ROTATIONAL SPECTRA OF SULFUR-CARBON CHAINS.
I. THE RADICALS C_4S, C_5S, C_6S, C_7S, C_8S, AND C_9S

V. D. GORDON, M. C. MCCARTHY, A. J. APPONI, AND P. THADDEUS

Harvard-Smithsonian Center for Astrophysics, 60 Garden Street, Cambridge, MA 02138; and Division of Engineering and Applied Sciences,
Harvard University, 29 Oxford Street, Cambridge, MA 02138

ABSTRACT

The linear carbon-chain radicals C_6S, C_7S, C_8S, and C_9S have been detected in a supersonic molecular beam by Fourier transform microwave spectroscopy, and measurements of the previously studied chains C_4S and C_5S have been extended using the same technique. The electronic ground state, as predicted, is found to be a triplet for those with an even number of carbon atoms and a singlet for those with an odd number. The microwave spectra of all six chains have been fully characterized, and spectroscopic constants, including fine-structure constants where applicable, have been determined to high precision. Transitions from the $J = N$ and $J = N - 1$ fine-structure levels of C_4S have been detected for the first time, and the lengths of the individual bonds of C_5S have been determined from its isotopic species. The carbon-sulfur chains here are all highly polar, calculated to possess dipole moments in the 4–7 D range; all are plausible candidates for astronomical detection. The spectroscopic constants determined from this work allow transitions up to 40 GHz to be calculated with an uncertainty of less than 1 km s^{-1} for each chain.

Subject headings: ISM: molecules — line: identification — molecular data — molecular processes — radio lines: ISM

1. INTRODUCTION

Many carbon-chain molecules, including several terminated with a sulfur atom, have been detected in interstellar clouds and circumstellar envelopes of late-type stars. The carriers of strong unidentified astronomical lines (Suzuki et al. 1984; Kaifu et al. 1987) were shown to be the radicals C_2S (Saito et al. 1987) and C_3S (Yamamoto et al. 1987) on the basis of laboratory rotational spectroscopy. Subsequent observations show that C_2S and C_3S are surprisingly abundant in TMC-1 (Hirahara et al. 1992); C_2S is only 2 times less abundant than CS, while C_3S is only 4 times less abundant than C_2S. Although oxygen is cosmically more abundant than sulfur, C_2S and C_3S are much more abundant in TMC-1 than the isovalent chains C_2O (Ohishi et al. 1991) and C_3O (Brown et al. 1985). C_2S and C_3S have also been observed in the circumstellar shell of the evolved carbon star IRC +10216 (Cernicharo et al. 1987), and C_5S has been tentatively identified there as well (Bell, Avery, & Feldman 1993).

The abundance of sulfur-containing chains in a cold, dense source such as TMC-1 has been explained on the assumption that S^+ plays an important role in the interstellar synthesis of C_nS chains (Suzuki et al. 1988; Smith et al. 1988; Millar & Herbst 1990). Because the reaction of S^+ with H_2 is endothermic while O^+ reacts exothermically with H_2 (Oppenheimer & Dalgarno 1974; Prasad & Huntress 1982), the sulfur cation is expected to be more abundant than that of oxygen in cold, dense interstellar clouds. The gas-phase model of Smith et al. (1988), for example, invokes reactions between S^+ and neutral hydrocarbons to synthesize C_2S and C_3S; by extension, the same mechanism is thought to form even longer chains. The same authors propose similar synthetic pathways to form closely related chains such as HC_3S and H_2C_3S.

Here we present the first laboratory detections of four new carbon-sulfur chains, C_7S and C_9S, with singlet ($^1\Sigma$) electronic ground states, and C_6S and C_8S, with triplet ($^3\Sigma$)

states; all were detected by Fourier transform microwave (FTM) spectroscopy in a supersonic molecular beam. We also have been able to refine and extend the rotational spectroscopy of C_4S (Hirahara, Ohshima, & Endo 1993) and C_5S (Kasai et al. 1993). Rotational transitions from two high-lying fine-structure levels of C_4S have been measured for the first time, and the rotational spectra of all the singly substituted rare isotopic species of C_5S have been observed in natural abundance, allowing a precise determination of all the individual bond lengths. Laboratory detection of the carbon-sulfur chains HC_nS ($n = 5$–8) and H_2C_nS ($n = 4$–7) will be described elsewhere.

2. EXPERIMENT

Searches for the rotational transitions of the four longer chains here were based on geometries obtained from density functional theory (Lee 1997). Rotational constants B were calculated from the ab initio bonds and then scaled by the ratio of the experimental B value to the calculated B value for either C_4S or C_5S, depending on whether the longer chain had a singlet or triplet electronic ground state. Rotational transitions predicted in this way turned out to be accurate to better than 1%.

