

Coupled-cluster *ab initio* investigation of singlet/triplet CH₂S isomers and the reaction of atomic carbon with hydrogen sulfide to HCS/HSC

Christian Ochsenfeld^{a)}

Department of Chemistry, University of California at Berkeley, Berkeley, California 94720,
and Institut für Physikalische Chemie, Universität Mainz, D-55099 Mainz, Germany

Ralf I. Kaiser^{b)}

Department of Chemistry, University of California at Berkeley, Berkeley, California 94720, and Academia Sinica, Institute of Atomic and Molecular Sciences, 1, Section 4, Roosevelt Road, Taipei, 106, Taiwan, Republic of China, and Institut für Physik, Technische Universität Chemnitz-Zwickau, D-09107 Chemnitz, Germany

Yuan T. Lee^{c)}

Department of Chemistry, University of California at Berkeley, Berkeley, California 94720, and Academia Sinica, Institute of Atomic and Molecular Sciences, 1, Section 4, Roosevelt Road, Taipei, 106, Taiwan, Republic of China

Martin Head-Gordon

Department of Chemistry, University of California at Berkeley, Berkeley, California 94720, and Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720.

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The reaction of C(³P) with H₂S to HCS/HSC isomers is investigated with high level *ab initio* methods. Besides reaction energies to form HCS/HSC, the energetics and properties of different singlet/triplet H₂CS reaction intermediates are studied. The combination of *ab initio* theory and crossed molecular beams experiments leads to the conclusion that mainly HCS is formed under single collision conditions and that the reaction is indirect and proceeds through a thiohydroxycarbene intermediate. © 1999 American Institute of Physics.

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I. INTRODUCTION

Reactions of atomic carbon in its ³P_j electronic ground state with unsaturated hydrocarbons have been subject of a multitude of both theoretical and experimental investigations, motivated by their importance for hydrocarbon syntheses, astrophysical chemistry, and combustion processes. Although these reactions involve quite small molecules, usually with fewer than five to ten atoms, and despite progress in experimental and theoretical techniques, it is still often very difficult to obtain an understanding of the reaction mechanisms involved.

It has been well established that crossed molecular beams experiments are excellent tools to investigate the dynamics of chemical reactions under single collision conditions.¹ In these studies, the reaction products are mass detected. The center of mass angular distribution and translational energy distributions are inferred from the experimental data, and the reaction product as well as involved collision complexes characterized. However, in some cases, the nature of the reaction product(s) and/or of the decomposing complex(es) might remain unclear if we consider the experimental data alone. To simplify and even to allow for their identification, an exact knowledge of energetics, symmetries, and structural properties of the products and intermediates is

required—a task for which *ab initio* quantum chemistry can be often of important help.

From the theoretical point of view, a treatment of reaction dynamics is certainly in principle as well possible, however, a multitude of difficulties occur, which often prohibit a reliable theoretical study. Here, the most important basic problem is the quality of the potential energy surface (PES), which is crucial for a reliable theoretical treatment of reaction or molecular dynamics. Although modern developments in *ab initio* quantum chemistry have enabled a more and more efficient and accurate investigation of molecular properties, severe difficulties can be encountered already for the investigation of selected isomers of small, but complicated, molecules. Complicated means here that the electronic wavefunction is difficult to describe theoretically and therefore computationally demanding, high level electron correlation or even multireference techniques are required. These difficulties can frequently prohibit a reliable theoretical treatment with molecular dynamics methods, since here the necessary number of data points on the PES can become excessive and therefore computationally impossible to obtain.

One solution to the problem is to exploit both the strengths of theoretical and experimental techniques in combining them. In this way, high level *ab initio* calculations are able to provide reliable information on static properties, such as structure, energetics, symmetries of intermediates and reaction products, and the crossed molecular beams experiments allow to obtain information about the missing chemical dynamics as well as some of the reaction energetics.

^{a)}Present address: University of Mainz.

^{b)}Present address: Academia Sinica and University of Chemnitz-Zwickau.

^{c)}Present address: Academia Sinica.

