# Heats of formation of $SiH_mF_n$ calculated by *ab initio* molecular orbital methods

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Reliable heats of formation are known for $SiH_n$ and $SiF_4$, but experimental data for some of the other perfluorosilanes and the mixed $SiH_mF_n$ compounds are less reliable or unavailable. Because of the importance of these compounds in chemical vapor deposition (CVD) and etching silicon and because of the continued uncertainty in some of the heats of formation, we have extended our previous calculations [J. Phys. Chem. **88**, 6254 (1988)] on the $\Delta H_f^0$ of these compounds. The present calculations have been carried out at a higher level of theory [Møller–Plesset perturbation theory including single, double, triple, and quadruple (MP4SDTQ)] with larger basis sets [6-31G(2$d$,2$p$), 6-31 + + G($d$,$p$), 6-31 + + G(2$d$,2$p$)] for the entire set of molecules. To establish accurate theoretical estimates of $\Delta H_f^0$ for $SiH_n$ and $SiF_n$ additional calculations were performed on SiX, SXY, $SiH_3$, and $SiH_2XY$ (X,Y = H,F) at the MP4SDTQ level with even larger basis sets [6-31G(3$d$,3$p$), 6-31G($df$,$p$), 6-311G($d$,$p$), 6-311G(2$df$,2$p$), 6-311 + + G(2$df$,2$p$)]. Based on the experimental $\Delta H_f^0$ for $SiH_n$ and $SiF_4$ and the calculated $\Delta H_r$ for isodesmic reactions, SiF is found to be 9 kcal/mol more stable and $SiF_2$ is found to be 12 kcal/mol more stable than the currently accepted values; the calculated $\Delta H_f^0$ of $SiH_n$ and $SiF_3$ agree with the value advocated by Walsh. The theoretical estimated heats of formation (298 K, ideal gas) are: SiH, $89.9 \pm 2$; SiF, $-14.2 \pm 2$; $SiH_2$, $65.7 \pm 2$; SiHF, $-37.8 \pm 2$; $SiF_2$, $-153.0 \pm 2$; $SiH_3$, $47.7 \pm 2$; $SiH_2F$, $-44.9 \pm 2$; $SiHF_2$, $-142.6 \pm 2$; $SiF_3$, $-240.7 \pm 2$; $SiH_3F$, $-85.8 \pm 2$; $SiH_2F_2$, $-186.3 \pm 2$; $SiHF_3$, $-288.2 \pm 2$ kcal/mol.

## INTRODUCTION

The thermochemistry of small silicon and fluorine containing molecules is of considerable interest, especially in the deposition of amorphous silicon films[1] and in the etching of silicon surfaces.[2] In connection with a study of the heats of formation of $SiH_mF_n$ cations,[3] we have extended our previous study of the $\Delta H_f^0$ of the neutral compounds.[4] The experimental $\Delta H_f^0$ of $SiH_mX_n$ (X = F, Cl, Br, I, $CH_3$) have been reviewed by Walsh.[5] The heats of formation of $SiH_n$ are firmly established[6] and there is good agreement between experiment and theory.[7] For the perfluoro derivatives, there is still some uncertainty in the heats of formation of SiF and $SiF_3$.[5,8,9] Dissociation and excitation energies of $SiF_n$ systems have also been examined theoretically by generalized valence-bond (GVB) methods.[10] For some of the mixed $SiH_mF_n$ compounds, thermodynamic information from theoretical studies[4,11] may be more reliable than from some experimental studies.[12] In previous work,[4] we examined the $\Delta H_f^0$ of $SiH_mF_n$ by *ab initio* molecular orbital methods at the Møller–Plesset perturbation theory including single, double, and quadruple excitations (MP4SDQ)/6-31G($d$,$p$). The present study extends these calculations and incorporates recent experimental data, in an attempt to establish revised heats of formation for SiF, $SiF_2$, and $SiF_3$ and to compile a consistent set of heats of formation for the mixed $SiH_mF_n$ compounds.

## METHOD

*Ab initio* molecular orbital calculations were performed with the GAUSSIAN 88 series of programs.[13] Previous calculations[4] were carried out at the MP4SDQ/6-31G($d$,$p$) level with frequencies at the HF/3-21G level. The present calculations were performed at the HF/6-31G($d$) optimized geometry with larger basis sets that include diffuse functions and two sets of polarization functions[14] [6-31 + + G($d$,$p$), 6-31G(2$d$,2$p$), and 6-31 + + G(2$d$,2$p$)]. Correlation corrections were computed by fourth order Møller–Plesset perturbation theory including single, double, triple, and quadruple excitations (MP4SDTQ, frozen core). If spin contamination is significant, unrestricted Møller–Plesset perturbation theory used for open shell systems can be slow to converge. Comparision of projected, unrestricted MP$n$ calculations with restricted MP$n$ indicates that spin projection provides a good estimate of the error in the energy resulting from the fact that the unrestricted wave function is not an eigenfunction of spin.[15(a)] As pointed out in a footnote in Table I, the spin contamination for the open shell species (Si, SiH, SiF, and $SiH_{3-n}F_n$) is quite small. Spin projection at the PMP4 level[15(a)] was found to change the $\Delta H$ for the isodesmic reactions involving $SiH_mF_n$ by $\pm 0.5$ kcal/mol or less.[15(b)] Therefore, it was considered safe to use unprojected HF and MP$n$ energies for the reactions discussed in this paper. Vibrational frequencies and thermal corrections were computed at the HF/6-31G($d$) level. For a subset of the molecules (SiX, SiXY, $SiH_3$, and $SiH_2XY$; X, Y = H, F), calculations were carried out with a number of additional basis sets to probe the convergence of the calcula-

TABLE I. Total energies.[a]

| Basis set | HF | $E_2$ | $E_3$ | $E_{4SDQ}$ | $E_{4T}$ |
|---|---|---|---|---|---|
| **Si** | | | | | |
| 6-31G($d,p$) | − 288.831 79 | − 0.040 24 | − 0.011 87 | − 0.003 30 | − 0.000 45 |
| 6-31G($2d,2p$) | − 288.833 20 | − 0.047 35 | − 0.014 93 | − 0.004 16 | − 0.000 65 |
| 6-31G($3d,3p$) | − 288.833 79 | − 0.048 01 | − 0.014 75 | − 0.004 06 | − 0.000 76 |
| 6-31G($df,p$) | − 288.831 80 | − 0.045 78 | − 0.011 64 | − 0.002 81 | − 0.000 79 |
| 6-31 + + G($d,p$) | − 288.832 20 | − 0.040 66 | − 0.011 88 | − 0.003 29 | − 0.000 47 |
| 6-31 + + G($2d,2p$) | − 288.833 46 | − 0.047 64 | − 0.014 90 | − 0.004 14 | − 0.000 67 |
| 6-311G($d,p$) | − 288.850 35 | − 0.041 85 | − 0.011 81 | − 0.003 27 | − 0.000 51 |
| 6-311G($2df,2p$) | − 288.851 83 | − 0.054 78 | − 0.014 20 | − 0.003 29 | − 0.001 35 |
| 6-311 + + G($d,p$) | − 288.850 51 | − 0.041 98 | − 0.011 80 | − 0.003 26 | − 0.000 52 |
| 6-311 + + G($2df,2p$) | − 288.852 00 | − 0.054 85 | − 0.014 16 | − 0.003 27 | − 0.001 36 |
| 6-311 + + G($3df,3p$) | − 288.852 09 | − 0.055 42 | − 0.014 12 | − 0.003 23 | − 0.001 44 |
| **SiH** | | | | | |
| 6-31G($d$) | − 289.409 86 | − 0.052 85 | − 0.014 53 | − 0.004 34 | − 0.000 72 |
| 6-31G($d$)[b] | − 289.409 82 | − 0.052 93 | − 0.014 56 | − 0.004 36 | − 0.000 72 |
| 6-31G($d,p$) | − 289.411 39 | − 0.059 54 | − 0.015 05 | − 0.004 19 | − 0.000 77 |
| 6-31G($2d,2p$) | − 289.414 33 | − 0.068 31 | − 0.018 00 | − 0.004 96 | − 0.001 04 |
| 6-31G($3d,3p$) | − 289.415 29 | − 0.069 79 | − 0.017 92 | − 0.004 88 | − 0.001 20 |
| 6-31G($df,p$) | − 289.412 20 | − 0.067 50 | − 0.015 79 | − 0.004 01 | − 0.001 09 |
| 6-31 + + G($d,p$) | − 289.412 30 | − 0.060 15 | − 0.015 08 | − 0.004 19 | − 0.000 80 |
| 6-31 + + G($2d,2p$) | − 289.414 93 | − 0.068 70 | − 0.018 00 | − 0.004 92 | − 0.001 08 |
| 6-311G($d,p$) | − 289.430 86 | − 0.063 97 | − 0.015 58 | − 0.004 22 | − 0.000 92 |
| 6-311G($2df,2p$) | − 289.434 42 | − 0.077 31 | − 0.017 98 | − 0.004 48 | − 0.001 68 |
| 6-311 + + G($d,p$) | − 289.431 43 | − 0.064 09 | − 0.015 58 | − 0.004 21 | − 0.000 93 |
| 6-311 + + G($2df,2p$) | − 289.434 87 | − 0.077 33 | − 0.017 95 | − 0.004 46 | − 0.001 68 |
| 6-311 + + G($3df,3p$) | − 289.435 32 | − 0.078 35 | − 0.017 89 | − 0.004 42 | − 0.001 76 |
| **SiF** | | | | | |
| 6-31G($d$) | − 388.342 44 | − 0.229 30 | − 0.005 47 | − 0.008 67 | − 0.005 22 |
| 6-31G($d$)[b] | − 388.342 14 | − 0.229 93 | − 0.005 31 | − 0.008 85 | − 0.005 33 |
| 6-31G($d,p$) | − 388.342 44 | − 0.229 30 | − 0.005 47 | − 0.008 67 | − 0.005 22 |
| 6-31G($2d,2p$) | − 388.350 08 | − 0.268 44 | −0.007 74 | − 0.008 84 | − 0.007 44 |
| 6-31G($3d,3p$) | − 388.356 14 | − 0.280 86 | − 0.006 63 | − 0.008 57 | − 0.008 44 |
| 6-31G($df,p$) | − 388.346 16 | − 0.254 21 | − 0.007 71 | − 0.008 14 | − 0.006 26 |
| 6-31 + + G($d,p$) | − 388.352 56 | − 0.236 04 | − 0.004 04 | − 0.010 04 | − 0.006 39 |
| 6-31 + + G($2d,2p$) | − 388.358 39 | − 0.272 98 | − 0.006 41 | − 0.009 63 | − 0.008 30 |
| 6-311G($d,p$) | − 388.387 32 | − 0.264 21 | − 0.003 63 | − 0.008 91 | − 0.007 07 |
| 6-311G($2df,2p$) | − 388.403 86 | − 0.320 78 | − 0.006 66 | − 0.007 66 | − 0.010 55 |
| 6-311 + + G($d,p$) | − 388.393 53 | − 0.268 28 | − 0.002 56 | − 0.009 91 | − 0.008 06 |
| 6-311 + + G($2df,2p$) | − 388.407 88 | − 0.323 46 | − 0.005 63 | − 0.008 20 | − 0.011 34 |
| **SiH$_2$** | | | | | |
| 6-31G($d$) | − 289.999 78 | − 0.067 28 | − 0.017 07 | − 0.004 91 | − 0.000 99 |
| 6-31G($d$)[b] | − 289.999 70 | − 0.067 44 | − 0.017 14 | − 0.004 95 | − 0.000 99 |
| 6-31G($d,p$) | − 290.002 63 | − 0.080 75 | − 0.018 20 | − 0.004 64 | − 0.001 09 |
| 6-31G($2d,2p$) | − 290.005 56 | − 0.093 10 | − 0.021 60 | − 0.005 17 | − 0.001 46 |
| 6-31G($3d,3p$) | − 290.006 61 | − 0.095 60 | − 0.021 57 | − 0.005 06 | − 0.001 69 |
| 6-31G($df,p$) | − 290.003 53 | − 0.091 01 | − 0.019 50 | − 0.004 55 | − 0.001 45 |
| 6-31 + + G($d,p$) | − 290.003 80 | − 0.081 54 | − 0.018 25 | − 0.004 64 | − 0.001 13 |
| 6-31 + + G($2d,2p$) | − 290.006 32 | − 0.093 54 | − 0.021 59 | − 0.005 14 | − 0.001 50 |
| 6-311G($d,p$) | − 290.023 03 | − 0.087 76 | − 0.019 28 | − 0.004 72 | − 0.001 32 |
| 6-311G($2df,2p$) | − 290.026 36 | − 0.103 69 | − 0.021 65 | − 0.004 74 | − 0.002 18 |
| 6-311 + + G($d,p$) | − 290.023 63 | 0.087 98 | − 0.019 31 | − 0.004 73 | − 0.001 33 |
| 6-311 + + G($2df,2p$) | − 290.026 81 | − 0.103 78 | − 0.021 63 | − 0.004 73 | − 0.002 19 |
| 6-311 + + G($3df,3p$) | − 290.027 44 | − 0.105 31 | − 0.021 57 | − 0.004 64 | − 0.002 29 |
| **SiHF** | | | | | |
| 6-31G($d$) | − 388.931 90 | − 0.242 22 | − 0.008 71 | − 0.008 95 | − 0.005 15 |
| 6-31G($d$)[b] | − 388.931 50 | − 0.243 06 | − 0.008 57 | − 0.009 16 | − 0.005 31 |
| 6-31G($d,p$) | − 388.933 41 | − 0.249 12 | − 0.009 36 | − 0.008 89 | − 0.005 26 |
| 6-31G($2d,2p$) | − 388.940 29 | − 0.292 12 | − 0.012 10 | − 0.008 87 | − 0.007 53 |
| 6-31G($3d,3p$) | − 388.945 83 | − 0.305 30 | − 0.011 06 | − 0.008 61 | − 0.008 58 |
| 6-31G($df,p$) | − 388.937 17 | − 0.276 35 | − 0.012 08 | − 0.008 42 | − 0.006 34 |
| 6-31 + + G($d,p$) | − 388.941 87 | − 0.256 15 | − 0.007 98 | − 0.010 19 | − 0.006 44 |
| 6-31 + + G($2d,2p$) | − 388.947 69 | − 0.296 66 | − 0.010 82 | − 0.009 64 | − 0.008 39 |
| 6-311G($d,p$) | − 388.978 28 | − 0.286 75 | − 0.008 25 | − 0.009 15 | − 0.007 12 |
| 6-311G($2df,2p$) | − 388.994 04 | − 0.346 05 | − 0.011 08 | − 0.007 71 | − 0.010 69 |
| 6-311 + + G($d,p$) | − 388.983 76 | − 0.290 91 | − 0.007 14 | − 0.010 14 | − 0.008 12 |
| 6-311 + + G($2df,2p$) | − 388.999 76 | − 0.348 65 | − 0.010 15 | − 0.008 24 | − 0.011 47 |

