

# A Mechanistical Study on the Formation of Dimethyl Ether (CH<sub>3</sub>OCH<sub>3</sub>) and Ethanol (CH<sub>3</sub>CH<sub>2</sub>OH) in Methanol-containing Ices and Implications for the Chemistry of Star-forming Regions

Alexandre Bergantini<sup>1,2</sup>, Sándor Góbi<sup>1,2</sup>, Matthew J. Abplanalp<sup>1,2</sup>, and Ralf I. Kaiser<sup>1,2</sup> <sup>1</sup>Department of Chemistry, University of Hawaii at Mānoa, Honolulu, HI 96822, USA; ralfk@hawaii.edu <sup>2</sup>W.M. Keck Laboratory in Astrochemistry, University of Hawaii at Mānoa, Honolulu, HI 96822, USA

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## Abstract

The underlying formation mechanisms of complex organic molecules (COMs)—in particular, structural isomers in the interstellar medium (ISM) are largely elusive. Here, we report new experimental findings on the role of methanol (CH<sub>3</sub>OH) and methane (CH<sub>4</sub>) ices in the synthesis of two C<sub>2</sub>H<sub>6</sub>O isomers upon interaction with ionizing radiation: ethanol (CH<sub>3</sub>CH<sub>2</sub>OH) and dimethyl ether (CH<sub>3</sub>OCH<sub>3</sub>). The present study reproduces the interstellar abundance ratios of both species with ethanol to dimethyl ether branching ratios of  $(2.33 \pm 0.14)$ :1 suggesting that methanol and methane represents the key precursor to both isomers within interstellar ices. Exploiting isotopic labeling combined with reflectron time-of-flight mass spectrometry (Re-TOF-MS) after isomer selective vacuum ultra-violet (VUV) photoionization of the neutral molecules, we also determine the formation mechanisms of both isomers via radical–radical recombination versus carbene (CH<sub>2</sub>) insertion with the former pathway being predominant. Formation routes to higher molecular weight reaction products such as ethylene glycol (HOCH<sub>2</sub>CH<sub>2</sub>OH), dimethyl peroxide (CH<sub>3</sub>OOCH<sub>3</sub>), and methoxymethanol (CH<sub>3</sub>OCH<sub>2</sub>OH) are discussed briefly as well.

*Key words:* astrochemistry – cosmic rays – infrared: general – ISM: molecules – methods: laboratory: solid state – radiation mechanisms: non-thermal

## 1. Introduction

Untangling the formation mechanisms of complex organic molecules (COMs) in the interstellar medium (ISM), in particular, in star-forming regions, is one of the great challenges in experimental physical chemistry and in astrochemistry. Since even sophisticated models of exclusive gas phase reactions are not able to reproduce the molecular abundances of COMs observed in the ISM (Watanabe & Kouchi 2008; Herbst & Van Dishoeck 2009), the study of the exposure of model ices of astrophysical relevance to ionizing radiation and the inherent formation of new (organic) molecules in these processes is of fundamental importance for the laboratory astrophysics and astrochemistry communities (Garrod & Herbst 2006; Abplanalp et al. 2016; Bergantini et al. 2017). Among the organic molecules observed in the ISM so far, structural isomers-molecules with the same chemical formula but with different connectivities of atoms-have received considerable attention as the relative abundances of structural isomers relies strongly on the physical and chemical conditions such as temperature, pressure, radiation sources, and molecular composition of the interstellar and/or circumstellar region of interest. In this sense, structural isomers can act as molecular tracers to expose temperature and density-dependent formation routes in the synthesis of interstellar COMs (Bacmann et al. 2012; Bennett et al. 2007).

