Tracing Prebiotic Molecules: Rotational Spectroscopy of Deuterated Glycolaldehyde and (Z)-1,2-Ethenediol

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Abstract

Glycolaldehyde, an important prebiotic molecule, along with its mono deuterated species and its higher energy tautomer, (*Z*)-1,2-ethenediol, have been detected in the Interstellar Medium. Although the elemental D/H ratio in the Universe is only $\sim 1.6\times10^{-5}$, the deuterium relative abundance in interstellar molecules might be by far larger than this. As such it provides a remarkable and almost unique diagnostic tool. In particular, it might help to elucidate the reaction mechanisms that lead to the formation of the so-called Complex Organic Molecules. It is therefore crucial to extend the census of the interstellar deuterated molecules. To this aim, in this work, we present for the first time a spectroscopic investigation of the rotational spectra of the CHDOD−CHO bi-deuterated variant of glycolaldehyde and of mono- and bi-deuterated species of (*Z*)-1,2-ethenediol (CHOD=CHOD, CHOD=CHOH, CHOH=CHOD). For each species, more than a hundred transitions have been assigned. Their analysis led to the accurate determination of all rotational constants as well as quartic and sextic centrifugal distortion terms, thus providing spectroscopic line catalogues suitable for supporting astronomical searches. In addition, the rotational constants of the bi-deuterated glycolaldehyde isotopologue studied in this work allowed us to improve the semi-experimental equilibrium structure determination for this molecule.

Introduction

Deuterium fractionation, namely the enrichment of the deuterium abundance ratio in the isotopic distribution of molecules, is a powerful tool to investigate the chemistry occurring in the Interstellar Medium (ISM). In those regions of the ISM characterized by extremely low temperature and pressure, the D/H ratio of molecules has been found to be much higher than the elemental one,[1] which is estimated to be on the order of 10^{-5}.[2] This is due to several factors that make the enrichment of deuterium atoms in molecules favorable. In particular, in cold molecular clouds –where the average temperature is about 10 K– the abundance of the main source of deuterium atoms, namely H_2D^+, is enhanced with respect to that of H_3^+. In fact, H_2D^+ is formed from the H_3^+ + HD reaction, and the reverse process is endothermic due to the lower zero-point energy (ZPE) contribution of H_2D^+ with respect to H_3^+ (mainly related to the higher mass of the former).[1]

The knowledge of the deuteration degree of molecules can provide information on their formation mechanisms and can reveal whether they have been formed in the gas phase or on the icy surface of interstellar dust grains.[3,4] It is also a valuable tool to study and understand the complex processes that lead to the formation of new protostars and planetary systems as well as asteroids, meteorites, and comets.[5] Interestingly, the chemical composition of these objects might help to obtain relevant information concerning ques-

tions related to the origin of life. Indeed, interstellar Complex Organic Molecules (COMs) –that is, carbon-containing molecular species with six atoms or more[6]– formed during the protostellar phase could have been delivered to early Earth through some heavy meteorite or cometary bombardments when its atmosphere was still very rarefied.[7–10] In this respect, a valuable support in elucidating interstellar chemistry and its role in the origin of life is the detection of new deuterated COMs.

Glycolaldehyde ($CH_2OH-CHO$) is one of the most studied COMs. In terms of chemical structure, it is the simplest α-hydroxy-aldehyde and can be considered an important prebiotic molecule. Indeed, experimental studies have proven that simple organic molecules, such as glycolaldehyde, are key ingredients for the synthesis of ribonucleotides, the building blocks of RNA.[11] Within the RNA-World theory,[12] RNA is thought to be the precursor of DNA in its genetic and metabolic functions on the prebiotic Earth. Glycolaldehyde has been detected in the ISM for the first time in 2000, towards the Galactic center source Sagittarius B2(N) through millimeter-wave rotational transitions[13] and, later on, in the G31.41+0.31 hot molecular core.[14] Glycolaldehyde has also been detected towards the Solar-type protostar Class 0 protostellar binary IRAS 16293-2422A and IRAS 16293-2422B,[15,16] the star forming regions MM1 and MM2 in the NGC6334I complex,[17] and the Class 0 young stellar object NGC 1333 IRAS2A.[18] In 2016, all possible forms of singly-deuterated glycolaldehyde ($CH_2OD-CHO$, $CH_2OH-CDO$, and $CHDOH-CHO$) have been detected as well in the ISM, more precisely in the Class 0 protostellar binary IRAS 16293-2422B.[19] These observations prompted new studies on the deuterium fractionation of glycolaldehyde with the aim of understanding whether the formation route of this COM involves a gas-phase path or occurs on dust grains.[20] These two hypotheses are still highly debated and several chemical models have been proposed and compared with the observed abundances in various regions of the ISM.[21–23]

Very recently, the less stable enol form of glycolaldehyde, namely (*Z*)-1,2-ethenediol (CHOH=CHOH), has also been detected in the ISM, towards the G+0.693-0.027 molecular cloud located in the Galactic center.[24] According to Rivilla et al.,[24] glycolaldehyde and (*Z*)-1,2-ethenediol have an abundance ratio of ~ 5 in such molecular cloud. Ethenediol is thought to be a highly reactive, key intermediate in the synthesis of prebiotic sugars.[25] Although its formation mechanism in the ISM has not been disclosed yet, there is some evidence that 1,2-ethenediol can be formed upon cosmic-ray irradiation of interstellar ice containing methanol or methanol-carbon monoxide mixture.[26] However, to shed light on the formation routes of both glycolaldehyde and 1,2-ethenediol as well as to unveil the interstellar chemistry linking them, more astronomical observations of these species are needed, also including their deuterated isotopologues.

