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SEARCH FOR INTERSTELLAR PYRROLE AND FURAN

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ABSTRACT

We report unsuccessful searches for the organic ring molecules pyrrole (C_4H_4N) and furan (C_4H_4O). In TMC-1, we find an upper limit to the pyrrole column density of 4×10^{12} cm^{-2}, an order of magnitude less than the column density of HC_5N in this source. In Sgr B2, the upper limit to the pyrrole column density is 6×10^{13} cm^{-2}, about 0.4 times the HC_5N column density. These results suggest that chemical processes in these clouds favor the formation of chains over rings of comparable molecular weight. During these searches, a number of unidentified millimeter wavelength lines were also found; their frequencies are reported here.

Subject headings: interstellar: molecules — line identifications — radio sources: lines

I. INTRODUCTION

Despite the rich chemistry of the interstellar medium, attempts to detect simple organic rings have been unsuccessful (see, e.g., de Zafra *et al.* 1971; Fertel and Turner 1975). However, these negative results have generally not been converted into meaningful upper limits on the molecular column densities, because rings tend to have large partition functions, even at relatively low interstellar temperatures. However, with more sensitive receivers the limits are now becoming significant in evaluating models for interstellar chemistry.

The attempt to find rings becomes more important with the discovery of several carbon chain molecules, such as HC_5N (Avery *et al.* 1976), HC_7N (Kroto *et al.* 1978), and HC_9N (Broten *et al.* 1978), with molecular weights greater than those of most of the rings that have been sought. In particular, the discovery of these chain molecules in the source TMC-1 raises an interesting possibility: excitation temperatures are sufficiently low in this source (~ 10 K) that rings, if they are as abundant as the chains, should be detectable. If no detections are made, one then has the possibility of establishing the existence of a true deficiency of rings with respect to chains.

In this paper, we report an unsuccessful search for two similar ring molecules, pyrrole (C_4H_4N) and furan (C_4H_4O). The upper limits, especially for pyrrole, allow us to make important comparisons with chains of comparable complexity.

II. OBSERVATIONS

The pyrrole transitions searched for are listed in Table 1, and the furan transitions are listed in Table 2. Most of these transitions lie at millimeter wavelengths and were searched for with the 11 m telescope of the National Radio Astronomy Observatory,[2] located on Kitt Peak. All observations were done in a position-switching mode, in which 30 s integrations are alternately performed on and off source. Spectral resolution was provided by 256 channel filter banks, the resolution in each source being chosen to provide at least five channels over the expected line width. Calibration was done using a chopper wheel at ambient temperature, with the scale of radiation temperature, T_R, established as described by Kutner (1978). No image sideband rejection was employed, and it was assumed that gains in the signal and image sidebands were equal. Observations of known lines at frequencies not far from those observed indicate that this assumption probably does not introduce an error larger than 30% in absolute intensity for the particular lines observed.

Some observations (the 22.7 GHz line of pyrrole and the 10.6 GHz line of furan) were done on the NRAO 43 m telescope at Green Bank, West Virginia. Observations of Sgr B2 were made with position-switching, sampling on and off source positions once every 15 minutes. All other observations were frequency-switched. Spectral analysis was performed by the 384 channel autocorrelator, with resolutions chosen to be less than one-fifth the expected line width. Calibration was done with a noise tube, and

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TABLE 1

PYRROLE UPPER LIMITS (T_R)

Transition	2_{02}–1_{01} ...	4_{14}–3_{13} 4_{04}–3_{03}	5_{15}–4_{14} 5_{05}–4_{04}	8_{27}–7_{26} 8_{17}–7_{16}	5_{41}–4_{22} ...	6_{60}–5_{41} ...
ν(MHz)[a]	22,724	40,790	49,855	86,114	103,351	114,467
E/k(K)[b]	2	5	7	20	12	17
B335[c]	...	0.5	...	0.10	...	...
TMC-1[d]	0.02	0.06	0.13	...	...	...
Ori A	0.05	0.08	0.05	...	...	...
NGC 2264	...	...	...	...	0.15	...
IRC+10,216	0.02	0.08	0.03	...	...	...
Sgr B2	0.02	0.10	0.04	0.03	0.08	0.19
W51	...	0.10	...	...	...	...
DR 21	0.02	0.15	0.2	...	...	...

[a] Using rigid rotor constants of Nygaard *et al.* 1968.

[b] Energy above ground state of upper level.

[c] Entries in this section of table are upper limits to T_R for the given transitions in the indicated sources. Upper limits are half the peak-to-peak noise.

[d] 1950 coordinates $4^h38^m42^s$, 25°35′46″.

conversion to radiation temperatures accomplished by comparison with continuum sources of known intensity. This was particularly important at 1 cm, where the antenna gain changes significantly with hour angle, even with the deformable subreflector (which was in use). Because of these beam shape problems, radiation temperatures for the 1 cm lines are highly uncertain and difficult to interpret. Consequently, they are not used in the final column density determinations discussed in the next section. (This is not a serious loss since other transitions generally provide lower column density limits).

