ENERGY PARTITIONING IN THE REACTION ${}^{16}O({}^{1}D) + H_{2}{}^{18}O \rightarrow {}^{16}OH + {}^{18}OH - VI$. THE u.v.-SPECTRUM OF ${}^{16}OH$ AND ${}^{18}OH$

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Abstract—Highly resolved observations of the u v spectrum of ¹⁶OH and ¹⁸OH have been made in the absorption mode by means of a narrow bandwidth dye laser $(\nu/\Delta\nu = 10^6)$. The spectrum of the transition from the electronic ground state to the first excited electronic state, $A^2\Sigma^+ \leftarrow X^2\Pi$, in the $O \rightarrow O$ vibrational band yielded molecular constants for these rotational systems in both isotopic modifications. The determination of these constants was based on a linearized least squares procedure. The term value formulas employed take into account the Λ -splitting and the centrifugal distortion of the molecule. The computer procedure revealed that the theoretically calculated transitions agree with the measured absorption lines to better than $0 \ 1 \ cm^{-1}$. The following molecular constants of the Λ -type doubling of the ²II and ²\Sigma⁺ state, *A*, *A_j*, the constants of the splitting of the ²II state, γ_0 , the constant of the ρ -splitting of the ²\Sigma⁺ state. Furthermore, term values up to *J*'' and *J*' = 30.5 are reported for both spin systems and isotopes

INTRODUCTION

The OH radical is a species of considerable interest, since it is an important trace constituent of the atmosphere,¹ is of decisive significance in combustion,² and is known to be a maser source in interstellar space.³ Its simple structure permits complete analysis of all quantum states and offers the possibility of more closely investigating the Λ -type doubling. In discussing the dynamics of chemical reactions of the 4-center type in which the OH radical is a participant, namely,

${}^{16}O({}^{1}D) + H_{2}{}^{18}O \rightarrow {}^{16}OH + {}^{18}OH$

in the present experiments, knowledge of all possible transitions of the radical allows detailed statements to be made.⁴ Furthermore, OH is a good model molecule for testing methods of theoretical calculation of molecular states, as Destombes *et al.*⁵ have shown in their work For these reasons, it is not surprising that OH has been the subject of numerous intensive experimental and theoretical studies

The first fundamental and comprehensive spectroscopic study was done by Dieke and Crosswhite,⁶ whose results were later reanalyzed by Moore and Richards.⁷

The theoretical analysis of hydroxyl radical spectra has been carried out either by direct diagonalization⁸ or by perturbation calculations.⁹ Basically, the two methods use the same Hamiltonian derived from Van Vleck's early work.¹⁰

Until now, however, there have been no experimental data on transitions of ¹⁸OH to parallel the quite precise knowledge of the u v. spectrum of ¹⁶OH. Only a small number of microwave transitions in the $X^2\Pi$ state have been determined.¹¹

THEORY

A first attempt at a term value formula for diatomic molecules is due to Hill and Van Vleck.¹² Taking Hund's case (b) as a point of departure, they employ first-order perturbation theory to calculate, from the terms neglected in separating the Schrödinger equation, those matrix elements that cause the spin-splitting of the doublet state. Their term value formula takes the following form for both spin states:

$$F_{J^{\pm 1/2}} = \nu_0 + B \left[\left(J + \frac{1}{2} \right)^2 - \Lambda^2 \pm \frac{1}{2} \sqrt{(\Lambda^2 Y(Y - 4) + 4(J + 1/2)^2)} \right], \tag{1}$$

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where Y = A/B, B is the rotational constant, and A is the constant of spin-orbit coupling; Λ is the projection of the electronic orbital angular momentum on the bond axis of the molecule, and J represents the total angular momentum of the molecule. By taking into account centrifugal distortion and spin-rotation interaction, following Mulliken and Christy,¹³ with the terms

$$-D[N(N+1) - \Lambda^{2}] \begin{cases} +\frac{1}{2}\gamma N, & N = J - \frac{1}{2}, \\ -\frac{1}{2}\gamma(N+1), & N = J + \frac{1}{2}, \end{cases}$$

where D is the rotational constant of centrifugal distortion and γ is the constant of ρ -splitting, an essentially exact term value formula is obtained for the ${}^{2}\Sigma^{+}$ state. $N = |\Lambda|, |\Lambda| + 1, ...$ represents the sum of the angular momentum of rotation of the nuclei and the angular momentum vector component Λ .

