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ACCURATE SPECTROSCOPIC CHARACTERIZATION OF ETHYL MERCAPTAN AND DIMETHYL SULFIDE ISOTOPOLOGUES: A ROUTE TOWARD THEIR ASTROPHYSICAL DETECTION

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ABSTRACT

Using state-of-the-art computational methodologies, we predict a set of reliable rotational and torsional parameters for ethyl mercaptan and dimethyl sulfide monosubstituted isotopologues. This includes rotational, quartic, and sextic centrifugal-distortion constants, torsional levels, and torsional splittings. The accuracy of the present data was assessed from a comparison to the available experimental data. Generally, our computed parameters should help in the characterization and the identification of these organo-sulfur molecules in laboratory settings and in the interstellar medium.

Key words: astrochemistry – catalogs – ISM: abundances – ISM: molecules – molecular data

1. INTRODUCTION

Given the improved capabilities of new astronomical observatories in terms of spectral coverage and spatial resolution, the corresponding surveys cover large frequency ranges and can contain many unidentified lines. The latter features usually correspond to “new” molecules and/or rare isotopologues of previously detected species. The “cleaning” of the corresponding spectral confusion implies the full assignment of astronomical spectra, which in turn requires a complete spectroscopic characterization of all of the involved species at different temperatures.

Organic molecules can be detected in low-energy, excited vibrational states in hot molecular cores through their rotational spectra. Furthermore, nonrigid species such as ethyl mercaptan and dimethyl sulfide present internal rotation motions restricted by energy barriers. These motions can produce splitting of the ground and low-excited vibrational levels through the tunneling effect. Their complete characterization at low temperatures requires analysis of the vibrational spectrum in the far-infrared region. Unfortunately, a large number of detectable molecules are not well characterized. For many species, although accurate spectroscopic data are available, they are limited to the vibrational ground state and to the most abundant isotopologues. The effect of temperature and the fact that isotopic composition can be very different from one extraterrestrial source to another are often not considered. However, species containing less abundant isotopes or molecules with populated low vibrational states can play important chemical roles in many sources. An example is provided by methyl formate (a nonrigid molecule), for which investigations have been reported for the rotational spectrum in the vibrational ground state for the main isotopic species (Brown et al. 1975; Churchwell & Winnewisser 1975) as well as for several isotopologues (Carvajal et al. 2009; Margulès et al. 2010; Tercero et al. 2012). Features due to the first excited torsional state have also been detected for the main isotopologue (Kobayashi et al. 2007; Demyk et al. 2008) and ^{13}C-containing (Carvajal et al. 2010) isotopologues. The main isotopic species was also observed in the second excited torsional state (Takano et al. 2012).

State-of-the-art ab initio methods can be used to compute highly accurate spectroscopic constants, even for nonrigid molecules (Brites et al. 2008; Halvick et al. 2011; Puzzarini et al. 2014a; Senent et al. 2009, 2014). Today, these constants are known to provide the required accuracy to guide experimental investigations of rotational and far-infrared spectra. While experimental determinations for rare isotopic species can be hampered by their low natural abundance, computations provide the same accuracy for all isotopologues. Therefore, quantum-chemical calculations are well suited to support and complement experimental and astronomical studies that also involve rare isotopic species. Examples can be found in investigations of the main isotopologues and several other isotopologues containing D and ^{13}C of dimethyl-ether (DME; Senent et al. 2012; Carvajal et al. 2012, 2014) or propane (Villa et al. 2013).

Recently, we conducted a study of the main isotopic species of dimethyl sulfide (DMS) and ethyl mercaptan (ETSH) at low temperatures (Senent et al. 2014) considering their potential astrophysical relevance. In particular, the latter molecule was considered to be a potential detectable sulfur organic compound based on different arguments: the importance of sulfur chemistry in the interstellar medium (Charnley 1997) and because the O-analog of ethyl mercaptan, ethanol, is a well-known astrophysical molecule. We should consider that usually, with few exceptions (Cernicharo et al. 1987), the detection of S-bearing species follows the detection of corresponding O-analogs. The expectations of astrophysicists were recently satisfied when an exhaustive search led to the detection of ethyl-mercaptan in Orion in 2014 (Kolesniková et al. 2014). For many years, methyl mercaptan was the only sulfur nonrigid molecule detected in astrophysical sources (Linke et al. 1979).

Differences in their formation processes have made determination of the isotopic abundances of different sources particularly interesting as a means of investigating interstellar and galactic evolution (Mauersberger et al. 2004). In addition, fluctuations of the relative isotopic abundances are tools for identifying chemical, geophysical, and biological processes (Canfield 2001; Farquhar & Wing 2003; Mauersberger et al. 2004). Hence, relative isotopic abundances have been estimated for meteorites, the moon, cosmic rays, and stars (Mauersberger et al. 2004). There is some evidence demonstrating that isotope yields follow different synthesis procedures. Whereas ^{32}S, ^{34}S, and ^{33}S are the primary products of oxygen burning in a star, ^{36}S is produced when the primary sulfur isotopes capture neutrons during helium and carbon burning (Mauersberger et al. 1996).

