A Search for Interstellar Monohydric Thiols

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Abstract

It has been pointed out by various astronomers that a very interesting relationship exists between interstellar alcohols and the corresponding thiols (sulfur analog of alcohols) as far as the spectroscopic properties and chemical abundances are concerned. Monohydric alcohols such as methanol and ethanol are widely observed and 1-propanol was recently claimed to have been seen in Orion KL. Among the monohydric thiols, methanethiol (chemical analog of methanol) has been firmly detected in Orion KL and Sgr B2(N2) and ethanethiol (chemical analog of ethanol) has been observed in Sgr B2(N2), though the confirmation of this detection is yet to come. It is very likely that higher order thiols could be observed in these regions. In this paper, we study the formation of monohydric alcohols and their thiol analogs. Based on our quantum chemical calculation and chemical modeling, we find that the $T_g$ conformer of 1-propanethiol is a good candidate of astronomical interest. We present various spectroscopically relevant parameters of this molecule to assist in its future detection in the interstellar medium.

Key words: astrochemistry – evolution – ISM: abundances – ISM: molecules – methods: numerical – techniques: spectroscopic

Supporting material: tar.gz file

1. Introduction

Starting from the detection of the first carbon containing molecule, the methyldiene radical (CH) in 1937 (Swings & Rosenfeld 1937), almost 200 molecules including neutrals, radicals, and ions have been observed in the interstellar medium (ISM) or in circumstellar shells, and almost 60 molecules have been observed in comets. A mismatch between the cosmic abundance of sulfur and observed abundances of S-bearing species is well known (Palumbo et al. 1997). Particularly around the dense cloud regions, this inequality is pronounced (Tielens & Allamandola 1987; Palumbo et al. 1997).

Around the diffuse cloud and highly ionized regions, sulfur related species roughly resemble the cosmic abundance $\sim 10^{-5}$ (Savage & Sembach 1996; Howk et al. 2006). Earlier, Millar & Herbst (1990) and Jansen et al. (1995) suggested that S, SO, CS, and H$_2$S may explain the missing sulfur problem, though our knowledge of the CS related species is very limited. Recently, Müller et al. (2016) suggested that at 400 K more than 50% of the sulfur budget is shared by CS and H$_2$CS and that a remainder resides in the form of SO and SO$_2$ for hot source Sgr B2(N). Several experiments were carried out to determine the abundant S-bearing species on interstellar grains. The proposed outcome of these experiments is that OCS (Garozzo et al. 2010), CS$_2$ (Ferrante et al. 2008), and hydrated sulfuric acid (Scappini et al. 2003) would act as a sink for the interstellar sulfur. To date, only two sulfur related molecules (OCS and SO$_2$) have been detected on grain surfaces with full confidence, thus the exact reservoir of sulfur is not yet known with certainty (Palumbo et al. 1995; Boogert et al. 1997; Woods et al. 2015).

Among the monohydric alcohols, methanol (CH$_3$OH) is the simplest alcohol that is widely observed in both the gas and solid phases (Tielens & Allamandola 1987) of the ISM. A major portion of the interstellar grain mantle is found to be covered with methanol (Gibb et al. 2004; Das et al. 2008a, 2010; Das & Chakrabarti 2011; Das et al. 2016). The gas-phase abundance of methanol relative to H$_2$ is found to be in the range from 10$^{-9}$ in cold dark clouds to 10$^{-6}$ in hot molecular cores (Charnley et al. 1995). The presence of ethanol (C$_2$H$_5$OH) (the second alcohol in this homologous series) is observed in star-forming regions in the range of 10$^{-8}$ – 10$^{-6}$ (Millar et al. 1988; Turner 1991). Propanol is the next alcohol in the series of monohydric alcohols which may appear in two different forms: normal(n)-propanol (CH$_3$CH$_2$CH$_3$OH) and 2-propanol (CH$_3$CHOHCH$_3$). Recently n-propanol (1-propanol) was claimed to be detected toward Orion KL by Tercero et al. (2015) with a column density of $\lesssim (1.0 \pm 0.2 \times 10^{15})$ cm$^{-2}$, whereas the presence of 2-propanol has not yet been verified.

It is now confirmed that methanol and ethanol are mainly produced on dust grains in the cold phase, and evaporate from warm dust grains in later stages of evolution. Following this trend, even higher order alcohols would be produced on interstellar grains. In the case of thiols, sulfur takes the place of oxygen in the hydroxyl group of an alcohol. Like their alcohol analogs, these thiols are mainly produced on the grain surface and are evaporated in suitable time. A tentative detection of methanethiol (CH$_3$SH) in Sgr B2 was done by Turner (1977). Later this claim was confirmed by Linke et al. (1979) and showed that the CH$_3$SH/CH$_3$OH ratio is close to the cosmic S/O ratio. Recently, Majumdar et al. (2016) detected CH$_3$SH in IRAS 16293-2422, and Kolessniková et al. (2014) reported the detection of C$_2$H$_4$SH in the hot core of Orion KL, but very recent observations by Müller et al. (2016) suggested that the detection of C$_2$H$_5$SH in Orion KL is uncertain. The presence of higher order thiols is yet to be seen.
In this paper, we discuss the formation of monohydric alcohols and their thiol analogs. First, we identify the most stable conformers of alcohols and their thiols. Then we develop a chemical network to study the formation of all these species. From the outcome of our chemical modeling, the most probable new candidate for the astronomical detection is determined. Moreover, a detailed spectroscopic study is carried out to set a guideline for observing this species in the near future. This

