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[1] R. Bass, Nucl. Phys. A231, 45 (1974), and Phys. Rev. Lett. 39, 265 (1977).

[2] J. Galin *et al.*, Phys. Rev. C 9, 1018 (1974).

[3] D. Glas and U. Mosel, Nucl. Phys. A237, 429 (1975).

[4] D. Horn and A. J. Ferguson, Phys. Rev. Lett. 41, 1529 (1978), and Nucl. Phys. A311, 238 (1978).

[5] R. G. Stokstad *et al.*, Phys. Rev. Lett. 37, 888 (1976).

[6] P. Sperr *et al.*, Phys. Rev. Lett. 37, 321 (1976).

[7] M. Conjeaud *et al.*, Nucl. Phys. A309, 515 (1978).

[8] D. G. Kovar, in Proceedings of the IPCR (Institute of Physical and Chemical Research) Symposium on Macroscopic Features of Heavy-Ion Collisions and Pre-Equilibrium Process, Hakone, Japan, 1977, edited by H. Kamitsubo and M. Ishihara (unpublished).

[9] D. Glas and U. Mosel, Phys. Lett. 78B, 9 (1978).

[10] A. M. Zebelman and J. M. Miller, Phys. Rev. Lett. 30, 27 (1973).

[11] M. N. Namboodiri *et al.*, Nucl. Phys. A263, 491 (1976).

[12] R. G. Stokstad *et al.*, Phys. Rev. Lett. 36, 1529 (1976).

[13] R. G. Stokstad *et al.*, Phys. Lett. 70B, 289 (1977).

[14] J. Gomez del Campo *et al.*, Phys. Rev. C 19, 2170 (1979).

[15] S. Cohen *et al.*, Ann. Phys. (N.Y.) 82, 557 (1974).

[16] D. Shapira *et al.*, to be published.

[17] J. Gomez del Campo and R. G. Stokstad, Monte Carlo Hauser-Feshbach Code LILITA.

[18] R. Satchler and W. G. Love, Phys. Lett. 65B, 415 (1976).

[19] J. R. Birkelund *et al.*, Phys. Rev. Lett. 40, 1123 (1978).

[20] D. Glas and U. Mosel, Phys. Lett. 49B, 301 (1974).

[21] C. Von Charzewski *et al.*, Nucl. Phys. A307, 309 (1978).

[22] P. Bonche *et al.*, Phys. Rev. C 17, 1700 (1978); R. Y. Cusson *et al.*, Phys. Rev. C 18, 2589 (1978).

[23] K. H. Ziegenhain *et al.*, Fisica 9, 559 (1977).

[24] T. Tamura *et al.*, Phys. Lett. 66B, 109 (1977).

Determination of the Hyperfine Structure in the $A\,^2\Sigma_{1/2}{}^+$ State of OH by Frequency-Doubled Dye-Laser Radiation

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The hyperfine structure of OH in the $A\,^2\Sigma_{1/2}{}^+$ state has been measured by exciting a molecular beam with cw intracavity frequency-doubled dye-laser radiation. The splittings are 778 MHz for $N'=0$ and 200 to 500 MHz for $1 \le N' \le 5$. The values for the hyperfine and ρ doubling are $b+\frac{1}{3}c = 777.8 \pm 2.0$ MHz, $c = 165.8 \pm 2.8$ MHz, and $\gamma = 7.13 \pm 0.03$ GHz. Also the hyperfine splitting of OD in the $N'=0$ state has been measured yielding $b+\frac{1}{3}c = 119 \pm 2$ MHz.

The hydroxyl radical (OH) is one of the fundamental molecules in chemistry, physics, and astrophysics. It is the simplest diatomic open-shell system, readily accessible for a wide range of spectroscopic techniques (optical,[1] infrared,[2] microwave,[3] and molecular beam-maser and -resonance[4,5]) and accurate calculations. The radical plays an important role in laboratory and atmospheric chemistry and its maser emission in interstellar clouds forms a major unsolved problem in astrophysics.

