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Theoretical spectroscopic characterization at low temperatures of methyl hydroperoxide and three S-analogs

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The low temperature spectra of the detectable species methyl hydroperoxide (CH₃OOH) and three sulfur analogs, the two isomers of methanesulfenic acid (CH₃SOH and CH₃OSH) and the methyl hydrogen disulfide (CH₃SSH), are predicted from highly correlated *ab initio* methods (CCSD(T) and CCSD(T)-F12). Rotational parameters, anharmonic frequencies, torsional energy barriers, torsional energy levels, and their splittings are provided. Our computed parameters should help for the characterization and the identification of these organic compounds in laboratory and in the interstellar medium. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4907941>]

INTRODUCTION

Methyl hydroperoxide (CH₃OOH, MeOOH, MHP), the simplest organic peroxide, plays an important role in the atmospheric chemistry because it is a source of HOx radicals through photodissociation.¹ It is considered as the most abundant organic peroxide in the atmosphere, with a maximum concentration approaching or even higher than that of H₂O₂. It presents a longer lifetime and a lower solubility in water, compared to H₂O₂.² Its contribution to the atmospheric oxidizing capacity has motivated previous collisional and spectroscopic studies devoted to the photofragmentation processes and to the measurement and analysis of the infrared spectra in the N_νOH (N = 2,6) regions.^{3–6}

The main source of MeOOH in the earth atmosphere is the combination of HO₂ and CH₃O₂ radicals.¹ It has not been discovered in gas phase extraterrestrial sources and planetary atmospheres but it represents a good candidate to be detected with the new radioastronomical observatories. Numerous arguments make reasonable its search in the interstellar medium. For example, molecules containing rotating methyl groups are abundant in many sources such as star formation regions; the simplest peroxide, H₂O₂ has been already detected⁷ and various observed radicals, HO,⁸ HO₂,⁹ and CH₃O,¹⁰ as well as several abundant observed molecules such as methanol¹¹ are products of methyl hydroperoxide fragmentation.¹

Given its relevance for astrophysics, various laboratories dealing with rotational spectroscopy have confirmed their interest for MeOOH. This species has not been fully characterized at low temperatures. With the exceptions of the measurement of the rotational spectra,¹² the main available spectroscopic data arise from the analysis the OH stretch-

ing bands in the near infrared and ultraviolet regions. These previous works focus on the study of the photodissociation processes where the OH stretching excitations play important roles. Because other spectral regions such as the far infrared (FIR) have not been explored, all the available data corresponding to the large amplitude vibrational motions have not been directly observed. They have been obtained in the analysis of the spectra of the OH overtones by fitting the two-dimensional effective Hamiltonian parameters using transitions involving combination levels for the OH stretching and the OH-torsional modes.⁶

Following these considerations, the aim of the present paper is to use state-of-the-art *ab initio* calculations to obtain spectroscopic rotational and torsional properties that can help future assignments. Our main goal is the study of the MeOOH spectra at low temperatures along with those of its sulfur analogs (S-analogs). These are the methanesulfenic acid (CH₃SOH, MeSOH) and its isomer CH₃OSH (MeOSH) and the methyl hydrogen disulfide (methyl hydrosulfide, CH₃SSH, MeSSH). We believe that a common study for these four species can help to understand the effect of the O → S substitutions on the molecular and spectroscopic properties. We take into account that sulfur chemistry plays an important role in the chemical evolution of many extraterrestrial sources.¹³ Recent detections of new sulfur molecules showing methyl groups¹⁴ represent significant arguments to justify this research.

Since the search for S-analogs of abundant detected species is a common strategy of astrophysicists, we have accomplished several theoretical studies of organo-sulfur compounds related to relevant interstellar molecules.^{15–17} All of them present non-rigid properties. In parallel of the fruitful observation,¹⁴ we have published our theoretical study on the main isotopic species of ethyl mercaptan and dimethyl sulfide,¹⁵ while the manuscript on the corresponding rare isotopic species has been submitted for publication.¹⁷ Another recent work focuses on the S-analogs of methyl formate.¹⁶ All these species are considered to be detectable although, to the present, only the

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S-analogs of methanol and ethanol, the methyl mercaptan, and the ethyl mercaptan have been already detected.^{14,18}

In this paper, we provide a detailed spectroscopic characterization of MeOOH and S-analogs to help their detection in the interstellar medium (ISM). Properties have been obtained using state-of-the-art methodologies suitable for the molecular size. To assess their accuracy, the computed properties were compared with the available experimental data, in particular for MeOOH. Given the lack of previous studies, many of our results, mainly for the sulfur compounds, are predictions that cannot be compared with experimental data. We believe that they can be useful for future spectral analysis. Although the discovery of a new species requires its previous characterization at the laboratory level, available studies for the sulfur compounds MeSOH, MeSOH, and MeSSH are not common,^{19–22} to our knowledge, only for MeSSH, a published study of the rotational spectrum is available.²¹ The structural parameters of MeSOH were previously determined comparing microwave spectroscopy data for several isotopic varieties.¹⁹

THEORETICAL AND COMPUTATIONAL DETAILS

Equilibrium structures, rotational constants, and harmonic frequencies have been computed using the explicitly correlated coupled-cluster method CCSD(T)-F12b,^{23,24} as implemented in MOLPRO (2010).²⁵ The atoms were described by the cc-pVTZ-F12 basis set of Peterson *et al.*²⁶ The AVTZ/MP2FIT and VTZ/JKFIT basis sets were used for the density fitting integral evaluation of the F12 integrals and for the resolution of the identity expansions, respectively.²⁷ In this paper, this basis set is denoted by VTZ. Default options of the MOLPRO package have been employed to define parameters such as the pair specific geminal exponents. Triples energy contributions were not scaled in connection with the corresponding resolutions of the identity and density fitting functions.²⁷ Because the rotational constants are the most relevant molecular properties for radioastronomy, the CCSD(T)-F12 parameters have been improved adding a core-valence correlation correction to obtain reliable equilibrium rotational constants

$$\Delta B_e^{\text{core}} = B_e(\text{CV}) - B_e(\text{V}). \quad (1)$$

Here, $B_e(\text{CV})$ and $B_e(\text{V})$ are calculated correlating both core and valence electrons (CV) or just the valence electrons (V) in the post-SCF process. ΔB_e^{core} has been determined with CCSD(T) (coupled-cluster theory with singles and doubles substitutions, augmented by a perturbative treatment of triple excitations)²⁸ and the cc-pCVTZ basis set.^{29,30}

