

## DIRECT MEASUREMENT OF THE FUNDAMENTAL ROTATIONAL TRANSITIONS OF THE OH RADICAL BY LASER SIDEBAND SPECTROSCOPY

JAM FARHOOMAND,<sup>1</sup> GEOFFREY A. BLAKE,<sup>2</sup> AND HERBERT M. PICKETT<sup>1</sup>

*Received 1984 November 30; accepted 1985 January 8*

### ABSTRACT

We report for the first time the direct (zero-field) spectra of the fundamental rotational transitions of the OH radical in its  $\Omega = 3/2$  and  $1/2$  states at 2509.9 and 1834.7 GHz using a recently developed far-infrared laser sideband spectrometer. These measurements have verified and refined the predictions of previous laser magnetic resonance (LMR) work, thereby confirming the far-infrared detection of interstellar OH. The increased accuracy of these direct measurements will be useful to future astronomical and atmospheric studies of these important transitions.

*Subject headings:* laboratory spectra — molecular processes

### 1. INTRODUCTION

The ubiquitous OH radical is a fundamental participant in a wide variety of chemical and physical processes. In addition to being a widespread constituent of the interstellar medium, OH also regulates stratospheric chlorine and nitrogen oxide catalytic ozone destruction cycles via reactions with HCl and NO<sub>2</sub>. Because of its importance to so many systems, and because it is relatively easy to generate in the laboratory, OH has long served as the prototypical free radical for a number of spectroscopic techniques and theoretical models. Perhaps the most well-studied transitions are the microwave lambda doublets first detected in the laboratory by Dousmanis, Sanders, and Townes (1955) and subsequently detected astronomically 8 yr later by Weinreb *et al.* (1963)—the first interstellar molecule detected using radioastronomical techniques. Observations of the ground-state lambda doublets also produced the first interstellar maser (Weaver *et al.* 1965).

It is only recently, however, that the far-infrared (FIR) pure rotational transitions of OH shown in Figure 1 have become accessible to laboratory and astronomical study. Spectral lines in this region are important because they provide powerful, and often unique, probes into the chemical and physical nature of the interstellar gas (Phillips and Huggins 1981; Watson 1982). For example, thermal FIR emission from OH at 119 and 84  $\mu\text{m}$  in Orion has shown that the hydroxyl radical abundance is increased dramatically by the passage of shock fronts through molecular clouds (Watson *et al.* 1985), a feature not observable with the lambda doubling transitions. Searches for, and definitive identification of, various species in the relatively unexplored FIR region must rely on the presence of accurate laboratory rest frequencies. To date, the bulk of this limited data on transient species has been provided by laser magnetic resonance (LMR) studies due to the almost complete lack of tunable sources of radiation at FIR wavelengths. In this pioneering technique, atomic or molecular transitions are tuned into resonance with various fixed

frequency FIR lasers by applying a variable magnetic field to the sample (Evenson 1981). As such, zero-field frequencies are not directly measured but must be reconstructed from fits of the magnetic field data using sophisticated effective Hamiltonians. Errors in the zero-field transition frequencies are therefore higher than can be obtained with swept frequency techniques. In addition, the method is inapplicable to non-magnetic molecules like CO or NH<sub>3</sub>.

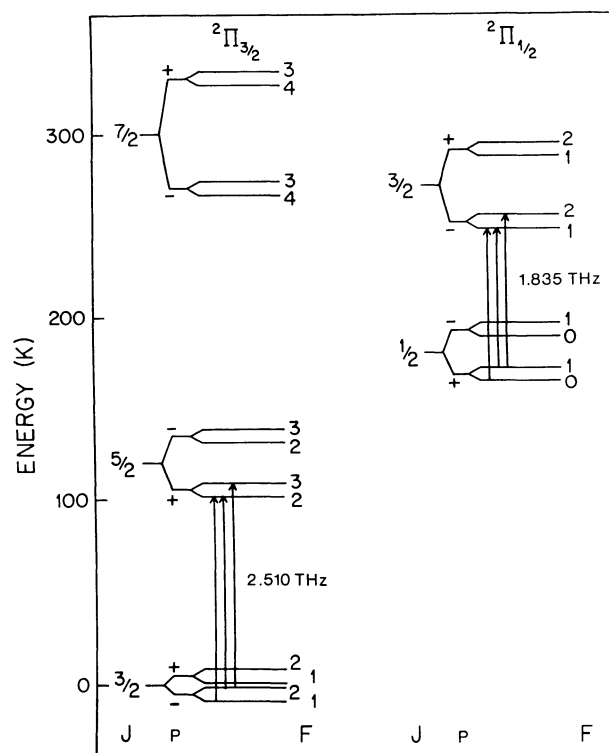


FIG. 1.—Energy level diagram of the lowest rotational states of the OH radical. The hyperfine and lambda doubling splittings have been exaggerated here for clarity. Arrows mark the observed transitions.

