The uv Spectrum of ^{18}OD

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The combined high-resolution ultraviolet (uv) absorption spectrum of ^{16}OD and ^{18}OD was obtained. State selective measurements of the transitions from the electronic ground state to the first excited electronic state, $\tilde{A}^2\Sigma^+ \leftarrow \tilde{X}^2\Pi$, in the 0–0 vibronic band were performed by means of a narrow bandwidth dye laser system. Evaluation of these transition frequencies in wavenumbers yielded molecular constants as well as rotational term values for each of the isotopic species. A computer program based on a linearized least-squares procedure was used to determine the molecular constants and term values. The term value formulas which were employed for this purpose, take into account the Λ splitting and the centrifugal distortion of the diatomic species. The transitions, recalculated from the semiempirically determined term values agree with the measured absorption lines to better than 0.1 cm^{-1}. The following molecular constants are reported: B, D, H, the rotational constants of the $^2\Pi$ and $^2\Sigma^+$ states; O_0, P_0, Q_0, the constants of the Λ splitting of the $^2\Pi$ state; A and A_J; the constants of the spin–orbit coupling of the $^2\Pi$ state; and γ_0, the constant of the ρ doubling of the $^2\Sigma^+$ state. Futhermore, term values up to J'' and J' of 25.5 and the corresponding uv transitions are given.

INTRODUCTION

Due to the importance of the hydroxyl radical as a trace constituent of the atmosphere (*1*), as a short-lived molecule in a wide variety of combustion and flame processes (*2*), and as a maser source in astrophysical objects (*3*), numerous experimental and theoretical investigations of its electronic structure have been performed. The chemical kinetics as well as dynamics of the four-center reaction involving the OD radical

$$^{16}\text{O}(^1\text{D}) + \text{D}_2{}^{18}\text{O} \rightarrow {}^{16}\text{OD} + {}^{18}\text{OD} \tag{1}$$
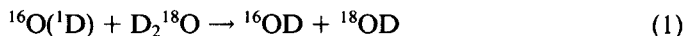
has been analyzed (*4*). The present paper is concerned with the spectral analysis of the experimental frequencies of OD radicals produced in reaction (1), and thus with the computation of a self-consistent set of term values. The computational procedure was originally developed to analyze the uv spectrum of OH, but the analogous electronic structure of OD also allows the use of computer program for the UV spectrum of OD as well (*5*).

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The first fundamental and comprehensive study of the OH uv spectrum, which included term values and molecular constants, was reported by Dieke and Crosswhite (6). Similar sets of term values have been derived for ^{16}OD by Clyne, Coxon, and Woon Fat (7), and reanalyzed for ^{16}OH by Moore and Richards (8). Experimental data as well as calculated energy levels and constants of ^{18}OH were recently given by Nuss, Gericke, and Comes to parallel the precisely known uv spectrum of ^{16}OH (5).

The structure of the rotational transitions in the $\tilde{A}^2\Sigma^+ \leftarrow \tilde{X}^2\Pi$ bands of OD and OH is complex because of a change in the $^2\Pi$ ground state from coupling according to Hund's case (a) to case (b) with increasing rotation. Furthermore, the electronic ground state $^2\Pi$ is split into two Λ levels by a distortion of the first excited electronic state (9). Since this splitting shows a characteristic J dependence, and because of finer details of spin–orbit and spin–rotation interaction in both states (10), it is necessary to use perturbation (11) theory or direct diagonalization of the Hamiltonian. Perturbation theory up to the third order takes into account most of these interactions and results in term value formulas for the $^2\Pi$ and the $^2\Sigma^+$ set.

EXPERIMENTAL DETAILS

Absorption measurements have a great advantage in comparison with measurements by the usual resonance fluorescence technique (12). In the case of absorption, predissociation has less influence on the intensity of the transition than it does in the case of emission. While the intensity of emission lines is strongly reduced by a ra-
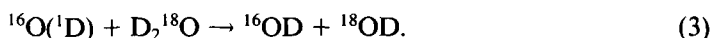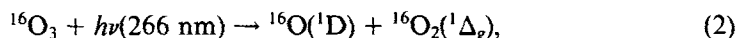
TABLE I

Energy levels of the electronic ground state of ^{18}OD ($\tilde{X}^2\Pi(v = 0)$). The f_1 levels correspond to the Λ components of the $^2\Pi_{3/2}$ state as do the f_2 levels to the $^2\Pi_{1/2}$ state

