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Laboratory Rotational Spectroscopy of Methyl n-Propyl Sulfide: Conformational Analysis and Methyl Internal Rotations

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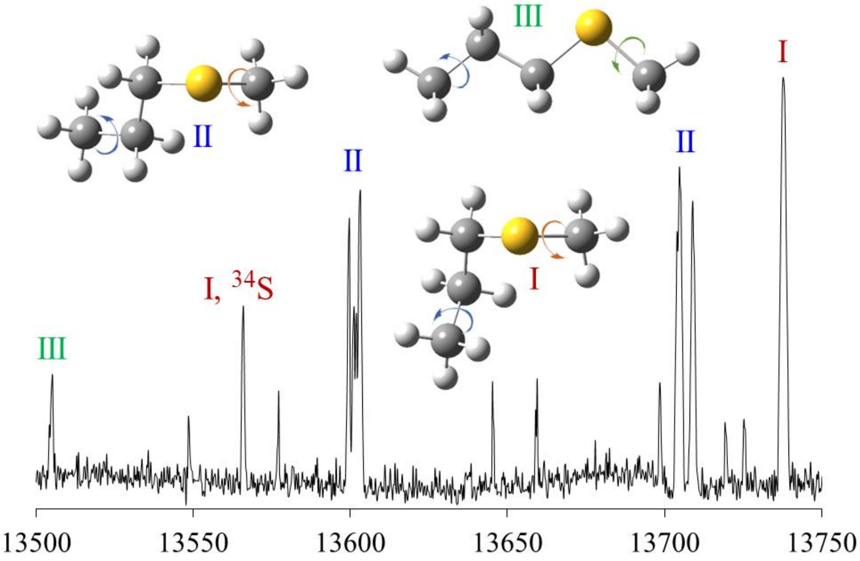
** This paper is dedicated to Dr. F. J. Lovas.

Abstract

The microwave spectra of methyl n-propyl sulfide, CH_3-S-CH_2-CH_2-CH_3, were recorded in the frequency region from 2.0 to 26.5 GHz, revealing three conformers. Quantum chemical calculations were carried out to support experimental work. Fine splittings arising from the internal rotation of the methyl group attached to the sulfur atom were resolved and analyzed. Torsional barriers of about 600 cm^{-1} for the two conformers with C_1 symmetry and about 700 cm^{-1} for the C_s conformer could be deduced, showing that conformations affect the methyl internal rotation. Torsional splittings of the methyl group at the end of the propyl moiety were observed for some transitions, leading to the determination of barrier heights close to 1000 cm^{-1}. The spectrum of the ^{34}S isotopologue of the most stable conformer could be measured in natural abundance. The present laboratory work provides highly accurate spectroscopic parameters, which serve as reliable starting values for extrapolation in higher frequency ranges and for the search of this sulfur-containing molecule in the interstellar medium.

Keywords: rotational spectroscopy, microwave structure, conformational analysis, internal rotation

Graphical abstract



1. Introduction

The past decade has seen an extraordinary progress in astrophysical observation both in sensitivity and operational frequency range. Observatories such as the Atacama Large Millimeter/submillimeter Array (ALMA) has enabled the detection of large and complex molecules in circumstellar envelopes and interstellar medium (ISM) [1-3], and still shows a great potential towards even larger and more dynamic systems for the future.

More than 200 molecules have been found in the circumstellar shells or ISM according to the Cologne Database for Molecular Spectroscopy (CDMS) [4]. A number of them show internal rotation with observable splittings. The classical example is methanol, one of the simplest molecules showing methyl internal rotation with a barrier height of about 380 cm^{-1}, which was detected in Orion-A by Lovas et al. in 1976 [5]. About at the same time, Churchwell and Winnewisser found methyl formate in Sgr B2 with the A-E doublet of the $1_{10} \leftarrow 1_{11}$ transition [6]. Acetaldehyde was also found in Sgr B2, and then in two other clouds TMC-1 and L134N [7]. Many internal rotor molecules were observed in Orion-KL such as dimethyl ether [8]. Larger molecules like acetone [9] and methyl acetate [10] showing two methyl internal rotations have been detected in the ISM as well. Most of the identifications were enabled by the interplay between laboratory studies of the rotational spectra and observations of interstellar surveys in the microwave, sub-millimeter wave, and millimeter wave frequency ranges. The laboratory investigations yield reliable data such as line lists and intensity needed for the interpretation of interstellar surveys, which are available in several databases like CDMS [4], Jet Propulsion Laboratory (JPL) [11], Splatalogue [12], the Toyama Microwave Atlas [13], and the Observed Interstellar Molecular Microwave Transitions NIST database [14].

