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INTERSTELLAR O_2. I. ABUNDANCE, EXCITATION, AND PROSPECTS FOR DETECTION OF $^{16}O^{18}O$ AT RADIO FREQUENCIES

JOHN H. BLACK AND PETER L. SMITH
Harvard-Smithsonian Center for Astrophysics
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ABSTRACT

Molecular oxygen, O_2, is predicted to be an important constituent of the interstellar gas, but it has not yet been detected in interstellar clouds. In this paper, the gas-phase production and destruction of O_2 are reconsidered, a non-LTE calculation of level populations at cloud temperatures is presented, and O_2 column densities in diffuse and dark clouds are predicted. Ground-based detection of the 234 GHz line of $^{16}O^{18}O$ is shown to be feasible; if CO and O_2 are comparable in abundance in clouds similar to the Taurus molecular cloud or in giant molecular clouds, the brightness temperature is predicted to be 0.1 K.

Subject headings: interstellar: abundances — interstellar: molecules — molecular processes

I. INTRODUCTION

The prospects for detection of interstellar O_2 depend upon its abundance, its excitation, and the intrinsic strengths of its spectral lines. We consider each of these matters, with reference to radio wavelength observations, in this paper. The following paper (Smith *et al.* 1984, hereafter Paper II) presents oscillator strengths for vacuum ultraviolet lines of O_2 and discusses prospects for observation of interstellar O_2 with Space Telescope.

Considerations of cosmic abundances suggest that, at most, half of the gas phase oxygen in interstellar clouds might be in the form of CO, which is currently thought to be the most abundant molecule after H_2. The remaining gaseous oxygen will exist as O, O_2, OH, H_2O, and other less abundant species. Theories of interstellar molecule formation predict that the abundance of O_2 may approach that of CO deep inside molecular clouds (Herbst and Klemperer 1973; Viala and Walmsley 1976; Mitchell, Ginsburg, and Kuntz 1978; Prasad and Huntress 1980*a*). More importantly, O_2 plays a prominent role in reaction schemes that are thought to govern the abundances of various other interstellar molecules (e.g., Prasad and Huntress 1982); in this sense, O_2 is a significant missing link in our understanding of interstellar chemistry. Observations of O_2 would therefore provide a test of theories of interstellar chemistry and would yield important information about the overall oxygen abundance. The chemistry, excitation, and predicted abundances of interstellar O_2 are discussed in § II of this paper.

Although the presence of a large quantity of O_2 in the terrestrial atmosphere is a necessary condition for all human efforts in astronomy, it presents a major obstacle to the detection of interstellar O_2 by ground-based techniques. The magnetic dipole transitions between rotational levels of the $X\ ^3\Sigma_g^-$ ground state have not been detected because of overwhelming atmospheric attenuation (cf. Rudnitskii 1974); although Matsakis *et al.* (1982) have reported the possible detection of a redshifted, 119 GHz line in absorption in the peculiar galaxy 3C 84. Atmospheric attenuation is reduced at the wavelengths of the rare isotopic species $^{16}O^{18}O$. In § III of this paper, we consider ground-based observations of millimeter wavelength line emission from this molecule.

II. INTERSTELLAR CHEMISTRY, EXCITATION, AND COLUMN DENSITIES OF O_2

Theories of interstellar molecule formation can be used to predict the abundance of O_2, to anticipate locations where O_2 might be detectable, and to show how observations can be used to test models of interstellar chemistry. In order to relate measured line intensities to a molecular abundance, the excitation of the molecule must also be considered, i.e., the fractional populations of the states that participate in each transition must be characterized.

a) Interstellar Chemistry of O_2

The gas phase chemistry that determines the abundance of interstellar O_2 is relatively straightforward and has been understood in basic outline for some time (Herbst and Klemperer 1973; Viala and Walmsley 1976). The only significant source of O_2 is thought to be

$$O + OH \rightarrow O_2 + H\,, \tag{1}$$

while

$$O^- + O \rightarrow O_2 + e \tag{2}$$

may be a minor source in diffuse clouds.

The principal destruction mechanisms are photodissociation,

$$O_2 + h\nu \rightarrow O + O\,, \tag{3}$$

photoionization,

$$O_2 + h\nu \rightarrow O_2^+ + e\,, \tag{4}$$

reactions with various positive ions,

$$H^+ + O_2 \rightarrow O_2^+ + H \tag{5}$$

$$He^+ + O_2 \rightarrow \begin{cases} O^+ + O + He & \text{(6a)} \\ O_2^+ + He & \text{(6b)} \end{cases}$$

$$C^+ + O_2 \rightarrow \begin{cases} CO + O^+ & \text{(7a)} \\ CO^+ + O & \text{(7b)} \end{cases}$$

$$H_3^+ + O_2 \rightarrow O_2H^+ + H_2 \tag{8}$$

$$CH_3^+ + O_2 \rightarrow HCO^+ + H_2O\,, \tag{9}$$

and at least one neutral-neutral reaction

$$C + O_2 \rightarrow CO + O \,. \tag{10}$$

Reaction (8) is nearly thermoneutral and has comparable rates in both directions; therefore, any product O_2H^+ ions are very likely to re-form O_2 by the reverse of reaction (8) or by

$$O_2H^+ + e \rightarrow O_2 + H \,. \tag{11}$$

Reaction (8) can thus be ignored as a net destruction process.

The $O_2{}^+$ ions produced in reactions (4), (5), and (6b) will not re-form O_2 efficiently in subsequent reactions because the rate coefficient of

$$O_2{}^+ + H_2 \rightarrow O_2H^+ + H \tag{12}$$

is small, $k_{12} < 10^{-13}$ cm^3 s^{-1} (Ferguson 1973), and the O–O bond will tend to be broken in most of the probable reactions involving $O_2{}^+$. The ion $C_2H_2{}^+$ does not react with O_2 (Huntress 1977), and there is probably no important reaction of HCO^+ with O_2, proton transfer and charge transfer both being endoergic.