Considering their potential importance, in the present work, we investigated several rare monosubstituted isotopologues of ethyl mercaptan and dimethyl sulfide containing either a rare S-isotope or deuterium. Sulfur, the tenth most abundant cosmological element, presents four stable isotopes ^{32}S, ^{34}S, ^{33}S, and ^{36}S whose abundance ratios in the solar system were estimated to be 95.02%, 4.21%, 0.75%, and 0.021% (Anders & Grevesse 1989), respectively. Their relative abundances in Orion KL were determined to be $^{32}\mathrm{S}/^{34}\mathrm{S} = 20 \pm 6$, $^{32}\mathrm{S}/^{33}\mathrm{S} = 75 \pm 29$ (Tercero et al. 2010a, 2010b). The first molecule containing ^{36}S,C^{36}S, was detected in Galactic molecular hot cores by Mauersberger et al. (1996), who estimated a relative abundance of $^{34}\mathrm{S}/^{36}\mathrm{S} = 115 \pm 17$, which is smaller than that in the solar system. This ratio is consistent with what was later determined by Mauersberger et al. (2004), 107 ± 15, in the carbon star IRC + 10216 based on the detection of the rotational transitions of C^{36}S and Si^{36}S. Moreover, several S-containing molecules were detected in the ISM raging from diatomics (e.g. NS, SO, and SH) to more complex small organic molecules (e.g. C_2S, H_2S, OCS, C_3S, H_2CS, HSCN, HNCS, CH_3CS, etc.; Ziurys 2006; Millar et al. 1986; Irvine et al. 1988; Goldsmith et al. 1981; Minh et al. 1991; Frerking et al. 1979; Linke et al. 1979). Si^{36}S is the first compound containing ^{36}S detected in a star (Mauersberger et al. 2004).

In the present work, by following the procedures of Senent et al. (2014), we have investigated the ^{34}S-, ^{36}S-, ^{33}S-, and deuterium-containing ETSH and DMS species, considering them not only in the vibrational ground state, but also in their excited torsional states because at the temperature of the hot molecular cores, these excited states and their splittings can be populated. Hence, we provide a detailed spectroscopic characterization of these S-containing molecules and isotopologues to help their detection in the ISM. Thus, the aim of this paper is to predict the isotopic substitution effect on the rotational and torsional parameters. To assess their accuracy, the computed properties were compared with the available experimental data, in particular, for the main isotopologues (Senent et al. 2014). While for the latter we refer to Senent et al. (2014) for an account on previous theoretical and experimental studies, here we mention that for other isotopic species, only a few studies are available (Hayashi et al. 1989; Schmidt & Quade 1975; Wolff & Szydlowski 1985; Manocha et al. 1973; Kretschmer et al. 1995; Kolesniková et al. 2014).

2. METHODOLOGY

In this study, we followed the methodologies described in Puzzarini et al. (2010), Puzzarini (2013), and Senent (1998a, 1998b, 2001). In particular, we refer interested readers to Puzzarini et al. (2010) and Puzzarini (2013) for rotational spectroscopy and to Senent (1998a, 1998b, 2001) for torsional analysis. In particular, concerning the spectroscopic characterization of ETSH and DMS, all computational details can be found in Senent et al. (2014). In the following, only a brief summary is provided. Here, we also point out that DMS has two equivalent methyl groups leading to nine equivalent minima in the potential energy surface (PES), while ETSH has a unique methyl group which is responsible for three equivalent minima. In addition, for the latter, a second torsional coordinate, the thiol torsion (SH torsion), leads to two conformers, the gauche and trans forms. Then, the coupling of the two torsional motions in ETSH (methyl and thiol torsions) generates a PES with nine minima (for further details, see Senent et al. 2014).

2.1. Rotational Spectroscopy

To obtain accurate equilibrium rotational constants, the equilibrium structures of ETSH and DMS were determined by means of a composite scheme (see Senent et al. 2014) which is based on additivity at an energy-gradient level (Heckert et al. 2005, 2006) and employs the coupled-cluster singles and doubles approximation (CCSD) augmented by a perturbative treatment of triple excitations [CCSD(T)] (Raghavachari et al. 1989) in conjunction with correlation-consistent basis sets, cc-p(C)VnZ (n = T, Q, 5) (Dunning 1989; Woon & Dunning 1995). Second, to derive vibrational ground-state and torsional-excited-state rotational constants, the equilibrium rotational constants were corrected for vibrational effects with the corresponding corrections being obtained by means of second-order vibrational perturbation theory (VPT2; Mills 1972) at the MP2/cc-pVTZ, CCSD/cc-pVTZ, and CCSD(T)/cp-VTZ levels (for details, see Senent et al. 2014), where MP2 stands for the Møller–Plesset theory to the second order (Møller & Plesset 1934). These calculations implied the evaluation of cubic force fields, and therefore they also allowed us to determine quartic and sextic centrifugal-distortion constants. Different levels of theory were considered in order to verify the cheapest one while still providing reliable and accurate results. All of these calculations were carried out with the quantum-chemical CFOUR program package (2012).

To further improve the predictive capabilities of our computed parameters (i.e., rotational and centrifugal-distortion constants), an empirical scaling procedure was employed for the ground-state parameters. For a generic parameter X, the latter procedure is based on multiplying the computed value of X for a monosubstituted isotopologue (denoted by the superscript iso) for the corresponding experiment/theory ratio for the main (^{32}S-containing) isotopic species (denoted by the superscript main):

$$X^{\mathrm{iso}}_{\mathrm{scal}} = X^{\mathrm{iso}}_{\mathrm{calc}} \times \left(X^{\mathrm{main}}_{\mathrm{exp}} / X^{\mathrm{main}}_{\mathrm{cal}} \right), \qquad (1)$$

where scal, exp, and calc denote the scaled, experimental, and quantum-chemically calculated values for X, respectively. This approach is extensively used in the field of rotational spectroscopy, and its validity has been discussed, for example, in Puzzarini et al. (2012). For gauche-ETSH, for which a complete set of experimental rotational and quartic centrifugal-distortion constants is available for the ^{34}S-containing species, the latter was used for the reference isotopologue in order to derive the scaled parameters for the main isotopic species.

