A Molecular Beam Electric Resonance Study of the Hyperfine Λ Doubling Spectrum of OH, OD, SH, and SD

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The molecular beam electric resonance method was employed to obtain a complete set of hyperfine Λ doubling transitions of the free radicals OH, OD, SH, and SD. The observed spectra could be explained very well by the degenerate perturbation theory adapted to the $^2\Pi$ state. The experimental results include fine and hyperfine coupling constants, the electric dipole moments could be explained very well by the degenerate perturbation theory adapted to the $^2\Pi$ state. The constants agree well with *ab initio* calculations.

On a utilisé la méthode de résonance électrique d'un faisceau moléculaire afin d'obtenir un ensemble complet de transitions hyperfines à dédoublement Λ pour les radicaux libres OH, OD, SH et SD. Les spectres observés pouvaient très bien être expliqués par la théorie des perturbations pour un état dégénéré appliqué à l'état $^2\Pi$. Les résultats expérimentaux incluent les constantes du couplage de structure fine et de structure hyperfine, ainsi que le moment de dipôle électrique pour les quatre molécules, de même que certaines propriétés magnétiques de SH. Les constantes de couplage de structure hyperfine déduites des mesures sont en bon accord avec les résultats de calculs théoriques.

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1. Introduction

The structure and spectra of free radicals, defined here as molecules with one or more unpaired electrons, have been the subject of a large number of theoretical studies and of experimental investigations using practically all available spectroscopic techniques. In contrast to the vast majority of stable molecules, the ground electronic state of many free radicals is a state with a nonzero electronic orbital and/or spin angular momentum. Because of these angular momenta, the energy levels of the radicals show fine structure and the effects of the coupling between rotation and electronic motion, such as Λ doubling in a $^2\Pi$ state and ρ doubling in a $^2\Sigma$ state. The experimental investigations of the spectra of free radicals range from classical vacuum ultraviolet (UV) spectroscopy to gas phase electron paramagnetic resonance (EPR) and microwave spectroscopy. The present communication describes a study of the OH, OD, SH, and SD radicals by the molecular beam electric resonance (MBER) technique. These radicals all have the $^2\Pi_{3/2}$ ground electronic state.

The most extensive measurements and analyses of the UV band spectra of OH were performed by Dieke and Crosswhite (1962). The UV spectrum of OD was measured recently by

Clyne *et al.* (1973). The first measurements of the microwave Λ doubling spectra of OH and OD radicals were reported by Dousmanis *et al.* (1955). The observed spectra originate from direct transitions between the Λ doublet levels of rotational states in the $^2\Pi_{1/2}$ and the $^2\Pi_{3/2}$ electronic levels. The observed spectra are in the frequency range of 7.7 to 37 GHz. The experimental accuracy of the observed frequencies of Dousmanis *et al.* (1955) varied between 0.05 and 0.5 MHz. An extension (to the order of $(E_{rot}/E_{el})^2$ or $(E_{finc}/E_{el})^2$) of Van Vleck's (1929) theory of molecular energies in the $^2\Pi$ states was employed to explain the observed spectra. Subsequent investigations of OH by Poynter and Beaudet (1968) on the $^2\Pi_{3/2}, J = 7/2, 9/2$, and 11/2 states, by Radford (1968) on the $^2\Pi_{1/2}, J = 1/2$ and $^2\Pi_{3/2}, J = 5/2$ states, and by Ball *et al.* (1970, 1971) on the $^2\Pi_{1/2}, J = 3/2$ and 5/2 states considerably improved the accuracy of the zero field transitions. Recently, ter Meulen and Dymanus (1972) used a beam–maser spectrometer to obtain very accurate hyperfine Λ doubling transition frequencies of the $^2\Pi_{3/2}, J = 3/2$ state of OH. The magnetic properties of OH in the $^2\Pi_{1/2}, J = 3/2$ and 5/2 states and in the $^2\Pi_{3/2}, J = 3/2, 5/2$, and 7/2 states were investigated by Radford (1961, 1962) using the

gas phase EPR technique. From the analysis of the EPR spectra Radford deduced the g_J values, the values for the hyperfine constants of OH, and the g_J factor for OD in the $^2\Pi_{3/2}$, $J = 3/2$ state. Accurate hyperfine Λ doubling transition frequencies of OD in the $^2\Pi_{1/2}$, $J = 1/2$ state and in the $^2\Pi_{3/2}$, $J = 3/2$, $5/2$, and $7/2$ states were obtained by Meerts and Dymanus (1973a) from an MBER investigation. This investigation also yielded accurate values of the electric dipole moments of both radicals (Meerts and Dymanus 1973b).

The free radicals SH and SD have not been as extensively investigated as OH and OD. Ramsay (1952) obtained and analyzed the $A^2\Sigma \leftarrow X^2\Pi$ band spectra of SH and SD and determined the rotational and vibrational constants of both radicals. The EPR techniques were used on SH by Radford and Linzer (1963) for the $^2\Pi_{3/2}$, $J = 3/2$ state, by Tanimoto and Uehara (1973) for the $^2\Pi_{3/2}$, $J = 3/2$ and $5/2$ states, and by Brown and Thistlethwaite (1972) for the $^2\Pi_{3/2}$, $J = 5/2$ state. However, neither for SH nor for SD were hyperfine Λ doubling transitions observed. Those of SH have recently been obtained by Meerts and Dymanus (1974) for the $^2\Pi_{3/2}$, $J = 3/2$, $5/2$, $7/2$, $9/2$, and $11/2$ states using the MBER technique.

In the present investigation we used the molecular beam electric resonance technique on OH, OD, SH, and SD in order to obtain a set, as complete as possible, of accurate experimental data on the $\Delta J = 0$ hyperfine Λ doubling transitions in the lower rotational states of the ground vibrational state and the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ electronic states of the four radicals. This was a logical step in a program on the hyperfine structure of open shell molecules using the MBER method, which was started with a study of the only stable diatomic radical, NO (Meerts and Dymanus 1972). The MBER technique furnished high resolution hyperfine Λ doubling spectra of the investigated radicals. The project was undertaken to investigate the feasibility of using the MBER technique on short living radicals like OH and SH and to provide accurate hyperfine Λ doubling spectra for a larger number of open shell molecules. The experimental spectra could be used as a test of the current theories on the fine and hyperfine interactions in a molecule in a $^2\Pi$ state.

A degenerate perturbation theory developed previously for the interpretation of the spectra of NO (Meerts and Dymanus 1972) was employed to explain the hyperfine Λ doubling spectra of OH, OD, SH, and SD. It turned out that the theory, extended to third order in fine and hyperfine structure, was well capable of explaining the observed spectra for most transitions within the experimental accuracy. Only for the interpretation of the spectrum of OH do we suspect that higher order hyperfine structure contributions should be included to improve the agreement between the experimental and the calculated spectrum.

From the analysis of the spectra, the molecular properties, related specifically either to the properties of the unpaired π electron or to the charge distribution of all the electrons in the molecules, could be determined. *Ab initio* molecular orbital calculations are available only for the properties of OH and SH directly related to the π electron distribution. It was found that the *ab initio* results of Kayama (1963) for OH and of Kotake et al. (1971) and Bendazzoli et al. (1972) for OH and SH are in reasonably good agreement with the present experimental results.

The observed laboratory transition frequencies may be of help in the identification of observed spectra from interstellar radio sources and increase the chance of detecting the presence of the OD, the SH, or maybe even the SD radicals in space. Especially the chance of detecting the SH radical has been considerably improved by the reliable hyperfine Λ doubling transition frequencies obtained in the present investigation. A search for the emission lines of the SH molecule has already been undertaken by Meeks et al. (1969) and by Heiles and Turner (1971). The attempts were unsuccessful, partly because of the errors in the Λ doublet transition frequencies available at that time.

The values of the electric dipole moments of the four radicals have been obtained from the observed Stark shifts of some transitions. Significant isotopic effects were found. Unfortunately, it is not possible to deduce reliable information about vibrational and centrifugal effects on the electric dipole moments from the isotopic dependence alone. Therefore, measurements in excited vibrational states are needed.

The SH radical in the $^2\Pi_{1/2}$, $J = 1/2$ state was also investigated in a magnetic field. An

analysis of the spectrum is given and the g_J factors of this state are reported. A large difference between the g_J values for the upper and the lower Λ doublet levels is found. This effect can be explained by the breaking of the symmetry of the electronic charge distribution around the molecular axis by the rotation of the molecule.

2. Experimental Techniques

The experiments were performed using a molecular beam electric resonance spectrometer described in detail elsewhere (de Leeuw 1971; de Leeuw and Dymanus 1973). Only the features pertinent to the present investigation are discussed here. In the experiments we used two types of C fields: (1) a 30 cm long field for high precision Stark measurements at low frequencies and (2) a short (about 8 cm) transition field for measurements at frequencies above about 2 GHz. The latter field, constructed of two flat copper plates, was unsuitable for Stark measurements because of poor DC field homogeneity. Its small dimensions permitted good shielding of the earth's magnetic field for measurements of the zero field transition frequencies. We succeeded in shielding the earth's magnetic field to about 5 mG, which was enough even for accurate measurements on the $\Delta F = \pm 1$ transitions (Meerts and Dymanus 1972). The long field consisted of two optically flat quartz plates coated with a thin gold layer (de Leeuw 1971). The microwave power for inducing the transitions was obtained from a Hewlett-Packard 8660B synthesizer for frequencies below 1 GHz. Three Varian backward wave oscillators were used for the generation of frequencies in the GHz range. These oscillators were frequency stabilized by phase locking techniques.

The beam was detected by an electron bombardment ionizer designed by Stolte (1972), followed by an electric quadrupole mass selector. The overall efficiency of the detection system was of the order of 2×10^{-3}.

