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UPPER LIMITS ON THE O_2/CO RATIO IN TWO DENSE INTERSTELLAR CLOUDS

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ABSTRACT

We have searched for a magnetic-dipole rotation transition of the isotope $^{16}O^{18}O$ toward ρ Oph and Orion A at a wavelength of 1.3 mm. Upper limits on the intensity of this line imply that $N_{O_2}/N_{CO} \leq 0.13$ and 0.67 in the two sources, respectively, so that neither harbors a hitherto-undetected reservoir of oxygen in molecular form.

Subject headings: interstellar: abundances — interstellar: molecules

I. INTRODUCTION

As the rich chemistry of interstellar clouds continues to unfold, models of the molecular behavior of dense material grow ever more complicated. Recent gas-phase schemes (Prasad and Huntress 1980; Graedel, Langer, and Frerking 1982) trace the time-dependence of reaction networks containing thousands of detailed interactions in the hope of understanding the abundances of perhaps two dozen species containing four to five atoms chosen from the elements H, C, N, O, S, and Si. Still, important new physical effects are proposed more quickly than they can be fully incorporated in computer codes, while other clearly important processes such as gas-grain coupling are usually regarded as intractable (however, see Watson 1977 and Liszt 1979).

Another problem for chemical models, but one which is not usually considered seriously, is the input set of elemental abundances on which the reaction network operates. All calculations start with a set of abundances determined in the interstellar medium toward moderately reddened stars such as ζ Oph (Morton 1975) but the physical conditions in these directions are no longer believed to be as nearly typical of dense, shielded cloud cores as was once the case (Liszt 1979; Crutcher and Watson 1981). The CNO elemental depletions inferred for such regions have generally been reduced in the past few years (de Boer 1981; Liszt 1981; Jenkins, Jura, and Loewenstein 1983) and the effect of these changes is to leave us with no reliable guide to the gaseous abundances in dark and molecular clouds.

Uncertainty in the input elemental abundances arises because none of the molecules presently studied in dense clouds contains more than a small fraction of the undepleted quantity of any of its constituents. Carbon monoxide, which accounts for the vast majority of the observable oxygen, contains perhaps 5% of the quantity of that element. It is entirely possible that the greatest part of the available heavy nuclei is simply not accessible to observation, and this situation will not be alleviated until a wider variety of species in both atomic and molecular form is observable.

Here, we present results of a search for molecular oxygen, which in some chemical models is expected to contain much or most of the free oxygen. The chemistry of O_2, and prospects for its detection in the interstellar medium, have recently been discussed by Black and Smith (1984). Our negative results, which are particularly sensitive toward ρ Oph, indicate that the abundance of O_2 is much less than that of CO.

II. OBSERVATIONS

We observed the $^{16}O^{18}O$ line at 234 GHz (see § III) in the spring of 1981 and 1982 at the Millimeter Wave Observatory[2] (MWO) in Fort Davis, Texas, but unfavorable weather conditions prevented us from reaching adequate limits. The observations reported here were taken in 1984 February at the 12 m NRAO telescope on Kitt Peak. Weather conditions were very good, with zenith optical depths below 0.15 on most days. System temperatures in the two receiver polarizations discussed here were taken with 256 channel filter banks of width 0.25 and 0.5 MHz, corresponding in the first case to velocity resolutions of 0.32 and 0.34 km s^{-1} at the $^{16}O^{18}O$ and $C^{18}O$ $J = 2$–1 transitions. On most days, the filter banks were split to accept both receiver channels.

The 12 m telescope is still in the process of final testing, and it is to be expected that improvements in its optics and surface during the next year will change its observing characteristics somewhat. Some of the telescope and observational parameters relevant at the time of our observations are summarized in Table 1 (see Kutner and Ulich 1981 for definitions of the tabulated quantities).