The same FTM spectrometer recently used to detect the rotational spectra of a number of carbon chains and other reactive molecules (McCarthy et al. 1999) was used in the present investigation. This instrument was designed specifically to study rotationally cold reactive molecules in a supersonic molecular beam; recent upgrades have improved its sensitivity and extended its operating range to 43 GHz.

The strongest lines of the two known chains C_4S and C_5S were observed using a low-current discharge at 1300–1500 V through a precursor gas mixture of 0.5% diacetylene (HCCCCH) and 0.3% carbon disulfide (CS_2), diluted in Ne or Ar, at a nozzle backing pressure of 2.5 ktorr. This mixture very efficiently produces carbon-sulfur chains;
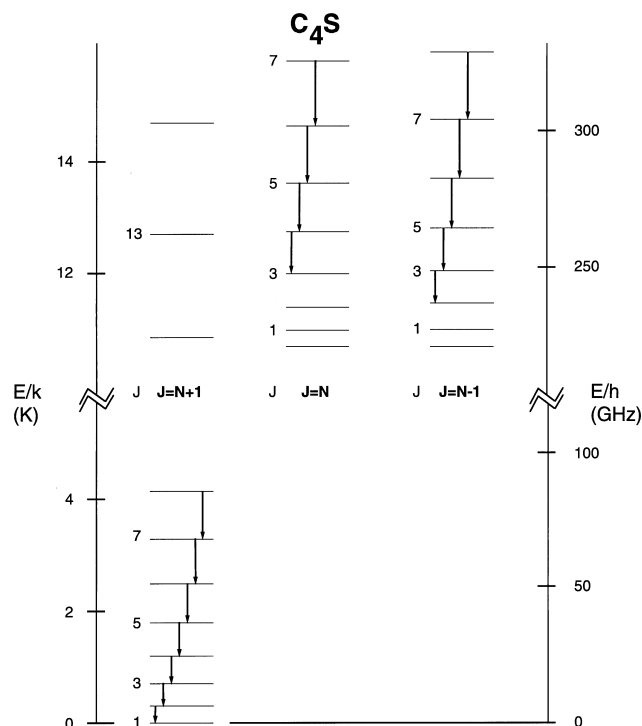
FIG. 1.—Energy level diagram of triplet C_4S with arrows indicating measured transitions. C_6S and C_8S have similar energy-level patterns, but since they have larger λ-values than C_4S, the $J = N$ and $J = N - 1$ ladders are displaced higher in energy relative to the $J = N + 1$ ladder.

under these conditions, for example, the strongest lines of C_4S were observed with a signal-to-noise ratio of more than 100 in 1 minute of integration. The same experimental conditions were used in searches for longer such chains; once found, the production of each molecule was then optimized individually. The best conditions for the longer chains are

TABLE 1

ROTATIONAL TRANSITIONS OF SINGLET C_7S AND $C_7^{34}S$

	C_7S		$C_7^{34}S$	
$J \to J'$	Frequency (MHz)	$O - C$ (kHz)	Frequency (MHz)	$O - C$ (kHz)
$7 \to 6$	5801.990	0	...	...
$8 \to 7$	6630.844	−1	...	...
$9 \to 8$	7459.700	1	7281.746	1
$10 \to 9$	8288.554	1	8090.828	1
$11 \to 10$	9117.405	−1	8899.907	−1
$12 \to 11$	9946.258	−1	9708.987	−1
$13 \to 12$	10775.110	−1	10518.068	0
$14 \to 13$	11603.965	2	11327.148	1
$15 \to 14$	12432.813	−1	12136.226	0
$16 \to 15$	13261.664	0	12945.305	1
$17 \to 16$	14090.515	2	13754.381	0
$18 \to 17$	14919.362	0	14563.455	−2
$19 \to 18$	15748.210	0	...	...
$20 \to 19$	16577.054	−3	...	...
$21 \to 20$	17405.903	1	16990.682	1
$22 \to 21$	18234.748	1	...	...
$23 \to 22$	19063.591	0	...	...
$24 \to 23$	19892.434	0	...	...

NOTE.—Estimated measurement uncertainty: 2 kHz. Observed minus calculated derived from best-fit constants in Table 3.

TABLE 2

ROTATIONAL TRANSITIONS OF SINGLET C_9S

$J \to J'$	Frequency (MHz)	$O - C$ (kHz)
$19 \to 18$	8463.351	2
$20 \to 19$	8908.788	1
$21 \to 20$	9354.224	−1
$22 \to 21$	9799.662	0
$23 \to 22$	10245.100	1
$24 \to 23$	10690.536	0
$25 \to 24$	11135.972	−1
$26 \to 25$	11581.410	1
$27 \to 26$	12026.845	0
$28 \to 27$	12472.279	−2
$30 \to 29$	13363.152	0
$31 \to 30$	13808.586	−1
$32 \to 31$	14254.021	0
$33 \to 32$	14699.456	1
$34 \to 33$	15144.889	0

NOTE.—Estimated measurement uncertainty: 2 kHz. Observed minus calculated frequencies derived from best-fit constants in Table 3.

very similar to those that optimize C_4S and C_5S, except with (1) slightly lower carbon disulfide concentration (0.2%) and (2) slightly higher discharge voltage, successively increasing by about 100 V for each additional carbon atom beyond C_5S. The singly substituted ^{34}S and ^{13}C isotopic species of C_5S were observed in natural abundance, as were the ^{34}S species of C_6S and C_7S.