The beams of short lived free radicals were produced in a reaction type source schematically shown in Fig. 1. The OH radicals were formed in the reaction between atomic hydrogen and NO_2 by (Del Greco and Kaufman 1962)

[1] $H + NO_2 \rightarrow OH + NO$
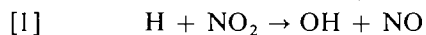
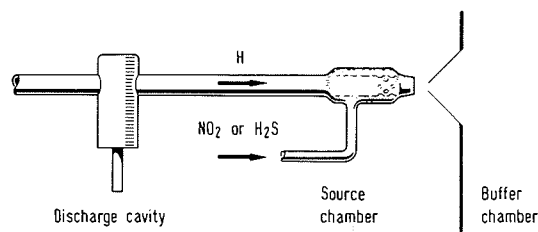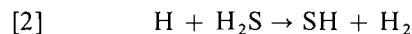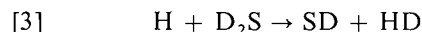For the production of the OD radicals the

FIG. 1.   Schematic diagram of the reaction source.

hydrogen atoms were replaced by deuterium atoms. The SH and SD radicals were produced in the reaction of atomic hydrogen with H_2S and D_2S respectively by

[2] $H + H_2S \rightarrow SH + H_2$

for SH and

[3] $H + D_2S \rightarrow SD + HD$

for SD. The atomic hydrogen was obtained from a microwave discharge at 2.45 GHz in water at the entrance of the tube. The power fed into the discharge was usually about 150 W. The deuterium atoms were obtained from a microwave discharge in D_2O. For D_2S we used a 98% enriched sample. Because the D_2S sample had to be recovered, we also replaced H_2O by D_2O in the production of the SD radicals to reduce contamination of the D_2S sample by H_2S. A reaction of atomic deuterium and H_2S resulted in only a small number of SD radicals and almost the same number of SH radicals as obtained in the reaction [2]. This indicates that the hydrogen atoms probably strip off one of the hydrogen atoms from the H_2S molecule forming H_2 and SH as proposed by McDonald (1963).

To handle the large gas flows, the source chamber was pumped by a mechanical pump system with a capacity of 500 m^3/h. The source chamber was separated from the resonance part of the machine by two buffer chambers, pumped by diffusion pumps. The beam was formed by a conical diaphragm 2 mm in diameter between the source chamber and the first buffer chamber. The distance between this diaphragm and the end of the reaction tube could be varied during the experiment but was usually 5 to 20 mm.

The observed full linewidth of one half of the peak intensity varied between 3 and 25 kHz, depending on the type of C field and on the

observed transitions. The linewidths for the $\Delta F = 0$ transitions were determined essentially by the transit time of the molecules through the resonance region (C field). However, the linewidths for the $\Delta F = \pm 1$ transitions were largely determined by the residual earth's magnetic field (Meerts and Dymanus 1972). The observed signal to noise ratio at $RC = 5$ s for the transitions of OH, OD, SH, and SD was typically 100, 40, 20, and 6 respectively.

3. Theory

The Hamiltonian for the interpretation of high resolution spectra of the open shell diatomic molecules can be written formally as

[4] $$H = H_0 + H_F + H_{hf} + H_{ST}$$

where H_0 is the nonrelativistic Hamiltonian for electronic energies in the Born–Oppenheimer approximation; H_F contains the spin–orbit and the rotational and gyroscopic terms which give rise to the Λ splitting and the fine structure; H_{hf} describes the hyperfine contributions; and the last term $H_{ST} = -\mathbf{\mu} \cdot \mathbf{E}$ gives the interaction of the electric dipole moment, $\mathbf{\mu}$, of the molecule with an external electric field, $\mathbf{E}$ (Stark effect). For H_F we used the expression of Van Vleck (1929)

[5] $H_F = B(J^2 - L_z{}^2 + S^2) + AL_zS_z - 2BJ \cdot S + (B + \tfrac{1}{2}A)(L_+S_- + L_-S_+) - B(J_+L_- + J_-L_+)$

Here A is the spin–orbit constant; B is the rotational constant; L and S represent the orbital and spin angular momentum of the electrons respectively; J stands for the total rotational angular momentum including the rotation of the nuclear frame, but excluding the nuclear spins. The hyperfine Hamiltonian H_{hf} expressed in spherical tensor operators is (Freed 1966):

[6] $H_{hf} = \zeta \sum_q (-1)^q T_q{}^{(1)}(I) T_{-q}{}^{(1)}(L_1)/r_{11}{}^3$

$$+ \zeta \sqrt{30} \sum_{q,\mu} \begin{pmatrix} 1 & 1 & 2 \\ \mu & q-\mu & -q \end{pmatrix} T_\mu{}^{(1)}(S_1) T_{q-\mu}{}^{(1)}(I) C_{-q}{}^{(2)}(\theta_{11}, \phi_{11})/r_{11}{}^3$$

$$+ \frac{8}{3}\pi\zeta \sum_q (-1)^q T_q{}^{(1)}(I) T_{-q}{}^{(1)}(S_1)\delta(r_{11}) + \sum_q (-1)^q T_q{}^{(2)}(Q) T_{-q}{}^{(2)}(V_1) + C_{RS}I \cdot J$$

Here $\zeta = gg_I\mu_0\mu_N$, where g, g_I, μ_0, and μ_N are the g value for the free electron, the nuclear g factor, the Bohr magneton, and nuclear magneton respectively; r_{11} is the distance between electron 1 and the nucleus I and $T^{(1)}(M)$ is the spherical tensor of rank 1 constructed from the components of an angular momentum $M = (I, L_1, S_1)$, while:

[7] $$T^{(2)}(Q) = \sum_{\text{protons } p} e_p r_p{}^2 C^{(2)}(\theta_p, \phi_p)$$

[8] $$T^{(2)}(V_1) = -eC^{(2)}(\theta_{11}, \phi_{11})/r_{11}{}^3 + Z_K C^{(2)}(\theta_{KI}, \phi_{KI})/R_{KI}{}^3$$

are spherical tensor operators of rank two describing the nuclear quadrupole moment (tensor) and the gradient of the electric field at the position of the nucleus I in the molecule. In expressions [7] and [8], Z_K is the atomic number of the second nucleus K ($K \neq I$) and R_{KI} is the distance between the two nuclei, $\theta_{11}(\theta_{KI})$ is the angle between $r_{11}(R_{KI})$ and the bond axis (z axis), and $\phi_{11}(\phi_{KI})$ is the azimuthal angle. The hyperfine interactions of [6] are written in one electron notation as used in the reduced density matrix formulation (McWeeny 1960, 1965).

The first contribution to the hyperfine Hamiltonian of [6] represents the interaction between the magnetic moment, μ_I, associated with nuclear spin, I, and the orbital angular momentum, L, of the electrons. The second term describes the interaction of μ_1 with the spin angular momentum, S, of the electrons with zero density at the nucleus I. The third term is the Fermi contact term. The fourth contribution to H_{hf} is due to the nuclear electric quadrupole interaction. The last term represents the interaction between μ_I and the orbital motion of the nuclei due to the rotation of the molecule (spin–rotation interaction); C_{RS} is the coupling constant of this interaction.

With the Hamiltonian of [5] and [6] the spectrum has been calculated using the degenerate perturbation theory described by Freed (1966), extended and adapted to a $^2\Pi$ state by Meerts and

Dymanus (1972). Application of this theory to the Hamiltonians H_F and H_{hf} (zero external field) involves the solution of a 4×4 secular equation. However, these Hamiltonians are invariant under reflections of the coordinates and spins of all the particles in a plane containing the nuclei. Consequently, if wave functions are used with the proper Kronig symmetry (Van Vleck 1929) with respect to these reflections, the secular determinant factors into two 2×2 determinants.

The coupling scheme for the electronic and rotational part of the wave function adopted in the calculations is the Hund's case (a). Wave functions, $|^2\Pi_{|\Omega|}{}^{\pm}, J\rangle$, including nuclear rotation are in this coupling scheme defined as:

[9]
$$|^2\Pi_{|\Omega|}{}^{\pm}, J\rangle = (1/\sqrt{2})[|J\Lambda\Sigma\Omega\rangle \pm |J - \Lambda - \Sigma - \Omega\rangle]$$

with $\Omega = \Lambda + \Sigma$; Λ, Σ, and Ω are the projections on the molecular axis of L, S, and J respectively; $|\Omega|$ can take the values of $1/2$ and $3/2$. The wave functions $|J\Lambda\Sigma\Omega\rangle$ are given by Freed (1966). The total wave function, $|^2\Pi_{|\Omega|}{}^{\pm} JIFM_F\rangle$, of the molecule including the nuclear part is obtained as a product of the electronic–rotational wave function, $|^2\Pi_{|\Omega|}{}^{\pm}, J\rangle$, and of the nuclear spin wave function, $|IM_I\rangle$, corresponding to the coupling scheme: $F = J + I$, where F is the total angular momentum of the molecule. These wave functions are used as a basis for the degenerate perturbation calculation of the energy matrix.

All molecules investigated can be described by a coupling which is intermediate between the Hund's case (a) and case (b). The proper wave functions are obtained automatically by solving the secular problem. The contributions of the fine and hyperfine interactions to the energy are taken into account up to third order. In the final expressions for the state energies we separate terms with different dependence on the rotational quantum number J, as only these terms can be determined from the experimental data. The matrix elements of H_F and H_{hf} in terms of J and a number of coupling constants were obtained using the degenerate perturbation theory developed in a previous paper (Meerts and Dymanus 1972). The results are

[10] $\langle^2\Pi_{\frac{1}{2}}{}^{\pm}|H_F + H_{hf}|^2\Pi_{\frac{1}{2}}{}^{\pm}\rangle = -\frac{1}{2}\alpha_1 + \alpha_2(J + \frac{1}{2})^2 + \alpha_{10}(J + \frac{1}{2})^4 \pm \alpha_3(2J + 1) \pm \alpha_4(J + \frac{1}{2})^3$

$$\pm \alpha_5(J + \tfrac{1}{2})z^2 + y\{(\chi_1 + z^2\chi_5) \pm (J + \tfrac{1}{2})(\chi_2 + z^2\chi_6)\} + u\{(\tfrac{3}{4} - x)(\zeta_1 + \zeta_4 J(J + 1))$$

$$\pm \zeta_5 z^2(J + \tfrac{1}{2})\}$$

[11] $\langle^2\Pi_{\frac{3}{2}}{}^{\pm}|H_F + H_{hf}|^2\Pi_{\frac{3}{2}}{}^{\pm}\rangle = \frac{1}{2}A_\Pi + B_\Pi(J(J + 1) - (7/4)) + \alpha_9 z^2 + \alpha_{10}(J + \frac{1}{2})^2 z^2$

$$\pm \alpha_8(J + \tfrac{1}{2})z^2 + y\{\chi_3 + z^2\chi_7\} + u\{((27/4) - x)(\zeta_2 + \zeta_4 J(J + 1)) + (\zeta_7 \pm \zeta_5(J + \tfrac{1}{2}))z^2\}$$

