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A Microwave and Quantum Chemical Study of Cyclopropanethiol

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The microwave spectra of cyclopropanethiol, C_3H_5SH, and one deuterated species C_3H_5SD, have been investigated in the 20 − 80 GHz frequency range. The spectra of the ground vibrational state and of three vibrationally excited states of the parent species of a conformer which has a *synclinal* ("*gauche*") arrangement for the H−C−S−H chain of atoms, was assigned. The H−C−S−H dihedral angle is 76(5)° from *synperiplanar* (0°). The *b*-type transitions of the ground and of the vibrationally excited states of the parent species were split into two components, which is assumed to arise from tunneling of the proton of the thiol group between two equivalent *synclinal* potential wells. No splitting was resolved in the spectrum of C_3H_5SD. The tunneling frequency of the ground vibrational state of C_3H_5SH is 1.664(22) MHz. The tunneling frequency of the first excited-state of the C−S torsion is 52.330(44) MHz, whereas this frequency is 26.43(13) and 3.286(61) MHz, respectively, for the first excited states of the two lowest bending vibrations. The dipole moment of the ground vibrational state of the parent species is $\mu_a = 4.09(5)$, $\mu_b = 2.83(11)$, $\mu_c = 0.89(32)$, and $\mu_{tot} = 5.06(16) \times 10^{-30}$ C m. The microwave study has been augmented by high-level density functional and *ab initio* quantum chemical calculations.

Introduction

Conformational properties of substituted cyclopropanes have interested chemists for a long time. It has been shown that the preferred forms of cyclopropane derivatives, which contain substituents with unsaturated groups such as CHO,[1] CFO,[2] CClO,[3] COOH,[4] $CH{=}CH_2$,[5] and NO_2,[6] have a symmetry plane (C_s symmetry), with the substituent lying in this plane. A different conformational preference is observed for cyclopropanols. The H−C−O−H chain of atoms is *synclinal* (obsolete "*gauche*") in the favored forms of cyclopropanol (C_3H_5OH),[7] 1-cyclopropylcyclopropanol ($C_3H_4(OH)C_3H_4$),[8] and in the two rotamers found for 1-ethenylcyclopropan-1-ol ($C_3H_4(OH)C{=}CH_2$).[9] The related compound cyclopropyl methyl ether ($C_3H_5OCH_3$) also prefers a *synclinal* conformation for the $H{-}C{-}O{-}CH_3$ link of atoms.[6,10]

No experimental studies of the conformational properties have previously been reported for the title compound, cyclopropanethiol (C_3H_5SH), but quantum chemical calculations[11–13] predict that the conformer with a *synclinal* conformation for the H−C−S−H link of atoms is favored. These calculations[11–13] also indicate that a second high-energy rotamer, which has an *antiperiplanar* arrangement for the said atoms, exists as a high-energy form. These two conformers are henceforth called ***sc*** and ***ap***, respectively, and they are sketched in Figure 1. It should be mentioned that the preferred form of the related molecule cyclopropylmethylthioether ($C_3H_5SCH_3$) has a *synclinal* arrangement for the $H{-}C{-}S{-}CH_3$ chain, according to a microwave (MW) study.[14]

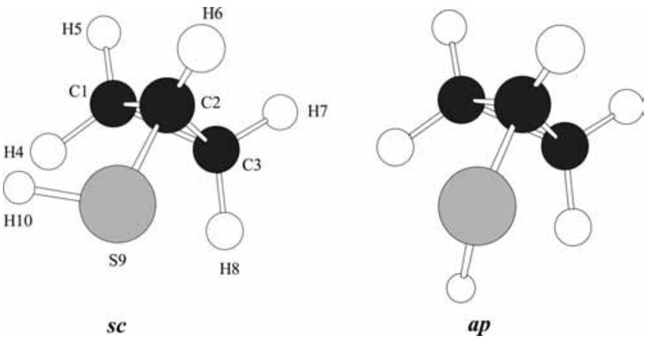

Figure 1. Models of the two "stable" conformers, ***sc*** and ***ap***, of cyclopropanethiol according to the quantum chemical predictions. Atom numbering is given on ***sc***. The H6−C2−S9−H10 dihedral angle is *synclinal* in ***sc*** and *antiperiplanar* in ***ap***. The MW spectrum of ***sc*** has been assigned in this work.

Interestingly, ***sc*** would be expected to exhibit the ability to undergo rovibrational transitions between states of opposite parity in the torsional vibration of the thiol top resulting in "tunneling" between the two equivalent *synclinal* potential wells. This phenomenon has already been observed in cyclopropanol[7] and has also been seen in several thiols such as propargyl mercaptan ($HSCH_2C{\equiv}CH$),[15,16] ethyl mercaptan (CH_3CH_2SH),[17] isopropyl mercaptan ($(CH_3)_2CHSH$),[18] and 1,2-ethanedithiol ($HSCH_2CH_2SH$).[19] The rovibrational transitions allowed the determination of accurate torsional energy differences in these cases.

