# ROTATIONAL SPECTRA OF SULFUR-CARBON CHAINS. II. HC<sub>5</sub>S, HC<sub>6</sub>S, HC<sub>7</sub>S, AND HC<sub>8</sub>S, AND H<sub>2</sub>C<sub>4</sub>S, H<sub>2</sub>C<sub>5</sub>S, H<sub>2</sub>C<sub>6</sub>S, AND H<sub>2</sub>C<sub>7</sub>S

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 *Received 2000 October 30; accepted 2001 September 7* 

## ABSTRACT

The linear carbon chain radicals HC<sub>5</sub>S, HC<sub>6</sub>S, HC<sub>7</sub>S, and HC<sub>8</sub>S and the asymmetric top chains H<sub>2</sub>C<sub>4</sub>S, H<sub>2</sub>C<sub>5</sub>S, H<sub>2</sub>C<sub>6</sub>S, and H<sub>2</sub>C<sub>7</sub>S have been detected in a supersonic molecular beam by Fourier transform microwave spectroscopy. Like the shorter HC<sub>n</sub>S chains, the electronic ground states of the four longer chains here alternate with even and odd number of carbon atoms: HC<sub>5</sub>S and HC<sub>7</sub>S have  ${}^{2}\Pi_{1/2}$  ground states, while HC<sub>6</sub>S and HC<sub>8</sub>S have  ${}^{2}\Pi_{3/2}$  ground states. Each of the four new thiocumulene chains possesses a rotational spectrum characteristic of a molecule with C<sub>2v</sub> symmetry, in agreement with that observed for the two shorter chains H<sub>2</sub>C<sub>2</sub>S and H<sub>2</sub>C<sub>3</sub>S. The microwave spectra of all eight chains have been fully characterized, and spectroscopic constants, including fine and hyperfine structure constants where applicable, have been determined to high precision. The eight new chains are probably all highly polar and all are plausible candidates for astronomical detection. For the radical chains, the spectroscopic constants determined from the present work allow the astronomically most relevant lines to be calculated with an uncertainty of less than 1 km s<sup>-1</sup> up to 40 GHz; for the asymmetric top chains, the same transitions can be calculated with an uncertainty of less than 0.5 km s<sup>-1</sup> up to 55 GHz.

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

### 1. INTRODUCTION

Carbon chain molecules are known to play an important role in the chemistry of the interstellar medium; many have been detected in interstellar molecular clouds and circumstellar envelopes of late-type stars (Thaddeus et al. 1998). Chains of the form HC<sub>n</sub>S and H<sub>2</sub>C<sub>n</sub>S are plausible candidates for detection by radio astronomers because they are closely related in structure and composition to families of known astronomical molecules, such as C<sub>n</sub>S, C<sub>n</sub>H, and H<sub>2</sub>C<sub>n</sub>, and because hydrogenated carbon-sulfur chains with one or two hydrogen atoms are probably highly polar. In TMC-1, C<sub>2</sub>S and C<sub>3</sub>S (Hirahara et al. 1992) are much more abundant than the isovalent chains C<sub>2</sub>O (Ohishi et al. 1991) and C<sub>3</sub>O (Brown et al. 1985), even though oxygen is cosmically more abundant than sulfur by a factor of about 40.

Several astrochemical gas-phase models also indicate that hydrogenated carbon-sulfur chains might be present at detectable abundances in the interstellar medium. Models of interstellar synthesis which incorporate sulfur chemistry have been reviewed briefly in the first paper in this series (Gordon et al. 2001); some of these models include cations of the form HC<sub>n</sub>S<sup>+</sup> (Smith et al. 1988; Wlodek, Bohme, & Herbst 1988; Millar & Herbst 1990). The model of Smith et al., for example, suggests synthetic pathways for the formation of HC<sub>3</sub>S and H<sub>2</sub>C<sub>3</sub>S, shorter analogs to the chains studied here. Radioastronomical searches for longer such chains would be greatly aided if precise rest frequencies were available from laboratory measurements.

Here we present the first laboratory detections of eight new carbon-sulfur molecules: the linear radicals HC<sub>5</sub>S and HC<sub>7</sub>S (with  ${}^{2}\Pi_{1/2}$  electronic ground states), HC<sub>6</sub>S and HC<sub>8</sub>S (with  ${}^{2}\Pi_{3/2}$  ground states), and the four asymmetric top thiocumulenes H<sub>2</sub>C<sub>4</sub>S, H<sub>2</sub>C<sub>5</sub>S, H<sub>2</sub>C<sub>6</sub>S, and H<sub>2</sub>C<sub>7</sub>S. All were detected by Fourier transform microwave (FTM) spectroscopy in a supersonic molecular beam. From six to 18 rotational transitions of each chain have been measured between 6 and 20 GHz. Laboratory spectroscopy of the  $C_nS$  (n = 4-9) chains was discussed in the first paper in this series.

