ON THE MICROWAVE SPECTRUM OF THE X $^2\Pi$ STATE OF THE HYDROXYL RADICAL

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A refit of the observed hyperfine Λ-doubling spectrum of OH is presented using an expansion of the fine structure matrix elements in a power series up to the fifth degree in the rotational quantum number J. Almost all observed transitions of the microwave spectrum of the OH molecule in the X $^2\Pi$ state could be predicted within their experimental inaccuracies. Reliable predictions for the non-observed transitions originating in the rotational states for $J \leqslant 17/2$ are also presented.

1. Introduction

The interpretation of high resolution spectra of diatomic molecules in a $^2\Pi$ state as obtained with molecular beam techniques requires a more refined theoretical description than used for the interpretation of the microwave absorption spectra [1]. The spectra of the NO molecule obtained by the molecular beam electric resonance spectroscopy were interpreted in a previous paper [2] using a degenerate perturbation calculation introduced by Freed [3]. However, the calculated and observed spectra could not be brought into agreement within the experimental accuracies.

The hyperfine Λ-doubling spectrum of the ground electronic $^2\Pi$ state of the OH radical has recently been investigated experimentally and theoretically by Meerts and Dymanus [4]. The spectrum was calculated using the perturbation theory developed up to third order in fine and hyperfine structure. In the final fit also spectra obtained by other investigators were included [5–9]. The agreement between the calculated and observed transition frequencies of the OH molecule was found to be quite unsatisfactory. Differences between the predicted and measured frequencies were for some transitions as large as 100 times the experimental precision. Recently observed transitions by Destombes et al. [10] originating in the higher rotational states $J = 11/2$ through 15/2 of OH showed even larger discrepancies with the calculated spectrum.

In a refit of the spectrum of the NO molecule [11], excellent agreement between the measured and predicted spectrum was achieved. In this refit the third order perturbation theory was applied and hyperfine contributions originating from the matrix elements off-diagonal in the rotational quantum number (J) were included. Unfortunately this approach failed to remove the discrepancies between the observed and calculated spectrum of OH. This can, however, be easily understood by simple order of magnitude consideration. The magnitude of the contributions off-diagonal in J is determined by $\langle H_{hf}\rangle^2/4B_\Pi$, where $\langle H_{hf}\rangle$ is the average hyperfine structure contribution and B_Π the rotational constant of the molecule in its $^2\Pi$ state. For the NO molecule $\langle H_{hf}\rangle^2/4B_\Pi$ is approximately 35 kHz, for OH this quantity is only 3 kHz. On the other hand, the fine structure (Λ-doubling) in OH is rather large: the second order Λ-splitting coupling constants are 600–2200 MHz, while the third order constants are still about 200 kHz. So it is plausible that the fourth order fine structure contributions are not negligible in OH, especially in the higher rotational states ($J \geqslant 7/2$).

The present work gives an extension of the previous perturbation calculations [2,4] in order to include the major part of the fourth order Λ-splitting effects in an easy and straightforward way without going into detail of the extremely complicated fourth order perturbation calculation. It has been achieved by expanding the Λ-splitting parameters in a power

series of $(J + \frac{1}{2})$. The available experimental transition frequencies of OH, which cover rotational states from $J = 1/2$ to $13/2$ of the $^2\Pi_{1/2}$ state and from $J = 3/2$ to $15/2$ of the $^2\Pi_{3/2}$ state were used in a least squares fit to determine the fine and hyperfine coupling constants. An excellent agreement between the experimental and calculated spectrum of the OH molecule was obtained. Furthermore all the non-observed hyperfine Λ-doubling transitions of the OH radical originating in the rotational states with $J \leqslant 17/2$ were calculated with estimated uncertainty of 20–40 kHz.

