

Fourier transform millimeter-wave spectroscopy of the HCS radical in the $^2A'$ ground electronic state

Hideta Habara and Satoshi Yamamoto

Department of Physics, The University of Tokyo, Bunkyo-ku, Tokyo 113-0033, Japan

Christian Ochsenfeld and Martin Head-Gordon

Department of Chemistry, University of California, Berkeley, California 94720

and Chemical Science Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720

Ralf I. Kaiser^{a)} and Yuan T. Lee

Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei 106, Taiwan, Republic of China

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The $1_{01}-0_{00}$ rotational transition of the HCS radical in the \tilde{X}^2A' ground electronic state has been observed with a Fourier transform millimeter-wave spectrometer in combination with a pulsed discharge nozzle. The radical is produced by discharging a mixture of CH_4 and H_2S diluted in Ar. Six fine and hyperfine components are detected, and the effective rotational constant, spin-rotation interaction constant, and hyperfine interaction constants are determined accurately. The Fermi contact term of the hydrogen nucleus is found to be much smaller than that for the isovalent radical, HCO, indicating that the HCS radical is more close to a linear structure than the HCO radical.

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INTRODUCTION

The HCS radical is a fundamental reaction intermediate containing a single sulfur atom in combustion processes,¹ interstellar chemistry,² and during the collision of comet Shoemaker-Levy 9 with Jupiter.³ This radical was also identified as a reactive intermediate in hydrogen abstraction reactions of methyl mercaptane (CH_3SH) with F atoms by means of photoionization mass spectroscopy.⁴ In extraterrestrial environments like cold, molecular clouds, the sulfur chemistry is closely related to the carbon chemistry, and hence, a number of sulfur-bearing neutral species such as H_2S , CS, H_2CS , OCS, C_2S , and C_3S are known to be abundant in various astronomical sources.^{5,6} A chemical model calculation of interstellar molecular clouds predicts a moderate abundance of HCS; Lee *et al.*² estimated the fractional abundance of HCS relative to the H_2 abundance to be 10^{-11} , about 1/10 of H_2CS . Therefore HCS should be detectable in molecular clouds by radioastronomical observations, and its abundance would be of crucial importance to test chemical models of molecular clouds.

Despite the importance of the HCS radical, no spectroscopic study has been reported for this important reaction intermediate until recent, tentative detection by the far-infrared laser magnetic resonance spectroscopy.⁷ In this study, a number of resonances were observed in a discharge plasma of H_2S and CO, but they were too complicated to be assigned definitively. Although the observed resonance lines are considered to be due to HCS on the basis of the production chemistry and the isotopic studies, no molecular constants have been determined. A few *ab initio* calculations

have been reported for geometrical structure, vibrational frequencies, and dipole moment of the HCS radical.^{3,8-10}

On the other hand, the rotational spectra of the related isovalent species have been studied extensively. The pure rotational spectrum of the HCO radical was first detected by Saito,¹¹ and further measurements including the submillimeter-wave lines were carried out by Austin *et al.*¹² and Blake *et al.*¹³ The rotational spectrum of the HSiO radical was recently detected by Izuha *et al.*¹⁴ They produced the HSiO radical in a discharge plasma of SiH_4 and N_2O , and reported detailed molecular constants including hyperfine interaction constants. The rotational spectrum of the HSiS radical was found in a discharge plasma of SiH_4 and OCS by Brown *et al.*¹⁵

A reason why the rotational spectrum of HCS has not been detected so far seems to be a small dipole moment along the *a* axis (0.4 D).^{3,8} As a result, the *a*-type transitions of HCS are fairly weak. On the other hand, a search for the *b*-type transitions would be difficult because of a large uncertainty in the rotational constant, *A*. The Fourier transform millimeter-wave spectroscopy combined with a pulsed discharge nozzle is a powerful method for studying a free radical with a small dipole moment. We have recently extended the observable frequency of our spectrometer up to 52 GHz with sufficient sensitivity for transient species. With this new spectrometer, we have detected the $1_{01}-0_{00}$ rotational transition of HCS for the first time.