2.2. Torsional Analysis

For the analysis of the vibrational spectrum in the far-infrared region, we have performed a torsional analysis following the theoretical methodology described in our previous paper

Table 1
Computed, Scaled, and Experimental Rotational Parameters[a] for *gauche*-ethyl Mercaptan

gauche-$CH_3CH_2{}^{32}SH$

Parameter	Calculated			Scaled[e]	Experiment Kolesniková et al. (2014)	
	MP2[b]	CCSD[c]	CCSD(T)[d]	CCSD	0^+	0^-
A_0	28783.924	28779.449	28775.409	28748.096	28747.4104(66)	28747.2715(65)
B_0	5300.793	5300.891	5298.833	5295.107	5295.1422(36)	5295.0008(36)
C_0	4850.955	4850.923	4849.312	4845.829	4845.9421(36)	4845.9689(36)
Δ_J	3.362	3.287	3.364	3.328	3.326369(20)	3.323582(20)
Δ_{JK}	−20.330	−19.571	−19.809	−18.402	−18.39280(60)	−18.35859(60)
Δ_K	205.641	205.263	206.297	206.932	204.1591(82)	203.9217(81)
δ_J	0.537	0.518	0.534	0.514	0.514429(12)	0.513170(14)
δ_K	10.016	9.592	9.960	8.482	8.781(12)	8.555(12)
Φ_J	−0.0027	−0.0027	−0.0029		0.0029872(28)	0.0029225(31)
Φ_{JK}	−0.1125	−0.1182	−0.1201		0.0790(13)	0.0661(13)
Φ_{KJ}	0.9420	1.0045	0.9973		−1.3341(45)	−1.2955(44)
Φ_K	−3.3603	−3.6061	−3.5997		6.341(48)	5.171(46)
ϕ_J	−0.0011	−0.0011	−0.0012		0.0012107(15)	0.0011805(16)
ϕ_{JK}	−0.0597	−0.0631	−0.0647		0.04561(63)	0.04326(65)
ϕ_K	1.9055	1.9526	2.0270		5.858(95)	4.825(97)

gauche-$CH_3CH_2{}^{34}SH$

Parameter	Calculated			Scaled[e]	Experiment Kolesniková et al. (2014)	
	MP2[b]	CCSD[c]	CCSD(T)[d]	CCSD	0^+	0^-
A_0	28745.294	28741.143	28737.106	28709.078	28709.699(24)	28708.964(26)
B_0	5181.142	5181.156	5179.154	5175.469	5175.5685(36)	5175.4383(36)
C_0	4749.762	4749.706	4748.131	4744.843	4744.7050(36)	4744.7310(36)
Δ_J	3.215	3.143	3.217	3.179	3.18351(18)	3.18084(18)
Δ_{JK}	−19.798	−19.064	−19.290	−17.899	−17.9512(15)	−17.8994(14)
Δ_K	204.658	204.289	205.308	203.072	206.8(14)	205.1(14)
δ_J	0.502	0.484	0.499	0.480	0.481132(82)	0.480129(71)
δ_K	9.628	9.214	9.569	8.326	8.271(34)	8.024(35)
Φ_J	−0.0024	−0.0024	−0.0025			
Φ_{JK}	−0.1066	−0.1111	−0.1129			
Φ_{KJ}	0.8831	0.9400	0.9328			
Φ_K	−3.1091	−3.4068	−3.4003			
ϕ_J	−0.0010	−0.0010	−0.0011			
ϕ_{JK}	−0.0545	−0.0577	−0.0592			
ϕ_K	1.8209	1.8821	1.9542			

	gauche-$CH_3CH_2{}^{33}SH$			*gauche*-$CH_3CH_2{}^{36}SH$		
Parameter	Calculated		Scaled	Calculated		Scaled
	CCSD[c]	CCSD(T)[d]	CCSD[e]	CCSD[c]	CCSD(T)[d]	CCSD[e]
A_0	28759.688	28755.646	28727.602	28707.028	28702.999	28675.000
B_0	5239.310	5237.282	5233.559	5073.263	5071.311	5067.6946
C_0	4798.905	4797.313	4793.991	4658.229	4656.686	4653.4594
Δ_J	3.210	3.288	3.247	3.010	3.087	3.045
Δ_{JK}	−19.208	−19.541	−18.034	−18.744	−18.833	−17.599
Δ_K	204.239	205.786	203.023	204.271	204.428	203.054
δ_J	0.500	0.515	0.496	0.454	0.469	0.451
δ_K	9.402	9.758	8.496	8.846	9.222	7.994
Φ_J	−0.0026			−0.0022		
Φ_{JK}	−0.1145			−0.1048		
Φ_{KJ}	0.9711			0.8833		
Φ_K	−3.5034			−3.2284		
ϕ_J	−0.0011			−0.0009		
ϕ_{JK}	−0.0603			−0.0531		
ϕ_K	1.9160			1.8202		

gauche-$CH_3CH_2{}^{32}SD$

Parameters	Calculated		Scaled	Experiment Schmidt & Quade (1975)
	CCSD[c]	CCSD(T)[d]	CCSD[e]	
A_0	26092.013	26087.580	26062.904	26064.003
B_0	5195.122	5193.214	5189.419	5190.090
C_0	4773.556	4772.141	4768.672	4768.620
Δ_J	3.378	3.521	3.416	

Table 1
(Continued)

gauche-$CH_3CH_2{}^{32}SD$				
Parameters	Calculated		Scaled	Experiment Schmidt & Quade (1975)
	CCSD[c]	CCSD(T)[d]	CCSD[e]	
Δ_{JK}	−13.104	−13.931	−12.303	
Δ_K	140.806	143.593	139.967	
δ_J	0.585	0.626	0.580	
δ_K	13.190	22.893	11.919	
Φ_J	−0.0102			
Φ_{JK}	−0.0664			
Φ_{KJ}	0.8960			
Φ_K	−4.1109			
ϕ_J	−0.0046			
ϕ_{JK}	−0.1203			
ϕ_K	4.7852			

Notes.

[a] Rotational constants in MHz; quartic and sextic centrifugal-distortion constants in kHz and Hz, respectively. Watson A-reduction in the I^r representation is used.