Combining eqs. (1) and (2) for OH gives for the $A^2\Sigma^+$ state ($\Lambda = 0$ and Y = 0)

$$F_{J-1/2} = F_1 = \nu_0 + BN(N+1) - DN^2(N+1)^2 + \frac{1}{2}\gamma N,$$

$$F_{J+1/2} = F_2 = \nu_0 + BN(N+1) - DN^2(N+1)^2 - \frac{1}{2}\gamma(N+1).$$
(3)

Adding a term $HN^{3}(N + 1)^{3}$ and expressing the N-dependence of the constant γ in the form given by Moore and Richards,⁷

$$\gamma = \gamma_0 (1 - kN(N+1)); \ k = 2D_e/B_e - A_f/A + (B_{\xi} - B_{\pi})/W_o, \tag{4}$$

where W_o is the energy spacing of the electronic states under consideration, we are able to obtain the final term value formula for the ${}^{2}\Sigma^{+}$ state.

Equation (1) is also the point of departure for the case of the $X^2\Pi$ state, this time for second-order perturbation calculations. Since here $\Lambda > 0$, the twofold splitting of the term values of both spin systems must be taken into account. In the case of OH, the perturbations of the ${}^{2}\Sigma^{+}$ system are substantially responsible for the splitting of these levels. If, in the perturbation calculation, once again those terms are taken into consideration which were neglected in separating the wave equation¹⁴ and also the matrix elements of the spin-orbit coupling (see Table 1), the perturbation calculation gives the following two matrices:

		${}^{2}\Sigma^{+}{}_{J-1/2}$	${}^{2}\Pi^{+}_{J-1/2}$	${}^{2}\Pi^{-}_{J+1/2}$
		${}^{2}\Sigma^{+}_{J+1/2}$	${}^{2}\Pi^{-}{}_{J-1/2}$	$^{2}\Pi^{+}_{J-1/2}$
${}^{2}\Sigma^{+}{}_{J-1/2}$	${}^{2}\Sigma^{+}{}_{J+1/2}$	к	μ	ν
${}^{2}\Pi^{+}{}_{J-1/2}$	${}^{2}\Pi^{-}{}_{J-1/2}$	μ	β	ε
${}^{2}\Pi^{-}_{J-1/2}$	${}^{2}\Pi^{+}_{J+1/2}$	ν	ε	γ

The states for the first set of matrix elements refer to term values Π_f , and those in the second set to Π_e (following the notation of Kopp and Hougen¹⁵). A-type doubling arises from the elements μ and ν . The constants of the A-splitting are defined as follows:

$$o = -\xi^2 / W_o, \quad p = -8\xi\eta / W_o, \quad q = -8\eta^2 / W_o.$$

We have used the concise notation

$$o = -\xi'^2$$
, $p = -8\xi'\eta'$, $q = -8\eta'^2$.

To obtain the energy values of the system, the secular equation

$$\begin{vmatrix} W_o & \mu & \nu \\ \mu & \beta - E & \epsilon \\ \nu & \epsilon & \gamma - E \end{vmatrix} = 0$$



must be solved, in which the matrix element $\kappa - E$ has been approximated by the constant energy difference W_o . The following solution (compare Ref. 13) neglects only terms whose numerator contains the square of this energy difference, W_o^2 :

$$f_{1/2}^{[\pm]} = BX + \frac{1}{2}(o + \frac{1}{2}p + q(J + \frac{1}{2})^2) + [\pm]\frac{1}{2}(\frac{1}{2}p + q)(J + \frac{1}{2}) + \\\pm [(A - 2B)^2/2 + B^2X + BX(\frac{1}{2}p + q) + (2B - A)(o + \frac{1}{2}p + q)/2 + \\[\pm]BXq(J + \frac{1}{2}) + [\pm](2B - A)(\frac{1}{2}p + q)(J + \frac{1}{2})/2]^{1/2}$$
(5)