EXPERIMENT

A Balle-Flygare type Fourier transform millimeter-wave spectrometer newly developed at the University of Tokyo was used in combination with a pulsed discharge nozzle. Details of the spectrometer will be described elsewhere. A

^{a)}Also at: Department of Physics, Technical University Chemnitz-Zickau, 09107 Chemnitz, Germany.

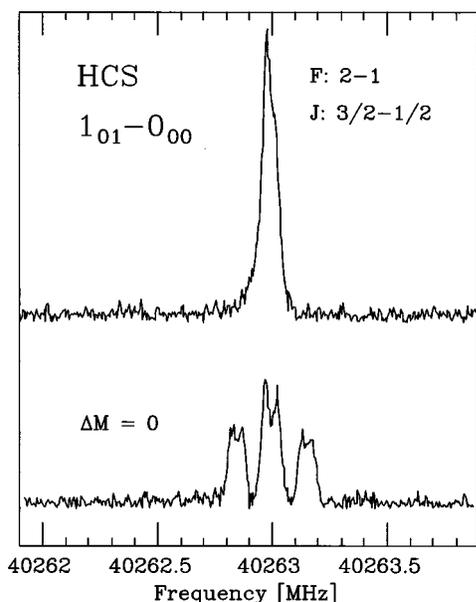


FIG. 1. A typical example of the $F=2-1$ and $J=3/2-1/2$ component of the $1_{01}-0_{00}$ transition of HCS. The lower trace is obtained without correction of the earth magnetic field parallel to the polarization of the free induction decay. Three Zeeman components with $M=1-1$, $M=0-0$, and $M=(-1)-(-1)$ are observed.

gaseous mixture of CH_4 and H_2S was diluted in Ar, and released into the vacuum chamber from the pulsed discharge nozzle. A pulsed high voltage of 1.5 kV was added to the discharge electrodes attached to the nozzle. For measurements of paramagnetic lines, the earth magnetic field was compensated by using three Helmholtz coils placed perpendicularly to one another. The production conditions were first optimized by monitoring the $1_{01}-0_{00}$ line of H_2CS .

The rotational constants of HCS were estimated by using the geometrical structure reported by the *ab initio* calculations.^{3,8,9} We predicted the frequencies of the hyperfine components of the $1_{01}-0_{00}$ transition with aid of the spin-rotation interaction constants and hyperfine interaction constants taken from those of HCO^{13} with corrections for difference in the rotational constants. We searched for the HCS line on the basis of the prediction. After scanning over the 200 MHz range, we first found a paramagnetic line at 40 263 MHz as shown in Fig. 1. This line was also observed by discharging a mixture of CS_2 and CH_4 , H_2S and CO , or $(\text{CH}_2)_3\text{S}$, diluted in Ar. However, the line was not observed with CH_4 or CS_2 diluted in Ar. These chemical behaviors indicate that the molecule responsible for the line contains the C, S, and H atoms. The CH_3S radical (2E) is expected to give a number of hyperfine components of the $J=3/2-1/2$ transition around the 40 GHz region. Although we calculated transition frequencies of all the fine and hyperfine components of CH_3S by use of the molecular constants reported in Ref. 16, none of them corresponds to the 40 263 MHz line. In fact we observed one of the CH_3S lines, and found that it is much weaker than the 40 263 MHz line in the above discharge system. Therefore the line observed at 40 263 MHz was thought to be a good candidate for one of the hyperfine components of the HCS radical.

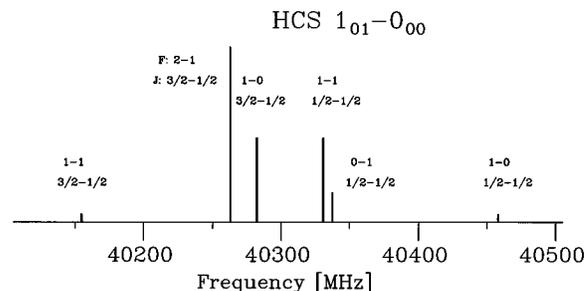


FIG. 2. Fine and hyperfine structure pattern observed for the $1_{01}-0_{00}$ transition. All the six components are detected in the present study.