The current study of the MW spectrum of C_3H_5SH and its isotopologue C_3H_5SD was undertaken to determine the conformational and dynamical properties of this compound. The MW study has been augmented by quantum chemical calculations performed at a much higher level of theory than applied in previous work.[11–13] The current calculations were conducted to obtain information for use in assigning the MW spectrum and investigating the properties of the potential-energy hypersurface.

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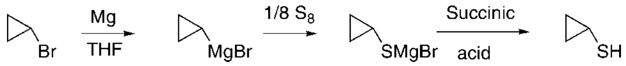
Experimental Section

Preparation. *Cyclopropanethiol is malodorous and potentially toxic. All reactions and handling should be carried out in a well-ventilated hood.*

The synthesis of cyclopropanethiol has already been reported.[20–22] The method of Block et al.[21] was modified to produce a pure sample. The steps of the present synthesis are indicated in the scheme below, and the full experimental procedure is reported in the Supporting Information.



The deuterated species, C_3H_5SD, was produced by mixing fumes of heavy water with fumes of the parent species. The intensity of the MW spectrum indicated that roughly 50% of the hydrogen atom of the thiol group had been exchanged with deuterium.

MW Experiment. The spectrum of cyclopropanethiol was recorded in the 20−80-GHz frequency interval by Stark modulation spectroscopy, using the MW spectrometer of the University of Oslo, which measures the frequency of individual transitions with an estimated accuracy of 0.10 MHz. Details of the construction and operation of this spectrometer has been given elsewhere.[23,24] While recording the spectrum, the Stark cell was cooled to about −35 °C with solid CO_2 in an attempt to increase the intensity of the spectrum.

Results and Discussion

Quantum Chemical Calculations. The present ab initio and density functional theory (DFT) calculations were conducted employing the Gaussian 03 suite of programs,[25] running on the 64 processor HP "superdome" computer in Oslo. Electron correlation was taken into consideration in the ab initio calculations using Møller−Plesset second-order perturbation calculations (MP2).[26] Becke's three-parameter hybrid functional[27] employing the Lee, Yang, and Parr correlation functional[28] (B3LYP) was employed in the DFT calculations. The aug-cc-pVTZ basis set,[29] which is of triple-ζ quality and includes polarization and diffuse functions, was used throughout the calculations. The default convergence criteria of Gaussian 03 were employed.

Rotation about the C2−S9 bond (see Figure 1) may produce rotational isomerism in this compound. B3LYP calculations were performed in an attempt to predict which rotameric forms are minima ("stable" conformers) of the potential-energy hypersurface. Calculations of energies were performed for the 0 to 180° interval in steps of 10° of the H6−C2−S9−H10 dihedral angle, employing the scan option of the Gaussian 03 program, allowing all remaining structural parameters to vary freely. The resulting potential function, which is shown in Figure 2, has two minima close to 75 (***sc***) and 180° (***ap***) of the H6−C2−S9−H10 dihedral angle and two maxima at about 0 and 150°. These predictions are in semiquantitative agreement with previous calculations.[11–13]

Separate B3LYP calculations of the structures, energies, dipole moments, vibrational frequencies, and Watson's A-reduction centrifugal distortion constants were then performed for ***sc*** and ***ap***. The starting values of the H6−C2−S9−H10 dihedral angles were chosen to be close to 75 and 180°, respectively. Full geometry optimizations with no symmetry restrictions were undertaken. The H6−C2−S9−H10 dihedral angle was found to be 74.7° for ***sc*** and exactly 180° for ***ap***. Only positive values were found for the harmonic vibrational frequencies of each of these conformers, as expected for minima on the potential-energy hypersurface. The B3LYP structures of ***sc*** and ***ap*** found in these calculations are listed in Table 1.

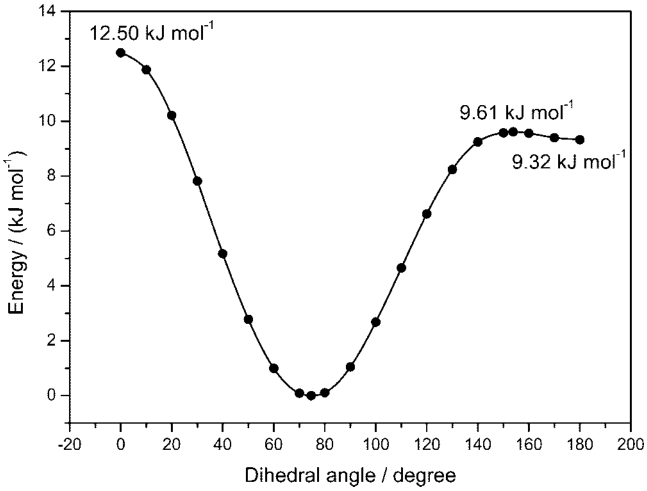


Figure 2. The B3LYP/aug-cc-pVTZ potential function for rotation about the C2−S9 bond. The values of the H6−C2−S9−H10 dihedral angle are given on the abscissa. This dihedral angle is 74.7° for ***sc***, whose MW spectrum was assigned in this work. The B3LYP and MP calculations predict that a second rotamer, ***ap***, exists with a H6−C2−S9−H10 dihedral angle of exactly 180°.