III. THE SPECTRUM OF O_2

Because the $^{16}O_2$ molecule is homonuclear, it possesses no permanent electric dipole moment and no spectrum of electric-dipole rotation transitions with $\Delta J = \pm 1$; because ^{16}O is a boson, levels of odd total angular momentum J are absent. However, the electronic ground state is $^3\Sigma_g{}^-$ and the triplet symmetry is manifested in fine-structure splitting $J = N$, $N \pm 1$, N being the rotational angular momentum of the nuclei. Levels of equal N are connected radiatively by magnetic-dipole fine-structure transitions $\Delta J \pm 1$; these occur

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TABLE 1

OBSERVING PARAMETERS OF THE 12 METER TELESCOPE

Quantity[a]	Value	How Obtained
η_c	0.85	Antenna tips
η_{fss} (Moon)	0.74	Coupling to moon
η_B	0.61	Coupling to Jupiter
η_A	0.13	Jupiter, other sources
HPBW (arcsec)	34	(NRAO value)
T_c (K)	740	$2 \times 273\ K/\eta_{fss}$
T_r^* (K)	90	Orion A, CO $J = 2$–1
T_r^* (K)	9.7	IRC +10216, CO $J = 2$–1

[a] For definitions see Kutner and Ulich 1981.

at 119 and 55–65 GHz and are responsible for high telluric opacity in the ranges 50–70 and 117–122 GHz. Levels of differing N are connected by magnetic-dipole rotation transitions having the upward selection rules $\Delta N = 2$, $\Delta J = 0, +1$, with wavelengths in the submillimeter band. The spectrum of $^{16}O_2$ for the two lowest N levels is illustrated in Figure 1*a*, with parameters from Steinbach (1974; see also Steinbach and Gordy 1975).

The isotope $^{16}O^{18}O$ is not homonuclear and even-N levels (except $J = N = 0$) exist in its rotation ladder. Thus, although its fine-structure transitions occur in spectral regions of high telluric opacity, the magnetic-dipole rotation transitions having even-N are not obscured by analogous features in the main isotope. The strongest and most accessible of the $^{16}O^{18}O$ transitions arises from the ground state and occurs at 233.94618 GHz, as shown in Figure 1*b*. It is this line for which we have searched.

The relevant dipole moment for any of the O_2 transitions is $4\mu_B{}^2S^2$ ($\mu_B = eh/4\pi m_e c = 9.26 \times 10^{-21}$ esu) and the integrated optical depth of a line in velocity units is

$$\int \tau dv = \frac{8\pi^3}{3h}\, 4\mu_B{}^2 S^2 \frac{N_\iota}{2J_\iota + 1}\,(1 - e^{-h\nu/kT})\,.$$

The subscript ι refers to the lower state of the transition, and N_ι to the column density in that state. T is an excitation temperature characterizing the level population and the line strengths S^2 are given in Figure 1. Spontaneous emission coefficients in O_2 are relatively small, lower even than those of CO, and approximation of the rotation level population by a single temperature near the assumed kinetic value is reasonable given the high particle densities (much above 10^4 cm^{-3}) in the sources we observe (see Black and Smith 1984 for a verification of this assertion).

For the 234 GHz line of $^{16}O^{18}O$ ($h\nu/k = 11.22$ K) we obtain, the units of km s^{-1},

$$\int \tau dv = 2.2 \times 10^{-17} \frac{(1 - e^{-11.22/T})}{T} N_{^{16}O^{18}O}$$

after replacing the partition function $[Q(T)]$ by $1.52T$, valid for $T \geq 20$ K. Observationally, the rms optical depth fluctuation arising in the search for a weak line at 234 GHz is $\Delta T_r^*/\eta_s(T - 5.5\ \mathrm{K})$, with ΔT_r^* the rms fluctuation in the corrected radi-

