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Theoretical Calculation of Thermochemistry for Molecules in the Si−P−H System

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Ab initio molecular orbital calculations have been performed on species belonging to the Si−P−H system. These computations have been coupled to a bond additivity correction procedure to obtain heats of formation for 27 species. The Si−P single bond energy was found to be nominally about 300 kJ/mol, which is somewhat weaker than a Si−Si single bond. Multiple bond character in Si−P was found to be relatively weak.

Introduction

Silane decomposition chemistry has received considerable attention owing to its importance in semiconductor manufacturing. However, it is well-known that when dopants such as phosphorus or boron are added in small quantities, significant effects on growth rates are observed. In the case of phosphorus dopants, small quantities of PH_3 can lead to a factor of 20 decrease in polysilicon growth rate.[1] Understanding this behavior requires a knowledge of both surface and gas phase chemistries that might account for such a striking result. Unfortunately, no experimental thermochemical data are available to develop models for some of the effects observed in the growth of silicon films. In this paper we develop the thermochemical data base for the vapor phase interaction between silicon and phosphorous species that may be used in models to describe vapor deposition of silicon.

Calculation Methodology

All calculations were performed using the BAC-MP4 procedure outlined by Melius.[2] This procedure involves ab initio molecular orbital calculation using the Gaussian series of programs[3] followed by application of a bond additivity correction (BAC) procedure to the calculated energy. The essence of the BAC procedure is to enable one to calculate energies at accuracies sufficient for chemical applications without the need to resort to large basis sets or configuration interaction terms. This is a particularly important issue where the goal is generation of a sufficiently complete data set of consistent thermochemical data necessary for detailed chemical modeling. In a recent study, thermochemical data on about 100 closed and open shelled C1 and C2 fluorocarbon and fluoroxy hydrocarbons species were obtained by the BAC-MP4 method. For about 70 of these species, literature values for enthalpies of formation were available for comparison to the calculated values. The average difference between the calculated and literature values was about 9 kJ/mol.[4]

Equilibrium geometries, vibrational frequencies, and zero-point energies were calculated at the HF/6-31G(d) level. Single point energies were calculated at the MP4/6-31G(d,p) level to which the BAC procedure was applied. In the BAC method, errors in the electronic energy of a molecule are treated as systematic bondwise additive corrections that depend on bonding partner, distance, and next nearest neighbors. The energy per bond is corrected by calibration against reference molecules of known heats of formation.

Melius[2] has shown that for any molecule with bond connectivity $A_k{-}A_i{-}A_j{-}A_l$, the error in calculating the electronic energy can be estimated through the use of an empirical correction E_{BAC} to each bond $A_i{-}A_j$, where

$$E_{BAC}\,(A_i{-}A_j) = f_{ij}\, g_{kij}\, g_{ijl} \tag{1}$$

and

$$f_{ij} = A_{ij} \exp(-\alpha_{ij}\, r_{ij}) \tag{2}$$

A_{ij} and α_{ij} are calibration constants that depend on bond type. r_{ij} is the bond length at the Hartree−Fock level. g_{kij} is a correction to each second-nearest neighbor A_k, where

$$g_{kij} = (1 - h_{ik}\, h_{ij}) \tag{3}$$

and

$$h_{ik} = B_k \exp[-\alpha_{ik}(r_{ik} - 1.4\ \text{Å})] \tag{4}$$

B_k is a calibration constant that depends on the atom type. For open shell molecules, an additional correction is needed owing to contamination from higher spin states. This error E_{spin} is estimated using an approach developed by Schlegel in which the spin energy correction is obtained from the difference between the energy at the MP3 level using the UHF wave function and the projected energy[5] or

$$E_{spin} = E(\text{UMP3}) - E(\text{PUMP3}) \tag{5}$$

For closed-shell species having a UHF instability, the spin

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TABLE 1: Bond Additivity Correction Parameters (MP4/6-31G(d,p)//HF/6-31G(d))

bond	calibration species	A_{ij}[a]	α_{ij}	atom type	B_k
Si−H	SiH_4	38.6	2.0	H	0
P−H	PH_3	137.5	2.0	Si	0
Si−P	PH_2-SiH_3; $PH=SiH_2$	7085.2	2.91	P	0
H−H	H_2	18.98	2.0		

[a] kcal/mol.

TABLE 2: Heat of Formation (298 K): Literature and Computation

	theory		recommended literature	
species	CBS-Q	G2	JANAF[a]	Gurvich
PH_3	7.1	8.3	7.1	5.0
PH_2	132.5	137.1	110.3	119.5
PH	237.4	240.8	237.4	230.7

[a] JANAF value adjusted to account for correct reference state.

