Vibrational effects in the hydroxyl radical by molecular beam electric resonance spectroscopy

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The hyperfine Λ-doubling transitions of OH in the $^2\Pi_{1/2}$, $J = 1/2$ and $3/2$ and in the $^2\Pi_{3/2}$, $J = 3/2$ and $5/2$ levels of the $v = 1$ and $v = 2$ excited vibrational states have been measured in a molecular beam electric resonance spectrometer. Vibrational effects in the deduced Λ-doubling and hyperfine structure constants have been determined. A comparison is made with *ab initio* calculations.

1. INTRODUCTION

The hyperfine Λ-doubling spectrum in the ground vibrational state of the hydroxyl radical has been the subject of extensive theoretical and experimental studies. A summary of the results can be found in several papers [1, 2, 3]. Many less experimental data are available for the excited vibrational states of OH. The paramagnetic resonance spectra were investigated up to $v = 9$ [4, 5, 6, 7]. However, these measurements were restricted to the $J = 3/2$ and $5/2$ (for $v \leqslant 4$) levels in the $^2\Pi_{3/2}$ electronic state. This limits seriously the possibility of deducing the Λ-doubling and the hyperfine structure constants in the vibrationally excited states and their dependence on the internuclear distance in the OH molecule.

This paper reports a molecular beam electric resonance (MBER) study of the hyperfine Λ-doubling spectra originating in the $v = 1$ and $v = 2$ vibrational states. The complete set of microwave transitions has been obtained for the $J = 1/2$ and $3/2$ rotational levels of the $X^2\Pi_{1/2}$ electronic state and for the $J = 3/2$ and $5/2$ levels of the $X^2\Pi_{3/2}$ state. The electric resonance data are interpreted in terms of the theory for a $^2\Pi$ state, developed previously [1, 8]. All Λ-doubling and hyperfine structure constants could independently be determined for the $v = 1$ and $v = 2$ vibrational states. Together with the results for the $v = 0$ state, accurate and rather complete experimental information about the variation of these constants with the internuclear distance has become available. The experimental results are compared with *ab initio* calculations performed by Hinkley *et al.* [9] and Coxon and Hammersley [10] for the Λ-doubling constants p and q and by Kayama [11] for the hyperfine constants. The overall agreement is satisfactory.

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2. EXPERIMENT

The experiments were performed using a molecular beam electric resonance spectrometer described in detail elsewhere [8, 12]. Only some features relevant to the present work are discussed here.

Previous investigators have produced the vibrationally excited OH radical by the reaction of atomic hydrogen with ozone [5, 6] or with F_2O [4]. Although the techniques of producing beams of ozone were well developed in our laboratory [13], the reaction between atomic hydrogen and NO_2 was preferred for reasons of convenience and safety. The expected low signal-to-noise ratio for the transitions in excited vibrational states, and consequently integration times up to a few hours (see below) for a single transition, would require production and storage of large quantities of ozone. The reaction

$$H + NO_2 \rightarrow OH + NO$$
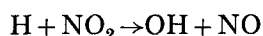
[14] was found to be quite effective in producing vibrationally excited OH radicals under optimized experimental conditions. Two different types of reaction sources were used. The type (a) source (figure 1 (*a*)) consisted of a quartz tube (inner diameter 9 mm) in which the NO_2 gas is injected through a ring of small holes 10 mm from the end. The type (b) source (figure 1 (*b*)), similar to the one used by ter Meulen in a beam maser [15], is made of a Pyrex tube (inner diameter 17 mm) in which the NO_2 gas is injected in the direction of the molecular flow via a fine glass capillary array 10 mm from the end of the tube. In both sources the beam was formed by a conical diaphragm (skimmer)
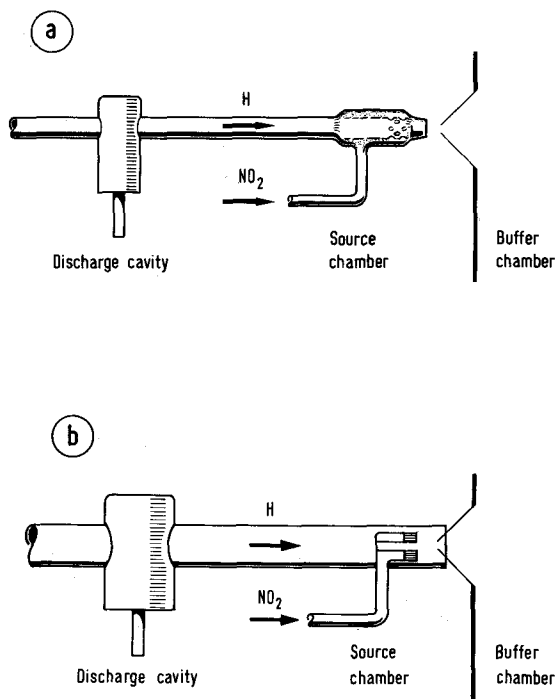

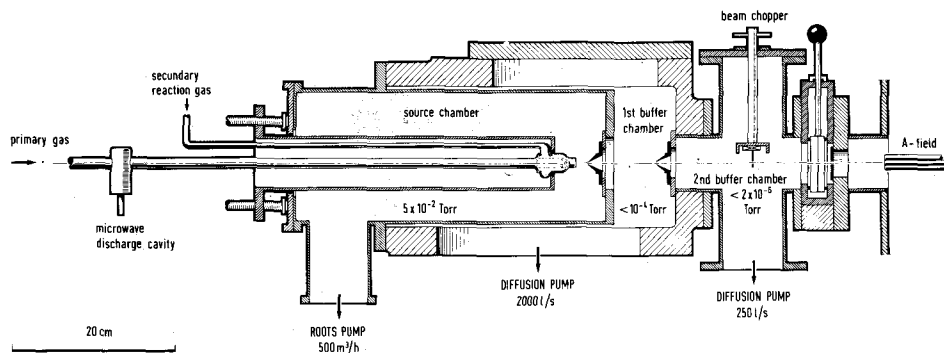Figure 1.   The two types of reaction sources for OH.

