Quantum Chemical Computations of Gas-phase Glycolaldehyde Deuteration and Constraints on Its Formation Route

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Abstract

Despite the detection of numerous interstellar complex organic molecules (iCOMs) for decades, it is still a matter of debate whether they are synthesized in the gas phase or on the icy surface of interstellar grains. In the past, molecular deuteration has been used to constrain the formation paths of small and abundant hydrogenated interstellar species. More recently, the deuteration degree of formamide, one of the most interesting iCOMs, has also been explained with the hypothesis that it is formed by the gas-phase reaction NH₂ + H₂CO. In this paper, we aim at using molecular deuteration to constrain the formation of another iCOM, glycolaldehyde, which is an important prebiotic species. More specifically, we have performed dedicated electronic structure and kinetic calculations to establish the glycolaldehyde deuteration degree in relation to that of ethanol, which is its possible parent species according to the suggestion of Skouteris et al. We found that the abundance ratio of the species containing one D atom over the all-protium counterpart depends on the produced D isotopomer and varies from 0.9 to 0.5. These theoretical predictions compare extremely well with the monodeuterated isotopomers of glycolaldehyde and that of ethanol measured toward the solar-like protostar IRAS 16293–2422, supporting the hypothesis that glycolaldehyde could be produced in the gas phase for this source. In addition, the present work confirms that the deuterium fractionation of iCOMs cannot be simply anticipated based on the deuteration fractionation of the parent species but necessitates a specific study, as already shown for the case of formamide.

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1. Introduction

Among the more than 270 species that have been detected in the interstellar medium (ISM) so far (McGuire 2022), about 40% are composed of six or more atoms and contain at least a carbon atom. They are referred as interstellar complex organic molecules (iCOMs; Herbst & van Dishoeck 2009; Ceccarelli et al. 2017), where the “i” emphasizes that the “complex” adjective only holds in the ISM context. The iCOMs are significant in prebiotic chemistry research, whose goal is to understand how life could appear on an originally inorganic Earth. They can be considered as precursors or intermediates in the formation of the building blocks of life, such as amino acids or nucleobases. The question of their formation in the harsh ISM conditions is, therefore, of paramount importance and far-reaching.

So far, two major processes responsible for iCOM synthesis have been invoked in the literature: reactions occurring on the interstellar icy grain surfaces or in the gas phase (e.g., Garrod & Herbst 2006; Balucani et al. 2015; Ceccarelli et al. 2022). Which one dominates and where has been a decades-long quarel that started soon after the first detection of iCOMs in massive hot cores (Rubin et al. 1971; Blake et al. 1987) and was revived when iCOMs were detected in hot coronas (Cazaux et al. 2003; Ceccarelli et al. 2004). Traditionally, a major argument to distinguish the gas-phase versus grain-surface origin of the gaseous species observed in hot cores/corinos has been the molecular deuteration or deuterium fractionation, namely, the abundance ratio between the species containing D atoms with respect to the same containing H atoms (e.g., Tielens 1983; Charnley et al. 1992; Roberts & Millar 2000a, 2000b; Ceccarelli et al. 2001, 2014). Indeed, since the D/H ratio at the birth of the universe is AD = 2.4 × 10⁻⁵ (Cooke et al. 2016; Planck Collaboration et al. 2016), the abundance of D-bearing molecules would be extremely low without a chemistry-triggered deuteration fractionation. Instead, since the 1970s, it has been known that many interstellar di- and triatomic molecules show an enhanced abundance of D-bearing molecules with respect to the elemental D/H abundance (e.g., Hollis et al. 1976; Penzias et al. 1977; Snyder et al. 1977). This is (mainly) caused by the dense ISM low temperatures that enhance the H₂D⁺/H₂⁺ abundance ratio because of the different zero-point energy (ZPE) of the two species; then, all other small deuterated molecules inherit the deuteration from H₂D⁺ (Watson 1974; Dalgarno & Lepp 1984).

At the beginning of the 2000s, formaldehyde and methanol were the most complex deuterated species detected in the ISM, and the detection of doubly deuterated formaldehyde and even triply deuterated methanol (Turner 1990; Ceccarelli et al. 1998; Parise et al. 2004) were used to assess their grain-surface origin (e.g., Ceccarelli et al. 2001; Parise et al. 2006; Taquet et al. 2013). Indeed, both molecules are (mostly) produced on the grain surfaces thanks to the hydrogenation of frozen CO (Watanabe & Kouchi 2002; Watanabe et al. 2003; Rimola et al. 2014), so the crucial parameter is the D/H abundance ratio of atoms landing on the grain surfaces (Tielens 1983), which in turn depends on the H₂D⁺/H₂⁺ abundance ratio in the gas (see, e.g., the review by Ceccarelli et al. 2014). In summary, until
recently, the deuteration of the observed molecules was only connected to the enhanced H₂D⁺/H₂⁺ abundance in cold gas,⁴ which, in turn, is controlled by the so-called thermodynamic isotope effect (TIE; the difference in the ZPE is such that the isotopic variant H₂⁺ + HD → H₂D⁺ + H₂ is slightly exothermic, while the reverse process is slightly endothermic).

The situation has changed in recent years with the detection of D-enriched iCOMs (Coudert et al. 2013; Coutens et al. 2016; Jørgensen et al. 2018; Manigand et al. 2019) because, whatever their formation route, iCOM deuteration is no longer directly connected to the enhanced (gaseous) H₂D⁺/H₂⁺ abundance ratio but rather to the deuteration of their parent species. In this case, the question is whether the iCOM deuteration is directly inherited from their parent species without any alteration or whether the processes leading from the parent to the daughter species can induce an enrichment or a decrease in the deuteration degree.