#### 2. EXPERIMENT

To our knowledge, no ab initio structures are available for the chains studied here. Searches for rotational transitions were therefore based on calculated geometries of the linear  $C_n$ S chains (Lee 1997) modified by appending one or two hydrogen atoms as appropriate. For the  $HC_nS$  chains, a hydrogen atom was added to the terminal carbon atom assuming a C—H bond length of 1.06 Å. For the  $H_2C_nS$ chains, two axially symmetric hydrogen atoms were added to the terminal carbon atom at a distance of 1.095 Å and an internal HCH angle of 118°, according to the H<sub>2</sub>C<sub>3</sub>S geometry derived by Brown et al. (1988). Rotational constants B for each chain were then calculated from these structures and scaled by the ratio of the experimental B value to the calculated B value for one of the shorter known chains HC<sub>3</sub>S, HC<sub>4</sub>S, or H<sub>2</sub>C<sub>4</sub>S, depending on the type of chain and its ground state. Rotational transitions predicted in this way turned out to be accurate to about 1%.

The same FTM spectrometer recently used to detect the rotational transitions of a number of carbon chains and other reactive molecules (McCarthy et al. 1997, 2000), including the longer  $C_nS$  chains up to  $C_9S$  (Gordon et al. 2001), 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 known chains  $HC_4S$  (Hirahara, Ohshima, & Endo 1994) and  $H_2C_3S$  (Brown et al. 1988) were observed and optimized 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<sub>2</sub>) in Ne at a nozzle backing pressure of 2.5 ktorr. These conditions were used in initial searches for longer chains; once found, the production of each molecule was then optimized individually. The best conditions for the longer radical and cumulene chains are very similar to those that optimize HC<sub>4</sub>S and H<sub>2</sub>C<sub>4</sub>S, except with (1) a slightly lower carbon disulfide concentration (0.1%–0.2%) and (2) a somewhat higher discharge voltage, increasing by about 100 V for each additional carbon atom in the chain.

# 3. RESULTS AND ANALYSIS

## 3.1. The Radical Chains: HC<sub>5</sub>S, HC<sub>6</sub>S, HC<sub>7</sub>S, and HC<sub>8</sub>S

Eight fairly intense rotational transitions of  $HC_5S$  (Table 1) and 10 of  $HC_7S$  (Table 2) have been measured between 6 and 20 GHz. Each transition is split into four strong lines by widely spaced  $\Lambda$ -type doubling and closely spaced proton

TABLE 1 Microwave Transitions of HC5S in the  $^{2}\Pi_{1/2}$  Ground State

TRANSITION		a/f	FREQUENCY	0 0
J  ightarrow J'	$F \to F'$	$\Lambda \operatorname{Comp.}^{a}$	(MHz)	(kHz)
3.5→2.5	4→3	е	6127.455	2
	$3 \rightarrow 2$	е	6127.993	-6
	4→3	f	6133.153	1
	$3 \rightarrow 2$	f	6133.795	0
4.5→3.5	5→4	е	7879.130	3
	4→3	е	7879.453	1
	5→4	f	7884.778	-2
	4→3	f	7885.150	0
5.5→4.5	$6 \rightarrow 5$	е	9630.755	2
	5→4	е	9630.973	3
	$6 \rightarrow 5$	f	9636.378	-5
	5→4	f	9636.623	0
6.5→5.5	7→6	е	11382.356	-1
	$6 \rightarrow 5$	е	11382.516	5
	7→6	f	11387.968	-3
	$6 \rightarrow 5$	f	11388.140	-1
7.5→6.5	$8 \rightarrow 7$	е	13133.946	-1
	7→6	е	13134.066	3
	$8 \rightarrow 7$	f	13139.550	-2
	7→6	f	13139.680	3
8.5→7.5	$9 \rightarrow 8$	е	14885.525	-3
	$8 \rightarrow 7$	е	14885.620	1
	$9 \rightarrow 8$	f	14891.123	-4
	$8 \rightarrow 7$	f	14891.228	4
9.5→8.5	10→9	e	16637.100	-3
	9→8	е	16637.177	2
	10→9	f	16642.695	-2
	9→8	f	16642.775	1
10.5→9.5	$11 \rightarrow 10$	е	18388.667	-5
	10→9	е	18388.729	-3
	$11 \rightarrow 10$	f	18394.266	3
	10→9	$\tilde{f}$	18394.331	6

Notes.—Estimated 1  $\sigma$  measurement uncertainty: 2 kHz. Calculated frequencies derived from best-fit constants in Table 5.

