

In this type of laser, self-phase-locking between transverse modes occurs more easily than in other lasers for the following reason: The discharge tube being cooled with liquid nitrogen presents a great radial gradient of temperature; therefore, a higher population inversion is built up near the walls of the tube than on the axis, and this circumstance makes the oscillation of transverse modes easier.

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## CH FREE RADICALS DETECTED BY INFRARED LASER MAGNETIC RESONANCE

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CH radicals in an oxyacetylene flame have been detected by a magnetic resonance absorption method, with a water-vapor laser as the source oscillator at a frequency of 2.5 THz. The absorption spectrum is identified with the pure rotational transition,  $J, K = (5/2, 2) \rightarrow (7/2, 3)$  at a wavelength of 118.6  $\mu\text{m}$ .

CH, the fundamental hydrocarbon radical, is familiar to optical astronomers by its interstellar absorption lines, but it has been a source of continuing frustration to radio astronomers. Laboratory searches for the 10-cm  $\Lambda$ -type doubling spectrum of CH have failed and astronomical searches for the same spectrum, necessarily over wide frequency ranges because of the lack of laboratory data, have been no more successful.<sup>1</sup> Laboratory experiments are difficult because there is no good way known by which to make large quantities of CH. Although the optical emission spectrum of CH can be measured easily in hydrocarbon flames, a source more productive of ground-state molecules is needed for measurements of the microwave spectrum. High-temperature flames have looked promising since Bleekrode and Nieuwpoort<sup>2</sup> showed that optical absorption by CH (and OH and C<sub>2</sub>) was observable in oxyacetylene flames burning at low pressure. Their measured concentration of CH is, however, not quite large enough to give detectable microwave absorption signals, and, furthermore, there are serious technical difficulties in operating a high-temperature heavily ionized flame in a microwave absorption cell. The recently developed technique of laser magnetic resonant spectroscopy<sup>3-5</sup> offers a possibility, provided there existed the necessary near coincidence between a CH infrared absorption and a convenient laser line. The optically-determined<sup>6</sup> energy levels of CH indicate a coincidence between the  $F_1$  rotational levels  $J, K = (5/2, 2)$  and  $J, K = (7/2, 3)$  and the 118.6- $\mu\text{m}$  line of the water-

vapor laser. These are not the rotational levels most important to radio astronomy, but the successful detection of this 118.6- $\mu\text{m}$  resonance, which we report here, encourages us to believe that the lowest level, the one responsible for the long-sought 10-cm spectrum, can also be measured by the same method.

The experimental results are given by Fig. 1, which is a pen recording of the 118.6- $\mu\text{m}$  magnetic resonance spectrum over a field range of 0-25 kG, and by Table I, which lists measurements on the individual lines of the spectrum. The spectrum was obtained by monitoring the power level of a water-vapor laser, within which a low-pressure oxyacetylene flame burned, while slowly increasing the strength of a magnetic field applied to the flame. (The derivative line shape is due, as is usual in magnetic resonance spectra, to the use of field modulation and lock-in detection.) A Brewster-angle diaphragm divides the 5-m-long laser tube into two sections, one for the flame and one for the water-vapor electric discharge, each having its own gas inlets and vacuum pump. The diaphragm, made of polypropylene film approximately 15  $\mu\text{m}$  thick, has two other functions as well: It polarizes the laser radiation and it reflects a small fraction of the laser radiation to two Golay infrared detectors located outside and on either side of the laser tube. One of these detectors monitors the laser power and the other detects the absorption signal. To change the polarization the entire beam splitter assembly may be rotated about the laser axis, and the cou-

