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¹⁶For a diatomic molecule at the equilibrium distance, the virial theorem states that $\langle E \rangle = -\langle T \rangle = \frac{1}{2} \langle V \rangle$. By definition of correlation, the energy of a correlated wave function is less than the HFSCF energy.
¹⁷This is not rigorously true, as the Das-Wahl wave function demonstrates. However, previous work with very accurate wave functions have always given this intuitive result (Ref. 8).

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Molecular Parameters of OH Free Radical*

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Theoretical formulas with higher-order perturbation terms are given for the rotational levels of ²Π states, and are applied to the OH free radical. By analyzing existing data values of several molecular parameters including the rotational constant *B*, the spin-orbit coupling constant *A* and Λ-doublet constants *α* and *β* are obtained for some vibrational states. The magnetic *g* factors are discussed and analyzed. A recent experiment on laser magnetic resonance (LMR) is also discussed.

I. INTRODUCTION

Diatomic molecules, including diatomic free radicals such as OH, are more complicated than atoms but still simple enough to allow detailed theoretical treatment. The rotational and vibrational levels of a diatomic molecule are particularly simple, because the Born-Oppenheimer approximation,¹ namely, the semirigid body model, is known to be applicable. Many data are carefully analyzed according to this model.^{2,3}

Most stable diatomic molecules are in the ¹Σ electronic state, but there are some which have finite electronic angular momenta in their ground states. The oxygen molecule has electron spin angular momentum *S* = 1 in its electronic ground states, which makes each rotational level a triplet. The triplet separations in this case are measured and analyzed, and some molecular parameters for that molecule are obtained.⁴⁻⁶ The OH free radical, our present subject, is another typical case. Its electronic ground state is ²Π; namely, the electronic orbital

angular momentum around the molecular axis is + 1 or - 1, and the electronic spin angular momentum *S* is $\frac{1}{2}$.

Because of the spin-orbit coupling, the spin can orient itself either in parallel or antiparallel direction to the orbital angular momentum, producing the splitting into the Π_{3/2} and Π_{1/2} states. Since the coupled electronic angular momenta can be either in parallel or antiparallel direction to the molecular axis, which we call the *z* axis, each of these two states is doubly degenerate. The degeneracy is slightly removed due to the end-over-end rotation, and gives the so-called Λ doublet. The theory of rotational states of a ²Π molecules was given by Van Vleck⁷ and by Mulliken and Christy.⁸

The uv spectrum of OH was measured and analyzed by Johnston, Dawson, and Walker many years ago.^{9,10} Much more extensive and accurate measurement was done by Dieke and Crosswhite,¹¹ who reported many rotational and vibrational levels of the ground ²Π states. Transitions within each Λ doublet can be observed in microwave spectroscopy.

Dousmanis, Sanders, and Townes¹² first observed such transitions for five rotational levels of O¹⁶H. Ehrenstein, Townes, and Stevenson,¹³ Radford,^{14,15} and Poynter and Beaudet¹⁶ observed them for other rotational levels. Those microwave measurements were all for the vibrational ground state. Radford^{17,18} observed EPR of OH in the X band, while Evenson, Wells, and Radford¹⁹ observed laser magnetic resonance (LMR) using the 79- μ m line of the H₂O laser. Evenson²⁰ improved the LMR data and observed additional lines using other lines of the H₂O laser. Radford¹⁸ observed and analyzed the hyperfine structure (hfs).

Van Vleck's theory⁷ is only the first-order approximation and is not enough to explain these new precise data. Dousmanis, Sanders, and Townes¹² presented a higher-order theory of Λ doublet, by which they explained their own data to some extent. However, they could not develop a satisfactory theory because Dieke and Crosswhite's data were not available to them. Thus, for example, they obtained -7.444 for A/B , where A and B are the spin-orbit coupling constant and the end-over-end rotational constant, respectively, but this value deviates much from -7.547 which is obtained by Dieke and Crosswhite¹¹ from their more direct observation. Radford,¹⁷ when the former value of A/B was used, had to conclude that the electron spin g factor g_s was almost exactly 2, instead of 2.0023. Later Radford found¹⁸ that better agreement with his data could be achieved when -7.504 was taken for this ratio.

II. HAMILTONIAN

For a linear molecule the perturbation Hamiltonian which we are interested in is^{7,21}

$$\hat{H} = \hat{A}_z \hat{L}_z \hat{S}_z + \hat{A}_1 (\hat{L}_x \hat{S}_x + \hat{L}_y \hat{S}_y) + \hat{B} (\hat{N}_x^2 + \hat{N}_y^2) + \hat{\mu}_L \hat{N} \cdot \hat{L} + \hat{\mu}_S \hat{N} \cdot \hat{S}, \quad (1)$$

where \hat{L} , \hat{S} , and \hat{N} are the electronic orbital, spin, and end-over-end rotational angular momenta, respectively, and the subscripts x , y , and z designate their components along the molecule-fixed coordinates, of which the z axis is taken along the molecular axis. The first terms in (1) with coefficients \hat{A}_z and \hat{A}_1 are the spin-orbit interaction, the next terms with coefficient \hat{B} are the end-over-end rotational energy, and the last two terms are the magnetic coupling terms between the end-over-end rotation and the electronic angular momenta. The hyperfine interaction terms are neglected in our discussions.

By means of the total angular momentum

$$\hat{J} = \hat{N} + \hat{L} + \hat{S} \quad (2)$$

we can rewrite (1) as

$$\begin{aligned} \hat{H} = & (\hat{A}_z - \hat{\mu}_L - \hat{\mu}_S) \hat{L}_z \hat{S}_z \\ & + (\frac{1}{2} \hat{A}_1 + \hat{B} - \frac{1}{2} \hat{\mu}_L - \frac{1}{2} \hat{\mu}_S) (\hat{L}_+ \hat{S}_- + \hat{L}_- \hat{S}_+) \\ & + \hat{B} (\hat{J}^2 - \hat{J}_z^2) - (\hat{B} - \frac{1}{2} \hat{\mu}_L) (\hat{J}_+ \hat{L}_- + \hat{J}_- \hat{L}_+) \\ & - (\hat{B} - \frac{1}{2} \hat{\mu}_S) (\hat{J}_+ \hat{S}_- + \hat{J}_- \hat{S}_+) + \hat{\mu}_L \hat{J}_z \hat{L}_z + \hat{\mu}_S \hat{J}_z \hat{S}_z \\ & + \hat{B} \{ (\hat{L}^2 - \hat{L}_z^2) + (\hat{S}^2 - \hat{S}_z^2) \} - \hat{\mu}_L \hat{L}^2 - \hat{\mu}_S \hat{S}^2, \quad (3) \end{aligned}$$

where we used the conventional notations

$$\hat{J}_\pm = \hat{J}_x \pm i \hat{J}_y, \quad \text{etc.} \quad (4)$$

There are four independent base functions for a given set of v , vibrational quantum number, and J , rotational quantum number, in the Π states. If we take²²

$$|\Pi_{3/2} c v J\rangle = \frac{\sqrt{2}}{2} (|\Pi_{3/2} + v J\rangle + |\Pi_{3/2} - v J\rangle), \quad (5a)$$

$$|\Pi_{1/2} c v J\rangle = \frac{\sqrt{2}}{2} (|\Pi_{1/2} + v J\rangle + |\Pi_{1/2} - v J\rangle), \quad (5b)$$

$$|\Pi_{3/2} d v J\rangle = \frac{\sqrt{2}}{2} (|\Pi_{3/2} + v J\rangle - |\Pi_{3/2} - v J\rangle), \quad (5c)$$

and

$$|\pi_{1/2} d v J\rangle = \frac{\sqrt{2}}{2} (|\pi_{1/2} + v J\rangle - |\pi_{1/2} - v J\rangle), \quad (5d)$$

this part of the Hamiltonian matrix is reduced into two identical matrices, each of which is

$$\begin{pmatrix} \frac{1}{2} A_z - B - (B - \frac{1}{2} \mu_S) [(J + \frac{1}{2})^2 - 1]^{1/2} \\ - (B - \frac{1}{2} \mu_S) [(J + \frac{1}{2})^2 - 1]^{1/2} - (\frac{1}{2} A_z - B) \end{pmatrix} + B(J + \frac{1}{2})^2 - \mu_L - \frac{1}{2} \mu_S. \quad (6)$$

In (5) we defined

$$\hat{S}_z |\Pi_{3/2} \pm J\rangle = \pm \frac{1}{2} |\Pi_{3/2} \pm J\rangle, \quad \hat{J}_z |\Pi_{3/2} \pm J\rangle = \pm \frac{3}{2} |\Pi_{3/2} \pm J\rangle, \quad (7)$$

$$\hat{S}_z |\Pi_{1/2} \pm J\rangle = \mp \frac{1}{2} |\Pi_{1/2} \pm J\rangle, \quad \hat{J}_z |\Pi_{1/2} \pm J\rangle = \pm \frac{1}{2} |\Pi_{1/2} \pm J\rangle.$$

Note that the rotational energy appears in (6) as $B(J + \frac{1}{2})^2$ instead of $BJ(J + 1)$ when the $B[(\hat{L}^2 - \hat{L}_z^2) + (\hat{S}^2 - \hat{S}_z^2)]$ term in (3) is taken into account assuming that $L = 1$ in the Π state. This assumption may not be exactly correct but is better than simply neglecting this term.

