Microwave Detection of Thioformaldehyde

Abstract. *Thioformaldehyde (H_2CS) has been detected and characterized from its microwave spectrum. Preliminary analysis of rotational transitions for the sulfur-32-containing form of H_2CS shows this new species to have* C_{2v} *symmetry with rotational constants (in megahertz) of* A = *292,729,* B = *17,698, and* C = *16,652. The possibility of detection of thioformaldehyde in the interstellar medium is discussed, and a table of transitions expected to be of importance for that detection is presented.*

Thioformaldehyde (H_2CS) has been successfully generated and characterized from its gas-phase rotational spectrum. It seems likely that this new species will be an astronomically important molecule in view of the recent detection of the spectrum of interstellar formaldehyde (H_2CO) in a large number of radio sources in our galaxy (*1*). For this reason we report the preliminary results of our study of this sulfur-containing analog of formaldehyde. Efforts to determine an accurate structure from a study of the spectra of isotopically substituted species are now under way and will be reported when complete.

A trimer of thioformaldehyde under the name *s*-trithiane has been available commercially for some time. Attempts to isolate the monomer by a variety of techniques have been reported (*2*). In a recent note on the flash photolysis of simple sulfur-containing molecules in the gas phase, an observed ultraviolet band has been tentatively assigned to the electronic spectrum of thioformaldehyde (*3*). This assignment was based primarily on chemical evidence and no detailed analysis was reported.

Table 1. Microwave spectrum and rotational constants of H_2CS^{32}. The rotational constants were determined from a least-squares fit of a larger group of transitions (including those listed here) to a rigid rotor formulation. Standard errors were obtained from the least-squares fit and may be several times too small because of contributions from centrifugal distortion.

Transition	Observed frequency* (Mhz)	Calculated frequency (Mhz)
$1_{01} \leftarrow 0_{00}$	34,351.43 ± 0.02	34,350.74
$1_{10} \leftarrow 1_{11}$	(Not measured)	1046.48 ± 0.02†
$2_{11} \leftarrow 2_{12}$	3139.38 ± 0.03	3138.57
$3_{12} \leftarrow 3_{13}$	6278.65 ± 0.01	6277.15
$4_{13} \leftarrow 4_{14}$	10,463.97 ± 0.01	10,461.89
$5_{14} \leftarrow 5_{15}$	15,695.12 ± 0.02	15,692.74
$6_{15} \leftarrow 6_{16}$	21,971.71 ± 0.02	21,969.60

A = 292,729.16 ±35.99 Mhz
B = 17,698.47 ± 0.29 Mhz
C = 16,652.27 ± 0.29 Mhz
$\Delta = I_c - I_a - I_b = +0.0676$ amu Å^2

* These errors are an estimate of the accuracy of the measurements. † This value has been adjusted to include the effect of centrifugal distortion as outlined in the text.

In the investigation reported here a microwave spectrometer with a parallel-plate absorption cell coupled to a fast-flow pumping system was used (*4*). We were able to observe thioformaldehyde initially under continuous-flow conditions by reacting the products of a radio-frequency discharge in methane (CH_4) with carbon disulfide (CS_2) downstream from the discharge zone.

Subsequent experiments demonstrated that the discharge products of methane would react with nearly any small sulfur-containing molecule to produce the species in question. Even the reaction of hydrogen atoms with weakly discharged carbon disulfide produced detectable results. Clearly the species being generated was a significant reaction product and appeared reasonably stable, with a lifetime dependent on the reactive surroundings in which it was produced. Dimethyldisulfide (CH_3SSCH_3), passed through a weak radio-frequency discharge at low pressures (~ 10 μm of Hg), was finally settled upon as the easiest and most efficient generator of the new species.

We obtained initial predictions of the thioformaldehyde spectrum by assuming a carbon-hydrogen geometry similar to that of formaldehyde with a carbon-sulfur bond estimated by analogy with other similar compounds. Observation of the $1_{01} \leftarrow 0_{00}$ transition and its subsequent identification from the Stark effect allowed slight adjustments to the parameters and fairly accurate predictions of a number of other transitions. Observed transitions thought to be of astronomical importance are reported in Table 1. The calculated frequencies were obtained by fitting the observed frequencies listed in Table 1, together with some observed transitions of the $K_p = 2$ series (for example $15_{2,13} \leftarrow 15_{2,14}$) and a few other transitions at higher frequencies, to a standard rigid rotor formulation. The $K_p = 2$ series transitions must be included in this fit in order to determine the value of the rotational constant about the axis of symmetry of the molecule.

