

## LABORATORY MEASUREMENT OF THE ROTATIONAL SPECTRUM OF THE OH RADICAL WITH TUNABLE FAR-INFRARED RADIATION<sup>1</sup>

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### ABSTRACT

Rotational and fine-structure transitions between the low rotational levels of the OH radical in its  $X^2\Pi$  state have been observed in absorption in the laboratory. It has thus been possible to measure the frequencies of these transitions directly. The observations were made with tunable far-infrared radiation generated by mixing two chosen CO<sub>2</sub> laser frequencies in a metal-insulator-metal diode; the far-infrared difference frequency was radiated from the diode's whisker antenna. The measurements have an accuracy of a few hundred kHz. They both confirm and improve on the best previous estimates, which were obtained by extrapolation of laser magnetic resonance data.

*Subject headings:* laboratory spectra — molecular processes

The OH radical is a particularly important species in astrophysical and aeronomical environments. It was the first molecule to be identified in the interstellar medium by radio astronomy (Weinreb *et al.* 1963). Since then it has been the subject of intensive study. It has also been detected more recently at far-infrared wavelengths (Storey, Watson, and Townes 1981; Watson *et al.* 1985). Although microwave observations are restricted to the cold molecular cloud regions, the far-infrared spectrum can be used to monitor species in a much greater range of different physical conditions. Thus there are considerable advantages to observing a molecular species by means of its far-infrared transitions. However, the identification and exploitation of individual observations depend heavily on preliminary spectroscopic work in Earth-based laboratories.

For a long time, the far-infrared (FIR) region had been rather poorly served by both radiation sources and detectors. Until very recently, almost all very high resolution spectroscopic work has been performed with fixed-frequency lasers. In these experiments, the molecular transition is tuned into coincidence with a nearby fixed-frequency laser line by some suitable means. Paramagnetic species, for example, can be detected by the application of a variable magnetic field, in a technique called laser magnetic resonance (LMR; Evenson 1981). The FIR spectrum of the OH radical has been studied in this way (Evenson, Wells, and Radford 1970; Brown *et al.* 1981), and the observations were used to predict the zero-field spectrum to an accuracy of a few MHz by means of a model-dependent extrapolation (Brown *et al.* 1982). During the past few years, methods of generating tunable continuous wave (cw) FIR radiation have been developed. For example, it is possible to add tunable sidebands to a FIR laser by mixing with microwave

radiation from a klystron in a Schottky barrier diode (Bičanić, Zuidberg, and Dymanus 1978). More recently, tunable cw FIR radiation has been generated by nonlinear mixing of radiation from two CO<sub>2</sub> lasers in a metal-insulator-metal (MIM) diode (Evenson, Jennings, and Petersen 1984). The radiation is tuned by varying the output of one of the two lasers over its gain profile. The frequency generated depends on the choice of CO<sub>2</sub> laser lines. By using all readily available isotopic modifications, it is possible to cover over 80% of the FIR region, with gaps appearing at frequencies greater than 2 THz. This latest method of generating tunable FIR radiation thus appears to have considerable advantages as a spectroscopic source. We have used it to observe nearly all the transitions between the lowest few rotational levels of the OH radical. The transitions detected and measured are shown in the energy level diagram in Figure 1.

Brief details of the experimental apparatus are as follows: The FIR radiation was emitted from the MIM diode with a long wire antenna. After making a single pass through a Pyrex absorption cell (55 cm long and 19 cm in diameter), the radiation was detected with a bolometer, either a <sup>4</sup>He cooled germanium bolometer or a <sup>3</sup>He composite bolometer cooled to 0.4 K (Radostitz *et al.* 1978). Flowing OH radicals were generated in three ways. First, H atoms from a microwave discharge through wet hydrogen were reacted with nitrogen dioxide (H + NO<sub>2</sub> → OH + NO) at a total pressure of ~100 Pa (750 mtorr). Second, we produced OH by dissociation of H<sub>2</sub>O vapor in the microwave discharge mounted on a sidearm to the cell (the optimum pressure was ~40 Pa or 300 mtorr, and the microwave power ~50 W). Finally, we also produced OH in a DC discharge through water vapor running the whole length of the cell, again at a total pressure of ~40 Pa. The OH signals recorded increased roughly in the ratio 1:3:30 for these three methods. An example of a recorded spectrum is shown in

<sup>1</sup> Contribution of the National Bureau of Standards.

