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THE RADIO SPECTRA OF S_3 AND S_4

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ABSTRACT

The pure rotational spectra of the polar asymmetric top molecules S_3 and S_4 have recently been observed in the laboratory for the first time. Approximately 150 transitions of S_3 between 10 and 458 GHz and a similar number for S_4 between 6 and 271 GHz have been measured. Many transitions of both molecules are accessible with existing telescopes across the entire radio band. The most interesting astronomical lines to 300 GHz are calculated here from the derived spectroscopic constants to an uncertainty of 1 km s^{-1} or better in equivalent radial velocity, and even at 700 GHz uncertainties are probably worse by only an order of magnitude. Both S_3 and S_4 are plausible candidates for detection in Galactic molecular sources, the atmosphere of the Jovian moon Io, and comets.

Subject headings: ISM: molecules — molecular data — molecular processes — radio lines: ISM — stars: formation

Online material: machine-readable tables

Fourteen molecules containing sulfur have been observed in the radio band in a variety of Galactic sources, including cold dense clouds, hot molecular cores, and circumstellar envelopes around late-type stars (Thaddeus & McCarthy 2001); at least five of these have been found in external galaxies as well. Recently we detected the rotational spectra of S_3 and S_4 in the laboratory for the first time (McCarthy et al. 2004a, 2004b). These are the smallest sulfur clusters with electric dipole transitions in the radio band (the lowest transition of atomic sulfur is in the far-IR, and S_2, like O_2, has only magnetic dipole transitions). Pure sulfur molecules are of astronomical interest because sulfur is one of the most cosmically abundant second-row elements, and S and S_2 have been detected at UV wavelengths in the atmosphere of Jupiter's Galilean moon Io (Spencer et al. 2000) and in comets (Bockelée-Morvan & Crovisier 2001). There is tentative evidence for S_3 and S_4 in the lower atmosphere of Venus (Prinn 1979; Krasnopolsky 1987), but rotational lines there will probably be too broad to be detected. Although the radio astronomical observations of small sulfur molecules are very extensive, sulfur chemistry in space is still not very well understood, largely because the identity of the major reservoir of sulfur in dense molecular clouds has not been established (see Wakelam et al. 2004a). Here we describe the laboratory measurements of S_3 and S_4 at millimeter and submillimeter wavelengths and provide spectroscopic constants and a tabulation of the most relevant lines that will allow deep radio astronomical searches in molecular clouds, circumstellar shells, Io, and comets.

Both S_3 and S_4 are prolate asymmetric top molecules with C_{2v} symmetry and *b*-type rotational transitions. The dominant sulfur isotope on earth (95%) is ^{32}S, and that appears to be true in astronomical sources as well. Owing to the equivalent off-axis ^{32}S atoms in the most abundant isotopic species of both molecules (Fig. 1), half of the rotational levels do not exist, the Bose-Einstein statistics restricting the rotational wave function ($J_{K_aK_c}$) to levels with K_aK_c either *ee* or *oo*. We first detected the rotational spectra of S_3 and S_4 at centimeter wavelengths with a Fourier transform microwave (FTM) spectrometer in a supersonic molecular beam (McCarthy et al. 2004a, 2004b). For both molecules, the strongest lines were obtained by heating powdered sulfur in a stream of neon to yield mainly cyclic S_8 (Meyer 1976), which then was cracked in a DC discharge to produce S_3, S_4, and other small clusters. To better determine centrifugal distortion constants, the millimeter- and submillimeter-wave lines of S_3 and S_4 were subsequently observed in a 1.5 m long free-space glass absorption cell with a spectrometer similar to that described by Gottlieb et al. (2003). Both molecules were produced in this cell under essentially the same conditions: a low-current DC discharge (20 mA) through argon flowing over a sulfur sample that was heated (along with the entire cell) to 70° C. A fairly high flow rate of Ar (9 cm^3 $minute^{-1}$) was required to maintain a stable discharge, and as a result the total pressure was fairly high (45 mtorr). Under these conditions the signal-to-noise ratio of S_3 lines was $\sim$100 at a typical integration time of 10 minutes; lines of S_4 were 5–10 times weaker. Significantly stronger lines were observed when the sample was heated to a slightly higher temperature, but the discharge then became unstable and data could not be reliably obtained.

