

An accurate description of the ground and excited states of SiH

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The astrophysical importance of the SiH radical has motivated significant experimental and theoretical work. However, only the $X^2\Pi$ and $A^2\Delta$ states of SiH have been extensively investigated experimentally, while the study of higher excited states is rather limited. From a theoretical point of view, most of the studies have been focused on spectroscopic and thermochemical quantities of the ground state. The lack of accurate spectroscopic parameters ($r_e, D_e, \omega_e, \omega_e x_e, \alpha_e, \bar{D}_e, T_e$) pertaining to higher excited states was the driving force of the present work, in line with our previous study of the isovalent CH molecule [A. Kalamos, A. Mavridis, and A. Metropoulos, *J. Chem. Phys.* **111**, 9536 (1999)]. Using the multireference configuration interaction approach coupled with very large correlation-consistent basis sets, we have constructed potential energy curves for 18 molecular states correlating to $\text{Si}(^3P, ^1D, ^1S, ^5S, ^3P, ^1P) + \text{H}(^2S)$. At the same level, the potential energy curve of the ground SiH^+ state ($X^1\Sigma^+$) has also been constructed. We report total energies, dissociation energies, and the usual spectroscopic constants for $^{28}\text{Si}-^{1,2}\text{H}$ and for all states studied. Most of our results are in excellent agreement with existing experimental values. In particular, we believe that our dissociation energy for the X state, $D_e = 73.28$ kcal/mol, is the most reliable reported so far in the literature. © 2002 American Institute of Physics.

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I. INTRODUCTION

The SiH radical was first observed by optical spectroscopy in the 1930's.¹⁻⁴ It is the simplest of the four silicon hydrides and its role in the chemistry of these hydrides as well as in the process of chemical vapor deposition (CVD) of hydrogenated amorphous silicon thin films is well documented.⁵⁻³⁴ References 31 and 33 list many papers, up to 1991 and 1995, respectively, pertaining to various aspects of silicon hydride chemistry. SiH is also of astrophysical importance because of its presence in stellar atmospheres and its suspected, but not yet proven, presence in interstellar clouds.³⁵⁻⁵¹

SiH has been studied by optical, infrared, and far-infrared spectroscopy, by radio frequency transitions, and by mass spectroscopy. It is usually produced from the silane (SiH_4) molecule by flash photolysis, laser-induced photolysis, rf discharge, or by reaction with fluorine atoms. Because of its importance, the assignments of spectral lines and the determination of accurate spectroscopic and thermochemical quantities comprise a large body of experimental⁵²⁻⁸⁴ and theoretical⁸⁵⁻¹³¹ work on SiH and SiD.

Only the $X^2\Pi$ and the $A^2\Delta$ states of SiH and SiD have been extensively investigated experimentally. Work on these two states includes the determination of Λ -doubling transition frequencies for $X^2\Pi$,^{38,63,65,76} radiative lifetimes and oscillator strengths of the $A^2\Delta-X^2\Pi$ system,^{43,45,47,61,64,74}

various molecular constants,^{55,56,67,72,78,79,84} transition moments,⁶⁶ ionization potentials,^{55,80,81} and dissociation energies and enthalpies of formation.^{55,59,64,68,80,81,83} To our knowledge, only a limited number of experimental papers deal with the higher excited states, but the extracted parameters useful to the present theoretical work are very few, limited mostly to term values. These papers include the work of Verma,⁵⁵ Herzberg *et al.*,⁶⁰ Bollmark *et al.*,⁶² and Johnson and Hudgens.⁸² The latter authors have located a state at $46\,700 \pm 10$ cm^{-1} and identified it as either a $^2\Pi$ or a $^2\Sigma^+$ state. Based on our present work (*vide infra*) it is the $F^2\Pi$ state. It is noteworthy that there is no experimental value for the dipole moment of SiH and that the values of its dissociation energy vary significantly. A list of papers on the SiH and SiD spectroscopy up to 1998 and a brief summary of each work is given by Ram *et al.*⁸⁴

The first theoretical treatment of SiH appeared in the literature in 1966 and reported its energy of formation and the excitation energies of the ground- and the low-lying excited states using a semiempirical method.⁸⁶ *Ab initio* calculations soon followed, first at the SCF level and then at levels of accuracy beyond SCF. Table I shows results of such calculations relevant to the present work along with the corresponding latest experimental values. Often, work on SiH was part of a larger investigation on silicon hydrides. Oikawa *et al.*¹⁰⁹ investigated the mechanism of formation of SiH during plasma CVD. Allen and Schaefer¹¹¹ did an extensive investigation of the ground-state properties of the silicon hydrides and gave extensive references to related experimental

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TABLE I. Previous theoretical estimates of total energies E (hartree), dissociation energies D_e (kcal/mol), bond distances r_e (Å), harmonic frequencies ω_e (cm⁻¹), anharmonic corrections $\omega_e x_e$ (cm⁻¹), rotational-vibrational coupling constants α_e (cm⁻¹), centrifugal distortions \bar{D}_e (cm⁻¹), dipole moments μ (D), and energy separations T_e (kcal/mol) along with recent experimental values of the SiH molecule and in different states.

$-E$	D_e	r_e	ω_e	$\omega_e x_e$	α_e	$\bar{D}_e(10^4)$	μ	T_e	Ref./year
$(X^2\Pi)$									
	76.33								86/1966 ^a
289.436 2	51.43	1.521							87/1967 ^b
289.323 4		1.561	2200						90/1971 ^c
289.540 770	71.26	1.526	2034.7	36.0	0.216		0.141		96/1975 ^d
289.505 20	65.72	1.552	1965.9	37.2	0.215 1	3.9			104/1982 ^e
289.518 0	70.11	1.544	2015	39.0	0.208		0.124		105a/1983 ^f
289.513 87	72.60	1.515 21	1949						107/1985 ^g
	65.93		2181.24						108/1985 ^h
		1.520	2044				0.160		110/1986 ⁱ
		1.523	2022				0.118		110/1986 ^j
289.528 786		1.521 42	2062	38.5	0.217 55		0.077		111/1986 ^k
289.541 256	72.09	1.520	2057.8	37.8	0.218		0.123		113/1987 ^l
289.533 59		1.541	1996.4	28.94			0.080		114/1987 ^m
		1.520 1					0.1218		122/1992 ⁿ
289.554 544	73.20	1.521 42							123/1992 ^o
289.546 30	70.61	1.525 9							124/1993 ^p
289.529 03		1.510 8							125a/1993 ^q
289.552 25	72.90	1.523 6	2036.2	35.8	0.214 7				126/1993 ^r
		1.533	2050						127/1994 ^s
289.524 369		1.520 1					0.091		128/1996 ^t
289.556 8	73.61	1.521							131/1999 ^u
		1.503					0.140		132/1999 ^v
	$D_0^o \leq 70.57$	1.520 1 ₀	2041.80	35.51	0.219 0	3.97			67/1979 ^w
	72.35–73.46	1.519 66(7)	2042.5229(8)	36.0552(5)	0.218 14(2)	4.0556(45)			78/1986 ^x
$(a^4\Sigma^-)$									
								61.57	86/1966 ^a
289.285 7		1.522	2255					23.98	90/1971 ^c
289.447 68	29.70	1.522	1982.5	60.6	0.285 8	4.3		36.09	104/1982 ^e
	33.90	1.511	2030	65.0	0.313			36.44	105a/1983 ^f
		1.520 1					0.1383		122/1992 ⁿ
289.472 80		1.510 8						35.28	125a/1993 ^q
		1.501	2086					38.97	127/1994 ^s
								14.30	66/1979 ^y
$(A^2\Delta)$									
289.209 6		1.554	1955					71.49	90/1971 ^c
	20.06	1.546	1797	91.0	0.420		0.118	71.26	105a/1983 ^f
289.426 924		1.517	1884.4	68.4	0.242			71.72	113/1987 ^l
		1.520 1					0.1451		122/1992 ⁿ
289.415 11		1.510 8						71.49	125a/1993 ^q
		1.523 4 ₇	1858.90	99.17 ₅	0.344 5	5.24		69.48	67/1979 ^w
	20.58–21.69	1.519 781 6(21)			0.215 119(15)			69.35	84/1998 ^z
$(B^2\Sigma^-)$									
289.201 1								70.71	86/1966 ^a
								76.75	90/1971 ^c
								75.64	105a/1983 ^f
289.408 49		1.510 8						75.64	125a/1993 ^q
								73.31–76.24	53/1960 ^{aa}
$(C^2\Sigma^+)$									
289.178 0		1.585	1710					100.78	86/1966 ^a
		1.553	1550±50					91.09	90/1971 ^c
		1.520 1					0.171	89.71	105a/1983 ^f
		1.510 8					0.114 1		122/1992 ⁿ
289.383 14		1.510 8						91.55	125a/1993 ^q
1st min		3.8 ₅						91.01	67/1979 ^w
2nd min		1.61 ₈						91.04	67/1979 ^w
$(D^2\Sigma^+)$								104.70	105a/1983 ^f
$(E^2\Sigma^+)$								114.61	105a/1983 ^f
$(c^4\Sigma^-)$									
		1.970	1245	22.0	0.094			150.13	105a/1983 ^f
								131.5	66/1979 ^y
$(F^2\Pi)$									
289.048 9		1.571	1944					172.27	90/1971 ^c
								132.14	105a/1983 ^f
								133.52	82/1989 ^{bb}

TABLE I. (Continued.)

