a sizable barrier for the back reaction. The threshold for reaction 18<sup>23</sup> sets a definite upper bound on the heat of formation of  $\text{SiF}_3^+$ , since the  $\Delta H_f^\circ$  for  $\text{SiF}_4$  and F atom are well established;<sup>9,51</sup> the agreement between theory and experiment is quite good. The threshold for direct ionization of  $\text{SiF}_3$  is difficult to determine accurately because a large amount of curvature in the ionization cross-section;<sup>33</sup> this has been interpreted in terms of the energetics involved in changing the pyramidal radical to the planar cation.<sup>33</sup> The calculated ionization potential of  $\text{SiF}_3$ , 9.12 eV, is in agreement with a number of experimental values,  $9.0 \pm 0.24$  eV,<sup>23</sup>  $9.4 \pm 0.23$  eV,<sup>27</sup> and  $9.6 \pm 0.6$  eV;<sup>33</sup> the disagreement with the Weber and Armentrout recommended value,  $9.99 \pm 0.24$  eV,<sup>4</sup> can be traced in part to the assumption that reaction 14 proceeds without activation. The ionization energies of  $\text{SiF}$  7.26 eV<sup>21</sup> and  $\text{SiF}_2$  10.78 eV<sup>26</sup> are more firmly established and the calculated values ( $\text{IP}(\text{SiF}) = 7.30$  eV and  $\text{IP}(\text{SiF}_2) = 10.90$  eV) are in very good agreement with experiment.

## Conclusions

The optimized structures of  $\text{SiH}$ ,  $\text{SiF}$ , and  $\text{SiH}_{2-n}\text{F}_n^+$  are similar to those of the neutral molecules. The tricoordinate cations are planar, whereas the neutral radicals are pyramidal. The  $\text{SiH}_{4-n}\text{F}_n^+$

distort to form a complex between a silicon-containing cation and a neutral atom or diatom; the lowest energy structures are  $\text{SiH}_2^+-\text{H}_2$ ,  $\text{SiHF}^+-\text{H}_2$  or  $\text{SiH}_2^+-\text{HF}$ ,  $\text{SiHF}^+-\text{HF}$ ,  $\text{SiF}_2^+-\text{HF}$ , and  $\text{SiF}_3^+-\text{F}$ . Adiabatic ionization potentials, proton affinities, and heats of formation have been calculated by using isodesmic and isogyric reactions at the MP4SDTQ/6-31G\*\* level. The calculations on  $\text{SiH}_n^+$  agree well with higher level theoretical computations and with experiment. The theoretical values for  $\text{SiF}_n^+$  agree with experimental thresholds and ionization potentials. The

present work, combined with our previous calculations, provides a consistent set of heats of formation for the interpretation of the thermodynamics of  $\text{SiH}_n\text{F}_m$  and  $\text{SiH}_n\text{F}_m^+$ .

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## ESR Spectra of Mixed Group IA–IIA Compounds in Argon Matrices

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Electron spin resonance (ESR) spectra assigned to NaMg, NaCa, NaSr, KMg, and KCa radicals have been produced by codepositing suitable combinations of group IA and group IIA atoms in Ar matrices. The ESR spectra establish a  $^2\Sigma$  ground state in which the unpaired electron is substantially delocalized over the group IIA atom (ca. 25% in the case of NaCa and NaSr), thus implying chemical bond formation between the two metallic moieties. Additional ESR transitions, corresponding to  $\text{KMg}_k$  and  $\text{NaMg}_k$  molecules ( $k$  not determined), were observed when Na and K were codeposited with Mg atoms.

### Introduction

While alkali-metal clusters are chemically bound even at sizes as small as the dimer, small aggregates of the group IIA (and group IIB) metals are relatively weakly bound and only develop their metallic stability (as a result of hybridization) after reaching a certain critical size.<sup>1–7</sup> Thus, in the case of dimers (for example), the ground-state configuration is  $\dots\sigma^2$  for the alkali metals but  $\dots\sigma^2\sigma^{*2}$  for the group IIA elements. This leads to a bond order<sup>8</sup> of 1 in the former and 0 in the latter which may, therefore, be bound only by weak van der Waals forces.<sup>9,10</sup> For beryllium, *ab initio* calculations<sup>2</sup> predict that the binding energy per atom rises rapidly from about 0.1 eV for the dimer (a value confirmed by experiment<sup>10</sup>) to over 0.6 eV for  $\text{Be}_4$ . For Hg clusters, on the other hand, the transition to metallic behavior occurs at much larger sizes: in the range of 20–70 atoms.<sup>6,7</sup> Mixed group IA–IIA dimers (configuration  $\dots\sigma^2\sigma^*$ ) would be expected to have intermediate bond strengths and could be relatively stable even without significant hybridization. In general, the addition of a single alkali-metal atom might well provide a mechanism for substantially stabilizing a homonuclear group IIA cluster. While there have been several experimental<sup>11</sup> and calculational<sup>12,13</sup> studies on mixed metal clusters such as  $\text{Na}_k\text{Mg}$  ( $k \approx 2-8$ ), there is a relative dearth of information on the species  $\text{NaMg}_k$ ,  $\text{KMg}_k$ , etc. However,  $\text{NaMg}_k$  (for example) is isoelectronic with  $\text{Mg}_{k+1}^+$  (recently observed in rare gas matrices<sup>14</sup>) which (for  $k = 1-6$ ) are predicted to have binding energies in the range of 0.5 eV/atom as compared to only about 0.1 eV/atom for the corresponding neutral Mg clusters.<sup>15</sup>

In this paper we present electron spin resonance (ESR) evidence for the formation of NaMg, NaCa, NaSr, KMg, and KCa radicals during cocondensation of the group IA and group IIA metal vapors in argon matrices. The ESR spectra show that the dimers have  $^2\Sigma$  ground states and that the wave function for the unpaired electron is delocalized over the group IIA atom (ca. 25% in the case of NaCa and NaSr), thus implying a significant, chemical interaction between the two atomic moieties. There are strong similarities between the spectra analyzed here and those of the

isovalent Ag–group IIA and Ag–group IIB species.<sup>16</sup> Thus, (i) alkali-metal hyperfine (hf) constants decrease (i.e., greater delocalization) as the difference in ionization potential between the two metal atoms decreases and (ii) measured  $g$  shifts increase linearly with the spin–orbit coupling constant of the group IIA atom. When Na and K were codeposited with Mg (but not with Ca or Sr), ESR transitions in addition to those assigned to the dimer were observed. The spectra imply the formation of  $\text{KMg}_k$  and  $\text{NaMg}_k$  molecules ( $k$  not determined) and a further delocalization of the unpaired electron over the magnesium nuclei.

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