N"	f_{1e}	f_{1f}	f_{2e}	f_{2f}
1	.00	.01	131.04	130.92
2	45.79	45.83	162.11	161.89
3	110.03	110.12	213.75	213.45
4	192.81	192.98	285.82	285.45
5	294.23	294.50	378.14	377.75
6	414.34	414.74	490.55	490.15
7	553.20	553.77	622.87	622.48
8	710.83	711.58	774.91	774.57
9	887.22	888.17	946.50	946.23
10	1082.32	1083.50	1137.47	1137.30
11	1296.07	1297.51	1347.66	1347.60
12	1528.40	1530.11	1576.86	1576.95
13	1779.17	1781.17	1824.91	1825.16
14	2048.26	2050.56	2091.61	2092.04
15	2335.49	2338.12	2376.73	2377.35
16	2640.68	2643.65	2680.04	2680.88
17	2963.61	2966.93	3001.30	3002.37
18	3304.02	3307.71	3340.23	3341.55
19	3661.65	3665.71	3696.53	3698.10
20	4036.17	4040.61	4069.86	4071.70
21	4427.25	4432.08	4459.87	4461.98
22	4834.50	4839.72	4866.16	4868.55
23	5257.50	5263.12	5288.29	5290.97
24	5695.79	5701.80	5725.79	5728.77
25	6148.85	6155.25	6178.14	6181.42

diationless transition into another dissociative electronic state, the consequences to the intensity of absorption transitions are less severe; namely, only a reduced mean lifetime of the excited electronic state. Even though broadening of the term values and of the transitions results, this broadening is not apparent in the measured spectrum because the room temperature Doppler width amounts to 0.1 cm^{-1} and thus is several orders of magnitude larger than the broadening caused by predissociation.

A detailed description of the experimental setup is given in a previous publication (5). The absorption spectrum of ^{16}OD and ^{18}OD was obtained by the use of a tunable dye laser with a resolving power of at least 10^6. This high resolution guaranteed that the precision of the measured wavenumbers was not instrument limited, but by Doppler broadening of the OD transitions.

The dye laser system was pumped by the second harmonic frequency (532 nm) of a Q-switched Nd:YAG laser. The fourth harmonic (266 nm) of the Nd:YAG laser was used to photolyze ozone (O_3) in the production of $O(^1D)$ atoms. The $O(^1D)$ atoms react with D_2O at a rate which is essentially gas kinetic. This fast photochemical production cycle is shown in the reaction scheme

$$^{16}O_3 + h\nu(266 \text{ nm}) \rightarrow {}^{16}O(^1D) + {}^{16}O_2(^1\Delta_g), \tag{2}$$

$$^{16}O(^1D) + D_2{}^{18}O \rightarrow {}^{16}OD + {}^{18}OD. \tag{3}$$

The excited oxygen atoms react with $D_2{}^{18}O$ according to Eq. (3), producing both of the isotopically differing molecules.

TABLE II

Energy levels of the first electronic excited state of ^{18}OD ($\tilde{A}^2\Sigma^+(v = 0)$)

N'	F$_2$	F$_2$
0	32530.12	
1	32548.03	32547.85
2	32583.77	32583.48
3	32637.33	32636.92
4	32708.67	32708.14
5	32797.75	32797.11
6	32904.52	32903.75
7	33028.90	33028.01
8	33170.81	33169.80
9	33330.15	33329.03
10	33506.83	33505.59
11	33700.70	33699.35
12	33911.64	33910.18
13	34139.48	34137.90
14	34384.04	34382.35
15	34645.13	34643.32
16	34922.52	34920.60
17	35215.96	35213.93
18	35525.20	35523.06
19	35849.93	35847.68
20	36189.83	36187.47
21	36544.55	36542.08
22	36913.69	36911.11
23	37296.84	37294.15
24	37693.52	37690.73
25	38103.25	38100.35

The OD radicals are detected by means of absorption around 308 nm resulting from the $\tilde{A}^2\Sigma^+ \leftarrow \tilde{X}^2\Pi$ transition. At the gas pressures in the reaction chamber, 10 Torr of $D_2^{18}O$ and 2 Torr of $^{16}O_3$, conditions in the present study lead (4) to reaction times around 13 nsec. In order to allow the $O(^1D)$ atoms an opportunity to form OD radicals as in Eq. (3), the uv pulse of the narrow-bandwidth frequency-doubled dye laser ($\Delta\nu$ = 1.5 GHz, Δt = 5 nsec) is delayed by 10 nsec relative to the photolysis flash (13).

To compensate for intensity fluctuations of the monitoring dye laser beam, it was separated by a partially transmitting mirror in front of the reaction cell into two beams, one of which bypassed the cell. Both signals were detected by uv diodes but only the differential signal was registered and amplified. This signal was stored and averaged by a boxcar integrator and displayed by an X-Y recorder.