$-E$	D_e	r_e	ω_e	$\omega_e x_e$	α_e	$\bar{D}_e(10^4)$	μ	T_e	Ref./year
$(G^2\Sigma^+)$								130.06	105a/1983 ^f
$(H^2\Delta)$								139.52	105a/1983 ^f
		1.48 ₁						141.59	67/1979 ^w
$(I^2\Pi)$								140.44	105a/1983 ^f
$(J^2\Pi)$								$\sim 148.74^{\text{cc}}$	105a/1983 ^f
$(^2\Sigma^+)$								149.44	105a/1983 ^f
		1.517 ₂				3.92		152.66	67/1979 ^w
$(e^4\Pi)$								163.73	105a/1983 ^f

^aSemiempirical calculations at $r = 1.48 \text{ \AA}$.

^bSCF with a large basis set of STFs ($6s5p1d/3s1p$), and extensive optimization of the orbital exponents; the total energy reported has been calculated at the experimental r_e . An "experimental" energy value of -290.549 hartree is also reported.

^cSCF/CISD [$6s3p/1s$] basis; reported energies and T_e 's at $r = 2.87$ bohr.

^dCEPA [$13s10p2d1f/6s2p1d_{\sigma}$] basis set; the reported r_e value is estimated to be reduced by 0.004 \AA when core–valence correlation effects are taken into account.

^eMCSCF+1+2, [$4s3p1d/3s1p$] basis set.

^fFull-CI estimate of the MRD-CI results using two different basis sets, [$7s5p4d1f/3s1p1d$], and [$7s5p2d1f/3s1p1d$] for the description of Rydberg and valence states, respectively. T_e 's are vertical excitations from the ground state at the equilibrium geometry of the $a^4\Sigma^-$ state; dipole moments are also calculated at this internuclear separation.

^gMP4/6-31+G(2df,p)//HF/6-31G(d) results; the r_e was not optimized to five significant figures but is given to this precision for reasons of reproducibility.

^hMP4/6-31G**//HF/6-31G* results, coupled with empirical correction factors to account for systematic deficiencies due to basis set truncation.

ⁱSCF+1+2 (= CISD) using large STO basis sets ($8s6p3d2f/4s3p2d$).

^jCoupled pair functional (CPF) calculations, basis set the same as in i.

^kCISD/[$6s5p2d/4s2p$].

^lCASSCF+contracted CI/[$8s6p4d2f/7s4p1d$].

^mCI4(SDQ)/[$6s5p2d/4s2p$].

ⁿValence–shell Hamiltonian method based on quasidegenerate MBPT; [$7s5p2d/3s1p1d$] basis set. All calculations at the r_e of the X -state.

^oCCSD(T)/[$6s5p3d2f1g/4s3p2d1f$]/CISD/[$6s5p2d/4s2p$].

^pG1/MP2/6-31G(d).

^qMRCI/TZP; reported T_e 's are vertical excitation energies calculated at $r = 2.855$ bohr.

^rCASSCF+1+2/cc-pV5Z.

^sMRCI+Q//MCSF results using pseudopotential on Si.

^tCISDT⁺/POL1; [$7s5p2d/3s2p$] basis at the experimental $r_e = 1.5201 \text{ \AA}$ from Ref. 67.

^uUGA-CCSD(T)/aug-cc-pV6Z results for the total energy and r_e , while the D_e value takes into account the CBS limit. Corrections for core–valence correlation effects, scalar relativistic, and spin–orbit effects give a D_e value of 73.3 kcal/mol.

^vMulti-reference CC approach/[$7s5p2d/3s2p$].

^wExperimental results.

^xExperimental results from analysis of the infrared emission spectrum of the ^{28}SiH radical; D_e value from Ref. 113.

^yShock-tube determination of absorption cross sections.

^zFourier transform emission spectroscopy on the $A^2\Delta \leftarrow X^2\Pi$ transitions of SiH; $T_e (= 24\,257.127(1) \text{ cm}^{-1})$ from Ref. 65.

^{aa}Experimental value from absorption spectroscopy.

^{bb}Experimental value from resonance-enhanced multiphoton ionization spectroscopy.

^{cc}Approximately obtained from Fig. 4 of Ref. 105a.

and theoretical work. Kalcher¹¹⁴ did extensive comparisons between *ab initio* and pseudopotential calculations at various levels of accuracy for the neutral and anionic species of SiH_n ($n = 1, 2, 3$), trying to judge the validity of pseudopotentials for calculations on larger silicon hydride clusters. Greeff and Lester¹²⁹ have done a Monte Carlo (MC) calculation on SiH as a means of estimating the advisability of MC calculations on larger silicon hydride molecules where huge basis sets would be required for accuracy comparable to MC. Other papers deal exclusively with the ground- and the low-lying excited states of SiH. Meyer and Rosmus^{96,98} used large basis sets with the pseudonatural orbitals-configuration interaction (PNO-CI) and coupled electron pair approximation (CEPA) methods to calculate energies, ionization potentials, and spectroscopic constants of the ground state. Richards and co-workers^{97,102,103} calculated the Λ -doubling in the lowest rotational level of the $X^2\Pi$. Mavridis and Harrison¹⁰⁴ have done *ab initio* calculations on the $X^2\Pi$ and $a^4\Sigma^-$ states. Petterson and Langhoff¹¹⁰ calculated dipole moments of the

TABLE II. Total energies E (hartree) of the $^3P(3s^23p^2)$, $^1D(3s^23p^2)$, $^1S(3s^23p^2)$, $^3S(3s^13p^3)$, $^3P(3s^23p^14s^1)$, $^1P(3s^23p^14s^1)$, $^3D(3s^13p^3)$, and $^3D(3s^23p^14p^1)$ Si states and corresponding energy gaps ΔE (eV) with respect to the ground state at the MRCI level of theory. Experimental values in parentheses.

State	$-E^b$	ΔE^c
$^3P(3s^23p^2)^a$	288.940 143	0.0(0.0)
$^1D(3s^23p^2)$	288.911 836	0.770(0.762)
$^1S(3s^23p^2)$	288.870 350	1.899(1.890)
$^5S(3s^13p^3)$	288.795 048	3.948(4.113)
$^3P(3s^23p^14s^1)$	288.757 063	4.982(4.923)
$^1P(3s^23p^14s^1)$	288.751 215	5.141(5.064)
$^3D(3s^13p^3)$	288.735 503	5.569(5.598)
$^3D(3s^23p^14p^1)$	288.720 387	5.980(5.953)

^aThe SCF energy of the 3P state is $-288.854\,346h$ as compared to the numerical HF value of $-288.854\,3624h$, Ref. 138.

^bThe active space of the CASSCF wave functions includes 13 orbitals related to the $3s$, $3p$, $3d$, $4s$, and $4p$ atomic orbitals. Spherical symmetry was induced by performing state-average CASSCF calculations.

^cExperimental values, averaged over M_J , are taken from the Atomic Spectra Database of NIST, Ref. 140. 1 hartree = 27.2114 eV.

TABLE III. Total energies E (hartree), dissociation energies D_e (kcal/mol), bond distances r_e (Å), dipole moments μ (D), and energy separations T_e (kcal/mol) of all bound calculated states of the SiH system. Existing experimental results are also included.