It is worth mentioning here that the rate coefficient of a chemical reaction is expected to change when one of the atoms in the reactants is replaced by one of its isotopes. This is the so-called kinetic isotope effect (KIE), not to be confused with the TIE ruling the H₂D⁺/H₂⁺ abundance. A further distinction is made between the primary kinetic isotope (in this case, a bond involving the isotopically labeled atom being formed or broken) and secondary KIE (when no bond to the isotopically labeled atom in the reactant is being broken or formed). Secondary KIEs are much smaller than primary KIEs. Finally, and perhaps more importantly, if there is competition between the formation of a D product or an H product, it is very important to characterize the reaction mechanism. As a matter of fact, if the reaction is an impulsive direct reaction, H products are favored, while if the reaction is an indirect reaction featuring the formation of a reaction intermediate (RI), since X–D bonds are stronger than X–H bonds (where X is an atomic species like carbon or oxygen), D products are favored. In other words, to assess the relationship between the deuteration degree of one iCOM and its parent species, the reaction mechanism has to be characterized.

For instance, in a recent example, Skouteris et al. (2017) showed that the reaction mechanism of the gas-phase reaction NH₂ + H₂CO → NH₂CHO + H can explain the measured D/H abundance ratios of formamide (NH₂CHO) toward IRAS 16293–2422 B. This is due to a combination of the D-/H-product branching ratio and KIE.

To the best of our knowledge, the case of formamide is the only case reported in the literature. The detection of its D isotopomers was first reported by Coutens et al. (2016) toward the solar-like protostar IRAS 16293–2422 B (hereafter IRAS 16293 B) hot corino. Skouteris et al. (2017) showed that, if formamide is formed in the gas phase by the NH₂ + H₂CO reaction, then trans-HCONHD/HCONH₂ ~ 1/3 NH₂/ND₂, cis-HCONHD/HCONH₂ ~ 1/3 NH₂/ND₂, and DCONH₂/HCONH₂ ~ 1/3 = HDCO/H₂C. In other words, (i) the singly deuterated formamide abundance will be a factor of 3 lower than that characterizing the parent species NH₂ and H₂CO, respectively, while (ii) the relative abundance ratios will reflect those of the parent species (NH₂ and H₂CO). Therefore, the strong message from the Skouteris et al. (2017) study is that the deuterium fractionation of iCOMs from gas-phase reactions depends on the specific characteristics of the formation reaction and cannot be anticipated simply based on the mother species deuteration. Incidentally, the Coutens et al. observations agree with these theoretical predictions, supporting the case for a gas-phase formation of formamide in the IRAS 16293 B hot corino.

In this paper, following the Skouteris et al. (2017) study, we report on the case of glycolaldehyde, the deuterated forms of which have been detected in IRAS 16293 B by Jørgensen et al. (2016). As for other iCOMs, two possible formation routes are invoked in the literature: (i) in the gas phase from gaseous ethanol (CH₃CH₂OH) following the scheme by Skouteris et al. (2018), reported in Figure 1, or (ii) by the combination of radicals on the grain surfaces as predicted by Garrod et al. (2008; see also Simons et al. 2020, and references therein). In the present work, we focus on the gas-phase route only and provide theoretical calculations to predict the deuteration of glycolaldehyde when it is synthesized starting from monodeuterated ethanol.

To this end, we separately follow the effect on the deuteration degree of the two steps shown in Figure 1: first, the reactions of partially deuterated ethanol with OH that lead to a combination of five isotopomers/rotamers of CH₂D₂CH₂OH, and second, their reactions with atomic oxygen leading to the three deuterated isotomers of glycolaldehyde. While we discuss the consequences of the first step starting from the data available in the literature, we have calculated the rate coefficients and H-/D-product branching ratios associated with the second step in this work. The studied reactions are listed in Table 1, and their scheme is shown in Figure 2.

The paper is organized as follows. In Section 2, we provide some considerations on the first step, namely, the hydrogen or deuterium abstraction from deuterated ethanol. We then describe the theoretical methods used for this study in Section 3 and show the results we obtained in Section 4. Section 5 is dedicated to a discussion about the astronomical relevance of this study and the comparison between our predictions and observations. Section 6 concludes the paper.

### 2. The First Abstraction Step and Implications for the Deuteration Degree

Following the suggestion by Skouteris et al. (2018), the first step of the envisaged reaction sequence consists of an H-atom abstraction from ethanol by OH. The all-proton reaction \( \text{OH} + \text{CH}_3\text{CH}_2\text{OH} \) has been investigated from an experimental and theoretical point of view (Galano et al. 2002; Xu & Lin 2007; Sivaramakrishnan et al. 2010; Elm et al. 2013). The rate coefficient as a function of the temperature (encompassing the range of temperature of interest in the ISM) was determined

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⁴ Additionally and/or alternatively, CH₃D⁺ and OD can also enhance molecular deuteration in some species in somewhat warmer gas (~30–100 K; Roberts & Millar 2000a; Thi et al. 2010).
Note. The structural formula of each isotopomer is shown in Figure 2. The reaction numbers follow the sequence of reactions shown in Figure 2. Note that the radical CHDCH2OH can be generated by both reactions 3 and 4; therefore, reaction 9 accounts for both. Note that reactions 6 and 7 produce the same isotopomer of glycolaldehyde, as well as reactions 8 and 9.

Let us now consider the relation between the four isotopomers of ethanol and the isotopomers of the 2-hydroxyethyl radical that can be formed by H (or D) abstraction. In all cases, we are considering only the abstraction from the methyl group of ethanol because this is the step that later leads to glycolaldehyde. Also, since the gauche-2-hydroxyethyl radical is the most stable rotamer and the calculations have been done starting from this species (see below), the relation will be shown for this species only. Similar reasoning can also be applied to the case of the anti rotamers. If we start from CH3CHDOH, the degree of deuteration remains unchanged in this first step because the D atom is not directly involved in the process, and the mechanism is of the direct type (impulsive reaction). If compared to the all-protium reaction, the rate coefficient could be slightly affected by secondary KIE, but the effect is expected to be minor.

If we start from CH3CHDOH, the H abstraction from the terminal methyl group leads to the formation of two isotopomic radicals (Figure 3, panel (c)): CH2CHDOH (D2') and CH3CHDOH (D2-). In this case, there is no direct competition between the H or D abstraction, and the deuteration degree is not going to be affected. Given the chemical equivalence of the D2 position, we assign a branching ratio of 0.1 to both CH2CHDOH and CH3CDHOH. Also in this case, secondary KIEs are expected to be negligible.

