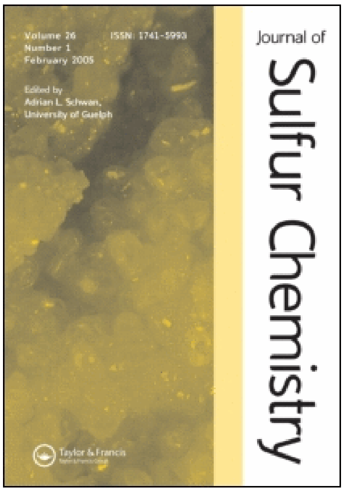

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SULFUR-BEARING CARBON-CHAIN MOLECULES IN SPACE AND IN THE LABORATORY

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This review introduces the present status of interstellar chemistry and shows why various carbon-chain molecules occupy a key position among hundred or more interstellar molecules so far identified. Then, several series of sulfur-bearing carbon-chain molecules such as C_nS, HC_nS, C_nS_2, C_nOS, and C_nO_2 are reviewed especially by paying attention to their generation and spectroscopic characterization in the laboratory.

Keywords: Interstellar chemistry; interstellar molecules; ion–molecule reaction; microwave spectroscopy; sulfur-bearing carbon-chain molecules; transient molecules

CONTENTS

1. INTRODUCTION – INTERSTELLAR CHEMISTRY AND CARBON-CHAIN MOLECULES

Hundred or more molecules have now been identified to exist in space by close collaboration of radio astronomy and laboratory spectroscopy since 1963. The molecules identified in space are called "interstellar molecules", and they are various kinds of organic and inorganic compounds, as listed in Table I. About half of them are transient molecules in terrestrial conditions, including several simple molecular ions, free radicals and unstable molecules.[1,2] As Table I shows, one of the outstanding features of the interstellar molecules is that they include several kinds of heteroatom-containing carbon-chain molecules which have rarely been encountered in the laboratory prior to the detection of interstellar molecules.

The interstellar molecules exist in very sparse regions of space, 100 molecules $(H, H_2)/cm^3$–10^7 molecules/cm^3, and a large number of interstellar molecules with interstellar dusts sometimes form a cloud, a molecular cloud. In the molecular clouds denser regions or cores are formed by their own gravity or mechanical shock, and some of the dense cores proceed on the way to star formation, along which molecules are deeply involved as masses and energy exchangers. As a result, the interstellar spectral lines of various molecules have been used to monitor the physical conditions of the molecular cloud and the process of star formation, and the chemistry of interstellar molecules in the molecular clouds is essential to a deeper understanding of the physical conditions in the clouds.

Since the first detection of the interstellar molecules, chemistry in space has been presented and discussed. The physical conditions of the interstellar space are quite different from the well-known conditions in the laboratory. The typical physical conditions of the dark molecular clouds are their very low temperature of less than 10 K, a density of 10^3–10^6 molecules/cm^3 and the lack of ultraviolet radiation. Therefore, chemical reactions such as endothermic reactions, neutral–neutral reactions with an activation energy, third body reactions and photoreactions which are familiar in the laboratory are not effective. The only energy source available for the reactions in the dark clouds is cosmic-ray ionization. The ion–molecule reaction initiated by the cosmic-ray ionization is the only rapid reaction in the cold dark clouds, because the charge of the ion polarizes its counterpart, and the electrostatic attraction between the positive charge and the polarized negative charge makes the cross section very large; it is the well known temperature-independent Langevin rate of $10^{-9}\,cm^3\,s^{-1}$. Thus, this ion–molecule reaction scheme has been put forward to explain the formation and destruction of molecules in the interstellar molecular clouds.[3]

Molecular hydrogen is by far the most abundant species in the molecular clouds. A high energy cosmic ray with 100 MeV or more energy can penetrate even the central region of dense molecular clouds and ionize molecular hydrogen and helium nearby, producing H_2^+, H^+, and He^+ ions. The H_2^+ ion immediately reacts with surrounding H_2 to generate the very stable molecular ion H_3^+. When a molecule having a higher proton affinity than H_2 encounters H_3^+, the proton transfer occurs from H_3^+ to the molecule. Interstellar HCO^+ and HN_2^+ are such examples which have been considered as strong evidence of the ion–molecule reaction scheme in space. Ions further react with surrounding H_2, generating more complex and heavier molecular ions:

$$HX^+ + H_2 \rightarrow H_2X^+ + H$$
$$H_2X^+ + H_2 \rightarrow H_3X^+ + H$$

and so on. A carbon-chain backbone is formed by carbon ion insertion into hydrocarbons:

$$\begin{aligned} C^+ + CH_4 &\rightarrow C_2H_3^+ + H \\ &\rightarrow C_2H_2^+ + H_2 \end{aligned}$$

The condensation of a hydrocarbon ion with a hydrocarbon molecule is important for the formation of more complex molecules:

$$CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2$$

Longer carbon chains grow via radiative association reactions:[4]

$$C^+ + C_n \rightarrow C_{n+1}^+ + h\nu$$

Finally, molecular ions react with electrons generating neutral molecules. The neutralization of a positive ion and an electron generates a large amount of energy. The energy generated is generally dissipated by breaking one or two weak chemical bonds of the parent molecular ions, that is, bonds to hydrogen. Thus, unsaturated hydrocarbons are generated and carbon-chain molecules are unique and ubiquitous in interstellar space, as indicated in Table I.