Recently, we have shown the usefulness of this approach and we employed this highly useful symbiosis of theory and experiment to clarify the formation mechanism of C_3H isomers²⁻⁴ via atom-neutral reactions of triplet carbon atoms with C_2H_2 . This formation mechanism is especially important for interstellar chemistry and our investigation yields a possible explanation for the astronomically observed isomer ratios of linear to cyclic C_3H .²

In the present study, we investigate the reaction of triplet carbon with hydrogen sulfide to form HCS or HSC:



There are several reasons why this reaction is important and needs to be investigated. First, some sulfur containing molecules are known in interstellar space, however, the HCS radical has so far not been detected astronomically. Our combined theoretical and experimental study shows that it can possibly be formed in extraterrestrial environments. This is in agreement with model calculations of interstellar molecular clouds predicting that HCS should be detectable.⁵ Very recently, the microwave spectrum of the HCS isomer has been characterized by Habara *et al.*⁶ in the laboratory, and efforts for the astronomical detection are in progress. A second aspect of importance for reaction (1) is found in another extraterrestrial environment: In 1994 the comet Shoemaker-Levy-9 (SL9)⁷ impacted on Jupiter.⁸ As a result, a multitude of new sulfur compounds not indigenous to Jupiter's atmosphere were detected. Reaction networks trying to simulate the impact-induced sulfur chemistry suffered from the lack of laboratory data on reaction intermediates and products involved. To match observed data qualitatively, reaction models had to include postulated reactions involving transient species such as HCS and H_2CS .^{9,10} However, a precise knowledge of how and if those molecules could have been formed remained unclear and served as motivation for the present study of reaction (1). A third aspect is that reaction (1) could play a role in combustion processes (see, for example, Ref. 11 for more details).

The crossed molecular beams experiments described elsewhere in detail¹¹ indicate that the reaction of triplet carbon with H_2S proceeds through an intermediate H_2CS collision complex. Therefore, we study the different possible isomers on the H_2CS PES, as well as the reaction energies and properties of the final reaction products, HCS and HSC.

II. COMPUTATIONAL DETAILS

All *ab initio* calculations have been performed using the ACES II program package.¹² All calculations were carried out at the CCSD(*T*) (single- and double-excitation coupled cluster with a perturbational estimate of triple excitations) level¹³ and all electrons correlated (no frozen core approximation). Throughout this paper Unrestricted Hartree-Fock (UHF) reference wave functions have been used and only pure spherical harmonic basis functions were employed. For the sake of comparison, we list as well some self-consistent field (SCF), MP2 (Møller-Plesset second-order perturbation theory),¹⁴ and CCSD¹⁵ data. The stability of the zeroth-order wave function has always been checked.¹⁶

In selected cases, we compare with Brueckner CC methods.¹⁷⁻²¹ In these, the reference function is chosen such that the T_1 amplitudes vanish. Since the T_1 amplitudes account for most of the orbital relaxation effects in CC methods,²² data obtained with Brueckner methods are useful to compare with, in case symmetry-breaking effects occur in the zeroth-order wave function.

All structures were fully optimized at the CCSD(*T*) level imposing proper point group symmetries of D_{2h} and subgroups. The stationary points were characterized by vibrational frequencies, providing as well zero-point vibrational energies (ZPE). The second derivatives of the energy with respect to nuclear displacements were computed numerically within the harmonic approximation using analytic CCSD(*T*) gradients.²³ Since numerical differentiation can lead to difficulties in case of unstable or differing zeroth-order wavefunctions, frequencies have been computed in addition at the SCF level both analytically and numerically at the corresponding CCSD(*T*) structure. This simple check indicates if there is a serious problem with the zeroth-order wave function. In the future, it is of course highly preferable and easier to calculate vibrational frequencies analytically, a new development for CCSD(*T*) recently introduced by Gauss and Stanton.^{24,25}

Throughout this study the following basis sets were used:

TZP:	H (Ref. 26):	(5s1p)/[3s1p]
	C:	(10s6p1d)/[6s3p1d]
	S:	(12s9p1d)/[7s5p1d]
TZ2P:	H (Ref. 26):	(5s2p1d)/[3s2p1d]
	C:	(10s6p2d1f)/[6s3p2d1f]
	S:	(12s9p2d1f)/[7s5p2d1f]
QZ2P:	H (Ref. 26):	(7s2p1d)/[4s2p1d]
	C:	(11s7p2d1f)/[6s4p2d1f]
	S:	(15s12p2d1f)/[10s7p2d1f]
QZ3P:	H (Ref. 26):	(7s3p2d1f)/[4s3p2d1f]
	C:	(11s7p3d2f1g)/[6s4p3d2f1g]
	S:	(15s12p3d2f1g)/[10s7p3d2f1g]

