SEARCH FOR INTERSTELLAR METHANE

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ABSTRACT

Upper limits to the column abundance of methane have been determined for the Orion molecular cloud in front of the BN object and for the cloud obscuring AFGL 490. Observations of the P(2) line of the ν_3 fundamental of CH₄ at 3.3 μ m give a column density of $N < 6 \times 10^{16}$ cm⁻² to BN. The resulting abundance ratio, (CH₄)/(CO) < 1 × 10⁻², is consistent with current chemical models of molecular clouds, and confirms that little interstellar carbon is contained in CH₄.

Subject headings: interstellar: abundances - interstellar: molecules - nebulae: Orion Nebula

I. INTRODUCTION

The abundance of methane in molecular clouds has been difficult to establish observationally because of the weak radio spectrum of this symmetric molecule. Recent radio searches found no evidence for the molecule in the Orion region despite earlier tentative claims (Wilson and Snyder 1985; Elldér *et al.* 1980). The single nonplanetary detection of CH_4 of which we are aware is by Hall and Ridgway (1978) in IRC +10°216 where, however, the molecule is clearly located in a circumstellar cloud.

Although CH₄ is the dominant form of carbon in a reducing environment in equilibrium at low temperatures, the highly nonequilibrium situation in molecular clouds drives up the abundance of carbon monoxide and other organic molecules relative to methane. Ion-molecule calculations by Leung, Herbst, and Leubner (1984) and Prasad and Huntress (1980) give (CH₄)/(CO) abundance ratios of order 10^{-4} to 10^{-6} in dense ($n[H_2] = 10^4 - 10^5$) molecular clouds.

These predictions are dependent on sometimes poorly known reaction rates of the complicated carbon chemistry, and uncertainty also remains about the reaction networks. Prasad and Huntress (1980) suggested that these uncertainties could allow methane abundances as high as 7×10^{-6} relative to H₂ corresponding to a (CH₄)/(CO) ratio on the order of 10^{-2} to 10^{-1} . Smith and Adams (1978) suggested that the CH₄ abundance could even exceed that of CO, although later results would revise this downward (Adams and Smith 1981).

In view of the central importance of the reduced forms of carbon in molecular clouds, we initiated a search for CH_4 in the infrared region of the spectrum.

II. THE METHANE SPECTRUM

The ν_3 fundamental rotation-vibration band of the C-H stretch is the strongest CH₄ band accessible to ground-based observations. The P(2) manifold at 2999.10 cm⁻¹ and the

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R(1) manifold at 3038.58 cm⁻¹ are both favorably situated with respect to Earth atmosphere lines other than telluric CH₄, and should be among the stronger bands at temperatures characteristic of the molecular cloud sources.

Observations were made at the United Kingdom Infrared Telescope Facility at Mauna Kea. We searched for CH_4 in absorption against point sources in molecular clouds. The spectrometer was the UKIRT Fabry-Perot with a grating order sorter, described by Wade (1983). The resolution was 0.4 cm⁻¹. A beam diameter of 5''.4 was used in all the observations, with a chopper throw of 10'' to 30''.

We observed the BN object in Orion on 1985 March 9–10 (UT) and the infrared source, AFGL 490, on 1984 September 5–8 (UT). BN is well known to be located in a complex of CO absorption and emission sources including outflowing material. The CO fundamental lines near 4.7 μ m observed by Hall *et al.* (1978) show that infrared absorption originates in the extended OMC-1 molecular cloud. AFGL 490 is embedded in a dense molecular cloud and is another source with high-velocity outflow (Lada and Harvey 1981).

A typical data set is shown in Figure 1 where we compare a spectrum of the BN object, a reference star, and the ratio of the two. Both spectral regions are dominated by the strong P(2) manifold of Earth atmosphere methane. The expected positions of the P(2) manifold as Doppler-shifted (LSR velocity 8.9 and -16.1 km s⁻¹) in the two velocity components in BN are also shown on the plots. The BN spectrum is an average of data taken over a 3 hr period.

