### THE OBSERVATION OF THE HIGH-RESOLUTION INFRARED SPECTRUM OF SH3

T. NAKANAGA and T. AMANO

Herzberg Institute of Astrophysics, National Research Council, Ottawa, Ontario, Canada K1A 0R6

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The  $v_3$  fundamental band of SH<sub>3</sub><sup>+</sup> has been observed in absorption in a hollow cathode discharge with a difference frequency laser system. The molecular constants of the ground state have been determined through a fit of the ground-state combination differences (from the observed transition frequencies). The band is perturbed and a preliminary analysis is made to obtain the molecular constants for the excited state. The lowest rotational transition frequency useful for astrophysical searches is predicted to be 293464(3) MHz.

### 1. Introduction

 $SH_3^+$  is little known spectroscopically, while its isovalent ion  $H_3O^+$  has been a subject of extensive spectroscopic interest in recent several years [1]. Christe [2] observed the infrared and Raman spectra of the  $SH_3^+SbF_6^-$  salt, and measured all the infrared active fundamentals as well as an overtone. There has been, however, no high-resolution spectroscopic detection of  $SH_3^+$  until our detection with a difference frequency laser spectrometer system.

Mass-spectroscopically,  $SH_3^+$  is a rather ubiquitous ion [3], and the absolute proton affinity of  $H_2S$ was measured with ion cyclotron resonance technique to be 173 kcal/mol which compares with 170 kcal/mol for  $H_2O$  [4,5]. There are a fairly large number of ab initio calculations of various physical properties of this ion, including the molecular structure [6–11], the vibrational frequencies [11–13], the proton affinity [6–12], the barrier to the inversion [6,9–11], and the electric dipole moment [11].

Hydrogen sulfide  $H_2S$  has been found to be abundant in the interstellar clouds especially in the Orion plateau [14]. Since ion-molecule reactions play an important role in the chemistry in interstellar space, it is important to detect the related ionic species to deepen our understanding of the sulfur chemistry in the clouds. The observation of  $SH_3^+$  in the same interstellar clouds seems to be promising in view of the large proton affinity of  $H_2S$  [15].

## 2. Experiment

The experimental arrangement is similar to that described in our previous work [16].  $SH_3^+$  was generated in a hollow cathode discharge through a mixture of  $H_2S(\approx 30 \text{ mTorr})$  and  $H_2(\approx 300 \text{ mTorr})$ . The discharge was cooled by flowing cooled methanol  $(-50 \text{ to } -60^\circ\text{C})$  through copper tubing wound around the copper cathode. The discharge was modulated to attain high sensitivity as described in ref. [16]. The modulation frequency was 19 kHz, and the optimum discharge current (level to peak) was found to be about 400 mA. Fig. 1 shows an example of a section of the infrared spectrum of  $SH_3^+$ . The transition wavenumbers were measured using frequency



Fig. 1. The Q-branch lines of SH<sub>3</sub><sup>+</sup> around 2525 cm<sup>-1</sup>.

markers with a 150 MHz interval from a temperature stabilized etalon together with lines of  $N_2O$  as a reference gas [17]. The accuracy of the wavenumber measurement is estimated to be better than 0.001 cm<sup>-1</sup>.

### 3. Observation of the spectra

The S-H stretching vibrational bands were expected to locate around 2550 cm<sup>-1</sup> from the infrared spectrum of the salt [2] and ab initio MO calculations [11,13,18]. We started the measurement from 2600 cm<sup>-1</sup> downwards, and found at first a series of R-branch lines of a perpendicular band. There were, however, no Q- and P-branch lines which should appear with the abovementioned R-branch lines. Instead another series of lines appeared in the region of 2450–2550 cm<sup>-1</sup>, which were clearly the Q- and P-branch lines of a typical perpendicular band. These lines were, in general, stronger than those described above. Eventually we found much weaker R-branch lines which belonged to the same band as

### Table 1 Molecular constants of SH<sub>3</sub><sup>+</sup> (in MHz)<sup>a)</sup>

the above mentioned P- and Q-branch lines. This
band was assigned to the $v_3$ band, whose intensities
as well as line positions turned out to be perturbed as
is well known in PH <sub>3</sub> [19], an isoelectronic molecule
of SH <sup>+</sup> .

