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Theoretical rovibrational characterization of the *cis*/*trans*-HCSH and H_2SC isomers of the known interstellar molecule thioformaldehyde

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ABSTRACT

The missing sulfur of the interstellar medium may be hiding in molecules for which there are no spectral data yet available for any astrophysical observation, molecules like isomers of H_2CS a known interstellar compound. Every known interstellar molecule is a pointer to the presence and detectability of related molecules in the ISM. This quantum chemical study provides the necessary spectral data for the observation of *cis*-, *trans*-, and ^3A HCSH as well as for $^1A_1$ and $^3A''$ H_2SC. Benchmarks of the CCSD(T)-F12/cc-pVTZ-F12 quartic force field for the known thioformaldehyde provide anharmonic vibrational frequencies of with an average of 1.9 cm^{-1} of gas-phase experiment demonstrating reliability for the computed fundamental frequencies. The $^1A_1$ H_2SC form has bright spectral features in the infrared and millimeter-wave regimes, but is the highest-energy species of this set. The *trans*-HCSH isomer is the lowest-energy (43.69 kcal/mol or 1.90 eV) isomer next to thioformaldehyde, but the slightly higher *cis*-HCSH isomer has greater intensities for its brightest fundamental frequencies and a larger dipole moment making it potentially more likely to be observed. These data determined here may also assist in laboratory characterization of these molecules and how their chemistry will likely progress.

1. Introduction

Of the 18 known S-containing interstellar molecules, 15 of them have the corresponding O-analogues as known interstellar molecules [1]. Thus, every known O-containing species in the interstellar medium (ISM) is an indication for the presence and possible detection of the corresponding S-analogue. One of the first interstellar sulfur molecules was thioformaldehyde (H_2CS) in 1973 [2], the sulfur-analogue of the well known biological preservative formaldehyde (H_2CO) which itself was observed in the ISM in 1969 [3]. Sulfur is also one of the ten-most abundant elements in space [4,5] and is a portion of the essential amino acid cysteine and also in methionine [6]. Sulfur-containing molecules are used to probe the physical and chemical conditions of the ISM, and their chemistry is strongly related to the evolution of various astrophysical regions. For instance, younger molecular clouds possess sulfoxides while more evolved molecular clouds contain greater amounts of hydrogen-rich compounds like H_2CS [5,7–9]. Sulfur-bearing molecules also have the unique traits of being necessary in both refractory and volatile chemistry making their appearance a novel means to explore the chemical evolution of both pathways [10].

Current astrochemical reaction models have to treat sulfur specially. While thioformaldehyde, HCS, and methyl mercaptan, among other species, are known in the ISM, most reaction models have this element significantly depleted in the gas phase in order to match observations both molecularly and atomically [11]. The sequestration of sulfur in refractories or minerals is certainly possible, and H_2S and OCS may be reservoirs on interstellar grain surfaces [12]. Even so, other gas phase molecular species containing element-16 are likely additional harbors for this material [13], especially if they play a role in the formation or destruction of known astrochemicals. Recent searches for H_2CCS (thioketene) and HCCSH have returned with only possible upper bounds in regions searched [14], but further oxygen-analogue molecules like H_2S^+ [15,16] and even unique sulfur compounds are likely still present in the ISM or in the atmospheres of carbon-rich stars.

One proposed formation pathway of astrochemically-known H_2CS is through collisions of sulfur atoms with methane or methyl radicals [17]. Differently, this molecule is also modeled to form in the gas phase through a myriad of chemical reactions such as from collisions of H_2 with known interstellar molecules like methyl mercaptan or HCS [18,19,13]. However, many pathways explored

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quantum chemically produce the HCSH isomer as an intermediate en route to H_2CS [20]. Surprisingly, little is known about this molecule and its role in the larger chemistry of thioformaldehyde.