Figure 2. Schematic view of the reaction source section of the spectrometer.

2 mm in diameter. The hydrogen atoms were produced by a 2·45 GHz microwave discharge in water vapour ; the typical microwave power dissipated was 175 W. The source chamber was separated from the high vacuum of the electric resonance machine by two buffer chambers pumped by oil diffusion pumps, shown schematically in figure 2. The distance between the skimmer and the end of the source tube could be varied, which turned out to be of utmost importance for the production of a beam of vibrationally excited OH radicals. Under optimum flow conditions, typically $1·5 \times 10^{19}$ mol/s water and 1×10^{19} mol/s NO_2 through the reaction tube, the intensity of the $v = 0$ spectrum was found to be almost equal for the two sources. However, the optimum intensity ratio between the $v = 1$ and $v = 0$ spectra was 1·5 per cent and 6 per cent for the type (a) and type (b) sources, respectively. The maximum intensities were obtained for both sources when the distance between the end of the source tube and the skimmer was as short as possible, sometimes the skimmer was even inside the tube. Since the tube diameter of the type (b) source is larger the beam could be skimmed in the region where the reaction between atomic hydrogen and NO_2 took place. A displacement of a few millimeters of the skimmer downstream from the reaction zone reduced the intensity of the $v = 1$ spectrum considerably, while the intensity of the $v = 0$ spectrum was almost unchanged. This phenomenon can be understood by assuming that a large fraction of the OH radicals formed in the reaction is produced in excited vibrational states. The OH molecules cascade down the vibrational ladder by collisions with the gas molecules and the walls inside the reaction tube. Since the ratio of the number of OH radicals in the $v = 1$ and $v = 0$ state depends so strongly on the geometry of the source and skimmer it is not very sensible to define a vibrational temperature for the OH molecules in the beam. The $v = 2$ state of OH has only been investigated with the type (b) source and its spectrum was approximately 2·4 times weaker than the $v = 1$ spectrum. These results show that a beam of vibrationally excited OH radicals can be produced quite efficiently using the reaction between H and NO_2, while it is even competitive with the production by ozone reactions used by other investigators [5, 7] or by reaction with F_2O [4].

The microwave power for inducing the transitions was obtained from two Varian backward wave oscillators (BWO) type VA-183GA and VA-185M for

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the region 1–2 GHz and 4–8 GHz, respectively. The most prominent features
of these BWO's are the flat power response as a function of the frequency and
the helix voltage as the only tuning element which completely determines the
frequency. These features enabled searches for lines over wide frequency
regions, 100 MHz or more. Since the instrumental linewidth of the electric
resonance spectrometer varies between 8 and 25 kHz such a large frequency
region can not normally be covered in a single scan. The reason is that the
lines are wiped out by a fast scan (e.g. 20 kHz is scanned in about 10^{-2} s). A
way out is line broadening by a random frequency modulation of the microwave
power from the BWO, for example by superimposing a white noise voltage upon
the helix voltage. This method of line broadening does not affect its peak
intensity. The linewidth is controlled by the RMS value of the voltage from
the noise generator. We were able to broaden the spectral lines up to 20 MHz
allowing a scan over 150 MHz in 50 s when the RC-time of the lock-in
amplifier was 1 s. Once a line was located roughly from a wide scan an accurate
frequency measurement was performed with the normal linewidth. For this
measurement the BWO frequency was stabilized by phase locking the 30 MHz
beat signal between the BWO frequency and that of a Hewlett-Packard 8660B
synthesizer to a 30 MHz reference signal by means of a Schomandl FDS 30
syncriminator.

The signal-to-noise of the transitions originating in the excited vibrational
states of OH was smaller than unity at an RC time of 1 s, which forced us to use
signal averaging techniques. For this purpose a Hewlett–Packard 5480B signal
analyser has been interfaced either directly with the power supply of the helix
voltage for wide scans or with the HP synthesizer for narrow scans. The
typical time for a single scan over a spectral region was 50 s with RC of the lock-in
set at 1 s, while usually 0·5 and 1·5 hour of signal averaging was required for the
spectra from the $v = 1$ and $v = 2$ states, respectively. Figure 3 shows the strongest
transitions observed in the $v = 0$, 1 and 2 states of OH. The search for the
spectra originating in the excited vibrational states of OH was only possible by
using the combination of the wide frequency region scan facility and the averaging
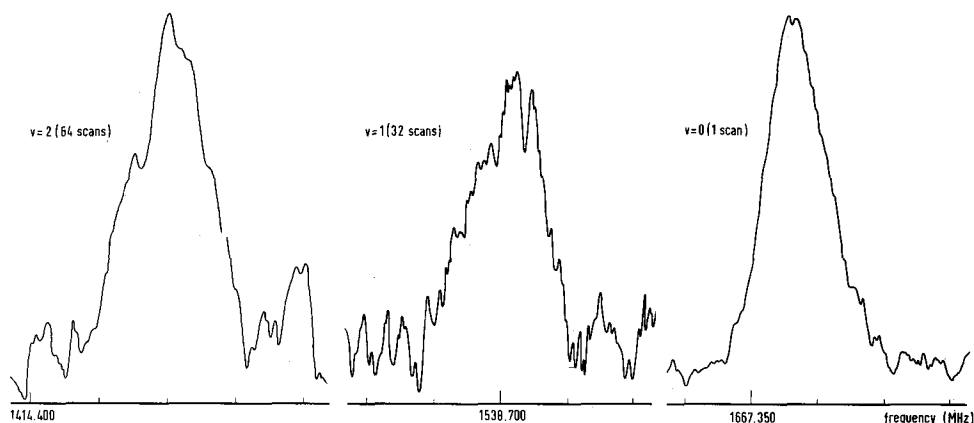techniques.

