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Fourier Transform Emission Spectroscopy of the $A^2\Delta$–$X^2\Pi$ Transition of SiH and SiD

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The emission spectra of the $A^2\Delta$–$X^2\Pi$ transition of SiH and SiD have been observed at high resolution using a Fourier transform spectrometer. The molecules were excited in a Si hollow cathode lamp by passing a discharge through a mixture of Ne and a trace of H_2 or D_2. The present data, combined with the previous infrared vibration–rotation measurements, have been used to determine improved molecular constants for the ground and excited states of SiH and SiD. © 1998 Academic Press

INTRODUCTION

SiH is a free radical of fundamental importance. In recent years, there have been numerous experimental and theoretical studies of SiH because of its importance in astrophysics (*1*) and chemical vapor deposition of thin films (*2–4*). Because of significant cosmic abundances of Si and H, there is a strong possibility that the SiH radical may be found in the interstellar medium and stellar atmospheres (*5*). SiH has already been identified in the spectra of sunspots (*6–8*). As a chemical intermediate this radical plays an important role in many industrial processes such as plasma vapor deposition, thin film formation, and semiconductor manufacturing. The primary diagnostic of silane plasmas has been the observation of the $A^2\Delta$–$X^2\Pi$ transition of SiH by optical emission spectroscopy (*9–13*), laser spectroscopy (*14, 15*), and laser optogalvanic spectroscopy (*16*).

The emission spectrum of SiH has been known since 1930 when Jackson (*17*) observed a strong transition of SiH near 410 nm using an arc source. He obtained a rotational analysis of the 0–0 band and assigned it as the $A^2\Delta$–$X^2\Pi$ transition. This analysis was later modified by Mulliken (*18*). The spectra of SiH and SiD were reinvestigated by Rochester (*19*), Douglas (*20*), and Klynning and Lindgren (*21*). Rochester (*19*) obtained an analysis of the 0–0 and 1–1 bands of SiH and the 0–0 band of SiD, whereas Douglas (*20*) observed the SiH bands at a higher dispersion and analyzed 0–0, 1–0, 2–1, and 2–2 bands. In a more recent study Klynning and Lindgren (*21*) provided an analysis for 1–1 band of SiH and the 0–0, 1–1, 2–2, 1–0, and 2–1 bands of SiD. Several higher-lying excited electronic states, $B^2\Sigma^+$, $C^2\Sigma^+$, $D^2\Delta$, and $E^2\Sigma^+$, have also been observed for SiH and SiD (*22–24*). The $B^2\Sigma^+$ and $D^2\Delta$ states were found to be strongly predissociated (*22, 23*). More recently, a new electronic state of SiH and SiD was detected near 46 700 cm^{-1} by resonance-enhanced multiphoton ionization spectroscopy (*25*). This state was tentatively assigned as a $^2\Pi$ state based on a computer simulation of the spectrum.

Because of astrophysical interest in SiH, transitions in other spectral regions have also been investigated extensively. The lowest pure rotational transition lies outside of the spectral range available to radio astronomers, but lambda doubling transitions can be used to detect SiH. Similar radiofrequency transitions have been successfully used for the detection of OH and CH in the interstellar medium (*26, 27*). Wilson and Richards (*28*) obtained a Λ-doubling frequency of 2940 $\pm$ 300 MHz for $J = 0.5$ by extrapolating the Λ-doubling from high rotational levels populated in the optical experiment of Douglas and Elliott (*5*). Klynning *et al.* (*29*) remeasured their high dispersion plates in order to obtain the more precise values of the Λ-doubling constants for the ground $X^2\Pi$ state. From these measurements a value of 2968 $\pm$ 6 MHz was predicted for the Λ-doubling transition. Cooper and Richards (*30*) also carried out an ab initio calculation of this frequency. Freedman and Irwin (*31*) have refitted the line positions of the 0–0 and 1–0 bands of Douglas (*20*) without first deriving term values [direct approach of Zare *et al.* (*32*)] and provided a value of 2932 MHz.

The SiH vibration–rotation bands were observed by Knights *et al.* (*33*) in an emission study of a silane plasma in the 1800–2300 cm^{-1} region. From this study the vibrational and rotational temperatures of 2000 and 485 K were obtained. The infrared spectra of SiH were also observed by Brown and Robinson (*34*), Brown *et al.* (*35*), Davies *et al.* (*36*), and Betrencourt *et al.* (*37*). Brown and Robinson (*34*) detected the fundamental 1–0 band of SiH by laser magnetic resonance spectroscopy, while Betrencourt *et al.* (*37*) observed the 1–0, 2–1, and 3–2 vibration–rotation bands at a resolution of 0.005

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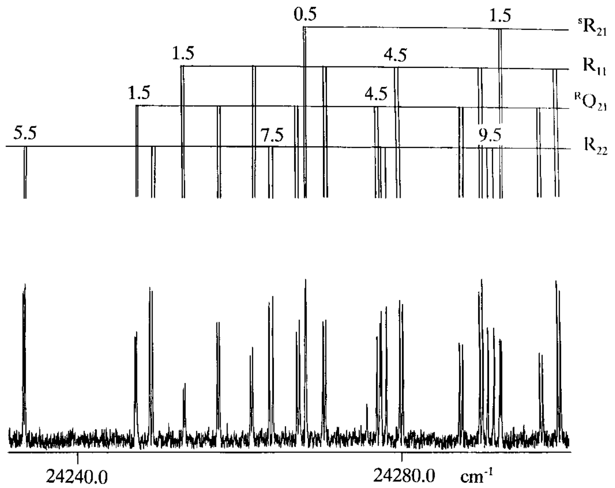

FIG 1. A portion of the 0–0 band showing some low *J* lines in R_{11}, R_{22}, $^{R}Q_{12}$, and $^{S}R_{21}$ branches of SiH.

cm^{-1} using a Fourier transform spectrometer and provided much improved constants for the ground state. In the most recent study of this radical, Seebass *et al.* (*38*) have measured several vibration–rotation lines in the 1–0, 2–1, 3–2, 4–3, and 5–4 bands of five isotopomers of SiH and have determined a very precise set of ground state molecular constants including the spin-orbit constant of $A_0 = 142.8957$ (8) cm^{-1}.

The intensity of the $A^2\Delta$–$X^2\Pi$ electronic transition of SiH is of concern to astronomers and to material scientists. The absorption cross section and electronic transition moment of the $A^2\Delta$–$X^2\Pi$ transition have been determined by Park (*39*) using a shock tube absorption technique, and a transition moment of 0.12 ± 0.04 au has been obtained. The $A^2\Delta$–$X^2\Pi$ transition of SiH has also been observed in vacuum UV photolysis experiments of silane (SiH_4) and dichlorosilane (SiH_2Cl_2) by Washida *et al.* (*40*). In a recent paper Stamou *et al.* (*41*) have simulated the rotational intensity distribution of the 0–0 band of the $A^2\Delta$–$X^2\Pi$ transition of SiH observed in emission from a radio frequency discharge and proposed a new set of molecular constants. There are several studies of the radiative lifetimes of the $A^2\Delta$ state of SiH (*7, 8, 42–45*) using the solar spectrum (*7, 8, 41*), electron bombardment (*43–45*), and laser-induced fluorescence (*14, 46*). The solar values, ranging from 569 to 3200 ns, have been estimated from the oscillator strengths f_{00} and are less reliable. The other experimental values range from 518 to 700 ns. A recent value of 534 ± 23 ns has been obtained using the laser-induced fluorescence technique (*46*). There are several calculations providing the estimates of dissociation energy of SiH between 3.0 to 3.35 eV. An upper limit of 3.06 eV has been obtained from the analysis of predissociation in the $^2\Sigma^+$ state (*22*), while a value of 3.34 eV was obtained from an analysis of the fluorescence lifetimes of the $v = 1$ rotational levels of the $A^2\Delta$ state (*45*). A summary of the experimental and theoretical heats of formation of SiH are tabulated by Jasinski *et al.* (*2*).

There are several theoretical predictions of the spectroscopic properties of the SiH radical (*47–54*). A dipole moment of 0.118 D was predicted by Petterson and Langhoff (*47*), in excellent agreement with the calculated values of Lewerenz *et al.* (*48*) (0.124 D) and Meyer and Rosmus (*49*) (0.115 D). Park and Sun (*50*) have applied the valence shell Hamiltonian method base on quasi-degenerate many-body perturbation theory to calculate the molecular properties including the valence state energies. Theoretical calculations have also been focused on the study of geometrical structures, force constants, and vibrational spectra and heats of formation of silane (SiH_n) and chlorinated silane molecules (SiH_nCl_m) (*51–55*).

EXPERIMENTAL

The SiH and SiD molecules were made in a demountable silicon hollow cathode lamp (*56*). The cathode was prepared by inserting a solid rod of boron-doped silicon into a hole in a copper block. The central part of the rod was then bored through to provide a uniform layer of silicon inside the cathode. The addition of 0.02% of boron to the silicon provided a material with good electrical conductivity. The lamp was operated at 470 V and 610 mA current with a slow flow of neon. Strong SiH bands were initially observed using neon carrier gas at 2 Torr without any added hydrogen. The hydrogen apparently came as impurity in the neon gas or in the vacuum system. The addition of more hydrogen did not increase the intensity of SiH bands. The SiD bands were observed by adding a trace of D_2 gas to the neon flow.

