

## OBSERVATION OF $\rho$ -DOUBLET TRANSITIONS IN OH( $A^2\Sigma_{1/2}^+$ ) BY UV-MICROWAVE DOUBLE RESONANCE IN A MOLECULAR BEAM

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In a molecular-beam experiment on OH several  $\rho$ -doublet transition frequencies in the  $A^2\Sigma_{1/2}^+$  state have been measured by a UV-microwave double-resonance technique. Accurate values for the  $\rho$ -doubling and hyperfine constants have been obtained.

### 1. Introduction

The first excited electronic state  $A^2\Sigma_{1/2}^+$  of OH has been the subject of various high-resolution studies. From Hanle effect and optical-rf double-resonance measurements accurate  $g$ -factors and lifetimes were obtained [1]. In a molecular-beam apparatus we determined the hyperfine structure by laser-induced fluorescence (LIF) detection [2,3]. Raab et al. [4] reported more accurate values for the hyperfine constants from the observation of quantum beats in LIF signals.

The  $\rho$ -doubling, which is more than an order of magnitude larger than the hyperfine splittings, was more difficult to determine accurately. In a previous experiment [3] we succeeded in scanning the laser frequency continuously over the frequency separation of  $Q_1(N)$  and  $Q_{P_{21}}(N)$  transitions up to  $N=7$  and obtained values for the  $\rho$ -doubling constant and its centrifugal distortion. The accuracy was limited by residual Doppler broadening of the LIF signals due to the divergence of the molecular beam and by the inaccuracy of the free spectral range of the interferometer used for the calibration of observed splittings.

In the present investigation we have developed a new optical-microwave double-resonance technique by means of which microwave transitions in excited electronic states can be measured in a molecular beam. The underlying idea was a precise determination of the free spectral range of the interferometer. The working principle is essentially different from other

optical-microwave double-resonance experiments which are usually based on saturation of the electronic transition causing an increase of fluorescence intensity in the case of microwave resonance. Most of these experiments are performed in gas cells [5] but also molecular-beam techniques are applied [6] with the possibility of state selection [7]. In the present method, however, the excitation is weak and the total fluorescence is not influenced by the microwave transition. The detection is based on a change in the allowed spontaneous decay channels.

We have measured hyperfine resolved  $\rho$ -doublet transitions in the  $N=1, 3$  and  $4$  states of OH( $A^2\Sigma_{1/2}^+$ ). In comparison with the LIF results, the accuracy of the  $\rho$ -doubling constant obtained is improved by two orders of magnitude because the transition frequencies are measured directly and the linewidth is no longer determined by residual Doppler effects. Also the hyperfine constants were obtained with a much larger precision compared to our previous values.

The observation of  $\rho$ -doublet transitions in the  $A^2\Sigma_{1/2}^+$  state of OH is complicated for two reasons. First the transitions are parity-conserving and have to be induced via the magnetic dipole moment; this is relatively large in open-shell molecules, but still the transition probability is a factor  $10^4$  smaller than for electric dipole transitions. Second, since the lifetime of the excited state is only  $0.7 \mu\text{s}$ , the weak microwave transition must take place within a path length of about  $0.5 \text{ mm}$ . These problems have been overcome

by the application of small resonant microwave cavities with internal UV excitation.

## 2. Experiment

A schematic view of the experimental arrangement is given in fig. 1. The OH beam formation and LIF detection have been described [2,3]. The OH was produced by the reaction between H and NO<sub>2</sub> or by a coaxial microwave discharge in H<sub>2</sub>O [8]. The latter method is cleaner and yields comparable amounts of hydroxyl radicals. Inside a microwave cavity resonant at a  $\rho$ -doublet transition the radicals were excited from the ground to the excited electronic state by a perpendicularly incident UV beam at 309 nm. The UV radiation with a power around 1 mW was obtained from a stabilized single-frequency ring dye laser with intra-cavity frequency doubling. A fraction of the UV beam was used to probe the OH radicals by LIF detection at about 5 cm from the first excitation zone. In some of the measurements the full laser beam was used both for probing and, after traversing the beam ma-

chine, for pumping. For phase-sensitive detection the pump beam was modulated at 3000 Hz by a mechanical chopper.

