THE JOURNAL OF CHEMICAL PHYSICS VOLUME 58, NUMBER 10 15 MAY 1973

High-field level-crossing and Stark studies of the $A\ ^2\Sigma^+$ state of OD

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(Received 27 July 1972)

We have carried out a high-field level-crossing experiment on the $v=0$, $N=1$, $J=3/2$ ot the OD $A\ ^2\Sigma^+$ state. A precise measurement of the magnetic fields at which three crossovers are observed permits a determination of the three hyperfine constants $b=110.4\pm2.6$ MHz, $c=22\pm14$ MHz, and $eQq=0.09\pm0.05$ MHz (3σ). In addition, we have applied a static electric field parallel to the magnetic field and observed a shift in the location of the high-field level crossings from which we calculate the dipole moment of this excited state to be 1.72 ± 0.10 D (3σ). A comparison of these structural parameters is made with *ab initio* calculations.

I. INTRODUCTION

The experimental apparatus required to observe a molecular high-field level crossing (hereafter referred to as HFLC) is the same as that required in a zero-field level crossing (Hanle effect).[1] However, the expected weakness of the HFLC signal and the associated search problem in locating its position makes high-field level-crossing studies much more difficult. The HFLC signal strength is at least $2J+1$ times weaker than a Hanle-effect signal from the same rotational level because the HFLC signal arises from the crossover of only two Zeeman levels. Moreover, the fluorescence originating from the other Zeeman levels adds to the background light intensity, thereby further reducing the signal-to-noise expected in an HFLC experiment.

In spite of the problems inherent in molecular HFLC experiments, there have been several successes to date: Silvers, Bergeman, and Klemperer[2] carried out a Stark-Zeeman recrossing experiment on the $A\ ^1\Pi$ state of CS; Levy[3] has observed high-field anticrossing signals involving the mutual perturbations between the $B\ ^2\Sigma^+$ and $A\ ^2\Pi$ states of CN when an electric field is applied; and Baltayan and Nédélec[4] have measured high-field level crossings in the $v=0$, 1, 2, 3, $N=1$ levels of the $1s3p\ ^3\Pi_u$ state of parahydrogen ($I=0$) when the Zeeman levels of adjacent J levels cross at various applied magnetic fields. In the latter study, the search problem was largely eliminated by using preliminary fine structure parameters determined from optical radio-frequency double resonance experiments in which the uncoupling of $\mathbf{N}$ and $\mathbf{S}$ is observed.[5] In a similar manner, we have carried out optical radio-frequency double resonance studies on the $v=0$, $N=1$, $J=3/2$ level of the OD $A\ ^2\Sigma^+$ state in which the uncoupling of $\mathbf{I}$ and $\mathbf{S}$ is used to calculate preliminary hyperfine splittings (see preceding paper[6]). Using the value $b+c/5=121\pm14$ MHz, we predict $\Delta M=2$ high-field level crossings to occur at the positions indicated in Fig. 1.

We report here the observation of three HFLC signals corresponding to the three $\Delta M=2$ crossovers shown in Fig. 1. In addition, we obtain the dipole moment of the $v=0$ level of the OD $A\ ^2\Sigma^+$ state by measuring the shift in the position of the HFLC signal when a dc electric field is applied parallel to the magnetic field. By making a simultaneous fit to all HFLC data, we determine values for the hyperfine constants b, c, eQq, and the dipole moment μ. These excited-state structural parameters are then compared with recent *ab initio* calculations.

II. EXPERIMENTAL

The OD molecules are generated by the chemical reaction of $D+NO_2$ in a flow system. The 3071.60-Å resonance line from a microwave-driven barium flowlamp excites OD to the $v=0$, $N=1$, $J=3/2$ level of the $A\ ^2\Sigma^+$ state.[7] The fluorescence is observed at right angles to the excitation beam and to the magnetic field. For the HFLC studies we replace the exit window of the flow cell in the excitation path by a Wood's horn. This decreases the reflected light sufficiently to allow a Corning 7-54 filter to be used in place of a narrow band interference filter. Other than this change, the experimental setup is the same as that described previously (see Fig. 1 of Ref. 6).

A. High-Field Level-Crossing Measurements

Figure 2 is a typical trace of a high-field level crossing observed at 66.67 G. This corresponds to the crossover of the ($F=\frac{5}{2}$, $M_F=-\frac{3}{2}$) and the ($F=\frac{3}{2}$, $M_F=\frac{1}{2}$) Zeeman levels (see Fig. 1). The magnetic field at the terminal points of the sweeps is determined by measuring with a model 266 Digitec[8] DVM the voltage drop across an air-cooled constantan resistor that is in series with the Helmholtz coils. The magnetic field is calibrated by measuring the Hg double resonance signal at a number of different fields and by fitting the data in a least squares manner to a straight line.[9] Care is taken to minimize the Bloch–Siegert shift by using low rf power levels.