Under the usual molecular beam expansion conditions, using Ne or Ar as the buffer gas, rotational transitions from only one of the three fine-structure levels of C_6S were observed. The rotational temperature of molecules in our supersonic beam is generally quite low, in the vicinity of 3 K, and there is evidence that the excitation of the fine-structure levels of open-shell molecules like those here is characterized by an excitation temperature that is comparably low. Figure 1 shows an energy level diagram of the lower rotational levels of C_4S; for C_6S and C_8S, the level diagram is similar except that λ is somewhat larger, and consequently the energy separations between fine-structure levels are even greater.

Lines of C_4S are strong enough in our spectrometer that rotational transitions from all three fine-structure levels can be observed in an Ar beam, even though lines from the $J = N$ and $J = N - 1$ levels are more than 85 times weaker than those from the $J = N + 1$ level. Each $^3\Sigma$ chain here is well described by Hund's case a. Because the spin-spin constant λ is positive and much larger than both B and the spin-rotation constant γ, at low J the $J = N + 1$ fine-structure levels are more than 10 K lower in energy than the $J = N$ and $J = N - 1$ levels, both of which have comparable energies for low N (Townes & Schawlow 1955). Consequently, the $J = N + 1$ level is significantly more populated in our cold beam than the other two levels.

Transitions within the two higher lying fine-structure levels of C_4S were also detected using He as the buffer gas. Figure 2 shows rotational transitions from the $J = N + 1$ and $J = N$ levels of C_4S measured first with Ne and then with He. With Ne, the $J = N + 1$ line is about 90 times stronger than that of $J = N$; with He, the intensity ratio
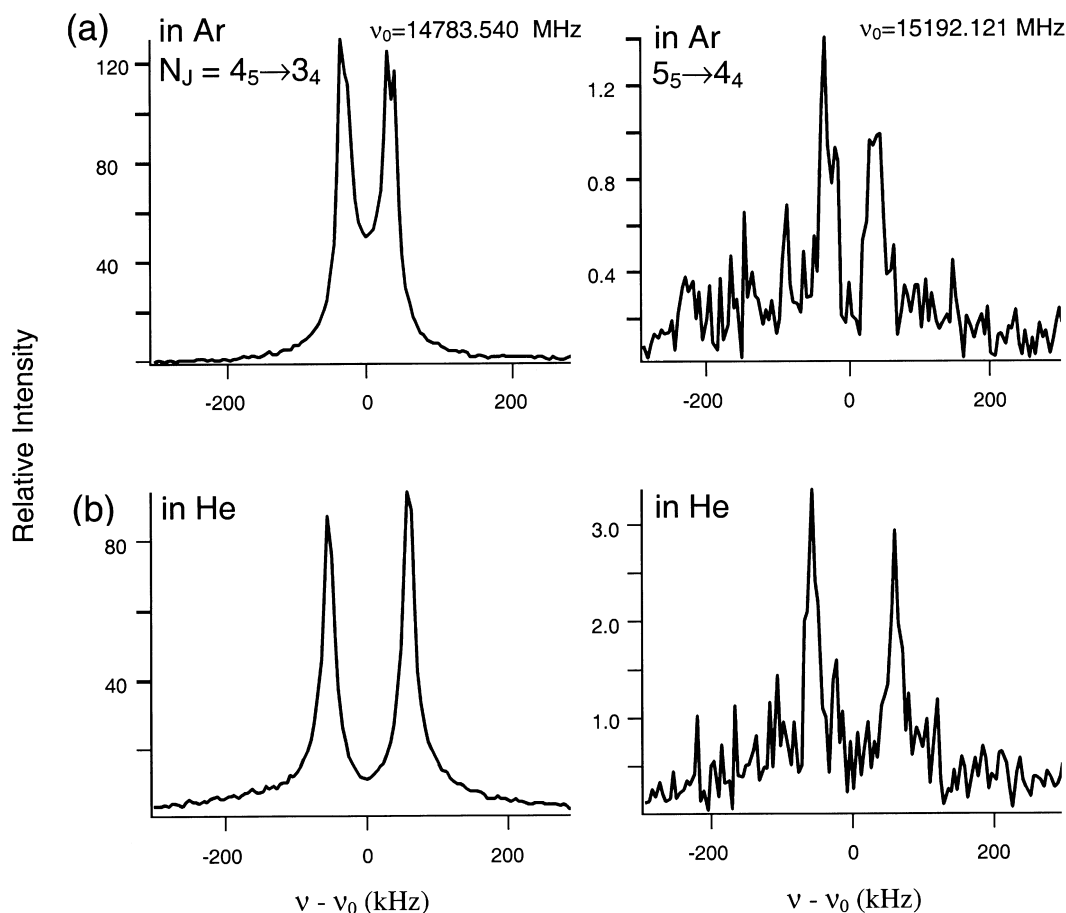
Fig. 2.—C_4S transitions from the $J = N + 1$ and the $J = N$ fine-structure levels. (a) Lines measured with Ar as the carrier gas. The $J = N$ fine-structure level lies 10.8 K above the $N_J = 4_5$ level. (b) Lines measured with He as the carrier gas. Note the increase in line strength for the $J = N$ transition relative to the $J = N + 1$ transition. Larger Doppler doubling indicates that the translational velocity along the cavity axis of the He-carried beam is higher than that of the Ar-carried beam.

