

## FAR-INFRARED LMR DETECTION OF HYDROXYMETHYL

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Laser magnetic resonance spectra of the free hydroxymethyl radical, produced by the reaction of atomic chlorine with methanol vapor, have been observed at several laser wavelengths between 118 and 657  $\mu\text{m}$ . The spectra are identified by chemical tests and by comparison with the ESR spectrum of hydroxymethyl in solids and liquids.

Hydroxymethyl ( $\text{CH}_2\text{OH}$ ) has long been known as a product of photolysis or fluorine atom reaction in liquid and solid methanol, where it is recognized by its electron spin resonance (ESR) [1,2] and infrared spectra [3]. As one of the simplest organic free radicals, its presence is also predictable in gaseous laboratory reactions, in the upper atmosphere, and in the interstellar gas. No direct detection of  $\text{CH}_2\text{OH}$  in these sources has been possible, however, in the absence of knowledge of its gas-phase spectra. We have now observed far-infrared Zeeman spectra of gaseous  $\text{CH}_2\text{OH}$  by the laser magnetic resonance (LMR) method. Identification of the spectra is based on their chemical behavior and on hyperfine structure; there is as yet insufficient data for an energy level analysis. One of the spectra, at a laser wavelength of 118.8  $\mu\text{m}$ , is intense enough to permit measurements of reaction rate coefficients by the LMR flow-tube method.

The LMR spectrometer is of the transverse optically pumped type [4], with an intracavity absorption cell that is part of a fast gas-flow system.  $\text{CH}_2\text{OH}$  was made in the absorption cell by mixing methanol vapor with the products of a microwave discharge in a flowing gas mixture of 3% chlorine in helium; the gas conditions were preset for maximum  $\text{CH}_2\text{OH}$  production in accord with a recent study of  $\text{CH}_2\text{OH}$

chemistry [5]. The total pressure in the absorption cell was 0.23 Torr, of which 0.03 Torr was methanol.

Searches for spectra were made with 47 different laser wavelengths between 118 and 920  $\mu\text{m}$ . The field search range was limited to 0–2 kG, after preliminary scans showed  $\text{CH}_2\text{OH}$  absorption signals only in the vicinity of zero field. In addition to many spectra of HCO and  $\text{HO}_2$ , spectra attributable to  $\text{CH}_2\text{OH}$  were found with the 21 laser wavelengths listed in table 1. Most of these consisted of a few weak and unresolved features near zero field; notable exceptions are shown by fig. 1. Each of the 21 spectra was subjected to two chemical tests, based on the known properties of the methanol–atomic chlorine system [5]: these tests were the addition of oxygen to the gas mixture, and the substitution of  $\text{CH}_3\text{OD}$  for  $\text{CH}_3\text{OH}$ . Both reduce markedly the density of  $\text{CH}_2\text{OH}$ , but oxygen addition increases the density of  $\text{HO}_2$  and  $\text{CH}_3\text{OD}$  substitution does not affect the density of HCO. Spectra that passed these tests were, in addition, all found able to tolerate a large excess of methanol relative to atomic chlorine, a result which is consonant with their assignment to a primary reaction product. The possibility that a chlorine-containing radical was responsible for the new spectra was eliminated by substituting atomic fluorine for atomic chlorine. The same spectra, and in addition the well-known spectra

Table 1  
Wavelengths of CH<sub>2</sub>OH LMR spectra

$\lambda$ ( $\mu\text{m}$ )	Laser gas	CO <sub>2</sub> laser pump line ( $\mu\text{m}$ )
117.7	CH <sub>2</sub> F <sub>2</sub>	R(20), 9.3
118.8	CH <sub>3</sub> OH	P(36), 9.7
166.6	CH <sub>2</sub> F <sub>2</sub>	R(20), 9.3
170.6	CH <sub>3</sub> OH	P(36), 9.7
191.8	CH <sub>2</sub> F <sub>2</sub>	P(22), 9.6
302.3	HCOOH	R(4), 9.4
304.1	DCOOD	R(24), 10.2
353.1	HCOOH	R(6), 10.4
355.1	CH <sub>2</sub> F <sub>2</sub>	P(8), 9.5
370.0	HCOOH	R(28), 10.2
375.5	C <sub>2</sub> H <sub>2</sub> F <sub>2</sub>	P(12), 10.5
380.6	DCOOD	R(12), 10.3
407.3	C <sub>2</sub> H <sub>2</sub> F <sub>2</sub>	P(14), 10.5
432.1	HCOOH	R(22), 9.3
479.9	DCOOH	P(14), 10.5
511.4	CH <sub>2</sub> F <sub>2</sub>	R(28), 9.2
515.0	DCOOD	P(34), 10.7
554.4	C <sub>2</sub> H <sub>2</sub> F <sub>2</sub>	P(14), 10.5
556.9	CD <sub>3</sub> I	P(36), 10.8
567.9	DCOOD	R(26), 10.2
657.2	CH <sub>2</sub> F <sub>2</sub>	P(10), 9.5

of CH<sub>3</sub>O [6], were produced.