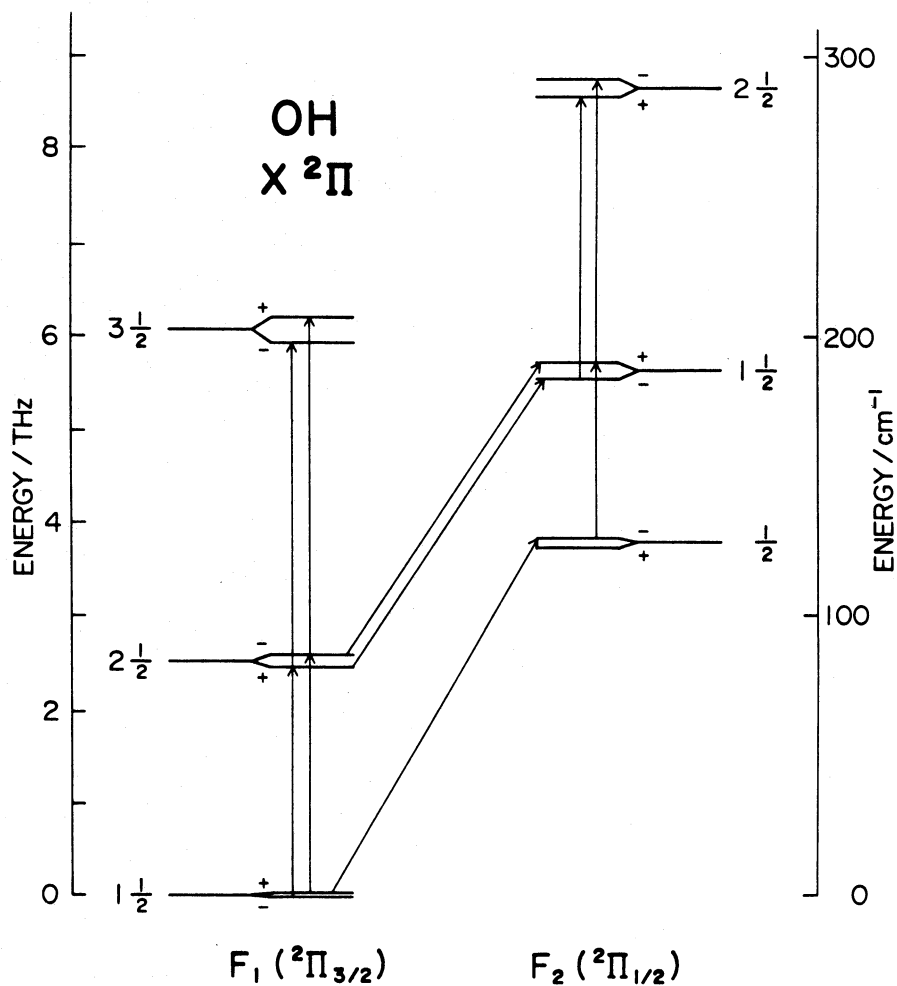


FIG. 1.—Energy level diagram of the lower rotational levels of the OH radical, showing the transitions detected and measured in the present work. The  $\lambda$ -doubling splittings have been exaggerated for the sake of clarity.