[12] $\langle^2\Pi_{\frac{1}{2}}{}^{\pm}|H_F + H_{hf}|^2\Pi_{\frac{3}{2}}{}^{\pm}\rangle = \alpha_6 z + \alpha_{11}z(J + \frac{1}{2})^2 \pm \alpha_7 z(J + \frac{1}{2}) \pm \alpha_8 z(J + \frac{1}{2})^3$

$$+ zy\{(\chi_4 + z^2\chi_8) \pm \chi_9(J + \tfrac{1}{2})\} + zu\{\pm(\zeta_3 + \zeta_5 J(J + 1))(J + \tfrac{1}{2}) + (\zeta_6 - \zeta_4 J(J + 1))\}$$

Herein $z = \sqrt{(J - \frac{1}{2})(J + \frac{3}{2})}$, $x = J(J + 1)$, $y = (F(F + 1) - J(J + 1) - I(I + 1))/(2J(J + 1))$, $u = (\frac{3}{4}C(C - 1) - J(J + 1)I(I + 1))/2I(2I - 1)J(J + 1)(2J - 1)(2J + 3)$, and $C = I(I + 1) + J(J + 1) - F(F + 1)$. The upper signs in [10], [11], and [12] are appropriate for the states with $(-1)^{J - (1/2)}$ Kronig symmetry, the lower signs for states with $(-1)^{J + (1/2)}$ Kronig symmetry.

The coupling constants A_Π, B_Π, and α_i describe the contributions to the fine structure and the Λ splitting in the various orders of approximation. In the first order, α_1 can be approximated by A_Π, the spin orbit coupling constant of a Π state; α_2 and α_6 can be approximated by B_Π, the rotational constant of a Π state. In the second and third order, all α_i's are essentially different but to a good approximation $\alpha_1 \simeq A_\Pi, \alpha_2 \simeq B_\Pi + \alpha_7, \alpha_6 \simeq B_\Pi + \alpha_3, \alpha_9 \simeq \alpha_7$, and $\alpha_8 \simeq \alpha_5(B_\Pi - B_\Sigma)/B_\Pi$ where B_Σ is the rotational constant of a Σ state. The coupling constants $\alpha_4, \alpha_5, \alpha_8, \alpha_9, \alpha_{10}$, and α_{11} contain only third order effects, but only α_4, α_5, and α_8 contribute directly to the Λ splitting. The coupling constants α_{10} and α_{11} are set to zero because they do not contribute directly to the Λ splitting and their effects are too small to be detected. The coupling constants χ_i are associated with

the magnetic hyperfine interactions and ζ_i's with the electric quadrupole interaction. The coupling constants χ_5, χ_6, χ_7, χ_8, χ_9, and ζ_4, ζ_5, ζ_6, ζ_7 contain only third order effects, while the others contain second as well as third order contributions. From the observed spectra it was found that the contributions to the energy of χ_8, ζ_4, ζ_6, and ζ_7 were too small to be determined and the constants were taken equal to zero.

The coupling constants α_i, χ_i, and ζ_i are rather complex expressions containing first and second as well as third order contributions. They are tabulated by Meerts and Dymanus (1972). A comparison of the present hyperfine coupling constants χ_i and ζ_i with those of the conventional theory (Dousmanis et al. 1955; Radford 1961, 1962; Lin and Mizushima 1955) can only be made if the third order effects are neglected. In this approximation the relations between the present and the conventional hyperfine structure coupling constants are:

[13, 14] $\chi_1 = \frac{1}{2}(a - \frac{1}{2}(b + c))$; $\chi_2 = \frac{1}{2}d$

[15, 16] $\chi_3 = \frac{3}{2}(a + \frac{1}{2}(b + c))$; $\chi_4 = -\frac{1}{2}b$

[17, 18] $\zeta_1 = \zeta_2 = eQq_1$; $\zeta_3 = \frac{1}{2}eQq_2$

If third order effects are neglected, the relations between the present Λ splitting parameters and those used by other investigators are:

[19, 20] $\alpha_3 = -\frac{1}{2}\alpha = \frac{1}{4}p + \frac{1}{2}q$; $\alpha_7 = -\beta = \frac{1}{2}q$

α, β were used by Dousmanis et al. (1955) and p, q were introduced by Mulliken and Christy (1931).

The contributions to the energy of the last term of the Hamiltonian [3], the Stark effect, is extensively discussed by Meerts and Dymanus (1973b) and the formulas are not reproduced here.

The observed spectra of OH, OD, SH, and SD are analyzed using the theory outlined above. However, in this theory developed primarily for NO, the centrifugal distortion effects are neglected. The neglect was fully justified for NO but such is not the case for the light molecules of the present investigation. A simple replacement of B_Π by $B_\Pi - D_\Pi J(J + 1)$, with D_Π the centrifugal distortion constant, in the above equations is not correct. Problems arise because in the present calculations the values of B_Π and D_Π, accepted for all four molecules and for SH and SD also the value of A_Π are those obtained from analyses of rovibronic or electronic spectra. As these analyses are based on an effective Hamiltonian which is slightly different from the present one, the spectroscopic constants derived are different. In order to obtain compatible constants A_Π, B_Π, and D_Π for the calculations of the state energies, we have to use a Hamiltonian compatible with the one used in the analyses of the electronic or rovibronic spectra.

The electronic spectra of SH and SD were analyzed by Ramsay (1952) using the expressions given by Almy and Horsfall (1937). These expressions are based on the Hund's case (a) representation, which we also used. Therefore, for the interpretation of the spectra of SH and SD, our expressions [10], [11], and [12] are compatible (in this case identical) with those of Almy and Horsfall. The centrifugal distortion effects are taken care of simply by adding the contributions of D_Π in [10], [11], and [12] with the value of D_Π determined by Ramsay (1952). The rotational constants B_Π and D_Π of OH and OD were obtained by Dieke and Crosswhite (1962) from a fit of the ultraviolet band spectrum to the theoretical spectrum calculated using a Hund's case (b) representation. In order to take correctly into account the contributions of B_Π and D_Π for OH and OD, we have to use the Dieke and Crosswhite (1962) expression for the rotational energy, or what comes to the same, to transform the Hund's case (b) rotational Hamiltonian used by Dieke and Crosswhite to the case (a) representation. The rotational energy of a $^2\Pi$ molecule in the Hund's case (b) representation is given by $B(K(K + 1) - 1)$, where $B = B_\Pi(1 - D_\Pi/B_\Pi K(K + 1))$ and K can take the values $J + \frac{1}{2}$ and $J - \frac{1}{2}$. In this representation the 2×2 rotational energy matrix can be written in the form

[21] $(H_R)_b = \begin{bmatrix} B_1((J - \frac{1}{2})(J + \frac{1}{2}) - 1) & 0 \\ 0 & B_2((J + \frac{3}{2})(J + \frac{1}{2}) - 1) \end{bmatrix}$

where $B_1 = B_\Pi - D_\Pi(J - \frac{1}{2})(J + \frac{1}{2})$ and $B_2 = B_\Pi - D_\Pi(J + \frac{1}{2})(J + \frac{3}{2})$. This matrix can be transformed to the Hund's case (a) representation by the transformation:

[22]
$$(H_R)_a = R^+(H_R)_b R$$

where

[23]
$$R = \frac{1}{\sqrt{2J + 1}}\begin{bmatrix} -\sqrt{J - \frac{1}{2}} & \sqrt{J + \frac{3}{2}} \\ \sqrt{J + \frac{3}{2}} & \sqrt{J - \frac{1}{2}} \end{bmatrix}$$

The matrix $(H_R)_a$ contains the contributions of B_Π which are the same as [10], [11], and [12].

All molecules discussed in this paper are properly described in a Hund's case intermediate between (a) and (b). The ratio between the spin–orbit energy and the rotational energy (λ) is a measure for the mixing of the $^2\Pi_{1/2}$ and the $^2\Pi_{3/2}$ levels. The smaller the value of $|\lambda|$ is, the stronger is the effect of the mixing. This mixing also depends on D_Π. As pointed out by Meerts and Dymanus (1973b), the determination of molecular constants which are sensitive to this mixing, e.g., α_4, α_5, χ_4, χ_9, ζ_3, and the electric dipole moment μ will be affected by the value of B_Π, D_Π, and A_Π. However, only for OH $(\lambda = -7.5)$, these mixing effects do play a role in the determination of the molecular constants and the values as obtained from the least squares fit of the spectra depend slightly on the choice of B_Π and D_Π. For OD $(\lambda = -14.0)$, SH $(\lambda = -39.8)$, and SD $(\lambda = -76.9)$, the effects of the mixing of the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ levels on the determination of the molecular constants can be neglected.

4. Experimental Results and Analysis of the Spectra

All the observed transitions involved the electric dipole transitions between hyperfine sublevels in zero magnetic field from a + Kronig symmetry level to a − Kronig symmetry level within one J state of the $^2\Pi_{1/2}$ or the $^2\Pi_{3/2}$ electronic level. The molecular and hyperfine constants were obtained from the fit of the observed spectra to the spectra calculated using the theory outlined in the previous section. The values of the molecular constants taken from other sources and used in the analysis of the spectra are reproduced in Table 5. The physical constants were taken from Taylor *et al.* (1969). The measurements and results are reported below for the individual molecules.