Second order vibrational perturbation theory (VPT2) implemented in the Gaussian 09 package³¹ has been applied to establish the anharmonic frequencies, the α_r^i vibration-rotation interaction parameters, as well as the quartic and sextic centrifugal distortion constants. The anharmonic cubic and quartic force fields have been computed with Möller-Plesset theory (MP2) using the cc-pVTZ correlation-consistent basis set.³²

For the variational determination of the torsional energy levels and their splittings, four two-dimensional potential energy surfaces depending on the torsional degrees of freedom have been computed using CCSD(T) theory and the aug-cc-

pVTZ basis set.³³ They have been vibrationally corrected at the MP2/aug-cc-pVTZ level of theory. The kinetic parameters of the corresponding two-dimensional Hamiltonians (see below) have been obtained from a set of 26 CCSD/aug-cc-pVTZ geometries. For this purpose, all the required *ab initio* calculations have been performed with the Gaussian 09 package.³¹ Our code ENEDIM (2001)³⁴ has been used for the calculation of all the torsional Hamiltonian parameters, the torsional transitions, and for the assignments of the torsional energy levels.

RESULTS AND DISCUSSION

Equilibrium structures and rotational parameters

The equilibrium geometries of the four species, MeOOH, MeOSH, MeSOH, and MeSSH, have been optimized using explicitly correlated couple cluster theory (CCSD(T)-F12/cc-pVTZ). The corresponding energies and structural parameters are shown in Table I. Figure 1 displays the minimum energy geometry of MeOOH and helps the understanding of the definition of the internal coordinates and the two torsional degrees of freedom, θ (methyl torsion) and α (OH or SH torsion). The symbols X1 and Y2 of Table I correspond to oxygen or sulfur atoms.

Unfortunately, there are few experimental data to discuss the present results. For MeOSH and MeSOH, our data have to be considered as accurate predictions. Our experience shows that the very efficient explicitly correlated method provides very realistic results with a relatively low computational cost. Energies and structural parameters obtained with RCCSD(T)-F12/VTZ are always as accurate as those obtained using CCSD(T) theory and very large basis sets (i.e., cc-pV5Z).³⁷ For MeOOH and MeSSH, the calculated rotational constants for the ground vibrational state, A_0 , B_0 , and C_0 , are compared with the experimental values of Tyblewski *et al.*^{12,21} For their estimation, we have used the CCSD(T)-F12 equilibrium rotational constants, B_e (or A_e or C_e), and the formula

$$B_0 = B_e + \Delta B_e^{\text{core}} + \Delta B^{\text{vib}}. \quad (2)$$

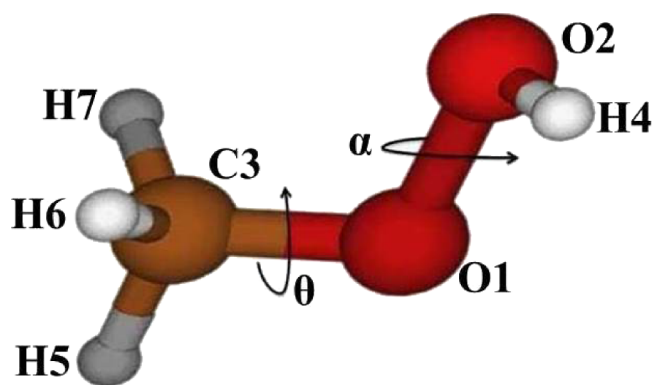
The core-electron correlation correction ΔB_e^{core} has been computed with CCSD(T)/cc-pCVTZ. The two electrons of 1s internal orbitals of the sulfur atoms have never been correlated. In Eq. (2), ΔB^{vib} represents the vibrational contribution to the rotational constants derived from the VPT2 α_r^i vibration-rotation interaction parameters determined using the MP2 cubic force field (see below). Values for both corrections are shown in Table II.

The procedure for the estimation of the rotational constants at the vibrational ground state combines different levels of *ab initio* calculations (CCSD(T)-F12, CCSD(T), and MP2). It represents an efficient way to approach to the experimental values. We avoid the use more expensive computations for the corrections that are relatively small.

The concluding ground vibrational state rotational constants of the four species (see Figure 2) are shown in Table I. For MeOOH and MeSSH, they have been calculated to be $A_0 = 42\,822.23$ MHz, $B_0 = 10\,564.08$ MHz, and $C_0 = 9149.3$ MHz and to be $A_0 = 16\,795.83$ MHz, $B_0 = 4441.34$ MHz, and

TABLE I. Total electronic energies E (in Hartrees), structural parameters (distances in Å; angles in degrees; X, Y = O, S), dipole moment^a (in debyes), equilibrium rotational constants (in MHz) of the MeOOH, MeOSH, MeSOH, and MeSSH equilibrium geometries calculated with CCSD(T)-F12/VTZ.