We carried out a deep search for the other hyperfine components around the 40 263 MHz line, and successively found five other paramagnetic lines as shown in Fig. 2. The lines show a typical pattern for the fine and hyperfine structures of the doublet radical with the hyperfine structure of the $I=1/2$ nucleus. This pattern is very similar to that expected for the $1_{01}-0_{00}$ line of HCS, and hence, we finally concluded that the observed lines are due to the HCS radical. On the basis of the observed intensity, we assigned the individual components as indicated in Fig. 2.

We inspected the Zeeman effect of the observed lines for further confirmation. For this purpose, the power supply for one of the Helmholtz coils was turned off, giving the residual earth magnetic field parallel to the polarization of the microwave. In this condition, the Zeeman component lines with $\Delta M=0$ are observed. Since the 40 263 MHz line is assigned to the $F=2-1$ component, we expect three Zeeman components with $M=0$ and $M=\pm 1$. The observed Zeeman pattern shown in the lower trace of Fig. 1 is consistent with this expectation. On the other hand, the 40 331 MHz line is assigned to the $F=1-1$ component, and we expect two Zeeman components with $M=\pm 1$. Note that the $M=0$ component has no intensity. In fact we observed two Zeeman components as shown in Fig. 3. These results further strengthen our conclusion that the lines are due to the HCS radical.

The optimum condition for production of HCS in our system is as follows; H_2S (0.5%) and CH_4 (0.5%) are diluted in Ar, and are introduced into the pulse discharge nozzle with the stagnation pressure of 2.0–2.5 atm. We integrated 1000–6000 shots with a repetition rate of 5 Hz to obtain the spectral lines with sufficient signal-to-noise ratio for precise measurements. The line frequency was determined by averaging at least three measurements. The results are summarized in Table I.

On the basis of the present data, we have just succeeded detecting the high N rotational lines with $K_a=0$ with a millimeter- and submillimeter-wave absorption spectrometer, details of which will be described separately.

RESULTS AND DISCUSSION

The HCS radical is an asymmetric top molecule which is very close to a prolate symmetric top. Since the rotational levels of $K_a=0$ are well isolated from the other K_a levels because of a large A rotational constant, we can treat the

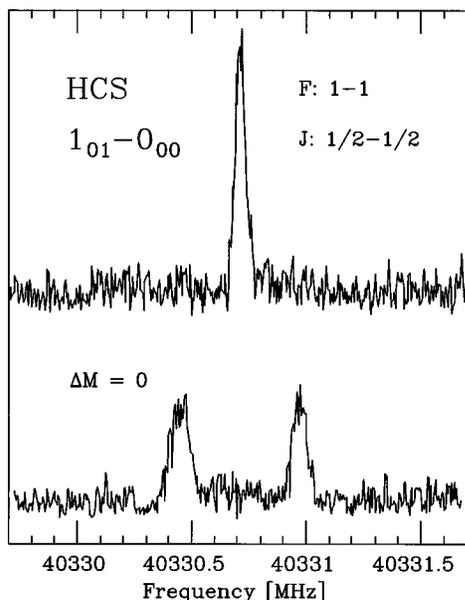


FIG. 3. A typical example of the $F=1-1$ and $J=1/2-1/2$ component of the $1_{01}-0_{00}$ transition of HCS. The lower trace is obtained without correction of the earth magnetic field parallel to the polarization of the free induction decay. Two Zeeman components with $M=1-1$ and $M=(-1)-(-1)$ are observed. Note that the $M=0-0$ component has no intensity, and hence, it is not observed.