Sulfur is often incorporated into interstellar silicates, as this element has been found in interstellar grains extracted from dust particles brought by meteorites [15]. Furthermore, molecules with sulfur might play an important role to study the chemical evolution and to determine the age of hot cores [16] and massive stars [17]. To date, about 20 molecules containing a sulfur atom have been detected in space, among them only one, methyl mercaptan (CH_3SH), shows observable splittings arising from methyl internal rotation [18,19]. In 2014, Kolesniková et al. found ethyl mercaptan in the Orion Cloud [20], but the torsional splittings of the methyl group in the ethyl moiety could not be resolved. Ethyl methyl sulfide, present as a *trans* and a *gauche* conformer with torsional barriers of 692 cm^{-1} [21] and 598 cm^{-1} [22], respectively, of the S-**CH_3**, henceforward called the thiomethyl group, has not yet been observed in space, though its oxygen analogue ethyl methyl ether was (tentatively) detected in W51e2 employing the IRAM 30m and SEST 15m telescopes [23,24]. Knowledge about the chemistry of sulfur in the ISM is still vague despite its importance. Many more sulfur-containing compounds have been detected in diffuse regions than in dense regions [25], and astronomers are searching intensively for this missing sulfur and its reservoir.

In the methyl *n*-alkyl sulfide family, methyl propyl sulfide is the third member with an *n*-propyl chain attached to the sulfur atom. This alliaceous smelling thioether can be obtained from the reaction of methyl iodide with *n*-propyl mercaptan [26]. To the best of our knowledge, no rotational studies of methyl propyl sulfide have been reported. Therefore, it is worthwhile to investigate its microwave spectrum to obtain accurate geometry parameters such as the rotational and centrifugal constants of the molecule with support from quantum chemical calculations. This will serve fundamental information for possible astrophysical searches of this sulfur containing molecule in the future.

The internal rotation of the methyl group attached to the sulfur atom is an additional motivation for this work. Previous studies on ethyl methyl sulfide have reported quite different torsional barriers for the *trans* (692 cm^{-1}) [21] and the *gauche* conformer (598 cm^{-1}) [22]. In a systematic investigation on linear aliphatic ketones, Andresen *et al.* have pointed out that the methyl torsion is conformation-dependent. The "pseudo-C_s" conformer always shows a torsional barrier of about 180 cm^{-1} of the acetyl methyl group, while that of the C_1 conformer where the alkyl chain is bent at the γ carbon position has a higher barrier around 240 cm^{-1} [27-29]. These observations contrast with the results on a series of linear aliphatic acetates which indicate that the barrier hindering the methyl internal rotation is always around 100 cm^{-1}, independent of the molecular geometry [30]. The significant difference in barrier height between the *trans* and the *gauche* conformer of ethyl methyl sulfide hints about conformational effects on the methyl torsion in methyl *n*-alkyl sulfide. Information obtained from methyl propyl sulfide will provide valuable data to explore and validate these effects.

Comparison between torsional barriers of oxygen and sulfur analogues has shown that the barrier height is always larger in the oxygen analogue, for example 2-methylfuran (413 cm^{-1}) [31] vs. 2-methylthiophene (194 cm^{-1}) [32] and dimethylfuran (439 cm^{-1}) [33] vs. dimethylthiophene (248 cm^{-1}) [34]. In a previous study on methyl propyl ether, only one conformer with C_s symmetry was observed where the barrier to internal rotation of the methoxy methyl group was determined to be 1154(21) cm^{-1} [35]. We will also compare the conformations and methyl torsional barriers of methyl propyl sulfide with those of methyl propyl ether.

2. Quantum chemical calculations

2.1. Conformational analysis

Theoretical calculations were performed using the *Gaussian 16* [36] program package to obtain the molecular geometries and electronic energies of different conformers of methyl propyl sulfide. The starting geometries were generated systematically through step-wise rotation around the sp^3 hybridized bonds, in other to efficiently sample the conformational landscape. The energies of the resulting energy minima were used to estimate which conformers could be observed in the microwave spectrum. The starting geometries were generated by setting the dihedral angles $\theta_1 = \angle(C_1,S_5,C_6,C_9)$ and $\theta_2 = \angle(S_5,C_6,C_9,C_{12})$ to 0°, ±60°, ±120°, and 180°, corresponding to rotations about the S_5-C_6 and C_6-C_9 bonds, respectively (for atom numbering, see Figure 1). Optimizations were first carried out at the MP2/6-311++G(d,p) level of theory, as this level has yielded reliable results for many classes of molecules reported in the literature [37-39]. In total, five conformers were found as minima, all of which were closer than 5 kJ/mol in energy. Therefore, we assumed several of them to be present in the spectrum recorded under molecular jet conditions. The optimized geometries of all conformers are illustrated in Figure 1. The rotational constants, dipole moment components, optimized dihedral angles θ_1 and θ_2, and energies relative to the energetically lowest conformer including zero-point corrections are given in Table 1. The nuclear coordinates in the principal inertial axis system are given in Table S1 in the Supplementary Material. Optimizations were later repeated at different levels of theory with the MP2, B3LYP, M06-2X, and coupled cluster (CCSD) methods to explore the method-basis set combination that predicts rotational constants that are in best agreement with the experimental ones. The results are collected in Table S2.