The electronic energy difference between the two rotamers was predicted to be 9.32 kJ/mol, with ***sc*** as the more stable rotameric form. This energy difference becomes 8.13 kJ/mol when the effect of the harmonic zero-point vibrational energy is taken into consideration. The latter value for the energy difference is listed in Table 2, together with the rotational and quartic centrifugal distortion constants and principal-axes dipole moment components of ***sc*** and ***ap***.

The two maxima of the potential function were explored next using the transition-state option of Gaussian 03. The first transition state was found for a value of exactly 0° of the H6−C2−S9−H10 dihedral angle and an electronic energy that is 12.50 kJ/mol higher than the electronic energy of ***sc***. The second transition state was found at 153.8° (9.61 kJ/mol above the energy of ***sc***). Each of these maxima has one imaginary vibrational frequency (262*i* and 146*i*, respectively) associated with the torsion about the C2−S9 bond, which indicates that they are first-order transition states. The full potential function for rotation about the C2−S9 bond not corrected for zero-point energies could now be constructed, as shown in Figure 2.

MP2/aug-cc-pVTZ calculations of the energies, structures, dipole moments, harmonic vibrational frequencies and quartic centrifugal distortion constants were repeated for ***sc*** and ***ap***, because we wanted to compare the results obtained by the B3LYP and MP2 methods with each other as well as with the experimental results. Selected MP2 results are therefore included in Tables 1 and 2.

It is seen from Table 2 that the MP2 energy difference corrected for zero-point vibrational effects was predicted to be 9.23 kJ/mol, with ***sc*** as the more stable, fairly close to the B3LYP result (8.13 kJ/mol). The ***ap*** form is found to have a symmetry plane (C_s symmetry) in both procedures, whereas the MP2 H6−C2−S9−H10 dihedral angle of ***sc*** was predicted to be 76.3°, close to the B3LYP result (74.7°).

The C−H bond lengths (Table 1) are predicted to be 108.0−108.2 pm compared to the experimental equilibrium distance of 107.42(29) pm found in cyclopropane.[31] The three

TABLE 1: B3LYP and MP2 Geometries[a,b] of the sc and ap Conformers of C_3H_5SH

method	B3LYP		MP2	
conformer	***sc***	***ap***	***sc***	***ap***
	Bond Length (pm)			
C1−C2	150.4	149.8	150.5	149.9
C1−C3	150.3	151.3	150.5	151.5
C1−H4	108.0	108.1	107.9	108.0
C1−H5	108.1	108.2	108.0	108.0
C2−C3	150.4	149.8	150.6	149.9
C2−H6	108.1	108.1	108.0	108.1
C2−S9	180.1	180.9	178.4	179.2
C3−H7	108.1	108.2	107.9	108.0
C3−H8	108.0	108.1	108.0	108.0
S9−H10	134.7	134.6	133.9	133.9
	Angles (deg)			
C2−C1−H4	117.5	117.7	116.7	116.9
C2−C1−H5	117.3	118.2	117.1	118.2
C3−C1−H4	117.6	117.7	117.3	117.4
C3−C1−H5	118.5	118.7	118.0	118.2
H4−C1−H5	115.0	114.3	116.0	115.3
C1−C2−H6	117.2	117.2	117.3	117.3
C1−C2−S9	121.1	123.3	119.9	121.9
C3−C2−H6	116.6	117.2	116.6	117.3
C3−C2−S9	117.3	123.3	116.0	121.9
H6−C2−S9	114.1	108.5	115.5	110.1
C1−C3−H7	118.8	118.7	118.4	118.2
C1−C3−H8	117.5	117.7	117.2	117.4
C2−C3−H7	117.4	118.2	117.3	118.2
C2−C3−H8	117.6	117.7	116.8	116.9
H7−C3−H8	114.7	114.3	115.7	115.3
C2−S9−H10	97.7	97.0	97.3	95.7
	Dihedral Angle (deg)			
H4−C1−C2−H6	−145.8	−145.0	−145.9	−144.8
H4−C1−C2−S9	2.1	−5.1	3.0	−3.8
H5−C1−C2−H6	−2.3	−1.0	−1.9	−0.3
H5−C1−C2−S9	145.6	138.9	147.0	140.7
H4−C1−C3−H7	145.7	144.7	146.5	145.5
H4−C1−C3−H8	0.1	0.0	0.1	0.0
H5−C1−C3−H7	0.0	0.0	0.0	0.0
H5−C1−C3−H8	−145.6	−144.7	−146.4	−145.5
H6−C2−C3−H7	1.6	1.0	0.9	0.3
H6−C2−C3−H8	144.9	145.0	144.9	144.8
S9−C2−C3−H7	−138.9	−138.9	−140.4	−140.7
S9−C2−C3−H8	4.4	5.1	3.5	3.8
C1−C2−S9−H10	−74.1	37.2	−73.1	36.5
C3−C2−S9−H10	−143.9	−37.2	−141.9	−36.5
H6−C2−S9−H10	74.7	180.0	76.3	180.0

[a] Basis set was aug-cc-pVTZ. [b] Atom numbering is given in Figure 1.

