

## THE MICROWAVE AND FAR-INFRARED SPECTRA OF THE $^{18}\text{OH}$ RADICAL<sup>1</sup>

E. R. COMBEN AND J. M. BROWN  
Physical Chemistry Laboratory, Oxford

T. C. STEIMLE  
Department of Chemistry, Arizona State University

AND

K. R. LEOPOLD AND K. M. EVENSON  
National Bureau of Standards

Received 1985 September 20; accepted 1985 November 25

### ABSTRACT

The frequencies, wavelengths, and line strengths for transitions of the  $^{18}\text{OH}$  molecule at microwave and far-infrared frequencies have been calculated from an analysis of its far-infrared laser magnetic resonance spectrum.

*Subject headings:* infrared: spectra — line identifications — molecular processes

The OH radical was the first molecule to be detected at radio frequencies in the interstellar medium (Weinreb *et al.* 1963). In the intervening 20 yr, literally thousands of different microwave observations of OH have been made in a wide variety of astrophysical sources. These observations have yielded valuable information about the physical conditions in the sources concerned and have prompted many studies of the chemical processes involved in the diffuse, interstellar clouds. In addition to the dominant isotope,  $^{16}\text{OH}$ , some lines from the two minor isotopic modifications,  $^{18}\text{OH}$  and  $^{17}\text{OH}$ , have also been observed (Barrett and Rogers 1964; Gardner, McGee, and Sinclair 1970; Wilson and Barrett 1970; Gardner and Whiteoak 1976). Such observations can lead to a determination of the relative isotopic abundances in the sources involved. The differences between these values and those obtained on Earth have important implications for the processes involved in nucleosynthesis, stellar mass loss and galactic evolution (Audouze, Lequeux, and Vigroux 1975). More recently, rotational transitions of OH have also been detected in the direction of Sgr B2 and Orion-KL at far-infrared wavelengths (Storey, Watson, and Townes 1981; Watson *et al.* 1985). While microwave observations are restricted to the cold, molecular cloud regions, the far-infrared spectrum can be used to monitor molecules in a much wider range of physical conditions.

Further astrophysical searches for molecules in both the microwave and far-infrared regions can be aided considerably by laboratory measurements of their spectra. Previous studies of  $^{16}\text{OH}$ , CH, and SiH by far-infrared laser magnetic resonance (LMR) spectroscopy have enabled us to predict zero field frequencies with an accuracy of a few MHz for these molecules (Brown *et al.* 1982; Brown and Evenson 1983; Brown, Curl, and Evenson 1985). In this paper, we extend the studies to  $^{18}\text{OH}$ . In the LMR experiment, a molecular transition frequency is tuned into coincidence with that of a fixed frequency laser by the application of a variable magnetic field (0–2 tesla).

The  $^{18}\text{OH}$  radicals, produced by the reaction of hydrogen atoms with nitrogen dioxide, have been detected in natural abundance (0.20%) with good signal-to-noise ratios. Details of the laser lines used and of the  $^{18}\text{OH}$  transitions observed are summarized in Table 1. These data and the microwave frequencies of Gottlieb, Radford, and Smith (1974) were used to determine the parameters of an effective Hamiltonian described by Brown *et al.* (1978). Some of the smaller parameters required in the fit were constrained at values obtained by appropriate scaling (Brown *et al.* 1979) of the  $^{16}\text{OH}$  values. The values of the parameters determined in the fit are close to those predicted by the use of isotopic scaling factors and are given in Table 2.

We have used the parameter values determined by the fit to compute microwave and far-infrared transition frequencies, wavelengths, and line strengths for individual hyperfine transitions in  $^{18}\text{OH}$  involving rotational levels up to  $J = 5\frac{1}{2}$ . The results are given in Tables 3 and 4 and are summarized in the diagram of Figure 1 which shows the low-lying energy levels of  $^{18}\text{OH}$ . The frequencies of transitions between levels studied directly in the LMR experiment are quite reliable. The standard deviation of the fit for an observation of unit weight was 1.7 MHz and, allowing for some uncertainty in the model-dependent extrapolation to zero magnetic field, we estimate the  $1\sigma$  uncertainty of such transition frequencies to be  $\pm 3$  MHz. The energy levels involved in other transitions are extrapolated in  $J$  value, and consequently their frequencies are less reliable (see Tables 3 and 4). The reliability of the procedure for extrapolation to zero field has been supported recently by the direct measurement of several zero field frequencies of  $^{16}\text{OH}$  in experiments using sources of tunable far-infrared radiation (Farhoomand, Blake, and Pickett 1985; Brown *et al.* 1985).

