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Fourier Transform Infrared Emission Spectroscopy of SH

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The infrared emission spectrum of SH has been observed in the 1850–2800 cm^{-1} spectral region using a Fourier transform spectrometer. The molecules were excited in a microwave discharge source and the spectra have been recorded at a resolution of 0.005 cm^{-1}. The observed spectra consist of 1–0, 2–1, and 3–2 vibration–rotation bands of the $X^2\Pi_{1/2}$ spin component and 1–0, 2–1, 3–2, and 4–3 bands of the $X^2\Pi_{3/2}$ spin component. The present data were combined with the previous vibration–rotation, pure rotation, and Λ-doubling measurements in the ground state to yield an improved set of molecular constants. The principal equilibrium constants obtained from this work are: ω_e = 2696.2475(58) cm^{-1}, $\omega_e x_e$ = 48.7420(28) cm^{-1}, B_e = 9.600247(51) cm^{-1}, α_e = 0.27990(10) cm^{-1}, and r_e = 1.340614(4) Å. © 1995 Academic Press, Inc.

INTRODUCTION

There are many previous spectroscopic studies of the SH free radical. The electronic spectrum of SH has been investigated over the past several decades from the near ultraviolet to the vacuum ultraviolet regions and eight electronic transitions have been identified, all involving the ground electronic state (*1*). Initial rotational constants for the ground state were obtained from the analysis of the $A^2\Sigma^+$–$X^2\Pi$ transition (*2–4*). In addition, several electronic transitions of SH have been observed in the vacuum ultraviolet region by Morrow (*5*).

SH is a molecule of astrophysical importance (*6*). Several sulfur-containing molecules have already been observed in space (*7–9*). Since the isovalent OH radical has also been observed in the interstellar medium, there is a strong possibility that SH may also be found. So far the search for SH in the interstellar medium has been unsuccessful (*10, 11*). Precise ground state molecular parameters and Λ-doubling measurements are required for a successful search and there have been several studies of the Λ-doubling, vibration–rotation, and pure rotation transitions (*12–24*).

Transitions in the ground state have been investigated using different experimental techniques, such as electron paramagnetic resonance (*12–15*), molecular beam electric resonance (*17, 18*), and far-infrared laser magnetic resonance (*19, 20*). Meerts and Dymanus (*18*) have observed several Λ-doubling transitions using the molecular beam electric resonance technique and determined the hyperfine coupling constants and the dipole moment.

Bernath *et al.* (*21*) have reported the observation of the 1–0 vibration–rotation band of SH using a tunable difference frequency spectrometer. The SH molecules were formed in an electrical discharge through H_2S. Winkel and Davis (*22*) have observed the 1–0, 2–1, and 3–2 bands excited in a King furnace at 2300°C, but this spectrum contained only *R*-branch lines. The *P*-branch lines were either overlapped by the very strong $\Delta v = 2$ vibration–rotation overtone bands of CS or they

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TABLE I

Observed Wavenumbers (in cm^{-1}) of the Vibration–Rotation Bands of SH

$X^2\Pi_{1/2}$ 1-0

J	Ree	O-C	Rff	O-C
1.5	2644.6542	-0.0026	2644.8974	0.0016
2.5	2661.9319	-0.0012	2662.1507	-0.0012
3.5	2678.5757	-0.0004	2678.7713	-0.0010
4.5	2694.5735	0.0007	2694.7430	-0.0016
5.5	2709.9107	-0.0004	2710.0568	-0.0006
6.5	2724.5789	-0.0008	2724.6997	-0.0002
7.5	2738.5679	0.0001	2738.6609	-0.0010
8.5	2751.8665	0.0005	2751.9344	0.0004
9.5	2764.4656	0.0006	2764.5060	-0.0016
10.5	2776.3548	-0.0013	2776.3766	0.0022
11.5	2787.5323	0.0011	2787.5255	-0.0008
12.5	2797.9822	-0.0003	2797.9575	0.0017
13.5	2807.6990	-0.0036	2807.6579	0.0022
14.5			2816.6194	0.0006