<sup>a</sup> Designation of e and f levels is based on the assumption that the hyperfine coupling constant d is positive.

TABLE 2 Microwave Transitions of HC7S in the  $^2\Pi_{1/2}$  Ground State

Transit	ION	- / £	Ennorm	0 0
J  ightarrow J'	$F \to F'$	e/f $\Lambda$ Comp. <sup>a</sup>	(MHz)	(kHz)
10.5→9.5	11→10	е	8358.101	-2
	$10 \rightarrow 9$	е	8358.136	-5
	$11 \rightarrow 10$	f	8360.653	1
	$10 \rightarrow 9$	f	8360.690	1
$11.5 \rightarrow 10.5$	12→11	е	9154.236	-1
	$11 \rightarrow 10$	е	9154.266	-2
	$12 \rightarrow 11$	f	9156.785	-1
	$11 \rightarrow 10$	f	9156.818	1
12.5→11.5	13→12	е	9950.368	-2
	12	е	9950.398	1
	13→12	f	9952.918	-1
	12→11	f	9952.943	-2
13.5→12.5	14→13	е	10746.500	-2
	13→12	е	10746.525	0
	14→13	f	10749.047	-4
	13→12	f	10749.072	-1
14.5→13.5	$15 \rightarrow 14$	е	11542.633	-1
	14→13	е	11542.650	-3
	$15 \rightarrow 14$	f	11545.178	-4
	14→13	f	11545.198	-3
15.5→14.5	$16 \rightarrow 15$	е	12338.762	8
	$15 \rightarrow 14$	е	12338.777	5
	$16 \rightarrow 15$	f	12341.306	4
	$15 \rightarrow 14$	f	12341.326	6
16.5→15.5	$17 \rightarrow 16$	е	13134.888	3
	16→15	е	13134.905	4
	17→16	$f_{-}$	13137.434	1
	16→15	f	13137.454	5
17.5→16.5	18→17	е	13931.014	-1
	17→16	е	13931.031	2
	18→17	f	13933.561	-2
	17→16	f	13933.581	4
18.5→17.5	19→18	е	14/27.142	-2
	18-17	e	14/27.158	2
	$19 \rightarrow 18$	$f_{c}$	14729.690	-2
	18-17	f	14/29.705	0
19.5→18.5	20→19	е	15523.267	-5
	$19 \rightarrow 18$	е	15523.284	1
	$20 \rightarrow 19$	f	15525.815	-5
	$19 \rightarrow 18$	f	15525.830	-1

Notes.—Estimated 1  $\sigma$  measurement uncertainty: 5 kHz. Calculated frequencies derived from best-fit constants in Table 5.

<sup>a</sup> Designation of *e* and *f* levels is based on the assumption that the sign of the lambda-type doubling constant p + 2q is positive.

hyperfine structure (hfs), as shown in Figure 1. A similar pattern of lines was observed for each rotational transition of  $HC_3S$  (Hirahara et al. 1994).

Six transitions of HC<sub>6</sub>S (Table 3) and 18 of HC<sub>8</sub>S (Table 4) have also been measured. Because the  $\Lambda$ -type doubling is apparently so small that it is unresolved in the  ${}^{2}\Pi_{3/2}$  fine-structure ladder, each rotational transition (see Fig. 2) consists of only two closely spaced lines split by hydrogen hyperfine splitting—the same pattern observed for HC<sub>4</sub>S. For HC<sub>8</sub>S, the two hyperfine components collapse to an unresolved line for J > 14.5.

For each new radical chain, a theoretical spectrum calculated from a standard Hamiltonian for a linear molecule in an isolated  ${}^{2}\Pi$  electronic state with hfs (Brown et al. 1979;



FIG. 1.—Rotational transitions of HC<sub>5</sub>S in the  ${}^{2}\Pi_{1/2}$  ground state. While the  $\Lambda$ -type doubling remains nearly constant with increasing *J*, the hyperfine structure collapses significantly. The double-peaked line profile is an instrumental artifact; Doppler splitting results from the interaction of the supersonic axial molecular beam with the standing wave in the confocal Fabry-Perot microwave cavity. Spectra were obtained after 2–3 minutes of integration.

