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Weixiu Pang  
Baotou Teachers College

Xiaomin Song  
Ludong University

Yunbin Sun  
Baotou Teachers College

Meishan Wang  (mswang1971@163.com)  
Ludong University  https://orcid.org/0000-0001-8085-2657

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Spectroscopic constants and anharmonic force field of dithioformic acid and its isomers: a theoretical study

Weixiu Pang¹, Xiaomin Song³, Yunbin Sun¹, Meishan Wang²,³†

1. Department of Physics, Baotou Teacher’s College, Baotou 014030, China
2. School of Integrated Circuits, Ludong University, Yantai 264025, China
3. School of Physics and Optoelectronics Engineering, Ludong University, Yantai 264025, China

Abstract

The potential astronomical interest dithioformic acid (trans-HC(=S)SH) exists five isomers and has received considerable attention of astronomical observation in recent years. The different positions of H atoms of five isomers lead to diverse point groups, dipole moments, and spectroscopic constants. The anharmonic force field and spectroscopic constants of them are calculated using CCSD(T) and B3LYP employing correlation consistent basis sets. Molecular structures, dipole moments, rotational constants, and fundamental frequencies of trans-HC(=S)SH are compared with the available experimental data. The B3LYP/Gen=5 and CCSD(T)/Gen=Q results can reproduce them well. Molecular structures, dipole moments, relative energies, spectroscopic constants of cis-HC(=S)SH and dithiohydroxy carbene (DTHC) are also calculated. The new data obtained in this study are expected to guide the future high resolution experimental work and to assist astronomical search for CH₂S₂.

Keywords: anharmonic force field; spectroscopic constants; molecular structures; CH₂S₂ isomers

1. Introduction

Sulfur is a highly abundant element in the galaxy, and more than 20 sulfur compounds have been detected in some astrophysical environments[1, 2]. Especially, some C₃H₇S₂ isomers have received considerable attention of astronomical observation in recent years. So far, some sulfur-bearing
molecules$^{[2-7]}$ have been identified in the interstellar medium (ISM). In order to systematacially understand the sulfur chemistry in the astrophysical environment, new molecules with multiple sulfur atoms are required to search in some planetary atmospheres or surfaces. The astronomical search of one molecule can be achieved directly by the pure rotational spectroscopy$^{[8]}$, thus the potential astronomical interest molecules, CH$_2$XY (X, Y=O, S) isomers (such as HC(=O)SH, HC(=S)OH, and HC(=S)SH) have received experimental or theoretical investigations of its physical properties and rotational transitions$^{[9, 10]}$. Although none of the CH$_2$S$_2$ isomers has been detected in the space, they are also expected to exist in L183 or Barnard 1, which are both S-rich prestellar cores$^{[10]}$.

There are five isomers for the simplest dithio carboxylic homologue CH$_2$S$_2$: dithioformic acid (DTFA) exhibits trans- and cis-HC(=S)SH conformations and dithiohydroxy carbene (DTHC) contains 2tt-, 2cc-, and 2tc-CH$_2$S$_2$ conformers (collected in Figure 1). These isomers have same backbone of S-C-S and different position of H atoms. The shift of intramolecular hydrogen makes them have different total energies and dipole moments. The energy difference of CH$_2$S$_2$ isomers can be used as a “thermometer” in the astrophysical environments, which is extremely cold conditions and usually too harsh to reproduce it on the earth$^{[11]}$. On the other hand, the various styles of molecular dipole moment lead to the diverse rotational spectrum. Thus the geometry structures, total energies, dipole moments, vibrational and rotational spectra of CH$_2$S$_2$ isomers were investigated$^{[9, 10, 12-24]}$.

As far as the authors know, there are some experimental papers which focused on vibrational or rotational spectra for CH$_2$S$_2$ isomers$^{[10, 18, 22-24]}$. In 1971, the IR spectrum of trans-HC(=S)SH was firstly reported in a short communication$^{[24]}$, and several vibrational wave numbers were determined without band assignment. In 1989, the low resolution IR spectrum of DTFA was observed at the range of 475-3100 cm$^{-1}$$^{[18]}$. Six and four fundamental frequencies were assigned for trans- and cis-HC(=S)SH, respectively. In 1978, the rotational transitions of ground state of DTFA were firstly identified using microwave spectrum in the region of 18-40 GHz by Bak et al$^{[23]}$. The original rotational spectroscopy parameters of DTFA were determined, such as ground state rotational constants (A$_0$, B$_0$, and C$_0$), two quartic centrifugal distortion constants (A, and A$_{jk}$), asymmetry
parameter $\kappa$, and inertial defects $\Delta$. The “iterative” structure of $\text{trans-}HC(=S)SH$ isomer was reported using Kraitchman technique. Additionally, the dipole moments $\mu$ and $\mu_a$ of DTFA were derived using rigid model. However, only $a$-type transitions were measured and the estimated uncertainties of rotational constants $A_v$ were 86 and 380 MHz for $\text{trans-}$ and $\text{cis-}HC(=S)SH$, respectively. One year later, Bak and his coworkers reinvestigated the microwave spectrum of DTFA in the region of 18.6-40 GHz\textsuperscript{[22]}. The same parameters were obtained for $\text{trans-}HC(=^{32}\text{S})^{32}\text{SH}$, $HC(=^{34}\text{S})^{32}\text{SH}$, $HC(=^{32}\text{S})^{34}\text{SH}$, $HC(=^{32}\text{S})^{32}\text{SD}$, and $\text{cis-}HC(=^{32}\text{S})^{32}\text{SD}$. In order to improve the accuracy of rotational spectroscopic constants of DTFA, more than 300 lines of rotational transitions were measured by Prudenzano \textit{et al}\textsuperscript{[10]}. The ground state rotational constants, complete quartic and four sextic centrifugal distortion constants were obtained accurately in the range of the millimeter and sub-millimeter.

With the development of quantum-chemical calculations, it is possible to obtain the spectroscopic constants of astrochemical molecules by quantum-chemical calculations. And the computational spectroscopy is important to investigate astrochemistry as the molecular complexity in space\textsuperscript{[11]}. In 1979, the optimized geometries, relative energies, and dipole moment components of DTFA were calculated using LCAO-MO-SCF theory\textsuperscript{[22]}. The theoretical calculations of molecular structure parameters of DTFA have been reported\textsuperscript{[9, 10, 13-18]}. The main methods used by them were SCF, SCF-MO, and CCSD(T); and the main basis sets were 3-21G*, 6-31G*, 6-31G**, and CBS+CV. For the vibrational spectra of DTFA isomers, only harmonic wave numbers were calculated using SCF/6-31G*\textsuperscript{[18]}, SCF-MO/6-31G*\textsuperscript{[19]}, and STO-3G/DZP\textsuperscript{[16]} levels of theory. The existence of several isomers implies the potential large amplitude motions (LAMs) in molecules\textsuperscript{[11]}. The accurate prediction of the vibrational spectra might therefore be required using high-level quantum-chemical theory for these isomers. For the rotational spectra of DTFA, the three equilibrium rotational constants $A_v$, $B_v$, and $C_v$, were predicted using SCF/6-31G* level of theory\textsuperscript{[18]}. In order to obtain rotational constants and to predict quartic and sextic centrifugal distortion constants theoretically, the high level of theory is needed for DTFA. Only structural parameters and relative energies of the three isomers
of DTHC have been theoretically studied\cite{13, 17}. The relative energies of the lowest-excited vibrational states for the most stable isomer are similar to those of the vibrational ground states for less stable ones\cite{11}. This maybe a reason to be difficult to observe the rotational or vibrational spectra of the three DTHC isomers.

These quantum-chemical calculations of CH$_2$S$_2$ mentioned above have paralleled the experimental measurements and only molecular geometry parameters of DTFA were determined employing CCSD(T) method. All the previous studies show that some key spectral parameters of the five isomers of CH$_2$S$_2$ are still absent. Therefore, the purpose of this paper is to obtain the vibrational and rotational spectra with quantum-chemical computations for trans-HC(=S)SH, cis-HC(=S)SH, 2tt-CH$_2$S$_2$, 2cc-CH$_2$S$_2$, and 2tc-CH$_2$S$_2$.