In all, 152 lines of S_3 with rotational quantum numbers $J \leq 87$ and $K_a \leq 12$ were measured at frequencies up to 458 GHz. The data were analyzed with Watson's *S*-reduced Hamiltonian with the full set of five fourth-order and seven sixth-order centrifugal distortion constants. With 15 spectroscopic constants, the observed lines were generally fitted to within the measurement uncertainties: 2–4 kHz in the centimeter-wave region up to 40 GHz and 20–50 kHz in the millimeter- and submillimeter-wave bands. Similarly for S_4, 147 lines with $J \leq 89$ and $K_a \leq 28$ were measured at frequencies up to 271 GHz. A global fit of the combined centimeter-wave (FTM) and the millimeter- and submillimeter-wave measurements of S_4 is of similar quality to that of S_3 when an additional term to account for small ($\sim$15 kHz) shifts in the line frequencies owing to interchange tunneling is included in the Hamiltonian (see McCarthy et al. 2004b). In the final fit to the S_4 measurements, only five of the possible seven sixth-order centrifugal distortion constants were required to reproduce the measured frequencies. A more complete account of the spectroscopic investigation and the full analysis of both molecules, including some of the isotopic species, will be given elsewhere. The derived spectroscopic constants of S_3 and S_4 are given in Table 1.

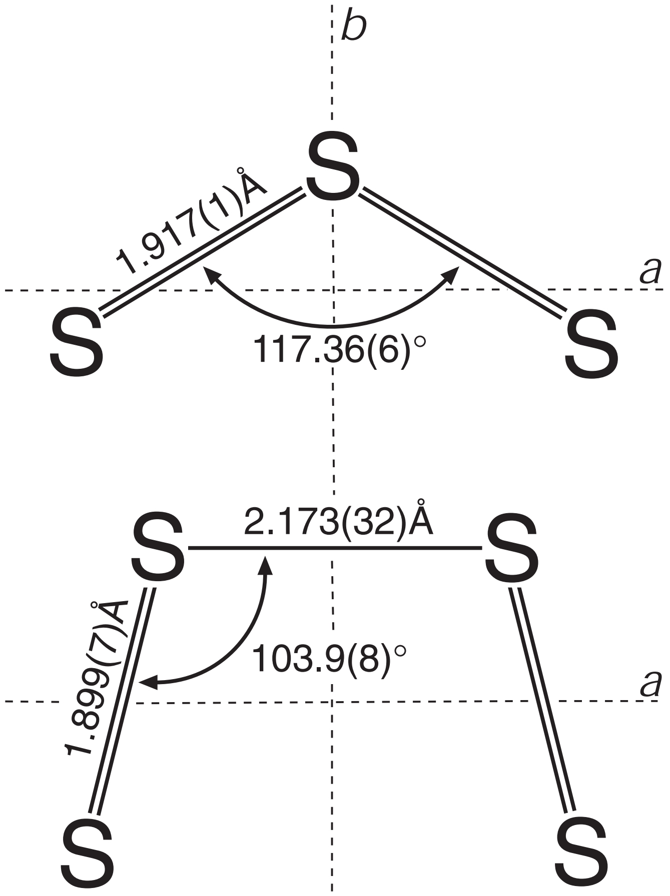

FIG. 1.—Molecular geometries of S_3 and S_4. Both are planar asymmetric top molecules with C_{2v} symmetry and *b*-type rotational transitions. The dipole moments calculated at the CCSD(T)/cc-pVTZ level of theory are 0.51 D for S_3 and 1.15 D for S_4 (estimated uncertainties 10%; J. F. Stanton & H. Gupta 2004, private communication). Bond lengths and angles are from the experimental (r_0) structures determined by isotopic substitution (McCarthy et al. 2004a, 2004b).

Many allowed transitions of S_3 and S_4 are accessible throughout the millimeter- and submillimeter-wave bands, owing to the fairly large moments of inertia and small rotational constants of both molecules. This is illustrated in Figure 2, which shows the calculated line intensities of S_3 and S_4 on the assumption of rotational equilibrium at $T_{\rm rot} = 20$ and 150 K. In the cooler astronomical sources with $T_{\rm rot} \sim 20$ K [such as Sgr B2(OH) and IRC+10216] the strongest lines of S_3 are near 250 GHz in frequency, but in hot molecular cores with $T_{\rm rot} \geq 150$ K (as in the molecular cloud associated with the Orion Nebula) the peak intensity falls in the submillimeter-wave band near 700 GHz. Owing to its higher mass, the lines of S_4 peak about 2.5 times lower in frequency than those of S_3, i.e., near 100 GHz for $T_{\rm rot} = 20$ K and 300 GHz for 150 K. Figure 2 should serve as a useful guide for future astronomical searches for S_3 and S_4.

