

THE ZEEMAN SPECTRUM OF THE OH $^2\Pi_{1/2}$ STATE

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The $J = 1/2$ and $J = 3/2$ states of the X $^2\Pi_{1/2}$ level of OH have been studied in magnetic fields up to 0.8 T. The molecular beam electric resonance method was used. The Λ -doubling Zeeman transitions have been observed for the $J = 1/2$ singular level for the first time. The results were combined with data from the literature, which enabled a rather uncorrelated fit of all the g -factors with improved accuracies. The experimental value of the electronic spin g -factor is compared with the theoretical prediction.

1. Introduction

The OH radical in its $^2\Pi$ ground state has been extensively investigated by various high-precision spectroscopic techniques. The list of accurate molecular parameters obtained from the OH data in the literature might seem quite complete, and the theoretical model well understood. There is, however, one crucial parameter which is not well determined from experiment so far, and that is the electronic spin g -factor, g_s . An accurate set of values for all the six g -factors needed to describe the Zeeman effect of a $^2\Pi$ state is furthermore required to extract accurate rotational and fine structure constants from laser magnetic resonance spectra [1].

A fitted value of g_s was presented by Brown and co-workers [2]. However, with the data available very high correlations among the g -factors were encountered, and their result $g_s = 2.00152(36)$ is not accurate enough to enable a significant comparison with theory. The ab initio result $g_s = 2.002114$ is expected to be accurate to about 5 ppm [3]. The fitted value of g_s is very sensitive to deficiencies in the theoretical model as well as to inaccuracies in the magnetic field measure-

ments. Hence, the electronic spin g -factor g_s yields the opportunity to compare an experimentally derived parameter with more reliable theoretical prediction.

The main objective of the present work is to reinvestigate the Zeeman spectrum of the OH $^2\Pi_{1/2}$ sub-state. Λ -doubling Zeeman transitions have been observed for the $J = 1/2$ singular level for the first time, and Zeeman data of improved quality are presented for the $J = 3/2$ level. Combining the zero-field and Zeeman data available in the literature with the present observations has enabled a rather uncorrelated fit of all the g -factors, and thereby individual g -factors of improved accuracy.

2. Experimental details

The experiments were performed with a molecular beam electric resonance spectrometer, previously used for obtaining Zeeman data on NO [4] and described in detail elsewhere [5]. We will only discuss some features relevant to the present work.

OH radicals have been produced in a number of different reactions. Under optimized conditions we found

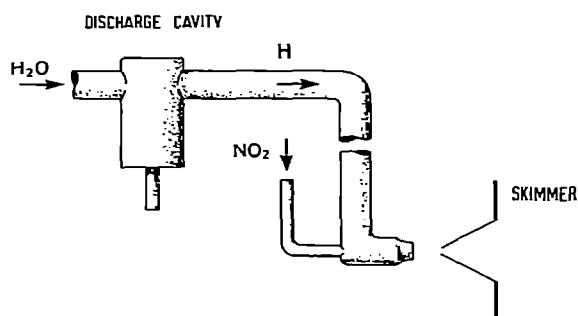
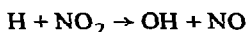


Fig. 1. Diagram of the reaction source for OH molecular beam production.

the reaction



described by Del Greco [6] to be effective in producing OH radicals [7]. The molecular beam was formed in a reaction source (fig. 1) also used in experiments on the iodine oxide radical [8]. Hydrogen atoms were produced in a 2.45 GHz microwave discharge in water vapour flowing through a 10 mm inner diameter tube. Typically 100 W of microwave power was dissipated. The NO₂ gas was injected at the reaction zone close to the end of the source. This end, contracted to a diameter of 6 mm, was placed some 15 mm in front of a conical skimmer with a 2 mm aperture. This distance could be varied to optimize the conditions. The source chamber (pumped by a 500 m³/h Roots pump) was at a typical pressure of 4×10^{-2} mbar.

The transitions were induced by microwave power from two backward wave oscillators (BWO) in the region 4–8 and 8–12 GHz (Varian type VA-185M and VA-175T, respectively). For stabilization the 30 MHz beat signal of the BWO frequency and of a synthesizer (Hewlett-Packard 8660B) was phase-locked to a 30 MHz reference signal by means of a synchronizer (Schomandl FDS 30). Transitions in NO below 500 MHz, used for field calibration purposes, could be induced directly by the synthesizer. In most cases four scans (each scan took about one minute at a 1 s time constant) were averaged yielding a signal-to-noise ratio of 3.