2. Computational methods

The quantum-chemical calculations of B3LYP\cite{25, 26} method are carried out using program GAUSSIAN 09\cite{27}. The B3LYP calculations employ correlation consistent basis sets\cite{28-30}, cc-pVnZ, $d$-augmented valence cc-pV(n+d)Z, and aug-cc-pVnZ (n=Q, 5). The abbreviations of them are VnZ, V(n+d)Z, and AVnZ, respectively. The mixed basis set Gen=Q presented below is denoted that: cc-pVQZ basis set is employed for the carbon and hydrogen atoms and the $d$-augmented basis set cc-pV(Q+d)Z for sulfur atoms. Similarly with the denotation of Gen=Q, the mixed basis set Gen=5 is denoted that: cc-pV5Z basis set is employed for the light atoms (H and C), cc-pV(5+d)Z basis set for sulfur atoms. No orbital has been kept frozen during the B3LYP calculations.

CCSD(T) (CC singles and doubles augmented by a perturbative treatment of triple excitations) is performed with the help of CFOUR\cite{31} program. The CCSD(T) calculations employ correlation consistent basis sets\cite{28-30}, cc-pVQZ, and above mentioned Gen=Q mixed basis set. The cc-pVQZ basis set is abbreviated as VQZ in the following sections. The frozen-core approximation is employed for the calculation of all the CCSD(T) method.

Within the constraint of C$_s$ (DTFA and 2tc-CH$_2$S$_2$) and C$_{2v}$ (2tt- and 2cc-CH$_2$S$_2$) point groups, the geometries of the five CH$_2$S$_2$ isomers are optimized with analytic gradients. Based on the
optimized geometries, harmonic force fields of these isomers are evaluated analytically. The normal modes and the harmonic spectroscopic constants are computed in the usual manner\cite{32-35}. Cubic and semidiagonal quartic normal coordinate force constants are calculated using the two methods. The anharmonic spectroscopic constants are derived from the theoretical force fields applying standard formulas based on the second-order rovibrational perturbation theory.

3. Results and discussion

The spectroscopic constants and geometry structures for CH₂S₂ isomers are given in Tables 1-8. They are compared with the corresponding experimental\cite{10, 18, 22-24} or theoretical data\cite{10, 13, 16-19} whenever available. Figures 2 and 4 are given by the virtual multi-frequency spectrometer, VMS\cite{36, 37}.

3.1 Geometry structures, dipole moments and energies

The \textit{ab initio} structures of five CH₂S₂ isomers are calculated at B3LYP and CCSD(T) methods using mixed basis sets Gen=5 and Q, respectively. The computed equilibrium structures, experimentally derived results\cite{22} and previously calculated values\cite{10, 13, 17} are shown in Table 1. Figure 1 illustrates the molecular structures, and all the five isomers have a planar form, because only zero torsional angle has the minima torsional potential\cite{13, 18}.

Geometry parameters vary little with two level of theory for the five CH₂S₂ isomers. Precisely, the biggest discrepancy of bond angels (bond lengths) is about 2.44° (0.012Å), which can be found between B3LYP/Gen=5 and CCSD(T)/Gen=Q for S-C-S (C-S) in \textit{2t}-CH₂S₂. Generally, the S-C-S bond angel is sensitive to basis set and method, for example, the difference is about 8.9° between STO-3G and 3-21G*\cite{17}. Meanwhile, it is known that CCSD(T) theory typically estimates bond length more higher by about several thousands of one angstrom\cite{38}. By comparing our calculated equilibrium geometries to the experimental results\cite{22} of \textit{trans}-HC(=S)SH, a good agreement can be found: the most calculated results agree within the uncertainties. Hence, the B3LYP/Gen=5 level of theory can give reliable results.

For the five isomers, the bond angles are influenced obviously by the position of H atoms, while
the bond lengths are not sensitive to it. The values of C-H and S-H bond length are similar, which are about 1.08 and 1.34Å, respectively. Relatively, the bond angles lie in a wide range. Especially, the discrepancies of S-C-S bond angle at B3LYP/Gen=5 level of theory are about 5° and 13° for DTFA and DTHC, respectively. The opening of heavy-atom backbone S-C-S and giving way to H atoms lead to larger S-C-S bond angle in trans-HC(=S)SH (2cc-CH₂S₂) than in cis-HC(=S)SH (2tt- and 2tc-CH₂S₂). And it is suggested that the cis-HC(=S)SH, 2tt-, and 2tc-CH₂S₂ isomers can be formed by adding a hydrogen atom to the trans-HSCS radical. Similarly, adding a hydrogen atom to the cis-HSCS radical can form trans-HC(=S)SH and 2cc-CH₂S₂ isomers.

The molecular dipole moment is related to charge distribution in molecules, which can influence the intensity of rotational spectrum. Thus the dipole moments of the five isomers are also collected in Table 1, which have great differences affected by the position of H atoms. The Cs point group molecules have a- and b-dipole moment components, and there is a large variation between these two components. In particular, the difference between and is about 1.29 D for trans-HC(=S)SH, which is a near-prolate asymmetric rotor with the asymmetry parameter (can be seen in Table 2). As expected, the 2tt- and 2cc-CH₂S₂ isomers have only b- components, the calculated values are 0.2649 D and 2.5602 D, respectively. The dipole moments of cis-HC(=S)SH and 2cc-CH₂S₂ are larger than 2.5 D, which lead to more higher intensity of rotational spectrum in the same abundance. Figure 2 gives the intensity of rotational spectrum in the range of 0-3100 GHz at 300 K using the virtual multi-frequency spectrometer. And the parameters of the five isomers are taken from B3LYP/Gen=5 level of theory. It can also be seen in Figure 2 that the intensity of 2tt-CH₂S₂ isomer is weakest, because its dipole moment is smallest. And it can be predicted that the b-type transitions of trans-HC(=S)SH and 2tt-CH₂S₂ isomers will be difficult to determine experimentally, which have small b-components (0.1623 D and 0.2239 D).

Figure 3 gives the relative energies of CH₂S₂ isomers relative to trans-HC(=S)SH, and they are calculated using B3LYP/Gen=5 level of theory. The unit of kJ/mol is used for the sake of expressing the relative energy clearly. The order of energy is in agreement with the results from Refs. [13, 17,
The most stable isomer is trans-HC(=S)SH as the intramolecular effects of $\pi$ conjugation and hydrogen bonding\cite{14, 19}. The second one cis-HC(=S)SH lies energetically about 4 kJ/mol above trans-HC(=S)SH, and the experimental value is 4.2 kJ/mol\cite{23}. The energy difference between DTFA and DTHC is about 145 kJ/mol, while the differences are less than 7 kJ/mol between trans- and cis-HC(=S)SH, or among 2tt-, 2cc-, and 2tc-CH$_2$S$_2$. The relatively small differences make them have high sensitivity of temperature\cite{11}.

### 3.2 Rotational spectra parameters

Several levels of theory are used to calculate the rotational constants for the five isomers which are summarized in Tables 2 and 3, together with the corresponding asymmetry parameters and inertial detects. Rotational constants $B$ and $C$ are predicted well with any level of theory for trans-HC(=S)SH: slightly smaller than experimental values\cite{10}. The opposite is find for the largest $A$ rotational constant, the deviation is about several hundred MHz. That is not surprising, because the experimental uncertainties for rotational constants $A$ are larger than the values for $B$ or $C$ constants by three orders of magnitude. On the other hand, the effect of mixed basis set is significantly. In particular, for rotational constants $A$, the adding of $d$ function on S atoms increases about 171 and 140 MHz using B3LYP and CCSD(T), respectively. The rotational constants of trans-HC(=S)SH are well reproduced the most recent experimental values\cite{10} with CCSD(T)/Gen=Q level of theory, which gives the deviation within 0.8%. Thus the B3LYP/Gen=5 and CCSD(T)/Gen=Q results of the other four isomers are presented in Table 3. The deviations of the corresponding rotational constants among the five isomers are very tiny, which suggests that the five isomers have similar mass distributions and the position change of H atoms slightly affects the inertia tensor.

Moving to the asymmetry parameter, the five isomers are all near-prolate asymmetric rotors with the $\kappa = \frac{2B - A - C}{A - C} = -0.99$, which is very close to the symmetric prolate limit, -1. As shown in Tables 2 and 3, all the calculated results of DTFA can well reproduce the experimental values\cite{10, 22}, and the percentage deviations are within 0.08%.
Planar structure of one molecule can be confirmed by the inertial defect, which is defined as
\[ \Delta = I_c - (I_A + I_B) \] \[\text{[10]}\]. The inertial defect calculated from ground state rotational constants of the five isomers are given in Tables 2 and 3. The CCSD(T)/Gen=Q level of theory predicts small positive inertial defects, which agree well with planar structures for the five isomers. For the results of B3LYP/Gen=5, DTFA have planar structure significantly (with the inertial defect values 0.123, 0.186), while the inertial defects of DTHC are slightly larger (0.625, 0.548, 0.576).