2. Theory

The perturbation calculations up to third order in fine and hyperfine structure were discussed in previous papers [2,4] for contributions diagonal in the rotational quantum number J. The results of ref. [11] have been used as far as the hyperfine structure is concerned for both diagonal and off-diagonal contributions in J. It was found in ref. [2] that the matrix elements due to the Λ-splitting in a $^2\Pi$ state up to third order are expressible as a power series in $(J + \frac{1}{2})$:

$$\langle ^2\Pi^{\pm}_{1/2} J | H_F | ^2\Pi^{\pm}_{1/2} J \rangle$$
$$= \pm (-)^{J-1/2}(J + \tfrac{1}{2})[p + D_p(J + \tfrac{1}{2})^2],$$
$$\langle ^2\Pi^{\pm}_{1/2} J | H_F | ^2\Pi^{\pm}_{3/2} J \rangle \qquad\qquad (1)$$
$$= \pm (-)^{J-1/2} z (J + \tfrac{1}{2})[q + D_q(J + \tfrac{1}{2})^2],$$
$$\langle ^2\Pi^{\pm}_{3/2} J | H_F | ^2\Pi^{\pm}_{3/2} J \rangle = \pm (-)^{J-1/2} z^2 (J + \tfrac{1}{2}) D_q,$$

where $z = [(J - \frac{1}{2})(J + \frac{3}{2})]^{1/2}$. The coupling constants p, D_p, q and D_q are expressible in terms of matrix elements between the ground $^2\Pi$ state and the excited electronic $^2\Sigma$ states [2]. The coupling constants defined above describe the contributions to the Λ-splitting in the various orders of approximation. The constants D_p and D_q contain only third order effects, while p and q contain second as well as third order contributions.

In order to obtain the fine structure contributions correct up to fourth order it is in principle possible to extend the perturbation calculation up to fourth order. The relevant expressions are given by Freed [3, eq. (3.2)]. However, this calculation is very complicated and would necessitate the introduction of a number of new molecular parameters. In view of the

results of the pure third order perturbation treatment it is expected that the coupling constants describing the Λ-splitting correct up to fourth order again can be written as a power series in $(J + \frac{1}{2})$. No detailed fourth order calculations were performed, but a reasonable assumption about the Λ-splitting expansion can be made by writing

$$\langle ^2\Pi^{\pm}_{1/2} J | H_F | ^2\Pi^{\pm}_{1/2} J \rangle$$
$$= \pm (-)^{J-1/2}(J + \tfrac{1}{2})[p + D_p(J + \tfrac{1}{2})^2 + \delta_p(J + \tfrac{1}{2})^4],$$
$$\langle ^2\Pi^{\pm}_{1/2} J | H_F | ^2\Pi^{\pm}_{3/2} J \rangle \qquad\qquad (2)$$
$$= \pm (-)^{J-1/2} z (J + \tfrac{1}{2})[q + D_q(J + \tfrac{1}{2})^2 + \delta_q(J + \tfrac{1}{2})^4],$$
$$\langle ^2\Pi^{\pm}_{3/2} J | H_F | ^2\Pi^{\pm}_{3/2} J \rangle = \pm (-)^{J-1/2} z^2 (J + \tfrac{1}{2}) D'_q.$$

The justification of this expansion is found in the results of the least squares fit of the spectrum of OH. Firstly the observed spectrum was reproduced within the experimental uncertainties using eq. (2). Secondly δ_p and δ_q (table 2) are a few orders of magnitude smaller than D_p and D_q, illustrating the converging character of the expansion coefficients of eq. (2). Although the choice of the form of the series expansion for the Λ-splitting is not unique, the number of independent parameters which could be deduced from the experimental spectra turned out to be six, assuming an expansion up to fifth degree in $(J + \frac{1}{2})$. The molecular parameters p and q defined in eq. (1) are slightly different from those in eq. (2), as the last ones contain also fourth order contributions. Similarly D_p and D_q in eq. (2) contain third and fourth order terms, while δ_p and δ_q are purely fourth order contributions. An independent determination of D'_q from the observed spectra of OH turned out to be impossible. In the actual fit of the spectrum D'_q is replaced by D_q, which is an acceptable approximation since D'_q is equal to D_q in third order perturbation treatment.