[b] Equilibrium constants corresponding to the best-estimated equilibrium structure (see text; Senent et al. 2014). Vibrational corrections to rotational constants, and quartic and sextic centrifugal-distortion constants at the MP2/cc-pVTZ level.

[c] Equilibrium constants corresponding to the best-estimated equilibrium structure (see text; Senent et al. 2014). Vibrational corrections to rotational constants, and quartic and sextic centrifugal-distortion constants at the CCSD/cc-pVTZ level.

[d] Equilibrium constants corresponding to the best-estimated equilibrium structure (see text; Senent et al. 2014). Vibrational corrections to rotational constants, and quartic and sextic centrifugal-distortion constants at the CCSD(T)/cc-pVTZ level.

[e] For ^{32}S, the experimental data of the ^{34}S-containing isotopologue were used for the scaling procedure; for ^{34}S, ^{33}S, ^{36}S, and D, the experimental values of ^{32}S were employed. For experiment, the averaged 0^+ and 0^- values are used.

(Senent et al. 2014). The energy levels are determined variationally by solving the following two-dimensional Hamiltonian:

$$\hat{H}(q_i,q_j) = -\sum_{i=1}^{2}\sum_{J=1}^{2}\left(\frac{\partial}{\partial q_i}\right)B_{q_iq_j}(q_i,q_j)\left(\frac{\partial}{\partial q_j}\right) + V(q_{i,}\, q_j)+V'(q_i,\, q_j)+V^{\mathrm{ZPVE}}(q_i,q_j),$$

which depends on two independent coordinates q_i and q_j. For ETSH, q_i and q_j are identified as the CH_3 torsion (θ) and the SH torsion (α), respectively. In DMS, both coordinates correspond to methyl internal rotations (θ_1 and θ_2). $V(q_i, q_j)$ represents the two-dimensional potential energy surface (2D-PES). $V^{\mathrm{ZPVE}}(q_i, q_2)$, B_{qiqj}, and V' (q_i, q_j) denote the zero-point vibrational energy correction, the kinetic energy parameters, and the Podolsky pseudopotential, respectively. For their definition, the readers are referred to Senent (1998a, 1998b).

Since the 2D-PES is isotopically invariant, here we use the surfaces generated in our previous study to treat the main isotopologue. These surfaces were obtained from the total electronic energies calculated at the CCSD(T)/aug-cc-pVTZlevel of theory (Kendall et al. 1992) for a number NS of selected geometries defined for different values of the independent coordinates (NS = 26 for ETSH and NS = 7 for DMS). For each point of the PES, the remaining 3Na-6-*n* internal coordinates (Na = number of atoms, *n* = 2 dihedral angles) were optimized at the CCSD/aug-cc-pVTZ level.

$V^{\mathrm{ZPVE}}(q_i, q_2)$, B_{qiqj}, and $V'(q_i, q_j)$ are, however, isotopically dependent. For each NS structure and for each isotopologue, B_{qiqj} and $V'(q_i, q_j)$ were determined using the code ENEDIM, also employed in the variational calculation of the energy levels. $V^{\mathrm{ZPVE}}(q_i, q_2)$ was calculated within the harmonic approximation at the MP2/aug-cc-pVTZ level using the Gaussian 09 package. For all details, the reader is referred to Senent et al. (2014).

3. RESULTS

3.1. Rotational Parameters

The computed vibrational-ground-state rotational and centrifugal-distortion constants of the isotopologues considered for gauche-ETSH, trans-ETSH, and DMS are collected in Tables 1–3, with the Watson's *A* reduction in the I^r representation (Watson 1977) taken into consideration. Tables 1 and 2 summarize in detail the spectroscopic parameters obtained for the isotopologues considered for gauche-ETSH and trans-ETSH. Table 3 reports the results for DMS isotopic species. While in Tables 1–3 we only report our best-computed values (i.e., those based on CCSD(T) calculations), the CCSD parameters scaled according to Equation (1), and the available experimental data, the complete set of our results is supplied in our tables. In particular, we present the comparison of the MP2, CCSD, and CCSD(T) results.

Based on comparison with experiments, we note very good agreement between the latter and our best data. Indeed, we note mean discrepancies of about 0.12% and 0.07% when the best-estimated equilibrium constants (from the best-estimated equilibrium structures computed in Senent et al. 2014) are corrected for vibrational corrections at the CCSD/cc-pVTZ and CCSD(T)/cc-pVTZ levels, respectively. Employing MP2/cc-pVTZ corrections does not worsen the agreement, with mean discrepancies still on the order of 0.12%. Moving to quartic centrifugal-distortion constants, the MP2, CCSD, and CCSD(T) levels in conjunction with the cc-pVTZ basis set show averaged discrepancies of about 6.4%, 5.0%, and 6.1%, respectively. Sextic centrifugal-distortion constants deserve special note since, to our knowledge, only a few experimental values are available for the main isotopologue of DMS (Vacherand et al. 1987, see Table 1) and for the ^{32}S- and ^{34}S-containing isotopologues of gauche-ETSH and for ^{32}S-trans-ETSH. While for DMS only a limited number of sextics are

