

COMPUTATIONAL PREDICTION OF THE SPECTROSCOPIC PARAMETERS OF METHANEDIOL, AN ELUSIVE MOLECULE FOR INTERSTELLAR DETECTION

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ABSTRACT

The molecular structure of methanediol has been investigated by means of quantum chemical calculations. Two conformers, corresponding to C_2 and C_s symmetries, respectively, were considered. The C_2 conformer is found to lie about 1.7 (at 298 K) or 2.3 (at 0 K) kcal mol⁻¹ below the C_s conformer. Predictions for their rotational constants, vibrational frequencies, IR intensities, and dipole moments have been provided. The lowest-lying isomer has a very low dipole moment, around 0.03 D, whereas the C_s conformer has a relatively high dipole moment, namely, 2.7 D. The barrier for the $C_s \rightarrow C_2$ process is predicted to be around 0.7–1 kcal mol⁻¹. Based on the energetic results the proportion of the C_s conformer is likely to be negligible under low temperature conditions, such as in the interstellar medium. Therefore, it is predicted that detection by radioastronomy of methanediol would be rather unlikely.

Key words: astrochemistry – infrared: ISM – ISM: molecules – molecular data

Online-only material: color figure

1. INTRODUCTION

Methanediol, also known as methylene glycol, is a rather interesting molecule in different fields. Being the smallest diol, methanediol has been employed as a model compound for the study of the anomeric effect and consequently several theoretical studies (Rodler 1986; Pichon-Pesme & Hansen 1989; Grein & Deslongchamps 1992a, 1992b; Salzner & Schleyer 1993; Chang & Su 1996; Vila & Mosquera 2007; Vila et al. 2011) have been carried out with this purpose. Further, as pointed out by Hazra et al. (2013), methanediol is of atmospheric relevance, because diols are species potentially involved in aerosol growth.

Methanediol is also an interesting molecule in astrochemistry. Some related molecules, such as methanol (Johansson et al. 1984) or ethyl alcohol (Zuckerman et al. 1975), have already been observed in space. Other molecules containing oxygen, including alcohols or aldehydes, have been detected in the interstellar medium. Methanediol is thought to be formed on the surface of interstellar grains through reactions initiated by UV radiation or cosmic rays (Schutte et al. 1993). A suggested synthetic pathway is the reaction between OH and CH₂OH, since these radicals form from water and methanol after photolysis (Garrod et al. 2008). Once in the gas phase after evaporation, methanediol could lead to more complex molecules, some of them of interest in prebiotic chemistry, through ion–molecule reactions. Therefore, knowledge of its molecular structure is important to provide information that could be useful for its eventual conclusive detection in the interstellar medium.

Nevertheless, there are no high-resolution spectroscopic studies of methanediol in the gas phase. Even though it is well known that aqueous solutions of formaldehyde at low concentrations contain methanediol as their major component (Le Botlan 1983), its production in the gas phase has encountered more difficulties. In the liquid phase formaldehyde reacts easily with water to produce methanediol, a process which is subject to considerable barrier in the gas phase (Hazra et al. 2013; Williams 1987;

Wolfe et al. 1995; Böhm et al. 1996). In this context it should be pointed out that a theoretical study by Kent et al. (2003) predicts that methanediol should be thermodynamically and kinetically stable at temperatures lower than 300 K, and in particular for temperatures below 100 K, which are typical of the interstellar medium. This prediction opens the possibility of high-resolution spectroscopic studies, as well as for detecting methanediol in space.

The experimental information about the structure of methanediol is limited to two studies. A matrix-isolation infrared (IR) spectroscopy study carried out by Lugez et al. (1994) where methanediol was produced by the reaction of methanol with ozone upon irradiation. The photolysis of ozone produces O(¹D) atoms which react with methanol. The insertion reaction of O(¹D) atoms with methanol has been very recently studied by Hays & Widicus-Weaver (2013) through computational techniques. These authors conclude that insertion into the C–H bond is the most favored reaction pathway, proceeding through a direct and barrierless mechanism.

Previous theoretical studies (Rodler 1986; Pichon-Pesme & Hansen 1989; Grein & Deslongchamps 1992a, 1992b; Salzner & Schleyer 1993; Chang & Su 1996; Vila & Mosquera 2007; Vila et al. 2011) have concluded that the lowest-lying conformer of methanediol has a gauche conformation (C_2 symmetry) instead of an anti conformation due to the anomeric effect. Another low-lying isomer exists with C_s symmetry corresponding to gauche conformation but with the two hydrogen atoms of the O–H groups pointing to the same side of the OCO plane.