$X^2\Pi_{3/2}$ 1-0

J	Ree	O-C	Rff	O-C
1.5	2642.8282	-0.0013	2642.8388	-0.0007
2.5	2659.3950	-0.0003	2659.4136	-0.0007
3.5	2675.4007	-0.0004	2675.4302	-0.0010
4.5	2690.8369	-0.0009	2690.8800	-0.0007
5.5	2705.6952	-0.0007	2705.7517	-0.0009
6.5	2719.9649	-0.0006	2720.0359	-0.0002
7.5	2733.6352	-0.0004	2733.7209	0.0004
8.5	2746.6954	-0.0004	2746.7940	-0.0002
9.5	2759.1348	0.0002	2759.2460	0.0002
10.5	2770.9409	0.0001	2771.0647	0.0010
11.5	2782.1030	0.0001	2782.2355	-0.0004
12.5	2792.6100	0.0004	2792.7502	-0.0010
13.5	2802.4501	0.0009	2802.5996	0.0018
14.5	2811.6111	0.0001	2811.7643	-0.0002
15.5	2820.0814	-0.0023	2820.2386	-0.0015
J	Pee	O-C	Pff	O-C
2.5	2551.8960	-0.0009	2551.8846	-0.0004
3.5	2532.1454	0.0011	2532.1252	-0.0004
4.5	2511.8953	0.0025	2511.8598	0.0034
J	Qef	O-C	Qfe	O-C
1.5	2598.0237	-0.0001	2598.0318	0.0006
2.5	2596.6849	0.0010	2596.7138	0.0002

TABLE I—*Continued*

$X^2\Pi_{1/2}$ 2-1

J	Ree	O-C	Rff	O-C
3.5			2579.2191	-0.0002
4.5	2594.4601	-0.0001	2594.6223	-0.0003
5.5	2609.2315	-0.0003	2609.3706	0.0011
6.5	2623.3359	-0.0009	2623.4497	0.0004
7.5	2636.7651	0.0006	2636.8540	0.0024
8.5	2649.5047	-0.0003	2649.5673	0.0002
9.5	2661.5517	0.0028	2661.5849	-0.0017
10.5	2672.8875	0.0002	2672.9006	-0.0009
11.5	2683.5080	-0.0034	2683.5080	0.0046
12.5	2693.4146	0.0013		

$X^2\Pi_{3/2}$ 2-1

J	Ree	O-C	Rff	O-C
1.5	2544.5614	-0.0045	2544.5747	-0.0004
2.5	2560.6003	-0.0010	2560.6182	-0.0006
3.5	2576.0763	0.0003	2576.1038	-0.0000
4.5	2590.9809	-0.0003	2591.0205	-0.0001
5.5	2605.3065	-0.0004	2605.3588	-0.0001
6.5	2619.0429	-0.0003	2619.1087	0.0006
7.5	2632.1803	0.0008	2632.2576	0.0003
8.5	2644.7051	0.0003	2644.7951	0.0001
9.5	2656.6069	-0.0012	2656.7111	0.0014
10.5	2667.8778	-0.0000	2667.9904	0.0006
11.5	2678.5039	0.0012	2678.6249	0.0011
12.5	2688.4716	0.0003	2688.5997	-0.0001
13.5	2697.7700	-0.0021	2697.9063	0.0001
14.5	2706.3954	0.0018	2706.5328	0.0010
15.5	2714.3246	-0.0003	2714.4671	0.0020
J	Pee	O-C	Pff	O-C
2.5	2456.2835	-0.0009		
3.5	2437.0665	-0.0011	2437.0466	0.0003
4.5	2417.3455	-0.0033	2417.3133	0.0000
5.5	2397.1367	0.0009	2397.0812	-0.0013

were too weak to be detected because of the Herman–Wallis effect (*23*). This prevented them from obtaining band origins and they reported only estimates for the Λ-doubling parameters $p + 2q$ and p_D. Benidar *et al.* (*23*) also observed the same bands and carried out intensity measurements in order to study the Herman–Wallis effect. Very recently, Morino and Kawaguchi (*24*) have observed the far-infrared pure rotational transitions of SH using a Fourier transform spectrometer.