In the past considerable effort has been spent to unravel the structure and properties of OH. The structure of the ground electronic state ($X\,^2\Pi$), its vibrational and rotational levels, the ρ doubling, and the hyperfine structure are all well known.[6] This is, however, not the case for the first excited electronic state $A\,^2\Sigma_{1/2}{}^+$ where only the rotational and Λ-doubling energies are known from old optical work. The hyperfine structure due to the interaction between the magnetic moment $I=\frac{1}{2}$ of the hydrogen nucleus and the electronic spin has not been measured yet. In level-crossing experiments German *et al.*[7,8] determined the hyperfine structure of OD in the $A\,^2\Sigma_{1/2}{}^+$ state from which they calculated the splittings for OH. The estimated values are on the order of 300 MHz which is beyond the resolution of conventional Doppler-limited spectroscopy (4 GHz at 300 K).

The knowledge of the hyperfine structure is important not only for a theoretical understanding of the excited structure but also for the uv excitation models of interstellar OH radicals. As proposed by Litvak *et al.*,[9] uv pumping might cause a population inversion between the Λ-doublet levels in the rotational ground state $^2\Pi_{3/2}$, $J=\frac{3}{2}$, leading to the observed maser emissions. Turner[10] has pointed out that the hyperfine structure forms a crucial parameter in Litvak's model.

We report here the determination of the hyperfine structure in the $A\,^2\Sigma_{1/2}^+$ state of OH by exciting a molecular OH beam by uv radiation from a single-frequency cw dye laser with intracavity frequency doubling. Because the second-harmonic power is proportional to the square of the fundamental power, the uv intensity obtained is usually several orders of magnitude larger than in the case of extracavity frequency doubling. This makes experiments on molecular beams in the uv region possible especially in the case of free radicals or other unstable molecules. In combination with the very sensitive detection of fluorescence radiation, the present experimental technique opens large perspectives for high-resolution molecular spectroscopy between 200 and 400 nm.

The basic outline of the laser system is shown in Fig. 1. The frequency doubling takes place inside the cavity of a modified single-frequency Spectra Physics dye laser (model 580A). The intracavity laser radiation is focused in the center of an ammonium dihydrogen arsenate crystal mounted in a temperature stabilized oven to permit 90° phase matching by temperature tuning. Unfortunately, it turned out that at 307 nm, 90° phase matching was just not possible because damage at the crystal coatings occurred at the temperature required (> 110°C). Therefore the temperature was kept below 110°C and phase matching was obtained by rotating the crystal slightly with respect to the laser axis, whereby the frequency-doubling efficiency decreased by a factor of 2. The generated uv radiation is coupled out via the concave end mirror which is highly reflectant for the fundamental radiation. A single-frequency second-harmonic power of 0.1 mW is obtained at 615 nm for Rhodamine *B* pumped by 4-W argon-ion-laser power at 514 nm. At a somewhat lower power (~ 30 μW) the fundamental frequency can be swept linearly over 3 GHz in a single scan without the occurrence of mode hops. This is achieved by an active stabilization system in which the laser frequency is controlled by an external reference cavity. In addition the electronically tunable etalon is locked to the cavity mode. Details of the complete laser system will be published in a forthcoming paper.

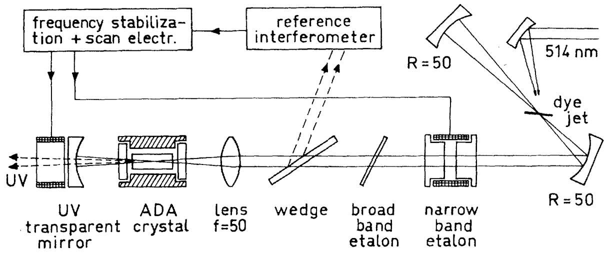

FIG. 1. A schematic view of the single-frequency dye laser with intracavity frequency doubling.