drops by almost a factor of 3, to about 30:1. This $J = N + 1$ level lies about 11 K lower than the $J = N$ level, so if the level populations are described by a Boltzmann distribution, C_4S in the Ne expansion has an excitation temperature between the fine-structure levels of 2.1 ± 0.4 K; in the He expansion, the same chain has an excitation temperature of 3.4 ± 0.5 K. The $J = N$ and $J = N - 1$ transitions of C_6S were first detected in the He expansion;

TABLE 3

ROTATIONAL AND CENTRIFUGAL DISTORTION CONSTANTS OF SINGLET C_7S, $C_7^{34}S$, AND C_9S (IN MHz)

	C_7S		$C_7^{34}S$		C_9S	
CONSTANT	Measured	Expected	Measured	Expected	Measured	Expected
B..........	414.42804(4)	415.167	404.54173(5)	405.241	222.72006(3)	223.382
10^6D......	2.03(5)	...	1.93(9)	...	0.48(2)	...

NOTE.—Statistical 1σ uncertainties, in units of the last significant digit, are given in parentheses. Expected B values are scaled from density functional calculations (Lee 1997).

TABLE 4

ROTATIONAL TRANSITIONS OF THE SINGLY SUBSTITUTED ISOTOPIC SPECIES OF SINGLET C_5S (IN MHz)

$J \to J'$	C_5S	$C_5^{34}S$	$CCCC^{13}CS$	$CCC^{13}CCS$	$CC^{13}CCCS$	$C^{13}CCCCS$	$^{13}CCCCCS$
$5 \to 4$.......	...	...	9205.739	9226.351	9193.603	9105.729	8968.501
$6 \to 5$.......	11072.428	10796.581	11046.881	11071.618	11032.321	10926.869	10762.197
$7 \to 6$.......	12917.826	12596.007	12888.024	12916.884	12871.038	...	12555.893
$8 \to 7$.......	14763.227	14395.431	14729.163	14762.148	14709.750	14569.149	14349.587
$9 \to 8$.......	16608.621	16194.852	16570.301	...	...	16390.281	16143.274
$10 \to 9$......	18454.012	17994.268	...	...	...	...	...

NOTE.—Estimated measurement uncertainty: 2 kHz. Observed minus calculated frequencies are 0–2 kHz; the best-fit constants are given in Table 5.

TABLE 5

ROTATIONAL AND CENTRIFUGAL DISTORTION CONSTANTS OF SINGLET C_5S ISOTOPIC SPECIES (IN MHz)

Constant	C_5S	$C_5^{34}S$	$CCCC^{13}CS$	$CCC^{13}CCS$	$CC^{13}CCCS$	$C^{13}CCCCS$	$^{13}CCCCCS$
B..........	922.7033(2)	899.7161(2)	920.5745(2)	922.6356(3)	919.3610(3)	910.5736(2)	896.8508(2)
$10^6 D$......	13(1)	13(1)	14(2)	11(3)	12(3)	15(2)	13(2)

NOTE.—Statistical 1 σ uncertainties, in units of the last significant digit, are given in parentheses.

the relative intensities of the $J = N + 1$ and $J = N$ lines indicate that C_6S has an excitation temperature of 8.1 ± 1.0 K. A search for lines of the $J = N$ component of C_8S, with He as the buffer gas, was unsuccessful. The use of He in a supersonic expansion like ours is evidently an effective technique for heating molecules as a way to study high-lying energy levels that might result from fine-structure splitting or from other interactions such as spin-orbit splitting.