The effect of all excited ${}^2\Sigma$ states and other vibrational states in the ${}^2\Pi$ state can be taken into account by means of the perturbation theory as shown in the Appendix of this paper. As a result we obtain the following four energy levels for a given vibrational-rotational state:

$$f_{c2}(J) = \xi_J + \eta_J + \frac{1}{2} (X_J^2 + Y_J)^{1/2}, \quad (8a)$$

$$f_{d2}(J) = \xi_J - \eta_J + \frac{1}{2} (X_J^2 - Y_J)^{1/2}, \quad (8b)$$

$$f_{c1}(J) = \xi_J + \eta_J - \frac{1}{2} (X_J^2 + Y_J)^{1/2}, \quad (8c)$$

$$f_{d1}(J) = \xi_J - \eta_J - \frac{1}{2} (X_J^2 - Y_J)^{1/2}, \quad (8d)$$

where

$$\begin{aligned} \xi_J &= (B - \beta - D)(J + \frac{1}{2})^2 - D(J + \frac{1}{2})^4 \\ &\quad + H(J + \frac{1}{2})^6 - P(J + \frac{1}{2})^8 + \dots \\ &= B_{\text{eff}} J(J+1) - D_{\text{eff}} J^2(J+1)^2 + HJ^3(J+1)^3 \\ &\quad - PJ^4(J+1)^4 + \frac{1}{4}(B - \beta - D), \quad (9a) \end{aligned}$$

$$\eta_J = \frac{1}{2}(\alpha + \lambda - 2\epsilon - 2\kappa)(J + \frac{1}{2}) - (\epsilon + \kappa)(J + \frac{1}{2})^3, \quad (9b)$$

$$\begin{aligned} X_J^2 &= \bar{A}_J^2 + 4\bar{B}_J^2 [(J + \frac{1}{2})^2 - 1] = \bar{A}^2 - 4\bar{B}^2 \\ &\quad + 4(\bar{B}^2 + 4\bar{B}D - \bar{A}\bar{\delta})(J + \frac{1}{2})^2 \\ &\quad - (16\bar{B}D - 4\bar{\delta}^2)(J + \frac{1}{2})^4 + 8(2D^2 + 3\bar{B}H)(J + \frac{1}{2})^6 \\ &\quad - 16(3DH + 2\bar{B}P)(J + \frac{1}{2})^8, \quad (9c) \end{aligned}$$

$$\begin{aligned} Y_J &= -2\bar{A}_J \alpha_J (J + \frac{1}{2}) + 8\bar{B}_J \beta_J (J + \frac{1}{2}) [(J + \frac{1}{2})^2 - 1] \\ &= -2[\bar{A}(\alpha + \lambda + 2\kappa) + 4\bar{B}(\beta - \epsilon)](J + \frac{1}{2}) \\ &\quad + 8[\bar{B}(\beta - \epsilon) + \frac{1}{2}\bar{\delta}(\alpha + \lambda + 2\kappa)](J + \frac{1}{2})^3 \\ &\quad - 16(D\beta + B\kappa)(J + \frac{1}{2})^5 + 8(3H\beta + 4D\kappa)(J + \frac{1}{2})^7. \quad (9d) \end{aligned}$$

In (9a)

$$B_{\text{eff}} = B - \beta - \frac{3}{2}D \quad \text{and} \quad D_{\text{eff}} = D - \frac{3}{4}H, \quad (10)$$

in (9c) and (9d)

$$\begin{aligned} \bar{A}_J &= \bar{A} - 2(\bar{\delta} - 2D)(J + \frac{1}{2})^2 + 3(\bar{h} - 2H)(J + \frac{1}{2})^4 \\ &\quad (\bar{\delta} \equiv \bar{\delta} - 2D), \quad (11) \end{aligned}$$

$$\bar{B}_J = \bar{B} - 2D(J + \frac{1}{2})^2 + 3H(J + \frac{1}{2})^4 - 4P(J + \frac{1}{2})^6, \quad (12)$$

and in (9d)

$$\alpha_J = \alpha + \lambda - 2\epsilon + 2\kappa - 2(\epsilon - \kappa)(J + \frac{1}{2})^2 \quad (13)$$

and

$$\beta_J = \beta - \epsilon - 2\kappa(J + \frac{1}{2})^2. \quad (14)$$

We define

$$\bar{A} = A - 2B + \beta + \frac{1}{4}\gamma + \frac{1}{2}\iota \quad (15)$$

and

$$\bar{B} = B - \frac{1}{2}\mu_S - \frac{1}{2}\alpha - \kappa + \frac{1}{4}\iota \quad (16)$$

in the above formulas. Definition of all molecular constants we use are given in Table I.

When $J = \frac{1}{2}$ we have a special case, since in this case we have only two states which are both pure $\Pi_{1/2}$ states. The previous formulas (8a)–(8d) are not applicable here; instead we obtain

$$f_{c2}(\frac{1}{2}) = -\frac{1}{2}\bar{A} + B - \beta + \bar{\delta} - 3D - (\alpha - 2\epsilon) \quad (17a)$$

and

$$f_{d2}(\frac{1}{2}) = -\frac{1}{2}\bar{A} + B - \beta + \bar{\delta} - 3D + (\alpha - 2\epsilon). \quad (17b)$$

TABLE I. Definition of coupling constants.

Electronic first order	$A = \langle \Pi + v \hat{A}_\pi \Pi + v \rangle$ $B = \langle \Pi + v \hat{B} \Pi + v \rangle$ $\mu_L = \langle \Pi + v \hat{\mu}_L \Pi + v \rangle$ $\mu_S = \langle \Pi + v \hat{\mu}_S \Pi + v \rangle$
Electronic second order ^a	$\hat{\alpha} = \sum \langle \Pi + v \hat{A}' \hat{L}_+ \Sigma \rangle \langle \Sigma \hat{B}' \hat{L}_- \Pi + v \rangle / E(\Sigma)$ $\hat{\beta} = \sum \langle \Pi + v \hat{B}' \hat{L}_+ \Sigma \rangle \langle \Sigma \hat{A}' \hat{L}_- \Pi + v \rangle / E(\Sigma)$ $\hat{\gamma} = \sum \langle \Pi + v \hat{A}' \hat{L}_+ \Sigma \rangle \langle \Sigma \hat{A}' \hat{L}_- \Pi + v \rangle / E(\Sigma)$ $\hat{\psi} = \sum \langle \Pi + v \hat{L}_+ \Sigma \rangle \langle \Sigma \hat{A}' \hat{L}_- \Pi + v \rangle / E(\Sigma)$ $\hat{\phi} = \sum \langle \Pi + v \hat{L}_+ \Sigma \rangle \langle \Sigma \hat{B}' \hat{L}_- \Pi + v \rangle / E(\Sigma)$ $\hat{\theta} = \sum \langle \Pi \hat{A}_\pi \Pi \rangle / E(\Pi')$
Vibrational first order	$\alpha = \langle v \hat{\alpha} v \rangle$ $\beta = \langle v \hat{\beta} v \rangle$ $\gamma = \langle v \hat{\gamma} v \rangle$ $\psi = \langle v \hat{\psi} v \rangle$ $\phi = \langle v \hat{\phi} v \rangle$ $\theta = \langle v \hat{\theta} v \rangle$
Vibrational second order ^b	$\delta = \sum_{v' \neq v} \langle \Pi + v \hat{A}_\pi \Pi + v' \rangle \langle \Pi + v' \hat{B} \Pi + v \rangle / E(v')$ $D = \sum_{v' \neq v} \langle \Pi + v \hat{B} \Pi + v' \rangle ^2 / E(v')$ $\epsilon = \sum_{v' \neq v} \langle v \hat{\alpha} v' \rangle \langle \Pi + v' \hat{B} \Pi + v \rangle / E(v')$ $\Lambda = \sum_{v' \neq v} \langle v \hat{\beta} v' \rangle \langle \Pi + v \hat{B} \Pi + v \rangle / E(v')$ $\iota = \sum_{v' \neq v} \langle v \hat{\gamma} v' \rangle \langle \Pi + v \hat{B} \Pi + v \rangle / E(v')$ $\lambda = \sum_{v' \neq v} \langle v \hat{\alpha} v' \rangle \langle \Pi + v' \hat{A}_\pi \Pi + v \rangle / E(v')$
Vibrational third order ^b	$h = \sum_{v'' \neq v} \langle v \hat{A}_\pi v'' \rangle \langle v'' \hat{B} v' \rangle \langle v' \hat{B} v \rangle / E(v')E(v'')$ $H = \sum_{v'' \neq v} \langle v \hat{B} v' \rangle \langle v' \hat{B} v'' \rangle \langle v'' \hat{B} v \rangle / E(v')E(v'')$
Vibrational fourth order ^b	$P = \sum_{v'' \neq v} \langle v \hat{B} v' \rangle \langle v' \hat{B} v'' \rangle \langle v'' \hat{B} v''' \rangle \langle v''' \hat{B} v \rangle / E(v')E(v'')E(v''')$

^aSummations are over all Σ states. $E(\Sigma) = E(\Sigma) - E(\Pi)$.

In $\hat{\theta}$ the summation is over all excited Π states (Π' states) and $E(\Pi') = E(\Pi') - E(\Pi)$. $\hat{A}' = \hat{A}'_1 + 2\hat{B}' - \hat{\mu}_L - \hat{\mu}_S$ and $\hat{B}' = \hat{B}' - \frac{1}{2}\hat{\mu}_L$.

^b $E(v') = E(v') - E(v)$.

III. ROTATIONAL ENERGY

The ξ_J term given by (9a) corresponds to the rotational-energy term of simpler molecules. From (8a)–(8d) we obtain

$$\xi_J = \frac{1}{4} [f_{c2}(J) + f_{d2}(J) + f_{c1}(J) + f_{d1}(J)]. \quad (18)$$

The energy levels f_{c2} , f_{d2} , f_{c1} , and f_{d1} are observed by Dieke and Crosswhite.¹¹ (They are their f'_{2s} , f_{2s} , f_{1s} , and f'_{1s} , respectively.) From their data and (18) we find “observed values” of ξ_J , and fitting these observed values to the formula (9a) we obtain the rotational constants B_{eff} , D_{eff} , H , and P . The obtained values of the rotational constants are given in Table II, and the comparison between the observed values and the calculated values using these constants and formula (9a) is shown in Table III.

Our values of the rotational constants are somewhat different from those given by Dieke and Crosswhite.¹¹ For example, their values of B and D for $v = 0$ are 18.515 and 1.87×10^{-3} , respectively. Disagreement is simply due to different ways of analysis. Our way is theoretically more sound since it is based on more accurate perturbation theory.