<sup>1</sup>Jet Propulsion Laboratory, California Institute of Technology.

<sup>2</sup>Department of Chemistry, California Institute of Technology.

As part of the continuing effort in this laboratory to measure the submillimeter spectra of molecules of astronomical and atmospheric interest, we present for the first time the zero-field spectra of the fundamental rotational transitions of the OH radical using a frequency-agile FIR laser sideband spectrometer. The high accuracy of these measurements verifies the predictions of previous LMR work and will be of use to the generation of FIR heterodyne receivers which, unlike current astronomical instruments, will be able to fully resolve the OH line profiles in the interstellar medium.

## II. EXPERIMENTAL

The laser sideband spectrometer used in these experiments has been described in detail elsewhere (Farhoomand *et al.* 1985). Briefly, radiation from tunable millimeter-wave klystrons is mixed with that from FIR lasers in a Schottky-barrier diode (Mattauch log 1V1) located at the apex of an open structure corner cube mount. A commercial CO<sub>2</sub>-pumped FIR molecule laser (Apollo model 560) in which the CO<sub>2</sub> laser is stabilized with an external Fabry-Perot etalon serves as the fixed frequency source. The millimeter-wave klystrons are phase locked to a stabilized X-band source (Hewlett-Packard model 8762A) which may be swept under computer control.

As shown in the optical layout of Figure 2, a polarizing Michelson interferometer is used both to couple laser radiation onto the mixing diode and also to separate the tunable sidebands from the laser carrier. Separation of the upper and lower sidebands as well as suppression of any laser leakage from the Michelson interferometer is achieved with an adjustable Fabry-Perot cavity. In earlier experiments a Fabry-Perot with a finesse of about 15 was used in conjunction with an angle-tuned mesh filter, but in these experiments a single Fabry-Perot with a finesse of approximately 80 sufficed. After passing through a free-space absorption cell containing the species of interest, the sideband radiation is detected by a Ge

bolometer operating at 2.2 K. Supplying the Schottky diode with a square wave bias voltage in the 50–500 Hz range amplitude modulates the sideband power to provide a phase-sensitive signal. Since this technique monitors the total power received by the detector, a true line shape is produced. Toneburst (frequency) modulation of the klystron may also be employed, which yields a second derivative line shape.

Two difluoromethane laser lines have been used to measure the OH spectra at 1834.7 and 2509.9 GHz. The  $\Omega = 1/2$ ,  $J = 1/2 \rightarrow 3/2$  transitions were recorded using the lower laser sideband produced by the 1891.3 GHz CH<sub>2</sub>F<sub>2</sub> laser line and klystrons in the 50–55 GHz range, while the  $\Omega = 3/2$ ,  $J = 3/2 \rightarrow 5/2$  lines were detected using the upper sideband of the 2448.0 GHz CH<sub>2</sub>F<sub>2</sub> laser and 60–65 GHz klystrons. OH radicals were produced by a 1.5 m DC glow discharge cell through which a slow flow of water vapor was established. Although detected under a wide range of conditions, highest OH signal-to-noise ratios were obtained with water vapor pressures of 65–80  $\mu$ m and discharge currents of 100–200 mA. Figure 3 shows a typical spectrum of the  $\Omega = 3/2$ ,  $J^P = 3/2^- \rightarrow 5/2^+$  transition.