Quartic and sextic centrifugal distortion constants of a molecule are very important for determining rotational spectra, as molecules at higher rotational energies are not rigid rotors and the vibration-rotation couplings are more significant. The S-reduction is used in this work as the five isomers are all near-prolate asymmetric rotors (see the asymmetry parameters in Tables 2 and 3). The calculated quartic and sextic centrifugal distortion constants (S-reduction) for \textit{trans-HC(=S)SH} isomer are collected in Table 4 containing experimental data\[\text{[10]}\]. The effects of basis set extension for \textit{trans-HC(=S)SH} isomer are clear from cc-pVQZ to cc-pV5Z using B3LYP method: the differences show up in symbol and magnitude. For example, the values of \[ D_{jk} \] are 247.51 and -38.77 MHz using B3LYP/cc-pVQZ and B3LYP/cc-pV5Z, respectively. While the similar results are found between Gen=\(n\) and cc-p\(VnZ\) (\(n=Q, 5\)) basis sets with B3LYP or CCSD(T) method. It suggests that the improvement of basis set can obtain reliable data than adding \(d\) function to S atoms for these parameters, which are not the case with rotation constants in Table 2. The differences of quartic centrifugal distortion constants between CCSD(T)/Gen=Q results and experimental values are less than 2.7\% except for \(d_2\), which has a large deviation of 12.5\%. This outcome is also considered a good result as the presence of large amplitude motions and the extremely small value of \(d_2\) (about -3 Hz)\[\text{[11]}\]. The results of B3LYP/Gen=5 are similar with the data of CCSD(T)/Gen=Q for the five quartic centrifugal distortion constants. The sextic centrifugal distortion constants of \textit{trans-HC(=S)SH} isomer are calculated by B3LYP method and the data of Gen=5 or cc-pV5Z basis sets are more reliable than the values of \(n=Q\) basis sets.

Table 5 lists the calculated quartic and sixthic centrifugal distortion constants of other isomers.
determined by B3LYP/Gen=5 and CCSD(T)/Gen=Q levels of theory and the experimental data\textsuperscript{[10]} for cis-HC(=S)SH. The quartic centrifugal distortion constants calculated by CCSD(T) is not sensitive to the choice of the structure. A satisfactory agreement for cis-HC(=S)SH isomer can be found in CCSD(T)/Gen=Q, and the predictions of quartic and sextic centrifugal distortion constants for 2tt- and 2tc-CH\textsubscript{2}S\textsubscript{2} isomers are reliable.

3.3 Vibrational spectra parameters

Table 6 contains 9 vibrational frequencies of trans-HC(=S)SH isomer, which has 7 of in-molecular-plane A’ and the remaining 2 of out-of-plane A’’ symmetry species. The agreement of fundamental frequencies between B3LYP/Gen=5 and experimental ones\textsuperscript{[18]} is excellent with less than 2.2%. The results of B3LYP/Gen=5 and CCSD(T)/Gen=Q are consistent within 1.8% for other harmonic frequencies except for \(\omega_9\). The effect of cc-pV(Q+d)Z basis set on S atoms is slightly stronger than basis set improvement from cc-pVQZ to cc-pV5Z. The largest difference between cc-pVQZ and Gen=Q for the 9 harmonic frequencies is about 5.5 cm\textsuperscript{-1} which appears in the S-H stretching mode \(\omega_2\). The calculated value \(\omega_2\) of 2655.2 cm\textsuperscript{-1} in the range of characteristic bond frequencies for S-H stretching is similar to the same vibrations of MgSH\textsuperscript{[39]}, AuSH\textsuperscript{[40]}, and CuSH\textsuperscript{[41]} molecules, which are 2674.9, 2688, and 2649.9 cm\textsuperscript{-1}, respectively. Similarly, the characteristic bond frequency \(\omega_1\) of 3085.9 cm\textsuperscript{-1} for C-H bond stretching is close to the value of 3105.9 cm\textsuperscript{-1} for trans-HC(=O)OH\textsuperscript{[42]}, where it is also adjacent to one single and one double bond. The characteristic bond frequencies \(\omega_1\) and \(\omega_2\) suggest that the two frequencies mainly depend on the binding force of H and other heavy atoms as the small mass of H nucleus. The other thing that we have to notice is that the C=S stretching mode \(\omega_4\) is the strongest band (see Figure 4) with the intensity of 112.9 and 135.8 km/mol using CCSD(T)/Gen=Q and B3LYP/Gen=5, respectively.

The calculated harmonic and fundamental frequencies of cis-HC(=S)SH and DTHC are listed in Table 7 together with previous data for cis-HC(=S)SH isomer\textsuperscript{[14, 16, 18, 24]}. The harmonic and fundamental frequencies of DTFA are similar to each other, because only the positions of the hydrogens in sulphydryl are different for these two isomers. The \(\omega_1\) and \(\omega_2\) of two isomers for
DTFA are also S-H and C-H stretching characteristic bond frequencies, respectively. The $\omega_g$ is very sensitive to geometrical isomerism. In the results of CCSD(T)/Gen=Q level of theory, the frequency $\omega_g$ of trans-HC(=S)SH decreases from 428.7 cm$^{-1}$ to 360.6 cm$^{-1}$ of cis-HC(=S)SH. The most intense fundamental frequency $v_4$ is also sensitive to geometrical isomerism: the B3LYP/Gen=5 result of trans-HC(=S)SH is 23.5 cm$^{-1}$ higher than that of cis-HC(=S)SH, the corresponding experimental difference is also 23.5 cm$^{-1}$[18], which agrees with that the C=S bond length of cis-HC(=S)SH is 0.0013 Å shorter than that of trans-HC(=S)SH. It is similar for $\nu$(C=O) stretching frequency with the C=O bond of cis-HC(=O)OH, which bond length is 0.006 Å shorter than that of trans-HC(=O)OH isomer[42]. The frequencies of $v_7$ and $v_9$ of DTFA lie below 475 cm$^{-1}$ and are not detected so far, thus the results of this work can be considered valuable prediction.

On the other hand, neither theoretical nor experimental results of harmonic or fundamental frequencies of DTHC exists until now. It can be seen from Table 7 that the B3LYP and CCSD(T) results of harmonic or fundamental frequencies for 2tt- and 2tc-CH$_2$S$_2$ are consistent. Similarly to DTFA, 2tc-CH$_2$S$_2$ isomer has seven vibrational modes belonging to $A'$ symmetry species and two vibrational modes belonging to $A''$ species. The most intense frequency for 2tc-CH$_2$S$_2$ (see Figure 4) is $v_2$, which provides a plausible support to detect the spectral feature of 2tc-CH$_2$S$_2$.

2tt- and 2cc-CH$_2$S$_2$ isomers belong to the C$_{2v}$ point group, and their corresponding frequencies lie close to each other. $v_1$ (totally symmetric specie, $A_1$) and $v_7$ (anti-symmetric with respect to molecular plane, $B_2$) of 2tt- and 2cc-CH$_2$S$_2$ are S-H wagging and twisting vibrations, respectively. The fundamental frequency $v_7$ of 2tt- and 2cc-CH$_2$S$_2$ is sensitive to geometrical isomerism. The difference of $v_7$ between 2tt- and 2cc-CH$_2$S$_2$ is about 300 cm$^{-1}$ using B3LYP/Gen=5 level of theory.

While, the differences of $v_2$, $v_3$, and $v_4$ between 2tt- and 2cc-CH$_2$S$_2$ are all less than 10 cm$^{-1}$. The values of $v_1 - v_7$ of 2tt- and 2cc-CH$_2$S$_2$ isomers are 1.9 cm$^{-1}$ and 16.7 cm$^{-1}$, respectively. The small difference of 1.9 cm$^{-1}$ suggests that the coupling of two S-H bonds in 2tt-CH$_2$S$_2$ isomer is weaker, which corresponds to longer bond length of S-H (see Figure 1)[43]. Furthermore, it is worth noting
that the calculated IR intensity of $\omega_5$ is zero, which suggests that the dipole moment in this vibration mode does not change.