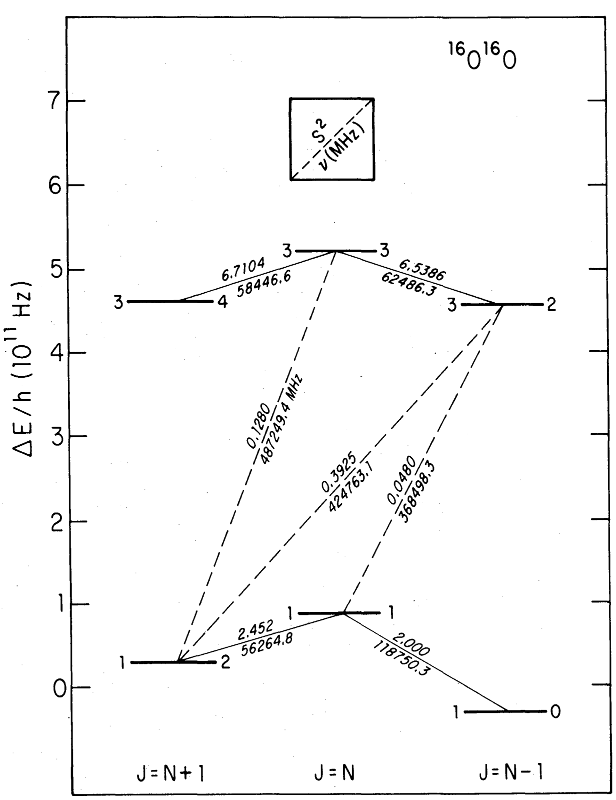

FIG. 1*a*

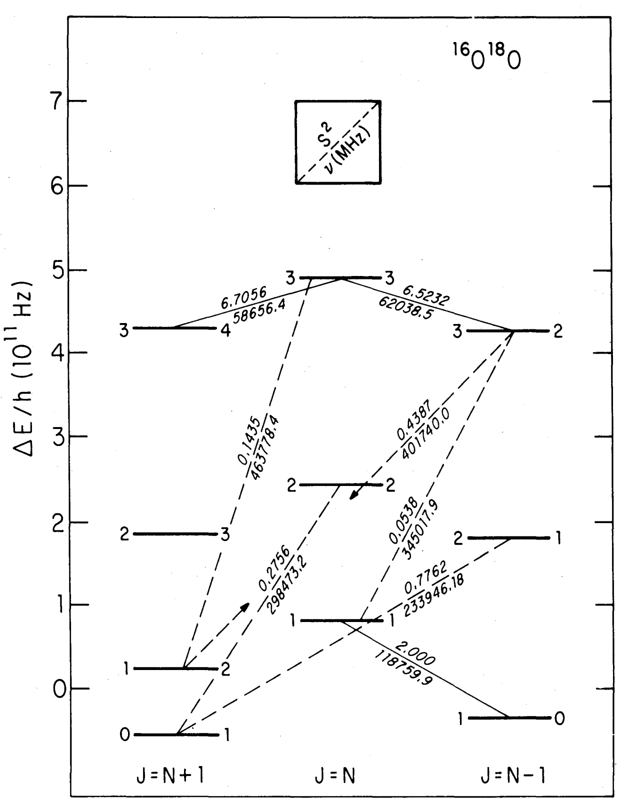

FIG. 1*b*

FIG. 1.—(*a*) An energy level diagram showing the magnetic-dipole transitions in the two lowest rotation levels of $^{16}O_2$. Frequencies and line strengths (see § III) are from Steinbach (1974) and Steinbach and Gordy (1975). (*b*) As in Fig. 1*a*, but now for the rare isotopic species $^{16}O^{18}O$. Most fine-structure transitions have been ignored.

ation temperature defined by Kutner and Ulich (1981), η_s a geometrical factor accounting for the source-beam coupling, and $T - 5.5$ K the maximum brightness temperature above the blackbody background of a gas at temperature $T \geq 20$ K. Thus we have

$$N_{^{16}\mathrm{O}^{18}\mathrm{O}} \leq 4.6 \times 10^{16}\ \mathrm{cm}^{-2}\ (1 - e^{-11.22/T})^{-1} \times \frac{T}{(T - 5.5\ \mathrm{K})} \int \frac{\Delta T_r^*}{\eta_s}\, dv$$

and

$$N_{^{16}\mathrm{O}_2} \leq 250 N_{^{16}\mathrm{O}^{18}\mathrm{O}}\ ,$$

assuming that the rarer isotope is not preferentially destroyed in dense, shielded regions. Fractionation effects, which are not believed to be important (Watson 1977); Langer *et al.* 1984), act to strengthen the upper limit.