Figure 1. Relaxed potential energy surface scan of the dihedral angle of monohydric alcohols and their thiol analogs using the MP2/cc-pVTZ level of theory.
Relative Energies of Various Conformers of Alcohols and Their Thiol Analogs

| Species     | Conformer     | ΔE in cm⁻¹ (Kcal/mol) |
|-------------|---------------|-----------------------|
| Methanol    | HCOH ± 180°   | 0 (0)                 |
|             | HCOH ± 60°    | 0.4389 (0.0013)       |
|             | HCOH 120°     | 395 (1.13)            |
|             | HCOH 0°       | 395 (1.13)            |
| Methanethiol| HCSH ± 180°   | 0 (0)                 |
|             | HCSH ± 60°    | 0.877 (0.0025)        |
|             | HCSH ± 120°   | 445 (1.27)            |
|             | HCSH 0°       | 445 (1.27)            |
| Ethanol     | trans         | 0 (0)                 |
|             | gauche        | 23 (0.066)            |
|             | eclipsed      | 415 (1.19)            |
|             | cis           | 456 (1.30)            |
| Ethanethiol | gauche CCSH   | 0 (0)                 |
|             | trans CCSH    | 170.0 (0.49)          |
|             | eclipsed      | 524.0 (1.50)          |
|             | cis           | 541 (1.55)            |
| 1-propanol  | Gt            | 0 (0)                 |
|             | Gg            | 67 (0.19)             |
|             | Gg'           | 3.5 (0.01)            |
|             | Tt            | 95 (0.27)             |
|             | Tg            | 80 (0.23)             |
| 1-propanethiol| Gt            | 0 (0)                 |
|             | Gg            | 318 (0.91)            |
|             | Gg'           | 63 (0.18)             |
|             | Gg'           | 46 (0.13)             |
| 2-propanol  | Tt            | 0 (0)                 |
|             | 216 (0.62)    |
| 2-propanethiol| Tt            | 0 (0)                 |
|             | 83.6 (0.24)   |
|             | 2 (0.034)     |

Table 1

Figure 2. Five possible conformers of 1-propanethiol.

2. A Search for the Most Stable Conformational Isomers

All the quantum chemical calculations reported here are calculated with the Gaussian 09 program (Foresman & Frisch 1996; Frisch et al. 2009). Each optimized structure is verified by avoiding the imaginary frequency. With the advance of quantum chemical calculations, proper choices of method and basis sets are required to compute the molecular properties.

According to the IUPAC definition of a conformer, conformational isomerism is a form of stereo isomerism in which the isomers can be interconverted exclusively by rotations about formally single bonds. It is expected that the most stable conformer would be the most probable candidate for the astronomical detection. In the attempt here, before constructing our chemical model we searched for the various conformers of the monohydric alcohols and their thiols through a relaxed potential energy surface (PES) scan of dihedral angles. PES scan results are displayed in Figure 1 and the relative energies of the conformers are listed in Table 1. 2-propanol/2-propanethiol is the structural isomer of 1-propanol/1-propanethiol, and for the sake of completeness we discuss their conformers as well. For all these calculations, we use Møller-Plesset perturbation theory (MP2) with the Peterson and Dunning correlation consistent basis set (cc-pVTZ) (Peterson & Dunning 2002) of the Gaussian 09 software. The results of the PES scans are presented below.

2.1. Methanol and Methanethiol

Methanol and methanethiol both show internal rotation of the CH₃ group. From a relaxed PES scan (~180° to +180° of dihedral angle ∠(H₅, C₁, O₁, H₃)), we have shown that methanol and methanethiol both exist in the most stable state at ±180° of the dihedral angle on PES. On the other hand, there are three different maxima for both methanol and methanethiol at ±120° and at 0°. Relative energies are listed in Table 1.

2.2. Ethanol and Ethanethiol

In the case of ethanol and ethanethiol, both have two types of internal rotation: around the OH/SH group and the CH₃ group. Due to the internal rotation of the OH/SH group of ethanol/ethanethiol, there may be four different forms. For ethanol, the trans/anti conformation (dihedral angle ∠(C₁, C₅, O₁, H₃) = 180°) is the minimum energy state on PES. The gauche conformer (dihedral angle ∠(C₁, C₅, O₁, H₃) = ±60°) is situated slightly higher on the PES. The relative energy between the trans and gauche conformer is 0.877 cm⁻¹. When the dihedral angle is ±120°, conformers are called eclipsed. The relative energy between trans and eclipsed conformers is 415 cm⁻¹. When the dihedral angle is 0°, it is called a cis conformer, which is also
Table 2