## III. RESULTS AND DISCUSSION

Figure 1 shows an energy level diagram of the OH radical and the transitions studied in this work, which are listed in Table 1. The lambda doubling and hyperfine splittings have been exaggerated for clarity in Figure 1. In most cases the nuclear hyperfine splittings are easily resolved. The hyperfine and lambda doubling intervals of the OH rotational transitions are known to an accuracy of  $\sim 5$  kHz from the beam maser work of Meerts and Dymanus (1975). We have therefore obtained the frequencies listed in Table 1 by fitting the overall spectrum with Gaussian components whose separations are fixed to the hyperfine splittings measured previously. The quality of the data is such, however, that

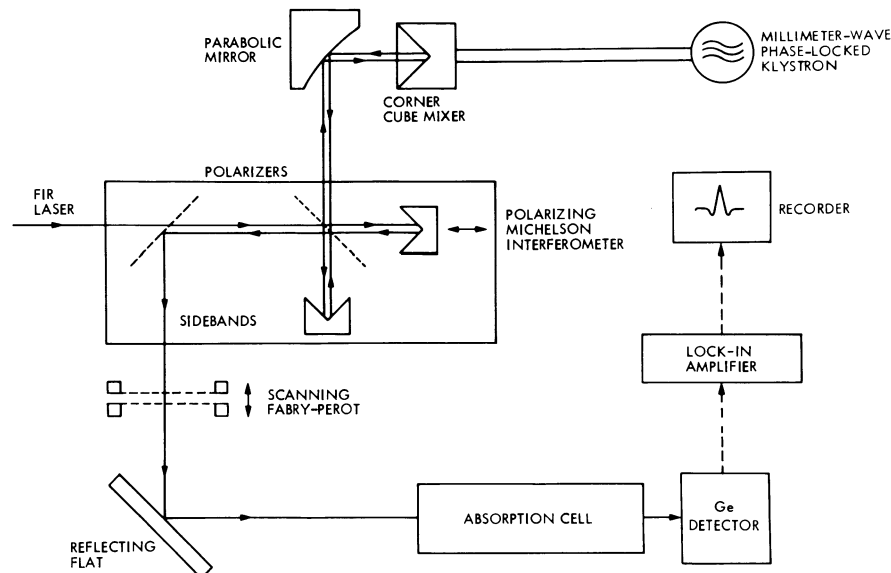


FIG. 2.—Optical layout of the tunable laser sideband spectrometer

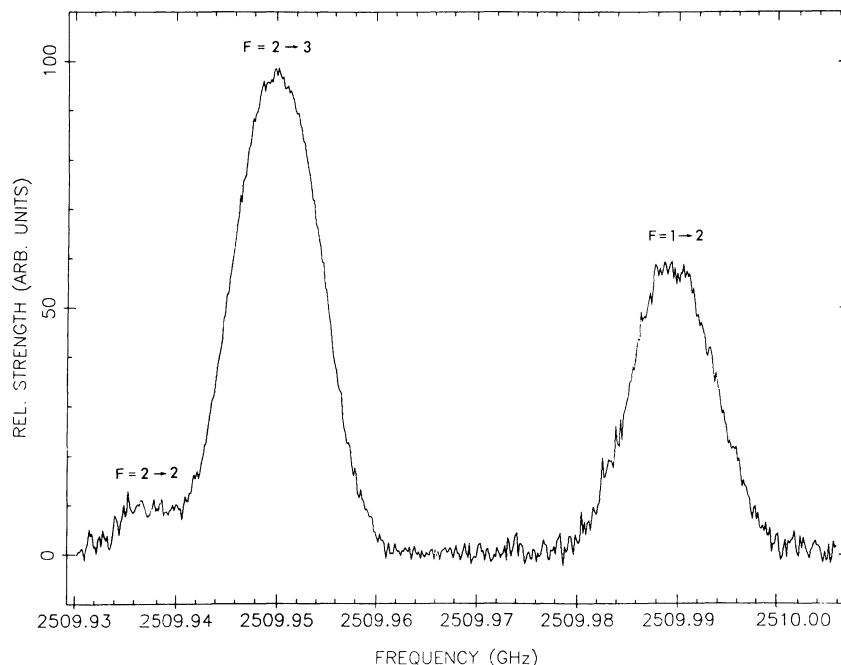


FIG. 3.—Observed spectrum of the  $J^P = 3/2^- \rightarrow 5/2^+$  transition obtained by averaging four sweeps taken with a 1 s time constant. Amplitude modulation of the laser sidebands produces a true lineshape profile.