Hyperfine structure is clearly visible in the 407.3  $\mu\text{m}$  spectrum of fig. 1a as two groups of six lines, one in each polarization. A similar pattern is found in the ESR spectrum of CH<sub>2</sub>OH in methanol [1,2]. The tripling is caused by hyperfine interaction of the unpaired electron with the two equivalent protons of the CH<sub>2</sub> group, and the small doubling is caused by interaction with the single proton of the OH group. The line splittings are  $\approx 18$  and 2 G in the ESR spectrum, and are 16 and 2 G in fig. 1a. The near equality of these splittings implies that in this gas-phase spectrum the Paschen-Back effect is nearly complete at a field strength of 200 G; that is, the Zeeman energy at this field strength has become considerably larger than both the fine structure and the hyperfine structure energies. It is this condition which often makes strong-field Zeeman spectra unobservable in asymmetric rotor radicals, and indeed the six-line hyperfine patterns are the last detectable features in the 407.3  $\mu\text{m}$  spectrum. Fig. 1a thus represents a complete transition of CH<sub>2</sub>OH from the weak-field limit to the strong-field (Paschen-Back) limit.

The most intense of the 21 CH<sub>2</sub>OH spectra, and also the simplest in appearance, is shown by fig. 1b.

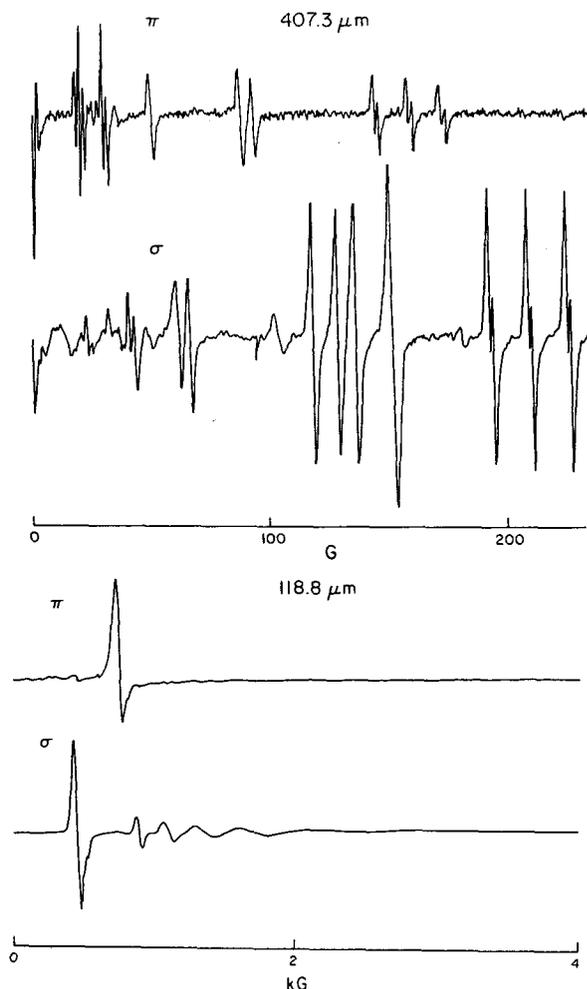


Fig. 1. Selected LMR spectra of CH<sub>2</sub>OH. Traces labelled  $\pi$  and  $\sigma$  are recorded with the far-infrared electric field polarized parallel and perpendicular, respectively, to the dc magnetic field. Line shapes are in derivative form because of the use of ac field modulation and phase-sensitive detection. (a) Laser wavelength 407.3  $\mu\text{m}$ ; (b) laser wavelength 118.8  $\mu\text{m}$ .

Here, as demonstrated by detuning the laser slightly, the laser frequency lies between two molecular transitions, one giving the large single lines and the other giving the resolved series of lines, apparently six in number. Structure on the high-field side of the large lines indicates that they are actually superpositions of several components. The observability of LMR lines at relatively high field strength, as well as the shortness of the observing wavelength, suggests that

this spectrum represents  $\Delta K_a = 1$  transitions between excited axial rotation levels. The theoretical structure of  $\text{CH}_2\text{OH}$  [7,8] predicts the values  $A = 6.5 \text{ cm}^{-1}$ ,  $B = 1.0 \text{ cm}^{-1}$  and  $C = 0.9 \text{ cm}^{-1}$  for its rotation constants, and these would place the transition  $N, K_a = 6,6 \leftarrow 5,5$  at a wavelength near  $120 \mu\text{m}$ . Another possible assignment of the spectrum, one which might account better for its exceptional intensity, is to a low-frequency vibrational transition. Again according to the theoretical structure, the molecule is non-planar but its barrier to pyramidal inversion is less than  $200 \text{ cm}^{-1}$  high. The corresponding inversion-rotation spectrum could have a long-wavelength limit in the far infrared, as compared to a long-wavelength limit of  $5 \text{ mm}$  for the pure rotation spectrum.

A rotational analysis of  $\text{CH}_2\text{OH}$  from the LMR data, similar to that performed for  $\text{CH}_3\text{O}$  [6], may be possible when a sufficient number of resolved spectra are in hand, and with this goal further searches for new spectra are in progress.

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