State	Method ^a	$-E$	D_e	r_e	μ	T_e
$X^2\Pi$	SCF	289.437 788	52.25	1.512 7	0.269	0.0
	CASSCF	289.533 299	65.63	1.519 6	0.150	0.0
	MRCI	289.557 373	73.55	1.522 3	0.124	0.0
	MRCI+Q	289.557 7	73.73	1.522 7		0.0
	CCSD(T)	289.556 482	73.57	1.522 1		0.0
	Expt.			72.35–73.46 ^b	1.519 66 ^c	
$a^4\Sigma^-$	SCF	289.406 304	32.49	1.465 3	-0.144	19.76
	CASSCF	289.476 683	29.69	1.500 6	-0.022	35.53
	MRCI	289.495 594	34.73	1.497 4	-0.027	38.77
	MRCI+Q	289.495 7	34.79	1.497 4		38.90
	CCSD(T)	289.494 509	34.68	1.495 3		38.89
	Expt. ^d					
$A^2\Delta$	CASSCF	289.418 798	15.86	1.535 1	0.110	71.85
	MRCI	289.447 424	22.28	1.524 0	0.098	68.99
	MRCI+Q	289.447 9	22.45	1.523 7		68.91
	Expt.		20.58–21.69 ^e	1.5197 816 ₂₁ ^f		69.35 ^g
$B^2\Sigma^-$	MRCI	289.440 547	0.19	3.440	0.093	73.31
	MRCI+Q	289.440 6	0.20	3.426		73.49
	Expt. ^b					73.31–76.24
	Local minimum					
$C^2\Sigma^+$	MRCI	289.439 778		1.7154	0.621	
	MRCI+Q	289.440 0		1.7128		
	MRCI	289.416 551	2.89	1.5338	0.178	88.37
	MRCI+Q	289.417 1	3.17	1.5328		88.26
	Expt. ⁱ					
$D^2\Sigma^+$	Local minimum					
	MRCI	289.414 926		2.40	-1.245	
	MRCI+Q	289.415 3		2.38		
	Expt. ⁱ					
$E^2\Sigma^+$	MRCI	289.402 681	20.29	1.7923	-0.279	97.07
	MRCI+Q	289.403 6	20.94	1.7943		96.73
$F^2\Pi$	MRCI	289.374 571	73.67	1.5374	-0.975	114.71
	MRCI+Q	289.375 7	74.30	1.5346		114.22
	Local minimum					
	MRCI	289.303 480		3.1824	-9.552	
$c^4\Sigma^-$	MRCI+Q	289.304 9		3.1949		
	CASSCF	289.325 673	22.60	1.9802	-0.031	130.29
	MRCI	289.343 814	30.60	1.9453	0.049	134.01
	MRCI+Q	289.344 1	30.74	1.9428		134.08
	Expt. ^d					131.5
$G^2\Sigma^+$	MRCI	~289.341 2		~1.43	-0.363	~135
	MRCI+Q	~289.342		~1.43		
	Expt. ^j					133.52
$H^2\Delta$	MRCI	289.279 506	17.66	2.5387	-2.009	
	MRCI+Q	289.280 9	18.38	2.5340		
$I^2\Pi$	MRCI	~289.322 8	~54.8	~1.56	0.331	~147.2
	MRCI+Q	~289.382	~81.6	~1.56		~110
	Expt. ^k					141.59
	MRCI	289.310 652	33.63	3.175	-9.543	154.82
$e^4\Pi$	MRCI+Q	289.311 6	34.15	3.17		154.43
	CASSCF	289.277 442	19.67	1.5157	-2.301	160.55
	MRCI	289.300 964	27.53	1.5081	-2.316	160.90
$f^4\Delta$	MRCI+Q	289.301 3	27.68	1.5082		160.9
	MRCI	289.263 953	17.86	1.5497	-2.149	181.12
	MRCI+Q	289.264 6	7.86	1.5545		183.9
$J^2\Pi$	MRCI	~289.257 7	~4.06	~2.33		~188
	MRCI	289.259 725	1.60	1.5483	-1.847	186.78
$g^4\Sigma^+$	MRCI	289.260 2	1.78	1.551		186.7
	MRCI+Q					

^a+Q, refers to the multireference Davidson correction.^bReference 113.^cReference 84.^dReference 66.^eReference 113; see also the text.^fReference 84.^gReference 65.^hReference 53.ⁱSee the text.^jReference 82.^kReference 67.

TABLE IV. Harmonic frequencies ω_e , anharmonicities $\omega_e x_e$, rotational vibrational couplings α_e , and centrifugal distortions \bar{D}_e in cm^{-1} of the $^{28}\text{Si}-^{1,2}\text{H}$ system in different states at the MRCI level.

State	ω_e	$\omega_e x_e$	α_e	$\bar{D}_e \times 10^4$
		$^{28}\text{Si}-^1\text{H}$		
$X^2\Pi$	2043.15	35.09	0.213	4.01
Expt. ^a	2042.52	36.06	0.218	4.06
$a^4\Sigma^-$	2059.16	61.07	0.287	4.44
$A^2\Delta$	1853.15	78.39	0.375	5.39
Expt. ^b	1858.90	99.17	0.344	5.24
$B^2\Sigma^-$	81.74			
$C^2\Sigma^+$	285.12			
$D^2\Sigma^+$	2147.31	402.51		
$E^2\Sigma^+$	647.85	20.40	0.021	0.506
$E^2\Sigma^+$	2410.86	70.76	0.257	2.59
$c^4\Sigma^-$	1253.63	15.60	0.042	2.47
$I^2\Pi$	599.33	-0.815	-0.007	0.48
$e^4\Pi$	1925.53	61.61	0.349	4.89
$f^4\Delta$	1661.86	65.66	0.319	4.37
$g^4\Sigma^+$	1639.63	32.94	0.217	3.92
		$^{28}\text{Si}-^2\text{H}$		
$X^2\Pi$	1470.75	18.54	0.080	1.07
Expt. ^b	1469.32	18.23	0.078	1.054
$a^4\Sigma^-$	1480.17	30.65	0.107	1.17
$A^2\Delta$	1333.66	40.79	0.137	1.33
Expt. ^b	1328.08	48.11	0.132	1.379
$B^2\Sigma^-$	60.59			
$C^2\Sigma^+$	229.71			
$D^2\Sigma^+$	1570.38	253.34		
$E^2\Sigma^+$	456.33	3.18	0.011	0.125
$E^2\Sigma^+$	1725.99	27.66	0.101	0.699
$c^4\Sigma^-$	902.85	9.09	0.015	0.66
$I^2\Pi$	435.33	2.15	0.002	0.14
$e^4\Pi$	1384.93	31.79	0.123	1.29
$f^4\Delta$	1210.50	44.81	0.154	1.42
$g^4\Sigma^+$	1219.23	45.62	0.153	1.39

^aReference 78.

^bReference 67.

^c“g” and “l” refer to global and local minima; see the text.

$X^2\Pi$ state using a large Slater-type orbitals (STO) basis set with a singlereference CISD. Larsson¹¹³ used a complete active space self-consistent field (CASSCF)-contracted CI method and calculated the potential curves of the $X^2\Pi$ and $A^2\Delta$ states, transition moments, and dipole moments as functions of internuclear separation, as well as useful spectroscopic parameters. Winter and Millié¹²⁵ explained in terms of hybridization the differences in the $X^2\Pi-a^4\Sigma^-$ gaps between the states of SiH and CH. Calculations on higher excited states of SiH were first done by Wirsam,⁹⁰ who studied six states by a low-accuracy calculation employing a limited CI and a double-zeta basis but without polarization functions. Lewerenz *et al.*,¹⁰⁵ were the first to do extensive calculations on SiH at an acceptable accuracy including many excited states. They used DZP-type basis sets with the multireference double configuration interaction (MRDCI) package and a selection threshold resulting in about 10 000 spin-adapted functions. They computed the potential energy curves for all valence- and many Rydberg states, as well as dipole moments, electronic transition moments, spin-orbit coupling parameters, and other spectroscopic and thermochemical properties. They also did a charge distribution analysis. Other workers have computed, at various degrees of

