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HIGH-RESOLUTION MOLECULAR-BEAM SPECTROSCOPY ON THE A $^2\Sigma^+_{1/2}$, $v = 0$ STATE OF SH

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In a molecular-beam laser-induced fluorescence experiment on SH, the hyperfine and spin–rotation structure in the A $^2\Sigma^+_{1/2}$, $v = 0$ state has been determined. From linewidth measurements, a rotationally dependent predissociation is shown to be present. A natural lifetime of 3.2 ± 0.3 ns is obtained for $N = 0$.

1. Introduction

Over the past few years, the SH radical has received increasing interest because of its intermediate role in reactions producing sulphur-containing pollutants. From the combustion of fossil fuel, large amounts of sulphur escape into the air, predominantly in the form of SO_2 but also as H_2S. In the upper layers of the earth's atmosphere, SH is produced by photodissociation of H_2S. In the interstellar medium, the SH radical has not been discovered yet despite the observed presence of H_2S. No high-resolution laser spectroscopy has been performed on SH due to its chemical instability, predissociation in the excited A $^2\Sigma^+_{1/2}$ state and the lack of a tunable single-frequency laser at the excitation wavelength of 324 nm.

The rotational and fine structure of the X $^2\Pi$ ground and A $^2\Sigma^+_{1/2}$ excited electronic states has been determined by Ramsay [1] and by Johns and Ramsay [2] from the absorption spectrum produced by flash photolysis of H_2S. They observed strong predissociation effects on the A $^2\Sigma^+_{1/2}$, $v = 1$ and 2 states. The hyperfine structure of the X $^2\Pi$, $v = 0$ ground state is well known from the molecular-beam electric-resonance measurements by Meerts and Dymanus [3].

In the present investigation, the hyperfine structure in the A $^2\Sigma^+_{1/2}$, $v = 0$ state has been measured for the first time in a molecular-beam laser-induced fluorescence (LIF) experiment. We observed 18 hyperfine splittings in the upper and lower ρ-doublet states in the rotational states with $N = 0$–9. The ρ-doublet splittings were measured for $N = 1$–7. From these data, we derived the hyperfine and spin–rotation coupling constants and the effect of centrifugal distortion upon the spin–rotation coupling.

From linewidth measurements, we discovered that the natural lifetime decreased significantly for higher rotational states, indicating an N-dependent predissociation in the A $^2\Sigma^+_{1/2}$, $v = 0$ state. The natural lifetime turns out to be considerably smaller than the radiative lifetime found in fluorescence-decay measurements by Becker and Haaks [4].

2. Experimental

The experimental apparatus is similar to the one used in OH experiments [5,6]. A view of the molecular-beam apparatus is given in fig. 1. The sulphur hydride radicals were produced in the reaction

$$H + H_2S \rightarrow SH + H_2 .$$

The atomic hydrogen obtained from a microwave discharge in H_2O was mixed with H_2S gas in front of the molecular-beam source. The fraction of SH radicals in the beam was estimated by Meerts and Dymanus [3], using essentially the same apparatus, to be 0.5%.

An adjustable slit diaphragm was installed 6.5 cm behind the beam source with an opening of 1.9 mm. The SH molecules were excited by a perpendicularly incident UV beam at a distance of 15 cm from the source. Via collecting optics, including a concave mir-