The goal of the present work is to elucidate the formation mechanisms of the  $C_2H_6O$  isomers ethanol (CH<sub>3</sub>CH<sub>2</sub>OH) and dimethyl ether (CH<sub>3</sub>OCH<sub>3</sub>) in interstellar analog ices containing methanol (CH<sub>3</sub>OH) and methane (CH<sub>4</sub>) via the interaction of energetic electrons, thus mimicking the effects of secondary electrons generated in the track of galactic cosmic rays interacting with ice-coated interstellar grains (Kaiser & Roessler 1998; Bennett et al. 2005; Alizadeh et al. 2015). It

is important to notice that previous investigations on the irradiation of water (H<sub>2</sub>O)/methane (CH<sub>4</sub>) ices (Bergantini et al. 2017) yielded an ethanol-to-dimethyl ether abundance ratio of  $31 \pm 11$  to 1, which is quite distinct compared to abundance ratios derived from astronomical observations toward several star-forming regions from a minimum of 0.03 to 1 toward NGC 6334 IRS1 (Bisschop et al. 2007) to a maximum of 3.4 to 1 toward Orion-KL (White et al. 2003). These findings suggest that alternative precursor molecules to ethanol (CH<sub>3</sub>CH<sub>2</sub>OH) and/or dimethyl ether (CH<sub>3</sub>OCH<sub>3</sub>) might exist in interstellar ices, a possibility that is yet to be investigated.

Here, methanol (CH<sub>3</sub>OH) and methane (CH<sub>4</sub>) were chosen as potential precursors of the  $C_2H_6O$  isomers ethanol and dimethyl ether after considering that the molecular structures of both isomers incorporated CH<sub>2</sub>OH/CH<sub>3</sub>O moieties, respectively, along with the methyl (CH<sub>3</sub>) group (Bennett et al. 2007; Maity et al. 2015; Bergantini et al. 2017). Besides simple radical-radical recombination reactions within interstellar ices (reactions R1 and R2), it is also possible that ethanol and dimethyl ether can be formed by the barrierless insertion of singlet carbene (CH<sub>2</sub>) into a carbon–hydrogen or oxygen– hydrogen bond of methanol ((R3) and (R4); Turner et al. 2016; Förstel et al. 2017); however, until now, no studies were available in the literature to clarify quantitatively the role of these two mechanisms—radical–radical reaction versus CH<sub>2</sub> insertion—on the formation of ethanol and dimethyl ether.

$$CH_2OH + CH_3 \rightarrow CH_3CH_2OH,$$
 (R1)

$$CH_{3}O + CH_{3} \rightarrow CH_{3}OCH_{3}, \tag{R2}$$

 $CH_3OH + CH_2 \rightarrow CH_3CH_2OH, \tag{R3}$ 

$$CH_3OH + CH_2 \rightarrow CH_3OCH_3.$$
 (R4)

Both methanol and methane are commonly found in the interstellar medium in gas and in the solid phase (Martín-Doménech et al. 2016 and references therein; Boogert et al. 1996). Methanol was first detected toward Sgr B2 (Ball et al. 1970), and methane was first reported toward the objects NGC 7538 IRS 9, OMC-1 IRc2, and W33A (Lacy et al. 1991). Both species were probed subsequently toward low-, intermediate-, and high-mass star-forming regions (see Boogert et al. 1998; Ikeda et al. 2002; White et al. 2003; Fuente et al. 2014; Graninger et al. 2016). Methanol holds abundances relative to water of up to 30% in star-forming regions such as RAFGL7009S and W33A (Dartois et al. 1999); methane is present at levels of up to 7% in ices observed toward the objects SVS 4-5, L1014 IRS, IRAS 03235 + 3004, and L1489 IRS (Graninger et al. 2016). Observations show that the individual abundances of methanol and methane increases in regions around protostars as the level of thermal processing of the ices surrounding the protostar increases and methane sublimes (Gibb et al. 2000; Boogert et al. 2015); which supports the idea that the formation of methanol in molecular clouds occurs by sequential CO hydrogenation reactions  $(CO \rightarrow HCO \rightarrow H_2CO \rightarrow CH_2OH \rightarrow CH_3OH)$  on the surface of grains (Tielens & Hagen 1982; Dartois et al. 1999), since some of these reactions have activation barriers. Methane is believed to be formed in the ISM through hydrogenations of carbon atoms released from the stars (Brown et al. 1988; Gibb et al. 2000).