We measure the magnetic fields for the three high-

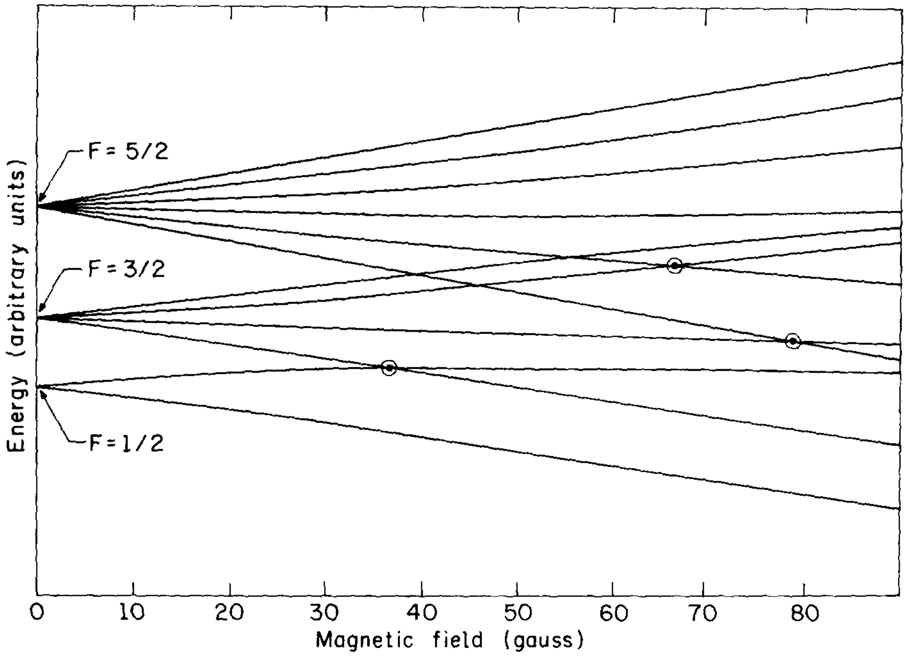

FIG. 1. Zeeman energy level pattern for the OD $A\,^2\Sigma^+$ $v=0$, $N=1$, $J=\frac{3}{2}$ level as a function of magnetic field. This figure is constructed using the previously determined value of $b+c/5=121$ MHz. The circles denote the $\Delta M=2$ crossovers that occur at fields less than 80 G.

field level crossings circled in Fig. 1. The results are presented in Table I. Our determination of the magnetic field location of the crossing points is subject to the following three errors:

(1) magnetic field calibration (0.1% three standard deviations),

(2) uncertainty in the determination of the line center of the HFLC signal (0.3% three standard deviations),

(3) reading error (one unit uncertainty in last digit) of the DVM (0.07% maximum, three standard deviations),

of which the last uncertainty is negligible in most cases. Note that throughout this paper we quote three standard deviations unless otherwise stated. Taking into account these errors, we find that: the $F=\frac{1}{2}$, $M_F=\frac{1}{2}$, and the $F=\frac{3}{2}$, $M_F=-\frac{3}{2}$ levels cross at 36.59 G; the $F=\frac{3}{2}$, $M_F=\frac{1}{2}$ and the $F=\frac{5}{2}$, $M_F=-\frac{3}{2}$ levels cross at 66.66 G; and the $F=\frac{3}{2}$, $M_F=-\frac{1}{2}$ and the $F=\frac{5}{2}$, $M_F=-\frac{5}{2}$ levels cross at 79.01 G. No attempt is made