The working principle of the double-resonance method is explained in fig. 2. For the levels shown molecules are excited from the X<sup>2</sup>Π<sub>3/2</sub>,  $J = 9/2$ ,  $F = 5$  state to A<sup>2</sup>Σ<sub>1/2</sub>,  $N = 3$ ,  $J' = 7/2$ ,  $F' = 4$  from which they decay back to the X<sup>2</sup>Π state within 1 μs. About one third of the excited molecules returns to the initial state and contributes to the LIF signal produced by the probe beam. When the excited molecules are pumped by microwave radiation from  $J' = 7/2$ ,  $F' = 4$  to  $J' = 5/2$ ,  $F' = 3$  the decay follows other ways back to the ground electronic state. The transition to the Π<sub>3/2</sub>,  $J = 9/2$  state is then forbidden by the selection rule  $\Delta J = 0, \pm 1$ . Consequently the population of the initial state as probed in the LIF zone will be reduced. Because the UV pump beam is modulated this results in an increase of the (negative) phase-sensitive signal.

Cylindrical microwave cavities were used, resonating at the frequency of the  $N = 1, 3$  and 4 transitions. The cavities were oscillating in the TE<sub>011</sub> mode with a maximum magnetic field along the axis. Coarse tuning

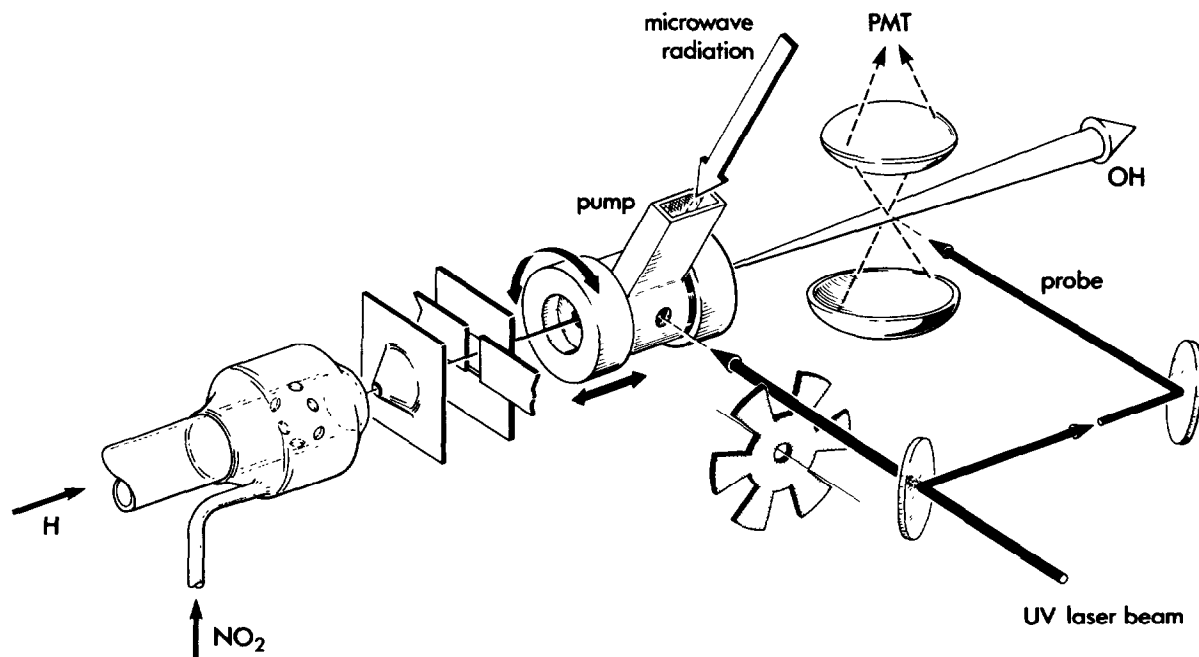


Fig. 1. Schematic view of the experimental arrangement.