The rearrangement (or isomerization) of H_2CS is not limited just to HCSH (which has both *cis* and *trans* conformers), but the total proton rearrangement is possible in isothioformaldehyde, H_2SC. Though interstellar chemical processes are typically far away from the thermodynamic equilibrium, isomerism can be used to initially select some most probable candidates from an isomeric group for astronomical detection. The reaction of carbon atoms with hydrogen sulfide, the latter of which was detected in the ISM in 1972 [21–23], has been shown to proceed through HCSH and eventually produces H_2SC in the gas phase, as well [24]. Hence, the potential energy surface for two hydrogen atoms, one sulfur atom, and one carbon atom has other possibilities for molecules of potential importance to interstellar sulfur chemistry. The true test comes in whether any of these molecules actually are present in extraterrestrial environments, and that confirmation can only be realized via astronomical spectral characterization.

Observation of any molecule in space is done through comparison with known standards, typically laboratory spectra. However, quantum chemical predictions for spectral data are growing in accuracy as the methods develop, and the hardware becomes more capable of performing more sophisticated computations. Quantum chemistry has greatly informed laboratory spectral characterization for decades, and it has recently preceded such analysis for molecules like *c*-$C_3H_3^+$ and $ArOH^+$ [25–29]. The astrophysical detection of S_2H, a sulfur-containing molecule no less, was also informed by quantum chemical computations [30,31]. Quantum chemistry also provides a full spectral characterization that is often impossible to acheive in the laboratory for reasons ranging from symmetry to the available experimental techniques.

The most accurate quantum chemical methodology for computing rovibrational spectral data of small molecules involves fourth-order Taylor series expansions of the potential within the intermolecular Hamiltonian called quartic force fields or QFFs [32]. Vibrational frequencies of within 1.0 cm^{-1} and rotational constants within 15 MHz of gas phase experiment have been acheived numerous times [33,34,25,35–37,26,38–41,16]. However, these methods are costly and time-consuming. More modern and advanced quantum chemical methods like explicitly correlated coupled cluster theory at the singles, doubles, and perturbative triples level, CCSD(T)-F12 [42,43], have been combined with QFFs to give vibrational frequencies within an average of 7.0 cm^{-1} of higher-level theory for closed-shell molecules in the span of hours as opposed to months for the higher-level approaches [44–47]. Additionally, most fundmanetal frequencies of formaldehyde have been shown to be within 5.0 cm^{-1} or better (often within 2.0 cm^{-1}) of experiment [47]. Hence, CCSD(T)-F12 QFFs are employed in this present work to produce the rotational, vibrational, and rovibrational spectral data for *cis*-HCSH, *trans*-HCSH, and H_2SC in order to facilitate their potential observation in the laboratory or even in the ISM via observations from the *Stratospheric Observatory for Infrared Astronomy* or the upcoming the *James Webb Space Telescope*. Finally, these computations will be benchmarked against known experimental data for H_2CS itself [48–50].

2. Computational details

The coupled cluster computations utilize the MOLPRO2015.1 quantum chemical program [51,52] and the cc-pVTZ-F12 basis set [53]. Density functional theory (DFT) in the form of B3LYP and MP2 computations along with the aug-cc-pVTZ basis set all utilize the Gaussian16 program [54–59]. The latter are used only to compute the optimized geometry of the transition states (TSs), and the double-harmonic vibrational intensities. Good agreement with higher-level theory and significant reductions in computational cost have been previously reported for this approach in determining the intensities [60,61].