Over the last decades, Fourier transform infrared spectroscopy (FTIR) was exploited to successfully monitor the evolution of astrophysical ice analogs in the laboratory during exposure to ionizing radiation. FTIR spectroscopy presents an ideal tool to investigate the processing and decay kinetics of "simple" molecules such as water (H<sub>2</sub>O), carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>), methane (CH<sub>4</sub>), formaldehyde (H<sub>2</sub>CO), and methanol (CH<sub>3</sub>OH) as detected in the ISM. However, limitations that are inherent to infrared spectroscopy require the use of additional spectrometric techniques (see, e.g., Abplanalp & Kaiser 2017). For instance, FTIR does not allow the identification of individual complex molecules due to overlapping fundamentals, but only the functional groups of COMs. The use of quadrupole mass spectrometry (QMS) in residual gas analyzer (RGA) mode-an alternative approach to detect newly formed molecules in laboratory simulation experimentsintroduces two new challenges: the first one is the fragmentation of the molecules caused by the excess of energy from the ionization source (70 eV), which might be overcome by the comparison of the fragmentation patterns measured with data available from the literature, even though such an approach is complicated for convoluted systems with dozens of products like ours; the second challenge is the low sensibility of the instrument, i.e., given the fact that in such experiments the concentration of most of the products is extremely lower if compared to the concentration of the reactants, the signal of the molecules of interest is simply not measurable in many cases. Here, a different approach to understand the formation of COMs upon interaction of ionizing radiation with model ices was used, employing fragment-free tunable photoionization coupled with photoionization reflectron time-of-flight mass spectrometry (PI-ReTOF-MS) to unravel the complex chemistry taking place

in the irradiated binary ice of mixed methanol and methane. This method has previously demonstrated to be extremely sensitive, as it has the power to resolve the existence of distinct structural isomers with distinct ionization energies (Jones & Kaiser 2013; Kaiser et al. 2015; Abplanalp & Kaiser 2016; Bergantini et al. 2017).

Methanol (CH<sub>3</sub>OH), a key species in the formation of COMs, was exhaustively studied experimentally over the last decades. For instance, Johnson & Stanley (1988) detected formaldehyde (CH<sub>2</sub>O) and methoxymethanol (CH<sub>3</sub>OCH<sub>2</sub>OH) upon the laserinduced dissociation of gaseous methanol samples. Upon VUVphotolysis of CH<sub>3</sub>OH ice and CH<sub>3</sub>OH:CH<sub>4</sub>/CO ice mixtures at 20–70 K, Öberg et al. (2009) have detected  $C_2H_6$ ,  $CH_3CHO$ , CH<sub>3</sub>CH<sub>2</sub>OH, CH<sub>3</sub>OCH<sub>3</sub>, HCOOCH<sub>3</sub>, and HOCH<sub>2</sub>CHO using Reflection Absorption Infrared Spectroscopy (RAIRS) and QMS. The irradiation of pure methanol ices by 5 keV electrons by Bennett et al. (2007) showed that the decomposition of methanol proceeds via the formation of hydroxymethyl radical (CH<sub>2</sub>OH), methoxy radical (CH<sub>3</sub>O), formaldehyde (H<sub>2</sub>CO), and methane (CH<sub>4</sub>)-the latter species via retro-insertion of electronically excited atomic oxygen; upon heating of the sample, methyl formate (CH<sub>3</sub>OCHO), glycolaldehyde (CH<sub>2</sub>OHCHO), and ethylene glycol (HOCH<sub>2</sub>CH<sub>2</sub>OH) were also detected. Irradiation of pure methanol ices by a pulsed beam of 800 eV electrons by Bergantini et al. (2013) revealed the formation of several  $C_m H_n$  (m = 1-2, n = 1-4) species, in addition to a few oxygen-bearing fragments such as CH<sub>2</sub>OH. Ice mixtures of methanol and water (CH<sub>3</sub>OH/H<sub>2</sub>O) irradiated by heavy and energetic ions (40 MeV) was analyzed by de Barros et al. (2014) using FTIR spectroscopy; this work detected smaller species such as H<sub>2</sub>CO (formaldehyde), CH<sub>4</sub> (methane), CO (carbon monoxide), CO<sub>2</sub> (carbon dioxide), HCO (formyl radical), and HCOOCH<sub>3</sub> (methyl formate). Paardekooper et al. (2016) exploited laser desorption post-ionization TOF-MS to study vacuum ultra-violet (VUV) photo-processed methanol ices, suggesting the formation of formic acid (HCOOH) and acetic acid (CH<sub>3</sub>COOH). Maity et al. (2014, 2015) achieved outstanding results using tunable PI-ReTOF-MS to investigate methanol and mixtures of methanol and carbon monoxide (CH<sub>3</sub>OH/CO) ice irradiated by energetic electrons. This unveiled the mechanisms of formation of glycolaldehyde (HOCH2CHO) in models of astrophysical ices, in addition to the detection of a large number of new COMs containing up to five carbon atoms including potentially sugar-related molecules. Until now, the study of irradiated binary methanol and methane mixed ices has been mostly limited to FTIR analysis, which comes with limitations in providing information about the formation mechanisms of such COMs as ethanol and dimethyl ether. As a result, the complimentary method of PI-ReTOF-MS was utilized in this study to further the understanding of such important interstellar isomers. More importantly, there are no previous studies in the literature unveiling the formation mechanisms of the C2H6O isomers ethanol and dimethyl ether, or even measuring the relative abundance ratios (branching ratios) of these species from the non-thermal processing of astrophysical ices (Kaiser et al. 2015).

