

# A Crossed Beam and *ab Initio* Investigation of the Reaction of Hydrogen Sulfide, $\text{H}_2\text{S}(\text{X}^1\text{A}_1)$ , with Dicarbon Molecules, $\text{C}_2(\text{X}^1\Sigma_g^+)$

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The reaction of the dicarbon molecule  $\text{C}_2(\text{X}^1\Sigma_g^+)$  with hydrogen sulfide,  $\text{H}_2\text{S}(\text{X}^1\text{A}_1)$ , was investigated under single collision conditions in a crossed beam setup with mass spectrometric detection at an averaged collision energy of  $46.0 \text{ kJ mol}^{-1}$ . The experiment was supplemented by electronic structure calculations. The reaction dynamics are dictated by a barrierless addition of dicarbon to the sulfur atom to form a bound  $\text{H}_2\text{SCC}$  intermediate followed by two successive hydrogen migrations on the singlet surface to give a singlet thiohydroxyacetylene ( $\text{HCCSH}$ ) species. The latter emits atomic hydrogen to yield the  $\text{HCCS}(\text{X}^2\Pi_\Omega)$  isomer. Possible alternative pathways, the elimination of atomic and molecular hydrogen from a thioketene ( $\text{H}_2\text{CCS}$ ) intermediate, to synthesize  $\text{HCCS}$  and  $\text{CCS}$  are also discussed.

## 1. Introduction

Investigating the formation of sulfur bearing molecules in extraterrestrial environments is an important means to understand the history and chemical evolution of star forming regions, cold molecular clouds, and circumstellar envelopes of carbon stars.<sup>1</sup> Compared to the cosmic carbon versus sulfur ratio of 15:1,<sup>2</sup> sulfur is severely depleted in carbon containing molecules. So far, only  $\text{CS}$ ,  $\text{COS}$ ,  $\text{HNCS}$ ,  $\text{CH}_3\text{SH}$ ,  $\text{H}_2\text{CS}$ ,  $\text{HCS}^+$ ,  $\text{CS}^+$ , together with the cummulenes  $\text{C}_2\text{S}$  and  $\text{C}_3\text{S}$  have been observed astronomically.<sup>3</sup> The homologous row  $\text{C}_n\text{S}$  ( $n = 1-3$ ) is of particular astrochemical interest. Although these molecules are ubiquitous in cold molecular clouds  $\text{OMC-1}$  and  $\text{TMC-1}$ ,<sup>4,5,6</sup> in circumstellar envelopes of the protostellar object  $\text{B3357}$  and in the outflow of the carbon star  $\text{IRC+10216}$ ,<sup>8</sup> their hydrogen terminated species  $\text{HC}_n\text{S}$  and  $\text{C}_n\text{SH}$  have neither been searched for nor included into astrochemical models. Therefore, these molecules might represent the missing source of molecular-bound sulfur in the interstellar medium. Besides the significant role of the  $\text{H-C-S}$  system in astrochemical processes, organosulfur molecules are also thought to be of fundamental importance in the combustion of sulfur containing fuel and coal. Hitherto, only simple di- and triatomic sulfur bearing species  $\text{S}_2$ ,  $\text{SH}$ ,  $\text{CS}$ ,  $\text{H}_2\text{S}$ ,  $\text{OCS}$ , and  $\text{SO}_2$  have been identified explicitly in combustion flames.<sup>9,10</sup> However, as pointed out recently, more complex hydrogen deficient organosulfur molecules such as  $\text{HCS}(\text{X}^2\text{A}')$  could present important reaction intermediates in combustion processes which might ultimately lead to acetic rain and to sulfur carrying aromatic molecules.<sup>11</sup>

However, despite the potential key role of  $\text{HC}_n\text{S}$  isomers to understand the organosulfur chemistry in terrestrial and interstellar environments, the underlying potential energy surfaces (PESs) involved are poorly characterized. Previous mechanistic information are limited to the  $\text{C}(\text{P}_1)/\text{H}_2\text{S}$  system which accessed

the  $\text{HCS}$  and  $\text{H}_2\text{CS}$  PESs. Crossed molecular beam experiments combined with *ab initio* calculations demonstrated the initial formation of a  $\text{H}_2\text{SC}$  addition complex, which undergoes hydrogen migration to the thiohydroxycarbene isomer,  $\text{HSCH}$ . The latter was found to fragment to atomic hydrogen and the thiohydroxyformyl radical  $\text{HCS}(\text{X}^2\text{A}')$ . At lower collision energies, a [1,2] H shift in  $\text{HCSH}$  was suggested to form the  $\text{HCS}$  isomer via a decomposing thioformaldehyde ( $\text{H}_2\text{CS}$ ) intermediate. Upper limits of 10% to form the less stable  $\text{HSC}(\text{X}^2\text{A}'')$  isomer were also derived. A recent theoretical investigation supports these conclusions indicating that  $\text{HSC}$  should be only synthesized to a minor amount at higher collision energies.<sup>12</sup>

Compared to the  $\text{C}(\text{P}_1)/\text{H}_2\text{S}$  system, the characterization of the  $\text{H}_x\text{C}_2\text{S}$  ( $x = 0-2$ ) PES is less complete. Li and Iwata investigated the electronic states of the thioketenyl radical ( $\text{HCCS}$ ) theoretically.<sup>13</sup> Their computations suggest a  $\text{C}_{\infty v}$  structure and a  $^2\Pi$  electronic ground state. The linearity and the bond lengths of  $\text{H-CCS}$  ( $1.057-1.064 \text{ \AA}$ ),  $\text{HC=CS}$  ( $1.225-1.223 \text{ \AA}$ ), and  $\text{HCC=S}$  ( $1.612-1.633 \text{ \AA}$ ) imply that the  $\text{HCCS}$  isomer exhibits a Renner-Teller effect.<sup>13-15</sup> The first electronically excited state,  $\text{A}^2\Pi$ , was found to be  $290 \text{ kJ mol}^{-1}$  above the ground state. Vibrational frequencies were calculated to be  $336, 353, 445, 649, 775, 1923, \text{ and } 3455 \text{ cm}^{-1}$ ,<sup>13</sup> whereas the spin-orbit splitting in  $\text{HCCS}$  was derived to  $185^{19}-270 \text{ cm}^{-1}$ .<sup>16</sup> Tang and Saito recorded the microwave spectra of the thioketenyl radical in the  $160-400 \text{ GHz}$  range.<sup>16</sup> The authors determined the  $\nu_4$  and  $\nu_5$  vibration modes to be  $565$  and  $380 \text{ cm}^{-1}$ , respectively. The carbon-sulfur stretching mode was assigned to be  $740 \text{ cm}^{-1}$ ,<sup>17</sup> whereas the dipole moment was estimated to  $1.23-1.43 \text{ D}$ .<sup>18</sup> Vritilek determined the rotational constant of  $\text{HCCS}$  to  $0.19578-0.19575 \text{ cm}^{-1}$ <sup>19</sup> versus a computed value of  $0.19289 \text{ cm}^{-1}$ .<sup>18</sup> Very recently, Flores et al. explored the reaction of atomic sulfur with ethynyl radicals theoretically.<sup>20</sup> They concluded that  $\text{HCCS}(\text{X}^2\Pi)$  represents the global minimum; the cyclic isomer was found to be less stable

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by about 117 kJ mol<sup>-1</sup>, whereas the bent structure HSCC(X<sup>2</sup>A') ranges about 192 kJ mol<sup>-1</sup> above the thioketenyl radical.