The spectra were recorded using the 1-m Fourier transform spectrometer associated with the McMath-Pierce Solar Telescope of the National Solar Observatory. The spectra in the 17 000–35 000 cm^{-1} region were recorded using Si photodiode detectors and a $CuSO_4$ filter. The SiH bands were recorded at 0.016 cm^{-1} resolution after coadding five scans in about 75 min of integration, while the SiD bands were recorded at 0.05 cm^{-1} after coadding 25 scans in 130 min of integration.

The spectral line positions were extracted from the observed spectra using data reduction programs called PC-DECOMP and GREMLIN developed by J. Brault. The peak positions were determined by fitting a Voigt line shape function to each spectral feature.

In addition to the SiH/SiD bands, the final spectra also contained Si and Ne atomic lines. The spectra were calibrated using the measurements of Ne atomic lines made by Palmer and Engleman (*57*). The SiH/SiD lines have widths of about 0.103 ± 0.005 cm^{-1} and appear with a maximum signal-to-noise ratio of about 30:1 in the 0–0 band. Because of large widths and weak intensity, the high-*J* and weaker lines appear to be diffuse and slightly distorted. Part of the strange appearance of the lines could be due to the presence of unresolved

TABLE 1
Vacuum Wavenumbers (in cm^{-1}) of the $A^2\Delta$–$X^2\Pi$ System of SiH

SiH 0-0											
Line	**Obs.**	**O-C**	**Line**	**Obs.**	**O-C**	**Line**	**Obs.**	**O-C**	**Line**	**Obs.**	**O-C**
R_{11e}(1.5)	24253.164	-4	6.5	24111.326	-5	$^SR_{21f}$(0.5)	24267.965	0	4.5	24217.099	2
2.5	24261.477	0	7.5	24092.832	2	1.5	24292.016	3	5.5	24233.569	-1
3.5	24270.503	-1	8.5	24074.515	-2	2.5	24315.827	7	6.5	24249.177	-0
4.5	24280.014	2	9.5	24056.311	-2	3.5	24339.816	1	7.5	24263.974	-2
5.5	24289.836	3	10.5	24038.147	2	4.5	24364.025	8	8.5	24277.995	-3
6.5	24299.838	4	11.5	24019.945	-9	5.5	24388.355	-0	9.5	24291.264	-0
7.5	24309.897	-1	12.5	24001.678	-3	6.5	24412.733	1	10.5	24303.775	-4
8.5	24319.919	1	13.5	23983.274	3	7.5	24437.052	9	11.5	24315.527	-3
9.5	24329.797	0	14.5	23964.671	0	8.5	24461.183	-2	12.5	24326.494	-7
10.5	24339.448	1	15.5	23945.819	-5	$^QP_{21e}$(3.5)	24208.526	-6	13.5	24336.661	2
11.5	24348.789	6	16.5	23926.664	-11	4.5	24204.302	0	R_{22f}(1.5)	24161.498	7
12.5	24357.727	2	Q_{11e}(2.5)	24218.338	-8	5.5	24200.138	3	2.5	24181.185	-2
13.5	24366.189	-4	3.5	24212.625	-1	6.5	24196.073	4	3.5	24199.614	0
14.5	24374.114	8	4.5	24207.566	-2	7.5	24192.063	-1	4.5	24216.969	3
15.5	24381.386	0	5.5	24202.936	-4	8.5	24188.053	-6	5.5	24233.350	-2
16.5	24387.950	-0	6.5	24198.589	-2	9.5	24183.986	-5	6.5	24248.849	-4
17.5	24393.714	2	7.5	24194.406	-1	10.5	24179.780	-13	7.5	24263.521	0
18.5	24398.582	-3	8.5	24190.286	-0	11.5	24175.408	6	8.5	24277.388	-4
R_{11f}(1.5)	24252.971	-5	9.5	24186.143	-1	12.5	24170.742	-11	9.5	24290.485	-2
2.5	24261.208	1	10.5	24181.899	-3	$^QP_{21f}$(3.5)	24208.205	2	10.5	24302.808	-3
3.5	24270.177	1	11.5	24177.493	6	4.5	24203.936	-0	11.5	24314.354	-3
4.5	24279.649	3	12.5	24172.830	-2	5.5	24199.750	-7	12.5	24325.105	1
5.5	24289.460	5	13.5	24167.869	0	6.5	24195.700	-2	13.5	24335.025	2
6.5	24299.470	3	14.5	24162.532	1	7.5	24191.733	3	14.5	24344.076	1
7.5	24309.568	3	15.5	24156.754	1	8.5	24187.788	5	P_{22e}(3.5)	24068.071	-1
8.5	24319.641	1	16.5	24150.466	0	9.5	24183.780	-10	4.5	24057.018	1
9.5	24329.598	1	Q_{11f}(2.5)	24218.075	-0	10.5	24179.690	0	5.5	24044.971	-0
10.5	24339.346	2	3.5	24212.304	7	11.5	24175.408	-6	6.5	24032.148	1
11.5	24348.789	-7	4.5	24207.201	-2	12.5	24170.903	4	7.5	24018.664	1
12.5	24357.874	3	5.5	24202.562	1	$^RQ_{21e}$(1.5)	24247.219	-0	8.5	24004.599	3
13.5	24366.488	-1	6.5	24198.224	0	2.5	24257.381	-2	9.5	23989.999	-0
14.5	24374.564	-5	7.5	24194.074	1	3.5	24267.240	1	10.5	23974.905	-1
15.5	24382.026	-5	8.5	24190.009	1	4.5	24277.212	5	11.5	23959.335	-2
P_{11e}(2.5)	24212.396	-3	9.5	24185.942	-1	5.5	24287.313	2	12.5	23943.304	4
3.5	24169.502	7	10.5	24181.791	-7	6.5	24297.496	4	13.5	23926.791	-2
4.5	24149.691	3	11.5	24177.493	-7	7.5	24307.676	5	14.5	23909.803	4
5.5	24130.498	2	12.5	24172.978	0	8.5	24317.763	-2	15.5	23892.296	-2
6.5	24111.706	8	13.5	24168.165	0	9.5	24327.690	2	P_{22f}(3.5)	24067.999	-2
7.5	24093.160	-3	14.5	24162.994	-1	10.5	24337.355	-7	4.5	24056.881	-3
8.5	24074.798	3	15.5	24157.399	0	$^RQ_{21f}$(1.5)	24247.027	-1	5.5	24044.753	-1
9.5	24056.514	2	16.5	24151.311	4	2.5	24257.115	2	6.5	24031.817	-5
10.5	24038.251	2	17.5	24144.654	6	3.5	24266.909	-1	7.5	24018.206	-2
11.5	24019.945	3	18.5	24137.347	2	4.5	24276.843	1	8.5	24003.988	-1
12.5	24001.530	-5	19.5	24129.317	-1	5.5	24286.937	5	9.5	23989.220	-2
13.5	23982.970	-5	$^SR_{21e}$(0.5)	24268.061	-4	6.5	24297.128	3	10.5	23973.939	-0
14.5	23964.201	-7	1.5	24292.207	2	7.5	24307.343	5	11.5	23958.167	3
15.5	23945.175	-3	2.5	24316.093	3	8.5	24317.486	-1	12.5	23941.901	-3
16.5	23925.835	2	3.5	24340.147	3	9.5	24327.485	-3	13.5	23925.154	-3
17.5	23906.112	-1	4.5	24364.382	-0	10.5	24337.256	-2	14.5	23907.915	5
P_{11f}(2.5)	24212.123	-5	5.5	24388.728	-5	11.5	24346.715	-2	15.5	23890.141	-4
3.5	24169.166	0	6.5	24413.095	-4	R_{22e}(1.5)	24161.498	-1	16.5	23871.823	-5
4.5	24149.324	0	7.5	24437.375	-2	2.5	24181.214	-2	Q_{22e}(2.5)	24122.509	0
5.5	24130.116	-2	8.5	24461.466	4	3.5	24199.684	-0	5.5	24132.147	0

isotope structure for high-J lines. The absolute accuracy and precision of the measurements of sharp and unblended lines is expected to be of the order of ± 0.003 cm^{-1}. However, the uncertainty of the weaker and blended lines could be as high as ± 0.005 cm^{-1}.