Finally, in the case of the CH2DCH2OH isotopomers, there is a competition between D and H abstraction. However, the H/D abstraction in the reaction OH + ethanol is characterized by a significant entrance barrier, and, while the H abstraction process is made possible at low temperatures by quantum tunneling through that barrier (Caravan et al. 2015; Ocaña et al. 2018), the same is not valid for the D abstraction. The tunneling probability shows exponential dependency on the mass of the particle, and doubling the mass of a tunneling H atom by replacing it with deuterium drastically reduces the rate. Therefore, only the H atom will be abstracted by OH, since the same process involving D will not benefit from the tunneling effect (primary KIE). In this case, as well, the original deuteration degree of ethanol will be retained in the 2-hydroxyethyl radical.

In conclusion, we can say that, for different reasons, the first step does not alter the deuteration degree or the position of the deuteron atom in the 2-hydroxyethyl radical with respect to its parent ethanol molecule. Secondary KIEs are expected to be negligible in all cases and we can assume that reactions 1–4 are characterized by the same rate coefficients as the all-protium reaction.

After the first step, therefore, we have five possible monodeuterated species of 2-hydroxyethyl radical (there is no symmetry in this case): CH3CHDOH (D1), CH2CHDOH (D2'), CH3CDHOH (D2-), CHDCH2OH (D3), and CDHCH2OH (D4). In the ISM, only the anti ethanol rotamer has been observed so far, but the gauche-ethanol is expected to be more abundant because of its degeneracy and little energy difference. Considering also that the gauche-2-hydroxyethyl radical is the more stable rotamer, our theoretical study was performed starting from it. This is also motivated by the fact that the H abstraction is an exothermic reaction that will liberate a large excess energy allowing all possible rotations to occur. In any case, we have verified that, if we consider the anti-2-hydroxyethyl radical as a starting reactant, the global outcome is not changing (see Figure 4). The addition of atomic oxygen to the anti-2-hydroxyethyl radical indeed leads to the addition of RI2 rather than RI1, but RI1 and RI2 easily

### Table 1

| No. | Reactants | Products |
|-----|-----------|----------|
| 1   | CH3CHOD + OH | CH3CHOD + H2O |
| 2a  | CH3CHDOH + OH | CH3CHDOH + H2O |
| 2b  |             | CH3CDHOH + H2O |
| 3a  | a-a-CH2DCH2OH + OH | CHDCH2OH + H2O |
| 3b  |             | CHDCH2OH + H2O |
| 4   | a-a-CH2DCH2OH + OH | CHDCH2OH + H2O |

Note. The structural formula of each isotopomer is shown in Figure 2. The reaction numbers follow the sequence of reactions shown in Figure 2. Note that the radical CHDCH2OH can be generated by both reactions 3 and 4; therefore, reaction 9 accounts for both. Note that reactions 6 and 7 produce the same isotopomer of glycolaldehyde, as well as reactions 8 and 9.

in two different Cintique de Raction en Ecoulement Supersonic Uniforme experiments (Caravan et al. 2015; Ocaña et al. 2018). However, this technique is not able to give information on the branching ratios of the different products (Cooke & Sims 2019). Theoretical calculations and experimental work have pointed out that both CH3CHOH and CH2CH2OH can be formed (Marinov 1999; Carr et al. 2011), while the formation of CH3CHOH has been ruled out (Caravan et al. 2015). Given the uncertainty on the product branching ratios at low temperatures, Skouteris et al. (2018) adopted two sets of branching ratios, that is, 0.9/0.7 for CH3CHOH and 0.1/0.3 for CH2CH2OH (see the two scenarios in Skouteris et al.). Here we have adopted an intermediate value using a yield of 0.8 for CH3CHOH and 0.2 for CH2CH2OH.

In this work, we are interested only in the formation of deuterated glycolaldehyde; therefore, we will consider the part of the ethanol tree that leads to it, i.e., the H abstraction from the methyl group with the formation of the 2-hydroxyethyl radical (the red boxes of Figure 1). Note that abstraction reactions are impulsive direct processes.

Ethanol and the 2-hydroxyethyl radical exist under the form of three rotamers regarding the CO bond: the anti-, +gauche-, and -gauche- isomers (see Figure 3). The two gauche isomers are chemically indistinguishable. In the case of ethanol, the anti-rotamer is the one with the lowest energy content, while in the case of CH2CH2OH, the most stable rotamer is the gauche-2-hydroxyethyl radical.

If we consider the monodeuterated species of ethanol, because of its four distinct types of hydrogen atoms, we have four isotopomers (Figure 3, panels (a) and (b)): CH3CH2OD (D1), CH3CHDOH (D2), a-a-CH2DCH2OH (D3), and a-a-CDH2CH2OH (D4). Note that a-a-CH2DCH2OH and a-a-CDH2CH2OH have different spectroscopic properties and, therefore, are distinguishable when observed in the ISM. However, they are characterized by a very similar chemical behavior.
Figure 2. Summary of the multistep reactions with their respective major products. Reactions are numbered as in Table 1. The colored boxes show the parent–daughter relationship. The magenta boxes show the channels that lead to undeuterated glycoaldehyde products (8b and 9b). Note that the two types of CH$_2$DCH$_2$OH (a-a and a-s) are characterized by different spectroscopic properties that make them observationally distinguishable. They are characterized, however, by very similar chemical behavior. Branching ratios are also indicated (see text).

Figure 3. Different types of deuterated ethanol (left) and deuterated 2-hydroxyethyl radical (CH$_2$CH$_2$OH; right).
interconvert through TS1 (where TS stands for transition state) and are expected to be in equilibrium. Therefore, no changes are expected whether we start from the anti or the gauche radical.