TABLE I (*continued*).

| Basis set | HF | $E_2$ | $E_3$ | $E_{4SDQ}$ | $E_{4T}$ |
|---|---|---|---|---|---|
| **SiF₂** | | | | | |
| 6-31G(*d*) | − 487.884 67 | − 0.418 79 | − 0.000 30 | − 0.012 55 | − 0.009 61 |
| 6-31G(*d*)[b] | − 487.883 77 | − 0.420 64 | 0.000 22 | − 0.013 00 | − 0.009 89 |
| 6-31G(*d,p*) | − 487.884 67 | − 0.418 79 | − 0.000 30 | − 0.012 55 | − 0.009 61 |
| 6-31G(2*d*,2*p*) | − 487.895 40 | − 0.492 74 | − 0.002 52 | − 0.011 74 | − 0.013 73 |
| 6-31G(3*d*,3*p*) | − 487.904 66 | − 0.516 94 | − 0.000 73 | − 0.011 27 | − 0.015 60 |
| 6-31G(*df,p*) | − 487.892 03 | − 0.463 01 | − 0.004 46 | − 0.011 72 | − 0.011 43 |
| 6-31 + + G(*d,p*) | − 487.898 24 | − 0.431 22 | 0.002 21 | − 0.014 95 | − 0.011 88 |
| 6-31 + + G(2*d*,2*p*) | − 487.907 29 | − 0.500 97 | − 0.000 24 | − 0.013 17 | − 0.015 30 |
| 6-311G(*d,p*) | − 487.953 87 | − 0.487 36 | − 0.003 26 | − 0.013 06 | − 0.013 21 |
| 6-311G(2*df*,2*p*) | − 487.982 57 | − 0.590 08 | − 0.000 77 | − 0.009 96 | − 0.019 40 |
| 6-311 + + G(*d,p*) | − 487.961 69 | − 0.495 04 | 0.005 07 | − 0.014 74 | − 0.015 06 |
| **SiH₃** | | | | | |
| 6-31G(*d*) | − 290.606 12 | − 0.068 33 | − 0.016 07 | − 0.004 22 | − 0.001 01 |
| 6-31G(*d,p*) | − 290.610 58 | − 0.087 66 | − 0.017 82 | − 0.003 80 | − 0.001 16 |
| 6-31G(2*d*,2*p*) | − 290.614 86 | − 0.099 44 | − 0.021 03 | − 0.004 38 | − 0.001 46 |
| 6-31G(3*d*,3*p*) | − 290.616 28 | − 0.101 93 | − 0.020 98 | − 0.004 32 | − 0.001 66 |
| 6-31G(*df,p*) | − 290.612 40 | − 0.098 47 | − 0.019 81 | − 0.004 00 | − 0.001 49 |
| 6-31 + + G(*d,p*) | − 290.611 70 | − 0.088 37 | − 0.017 87 | − 0.003 81 | − 0.001 20 |
| 6-31 + + G(2*d*,2*p*) | − 290.615 44 | − 0.099 84 | − 0.021 04 | − 0.004 37 | − 0.001 50 |
| 6-311G(*d,p*) | − 290.632 01 | − 0.095 97 | − 0.019 43 | − 0.004 03 | − 0.001 41 |
| 6-311G(2*df*,2*p*) | − 290.636 97 | − 0.109 53 | − 0.021 49 | − 0.004 30 | − 0.002 08 |
| 6-311 + + G(*d,p*) | − 290.632 39 | − 0.096 17 | − 0.019 47 | − 0.004 05 | − 0.001 42 |
| 6-311 + + G(2*df*,2*p*) | − 290.637 21 | − 0.109 55 | − 0.021 48 | − 0.004 31 | − 0.002 07 |
| 6-311 + + G(3*df*,3*p*) | − 290.638 24 | − 0.111 04 | − 0.021 42 | − 0.004 28 | − 0.002 15 |
| **SiH₂F** | | | | | |
| 6-31G(*d*) | − 389.522 83 | − 0.238 41 | − 0.008 11 | − 0.007 63 | − 0.004 59 |
| 6-31G(*d,p*) | − 389.525 90 | − 0.251 48 | − 0.009 42 | − 0.007 50 | − 0.004 69 |
| 6-31G(2*d*,2*p*) | − 389.535 41 | − 0.294 33 | − 0.012 26 | − 0.007 55 | − 0.006 78 |
| 6-31 + + G(*d,p*) | − 389.534 82 | − 0.258 17 | − 0.008 12 | − 0.008 73 | − 0.005 79 |
| 6-31 + + G(2*d*,2*p*) | − 389.542 64 | − 0.298 82 | − 0.011 06 | − 0.008 34 | − 0.007 62 |
| **SiHF₂** | | | | | |
| 6-31G(*d*) | − 488.450 82 | − 0.410 30 | − 0.000 36 | − 0.011 03 | − 0.008 34 |
| 6-31G(*d,p*) | − 488.452 37 | − 0.416 73 | − 0.001 04 | − 0.011 01 | − 0.008 40 |
| 6-31G(2*d*,2*p*) | − 488.466 39 | − 0.491 05 | − 0.003 56 | − 0.010 39 | − 0.012 28 |
| 6-31 + + G(*d,p*) | − 488.466 80 | − 0.428 22 | 0.001 52 | − 0.013 29 | − 0.010 52 |
| 6-31 + + G(2*d*,2*p*) | − 488.478 29 | − 0.498 92 | − 0.001 38 | − 0.011 82 | − 0.013 80 |
| **SiF₃** | | | | | |
| 6-31G(*d*) | − 587.381 23 | − 0.581 60 | 0.006 97 | − 0.014 01 | − 0.012 06 |
| 6-31G(*d,p*) | − 587.381 23 | − 0.581 60 | 0.006 97 | − 0.014 01 | − 0.012 06 |
| 6-31G(2*d*,2*p*) | − 587.399 53 | − 0.687 67 | 0.004 57 | − 0.012 66 | − 0.017 69 |
| 6-31 + + G(*d,p*) | − 587.399 92 | − 0.597 21 | 0.010 61 | − 0.017 15 | − 0.015 13 |
| 6-31 + + G(2*d*,2*p*) | − 587.414 87 | − 0.698 40 | 0.007 53 | − 0.014 63 | − 0.019 77 |
| **SiH₄** | | | | | |
| 6-31G(*d*) | − 291.225 13 | − 0.081 89 | − 0.018 38 | − 0.004 70 | − 0.001 18 |
| 6-31G(*d*)[b] | − 291.225 05 | − 0.082 07 | − 0.018 46 | − 0.004 75 | − 0.001 18 |
| 6-31G(*d,p*) | − 291.230 84 | − 0.108 15 | − 0.021 00 | − 0.004 26 | − 0.001 35 |
| 6-31G(2*d*,2*p*) | − 291.235 06 | − 0.122 92 | − 0.024 85 | − 0.004 91 | − 0.001 71 |
| 6-31G(3*d*,3*p*) | − 291.236 52 | − 0.126 03 | − 0.024 68 | − 0.004 78 | − 0.001 96 |
| 6-31G(*df,p*) | − 291.232 72 | − 0.120 94 | − 0.023 46 | − 0.004 53 | − 0.001 70 |
| 6-31 + + G(*d,p*) | − 291.232 03 | − 0.109 06 | − 0.021 05 | − 0.004 26 | − 0.001 40 |
| 6-31 + + G(2*d*,2*p*) | − 291.235 58 | − 0.123 39 | − 0.024 85 | − 0.004 89 | − 0.001 76 |
| 6-311G(*d,p*) | − 291.253 17 | − 0.118 76 | − 0.023 18 | − 0.004 61 | − 0.001 68 |
| 6-311G(2*df*,2*p*) | − 291.257 78 | − 0.134 20 | − 0.025 18 | − 0.004 78 | − 0.002 39 |
| 6-311 + + G(*d,p*) | − 291.253 30 | − 0.119 04 | − 0.023 23 | − 0.004 62 | − 0.001 69 |
| 6-311 + + G(2*df*,2*p*) | − 291.257 83 | − 0.134 29 | − 0.025 18 | − 0.004 78 | − 0.002 39 |
| 6-311 + + G(3*df*,3*p*) | − 291.259 15 | − 0.136 05 | − 0.025 07 | − 0.004 73 | − 0.002 48 |
| **SiH₃F** | | | | | |
| 6-31G(*d*) | − 390.148 40 | − 0.251 30 | − 0.010 83 | − 0.007 77 | − 0.004 55 |
| 6-31G(*d*)[b] | − 390.147 89 | − 0.252 36 | − 0.010 74 | − 0.007 97 | − 0.004 65 |
| 6-31G(*d,p*) | − 390.152 84 | − 0.271 35 | − 0.013 04 | − 0.007 68 | − 0.004 69 |
| 6-31G(2*d*,2*p*) | − 390.160 96 | − 0.317 46 | − 0.016 62 | − 0.007 81 | − 0.006 83 |
| 6-31G(3*d*,3*p*) | − 390.167 20 | − 0.331 69 | − 0.015 57 | − 0.007 49 | − 0.007 90 |
| 6-31G(*df,p*) | − 390.157 51 | − 0.301 29 | − 0.016 95 | − 0.007 66 | − 0.005 75 |
| 6-31 + + G(*d,p*) | − 390.159 63 | − 0.278 20 | − 0.011 89 | − 0.008 80 | − 0.005 76 |
| 6-31 + + G(2*d*,2*p*) | − 390.167 09 | − 0.321 89 | − 0.015 50 | − 0.008 54 | − 0.007 63 |