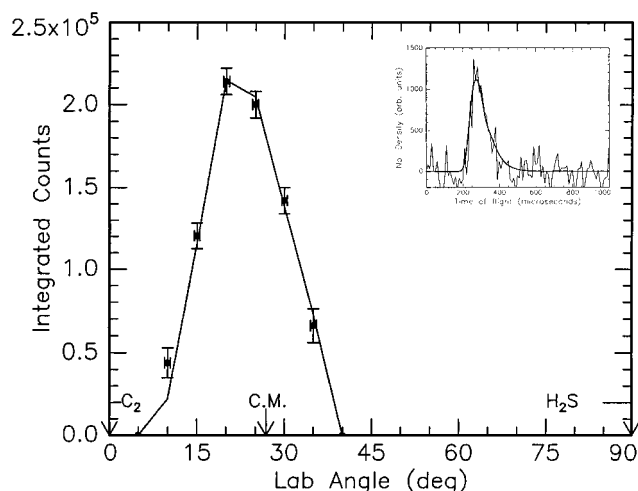
Data on the related carbon-sulfide cluster CCS are also sparse. The linear CCS molecule has a <sup>3</sup>Σ<sup>-</sup> ground state,<sup>21</sup> whereas the excited singlet state <sup>1</sup>Δ was found to be 47.0,<sup>21</sup> 45.7,<sup>22</sup> or 44.8–56.7 kJ mol<sup>-1</sup> higher in energy.<sup>20</sup> The lengths of the carbon–carbon and sulfur–carbon bonds of 1.314 and 1.575 Å suggest a cummulene structure holding a dipole moment of 2.88 D.<sup>21</sup> These data are in good agreement with Murakami's investigation (2.8 D).<sup>23</sup> The cyclic, C<sub>2v</sub>, isomer of C<sub>2</sub>S in its <sup>1</sup>A<sub>1</sub> electronic ground state is 90–100 kJ mol<sup>-1</sup> less stable than the linear structure.<sup>20,24</sup> This limited information clearly indicates the necessity to investigate the H<sub>x</sub>C<sub>2</sub>S (x = 0–2) PESs systematically to understand the astrophysical and combustion chemical applications of these important sulfur bearing molecules. In this paper, we present the first results of a combined crossed beam and ab initio investigation on the reaction of the dicarbon molecule, C<sub>2</sub>, in its electronic ground state <sup>1</sup>Σ<sub>g</sub><sup>+</sup> with hydrogen sulfide, H<sub>2</sub>S(X<sup>1</sup>A<sub>1</sub>).

## 2. Experimental Setup and Data Processing

The reactive scattering experiment was performed at a collision energy of 46.0 ± 2.0 kJ mol<sup>-1</sup> employing the 35'' universal crossed molecular beam apparatus described in ref 25. A dicarbon beam of C<sub>2</sub>(X<sup>1</sup>Σ<sub>g</sub><sup>+</sup>/a<sup>3</sup>Π<sub>u</sub>) was prepared via laser ablation of graphite and seeding the ablated species in helium carrier gas.<sup>26</sup> A chopper wheel located after the ablation zone and the skimmer selected a slice of the pulsed beam with a peak velocity of 2380 ± 10 ms<sup>-1</sup> and speed ratio of 4.3 ± 0.3. At this velocity, the beam contains ground state <sup>1</sup>Σ<sub>g</sub><sup>+</sup> and small amounts of electronically excited dicarbon molecules in the <sup>3</sup>Π<sub>u</sub> state.<sup>27</sup> However, the latter does not interfere as the electronic structure calculations suggest that the potential between triplet C<sub>2</sub> and H<sub>2</sub>S is nonreactive (section 3). The pulsed dicarbon beam crossed a hydrogen sulfide beam with a peak velocity of 940 ± 10 ms<sup>-1</sup> and a speed ratio of 9.2 ± 0.2 at 90° in a scattering chamber held at 1–2 × 10<sup>-7</sup> mbar. Reaction products were detected via a quadrupole mass spectrometer rotatable in the plane defined by both beams and coupled to an electron impact ionizer. The detector unit is placed in an ultrahigh-vacuum (<8 × 10<sup>-13</sup> mbar) chamber. By employing the time-of-flight (TOF) technique, the product velocity distributions were measured at different laboratory scattering angles and for distinct mass-to-charge ratios (*m/e*); up to 800 000 TOF spectra were averaged per lab angle. To extract quantitative information on the reaction dynamics, a transformation of coordinates from the laboratory system to the center-of-mass (CM) reference frame is employed.<sup>9</sup> This was actually achieved by a forward convolution of trial CM functions, the product angular, *T*(θ), and translational energy, *P*(*E*<sub>T</sub>), flux distributions, until the best fit of the laboratory data is obtained.