The geometry of the molecule in question is optimized via CCSD(T)-F12/cc-pVTZ-F12 (with each given in Fig. 1) and then displacements about a set of coordinates produce the energy points necessary to define the QFF. The displacements are 0.005 Å for bond lengths and 0.005 radians for the bond angles or torsions (τ). The symmetry-internal coordinates for thioformaldehyde (Fig. 1A) and $^1A_1$ H_2SC (Fig. 1B) are similar to those for other C_{2v} tetraatomic systems [62–66] and are defined below where the out-of-plane bend is denoted as OPB:

$$S_1(a_1) = r(\mathrm{C}-\mathrm{S}) \tag{1}$$

$$S_2(a_1) = \frac{1}{\sqrt{2}}[r(\mathrm{H}_a-\mathrm{C}) + r(\mathrm{H}_b-\mathrm{C})] \tag{2}$$

$$S_3(a_1) = \frac{1}{\sqrt{2}}[\angle(\mathrm{H}_a-\mathrm{C}-\mathrm{S}) + \angle(\mathrm{H}_b-\mathrm{C}-\mathrm{S})] \tag{3}$$

$$S_4(b_2) = \frac{1}{\sqrt{2}}[r(\mathrm{H}_a-\mathrm{C}) - r(\mathrm{H}_b-\mathrm{C})] \tag{4}$$

$$S_5(b_2) = \frac{1}{\sqrt{2}}[\angle(\mathrm{H}_a-\mathrm{C}-\mathrm{S}) - \angle(\mathrm{H}_b-\mathrm{C}-\mathrm{S})] \tag{5}$$

$$S_6(b_1) = OPB(\mathrm{S}-\mathrm{C}-\mathrm{H}_a-\mathrm{H}_b), \tag{6}$$

where H_a and H_b are simply used to denote opposite hydrogens. The *cis* and *trans*-HCSH coordinates (Fig. 1D & E) are similar to those utilized for the oxygen analogue and other C_s tetraatomic systems where the plane of symmetry contains all of the atoms [67–69]:

$$S_1(a') = r(\mathrm{H}_a-\mathrm{C}) \tag{7}$$

$$S_2(a') = r(\mathrm{C}-\mathrm{S}) \tag{8}$$

$$S_3(a') = r(\mathrm{S}-\mathrm{H}_b) \tag{9}$$

$$S_4(a') = \angle(\mathrm{H}_a-\mathrm{C}-\mathrm{S}) \tag{10}$$

$$S_5(a') = \angle(\mathrm{C}-\mathrm{S}-\mathrm{H}_b) \tag{11}$$

$$S_6(a'') = \tau(\mathrm{H}_a-\mathrm{C}-\mathrm{S}-\mathrm{H}_b). \tag{12}$$

The above coordinates are also used for the skew C_1 structure (Fig. 1F), as well. The H_2SC structure is C_s as well (Fig. 1C) but with the plane of symmetry bisecting the H—S—H angle. These coordinates are similar to studies on the oxywater cation (H_2OO^+) and its sulfur analogue as well as argon-containing species [70–73]:

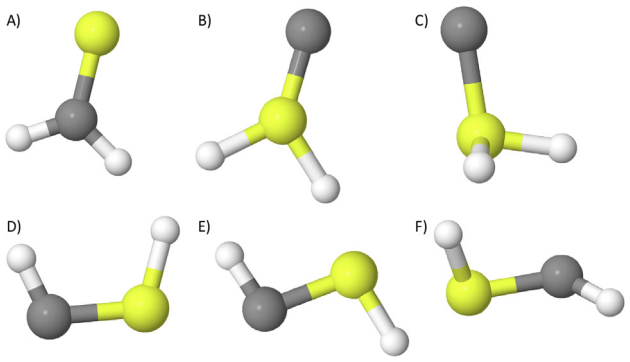

Fig. 1. The Structures (Carbon-Gray, Sulfur-Yellow, & Hydrogen-White) of (A) H_2CS, (B) $^1A_1$ H_2SC, (C) $^3A''$ H_2SC, (D) *cis*-HCSH, (E) *trans*-HCSH, and (F) ^3A HCSH. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

$$S_1(a') = r(\mathrm{S}-\mathrm{C}) \quad (13)$$

$$S_2(a') = \frac{1}{\sqrt{2}}[r(\mathrm{H}_a-\mathrm{S}) + r(\mathrm{H}_b-\mathrm{S})] \quad (14)$$