If a J-dependence of the constants of the Λ -splitting is included in the calculation, there results appreciably improved accuracy of the term values, as well as a remarkable diminution of the standard deviation of the molecular constants, especially those for the Λ -splitting. Introduction of the rotational constants D and H for the centrifugal distortion and of the substitution $A \rightarrow A + A_J X$, as suggested by Mulliken and Christy,¹³ Kovács¹⁴ and Veseth,¹⁶ leads to (compare Ref. 7) the following relation used by us:

$$f_{1/2}^{[\frac{1}{2}]} = BX - D(X^{2} + X + 1) + HX^{3} + \frac{1}{2}(o + \frac{1}{2}p + q(X + 1)) + [\pm]\frac{1}{2}(\frac{1}{2}p + q)(J + \frac{1}{2}) \pm [\frac{1}{4}((2B - 4DX + 6HX^{2}) - (A + A_{J}X))^{2} + + (B - 2DX + 3HX^{2})^{2}X + \frac{1}{2}(2B - 4DX + 6HX^{2})(o + \frac{1}{2}p + q) - -\frac{1}{2}(A + A_{J}X)(o + \frac{1}{2}p + q) + [\pm]\frac{1}{2}(2B - 4DX + 6HX^{2})(\frac{1}{2}p + q)(J + \frac{1}{2}) - [\pm]\frac{1}{2}(A + A_{J}X)(\frac{1}{2}p + q)(J + \frac{1}{2}) + \frac{1}{2}(2B - 4DX + 6HX^{2})(\frac{1}{2}p + q)X + [\pm]\frac{1}{2}(2B - 4DX + 6HX^{2})(J + \frac{1}{2})qX + (o + \frac{1}{2}p + q(X + 1) + [\pm](\frac{1}{2}p + q)(J + \frac{1}{2}))^{2}]^{1/2}.$$
(6)

DESCRIPTION OF THE SPECTRUM

The electronic spin in the OH radical is $s = \frac{1}{2}$, resulting in doublet states These are denoted by the indices 1 and 2, respectively, so that for

$$F_1, f_1, J = N + \frac{1}{2};$$

 $F_2, f_2: J = N - \frac{1}{2}$

 $F_{1,2}$ refers to the ${}^{2}\Sigma^{+}$ state and $f_{1,2}$ to the ${}^{2}\Pi$ state.

The Λ -splitting occurring in the ground state is identified by $[\pm]$ in the term value formula, and is labeled with the indices c and d in the listing of term values (Tables 2-5). Knowledge of the possible transitions is a prerequisite for the calculation of the molecular constants and term values Selection rules for dipole transitions of the free molecule: $N \rightarrow N$ and $N \rightarrow N \pm 1$, together with the symmetry selection rule: even \rightleftharpoons odd, define the main branches.

For Hund's case (b), we find a P branch for $N \rightarrow N - 1$, a Q branch for $N \rightarrow N$, and an R branch for $N \rightarrow N + 1$. The resulting transitions are P_1 , P_2 , Q_1 , Q_2 , R_1 , R_2 , In addition to the principal branches, there are also six satellite branches, for which $\Delta J \neq \Delta N$ Thus these satellite lines arise only when the spin system is altered. Among these, there are transitions which do not obey the N-selection rule for dipole transitions. These are the 0 branch for $N \rightarrow N - 2$ and the S branch for $N \rightarrow N + 2$.