Prasad and Huntress (1980*b*, 1982) have suggested that the interstellar oxygen and sulfur chemistries are coupled through reactions such as

$$S + O_2 \rightarrow SO + O \tag{13}$$

and

$$S + OH \rightarrow SO + H \,. \tag{14}$$

It is uncertain whether reaction (13) has a significant rate coefficient at low temperature. If it does and if sulfur is not highly depleted, then it may be an additional sink of O_2.

b) Rates of Processes Involving O_2

In steady state, the concentration of O_2, $n(O_2)$, is given approximately by

$$n(O_2) \approx n(O)n(OH)k_1/k_d$$

where

$$k_d = k_3(\tau_v) + k_4(\tau_v) + n(H^+)k_5 + n(He^+)k_6 + n(C^+)k_7 + n(CH_3{}^+)k_9 + n(C)k_{10} \,.$$

Here, k_i is the rate coefficient of reaction (i), $n(X)$ is the number density of species X, and the photodestruction rates k_3 and k_4 are written as explicit functions of the visual optical depth, τ_v, into a cloud.

The rate of formation of interstellar O_2 depends upon the low-temperature behavior of reaction (1). Although the rate coefficient k_1 has never been measured at the temperatures of interest, $T \lesssim 100$ K, results of recent laboratory studies permit useful constraints to be placed upon the value of k_1. The measurements of Howard and Smith (1981) in the temperature range 250 K $\leq T \leq$ 515 K are represented well by

$$k_1{}^A = (6.65 \pm 0.23) \times 10^{-10} T^{-(0.50 \pm 0.12)} \text{ cm}^3 \text{ s}^{-1} \,, \qquad \text{[form A]}$$

and the measurements of Lewis and Watson (1980) give a similar, though slightly lower, result

$$k_1{}^B = (2.37^{+1.23}_{-0.81}) \times 10^{-10} T^{-(0.362 \pm 0.072)} \text{ cm}^3 \text{ s}^{-1} \,. \qquad \text{[form B]}$$

In such a neutral-neutral reaction, an inverse temperature dependence is unlikely to persist at cloud temperatures because of the absence of any strong attractive force in the interaction. The most extreme—yet smooth—behavior at $T < 100$ K that would be consistent with the measured rates at $T \geq 250$ K is

$$k_1{}^C = 7.55 \times 10^{-10} T^{-1/2} \exp(-83.6/T) \text{ cm}^3 \text{ s}^{-1} \,. \qquad \text{[form C]}$$

We thus use forms A and C to assign upper and lower limits, respectively, to the values of k_1 at interstellar temperatures: $0.33 \leq 10^{10}k_1 \leq 0.66$ at $T = 100$ K; $0.20 \leq 10^{10}k_1 \leq 0.94$ at $T = 50$ K; and $0.26 \leq 10^{10}k_1 \leq 1.5$ at $T = 20$ K.

Deep inside dark clouds, where both destructive positive ions and dissociating photons are scare, reaction (1) can be the principal destruction mechanism for OH. In that case, the O_2 abundance will depend upon the rate of formation of OH and will be relatively insensitive to the exact value of k_1. At the same time, the predicted OH abundance will be inversely proportional to the adopted value of k_1.

The negative ion O^- is formed inefficiently by radiative association in a gas of low fractional ionization and is destroyed rapidly by long-wavelength photons and by reactions with H and H_2; therefore, its concentration will be very small, $n(O^-) < 10^{-8}n(e)n(O)$ (cf. Prasad and Huntress 1980*a*), and reaction (2) will be a negligible source of O_2.

We have computed the rates of processes (3) and (4) in the mean interstellar radiation field adopted by Roberge, Dalgarno, and Flannery (1981). Photodissociation of O_2 has contributions from the Schumann-Runge (S-R) continuum at wavelengths $\lambda \lesssim 1750$ Å, from the S-R bands—virtually all of which are predissociated—at 1750 Å $\leq \lambda \leq$ 2026 Å, and from a number of bands at shorter wavelengths. For the S-R continuum, we adopt the differential oscillator strengths of Huebner *et al.* (1975). For the S-R bands, we use the band oscillator strengths of Yoshino *et al.* (1983) for $v' \leq 12$, those given in Paper II for $13 \leq v' \leq 16$, and those of Geis *et al.* (1981) for $v' > 16$. Oscillator strengths of Huebner *et al.* (1975) have been adopted for 25 EUV bands with $917 \leq \lambda(\text{Å}) \leq 1294$; for all of these we assume 100% predissociation. To calculate the rates for photoionization of O_2, reaction (4), at wavelengths 912 Å to 1027 Å, we have adopted the cross sections tabulated by Kirby *et al.* (1979).

Under conditions of uniform illumination by the unattenuated interstellar radiation field, the photodestruction rates are 6.3×10^{-10} s^{-1} (S-R bands and continuum), 1.6×10^{-10} s^{-1} (EUV bands), and 0.9×10^{-10} s^{-1} (photoionization). The total rate of destruction of O_2 by photons, $k_3 + k_4 = 8.8 \times 10^{-10}$ s^{-1}, is approximately 2.5 times larger than the corresponding rate of photodissociation of OH (van Dishoeck and Dalgarno 1983). The destruction rates of O_2 are shown as functions of visual extinction, $A_v = \tau_v/1.086$, through a very thick, plane-parallel cloud in Figure 1.

c) O_2 *in Diffuse Clouds*

It is crucial to recognize that the observable strengths of interstellar lines of O_2 are directly related to its column density, $N(O_2) = \int n(O_2)dr$, i.e., the integrated density along an observer's line of sight. In order to predict $N(O_2)$, or to relate it to a measured column density of another molecule, it is necessary to construct models of interstellar clouds that