spectral lines with $K_a=0$ as if they were of a linear molecule. Since we only observed the $1_{01}-0_{00}$ transition, we analyzed the observed frequencies by using the conventional Hamiltonian for a linear free radical with the $^2\Sigma$ state including hyperfine interaction;^{17,18}

$$H = B_{\text{eff}}\mathbf{N}^2 + \gamma_{\text{eff}}\mathbf{N}\cdot\mathbf{S} + b\mathbf{I}\cdot\mathbf{S} + cI_zS_z, \quad (1)$$

where \mathbf{N} , \mathbf{S} , and \mathbf{I} represent the angular momentum operators for the end-over-end rotation, the electron spin, and the nuclear spin of the hydrogen nucleus, respectively. We employed the Hund's case (b) _{βJ} basis set for constructing the Hamiltonian matrix,¹⁸ where the coupling scheme of the angular momenta is as follows:

$$J = N + S, \quad (2a)$$

and

$$F = J + I. \quad (2b)$$

The energy levels were obtained by numerical diagonalization of the Hamiltonian matrix. The effective rotational constant, spin-rotation interaction constant, Fermi contact term, and dipolar hyperfine interaction constant were determined by a least-squares fit. The result of the fit is shown in Table

TABLE I. Observed $1_{01}-0_{00}$ transition frequencies of HCS (MHz).

F	J	Obs.	Obs.-Calc.
0-1	1/2-1/2	40 337.535	0.000
1-0	1/2-1/2	40 458.131	-0.004
1-1	1/2-1/2	40 330.713	0.004
1-0	3/2-1/2	40 282.098	0.003
1-1	3/2-1/2	40 154.665	-0.004
2-1	3/2-1/2	40 262.996	0.001

TABLE II. Molecular constants of HCS(MHz).^a

Constants	
B_{eff}	20 145.4550(36)
γ_{eff}	-54.2962(127)
b	119.755(24)
c	23.014(43)

^aNumbers in parentheses represent three times the standard deviation in units of the last significant digits.

I, and the obtained molecular constants are listed in Table II. The standard deviation of the fit was 5 kHz, which is comparable to the frequency measurement error. The correlation matrix is given in Table III. The maximum correlation coefficient is 0.817 between two hyperfine interaction constants, indicating that the constants are well determined in the fit.

The effective rotational constant determined above corresponds to $(B_0 + C_0)/2$ in the asymmetric top representation. Senekowitsch *et al.*⁹ reported the equilibrium rotational constants, vibration-rotation interaction constants, and centrifugal distortion constants by *ab initio* calculations. From their result, the effective rotational constant is calculated to be 19 800 MHz. This value is about 2% smaller than the observed value [20 145.4550(36) MHz]. On the other hand, it is calculated to be 20 099 MHz on the basis of the geometry reported by Kaiser *et al.*,³ which is in good agreement with the observed value.

The Fermi contact term, $b + c/3$, is determined to be 127.427 MHz in the present study. The positive value indicates that the HCS radical is the σ radical, in which the unpaired electron occupies the molecular orbital extending within a molecular plane. This further supports that the HCS radical has a bent structure with the $^2A'$ ground electronic state. However, the observed Fermi contact term of HCS is much smaller than the corresponding value for the related molecules; 388.89 MHz for HCO,¹³ 451.32 MHz for HSiO,¹⁴ and 335.74 MHz for HSiS.¹⁵ Since no *ab initio* calculation for the hyperfine coupling constants of HCS has been reported so far, we qualitatively discuss the relatively small Fermi contact term of HCS in terms of its geometrical structure as follows. The HCO radical is known to have a bent structure with the HCO angle of 124°. According to the *ab initio* calculation,^{3,8} the corresponding angle for HCS is estimated to be 132°, which is somewhat larger than that for HCO. If the molecule were in the linear form, the Fermi contact term would take a small negative value. In this case, the molecular orbital of the unpaired electron has a node along the molecular axis, and hence, the orbital has no s character. Instead an effect of spin polarization makes the

TABLE III. Correlation matrix.