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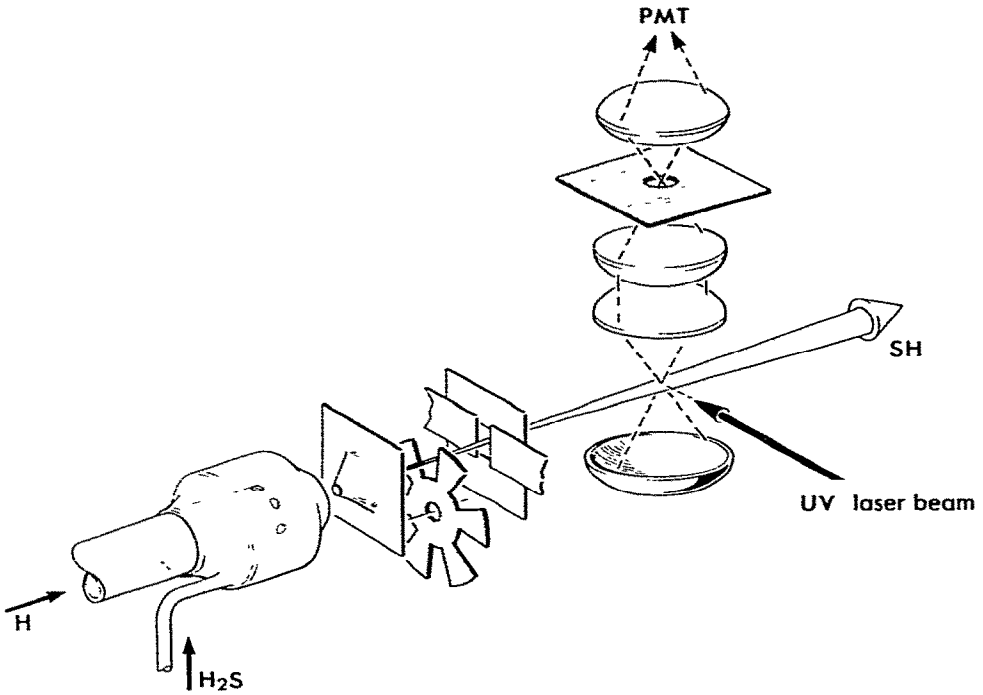


Fig. 1. View of the laser–molecular-beam spectrometer.

ror opposite to the detector, 10% of the emitted fluorescence radiation was focused on a photomultiplier tube (EMI, 9635QA). The molecular beam was chopped at 120 Hz so that phase-sensitive detection could be applied at time constants of 0.3–3 s.

A stabilized single-frequency ring dye laser (Spectra Physics, modified model 380D) was used operating with DCM at 648 nm. The laser frequency was doubled in a 1 mm thick angle-tuned $LiIO_3$ crystal (Gsänger GmbH), positioned inside the cavity under the Brewster angle in the second focus of the ring laser [7]. A typical UV power of ≈2 mW was obtained at 3 W (all lines) pump power from an Ar^+ laser. The UV linewidth was ≈0.5 MHz rms. The frequency could be scanned continuously over more than 100 GHz. During the scan, frequency markers were produced by a pressure and temperature stabilized interferometer. The free spectral range (FSR) was calibrated in a UV–microwave double-resonance experiment on OH [8]. Herein, the ρ-doublet splittings in the $A\,^2\Sigma^+_{1/2}$ state were measured directly for $N = 3$ and 4 with a microwave cavity inducing magnetic dipole transitions between the hyperfine states of the upper and lower ρ-doublet state. The resulting value of the FSR is 299.41 ± 0.02 MHz.

3. Measurements and interpretation

The $A\,^2\Sigma^+_{1/2} \leftarrow X\,^2\Pi_{3/2}$ transitions investigated were $P_1(3/2)$, $Q_1(J)$ and $^QP_{21}(J)$ for $J = 3/2$ to 15/2, $R_1(15/2)$ and $^RQ_{21}(J)$ for $J = 15/2$ and 17/2, where J is the total angular momentum in the ground state. For $J = 17/2$ and 19/2, the $Q_1(J)$ and $^QP_{21}(J)$ lines overlap with unknown lines, probably of S_2. The signal-to-noise ratio was typically 100 at $RC = 0.3$ s for transitions to the low-N states, and decreased to ≈10 at $RC = 3$ s for transitions to the highest states. For each J, the separation in frequency between the $Q_1(J)$ and $^QP_{21}(J)$ transitions was covered in continuous scans without mode hops of the laser. From this, the ρ-doublet and hyperfine splittings in the states with $N = 1$–7 were obtained. The P_1, R_1 and $^RQ_{21}$ transitions gave the hyperfine splittings of the $N = 0$, 8 and 9 states.

The measured hyperfine splittings are equal to either the sum of or the difference between the hyperfine splittings of the ground and excited states, depending on the sequence of the hyperfine levels in both states. The hyperfine states in the $X\,^2\Pi_{3/2}$, Λ-doublet states are separated by not more than 10 MHz [3], which cannot be resolved in the present experiment in the case of transitions to the same ρ-doublet hyperfine state. So, for each pair of $Q_1(J)$ and $^QP_{21}(J)$ transitions, only four spectral lines were observed of the seven possible $\Delta F = 0, \pm 1$ hyperfine transitions from a ground J state to an excited N state. For the overlap of the unresolved hyperfine pairs, a small correction (<4 MHz) was applied as obtained from calculated intensity ratios. The values obtained for the $A\,^2\Sigma^+_{1/2}$ hyperfine and ρ-doublet splittings are listed in tables 1 and 2, respectively. Each value is the result of at least six measurements. The quoted error corresponds to one standard deviation.