3. RESULTS AND ANALYSIS

3.1. C_7S and C_9S

A total of 18 rotational transitions of C_7S, 11 of $C_7^{34}S$ (Table 1), and 15 of C_9S (Table 2) have been measured between 5 and 20 GHz to an uncertainty of 2 kHz or less. For each molecule, the Hamiltonian for a closed-shell linear molecule, $v = 2BJ - 4DJ^3$, was least-squares fitted to

TABLE 6

ROTATIONAL TRANSITIONS OF TRIPLET C_4S

	$J = N + 1$		$J = N$		$J = N - 1$	
$N \rightarrow N'$	Frequency (MHz)	$O - C$ (kHz)	Frequency (MHz)	$O - C$ (kHz)	Frequency (MHz)	$O - C$ (kHz)
$1 \rightarrow 0$......	5912.177	4	...	...	...	...
$2 \rightarrow 1$......	8868.708	1	...	...	...	...
$3 \rightarrow 2$......	11825.770	-3	...	...	...	...
$4 \rightarrow 3$......	14783.540	0	12153.703	0	...	...
$5 \rightarrow 4$......	17742.169	1	15192.121	1	12481.436	4
$6 \rightarrow 5$......	20701.809	0	18230.531	0	15600.446	-3
$7 \rightarrow 6$......	23662.606	1	21268.935	-1	18718.594	0
$8 \rightarrow 7$......	...	...	...	...	21835.709	-3
$9 \rightarrow 8$......	...	...	...	...	24951.661	2

NOTE.—Estimated measurement uncertainty: 5 kHz. Observed minus calculated derived from best-fit constants in Table 9.

TABLE 7

ROTATIONAL TRANSITIONS OF TRIPLET C_6S AND $C_6^{34}S$

	C_6S						$C_6^{34}S$	
	$J = N + 1$		$J = N$		$J = N - 1$		$J = N + 1$	
$N \rightarrow N'$	Frequency (MHz)	$O - C$ (kHz)	Frequency (MHz)	$O - C$ (kHz)	Frequency (MHz)	$O - C$ (kHz)	Frequency (MHz)	$O - C$ (kHz)
$4 \rightarrow 3$	5927.072	0	...	...	...	...	...	...
$5 \rightarrow 4$	7112.500	-1	...	...	...	...	...	...
$6 \rightarrow 5$	8297.940	2	...	...	...	...	...	...
$7 \rightarrow 6$	9483.384	-1	...	...	...	...	9252.797	2
$8 \rightarrow 7$	10668.840	-2	9554.079	0	...	...	10409.425	0
$9 \rightarrow 8$	11854.313	3	10748.337	1	9624.485	0	11566.065	-1
$10 \rightarrow 9$	13039.792	-1	11942.593	0	10827.507	0	12722.719	0
$11 \rightarrow 10$	14225.288	-1	13136.847	-1	12030.515	0	13879.385	0
$12 \rightarrow 11$	15410.802	0	14331.102	0	13233.507	0	15036.066	1
$13 \rightarrow 12$	16596.329	-2	...	...	14436.484	1	...	...
$14 \rightarrow 13$	17781.879	1	...	...	...	...	...	...
$15 \rightarrow 14$	18967.445	0	...	...	...	...	...	...
$16 \rightarrow 15$	20153.032	-1	...	...	...	...	...	...
$17 \rightarrow 16$	21338.641	-1	...	...	...	...	...	...
$18 \rightarrow 17$	22524.274	-1	...	...	...	...	...	...
$19 \rightarrow 18$	23709.932	1	...	...	...	...	...	...
$20 \rightarrow 19$	24895.615	2	...	...	...	...	...	...