Amiot, Maillard, & Chauville 1981) was least-squares fitted to the observed transitions. The spectroscopic constants of HC<sub>5</sub>S and HC<sub>7</sub>S are given in Table 5, and those of HC<sub>6</sub>S and HC<sub>8</sub>S are given in Table 6. Each fit required at most five adjustable parameters to reproduce the observed lines to an rms deviation of about 3 kHz. The rotational constant *B* and the centrifugal distortion constant *D* were determined for all molecules; for HC<sub>5</sub>S and HC<sub>7</sub>S, the effective  $\Lambda$ -type doubling constant p + 2q and hyperfine coupling constants a - (b + c)/2 and *d* (for HC<sub>5</sub>S) were determined, and for HC<sub>6</sub>S and HC<sub>8</sub>S the effective hyperfine coupling constant a + (b + c)/2 was determined. The hfs constants determined here are similar in magnitude to those determined for the  $C_nH$  chains of comparable size (Pearson et al. 1988; McCarthy et al. 1999). Because the lower fine-structure level is the only one thermally populated in our rotationally cold ( $T_{rot} = 3$  K) molecular beam, it has not been possible to determine the individual hyperfine constants *a*, *b*, and *c*. For the same reason, the fine-structure constant *A* could not be derived with the data at hand, so its value was fixed to the HC<sub>3</sub>S value (McCarthy et al. 1994) in the analysis of the HC<sub>5</sub>S and HC<sub>7</sub>S data, and to the value assumed for HC<sub>4</sub>S (Hirahara et al. 1994) in the analysis of the HC<sub>6</sub>S and HC<sub>8</sub>S data. For HC<sub>5</sub>S and HC<sub>7</sub>S, because *A* is probably much greater than 2*BJ* for the rotational transitions measured here, it is more appropriate to use the Hund's case *a* combi-

TABLE 3
Microwave Transitions of $HC_6S$ in the ${}^2\Pi_{3/2}$
GROUND STATE

Transition		EDEOLIENCY	0 0
J  ightarrow J'	$F \to F'$	(MHz)	(kHz)
10.5→9.5	$11 \rightarrow 10$	12007.630	-1
	$10 \rightarrow 9$	12007.658	-2
11.5→10.5	12→11	13151.217	1
	$11 \rightarrow 10$	13151.242	2
12.5→11.5	13→12	14294.801	2
	12→11	14294.818	-1
13.5→12.5	14	15438.376	-5
	13→12	15438.398	0
14.5→13.5	15→14	16581.956	4
	14	16581.971	3
15.5→14.5	16→15	17725.532	-1
	15→14	17725.544	-3

Notes.—Estimated 1  $\sigma$  measurement uncertainty: 5 kHz. Calculated frequencies derived from best-fit constants in Table 6.

nation p + 2q and q instead of the individual parameters p and q.

All of the data here and the various checks made demonstrate that the observed lines are carried by the assigned radicals and no others. The  $\Lambda$ -type doubling and hyperfine structure pattern constitute a distinctive spectroscopic signature for each chain. As expected, lines of HC<sub>6</sub>S and HC<sub>8</sub>S show a marked Zeeman effect when a permanent magnet is

TABLE 4 Microwave Transitions of  $HC_8S$  in the  $^2\Pi_{3/2}$  Ground State

TRANSITION		Ennorm	0 0
J  ightarrow J'	$F \to F'$	(MHz)	(kHz)
10.5→9.5	$11 \rightarrow 10$	6030.156	-2
	$10 \rightarrow 9$	6030.169	-2
$11.5 \rightarrow 10.5$	12	6604.458	-1
	$11 \rightarrow 10$	6604.468	-2
12.5→11.5	13→12	7178.758	-2
	12	7178.768	-1
13.5→12.5	14→13	7753.058	-3
	13→12	7753.068	-1
14.5→13.5		8327.363	3
15.5→14.5		8901.665	5
16.5→15.5		9475.958	-1
17.5→16.5		10050.260	3
18.5→17.5		10624.555	-2
19.5→18.5		11198.854	0
20.5→19.5		11773.151	0
21.5→20.5		12347.446	-3
22.5→21.5		12921.743	-2
23.5→22.5		13496.042	2
24.5→23.5		14070.336	1
25.5→24.5		14644.630	-1
26.5→25.5		15218.927	3
27.5→26.5		15793.216	-2

Notes.—Estimated 1  $\sigma$  measurement uncertainty: 5 kHz. Calculated frequencies derived from best-fit constants in Table 6.



FIG. 2.—Rotational transitions of HC<sub>8</sub>S in the  ${}^{2}\Pi_{3/2}$  ground state showing fully resolved, partially blended, and fully blended hfs for three values of *J*. A-doubling is so small that it is not resolved in these spectra. The integration time of each spectrum was approximately 3 minutes. The rest frequencies ( $\nu_{0}$ ) are 6030.162 MHz for the  $J = 10.5 \rightarrow 9.5$  transition, 7178.763 MHz for the  $J = 12.5 \rightarrow 11.5$ , and 15793.216 MHz for the  $J = 27.5 \rightarrow 26.5$ .

brought near the molecular beam, as do lines of HC<sub>4</sub>S owing to the large magnetic *g* factor of  ${}^{2}\Pi_{3/2}$  states. Lines of HC<sub>5</sub>S and HC<sub>7</sub>S, however, are insensitive to a magnetic field applied in the same way, as are lines of HC<sub>3</sub>S, owing to the very small magnetic *g* factor of  ${}^{2}\Pi_{1/2}$  states. Rotational transitions of each chain are related by half-integer quantum numbers with a small harmonic defect, with rotational constants that are within 1.2% of those predicted from the modified C<sub>n</sub>S structures.