3. Methods

All of the computations were carried out using the Gaussian16 suite of programs (Frisch et al. 2016). Geometry optimizations were performed for every involved species employing the B2PLYP double hybrid functional (Grimme 2006) in conjunction to the aug-cc-pVTZ triple-ζ basis set (Kendall et al. 1992; Woon & Dunning 1993). Semiempirical dispersion effects were included by means of the D3BJ model of Grimme (Grimme et al. 2011), leading to the so-called B2PLYP-D3/aug-cc-pVTZ level of theory. These optimizations were followed by harmonic vibrational calculations adopting the same method, in order to verify that all intermediates were true minima of the potential energy surface (PES) and that all TSs exhibited a single imaginary frequency. The electronic energies were then reevaluated via the coupled-cluster singles and doubles approximation augmented by a perturbative treatment of triple excitations (CCSD(T); Raghavachari et al. 1989) in conjunction with the same basis set. This composite method will be hereafter named CCSD(T)// aug-cc-pVTZ//B2PLYP-D3/aug-cc-pVTZ.

As in previous works (Balucani et al. 2012; Leonori et al. 2013; Skouteris et al. 2015; Vazart et al. 2015; Skouteris et al. 2018), a combination of capture theory and the Rice–Ramsperger–Kassel–Marcus (RRKM) calculations was used to determine the relevant rate coefficients and branching ratios regarding the reactions following the oxygen addition to the radicals. We have used capture theory for the addition of the O(3P) atom to the various forms of deuterated hydroxyethyl radicals, whereas for the subsequent steps (isomerizations or bond fissions), energy-dependent rate constants were calculated using the RRKM scheme. We used an in-house code to solve the master equation in the zero pressure limit. The quantum tunneling effects were computed following the symmetric Eckart potential treatment, which provides results that do not deviate much from the more accurate instanton method (e.g., Seneviratne et al. 2017).

Given the critical role of the long-range interaction in the capture model, we decided to employ a higher-accuracy theoretical method based on CASSCF and CASPT2 calculations (OpenMolcas 18.09). However, we met with considerable difficulty in identifying the van der Waals minima in the entrance valley and possible TSs from the van der Waals complex(es) to the first covalently bound intermediate. Therefore, as a guide to locate the position of the van der Waals energy minimum, we resorted to a semiempirical method developed by Pirani et al. (2008), as recently done for other systems by de Aragão et al. (2021) and Marchione et al. (2022). This treatment of the entrance channel leads to some variation in the rate coefficient values with respect to those reported in Skouteris et al. (2018). Since the focus of this paper is on the deuteration degree of the reaction products, which is not affected by the long-range potential, the details of these calculations and the effect on the global rate coefficients will be the subject of a future publication.

Finally, to obtain the product branching fractions, the master equation was solved at all relevant energies for all systems (to consider the overall reaction scheme), and Boltzmann averaging was carried out to obtain temperature-dependent values.

4. Results

4.1. Electronic Structure: PESs

Figure 4 shows the minimum energy path following the addition of atomic oxygen O(3P) on the 2-hydroxyethyl radical CH2CH2OH already proposed by Skouteris et al. (2018). All of
the energies and the coordinates of the involved species are reported in the Appendix.

As both fragments approach each other, the barrierless addition of oxygen on the gauche-2-hydroxyethyl radical leads to the RI1, which is about 370 kJ mol$^{-1}$ more stable than the reactants. Its trans counterpart, the slightly less stable (by 5 kJ mol$^{-1}$) compound RI2, can easily be reached from the cis through TS1 reflecting a 15 kJ mol$^{-1}$ barrier. It is also possible to start from the anti-conformer of the radical (ca. 2 kJ mol$^{-1}$ less stable than the gauche) that would lead to RI2. Both RI1 and RI2 species are then able to undergo a dissociation into formaldehyde and the CH$_2$OH radical through TS5 and TS6. These dissociation channels exhibit barriers of around 50 kJ mol$^{-1}$. Other dissociations can also be observed from both RI1 and RI2, leading this time to cis- or trans-glycolaldehyde and H through TS2 and TS3, respectively, that are about 95 kJ mol$^{-1}$ higher in energy than their corresponding RIs.

Cis- and trans-glycolaldehyde are connected by TS4 and require a 30 kJ mol$^{-1}$ energy to go from one to the other. The cis conformer is the marginally most stable one, by 13 kJ mol$^{-1}$. Two epoxidations can also be envisaged. The first one, starting from RI1, leads to the epoxide CH$_2$OCHO + H and exhibits a barrier (represented by TS13) of ca. 220 kJ mol$^{-1}$. The second one starts from RI2, leads to ethylene oxide and OH, and has to go through a ca. 200 kJ mol$^{-1}$ barrier, represented by TS14. Again starting from both RI1 and RI2 species, one can observe hydrogen migrations from carbon atoms to the oxygen atom bearing the lone electron. Both TS7 and TS8 correspond to hydrogen migrations from the carbon atom linked to the oxygen atom bearing the lone electron and are around 120 kJ mol$^{-1}$ more energetic than their corresponding intermediates.

The TS9 can be reached from both RI1 and RI2 and consists of a hydrogen migration from the carbon that is not linked to the oxygen atom bearing the lone electron. It is ca. 115 kJ mol$^{-1}$ energetically higher than RI1 and RI2. The TS7 and TS8 lead to RI3 and RI4, respectively, while TS9 leads to RI4. These intermediates are found to be more than 400 kJ mol$^{-1}$ more stable than the precursors and can be linked to each other thanks to the TS10 with a small barrier of around 20 kJ mol$^{-1}$. Starting from both RI3 and RI4 compounds, an epoxidation leading to the epoxide CH$_2$OCHO and H can be envisaged and exhibits ca. 250 kJ mol$^{-1}$ barriers (TS15). The other possible reaction is a dissociation from both RI3 and RI4 into Z- and E-ethene-1,2-diol isomers and H, respectively. The step from RI3 to Z-ethene-1,2-diol + H and the one from RI4 to E-ethene-1,2-diol + H exhibit barriers of about 150 kJ mol$^{-1}$ (through TS11 and TS12, respectively), both isomers being found around 260 kJ mol$^{-1}$ more stable than the precursors and the Z one slightly more stable (by 20 kJ mol$^{-1}$) than its E counterpart.