RESULTS AND DISCUSSION

The SiH and SiD bands are located in the 21 000–25 000 cm^{-1} region that covers the $\Delta v = 0$ and $\Delta v = \pm 1$ sequences. The bands in the $\Delta v = \pm 1$ sequences are very weak and could

TABLE 1—*Continued*

Line	Obs.	O-C	Line	Obs.	O-C	Line	Obs.	O-C	Line	Obs.	O-C
6.5	24133.575	4	12.5	24126.791	-2	5.5	23975.332	-0	8.5	24006.821	-2
8.5	24134.301	0	13.5	24123.473	5	6.5	23947.776	-0	9.5	23992.153	1
9.5	24133.695	-2	14.5	24119.471	5	7.5	23919.763	-0	10.5	23977.021	6
10.5	24132.472	-3	15.5	24114.754	1	8.5	23891.331	-0	11.5	23961.416	-8
11.5	24130.644	3	${}^{Q}R_{12e}(1.5)$	24122.462	0	9.5	23862.526	5	12.5	23945.380	1
12.5	24128.194	4	2.5	24126.588	-15	10.5	23833.365	3	13.5	23928.878	3
13.5	24125.109	6	3.5	24130.043	-1	${}^{O}P_{12f}(4.5)$	24002.271	-0	${}^{P}Q_{12f}(2.5)$	24083.436	-6
14.5	24121.357	3	4.5	24132.722	-4	5.5	23975.117	2	3.5	24072.095	0
16.5	24111.709	-8	5.5	24134.665	-4	6.5	23947.448	-3	4.5	24060.145	-6
17.5	24105.733	1	6.5	24135.907	-6	7.5	23919.303	-4	5.5	24047.554	-5
$Q_{22f}(2.5)$	24122.478	-2	7.5	24136.486	-11	8.5	23890.713	-12	6.5	24034.346	2
4.5	24129.782	-8	${}^{Q}R_{12f}(1.5)$	24122.462	8	9.5	23861.738	-6	7.5	24020.550	-1
5.5	24131.932	3	2.5	24126.588	15	10.5	23832.396	1	8.5	24006.219	3
6.5	24133.246	1	3.5	24129.966	-9	${}^{P}Q_{12e}(2.5)$	24083.474	2	9.5	23991.376	1
7.5	24133.817	2	4.5	24132.596	1	3.5	24072.165	0	10.5	23976.048	0
8.5	24133.695	0	5.5	24134.449	-3	4.5	24060.284	1	11.5	23960.250	0
9.5	24132.918	-1	6.5	24135.587	-1	5.5	24047.772	-4	12.5	23943.986	4
10.5	24131.513	5	7.5	24136.035	-7	6.5	24034.670	-0	13.5	23927.244	5
11.5	24129.469	1	${}^{O}P_{12e}(4.5)$	24002.408	4	7.5	24021.006	0			

SiH 1-1

Line	Obs.	O-C	Line	Obs.	O-C	Line	Obs.	O-C	Line	Obs.	O-C
$R_{11e}(1.5)$	23942.917	-3	12.5	23669.101	-8	$Q_{11f}(2.5)$	23908.779	-6	12.5	24000.741	-19
2.5	23949.661	3	13.5	23645.272	1	3.5	23901.828	-1	${}^{R}Q_{21f}(1.5)$	23937.506	-5
3.5	23956.611	5	14.5	23620.644	1	4.5	23895.053	-3	2.5	23945.780	5
4.5	23963.552	9	15.5	23595.140	-2	5.5	23888.253	-1	3.5	23953.382	-3
5.5	23970.311	-0	16.5	23568.670	-10	6.5	23881.278	0	4.5	23960.681	-5
6.5	23976.776	0	17.5	23541.151	-8	7.5	23874.007	-1	5.5	23967.684	1
7.5	23982.811	-3	$P_{11f}(2.5)$	23903.572	11	8.5	23866.334	-3	6.5	23974.310	0
8.5	23988.306	-1	3.5	23861.218	1	9.5	23858.165	-2	7.5	23980.476	1
9.5	23993.149	3	4.5	23840.600	3	10.5	23849.400	-3	8.5	23986.086	4
10.5	23997.223	-0	5.5	23820.121	-1	11.5	23839.950	-2	9.5	23991.026	-3
11.5	24000.430	-2	6.5	23799.588	0	12.5	23829.725	2	10.5	23995.214	-1
12.5	24002.676	10	7.5	23778.871	3	13.5	23818.621	-0	$R_{22e}(2.5)$	23865.748	-12
$R_{11f}(1.5)$	23942.735	1	8.5	23757.847	-11	14.5	23806.550	-1	3.5	23881.530	-2
2.5	23949.393	-5	9.5	23736.476	5	16.5	23779.091	1	4.5	23895.838	-3
3.5	23956.286	-3	10.5	23714.625	-0	17.5	23763.479	-0	5.5	23908.776	6
4.5	23963.190	1	11.5	23692.238	-3	${}^{S}R_{21e}(1.5)$	23979.912	2	6.5	23920.379	1
5.5	23969.941	-3	12.5	23669.229	-11	2.5	24001.216	3	7.5	23930.696	2
6.5	23976.416	-1	13.5	23645.543	-4	3.5	24022.227	-8	8.5	23939.732	0
7.5	23982.488	2	14.5	23621.083	3	4.5	24042.974	3	9.5	23947.477	-8
8.5	23988.035	2	15.5	23595.755	0	5.5	24063.340	-3	10.5	23953.934	1
9.5	23992.942	-3	$Q_{11e}(2.5)$	23909.044	-2	${}^{S}R_{21f}(1.5)$	23979.724	-0	11.5	23959.040	1
10.5	23997.118	3	3.5	23902.148	1	2.5	24000.959	6	12.5	23962.751	-1
11.5	24000.430	-5	4.5	23895.411	1	3.5	24021.923	5	13.5	23965.005	-1
12.5	24002.799	2	5.5	23888.626	5	4.5	24042.624	7	$R_{22f}(2.5)$	23865.748	15
13.5	24004.083	-9	6.5	23881.637	0	5.5	24062.976	0	3.5	23881.473	6
$P_{11e}(2.5)$	23903.809	-12	7.5	23874.331	-4	${}^{R}Q_{21e}(1.5)$	23937.695	0	4.5	23895.715	-2
3.5	23861.547	13	8.5	23866.613	1	2.5	23946.033	-3	5.5	23908.569	2
4.5	23840.939	-12	9.5	23858.367	-1	3.5	23953.702	-0	6.5	23920.076	4
5.5	23820.486	-3	10.5	23849.504	-7	4.5	23961.044	5	7.5	23930.262	-2
6.5	23799.943	-3	11.5	23839.950	1	5.5	23968.049	-1	8.5	23939.152	-5
7.5	23779.201	6	12.5	23829.590	-1	6.5	23974.672	4	9.5	23946.743	-5
8.5	23758.131	-2	13.5	23818.343	-2	7.5	23980.804	1	10.5	23953.013	-1
9.5	23736.670	-2	14.5	23806.116	3	8.5	23986.364	8	11.5	23957.926	4
10.5	23714.731	-2	15.5	23792.798	1	9.5	23991.225	-5	12.5	23961.416	-5
11.5	23692.238	0	16.5	23778.287	-2	11.5	23998.538	4	13.5	23963.446	-0

not be measured. In the $\Delta v = 0$ sequence the 0–0 band is the strongest and the 1–1 band is about 20% of the intensity of the 0–0 band. In this analysis we have only included the lines of these two bands. The 2–2 band is very weakly present in our spectra and a few *Q*-branch lines were seen near the heads, but the data were not sufficient for a meaningful analysis.

In a ${}^{2}\Delta$–${}^{2}\Pi$ transition there are six strong main branches, P_1, P_2, Q_1, Q_2, R_1, and R_2, each of which is doubled by lambda

TABLE 1—*Continued*

Line	Obs.	O-C	Line	Obs.	O-C	Line	Obs.	O-C	Line	Obs.	O-C
P_{22e}(4.5)	23745.374	-2	11.5	23624.373	3	14.5	23756.139	3	4.5	23748.281	2
5.5	23731.540	-6	12.5	23602.902	5	15.5	23743.518	0	5.5	23734.048	-1
6.5	23716.505	-4	13.5	23580.355	1	Q_{22f}(2.5)	23810.538	-16	6.5	23718.768	-2
7.5	23700.365	2	14.5	23556.702	4	3.5	23812.939	4	7.5	23702.474	3
8.5	23683.162	-2	15.5	23531.875	2	4.5	23813.794	10	9.5	23666.900	4
9.5	23664.938	-7	Q_{22e}(1.5)	23806.147	-3	5.5	23813.270	-4	10.5	23647.634	-3
10.5	23645.717	-3	2.5	23810.577	-5	6.5	23811.498	1	11.5	23627.392	4
12.5	23604.233	4	3.5	23813.000	-1	7.5	23808.511	2	${}^PQ_{12f}$(2.5)	23773.576	11
13.5	23581.915	1	4.5	23813.914	6	8.5	23804.347	1	3.5	23761.381	1
14.5	23558.496	-5	5.5	23813.476	-2	9.5	23799.017	-3	4.5	23748.157	2
15.5	23533.934	3	6.5	23811.806	3	10.5	23792.528	-2	5.5	23733.847	2
P_{22f}(4.5)	23745.243	-9	7.5	23808.941	2	11.5	23784.856	1	6.5	23718.466	2
5.5	23731.337	-4	8.5	23804.920	1	12.5	23775.963	-2	7.5	23702.039	-2
6.5	23716.211	7	9.5	23799.759	2	13.5	23765.809	-1	8.5	23684.604	3
7.5	23699.942	8	10.5	23793.445	-3	14.5	23754.334	1	9.5	23666.160	2
8.5	23682.588	-2	11.5	23785.972	-0	15.5	23741.458	-2	10.5	23646.721	3
9.5	23664.203	-4	12.5	23777.298	1	${}^PQ_{12e}$(2.5)	23773.589	-3			
10.5	23644.795	-6	13.5	23767.370	-1	3.5	23761.444	-0			

doubling in the $^2\Pi$ state. These are the only branches that are allowed if both states obey pure Hund's case (a) coupling or if both states have pure Hund's case (b) coupling. For SiH, however, the $A^2\Delta$ state changes from approximately Hund's case (a) to Hund's case (b) as J increases and several satellite branches become allowed. In total six additional satellite branches (${}^QR_{12}$, ${}^PQ_{12}$, ${}^OP_{12}$, ${}^SR_{21}$, ${}^RQ_{21}$, and ${}^QP_{21}$) are expected in each band. In the 0–0 band all of these branches have been identified. In the 1–1 band some of the satellite branches, such as ${}^OP_{12}$ and ${}^QP_{21}$, could not be identified because of their very weak intensity. In SiD some of the satellite branches also were not observed in the 0–0 and 1–1 bands. Although Klynning and Lindgren (*21*) observed more bands in their study, the Fourier transform measurements are expected to be more precise by about an order of magnitude. A part of the 0–0 band of SiH showing some low J lines of a few branches has been provided in Fig. 1. As shown, the Λ-doubling is resolved even for the lowest J lines observed. The observed line positions of SiH and SiD bands have been provided in Tables 1 and 2.

