Observation of the $v = 1 \leftarrow 0$ Band of SH ($X^2\Pi$) with a Difference Frequency Laser

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The fundamental vibration–rotation band of SH ($X^2\Pi$) has been studied in absorption at Doppler-limited resolution with an estimated accuracy of 0.002 cm⁻¹. The band origin ($\nu_0 = 2598.7675 \pm 0.0003$ cm⁻¹) and the molecular constants for the excited vibrational state ($v = 1$), as well as improved molecular constants for the ground vibrational state, have been determined in a least-squares fit.

INTRODUCTION

Many spectroscopic studies of the SH free radical have been made. Flash photolysis of H_2S was used to observe the $A^2\Sigma^+-X^2\Pi_i$ absorption spectrum (*1–3*). Electron paramagnetic resonance spectra of SH for the $J = 3/2$ and $J = 5/2$ rotational levels of the $^2\Pi_{3/2}$ state have been analyzed (*4–9*). Meerts and Dymanus (*10*), using the molecular beam electric resonance technique, have observed several Λ-doubling transitions in both the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ states. Davies *et al.* (*11*) have observed the $J = 5/2 \leftarrow 3/2$ transition for $X^2\Pi_{3/2}$ with far-infrared laser magnetic resonance. Vacuum ultraviolet absorption spectra have been recorded by Morrow (*12*).

In spite of this considerable experimental activity, there are almost no data for $v = 1$ of the ground state of SH. The optical emission spectrum of the $v = 0-1$, $A-X$ band has not been observed at high resolution, although low resolution laser induced fluorescence observations have been made (*13, 14*). Pathak and Palmer (*15*), however, were able to record the $v = 0-1$, $A-X$ band of SD in emission from a low-pressure flame made by reacting $SOCl_2$ and $CDCl_3$ with potassium vapor, and estimated ν_0 for SH to be 2591.8 cm⁻¹. More recently, SD has been observed by midinfrared laser magnetic resonance (*16, 17*). The predicted ν_0 from the electronic emission spectrum was 2582 cm⁻¹ (*2*). There has also been an infrared absorption measurement on argon matrix isolated SH (observed $\nu_0 = 2540.8$ cm⁻¹) (*18*).

Employing a tunable infrared radiation from a difference frequency laser system (*19*), we have detected the $v = 1 \leftarrow 0$ vibration–rotation transition of SH. The SH radical was produced by an electric discharge through H_2S in a multiple reflection cell. The observed lines were simultaneously fit with the accurate Λ-doubling transition frequencies of Meerts and Dymanus (*10*). The parameters in the $v = 1$ and $v = 0$ states allowed the estimation of equilibrium molecular constants of SH.

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EXPERIMENTAL DETAILS

The difference frequency laser system and multiple-reflection discharge cell used in the present work have been described previously (20) in detail. Briefly, CW tunable infrared radiation was generated by mixing the output from a tunable dye laser (Coherent Radiation CR-699-21) and that from a single-mode argon ion laser (Spectra Physics 165) in a temperature controlled $LiNbO_3$ oven (Chromatix). The infrared beam was passed 16 times through a 2-m discharge cell. About 1 m of the cell was wound with a coil for Zeeman modulation. Both frequency and Zeeman modulation were employed. Zeeman modulation was essential to distinguish paramagnetic lines of SH $X^2\Pi_{3/2}$ from diamagnetic absorption features of H_2S and SH $X^2\Pi_{1/2}$.

The estimated band origin of SH (~ 2592 cm^{-1} (15)) served to guide our initial search for $^2\Pi_{3/2}$ transitions using Zeeman modulation. A 15-mA DC discharge in 500 mTorr of H_2S was used. A doublet was observed at 2642.83 cm^{-1}. The signal was optimized at a discharge current of 30 mA in a 1:1 mixture of H_2 and H_2S at 800 mTorr. Under these conditions there was considerable deposition of sulphur on the wall of the cell. A second doublet was located at 2659.4 cm^{-1}. These lines were assigned as $J = 3.5 \leftarrow 2.5$ Λ-doublet while the lines at 2642.83 were $J = 2.5 \leftarrow 1.5$. Other lines were then predicted and measured using, mainly, frequency modulation. The reference molecules used for infrared wavenumber calibration were H_2CO (21), N_2O (22), and H_2S (23). Relative frequency calibration was accomplished with markers from a 300-MHz Fabry–Perot etalon. Our absolute accuracy was estimated to be about ± 0.002 cm^{-1}.