TABLE I *(continued)*.

| Basis set | HF | $E_2$ | $E_3$ | $E_{4SDQ}$ | $E_{4T}$ |
|---|---|---|---|---|---|
| 6-311G($d,p$) | − 390.200 47 | − 0.313 03 | − 0.012 95 | − 0.008 23 | − 0.006 64 |
| 6-311G($2df,2p$) | − 390.217 62 | − 0.372 57 | − 0.015 90 | − 0.007 06 | − 0.010 00 |
| 6-311 + + G($d,p$) | − 390.203 43 | − 0.316 85 | − 0.012 25 | − 0.008 96 | − 0.007 44 |
| 6-311 + + G($2df,2p$) | − 390.219 68 | − 0.374 99 | − 0.015 17 | − 0.007 49 | − 0.010 64 |
| **$SiH_2F_2$** | | | | | |
| 6-31G($d$) | − 489.081 81 | − 0.422 88 | − 0.003 57 | − 0.010 94 | − 0.008 33 |
| 6-31G($d$)[b] | − 489.080 88 | − 0.424 82 | − 0.003 23 | − 0.011 29 | − 0.008 35 |
| 6-31G($d,p$) | − 489.084 83 | − 0.436 26 | − 0.005 14 | − 0.010 99 | − 0.008 26 |
| 6-31G($2d,2p$) | − 489.096 59 | − 0.513 88 | − 0.008 48 | − 0.010 47 | − 0.012 16 |
| 6-31G($3d,3p$) | − 489.106 34 | − 0.539 06 | − 0.006 69 | − 0.009 90 | − 0.014 01 |
| 6-31G($df,p$) | − 489.093 21 | − 0.483 29 | − 0.010 49 | − 0.010 67 | − 0.010 04 |
| 6-31 + + G($d,p$) | − 489.095 41 | − 0.447 66 | − 0.002 89 | − 0.013 07 | − 0.010 28 |
| 6-31 + + G($2d,2p$) | − 489.106 62 | − 0.521 47 | − 0.006 47 | − 0.011 80 | − 0.013 60 |
| 6-311G($d,p$) | − 489.156 31 | − 0.509 31 | − 0.002 72 | − 0.011 67 | − 0.011 85 |
| 6-311G($2df,2p$) | − 489.186 81 | − 0.612 82 | − 0.006 93 | − 0.009 09 | − 0.009 09 |
| 6-311 + + G($d,p$) | − 489.161 37 | − 0.515 74 | − 0.001 28 | − 0.013 01 | − 0.013 35 |
| **$SiHF_3$** | | | | | |
| 6-31G($d$) | − 588.018 33 | − 0.594 58 | 0.003 17 | − 0.013 87 | − 0.011 79 |
| 6-31G($d,p$) | − 588.019 85 | − 0.601 15 | 0.002 36 | − 0.013 93 | − 0.011 85 |
| 6-31G($2d,2p$) | − 588.035 40 | − 0.710 45 | − 0.000 90 | − 0.012 70 | − 0.017 50 |
| 6-31 + + G($d,p$) | − 588.033 42 | − 0.616 48 | 0.005 53 | − 0.016 82 | − 0.014 78 |
| 6-31 + + G($2d,2p$) | − 588.048 48 | − 0.720 77 | 0.001 83 | − 0.014 51 | − 0.019 47 |
| **$SiF_4$** | | | | | |
| 6-31G($d$) | − 686.949 84 | − 0.764 61 | 0.009 17 | − 0.016 37 | − 0.015 35 |
| 6-31G($d,p$) | − 686.949 84 | − 0.764 62 | 0.009 17 | − 0.016 37 | − 0.015 34 |
| 6-31G($2d,2p$) | − 686.969 38 | − 0.905 91 | 0.005 82 | − 0.014 43 | − 0.022 69 |
| 6-31 + + G($d,p$) | − 686.965 81 | − 0.783 14 | 0.013 12 | − 0.019 89 | − 0.019 06 |
| 6-31 + + G($2d,2p$) | − 686.985 09 | − 0.918 46 | 0.009 11 | − 0.016 61 | − 0.025 08 |

[a] In hartree; unless otherwise specified, calculations were carried out at the HF/6-31G($d$) optimized geometry; 6-31G($d$) and 6-31G($d,p$) energies from Ref. 4; $\langle \hat{S}^2 \rangle_0$ = 2.000–2.015 for Si, 0.761–0.773 for SiH, 0.754–0.774 for SiF, and 0.751–0.754 for $SiH_nF_{3-n}$.

[b] At the MP2/6-31 G($d$) optimized geometry.

tions with respect to further expansion of the basis set. These included triple split valence basis set with polarization functions (6-311G[16]), multiple polarization functions [6-31G($3d,3p$), 6-311G($2d,2p$)], $f$ functions [6-31G($df,p$), 6-311G($2df,2p$)], and diffuse functions [6-311 + + G($d,p$)]. For reactions involving difluoro species, the effects of the different basis set extensions were assumed to be additive and were combined to give an estimate of the relative energetics with the 6-31 + + G($3df,3p$) and 6-311 + + G($2df,2p$) basis sets.

estimated 6-31 + + G($3df,3p$)

$$= \text{6-31} + + \text{G}(2d,2p)$$
$$+ \text{6-31G}(3d,3p) - \text{6-31G}(2d,2p)$$
$$+ \text{6-31G}(df,p) - \text{6-31G}(d,p), \qquad (1)$$

estimated 6-311 + + G($2df,2p$)

$$= \text{6-311G}(2df,2p)$$
$$+ \text{6-311} + + \text{G}(d,p) - \text{6-311G}(d,p).$$

For $SiH_n$, both of these estimates are within 0.1–0.3 kcal/mol of full 6-311 + + G($2df,2p$) and 6-311 + + G($3df,3p$) calculations. When the reactions involve SiF and $SiH_3F$, these estimated heats of reaction are within 1 kcal/mol of the full basis set calculations. Similar results are found for HF dissociation and

$F + H_2 \rightarrow HF + H$.[17] Finally, the effects of correlation corrections on the geometry were examined by reoptimizing a subset of the molecules at the MP2/6-31G($d$) level.

## RESULTS AND DISCUSSION

The total energies for $SiH_mF_n$ at the HF, MP2, MP3, and MP4 levels for the various basis sets used in the present study are collected in Table I. The HF/6-31G($d$) optimized geometries have been published previously.[4,18] To test the effects of electron correlation on geometry, a subset of the molecules (SiX, SiXY, and $SiH_2XY$; X, Y = H, F) was reoptimized at the MP2/6-31G($d$) level. As shown in Table II, correlation corrections make the agreement between theory and experiment better for bond angles (mean absolute error 0.6°, MP2 optimized vs 1.1°, HF optimized) and SiH bond lengths (0.004 Å, MP2 vs 0.010 Å, HF), but poorer for SiF bond lengths (0.026 Å, MP2 vs 0.003 Å, HF). As will be seen below, the use of the MP2 optimized geometries instead of the HF geometries changes the energetics of the isodesmic reactions by 0.1 kcal/mol or less. Because the number of bonds of each type are conserved in isodesmic reactions, errors due to systematic differences tend to cancel. Since the choice of optimized geometry seems to have little effect on the $\Delta H_r$ for isodesmic reactions and since the agreement between theory and experiment for SiF bond lengths is (for-

tuitously) better at the HF/6-31G($d$) level, the HF/6-31G($d$) optimized geometries are used for all of the larger basis set calculations.

The HF/6-31G($d$) vibrational frequencies are listed in Table III, along with the zero point energies and the thermal corrections to the enthalpies. The calculated harmonic frequencies are plotted vs the available experimental anharmonic frequencies in Fig. 1. On average, the theoretical values are $\sim 8\%$ higher than the experimental frequencies. A scale factor of 0.93 has been applied to all of the zero point energies to correct for this overestimation. The HF/6-31G($d$) frequencies show somewhat less scatter in the correlation with experiment than the HF/3-21G frequencies computed in our previous study. Dixon[11] has found similar agreement with experimental vibrational frequencies $CH_{4-n}F_n$ and $SiH_{4-n}F_n$ at a comparable level of theory.

## $\Delta H_f^0$ for $SiH_n$

The heats of formation of $SiH_n$ are well known[5,6,19–26] and are adopted as reference values for the calculations discussed below. For $SiH_4$, $\Delta H_{f298}^0 = 8.2 \pm 0.5$ kcal/mol[19] was obtained from the decomposition of silane into Si and $H_2$. Kinetic studies of $D(H_3Si-H)$ lead to $46.6 \pm 1.5$ kcal/mol for $\Delta H_{f298}^0$ $SiH_3$.[20] Recent experimental results for $SiH_2$ are in good agreement with each other ($\Delta H_{f298}^0 = 65.6 \pm 0.7$,[6] $64.1 \pm 2$,[21] $64.8 \pm 2$,[21] $65.1 \pm 2$,[21] $65.5 \pm 1.5$,[21,22] $65.4 \pm 1.6$,[23] $66 \pm 3$,[6,24] and $63.6 \pm 2.8$[25] kcal/mol) and yield an average value of $\Delta H_{f298}^0 = 65.0 \pm 2$ kcal/mol. For $SiH$, spectroscopic studies give to $\Delta H_{f298}^0 = 90 \pm 2$ kcal/mol[26] and photoionization experiments yield $89.6 \pm 1.2$ kcal/mol.[6] Calculations based on the bond additivity corrections at the MP4/6-31G($d,p$) level (BAC-MP4)[27] are within $\pm 3$ kcal/mol of experiment. Higher level, direct calculations of the heats of formation of $SiH_n$ by Curtiss and Pople[7(a)] are within $\pm 2$ kcal/mol of the experimental values.