TABLE I Interstellar molecules

Molecular ions	CH^+, CO^+, SO^+, H_3^+, HCO^+, HOC^+, HCS^+, HN_2^+, HCO_2^+, H_2CN^+, H_3O^+, HC_3NH^+, H_2COH^+
Inorganic molecules	H_2, NH*, OH*, NO*, NS*, SO*, SiO, SiN*, SiS, HCl, HF, NaCl, KCl, AlF, AlCl, H_2O, H_2S, H_2Si, HNO, N_2O, SO_2, NH_2*, NH_3, SiH_4
Organic molecules	Saturated hydrocarbons, CH_4 Alcohols, Ethers, CH_3OH, C_2H_5OH, $(CH_3)_2O$ Aldehydes, Ketones, HCO*, H_2CO, H_2CCO, CH_3CHO, HCCCHO, $(CH_3)_2CO$ Acids, Esters, HCOOH, CH_3COOH, CH_3OCHO Amines, Imines, NH_2CN, NH_2CHO, CH_2NH, CH_3NH_2 Cyanides, Isocyanides, MgCN, MgNC, NaCN, HNC, CH_2N*, CH_2CN*, CH_3CN, CH_3NC, C_2H_5CN, C_2H_3CN, HNCO S-Bearing molecules, OCS, HNCS, H_2CS, CH_3SH P-Bearing molecules, CP*, PN Cyclic molecules, C_3H_2, C_3H*, C_2Si, $(CH_2)_2O$ Carbon-chain molecules C*, C_2, C_3, C_5 HCN, HC_2CN, HC_4CN, HC_6CN, HC_8CN, $HC_{10}CN$ HCCN*, HCCNC, CCCNH CH*, C_2H*, C_3H*, C_4H*, C_5H*, C_6H*, C_7H*, C_8H* CH_2*, CH_2CC, CH_2C_3, CH_2C_5 CO, C_2O*, C_3O CN*, C_3N* CS, CCS*, C_3S CSi*, C_4Si CH_3CCH, CH_3C_4H

*Free radical.

2. C_nS

Up to the middle of the 1980s, only two series of interstellar carbon-chain molecules have been known: $H(C{\equiv}C)_nCN$ and C_nH. There had been no spectroscopic studies and no theoretical predictions on the sulfur containing carbon-chain family, C_nS, though the unstable diatomic molecule CS has been extensively studied mainly by microwave spectroscopy since 1955.[5,6] The sulfur-bearing carbon-chain family first appeared in radio astronomy and then in laboratory spectroscopy.

2.1. *CCS (Thioxoethenylidene) and C_3S (3-Thioxo-1,2-propadienylidene)*

In 1984, Suzuki and her collaborators detected a strong interstellar spectral line at 45 379 MHz toward a dark molecular cloud TMC-1 and our Galactic Center Sgr B2 by using the 45 m radio telescope of the Nobeyama Radio Observatory (NRO),[7] as shown in Figure 1. This interstellar line could not be assigned to any transitions of known molecules. As a single line without hyperfine structure it gave no information regarding molecular transitions. Its identification took almost three years. In 1987, Saito *et al.*[8] studied a glow-discharge chemical system of carbon disulfide and helium with laboratory microwave spectroscopy and found a set of strong lines showing triplet patterns of a paramagnetic molecule with every 13 GHz. These lines were assigned to

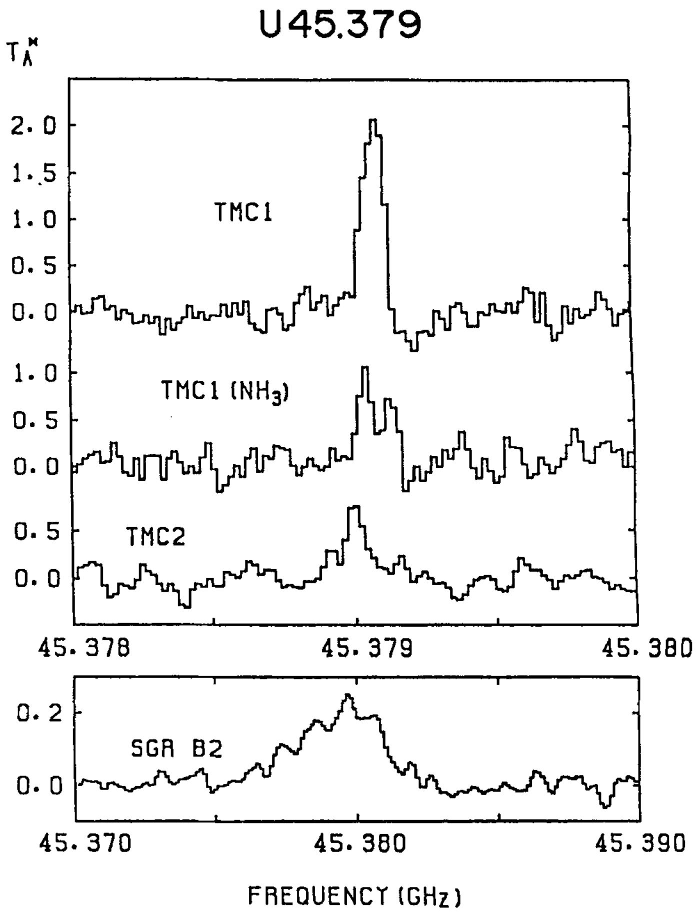


FIGURE 1 The line profile of U45379 toward TMC (upper) and Sgr B2 (lower).[7]

a biradical, CCS, in the $^3\Sigma^-$ ground electronic state, which was a completely new molecule never before studied spectroscopically or theoretically. On the basis of the precise molecular constants determined from the measured millimeter-wave line frequencies, one fine-structure component of the $N = 3\text{-}2$ rotational transition was found to correspond exactly to the strong and unidentified interstellar line at 45 379 MHz reported by Suzuki *et al.*[7] as shown in Figure 2. Furthermore, three other lines among seven unidentified lines detected toward TMC-1 by the NRO telescope[9] and seven lines among unidentified lines reported by Cummins *et al.*[10] in the line survey observations toward Sgr B2 were assigned to the spectral lines of CCS.

