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UPPER LIMITS ON THE ABUNDANCE OF THE SULFUR DIMER IN MOLECULAR CLOUDS

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ABSTRACT

We have searched for magnetic-dipole transitions among spin-split rotational levels in $^{32}S_2$. The absence of such emission shows that less than a few percent of the presumably available sulfur nuclei resides in this species. Several other lines observed during the search are briefly discussed.

Subject headings: interstellar: abundances — interstellar: molecules — radio sources: lines

I. INTRODUCTION

With the slight exceptions of carbon and oxygen, some 5%–10% of which can be accounted for in the form of carbon monoxide, the vast majority of particles present in molecular clouds simply go unobserved. For instance, in Orion A, where the inferred column density of H_2 is greater than $\sim 2 \times 10^{23}$ cm^{-2}, a solar-system abundance of sulfur nuclei is $N_s \gtrsim 6 \times 10^{18}$ cm^{-2} (Allen 1973). Because sulfur-bearing molecules have column densities less than $\sim 3 \times 10^{15}$ cm^{-2}, less than 0.1% of the likely sulfur has been detected. The alternatives usually presented to account for this state of affairs involve either depletion from the gas phase or concealment in species which lack accessible spectra. However, most sulfur-bearing compounds have the prerequisite spectra and some, like SO_2, which would be unobservable if carbon or oxygen were substituted, are already known to be fairly low in abundance (Snyder *et al.* 1975). We have searched for lines of the sulfur dimer (S_2), a species which could, in principle, contain an appreciable fraction of the available S nuclei. S_2 is the only such dimer with an accessible radio spectrum. The silicon dimer is thought to have a triplet ground state, but no details concerning its rotational spectrum are available (Rosen 1970). The ground state of C_2 is now classified as a singlet (Rosen 1970), although Herzberg (1967) gave it as $^3\Pi$.

II. THE ROTATION SPECTRUM OF $^{32}S_2$

Like $^{16}O_2$, the $^{32}S_2$ ground state is $^3\Sigma_g^-$; even-numbered rotation (N) levels are absent, and those with N odd are split into triplets $J = N$, $N \pm 1$. As shown in Figure 1, radiative transitions are magnetic-dipole-allowed for $\Delta N = 0$, $\Delta J = \pm 1$ (quadrupole interactions connecting levels with $\Delta N = 2$ are much weaker and can be ignored here). The dipole moments for these transitions are given by Townes and Schawlow (1955) and are approximately equal to $4\mu_B{}^2$, where μ_B is the Bohr magneton, 9×10^{-21} emu.

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Calculation of the energy levels in S_2 involves knowledge of four constants (Townes and Schawlow 1955): $B_0 = 8.8386 \pm 0.002$ GHz, $D_0 = 6.4 \times 10^{-6}$ GHz (Rosen 1970), $\lambda = 352.97 \pm 0.18$ GHz, and $\gamma = -0.257 \pm 0.009$ GHz (Wayne, Davies, and Thrush 1974). Using them, one obtains

$$\nu[(J = N = 5)\text{–}(J = N - 1 = 4)] = 79.158 \pm 0.030 \text{ GHz}$$

and

$$\nu[(J = N = 7)\text{–}(J = N - 1 = 6)] = 104.633 \pm 0.030 \text{ GHz},$$

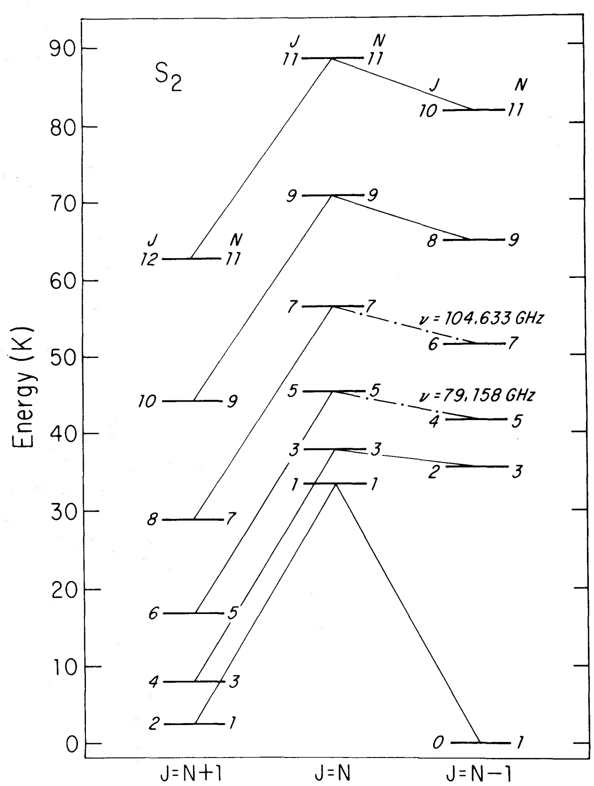

FIG. 1.—The energy-level structure of $^{32}S_2$. Lines connecting different levels indicate magnetic-dipole–allowed transitions. The two lines searched for during this work are indicated by chained lines.