The lines we encountered at the earlier stage of our search exhibit the characteristics of a perpendicular band. We made a fit of these lines with the groundstate constants fixed at the values which will be given in section 4, and it yielded a band origin of this band (only the R-branch lines) to be about  $2549.4 \text{ cm}^{-1}$ . According to ab initio calculations, the  $v_4$  band is at around 1208 cm<sup>-1</sup> [13]. Also very recently, the  $v_2$ band was observed at 1033  $\text{cm}^{-1}$  [20]. Therefore it is very unlikely that the perturbing state is either the  $v_4=2$  state or the  $(v_2=1, v_4=1)$  state of SH<sub>3</sub><sup>+</sup>. At the present stage, the assignment of the mystery band is a puzzle. According to the ab initio predictions [11,13], the v<sub>1</sub> parallel band should be very close to the  $v_3$  band. However, as described above, the observed R-branch pattern does not look like a parallel band.

	Ground state		$v_3 = 1$ state	
	exp.	theory [11]	exp.	
В	146740.8(15)	146830	145278.7(43)	<u></u>
С	126630 <sup>b)</sup>	126630	126018 (15)	
D,	4.676(62)	4.323	3.432(60)	
$D_{JK}$	-6.428(170)	- 5.858	-7.82(72)	
$D_K$	4.633 <sup>b)</sup>	4.633	4.633 <sup>b)</sup>	
$H_J$	0.0021(7)		0.0021 b)	
H <sub>JK</sub>	-0.0070(29)		-0.0070 <sup>b)</sup>	
H <sub>KJ</sub>	0.0134(68)		0.0134 <sup>b)</sup>	
$H_{\kappa}$	0 <sup>b)</sup>		0 ь)	
$C_{t}$			2679 (18) °)	
$\eta_{x}$			29.8(20)	
$\eta_{K}$			-16.8(52)	
q			-337.1(96)	
$q_D$			1.41(21)	
$\nu_{0}$			75719890 (56) <sup>d)</sup>	

<sup>a)</sup> Values in parentheses are one standard error to the last digits of the constants.

<sup>b)</sup> Fixed at an assumed value (see text).

<sup>c)</sup> Theoretical value: 2772 GHz [11].

<sup>d)</sup> 2525.7437(2) cm<sup>-1</sup> in wavenumber. This value can be compared with the solid salt value (2520 cm<sup>-1</sup> [2]), and theoretical values (2529 [11], 2459 [18], and 2589 [13] cm<sup>-1</sup>).

# 4. The ground-state molecular constants

The forty-seven ground-state combination differences were fit to an ordinary oblate symmetric top rotational energy expression. The constants C,  $D_K$ , and  $H_K$  are not determinable without observing the "forbidden" lines. In the fit, C and  $D_K$  were thus fixed at the values given by Botschwina and co-workers [11] and  $H_K$  at zero. Table 1 shows the molecular constants thus determined. Although the sextic centrifugal distortion constants are only marginally determined as shown in table 1, the quality of the fit is slightly better than that without them. The stan-

Table 2 Term values for the  $v_3 = 1$  state (in cm<sup>-1</sup>)

dard deviation of the fit was  $8.5 \times 10^{-4}$  cm<sup>-1</sup>. In table 1 several calculated values are listed for comparison. As seen in table 1, the agreement is in general very good.

# 5. A preliminary determination of the molecular constants for the $vv_3=1$ state

Table 2 lists the term values for the levels in the  $v_3=1$  state which were derived from the observed transition frequencies and the term values for the ground state calculated with the molecular constants

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	J	(K=0, l=-1)	$(K=1, l=1)^+$	$(K=1, l=1)^{-}$	(K=1, l=-1)
	0	2525.7434			
	1	2535.4347	2534.6052	2534.6267	2534.9695
	2	2554.8156	2553.9693	2554.0331	2554.3475
	3	2583.8802	2583.0087	2583.1344	2583.4102
	4	2622.6217	2621.7175	2621.9197	2622.1498
	5	2671.0294	2670.0874	2670.3810	2670.5549
	6	2729.0899	2728.1115	2728.5047	2728.6152
	7	2796.7895	2795.7844	2796.2636	2796.3164
	8	2874.1122			2873.6432
	9	2961.0395			2960.5810
	10				3057.1926
	J	(K=2, l=1)	(K=2, l=-1)	(K=3, l=1)	(K=3, l=-1)
	2	2551.8987	2552.5993		
	3	2580.9823	2581.6567	2577.6151	2578.6702
	4	2619.7475	2620.3846	2616.4359	2617.4776
	5	2668.1806	2668.7684	2664.9320	2665.9596
	6	2726.2676	2726.7892	2723.0706	2724.0903
	7	2793.9904	2794.4293		2791.8416
	8	2871.3272	2871.6607		2869.1858
	9		2958.4629		2956.0939
	J	(K=4, l=1)	(K=4, l=-1)	(K=5, l=1)	(K=5, l=-1)
	4		2613.0498		
	5		2661.4272		2655.8781
	6		2719.4224		2713.9240
	7		2786.9985		2781.5792
	8		2864.1262		2858.8093
	9		2950.7684		2945.5820
	J	(K=6, l=1)	(K=6, l=-1)		
	6		2707.0941		
	7		2774.7985		