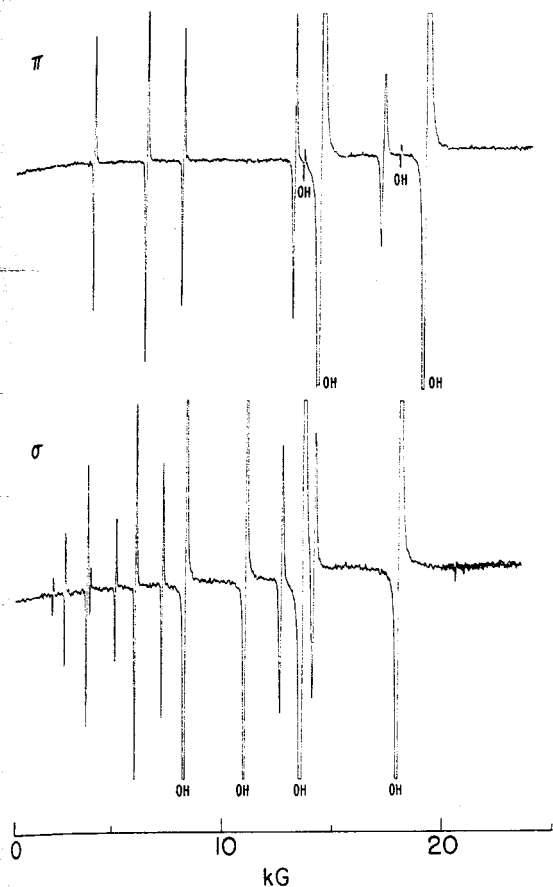


FIG. 1. The 118.6- $\mu\text{m}$  magnetic resonance spectrum of a low-pressure oxyacetylene flame. The source oscillator is a water-vapor laser operating at 2527.95 GHz, and pen recordings are shown for two orthogonal polarizations of the infrared electric field relative to the dc magnetic field. The six square-topped lines ( $2\pi$  and  $4\sigma$ ) are OH resonances that overdrive the recorder. The two small lines in the  $\pi$  spectrum are  $\sigma$  resonances of OH, detectable because of imperfect orientation of the polarizer.

pling may be changed by rotating the beam splitter itself a few degrees from the Brewster angle.

The oxyacetylene diffusion flame burns between the poles, tapered to 6 in. in diameter at a gap, of a 15-in. precision electromagnet. At the typical operating pressure of 3.5 Torr the flame is a bright blue-green ball that fills the bore of the laser tube for a distance of about 5 cm. The burner, a coaxial quartz tube assembly mounted in a side arm of the laser tube, was fed with welding-grade oxygen and acetylene. The flame was ignited by subjecting the inlet oxygen to a microwave discharge. This produces an "atomic flame" which, with increasing gas supply, goes over smoothly to the much hotter diffusion flame.

The strongest lines in Fig. 1 are due to the OH molecule, which also has a rotational transition ( ${}^2\Pi_{3/2}$ ,  $J = 3/2 \rightarrow 5/2$ ) nearly coincident with the 118.6- $\mu\text{m}$  laser line.<sup>5</sup> When the flame is replaced by other known sources of OH, such as an electric

discharge in water vapor or the chemical reaction  $\text{H} + \text{NO}_2$ , these strong absorptions get much stronger (and even extinguish the lasing action), but the other 14 principal lines in Fig. 1 vanish. This group of lines numbering five  $\pi$  lines and nine  $\sigma$  lines are due to CH. The basis for the identification is shown by Fig. 2, which is a diagram of the Zeeman effect of the levels  $J, K = (5/2, 2)$  and  $J, K = (7/2, 3)$  of CH, drawn from the optical data of Douglas and Elliott<sup>6</sup> and the theoretical Zeeman-energy formula of Hill.<sup>7</sup> The  $\Lambda$ -type doubling separations and Zeeman splittings of the two levels are drawn to scale, but the infrared energy difference is shown much reduced. Curvature of the sublevels is caused by magnetic interactions with the nearby spin doublet levels  $J, K = (3/2, 2)$  and  $(5/2, 3)$ . Hyperfine structure is disregarded, as are the small magnetic perturbations off-diagonal in  $K$ . The length of the transition arrows is scaled to the energy of the water-vapor laser line, and the positions of these arrows give a rough prediction of the magnetic resonance spectrum. The predicted spectrum, with theoretical relative intensities, is given at the bottom of Fig. 2. There is good agreement with the observed flame spectrum: Every predicted CH line is found in Fig. 1 with the right polarization and at approximately the right field strength. The relative intensities are also roughly correct, when allowance is made for the lower modulation sensitivities of the broader

TABLE I. Magnetic resonance data. Oscillator frequency:  $2527.953 \pm 0.001$  GHz.