The line strengths of the transitions are also given in Tables 3 and 4. The line strength  $S_{F'F''}$  can be used to assess the relative intensity of an individual transition. It is defined by

$$S_{F'F''} = |\langle \gamma' F' || \mathcal{D}_q^{(1)}(\omega) || \gamma F \rangle|^2, \quad (1)$$

where the quantity on the right-hand side is the reduced matrix element of the rotation matrix (Brink and Satchler 1968), and  $\gamma$

<sup>1</sup> Work supported in part by NASA contract W-15,047.

TABLE I  
SUMMARY OF OBSERVATIONS IN THE FAR-INFRARED LMR SPECTRUM  
OF THE  $^{18}\text{OH}$  RADICAL IN ITS GROUND STATE

PUMP	Gain Medium	LASER LINE		$^{18}\text{OH}$ TRANSITION	
		$\lambda/\mu\text{m}$	$\nu/\text{GHz}$	$J$	$F_i$
9P(22) .....	$^{13}\text{CH}_3\text{OH}$	85.3	3513.8530	$3\frac{1}{2} \leftarrow 2\frac{1}{2}$	$F_1 \leftarrow F_1$
9R(10) .....	$\text{CH}_3\text{OH}$	96.5	3105.9368	$1\frac{1}{2} \leftarrow 2\frac{1}{2}$	$F_2 \leftarrow F_1$
10R(16) .....	$^{13}\text{CH}_3\text{OH}$	115.8	2588.3617	$2\frac{1}{2} \leftarrow 3\frac{1}{2}$	$F_2 \leftarrow F_1$
9P(36) .....	$\text{CH}_3\text{OH}$	118.8	2522.7816	$2\frac{1}{2} \leftarrow 1\frac{1}{2}$	$F_1 \leftarrow F_1$
10R(36) .....	$\text{CD}_2\text{F}_2$	120.5	2488.5534		
9P(16) .....	$\text{CH}_3\text{OH}$	164.6	1821.3352	$1\frac{1}{2} \leftarrow \frac{1}{2}$	$F_2 \leftarrow F_2$
9R(10) .....	$\text{CH}_3\text{OH}$	164.8	1819.3140		