Of course η_s and T are always uncertain, but the only meaningful comparison we can make is with CO and the inferred column density of $C^{18}O$ has similar dependences on both these quantities. The derived O_2/CO ratio is nearly unaffected and the assumptions of LTE level populations also act equally on both species. For the $J = 2$–1 line of $C^{18}O$ at 219.6 GHz

$$\int \tau dv = 4.0 \times 10^{-15} \frac{(1 - e^{-10.53/T})}{T} e^{-5.3/T} N_{\mathrm{C}^{18}\mathrm{O}}$$

and

$$\tau = -\ln \{1 - T_r^*/[\eta_s(T - 5.3\ \mathrm{K})]\}\ .$$

IV. LIMITS ON THE O_2/CO RATIO IN RHO OPHIUCHI AND ORION A

a) *Observational Limits*

To obtain meaningful upper limits on N_{O_2}, which we sample through the weak line of a rare isotope, requires high column density concentrated in a fairly narrow line profile. It also requires that we observe sources in which we will not run into a forest of contaminating features. Probably the best source in the sky is ρ Oph (Lada and Wilking 1980; Wilking and Lada 1983; Loren *et al.* 1980), which has column densities comparable to those seen in Orion, concentrated in a much narrower line. The brightest $C^{18}O$ $J = 2$–1 lines in the sky occur toward this source.

At both the MWO and Kitt Peak, we found the $C^{18}O$ $J = 2$–1 line to be substantially brighter at the position of ρ Oph A ($16^h23^m25^s$, $-24°15'49''$) than further south where the $J = 1$–0 $C^{18}O$ map of Wilking and Lada (1983) has its most extended peak. Because of this we chose ρ Oph A as the target position and reached an rms noise level $\Delta T_r^* = 0.0175$ K, as shown in Figure 2*a*. In spite of the high column density implied by $C^{18}O$, the spectral regions around 233.946 GHz (and 230.946 GHz in the other sideband) are free of extraneous features.

For this source we take $T = 32$ K (Loren *et al.* 1980), $\eta_s = 0.8$ (a nominal value) and obtain for $C^{18}O$