### TABLE III. Vibrational frequencies.[a]

| Molecule | ZPE | Thermal | Frequencies |
|---|---|---|---|
| SiH | 2.90 | 1.62[b] | 2181(2042) |
| SiF | 1.22 | 1.66[c] | 919(857) |
| $SiH_2$ | 7.38 | 1.79 | 1130,2207,2218(1005,2022) |
| SiHF | 5.39 | 1.84 | 922,964,2169(834,859,1913) |
| $SiF_2$ | 2.99 | 2.05 | 373,932,950(345,885,872) |
| $SiH_3$ | 13.35 | 1.85 | 875,1015′,2364,2383′ |
| $SiH_2F$ | 11.15 | 1.92 | 773,887,954,1023,2367,2387 |
| $SiHF_2$ | 8.43 | 2.15 | 332,843,847,932,1017,2367 |
| $SiF_3$ | 5.36 | 2.54 | 307′,437,901,1040′(290′,406,832, 954′) |
| $SiH_4$ | 19.55 | 1.88 | 1016″,1051′,2386″,2393(913″, 972′,2186″,2189) |
| $SiH_3F$ | 17.31 | 1.96 | 795′,943,1051′,1111,2421′,2428(728′, 872,961′,990,2196′,2206) |
| $SiH_2F_2$ | 14.60 | 2.20 | 342,780,808,932,983,1083,1093, 2480,2481(322,730,730,870,903,981, 982,2225,2246) |
| $SiHF_3$ | 11.42 | 2.57 | 320′,448,913,932′,1083′,2556(305′, 425,844′,858,998′,2316) |
| $SiF_4$ | 7.90 | 3.00 | 274′,406″,849,1107″(266′,389″,800, 1032″) |

[a] At the HF/6-31G($d$) optimized geometry; zero point energy and thermal corrections to the enthalpy are in kcal/mol; frequencies are in $cm^{-1}$, doubly degenerate modes are indicated by a ′ and triply degenerate modes by ″; theoretical frequencies unscaled, experimental frequencies (quoted in Refs. 11 and 18) are in parentheses; zero point energies calculated with theoretical frequencies scaled by 0.93 (see the text).

[b] Electronic contribution to the thermal correction computed using 142.83 $cm^{-1}$ for the $^2\Pi_{3/2}-^2\Pi_{1/2}$ separation (Ref. 19).

[c] Electronic contribution to the thermal correction computed using 161.93 $cm^{-1}$ for the $^2\Pi_{3/2}-^2\Pi_{1/2}$ separation.[19]

## $\Delta H_f^0$ for $SiF_n$

A recent fluorine bomb calorimetry study has reconfirmed $\Delta H_{f298}^0 = 386.18$ kcal/mol for $SiF_4$.[28] Doncaster and Walsh[29] obtained $D(F_3Si-H) = 100.1 \pm 1.2$ kcal/mol and recommend $\Delta H_f^0 = -239 \pm 5$ kcal/mol for $SiF_3$. Mass-spectrometric effusion studies by Farber and Srivas-

### TABLE II. Optimized geometries of SiX, SiXY, and $SiH_2XY$ (X,Y = H,F).[a]

| Molecule | Symmetry | Parameter | HF | MP2 | Expt. |
|---|---|---|---|---|---|
| SiH | $D_{\infty h}$ | $R(SiH)$ | 1.515 | 1.526 | 1.520 |
| SiF | $D_{\infty h}$ | $R(SiF)$ | 1.605 | 1.627 | 1.601 |
| $SiH_2$ | $C_{2v}$ | $R(SiH)$ | 1.508 | 1.519 | 1.521 |
|  |  | ∠HSiH | 93.3 | 92.6 | 92.1 |
| SiHF | $C_s$ | $R(SiH)$ | 1.516 | 1.530 |  |
|  |  | $R(SiF)$ | 1.602 | 1.626 |  |
|  |  | ∠HSiF | 97.3 | 97.7 |  |
| $SiF_2$ | $C_{2v}$ | $R(SiF)$ | 1.592 | 1.616 | 1.591 |
|  |  | ∠FSiF | 98.9 | 100.9 | 101.0 |
| $SiH_4$ | $T_d$ | $R(SiH)$ | 1.475 | 1.483 | 1.481 |
| $SiH_3F$ | $C_{3v}$ | $R(SiH)$ | 1.470 | 1.480 | 1.486 |
|  |  | $R(SiF)$ | 1.594 | 1.617 | 1.593 |
|  |  | ∠HSiF | 108.8 | 109.0 | 108.5 |
| $SiH_2F_2$ | $C_{2v}$ | $R(SiH)$ | 1.461 | 1.472 | 1.471 |
|  |  | R(SiF) | 1.581 | 1.604 | 1.577 |
|  |  | ∠HSiH | 113.4 | 113.7 | 112.0 |
|  |  | ∠FSiF | 107.6 | 108.1 | 107.9 |

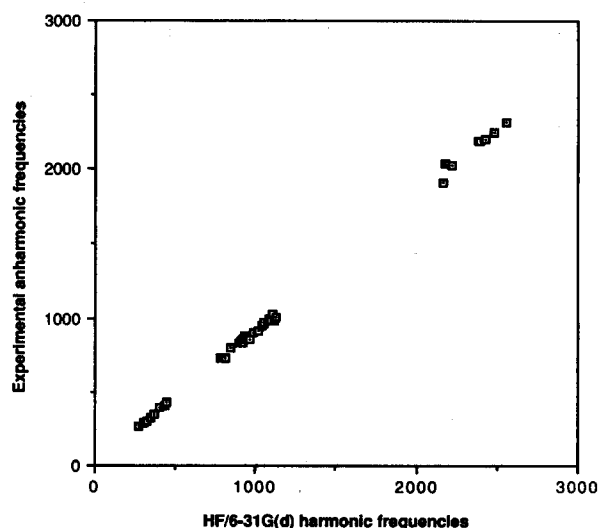[a] Bond lengths are in Å, angles are in degrees; experimental geometries in parentheses from JANAF Tables (Ref. 19).



FIG. 1. Comparison of the harmonic frequencies calculated at the HF/6-31G($d$) level with the experimental, anharmonic frequencies for $SiH_mF_n$.

tava[8] and ion beam/mass spectroscopy studies of $Si^+ + SiF_4$ by Weber and Armentrout[9] give $\Delta H_f^0 = -257$ to $-259$ kcal/mol. Our previous computations[4] at the MP4SDQ/6-31G($d,p$) level (as well as the present work, see below) support $\Delta H_f^0 = -239$ kcal/mol. The experimental heat of formation of $SiF_2$ appears to be well established at $-140.5 \pm 2$ kcal/mol[5,8,19] (however, see below). A fairly wide range of values is available for $\Delta H_f^0$ of SiF and Walsh recommends $-5 \pm 6$ kcal/mol "with caution, but with no great confidence."[5]

Table IV lists the energetics for a series of isodesmic reactions used to calculate the heats of formation of $SiH_n$ and $SiF_n$, $n = 1-3$. The one set relates the $\Delta H_f^0$ of $SiF_n$ to the $\Delta H_f^0$ of $SiH_n$:

$$\tfrac{1}{4}nSiF_4 + SiH_n \to \tfrac{1}{4}nSiH_4 + SiF_n . \qquad (2)$$
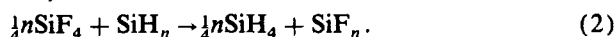
Since these reactions are both isodesmic and isogyric, the results should be quite reliable. A closely related set of reactions

$$SiH_{4-n}F_n + SiH_n \to SiH_4 + SiF_n \qquad (3)$$
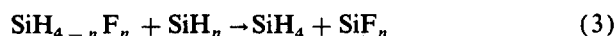
is more practical for larger basis set calculations, since the reactants contain fewer fluorines. However, inconsistencies in the experimental heats of formation of $SiH_{4-m}F_m$ have been pointed out previously.[4,5] As discussed below, the $\Delta H_f^0$ of $SiH_{4-m}F_m$ can be obtained reliably from the following isodesmic reaction:

$$\frac{4-m}{4} SiH_4 + \frac{m}{4} SiF_4 \to SiH_{4-m}F_m . \qquad (4)$$
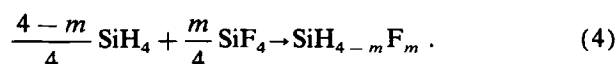
Note that reaction (3) plus reaction (4) yields reaction (2).

Independent of reactions (2) and (3), a third set of isodesmic reactions can be used to estimate of the heats of formation of both $SiH_n$ and $SiF_n$, $n = 1-3$:

$$\frac{n}{4}SiX_4 + \frac{4-n}{4} Si \to SiX_n, \quad X = H, F . \qquad (5)$$
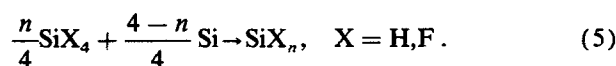
This is directly related to the bond additivity correction (BAC) method of Binkley and Melius.[27] In the BAC approach, the calculated and experimental atomization energies for a set of reference compounds are used to compute correction factors for each bond type. The correction for an SiX bond can be calculated from $SiX_4$:

$$SiX_4 \to Si + 4X,$$

$$BAC(Si-X) = \tfrac{1}{4}[\Delta H_r(exp) - \Delta H_r(calc)] . \qquad (6)$$
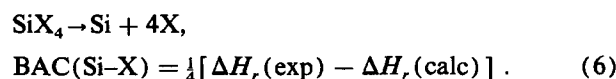
A reliable estimate of the atomization energy of other $SiX_n$ species can then be obtained by combining the calculated atomization energy and the corrections for each bond

$$SiX_n \to Si + nX,$$

$$\Delta H_r(est\ exp) = \Delta H_r(calc) + nBAC(Si-X) . \qquad (7)$$
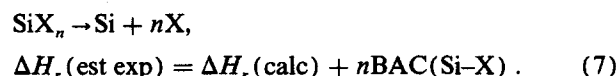
Note that $n/4$ times reaction (6) minus reaction (7) gives reaction (5).

A fourth set of reactions more suitable for large basis set calculations can be obtained by combining reactions (4) and (5):

$$SiH_{4-n}F_n + \frac{4-n}{4} Si \to \frac{4-n}{4} SiH_4 + SiF_n . \qquad (8)$$
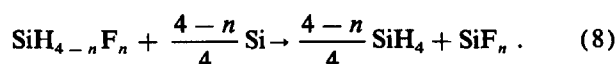
Despite the fact that reactions (2), (3), (5), and (8) are

isodesmic, the correlation corrections to $\Delta H_r$ are sizeable, ranging from 1 to 13 kcal/mol (Table IV). However, most of the correlation energy is recovered at the MP2 level, with $E_3$ and $E_4$ contributing only 0–2 kcal/mol. The triples contribution $E_{4T}$, is 0.2–1.5 kcal/mol. A second set of polarization functions [6-31G($d,p$) → 6-31G($2d,2p$) and 6-31 + + G($d,p$) → 6-31 + + G($2d,2p$)] changes the heats of reaction by 0–2 kcal/mol; adding a third set of polarization functions [6-31G($2d,2p$) → 6-31G($3d,3p$)] or adding a set of $f$ functions to the heavy atoms [6-31G($d,p$) → 6-31G($df,p$)] changes the heats of reaction by ~0.3 kcal/mol each. The effect of diffuse functions [6-31G($d,p$) → 6-31 + + G($nd,np$) and 6-311G($d,p$) → 6-311 + + G($d,p$)] is surprisingly large, 3–5 kcal/mol for some reactions; this is almost entirely due to fluorine and its main effect is on the Hartree–Fock energy, with only small changes in the correlation corrections. Increasing the basis set to triple split valence [6-31 + + G($d,p$) → 6-311 + + G($d,p$)] contributes 0–1 kcal/mol to the heats of reaction. When MP2 optimized geometries are used instead of HF optimized geometries, the heats of reaction change 0.1 kcal/mol or less. Where applicable, the contributions from the various basis set extensions are combined according to Eq. (1) to yield an estimate of the heats of reaction at the MP4/6-31 + + ($3df,3p$) and MP4/6-311 + + ($2df,2p$) levels. These two estimates agree with the full calculations to within $\pm 0.3$ kcal/mol for $SiH_n$ and within $\pm 1.0$ kcal/mol for reactions involving fluorinated species [e.g., reactions (5a) and (8a)].