To support astronomical observations, in this work, we present the first spectroscopic characterization of the CHDOD−CHO variant for doubly-deuterated glycolaldehyde and of the mono- and bi-deuterated forms of (*Z*)-1,2-ethenediol. In all its steps, experiment has been supported by highly-accurate quantum-chemical calculations. Using the newly determined spectroscopic parameters of CHDOD−CHO, we have also improved the semi-experimental (SE) equilibrium structure of glycolaldehyde available in the literature.[27]

This paper is organized as follows. In the next section, the methodology is introduced in some detail. This concerns the sample preparation, experimental measurements, and quantum-chemical calculations. Subsequently, the results are presented and discussed. In Results section, starting from the spectral assignments of the gas mixture (*vide infra*), we proceed toward the accurate spectroscopic characterization of the species considered in this work. In the Discussion section, the comparison between experiment and theory is addressed together with the presentation of the revised SE equilibrium structure of glycolaldehyde. The main outcomes of this work are summarized in the Conclusion section.

Methodology

Chemical Preparation

Bis-*exo*-5-norbornene-2,3-diol was synthesized as described by Maier et al..[28] Subsequently, to obtain its deuterated form, deuteromethanol (CH_3OD, 5.0 g, 150 mmol) was added under dry nitrogen to a small amount of the former compound (5.0 g, 40 mmol) and stirred for 5 min at room temperature. Methanol was removed under vacuum (0.1 mbar, room temperature) and the sequence repeated twice, thus leading to bis-*exo*-5-norbornene-

2,3-diol-d_2 in a 98% yield and an isotopic purity better than 97%. The target molecules of this work, namely deuterated forms of glycolaldehyde and its tautomer (*Z*)-1,2-ethenediol, were produced through retro Diels-Alder reaction of bis-*exo*-5-norbornene-2,3-diol-d_2 induced by flash vacuum pyrolysis (FVP). The process led to the formation of cyclopentadiene, mono- and bi-deuterated glycolaldehyde, and mono- and bi-deuterated (*Z*)-1,2-ethenediol. To exploit FVP at best, the solid precursor was heated, using a heating-tape, at temperatures around 50°C in order to make its vapors flowing inside a 30 cm long quartz tube surrounded by a tubular oven set at 750°C. The same setup was already employed to produce other unstable species of astrochemical interest.[29–31] As in previous experiments, the quartz tube was connected to the millimiter/submillimiter-wave frequency-modulation spectrometer (see next section), so that the vapors of the pyrolysis products could flow directly through the absorption cell. The optimal working-pressure inside the cell was found to be in the 10-20 μbar range.

Experimental Details

The rotational spectrum of the gas mixture resulting from FVP was acquired in two distinct frequency regions, namely 80-115 GHz and 250-300 GHz, using a millimeter/submillimeter-wave frequency-modulation spectrometer.[32,33] The radiation source consists of a Gunn diode emitting in the 80-115 GHz range, whose spectral coverage has also been extended up to 240-345 GHz owing to a passive frequency tripler (Virginia Diodes Inc., WR3.4X3). A Phase Lock Loop (PLL) system ensured the stability and accuracy of the emitted radiation, which was sine-wave modulated at $f = 16$ kHz. All the frequency synthesizers used in the PLL were referred to a rubidium atomic clock which guaranteed a frequency accuracy of 0.001 ppb. The output radiation was detected by two zero-bias detectors (Virginia Diodes Inc.), WR10ZBD in the 80-115 GHz spectral range and WR3.4ZBD for the frequency interval between 250 and 300 GHz. The detected signal was finally amplified, filtered, and de-modulated at twice the modulation frequency ($2f$ detection scheme) by a lock-in amplifier. Based on the signal-to-noise ratio (S/N) in the different frequency ranges and the recorded linewidths, the experimental uncertainties of the measured lines were estimated to range between 15 and 30 kHz.

Computational Details

The assignment of the rotational spectra of doubly-deuterated glycolaldehyde, and those of the singly- and doubly-deuterated isotopologues of (*Z*)-1,2-ethenediol, was supported by simulations based on computed spectroscopic parameters.

As far as the singly- and doubly-deuterated isotopologues of (*Z*)-1,2-ethenediol are concerned, the computational characterization followed the same strategy adopted by Melosso et al.[34] to assign the rotational spectrum of their parent species. To summarize, the equilibrium structure obtained in ref. 34 by exploiting the so-called CCSD(T)/CBS+CV composite scheme[35,36] was employed to straightforwardly derive the equilibrium rotational constants. In the scheme above, CCSD(T) stands for coupled-cluster singles and doubles and a perturbative treatment of triple excitations,[37] CBS denotes the extrapolation to the complete basis set and CV indicates the incorporation of the core-correlation effects (the reader is referred to refs. 34,35 for more details). Equilibrium rotational constants were then augmented by vibrational corrections to estimate the ground-state rotational constants required for spectral simulations. Calculations of such corrections required the exploitation of the VPT2 treatment based on a cubic force field (VPT2 stands for vibrational perturbation theory to second order),[38] which was evaluated at the fc-MP2/cc-pVTZ[39] level of theory (MP2 is second-order Møller-Plesset perturbation theory[40] and fc denotes the frozen-core approximation). As a byproduct, quartic and sextic centrifugal distortion constants were also obtained.