An extensive list of calculated line frequencies for S_3 and S_4 up to 700 GHz is available in the electronic edition of this paper. Lines between 500 and 600 GHz have been omitted owing to the high atmospheric opacity. To illustrate the types of transitions that might be found in space and the format of the tables, a few of the strongest lines of both molecules in the 3 and 2 mm bands are given in Tables 2 and 3. In the cooler astronomical sources with $T_{\rm rot} \sim 20$ K, the most intense lines in S_3 (Table 2) are predicted to be *Q*-branch ($\Delta J = 0$) and *R*-branch ($\Delta J = 1$) transitions from levels that are close to ground and line strengths (*S*) that are a substantial fraction of the rotational quantum number *J*. In the hot molecular sources with $T_{\rm rot} \sim 150$ K, *R*-branch transitions with fairly large *E*/*k* and large line strengths ($S \sim J$) are predicted to be the most intense. As can be seen in Table 2, *R*-branch progressions with $K'_a = 0$ or 1 occur every few GHz in frequency in S_3. Interspersed with these strong *R*-branch transitions are long *Q*-branch progressions. There are many such *Q*-branch progressions in S_3, but lines in each are spaced well apart in frequency. In S_4, the two or three most intense members of the *R*-branch series with low K'_a are separated by less than 10 MHz and would appear as broad unresolved features in sources like IRC+10216 with line widths greater than 15 km s^{-1}. In addition, there are *R*-branch series in S_4 with fairly low *J* and high K_a that are nearly as intense as those with high *J* and low K_a. To restrict the number of tabulated lines, we adopted the following selection criteria generally for inclusion in the electronic table: $\nu < 700$ GHz, $E_u/k \leq 600$ K, and $S/J' \geq 0.3$. Because these criteria yield no lines for S_4 above 475 GHz, in particular in the last good atmospheric window at 600–700 GHz, somewhat relaxed selection criteria were employed in this band: $E_u/k \leq 1300$ K and $S/J' \geq 0.9$, so some lines of S_4 in this window are included in Table 3.

TABLE 1

Spectroscopic Constants of S_3 and S_4

Constant	S_3	S_4
A	23972.5807(4)	4655.33365(7)
B	2948.54679(7)	2221.53896(5)
C	2622.29112(7)	1502.37880(3)
$10^3 D_J$	0.79967(3)	0.8742(2)
$10^3 D_{JK}$	−20.279(1)	−1.882(1)
D_K	0.50344(1)	0.00304(2)
$10^3 d_1$	−0.163171(7)	−0.3413(1)
$10^6 d_2$	−7.232(4)	−35.34(4)
$10^9 H_J$	0.461(4)	−1.13(4)
$10^9 H_{JK}$	−9.17(9)	9.3(4)
$10^6 H_{KJ}$	−1.59(1)	−0.027(1)
$10^6 H_K$	34.02(8)	0.028(2)
$10^9 h_1$	0.216(1)	−0.48(2)
$10^{12} h_2$	24.2(9)	. . .
$10^{12} h_3$	6.1(2)	. . .
$10^3 \Delta E$	. . .	14.1(2)

NOTES.—Constants (in units of MHz) derived from a numerical fit with Watson's *S*-reduced Hamiltonian. Uncertainties in parentheses are 1 σ in units of the least significant digit.

In the submillimeter-wave band the quoted uncertainties in the calculated frequencies of S_3 are fairly small (<0.2 km s^{-1} near 700 GHz), but the actual uncertainties are likely to be somewhat larger because of the missing higher order centrifugal distortion terms. Line frequencies above 460 GHz were obtained by extrapolation of a truncated Hamiltonian containing all fourth- and sixth-order centrifugal distortion constants, but no eighth-order constants. All sixth-order constants of S_3 (except h_{JK}) are approximately 10 times smaller than those of the structurally similar SO_2 and have the same signs. On the assumption that the same ratio applies to the eighth-order distortion constants of S_3 and SO_2, line frequencies of S_3 near 700 GHz predicted with the truncated Hamiltonian were compared with those calculated with a Hamiltonian that contained seven eighth-order constants that were 10 times smaller than those of SO_2 (Müller et al. 2000). We find that the calculated line frequencies of S_3 near 700 GHz differ by ≤ 5 km s^{-1} in the two cases. We conclude that even at frequencies this high, the S_3 predictions are quite adequate for a deep search.