Polarization	Line center <sup>a</sup> (G)	Line width <sup>b</sup> (G)	Relative signal amplitude
$\pi$	4258	47	9.3
	6628	62	13.0
	8242	58	9.6
	13221	93	8.7
	17147	140	4.3
$\sigma$	2316	21	1.0
	2924	29	3.3
	3968	36	5.2
	4116	33	1.0
	5275	33	2.4
	6171	48	5.3
	7377	47	3.8
	12694	83	3.9
14173	113	3.7	

<sup>a</sup>Estimated uncertainties are  $\pm 5$  G for lines below 10 kG and  $\pm 10$  G for lines above 10 kG.

<sup>b</sup>Measured between peaks of the derivative line shape. Some of the narrower lines may be somewhat modulation broadened. These field widths are consistent with a frequency width of 21.5 MHz.

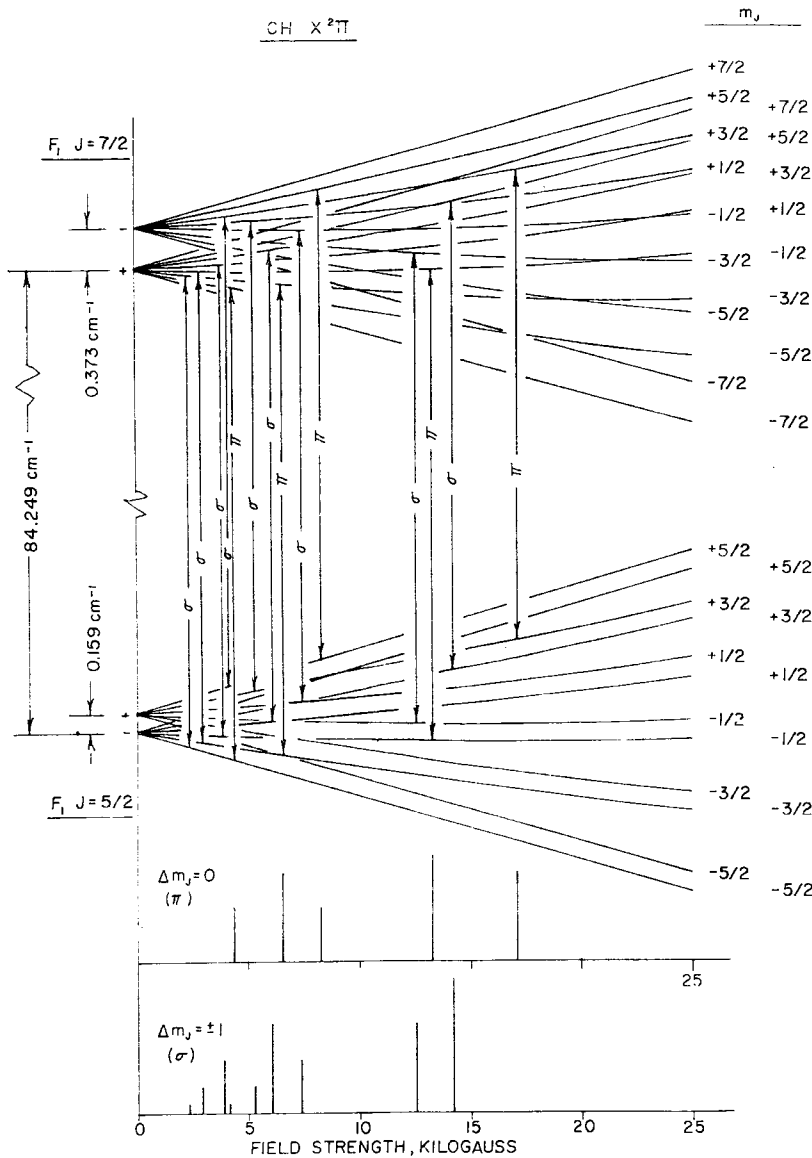


FIG. 2. Zeeman splittings of the  $J, K = (5/2, 2)$  and  $(7/2, 3)$  levels of the ground state of CH, and the predicted magnetic resonance spectrum for an oscillator frequency of 2527.953 GHz ( $84.323 \text{ cm}^{-1}$ ). Energies at zero field are taken from measurements on the optical spectrum of CH (Ref. 6).