TABLE 3: Heat of Formation (298 K) for PH_2-SiH_3[a]

	CBS-Q	G2
from $PH_3 + SiH_2 = PH_2-SiH_3$	36.8	44.9
from $PH_2 + SiH_3 = PH_2-SiH_3$	39.3	38.5
from $PH_3 + SiH_4 = PH_2-SiH_3 + H_2$	35.1	38.0

[a] Heats of formation based on previously computed heats of formation by BAC-MP4 for the following species: SiH_4 = 34.3, SiH_3 = 198.1, SiH_2 = 270.9 (kJ/mol).

correction is

$$E_{\mathrm{spin}} = KS(S + 1) \tag{6}$$

where K = 41.8 kJ/mol.

Bond Correction Parameters

Implementation of the BAC procedure requires calibration against molecules of known heats of atomization in order to define the parameters. Table 1 lists the parameters used for the calculations. The Si−H BAC parameters listed are based on calibration against the known heat of formation of silane.[2] For the P−H bond we reference against the PH_3 molecule. One area of confusion, however, is the accepted standard state of solid phosphorus. The crystalline forms of red phosphorus are thermodynamically more stable than the white phosphorus. However, conversion of the white to the red is extremely slow, and it is generally believed that better data exist for the white. The most recent thermochemical compilations in the JANAF tables[6] have defined the white phosphorus as the standard reference state, a change from the previous edition that used the red. However, by conversion of standard states, it appears that the change in reference state was not carried through to some of the phosphorus-containing compounds listed in the latest JANAF edition, in particular, to the relevant species in this study—PH(g), PH_2(g), and PH_3(g). The change in reference state implies that the heats of formation for these three species should be lowered by 15.8 kJ/mol (3.78 kcal/mol) at 298 K relative to the numbers quoted in the JANAF tables. When the correct standard state is accounted for, the new defined JANAF value for PH_3 would be 7.1 kJ/mol, which is slightly higher than the recommended value of 5.0 kJ/mol suggested by Gurvich et al.[7] Because of this discrepancy, we have also implemented some of the higher level computational approaches (G2,[8] CBS-Q[9]) and obtain excellent agreement between the two computational methods and the JANAF recommendation. The results for the simple phosphorous hydrides are summarized in Table 2. For the purposes of calibration of the BAC parameter for the P−H bond, we use the G2 method, since it is consistent with bond literature reviews and the less known CBS method.[9] Quite good agreement is also obtained between the computation and the recommended value for PH. The PH_2 radical has a quoted literature recommendation of between 20 and 30 kJ/mol lower than the G2 method. However, the stated uncertainty in the JANAF recommendation is 96 kJ/mol!

Since no experimental data are available to define the strength of the Si−P bond, we rely on high-level G2 computation for the calibration. We based calibration of the Si−P bond on the most likely closed shell species to form in the gas phase during

TABLE 4: Energies, Bond Corrections, and Heats of Formation[a]

species	E(MP4)	E(HF)	E(ZP)	E(BAC)	$H_{f,298}$
PH [singlet]	−341.303 955	−341.192 413	0.005 846	34.2	402.1
PH [triplet]	−341.362 976	−341.267 334	0.005 818	36.9	244.4
PH_2	−341.977 722	−341.854 065	0.014 618	71.3	140.1
PH_3	−342.605 927	−342.454 193	0.026 181	104.3	8.1
PH_2-SiH_3	−632.804 811	−632.543 641	0.045 674	170.8	37.7
PH_3-SiH_2 [adduct]	−632.748 047	−632.482 056	0.045 529	171.6	186.6
PH_2-SiH_2	−632.161 865	−631.924 805	0.035 497	151.5	198.4
PH_2-SiH	−631.562 134	−631.327 026	0.026 484	131.9	247.9
PH_2-Si	−630.946 777	−630.737 061	0.018 383	117.7	335.6
$PH-SiH_3$	−632.177 368	−631.944 214	0.035 113	138.0	170.0
$P-SiH_3$ [singlet]	−631.511 047	−631.288 696	0.026 523	104.9	408.6
$P-SiH_3$ [triplet]	−631.562 988	−631.357 849	0.026 969	103.4	274.5
$PH-SiH_2$ [singlet]	−631.584 656	−631.339 051	0.026 765	149.4	171.4
$PH-SiH_2$ [triplet]	−631.536 316	−631.326 051	0.025 177	151.7	293.1
$P-SiH_2$	−630.952 026	−630.734 558	0.016 819	106.8	328.8
PH−SiH	−630.937 683	−630.736 023	0.016 955	140.5	332.9
P−SiH [singlet]	−630.364 8991	−630.131 5055	0.008 011	130.6	304.5
P−SiH [triplet]	−630.318 665	−630.124 207	0.008 095	90.6	463.9
PH_2-Si	−630.946 777	−630.737 061	0.018 383	117.7	335.6
PH−Si [singlet]	−630.376 282	−630.154 785	0.007 354	108.8	293.7
PH−Si [triplet]	−630.296 387	−630.118 286	0.008 701	105.5	509.2
P−Si	−629.757 081	−629.542 053	0.001 666	101.7	388.8
$SiH_3-PH-SiH_3$	−923.006 531	−922.634 583	0.064 674	238.5	59.3
$PH_2-SiH_2-PH_2$	−974.245 728	−973.856 384	0.057 263	260.0	36.9
c-$SiH_2-PH-SiH_2$	−921.793 152	−921.438 111	0.046 921	223.3	170.4
c-$SiH_2-PH-SiH_2-PH$	−1263.267 456	−1262.788 696	0.059 423	311.7	83.6
c-Si−PH−Si	−919.363 342	−919.048 828	0.011 327	173.6	424.1