It is surprising to note that despite such extensive interest in this molecule, reliable experimental values of the ground state vibrational constants are not available. This is mainly because the electronic transitions involving vibrational levels with $v'' > 0$ have not been studied at high resolution. Indirect estimates of the vibrational con-

TABLE I—*Continued*

$X^2\Pi_{1/2}$ 3-2

J	Ree	O-C	Rff	O-C
2.5			2464.0678	-0.0017
3.5	2479.3627	0.0001	2479.5383	-0.0002
4.5	2494.2141	0.0031	2494.3654	0.0015
5.5	2508.4074	0.0023	2508.5343	0.0001
6.5	2521.9343	0.0006	2522.0377	-0.0005
7.5	2534.7858	0.0000	2534.8673	0.0016
8.5	2546.9504	-0.0008	2547.0066	-0.0002
9.5	2558.4193	-0.0006		
10.5	2569.1809	-0.0021		

$X^2\Pi_{3/2}$ 3-2

J	Ree	O-C	Rff	O-C
4.5	2490.9976	-0.0002	2491.0342	0.0002
5.5	2504.7807	0.0004	2504.8278	-0.0000
6.5	2517.9704	-0.0002	2518.0302	0.0003
7.5	2530.5584	0.0003	2530.6296	0.0006
8.5	2542.5318	0.0001	2542.6133	-0.0005
9.5	2553.8799	-0.0005	2553.9720	-0.0008
10.5	2564.5933	0.0007	2564.6942	0.0000
11.5	2574.6551	-0.0016	2574.7649	-0.0011
12.5	2584.0603	-0.0009	2584.1771	0.0006
13.5	2592.7948	0.0006	2592.9155	0.0014
14.5	2600.8409	-0.0036	2600.9656	-0.0013

$X^2\Pi_{3/2}$ 4-3

J	Ree	O-C	Rff	O-C
3.5	2376.6704	-0.0010	2376.6944	0.0000
4.5	2390.4828	0.0007	2390.5151	0.0004
5.5	2403.7055	-0.0006	2403.7489	0.0002
6.5	2416.3329	0.0002	2416.3871	0.0013
7.5	2428.3514	-0.0000	2428.4137	-0.0009
8.5	2439.7495	-0.0011	2439.8243	0.0009
9.5	2450.5184	-0.0008	2450.6033	0.0028
10.5	2460.6464	0.0014	2460.7302	-0.0037

stants have been obtained using the known data for SH and SD and the isotopic relations.

In the present paper we report the high-resolution observation of the 1–0, 2–1, 3–2, and 4–3 infrared vibration–rotation bands using a Fourier transform spectrometer. In addition to *R*-branch lines we have also observed a few *P*- and *Q*-branch lines in the 1–0 and 2–1 bands. The present data, when combined with previous infrared vibration–rotation (*21, 22*), pure rotation (*24*), and Λ-doubling (*18*) measurements,

TABLE II

Molecular Constants (in cm^{-1}) for the $X^2\Pi$ State of SH

Constants	v=0	v=1	v=2	v=3	v=4
T_v	0.0	2599.04755(14)	5101.15171(29)	7506.20703(50)	9813.7181(11)
A_v	-376.832[a]	-377.28439(28)	-377.72698(59)	-378.14546(98)	-378.5256[b]
B_v	9.4605138(71)	9.1820255(75)	8.9040175(81)	8.6256403(95)	8.345844(31)
$10^4 \times D_v$	4.84769(34)	4.79953(32)	4.75956(29)	4.73131(32)	4.7203(19)
$10^8 \times H_v$	1.7058(31)	1.5795(27)	1.4389(23)	1.2912(27)	1.1309[b]
γ_v	-0.15263(29)	-0.14317(32)	-0.13269(35)	-0.12162(38)	-0.10962[b]
$10^5 \times \gamma_{Dv}$	1.561(110)	1.663(103)	1.773(97)	2.026(91)	2.521[b]
$10^3 \times q_v$	-9.48949(25)	-9.1080(34)	-8.7187(49)	-8.3290(59)	-7.9317[b]
$10^6 \times q_{Dv}$	1.8284(62)	1.7845(109)	1.740(15)	1.752(14)	1.752[b]
$10^{11} \times q_{Hv}$	-4.8(17)	-3.1(16)	--	--	--
p_v	0.30044822(85)	0.289061(44)	0.277258(69)	0.265211(91)	0.2490(16)
$10^4 \times p_{Dv}$	-0.3933(49)	-0.3927(46)	-0.3872(46)	-0.3954(44)	-0.3922[b]
$10^9 \times p_{Hv}$	1.27(45)	1.00(39)	--	--	--