If we look more carefully at the products that can be obtained via this path, one can see that the most stable ones are formaldehyde + H$_2$COH. The following ones, in decreasing order of stability, are glycolaldehyde + H, Z- and E-ethene-1,2-diol + H, ethylene oxide + OH, and CH$_2$OCHO + H.

When the deuteration of a species is considered, only ZPEs are affected, as the electronic energy remains identical. Indeed, isotopomers carry the same number of electrons, and this is the reason why the reaction path of Figure 4 is valid for all isotopic variants, since the electronic energies remain identical for all five reactions that involve one of the monodeuterated 2-hydroxyethyl radicals. The energetic distinction between the five paths is then made thanks to zero-point corrections originating from frequency computations that take into account the masses of the atoms. These differences of zero-point-corrected energies are reported in Appendix A for each case.

The only difference originates from to the presence of a loop between RI1/RI2 and RI3/RI4 through TS7, TS8, and TS9. Indeed, for each stage of a reaction, one has to consider the backward and forward steps, and if, in the all-protium reaction, TS9 and TS7/TS8 link the same intermediates, it is no longer the case when deuterated species are involved. An example of this loop regarding reaction 1 is described in Appendix C, together with figures representing all the cases (Figures 8–11), and were all taken into account for the kinetics calculations. The deuteration propagation between the hydroxyethyl radical and glycolaldehyde in every case is also given in Appendix C. We have verified that these loops are not affecting the final outcome, as the dominant channels are those leading from RI1 and RI2 to cis- and trans-glycolaldehyde.

4.2. Kinetics

The main goal of these new calculations is to evaluate the variation of the rate coefficients due to KIE and the D-product branching ratios. In Figure 5, we have reported the decomposition rate coefficients of the different monodeuterated RI1 into monodeuterated glycolaldehyde (H) for reactions 5–7, 8a, and 9a. A first aspect to be noted is that the decomposition rate coefficient of RI1 is not very different when the all-protium reaction is compared to reactions 5 and 6. A rather small difference is visible in the case of reactions 7 and 9a, while a more pronounced difference is visible for reaction 8a. An inspection of Figure 6 can help to clarify this trend. Reactions 5–7 can only form one isotopomer of glycolaldehyde without competition. Furthermore, the C–H bond which is going to be broken does not involve the deuterium atom. The similarity with the rate coefficient of the all-protium reaction clearly indicates a very minor contribution from secondary KIE, as expected, with the exception of reaction 7, where a small effect can be noted.

The situation is different for reactions 8 and 9, as in this case, we expect competition between the fission of a C–H bond and that of a C–D bond. As expected for an indirect reaction, this competition favors the C–H bond breaking over that of C–D. Having said that,
however, there is a significant difference between the cases of reactions 8 and 9. In the case of reaction 9, the fission of the C–H bond is so favored that the rate coefficient of the 9a channel is almost the same as the other rate coefficients of Figure 5. Instead, the rate coefficient for reaction 8a is significantly smaller. An inspection of the characteristics of the TSs reported in Figure 6 can help in understanding the reason; in order for the H atom to reach the appropriate geometry of the TS2-8a, a significant amount of internal rotation must also occur simultaneously with the bond breaking, increasing the height of the barrier and the rate of its surmounting. As a consequence, the yield of the undeuterated glycolaldehyde + D is significant for reaction 8. In the case of reaction 9, instead, the opposite is true because it is the mechanism leading to undeuterated glycolaldehyde + D that features a reorientation of RI1 to reach the critical configuration of TS2-9a. Indeed, the yield of HOCH2CHO + D is much smaller than in the case of reaction 8.

In conclusion, the effect of secondary KIE is small in all the cases considered, while primary KIE affecting reactions 8 and 9 has a rather different outcome depending on the details of the PES and, more specifically in this case, the difference in the geometry of the intermediates with respect to that of the TSs connecting the intermediates to the products.

In order to be able to compare our new computations with astronomical observations, it is necessary to figure out the amount of every type of deuterated glycolaldehyde that is formed starting from each radical of deuterated ethanol. Therefore, we have considered the effect of the first step and multiplied the global rates obtained from each reaction 5–9 by their respective branching ratios resulting from the first step, according to the scheme depicted in Figure 2. In the cases where the same isotopomer of glycolaldehyde has more than one formation reaction, the contributions have been summed up.

5. Discussion

5.1. How to Compare the Theoretical Values with Astronomical Observations

In this section, we aim to provide guidelines to compare the results of our new computations with astronomical observations.
As mentioned in Section 2, ethanol exists in the form of three rotamers: the anti- (CH₃CH₂OD), gauche- (CH₂ODCHO) and -gauche- (CH₂OHCHO). However, in the ISM, so far the only detected deuterated conformer is the anti-one. To derive the total abundance of deuterated ethanol (i.e., including the gauche rotamers), Jørgensen et al. (2018) suggested applying a factor of 2.69 to the measured anti rotamer abundance (see also Manigand et al. 2020). This practically means that having (so far) only the abundance of the anti deuterated conformers, it is necessary to multiply by 2.69 to account for the entire abundance of monodeuterated ethanol. Indeed, since we want to compare the abundances of monodeuterated glycolaldehyde and monodeuterated ethanol, we have to keep in mind that all three starting rotamers of ethanol can lead to glycolaldehyde. If a total abundance of the various ethanol isotopologues is ever measured, the factor is not needed anymore.

Given the very close energies of the rotamers of both ethanol and the 2-hydroxyethyl radical, we can say that the proposed chemical schemes hold for all rotamers. In particular, the very low energy of TS1 warrants an equilibrium population between R11 and R12, which are the intermediates formed by the addition of the O atom to either the gauche- or anti- rotamers of 2-hydroxyethyl radical. To address the astrophysical implications, the rate coefficients obtained for reactions 5–9 will be divided by the rate coefficient derived for the all-proton reaction. Any correction factor necessary to recover the global abundance from the anti rotamer is therefore simplified.