The satellite lines O_{12} , P_{12} , Q_{12} , Q_{21} , R_{21} , S_{21} are thus obtained The satellite lines are of particular interest since a main and satellite line belonging to the same rotational quantum number lead directly to the ρ -splitting of the $^{2}\Sigma^{+}$ system. Agreement of experimental results with the theoretically calculated rotational constant γ_{0} for this splitting confirms the validity of the computational procedure



Fig 1 Energy level diagram of OH The different branches of the rotational structure of the transitions $A^2\Sigma^+(v'=0) \leftarrow X^2\Pi_{3/2,1/2}(v''=0)$ are shown

COMPUTATIONAL PROCEDURE

To compute term values and molecular constants for ¹⁶OH from the wave numbers of the absorption lines, a least-squares procedure was employed that compares the observed wave numbers with those calculated from the specified formulas until the new constants produce an absolute minimum sum of squared errors. The initial trial values required for this procedure were taken from the work of Maillard and Chauville ¹⁷

The procedure involves the following sequence:



The newly calculated constants for ¹⁶OH, in turn, served as initial trial values for the constants of ¹⁸OH. Finally, the term values obtained, together with the applicable selection rules, permit back calculation to the wave numbers of the absorption lines. For most lines, the discrepancy between experiment and theory proves to be less than 0.1 cm⁻¹

1	N	Fir	Fid	Fa	Fa.
$ \begin{bmatrix} 1 & .00 & .06 & 126 46 & 126 3 \\ 2 & 83.72 & 83 92 & 187.76 & 187.4 \\ 3 & 201 91 & 202.36 & 289.03 & 288.7 \\ 4 & 355.08 & 355.88 & 429.42 & 429 \\ 5 & 543 54 & 544.78 & 608 12 & 608 0 \\ 6 & 767.40 & 769.17 & 824 43 & 824.6 \\ 7 & 1026.65 & 1029.03 & 1077 72 & 1078 3 \\ 8 & 1321 15 & 1324 21 & 1367 46 & 1368.5 \\ 9 & 1650.67 & 1654.48 & 1693 10 & 1694 6 \\ 10 & 2014.89 & 2019.52 & 2054.14 & 2056 2 \\ 11 & 2413.45 & 2418.95 & 2450 04 & 2452.8 \\ 12 & 2845.91 & 2852.34 & 2880 28 & 2883.8 \\ 13 & 3311.78 & 3319.20 & 3344 26 & 3346 5 \\ 14 & 3810.55 & 3819.00 & 3841 42 & 3846.5 \\ 15 & 4341.64 & 4351 15 & 4371 11 & 4377.1 \\ 16 & 4904.42 & 4915.05 & 4932.70 & 4939 6 \\ 17 & 5498 25 & 5510.02 & 5525.49 & 5533.3 \\ 18 & 6122.44 & 6135.38 & 6148 76 & 6157.6 \\ 19 & 6776.26 & 6790.39 & 6801.78 & 6811.6 \\ 20 & 7458.95 & 7474.29 & 7483 77 & 7494 8 \\ 21 & 8169.73 & 8186 29 & 8193 93 & 8205 9 \\ 22 & 8907.77 & 8925 56 & 8931.43 & 8944 4 \\ 23 & 9672 24 & 9691.26 & 9695 41 & 9709.5 \\ 24 & 10462 26 & 10482.50 & 10484.99 & 10500 2 \\ 25 & 11276 95 & 11298 39 & 1299 29 & 11315 5 \\ 26 & 12115 38 & 12138.02 & 12137.37 & 12154.7 \\ 27 & 12976 62 & 13000.43 & 12998.30 & 13016 7 \\ 28 & 13859 74 & 13084.69 & 13881.13 & 13900.6 \\ 29 & 14763 75 & 14789 82 & 14784 89 & 144805 3 \\ 30 & 15687 70 & 15714 84 & 15708 60 & 15730 \\ \end{bmatrix}$	<u> </u>	10		<u> </u>	*2d
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	3	201 91	202.36	289.03	288.73
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	5	543 54	544.78	608 12	608 09
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$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	8	1321 15	1324 21	1367 46	1368,51
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	30	15687 70	15714 84	15708 60	15730 06
31 16630.58 16658 75 16651 27 16673 6	31	16630.58	16658 75	16651 27	16673 67