[a] Fixed to the value in reference 20.
[b] Extrapolated value.

provide an improved set of ground state molecular constants including the equilibrium vibrational constants.

EXPERIMENTAL

The emission bands of SH were excited in an electrodeless discharge lamp with a flowing mixture of 2.24 Torr of helium and 0.36 Torr of H_2S. The lamp was operated with 80 W of power from a 2450-MHz microwave oscillator. The bands were observed with the Fourier transform spectrometer associated with the McMath-Pierce solar telescope of the National Solar Observatory at Kitt Peak. The spectrometer was operated with a CaF_2 beam splitter, Ge filters, and InSb detectors. The spectrum in the 1700–5500 cm^{-1} region was recorded at 0.005 cm^{-1} resolution by coadding 10 scans in about 1.4 hr of integration.

In addition to the molecular lines of SH, the observed spectra also contained the lines of the $\Delta v = 1$ vibration–rotation bands of CO and strong atomic lines of neutral sulfur. An analysis of the infrared transitions of S *I* will be published elsewhere (*25*). The lines of the strong vibration–rotation bands of CO have been used to calibrate the SH spectra using the measurements of Brown and Toth (*26*). The SH molecular lines have an approximate width of 0.015 cm^{-1} and stronger lines appear with a typical signal-to-noise ratio of 10. Therefore, the precision of measurement for the strong and unblended lines is expected to be better than 0.001 cm^{-1}.

TABLE III

Equilibrium Constants (in cm^{-1}) for the $X^2\Pi$ State of SH

ω_e	2696.2475(58)	$10^4 \times D_e$	4.8766(18)
$\omega_e x_e$	48.7420(28)	$10^6 \times \beta_e$	-5.98(20)
$\omega_e y_e$	0.1124(6)	$10^7 \times \delta_D$	5.23(48)
$\omega_e z_e$	-0.0163(1)	$10^3 \times q_e$	-9.6788(11)
A_e	-376.6001(19)	$10^4 \times \alpha_q$	3.774(25)
α_A	-0.4674(44)	$10^6 \times \gamma_q$	2.41(73)
γ_A	0.0072(15)	p_e	0.306009(61)
B_e	9.600247(51)	α_p	-0.01103(14)
α_e	0.27990(10)	$10^4 \times \gamma_p$	-1.82(43)
$10^3 \times \gamma_e$	0.953(54)		
$10^3 \times \delta_e$	-0.1549(81)	r_e(Å)	1.340614(4)

[a]The expressions used are:

$A_v = A_e + \alpha_A(v+1/2) + \gamma_A(v+1/2)^2$

$B_v = B_e - \alpha_e(v+1/2) + \gamma_e(v+1/2)^2 + \delta_e(v+1/2)^3$

$D_v = D_e + \beta_e(v+1/2) + \delta_D(v+1/2)^2$

$q_v = q_e + \alpha_q(v+1/2) + \gamma_q(v+1/2)^2$

$p_v = p_e + \alpha_p(v+1/2) + \gamma_p(v+1/2)^2$.

The spectral line positions have been measured using a data reduction program called PC-DECOMP developed at the National Solar Observatory. The peak positions were determined by fitting a Voigt lineshape function to each spectral feature. The branches in the different bands were identified using a color Loomis–Wood program running on a PC computer.