The observed Zeeman spectra involve $\Delta J = 0$ electric dipole allowed transitions between the two Λ -doubling components in the $J = 1/2$ and $J = 3/2$ rotational

states of the $^2\Pi_{1/2}$ level. In the magnetic field region three different configurations were used to induce transitions, depending on the frequency range and transition type. In the $J = 1/2$ state Λ -doubling transitions were studied by a stripline system. Two parallel conducting plates (10 mm spaced and 50 mm wide) acted as a transmission line with the electric field component perpendicular to the molecular beam and parallel to the homogeneous magnetic field, thus allowing $\Delta M_F = 0$ transitions. The observed linewidths were 10–15 kHz.

For the $\Delta M_F = 0$ transitions in the $J = 3/2$ state we used a rectangular waveguide with the end expanded in the direction parallel to the beam and contracted in the magnetic field direction. The microwave power was launched between two parallel plates (10 mm spaced, 10 cm wide). A travelling wave was obtained by obstructing reflections at the end of the parallel plate system with the help of foam microwave absorbers. The electric component of the microwave field was parallel to the magnetic field direction. We observed linewidths of 10–15 kHz with this apparatus.

To induce $\Delta M_F = \pm 1$ transitions in the $J = 3/2$ state, the waveguide was rotated 90° to obtain an electric component perpendicular to the magnetic field direction. The waveguide was again expanded in the beam direction; however, so as not to affect the cutoff frequency it is not allowed to contract in the magnetic field direction. The parallel plates were now separated by 23 mm and the observed linewidths 20–25 kHz.

The magnetic field was produced by an electromagnet (Bruker Physik) capable of yielding a homogeneous field up to 0.87 T in the transition region. The magnetic fields have been calibrated relative to previous Zeeman measurements on NO [4] in the $X^2\Pi_{1/2}$, $J = 1/2$ state around 430 MHz. Transitions at these frequencies could be induced directly by the stripline system. For the waveguide systems we had to connect the rf signal separately to the parallel plates. The NO molecule is formed in a sufficient amount in the same reaction as the OH radical. With this method the magnetic field strength could be determined to 4 parts in 10^5 for relative purposes. However, the absolute field uncertainty was limited to 2 parts in 10^4 inherent to the calibration of the NO measurements [4].

Table 1 presents the results. The errors indicated on the frequencies are determined by a combination of the spectral linewidths and stability of the magnetic

Table 1
Observed transition frequencies and magnetic flux densities of the ${}^2\Pi_{1/2}$, $J = 1/2$ and ${}^2\Pi_{1/2}$, $J = 3/2$ states in OH

J	F'	$M'_{F'}$	F''	$M''_{F''}$	B (T)	ν (MHz)	
1/2	1	1	1	1	0.80003 (16)	4717.874 (5)	
	1	0	1	0		4721.656	
	1	-1	1	-1		4783.040	
	1	0	0	0		4794.353	
	0	0	1	0		4631.052	
3/2	2	2	2	2	0.79991 (16)	7802.352 (4)	
	2	1	2	1		7799.887	
	2	0	2	0		7797.150	
	2	-1	2	-1		7794.107	
	2	-2	2	-2		7837.196	
	1	1	1	1	0.79994 (16)	7757.913	
	1	0	1	0		7783.766	
	1	-1	1	-1		7810.180	
	1	0	2	0		0.022567 (90)	7728.721 (5)
	2	0	2	-1		0.39994 (8)	7052.693 (8)
	2	0	2	1		8539.505 (5)	
	2	1	2	2		8549.298 (8)	
	1	0	1	1		8537.745 (5)	
	2	2	2	1	0.59998 (11)	6685.782 (4)	
	1	0	1	-1		6661.485 (4)	

field, while the field strength uncertainties represent the absolute error.

3. Determination of molecular parameters

The present Zeeman data on the ${}^2\Pi_{1/2}$, $J = 1/2$ and $J = 3/2$ levels were combined with all available high-precision data for the lowest vibrational level in a weighted non-linear least-squares fit. The experimental data used in addition to the present ones are as follows: microwave Λ -doubling transitions for the ${}^2\Pi_{1/2}$ and ${}^2\Pi_{3/2}$ substates (as compiled by Coxon et al. [9]), laser magnetic resonance (LMR) rotational and fine structure transitions [1], electron paramagnetic resonance (EPR) data for the ${}^2\Pi_{1/2}$ and ${}^2\Pi_{3/2}$ substates [2], and combination differences from the $\nu = 1 \leftarrow 0$ band observed by difference frequency laser spectroscopy [10].