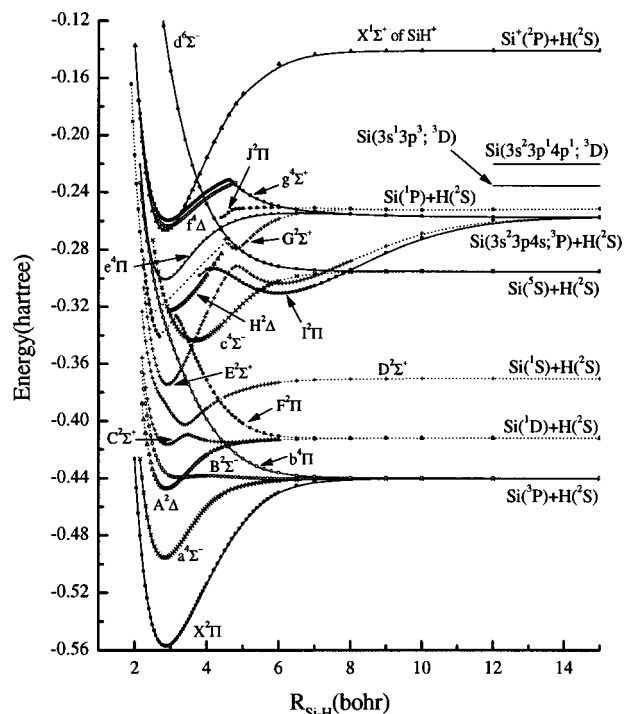


FIG. 1. Potential energy curves of all calculated states of SiH and the $X^1\Sigma^+$ state of SiH^+ at the MRCI level of theory. All energies have been shifted by +289.00 hartree.

accuracy, values for the ionization energy,^{87,90,98,115,123} the electron affinity,^{88,105,114,124} the transition probabilities and f -factors ($A^2\Delta \leftarrow X^2\Pi$),^{92,100,113} the Λ -doubling,^{97,102,103} the spin-orbit constant (for $X^2\Pi$),^{102,119} and the enthalpy of formation.^{107,108,116-118,120,121,123,124} Notice that not all states have been identified in the literature and there is a confusion regarding their labeling.

The aim of the present work is to construct with the highest accuracy presently possible the potential energy curves (PEC) for all molecular states arising from the lowest six states of Si plus the ground state of H. In particular, we have generated curves for all states emanating from the 2S of H and the 3P , 1D , 1S , 5S , $^3P(3s^2 3p^1 4s^1)$, $^1P(3s^2 3p^1 4s^1)$ states of the Si atom. Two more states, a $^2\Delta$ and a $^4\Delta$, originating from the Si $^3D(3s^1 3p^3)$ have also been computed. Overall, 18 PECs have been constructed spanning an energy range of about 8 eV, at the same accuracy, we also report the potential energy curve of the SiH^+ ground state, $X^1\Sigma^+$. For all states studied we report absolute and binding energies, equilibrium distances, dipole moments, and usual spectroscopic parameters.

II. METHODS AND COMPUTATIONAL DETAILS

The one electron correlation-consistent basis set of Dunning and co-workers¹³² was used throughout the present work. In particular, for the Si atom the aug-cc-pV6Z basis set was employed, while for the H atom the plain cc-pV5Z. The final one electron generally contracted orbital space, $[9s8p6d5f4g3h2i/s;5s4p3d2f1g/H]$, contains 248 spherical Gaussian functions.

Our goal to construct accurate potential energy curves for all states examined dictated a multireference approach.

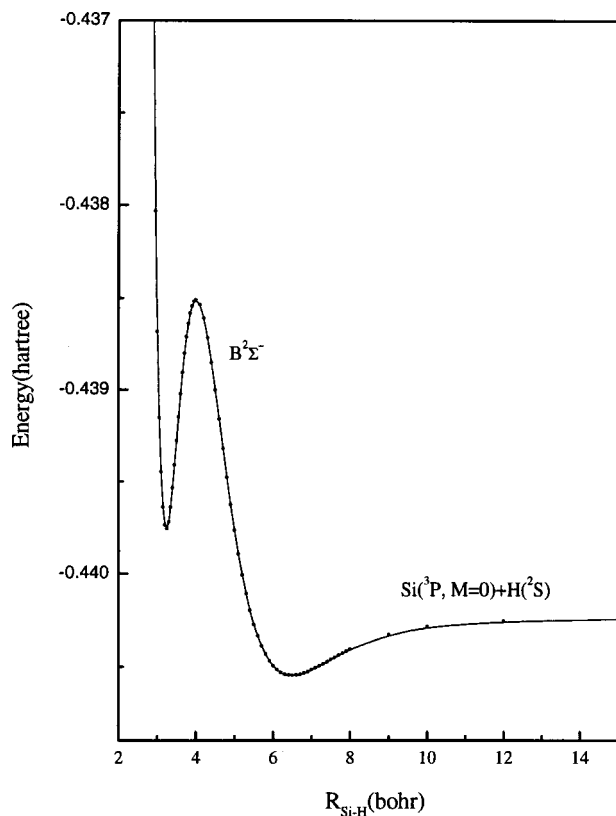


FIG. 2. Potential energy curve of the $B^2\Sigma^-$ state of SiH at the MRCI level of theory.

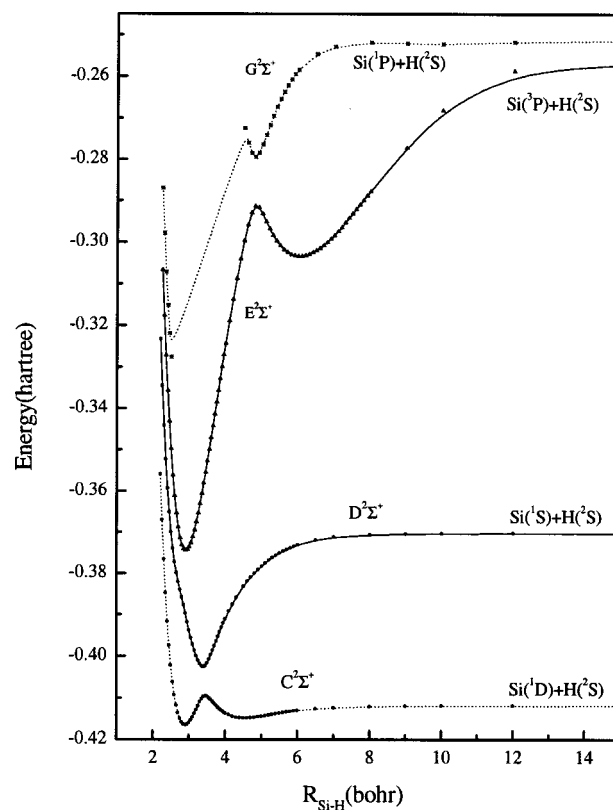


FIG. 3. Potential energy curves of the C -, D -, E -, and $G^2\Sigma^+$ states of SiH at the MRCI level of theory.

Our zero-order function, namely a complete active space SCF (=CASSCF), correlates at infinity to $(3s+3p_{\sigma,\pi}+3d_{\sigma,\pi,\delta}+4s+4p_{\sigma,\pi})_{\text{Si}}+(1s)_{\text{H}}=14$ atomic functions, providing a common orbital space for both valence- and Rydberg molecular states. By distributing the five “valence” (active) electrons among the 14 orbitals of the active space, configuration functions (CF) of $|\Lambda|=0^\pm, 1$, and 2 symmetry are generated. Additional valence correlation was obtained by single and double excitations out of the CASSCF space (CASSCF+1+2=MRCI), using at the same time the internal contraction (ic) scheme as implemented in the MOLPRO package.¹³³ For the $X^2\Pi$ and the first excited $a^4\Sigma^-$ states the coupled-cluster CCSD(T) method was also used for comparison purposes.

For excited states of $^2\Sigma^+$ and $^2\Pi$ symmetry and for purely technical reasons, the state average¹³⁴ methodology was followed. The large size of the one-electron basis set precludes significant basis-set superposition errors (BSSE). Indeed, the BSSE error of the ground SiH $X^2\Pi$ state, calculated by the usual counterpoise technique,¹³⁵ does not exceed 10 cm^{-1} ($=0.03\text{ kcal/mol}$). Also, size nonextensivity errors are practically negligible due to the small number of active electrons.