where the uncertainties are conservative limits derived from varying all quantities.[1] The spontaneous emission probabilities for these two transitions are $1.9 \times 10^{-9}\ s^{-1}$ and $4.5 \times 10^{-9}\ s^{-1}$, respectively, a factor of 15–35 weaker than for the $J = 1$–0 lines of carbon monoxide. The transitions $(J = N)$–$(J = N + 1)$ have higher rates; but even for these, $A < 10^{-6}\ s^{-1}$. Such small values indicate that the level populations should be characterized by near-thermal excitation, and in the discussion below we assume that they are indeed thermalized. This simplifies the analysis considerably and, because it tends to raise the upper limits derived from the data, also seems to be a conservative assumption.

When the partition function is calculated for the lowest 40 levels, it is found that the lower states of both the $N = 5$ and $N = 7$ transitions are expected to have a fraction $f = 3.5 \pm 0.4\%$ of the total population for kinetic temperatures between 20 and 60 K. Taking the nominal value $f = 0.035$ and using the assumption that the excitation temperatures in S_2 are much greater than the values of $h\nu/k$ considered here, one obtains the result

$$N(S_2) = 1.5 \times 10^{17} \int I dv \equiv 1.5 \times 10^{17}\, I_{max} \Delta v\ \mathrm{cm}^{-2},$$

where I is the line brightness temperature above the blackbody background (see below), I_{max} its maximum value, and Δv is the line equivalent width expressed in km s^{-1}. Numerical coefficients for the two transitions differ by only 25%, and we have taken the larger of them. To complete the derivation of limits on the ratio $N(S_2)/N(H_2)$, we assume that the equivalent width of S_2 is the same as that of ^{13}CO, from which $N(H_2)$ is inferred.

[1] Line frequencies for the transitions $J = 9$–8 and $J = 11$–10 are 126.932 and 156.374 GHz, respectively, with 40 MHz uncertainty. The $J = 3$–2 line is masked by telluric absorption.

III. OBSERVATIONAL TECHNIQUES

The observations were taken during 1977 March at the 36′ radio telescope on Kitt Peak with the cooled mixer receiver and, at 79.2 GHz, with the Fabry-Perot image rejection filter (FPI). The system temperature was fairly high at this frequency (~1700 K single sideband) because of transmission losses in the FPI (72% transmission, see Wannier *et al.* 1976) and proximity to the low-frequency cutoff of the receiver as it was then configured. Use of the FPI was an unfortunate necessity not only for calibration but also because the $J = 1$–0 transition of HCN lay near the center of the image sideband. The absence of this line through the FPI in the direction of Orion A at a level of 0.1 K showed the image rejection characteristics of this device to be greater than ~20 db, as claimed. At 104.6 GHz the present observations were calibrated against the 3_{13}–2_{12} line of H_2CS, which had earlier been observed through the FPI.

The intensity scale given below is in terms of $I \equiv T_A^*/\eta$ ($\eta = 0.65$, a nominal value), where T_A^* is the antenna temperature corrected for atmospheric and telescope losses (Ulich and Haas 1976) and η accounts for the coupling between source and antenna response pattern. The upper limits presented below are 3 σ deviations in I, obtained by using 1 MHz filters in Sgr B2(OH) and IRC +10216 and 500 kHz filters in the other sources. In all cases we searched over a range of 256 MHz centered on the nominal line frequencies.

IV. OBSERVATIONAL RESULTS

The salient features of the observations can be summarized as follows:

1. Identifiable but previously unobserved features. These include the H54β line which occurs in Sgr B2(OH) (Fig. 2) and Orion A, the 3_{13}–2_{12} line of H_2CS (results for which are given in Table 1), and the 7_{26}–7_{17} line of $(CH_3)_2O$ (dimethylether) which occurs in Sgr B2(OH)