C−C bonds lengths in ***sc*** are predicted to be 150.3−150.6 pm, a little shorter than the equilibrium bond length of 151.01(23) pm in cyclopropane.[31] Interestingly, while all the three C−C distances in ***sc*** are found to be very similar in the calculations (Table 1), this is not the case for ***ap***. In this conformer, the C1−C3 bond, which is opposite to the SH substituent, is approximately 1.6 pm longer than the C1−C2 and C1−C3 bonds, which is adjacent to the thiol group. This difference between the lengths of the carbon bonds of a substituted cyclopropane with C_s symmetry is typical.[32]

Moreover, it is seen from Table 1 that the B3LYP C−S bond lengths are longer than the MP2 counterparts by about 1.5 pm and that S−H bond lengths are roughly 1 pm longer in the B3LYP calculations. The experimental S−H bond length in CH_3SH is 1.336(10) pm,[33] which is close to the MP2 predictions for both ***sc*** and ***ap***, which are the same (133.9 pm, Table 1). The B3LYP method predicts a longer S−H bond length (134.7 (***sc***) and 134.6 pm (***ap***)).

It is also noted that bond angles and dihedral angles calculated with the two procedures generally agree to within about 1.5° (Table 1) and that there is satisfactory agreement between the theoretical quartic centrifugal distortion constants, dipole moments, and energy differences, as presented in Table 2.

Three vibrationally excited states belonging to three different normal vibrational modes of ***sc*** were assigned in the course of this work, which makes it possible to obtain the vibration−rotation constants (α) of these three normal modes.[34] Comparison of the experimental and theoretical vibration−rotation constants is of interest. Calculation of these constants is very expensive and could therefore not be conducted using the comparatively large aug-cc-pVTZ basis set, and the smaller basis set 6−311++G**, which is of triple-ζ quality and includes diffuse and polarized functions had to be used instead in B3LYP calculations. The results are discussed below in the section on vibrationally excited states.

MW Spectrum and Assignment of the Ground Vibrational State. The quantum chemical calculations above strongly indicate that ***sc*** is preferred over ***ap***. This rotamer is a prolate rotor (Ray's asymmetry parameter[35] $\kappa \approx -0.95$) and has its major dipole-moment component along the *a* inertial axis, with lesser components along the *b* and *c* inertial axes (Table 2). The approximate disposition of the inertial axes in ***sc*** is indicated in Figure 3.

It is seen from this figure that μ_b is antisymmetrical with respect to the torsion of the thiol group and *b*-type rotational transitions therefore connect energy levels in torsional states of opposite parity and will depend strongly on the energy of the separation, Δ, of these states. The selection rules of the *b* type lines are therefore those of a rigid rotor plus $(+) \leftarrow (-)$, or $(-) \leftarrow (+)$, whereas the *a*- and *c*-type transitions occur between states of the same parity and will therefore depend little on Δ. The present quantum chemical calculations are not sufficiently accurate to allow a quantitative prediction of Δ, so no indication of its value was available from the theoretical calculations.

The spectrum of the normal isotopic species exhibit a number of fairly intense absorptions, many of which have well-resolved Stark effects, amid a background of lines of moderate intensity. A search for ^aR transitions using the B3LYP spectroscopic constants (Table 2) to predict their approximate frequencies soon met with success. The preliminary spectroscopic constants obtained from these lines were used to predict the frequencies of *b*- and *c*-type transitions, which involved low or intermediate values of the *J* principal quantum number. These lines were generally found within a few megaHertz from the predicted frequencies. Additional transitions involving higher values of *J* were successively included in the fit. Lines with a maximum of $J = 60$ were assigned in this manner.

All the *b*-type lines were split by roughly 3 MHz, corresponding to $2 \times \Delta$, whereas no resolved splittings were seen for the *a*- and *c*-type lines. It was therefore assumed that the tunneling frequency is about 1.5 MHz.

A computer program, Asmix, by Nielsen,[36] deals with spectra of this type. This program is based on the reduced Hamiltonian defined as follows[36]

$$H_{\mathrm{red}} = |0\rangle\{H_r^{(0)} + H_d^{(0)}\}\langle 0| + |1\rangle H_r^{(1)} + H_d^{(1)} + W_{01}\}\langle 1| + |0\rangle H_c\langle 1| + |1\rangle H_c\langle 0|$$

where the label 0 corresponds to the (+) state and the label 1 corresponds to the (−) state.