The obvious anharmonic effects of DTFA are about 140 and 180 cm$^{-1}$, which happened in $v_1$ (C-H) and $v_2$ (S-H) (see Tables 6 and 7). All the anharmonic constants of the five isomers are given in Table S1. It can be seen from the B3LYP/Gen=5 results that the anharmonic effects of DTFA are mainly due to $x_{11}$, $x_{22}$, and $x_{29}$ constants, which are all larger than 65 cm$^{-1}$. However, the anharmonic effects of $v_1$ (S-H) and $v_7$ (S-H) for 2tt-CH$_2$S$_2$ and 2cc-CH$_2$S$_2$ isomers are about 160 cm$^{-1}$ and 210 cm$^{-1}$, respectively. Similarly, It can be seen from Table S1 that this anharmonic effects of 2tt-CH$_2$S$_2$ and 2cc-CH$_2$S$_2$ isomers are mainly contributed by $x_{11}$, $x_{17}$, and $x_{77}$ constants. The above vibrations all involve the motion of H atoms: C-H or S-H.

The $ab initio$ ro-vibration interaction constants ($\alpha_i^A$, $\alpha_i^B$, and $\alpha_i^C$, $i=1-9$) of the five CH$_2$S$_2$ isomers are given in Table 8. These constants may be perturbed by Coriolis coupling constants, thus the values of $\sum \alpha_i^A / 2 = A_\alpha - A_\beta$ are also given in Table 8. Similar expressions also hold for the $\sum \alpha_i^B$ and $\sum \alpha_i^C$. As shown in Table 8, the B3LYP and CCSD(T) theory give internal agreements for $\sum \alpha_i^B$ and $\sum \alpha_i^C$ in DTFA isomers. Thus the B3LYP/Gen=5 and CCSD(T)/Gen=Q data can provide the reliable predictions of spectroscopic constants for CH$_2$S$_2$ isomers. In addition, the cubic and quartic force constants of CH$_2$S$_2$ isomers using B3LYP/Gen=5 level of theory are shown in Tables S2 and S3, respectively. These data are calculated in the normal coordinate and can be used for reference.

4. Conclusion

The equilibrium geometry, dipole moments, total energies, spectroscopic constants, and force fields of five CH$_2$S$_2$ isomers are obtained at B3LYP and CCSD(T) methods with correlation consistent basis sets. Comparing the calculated results with available experimental data, the B3LYP/Gen=5 and CCSD(T)/Gen=Q levels of theory can give the reliable prediction. The adding of $d$ function on S
atoms has significant effect for rotational constants (about 150 MHz). The extension from Gen=Q to Gen=5 with B3LYP method is very essential for the centrifugal distortion constants. The rotational constants of five isomers are similar because the position of H atoms slightly influences moment of inertia, while, the position of H significantly affects the bond angles, dipole moments, and molecular point groups of five isomers. Thus the large variety exists in the intensity of rotational spectra of CH$_2$S$_2$ isomers. The frequencies of CH$_2$S$_2$ isomers have diverse values and symmetry species, which determined by molecular point group. The characteristic bond frequencies exist in the C-H and S-H stretching vibrations of DTFA. These new spectroscopic data might be used for the astronomical search in some S-rich prestellar cores and then understand the sulfur chemistry in astrophysical environment.

Declarations

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Authors' contributions: Weixiu Pang: Writing-original draft, Methodology, Data curation. Xiaomin Song: Formal analysis, Writing-review & editing. Yunbin Sun: Software, Writing-review & editing. Meishan Wang: Supervision, Writing-review & editing, Project administration.
References

[1] M. A. Martin-Drumel, K. L. K. Lee, A. Belloche, O. Zinsheim, S. Thorwirth, H. S. P. Müller, F. Lewen, R. T. Garrod, K. M. Menten, M. C. McCarthy, S. Schlemmer. Submillimeter spectroscopy and astronomical searches of vinyl mercaptan, C$_2$H$_3$SH. A&A 632 (2019) A167. DOI: 10.1051/0004-6361/201935032

[2] L. Margulès, V. V. Ilyushin, B. A. McGuire, A. Belloche, R. A. Motiyenko, A. Remijan, E. A. Alekseev, O. Dorovskaya, J. C. Guillemin. Submillimeter-wave spectroscopy of and interstellar search for thioacetaldehyde. J. Mol. Spectrosc. 371 (2020) 111304. DOI: 10.1016/j.jms.2020.111304

[3] M. W. Sinclair, N. Fourikis, J. C. Ribes, B. J. Robinson, R. D. Brown, P. D. Godfrey. Detection of interstellar thioformaldehyde. Aust. J. Phys. 26 (1973) 85-92. DOI: 10.1071/PH730085

[4] L. Kolesniková, B. Tercero, J. Cernicharo, J. L. Alonso, A. M. Daly, B. P. Gordon, S. T. Shipman. Spectroscopic characterization and detection of Ethyl Mercaptan in Orion. Astrophys. J. Lett. 784 (2014) L7. DOI: 10.1088/2041-8205/784/1/L7

[5] V. Ilyushin, I. Armieieva, O. Dorovskaya, M. Pogrebnyak, I. Krapivin, E. Alekseev, L. Margulès, R. Motiyenko, F. K. Tchana, A. Jabri, L. Manceron, E. S. Bekhtereva, S. Bauerecker, C. Maul. Microwave and FIR spectroscopy of dimethylsulfide in the ground, first and second excited torsional states. J. Mol. Struct. 1200 (2020) 127114. DOI: 10.1016/j.molstruc.2019.127114

[6] J. Cernicharo, C. Cabezas, Y. Endo, N. Marcelino, M. Agüindez, B. Tercero, J. D. Gallego, P. de Vicente. Space and laboratory discovery of HC$_3$S$^+$. A&A 646 (2021) L3. DOI: 10.1051/0004-6361/202040013

[7] J. Cernicharo, C. Cabezas, M. Agün.dez, B. Tercero, J. R. Pardo, N. Marcelino, J. D. Gallego, F. Tercero, J. A. López-Pérez, and P. de Vicente. TMC-1, the starless core sulfur factory: Discovery
of NCS, HCCS, H₂CCS, H₂CCCS, and C₄S and detection of C₅S. A&A \textbf{648}, (2021) L3.

DOI: 10.1051/0004-6361/202140642

[8] S. L. W. Weaver. Millimeterwave and submillimeterwave laboratory spectroscopy in support of observational astronomy. Annu. Rev. Astron. Astrophys. \textbf{57} (2019) 79-112.

DOI: 10.1146/annurev-astro-091918-104438

[9] J. H. Huang, K. L. Han, R. S. Zhu, G. Z. He, N. Q. Lou, Unimolecular pyrolysis mechanisms of monothioformic and dithioformic acids. An \textit{ab initio} study and evaluation of rate constant. J. Phys. Chem. A \textbf{102} (1998) 2044-2049.

DOI: 10.1021/jp973213s

[10] D. Prudenzano, J. Laas, L. Bizzocchi, V. Lattanzi, C. Endres, B. M. Giuliano, S. Spezzano, M. E. Palumbo, P. Caselli, Accurate millimetre and submillimetre rest frequencies for \textit{cis}- and \textit{trans}-dithioformic acid, HCSSH. A&A \textbf{612} (2018) A56.

DOI: 10.1051/0004-6361/201732397

[11] M. Biczysko, J. Bloino, C. Puzzarini, Computational challenges in Astrochemistry. WIREs Comput Mol Sci (2017) e1349.

DOI: 10.1002/wcms.1349

[12] S. Vivekananda, R. Srinivas, M. Manoharan, E. D. Jemmis, Generation and identification of ionic and neutral dithioformic acid [HC(S)SH], dimercaptocarbene [HSCSH], and dithiirane [H₂C(S₂)]: a neutralization-reionization mass spectrometry and theoretical study. J. Phys. Chem. A \textbf{103} (1999) 5123-5128.

DOI: 10.1021/jp984558t

[13] M. T. Nguyen, T. L. Nguyen, H. T. Le, Theoretical study of dithioformic acid, dithiohydroxy carbene and their Radical cations: Unimolecular and assisted rearrangements. J. Phys. Chem. A \textbf{103} (1999) 5758-5765.

DOI: 10.1021/jp983658w

[14] Y. G. Smeyers, M. Villa, G. I. Cárdenas-Jirón, A. Toro-Labbé, Dynamical and spectroscopic
study of internal rotation in formic, thiolformic, thionformic and dithioformic acids using a reduced potential model. J. Mol. Struct. (Theochem) 426 (1998) 155-163.