[a] E(MP4) = MP4 energy (hartrees); E(HF) = Hartree−Fock energy (hartrees); E(ZP) = zero-point energy (hartrees); E(BAC) = bond additivity correction (kJ/mol); $H_{f,298}$ = enthalpy of formation at 298.15 K. All in kJ/mol.

TABLE 5: Vibrational Frequencies (cm^{-1})[a]

PH [singlet]	2291														
PH [triplet]	2280														
PH_2	1123	2302	2304												
PH_3	1018	1135	1135	2323	2323	2327									
PH_2-SiH_3	156	434	465	481	729	776	899	920	931	1100	2123	2129	2130	2313	2315
PH_3-SiH_2 [adduct]	165	258	359	361	708	724	948	1021	1105	1121	1932	1943	2380	2407	2412
PH_2-SiH_2	143	431	482	524	723	759	901	1101	2106	2119	2309	2314			
PH_2-SiH	363	404	490	535	817	1093	1981	2344	2354						
PH_2-Si	363	483	595	1089	2335	2339									
$PH-SiH_3$	164	432	482	508	771	899	922	924	2120	2121	2134	2286			
$P-SiH_3$ [singlet]	354	489	516	864	883	957	2087	2119	2127						
$P-SiH_3$ [triplet]	432	517	517	897	920	920	2122	2122	2123						
$PH-SiH_2$ [singlet]	466	519	586	597	763	938	2157	2175	2289						
$PH-SiH_2$ [triplet]	192	425	530	561	762	900	2095	2106	2298						
$P-SiH_2$	363	501	536	855	2147	2191									
$PH-SiH$	461	487	516	780	2108	2293									
$P-SiH$ [singlet]	298	298	730	2191											
$P-SiH$ [triplet]	538	595	2039												
PH_2-Si	363	438	595	1089	2335	2339									
$PH-Si$ [singlet]	137	633	2111												
$PH-Si$ [triplet]	416	720	2274												
$P-Si$	653														
$SiH_3-PH-SiH_3$	74	97	119	403	451	466	483	549	615	708	808	882	913	917	927
	930	934	2114	2122	2126	2133	2134	2136	2307						
$PH_2-SiH_2-PH_2$	116	129	129	395	425	463	529	593	718	729	774	819	924	1095	1099
	2117	2119	2313	2315	2320	2322									
c-$SiH_2-PH-SiH_2$	326	351	385	388	478	510	540	601	693	699	732	888	896	2142	2147
	2156	2162	2294												
c-$SiH_2-PH-SiH_2-PH$	66	232	381	410	422	431	435	460	519	553	673	676	702	761	798
	811	911	924	2123	2128	2135	2137	2288	2316						
c-$Si-PH-Si$	193	312	432	543	597	2363									

[a] Frequencies calculated at HF/6-31g(d) geometry and scaled by 0.89.