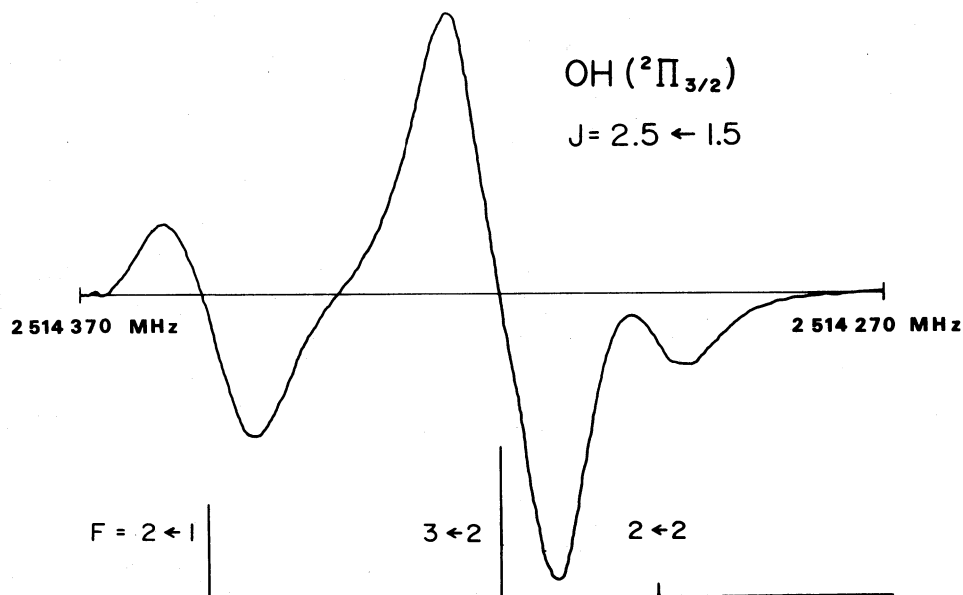


FIG. 2.—Observed spectrum of the  $F_1-F_1$ ,  $J = 2\frac{1}{2} \leftarrow 1\frac{1}{2}$  transition of the OH radical in its ground state. The spectrum is a single scan recorded with a 100 ms output time constant. The signals are displayed with a first derivative line shape caused by frequency modulation of the FIR radiation and detection at the modulation frequency.

TABLE 1

MEASURED FREQUENCIES OF TRANSITIONS IN THE FAR-INFRARED SPECTRUM OF THE OH RADICAL IN ITS GROUND STATE

$\nu$	TRANSITION <sup>a</sup>			FREQUENCY (MHz)		
	$F'_i - F''_i$	$J' - J''$	$F' - F''$	Previous Calculation <sup>b</sup>	Measured <sup>c</sup>	$O - C^d$
$F_1 - F_1$	$2\frac{1}{2} - 1\frac{1}{2}$	$3^+ - 2^-$	.....	2509947.7	2509948.69(12) <sup>e</sup>	+0.07
		$2^+ - 1^-$	.....	2509986.7	2509987.80(20) <sup>e</sup>	+0.01
		$2^- - 2^+$	.....	2514297.1	2514296.0(16) <sup>f</sup>	-2.00
		$3^- - 2^+$	.....	2514315.5	2514316.34(07)	0.00
$F_1 - F_1$	$3\frac{1}{2} - 2\frac{1}{2}$	$2^- - 1^+$	.....	2514352.3	2514353.12(06)	0.00
		$4^- - 3^+$	.....	3543781.2	3543779.37(20)	+0.32
		$3^- - 2^+$	.....	3543802.7	3543800.64(20)	+0.12
		$4^+ - 3^-$	.....	3551187.6	3551185.25(15)	-0.10
$F_2 - F_2$	$1\frac{1}{2} - \frac{1}{2}$	$3^+ - 2^-$	.....	3551206.6	3551204.24(15)	-0.15
		$2^+ - 1^-$	.....	1837816.0	1837816.39(05)	+0.03
		$1^+ - 0^-$	.....	1837836.2	1837836.52(06)	-0.05
$F_2 - F_2$	$2\frac{1}{2} - 1\frac{1}{2}$	$2^+ - 2^-$	.....	3036260.	3036257.0(16) <sup>f</sup>	-0.91
		$2^+ - 1^-$	.....	3036272.		+4.51
		$3^+ - 2^-$	.....	3036278.	3036274.30(14) <sup>f</sup>	-1.47
		$2^- - 1^+$	.....	3036646.	3036644.93(17) <sup>f</sup>	+1.06
$F_2 - F_1$	$\frac{1}{2} - 1\frac{1}{2}$	$3^- - 2^+$	.....	3036647.		-0.26
		$0^- - 1^+$	.....	3789180.2	3789179.79(27)	-0.01
		$1^- - 2^+$	.....	3789215.5	3789214.99(40)	-0.10
$F_2 - F_1$	$1\frac{1}{2} - 2\frac{1}{2}$	$2^- - 3^+$	.....	3110931.0		+1.06
		$1^- - 2^+$	.....	3110933.2	3110931.13(50) <sup>f</sup>	-1.10
		$1^+ - 2^-$	.....	3112664.2	3112663.41(21)	+0.16
		$2^+ - 3^-$	.....	3112716.0	3112715.01(19)	-0.10

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

<sup>b</sup> From Brown *et al.* 1982.

<sup>c</sup> Parentheses enclose estimates ( $1 \sigma$ ) of the total measurement error, in units of the last quoted decimal place.