DOI: 10.1016/S0166-1280(97)00316-3

[15] X. G. Xie, Y. Q. Tao, H. Cao, W. G. Duang, *Ab initio* study of unimolecular pyrolysis mechanisms of dithioformic acid. Chem. Phys. 213 (1996) 133-137.

DOI: 10.1016/S0301-0104(96)00286-8

[16] R. B. Bohn, G. D. Brabson, L. Andrews, Reaction of atomic hydrogen and carbon disulfide. Infrared spectra of HSCS and HSHCS in solid Argon. J. Phys. Chem. 96 (1992) 1582-1589.

DOI: 10.1021/j100183a019

[17] Y. Q. Tao, Isomerization and unimolecular rearrangement channels of dithioformic acid. Chem. Phys. 154 (1991) 221-225.

DOI: 10.1016/0301-0104(91)80073-Q

[18] F. Ioannoni, D.C. Moule, J. D. Goddard, D. J. Clouthier, Thiocarbonyl spectroscopy: The infrared spectrum and *ab initio* vibrational frequencies of *cis* - and *trans*-dithioformic acid in the $\tilde{X}^{1}A'$ ground state. J. Mol. Struct. 197 (1989) 159-170.

DOI: 10.1016/0022-2860(89)85159-2

[19] R. Fausto, L. A. E. Batista de Carvalho, J. J. C. Teixeira-Dias, M. N. Ramos, s-*cis* and s-*trans* conformers of formic, thioformic and dithioformic acids. J. Chem. Soc. 85 (1989) 1945-1962.

DOI: 10.1039/F29898501945

[20] R. Fausto, J. J. C. Teixeira-Dias, P. R. Carey, *Ab initio* structural and conformational studies of HCSSH, CH$_3$CSSH and HCSSCH$_3$. J. Mol. Struct (Theochem) 152 (1987) 119-135.

DOI: 10.1016/0166-1280(87)87010-0

[21] S. P. So, Structures, relative stabilities and barriers to internal rotation of dithioformic acid and its isomers. J. Mol. Struct. (Theochem) 148 (1986) 153-161.

DOI: 10.1016/0166-1280(86)85013-8

[22] B. Bak, O. Nielsen, H. Svanholt, Rotational spectra of isotopic di-thioformic acids with a
structure of trans HCSSH: *Ab initio* estimates of cis/trans structures, energies, dipole moments, and torsional barrier. J. Mol. Spectr. 75 (1979) 134-143.

DOI: 10.1016/0022-2852(79)90154-1

[23] B. Bak, O. J. Nielsen, H. Svanholt, Production and microwave spectra of dithioformic acid, HCSSH. J. Mol. Spectr. 69 (1978) 401-408.

DOI: 10.1016/0022-2852(78)90233-3

[24] G. Gattow, R. Engler. Über die Dithioameisensäure. Naturwissenschaften. 58 (1971) 53.

DOI: 10.1007/BF00620806

[25] A. D. Becke, Density-functional Thermochemistry. III. The Role of Exact Exchange. J. Chem. Phys. 98 (1993) 5648-5652.

DOI: 10.1063/1.464913

[26] C. T. Lee, W. T. Yang, R. G. Parr, Development of the Colle-Salvetti Correlation-energy Formula into a Functional of the Electron Density. Phys. Rev. B 37 (1988) 785-789.

DOI: 10.1103/PhysRevB.37.785

[27] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, *Gaussian 09, Revision D.01*. 2013.
[28] T. H. Dunning Jr., Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen. J. Chem. Phys. 90 (1989) 1007-1023.
DOI: 10.1063/1.456153

[29] T. H. Dunning Jr., K. A. Peterson, A. K. Wilson, Gaussian basis sets for use in correlated molecular calculations. X. The atoms aluminum through argon revisited. J. Chem. Phys. 114 (2001) 9244-9253.
DOI: 10.1063/1.1367373

[30] K. A. Peterson, T. H. Dunning Jr., Accurate correlation consistent basis sets for molecular core-valence correlation effects: The second row atoms Al-Ar, and the first row atoms B-Ne revisited. J. Chem. Phys. 117 (2002) 10548-10560.
DOI: 10.1063/1.1520138

[31] CFOUR (Coupled Cluster Techniques for Computational Chemistry), a quantum-chemical program package by J. F. Stanton, J. Gauss, M. E. Harding, and P. G. Szalay with contributions from A. A. Auer, R. J. Bartlett, U. Benedikt, C. Berger, D. E. Bernholdt, Y. J. Bomble, O. Christiansen, M. Heckert, O. Heun, C. Huber, T. C. Jagau, D. Jonsson, J. Jusélius, K. Klein, W. J. Lauderdale, D. Matthews, T. Metzroth, D. P. O’Neill, D. R. Price, E. Prochnow, K. Ruud, F. Schiffmann, S. Stopkowicz, M. E. Varner, J. Vázquez, J. D. Watts, F. Wang and the integral packages MOLECULE (J. Almlöf and P. R. Taylor) PROPS (P. R. Taylor), ABACUS (T. Helgaker, H. J. Aa. Jensen, P. Jørgensen, and J. Olsen), and ECP routines by A. V. Mitin and C. van Wullen. For the current version, see http://www.cfour.de.

[32] W. X. Pang, M. S. Wang, C. L. Yang, Y. F. Zhang. Ab initio study of spectroscopic constants and anharmonic force field of $^{74}$GeCl$_2$. J. Chem. Phys. 126 (2007) 194301.
DOI: 10.1063/1.2733654

[33] W. X. Pang, Y. B. Sun, J. J. Zhao, Y. Lu. Ab initio study of anharmonic force field and spectroscopic constants for germanium dichloride. Chin. J. Chem. Phys. 29 (2016) 657-662.
DOI:10.1063/1674-0068/29/cjcp1604076
[34] W. X. Pang, H. Y. Wu, J. J. Zhao, Y. Lu, Y. B. Sun. DFT anharmonic force field, and spectroscopic constants for phosphaethene, CH$_2$PH. Main Group Chem. 16 (2017) 207-216. DOI: 10.3233/MGC-170237

[35] W. X. Pang, H. Y. Wu, J. J. Zhao, Y. B. Sun. Theoretical study of anharmonic force field and spectroscopic constants for 1-chlorophosphaethene, CH$_2$PCl and CD$_2$PCl. Phosphorus, Sulfur and Silicon Relat. Elem. 194 (2019) 69-75. DOI: 10.1080/10426507.2018.1490283

[36] V. Barone, The virtual multifrequency spectrometer: a new paradigm for spectroscopy. WIREs Comput. Mol. Sci. 6 (2016) 86-110. DOI: 10.1002/wcms.1238

[37] V. Barone, A. Baiardi, M. Biczysko, J. Bloino, C. Cappelli, F. Lipparini, Implementation and validation of a multi-purpose virtual spectrometer for large systems in complex environments. Phys. Chem. Chem. Phys. 14 (2012) 12404-12422. DOI: 10.1039/c2cp41006k

[38] P. Dréan, M. Paplewski, J. Demaison, J. Breidung, W. Thiel, H. Beckers, H. Bürger, Millimeter-wave spectra, ab initio calculations, and structures of fluorophosphane and chlorophosphane. Inorg. Chem. 35 (1996) 7671-7678. DOI: 10.1021/ic960546f

[39] A. Zaidi, S. Lahmar, Z. B. Lakhdar, P. Rosmus, J. P. Flament, Theoretical study of the MgSH radical. J. Mol. Struct. (Theochem) 634 (2003) 299-304. DOI: 10.1016/S0166-1280(03)00382-8

[40] Y. L. Zhao, M. S. Wang, C. L. Yang, X. G. Ma, Z. L. Zhu, The spectroscopic constants and anharmonic force field of AgSH: An ab initio study. Spectrochim. Acta A 164 (2016) 89-92. DOI: 10.1016/j.saa.2016.03.033

[41] Y. L. Zhao, M. S. Wang, C. L. Yang, X. G. Ma et al. Computational anharmonic force fields of CuSH and CuSD. J. Phys. B: At. Mol. Opt. Phys. 50 (2017) 155102 1-9.
[42] J. Demaison, M. Herman, J. Lievin, Anharmonic force field of cis- and trans-formic acid from high-level *ab initio* calculations, and analysis of resonance polyads. J. Chem. Phys. **126**(2007)164305.