## 3. Electronic Structure Calculations

The singlet potential energy surface (PES) of the reaction of C<sub>2</sub>(X<sup>1</sup>Σ<sub>g</sub><sup>+</sup>) with hydrogen sulfide H<sub>2</sub>S was examined in terms of ab initio molecular orbital methods. We have employed the hybrid density functional B3LYP method, i.e., Becke's three parameter nonlocal exchange functional<sup>28</sup> with the nonlocal correlation functional of Lee, Yang, and Parr<sup>29</sup> and the 6-311G(d,p) basis set.<sup>30</sup> The structures of the intermediates and transition states have been confirmed with the vibrational analysis; all relative energies are the corrected values of the zero-point vibrational energies with the B3LYP/6-311G(d,p) level of calculation. The coupled cluster CCSD(T)<sup>31,32</sup> calcula-

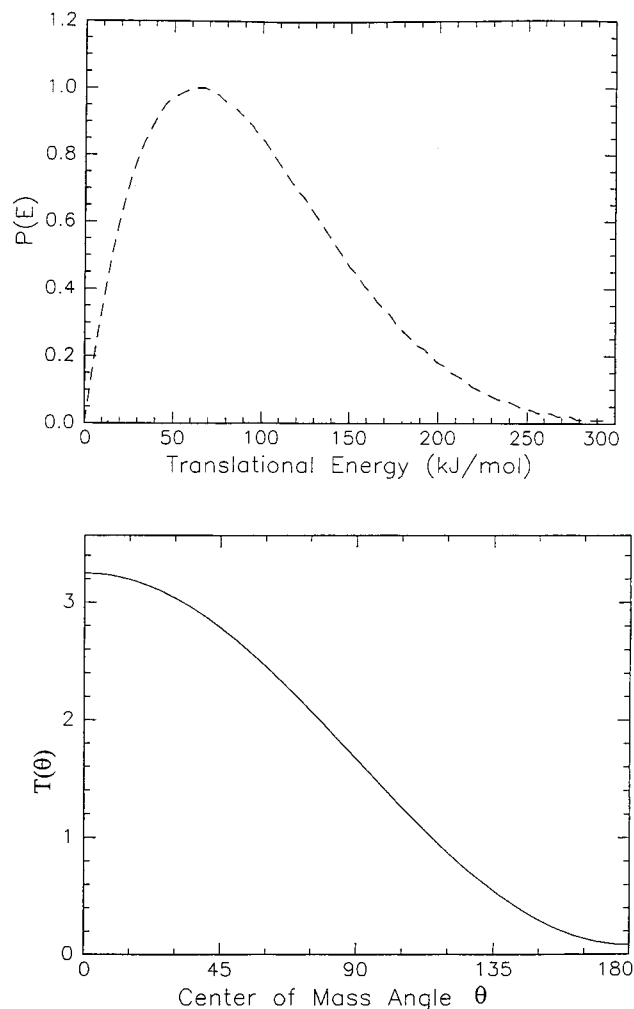


**Figure 1.** Laboratory angular distribution at *m/e* = 57 obtained for the C<sub>2</sub> + H<sub>2</sub>S reaction. Open circles and 1σ error bars indicate the experimental data whereas the solid line represents the best fit. The time-of-flight spectrum of *m/e* = 57 recorded at the center-of-mass angle of 27.0° is shown in the upper right corner (light line: experimental data; fat line: calculated fit). CM indicates the center-of-mass angle.

tions with the aug-cc-pVTZ basis set<sup>33</sup> have also been performed at the optimized structures obtained with the B3LYP method in order to refine the energetics. All computations have been carried out using the Gaussian 98 program package.<sup>34</sup> The relative energies stated in the text are the values obtained with the CCSD(T) method. Note that the interaction of triplet dicarbon with the hydrogen sulfide molecule forms a van der Waals complex; the latter was found to lead via hydrogen abstraction to SH + C<sub>2</sub>H. The energy of this transition state involved is slightly higher than the energy of the separated reactants. No reaction pathway has been found on the triplet PES leading to HC<sub>2</sub>S or C<sub>2</sub>S isomers. Therefore, we do not present detailed data on the reaction of C<sub>2</sub>(a<sup>3</sup>Π<sub>u</sub>) with H<sub>2</sub>S(X<sup>1</sup>A<sub>1</sub>) in this paper.

## 4. Experimental Results

**A. Laboratory Data.** The crossed beam experiments were complicated by the fact that sulfur has four isotopes of *m/e* = 36 (0.02%), 34 (4.21%), 33 (0.75%), and 32 (95.02%); the natural abundances are given in parentheses. Carbon possess the isotopes <sup>12</sup>C (98.9%) and <sup>13</sup>C (1.1%). To minimize the background of higher sulfur and carbon isotopes, we investigated a possible H atom elimination channel at *m/e* = 57 (H<sup>12</sup>C<sub>2</sub><sup>32</sup>S<sup>+</sup>) and a molecular H<sub>2</sub> loss pathway at *m/e* = 56 (<sup>12</sup>C<sub>2</sub><sup>32</sup>S<sup>+</sup>). This guarantees no interferences at *m/e* = 56 and only a marginal background from <sup>12</sup>C<sub>2</sub><sup>33</sup>S<sup>+</sup> together with fragmentation of H<sup>13</sup>C<sup>12</sup>C<sup>32</sup>S<sup>+</sup> (*m/e* = 58) to *m/e* = 57. The reactive scattering signal was observed at *m/e* = 57 (H<sup>12</sup>C<sub>2</sub><sup>32</sup>S<sup>+</sup>) and 56 (<sup>12</sup>C<sub>2</sub><sup>32</sup>S<sup>+</sup>) at distinct laboratory angles between 10° and 35°. To obtain the laboratory angular distribution (LAB) displayed in Figure 1, TOF spectra of *m/e* = 57 taken at identical laboratory angles were added, weighted by their data accumulation time, and integrated. This yields a LAB distribution at *m/e* = 57 which is relatively narrow, extends only 40° in the scattering plane, and peaks at a laboratory angle of 20°. Compared to the CM angle θ of 27.2° ± 0.5°, Figure 1 shows a preferential “forward” scattering with respect to the dicarbon beam. These data suggest that at least a dicarbon versus atomic hydrogen pathway is open. At *m/e* = 56, the intensity of the reactive scattering signal was very low; data had to be accumulated at the center-of-mass angle



**Figure 2.** Top: Best fit center-of-mass translational energy flux distributions for the HCCS + H pathway. Bottom: Best fit angular flux distributions for the HCCS + H pathway.

up to 86 h. No complete angular distribution could be acquired for  $m/e = 56$  within reasonable error bars. So far, the raw data indicate that the TOF of  $m/e = 57$  and 56 differ slightly in the fast part of the spectra; however, because of the lack of a complete angular distribution at  $m/e = 56$ , the weak C<sub>2</sub> beam, and the limited signal-to-noise ratio of the data, we cannot extract detailed dynamical information on the H<sub>2</sub> loss pathway from the experiments.