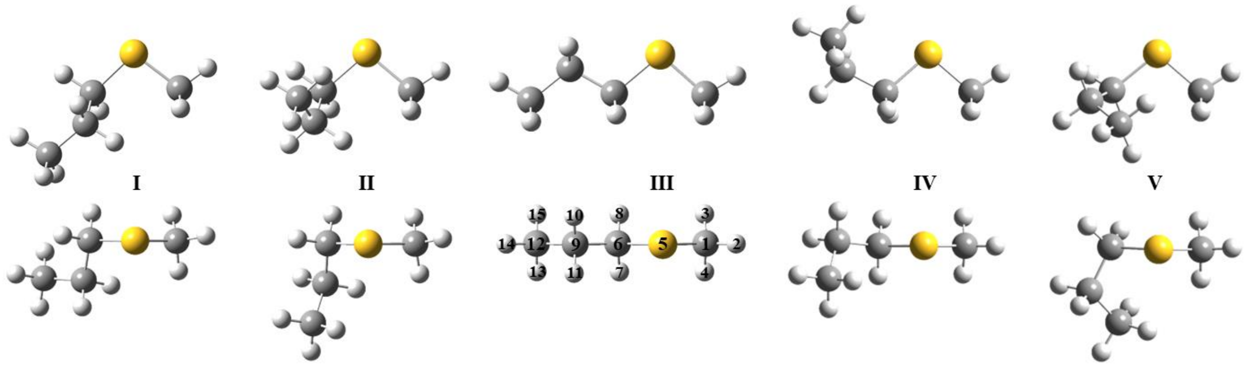


Figure 1: Geometries of the five stable conformers of methyl propyl sulfide optimized at the MP2/6-311++G(d,p) level of theory. Upper trace: view onto the C−S−C plane. Lower trace: view along the C−S−C plane. The atom labeling is given at the C_s conformer III.

Table 1. Rotational constants in GHz, dipole moment components in Debye, optimized dihedral angles $\theta_1 = \angle(C_1,S_5,C_6,C_9)$ and $\theta_2 = \angle(S_5,C_6,C_9,C_{12})$ in degree, relative energies with (ZPE) and without (E) zero-point corrections in kJ/mol, and the $V_{3,1}$ term of the potential energy of the thiomethyl torsion in cm^{-1} of five stable conformers of methyl propyl sulfide calculated at the MP2/6-311++G(d,p) level of theory.

	A	B	C	$\lvert\mu_a\rvert$	$\lvert\mu_b\rvert$	$\lvert\mu_c\rvert$	θ_1	θ_2	E^a	ZPE^b	$V_{3,1}$
I	8.7182	1.8804	1.6851	1.02	1.26	0.50	67.32	177.2	0.00	0.00	526.8
II	6.4822	2.2475	2.1640	0.58	1.26	0.89	66.79	63.93	0.15	0.34	551.8
III	12.2844	1.6527	1.5121	0.38	1.50	0.00	180.00	180.00	1.80	1.30	617.3
IV	9.6799	1.9654	1.7955	0.14	1.42	0.56	174.10	64.01	2.87	2.80	642.5
V	5.9824	2.5410	2.0728	0.82	0.81	1.14	–96.26	63.00	4.54	5.01	515.8

[a] Referring to the absolute energy of *E* = –555.625578 Hartree of conformer I. [b] Referring to the zero-point corrected energy of *E* = –555.490686 Hartree of conformer I.

2.2. Methyl internal rotations

The torsional potentials of the thiomethyl group, and the CH_2-CH_2-$\mathbf{CH_3}$, called the propyl methyl group, were calculated by varying the dihedral angles $\alpha_1 = \angle(H_2,C_1,S_5,C_6)$ and $\alpha_2 = \angle(C_6,C_9,C_{12},H_{14})$ in a step width of 10°, while all other geometry parameters were optimized at the MP2/6-311++G(d,p) level of theory. For all conformers, three-fold potentials were observed and the barrier heights for the thiomethyl group range from 515 cm^{-1} to 642 cm^{-1}. Therefore, torsional splittings in the microwave spectrum should be, though small, observable with the resolution of our spectrometer. For conformer I and II, the shape of the potential curve is not symmetric as for conformer III. We noticed that the torsion of the methyl group induced an oscillation of the entire n-propyl chain, which is reflected by changes of up to 10° of the dihedral angle θ_1, as shown in the lower part of Figure 2. For the propyl methyl group, the calculated barrier height is over 1000 cm^{-1}, and we expect that the effects of the internal rotation of this methyl group will not be visible in the spectrum.