RESULTS AND DISCUSSION

Since the present excitation source is much cooler than the carbon furnace used by Winkle and Davis (*22*), we observed only the lower J transitions ($J < 15.5$). The SH molecular lines were easily identified by their characteristic doublet structure caused by Λ-doubling. The assignment of lines in different bands was straightforward, using the previous infrared measurements of Bernath *et al.* (*21*) and Winkel and Davis (*22*). A few low-J P and Q lines were also found but the higher-J P lines are too weak to be observed, due to the Herman–Wallis effect. Some of these P- and Q-branch lines were also observed by Bernath *et al.* (*21*) in the 1–0 band. In addition to the bands observed by Winkel and Davis (*22*), we have also observed the 4–3 band for the $X^2\Pi_{3/2}$ spin component. The corresponding $X^2\Pi_{1/2}$ subband could not be measured due to its weaker intensity. In general the $X^2\Pi_{1/2}$ subbands are half the intensity of the $X^2\Pi_{3/2}$ subbands. The observed transition wavenumbers and their rotational assignments are provided in Table I.

The lines of the different bands were simultaneously fit using the effective N^2 Hamiltonian of Brown *et al.* (*27*) for a $^2\Pi$ state. The matrix elements for this Hamiltonian are provided by Amiot *et al.* (*28*). In this fit the observed wavenumbers of all the bands, together with the infrared line positions of Bernath *et al.* (*21*) and Winkel and Davis (*22*), the pure rotational transitions of Morino and Kawaguchi (*24*), and the

TABLE IV

Term Values (in cm^{-1}) for the v = 0, 1, 2, 3, and 4 Vibrational Levels of SH($^2\Pi$)