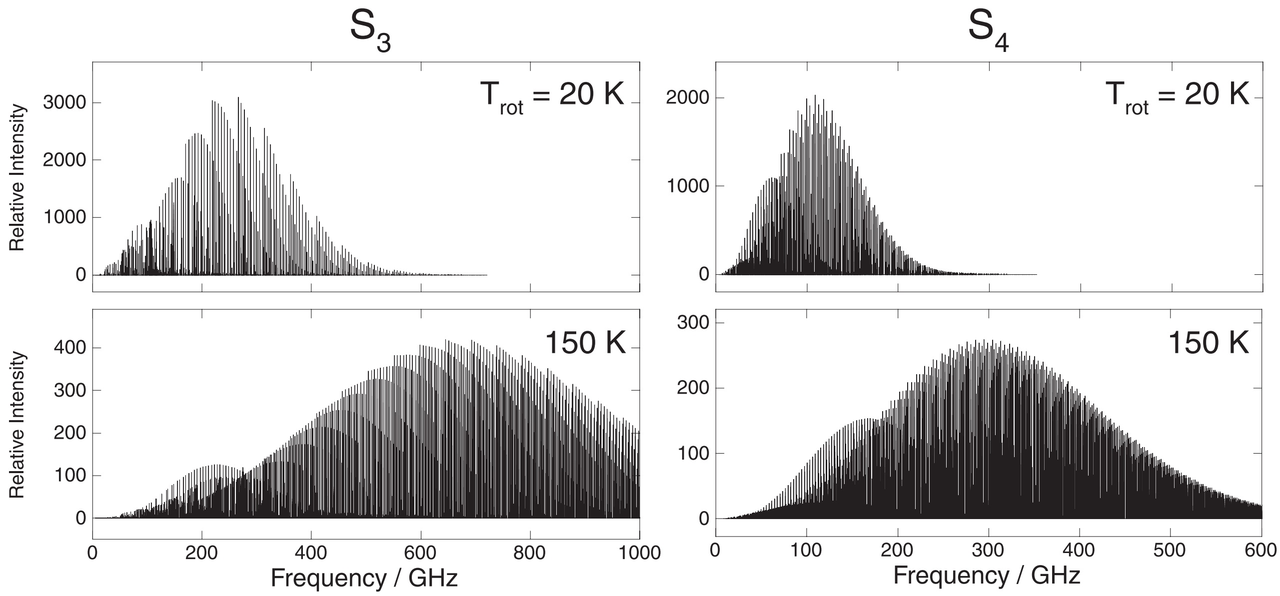

FIG. 2.—Relative intensities of rotational transitions vs. frequency of S_3 and S_4 at 20 and 150 K. The intensities were calculated on the assumption that the populations of all the rotational levels are described by a single temperature, and only the ground vibrational state is populated.

A similar estimate of the actual uncertainties of the S_4 frequencies in the submillimeter-wave band was not possible, because no structurally related molecule has been measured in the laboratory to the required accuracy. Instead, to check the reliability of the submillimeter-wave predictions we compared two different sets of predictions: one set of frequencies was calculated with a Hamiltonian with five fourth-order centrifugal distortion constants derived from the centimeter-wave measurements up to 40 GHz; the second set was calculated with the spectroscopic constants in Table 1. We found that the two sets differed by less than 15 km s^{-1} at frequencies near 475 GHz and less than 50 km s^{-1} at 700 GHz. The contribution of the eighth-order centrifugal distortion terms is apparently fairly small even at frequencies this high, and our S_4 predictions in the submillimeter-wave band are therefore probably adequate for a deep, unambiguous search.

We find no evidence for either S_3 or S_4 in published astronomical surveys of Galactic molecular sources. The sulfur bearing molecules in space most widely studied are CS, SO, and SO_2, so here we compare the upper limits of the column densities of S_3 and S_4 with the known abundances of these molecules in IRC+10216, Sgr B2, Orion, and TMC-1. In sources in which SO_2 is not exceptionally abundant [such as IRC+10216 and Sgr B2(OH)] our upper limits for S_3 are significantly higher

TABLE 2

PREDICTED ROTATIONAL TRANSITION FREQUENCIES OF THIOZONE, S_3

J'	K'_a	K'_c	J''	K''_a	K''_c	Frequency (MHz)	$\Delta\nu$ (MHz)	$c\Delta\nu/\nu$ (km s^{-1})	E_u/k (K)	S
18	0	18	17	1	17	91387.669	0.002	0.007	45.0	13.1
17	1	17	16	0	16	98254.896	0.003	0.008	40.6	12.3
8	3	5	8	2	6	105355.987	0.002	0.005	18.8	4.0
11	3	9	11	2	10	106650.501	0.002	0.004	26.8	5.7
15	3	13	15	2	14	108277.146	0.002	0.004	41.3	7.9
17	3	15	17	2	16	109660.149	0.002	0.005	50.1	9.0
19	3	17	19	2	18	111521.799	0.002	0.005	60.0	10.0
21	3	19	21	2	20	113928.566	0.002	0.006	71.0	11.0
26	0	26	25	1	25	137496.086	0.003	0.006	91.4	21.5
7	3	5	6	2	4	144742.029	0.002	0.005	16.6	3.1
27	1	27	26	0	26	145469.451	0.003	0.006	98.4	22.5
28	0	28	27	1	27	148433.462	0.003	0.005	105.5	23.5
29	1	29	28	0	28	155557.582	0.003	0.006	112.9	24.5
30	0	30	29	1	29	159234.483	0.003	0.005	120.6	25.6
10	3	7	9	2	8	162083.539	0.003	0.005	23.9	3.7
31	1	31	30	0	30	165760.454	0.003	0.005	128.5	26.6
4	4	0	3	3	1	170510.174	0.002	0.004	18.9	3.5