In order to determine the rotational constants, the observed line positions of different bands were fitted with the effective N^2 Hamiltonian of Brown *et al.* (*58*). The $^2\Pi$ matrix element of this Hamiltonian is provided by Amiot *et al.* (*59*), and those for a $^2\Delta$ state are provided by Brown *et al.* (*60*). The lines in each of the vibrational bands were initially fitted separately using a nonlinear least-squares procedure. In the final fit the zero field wavenumbers of the 1–0 and 2–1 vibration–rotation bands calculated by Brown (*61*) (provided for convenience in Table 3), the infrared vibration–rotation bands of Betrencourt *et al.* (*37*), and far infrared frequencies calculated from the constants of Brown *et al.* (*35*) provided in the Table 2 of Betrencourt *et al.* (*37*) were combined with our present measurements. These infrared and far infrared frequencies were weighted by the estimated uncertainties provided in the original papers. The weights for the weaker and blended lines were chosen according to the signal-to-noise ratio and extent of blending. The constants for SiH and SiD obtained in this fit are provided in Tables 4 and 5. The final reduced standard deviations are 1.20 for SiH and 1.14 for SiD. For convenience, the ground and excited state term values for SiH and SiD are also provided in Tables 6 and 7, respectively. The spectroscopic parameters T_v (except $v = 0$), A_v, γ_v, γ_{Dv} (except $v = 0$), B_v, D_v, H_v, q_v, q_{Dv}, p_v, and p_{Dv} were determined in the ground state. The term value for the $v = 0$ vibrational level of the ground state (T_0) was held fixed to zero. Except for q_v, q_{Dv}, p_v, and p_{Dv}, all the above parameters were determined in the excited $A^2\Delta$ state. The inclusion of high-J vibration–rotation lines from Betrencourt *et al.* (*37*) is expected to improve the determination of distortion constants in the ground state and hence help break the strong correlations with the excited state. The present ground state values are in excellent agreement with the previously reported values (*35–38*), partly because of the inclusion of all the previous infrared measurements. In particular the present values of $\Delta G''(1/2) = 1971.03904(35)$ cm^{-1}, $A''_0 = 142.88778(39)$ cm^{-1} can be compared by the recent values of $\Delta G''(1/2) = 1971.0413$ cm^{-1}, $A''_0 = 142.8952$ cm^{-1} obtained by Seebass *et al.* (*38*) in their laser magnetic resonance experiment. The values of $\Delta G''(1/2) = 1970.78$ cm^{-1}, $A''_0 = 142.83$ cm^{-1} were obtained by Klynning and Lindgren (*21*). Some of the discrepancies are caused by our adoption of the N^2 Hamiltonian rather than the energy level expressions used by Klynning and Lindgren (*21*). It has been shown by Brown and Watson (*62*) that the A_{Dv} and γ_v parameters cannot be determined simultaneously for a $^2\Pi$ state. In their analysis Klynning and Lindgren (*21*) determined A_{Dv} (A_J in their notation) instead of γ_v. The separation of these two parameters is possible only by isotopic substitution, and Betrencourt *et al.* (*37*) decided to determine γ_v rather than A_{Dv}. In the most recent infrared study of this radical, Seebass *et al.* (*38*) observed the spectra of five isotopic species ^{28}SiH, ^{29}SiH, ^{30}SiH, ^{28}SiD, and ^{29}SiD and found an appreciable magnitude for

TABLE 2
Vacuum Wavenumbers (in cm^{-1}) of the $A^2\Delta$–$X^2\Pi$ System of SiD

SiD 0-0											
Line	**Obs.**	**O-C**	**Line**	**Obs.**	**O-C**	**Line**	**Obs.**	**O-C**	**Line**	**Obs.**	**O-C**
R_{11e}(2.5)	24305.365	3	20.5	24078.383	-14	9.5	24260.038	1	10.5	24255.619	4
3.5	24309.328	3	21.5	24067.621	9	10.5	24257.159	1	11.5	24252.806	3
4.5	24313.503	5	22.5	24056.681	6	11.5	24254.303	4	12.5	24249.974	-1
5.5	24317.812	-3	23.5	24045.564	-0	12.5	24251.438	1	13.5	24247.098	-13
6.5	24322.236	2	25.5	24022.745	13	13.5	24248.554	3	$^{R}Q_{21e}$(3.5)	24306.531	-5
7.5	24326.729	2	P_{11f}(6.5)	24223.628	14	14.5	24245.622	0	4.5	24311.163	-7
8.5	24331.265	1	7.5	24212.986	6	15.5	24242.626	-3	5.5	24315.780	4
9.5	24335.826	2	8.5	24202.466	-1	16.5	24239.544	-8	6.5	24320.390	-0
10.5	24340.381	1	9.5	24192.054	3	17.5	24236.364	-4	7.5	24325.025	6
11.5	24344.911	1	10.5	24181.708	-0	18.5	24233.054	-4	8.5	24329.649	-3
12.5	24349.386	-3	11.5	24171.422	3	19.5	24229.602	3	9.5	24334.283	3
13.5	24353.798	3	12.5	24161.173	6	20.5	24225.969	2	10.5	24338.889	4
14.5	24358.102	-2	13.5	24150.932	-0	21.5	24222.150	8	11.5	24343.439	-9
15.5	24362.293	0	15.5	24130.444	-5	22.5	24218.086	-13	12.5	24347.953	3
16.5	24366.345	7	16.5	24120.161	-3	23.5	24213.810	-2	13.5	24352.357	-13
17.5	24370.208	-6	17.5	24109.832	4	24.5	24209.259	3	14.5	24356.682	-3
18.5	24373.902	6	18.5	24099.423	0	25.5	24204.409	5	15.5	24360.873	-2
19.5	24377.356	-5	19.5	24088.925	-4	26.5	24199.223	-6	16.5	24364.921	5
21.5	24383.544	11	20.5	24078.324	-3	27.5	24193.706	7	17.5	24368.791	7
22.5	24386.199	13	21.5	24067.603	5	28.5	24187.795	11	18.5	24372.469	11
23.5	24388.513	-2	22.5	24056.728	6	29.5	24181.444	-8	$^{R}Q_{21f}$(2.5)	24301.604	3
R_{11f}(3.5)	24309.150	7	23.5	24045.690	13	30.5	24174.664	-4	3.5	24306.338	-15
4.5	24313.270	-8	24.5	24034.448	7	$^{S}R_{21e}$(4.5)	24356.842	-3	4.5	24310.944	-5
5.5	24317.556	-4	25.5	24023.007	18	5.5	24368.931	6	5.5	24315.525	4
6.5	24321.945	-6	Q_{11e}(2.5)	24283.105	-7	6.5	24381.008	-5	6.5	24320.112	5
7.5	24326.422	3	3.5	24279.229	-6	7.5	24393.097	-3	7.5	24324.715	4
8.5	24330.947	7	4.5	24275.723	-4	8.5	24405.177	5	8.5	24329.331	3
9.5	24335.490	2	5.5	24272.426	-5	9.5	24417.208	0	9.5	24333.953	9
10.5	24340.029	-10	6.5	24269.284	3	10.5	24429.188	0	10.5	24338.549	6
11.5	24344.573	4	7.5	24266.238	-2	11.5	24441.098	9	11.5	24343.111	4
12.5	24349.049	-6	8.5	24263.279	-0	12.5	24452.891	4	12.5	24347.636	20
13.5	24353.469	-5	9.5	24260.370	-3	13.5	24464.554	-2	13.5	24352.051	3
14.5	24357.802	-1	10.5	24257.498	-3	$^{S}R_{21f}$(4.5)	24356.625	2	14.5	24356.371	-12
15.5	24362.015	-1	11.5	24254.643	3	5.5	24368.680	11	15.5	24360.585	-13
16.5	24366.083	-8	12.5	24251.771	1	7.5	24392.786	-6	16.5	24364.657	-12
17.5	24369.994	-9	13.5	24248.871	-1	8.5	24404.849	2	17.5	24368.570	-5
18.5	24373.729	2	14.5	24245.923	-1	9.5	24416.867	-5	18.5	24372.297	7
19.5	24377.236	-3	15.5	24242.901	-5	10.5	24428.845	-2	R_{22e}(1.5)	24184.644	-17
20.5	24380.522	10	16.5	24239.792	-5	11.5	24440.748	-0	2.5	24195.803	-8
21.5	24383.521	2	17.5	24236.578	-0	12.5	24452.546	-7	3.5	24206.362	-20
22.5	24386.234	0	18.5	24233.226	-0	13.5	24464.256	21	4.5	24216.508	-14
23.5	24388.626	-2	19.5	24229.713	-7	14.5	24475.779	8	5.5	24226.277	-6
P_{11e}(5.5)	24234.655	-4	20.5	24226.038	-0	$^{Q}P_{21e}$(5.5)	24270.098	-5	6.5	24235.687	-5
6.5	24223.891	-7	21.5	24222.150	-6	6.5	24267.242	-1	7.5	24244.763	-2
7.5	24213.295	8	22.5	24218.057	6	7.5	24264.398	2	8.5	24253.509	1
8.5	24202.806	13	23.5	24213.691	-8	8.5	24261.574	3	9.5	24261.927	-3
9.5	24192.396	9	24.5	24209.082	9	9.5	24258.773	12	10.5	24270.044	10
10.5	24182.055	5	25.5	24204.153	6	10.5	24255.953	-3	11.5	24277.821	2
11.5	24171.758	-2	26.5	24198.892	-1	11.5	24253.127	-17	12.5	24285.295	7
12.5	24161.506	5	27.5	24193.274	-8	12.5	24250.321	12	13.5	24292.441	5
13.5	24151.241	-12	Q_{11f}(2.5)	24282.944	-28	13.5	24247.436	3	14.5	24299.264	4
14.5	24141.001	0	3.5	24279.042	-10	$^{Q}P_{21f}$(4.5)	24272.710	-6	15.5	24305.749	-3
15.5	24130.723	-3	4.5	24275.510	5	5.5	24269.852	5	16.5	24311.902	-5
16.5	24120.403	-8	5.5	24272.170	-6	6.5	24266.954	-6	17.5	24317.704	-9
17.5	24110.027	-12	6.5	24268.998	1	7.5	24264.089	-1	18.5	24323.152	-7
18.5	24099.585	-7	7.5	24265.934	1	8.5	24261.252	6	19.5	24328.237	4
19.5	24089.045	-5	8.5	24262.956	1	9.5	24258.427	2	20.5	24332.920	3