Figure 3.   Spectral lines of the $^2\Pi_{3/2}$, $J = 3/2$, $F = 2 \to 2$ transition in the $v = 0$, 1 and 2
vibrational states of OH.   Separation between markers is 10 kHz.

3. THEORY

Since the theory used for the interpretation of the high resolution microwave spectrum of OH has been discussed in detail previously [1, 8, 16], only a short summary is given here. The hamiltonian for the microwave spectra of open shell molecules can be written formally as

$$H = H_{\mathrm{F}} + H_{\mathrm{hf}}, \tag{1}$$

where H_{F} contains the spin-orbit, rotational and gyroscopic terms which give rise to the Λ-splitting ; H_{hf} describes the hyperfine contributions induced by the interactions between the magnetic moments associated with the nuclear spin (**I**) and the orbital (**L**) and spin (**S**) angular momenta of the electrons. The explicit form of H_{F} and H_{hf} can be found in a previous paper [8]. The coupling scheme for the electronic and rotational part of the wavefunctions used here is Hund's case (a). The basis wavefunctions symmetrized with respect to a reflection (σ_{xz}) of the coordinates and spins of all particles in a plane containing the nuclei can be expressed as

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

where $\Omega = \Lambda + \Sigma$ is taken to be positive ; Λ, Σ, Ω is the projection on the molecular axis of **L**, **S** and **J**, respectively, with **J** as the total angular momentum excluding nuclear spin. The Kronig symmetry of the functions of equation (2) is ± 1, the eigenvalues of the operator $\sigma_{xz}(\sigma_{xz}|{}^{2}\Pi_{\Omega}{}^{\pm}\ J\rangle = \pm\,|{}^{2}\Pi_{\Omega}{}^{\pm}\ J\rangle)$. The total wavefunction $|{}^{2}\Pi_{\Omega}{}^{\pm}\ JIF\rangle$ including the nuclear part is constructed as a product of the functions $|{}^{2}\Pi_{\Omega}{}^{\pm}\ J\rangle$ and the nuclear spin functions $|IM_{I}\rangle$ according to the coupling scheme $\mathbf{F} = \mathbf{J} + \mathbf{I}$, where **F** is the total angular momentum.

The OH molecule can be described by a coupling which is intermediate between Hund's case (a) and (b). The proper energies are obtained automatically by solving the secular equation. This equation can be set up using a degenerate perturbation calculation [17, 18]. The dimension of the secular equation is two in the absence of hyperfine effects and $2(2I+1)$ if hyperfine contributions diagonal and off-diagonal in J are included. The relevant equations discussed in earlier studies [1, 8, 16, 17] are summarized below. In these equations the generally accepted notation for the Λ-doubling constants p and q [19] and for the hyperfine structure constants a, b, c and d [20] is used. This is felt necessary to achieve a more uniform notation. However, while Mulliken and Christy [19] and Frosch and Foley [20] define the parameters in terms of expressions from second and first order perturbation theory, respectively, our definitions contain also contributions from higher order perturbations. The matrix elements for the hamiltonian of equation (1) containing contributions up to fourth order take the form :

$$\langle {}^{2}\Pi_{1/2}{}^{\pm}\ JIF|H|{}^{2}\Pi_{1/2}{}^{\pm}\ J'IF\rangle$$
$$= \delta_{JJ'}[-1/2A_{\Pi_{v}} + B_{\Pi_{v}}(J+1/2)^{2} \pm (-1)^{J-1/2}(J+1/2)\{(1/2p_{v}+q_{v})$$
$$+ D_{p_{v}}(J+1/2)^{2} + \delta_{p_{v}}(J+1/2)^{4}\}] + G(J, J', I, F)$$
$$\times \left[(-1)^{J'-1/2}\begin{pmatrix} J & 1 & J' \\ -1/2 & 0 & 1/2 \end{pmatrix}\{(a_{v}-1/2(b_{v}+c_{v})) + \delta_{JJ'}2C_{I,v}z^{2}\}\right.$$
$$\left.\pm \frac{(-1)}{\sqrt{2}}\begin{pmatrix} J & 1 & J' \\ -1/2 & 1 & -1/2 \end{pmatrix}(d_{v}+\delta_{JJ'}D_{d,v}z^{2})\right], \tag{3}$$

$$\langle {}^2\Pi_{3/2}{}^{\pm} \; JIF|H|{}^2\Pi_{3/2}{}^{\pm} \; J'IF\rangle = \delta_{JJ'} \; [1/2A_{\Pi_v} + B_{\Pi_v}((J+1/2)^2 - 2)$$