	CH_3OOH		CH_3OSH	CH_3SOH		CH_3SSH	
	Calc.	Exp. ^{b,c}		Calc.	Exp. ^d	Calc.	Exp. ^e
E	-190.651 161		-513.314 679	-513.334 115		-835.956 908	
X1Y2	1.4463		1.6501	1.6625	1.658	2.0477	
C3X1	1.4117		1.4259	1.7924	1.806	1.8097	
H4Y2	0.9631		1.3476	0.9610	0.957	1.3438	
H5C3	1.0894		1.0882	1.0916		1.0907	
H6C3	1.0919		1.0925	1.0890		1.0877	
H7C3	1.0904		1.0907	1.0883		1.0873	
C3X1Y2	105.5		113.6	100.2	100.1	102.0	
H4Y2X1	100.0		98.6	107.0	107.7	98.7	
H5C3X1	104.9		106.1	106.0		106.2	
H6C3X1	111.3		110.7	111.6		110.8	
H7C3X1	64.2		110.9	110.4		110.4	
H4Y2X1C3	111.9		80.9	91.3	93.9	87.4	
H5C3X1Y2	177.1		174.8	175.9		175.7	
H6C3X1H5	118.8		118.9	-118.6		118.7	
H7C3X1H5	-118.5		-119.5	-118.1		-118.7	
μ	1.6670		1.7513	1.9707	1.87	1.7543	1.796 (42)
A_e	42 808.35		39 305.70	21 025.46		16 777.69	
B_e	10 637.36		6 261.54	8 085.68		4 454.93	
C_e	9 246.66		5 803.52	6 181.73		3 690.55	
A_0	42 822.23	42 828.465 (56) ^b 42 686.115 (45) ^c	39 322.72	21 009.80		16 795.83	16 865.3758 (71)
B_0	10 564.08	10 500.200 (23) ^b 10 478.244 (19) ^c	6 217.42	8 062.46		4 441.34	4 442.1185 (18)
C_0	9 149.30	9 055.058 (9) ^b 9 075.021 (13) ^c	5 764.73	6 153.07		3 676.48	3 680.3640 (16)

^aDipole moment calculated at the MP2/cc-pVTZ level.^b(0 0⁺) OH torsional, Ref. 12.^c(0 0⁻) torsional component, Ref. 12.^dReference 19.^eReference 21.FIG. 1. CH_3OOH equilibrium geometry; torsional coordinates θ and α .

$C_0 = 3676.48$ MHz, respectively (see Table I). For MeOOH, our values differ slightly from the previous QCISD(T)/aug-cc-pVTZ results of Watts and Francisco³⁸ ($A_0 = 42\,289.6$ MHz, $B_0 = 10\,493.9$ MHz, and $C_0 = 9104.4$ MHz). To compare them with the available experimental data, some aspects need to be considered. For example, Tyblewski *et al.*¹² have fitted the effective Hamiltonian parameters independently for each one of the two OH components (0 0⁺) and (0 0⁻) of the ground vibrational state. These components split by tunneling effect in the OH torsional barrier. The same paper¹² provides a unique set of averaged rotational constants for both components ($A_e = 43\,006.5$ MHz, $B_e = 10\,517.5$ MHz, and $C_e = 9053.3$ MHz). For MESSH, the parameters of Tyblewski *et al.*²¹ were

TABLE II. The core-electron correlation correction (in MHz) and vibrational correction (in MHz) of the equilibrium rotational constants.

	ΔA^{vib}	ΔA_e^{core}	ΔB^{vib}	ΔB_e^{core}	ΔC^{vib}	ΔC_e^{core}
MEOOH	-176.34	190.22	-97.82	24.54	-120.85	23.48
MEOSH	-120.55	137.57	-61.04	16.92	-58.19	19.40
MESOH	-87.75	72.09	-47.16	23.94	-48.03	19.37
MESSH	-38.43	56.57	-28.51	14.92	-26.62	12.55

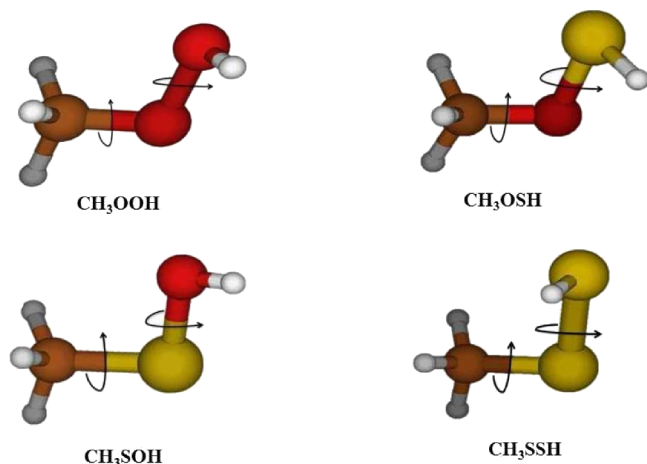


FIG. 2. The equilibrium geometries of the four molecules: CH₃OOH, CH₃OSH, CH₃SOH, and CH₃SSH.

obtained using the Internal Axis Method (IAM) instead of the Principal Axis Method (PAM). It stands out that there is a very good agreement between calculations and experiments.

Full-dimensional analysis

In Table II, the RCCSD(T)-F12 harmonic fundamental frequencies are shown. In addition, harmonic and anharmonic frequencies have been calculated with MP2/aug-cc-pVTZ to evaluate the effect of the anharmonicity on the vibrational band center positions. On the basis of our experience, we consider that anharmonic effects are less sensitive to the level of calculation than the harmonic contribution. As has been demonstrated, the accuracy of the RCCSD(T)-F12 harmonic fundamentals is of the same order of magnitude than those determined with RCCSD(T) and a complete basis set.^{39,40}

To our knowledge, there are no previous experimental data to be compared with our results with the exception of the OH-stretching fundamental of MeOOH predicted to lie at $\nu_1 = 3679 \text{ cm}^{-1}$ ($\omega = 3773 \pm 15 \text{ cm}^{-1}$; anharmonicity = $94 \pm 3 \text{ cm}^{-1}$) by Haynes *et al.* (2005).³ The theoretical value of $\nu_1 = 3610 \text{ cm}^{-1}$ ($\omega = 3797 \text{ cm}^{-1}$; anharmonicity = 187 cm^{-1}) is in a very good agreement with the experimental one.