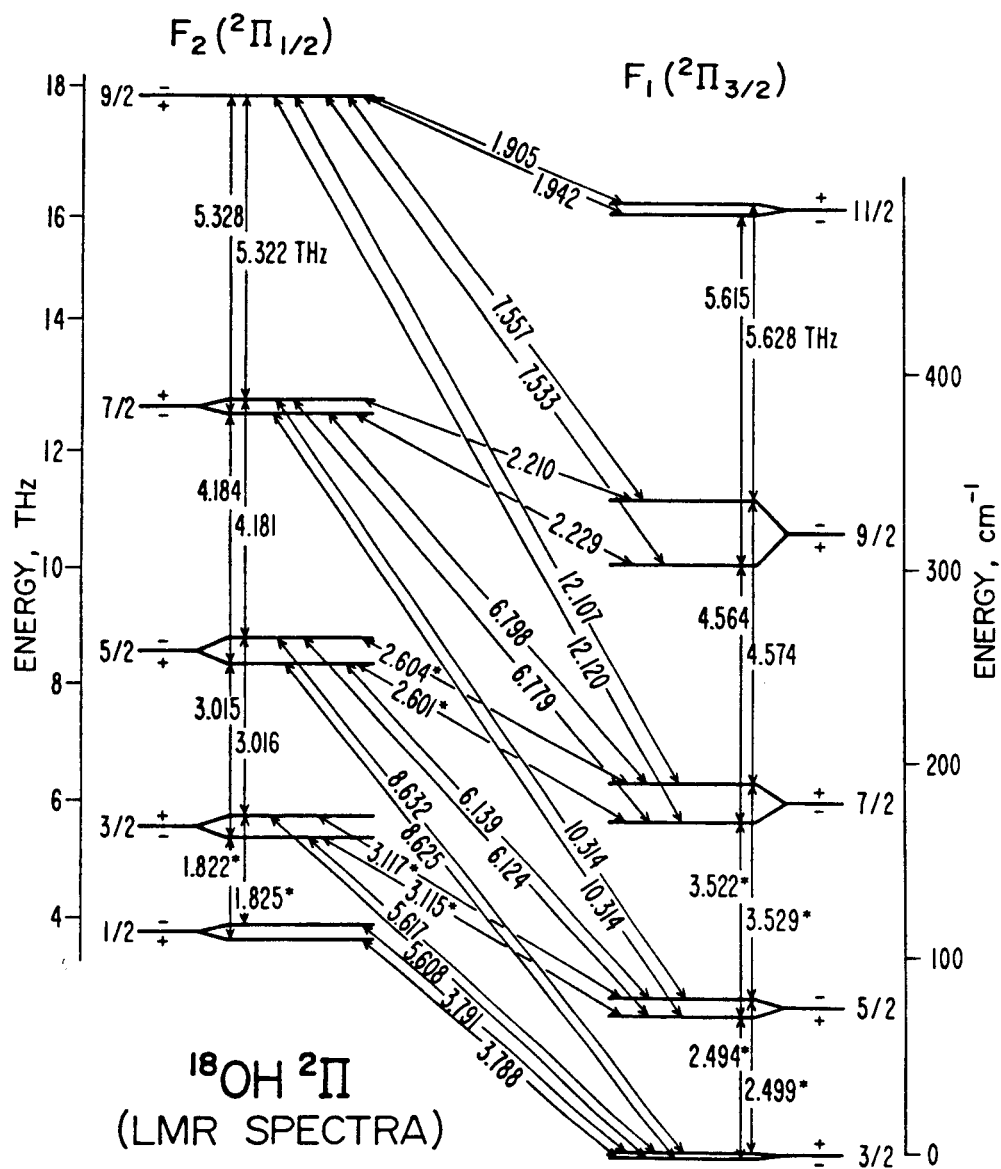


FIG. 1.—The low-lying energy levels of the  $^{18}\text{OH}$  radical, connected by electric dipole transitions ( $\leftrightarrow$ ) in the far-infrared. The parity doubling (or lambda doubling) has been exaggerated for the sake of clarity. The transition frequencies are given in MHz. The transitions observed in the LMR experiment are marked with an asterisk.

TABLE 2  
PARAMETERS FOR THE <sup>18</sup>OH IN THE  $v = 0$  LEVEL  
OF THE  $X^2\Pi$  STATE<sup>a</sup>

Parameter	Value
A. Parameter Values Constrained in the Least-Squares Fit	
$10^2 H$	0.4153
$\gamma_D$	0.7219
$P_D$	-1.5305559
$10^2 P_H$	0.1615
$q_D$	0.433337
$10^4 q_H$	-0.8022
$a$	86.1116
$b_F$	-73.2537
$c$	130.641
$d$	56.6838
$10 C_i$	-0.9971
$10^2 C_i'$	0.643
$10 d_D$	-0.2276
$\theta_L'$	1.00106
$\theta_S$	2.00153
$10^2 g_i$	0.399
$10^3 g_i'$	-0.630
$10^2 g_i'$	0.6386
$10^2 g_i e'$	0.20309
B. Parameter Values Determined in the Least-Squares Fit	
$\bar{A}^b$	-4168644.90(212) <sup>c</sup>
$B$	552032.89(18)
$D$	56.4565(135)
$\bar{\nu}^b$	-3552.48(72)
$p$	7007.1767(58)
$q$	-1144.8298(15)

<sup>a</sup> Values in MHz, where appropriate.

<sup>b</sup> Effective parameter. The fit was performed with the parameter  $A_D$  constrained to zero.

<sup>c</sup> The numbers in parenthesis represent one standard deviation of the least-squares fit, in units of the last quoted decimal place.

