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LABORATORY MEASUREMENT OF THE 4_{04}–3_{13} 70 GHz TRANSITION OF GROUND-STATE METHYLENE (CH_2)

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ABSTRACT

Measurement of the $N_{KK} = 4_{04}$–3_{13} rotational transition of $X\,^3B_1$ CH_2 is reported. The rotational transition is split into three fine-structure components due to electron spin and spin-rotation interactions. These were observed at 68.37 GHz, 69.01 GHz, and 70.68 GHz, each line within 20 MHz of the values predicted from a prior analysis of the far-infrared rotational spectrum. Also, the triplet hyperfine structure due to the proton nuclear spin was well resolved.

Subject headings: laboratory spectra — molecular processes

I. INTRODUCTION

The present study of the methylene radical (CH_2) in the microwave region is an outgrowth of several preceding high-resolution spectroscopic studies. Observation of rotational transitions from the $^3B_1$ electronic ground state of CH_2 were first reported by Mucha *et al.* (1979) although spectral assignments were not possible at that time. A subsequent analysis of several rovibrational transitions from the v_2 fundamental band by Sears, Bunker, and McKellar (1981) yielded parameters which allowed the prediction of the far-infrared rotational spectrum of CH_2. Very recently, Sears *et al.* (1982) measured and analyzed 13 rotational transitions by far-infrared laser magnetic resonance (LMR). These results provided rather accurate predictions for the present study of the 4_{04}–3_{13} microwave transition.

Since the 4_{04}–3_{13} transition is the only rotational line of CH_2 occurring below 400 GHz and arising from relatively low energy states ($\sim$ 150 cm^{-1}), it is perhaps the only transition by which methylene might be detectable at microwave frequencies in interstellar molecular clouds. Thus, one of the incentives of the current study was to obtain accurate rest frequencies for guiding interstellar searches for CH_2.

II. EXPERIMENTAL

An 80 kHz Stark modulated microwave spectrometer and parallel plate absorption cell were employed in the measurements reported here. A block diagram of the computer-controlled spectrometer was described previously (Suenram and Lovas 1980). The parallel plates employed were 25 cm in length and separated by 3 mm.

The chemical production method was identical to that used for the far-infrared LMR experiments. A microwave discharge (2450 MHz, 50 Watts) of 90% He/10% F_2 on a side-arm of the discharge tube generates fluorine atoms which abstract hydrogen atoms from methane (CH_4) which is injected through a 1 mm nozzle located between the parallel plates. In order to minimize the loss of CH_2 through chemical reactions on the metal plates, the plates were coated with tetrafluoroethylene polymer (TFP) (a commercial lubricant spray was used). This coating enhanced the signal intensity by nearly a factor of 3 over uncoated plates. The reactants were passed through the cell in a continuous flow at a total pressure of 20 mtorr ($\sim$ 2.5 Pa) with a partial pressure of CH_4 of approximately 4 mtorr ($\sim$ 0.5 Pa) for optimum production of CH_2.

III. SPECTRAL OBSERVATIONS

Our laboratory search for CH_2 was guided by predicted frequencies from the analysis of the far-infrared rotational spectrum (Sears *et al.* 1982). The $N_{KK} = 4_{04}$–3_{13} transition has three fine-structure components predicted as follows: $J = 5 \leftarrow 4$ at 68.400 GHz, $J = 3 \leftarrow 2$ at 69.040 GHz, and $J = 4 \leftarrow 3$ at 70.688 GHz, all with estimated uncertainties of $\pm$100 MHz. Each of these components was expected to be split into three hyperfine structure components separated by several MHz. The search was initiated with the strongest component, $J = 5 \leftarrow 4$, near 68.4 GHz. The spectral window employed for the computer-controlled frequency scans was 60 MHz at a resolution of 30 kHz and a time constant of 0.1 s for the phase-sensitive detector. The