In the present work we provide a computational study of methanediol and its low-lying conformer in order to provide information about its molecular structure which could be helpful for its eventual observation in the laboratory or in the interstellar medium.

2. COMPUTATIONAL METHODS

We have applied several theoretical methods with different basis sets. Only the most interesting results will be reported.

Geometries were optimized at the density functional theory level, employing the popular B3LYP functional (Becke 1988; Lee et al. 1988), as well as different ab initio methods: second-order Møller–Plesset (MP2; Møller & Plesset 1934), quadratic configuration interaction including single and double excitations (QCISD; Pople et al. 1987), and coupled-cluster with singles and doubles and a perturbative inclusion of triple excitations (CCSD(T); Raghavachari et al. 1989). Harmonic vibrational frequencies were also computed at these levels of theory, except for the CCSD(T) method. Anharmonic corrections for vibrational frequencies were estimated at the MP2 level. We have employed the correlated-consistent basis sets of Dunning as well as those from Pople’s group. Only the results obtained with the triple-zeta basis sets augmented with diffuse and polarization functions denoted as aug-cc-pVTZ (Dunning 1989) and 6–311++G(2d, 2p) (Krishnan et al. 1980) will be presented. In the case of CCSD(T) optimizations, we will also report the results obtained with Dunning’s quadruple-zeta (aug-cc-pVQZ) basis set. This level should be reliable enough for predicting the energetics of the system under study.

One of the main objectives of the present work is to provide predictions for the rotational constants of the two lowest-lying conformers of methanediol. For that purpose we have also applied a composite procedure. In the composite scheme the different contributions are evaluated separately and are combined assuming additivity. This type of schemes have been developed at the coupled-cluster level (Heckert et al 2005, 2006; Huang & Lee 2008) providing very good results. In addition, there is another more affordable version of the method from the computational point of view involving essentially geometry optimizations at the MP2 level. This procedure has been successfully applied recently by Barone et al. (2013) and will be adopted in the present work. We refer to the paper by Barone et al. (2013) for a detailed account of the method although a brief outline is given.

The composite scheme assumes additivity of the different contributions for computing the geometrical parameters. The estimated geometrical parameter through the composite scheme, which we will denote as $r(\text{comp})$ is obtained using the following expression (Barone et al. 2013):

$$r(\text{comp}) = r(\text{CBS}) + \Delta r(\text{CV}) + \Delta r(\text{aug}) + \Delta r(T), \quad (1)$$

where the different contributions are defined by the following procedures:

1. $r(\text{CBS})$ corresponds to the complete basis set limit evaluated through the n^{-3} extrapolation formula (Helgaker et al. 1997) applied to the case $n = T, Q$, that is employing the MP2/cc-pVTZ and MP2/cc-pVQZ optimized parameters.
2. $\Delta r(\text{CV})$ accounts for the core–valence electron correlation and is evaluated as

$$\Delta r(\text{CV}) = r(\text{CVTZ, all}) - r(\text{CVTZ, fc}), \quad (2)$$

where $r(\text{CVTZ, full})$ and $r(\text{CVTZ, fc})$ are the optimized geometrical parameters at the MP2 level with the cc-pCVTZ basis set correlating all electrons (full) or only the valence electrons (frozen core, fc). cc-pCVTZ denotes the core–valence correlated-consistent triple-zeta basis set (Woon & Dunning 1995).

3. $\Delta r(\text{aug})$ denotes the correction due to the inclusion of diffuse functions in the basis set and is computed as

$$\Delta r(\text{aug}) = r(\text{augVTZ}) - r(\text{VTZ}), \quad (3)$$

where $r(\text{augVTZ})$ and $r(\text{VTZ})$ correspond to the geometrical parameters optimized at the MP2 level, within the frozen core approximation, with the aug-cc-pVTZ and cc-pVTZ basis sets, respectively.

4. Finally, $\Delta r(T)$ represents a higher-order correlation energy contribution and is evaluated as

$$\Delta r(T) = r(\text{CCSD}(T)) - r(\text{MP2}), \quad (4)$$

thus corresponding to the difference between the optimized geometrical parameters at the CCSD(T)/cc-pVTZ and MP2/cc-pVTZ levels of theory.

For the different levels of calculations employed, as well as for the composite scheme, we have checked its accuracy, evaluating the relative error taking as reference a well-known related molecule such as methanol. We have not scaled the predicted rotational constants. Earlier work for predicting rotational constants for unobserved molecules in the laboratory or in space (DeFrees et al. 1984) employed scaling factors for improving the theoretical predictions. In the present case, the relative errors obtained for a reference molecule, methanol, should be enough to calibrate the accuracy of the employed methods. In the case of vibrational frequencies, for reasons of brevity, we will only provide the unharmonic MP2/aug-cc-pVTZ vibrational frequencies and the scaled harmonic QCISD/aug-cc-pVTZ vibrational frequencies, taking the standard scaling factor for the QCISD level of theory, namely 0.9624. All the calculations were carried out with the Gaussian 09 program package (Frisch et al. 2009).