To improve the computed spectroscopic parameters, a scaling procedure based on the available data for the main isotopic species has been performed:

$$X^i_{scal} = X^i_{calc} \times (X^p_{exp}/X^p_{calc}) \,, \qquad (1)$$

where X represents a generic rotational constant, i and p refer to isotopic substituted and parent molecule, respectively; *scal*, *exp* and *calc* denote the scaled, experimental, and calculated values, respectively.

Moving to glycolaldehyde, the availability of the SE equilibrium structure (*vide infra*)[27] allowed us to straightforwardly derive accurate equilibrium rotational constants for the bi-deuterated

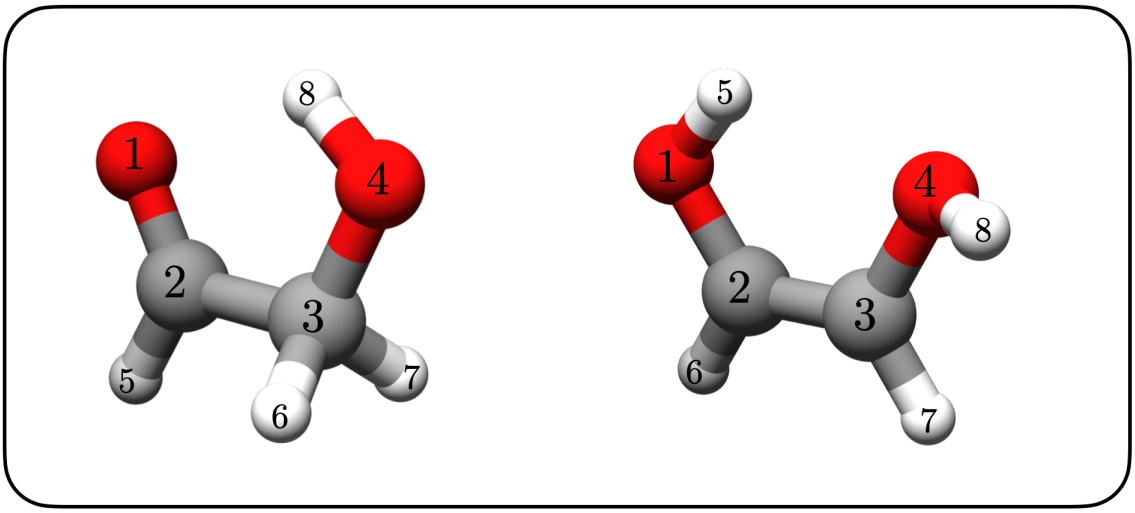

Figure 1: Structure and atom labeling of the most stable conformers of glycolaldehyde (left) and (*Z*)-1,2-ethenediol (right). In this work, the isotopologue of glycolaldehyde deuterated in positions 6 (or 7, these being equivalent) and 8 is labeled as CHDOD−CHO. (*Z*)-1,2-ethenediol deuterated in positions 5 and 8 is denoted as CHOD=CHOD, while when deuterated in position 5 or 8 is labeled as CHOD=CHOH and CHOH=CHOD, respectively.

species. As above, vibrational corrections to these latter as well as quartic and sextic centrifugal distortion constants were computed at the fc-MP2/cc-pVTZ level. For comparison purposes, the CCSD(T)/CBS+CV equilibrium geometry was also calculated.

As mentioned in the Introduction, the data obtained for CHDOD−CHO were employed to further improve the SE equilibrium structure (r_e(SE)) of glycolaldehyde. This type of equilibrium geometry is determined from a least-squares (LSQ) fit of the molecular structural parameters to the SE equilibrium inertia moments I_e for a significant number of isotopologues of the considered molecule, with the SE I_e values being straightforwardly derived from the corresponding SE equilibrium rotational constants B_e(SE).[41,42] These latter are obtained by correcting the experimental ground-state rotational constants for computed vibrational corrections, as follows:

$$\begin{aligned} B_e^i(\mathrm{SE}) &= B_0^i(\mathrm{exp}) - \Delta B_{\mathrm{vib}}^i(\mathrm{theo}) \qquad (2) \\ &= B_0^i(\mathrm{exp}) + \frac{1}{2}\sum_r \alpha_r^i(\mathrm{theo}) d_r \ , \end{aligned}$$

where i refers to the inertial axis ($i = a, b, c$); B_0^i(exp) and $\Delta B_{\mathrm{vib}}^i$(theo) are the experimental ground-state rotational constants and the computed vibrational corrections, respectively. In the equation above, α_r^i(theo) denotes the calculated vibration-rotation interaction constants. The sum runs over all the r vibrational modes, d_r being their degeneracy.