Spectroscopic constants for the isotopomers $^{28}\text{Si}-^{1,2}\text{H}$ were extracted by obtaining rovibrational energy levels through a numerical rovibrational solution of the nuclear Schrödinger equation, and then by a least-squares fit to the expansion $E(v,J)=\sum_{k,l}Y_{kl}(v+\frac{1}{2})^k[J(J+1)]^l$, where Y_{kl} represent the unknown spectroscopic constants.¹³⁶

III. ATOMIC STATES

Table II lists the MRCI absolute and relative (to 3P) energies of the Si atom for all states involved in the formation of SiH either explicitly or implicitly. With the exception of the 5S state, the agreement between the experimental and theoretical energy levels is excellent. The theoretical level of the 5S state is lower than the experimental one by 0.165 eV ($=1331\text{ cm}^{-1}$). This is attributed to the spin difference between the 3P and 5S states, which produces unbalanced correlation effects. It is noteworthy that the Si 5S state is not listed in the 1971 Moore tables.¹³⁷

IV. RESULTS AND DISCUSSION

Total energies (E), binding energies (D_e), equilibrium bond distances (r_e), dipole moments (μ), and energy separations (T_e) with respect to the ground SiH state are presented in Table III at different levels of theory. Table IV lists spectroscopic constants ($\omega_e, \omega_e x_e, \alpha_e, \bar{D}_e$) of the isotopomers $^{28}\text{Si}-^{1,2}\text{H}$ for all bound states. Potential energy curves for all computed states of SiH and the ground state of SiH^+ are shown in Fig. 1.

In what follows we analyze the important characteristics of every state, contrasting them at the same time with the corresponding states of the CH molecule,¹³⁹ isovalent to SiH.

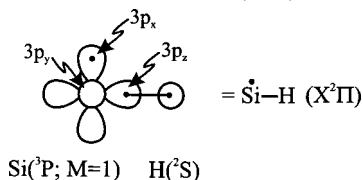
TABLE V. D_e (kcal/mol), r_e (Å), and T_e (kcal/mol) values of SiH contrasted to the corresponding values of the CH system at the MRCI level of theory.

CH ^a				SiH			
State	D_e	r_e	T_e	State	D_e	r_e	T_e
$X^2\Pi$	83.37	1.1204	0.0	$X^2\Pi$	73.55	1.5223	0.0
$a^4\Sigma^-$	66.03	1.0892	17.22	$a^4\Sigma^-$	34.73	1.4974	38.77
$A^2\Delta$	45.54	1.1056	66.89	$A^2\Delta$	22.28	1.5240	68.99
$B^2\Sigma^-$	8.59	1.1468	74.74	$B^2\Sigma^-$	0.19	3.440	73.31
$C^2\Sigma^+$	20.98	1.1164	91.85	$C^2\Sigma^+$	2.89	1.5338	88.37
$D^2\Sigma^+$	9.35	1.6635	136.11	$D^2\Sigma^+$	20.29	1.7923	97.07
$c^4\Sigma^-$	22.31	1.7866	157.38	$c^4\Sigma^-$	30.60	1.9453	134.01
$E^2\Pi$		1.1437	169.68	$F^2\Pi$		~1.43	~135
$F^2\Pi$	75.22	1.3751	181.57	$I^2\Pi$			
$G^2\Sigma^+$	69.30	1.1482	187.36	$E^2\Sigma^+$	73.67	1.5374	114.71
$H^2\Pi$	61.03	1.3762	201.14	$J^2\Pi$			
$I^2\Sigma^+$	57.85	1.2639	204.15	$G^2\Sigma^+$			
$J^2\Delta$	48.92	1.6661	221.05	$H^2\Delta$	~54.8	~1.56	~147.2
				$e^4\Pi$	27.53	1.5081	160.90
				$f^4\Delta$	17.86	1.5497	181.12
				$g^4\Sigma^+$	1.60	1.5483	186.78

^aReference 139.

A. $X^2\Pi$ state

The bonding in the $X^2\Pi$ state can be clearly pictured by the following valence-bond Lewis (vbL) icon:



supported by the CASSCF equilibrium Mulliken populations (Si/H)

$$3s^{1.80}3p_z^{0.96}3p_x^{0.98}3p_y^{0.06}3d^{0.12}/1s^{1.04}2p^{0.03}.$$

The accurate experimental dissociation energy of SiH($X^2\Pi$) is still questionable; its chronological evolution is given in detail by Larsson,¹¹³ who concluded that $3.012 \leq D_0 \leq 3.06eV$. Using the experimental spectroscopic constants⁷⁸ $\omega_e = 2042.5229(8) \text{ cm}^{-1}$, and $\omega_e x_e = 30.0552(5) \text{ cm}^{-1}$, the corresponding $D_e (= D_0 + \omega_e/2 - \omega_e x_e/4)$ inequality (in kcal/mol) is $72.35 \leq D_e \leq 73.46$. In Table III we report $D_e = 73.55, 73.73,$ and 73.57 kcal/mol at the MRCI, MRCI + Davidson correction (+ Q), and CCSD(T) levels of theory, respectively. According to Feller and Dixon,¹³⁰ scalar relativistic effects $\Delta E(\text{sr})$ decrease the binding energy by $\Delta E(\text{sr}) = 0.1 \text{ kcal/mol}$, while core-valence $\Delta E(\text{cv})$ contributions do not affect the D_e value.¹³⁰ Taking into account the experimental atomic¹³⁷ and molecular⁸⁴ spin-orbit splittings, $\text{Si}(^3P_2 - ^3P_0) = 223.31 \text{ cm}^{-1}$, $\text{SiH}(^2\Pi_{+3/2} - ^2\Pi_{+1/2}) = 151.5508 \text{ cm}^{-1}$, the binding energy should also be corrected by

$$\Delta E(\text{so}) = \frac{E(^2\Pi_{3/2}) \times 4 + E(^2\Pi_{1/2}) \times 2}{6} - \frac{E(^3P_0) \times 1 + E(^3P_1) \times 3 + E(^3P_2) \times 5}{9}$$

$= 101.0338 - 149.68007 \text{ cm}^{-1} = -48.646 \text{ cm}^{-1} (= -0.14 \text{ kcal/mol})$. Finally, including the BSSE correction of -0.03 kcal/mol we obtain D_e (corrected) $= D_e(\text{MRCI}) + \Delta E(\text{so}) + \Delta E(\text{sr}) + \Delta E(\text{cv}) + \Delta E(\text{BSSE}) = 73.55 - 0.27 = 73.28 \text{ kcal/mol}$, in complete agreement with the (corrected) results of Feller and Dixon.¹³⁰ Our MRCI bond distance, $r_e = 1.5223 \text{ \AA}$, obtained by a Dunham analysis, is by 0.0026 \AA longer as compared to the experimental value of $1.51966(7) \text{ \AA}$,⁷⁸ probably because the core-valence correlation effects⁹⁶ are not included in the present calculations.

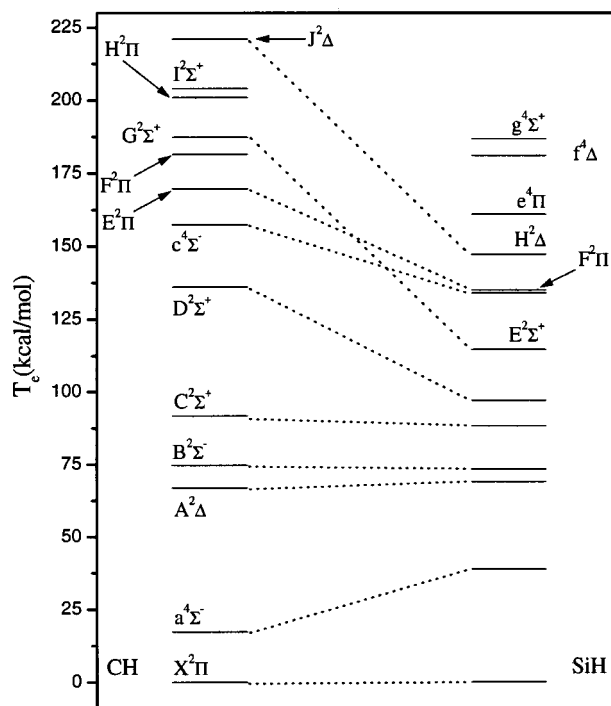


FIG. 4. Relative energy levels of the isovalent species of CH and SiH at the MRCI level of theory. Dotted lines connect corresponding states between the two species.

By solving the radial Schrödinger equation numerically, the rovibrational levels are obtained; it is found that the SiH($X^2\Pi$) potential (Fig. 1) can sustain 20 vibrational levels, $v=0-19$. In particular, for the vibrational transitions 0-1, 1-2, and 2-3 we predict 1972.84, 1902.30, and 1831.54 cm^{-1} , respectively, in excellent agreement with the corresponding experimental values,⁷⁹ 1971.0413, 1900.0585, and 1829.8196 cm^{-1} , reflecting the accuracy of the potential energy function.