TABLE 3

CALCULATED LAMBDA DOUBLING TRANSITION FREQUENCIES FOR THE <sup>18</sup>OH RADICAL IN ITS GROUND STATE

TRANSITION <sup>a</sup>			FREQUENCY (MHz)	LINE STRENGTH <sup>b</sup>	
$F_i$	$J$	$F'-F''$			
$F_1$ .....	$1\frac{1}{2}$	$1^+-2^-$	1584.2740 <sup>c</sup>	0.2881	
		$1^+-1^-$	1637.5640 <sup>c</sup>	1.4405	
		$2^+-2^-$	1639.5030 <sup>c</sup>	2.5929	
		$2^+-1^-$	1692.7950 <sup>c</sup>	0.2881	
	$2\frac{1}{2}$	$2^--3^+$	5920.5050 <sup>c</sup>	$0.7791 \times 10^{-1}$	
		$2^--2^+$	5934.6440 <sup>c</sup>	1.0908	
		$3^--3^+$	5938.9670 <sup>c</sup>	1.5582	
		$3^--2^+$	5953.1160 <sup>c</sup>	$0.7790 \times 10^{-1}$	
		$4^+-3^-$	13229.9 <sup>d</sup>	$0.3059 \times 10^{-1}$	
		$3^+-3^-$	13230.5	0.8261	
	$4\frac{1}{2}$	$4^+-4^-$	13237.3	1.0708	
		$3^+-4^-$	13237.8	$0.3059 \times 10^{-1}$	
		$5^--4^+$	23458.4	$0.1471 \times 10^{-1}$	
		$4^--4^+$	23470.6	0.6474	
		$5^--5^+$	23479.5	0.7944	
		$4^--5^+$	23491.8	$0.1471 \times 10^{-1}$	
		$6^+-5^-$	36443.0	$0.8061 \times 10^{-2}$	
		$5^+-5^-$	36462.9	0.5238	
	$5\frac{1}{2}$	$6^+-6^-$	36473.8	0.6204	
		$5^+-6^-$	36493.7	$0.8055 \times 10^{-2}$	
$F_2$ .....		$\frac{1}{2}$	$0^- - 1^+$	4644.6500 <sup>c</sup>	0.3334
			$1^- - 1^+$	4735.0730 <sup>c</sup>	0.6667
$1\frac{1}{2}$	$1\frac{1}{2}$	$1^- - 0^+$	4749.9710 <sup>c</sup>	0.3333	
		$1^+-2^-$	7746.6	$0.3745 \times 10^{-1}$	
	$2\frac{1}{2}$	$1^+-1^-$	7758.3	0.1873	
		$2^+-2^-$	7816.7	0.3372	
		$2^+-1^-$	7828.4	$0.3746 \times 10^{-1}$	
		$2^--3^+$	8167.2	$0.1238 \times 10^{-1}$	
	$3\frac{1}{2}$	$2^--2^+$	8184.8	0.1732	
		$3^--3^+$	8238.6	0.2475	
		$3^--2^+$	8256.3	$0.1237 \times 10^{-1}$	
		$3^+-4^-$	5590.5	$0.5937 \times 10^{-2}$	
		$3^+-3^-$	5613.9	0.1603	
		$4^+-4^-$	5664.4	0.2078	
$4\frac{1}{2}$	$4^+-3^-$	5687.8	$0.5939 \times 10^{-2}$		
	$4^--5^+$	74.5	$0.3423 \times 10^{-2}$		
	$4^--4^+$	102.6	0.1505		
	$5^--5^+$	150.3	0.1848		
$5\frac{1}{2}$	$5^--4^+$	178.3	$0.3420 \times 10^{-2}$		
	$5^--6^+$	8079.2	$0.2190 \times 10^{-2}$		
	$6^--6^+$	8110.7	0.1686		
	$5^--5^+$	8156.1	0.1423		
$6^--5^+$	$6^--5^+$	8187.6	$0.2190 \times 10^{-2}$		

<sup>a</sup> Quantum numbers for the upper and lower states are denoted by single and double primes, respectively. The superscripts on the  $F$  quantum number values indicate the parities of the states involved in accordance with the definition in Brown *et al.* 1978.

<sup>b</sup> For definition see eq. (1).

<sup>c</sup> Laboratory observation by Gottlieb, Radford, and Smith 1974.

<sup>d</sup> Estimated uncertainty of 3 MHz for transitions studied in the LMR spectrum and 5 MHz for those not studied directly.

<sup>e</sup> Transition involves level(s) not studied directly in the LMR spectrum.

stands for subsidiary quantum numbers. The intensity of a line in absorption can be obtained by multiplying the line strength by the square of the dipole moment  $\mu$  (1.668 debye for <sup>16</sup>OH; Meerts and Dymanus 1973), by the transition frequency and by the population factor for the lower level. The Einstein  $A$ -coefficients for spontaneous emission from state  $i$  to  $j$  can also be calculated from the line strengths by use of

$$A_{i \rightarrow j} = (16\pi^3 \nu_{ij} / 3\epsilon_0 hc^3) (2F_i + 1)^{-1} S_{ij} \mu^2 \quad (2)$$

We are grateful to Dr. H. E. Radford for suggesting this project and to the Science and Engineering Research Council for the support of E. R. C.