The triple zeta polarization (TZP) basis²⁶ was used for all structure optimizations and calculations of vibrational frequencies (and ZPE) at the CCSD(*T*) level. In addition, for the HCS/HSC isomers structures and vibrational frequencies, and for the most stable isomer of H_2CS only structures, were computed using the quadruple zeta double polarization (QZ2P) basis²⁶ at the CCSD(*T*) level. In addition, the QZ3P basis was used for determining relative and reaction energies of HCS/HSC isomers. For the QZ2P and the quadruple zeta triple polarization (QZ3P) basis, only polarization functions from Dunning's correlation consistent bases²⁷ were used.²⁶

III. DISCUSSION OF RESULTS

The crossed molecular beams experiments described elsewhere¹¹ show that the reaction of $C(^3P)$ with H_2S proceeds through an intermediate H_2CS collision complex. Therefore, we investigate different singlet and triplet isomers first.

TABLE I. Relative energies of H₂CS isomers depicted in Fig. 1 with respect to the most stable H₂CS(¹A₁) isomer for which total energies are listed.

Method/Basis	H ₂ CS(¹ A ₁) (C _{2v}) (Hartree)	H ₂ CS(³ A'') (C _s) (kJ/mol)	HCSH _{trans} (¹ A') (C _s) (kJ/mol)	HCSH _{cis} (¹ A') (C _s) (kJ/mol)	HCSH(³ A) (C ₁) (kJ/mol)	H ₂ SC(¹ A ₁) (C _{2v}) (kJ/mol)	H ₂ SC(³ A'') (C _s) (kJ/mol)
CCSD(T)/TZP	-436.990889	172.6	206.5	214.5	275.0	537.6	512.1
CCSD(T)/QZ2P ^a	-437.110680	174.2	193.3	200.2	273.1	514.3	505.3
CCSD(T)/QZ2P/ZPE ^{a,b}	-437.085727	167.5	184.8	189.8	260.9	493.1	486.9
SCF/QZ2P ^a	-436.531084	87.5	186.1	194.0	170.8	548.5	408.9
MP2/QZ2P ^a	-436.994810	147.9	169.6	176.8	245.7	495.5	489.4
CCSD/QZ2P ^a	-437.028888	162.1	192.1	199.2	261.0	521.0	495.4

^aSingle-point calculations at the CCSD(T)/TZP structure.^bZero-point vibrational energies included as computed at the CCSD(T)/TZP level.

A. Intermediate H₂CS collision complexes

Table I shows the relative energies of the different singlet and triplet isomers studied (depicted in Fig. 1) in this work. Structural data and vibrational frequencies are listed in Table II–IV. The most stable isomer is singlet H₂CS, denoted as H₂CS(¹A₁). It is 167.5 kJ/mol [CCSD(T)/QZ2P/ZPE] more stable than the other structures of H₂CS (or HCSH/H₂SC). This energy difference of 167.5 kJ/mol corresponds to the singlet-triplet gap of H₂CS. The triplet isomer shows only C_s symmetry. However, the energy difference between the corresponding C_{2v} structure (³A₂; a saddle point at the CCSD(T)/TZP level) and the final minimum is very small (less than 1 kJ/mol). This indicates a very flat PES (the imaginary mode of H₂CS(³A'') with C_{2v} sym-

metry is 276.6i cm⁻¹). The observation of a very flat surface is in agreement with a recent multireference configuration interaction (MR-CI) study of Hachey and Grein,²⁸ although they found the triplet isomer to be planar. There have been a multitude of theoretical and experimental studies on the question of whether triplet H₂CS in its (*n*, π*) state is planar or not, and the recent paper of Hachey and Grein²⁸ gives a nice survey. For the present study with the focus on understanding the reaction of triplet carbon with hydrogen sulfide this question is of minor importance, a fact which will become clear later in this paper, where we discuss the experimental implications of our calculations.

Other isomers to be considered as possible intermediates for reaction (1) are those with hydrogen atoms attached to both C and S, respectively, the thiohydroxycarbenes. The corresponding singlet HCSH structures, *cis* and *trans*, are by 184.8 and 189.8 kJ/mol, respectively, energetically higher than the most stable H₂CS structure. For the thiohydroxycarbenes, however, only one triplet structure is found, HCSH(³A), which shows no point group symmetry. It is obtained from both *cis* or *trans* triplet HCSH structures with imposed C_s symmetry upon distortion along the corresponding imaginary mode (destroying the point group symmetry) and structure optimization. The HCSH(³A) isomer is 260.9 kJ/mol less stable than the most favored H₂CS structure. The symmetries of the so far considered H₂CS structures agree with an older *ab initio* study of 1985 by Pope *et al.*²⁹ The relative energies are also in surprisingly good agreement (deviations of roughly 10 kJ/mol or less) considering the fact that in the older study smaller basis sets than in the present investigation were used within the MRCI and CISD approach (including approximate quadruples corrections) and only the HF method with a 3-21G basis was employed to obtain the zero-point energies. Finally, we considered singlet and triplet states of H₂SC. These are 493.1 and 486.9 kJ/mol higher in energy than H₂CS(¹A₁).