The production of the OH beam takes place in the same way as described previously.[4] The OH radicals are obtained by the reaction

$$H + NO_2 \rightarrow OH + NO$$

taking place in front of the molecular beam source. The OH radicals are excited by the perpendicularly incident uv beam at about 10 cm from the beam source. Part of the emitted fluorescence radiation is reflected by a spherical mirror and detected by a photomultiplier tube (EMI, 9789Q). Phase-sensitive detection is possible by 120-Hz modulation of the molecular beam.

In total eleven rotational transitions with wavelengths[1] between 306.8 and 308.3 nm were induced to the $^2\Sigma_{1/2}^+$ states with J' up to $\frac{11}{2}$; five transitions from the ground state (P_1, Q_1, Q_{21}, R_1, and R_{21}) and six of the R_1 and R_{21} type from the lower Λ-doublet levels of the $^2\Pi_{3/2}$, $J=\frac{5}{2}$, $\frac{7}{2}$, and $\frac{9}{2}$ states. In the case of $\Delta J=0$ the transitions are split into four hyperfine components of which the two $\Delta F=0$ transitions are a factor of 5 or more stronger than the $\Delta F=\pm 1$ components. The reverse is the case for $\Delta J=\pm 1$ transitions. It turned out that the weak transitions coincided with the strong ones within the experimental linewidth which is equal to about 150 MHz, deter-

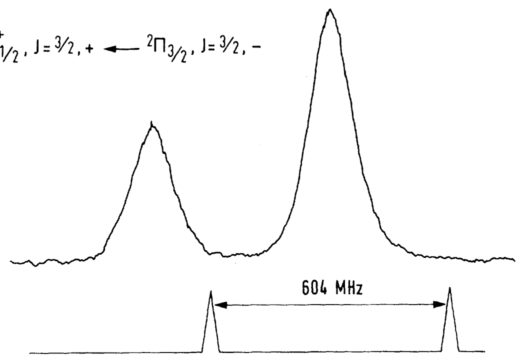

FIG. 2. Typical recordings of the $Q_1(1)$ transition of OH.

mined by the divergency of the molecular beam. A typical spectrum observed is shown in Fig. 2 for the $^2\Sigma_{1/2}{}^+$, $J'=\frac{3}{2}^+ \leftarrow {}^2\Pi_{3/2}$, $J=\frac{3}{2}^-$ transition. During the frequency scan, markers are produced by an interferometer at intervals of 604 MHz, equal to twice the free spectral range at the fundamental wavelength. The interferometer has been calibrated by measuring the hyperfine splitting in the D_2 line of sodium at 589 nm in an atomic-beam setup.

If the weak components are neglected the splittings observed would be 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. This depends on the sequence of the levels with the quantum number for the total angular momentum F and F' of the Π and Σ levels involved, respectively. In the $^2\Pi_{3/2}$ rotational states up to $J=\frac{5}{2}$ the lower hyperfine levels correspond to $F=J-\frac{1}{2}$. At $J=\frac{7}{2}$ the sequence is reversed, i.e., $F=J+\frac{1}{2}$ for the lower levels.[6] For the $^2\Sigma_{1/2}{}^+$ states with $J'=N'+\frac{1}{2}$ the lower hyperfine levels have the quantum number $F'=J'-\frac{1}{2}$, whereas for $J'=N'-\frac{1}{2}$ the upper level corresponds to $F'=J'-\frac{1}{2}$. The inclusion of the weak components causes a correction which is quite large (up to 13 MHz) for some of the transitions from the lowest state $^2\Pi_{3/2}$, $J=\frac{3}{2}$, but smaller than 1 MHz for the transitions from $J\geqslant\frac{5}{2}$ states. The hyperfine splittings obtained for the $A\,^2\Sigma_{1/2}{}^+$ states are given in Table I. The experimental accuracy is about 0.5%. Also measured is the energy separation between the $J'=\frac{1}{2}$, $F'=0$ and $J'=\frac{3}{2}$, $F'=2$ hyperfine levels of the $N'=1$ state, which turned out to be equal to 10745(45) MHz. From this the ρ-doubling constant γ can be determined when the values for the hyperfine constants are known.