Table 2 Term levels of ${}^{16}\text{OH}, {}^{2}\Pi_{3/2-1/2}(v''=0)$

Table 3 Term levels of ${}^{16}\text{OH}, {}^{2}\Sigma^{+}(v'=0)$

N	F ₁	F ₂
0	32440.62	<u> </u>
	32474.65	32474 31
2	32542.54	32541 98
3	32644.19	32643.41
4	32779.47	32778 47
5	32948,17	32946.95
6	33150.05	33148.61
7	33384.82	33383.17
8	33652.14	33650,27
9	33951.63	33949.54
10	34282.84	34280.54
11	34645.30	34642,80
12	35038.49	35035.79
13	35461.84	35458.93
14	35914.72	35911.62
15	36396.49	36393.20
16	36906 45	36902.97
17	37443 85	37440 19
18	38007 92	38004 08
19	38597.83	38593 82
20	39212 73	39208.54
21	39851.71	39847 37
22	40513.86	40509.36
23	41198,19	41193.55
24	41903 73	41898 94
2.5	42629.43	42624.50
26	43374.23	43369.18
27	44137.05	44131.68
28	44916.77	44911.48
29	45712.25	45706.86
30	46522.33	46516.85
31		47340.25

N	Fje	F _{Jd}	F2c	F2d
1	.00	.06	125.56	125.40
2	83.20	83.40	186.50	186.23
3	200.68	201.12	287.20	286 91
4	352.91	353.70	426.77	426.57
5	540.21	541.43	604.43	604.40
6	762.69	764.44	819.44	819.69
7	1020.33	1022.67	1071.20	1071.81
8	1312.98	1315.99	1359.16	1360.20
9	1640.41	1644.16	1682.78	1684.33
10	2002.31	2006.86	2041.56	2043.68
11	2398.31	2403.72	2434.96	2437.73
12	2827.98	2834.31	2862.47	2865.93
13	3290.86	3298.16	3323.51	3327.73
14	3786.45	3794.76	3817.53	3822.56
15	4314.18	4323.55	4343.93	4349.82
16	4873.49	4883.96	4902.10	4908.88
17	5463.78	5475.38	5491.40	5499.12
18	6084.41	6097.18	6111.17	6119 87
19	6734.74	6748.70	6760.76	6770 46
20	7414.10	7429.28	7439.48	7450.21
21	8121.82	8138.24	8146 65	8158,43
22	8857.22	8874.88	8881.56	8894,42
23	9619.59	9638.52	9643.51	9657.47
24	10408.26	10428.47	10431.82	10446 88
25	11222.54	11244.03	11245.79	11261.96
26	12061.75	12084.52	12084.74	12102.03
27	12925.23	12949 30	12948 00	12966.42
28	13812.34	13837.70	13834.93	13854.47
29	14722.45	14749.10	14744,89	14765.56
30	15654.98	15682.92	15677.30	15699.10
31	16609.36	16638 60	16631.60	16654.53

Table 4 Term levels of ${}^{18}\text{OH}, {}^{2}\Pi_{3/2,1/2}(v'=0)$

Table 5 Term levels of ${}^{18}\text{OH}, {}^{2}\Sigma^{+}(v'=0)$

N	F	F ₂
0	32440.62	
1	32474.48	32474.14
2	32542.03	32541.46
3	32643.17	32642.38
4	32777.74	32776.72
5	32945.54	32944.30
6	33146.30	33144.84
7	33379.74	33378.06
8	33645.49	33643.59
9	33943.16	33941.05
10	34272.32	34269.99
11	34632.48	34629.94
12	35023.12	35020.37
13	35443.70	35440.74
14	35893.62	35890.46
15	36372.28	36368,92
16	36879.03	36875.48
17	37413.22	37409.48
18	37974.16	37970.23
19	38561.17	38557.05
20	39173.53	39169.24
21	39810.56	39806.09
22	40471.54	40466.91
23	41155.78	41150.99
24	41862.60	41857 65
25	42591.33	42586.23
26	43341.33	43336.08
27	44111.98	44106.60
28	44902.72	44897.20
29	45713.01	45707.37
30	46542.37	46536.61
31		47384.52
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EXPERIMENTAL