Table 2

Computed, Scaled, and Experimental Rotational Parameters[a] for *trans*-ethyl Mercaptan

		trans-$CH_3CH_2{}^{32}SH$		
Parameters	Calculated			Experiment Kolesniková et al. (2014)
	MP2[b]	CCSD[c]	CCSD(T)[d]	
A_0	28460.983	28460.659	28451.975	28416.7604 (18)
B_0	5492.059	5491.347	5489.912	5485.77901 (15)
C_0	4886.820	4886.618	4885.345	4881.81770 (15)
Δ_J	3.795	3.679	3.767	3.83217 (27)
Δ_{JK}	−23.558	−22.847	−23.107	−22.4549 (58)
Δ_K	196.710	197.969	198.873	210.03 (18)
δ_J	0.646	0.617	0.634	0.65664 (11)
δ_K	6.091	5.807	5.967	7.342 (20)
Φ_J	−0.0116	−0.0120	−0.0130	−0.00086 (17)
Φ_{JK}	−0.0415	−0.0467	−0.0423	0.367 (18)
Φ_{KJ}	0.9175	1.0659	1.0607	−2.717 (106)
Φ_K	−4.6243	−5.3975	−5.4647	26.7 (80)
ϕ_J	−0.0057	−0.0059	−0.0064	−0.000935 (91)
ϕ_{JK}	−0.2014	−0.2136	−0.2265	−0.164 (26)
ϕ_K	−1.0809	−1.2489	−1.3450	28.89 (97)
		trans-$CH_3CH_2{}^{34}SH$		
Parameters	Calculated			Scaled
	MP2[b]	CCSD[c]	CCSD(T)[d]	CCSD[e]
A_0	28374.015	28373.744	28365.113	28329.979
B_0	5373.179	5372.489	5371.085	5367.041
C_0	4789.981	4789.783	4788.536	4785.077
Δ_J	3.659	3.541	3.634	3.688
Δ_{JK}	−23.153	−22.564	−22.585	−22.177
Δ_K	195.493	197.344	196.995	209.367
δ_J	0.613	0.585	0.602	0.622
δ_K	5.948	5.624	5.868	7.110
Φ_J	−0.0105	−0.0109	−0.0117	
Φ_{JK}	−0.0408	−0.0457	−0.0418	
Φ_{KJ}	0.8413	0.9788	0.9735	
Φ_K	−4.2527	−4.9684	−5.0279	
ϕ_J	−0.0051	−0.0053	−0.0057	
ϕ_{JK}	−0.1854	−0.1966	−0.2085	
ϕ_K	−0.9751	−1.1294	−1.2178	
		trans-$CH_3CH_2{}^{33}SH$		
Parameters		Calculated		Scaled
		CCSD[c]	CCSD(T)[d]	CCSD[e]
A_0		28415.795	28407.139	28371.966
B_0		5430.260	5428.841	5424.754
C_0		4836.877	4835.617	4832.125
Δ_J		3.610	3.699	3.761
Δ_{JK}		−22.716	−22.838	−22.326
Δ_K		197.693	197.905	209.737
δ_J		0.601	0.617	0.639
δ_K		5.716	5.917	7.227
Φ_J		−0.0114	−0.0123	
Φ_{JK}		−0.0462	−0.0431	
Φ_{KJ}		1.0204	1.0182	
Φ_K		−5.1738	−5.2391	
ϕ_J		−0.0056	−0.0060	
ϕ_{JK}		−0.2048	−0.2167	
ϕ_K		−1.1869	−1.3222	
		trans-$CH_3CH_2{}^{36}SH$		
Parameters		Calculated		Scaled
		CCSD[c]	CCSD(T)[d]	CCSD[e]
A_0		28296.527	28287.940	28252.881
B_0		5265.097	5263.722	5259.759
C_0		4702.094	4700.871	4697.475
Δ_J		3.400	3.514	3.542

Table 2
(Continued)

trans-$CH_3CH_2{}^{36}SH$

Parameters	Calculated		Scaled
	CCSD[c]	CCSD(T)[d]	CCSD[e]
Δ_{JK}	−22.202	−22.115	−21.821
Δ_K	196.451	195.316	208.420
δ_J	0.553	0.573	0.588
δ_K	5.437	5.774	6.874
Φ_J	−0.0099	−0.0106	
Φ_{JK}	−0.0447	−0.0422	
Φ_{KJ}	0.9050	0.9026	
Φ_K	−4.6015	−4.6568	
ϕ_J	−0.0048	−0.0052	
ϕ_{JK}	−0.1820	−0.1926	
ϕ_K	−1.0252	−1.1520	

trans-$CH_3CH_2{}^{32}SD$

Parameters	Calculated		Scaled	Experiment Schmidt & Quade (1975)
	CCSD[c]	CCSD(T)[d]	CCSD[e]	
A_0	27202.948	27194.339	27160.989	27155.91
B_0	5308.668	5307.475	5303.285	5304.36
C_0	4706.623	4705.557	4701.999	4702.60
Δ_J	3.166	3.253	3.298	
Δ_{JK}	−16.455	−17.670	−16.172	
Δ_K	147.484	154.696	156.469	
δ_J	0.524	0.541	0.557	
δ_K	3.826	3.671	4.838	
Φ_J	−0.0417	−0.0452		
Φ_{JK}	−0.0860	−0.0814		
Φ_{KJ}	5.2740	5.4727		
Φ_K	−24.3435	−25.1609		
ϕ_J	−0.0208	−0.0225		
ϕ_{JK}	−0.6558	−0.7025		
ϕ_K	−6.3870	−6.8136		

Notes.

[a] Rotational constants in MHz; quartic and sextic centrifugal-distortion constants in kHz and Hz, respectively. Watson A-reduction in the I^r representation is used.

[b] Equilibrium constants corresponding to the best-estimated equilibrium structure (see text; Senent et al. 2014). Vibrational corrections to rotational constants, and quartic and sextic centrifugal-distortion constants at the MP2/cc-pVTZ level.

[c] Equilibrium constants corresponding to the best-estimated equilibrium structure (see text; Senent et al. 2014). Vibrational corrections to rotational constants, and quartic and sextic centrifugal-ditortion constants at the CCSD/cc-pVTZ level.

[d] Equilibrium constants corresponding to the best-estimated equilibrium structure (see text; Senent et al. 2014). Vibrational corrections to rotational constants, and quartic and sextic centrifugal-ditortion constants at the CCSD(T)/cc-pVTZ level.