TABLE I. The observed and calculated hyperfine splittings in the $A^2\Sigma_{1/2}{}^+$ state of OH.

N'*, *J'	Observed splitting (MHz)	Calculated splitting (MHz)	Observed minus calculated splitting (MHz)
0, 1/2	777.9	777.8	0.1
1, 1/2	198.1	199.4	− 1.3
1, 3/2	490.1	490.0	0.1
2, 3/2	276.5	275.7	0.8
2, 5/2	436.0	438.9	− 2.9
3, 5/2	303.4	301.8	1.6
3, 7/2	415.9	417.0	− 1.1
4, 7/2	319.1	315.6	3.5
4, 9/2	404.4	404.8	− 0.4
5, 9/2	323.2	324.2	− 1.0
5, 11/2	398.3	397.0	1.3

The hyperfine-interaction Hamiltonian for the $A\,^2\Sigma_{1/2}{}^+$ state can be written as[11]

$$H_{\mathrm{hf}} = b(\vec{I}\cdot\vec{S}) + cI_zS_z, \tag{1}$$

where to a good approximation the constants b and c are equal to

$$b = g_I\,\mu_0\mu_N\left\langle \frac{4}{3}\,\frac{\delta(r)}{r^2} - \frac{3\cos^2\chi - 1}{r^3}\right\rangle_{\mathrm{av}},$$

$$c = 3g_I\,\mu_0\mu_N\left\langle \frac{3\cos^2\chi - 1}{r^3}\right\rangle_{\mathrm{av}}$$

averaged over the electronic space coordinates r and χ. Matrix elements exist only between states with the same parity for which $\Delta J'=0$, ± 1 and $\Delta F'=0$. The coupling between states with $\Delta J'=\pm 1$ and $\Delta N'=\pm 2$ gives a contribution to the hyperfine splittings of the order of 10 kHz which is far below the present experimental accuracy. So the problem is reduced to the diagonalization of the 2×2 matrix obtained for each N' state. The matrix elements were evaluated with symmetrized Hund's case-(b) Σ-state basis functions. The interaction of the $\Pi_{1/2}$ and $\Pi_{3/2}$ states is expected to give a contribution less than 100 kHz. For a given N' state the expressions are obtained as given by Radford.[12] The hyperfine matrices are diagonalized by a computer program and the values for $b+\frac{1}{3}c$ and c are determined in a least-squares fit. The results along with the value obtained for γ are given in Table II. The hyperfine splittings in this fit and given in Table I are in good agreement with the experimental results.

From measurements on the $N'=1$ state of OD in the $A\,^2\Sigma_{1/2}{}^+$ state German *et al.*[7] derived for the $N'=1$ state of OH a value of 509 MHz for the hyperfine splitting of the $J'=\frac{3}{2}$ level and 227 MHz for the $J'=\frac{1}{2}$ level, which is somewhat higher than the present results. The value of γ has been determined by Dieke and Crosswhite.[1] Their result of 6.73 GHz deviates strongly from our value. From theory German *et al.* obtained a value

TABLE II. The hyperfine coupling and ρ-doubling constants of OH in the $A^2\Sigma_{1/2}{}^+$ state.

Molecular constant	Value (MHz)
$b+\frac{1}{3}c$	777.8 ± 2.0
c	165.8 ± 2.8
γ	7130.0 ± 30.0

of 7.05 GHz which is in closer agreement with the present value.