3. RESULTS AND DISCUSSION

As mentioned in the Introduction, there are two low-lying isomers for methanediol. Both structures, denoted respectively as methanediol- C_2 and methanediol- C_s , are schematically represented in Figure 1, along with the transition state connecting them, denoted methanediol-TS.

We have checked the theoretical methods employed in the present work taking methanol, a closely related molecule to methanediol, as reference. The results for the rotational constants and dipole moment of methanol at different levels of theory are given in Table 1. The computed rotational constants correspond to equilibrium structures. According to the mean relative error all the theoretical methods provide reasonably good results. Perhaps the best results are obtained with the CCSD(T)/aug-cc-pVTZ method, with a mean relative error of 0.13, whereas the aug-cc-pVQZ provides rotational constants slightly different from the experimental values. The composite method also has a small relative error, namely 0.34, suggesting a rather similar quality of predicted rotational constants than the CCSD(T) method. Since the CCSD(T) optimizations are made numerically and can become computationally expensive with large basis sets, the composite method could be a reasonable compromise between quality and cost. It involves also an optimization at the CCSD(T) level, but without inclusion of diffuse functions which can increase sensibly the size of the basis set.

Concerning the dipole moment, all methods provide values close to the experimental one, although it seems that generally the results are better when the aug-cc-pVTZ basis set is employed. Especially, the MP2, QCISD, and CCSD methods with the aug-cc-pVTZ basis set lead to dipole moments in very good agreement with the experimental value of 1.7 D.

The rotational constants and dipole moment for the lowest-lying conformer of methanediol (methanediol- C_2) at different

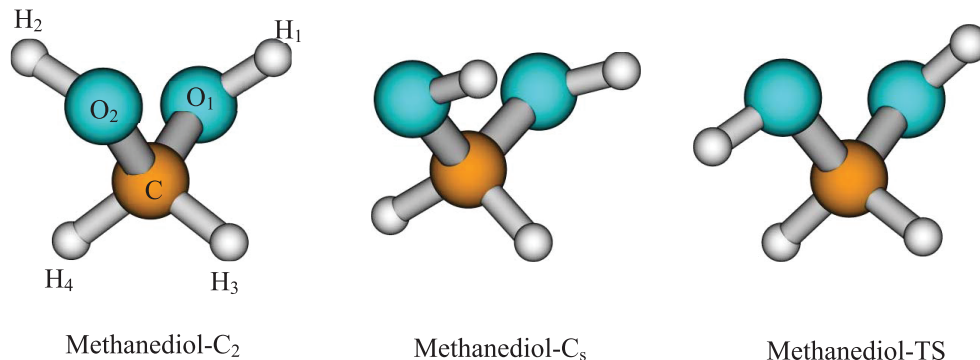


Figure 1. Schematic representation with atom numbering of the methanediol conformers and the transition state for their interconversion. (A color version of this figure is available in the online journal.)

Table 1
Equilibrium Rotational Constants (GHz), Percentage of Mean Relative Error (Denoted as %RE), and Dipole Moment (debye) for Methanol Obtained at Different Levels of Theory

Method	Basis Set	<i>A</i>	<i>B</i>	<i>C</i>	%RE	μ
B3LYP	6-311++G(2 <i>d</i> , 2 <i>p</i>)	128.6912	24.6558	23.8101	0.38	1.7442
	aug-cc-pVTZ	128.6206	24.6747	23.8254	0.36	1.6573
MP2	6-311++G(2 <i>d</i> , 2 <i>p</i>)	129.2598	24.6658	23.8116	0.51	1.7946
	aug-cc-pVTZ	128.5897	24.7449	23.8773	0.49	1.7052
QCISD	6-311++G(2 <i>d</i> , 2 <i>p</i>)	129.0699	24.7056	23.8551	0.53	1.7765
	aug-cc-pVTZ	128.4931	24.8041	23.9404	0.64	1.6951
CCSD(T)	aug-cc-pVTZ	127.8373	24.6803	23.8161	0.13	1.7102 ^a
	aug-cc-pVQZ	128.4743	24.7976	23.9339	0.61	
Composite		128.5462	24.6448	23.7968	0.34	
Experiment ^b		127.6308	24.6842	23.7654		1.700 ^c

Notes.

^a Dipole moment computed at the CCSD level.

^b Herbst et al. (1984).

^c Nelson et al. (1967).