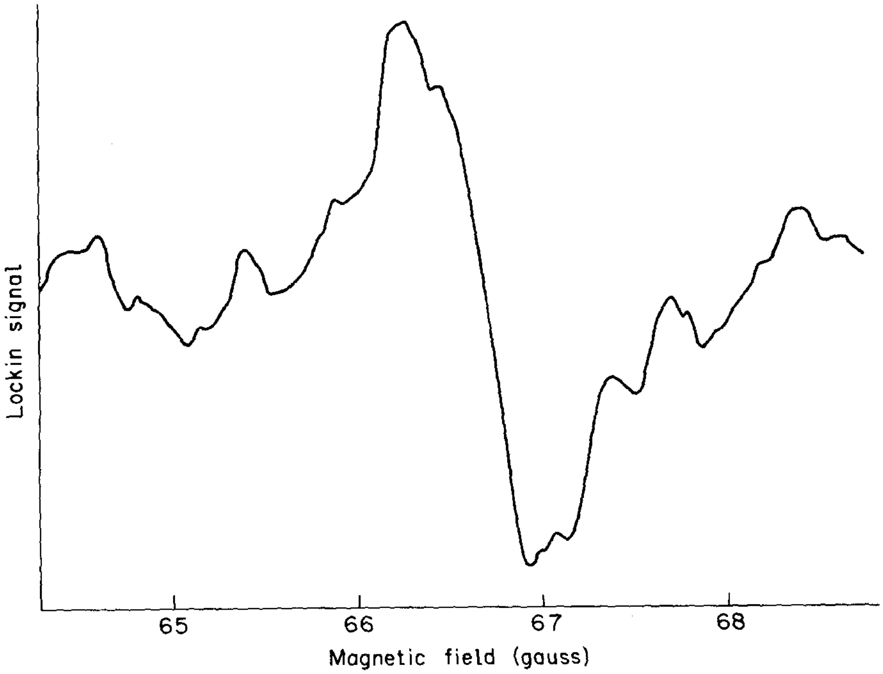

FIG. 2. A high-field level-crossing signal, centered at 66.67 G corresponding to the crossover of the $F=\frac{5}{2}$, $M_F=-\frac{3}{2}$ and $F=\frac{3}{2}$, $M_F=-\frac{1}{2}$ levels.

to search for additional $\Delta M=2$ crossovers at higher fields.

B. Stark Shift Measurements

In order to measure the dipole moment in the $v=0$, $N=1$ level of the OD $A\,^2\Sigma^+$ state, a static dc electric field is applied parallel to the magnetic field. This is achieved by parallel Stark plates that are positioned above and below the flow cell windows and are held in place by tungsten pins sealed in and passing through the walls of the flow cell. The parallelism with the magnetic field is better than 1 deg. The Stark plates are made of stainless steel mesh having a wire diameter of 0.46 mm and a spacing of 1.14 mm. The separation of the plates is measured in two different ways. First, calipers are used to measure the spacing over the central portion of the plates. Second, an optical comparator is used to determine the separation at the edges of the plates.

The two determinations give values of 22.5±0.5 mm (3σ) and 22.5±0.6 mm (3σ), respectively. This agreement is indicative of the high degree of parallelism of the plates. By taking the average of these two types of determinations, we arrive at a measured separation of 22.5±0.4 mm (3σ). Since the optical setup is such that the observed fluorescence originates from a sphere of at most 10 mm in diameter, the actual field can be considered to be 99.7%±0.3% of the applied field,[10] i.e., the fringing effect caused by the finite extent of the plates is almost negligible. The reduction of the electric field caused by the grid spacing is estimated to be 0.36%. This is determined by averaging different line integrals along the lines of force of the electric field.

It is well known that hydrogen (or deuterium) atoms recombine very efficiently on metal surfaces. It is also suspected that the OH (or OD) radical is efficiently destroyed by the presence of metal surfaces. Not surprisingly, our initial attempts to detect OD fluorescence in the Stark cell proved futile, and no fluorescence is observed even when the mixing of the D atoms and NO_2 takes place between the Stark plates. Our speculation that the OD is produced in the reaction and then effectively removed by the plates is confirmed by the observation of NO fluorescence excited by the 2145-Å Te line[11] under the same conditions in which no OD fluorescence is detectable.

The destruction of deuterium atoms and OD molecules is greatly inhibited by coating the Stark plates with a 10% aqueous solution of phosphoric acid. When the system is put under vacuum, an invisible coating of phosphoric acid remains on the plates. Unfortunately, there is concern that the presence of such a coating may reduce the value of the electric field applied across the Stark plates. There are two conceivable ways for this to happen: (1) the phosphoric-acid coating behaves as a dielectric layer inserted between the two capacitor plates, and (2) free charges produced in the rf discharge used to dissociate D_2 migrate into the region of the Stark plates and build up on the coating in such a way as to oppose the electric field. The first of these effects is estimated to be negligible. If we assume a dielectric constant of 10 for the H_3PO_4 coating and a film thickness of 0.05 mm, we calculate a decrease of only 0.04% in the applied field.

Table I. High-field level-crossing data taken with no applied electric field.

F_1, M_1	F_2, M_2	Magnetic field (G)[a]
1/2, 1/2	3/2, −3/2	36.60±0.05
		36.60±0.05
		36.57±0.05
3/2, 1/2	5/2, −3/2	66.67±0.08
		66.67±0.08
		66.71±0.05
		66.64±0.05
3/2, −1/2	5/2, −5/2	79.01±0.06
		79.01±0.06
		79.01±0.06
		79.03±0.06

[a] The uncertainty represents one standard deviation.