| Reaction                      | Energy Barrier (K) | References |
|-------------------------------|-------------------|------------|
| Methanethiol                  |                   |            |
| H + CO → HCO                   | 1000              | H          |
| H + CO → HOC                   | 1000              | H          |
| H + HCO → H2CO                 | 0                 | H          |
| H + HOC → CHOH                 | 0                 | H          |
| CH + OH → CHOH                 | 0                 | H          |
| H + H2CO → HCO + H2           | 1850              | H          |
| H + CHOH → CH2OH              | 0                 | H          |
| OH + CH2 → CH2OH              | 0                 | H          |
| O + CH2 → CH2OH               | 0                 | H          |
| H + CH2OH → CH3OH             | 0                 | H          |
| Methanol                      |                   |            |
| H + CS → HCS                  | 1000              | H          |
| H + HCS → H2CS                | 0                 | H          |
| H + H2CS → CH3S               | 1000              | M          |
| S + CH2 → CH3S                | 0                 | ...        |
| H + H2CS → HCS + H2           | 1000              | M          |
| H + H2CS → CH3SH              | 1000              | M          |
| CH2 + HS → CH3SH              | 0                 | ...        |
| H + CH3S → CH3SH              | 0                 | M          |
| H + CH2SH → CH3SH             | 0                 | ...        |
| Ethanol                       |                   |            |
| C2H5 + OH → C2H4OH            | 0                 | H          |
| CH2OH + CH2 → C2H4OH          | 0                 | ...        |
| C2H5 + O → C2H4O              | 0                 | ...        |
| H + C2H2O → C2H4OH            | 0                 | ...        |
| Ethanolithiol                 |                   |            |
| C2H5 + HS → C2H4SH            | 0                 | M          |
| CH3SH + CH2 → C2H4SH          | 0                 | M          |
| S + C2H5 → C2H4S              | 0                 | M          |
| H + C2H4S → C2H4SH            | 0                 | M          |
| CH2 + CH3S → C2H4SH           | 0                 | ...        |
| 1-propanol(CH3CH2CH2OH)       |                   |            |
| C2H + H2O → HCCCHHO + H      | 0                 | ...        |
| O + C2H5 → HCCCHHO + H       | 0                 | ...        |
| H + HCCCHHO → HCCCHCHO        | 1688              | ...        |
| H + HCCCHCHO → H2CCCHCHCHO    | 2891              | ...        |
| H + CH2CH2CHO → CH3CH2CHO    | 2274              | ...        |
| H + CH2CH2CHO → CH3CH2CHO    | 0                 | ...        |
| H + CH3CH2CHO → CH3CH2CH3O   | 0                 | ...        |
| C2H5 + CH2OH → CH3CH2CH2OH   | 0                 | ...        |

Note. H: reaction taken from Hasegawa et al. (1992); M: reaction taken from Müller et al. (2016).

Maeda et al. (2006) discussed five possible conformational isomers of 1-propanol originating from alternate structures of the central (C1, C5, O8, H6) and (O8, C5, C1, H2) skeletal chains. These five forms are Trans–trans (Tt), Trans–gauche (Tg), Gauche–trans (Gt), Gauche–gauche (Gg), and Gauche–gauche$^c$ (Gg$^c$). Based on the relative energies of these conformers, Abdurakhmanov & Ismailzade (1984) determined that the Tg conformer has the lowest energy. However, Lotta et al. (1984) and Kisiel et al. (2010) predicted that the Gt conformer has the lowest energy. Our quantum chemical study also finds that the Gt conformer has the lowest energy. As in earlier studies, in terms of their relative energies, we find that the 1-propanol conformer follows the sequence of Gt, Gg, Gg$^c$, Tg, Tt in ascending order of relative energies.

Similar studies have been carried out for 1-propanethiol. Since 1-propanethiol has not yet been detected in the ISM, perspective views of its possible staggered conformers, originating from the combination of trans and gauche conformations, is shown in Figure 2. Our calculation reveals that the Tg configuration has the lowest energies. The relative energies of all the conformers with respect to the Tg conformer are shown in Table 1.

2.4. 2-propanol and 2-propanethiol

Depending on the rotation of the dihedral angle $\angle$(C8, C9, O11, H12)/$\angle$(H10, C9, S11, H2). 2-propanol/2-propanethiol may exist in two forms: gauche and trans. The gauche conformer is found to be stable for 2-propanol, whereas in the case of 2-propanethiol the trans conformer is found to be stable. Since 2-propanol/2-propanethiol is a secondary alcohol/thiol, we do not consider this in our chemical modeling.