**B. Center-of-Mass Functions.** The reaction dynamics are inferred by transforming the data from the laboratory system to the CM reference frame, cf. section 2. The bold lines superimposed on the TOF data are the calculated curves when using the best-fit CM functions. Data at  $m/e = 57$  were fit with one channel of products with the masses 57 (HC<sub>2</sub>S) and 1 (H). The corresponding translational energy distribution,  $P(E_T)$ , and angular distribution,  $T(\theta)$ , are shown in Figure 2. We obtained best fit with a  $P(E_T)$  extending to a maximum translational energy release  $E_{\max}$  of 300 kJ mol<sup>-1</sup>. The high-energy cutoff is relatively insensitive, and increasing  $E_{\max}$  by up to 30 kJ mol<sup>-1</sup> does not change the fit significantly. Because  $E_{\max}$  presents the sum of the reaction energy plus the collision energy, a subtraction of the latter from the maximum translational energy release gives a reaction exothermicity of about 254 kJ mol<sup>-1</sup>. Second, the  $P(E_T)$  peaks at 60 kJ mol<sup>-1</sup>.

The shape of the CM angular flux distribution of the atomic hydrogen loss pathway can be employed to collect further

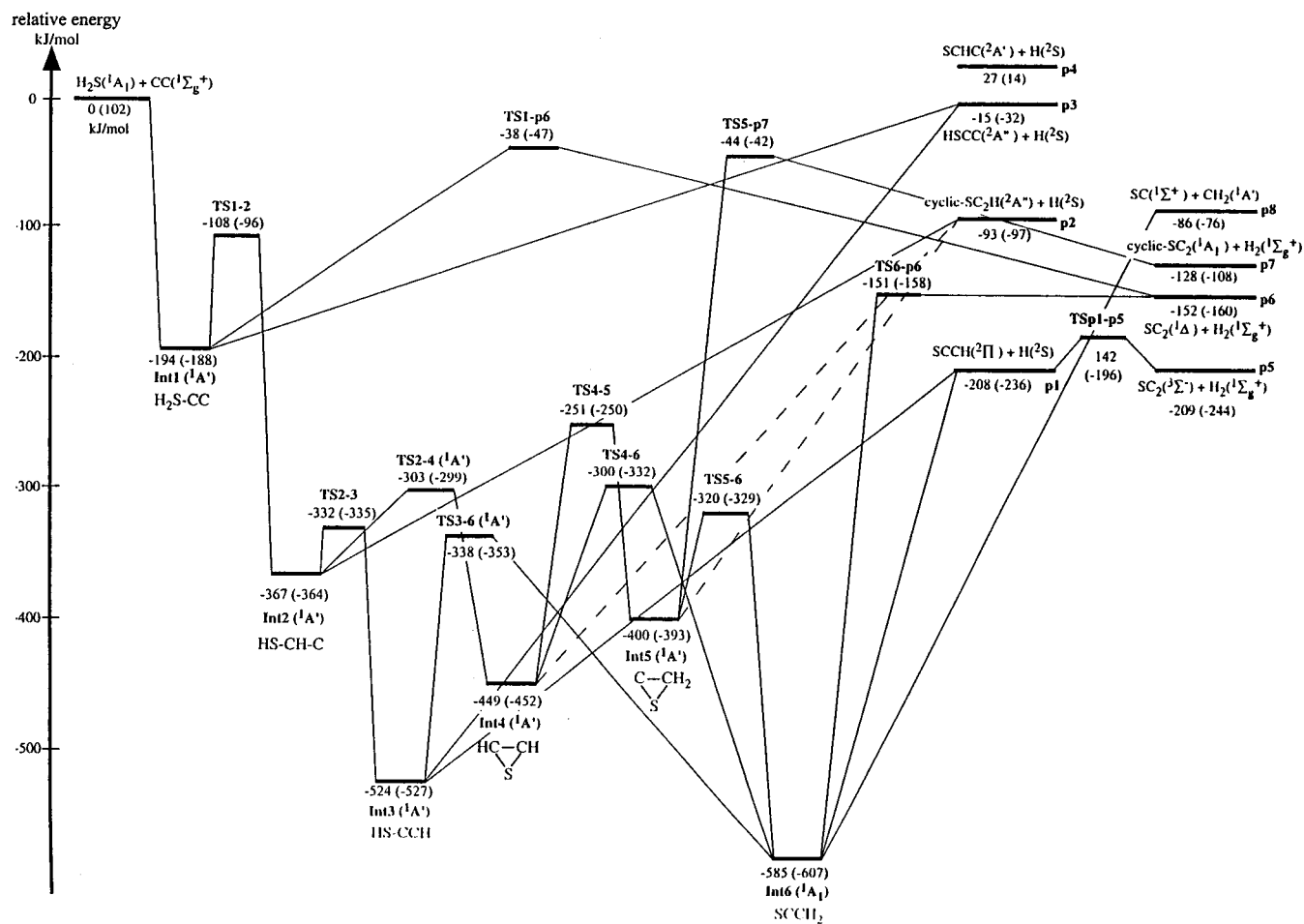
information on the chemical dynamics. This channel was fit with a forward-scattered distribution and does not change significantly if the intensity ratio at the poles, i.e.,  $I(0^\circ)/I(180^\circ)$ , is varied between 43.0 and 36.0. This suggests that this reaction pathway is indirect (complex forming reaction dynamics) and involves an oscillating complex, i.e., an intermediate with a lifetime of less than the rotational period. Alternatively, two microchannels which lead both to a molecule of the generic formula HC<sub>2</sub>S might be present: an isotropic distribution which is indicative of a long-lived complex plus a forward-scattered distribution.

## 5. Computational Results

Figure 3 shows the potential energy diagram of the reaction between H<sub>2</sub>S and the singlet ground state of C<sub>2</sub>. The relative energies are the values calculated with the CCSD(T) method with the aug-cc-pVTZ basis set at the geometries obtained with the B3LYP/6-311G(d,p) level. The values in parentheses are the relative energies calculated with the B3LYP method. All values of the relative energies were corrected with the zero-point vibrational energies calculated with the B3LYP/6-311G(d,p) level of method without scaling. The dashed lines in the potential energy diagram indicate that the reaction pathways were unable to be completed between two species because of the convergence problem during the optimization procedure, but they could be connected from the electronic structure point of view.