The second effect depends to what extent the phosphoric acid coating is conductive. A Pyrex plate was coated with phosphoric acid in the same manner as the Stark plates and two probes were placed 1 cm apart. A finite resistance of about 100 kΩ was measured using a VTVM whereas without the coating there was an open circuit. These measurements were repeated for various coating thicknesses and the resistance was found to increase with decreasing thickness, as expected. Note that in these measurements care was taken to remove all water from the coating.

At the suggestion of the referee, it was decided to test the effect of the phosphoric acid coating on a conventional microwave Stark cell. The following series of measurements were carried out in the laboratory of Professor S. G. Kukolich at MIT. First, the Stark separation was measured between two $\Delta M=0$ absorption lines of HOD,[12] $K=1$, $J=2\rightarrow K=2$, $J=2$ at zero applied field, and $K=1$, $J=2$, $M=\pm2\rightarrow K=2$, $J=2$, $M=\pm2$ at an applied field of 1000 V/cm. A value of 9.83±0.06 MHz (1σ) was found. The Stark plates were then coated with phosphoric acid in the same manner as in the OD Stark measurements, and the above HOD Stark separation was remeasured, yielding a value of 9.86±0.03 MHz (1σ). Finally, a number of determinations of this Stark separation was made immediately after a Tesla discharge was struck in the system for various periods of time (up to two minutes). For these runs, the HOD

TABLE II. High-field level-crossing data taken with an applied electric field.

F_1, M_1	F_2, M_2	Magnetic field[a] (G)	Electric field[a] (V/cm)
1/2, 1/2	3/2, −3/2	36.02±0.14[b]	2219±14
		36.09±0.17[b]	2219±14
		36.02±0.05	2219±14
		36.02±0.05	2219±14
3/2, −1/2	5/2, −5/2	77.98±0.08	2239±14
		78.03±0.14[b]	2239±14
		77.96±0.19[b]	2219±14
		77.98±0.16	2219±14

[a] The uncertainty represents one standard deviation.

[b] The larger uncertainties in these line center measurements are caused by instabilities in the magnetic field sweep that occurred during these runs.

Stark separation was found to be independent of the duration of the discharge and to have the value 9.80± 0.06 MHz (1σ). We conclude that the effects of charge build up in our OD Stark measurements are also negligible.

For a $^2\Sigma$ state, the Stark shift is second-order in the electric field. Consequently, it is desirable to apply a large field subject to the constraint of electrical breakdown. For this purpose, it is advantageous to reduce the Stark plate separation. However, this limits the volume of OD molecules that can be studied and further increases the reflected light level while decreasing the effective intensity of our excitation source in the active volume. As a compromise to these design problems we use a spacing of 22.5 mm corresponding roughly to the entrance and observation window diameter. Even under these conditions, we must work at reduced OD concentrations (6 mtorr D_2, 3 mtorr NO_2) in order to avoid breakdown at electric fields of about 2000 V/cm.

The electric field is supplied by a Spellman 10 kV dc power supply (less than 200 mV rms ripple). The voltage across the Stark plates is measured to an accuracy of ±1 V using a Fluke 80E voltage divider in conjunction with the previously mentioned Digitec DVM. The apparent voltage is corrected for the presence of fringing fields caused by the finite size of the plates and the use of a mesh.

Only shifts in the positions of the first and third crossovers (see Fig. 1) are studied as a function of applied electric field and the data obtained are summarized in Table II. The middle crossover is the least sensitive to applied electric field (see Fig. 3 in Sec. III), and consequently no attempt is made to measure its Stark shift quantitatively.

III. ANALYSIS OF THE DATA

A. Calculation of Molecular Energy Levels

The molecular Hamiltonian is a sum of the fine structure, hyperfine structure, Zeeman, and Stark Hamiltonians

$$\mathcal{H}=\mathcal{H}_{\mathrm{fs}}+\mathcal{H}_{\mathrm{hfs}}+\mathcal{H}_Z+\mathcal{H}_S, \tag{1}$$

where

$$\mathcal{H}_{\mathrm{fs}}=\gamma\mathbf{N}\cdot\mathbf{S}, \tag{2}$$

$$\mathcal{H}_{\mathrm{hfs}}=b\mathbf{I}\cdot\mathbf{S}+cI_zS_z+eQq \times[3I_z^2-I(I+1)/4I(2I-1)], \tag{3}$$

$$\mathcal{H}_Z=[\mu_0(g_e\mathbf{S}+\mathbf{L})+\mu_N(g_I\mathbf{I}+g_J\mathbf{J})]\cdot\mathbf{H}, \tag{4}$$

and

$$\mathcal{H}_S=-\boldsymbol{\mu}\cdot\mathbf{E}. \tag{5}$$

In Eq. (2) γ is the rho-doubling constant; in Eq. (3) b and c are the hyperfine parameters given by