TABLE 2—*Continued*

Line	Obs.	O-C	Line	Obs.	O-C	Line	Obs.	O-C	Line	Obs.	O-C
21.5	24337.210	13	11.5	24089.884	8	5.5	24173.148	13	4.5	24135.404	-0
22.5	24341.059	8	12.5	24082.717	7	7.5	24176.678	-4	5.5	24129.787	-2
23.5	24344.454	-5	13.5	24075.320	7	8.5	24177.986	-3	6.5	24123.951	-10
24.5	24347.396	-3	14.5	24067.682	-2	9.5	24179.007	5	7.5	24117.897	-7
25.5	24349.853	7	15.5	24059.826	-2	10.5	24179.731	1	8.5	24111.615	-0
$R_{22f}(1.5)$	24184.644	-16	16.5	24051.729	-14	11.5	24180.194	15	9.5	24105.104	8
2.5	24195.803	-4	17.5	24043.428	3	14.5	24179.870	-2	10.5	24098.357	11
3.5	24206.362	-10	18.5	24034.860	-12	15.5	24179.214	-3	11.5	24091.379	8
4.5	24216.508	5	19.5	24026.065	-9	16.5	24178.297	17	12.5	24084.183	11
5.5	24226.244	-6	20.5	24017.029	3	17.5	24177.047	-7	13.5	24076.760	9
6.5	24235.637	-4	21.5	24007.712	-5	18.5	24175.532	1	14.5	24069.122	12
7.5	24244.691	1	22.5	23998.139	6	19.5	24173.702	-1	15.5	24061.247	-1
8.5	24253.408	4	23.5	23988.287	24	20.5	24171.549	-7	16.5	24053.159	-2
9.5	24261.791	-0	$P_{22f}(6.5)$	24121.852	-19	21.5	24169.081	3	17.5	24044.832	-15
10.5	24269.852	-2	7.5	24115.986	1	22.5	24166.249	-3	$^{R}Q_{12f}(3.5)$	24140.847	8
11.5	24277.595	1	8.5	24109.811	8	23.5	24163.057	-5	4.5	24135.378	-6
12.5	24285.009	-1	9.5	24103.352	8	$Q_{22f}(5.5)$	24173.109	6	5.5	24129.757	0
13.5	24292.100	-1	10.5	24096.620	-3	6.5	24175.022	3	6.5	24123.912	3
14.5	24298.866	5	11.5	24089.644	-6	7.5	24176.612	4	7.5	24117.825	-4
15.5	24305.289	3	12.5	24082.430	-3	8.5	24177.885	-0	8.5	24111.517	5
16.5	24311.370	2	13.5	24074.965	-12	13.5	24179.915	1	9.5	24104.956	-0
17.5	24317.090	-6	14.5	24067.290	4	14.5	24179.473	-0	10.5	24098.174	8
18.5	24322.455	-5	15.5	24059.364	1	15.5	24178.755	5	11.5	24091.156	11
19.5	24327.456	10	16.5	24051.192	-12	16.5	24177.748	8	12.5	24083.901	6
20.5	24332.036	-3	17.5	24042.806	-2	17.5	24176.444	8	13.5	24076.412	-5
21.5	24336.220	-4	18.5	24034.171	-1	18.5	24174.826	-5	14.5	24068.728	16
22.5	24339.977	-2	19.5	24025.278	-9	19.5	24172.924	8	15.5	24060.791	10
24.5	24346.123	4	20.5	24016.129	-19	20.5	24170.681	3	16.5	24052.625	4
25.5	24348.461	4	21.5	24006.733	-10	22.5	24165.165	-15	17.5	24044.222	-8
$P_{22e}(5.5)$	24127.469	8	22.5	23997.054	-7	23.5	24161.874	-13	18.5	24035.602	2
6.5	24121.917	-6	23.5	23987.103	14	24.5	24158.212	4	19.5	24026.726	-0
7.5	24116.062	1	24.5	23976.815	5	25.5	24154.140	21	20.5	24017.588	-11
8.5	24109.901	-6	$Q_{22e}(2.5)$	24164.882	-7	26.5	24149.596	-4			
9.5	24103.478	-5	3.5	24168.141	-8	$^{R}Q_{12e}(2.5)$	24146.254	-7			
10.5	24096.799	-3	4.5	24170.847	0	3.5	24140.847	-1			
SiD 1-1											
$R_{11e}(2.5)$	24103.949	-1	12.5	24040.310	3	7.5	24035.647	6	16.5	23953.831	14
3.5	24107.222	-12	13.5	24035.406	6	8.5	24042.724	13	$Q_{22f}(4.5)$	23967.698	2
4.5	24110.557	-6	14.5	24030.286	19	$R_{22f}(3.5)$	24002.482	11	5.5	23969.042	-5
5.5	24113.860	-16	15.5	24024.886	4	4.5	24011.518	9	10.5	23968.692	3
6.5	24117.130	-0	16.5	24019.209	-10	5.5	24020.046	20	11.5	23967.271	8
8.5	24123.345	-1	$Q_{11f}(4.5)$	24074.108	10	6.5	24028.046	3	12.5	23965.394	5
9.5	24126.257	4	5.5	24070.067	-11	7.5	24035.575	5	13.5	23963.048	-14
10.5	24128.995	3	6.5	24066.066	18	8.5	24042.627	14	14.5	23960.281	4
$R_{11f}(2.5)$	24103.829	20	7.5	24061.978	5	$P_{22e}(5.5)$	23925.281	17	15.5	23957.024	-3
3.5	24107.055	5	8.5	24057.829	6	6.5	23918.961	-8	16.5	23953.299	1
4.5	24110.343	2	9.5	24053.562	-9	7.5	23912.195	-12	$^{R}Q_{12e}(3.5)$	23939.515	-5
6.5	24116.833	-11	10.5	24049.209	12	8.5	23905.017	8	4.5	23933.612	-21
8.5	24123.034	14	11.5	24044.668	-6	$P_{22f}(5.5)$	23925.245	12	5.5	23927.402	-23
9.5	24125.917	-0	12.5	24039.973	-7	6.5	23918.921	0	6.5	23920.880	22
10.5	24128.650	-2	13.5	24035.099	8	8.5	23904.908	-2	7.5	23913.911	-3
$Q_{11e}(4.5)$	24074.328	7	14.5	24029.975	-6	$Q_{22e}(4.5)$	23967.698	-16	8.5	23906.577	-10
5.5	24070.340	6	15.5	24024.638	10	5.5	23969.090	13	9.5	23898.897	23
6.5	24066.336	2	16.5	24019.000	-3	10.5	23968.859	-1	$^{R}Q_{12f}(3.5)$	23939.515	4
7.5	24062.278	-4	$R_{22e}(2.5)$	23992.866	-4	11.5	23967.469	-9	4.5	23933.612	-3
8.5	24058.141	-7	3.5	24002.482	2	12.5	23965.648	-6	5.5	23927.402	8
9.5	24053.900	-7	4.5	24011.518	-10	13.5	23963.369	-14	6.5	23920.826	16
10.5	24049.537	1	5.5	24020.046	-11	14.5	23960.659	0	8.5	23906.501	13
11.5	24045.018	8	6.5	24028.107	16	15.5	23957.474	-0	9.5	23898.752	10