$$S_3(a') = \frac{1}{\sqrt{2}}[\angle(\mathrm{H}_a-\mathrm{S}-\mathrm{C}) + \angle(\mathrm{H}_b-\mathrm{S}-\mathrm{C})] \quad (15)$$

$$S_4(a') = \angle(\mathrm{H}_a-\mathrm{S}-\mathrm{H}_b) \quad (16)$$

$$S_5(a'') = \frac{1}{\sqrt{2}}[r(\mathrm{H}_a-\mathrm{S}) - r(\mathrm{H}_b-\mathrm{S})] \quad (17)$$

$$S_6(a'') = \frac{1}{\sqrt{2}}[\angle(\mathrm{H}_a-\mathrm{S}-\mathrm{C}) - \angle(\mathrm{H}_b-\mathrm{S}-\mathrm{C})]. \quad (18)$$

A fitting of the points produces the QFF, equilibrium geometry, and rotational constants of each molecule and each has a sum of squared residuals on the order of 10^{-17} a.u.[2] The force constants are transformed with the Intder2005 program [74] from symmetry- or simple-internal coordinates into Cartesian coordinates. The Spectro program [75] utilizes these transformed force constants via second-order rotational [76] and vibrational perturbation theory (VPT2) [77,78] to produce the desired spectral data. Full treatment of Fermi resonance polyads are also included for each molecule [79,80].

The relative energies are also computed from these equilibrium minima corrected for the anharmonic zero-point vibrational energies (ZPVEs). The energies of the TSs are determined from CCSD(T)-F12/cc-pVTZ-F12 energies at the B3LYP/aug-cc-pVTZ optimized transition state geometries including the DFT ZPVEs. The dipole moments for each minimum are computed with CCSD(T)-F12/cc-pVTZ-F12.

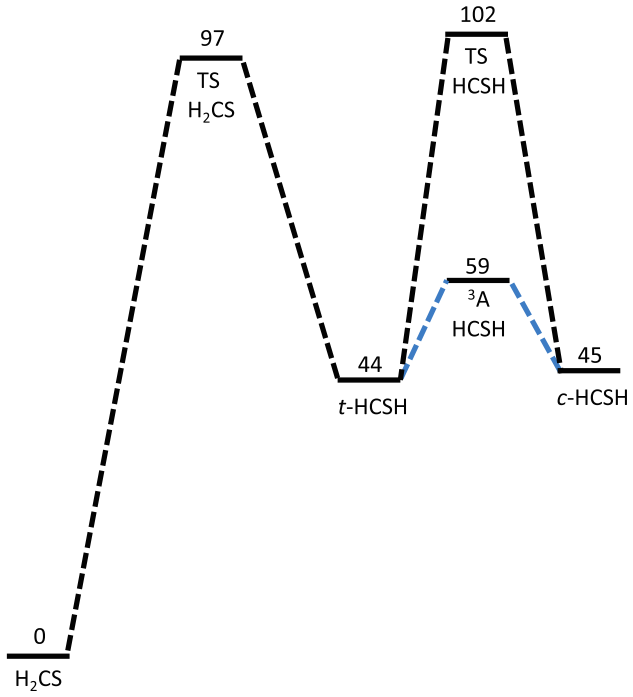

Fig. 2. The potential energy surface for conversion of H_2CS into *cis*- and *trans*-HCSH in kcal/mol.