ANALYSIS

The Hamiltonian appropriate for a $^2\Pi$ state has been derived by many authors. The Hamiltonian (24) used in the present analysis was

$$\left\langle ^2\Pi_{3/2}, J, \frac{e}{f} | H_{\text{rot}} | ^2\Pi_{3/2}, J, \frac{e}{f} \right\rangle$$

$$= T_v + A_v/2 + q/2 - D_v + (B_v - D_v + q/2 + A_D/2)(x^2 - 2) - D_v(x^2 - 2)^2$$

$$\left\langle ^2\Pi_{1/2}, J, \frac{e}{f} | H_{\text{rot}} | ^2\Pi_{1/2}, J, \frac{e}{f} \right\rangle = T_v - A_v/2 + D_v + (B_v - D_v - A_D/2)x^2$$

$$- D_v x^4 + [p + p_D(x^2 - 1/4)](1 \mp x)/2 + q(1 \mp x)^2/2$$

$$\left\langle ^2\Pi_{3/2}, J, \frac{e}{f} | H_{\text{rot}} | ^2\Pi_{1/2}, J, \frac{e}{f} \right\rangle$$

$$= [-B_v - p/4 - p_D(x^2 - 1/4)/4 - q(1 \mp x)/2 + 2D_v(x^2 - 1)](x^2 - 1)^{1/2}.$$

where $x = J + 1/2$ and the upper (lower) sign refers to the e (f) parity. It was not possible to determine A_v for both the $v = 0$ and $v = 1$ states because only $\Delta\Omega = 0$ transitions were observed. The value of A_0 was determined by refitting the optical $A^2\Sigma^+$–$X^2\Pi$ 0–0 band, recorded by Ramsay (2), with our Hamiltonian. The A_D and

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TABLE I

Observed Wavenumbers of the $v = 1 \leftarrow 0$ Band of SH ($X^2\Pi$) (in cm^{-1})

Transition		obs	(o-c)×10^4
$^2\Pi_{3/2} - {}^2\Pi_{3/2}$			
P(4.5)	f	2511.8627	8
	e	2511.9000	0
P(3.5)	f	2532.1253	-12
	e	2532.1497	4
P(2.5)	f	2551.8851	-3
	e	2551.8959	-8
Q(2.5)	ef	2596.6865	5
	fe	2596.7142	-2
Q(1.5)	ef	2598.0223	-2
	fe	2598.0301	5
R(1.5)	e	2642.8324	22
	f	2642.8420	19
R(2.5)	e	2659.3954	-6
	f	2659.4152	1
R(3.5)	e	2675.4018	0
	f	2675.4306	-14
R(4.5)	e	2690.8371	-14
	f	2690.8803	-11
R(5.5)	e	2705.6962	-3
R(6.5)	e	2719.9655	-2
	f	2720.0362	-5
R(7.5)	e	2733.6365	8
	f	2733.7221	11
R(8.5)	e	2746.6961	7
	f	2746.7945	-4
R(9.5)	e	2759.1326	-13
	f	2759.2485	16
R(10.5)	e	2770.9403	6
	f	2771.0645	-9
$^2\Pi_{1/2} - {}^2\Pi_{1/2}$			
P(3.5)	e	2528.8111	-9
P(2.5)	f	2549.2915	8
	e	2549.5781	20
P(1.5)	e	2569.7950	-4
Q(0.5)	ef	2598.4307	-16
	fe	2598.9841	-15
R(1.5)	e	2644.6590	18
	f	2644.8979	0
R(2.5)	e	2661.9342	6
	f	2662.1532	-3
R(3.5)	e	2678.5768	1
	f	2678.7726	-8
R(4.5)	e	2694.5731	-3
	f	2694.7453	1
R(5.5)	e	2709.9106	-10
	f	2710.0578	4
R(6.5)	e	2724.5800	0
	f	2724.7006	12
R(7.5)	e	2738.5690	9
R(8.5)	e	2751.8658	-5
	f	2751.9335	-7

γ parameters could not be determined simultaneously (*25*). Therefore γ was set to zero and A_D was taken as an adjustable parameter. Meerts and Dymanus (*10*) precisely measured six Λ-doubling splittings for $v = 0$ of SH by the molecular beam electric resonance technique. Their data were corrected for the hyperfine splittings and were included in the least-squares fit.