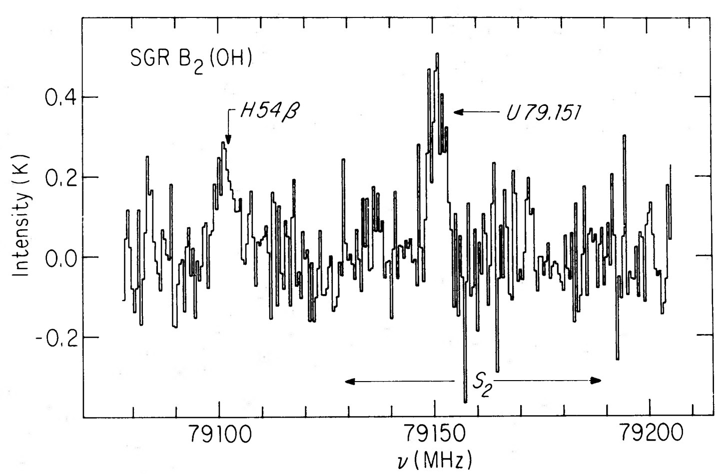

FIG. 2.—The spectrum of Sgr B2(OH) near 79.150 GHz. The range of possible S_2 line frequency is indicated at the bottom of the figure.

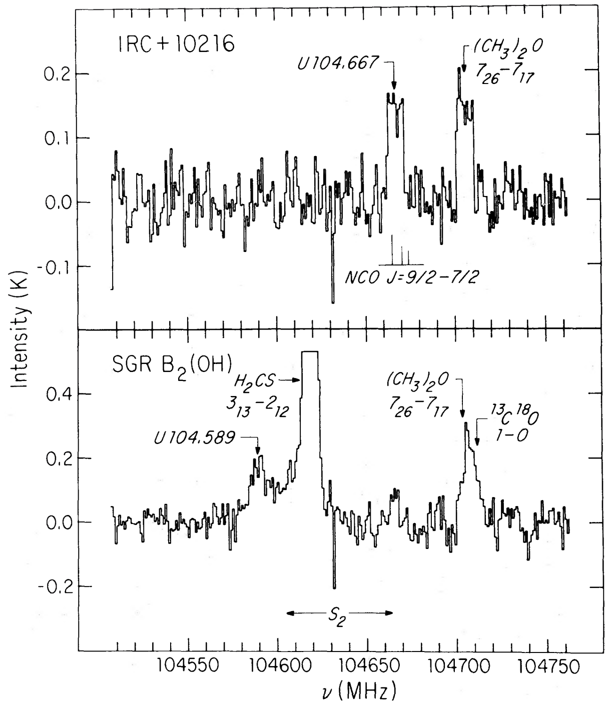

FIG. 3.—Spectra of Sgr B2(OH) and IRC +10216 near 104.650 GHz. The positions of several expected or possible lines are indicated. The range of possible S_2 line frequency is indicated at the bottom of the figure.

(Fig. 3). As no other lines of this last species have been found toward IRC +10216 (Clark 1977), it is likely that the feature at 104.704 GHz in this source is simply another U line, perhaps part (with U104.667) of a spin doublet. Also shown in Figure 3 is the expected position of the $J = 1–0$ line of $^{13}C^{18}O$, which is apparently overlapped by the wing of the lower-frequency dimethyl ether line.

2. Negative results for S_2 outside the galactic center. In all molecular clouds except Sgr B2, no features corresponding to either S_2 line were detected at 3 σ limits in $I_{max} = 0.1$ K. Using the measured ^{12}CO column densities in these sources as given by Liszt (1973) and an abundance $^{12}CO/H_2 = 6 \times 10^{-5}$, we derive upper limits on the ratio $N(S_2)/N(H_2)$ as given in Table 2. Taking the ratio of this quantity to the solar-system abundance $[S/H]_\odot = 1.6 \times 10^{-5}$ (Allen 1973) leads to the figures in the last column of this table. Typically, less than 2%–3% of a solar, gas-phase sulfur abundance can be in the form of S_2, with a limit of 1% in Orion A.

3. Sgr B2(OH) and IRC +10216. A line is clearly present in Sgr B2 at 79.151 GHz, well within the 30 MHz uncertainty in S_2 frequency. A line also appears at 104.667 GHz in IRC +10216 and, perhaps, in Sgr B2. It is unlikely that both of these U lines can be ascribed to S_2. Uncertainties in the spectroscopic constants from which the frequencies were calculated are expected to displace *both* the $N = 5$ and $N = 7$ lines in the same direction from the nominal values of 79.158 and 104.633 GHz. Also, as noted in Figure 3, U104.667 coincides quite closely with the strongest components of the $J = 9/2–7/2$ transition of NCO (S. Saito 1975, private communication by N. Kaifu), which precludes a definite assignment. Although searches for the 7/2–5/2 transition of NCO have proved negative (Turner 1977; Zuckerman and Kuiper 1977), this is merely consistent with the strength of the presently observed U line and the local thermodynamic equilibrium (LTE) line strengths for this molecule. Until the S_2 line frequencies are measured, it will not be possible to remove the ambiguities noted here. If U79.151 is indeed a line arising from S_2, it would indicate that 5%–7% of the sulfur nuclei in this source reside in the sulfur dimer.