TABLE II. Rotational constants of OH in the ground Π states (cm^{-1}).

v	0	1	2	3
B_{eff}	18.5215	17.8208	17.1202	16.4589
D_{eff}	1.9074×10^{-3}	1.8696×10^{-3}	1.8425×10^{-3}	2.425×10^{-3}
H	1.4074×10^{-7}	1.3883×10^{-7}	1.566×10^{-7}	4×10^{-6}
P	1.23×10^{-11}	1.68×10^{-11}	4×10^{-11}	

IV. SPIN-ORBIT COUPLING

Because of the spin-orbit coupling terms given in (1), the ${}^2\Pi$ states split into $\Pi_{1/2}$ and $\Pi_{3/2}$ states. In the case of OH the $\Pi_{1/2}$ states have higher energies than the $\Pi_{3/2}$ states because the coupling constant A is negative. The end-over-end rotation, however, produces a coupling between these Π

TABLE III. Observed values of $\epsilon_J - \epsilon_{J-1}$ compared to its theoretical values given by $2B_{\text{eff}}J - 4D_{\text{eff}}J^3 + 6H(J^5 + J^3) - 8P(J^7 + J^5)$.

J	$v=0$		$v=1$		$v=2$		$v=3$	
	Obs.	Theor.	Obs.	Theor.	Obs.	Theor.	Obs.	Theor.
$\frac{5}{2}$	92.56	92.54	88.99	88.99	85.43	85.49	82.03	82.15
$\frac{7}{2}$	129.38	129.39	124.42	124.43	119.54	119.53	115.05	114.81
$\frac{9}{2}$	166.08	166.09	159.70	159.71	153.39	153.41	147.20	147.29
$\frac{11}{2}$	202.60	202.58	194.80	194.79	187.14	187.10	179.52	179.56
$\frac{13}{2}$	238.80	238.82	229.63	229.63	220.56	220.55	211.55	211.58
$\frac{15}{2}$	274.78	274.77	264.18	264.18	253.70	253.72	243.34	243.33
$\frac{17}{2}$	310.37	310.38	298.40	298.40	286.55	286.56	274.79	274.77
$\frac{19}{2}$	345.62	345.62	332.22	332.25	319.04	319.04	305.90	305.90
$\frac{21}{2}$	380.44	380.44	365.71	365.68	351.11	351.11	336.71	336.67
$\frac{23}{2}$	414.83	414.79	398.69	398.67	382.76	382.74	366.93	366.99
$\frac{25}{2}$	448.59	448.64	431.12	431.16	413.88	413.88	396.76	396.74
$\frac{27}{2}$	482.00	481.95	463.11	463.13	444.49	444.51		
$\frac{29}{2}$	514.69	514.68	494.51	494.52	474.58	474.58		
$\frac{31}{2}$	546.83	546.81	525.37	525.31	504.15	504.05		
$\frac{33}{2}$	578.30	578.28	555.46	555.47	532.78	532.90		
$\frac{35}{2}$	608.93	609.05	584.95	584.95	561.11	561.08		
$\frac{37}{2}$	639.23	639.12	613.74	613.73	588.55	588.57		
$\frac{39}{2}$	668.43	668.44	641.74	641.77	615.33	615.33		
$\frac{41}{2}$	697.00	696.98	669.05	669.04	641.38	641.32		
$\frac{43}{2}$	724.67	724.71	695.50	695.52	666.49	666.52		
$\frac{45}{2}$	751.63	751.60	721.20	721.17				
$\frac{47}{2}$	777.61	777.64	745.96	745.97				
$\frac{49}{2}$	802.83	802.79	769.38	769.89				
$\frac{51}{2}$	827.03	827.03	793.58	793.03				
$\frac{53}{2}$	850.29	850.34	816.52	815.00				
$\frac{55}{2}$	872.67	872.69	834.72	836.13				
$\frac{57}{2}$	894.13	894.08						
$\frac{59}{2}$	914.40	914.47						
$\frac{61}{2}$	933.94	933.85						
$\frac{63}{2}$	952.17	952.21						

states, and as a result each level is not a pure $\Pi_{1/2}$ nor $\Pi_{3/2}$ state. Since $|A| > 7B$, as we will see later, the upper states f_{c2} and f_{d2} are mostly $\Pi_{1/2}$ with a small amount of $\Pi_{3/2}$ mixed in, while the lower states f_{c1} and f_{d1} are mostly $\Pi_{3/2}$ with a small amount of $\Pi_{1/2}$ mixed in.

The energy difference between the upper and the lower components is essentially given by X_J of (9c), since η_J and Y_J are much smaller. From (8) we see that X_J^2 can be obtained from experiment

as

$$X_J^2 = \frac{1}{2}[(f_{c2}(J) - f_{c1}(J))^2 + (f_{d2}(J) - f_{d1}(J))^2]. \quad (19)$$

Observed values of X_J are obtained by combining Dieke and Crosswhite's data according to (19), and are shown in Table IV. From (9c) we expect that

$$X_J^2 = k + l(J + \frac{1}{2})^2 - m(J + \frac{1}{2})^4 + n(J + \frac{1}{2})^6 - q(J + \frac{1}{2})^8 \quad (20)$$

TABLE IV. X_J . Observed values are obtained from (19) and Dieke and Crosswhite's data, while calculated values are obtained from (20) and Table V (cm^{-1}).

J	$v=0$		$v=1$		$v=2$		$v=3$	
	Obs.	Theor.	Obs.	Theor.	Obs.	Theor.	Obs.	Theor.
$\frac{3}{2}$	187.57	187.5824	185.65	185.37	184.06	183.83	180.66	181.01
$\frac{5}{2}$	205.12	205.0760	202.05	201.82	199.10	199.14	196.10	195.68
$\frac{7}{2}$	227.20	227.2115	222.85	222.72	218.60	218.68	214.37	214.32
$\frac{9}{2}$	252.68	252.6790	246.87	246.84	241.23	241.33	235.77	235.82
$\frac{11}{2}$	280.45	280.4652	273.23	273.23	266.25	266.21	259.26	259.34
$\frac{13}{2}$	309.83	309.83	301.12	301.17	292.61	292.63	284.23	284.25
$\frac{15}{2}$	340.22	340.24	330.07	330.14	320.06	320.09	310.16	310.15
$\frac{17}{2}$	371.26	371.31	359.65	359.77	348.20	348.23	336.79	336.78
$\frac{19}{2}$	402.75	402.75	389.60	389.77	376.75	376.76	363.95	363.93
$\frac{21}{2}$	434.36	434.35	419.81	419.93	405.49	405.48	391.40	391.39
$\frac{23}{2}$	465.95	465.93	449.94	450.09	434.20	434.22	418.85	418.88
$\frac{25}{2}$	497.39	497.37	480.05	480.10	462.90	462.85	445.94	445.93
$\frac{27}{2}$	528.54	528.56	509.80	509.87	491.28	491.26		
$\frac{29}{2}$	559.46	559.39	539.31	539.29	519.47	519.36		
$\frac{31}{2}$	589.84	589.80	568.34	568.30	546.93	547.07		
$\frac{33}{2}$	619.77	619.72	596.98	596.84	574.33	574.32		
$\frac{35}{2}$	648.90	649.08	624.95	624.84	601.10	601.06		
$\frac{37}{2}$	677.86	677.83	652.40	652.26	627.14	627.22		
$\frac{39}{2}$	705.95	705.93	679.14	679.05	652.71	652.75		
$\frac{41}{2}$	733.34	733.33	705.30	705.17	677.72	677.59		
$\frac{43}{2}$	759.96	759.99	730.76	730.60	701.62	701.67		
$\frac{45}{2}$	785.88	785.87	755.28	755.29				
$\frac{47}{2}$	810.95	810.94	779.10	779.22				
$\frac{49}{2}$	835.22	835.17	801.09	802.37				
$\frac{51}{2}$	858.57	858.53	824.40	824.71				
$\frac{53}{2}$	881.06	880.98	848.44	846.21				
$\frac{55}{2}$	902.57	902.51	865.85	866.85				
$\frac{57}{2}$	922.96	923.08						
$\frac{59}{2}$	942.69	942.67						
$\frac{61}{2}$	961.28	961.25						
$\frac{63}{2}$	978.90	978.79						

TABLE V. Constants for X_J [formula (20)] (cm^{-1})².

	$v=0$	$v=1$	$v=2$	$v=3$
k	29 671.5	29 245.2	29 087.0	28 297.8
l	1 381.20	1 281.32	1 179.08	1 122.06
m	0.570 845	0.560 298	0.5208	1.4
n	1.256×10^{-4}	1.523×10^{-4}	1.70×10^{-4}	
q	2.026×10^{-8}	3.01×10^{-8}	8×10^{-8}	

will be able to express its J dependence. We determined the coefficients k , l , m , n , and q by the least-squares fit, and the resulting fits are shown in Table IV, while the values of the coefficients are shown in Table V.

Since Y_J and η_J are both much smaller than X_J , levels f_{c2} and f_{d2} are close to each other and are separated by about X_J from levels f_{c1} and f_{d1} , which are close to each other. Thus,

$$2X_J \cong f_{c2} + f_{d2} - f_{c1} - f_{d1}. \quad (21)$$

X_J calculated from (21) are about the same as those calculated from (20) for J less than $\frac{19}{2}$, but deviate more as J increases. For $J = \frac{69}{2}$ of $v=0$, for example, X_J calculated from (20) is 978.90, while that calculated from (21) is 978.55. The deviation was less in all other cases. Table IV, of course, shows values calculated using (20).

V. Λ DOUBLETS FOR HIGH- J VALUES

The Λ -doublet separations are given by $f_{c2}(J) - f_{d2}(J)$ and $f_{c1}(J) - f_{d1}(J)$. In our formulas (8) we see that they are given by two terms η_J and Y_J , which can be obtained separately as

$$\eta_J = \frac{1}{4}[f_{c2}(J) - f_{d2}(J) + f_{c1}(J) - f_{d1}(J)] \quad (22)$$

and

$$Y_J = \frac{1}{2}\{[f_{c2}(J) - f_{c1}(J)]^2 - [f_{d2}(J) - f_{d1}(J)]^2\} \quad (23)$$

from experimental data. Since Y_J is much smaller than X_J^2 we see that

$$Y_J \cong X_J \{f_{c2}(J) - f_{c1}(J) - f_{d2}(J) + f_{d1}(J)\} \quad (24)$$

holds approximately. It turns out, at least in the case of OH, that (24) is accurate enough for low- J states. For J of over $\frac{17}{2}$, however, we have to use (23) instead of (24).