TABLE II

Molecular Beam Electric Resonance Data of Meerts and Dymanus (*11*) Corrected for
Hyperfine Structure (Transitions Occur between Λ-Doubling Components)

Ω	J	frequency (MHz)
1.5	1.5	111.523 (-4)[a]
1.5	2.5	442.566 (-9)
1.5	3.5	1094.341 (-5)
1.5	4.5	2158.533 (11)
1.5	5.5	3715.214 (-3)
0.5	0.5	8436.097 (0)

[a]Obs.-calc. in kHz using the constant of

Table III.

Table I lists the wavenumbers and assignments of the fundamental vibration–
rotation band of SH. Only transitions with $\Delta\Omega = 0$ were observed ($^2\Pi_{1/2}-^2\Pi_{1/2}$,
$^2\Pi_{3/2}-^2\Pi_{3/2}$). Most of the lines belong to the R branch, and the Q-branch lines were
observed only for low-J states, because of rapidly decreasing line strengths. Relatively

TABLE III

Spectroscopic Constants for $v = 0, 1$ of $X^2\Pi$ State of SH (in cm^{-1})

	v=0	v=1
B_v	9.464308(56)[a]	9.185702(63)
$D_v \times 10^4$	4.939(21)	4.861(16)
A_v	-376.834(8)[b]	-377.28354(46)
$A_D \times 10^4$	0.96(81)	2.38(64)
P_v	0.3006270(33)	0.29036(19)
$P_{Dv} \times 10^4$	-1.822(19)	-1.525(31)
$q_v \times 10^3$	-9.54621(72)	-9.136(13)
ν_0	2598.7675(3)	

[a]Uncertainty estimates (one standard deviation)

are quoted in parenthesis.

[b]Fixed in the final fit. The value for A_0

along with the corresponding uncertainty, was

obtained in a preliminary simultaneous fit of

Ramsay's $A^2\Sigma^+-X^2\Pi$ 0-0 data (Ref. 3) and our

infrared data.

TABLE IV

Equilibrium Molecular Constants for $X^2\Pi$ State of SH (in cm^{-1}, except for r_e Which Is in Å)
(One Standard Deviation is Quoted in Parentheses)

B_e	9.603611(71)[a]	A_e[b]	−367.609(8)
α_e	0.278606(85)[a]	α_A	0.4495(5)
$D_e \times 10^4$	4.978(25)	P_e	−0.30576(10)
$\beta_e \times 10^4$	−0.078(26)	α_p	0.01027(19)
ω_e	2695.8(40)	$q_e \times 10^3$	9.7513(7)
$\omega_e x_e$	48.5(20)	$\alpha_q \times 10^3$	−0.410(13)
	r_e 1.340379(5)[a] Å		

[a] Uncertainty estimates are too small because of the neglect of γ_e in B_v expansion.

[b] $X_v = X_e - \alpha_x(v+\frac{1}{2})$, X=A,p,q.

few *P*-branch lines were observed because of experimental difficulties involved in generating the infrared radiation near the LiNbO$_3$ phonon absorption edge (about 2400 cm^{-1}). Table II reproduces the frequencies for the Λ-type doubling transitions

TABLE V

Term Values for the $v = 0$ and $v = 1$ States of SH ($X^2\Pi$) (in cm^{-1})