5.2. Application to IRAS 16293 B

As mentioned in the Introduction, molecular deuteration has proven to be an efficient way to discriminate among the possible different routes of formation of interstellar molecules. Until very recently, this could only be done for small (≤5 atoms) molecules and methanol, in which the molecular deuteration is basically set by the H₂D⁺/H₂ abundance ratio, which, in turn, is due to the TIE. In large molecules, such as the iCOMs, instead, the deuteration is governed by the KIE.

The new calculations reported in the present work allow us to test whether the observed deuteration of glycolaldehyde is compatible with its formation in the gas phase from ethanol, following the chain of reactions suggested by Skouteris et al. (2018) and schematically shown in Figure 1. This is also possible thanks to the very sensitive ALMA observations toward the solar-like protostar IRAS 16293 B hot corino obtained by the PILS project (Jørgensen et al. 2016), which detected various isotopomers of deuterated ethanol and glycolaldehyde (Jørgensen et al. 2016, 2018).

Table 2 summarizes the measured D/H abundance ratios of the three deuterated ethanol isotopomers and the three isotopomers of deuterated glycolaldehyde that would originate from them according to the scheme illustrated in Figure 2. Note that the abundances of a-a and a-s CH₂DCH₂OH have been added because, even if they can be spectroscopically identified, they are chemically indistinguishable. In the same table, we report the abundance ratios of the measured and computed (CH₂ODCHO/CH₂OHCHO)/(CH₃CH₂OD/CH₃CH₂OH), (CHDOHCHO/CH₂OHCHO)/(CH₃CHDOH/CH₃CH₂OH), and (CH₂OHCDO/CH₂OHCHO)/(CH₂DCH₂OH/CH₂CH₂OH). Note that by “measured D/H abundance ratios,” we mean the ratios of the measured column densities of each D-bearing isotopomer with respect to the H-bearing glycolaldehyde.

Table 2. Comparison of the Computed D/H Ratios with Respect to the Observations toward IRAS 16293–2422 by Jørgensen et al. (2016; Glycolaldehyde) and Jørgensen et al. (2018; Ethanol).

| Isotopomers | Observed D-ethanol | Observed D-glycolaldehyde | D-glycol/D-ethanol |
|-------------|---------------------|---------------------------|-------------------|
| CH₃CH₂OD  | 0.05                | CH₂ODCHO                  | 1.0 ± 0.8          | 0.90              |
| CH₃CHDOH | 0.10                | CHDOHCHO                  | 1.0 ± 0.8          | 0.95              |
| CH₂DCH₂OH | 0.17                | CH₂OHCDO                  | 0.30 ± 0.24        | 0.54              |

Notes. The first two columns report the observed ratio of the measured column densities of the three D-bearing isotopomers of ethanol (D-ethanol) with respect to the H-bearing ethanol (CH₃CH₂OH). The third and fourth columns report the observed ratio of the measured column densities of the three D-bearing isotopomers of glycolaldehyde (D-glycolaldehyde) with respect to the H-bearing glycolaldehyde (CH₂OHCHO). Following the scheme of Figure 2, we then compare the observed and predicted ratios of (CH₂ODCHO/CH₂OHCHO)/(CH₃CH₂OD/CH₃CH₂OH), (CHDOHCHO/CH₂OHCHO)/(CH₃CHDOH/CH₃CH₂OH), and (CH₂OHCDO/CH₂OHCHO)/(CH₂DCH₂OH/CH₂CH₂OH).

* Jørgensen et al. (2018) reported an uncertainty of 20% on the estimates of the ethanol isotopologue column densities, which translates into 40% on their column density ratio. We assumed the same for glycolaldehyde. Then, propagating to the ratio of the ratios in the penultimate column gives an approximate uncertainty of 80% on each quoted value.
extremely important, if not essential, to also have those computations so as to be able to really understand if the two pathways lead to different molecular deuteration and, consequently, if iCOM deuteration can be used to discriminate their formation route.

Finally, an important result of our new calculations is that, in gas-phase reactions, the molecular deuteration of the parent species is not just passed to the daughter one, as already found by Skouteris et al. (2017) for formamide. Furthermore, it is impossible to predict a priori the molecular deuteration of different isomers; only specific calculations can provide the correct values. For example, for the NH$_2$ + H$_2$CO $\rightarrow$ NH$_2$CHO + H$_2$ reaction, the rate coefficient to form NH$_2$CDO from HDCO is about a factor of 3 smaller than that to form NH$_2$CHO, whereas the formation of CH$_3$OHDCO from CH$_3$DCH$_2$OH is a factor of 2 smaller. Therefore, specific calculations need to be carried out for the systems where deuterated iCOM isomers are detected to have the deuterium fractionation from both gas-phase and grain-surface reactions.

6. Conclusions

In this work, we present a theoretical study of the gas-phase formation of the deuterated glycolaldehyde isotopomers using the deuterated ethanol isotopomers as mother species. This work is based on the original scheme proposed by Skouteris et al. (2018; see Figure 1). The list of reactions between the deuterated isotopomers of ethanol and glycolaldehyde is summarized in Table 1, and their scheme is shown in Figure 2. It involves two steps that lead first from ethanol to the 2-hydroxyethyl radical (CH$_2$CH$_2$OH) and then from the latter to glycolaldehyde. Here we report new computations of the second step, which allow us to provide theoretical predictions of the abundance ratios of the different D isotopomers of glycolaldehyde with respect to those of ethanol.

We have found a significant primary KIE for the case of the reaction CHDCH$_2$OH + O, while in the cases of the other reactions, the KIE is modest. Starting from CH$_3$CH$_2$OH, CH$_3$CH$_2$OD, or CH$_3$CHDOH, similar rates for the formation of the major monodeuterated glycolaldehyde products are obtained, due to the deuterium atom being only an onlooker in these reaction paths. On the contrary, starting from CH$_3$DCH$_2$OH, a competition between hydrogen and deuterium loss leads to a depletion of the corresponding deuterated glycolaldehyde but with a significant difference in the case of reaction CHDCH$_2$OH + O, where the yield of undeuterated glycolaldehyde is not negligible.