$$b=(16\pi/3)(\mu_0\mu_I/I)\Psi^2(0) -(\mu_0\mu_I)\langle(3\cos^2\theta-1)/r^3\rangle \tag{6}$$

and

$$c=3(\mu_0\mu_I/I)\langle(3\cos^2\theta-1)/r^3\rangle, \tag{7}$$

and eqQ is the product of the nuclear electric quadrupole moment Q, the proton charge e, and the electric field gradient at the nucleus

$$q=\sum_i e_i\langle(3\cos^2\theta_i-1)/r_i^3\rangle; \tag{8}$$

in Eq. (4) the expression in square brackets is the magnetic moment and $\mathbf{H}$ is the magnetic field; and in Eq. (5) $\boldsymbol{\mu}$ is the electric dipole moment and $\mathbf{E}$ is the electric field. Matrix elements of $\mathcal{H}_{\mathrm{fs}}$, $\mathcal{H}_{\mathrm{hfs}}$, and $\mathcal{H}_Z$ have been given in the NSJIFM$_F$ representation in the preceding paper[6] and will not be repeated here. The matrix elements of $\mathcal{H}_S$ in this representation may be found from the results of Miller, Levy and Carrington.[13]

The energy levels are calculated as a function of magnetic and electric field by diagonalizing the Hamiltonian given in Eq. (1) for assumed values of the parameters b, c, eQq, and μ. A computer program has been written that numerically solves the resulting secular equations. In Fig. 1, we have plotted the Zeeman levels as a function of magnetic field. In Fig. 3, we show how the three $\Delta M=2$ crossovers circled in Fig. 1 shift with an applied electric field of 2000 V/cm and an assumed dipole moment of 2.0 D. With predicted shifts up to 1 G and with the ability to measure individual line centers of HFLC signals to ±0.05 G, we are encouraged to believe that the measurement of HFLC Stark shifts would yield an accurate value of the excited-state dipole moment.

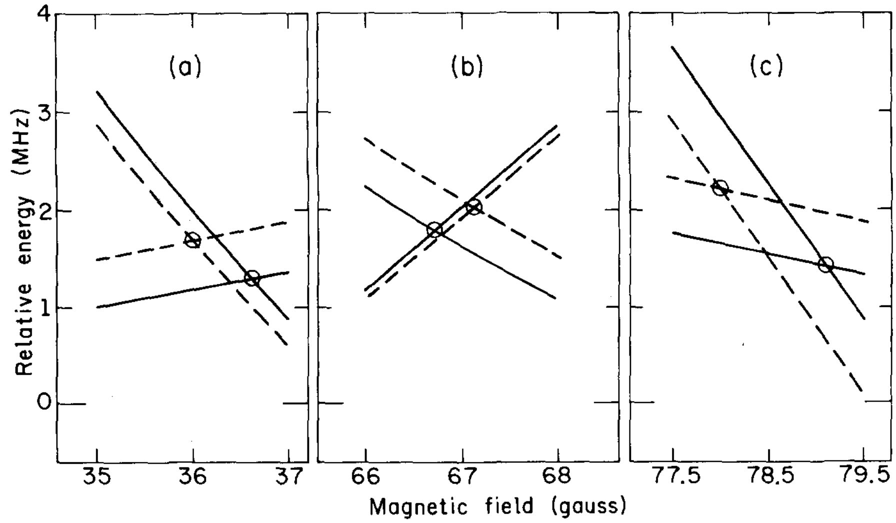

FIG. 3. Calculated shift in the position of the three observed $\Delta M=2$ crossovers when a 2000 V/cm electric field is applied parallel to the magnetic field. This figure is constructed using an assumed excited-state dipole moment of 2.0 D.

B. Determination of Excited-State Parameters

A nonlinear least squares fit of the data given in Tables I and II is made to the energy levels calculated with adjustable parameters b, c, eQq, and μ. We find that

$$b=110.4\pm2.6 \text{ MHz}, \tag{9}$$

$$c=22\pm14 \text{ MHz}, \tag{10}$$

$$eQq=0.09\pm0.05 \text{ MHz}, \tag{11}$$

and

$$\mu=1.72\pm0.10 \text{ D}. \tag{12}$$

It should be noted that values of these structural parameters can also be derived from the experimental data using the following two step procedure: (1) a nonlinear least squares fit to the data in Table I is made to the energy levels calculated with the adjustable hyperfine parameters b, c, and eQq; and (2) using these determined hyperfine parameters, a nonlinear least squares fit of the data in Table II is made to ascertain the value of the dipole moment, μ. The values of the parameters obtained in this manner are negligibly different from those quoted, but have slightly larger uncertainties. The agreement of these two procedures increases our confidence in the results presented in Eqs. (9)–(12) which are based on a fit to all measurements.