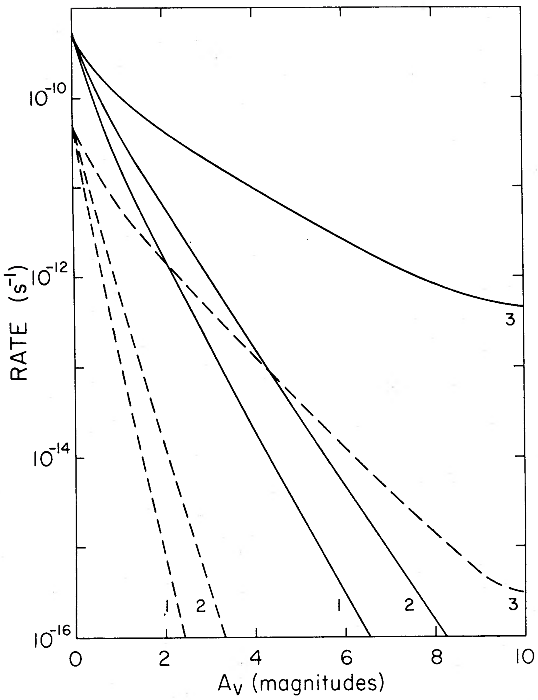

FIG. 1.—O_2 destruction rate. Solid curves show the total photodestruction rate, photodissociation plus photoionization, as a function of visual extinction into a cloud of total thickness $A_v = 20$ mag for grain models 1–3 of Roberge, Dalgarno, and Flannery (1981). Dashed curves show the photoionization rate.

realistically represent the depth dependences of the O_2 formation and destruction rates and of the abundances of related species (cf. Viala and Walmsley 1976; Black and Dalgarno 1977; de Jong, Dalgarno, and Boland 1981).

The depth dependence of the O_2 concentration is linked to that of OH, the principal source of O_2 (cf. reaction [1]). The abundances of C^+ and C, which compete with photons in destroying O_2 (cf. reactions [7] and [10]), are severely affected by the conversion of carbon into molecules like CO. In particular, the depth dependences of the photodestruction rates are affected both by the scattering properties of the interstellar grains and by the total thickness of the cloud (Roberge, Dalgarno, and Flannery 1981). Chemical models of interstellar clouds that ignore the effects of UV photons or that neglect the depth-dependences of predicted abundances (e.g., Herbst and Klemperer 1973; Iglesias 1977; Prasad and Huntress 1980*a*) are therefore of limited value in interpreting observations.

In diffuse clouds, the growth of O_2 is inhibited because it is formed in only a small fraction of the destructions of its parent OH, which is more likely to be removed by photodissociation and by reactions with the abundant ion C^+. We have computed diffuse cloud models that treat accurately the balance between H and H_2 and that incorporate a chemical reaction network large enough to describe the equilibrium among the other major species: C, C^+, CO, OH, O_2, H^+, He^+, and $H_3{}^+$. The construction of the models and the details of the reaction network will be described in a future paper. Some representative values of model column densities of H_2, OH, O_2, and CO in diffuse clouds are presented in Table 1. Each cloud model is specified by a total density of hydrogen nuclei, $n = n(H) + 2n(H_2)$; a temperature T; and a total visual extinction (i.e., optical thickness), A_v, in magnitudes. These results suggest that the O_2 column density will be $N(O_2) \approx 10^{10}$–10^{11} cm^{-2} in diffuse clouds where $A_v \approx 1$ mag and $N(O_2) \approx 10^{12}$–10^{13} cm^{-2} in more highly obscured regions where $A_v \gtrsim 3$ mag. These column densities are consistent with those obtained from a partial revision of the chemical model of the well-studied diffuse cloud toward ζ Oph (Black and Dalgarno 1977) which indicates $N(O_2) \approx 3 \times 10^{11}$ cm^{-2}.

TABLE 1

LOG$_{10}$ PREDICTED COLUMN DENSITIES $N(X)$ (IN cm^{-2}) FOR DIFFUSE CLOUDS FOR VARIOUS VALUES OF TOTAL DENSITY n

		log$_{10}$ N:			
T(K)	n(cm^{-3})	H_2	OH	O_2	CO
Diffuse Cloud (A_v = 1.0)					
100	100	20.6	13.5	11.0	14.4
	300	20.8	13.5	11.1	15.8
	1000	20.9	12.9	11.0	17.1
50	300	20.8	12.6	10.2	15.7
	1000	20.9	12.5	10.4	17.1
20	1000	20.9	11.8	8.8	17.1
Thick Diffuse Cloud (A_v = 3.0)					
50	300	21.4	13.6	11.8	17.6
	1000	21.5	13.9	12.7	17.8
	3000	21.5	14.2	13.5	17.9
20	1000	21.5	13.4	11.3	17.8
	10,000	21.5	13.9	12.6	17.9

d) O_2 *in Dark Clouds*

The formation of O_2 in dark clouds has been considered by numerous investigators, including Herbst and Klemperer (1973); Viala and Walmsley (1976); Viala, Bel, and Clavel (1979); Iglesias (1977); Mitchell, Ginsburg, and Kuntz (1978); and Prasad and Huntress (1980*a*, *b*). Rather than present the results of one specific model of O_2 abundance in a particular cloud, we have chosen to survey previous work, to point out and explain some discrepancies, and to draw general conclusions about predicted O_2 column densities relative to those for CO and OH. Several of the above-mentioned studies predict that $n(O_2) \gg n(OH)$ and $n(O_2) \approx n(O) \gtrsim 0.1\ n(CO)$ deep inside dark clouds.[1]