Two kinds of data are available for the Λ doublets of OH. Microwave data are very accurate but cover only up to $J = \frac{11}{2}$ at present. On the other hand uv data, obtained by Dieke and Crosswhite,¹¹ are not so accurate for the present purpose but cover up to very high- J values. Therefore the latter are suitable for finding expansion coefficients of higher powers of J , while the former are suitable for finding those of lower powers of J .

According to (9b) and (9d) we expect that η_J and Y_J can be expressed in the forms of

$$\eta_J = -s(J + \frac{1}{2}) + t(J + \frac{1}{2})^3, \quad (25)$$

$$Y_J = -u(J + \frac{1}{2}) + v(J + \frac{1}{2})^3 - w(J + \frac{1}{2})^5 + x(J + \frac{1}{2})^7. \quad (26)$$

In Fig. 1 we plot $\eta_J/(J + \frac{1}{2})$ obtained from Dieke and Crosswhite's data against $J + \frac{1}{2}$. We see here that $\eta_J/(J + \frac{1}{2})$ is a constant for each v within experimental error showing that

$$s = \begin{cases} 0.0395 \text{ (cm}^{-1}\text{)}^2 & \text{for } v=0 \\ 0.038 \text{ (cm}^{-1}\text{)}^2 & \text{for } v=1 \\ 0.036 \text{ (cm}^{-1}\text{)}^2 & \text{for } v=2 \\ 0.0325 \text{ (cm}^{-1}\text{)}^2 & \text{for } v=3 \end{cases} \quad (27)$$

and

$$|t| < 10^{-5} \text{ (cm}^{-1}\text{)}^2 \quad (28)$$

in (25).

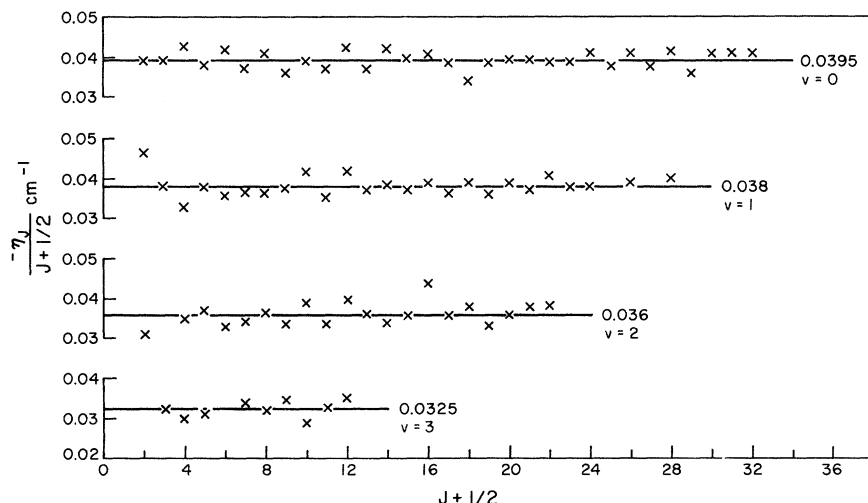


FIG. 1. $-\eta_J/(J + \frac{1}{2})$ plotted against $J + \frac{1}{2}$. Crosses are experimental values and horizontal straight lines are theoretical values.

TABLE VI. $Y_J/(J + \frac{1}{2})$, observed and calculated values in $(\text{cm}^{-1})^2$.

J	$v=0$		$v=1$		$v=2$		$v=3$	
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
$\frac{7}{2}$	15	18	12	17	13	13		
$\frac{9}{2}$	40	43	33	40	36	34		
$\frac{11}{2}$	72	73	64	67	59	60	55	56
$\frac{13}{2}$	106	108	97	98	85	89	84	81
$\frac{15}{2}$	139	149	136	135	124	123	106	111
$\frac{17}{2}$	193	193	178	175	162	161	147	146
$\frac{19}{2}$	240	242	218	219	204	202	185	184
$\frac{21}{2}$	294	295	272	267	250	246	228	226
$\frac{23}{2}$	351	352	324	318	294	294	264	267
$\frac{25}{2}$	412	411	377	373	336	344	306	306
$\frac{27}{2}$	476	474	428	430	389	396		
$\frac{29}{2}$	540	539	492	490	448	449		
$\frac{31}{2}$	624	606	556	552	520	505		
$\frac{33}{2}$	674	674	617	615	559	561		
$\frac{35}{2}$	780	744	676	680	615	617		
$\frac{37}{2}$	810	814	742	745	677	674		
$\frac{39}{2}$	878	884	805	810	728	730		
$\frac{41}{2}$	951	954	870	875	778	785		
$\frac{43}{2}$	1025	1023	933	939	842	838		
$\frac{45}{2}$	1092	1091	994	1001				
$\frac{47}{2}$	1154	1157	1047	1061				
$\frac{49}{2}$	1226	1221	1170	1119				
$\frac{51}{2}$	1277	1282	1159	1172				
$\frac{53}{2}$	1344	1340	1016	1222				
$\frac{55}{2}$	1395	1396	1260	1266				
$\frac{57}{2}$	1445	1447						
$\frac{59}{2}$	1500	1493						
$\frac{61}{2}$	1532	1536						

Table VI shows observed values of Y_J obtained by (23) from Dieke and Crosswhite's data. The table also shows the least-squares fit calculated by using the constants given in Table VII. In Table VI, $J = \frac{3}{2}$ and $\frac{5}{2}$ states are neglected because Y_J in these states is too small to find any meaningful numbers in the present scale. These states will be discussed in Sec. VI.

VI. A DOUBLETS FOR LOW- J VALUES ($v=0$)

Transitions from the c to d state of each Λ doublet are observed in microwave spectroscopy. Their frequencies are accurately measured, but these kinds of data are available only for $v=0$ and $J \leq \frac{11}{2}$ states at present. Table VIII summarizes all ex-

isting data.

Since J values are low in these microwave data, we can use the approximation formulas

$$f_{c2}(J) - f_{d2}(J) = 2\eta_J + (Y_J/2X_J), \quad (29a)$$

$$f_{c1}(J) - f_{d1}(J) = 2\eta_J - (Y_J/2X_J) \quad (29b)$$

to fit these data. Results of the fit with our expansion formulas (25) and (26) are shown in Table VIII. Since we used six adjustable parameters for seven data, the fit is naturally almost perfect. Table IX gives the values of the constants s and t for η_J obtained in this way. We see that they agree very well with those given by (27) and (28) which are obtained from uv data. On the other hand the values

TABLE VII. Constants for Y_J from high J data in $(\text{cm}^{-1})^2$.

	$v=0$	$v=1$	$v=2$	$v=3$
u	27	23	25	5
v	2.844	2.531	2.408	1.48
w	1.518×10^{-3}	1.11×10^{-3}	1.35×10^{-3}	7.14×10^{-3}
x	2.61×10^{-7}	-2.5×10^{-8}	1.3×10^{-7}	

of constants for Y_J obtained here and shown in Table X are close to those obtained previously in Table VII, but the agreement is not very good. We believe that true values of u and v must be very close to those given in Table X, but true values of w and x are somewhere between those given in Tables VII and X.

A large disagreement between observed and calculated frequencies is noticed for $J = \frac{5}{2}$, $f_{c2} - f_{d2}$.

VII. VALUES OF MOLECULAR PARAMETERS

We can obtain the values of the molecular parameters by comparing the theoretical formulas (9a)–(16) with the values of the expansion coefficients given in Tables II, V, VII, IX, and X, and formula (27).

Comparing (9a) and (10) with Table II we obtain the values of $B - \beta$, D , H , and P . The values of D , H , and P are given in Table XI, while

$$B - \beta = \begin{cases} 18.5243 \text{ cm}^{-1} & \text{for } v=0 \\ 17.8236 \text{ cm}^{-1} & \text{for } v=1 \\ 17.1229 \text{ cm}^{-1} & \text{for } v=2 \\ 16.4625 \text{ cm}^{-1} & \text{for } v=3. \end{cases} \quad (30)$$

In order to find the values of B from this result we need to know the values of β . However, only an approximate value of β are necessary here, and they can be obtained from the known values of the coefficient l since l is approximately equal to $8(B - \beta)$. The values of B obtained in this way are given in Table XII. These values are expressed as

$$B_v = 18.895 - 0.704(v + \frac{1}{2}) + 0.0007(v + \frac{1}{2})^2 - \dots, \quad (31)$$

TABLE VIII. Λ -doublet separations in MHz ($v=0$ states).

J	$f_{d2} - f_{c2}$		Obs.	$f_{d1} - f_{c1}$	
	Obs.	Ref.		Calc.	Ref.
$\frac{1}{2}$	4731.78	15			
$\frac{3}{2}$	7797.59	12	7797.63	1666.625508	13,14,23
$\frac{5}{2}$	8166.08	12	8160.18	6033.60	12,15
$\frac{7}{2}$...		5480.83	13438.41	12,16
$\frac{9}{2}$...		182.12	23822.568	12,16,23
$\frac{11}{2}$...		-8633.39	36989.41	12,16

TABLE IX. Constants for η_J ($v=0$ states).

s	t	
1183.2285	0.048	MHz
0.03946825	1.785×10^{-6}	cm^{-1}

$$D_v = (1.930 - 0.0483(v + \frac{1}{2}) + 0.0053(v + \frac{1}{2})^2) \times 10^{-3}, \quad (32)$$

as functions of the vibrational quantum number v . One can obtain the adiabatic potential from these results.