TABLE 2: B3LYP[a] and MP2[b] Parameters of Spectroscopic Interest of C_3H_5SH

method	B3LYP		MP2		experimental[c]
conformer	***sc***	***ap***	***sc***	***ap***	***sc***
			Rotational Constants (MHz)		
A	15884.2	16053.3	15796.8	15966.4	15702.3660(50)
B	3832.6	3705.8	3916.2	3789.2	3894.7246(11)
C	3529.8	3477.8	3606.4	3556.8	3585.1683(11)
			Quartic Centrifugal Distortion Constants[a] (kHz)		
Δ_J	1.28	1.17	1.31	1.22	1.3040(22)
Δ_{JK}	2.03	3.01	1.76	2.50	2.0231(84)
Δ_K	14.6	14.3	14.2	14.1	12.00(29)
δ_J	0.0603	0.0393	0.0580	0.0371	0.06137(13)
δ_K	2.07	−10.8	1.88	−9.29	1.982(20)
			Dipole Moment[d] (10^{-30} C m)		
μ_a	4.4	5.3	4.6	5.7	4.09(5)
μ_b	2.5	0.0	2.8	0.0	2.83(11)
μ_c	1.7	0.9	1.7	0.9	0.89(32)
μ_{tot}	5.3	5.4	5.6	5.8	5.06(16)
			Energy Difference[e] (kJ/mol)		
ΔE	0.0[f]	8.1	0.0	9.2[g]	0.0[h]

[a] Basis set aug-cc-pVTZ. [b] A reduction.[30] [c] 0^+ state. Uncertainties represent one standard deviation. [d] 1 debye = 3.33564 × 10^{-30} C m. [e] Corrected for zero-point vibrational energy. [f] Electronic energy = −1355 196.34 kJ/mol. [g] Electronic energy = −1353 046.16 kJ/mol. [h] Lowest energy state.

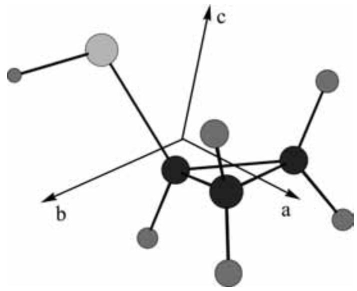


Figure 3. Model showing approximate principal inertial axes in ***sc***.

By use of I^r representation,[34] one has

$$H_r(v) = B^{(v)}J_b^{\,2} + C^{(v)}J_c^{\,2} + A^{(v)}J_a^{\,2}$$

where v refers to the (+) or the (−) state, respectively.

H_d = {Watson[30] quartic and sextic centrifugal distortion constants}$^{(v)}$

$$W_{01} = \langle 1|H_{\text{vib}}^{\ 0}|1\rangle - \langle 0|H_{\text{vib}}^{\ 0}|0\rangle$$

where W_{01} corresponds to Δ above.

H_c is the coupling term of the form

$$H_c = \mu_{ij}\langle J_iJ_j + J_jJ_i\rangle$$

where i and j refer to the principal inertial axis. μ_{ij} is the reduced moment of inertia.

A total of 589 transitions, which are listed in Table 1S in the Supporting Information, were used to determine the spectroscopic constants shown in Table 3. The effect of centrifugal distortion is not very prominent in this spectrum and only quartic centrifugal distortion constants were therefore included in the least-squares fit. The rotational and quartic centrifugal distortion constants were varied in the least-squares fit together with the tunneling frequency Δ. Attempts to determine the μ_{ij} coupling constants failed, presumably because of the rather small energy difference between the (+) and (−) tunneling states. The root-mean-square deviation of the fit was 0.171 MHz, somewhat more than the experimental uncertainty of ±0.10 MHz. The tunneling frequency, Δ, was determined to be 1.664(22) MHz. The B and C rotational constants (Table 3) of the 0^+ and 0^- substates are the same within the stated uncertainties, whereas a minor, but significant, difference is seen for the A rotational constants of the two states.

The tunneling frequency of 1.664(22) MHz is much smaller than 4115.26(42) MHz in the oxygen analogue (C_3H_5OH).[7] A large decrease in the tunneling frequency on going from alcohols to thiols seems to be typical. For example, the tunneling frequency, which is 644319.69 MHz in $HOCH_2C{\equiv}H$,[37] is reduced to 6895 MHz in $HSCH_2C{\equiv}CH$.[15,16] In the *synclinal* conformer of CH_3CH_2OH it is 97734.3 MHz,[38] while in the similar rotamer of CH_3CH_2SH, a value of 1753.84(29) has been[17] determined. Similarly, the reduction of Δ from 46798.50(11) MHz in $(CH_3)_2CHOH$[39] to 562.4 MHz was seen in $(CH_3)_2CHSH$.[18]