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[1] Several previous investigators comment on the difficulty of reproducing the observed amounts of OH. In particular, Viala, Bel, and Clavel (1979) claimed that gas phase processes alone are insufficient and that formation of OH on grain surfaces is required to produce column densities as large as those observed in dark clouds, $N(OH) \gtrsim 10^{15}$ cm^{-2}. We can identify two possible explanations for these small predicted abundances: overestimation of the low-temperature rate of reaction (1) and underestimation of the OH/H_2O product ratio in dissociative recombination of H_3O^+,

$$H_3O^+ + e \rightarrow \begin{cases} OH + 2H \text{ (or } H_2) \\ H_2O + H\,. \end{cases} \tag{15}$$

All of the above investigators adopted $k_1 \approx 4 \times 10^{-11}$ cm^3 s^{-1}, independent of T, with the exception of Prasad and Huntress (1980*a*, *b*) who assumed $k_1 = 2.3 \times 10^{-12} T^{1/2}$. As suggested above, a small activation energy and a rate as low as $k_1 = 3 \times 10^{-12}$ cm^3 s^{-1} at $T = 20$ K would be consistent with the best laboratory data on reaction (1). A low value of k_1 would imply a lower destruction rate and thus a larger abundance of OH in cold, dark clouds. Observational limits on the H_2O abundance in diffuse clouds imply a conservative lower limit of 0.7 on the OH/H_2O product ratio in reaction (15) (Smith *et al.* 1981) and theoretical estimates favor a value of the order of 10 (Herbst 1978). With these adjustments, known gas phase processes can reproduce observed OH abundances.

From the calculations of Herbst and Klemperer (1973) and of Viala and Walmsley (1976), it is clear that the O_2 abundance will be extremely sensitive to the total abundance of oxygen in the gas phase. If O_2 is eventually observed, this sensitivity might be exploited to establish whether the accretion of elements such as O and C to form grain mantles is inexorable in quiescent, dark clouds (cf. de Jong, Dalgarno, and Boland 1981), or whether there exists a mechanism that limits depletion (Boland and de Jong 1982).

In the interiors of thicker clouds, the rates of photodissociation and photoionization are reduced by attenuation; thus, most of the gaseous carbon exists as CO and the abundance of C^+ diminishes. Consequently, reaction (1) begins to account for a significant fraction of the destruction of OH. With increasing depth, the production rate of O_2 approaches that of OH, while the destruction rate of OH will tend to exceed that of O_2; thus, the predicted density of O_2 can greatly exceed that of OH near the heart of a dark cloud. The column density of OH is found to exceed 10^{15} cm^{-2} in a number of cloud complexes (Wouterloot 1981; Baud and Wouterloot 1980). If $N(O_2) \gtrsim 100N(OH)$, then column densities $N(O_2) \gtrsim 10^{17}$ cm^{-2} can be expected.

In realistic models of the dark cloud L134 (de Jong, Dalgarno, and Boland 1981), the predicted column density of O_2 always exceeds that of OH and ranges from 8.7×10^{15} to 1.8×10^{17} cm^{-2}, depending upon the total density and the degree of oxygen depletion in the interior. Comparison of observations with two of these models shows that the column density of OH is only slightly larger (viz., factors 1.3 and 2.4) than the theoretical values and that even better agreement could be achieved by a modest increase in the cosmic ray ionization rate (from 5×10^{-18} s^{-1}) or a modest decrease in the rate of reaction (1) (from 5×10^{-11} cm^3 s^{-1}, independent of T).

Myers, Linke, and Benson (1983) infer $N(CO) \approx 3 \times 10^{18}$ cm^{-2} in the cores of dark clouds. As mentioned above, several models predict $n(O_2) \geq 0.1n(CO)$, and it is possible that the column densities of these two species are comparable. Thus, $N(O_2) \gtrsim 10^{18}$ cm^{-2} could be expected in such clouds. The very largest column densities of CO are observed in giant molecular clouds, where they can be as large as $N(CO) \approx 2 \times 10^{19}$ cm^{-2} (cf. Phillips *et al.* 1980). In such regions, the corresponding column densities of O_2 may also be 10^{18} cm^{-2} or more.

Prasad and Huntress (1982) have suggested that the abundances of O and O_2 may be rather smaller than previously predicted if the observed abundances of sulfur-bearing species in some interstellar clouds are to be understood in terms of known reaction schemes. Questions raised by such investigations emphasize the need for direct observations of O_2.

The above presentation suggests that the abundance of O_2 cannot be predicted confidently for any particular molecular cloud, but that order of magnitude estimates can be made. If $n(O_2) \approx 100n(OH)$, which is likely, then $N(O_2) \approx 10^{17}$ cm^{-2}. If $n(O_2) \approx n(CO)$, then $N(O_2) \gtrsim 10^{18}$ cm^{-2}. The uncertainties in predicted O_2 abundances lie in the uncertainties in the concentrations of positive ions and in the oxygen depletion in the interiors of dark clouds rather than in details of the reactions and reaction rates. We assert that if the basic chemistry of interstellar O_2 is as outlined above, then observations of O_2 and related species can be used to refine our knowledge of the overall oxygen abundance and ion chemistry in molecular clouds.

e) Level Populations

Even at low interstellar temperatures, a number of rotational states of O_2 can be populated. Because it is a homonuclear species, $^{16}O_2$ has no permanent electric dipole moment; hence, excited rotational levels decay spontaneously only by relatively slow, higher order transitions and will be long-lived. Because the strong ultraviolet transitions in O_2 produce dissociation rather than fluorescence, fluorescent excitation makes no contribution to the rotational level populations in O_2. In contrast, fluorescence following absorption of starlight has significant effects on the rotational excitation of the previously studied homonuclear interstellar molecules H_2 and C_2 (Black and Dalgarno 1976; van Dishoeck and Black 1982). The rotational populations of O_2 are determined by a statistical equilibrium among the following processes: spontaneous magnetic dipole transitions, emission stimulated by and absorption of the ambient background radiation in the magnetic dipole transitions, and collisional excitation and de-excitation.