RESULTS AND DISCUSSION

The results of the present analysis are shown in Tables I–III, which list term values of the $^2\Pi$ ground state, v'' = 0 and of the $^2\Sigma^+$ state, v' = 0, as well as the molecular

TABLE III

Molecular constants of ^{18}OD in the electronic ground state, $X^2\Pi$, and in the first electronic excited state, $A^2\Sigma^+$, from direct fit of the 0–0 band. Errors are two standard deviations

^{18}OD (this work)	^{16}OD (J.A. Coxon)[7]
Rotation	
B_Π 9.749 $\pm$ 6.0'-3	9.8831 $\pm$ 1.1'-6
D_Π 3.86'-4 $\pm$ 3.3'-5	5.3742'-4 $\pm$ 2.5'-9
H_Π -1.7'-7 $\pm$ 5.6'-8	1.935'-8 $\pm$ 2.1'-12
Λ-Splitting	
ξ' -4.7'-1 $\pm$ 3.3'-2	
η' 3.4'-2 $\pm$ 1.3'-3	
o_0 -2.24'-1	
p_0 1.32'-1	1.266'-1 $\pm$ 4.6'-6
q_0 -9.79'-3	-1.093'-2 $\pm$ 1.9'-7
Spin-Orbit-Interaction	
A -139.08 $\pm$ 5.9'-2	-139.230 $\pm$ 4'-4
A_J -2.1'-3 $\pm$ 1.2'-3	-4.36'-4
Rotation	
B_Σ 8.924 $\pm$ 5.8'-3	9.0435 $\pm$ 1.2'-6
D_Σ 4.48'-4 $\pm$ 2.7'-5	5.7626'-4 $\pm$ 2.7'-8
H_Σ -1.4'-7 $\pm$ 4.2'-8	1.645'-8 $\pm$ 2.8'-12
ρ-Splitting	
γ_0 1.18'-1 $\pm$ 8.5'-3	1.201'-1 $\pm$ 2.1'-6

TABLE IV

Transition frequencies in wavenumbers for the Q_2, Q_{12}, R_1, and R_2 branches of the $A^2\Sigma^+(v' = 0, N') \leftarrow$ $X^2\Pi(v'' = 0, N'')$ system. The notation is from Dieke and Crosswhite (6)

N''	Q_2	Q_{12}	R_1	R_2
1	---	---	---	32452.35
2	---	---	---	32474.52
3	---	---	---	32494.27
4	---	---	---	32511.33
5	---	---	---	32525.72
6	32413.47	---	---	32537.74
7	32405.47	32406.49	---	---
8	32395.18	32396.37	---	---
9	32382.84	---	---	---
10	32368.19	---	---	---
11	32351.29	---	---	---
12	32333.55	---	---	---
13	32312.79	---	---	---
14	---	---	---	32551.66
15	32266.36	---	---	32543.56
16	32239.56	---	---	---
17	32211.20	---	---	---
18	---	---	---	32507.41
19	---	---	32528.18	32491.21
20	32115.98	---	32508.41	---
21	---	---	---	---
22	---	---	---	---
23	---	---	---	---
24	---	---	---	32374.51

constants which belong to each of these energy levels. Additionally, Tables IV and V give the measured ^{18}OD absorption transitions. The ^{18}OD spectrum was determined by recording the combined uv spectrum of ^{16}OD and ^{18}OD and using the known transition frequencies in wavenumbers of ^{16}OD as a standard.

TABLE V

Transition frequencies in wavenumbers for the P_1, P_2, P_{12}, Q_1, and Q_{21} branches of the $A^2\Sigma^+(v' = 0, N') \leftarrow X^2\Pi(v'' = 0, N'')$ system. The notation is from Dieke and Crosswhite (6)

N''	P_1	P_2	P_{12}	Q_1	Q_{21}
1	32530.12	---	32399.00	32548.27	32548.20
2	32502.31	32385.92	32386.13	32538.28	32537.96
3	32473.84	32369.60	32369.76	32527.21	32526.83
4	32444.45	32351.36	32351.29	32515.86	32515.33
5	32414.66	32329.94	32330.82	32503.34	32502.80
6	32383.65	32306.68	32307.21	32489.84	32489.14
7	32351.29	32280.88	32281.64	32475.10	32474.34
8	32317.82	32253.38	32254.25	32459.16	32458.24
9	32283.48	32222.94	32224.13	32441.72	32440.89
10	32247.93	---	---	---	---
11	32210.39	32157.77	---	32403.04	---
12	32172.48	32122.64	---	32381.54	---
13	32132.60	---	---	32358.42	32356.64
14	---	---	---	32333.79	---
15	---	---	---	---	---
16	---	---	---	---	---
17	---	---	---	32249.17	---
18	---	---	---	32217.14	---

