

DETERMINATION OF THE SPIN-ROTATION AND HYPERFINE STRUCTURE IN THE $A^2\Sigma_{1/2}^+$, $v=0$ AND $v=1$ STATES OF OH

J.J. TER MEULEN, W.A. MAJEWSKI *, W. Leo MEERTS and A. DYMANUS

Fysisch Laboratorium, Katholieke Universiteit, 6525 ED Nijmegen, The Netherlands

Received 19 August 1982, in final form 11 October 1982

The spin-rotation (ρ -doubling) and hyperfine structure in the $A^2\Sigma_{1/2}^+$, $v=0$ and $v=1$ states of OH has been determined in a molecular beam laser-induced fluorescence experiment. High-resolution measurements have been performed for N up to 7 in $v=0$ and N up to 6 in $v=1$ using a ring dye laser with intracavity frequency doubling.

1. Introduction

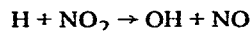
The rotational and fine structure of the $A^2\Sigma_{1/2}^+$ excited electronic state of OH has been determined by Dieke and Crosswhite [1] from the emission spectrum to the ground state, $X^2\Pi_{1/2,3/2}$. Several authors [2-4] have used their data to derive more accurate values for the rotational and ρ -doubling constants. In a previous experiment [5] we obtained the hyperfine structure of the $v=0$ state of $A^2\Sigma_{1/2}^+$ in a laser-induced fluorescence (LIF) measurement on a molecular OH beam. Recently Raab et al. [6] reported more accurate values for the hyperfine constants of the same state obtained in a quantum beat experiment. In addition they measured the ρ -doubling constant γ for low rotational states in $A^2\Sigma_{1/2}^+$, $v=0$. In our experiment γ was determined from a measurement of the lowest ($N=1$) ρ -doublet splitting. As this splitting was larger than the maximum attainable continuous scan of the standing wave dye laser used the frequency was scanned by mode hopping. It was realized later that this method was not reliable.

In the present experiment the hyperfine and ρ -doublet splittings in $A^2\Sigma_{1/2}^+$ have been measured using a ring dye laser with intracavity frequency doubling. This laser allows for a single continuous scan large enough for the ρ -doubling splittings. Mea-

surements have been performed for $N=1$ to 7 in the ground ($v=0$) and for $N=1$ to 4 and $N=6$ in the first excited ($v=1$) vibrational state of the $A^2\Sigma_{1/2}^+$ level. The new results not only made it possible to improve significantly the accuracies of the molecular parameters in the $v=0$ state but also to determine these parameters for the $v=1$ state of the same level.

2. Experiment

The OH beam was produced in the same way as described in ref. [5]. The hydroxyl radicals were obtained from the reaction



in front of a skimmer-type beam source with a hole of 0.7 mm. The OH concentration in the beam was estimated to be $\approx 1\%$ of which a fraction of the order of 5% was in the $X^2\Pi_{1/2,3/2}$, $v=1$ state. At ≈ 30 cm from the beam source the OH molecules were excited by the perpendicularly incident UV beam. Via collecting optics, $\approx 5\%$ of the emitted fluorescence radiation was focused on a photomultiplier tube (EMI 9864 Q). A photon counter (Ortec-Brookdeal 5C1) was used at an effective integration time of 0.2 s. The linewidth was determined by the molecular beam divergence which was reduced by a diaphragm halfway between the beam source and the UV excitation zone. The residual Doppler width was 35 MHz (fwhm).

* Permanent address: IFD, Warsaw University, 00-681 Warsaw Hoza 69, Poland

A stabilized single-frequency ring dye laser (Spectra Physics, modified model 380D) was used operating with rhodamine 6G at 615 nm for the $v' = 0 \leftarrow v = 0$ transitions and with DCM (4-dicyanomethylene-2-methyl-6-*p*-dimethylaminostyryl-4H-pyran) at 628 nm for $v' = 1 \leftarrow v = 1$. The laser frequency was doubled in a 0.5 mm thick angle-tuned LiIO_3 crystal inside the laser cavity. With the normal output coupler of the ring laser exchanged for a high reflecting mirror ($R \approx 0.25\%$) a UV power of typically 1 mW was obtained at 2 W pump power from an Ar^+ laser. It turned out that at 307 nm the efficiency of the LiIO_3 crystal for second-harmonic generation is about half of that of the previously used ADA (ammonium-dihydrogen-arsenate) crystals at 90° phase matching. The use of LiIO_3 made it possible to generate UV from 295 to 330 nm. The UV linewidth was smaller than 0.5 MHz rms. The maximum possible frequency scan of the UV radiation was ≈ 120 GHz with a power variation smaller than 5%. A detailed description of the intracavity frequency doubled ring dye laser will be given elsewhere.