high-field lines. Using Fig. 2 to assign quantum numbers, we have made a least-squares computer fit of the 14-line flame spectrum to Hill's energy formula. The adjustable parameters in this fit are the rotational constant  $B$ , the spin-uncoupling constant  $Y (=A/B, \text{ where } A \text{ is the spin-orbit constant})$ , and the difference in the  $\Lambda$ -type doubling frequencies of the two rotational levels,  $\nu_A(7/2) - \nu_A(5/2)$ . The input data are the measured magnetic field strengths of the line centers given in Table I and the frequency of the  $118.6\text{-}\mu\text{m}$  laser line,  $2.5279528 \text{ THz}$ .<sup>8</sup> Best values of the fitted parameters are listed in Table II, along with corresponding values from the optical emission spectrum of CH. The agreement between the two sets of numbers is conclusive proof that the 14-line flame spectrum is due to CH. Hill's Zeeman theory was meant for optical spectra, and it cannot be expected to match the precision of the laser res-

onance technique. Accordingly, the fitted parameters of Table II should be regarded as preliminary values.

This work shows clearly the sensitivity of the laser magnetic resonance technique. CH concentrations of  $\sim 10^{12}/\text{cm}^3$  in the ground vibrational and electronic state<sup>2</sup> yield signals of 260 times noise in an absorption path of 5 cm; this is roughly 30 times the signal-to-noise ratio reported using broad-band optical techniques.<sup>2</sup> Due to the frequency dependence of line absorption coefficients, an increase in sensitivity by a factor between 250 and  $(250)^2$ , depending on sources of linewidth, might be expected when comparing the laser resonance technique at 2.5 THz with microwave absorption at 10 GHz. The actual increase, determined by comparing OH signals observed at the two frequencies, is approximately 300, and this suggests that there is room for even further

TABLE II. Comparison of molecular parameters.

Parameter	From flame spectrum <sup>a</sup>	CH <sup>b</sup>
$B_0$ (rotational constant)	$14.162 \pm 0.001 \text{ cm}^{-1c}$	$14.191 \text{ cm}^{-1}$
$Y$ (spin-coupling constant)	$1.99 \pm 0.2$	2.00
$\nu_A(7/2) - \nu_A(5/2)$	$0.213 \pm 0.002 \text{ cm}^{-1}$	$0.214 \text{ cm}^{-1}$

<sup>a</sup>Least-squares fit of the data in Table I to Hill's Zeeman-energy formula [Eq. (22) of Ref. 7]. The rms deviation is  $0.001 \text{ cm}^{-1}$ , and the quoted errors are the variations of the parameters, one at a time, that are necessary to double this rms deviation.

<sup>b</sup>Reference 6.

<sup>c</sup>A correction for centrifugal distortion, not applied, would increase this value.

improvement in sensitivity. The main source of noise at present is the infrared detector, a Golay cell, which might well be replaced by a cryogenic detector.

With improved sensitivity, one could hope to detect the weaker magnetic dipole spectrum (the  $+-+$  and  $---$  transitions in Fig. 2) and to resolve hyperfine structure in the electric dipole spectrum of Fig. 1. Frequency-difference equations could then be applied to determine the microwave

spectra of the  $J, K$  (5/2, 2) and (7/2, 3) levels separately, to a precision of about  $\pm 1 \text{ MHz}$ . Similar observations on the  $560\text{-}\mu\text{m}$  rotational transition  $J, K = (1/2, 1) \rightarrow (3/2, 1)$  would make it possible to determine, to similar precision, the 10-cm astronomical spectrum of CH.

We thank Dr. H. P. Broida for advice on the technique of operating low-pressure flames and his continuing enthusiasm for these experiments.

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