Comparing (9c) with Table V for the coefficients k , l , and m we obtain

$$\bar{A} - 2\bar{\delta} = \begin{cases} -176.216 \text{ cm}^{-1} & \text{for } v=0 \\ -174.717 \text{ cm}^{-1} & \text{for } v=1 \\ -173.970 \text{ cm}^{-1} & \text{for } v=2 \\ -171.532 \text{ cm}^{-1} & \text{for } v=3. \end{cases} \quad (33)$$

We know, from (16), that \bar{B} is slightly different from B , and that $\bar{A} - 2\bar{\delta}$ is of course different from \bar{A} . Since the differences in both cases are expected to be about 10^{-2} cm^{-1} , we can use $\bar{A} - 2\bar{\delta}$ and B for \bar{A} and \bar{B} , respectively, in (9c) to calculate the theoretical values of the coefficients k , l , m , n , and q of (20). The results are shown in Table XI. We see that agreements in the coefficients m , n , and q are not perfect, which may be due to the errors in our perturbation formula or in experimental data, or both. The difference between calculated and observed values in k is seen to be the same in magnitude and opposite in sign to that in l for each v , except for $v=3$. Since that magnitude is expected to be $-4\bar{A}\bar{\delta} + 8B(\bar{B} - B)$ in both k and l , as can be seen from (9a), we believe that the small differences between calculated and observed values of k and l as seen in Table XI are real. We, therefore, obtain

$$\bar{B} - B + \begin{cases} 4.73\bar{\delta} = 0.035 \text{ cm}^{-1} & \text{for } v=0 \\ 4.88\bar{\delta} = 0.053 \text{ cm}^{-1} & \text{for } v=1 \\ 5.07\bar{\delta} = 0.026 \text{ cm}^{-1} & \text{for } v=2. \end{cases} \quad (34)$$

From η_J and Y_J terms we obtain the values of α , β , and their higher-order terms. Since available data are not accurate for $v=1, 2$, and 3 , we may approximate

$$\eta_J \cong -\frac{1}{2}\alpha(J + \frac{1}{2}), \quad (9b')$$

$$Y_J \cong (2\bar{A}\alpha + 4B\beta)(J + \frac{1}{2}) - 8B\beta(J + \frac{1}{2})^3 + \dots \quad (9d')$$

TABLE X. Constants for Y_J ($v=0$ states).

u	v	w	x	
27596.07	2595.10	1.4635	1.25×10^{-4}	GHz^2
30.70476	2.88744	1.6284×10^{-3}	1.38×10^{-7}	$(\text{cm}^{-1})^2$

TABLE XI. Calculated and observed values of k , l , m , n , and q . (Observed values are taken from Table V.)

v		0	1	2	3
k	Calc.	29 676.63	29 252.8	29 090.4	28 336.8
	Obs.	29 671.5	29 245.2	29 087.0	28 297.8
l	Calc.	1 376.01	1 273.74	1 175.62	1 090.0
	Obs.	1 381.20	1 281.32	1 179.08	1 122.06
m	Calc.	0.565 829	0.533 603	0.5052	0.6
	Obs.	0.570 845	0.560 298	0.5208	1.4
n	Calc.	1.208×10^{-4}	1.154×10^{-4}	1.19×10^{-4}	
	Obs.	1.256×10^{-4}	1.523×10^{-4}	1.70×10^{-4}	
q	Calc.	2.018×10^{-8}	2.20×10^{-8}		
	Obs.	2.026×10^{-8}	3.01×10^{-8}		

We obtain the values of α and β from these simplified expressions of the coefficients s and v using (27) and Table VII for $v=1, 2$, and 3 . The results are shown in Table XII. Comparing the observed values of w as shown in Table VII with formula (9d) we obtain the values of κ for $v=1$ and 2 , as shown in Table XII. The observed value of x for $v=1$ is seen to be negative which indicates some experimental error. In any case the order of magnitude of the coefficient x can be explained by our theoretical formula (9d).

Since much more accurate data is available for $v=0$ we can apply our theory more carefully here. From (9b) and Table IX we obtain

$$\left. \begin{aligned} \alpha + \lambda &= -0.078\,938\,29 \text{ cm}^{-1} \\ \epsilon + \kappa &= -1.785 \times 10^{-6} \text{ cm}^{-1} \end{aligned} \right\} \text{ for } v=0. \quad (35)$$

Since

$$u - v = 2(A - 2\delta)(\alpha + \lambda + 2\kappa), \quad (36)$$

we obtain from Table X and (34) that

$$\alpha + \lambda + 2\kappa = -0.078\,929\,6 \text{ cm}^{-1} \text{ for } v=0. \quad (37)$$

One piece of important information comes from the Λ -doublet splitting in $J = \frac{1}{2}$ state. From (17) and Table VIII we obtain

$$\begin{aligned} \alpha - 2\epsilon &= -2365.89 \text{ MHz} \\ &= -0.078\,917\,6 \text{ cm}^{-1} \text{ for } v=0. \end{aligned} \quad (38)$$

From (35), (36), (37), and (38), we obtain α , λ , κ , and ϵ which are given in Table XII.

Putting (33) and (34) into the expressions of u and v given in (9d) and comparing the result with Table VII, we obtain

$$\begin{aligned} \beta &= (0.019\,454\,1 - 0.002\,128\bar{\delta}) / (1 - 0.255\bar{\delta}) \\ &= 0.019\,454\,1 + 0.002\,832\bar{\delta} \text{ cm}^{-1} \text{ for } v=0. \end{aligned} \quad (39)$$

It is necessary to know the value of $\bar{\delta}$ in order to

determine the values of \bar{A} , \bar{B} , and β accurately. None of the data we used so far are accurate enough for this purpose, but it is found that the magnetic g factors are rather sensitive functions of $\bar{\delta}$, as will be discussed in Sec. VIII. It is found that the best value of $\bar{\delta}$ obtained from the magnetic g factors is

$$\bar{\delta} = -0.0038 \text{ cm}^{-1} \text{ for } v=0, \quad (40)$$

which corresponds to the value of δ shown in Table XII. Once $\bar{\delta}$ is found in this way the value of β is obtained from (39), and the result is given in Table XII. From (15) and (33) then we obtain

$$A = -139.150 - \frac{1}{4}\gamma \text{ cm}^{-1} \text{ for } v=0, \quad (41)$$

where ι is neglected since ι must be of the order of 10^{-6} cm^{-1} . We cannot obtain the value of γ from experiment, but from Table I we expect that

$$\gamma \cong \alpha^2 / \beta. \quad (42)$$

The value of γ estimated in this way, and the value of A obtained by using the estimated value of γ in (41), are given in Table XII. The values of A for vibrationally excited states are obtained by assuming the same value of $\bar{\delta}$ as in the ground state.

TABLE XII. Values of molecular parameters for O^{16}H in cm^{-1} .

v	0	1	2	3
A	-139.235	-139.13	-139.77	-138.5
B	18.5435	17.841	17.140	16.48
μ_s	-0.027			
α	-0.078 929 8	-0.076	-0.072	
β	0.019 443	0.0177	0.0175	
γ	0.317 ^a	0.33 ^a	0.30 ^a	
δ	0.0000 ^b			
D	1.9071×10^{-3}	1.8693×10^{-3}	1.842×10^{-3}	2.4×10^{-3}
ϵ	-6.13×10^{-6}			
κ	4.345×10^{-6}			
λ	-8.45×10^{-6}			
H	1.4074×10^{-7}	1.3883×10^{-7}	1.566×10^{-7}	
P	1.23×10^{-11}	1.68×10^{-11}	4×10^{-11}	

^aEstimated by (42).

^bObtained from the g factors.

Finally, from (16) and (34) we obtain the value of μ_s which is shown in Table XII.

Previous values obtained by Dousmanis, Sanders, and Townes¹² for $v=0$ are $\alpha = -0.0787668 \text{ cm}^{-1}$, $\beta = 0.019219 \text{ cm}^{-1}$, and $A/B = -7.444$. Other values for A/B are reported^{18,16} as -7.504 and -7.5009 , but they are all based on conventional theories. Our value of A/B is -7.50856 , but this ratio in conventional theories corresponds to our $(\bar{A} + 2\bar{B})/\bar{B}$ more closely, and our value for this ratio is -7.4759 .

It is interesting to note that δ is very small. When the internuclear distance is made zero and infinity, the OH free radical reduces to the F atom and to the O and H atoms, respectively. The spin-orbit coupling constants for the F and O atoms are²⁴ -269 and -150 cm^{-1} , respectively. We found that this constant is -139 cm^{-1} for the OH free radical at its equilibrium internuclear distance. The fact that δ is very small implies that the spin-orbit coupling constant as a function of the internuclear distance takes its maximum value at near the equilibrium internuclear distance. When $|\delta| < |D|$ we expect that $|\lambda| < |\epsilon|$ from Table I, but Table XII shows that $\epsilon \approx \lambda$. This is a contradiction and exhibits the inaccuracy of the present theory. If $\lambda \epsilon > 0$ as Table XII shows then $\delta > 0$ which implies that the spin-orbit coupling constant decreases as the internuclear distance increases from its equilibrium value.

The molecular constant μ_s is observed⁴⁻⁶ for the O_2 molecule as -0.008 cm^{-1} .