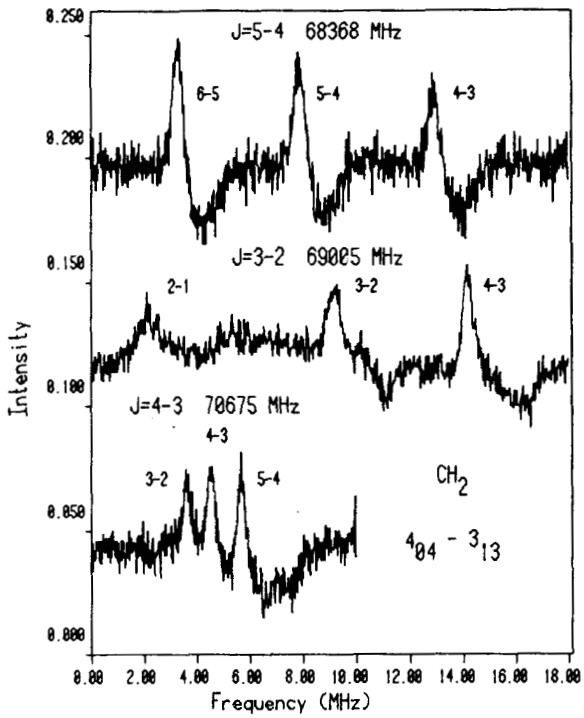

FIG. 1.—Laboratory traces of the three hyperfine triplets of the 4_{04}–3_{13} transition of CH_2. The frequency axis is relative to the initial frequency shown above each trace.

region from 68.34 GHz to 68.52 GHz was searched, and the only transitions observed were the triplet shown in the upper trace of Figure 1. After optimizing the chemical reaction, the predicted regions for the $J = 3 \leftarrow 2$ and $J = 4 \leftarrow 3$ were searched. These searches yielded the triplet features shown in the middle and lower traces of Figure 1. Each of these was tested for sensitivity to an applied magnetic field (~ 200 gauss) and found to be quite paramagnetic, which is expected for triplet CH_2. Each of these regions was examined with higher resolution and longer integration time in order to obtain better signal-to-noise ratios and accurate line positions. Table 1 summarizes the final measurements (discussed below), the assignments, and relative intensities. The strongest transitions were also studied at various applied electric fields in an attempt to measure the Stark effect, to determine the dipole moment. This was unsuccessful due to insufficient signal intensity. The observed signals shown in Figure 1 represent thirty 3.5 minute scan averages, i.e., approximately 2 hours. Even an average of 75 scans on the strongest line did not allow us to obtain any resolvable Stark-shifted components.

After the first set of measurements was complete, we had some concern about line broadening or frequency shift due to the Earth's magnetic field in the absorption cell. We measured it to be a maximum of 0.3 gauss along the entire path. Then we shielded the entire cell with mu-metal (to the extent possible) and thus reduced the maximum field to 0.1 gauss. All nine hyperfine transitions were then remeasured. We obtained slightly improved line widths of $\Delta\nu_{avg} = 0.40$ MHz (vs. 0.45 MHz when unshielded) and frequency differences of less than 0.04 MHz for all lines. These differences, which were within our original measurement uncertainty, may have resulted from improved signal-to-noise ratios due to improvement in some equipment rather than being indicative of magnetic field effects which undoubtedly are not significant.

An effort was made to estimate the total peak absorption of CH_2 by comparison with OCS. The $\nu_2 = 2$ $^{16}O^{12}C^{34}S$ $J = 6$–5 transition near 71.439 GHz, which has a peak absorption coefficient $\gamma = 7.17 \times 10^{-7}$ cm^{-1},

TABLE 1

MEASURED FREQUENCIES FOR THE $N_{KK} = 4_{04}$–3_{13} TRANSITION OF CH_2

TRANSITION		MEASURED FREQUENCY	OBS. – CALC.[a]	RELATIVE INTENSITY	
J'–J''	F'–F''	(MHz)	(MHz)	Obs.	Calc.
5–4	6–5.....	68371.278(41)[b]	–0.015	0.17	0.18
	5–4.....	68375.875(39)	–0.074	0.14	0.14
	4–3.....	68380.873(41)	0.088	0.10	0.12
4–3	5–4.....	70680.720(38)	0.061	0.13	0.14
	4–3.....	70679.543(45)	–0.128	0.11	0.11
	3–2.....	70678.633(42)	0.067	0.08	0.08
3–2	4–3.....	69019.187(44)	–0.079	0.13	0.11
	3–2.....	69014.202(37)	–0.066	0.08	0.08
	2–1.....	69007.179(37)	0.013	0.06	0.05

[a]Analysis by Brown (1982) yielded: $a_{FC} = -12.48(90)$ MHz, $T_{aa} = 42.09(98)$ MHz, with $T_{bb} - T_{cc}$ constrained to 0.72 MHz.