Since all the crossovers we observe are within one J level, at first glance it might appear doubtful that the HFLC data would yield values of both b and c. Fortunately, however, off-diagonal matrix elements between the $N=1, J=\frac{3}{2}$ level and the $N=1, J=\frac{1}{2}$ level [see Eq. (11), Ref. 6] introduce a different dependence on c. Since the perturbation is across the spin–doublet, an accurate knowledge of the value of γ is necessary. We use the value of $\gamma=0.1200\pm0.0023$ cm^{-1} as determined by Clyne, Coxon, and Woon Fat[14] from a high-resolution study of the OD A–X band system. The error represents a spread of γ values with fitting procedure. This lack of precision in γ introduces an uncertainty in the value of c that is comparable to the uncertainty (1σ) in the fit to the data.

We note from Eqs. (9)–(12) that the value of eQq also has a relatively large uncertainty. This is not unexpected because the quadrupole moment of the deuteron is so small. Although the matrix elements of eQq have a different F, M_F dependence within the same J level, there are also matrix elements of eQq that connect the two spin–doublets, thus causing the value of eQq to depend on the value of γ.

In addition to the uncertainty in γ, we must also take into account the deviation of the g_F values from those calculated assuming a pure $^2\Sigma$ state. The slight mixing of the $X\,^2\Pi$ state with the $A\,^2\Sigma^+$ state causes a correction of 0.4% to the g_F values. (See Appendix A of Ref. 6.) We estimate a 30% uncertainty in this correction. It should be noted that the accuracy of our data does not warrant retaining the nuclear Zeeman effect, $\mu_N g_I \mathbf{I}\cdot\mathbf{H}$, appearing in Eq. (4) because $\mu_N g_I$ is about 2000 times smaller than $g_e\mu_0$. For similar reasons, the rotational Zeeman effect, $\mu_N g_J \mathbf{J}\cdot\mathbf{H}$ appearing in Eq. (4) is also omitted. We present in Table III the variation of the excited-state parameters with a 2% variation in the assumed value of γ, and a 20% variation in the assumed g-factor correction. We see from Table III that all the parameters are rather insensitive to the uncertainty in the g-factor correction. However, the uncertainty in γ causes c and eQq to vary by as much as 25%, although b and μ are relatively unaffected. The quotation of values of c and eQq to 1σ (70% confidence level) must await a more accurate determination of the spin–doublet separation characterized by the parameter γ. However, we believe such a redetermination of γ will not change the values of b, c, eQq, and μ within the three standard deviations (99% confidence level) given in Eqs. (9)–(12). Nevertheless, we suspect that eQq, by far

TABLE III. Variation of the hyperfine parameters b, c, eQq with a 2% variation in the rho-doubling constant, γ, and a 20% variation in the correction to the g_F values.

γ (MHz)	g_F Correction	b (MHz)	c (MHz)	eQq (MHz)
3528	0.32	109.2±2.5	28±13	0.06±0.05
3528	0.40	109.4±2.6	28±13	0.06±0.06
3528	0.48	109.6±2.6	27±13	0.06±0.06
3600	0.32	110.2±2.6	23±14	0.08±0.05
3600	0.40	110.4±2.6	22±14	0.09±0.05
3600	0.48	110.6±2.6	22±14	0.09±0.06
3702	0.32	111.2±2.6	17±14	0.11±0.05
3702	0.40	111.4±2.6	17±14	0.11±0.05
3702	0.48	111.6±2.7	16±14	0.11±0.05

the smallest quantity, might be more inaccurate than suggested. Because we have made an exact fit to the data, small deviations from the model Hamiltonian might be expected to alter the apparent value of eQq.

IV. DISCUSSION

A. Excited-State Hyperfine Structure

The hyperfine parameters for the $v=0$, $N=1$, $J=3/2$ level of the OD $A\ {}^2\Sigma^+$ state obtained from the HFLC data yield a value of $b+c/5=115\pm6$ MHz. This is in excellent agreement with the value of $b+c/5=121\pm14$ MHz obtained previously from the optical radio-frequency double resonance measurements.[6] It is of interest to compare these two methods. By following the double resonance signal into the nonlinear Zeeman region, the search problem associated with the location of high-field crossovers is circumvented. On the other hand, the HFLC technique offers the advantage of avoiding the problem associated with coupling radio-frequency radiation into the molecular sample. Once preliminary hyperfine structure splittings can be obtained from optical double resonance studies, a more accurate determination of the hyperfine parameters can generally be carried out using the HFLC technique, which is free of such experimental difficulties as rf breakdown, rf pickup, and the need to construct stable sweeping rf oscillators.