Therefore, given the fact that interstellar molecules—COMs, in particular—play an essential role in the understanding of the evolutionary stages of star-forming regions (Herbst 2017) and that an understanding of the mechanisms of formation of most of the COMs is still in its infancy, the first objective of this work is to determine experimentally, using PI-ReTOF-MS, the efficiency of radical–radical reaction versus carbene insertion on the formation of ethanol (CH<sub>3</sub>CH<sub>2</sub>OH) and dimethyl ether (CH<sub>3</sub>OCH<sub>3</sub>) within interstellar ices containing methanol and methane exposed to ionizing radiation. The second objective was to determine the branching ratio of ethanol to dimethyl ether, which will then be compared with observed abundance ratios of these species toward star-forming regions. Additionally, we have also analyzed the formation routes to the higher molecular weight products ethylene glycol (HOCH<sub>2</sub>CH<sub>2</sub>OH) and dimethyl peroxide (CH<sub>3</sub>OOCH<sub>3</sub>) using PI-ReTOF-MS. The results presented here will provide valuable information regarding the mechanistical processes taking place on the formation of COMs in star-forming regions.

### 2. Experimental Methods

The experiments were carried out in a contamination-free stainless steel ultra-high-vacuum chamber (UHV) evacuated to a base pressure of a few  $10^{-11}$  Torr exploiting oil-free magnetically suspended turbomolecular pumps backed by dry scroll pumps. Ice mixtures were prepared via deposition of premixed gases onto a polished silver substrate coupled to a cold finger at 5.5  $\pm$  0.2 K of temperature. The cold finger, machined from oxygen-free high conductivity copper, is connected to a closed-cycle helium cryostat (Sumitomo Heavy Industries, RDK-415E), interfaced to the UHV chamber so that it is rotatable in the horizontal plane and translatable vertically. The compounds used in the experiment—methanol (CH<sub>3</sub>OH, 99.9%+, Sigma-Aldrich; CD<sub>3</sub>OD, 99.8% atom D, Sigma-Aldrich), and methane (CH<sub>4</sub>, 99.999% Specialty Gases of America; CD<sub>4</sub>, Aldrich, 99%+ atom D) were premixed in a gas mixing chamber (GMC) kept at pressures of a few  $10^{-8}$  Torr. The partial pressures of methanol  $(CH_3OH)$  and methane  $(CH_4)$  in the GMC prior to the deposition were  $12.0 \pm 0.1$  Torr and  $10.0 \pm 0.1$  Torr, respectively. The gas mixture was deposited using a glass capillary array located  $(30.0 \pm 0.5)$  mm away from the silver substrate. A leak valve was used to control the gas flow into the chamber during the deposition at pressures in the main chamber of  $(2.0 \pm 0.2) \times$  $10^{-8}$  Torr for 600  $\pm$  20 s until the ice thickness of 620  $\pm$  20 nm was achieved. The ice growth was monitored online and in situ by measuring the interference pattern (fringes) produced by a 632.8 nm HeNe laser (CVI Melles Griot; 25-LHP-230) as the laser beam was being reflected off the substrate into a photodiode interfaced to a picoammeter (Keithley 6485). The signal was recorded by a personal computer using LabVIEW (Turner et al. 2015). The ice thickness (d) was calculated using Equation (1), which takes into account the number of fringes (m) measured during the deposition, the wavelength ( $\lambda$ ) of the HeNe laser (632.8 nm), the refractive index of the ice (n) and the angle of incidence of the laser beam ( $\theta = 4^{\circ}$ ) (Turner et al. 2015; Förstel et al. 2016):