3. Chemical Modeling

3.1. Chemical Network

For the purpose of chemical modeling, we use our large gas-grain chemical network (Das et al. 2008b, 2013a, 2013b; Gorai et al. 2017). Gas-grain interactions are considered to mimic the most realistic scenario of the ISM. We assume that gas and grains are coupled through accretion and various desorption mechanisms such as thermal, nonthermal (Garrod & Herbst 2006), and cosmic-ray desorption processes. Our present gas-phase chemical network consists of 6628 reactions between 684 gas-phase species, and our surface chemical network consists of 487 reactions between 316 surface species. We adopt our gas-phase chemical network from the UMIST 2006 database (Woodall et al. 2007). Our gas-phase network contains some deuterated reactions as well (Das et al. 2015a, 2015b; Sahu et al. 2015). For the grain surface reaction network, we primarily follow Hasegawa et al. (1992) and for the ice-phase deuterium fractionation reactions, we follow Caselli et al. (2002), Cazaux et al. (2010), and Das et al.
Though we have the deuterated species in our network, we do not consider the deuterium chemistry here for the sake of simplicity. Here, we concentrate on the formation of monohydric alcohols and their thiol analogs. These molecules are mainly formed on the dust surface. Chemical enrichment of the interstellar grain mantle depends on the binding energies ($E_d$) and barriers against diffusion ($E_b$) of the adsorbed species. The binding energies of these species are available from past studies (Allen & Robinson 1977; Tielens & Allamandola 1987; Hasegawa et al. 1992; Hasegawa & Herbst 1993), but these binding energies mostly pertain to silicates. The binding energy of the most important surface species (with ice), which control the chemical composition of the interstellar grain mantle, are available from some recent studies (Cuppen & Herbst 2007; Garrod 2013). We used these energies in our model. For the species whose binding energies were unavailable from these papers, we kept the same values as in the past studies. We used the binding energies against diffusion equal to $E_d^{0.5}$ (Garrod 2013) for our calculations.

Our ice-phase network contains other reactions mentioned in Hasegawa et al. (1992). In Table 2, we only show some grain phase reactions that may lead to the formation of these alcohols and their thiol analogs. Druard & Wakelam (2012) show that the chemistry of sulfur may be very different from the chemistry of other chemical elements. They considered sulfur polymers ($S_n$) and polysulphanes ($H_2S_n$) as the potential candidates of the sulfur refractory residue. Here we considered all the sulfur related reactions used in Druard & Wakelam (2012). For the formation of methanol, we used the pathways

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**Table 3**

Peak Abundance of Ice-phase Alcohols and Their Thiols with Respect to H Nuclei in all Forms

| Species          | Isothermal Phase | Warm-up Phase |
|------------------|------------------|---------------|
|                  | Gas Phase        | Ice Phase     | Gas Phase (Temp in K) | Ice Phase (Temp in K) |
| Methanol         | $1.75 \times 10^{-9}$ | $2.12 \times 10^{-5}$ | $6.98 \times 10^{-6}(106.0)$ | $1.86 \times 10^{-5}(10.24)$ |
| Ethanol          | $8.38 \times 10^{-11}$ | $4.66 \times 10^{-11}$ | $1.26 \times 10^{-4}(120.2)$ | $2.00 \times 10^{-5}(71.4)$ |
| 1-propanol       | $6.45 \times 10^{-20}$ | $1.84 \times 10^{-17}$ | $4.29 \times 10^{-7}(120.6)$ | $4.76 \times 10^{-7}(106.1)$ |
| Methanethiol     | $1.06 \times 10^{-20}$ | $1.62 \times 10^{-8}$ | $2.16 \times 10^{-8}(107.3)$ | $4.58 \times 10^{-8}(31.2)$ |
| Ethanethiol      | $3.04 \times 10^{-22}$ | $5.23 \times 10^{-20}$ | $5.45 \times 10^{-9}(120.0)$ | $1.02 \times 10^{-9}(66.2)$ |
| 1-propanethiol   | $2.94 \times 10^{-27}$ | $6.00 \times 10^{-25}$ | $3.71 \times 10^{-10}(122.7)$ | $3.73 \times 10^{-10}(108.4)$ |

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proposed by Hasegawa et al. (1992); for the production of methanol we followed Müller et al. (2016). For ethanol production, we assumed a barrierless addition between the C₂H₃ and OH radicals (Hasegawa et al. 1992), the CH₂OH and CH radicals, and a hydrogenation reaction with C₂H₂O. For the production of ethanethiol, we used the pathways proposed by Müller et al. (2016). Reaction references are also noted in Table 2. Since no pathways were available for the formation of 1-propanol and 1-propanethiol, we used some new pathways for the formation of these species in the ice phase. For the formation of 1-propanol we considered two radical-molecular ice-phase reactions followed by four successive hydrogen addition reactions. A similar sequence was also considered for the formation of 1-propanethiol. In addition, we also considered the radical–radical reaction between C₂H₃ and CH₂OH for the formation of 1-propanol and the radical–radical reaction between C₂H₂ and CH₂SH for the formation of 1-propanethiol. As for the other radical-molecular reactions considered in Hasegawa et al. (1992), here we also assumed the barrierless nature of these reactions. Rate coefficients of these types of reactions thus depend upon the adopted adsorption energies and would be processed in each encounter. Among the four successive hydrogen addition reactions considered here, the hydrogen addition reaction in the second and fourth steps of 1-propanol and 1-propanethiol would be considered radical–radical interactions and thus barrierless in nature. But the first and third steps of this sequence are the neutral-neutral reactions that must contain some activation barrier. We carried out a quantum chemical calculation to determine the suitable transition states for these neutral-neutral reactions. A QST2 calculation with the B3LYP/6-31+G(d) method was employed for this computation and the activation barriers obtained for these neutral-neutral reactions are listed in the second column of Table 2. Though 2-propanol and 2-propanethiol are the structural isomers of 1-propanol and 1-propanethiol, respectively, we do not consider their formation in the present study. For the destruction of ice-phase species, we consider the photodissociation reactions by direct interstellar photons and cosmic-ray induced photons.