This new study confirms that the molecular deuteration of the parent species is not just passed to the daughter one, as also found in the case of formamide when formed in the NH$_2$ + H$_2$CO gas-phase reaction (Skouteris et al. 2017).

Finally, the comparison of the new predicted deuterated glycolaldehyde over ethanol isotopomers with those measured toward the solar-like protostar IRAS 16293 B suggests a gas-phase origin for the glycolaldehyde. However, lacking similar computations for the glycolaldehyde grain-surface formation route, the latter cannot be excluded.

We conclude by emphasizing that new facilities like ALMA and IRAM/NOEMA are now so sensitive that the deuterated iCOM isomers can be detected. Their observed ratios can potentially be used to discriminate their formation routes if, and only if, computations similar to those reported here are carried out for both the gas-phase and grain-surface reactions.

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Appendix A

Energies

In the following Tables (3-5), we report the energies of the reaction path, starting from CH$_3$CH$_2$OH + O (e.g., Figure 4 of the main text).
Table 3
Involved Energies Part 1, in Hartrees

| Electronic Energies | Undeuterated | D1 |
|---------------------|--------------|----|
|                     | ZPE B | ZPE-corr B | ZPE-corr B₂/CCSD(T) | ZPE B | ZPE-corr B | ZPE-corr B₂/CCSD(T) |
| CH₃CH₂OH          | -154.1363 | -154.31015 | 0.065377849 | -154.2447744 | -154.0709822 | 0.0620758 | -154.2480766 | -154.0742842 |
| O                   | -74.9785 | -75.0509996 | 0.071620018 | -229.4399420 | -229.1911422 | 0.0682610 | -229.4433010 | -229.1945012 |
| RI1                 | -229.26 | -229.51156 | 0.070337589 | -229.4383720 | -229.1893311 | 0.0670636 | -229.4416460 | -229.1926050 |
| R2                  | -229.25 | -229.50761 | 0.070431348 | -229.43433 | -229.1851619 | 0.0671333 | -229.4376280 | -229.1884599 |
| R3                  | -229.28 | -229.53008 | 0.072307655 | -229.45775 | -229.2079963 | 0.0689597 | -229.4611230 | -229.2113443 |
| R4                  | -229.27 | -229.55250 | 0.071691112 | -229.45559 | -229.2035984 | 0.0683771 | -229.456873 | -229.2069124 |
| TS10                | -229.27 | -229.51204 | 0.070910492 | -229.45049 | -229.2005771 | 0.0676605 | -229.45374 | -229.2038271 |
| cis-glycol.         | -228.72 | -228.97972 | 0.061282384 | -228.91795 | -228.6671163 | 0.0579184 | -228.9213170 | -228.6704083 |
| trans-glycol.       | -228.72 | -228.97374 | 0.06060706 | -228.91314 | -228.6643414 | 0.0573357 | -228.9164110 | -228.6657024 |
| TS4                 | -228.71 | -228.96624 | 0.060708204 | -228.90553 | -228.6550636 | 0.0574292 | -228.9088180 | -228.6583426 |
| TS2                 | -229.21 | -229.46801 | 0.063386520 | -229.40641 | -229.1556054 | 0.0600995 | -229.4097920 | -229.1598924 |
| TS3                 | -229.21 | -229.46556 | 0.062653149 | -229.40291 | -229.1521423 | 0.0593911 | -229.4061750 | -229.1554043 |
| TS6                 | -229.24 | -229.49193 | 0.068737806 | -229.42645 | -229.1730995 | 0.0653728 | -229.4298210 | -229.1764645 |
| TS5                 | -229.23 | -229.49221 | 0.068636375 | -229.42357 | -229.1702044 | 0.0652584 | -229.4269570 | -229.1735824 |
| TS13                | -229.17 | -229.42115 | 0.064329474 | -229.35678 | -229.1066454 | 0.0610465 | -229.3600690 | -229.1099284 |
| TS14                | -229.18 | -229.42399 | 0.068804454 | -229.36359 | -229.113547 | 0.0658265 | -229.3665730 | -229.1165250 |
| TS7                 | -229.21 | -229.46291 | 0.066841945 | -229.39611 | -229.1466319 | 0.0634669 | -229.3994850 | -229.1500069 |
| TS8                 | -229.20 | -229.45945 | 0.066667631 | -229.39279 | -229.1431152 | 0.0633656 | -229.3960920 | -229.1464172 |
| TS9                 | -229.21 | -229.46596 | 0.067715499 | -229.39825 | -229.1479407 | 0.0643525 | -229.4016165 | -229.1513037 |
| TS15                | -229.17 | -229.42550 | 0.063381787 | -229.36212 | -229.1094227 | 0.0600308 | -229.3654730 | -229.1127377 |
| TS11                | -229.21 | -229.46599 | 0.063609818 | -229.40238 | -229.1505795 | 0.0603338 | -229.4056610 | -229.1538555 |
| ep-CH₃OCHOH         | -229.69 | -229.70860 | 0.062141192 | -228.866228 | -228.637091 | 0.0588422 | -228.8895270 | -228.6403900 |
| E-ethen-1,2-diol    | -228.70 | -228.95950 | 0.061060253 | -228.89849 | -228.6473018 | 0.0577773 | -228.9017730 | -228.6505848 |
| Z-ethen-1,2-diol    | -228.71 | -228.96699 | 0.061556193 | -228.90543 | -228.6543449 | 0.0581452 | -228.9088440 | -228.6577559 |
| H                   | -0.4998 | -0.498668238 | 0.0 | ... | ... | ... | ... | ... |
| Ethylene oxide      | -153.56 | -153.7306 | 0.057803599 | -153.67300 | -153.4989789 | 0.0543794 | -153.6763030 | -153.5021988 |
| OH                  | -75.64 | -75.71936 | 0.008111898 | -75.71085 | -75.63707287 | 0.0061969 | -75.7317120 | -75.6393879 |
| Formaldehyde        | -114.34 | -114.46857 | 0.02675717 | -114.42218 | -114.3162043 | 0.0238247 | -114.4450303 | -114.3190553 |
| H₂COH               | -114.89 | -115.02458 | 0.037422909 | -114.98716 | -114.8614284 | 0.0341269 | -114.9904610 | -114.8647244 |
### Table 4