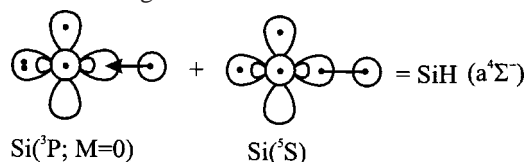
B. $a^4\Sigma^-$ and $c^4\Sigma^-$ states

In essence, for both states above there are no experimental findings (but see below). The $a^4\Sigma^-$ state correlates to Si($^3P;M=0$) + H(2S), Fig. 1. The CASSCF leading equilibrium configuration is $\sim 0.97|1\sigma^2 2\sigma^1 1\pi_x^1 1\pi_y^1\rangle$ (counting only “valence” electrons), with $1\sigma \sim 0.72(3s) + 0.30(3p_z) + 0.66(1s)$, and $2\sigma \sim 0.62(3s) - 0.67(3p_z) - 0.54(1s)$. The atomic CASSCF Mulliken atomic populations at infinity and equilibrium are

$$r_\infty: 3s^{1.91}3p_z^{0.05}3p_x^{0.99}3p_y^{0.99}3d^{0.06}/1s^{1.0},$$

$$r_e: 3s^{1.45}3p_z^{0.56}3p_x^{0.99}3p_y^{0.99}3d^{0.09}/1s^{0.90}2p^{0.04}.$$

Upon bonding, a strong $3s3p_z$ hybridization occurs caused by the promotion of $0.46e^-$ from the Si $3s$ to the $3p_z$ orbital; thus, the *in situ* Si atom acquires a partial 5S character. The emerging bonding picture can be described as a superposition of two limiting vbL icons



The D_e value obtained at the MRCI, MRCI+Q, and CCSD(T) level is practically the same (Table III), the MRCI value being 34.73 kcal/mol compared to 32.49 kcal/mol at the SCF level.

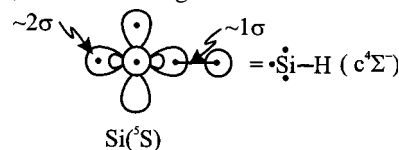
An experimental $a^4\Sigma^- \leftarrow X^2\Pi$ separation of $\sim 5000 \text{ cm}^{-1}$ ($= 14.3 \text{ kcal/mol}$) has been reported by Park,⁶⁶ based on a separation $X^2\Pi \rightarrow b^4\Pi$ (repulsive) of 24 800 cm^{-1} , and to the observed transition $b^4\Pi \leftarrow a^4\Sigma^-$ of about 20 000 cm^{-1} . Our $T_e(a^4\Sigma^- \leftarrow X^2\Pi) = 13 559 \text{ cm}^{-1}$ ($= 38.77 \text{ kcal/mol}$) at the MRCI level, leaves no doubt that the experimental value is wrong. Our corresponding vertical transitions $b^4\Pi \leftarrow X^2\Pi$, and $b^4\Pi \leftarrow a^4\Sigma^-$ are 48 607 and 35 913 cm^{-1} , respectively.

The $c^4\Sigma^-$ state traces its origin to Si(5S) + H(2S), and in contrast to the $a^4\Sigma^-$ is not dominated by a single configuration function. Indeed, the leading equilibrium CASSCF configurations are

$$|c^4\Sigma^- \rangle \sim |(0.86 \times 1\sigma^2 2\sigma^1 - 0.39 \times 2\sigma^2 3\sigma^1 - 0.19 \times 2\sigma^1 3\sigma^2) 1\pi_x^1 1\pi_y^1\rangle,$$

with $1\sigma \sim 0.41(3s) - 0.57(3p_z) - 0.70(1s)$, $2\sigma \sim 0.90(3s) + 0.12(3p_z) + 0.35(1s)$, $3\sigma \sim 0.20(3s) + 0.98(3p_z) - 0.76(1s)$, and the following atomic CASSCF populations: $3s^{1.21}3p_z^{0.76}3p_x^{0.98}3p_y^{0.98}3d^{0.10}/1s^{0.96}2p^{0.02}$. Based on the

atomic distributions we can claim that the *in situ* Si atom is in a 5S state, so the bonding can be described by the icon



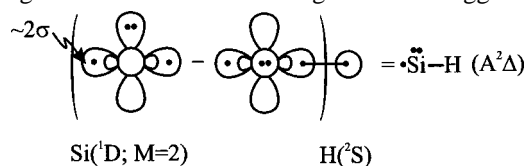
At the MRCI level $T_o(c^4\Sigma^- \leftarrow X^2\Pi) = T_e + 1/2[\omega_e(c^4\Sigma^-) - \omega_e(X^2\Pi)] = 134.0 - 1.14 = 132.9 \text{ kcal/mol}$ (Tables III and IV) is in very good agreement with the corresponding experimental T_o separation of 46 000 cm^{-1} ($= 131.52 \text{ kcal/mol}$).⁶⁶ With respect to Si(5S) + H(2S), $D_e = 30.60(30.74) \text{ kcal/mol}$ and $r_e = 1.945(1.943) \text{ \AA}$ at the MRCI(+Q) level, Table III.

C. $A^2\Delta$ state

As the PEC of Fig. 1 shows, the $A^2\Delta$ state correlates to Si($^1D;M=\pm 2$) + H(2S). The dominant CASSCF configurations are

$$|A^2\Delta \rangle \sim 0.67(|1\sigma^2 2\sigma^1 1\pi_x^2\rangle - |1\sigma^2 2\sigma^1 1\pi_y^2\rangle),$$

dictating a σ bond as the following vbL icon suggests



very similar to that of the CH $A^2\Delta$ state.¹³⁹ The above picture is corroborated by the atomic equilibrium and asymptotic CASSCF distributions

$$r_\infty: 3s^{1.91}3p_z^{0.05}3p_x^{1.0}3p_y^{1.0}3d^{0.07}/1s^{1.0},$$

$$r_e: 3s^{1.55}3p_z^{0.50}3p_x^{0.96}3p_y^{0.96}3d^{0.10}/1s^{0.88}2p^{0.04},$$

indicating a promotion of $0.36e^-$ from the Si $3s$ to $3p_z$ resulting in a $3s3p_z$ hybrid orbital, with the synchronous transfer to that hybrid of $0.09e^-$ from the $1s$ hydrogen function.

Although the experimental dissociation energy of the $A^2\Delta$ state is not explicitly reported in the literature, it can be deduced by the relationship $D_e(A^2\Delta) = D_e(X^2\Pi) + \Delta E(\text{Si}; ^1D \leftarrow ^3P) - T_e(A^2\Delta \leftarrow X^2\Pi)$. Employing the experimental values (in kcal/mol), $72.35 \leq D_e(X^2\Pi) \leq 73.46$,¹¹³ $\Delta E(\text{Si}; ^1D \leftarrow ^3P) = 17.58$,¹³⁷ and $T_e(A^2\Delta \leftarrow X^2\Pi) = 69.35$,⁶⁵ one obtains $20.58 \leq D_e^{\text{exp}}(A^2\Delta) \leq 21.69$. This range of values should be contrasted with our $D_e = 22.28 \text{ kcal/mol}$ at the MRCI level, Table III. Now, the MRCI(+Q) $r_e = 1.5240(1.5237) \text{ \AA}$ is longer by 0.0042 \AA than the latest experimental value of $1.519 781 6(21) \text{ \AA}$.⁸⁴ As already mentioned, this discrepancy is rather caused by core-valence correlation effects not taken into account in the present study.

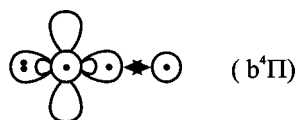
D. $B^2\Sigma^-$ state

By coupling the electrons of the $a^4\Sigma^-$ state into a doublet, the “quasirepulsive” $B^2\Sigma^-$ state is obtained, correlating to Si($^3P;M=0$) + H(2S), Figs. 1 and 2. By following its PEC (Fig. 2) more closely, two minima are observed, the first

one at $r_e=6.5$ bohr, displaying an interaction of just 66.5 cm^{-1} ($=0.19\text{ kcal/mol}$), clearly of van der Waals origin. As we move closer, an energy barrier of 1.28 kcal/mol ($r=4.0$ bohr) with respect to the van der Waals minimum is developed, followed by a second, non-van der Waals minimum of 0.79 kcal/mol at $r_e=1.715\text{ \AA}$. The situation is closely analogous to the $B^2\Sigma^-$ state of CH;¹³⁹ hence, it is conjectured that the second SiH minimum is caused by the intervention of a $^2\Sigma^-$ state correlating to $\text{Si}(^3D)+\text{H}(^2S)$.

