Ultraviolet-Microwave Double Resonance Spectroscopy on OH

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The spin-rotation and hyperfine structure of OH in the first excited electronic state $A^2\Sigma^+_{1/2}$ has been investigated by molecular beam LIF [1] and quantum beat [2] spectroscopy. In the present work the N' = 3 and N' = 4 splittings in $A^2\Sigma^+_{1/2}$, v' = 0 have been measured with a much higher accuracy by inducing magnetic dipole transitions between the ρ-doublet states in a microwave – UV double resonance experiment.

The experimental set-up is shown schematically in fig. 1. The OH radicals are produced in the reaction $H + NO_2 \rightarrow OH + NO$ in front of the molecular beam source. The fraction of OH radicals in the molecular beam is about 1%. The radicals are excited from the ground state $X^2\Pi_{3/2}$ to the $A^2\Sigma^+_{1/2}$ state by a perpendicularly incident UV beam at 307 nm. The UV radiation is obtained by frequency doubling in an angle-tuned $LiIO_3$ crystal inside the cavity of a stabilized ring dye laser operating with R6G. The $^2\Sigma_{1/2} \leftarrow {}^2\Pi_{3/2}$ transitions induced are N' = 3, J' = 7/2, F' = 3 or 4 ← J = 9/2, F = 4 or 5 and N' = 4, J' = 9/2, F' = 4 or 5 ← J = 11/2, F = 5 or 6. The UV excitation takes place inside a microwave cavity resonating in the TE_{011} mode. The excited OH radicals decay back to the $X^2\Pi$ state within 1 μs. About 1/3 of them return to the initial state. At 5 cm from the cavity the population of the initial state is probed by LIF. In the microwave cavity magnetic dipole transitions are induced between the upper and lower

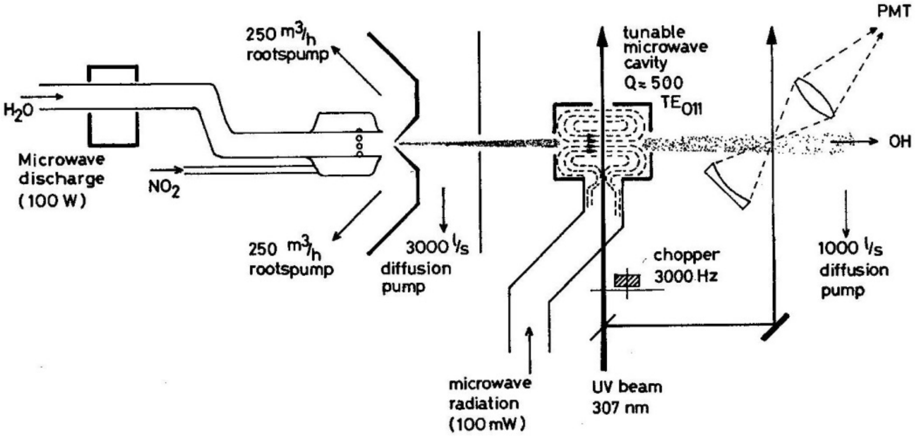

Fig. 1.: Schematic view of the OH beam double resonance set-up

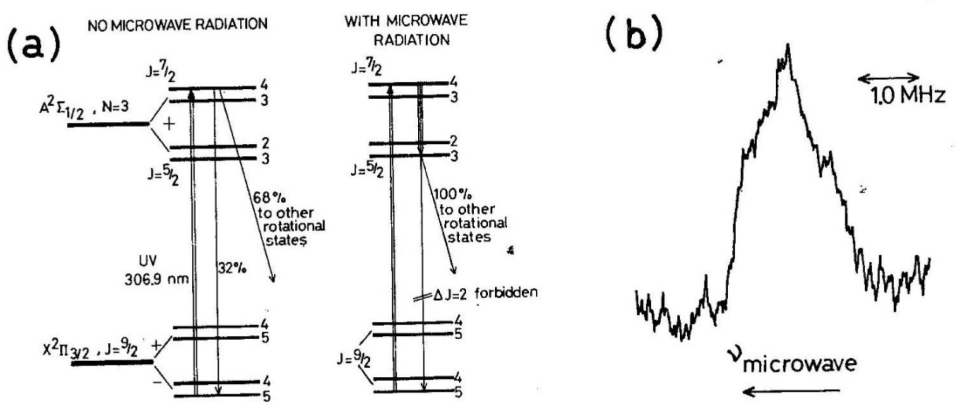

Fig. 2: (a) Working principle of the double resonance experiment. (b) The J = 7/2, F = 4 → J = 5/2, F = 3 transition in $A^2\Sigma^+_{1/2}$, N' = 3 at 23 975.2 MHz

ρ-doublet hyperfine states. Molecules that have made a microwave transition cannot decay back to the initial state because of the selection rule $\Delta J = 0, \pm 1$. This is shown schematically in fig. 2a. As a result the population of the initial state as measured by the probe laser beam decreases in case of a microwave resonance.

In the measurements the UV pump beam was modulated and the microwave frequency was scanned. The signal-to-noise ratio varied between 5 and 20 at integration times of about 20 minutes. The linewidth (FWHM) was equal to 1.8 MHz. A typical result is given in fig. 2b. The observed transitions and their frequencies are listed in table 1. The frequencies have been fitted to an effective Hamiltonian for a $^2\Sigma^+_{1/2}$ diatomic molecule [1]

$$H = BN^2 + (\gamma+\gamma_D N^2)\mathbf{N}\cdot\mathbf{S} + b\mathbf{I}\cdot\mathbf{S} + cI_zS_z.$$

The preliminary results for the spin-rotation coupling constants γ and γ_D and the hyperfine coupling constants b and c are (in MHz) b = 718.05 ± 0.09, c = 158.6 ± 1.2, γ = 6776.69 ± 0.07, $\gamma_D = -1.418 \pm 0.004$. The accuracy will be improved further by the measurement of the N' = 1 and N' = 2 transitions at 10 and 17 GHz respectively.

Table 1: The ρ-doublet transition frequencies (in MHz) of OH in $A^2\Sigma^+_{1/2}$, v' = 0

	J, F → J, F'	observed frequency	previous work [1]
N' = 3	7/2, 3 → 5/2, 2	23 260.80 ± 0.05	23 258.9 ± 12.0
	7/2, 3 → 5/2, 3	23 561.49 ± 0.08	23 559.8 ± 12.0
	7/2, 4 → 5/2, 3	23 975.20 ± 0.05	23 974.9 ± 12.0
N' = 4	9/2, 5 → 7/2, 4	30 695.08 ± 0.05	30 695.9 ± 6.0
	9/2, 4 → 7/2, 3	29 979.02 ± 0.08	29 978.3 ± 6.0

References

1. J.J. ter Meulen, W.A. Majewski, W.L. Meerts and A. Dymanus: Chem. Phys. Lett. 94, 25 (1983)
2. F. Raab, T. Bergeman, D. Lieberman and H. Metcalf: Phys. Rev. A24, 3120 (1981)