In the present approach the Λ-splitting in the OH molecule is described by six molecular parameters, the hyperfine structure (nuclear spin $I = 1/2$) by eight coupling constants [11], while the rotational and spin–orbit contributions are taken into account by the rotational constant B_Π, the centrifugal distortion constant D_Π, and the spin–orbit constant A_Π [4]. The quantities B_Π and D_Π were taken from the analysis of Dieke and Crosswhite [12] and A_Π was determined in the fit.

Table 1

Observed hyperfine Λ-doubling transitions of OH together with the results of the present least squares fit of the spectrum as calculated using the molecular constants from table 2

J	Ω	F_+ [a]	F_-	Observed frequency (MHz)	Ref.	Observed minus calculated frequency [b] (kHz)
1/2	1/2	1	1	4750.656(3)	[6]	−2.0
		0	1	4660.242(3)	[6]	−3.1
		1	0	4765.562(3)	[6]	−3.5
3/2	1/2	1	1	7761.747(5)	[7]	−2.2
		2	2	7820.125(5)	[7]	1.8
		2	1	7749.909(5)	[7]	−1.3
		1	2	7831.962(5)	[7]	−0.1
5/2	1/2	2	2	8135.870(5)	[4]	2.2
		3	3	8189.587(5)	[4]	3.9
		2	3	8118.051(5)	[4]	0.0
		3	2	8207.402(5)	[4]	2.1
7/2	1/2	3	3	5473.045(5)	[4]	8.6
		4	4	5523.438(5)	[4]	−1.1
		4	3	5449.436(5)	[4]	−0.8
		3	4	5547.042(5)	[4]	3.3
9/2	1/2	4	4	164.7960(10)	[14]	−0.2
		5	5	117.1495(10)	[14]	0.0
		4	5	192.9957(10)	[14]	0.1
		5	4	88.9504(10)	[14]	0.3
11/2	1/2	5	5	8580.170(20)	[10]	38.1
		6	6	8534.860(20)	[10]	26.5
13/2	1/2	6	6	19561.897(20)	[10]	−16.3
		7	7	19518.612(20)	[10]	−18.8
3/2	3/2	1	1	1665.40184(20)	[9]	0.1
		2	2	1667.35903(20)	[9]	0.1
		2	1	1612.23101(20)	[9]	0.1
		1	2	1720.52998(20)	[9]	0.1
5/2	3/2	2	2	6030.7485(2)	[13]	−0.1
		3	3	6035.0932(2)	[13]	−0.2
		2	3	6016.746(5)	[6]	−7.2
		3	2	6049.084(5)	[6]	−4.9
7/2	3/2	3	3	13434.6374(2)	[13]	0.2
		4	4	13441.4173(2)	[13]	0.0
		3	4	13433.930(25)	[10]	−10.8
		4	3	13442.030(25)	[10]	−83.7
9/2	3/2	4	4	23817 6153(2)	[15]	−0.1
		5	5	23826.6211(2)	[15]	0.1
		5	4	23805.297(10)	[10]	−5.0
		4	5	23838.933(10)	[10]	−1.4
11/2	3/2	5	5	36983.470(20)	[10]	−6.9
		6	6	36994.430(20)	[10]	24.1
		5	6	36963.480(30)	[10]	−16.5
		6	5	37014.420(30)	[10]	33.7
13/2	3/2	6	6	52722.040(20)	[10]	23.5
		7	7	52734.560(20)	[10]	−1.8
		7	6	52696.720(30)	[10]	12 5
		6	7	52759.890(30)	[10]	19.3
15/2	3/2	7	7	70845.081(20)	[10]	17.3
		8	8	70858.930(20)	[10]	−17.9

[a] The subscript + (−) refers to even (odd) Kronig symmetry [4].

[b] The number of transitions is 49 and the χ^2 of the fit 32.6.