	B_{eff}	γ_{eff}	b	c
B_{eff}	1.000	0.426	0.182	-0.082
γ_{eff}		1.000	0.480	-0.265
b			1.000	-0.817
c				1.000

Fermi contact term of the hydrogen atom negative. In fact the negative Fermi contact term is obtained for the isovalent species, HCCCS, which has definitively a linear structure with the $^2\Pi$ ground electronic state.¹⁹ On the other hand, the Fermi contact term of the hydrogen atom becomes large positive value if the molecule is in the bent form as in the case of HCO.¹³ The relatively small Fermi contact term supports that the HCS radical is more close to a linear structure than the HCO radical.

The dipolar interaction term, c , which corresponds to $(3/2)T_{aa}$ for the asymmetric top case, is determined to be 23.014(43) MHz. This value is slightly larger than the $(3/2)T_{aa}$ of the HCO radical (17.34 MHz).¹³ The dipolar interaction of the hydrogen nucleus mainly originates from the interaction with the unpaired electron localized on the carbon atom. The tensor component along the C–H bond therefore takes a large positive value, whereas that perpendicular to the C–H bond a negative value. The angle between the a axis and the C–H bond in HCS is smaller than that in HCO, the T_{aa} constant of HCS is expected to take a larger value than that of HCO. This is consistent with the observed trend in the c constant.

Both the HCS and HCO radicals should have the $^2\Pi$ ground electronic state in the linear configuration. However a mechanism of the Renner–Teller interaction removes the degeneracy, and stabilizes the bent structure with A' symmetry for both species. The large HCS angle implies that the Renner–Teller interaction in HCS is weaker than that in HCO. As a result, the first electronic state of HCS, A^2A'' , which is a counterpart of the Renner–Teller pair, is expected to be lower in energy than in the case of HCO. If so, the spin–rotation interaction constant about the a axis, ϵ_{aa} , should have a large value.^{20,21} This can also be regarded as an effect of the residual spin–orbit interaction. However, the effect of ϵ_{aa} is not visible in the present study, since we only observed the $1_{01}-0_{00}$ transition. The γ_{eff} constant determined here corresponds to $(\epsilon_{bb} + \epsilon_{cc})/2$ in the asymmetric top representation, and is mainly related to the electronic excited states with A' symmetry within the second-order approximation. Thus the γ_{eff} constant is not affected by the low-lying A^2A'' state. In fact the γ_{eff} constant is $-54.2962(127)$ MHz, which is even smaller than that for HCO (-93.365 MHz).¹³ For further understanding of electronic structure of HCS, it is therefore important to observe the $K_a = 1$ lines by millimeter- and submillimeter-wave spectroscopy. Such a study is now in progress.

ASTROCHEMICAL IMPLICATION

The HCS radical is a potential candidate for an interstellar molecule. Three mechanisms can contribute to its formation. First, ion molecule reactions could account for HCS. The H_2CS molecule is found in various astronomical sources, and it is speculated to be produced by the dissociative electron recombination reaction of the H_2CSH^+ ion;²²



In this reaction, the following pathway detaching two hydrogen atoms may also be possible;



However, we like to point out that reactions (3) and (4) have never been studied in the laboratory, and hence, branching ratios are completely unknown. Second, a more realistic route seems to be the reaction of atomic carbon in its 3P ; electronic ground state with interstellar hydrogen sulfide, H_2S^3 ,



Recent crossed molecular beam studies of this reaction detected the HCS radical as the reaction product.^{1,3} Finally, photolyses of thioformaldehyde, H_2CS , to HCS and H could contribute to interstellar HCS in photon dominated regions.

The a component of the dipole moment is expected to be small, and hence, the spectral lines of HCS from interstellar molecular clouds may not be very strong. However it is worth searching for them with a sensitive radiotelescope, since the related species, H_2CS and H_2S , are abundant in interstellar molecular clouds.^{23,24} The abundance, or at least the upper limit to the abundance, of HCS will provide us with important information for modeling the production chemistry of sulfur bearing organic species in molecular clouds.

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