DOI: 10.1063/1.2722752

[43] G. Herzberg, Molecular Spectra and Molecular Structure, II. Infrared and Raman Spectra of Polyatomic Molecules (Van Nostrand Reinhold, New York, 1945), p196.
Figure 1. Molecular geometries of CH$_2$S$_2$ isomers: trans-, cis-dithioformic acid (DTFA), and 2tt-, 2cc-, 2tc-dithiohydroxy carbene (DTHC). The horizontal and vertical axes are the $a$ and $b$ principal inertial axes, respectively.
Figure 2. Intensity of rotational spectra for CH$_2$S$_2$ isomers at the B3LYP/Gen=5 level of theory.
Figure 3. Energetics of CH$_2$S$_2$ isomers relative to trans-HC(=S)SH at the B3LYP/Gen=5 level of theory.
Figure 4. The intensity of nine frequencies for CH$_2$S$_2$ isomers at the B3LYP/Gen=5 level of theory.
Table 1. Molecular equilibrium geometry structures and dipole moments of CH$_2$S$_2$ isomers (Bond lengths in Å, bond angles in deg, dipole moments in Debye, and total energies in Hartree).^a

|                  | trans-HC(=S)SH | cis-HC(=S)SH |
|------------------|---------------|-------------|
|                  | B3LYP        | CCSD(T)    | Exp$^{[22]}$ | Pre$^{[10]}$ | B3LYP        | CCSD(T)    | Pre$^{[10]}$ |
| r(C1-S2)         | 1.6191       | 1.6224     | 1.625       | 1.6161       | 1.6181       | 1.6211     | 1.6149       |
| r(C1-S3)         | 1.7326       | 1.7352     | 1.733       | 1.7270       | 1.7368       | 1.7391     | 1.7309       |
| r(C1-H4)         | 1.0885       | 1.0891     | 1.10        | 1.0877       | 1.0869       | 1.0878     | 1.0862       |
| r(S3-H5)         | 1.3453       | 1.3421     | 1.357       | 1.3398       | 1.3457       | 1.3457     | 1.3389       |
| A(S2-C1-S3)      | 129.16       | 128.09     | 127.8       | 127.99       | 124.20       | 123.59     | 123.45       |
| A(S2-C1-H4)      | 121.38       | 121.47     | 121.2       | 122.07       | 122.07       | 122.09     |              |
| A(C1-S3-H5)      | 96.77        | 95.61      | 94.3        | 95.66        | 97.52        |            | 96.88        |
| $\mu_a$          | 1.7165       | 1.4679     | 1.53$^{[23]}$ | 1.4766       | 2.2955       | 2.0768     | 2.0829       |
| $\mu_b$          | 0.1623       | 0.1860     |            | 0.1924       | 1.6194       | 1.6569     | 1.6403       |
| $\mu$            | 1.7242       | 1.4770     | 1.90$^{[23]}$ | 1.4890       | 2.8093       | 2.6567     | 2.6512       |
| $E_T$            | -835.7780    | -834.7396  |            | -835.4578    | -835.7764    | -835.7776  | -835.4559    |

|                  | 2tc-CH$_2$S$_2$ | 2tt-CH$_2$S$_2$ | 2cc-CH$_2$S$_2$ |
|------------------|---------------|---------------|---------------|
|                  | B3LYP        | CCSD(T)     | Pre$^{[15]}$ | B3LYP        | CCSD(T)     | Pre$^{[15]}$ | B3LYP        | Pre$^{[15]}$ |
| r(C1-S2)         | 1.6588       | 1.6910       | 1.6891       | 1.7011       | 1.703        | 1.6468      | 1.658        |
| r(C1-S4)         | 1.6771       | 1.6751       | 1.6724       | 1.6891       | 1.7011       | 1.6468      | 1.668        |
| r(S2-H3)         | 1.3762       | 1.3656       | 1.3443       | 1.3470       | 1.3412       | 1.3792      |              |
| r(S4-H5)         | 1.3483       | 1.3425       | 1.3259       | 1.3470       | 1.3412       | 1.3792      |              |
| A(S2-C1-S4)      | 119.39       | 121.7        | 113.28       | 110.84       | 111.9        | 126.44      | 124.0        |
| A(C1-S2-H3)      | 108.05       | 106.69       | 106.6        | 97.40        | 96.48        | 105.47      |              |
| A(C1-S4-H5)      | 98.72        | 97.86        | 98.4         | 97.40        | 96.48        | 105.47      |              |
| $\mu_a$          | 0.8401       | 0.8529       | 0.000        | 0.000        | 0.000        | 0.000       |              |
| $\mu_b$          | 1.4577       | 1.5209       | 0.2649       | 0.2239       | 2.5602       | 2.5602      |              |
| $\mu$            | 1.6825       | 1.7438       | 0.2649       | 0.2239       | 2.5602       | 2.5602      |              |
| $E_T$            | -835.7207    | -834.6805    | -830.0539    | -835.7192    | -834.6797    | -835.6718   | -835.7220    | -835.6721    |

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$^a$ This work, the parameters are determined by B3LYP and CCSD(T) methods employing Gen=5 and Gen=Q, respectively.

$^b$ The molecular parameter r(C1-H4) was the assumed value in the Ref. [22].

$^c$ The calculated results of DTFA were obtained by CCSD(T)/CBS+CV level of theory with the CFOUR program.

$^d$ MP2/3-21G* level of theory was employed using Gaussian82 program.

$^e$ The MP2/6-31G(d,p) and B3LYP/6-311++G** levels of theory were employed for the determination of geometries and total energy, respectively.
Table 2. Equilibrium and ground states rotational constants (in MHz), asymmetry parameters, and inertial defects (in amu*Å^2) for trans-HC(=S)SH.

|       | B3LYP | CCSD(T) | Exp[10] | Exp[22, 23] | Pre[18] |
|-------|-------|---------|---------|-------------|---------|
|       | VQZ   | Gen=Q   | AVQZ    | V5Z Gen=5   | VQZ Gen=Q |         |
| \(A_e\) | 50314.65 | 50485.66 | 50306.76 | 50407.20 | 50424.45 | 49118.14 | 49254.09 | 50466    |
| \(B_e\) | 3408.99  | 3418.22  | 3409.37  | 3416.73  | 3418.49  | 3431.02  | 3439.10  | 3438     |
| \(C_e\) | 3192.67  | 3201.46  | 3192.97  | 3199.83  | 3201.45  | 3207.01  | 3214.64  | 3219     |
| \(A_0\) | 49446.56 | 49618.30 | 49435.46 | 50293.96 | 50311.59 | 48950.19 | 49094.76 | 49206.11 | 49226.804|
| \(B_0\) | 3405.73  | 3414.94  | 3406.08  | 3397.29  | 3399.07  | 3411.67  | 3419.63  | 3447.53 | 3447.5312 |
| \(C_0\) | 3172.84  | 3181.56  | 3173.11  | 3179.87  | 3181.50  | 3186.99  | 3194.55  | 3219.47256 | 3219.4954 |
| \(\kappa\) | -0.99082 | -0.99083 | -0.99081 | -0.99081 | -0.99081 | -0.99024 | -0.99019 | -0.99008 | -0.99009 |
| \(\Delta\) | 0.67124  | 0.67018  | 0.67081  | 0.12253  | 0.12255  | 0.11887  | 0.11879  | 0.11362 | 0.11669  |

\(a\) The inertial defect was calculated using conversion factor 505376 MHz amu Å^2 and the asymmetry parameter was also calculated by the definition.

\(b\) The values were obtained by the microwave spectrum in the range of 18-40 GHz.