$$\pm (-1)^{J-1/2} \; z^2(J+1/2)D_{q_v}] + G(J, J', I, F)(-1)^{J'-1/2}$$

$$\times \begin{pmatrix} J & 1 & J' \\ -3/2 & 0 & 3/2 \end{pmatrix} \{(a_v + 1/2(b_v + c_v)) + \delta_{JJ'} \cdot 2/3C_{I_v}z^2\}, \qquad (4)$$

$$\langle {}^2\Pi_{3/2}{}^{\pm} \; JIF|H|{}^2\Pi_{1/2}{}^{\pm} \; J'IF\rangle$$

$$= \delta_{JJ'} \cdot z[B_{\Pi_v} \pm (-1)^{J-1/2}(J+1/2)\{1/2q_v + D_{q_v}(J+1/2)^2 + \delta_{q_v}$$

$$\times (J+1/2)^4\}] + G(J, J', I, F)(-1)^{J'+1/2} \begin{pmatrix} J & 1 & J' \\ -3/2 & 1 & 1/2 \end{pmatrix}$$

$$\times \frac{1}{\sqrt{2}} \{b_v \pm \delta_{JJ'} \cdot (-1)^{J-1/2}(J+1/2)C'_{I_v}\}, \qquad (5)$$

where

$$G(J, J', I, F) = [(2J+1)(2J'+1)I(I+1)(2I+1)]^{1/2}(-1)^{J+I+F} \begin{Bmatrix} F & J & I \\ 1 & I & J' \end{Bmatrix}$$

and $z = \sqrt{(J-1/2)(J+3/2)}$. In these expressions the third-order hyperfine constants C_{I_v}, D_{d_v} and C'_{I_v} replace the constants $X_5 + X_7$, X_6 and X_9 defined in the original work [17] similar to recent work of Coxon *et al.* [29]; A_{Π_v} represents the spin-orbit coupling constant, B_{Π_v} is the rotational constant while the other coupling constants D_{p_v}, δ_{p_v}, D_{q_v} and δ_{q_v} are third- and fourth-order Λ-doubling parameters discussed by Meerts [1]. The centrifugal distortion contributions were included by taking the square of the pure rotational matrix and multiplying the result by $-D_{\Pi_v}$ [21].

It was shown by Meerts [1] that this model discussed is capable of explaining all the available high precision microwave data of the vibrational ground state of OH. In the present study we shall use the model to deduce the molecular constants in the excited vibrational states of OH from the corresponding experimental spectra.

4. EXPERIMENTAL RESULTS

All the transitions observed are electric dipole transitions between hyperfine sublevels in zero electric and magnetic fields from a (+) Kronig symmetry level to a (−) Kronig symmetry level within one rotational state. The spectra of the $v = 1$ and $v = 2$ vibrational states of OH were investigated in the rotational levels $J = 1/2$ and $3/2$ of the ${}^2\Pi_{1/2}$ state and in the rotational levels $J = 3/2$ and $5/2$ of the ${}^2\Pi_{3/2}$ state. The observed transition frequencies are reproduced in table 1. The molecular constants for each vibrational state were adjusted in a least squares fit of the observed spectra to the spectra calculated using the theory outlined in the previous section. However, not all the necessary constants could be determined from only Λ-doubling spectra. We have taken the B_{Π_v} and D_{Π_v} constants from Veseth's [22] analysis of the U.V. spectra measured by Dieke and Crosswhite [23]. Our rotational hamiltonian including distortional effects is equivalent to that of Veseth [22].

Table 1. Observed and calculated hyperfine Λ-doubling transitions of OH in the $v = 1$ and $v = 2$ vibrational states.

Electronic state	J	F_{+}†	F_{-}	$v = 1$ Observed frequency (MHz)	$v = 1$ Observed − calculated frequency (kHz)	$v = 2$ Observed frequency (MHz)	$v = 2$ Observed − calculated frequency (kHz)
$^2\Pi_{1/2}$	1/2	1	1	4537·381 (5)	−0·1	4319·938 (5)	−0·2
		0	1	4449·064 (5)	0·1	4233·346 (5)	0·1
		1	0	4553·998 (5)	0·1	4338·543 (6)	0·1
$^2\Pi_{1/2}$	3/2	1	1	7467·323 (8)	3·9	7160·046 (7)	0·7
		2	2	7522·842 (6)	2·5	7212·791 (6)	0·8
		2	1	7454·592 (6)	−2·3	7146·208 (6)	−0·6
		1	2	7535·563 (5)	−1·6	7226·627 (5)	−0·4
$^2\Pi_{3/2}$	3/2	1	1	1536·944 (3)	−2·0	1412·850 (3)	−0·9
		2	2	1538·702 (3)	−0·4	1414·424 (3)	0·9
		2	1	1489·438 (3)	1·2	1371·377 (3)	0·0
		1	2	1586·213 (3)	1·2	1455·896 (3)	0·0
$^2\Pi_{3/2}$	5/2	2	2	5594·246 (5)	1·4	5168·657 (6)	−1·8
		3	3	5598·168 (5)	−0·3	5172·192 (6)	−4·6
		2	3	5583·476 (7)	−1·1	5161·489 (7)	4·4
		3	2	5608·935 (6)	−0·8	5179·376 (8)	5·7

† The subscript $+ (-)$ refers to the even (odd) Kronig symmetry.

The OH molecule is described properly in a Hund's case intermediate between (a) and (b) resulting in a strong mixing between the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ states determined by the value of the parameter $\lambda_v (\equiv A_{\Pi_v}/B_{\Pi_v})$ and the rotational quantum number. For the $v = 0$ state it was possible [1] to determine an effective value for λ_0 because data from many rotational levels were available. This was not possible for the $v = 1$ and $v = 2$ states as only a limited number of rotational levels have been investigated. The value of λ_v for these states has been fixed in the least squares fit at the values obtained by extrapolation from the $v = 0$ value [1] using the vibrational effects in A_{Π_v} and B_{Π_v} as deduced by Veseth [22].