TABLE 6: Moments of Inertia (au)

PH [singlet]	0.0	3.2	3.2
PH [triplet]	0.0	3.2	3.2
PH_2	2.9	3.5	6.4
PH_3	6.0	6.0	7.2
PH_2-SiH_3	16.0	152.4	153.4
PH_3-SiH_2 [adduct]	15.0	168.9	170.0
PH_2-SiH_2	12.4	145.8	148.8
PH_2-SiH	9.6	135.2	140.5
PH_2-Si	5.9	132.4	134.1
$PH-SiH_3$	12.9	146.7	149.9
$P-SiH_3$ [singlet]	9.6	140.2	140.2
$P-SiH_3$ [triplet]	9.7	144.1	144.1
$PH-SiH_2$ [singlet]	8.2	117.5	125.7
$PH-SiH_2$ [triplet]	8.2	117.5	125.7
$P-SiH_2$	5.8	120.9	126.7
$PH-SiH$	5.7	120.0	125.7
$P-SiH$ [singlet]	0.0	100.5	100.5
$P-SiH$ [triplet]	2.6	111.6	114.2
PH_2-Si	5.9	132.4	134.1
$PH-Si$ [singlet]	3.2	103.1	106.3
$PH-Si$ [triplet]	3.2	118.6	121.7
$P-Si$	0.0	94.5	94.5
$SiH_3-PH-SiH_3$	94.8	350.6	420.0
$PH_2-SiH_2-PH_2$	81.1	394.9	454.7
c-$SiH_2-PH-SiH_2$	153.5	157.4	284.5
c-$SiH_2-PH-SiH_2-PH$	262.8	330.2	545.2
c-$Si-PH-Si$	110.0	141.8	251.8

TABLE 7: Bond Dissociation Energies (kJ/mol)

BOND	BDE (kJ/mol)	BOND	BDE (kJ/mol)
H_2P-H	350	$H_2PSiH-H$	268
^3HP-H	322	$H_3SiPH-H$	350
^3P-H	289	$^1HP{=}SiH_2 = {^1HP} + {^1SiH_2}$	502
H_2P-SiH_3	300	$= {^3HP} + {^3SiH_2}$	427
$SiH_3PH-SiH_3$	309	$= {^3HP} + {^1SiH_2}$	344
$H_2PSiH_2-PH_2$	349	$^3HP{=}SiH_2 = {^3HP} + {^1SiH_2}$	222
$HP-SiH_3$	272	$P-SiH$	396
$P-SiH_3$	240	$HP-Si$	401
H_2P-SiH_2	213	H_3P-SiH_2	92
$P-SiH_2$	258	SiH_3-H	382
H_2PSiH_2-H	379	$H_3Si-SiH_3$	316

SiH_4/PH_3 pyrolysis: PH_2-SiH_3. Heats of formation were determined by three reactions, $PH_3 + SiH_2$, $PH_2 + SiH_3$, and the isogyric reaction $PH_3 + SiH_4 = PH_2-SiH_3 + H_2$, summarized in Table 3. As expected, the largest discrepancy in the calculated heat of formation between G2 and CBS occurs for the reaction $PH_3 + SiH_2$, presumably because of the multireference character of SiH_2. Agreement between G2 and CBS is considerably better when using $PH_2 + SiH_3$ and consistent with what should be the more accurate isodesmic reaction. In either case the largest deviation is still only 7 kJ/mol, certainly within common experimental error. For the purposes of defining the BAC parameter for the Si−P bond, we used the G2 value of 38 kJ/mol (9.1 kcal/mol) corresponding to the isogyric reaction. The Si═P double bond was calibrated from the species $PH{=}SiH_2$. Agreement between G2 and CBS for the heat of formation calculated for $PH{=}SiH_2$ from the reaction $^3PH + {^3SiH_2} = {^1PH}{=}SiH_2$ was excellent and gave a value of 172 kJ/mol based on BAC-MP4 numbers for the heat of formation of ^3PH and $^3SiH_2$ of 244 and 354 kJ/mol, respectively.

Molecular Properties

Tables 4−7 list the total energies, heats of formation, bond corrections, vibrational frequencies, moments of inertia, and bond dissociation energies for the species computed. Molecular geometries and NASA type polynomial fits[10] for C_p, H, and S are included in Charts 1 and 2, respectively.

The P−H bond (in PH_3) is nominally slightly shorter (1.40 vs 1.48 Å) and the bond energy smaller (350 vs 382 kJ/mol) than for Si−H (SiH_4). Mulliken charge analysis indicates that although the P−H bond is essentially covalent, the Si−H bond is slightly ionic with silicon being the electron donor. Neither the P−H nor the Si−H bond dissociation energy (BDE) was found to be sensitive to P or Si substitution on the central atom relative to the corresponding hydride. The Si−P single BDE in PH_2-SiH_3 is about 23% weaker than the Si−Si single BDE

CHART 1: Atom Coordinates (angstroms)