All calculations were performed by employing the CFOUR quantum-chemistry package.[43,44] The `xrefit` module of CFOUR was employed for the LSQ fit.

Results

FVP of bis-*exo*-5-norbornene-2,3-diol-d_2 led to the production of a large number of species, some of which were readily identified in the recorded spectra. They include cyclopentadiene, all the singly-deuterated forms of glycolaldehyde as well as its doubly-deuterated form CHDOH−CDO. The identification has been made possible thanks to extensive literature data[45–47] and with the help of the Cologne Database for Molecular Spectroscopy (CDMS).[48] The analysis of unknown features started with the search of one of our target molecules: the CHDOD−CHO variant of deuterated glycolaldehyde. To this aim, its rotational spectrum has been simulated, based on computed spectroscopic constants (see previous section), using the `PGOPHER` software.[49]

Glycolaldehyde, shown in the left panel of Fig-

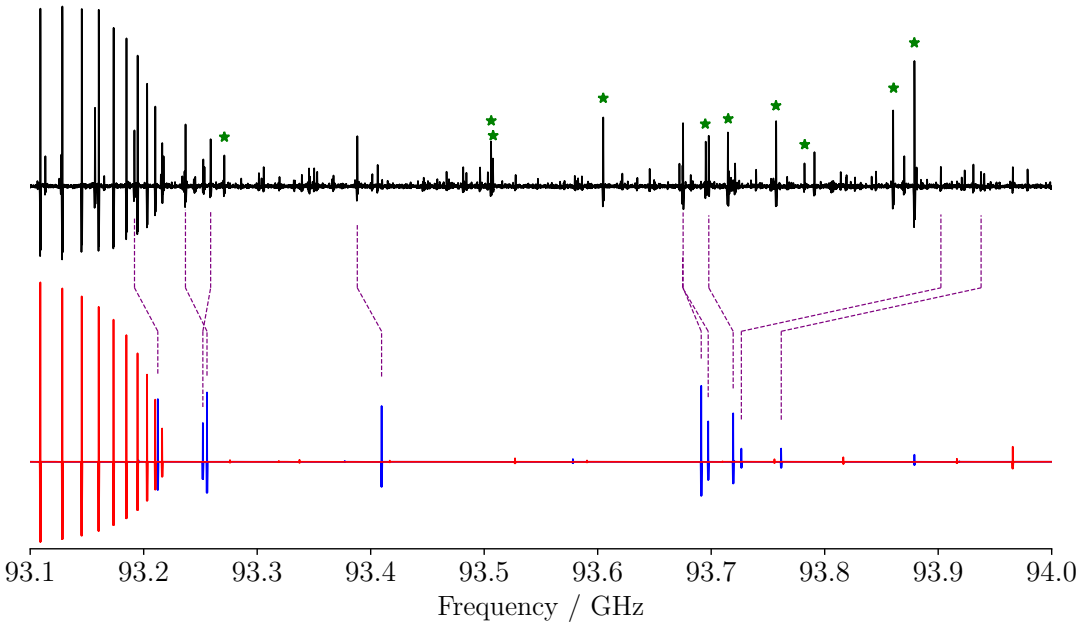

Figure 2: Portion of the millimeter-wave spectrum between 93 and 94 GHz. The experimental spectrum (black trace) is compared with the spectral simulation of cyclopentadiene (red trace) and the CHDOD−CHO deuterated variant of glycolaldehyde (blue trace, based on computed spectroscopic parameters), assuming a relative abundance of 30:1. The dashed lines indicate the correspondence of each computed transition to the experimental feature. Asterisks mark those lines that were later assigned to doubly-deuterated ethenediol.

ure 1, is a nearly prolate asymmetric rotor (the asymmetry parameter κ being about -0.7) with a large dipole moment component along the b axis, $\mu_b = 2.33(1)$ D, and a small component along the a axis, $\mu_a = 0.262(2)$ D.[50] According to this, in the simulation of the lowest frequency interval considered (i.e. 80-115 GHz), the most intense features of CHDOD−CHO are the Q-branch ($\Delta J = 0$), b-type transitions with $\Delta K_a = 1$. The accuracy of our calculations allowed us to easily identify many of these lines in the experimental spectra, with deviations from the computed values of few tens of MHz. As an example, Figure 2 shows the comparison between experimental and predicted transitions in a portion of spectrum between 93 and 94 GHz; for the features belonging to CHDOD−CHO, the correct correspondence between experiment and simulation is made evident. All the assigned lines are b-type transitions with J values ranging from 6 to 30 and K_a values from 1 to 20, all belonging to the Q branch. These assignments permitted to refine some of the initial spectroscopic constants, such as A, C, and few centrifugal distortion constants, but the B rotational constant remained not determinable. At higher frequencies (250-300 GHz), instead, the spectrum is dominated by R branch transitions ($\Delta J = +1$) which involve J values up to 65. Therefore, their assignment allowed the determination of the B rotational constant and several additional centrifugal distortion terms. No a-type transitions could be identified unambiguously. The final fit was carried out using the `SPFIT` subroutine of the `CALPGM` suite of programs,[51] with all rotational constants, the entire set of quartic centrifugal distortion parameters, and all sextic terms but h_3 of CHDOD−CHO being accurately determined for the first time. The results are collected in Table 1.