A better comparison with the experimental results of German *et al*. would be the measurement of the hyperfine splittings of OD in the $A\,^2\Sigma_{1/2}{}^+$ state. Unfortunately, we could only resolve the splitting between the $F'=\frac{1}{2}$ and $F'=\frac{3}{2}$ levels of the $N'=0$ state, being equal to $\frac{3}{2}(b+\frac{1}{3}c)$. The transition induced, the $P_1(1)$ transition from the $\Pi_{3/2}$, $J=\frac{3}{2}$ state at 307.3 nm,[13] consists of five components of which three coincide within 19 MHz and two with 7 MHz as follows from microwave data.[14] A least-squares fit in which the theoretical values for the relative strengths of the five transitions were input yielded $b+\frac{1}{3}c=119\pm 2$ MHz. This is in agreement with the value of 118.31 ± 0.14 MHz given by German.[8]

Except for the $N'=0$ state the hyperfine splittings in the $A\,^2\Sigma_{1/2}{}^+$ state of OH are all less than 500 MHz. This value is equal to the Doppler broadening at a temperature of 8 K. The splitting of 778 MHz of the $N'=0$ state is equal to the Doppler width at 20 K. This implies that for the uv-excited interstellar OH radicals the overlap of the hyperfine states at temperatures up to 20 K is much smaller for the lowest state, $N'=0$, than for the higher levels. Preliminary calculations in which for simplicity complete overlap is assumed for the states with $N'\geqslant 1$ and no overlap at all for $N'=0$ show that at optical depths larger than about 0.5, as defined according to Litvak *et al*.,[9] the ground-state hyperfine transition $F=1\rightarrow F=1$ at 1665 MHz becomes anomalously strong, in agreement with the observed spectra. However, also the satellite transition $F=2\rightarrow F=1$ at 1720 MHz would be strong in emission which has not been observed for class-I sources. More accurate calculations are in progress.

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[1] G. H. Dieke and H. M. Crosswhite, J. Quant. Spectrosc. Radia. Transfer 2, 97 (1962); B. G. Elmergreen and W. H. Smith, Astrophys. J. 178, 557 (1972).

[2] T. W. Ducas, L. D. Geoffrion, R. M. Osgood, and A. Javan, Appl. Phys. Lett. 21, 42 (1972).

[3] G. C. Dousmanis, T. M. Sanders, and C. H. Townes, Phys. Rev. 100, 1735 (1955); R. L. Poynter and R. A. Beaudet, Phys. Rev. Lett. 21, 305 (1968); H. E. Radford, Rev. Sci. Instrum. 39, 1687 (1968).

[4] J. J. ter Meulen and A. Dymanus, Astrophys. J. 172, L21 (1972); J. J. ter Meulen, W. L. Meerts, G. W. M. van Mierlo, and A. Dymanus, Phys. Rev. Lett. 36, 1031 (1976).

[5] W. L. Meerts and A. Dymanus, Can. J. Phys. 53, 2123 (1975).

[6] J. L. Destombes, C. Marlière, A. Beaudry, and J. Brillet, Astron. Astrophys. 60, 55 (1977).

[7] K. R. German, T. H. Bergeman, E. M. Weinstock, and R. N. Zare, J. Chem. Phys. 58, 4304 (1973).

[8] K. R. German, J. Chem. Phys. 64, 4192 (1976).

[9] M. M. Litvak, A. L. McWorther, M. L. Meeks, and H. J. Zeiger, Phys. Rev. Lett. 17, 821 (1966).

[10] B. E. Turner, J. R. Astron. Soc. Can. 64, 221 (1970).

[11] R. A. Frosch and H. M. Foley, Phys. Rev. 88, 1337 (1952).

[12] H. E. Radford, Phys. Rev. A 136, 1571 (1964).

[13] M. A. A. Clyne, J. A. Coxon, and A. R. Woon Fat, J. Mol. Spectrosc. 46, 146 (1973).

[14] W. L. Meerts and A. Dymanus, Astrophys. J. 180, L93 (1973).