Of greater interest than the quantity $b+c/5$ is the Fermi contact term, $b+c/3$, which is proportional to $\Psi^2(0)$, the unpaired electron spin density at the magnetically active nucleus. From HFLC data we obtain the value

$$b+c/3=118\pm7 \text{ MHz}, \qquad (13)$$

corresponding to an unpaired electron spin density at the deuteron of

$$\Psi^2(0)=0.173\pm0.011\ a_0^{-3}. \qquad (14)$$

Equation (13) shows that in this ${}^2\Sigma$ molecular state the Fermi contact term rather than the nuclear-spin electron-spin dipole–dipole term, c, controls the magnitude of the hyperfine splittings.

To obtain a simple interpretation of the size of the zero-field hyperfine splittings, let us use the molecular orbital picture for diatomic hydrides first proposed by Mulliken.[15] He suggested that the ground-state electron configuration of any state of a diatomic hydride can be accounted for by assuming that the electrons of the heavier atom are unchanged with respect to their quantum numbers except that they make well-defined projections λ on the internuclear axis while the electron from the H atom is promoted to the lowest-lying unoccupied orbital of σ-type symmetry. Thus, the electron configuration of the OH ground state becomes

$${}^2\Pi_i:\quad (1s\sigma)^2(2s\sigma)^2(2p\sigma)^2(2p\pi)^3 \qquad (15)$$

while the electron configuration of the lowest-lying excited state would be expected to be

$${}^2\Sigma^+:\quad (1s\sigma)^2(2s\sigma)^2(2p\sigma)(2p\pi)^4. \qquad (16)$$

In this model the A–X electronic band system corresponds to the excitation of an electron from the $2p\sigma$ orbital to the $2p\pi$ orbital, which causes the $2p\pi$ shell to become filled. The hfs splittings of the $A\ {}^2\Sigma^+$ states of OH or OD are, according to this model, a measure of the charge distribution of the unpaired electron in the $2p\sigma$ orbital.

The simplest approximation to the form of the $2p\sigma$ orbital is to write it as a linear combination of an atomic $1s$ orbital centered on hydrogen (deuterium) and an atomic $2p_z$ orbital centered on oxygen:

$$\Psi_{2p\sigma}=2^{-1/2}[(1s)_{\mathrm{H}}+(2p_z)_{\mathrm{O}}], \qquad (17)$$

where we have neglected the overlap between the two atomic orbitals. Using Eq. (17) we obtain an unpaired electron spin density of $\frac{1}{2}(\pi a_0^3)^{-1}=0.159\ a_0^{-3}$, corresponding to a Fermi contact term of 711 MHz at the proton or 109 MHz at the deuteron. The close agreement of this simple calculation with our experimental measurements suggests to us that most of the unpaired electron spin density arises from the $2p\sigma$ orbital.

Restricted Hartree–Fock SCF calculations have been performed for the ground and excited state configurations[16,17] given in Eqs. (15) and (16). The total energy for the ground state agrees within 0.36 a.u. (the correlation energy) with experiment, while SCF calculations on the A state reproduce the observed excitation energy to within 5%. A detailed analysis of the electron distribution and binding in the X and A states has been presented by Cade, Bader, and Pelletier.[18] From their tabulated "partial forces" we see that the strong bonding character of the $2s\sigma$ orbital explains the small (4%) increase in internuclear distance in the X to A excitation.

Table IV presents a comparison of our measured $A\,^2\Sigma^+$ state hyperfine parameters with those calculated from SCF wavefunctions by S. Green. While our experimentally determined value of c agrees with the calculation within our error, we find that the SCF value for $b+c/3$ is about 10% too low. We also note that eQq is very sensitive to internuclear separation and a valid comparison is difficult. The agreement with the SCF calculation of $b+c/3$ with our measurement confirms our belief that the $2p\sigma$ orbital is the overwhelming contributor to the Fermi contact term.

Recently, Rogers, Lee, Das, and Ikenberry[19] have applied linked-cluster many-body perturbation theory (LCMBPT) to calculate the hyperfine structure of small heteronuclear diatomic molecules using a variational Hartree–Fock molecular orbital basis set. At our request they have applied this method to the OH $A\,^2\Sigma^+$ state using their V^N potential. They find that $b+c/3=751$ MHz at proton, corresponding to a value of $b+c/3=115$ MHz at the deuteron. This is almost within one standard deviation of our value.