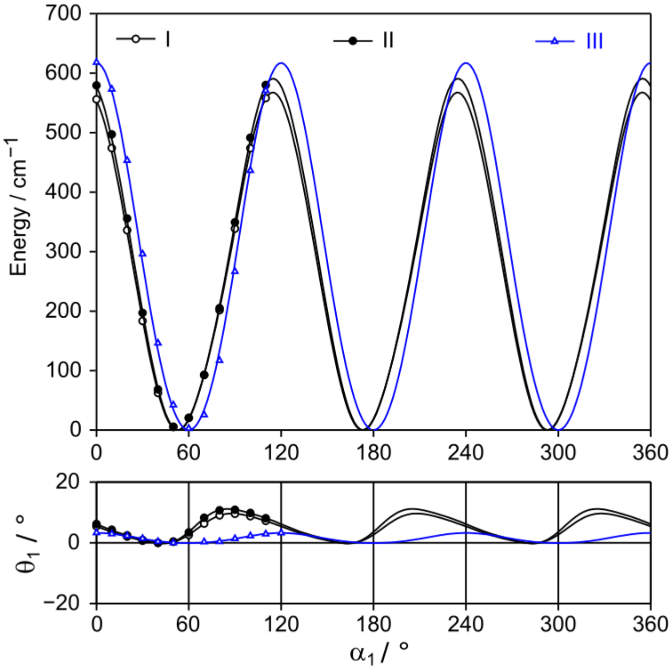


Figure 2: Upper trace: Potential energy curves of three conformer of methyl n-propyl sulfide obtained by rotating the thiomethyl group while all other geometry parameters were optimized at the MP2/6-311++G(d,p) level of theory. The energies are given relative to the lowest energy

conformations. Lower trace: Oscillation of the propyl group upon the thiomethyl torsion visualized by changes in the dihedral angle $\theta_1 = \angle(C_1,S_5,C_6,C_9)$ relative to the smallest value of $\theta_1 = 65.81°$ at $\alpha_1 = 40°$ (conformer II), and $\theta_1 = 176.67°$ at $\alpha_1 = 50°$ (conformer III).

3. Microwave spectroscopy

3.1. Measurements

The rotational spectrum of methyl propyl sulfide was recorded using a molecular jet Fourier transform microwave (MJ-FTMW) spectrometer operating in the frequency range from 2.0-26.5 GHz [40]. The spectrometer can be used in two different modes: the high resolution mode and the scan mode. A survey spectrum was recorded from 10.0 to 14.0 GHz using the scan mode, and all observed transitions were subsequently remeasured in the high resolution mode. Figure 3 illustrates a portion of the broadband scan, and Figure 4 a typical spectrum recorded at high resolution. Methyl propyl sulfide was purchased from Alfa Aesar GmbH & Co. KG, Germany, with a stated purity of 99% and used without further purification. A mixture of approximately 1% of methyl propyl sulfide in helium at a total pressure of 70-110 kPa was expanded through a pulsed nozzle into the cavity. Helium was chosen as a carrier gas and favored over neon and argon because of the warmer molecular jet which enables the observation of relatively high *J* transitions with satisfactory intensity.

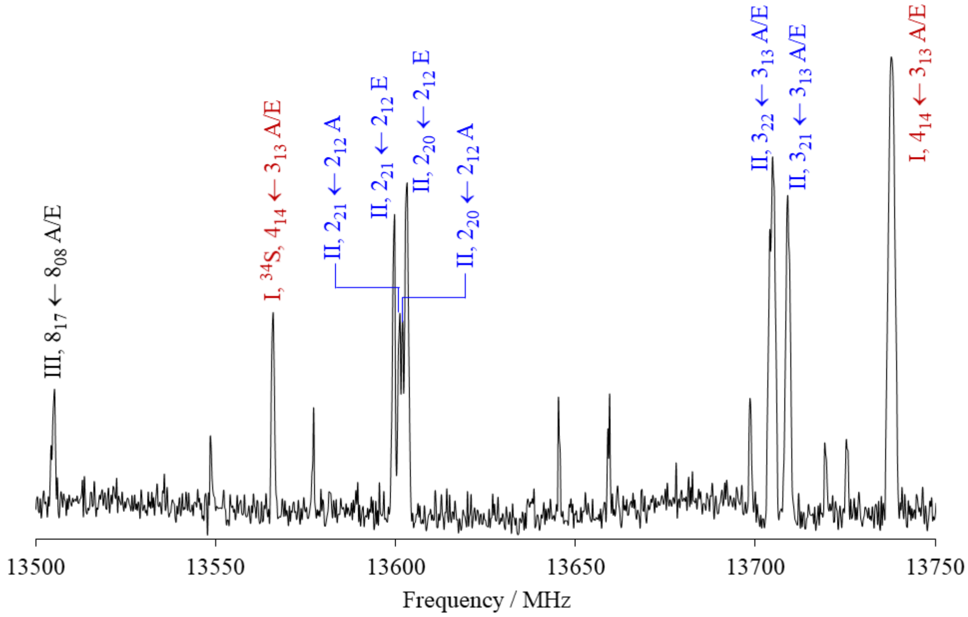


Figure 3: A portion of the broadband scan of methyl propyl sulfide in the frequency range from 13500 to 13750 MHz. The intensities are given in arbitrary unit and a logarithmic scale. Each

assigned line is labelled by the conformer, the corresponding quantum numbers of the transition $J''_{K_a''K_c''} \leftarrow J'_{K_a'K_c'}$, and the torsional species. Except for the $4_{14} \leftarrow 3_{13}$ transition of the ^{34}S isotopologue of conformer I, all other transitions are those of the main isotopologue.