The rotational and centrifugal distortion constants of the 0^+ state are listed in Table 2 for convenient comparison with the calculated values. The B3LYP rotational constants deviate from the experimental rotational constants by 1.1, −1.6, and −1.6% in the cases of A, B, and C, respectively, as can be seen from this Table 2. The corresponding MP2 rotational constants deviate by 0.6, −0.6, and −0.6%, respectively. The theoretical B3LYP and MP2 rotational constants have been obtained from approximate equilibrium structures, whereas the experimental rotational constants reflect an effective r_0 structure, which by definition is different from the equilibrium structure. However, the good agreement between the experimental and calculated rotational constants is an indication that the structure associated with the experimental rotational constants is close to the B3LYP and the MP2 structures. The MP2 rotational constants are slightly closer to the experimental counterparts than the B3LYP rotational constants are. Interestingly, MP2 structures obtained using a large basis set are close to the true equilibrium structures.[40]

Vibrationally Excited States. The three lowest vibrational fundamentals of ***sc*** corrected for anharmonicity (not given in Tables 1 or 2) were predicted at v_{24} = 169, v_{23} = 292, and v_{22} = 318 cm^{-1}, according to the B3LYP/6−311++G** calculations (the corresponding B3LYP/aug-cc-pVTZ harmonic frequencies were 225, 304, and 321 cm^{-1}, respectively). v_{24} is the

TABLE 3: Spectroscopic Constants[a,b] of the Ground and Vibrationally Excited States of the *sc* Conformer of C_3H_5SH

vibrational state	ground[c]		first excited torsion[c]		lowest bending[c]		second lowest bending[c]	
species	0^+	0^-	$v_{24}{}^-$	$v_{24}{}^+$	$v_{23}{}^+$	$v_{23}{}^-$	$v_{22}{}^+$	$v_{22}{}^-$
A (MHz)	15702.3660(50)	15702.3181(50)	15707.175(13)	15706.164(13)	15557.635(41)	15557.288(32)	15898.793(28)	15898.744(28)
B (MHz)	3894.7246(11)	3894.7246(11)	3881.9788(24)	3881.9805(24)	3891.4770(48)	3891.4702(48)	3891.4373(56)	3891.4374(56)
C (MHz)	3585.1683(11)	3585.1683(11)	3579.9811(24)	3579.9691(24)	3571.5678(48)	3571.5806(48)	3589.4647(56)	3589.4649(56)
Δ_J (kHz)	1.3040(22)	1.3047(22)	1.1281(95)	1.1285(95)	1.139(34)	1.123(34)	1.365(37)	1.365(37)
Δ_{JK} (kHz)	2.0231(84)	2.0087(84)	2.058(23)	1.979(24)	3.93(19)	4.25(12)	0.141(86)	0.160(81)
Δ_K (kHz)	12.00(29)	11.02(29)	10.9(12)	7.8(12)	12.00[d]	11.02[d]	53.1(48)	50.0(46)
δ_J (kHz)	0.6137(13)	0.06107(13)	0.06099(27)	0.06075(28)	0.1074(25)	0.1110(20)	0.02250(56)	0.02236(55)
δ_K (kHz)	1.982(20)	2.044(20)	1.958(41)	2.044(42)	3.83(45)	1.85(33)	0.77(10)	0.78(10)
Δ^e (MHz)	1.664(22)		52.330(44)		26.43(16)		3.286(61)	
rms[f] (MHz)	0.171		0.221		0.179		0.245	
no transitions in fit	589		326		103		192	
maximum *J* value	60		48		40		45	

[a] As defined by Nielsen.[36] [b] Uncertainties represent one standard deviation. [c] The full spectra are given in Tables 1−4S in the Supporting Information. [d] Fixed. [e] $\Delta = W_{01}$ (energy separation between tunneling states).[36] [f] Root-mean-square deviation.

torsion about the C2−S9 bond, while v_{23} and v_{22} are the two lowest bending vibrations. The spectra of these three states should therefore have sufficient intensity to allow their assignments. The next fundamental frequency is predicted to occur at 639 cm^{-1} according to the B3LYP/6−311++G** calculations, and its microwave spectrum would therefore have a very low intensity compared to the intensity of the ground-state spectrum.

The spectra of the first excited states of v_{24}, v_{23}, and v_{22} were indeed assigned and are listed in the Supporting Information, Tables 2S − 4S. The spectroscopic constants obtained from 326, 103 and 192 transitions, respectively, are reported in Table 3. These excited-state spectra displayed splittings caused by tunneling, and they were therefore fitted in the same manner as described above for the ground-state spectrum, using Asmix.[36]

The splittings of the *b*-type lines of the first excited-state of the C2−S9 torsion (v_{24}) were approximately 105 MHz, 35 times larger than the splittings of the ground state. An increase of this order of magnitude was expected for the first excited state of this mode. None of the *a*-type lines of this excited state displayed a resolved splitting, whereas the *c*-type lines were split by a few MHz. The splittings observed for the *c*-type lines do not result from tunneling but from the fact that the rotational constants, in particular the *A* rotational constant of the (+) and (−) states differ by about 1 MHz, as can be seen from Table 3. The *c*-type transitions depend strongly upon *A*, whereas this is not the case for the *a*-type lines, and this explains why resolved splittings were observed for the *c*- but not for the *a*-type transitions. Δ was determined to be 52.330(44) MHz for the first excited state of the C2−S9 torsion. No significant value could be determined for the μ_{ij} coupling constants in this case too.