The reaction of the dicarbon molecule C<sub>2</sub> in its <sup>1</sup>Σ<sub>g</sub><sup>+</sup> ground state with hydrogen sulfide, H<sub>2</sub>S(X<sup>1</sup>A<sub>1</sub>), represents a barrierless pathway to enter the C<sub>2</sub>H<sub>2</sub>S PES (Figures 3 and 4). An initial addition of C<sub>2</sub>(X<sup>1</sup>Σ<sub>g</sub><sup>+</sup>) to the sulfur atom of hydrogen sulfide forms a 3,3-dihydrodicarbonylsulfide complex, H<sub>2</sub>SCC(X<sup>1</sup>A') (**Int1**), which is bound by 194 kJ mol<sup>-1</sup> with respect to the separated reactants. This intermediate has a C<sub>s</sub> symmetry and exhibits a S–C bond of 1.648 Å compared to typical sulfur–carbon single bond lengths of typically 1.71–1.8 Å. The C=C bond length of 1.256 Å in **Int1** remains almost unchanged to 1.251 Å in the dicarbon molecule. A [3,2] hydrogen migration transforms **Int1** via transition state **TS1–2** to thiohydroxyvinylidene carbene, HS(CH)C(X<sup>1</sup>A', C<sub>s</sub>) (**Int2**). This transition state is characterized by a hydrogen bridged carbon–carbon double bond and lies 86 kJ mol<sup>-1</sup> above **Int1**. Note that no insertion pathway of the C<sub>2</sub> molecule into the S–H bond of hydrogen sulfide forming **Int2** from the reactants could be located. Compared to **Int1**, **Int2** is energetically favored by 173 kJ mol<sup>-1</sup> and either rearranges via a subsequent hydrogen migration to the bent thiohydroxyacetylene isomer, HCCSH(X<sup>1</sup>A', C<sub>s</sub>) (**Int3**), or undergoes a combined H migration/ring-closure to form cyclothiopropene, *c*-SC<sub>2</sub>H<sub>2</sub>(X<sup>1</sup>A<sub>1</sub>, C<sub>2v</sub>) (**Int4**). Both intermediates are stabilized by 524 and 449 kJ mol<sup>-1</sup> compared to the separated reactants. Thiohydroxyketene, H<sub>2</sub>CCS (**Int6**), in its <sup>1</sup>A<sub>1</sub> electronic ground state presents the global minimum of the PES and resides in a deep potential energy well of 585 kJ mol<sup>-1</sup> with respect to the separated reactants. The calculated infrared frequencies are in good agreement with experimental assignments of the ν<sub>9</sub> (357.4 cm<sup>-1</sup>) and ν<sub>6</sub> modes (413.8 cm<sup>-1</sup>), cf. Table 1.<sup>35</sup> **Int6** can be formed via isomerization of **Int4** and connects the latter to **Int5**.

The structures **Int1–Int6** can form various HC<sub>2</sub>S and C<sub>2</sub>S isomers via atomic and molecular hydrogen elimination. We investigate the atomic hydrogen loss pathways first. All H atom emissions were found to proceed barrierlessly. The linear thiohydroxyketenyl radical, HCCS(X<sup>2</sup>Π<sub>Ω</sub>), represents the global minimum of the HC<sub>2</sub>S PES. The calculated bond lengths,



**Figure 3.** Schematic representation of the singlet  $C_2H_2S$  potential energy surface. Computational details are given in the text.

vibrational frequencies, and rotational constants are in good agreement with earlier studies cf. Figure 4 and refs 13–15. The cyclic  $c\text{-HC}_2\text{S}(X^2A'')$  and bent  $\text{CCSH}(X^2A'')$  radicals are 115 and 193  $\text{kJ mol}^{-1}$  higher in energy than  $\text{HCCS}(X^2\Pi_Q)$ . These energetics agree well with the previous data of 177 and 192  $\text{kJ mol}^{-1}$ , respectively.<sup>20</sup> Our theoretical investigations show further that all reactions to form  $\text{HCCS}(X^2\Pi_Q)$ ,  $c\text{-HC}_2\text{S}(X^2A'')$ , and  $\text{CCSH}(X^2A'')$  plus atomic hydrogen from the reactants are exothermic by 208, 93, and 15  $\text{kJ mol}^{-1}$ , respectively.

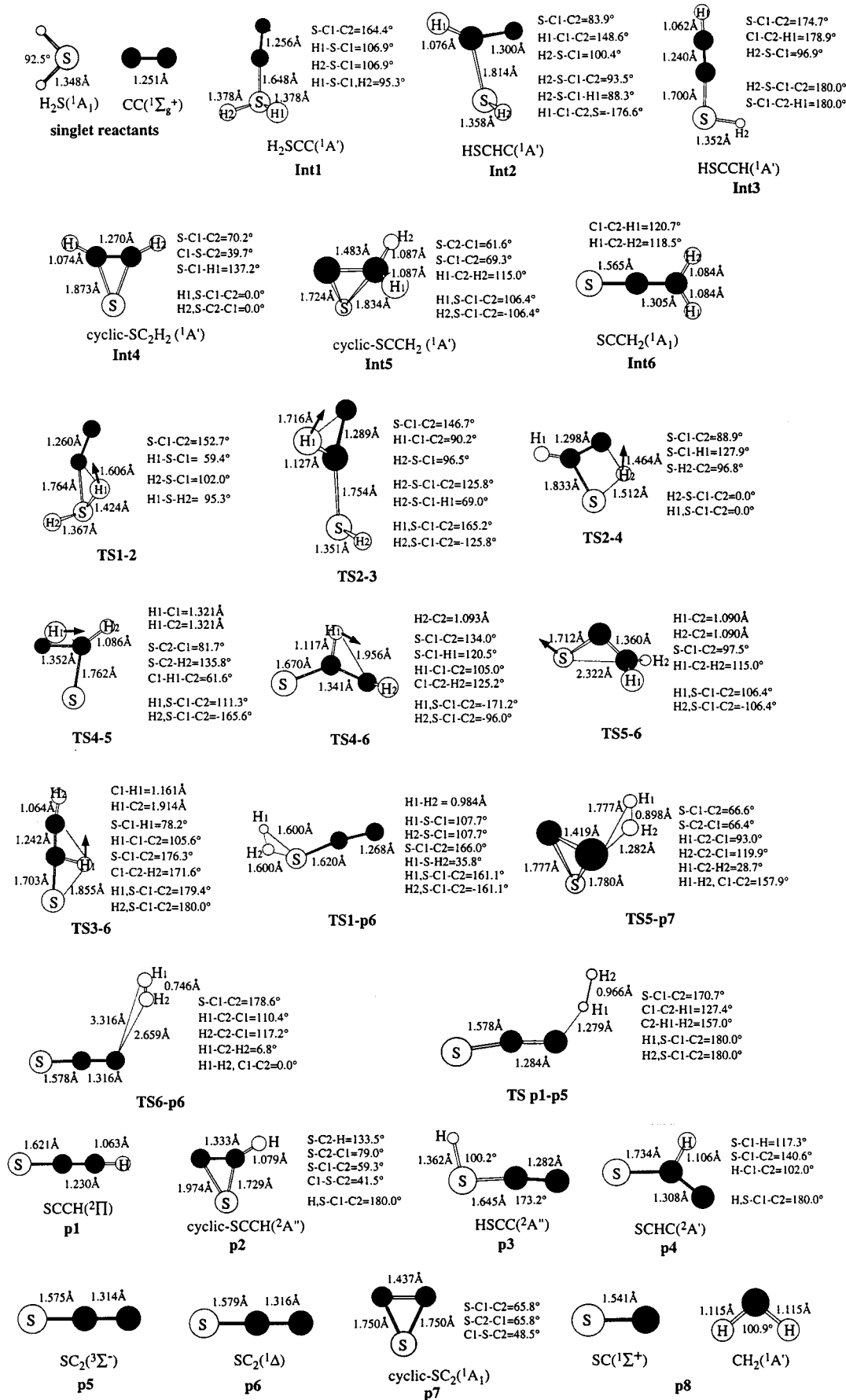
We investigated also the energetics to form linear and cyclic  $C_2S$  isomers via molecular hydrogen elimination. The molecular hydrogen can eliminate from **Int1** and **Int6** producing  $\text{CCS}$  in the excited  $^1\Delta$  state via **TS1-p6** and **TS6-p6**, respectively. The linear  $\text{CCS}$  molecule in its ground  $^3\Sigma^-$  state is 81  $\text{kJ mol}^{-1}$  more stable than the cyclic isomer in the  $^1A_1$  state; the excited singlet state of linear  $\text{CCS}$ ,  $^1\Delta$ , lies 57  $\text{kJ mol}^{-1}$  above the triplet ground state. Earlier investigations provided energy separations of 90–100 (linear versus cyclic)<sup>23,24</sup> and 40–60  $\text{kJ mol}^{-1}$  (triplet–singlet splitting), respectively. The present CCSD(T) calculation agrees well with the previous CISD calculation by Xie and Schaefer but not with the B3LYP density functional calculation. The reaction energies to form  $\text{CCS}(X^3\Sigma^-)$ ,  $\text{CCS}(a^1\Delta)$ , and  $c\text{-C}_2\text{S}(X^1A_1)$  plus molecular hydrogen were computed to be  $-209$ ,  $-152$ , and  $-128$   $\text{kJ mol}^{-1}$ , respectively.

