ELECTRIC DIPOLE MOMENTS OF OH AND OD 
BY MOLECULAR BEAM ELECTRIC RESONANCE

W.L. MEERTS and A. DYMANUS
Fysisch Laboratorium, Katholieke Universiteit, Nijmegen, The Netherlands

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The Stark shifts of hyperfine A-doubling transitions originating from the $^2\Pi_{3/2}$ level of OH and OD are observed. From these shifts we calculated the values of the electric dipole moments: 1.6676(9) D for OH and 1.65312(14) D for OD.

1. Introduction

The electric dipole moment of the hydroxyl radical (OH) has been investigated by several authors [1–3]. The most accurate value is reported by Powell and Lide [4] $\mu = 1.660(10)$ D obtained from the Stark shifts of the microwave A-doublet transition of the $^2\Pi_{3/2}, J = 7/2$ level at 13438 MHz.

After a molecular beam electric resonance study of the hyperfine A-doubling spectrum of OD in zero external fields [5] we decided to investigate the Stark effect of OH and OD in order to obtain more accurate values of the dipole moments for both molecules as a first step in an investigation of their vibrational dependence.

2. Theory

The hamiltonian used for the interpretation of the observed spectra is

$$H = H_F + H_{hf} - \mu \cdot E.$$  
(1)

Herein $H_F$ and $H_{hf}$ describe the fine, hyperfine structure contributions, respectively, the last term gives the Stark effect, where $\mu$ is the permanent dipole moment of the molecule, and $E$ the external electric field.

For the interpretation of the spectra in zero electric field we used the theory developed in a previous paper [6]. The lowest electronic state of the hydroxyl radical is a $^2\Pi$ state. The rotational wavefunctions can be formally written [6] as $|^2\Pi_{|\Omega|}, J\rangle$, where $|\Omega|$ takes the values 1/2 and 3/2, and $p$ stands for $\pm$. The nuclear spin $I$ of the hydrogen or deuteron nucleus is coupled with the rotational angular momentum $J$ to $F$ in the conventional way: $J + I = F$.

The basic hyperfine wavefunctions take the form $|^2\Pi_{|\Omega|}, JFM_F\rangle$. Their Kronig symmetry is $p (-1)^{I+J}$. The matrix elements of $H_F$ and $H_{hf}$ on these basic wavefunctions are extensively discussed by Meerts and Dymanus [6]. The matrix elements of the Stark contribution can easily be calculated (see also Freed [7]). The result is

$$\langle^2\Pi_{|\Omega|}, JFM_F | -\mu \cdot E | ^2\Pi_{|\Omega'|}, J'F'M'_{F'}\rangle$$

$$= \delta(|\Omega|, |\Omega'|) f_{\mu} E [(2J+1)(2J'+1)(2F+1)(2F'+1)]^{1/2}$$

$$\times \left\{ \begin{array}{c} J \ F \ 1 \ \ F' \ \ 1 \ \ J' \end{array} \right\} \left\{ \begin{array}{c} F' \ F \ J' \ J \end{array} \right\} \left\{ \begin{array}{c} \mu \cdot E \ M_{F'} \ 0 \ M_{F'} \end{array} \right\} \left\{ \begin{array}{c} -|\Omega| \ 0 \ |\Omega'| \end{array} \right\}.$$  
(2)

In this expression $E$ is taken parallel to the $z$ axis. As the Stark effect operator has non-zero matrix elements only between states with a different Kronig symmetry, the constant $f$ takes the values:

$$f = 0 \quad \text{if } |J - J'| = 0 \text{ and } p = p',$$

$$\text{or } |J - J'| = 1 \text{ and } p \neq p;$$

$$= (-1)^{2J+F+F'-M_F-|\Omega|} \quad \text{otherwise.}$$
The energy matrix for the fine and hyperfine structure contributions involve a simple 2 X 2 secular equation. The Stark effect enlarges the secular problem considerably, because of the coupling between states with different symmetry and matrix elements off-diagonal in J and F. The only good quantum-number of the hamiltonian (1) is \( M_F \). We calculated for each \( M_F \) value the total matrix of \( H \) including \( \Delta J = \pm 1 \) coupling terms. The latter terms are responsible for second order contributions to the Stark energy. Higher-order terms turned out to be far below the experimental accuracy. The calculations were performed using a computer program, which diagonalizes the complete hamiltonian matrix.

3. Results and discussion

The measurements were performed using a molecular-beam electric resonance spectrometer (MBER) described elsewhere [8]. Initially, attempts were made to measure the Stark splitting of the lowest rotational level \( (J = 3/2) \) of the \( 2\Pi_{3/2} \) state. This state has a very strong Zeeman effect. Although the earth's magnetic field has been compensated for with extreme care, internal inconsistencies in the order of \( 1 \times 10^3 \) in the measured Stark splittings were observed. These are caused probably by the component of the earth's magnetic field perpendicular to the electric field, estimated to be 15-30 mG. As an alternative we decided to measure the Stark effect of the transitions belonging to the \( 2\Pi_{1/2} \) state, which is essentially non-magnetic. However, the conditions for MBER are not favourable, because of the relatively high transition frequencies in zero external fields: 4.7 GHz for OH [9] and 3.1 GHz for OD [5], respectively, in their lowest rotational state \( J = 1/2 \). It turned out that the Stark splitting for OD could very well be observed at 3.1 GHz, but the OH transition at 4.7 GHz could not be observed. Fortunately, the zero-field transitions of the \( J = 9/2 \), \( 2\Pi_{1/2} \) state of OH are at easy MBER frequencies between 88 and 165 MHz. So for OH the Stark splitting of these transitions is observed. The zero-field transition frequencies are given in table 1.