The MP2/aug-cc-pVTZ anharmonic force field has been applied for the computation of the α_r^i vibration-rotation interaction parameters and the centrifugal distortion constants, which are shown in Table III. These last are parameters of the Watson A-reduced Hamiltonian in the Γ representation. The MP2 rotational constants in the ground vibrational state and the first excited torsional states are also provided. Obviously, the MP2 equilibrium rotational constants are less accurate than those determined with CCSD(T)-F12 which are shown in Table I. However, we provide them in the same section than the parameters for the excited vibrational states, to help the comparison of all of them. Since anharmonic effects are less dependent on the level of theory, the MP2 dependence of the rotational constants on the vibrational quanta is believable.

VPT2 is not a suitable theory for the study of the torsional motions of non-rigid molecules since it has been developed for semi-rigid species. For this reason, in this pa-

per, we determine the torsional frequencies variationally (see below). However, VPT2 provides a preliminary description of the far infrared spectra and allows us to predict Fermi resonances between all the 3Na-6 vibrational modes. These results are useful to validate the variational results derived from a theoretical model of a reduced dimensionality. If strong resonances are present, but they are neglected by the 2D-model, the 2D-levels are not realistic. Fortunately, it can be concluded that resonances between the torsional motions and the remaining vibrational modes are not expected. A unique low energy level of MeOOH ($\nu = 1, \nu' = 1$) is very slightly displaced by the fundamental COO bending mode.

With VPT2, the two torsional harmonic fundamentals of the CH₃ and OH (or SH) torsions of MeOOH are predicted to lie at 254 cm^{-1} and 200 cm^{-1} , respectively. For MeOSH, MeSOH, and MeSSH, they have found to be at 192 cm^{-1} and 270 cm^{-1} , 191 cm^{-1} and 297 cm^{-1} , and 172 cm^{-1} and 244 cm^{-1} , respectively. In the unique case of MeOOH, the OH torsion lies below the CH₃ torsion.

Torsional analysis

The ground and excited vibrational states of molecules with internal rotors split into various components as a consequence of the tunneling effects in the potential energy barriers. It has to be considered that some hot astrophysical bodies, such as the hot molecular cores, are sources of many discovered organic molecules. At their temperatures, vibrational species showing large amplitude motions can be found in excited vibrational states. Their complete spectroscopic characterization requires the determination of the low torsional states and their splittings.

The analysis of the far infrared region of the spectra of MeOOH and sulfur derivatives has been achieved assuming the independence of the torsional motions and the remaining vibrational modes. Then, a two-dimensional Hamiltonian can be defined as^{35,36}

$$\hat{H}(q_i, q_j) = - \sum_{i=1}^2 \sum_{j=1}^2 \left(\frac{\partial}{\partial q_i} \right) B_{ij}(q_i, q_j) \left(\frac{\partial}{\partial q_j} \right) + V(q_i, q_j) + V'(q_i, q_j) + V^{ZPVE}(q_i, q_j), \quad (3)$$

where the independent coordinates q_i and q_j are identified as the CH₃ torsion (θ) and the OH (or SH) torsion (α), respectively (see Figure 1). For their definition, we have used the following equations:

$$\begin{aligned} \theta &= (\text{H5C3X1Y2} + \text{H6C3X1Y2} + \text{H7C3X1Y2})/3 - 180^\circ, \\ \alpha &= \text{H4Y2X1C3} - 180^\circ (\text{X, Y} = \text{O, S}). \end{aligned} \quad (4)$$

In Eq. (3), $V(q_i, q_j)$ represents the two-dimensional potential energy surface (2D-PES). In this paper, the four required PESs have been computed from the CCSD(T)/aug-cc-pVTZ total electronic energies of 26 selected geometries defined for different values of the independent coordinates ($\theta = 0^\circ, 90^\circ, 180^\circ, -90^\circ; \alpha = 0^\circ, 30^\circ, 60^\circ, 90^\circ, 120^\circ, 150^\circ, \text{ and } 180^\circ$). For the planar structures ($\alpha = 0^\circ, 180^\circ$), $E(\alpha, \theta) = E(\alpha, -\theta)$. For each structure, 3Na-6-n internal coordinates (Na = number of atoms, n = 2 dihedral angles) were optimized at the CCSD/aug-cc-pVTZ level of theory.

TABLE III. Harmonic and anharmonic fundamental frequencies (ω , ν , in cm^{-1}) of MeOOH, MeOSH, MeSOH, and MeSSH equilibrium geometries.^a