	2		PH, singlet		
P		1	0	0	0
H		2	0	0	1.411
	2		PH, triplet		
P		1	0	0	0
H		2	0	0	1.411
	3		PH_2		
P		1	0	0	0
H		2	0	0	1.407
H		3	1.4044	0	−0.0852
	4		PH3		
P		1	0	0	0
H		2	0	0	1.4031
H		3	1.3969	0	−0.1319
H		4	−0.145	−1.3893	−0.1319
	7		PH_2-SiH_3		
P		1	0	0	0
Si		2	0	0	2.2663
H		3	1.3922	0	−0.1809
H		4	−0.162	1.383	−0.1796
H		5	0.8979	1.0146	2.8513
H		6	−1.3791	0.2587	2.7215
H		7	0.4223	−1.337	2.7244
	7		PH_3-SiH_2 adduct		
P		1	0	0	0
Si		2	0	0	2.4041
H		3	1.2685	0	−0.5701
H		4	−0.5233	−1.1555	−0.5701
H		5	0.3973	1.4575	2.356
H		6	−1.4914	0.2401	2.3561
H		7	−0.6238	0.9676	−0.7858
	6		PH_2-SiH_2		
P		1	0	0	0
Si		2	0	0	2.2658
H		3	1.3886	0	−0.2077
H		4	−0.1618	−1.3839	−0.1726
H		5	1.0018	−0.8838	2.8958
H		6	0.1637	1.3798	2.7666
	5		PH_2-SiH		
P		1	0	0	0
Si		2	0	0	2.2493
H		3	1.3437	0	−0.3879
H		4	−0.3329	−1.314	−0.341
H		5	1.0667	1.0618	2.316
	4		PH_2-Si		
P		1	0	0	0
Si		2	0	0	2.2491
H		3	1.348	0	−0.3757
H		4	−0.3289	−1.3069	−0.3768
	6		$PH-SiH_3$		
P		1	0	0	0
Si		2	0	0	2.267
H		3	1.4039	0	−0.119
H		4	0.6864	1.201	2.7826
H		5	−1.397	0.0007	2.7383
H		6	0.6851	−1.2017	2.7826
	5		$P-SiH_3$		
P		1	0	0	0
Si		2	0	0	2.2353
H		3	1.4672	0	2.453
H		4	−0.5961	−1.1944	2.8636
H		5	−0.5942	1.1962	2.8624
	5		$P-SiH_3$, triplet		
P		1	0	0	0
Si		2	0	0	2.2681
H		3	1.3876	0	2.7713
H		4	−0.6938	−1.2017	2.7713
H		5	−0.6938	1.2017	2.7713
	5		$PH-SiH_2$, singlet		
P		1	0	0	0
Si		2	0	0	2.0601
H		3	1.4057	0	−0.0899
H		4	1.1835	−0.0001	2.9322
H		5	−1.2498	−0.0003	2.8307
	5		$PH-SiH_2$, triplet		
P		1	0	0	0
Si		2	0	0	2.0601
H		3	1.4057	0	−0.0899
H		4	1.1835	−0.0001	2.9322
H		5	−1.2498	−0.0003	2.8307
	4		$P-SiH_2$		
P		1	0	0	0
Si		2	0	0	2.131
H		3	1.3228	0	2.7683
H		4	−1.3062	0.168	2.7775
	4		$PH-SiH$ (cis)		
P		1	0	0	0
Si		2	0	0	2.1398
H		3	1.4025	0	−0.119
H		4	−1.2879	0	2.8627
	3		$P-SiH$, singlet		
P		1	0	0	0
Si		2	0	0	1.9233
H		3	0	0	3.3869
	3		$P-SiH$, triplet		
P		1	0	0	0
Si		2	0	0	2.0826
H		3	1.2905	0	2.8256
	4		PH_2-Si		
P		1	0	0	0
Si		2	0	0	2.2491
H		3	1.348	0	−0.3757
H		4	−0.3289	−1.3069	−0.3768
	3		$PH-Si$, singlet		
P		1	0	0	0
Si		2	0	0	2.0484
H		3	1.3962	0	0.3467
	3		$PH-Si$, triplet		
P		1	0	0	0
Si		2	0	0	2.1814
H		3	1.4002	0	−0.1615
	2		$P-Si$		
P		1	0	0	0
Si		2	0	0	1.9678
	10		$SiH_3-PH-SiH_3$		
P		1	0	0	0
Si		2	0	0	2.2625
H		3	1.3909	0	−0.1944
Si		4	−0.3829	2.1787	−0.4751
H		5	0.8414	1.0631	2.8472
H		6	−1.3919	0.1952	2.71
H		7	0.4896	−1.3102	2.7272
H		8	−0.1725	2.3838	−1.9193
H		9	−1.7877	2.4708	−0.1334
H		10	0.4914	3.1027	0.2745
	9		$PH_2-SiH_2-PH_2$		
P		1	0	0	0
Si		2	0	0	2.2684
H		3	1.391	0	−0.1827
H		4	−0.1667	−1.3834	−0.1706
H		5	0.9633	−0.9595	2.8433
H		6	−1.3583	−0.3806	2.7032
P		7	0.6083	2.066	2.981
H		8	−0.5856	2.729	2.6597
H		9	0.3049	1.8743	4.3381
	8		*c*-$SiH_2-PH-SiH_2$		
P		1	0	0	0
Si		2	0	0	2.285
H		3	1.3984	0	−0.1488
Si		4	−0.1214	1.97	1.15
H		5	1.2536	−0.3862	2.9483
H		6	−1.1922	−0.5986	2.9007
H		7	1.0526	2.8517	1.0839
H		8	−1.3941	2.6904	1.0066
	10		*c*-$SiH_2-PH-SiH_2-PH$		
P		1	0	0	0
Si		2	0	0	2.2814
H		3	1.4016	0	−0.1269
Si		4	−0.1763	2.2446	0.3664
H		5	0.9281	−0.9648	2.8955
H		6	−1.3657	−0.2566	2.7748
H		7	0.6071	3.0841	−0.556
H		8	−1.5947	2.6428	0.3012
P		9	−0.6111	2.181	2.5007
H		10	−0.4656	2.7145	3.2244
	4		*c*-$Si-PH-Si$		
P		1	0	0	0
Si		2	0	0	2.1294
H		3	0.8114	0	−1.1333
Si		4	−2.0124	−0.0029	0.6959