B. Methodological aspects

Before presenting the results for the HCS/HSC isomers, it is worthwhile to discuss some methodological aspects of the investigation of the H₂CS intermediates presented in the previous section. The zeroth-order wave function (HF/TZP) of the isomers H₂SC(¹A₁), HCSH_{cis}(¹A'), and HCSH_{trans}(¹A'), suffers from symmetry-breaking problems

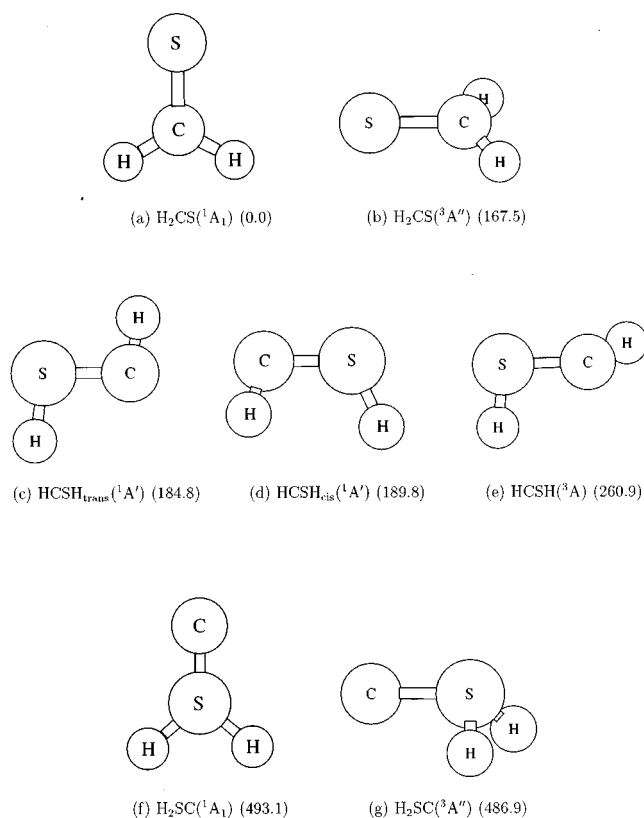


FIG. 1. Computed singlet and triplet isomers of H₂CS. Relative energies with respect to the most stable isomer, H₂CS(¹A₁) (C_{2v} symmetry), are listed in kJ/mol [CCSD(T)/QZ2P/ZPE].

TABLE II. Structural data, dipole moments (μ in Debye), and rotational constants (A, B, C) in cm^{-1} of H_2CS isomers (Fig. 1) as computed at the CCSD(T)/TZP level.

Isomer	Symmetry	Structural data ^a		$\ \mu\ $	$A/B/C$ (cm^{-1})
$\text{H}_2\text{CS}(^1A_1)$	$C_{2v}(^1A_1)$	(S–C)=162.2 (S, C, H)=122.0°	(C–H)=108.8	1.57	9.840/0.583/0.550
$\text{H}_2\text{CS}(^3A'')$	$C_s(^3A'')$	(S–C)=171.5 (S, C, H)=118.3°	(C–H)=108.2 (S, H, H, C)=20.3°	0.55	9.295/0.532/0.505
$\text{HCSH}_{\text{trans}}(^1A')$	$C_s(^1A')$	(H–C)=110.8 (S–H)=135.4 (C, S, H)=99.6°	(C–S)=168.3 (H, C, S)=100.8°	2.02	6.164/0.613/0.558
$\text{HCSH}_{\text{cis}}(^1A')$	$C_s(^1A')$	(H–C)=110.0 (S–H)=137.7 (C, S, H)=109.4°	(C–S)=166.2 (H, C, S)=109.5°	2.97	6.347/0.615/0.560
$\text{HCSH}(^3A)$	$C_1(^3A)$	(H–C)=108.4 (S–H)=135.3 (C, S, H)=98.5°	(C–S)=171.7 (H, C, S)=129.6° (H–C–S–H)=97.2°	1.19	7.251/0.550/0.530
$\text{H}_2\text{SC}(^1A_1)$	$C_{2v}(^1A_1)$	(C–S)=160.8 (C, S, H)=132.1°	(S–H)=139.6	3.83	7.787/0.643/0.594
$\text{H}_2\text{SC}(^3A'')$	$C_s(^3A'')$	(C–S)=196.5 (C, S, H)=104.6°	(S–H)=135.4 (C, H, H, S)=68.7°	4.41	5.067/0.460/0.454