Even though the effects of centrifugal distortion were neglected in the present treatment, the agreement between the calculated and observed transitions is quite reasonable. Preliminary calculations including the effects of centrifugal distortion indicate that the $1_{10} \leftarrow 1_{11}$ frequency calculated from the rigid rotor model was low by 0.30 Mhz. The calculated value for the $1_{10} \leftarrow 1_{11}$ transition of 1046.48 ± 0.02 Mhz (Table 1) includes a correction for distortion; the variation limits are based on the estimated accuracy of this correction.

Since the present observations on thioformaldehyde are all spectroscopic in nature, we shall summarize the arguments establishing the existence of this new molecule. Important structural information may be obtained directly from the rotational constants (*A, B, C*) presented in Table 1. The magnitude of *A* clearly indicates that the contribution to the moment of inertia from the atoms lying off the corresponding principal axis is small, a result which is quite compatible with the initial assumption of a formaldehyde-like structure. The inertial defect ($I_c - I_a - I_b$) obtained from these rotational constants was found to be a small positive number, comparing very favorably with the value of + 0.0574 atomic mass unit Å^2 obtained for formaldehyde (*5*). This small positive inertial

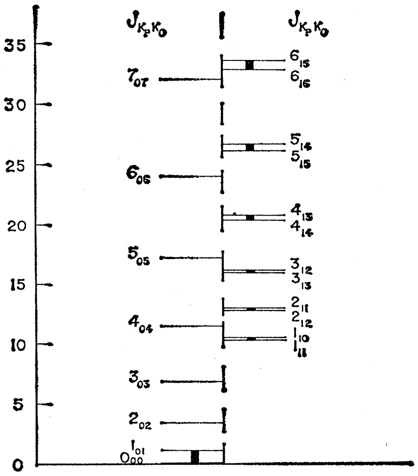

Fig. 1. The lowest lying rotational energy levels of thioformaldehyde (H_2CS^{32}).

defect provides strong evidence that the new species is planar.

All the transitions listed in Table 1 are active through a component of the permanent electric dipole moment lying along the axis of the smallest moment of inertia, designated as the *a* axis. Transitions active through a dipole moment along the other principal axis in the plane of the molecule were not detected, thus suggesting a twofold symmetry (C_{2v}) about the *a* axis. Preliminary measurements of the Stark effect place the permanent electric dipole moment near 1.6 debye.

A comparison of the relative intensities between the $K_p = 1$ and $K_p = 2$ series Q branch transitions ($\Delta J = 0$) indicated that the observed intensities were being altered by the effects of nuclear spin statistics. An arrangement in which two hydrogen atoms with the nuclear spin $I = \frac{1}{2}\hbar$ were placed symmetrically off the *a* axis brought the observed relative intensities into agreement with theory. Isotopic studies now under way have established that the atoms lying on the symmetry axis are indeed carbon and sulfur. The assignment of this newly observed species to thioformaldehyde has therefore been positively confirmed.

The lowest-lying rotational energy levels of thioformaldehyde are illustrated schematically in Fig. 1, with the transitions listed in Table 1 indicated by heavy black lines. The diagram has been divided into two "stacks" to illustrate that electric dipole transitions between the two sets of levels are forbidden by selection rules. In the absence of collisional transfer, the 1_{11} level will, therefore, become metastable with respect to lower lying levels. This feature of the energy structure will considerably increase the chances of observing the $1_{10} \leftarrow 1_{11}$ transition of thioformaldehyde in the interstellar medium as it did for the same transition in formaldehyde (*1*).

The $1_{10} \leftarrow 1_{11}$ transition in formaldehyde has been detected in absorption in an estimated 50 galactic sources (*6*). At least three of these sources proved intense enough to allow the detection of signals due to the less abundant carbon-13 isotopic form of formaldehyde (*7*). This fact coupled with current estimates of stellar oxygen-sulfur abundance ratios ranging from 10 to 1 (*8*) to 50 to 1 (*9*) provide a strong case for the prediction of detectable signals from interstellar thioformaldehyde.