In total, laboratory spectroscopy accomplished assignments of eleven unidentified interstellar lines to the lines of CCS, whose identifications had been discussed by many researchers for years. This is because the rotational energy structure of CCS in the $^3\Sigma^-$ state is relatively simple for molecular spectroscopy as shown in Figure 3. However, it is reasonably complicated for astronomical spectroscopy of molecules in sources of

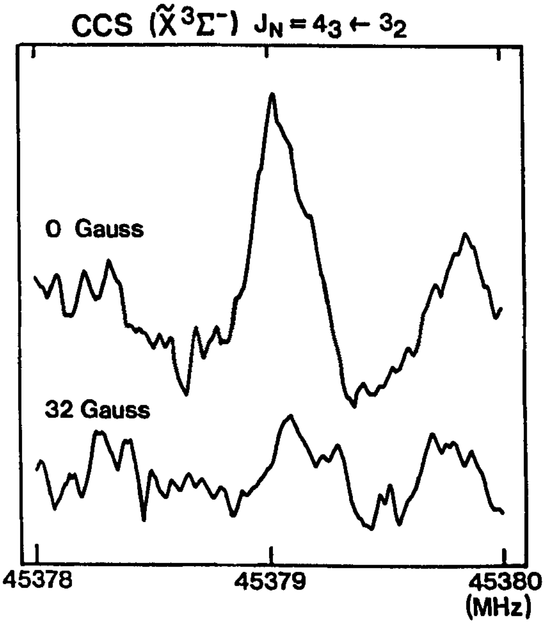


FIGURE 2 Laboratory spectra of the F_1 fine-structure component of the $N = 3\text{-}2$ rotational transition of CCS, corresponding to the U45379 interstellar line.[8]

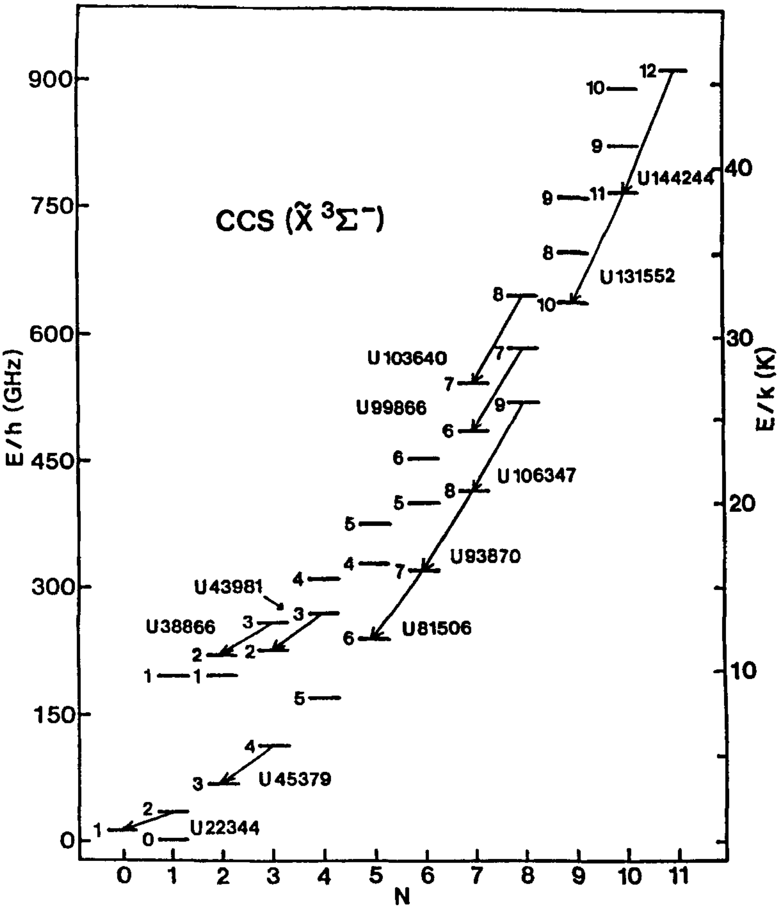


FIGURE 3 The energy level diagram of CCS ($^3\Sigma^-$) with the astronomically identified transitions in TMC-1 and Sgr B2.[8] *N* is the rotational quantum number and the number attached to the energy levels represents the fine structure component.

different physical conditions. The four lines detected toward TMC-1 are located in the energy region of a few to 10 K, whereas the seven lines toward Sgr B2 are found in the region of 10–40 K. These temperatures correspond to the kinetic temperature of H_2 in the sources observed. These features made it difficult to assign the interstellar spectral lines in different astronomical sources.