A fast photochemical production-detection cycle, provided by nanosecond spectroscopy, was used to study the absorption spectrum of ¹⁶OH and ¹⁸OH.¹⁸ In the present experiments, the OH radicals were produced by the reaction of oxygen atoms with water. The following reaction scheme shows the formation of the isotopically differing molecules

$${}^{16}\text{O}_3 + h\nu(266 \text{ nm}) \rightarrow {}^{16}\text{O}({}^1D) + {}^{16}\text{O}_2({}^1\Delta_g),$$

 ${}^{16}\text{O}({}^1D) + H_2{}^{18}\text{O} \rightarrow {}^{16}\text{OH} + {}^{18}\text{OH}.$

The O(¹D) atoms are generated by photolysis of ozone with the fourth harmonic of the radiation of a Nd: YAG laser (266 nm). The O(¹D) atoms react with the isotopically labeled water at a gas-kinetically controlled rate ¹⁹ and form the two OH radicals. At the gas pressures employed, 10 torr for H₂¹⁸O and 2 torr for ¹⁶O₃, the reaction time is 13 ns. The experimental setup is shown in Fig 2 The OH radicals are detected by means of the absorption above 308 nm resulting from their resonant transitions $A^2\Sigma^+ \leftarrow X^2\Pi$. The dye laser that produces the resonant radiation is pumped by the second harmonic of the YAG laser light with a delay of 10 ns. The bandwidth of the dye laser is narrowed by use of an etalon. The resulting line width was determined to be 0.05 cm^{-1} by means of an external Fabry-Perot. For the ${}^{2}\Sigma^{+}(v' = 0) \leftarrow {}^{2}\Pi(v'' = 0)$ transition of the OH radicals, the Doppler width amounts to 0.1 cm⁻¹, so that the resolution of the spectrum is limited only by the Doppler broadening

The dye laser is tuned by varying the pressure of a gas in the optical resonator.²⁰ These operating conditions, using propane at 0-760 torr as a tuning gas, offer reproducible frequency tuning over a continuous range of more than 30 cm^{-1} with a nonlinearity of less than 5×10^{-4}

Since the absorption of the OH radicals lies in the uv, the light of the dye laser is frequency doubled. To compensate for intensity fluctuations, the monitoring laser beam is split into two beams, one of which bypasses the cell (Fig 2) Both signals are detected by u.v diodes but only the differential signal is registered and amplified ⁴. The signal is stored and averaged by a boxcar integrator and read out by a recorder. A pressure scan of the observed OH absorption spectrum is shown in Fig 3. This scan exhibits absorption lines due to the $v'' = 0 \rightarrow v' = 0$ transition for both isotopes. The isotopic lines are well resolved from each other.



Fig 2 Schematic diagram of the experimental setup A, aperature, BS, beam splitter, C, chamber, DYE, pressure-tuned dye laser, F, filter; M, mirror, MC, mixing chamber, OSC, oscilloscope, PD, photodiode, REC, recorder, S(F)HG, second (fourth) harmonic generator

Fig 3 A portion of the u v absorption spectrum including the $Q_2(11)$ and $P_1(6)$ lines of the isotopically different species ¹⁶OH and ¹⁸OH

RESULTS AND DISCUSSION

The molecular constants calculated by the computational procedure described are presented in Table 6. There are various methods for experimentally obtaining the quantities that are theoretically derived by the computer procedure. One approach is to determine the constant γ_0 of the ρ -type doubling from the difference between a main and a satellite line. From the term value formulas this can be seen to be $\gamma(N + 1/2)$, which, by invoking Eqn (4), gives a value for γ_o In this way, we find $\gamma_o = 2.23$ cm⁻¹ for ¹⁶OH and $\gamma_o = 2.30$ cm⁻¹ for ¹⁸OH, both of which lie within the confidence intervals of our molecular constants

As a second approach, we calculated backwards to the spectrum of ¹⁶OH from its published term values, and then compared with its lines as given in the work of Dieke and Crosswhite. For the great majority of transitions, agreement to better than 0.1 cm⁻¹ was found. In individual



Fig. 4 Calculated Λ -type $({}^{2}\Pi_{3/2,1/2})$ and ρ -type $({}^{2}\Sigma^{+})$ doubling of ${}^{16}OH$ and ${}^{18}OH$; (a), Λ -doubling; (b), ρ -doubling, \bigoplus , ${}^{18}OH$, \bigcirc , ${}^{16}OH$