Involved Energies Part 2, in Hartrees

|     | D2       | D3       | D4       |
|-----|----------|----------|----------|
|     | ZPE B2   | ZPE-corr | ZPE B2   |
|     | B2PLYPD3 | B2//CCSD(T) | B2/CCSD(T) |
|     | ZPE-corr | ZPE-corr | ZPE B2   |
|     | B2PLYPD3 | B2//CCSD(T) | B2/CCSD(T) |
| CH2CH2OH | 0.0620798 | −154.2480720 | −154.0742802 |
| O     | ...       | ...       | ...       |
| R11   | 0.0682290 | −229.4433330 | −229.1945332 |
| R12   | 0.0669806 | −229.4417290 | −229.1926880 |
| TS1   | 0.0670293 | −229.4377320 | −229.1885639 |
| R3    | 0.0689817 | −229.4610100 | −229.2113223 |
| R4    | 0.0683701 | −229.4568800 | −229.2069194 |
| TS10  | 0.0675495 | −229.4538550 | −229.2039381 |
| cis-glycol. | 0.0580094 | −228.9212260 | −228.6703893 |
| trans-glycol. | 0.0573127 | −228.9164340 | −228.6657254 |
| TS4   | 0.0573502 | −228.9088970 | −228.6584216 |
| TS5   | 0.0600335 | −229.4097680 | −229.1589584 |
| TS3   | 0.0593101 | −229.4062560 | −229.1554853 |
| TS6   | 0.0655148 | −229.4296790 | −229.1763225 |
| TS11  | 0.0653994 | −229.4268160 | −229.1734414 |
| TS13  | 0.0609195 | −229.3601960 | −229.1100554 |
| TS14  | 0.0653815 | −229.3670180 | −229.1169700 |
| TS7   | 0.0634699 | −229.3994910 | −229.1500129 |
| TS8   | 0.0633366 | −229.3961210 | −229.1464462 |
| TS9   | 0.0644655 | −229.4015020 | −229.1511907 |
| TS15  | 0.0600888 | −229.3654950 | −229.1127957 |
| TS11  | 0.0603418 | −229.4056530 | −229.1538475 |
| TS12  | 0.0596056 | −229.3983880 | −229.1466282 |
| ep-CH$_2$OCHO | 0.0586722 | −228.889970 | −228.6405600 |
| E-ethen-1,2-diol | 0.0578453 | −228.9017050 | −228.6501680 |
| Z-ethen-1,2-diol | 0.0582662 | −228.9087230 | −228.6576349 |
| H     | ...       | ...       | ...       |
| Ethylene oxide | ...       | ...       | ...       |
| OH    | ...       | ...       | ...       |
| Formaldehyde | 0.0345569 | −114.9900310 | −114.8642944 |
| H$_2$COH | 0.0345569 | −114.9900310 | −114.8642944 |

**Note:** The entries include zero-point energies (ZPE) corrected for both B2PLYPD3 and B2//CCSD(T) levels of theory. The final columns represent the corrected total energies (ZPE-corr) for comparison.


Appendix B Geometries

\[
\begin{array}{llll}
\text{CH}_2\text{CH}_2\text{OH} & C & 1.232920-0.271107-0.008952 \\
& H & 2.125654 0.101853 0.485779 \\
& H & 1.288279-1.185206 0.562369 \\
& C & -0.005441 0.539806 0.032131 \\
& H & -0.024020 1.252402 -0.796671 \\
& H & -0.062224 1.126275 0.954803 \\
& O & -1.192797-0.255687 0.041870 \\
& H & -1.150186-0.856623-0.708756 \\
& C & -0.665516 0.600616-0.243231 \\
& H & -0.680218 0.705686-1.332409 \\
& H & -1.141144 1.479384 0.188953 \\
& O & -1.413347-0.525848 0.171215 \\
& H & -0.917795-1.308661-0.94782 \\
& C & 0.780402 0.508725 0.231273 \\
& H & 1.370941 1.396615-0.029110 \\
& H & 0.790069 0.440096 1.334495 \\
& O & 1.399450-0.645306-0.170639 \\
& C & 0.000000 0.740070 0.000000 \\
& H & -0.485785 1.154026 0.886696 \\
& H & -0.485785 1.154026-0.886696 \\
\end{array}
\]
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Appendix C
Deuteration Loops of Reactions 1–5

It is noticeable that RI₁/R₁₂-D₁ leads to RI₃/R₄-D₃ through TS₉-D₃ and that RI₃/R₄-D₅ leads to RI₁/R₁₂-D₄ through TS₇/TS₈-D₅. The last step of the loop is the passage from both RI₁/R₁₂-D₄ and RI₁/R₁₂-D₃ to RI₃/R₄-D₃ through TS₉-D₅ and TS₇/TS₈-D₃, respectively. For this reaction, it is therefore required to consider RI₁/R₁₂-D₁/D₃/D₄ and RI₃/R₄-D₁/D₃/D₅ for the remaining rearrangements and dissociations. With all of this, one should be keeping in mind that all RI₁ and RI₂ are connected by their corresponding TS₁, and that all RI₃ and RI₄ are connected by their corresponding TS₁₀.

Figure 7. Loop of deuteration regarding reaction 1.

Figure 8. Loop of deuteration regarding reaction 2.
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Figure 9. Loop of deuteration regarding reaction 3.

Figure 10. Loop of deuteration regarding reaction 4.

Figure 11. Loop of deuteration regarding reaction 5.

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