[e] Empirically scaled parameters (see text) starting from those computed as at footnote c.

experimentally known, and therefore the poor agreement can be ascribed to limitations in the experimental work, for both gauche-and trans-ETSH the full sets of sextic centrifugal-distortion constants were determined in conjunction with higher-order terms. Therefore, a thorough inspection of this disagreement is required, especially because a sign inversion is observed in almost all cases. The corresponding discussion is reported later in the text.

Based on the results of Tables 1–3, we also note improved accuracy once we apply the empirical scaling procedure described above. In fact, the discrepancies decrease to less than 0.01% for rotational constants and to 3.1% (<2.0% in most cases) on average for quartic centrifugal-distortion terms. This improvement also has repercussions for the prediction of rotational transitions. In fact, our best-estimated computed parameters provide predictions with a relative accuracy of ∼0.1% in the centimeter/millimeter-wave region. Therefore, a rotational frequency of 200 GHz is currently predicted with an accuracy of 200 MHz. For the same frequency, the relative error decreases to ∼0.01%, resulting in an accuracy of 20 MHz for our prediction of a rotational transition at 200 GHz.

Our overall conclusion is that our predicted parameters, also the nonscaled ones, are reliable. We thus consider them to be sufficiently accurate for supporting laboratory or astronomical assignments and identifications. From the discussion above and from a methodological point of view, we would like to point out that the MP2/cc-pVTZ level is suitable for obtaining vibrational corrections to rotational constants and centrifugal-distortion parameters with an accuracy that allows for quantitative predictions.

Table 3

Computed, Scaled, and Experimental Rotational Parameters[a] for Dimethyl-Sulfide

$CH_3{}^{32}SCH_3$

Parameter	Calculated			Experiment Vacherand et al. (1987)	Experiment Hayashi et al. (1989).
	MP2[b]	CCSD[c]	CCSD(T)[d]		
A_0	17836.230	17832.456	17825.867	17810.0389(35)	17809.734(8)
B_0	7630.756	7631.159	7629.422	7621.12253(110)	7621.098(2)
C_0	5725.777	5725.526	5724.127	5717.76282(101)	5717.769(2)
Δ_J	8.692	8.324	8.609	8.04258(118)	8.06(4)
Δ_{JK}	−40.406	−38.073	−39.071	−35.2214(103)	−35.45(43)
Δ_K	140.456	138.442	139.591	139.572(49)	140.88(165)
δ_J	3.139	2.970	3.086	2.82209(21)	2.84(2)
δ_K	3.635	3.396	3.440	3.8458(156)	3.29(49)
Φ_J	−0.0457	−0.0485	−0.0519		
Φ_{JK}	−0.0436	−0.0571	−0.0528	−0.1152(138)	
Φ_{KJ}	1.3772	1.5930	1.6203	0.462(82)	
Φ_K	−3.8297	−4.4210	−4.4775		
ϕ_J	−0.0227	−0.0241	−0.0258		
ϕ_{JK}	−0.2395	−0.2654	−0.2759	0.2277(161)	
ϕ_K	0.8114	0.7648	0.7885		

$CH_3{}^{34}SCH_3$

Parameter	Calculated		Scaled	Experiment Hayashi et al. (1989).
	CCSD[c]	CCSD[d]	CCSD[e]	
A_0	17420.928	17414.496	17399.028	17398.825(9)
B_0	7631.361	7629.625	7621.324	7621.335(4)
C_0	5682.329	5680.944	5674.624	5674.658(8)
Δ_J	8.274	8.558	8.011	8.46(5)
Δ_{JK}	−37.506	−38.496	−34.697	−35.12(40)
Δ_K	134.375	135.486	135.472	17398.825(9)
δ_J	2.995	3.112	2.846	
δ_K	3.198	3.230	3.621	
Φ_J	−0.0472			
Φ_{JK}	−0.0411			
Φ_{KJ}	1.4401			
Φ_K	−4.0653			
ϕ_J	−0.0234			
ϕ_{JK}	−0.2445			
ϕ_K	0.7414			

$CH_3{}^{33}SCH_3$

Parameter	Calculated		Scaled	Experiment Kretschmer et al. (1995)
	CCSD[c]	CCSD(T)[d]	CCSD[e]	
A_0	17620.725	17614.217	17598.574	17598.3002(14)
B_0	7631.263	7629.527	7621.2264	7622.2643(24)
C_0	5703.472	5702.080	5695.7379	5694.7067(24)
Δ_J	8.582	8.582	8.034	8.115(32)
Δ_{JK}	−38.776	−38.776	−34.955	−35.36(16)
Δ_K	137.481	137.481	137.462	137.07(27)
δ_J	3.099	3.099	2.834	2.845(8)
δ_K	3.335	3.335	3.728	3.63(25)
Φ_J	−0.0478			
Φ_{JK}	−0.0488			
Φ_{KJ}	1.5135			
Φ_K	−4.2362			
ϕ_J	−0.0238			
ϕ_{JK}	−0.2546			
ϕ_K	0.7530			

$CH_3{}^{36}SCH_3$

Parameter	Calculated		Scaled
	CCSD[c]	CCSD(T)[d]	CCSD[e]
A_0	17050.624	17044.335	17029.190
B_0	7631.541	7629.806	7621.504
C_0	5642.268	5640.897	5634.618
Δ_J	8.513	8.513	7.969

Table 3
(Continued)

$CH_3{}^{36}SCH_3$

Parameter	Calculated		Scaled
	CCSD[c]	CCSD(T)[d]	CCSD[e]
Δ_{JK}	−37.977	−37.977	−34.235
Δ_K	131.786	131.786	131.768
δ_J	3.134	3.134	2.866
δ_K	3.024	3.024	3.381
Φ_J	−0.0460		
Φ_{JK}	−0.0276		
Φ_{KJ}	1.3083		
Φ_K	−3.7576		
ϕ_J	−0.0229		
ϕ_{JK}	−0.2262		
ϕ_K	0.7187		