Since the interstellar CS and CCS molecules show strong signals from the molecular clouds, the identification of CCS in space suggested the possibility of the existence of the next member of the sulfur-bearing carbon-chain molecule series. Actually three unidentified lines left in the NRO line survey data for TMC-1 were suspected to be the lines of C_3S. This was confirmed by observing several spectral lines of C_3S generated in the same dc-glow discharge of CS_2 and He in the laboratory.[11] The molecular constants of C_3S determined by laboratory spectroscopy are also listed in Table II.

These findings showed the importance of heteroatom-containing carbon-chain molecules in space and urged a full spectroscopic characterization of these molecules. The isotopic species of these molecules were subsequently studied in the laboratory[12,13] and their structures determined as listed in Table III. The dipole moment of a molecule is important to laboratory spectroscopy and radioastronomy observations. However, there have been no laboratory measurements of the dipole moment of CCS and it has been predicted to be 2.81–3.18 D by *ab initio* calculations.[22,25] The dipole moment of C_3S was experimentally determined to be 3.704 D.[14,15] Thus, the two new members of the C_nS family, CCS and C_3S, were fully characterized by laboratory microwave spectroscopy. Although the concentrations of both species in the glow-discharge chemical system described above were estimated to be very low,

TABLE II Molecular constants of C_nS ($n = 1-5$)

Constant	CS^a	$CCS\ (^3\Sigma^-)^b$	C_3S^c	$C_4S\ (^3\Sigma^-)^d$	C_5S^e
B_0 (MHz)	24495.574	6477.75036	2890.38000	1519.165	922.70348
D (kHz)	40.24	1.72796	0.224158	0.056^f	0.0145
γ (MHz)		− 14.737			
γ_D (kHz)		0.055			
λ (MHz)		97196.07		113603	
λ_D (kHz)		27.00			
μ (D)	1.958		3.704^g		

[a]Ref. [6]; [b]Refs. [8,12]; [c]Ref. [11]; [d]Ref. [27]; [e]Ref. [28]; [f]Fixed; [g]Ref. [15].

TABLE III Bond lengths of C_nS ($n = 1-5$) (Å)

Molecule	$r\,(S\text{–}C_1)$	$r\,(C_1\text{–}C_2)$	$r\,(C_2\text{–}C_3)$	$r\,(C_3\text{–}C_4)$	$r\,(C_4\text{–}C_5)$
CS^a	1.535152				
CCS^b	1.5669	1.3101			
C_3S^c	1.5323	1.3028	1.2724		
C_4S					
C_5S^d	1.5424	1.2857	1.2660	1.2988	1.2993

[a]Ref. [30], r_e; [b]Ref. [12], r_s; [c]Ref. [13], r_s; [d]Ref. [28], r_e; MP3/6-31G**.

less than 1%, their spectroscopic and molecular structural characterization was substantiated by the high sensitivity and high resolution of laboratory microwave spectroscopy.[1,16,17]

The formation and destruction of CCS and C_3S in space have been discussed.[18] Sulfur-bearing hydrocarbon ions are generated by the following reactions:

$$\begin{aligned}
S^+ + C_2H_2 &\rightarrow HC_2S^+ + H\\
S^+ + C_2H_3 &\rightarrow HC_2S^+ + H_2\\
S^+ + C_3H_2 &\rightarrow HC_3S^+ + H\\
S + C_2H_3^+ &\rightarrow HC_2S^+ + H_2\\
S + C_2H_4^+ &\rightarrow HC_2S^+ + H_2 + H\\
S + C_3H_2^+ &\rightarrow HC_3S^+ + H\\
S + C_3H_3^+ &\rightarrow HC_3S^+ + H_2
\end{aligned}$$

and

$$\begin{aligned}
HC_2S^+ + e &\rightarrow CCS + H\\
HC_3S^+ + e &\rightarrow C_3S + H\\
C_nS + O &\rightarrow CO + C_{n-1}S
\end{aligned}$$

Millar and Herbst[18] concluded that the observed high abundances of CCS and C_3S in TMC-1 could be explained by the ion–molecule reaction scheme if the elemental sulfur abundance is about 2×10^{-7} with respect to H_2 and if the dissociative recombination of HC_2S^+ and HC_3S^+ with electrons produces mainly CCS and C_3S.

The high resolution of laboratory microwave spectroscopy and also of radio astronomy makes it possible to discriminate the spectral lines of molecules in a gaseous mixture. However, infrared spectroscopy of lower resolution needs an efficient production of C_nS for its observations. Maier *el al.*[19] prepared C_3S in an Ar matrix by photolyzing C_4OS with UV radiation and measured three infrared Σ bands of C_3S. Sample of C_4OS was produced from 7-diazo-2-thia-3,4-diazabicyclo[3.3.0]hepta-1(5),3-diene-6,8-dione by UV photolysis. Takano *et al.*[20] measured the ν_1 and $\nu_1 + \nu_5 - \nu_5$ bands of C_3S by using an infrared diode-laser spectrometer combined with a dc glow discharge. This new sulfur-bearing carbon-chain molecule also stimulated several quantum chemical calculations.[21–26]

Longer carbon-chain members of C_nS were looked for in space and in the laboratory immediately after the identification of CCS and C_3S, but their identification was not straightforward. The spectral lines of C_4S (4-thioxo-1,2,3-butatrienylidene)[27] and C_5S (5-thioxo-pentatetraenylidene)[28] were observed in the laboratory in 1993 by using a new microwave spectroscopic method: pulsed-discharge nozzle Fourier transform microwave spectroscopy. This microwave spectroscopic method is mainly operated in the centimeter wave region and suitable for high-sensitivity observations of medium sized molecules, especially combined with free-jet molecular production in the absorption cavity. Consequently one interstellar line detected toward the circumstellar envelope of a late-type carbon star, IRC + 10216, was tentatively assigned to that of C_5S,[29] but this requires a further confirmation.