Table 2
Equilibrium Rotational Constants (GHz) and Dipole Moment (debye) for Methanediol-C₂ Obtained at Different Levels of Theory

Method	Basis Set	<i>A</i>	<i>B</i>	<i>C</i>	μ
B3LYP	6-311++G(2 <i>d</i> , 2 <i>p</i>)	41.9569	10.1199	8.9791	0.0582
	aug-cc-pVTZ	41.9718	10.1165	8.9791	0.0534
MP2	6-311++G(2 <i>d</i> , 2 <i>p</i>)	41.9817	10.1490	9.0012	0.0198
	aug-cc-pVTZ	41.9021	10.1956	9.0367	0.0369
QCISD	6-311++G(2 <i>d</i> , 2 <i>p</i>)	41.9383	10.1945	9.0326	0.0205
	aug-cc-pVTZ	41.8914	10.2510	9.0765	0.0368
CCSD(T)	aug-cc-pVTZ	41.6691	10.1835	9.0177	0.0290 ^a
	aug-cc-pVQZ	41.8526	10.2401	9.0669	
Composite		41.9473	10.2610	9.0825	

Note. ^a Dipole moment computed at the CCSD level.

levels of theory are given in Table 2, whereas the corresponding values for methanediol-C_s are provided in Table 3. It is interesting to note that, whereas B3LYP and MP2 rotational constants differ slightly from the rest, the QCISD and composite results are not too different. The CCSD(T)/aug-cc-pVTZ values also differ slightly from those obtained with the composite method. This led us to compute rotational constants for methanediol isomers at the CCSD(T) level with a quadruple-zeta basis set, namely aug-cc-pVQZ. Rotational constants at QCISD/aug-cc-pVTZ, CCSD(T)/aug-cc-pVQZ, and composite levels differ

Table 3
Equilibrium Rotational Constants (GHz) and Dipole Moment (debye) for Methanediol-C_s Obtained at Different Levels of Theory

Method	Basis Set	<i>A</i>	<i>B</i>	<i>C</i>	μ
B3LYP	6-311++G(2 <i>d</i> , 2 <i>p</i>)	43.4129	9.8412	8.8532	2.7961
	aug-cc-pVTZ	43.3832	9.8449	8.8571	2.7152
MP2	6-311++G(2 <i>d</i> , 2 <i>p</i>)	43.4682	9.8629	8.8726	2.8252
	aug-cc-pVTZ	43.5960	9.9563	8.9551	2.7381
QCISD	6-311++G(2 <i>d</i> , 2 <i>p</i>)	43.3707	9.9021	8.9069	2.8039
	aug-cc-pVTZ	43.3309	9.9592	8.9453	2.7255
CCSD(T)	aug-cc-pVTZ	43.1162	9.8908	8.8891	2.7445 ^a
	aug-cc-pVQZ	43.3263	9.9432	8.9345	
Composite		43.4301	9.9578	8.9501	

Note. ^a Dipole moment computed at the CCSD level.

roughly in around 0.01 GHz. The agreement between these three levels of theory gives reliability to their predictions. This means that the QCISD/aug-cc-pVTZ level and the composite method can be reasonable alternatives to the more expensive CCSD(T)/aug-cc-pVQZ method, since they provide quite similar results.

It is worth mentioning that the CCSD(T)/aug-cc-pVTZ level, which has a good performance for methanol, differs in its predictions of the rotational constants for both methanediol conformers. The predicted values for the *B* and *C*

Table 4
Vibrational Frequencies (cm^{-1}) for the Two Methanediol Conformers

Symmetry	Methanediol- C_2			Methanediol- C_s		
	MP2/aug-cc-pVTZ	QCISD/aug-cc-pVTZ		MP2/aug-cc-pVTZ	QCISD/aug-cc-pVTZ	
	Frequency	Frequency	Intensity	Frequency	Frequency	Intensity
a/a'' OH stret.	3648	3711	27.5	3669	3725	18.4
b/a' OH stret.	3648	3710	47.5	3667	3724	43.1
b/a' CH ₂ stret.	3020	3007	33.5	3053	3042	20.4
a/a' CH ₂ stret.	2807	2956	49.9	2846	2926	61.5
a/a' CH ₂ sciss.	1374	1498	0.3	1451	1487	0.3
b/a'' CH ₂ wag	1441	1413	60.7	1416	1405	31.5
a/a' CH ₂ twist	1350	1360	3.4	1359	1380	19.9
b/a'' COH bend	1329	1341	28.7	1336	1343	3.5
a/a'' COH bend	1188	1178	1.6	1131	1138	74.1
b/a'' OCO stret.	1048	1070	243.7	1040	1065	277.5
a/a' OCO stret.	1019	1024	95.2	1048	1044	41.9
b/a' CH ₂ rock	1010	985	20.5	995	976	41.6
a/a' OCO bend	538	545	62.7	530	525	26.4
a/a' COH torsion	368	366	57.5	331	363	116.7
b/a'' COH torsion	333	349	161.9	112	155	72.3