We did not use any new gas-phase formations of these species. In our model, gas and grains are continuously interacting with each other and exchanging their chemical components. Surface species could populate the gas phase by various evaporation mechanisms considered here, namely thermal desorption, cosmic-ray induced desorption, and reactive nonthermal desorption (here we assume a nonthermal desorption factor to be 0.01). For the destruction of gas-phase alcohols and their corresponding thiols, we used destruction by the most abundant ions (H₃⁺, CH₄⁺, C⁺, HCO⁺, N⁺, O⁺, H₂O⁺, CH⁺, O₂⁺, H⁺, He⁺, CH₃⁺), dissociative recombination, photodissociation, and dissociation by cosmic rays.

### 3.2. Physical Condition

In order to realistically model the physical parameters, we consider a warm-up model (Quan et al. 2016). Initial phase of this model is the isothermal phase (T = 10 K) followed by a warm-up phase. Both phases have the same constant density (n_H = 10⁴ cm⁻³) and a visual extinction of 10. The second phase starts with 10 K and ends at 200 K. Here, it is assumed that the isothermal phase lasts for 10⁴ years and the warm-up phase for another 10⁴ years. Initial abundances are taken from Druard & Wakelam (2012), except the sulfur abundance. Druard & Wakelam (2012) considered the abundance of S²⁻ in its cosmic value ~1.5 × 10⁻³ (Sofia et al. 1994). Here, we are assuming much reduced S²⁻ abundance (8.0 × 10⁻⁶) as used in Leung et al. (1984). Hydrogens are mostly assumed to be in the form of molecular hydrogen. These molecular hydrogens were mainly formed on the dust surfaces (Bihlm et al. 2001; Chakrabarti et al. 2006a, 2006b) in earlier stages. For the ionization of the medium, we assume a cosmic ray ionization rate of 1.3 × 10⁻¹⁷ s⁻¹.

### 3.3. Modeling Results

In Figure 3, we show the time evolution of gas-phase (solid curve) and ice-phase (dotted curve) alcohols and their thiol analogs. The upper panel shows the isothermal phase and the lower panel shows the warm-up phase. In the isothermal phase, it is clear that ice-phase methanol, ethanol, and methanethiol are efficiently produced. Some portions of these abundant ice-phase species are readily transferred to the gas phase via various desorption mechanisms. At the beginning of the warm-up phase, the ice phase production of ethanol, ethanethiol, 1-propanol, and 1-propanethiol increases, due to the increase in the mobility of the surface species involved in the reactions. In Table 3, we list the peak abundances of these alcohols and their thiol analogs for both phases. In the warm-up phase, the peak abundances of these species, along with the temperatures related to these peak values, are also given.

It is fascinating that among all the species shown in Table 3, methanol is the only one that is most efficiently produced in the isothermal (T = 10 K) phase compared to the warm-up phase. Its peak ice-phase abundance in the isothermal phase is found to be 2.12 × 10⁻⁵ with respect to total H nuclei, whereas in the warm-up phase, its peak abundance of 1.86 × 10⁻⁵ appears around 10.24 K. In comparison to the isothermal phase, abundances of the other ice-phase species seem to be significantly higher in the warm-up phase. For example, the peak abundance of ice-phase methanethiol appears around 31

### Table 4: Molecular Ratio of Some Species

| Species | After 1.0 × 10⁶ Years | After 1.5 × 10⁶ Years | After 2.0 × 10⁶ Years | Observed |
|---------|----------------------|----------------------|----------------------|----------|
| CH₃OH   | 2663                 | 1879                 | 3.24                 | 45⁰, 78⁰ |
| CH₃CH₂OH| 2.08 × 10⁹           | 3485                 | 7.79                 | 2700⁰    |
| CH₃CH₂SH| 773843               | 1.85                 | 2.40                 | 60⁰      |
| CH₃SH   | 2.61 × 10¹¹          | 708                  | 4.55                 | ≥21⁰, 3.1⁰ |
| CH₃OH   | 2.69                 | 344.3                | 112.7                | 120⁰, 5700⁰ |
| CH₃CH₂SH| 2.62 × 10⁸           | 129                  | 157                  | 125⁰, 225⁰ |

**Notes.**

* Tercero et al. (2015) from observation.
* Müller et al. (2016) from modeling.
* Müller et al. (2016) from observation.
K, the production of ethanol and ethanethiol is found to be efficient around 66–71 K, and the efficient production of 1-propanol and 1-propanethiol is found to be around 106–108 K. The formation of ethanol, ethanethiol, 1-propanol, and 1-propanethiol at such high temperatures is mainly due to the radical–radical reactions. It is essential to point out that the
adopted adsorption energies (1175 K, 2110 K, 2850 K, 1500 K, 5080 K, 5084 K) of some of these key radicals (respectively CH₃, C₂H₅, OH, SH, CH₂OH, CH₂SH) are available from some earlier studies (Hasegawa & Herbst 1993; Cuppen & Herbst 2007; Garrod 2013).