TABLE 3
Hyperfine-Free Vibration-Rotation Lines (in cm^{-1}) of SiH and SiD (*61*)

J′	Level	J″	Level	Obs.	O-C	J′	Level	J″	Level	Obs.	O-C
SiH 1-0											
2.5	F_2 e	1.5	F_2 e	2008.3766	-0.0015	1.5	F_2 f	2.5	F_2 f	1931.5825	-0.0012
2.5	F_2 f	1.5	F_2 f	2008.3985	0.0008	3.5	F_2 f	4.5	F_2 f	1897.8800	-0.0018
2.5	F_2 e	2.5	F_2 f	1969.3560	-0.0027	4.5	F_2 f	5.5	F_2 f	1880.5289	-0.0001
2.5	F_2 f	2.5	F_2 e	1969.4170	0.0016	5.5	F_2 f	6.5	F_2 f	1862.8662	0.0015
1.5	F_2 e	2.5	F_2 e	1931.6058	-0.0003	6.5	F_2 f	7.5	F_2 f	1844.9022	0.0040
3.5	F_2 e	4.5	F_2 e	1897.9489	0.0000	5.5	F_1 f	6.5	F_1 f	1872.3352	-0.0005
4.5	F_2 e	5.5	F_2 e	1880.6228	0.0000	0.5	F_1 e	1.5	F_2 e	1818.7695	0.0008
5.5	F_2 e	6.5	F_2 e	1862.9860	-0.0000	1.5	F_1 e	2.5	F_2 e	1800.0617	0.0010
6.5	F_2 e	7.5	F_2 e	1845.0475	0.0000	0.5	F_1 f	1.5	F_2 f	1818.8584	0.0013
8.5	F_2 e	9.5	F_2 e	1808.2864	0.0012	1.5	F_1 f	2.5	F_2 f	1800.2167	0.0005
SiH 2-1											
2.5	F_2 e	1.5	F_2 e	1936.2085	0.0003	4.5	F_2 f	5.5	F_2 f	1812.2053	-0.0002
2.5	F_2 f	1.5	F_2 f	1936.2253	-0.0011	4.5	F_1 e	5.5	F_1 e	1819.8522	-0.0008
1.5	F_2 e	2.5	F_2 e	1861.8364	-0.0000	4.5	F_1 f	5.5	F_1 f	1819.8294	0.0014
2.5	F_2 e	3.5	F_2 e	1845.6655	-0.0007	1.5	F_2 f	1.5	F_2 e	1899.6255	0.0006
4.5	F_2 e	5.5	F_2 e	1812.2957	0.0015	1.5	F_2 e	1.5	F_2 f	1899.6126	0.0012
2.5	F_2 f	3.5	F_2 f	1845.6258	-0.0004	3.5	F_1 e	3.5	F_1 f	1896.1889	0.0013
SiD 1-0											
1.5	F_2 f	1.5	F_2 e	1432.9958	0.0002	2.5	F_2 f	1.5	F_2 f	1452.3433	0.0027
2.5	F_2 f	2.5	F_2 e	1432.5704	0.0003	3.5	F_2 f	2.5	F_2 f	1459.6317	-0.0032
3.5	F_2 f	3.5	F_2 e	1431.9771	0.0002	4.5	F_2 f	3.5	F_2 f	1466.7406	-0.0022
1.5	F_2 e	1.5	F_2 f	1432.9938	0.0002	1.5	F_2 e	2.5	F_2 e	1413.2208	-0.0022
2.5	F_2 e	2.5	F_2 f	1432.5626	0.0002	2.5	F_2 e	3.5	F_2 e	1404.9034	-0.0010
3.5	F_2 e	3.5	F_2 f	1431.9581	0.0001	3.5	F_2 e	4.5	F_2 e	1396.4341	0.0012
2.5	F_2 e	1.5	F_2 e	1452.3405	0.0026	1.5	F_2 f	2.5	F_2 f	1413.2179	-0.0022
3.5	F_2 e	2.5	F_2 e	1459.6308	0.0012	2.5	F_2 f	3.5	F_2 f	1404.8976	-0.0008
4.5	F_2 e	3.5	F_2 e	1466.7317	-0.0028	3.5	F_2 f	4.5	F_2 f	1396.4254	0.0025
SiD 2-1											
1.5	F_2 f	1.5	F_2 e	1396.0475	0.0014	2.5	F_2 f	1.5	F_2 f	1414.9743	0.0018
2.5	F_2 f	2.5	F_2 e	1395.6296	-0.0007	3.5	F_2 f	2.5	F_2 f	1422.1072	-0.0001
3.5	F_2 f	3.5	F_2 e	1395.0468	-0.0010	4.5	F_2 f	3.5	F_2 f	1429.0549	-0.0003
1.5	F_2 e	1.5	F_2 f	1396.0456	0.0014	1.5	F_2 e	2.5	F_2 e	1376.7008	-0.0010
2.5	F_2 e	2.5	F_2 f	1395.6220	-0.0007	2.5	F_2 e	3.5	F_2 e	1368.5616	-0.0016
3.5	F_2 e	3.5	F_2 f	1395.0281	-0.0012	3.5	F_2 e	4.5	F_2 e	1360.2735	0.0019
2.5	F_2 e	1.5	F_2 e	1414.9716	0.0018	1.5	F_2 f	2.5	F_2 f	1376.6980	-0.0012
3.5	F_2 e	2.5	F_2 e	1422.1018	0.0001	2.5	F_2 f	3.5	F_2 f	1368.5559	-0.0019
4.5	F_2 e	3.5	F_2 e	1429.0462	0.0001	3.5	F_2 f	4.5	F_2 f	1360.2642	0.0013

the γ_v parameter. Our results are consistent with the results of these two groups.

Since the ground state molecular parameters are known with excellent precision from the previous infrared studies (*35–38*), the main purpose of the present study was to improve the molecular constants for the excited $A^2\Delta$ state. It is therefore more interesting to compare the present excited state constants for the $A^2\Delta$ state with the values obtained previously by Klynning and Lindgren (*21*) and Klynning *et al.* (*29*). Our $\Delta G'(1/2) = 1662.36001(82)$ cm^{-1}, $A'_0 = 3.54137(82)$ cm^{-1} are significantly different from the values of $\Delta G'(1/2) = 1660.58$ cm^{-1}, $A'_0 = 3.62$ cm^{-1} obtained by Klynning and Lindgren (*21*). The rotational constants for the $v = 0$ vibrational level of the $A^2\Delta$ state from their revised analysis of the 0–0 band [Klynning *et al.* (*29*)], however, compare better with our values. In this work they determined γ_0 instead of A_{D0} in the excited state while still keeping A_{D0} in the ground state. Their $B'_0 = 7.28280(8)$ cm^{-1}, $D'_0 = 5.203(3) \times 10^4$ cm^{-1}, $A'_0 = 3.544(2)$ and $\gamma_0 = 0.0871$ cm^{-1} compare well with our values of $B'_0 = 7.287599(14)$ cm^{-1}, $D'_0 = 5.1881(13) \times 10^4$ cm^{-1}, $A'_0 = 3.54137(82)$ and $\gamma_0 = 0.089983(99)$ cm^{-1}.

The molecular constants of the $v = 0$ and $v = 1$ vibrational levels have been used to determine the equilibrium constants for SiH and SiD from an exact fit. The excited state equilibrium rotational constants obtained from this work are $B_e = 7.502718(21)$ cm^{-1}, $\alpha_e = 0.215119(15)$ cm^{-1} for SiH and B_e

TABLE 4
Spectroscopic Constants (in cm^{-1}) for the $A^2\Delta$–$X^2\Pi$ System of SiH

Constants[a]	$X^2\Pi$ (v=0)	$X^2\Pi$ (v=1)	$A^2\Delta$ (v=0)	$A^2\Delta$ (v=1)
T_v	0	1971.03904(35)	24171.36819(44)	25833.72820(69)
A_v	142.88778(39)	143.46046(46)	3.54137(82)	3.0935(11)
$10^2 \times \gamma_v$	-4.5762(54)	-4.2215(89)	8.9983(99)	8.527(13)
$10^5 \times \gamma_{Dv}$	--	--	-2.158(49)	-2.382(71)
B_v	7.3917453(62)	7.175928(17)	7.287599(14)	6.857362(26)
$10^4 \times D_v$	4.0174(10)	3.9624(19)	5.1881(13)	5.8242(25)
$10^8 \times H_v$	1.545(25)	1.378(50)	-1.335(28)	-4.711(64)
$10^3 \times q_v$	8.3656(80)	8.147(13)	--	--
$10^6 \times q_{Dv}$	-1.648(36)	-1.733(60)	--	--
$10^2 \times p_v$	8.3316(59)	7.980(11)	--	--
$10^5 \times p_{Dv}$	-1.572(44)	-1.548(68)	--	--

[a]Numbers in parentheses are one standard deviation in last two digits.