^aNotation: (S–C)=162.2 denotes bond length in pm, (S, C, H)=122.0° denotes bond angle with apical atom C, (S, H, H, C)=20.3° stands for the out of plane angle between the bond S–C and the plane H–H–C, and (H–C–S–H)=97.2° stands for the torsion angle H–C–S–H.

within the imposed point-group symmetry. However, as discussed in an earlier paper more extensively,⁴ the CC method largely compensates for these effects. To check the behavior, the following data list energy differences between the true symmetry wavefunction and the HF-stable C_1 zeroth-order wave function (negative sign if symmetric solution is lower in energy; all data obtained at the CCSD(T)/TZP structures using the TZP basis):

$$\begin{aligned} \text{H}_2\text{SC}(^1A_1) &+ 2.2/-15.9/-0.2/-0.1 \quad (\text{SCF/MP2/CCSD/CCSD}(T)), \\ \text{HCSH}_{\text{cis}}(^1A') &+ 5.8/-17.9/-1.3/-1.2 \quad (\text{SCF/MP2/CCSD/CCSD}(T)), \\ \text{HCSH}_{\text{trans}}(^1A') &+ 8.3/-19.1/-1.6/-1.6 \quad (\text{SCF/MP2/CCSD/CCSD}(T)). \end{aligned}$$

These data indicate that the symmetry-breaking effects in the zeroth-order wave function are largely compensated at the CC level, whereas MP2 tends to overshoot quite strongly. A second indication for the reliability of the CC data using the true symmetry (but HF unstable) wave function is given by comparison of CCSD/TZP and B-CCD/TZP (Brueckner CCD/TZP) data. Here we consider the relative energies in kJ/mol of $\text{H}_2\text{CS}(^3A'')$ versus $\text{HCSH}_{\text{trans}}(^1A')$, $\text{HCSH}_{\text{cis}}(^1A')$, and $\text{H}_2\text{SC}(^1A_1)$:

$$\begin{aligned} \text{CCSD/TZP:} & \quad (0.0/43.7/52.2/382.4) \quad [\text{H}_2\text{CS}(^3A'')/\text{HCSH}_{\text{trans}}(^1A')/\text{HCSH}_{\text{cis}}(^1A')/\text{H}_2\text{SC}(^1A_1)], \\ \text{B-CCD/TZP:} & \quad (0.0/45.0/53.5/385.0) \quad [\text{H}_2\text{CS}(^3A'')/\text{HCSH}_{\text{trans}}(^1A')/\text{HCSH}_{\text{cis}}(^1A')/\text{H}_2\text{SC}(^1A_1)]. \end{aligned}$$

The small differences between the CCSD and B-CCD relative energies of 1.3–2.6 kJ/mol indicate that the conventional CCSD method already provides a sufficiently good description and supports as well the use of the CCSD(T) approach.

The additionally listed SCF and MP2 data in Table I show that relative energies at the SCF level deviate strongly by up to 102.3 kJ/mol [$\text{HCSH}(^3A)$] from our most reliable CCSD(T) data, which illustrates the necessity for high level electron correlation methods for an accurate treatment. At the MP2 level, the differences are already smaller, but they still remain significant with values of up to 27.4 kJ/mol.

Furthermore, it is well known that unstable zeroth-order wave functions may have dramatic effects on the calculation of properties such as vibrational frequencies:^{30,31} Singularities in the orbital rotation hessian can lead to unphysical frequencies.

TABLE III. Harmonic vibrational frequencies computed at the CCSD(T)/TZP level of H_2CS singlet isomers depicted in Fig. 1. Symmetry of modes, wave numbers (cm^{-1}), and IR intensities (km/mol ; in parentheses) are listed.