<sup>d</sup> Calculated value obtained using the parameters given in Table 2.

<sup>e</sup> Measured using microwave sideband of  $\text{CO}_2$  difference frequency.

<sup>f</sup> Hyperfine lines not resolved, hence excluded from the fit.

Figure 2. The line shape is the first derivative of an absorption line, because the FIR radiation was frequency-modulated by the modulation of one of the  $\text{CO}_2$  lasers, and the signal was detected at this frequency. In addition to generating a difference frequency, the MIM diode can also be used to add microwave sidebands to the difference frequency (Evenson *et al.* 1986). This technique was particularly useful when the difference between pairs of  $\text{CO}_2$  lines did not fall close enough to the OH transition frequency to be studied. Two of the OH frequencies were measured in this way (see Table 1).

The details of the transitions observed and the measurements made are given in Table 1. Both rotational and fine-structure transitions have been detected, although the latter are much weaker. The accuracy of each measurement is also given, a typical value ( $1 \sigma$ ) for an isolated line being between 100 and 200 kHz. This can be confirmed experimentally because there is some redundancy in the measurements; this allows independent determination of the separation between pairs of energy levels. The accuracy of these measurements is limited by determining the center of each absorption line (i.e., it is a function of the line width and the signal-to-noise ratio). The FIR frequency uncertainty is the quadrature sum of the uncertainties of the  $\text{CO}_2$  pair used to synthesize the FIR radiation (35 kHz). The line widths have been measured for all the transitions and are consistent with the expectations of Doppler broadening at 300 K (for example, the FWHM of the 2.5 THz lines was 9.5 MHz).

The best previous estimates of the OH frequencies obtained by extrapolation of the LMR data are also given in Table 1. The agreement with the present values is within the estimated uncertainty of the LMR results (3 MHz) and provides an important confirmation of the model used in the extrapolation procedure (Brown *et al.* 1978). This model has not previously been tested.

During the course of our work, we learned of a parallel study of OH by Farhoomand, Blake, and Pickett (1985). These authors detected the hyperfine components of two rotational transitions with radiation generated by mixing the outputs of a fixed frequency FIR laser and a tunable, millimeter-wave klystron in a Schottky barrier diode. The agreement between the two sets of measurements is consistent with the quoted uncertainties: 500 kHz (Farhoomand *et al.*) and 200 kHz (present work).

The measurements in Table 1 allow a refinement of the molecular parameters for OH. We used all the reasonably well resolved lines to determine the appropriate parameters in the molecular Hamiltonian (Brown *et al.* 1981) in a weighted least-squares fit. The lambda-doubling and proton hyperfine parameters were constrained to the values determined previously (Brown *et al.* 1981). The weights were taken as the inverse square of the experimental uncertainties given in Table 1. The data were fitted to experimental precision by adjustment of just four parameters,  $A$ ,  $\gamma$ ,  $B$ , and  $D$ . The results of the fit are given in Table 1 and the resultant parameter set in Table 2. The standard deviation of the fit relative to the experimental uncertainty is 0.84. Comparison with the corresponding table in the earlier paper (Brown *et al.* 1981) shows that the required changes in the parameters are very small.

TABLE 2

PARAMETERS (MHz) FOR OH IN THE  $v = 0$  LEVEL OF THE  $X^2\Pi$  STATE

Parameter	Value
Constrained in the Least-Squares Fit <sup>a</sup>	
$10^2 H$	0.4236
$p$	7053.09846
$p_D$	-1.550962
$10^3 p_H$	0.1647
$a$	86.1116
$b_F$	-73.2537
$c$	130.641
$d$	56.6838
$\gamma_D$	0.7315
$q$	-1159.991650
$q_D$	0.4420320
$10^4 q_H$	-0.8237
$10 C_I$	-0.9971
$10^2 C_I$	0.643
$10 d_D$	-0.2276
Determined in the Least-Squares Fit	
$\bar{A}^b$	-4168640.221(82) <sup>c</sup>
$\bar{\gamma}^b$	-3573.805(46)
$B$	555661.584(11)
$D$	57.23246(98)

<sup>a</sup> From Brown *et al.* 1981.

<sup>b</sup> Effective parameter. The fit was performed with the parameter  $A_D$  constrained to zero (Brown *et al.* 1979).

<sup>c</sup> Parentheses enclose one standard deviation of the least-squares fit, in units of the last quoted decimal place.

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