4.1. The Spectrum of the OH Radical

The first measurements of the Λ doubling transitions of OH were performed by Dousmanis *et al.* (1955) on the $^2\Pi_{1/2}$, $J = 3/2$ and $5/2$ states and on the $^2\Pi_{3/2}$, $J = 7/2$, $9/2$, and $11/2$ states. The spectra of these transitions have been reinvestigated using improved experimental techniques by several investigators (Poynter and Beaudet 1968; Radford 1968; Ball *et al.* 1970, 1971; ter Meulen and Dymanus 1972) (see also Table 1). We investigated the $J = 5/2$ state of the $^2\Pi_{3/2}$ level and the $J = 5/2$, $7/2$, and $9/2$ states of the $^2\Pi_{1/2}$ level in order to obtain a complete set of the zero field transition frequencies of the lower J states of the $^2\Pi_{1/2}$ and the $^2\Pi_{3/2}$ levels. The transition frequencies of the $^2\Pi_{1/2}$, $J = 9/2$ state have already been reported in a previous communication (Meerts and Dymanus 1973b). A list of all the available data and the references on the hyperfine Λ doubling transitions of OH is given in Table 1. A few remarks should be made about this table. The $\Delta F = 0$ transitions of the $J = 9/2$, $^2\Pi_{3/2}$ state have also been measured by Poynter and Beaudet (1968), but only the much more accurate frequencies obtained by ter Meulen (1970) with a beam maser are reproduced in Table 1. We also remeasured the transitions of the $^2\Pi_{3/2}$, $J = 5/2$ state and found that the $\Delta F = 0$ transitions slightly deviate from the results of Radford (1968). The transitions observed in the $J = 5/2$ state of the $^2\Pi_{1/2}$ level are in agreement with those of Ball *et al.* (1971).

The transition frequencies of Table 1 were used in a least squares fit to the calculated spectrum. The fine structure contributions are determined by B_Π, D_Π, A_Π, α_3, α_7, α_4, and α_5. The first two constants were taken from the results of Dieke and Crosswhite (1962) and the remaining five were varied in the fit. For the hyperfine contributions we used essentially the same approach as in the analysis of the spectra of NO (Meerts and Dymanus 1972) but with a modification for the hyperfine

TABLE 1. Observed and calculated hyperfine Λ doubling transitions of OH.
PI stands for present investigations

J	Ω	F_+	F_- [a]	Observed frequency (MHz)	Reference	Observed minus calculated frequency (kHz)
1/2	1/2	1	1	4 750.656(3)	[b]	27.5
		0	1	4 660.242(3)	[b]	24.7
		1	0	4 765.562(3)	[b]	19.3
3/2	1/2	1	1	7 761.747(5)	[c]	−7.5
		2	2	7 820.125(5)	[c]	0.3
		2	1	7 749.909(5)	[c]	−9.2
		1	2	7 831.962(5)	[c]	1.1
5/2	1/2	2	2	8 135.870(5)	PI[d]	0.8
		3	3	8 189.587(5)	PI[d]	4.6
		2	3	8 118.051(5)	PI[d]	−4.5
		3	2	8 207.402(5)	PI[d]	5.8
7/2	1/2	3	3	5 473.045(5)	PI	−4.3
		4	4	5 523.438(5)	PI	−12.6
		4	3	5 449.436(5)	PI	−12.8
		3	4	5 547.042(5)	PI	−9.1
9/2	1/2	4	4	164.7960(10)	PI[e]	−4.1
		5	5	117.1495(10)	PI[e]	−5.6
		4	5	192.9957(10)	PI[e]	−11.3
		5	4	88.9504(10)	PI[e]	2.1
3/2	3/2	1	1	1 665.40184(20)	[f]	26.0
		2	2	1 667.35903(20)	[f]	27.4
		2	1	1 612.23101(20)	[f]	28.0
		1	2	1 720.52998(20)	[f]	25.4
5/2	3/2	2	2	6 030.747(5)	PI	−20.2
		3	3	6 035.092(5)	PI	−18.2
		2	3	6 016.746(5)	PI[b]	−25.7
		3	2	6 049.084(8)	[b]	−21.7
7/2	3/2	3	3	13 434.62(1)	[g]	−65
		4	4	13 441.36(1)	[g]	−100
9/2	3/2	4	4	23 817.6153(20)	[h]	6.3
		5	5	23 826.6211(30)	[h]	5.5
		4	5	23 838.46(1)	[g]	−480
		5	4	23 805.13(1)	[g]	−150
11/2	3/2	5	5	36 983.47(3)	[g]	−940
		6	6	36 994.43(5)	[g]	−910

[a]The subscript + (−) refers to the even (odd) Kronig symmetry.
[b]Radford (1968).
[c]Ball et al. (1970).
[d]Also reported by Ball et al. (1971).
[e]Reported by Meerts and Dymanus (1973b).
[f]Ter Meulen and Dymanus (1972).
[g]Poynter and Beaudet (1968).
[h]Ter Meulen (1970).

constants χ_4, χ_5, and χ_7. As shown by Meerts and Dymanus (1972), these constants are related:

[24, 25]
$$\chi_5{}' = \chi_5 - \alpha\chi_4; \quad \chi_7{}' = \chi_7 + \alpha\chi_4$$

In a molecule, which can well be described by the Hund's case (a) approximation, α depends weakly on J. However, the OH radical belongs to the class intermediate between Hund's case (a) and (b). Because of the very strong coupling between the $^2\Pi_{1/2}$ and the $^2\Pi_{3/2}$ level (small absolute value of A_Π/B_Π), α varies by about 10% for the investigated J states. Therefore, χ_4, χ_5, and χ_7 can, in principle, be determined independently. Unfortunately the correlation between these three constants was still too large to calculate all of them from the observed spectra. We decided to choose for a variation of χ_4 and of $\chi_5 + \chi_7$. The other hyperfine constants varied in the least squares fit were χ_1, χ_2, χ_3, χ_6, and χ_9. The molecular constants of OH obtained in this way are given in

TABLE 2. Observed and calculated hyperfine Λ doubling transitions of OD as obtained in the present experiments

J	Ω	F_+ [a]	F_-	Observed frequency (MHz)	Observed minus calculated frequency (kHz)
3/2	1/2	1/2	1/2	5887.741(5)	−0.3
		3/2	3/2	5894.680(5)	0.4
		5/2	5/2	. 5906.215(5)	1.8
		3/2	1/2	5887.282(5)	−2.1
		1/2	3/2	5895.135(5)	−1.8
		5/2	3/2	5894.179(5)	−1.5
		3/2	5/2	5906.712(5)	−0.3
5/2	1/2	3/2	3/2	8110.717(5)	2.8
		5/2	5/2	8118.013(5)	7.5
		7/2	7/2	8128.181(5)	7.0
		3/2	5/2	8109.994(5)	3.8
		5/2	3/2	8118.733(5)	3.5
		5/2	7/2	8117.228(5)	5.3
		7/2	5/2	8128.961(5)	4.2
9/2	3/2	7/2	7/2	5304.015(5)	−4.1
		9/2	9/2	5304.600(5)	−3.7
		11/2	11/2	5305.372(5)	−1.0
		7/2	9/2	5304.681(5)	3.1
		9/2	11/2	5305.619(5)	−0.4
		11/2	9/2	5304.359(5)	1.8

[a]The subscript + (−) refers to the even (odd) Kronig symmetry.

Table 4. A comparison between the experimental spectrum and the spectrum calculated using the best fit constants is shown in Table 1. The agreement between experimental and predicted frequencies is satisfactory. However, the results are not as good as we hoped, especially if compared with the results for OD (Table 2 and next section). The experimental results obtained by Poynter and Beaudet (1968) deviate strongly from the calculated frequencies. These results are not self-consistent. The transitions of the $J = 9/2$ state of the $^2\Pi_{3/2}$ level have to fulfil the following sum rule

[26] $$v(5_+ \to 4_-) = v(4_+ \to 4_-) + v(5_+ \to 5_-) - v(4_+ \to 5_-)$$

Herein $v(F_+ \to F_-')$ is the frequency of the transition from F_+ to F_-'. The observed transitions of Poynter and Beaudet (1968) violate this rule by 670 kHz in spite of the claimed experimental accuracy of 10 kHz. As we used their results in the fit, we decided to increase the quoted errors to 200 kHz. Unfortunately, we are not able to measure these transitions at this moment to check the reliability of the calculations. However, in view of the results on the spectra of the other radicals discussed in the next sections, we feel that the employed theory is capable of predicting the transitions of the $J = 7/2$, $9/2$, and $11/2$ states of the $^2\Pi_{3/2}$ level to within 30 kHz.

Recently, Destombes et al. (1974) reanalyzed the spectrum of OH by applying the theory of Poynter and Beaudet (1968) to the observed Λ doubling transitions of OH presented in Table 1, excluding those of the $^2\Pi_{1/2}$, $J = 7/2$ and $9/2$ states. The disagreement between the observed frequencies and those calculated by Destombes et al. (1974) is an order of magnitude larger than obtained from the present calculations. This is due to the neglect of third order hyperfine structure contributions in the calculations of Destombes et al. (1974).

4.2. The Spectrum of the OD Radical

In a previous investigation on the OD radical (Meerts and Dymanus 1973a) we reported the hyperfine Λ doubling transitions in a number of rotational states of the $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ electronic states. In the latter state only the transitions in the rotational state of $J = 1/2$ were measured from which only limited information about the fine and hyperfine structure of the $^2\Pi_{1/2}$ level could be

TABLE 3.   Observed and calculated hyperfine Λ doubling transitions of SD in
the $\Pi_{3/2}$ state obtained in the present measurements

J	F_+ [a]	F_-	Observed frequency (MHz)	Observed minus calculated frequency (kHz)
3/2	5/2	5/2	16.120(3)	−0.1
	3/2	1/2	14.719(5)	−2.1
	7/2	5/2	13.643(3)	−2.0
	5/2	7/2	18.591(3)	0.6
5/2	3/2	3/2	64.295(1)	0.3
	5/2	5/2	64.299(1)	0.5
	7/2	7/2	64.307(1)	−0.2
	3/2	5/2	63.410(5)	−2.1
	5/2	3/2	65.181(1)	−0.1
	5/2	7/2	63.096(3)	−2.0
	7/2	5/2	65.505(2)	−2.6
7/2	5/2	5/2	160.1546(10)	0.3
	7/2	7/2	160.1617(10)	−1.1
	9/2	9/2	160.1767(7)	−1.2
	7/2	5/2	159.635(2)	−0.8
	5/2	7/2	160.6807(10)	−0.6
	9/2	7/2	159.5752(10)	0.5
	7/2	9/2	160.7660(10)	0.0
9/2	7/2	7/2	318.8188(7)	−0.3
	9/2	9/2	318.8334(7)	−0.2
	11/2	11/2	318.8568(7)	0.2
	7/2	9/2	318.583(2)	0.9
	9/2	7/2	319.071(1)	0.5
	9/2	11/2	318.640(1)	0.6
	11/2	9/2	319.052(1)	1.2
11/2	13/2	13/2	554.8335(1)	0.5
13/2	11/2	11/2	881.757(2)	−0.3
	13/2	13/2	881.788(2)	−0.4
	15/2	15/2	881.831(1)	−0.2
	11/2	13/2	881.959(5)	−0.1