NOTE.—Estimated measurement uncertainty: 5 kHz. Observed minus calculated derived from best-fit constants in Table 9.
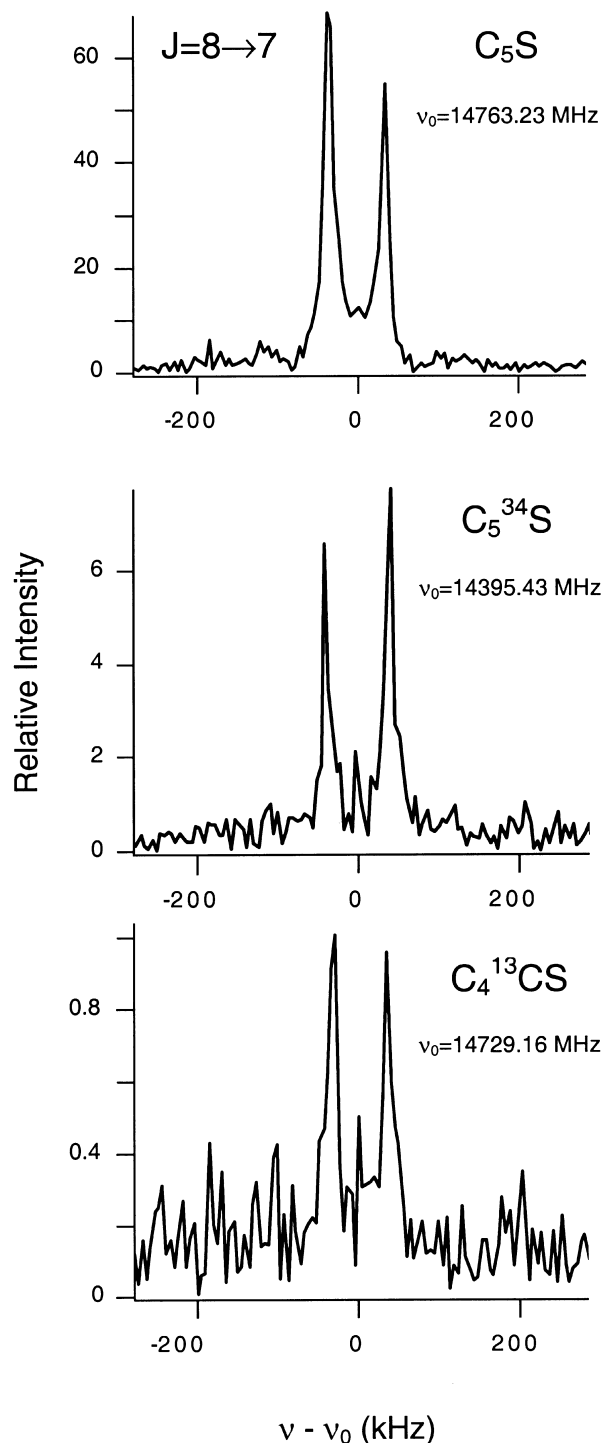
FIG. 3.—The $J = 8 \rightarrow 7$ transitions of C_5S, $C_5^{34}S$, and $CCCC^{13}CS$, observed in natural abundance. The spectra shown were obtained with 8 s of integration for C_5S, 25 s for $C_5^{34}S$, and 3 minutes for $CCCC^{13}CS$. The double-peaked line shape results from the Doppler splitting of the fast-moving supersonic molecular beam relative to the two traveling waves that compose the confocal mode of the Fabry-Perot cavity.

TABLE 8

ROTATIONAL TRANSITIONS OF
TRIPLET C_8S

	$J = N + 1$	
$N \rightarrow N'$	Frequency (MHz)	$O - C$ (kHz)
$10 \rightarrow 9$	6532.462	1
$11 \rightarrow 10$	7126.323	2
$12 \rightarrow 11$	7720.180	−1
$13 \rightarrow 12$	8314.040	0
$14 \rightarrow 13$	8907.898	−2
$15 \rightarrow 14$	9501.760	0
$16 \rightarrow 15$	10095.620	1
$17 \rightarrow 16$	10689.478	−1
$18 \rightarrow 17$	11283.338	0
$19 \rightarrow 18$	11877.198	1
$20 \rightarrow 19$	12471.056	0
$21 \rightarrow 20$	13064.915	0
$22 \rightarrow 21$	13658.774	0
$23 \rightarrow 22$	14252.630	−2
$24 \rightarrow 23$	14846.492	0
$25 \rightarrow 24$	15440.349	0
$26 \rightarrow 25$	16034.209	1
$27 \rightarrow 26$	16628.066	0

NOTE.—Estimated measurement uncertainty: 5 kHz. Observed minus calculated frequencies derived from best-fit constants in Table 9.

magnet is brought near the supersonic molecular beam, as expected for lines of a closed-shell molecule. For C_7S, no transitions were observed at frequencies corresponding to the 1/2 or 1/3 subharmonics, indicating that the assigned transitions do not belong to a much longer or heavier molecule. Finally, transitions of the rare isotopic species $C_7^{34}S$ were observed in natural abundance at precisely the frequency shift expected for a molecule with the linear geometry and molecular structure of C_7S.

3.2. C_5S Isotopic Species and Experimental Structure

Rotational transitions of the leading singly substituted rare isotopic species of C_5S have been observed in natural abundance (Table 4). Rotational constants for each isotopic species were well predicted from ab initio calculated bond lengths (Lee 1997) by scaling the resulting calculated rotational constants by the ratio of the experimentally determined B value to the calculated B value for the normal isotopic species—the same procedure used for the long carbon-sulfur chains. Figure 3 shows sample spectra of the same rotational transition of C_5S, $C_5^{34}S$, and $CCCC^{13}CS$. Rotational constants B and D determined from the isotopic data are listed in Table 5.

An experimental structure (r_0) for C_5S (Fig. 4) was derived by a least-squares adjustment of the bonds to reproduce the measured rotational constants of all singly substituted isotopic species on the assumption that C_5S is a linear chain. The experimentally determined bond lengths have estimated errors of less than 1%, and each agrees well with scaled ab initio predictions (Lee 1997) and an optimized ab initio structure calculated at a higher level of theory (P. Botschwina 2000, private communication). As expected, the C—C bond lengths are fairly uniform, indicating that C_5S is best characterized by cumulenic double bonding.

observed transitions to determine B and D (Table 3). The rms error of each fit is about 1 kHz, or about half the estimated measurement uncertainty.