Since we mainly consider the ice phase production of these species, the appearance of the peak gas-phase abundance is closely related to their respective adsorption energies. For example, in the case of methanol and methanethiol, we assumed the adsorption energy of 5530 K and 5534 K, respectively, and from Table 3 the resulting peak gas-phase abundances of methanol and methanethiol seem to be around 10⁶–10⁷ K. For ethanol, ethanethiol, propanol, and 1-propanethiol much higher adsorption energies are assumed, respectively 6260 K, 6230 K, 6260 K, and 6260 K, which ensures the peak gas-phase abundance of these species around 120–123 K.

In Table 4, we show the molecular ratio (gas phase) of these alcohols and their thiol analogs. Since chemical evolution is a highly time-dependent phenomenon, ratios are shown for various timescales: 1.0 × 10⁶ years corresponds to the end of the isothermal phase, 1.5 × 10⁶ years corresponds to the middle age of the warm-up phase, and 2.0 × 10⁶ years is related to the end of the warm-up phase. The gas-phase ratios of the observed and other modeling results are also shown. The gas-phase observational ratios are taken from Tercero et al. (2015) and Müller et al. (2016), whereas hot-core modeling results are taken from Müller et al. (2016). It is interesting to note that around the isothermal phase, the gas-phase abundances of methanol, methanethiol, and ethanol are in the range of 10⁻⁹–10⁻¹¹, whereas the gas-phase abundances of the other species are negligible, which yields much higher molecular ratios for some species. Beyond 1.0 × 10⁶ years, the mobility of the surface species rapidly increases and yields a significant production of negligible species. At the end of the warm-up phase, we obtain reasonable values for these ratios.

4. Spectroscopy

4.1. Vibrational Spectroscopy

Our results suggest that 1-propanethiol would be a probable candidate for the astronomical detection. Here we calculate the IR spectrum of 1-propanethiol for the sake of completeness. Moreover, vibrational spectral information of its one structural isomer, 2-propanethiol, is also presented. In Table 5 we assign different modes of vibrations along with the frequency and intensity of these species. Ice-phase absorbance is shown in terms of the integral absorption coefficient in cm molecule⁻¹. We compare our results with the existing experimental results. The Gaussian 09 program was used for all these calculations. Water is used as a solvent to compute vibrational spectroscopy using the Polarizable Continuum Model (PCM) with the integral equation formalism variant (IEFPCM) as a default Self-consistent Reaction Field (SCRF) method. The IEFPCM model is considered convenient because the second derivative of energy with respect to the coordinate (bond distance, bond angle) is available for this model and also because its analytic form is available. For these computations, we used the DFT
method with B3LYP functional and the higher order basis set to 6-311g+++(2df, 2pd) (Choi et al. 2008) for better accuracy. A comparison between our calculated IR spectrum band with the existing experimental results of 1-propanethiol and 2-propanethiol (Smith et al. 1968; Torgrimsen et al. 1970) are shown in Table 5. It is clear from the table that our results are in excellent agreement with the existing experimental values. The most intense band of 1-propanethiol appears at 3.23 μm (3091.47 cm⁻¹) and 3.24 μm (3085.19 cm⁻¹), due to CH₂ and CH₃ bands stretching with the integral absorbance coefficient of 8.81 × 10⁻¹⁸ and 8.41 × 10⁻¹⁸ cm molecule⁻¹, respectively. The most intense band of 2-propanethiol belongs to 3.25 μm (3078.79 cm⁻¹), which corresponds to the integral absorbance coefficient of 1.50 × 10⁻¹⁷ cm molecule⁻¹.

Table 6
Rotational, Quartic, and Sextic Centrifugal Distortion Constants of 1-propanethiol and 2-propanethiol

