# A Predicted Spectrum of HCS, an Intermediate in the Production of the Sulfur Compounds Observed in the Collision of Comet Shoemaker-Levy 9 with Jupiter

Dennis J. Clouthier and Roger S. Grev*

*Department of Chemistry, University of Kentucky*
*Lexington, Kentucky 40506-0055*

When comet Shoemaker-Levy 9 (SL9) collided with Jupiter, large amounts of $H_2S$, COS, $CS_2$, $S_2$, and CS were detected, although such sulfur species are not normally present in the Jovian atmosphere.[1,2] To obtain reasonable concentrations of the reduced species CS and $CS_2$, modelers had to include postulated reactions involving the transient species HCS and $H_2CS$, although little was known about their chemistry.[3,4] Recently, Kaiser et al.[5,6] reported molecular beam studies of the reaction of $H_2S$ with ground-state carbon atoms. They showed that HCSH was formed as a reactive intermediate, which then immediately fragmented into hydrogen atoms and HCS radicals. This process could have been the source of HCS in the SL9–Jupiter collision, and subsequent reactions could generate the other observed sulfur-containing molecules. Unfortunately, little is known[7] about the microwave, infrared, or UV–visible spectra of HCS—primarily because of a lack of suitable precursors—although the spectroscopy of the formyl radical (HCO) is well studied.[8] Laser-induced fluorescence (LIF) or resonance-enhanced multiphoton ionization (REMPI) techniques would be ideal for studying HCS, but theory predicts that the lowest electronic transition ($\tilde{A}^2A''$–$\tilde{X}^2A'$) is in the infrared, making it unsuitable.[9,10] The $\tilde{B}^2A'$–$\tilde{X}^2A'$ transition, analogous to the hydrocarbon flame bands of HCO,[11] is likely to be more useful. Here we study the $\tilde{B}$–$\tilde{X}$ spectrum of HCS using reliable theoretical methods to guide future experimental searches.

Because the $\tilde{B}^2A'$ and $\tilde{X}^2A'$ states have the same spin and spatial symmetry, we studied them using the full-valence (11 electrons in 9 orbitals) complete-active-space self-consistent-field method[12] (CASSCF), which can describe excited states of the

**Table 1.** Equilibrium Geometries, Rotational Constants, and Harmonic Vibrational Frequencies of the $\tilde{X}$ and $\tilde{B}$ Electronic States of HCS Determined at the TZ(2df,2p) CASSCF Level of Theory[a]

|  | $\tilde{X}^2A'$ | $\tilde{B}^2A'$ |
|---|---|---|
| $r$(C–H) | 1.101 Å | 1.088 Å |
| $\theta$(H–C–S) | 132.0° | 107.3° |
| $r$(C–S) | 1.582 Å | 1.779 Å |
| $T_e$ | 0.0 | 25148 cm$^{-1}$ |
| $A$ | 29.770 cm$^{-1}$ | 17.389 cm$^{-1}$ |
| $B$ | 0.66238 cm$^{-1}$ | 0.55638 cm$^{-1}$ |
| $C$ | 0.64796 cm$^{-1}$ | 0.53913 cm$^{-1}$ |
| $\nu_1$(C–H str) | 3006 cm$^{-1}$ | 3151 cm$^{-1}$ |
| $\nu_2$(bend) | 886 cm$^{-1}$ | 1162 cm$^{-1}$ |
| $\nu_3$(C–S str) | 1146 cm$^{-1}$ | 752 cm$^{-1}$ |

[a] The relative energies are from MRCI energies at the CASSCF Geometries

same symmetry as the ground state.[13] Final excitation energies were obtained using the multireference configuration interaction (MRCI) method.[14] We simulated the cold absorption spectrum for the $\tilde{B}$–$\tilde{X}$ transition by determining the Franck–Condon factors (FC)—and thus the relative transition probabilities for each vibronic band, within the harmonic oscillator approximation—using the program of Yang et al.,[15,16] which allows simultaneous excitation of all three normal modes.