For $^{16}O_2$ we consider all such transitions between levels of a 15-level molecule with rotational quantum numbers $N = 1$, 3, 5, 7, and 9. Term values have been determined for all $N = 1$ and 3 levels from microwave transition frequencies tabulated by Lovas and Tiemann (1974). Rotational separations between higher levels with $N = J$ are from Veseth and Lofthus (1974), and the splittings for $\Delta N = 0$, $\Delta J = \pm 1$ are taken from the accurate microwave transition frequencies. Somewhat more accurate separations $\Delta N = 2$ for the higher levels can be derived from the analysis of Johns and Lepard (1975).

The probability of a spontaneous magnetic dipole transition from upper state, u, to lower state, l, is given by

$$\begin{aligned}(2J_u + 1)A_{ul} &= (64\pi^4/3h)\tilde{\nu}^3\mu_m^2 S_{ul} \\ &= 1.079 \times 10^{-10}\tilde{\nu}^3 S_{ul}\ \mathrm{s}^{-1}\ ,\end{aligned}$$

where $\tilde{\nu} = \nu/c$ is the transition frequency in cm^{-1}; μ_m is the magnetic dipole moment of O_2, $\mu_m = 2$ Bohr magnetons; and S_{ul} is the magnetic dipole line strength as defined by Tinkham and Strandberg (1955). Gebbie, Burroughs, and Bird (1969) have pointed out that the line strengths tabulated by Tinkham and Strandberg (1955) for transitions with $N'' = N'-2$ and $J'' = J'-1$ are erroneous; accordingly, we have recomputed these from the basic matrix elements.

The radiation field governing the rates of absorption and stimulated emission is a combination of the $T = 2.7$ K cosmic blackbody radiation and thermal emission by local dust grains. In a cloud of small optical depth at submillimeter wavelengths and of dust grains at a temperature $T_{\mathrm{dust}} = 15$ K, the local dust emission can provide a brightness temperature $T_{\mathrm{rad}} \approx 5$–6 K at the frequencies of the $N = 9 \rightarrow 7$ (1500 GHz) and $N = 7 \rightarrow 5$ (1100 GHz) transitions.

Collisional excitation rates can be estimated from experimental data on pressure broadening of microwave lines (cf. Schwartz 1979). Pressure broadening linewidth parameters for O_2 in collisions with N_2 have been measured for both the $N = 1 \rightarrow 1$, $J = 1 \rightarrow 0$ (118.75 GHz) and $N = 3 \rightarrow 1$, $J = 2 \rightarrow 2$

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TABLE 2

FRACTIONAL POPULATIONS OF ROTATIONAL LEVELS OF O_2 IN STATISTICAL EQUILIBRIUM (SE) AND THERMODYNAMIC EQUILIBRIUM (TE)

Density (cm^{-3})			500		1000		10,000	
Temperature (K)			50		20		10	
N	J	Energy (cm^{-1})	SE	TE	SE	TE	SE	TE
1	0	0.00	0.0458	0.0270	0.0793	0.0649	0.1207	0.1204
	2	2.08	0.2320	0.1272	0.4125	0.2793	0.4475	0.4460
	1	3.96	0.1206	0.0723	0.1777	0.1464	0.2047	0.2043
3	2	16.25	0.1310	0.0846	0.0881	0.1008	0.0580	0.0581
	4	16.39	0.2306	0.1517	0.1432	0.1796	0.1022	0.1025
	3	18.34	0.1691	0.1115	0.0959	0.1214	0.0601	0.1602
5	4	42.20	0.0192	0.0722	0.0092	0.0281	0.0020	0.0025
	6	42.22	0.0275	0.1042	0.0013	0.0405	0.0029	0.0036
	5	44.21	0.0220	0.0832	0.0009	0.0297	0.0019	0.0023
7	8	79.56	0.0008	0.0465	...	0.0036	...	...
	6	79.61	0.0006	0.0355	...	0.0027	...	...
	7	81.58	0.0007	0.0387	...	0.0027	...	...
9	10	128.40	...	0.0141	...	0.0001	...	...
	8	128.49	...	0.0114	...	0.0001	...	...
	9	130.44	...	0.0120	...	0.0001	...	...

(425 GHz) lines by Pickett, Cohen, and Brinza (1981). After the N_2-O_2 broadening parameters have been converted to collisional de-excitation rates, scaled for the smaller reduced mass of the H_2-O_2 system, and extrapolated to low temperatures, it is found that the rates for the 119 and 425 GHz transitions are in approximately the same ratio as their magnetic dipole line strengths. Therefore, we adopt a set of very approximate H_2-O_2 collision rates prescribed by the following rules:

1. Only transitions that obey the selection rules $\Delta N = 0$ or ± 2 and $\Delta J = 0$ or ± 1 are considered;
2. The de-excitation rate for the $N = 1 \rightarrow 1$, $J = 1 \rightarrow 0$ (119 GHz) transition is taken to be $k = 5.3 \times 10^{-10}(T/20)^{0.3}$ $cm^3\ s^{-1}$;
3. All other downward rates scale in proportion to $S_{ul}/(2J_u + 1)$; and
4. Excitation rates are computed from corresponding downward rates according to the principal of detailed balance. The collision rates are uncertain by as much as a factor of 2.