Because transitions in only a few low J levels have been observed in the $v = 1$ and $v = 2$ states the fourth order Λ-doubling parameters δ_{p_v} and δ_{q_v} were assumed to be zero. All other molecular parameters for $v = 1$ and $v = 2$ could be determined from the observed spectra. The results are given in table 2 together with the values used for B_{Π_v}, D_{Π_v} and λ_v. In this table we list the value for $(b_v + \frac{1}{3}c_v)$ rather than b_v because $(b_v + \frac{1}{3}c_v)$ is proportional to the Fermi contact term [8] and has consequently a more direct physical significance than b_v itself. The differences between the calculated spectra using the best fit constants from table 2 and the observed frequencies are given for both the $v = 1$ and $v = 2$ states in table 1. The differences lie within the quoted experimental accuracy. For comparison the coupling constants for the $v = 0$ state are also reproduced in table 2.

Table 2. Molecular constants of OH in the $v=0$, 1 and 2 vibrational states and the vibrational dependences derived from the present investigation (all values in MHz).

Quantity	$v=0$†	$v=1$†	$v=2$†	O_e	$O^{(1)}$	$O^{(2)}$
B_{Π_v}‡	556100·0	534827·0	513664·0			
D_{Π_v}‡	57·1	56·0	54·9			
λ_v§	$-7\cdot4794$	$-7\cdot7893$	$-8\cdot1230$			
p_v	7052·600 (4)	6734·080 (9)	6411·516 (9)	7210·344	$-314\cdot48$	$-2\cdot02$
q_v	$-1160\cdot298$ (1)	$-1107\cdot200$ (2)	$-1054\cdot166$ (2)	$-1186\cdot871$	53·162	$-0\cdot032$
D_{p_v}	$-0\cdot1122$ (6)	$-0\cdot112$ (1)	$-0\cdot123$ (1)			
D_{q_v}	0·2206 (1)	0·2080 (2)	0·2027 (3)			
a_v	86·011 (6)	81·976 (9)	78·035 (9)	88·064	$-4\cdot129$	0·047
$b_v+\frac{1}{3}c_v$	$-73\cdot746$ (43)	$-77\cdot679$ (43)	$-82\cdot518$ (57)	$-72\cdot119$	$-3\cdot03$	$-0\cdot45$
c_v	131·681 (42)	126·346 (42)	121·194 (56)	134·417	$-5\cdot518$	0·092
d_v	56·632 (8)	53·774 (14)	50·990 (16)	58·089	$-2\cdot932$	0·037
C_{I_v}	$-0\cdot100$ (3)	$-0\cdot099$ (3)	$-0\cdot097$ (4)			
C'_{I_v}	0·0166 (4)	0·010 (6)	0·008 (6)			
D_{d_v}	$-0\cdot0226$ (6)	$-0\cdot026$ (6)	$-0\cdot022$ (6)			

† The uncertainties in the molecular constants represent one standard deviation, based on a confidence level of the fit of 95 per cent.
‡ Parameter held fixed at this value [22].
§ See text.

Table 3. Experimental Λ-splittings (ν_Λ) in the $J=3/2$ and $J=5/2$ rotational levels of the $^2\Pi_{3/2}$ state.

		$v=0$	$v=1$	$v=2$†	$v=3$†	$v=4$†
$J=3/2$	present work	1666·625 (10)	1538·044 (10)	1413·833 (10)	1294·12 (10)	1178·80 (30)
	Clough et al. [5]	1666·20 (20)	1537·84 (30)	1413·46 (30)	1293·23 (30)	1176·37 (30)
	Lee et al. [6]	1666·5 (1·3)	1537·1 (1·5)	1413·5 (1·5)	1293·1 (1·5)	1176·2 (1·5)
$J=5/2$	present work	6033·282 (30)	5596·533 (30)	5170·723 (30)	4756·75 (30)	4354·59 (90)
	Clough et al. [5]	6032·0 (1·5)	5593·3 (1·5)		4751·3 (2·0)	4346·3 (2·0)

† The values from the present investigation for $v=3$ and $v=4$ are obtained using extrapolated values of the Λ-doubling constants from table 2.

5. DISCUSSION

In the Born–Oppenheimer approximation it is assumed that the average value for an arbitrary operator O of a diatomic molecule in a given electronic state is a function of the internuclear distance (R) only. Expanding O in a Taylor series about R_e yields

$$\langle O \rangle = O_e + O_e' R_e \langle \xi \rangle + \tfrac{1}{2} O_e'' R_e^2 \langle \xi^2 \rangle + \dots \quad (6)$$

The primed quantities are the successive derivatives of the operator O with respect to R at the equilibrium internuclear distance R_e, $\xi = (R - R_e)/R_e$, and O_e is the expectation value at $R = R_e$. Using Dunham's rotation-vibration theory [24] and restricting the problem to the vibrational dependence equation (6) can be approximated by

$$\langle O \rangle_v \simeq O_e + O^{(1)}(v + \tfrac{1}{2}) + O^{(2)}(v + \tfrac{1}{2})^2. \quad (7)$$