The experimental results have been fitted to an effective hamiltonian for the $A\,^2\Sigma^+_{1/2}$ states [5,6]:

$$H = BN^2 + (\gamma + \gamma_D N^2)N\cdot S + bI\cdot S + cI_zS_z\,.$$

The first term represents the rotational energy and the second the spin–rotation interaction including centrifugal distortion. The last two terms describe the hyperfine interaction between the spins of the electrons and the hydrogen nucleus. The constans b, c, γ and γ_D were calculated by diagonalizing the hamiltonian in symmetrized Hund's-case-(b) basis functions. The values from a least-squares fit over all data are given in table 3. The value for γ (9.38 GHz) as reported by Ramsay [1] agrees roughly with our more accurate result. In tables 1 and 2 the differences between calculated and observed frequencies are given, showing a good agreement. Only the $N = 7, J = 15/2$ hyperfine splitting gave too large a deviation.

The constant $b + \frac{1}{3}c$ is proportional to $\langle\psi^2(0)\rangle$, the density of the spin-contributing electrons at the hydro-

Table 1
Hyperfine splittings (in MHz) in the $A\,^2\Sigma^+_{1/2}, v = 0$ states of SH and deviations from a least-squares fit

N	J	Observed splitting	Obs. – calc.
0	1/2	898.6(2.5)	0.07
1	1/2	289.8(2.2)	−0.14
1	3/2	581.7(1.4)	0.30
2	3/2	355.8(4.1)	1.61
2	5/2	523.7(5.3)	−1.22
3	5/2	379.4(2.6)	−0.12
3	7/2	500.5(2.8)	−0.39
4	7/2	394.7(4.1)	1.38
4	9/2	486.5(2.5)	−1.05
5	9/2	405.4(2.7)	3.36
5	11/2	478.7(1.7)	−0.36
6	11/2	406.0(3.2)	−2.05
6	13/2	473.7(3.0)	0.52
7	13/2	415.0(5.6)	2.56
7	15/2	450.7(5.0)	−8.16
8	15/2	416.2(4.0)	0.40
8	17/2	466.7(4.0)	1.13
9	17/2	417.3(8.4)	−1.15

Table 2
ρ-doublet splittings (in MHz) for SH in the $A\,^2\Sigma^+_{1/2}, v = 0$ states and deviations from the values obtained in a least-squares fit. The quantum numbers J_1, F_1 and J_2, F_2 refer to the upper and lower ρ-doublet states, respectively

N	J_1	F_1	J_2	F_2	Observed splitting	Obs. – calc.
1	3/2	1	1/2	1	13977.2 (5.7)	−4.13
	3/2	2	1/2	0	14273.2 (5.5)	0.41
2	5/2	2	3/3	2	23593.5 (7.0	4.37
	5/2	3	3/2	1	23760.8 (5.3)	0.94
3	7/2	3	5/2	3	33118.6(12.4)	−1.04
	7/2	4	5/2	2	33238.6(13.8)	−2.41
4	9/2	4	7/2	4	42612.5 (7.8)	1.70
	9/2	5	7/2	3	42704.4 (7.8)	−0.62
5	11/2	5	9/2	5	52074.3(10.8)	5.36
	11/2	6	9/2	4	52146.7 (7.2)	0.75
6	13/2	6	11/2	6	61490.5 (3.1)	−2.75
	13/2	7	11/2	5	61560.6 (4.2)	2.22
7	15/2	7	13/2	7	70882.9 (6.2)	2.31
	15/2	8	13/2	6	70937.9 (7.6)	0.89

Table 3
Hyperfine and ρ-doubling constants (in MHz) for SH in the $A\,^2\Sigma^+_{1/2}, v = 0$ state. For comparison, the hyperfine constants in the ground state as obtained by Meerts and Dymanus [3] are given also