 $\begin{array}{c} TABLE \ 5 \\ Spectroscopic \ Constants \ of \ HC_5S \ and \ HC_7S \ in \\ The \ X^2\Pi_r \ State \ (in \ MHz) \end{array}$ 

Constant	HC <sub>5</sub> S	HC <sub>7</sub> S
A	1,328,800 <sup>a</sup>	1,328,800 <sup>a</sup>
<i>B</i>	876.36692(7)	398.18614(9)
10 <sup>6</sup> D	12.3(4)	1.5(2)
p + 2q	5.575(1)	2.548(2)
a - (b + c)/2	13.37(3)	8.2(6)
<i>d</i>	7.8(1)	•••

Note.—Uncertainties (in parentheses) are 1  $\sigma$  in the last significant digit.

<sup>a</sup> Constrained to the  $HC_3S$  value (McCarthy et al. 1994).

TABLE 6
Spectroscopic Constants of $HC_6S$ and $HC_8S$ in
THE $X^2 \Pi_i$ State (in MHz)

Constant	$HC_6S$	$HC_8S$
A	$-1,000,000^{a}$	-1,000,000 <sup>a</sup>
<i>B</i>	572.1202(2)	287.23333(4)
10 <sup>6</sup> D	3.1(4)	1.00(4)
a + (b + c)/2	2.1(2)	1.0(2)

Note.—Uncertainties (in parentheses) are 1  $\sigma$  in the last significant digit.

<sup>a</sup> Constrained to the  $HC_4S$  value (Hirahara et al. 1994).

 $\begin{array}{c} TABLE \ 7 \\ Microwave \ Transitions \ of \ H_2C_4S \ \text{and} \ H_2C_5S \end{array}$ 

	$H_2C_4S$		$H_2C_5S$	
$J_{K_a,K_c}  ightarrow J'_{K'_a,K'_c}$	Frequency (MHz)	O - C (kHz)	Frequency (MHz)	0 – C (kHz)
$3_{1,3} \rightarrow 2_{1,2} \dots \dots$	8335.965	2		
$3_0 \xrightarrow{3}{} 2_0 \xrightarrow{2}{} \dots$	8346.605	-2		
$3_{1,2} \rightarrow 2_{1,1}$	8357.047	1		
$4_{1,4} \rightarrow 3_{1,3}$	11114.613	0	6771.030	-1
$4_{0,4} \rightarrow 3_{0,3}$	11128.805	0	6776.430	1
$4_{1,3} \rightarrow 3_{1,2}$	11142.723	-1	6781.690	-2
$5_{1,5} \rightarrow 4_{1,4}$	13893.259	-1	8463.787	0
$5_{0.5} \rightarrow 4_{0.4}$	13910.999	0	8470.536	2
$5_{1,4} \rightarrow 4_{1,3}$	13928.397	-1	8477.113	0
$6_{1.6} \rightarrow 5_{1.5} \dots \dots$	16671.901	-1	10156.540	-2
$6_{0,6} \rightarrow 5_{0,5} \dots \dots$	16693.188	1	10164.638	0
$6_{1,5} \rightarrow 5_{1,4}$	16714.068	1	10172.535	2
$7_{1,7} \rightarrow 6_{1,6} \dots \dots$			11849.295	0
$7_{0.7} \rightarrow 6_{0.6} \dots \dots$			11858.739	-1
$7_{1.6} \rightarrow 6_{1.5} \dots \dots$			11867.950	-1
$8_{1,8} \rightarrow 7_{1,7}$			13542.046	0
$8_{0.8} \rightarrow 7_{0.7}$			13552.841	0
$8_{1,7} \rightarrow 7_{1,6}$			13563.368	1
$9_{1,9} \rightarrow 8_{1,8}$			15234.795	0
$9_{0,9} \rightarrow 8_{0,8} \dots \dots$			15246.939	1
$9_{1,8} \rightarrow 8_{1,7}$			15258.781	0
$10_{1,10} \rightarrow 9_{1,9} \dots \dots$			16927.542	1
$10_{0,10} \rightarrow 9_{0,9} \dots \dots$			16941.033	-1
$10_{1,9} \rightarrow 9_{1,8}$			16954.191	-1

Notes.—Estimated 1  $\sigma$  measurement uncertainty: 5 kHz. Calculated frequencies derived from best-fit constants in Table 9.