The structures of C_nS are summarized in Table III. When the appropriate bonding structure is applied to C_nS, the number of the π electrons is accounted to be $2n+2$ for C_nS. Hence, a member of this series with an odd number of carbon atoms has an electronic configuration of $(\pi)^4$, a closed shell, whereas one with an even number a configuration of $(\pi)^2$. According to Hund's rule, the half filled π orbital gives the lowest electronic state of $^3\Sigma^-$. The ground electronic states and the molecular structures concluded from spectroscopic and theoretical studies are consistent with this prediction; linear molecules in the $^1\Sigma$ state for the $n=$ odd members and in the $^3\Sigma$ state for the $n=$ even ones. Table III also shows the relatively small variation in the C–C bond lengths.[13,28] This means that the bonding between the carbon atoms is of a cumulene type rather than of a type with alternating triple and single bonds.

3. HC_nS

The discovery of CCS and C_3S in space has stimulated much interest in other carbon-chain molecules. Another sulfur-bearing carbon-chain molecule series HC_nS is such an example and its spectroscopic studies have been started mainly in the laboratory.

When one hydrogen atom combines to form a σ bond with the terminal carbon atom of C_nS, the molecule has a π electronic configuration for members with an odd number of carbon atoms and a π^3 configuration for members with an even number. According to Van Vleck's theory[31] the HC_nS members with an odd number of carbon atoms have a $^2\Pi_r$ ground electronic state with a positive (regular) spin–orbit coupling constant and the members with an even-number a $^2\Pi_i$ state with a negative (inverted) constant.

The linear structure of HC_nS is an interesting feature. When the unpaired electron is located at one of the carbon atoms, the chain should show some deviation from a linear structure, $\mathrm{H{-}\dot{C}{=}C{=}}$, or $\mathrm{{\equiv}C{-}\dot{C}{=}C{=}}$, whereas the molecule must be linear when the unpaired electron is localized at the terminal sulfur, $\mathrm{{\equiv}C{-}\dot{S}}$. Therefore, the linearity of the molecule depends on the delocalization of the unpaired electrons.

From the viewpoint of molecular spectroscopy, another interesting feature of HC_nS is the Renner–Teller effect in linear molecules having a degenerate ground electronic state. A linear molecule has one or more degenerate bending modes, and the strong vibronic interaction between orbital electrons and vibrational angular momenta stabilizes the molecule if it has a bent structure. The experimental and theoretical studies so far reported have been limited to triatomic molecules with one degenerate bending mode such as NCO and NCS.[32,33]

3.1. HCS (Thioxomethyl)

The first member of the HC_nS family, HCS, is expected to have a bent structure in the $^2A'$ ground electronic state similar to that of the well-known free radical HCO. The bent structure is brought about by the strong Renner–Teller interaction which removes the degeneracy of the $^2\Pi$ ground electronic state in the linear configuration of HCO and HCS. HCO has been spectroscopically well studied, but HCS has been a difficult target, although its spectroscopic properties have been predicted by several sophisticated *ab initio* calculations.[34–36]

The existence of HCS in the gas phase was reported only a few years ago. Anacona[37] reported the detection of the HCS radical by far-infrared laser magnetic resonance spectroscopy. He presented several chemical tests and a qualitative description of the identification of its transitions, but did not show any definite assignment of the spectral lines detected. In 1993 Ruscic and Berkowitz[38] reported a study of the photoionization mass spectrometry of HCS. They prepared HCS from CH_3SH by sequential hydrogen abstraction with fluorine and determined its formation enthalpy to be 71.7 ± 2.0 kcal/mol. Very recently

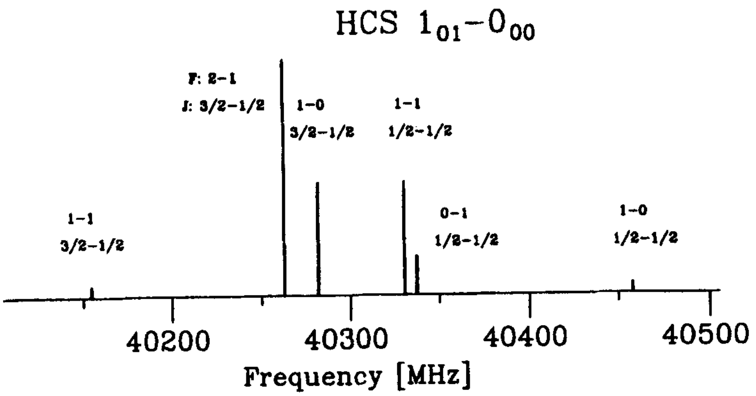


FIGURE 4 Fine and hyperfine structure pattern observed for the 1_{01}-0_{00} transition of HCS.[40]

Kaiser *et al.*[39] carried out molecular cross beam experiments of atomic carbon with H_2S and verified the existence of HCS in the X^2A' ground electronic state.