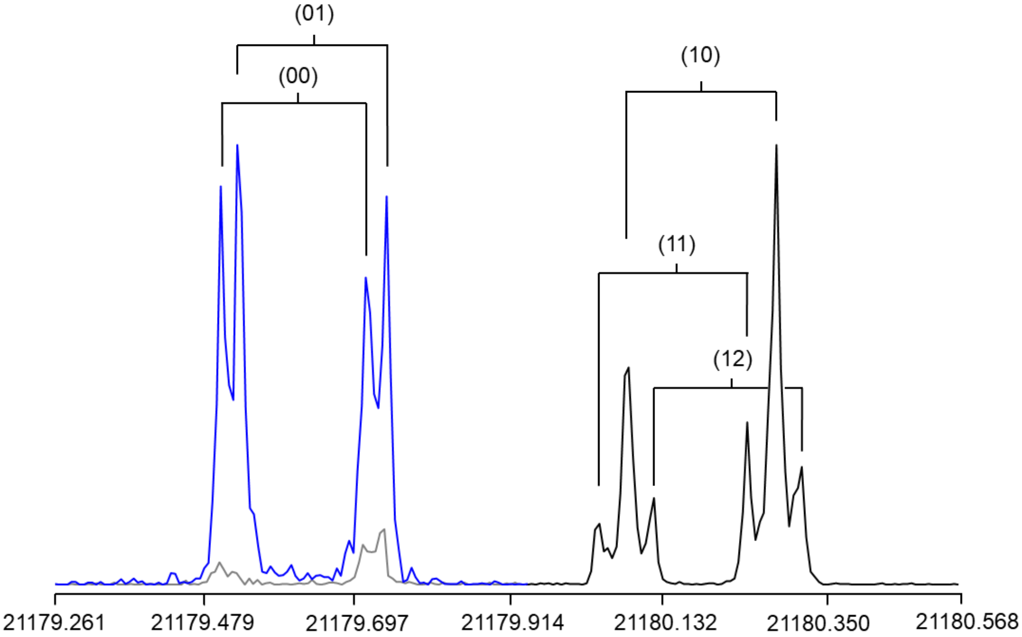


Figure 4: Two spectra of conformer I of methyl n-propyl sulfide recorded at high resolution, capturing all five torsional components (00), (01), (10), (11), and (12) of the rotational transition $6_{34} \leftarrow 5_{33}$. The frequencies are in MHz; the Doppler pairs are marked by brackets. The spectra are overlapped as can be distinguished by different colors, and the intensity is normalized. For the blue spectrum, 69 free induction decays were co-added, and 124 decays for the black spectrum.

3.2. Spectral assignments and fits

3.2.1. Conformer I

To start the assignment of the spectrum we predicted the theoretical microwave spectrum of the most stable conformer I of methyl propyl sulfide with the program *XIAM* [41] using the theoretical rotational constants obtained from the quantum chemical calculations at the MP2/6-311++G(d,p) level of theory.

By treating the molecule as a rigid rotor, we succeeded to determine the transitions belonging to the A symmetry species of the molecule. The *a*-type transitions of this conformer could be identified yielding *B* and *C* rotational constants. Subsequently, *b*- and *c*-type transitions were included in the fit to determine the *A* rotational constant. 63 A species lines were found and fitted with a standard deviation of 4.1 kHz. This value indicates the measurement accuracy of conformer I. Though the transition frequencies can be determined with an accuracy of better than 2 kHz for some strong, isolated lines, most of the transitions appear quite broad, most probably due to unresolved splittings arising from the internal rotation of the propyl methyl group. Especially, a vast number of transitions show clearly resolved splittings due to this large amplitude motion, as will be described later in section 3.2.5.

In the next step both, A and E species transitions were predicted with a one-top approach using the estimated value of 526.8 cm^{-1} of the torsional barrier of the thiomethyl group calculated at the MP2/6-311++G(d,p) level. This was in reasonable agreement with the experimentally determined barrier of 586.15(41) cm^{-1}. Altogether, 127 torsional components with $J \leq 11$ and $K_a \leq 4$ were assigned and fitted, yielding a set of highly accurate rotational and centrifugal distortion constants, as well as the molecular parameters describing the internal rotational motion of the thiomethyl group. The standard deviation of the fit is 3.9 kHz, which is essentially the same as that of the A species fit and the measurement accuracy of conformer I.

3.2.2. Conformer II

Conformer II, which has an energy of 0.34 kJ/mol relative to that of conformer I, was our second candidate for the assignment. Using its rotational constants obtained at the MP2/6-311++G(d,p) level, the rigid rotor spectrum was predicted and 67 A species lines consisting of *a*-, *b*-, and *c*-type transitions could be identified and fitted with a standard deviation of 3.0 kHz. Accordingly, we considered the internal rotation of the thiomethyl methyl group by using its theoretically calculated torsional barrier of 551.8 cm^{-1} to predict the A and E transitions. In total 67 A species and 70 E species lines with $J \leq 9$ and $K_a \leq 3$ were assigned and fitted with the program *XIAM* to a standard deviation of 2.9 kHz, close to the value found for the A species fit. The experimental barrier to internal rotation was determined to be 595.31(37) cm^{-1}.