	$\text{H}_2\text{CS}(^1A_1)$		$\text{HCSH}_{\text{trans}}(^1A')$		$\text{HCSH}_{\text{cis}}(^1A')$		$\text{H}_2\text{SC}(^1A_1)$				
b_1	1027.0	(3.2)	a'	845.9	(31.7)	a'	786.7	(20.7)	b_2	218.0	(44.3)
b_2	1032.3	(44.1)	a'	943.7	(16.3)	a''	928.0	(9.7)	b_1	573.4	(58.8)
a_1	1078.1	(5.6)	a''	976.1	(26.8)	a'	934.3	(33.5)	a_1	982.6	(12.5)
a_1	1533.1	(5.1)	a'	1185.8	(8.8)	a'	1107.2	(1.6)	a_1	1389.9	(108.7)
a_1	3096.1	(27.0)	a'	2615.1	(15.0)	a'	2418.1	(136.6)	b_1	2052.0	(567.6)
b_1	3186.2	(12.6)	a'	2968.0	(63.9)	a'	3030.2	(43.8)	a_1	2200.9	(281.2)

TABLE IV. Harmonic vibrational frequencies computed at the CCSD(*T*)/TZP level of H₂CS triplet isomers depicted in Fig. 1. Symmetry of modes, wave numbers (cm⁻¹), and IR intensities (km/mol, in parentheses) are listed.

H ₂ CS(³ A'')			HCSH(³ A)			H ₂ SC(³ A'')		
<i>a'</i>	377.3	(96.2)	<i>a</i>	418.6	(18.8)	<i>a'</i>	305.3	(21.7)
<i>a''</i>	799.6	(0.0)	<i>a</i>	823.6	(10.0)	<i>a''</i>	519.5	(2.5)
<i>a'</i>	840.5	(4.2)	<i>a</i>	920.8	(5.1)	<i>a'</i>	607.9	(2.3)
<i>a'</i>	1393.4	(0.6)	<i>a</i>	938.9	(11.0)	<i>a'</i>	1203.7	(10.0)
<i>a'</i>	3149.6	(0.4)	<i>a</i>	2616.9	(11.3)	<i>a'</i>	2614.9	(12.1)
<i>a''</i>	3269.3	(0.4)	<i>a</i>	3194.1	(10.3)	<i>a''</i>	2629.1	(2.4)

The size of the negative eigenvalues occurring in the orbital rotation Hessians of the concerned isomers are -0.01 a.u. in A_2 symmetry for H₂SC(¹A₁) and -0.03 a.u. in A'' symmetry for HCSH_{trans}(¹A') and HCSH_{cis}(¹A'), which can serve as indication on the proximity to a point of singularity.³¹ To investigate the effects of orbital instabilities more specifically, we calculated the vibrational frequencies within the same problematic symmetry block (A'' symmetry for HCSH_{trans}(¹A') and HCSH_{cis}(¹A')); compare Table III) on both CCSD and B-CCD level. The obtained frequencies agree within less than 6 cm⁻¹, so that no influence of the orbital instabilities on to the force constants of the considered isomers is found. In addition, the agreement of vibrational frequencies computed both numerically and analytically at the CCSD(*T*) level hints to no difficulties with symmetry-broken zeroth-order wave functions in the present case.

C. HCS/HSC isomers and reaction energies

The relative energies of HCS and HSC as well as the reaction energies for (1) are listed in Table V. The HCS isomer is favored by 165.6 kJ/mol at the CCSD(*T*)/

QZ3P/ZPE level. The relative energy of the two isomers changes by 2.5 kJ/mol in increasing the basis from QZ2P to QZ3P.

The comparison of structural data, rotational constants, vibrational frequencies listed in Tables VI and VII for HCS and HSC, respectively, as obtained by using different basis sets indicates that the QZ2P basis is reliable at the CCSD(*T*) level. Bond lengths change by less than 0.2 pm and angles by less than 0.5° in increasing the basis from TZ2P to QZ2P. Our structural data for the HCS isomer differs by less than 0.9 pm and 0.5° from older *ab initio* data (MCSCF CI) of Senekowitsch *et al.*³² The energy for the reaction of triplet carbon with hydrogen sulfide (1) to form HCS and HSC is exothermic by 183.9 and 18.3 kJ/mol, respectively [CCSD(*T*)/QZ3P/ZPE].

IV. EXPERIMENTAL IMPLICATIONS

In the following, we briefly outline the experimental implications of our electronic structure calculations on the crossed beams reaction of atomic carbon, C(³P), with hydrogen sulfide, H₂S. Experiments were performed at four

TABLE V. Relative energies of HCS and HSC. For HCS as well total energies in a.u. are given. In addition, reaction energies of C(³P) with H₂S to form HCS, HSC, or ¹H₂CS are listed.