Finally, Habara *et al.*[40] detected the 1_{01}-0_{00} rotational transition of HCS (X^2A') by using a Fourier transform microwave spectrometer, as shown in Figure 4. The HCS radical was produced by a dc discharge in a mixture of CH_4 and H_2S diluted with Ar. Only the lowest a-type R-branch transition was measured in this study. The Fermi contact term of 127.427 MHz derived from the hyperfine structure of the hydrogen nucleus (Figure 4) indicates that the HCS radical is a σ radical with $^2A'$ symmetry, and the observed effective rotational constant $(B_0 + C_0)/2$ of 20 145.455 MHz is in good agreement with the 20 099 MHz calculated from the latest theoretical prediction by Kaiser *et al.*[41] Further detailed information regarding HCS will be available from its millimeter-wave spectrum.[42]

3.2. *HCCS (Thioxoethenyl)*

The identification of HCCS in the gas phase was reported in 1978 by Krishnamachari and his collaborators[43,44] who observed the absorption spectrum of HCCS and DCCS generated by flash photolysis of thiophene and deuterated thiophene, respectively. Later, rotationally resolved emission spectroscopy[45] and laser induced fluorescence spectroscopy[46] were also reported and vibrational assignments were proposed, but the determination of the spin–orbit coupling constant was inconclusive. A full characterization of HCCS was achieved by microwave spectroscopic studies,[47,48] reporting detailed molecular constants. Vrtilek *et al.*[48] studied the microwave spectra of three isotopic species DCCS, $HC^{13}CS$ and $HCC^{34}S$ as well as the main species and confirmed that the molecular structure predicted theoretically by Goddard[49] reproduces the observed rotational constant to 0.1%. They also reported the spin–orbit coupling constant to be $-185\,cm^{-1}$, which largely deviated from a predicted value of $-360\,cm^{-1}$.[50]

Tang and Saito[51] measured and analyzed the microwave spectra of HCCS and DCCS in excited vibronic states. The spectral lines of vibrationally excited states appear as weak satellite lines around the line of the vibrational ground state and their intensities are proportional to the Boltzmann factor of the excited states, as exemplified in Figure 5. They developed the theory of the Renner–Teller effect for two bending modes

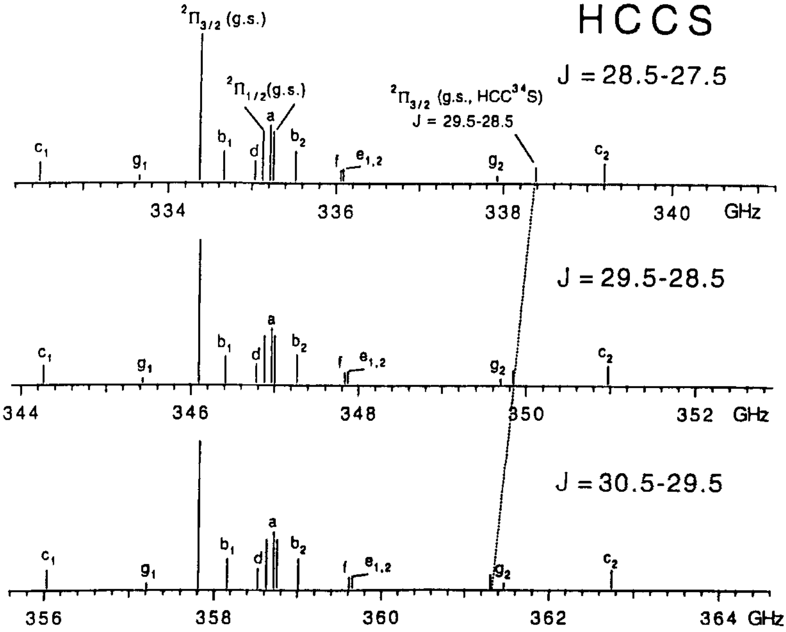


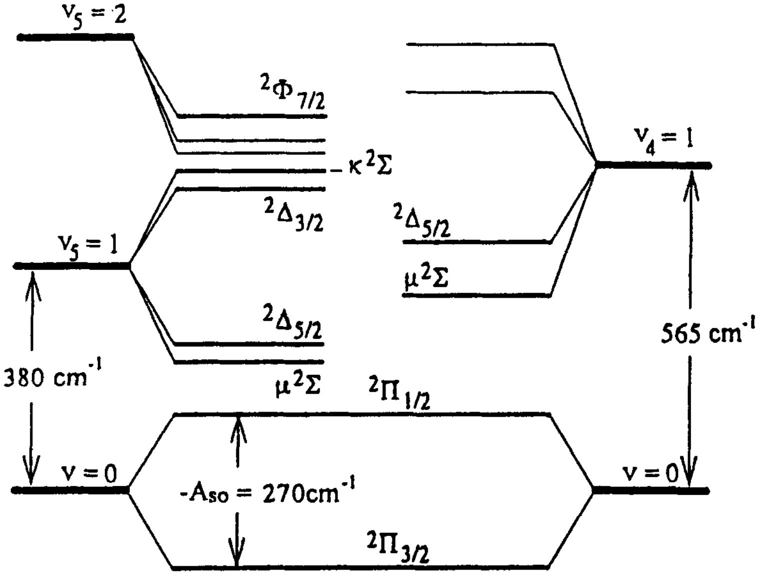
FIGURE 5 Spectral diagram of the rotational transition series observed for the low-lying vibronic states of HCCS. The satellite lines named as a–g are the lines of the vibrationally excited levels of the bending modes.