Generally $O^{(2)}$ is much smaller than $O^{(1)}$. Consequently for the discussion of the vibrational effects, that is the dependence of the molecular constants on the internuclear distance, we will consider only O_e and $O^{(1)}$. This restriction is legitimate because, as will be shown later, the theoretical predictions for the vibrational behaviour of both the Λ-doubling and the hyperfine structure constants are only in agreement with the experimental results to first order and are yet far from capable of explaining higher order effects described by $O^{(2)}$. However, for an accurate calculation of the molecular constants relevant, for example for prediction of transitions in higher vibrational states, the effect of $O^{(2)}$ cannot be neglected. In table 2 are listed O_e, $O^{(1)}$ and $O^{(2)}$ determined from a fit of the $v = 0$, 1 and 2 constants to equation (7) for p_v, q_v, a_v, $(b_v + \tfrac{1}{3}c_v)$, c_v and d_v. Only for the first-order Λ-doubling and hyperfine coupling constants is the experimental error small enough to extract significant vibrational effects. It is interesting to note that the relative vibrational effect $(O^{(1)}/O_e)$ is almost the same for both the Λ-doubling and the hyperfine structure constants. Predictions of the frequencies of the hyperfine Λ-doubling transitions in the $^2\Pi_{3/2}$, $J = 3/2$, $v = 3$ and $v = 4$ states based on the constants of table 2 have been given in a separate paper [25].

5.1. *The lambda doubling constants p and q*

Previous investigations of the E.P.R. spectrum of vibrationally excited OH in the $J = 3/2$ and $J = 5/2$ rotational levels of the $^2\Pi_{3/2}$ state [5, 6] yielded the experimental values for the zero field Λ-doublet splittings in these states. The results, together with the values deduced from the present investigation, are given in table 3. The agreement is reasonable although the E.P.R. values tend to be somewhat lower than the electric resonance data. Rather than expressing the Λ-splitting in p_v and q_v Clough *et al.* [5] deduced this splitting by solving a 3×3 secular matrix involving the lowest electronically excited $A^2\Sigma^+$ state [26, 27] and the $X^2\Pi_{1/2}$ and $X^2\Pi_{3/2}$ states. In this solution the matrix elements $\langle \Pi v | AL_+ + 2BL_+ | \Sigma v \rangle$ and $\langle \Pi v | BL_+ | \Sigma v \rangle$ were considered as fit parameters for each vibrational state and were varied until the best agreement was obtained with the observed splittings. The best fit parameters in this procedure may be considered as effective matrix elements. Since separate values for those matrix elements cannot be obtained from Λ-splitting in the

Table 4. Lambda-doubling constants p_v, p_e and q_v, q_e (all in MHz), the value for $O^{(1)}/O_e$ (dimensionless), and the average internuclear distance R (in Å).

Quantity	$v=0$	$v=1$	$v=2$	$v=3$	$v=4$	O_e‖	$O^{(1)}/O_e$ (per cent)‖
R†	0.9791	0.9984	1·0187	1·0385	1·0583		
p_v Present work	7025·600	6734·080	6411·516	6084·91‡	5762·85‡	7216·36	−4·47
Observed [5]	7045	6895	6775	6625	6476	7115	−2·0
Calculated [9]	7255	6985	6835	6625	6296	7369	−3·1
Calculated§ [10]	6922	6673	6455			7034	−3·3
q_v Present work	−1160·298	−1107·200	−1054·166	−1001·20‡	−948·15‡	−1186·78	−4·47
Observed [5]	−1160	−1097	−1034	−974	−908	−1191	−5·3
Calculated [9]	−1172	−1118	−1085	−1046	−995	−1190	−3·6
Calculated§ [10]	−1141	−1084	−1035			−1166	−4·5

† Calculated from the rotational constants quoted by Veseth [22] for $v=0$ through $v=2$ and extrapolated from these results to $v=3$ and 4.
‡ Values predicted by extrapolation from results of table 2 and equation (7).
§ Deduced from the *ab initio* calculations for OD [10] by isotopic substitution.
‖ The values for O_e and $O^{(1)}/O_e$ have been determined from a least squares fit of the data for $v=0$ through $v=4$ to a straight line.
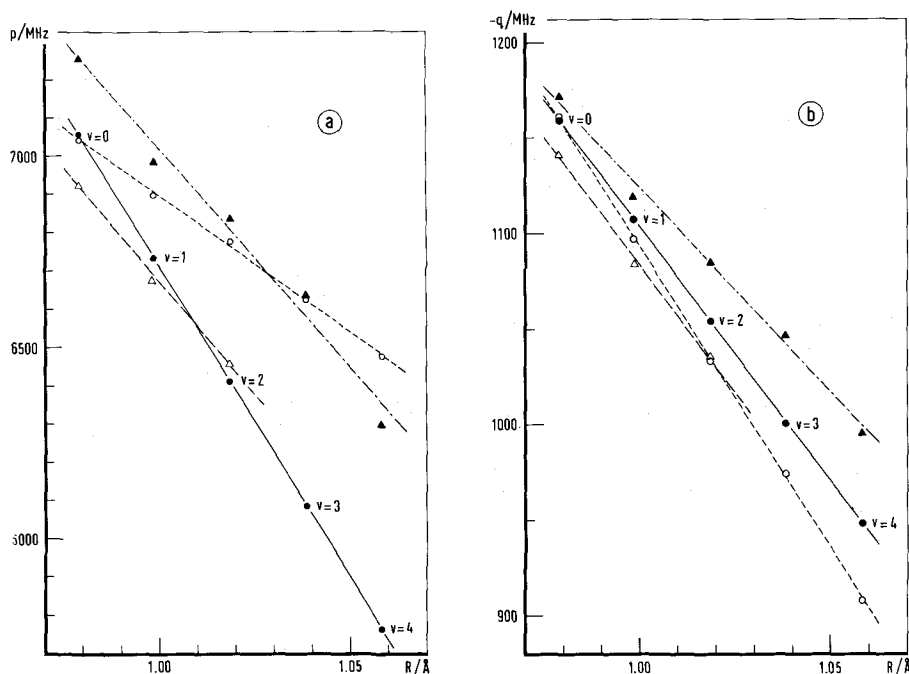
Figure 4. The Λ-doubling constants p (a) and q (b) as a function of the average internuclear distance R with ● for : observed in the present investigation, the values for $v=3$ and $v=4$ are obtained by extrapolation from table 2 ; ○ for : results of Clough et al. [5] ; ▲ for : ab initio calculations of Hinkley et al. [9] ; △ for : values obtained by isotopic substitution from the ab initio calculations for OD by Coxon and Hammersley [10].