Method/Basis	HCS (Hartree)	HSC (kJ/mol)	ΔE_{R1}^a (kJ/mol)	ΔE_{R2}^b (kJ/mol)	ΔE_{R3}^c (kJ/mol)
CCSD/TZ2P	-436.394262	165.0	-142.0	+23.1	...
CCSD(<i>T</i>)/TZP	-436.336679	173.9	-158.2	+15.7	-563.6
CCSD(<i>T</i>)/TZ2P	-436.413889	169.7	-164.6	+5.1	...
CCSD(<i>T</i>)/QZ2P	-436.454018	169.4	-164.2	+5.2	-575.8
CCSD(<i>T</i>)/QZ3P ^d	-436.489099	171.9	-175.0	-3.1	...
CCSD(<i>T</i>)/QZ2P/ZPE	-436.442170	163.1	-173.1	-10.0	-550.4 ^e
CCSD(<i>T</i>)/QZ3P/ZPE ^{d,f}	-436.477251	165.6	-183.9	-18.3	...
SCF/QZ2P ^d	-435.938034	141.0	-75.4	+65.6	-407.1
SCF/QZ3P ^d	-435.940386	140.8	-77.3	+63.5	...
MP2/QZ2P ^d	-436.397938	154.9	-159.8	-4.9	-565.5
MP2/QZ3P ^d	-436.434124	156.5	-169.0	-12.5	...
CCSD/QZ2P ^d	-436.433771	164.6	-141.2	+23.5	-553.7
CCSD/QZ3P ^d	-436.466521	166.9	-151.1	+15.7	...

^aH₂S+C→HCS+H.

^bH₂S+C→HSC+H.

^cH₂S+C→H₂CS(¹A₁).

^dComputed at the CCSD(*T*)/QZ2P structures.

^eCCSD(*T*)/TZP-ZPE is used.

^fCCSD(*T*)/QZ2P-ZPE is used.

TABLE VI. Structural data, dipole moments, rotational constants, vibrational frequencies, and zero-point energies (ZPE) of HCS($^2A'$).

		CCSD TZ2P	CCSD(T) TZP	CCSD(T) TZ2P	CCSD(T) QZ2P
$r(\text{H-C})$	(pm)	108.3	108.8	108.6	108.7
$r(\text{C-S})$	(pm)	155.9	157.5	156.6	156.4
$\angle(\text{H, C, S})$		132.8°	131.9°	131.8°	132.3°
$\ \mu\ $	(Debye)	1.02	1.07	1.01	1.02
A	(cm^{-1})	31.644	30.323	30.424	30.783
B	(cm^{-1})	0.681	0.669	0.677	0.678
C	(cm^{-1})	0.667	0.655	0.662	0.663
$\omega(a')$	(cm^{-1}) (km/mol)	3171.0 (6.6)	3135.3 (10.9)	3133.9 (7.2)	3145.9 (6.3)
$\omega(a')$	(cm^{-1}) (km/mol)	1237.5 (15.0)	1190.9 (8.0)	1214.3 (9.5)	1217.7 (9.9)
$\omega(a')$	(cm^{-1}) (km/mol)	861.1 (64.3)	883.3 (61.6)	851.2 (65.9)	837.0 (68.3)
ZPE	(kJ/mol)	31.52	31.16	31.10	31.11

different average collision energies between 16.7 and 42.8 kJ/mol. We limit ourselves here to a brief discussion of the reaction products formed (HCS or HSC isomer(s)), the involved H_2CS (or $\text{HCSH}/\text{H}_2\text{SC}$) reaction intermediates, and some aspects of the chemical dynamics of the reaction. Details of the experiments are given elsewhere.¹¹ For the physical interpretation of the scattering data, the laboratory data was transformed into the center-of-mass (CM) reference frame.³³ This procedure initially guesses the angular flux distribution $T(\Theta)$ and the translational energy flux distribution $P(E_T)$ in the center-of-mass system, which are then iteratively refined.¹¹

Comparison of the computed *ab initio* reaction energies and the experimentally obtained high energy cutoffs of the $P(E_T)$ s allow to determine the product isomer(s), since the reaction energies to the two possible isomers HCS/HSC differ significantly. The comparison clearly indicates that the HCS isomer is formed as the major product, rather than the (165.6 kJ/mol) less stable HSC isomer.