$X^2\Pi_{1/2}$

	v=0		v=1		v=2		v=3		v=4	
J	e	f	e	f	e	f	e	f	e	f
0.5	207.3470	207.6284	2806.0596	2806.3304	5307.8241	5308.0839	7712.5265	7712.7750	10019.6637	10019.8968
1.5	236.2655	236.8244	2834.1080	2834.6459	5335.0051	5335.5213	7738.8403	7739.3341	10045.1090	10045.5724
2.5	284.5330	285.3617	2880.9223	2881.7202	5380.3708	5381.1367	7782.7573	7783.4904	10087.5738	10088.2618
3.5	352.1118	353.1990	2946.4661	2947.5135	5443.8856	5444.8915	7844.2429	7845.2062	10147.0241	10147.9284
4.5	438.9489	440.2801	3030.6879	3031.9712	5525.4994	5526.7328	7923.2482	7924.4300	10223.4119	10224.5218
5.5	544.9764	546.5342	3133.5217	3135.0247	5625.1481	5626.5938	8019.7104	8021.0967	10316.6758	10317.9784
6.5	670.1120	671.8766	3254.8875	3256.5916	5742.7535	5744.3942	8133.5532	8135.1279	10426.7407	10428.2211
7.5	814.2597	816.2092	3394.6917	3396.5765	5878.2243	5880.0409	8264.6872	8266.4324	10553.5187	10555.1604
8.5	977.3100	979.4212	3552.8275	3554.8710	6031.4562	6033.4281	8413.0101	8414.9066	10696.9090	10698.6943
9.5	1159.1412	1161.3897	3729.1760	3731.3552	6202.3326	6204.4382	8578.4073	8580.4348	10856.7989	10858.7088
10.5	1359.6196	1361.9803	3923.6062	3925.8974	6390.7250	6392.9419	8760.7526	8762.8900	11033.0635	11035.0785
11.5	1578.6001	1581.0474	4135.9757	4138.3546	6596.4935	6598.7988	8959.9080	8962.1339	11225.5665	11227.6665
12.5	1815.9265	1818.4350	4366.1313	4368.5737	6819.4872	6821.8581	9175.7246	9178.0173	11434.1603	11436.3252
13.5	2071.4325	2073.9770	4613.9090	4616.3909	7059.5447	7061.9582	9408.0429	9410.3808	11658.6867	11660.8962
14.5	2344.9415	2347.4972	4879.1351	4881.6327	7316.4941	7318.9277	9656.6929	9659.0547	11898.9767	11901.2108
15.5	2636.2674	2638.8101	5161.6257	5164.1160	7590.1540	7592.5856	9921.4946	9923.8592	12154.8511	12157.0902
16.5	2945.2146	2947.7211	5461.1877	5463.6482	7880.3329	7882.7412	10202.2580	10204.6052	12426.1209	12428.3459
17.5	3271.5787	3274.0263	5777.6187	5780.0278	8186.8303	8189.1945	10498.7837	10501.0938	12712.5870	12714.7794
18.5	3615.1461	3617.5134	6110.7072	6113.0443	8509.4363	8511.7367	10810.8630	10813.1173	13014.0409	13016.1830
19.5	3975.6949	3977.9615	6460.2332	6462.4786	8847.9322	8850.1500	11138.2780	11140.4586	13330.2645	13332.3396
20.5	4352.9947	4355.1413	6825.9680	6828.1032	9202.0908	9204.2080	11480.8020	11482.8918	13661.0308	13663.0229
21.5	4746.8071	4748.8155	7207.6749	7209.6822	9571.6760	9573.6760	11838.1993	11840.1825	14006.1036	14007.9978
22.5	5156.8857	5158.7390	7605.1088	7606.9720	9956.4438	9958.3108	12210.2259	12212.0877	14365.2379	14367.0203
23.5	5582.9766	5584.6589	8018.0168	8019.7208	10356.1418	10357.8614	12596.6294	12598.3561	14738.1799	14739.8377
24.5	6024.8182	6026.3151	8446.1387	8447.6694	10770.5100	10772.0688	12997.1493	12998.7283	15124.6674	15126.1891
25.5	6482.1418	6483.4401	8889.2064	8890.5513	11199.2806	11200.6665	13411.5170	13412.9369	15524.4300	15525.8049
26.5	6954.6721	6955.7596	9346.9451	9348.0925	11642.1784	11643.3805	13839.4561	13840.7068	15937.1888	15938.4078
27.5	7442.1266	7442.9926	9819.0728	9820.0126	12098.9209	12099.9296	14280.6829	14281.7556	16362.6572	16363.7122
28.5	7944.2167	7944.8519	10305.3069	10306.0242	12569.2188	12570.0257	14734.9062	14735.7931	16800.5409	16801.4249
29.5	8460.6478	8461.0439	10805.3346	10805.8336	13052.7760	13053.3740	15201.8277	15202.5225	17250.5376	17251.2452
30.5	8991.1194	8991.2694	11318.8729	11319.1413	13549.2899	13549.6733	15681.1423	15681.6399	17712.3382	17712.8651
31.5	9535.3255	9535.2240	11845.6089	11845.6417	14058.4518	14058.6162	16172.5381	16172.8349	18185.6260	18185.9692
32.5	10092.9551	10092.5978	12385.2305	12385.0240	14579.9471	14579.8894	16675.6970	16675.7907	18670.0776	18670.2356
33.5	10663.6925	10663.0763	12937.4203	12936.9720	15113.4555	15113.1741	17190.2949	17190.1844	19165.3628	19165.3352
34.5	11247.2173	11246.3408	13501.8561	13501.1651	15658.6517	15658.1463	17716.0016	17715.6874	19671.1450	19670.9331
35.5	11843.2055	11842.0683	14078.2113	14077.2780	16215.2052	16214.4770	18252.4815	18251.9655	20187.0814	20186.6877