$^2\Pi_{3/2}$ state alone Clough et al. assumed the vibrational dependence of $\langle \Pi v | AL_+ + 2BL_+ | \Sigma v \rangle$ to be the same as that of the diagonal matrix element $(A_\Pi + 2B_\Pi)_v$. Only the value of $\langle \Pi v | BL_+ | \Sigma v \rangle$ was then varied in the fit. Values for p_v and q_v can be deduced from these matrix elements and the results [9] are shown in table 4 and also in figure 4 which displays clearly their v-dependence. It is seen from this figure that p_v and q_v deduced from the results of Clough et al. deviate systematically from the values obtained in the present investigation. The most likely explanation of these deviations is an unsatisfactory vibrational dependence of $\langle \Pi v | AL_+ + 2BL_+ | \Sigma v \rangle$ adopted by Clough et al. [5].

Ab initio calculations of p_v and q_v defined as

$$p_v = 2 \sum_{v'} \frac{\langle \Pi v | AL_+ | \Sigma v' \rangle \langle \Pi v | BL_+ | \Sigma v' \rangle}{E_{\Pi v} - E_{\Sigma v'}}, \tag{8}$$

$$q_v = 2 \sum_{v'} \frac{|\langle \Pi v | BL_+ | \Sigma v' \rangle|^2}{E_{\Pi v} - E_{\Sigma v'}}, \tag{9}$$

have been performed by Hinkley et al. [9, 28]. In these definitions $(E_{\Pi v} - E_{\Sigma v'})$ is the energy separation between the $X^2\Pi v$ and the $A^2\Sigma^+v'$ states, the only states taken into account. Hinkley et al. assumed that the electronic and nuclear

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motions are completely separable and the expressions (8) and (9) reduce to

$$p_v = 2\langle AL_+ \rangle \langle L_+ \rangle \sum_{v'} \frac{\langle v|v' \rangle \langle v|B|v' \rangle}{E_{vv'}} \tag{10}$$

and

$$q_v = 2\langle L_+ \rangle^2 \sum_{v'} \frac{\langle v|B|v' \rangle^2}{E_{vv'}}, \tag{11}$$

where $\langle AL_+ \rangle$, $\langle L_+ \rangle$ and $E_{vv'}$ are abbreviations for $\langle \Pi|AL_+|\Sigma \rangle$, $\langle \Pi|L_+|\Sigma \rangle$ and $(E_{\Pi v} - E_{\Sigma v'})$, respectively. The off-diagonal electronic matrix elements $\langle AL_+ \rangle$ and $\langle L_+ \rangle$ were calculated at R_e only and all two-centre integrals were neglected. Restricted Hartree–Fock (RHF) orbitals computed for the electronic ground state were employed in constructing the wavefunctions for the $A^2\Sigma^+$ state (invariant orbital approximation). The Franck–Condon factors $\langle v|v' \rangle$, the expectation values of $\langle v|B|v' \rangle$ and $E_{vv'}$ were computed using numerical vibrational wavefunctions obtained from Rydberg–Klein–Rees (RKR) potential curves. The calculated values for p_v and q_v are given in table 4 and plotted in figure 4 assuming that the electronic matrix elements were independent of R.

Coxon and Hammersley [10] performed more accurate *ab initio* calculations for p_v and q_v for the OD radical defined as (see equations (8) and (9))

$$p_v = 2 \sum_{v'} \frac{\langle AL_+ \rangle_{\bar{R}_{vv'}} \langle v|v' \rangle \langle L_+ \rangle_{R_{\mathrm{eff}}} \langle v|B|v' \rangle}{E_{vv'}} \tag{12}$$

and

$$q_v = 2 \sum_{v'} \frac{\langle L_+ \rangle_{R_{\mathrm{eff}}}^2 \langle v|B|v' \rangle^2}{E_{vv'}}. \tag{13}$$

Herein $\langle L_+ \rangle_{R_{\mathrm{eff}}}$ and $\langle AL_+ \rangle_{\bar{R}_{vv'}}$ is the value of $\langle L_+ \rangle$ at an effective internuclear distance $(R_{\mathrm{eff}} = \langle v|1/R|v' \rangle / \langle v|1/R^2|v' \rangle)$ and of $\langle AL_+ \rangle$ at the R-centroid $(\bar{R}_{vv'})$, respectively, for each vibrational state v'. Using a different set of RHF orbitals for each electronic state the off-diagonal matrix elements $\langle L_+ \rangle$ and $\langle AL_+ \rangle$ were calculated over a much larger range of internuclear distances than the region $R_{v=0}$ to $R_{v=4}$ to allow for an R-dependence. Two-centre integrals were taken into account for $\langle L_+ \rangle$ but not for the spin-orbit integrals $\langle AL_+ \rangle$. The former quantity was found to be nearly independent of R, while $\langle AL_+ \rangle$ varied considerably and showed an almost linear dependence on R. All expectation values over vibrational wavefunctions were obtained from RKR curves.