E. $b^4\Pi$ and $e^4\Pi$ states

The $b^4\Pi$ is a purely Pauli repulsive state succinctly described by the picture



Si($^3P; M=1$) H(2S)

and displaying a van der Waals interaction of 8.1 cm^{-1} at about 10 bohr. The corresponding CH values are 4.5 cm^{-1} at $r=9$ bohr.¹³⁹ It is interesting to observe that an avoided crossing occurs at 2.4 bohr with the repulsive part of the $e^4\Pi$ Rydberg state (see below), tracing its lineage to $\text{Si}(3s^23p^14s^1; ^3P; M=\pm 1)+\text{H}(^2S)$, Fig. 1.

Now, the $e^4\Pi$ (Rydberg) state shows a repulsive character up to 6.5 bohr, giving rise to an energy barrier of 1.72 kcal/mol . Passing this point the PEC plummets, resulting in an equilibrium distance $r_e=1.5081\text{ \AA}$ and $D_e=27.53\text{ kcal/mol}$ with respect to the adiabatic products. The dominant equilibrium MRCI configuration and corresponding Mulliken atomic populations are $|e^4\Pi\rangle\sim 0.96|1\sigma^22\sigma^13\sigma^11\pi_x^1\rangle$, and $(3s+4s)^{2.45}3p_z^{0.64}3p_x^{0.99}3p_y^{0.04}3d^{0.12}/1s^{0.73}2p^{0.04}$, showing a significant total transfer of $0.23e^-$ from H to Si, and in particular to the $3p_z$ orbital, causing the creation of a half (one electron) σ bond.

F. $C^2\Sigma^+$, $D^2\Sigma^+$, $E^2\Sigma^+$, and $G^2\Sigma^+$ states

The C and $D^2\Sigma^+$ states correlate adiabatically to

$$\text{Si}(^1D; M=0) = \frac{1}{\sqrt{6}}[2|3s^23p_z^2\rangle - |3s^23p_x^2\rangle - |3s^23p_y^2\rangle],$$

and

$$\text{Si}(^1S) = \frac{1}{\sqrt{3}}[|3s^23p_z^2\rangle + |3s^23p_x^2\rangle + |3s^23p_y^2\rangle],$$

respectively. The $C^2\Sigma^+$ PEC presents two minima: one at $r_e=2.40\text{ \AA}$ and an interaction energy of 1.87 kcal/mol , maintaining in essence the character of the asymptote, and a second one at $r_e=1.534\text{ \AA}$ with an interaction energy of 2.89 kcal/mol with respect to the asymptotic products, Fig. 3. The second minimum results from an avoided crossing with the $D^2\Sigma^+$ state, so the internal bond strength of the C state is $2.89 + \Delta E[\text{Si}(^1S) \leftarrow \text{Si}(^1D)] = 29.0\text{ kcal/mol}$. The minimum

(equilibrium) of the $D^2\Sigma^+$ state is located at the top of the avoided crossing ($r=1.792\text{ \AA}$), corresponding to $D_e=20.3\text{ kcal/mol}$ with respect to $\text{Si}(^1S)+\text{H}(^2S)$.

Experimental results exist for, presumably, two states tagged B^- and $C^2\Sigma^+$ (see Ref. 67, and Table I): $T_e^{\text{exp}}(C \leftarrow X) = 31\,832.4\text{ cm}^{-1}$, $r_e = 3.85\text{ \AA}$, and $T_e^{\text{exp}}(B^- \leftarrow X) = 31\,842.2\text{ cm}^{-1}$, $r_e = 1.618\text{ \AA}$. We believe that the B^- and $C^2\Sigma^+$ experimental states correspond to the two minima of our $C^2\Sigma^+$ state. Indeed, at $r_e=2.40$ and 1.53 \AA mentioned above, the corresponding T_e values are 89.4 kcal/mol ($=31\,263\text{ cm}^{-1}$), and 88.4 kcal/mol ($=30\,918\text{ cm}^{-1}$), respectively, with respect to the $X^2\Pi$ state. Finally, it is worth mentioning that the PEC morphologies and their explanation of the C^- and $D^2\Sigma^+$ SiH states are, *mutatis mutandis*, identical to the C^- and $D^2\Sigma^+$ states of CH.¹³⁹

The $E^2\Sigma^+$ state correlates to the Rydberg $\text{Si}(^3P; M=0)+\text{H}(^2S)$ fragments, with its PEC presenting a local (l) and a global (g) minima, Fig. 3. The leading CAS configurations for the l - and g -minima are

$$|E^2\Sigma^+; l\rangle \sim 0.60|1\sigma^22\sigma^13\sigma^2\rangle + 0.56|1\sigma^22\sigma^23\sigma^1\rangle - 0.16|1\sigma^22\sigma^24\sigma^1\rangle,$$

with

$$1\sigma \sim 3s, \quad 2\sigma \sim 0.44(3p_z) + 0.79(1s),$$

$$3\sigma \sim 1.0(3p_z) - 0.45(1s),$$

$$4\sigma \sim 4s,$$

$$|E^2\Sigma^+; g\rangle \sim 0.76|1\sigma^22\sigma^23\sigma^1\rangle + 0.54|1\sigma^22\sigma^24\sigma^1\rangle,$$

with

$$1\sigma \sim 0.83(3s) + 0.25(3p_z) + 0.56(1s),$$

$$2\sigma \sim 0.58(3s) - 0.68(3p_z) - 0.59(1s),$$

$$3\sigma \sim 0.23(3s) + 0.77(3p_z) - 0.52(1s), \quad 4\sigma \sim 4s.$$

The r_e and D_e parameters of the l - and g -minima are (in \AA and kcal/mol) 3.18, 29.1, and 1.537, 73.7, respectively. The bonding in the l -min can be attributed to the 2σ orbital, the 3σ being simply the orthogonal counterpart of the 2σ with no practical participation of the $3s$ or $4s$ atomic Si orbitals. It is interesting that the dipole moment is $\mu = -9.55\text{ D}$, with $0.25e^-$ transferred from the Si to the H atom. Due to an avoided crossing of the E^- with the $G^2\Sigma^+$ (Rydberg) state at 4.8 bohr, an energy barrier of about 7.6 kcal/mol is created with respect to the l -minimum (Fig. 3); thus, the $g-E^2\Sigma^+$ minimum correlates diabatically to $\text{Si}(3s^23p^14s^1; ^1P)+\text{H}(^2S)$. A second avoided crossing is observed in the repulsive part of the E state with the previously discussed $D^2\Sigma^+$ state, and close to 2.8 bohr, Fig. 3. From the CAS configurations and the explicit form of the orbitals, we can speak of two ‘‘bonding’’ orbitals, namely the 1σ and 2σ , with the 3σ and 4σ ($\sim 4s$) carrying the spin symmetry. Overall, less than $0.1e^-$ are transferred from Si to H, resulting in a (relative) negative dipole moment ten times smaller than that of the l -minimum. Finally, the similarity

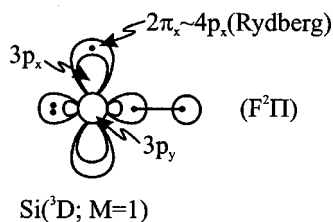
between the SiH $E^2\Sigma^+$ state and the corresponding CH state ($G^2\Sigma^+$), is remarkable: instead the CH PEC barrier is 9.1 kcal/mol and the $g-D_e=69.3$ kcal/mol.¹³⁹

Due to severe technical difficulties, only part of the PEC of the Rydberg $G^2\Sigma^+$ state has been computed, Fig. 3. The only certain thing that can be said about the G state is that its l -minimum occurs at 4.8 bohr (the point of the avoided crossing), giving rise to $D_e=17.7$ kcal/mol with respect to Si(1P) + H(2S). A global minimum surely exists as indicated from a few calculated energy points in the PEC's repulsive part, and the work of Lewerenz *et al.*^{105(a)}

G. $F^2\Pi$, $I^2\Pi$, and $J^2\Pi$ states

None of the PECs of the above SiH states has been fully calculated in the present work due to severe technical problems, with the most complete among the three being that of the $F^2\Pi$ state, Fig. 1.