$= 3.878272(77)$ cm^{-1}, $\alpha_e = 0.076744(68)$ cm^{-1} for SiD. The values reported in parentheses are estimated uncertainties. Since these values have been determined from exact fits, the actual uncertainties in these values are expected to be much higher than the quoted values. The equilibrium bond lengths for the excited $A^2\Delta$ state of SiH and SiD using these values are 1.5197816(21) Å and 1.521017(15) Å, respectively.

In a previous study of this molecule, Verma (*22*) observed strong predissociation in the $B^2\Sigma^+$ and $D^2\Delta$ states. From an analysis of these predissociations, Verma (*22*) estimated an upper limit of the dissociation energy of 3.06 eV for this molecule. The lifetimes of a number of rotational levels of the $v = 0$, 1, and 2 vibrational levels were measured by Carlson *et al.* (*45*) using the high-frequency deflection technique. They observed some decrease in the lifetimes of rotational levels at $N' \geq 12$ in $v = 1$ F_1 and F_2 components. They found that the rotational levels up to $N' \approx 11$ of $v = 1$ have average lifetimes of 594 ± 10 ns, and for higher N' this value decreases slowly to 470 ns in F_1 (at $N' = 18$) and 405 ns in F_2 (at $N' = 16$). They also found that the $v = 2$ vibrational level has a very short lifetime of about 160 ns. From this observation, they concluded that the $v = 1$ and 2 vibrational levels of SiH are affected by

TABLE 5
Spectroscopic Constants (in cm^{-1}) for the $A^2\Delta$–$X^2\Pi$ System of SiD

Constants[a]	$X^2\Pi$ (v=0)	$X^2\Pi$ (v=1)	$A^2\Delta$ (v=0)	$A^2\Delta$ (v=1)
T_v	0	1433.0351(23)	24224.41130(93)	25456.9993(43)
A_v	142.7487(13)	143.1823(43)	3.6159(41)	3.333(14)
$10^2 \times \gamma_v$	-2.832(18)	-3.12(22)	4.725(16)	4.244(89)
$10^6 \times \gamma_{Dv}$	--	--	-5.94(39)	-9.4(42)
B_v	3.846656(35)	3.765807(81)	3.801528(37)	3.64804(13)
$10^4 \times D_v$	1.0916(12)	1.0656(86)	1.3769(12)	1.468(11)
$10^9 \times H_v$	2.98(12)	7.7(19)	-1.11(12)	--
$10^3 \times q_v$	2.236(12)	2.149(28)	--	--
$10^7 \times q_{Dv}$	-2.29(22)	--	--	--
$10^2 \times p_v$	4.375(15)	4.436(50)	--	--
$10^5 \times p_{Dv}$	-0.604(38)	-1.85(29)	--	--

[a]Numbers in parentheses are one standard deviation in last two digits.

TABLE 6
Term Values (in cm^{-1}) for the Ground and Excited States of SiH

	$A^2\Delta_{3/2}$				$A^2\Delta_{5/2}$			
	v=0		v=1		v=0		v=1	
J	e	f	e	f	e	f	e	f
1.5	24211.3990	24211.3990	25871.6302	25871.6302				
2.5	24217.3466	24217.3466	25876.8545	25876.8545	24256.3836	24256.3836	25913.8446	25913.8446
3.5	24260.4771	24260.4771	25917.4672	25917.4672	24315.0907	24315.0907	25969.0230	25969.0230
4.5	24318.3566	24318.3566	25971.9264	25971.9264	24387.9959	24387.9959	26037.5553	26037.5553
5.5	24390.8003	24390.8003	26040.0589	26040.0589	24475.1713	24475.1713	26119.4877	26119.4877
6.5	24477.6936	24477.6936	26121.7486	26121.7486	24576.5941	24576.5941	26214.7807	26214.7807
7.5	24578.9365	24578.9365	26216.8886	26216.8886	24692.2014	24692.2014	26323.3564	26323.3564
8.5	24694.4279	24694.4279	26325.3671	26325.3671	24821.9064	24821.9064	26445.1118	26445.1118
9.5	24824.0593	24824.0593	26447.0624	26447.0624	24965.6036	24965.6036	26579.9240	26579.9240
10.5	24967.7125	24967.7125	26581.8403	26581.8403	25123.1721	25123.1721	26727.6519	26727.6519
11.5	25125.2581	25125.2581	26729.5522	26729.5522	25294.4759	25294.4759	26888.1371	26888.1371
12.5	25296.5546	25296.5546	26890.0347	26890.0347	25479.3653	25479.3653	27061.2042	27061.2042
13.5	25481.4481	25481.4481	27063.1090	27063.1090	25677.6764	25677.6764	27246.6605	27246.6605
14.5	25679.7721	25679.7721	27248.5796	27248.5796	25889.2318	25889.2318	27444.2957	27444.2957
15.5	25891.3468	25891.3468	27446.2345	27446.2345	26113.8403	26113.8403	27653.8820	27653.8820
16.5	26115.9794	26115.9794	27655.8442	27655.8442	26351.2966	26351.2966	27875.1731	27875.1731
17.5	26353.4634	26353.4634	27877.1614	27877.1614	26601.3820	26601.3820	28107.9041	28107.9041
18.5	26603.5788	26603.5788	28109.9201	28109.9201	26863.8632	26863.8632	28351.7908	28351.7908
19.5	26866.0917	26866.0917	28353.8353	28353.8353	27138.4933	27138.4933	28606.5291	28606.5291
20.5	27140.7542	27140.7542	28608.6024	28608.6024	27425.0105	27425.0105	28871.7945	28871.7945
21.5	27427.3042	27427.3042	28873.8963	28873.8963	27723.1388	27723.1388	29147.2413	29147.2413
22.5	27725.4650	27725.4650	29149.3706	29149.3706	28032.5875	28032.5875	29432.5019	29432.5019
23.5	28034.9455	28034.9455	29434.6575	29434.6575	28353.0509	28353.0509	29727.1862	29727.1862
24.5	28355.4396	28355.4396	29729.3663	29729.3663	28684.2081	28684.2081	30030.8806	30030.8806
25.5	28686.6260	28686.6260	30033.0833	30033.0833	29025.7229	29025.7229	30343.1475	30343.1475
	$X^2\Pi_{1/2}$				$X^2\Pi_{3/2}$			
0.5	-56.6662	-56.5662	1913.6533	1913.7493				
1.5	-35.8208	-35.6286	1933.9353	1934.1202	94.8846	94.8922	2065.4806	2065.4877
2.5	-0.9994	-0.7293	1967.8093	1968.0696	133.8745	133.9039	2103.2626	2103.2899
3.5	47.8518	48.1804	2015.3205	2015.6381	188.3121	188.3821	2156.0227	2156.0879
4.5	110.7888	111.1539	2076.5162	2076.8700	258.0738	258.2061	2223.6471	2223.7709
5.5	187.8607	188.2386	2151.4374	2151.8050	343.0244	343.2418	2306.0098	2306.2138
6.5	279.1021	279.4693	2240.1125	2240.4711	443.0237	443.3491	2402.9783	2403.2845
7.5	384.5300	384.8634	2342.5537	2342.8810	557.9308	558.3862	2514.4177	2514.8475
8.5	504.1416	504.4191	2458.7555	2459.0300	687.6052	688.2118	2640.1926	2640.7664
9.5	637.9152	638.1157	2588.6943	2588.8954	831.9073	832.6848	2780.1669	2780.9041
10.5	785.8107	785.9142	2732.3292	2732.4374	990.6973	991.6644	2934.2037	2935.1225
11.5	947.7708	947.7586	2889.6030	2889.6000	1163.8343	1165.0084	3102.1646	3103.2817
12.5	1123.7228	1123.5769	3060.4434	3060.3118	1351.1751	1352.5724	3283.9081	3285.2395
13.5	1313.5796	1313.2831	3244.7642	3244.4876	1552.5731	1554.2089	3479.2896	3480.8498
14.5	1517.2408	1516.7775	3442.4659	3442.0287	1767.8777	1769.7661	3688.1598	3689.9625
15.5	1734.5935	1733.9485	3653.4370	3652.8247	1996.9335	1999.0876	3910.3646	3912.4224
16.5	1965.5137	1964.6726	3877.5548	3876.7535	2239.5797	2242.0117	4145.7446	4148.0691
17.5	2209.8666	2208.8158	4114.6856	4113.6826	2495.6496	2498.3708	4394.1345	4396.7362
18.5	2467.5071	2466.2340	4364.6858	4363.4690	2764.9710	2767.9916	4655.3629	4658.2514
19.5	2738.2807	2736.7735	4627.4022	4625.9605	3047.3652	3050.6945	4929.2524	4932.4363
20.5	3022.0239	3020.2715	4902.6724	4900.9956	3342.6474	3346.2938	5215.6189	5219.1058
21.5	3318.5645	3316.5567	5190.3252	5188.4039	3650.6266	3654.5974	5514.2725	5518.0689
22.5	3627.7220	3625.4495	5490.1814	5488.0071	3971.1056	3975.4073	5825.0167	5829.1280
23.5	3949.3082	3946.7626	5802.0534	5799.6187	4303.8814	4308.5192	6147.6487	6152.0794
24.5	4283.1273	4280.3012	6125.7462	6123.0445	4648.7446	4653.7229	6481.9597	6486.7132
25.5	4628.9766	4625.8634	6461.0574	6458.0832	5005.4806	5010.8024	6827.7350	6832.8133