3.2.3. Conformer III

The third conformer with all heavy atoms lying on a symmetry plane was also assigned. A total of 36 A symmetry species could be measured and fitted to a standard deviation of 4.3 kHz. Since conformer III is about 1.30 kJ/mol higher in energy than conformer I, many of its transitions are of weak intensity. This significantly affects the measurement accuracy. The assigned lines belong to *a*- and *b*-type transitions, since the dipole moment component in the *c*-direction is zero. Subsequently, we assigned also the E lines using the estimated torsional barrier of 617.3 cm^{-1}. Fitting 36 A and 34 E species lines with $J \leq 9$ and $K_a \leq 3$ yielded a standard deviation of 4.0 kHz and the experimental barrier to internal rotation of 699.4(37) cm^{-1}.

Because only transitions in the vibrational ground state are available in the data set, the rotational constant F_0 of the thiomethyl rotor correlates with the V_3 term and was fixed to the predicted value of 159 GHz for all three assigned conformers. The fitted molecular parameters are represented in Table 2. The lists of the observed frequencies along with their residuals obtained from the *XIAM* fits are given in Table S3 in the Supplementary Material.

Table 2. Molecular parameters of the three most stable conformers I, II, and III of methyl n-propyl sulfide obtained using the program *XIAM*. Parameters of the ^{34}S isotopologue of conformer I are also given.

Par.[a]	Unit	I	I-^{34}S	II	III
A_0	MHz	8.79945137(76)	8.7047601(24)	6.66026284(29)	12.4009811(21)
B_0	MHz	1.85424558(14)	1.83191109(31)	2.19515581(12)	1.64749077(71)
C_0	MHz	1.67272634(12)	1.65151148(28)	2.12638499(12)	1.51000119(70)
D_J	kHz	0.3827(14)	0.3827	2.5354(12)	0.1555(31)
D_{JK}	kHz	0.7591(73)	0.7591	−13.1141(34)	-0.980(17)
D_K	kHz	17.601(61)	17.601	59.973(19)	0.0[e]
d_1	kHz	−0.07907(27)	−0.07907	0.03941(42)	-0.02321(84)
d_2	kHz	−0.00333(22)	−0.00333	0.072676(93)	0.0[e]
$D_{\pi 2K}$	MHz	0.0[e]	0.0[e]	−1.432(60)	16.8(21)
$V_{3,1}$	cm^{-1}	586.15(41)	591.8(28)	595.21(37)	699.4(37)
$\angle(i_1,a)$[b]	°	72.436(73)	73.49(49)	62.91(11)	141.1(15)
$\angle(i_1,b)$[b]	°	160.069(64)	19.02(42)	152.051(99)	51.1(15)
$\angle(i_1,c)$[b]	°	99.1236(37)	80.825(23)	96.3664(58)	90.0
$N_{A/E}$[c]		63/64	14/17	67/70	36/34
σ[d]	kHz	3.9	4.1	2.9	4.0

[a] All parameters refer to the principal axis system. Watson's S reduction and I^r representation were used. Standard errors are in the units of the last digits. [b] Derived from the parameters δ and ε, where only δ was fitted and ε was fixed

to the *ab initio* value of 0.1670 for conformer I, 3.2665 for conformer II, and zero for conformer III due to symmetry. [c] Number of the A and E species lines. [d] Standard deviation of the fit. [e] Set to zero.

3.2.4. ^{34}S isotopologue

After the spectra of conformers I, II, and III were assigned, some weak transitions at about the level of conformer III remained in the broadband scan (see for example the portion given in Figure 3). We suspected that they belong to the ^{34}S and ^{13}C isotopologues of conformer I and II and started with the spectrum of the ^{34}S isotopologue of the most stable conformer I. The assignment was straightforward as a sufficient number of transitions of this species are visible in the scan. The molecular parameters are collected in Table 2 along with those of the main isotopologue. The frequency list is also given in Table S3 in the Supplementary Material.

We found some transitions which probably belong to the ^{34}S isotopologue of conformer II. However, the weak intensity of the spectrum inhibited confident assignment. Therefore, we decided to neglect this species as well as the spectra of all ^{13}C isotopologues in the present study.

3.2.5. Two-top fits

At the beginning, we expected that splittings arising from the internal rotation of the propyl methyl group could not be resolved due to the high torsional barrier. This turned out to be wrong as a significant number of transitions showed additional splittings up to some hundreds of kHz. In order to take into account these splittings, methyl n-propyl sulfide was treated as a two-top molecule where all rotational transitions split into quintets. We will use the labeling ($\sigma_1\sigma_2$) = (00), (01), (10), (11), and (12) for the five torsional components where the numbers σ = 0, 1, 2 represent the three symmetry species A, E_a, E_b of the C_3 group. σ_1 and σ_2 refer to the thiomethyl and the propyl methyl group, respectively [42]. The F_0 value of the propyl methyl group was also fixed to 159 GHz, and the angles between the internal rotor axis and the principal axes of inertia were fixed to the calculated values. The V_3 potential of 991.31(90) cm^{-1} could be deduced for conformer I in a *XIAM* fit with a satisfactory standard deviation of 4.1 kHz, and a similar value of 965.31(63) cm^{-1} was found for conformer II. For conformer III, the number of observed lines is significantly smaller than that of conformer I and II, and only a few transitions show splittings from the internal rotation of the propyl methyl group. Table 3 presents the fitted molecular parameters obtained from the three two-top fits. The frequency lists are available in Table S4 in the Supplementary Material.