Calculated fractional equilibrium level populations are shown in Table 2 for the conditions $n(H_2) = 500$ cm^{-3}, $T = 50$ K; $n(H_2) = 10^3$ cm^{-3}, $T = 20$ K; and $n(H_2) = 10^4$ cm^{-3}, $T = 10$ K. The uncertainties in the collision rates could produce a 30% uncertainty in the level populations. Fractional populations in local thermodynamic equilibrium (LTE) are listed for comparison. It is evident that the higher levels are not thermalized at densities as low as $n(H_2) = 500$ cm^{-3}, even though the radiative transitions are electric-dipole forbidden. Note that the population distribution at $T = 50$ K in a low-density cloud is not very different from that at $T = 20$ K in a high-density cloud.

III. PROSPECTS FOR GROUND-BASED DETECTION OF O_2 AT RADIO FREQUENCIES

The abundances, level populations, and transition probabilities derived in §§ II*d* and II*e* were used to predict intensities of some O_2 radio frequency lines for several values of the total O_2 column density. Table 3 lists the quantum numbers of the upper (N', J') and lower (N'', J'') states, the frequencies in GHz, the transition probabilities A_{ul} in s^{-1}, and the predicted peak brightness temperatures in excess of background for lines of width $\Delta v = 1.0$ km s^{-1}. All of these lines are, of course, coincident with strong atmospheric

TABLE 3

BRIGHTNESS TEMPERATURES (IN K) OF SELECTED RADIO LINES OF O_2 FOR TWO CLOUD MODELS FOR VARIOUS VALUES OF $N(O_2)$ IN CENTIMETERS^{-2}

Density (cm^{-3})			500			10,000			
Temperature (K)			50			20			
			T_b			T_b			
TRANSITION N', J'-N'', J''	FREQUENCY (GHz)	A (s^{-1})	$N(O_2) = 10^{15}$	10^{16}	10^{17}	$N(O_2) = 10^{15}$	10^{16}	10^{17}	10^{18}
1, 1-1, 2	56.265	5.83(−10)	0.011	0.11	1.07	0.014	0.14	1.32	9.20
3, 3-3, 4	58.447	7.66(−10)	0.021	0.21	1.95	0.014	0.14	1.34	9.34
1, 1-1, 0	118.750	4.47 (−9)	0.027	0.27	2.29	0.033	0.32	2.61	13.2
3, 3-3, 2	62.486	9.13(−10)	0.022	0.21	2.01	0.015	0.15	1.41	9.61
3, 2-1, 1	368.498	1.92 (−9)	0.013	0.12	0.78	0.009	0.09	0.63	2.70
3, 2-1, 2	424.763	2.41 (−8)	0.177	0.99	3.55	0.120	0.78	3.01	9.89
3, 3-1, 2	487.249	8.47 (−9)	0.097	0.63	2.35	0.057	0.43	1.87	6.06

TABLE 4

BRIGHTNESS TEMPERATURE (K) FOR $C^{18}O$, $J = 2 \rightarrow 1$, AND $O^{18}O$, $N = 2 \rightarrow 0$, $J = 1 \rightarrow 1$

COLUMN DENSITY OF $O^{18}O$ OR $C^{18}O$		$T = 10$ K, $\Delta v = 0.5$ km s^{-1}				$T = 40$ K, $\Delta v = 3.0$ km s^{-1}			
		$n(H_2) =$ 10^2	10^3	10^4	10^5	$n(H_2) =$ 10^2	10^3	10^4	10^5
10^{14} cm^{-2}	$T_b(O^{18}O)$	0.003	0.003	0.003	0.003	0.0006	0.0005	0.0004	0.0003
	$T_b(C^{18}O)$	0.024	0.188	0.593	0.714	0.016	0.106	0.197	0.145
10^{15} cm^{-2}	$T_b(O^{18}O)$	0.028	0.034	0.034	0.034	0.006	0.005	0.004	0.003
	$T_b(C^{18}O)$	0.195	1.159	3.047	3.660	0.145	0.830	1.422	1.115
10^{16} cm^{-2}	$T_b(O^{18}O)$	0.256	0.306	0.308	0.307	0.057	0.047	0.036	0.034
	$T_b(C^{18}O)$	0.891	3.489	6.559	7.195	0.899	4.011	7.826	6.506

absorption features due to O_2 and will be unobservable from the Earth's surface.

Rudnitskii (1974) had previously discussed the observability of interstellar O_2. Rudnitskii ignored the submillimeter rotational transitions and assumed that the level populations are in thermodynamic equilibrium (although the levels of lower statistical weight unaccountably have larger relative populations in Table 2 of Rudnitskii's paper). We believe our predictions to be more reliable than those of Rudnitskii.

The principal isotopic form of molecular oxygen, $^{16}O_2$, is homonuclear with nuclear spin $I = 0$. Hence all ground-state rotational levels with even values of N are absent in accordance with the Pauli exclusion principle. Because the nuclei are distinguishable in the rare species $^{16}O^{18}O$, it possesses the full complement of rotational levels and, therefore, has magnetic-dipole rotational transitions that do not coincide with any transitions of $^{16}O_2$.[2] Because the center of mass and center of charge do not coincide exactly in $O^{18}O$, this molecule will possess a small permanent electric dipole moment (cf. Bates 1953). The magnitude of this dipole moment can be estimated by scaling the corresponding dipole moment of isotopic hydrogen, HD, according to the isotopic mass difference (Bunker 1973), with the result that $\mu_e(O^{18}O) \approx 8 \times 10^{-6}$ Debye. The line strengths of magnetic dipole transitions will exceed those of electric dipole transitions by factors of the order of $(\mu_m/\mu_e)^2 \approx 10^6$; therefore, we may safely ignore the electric dipole transitions in $O^{18}O$.