CHART 2: NASA Polynomial Coefficients for C_p, H, and S as a Function of Temperature[9] [a]

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PH
 0.27950157E+01 0.17922738E-02-0.80989109E-06 0.17532626E-09-0.14975313E-13
 0.47486739E+05 0.60994191E+01 0.37502027E+01-0.18229677E-02 0.40506209E-05
 -0.25691441E-08 0.52682452E-12 0.47296838E+05 0.14656557E+01
PH
0.24986682E+01 0.24383019E-02-0.13056343E-05 0.33655625E-09-0.33904679E-13
 0.28616991E+05 0.88082001E+01 0.38440816E+01-0.25051985E-02 0.57320095E-05
 -0.42458632E-08 0.11108862E-11 0.28314027E+05 0.21803029E+01
PH2
 0.24764083E+01 0.52941967E-02-0.26891816E-05 0.65443120E-09-0.62245769E-13
 0.15933902E+05 0.10018891E+02 0.40314478E+01-0.15044608E-02 0.80168646E-05
-0.66282287E-08 0.17562011E-11 0.15666541E+05 0.26956889E+01
PH3
 0.17400687E+01 0.10091725E-01-0.53111977E-05 0.13274015E-08-0.12860052E-12
 0.18498737E+020.13605277E+020.31738113E+010.23255312E-020.90325372E-05
-0.98058586E-080.29938095E-11-0.15459092E+03 0.72261132E+01
PH2SIH3
 0.57746754E+01 0.16443327E-01-0.87791891E-05 0.22242549E-08-0.21847862E-12
 0.18691263E+04-0.43024180E+01 0.13793247E+01 0.32249198E-01-0.32077909E-04
 0.18606620E-07-0.47294991E-11 0.29349786E+04 0.17570614E+02
PH3SIH2
 0.55977176E+01 0.16711918E-01-0.89711059E-05 0.22868450E-08-0.22596871E-12
 0.19895800E+05-0.24024293E+01 0.30988665E+01 0.24093612E-01-0.17761936E-04
 0.74781463E-08-0.15194120E-11 0.20595284E+05 0.10466002E+02
PH2SIH2
 0.61938267E+01 0.11749686E-01-0.60301377E-05 0.14674155E-08-0.13858742E-12
 0.21298701E+05-0.48992577E+01 0.24448967E+01 0.25832340E-01-0.28051226E-04
 0.17856594E-07-0.48585304E-11 0.22193995E+05 0.13642869E+02
PH2SIH
 0.58296168E+01 0.85104188E-02-0.43359878E-05 0.10487613E-08-0.98469928E-13
 0.27547702E+05-0.37300542E+01 0.29865869E+01 0.19747821E-01-0.22699009E-04
 0.15118785E-07-0.42143495E-11 0.28199219E+05 0.10192470E+02
PH2SI
 0.48411597E+01 0.62423109E-02-0.32807976E-05 0.82488906E-09-0.80856425E-13
 0.38608081E+05 0.25162469E+01 0.33234908E+01 0.13095582E-01-0.15492257E-04
 0.10596951E-07-0.29848094E-11 0.38907656E+05 0.97212983E+01
PHSIH3
 0.58624570E+01 0.12665906E-01-0.67888673E-05 0.17241016E-08-0.16950300E-12
 0.17961190E+05-0.33634990E+01 0.22791585E+01 0.26012526E-01-0.27166442E-04
 0.16452185E-07-0.42977709E-11 0.18807840E+05 0.14354415E+02
P-SIH3
 0.54188111E+01 0.94550220E-02-0.50266430E-05 0.12616618E-08-0.12242409E-12
 0.46915647E+05-0.21005051E+01 0.22064631E+01 0.20820916E-01-0.21491471E-04
0.12671748E-07-0.32332217E-11 0.47703376E+05 0.13930870E+02
P-SIH3
 0.52694607E+01 0.96754139E-02-0.51733778E-05 0.13089297E-08-0.12825772E-12
 0.30840866E+05-0.14755917E+01 0.18431843E+01 0.21953520E-01-0.23093973E-04
 0.13747093E-07-0.35097996E-11 0.31668809E+05 0.15574220E+02
PHSIH2
 0.56714705E+01 0.89028654E-02-0.46527360E-05 0.11566613E-08-0.11176266E-12
 0.18793064E+05-0.36613194E+01 0.17240997E+01 0.25113829E-01-0.31467153E-04
PHSIH2
 0.59287190E+01 0.87356225E-02-0.46565862E-05 0.11828377E-08-0.11685561E-12
 0.32966518E+05-0.28951437E+01 0.31692030E+01 0.20035958E-01-0.23512385E-04
 0.15741808E-07-0.43743014E-11 0.33573357E+05 0.10506319E+02