TABLE 1  
OBSERVED SPIN-ROTATION TRANSITION FREQUENCIES  
OF  $^2\Pi_{3/2}$  AND  $^2\Pi_{1/2}$  OH

$\Omega$	TRANSITION <sup>a</sup>		MEASURED FREQUENCY <sup>b</sup> ( $\sigma$ ) (MHz)	LMR PREDICTIONS <sup>c</sup> ( $\sigma$ ) (MHz)	VACUUM WAVELENGTH ( $\mu\text{m}$ )
	$J^{P'} \rightarrow J^{P''}$	$F' \rightarrow F''$			
1/2 .....	$3/2^- \rightarrow 1/2^+$	1 $\rightarrow$ 1	1834735.51(0.50) <sup>m</sup>	1834734.7(3.0)	163.3983
		2 $\rightarrow$ 1	1834747.35(0.50) <sup>m</sup>	1834746.6(3.0)	163.3972
		1 $\rightarrow$ 0	1834750.42(0.50) <sup>m</sup>	1834749.6(3.0)	163.3969
1/2 .....	$3/2^+ \rightarrow 1/2^-$	1 $\rightarrow$ 1	1837746.60(0.50) <sup>c</sup>	1837745.8(3.0)	163.1305
		2 $\rightarrow$ 1	1837816.82(0.50) <sup>c</sup>	1837816.0(3.0)	163.1243
		1 $\rightarrow$ 0	1837837.02(0.50) <sup>c</sup>	1837836.2(3.0)	163.1225
3/2 .....	$5/2^+ \rightarrow 3/2^-$	2 $\rightarrow$ 2	2509935.44(0.50) <sup>m</sup>	2509933.7(3.0)	119.4424
		3 $\rightarrow$ 2	2509949.43(0.50) <sup>m</sup>	2509947.7(3.0)	119.4417
		2 $\rightarrow$ 1	2509988.61(0.50) <sup>m</sup>	2509986.9(3.0)	119.4398
		2 $\rightarrow$ 2	2514298.83(0.50) <sup>c</sup>	2514297.1(3.0)	119.2351
3/2 .....	$5/2^- \rightarrow 3/2^+$	3 $\rightarrow$ 2	2514317.17(0.50) <sup>c</sup>	2514315.5(3.0)	119.2342
		2 $\rightarrow$ 1	2514353.96(0.50) <sup>c</sup>	2514352.3(3.0)	119.2325

<sup>a</sup>Quantum numbers for the upper state are denoted by primes and those for the lower state by double primes. Superscripts on the  $J$  quantum numbers indicate the parity of the states according to Brown *et al.* 1982.

<sup>b</sup>The m superscript denotes those transitions that have been measured directly, while the c superscript indicates transition frequencies that have been calculated from our observed data and the beam maser measurements of Meerts and Dymanus 1975.  $\sigma$  in MHz.

<sup>c</sup>Taken from Brown *et al.* 1982.  $\sigma$  in MHz.

unrestricted fits of the  $J^P = 3/2^- \rightarrow 5/2^+$  transitions reproduce the beam maser hyperfine splittings to within 200 kHz. Thus, the error bars quoted in Table 1 apply to the measured frequency of the entire pattern and not to the individual splittings of the hyperfine and lambda doubling components. Only the  $J^P = 1/2^+ \rightarrow 3/2^-$  and  $J^P = 3/2^- \rightarrow 5/2^+$  transition frequencies have been measured directly; frequencies for the other lambda doubling components have been calculated

using the beam maser splittings noted above. Table 1 also lists the predicted zero-field transition frequencies of Brown *et al.* (1982), derived from earlier LMR measurements (Brown *et al.* 1981). As can be seen, our measured frequencies lie slightly above the LMR predictions but within their 3 MHz error bars in all cases. Identification of the astronomical features at 2509.9 and 2514.3 GHz as OH is therefore quite secure.

The major uncertainty in these experiments is that of the

FIR laser frequency as the klystrons are referenced to an extremely stable 5 MHz source. The uncertainties stem from the broad gain profiles of FIR lasers and are manifested as follows:

1. The absolute laser frequencies for each FIR system may differ significantly from the reported values because of differences in resonator geometry, CO<sub>2</sub> pump power, etc.

2. As determined mainly by the stability of a particular FIR cavity, the fractional accuracies reported may not be applicable to different FIR systems.

For example, we have found that for lower frequency HCOOH and CH<sub>3</sub>F lasers the measured frequency may be altered approximately  $\pm 0.3$ – $0.5$  MHz by adjusting the FIR cavity length to produce a 10% drop in the output power level. These measurements were performed using the corner cube as a harmonic mixer. Inguscio *et al.* (1984) have obtained similar results with higher frequency laser lines used to record the LMR spectra of Si atoms for which they report a fractional accuracy of  $2 \times 10^{-7}$ . Therefore, to fully utilize the high-resolution capabilities of this technique, it is essential to monitor the laser frequencies used in each experiment.