The excitation of $O^{18}O$ was calculated as for O_2 (cf. § II*e*) except that all 28 rotational levels with $N \leq 9$ were taken into account. The most favorable transition in $O^{18}O$ is $N = 2 \rightarrow 0$, $J = 1 \rightarrow 1$ at a frequency of 233.946179 GHz (Steinbach and Gordy 1975). Predicted brightness temperatures are tabulated for several values of column density of $O^{18}O$ and for two types of clouds in Table 4. A typical cold, dark cloud is characterized by $T = 10$ K and a line width $\Delta v = 0.5$ km s^{-1}, and a warmer, giant molecular cloud, by $T = 40$ K and $\Delta v = 3.0$ km s^{-1}. Peak brightness temperatures in excess of background are listed at various H_2 densities. A column density $N(O_2) \approx 10^{18}$ cm^{-2} would yield $T_b(0^{18}O) \approx 0.07$ K in the 234 GHz line in a cold, dark cloud.

The Earth's atmosphere is relatively transparent at this frequency. For an abundance ratio $n(^{18}O)/n(O_2) = 1/250$ in the atmosphere and an assumed pressure-broadened line width of 1 GHz (similar to that of the 425 GHz line of O_2: Pickett, Cohen, and Brinza 1981), the peak optical depth in the 234 GHz atmospheric line itself is predicted to be $\tau = 0.024$ through a vertical column from sea level. For comparison, the optical depth due to atmospheric water vapor absorption at 230 GHz is $\tau = 0.067$, under favorable conditions of 1 mm of precipitable H_2O from an elevation of 2400 m (Brand 1982).

It is instructive to compare predicted brightness temperatures of the 234 GHz line, $T_b(O^{18}O)$, with those of the $J = 2 \rightarrow 1$ line of $C^{18}O$ at 219.560 GHz, $T_b(C^{18}O)$. Not only are these two lines close in frequency, but the abundance ratio $n(O^{18}O)/n(C^{18}O)$ should be approximately equal to the overall ratio $n(O_2)/n(CO)$.[3]

The brightness temperatures in the $C^{18}O$ lines have been calculated for a 10-level molecule using the He-CO collisional excitation rates of Green and Chapman (1978) scaled for H_2-CO collisions. Values of $T_b(C^{18}O)$ for the $J = 2 \rightarrow 1$ line under various conditions are also given in Table 4. The tabulated results could be used to infer ratios of column densities from ratios of brightness temperatures in the lines of $O^{18}O$ and $C^{18}O$.

Observations suggest $C^{18}O$ column densities of 10^{15} cm^{-2} to 5×10^{15} cm^{-2} in the cores of cold, dark clouds (Myers, Linke, and Benson 1983; Frerking, Langer, and Wilson 1982), and $N(C^{18}O)$ of 10^{16} cm^{-2} to 4×10^{16} cm^{-2} in several warm, giant molecular clouds (Phillips *et al.* 1980). Observations of the $C^{18}O$ $J = 2 \rightarrow 1$ line itself yield peak line temperatures $T_A^* = 2$–10 K in several giant molecular clouds (Plambeck and Williams 1979; Phillips *et al.* 1979).

It is evident from Table 4 that the 234 GHz line of $O^{18}O$ will have a larger peak temperature for a given column density in a cold, dark cloud than in a warm, giant molecular cloud. This occurs in part because the lines are assumed to be narrower in cold clouds, and in part because the upper state of the transition contains a larger fraction of the total $O^{18}O$ abundance at the lower temperature. On the other hand, the larger column densities of some giant molecular clouds will probably compensate for the smaller peak line strengths. If frequency resolution is chosen to match the expected line widths, then searches for broad lines ($\Delta v = 3$ km s^{-1}) in giant molecular clouds will have an added advantage over

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[2] Henceforth we will refer to the principal isotopic species, O_2, without a superscript, and we will refer to the rare species, $^{16}O^{18}O$, as $O^{18}O$.

[3] From a naive consideration of the interstellar chemistry, one would conclude that, because O_2 is homonuclear, $n(O^{18}O)/n(O_2) = 2n(^{18}O)/n(^{16}O) \approx 2/500$ (cf. Wannier 1980) and, thus, that $n(O^{18}O)/n(C^{18}O) = 2n(O_2)/n(CO)$. However, the detailed fractionation of O-bearing molecules has not yet been considered, and, therefore, we will use the conservative estimate that $0.1 \leq n(O^{18}O)/n(C^{18}O) \approx n(O_2)/n(CO) \leq 1$.

searches for narrow lines ($\Delta v = 0.5$ km s^{-1}) in dark clouds. The noise level is proportional to $(\Delta v t)^{-1/2}$, so that a higher signal-to-noise ratio can be achieved on broad-line sources in a given integration time, t. At worst, it should be possible to establish an upper limit $T_b(\mathrm{O^{18}O})/T_b(\mathrm{C^{18}O}) \leq 10^{-2}$, which would imply $N(\mathrm{O_2})/N(\mathrm{CO}) < 1$. An upper limit at this level would provide an interesting constraint upon models of interstellar chemistry.

The above discussion shows that the previously unobserved interstellar molecule, O_2, could be detected through ground-based observations of the 234 GHz line of $^{16}O^{18}O$ if the column density of O_2 is of the order of 10^{18} cm^{-2} in molecular clouds. Paper II discusses prospects for observation of interstellar O_2 at vacuum ultraviolet wavelengths using the High Resolution Spectrograph on Space Telescope to search for absorption in the spectra of background stars. Such observations would be limited to very few lines of sight but could be about 10 times more sensitive than the ground-based, radio frequency observations suggested here. The UV observations should also detect absorption from several lower levels; thus, models of the excitation of interstellar O_2 could be assessed. Determination of O_2 column densities in dark clouds, or an upper limit to them, by either method would permit an assessment of the accuracy of models of the chemistry and excitation of oxygen-bearing species in interstellar clouds.