The predicted geometries and properties of the $\tilde{X}^2A'$ and $\tilde{B}^2A'$ states of HCS are listed in Table 1. Our HCS ground-state geometry is similar to that of Kaiser et al.,[6] who used coupled cluster methods and similar basis sets, and is about what would be predicted for a carbon centered radical H$\dot{\text{C}}$S, derived from thioformaldehyde. For example, HCS has a larger H–C–S bond angle than that of thioformaldehyde (132 versus 122°), and a smaller C–S bond length (1.582 Å versus 1.62 Å), consistent with an increase in s-character in the C–S bond.

The excited-state geometry of HCS differs significantly from that of the ground state. The H–C–S bond angle in the $\tilde{B}$ state is 107.3°, 25° less than in the $\tilde{X}$ state, while the C–S bond length is 1.779 Å, 0.2 Å longer than in the ground state and close to that of $H_3C$–S–H[17] (1.819 Å), suggesting that the C–S bond in the $\tilde{B}$ state of HCS is essentially a single bond. HCO and HCS have similar decreases in the bond angle and increases in the CO or CS bond length on electronic excitation to the $\tilde{B}$ state.

Tanaka and Davidson[18] described the electronic structure of HCO by the interaction of a hydrogen atom with excited states of CO, and an analogous model works well for HCS. The first excited state ($\tilde{a}^3\Pi$) of CS has the configuration

$$...(5\sigma)^2(6\sigma)^2(2\pi)^4(7\sigma)^1(3\pi)^1$$

Attaching a hydrogen atom at the preferred nonlinear geometry gives the ground-state electron configuration of HCS

$$...(6a')^2(7a')^2(8a')^2(2a'')^2(9a')^2(10a')^1 \qquad (1)$$

while the first excited state of HCS ($^2\Pi$) arises from bonding to

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(7) To date, the only spectroscopic studies of HCS are those of Anacona (Anacona, J. R. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 1507.) who attributed a series of new far-infrared laser magnetic resonance transitions to the radical, without making definitive assignments, and Ruscic and Berkowitz (Ruscic, B.; Berkowitz, J. *J. Chem. Phys.* **1993**, *98*, 2568), who determined the heat of formation and ionization potential of HCS using photoionization mass spectrometry.

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(12) Roos, B. O. *Adv. Chem. Phys.* **1987**, *69*, 399.

(13) The basis sets were of polarized triple-$\zeta$ quality, TZ(2df,2p). Specifically, we used hydrogen (5s/3s), carbon (10s6p/5s3p), and sulfur (12s9p/6s5p) contractions (Dunning, T. H. *J. Chem. Phys.* **1971**, *55*, 716; McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72*, 5639) of Huzinaga's primitive basis sets (Huzinaga, S. *J. Chem. Phys.* **1965**, *42*, 1293. Huzinaga, S. Approximate Atomic Functions. II; Department of Chemistry Report, University of Alberta: Edmonton, Alberta, Canada, 1971.) with the following polarization functions: $\alpha_p$(H) = 1.5 and 0.375; $\alpha_d$(C) = 1.5 and 0.375; $\alpha_f$(C) = 0.8; $\alpha_d$(S) = 1.4 and 0.35; and $\alpha_f$(S) = 0.55.

(14) The reference space in these MRCIs included all configurations (in all possible spin couplings) with coefficients of $\geq 0.05$ in the CASSCF wave function expanded in the natural orbital basis. For the ground state, the MRCI included 14 references and 1 066 044 configuration state functions (CSFs), while the $\tilde{B}$ state used 14 references and 876 430 CSFs. In all cases, the lowest lying core orbitals (carbon 1s, sulfur 1s, 2s, and 2p) were constrained to be doubly occupied. The PSI suite of electronic structure programs (PSITECH Inc., Watkinsville, GA, 30677) was used throughout.