P-SIH2
 0.54522761E+01 0.54722954E-02-0.28267596E-05 0.69467804E-09-0.66492143E-13
 0.37599821E+05-0.87037530E+00 0.32871783E+01 0.14426181E-01-0.17891515E-04
 0.12392106E-07-0.34987023E-11 0.38072028E+05 0.96233647E+01
PHSIH
 0.53897940E+01 0.56028674E-02-0.29416268E-05 0.73657010E-09-0.71757620E-13
 0.38080475E+05-0.62039843E+00 0.30072673E+01 0.16102234E-01-0.21222634E-04
 0.15103389E-07-0.42852629E-11 0.38558375E+05 0.10743468E+02
P-SIH
 0.48148578E+01 0.25982013E-02-0.13351930E-05 0.32927239E-09-0.31891512E-13
 0.35155630E+05 0.36784244E-01 0.40535314E+01 0.56646212E-02-0.64451574E-05
 0.43054061E-08-0.12072979E-11 0.35328263E+05 0.37530200E+01
P-SIH
 0.46821781E+01 0.30046520E-02-0.16698662E-05 0.43863072E-09-0.44449499E-13
 0.54238121E+05 0.34648458E+01 0.33503537E+01 0.86229384E-02-0.11087862E-04
 0.76351014E-08-0.21146756E-11 0.54515251E+05 0.98743920E+01
PH2SI
 0.48411597E+01 0.62423109E-02-0.32807976E-05 0.82488906E-09-0.80856425E-13
 0.38608081E+05 0.25162469E+01 0.33234908E+01 0.13095582E-01-0.15492257E-04
 0.10596951E-07-0.29848094E-11 0.38907656E+05 0.97212983E+01
PHSI
 0.48883561E+01 0.26121572E-02-0.13962448E-05 0.35572372E-09-0.35224768E-13
 0.33741612E+05 0.25271264E+01 0.45487208E+01 0.40434582E-02-0.40943290E-05
 0.27333436E-08-0.81025780E-12 0.33825695E+05 0.41923357E+01
PHSI
 0.45988368E+01 0.29132934E-02-0.15251227E-05 0.37916173E-09-0.36483084E-13
 0.59725288E+05 0.42668944E+01 0.35307246E+01 0.77901189E-02-0.10114821E-04
 0.71154457E-08-0.19959498E-11 0.59926195E+05 0.93077626E+01
P-SI
 0.42317086E+01 0.30871502E-03-0.13027386E-06 0.20906734E-10-0.68700095E-15
 0.45424554E+05 0.32997315E+01 0.28705045E+01 0.56926977E-02-0.83084440E-05
 0.56323608E-08-0.14585357E-11 0.45708594E+05 0.99017388E+01
SIH3PHSIH3
 0.95200010E+01 0.23249421E-01-0.12530571E-04 0.31989525E-08-0.31620432E-12
 0.28893987E+04-0.20446285E+02 0.11566774E+01 0.54324341E-01-0.59337766E-04
 0.36391642E-07-0.94425295E-11 0.48457735E+04 0.20872532E+02
PH2SIH2PH2
 0.92038017E+01 0.19197172E-01-0.10025384E-04 0.24870209E-08-0.23954635E-12
 0.52997109E+03-0.18305856E+02 0.22497758E+01 0.46056646E-01-0.52103502E-04
 0.33297604E-07-0.89040900E-11 0.21114996E+04 0.15807294E+02
C_SI2H4PH2
 0.99498965E+01 0.14364696E-01-0.73150810E-05 0.17644415E-08-0.16510427E-12
 0.16486002E+05-0.24860988E+02 0.79066904E+00 0.51554351E-01-0.67932970E-04
 0.47298881E-07-0.13147883E-10 0.18470583E+05 0.19596793E+02
C_SI2H4P2H
 0.12389566E+02 0.19206459E-01-0.10137223E-04 0.25399320E-08-0.24702705E-12
 0.49829009E+04-0.35685598E+02 0.19756769E+00 0.68795973E-01-0.90253402E-04
 0.61896621E-07-0.16925972E-10 0.75836112E+04 0.23387917E+02
CY_SIPHSI
 0.75934391E+01 0.27031430E-02-0.13059680E-05 0.30116059E-09-0.27174506E-13
 0.48490043E+05-0.91110117E+01 0.42557954E+01 0.17551523E-01-0.26921673E-04
PH2SIH2SIH
 0.98899588E+01 0.22452839E-01-0.11931503E-04 0.30053522E-08-0.29336058E-12
 0.52867670E+04-0.22058300E+02 0.19160508E+01 0.52126200E-01-0.57028869E-04
 0.35393904E-07-0.93146984E-11 0.71646510E+04 0.17359022E+02
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[a] These fits can be used with the CHEMKIN package of software.[11]