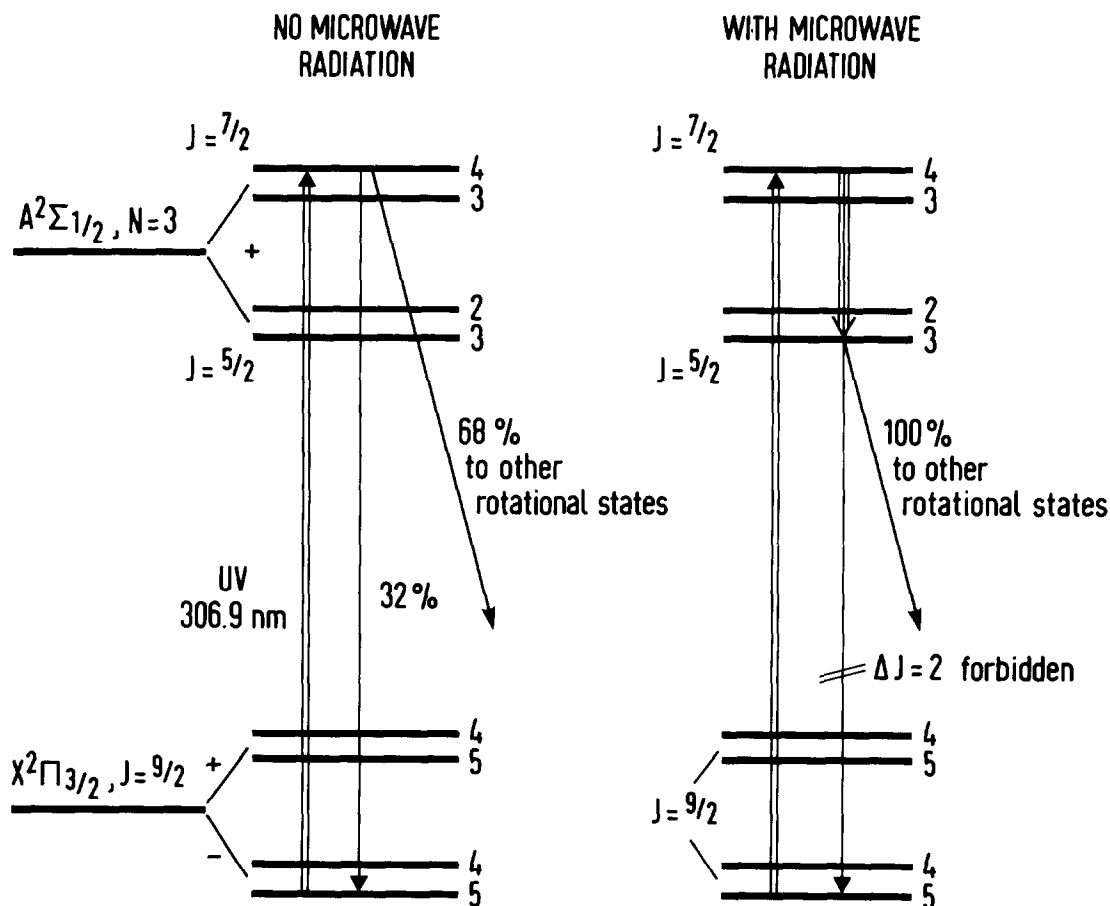


Fig. 2. Working principle of the double-resonance experiment.

was possible by varying the cavity length. A small bolt in the middle of the cavity served for fine tuning. The cavity length varied between 26 mm for  $N=1$  and 7 mm for  $N=4$ . The entrance and exit holes for the molecular beam were 3 mm in diameter. In the middle of the cavity wall two opposite holes with a diameter of 5 mm were present to transmit the laser beam. The quality factor varied between 100 and 1000.