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A Search for the $1_{10} \leftarrow 1_{11}$ Transition of Interstellar Thioformaldehyde

Abstract. *A search has been made for the $1_{10} \leftarrow 1_{11}$ transition of thioformaldehyde in interstellar clouds where formaldehyde is known to exist. Failure to detect this transition indicates that the ratio of thioformaldehyde abundance to that of formaldehyde is probably less than the abundance ratio of sulfur to oxygen.*

Formaldehyde ($H_2C^{12}O$) absorption has been observed by Snyder *et al.* in many directions in the galaxy (*1*). Zuckerman *et al.* (*2*) have found interstellar absorption by the isotopic species $H_2C^{13}O$. The microwave spectrum of the analog thioformaldehyde ($H_2C^{12}S$) has recently been observed in the laboratory by Johnson and Powell (*3*). Since the cosmic abundance of sulfur is about 1/40 that of oxygen (*4*), we might expect to detect absorption by $H_2C^{12}S$ in the interstellar medium. Our failure to detect the $1_{10} \leftarrow 1_{11}$ transition of $H_2C^{12}S$ at 1046.48 Mhz indicates that the abundance of $H_2C^{12}S$ is, in fact, less than 1/40 that of $H_2C^{12}O$.

The expected optical depth of $H_2C^{12}S$ may be calculated by comparison with $H_2C^{12}O$. We consider the relative abundance of $H_2C^{12}S$ to $H_2C^{12}O$ to be 1/40, the cosmic abundance of S to O, and assume an excitation mechanism which populates the relevant levels in $H_2C^{12}S$ in the same ratio as those in $H_2C^{12}O$. The same ratio for the populations of the two levels, rather than the same excitation temperature, is assumed, because interstellar $H_2C^{12}O$ is not generally in equilibrium with its surroundings. Johnson and Powell (*3*) report that the dipole moment of H_2CS is 0.7 times that of $H_2C^{12}O$. Thus the relation between the two optical depths is $\tau(H_2C^{12}S) = 1.2 \times 10^{-2}\, \tau\,(H_2C^{12}O)$. On the other hand, if equal excitation temperatures are assumed, rather than equal population ratios, $\tau\,(H_2C^{12}S) = 2.6 \times 10^{-3}\, \tau\,(H_2C^{12}O)$. We use the former assumption, that of equal relative populations, in all of the ensuing discussion.

Because absorption due to the lowest rotational doublet of $H_2C^{12}O$ may show saturation in some cases, we have also estimated the optical depth of $H_2C^{12}S$ by comparisons with other lines. Saturation effects should be much less in the case of absorption by $H_2C^{13}O$; absorption lines from this molecule have been detected in several of the sources we examined (*2*). If we assume that $H_2C^{12}O$ and $H_2C^{13}O$ exist in the ratio 89 : 1 (the ratio of terrestrial abundances of C^{12} and C^{13}), we find $\tau\,(H_2C^{12}S) = 1.1\, \tau\,(H_2C^{13}O)$.

The expected optical depths for H_2CS may also be estimated by comparison with measurements of $H_2C^{12}O$ in the $2_{11} \leftarrow 2_{12}$ transition (*5*) or in the $3_{12} \leftarrow 3_{13}$ transition (*6*). By direct comparison, $\tau\,(H_2C^{12}S) = 1.2 \times 10^{-2} R\, \tau\,(H_2C^{12}O;\, 2_{11} \leftarrow 2_{12})$, where R is defined as the theoretical ratio of optical depths $\tau\,(H_2C^{12}O;\, 1_{10} \leftarrow 1_{11})/\tau\,(H_2C^{12}O;\, 2_{11} \leftarrow 2_{12})$, which is also roughly equal to the ratio of the populations in the $J = 1$ and $J = 2$ levels. We have used a Boltzmann population ratio, assuming that the two levels are in equilibrium with the radiation flux at 2 mm. If we assume a radiation temperature of 2.7°K, we find $R = 12$; if the radiation temperature is 5°K, we find $R = 4$.

Our search for the $1_{10} \leftarrow 1_{11}$ line of $H_2C^{12}S$ at 1046.48 Mhz was made with the 85-foot (26-m) antenna at the Hat Creek Radio Observatory. The