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(16) Yang, D.-S.; Zbierski, M. Z.; Berces, A.; Hackett, P. A.; Roy, P.-N.; Martinez, A.; Carrington, T., Jr.; Salahub, D. R.; Fournier, R.; Pang, T.; Chen, C. *J. Chem. Phys.* **1996**, *105*, 10663.

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the $7\sigma$ orbital at a linear geometry. The *second* excited state of HCS arises from the $^3(\pi^3\pi*)$ configuration of CS,

$$...(5\sigma)^2(6\sigma)^2(7\sigma)^2(2\pi)^3(3\pi)^1$$

If a hydrogen atom bonds to the $3\pi$ orbital, the occupancies represented by

$$...(6a')^2(7a')^2(8a')^2(2a'',9a')^3(3a'', 10a')^2$$

give three configurations of $^2A'$ symmetry

$$...(6a')^2(7a')^2(8a')^2(2a'')^2(9a')^1(10a')^2 \qquad (2)$$

$$...(6a')^2(7a')^2(8a')^2(2a'')^1(9a')^2(10a')^1(3a'')^1$$

$$...(6a')^2(7a')^2(8a')^2(2a'')^2(9a')^1(3a'')^2$$

Tanaka and Davidson noted that the first two configurations are the most important for HCO, and they are the most important for $\tilde{B}^2A'$ of HCS as well, but the third configuration also contributes significantly (coefficient >0.1) in the CASSCF and MRCI description of the $\tilde{B}$ state of HCS.

This description of the electronic structure of HCS explains the large geometry change upon excitation. First, as originally noted by Walsh[19] for HCO, a state from configuration 2 should be more strongly bent than a state from configuration 1, because the $10a'$ orbital is strongly stabilized on bending, while $9a'$ is mostly unaffected by bending. This explains why the $\tilde{B}$ state is more strongly bent than the $\tilde{X}$ state. Second, the bond distances in the $^3(\pi^3\pi*)$ states are 1.73−1.77 Å,[20] or about 0.2 Å longer than bond lengths in the $\tilde{X}$ or $\tilde{a}$ states of CS. This explains the large bond distance increase upon excitation to the $\tilde{B}$ state.

The $\tilde{B}-\tilde{X}$ excitation energy, $T_e$, is 25 148 cm$^{-1}$ at the MRCI level of theory (see Table 1). At the TZ(2df,2p) CASSCF level of theory, the excitation energy is slightly larger at 25 891 cm$^{-1}$, and using a smaller double-$\zeta$ polarized (DZP) basis set gives a CASSCF excitation energy of 24 762 cm$^{-1}$. Thus, the excitation energy is relatively insensitive to both enlarging the one-particle basis set and including dynamical electron correlation. In this regard, HCS is unlike HCO; our analogous studies of HCO give excitation energies of 39 513 (DZP CASSCF), 41 089 [TZ-(2df,2p) CASSCF], and 37 899 cm$^{-1}$ [TZ(2df,2p) MRCI], which shows greater dependence on the basis set and, especially, the electron correlation method. For HCO, the experimental result is $T_0 = 38$ 695 cm$^{-1}$ and $T_e$ is ∼200 cm$^{-1}$ higher.[21,22] Thus, the TZ(2df,2p) MRCI excitation energy is too low by ∼1000 cm$^{-1}$ in HCO. On the basis of the above trends, we estimate that the converged value for HCS will be perhaps 500 cm$^{-1}$ above our predicted value, giving a best estimate for $T_e$ of ∼25 700 cm$^{-1}$.