[a]The subscript + (−) refers to the even (odd) Kronig symmetry.

obtained. Thus we decided to investigate also the $J = 3/2$ and $5/2$ rotational states of the $^2\Pi_{1/2}$ level and also the $J = 9/2$ state of the $^2\Pi_{3/2}$ level. The observed transition frequencies are given in Table 2. A recalculation of the molecular constants in a least squares fit was performed using the new experimental transition frequencies, $v_{ex}(i, w)$, and those obtained previously, $v_{ex}(i, p)$ (Meerts and Dymanus 1973a). We used essentially the same theory as for OH, extended to include the electric quadrupole interaction due to the nuclear spin of the deuteron ($I = 1$). The contributions of this interaction are described by ζ_1, ζ_2, ζ_3, and ζ_5. A comparison between $v_{ex}(i, w)$ and the calculated spectrum using the best fit constants is shown in Table 2. It is seen that the overall agreement is quite good, while for $v_{ex}(i, p)$ the differences with the calculated frequencies are generally smaller than 1 kHz. Therefore, the $v_{ex}(i, p)$ values are not reproduced here. The molecular constants of OD obtained from the least squares fit of all the available transitions are given in Table 4.

4.3. The Spectrum of the SH Radical

The Λ doubling transitions in the lowest rotational states of $J = 3/2$, $5/2$, $7/2$, $9/2$, and $11/2$ of the $^2\Pi_{3/2}$ level of SH were measured recently by Meerts and Dymanus (1974). In order to obtain information about the $^2\Pi_{1/2}$ level, we measured two transitions in the $J = 1/2$ state of the $^2\Pi_{1/2}$ level at about 8.4 GHz. The transitions could unambiguously be identified from the splittings in a magnetic field of 100 G. The transition frequency is 8445.211(5) MHz for the $F_+ \rightarrow F_- = 1_+ \rightarrow 1_-$ transition and 8459.034(5) MHz for the $F_+ \rightarrow F_- = 1_+ \rightarrow 0_-$ transition. The details of the procedure are given in an internal report (Meerts 1974). The observed magnetic spectrum of the $^2\Pi_{1/2}$ level of SH is discussed in Sect. 4.6.

TABLE 4. Molecular constants of OH, OD, SH, and SD obtained from a least squares fit of the observed spectra

Quantity	Molecule			
	OH	OD	SH	SD
$A_\Pi{}^a$ (cm^{-1})	$-139.38(2)$	$-139.22(2)$		
α_3 (MHz)	$1184.407(2)$	$776.588(2)$	$2108.0(2)$	
α_7 (MHz)	$-582.61(2)$	$-164.69(2)$	$-141.9(1)$	
α_4 (MHz)	$-2.937(4)$	$-0.527(3)$	$2.1(4)$	
α_5 (MHz)	$2.813(4)$	$0.407(3)$	$0.50(4)$	
χ_1 (MHz)	$39.497(8)$	$6.078(1)$	$24.04(6)$	
χ_2 (MHz)	$28.311(9)$	$4.384(1)$	$13.68(6)$	$2.10(8)$
χ_3 (MHz)	$139.55(4)$	$21.654(7)$	$25.617(8)$	$4.022(5)$
χ_4 (MHz)	$59.04(4)$	$9.034(10)$	$31.72(2)$	$4.824(15)$
$\chi_5 + \chi_7$ (kHz)	$-201(8)$	$-16(3)$		
χ_6 (kHz)	$-11(1)$	$-1.2(7)$		
χ_9 (kHz)	$-16(3)$	$-1.2(7)$		
ζ_1 (kHz)		$284(7)$		
ζ_2 (kHz)		$286(7)$		$149(4)$
ζ_3 (kHz)		$-62(6)$		$-25(12)$
ζ_4 (kHz)		$0(2)$		

^{a}The values of B_Π and D_Π were taken from Table 5.

In the fit, both the transition frequencies in the $^2\Pi_{1/2}$, $J = 1/2$ state obtained in the present investigation and those of the $^2\Pi_{3/2}$, $J = 3/2, 5/2, 7/2, 9/2$, and $11/2$ states reported previously (Meerts and Dymanus 1974) were used. The least squares fit procedure differed slightly from that used in the analyses of the spectra of OH and OD. It was found that the spin–orbit coupling constant, A_Π, could not be obtained from the observed SH spectrum and had to be kept constant. The value derived by Ramsay (1952) was used. As only one J state of the $^2\Pi_{1/2}$ level was measured, only the hyperfine constants χ_1, χ_2, χ_3, and χ_4 could be deduced. The remaining constants ($\chi_5 + \chi_7$, χ_6, and χ_9) describe the third order hyperfine contributions and can only be obtained if transitions in higher rotational states are also measured. The molecular constants obtained for SH are given in Table 4. The differences between the calculated spectra using the best fit constants of Table 4 and the observed frequencies lie within the quoted experimental accuracy of 0.5–5 kHz for each transition in the $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ states. This indicates a very good agreement between theory and experiment for SH.

4.4. The Spectrum of the SD Radical

Serious problems were encountered in obtaining the Λ doubling spectrum of SD mainly because of the poor signal to noise ratio. The total number of SD radicals produced in the beam was the same as the number of SH radicals. However, the population of the rotational states for SD is lower than for SH by a factor of about two. Moreover, the J states of SD are split into more hyperfine levels than those of SH. The observed signal to noise ratio varied between 1 and 10 at $RC = 5$ s. The frequencies of the weakest transitions were obtained by applying signal averaging techniques. We investigated the $J = 3/2$ to $J = 13/2$ states of the $^2\Pi_{3/2}$ level of SD. An unsuccessful search was made for the transitions in the lowest rotational state, $J = 1/2$ of $^2\Pi_{1/2}$. The observed transitions of the $^2\Pi_{3/2}$ level of SD are given in Table 3. For the $J = 11/2$ state, only one transition is reported because only this transition could be seen as a single line. Calculations showed that for the $J = 11/2$ state a number of transitions have accidentally almost the same frequencies.

The transition frequencies of SD, in Table 3, were used in a least squares fit to obtain the molecular constants. Only some of the molecular constants could be obtained because no transitions of the $^2\Pi_{1/2}$ level were available. The results are given in Table 4. The agreement between the calculated and experimental frequencies is excellent (Table 3).

4.5. The Electric Dipole Moment

The electric dipole moments of the four radicals were determined from the Stark shifts of transi-

tions in a given rotational state. The results for OH and OD were discussed by Meerts and Dymanus (1973b) in a previous communication. In the present investigation we observed the Stark shifts of the transitions originating in the $J = 5/2$ state of the $^2\Pi_{3/2}$ level of both SH and SD. The values obtained for the electric dipole moments are given in Table 7 together with the values for OH and OD obtained previously by Meerts and Dymanus (1973b).

4.6. The Magnetic Spectrum of the $^2\Pi_{1/2}$, $J = 1/2$ State of SH

The splitting of the Λ doubling transitions of SH in the $J = 1/2$ state of the $^2\Pi_{1/2}$ level at 8.4 GHz was investigated in a weak external magnetic field. Although the primary object of the measurements was identification of the transitions, some information about the magnetic properties of SH could be deduced from the observed splitting. A brief outline of the theory used for the interpretation of the splittings is given below.

The Zeeman Hamiltonian H_Z of a diatomic molecule in a Π state in an external magnetic field is given by Carrington *et al.* (1968)

$$[27] \qquad H_Z = \mu_0 H \cdot (L + gS) - g_N \mu_N H \cdot I - g_R \mu_0 H \cdot (J - L - S)$$

The first and second terms represent the electronic and nuclear Zeeman effect respectively, while the last term describes the Zeeman effect of the rotating nuclei. For the rotational state $J = 1/2$ of the $^2\Pi_{1/2}$ level, the paramagnetic contributions of the spin and orbital angular momentum almost cancel. At low (100 G) magnetic fields, H_Z for this state can be treated as a first order perturbation of the hyperfine Λ doublet levels. From the results of Carrington *et al.* (1968), we obtain for the Zeeman energy:

$$[28] \quad \langle ^2\Pi_{1/2} {}^\pm JIFM_F | H_Z | ^2\Pi_{1/2} {}^\pm JIFM_F \rangle = (-1)^{F-M_F} \begin{pmatrix} F & 1 & F \\ -M_F & 0 & M_F \end{pmatrix} (2F + 1)$$

$$\times \left[\mu_0 H g_J {}^\pm (-1)^{J+I+F+1} \begin{Bmatrix} J & F & I \\ F & J & 1 \end{Bmatrix} [J(J + 1)(2J + 1)]^{1/2} \right.$$

$$\left. + \mu_N H g_N (-1)^{J+I+F} \begin{Bmatrix} I & F & J \\ F & I & 1 \end{Bmatrix} [I(I + 1)(2I + 1)]^{1/2} \right]$$

In deriving [28], the interactions between the $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ states have been neglected. Consequently, [28] is correct only for the lowest rotational state, $J = 1/2$, for which this assumption is fully justified. The molecular g factor $g_J {}^\pm$ is defined as

$$[29] \qquad g_J {}^\pm = (1/2J(J + 1))\{(1 + g_R)\langle \Pi^\pm | T_0 {}^{(1)}(L) | \Pi^\pm \rangle - (1/2)(g + g_R)\} - g_R$$