## 6. Discussion

**A. Chemical Reaction Dynamics.** Our crossed beam experiments suggested the formation of a molecule with the formula  $\text{HC}_2\text{S}$ . This pathway is exothermic by 254  $\text{kJ mol}^{-1}$ . To identify

the isomers, we compare the computed reaction energies with the experimental ones. The data suggest that at least the thermodynamically most stable  $\text{HCCS}$  isomer is formed in its  $^2\Pi$  electronic ground state; the computed exothermicity of 208  $\text{kJ mol}^{-1}$  underestimates the experimental data of 254  $\text{kJ mol}^{-1}$  slightly.

The energetics and the shape of the center-of-mass functions aid us to unravel the chemical reaction dynamics involved in the formation of  $\text{HCCS}$ . Our findings suggest that  $C_2(X^1\Sigma_g^+)$  adds without entrance barrier to form the **Int1** collision complex. This process supports an optimum overlap of the vacant  $3\sigma_g^+$  orbital of the dicarbon molecule with the doubly occupied, nonbonding ( $2b_1$  or  $5a_1$ ) orbitals of hydrogen sulfide. Because  $\text{H}_2\text{S}$  has an  $\text{H-S-H}$  angle of only  $92.1^\circ$ , both nonbonding orbitals have a high p-orbital character.<sup>36</sup> Compared to the  $4a_1$  and  $2b_2$   $\text{H-S}$   $\sigma$  orbitals, the p-electron density extends to larger radii, thus making the  $2b_1$  and  $5a_1$  orbitals more accessible because of the enhanced cone of acceptance in contrast to attacks of  $4a_1$  and  $2b_2$  orbitals. Figure 5 sketches distinct approach geometries of the dicarbon molecule toward hydrogen sulfide. In the limiting case of  $b = 0$  Å (Figure 5a), we expect (i) no rotational excitation of **Int1** and (ii) a direct reaction mechanism via an extremely short-lived **Int1** intermediate (rebound dynamics). Upon emission of atomic hydrogen, a  $\text{HSCC}$  radical would be backward-scattered with respect to the dicarbon beam. This pattern was clearly not observed experimentally. However, trajectories with large impact parameters of around 1.5 Å (Figure 5b) lead to a maximum overlap of the  $3\sigma_g^+$  with the  $2b_1$  orbital and could lead to the formation of **Int1**.



**Figure 4.** Optimized geometries of reactants, intermediates, products, and transition states of the C<sub>2</sub>H<sub>2</sub>S potential energy surface calculated with the B3LYP/6-311G(d,p) level. Bond distances are in Angstrom and bond angles in degrees; electronic states are given in parentheses.

**TABLE 1: Vibration Frequencies, Rotational Constants, and Dipole Moments of Various C<sub>2</sub>H<sub>2</sub>S Intermediates and Reaction Products**

Vibrational frequencies (cm <sup>-1</sup> )			rotational constants (GHz)	dipole moment (Debye)
<b>Int1 H<sub>2</sub>SCC</b>				
101	159	747	145.08	7.34
904	921	1209	5.96	
1987	2383	2416	5.93	
<b>Int2 HSCHC</b>				
324	535	659	36.17	3.00
680	957	996	9.64	
659	2579	3285	8.03	
<b>Int3 HSCCH</b>				
275	331	560	287.82	0.94
706	708	979	5.52	
2161	2639	3478	5.42	
<b>Int4 c-SC<sub>2</sub>H<sub>2</sub></b>				
435	595	656	34.20	2.50
761	901	929	10.77	
1757	3282	3339	8.19	
<b>Int5 c-CSCH<sub>2</sub></b>				
603	767	893	29.68	2.31
958	992	1141	12.13	
1464	3086	3169	9.14	
<b>Int6 SCCH<sub>2</sub></b>				
360	416	721	288.85	1.20
857	928	1373	5.64	
1826	3140	3219	5.54	
<b>SCCH</b>				
335	350	430	5.86	1.45
650	799	1919		
3461				
<b>c-SC<sub>2</sub>H</b>				
434	708	790	38.96	2.60
1001	1512	3253	11.74	
			9.12	
<b>HSCC</b>				
165	217	744	288.57	4.48
985	1891	2552	6.09	
			5.97	
<b>SCHC</b>				
224	680	683	121.48	1.94
842	1651	2981	6.30	
			5.99	
<b>CCS(<sup>3</sup>Σ<sup>+</sup>)</b>				
274	274	859	6.43	2.88
1722				
<b>CCS(<sup>1</sup>Δ)</b>				
202	341	852	6.40	2.64
1742				
<b>c-C<sub>2</sub>S (<sup>1</sup>A<sub>1</sub>)</b>				
719	746	1183	40.77	2.32
			14.48	
			10.68	