# 3.2. The Thiocumulene Chains: $H_2C_4S$ , $H_2C_5S$ , $H_2C_6S$ , and $H_2C_7S$

Twelve rotational transitions of  $H_2C_4S$  and 21 of  $H_2C_5S$ have been measured (Table 7), as have 33 of  $H_2C_6S$  and 34 of  $H_2C_7S$  (Table 8). All of our measured lines lie between 6 and 18 GHz, and originate from either the  $K_a = 0$  or the metastable  $K_a = \pm 1$  ladders. Owing to the low rotational temperature in our supersonic molecular beam, transitions from higher lying ladders ( $K_a > 1$ ) are extremely weak and therefore have not been observed. The theoretical spectrum calculated from the Hamiltonian for an asymmetric top

 $TABLE \ 8 \\ Microwave Transitions of H_2C_6S \ \text{and} \ H_2C_7S$ 

	$H_2C_6S$		$H_2C_7S$	
$J_{K_a,K_c}  ightarrow J'_{K'_a,K'_c}$	Frequency (MHz)	O - C (kHz)	Frequency (MHz)	0 – C (kHz)
$6_{1,6} \rightarrow 5_{1,5}$	6714.287	0		
$6_{0,6} \rightarrow 5_{0,5} \dots \dots$	6717.745	2		
$6_{1,5} \rightarrow 5_{1,4}$	6721.111	-1		
$7_{1,7} \rightarrow 6_{1,6}$	7833.333	0		
$7_{0,7} \rightarrow 6_{0,6} \dots \dots$	7837.365	-1		
$7_{1.6} \rightarrow 6_{1.5} \dots \dots$	7841.295	0		
$8_{1,8} \rightarrow 7_{1,7}$	8952.379	1		
$8_{0.8} \rightarrow 7_{0.7} \dots$	8956.987	0		
$8_{1,7} \rightarrow 7_{1,6} \dots \dots$	8961.477	-1		
$9_{1,9} \rightarrow 8_{1,8}$	10071.423	0	6998.106	0
$9_{0,9} \rightarrow 8_{0,8}$	10076.608	0		
$9_{1,8} \rightarrow 8_{1,7}$	10081.659	-1	7003.168	-3
$10_{1,10} \rightarrow 9_{1,0} \dots$	11190.467	0	7775.673	1
$10_{0,10} \rightarrow 9_{0,0} \dots \dots$	11196.229	1	7778.527	1
$10_{10} \rightarrow 9_{10}$	11201.841	-1	7781.298	-1
$11_{1,1} \rightarrow 10_{1,10}$	12309 509	0	8553 238	1
$11_{0,11} \rightarrow 10_{0,10}$	12315 847	Ő	8556 377	0
$11_{0,11} \rightarrow 10_{0,10}$	12322 023	1	8559 427	Ő
$12_{1,10} \rightarrow 10_{1,9} \dots 12_{1,10}$	13428 551	0	9330 804	2
$12_{1,12} \rightarrow 11_{1,11} \dots$	13435 464	0	9334 226	_1
$12_{0,12} \rightarrow 11_{0,11} \dots$	13442 202	1	9337 554	_1
$12_{1,11} \rightarrow 11_{1,10} \dots 13_{1,12} \dots 12_{1,12}$	14547 501	0	10108 367	0
$13_{1,13} \rightarrow 12_{1,12} \dots$	14555 078	_2	10103.307	1
$13_{0,13} \rightarrow 12_{0,12} \dots$	14555.078	-2	10112.078	1
$13_{1,12} \rightarrow 12_{1,11} \dots 12_{1,12}$	14502.578	-1	10115.080	4
$14_{1,14} \rightarrow 15_{1,13} \dots$	15674 607	-1	10883.928	-5
$14_{0,14} \rightarrow 15_{0,13} \dots$	150/4.09/	2	10869.923	-1
$14_{1,13} \rightarrow 13_{1,12} \dots$	15682.554	-1	10893.807	-2
$15_{1,15} \rightarrow 14_{1,14} \dots$	16785.667	-1	11663.493	-1
$15_{0,15} \rightarrow 14_{0,14} \dots$	16794.310	1	11667.778	3
$15_{1,14} \rightarrow 14_{1,13} \dots$	16802.732	2	11671.933	-2
$16_{1,16} \rightarrow 15_{1,15} \dots$	17904.705	1	12441.057	0
$16_{0,16} \rightarrow 15_{0,15} \dots$	17913.919	-2	12445.624	1
$16_{1,15} \rightarrow 15_{1,14} \dots$	17922.904	0	12450.062	1
$17_{1,17} \rightarrow 16_{1,16} \dots$			13218.620	1
$17_{0,17} \rightarrow 16_{0,16} \dots$			13223.469	-1
$17_{1,16} \rightarrow 16_{1,15} \dots$			13228.185	0
$18_{1,18} \rightarrow 17_{1,17} \dots$			13996.182	2
$18_{0,18} \rightarrow 17_{0,17} \dots$			14001.316	-1
$18_{1,17} \rightarrow 17_{1,16} \dots$			14006.309	0
$19_{1,10} \rightarrow 18_{1,18} \dots$			14773.740	0
$19_{0,10} \rightarrow 18_{0,18} \dots$			14779.161	-2
$19_{1,10} \rightarrow 18_{1,17}$			14784 434	- 1
$20_{1,20} \rightarrow 19_{1,10}$			15551.298	-2
$20_{1,10} \rightarrow 19_{1,18} \dots$			15562.557	2