To profit from the higher accuracy of the *ab initio* calculations by Coxon and Hammersley, their results for OD were converted to OH by isotopic substitution [8] and are shown in table 4 and figure 4. Only a small error in the absolute magnitudes is introduced in this way. However, the most interesting feature, the vibrational dependence is practically unaffected.

From table 4 and figure 4 (*b*) it follows that the *ab initio* results of Coxon and Hammersley for q_v are somewhat lower than those of Hinkley *et al.* The dependence of q_v on the internuclear distance as found by Coxon and Hammersley agrees very well with the results of the present investigation (figure 4 (*b*)). This is most probably a consequence of the fact that Coxon and Hammersley allowed for the R-dependence and included two-centre integrals in their calculations of $\langle L_+ \rangle$.

It is seen from table 4 and figure 4 (*a*) that the *ab initio* results of Hinkley *et al.* for p_v are also somewhat too high. Coxon and Hammersley concluded that the invariant orbital approximation applied by Hinkley *et al.* is responsible for the value of p_v being too high, and also that of q_v. The *ab initio* calculations of both Hinkley *et al.* [9] and of Coxon and Hammersley [10] show a weaker *R*-dependence than observed experimentally. However, the vibrational dependence of p_v found by Coxon and Hammersley is in slightly better agreement with the experimental results than that found by Hinkley *et al.* as expected from the arguments given for q_v. The remaining difference between the *ab initio* calculations of Coxon and Hammersley and the experimentally observed *R*-dependence in p_v might be due to the neglect of two-centre spin-orbit integrals in the evaluation of $\langle AL_+ \rangle$. . A similar argument was used by Coxon and Hammersley to explain discrepancy between their *ab initio* values for A_v of OD and the experimental results [10].

The overall agreement between the *ab initio* calculations of p_v and q_v and the experiment is satisfactory indicating that extended *ab initio* calculations can be used to predict Λ-splittings in various vibrational states with an accuracy of about 1 per cent.

5.2. *The hyperfine structure constants*

The magnetic hyperfine constants a_v, $(b_v + \frac{1}{3}c_v)$, c_v and d_v are proportional to $\langle 1/r^3 \rangle_U$, $\langle \psi^2(0) \rangle_U$, $\langle (3\cos^2 \chi - 1)/r^3 \rangle_U$ and $\langle \sin^2 \chi/r^3 \rangle_U$, respectively [8]. The last four quantities are related to the properties of the unpaired π-electron. Their values deduced from the results of table 2 for the different vibrational states are given in table 5 together with the value at R_e and the relative vibrational changes $(O^{(1)}/O_e)$.

Table 5. Hyperfine structure constants (in units of 10^{24} cm^{-3}, except $O^{(1)}/O_e$ which is dimensionless).

Quantity		$v = 0$†	$v = 1$†	$v = 2$†	O_e	$O^{(1)}/O_e$ (per cent)
$\langle 1/r^3 \rangle_U$	obs	1·089	1·038	0·988	1·115	−4·7
	calc‡	0·993	0·945	0·896	1·015	−4·4
$\langle (3\cos^2 \chi - 1)/r^3 \rangle_U$	obs	1·112	1·067	1·023	1·135	−4·1
	calc‡	1·022	0·990	0·957	1·038	−2·9
$\langle \sin^2 \chi/r^3 \rangle_U$	obs	0·478	0·454	0·431	0·490	−5·0
	calc‡	0·320	0·299	0·278	0·330	−6·0
$\langle \Psi^2(0) \rangle_U$	obs	−0·111	−0·117	−0·125	−0·109	+4·2
	calc‡	−0·105	−0·109	−0·113	−0·103	+3·7

† The corresponding internuclear distances are given in table 4.
‡ Kayama [11].

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Kayama [11] has performed *ab initio* LCAO MO CI calculations in which he
determined the magnetic hyperfine structure constants at two different inter-
nuclear distances R_e and $1{\cdot}0584$ Å ($\equiv R_1$). Table 5 summarizes the predicted
values for the $v = 0$, 1 and 2 states obtained by interpolation between R_e and
R_1 using the relation

$$O(R) = O(R_e) + (R - R_e) \frac{O(R_1) - O(R_e)}{R_1 - R_e}, \qquad (14)$$

where $O(R_e) \equiv O_e$, while R in each vibrational state has been deduced from the
corresponding rotational constants B_{Π_v}. The calculated values for $\langle 1/r^3 \rangle_U$,
$\langle (3\cos^2 X - 1)/r^3 \rangle_U$ and $\langle \psi^2(0) \rangle_U$ at the equilibrium distance agree quite well
with the experimental values. The calculated value of $\langle \sin^2 X/r^3 \rangle_U$ deviates,
however, considerably from the experimental results for all vibrational states
and for the equilibrium distance. The reason of this disagreement is not clear.
The rather strong variation with the internuclear distance of these four quantities
predicted by Kayama's calculations is very well confirmed experimentally.
This can be clearly seen from the $(O^{(1)}/O_e)$ column of table 5.

In summary the present measurements show a gratifying agreement with the
vibrational dependence of the Λ-doubling and hyperfine constants of OH pre-
dicted by the *ab initio* calculations.

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