	$A\,^2\Sigma^+_{1/2}$	$X\,^2\Pi$
$b + \frac{1}{3}c$	898.5 ± 1.0	−52.63 ± 0.07
c	51.0 ± 2.7	32.44 ± 0.14
γ	9506.7 ± 1.2	
γ_D	−0.870 ± 0.014	

gen nucleous, while c is a measure of the non-sphericity of the electronic charge distribution. Both constants are predominantly determined by the unpaired electrons. The electronic configuration of the ground $X\,^2\Pi$ of SH is $(1s\sigma)^2\,(2s\sigma)^2\,(2p\sigma)^2\,(2p\pi)^4\,(3s\sigma)^2\,(3p\sigma)^2\,(3p\pi)^3$. The $3p\pi$ orbitals vanish on the internuclear axis, but polarization of the σ orbitals causes a non-zero value of $\langle\psi^2(0)\rangle$ [9]. In the excitation to the $A\,^2\Sigma^+_{1/2}$ state, a $3p\sigma$ electron is promoted to a $3p\pi$ orbital. As a consequence, the hyperfine interaction of this state is caused mainly by an inner-shell $3p\sigma$ electron having a non-vanishing charge distribution on the internuclear axis, which may result in a much larger Fermi contact term. Indeed, when compared to the value for $b + \frac{1}{3}c$ in the ground state as obtained by Meerts and Dymanus [3], the present result for the excited state is more than one order of magnitude larger. On the other hand, the c constant differs much less between the electronic ground and excited states as may be expected since the sphericity of the electron cloud will not change drastically in the $3p\sigma \rightarrow 3p\pi$ excitation.

There are no calculations available for the $A\,^2\Sigma^+_{1/2}$ state of SH, so the present results cannot be discussed quantitatively. The differences between the hyperfine constants in the electronic ground and excited states of SH are comparable with the analogous case of OH where, in the excitation to the $A\,^2\Sigma^+_{1/2}$ state, a $2p\sigma$ electron is promoted to a $2p\pi$ orbital.

The linewidths (fwhm) $\Delta\nu_{tot}$ of the spectral lines of SH increased from 95 MHz for the low-N states to 200 MHz for $N = 9$, indicating the presence of predissociation effects. The linewidths for transitions to the upper ρ-doublet states seemed persistently larger than for transitions to the lower ρ-doublet states.

The line broadening $\Delta\nu_\tau$ due to the natural lifetime, including both a radiative and a predissociative decay, can be deduced from the formula [10]

$$\Delta\nu_\tau = \Delta\nu_{tot} - (\Delta\nu_D)^2/\Delta\nu_{tot} \qquad (2)$$

valid for a lorentzian and a gaussian curve with linewidths (fwhm) $\Delta\nu_\tau$ and $\Delta\nu_D$, respectively. Because the SH molecules are produced in a chemical reaction, the translational velocity is poorly known. Therefore, it is not possible to calculate the Doppler contribution $\Delta\nu_D$, due to molecular-beam divergence, to the total linewidth. To determine the natural lifetime, we performed measurements on the $P_1(3/2)$ transition in which the Doppler contribution was reduced to a value much smaller than $\Delta\nu_\tau$ by installing a source with a diameter of 0.5 mm and reducing the slit diaphragm to 0.2 mm. A minimum value of 54 MHz for the total linewidth was obtained. With the same geometry, a measurement on OH, where the linewidth is determined only by Doppler broadening, yielded the much smaller value of 18 MHz.

As a result, we estimate the line broadening due to the natural lifetime $\Delta\nu_\tau$ to be 50 ± 5 MHz for the $N = 0$ state with a Doppler broadening $\Delta\nu_D$ of 66 ± 5 MHz for the measurements with source opening 1.9 mm and a full diaphragm. For the other N states, the broadening $\Delta\nu_\tau$ due to the natural lifetime is determined by subtracting this Doppler contribution from the total linewidth via eq. (2). The results are given in fig. 2.