Notes.—Estimated 1  $\sigma$  measurement uncertainty: 5 kHz. Calculated frequencies derived from best-fit constants in Table 9.

Spectroscopic Constants of  $H_2C_4S,\,H_2C_5S,\,H_2C_6S,\,\text{and}\,H_2C_7S$  (in MHz)

Constant	$H_2C_4S$	$H_2C_5S$	$H_2C_6S$	$H_2C_7S$
A	275,400 <sup>a</sup>	269,200 <sup>a</sup>	275,500 <sup>a</sup>	268,800 <sup>a</sup>
<i>B</i>	1394.6158(2)	848.38660(7)	560.38102(3)	389.20803(4)
<i>C</i>	1387.5881(2)	845.72147(7)	559.24352(3)	388.64528(4)
$10^6 D_J$	36(2)	10.9(3)	4.24(6)	1.80(5)
$10^{3}D_{JK}$	17.20(8)	8.47(4)	3.71(2)	2.02(2)

NOTE.—Uncertainties (in parentheses) are 1  $\sigma$  in the last significant digit. <sup>a</sup> Derived assuming a planar structure (i.e.,  $1/C \cdot 1/A \cdot 1/B = 0$ ).

molecule has been least-squares fitted to the observed transitions for each species to determine rotational and centrifugal distortion constants (Table 9). The rms error of each fit is about 2 kHz, comparable or better than the estimated measurement uncertainty of 2-5 kHz.

The assignments of the four new chains again have been established with a high degree of confidence. Lines showed no appreciable Zeeman effect, as expected for closed-shell molecules. For each chain, the frequency spacing and intensity ratio of the three closely spaced transitions having different  $K_a$  values but the same J agree with that expected: for a molecule with  $C_{2v}$  symmetry, the nuclear spin statistics of the two equivalent hydrogen atoms result in a 3:2:3 intensity ratio between the  $K_a = +1, 0, -1$ , ladders as the sample lines of  $H_2C_5S$  demonstrate (Fig. 3). In an FTM spectrometer such as ours, relative intensities reliable to better than 15% are generally difficult to obtain, but an intensity ratio as large as 3:2:3 is readily detected. A better signature is provided by the nearly equal frequency spacing between transitions which originate from different  $K_a$  ladders; these were predicted a priori to better than 10 MHz for each molecule using the modified structures discussed earlier.

### 4. DISCUSSION

The HC<sub>n</sub>S and H<sub>2</sub>C<sub>n</sub>S chains are good candidates for detection by radio astronomers. The theoretical dipole moment of HCCS is predicted to be 1.22 D (Szalay 1996), and the experimental dipole moment of H<sub>2</sub>CCS is 1.01(3) D (Winnewisser & Schaefer 1980). Ab initio calculations on the closely related species C<sub>n</sub>H (n = 2-7; Woon 1995) and H<sub>2</sub>C<sub>n</sub> (n = 3-8; Maluendes & McLean 1992) indicate that the dipole moments increase with chain length, so we might anticipate that the longer chains detected here probably possess even larger dipole moments, and therefore strong rotational spectra.

In addition to the astronomical identification of C<sub>2</sub>S and C<sub>3</sub>S and a tentative detection of C<sub>5</sub>S by Bell, Avery, & Feldman (1993), ortho-H<sub>2</sub>CS has been observed in TMC-1 at a column density of  $24 \times 10^{12}$  cm<sup>-2</sup> and in L134N at a column density of  $4 \times 10^{12}$  cm<sup>-2</sup> (Irvine et al. 1989); para-H<sub>2</sub>C<sub>2</sub>S was not detected in these sources, but Irvine et al. established upper limits for the column density of  $7 \times 10^{12}$  cm<sup>-2</sup> for TMC-1 and  $11 \times 10^{12}$  cm<sup>-2</sup> for L134N. A radio search for HC<sub>3</sub>S in TMC-1, IRC +10216, and Sgr B2 was unsuccessful, but an upper limit of its column density ( $10^{13}$  cm<sup>-2</sup>) in TMC-1 was derived by McCarthy et al. (1994). Although astronomical detection of longer hydrogenated carbon-sulfur chains may not be easy, precise rest frequencies are now available with the present work to guide astronomical searches with large and sensitive radio telescopes. With the