VIII. MAGNETIC g FACTORS

When an external magnetic field $\vec{\mathfrak{B}}$ exists the additional Hamiltonian terms

$$\begin{aligned} \hat{H}' &= \mu_B \vec{\mathfrak{B}} \cdot (\hat{\mathbf{L}} + g_s \hat{\mathbf{S}} + g_n \hat{\mathbf{N}}) \\ &= \mu_B \vec{\mathfrak{B}} \cdot (g_n \hat{\mathbf{J}} + (1 - g_n) \hat{\mathbf{L}} + (g_s - g_n) \hat{\mathbf{S}}) \end{aligned} \quad (43)$$

appear. Here μ_B is the Bohr magneton, g_s and g_n are the electron spin and end-over-end rotational

g factors, respectively. The relevant matrix elements of \hat{H}' can be found in the literature.^{17,25}

To the first order in \mathfrak{B} we can write the energy of each state as

$$f_{c2}(J, M) = f_{c2}(J) + \mathfrak{B} \mu_B M g_{c2}, \quad (44a)$$

$$f_{a2}(J, M) = f_{a2}(J) + \mathfrak{B} \mu_B M g_{a2}, \quad (44b)$$

$$f_{c1}(J, M) = f_{c1}(J) + \mathfrak{B} \mu_B M g_{c1}, \quad (44c)$$

$$f_{a1}(J, M) = f_{a1}(J) + \mathfrak{B} \mu_B M g_{a1}, \quad (44d)$$

where the first term on the right-hand side of each equation is given by the corresponding formula in (8). Using the perturbation theory (see Appendix) we see that the g factors in the above formulas can be expressed as

$$g_{c2} = g_z(J) + g_n(J) + g_x(J) + g_y(J), \quad (45a)$$

$$g_{a2} = g_z(J) - g_n(J) + g_x(J) - g_y(J), \quad (45b)$$

$$g_{c1} = g_z(J) + g_n(J) - g_x(J) - g_y(J), \quad (45c)$$

$$g_{a1} = g_z(J) - g_n(J) - g_x(J) + g_y(J), \quad (45d)$$

where

$$g_z(J) = g_n + \frac{4 + g_s - 5g_n - 6\theta + 4\varphi [(J + \frac{1}{2})^2 - \frac{1}{2}]}{4J(J+1)}, \quad (46a)$$

$$g_n(J) = -\psi(J + \frac{1}{2}) / [4J(J+1)], \quad (46b)$$

$$\begin{aligned} g_x(J) &= \{ \bar{A}_J (1 + g_s - 2g_n - \varphi - 3\theta) - 2\bar{B}_J (g_s - g_n - \frac{1}{2}\psi) \\ &\quad \times [(J + \frac{1}{2})^2 - 1] \} / [2X_J J(J+1)], \end{aligned} \quad (46c)$$

$$g_y(J) = \{ \bar{A}_J \psi - 8\bar{B}_J \varphi [(J + \frac{1}{2})^2 - 1] \} (J + \frac{1}{2}) / 4X_J J(J+1). \quad (46d)$$

The molecular parameters ψ , φ , and θ are defined in Table I, and \bar{A}_J and \bar{B}_J are defined in (11) and (12). Note that excited Π states do not contribute to the zero-field energies but contribute to the g factors through the molecular parameter θ .

Again we have a special case when $J = \frac{1}{2}$, where

$$g_{c2}(\frac{1}{2}) = \frac{1}{3}(2 - g_s + 2g_n + 4\varphi - 2\psi), \quad (47a)$$

TABLE XIII. Experimental (Refs. 16 and 17) and theoretical g factors.^a

J	g_z	g_x	$g_z - g_x$	g_n	g_y	$g_n - g_y$
expt.	0.40082	-0.53475		0.00057	-0.00007	
$\frac{3}{2}$ theor. 1	0.40000	-0.53418		0	0	
theor. 2	0.40082	-0.53473		0.00057	0.00000	
expt.	0.17208	-0.31321		0.00036 ₅	-0.00057	
$\frac{5}{2}$ theor. 1	0.17143	-0.31293		0	0	
theor. 2	0.17208	-0.31327		0.00037	-0.00053	
expt.			0.32561			0.00107
$\frac{7}{2}$ theor. 1			0.32432			0
theor. 2			0.32556			0.00112

^aTheoretical estimate 1 is obtained by $g_s = 2$, $g_n = \psi = \varphi = \theta = 0$. Theoretical estimate 2 is obtained by using the values given in Table XIV.

TABLE XIV. Values of additional molecular parameters ($\nu=0$).

$g_s = 2.00190^a$	$g_n = -0.00110$	$\psi = -0.00430$	$\varphi = 0.00170$	$\theta = 0.00049$
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^aAssumed.

$$g_{d2}(\frac{1}{2}) = \frac{1}{3}(2 - g_s + 2g_n + 4\varphi + 2\psi). \quad (47b)$$

Radford^{17,18} observed EPR of this free radical at X band and obtained the g factors for several rotational states as shown in Table XIII. He analyzed his own data but based on a different theory.

As was pointed out in Sec. VII the value of $\bar{\delta}$ cannot be determined from zero-field data. We, therefore, express \bar{A} and \bar{B} as

$$\bar{A} = -176.216 + 2\bar{\delta}, \quad (48)$$

$$\bar{B} = 18.579 - 4.73\bar{\delta}, \quad (49)$$

and determine the value of $\bar{\delta}$ from the g factors. The values of φ and ψ can be obtained from g_n and g_Y directly, but those of other parameters are not so accurately determined. Since g_s is observed as 2.00190 in the case of the O_2 molecule,^{26,27} we assume the same value of g_s and determine the values of g_n and θ . In Table XIII we show theoretical values with $g_s = 2$, $g_n = \psi = \varphi = \theta = 0$, and those with the values of the molecular parameters given in Table XIV.

IX. LASER MAGNETIC RESONANCE

Evenson, Wells, and Radford¹⁹ observed several magnetic resonance lines of the OH free radical

using the 79 μm line of the H_2O laser. They made tentative assignments of these lines.

The observed lines can be divided into two categories. Those between 600 to 2045 G are due to the ($d1$, $J = \frac{3}{2}$) \rightarrow ($d2$, $J = \frac{1}{2}$) transitions, and those between 2183 to 6560 G are due to the ($c1$, $J = \frac{3}{2}$) \rightarrow ($c2$, $J = \frac{1}{2}$) transitions. A schematic diagram to show these transitions is given in their paper,¹⁹ while more detailed assignments are given here in Tables XVI and XVII, and Figs. 2 and 3. Those tables list all observed lines except for one very weak line. The experimental values of the resonance magnetic fields are improved by more recent measurement.²⁰

The energy levels for the ($d1$, $J = \frac{3}{2}$) and ($c1$, $J = \frac{3}{2}$) states are given by

$$f_{d1}(\frac{3}{2}) + \mu_B \mathcal{B} [g_{d1}(\frac{3}{2}) M_J + g_p M_I] + \mathcal{A}_{d1}(\frac{3}{2}) M_J M_I, \quad (50a)$$

$$f_{c1}(\frac{3}{2}) + \mu_B \mathcal{B} [g_{c1}(\frac{3}{2}) M_J + g_p M_I] + \mathcal{A}_{c1}(\frac{3}{2}) M_J M_I, \quad (50b)$$

respectively, for the magnetic field \mathcal{B} of over 600 G. Here

$$g_p = -0.003042 \quad (51)$$

is the proton g factor in terms of the Bohr magneton μ_B , which is 1.3995 MHz/G. The g factors and the hfs constants \mathcal{A} for the $J = \frac{3}{2}$ states are obtained by Radford,¹⁷ and we use his values in this analysis. The second-order effect due to an incomplete decoupling of hfs splits the two $M_F = -1$ levels further by 3 MHz in the 600-G region. When the field is stronger than 200 G the second-order effect due to the mixing of other rotational states

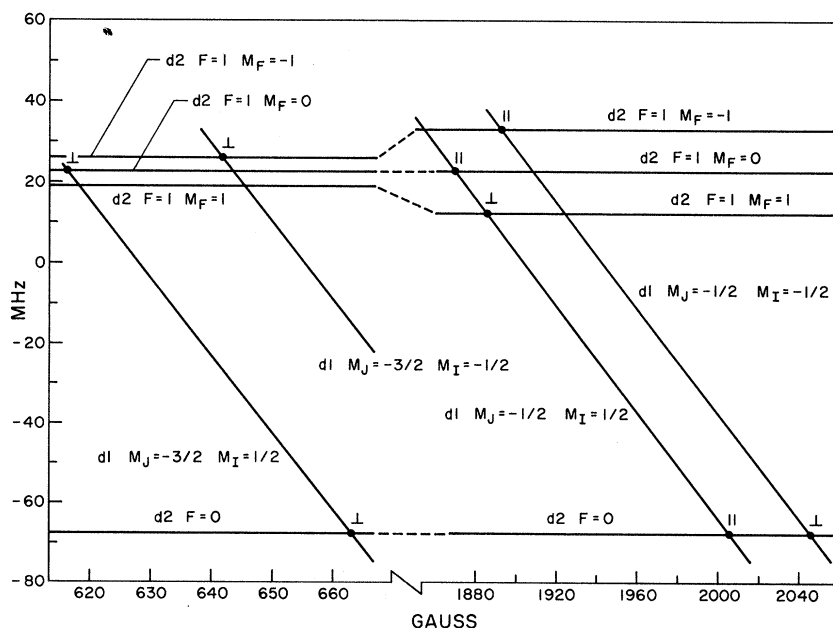


FIG. 2. Assignments of LMR lines. Horizontal lines show energy levels of $c2$ $J = \frac{1}{2}$ states, while slanted lines show energy levels of $d1$ $J = \frac{3}{2}$ states pushed up by the frequency of the laser line ν_0 . The circles show resonances while \perp and \parallel show their polarizations.