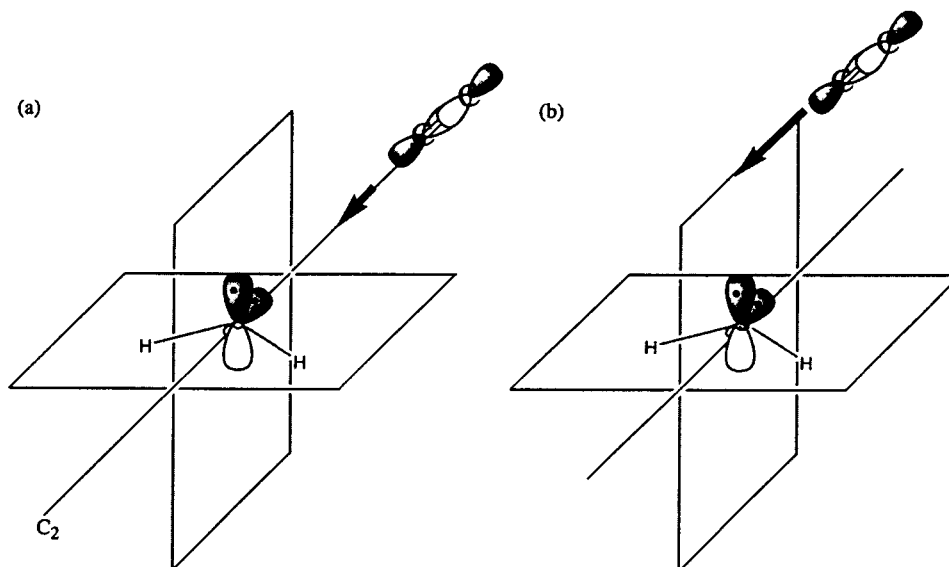
We now address the dynamics to form the HCCS(X<sup>2</sup>Π) radical. Neither **Int1** nor **Int2** can resemble the fragmenting complex because none of these intermediates shows a hydrogen atom attached to the terminal carbon atom. **Int4** and **Int5** can be eliminated also, because homolytic C–H bond cleavages would lead to the formation of the *c*-HC<sub>2</sub>S isomer. Therefore, only **Int3** and/or **Int6** remain. Each complex could emit a hydrogen atom to form the HCCS(X<sup>2</sup>Π) radical. Because an initial insertion of C<sub>2</sub> into the H–S bond to form **INT2** was excluded, at least two hydrogen migrations via the reaction sequence **Int1** → **Int2** → **Int3** are involved. A third hydrogen shift via **TS3–6** could yield **Int6**. The CM angular distribution suggests that at least one intermediate should have a lifetime of less than its rotational period following classical osculating complex pattern. Compared to **Int3**, **Int6** resides in a deeper potential energy well (585 kJ mol<sup>-1</sup> vs 524 kJ mol<sup>-1</sup>); therefore,

**Int3** could account for the experimentally found osculating complex behavior. We like to recall that a  $P(E_T)$  peaking at zero translational energy suggest the absence of any exit barrier; however, the reversed conclusion that a  $P(E_T)$  which peaks away from zero indicates an exit barrier does not always hold, in particular if the lifetime of the decomposing intermediate is relatively short compared to the rotation period. Therefore, the experimentally found “off-zero” peaking of channel 1 is not in contrast with the absence of an exit barrier. Alternatively, the heavy sulfur atom might facilitate an intersystem crossing to the triplet manifold. Here, triplets **Int3** and **Int6** were found to decompose via exit barriers leading to SCCH(<sup>2</sup>Π) + H.<sup>37</sup>

**B. Alternative Exit Channels.** We would like to discuss briefly possible routes of the molecular hydrogen loss. Our computations suggest that an H<sub>2</sub> loss is only feasible on the singlet surface from **Int1**, **Int5**, and **Int6**.<sup>38</sup> The cyclic intermediate **Int5** would form the *c*-C<sub>2</sub>S isomer in the <sup>1</sup>A<sub>1</sub> ground state, whereas **Int1** and **Int5** correlate with the linear CCS(a<sup>1</sup>Δ). Alternative reaction products will be addressed now (Table 2). Pathways 1 and 2b are closed because the reaction endothermicities cannot be compensated by the collision energy of 46 kJ mol<sup>-1</sup>. However, if intersystem crossing (ISC) to the triplet manifold occurs, the formation of ground state carbon atoms plus thioformaldehyde (pathway 2a) might represent a minor channel. Similar to (2a), pathway 3a might open up only if ISC is important. However, the formation of electronically excited sulfur atoms (pathway 3b) could proceed via **Int4**. Note that **Int6** might decay to vinylidene and S(<sup>1</sup>D<sub>2</sub>) in an almost thermoneutral reaction. Finally, pathways 4 and 5 should present minor fractions as **Int6** and **Int3** could decompose via carbon–carbon bond ruptures to form CH<sub>2</sub> + CS and SH + C<sub>2</sub>H, respectively. Note that our electronic structure calculations do not support the formation of C<sub>2</sub>H and SH via hydrogen abstraction. However, because of the inherent background counts at *m/e* = 14, 25, 32, 33, and 44 from the reactants and the residual gases (N<sub>2</sub>, CO<sub>2</sub>) in the detector, these channels could not be observed experimentally. Therefore, future investigations of this important reaction should focus on soft (vacuum) ultraviolet ionization of the hitherto undetected reaction products to unravel the underlying dynamics completely. Here, an identification of atomic carbon C(<sup>3</sup>P<sub>j</sub>) and/or S(<sup>3</sup>P<sub>j</sub>) would certainly suggest an ISC to the triplet surface, whereas the assignment of S(<sup>1</sup>D<sub>2</sub>) would be indicative of the existence of a cyclic intermediate **Int4** and, depending on the translational energy release, possibly of **Int6**. A detection of vinylidene (pathway 3c) and/or CS (pathway 4) would provide information on the role of **Int6** and perhaps **Int5**. Finally, because **Int3** was identified as a potential decomposing complex to form HCCS + H, pathway 5 could be also open.