| Species               | Rotational constants with equilibrium (e) and ground vibrational state (0) geometry | Values in MHz with DFT (HF method) | Experimentally obtained ground-state values in MHz | Distortional constants | Values in KHz with DFT(HF method) |
|-----------------------|------------------------------------------------------------------------------------|-----------------------------------|----------------------------------------------------|------------------------|-----------------------------------|
| 1-propanethiol (Tg)   | A⁺ 24213.642(24429.75)                                                            | ...                               | ΔJ                                                 | 0.296911(0.208512)     |
|                       | B⁺ 2312.864(2337.88)                                                              | ...                               | ΔK                                                 | 214.57798(618.4248)    |
|                       | C⁺ 2222.041(2245.40)                                                              | ...                               | ΔJK                                                | 28.91(42.2776)         |
|                       | ...                                                                                | ...                               | δ_j                                                | 0.0455(0.039844)       |
|                       | A₀ 23239.81(23632.75)                                                             | 23429.0^a                         | δ₁                                                 | 0.4518(9.96033)        |
|                       | B₀ 2301.32(2328.06)                                                               | 2345.29^a                         | Φ_J                                                | 0.90726 × 10⁻⁶(-0.2571 × 10⁻⁶) |
|                       | C₀ 2199.16(2226.75)                                                               | 2250.18^a                         | Φ_K                                                | 0.419723 × 10⁻⁴(0.45931 × 10⁻⁴) |
| 2-propanethiol (trans)| A⁺ 7886.965(7938.21)                                                              | ...                               | ΔJ                                                 | 1.246(1.043)           |
|                       | B⁺ 4341.565(4399.57)                                                              | ...                               | ΔK                                                 | 6.799(5.473)           |
|                       | C⁺ 3118.889(3152.54)                                                             | ...                               | ΔJK                                                | 2.184(3.312)           |
|                       | ...                                                                                | ...                               | δ_1                                                | 3.728(2.625)           |
|                       | A₀ 7782.14(7841.42)                                                               | 7892.65^a                         | δ₂                                                 | 0.3805(1.933)          |
|                       | B₀ 4306.51(4366.93)                                                               | 4441.42^a                         | Φ_J                                                | 0.108001 × 10⁻⁶(0.15733 × 10⁻⁶) |
|                       | C₀ 3087.77(3124.21)                                                               | 3158.03^b                         | Φ_K                                                | 0.144633 × 10⁻⁵(0.54329 × 10⁻⁵) |

Notes.

^a Ohashi et al. (1977)  
^b Griffith & Boggs (1975)

4.2. Rotational Spectroscopy

To date, most of the species have been observed in the ISM or circumstellar shells via their rotational transitions. Chakrabarti et al. (2015) and Majumdar et al. (2012, 2013, 2014a, 2014b) pointed out the need for theoretical calculations for a firm identification of some unknown species in the ISM. Species that have permanent dipole moments show their rotational transitions. Here we compute various rotational parameters (for equilibrium structures and for the ground vibrational state) for 1-propanethiol and 2-propanethiol. Here we employed the B3LYP/aug-cc-pVTZ and HF/cc-pVTZ methods in the Gaussian 09 program. The aug prefix basis set is used here to mean that the basis set is augmented with a consistent basis sets (Kendall et al. 1992, 2012, 2013, 2014a, 2014b). A comparison between our calculated IR spectrum band with the existing experimental results of 1-propanethiol and 2-propanethiol (Smith et al. 1968; Torgrimsen et al. 1970) are shown in Table 5. It is clear from the table that our results are in excellent agreement with the existing experimental values. The most intense band of 1-propanethiol appears at 3.23 μm (3091.47 cm⁻¹) and 3.24 μm (3085.19 cm⁻¹), due to CH₂ and CH₃ bands stretching with the integral absorbance coefficient of 8.81 × 10⁻¹⁸ and 8.41 × 10⁻¹⁸ cm molecule⁻¹, respectively. The most intense band of 2-propanethiol belongs to 3.25 μm (3078.79 cm⁻¹), which corresponds to the integral absorbance coefficient of 1.50 × 10⁻¹⁷ cm molecule⁻¹.

Figure 4 shows the isotopic variation of the vibrational spectra of 1-propanethiol. We show isotopic variation by changing the mass of carbon (C = 12 and 13 isotopic mass) and sulfur atoms (S = 32 and 34 isotopic mass). The result shows that the bending and stretching modes are shifted toward lower wavenumbers. The CS stretching mode for CH₃CH₂^{13}CH₂SH with wavenumber 700.4 cm⁻¹ is shifted to 698.01 cm⁻¹, the CH₂ wagging mode with wavenumber 1271.69 cm⁻¹ is shifted to 1265.14 cm⁻¹, and the CH₂ antisymmetric stretching with wavenumber 3111.92 cm⁻¹ is shifted to the wavenumber 3101.18 cm⁻¹ due to the change in isotopic mass of a carbon atom of the CH₂ group (CH₃CH₂^{13}CH₂^{32}SH).
| Species               | $\mu_a$       | $\mu_b$       | $\mu_c$ | $\mu_{\text{Total}}$ |
|----------------------|---------------|---------------|---------|----------------------|
| Methanol             | $-1.5406 (1.44^a)$ | $1.0537 (0.899^a)$ | 0.0     | $1.8665 (1.69^a)$    |
| Methanethiol         | 1.4683$(1.312^b)$ | 1.0152$(0.758^b)$ | $-0.0001$ | $1.7851(1.51^b)$    |
| Ethanol              | $-0.0541(0.046^c)$ | 1.7374$(1.438^c)$ | 0.0000  | $1.7838^{\text{HF}}, 1.53^{\text{DFT}}(1.441^c)$ |
| Ethanethiol          | 0.0431$(1.06^d)$ | 1.8597$(1.17^d)$ | 0.00    | $1.8602 (1.50^d)$    |
| 1-propanol (Gr)      | 0.8018, 0.574$^e$ (0.32$^h$, 0.4914$^i$) | 1.0022, 1.086$(1.23^h, 0.9705^i)$ | 1.0743, 0.922$(0.94^h, 0.9042^i)$ | $1.6737, 1.53^e(1.58^h, 1.4145^i)$ |
| 1-propanethiol (Tg)  | 1.7638        | $-0.0840$     | 0.8186  | $1.9463(1.6)^f$      |
| 2-propanol (gauche)  | $-1.2070(1.114^f)$ | $-0.7023(0.737^f)$ | 0.9868$(0.8129^f)$ | $1.9163(1.56^f)$    |
| 2-propanethiol (trans) | 0.4034     | 1.8685        | 0.00    | $1.9115 (1.61^f)$    |