The OH spectra were recorded relative to the transmission fringes of a pressure and temperature stabilized frequency interferometer. Measurements in frequency up and down direction yielded the same results showing the absence of possible thermal drift effects. The interferometer was calibrated both relative to a stabilized HeNe laser in a wavelength meter and against the iodine absorption spectrum [7] in a frequency scan of ≈ 400 GHz. The resulting value of the free spectral range (FSR) at 620 nm was equal to 299.4 ± 0.1 MHz.

3. Measurements and interpretation

The transitions induced were of the type $Q_1(N)$ and $Q_{2,1}(N)$ with $N = 1$ to 7 in the case of the $A^2\Sigma_{1/2}^+, v' = 0 \leftarrow X^2\Pi_{3/2}, v = 0$ excitation and $N = 1$ to 4 and $N = 6$ for $A^2\Sigma_{1/2}^+, v' = 1 \leftarrow X^2\Pi_{3/2}, v = 1$. In addition also the $P_1(1)$ transition was measured yielding the hyperfine splitting of the $N = 0$ states. The signal to noise ratio was typically 100 for the $v' = 0 \leftarrow v = 0$ spectra and 10 for $v' = 1 \leftarrow v = 1$. For each N the frequency distance between the $Q_1(N)$ and $Q_{2,1}(N)$ lines was measured in single continuous scans yielding the ρ -doublet splitting. Every

Table 1

The hyperfine splittings (in MHz) in the $A^2\Sigma_{1/2}^+, v = 0$ and $v = 1$ states of OH and the deviations from the values obtained in a least-squares fit. The experimental error is 2.5 MHz for all splittings except for $v = 0, N = 0, J = 1/2$ and $v = 1, N = 6, J = 1/2$ where the inaccuracy is equal to 1.5 MHz and 5 MHz respectively

N	J	v = 0		v = 1	
		observed splitting	observed - calculated	observed splitting	observed - calculated
0	1/2	776.3	1.2	775.6	-0.7
1	1/2	199.8	0.9	207.1	-0.3
1	3/2	484.7	-2.8	490.0	0.8
2	3/2	275.5	0.6	280.1	-0.2
2	5/2	434.9	-1.9	440.6	1.5
3	5/2	300.2	-0.7	304.6	-0.9
3	7/2	414.7	-0.4	416.3	-1.4
4	7/2	315.3	0.8	320.0	1.1
4	9/2	401.7	-1.3	404.8	-0.9
6	11/2			335.6	2.7
6	13/2			393.6	0.8

transition is split into two well-resolved components. This splitting is equal to either the sum of or the difference between the hyperfine splittings of the $^2\Pi_{3/2}$ and $^2\Sigma_{1/2}^+$ states involved, depending on the sequence of the hyperfine levels in both states [6]. Each component is either a single line or a doublet as a result of the hyperfine structure of the $X^2\Pi_{3/2}$ ground state. This structure could be resolved only for the transitions from the $^2\Pi_{3/2}, J = 3/2$ state. A correction for overlapping doublets [6] turned out to be smaller than 1 MHz for all transitions measured. In table 1 the hyperfine splittings of the $A^2\Sigma_{1/2}^+, v = 0$ and $v = 1$ states are given. The splittings are derived from the observed spectra using the hyperfine structure of the $X^2\Pi_{3/2}; v = 0$ and $v = 1$ states [3,8]. In table 2 the observed ρ -doublet splittings are presented. As in table 1 the quoted errors are based on the spread of the experimental results and do not include a systematic uncertainty due to the calibration of the FSR of the reference interferometer.