For this purpose we have used the  $J = 16 \rightarrow 17$  and  $21 \rightarrow 22$  lines of CO at 1956.0 and 2528.2 GHz as a calibrator to determine our absolute laser frequencies. The frequencies of these transitions are known to about 200 kHz from fits combining results from previous millimeter-wave spectroscopy with the recent high- $J$  measurements of Evenson (1985) using another tunable FIR spectrometer. Successive measurements were performed, alternating between the OH and CO lines, to ensure the consistency of the generated sideband frequencies.

Other molecules, namely the asymmetric rotors SO<sub>2</sub> and HDO which have a much richer FIR spectrum than CO, were used in the same manner as further insurance of the stability of the system. The 0.5 MHz error bar assigned to the measured frequencies listed in Table 1 is the maximum standard deviation of the independent measurements performed on each separate molecule mentioned above over a period of time. The average standard deviation for all these measurements is 0.3 MHz. In addition, fitting errors imposed by the spectral line-widths of OH at these frequencies ( $\Delta\nu_{\text{Doppler}} \approx 6$  MHz) also limits the accuracies to within 0.5 MHz. Using CO as the reference molecule, our CH<sub>2</sub>F<sub>2</sub> lasing frequencies lie within 3 MHz of the reported values (Peterson, Scalabrin, and Evenson 1980). Other possible systematic errors in the line frequency measurements include frequency shifts induced by Zeeman broadening by Earth's magnetic field and Stark effect by the electric discharge source. We have determined, however, that these effects are negligible under the conditions of our experiment.

We would like to thank Dr. K. M. Evenson of the National Bureau of Standards, Boulder, for providing his measured CO frequencies prior to publication, and Dr. E. A. Cohen for useful discussions during the course of this work. We would also like to thank M. Schaefer for his assistance on the Schottky diode mixer. The research described in this paper was performed by the Jet Propulsion Laboratory, California Institute of Technology, under contract with the National Aeronautics and Space Administration.

#### REFERENCES

- Brown, J. M., Kerr, C. M. L., Wayne, F. D., Evenson, K. M., and Radford, H. E. 1981, *J. Molec. Spectrosc.*, **86**, 544.  
 Brown, J. M., Schubert, J. E., Evenson, K. M., and Radford, H. E. 1982, *Ap. J.*, **258**, 899.  
 Dousmanis, G. C., Sanders, T. M., Jr., and Townes, C. H. 1955, *Phys. Rev.*, **100**, 1735.  
 Evenson, K. M. 1981, *J. Chem. Soc. Faraday Trans. I*, No. 71, p. 7.  
 ———. 1985, private communication.  
 Farhoomand, J., Blake, G. A., Frerking, M. A. and Pickett, H. M. 1985. *J. Appl. Phys.*, in press.  
 Inguscio, M., Evenson, K. M., Beltran-Lopez, H., and Ley-Koo, E. 1984, *Ap. J. (Letters)*, **278**, L127.  
 Meerts, W. L., and Dymanus, A. 1975, *Canadian J. Phys.*, **53**, 2123.  
 Peterson, F. R., Scalabrin, A., and Evenson, K. M. 1980, *Int. J. IR mm Waves*, **1**, 111.  
 Phillips, T. G., and Huggins, P. J. 1981, *Ap. J.*, **251**, 533.  
 Watson, D. M. 1982, Ph.D. thesis, University of California, Berkeley.  
 Watson, D. M., Genzel, R., Townes, C. H., and Storey, J. W. V. 1985, *Ap. J.*, submitted.  
 Weaver, H., Williams, D. R. W., Dieter, N. H., and Lum, W. T. 1965, *Nature*, **208**, 29.  
 Weinreb, S., Barret, A. H., Meeks, M. L., and Henry, J. C. 1963, *Nature*, **200**, 829.

GEOFFREY A. BLAKE: California Institute of Technology, 320-47, Pasadena, CA 91125

JAM FARHOOMAND and HERBERT M. PICKETT: Jet Propulsion Laboratory, 168-314, 4800 Oak Grove Drive, Pasadena, CA 91109