FIG. 3.—Rotational transitions of H<sub>2</sub>C<sub>5</sub>S in the  $K_a = 0$  and the  $K_a = \pm 1$  ladders. Note that the net line strength in the two  $K_a = \pm 1$  transitions is three times that of the  $K_a = 0$  transition as expected from the ortho-para nuclear spin statistics. Spectra were obtained after an integration time of 1 minute. The rest frequencies ( $\nu_0$ ) are 16927.542 MHz for the  $10_{1,10} \rightarrow 9_{1,9}$  transition; 16941.033 MHz for the  $10_{0,10} \rightarrow 9_{0,9}$  transition; and 16954.191 MHz for the  $J = 10_{1,9} \rightarrow 9_{1,8}$  transition.

spectroscopic constants listed in Tables 5 and 6 the  $HC_nS$ transitions can be calculated to an uncertainty of less than 1 km s<sup>-1</sup> up to 40 GHz, and with the constants listed in Table 9 the same transitions of  $H_2C_nS$  can be calculated to an uncertainty of less than 0.5 km  $s^{-1}$  up to 55 GHz.

If synthetic processes analogous to those that form formaldehyde ( $H_2CO$ ) and ketene ( $H_2C_2O$ ) in space form thioformaldehyde ( $H_2CS$ ) and thioketene ( $H_2C_2S$ ), we may be able to estimate the astronomical abundance of  $H_2C_2S$  from the ratio  $N(H_2C_2S)/N(H_2CS) = N(H_2C_2O)/N(H_2CS)$  $N(H_2CO)$ . In TMC-1, the column density of  $H_2CO$  is  $\sim 6 \times 10^{14} \text{ cm}^{-2}$  (Ohishi & Kaifu 1998), that of H<sub>2</sub>C<sub>2</sub>O is  $\sim 11 \times 10^{12} \text{ cm}^{-2}$  (Irvine et al. 1989), and that of ortho- $H_2CS$  is  $\sim 2.4 \times 10^{13}$  cm<sup>-2</sup> (Irvine et al. 1989), which implies a total (ortho + para)  $H_2C_2S$  column density of more than  $4 \times 10^{11}$  cm<sup>-2</sup>.

Laboratory detections of the optical and infrared spectra of the  $HC_nS$  and  $H_2C_nS$  chains may be possible. On the basis of our FTM measurements, we estimate that most of our new sulfur-bearing chains have high enough abundances in our molecular beam (> $10^8$  molecules per pulse) that their optical and infrared spectra may be detectable with present laser techniques, such as cavity ringdown spectroscopy or laser-induced florescence.

Lines of HC<sub>5</sub>S,  $H_2C_4S$ , and  $H_2C_5S$  are sufficiently strong in our spectrometer to encourage a number of future investigations. It should be possible to detect the leading singly substituted isotopic species of these chains in natural abundance, which would enable experimental determinations  $(r_0)$  of their molecular structure by the standard technique of isotopic substitution. Ab initio calculations (Liu et al. 1997) indicate that ionic chains of the form  $HSC_n^{\pm}$  are stable

but lie higher in energy than the isomeric  $HC_nS^{\pm}$  species; strong lines of the neutral  $HC_nS$  chains indicate that cations of both isomers may be detectable in a device such as ours. Although there are no ab initio calculations which might serve as a guide, isomers of  $HC_nS$  may also be found if they are polar and low-lying in energy.

Laboratory investigation of the isovalent chains  $HC_nO$ and  $H_2C_nO$  may also prove fruitful, especially given the ready availability of a  $CO_2 + HC_4H$  precursor gas mixture analogous to that used to produce strong lines of the sulfurbearing chains in the present investigation. Abundances of known astronomical oxygen-bearing carbon chains suggest that longer such chains may be detectable by radio astronomers once rest frequencies are available. Such detections would allow a systematic comparison between analogous sulfur- and oxygen-bearing molecules, provide additional data for gas-phase models of dense molecular clouds, and thereby help improve our understanding of the chemistry of rich interstellar and circumstellar sources.

Note added in manuscript.—Following completion of this work, we became aware of recent ab initio calculations on the thiocumulene chains  $H_2C_nS$  (n = 3-9) by Park et al. (2000). The rotational constants derived using density functional theory and MP2 methods are in good agreement with the experimental values measured here.

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