The matrix element $\langle \Pi^\pm | T_0 {}^{(1)}(L) | \Pi^\pm \rangle$ can be obtained by a perturbation theory similar to that employed for the explanation of the Λ splitting (Meerts and Dymanus 1972) and can be approximated by (Radford 1961)

$$[30] \qquad \langle \Pi^\pm | T_0 {}^{(1)}(L) | \Pi^\pm \rangle = 1 \pm \Delta_1$$

where Δ_1 is a correction originating from the second and higher order interactions of the ground $^2\Pi$ state with the excited $^2\Sigma$ states. In this approximation, the first term (1) is simply the first order expectation value of L_z for a $^2\Pi$ state. The correction Δ_1 has the same origin as the Λ splitting, breaking of the symmetry of the electronic charge distribution around the molecular axis by the rotation of the nuclear frame. This effect results in a different g_J factor for the states with $+$ and $-$ symmetry. From the observed splittings of the transitions of SH at 8.4 GHz in a magnetic field of 100 G, we obtained $\Delta_1 = -0.014(2)$ and $g_R = 6(2) \times 10^{-4}$ assuming $g = 2.00232$ and $g_N = 5.5856$, the g factor of the electron and the proton respectively. From [29] and [30] it follows

$$[31] \qquad g_J {}^+ - g_J {}^- = ((1 + g_R)/J(J + 1))\Delta_1$$

The g factor of a diatomic molecule in a $^2\Pi$ state has been discussed by Radford (1961). Using his results, the following expression is derived for $g_J {}^+ - g_J {}^-$:

$$[32] \qquad g_J {}^+ - g_J {}^- = (\langle \Pi | L_y | \Sigma \rangle / J(J + 1))(4\theta / E)$$

where E is the energy difference between the first excited $^2\Sigma$ state and the ground $^2\Pi$ state and $\theta = \langle \Pi | AL_y + 2BL_y | \Sigma \rangle$. This expression is correct only for the $J = 1/2$ state of the $^2\Pi_{1/2}$ level. The quantity θ/E can be expressed by the constants describing the Λ splitting if only one excited $^2\Sigma$ state is assumed:

[33]
$$\theta/E = -\alpha_3/\sqrt{|\alpha_7 E|}$$

With the results collected in Table 4 we obtain for SH: $\theta/E = -5.8 \times 10^{-3}$. With the derived values for Δ_1 and θ/E, we calculated the electronic matrix element $\langle \Pi | L_y | \Sigma \rangle$ using [31] and [32]. The result is $\langle \Pi | L_y | \Sigma \rangle = 0.60(8)$ for SH. In spite of the rather crude approximation performed in [32] and [33], this value compares well with that of OH found by Radford (1961) ($\langle \Pi | L_y | \Sigma \rangle = 0.68(1)$) and the theoretical value of $\frac{1}{2}\sqrt{2}$ calculated from the pure precession approximation (Dousmanis et al. 1955).

5. Discussion

The analysis of the hyperfine Λ doubling spectra yielded both the fine structure constants and the hyperfine coupling constants for all investigated molecules. From the least squares fit of the spectra of OH and OD, a value for the ratio A_Π/B_Π ($= \lambda$) could be deduced, assuming fixed values for B_Π and D_Π (Table 5). An independent value for A_Π can only be obtained from transitions between the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ levels. The value of $|\lambda|$ for OH and OD is rather small, indicating a strong mixing between the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ levels. This makes it possible to obtain a value for λ directly from the Λ doubling spectra. In SH and SD the coupling between $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ is much weaker and the value of A_Π had to be taken from other sources. The values of A_Π obtained in the present investigation for OH and OD (-139.38 cm^{-1} and -139.22 cm^{-1} respectively), both in the ground vibrational state, lend strong support for the reliability of the applied theory. The present value of λ for OH is $-7.528(2)$; other reported values are -7.547 (Dieke and Crosswhite 1962), $-7.444(17)$ (Dousmanis et al. 1955), $-7.504(3)$ (Radford 1962), and -7.5086 (Mizushima 1972). For OD we found $\lambda = -14.108(4)$ while other investigators reported the values of $-13.954(32)$ (Dousmanis et al. 1955) and $-14.08(1)$ (Radford 1961). When comparing these values it should be noted that, in all cases, λ is obtained as a parameter, which describes the mixing between the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ levels. The fact that this mixing is very strong in OH and OD makes it possible to determine λ, but the errors in the constants B_Π and D_Π strongly affect the value of λ. Especially the centrifugal distortion has a significant effect on λ: A variation of $+10\%$ in D_Π in OH results in a shift of $+0.08$ cm^{-1} in A_Π as obtained in the least squares fit of the spectrum.

A comparison between the α_3 and α_7 which describe the Λ splitting and the values obtained by other investigators is not simple because third order effects are absorbed in the parameters used in the present theory. Neglect of the third order contributions yields relations [19] and [20]. The result for the Λ doubling constant obtained by various investigators for OH and OD are collected in Table 6. As can be seen from this table, the present Λ splitting constants deviate from those of Dousmanis et al. (1955). The deviation can be explained partly by the poor accuracy of the experimental results of Dousmanis et al. (1955) which deviate for all transitions from the much more accurate present results. The deviations with the results of Mizushima (1972) for OH can be explained by the slight difference in the third order fine structure contributions to α_3 and α_7.

It is of interest to compare the experimentally determined Λ splitting parameters α_3 and α_7 in the different isotopic species. If third order effects are neglected, α_3 and α_7 can be written as (Meerts and Dymanus 1972)

[34]
$$\alpha_3 = \sum_i (-1)^s \frac{\langle ^2\Sigma(i)||BL_-||X^2\Pi\rangle\langle ^2\Sigma(i)||(B + \frac{1}{2}A)L_-||X^2\Pi\rangle}{E_\Pi - E_{\Sigma^s}}$$

[35]
$$\alpha_7 = \sum_i (-1)^s \frac{|\langle ^2\Sigma(i)||BL_-||X^2\Pi\rangle|^2}{E_\Pi - E_{\Sigma^s}}$$

where the sums are taken over all excited $^2\Sigma^s$ states; $s = \pm$; with $(-1)^s = 1$ for $s = +$, and $(-1)^s = -1$ for $s = -$. In the approximation that the reduced matrix elements in the above equations can be written as a product of the rotational constant B_Π and the matrix element $\langle ^2\Sigma(i)||L_-||X^2\Pi\rangle$,

TABLE 5. Molecular constants of OH, OD, SH, and SD accepted in the fit of the MBER spectra (in cm^{-1})

	Molecule			
Quantity	OH[a]	OD[b]	SH[c]	SD[c]
A_Π			-376.9_6	-376.7_5
B_Π	18.515	9.868	9.461_1	4.900_3
D_Π	0.00187	0.00052	0.00048_0	0.00013_5

[a]Dieke and Crosswhite (1962).
[b]Dousmanis et al. (1955).
[c]Ramsay (1952).

TABLE 6. The Λ doubling parameters for OH, OD, SH, and SD as obtained from various investigations (all values are in MHz)

Quantity	Present investigation	Dousmanis et al. (1955)	Mizushima (1972)	Ramsay (1952)
α_3(OH)	1184.407	1180.7(1.5)	1183.128	
α_7(OH)	-582.61	$-576.2(1.7)$	-582.89	
α_3(OD)	776.588	774.5(1.1)		
α_7(OD)	-164.69	$-161.9(1.7)$		
α_3(SH)	2108.0			$2100(50)^a$
α_7(SH)	-141.9			$-180(40)$
α_3(SD)	1127.3^b			1150(50)
α_7(SD)	-38.07^b			$-50(40)$

^{a}Estimated assuming uncertainties of 0.001 to 0.002 cm^{-1} in the constants p_0 and q_0 obtained by Ramsay (1952).
^{b}Obtained from the results for SH by isotopic substitution, see text.

and that $\langle {}^2\Sigma(i)||AL_-||X^2\Pi\rangle$ is the same for the two isotopes, $\alpha_3 - \alpha_7$ is proportional to B_Π whereas α_7 is proportional to $B_\Pi{}^2$. This is a part of the pure precession approximation (Dousmanis et al. 1955). The experimental value for

[36] $R_1(OH/OD) = (\alpha_3 - \alpha_7)_{OH}/(\alpha_3 - \alpha_7)_{OD}$

is 1.877 and the value for

[37] $R_2(OH/OD) = \sqrt{(\alpha_7)_{OH}/(\alpha_7)_{OD}}$

is 1.881, while $(B_\Pi)_{OH}/(B_\Pi)_{OD} = 1.876$. It may be concluded from these values that the pure precession approximation allows a good prediction of the Λ splitting parameters α_3 and α_7 from isotopic substitution in OH and OD. The relations [36] and [37] between $R_1(SH/SD)$ and $R_2(SH/SD)$ and the ratio between the B_Π values of isotopic species was applied to SH and SD in order to derive the values of α_3 and α_7 for SD from those of SH (Table 4). The value for $(B_\Pi)_{SH}/(B_\Pi)_{SD}$ is 1.931. Assuming that $R_1(SH/SD)$ and $R_2(SH/SD)$ are both equal to 1.931, the results for α_3 and α_7 of SD are $(\alpha_3)_{SD} = 1127.3(3.0)$ MHz and $(\alpha_7)_{SD} = -38.07(20)$ MHz. The errors are based on the estimated errors in $R_1(SH/SD)$ and $R_2(SH/SD)$. The values of α_3 and α_7 for SH and SD obtained in this way (Table 6) agree quite well with the Λ splitting parameters of Ramsay (1952).