$$\int \tau dv = 0.86\ \mathrm{km\ s^{-1}}$$

$$\sigma_v = 0.50\ \mathrm{km\ s^{-1}}$$

$$N_{\mathrm{C}^{18}\mathrm{O}} = 2.9 \times 10^{16}\ \mathrm{cm}^{-2}$$

$$N_{\mathrm{CO}} = 1.4 \times 10^{19}\ \mathrm{cm}^{-2}\ ,$$

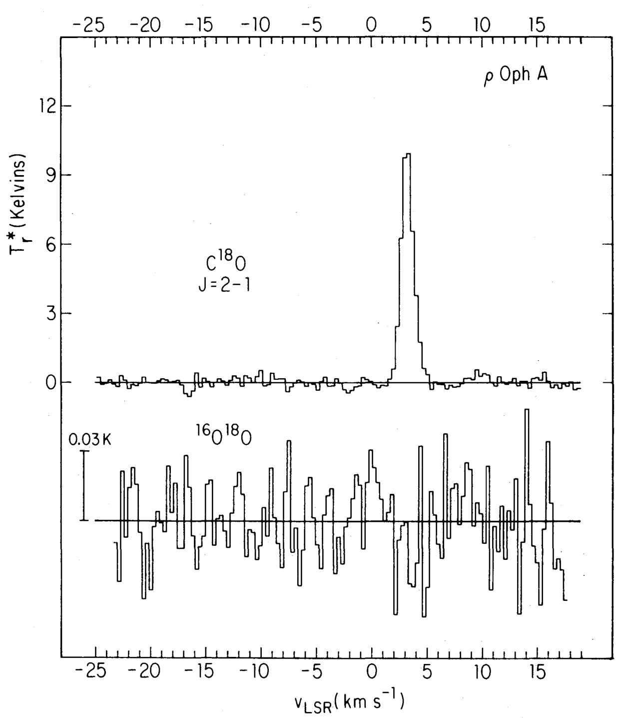

Fig. 2*a*

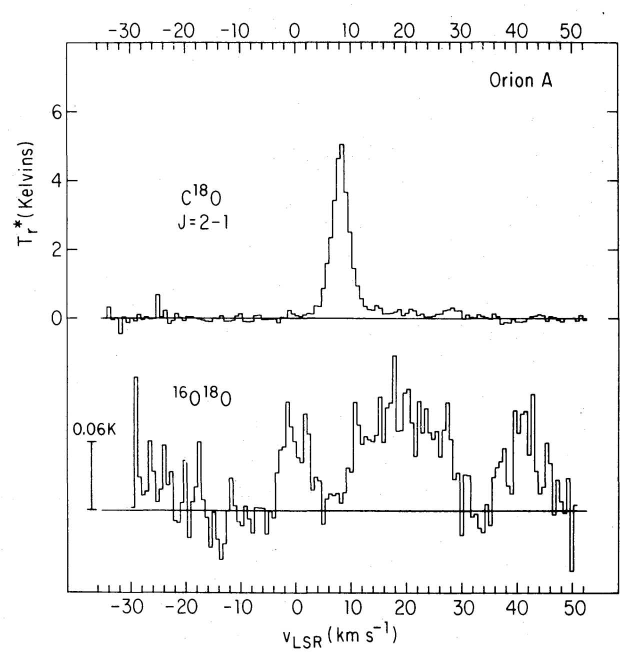

Fig. 2*b*

Fig. 2.—(*a*) Spectra of $C^{18}O$ $J = 2$–1 and the $^{16}O^{18}O$ transition at 233.94618 GHz toward ρ Oph A. The intensity scale is in terms of T_r^* as defined by Kutner and Ulich (1981), using the parameters quoted in Table 1. The rms noise measured across the $^{16}O^{18}O$ spectrum is 0.0175 K. (*b*) As in Fig. 2*a*, but now toward Orion A. Possible frequencies of the weak, unidentified lines in the lower spectrum are (*left to right*) 233.9532, 233.9306, and 233.9142 GHz in the signal sideband, and 230.9392, 230.9618, and 230.9781 GHz in the image sideband.

the final value being some 15% higher than the peak values in the $C^{18}O$ $J = 1$–0 map.

For $\Delta T_r^* = 0.0175$ K, and summing over a supposed eight channel wide region, a 2 σ limit is, ($\int \Delta T_r^* dv = 2 \times 8^{1/2} \times 0.32 \times 0.0175$ K km s^{-1})

$$N_{^{16}O^{18}O} \leq 7.4 \times 10^{15} \text{ cm}^{-2}$$

$$N_{O_2} \leq 1.8 \times 10^{18} \text{ cm}^{-2}$$

$$\frac{N_{O_2}}{N_{CO}} \leq 0.13 .$$

For Orion A, which we observed as a check on the sensitivity of the system, we take $T = 100$ K, $\eta_s = 0.9$ and find for $C^{18}O$ $J = 2$–1

$$\int \tau dv = 0.23 \text{ km s}^{-1}$$

$$\sigma_v = 1.6 \text{ km s}^{-1}$$

$$N_{C^{18}O} = 5.9 \times 10^{16} \text{ cm}^{-2}$$

$$N_{CO} = 3.0 \times 10^{19} \text{ cm}^{-2} .$$

If we assert that $\Delta T_r^* \leq 0.04$ K at the center of the $^{16}O^{18}O$ line, it follows that

$$N_{^{16}O^{18}O} \leq 8.1 \times 10^{16} \text{ cm}^{-2}$$

$$N_{O_2} \leq 2.0 \times 10^{19} \text{ cm}^{-2}$$

$$\frac{N_{O_2}}{N_{CO}} \leq 0.67 ,$$

which is much less sensitive than the result toward ρ Oph because the Orion line is broader, the gas is hotter, and we cannot integrate across the expected position of the $^{16}O^{18}O$ feature.

b) Discussion

The limits obtained in both ρ Oph and Orion are certainly sufficient to demonstrate that no substantial reservoir of hitherto-undetected oxygen resides in O_2 in two well-studied molecular clouds. A more sensitive limit could undoubtedly be derived in Orion, but detection of a weak line at 233.94618 GHz in either source would, unfortunately, not prove that O_2 had been detected. Species identifications based on a single line are simply too prone to error.

We now review briefly some aspects of interstellar cloud chemistry which are relevant to the abundance of O_2. Quantities X_s refer to the abundance, by number, of species s relative to H_2; ξ_a is the total available quantity of element a by number, relative to H_2, as is usual. Given these definitions, the maximum possible ratio of O_2 to CO is $X_{O_2}/X_{CO} = (\xi_O - X_{CO})/2X_{CO}) = [(\xi_O/\xi_C)(\xi_C/X_{CO}) - 1]/2$. Typically, chemical models take the input O/C ratio $\xi_O/\xi_C \approx 2.0$–2.5 and yield $X_{CO}/\xi_C \approx 1$, $X_{O_2}/X_{CO} \leq 0.5$–0.75, but values above unity can be obtained if 20%–50% of the gas-phase carbon resides outside CO.