NOTES.—Selected transition frequencies of S_3 in the 3 and 2 mm bands calculated with the spectroscopic constants in Table 1. $\Delta\nu$ is the 1 σ uncertainty in the calculated frequency (see text); $c\Delta\nu/\nu$ is the uncertainty in units of equivalent radial velocity (km s^{-1}); E_u/k is the energy of the upper level of the transition; and S is the asymmetric rotor line strength. Table 2 lists transitions with frequencies $\leq$700 GHz, $E_u/k \leq 600$ K, and $S/J' \geq 0.3$. Transitions between 500 and 600 GHz have not been tabulated owing to high atmospheric opacity. Table 2 is published in its entirety in the electronic edition of the *Astrophysical Journal*. A portion is shown here for guidance regarding its form and content.

TABLE 3

Predicted Rotational Transition Frequencies of Tetrasulfur, S_4

J'	K'_a	K'_c	J''	K''_a	K''_c	Frequency (MHz)	$\Delta\nu$ (MHz)	$c\Delta\nu/\nu$ (km s^{-1})	E_u/k (K)	S
9	9	1	8	8	0	81020.652	0.002	0.007	18.9	8.4
10	10	0	9	9	1	90329.356	0.003	0.009	23.2	9.4
11	10	2	10	9	1	94098.326	0.003	0.008	25.2	9.3
12	11	1	11	10	2	103406.865	0.003	0.010	30.2	10.3
34	0	34	33	1	33	103624.558	0.002	0.006	88.2	32.9
35	1	35	34	0	34	106625.464	0.002	0.006	93.3	33.9
12	12	0	11	11	1	108945.345	0.005	0.013	33.3	11.4
36	0	36	35	1	35	109626.091	0.002	0.006	98.6	34.9
15	14	2	14	13	1	131328.719	0.007	0.015	47.8	13.3
15	15	1	14	14	0	136864.988	0.008	0.018	51.6	14.4
48	0	48	47	1	47	145614.195	0.004	0.009	173.0	46.9
47	2	46	46	1	45	145621.512	0.004	0.008	172.7	43.8
46	2	44	45	3	43	145631.041	0.006	0.013	172.0	40.7
49	1	49	48	0	48	148611.389	0.005	0.009	180.1	47.9
50	0	50	49	1	49	151608.214	0.005	0.010	187.4	48.9
51	1	51	50	0	50	154604.775	0.005	0.010	194.8	49.9
52	0	52	51	1	51	157600.954	0.005	0.010	202.4	50.9
53	1	53	52	0	52	160596.855	0.006	0.010	210.1	51.9
54	0	54	53	1	53	163592.361	0.006	0.011	217.9	52.9
55	1	55	54	0	54	166587.578	0.006	0.011	225.9	53.9
56	0	56	55	1	55	169582.386	0.006	0.011	234.1	54.9

Notes.—Selected transition frequencies of S_4 in the 3 and 2 mm bands calculated with the spectroscopic constants in Table 1. $\Delta\nu$ is the 1 σ uncertainty in the calculated frequency (see text); $c\Delta\nu/\nu = \Delta v$ is the uncertainty in units of equivalent radial velocity (km s^{-1}); E_u/k is the energy of the upper level of the transition; and S is the asymmetric rotor line strength. Table 3 lists transitions with frequencies $\leq$475 GHz, $E_u/k \leq 600$ K, and $S/J' \geq 0.3$; a few lines between 600 and 700 GHz with $E_u/k \leq 1300$ K and $S/J' \geq 0.9$ are also tabulated (see text). Transitions between 500 and 600 GHz have not been tabulated owing to high atmospheric opacity. Table 3 is published in its entirety in the electronic edition of the *Astrophysical Journal*. A portion is shown here for guidance regarding its form and content.