	<i>MeOOH</i>				<i>MeOSH</i>				<i>MeSOH</i>				<i>MeSSH</i>			
	MP2 Cc-pVTZ		CCSD(T)-F12 VTZ		MP2 Cc-pVTZ		CCSD(T)-F12 VTZ		MP2 Cc-pVTZ		CCSD(T)-F12 VTZ		MP2 Cc-pVTZ		CCSD(T)-F12 VTZ	
	ω	ν	ω	Assignments ^a	ω	ν	ω	Assignments ^a	ω	ν	ω	Assignments ^a	ω	ν	ω	Assignments ^a
ν_1	3804	3617	3797	OH-s ^b	3182	3045	3140	CH ₃ -s	3817	3630	3816	OH-s	3191	3048	3154	CH ₃ -s
ν_2	3182	3045	3136	CH ₃ -s	3144	3006	3101	CH ₃ -s	3186	3043	3140	CH ₃ -s	3176	3036	3139	CH ₃ -s
ν_3	3152	3013	3104	CH ₃ -s	3056	3021	3025	CH ₃ -s	3174	3033	3128	CH ₃ -s	3072	2979	3047	CH ₃ -s
ν_4	3064	2955	3028	CH ₃ -s	2685	2581	2629	SH-s	3073	2984	3039	CH ₃ -s	2711	2605	2661	SH-s
ν_5	1533	1495	1522	CH ₃ -b	1519	1535	1510	CH ₃ -b	1497	1469	1490	CH ₃ -b	1494	1463	1487	CH ₃ -b
ν_6	1487	1446	1477	CH ₃ -b	1506	1475	1493	CH ₃ -b	1464	1424	1458	CH ₃ -b	1474	1432	1468	CH ₃ -b
ν_7	1464	1452	1459	CH ₃ -b	1474	1460	1471	CH ₃ -b	1348	1318	1351	CH ₃ -b	1351	1320	1353	CH ₃ -b
ν_8	1372	1348	1383	HOO-b	1201	1173	1205	HCO-b	1202	1170	1208	OH-b	989	970	982	CH ₃ -b
ν_9	1218	1185	1219	HCO-b	1180	1154	1183	CH ₃ -b	982	962	978	CH ₃ -b	985	967	978	HCS-b
ν_{10}	1187	1163	1183	CH ₃ -b	1073	1041	1083	CO-b	975	955	973	HCS-b	893	876	896	SSH-b
ν_{11}	1074	1043	1069	CO-b	1004	982	1012	HSO-b	789	784	796	SO-b	731	715	721	CS-b
ν_{12}	886	860	872	OO-b	733	717	744	OS-b	731	718	722	CS-b	531	522	527	SS-b
ν_{13}	451	445	453	COO-b	373	362	378	COS-b	389	375	398	OH-t	329	316	329	SH-t
ν_{14}	265	250	254	CH ₃ -t	264	255	270	SH-t	294	295	297	CSO-b	243	243	244	CSS-b
ν_{15}	182	127	200	OH-t	201	189	192	CH ₃ -t	193	185	191	CH ₃ -t	201	193	172	CH ₃ -t

^as = stretching; b = bending; t = torsion; **boldface** = important Fermi displacements.^bExperimental values ($\omega = 3773 \pm 15 \text{ cm}^{-1}$; anharmonicity = $94 \pm 3 \text{ cm}^{-1}$) from Ref. 3.

TABLE IV. Computed rotational parameters (in MHz) of the MeOOH, MeOSH, MeSOH, and MeSSH calculated with MP2/cc-pVTZ.

	MeOOH	MeOSH	MeSOH	MeSSH
K	-0.914 997	-0.971 878	-0.740 214	-0.880 625
A _e	42 613.64	38 686.39	20 798.98	16 608.47
B _e	10 645.75	6207.55	8043.00	4452.07
C _e	9226.71	5744.35	6138.73	3680.40
<i>Ground state</i>				
A ₀	42 437.30	38 565.54	20 711.22	16 570.04
B ₀	10 547.94	6146.54	7995.88	4423.56
C ₀	9105.87	5686.29	6090.67	3653.78
<i>Methyl torsion</i>				
ν (cm ⁻¹)	239	180	183	164
A _v	42 426.06	38 719.87	20 662.60	16 565.03
B _v	10 497.65	6119.75	7975.53	4409.11
C _v	9089.77	5663.52	6083.93	3647.45
<i>XH torsion (X = O, S)</i>				
ν (cm ⁻¹)	255	261	384	316
A _v	42 667.72	38 454.39	20 598.20	16 495.96
B _v	8144.19	6151.08	8033.24	4413.74
C _v	9066.41	5682.08	6089.00	3649.73
<i>Centrifugal-distortion constants^a</i>				
Δ_J	$0.116\,427 \times 10^{-1}$	$0.394\,874 \times 10^{-2}$	$0.869\,260 \times 10^{-2}$	$0.245\,173 \times 10^{-2}$
Δ_K	0.525 503	0.539 93	0.203 056	0.121 913
Δ_{JK}	$-0.283\,757 \times 10^{-1}$	$-0.259\,730 \times 10^{-1}$	$-0.432\,915 \times 10^{-1}$	$-0.122\,584 \times 10^{-1}$
δ_J	$0.225\,669 \times 10^{-2}$	$0.580\,484 \times 10^{-3}$	$0.297\,568 \times 10^{-2}$	$0.657\,466 \times 10^{-3}$
δ_K	$-0.105\,75 \times 10^{-1}$	$-0.312\,978 \times 10^{-2}$	$0.650\,356 \times 10^{-2}$	$0.572\,184 \times 10^{-2}$
Φ_J	$0.144\,581 \times 10^{-4}$	$0.344\,598 \times 10^{-5}$	$0.252\,594 \times 10^{-4}$	$0.208\,860 \times 10^{-5}$
Φ_{JK}	$-0.771\,664 \times 10^{-3}$	$-0.659\,904 \times 10^{-4}$	$-0.968\,00 \times 10^{-4}$	$0.217\,306 \times 10^{-4}$
Φ_{KJ}	$-0.363\,452 \times 10^{-2}$	$-0.312\,451 \times 10^{-2}$	$-0.161\,35 \times 10^{-2}$	$-0.717\,793 \times 10^{-3}$
Φ_K	$0.232\,663 \times 10^{-1}$	$0.243\,521 \times 10^{-1}$	$0.620\,526 \times 10^{-2}$	$0.347\,989 \times 10^{-2}$
φ_J	$0.888\,86 \times 10^{-5}$	$0.179\,049 \times 10^{-5}$	$0.131\,740 \times 10^{-4}$	$0.122\,079 \times 10^{-5}$
φ_{JK}	$0.216\,663 \times 10^{-4}$	$0.104\,097 \times 10^{-3}$	$0.133\,50 \times 10^{-4}$	$0.110\,053 \times 10^{-4}$
φ_K	$0.542\,302 \times 10^{-2}$	$0.989\,025 \times 10^{-2}$	$0.212\,025 \times 10^{-2}$	$0.782\,988 \times 10^{-3}$

^aParameters of the Watson A-reduced Hamiltonian in the I^r representation.