B. Excited-State Dipole Moment

The dipole moment of a molecular state is a sensitive measure of the total charge distribution within the state. For the ground state of OH the dipole moment has been measured by microwave spectroscopy using Stark modulation and by optical spectroscopy in which the Stark splittings are resolved. Powell and Lide[20] report the microwave value $\mu=1.660\pm0.010$ D for the $v=0$, $J=\frac{3}{2}$ level of the OH $X\,^2\Pi_{3/2}$ state while Phelps and Dalby[21] and Scarl and Dalby[22] report the optical values of $\mu=1.73_2\pm0.02$ and $\mu=1.72_1\pm0.02$ D, respectively, for the $v=0$, $J=\frac{1}{2}$ level of the OH $X\,^2\Pi_{1/2}$ state. The optical measurements are carried out in the cathode fall region of a discharge tube where electric fields up to 320 kV/cm are produced. The electric field is determined by photographing under high resolution the Stark splittings of the Balmer lines. By varying the electric field in the cathode fall region, Dalby and co-workers obtain the variation of the Stark-shifted line positions with field. From the linear variation of the line positions the ground state dipole moment is obtained.

The microwave and optical measurements disagree by more than their combined quoted uncertainties. Although we are in no position to discuss critically the source of error in the optical determination of μ, we find it difficult to fault the microwave measurement since this technique has proved to be so reliable. It is interesting to consider whether *ab initio* calculations can shed some light on these discrepant values of μ. Restricted Hartree–Fock SCF calculations by Cade and Huo[23] yield a value of $\mu=1.78$ D. However, configuration interaction calculations by Bender and Davidson[24] show that $\mu=1.633$ D. Moreover, Bender and Davidson have made a systematic study of their calculational procedure and they found the agreement of their calculated values of μ with experiment to be better than 3%. Thus, *ab initio* calculations strongly support the microwave determination of the X state dipole moment.

Table IV. Comparison of theoretical and experimental hyperfine constants in MHz. The theoretical calculations are carried out by Green[17] using restricted Hartree–Fock SCF wavefunctions at several values of the internuclear separation about r_e.

hfs Parameter	Calculated $r_e-0.05$ Å	r_e	$r_e+0.05$ Å	Observed (3σ) (this work)
$b+c/3$	105	107	108	118 ± 7
c	27	24	22	22 ± 14
eqQ	0.09	0.27	0.39	0.09 ± 0.05

In OH or OD, the $A\,^2\Sigma^+$ state differs from the ground state in that an electron in the $2p\sigma$ orbital in the X state is transferred to the $2p\pi$ orbital, centered primarily on the oxygen atom, in the A state. Since the polarity of the ground state dipole moment is O^-H^+, we expect the dipole moment of the A state to increase. However, because the $2p\sigma$ orbital is not strongly bonding, as witnessed by the small lengthening of the A state internuclear equilibrium distance, the increase in the magnitude of the A state dipole moment may not be dramatic.

From the HFLC data we find that $\mu=1.72\pm0.10$ D for the $v=0$ level of the OD A state. Previously, Scarl and Dalby determined the dipole moment of this level to be $\mu=2.15_9\pm0.07_6$ D from the second-order dependence of their measured Stark shifts. We see that there is substantial disagreement between the HFLC and optical values of the OD A state dipole moment.

Again, one might turn to the results of *ab initio* calculations to see whether they show a preference for one or the other of these discordant experimental determinations of the excited state dipole moment. Restricted Hartree–Fock SCF calculations of the A state dipole moment have been carried out by Cade[16] who finds $\mu=2.04$ D. Their calculations have been repeated by Green[17] with a larger basis set with a result that $\mu=1.96$ D. It might be anticipated from the behavior of the ground state dipole moment that the inclusion of configuration interaction (CI) would reduce the A state dipole moment from its Hartree–Fock SCF value. Moreover, the fact that the SCF calculation gives an unpaired electron spin density at the deuteron that is 10% low reinforces this belief. Preliminary CI calculations have been made by Mulder and Lester[25] who find a value of $\mu=1.9$ D. Most recently, after this study was completed, S. Green has performed CI calculations from which he concludes that $\mu=1.84\pm0.06$ D (see following paper). It would seem then that the trend of configuration interaction calculations is away from the restricted Hartree–Fock result towards our value.

ACKNOWLEDGMENTS

Our thanks go to T. H. Bergeman for his fringing field calculations and for his aid in the data analysis; to H. W. Cruse for suggesting the use of phosphoric acid for inhibiting radical recombination; to K. Schumann for constructing numerous versions of the Stark cell flow system; to R. C. Stern for lending us his high voltage power supply and digital voltmeter; and to P. E. Cade, T. P. Das, S. Green, W. Huo, and W. Lester for providing us with their unpublished calculations on OH and OD.

One of us (E. M. W.) extends his warm appreciation to S. G. Kukolich for the use of his facilities while carrying out the studies of the phosphoric acid coatings on the microwave Stark splittings of HOD.

This work was supported by the National Science Foundation.

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