$a\text{-}CH_3{}^{32}SCH_2{}^{f}$

Parameter	Calculated		Scaled	Experiment Hayashi et al. (1989)
	CCSD[c]	CCSD(T)[d]	CCSD[e]	
A_0	16578.647	16572.974	16557.528	16556.964(25)
B_0	7344.446	7342.763	7334.765	7335.312(5)
C_0	5519.346	5518.023	5511.869	5512.033(6)
Δ_J	8.124	8.404	7.865	8.02(11)
Δ_{JK}	−34.249	−35.179	−31.683	−32.27(116)
Δ_K	113.432	114.459	114.358	110.73(501)
δ_J	2.917	3.031	2.771	2.78(7)
δ_K	2.267	2.291	2.567	2.35(138)
Φ_J	−0.0610			
Φ_{JK}	0.0569			
Φ_{KJ}	1.1229			
Φ_K	−3.3337			
ϕ_J	−0.0304			
ϕ_{JK}	−0.2534			
ϕ_K	0.5996			

$s\text{-}CH_3{}^{32}SCH_2D^{g}$

Parameter	Calculated		Scaled	Experiment Hayashi et al. (1989)
	CCSD[c]	CCSD(T)[d]	CCSD[e]	
A_0	17819.084	17812.372	17796.684	17795.061(38)
B_0	7077.495	7076.097	7068.186	7068.973(10)
C_0	5408.647	5377.454	5401.313	5401.701(9)
Δ_J	6.504	6.721	6.297	6.87(21)
Δ_{JK}	−31.194	−31.985	−31.448	−27.50(85)
Δ_K	133.574	134.645	123.569	134.88(850)
δ_J	2.234	2.321	2.123	2.02
δ_K	3.475	3.540	3.935	
Φ_J	−0.0480			
Φ_{JK}	−0.1374			
Φ_{KJ}	2.8026			
Φ_K	−8.7476			
ϕ_J	−0.0239			
ϕ_{JK}	−0.3493			
ϕ_K	0.6581			

Notes.

[a] Rotational constants in MHz; quartic centrifugal-distortion constants in kHz; sextic centrifugal-distortion constants in Hz. Watson A-reduction in the I^r representation is used.

[b] Equilibrium constants corresponding to the best-estimated equilibrium structure (see text; Senent et al. 2014). Vibrational corrections to rotational constants, and quartic and sextic centrifugal-distortion constants at the MP2/cc-pVTZ level.

[c] Equilibrium constants corresponding to the best-estimated equilibrium structure (see text; Senent et al. 2014). Vibrational corrections to rotational constants, and quartic and sextic centrifugal-distortion constants at the CCSD/cc-pVTZ level.

[d] Equilibrium constants corresponding to the best-estimated equilibrium structure (see text; Senent et al. 2014). Vibrational corrections to rotational constants, and quartic and sextic centrifugal-distortion constants at the CCSD(T)/cc-pVTZ level.

[e] Empirically scaled parameters (see text) starting from those computed as at footnote c.

[f] Deuterium substitution leads to a complete symmetry loss: from the C_{2V} symmetry point group to C_1.

[g] Deuterium substitution leads to a limited symmetry loss: from C_{2V} to C_S.

Table 4

Low Torsional Energy Levels (in cm^{-1}) of Ethyl Mercaptan and Dimethyl Sulfide Isotopologues Calculated at the CCSD(T)/aug-cc-pVTZ Level

gauche- ethyl-mercaptan

		$CH_3CH_2{}^{32}SH$	$CH_3CH_2{}^{34}SH$	$CH_3CH_2{}^{36}SH$	$CH_3CH_2{}^{33}SH$	$CH_3CH_2{}^{32}SD$
ZPVE		226.898	226.773	226.661	226.834	201.658
ν_{20}, ν_{21}						
$0\ 0^+$	A_1, E	0.000	0.000	0.000	0.000	0.000
$0\ 0^-$	A_2, E	0.061	0.060	0.059	0.060	0.002
$0\ 1^+$	A_1, E	188.132	188.086	188.043	188.108	145.434
$0\ 1^-$	A_2, E	189.613	189.552	189.497	189.582	145.525
$1\ 0^+$	A_1	254.046	253.888	253.745	253.965	252.600
	E	254.045	253.887	253.746	253.964	252.600
$1\ 0^-$	A_2	254.068	253.910	253.769	253.986	252.599
	E	254.067	253.909	253.768	253.985	252.598
$0\ 2^+$	A_1, E	339.848	339.824	339.802	339.835	275.486
$0\ 2^-$	A_2, E	356.237	356.102	355.981	356.168	276.729
$1\ 1^+$	A_1	441.675	441.493	441.331	441.581	398.580
	E	441.677	491.496	441.334	441.584	398.581
$1\ 1^-$	A_2	441.334	441.175	441.033	441.252	398.982
	E	441.336	441.178	441.036	441.255	398.983
$2\ 0^+$	A_1	491.359	491.049	490.772	491.199	487.356
	E	491.145	491.074	490.797	491.223	487.369
$2\ 0^-$	A_2	491.120	490.804	490.521	490.957	487.343
	E	491.384	490.829	490.546	490.982	487.383

trans- ethyl-mercaptan

		$CH_3CH_2{}^{32}SH$	$CH_3CH_2{}^{34}SH$	$CH_3CH_2{}^{36}SH$	$CH_3CH_2{}^{33}SH$	$CH_3CH_2{}^{32}SD$
ν_{20}, ν_{21}						
0 0	A_1, E	157.835	157.991	158.133	157.915	160.083
0 1	A_2, E	313.572	313.669	313.760	313.622	283.577
1 0	A_2	403.069	403.146	403.218	403.108	403.069
	E	403.067	403.145	403.217	403.107	403.068
0 2	A_1, E	424.286	424.349	424.409	424.318	392.125
1 1	A_1	555.804	555.706	555.622	555.753	522.955
	E	555.807	555.709	555.624	555.756	522.956
2 0	A_1	632.303	632.332	632.362	632.317	628.722
	E	632.342	632.371	632.400	632.357	628.765