A total of 25 parameters were determined simultaneously by the fit, including 2 rotational, 2 fine structure, 8 Λ -doubling, 7 hyperfine, and 6 g -factors. The highest correlation coefficients encountered were respectively 0.98 and 0.94 between the higher-order Λ -

doubling parameters p_H and p_L , and between q_L and p_L (cf. ref. [9]). Among the g -factors the highest correlation (0.89) was found between g_S and g_T . The weighted rms error of the fit was 1.60, indicating that the frequency residuals on an average exceeded the estimated measurement errors by a factor of 1.6. We were in particular unable to fit the combination differences from the $\nu = 1 \leftarrow 0$ band within the experimental accuracy of 0.001 cm^{-1} claimed by Amano [10]. Systematic residuals up to five times the experimental accuracy were found for the highest J value ($J = 7.5$).

The model used to fit the OH data was described in a previous paper [4] (and references therein). Table 2 presents molecular parameters and g -factors as determined from the present fit. No new information was obtained on the Λ -doubling and hyperfine parameters, and their fitted values are not reproduced here. The rotational constants B and D and the fine structure constants A and A'_D are mainly determined by the LMR data, which in turn requires precise knowledge of the g -factors. The present work seems to be the first investigation for OH in which zero-field parameters and g -factors are determined simultaneously. Hence, the present values of the rotational and fine structure constants including their standard deviations should be the most reliable ones available. The values of B , D , and A obtained by Brown et al. [1] from the LMR data with constrained values of all Λ -doubling and hyperfine parameters and all g -factors are, however, in good agreement with those presented in table 2 (see also comparison by Amano [10]).

The effective spin-orbit parameter A'_D and the g -factor g_T take care of the well known correlation between A_D and the spin-rotation interaction constant γ [3,4]. The present value of A'_D was obtained with γ constrained to its theoretical estimate $\gamma \approx \gamma^{(1)} - \frac{1}{2}P = -3502 \text{ MHz}$, with the first-order spin-rotation constant $\gamma^{(1)}$ equal to 22 MHz [11]. For A_D the most reliable estimate seems to be the value $A_D = -21.39(50) \text{ MHz}$ obtained by Brown et al. [12] from a combination of data on OH and OD. Hence, the definition of A'_D ,

$$A'_D = A_D - 2[\gamma(\text{true}) - \gamma(\text{est.})]/(A - 2B),$$

indicates that the estimated value of γ is in error by just about 1%. The estimated constrained value of γ could be changed by as much as 5% with no significant effect on the fitted g -factors, except for g_T which has an explicit dependence on γ .

Table 2
Molecular parameters for the ${}^2\Pi$ ground state ($v = 0$) in OH as determined from the present fit. The lower part of the table presents derived quantities

Quantity	Experimental value ^{a)}	Theoretical value
B (MHz)	555546.20(12)	
D (MHz)	57.1369(99)	
A (MHz)	-4172215.96(53)	
A'_D (MHz)	-13.18(15)	
$g_{I,\text{eff}}$	1.000870(25)	0.999825 ^{b)}
g_s	2.001945(50)	2.002114 ^{b)}
$10^3 g_R$	0.6411(70)	
$10^3 g_B^*$	-1.02485(82)	
$10^3 g_A^*$	4.36890(71)	
$10^3 g_T$	-0.041(11)	
$10^3 g_R^N$		-0.5286
$10^3 g_R^c$	-1.1697(70)	
$10^3 g_R^e({}^2\Sigma^+)$	-1.0661(74)	-1.040 ^{c)}
$10^3 g_R^e({}^2\Sigma^-)$	-0.0412(74)	
$10^3 g_R^e({}^2\Delta)$	-0.062(13)	

a) Numbers in parentheses represent one standard deviation. The standard deviations in $g_{I,\text{eff}}$ and g_s have been enhanced to take account of the absolute uncertainties in the magnetic field measurements. The fit uncertainties are 1.1×10^{-5} and 2.2×10^{-5} , respectively.

b) Ab initio value of g_I and g_s [3].

c) Contribution (ab initio) from the $A {}^2\Sigma^+$ state [13].

In NO a combination of the fitted values of A'_D and g_T led to separate values of A_D and γ [4]. The accuracy of the fitted g_T value for OH is, however, too low for a similar successful separation in this case.