\(c\) The data were calculated using SCF/6-31G*.
Table 3. Equilibrium and ground states rotational constants (in MHz), asymmetry parameters, and inertial defects (in amu Å²) for CH₂S₂ isomers.¹

|                 | cis-HC(=S)SH | 2tc-CH₂S₂ | 2π-CH₂S₂ | 2cc-CH₂S₂ |
|-----------------|-------------|-----------|----------|-----------|
| Aₑ              |            |           |          |           |
| B3LYP           | 49834.38   | 48964.85  | 49470.85 | 46511.64  |
| CCSD(T)         | 50081.11   | 46333.39  | 49470.85 | 51550.36  |
| Bₑ              | 3468.83    | 3478.64   | 3666.53  | 3581.65   |
| Cₑ              | 3243.09    | 3247.90   | 3413.53  | 3348.97   |
| A₀              | 49288.81   | 48559.85  | 48774.65 | 50586.21  |
| B₀              | 3460.66    | 3467.00   | 3659.34  | 3567.44   |
| C₀              | 3229.77    | 3233.67   | 3425.67  | 3319.81   |
| κ               | -0.99031   | -0.98970  | -0.98950 | -0.99035  |
| Δ               | 0.18642    | 0.11069   | 0.10628  | 0.54838   |

¹This work, the parameters are determined by B3LYP and CCSD(T) methods employing Gen=5 and Gen=Q, respectively.
² The inertial defect was calculated using conversion factor 505376 MHz amu Å² and the asymmetry parameter was also calculated by the definition.
³ The values were obtained by the microwave spectrum in the range of 18-40 GHz.
⁴ The data were calculated using SCF/6-31G*. 
|                | B3LYP        |            | CCSD(T)       |            | Exp[^10^μ] |
|----------------|-------------|------------|---------------|------------|------------|
|                | VQZ Gen=Q   | AVQZ V5Z  | VQZ Gen=Q     | AVQZ       |
| $D_J$          | 0.5838      | 0.5858     | 0.5837        | 1.0198     | 1.0380     | 1.0408     | 1.063389   |
| $D_K$          | 4754.0797   | 4779.9882  | 4747.4996     | 1439.4154  | 1440.6304  | 1333.98    | 1342.24    | 1376       |
| $D_{JK}$       | 247.5104    | 248.6800   | 247.3512      | -38.7737   | -38.8076   | -38.5280   | -38.6907   | -38.9438   |
| $d_i$          | 0.0685      | 0.0687     | 0.0685        | -0.1110    | -0.1111    | -0.1164    | -0.1167    | -0.119787  |
| $d_i \times 10^3$ | -40.2280   | -40.3810   | -40.2310      | -3.0620    | -3.0655    | -3.1992    | -3.2092    | -3.609     |
| $H_J \times 10^3$ | -0.3520    | -0.3528    | -0.3514       | 0.3773     | 0.3781     | 0.5714     |
| $H_K$          | 952.3847    | 960.9374   | 947.4715      | 81.7881    | 81.8779    |
| $H_{JK}$       | 0.6586      | 0.6644     | 0.6582        | -0.0954    | -0.0955    | -0.00573   |
| $H_{KJ}$       | 64.8476     | 65.4416    | 64.5719       | 0.1221     | 0.1227     | -4.216     |
| $h_i \times 10^3$ | -0.2882    | -0.2898    | -0.2881       | 0.0990     | 0.0993     | 0.1673     |
| $h_i \times 10^3$ | 0.0199     | 0.0204     | 0.0201        | -0.0028    | -0.0028    |
| $h_i \times 10^3$ | 0.0476     | 0.0479     | 0.0475        | 0.0013     | 0.0013     |

[^10^μ]: The data were obtained by the measurements in the millimetre and submillimetre range.
Table 5. Equilibrium quartic (in KHz) and sextic (in Hz) centrifugal distortion constants ($S$-reduction) for CH$_2$S$_2$ isomers.$^a$

|            | cis-HC(=S)SH | 2tc-CH$_2$S$_2$ | 2tr-CH$_2$S$_2$ | 2cc-CH$_2$S$_2$ |
|------------|--------------|-----------------|-----------------|-----------------|
|            | B3LYP        | CCSD(T)         | B3LYP           | CCSD(T)         | B3LYP           |
| $D_J$      | 1.1427       | 1.2301          | 0.9203          | 1.5679          | 0.9538          | 1.5774          | 0.8633          |
| $D_K$      | 1097.8005    | 1421.36         | 1412            | 3531.8081       | 1436.24         | 2778.2492       | 1427.00         | 2857.6219       |
| $D_{JK}$   | 6.5031       | -46.8462        | -47.0807        | 284.9791        | -49.5975        | 246.0192        | -44.4907        | 252.8967        |
| $d_i$      | -0.1054      | -0.1418         | -0.1490         | 0.0578          | -0.1959         | 0.0414          | -0.1900         | 0.0392          |
| $d_j \times 10^3$ | -11.755 | -3.7664         | -4.343          | -58.0638        | -5.5228         | -52.8538        | -5.7706         | -48.3829        |
| $H_j \times 10^3$ | 0.5665 | 1.169           | -0.7796         | -0.6542         | -0.9410         |                   |                  |                  |
| $H_K$      | 17.4237      |                 | 689.5718        | 385.7140        | 390.6985        |                   |                  |                  |
| $H_{JK}$   | -0.1807      | -0.03601        | 1.1051          | 0.9171          | 0.5539          |                   |                  |                  |
| $H_{KJ}$   | 0.7554       | -4.109          | 84.6840         | 56.3746         | 44.6241         |                   |                  |                  |
| $h_j \times 10^3$ | 61.4275 | 0.288           | -727.8034       | -639.8516       | -574.8906       |                   |                  |                  |
| $h_j \times 10^3$ | 10.4368 | 91.6713         | 106.8727        | -6.8068         |                   |                   |                  |                  |

$^a$This work, the parameters are determined by B3LYP and CCSD(T) methods employing Gen=5 and Gen=Q, respectively.

$^b$The data were obtained by the measurements in the millimetre and submillimetre range.
Table 6. Harmonic and fundamental frequencies (in cm$^{-1}$) for trans-HC(=S)SH.

|       | B3LYP          | CCSD(T)       | Pre$^{[16]}_a$ | Pre$^{[19]}_b$ | Exp$^{[24]}_c$ | Ref$^{[18]}_d$ |
|-------|----------------|---------------|----------------|----------------|----------------|----------------|
|       | VQZ Gen=Q     | AVQZ V5Z Gen=5 VQZ Gen=Q |               |               |               |               |
| $A'$  | $\omega_1$   | 3087.2 3083.8 3087.0 3086.2 3085.9 3064.4 3062.0 | 3343 | 3341 | 3007 |
| $A'$  | $\omega_2$   | 2649.0 2654.0 2648.1 2654.0 2655.2 2685.2 2690.8 | 2875 | 2932 | 2639 |
| $A'$  | $\omega_3$   | 1319.4 1320.3 1319.2 1319.7 1319.7 1325.2 1326.2 | 1469 | 1478 | 1331 |
| $A'$  | $\omega_4$   | 1067.7 1068.6 1067.2 1067.7 1067.9 1076.9 1077.9 | 1166 | 1158 | 1042 |
| $A'$  | $\omega_5$   | 946.3 948.8 946.2 947.9 948.4 949.1 951.4 | 1054 | 1060 | 954  |
| $A'$  | $\omega_6$   | 684.5 685.2 684.8 684.1 684.2 695.4 696.2 | 759  | 757  | 680  |
| $A^*$ | $\omega_9$   | 851.0 852.0 850.8 851.4 851.3 862.3 863.3 | 951  | 955  | 860  |
| $A^*$ | $\omega_9$   | 448.6 450.5 447.6 449.0 449.2 427.2 428.7 | 449  | 447  | 402  |
| $A'$  | $v_1$         | 2943.2 2939.1 2942.5 2942.1 2941.6 | 2860 | 2988.8 |
| $A'$  | $v_2$         | 2475.5 2480.9 2474.8 2473.7 2474.1 | 2495 |
| $A'$  | $v_3$         | 1291.1 1291.8 1290.6 1290.2 1290.4 | 1432 | 1283.0 |
| $A'$  | $v_4$         | 1053.9 1054.9 1053.2 1053.9 1054.1 | 1048 | 1057.2 |
| $A'$  | $v_5$         | 916.5 919.0 917.0 922.1 922.6 | 922  | 935.5  |
| $A'$  | $v_6$         | 667.2 667.8 667.4 667.7 667.8 | 711  | 682.5  |
| $A^*$ | $v_9$         | 837.8 838.6 837.2 837.4 837.3 | 893  | 824.0  |
| $A^*$ | $v_9$         | 355.6 353.6 354.2 351.7 350.9 |      |       |

$^a$The results of Ref. [16] were calculated using DZP level of theory and scaled by a factor of 0.90.

$^b$The results of Ref. [19] were calculated using SCF-MO/6-31G* level of theory.

$^c$The values were measured by Ref. [24], while the order was from Ref. [19].