As shown in Table IV, the best calculations of $\Delta H_r$ for reaction (5) for $SiH_n$ are within 1 kcal/mol of the values obtained using the experimental $\Delta H_f^0$. This validates the accuracy of the level of theory adopted. Alternatively, these reactions provide theoretical heats of formation for $SiH_n$ at the MP4/6-311 + + G($3df,3p$) level without any assumptions of basis set effect additivity (i.e., a significantly higher level than previous work[7]). The accepted experimental values for $\Delta H_f^0$ for SiF and $SiF_2$ ( $-5$ and $-140.5$ kcal/mol, respectively)[5,19] lead to $\Delta H_r$ for reactions (2), (3), (5), and (8) that are more than 8 kcal/mol too high when compared to *any* of the calculated MP$n$ values. The best calculations predict that reactions (3a) and (8a) for SiF are 8 kcal/mol more exothermic than obtained with the accepted value for the $\Delta H_f^0$ of SiF (and $-84.9$ kcal/mol for $SiH_3F$; for other values of $\Delta H_f^0$ ($SiH_3F$), the agreement is even worse). Similarly for $SiF_2$, the best theoretical estimates predict $\Delta H_r$ to be 10 kcal/mol lower for reactions (3b) and (8b) than obtained with the accepted $\Delta H_f^0$ for $SiF_2$. By contrast, the differences between the calculated and experimental $\Delta H_r$ for reaction (5) for $SiH_n$ are only 0.4–0.8 kcal/mol. This indicates that the $\Delta H_f^0$ of SiF and $SiF_2$ should be revised downward by ~10 kcal/mol. For $SiF_3$, the agreement between the calculated and experimental $\Delta H_r$ is quite good when Doncaster and Walsh's value[29] is used for $\Delta H_f^0$ ($SiF_3$). At no level of calculation is there any support for $\Delta H_f^0$ ($SiF_3$) $\approx -259$ kcal/mol.[8,9]

## $\Delta H_f^0$ for $SiH_mF_n$

The heats of formation for the mixed hydrogen and fluorine compounds of silicon can be obtained from reaction

TABLE IV. Calculated and experimental $\Delta H_{r,298}$ for isodesmic reactions leading to the heats of formation of $SiH_n$ and $SiF_n$, $n = 1\text{–}3$.[a]

| Basis set | Theoretical | | | | | From Table VI | |
|---|---|---|---|---|---|---|---|
| | HF | MP2 | MP3 | MP4SDQ | MP4SDTQ | Literature[b] | Revised[c] |
| (5)$\frac{1}{4}$SiH$_4$ + $\frac{3}{4}$Si→SiH | | | | | | | |
| 6-31G($d$) | 11.21 | 9.83 | 9.19 | 8.75 | 8.70 | 6.89 | |
| 6-31G($d$)[d] | 11.22 | 9.83 | 9.17 | 8.73 | 8.67 | | |
| 6-31G($d,p$) | 11.15 | 9.69 | 9.13 | 8.72 | 8.66 | | |
| 6-31G($2d,2p$) | 10.63 | 9.33 | 8.96 | 8.58 | 8.50 | | |
| 6-31G($3d,3p$) | 10.53 | 9.10 | 8.67 | 8.27 | 8.18 | | |
| 6-31G($df,p$) | 10.94 | 9.10 | 8.35 | 7.87 | 7.83 | | |
| 6-31 + + G($d,p$) | 10.96 | 9.46 | 8.89 | 8.48 | 8.41 | | |
| 6-31 + + G($2d,2p$) | 10.46 | 9.13 | 8.74 | 8.37 | 8.28 | | |
| (6-31 + + G($3df,3p$))[e] | 10.15 | 8.31 | 7.67 | 7.21 | 7.13 | | |
| 6-311G($d,p$) | 11.17 | 9.35 | 8.76 | 8.38 | 8.31 | | |
| 6-311G($2df,2p$) | 10.36 | 8.68 | 8.03 | 7.52 | 7.47 | | |
| 6-311 + + G($d,p$) | 10.91 | 9.12 | 8.54 | 8.16 | 8.08 | | |
| (6-311 + + G($2df,2p$))[e] | 10.10 | 8.46 | 7.81 | 7.30 | 7.25 | | |
| 6-311 + + G($2df,2p$) | 10.16 | 8.51 | 7.87 | 7.36 | 7.31 | | |
| 6-311 + + G($3df,3p$) | 10.13 | 8.39 | 7.74 | 7.23 | 7.19 | | |
| (5)$\frac{1}{2}$SiH$_4$ + $\frac{1}{2}$Si→SiH$_2$ | | | | | | | |
| 6-31G($d$) | 16.01 | 12.11 | 10.89 | 10.32 | 10.21 | 7.12 | |
| 6-31G($d$)[d] | 16.03 | 12.09 | 10.85 | 10.26 | 10.15 | | |
| 6-31G($d,p$) | 16.02 | 11.90 | 10.79 | 10.25 | 10.14 | | |
| 6-31G($2d,2p$) | 15.94 | 10.94 | 9.87 | 9.47 | 9.30 | | |
| 6-31G($3d,3p$) | 15.93 | 10.54 | 9.38 | 8.97 | 8.77 | | |
| 6-31G($df,p$) | 16.04 | 11.24 | 10.02 | 9.47 | 9.34 | | |
| 6-31 + + G($d,p$) | 15.78 | 11.59 | 10.47 | 9.93 | 9.81 | | |
| 6-31 + + G($2d,2p$) | 15.71 | 10.67 | 9.60 | 9.21 | 9.03 | | |
| (6-31 + + G($3df,3p$))[e] | 15.72 | 9.61 | 8.33 | 7.92 | 7.70 | | |
| 6-311G($d,p$) | 16.04 | 11.36 | 10.24 | 9.74 | 9.60 | | |
| 6-311G($2df,2p$) | 15.85 | 10.08 | 8.85 | 8.41 | 8.21 | | |
| 6-311 + + G($d,p$) | 15.76 | 11.07 | 9.94 | 9.45 | 9.31 | | |
| (6-311 + + G($2df,2p$))[e] | 15.57 | 9.79 | 8.55 | 8.11 | 7.91 | | |
| 6-311 + + G($2df,2p$) | 15.65 | 9.87 | 8.64 | 8.20 | 8.01 | | |
| 6-311 + + G($3df,3p$) | 15.70 | 9.69 | 8.45 | 8.04 | 7.83 | | |
| (5)$\frac{3}{4}$SiH$_4$ + $\frac{1}{4}$Si→SiH$_3$ | | | | | | | |
| 6-31G($d$) | 11.88 | 13.85 | 14.28 | 14.36 | 14.35 | 13.56 | |
| 6-31G($d,p$) | 11.76 | 13.97 | 14.53 | 14.67 | 14.65 | | |
| 6-31G($2d,2p$) | 11.29 | 14.16 | 15.01 | 15.22 | 15.21 | | |
| 6-31G($3d,3p$) | 11.18 | 14.06 | 14.83 | 15.01 | 15.01 | | |
| 6-31G($df,p$) | 11.51 | 13.82 | 14.25 | 14.32 | 14.31 | | |
| 6-31 + + G($d,p$) | 11.69 | 13.94 | 14.50 | 14.63 | 14.60 | | |
| 6-31 + + G($2d,2p$) | 11.21 | 14.10 | 14.93 | 15.14 | 15.13 | | |
| (6-31 + + G($3df,3p$))[e] | 10.85 | 13.85 | 14.48 | 14.57 | 14.59 | | |
| 6-311G($d,p$) | 11.73 | 13.97 | 14.53 | 14.68 | 14.67 | | |
| 6-311G($2df,2p$) | 11.03 | 14.05 | 14.64 | 14.71 | 14.71 | | |
| 6-311 + + G($d,p$) | 11.58 | 13.85 | 14.41 | 14.55 | 14.54 | | |
| (6-311 + + G($2df,2p$))[e] | 10.88 | 13.92 | 14.52 | 14.58 | 14.61 | | |
| 6-311 + + G($2df,2p$) | 10.93 | 13.99 | 14.58 | 14.64 | 14.68 | | |
| 6-311 + + G($3df,3p$) | 10.91 | 13.96 | 14.53 | 14.58 | 14.62 | | |
| (2a)$\frac{1}{4}$SiF$_4$ + SiH→$\frac{1}{4}$SiH$_4$ + SiF | | | | | | | |
| 6-31G($d$) | 0.11 | − 3.51 | − 2.15 | − 3.03 | − 3.63 | 4.0 | − 5.20 |
| 6-31G($d, p$) | 0.17 | − 3.37 | − 2.09 | − 3.00 | − 3.60 | | |
| 6-31G($2d,2p$) | − 0.37 | − 3.12 | − 1.49 | − 2.43 | − 3.16 | | |
| 6-31 + + G($d, p$) | − 3.29 | − 7.91 | − 6.34 | − 7.56 | − 8.30 | | |
| 6-31 + + G($2d,2p$) | − 2.83 | − 6.29 | − 4.34 | − 5.46 | − 6.33 | | |
| (3a) SiH$_3$F + SiH→SiH$_4$ + SiF | | | | | | | |
| 6-31G($d$) | − 5.32 | − 9.74 | − 8.79 | − 9.58 | − 10.29 | − 1.5[f] | − 9.75 |
| 6-31G($d$)[d] | − 5.43 | − 9.64 | − 8.68 | − 9.48 | − 10.19 | 3.6[g] | |
| 6-31G($d, p$) | − 5.16 | − 9.28 | − 8.26 | − 8.93 | − 9.62 | 7.6[h] | |
| 6-31G($2d,2p$) | − 5.66 | − 9.17 | − 7.90 | − 8.51 | − 9.32 | | |
| 6-31G($3d,3p$) | − 5.86 | − 9.26 | − 7.89 | − 8.51 | − 9.32 | | |
| 6-31G($df, p$) | − 5.24 | − 9.23 | − 8.24 | − 8.87 | − 9.57 | | |
| 6-31 + + G($d, p$) | − 7.43 | − 11.66 | − 10.48 | − 11.30 | − 12.08 | | |
| 6-31 + + G($2d,2p$) | − 6.98 | − 10.61 | − 9.20 | − 9.87 | − 10.71 | | |
| (6-311 + + G($3df,3p$))[e] | − 7.26 | − 10.65 | − 9.18 | − 9.80 | − 10.67 | | |
| 6-311G($d, p$) | − 5.23 | − 8.97 | − 7.89 | − 8.56 | − 9.30 | | |

TABLE IV (continued).