Notes. MP2 values correspond to anharmonic frequencies, whereas QCISD values are harmonic frequencies scaled by a factor 0.9624. IR intensities (km mol^{-1}) have been computed at the QCISD level.

rotational constants employing the composite method or the CCSD(T)/aug-cc-pVQZ level differ from those obtained at the CCSD(T)/aug-cc-pVTZ level in 0.05–0.06 GHz, whereas for the *A* rotational constant a higher discrepancy (around 0.2 GHz) is observed.

This discrepancy is mainly due to the shorter bond distances predicted by the composite method. This fact can be clearly seen in Table 6 of the Appendix, where the geometrical parameters predicted at the CCSD(T) level and composite methods are shown. Most bond and dihedral angles are in reasonable agreement for both methods, but bond distances are always predicted to be shorter by the composite method. A careful analysis of the different contributions for bond distances in the composite method reveals that the main factor contributing to the shortening of the bond distances is the $r(\text{CBS})$ term in Equation (1), corresponding to the extrapolated basis set limit. It seems that increasing the basis set has an important effect, and therefore it is likely that the geometrical parameters obtained through the composite method could be more reliable.

As can be seen in Table 2, the dipole moment for the lowest-lying conformer of methanediol is predicted to be very low, around 0.02–0.04 D at the most reliable levels of theory, as a consequence of two hydroxyl groups directed along opposite sides of the O_1CO_2 plane. This fact suggests that its rotational spectrum should consist of very weak lines, making its detection difficult. This is particularly important for its eventual detection in the interstellar medium. Even if methanediol is produced in the interstellar medium in significant amounts, such a low dipole moment could in practice preclude its detection. On the other hand, the higher-lying isomer, methanediol- C_s , with two hydroxyl groups pointing to the same side of the O_1CO_2 plane, has a relatively high dipole moment (2.7–2.8 D at all levels of theory) which should favor its possible detection provided it can be formed in space. We will come back to this point later when discussing the energetic results.

The predicted vibrational frequencies and IR intensities for both conformers of methanediol are given in Table 4. This information could be useful for an eventual detection in the gas

phase of methanediol through IR spectroscopy. So far only the liquid phase Raman frequencies have been reported for methanediol (Matsuura et al. 1980). We have computed vibrational frequencies and IR intensities at different levels of theory, but in Table 4 we provide only unharmonic frequencies at the MP2/aug-cc-pVTZ and the harmonic values at the QCISD/aug-cc-pVTZ level scaled by a factor of 0.9624 (Computational Chemistry Comparison and Benchmark Data Base 2014). We have tested these levels of calculation for methanol and the results are given in the Appendix (Table 7). In this case a comparison with the gas phase results obtained through IR spectroscopy (Shimanuchi 1972) can be made. A reasonable agreement of vibrational frequencies at both theoretical levels with the experimental values for methanol is observed. In addition, the predicted IR intensities follow in general the experimental qualitative intensities (Shimanuchi 1972).

As can be seen in Table 4 the predicted vibrational frequencies for methanediol are rather similar for both conformers, with the exception of the low frequency torsion movement (349 cm^{-1} for methanediol- C_2 and 155 cm^{-1} for methanediol- C_s , respectively, at the QCISD level). Another difference between the predicted IR spectra for both conformers resides in the IR intensities in the region $1100\text{--}1400 \text{ cm}^{-1}$, as can be seen more clearly in Figure 2, where schematic predicted IR spectra for both conformers are depicted. In both cases the most intense line in the IR spectrum corresponds to the O–C–O asymmetric stretching normal mode. The corresponding frequency for this intense mode is virtually coincident for both conformers (1070 cm^{-1} for the C_2 conformer and 1065 cm^{-1} for the C_s one at the QCISD level). However, for the C_s conformer there is a relatively strong line at higher frequency (1138 cm^{-1}), whereas for the C_2 conformer a strong line is predicted at a lower frequency (1024 cm^{-1}).