3. Results and discussion

The relative energies for the six isomers/conformers/electronic states studied in this work are given in Table 1 and also in Fig. 2 with graphical representations of their structures given in Fig. 1. The H_2CS isomer is clearly the lowest energy form. The well containing it is rather deep with the TS to forming the *trans*-HCSH isomer lying 96.97 kcal/mol (4.205 eV) higher in energy as shown in Fig. 2. Hence, the accessibility of the other isomer in the gas phase would require UV photons, high-energy collisions, or a surface. However, once *trans*-HCSH is formed, the other isomers are more favored to form, as well. The difference between the *cis*- and *trans*-HCSH isomers is only 1.16 kcal/mol in excellent agreement with previous quantum chemical data [24]. While the TS between the *cis*- and *trans*-HCSH isomers is even larger at 101.53 kcal/mol (4.403 eV, relative to the H_2CS global minimum) than that from H_2CS to *trans*-HCSH, the ^3A HCSH state is requires a mere 15.17 kcal/mol (0.658 eV/1.89 μm) of energy suggesting that crossing over to the triplet surface via relativistic effects could be important. This pathway is in the blue dashed line of Fig. 2. Furthermore, the triplet skew/intermediate has a dihedral angle of 98.76° nearly exactly in between these two conformers, and an electron shifts from a n to π^* orbital in order to create the triplet likely with a fast rate from El Sayed's rule. Hence, ^3A HCSH almost certainly serves as the conduit between the two planar HCSH isomers. The H_2SC isomer is much higher than the HCSH isomers, and the $^3A''$ state is actually lower in energy than the $^1A_1$ as given in Table 1. Hence, H_2SC would likely need to form first in the gas phase before rearranging either through the HCSH isomer [24] or directly into thioformaldehyde. In any case, the spectral data provided in this work can help to follow the reaction pathway in the laboratory in order to provide better models for sulfur chemistry in the ISM.

Table 1
The H_2CS CCSD(T)-F12/cc-pVTZ-F12 Isomeric Relative Energies (in kcal/mol).

Isomer	This Work	Previous[a]
H_2CS	0.00	0.00
$^1A_1$ H_2SC	114.89	117.4
$^3A''$ H_2SC	111.38	–
cis-HCSH	44.85	46.1
trans-HCSH	43.69	45.2
^3A HCSH	58.86	–
H_2CS TS	96.97	69.1
HCSH TS	101.53	–

[a] CCSD(T)/cc-pVTZ//QCISD/cc-pVDZ including QCISD/cc-pVDZ ZPVE results from Ref. [24].

Of the five other forms of [H_2, C, S] beyond thioformaledyde studied here, *cis*-HCSH balances the most favorable energetics for the best spectroscopic data making it the most likely observed at least in the laboratory if not the ISM. The exceptionally bright (149 km/mol) ν_2 S—H stretching vibrational frequency is predicted to lie at 2280.5 cm^{-1} (4.385 μm) as given in Table 2, and its dipole moment is 2.66 D, (Table 3) greater than the *trans* conformer and even thioformaldehyde itself. The *trans*-HCSH isomer has a notably intense ν_1 C—H stretch at 2837.2 cm^{-1} (3.524 μm), but is less intense relative to the ν_2 for the *cis* isomer. Both conformers exhibit similar frequencies for the vibrational fundamentals, as would be expected, but the hydride bending motions (ν_3 in each) differ most notably due to the interference of the hydrogen atoms in the *cis*-HCSH conformer. The ν_6 modes also involve hydride bending and are further delineated from each other as a result of the steric hinderance not present in the *trans*. The unique frequencies of the skew ^3A HCSH are also provided in Tables 2 and 3 so that gas phase experiment may directly observe this molecule, as well, and potentially determine its role in the conformational progression of HCSH.

H_2SC on the other hand is actually much more active spectroscopically in both the $^1A_1$ and $^3A''$ electronic states. The $^3A''$ state arises from occupation of the π^* antibonding orbital in the C=S π

Table 2
The H_2CS CCSD(T)-F12/cc-pVTZ-F12 QFF Frequencies (in cm^{-1}) and Intensities in Parentheses (in km/mol).