($H_3Si-SiH_3$) despite the fact that the Si−P interaction should have an ionic contribution. The analogous isovalent Si−N bond gives a BDE of 439 kJ/mol or about 1.5 times the BDE of the Si−P bond. The computed Si−P single, double, and triple bond distances are 2.30, 2.06, and 1.92 Å, respectively. The corresponding Mulliken charge analysis indicates that the Si−P single bond is about as ionic as a Si−H bond. However, as the multiple bond character increases, the Si center becomes progressively less positively charged and the P center less negatively charged such that the net effect is to make the bond less ionic. Bond dissociation energies for Si−P multiple bonds indicate a low multiple bond order as expected for silicon. The BDE of $^1HP{=}SiH_2$ to form the most stable products (^3HP + $^1SiH_2$) only requires 344 kJ/mol and would necessitate curve crossing, while the adiabatic surface leading to singlet states requires 502 kJ/mol. Singlet−triplet splitting in $HP{=}SiH_2$ was only 122 kJ/mol, implying a very weak π bond contribution. The triple bond in P−SiH is also relatively weak at 396 kJ/mol and essentially degenerate in energy with its doubly bonded isomer HP−Si, which has a bond length slightly longer (2.04 vs 1.92 Å) than that of P−SiH. This degeneracy in energy is surprising, since from a valence bond view one expects the P−SiH isomer to be more stable than HP−Si. The P−SiH molecule is linear, indicating triple bond character, while the HP−Si isomer has a bond angle of only 750°, which would not indicate a strong bridge bond character as is known for HSi−SiH, where the Si−Si−H bond angle is about 49°. On the other hand, charge separation between phosphorus and silicon is greater in HP−Si owing to the higher electronegativity of H relative to Si. This increased ionicity in HP−Si combined with the fact that natural bond order analysis indicates that the p orbitals in phosphorus are less populated in the triply bonded case (presumably due to the electron-withdrawing nature of H when bonded to silicon) is sufficient to make the triple bond not as favored as one might expect. In terms of bond order (based on the most stable products), the double and triple bonds have orders of 1.15 and 1.34, respectively. For radicals the Si−H bond is actually weaker than the corresponding P−H bond, opposite to that seen for the closed-shell species. The cyclic structures presented are possible species that might form under CVD conditions as precursors to particle formation/contamination.

Conclusions

Ab initio computation of the electronic structure of molecules in the Si−P−H system, combined with a bond additivity correction procedure has been used to obtain a set of self-consistent thermochemical data. The Si−P single bond was found to be weaker than the Si−Si bond, and multiple bonds indicated weak π bond character. The results provide the basis for the construction of detailed chemical kinetic models for the interaction of silicon–phosphorus species in the gas phase during thermal deposition of doped silicon from silane and phosphine.

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