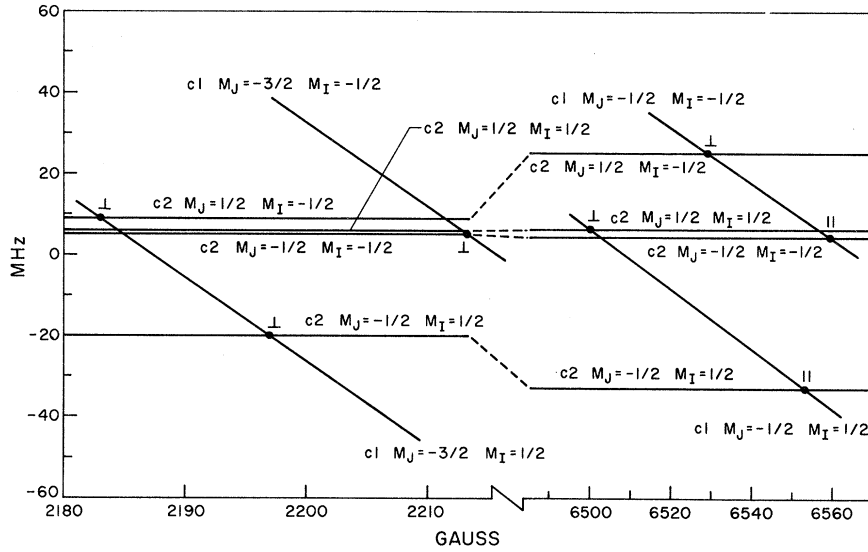


FIG. 3. Assignments of another set of LMR lines. Horizontal lines show energy levels of $c2 J = \frac{1}{2}$ states, while slanted lines show energy levels of $c1 J = \frac{3}{2}$ states pushed up by the frequency of the laser line ν_0 . The circles show resonances while \perp and \parallel show their polarizations.

amounts to

$$-1.16 \times 10^{-6} \mathcal{B}^2 \text{ MHz for } M_J = \pm \frac{1}{2}, \quad (52a)$$

$$-0.72 \times 10^{-6} \mathcal{B}^2 \text{ MHz for } M_J = \pm \frac{3}{2}. \quad (52b)$$

For the ($d2, J = \frac{1}{2}$) state, which is a pure $\Pi_{1/2}$ state, we find that

$$f_{d2}(\frac{1}{2}) + \frac{1}{2} \mathcal{A}_{d2}(\frac{1}{2}) [F(F+1) - \frac{3}{2}] + \frac{1}{2} \mu_B \mathcal{B} [g_{d2}(\frac{1}{2}) + g_p] M_F \quad (53)$$

is accurate enough without any second-order corrections even in the 2000-G region.

For the ($c2, J = \frac{1}{2}$) state we have

$$f_{c2}(\frac{1}{2}) + \frac{1}{4} \mathcal{A}_{c2}(\frac{1}{2}) + \frac{1}{2} \mu_B \mathcal{B} [g_{c2}(\frac{1}{2}) + g_p] \text{ for } M_F = \pm 1 \quad (54a)$$

and

$$f_{c2}(\frac{1}{2}) - \frac{1}{4} \mathcal{A}_{c2}(\frac{1}{2}) + \frac{1}{2} [\mathcal{A}_{c2}(\frac{1}{2})]^2 + \{\mu_B \mathcal{B} [g_{c2}(\frac{1}{2}) - g_p]\}^2)^{1/2} \text{ for } M_F = 0. \quad (54b)$$

In the 200-G region two $M_F = 0$ states, namely, the ($M_J = \frac{1}{2}, M_I = -\frac{1}{2}$) and ($M_J = -\frac{1}{2}, M_I = \frac{1}{2}$) states, are intermediately coupled. The asymmetric intensity distribution between the 2183- and 2197-G lines appears as a result. In the 6000-G region the hfs is completely decoupled. The second-order effect due to the ($d1, J = \frac{3}{2}$) state pushes up these states by 4 MHz at 600 G.

Using the known values^{14,15,17} of \mathcal{A} 's and the g factor for $J = \frac{3}{2}$ states we see that when $g_{d2}(\frac{1}{2})$, $g_{c2}(\frac{1}{2})$, and the zero-field energy are chosen as in Table XV a satisfactory fit is obtained as shown in Tables XVI and XVII.

When we use the values of molecular parameters given in Table XIV we obtain

$$g_{d2}(\frac{1}{2}) = -0.0020 \text{ and } g_{c2}(\frac{1}{2}) = 0.0037 \quad (55)$$

as their theoretical values. It is noted that $g_{d2}(\frac{1}{2}) + g_{c2}(\frac{1}{2})$ is negative in the observed values, but is positive in the theoretical values. It is found, however, that unless g_s is chosen to be greater than 2.003, which is unacceptable, we cannot find a set of molecular parameters which gives the correct sign here and still gives satisfactory agreement with the EPR data we discussed in Sec. VIII.

The observed zero-field energies give

$$f_{d2}(\frac{1}{2}) - f_{c2}(\frac{1}{2}) - [f_{d1}(\frac{3}{2}) - f_{c1}(\frac{3}{2})] = 3070 \text{ MHz} \quad (56)$$

The observed Λ -doublet separations as shown in Table VIII give 3065 MHz for this quantity. The laser frequency ν_0 is not measured yet, but the corresponding wave number is measured²⁸ as 126.44 cm^{-1} . Using the observed zero-field energies we obtain

$$\frac{1}{2} [f_{d2}(\frac{1}{2}) + f_{c2}(\frac{1}{2}) - f_{d1}(\frac{3}{2}) - f_{c1}(\frac{3}{2})] = 126.37 \text{ cm}^{-1}, \quad (57)$$

while from Dieke and Crosswhite's data¹¹ this value is expected to be 126.26 cm^{-1} . Our theoretical formulas (8c), (8d), (17a), and (17b) give 126.354 cm^{-1} for this quantity when the values of molecular parameters given in Table XII are used. When the laser frequency is measured more accurately our data of LMR will give two more digits for this value.

TABLE XV. Molecular parameters observed by LMR.

$g_{d2}(\frac{1}{2}) = -0.0025$	$g_{c2}(\frac{1}{2}) = 0.0033$
$f_{d2}(\frac{3}{2}) - f_{d1}(\frac{3}{2}) = \nu_0 - 1262 \text{ MHz}$	$\nu_0 = 3790.477 \text{ GHz}$
$f_{c2}(\frac{1}{2}) - f_{c1}(\frac{3}{2}) = \nu_0 - 4332 \text{ MHz}$	

TABLE XVI. Observed (Refs. 19 and 20) and theoretical LMR data for $(d1, J=\frac{3}{2})$ $(d2, J=\frac{1}{2})$ transitions.

Magnetic field (G)	Experiment Relative intensity	Polarization	Assignment				Theory		Magnetic field (G)
			$(d1, J=\frac{3}{2})$		$(d2, J=\frac{1}{2})$		Relative intensity		
			M_J	M_I	F	M_F			
617	7	\perp	$-\frac{3}{2}$	$\frac{1}{2}$	1	0	6	617	
638	15	\perp	$-\frac{3}{2}$	$-\frac{1}{2}$	1	-1	12	639	
663	7	\perp	$-\frac{3}{2}$	$\frac{1}{2}$	0	0	6	664	
1870	8	\parallel	$-\frac{1}{2}$	$\frac{1}{2}$	1	0	8	1871	
1893	14	\parallel	$-\frac{1}{2}$	$-\frac{1}{2}$	1	-1	16	1895	
2006	8	\parallel	$-\frac{1}{2}$	$\frac{1}{2}$	0	0	8	2008	
1887	3	\perp	$-\frac{1}{2}$	$\frac{1}{2}$	1	1	4	1887	
1908.5	0.7	\perp	$-\frac{1}{2}$	$-\frac{1}{2}$	1	0	2	1908	
2045	1.5	\perp	$-\frac{1}{2}$	$-\frac{1}{2}$	0	0	2	2046	

Note added in manuscript. A similar work was done by L. Veseth, J. Mol. Spectry. 38, 228 (1971).

Note added in proof. ν_0 is now measured by Evenson as 3790.477 GHz, which makes the value in (57) as 126.3435 cm^{-1} .

ACKNOWLEDGMENT

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APPENDIX: PERTURBATION THEORY

It is shown that²⁹ if $\hat{H} = \hat{H}_0 + \hat{H}_1$ and

$$\hat{H}_0 |n_1^0\rangle = \mathcal{E}_n^0 |n_1^0\rangle, \quad (58)$$

$$\hat{H}_0 |n_2^0\rangle = \mathcal{E}_n^0 |n_2^0\rangle, \dots, \hat{H}_0 |n_b^0\rangle = \mathcal{E}_n^0 |n_b^0\rangle,$$

or there exists a b -fold degeneracy for \hat{H}_0 , then the solutions of the secular equation

$$\begin{vmatrix} \langle n_1^0 | \hat{S}_N^0 \hat{H} \hat{S}_N^0 | n_1^0 \rangle - \mathcal{E} \langle n_1^0 | \hat{S}_N^0 \hat{S}_N^0 | n_1^0 \rangle & \dots & \langle n_b^0 | \hat{S}_N^0 \hat{H} \hat{S}_N^0 | n_1^0 \rangle - \mathcal{E} \langle n_b^0 | \hat{S}_N^0 \hat{S}_N^0 | n_1^0 \rangle \\ \langle n_1^0 | \hat{S}_N^0 \hat{H} \hat{S}_N^0 | n_2^0 \rangle - \mathcal{E} \langle n_1^0 | \hat{S}_N^0 \hat{S}_N^0 | n_2^0 \rangle & \dots & \dots \\ \dots & \dots & \dots \\ \langle n_1^0 | \hat{S}_N^0 \hat{H} \hat{S}_N^0 | n_b^0 \rangle - \mathcal{E} \langle n_1^0 | \hat{S}_N^0 \hat{S}_N^0 | n_b^0 \rangle & \dots & \langle n_b^0 | \hat{S}_N^0 \hat{H} \hat{S}_N^0 | n_b^0 \rangle - \mathcal{E} \langle n_b^0 | \hat{S}_N^0 \hat{S}_N^0 | n_b^0 \rangle \end{vmatrix} = 0 \quad (59)$$

are correct to the order of \hat{H}_1^3 . In this formula

$$\begin{aligned} \hat{S}_N^0 &= \hat{1} + (\mathcal{E}_n^0 - \hat{H}_0 - \hat{Q}_N \hat{H}_1)^{-1} \hat{Q}_N \hat{H}_1 \\ &= \hat{1} + (\mathcal{E}_n^0 - \hat{H}_0)^{-1} \hat{Q}_N \hat{H}_1 \hat{S}_N^0 \end{aligned} \quad (60)$$

is the space-contraction operator, and

$$\hat{Q}_N = \hat{1} - |n_1^0\rangle \langle n_1^0| - |n_2^0\rangle \langle n_2^0| - \dots - |n_b^0\rangle \langle n_b^0|. \quad (61)$$

It is also shown that when the theory is applied to the ground states the solutions of (59) give the upper limit of the corresponding exact solutions.²⁹

TABLE XVII. Observed (Refs. 19 and 20) and theoretical LMR data for $(c1, J=\frac{3}{2})$ $(c2, J=\frac{1}{2})$ transitions.