Table 3. Molecular parameters of the three most stable conformers I, II, and III of methyl propyl sulfide obtained using the program *XIAM*, taking into account the internal rotations of both the thiomethyl and the propyl methyl group.

Par.[a]	Unit	I-2tops	$\mathrm{I}_{\mathrm{calc.}}$[b]	II-2tops	$\mathrm{II}_{\mathrm{calc.}}$[b]	III-2tops	$\mathrm{III}_{\mathrm{calc.}}$[c]
A_0	MHz	8.79944660(71)	8711.0	6.66026232(26)	6542.3	12.4009769(23)	
B_0	MHz	1.85425869(13)	1849.3	2.19515693(11)	2197.4	1.64750763(81)	
C_0	MHz	1.67271319(12)	1664.6	2.12638389(12)	2125.5	1.50998420(80)	
D_J	kHz	0.3826(13)	0.3600	2.5365(13)	2.7379	0.1527(33)	
D_{JK}	kHz	0.7634(66)	1.1034	−13.1133(27)	−11.9338	−0.957(18)	
D_K	kHz	17.601(51)	12.5803	59.977(16)	50.0422	0.0[i]	
d_1	kHz	−0.07897(24)	−0.0765	0.03914(41)	−0.1745	−0.02329(91)	
d_2	kHz	−0.00304(18)	−0.0047	0.072718(85)	0.0776	0.0[i]	
$D_{\pi 2K}$	MHz	0.0[i]		−1.414(54)		14.4(24)	
$V_{3,1}$	cm^{-1}	585.91(35)	526.8	595.42(39)	551.8	706.7(44)	617.3
$\angle(i_1,a)$[d]	°	72.510(62)	76.54	62.89(11)	68.27	143.3(18)	132.20
$\angle(i_1,b)$[d]	°	160.133(54)	163.53	152.03(11)	157.17	53.3(18)	137.80
$\angle(i_1,c)$[d]	°	99.1274(31)	99.31	96.3653(61)	96.64	90.0	90.00
$V_{3,2}$	cm^{-1}	991.31(90)	1080.2	965.31(63)	1069.3	986.4(34)	1094.6
$\angle(i_2,a)$	°	160.10[e]	160.10	118.36[e]	118.36	32.64[e]	32.64
$\angle(i_2,b)$	°	86.37[e]	86.37	75.04[e]	75.04	122.64[e]	122.64
$\angle(i_2,c)$	°	109.54[e]	109.54	32.73[e]	32.73	90.0[f]	90.00
$\mathrm{N}_{(00)/(01)}$[g]		63/15		67/19		36/3	
$\mathrm{N}_{(01)/(11)/(12)}$[g]		64/14/14		70/36/36		34/4/4	
σ[h]	kHz	4.1		3.1		4.4	

[a] All parameters refer to the principal axis system. Watson's S reduction and I^r representation were used. Standard errors are in the units of the last digits. [b] Ground state rotational constants and centrifugal constants obtained from anharmonic frequency calculations at the MP2/6-311++G(d,p) level of theory. All other parameters are from geometry optimizations at the same level. [c] Ground state rotational constants and centrifugal constants not available. All given values are obtained from geometry optimizations at the MP2/6-311++G(d,p) level. [d] See footnote [b] of Table 2. [e] Fixed to the predicted values. [f] Fixed due to symmetry. [g] Number of the corresponding torsional species lines. [h] Standard deviation of the fit. [i] Set to zero.

4. Discussion

4.1. Geometries of the three assigned conformers

By combining MJ-FTMW spectroscopy with quantum chemical calculations, the three lowest energy conformers of methyl n-propyl sulfide could be assigned. The strongest signals in the spectrum belong to conformer I and II with C_1 symmetry, while the spectrum of conformer III with C_s symmetry is much weaker, at about the level of the ^{34}S isotopologue of conformer I.

Comparison of the experimental rotational constants B_0 with the equilibrium rotational constants B_e predicted at different levels of theory showed that the differences are within 3% or less for conformer I and III. For a large number of molecules, e.g., alkynols [43], acetates [44], or aromatic ring containing compounds [45], the agreement between the experimental and predicted values are often within less than 1%. However, the differences found for conformer I and III are acceptable. Pople's triple zeta basis set 6-311 [46] with the polarization function (3df,3pd) with or without diffuse function in combination with the B3LYP method including Grimme's dispersion corrections [47] with Becke-Johnson damping [48] or Truhlar's M06-2X method [49] predicts rotational constants which match best the experimental ones (see Table S2 in the Supplementary Material). The same observation was found for conformer III, where in this case the M06-2X method performs much better than the B3LYP-D3BJ method. For this planar conformer, Dunning's (aug)-cc-pVTZ basis set [50] also yielded quite reliable rotational constants.