V. CONCLUSIONS

Quite generally, the relative abundances of the atomic and dimerized forms of the most abundant heavier elements are not well understood theoretically. Herbst and Klemperer (1973) obtained $O_2/O \ll 1$ for $O/C = 1.2$ and $O_2/O \gtrsim 1$ for $O/C \approx 2$, which more closely resembles the terrestrial case. For N_2 they obtained $N_2/N \ll 1$ always; but Mitchell, Ginsburg, and Kuntz (1976) reached the opposite conclusion on the basis of a more extensive network of reactions. The abundances of C (or C^+) and C_2 are subject to the theoretical difficulties involved in obtaining an equilibrium abundance $CO/H_2 \approx 6 \times 10^{-5}$. All models of interstellar chemistry now available predict that essentially all free carbon should be bound up in

TABLE 1

OBSERVATIONS OF THE $3_{13}–2_{12}$ LINE OF H_2CS

Source	α(1950)	δ(1950)	I (K)	Δv (km s^{-1})	V_{LSR} (km s^{-1})
W3	02ʰ21ᵐ51ˢ0	+61°52′18″	< 0.10	...	...
Ori A	05 32 47.0	−05 24 30	1.42	4.5	+9.0
Ori B	05 39 12.0	−01 55 42	0.50	2.1	+10.5
NGC 2264	06 38 28.0	+09 32 12	< 0.10	...	...
Sgr B2(OH)	17 44 11.0	−28 22 30	1.46	23.5	+62.0
W51	19 21 23.0	+14 24 30	0.58	9.3	+63.0
DR 21(OH)	20 37 14.0	+42 11 59	0.78	4.5	−3.3
IRC +10216	09 45 14.8	+13 30 39	< 0.05	...	...

TABLE 2

UPPER LIMITS ON THE ABUNDANCE OF S_2

Source	$N(S_2)$ (cm^{-2})	$N(H_2)$* (cm^{-2})	$\log [N(S_2)/N(H_2)] - \log [S/H]_{\odot}$
W3	$< 6 \times 10^{16}$	6×10^{22}	-1.08
Ori A	$< 6 \times 10^{16}$	3×10^{23}	-1.90
Ori B	$< 6 \times 10^{16}$	2×10^{23}	-1.73
NGC 2264	$< 5 \times 10^{16}$	1×10^{23}	-1.51
W51	$< 15 \times 10^{16}$	3×10^{23}	-1.51
DR 21(OH)	$< 6 \times 10^{16}$	8×10^{22}	-1.33

* Taken from Liszt 1973.

carbon monoxide in the dense clouds we have searched. This may simply indicate a very low value for the gas-phase abundances of carbon and perhaps other species, owing to depletion.

If we argue by analogy to oxygen, to which sulfur is chemically similar, we might expect S_2 to be the preponderant form of free S nuclei in interstellar clouds. But, as Oppenheimer and Dalgarno (1974) have noted, this chemical similarity is not obviously relevant to molecular clouds, where the lower abundance of sulfur prevents it from competing effectively for reaction partners. Sulfur is essentially a trace element, and the abundances of its compounds are essentially perturbations on the basic cloud chemistry determined by H, C, N, and O. The reaction most obviously suited to producing S_2, SH(S, H)S_2, has not been studied; but the low value for SH/S found by Oppenheimer and Dalgarno indicates a low production rate via this mechanism. In any case, we have shown that no appreciable fraction of S nuclei is bound up in the sulfur dimer.

I am grateful to Dr. D. R. Johnson for identifying the dimethyl ether line detected here and to Dr. N. Kaifu for pointing out the possibility of detecting the 9/2–7/2 transition of NCO. Dr. B. E. Turner provided the negative results of his earlier search for NCO, and Drs. B. Zuckerman and T. Kuiper kindly undertook to search for the 7/2–5/2 line of this species in IRC +10216. Dr. S. Mufson participated in some earlier observations which first showed the existence of the U and dimethyl ether lines in IRC +10216.

Note added in manuscript.—Dr. F. Lovas has kindly pointed out to us that our line U79.151 lies within the uncertainty in the frequency calculated for the 4_{13}–3_{12} *A*-state line of acetaldehyde, 79.15025 ± 0.00090 GHz.

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