The *b*-type lines of the first excited-state of lowest bending vibration (v_{23}) were split by approximately 53 MHz, about 15 times as much as in the ground state. The *a*-type lines were not detectably split. No *c*-type lines were assigned, presumably because of too low intensities. The tunneling frequency was determined to be Δ = 26.43(13) MHz (Table 3), compared to 1.664(22) MHz in the ground state. No significant value was found for the μ_{ij} coupling constants of this vibration.

Transitions of the *a*, *b*, and *c* varieties were assigned for the first excited-state of v_{22}. The tunneling frequency was determined to be 3.268(61) MHz (Table 3), which is about twice as large as the splitting in the ground vibrational state. The splitting patterns of this state were similar to those of the ground vibrational state.

Relative intensity comparisons of the spectra of the ground state and of the vibrationally excited states were performed as described elsewhere[41] to determine the fundamental vibrational frequencies of the three excited states assigned in the current investigation. The results were 195(30) for ν_{24}, 336(40) for ν_{23}, and 345(40) cm^{-1} for ν_{22}, respectively, compared to the B3LYP/6−311++G** anharmonic values of 169, 292, and 318 cm^{-1}, as stated above.

The experimental vibration−rotation constants were calculated from $\alpha_X = X_0 - X_1$,[34] where α_X is the vibration−rotation constants using the entries in Table 3. X_0 is the *A*, *B*, or *C* rotational constant of the ground vibrational state, and X_1 is the corresponding value for the first excited-state under consideration. The average rotational constants of the ground and of the vibrationally excited states shown in Table 3 were used to determine the vibration−rotation constants, which were found to be $\alpha_A = -4.33$, $\alpha_B = 12.74$, and $\alpha_C = 5.20$ MHz for the ν_{24} state, compared to the B3LYP/6−311++G** result, −11.35, 12.81, and 2.66 MHz, respectively. The experimental values are $\alpha_A = 144.89$, $\alpha_B = 3.25$, and $\alpha_C = 13.60$ MHz for the ν_{23} state compared to the theoretical values of 117.26, 2.45, and 11.96 MHz. Finally, $\alpha_A = -196.43$, $\alpha_B = 4.29$, and $\alpha_C = -3.68$ MHz are determined for the ν_{22} state, whereas the theoretical counterparts are −171.33, 3.09, and −3.68 MHz, respectively. It can be concluded that there is satisfactory agreement between the experimental vibrational frequencies and the vibration−rotation constants and their B3LYP/6−311++G** counterparts.

The assignments described in this and in the previous section comprise all the strong lines of the spectrum as well as many weak ones. There is no indication of substantial amounts of a second form such as ***ap***. This is in agreement with the theoretical calculations (Table 2), which predicts an energy difference of 8−10 kJ/mol between ***ap*** and ***sc***. An energy difference of this size would result in a very small gas-phase fraction of ***ap***, in accordance with the present findings.

Spectrum of C_3H_5SD and Structure. Intensity comparisons indicated that the mixing of fumes of heavy water and cyclopropanethiol resulted in roughly 50% of C_3H_5SD. The assignment of the *a*- and *b*-type ground-state spectrum of this species was straightforward. None of the *b*-type transitions were detectably split in this case presumably because the substitution of hydrogen with deuterium leads to a much increased reduced

TABLE 4: Spectroscopic Constants[a] of C_3H_5SD

A (MHz)	15012.066(14)
B (MHz)	3812.9269(75)
C (MHz)	3480.9706(74)
Δ_J (kHz)	1.062(45)
Δ_{JK} (kHz)	1.339(30)
Δ_K (kHz)	12.00[b]
δ_J (kHz)	0.07827(98)
δ_K (kHz)	2.004(85)

[a] *A* reduction. I^r representation.[30] Uncertainties represent one standard deviation. The spectrum is given in Table 5S in the Supporting Information. [b] Fixed.