Dimethyl sulfide

		$CH_3{}^{32}SCH_3$	$CH_3{}^{34}SCH_3$	$CH_3{}^{36}SCH_3$	$CH_3{}^{33}SCH_3$
ZPVE		187.066	186.905	186.761	186.983
ν_{11}, ν_{15}					
0 0	A_1	0.000	0.000	0.000	0.000
	G, E_1, E_3	0.001	0.001	0.001	0.001
1 0	A_3	176.516	176.530	176.542	176.523
	G	176.500	176.514	176.526	176.507
	E_2, E_3	176.484	176.498	176.511	176.491
0 1	A_2	182.289	181.983	181.709	182.131
	G	182.273	181.967	181.694	182.116
	E_1, E_4	182.258	181.952	181.678	182.100
2 0	A_1	339.979	339.888	339.802	339.933
	G	340.213	340.114	340.018	340.163
	E_1, E_3	340.587	340.494	340.406	340.540
1 1	A_4	341.312	341.058	340.831	341.181
	G	341.712	341.462	341.240	341.583
	E_2, E_4	341.972	341.711	341.478	341.837
0 2	A_1	361.048	360.590	360.185	360.811
	G	361.044	360.584	360.177	360.806
	E_1, E_3	361.040	360.577	360.169	360.800

Concerning the sextic centrifugal-distortion constants of gauche- and trans-ETSH, as mentioned above, an essentially complete disagreement is observed. For the trans form, the experimental parameters are affected by large uncertainties and we also note that the quartic term Δ_K is enlarged as it moves from gauche to trans, while theory predicts the opposite trend. In the case of gauche-ETSH, however, the sextics are well determined. The sextics are very similar to our computed values but are opposite in sign. Based on the available literature for these topics (see, for example, Puzzarini et al. 2012a, 2012b, 2014b), sextic centrifugal-distortion constants computed at the CCSD(T)/cc-pVTZ level usually have an averaged accuracy of about 10% and show maximum discrepancies of about 20%. Therefore, we suggest that we further investigate the rotational spectra of gauche- and trans-ETSH.

3.2. Torsional Energy Levels and Splittings

Table 4 summarizes the lowest torsional energy levels (ground and first torsional states) corresponding to the various isotopic species of g-ETSH, t-ETSH, and DMS. Second torsional states, combination bands, and vibrational partition functions are also provided in our tables. The levels are classified using the representations of the G_6 (ETSH) and G_{36} (DMS) Molecular Symmetry Groups and using two vibrational quanta. For ETSH, ν_{20} and ν_{21} refer to the methyl torsion and the hydroxyl torsion, respectively. For DMS, ν_{15} represents the infrared active mode. For both g-ETSH and t-ETSH, the vibrational ground state A/E splitting caused by the methyl internal rotation is very small. Nevertheless, the vibrational ground state of the hydrogenated isotopologues of g-ETSH splits by $\sim$0.060 cm^{-1} as a consequence of the SH torsion; this splitting largely reduces and becomes very small (only 0.002 cm^{-1}) in the deuterated species. The vibrational ground state of DMS splits into nine components. The levy of degeneracy leads to energy separations of less than 0.001 cm^{-1}. This means that the rotational study of the vibrational ground state of DMS using a treatment for semi-rigid molecules is realistic. For the first and second excited states, non-rigidity needs to be considered.

The variation of the torsional energies with the substitution of ^{32}S for other sulfur isotopes is very small (less than 1 cm^{-1}) because only the hydrogen atoms are significantly displaced during the internal rotation. Nevertheless, the variation is very important for the SH→SD substitution. For example, the OH fundamental levels vary from 188.132 cm^{-1} and 189.613 cm^{-1} to 145.434 cm^{-1} and 145.525 cm^{-1}. The CH_3 fundamentals vary from 254.046 (5) cm^{-1} and 254.068(7) cm^{-1} to 252.600 cm^{-1} and 252.599(8) cm^{-1}. It must be considered that deuterium is a cosmological abundant isotope. CH_3CH_2SD represent the most probable detectable compound.

4. CONCLUDING REMARKS

The present contribution provides an accurate and reliable set of spectroscopic parameters for different isotopic species of DMS and ETSH. For this purpose, state-of-the-art computational methods and approaches have been employed. We thus determined highly accurate rotational and torsional parameters. Available experimental data were used to assess the reliability of our computations. For instance, relative accuracies of 0.1% and 5%–6% were observed for rotational and quartic centrifugal-distortion constants, respectively, and were further improved through empirical scaling. The rotational-spectroscopy characterization was complemented by the calculation of reliable sextic centrifugal-distortion terms. On the whole, our computed parameters allow us to predict rotational transitions with the proper accuracy for future laboratory and/or astronomical investigations.

The A/E splitting of the ground vibrational state of ETSH caused by the A/E torsion is almost negligible. However, a splitting of $\sim$0.060 cm^{-1} due to the SH torsion is observed for the hydrogenated isotopologues of g-ETSH; this splitting is negligible in the deuterated species. In DMS, the low-energy torsional states split into nine components with separations of less than 0.001 cm^{-1}. Therefore, the vibrational ground-state rotational study based on the semi-rigid rotor approximation should be considered reliable; meanwhile, an appropriate treatment accounting for non-rigidity is required to describe the first and second excited states.

The overall conclusion is that based on the good agreement and well-established computational techniques employed, we are confident that the spectroscopic data provided herein are highly accurate and can therefore be useful for the identification of rare isotopologues of DMS and ETSH in the interstellar medium.

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