Following the same strategy as above, the bi-deuterated CH_2OD−CDO and CD_2OH−CHO species have also been searched for, but we did not find any clear evidence of their rotational features in the recorded spectra. Instead, because of the good signal-to-noise ratio observed for CHDOD−CHO, it was possible to identify and assign about 150 rotational transitions belonging to this species in its $v_{18} = 1$ vibrational excited state, which lies 198 cm^{-1} above the ground state (at the fc-MP2/cc-pVTZ level of theory). To search for the rotational transitions in the $v_{18} = 1$ state, we employed our computed vibration-rotation interaction constants and the set of centrifugal distortion

Table 1: Spectroscopic parameters of bi-deuterated CHDOD−CHO glycolaldehyde (Watson's S reduction, I^r representation).

		Ground state		$v_{18}=1$	
Parameter	Unit	Experiment[a]	Theory[b]	Experiment[a]	Theory[c]
A	MHz	16125.7981(3)	16126.249	16133.4247(4)	16132.452
B	MHz	6364.9744(2)	6362.635	6323.0180(4)	6321.617
C	MHz	4760.3135(2)	4759.166	4753.6608(4)	4753.371
D_J	kHz	5.4539(2)	5.339	5.6143(3)	5.4539
D_{JK}	kHz	−11.8537(4)	−10.927	−12.149(1)	−11.8537
D_K	kHz	26.789(2)	24.370	27.576(2)	26.789
d_1	kHz	−1.71894(3)	−1.685	−1.75050(9)	−1.71894
d_2	kHz	−0.14457(1)	−0.141	−0.13907(5)	−0.14457
H_J	mHz	−8.32(8)	−8.725	−8.32	−8.32
H_{JK}	mHz	105.6(1)	103.957	109.3(5)	105.6
H_{KJ}	mHz	−403.(1)	−367.658	−403.	−403.
H_K	mHz	466.(2)	408.797	466.	466.
h_1	mHz	−2.80(1)	−2.904	−2.80	−2.80
h_2	mHz	0.464(5)	0.405	0.464	0.464
h_3	mHz	0.107	0.107	0.107	0.107
No. data		364		147	
$J_{\max}, K_{\mathrm{a}\max}$		65, 21		48, 15	
rms error	kHz	23.6		31.3	

[a] Values in parentheses are one standard deviation and refer to the last digits. Parameters without uncertainties are held fixed at the corresponding computed value.
[b] Equilibrium rotational constants from the SE equilibrium structure from ref. 27 augmented by vibrational corrections at the fc-MP2/cc-pVTZ level of theory. Quartic and sextic centrifugal distortion constants at the fc-MP2/cc-pVTZ level.
[c] Equilibrium rotational constants from the SE equilibrium structure from ref. 27 augmented by vibrational corrections (incorporating the additional contribution of α^i_{18}) at the fc-MP2/cc-pVTZ level of theory. For quartic and sextic centrifugal distortion constants, the experimental vibrational ground-state values are used.

constants obtained from the ground state analysis. A further confirmation of the correct assignment was provided by the line intensity of such transitions, which are expected to be about three times weaker than the corresponding ground state lines, in accordance with the energy difference between the states. Their analysis led to an accurate spectroscopic characterization and the resulting parameters are listed in Table 1 together with the corresponding estimated values.

While the comparison between experiment and theory is discussed in the next section, here we follow the thread of the spectral assignment. The next step consisted in investigating the presence of the other target molecule of this work. Moving to (*Z*)1,2-ethenediol, the first species considered is the bi-deuterated isotopologue, CHOD=CHOD, as this is supposedly the main product obtained in the pyrolysis of bis-*exo*-5-norbornene-2,3-diol-d_2.

(*Z*)-1,2-ethenediol, shown in the right panel of Figure 1, is an asymmetric rotor in the prolate limit ($\kappa = -0.8$) with a prominent *a*-type spectrum ($\mu_a = 1.96\,\mathrm{D}$, $\mu_b = 0.62\,\mathrm{D}$, and $\mu_c = 0.97\,\mathrm{D}$).[34] In both frequency ranges considered, *a*-type transitions belonging to the *R* branch could be identified within 30-200 MHz from the predicted line positions based on our best estimate spectroscopic parameters (with the rotational constants scaled as explained in the Computational detail section). As an example, Figure 3 shows a portion of rotational spectrum around 94 GHz where the correspondence between the predicted lines and their experimental counterparts is made evident. These are all *a*-type transitions of the *R* branch with upper $J = 11$ or

10. The assigned transitions involve rotational energy levels with J values ranging from 7 to 10 and K_a values from 0 to 10 in the 80-115 GHz frequency interval, and from J=21 to J=34 and from K_a=0 to K_a=24 in the 250-300 GHz range. No *b*- or *c*-type transitions could be assigned safely.