TABLE 7

Term Values (in cm^{-1}) for the Ground and Excited States of SiD

	$A^2\Delta_{3/2}$				$A^2\Delta_{5/2}$			
	v=0		v=1		v=0		v=1	
J	e	f	e	f	e	f	e	f
1.5	24243.5288	24243.5288	25475.4858	25475.4858				
2.5	24249.2749	24249.2749	25480.7970	25480.7970	24267.9033	24267.9033	25498.7977	25498.7977
3.5	24271.5245	24271.5245	25502.1638	25502.1638	24298.8250	24298.8250	25528.4502	25528.4502
4.5	24301.6148	24301.6148	25531.0431	25531.0431	24337.0582	24337.0582	25565.1248	25565.1248
5.5	24339.3864	24339.3864	25567.2863	25567.2863	24382.7325	24382.7325	25608.9383	25608.9383
6.5	24384.7706	24384.7706	25610.8277	25610.8277	24435.8801	24435.8801	25659.9179	25659.9179
7.5	24437.7238	24437.7238	25661.6240	25661.6240	24496.5017	24496.5017	25718.0611	25718.0611
8.5	24498.2101	24498.2101	25719.6386	25719.6386	24564.5834	24564.5834	25783.3513	25783.3513
9.5	24566.1958	24566.1958	25784.8368	25784.8368	24640.1026	24640.1026	25855.7636	25855.7636
10.5	24641.6466	24641.6466	25857.1825	25857.1825	24723.0307	24723.0307	25935.2671	25935.2671
11.5	24724.5261	24724.5261	25936.6376	25936.6376	24813.3342	24813.3342	26021.8258	26021.8258
12.5	24814.7959	24814.7959	26023.1615	26023.1615	24910.9752	24910.9752	26115.3994	26115.3994
13.5	24912.4145	24912.4145	26116.7106	26116.7106	25015.9120	25015.9120	26215.9433	26215.9433
14.5	25017.3378	25017.3378	26217.2379	26217.2379	25128.0990	25128.0990	26323.4094	26323.4094
15.5	25129.5181	25129.5181	26324.6935	26324.6935	25247.4870	25247.4870	26437.7454	26437.7454
16.5	25248.9049	25248.9049	26439.0239	26439.0239	25374.0231	25374.0231	26558.8957	26558.8957
17.5	25375.4444	25375.4444	26560.1722	26560.1722	25507.6510	25507.6510	26686.8007	26686.8007
18.5	25509.0792	25509.0792	26688.0782	26688.0782	25648.3109	25648.3109	26821.3974	26821.3974
19.5	25649.7489	25649.7489	26822.6782	26822.6782	25795.9394	25795.9394	26962.6191	26962.6191
20.5	25797.3894	25797.3894	26963.9049	26963.9049	25950.4694	25950.4694	27110.3957	27110.3957
21.5	25951.9335	25951.9335	27111.6878	27111.6878	26111.8307	26111.8307	27264.6533	27264.6533
22.5	26113.3102	26113.3102	27265.9525	27265.9525	26279.9493	26279.9493	27425.3146	27425.3146
23.5	26281.4454	26281.4454	27426.6215	27426.6215	26454.7476	26454.7476	27592.2987	27592.2987
24.5	26456.2612	26456.2612	27593.6136	27593.6136	26636.1448	26636.1448	27765.5212	27765.5212
25.5	26637.6765	26637.6765	27766.8440	27766.8440	26824.0562	26824.0562	27944.8940	27944.8940
26.5	26825.6064	26825.6064	27946.2247	27946.2247	27018.3936	27018.3936	28130.3258	28130.3258
27.5	27019.9626	27019.9626	28131.6638	28131.6638	27219.0653	27219.0653	28321.7214	28321.7214
28.5	27220.6532	27220.6532	28323.0662	28323.0662	27425.9759	27425.9759	28518.9822	28518.9822
29.5	27427.5826	27427.5826	28520.3332	28520.3332	27639.0264	27639.0264	28722.0062	28722.0062
30.5	27640.6518	27640.6518	28723.3625	28723.3625	27858.1142	27858.1142	28930.6878	28930.6878
	$X^2\Pi_{1/2}$				$X^2\Pi_{3/2}$			
0.5	-63.6773	-63.6290	1368.9821	1369.0307				
1.5	-52.4937	-52.3983	1379.9377	1380.0339	83.2427	83.2437	1516.2374	1516.2383
2.5	-33.8380	-33.6975	1398.2135	1398.3552	103.0143	103.0182	1535.5806	1535.5844
3.5	-7.7104	-7.5277	1423.8088	1423.9930	130.6762	130.6859	1562.6439	1562.6531
4.5	25.8882	26.1093	1456.7224	1456.9453	166.2111	166.2302	1597.4107	1597.4287
5.5	66.9558	67.2109	1496.9519	1497.2088	209.5973	209.6301	1639.8606	1639.8915
6.5	115.4893	115.7732	1544.4938	1544.7795	260.8097	260.8609	1689.9694	1690.0179
7.5	171.4834	171.7906	1599.3425	1599.6512	319.8193	319.8942	1747.7100	1747.7810
8.5	234.9310	235.2558	1661.4909	1661.8165	386.5944	386.6985	1813.0520	1813.1507
9.5	305.8226	306.1589	1730.9295	1731.2655	461.1006	461.2394	1885.9627	1886.0946
10.5	384.1460	384.4877	1807.6463	1807.9861	543.3007	543.4800	1966.4070	1966.5776
11.5	469.8862	470.2272	1891.6272	1891.9638	633.1556	633.3812	2054.3476	2054.5627
12.5	563.0254	563.3593	1982.8551	1983.1817	730.6241	730.9016	2149.7458	2150.0108
13.5	663.5426	663.8635	2081.3103	2081.6199	835.6630	835.9981	2252.5607	2252.8813
14.5	771.4138	771.7156	2186.9707	2187.2563	948.2274	948.6254	2362.7504	2363.1319
15.5	886.6120	886.8890	2299.8112	2300.0660	1068.2706	1068.7366	2480.2713	2480.7190
16.5	1009.1072	1009.3535	2419.8045	2420.0214	1195.7440	1196.2832	2605.0784	2605.5975
17.5	1138.8662	1139.0763	2546.9205	2547.0926	1330.5977	1331.2148	2737.1258	2737.7213
18.5	1275.8530	1276.0216	2681.1271	2681.2476	1472.7797	1473.4794	2876.3662	2877.0430
19.5	1420.0287	1420.1506	2822.3896	2822.4515	1622.2366	1623.0234	3022.7513	3023.5142
20.5	1571.3516	1571.4218	2970.6713	2970.6680	1778.9133	1779.7912	3176.2320	3177.0854
21.5	1729.7774	1729.7910	3125.9337	3125.8582	1942.7530	1943.7260	3336.7579	3337.7064
22.5	1895.2588	1895.2113	3288.1361	3287.9818	2113.6973	2114.7691	3504.2780	3505.3259
23.5	2067.7464	2067.6333	3457.2364	3456.9965	2291.6860	2292.8601	3678.7407	3679.8922
24.5	2247.1880	2247.0049	3633.1909	3632.8588	2476.6574	2477.9371	3860.0935	3861.3525
25.5	2433.5291	2433.2721	3815.9546	3815.5234	2668.5481	2669.9365	4048.2833	4049.6539
26.5	2626.7130	2626.3781	4005.4811	4004.9442	2867.2933	2868.7931	4243.2568	4244.7428
27.5	2826.6808	2826.2642	4201.7231	4201.0738	3072.8264	3074.4403	4444.9603	4446.5653
28.5	3033.3712	3032.8694	4404.6325	4403.8640	3285.0793	3286.8097	4653.3397	4655.0674
29.5	3246.7211	3246.1307	4614.1603	4613.2659	3503.9824	3505.8314	4868.3410	4870.1949
30.5	3466.6654	3465.9832	4830.2572	4829.2302	3729.4648	3731.4344	5089.9102	5091.8938

predissociation. We are unable to add much to these observations since our 1–1 band is weak in intensity and the 2–2 band is almost absent in our spectra.

CONCLUSION

The emission spectra of the $A^2\Delta$–$X^2\Pi$ electronic transition of SiH and SiD have been measured with improved precision. The high-resolution measurements from spectra recorded with a Fourier transform spectrometer have been combined with the previous infrared vibration–rotation measurements (*35–38*) to extract improved molecular constants for the ground and excited states of SiH and SiD.

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