THE HYPERFINE Λ -DOUBLING SPECTRUM OF SULFUR HYDRIDE IN THE ${}^2\Pi_{3/2}$ STATE

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ABSTRACT

The hyperfine Λ -doubling spectrum of the five lowest rotational states of the ${}^2\Pi_{3/2}$, v=0 state is measured using the molecular-beam electric-resonance method. From the Stark splittings of the observed transitions the value of the electric dipole moment of SH is determined: $\mu=0.7580(1)$ D.

Subject headings: molecules — hyperfine structure

A search for the emission lines of the sulfur hydride (SH) molecule in astronomical sources has been performed by Meeks, Gordon, and Litvak (1969) and by Heiles and Turner (1971). These attempts were unsuccessful, partly because of the inaccuracy of the Λ -doublet transition frequencies. The Λ -doublet transition of the lowest rotational states J = 3/2 and J = 5/2 of the ${}^{2}\Pi_{3/2}$, v = 0 state of SH were investigated by several authors using paramagnetic resonance spectroscopy (Radford and Linzer 1963; Brown and Thistlethwaite 1972; Tanimoto and Uehara 1973). The accuracy of the predicted frequencies was of the order of 100-200 kHz. In order to check reliability of the ESR predictions and to obtain more accurate Λ-doublet transition frequencies for the SH radical we used the molecular-beam electric-resonance method for the five

lowest rotational states of the ${}^2\Pi_{3/2}$ level. In addition the value of the electric dipole moment of SH is obtained.

The SH radical is produced by the reaction of hydrogen atoms with H_2S . The hydrogen atoms are produced by a 2.45-GHz microwave discharge in water. The signal-to-noise ratio of the SH transitions varied between 1 and 15 with a RC = 5 s. The observed frequencies correspond to the $\Delta J = 0$, $\Delta F = 0 \pm 1$, Λ -doubling transitions between states with different Kronig symmetry, originating in the five lowest J-states of the electronic ground state ${}^2\Pi_{3/2}$. The lowest transition frequencies of the ${}^2\Pi_{1/2}$ electronic state lie at about 8.4 GHz, beyond our present experimental possibilities. The observed transition frequencies are listed in table 1.

The theory discussed in an earlier paper (Meerts and

TABLE 1 $Observed \ \Lambda \hbox{-doubling Transition Frequencies (in MHz) of the} $^2\Pi_{3/2}$ Electronic State of SH$

J	F_+ *	F_{-}	Present Observation	Predicted from ES	SR Measurements
3/2	1	1	111.4862(5)	111.26(10)†	111.39(10)‡
	2	2	111 . 5452(5)	111.58(10)†	111.44(10)‡
	2	1	100,293(3)	` / '	
	1	2	122.737(3)		
5/2	$\bar{2}$	2	442.4781(5)	440.4(2)§	440.8(2)
,	3	2 3 3	442.6277(5)	441.2(2) §	440.9(2)
	2	3	437.9154(20)	1 - (1) 6	(-711
	3	2	447.1876(20)		
7/2	3	2 3	1094.1871(5)		
., =	4		1094.4596(10)		
	$\tilde{4}$	$\frac{4}{3}$	1093.5326(20)		
	3	4	1095.1179(20)		
9/2	4	$ar{4}$	2158.2986(10)		
,	Ŝ.	5	2158.7239(10)		
	4	5	2160.5318(10)		
	$\tilde{5}$	4	2156.4902(10)		
11/2	Š	4 5	3714.8864(20)		
~~, ~	6	6	3715.4892(20)		

^{*} The subscript + (-) refers to the even (odd) Kronig symmetry (Meerts and Dymanus 1972).

L45

[†] Radford and Linzer 1963.

[‡] Tanimoto and Uehara 1973.

[§] Brown and Thistlethwaite 1972.

^{||} Correction by J. M. Brown added as note in the paper of Tanimoto and Uehara 1973.

Dymanus 1972) is used to explain the observed spectrum. However, due to the lack of information about the ${}^{2}\Pi_{1/2}$ state, the fine-structure constants cannot be determined unambiguously. The following hyperfinestructure constants are obtained from the observed spectrum: $a + \frac{1}{2}(b + c)$, b, and d; a definition of these constants can be found in Meerts and Dymanus (1972). The obtained values for SH are given in table 2. In this table we also list the ESR results of Tanimoto and Uehara (1973). They are essentially in agreement with the present values. The Λ -doubling transition frequencies for the lowest J-states predicted from ESR investigations are shown in table 1. It should be noted that there are rather strong deviations from the present direct measurements.

From the observed Stark shifts of the ${}^{2}\Pi_{3/2}$, J = 5/2state and the theory discussed by Meerts and Dymanus (1973), we calculated the electric dipole moment of SH. The value obtained is 0.7580(1) debye. Previous measurements of this value by Byfleet, Carrington, and Russell (1971) yielded $\mu = 0.62(1)$ debye. This value is not in agreement with the present more accurate result. The calculated dipole moment of SH by Cade and Huo (1966), $\mu = 0.861$ debye, is in rather good agreement with the present experimental value.

TABLE 2 Hyperfine Structure Constants (in MHz) of SH

Constant	Present Investigation	Tanimoto and Uehara (1973)
$a+\frac{1}{2}(b+c)$	+17.075(6) $-63.540(40)$ $+27.386(60)$	+17.0(2) $-60(2)$ $+29(17)$

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