TABLE 5: Second-Order Stark Coefficients[a] and Dipole Moments of C_3H_5SH

		stark coefficients	
		$\Delta E^{-2}/(10^{-5}$ MHz V^{-2} $cm^2)$	
transition	|*M*|	obsd	calcd
$3_{1,3} \leftarrow 2_{1,2}$	1	1.10(6)	1.04
$3_{1,2} \leftarrow 2_{1,1}$	1	−1.10(10)	−1.03
$3_{0,3} \leftarrow 2_{0,2}$	1	−0.160(10)	−0.134
	2	0.580(20)	0.591
$4_{1,4} \leftarrow 3_{1,3}$	2	0.52(8)	0.468
	3	1.12(2)	1.12
$4_{0,4} \leftarrow 3_{0,3}$	0	−0.10(2)	−0.090
	2	0.12(1)	0.129
	3	0.40(5)	0.410
$4_{2,2} \leftarrow 3_{2,1}$	0	0.50(5)	0.465
	1	−34(5)	−29.7
$4_{1,3} \leftarrow 3_{1,2}$	0	−0.12(2)	−0.113
	1	−0.20(5)	−0.220
	2	−0.54(2)	−0.576
	3	−1.14(3)	−1.16

dipole moments: $\mu_a = 4.09(5)$, $\mu_b = 2.83(11)$, $\mu_c = 0.89(32)$, $\mu_{tot} = 5.06(16) \times 10^{-30}$ C m

[a] Uncertainties represent one standard deviation. $D = 3.33564 \times 10^{-30}$ C m.

mass of the tunneling motion leading to unresolved splittings. The spectrum, which was fitted to Watson's *A*-reduced Hamiltonian[30] in this case, using the computer program Rotfit by Sørensen,[42] is listed in the Supporting Information, Table 5S, and the spectroscopic constants are displayed in Table 4.

The substitution coordinates[43,44] of the hydrogen atom of the thiol group was determined to be $|a| = 163.9(2)$, $|b| = 121.5(3)$, and $|c| = 15.8(20)$ pm, respectively, using the rotational constants of the 0^+ state of C_3H_5SH and the rotational constants of the ground states of the deuterated species. The indicated uncertainties have been calculated as recommended by van Eijck.[45] The corresponding values calculated from the MP2 structure (Table 1) are $|a| = 166.1$, $|b| = 123.7$, and $|c| = 9.2$ pm, respectively. The agreement between the two sets of coordinates indicates that the H6−C2−S9−H10 dihedral angle is close to the MP2 value of 76.3°. It is therefore concluded that the H6−C2−S9−H10 dihedral angle is 76(5)° from *synperiplanar*, where a liberal uncertainty limit of ± 5° has been assigned. This value is almost identical with the value found for the corresponding dihedral angle in C_3H_5OH, namely, 75(5)°.[7]

Dipole Moment. The dipole moment was determined in a least-squares fit using the second-order Stark coefficient shown in Table 5. The weight of each Stark coefficient was taken to be the inverse squared value of its uncertainty, which is also shown in the same table. The cell was calibrated using OCS, whose dipole moment was taken to be $2.3857(68) \times 10^{-30}$ C m.[46] The theoretical values of the second-order Stark coefficients were calculated as described by Golden and Wilson,[47] employing the computer program MB04.[48] The tunneling splitting is small (1.664(22) MHz) and was therefore not taken into account in these calculations. The result is shown in Table 5 and repeated in Table 2 for convenient comparison with the MP2 and B3LYP predictions. Both theoretical methods predict a larger dipole moment than the experimental finding (Table 2), with the B3LYP results being somewhat closer to the experiment than MP2 predictions.

Conclusions

The MW spectra of cyclopropanethiol and its SD isotopologue have been assigned and shown to belong to a conformation that has a *synclinal* orientation of the H−S−C−H (D) chain of atoms. The corresponding dihedral angle is 76(5)° from *synperiplanar* (0°). There is no indication in the spectrum of substantial amounts of further rotameric forms.

The three lowest vibrationally excited states were assigned for the parent species and their frequencies have been determined by relative intensity measurements. The *b*-type transitions of the ground and of the vibrationally excited states of this species were found to be split into two components. This splitting is assumed to be caused by tunneling between two equivalent *synclinal* potential wells. The tunneling frequency of the ground vibrational state is 1.664(20) MHz, much less than its counterpart, 4115.26(42) MHz, in the oxygen analogue cyclopropanol (C_3H_5OH),[7] which also prefers a similar *synclinal* conformation. The tunneling frequencies of the vibrationally excited states are larger than in the ground state. The largest tunneling frequency (52.330(44) MHz) is found for the first excited state of the torsion about the C−S bond. No resolved tunneling splittings were observed for the ground state of the deuterated species, C_3H_5SD, presumably because the reduced mass of this motion is significantly larger than in the case of the parent species.

Quantum chemical calculations at the B3LYP/aug-cc-pVTZ and MP2/aug-cc-pVTZ levels predict structures that are in good agreement with each other. The rotational constants calculated from the B3LYP and MP2 structures deviate less than about 1.6% from the experimental value in each case, which is an indication that the B3LYP and MP2 structures are close to the structure associated with the experimental rotational constants. The theoretical quartic centrifugal distortion constants and dipole moment components are also in satisfactory agreement with their experimental counterparts.

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Supporting Information Available: Description of the preparation of cyclopropanethiol, the spectra of the ground and vibrationally excited of the parent species, and the spectrum of the ground state of the SD species. This material is available free of charge at http://pubs.acs.org.

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