| Basis set | Theoretical | | | | | From Table VI | |
| --- | --- | --- | --- | --- | --- | --- | --- |
| | HF | MP2 | MP3 | MP4SDQ | MP4SDTQ | Literature[b] | Revised[c] |
| 6-311G(2df,2p) | − 5.50 | − 8.71 | − 7.42 | − 7.99 | − 8.78 | | |
| 6-311 + + G(d, p) | − 6.99 | − 11.00 | − 9.72 | − 10.57 | − 11.44 | | |
| (6-311 + + G(2df,2p))[e] | − 7.27 | − 10.73 | − 9.25 | − 10.00 | − 10.91 | | |
| 6-311 + + G(2df,2p) | − 6.48 | − 9.89 | − 8.44 | − 9.09 | − 9.97 | | |
| **(5a) $\frac{1}{4}$ SiF$_4$ + $\frac{3}{4}$ Si→SiF** | | | | | | | |
| 6-31G(d) | 11.32 | 6.32 | 7.04 | 5.72 | 5.06 | 10.9 | 1.69 |
| 6-31G(d, p) | 11.32 | 6.32 | 7.04 | 5.72 | 5.06 | | |
| 6-31G(2d,2p) | 10.26 | 6.21 | 7.47 | 6.14 | 5.34 | | |
| 6-31 + + G(d, p) | 7.67 | 1.55 | 2.55 | 0.91 | 0.12 | | |
| 6-31 + + G(2d,2p) | 7.63 | 2.84 | 4.40 | 2.91 | 1.95 | | |
| **(8a) SiH$_3$F + $\frac{3}{4}$ Si→$\frac{3}{4}$ SiH$_4$ + SiF** | | | | | | | |
| 6-31G(d) | 5.89 | 0.09 | 0.39 | − 0.83 | − 1.60 | 5.3[f] | − 2.87 |
| 6-31G(d)[d] | 5.80 | 0.19 | 0.49 | − 0.75 | − 1.52 | 10.5[g] | |
| 6-31G(d, p) | 5.99 | 0.41 | 0.87 | − 0.21 | − 0.96 | 14.5[h] | |
| 6-31G(2d,2p) | 4.97 | 0.16 | 1.07 | 0.07 | − 0.82 | | |
| 6-31G(3d,3p) | 4.67 | − 0.15 | 0.78 | − 0.24 | − 1.14 | | |
| 6-31G(df, p) | 5.71 | − 0.12 | 0.11 | − 1.00 | − 1.74 | | |
| 6-31 + + G(d, p) | 3.53 | − 2.20 | − 1.59 | − 2.83 | − 3.66 | | |
| 6-31 + + G(2d,2p) | 3.48 | − 1.48 | − 0.46 | − 1.50 | − 2.43 | | |
| (6-31 + + G(3df,3p))[e] | 2.90 | − 2.34 | − 1.50 | − 2.59 | − 3.54 | | |
| 6-311G(d, p) | 5.94 | 0.37 | 0.87 | − 0.18 | − 1.00 | | |
| 6-311G(2df,2p) | 4.85 | − 0.03 | 0.61 | − 0.47 | − 1.31 | | |
| 6-311 + + G(d, p) | 3.92 | − 1.87 | − 1.17 | − 2.41 | − 3.35 | | |
| (6-311 + + G(2df,2p))[e] | 2.83 | − 2.27 | − 1.44 | − 2.70 | − 3.66 | | |
| 6-311 + + G(2df,2p) | 3.68 | − 1.37 | − 0.58 | − 1.73 | − 2.65 | | |
| **(2b) $\frac{1}{2}$ SiF$_4$ + SiH$_2$→$\frac{1}{2}$ SiH$_4$ + SiF$_2$** | | | | | | | |
| 6-31G(d) | − 13.00 | − 19.37 | − 17.49 | − 18.63 | − 19.61 | − 8.3 | − 20.82 |
| 6-31G(d, p) | − 13.01 | − 19.16 | − 17.39 | − 18.56 | − 19.51 | | |
| 6-31G(2d,2p) | − 13.09 | − 18.20 | − 15.85 | − 16.99 | − 18.11 | | |
| 6-31 + + G(d, p) | − 16.15 | − 24.08 | − 21.96 | − 23.53 | − 24.73 | | |
| 6-31 + + G(2d,2p) | − 15.31 | − 21.52 | − 18.78 | − 20.14 | − 21.49 | | |
| **(3b) SiH$_2$F$_2$ + SiH$_2$→SiH$_4$ + SiF$_2$** | | | | | | | |
| 6-31G(d) | − 17.20 | − 23.81 | − 22.58 | − 23.45 | − 24.40 | − 12.8[i] | − 23.55 |
| 6-31G(d)[d] | − 17.22 | − 23.78 | − 22.44 | − 23.39 | − 24.36 | − 8.3[j] | |
| 6-31G(d, p) | − 17.10 | − 23.33 | − 22.05 | − 22.80 | − 23.81 | − 5.3[k] | |
| 6-31G(2d,2p) | − 17.27 | − 22.71 | − 21.01 | − 21.65 | − 22.79 | | |
| 6-31G(3d,3p) | − 17.21 | − 22.43 | − 20.64 | − 21.33 | − 22.49 | | |
| 6-31G(df, p) | − 17.08 | − 23.13 | − 21.84 | − 22.48 | − 23.51 | | |
| 6-31 + + G(d, p) | − 18.99 | − 25.95 | − 24.50 | − 25.44 | − 26.62 | | |
| 6-31 + + G(2d,2p) | − 18.28 | − 24.15 | − 22.29 | − 22.99 | − 24.22 | | |
| (6-31 + + G(3df,3p))[e] | − 18.21 | − 23.67 | − 21.70 | − 22.36 | − 23.63 | | |
| 6-311G(d, p) | − 16.89 | − 22.56 | − 21.25 | − 22.05 | − 23.12 | | |
| 6-311G(2df,2p) | − 16.54 | − 21.42 | − 19.77 | − 20.34 | − 21.45 | | |
| 6-311 + + G(d, p) | − 18.32 | − 24.82 | − 23.30 | − 24.31 | − 25.61 | | |
| (6-311 + + G(2df,2p))[e] | − 17.98 | − 23.69 | − 21.82 | − 22.61 | − 23.94 | | |
| **(5b) $\frac{1}{2}$ SiF$_4$ + $\frac{1}{2}$ Si→SiF$_2$** | | | | | | | |
| 6-31G(d) | 3.01 | − 7.26 | − 6.60 | − 8.31 | − 9.40 | − 1.19 | − 13.69 |
| 6-31G(d, p) | 3.01 | − 7.26 | − 6.60 | − 8.30 | − 9.38 | | |
| 6-31G(2d,2p) | 2.85 | − 7.26 | − 5.98 | − 7.52 | − 8.81 | | |
| 6-31 + + G(d, p) | − 0.37 | − 12.49 | − 11.49 | − 13.60 | − 14.93 | | |
| 6-31 + + G(2d,2p) | 0.40 | − 10.85 | − 9.18 | − 10.94 | − 12.46 | | |
| **(8b) SiH$_2$F$_2$ + $\frac{1}{2}$ Si→$\frac{1}{2}$ SiH$_4$ + SiF$_2$** | | | | | | | |
| 6-31G(d) | − 1.19 | − 11.69 | − 11.68 | − 13.13 | − 14.18 | − 5.7[i] | − 16.42 |
| 6-31G(d)[d] | − 1.18 | − 11.69 | − 11.60 | − 13.13 | − 14.32 | − 1.2[j] | |
| 6-31G(d, p) | − 1.09 | − 11.43 | − 11.26 | − 12.54 | − 13.67 | 1.8[k] | |
| 6-31G(2d,2p) | − 1.32 | − 11.77 | − 11.14 | − 12.17 | − 13.49 | | |
| 6-31G(3d,3p) | − 1.29 | − 11.89 | − 11.27 | − 12.35 | − 13.72 | | |
| 6-31G(df, p) | − 1.03 | − 11.89 | − 11.82 | − 13.01 | − 14.17 | | |
| 6-31 + + G(d, p) | − 3.21 | − 14.35 | − 14.03 | − 15.52 | − 16.81 | | |
| 6-31 + + G(2d,2p) | − 2.57 | − 13.48 | − 12.69 | − 13.78 | − 15.19 | | |
| (6-31 + + G(3df,3p))[e] | − 2.48 | − 14.05 | − 13.37 | − 14.43 | − 15.92 | | |
| 6-311G(d, p) | − 0.84 | − 11.20 | − 11.01 | − 12.30 | − 13.52 | | |
| 6-311G(2df,2p) | − 0.69 | − 11.34 | − 10.92 | − 11.94 | − 13.24 | | |
| 6-311 + + G(d, p) | − 2.56 | − 13.75 | − 13.35 | − 14.87 | − 16.31 | | |
| (6-311 + + G(2df,2p))[e] | − 2.41 | − 13.90 | − 13.26 | − 14.50 | − 16.03 | | |

TABLE IV (continued).

| Basis set | Theoretical | | | | | From Table VI | |
|---|---|---|---|---|---|---|---|
| | HF | MP2 | MP3 | MP4SDQ | MP4SDTQ | Literature[b] | Revised[c] |
| (2c) $\frac{1}{3}$ SiF$_4$ + SiH$_3$ → $\frac{1}{3}$ SiH$_4$ + SiF$_3$ | | | | | | | |
| 6-31G($d$) | 12.16 | 11.39 | 12.88 | 12.23 | 11.97 | 10.2[l] | 8.47 |
| 6-31G($d,p$) | 12.27 | 11.28 | 12.63 | 11.92 | 11.67 | − 9.8[m] | |
| 6-31G($2d,2p$) | 10.69 | 10.07 | 11.70 | 10.98 | 10.67 | | |
| 6-31 + + G($d,p$) | 8.20 | 6.15 | 7.94 | 6.92 | 6.49 | | |
| 6-31 + + G($2d,2p$) | 8.57 | 7.15 | 9.10 | 8.17 | 7.69 | | |
| (3c) SiHF$_3$ + SiH$_3$ → SiH$_4$ + SiF$_3$ | | | | | | | |
| 6-31G($d$) | 11.49 | 11.13 | 12.06 | 11.67 | 11.40 | 9.6[l] | 9.07 |
| 6-31G($d,p$) | 11.66 | 11.07 | 11.97 | 11.63 | 11.38 | − 10.4[m] | |
| 6-31G($2d,2p$) | 9.97 | 9.53 | 10.56 | 10.26 | 9.98 | | |
| 6-31 + + G($d,p$) | 8.40 | 7.51 | 8.71 | 8.22 | 7.87 | | |
| 6-31 + + G($2d,2p$) | 8.59 | 7.85 | 9.04 | 8.64 | 8.28 | | |
| (5c) $\frac{2}{3}$ SiF$_4$ + $\frac{1}{3}$ Si → SiF$_3$ | | | | | | | |
| 6-31G($d$) | 24.04 | 25.24 | 27.16 | 26.59 | 26.32 | 23.8[l] | 22.04 |
| 6-31G($d,p$) | 24.04 | 25.24 | 27.16 | 26.59 | 26.32 | 3.8[m] | |
| 6-31G($2d,2p$) | 21.97 | 24.23 | 26.71 | 26.20 | 25.88 | | |
| 6-31 + + G($d,p$) | 19.89 | 20.08 | 22.43 | 21.55 | 21.10 | | |
| 6-31 + + G($2d,2p$) | 19.78 | 21.26 | 24.03 | 23.31 | 22.82 | | |
| (8c) SiHF$_3$ + $\frac{1}{3}$ Si → $\frac{1}{3}$ SiH$_4$ + SiF$_3$ | | | | | | | |
| 6-31G($d$) | 23.37 | 24.98 | 26.34 | 26.03 | 25.75 | 23.2[l] | 22.64 |
| 6-31G($d,p$) | 23.42 | 25.04 | 26.50 | 26.30 | 26.03 | 3.2[m] | |
| 6-31G($2d,2p$) | 21.26 | 23.70 | 25.57 | 25.48 | 25.19 | | |
| 6-31 + + G($d,p$) | 20.09 | 21.45 | 23.20 | 22.84 | 22.48 | | |
| 6-31 + + G($2d,2p$) | 19.80 | 21.95 | 23.97 | 23.78 | 23.41 | | |

[a] In kcal/mol; using the HF/6-31G($d$) optimized geometry unless indicated otherwise.