than the column densities of SO_2, in part because of the three-fold smaller dipole moment of S_3 and the five-fold greater rotational partition function. Our limits for S_3 and S_4 in IRC+10216 are comparable to the observed column density of CS, but are considerably higher than that of SO, which is not very abundant in the molecular envelope of this carbon-rich source. Similarly, our limits for S_3 are about 10 times higher than the column densities of SO and SO_2 in Sgr B2, and our limits for S_4 are 2–3 times higher. The earlier surveys of Sgr B2 were centered on the OH maser position (Cummins et al. 1986; Turner 1989), but recently Nummelin et al. (2000) showed that the abundances of SO and SO_2 are extremely high ($\geq 1\times10^{17}$ cm^{-2}) in the dense cores designated Sgr B2(N) and Sgr B2(M). The latter position is displaced by 30″ from Sgr B2(OH), so the earlier surveys with fairly large beamwidths sampled some emission from Sgr B2(M). We have found no evidence of either S_3 or S_4 in the survey of Sgr B2(M) by Nummelin et al. (1998); the Sgr B2(N) core was not considered because the density of unrelated lines there is very high. In Orion the column densities of SO and SO_2 are also high: $\sim1\times10^{17}$ cm^{-2}, so that the upper limit on S_3 is more than a factor of 10 less than the column densities of SO and SO_2 in both the compact ridge and the hot core; our limit for S_3 is much less than the column density of CS in the compact ridge but is comparable to that of CS in the hot core, although Wakelam et al. (2004a) have suggested that much of the CS emission attributed to the hot core is actually from the compact ridge. Our limits for S_4 in the compact ridge and hot core of Orion are about 3 times less than the observed column densities of SO and SO_2, but are greater than that of CS. In TMC-1, S_3 and S_4 are less abundant than SO and CS by at least a factor of 100; lines of SO_2 were not detected in the Nobeyama survey of TMC-1 because SO_2 is not very abundant in this source (Kaifu et al. 2004). We are not aware of any line surveys of the hot core in IRS 16293, a source in which the abundances of SO and SO_2 are comparable to those in Orion (Wakelam et al. 2004b), or of the circumstellar shell of OH231.8+4.2 (Rotten Egg Nebula), an oxygen-rich source with a very high SO_2 abundance (Omont et al. 1993). Upper limits of the column densities of S_3 and S_4 in Table 4 are compared with those of SO, SO_2, and CS in Table 5.

Although there are few published data on pure sulfur molecules in Galactic sources, the radio observations that have been made of molecules with a single sulfur suggest that hot cores and circumstellar envelopes might be good sources in which to detect S_3 and S_4. Dedicated searches in Orion at the frequencies provided by the present work might yield limits on the abundances for S_3 or S_4 that are 5–10 times lower than those obtained from the existing survey data (although the dense thicket of faint lines in this source, not instrumental noise, may be the limiting factor). At present our upper limits for S_3 and S_4 are at most only about 10 times lower than the observed column density of SO_2 in the Orion hot core (Table 4). Owing to the high reactivity of S with OH and O_2, Wakelam et al. (2004a) predicted on the basis of chemical model calculations that pure sulfur molecules are efficiently converted to SO and SO_2 in very short timescales of $\sim10^4$ yr, implying that searches for S_3 and S_4 should be undertaken in young hot cores. In IRC+10216, four diatomic molecules containing two second-row elements (SiS, AlCl, KCl, and NaCl) have been observed; the abundance of SiS is so high that seven rare isotopic species have been detected, including two doubly substituted species (Cernicharo et al. 2000; Mauersberger et al. 2004). Although no molecule containing two sulfur atoms has been observed in Galactic

TABLE 4
Column Density Limits on S_3 and S_4 in Four Sources

Source	S_3 Frequency (MHz)	S_3 T_{mb} (mK)	S_3 N_{limit} (cm^{-2})	S_4 Frequency (MHz)	S_4 T_{mb} (mK)	S_4 N_{limit} (cm^{-2})	T_{rot} (K)	Δv (km s^{-1})
IRC+10216[a]	40,305	23	2(15)	37,562	17	6(14)	20	29
Sgr B2[b]	89,490	128	3(16)	81,021	86	2(15)	20	20
	108,277	107	5(15)	105,376	54	1(15)	20	20
Orion compact ridge[c]	258,834	240	1(16)	238,351	330	4(16)	75	3.5
Orion hot core[d]	243,671	330	1(16)	232,381	440	2(16)	150	9
TMC-1[e]	27,263	50	3(13)	37,562	75	1(13)	10	0.5