listed in table 1. The levels with  $K' \ge 3$  and l = +1have not been detected. It should be noted here that these term values were obtained by assuming the calculated C and  $D_K$  values [11]. After several trial fits, we have found that the (K', l) = (0, -1),  $(1, \pm 1)$ , and  $(2, \pm 1)$  levels are fit reasonably well at least for the lower J levels. The fit was done with the  $(\Delta K = \Delta l = \pm 2)$  and  $(\Delta K = \pm 1, \Delta l = \mp 2)$  interaction terms included in the Hamiltonian. The matrix element of the latter is given by [21]

$$\langle v_3, l, J, K | H' | v_3, l \pm 2, J, K \mp 1 \rangle$$
  
=  $\mp r_3 [(v_3 \mp l)(v_3 \pm l + 2)]^{1/2}$   
×  $[(J \pm K)(J \mp K + 1)]^{1/2} (2K \mp 1)$ .

It was found that, although  $r_3$  could not be determined very well, we observed a slight improvement of the fit with inclusion of the  $r_3$  term and the optimum  $r_3$  was about 180 MHz. The definitions of the higher-order terms of the first-order Coriolis splitting and the *l*-type doubling are given by  $-[2C_{\zeta} - \eta_J J(J+1) - \eta_K K^2]Kl$  and  $q_3 + q_J J(J+1)$ . The sign of the *l*-type doubling constant was taken as defined by Cartwright and Mills [22].

Table 1 lists the spectroscopic parameters for the excited state thus determined with some comparison



Fig. 2. The plot of the residuals of the fit (obs. - calc.).

with calculated values. In the fit,  $D'_{K}$  and the *H* constants were fixed at the values for the ground state. As seen from table 1, the values for  $D'_{JK}$  and  $D'_{J}$  are quite reasonable, indicating that the levels included in the fit are not seriously perturbed. Fig. 2 shows the plot of the residuals of the fit (obs. -calc.). In the least-squares fit, the levels of (J, K=J, l=-1) were included, and it was found that they were fit very well except the (3, 3, -1) level. If the deviations are due to the Coriolis interaction with the  $v_1=1$  state, they should not be affected by this interaction. Further analysis including the Coriolis perturbation with the  $v_1=1$  is in progress, and a more detailed account of the spectrum will be presented in a separate paper.

### 6. Inversion splitting and forbidden transitions

None of the lines observed in the present work show any sign of inversion doubling or broadening. This is reasonable in view of the rather high barrier predicted by ab initio calculations [6,9–11], and the spectral resolution, which is limited by the Doppler width. The  $v_2$  band should be more susceptible to the inversion motion, but even there no sign of inversion splitting or broadening has been observed with Doppler-limited resolution [20]. We have also looked for the  $\Delta(K-l) = \pm 3$  transitions with no success so far.

### 7. Prediction of the rotational transition frequencies

It will be very interesting and important to observe the rotational transitions of SH<sub>3</sub><sup>+</sup>. From the molecular constants determined above, we have predicted some low-lying rotational transition frequencies: 293464(3) for the  $J=1 \leftarrow 0$ , K=0 line, 586815(8) for the  $J=2\leftarrow 1$ , K=0 line, and 586840(8) for the  $J=2\leftarrow 1, K=1$  line (values given in MHz with one standard deviation in parentheses). It should be noted that the error limit given above may be somewhat optimistic. From the fit where all the sextic centrifugal distortion constants were neglected, the rotational constant was determined to be 146737.40(84) MHz which is smaller than that listed in table 1. This model-dependent uncertainty is larger than the statistical error quoted above. Although we feel the constants determined from the fit with the H constants included as listed in table 1 are more reasonable, one should keep this uncertainty in mind in searching for the rotational lines in either the laboratory or in interstellar space. In this sense, laboratory observations of submillimeter-wave lines are important to give much more reliable frequencies for astrophysical search. Also they will give a more critical upper limit for the inversion splitting.

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