During the course of the millimeter observations, 24 other lines were encountered. These are listed in Table 3. For each line, the sideband in which it was detected was checked by shifting the local oscillator by 5 MHz and reobserving. Half of these lines remain unidentified. Rest frequencies were derived by assuming an LSR velocity of 8.5 km s^{-1} in Ori A and 60 km s^{-1} in Sgr B2. There is probably a larger uncertainty associated with the Sgr B2 velocity than with the Ori A velocity. Many of the lines were observed with the 1 MHz per channel filter bank, so there is a statistical uncertainty of 1 MHz attached to each derived frequency. Among the identified lines are (1) a number of lines of methyl formate, HCO_2CH_3; (2) two lines of dimethyl ether, $(CH_3)_2O$, arising from levels with $J = 15$, which should prove useful in excitation analyses; and (3) a new line of ethanol, CH_3CH_2OH.

TABLE 2

FURAN UPPER LIMITS (T_R)

Transition	8_{72}–8_{71}	9_{09}–8_{08}
ν(MHz)[a]	10,584.5	88,748.3
E/k(K)	31	21
Ori A	0.01	0.04
Sgr B2	0.05	...

[a] Based on rotation constants with centrifugal distortion of Bak *et al.* 1962.

III. DISCUSSION

For each transition in each source, upper limits to T_R were converted to column density, N, upper limits as follows: It was assumed that the transitions are optically thin with the populations of the molecular levels described by a single excitation temperature, T_x, which could be varied. The partition function was calculated using the classical approximation. (A comparison with a direct summation at $T_x = 10$ K shows that this is reasonable even at low temperature.) In calculating the fractional populations of various levels the effect of the spin statistics due to the two pairs of identical protons must be taken into account, giving a relative statistical weight of 10 : 6 for rotational states with odd and even K_{-1}. Note that for most of the millimeter lines in Table 1, two transitions with essentially identical frequencies, one with odd K_{-1} and one with even K_{-1}, were sought. In converting T_R to N, the strengths of the two transitions were taken together. Finally, it was assumed that the line width in each source was equal to that of other optically thin lines in the source. The pyrrole results are discussed below, source by source.

For the purposes of comparison with other molecules, TMC-1 is the most interesting source. Consistent with the analysis of the HC_5N abundance by MacLeod *et al.* (1979), we take $T_x = 10$ K. The best column density limit for pyrrole comes from the 40.8 GHz line. For the line width, we can assume that a single hyperfine component

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TABLE 3

OBSERVED LINES

Rest Frequency (GHz)	Source	T_R (K)	v(LSR) (km s^{-1})	Identification	Notes
40,880.0	Sgr B2	0.07	60.0[a]	unidentified	
88,668.6	Ori A	0.04	8.8	CH_3NH_2 2_{02}–1_{01}	1
88,707.64	Ori A	0.05	8.5	$(CH_3)_2O$ $15_{2,13}$–$15_{1,14}$ (EE)	2
88,709.07	Ori A	0.06	8.0	$(CH_3)_2O$ $15_{2,13}$–$15_{1,14}$ (AA)	2
88,741.8	Ori A	0.03	8.5	unidentified	
88,749.8	Ori A	0.03	8.5	unidentified	
88,770.8	Ori A	0.03	8.5	unidentified	
88,843.24	Ori A	0.09	7.7	HCO_2CH_3 7_{16}–6_{15} (E)	3
88,851.61	Ori A	0.07	8.8	HCO_2CH_3 7_{16}–6_{15} (A)	4
88,865.69	Ori A	0.03	9.0	$H^{15}NC$ 1–0	5
98,177.55	Ori A	0.08	4.4	CH_3CH_2CN $11_{2,10}$–$10_{2,9}$	6
98,190.60	Ori A	0.04	7.6	HCO_2CH_3 8_{72}–7_{71}; 8_{71}–7_{70} (A)	
98,230.2	Ori A	0.02	8.5	unidentified	
98,239.7	Ori A	0.03	8.5	unidentified	
98,257.7	Ori A	0.03	8.5	unidentified	
98,270.46	Ori A	0.06	7.8	HCO_2CH_3 8_{62}–7_{61} (E)	
98,279.7	Ori A	0.12	7.0	HCO_2CH_3 8_{62}–7_{61} (A); 8_{63}–7_{62} (A,E)	
98,333.9	Ori A	0.02	8.5	unidentified	
98,351.9	Ori A	0.02	8.5	unidentified	
112,805.5	Sgr B2	0.12	60.0	unidentified	
112,807.1	Sgr B2	0.12	56.0	CH_3CH_2OH 2_{12}–1_{10} (A,E)	7
112,837.5	Sgr B2	0.08	60.0	unidentified	
112,840.65	Sgr B2	0.06	60.4	CH_2CHCN $12_{0,12}$–$11_{0,11}$	8
112,889.5	Sgr B2	0.06	60.0	unidentified	9

[a] For unidentified lines LSR velocities were assumed to be 60.0 km s^{-1} for Sgr B2 and 8.5 km s^{-1} for Ori A.