Notes.—T_{mb} is the estimated 3 σ upper limit to the peak line intensity corrected for atmospheric absorption and beam efficiency. The upper limit to the column density N_{limit} was derived for an assumed line width Δv and rotational temperature T_{rot}, where the rotational partition function Z_{rot} is $6.20(T_{rot})^{1.5}$ for S_3 and $21.42(T_{rot})^{1.5}$ for S_4. For N_{limit}, $y(x)$ means $10^x y$. Each survey was examined at five or six frequencies; however, only one or two lines are indicated here.
[a] Nobeyama 45 m telescope (Kawaguchi et al. 1995).
[b] Kitt Peak 11 m telescope (Turner 1989).
[c] Owens Valley 10 m telescope (Blake et al. 1986).
[d] Owens Valley 10 m telescope (Sutton et al. 1985).
[e] Nobeyama 45 m telescope (Kaifu et al. 2004).

sources, S_3 and S_4 are plausible candidates for detection in IRC+10216, because the cosmic abundance of S is comparable to that of Si (Snow & Witt 1996) and the abundances of the doubly substituted species of SiS are $\sim 3\times10^{-3}$ lower than that of the main isotopic species.

The tenuous time-varying atmosphere of the Jovian moon Io is known to contain S, S_2, SO, and SO_2 (Feaga et al. 2002 and references therein), and it has been proposed on the basis of IR reflectance measurements with the *Hubble Space Telescope* (*HST*) that deposits on the surface of Io near the spectacular volcano Pele may be composed of S_3 and S_4 (Spencer et al. 1997). Millimeter-wave lines of SO and SO_2 have been observed in the atmosphere of Io with the IRAM 30 m telescope (Lellouch et al. 1996), but it could not be determined whether the atmosphere is spatially homogenous owing to insufficient angular resolution (a 12″ telescope beam at 220 GHz compared with the $\sim$1″ diameter of Io). Observations with the *HST* at much higher angular resolution (0″.35) established that the column density of S_2 is significantly higher in the plume of Pele (1.0×10^{16} cm^{-2}) than elsewhere in the atmosphere of Io (Spencer et al. 2000). The Pele plume extends about $\sim$350 km above Io, or only 0″.1 from Earth. Owing to the high column density of S_2, it is worth asking whether it would be possible to observe with existing radio-, millimeter-, and submillimeter-wave interferometers other sulfur species, such as S_3, in the Pele plume. We estimated the intensity of lines of S_3 in the Pele plume on the following assumptions: (1) the abundance of S_3 is comparable to that of S_2, (2) $T_{rot} = 300$ K (McGrath et al. 2000), (3) the line widths (0.6 km s^{-1}) are comparable to those of the millimeter-wave lines of SO and SO_2 (Lellouch et al. 1996), and (4) the source fills the telescope beam. Under those assumptions, the calculated brightness temperature of S_3 lines near 350 GHz is $\sim$2 K. It might therefore be possible to observe S_3 in the Pele plume with millimeter- and submillimeter-wave interferometers, provided the actual column density of S_3 is not much less than that of S_2. On the basis of a photochemical model of a volcanically driven atmosphere of Io, Moses et al. (2002) predicted that the abundances of S_3 and S_4 may be quite low; however, the rates of some of the crucial reactions in their model, such as the three-body reaction $S_2 + S_2 + M \rightarrow S_4 + M$, are uncertain. Detection of S_3 and S_4 would provide important new information on the composition of the atmosphere of Io.

Atomic sulfur and eight sulfur bearing molecules, including S_2, SO, SO_2, and CS, have been observed in comets (Bockelée-Morvan & Crovisier 2001). S_2 has been observed in several comets with satellites and with the Kitt Peak 4 m telescope in the UV near 300 nm, but interpretation of the fluorescence spectrum requires detailed model-specific calculations (Kim et al. 2003). Now that rotational spectra have been measured in the radio band it will be feasible to search for S_3 and S_4 in comets. Quantitative comparisons between molecular abundances in hot molecular cores and comets imply that a similar gas phase

TABLE 5
Column Densities of Five Sulfur Molecules in Units of 10^{14} cm^{-2}

Source	S_3	S_4	SO	SO_2	CS
IRC+10216	$\leq$20	$\leq$6	<0.2[a]	...	40[a]
Sgr B2	$\leq$100	$\leq$20	11[b]	8[b]	...
Orion compact ridge	$\leq$100	$\leq$400	100[c]	2000[c]	80[c]
Orion hot core	$\leq$100	$\leq$200	2000[c]	900[c]	50[c]
TMC-1	$\leq$0.3	$\leq$0.1	50[d]	<10[d]	100[d]
IRAS 16293 hot core	...	...	1000[e]	400[e]	...