## 7. Implications to Astrochemistry and Combustion Processes

The hydrogen sulfide and dicarbon molecules have both been detected in extraterrestrial environments<sup>39</sup> and sulfur rich hydrocarbon flames.<sup>9</sup> H<sub>2</sub>S is ubiquitous in the interstellar medium and has been observed in molecular clouds TMC-1 and OMC-1, toward the star forming region SgrB2, and in the circumstellar envelope of the carbon star IRC +10216.<sup>40,41,42</sup> Additionally, Eberhardt et al. identified hydrogen sulfide in comets.<sup>43</sup> The spectral lines of dicarbon in its <sup>1</sup>Σ<sub>g</sub><sup>+</sup> electronic ground state were first detected in comets more than a century ago<sup>44</sup> and in terrestrial hydrocarbon flames fifty years later.<sup>45</sup> In the decades following it became clear that C<sub>2</sub>(X<sup>1</sup>Σ<sub>g</sub><sup>+</sup>) is very abundant in the interstellar medium.<sup>46</sup> Transitions were observed



**Figure 5.** Schematic representation of approach geometries of the dicarbon molecule toward hydrogen sulfide.

**TABLE 2: Reaction Enthalpies of Various Exit Channels except Atomic and Molecular Hydrogen Losses of the C<sub>2</sub>(X<sup>1</sup>Σ<sub>g</sub><sup>+</sup>) Reaction with Hydrogen Sulfide in kJ mol<sup>-1</sup> 50**

pathway	products	reaction enthalpy, kJ mol <sup>-1</sup>
(1)	CH + HCS	+80
(2)	H <sub>2</sub> CS + C( <sup>3</sup> P <sub>j</sub> )	+24 ± 8
(3a)	C <sub>2</sub> H <sub>2</sub> + S( <sup>3</sup> P <sub>j</sub> )	-306
(3b)	C <sub>2</sub> H <sub>2</sub> + S( <sup>1</sup> D <sub>2</sub> )	-196
(3c)	CCH <sub>2</sub> + S( <sup>1</sup> D <sub>2</sub> )	0 ± 10
(4)	CH <sub>2</sub> ( <sup>1</sup> A <sub>1</sub> ) + CS	-76
(5)	SH + C <sub>2</sub> H	-102

toward warm carbons stars such as IRC+10126,<sup>47</sup> post AGB stars such as HD 56126,<sup>48</sup> and toward the HII region W40 IRS. Since the reaction of C<sub>2</sub>(X<sup>1</sup>Σ<sub>g</sub><sup>+</sup>) with hydrogen sulfide has no entrance barrier, is exothermic, and all transition states involved are below the energy of the separated reactants, the title reaction is strongly expected to form HCCS and possibly CCS even in cold, molecular clouds where average translational temperatures as low as 10 K prevail. Since the dipole moment of HCCS(X<sup>2</sup>Π<sub>Q</sub>) is 1.45 D (Table 1), this isomer should be observable at least in TMC-1 and OMC-1 as well as in circumstellar envelopes of IRC+10216. Further, comets approaching perihelion should be searched for HCCS. Previous calculations<sup>20</sup> suggest that an isomerization of HCCS via c-C<sub>2</sub>S to CSH involves a barrier which lies about 140 kJ mol<sup>-1</sup> above the CSH isomer. Therefore, once HCCS is formed in cold molecular clouds, no isomerization to HSCC should occur.

Although the physical parameters in cold molecular clouds and combustion flames, i.e., pressures of less than 10<sup>-11</sup> Torr versus 760 Torr and temperatures of 10 K versus up to 5000 K strongly differ, the sulfur chemistry in both environments is expected to be closely correlated. Current combustion models of sulfur containing coal include only small sulfur bearing molecules S<sub>2</sub>, H<sub>2</sub>S, OCS, SH, CS and SO<sub>2</sub>. Since dicarbon molecules and hydrogen sulfide are present in combustion flames, a reaction is strongly expected to form HCCS and perhaps C<sub>2</sub>S isomers. Due to the denser combustion environments, intermediates involved can be stabilized and primary products can undergo secondary reactions. As the HCCS radical holds a <sup>2</sup>Π electronic ground state, a reaction with the propargyl radical, HCCCH<sub>2</sub>, is strongly expected to form a linear HCCCH<sub>2</sub>-SCCH molecule or heterocycles in combustion

flames. This process might be closely related to the reaction of two propargyl radicals forming first linear C<sub>6</sub>H<sub>6</sub> isomers and in a later stage possibly benzene. Second, HCCS could react with acetylene to form a 1-thiophenyl radical;<sup>49</sup> this reaction is currently under investigation.

Finally, we like to discuss alternative pathways to HC<sub>2</sub>S isomers in the interstellar medium and combustion flames. First, a reaction of SH radicals with C<sub>2</sub>H(X<sup>2</sup>Σ<sup>+</sup>) is expected to be barrierless on the singlet surface leading to the **Int3** complex. If the energy can be distributed statistically, **Int3** should decompose predominantly to the HCCS(X<sup>2</sup>Π) isomer plus a hydrogen atom. Second, atomic carbon should add without entrance barrier to the C=S double bond of thioformaldehyde, H<sub>2</sub>CS(X<sup>1</sup>A<sub>1</sub>) to form a three membered ring intermediate on the triplet surface which ring opens to triplet thioketene. The latter might emit H and/or H<sub>2</sub>, or undergoes intersystem crossing to the singlet manifold to **Int6** prior to its fragmentation to HCCS(X<sup>2</sup>Π). Further, CH(<sup>2</sup>Π) radicals could react with HCS(<sup>2</sup>A') barrierless to form the cyclic **Int4** complex. Two alternatives, i.e., the reactions of S(<sup>3</sup>P) with acetylene and triplet carbene (CH<sub>2</sub>) with carbonmonosulfide, CS, likely involve entrance barriers and might be irrelevant to the chemistry of cold molecular clouds.

## 8. Conclusions

In this paper, the chemical dynamics of the reaction of the dicarbon molecule with hydrogen sulfide were explored. The reaction is dictated by a barrierless addition of dicarbon to the sulfur molecule via a bound intermediate followed by two successive hydrogen migrations on the singlet surface to give a singlet thiohydroxyacetylene (HCCSH) species. The latter emits atomic hydrogen to yield the HCCS(X<sup>2</sup>Π<sub>Q</sub>) isomer. These findings should pawn the way for future spectroscopic studies and identification of the complex, sulfur bearing HCCS molecule in combustion flames and interstellar environments.

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