3. Results and discussion

A least squares fit of the observed spectrum of the OH molecule was performed using all the available experimental microwave data listed in table 1. For transition frequencies which were observed in more than one investigation, only the most accurate results were used in the present fit. The fine structure was included as described in the previous section and the hyperfine structure was calculated using ref. [11] (contributions off-diagonal in J were included). The range of experimental data enabled firstly the determination of all Λ-splitting and hyperfine parameters involved, and secondly it demonstrates the usefulness of the applied expansion procedure. The results are excellent; as can be seen from table 1 the measured and calculated frequencies are practically all in agreement within their experimental uncertainties. There is only one exception: the $F_+ \rightarrow F_- = 4 \rightarrow 3$ transition of the $J = 7/2$, $\Pi_{3/2}$ state observed by Destombes et al. [10] who also observed the $\Delta F = 0$ transitions of this state. It should be noted that the latter transitions,

which are not shown in table 1, deviate 41 and 52 kHz for $F = 3$ and 4, respectively, from those of ref. [13]. The best fit constants given in table 2 can be used for a reliable prediction of non-observed Λ-doubling transitions of OH. Table 3 lists all those frequencies for the states with $J = 17/2$ calculated using the best fit constants, the frequencies are believed to be accurate within 20–40 kHz.

In summary the hyperfine Λ-doubling spectra of diatomic molecules in a $^2\Pi$ state can be explained within the accuracy of the high resolution molecular beam data. The method has proved its value for the spectra of the NO [11] and the OH radicals, as shown in the present work. The theory originally developed by Freed [3] as a perturbation calculation, adapted on the $^2\Pi$ state by Meerts and Dymanus [2] and extended to include contributions which are non-diagonal in the rotational quantum number [11] is now capable of describing the major fourth order Λ-splitting contributions. The last contributions cannot be neglected for molecules possessing a large Λ-splitting like the OH radical, or when transitions originating from states with high rotational quantum numbers have to be calculated.

Table 2
Molecular constants of OH as obtained in the present least squares fit of the spectrum [a]

Quantity	Value
A_Π (cm^{-1})	−138.4719(4) [b]
p (MHz)	2366.003(2)
D_p (MHz)	0.1123(2)
δ_p (Hz)	−165 (4)
q (MHz)	−580.100(2)
D_q (MHz)	0.22104(5)
δ_q (Hz)	−41.2(5)
χ_1 (MHz)	39.495(6)
χ_2 (MHz)	28.314(6)
χ_3 (MHz)	139.556(20)
χ_4 (MHz)	58.833(33)
$\chi_5 + \chi_7$ (kHz)	−199 (5)
χ_6 (kHz)	−11.3(3)
χ_8 (kHz)	−0.6(9)
χ_9 (kHz)	−7.8(2)

[a] The values for $B_\Pi = 18.515$ cm^{-1} and $D_\Pi = 0.00187$ cm^{-1} were fixed in the fit and were taken from Dieke and Crosswhite [12].

[b] The uncertainties in the molecular constants represent three standard deviations. Definition of standard deviation is based on the "error definition one" and confidence level of the fit of 95% [11].

Table 3
Predicted frequencies of the non-observed hyperfine Λ-doubling transitions of OH in the rotational states with $J \leq 17/2$ as calculated using the best fit constants of table 2

J	Ω	F_+	F_-	Predicted frequency (MHz)
11/2	1/2	6	5	8611.809
		5	6	8503.157
13/2	1/2	6	7	19596.192
		7	6	19484.352
15/2	1/2	7	7	32921.453
		8	8	32879.899
		8	7	32957.671
		7	8	32843.663
17/2	1/2	8	8	48494.472
		9	9	48454.467
		8	9	48532.200
		9	8	48416.739
15/2	3/2	7	8	70815.898
		8	7	70888.114
17/2	3/2	8	8	91188.617
		9	9	91203.601
		9	8	91156.560
		8	9	91235.658

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