

## THE HIGH-RESOLUTION HYPERFINE LAMBDA-DOUBLING SPECTRUM OF VIBRATIONALLY EXCITED OH

J. P. BEKOORY, W. L. MEERTS, AND A. DYMANUS

Fysisch Laboratorium, Katholieke Universiteit, Nijmegen, The Netherlands

Received 1978 May 8; accepted 1978 June 15

### ABSTRACT

The hyperfine  $\Lambda$ -doubling transitions of OH originating in the  $J = 3$  rotational, the  $v = 1$  and  $v = 2$  vibrational, and the  $X^2\Pi_{3/2}$  electronic ground state have been measured using the molecular beam electric resonance technique. Predictions for the frequencies of the transitions in the  $X^2\Pi_{3/2}$ ,  $J = 3/2$ ,  $v = 3$  and  $v = 4$  states are given.

*Subject heading:* hyperfine structure — laboratory spectra

Astronomical observations of radio spectra from excited vibrational states of OH may provide important information about the near-infrared pumping model as proposed by Litvak (1969). It is expected that emission of interstellar OH in these states is very weak, and a successful observation would depend critically on laboratory measurements of the rest frequencies of the transitions in question. The magnetic resonance spectroscopy has been used by Churg and Levy (1970), by Clough, Curran, and Thrush (1971), and by Lee *et al.* (1971; Lee and Tam 1974) to investigate the  $^2\Pi_{3/2}$ ,  $J = 3/2$  state of vibrationally excited OH up to  $v = 9$ . The zero-field frequencies of lambda-doubling transitions in the  $^2\Pi_{3/2}$ ,  $J = 3/2$  level could be predicted from magnetic resonance data by Churg and Levy (1970) for the  $v = 1$  state (uncertainty 0.1 MHz), and those for higher vibrational states can be deduced from the results of Clough, Curran, and Thrush (1971), Lee *et al.* (1971), and Lee and Tam (1974). Since these magnetic resonance data were obtained from the  $J = 3/2$  and  $J = 5/2$  (for  $v \leq 4$ ) levels in the  $^2\Pi_{3/2}$  state only, the possibility of deducing the  $\Lambda$ -doubling and the hyperfine-structure constants in the vibrationally excited states is seriously limited. It was felt that the predictions may be subject to a much larger uncertainty than claimed. A direct measurement of the zero-field transitions was considered well justified. The molecular-beam electric resonance spectrometer has been used to investigate the  $v = 1$  and  $v = 2$  vibrational states of OH. The electric dipole allowed transitions originating in the  $^2\Pi_{3/2}$ ,  $J = 3/2$  state for both vibrational states are reported here. These are the first direct measurements of the hyperfine  $\Lambda$ -doubling transitions in excited vibrational states of OH.

The OH radicals have been produced by the reaction  $H + NO_2 \rightarrow OH + NO$ . Hydrogen atoms were generated by passing water vapor through a microwave discharge at 2.45 GHz. The experimental setup previously used to investigate the ground vibrational state of OH has been discussed in detail elsewhere (Meerts and Dymanus 1975). The observed intensity ratio between the  $v = 1$  and  $v = 0$  spectra and between the

$v = 2$  and  $v = 0$  spectra was 6% and 2.5%, respectively. The maximum intensities of the transitions from the excited vibrational states were obtained when the beam-forming orifice was in the reaction zone. By moving it a few millimeters downstream from the reaction zone, the intensities of the  $v = 1$  and  $v = 2$  spectra were reduced considerably, while those of the  $v = 0$  spectra were almost unaffected. This suggests the occurrence of strong vibrational relaxation induced by collisions. Since the signal-to-noise ratio of the  $v = 1$  and  $v = 2$  spectra was very low, signal-averaging techniques had to be used. Typical integration times for the spectra from the  $v = 1$  and  $v = 2$  states were 0.5 and 1.5 hours, respectively. A single scan took 50 s. The signal-to-noise ratio after the averaging process varied between 3 and 5.