A complete set of six fitted g -factors is presented in table 2. The error bars given also include the absolute uncertainties in the magnetic field measurements of the present work, and in the EPR spectrum. The fitted effective rotational g -factor g_R contains both a nuclear and an electronic part [4],

$$g_R = g_R^N - g_R^e,$$

$$g_R^e = g_R^e({}^2\Delta) + g_R^e({}^2\Sigma^+) + g_R^e({}^2\Sigma^-) = (g_I - g_R^N) \times \left(\sum_{{}^2\Delta, v'} \frac{\langle {}^2\Delta v' | L_+ | {}^2\Pi v \rangle \langle {}^2\Delta v' | B L_+ | {}^2\Pi v \rangle}{E_{\Pi v} - E_{\Delta v'}} + \sum_{{}^2\Sigma, v'} \frac{\langle {}^2\Pi v | L_+ | {}^2\Sigma v' \rangle \langle {}^2\Pi v | B L_+ | {}^2\Sigma v' \rangle}{E_{\Pi v} - E_{\Sigma v'}} \right).$$

In previous work on NO [4] the fitted values of g_R , $g_{I,\text{eff}}$, and g_B^* were combined with the ab initio value of g_I to yield separate values of $g_R^e({}^2\Delta)$, $g_R^e({}^2\Sigma^+)$, and $g_R^e({}^2\Sigma^-)$. A similar successful separation of the contributions to g_R^e was obtained for OH, and the results are presented in the lower part of table 2. The present results are also in reasonable agreement with those of an earlier investigation based on a smaller set of experimental data, and in which the g -factor g_s had to be constrained to its ab initio value [3]. The derived value of $g_R^e({}^2\Sigma^+)$ is seen to be in reasonable agreement with the ab initio prediction [13]; the small difference may indicate a significant contribution from excited ${}^2\Sigma^+$ states different from the prominent $A {}^2\Sigma^+$ state. Furthermore, the good agreement obtained for $g_R^e({}^2\Sigma^+)$ also tends to confirm the fitted value of $g_{I,\text{eff}}$, and in particular its deviation from the adiabatic ab initio prediction.

4. Discussion

The great puzzle presented by the present results is the clear discrepancy between the fitted value of g_s and the ab initio prediction. Ab initio values of g_I and g_s are obtained by computing the Hartree-Fock expectation values of the relativistic and diamagnetic corrections to the Zeeman Hamiltonian [3,4]. From atomic work the accuracy of the ab initio value of g_s is expected to be 1×10^{-5} or better, whereas the present difference between the experimental and theoretical values is $-1.69(50) \times 10^{-4}$. Hence, it seems safe to rule out inaccuracy in the ab initio prediction as an explanation for the discrepancy.

The reason may be sought within the theoretical model used to fit the data. However, the model used is able to reproduce the observed frequencies down to their estimated accuracies for a wide variety of transitions and field strengths. Furthermore, no alarming

correlation coefficients were encountered in the least-squares fit.

Finally, it remains to question the accuracy of the experimental data, in particular the absolute uncertainties in the magnetic field measurements. The estimated absolute uncertainty in the present magnetic field measurements of 2×10^{-4} affects the fitted value of g_s well within its error limits. For determining $g_{I,\text{eff}}$ and g_s the crucial data are the EPR measurements of the $^2\Pi_{3/2}$ state, in particular those of the lowest rotational level. The error limits $\pm 5 \times 10^{-5}$ given for g_s in table 2 stem from the absolute uncertainties in the $^2\Pi_{3/2}$ EPR magnetic field measurements, estimated to be 2×10^{-5} by Radford [14]. Hence, unless considerably underestimated, the magnetic field strength uncertainties do not provide a plausible explanation either.

Various refinements of the theoretical model were tried, e.g. to include adjustable centrifugal distortion corrections in the second-order g -factors g_R^c , g_A^* , and g_B^* which depend on the molecular moment of inertia. No significant centrifugal distortion effect was, however, detected. In NO a significant value of the electronic quadrupole moment Q_{\parallel}^c was obtained [4]. For OH a similar attempt to obtain Q_{\parallel}^c failed due to insufficient accuracy of the fitted value of the anisotropy in the magnetic susceptibility $\chi_{\parallel} - \chi_{\perp}$ [4]. An attempt was also made to fit the higher-order centrifugal distortion constant H . Its significance turned out to be mar-

ginal, and in the final fit it was constrained to the value 0.424×10^{-2} MHz obtained by Coxon [15] from UV data.

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