The microwave klystrons were stabilized by phase locking to a rubidium frequency standard. During the measurements the microwave frequency was swept while the laser frequency was fixed at the top of the absorption line.

### 3. Experimental results

The transitions induced by pump and probe UV beam were  $P_1(2)$ ,  $P_1(4)$  and  $P_1(5)$ . The phase-sensitive signal observed when the pump beam is switched on is critically dependent on the alignment of the two laser beams with respect to each other. By comparing the LIF signals measured with and without pump beam it followed that the pump efficiency is equal to about 5% at 1 mW. The  $P_1(N)$  spectra consist of three hyperfine components; the  $\Delta F=0$  component is, however, weak and mostly overlapped by one of the strong  $\Delta F=-1$  lines. All three  $\Delta F=0, \pm 1$  hyperfine transitions between the  $\rho$ -doublet states were measured except for  $N=4$  where the  $F=4 \rightarrow 4$  transition was too weak to be detected. Most signals could be observed at  $RC$

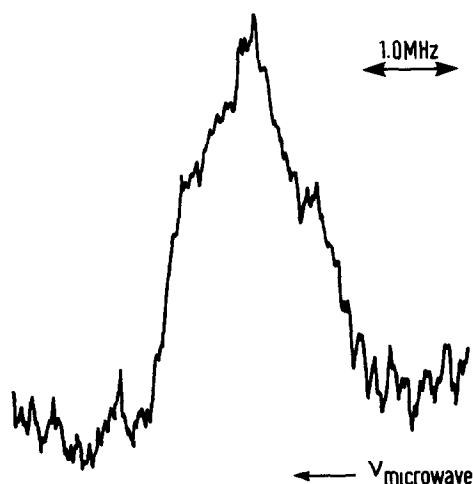


Fig. 3. The observed  $J = 7/2, F = 4 \rightarrow J = 5/2, F = 3$  transition in  $A^2\Sigma_{1/2}^+, N = 2$  at 23975.2 MHz.

= 3 s but signal averaging was applied to improve the signal to noise ratios. A typical example of a double-resonance signal is shown in fig. 3. The linewidths varied between 1.5 and 2.0 MHz. The intensities were proportional to the square of the UV power as expected since both the pump and the probe beam were far from saturating the absorption.

The measured frequencies are given in table 1. The experimental errors correspond to the spread of the results of at least four measurements. We have fitted these frequencies to an effective Hamiltonian for the  $A^2\Sigma_{1/2}^+$  state:

Table 1

Observed  $\rho$ -doublet transition frequencies (in MHz) for OH in the  $A^2\Sigma_{1/2}^+, v = 0$  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  $\rho$ -doublet state, respectively

$N$	$J_1, F_1$	$J_2, F_2$	Observed frequency	Observed - calculated
1	3/2, 1	1/2, 0	9724.84(15)	0.07
	3/2, 1	1/2, 1	9924.74(10)	-0.01
	3/2, 2	1/2, 1	10410.71(12)	0.08
3	7/2, 3	5/2, 2	23260.80(10)	-0.03
	7/2, 3	5/2, 3	23561.49(10)	0.09
	7/2, 4	5/2, 3	23975.20(10)	-0.11
4	9/2, 4	7/2, 3	29979.02(10)	-0.04
	9/2, 5	7/2, 4	30695.08(10)	0.05

Table 2

Hyperfine and  $\rho$ -doublet constants (in MHz) for OH in  $A^2\Sigma_{1/2}^+, v = 0$  and comparison with values obtained from quantum-beat spectroscopy [4] and ab initio calculations [9]

Molecular constant	This work	Quantum-beat spectroscopy	Ab initio calculations
$b + c/3$	771.74(22)	774.1(4)	775.5
$c$	161.01(55)	168.9(8)	150.3
$\gamma$	6777.749(36)		
$\gamma_D$	-1.4263(22)		