$X^2\Pi_{3/2}$

	v=0		v=1		v=2		v=3		v=4	
J	e	f	e	f	e	f	e	f	e	f
1.5	-160.7296	-160.7259	2437.2965	2437.2999	4938.3843	4938.3875	7342.4331	7342.4360	9648.9515	9648.9541
2.5	-114.6003	-114.5856	2482.1000	2482.1136	4981.8624	4981.8750	7384.5821	7384.5937	9689.7626	9689.7731
3.5	-50.0486	-50.0121	2544.7949	2544.8287	5042.7012	5042.7324	7443.5594	7443.5881	9746.8660	9746.8922
4.5	32.8975	32.9695	2625.3524	2625.4191	5120.8710	5120.9326	7519.3347	7519.3913	9820.2308	9820.2825
5.5	134.2015	134.3255	2723.7352	2723.8501	5216.3336	5216.4398	7611.8688	7611.9665	9909.8167	9909.9060
6.5	253.8188	254.0133	2839.8975	2840.0780	5329.0422	5329.2091	7721.1139	7721.2676	10015.5748	10015.7153
7.5	391.6953	391.9809	2973.7842	2974.0494	5458.9407	5459.1861	7847.0128	7847.2390	10137.4466	10137.6534
8.5	547.7677	548.1661	3125.3310	3125.7013	5605.9637	5606.3067	7989.4988	7989.8151	10275.3641	10275.6535
9.5	721.9627	722.4966	3294.4635	3294.9603	5770.0358	5770.4962	8148.4954	8148.9205	10429.2494	10429.6385
10.5	914.1965	914.8892	3481.0973	3481.7424	5951.0715	5951.6700	8323.9162	8324.4690	10599.0145	10599.5210
11.5	1124.3750	1125.2498	3685.1373	3685.9528	6148.9751	6149.7323	8515.6641	8516.3641	10784.5612	10785.2029
12.5	1352.3930	1353.4731	3906.4780	3907.4857	6363.6401	6364.5766	8723.6318	8724.4982	10985.7805	10986.5754
13.5	1598.1341	1599.4423	4145.0025	4146.2242	6594.9492	6596.0855	8947.7012	8948.7532	11202.5531	11203.5190
14.5	1861.4711	1863.0295	4400.5834	4402.0400	6842.7745	6844.1305	9187.7435	9188.9996	11434.7489	11435.9030
15.5	2142.2652	2144.0952	4673.0821	4674.7939	7106.9771	7108.5718	9443.6190	9445.0973	11682.2269	11683.5858
16.5	2440.3668	2442.4888	4962.3488	4964.3354	7387.4070	7389.2590	9715.1772	9716.8949	11944.8352	11946.4151
17.5	2755.6151	2758.0484	5268.2233	5270.5028	7683.9038	7686.0304	10002.2571	10004.2304	12222.4115	12224.2275
18.5	3087.8384	3090.6011	5590.5341	5593.1239	7996.2960	7998.7136	10304.6866	10306.9309	12514.7824	12516.8487
19.5	3436.8544	3439.9634	5929.0993	5932.0156	8324.4018	8327.1256	10622.2834	10624.8128	12821.7642	12824.0939
20.5	3802.4702	3805.9412	6283.7266	6286.9842	8668.0288	8671.0728	10954.8545	10957.6821	13143.1624	13145.7676
21.5	4184.4826	4188.3299	6654.2135	6657.8260	9026.9745	9030.3516	11302.1967	11305.3343	13478.7722	13481.6637
22.5	4582.6788	4586.9153	7040.3475	7044.3271	9401.0265	9404.7480	11664.0969	11667.5550	13828.3787	13831.5662
23.5	4996.8359	5001.4732	7441.9064	7446.2641	9789.9624	9794.0386	12040.3319	12044.1198	14191.7570	14195.2488
24.5	5426.7220	5431.7702	7858.6587	7863.4040	10193.5506	10197.9901	12430.6692	12434.7946	14568.6721	14572.4752
25.5	5872.0959	5877.5640	8290.3638	8295.5049	10611.5500	10616.3602	12834.8664	12839.3360	14958.8796	14962.9997
26.5	6332.7082	6338.6033	8736.7722	8742.3158	11043.7109	11048.8977	13252.6726	13257.4913	15362.1257	15366.5670
27.5	6808.3007	6814.6289	9197.6261	9203.5776	11489.7746	11495.3426	13683.8274	13688.9989	15778.1472	15782.9126
28.5	7298.6076	7305.3734	9672.6597	9679.0229	11949.4744	11955.4265	14128.0624	14133.5888	16206.6722	16211.7631
29.5	7803.3554	7810.5619	10161.5991	10168.3766	12422.5354	12428.8732	14585.1003	14590.9824	16647.4200	16652.8364
30.5	8322.2636	8329.9124	10664.1633	10671.3561	12908.6750	12915.3987	15054.6563	15060.8931	17100.1015	17105.8418
31.5	8855.0446	8863.1360	11180.0643	11187.6719	13407.6036	13414.7115	15536.4375	15543.0269	17564.4193	17570.4805
32.5	9401.4049	9409.9375	11709.0073	11717.0278	13919.0241	13926.5132	16030.1439	16037.0818	18040.0683	18046.4458
33.5	9961.0446	9970.0159	12250.6913	12259.1213	14442.6332	14450.4988	16535.4681	16542.7492	18526.7356	18533.4232
34.5	10533.6588	10543.0645	12804.8095	12813.6440	14978.1209	14986.3570	17052.0963	17059.7134	19024.1010	19031.0911
35.5	11118.9370	11128.7716	13371.0494	13380.2821	15525.1717	15533.7703	17579.7079	17587.6523	19531.8374	19539.1207