and introduced a new coupling term ε_{ij} between two separate vibronic interactions, ε_i and ε_j for the ν_i and ν_j levels, respectively. They applied the theory to the analysis of the observed spectra of HCCS and DCCS in the excited levels of two bending modes, ν_4 and ν_5, and found that the anomalously large spin-rotation coupling constants of the $^2\Sigma$ levels of HCCS in the $v_4 = 1$ and $v_5 = 1$ levels are nicely explained by considering a mixing parameter of Renner–Teller interaction ε_{45} between both the modes. This analysis correlated the vibronic energy levels with two bending modes for both the species as demonstrated in Figure 6. This result is consistent with the latest *ab initio* prediction by Szalay.[52]

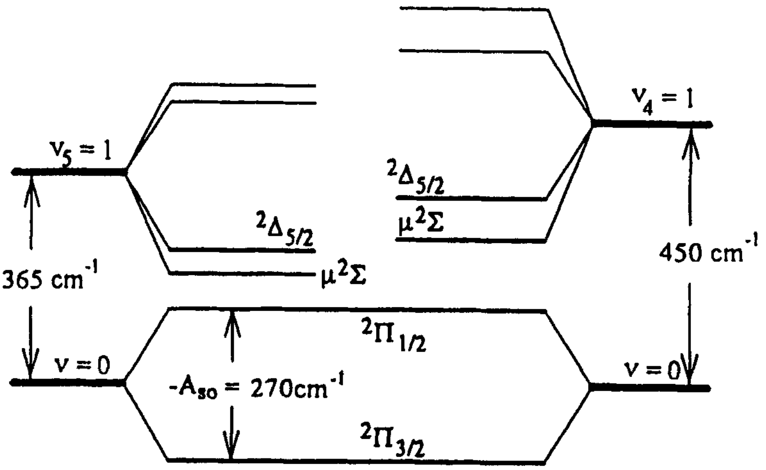
3.3. HC_3S (3-Thioxo-1,2-propadienyl) and HC_4S (4-Thioxo-1,2,3-butatrienyl)

Longer carbon-chain members of HC_nS have rarely been studied and discussed prior to the detection of HCCS. The compounds HC_3S and HC_4S have been identified in the gas phase only by microwave spectroscopic studies. McCarthy *et al.*[52] used almost the same conditions as for HCCS to generate HC_3S and DC_3S. They measured the spectral lines in the millimeter-wave region for both substates of $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$, and determined detailed molecular constants, finding that the spin–orbit coupling constant was only 44 cm^{-1}, which was compared with −270 cm^{-1} for HCCS,[51] 14.4 cm^{-1} for C_3H[54] or 23.7 cm^{-1} for C_5H.[55] This implies that the unpaired electron in HCCS is not localized on the sulfur atom. They also performed an *ab initio* calculation at the QCISD level for HC_3S and found that a form bent at the CCS backbone was the most stable geometrical isomer and that the linear $^2\Pi$ state was located only slightly higher in energy than the bent structure.

Hirahara *et al.*[56] observed the spectral lines of HC_3S and HC_45 in the 10 GHz region with Fourier transform microwave spectroscopy. They studied the spectral lines of the deuterium and ^{34}S species of HC_3S and determined the total bond length of HC_3S to be 5.107 Å which is slightly shorter than the 5.176 Å predicted by the QCISD calculations.[53] Based on the hyperfine structure of HC_3S they concluded a relatively large delocalization of the unpaired electron in the radical, which is consistent with a valence-bond structure composed of two canonical forms, $H-\dot{C}=C=C=S$ and $H-C\equiv C-\dot{C}=S$. They also measured several rotational transitions of HC_4S and DC_4S in the $^2\Pi_{3/2}$ state, indicating that the



(a) HCCS



(b) DCCS

FIGURE 6 Energy level diagrams for the vibronic structures of (a) HCCS and (b) DCCS.

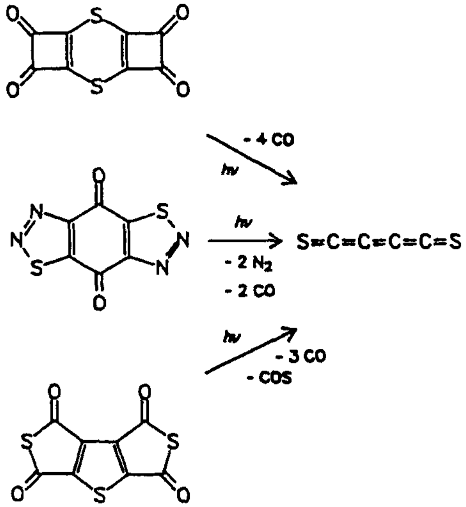
ground electronic state of HC_4S was $^2\Pi_i$, but the detailed molecular structure of HC_4S is not determinable only from the rotational constants of the two isomers HC_4S and DC_4S.

4. C_nS_2, C_nOS, AND C_nO_2

The simplest members of the series C_nS_2, C_nOS, and C_nO_2 are very familiar in the laboratory, i.e. CS_2, OCS, and CO_2, respectively. The ground electronic state of these two heteroatoms-bearing molecules is a singlet for an odd-number carbon-chain and a triplet for an even-number carbon-chain. Unlike the methods of generation for C_nS and HC_nS described above, the preparation of the members of the two heteroatoms-bearing carbon-chains is different for each member and only a limited number of two heteroatoms-bearing carbon-chain molecules are known. The preparation of C_3S_2 was reported in 1912, using an intermittent dc discharge in dry CS_2,[57] and that of C_3O_2 in 1954, using low-temperature dehydration of malonic acid with P_2O_5.[58]

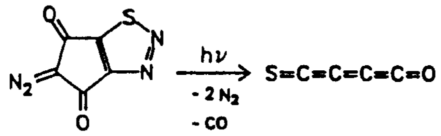
The preparation of higher members was reported very recently. Maier and his collaborators presented a unique preparation method for two heteroatoms-containing carbon-chain molecules.[19,59] They prepared C_4S_2 by photolyzing the following tricyclic compounds.