The repulsive part of the $F^2\Pi$ state shows a van der Waals interaction of 56.8 cm^{-1} correlating to Si($^1D;M=\pm 1$) = $|3s^23p_z^13p_x^1\rangle - |3s^23p_z^13p_y^1\rangle + \text{H}(^2S)$. This character is preserved along the PEC and up to 3.15 bohr, where an avoided crossing takes place with the incoming $I^2\Pi$ Rydberg state. The resulting energy barrier has a height of 9.1 kcal/mol with respect to the minimum; therefore, the latter acquires the character of the $I^2\Pi$ Rydberg state, and thus diabatically traces its lineage to the Rydberg Si($3s^23p^14p^1, ^3D$), 5.95 eV above the Si 3P state, Table II. Assuming that our lowest calculated point corresponds to the minimum, we predict $r_e=1.43\text{ \AA}$ and $T_e=135$ kcal/mol, in very good agreement with the experimental T_o value of $46\,700\pm 10\text{ cm}^{-1}$ ($=133.5$ kcal/mol).⁸² At r_e the dominant CASSCF configuration is $\sim 0.95|1\sigma^22\sigma^22\pi_x^1\rangle$, with the following atomic Mulliken densities $3s^{1.80}3p_z^{1.04}4p_x^{1.02}3p_y^{0.05}3d^{0.13}/1s^{0.94}2p^{0.02}$ displaying clearly the *in situ* 3D character of the Si atom. Notice that the bond length $r_e=1.43\text{ \AA}$ of the Rydberg minimum is the shortest of all states studied, 0.09 \AA shorter than the X state, with a diabatic bond strength [with respect to Si(3D)] of 75.8 kcal/mol. The bonding can be described by the diagram



indicating a single σ bond, with no participation of the symmetry-carrying Rydberg $2\pi_x\sim 4p_x$ electron, and, that, in essence, the H atom binds to a Si ^+2P state resulting in SiH $^+X^1\Sigma^+$ state plus a loosely bound π electron.

The $I^2\Pi$ Rydberg state correlates to Si($3s^23p^14s^1, ^3P;M=\pm 1$) + H(2S), with its PEC showing a broad minimum at $r_e=3.175\text{ \AA}$ and $D_e=33.6$ kcal/mol with respect to the asymptote. The interaction of the I - and $J^2\Pi$ states gives rise to the first avoided crossing of the I state at about 4.2 bohr, thus creating an energy barrier of 10.9 kcal/mol with respect to the minimum. A second avoided

crossing previously discussed with the F state occurs at 3.15 bohr. According to the present results and the results of Lewerenz *et al.*,^{105(a)} the complete $I^2\Pi$ PEC should exhibit three minima at distances 3.175 (present work), ~ 1.78 ,^{105(a)} and 1.52 \AA .^{105(a)O}

The $J^2\Pi$ Rydberg state correlates to Si($3s^23p^14s^1, ^1P;M=\pm 1$) + H(2S) with a few calculated points shown in Fig. 1.

H. $H^2\Delta$ state

A part of the PEC's $H^2\Delta$ is shown in Fig. 1, correlating to

$$\begin{aligned} & \text{Si}(^3D;M=\pm 2) \\ & \sim 0.54|3s^13p_z^1(3p_x^2-3p_y^2)\rangle \\ & - 0.41|3s^23p_z^13d_{x^2-y^2}^1\rangle + 0.21|3s^2(3p_x^13d_{xz}^1 \\ & - 3p_y^13d_{yz}^1)\rangle + \text{H}(^2S).^{140} \end{aligned}$$

Close to equilibrium, the dominant configurations are

$$|H^2\Delta\rangle \sim 0.61|1\sigma^22\sigma^21\delta_+^1\rangle + 0.24|1\sigma^12\sigma^2(1\pi_x^2-1\pi_y^2)\rangle,$$

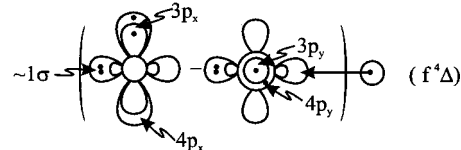
following the atomic character. Our numerical results, Table III, cannot be considered reliable enough, since the reference orbitals originate from a state average procedure of four $^2\Sigma^+$ states.

I. $f^4\Delta$ and $g^4\Sigma^+$ states

Only part of the PEC's $f^4\Delta$ state has been computed due to technical difficulties, Fig. 1. Adiabatically it should correlate to Si($3s^13p^3, ^3D;M=\pm 2$) + H(2S); however, the equilibrium character implies the entanglement of the Si($3s^23p^14p^1, ^3D$) Rydberg state through an (assumed) avoided crossing. At equilibrium ($r_e=1.550\text{ \AA}$), the dominant MRCI configurations read $|f^4\Delta\rangle \sim 0.67|1\sigma^22\sigma^1(1\pi_x^12\pi_x^1-1\pi_y^12\pi_y^1)\rangle$ with $1\sigma\sim 0.85(3s)+0.24(3p_z)+0.58(1s), 2\sigma\sim 0.60(3s)-0.73(3p_z)-0.62(1s), 1\pi\sim 3p_\pi, 2\pi\sim 4p_\pi$, and populations

$$\begin{aligned} & (3s+4s)^{1.56}3p_z^{0.54}(3p_x+4p_x)^{0.95}3d_{xz}^{0.05}(3p_y \\ & +4p_y)^{0.95}3d_{yz}^{0.05}3d^{0.16}/1s^{0.78}2p^{0.04}. \end{aligned}$$

A bonding picture consistent with the above orbitals and distributions is the following:



A total of $0.17 e^-$ are transferred from H to the Si atom.

The $g^4\Sigma^+$ state correlates to the (Rydberg) Si($3s^23p^14s^1, ^3P;M=0$) + H(2S), and as expected shows a repulsive character up to $r=4.6$ bohr, Fig. 1. At this point an avoided crossing is observed with a (not calculated) $^4\Sigma^+$ state, correlating to Si($3s^23p^14p^1, ^3D$) as evidenced from the equilibrium character of the $g^4\Sigma^+$ state, resulting to a minimum at $r_e=1.548\text{ \AA}$. The leading configurations, with a

“+” instead of a “-” sign, orbitals, distributions, and bonding are identical to those of the $f^4\Delta$ state. Finally, the $g^4\Sigma^+$ is bound with respect to its adiabatic asymptote by 1.60 kcal/mol, or by 24.7 kcal/mol with respect to $\text{Si}(3s^23p^14p^1,^3D)+\text{H}(^2S)$.

J. $d^6\Sigma^-$ state

A purely repulsive state correlating to $\text{Si}(^5S)+\text{H}(^2S)$, Fig. 1. A van der Waals attractive interaction of 9.5 cm^{-1} is recorded at about 9 bohr.

K. The $\text{SiH}^+ X^1\Sigma^+$ state

The fact that an accurate ionization energy (IE) of $\text{SiH}(X^2\Pi)$ has been reported,⁸¹ motivated us to examine the SiH^+ ground state. Its potential curve is depicted in Fig. 1. The following parameters are obtained at the MRCI/aug-cc-pV6Z level of theory (experimental results in parentheses): $E = -289.266\,576$ hartree, $r_e = 1.5057$ (1.5041)⁶⁷ Å, $D_e = 3.43$ (3.30)⁶⁷ eV with respect to $\text{Si}^+(^2P;M=0)+\text{H}(^2S)$, $\omega_e(^{28}\text{SiH}^+) = 2159.3$ (2157.17)⁶⁷ cm^{-1} , $\omega_e x_e = 33.72$ (34.24)⁶⁷ cm^{-1} , and $IE = 7.92$ (7.91 ± 0.01)⁸¹ eV.

V. SUMMARY

Employing large valence correlation-consistent basis sets, namely aug-cc-pV6Z/_{Si} cc-pV5Z/_H, and MRCISD techniques, we have constructed a series of 18 potential energy curves of the SiH radical, plus the PEC of the X state of the SiH^+ cation.

We report total energies, dissociation energies, bond lengths, dipole moments, and common spectroscopic parameters ($\omega_e, \omega_e x_e, \alpha_e, \bar{D}_e$) for the isotopic species $^{28}\text{Si}-^{1,2}\text{H}$. All our calculated values are in excellent agreement with the rather limited experimental results. In particular, we believe that our estimated $D_e(X^2\Pi)$ value of 73.28 kcal/mol is the most accurate value reported so far in the literature. The +0.0026 Å discrepancy between calculated and observed bond lengths for the X state could be attributed to core-valence correlation effects. D_e and r_e CCSD(T) results for the $X^2\Pi$ and $a^4\Sigma^-$ states are identical to those of the MRCI method.

Most of the SiH states are in close correspondence with the states of the isovalent CH system, as shown in Table V and visualized in Fig. 4.

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