The spectral analysis of CHOD=CHOD led to the assignment of 228 lines, which allowed the first determination of the entire set of rotational and quartic centrifugal distortion constants, and the H_J, H_{JK} and H_{KJ} sextic terms. The results are reported in Table 2. It should be noted that, while for the parent species a splitting of each rotational transition was observed because of a tunneling motion between two equivalent positions of the hydroxy groups,[34] for the doubly-deuterated species such a splitting is too small to be resolved. Indeed, the heavier masses involved in the case of CHOD=CHOD noticeably reduces the tunneling effects. This outcome is easily explained by considering the small splitting observed for the parent species ($\sim$ 300 kHz) and the fact that, for a similar rotor such as ethylene glycol, the splitting decreases by more than one order of magnitude when moving from the main species to the doubly-deuterated isotopologue.[52]

After the assignment of the transitions belonging to CHDOD−CHO and CHOD=CHOD, the acquired spectra were still dense of unassigned transitions. The identification of the singly-deuterated forms of glycolaldehyde suggested that the mono-deuterated forms of (*Z*)-1,2-ethenediol (CHOD=CHOH and CHOH=CHOD, not equivalent because of the conformation of this species; see Figure 1) could be present in the gas mixture as well. Therefore, their rotational spectra have been simulated based on the scaled-computed spectroscopic constants. While for the bi-deuterated species we could only rely on the parent isotopologue for the scaling procedure, in this case, the scaled rotational constants were obtained by taking the arithmetic mean of the scaled-theoretical values derived using the parent species and those exploiting the parameters of the doubly-deuterated form. Instead, the quartic centrifugal distortion constants were simply estimated as arithmetic mean of those of CHOH=CHOH and CHOD=CHOD. The predicted transition frequencies resulted to be accurate within a few dozen of MHz. Rotational transitions of both mono-deuterated species were identified in the frequency range 250-300 GHz and several transitions, all of them being *a*-type, have been assigned up to $J = 32$ and $K_a = 22$. Table 3 reports the spectroscopic parameters determined for these species, namely the rotational constants, the entire set of quartic centrifugal distortion constants, and the H_{JK} and H_{KJ} sextic terms.

Discussion

Although glycolaldehyde and 1,2-ethenediol are thought to be two important intermediates towards the formation of sugars in space, there is still much to understand about their interstellar chemistry. As mentioned in the Introduction, the D/H ratio for a given astrophysical object allows for gaining insights into its physical properties and chemical reactivity. It is therefore of crucial importance to detect deuterated species of glycolaldehyde and 1,2-ethenediol and derive their abundance. In this respect, to support their future astronomical observations, we have carried out a detailed analysis of their rotational spectra at millimeter-wavelengths. This allowed us to provide line catalogues that fulfil the accuracy requirements for radioastronomical searches: line transitions are predicted with uncertainties with 100–500 kHz up to 500 GHz.

Another important aspect of this work is the synergy between experiment and theory. Indeed, accurate quantum-chemical calculations provided a valuable support to the experimental characterization. Therefore, a discussion on the comparison between computed and experimental spectroscopic parameters is deserved. As far as the doubly-deuterated glycolaldehyde CHDOD−CHO is concerned, the availability of the SE equilibrium structure allows for obtaining very accurate prediction for rotational constants. Indeed, for the vibrational ground state, the average deviation between experimental and predicted rotational constants is around 0.02%; as far as the $v_{18} = 1$ state is concerned, the difference is lower than 0.03%. Such a comparison points out the importance of having accurate equilibrium structures when aiming at the reliable prediction of rotational spectra. Moving to the centrifugal distortion constants, for the ground state, quartic and sextic terms show average deviations of about 4.7% and 7.3%, respectively, which are in line with what expected from the literature on this topic.[42,53,54]

A good accuracy has also been obtained for the predicted spectroscopic constants of the mono- and bi-deuterated forms of (*Z*)-1,2-ethenediol. If the pure computational results are considered (i.e.,