In dense shielded regions, O_2 arises almost exclusively through the reaction $O + OH \rightarrow O_2 + H$, which is not believed to have an activation energy (cf. Black and Smith 1984). Molecular oxygen is fairly robust because some of its stronger reactions (mainly that with H_3^+) only recycle it; the main antagonists of O_2 are atomic ions like He^+, S^+, and C^+, as well as atomic carbon and CH_3^+ with which it reacts to form water. The abundances of O_2 and CO are actually strongly coupled because the same small values of X_{CO}/ξ_C which release additional oxygen will also increase the abundance of species which destroy O_2. Alternatively, when X_{O_2} is relatively large, molecular oxygen is the strongest reactant with many of its antagonists and provides a substantial additional source of CO through the reactions $C + O_2 \rightarrow CO + O$ and $C^+ + O_2 \rightarrow CO + O^+$. For these reasons, a general result obtains in available chemical models of dense, shielded regions having $\xi_O > \xi_C$: most of the available oxygen is in O_2 whenever X_{CO}/ξ_C is small, but the fraction of carbon in CO is never very low (much below 0.5) and X_{O_2}/X_{CO} is at most of order 1. A very clear demonstration of this behavior can be found in Figure 2*b* of Liszt (1978).

In the great majority of models, all but a trace amount of carbon resides in CO and X_O is substantial ($\sim$0.5) only when the density is large and X_e is very low; the O_2/CO ratio can be kept small at most densities in such models just by assuming the "high-metal" case in which the uncertain abundances of easily ionized species like sulphur are not assumed to be very heavily depleted (see, for instance, the results of Graedel, Langer, and Frerking 1982). The fractional electron abundance can be inferred to be very small in a few cases where strong deuteration effects are encountered (Guelin, Langer, and Wilson 1982), but there is no proof that such is generally the case. For many models, those having high X_{CO}/ξ_C, our observation of a low X_{O_2}/X_{CO} probably provides only indirect chemical constraints because the O_2 abundance is affected by too many uncertain conditions.

Of more interest in the present context are those conditions which yield low X_{CO}/ξ_C and are more likely to produce high values of X_{O_2}/X_{CO}. The notion that a substantial carbon abundance exists outside CO is strongly indicated by the high neutral atomic carbon column densities observed toward hotter clouds (Phillips and Huggins 1982); and several new ideas for providing large X_C/X_{CO} have recently been suggested. Prasad and Tarafdar (1983) (also see Roberge 1983) show that the ultraviolet photons produced in cosmic-ray–molecular hydrogen collisions provide a substantial dissociating flux even in heavily shielded regions. Boland and de Jong (1982) propose a scheme whereby turbulent motions in molecular regions are continually bringing new material to the cloud surface where it is exposed to the unattenuated interstellar radiation field. Unfortunately, neither of these mechanisms has been subjected to detailed numerical modeling and the photodissociation cross sections for CO are so poorly known that an accurate description of the carbon chemistry probably cannot be given under any conditions where photoprocesses are important.

Before summarizing our results, we note that there is another suggestion for maintaining high values of X_C, one which adheres more closely to our introductory remarks concerning the substantial uncertainties in elemental abundances applicable to dense regions. If $\xi_C > \xi_O$ (Langer *et al.* 1984), it would follow that free carbon could be plentiful without any tendency to produce appreciable amounts of O_2 (or, for that matter any other oxygen-bearing species except CO). This is clearly a very radical revision of the entire chemical scheme, but it is certainly proper to regard the oxygen/carbon ratio and ξ_C as test variables in chemical modeling.

To summarize most generally, the present results indicate that O_2 cannot account for any substantial fraction of the oxygen nuclei which would be present if the ρ Oph or Ori A molecular clouds contained undepleted solar elemental abundances in the gas phase. For the line of sight toward ρ Oph A we may make the stronger statement that the amount of oxygen in O_2 is small compared to that in CO. By themselves, these may or may not be significant considerations. In combination with expected results on O I, C I, C II, and perhaps other species (H_2O?) which together with CO must contain the bulk of the carbon and oxygen nuclei in dense clouds, they will help to remove one strong source of uncertainty in theoretical interpretation of interstellar chemistry.

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