	H_2CS			$^1A_1$ H_2SC		$^3A''$ H_2SC	
	Symm.	This Work	Exp.[a]	Symm.	Frequency	Symm.	Frequency
ω_1	b_2	3175.1 (6)		a_1	2283.1 (270)	a''	2499.8 (5)
ω_2	a_1	3083.2 (23)		b_2	2191.0 (472)	a'	2496.9 (10)
ω_3	a_1	1495.6 (5)		a_1	1361.0 (119)	a'	1181.8 (16)
ω_4	a_1	1076.4 (1)		a_1	1024.2 (23)	a'	692.0 (2)
ω_5	b_2	1004.6 (7)		b_2	584.5 (58)	a''	588.6 (2)
ω_6	b_1	1002.6 (62)		b_1	203.8 (46)	a'	514.6 (24)
ν_1	b_2	3021.6	3024.6	a_1	2079.2	a''	2326.4
ν_2	a_1	2976.8	2971.0	b_2	1988.6	a'	2327.4
ν_3	a_1	1455.3	1455.5	a_1	1321.3	a'	1129.9
ν_4	a_1	1061.4	1059.2	a_1	1000.1	a'	670.7
ν_5	b_2	990.9	991.0	b_2	575.8	a''	568.0
ν_6	b_1	990.3	990.2	b_1	268.0	a'	487.8
ZPVE		5354.8			3763.5		3912.6

	cis-HCSH		*trans*-HCSH		^3A HCSH
	Symm.	Frequency	Symm.	Frequency	Frequency
ω_1	a'	3050.5 (42)	a'	2983.9 (50)	3180.3 (14)
ω_2	a'	2429.6 (149)	a'	2599.3 (23)	2590.6 (14)
ω_3	a'	1107.0 (40)	a'	1176.9 (26)	936.2 (8)
ω_4	a'	963.6 (36)	a''	982.7 (21)	894.3 (9)
ω_5	a''	932.8 (12)	a'	954.2 (16)	834.4 (13)
ω_6	a'	788.8 (5)	a'	883.5 (36)	419.9 (20)
ν_1	a'	2908.9	a'	2837.2	3048.5
ν_2	a'	2280.5	a'	2471.5	2462.8
ν_3	a'	1078.5	a'	1146.5	916.1
ν_4	a'	947.8	a''	961.1	856.7
ν_5	a''	915.5	a'	932.0	815.6
ν_6	a'	769.1	a'	865.0	390.2
ZPVE		4574.9		4727.0	4356.8

[a] Gas phase experimental data from Refs. [48,49].

framework, but this is lower in energy than the singlet since the bond angles are closer to 90° as is preferred by sulfur and its third-row element colleagues [82,83]. The dipole moments of both electronic states are quite large at 3.98 D and 4.30 D, respectively of the singlet and triplet. The intensities of $^3A''$ are actually the smallest of the set, but the $^1A_1$ are the largest. The lowest intensity is 23 km/mol for the ν_4 C═S stretch while the largest is 472 km/mol for the 1988.6 cm^{-1} (5.029 μm) ν_2 antisymmetric S—H stretch. Hence, if this molecule can form, its position on the potential energy surface should be relatively easy to determine due to its intensities and dipole moment. The one caveat is that the ν_6 out-of-plane motion exhibits a positive anharmonicity. Such behavior has been experimentally corroborated before [36] indicating that the anharmonic frequency likely lies above the harmonic, but this behavior is rare.

Additionally, the CCSD(T)-F12/cc-pVTZ-F12 QFF VPT2 results are once again showcasing exceptional accuracy when compared to experiment, especially for fundamental vibrational frequencies. The gas-phase experimental data for H_2CS are given beside the present VPT2 results in Table 2. Once the Fermi resonances are included in the VPT2 computations, the present QFF results differ from experiment by no more than 5.8 cm^{-1} with the mean absolute error of 1.9 cm^{-1}. This corroborates previous analysis of this method [46,47,66] and implies that the anharmonic vibrational frequencies computed for the other systems in this work should be similarly accurate. The CCSD(T)-F12/cc-pVTZ-F12 dipole moment is 1.70 D, and experiment has this value at 1.647 D [81] a further statement regarding accuracy in the methods utilized.