For conformer II, the discrepancy between B_0 and B_e constants are up to 10%, especially in calculations using the M06-2X method, indicating that some interactions in this conformer are not correctly captured with this empirical method. In general, the agreements are much worse in comparison with results obtained for the other two conformers. This indicated that error compensations at some levels of theory, which accidentally yielded equilibrium constants close to ground state constants for many molecules, did not work for methyl n-propyl sulfide. The mentioned Pople's and Dunning's basis sets again perform best for conformer II, this time in combination with the B3LYP-D3 and B3LYP-D3BJ method. There is an *ab initio* level, MP2/6-31G(d,p), which yields good results for all three conformers of methyl n-propyl sulfide, as well as many other molecules such as 2-ethylfuran [51], ethyl valerate [52], quinoline and isoquinoline [53].

In oxygen analog methyl propyl ether, Kato et al. reported on only one conformer (*trans-trans*) with C_s symmetry, indicating that this conformer is the lowest in energy. In the jet-cooled spectrum of methyl n-propyl sulfide, the C_s conformer co-exists with two other more stable conformers with C_1 symmetry where the propyl chain is bent at the β-carbon position. Further studies on related molecules are needed to investigate the effect of oxygen and sulfur on the conformational stability.

4.2. Thiomethyl torsion

4.2.1. Conformational effects: Two-class concept

By comparing the results of the present work with that of methyl ethyl sulfide, and with knowledge gained from a systematic study on methyl n-alkyl ketones where the methyl torsion can be linked to the molecular structure, we propose a two-class concept for methyl n-alkyl sulfide. The first class includes sulfides where the β carbon of the alkyl chain is located on the C-S-C plane, and the torsional barrier of the thiomethyl group is around 700 cm^{-1}, as found for the *trans* conformer of methyl ethyl sulfide and conformer III of methyl n-propyl sulfide. The second class comprises of molecules in which the torsional barrier is around 600 cm^{-1} and the β carbon is tilted out to a gauche orientation. Current examples are *gauche* methyl ethyl sulfide and conformer I and II of methyl n-propyl sulfide. Even though the alkyl chain is branched, two conformers of isopropyl methyl sulfide also belong to this class as well. We suspect that the oscillation of the alkyl chain induced by the thiomethyl torsion is responsible for the lower barrier height (see Figure 2). The number of investigations on this class of molecules is still very limited, and studies on longer methyl n-alkyl sulfides are needed to verify and expand this two-class concept.

4.2.2. Thioethers vs ethers

In many previous investigations reported in the literature, the barrier height of methyl groups in oxygen analogues are usually higher than that of the sulfur analogues. The two equivalent methyl groups in dimethyl sulfide undergo internal rotations with a torsional barrier of 735.784(44) cm^{-1} [54], significantly lower than the value of 944.300(28) cm^{-1} found for dimethyl ether [55]. Similar observation was found while comparing the barrier heights of the thiomethyl group in *trans* methyl ethyl sulfide (692 cm^{-1}) [21] and *trans* methyl ethyl ether (893 cm^{-1}) [56]. For conformer III of methyl n-propyl sulfide, the value of 699.4(37) cm^{-1} of the thiomethyl group contributes a further data point to support this trend, as the ether methyl group in *trans-trans* methyl n-propyl ether also has a higher torsional barrier of 1154 cm^{-1} [35]. We expect the same observation in methyl n-alkyl sulfides and ethers with longer alkyl chain.

An interesting case is methyl isopropyl ether, for which Nakagawa et al. reported a torsional barrier of 603 cm^{-1} for the methoxy methyl group O-CH_3 determined by fitting the doublet structure observed for some transitions [57], which is unusually low for such methyl group and quite similar to the value of 601.642(65) cm^{-1} obtained for the *gauche* conformer of methyl isopropyl sulfide with comparable structure [58]. Currently, no conclusive statement could be made to explain the origin of different values of methyl torsional barrier in thioethers and ethers with the small number of available studies.

4.3. Propyl methyl torsion

The experimental deduced barriers of the propyl methyl torsion are between 950 and 1000 cm^{-1}, slightly lower than the calculated ones (over 1000 cm^{-1} for all three conformers). The values of all parameters of the two-top fits given in Table 3 are essentially the same as those of the one-top fits in Table 2, but the standard deviation of the later is about 2 kHz better. The barrier heights found for the propyl methyl group of methyl n-propyl sulfide are very similar to those obtained for methyl groups at the end of the alkyl chain in methyl n-alkyl ketones [27-29].

5. Conclusion

With support from quantum chemistry, the microwave spectra of three most stable conformers of methyl n-propyl sulfide were assigned and fitted with standard deviation close to measurement accuracy. Significant differences between the equilibrium and ground state rotational constants were observed for all conformers, but most pronounced for conformer II, indicating that error compensations did not work for methyl n-propyl sulfide. The value of this parameter could be linked to the molecular structure, suggesting that torsional barrier of methyl n-alkyl sulfide is always around 600 cm^{-1} if the β carbon is located in the C-S-C plane. If it is bent to a synclinal position, the barrier is approximately 700 cm^{-1}. Splittings arising from the propyl methyl torsion could also be resolved in some transitions, yielding barrier heights of 991.31(90) cm^{-1}, 965.31(63) cm^{-1}, and 986.4(34) cm^{-1} for conformers I, II, and III, respectively.

Disclosure statement

No potential conflict of interest was reported by the authors.

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