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REFERENCES

Bates, D. R. 1953, *Ap. J.*, **117**, 236.
Baud, B., and Wouterloot, J. G. A. 1980, *Astr. Ap.*, **90**, 297.
Black, J. H., and Dalgarno, A. 1976, *Ap. J.*, **203**, 132.
———. 1977, *Ap. J. Suppl.*, **34**, 405.
Boland, W., and de Jong, T. 1982, *Ap. J.*, **261**, 110.
Brand, J. 1982, *ESO Messenger*, No. 29, p. 20.
Bunker, P. R. 1973, *J. Molec. Spectrosc.*, **46**, 119.
de Jong, T., Dalgarno, A., and Boland, W. 1981, *Astr. Ap.*, **91**, 68.
Ferguson, E. E. 1973, *Atomic Data Nucl. Data Tables*, **12**, 159.
Frerking, M. A., Langer, W. D., and Wilson, R. W. 1982, *Ap. J.*, **262**, 590.
Gebbie, H. A., Burroughs, W. J., and Bird, G. R. 1969, *Proc. Roy. Soc. A.*, **310**, 579.
Gies, H. P. F., Gibson, S. T., McCoy, D. G., Blake, A. J., and Lewis, B. R. 1981, *J. Quant. Spectrosc. Rad. Transf.*, **26**, 469.
Green, S., and Chapman, S. 1978, *Ap. J. Suppl.*, **37**, 169.
Herbst, E. 1978, *Ap. J.*, **222**, 508.
Herbst, E., and Klemperer, W. 1973, *Ap. J.*, **185**, 505.
Howard, M. J., and Smith, I. W. M. 1981, *J. Chem. Soc. Faraday Trans. 2*, **77**, 997.
Huebner, R. H., Celotta, R. J., Mielczarek, S. R., and Kuyatt, C. E. 1975, *J. Chem. Phys.*, **63**, 241.
Huntress, W. T., Jr. 1977, *Ap. J. Suppl.*, **33**, 495.
Iglesias, E. 1977, *Ap. J.*, **218**, 697.
Johns, J. W., C., and Lepard, D. W. 1975, *J. Molec. Spectrosc.*, **55**, 374.
Kirby, K., Constantinides, E. R., Babeu, S., Oppenheimer, M., and Victor, G. A. 1979, *Atomic Data Nucl. Data Tables*, **23**, 63.
Lewis, R. S., and Watson, R. T. 1980, *J. Phys. Chem.*, **84**, 3495.
Lovas, F. J., and Tiemann, E. 1974, *J. Phys. Chem. Ref. Data*, **3**, 609.
Matsakis, D. N., Bologna, J. M., Schwartz, P. R., and Thacker, D. L. 1982, *Pub. A.S.P.*, **94**, 26.
Mitchell, G. F., Ginsburg, J. L., and Kuntz, P. J. 1978, *Ap. J. Suppl.*, **38**, 39.
Myers, P. C., Linke, R. A., and Benson, P. J. 1983, *Ap. J.*, **264**, 517.
Phillips, T. G., Huggins, P. J., Kuiper, T. B. H., and Miller, R. E. 1980, *Ap. J.* (*Letters*), **238**, L103.
Phillips, T. G., Huggins, P. J., Wannier, P. G., and Scoville, N. Z. 1979, *Ap. J.*, **231**, 720.
Pickett, H. M., Cohen, E. A., and Brinza, D. E. 1981, *Ap. J.* (*Letters*), **248**, L49.
Plambeck, R. L., and Williams, D. R. W. 1979, *Ap. J.* (*Letters*), **227**, L43.
Prasad, S. S., and Huntress, W. T., Jr. 1980*a*, *Ap. J. Suppl.*, **43**, 1.
———. 1980*b*, *Ap. J.*, **235**, 151.
———. 1982, *Ap. J.*, **260**, 590.
Roberge, W., Dalgarno, A., and Flannery, B. P. 1981, *Ap. J.*, **243**, 817.
Rudnitskii, G. M. 1974, *Soviet Astr.-A J*, **18**, 191.
Schwartz, P. R. 1979, *Ap. J.* (*Letters*), **229**, L45.
Smith, P. L., Griesinger, H. E., Black, J. H., Yoshino, K., and Freeman, D. E. 1984, *Ap. J.*, **277**, 569 (Paper II).
Smith, P. L., Yoshino, K., Griesinger, H. E., and Black, J. H. 1981, *Ap. J.*, **250**, 166.
Steinbach, W., and Gordy, W. 1975, *Phys. Rev. A*, **11**, 729.
Tinkham, M., and Strandberg, M. W. P. 1955, *Phys. Rev.*, **97**, 93.
van Dishoeck, E. F., and Black, J. H. 1982, *Ap. J.*, **258**, 533.
van Dishoeck, E. F., and Dalgarno, A. 1983, *J. Chem. Phys.*, **79**, 873.
Veseth, L., Lofthus, A. 1974, *Mol. Phys.*, **27**, 511.
Viala, Y. P., Bel, N., and Clavel, J. 1979, *Astr. Ap.*, **73**, 174.
Viala, Y. P., and Walmsley, C. M. 1976, *Astr. Ap.*, **50**, 1.
Wannier, P. G. 1980, *Ann. Rev. Astr. Ap.*, **18**, 399.
Wouterloot, J. G. A. 1981, Ph.D. thesis, University of Leiden.
Yoshino, K., Freeman, D. E., Esmond, J. R., and Parkinson, W. H. 1983, *Planet. Space Sci.*, **31**, 339.

JOHN H. BLACK: Steward Observatory, University of Arizona, Tucson, AZ 85721

PETER L. SMITH: Harvard College Observatory, 60 Garden Street, Cambridge, MA 02138