Unfortunately, the rotational constants (Table 3) are not behaving as well as the anharmonic vibrational frequencies. This has been shown in previous work [46] and is not surprising here. The QFF VPT2-computed *B* and *C* constants are known to be more accurate than the larger *A* constants in these near-prolate structures [35,36,29]. That trend is present here, as well, but the *B* and *C* constants differ from experiment by 93.1 MHz and 86.5 MHz, respectively, which is not as good as has been shown for more descriptive QFFs referenced previously. Even so, the rotational data here is an excellent starting guide for determining the rotational spectrum of these molecules especially for the vibrationally excited rotational spectra where variances in the rovibrational spectra should be effectively modeled by the differences in the vibrationally excited rotational constants provided here. As a bit of consolation, the quartic and sextic constants given in Table 3 and compared with those from [50] are some of the most accurate computed with this method thus far [62].

In addition to these data, the vibrational, rotational, and rovibrational spectral data are also reported in the supplemental information (SI) for the singly- and doubly-deuterated, ^{34}S, and mixtures of isotopes. The spectral accuracies should continue for these species and will help in giving further characterization of the isomers of thioformaldehyde. Finally, the force constants numbered according to the equations defined previously are also given in the SI. The most notable items are for Tables S11-S13 where the F_{11} values drop from 6.703 mdyne/AA^2 in H_2CS to 5.533 mdyne/$Å^2$ in $^1A_1$ H_2SC indicating a weakening of the C═S bond upon isomerization. This is further reduced in $^3A''$ H_2SC where F_{11} is 1.511 mdyne/AA^2.

4. Conclusions

While the lowest-energy isomer of H_2CS besides the astrochemically known thioformaldehyde is *trans*-HCSH, *cis*-HCSH may be the most likely isomer to be observed of this set. The *cis*-HCSH isomer can form readily from the *trans* through a low-lying triplet skew intermediate according to El Sayed's rule, and it has a larger

Table 3
The CCSD(T)-F12/cc-pVTZ-F12 Rotational Constants (in MHz unless otherwise marked).

	H_2CS						
	This Work	Exp.[a]	$^1A_1$ H_2SC	$^3A''$ H_2SC	*cis*-HCSH	*trans*-HCSH	^3A HCSH
A_e	293740.2		236715.5	155552.0	193396.5	187982.9	220576.3
B_e	17697.0		19783.5	16187.6	18950.1	18967.0	17073.2
C_e	16691.4		18257.6	15916.4	17258.9	17228.7	16437.5
A_0	291784.7	291613.34	229475.0	155027.4	192771.7	186192.2	221362.4
B_0	17622.4	17698.994	19651.8	16086.7	18851.8	18860.2	17012.0
C_0	16583.5	16652.498	18103.7	15802.8	17129.1	17084.7	16333.2
A_1	289229.7		224606.1	153545.9	189884.1	183157.0	218687.5
B_1	17605.9		19646.5	16275.5	18791.6	18826.7	16959.9
C_1	16566.0		18072.9	15995.3	17057.6	17033.1	16298.7
A_2	287210.0		225365.6	152318.3	190369.0	183027.6	216223.8
B_2	17610.2		19634.1	16267.2	18927.4	18906.5	17063.9
C_2	16559.2		18088.8	15971.6	17175.9	17099.9	16358.8
A_3	294582.4		230765.6	153376.3	194974.9	188839.6	224249.3
B_3	17670.7		19679.2	16162.5	18890.2	18891.8	16995.6
C_3	16542.9		18028.0	15845.2	17103.9	17073.0	16306.2
A_4	291465.2		229807.6	158367.5	194422.5	197491.2	231006.3
B_4	17517.0		19459.2	15915.4	18793.2	18801.0	16972.0
C_4	16482.7		17947.3	15683.0	17011.9	17053.2	16321.3
A_5	296670.2		242616.6	157250.9	190096.1	175506.5	222856.7
B_5	17635.3		19688.5	16006.1	18737.0	18762.3	16956.4
C_5	16544.3		18032.3	15662.5	17111.8	16991.0	16231.5
A_6	287639.5		209207.3	154256.4	195634.2	185549.6	216723.2
B_6	17546.6		19542.8	15692.7	18775.5	18760.1	17002.8
C_6	16589.2		18142.5	15431.7	17053.0	16969.2	16273.1
D_J (kHz)	18.658	19.01875	25.925	61.588	27.764	28.637	26.457
D_{JK}	0.520	0.5222938	1.267	0.701	0.448	0.444	0.579
D_K	22.099	23.34378	18.358	4.899	8.273	5.407	14.475
d_1 (kHz)	−1.126	−1.208429	−2.307	−1.089	−2.461	−2.567	−0.890
d_2 (kHz)	−0.148	−0.1773270	−0.658	−0.0948	−0.311	−0.318	0.257
H_J (mHz)	−1.588	−5.81	−45.194	−544.944	−29.857	−24.535	−2.186
H_{JK} (Hz)	1.463	1.50409	6.701	−1.365	0.940	1.223	−1.798
H_{KJ} (Hz)	−29.221	−28.155	−488.067	99.518	27.305	47.245	−10.862
H_K (kHz)	5.230	5.946	4.503	0.988	2.007	0.546	3.941
h_1 (mHz)	1.508	3.018	−2.973	−17.972	1.373	0.781	1.382
h_2 (mHz)	1.342	1.6472	9.505	2.708	3.340	3.198	−2.428
h_3 (mHz)	0.257	0.3619	3.354	0.175	0.640	0.639	−1.206
μ (D)	1.70	1.647	3.98	4.30	2.66	1.84	1.06