No methane lines were detected. Upper limit column densities were determined from

$$N(\text{cm}^{-2}) = (7.34 \times 10^{21} \text{ cm}^{-3} \text{ atm}^{-1} \text{ K}) \text{ EW}/TS_I(T),$$

where EW (cm⁻¹) is the equivalent width, $S_J(T)$ is the line strength, and T is the temperature. Equivalent width upper limits were estimated from the spectra by integrating the minimum observable deflection (taken as twice the rms noise for a 2 σ upper limit) over the 0.4 cm⁻¹ resolution element. The line strengths are from Varanasi, Pugh, and Bangaru (1974) and Toth, Brown, and Hunt (1977), evaluated at the

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FIG. 1.—Spectra of the BN object, the reference star BS 1713, and their ratio. The strong absorption is CH_4 in Earth's atmosphere. The expected positions of Doppler-shifted interstellar CH_4 absorption lines are shown by arrows.

molecular cloud temperatures following the procedure of Varanasi, Sarangi, and Pugh (1973).

Upper limit column depths are given in Table 1. For BN the strengths were evaluated at 70 K, the temperature of the KL molecular cloud complex as determined from radio and infrared CO studies and from the dust temperature. The temperature of the molecular cloud surrounding AFGL 490 is much less well determined. Lada and Harvey (1981) show that it is unlikely to be less than 10 K but consider that temperatures up to 100 K are possible. This temperature range is included in the column density upper limits tabulated in Table 1. The dust temperature determined from far-infrared emission is 30-40 K (Harvey *et al.* 1979), and in the absence of other information, this would seem to be the most probable value of the gas temperature.

III. DISCUSSION

Hall *et al.* (1978) derive column densities of $(5.6 \pm 2.0) \times 10^{18} \text{ cm}^{-2}$ and $(3.9 \pm 1.5) \times 10^{18} \text{ cm}^{-2}$ for red and blue components of CO in the BN object. With our upper limit of $6 \times 10^{16} \text{ cm}^{-2}$ for CH₄, we derive $(\text{CH}_4)/(\text{CO}) < 1 \times 10^{-2}$ for the red component. Column density measurements of CO in AFGL 490 do not seem to be available. An order of magnitude estimate of the gas density can be derived from the extinction observations of Merrill, Russell, and Soifer (1976). The ratio of optical depths in the 9.8 μ m silicate feature of AFGL 490 and BN is 0.7–0.8. If this is also representative of the CO relative column densities, we find $(\text{CH}_4)/(\text{CO}) < 3 \times 10^{-3}$ to 1×10^{-2} in AFGL 490, although these estimates are clearly uncertain.

The upper limits derived here are consistent with results of most modern calculations of gas-phase chemistry in molecular clouds. Leung, Herbst, and Huebner (1984) find $(CH_4)/(CO)$ ratios between 1.5×10^{-4} to 1.5×10^{-3} for evolving models of high and low metal abundances. Our upper limit marginally constrains the models with the higher abundances, although these are the unevolved clouds and the trend is to evolve to lower abundances. Prasad and Huntress (1980) find abundance ratios between 5×10^{-7} and 9×10^{-7} in their best estimates, far below our upper limits. However, the present results do show that the possibility of very high rates in the methane forming reactions, also considered by Prasad and Huntress (1980) and by Smith and Adams (1978), is unlikely. The issue centers on the radiative association reaction,

$$CH_3^+ + H_2 = CH_5^+ + h\nu.$$

Leung *et al.* estimated a rate constant for this reaction of $k = 10^{-14}$ cm³ s⁻¹; Prasad and Huntress took 6×10^{-16} to 10^{-15} , recently revised to 3×10^{-15} cm³ s⁻¹ (Tarafdar *et al.* 1985). The value of 4×10^{-13} cm³ s⁻¹ suggested by Smith and Adams (1978) in early work now appears too high in light of the present observations, if the chemical networks are correct. There are also laboratory (Adams and Smith 1981) and theoretical (Bates 1983) reasons to believe the lower