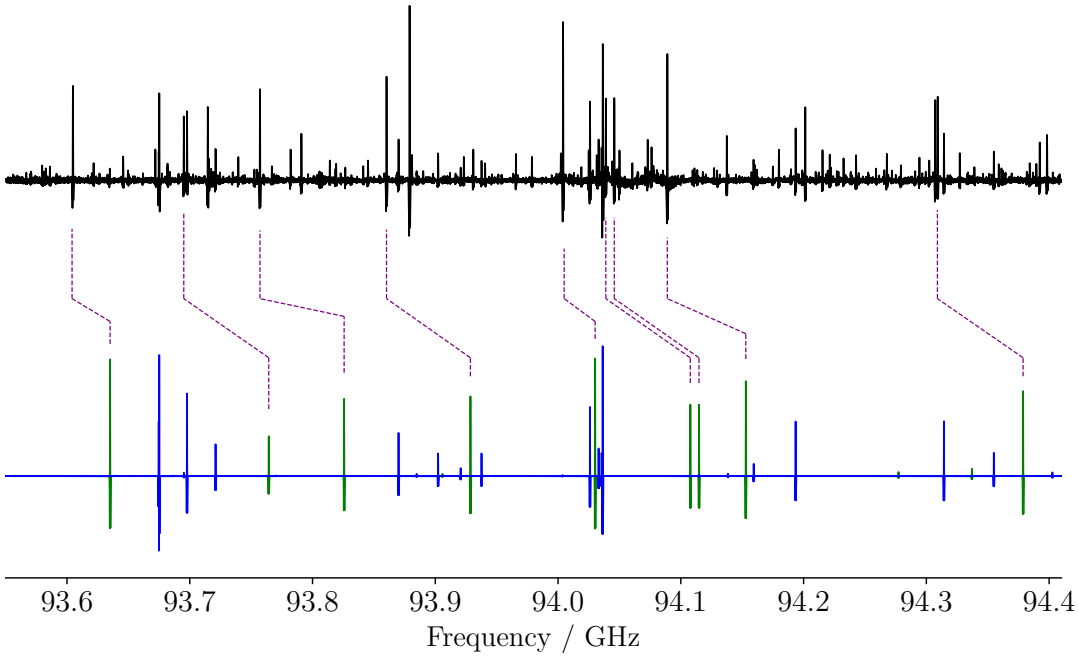

Figure 3: Portion of the millimeter-wave spectrum around 94 GHz. The experimental spectrum (black trace) is compared with the spectral simulation of doubly-deuterated glycolaldehyde (CHDOD−CHO, blue trace, based on our final fit of the ground and $v_{18} = 1$ states) and doubly-deuterated ethenediol (CHOD=CHOD, green trace, based on scaled spectroscopic parameters), assuming a relative abundance of 4:5. For this latter species, the dashed lines indicate the correspondence between predicted and experimental features.

CCSD(T)/CBS+CV equilibrium rotational constants corrected for vibrational effects at the fc-MP2/cc-pVTZ level), the difference between experimental and theoretical rotational constants is, on average, ∼0.2% for both the bi- and mono-deuterated species. Despite its empirical nature, the scaling procedure allowed us to further improve such a good accuracy, thereby obtaining a relative deviation from experiment of about 0.1% for CHOD=CHOD and 0.02% for CHOD=CHOH and CHOH=CHOD. It was somewhat expected that scaling would have led to a better improvement for mono-deuterated forms with respect to the bi-deuterated one; indeed, because of the great difference in mass between H and D, deuteration causes large changes in the rotational constants. Therefore, averaging the scaling for the parent and the bi-deuterated species allowed an accurate description of mono-deuteration. As already noted for glycolaldehyde, the computed centrifugal distortion constants are also in qualitative agreement with the corresponding experimental values, similarly to what observed for the parent species.[34]

The newly derived ground-state rotational constants of CHDOD−CHO have also been used in conjunction with our computed vibration-rotation interaction constants to improve the SE equilibrium structure of glycolaldehyde. The results are provided in Table 4, where they are compared with the previous determination (ref. 27). This latter was derived using a set of 27 rotational constants from 9 different isotopologues and vibration-rotation interaction constants computed at the B2PLYP/aug-cc-pVTZ level of theory (B2PLYP denoting the double-hybrid functional by Grimme[55]).[27] In this work, the SE equilibrium structure has been obtained using 30 rotational constants (10 isotopologues) in combination with vibrational corrections at the fc-MP2/cc-pVTZ level of theory. While the two computational methodologies employed for evaluating the vibration-rotation interaction constants are expected to provide results of similar quality and it is well-known that the accuracy of the SE equilibrium structure little depends on the level of theory used for the vibrational corrections,[27,56,57] our enlarged set of experimental data guarantees an improved accuracy on the determination of nearly all the geometrical parameters, mostly reducing the correlation among them. As can be seen from Ta-

Table 2: Spectroscopic constants of bi-deuterated ethenediol (Watson's S reduction, I^r representation).

		CHOD=CHOD		
Parameter	Unit	Experiment[a]	Theory[b]	Estimate[c]
A	MHz	18246.81(1)	18309.805	18225.08
B	MHz	5896.9235(5)	5889.912	5902.52
C	MHz	4466.8778(5)	4462.869	4468.22
D_J	kHz	6.2403(4)	6.775	
D_{JK}	kHz	−31.780(3)	−36.264	
D_K	kHz	89.8(2)	102.749	
d_1	kHz	−2.0030(1)	−2.110	
d_2	kHz	−0.13449(9)	−0.123	
H_J	mHz	3.0(2)	0.348	
H_{JK}	mHz	66.(2)	132.420	
H_{KJ}	Hz	−0.972(3)	−1.450	
H_K	Hz	3.110	3.110	
h_1	mHz	1.564	1.564	
h_2	mHz	0.724	0.724	
h_3	mHz	0.239	0.239	
No. data		228		
$J_{\max}, K_{\mathrm{a\,max}}$		34, 24		
rms error	kHz	29.8		

[a] Values in parentheses are one standard deviation and refer to the last digits. Parameters without uncertainties are held fixed at the corresponding computed value.
[b] Equilibrium rotational constants at the CBS+CV level augmented by vibrational corrections at the fc-MP2/cc-pVTZ level of theory. Quartic and sextic centrifugal distortion at the fc-MP2/cc-pVTZ level.
[c] Scaled values of the computed rotational constants; see Computational detail section.

ble 4, on average, the uncertainties affecting bond lengths and angles are nearly halved. The only notable differences are seen for the r(O4-H8) and r(C3-O4) distances, which –in our r_e(SE)– result longer than those obtained in ref. 27 by about 2 mÅ and 0.7 mÅ, respectively. In this respect, our isotopic substitution on H8 surely provides an important contribution to the determination of r(O4-H8). Therefore, the SE equilibrium structure of this work is the most accurate equilibrium geometry available so far for glycolaldehyde. The last comment concerns the comparison of r_e(SE) with the CCSD(T)/CBS+CV structure. It is remarkable that this latter agrees with the SE counterpart well within 1 mÅ for bond lengths and 0.1 degrees for angles. Such a good agreement further reinforces the suitability of the CCSD(T)/CBS+CV level of theory for computing very accurate equilibrium geometry, and thus accurate equilibrium rotational constants.