In the fit of the experimental results the following effective hamiltonian for the $A^2\Sigma_{1/2}^+$ states was used

$$H = BN^2 + (\gamma + \gamma_D N^2)N \cdot S + bI \cdot S + cI_z S_z \quad (1)$$

The first term is the rotational energy with N the an-

Table 2

Observed ρ -doublet splittings (in MHz) for OH in the $A^2\Sigma_{1/2}^+$, $v=0$ and $v=1$ states and Δ 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 state, respectively

N	J_1, F_1	J_2, F_2	$v=0$		$v=1$	
			observed splitting	observed - calculated	observed splitting	observed - calculated
1	3/2, 1	1/2, 1	9923.9 ± 6.0	1.4	9523.1 ± 20.0	10.4
	3/2, 2	1/2, 0	10210.5 ± 6.0	-0.6	9806.1 ± 20.0	11.6
2	5/2, 2	3/2, 2	16776.5 ± 6.0	-2.9	16094.2 ± 15.0	-1.9
	5/2, 3	3/2, 1	16937.1 ± 6.0	-4.2	16251.7 ± 15.0	-3.2
3	7/2, 3	5/2, 3	23558.3 ± 12.0	-1.5	22596.2 ± 15.0	-9.4
	7/2, 4	5/2, 2	23671.4 ± 12.0	-2.6	22703.6 ± 15.0	-14.2
4	9/2, 4	7/2, 4	30296.0 ± 6.0	3.1	29084.6 ± 15.0	13.5
	9/2, 5	7/2, 3	30378.0 ± 6.0	-3.3	29166.6 ± 15.0	8.6
5	11/2, 5	9/2, 5	36989.9 ± 12.0	9.5		
	11/2, 6	9/2, 4	37066.7 ± 12.0	14.1		
6	13/2, 6	11/2, 6	43620.9 ± 12.0	3.1	41873.9 ± 20.0	-0.3
	13/2, 7	11/2, 5	43684.1 ± 12.0	5.3	41928.1 ± 20.0	-6.0
7	15/2, 7	13/2, 7	50196.7 ± 12.0	-1.9		
	15/2, 8	13/2, 6	50240.1 ± 12.0	-11.3		

gular momentum of the overall nuclear rotation. The second term represents the interaction between N and the electronic spin S including centrifugal distortion [9]. The last two terms are the interaction between S and the spin I of the hydrogen nucleus [10].

The spin-rotation interaction causes the ρ -doublet splitting equal to $(N + 1/2) \bar{\gamma}(N)$ with [11]

$$\bar{\gamma}(N) = \gamma + \gamma_D N(N + 1). \quad (2)$$

The quantum number J of the angular momentum $J = N + S$ is equal to $N + 1/2$ for the upper ρ -doublet state and to $N - 1/2$ for the lower one. Every ρ -doublet level is split again into two hyperfine levels characterized by the quantum number $F = J \pm 1/2$ of the total angular momentum $F = J + I$.

The matrix elements were calculated with symmetrized Hund's case (b) basis functions [12]. The hyperfine matrix was diagonalized by a computer program yielding the energy distances between the four hyperfine states for each rotational state N . The constants b, c, γ and γ_D were determined from the observed splittings in a least-squares fit. The results for both $v=0$ and $v=1$ are given in table 2. The errors given represent one standard deviation, except for γ where the inaccuracy of the FSR of the calibrating interferometer is dominating. If the centrifugal distortion in the ρ -doubling is expressed as a function

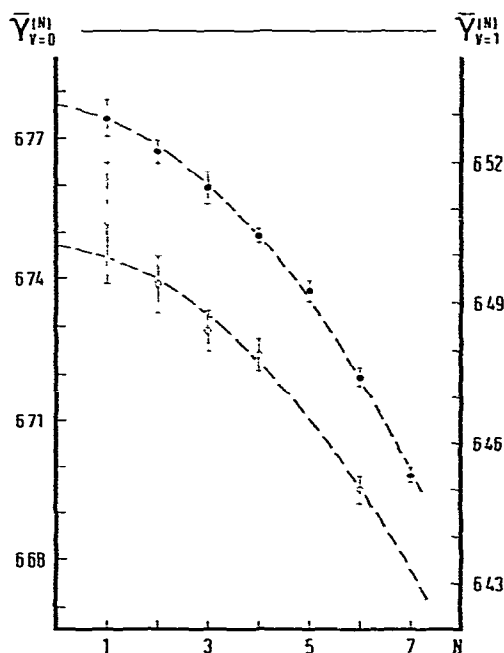


Fig. 1. Experimental values of $\bar{\gamma}(N)$ for the $A^2\Sigma_{1/2}^+$, $v=0$ (closed circles) and $v=1$ (open circles) states. The dashed curve gives the N dependence calculated from the least-squares fit.