B_{ij} and $V(q_i, q_j)$ in Eq. (3) represent the kinetic energy parameters and the Podolsky pseudopotential, respectively.^{35,36} The torsional Hamiltonian (Eq. (3)) contains a vibrational correction, $V^{ZPVE}(q_i, q_j)$, that can be defined as the torsional dependence of the contribution of the 3Na-6-n neglected modes to the zero point vibrational energy (ZPVE). In this paper, $V^{ZPVE}(q_i, q_j)$ has been determined within the harmonic approximation.^{15,16} For each isotopologue and for each geometry, $V^{ZPVE}(q_i, q_j)$ is computed using the corresponding MP2/aug-cc-pVTZ harmonic frequencies ω_i ,

$$E^{ZPVE} = \sum_{i=n+1}^{i=3N-6} \frac{\omega_i}{2}. \quad (5)$$

The sum starts with $n + 1$ because the contribution of the n independent modes to the ground vibrational state is considered explicitly in the variational calculations. Individual values of the ZPVE correction corresponding to the 26 conformations are fitted to totally symmetric series formally identical to the one used for the potential energy surface.

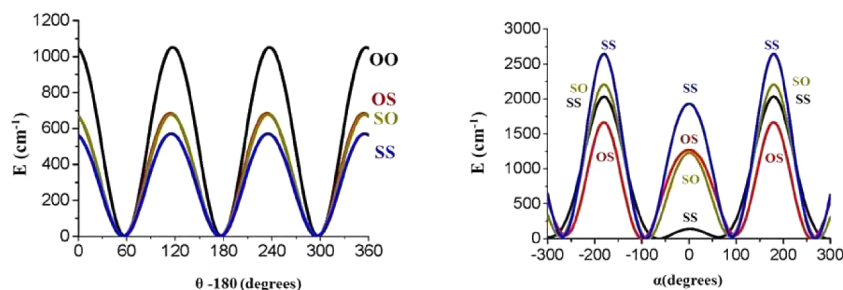


FIG. 3. One dimensional cuts of the torsional potential energy surfaces.

TABLE V. Effective potential parameters and internal rotation barriers (in cm^{-1}) calculated with CCSD(T)/aug-cc-pVTZ.

	MeOOH		MeOSH	MeSOH	MeSSH		HOOH	HSSH
	<i>Calc.</i>	<i>Exp.</i>	<i>Calc.</i>	<i>Calc.</i>	<i>Calc.</i>	<i>Exp.</i>	<i>Prev.works.</i>	<i>Exp.</i> ^a
V_3	1071.31	1117.0 (19) ^b 1123.4 (25) ^c	685.52	696.6	584.3	609.0 ^d		
V_{YH}^{trans}	162.74		1280.7	1249.8	1919.1		387.07 \pm 0.2 ^e 376 ^f	2037 \pm 12 2843 \pm 9
V_{YH}^{cis}	2012.43		1669.3	2170.6	2627.5		2562.8 \pm 60 ^e 2545 ^f	
B_1	6.702		6.483	5.890	5.592			
B_2	21.443		11.300	21.777	10.243			
B_{12}	-1.166		-1.243	-0.331	-0.263			

^aInfrared spectra, Ref. 43.^b(0 0⁺) component, Ref. 12.^c(0 0⁻) component, Ref. 12.^dReference 21.^eInfrared spectra; Ref. 42.^fCCSD(T)/aug-cc-pVTZ, Ref. 44.

For each one of the 26 structures, all the parameters of the Hamiltonian have been calculated with ENEDIM (2001),³⁴ also employed for the variational determination of the torsional energy levels and their classification. The main isotopologues of MeOOH and sulfur derivatives can be classified in the G_6 molecular symmetry group, the symmetry group of ethyl-mercaptan and S-methyl thioformate.^{15,16}

Then, the effective potential energy surfaces $V^{eff}(q_i, q_j) = V(q_i, q_j) + V'(q_i, q_j) + V^{ZPVE}(q_i, q_j)$ are the following:

TABLE VI. Torsional energy levels^a (in cm^{-1}) of MeOOH, MeOSH, MeSOH, and MeSSH calculated with CCSD(T)/aug-cc-pVTZ.

V, v'	Assignments	MeOOH			MeOSH	MeSOH	MeSSH
		Symmetric	E	E^{eff}	Exp. [OO1]	E^{eff}	E^{eff}
0 0 ⁺	A_1	0.000	0.000	0.0	0.000	0.000	0.000
	E	0.001	0.001		0.001	0.001	0.002
0 0 ⁻	A_2	14.805	10.978	14.97	0.000	0.001	0.000
	E	14.804	10.978		0.001	0.001	0.002
0 1 ⁺	A_1	119.048	121.108	130	257.030	347.247	297.419
	E	119.048	121.107		257.028	347.251	297.697
0 1 ⁻	A_2	203.518	199.357	191	257.030	347.291	297.419
	E	203.518	199.357		257.028	347.295	297.697
1 0 ⁺	A_1	257.478	255.853		185.882	183.359	158.726
	E	257.472	255.848		185.823	183.329	158.659
1 0 ⁻	A_2	243.212	245.581		185.882	183.359	158.726
	E	243.206	245.576		185.823	183.329	158.659
0 2 ⁺	A_1	316.255	310.235		673.697	669.244	584.945
	E	316.850	310.235		673.258	669.246	584.958
0 2 ⁻	A_2	438.802	430.400		673.709	670.673	584.945
	E	438.819	430.400		673.269	670.674	584.958
1 1 ⁺	A_1	445.582	443.932		436.721	348.844	302.649
	E	445.602	443.947		436.605	349.468	303.578
1 1 ⁻	A_2	361.844	365.753		436.721	348.845	302.649
	E	361.844	365.945		436.605	349.468	303.578
2 0 ⁺	A_1	467.752	472.326		353.137	498.291	432.193
	E	467.763	472.449		354.324	491.309	421.073
2 0 ⁻	A_2	467.763	480.613		353.137	498.291	432.193
	E	479.913	480.745		354.324	491.310	421.073
	ZPVE	166.644	208.839		229.839	272.172	233.854

^a(v, v') = CH₃-t, XH-t (X = O, S).