[b]Uncertainties shown in parentheses refer to the last two digits.

was observed to be approximately twice the intensity of the $J, F = 5,6 \leftarrow 4,5$ transition of CH_2.[1]

One of the questions which is difficult to answer is how much of the 25 cm long cell is filled by CH_2. In order to see if adding CH_4 from a number of nozzles along the entire path length would increase the CH_2 intensities, an experiment was carried out with a parallel plate cell which had 12 nozzle openings along the center axis of one plate. We obtained identical signals from this configuration and the single teflon nozzle flame configuration. This suggests that CH_2 fills the entire cell. Assuming this is true, then the strongest component of CH_2 has a total peak absorption $\gamma = 3.7 \times 10^{-7}$ cm^{-1}. This component is actually only 0.17 of the total intensity of the transition, so the total observed intensity is γ_{max} (4_{04}–3_{13}) = 2.18×10^{-6} cm^{-1}.

The theoretical intensity can be calculated using equation (1) (Kisiel and Millen 1982):

$$\gamma_{max} = \frac{8\pi^2 N}{3ckT} f_r f_v \mu_x^2 S_{ij} \nu_0^2 / \Delta\nu. \quad (1)$$

For CH_2, f_v was set equal to 1, and $f_r = 0.03$ was obtained by summing over all the energy levels with $E \leq 1000$ cm^{-1}. This is an approximation but should be close enough for use in equation (1). The electric dipole moment was assumed to be $0.5D$, and $N = 1.3088 \times 10^{14}$ molecules cm^{-3}, which was based on a CH_4 pressure of 4 mtorr (1 mtorr = 1.33 Pa) and 100% conversion to CH_2. From these assumptions, we obtain $\gamma_{max} = 3.9 \times 10^{-5}$ cm^{-1} for the 4_{04}–3_{13} transition of CH_2. Comparison of γ_{max} (Obs.) with γ_{max} (Theo.) indicates that the observed intensity is 5% of the expected intensity; thus the partial pressure of CH_2 in the absorption cell was on the order of 0.2 mtorr, and the concentration of CH_2 was $\sim 7.4 \times 10^{12}$ molecules cm^{-3}.

[1]Since the transition measured here was not presented in the tables by Kisiel and Millen (1982), we have calculated the absorption coefficient using their formulae and molecular constants.

IV. DISCUSSION

One of the principal objectives for measuring CH_2 in the microwave region is to provide radio astronomers with accurate transition frequencies for molecular cloud searches. A number of authors have examined the carbon-hydrogen gas phase chemistry of interstellar clouds. The methylene radical may be produced from the reactions:

$$CH_3 + h\nu \rightarrow CH_2 + H$$

or

$$CH_3^+ + e \rightarrow CH_2 + H.$$

Blint, Marshall, and Watson (1978) concluded that a high formation rate of CH_2 is unavoidable. Black, Hartquist, and Dalgarno (1978) have modeled the ζ Persei cloud and predict a CH_2 abundance larger than that observed for CH. Similarly, Prasad and Huntress (1980) model the Orion A cloud and predict substantially more CH_2 than C_2H which has been observed in this source.

The detection of the 4_{03}–3_{13} transition of CH_2 will be hampered by the fact that the levels lie near 150 cm^{-1}, a rather high energy for thermal excitation in most of the known molecular clouds. On the other hand, the next lowest frequency transition, 2_{12}–3_{03}, occurs near 444 GHz and may only be accessible via far-infrared astronomy techniques.

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REFERENCES

Black, J. H., Hartquist, T. W., and Dalgarno, A. 1978, *Ap. J.*, **224**, 448.
Blint, R. J., Marshall, R. F., and Watson, W. D. 1978, *Ap. J.*, **206**, 627.
Brown, J. M. 1982, private communication.
Kisiel, Z., and Millen, D. J. 1982, *J. Phys. Chem. Ref. Data*, **11**, 101.
Mucha, J. A., Evenson, K. M., Jennings, D. A., Ellison, G. B., and Howard, C. J. 1979, *Chem. Phys. Letters*, **66**, 244.
Sears, T. J., Bunker, P. R., and McKellar, A. R. W. 1981, *J. Chem. Phys.*, **75**, 4731.
Sears, T. J., Bunker, P. R., McKellar, A. R. W., Evenson, K. M., Jennings, D. A., and Brown, J. M. 1982, *J. Chem. Phys.*, **77**, 5348.
Suenram, R. D., and Lovas, F. J. 1980, *J. Am. Chem. Soc.*, **102**, 7180.
Prasad, S. S., and Huntress, W. T., Jr. 1980, *Ap. J. Suppl.*, **43**, 1.

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