The observed transition frequencies are given in Table 1. The experimental uncertainties were mainly determined by the signal-to-noise ratio. A full spectroscopic discussion including also observed transitions in the  $^2\Pi_{3/2}$ ,  $J = 5/2$  and the  $^2\Pi_{1/2}$ ,  $J = 1/2$  and  $3/2$  states is given in a separate paper (Meerts, Bekoory, and Dymanus 1978). In that paper vibrational effects in the  $\Lambda$ -doubling and hyperfine structure constants are discussed. The theoretical framework used has been described (for the  $v = 0$  state) by Meerts (1977). In this

TABLE 1  
 FREQUENCIES OF THE OBSERVED HYPERFINE  $\Lambda$ -DOUBLING  
 TRANSITIONS OF OH IN THE  $^2\Pi_{3/2}$ ,  $J = 3/2$ ,  
 $v = 1$  AND  $v = 2$  STATES

$F_+^*$	$F_-$	OBSERVED FREQUENCY (MHz)	
		$v=1$	$v=2$
1	1	1536.944(3)	1412.850(3)
2	2	1538.702(3)	1414.424(3)
2	1	1489.438(3)	1371.377(3)
1	2	1586.213(3)	1455.896(3)

\* The subscript + (–) refers to the even (odd) Kronig symmetry (Meerts and Dymanus 1975).

framework, by incorporating up to third-order perturbation contributions in fine and hyperfine structure and the major part of the fourth-order  $\Lambda$ -splitting, a prediction could be made for transitions in higher vibrational states by extrapolation of the molecular constants of the  $v = 0, 1,$  and  $2$  states. The results are presented in Table 2 for the  $v = 3$  and  $v = 4$  states. In this extrapolation the vibrational dependence of the molecular constants is approximated by an expansion up to second order in  $v$ . The expansion is found to converge very rapidly; the second-order term contributes an order of magnitude less for the  $v = 3$  and  $v = 4$  states than the first-order term. For the transition frequencies in the  $v = 3$  and in the  $v = 4$  state this yields an estimated reliability of 100 kHz and 300 kHz, respectively.

The technical assistance of Mr. F. A. van Rijn is gratefully acknowledged.

## REFERENCES

- Churg, A., and Levy, D. H. 1970, *Ap. J. (Letters)*, **162**, L161.  
 Clough, P. N., Curran, A. H., and Thrush, B. A. 1971, *Proc. Roy. Soc. London, A*, **323**, 541.  
 Lee, K. P., and Tam, W. G. 1974, *Chem. Phys.*, **4**, 434.  
 Lee, K. P., Tam, W. G., Larouche, R., and Woonton, G. A. 1971, *Canadian J. Phys.*, **49**, 2207.  
 Litvak, M. M. 1969, *Ap. J.*, **156**, 471.  
 Meerts, W. L. 1977, *Chem. Phys. Letters*, **46**, 24.  
 Meerts, W. L., Bekooy, J. P., and Dymanus, A. 1978, *Molec. Phys.*, in press.  
 Meerts, W. L., and Dymanus, A. 1975, *Canadian J. Phys.*, **53**, 2123.

J. P. BEKOOY, A. DYMANUS, and W. L. MEERTS: Fysisch Laboratorium, Katholieke Universiteit, Nijmegen, The Netherlands

TABLE 2  
 PREDICTED FREQUENCIES OF THE HYPERFINE  $\Lambda$ -DOUBLING  
 TRANSITIONS OF THE  ${}^2\Pi_{3/2}$ ,  $J = 3/2$ ,  $v = 3$   
 AND  $v = 4$  STATES OF OH

$F_+$	$F_-$	PREDICTED FREQUENCY (MHz)	
		$v=3^*$	$v=4^*$
1	1	1293.245	1178.024
2	2	1294.650	1179.269
2	1	1258.169	1148.906
1	2	1329.726	1208.387

\* Accuracy is estimated to be 100 kHz and 300 kHz for the frequencies in the  $v = 3$  and  $v = 4$  states, respectively.