The harmonic vibrational frequencies of HCS in Table 1 show that the character of the second and third highest frequency modes is different in the ground and excited states; in the ground state, the C−S stretching frequency is higher than the H−C−S bending frequency, while in the excited state, the opposite is true. HCO behaves similarly, as originally suggested by Milligan and Jacox[23] and later confirmed by experiment[24] and theory.[22]

The calculated absorption spectrum (Figure 1) shows extensive Franck−Condon activity in the excited-state bending ($\nu_2$) and C−S stretching ($\nu_3$) modes but only weak bands involving the C−S stretching mode $\nu_1$, consistent with the geometric changes on excitation. The most intense bands involve combinations of

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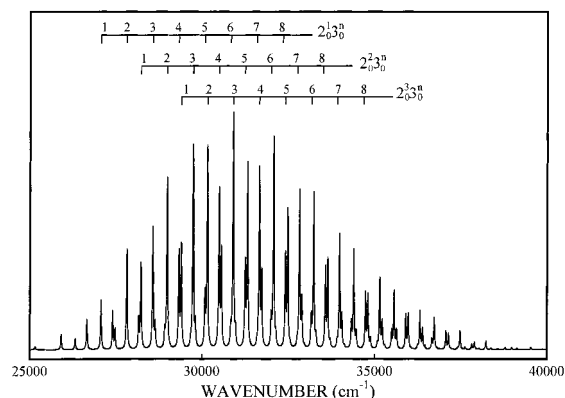


**Figure 1.** Calculated absorption spectrum of HCS radical. Each vibronic band was given a width of 30 cm$^{-1}$ (fwhm) and only transitions from the lowest vibronic level in the ground state were included, so the calculation simulates the spectrum under jet-cooled conditions at very low temperatures.
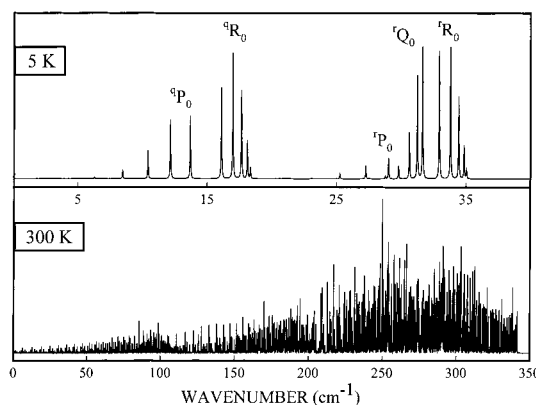


**Figure 2.** Calculated rotational structure of the $0_0^0$ band of HCS at 10 and 300 K. In each case, the ratio of the parallel to perpendicular transition moments was fixed at 1.4, and a resolution of 0.05 cm$^{-1}$ was assumed. Because the spin splittings (whose magnitude are unknown) were neglected in these calculations, the experimental spectra may differ significantly from the theoretical contours.

$\nu_2$ and $\nu_3$, with the maximum intensity occurring about ∼5700 cm$^{-1}$ above the electronic band origin predicted at 25 162 cm$^{-1}$.

In Figure 2, we show the approximate calculated rotational structure of the $0_0^0$ band at two different temperatures. These calculations used the equilibrium rotational constants in Table 1, neglected spin splittings, and assumed the ratio of the parallel to perpendicular transition moments to be similar to that of HCO.[8] At room temperature, each band extends over ∼350 cm$^{-1}$, with a pronounced head at higher energy and a maximum 50−100 cm$^{-1}$ from the band head. At 10 K, each band consists of a few well-separated rotational lines with the A- and B-type components ∼15 cm$^{-1}$ apart. The relative intensities of the two components will, of course, depend on the actual orientation of the transition moment.

These theoretical predictions, presented in Table 1 and Figures 1 and 2, should be sufficiently accurate to help experimentalists find the HCS spectrum. If the excited state does not suffer from extensive predissociation, then LIF studies should be feasible and we expect the electronic band origin to be at 25 700 ± 500 cm$^{-1}$, within a span of one or two laser dyes. The rovibronic structure of the band system is sufficiently distinctive that it should be readily identifiable at modest resolution.