[a] Gas phase spectroscopic constants from Refs. [48,50] and dipole moment from Ref. [81].

dipole moment as well as notable vibrational intensities. Even though the H_2SC states are more spectroscopically favorable, their formation requires significantly more energy and are most likely formed first (if at all) before preceding energetically downhill to rearrange into the lower-energy isomers like thioformaldehyde. In any case, these molecules represent noteworthy candidates for astronomical observation. The detection of new sulfur-containing molecules can give further insight into the depletion of sulfur, and H_2S in particular, in the gas phase and its role in gas-grain surface interactions [84]. More work along these lines is essential to explain the likely hidden sulfur reservoir in the ISM.

The present CCSD(T)-F12/cc-pVTZ QFF VPT2 vibrational frequencies for H_2CS compare excellently with experiment implying that the bright S—H stretch at 2280.5 cm^{-1} (4.385 μm) for *cis*-HCSH should be observed within a few cm^{-1} of this position. Furthermore, the $^1A_1$ H_2SC antisymmetric stretch at 1988.6 cm^{-1} (5.029 μm) would be confirmation of this isomer. The present work provides enough data for the [H_2, C, S] potential surface to be probed experimentally as the various isomers are formed and/or destroyed. Furthermore, the data given here also provide that which is necessary for the follow-up analysis of these molecules in the ISM with modern and upcoming infrared and radiotelescopes. Any of these isomers could contribute to the overall sulfur budget of any astrophysical region, and especially the HCSH forms are promising for future observation. However, more observations, experiments, and theoretical results are needed. The power of the upcoming *James Webb Space Telescope (JWST)* should be able to increase the amount of observable data and provide insights into the missing sulfur of the ISM.

CRediT authorship contribution statement

Natalia Inostroza-Pino: Conceptualization, Methodology, Investigation, Writing - original draft, Writing - review & editing. **C. Zachary Palmer:** Methodology, Investigation, Visualization, Formal analysis, Writing - original draft. **Timothy J. Lee:** Methodology, Writing - review & editing, Writing - original draft, Resources, Supervision. **Ryan C. Fortenberry:** Methodology, Visualization, Resources, Formal analysis, Writing - review & editing, Writing - original draft, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.jms.2020.111273.

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