Conclusions

To summarize, the spectroscopic constants obtained in this work enable the accurate prediction of the rotational spectra of all the investigated species in the whole millimeter region, covering the most relevant spectral windows used for astronomical observations. The most promising source of deuterated glycolaldehyde and 1,2-ethenediol is represented by the Class 0 protostellar binary IRAS 16293-2422, for which spectral line surveys are available at 3 mm and 1 mm. This protostellar core is known to be very rich in deuterated species, including glycolaldehyde, which has already been detected in all its singly-deuterated forms.[19] Future observations of this pair of COMs will be crucial in order to improve our understanding of the chemistry of interstellar sugars.

Table 3: Spectroscopic constants of both mono-deuterated forms of ethenediol (Watson's S reduction, I^r representation).

		CHOD=CHOH			CHOH=CHOD		
Parameter	Unit	Experiment[a]	Theory[b]	Estimate[c]	Experiment[a]	Theory[b]	Estimate[c]
A	MHz	18401.84(2)	18470.556	18396.054	19352.45(3)	19434.697	19356.295
B	MHz	6266.094(2)	6257.639	6268.065	5935.685(1)	5926.827	5936.704
C	MHz	4680.160(1)	4675.166	4680.060	4552.289(1)	4547.174	4551.946
D_J	kHz	7.0976(7)	6.613	6.594	6.0723(5)	7.384	6.594
D_{JK}	kHz	−32.865(5)	−40.669	−34.379	−35.714(4)	−34.945	−34.379
D_K	kHz	81.5(3)	128.802	96.498	111.9(4)	85.844	96.498
d_1	kHz	−2.3739(6)	−2.032	−2.147	−1.9258(4)	−2.432	−2.147
d_2	kHz	−0.1660(1)	−0.110	−0.147	−0.1220(1)	−0.152	−0.147
H_J	mHz	−0.623	−0.623		−0.548	−0.548	
H_{JK}	mHz	95.(4)	149.150		81.(3)	152.439	
H_{KJ}	Hz	−1.013(7)	−1.857		−1.244(4)	−1.296	
H_K	Hz	4.471	4.471		2.429	2.429	
h_1	mHz	1.613	1.613		1.713	1.713	
h_2	mHz	0.634	0.634		1.169	1.169	
h_3	mHz	0.214	0.214		0.268	0.268	
No. data		114			146		
$J_{\max}, K_{\mathrm{a}\max}$		31, 19			32, 22		
rms error	kHz	24.4			27.7		

[a] Values in parentheses are one standard deviation and refer to the last digits. Parameters without uncertainties are held fixed at the corresponding computed value.
[b] Equilibrium rotational constants at the CBS+CV level augmented by vibrational corrections at the fc-MP2/cc-pVTZ level of theory. Quartic and sextic centrifugal distortion at the fc-MP2/cc-pVTZ level.
[c] Scaled computed rotational constants (see text) and arithmetic mean of the experimental quartic centrifugal distortion constants for the main and doubly-deuterated species (see text).

Supporting Information Available

List of recorded transitions for each species and their residuals from the final fit.

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Table 4: Semi-experimental equilibrium structure of glycolaldehyde.

Parameter[a]	Ref. 27[b]	This work[b]	CBS+CV[c]
r(C2-O1)	1.2088(3)	1.2087(1)	1.2079
r(C2-H5)	1.1010(2)	1.1013(1)	1.1009
r(C2-C3)	1.5006(2)	1.5007(2)	1.5009
r(C3-H6)	1.0964(1)	1.09671(8)	1.0958
r(C3-O4)	1.3965(2)	1.3958(1)	1.3952
r(O4-H8)	0.9611(3)	0.9588(3)	0.9650
$\angle$(H5-C2-O1)	121.45(4)	121.41(2)	121.48
$\angle$(C3-C2-O1)	121.65(2)	121.67(1)	121.65
$\angle$(H6-C3-C2)	107.91(1)	108.03(1)	107.92
$\angle$(O4-C3-C2)	111.78(2)	111.719(7)	111.73
$\angle$(H8-O4-C3)	106.18(2)	106.35(2)	106.14
ϕ(H6-C3-C2-O1)	122.34(1)	122.378(5)	122.41
RMS $\times 10^4$	3.02	2.64	

[a] Bond lengths are given in Å, angles in degrees. For the atom labeling, the reader is referred to Figure 1. Root Mean Square (RMS) error in terms of moment of inertia ($u \times {a_0}^2$).
[b] Values in parentheses are one standard deviation and refer to the last digit.
[c] Computed equilibrium parameters at the CCSD(T)/CBS+CV level of theory.

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