Table 3
 Hyperfine and ρ -doubling constants (in MHz) for OH in the $A^2\Sigma_{1/2}^+$, $v = 0$ and $v = 1$ states

Molecular constant	$v = 0$		$v = 1$			
	this work		previous work		this work	previous work
γ	6776.9	± 3.0	6862	± 43 d)	6502.3	± 3.6
			6810	± 20 b)		
			6762	± 10 c)		
γ_D	-1.384 ± 0.019		1.430 ± 0.054 c,e)		-1.233 ± 0.051	-1.39 ± 0.09 c,e)
			-1.50 ± 0.03 d)			
$b + c/3$	775.1	± 1.1	774.1 ± 0.4 a)		776.3	± 1.1
c	166.4	± 2.8	168.9 ± 0.8 a)		149.2	± 2.4

a) Ref. [6]. b) Ref. [3]. c) Ref. [4]. d) Ref. [10]. e) The sign of γ_D given by Coxon [4] should be reversed [13].

of $J(J+1)$ rather than $N(N+1)$ (see e.g. ref. [4]) the same values for γ and γ_D were obtained within the present accuracy. The values for $\bar{\gamma}(N)$ derived from the observed splittings with the present values for b and c are plotted in fig. 1 as a function of N . As can be seen from fig. 1 the calculated N dependence is in excellent agreement with the experimental results for both $v = 0$ and $v = 1$. A comparison with other values reported for the ρ -doubling constants shows that our values for γ and γ_D are in agreement with the results of the most detailed analysis of the optical spectrum by Coxon [4] within their quoted uncertainties. The sign of γ_D given by Coxon should be reversed [13]. The other reported values for γ are too high which is remarkable since in all these cases the values obtained are averaged values for a number of rotational states so that a lower value than γ would be expected.

The values for the $v = 0$ hyperfine constants differ slightly from the previous reported values [5] and are close to the results of Raab et al. [6]. For $A^2\Sigma_{1/2}^+$, $v = 1$ the results for $b + c/3$ and c presented in table 3 are the first values reported. The change upon vibrational excitation found for the c constant is much larger than for $b + c/3$. A quantitative discussion of this effect has to await a theoretical calculation of the hyperfine structure in the $A^2\Sigma_{1/2}^+$ state.

Acknowledgement

The authors would like to thank Mr. W. Ubachs for

his assistance during the measurements. This work is part of the research program of the Stichting voor Fundamenteel Onderzoek der Materie (F.O.M.) and has been made possible by financial support from the Nederlandse Organisatie voor Zuiver-Wetenschappelijk Onderzoek (Z.W.O.).

References

- [1] G.H. Dieke and H.M. Crosswhite, *J. Quant. Spectry, Radiative Transfer* 2 (1962) 97.
- [2] L.A. Moore and W.G. Richards, *Physica Scripta* 3 (1971) 223.
- [3] J.L. Destombes, C. Marlière and F. Rohart, *J. Mol. Spectry.* 67 (1977) 93.
- [4] J.A. Coxon, *Can. J. Phys.* 58 (1980) 933.
- [5] J.J. ter Meulen, G.W.M. van Mierlo and A. Dymanus, *Phys. Rev. Letters* 43 (1979) 29.
- [6] I. Raab, T. Bergeman, D. Lieberman and H. Metcalf, *Phys. Rev. A* 24 (1981) 3120.
- [7] S. Gerstenkorn and P. Luc, *Atlas du spectroscopie d'absorption de la molécule d'hydrode* (CNRS, Paris, 1978).
- [8] W.L. Meerts, J.P. Bekooy and A. Dymanus, *Mol. Phys.* 37 (1979) 425.
- [9] J.M. Brown, E.A. Colbourn, J.K.G. Watson and F.D. Wayne, *J. Mol. Spectry.* 74 (1979) 294.
- [10] R.A. Irosch and H.M. Foley, *Phys. Rev.* 88 (1952) 1337.
- [11] L. Veseth, *J. Phys.* B3 (1970) 1677.
- [12] H.E. Radford, *Phys. Rev. A* 136 (1964) 1571.
- [13] J.A. Coxon, private communication.