To calculate the term values and molecular constants for ^{18}OD from the frequencies of the absorption lines, a least-squares procedure was employed. This computational procedure determines the molecular constants by a direct two-state fit approach. The entire data set constitutes an overdetermined set of simultaneous linearized equations. Together with the applicable selection rules, the fitted constants permit back calculation to the frequencies of the absorption lines. For most lines, the discrepancy between experiment and theory was less than 0.1 cm^{-1}.

The rotational structure of the electronic bands of OD contains six main branches (P_1, Q_1, R_1, P_2, Q_2, R_2) and has satellite branches (S_{21}, R_{21}, Q_{21}, Q_{12}, P_{12}, Q_{12}) for each band. The electronic spin in the OD radical is $s = 1/2$, resulting in doublet states. Each rotational level of the $\tilde{X}^2\Pi$ state is split by spin–orbit interaction into two components, and each spin component is split due to Λ doubling (Fig. 1). The spin splitting of the $\tilde{A}^2\Sigma^+$ state is caused by an interaction between the molecular rotation and the spin momentum and is referred to as ρ-type doubling in the earlier literature.

According to convention, the subscripts 1 and 2 for the spin components of both $\tilde{X}^2\Pi$ and $\tilde{A}^2\Sigma^+$ are defined such that

$$F_1(J), f_1(J); \qquad J = N + 1/2,$$

$$F_2(J), f_2(J); \qquad J = N - 1/2. \qquad (4)$$

The Λ splitting occurring in the ground state is identified by the indices e and f in the listing of term values.
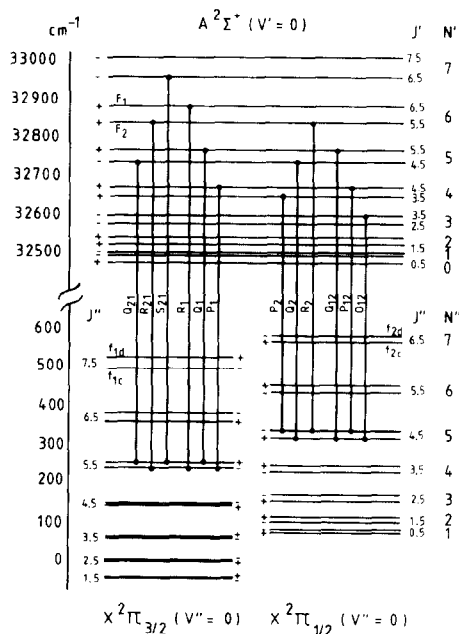

FIG. 1. Energy level diagram of OD, showing the different branches of the rotational structure of the transition $A^2\Sigma^+(v' = 0) \leftarrow X^2\Pi_{3/2,1/2}(v'' = 0)$. The zero energy is chosen as the arithmetic mean of the energies of the lowest $X^2\Pi_{3/2}$ and $X^2\Pi_{1/2}$ states.

Knowledge of all selection rules is a necessity for the computation of molecular constants and term values. Dipole transitions of the free molecule are possible if $N \to N$ or $N \to N \pm 1$. This rule, together with the symmetry selection rule, even $\rightleftarrows$ odd, defines the above-mentioned main branches. The six satellite branches arise only when the spin system is altered. Furthermore, they satisfy the inequality $\Delta J \neq \Delta N$. In addition, there are transitions which do not obey the N selection rules for dipole transitions. These give rise to O and S branches for $N \to N - 2$ and $N \to N + 2$, respectively.

All these possibilities for absorption transitions and the applicable restrictions have to be obeyed in employing the term value formulas which were taken from the work of Moore and Richards (8). These detailed formulas contain a J dependence on the Λ-splitting constants O, P, and Q; the rotational constant B, the constant for the centrifugal distortion D, and the third order constant H; the constant for spin–orbit coupling A is replaced by $A + A_J x$, where $x = (J + 1/2)^2 - 1$; and finally, the spin splitting constant γ, which causes the ρ doubling in the $\tilde{A}^2\Sigma^+$ state, is employed and correlated to the other constants.

The accurate molecular constants and especially the energy levels, provide applications in other areas, such as in energy transfer or chemical dynamics.

ACKNOWLEDGMENTS

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