C_4S_2:

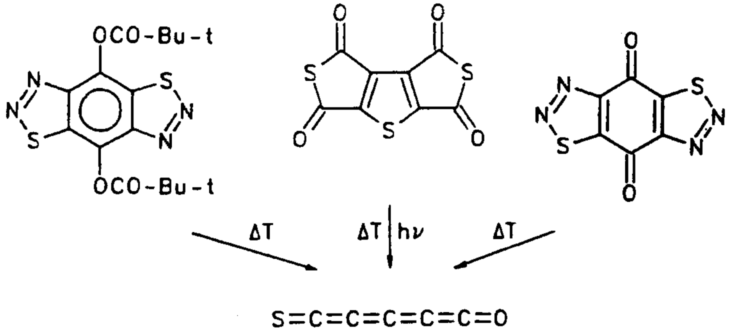


and measured its IR spectrum in an Ar matrix. They similarly prepared C_4OS and C_5OS by photolysis or thermal decomposition of the following tricyclic compounds.

C_4OS:



C_5OS:



and measured the IR and Vis/UV spectra of both species in an Ar matrix. Except C_4S_2, no even-number carbon-chain species have been studied by spectroscopic methods.

The main interesting spectroscopic feature of the two heteroatoms-bearing carbon-chain molecules is the linearity of their molecular frame. Most spectroscopic studies of C_3O_2[60–65] have focused on this point. However, the lowest bending frequency sensitive to the quasilinearity is estimated to be in the region below $100\,cm^{-1}$ where high-resolution and high-sensitivity spectroscopic methods are not easily available. Moreover, C_nO_2 has a center of symmetry and a zero dipole moment so that the microwave spectroscopic method is not applicable. The CCC bending frequency of C_3O_2, ν_7, was considered to be very low and a study by infrared and Raman spectroscopy allowed to observe its combination and hot bands.[60–64] In the 1970s, the electron diffraction method was applied to interpret the molecular structure and mean amplitude of C_3O_2 by a model of the shrinkage effect.[66,67] However, the estimated band origin of ν_7 was not definitely obtained, but seemed to be around 19 cm^{-1}. Finally the band origin was determined to be 18.2 cm^{-1} in 1979 by Burenin *et al.*[65] by direct measurement of the ν_7 mode with the submillimeter wave technique. The CCC bending mode of C_3S_2 was determined to be 94 cm^{-1} from its infrared and Raman spectra by Smith and Leroi,[68] which was interpreted as a bending mode of a rigid linear molecule. The studies of the quasilinearity of C_3S_2, C_3OS, and C_3O_2 have been summarized and discussed in a comprehensive review by Winnewisser.[69] Higher members of the C_nS_2 and C_nO_2 series have rarely been reported. Maier *et al.*[70] reported the preparation of C_5O_2 by UV photolysis or thermal decomposition of a tris(diazo) ketone and the observation of its IR absorption bands in an Ar matrix without their assignment. Holland *et al.*[71] studied the very unstable C_5O_2 molecule in the gas phase by FTIR spectroscopy. They assigned $\nu_2 - \nu_{10}$ bands of C_5O_2 and determined its molecular constants in the ground and $v_4 = 1$ vibrational levels.

On the other hand, C_nOS molecules have a permanent dipole moment and the $n = 3$ member C_3OS has been subjected to several microwave spectroscopic studies as well as infrared studies. Since the first microwave spectroscopic detection of C_3OS by Winnewisser and Christiansen,[72] a sample of which was prepared by the low-yield reaction of C_3O_2 with P_4S_{10}, C_3OS has been subjected to various spectroscopic studies[73–78] aimed at the determination of the CCC bending potential. Nicolaisen and Christiansen[75] recorded the IR spectrum of C_3OS in the region of 4000–200 cm^{-1} and performed an assignment of all fundamental bands. They reported that the ν_7 band of the CCC bending mode could be deduced to be 77 cm^{-1} from the difference band $\nu_2 - \nu_7$. Winnewisser and Peau[73] measured the relative intensities of the rotational transitions in the $v_7 = 1–7$ states and concluded the harmonic wave number to be 84.50 ± 0.63 cm^{-1}. In 1991 Holland and Winnewisser[77] measured the mid-infrared bands of C_3OS by high-resolution FTIR spectroscopy, determining ν_7 to be 77.63094(20) cm^{-1}, and finally concluded that C_3OS is a relatively rigid linear molecule with a low-lying but nevertheless harmonic CCC bending vibration. This conclusion shows a clear comparison with C_3O_2 which apparently indicates a quasilinear behavior in the lowest bending mode as described above. Holland *et al.*[78] measured the Zeeman effect on the rotational transitions of C_3OS and determined its magnetic susceptibility and g factors yielding the sign of the permanent electric dipole moment, $^{-}OCCCS^{+}$. The interstellar spectral lines of C_3OS have been searched for in cold dark clouds without success.[79] The various molecular properties of C_nOS including the even-number carbon-chain molecules with $n = 2{-}6$ have been predicted by *ab initio* calculations.[80]

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