(a) MeOOH (in cm^{-1})

$$V^{\text{eff}}(\theta, \alpha) = 1213.044 - 598.294\cos 3\theta - 11.005\cos 6\theta - 917.103\cos \alpha + 524.467\cos 2\alpha - 92.97\cos 3\alpha + 9.252\cos 4\alpha - 2.321\cos 5\alpha - 0.437\cos 6\alpha + 91.452\cos 3\theta\cos \alpha - 45.704\cos 3\theta\cos 2\alpha - 0.933\cos 3\theta\cos 3\alpha + 6.946\cos 3\theta\cos 4\alpha - 1.622\cos 3\theta\cos 5\alpha + 1.49\cos 3\theta\cos 6\alpha + 2.852\cos 6\theta\cos \alpha + 4.457\cos 6\theta\cos 2\alpha - 1.838\cos 6\theta\cos 3\alpha + 1.58\cos 6\theta\cos 4\alpha - 1.283\cos 6\theta\cos 5\alpha + 0.425\cos 6\theta\cos 6\alpha - 102.439\sin 3\theta\sin \alpha + 14.507\sin 3\theta\sin 2\alpha - 4.921\sin 3\theta\sin 3\alpha - 6.002\sin 3\theta\sin 4\alpha - 1.151\sin 3\theta\sin 5\alpha.$$

(b) MeOSH (in cm^{-1})

$$V^{\text{eff}}(\theta, \alpha) = 1127.044 - 407.880\cos 3\theta - 9.142\cos 6\theta - 90.791\cos \alpha + 790.859\cos 2\alpha - 163.138\cos 3\alpha + 6.839\cos 4\alpha - 13.091\cos 5\alpha - 0.93\cos 6\alpha + 75.565\cos 3\theta\cos \alpha - 87.261\cos 3\theta\cos 2\alpha - 8.812\cos 3\theta\cos 3\alpha + 6.448\cos 3\theta\cos 4\alpha + 0.449\cos 3\theta\cos 5\alpha + 1.349\cos 3\theta\cos 6\alpha + 6.072\cos 6\theta\cos \alpha + 1.426\cos 6\theta\cos 2\alpha + 2.522\cos 6\theta\cos 3\alpha - 0.614\cos 6\theta\cos 4\alpha + 0.404\cos 6\theta\cos 5\alpha - 0.339\cos 6\theta\cos 6\alpha - 82.374\sin 3\theta\sin \alpha + 48.925\sin 3\theta\sin 2\alpha - 2.785\sin 3\theta\sin 3\alpha - 3.132\sin 3\theta\sin 4\alpha - 2.334\sin 3\theta\sin 5\alpha.$$

(c) MeSOH (in cm^{-1})

$$V^{\text{eff}}(\theta, \alpha) = 1278.054 - 407.764\cos 3\theta - 3.351\cos 6\theta - 435.887\cos \alpha + 900.241\cos 2\alpha - 91.312\cos 3\alpha + 0.095\cos 4\alpha - 6.669\cos 5\alpha - 0.879\cos 6\alpha + 75.573\cos 3\theta\cos \alpha - 55.599\cos 3\theta\cos 2\alpha + 7.469\cos 3\theta\cos 3\alpha + 3.32\cos 3\theta\cos 4\alpha - 2.935\cos 3\theta\cos 5\alpha - 4.867\cos 3\theta\cos 6\alpha - 2.54\cos 6\theta\cos \alpha + 3.066\cos 6\theta\cos 2\alpha + 1.133\cos 6\theta\cos 3\alpha + 3.822\cos 6\theta\cos 4\alpha - 0.865\cos 6\theta\cos 5\alpha - 3.105\cos 6\theta\cos 6\alpha - 92.385\sin 3\theta\sin \alpha - 3.779\sin 3\theta\sin 2\alpha - 1.336\sin 3\theta\sin 3\alpha - 4.583\sin 3\theta\sin 4\alpha - 0.655\sin 3\theta\sin 5\alpha.$$

(d) MeSSH (in cm^{-1})

$$V^{\text{eff}}(\theta, \alpha) = 1546.331 - 378.957\cos 3\theta - 3.248\cos 6\theta - 247.120\cos \alpha + 1225.519\cos 2\alpha - 161.454\cos 3\alpha + 1.776\cos 4\alpha - 18.348\cos 5\alpha - 0.274\cos 6\alpha + 64.401\cos 3\theta\cos \alpha - 99.570\cos 3\theta\cos 2\alpha + 4.169\cos 3\theta\cos 3\alpha - 2.947\cos 3\theta\cos 4\alpha - 0.957\cos 3\theta\cos 5\alpha + 2.601\cos 3\theta\cos 6\alpha + 3.665\cos 6\theta\cos \alpha - 1.421\cos 6\theta\cos 2\alpha + 2.666\cos 6\theta\cos 3\alpha + 2.516\cos 6\theta\cos 4\alpha - 1.182\cos 6\theta\cos 5\alpha - 1.408\cos 6\theta\cos 6\alpha - 64.346\sin 3\theta\sin \alpha + 29.969\sin 3\theta\sin 2\alpha - 2.891\sin 3\theta\sin 3\alpha + 1.153\sin 3\theta\sin 4\alpha - 2.669\sin 3\theta\sin 5\alpha.$$