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

The first term gives the rotational energy with  $N$  the quantum number for the nuclear rotation; the second term represents the interaction between  $N$  and the electron spin  $S$ , responsible for the  $\rho$ -doubling; the last two terms represent the hyperfine interaction. The constants  $b$  and  $c$  are the hyperfine parameters introduced by Frosch and Foley [9]. Also included in the fit were the previously measured hyperfine splittings for  $N = 1$  through 4 and  $\rho$ -doublet splittings for  $N = 5, 6$  and 7 [3]. The  $P_1(1)$  transition, from which the hyperfine splitting in the  $N = 0$  state is obtained, was re-measured with all hyperfine components resolved (linewidth 12 MHz). The resulting  $N = 0$  splitting is equal to  $771.7 \pm 1.5$  MHz. This is somewhat lower than the previous value which must be due to a too small correction for the overlap of hyperfine components in our earlier measurements.

From the least-squares fit we obtained the values for the  $\rho$ -doubling and hyperfine constants as given in table 2. In the fit the relative weights of  $\rho$ -doublet and hyperfine splittings were taken according to their experimental uncertainties. In table 2 the errors correspond to one standard deviation. Calculations based on these constants yielded  $\rho$ -doublet transition frequencies which are in good agreement with the observed values as shown in table 1. Consideration of the second-order distortion constant  $\gamma_H$  in the fit had no influence on the results.

#### 4. Discussion

The present values for the  $\rho$ -doubling and hyperfine constants are much more precise than our previ-

ous results. The  $\gamma$ -constant is even a factor 100 more accurate as a result of the direct measurement of the  $\rho$ -doublet transition frequencies. Whereas our previous hyperfine constants are still in agreement with the present values within three standard deviations this is not the case for the quantum-beat results of Raab et al. [4]. This might be due to a larger inaccuracy in the extrapolation of their high-magnetic-field data to zero-field splittings than they quoted. Kristiansen and Veseth [10] have performed ab initio calculations of the hyperfine constants and obtained values which are close to the present results. The agreement is not as good as for the ground electronic state of OH indicating that ab initio calculations for excited states are open for improvement. No ab initio calculations are available for the  $\rho$ -doubling constants.

The accuracy of this double-resonance experiment is limited by the short lifetime  $\tau$  of the excited state. The probability for a microwave transition  $|i\rangle \rightarrow |j\rangle$  within this time is [11]

$$P_{ij} = \frac{\Omega_{ij}^2}{\Omega_{ij}^2 + \Delta\omega^2} \sin^2 \left[ \frac{1}{2} \tau (\Omega_{ij}^2 + \Delta\omega^2)^{1/2} \right], \quad (2)$$

with  $\Delta\omega/2\pi = \nu - \nu_0$ , the difference between the frequency of the stimulating field ( $\nu$ ) and the transition frequency ( $\nu_0$ ), and  $\Omega_{ij} = \langle i | \boldsymbol{\mu} \cdot \mathbf{B} | j \rangle / \hbar$ , the Rabi frequency for the interaction between the magnetic dipole moment  $\boldsymbol{\mu} = \mu_B g_s \mathbf{S}$  in the  $A^2\Sigma_{1/2}^+$  state and the microwave magnetic field. Inside the small laser excitation zone the Rabi frequency is practically constant and the transition probability at  $\nu = \nu_0$  is equal to unity at  $\Omega_{ij} = \pi/\tau$ . It follows that the full linewidth at half height is equal to  $\tau^{-1} = 1.4$  MHz. The observed linewidths are slightly larger, which is probably due to a larger degree of saturation by the microwave field and

to the velocity distribution of the OH radicals.

In view of the short lifetime of the excited state, the low laser excitation power, the weak microwave transition strength and the low density of OH radicals in the molecular beam, we conclude that the present double-resonance experiment is very sensitive. The method is essentially Doppler-free and therefore especially promising for molecules with excited-state lifetimes longer than  $1 \mu\text{s}$  resulting in linewidths smaller than 1 MHz which is impossible to obtain with LIF measurements even in beams due to residual Doppler broadening.

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