Ramsay [1] and Johns and Ramsay [2] have observed strong predissociation in the $A\,^2\Sigma^+_{1/2}$, $v = 1$ and 2 states and ascribed this to the interaction with a nearby repulsive $^2\Sigma^-$ state crossing the $A\,^2\Sigma^+_{1/2}$ state. This state dissociates into $S(^3P) + H(^2S)$ to which the ground state $X\,^2\Pi$ and the repulsive states $^4\Sigma^-$ and $^4\Pi$ are correlated also. From an ab initio potential calculation, Hirst and Guest [11] and Hirsch [12] have shown that

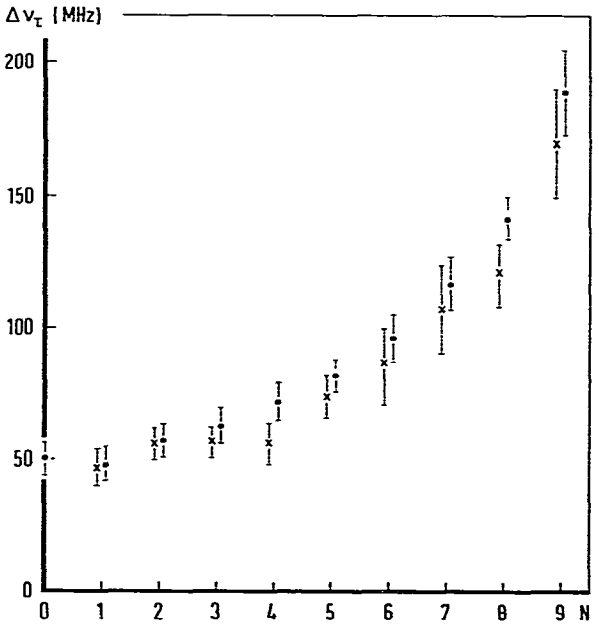


Fig. 2. The observed natural linewidths of the $A\,^2\Sigma^+_{1/2}$, $v = 0$, N states. The dots (•) refer to the upper ρ-doublet states, the crosses (×) to the lower ones.

the $^4\Sigma^-$ state crosses the $A\,^2\Sigma^+_{1/2}$ potential around $v = 1$, while the crossing of the $^2\Sigma^-$ state is in the region of $v = 3$. So the observed predissociation might be attributed to the interaction with the $^4\Sigma^-$ state, which is probably the main mechanism for the predissociation of OH [13] and OD [14].

The change in both spin and symmetry can be produced by spin–orbit and spin–nuclear rotation coupling. However, we could not explain the observed N dependence from the matrix elements derived by Freed [15] for the coupling between a $^2\Sigma^+$ and a $^4\Sigma^-$ state. Differences between dissociation rates for upper and lower ρ-doublet states have been observed also for OH and OD [13,14] and are ascribed to different overlap between the wavefunctions of the upper or lower ρ-doublet state and the $^4\Sigma^-$ continuum states.

Another mechanism that can cause predissociation is the interaction between the $A\,^2\Sigma^+_{1/2}$ state and the $X\,^2\Pi$ ground-state continuum. This has been suggested by Durmaz and Murrell [16] for the weak predissociation in the $A\,^2\Sigma^+_{1/2}$, $v = 2$ state of OH. In the case of SH, all $A\,^2\Sigma^+_{1/2}$, $v = 0$ levels are in the ground-state continuum. However, their lifetime is considerably shorter (by a factor of 10^3) than the $v = 2$ levels of OH. For CH, Brzozowski et al. [17] have shown that this type of interaction causes a weak predissociation of the $A\,^2\Delta$ states lying above the $X\,^2\Pi$ dissociation limit at a rate of $8.5 \times 10^5\ s^{-1}$, which is a factor of 400 smaller than the SH predissociation rate.

The linewidth of 50 ± 5 MHz for the $N = 0$ state corresponds to a natural lifetime of 3.2 ± 0.3 ns. This value fits well within the upper limit ($\leqslant 10$ ns) estimated by Tiee et al. [18] for the collision-free fluorescence lifetime of the $A\,^2\Sigma^+_{1/2}$ state of SH in LIF experiments with pulsed excitation. The estimate of Tiee et al. is, however, in sharp disagreement with the radiative lifetime of 550 ± 140 ns reported by Becker and Haaks [4]. Such a long radiation lifetime would imply that more than 99% of the excited molecules dissociate, which in turn would have important consequences for the SH concentration in the upper atmosphere and in interstellar regions with high UV radiation densities. Although the present measurements cannot exclude long radiative lifetimes, very high dissociation rates are rather improbable in view of the high fluorescence yields observed.

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