[b] Using the $\Delta H_f^0$ recommended by Walsh (Ref. 5) and/or JANAF (Ref. 19), as listed under the "Experimental" column in Table VI, unless indicated otherwise.

[c] Using the revised $\Delta H_f^0$ listed under the "Present calculations" column in Table VI, along with the experimental values for SiH$_n$ and SiF$_4$.

[d] Using the MP2/6-31G($d$) optimized geometry.

[e] Estimated using Eq. (1).

[f] Using $\Delta H_f^0$ (SiH$_3$F) = − 84.9 kcal/mol from our previous calculations (Ref. 4) (see Table VI).

[g] Using $\Delta H_f^0$ (SiH$_3$F) = − 90 kcal/mol obtained by linear interpolation in the *JANAF Tables* (Ref. 19).

[h] Using $\Delta H_f^0$ (SiH$_3$F) = − 94 kcal/mol measured by Farber and Srivastava (Ref. 12).

[i] Using $\Delta H_f^0$ (SiH$_2$F$_2$) = − 184.5 kcal/mol from our previous calculations (Ref. 4) (see Table VI).

[j] Using $\Delta H_f^0$ (SiH$_2$F$_2$) = − 189 kcal/mol obtained by linear interpolation in the *JANAF Tables* (Ref. 19).

[k] Using $\Delta H_f^0$ (SiH$_2$F$_2$) = − 192 kcal/mol measured by Farber and Srivastava (Ref. 12).

[l] Using $\Delta H_f^0$ (SiF$_3$) = − 192 kcal/mol measured by Doncaster and Walsh (Ref. 29).

[m] Using $\Delta H_f^0$ (SiF$_3$) = − 259 kcal/mol measured by Farber and Srivastava (Ref. 12).

(9), once the $\Delta H_f^0$ are known for SiH$_n$ and SiF$_n$:

$$\frac{n - m}{n} \text{SiH}_n + \frac{m}{n} \text{SiF}_n \rightarrow \text{SiH}_{n - m}\text{F}_m . \qquad (9)$$

As shown in Table V, basis set effects ( < 2 kcal/mol) and correlation corrections ( < 1 kcal/mol) are much smaller for these reactions than for reactions (2), (3), (5), and (8). The effect of triple excitations on the $\Delta H_r$ calculated at the MP4 level is less than 0.1 kcal/mol. Based on reactions (9a) and (9d), further extension of the basis set may change the heats of reaction for reactions (9b)–(9g) by ± 0.2 kcal/mol or less.

The final theoretical estimates for the heats of formation of SiH$_m$F$_n$ are listed in Table VI and were obtained by the following sequence: The $\Delta H_f^0$ for SiH$_n$, $n$ = 1–3 are calculated from reaction (5) in Table IV at the full MP4/6-311 + + G($3df,3p$) level. In subsequent calculations, the experimental values are used for the $\Delta H_f^0$ for SiH$_n$. The

$\Delta H_f^0$ for SiH$_2$F$_2$ and SiHF$_3$ are calculated from reactions (9f) and (9g) in Table V at the MP4/6-31 + + G($2d,2p$) level, yielding − 186.3 and − 288.2 kcal/mol, respectively. For SiH$_3$F, the estimated MP4/6-311 + + G($2df,2p$) enthalpy for reaction (9d) gives $\Delta H_f^0$ = − 85.8 kcal/mol. An average $\Delta H_f^0$ = − 240.7 kcal/mol for SiF$_3$ is obtained from reactions (2c), (3c), (5c), and (8c) in Table IV at the MP4/6-31 + + G($2d,2p$) level [extrapolation to MP4/6-311 + + G($2df,2p$) would suggest a value 0–1 kcal/mol lower]. For SiH$_2$F and SiHF$_2$, $\Delta H_f^0$ equals − 44.9 and − 142.6 kcal/mol, respectively, based on reactions (9b) and (9c) in Table V calculated at the MP4/6-31 + + G($2d,2p$) level. The heat of formation of SiF$_2$ is obtained from reactions (3b) and (5b) in Table IV at the estimated MP4/6-311 + + G($2df,2p$) level, $\Delta H_f^0$ = − 153.0 kcal/mol. Likewise, heat of formation of SiF from reactions (3a) and (5a) is $\Delta H_f^0$ = − 14.2 kcal/mol at the full MP4/6-31 + + G($2df,2p$) level. Last-

ly, $\Delta H_f^0 = -37.8$ kcal/mol for SiHF is obtained from reaction (9a) in Table V at the MP4/6-311 + + G($2d,2p$) level. When this revised set of $\Delta H_f^0$ has been used to recalculate the $\Delta H_r$'s for the reactions in Table IV, the mean absolute

error is 0.5 kcal/mol. The variations of the heats of reaction with basis set and electron correlation suggest that error bars of $\pm 2$ kcal/mol would be reasonable for the calculated $\Delta H_f^0$.

TABLE V. $\Delta H_{r,298}$ for isodesmic reactions leading to the heats of formation of $SiH_m F_n$.[a]

| Basis set | Theoretical | | | | | From Table VI | |
|---|---|---|---|---|---|---|---|
| | HF | MP2 | MP3 | MP4SDQ | MP4SDTQ | Previous calc[b] | Revised[c] |
| (9a) $\frac{1}{2}$ SiH$_2$ + $\frac{1}{2}$ SiF$_2 \rightarrow$ SiHF | | | | | | | |
| 6-31G($d$) | 6.60 | 7.12 | 7.10 | 6.96 | 7.06 | 6.69 | 6.20 |
| 6-31G($d$)[d] | 6.55 | 7.16 | 7.10 | 6.98 | 7.06 | | |
| 6-31G($d,p$) | 6.55 | 6.96 | 6.89 | 6.70 | 6.76 | | |
| 6-31G($2d,2p$) | 6.52 | 7.02 | 7.00 | 6.74 | 6.78 | | |
| 6-31G($3d,3p$) | 6.28 | 6.89 | 6.94 | 6.66 | 6.70 | | |
| 6-31G($df, p$) | 6.78 | 7.20 | 7.13 | 6.96 | 7.02 | | |
| 6-31 + + G($d, p$) | 5.86 | 6.01 | 6.03 | 5.78 | 5.83 | | |
| 6-31 + + G($2d,2p$) | 5.84 | 6.21 | 6.27 | 5.97 | 5.98 | | |
| (6-31 + + G($3df,3p$))[e] | 5.84 | 6.31 | 6.46 | 6.14 | 6.16 | | |
| 6-311G($d, p$) | 6.51 | 7.01 | 6.86 | 6.70 | 6.79 | | |
| 6-311G($2df,2p$) | 6.67 | 7.20 | 7.28 | 7.05 | 7.12 | | |
| 6-311 + + G($d, p$) | 5.71 | 6.09 | 6.07 | 5.82 | 5.87 | | |
| (6-311 + + G($2df,2p$))[e] | 5.88 | 6.27 | 6.49 | 6.17 | 6.19 | | |
| (9b) $\frac{2}{3}$ SiH$_3$ + $\frac{1}{3}$ SiF$_3 \rightarrow$ SiH$_2$F | | | | | | | |
| 6-31G($d$) | 5.53 | 6.17 | 6.34 | 6.25 | 6.32 | 6.06 | 4.30 |
| 6-31G($d, p$) | 5.47 | 5.99 | 6.08 | 5.89 | 5.96 | | |
| 6-31G($2d,2p$) | 5.12 | 5.87 | 6.02 | 5.76 | 5.82 | | |
| 6-31 + + G($d, p$) | 4.25 | 4.14 | 4.30 | 4.00 | 4.03 | | |
| 6-31 + + G($2d,2p$) | 4.04 | 4.37 | 4.66 | 4.32 | 4.30 | | |
| (9c) $\frac{1}{3}$ SiH$_3$ + $\frac{2}{3}$ SiF$_3 \rightarrow$ SiHF$_2$ | | | | | | | |
| 6-31G($d$) | 3.62 | 3.75 | 3.97 | 3.79 | 3.81 | 3.75 | 2.30 |
| 6-31G($d, p$) | 3.58 | 3.72 | 3.88 | 3.62 | 3.64 | | |
| 6-31G($2d,2p$) | 3.33 | 3.67 | 3.92 | 3.62 | 3.62 | | |
| 6-31 + + G($d, p$) | 2.58 | 2.19 | 2.44 | 2.07 | 2.05 | | |
| 6-31 + + G($2d,2p$) | 2.40 | 2.38 | 2.76 | 2.38 | 2.30 | | |
| (9d) $\frac{1}{2}$ SiH$_4$ + $\frac{1}{2}$ SiH$_2$F$_2 \rightarrow$ SiH$_3$F | | | | | | | |
| 6-31G($d$) | 3.33 | 4.01 | 4.11 | 4.14 | 4.27 | 3.31 | 3.19 |
| 6-31G($d$)[d] | 3.34 | 4.02 | 4.08 | 4.12 | 4.19 | | |
| 6-31G($d, p$) | 3.29 | 3.82 | 3.84 | 3.81 | 3.88 | | |
| 6-31G($2d,2p$) | 3.21 | 3.80 | 3.82 | 3.75 | 3.81 | | |
| 6-31G($3d,3p$) | 2.81 | 3.34 | 3.42 | 3.32 | 3.38 | | |
| 6-31G($df, p$) | 3.58 | 4.09 | 4.11 | 4.07 | 4.15 | | |
| 6-31 + + G($d, p$) | 2.72 | 2.82 | 2.87 | 2.78 | 2.84 | | |
| 6-31 + + G($2d,2p$) | 2.67 | 3.01 | 3.11 | 2.99 | 3.02 | | |
| (6-31 + + G($3df,3p$))[e] | 2.56 | 2.83 | 2.97 | 2.82 | 2.85 | | |
| 6-311G($d, p$) | 2.83 | 3.46 | 3.46 | 3.40 | 3.48 | | |
| 6-311G($2df,2p$) | 3.08 | 3.67 | 3.77 | 3.69 | 3.76 | | |
| 6-311 + + G($d, p$) | 2.60 | 2.94 | 2.94 | 2.85 | 2.90 | | |
| (6-311 + + G($2df,2p$))[e] | 2.86 | 3.16 | 3.26 | 3.15 | 3.19 | | |
| (9e) $\frac{3}{4}$ SiH$_4$ + $\frac{1}{4}$ SiF$_4 \rightarrow$ SiH$_3$F | | | | | | | |
| 6-31G($d$) | 5.43 | 6.23 | 6.65 | 6.55 | 6.66 | 5.55 | 4.56 |
| 6-31G($d, p$) | 5.34 | 5.91 | 6.17 | 5.93 | 6.03 | | |
| 6-31G($2d,2p$) | 5.29 | 6.05 | 6.40 | 6.08 | 6.16 | | |
| 6-31 + + G($d, p$) | 4.14 | 3.75 | 4.14 | 3.74 | 3.78 | | |
| 6-31 + + G($2d,2p$) | 4.15 | 4.32 | 4.86 | 4.41 | 4.38 | | |
| (9f) $\frac{1}{2}$ SiH$_4$ + $\frac{1}{2}$ SiF$_4 \rightarrow$ SiH$_2$F$_2$ | | | | | | | |
| 6-31G($d$) | 4.20 | 4.43 | 5.08 | 4.83 | 4.79 | 4.48 | 2.73 |
| 6-31G($d, p$) | 4.10 | 4.17 | 4.66 | 4.24 | 4.29 | | |
| 6-31G($2d,2p$) | 4.17 | 4.51 | 5.16 | 4.66 | 4.68 | | |
| 6-31 + + G($d, p$) | 2.84 | 1.86 | 2.54 | 1.91 | 1.88 | | |
| 6-31 + + G($2d,2p$) | 2.97 | 2.63 | 3.50 | 2.84 | 2.73 | | |