J		$v=0$ $^2\Pi_{3/2}$	$^2\Pi_{1/2}$	$v=1$ $^2\Pi_{3/2}$	$^2\Pi_{1/2}$
0.5	e		197.8808		2796.5944
	f		198.1622		2796.8664
1.5	e	−170.1952	226.7990	2427.8310	2824.6423
	f	−170.1915	227.3570	2427.8344	2825.1819
2.5	e	−124.0657	275.0661	2472.6350	2871.4563
	f	−124.0510	275.8912	2472.6487	2872.2549
3.5	e	−59.5143	342.6442	2535.3303	2936.9998
	f	−59.4778	343.7224	2535.3641	2938.0447
4.5	e	23.4302	429.4797	2615.8875	3021.2209
	f	23.5022	430.7928	2615.9542	3022.4958
5.5	e	124.7307	535.5035	2714.2687	3124.0531
	f	124.8547	537.0297	2714.3837	3125.5379
6.5	e	244.3411	660.6321	2830.4272	3245.4151
	f	244.5356	662.3461	2830.6078	3247.0871
7.5	e	382.2057	804.7673	2964.3068	3385.2121
	f	382.4913	806.6410	2964.5723	3387.0455
8.5	e	538.2593	967.7973	3115.8414	3543.3354
	f	538.6578	969.8002	3116.2124	3545.3024
9.5	e	712.4257	1149.5973	3284.9547	3719.6636
	f	712.9599	1151.6967	3285.4527	3721.7344
10.5	e	904.6181	1350.0295	3471.5596	3914.0627
	f	905.3113	1352.1911	3472.2068	3916.2059
11.5	e	1114.7380	1568.9438	3675.5578	4126.3863
	f	1115.6138	1571.1322	3676.3767	4128.5695
12.5	e	1342.6753	1806.1786	3896.8394	4356.4766
	f	1343.7571	1808.3569	3897.8526	4358.6660

together with the residuals of our final least-squares fit. The molecular constants thus obtained are listed in Table III.

DISCUSSION

The observation of both $v = 1$ and $v = 0$ allows the determination of equilibrium constants by assuming a linear vibrational dependence. The equilibrium molecular constants are presented in Table IV. For a hydride, like SH, the neglect of the γ term $((v + 1/2)^2)$ in the vibrational expansion of the B_v constant introduces considerable uncertainty in B_e and r_e. Therefore the quoted uncertainties are only lower limits.

The ω_e and $\omega_e x_e$ values were derived by using $\nu_0 = 1885.8$ cm^{-1} for SD (15–17) and the isotopic relationships (neglecting $\omega_e y_e$) (26). These values for ω_e (=2695.8(20) cm^{-1}) and $\omega_e x_e$ (=48.5(10) cm^{-1}) differ somewhat from the estimates of Pathak and Palmer ($\omega_e = 2711.6$ cm^{-1}, $\omega_e x_e = 59.9$ cm^{-1}) and those of Ramsay ($\omega_e = 2702$ cm^{-1}, $\omega_e x_e = 60$ cm^{-1}). For lack of data, these authors were obliged to use the rather unreliable relationship between $\omega_e x_e$ and the dissociation energy D_0 predicted by the Morse potential (26). The value of D_e predicted by the Kratzer relationship ($D_e = 4B_e^3/\omega_e^2$) is 4.88×10^{-4}cm^{-1} in reasonable agreement with the experimental $D_e = 4.978(25) \times 10^{-4}$ cm^{-1}.

There have been a number of ab initio calculations on the $X^2\Pi$ state of SH (27–29). The best theoretical estimate of the equilibrium properties of SH is that of Meyer and Rosmus (28). They predict $B_e = 9.55$ cm^{-1}, $\alpha_e = 0.285$ cm^{-1}, $\omega_e = 2676.4$ cm^{-1}, $\omega_e x_e = 50.0$ cm^{-1}, and $r_e = 1.344$ Å, in reasonable agreement with the values of Table IV. Cooper and Veseth (29) predict $p_0 = 0.3170$ cm^{-1}, $q_0 = -0.01019$ cm^{-1}, $p_D = -2.97 \times 10^{-5}$ cm^{-1}, and $D_0 = 4.93 \times 10^{-4}$ cm^{-1} at the ab initio SCF level. Considering the lack of configuration interaction, these numbers compare well with those of Table II.

In conclusion, we have observed the infrared vibration–rotation spectrum of SH. Accurate molecular constants for $v = 1$ were derived and used to estimate equilibrium molecular constants. To aid in the far-infrared and millimeter wave spectroscopy of SH, a set of term values has been provided in Table V. The infrared spectrum may assist the extraterrestrial detection of SH.

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