The methyl and OH (or SH) torsional barriers are shown in Table IV and represented in Figure 3. The vibrationally corrected methyl group barrier has been determined to be 1071.31 cm^{-1} (MeOOH), 685.5 cm^{-1} (MeOSH), 696.6 cm^{-1} (MeSOH), and 609 cm^{-1} (MeSSH). As was expected, it decreases with the enlargement of the C–X1 ($X1 = \text{O1}, \text{S1}$) bond distance during the O \rightarrow S substitution process, which reduces the non-bonding interactions responsible for the barriers.⁴¹ For MeOOH, the theoretical value compares well with the experimental ones of Tyblewski *et al.*¹² fitted for the (0 0⁺) and (0 0⁻) components of the vibrational ground state ($1117.0(19) \text{ cm}^{-1}$ and $1123.0(25) \text{ cm}^{-1}$), respectively.

The *trans* and *cis* barriers corresponding to the OH (or SH) torsion are also shown in Table IV and represented in Figure 3. For comparison, the equivalent parameters of the HOOH and HSSH peroxides, which were determined in assignments of the high resolution infrared spectra^{42,43} and

previous *ab initio* calculations,⁴⁴ are also shown. This last paper represents a significant full-dimensional analysis performed for a tetra-atomic molecule that, unfortunately, is too expensive to be employed for our species. For MeOOH, the OH *trans* barrier is very low (158.9 cm^{-1}). Thus, its ground vibrational state splits 10.978 cm^{-1} into the (0 0⁺) and (0 0⁻) components. This splitting is negligible for the sulfur compounds where the barriers are always higher than 1200 cm^{-1} .

Tables V and VI display the calculated torsional levels and their splittings classified following the representations of the G_6 group and the (v,v') vibrational quanta (v = methyl torsion, v' = Y2H torsion). The A/E splittings are derived from the tunneling effect in the methyl torsional barrier. For all the species, the splitting of the ground state is very small ($<0.002 \text{ cm}^{-1}$). For the fundamental levels (10⁺) and (10⁻), it starts to be noticeable (0.005 cm^{-1} (MeOOH), 0.04 cm^{-1} (MeOSH), 0.03 cm^{-1} (MeSOH), and 0.7 cm^{-1} (MeSSH)).

Finally, previous assignments of the torsional levels (Matthews *et al.*⁴) were performed neglecting interactions among the two torsional models although both are perpendicular vibrations. The kinetic parameter B_{12} and the coefficient of several interactions terms of the potential energy surface ($\cos 3\theta\cos \alpha$, $\cos 3\theta\cos 2\alpha$, $\sin 3\theta\sin \alpha$, or $\sin 3\theta\sin 2\alpha$) reflect these resonances. As was expected, given the bond distances, interactions are very small in MeSSH ($B_{12} = -0.26 \text{ cm}^{-1}$) but are not negligible for MeOOH ($B_{12} = -1.266 \text{ cm}^{-1}$).

CONCLUSIONS

In this paper, we describe highly correlated *ab initio* calculations performed to obtain realistic spectroscopic rotational and torsional properties of four species, MeOOH, MeSOH, MeOSH, and MeSSH, and focus to further astronomical detections through the rotational spectra. Given the lack of molecular data for the three sulfur compounds, these calculations represent a first full characterization at low temperatures and provide parameters relevant for the interpretation of observed spectra. Because we use very accurate methods (CCSD(T)-F12 for the rotational parameters and CCSD(T) for the potential energy surfaces), some of the calculated data, i.e., the torsional splittings (basic property for the interpretation of the rotational spectra), as well as the shift of the molecular properties with the O \rightarrow S substitution are really realistic parameters. Considering these shifts together with the available experimental data of MeOOH, for which experiments exist, many parameters can be estimated with considerable precision.

We provide parameters (barriers for the two torsional modes, kinetic energy parameters (B_1 , B_2 , and B_{12}), etc.) necessary for the definition of the effective Hamiltonian used in rotational spectroscopy. The VPT2 test of resonances reveals that Fermi interactions between the torsional motions and the remaining vibrational modes are not expected. A unique low energy level of MeOOH ($v = 1, v' = 1$) is very slightly displaced by the fundamental COO bending mode.

The torsional fundamental levels provided in Table V could be populated at low temperatures and need to be considered for the interpretation of the spectra. For all the

species, the A/E splitting of the ground state is very small ($<0.002\text{ cm}^{-1}$). For the fundamental levels, ($1\ 0^+$) and ($1\ 0^-$), it starts to be noticeable (0.005 cm^{-1} (MeOOH), 0.04 cm^{-1} (MeOSH), 0.03 cm^{-1} (MeSOH), and 0.7 cm^{-1} (MeSSH)). Whereas the splitting caused by the SH torsion is significant for MeOOH ($\sim 11.0\text{ cm}^{-1}$), for the other species, it is almost negligible.

The equilibrium and the ground vibrational state rotational parameters have been calculated with CCSD(T)-F12. For MeOOH and MeSSH, the last rotational constants have been calculated to be $A_0 = 42\ 822.23\text{ MHz}$, $B_0 = 10\ 564.08\text{ MHz}$, and $C_0 = 9149.3\text{ MHz}$ and to be $A_0 = 16\ 795.83\text{ MHz}$, $B_0 = 4441.34\text{ MHz}$, and $C_0 = 3676.48\text{ MHz}$, respectively. It has to be stand out that there is a very good agreement between calculations and previous experiments. For MeOSH and MeOSH, our computations have to be considered as predictions. Similar accuracy could be expected for all the species.

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