The relative energies of methanediol- C_s , taking methanediol- C_2 as reference and computed at different levels of theory, are given in Table 5. We provide the relative energies at 0 K (ΔE), thus including the electronic energy differences and the zero-point energy (ZPE) differences, as well as the relative Gibbs

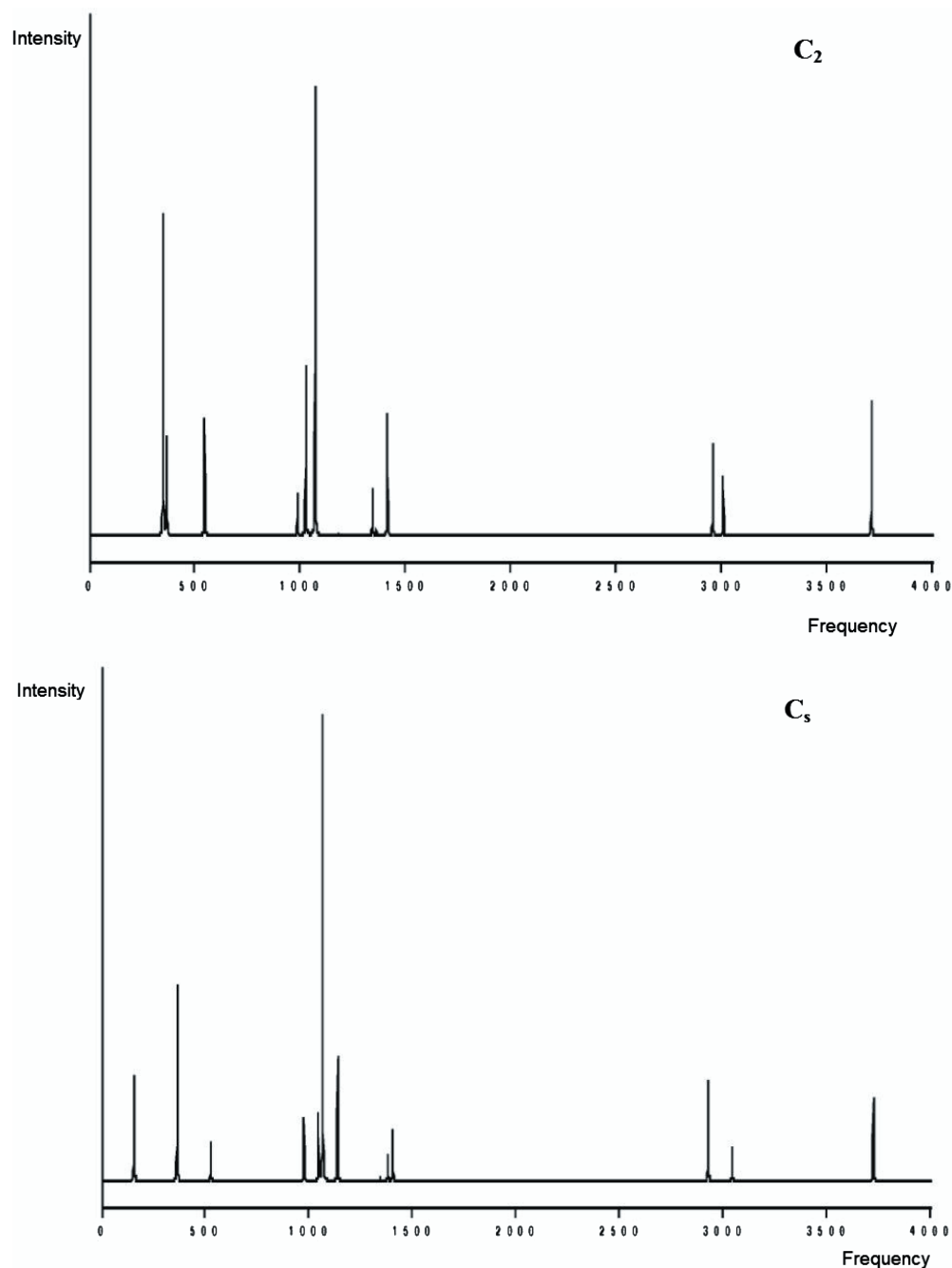


Figure 2. Schematic representation of the predicted IR spectra of the methanediol conformers at the scaled QCISD/aug-cc-pVTZ level.

free energies at 298 K (ΔG). It is readily seen in Table 5 that the relative energies are rather independent of the level of calculation employed, provided a good-quality basis set is used. This is not unexpected, since both conformers just differ in the value of a torsional angle. The final prediction at the highest level of theory, CCSD(T)/aug-cc-pVQZ, does not differ too much from the B3LYP values.

According to our results methanediol- C_s lies about $2.3 \text{ kcal mol}^{-1}$ above the lowest-lying conformer at 0 K, whereas at 298 K the energy difference is reduced to 1.66 K. A simple calculation, assuming equilibrium at 298 K, concludes that about 5.9% of methanediol should correspond to the higher-lying conformer. We have not considered higher temperatures, where the proportion of the C_s conformer would be higher,

because methanediol becomes highly unstable due to its unimolecular decomposition to give formaldehyde. On the other hand, for temperatures in the range of interstellar clouds, namely 20–40 K (which are also close to those relevant for supersonic expansion experiments), the amount of methanediol- C_s should be negligible.