$^d$The fundamental frequencies were experimental values, and the harmonic data were calculated by SCF/6-31G* with the scaled factor of 0.89 from Ref. [18].
Table 7. Harmonic and fundamental frequencies (in \text{cm}^{-1}) for CH$_2$S$_2$ isomers. $^a$

|          | cis-CH(=S)SH | 2tc-CH$_2$S$_2$ | 2tt-CH$_2$S$_2$ | 2cc-CH$_2$S$_2$ |
|----------|--------------|-----------------|-----------------|-----------------|
|          | B3LYP        | CCSD(T)         | Ref$^{[16]}$[b] | Pre$^{[18]}$[c] | B3LYP        | CCSD(T)         | B3LYP           |
| $A'$ $\omega_1$ | 3093.6  | 3067.8 | 3352 | 3010 | 3342 | 2611.3 | 2628.3 | 1021.6 | 1012.8 | 995.3 |
| $A'$ $\omega_2$ | 2650.0 | 2694.0 | 2862 | 2626 | 2918 | 2381.2 | 2466.4 | 651.0 | 678.5 | 644.4 |
| $A'$ $\omega_3$ | 1290.2 | 1299.0 | 1449 | 1313 | 1459 | 1075.9 | 1054.7 | 282.0 | 282.7 | 274.4 |
| $A'$ $\omega_4$ | 1095.2 | 1101.9 | 1202 | 1081 | 1202 | 986.8 | 983.3 | 492.9 | 447.5 | 603.2 |
| $A'$ $\omega_5$ | 724.9 | 733.9 | 785 | 707 | 784 | 641.6 | 655.7 | 549.4 | 539.1 | 536.8 |
| $A'$ $\omega_6$ | 301.9 | 300.7 | 335 | 302 | 533 | 264.3 | 276.1 | 2617.2 | 2706.3 | 2361.9 |
| $A^*$ $\omega_1$ | 818.7 | 827.4 | 915 | 825 | 918 | 565.7 | 566.3 | 1103.6 | 1072.4 | 1076.6 |
| $A^*$ $\omega_2$ | 390.4 | 360.6 | 365 | 329 | 365 | 521.2 | 525.2 | 848.0 | 825.9 | 939.4 |
| $A'$ $\nu_1$ | 2952.4 | 2424.5 | 2446.7 | 2136.6 |
| $A'$ $\nu_2$ | 2463.2 | 2163.9 | 971.0 | 962.9 |
| $A'$ $\nu_3$ | 1264.6 | 1255.5 | 1033.3 | 633.3 | 625.3 |
| $A'$ $\nu_4$ | 1077.6 | 1080.8 | 952.9 | 270.4 | 266.7 |
| $A'$ $\nu_5$ | 922.6 | 885.4 | 491.0 | 577.1 |
| $A'$ $\nu_6$ | 711.3 | 710.0 | 622.3 | 542.1 | 519.2 |
| $A^*$ $\nu_1$ | 300.5 | 253.3 | 2448.6 | 2153.3 |
| $A^*$ $\nu_2$ | 810.0 | 794.5 | 534.9 | 1060.2 | 1045.2 |
| $A^*$ $\nu_3$ | 294.7 | 489.8 | 801.3 | 895.3 |

$^a$This work, the parameters are determined by B3LYP and CCSD(T) methods employing Gen=5 and Gen=Q, respectively.

$^b$The results of Ref. [16] were calculated using DZP level of theory and scaled by a factor of 0.90.

$^c$The fundamental frequencies were experimental values, and the harmonic data were calculated by SCF/6-31G* with the factor of 0.89 from Ref. [18].

$^d$The results of Ref. [19] were calculated using SCF-MO/6-31G* level of theory.
Table 8. Ro-vibrational interaction constants (in MHz) for CH$_2$S$_2$ isomers.$^a$

| Mode $i$ | $2tc$-HC(=S)SH | $2nt$-HC(=S)SH | $2cc$-HC(=S)SH |
|----------|-----------------|-----------------|-----------------|
|          | B3LYP           | CCSD(T)         | B3LYP           | CCSD(T)         |
|          | $A$  | $B$  | $C$  | $A$  | $B$  | $C$  | $A$  | $B$  | $C$  |
| 1        | -7.08 | 2.83 | 2.34 | 4.12 | 4.03 | 3.42 | 105.34 | 0.70 | 0.93 | 102.42 | 2.48 | 2.49 |
| 2        | 118.53 | -0.30 | 0.10 | 154.10 | -0.46 | 0.14 | 216.48 | -6.14 | -4.61 | 309.29 | -4.84 | -2.99 |
| 3        | 353.53 | -4.73 | 0.78 | 342.48 | -3.89 | 1.49 | 296.81 | -5.18 | 0.48 | 327.09 | -4.06 | 1.47 |
| 4        | 320.87 | 5.84 | 4.77 | 377.44 | 4.54 | 3.94 | 260.25 | 1.45 | 1.48 | 369.61 | -0.17 | 0.87 |
| 5        | -199.99 | 4.72 | 10.56 | -209.67 | 4.44 | 9.87 | -48.34 | 5.32 | 8.32 | -27.30 | 4.20 | 7.62 |
| 6        | -496.20 | 16.87 | 16.81 | -427.03 | 15.84 | 15.75 | -59.55 | 16.48 | 17.77 | -125.24 | 16.88 | 16.45 |
| 7        | -242.61 | 1.04 | 2.29 | -218.54 | 1.76 | 2.73 | 203.40 | -7.75 | -1.45 | 127.77 | -3.14 | -1.23 |
| 8        | 183.59 | 6.97 | 0.78 | 183.99 | 6.47 | 0.79 | -21.59 | 5.16 | 0.73 | -119.24 | 4.79 | 0.41 |
| 9        | 195.08 | 5.65 | 1.45 | 111.78 | 6.22 | 2.06 | 138.35 | -301.24 | 3.15 | 5.85 | -23.52 | 0.22 | 6.94 |
| $\sum \alpha/2$ | 112.86 | 19.45 | 19.94 | 159.34 | 19.48 | 20.10 | 545.58 | 8.18 | 13.31 | 405.00 | 11.64 | 14.23 |

| Mode $i$ | $2tc$-CH$_2$S$_2$ | $2nt$-CH$_2$S$_2$ | $2cc$-CH$_2$S$_2$ |
|----------|-----------------|-----------------|-----------------|
|          | B3LYP           | CCSD(T)         | B3LYP           |
|          | $A$  | $B$  | $C$  | $A$  | $B$  | $C$  | $A$  | $B$  | $C$  |
| 1        | -247.65 | 3.31 | 1.54 | 19.20 | 3.70 | 3.14 | -68.91 | 1.59 | 0.85 | -264.36 | -3.64 | -3.98 |
| 2        | 155.61 | 2.74 | 2.91 | -51.77 | 1.21 | 5.55 | -301.24 | 3.15 | 5.85 | -23.52 | 0.22 | 6.94 |
| 3        | 242.00 | -1.24 | 0.23 | -101.54 | 17.67 | 24.03 | -854.23 | 24.95 | 23.10 | -355.82 | 11.77 | 20.77 |
| 4        | 182.70 | 6.14 | 10.75 | -400.40 | -18.01 | 1.11 | -281.39 | -0.07 | 1.54 | 10.29 | -5.24 | 13.00 |
| 5        | 205.49 | 2.24 | 6.68 | 491.42 | -2.85 | -4.76 | 894.69 | -9.07 | -7.46 | 575.17 | 3.05 | -1.13 |
| 6        | -73.16 | 10.81 | 21.70 | 836.28 | 9.55 | 6.13 | 393.00 | 10.41 | 5.08 | 796.31 | 6.11 | 14.41 |
| 7        | -447.83 | -16.51 | 3.44 | 25.99 | 3.89 | 3.33 | -64.06 | 1.71 | 0.97 | -165.15 | -0.18 | -1.58 |
| 8        | 419.23 | 5.55 | -1.34 | 285.61 | -2.48 | 0.68 | 569.93 | -4.73 | 0.03 | 930.52 | 7.23 | 7.35 |
| 9        | 931.88 | 1.68 | 1.20 | 287.60 | 1.92 | 4.99 | 504.23 | -0.35 | 4.13 | 424.84 | 9.10 | 15.52 |
| $\sum \alpha/2$ | 684.14 | 7.36 | 23.56 | 696.20 | 7.20 | 22.10 | 396.01 | 13.80 | 17.05 | 964.14 | 14.21 | 29.15 |

This work, the parameters are determined by B3LYP and CCSD(T) methods employing Gen=5 and Gen=Q, respectively.
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