NOTES. (1) This line previously detected at 0.2 K in Sgr B2 by Kaifu *et al.* 1975. (2) This series observed as high as $J = 4$ by Clark *et al.* 1979. (3) Churchwell *et al.* 1980. (4) Hollis *et al.* 1980. (5) Observed in DR 21(OH) at 0.15 K by Brown *et al.* 1977. (6) Observed at 0.15 K in Ori A by Johnson *et al.* 1977. (7) Three other transitions detected in Sgr B2 at about this level by Zuckerman *et al.* 1975. (8) $10_{0,10}$–$9_{0,9}$ line observed in Sgr B2 at 0.08 K by Johnson *et al.* 1977. (9) Possibly HCOOH 4_{22}–5_{23} at 65 km s^{-1}, but no other millimeter data available to see how reasonable this is.

(due to the nitrogen quadrupole splitting) would have a line width of 0.4 km s^{-1}, in agreement with other molecules in this source, or that the hyperfine manifold would have a width of about 1 km s^{-1}. We get essentially the same answer either way, with

$$N(C_4H_4N) \lesssim 4 \times 10^{12}\ \mathrm{cm}^{-2}\ . \qquad (1)$$

A comparison of this result with that of MacLeod *et al.* (1979) suggests an abundance ratio

$$[C_4H_4N]/[HC_5N] \lesssim 0.08\ . \qquad (2)$$

Even with the uncertainties in both abundance determinations this result suggests that the ring molecule is at least an order of magnitude less abundant than the chain with one more heavy atom. We note that the ratio might be even greater since our method of calculating level populations probably tends to overestimate the populations of the upper levels, relative to the method of MacLeod *et al.* (1979), which utilizes a statistical equilibrium calculation at a kinetic temperature, $T_k = 11$K.

In Sgr B2, the limits are not quite as stringent, because of the higher temperatures involved. Since we wish to compare our limit with the derived HC_5N abundance of Avery *et al.* (1979), we make assumptions consistent with their model. This model has three source components, with most of the HC_5N column density associated with the intermediate density region having $n_{H_2} \sim 3 \times 10^3$ cm^{-3} and $T_k = 25$–35 K. We therefore assume a constant $T_x = 30$ K for pyrrole and a line width of 20 km s^{-1} (probably a slight overestimate). This gives

$$N(C_4H_4N) \lesssim 6 \times 10^{13}\ \mathrm{cm}^{-2} \qquad (3)$$

and

$$[C_4H_4N]/[HC_5N] \lesssim 0.4\ . \qquad (4)$$

We note that the upper limit in equation (3) is consistent with that found by Myers, Thaddeus, and Linke (1980), $3 - 10 \times 10^{13}$ cm^{-2}, based on a different group of transitions.

In Ori A, there are no HC_5N observations for comparison. However, if we assume a line width of 3 km s^{-1} and $T_x = 30$ K, we get an upper limit of 3×10^{13} cm^{-2}. For IRC +10216, if the line width is 30 km s^{-1} and $T_x = 60$ K, $N(C_4H_4N) \lesssim 5 \times 10^{14}$ cm^{-2}. For comparison, at $T_x = 60$ K, the column densities of the radicals C_4H and C_3N are 4×10^{14} cm^{-2} and 1×10^{14} cm^{-2}, respectively (Guélin, Green, and Thaddeus 1978; Guélin and Thaddeus 1977).

Our furan observations are not quite as sensitive in terms of column density as those for pyrrole, partly because of furan's smaller dipole moment (0.7 vs. 1.8 debyes). Using the same assumptions as for calculating the pyrrole column densities, our furan observations translate into upper limits of 7×10^{13} cm^{-2} in Ori A and 2×10^{16} cm^{-2} in Sgr B2.

Our pyrrole observations, especially, suggest that interstellar chemistry may favor the production of chains over rings. Of course, this result is compelling for only one source, TMC-1, whose nature is not well known, However, at this time it may not be premature to assess the implications of an underabundance of rings relative to chains for interstellar chemistry. In general, various gas-phase chemical models do not produce observable quantities of the rings discussed here, but have been able to explain the formation of chains (e.g., Mitchell, Huntress, and Prasad 1979; Schiff and Bohme 1979). This has led to the assumption that if rings are produced in quantity, their production must be on grain surfaces. If this is true, then our results imply a greatly reduced role for grain-surface reactions relative to gas-phase reactions in producing complex molecules, even in dense regions such as TMC-1. However, much more will have to be known about the ability of both types of reactions to produce rings before such a strong conclusion can be firmly established.

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