If the third order effects are neglected, we can deduce values for the hyperfine constants used in the low order theories using the values of Table 4 and [13] through [18]. The results are given in Table 7. In this work all the hyperfine constants have been obtained that are needed to describe the structure of the investigated transitions of OH, OD, SH, and SD. Only for OH have these constants been obtained previously by Radford (1962) whose results are in agreement with the present more accurate values. The hyperfine constants $a + (1/2)(b + c)$, b, and d of SH were deduced by Tanimoto and Uehara (1973) from EPR spectra and their values agree with values obtained in this work. The electric quadrupole coupling constants for OD and SD were obtained in the present work for the

TABLE 7. Values of the conventional constants for OH, OD, SH, and SD as obtained
in the present work

Quantity	Molecule			
	OH	OD	SH	SD
a (MHz)	86.01(2)	13.296(3)	32.58(7)	5.03(3)[a]
b (MHz)	−118.08(8)	−18.07(2)	−63.44(4)	−9.65(3)
c (MHz)	132.12(9)	20.35(3)	32.44(14)	4.95(4)[a]
d (MHz)	56.62(2)	8.768(2)	27.36(12)	4.20(2)
eQq_1 (kHz)		285(5)[b]		149(4)
eQq_2 (kHz)		−124(12)		−50(24)
μ (D)	1.6676(9)[c]	1.65312(14)[c]	0.7580(1)	0.7571(1)
$g_J{}^+ - g_J{}^-$ (μ_0)			−0.019(3)[d]	
g_R (μ_0)			6(2) × 10^{-4}	
$\langle\Pi|L_y|\Sigma\rangle$			0.60(8)	

[a]Obtained from the results of SH from the ratio of the nuclear g factors.
[b]The value as given by Meerts and Dymanus (1973a) has to be multiplied by two.
[c]Meerts and Dymanus (1973b).
[d]Of the $J = 1/2$ state of $^2\Pi_{1/2}$.

first time. The ratios between the magnetic hyperfine structure constants of OH and OD and between those of SH and SD should be equal to the ratio of the nuclear g factors of proton and deuteron. Small deviations are observed which probably reflect the neglect of third and maybe of even higher order effects in the present derivation of the constants a, b, c, and d.

The hyperfine structure in the radicals OH and SH is mainly determined by the unpaired π electron. The fact that the hyperfine constants of OH are larger than those of SH may be explained partly by the larger average separation of the unpaired electron from the interacting hydrogen nucleus in SH.

The magnetic hyperfine constants a, b, c, and d are related to expectation values of electronic operators:

$$[38] \qquad a = gg_I\mu_0\mu_N \int \frac{1}{r_{11}{}^3}D_L(\Lambda, \Lambda|r_{11})\,dr_{11} = gg_I\mu_0\mu_N\langle 1/r^3\rangle_U$$

$$[39] \qquad b = -\tfrac{1}{2}gg_I\mu_0\mu_N \int \frac{3\cos^2\theta_{11} - 1}{r_{11}{}^3}D_S(\Sigma, \Sigma|r_{11})\,dr_{11} + (8/3)\pi\,gg_I\mu_0\mu_N D_S(\Sigma, \Sigma|0)$$

$$= -\tfrac{1}{2}gg_I\mu_0\mu_N\langle(3\cos^2\theta - 1)/r^3\rangle_U + (8/3)\pi\,gg_I\mu_0\mu_N\langle\psi^2(0)\rangle_U$$

$$[40] \qquad c = \tfrac{3}{2}gg_I\mu_0\mu_N \int \frac{3\cos^2\theta_{11} - 1}{r_{11}{}^3}D_S(\Sigma, \Sigma|r_{11})\,dr_{11}$$

$$= \tfrac{3}{2}gg_I\mu_0\mu_N\langle(3\cos^2\theta - 1)/r^3\rangle_U$$

$$[41] \qquad d = \tfrac{3}{2}gg_I\mu_0\mu_N \int \frac{\sin^2\theta_{11}}{r_{11}{}^3}e^{-2i\phi_{11}}D_S(\Sigma, -\Sigma|r_{11})\,dr_{11}$$

$$= \tfrac{3}{2}gg_I\mu_0\mu_N\langle\sin^2\theta/r^3\rangle_U$$

In these expressions $D_S(\Sigma, \Sigma'|r_{11})$ is the normalized spin density function of McWeeny (1960, 1965) and $D_L(\Lambda, \Lambda|r_{11})$ is its orbital analog with $\Lambda = 1$ and $\Sigma = 1/2$, $\Sigma' = \Sigma$ or $-\Sigma$; the average values are the differences between the average values for the part of the electron density with spin 'up' (α) and the part with the spin 'down' (β). In the 'spectroscopic approximation' it is assumed that the integrals in [38] through [41] are well approximated by averages only over the unpaired electron density as indicated by U. This approximation is only valid when the paired electrons have the same spatial density for the α and β spins. The electronic expectation values of $\langle 1/r^3\rangle_U$, $\langle(3\cos^2\theta - 1)/r^3\rangle_U$, $\langle\sin^2\theta/r^3\rangle_U$, and $\langle\psi^2(0)\rangle_U$ have been calculated from the present experimental magnetic hyperfine constants for all four molecules. The results for OH and OD are almost equal as can be

TABLE 8. Experimental and calculated molecular constants of OH (OD) and SH (SD) (in units of $10^{24}\,cm^{-3}$)

	$\langle 1/r^3 \rangle_U$	$\langle (3\cos^2\theta - 1)/r^3 \rangle_U$	$\langle \sin^2\theta/r^3 \rangle_U$	$\langle \psi^2(0) \rangle_U$	$\langle (3\cos^2\theta - 1)/r^3 \rangle_T$	$\langle \sin^2\theta/r^3 \rangle_T$
OH Obsd	1.093(4)	1.117(2)	0.480(2)	−0.1115(5)		
Calcd[a]	1.015	1.037	0.331	−0.103		
Calcd[b]	1.064	1.165		−0.111[f]		
Calcd[c]	1.014	1.018		−0.094[f]		
Calcd[d]				−0.128		
Calcd[e]				−0.115		
OD Obsd					14.18(5)	0.43(5)
SH Obsd	0.413(1)	0.274(1)	0.231(1)	−0.0795(5)		
Calcd[b]	0.379	0.276		−0.035[f]		
Calcd[c]	0.306	0.098		−0.009[f]		
Calcd[d]				−0.047		
Calcd[e]				−0.054		
SD Obsd					11.53(5)	0.17(8)

[a]Kayama (1963).
[b]Kotake et al. (1971) for Slater type orbitals.
[c]Kotake et al. (1971) for analytical Hartree–Fock orbitals.
[d]Bendazzoli et al. (1972) UHF approximation.
[e]Bendazzoli et al. (1972) RHF + CI.
[f]Derived from the calculated values for $\langle 1/r^3 \rangle_U$ and $\langle (3\cos^2\theta - 1)/r^3 \rangle_U$ and the experimental hyperfine constants.

expected from the fact that the replacement of hydrogen by deuterium in OH only slightly disturbs the electronic distribution in the molecule. Consequently, the corresponding results for OH and OD were averaged. The indicated errors cover the values obtained for OH as well as for OD. The same procedure was applied to SH and SD and the results are given in Table 8.

Valuable information about the character of interactions and about the electronic charge distribution in the molecule can be obtained from the quantities $\langle 1/r^3 \rangle_U$, $\langle (3\cos^2\theta - 1)/r^3 \rangle_U$, $\langle \sin^2\theta/r^3 \rangle_U$, and $\langle \psi^2(0) \rangle_U$. In an *ab initio* molecular orbital (MO) calculation of OH and SH the Fermi contact term can be used as a test of the quality of the applied configuration interaction (CI). In a single configuration MO approximation, the electronic configuration of OH is $(1\sigma)^2(2\sigma)^2 \times (3\sigma)^2(1\pi^+)^2(1\pi^-)$ and of SH is $(1\sigma)^2(2\sigma)^2(3\sigma)^2(1\pi)^4(4\sigma)^2(5\sigma)^2(2\pi^+)^2(2\pi^-)$. In the restricted Hartree–Fock approximation (RHF) the π^- orbital function vanishes on the intermolecular axis and $\langle \psi^2(0) \rangle_U = 0$. In the unrestricted Hartree–Fock (UHF) theory each doubly occupied spatial orbital function splits into two orbitals by the exchange polarization. The presence of the π^- orbital has a different effect on the density of the α and β core electrons. In the UHF theory, $\langle \psi^2(0) \rangle_U$ no longer vanishes due to polarization of the σ orbitals. Kayama (1963) used the UHF approximation to show that $\langle \psi^2(0) \rangle_U$ should be negative for OH. He also performed an *ab initio* MO–CI calculation using nine excited configurations. The result of this calculation is shown in Table 8. Bendazzoli et al. (1972) calculated $\langle \psi^2(0) \rangle_U$ for OH and SH with (1) the UHF wave functions and with (2) CI wave functions, denoted as RHF + CI since the one electron functions used were molecular orbitals obtained in a restricted Hartree–Fock approximation. The results for $\langle \psi^2(0) \rangle_U$ obtained by Bendazzoli et al. with a set of contracted Gaussian orbitals as the basis set are reproduced in Table 8. The calculated values for $\langle \psi^2(0) \rangle_U$ of Kayama (1963) and of Bendazzoli et al. (1972) agree quite well with the experimental value.

Contrary to $\langle \psi^2(0) \rangle_U$, the quantities $\langle 1/r^3 \rangle_U$, $\langle (3\cos^2\theta - 1)/r^3 \rangle_U$, and $\langle \sin^2\theta/r^3 \rangle_U$ do not vanish in a single configuration approximation. In this approximation it is readily seen that each of them is simply given by the average value over the unpaired π orbital ($1\pi^-$ for OH and $2\pi^-$ for SH). In the LCAO–MO approximation the unpaired electron is usually assigned to the np_x or to the np_y atomic orbital, both perpendicular to the molecular axis, with $n = 2$ for OH and $n = 3$ for SH. In *ab initio* LCAO–MO calculations these atomic orbitals are usually Slater orbitals or analytical Hartree–Fock (AHF) orbitals, the latter consisting of a linear combination of Slater type orbitals. The quantities $\langle 1/r^3 \rangle_U$ and $\langle (3\cos^2\theta - 1)/r^3 \rangle_U$ were calculated for OH in the single configuration approximation by Kayama (1963) using AHF orbitals and by Kotake et al. (1971) for OH and SH with Slater orbitals and AHF orbitals. The authors used different AHF orbitals as

the basis in their calculations on OH. The results are summarized in Table 8. It is seen from this table that the agreement between the experimental and calculated values for OH is quite good and that for SH the best results are obtained with Slater orbitals. The value for $\langle (3 \cos^2 \theta - 1)/r^3 \rangle_U$ for SH calculated with AHF orbitals differs markedly from the experimental value.