hyperfine-free Λ-doubling transitions of Meerts and Dymanus (*17, 18*), were combined with appropriate weights. The data of Winkel and Davis extend to higher J values up to $J = 33.5$ while the pure rotational transitions of SH, observed by Morino and Kawaguchi (*24*), extend up to $J = 13.5$. The combined infrared, far-infrared, and microwave data permit us to obtain the molecular parameters of SH from an unconstrained free fit. The lines of our present measurements were given weights based on their signal-to-noise ratio and the extent of blending. The $v = 0$ spin–orbit interaction constant A_0 was fixed to -376.832 cm^{-1} as determined by Ashworth and Brown (*20*) from a reanalysis of the $A^2\Sigma^+$–$X^2\Pi$ data of Ramsay (*3*). Since the 4–3 band was observed only for the $X^2\Pi_{3/2}$ spin component, the spin–orbit constant A_4 could not be determined independently and was fixed to -378.5256 cm^{-1}. This value was set by extrapolation of the constants A_0, A_1, A_2, and A_3. The H, γ, γ_D, q, and q_D parameters for $v = 4$ were also held fixed to values obtained by extrapolation. The constants obtained from this fit are provided in Table II. The values in the parentheses represent one standard deviation in the last digit. The molecular constants for $v = 0$ (Table II) are slightly different from those reported by Morino and Kawaguchi (*24*) because our data set includes a large number of high-J vibration–rotation lines measured by Winkel and Davis (*22*).

The molecular parameters obtained for the vibrational levels up to $v = 4$ (Table II) have enabled us to determine the equilibrium constants for the ground state which are provided in Table III. The equilibrium vibrational constants ω_e, $\omega_e x_e$, $\omega_e y_e$, and $\omega_e z_e$ determined by an exact fit are 2696.2475(58), 48.7420(28), 0.1124(6), and $-0.0163(1)$ cm^{-1}. The errors quoted for these constants are not statistical estimates but are obtained by the propagation of errors. The equilibrium rotational constant $B_e = 9.600247(51)$ cm^{-1} provides the equilibrium internuclear bond length of 1.340614(4) Å, which can be compared with the r_e value of 0.96966 Å for the $X^2\Pi$ state of the isoelectronic molecule OH (*1*). The molecular parameters for the different vibrational levels obtained in this work have been used to evaluate the corresponding term values, which are provided in Table IV. These predictions may prove useful in the infrared and microwave spectroscopy of this molecule.

SUMMARY

We have applied infrared Fourier transform emission spectroscopy to the observation of the vibration–rotation bands of SH in its ground ($X^2\Pi$) state. The spectra have been recorded at 0.005 cm^{-1} resolution. The present high-resolution data for the 1–0, 2–1, 3–2, and 4–3 bands, combined with the previous infrared and Λ-doubling measurements, have been used to determine a much improved set of the equilibrium constants for the ground state. In particular, our work provides the first direct determination of the equilibrium vibrational constants. The present spectroscopic data should prove useful in searches for SH in the interstellar medium.

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