It would be also important to know the magnitude of the barrier for the conversion between both conformers. We have characterized the transition state connecting conformers C_2 and C_s , whose qualitative structure is depicted in Figure 1. An intrinsic reaction coordinate procedure (Fukui 1981) was applied to check that the transition state connects both methanediol conformers. Its geometrical parameters at the QCISD/aug-cc-pVTZ level are given in the Appendix (Table 8). The energies

Table 5

Relative Energies (Including ZPE Corrections), ΔE , and Relative Gibbs Free Energies at 298 K, $\Delta G(298)$, for the Higher-energy Conformer of Methanediol (Methanediol- C_s) and the Transition State for the Conversion between Both Conformers (Methanediol-TS)

Method	Basis Set	Methanediol- C_s		Methanediol-TS	
		ΔE	$\Delta G(298)$	ΔE	$\Delta G(298)$
B3LYP	6-311++G(2d, 2p)	2.3	1.76	3.08	2.74
	aug-cc-pVTZ	2.26	1.65	2.9	2.56
MP2	6-311++G(2d, 2p)	2.48	1.83	3.25	2.90
	aug-cc-pVTZ	2.38	1.72	3.10	2.75
QCISD	6-311++G(2d, 2p)	2.43	1.77	3.11	2.75
	aug-cc-pVTZ	2.35	1.68	2.97	2.62
CCSD(T)	aug-cc-pVQZ	2.32	1.66	3.05	2.71

Note. All values, in kcal mol⁻¹, are given relative to the lowest-lying conformer, methanediol- C_2 .

at 0 K and Gibbs free energies of the transition state, relative to methanediol- C_2 , are also given in Table 5 at different levels of theory. Again, the relative energies are very similar at the different levels of theory employed. At the most reliable

level of theory, namely CCSD(T)/aug-cc-pVQZ, the barrier for the conversion methanediol- $C_2 \rightarrow$ methanediol- C_s is about 2.71 kcal mol⁻¹ at 298 K (3.05 kcal mol⁻¹ at 0 K), whereas for the inverse process amounts to 1.05 kcal mol⁻¹ at 298 K (0.73 kcal mol⁻¹ at 0 K). Roughly speaking these barriers correspond, depending on the temperature, to nearly 800–1000 cm⁻¹ for $C_2 \rightarrow C_s$ and 250–370 cm⁻¹ for $C_s \rightarrow C_2$. This would mean that the higher-lying isomer of methanediol could easily convert into the lowest-lying one even at low temperatures such as those reigning in the interstellar medium. In fact, it is difficult to imagine a feasible process under interstellar conditions (mainly exothermic) that could lead to methanediol- C_s and prevent its evolution toward the C_2 conformer.

Therefore, it seems that the laboratory characterization or even a radioastronomical observation of the higher-lying isomer would be quite unlikely. As we have mentioned before, it has a relatively high dipole moment, but its facile conversion into the most stable conformer should make this species difficult to detect. On the other hand, the lowest-lying isomer of methanediol is characterized by a very low dipole moment. This should make difficult a possible radioastronomical detection, and even its laboratory characterization through rotational spectroscopy, given the low intensity of its rotational lines.

Table 6

Geometrical Parameters (Distances in Angstroms, Angles in Degrees) for the Two Methanediol Conformers Obtained with the CCSD(T)/aug-cc-pVTZ (TZ), CCSD(T)/aug-cc-pVQZ (QZ), and Composite Methods

Parameter	Methanediol- C_2			Methanediol- C_s		
	CCSD(T)/TZ	CCSD(T)/QZ	Composite	CCSD(T)/TZ	CCSD(T)/QZ	Composite
$d(C-O)$	1.4085	1.4044	1.4027	1.4092	1.4052	1.4037
$d(O-H)$	0.9639	0.9612	0.9601	0.9624	0.9597	0.9590
$d(C-H_3)$	1.0922	1.0910	1.0884	1.0961	1.0951	1.0920
$d(C-H_4)$	1.0922	1.0910	1.0884	1.0876	1.0864	1.0845
$\angle O_1CO_2$	112.61	112.59	112.52	113.61	113.64	113.44
$\angle H_1O_1C$	107.42	107.59	108.48	108.87	109.06	109.97
$\angle H_3CO_2$	105.29	105.30	105.35	110.47	110.46	110.43
$\angle H_4CO_1$	105.29	105.30	105.35	106.00	106.01	106.08
$\angle H_1O_1CO_2$	61.75	61.83	61.93	78.63	78.48	79.98
$\angle H_2O_2CO_1$	61.75	61.83	61.93	-78.63	-78.48	-79.98
$\angle H_3CO_2O_1$	122.08	122.09	121.88	124.79	124.79	124.58
$\angle H_4CO_1O_2$	122.08	122.09	121.88	116.0	116.03	116.05