**Notes.**

- $^a$ Ivash & Dennison (1953).
- $^b$ Tsunekawa et al. (1989).
- $^c$ Takano et al. (1968).
- $^d$ Schmidt & Quade (1975).
- $^e$ calculation at MP2/cc-pVTZ level.
- $^f$ Lide (2001).
- $^g$ Hirota (1979).
- $^h$ Abdurakhmanov et al. (1970).
- $^i$ Kisiel et al. (2010).
Various components of dipole moments are computed for all the alcohols and their thiols considered in this study. In Table 7, we compare our calculated dipole moment components with the existing theoretical or experimental results. Previous studies found that calculations at the HF level would predict dipole moment components close to the experimental values. Thus, we used theoretical HF/6-31g(d) levels for this computation. It is expected that these complex molecules could be detected in hot-core regions. Charnley et al. (1995) pointed out that for an optically thin emission, the antenna temperature could be found by calculating the intensity of a given transition. This intensity is proportional to \( \frac{\mu^2}{Q(T_{\text{rot}})} \), where \( \mu \) is the electric dipole moment and \( Q(T_{\text{rot}}) \) is the partition function at rotational temperature \( T_{\text{rot}} \). In Table 8, we compare the intensities for all the species with respect to methanol. For the computation of \( Q(T_{\text{rot}}) \), we use \( \sqrt{T^3/(ABC)} \). Rotational constants of these species are taken from earlier studies (Takano et al. 1968; Griffith & Boggs 1975; Ohashi et al. 1977; Hirota 1979; Sastry et al. 1986; Lucia et al. 1989; Kisiel et al. 2010; Müller et al. 2011). Here we assume that all these species bear the same column density and rotational temperature. Since we are aiming to study these molecules around hot-core regions, we use \( T = 180 \) K for this calculation. All these ratios are shown in Table 8. A very nice correlation is seen as we go to higher order alcohols/thiols. The spectral intensities, along with the frequencies for rotational transitions of 1-propanethiol and 2-propanethiol in the submillimeter regime, are predicted by using quantum chemical calculations followed by the SPCAT program (Pickett 1991). For these calculations, we used the experimentally obtained constants from Table 6 and the theoretically obtained dipole moments from Table 7. We prepared these catalog files in JPL format; they are given as supplementary materials with this article.

5. Conclusions

In this paper we study the formation of monohydric alcohols and their thiols. The major highlights of our work are as follows.

1. Among the various conformational isomers, it is essential to determine the most stable conformer that might be a viable candidate for astronomical detections. Here we carried out a potential energy surface scan to find the most stable isomer of the monohydric alcohols and their thiol analogs. Among the alcohols, methanol, ethanol, and 1-propanol have been claimed to be detected in the ISM, whereas in thiols, methanethiol and ethanethiol were claimed to be detected in hot-core regions. Among the alcohols, 2-propanol has not yet been detected in any sources, and among the thiols, 1-propanethiol and 2-propanethiol have not yet been detected. Our calculations find that the gauche, \( T_g \), and trans conformers are the most stable isomers for 2-propanol, 1-propanethiol, and 2-propanethiol, respectively.

2. Reaction pathways in forming all stable isomers of monohydric alcohols and their thiols are prepared to study their chemical evolution.

3. Our study reveals that around the warmer region (\( T > 120 \) K), 1-propanethiol would be a viable candidate for astronomical detection in the gas phase.

4. Since 1-propanethiol has not yet been detected in space, we carried out quantum chemical calculations to study various spectral aspects (in the IR and the submillimeter) of this species. Band assignments were done for its various modes of vibration. Changes in absorbance spectra due to the isotopic effects were also noted. Moreover, we found the rotational and distortional constants of this species and compared them with existing experimental results. Experimentally obtained constants and our calculated dipole moment components are further utilized to predict various probable transitions, which should be useful for the future detection of this species in the ISM.

P.G. is grateful to D.S.T. (Grant No. SB/S2/HEP-021/2013) for the partial financial support. A.D. and S.K.C. would like to acknowledge the ISRO respond project (Grant No. ISRO/RES/2/402/16-17). E.E.E. acknowledges a research fellowship from the Indian Institute of Science, Bangalore. A.D. acknowledges the partial support of the Indian Centre for Space Physics.

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