The measurements are done at different electric field strengths, and for different hyperfine transitions for both OH and OD. The maximum Stark shift was 20 MHz and 15 MHz for OD and OH, respectively.

Using the theory discussed in the previous section the Stark shifts are calculated and values for the electric dipole moments for OH and OD are fitted to the experimental data. The obtained dipole moments were 1.66758(10) D and 1.65312(14) D for OH and OD, respectively. The agreement between experimental and calculated Stark shifts was excellent within experimental accuracy. The quoted errors are based on the experimental uncertainties.

However, difficulties encountered in fitting the zero-field spectrum force us to increase the inaccuracy in the reported value of the dipole moment of OH. The nucleus of the difficulties is the high accuracy of the measurements and the rather strong centrifugal distortion, which has to be taken into account when fitting the zero-field spectrum as well as the Stark spectrum. The OH molecule can be described by an intermediate Hund's case between (a) and (b). In the fit of the former spectrum we used an intermediate representation starting from the case (a) basic wavefunctions. For the rotational constant \( (B_\Pi) \) and the centrifugal distortion constant \( (D_\Pi) \) of the \( 2\Pi \) state we used the values reported by Díeke and Crosswhite [10]. These constants were obtained from a fit of the observed ultraviolet band spectrum of OH to the theoretical spectrum calculated in an intermediate representation starting from the Hund's case (b) wavefunctions.

This procedure is correct, but problems are introduced by an approximation: in the expressions for the rotational energy (functions \( f_{1,2}(K) \) of ref. [10]) the \( B_\Pi \) part is in an intermediate case, but the \( D_\Pi \) part in pure (b) case. This approximation is a good one for high \( J \) values for which OH is close to case (b), but not for low \( J \) values relevant to the present investigation. For the correct treatment of the rotational
energy in our representation we had to transform the Hamiltonian matrix of Dieke and Crosswhite. Essentially this is a transformation from the Hund's (b) to the Hund's (a) representation. However, when this is done an additional $D_\Pi$ contribution (proportional to $J(J+1)$) appears for the rotational energy. If Dieke and Crosswhite had used this approach their $B_\Pi$ and $D_\Pi$ values would have been slightly different.

The ratio between the rotational energy (including distortion effects) and the spin-orbit energy is a measure for the mixing of the $1\Pi_1,2$ and $2\Pi_{3/2}$ levels. As the Stark effect matrix elements are unequal for the two levels, the calculated Stark shifts depend on the mixing of the levels. A slight change of the $D_\Pi$ constant will cause a very small variation in the mixing of both $\Pi$ levels and consequently in the Stark shifts. The effect on the dipole moment can be $10^{-4}$. It is felt that the error in the dipole moment of OH should reflect this uncertainty (0.0009 D), resulting in $\mu = 1.6676(10)$ D for OH.

The observed Stark transitions are given in table 2. These transitions may be used to obtain a more accurate value of $\mu$(OH), when the uncertainty of $D_\Pi$ is removed.

There are no problems in the interpretation of the Stark spectrum of OD, because the lowest $J$-state, $J = 1/2$, is a pure $2\Pi_{1/2}$ state, without any mixing with the $2\Pi_{3/2}$ level. The obtained dipole moment for OD is $1.6531(14)$ D. For $B_\Pi$ and $D_\Pi$ of OD we used the values given by Dousmanis et al. [11].

For Planck's constant the recent value of Taylor et al. [12] is used: $h = 6.626196(50) \times 10^{-34}$ J sec.

The value of the anisotropy in the electric polarizability for OH is not known; however, the value will lie between 0.2 and $1.0 \times 10^{-24}$ cm$^3$. The effect on the Stark shifts is estimated for an assumed value of $1.0 \times 10^{-24}$ cm$^3$. This causes shifts or 10 Hz or less, which is far below the experimental accuracy (700 Hz).

The value of the dipole moment of OH as reported by Powell and Lide [4] has to be corrected for the incorrect value of the dipole moment of OCS they used to calibrate the electric field strength [13, 14]. The corrected value $1.667(10)$ D is in good agreement with the present more accurate value.

The observed isotopic effect in the dipole moment of OH and OD is about $8 \times 10^{-3}$, which is quite an acceptable value. This difference is caused by vibrational effects. It is, however, not possible to discuss these effects quantitatively only on the basis of the dipole moments for OH and OD in the ground vibrational state, one also needs the values for other vibrational states.

References