| Object | CH₄ Manifold | $(\mathrm{cm}^{-2}\mathrm{atm}^{-1})$ | Т (К) | $\frac{N^{a}}{(cm^{-2})}$ | (CH ₄)/(CO) (Number ratio) | | |
|----------|-----------------|---------------------------------------|----------|---------------------------|---|--|--|
| BN | P(2) | 41.6 | 70 | $< 6 \times 10^{16}$ | $< 1 \times 10^{-2}$ | | |
| AFGL 490 | P(2) | 96.5 | 10 | $< 2 \times 10^{17}$ | | | |
| | . , | 141.6 | 30 | $< 4 	imes 10^{16}$ | $< 1 \times 10^{-2} (?)^{b}$ | | |
| | | 73.9 | 50 | $< 4 	imes 10^{16}$ | | | |
| | | 20.9 | 100 | $< 7 \times 10^{16}$ | | | |
| AFGL 490 | R(1) | 1955.9 | 10 | $< 8 \times 10^{15}$ | | | |
| | . , | 387.1 | 30 | $< 1 	imes 10^{16}$ | $< 3 \times 10^{-3} (?)^{b}$ | | |
| | | 135.2 | 50 | $< 2 \times 10^{16}$ | () | | |
| | | 28.3 | 100 | $< 5 \times 10^{16}$ | | | |
| | | | | | | | |

| UPPER LIMIT | COLUMN | DENSITIES | OF | Methane |
|-------------|---------|-----------|----|-------------|
| OTTER LIMIT | COLOMIN | DENSITIES | or | IVIE I HANE |

^a2 σ upper limits; see text.

^bBased on CO column density estimated from extinction.

values of the rate constant, i.e., 10^{-14} to 10^{-15} cm³ s⁻¹ between 10 and 100 K.

Grain surface reactions might form CH₄ at rates comparable to the gas phase rates above (Duley and Williams 1984). However, such mechanisms need not be invoked to explain

Duley, W. W., and Williams, D. A. 1984, Intersteuar Cnemistry (New York: Academic Press), p. 102.
Elldér, J., et al. 1980, Ap. J. (Letters), 242, L93.
Hall, D. N. B., Kleinmann, S. G., Ridgway, S. T., and Gillett, F. C. 1978, Ap. J. (Letters), 223, L47.
Hall, D. N. B., and Ridgway, S. T. 1978, Nature, 273, 281.
Harvey, P. M., Campbell, M. F., Hoffmann, W. F., Thronson, H. A., Jr., and Gatley, I. 1979, Ap. J., 229, 990.
Lada, C. J., and Harvey, P. M. 1981, Ap. J., 245, 58.
Leung, C. M. Herbst, E., and Huebner, W. F. 1984, Ap. J. Suppl., 56,

Leung, C. M., Herbst, E., and Huebner, W. F. 1984, Ap. J. Suppl., 56, 231.

Adams, N. G., and Smith, D. 1981, Chem. Phys. Letters, 79, 563. Bates, D. R. 1983, *Ap. J.*, **270**, 564. Duley, W. W., and Williams, D. A. 1984, *Interstellar Chemistry* (New the present upper limits which are greater than the predictions of gas phase chemistry models.

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REFERENCES

- Merrill, K. M., Russell, R. W., and Soifer, B. T. 1976, Ap. J., 207, 763. Prasad, S. S., and Huntress, W. T., Jr. 1980, Ap. J., 239, 151. Smith, D., and Adams, N. G. 1978, Ap. J. (Letters), 220, L87. Tarafdar, S. P., Prasad, S. S., Huntress, W. T., Jr., Villere, K. R., and Black, D. C. 1985, Ap. J., 289, 220. Toth, R. A., Brown, L. R., and Hunt, R. H. 1977, J. Molec. Spectrosc., 67, 1.
- Varanasi, P., Pugh, L. A., and Bangaru, B. R. P. 1974, J. Quant. Spectrosc. Rad. Transf., 14, 829.
- Varanasi, P., Sarangi, S., and Pugh, L. 1973, Ap. J., 179, 977.
- Wade, R. 1983, Proc. Soc. Photo-Opt. Instr. Eng., 455, 47. Wilson, T. L., and Snyder, L. E. 1985, Ap. J. (Letters), 290, L63.

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L69