TABLE V (continued).

| Basis set | Theoretical | | | | | From Table VI | |
| | HF | MP2 | MP3 | MP4SDQ | MP4SDTQ | Previous calc[b] | Revised[c] |
|---|---|---|---|---|---|---|---|
| (9g) $\frac{1}{4}$ SiH$_4$ + $\frac{3}{4}$ SiF$_4$ → SiHF$_3$ | | | | | | | |
| 6-31G(d) | 0.67 | 0.26 | 0.82 | 0.56 | 0.57 | 0.53 | − 0.60 |
| 6-31G(d, p) | 0.61 | 0.20 | 0.67 | 0.29 | 0.29 | | |
| 6-31G(2d,2p) | 0.72 | 0.54 | 1.14 | 0.73 | 0.69 | | |
| 6-31 + + G(d, p) | − 0.20 | − 1.37 | − 0.77 | − 1.29 | − 1.38 | | |
| 6-31 + + G(2d,2p) | − 0.02 | − 0.70 | 0.06 | − 0.46 | − 0.60 | | |

[a] In kcal/mol; using the HF/6-31G(d) optimized geometry unless indicated otherwise.

[b] Using the $\Delta H_f^0$ calculated by Schlegel (Ref. 4) listed under the "Previous calc" column in Table VI, along with the experimental values for $SiH_n$, $SiF_3$, and $SiF_4$.

[c] Using the revised $\Delta H_f^0$ from our previous calculations (Ref. 4) (see Table VI), along with the experimental values for $SiH_n$ and $SiF_4$.

[d] Using the MP2/6-31G(d) optimized geometry.

[e] Estimated using Eq. (1).

The $\Delta H_f^0$ for SiF and SiF$_2$ are predicted to be 10–12 kcal/mol lower than the experimental $\Delta H_f^0$. As discussed above, all of the MP$n$ calculations on reactions (3a), (3b), (5a), and (5b) for SiF and SiF$_2$ are consistently more exothermic than the heats of reaction computed with the accepted, experimental $\Delta H_f^0$. The present calculations use much larger basis sets and more extensive corrections for electron

correlation than those in Ref. 10, indicating the good agreement with experiment found in the latter was fortuitous. In Ref. 10, $\Delta H_f^0$ for SiF is obtained from a direct calculation of $D_e$(SiF). Such calculations are notoriously sensitive to basis set size. With a DZP basis set, the generalized valence-bond + configuration interaction (GVB + CI) calculations give $D_e$(SiF) = 125.7 kcal/mol; the 6-31G(d,p) basis set is

TABLE VI. Heats of formation and entropies of $SiH_mF_n$ at 298 K.[a]

| Molecule | $\Delta H_f^0$ (298 K) | | | S (298 K) | |
| | Experiment | Previous calc | Present calc | Expt.[b] | Calc[d] |
|---|---|---|---|---|---|
| Si | 107.5 ± 2[b] | | | | |
| SiH | 90 ± 2,[b] 89.6 ± 1.2[c] | 88.5,[l] 91.7[m] | 89.9 | 47.3 | 47.2 |
| SiF | − 5 ± 6[d] | 2.0[n] | − 14.2 | 54.0 | 53.8 |
| SiH$_2$ | 65 ± 2[e] | 63.5,[l] 68.1[m] | 65.7 | | 49.5 |
| SiHF | − 41 ± 5[f] | − 31.1[o] | − 37.8 | | 57.0 |
| SiF$_2$ | − 140.5 ± 2[b,g] | − 136.9[n] | − 153.0 | 61.3 | 61.1 |
| SiH$_3$ | 46.6 ± 1.5[h] | 47.3,[l] 47.8[m] | 47.7 | | 51.6 |
| SiH$_2$F | − 49 ± 5[f] | − 42.5[o] | − 44.9 | | 59.4 |
| SiHF$_2$ | − 144 ± 5[f] | − 140.1[o] | − 142.6 | | 64.6 |
| SiF$_3$ | − 239 ± 5,[i] − 259 ± 5[g] | − 237.1,[o] − 257.2[n] | − 240.7 | 67.5 | 67.1 |
| SiH$_4$ | 8.2 ± 0.5[b] | 6.3[l] | | 48.9 | 48.7 |
| SiH$_3$F | − 90 ± 5,[f] − 94 ± 2[j] | − 84.9,[o] 85.6[p] | − 85.8 | 57.0 | 56.7 |
| SiH$_2$F$_2$ | − 189 ± 5,[f] − 192 ± 2[j] | − 184.5,[o] − 185.7[p] | − 186.3 | 62.6 | 62.3 |
| SiHF$_3$ | − 287 ± 5,[f] − 293 ± 2[j] | − 287.1,[o] − 287.7[p] | − 288.2 | 66.3 | 65.8 |
| SiF$_4$ | − 386.2 ± 0.1[k] | | | | |

[a] Heats of formation in kcal/mol, entropies in cal/(deg mol).

[b] From JANAF Tables (Ref. 19).

[c] Berkowitz, Greene, Cho, and Ruscic (Ref. 6).

[d] Recommended by Walsh (Ref. 5).

[e] An average of eight recent experimental values (see the text).

[f] Linear interpolation assumed in JANAF Tables (Ref. 19).

[g] Farber and Srivastava (Ref. 8).

[h] Doncaster and Walsh (Ref. 20).

[i] Doncaster and Walsh (Ref. 29).

[j] Farber and Srivastava (Ref. 12).

[k] Johnson (Ref. 28).

[l] Curtiss and Pople [Ref. 7(a)].

[m] Ho, coltrin, Binkley, and melius (Ref. 27).

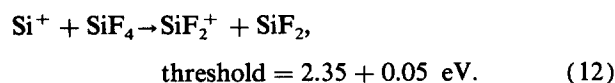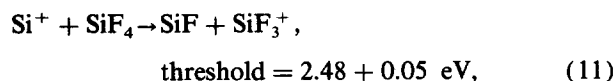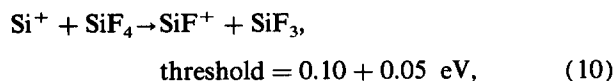[n] Garrison and Goddard (Ref. 10).

[o] Schlegel (Ref. 4).

[p] Dixon (Ref. 11).

[q] Present work.

roughly comparable in size and MP4 calculations yield a similar $D_e$ (SiF), 128.5 kcal/mol. Systematic improvements in the basis set result in a steady increase in $D_e$ (SiF), reaching a value of 136.4 kcal/mol at the MP4/6-311 + $G(2df,2p)$ level [data available in Table I and Ref. 17(a)]. Even this is only a lower bound, since further improvements in the calculation should lead to a better description of the bond, giving a higher dissociation energy. The revised $\Delta H_f^0$ (SiF) yields $D_e$ (SiF) = 141.2 kcal/mol. The other direct calculations of $D_e$'s in Ref. 10 and the $\Delta H_f^0$'s obtained from them suffer from the same shortcomings in the basis set. By contrast, the isodesmic reactions in Tables IV and V appear to be an order of magnitude less sensitive to basis set effects and, for a given level of theory, lead to more reliable estimates of $\Delta H_f^0$.

The average $\Delta H_f^0$ (SiF$_3$) of $-240.7$ kcal/mol obtained from reactions (2c), (3c), (5c), and (8c) is well within the error range of Doncaster and Walsh's value ($-239 \pm 5$ kcal/mol).[29] In a more direct comparison, the calculated $D(F_3Si–H) = 100.0 \pm 2$ kcal/mol is in very good agreement with $D(F_3Si–H) = 100.1 \pm 1.2$ kcal/mol determined experimentally by Doncaster and Walsh.[29] At no level in the present calculations is there any support for $\Delta H_f^0$ (SiHF$_3$) = $-259$ kcal/mol. Differences between the present work and Ref. 10 are again attributable to basis set deficiencies in the latter calculations. The computed $\Delta H_f^0$ for $SiH_{4-n}F_n$ are 0.5–2 kcal/mol lower than predicted by our previous study[4] and by Dixon[11] as a result of the larger basis sets and improved treatment of electron correlation; similarly, the $\Delta H_f^0$ for $SiH_{3-n}F_n$ are ~2.5 kcal/mol lower than our previous values.[4] The larger difference for SiHF is primarily due to the proposed changes in $\Delta H_f^0$ for SiF$_2$.

Recent experiments by Weber and Armentrout[9] provide a further test of the proposed revision of the $\Delta H_f^0$ of $SiF_n$. The reaction of Si$^+$ with SiF$_4$ yields the following thresholds:

$$Si^+ + SiF_4 \rightarrow SiF^+ + SiF_3,$$
$$\text{threshold} = 0.10 \pm 0.05 \text{ eV}, \qquad (10)$$

$$Si^+ + SiF_4 \rightarrow SiF + SiF_3^+,$$
$$\text{threshold} = 2.48 \pm 0.05 \text{ eV}, \qquad (11)$$

$$Si^+ + SiF_4 \rightarrow SiF_2^+ + SiF_2,$$
$$\text{threshold} = 2.35 \pm 0.05 \text{ eV}. \qquad (12)$$

These were interpreted to give $\Delta H_f^0 = -258$ kcal/mol for SiF$_3$ based on $\Delta H_f^0 = -5$ kcal/mol for SiF. When the revised values for $\Delta H_f^0$ of SiF and SiF$_3$ are used, these reactions lead to adiabatic ionization potentials of 7.22 and 9.60 eV for SiF and SiF$_3$, respectively. This is in good agreement with the accepted experimental ionization potential for SiF (7.26 eV[30]) and within the range of experimental values for SiF$_3$ (9.0–9.9 eV[31]). The threshold for reaction (12) is ~0.9 eV above the calculated heat of reaction (1.45 eV) based on the revised $\Delta H_f^0$ for SiF$_2$ and 10.78 eV for the adiabatic ionization potential.[32] This suggests that the rearrangement occurring in reaction (12) has a barrier of ~20 kcal/mol.

## SUMMARY

The computations discussed above indicate strongly that SiF and SiF$_2$ are more stable than previously thought. Calculations based on isodesmic reactions give $\Delta H_f^0(298 \text{ K}) = -14.2 \pm 2$ kcal/mol for SiF and $\Delta H_f^0(298 \text{ K}) = -153.0 \pm 2$ kcal/mol for SiF$_2$. The predicted heat of formation of SiF$_3$ ($-240.7$ kcal/mol) agrees with the value recommended by Walsh. The current calculations on the heats of formation for $SiH_n$, $n = 1$–3, are the highest level to date and are in excellent agreement with experiment. The present calculations lead to changes of 1–2 kcal/mol in the heats of formation of the mixed $SiH_mF_n$ compared to our previous study at a lower level. Calculations at the PMP4 level indicate that the effect of spin contamination contributes an uncertainty of less than $\pm 0.5$ kcal/mol to the $\Delta H_f^0$ of SiH, SiF, and $SiH_{3-n}F_n$.

## ACKNOWLEDGMENTS

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