Magnetic field (G)	Experiment Relative intensity	Polarization	Assignment				Theory		Magnetic field (G)
			$(c1, J=\frac{3}{2})$		$(c2, J=\frac{1}{2})$		Relative intensity		
			M_J	M_I	M_J	M_I			
2183	2	\perp	$-\frac{3}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	2	2185	
2197	11	\perp	$-\frac{3}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	10	2200	
2213	12	\perp	$-\frac{3}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	12	2213	
6500	5	\perp	$-\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	4	6499	
6528	5	\perp	$-\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	4	6527	
6553	22	\parallel	$-\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	16	6556	
6560		\parallel	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	16	6561	

We have a fourfold degeneracy as shown in (5a)–(5d), but since no matrix elements exist between c and d states, the problem is reduced to that of twofold degeneracy. The original matrix, before taking into account the perturbations due to other electronic and vibrational states, is shown in (6), which is the same for c and d states.

An excited ${}^2\Sigma$ state splits into c and d states in the same sense as in the ground states, and the matrix elements of \hat{H} of (1) or (3) are²¹

$$\left(\begin{array}{c} \frac{1}{2}A_c - B + \beta - \mathcal{E} - [B - \frac{1}{2}\mu_s - \frac{1}{2}\alpha \pm \beta(J + \frac{1}{2})][(J + \frac{1}{2})^2 - 1]^{1/2} \\ - [B - \frac{1}{2}\mu_s - \frac{1}{2}\alpha \pm \beta(J + \frac{1}{2})][(J + \frac{1}{2})^2 - 1]^{1/2} - \frac{1}{2}A_c + B - \frac{1}{4}\gamma \pm \alpha(J + \frac{1}{2}) - \mathcal{E} \end{array} \right) + (B - \beta)(J + \frac{1}{2})^2 - \mu_L - \frac{1}{2}\mu_s \quad (64)$$

for the transformed matrix of $\hat{H} - \mathcal{E}\hat{1}$. Since the first excited ${}^2\Sigma$ state is about $33\,000\text{ cm}^{-1}$ the difference between $\hat{S}_N^{0+}\hat{S}_N^0$ and $\hat{1}$ is less than 10^{-5} , and therefore neglected in (64).

The effect of other vibrational states is then taken into account in the same way. The result is

$$\left(\begin{array}{c} \frac{1}{2}[\bar{A}_J \mp \alpha_J(J + \frac{1}{2})] - \mathcal{E} - [\bar{B}_J \pm \beta_J(J + \frac{1}{2})][(J + \frac{1}{2})^2 - 1]^{1/2} \\ - [\bar{B}_J \pm \beta_J(J + \frac{1}{2})][(J + \frac{1}{2})^2 - 1]^{1/2} - \frac{1}{2}[\bar{A}_J \mp \alpha_J(J + \frac{1}{2})] - \mathcal{E} \end{array} \right) + \xi_J \pm \eta_J, \quad (65)$$

where $\bar{A}_J, \bar{B}_J, \alpha_J, \beta_J, \xi_J$, and η_J are defined in (11), (12), (13), (14), (9a), and (9b), respectively. The difference between $\hat{S}_N^{0+}\hat{S}_N^0$ and $\hat{1}$ is of the order of $D/E(v')$, where $E(v')$ is the vibrational excitation energy. Since $E(v')$ is about 3700 cm^{-1} and D is about $2 \times 10^{-3}\text{ cm}^{-1}$, this difference is of the order of 10^{-6} , and therefore neglected in (65).

When an external magnetic field exists the additional Hamiltonian \hat{H}' of (43) appears. Including this additional part, the matrix elements are

$$\langle {}^2\Pi_{\frac{3}{2}d}^c JM | (\hat{H} + \hat{H}') | {}^2\Pi_{\frac{3}{2}d}^c JM \rangle = \frac{1}{2}A - B + (B - \beta)(J + \frac{1}{2})^2 + \mathfrak{B}\mu_B M \left(\frac{3(2 + g_s - 3g_n)}{4J(J+1)} + g_n \right), \quad (66a)$$

$$\langle {}^2\Pi_{\frac{3}{2}d}^c JM | (\hat{H} + \hat{H}') | {}^2\Pi_{\frac{1}{2}d}^c JM \rangle = \left(- (B - \frac{1}{2}\mu_s) + \mathfrak{B}\mu_B M \frac{g_s - g_n}{2J(J+1)} \right) \times [(J + \frac{1}{2})^2 - 1], \quad (66b)$$

$$\langle {}^2\Pi_{\frac{1}{2}d}^c JM | (\hat{H} + \hat{H}') | {}^2\Pi_{\frac{1}{2}d}^c JM \rangle = -\frac{1}{2}A + B + (B - \beta)(J + \frac{1}{2})^2 + \mathfrak{B}\mu_B M \left(\frac{2 - g_s - g_n}{4J(J+1)} + g_n \right). \quad (66c)$$

The excited Σ states contribute through the matrix elements

$$\langle {}^2\Sigma_d^c JM | (\hat{H} + \hat{H}') | {}^2\Pi_{\frac{3}{2}d}^c JM \rangle = \left(- \langle \Sigma | \hat{B}' \hat{L}_- | \Pi + \rangle + \mathfrak{B}\mu_B M \frac{\langle \Sigma | \hat{L}_- | \pi + \rangle}{2J(J+1)} \right) \times [(J + \frac{1}{2})^2 - 1] \quad (67a)$$

$$\langle {}^2\Sigma_d^c JM | \hat{H} | {}^2\Pi_{\frac{3}{2}d}^c JM \rangle = - \langle \Sigma | \hat{B}' \hat{L}_+ | \Pi - \rangle [(J + \frac{1}{2})^2 - 1]^{1/2}, \quad (62)$$

$$\langle {}^2\Sigma_d^c JM | \hat{H} | {}^2\Pi_{\frac{1}{2}d}^c JM \rangle = \langle \Sigma | \frac{1}{2} \hat{A}' \hat{L}_+ | \Pi - \rangle \mp \langle \Sigma | \hat{B}' \hat{L}_+ | \Pi - \rangle (J + \frac{1}{2}), \quad (63)$$

and no matrix elements between c and d states.

Taking into account all ${}^2\Sigma$ states in the space-contraction operator \hat{S}_N^0 we obtain

$$\langle {}^2\Sigma_d^c JM | (\hat{H} + \hat{H}') | {}^2\Pi_{\frac{1}{2}d}^c JM \rangle = \frac{1}{2} \langle \Sigma | \hat{A}' \hat{L}_- | \Pi + \rangle \mp \langle \Sigma | \hat{B}' \hat{L}_- | \Pi + \rangle (J + \frac{1}{2}) \pm \mathfrak{B}\mu_B M \frac{\langle \Sigma | \hat{L}_- | \Pi + \rangle (J + \frac{1}{2})}{2J(J+1)}. \quad (67b)$$

In calculating the contributions by excited Π states (Π' states) we notice that since \hat{B} does not depend on any electronic coordinates

$$\langle \Pi | \hat{B} | \Pi' \rangle = \hat{B} \langle \Pi | \Pi' \rangle = 0. \quad (68)$$

Therefore

$$\langle {}^2\Pi_{\frac{3}{2}d}^c JM | (\hat{H} + \hat{H}') | {}^2\Pi_{\frac{3}{2}d}^c JM \rangle = \frac{1}{2} \langle \Pi | \hat{A}' | \Pi' \rangle + \mathfrak{B}\mu_B M \frac{3}{J(J+1)}, \quad (69a)$$

$$\langle {}^2\Pi_{\frac{3}{2}d}^c JM | (\hat{H} + \hat{H}') | {}^2\Pi_{\frac{1}{2}d}^c JM \rangle = \langle {}^2\Pi_{\frac{1}{2}d}^c JM | (\hat{H} + \hat{H}') | {}^2\Pi_{\frac{1}{2}d}^c JM \rangle = \mathfrak{B}\mu_B M \frac{[(J + \frac{1}{2})^2 - 1]^{1/2}}{J(J+1)}, \quad (69b)$$

Following the same procedure as before we obtain (46) and (47) when terms in the first order in \mathfrak{B} are taken. It is possible that g_s depends on J due to the second-order perturbation, but that is not taken into account in this paper.

It is not difficult to calculate the contributions due to excited Δ states, but they are presumably small since the ground state is known to be nearly

pure $L=1$ state. In contrast to excited Π states, excited Δ states contribute to the zero-field energies also, modifying

$(B - \beta - D)$ into $(B - \beta - \beta_\Delta - D)$ in (9a)

$$\text{into } \bar{A} = A - 2B + \beta + 3\beta_\Delta + \frac{1}{4}\gamma - \frac{1}{4}\gamma_\Delta \text{ in (15)}$$

$$\text{into } \bar{B} = B - \frac{1}{2}\mu_s - \frac{1}{2}\alpha - \frac{1}{2}\alpha_\Delta - \kappa \text{ in (16) ,}$$

$$(70)$$

where α_Δ , β_Δ , and γ_Δ are defined in the same way as α , β , and γ , except that $|\Sigma\rangle$ is replaced by $|\Delta\rangle$ and $E(\Sigma)$ is replaced by $E(\Delta)$. Note that Δ states do not contribute to α_r and β_r of (13) and (14). Ex-

cited Δ states also contribute to g_z and g_x , but not to g_y and g_r . The contributions modify g_z into

$$g_z + \varphi_\Delta \frac{(J + \frac{1}{2})^2 - \frac{5}{2}}{J(J+1)} \quad (71a)$$

and

$$\left. \begin{array}{l} \varphi \text{ into } \varphi + 3\varphi_\Delta \\ \psi \text{ into } \psi + \psi_\Delta \end{array} \right\} \text{ in } g_x, \quad (71b)$$

where φ_Δ and ψ_Δ are defined in the same way as φ and ψ except that $|\Sigma\rangle$ is replaced by $|\Delta\rangle$ and $E(\Sigma)$ is replaced by $E(\Delta)$. All these contributions are neglected in this paper.

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