Tanimoto and Uehara (1973) observed the EPR spectra of SH in the $^2\Pi_{3/2}$, $J = 3/2$ and $5/2$ states but were unable to deduce all the hyperfine constants independently from the experimental results. To solve this problem, Tanimoto and Uehara used the approximation

[42] $\langle \sin^2 \theta/r^3 \rangle_U : \langle (3 \cos^2 \theta - 1)/r^3 \rangle_U : \langle 1/r^3 \rangle_U = (4/5) : -(2/5) : 1$

which is derived assuming that the unpaired electron occupies a $2p$ (in OH) or $3p$ (in SH) atomic orbital of oxygen or sulfur respectively. However, the interacting nuclear spin is on the hydrogen atom and this approximation fails completely; it even predicts the wrong sign for $\langle (3 \cos^2 \theta - 1)/r^3 \rangle_U$.

The electric quadrupole coupling constants of OD and SD also provide information about the electronic charge distribution in the molecules. The coupling constants eQq_1 and eQq_2 can be expressed in the nuclear quadrupole moment Q and average values of $(3 \cos^2 \theta - 1)/r^3$ and $\sin^2 \theta/r^3$:

[43] $q_1 = \dfrac{2Z_K}{R_{IK}} - \displaystyle\int \dfrac{3 \cos^2 \theta_{11} - 1}{r_{11}^3} P_L(\Lambda, \Lambda | r_{11}) \, dr_{11} = \dfrac{2Z_K}{R_{IK}} - \langle (3 \cos^2 \theta - 1)/r^3 \rangle_T$

[44] $q_2 = -3 \displaystyle\int \dfrac{\sin^2 \theta_{11}}{r_{11}^3} e^{2i\phi_{11}} P_L(\Lambda, -\Lambda | r_{11}) \, dr_{11} = -3 \langle \sin^2 \theta/r^3 \rangle_T$

where $P_L(\Lambda, \Lambda' | r_{11})$ is the normalized electron density function of McWeeny (1969, 1965) with $\Lambda = 1$ and K stands for oxygen or sulfur for OD or SD respectively. The averages of $(3 \cos^2 \theta - 1)/r^3$ and $\sin^2 \theta/r^3$ marked with 'T' are over all electrons and are different from the average values in [38] through [41].

The quantities q_1 and q_2 are proportional to the component along and perpendicular to the bond axis respectively of the gradient of the electric field produced at the deuteron nucleus by the electronic charge distribution and by the other nucleus (K). The average value q_1 is well known for molecules in a $^1\Sigma$ state, while q_2 is only observable in molecules with $|\Lambda| = 1$.

The nuclear part in [43] can easily be calculated from the known molecular geometries and the results are 17.17×10^{24} cm^{-3} and 13.09×10^{24} cm^{-3} for OD and SD respectively. The electronic parts of q_1 and q_2 were obtained from the experimental quadrupole coupling constants of Table 7 and the value $Q = 0.002738 \times 10^{-24}$ cm^2 for the nuclear quadrupole moment of the deuteron (Ramsey 1956). The results are given in Table 8.

The average quantities $\langle (3 \cos^2 \theta - 1)/r^3 \rangle_T$ and $\langle \sin^2 \theta/r^3 \rangle_T$ can only be determined for OD and SD. However, these quantities depend only on electronic distribution. Within the Born–

Oppenheimer approximation assumed in the present theory, the charge distribution is the same in OD and OH. Consequently, $\langle (3 \cos^2 \theta - 1)/r^3 \rangle_T$ and $\langle \sin^2 \theta/r^3 \rangle_T$ should be the same for these molecules. The same arguments and conclusions apply also for SH and SD.

Unfortunately, no molecular orbital calculations are available of $\langle (3 \cos^2 \theta - 1)/r^3 \rangle_T$ and $\langle \sin^2 \theta/r^3 \rangle_T$ for OH (OD) or SH (SD). The values obtained in the present investigations may serve as a test for future calculations of the contributions of electrons occupying orbitals other than the unpaired π orbital.

It is interesting to note that $\langle \sin^2 \theta/r^3 \rangle_U$ and $\langle \sin^2 \theta/r^3 \rangle_T$ are almost equal for both OH and SH. This can be understood by considering the contributions to $\langle \sin^2 \theta/r^3 \rangle_U$ and to $\langle \sin^2 \theta/r^3 \rangle_T$ as sums of one electron contributions with each electron occupying a definite orbital. Electrons occupying σ orbitals do not contribute because integration over the azimuthal angle ϕ yields zero. Therefore, contributions of electrons occupying a π orbital remain. Electrons which can occupy an α state as well as a β state contribute to $\langle \sin^2 \theta/r^3 \rangle_U$ because $D_S(\Sigma, -\Sigma | r_{11})$ connects electron states with different spin values. Consequently, only an electron occupying an unpaired π orbital contributes to $\langle \sin^2 \theta/r^3 \rangle_U$. In the ground electronic

states of OH and SH, one π orbital is singly occupied ($1\pi^-$ for OH and $2\pi^-$ for SH). Therefore, $\langle\sin^2\theta/r^3\rangle_U$ effectively contains the contribution of one electron. The situation is quite similar for $\langle\sin^2\theta/r^3\rangle_T$. If we assume that the azimuthal dependence of a π^+ orbital is ($e^{i\phi} + e^{-i\phi}$) and of a π^- orbital ($e^{i\phi} - e^{-i\phi}$), then it is readily seen that the contributions to $\langle\sin^2\theta/r^3\rangle_T$ of an electron in a $n\pi^+$ orbital cancels the contribution of an electron in a $n\pi^-$ orbital. Therefore, effectively only one electron contributes to $\langle\sin^2\theta/r^3\rangle_T$ for OH $1\pi^+$ as well as for SH $2\pi^+$.

The observed isotopic effects in the dipole moments of OH and OD and SH and SD are 8×10^{-3} and 1.5×10^{-3} respectively. The order of magnitude agrees with the expectations but the isotopic effect for SH and SD is smaller than expected from the effect for OH and OD. Quantitative discussions have to await *ab initio* calculation of the dipole moment function or accurate measurements of the dipole moment in higher vibrational states.

Results from previous measurements of the dipole moments of OH and OD have already been extensively discussed by Meerts and Dymanus (1973*b*). The dipole moment of SH has been determined by Byfleet *et al.* (1971) using the gas phase EPR with an external electric field. The result $\mu_{SH} = 0.62(1)$ D disagrees with the present more accurate value. In our opinion, the origin of the discrepancy lies in the erroneous calibration of the electric field strength by Byfleet *et al.* This is supported by the fact that the value of the electric dipole moment of BrO obtained by Byfleet *et al.* (1971), $\mu = 1.61(4)$ D, also deviates from the recent values of Amano *et al.* (1972) (1.765(23) D, for ^{79}BrO and 1.794(49) D for ^{81}BrO).

The values for the electric dipole moments obtained by Cade and Huo (1966) from *ab initio* calculations ($\mu = 1.780$ D for OH and $\mu = 0.861$ D for SH) are in a quite good agreement with the experimental values. The calculated values, however, are 7 and 13% higher than the experimental values for OH and SH respectively.

6. Conclusions

The molecular beam electric resonance spectroscopy has proved to be a powerful technique in the investigation of spectra and properties of the free radicals OH, OD, SH, and SD via their Λ doubling transitions. The radicals are produced quite efficiently to obtain signal to noise ratios of the order of 100 for the transitions of OH and 20 for SH at $RC = 5$ s.

The spectrum calculated using the third order degenerate perturbation theory gives a very good agreement with the experimental results for OD, SH, and SD. However, for SD no transitions in the $^2\Pi_{1/2}$ level could be observed and for SH transitions only in the $J = 1/2$ of the $^2\Pi_{1/2}$ level. Consequently, the test of the theory is not complete for these molecules. For OH and OD we have measured transitions in a number of rotational states of both the $^2\Pi_{1/2}$ and the $^2\Pi_{3/2}$ levels. The agreement for OD is excellent, but for OH the differences between the calculated and observed transitions are larger than the experimental errors. A similar situation was found previously in the analysis of the hyperfine Λ doubling spectrum of ^{14}NO and ^{15}NO (Meerts and Dymanus 1972). The conclusion, based on the fact that the investigated molecules cover a large scale of different values of Λ splitting, is that the disagreement cannot be eliminated by taking into account higher order contributions in fine structure. The OH and OD radicals can be described by a representation intermediate between the Hund's case (*a*) and (*b*) and the molecules SH, SD, ^{14}NO, and ^{15}NO can be approximated by almost a pure Hund's case (*a*). The nature and the relative strength of the interactions responsible for the type of coupling apparently does not offer an explanation of the observed discrepancies between the experiment and the theory for ^{14}NO, ^{15}NO, and OH. The only significant difference between the group ^{14}NO, ^{15}NO, OH and the group OD, SH, SD is the magnitude of the hyperfine contributions, which are about an order of magnitude larger for the first group than for the second. It is possible that taking into account the fourth or even higher order contributions due to hyperfine structure may lift the observed differences between calculated and experimental spectra in OH, ^{14}NO, and ^{15}NO. However, this approach puts a heavy load on both the calculation of high order contributions and the experiment to measure a sufficient number of transitions for the fit with an increasing number of coupling constants. A possible solution of the problem

is to replace the zero order Hamiltonian ([4]) by an effective Hamiltonian which incorporates some of the lower order contributions.

From the present investigations the fine and hyperfine structure constants of OH, OD, SH, and SD were obtained. The relations between the fine structure parameters obtained by isotopic substitution of deuterium in OH could well be tested as well as their usefulness in deducing unknown molecular constants. The relevant relations ([36] and [37]) are actually based on the pure precession approximation (Dousmanis *et al.* 1955). By applying this approximation, the Λ splitting parameters of SD could be obtained from the isotopic substitution of deuterium in SH. The hyperfine structure constants obtained from the experiment show a gratifying agreement with the *ab initio* calculations.

NOTE ADDED IN PROOF: Recently we succeeded in observing transitions of the $^2\Pi_{1/2}$, $J = 1/2$ state. The measured transition frequency is 4518.328(6) MHz for the $F_+ \to F_- = 3/2 \to 3/2$ transition and 4521.476(7) MHz for the $F_+ \to F_- = 3/2 \to 1/2$. Some of the coupling constants of SD could be additionally calculated. The results are (in MHz) $\alpha_3 = 1128.8(2)$, $\alpha_7 = -38.0(1)$, $\alpha_4 = 0.25(4)$, $\alpha_5 = 0.05(1)$, and $\chi_1 = 3.68(8)$.

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