Table 7

Vibrational Frequencies (cm⁻¹) for Methanol

Symmetry	MP2/aug-cc-pVTZ	QCISD/aug-cc-pVTZ		Experiment ^a	
	Frequency	Frequency	Intensity	Frequency	Intensity
a' OH stret.	3687	3739	30.9	3681	Medium
a' CH ₃ stret.	3047	3026	23.7	3000	Medium
a'' CH ₃ stret.	2997	2971	46.6	2960	Strong
a' CH ₃ stret.	2901	2916	53.7	2844	Strong
a' CH ₃ deform.	1490	1477	4.7	1477	Medium
a'' CH ₃ deform.	1483	1468	3.0	1477	Medium
a' CH ₃ deform.	1442	1444	3.9	1455	Medium
a' \angle COH bend	1322	1339	25.6	1345	Strong
a'' CH ₃ rock	1155	1144	0.8	1165	
a' CH ₃ rock	1069	1054	5.1	1060	Weak
a' torsion	1029	1030	109.6	1033	Very strong
a'' torsion	241	277	103.3	200–295	

Notes. MP2 values correspond to anharmonic frequencies, whereas QCISD values are harmonic frequencies scaled by a factor 0.9624. IR intensities (km mol⁻¹) have been computed at the QCISD level.

^a Shimanuchi (1972).

Table 8
Geometrical Parameters (Distances in Angstroms, Angles in Degrees) for the Transition State Connecting Both Methanediol Conformers Obtained at the QCISD/aug-cc-pVTZ Level

Parameter	QCISD
$d(\text{C}-\text{O}_1)$	1.3919
$d(\text{C}-\text{O}_2)$	1.4151
$d(\text{O}_1-\text{H}_1)$	0.9605
$d(\text{O}_2-\text{H}_2)$	0.9589
$d(\text{C}-\text{H}_3)$	1.0954
$d(\text{C}-\text{H}_4)$	1.0906
$\angle \text{O}_1\text{CO}_2$	109.04
$\angle \text{H}_1\text{O}_1\text{C}$	107.95
$\angle \text{H}_2\text{O}_2\text{C}$	109.12
$\angle \text{H}_3\text{CO}_2$	109.47
$\angle \text{H}_4\text{CO}_1$	106.29
$\angle \text{H}_1\text{O}_1\text{CO}_2$	61.46
$\angle \text{H}_2\text{O}_2\text{CO}_1$	152.74
$\angle \text{H}_3\text{CO}_2\text{O}_1$	121.48
$\angle \text{H}_4\text{CO}_1\text{O}_2$	119.97

4. CONCLUSIONS

In this work we investigated by means of quantum chemical calculations the molecular structure of methanediol. The lowest-lying conformer, of C_2 symmetry with the two hydroxyl groups pointing in opposite directions of the OCO plane, is found to lie about 1.7 (298 K) or 2.3 kcal mol⁻¹ (0 K) below the C_s conformer, which has the two hydroxyl groups at the same side of the OCO plane. Predictions for their rotational constants, vibrational frequencies, IR intensities, and dipole moments have been provided. We have also studied the barrier for the interconversion between both conformers, which is predicted to be around 0.7–1 kcal mol⁻¹ for the $C_s \rightarrow C_2$ process.

It is found that the lowest-lying isomer has a very low dipole moment (around 0.03 D), which should hinder its possible detection by radioastronomy in space. On the other hand, the C_s conformer has a relatively high dipole moment (around 2.7 D). However, based on the energetic results for the relative stability of both conformers and the interconversion barrier, it is quite unlikely that the C_s conformer could be eventually detected in the interstellar medium. Only at temperatures approaching standard conditions would a significant proportion of the higher-lying conformer be present. Nevertheless, it should be taken into account that under such conditions methanediol is unstable toward the production of formaldehyde. It seems that methanediol would probably continue as an elusive molecule for high-resolution spectroscopy. IR spectroscopy is probably more likely to succeed in characterizing methanediol.

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APPENDIX

Additional tables (Tables 6, 7, and 8) providing detailed geometrical parameters for both methanediol conformers and the transition state connecting them, as well as the computed and experimental vibrational frequencies, are given in this appendix.

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