Comparison of the scattering behavior observed at different collision energies leads to conclusions on the chemical dynamics of the reaction and on the structure of intermediate collision complexes. At the lower collision energies, the $T(\Theta)$ s are isotropic and symmetric around $\pi/2$ which implies that either the decomposing H_2CS complex has a lifetime longer than its rotational period or that the exit transition state is symmetric.³⁴ As the collision energy rises, the

CM angular distribution peaks forward with respect to the carbon beam. These findings indicate a reduced lifetime of the H_2CS complex within the osculating complex model: a complex formation takes place, but the well depth along the reaction coordinate is too shallow to allow multiple rotations, and the complex decomposes with a random lifetime distribution before one full rotation elapses. To explain the forward peaking, the carbon atom and the leaving hydrogen atom have to be located on opposite sites of the rotation axis of the fragmenting complex. Detailed analyses suggest that the reaction begins by addition of $\text{C}(^3P_j)$ to the sulfur atom of H_2S to form a triplet H_2SC van der Waals complex. A successive [1,2]-H atom migration on the triplet or singlet surface forms a thiohydroxycarbene intermediate, HCSH, which dissociates to HCS and H. Therefore, three possible exit transition states from either singlet *trans/cis*- or triplet HCSH could contribute to the reactive scattering signal. However, the present investigations do not distinguish between those three possibilities, for which future work is required, such as investigating the exit transition states of these thiohydroxycarbenes to HCS and H as well as the possible contribution of thioformaldehyde at both lower collision energies.

V. CONCLUSION

In this paper, we have presented an *ab initio* study of H_2CS isomers (on both singlet and triplet surfaces) and the

TABLE VII. Structural data, dipole moments, rotational constants, vibrational frequencies, and zero-point energies (ZPE) of HSC($^2A'$).

		CCSD TZ2P	CCSD(T) TZP	CCSD(T) TZ2P	CCSD(T) QZ2P
$r(\text{H-S})$	(pm)	136.2	137.2	136.7	136.7
$r(\text{S-C})$	(pm)	165.6	167.0	165.8	165.6
$\angle(\text{H, S, C})$		102.3	102.6	102.7	102.7
$\ \mu\ $	(Debye)	2.55	2.64	2.59	2.62
A	(cm^{-1})	9.900	9.784	9.860	9.858
B	(cm^{-1})	0.688	0.676	0.685	0.687
C	(cm^{-1})	0.644	0.632	0.641	0.642
$\omega(a')$	(cm^{-1}) (km/mol)	2488.6 (16.6)	2417.0 (40.8)	2426.0 (22.6)	2428.8 (21.5)
$\omega(a')$	(cm^{-1}) (km/mol)	939.0 (43.2)	911.0 (43.2)	924.7 (37.2)	929.6 (40.3)
$\omega(a')$	(cm^{-1}) (km/mol)	810.3 (22.5)	785.2 (17.3)	782.4 (16.3)	785.1 (16.8)
ZPE	(kJ/mol)	25.35	24.60	24.72	24.78

reaction of triplet carbon with hydrogen sulfide to form HCS and/or HSC. The investigation of these molecules is crucial for an understanding of the corresponding reaction mechanisms observed in crossed molecular beams experiments and the study allows determination of which reaction products are formed under single collision conditions. This combination of theory and experiment allows us to establish that mainly the HCS radical is formed and that the reaction proceeds via HSCH intermediates, thiohydroxycarbenes, either on the singlet or triplet surface.

The studied reaction to form HCS via a one-step pathway implies that such reactions are able to form carbon-sulfur bonds in combustion processes, interstellar environments, and possibly in the collision of comet Shoemaker-Levy 9 with Jupiter. Here, the investigated reaction may account for the missing HCS source required for chemical reaction networks simulating the impact induced sulfur chemistry.¹⁰ Although the involved H₂CS intermediates cannot be stabilized under single collision conditions as encountered in crossed molecular beams experiments and the interstellar medium, denser planetary or cometary environments might supply third body collisions. These could divert the internal energy of the H₂CS intermediates and in this way stabilize them. The listed dipole moments and rotational constants might be of help for an astronomical detection of these intermediates as well as of the HCS/HSC isomers. However, to obtain a better understanding of the highly complicated processes involved in interstellar chemistry or the collision of comet Shoemaker-Levy 9 with Jupiter, much more work is necessary and even in the case of the reaction studied here, further work is needed to distinguish between the three suggested intermediate collision complexes.

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