	8 _{0H}	Ref. 11	3 18.4280	5 I.921E~3		2 -4.22 E-1	4 6.90 E-2	2	2	4	2 -138.661		3 16.815	5 2.023E-3		2
found in different studies		Тһів чогк	18.4380 ± 7.3 E-	1.952E-3 ± 4.8 E-	2.62 E-7 ± 9.2 E-	-4.33 E-1 <u>+</u> 2.7 E-	6.88 E-2 + 7.3 E-	-1.88 E-1 ± 2.3 E-	2.38 E-I ± 1.5 E-	-3.79 E-2 ± 8.0 E-	-138.26 ± 7.8 E-	3.5 E-3 + 4.2 E-	16.877 ± 6.9 E-	2.174 E-3 ± 4.5 E-	3.53 E-7 ± 8.6 E-	2,26 E-1 ± 1.8 E-
5 Comparison of molecular constants		Ref. 7	18.5474 <u>+</u> 2.1 E-4	1.9003E-3 ± 5.6 E-7	1.18 E-7 ± 4.1 E-10	-4.43 E-1 <u>+</u> 4.0 E-3	6.924E-2 <u>+</u> 4.8 E-5		2.46 E-1	-3.84 E-2	-139.37 <u>+</u> 4.1 E-2	4.5 E-3 <u>+</u> 2.9 E-4	16.9602 ± 5.0 E-4	2.039E-3 <u>+</u> 1.3 E-6	8.71 E-8 <u>+</u> 8.6 E-10	
Table (10 91	This work	JB 5469 ± 9.6 E-4	J.898E-3 ± 2.2 E-6	1.16 E-7 ± 1.5 E-9	-4.40 E-1 + 4.1 E-3	6.93 E-2 <u>+</u> 5.2 E-5	-1.937E-1 <u>+</u> 3.6 E-3	2.439E-1 ± 2.3 E-3	-3.841E-2 ± 5.8 E-5	-139.25 <u>+</u> 2.5 E-2	3.58 E-3 <u>+</u> 3.1 E-4	16.9609 ± 9.2 E-4	2.041 B-3 ± 2.1 E-6	8.78 E-8 ± 1.4 E-9	2.238E-1 ± 1.6 E-3
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cases exhibiting a deviation greater than 0.1 cm⁻¹, it was possible to provide the computer with more accurate wave numbers for the transitions taken from the measured ¹⁶OH spectrum, so that for these absorption lines, too, exact term values are shown with an uncertainty of about 0.1 cm⁻¹. Owing to the narrow bandwidth of the laser and the great accuracy with which the position of an ¹⁸OH line in the absorption spectrum can be measured relative to the position of the corresponding ¹⁶OH line, the accuracy of the term values of ¹⁸OH is determined by the accuracy of the ¹⁶OH term values

A further test of the accuracy of the term values for both states is a comparison of computed with observed values of the Λ -splitting Beaudet and Poynter¹¹ report such values measured by microwave spectrometry. Here, too, the differences were found to be less than 0.1 cm⁻¹ This is particularly remarkable in view of the fact that the present least-squares procedure employs the difference between two different electronic systems. Figure 4 shows graphically the ρ -type doubling of the ${}^{2}\Sigma^{+}$ state and the Λ -type doubling of the two spin systems of the ${}^{2}\Pi$ state for both isotopes

A comparison of molecular constants for ¹⁶OH and ¹⁸OH here reported with those found in previously published works is presented in Table 6. In most cases the values agree to within 5 parts per thousand The remaining discrepancy in the values of Moore and Richards may be a consequence of neglect of higher order terms in their computational procedure; this would also account for the particularly large deviation noted in A_J , in view of the great sensitivity of this parameter The modest disagreement of Beaudet and Poynter's values for ¹⁸OH can presumably be ascribed to their use of isotopic scaling instead of fitting the majority of their parameters; taking cognizance of the difference in computational approach and the fundamental dissimilarity of the underlying experiments, the reasonable agreement of the final results appears encouraging

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