There is little reason to question the present assignments. The best-fit B constants agree with those scaled from ab initio predictions. In addition, tested lines of each species display no significant change in intensity or width when a

$$C \equiv\!\equiv C \equiv\!\equiv C \equiv\!\equiv C \equiv\!\equiv C \equiv\!\equiv S$$

| exp. (Å) | 1.277(3) | 1.296(6) | 1.268(12) | 1.277(13) | 1.547(6) |
| theo. (Å) | 1.2836 | 1.2923 | 1.2661 | 1.2812 | 1.5439 |

Fig. 4.—Experimentally derived r_0 structure for C_5S obtained from the rotational constants of the normal and six singly substituted rare isotopic species; theoretical structure from CCSD(T) calculations plus corrections (P. Botschwina, 2000; private communication). Numbers in parentheses are estimated 1 σ bond length errors in units of the last significant digit.

3.3. C_4S, C_6S, and C_8S

The measured rotational transitions of C_4S are given in Table 6, those of C_6S and $C_6^{34}S$ are given in Table 7, and the measured $J = N + 1$ transitions of C_8S are given in Table 8. The spectroscopic constants obtained by least-squares fitting the Hamiltonian for a $^3\Sigma$ chain to line frequencies for each molecule are summarized in Table 9.

As before, there is very strong evidence that the carriers of the observed transitions are the assigned triplet carbon-sulfur chains and no other molecules. The best-fit B constants are closely predicted by scaling those calculated from ab initio theory. Lines exhibit a significant decrease in intensity when a permanent magnet is brought near the molecular beam, demonstrating the magnetic Zeeman effect expected of molecules with unpaired electrons. For C_6S, transitions of $C_6^{34}S$ have also been observed at the expected frequency shift, a further confirmation of this assignment.

4. DISCUSSION

Astrochemical models suggest that larger carbon-sulfur chains beyond C_3S are fairly abundant in space: Millar & Herbst (1990) predict a C_4S fractional abundance in TMC-1 only 1 order of magnitude less than that of C_3S, and Millar & Hatchell (1998) predict a high C_4S column density (about 10^{14} cm^{-2}) in the hot molecular core G34.3, a value only 8% of the C_3S column density predicted by the same model. A dipole moment of about 4 D has been calculated for C_4S, with even larger dipole moments for longer chains (Lee 1997; Pascoli & Lavendy 1998). From the constants given in Tables 3, 5, and 9, the strongest rotational transitions up to 40 GHz can be calculated to better than 1 km s^{-1} for each of the four chains here.

The substantial column densities of C_2S and C_3S in TMC-1 indicate that searches by radio astronomers for longer carbon-sulfur chains in this source are warranted. In

TMC-1, the $N_J = 3_4 \rightarrow 2_3$ transition of C_2S has an antenna temperature of over 2.2 K (Suzuki et al. 1992) and the $J = 8 \rightarrow 7$ transition of C_3S has an antenna temperature of over 0.8 K (Yamamoto et al. 1987; Kaifu et al. 1987).

The carbon-sulfur chains studied here are strong candidates for detection in IRC +10216. Bell et al. (1993) have reported a weak line (2 mK) in IRC +10216, which they tentatively assign to C_5S; from this assignment, the authors conclude that $N(C_5S)/N(C_3S) \approx 0.5$, on the assumption of a C_5S dipole moment of 4.5 D. Higher level ab initio calculations by Botschwina et al. (1994) find that the dipole moment of C_5S is even larger, about 5.38 D, implying a C_5S column density that is about three-fourths that estimated by Bell et al. (1993). If there is a similar abundance ratio between C_7S and C_5S, it may also be possible to detect C_7S in TMC-1 because the dipole moment of C_7S is slightly larger than that of C_5S at the same level of theory (Lee 1997).

Establishing column densities of C_5S and C_7S in IRC +10216 would be helpful in understanding carbon chemistry in this source, since present observations indicate that the column densities of the pure carbon chains C_n fall off more rapidly with increasing n than do the C_nS and the HC$_n$N chains (Bell et al. 1993). Detection of longer carbon-sulfur chains beyond C_3S may also provide useful physical probes of astronomical sources. For example, such species may be good chemical clocks; the relative abundances of different sulfur-bearing molecules (including H_2S, SO, and SO_2) may reflect the evaporation of grain mantle ices, and measured column densities have been combined with time-dependent chemical models to constrain the ages of hot molecular cores (Millar & Hatchell 1998). In addition, C_2S has been claimed to be a good tracer of physical conditions in preprotostellar cores (Wolkovitch et al. 1997). Other observations show that this chain is abundant in quiescent dark clouds but undetectable in active star-forming regions,

TABLE 9

SPECTROSCOPIC CONSTANTS OF TRIPLET C_4S, C_6S, $C_6^{34}S$, AND C_8S (IN MHz)