[a] Cernicharo et al. (1987).
[b] Turner (1991).
[c] Sutton et al. (1995).
[d] Ohishi et al. (1992).
[e] Wakelam et al. (2004b).

chemistry may occur in hot cores and comets (Bockelée-Morvan et al. 2000). Owing to uncertainties in the interstellar chemistry of sulfur bearing molecules and to the possible link between comets and the interstellar gas, detection of S_3 and S_4 in comets might yield useful information on the early solar nebula.

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REFERENCES

Blake, G. A., Sutton, E. C., Masson, C. R., & Phillips, T. G. 1986, ApJS, 60, 357

Bockelée-Morvan, D., & Crovisier, J. 2001, in The Promise of the *Herschel Space Observatory*, ed. G. L. Pilbratt, J. Cernicharo, A. M. Heras, T. Prusti, & R. Harris (ESA SP-460; Noordwijk: ESA), 279

Bockelée-Morvan, D., et al. 2000, A&A, 353, 1101

Cernicharo, J., Guélin, M., Hein, H., & Kahane, C. 1987, A&A, 181, L9

Cernicharo, J., Guélin, M., & Kahane, C. 2000, A&AS, 142, 181

Cummins, S. E., Linke, R. A., & Thaddeus, P. 1986, ApJS, 60, 819

Feaga, L. M., McGrath, M. A., & Feldman, P. D. 2002, ApJ, 570, 439

Gottlieb, C. A., Myers, P. C., & Thaddeus, P. 2003, ApJ, 588, 655

Kaifu, N., et al. 2004, PASJ, 56, 69

Kawaguchi, K., Kasai, Y., Ishikawa, S., & Kaifu, N. 1995, PASJ, 47, 853

Kim, S. J., A'Hearn, M. F., Wellnitz, D. D., Meier, R., & Lee, Y. S. 2003, Icarus, 166, 157

Krasnopolsky, V. A. 1987, Adv. Space Res., 7, 25

Lellouch, E., Strobel, D. F., Belton, M. J. S., Summers, M. E., Paubert, G., & Moreno, R. 1996, ApJ, 459, L107

Mauersberger, R., Ott, U., Henkel, C., Cernicharo, J., & Gallino, R. 2004, A&A, 426, 219

McCarthy, M. C., Thorwirth, S., Gottlieb, C. A., & Thaddeus, P. 2004a, J. Am. Chem. Soc., 126, 4096

———. 2004b, J. Chem. Phys., 121, 632

McGrath, M. A., Belton, M. J. S., Spencer, J. R., & Sartoretti, P. 2000, Icarus, 146, 476

Meyer, B. 1976, Chem. Rev., 76, 367

Moses, J. I., Zolotov, M. Y., & Fegley, B. Jr. 2002, Icarus, 156, 76

Müller, H. S. P., Farhoomand, J., Cohen, E. A., Brupbacher-Gatehouse, B., Schäfer, M., Bauder, A., & Winnewisser, G. 2000, J. Mol. Spectrosc., 201, 1

Nummelin, A., Bergman, P., Hjalmarson, Å., Friberg, P., Irvine, W. M., Millar, T. J., Ohishi, M., & Saito, S. 1998, ApJS, 117, 427

———. 2000, ApJS, 128, 213

Ohishi, M., Irvine, W. M., & Kaifu, N. 1992, in IAU Symp. 150, Astrochemistry of Cosmic Phenomena, ed. P. D. Singh (Dordrecht: Kluwer), 171

Omont, A., Lucas, R., Morris, M., & Guilloteau, S. 1993, A&A, 267, 490

Prinn, R. G. 1979, Geophys. Res. Lett., 6, 807

Snow, T. P., & Witt, A. N. 1996, ApJ, 468, L65

Spencer, J. R., Jessup, K. L., McGrath, M. A., Ballester, G. E., & Yelle, R. 2000, Science, 288, 1208

Spencer, J. R., McEwen, A. S., McGrath, M. A., Sartoretti, P., Nash, D. B., Noll, K. S., & Gilmore, D. 1997, Icarus, 127, 221

Sutton, E. C., Blake, G. A., Masson, C. R., & Phillips, T. G. 1985, ApJS, 58, 341

Sutton, E. C., Peng, R., Danchi, W. C., Jaminet, P. A., Sandell, G., & Russell, A. P. G. 1995, ApJS, 97, 455

Thaddeus, P., & McCarthy, M. C. 2001, Spectrochim. Acta A, 57, 757

Turner, B. E. 1989, ApJS, 70, 539

———. 1991, ApJS, 76, 617

Wakelam, V., Caselli, P., Ceccarelli, C., Herbst, E., & Castets, A. 2004a, A&A, 422, 159

Wakelam, V., Castets, A., Ceccarelli, C., Lefloch, B., Caux, E., & Pagani, L. 2004b, A&A, 413, 609