TABLE 4—Continued

TRANSITION <sup>a</sup>			FREQUENCY (GHz)	VACUUM WAVELENGTH (μm)	LINE STRENGTH <sup>b</sup>	TRANSITION <sup>a</sup>			FREQUENCY (GHz)	VACUUM WAVELENGTH (μm)	LINE STRENGTH <sup>b</sup>
F <sub>i</sub> '-F <sub>i</sub> "	J'-J"	F'-F"				F <sub>i</sub> '-F <sub>i</sub> "	J'-J"	F'-F"			
		4 <sup>+</sup> -5 <sup>-</sup>	2210.7645	135.6058	0.263 × 10 <sup>-1</sup>			5 <sup>-</sup> -5 <sup>+</sup>	1905.5355	157.3271	0.304 × 10 <sup>-3</sup>
		3 <sup>-</sup> -4 <sup>+</sup>	2228.5350	134.5245	0.214 × 10 <sup>-1</sup>			5 <sup>-</sup> -6 <sup>+</sup>	1905.5554	157.3255	0.198 × 10 <sup>-1</sup>
		4 <sup>-</sup> -4 <sup>+</sup>	2228.5585	134.5230	0.613 × 10 <sup>-3</sup>			4 <sup>+</sup> -5 <sup>-</sup>	1941.8201	154.3873	0.168 × 10 <sup>-1</sup>
		4 <sup>-</sup> -5 <sup>+</sup>	2228.5796	134.5218	0.269 × 10 <sup>-1</sup>			5 <sup>+</sup> -5 <sup>-</sup>	1941.8481	154.3851	0.312 × 10 <sup>-3</sup>
	4 <sub>1/2</sub> -5 <sub>1/2</sub> <sup>d</sup>	4 <sup>-</sup> -5 <sup>+</sup>	1905.4597	157.3334	0.164 × 10 <sup>-1</sup>			5 <sup>+</sup> -6 <sup>-</sup>	1941.8789	154.3827	0.203 × 10 <sup>-1</sup>

<sup>a</sup> Quantum numbers for the upper and lower states are denoted by single and double primes, respectively. The superscripts on the F quantum number values indicate the parities of the states involved in accordance with the definition in Brown *et al.* 1978.

<sup>b</sup> For definition, see eq. (1).

<sup>c</sup> Estimated uncertainty of 3 MHz for transitions studied in the LMR spectrum and 5 MHz for those not studied directly.

<sup>d</sup> Transition involves level(s) not studied directly in the LMR spectrum.

REFERENCES

Andouze, J., Lequeux, J., and Vigroux, L. 1975, *Astr. Ap.*, **43**, 71.  
 Barrett, A. H., and Rogers, A. E. E. 1964, *Nature*, **204**, 62.  
 Brink, D. M., and Satchler, G. R. 1968, *Angular Momentum* (Oxford: Oxford University Press).  
 Brown, J. M., Colbourn, E. A., Watson, J. K. G., and Wayne, F. D. 1979, *J. Molec. Spectrosc.*, **74**, 294.  
 Brown, J. M., Curl, R. F., and Evenson, K. M. 1985, *Ap. J.*, **292**, 188.  
 Brown, J. M., and Evenson, K. M. 1983, *Ap. J. (Letters)*, **268**, L51.  
 Brown, J. M., Kaise, M., Kerr, C. M. L., and Milton, D. J. 1978, *Molec. Phys.*, **36**, 553.  
 Brown, J. M., Schubert, J. E., Evenson, K. M., and Radford, H. E. 1982, *Ap. J.*, **258**, 899.  
 Brown, J. M., Zink, L. R., Jennings, D. A., Evenson, K. M., Hinz, A., and Nolt, I. G. 1985, to be published.  
 Farhoomand, J., Blake, G. A., and Pickett, H. M. 1985, *Ap. J. (Letters)*, **291**, L19.  
 Gardner, F. F., McGee, R. K., and Sinclair, M. W. 1970, *Ap. Letters*, **5**, 67.  
 Gardner, F. F., and Whiteoak, J. B. 1976, *M.N.R.A.S.*, **176**, 57P.  
 Gottlieb, C. A., Radford, H. E., and Smith, B. P. 1974, unpublished data given in Beaudet, R. A., and Poynter, R. L. 1978, *J. Phys. Chem. Ref. Data*, **7**, 311.  
 Meerts, W. L., and Dymanus, A. 1973, *Chem. Phys. Letters*, **23**, 45.  
 Storey, J. W. V., Watson, D. M., and Townes, C. H. 1981, *Ap. J. (Letters)*, **244**, L27.  
 Watson, D. M., Genzel, R., Townes, C. H., and Storey, J. W. V. 1985, *Ap. J.*, **298**, 316.  
 Weinreb, S., Barrett, A. H., Meeks, M. L., and Henry, J. C. 1963, *Nature*, **200**, 829.  
 Wilson, W. J., and Barrett, A. H. 1970, *Ap. Letters*, **6**, 231.

J. M. BROWN and E. R. COMBEN: Physical Chemistry Laboratory, South Parks Road, Oxford OX1 3QZ, England

K. M. EVENSON and K. R. LEOPOLD: National Bureau of Standards, Boulder, CO 80303

T. C. STEIMLE: Department of Chemistry, Arizona State University, Tempe, AZ 85287