CONSTANT	C_4S Measured	C_6S Measured	C_6S Expected	$C_6^{34}S$ Measured	$C_6^{34}S$ Expected	C_8S Measured	C_8S Expected
B	1519.2062(3)	597.12449(7)	599.041	582.51(4)	584.334	297.81(1)	298.981
$10^6 D$	48(3)	4.2(1)	...	4.2[a]	...	2.1[b]	...
γ	$-4.0(8)$	-4.1[c]	...	-4.1[c]	...	-4.1[c]	...
λ	113840(60)	163479(6)	...	163000(1000)	...	207000(3000)	...
$10^3 \lambda_D$	12(3)	9.0(1)	...	9[a]	...	9[a]	...

[a] Fixed to the C_6S value.
[b] Estimated from C_6S assuming that D is proportional to B.
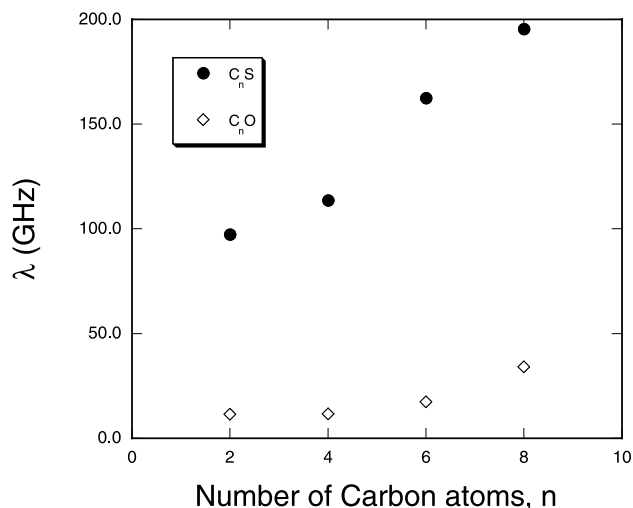[c] Fixed to the C_4S value.

FIG. 5.—Spin-spin coupling constants, λ, for the C_nS and C_nO chains ($n = 2, 4, 6, 8$) as a function of the number of carbon atoms. The C_nO coupling constants are from (Ohshima et al. 1995), and the C_2S constant is from Saito et al. (1987).

indicating that C_2S may trace preprotostellar cores in very early stages of star formation and the envelope of pre-protostellar cores in later stages (Lai & Crutcher 2000).

For the triplet carbon-sulfur chains studied here, the magnitude of the spin-spin constant λ increases steadily with chain length, similar to the trend found for the closely related triplet carbon chains C_n (Van Zee et al. 1988; Hwang et al. 1993), C_nO (Ohshima, Endo, & Ogata 1995), and SiC_n (McCarthy et al. 2000). Figure 5 shows this trend for the $C_{2n}S$ and isovalent $C_{2n}O$ chains (Ohshima et al. 1995). Since λ includes second-order magnetic interactions between the triplet ground state and a low-lying singlet electronic state (Gordy & Cook 1970), the increase in λ suggests that the energy gap between these two states narrows with n. This agrees with recent ab initio calculations by Pascoli & Lavendy (1998), who find that the energy gap between the ground electronic state and the first excited electronic state for $C_{2n}S$ ($n = 1$–10) decreases with chain length.

The work presented here suggests that additional laboratory investigations, as well as astronomical searches, may be worth pursuing. The high abundances (greater than 10^8 molecules per pulse) of these long carbon-sulfur chains in our molecular beam suggest that their optical and infrared spectra may be detectable with present laser techniques. Such investigations are worth pursuing in light of the recent assignment of several diffuse interstellar bands to C_7^- (Tulej et al. 1998), with the implication that carbon chains of similar size and structure may be carriers of the optical diffuse bands.

Lines of C_4S and C_5S, as well as possibly C_6S and C_7S, are strong enough in our FTM spectrometer that their energetic isomers may be detectable by the same technique. Pascoli & Lavendy (1998) have calculated the structures, dipole moments, and relative energies for cyclic isomers of C_nS; some lie only a very few eV above ground and are quite polar. Recent detections with our FTM device of four C_5H_2 isomers (Gottlieb et al. 1998) indicate that fairly high lying isomers are populated in our molecular beam with abundances that correlate fairly well with relative energy.

Rotational transitions from low-lying vibrationally excited states of shorter C_nS chains may be detectable as well. Calculations of vibrational frequencies (Lee 1997; Pascoli & Lavendy 1998) indicate that several of these chains possess fairly low lying bending modes, and the recent detection of vibrationally excited states of SiC_4 (Gordon et al. 2000) indicates that the vibrational temperature of this closely related chain is 40–60 K in our molecular beam, even though the rotational temperature is only a few K. Ab initio determination of the cubic force field constants for the C_nS chains would be a helpful guide in a search for such satellite transitions.

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