$$d = \frac{m \lambda}{2 \sqrt{n^2 - \sin^2 \theta}}.$$
 (1)

The refractive index (n) adopted for the methanol-methane ice mixture was  $1.33 \pm 0.02$  (Satorre et al. 2008; Maity et al. 2014). The achieved thickness of  $620 \pm 20$  nm is sufficient to ensure that no interaction occurs between the impinging electrons and the substrate, as the maximum penetration depth of the electrons was determined via Monte Carlo simulations using the CASINO software (v2.42) (Drouin et al. 2007) to  $550 \pm 50$  nm (Table 1).

 Table 1

 Data Applied in the Calculation of the Average Dose per Molecule in the CH<sub>3</sub>OH/CH<sub>4</sub> Ice

Initial kinetic energy of the electrons, $E_{\text{init}}$ (keV) <sup>a</sup>		5
Irradiation current, $I (nA)^{a}$		$19 \pm 1$
Total number of electrons <sup>a</sup>		$(1.1 \pm 0.5) \times 10^{14}$
Average penetration depth, $l (nm)^{a}$		$258 \pm 12$
Maximum penetration depth (nm) <sup>a</sup>		$550\pm50$
Average kinetic energy of backscattered		$3.53\pm0.21$
electrons, $E_{\rm bs}$ (keV) <sup>a</sup>		
Fraction of backscattered electrons, $f_{bs}^{a}$		$0.44\pm0.04$
Average kinetic energy of transmitted electrons,		0
$E_{\rm trans}  ({\rm keV})^{\rm a}$		
Fraction of transmitted electrons, $f_{\text{trans}}^{a}$		0
Density of the ice, $\rho$ (g cm <sup>-3</sup> )		$0.76\pm0.05$
Irradiated area, $A (cm^2)$		$1.0 \pm 0.1$
Dose (eV/molecule)	Methanol	$0.82\pm0.11$
	Methane	$0.41\pm0.06$

Note.

<sup>a</sup> Parameters obtained from CASINO software v2.42.

The methanol-to-methane ratio in the unirradiated ices was calculated based on the column density (*N*) of each reactant in the ice using the integrated infrared peak areas  $\int_{\tilde{\nu}_1}^{\tilde{\nu}_2} A(\tilde{\nu}) d\tilde{\nu}$  of the  $\nu_{11}$  band of methanol (1036 cm<sup>-1</sup>) and the  $\nu_4$  band of methane (1300 cm<sup>-1</sup>), and the absorption coefficients ( $A_{exp}$ ) of 1.07 × 10<sup>-17</sup> cm molecule<sup>-1</sup> and 8.00 × 10<sup>-18</sup> cm molecule<sup>-1</sup>, respectively (Bouilloud et al. 2015), via Equation (2) (Turner et al. 2016):

$$N = \frac{\ln(10) \int_{\tilde{\nu}1}^{\tilde{\nu}^2} A(\tilde{\nu}) d\tilde{\nu}}{2 A_{\exp}} \cos\left(\sin^{-1} \frac{\sin \alpha}{n_{ice}}\right).$$
(2)

The angle at which light passes through ice ( $\beta$ ) is related to the angle of the incoming beam ( $\alpha$ ) by Snell's law:  $n_v \sin \alpha = n_{ice} \sin \beta$ . This was incorporated into Equation (1), assigning the refractive index of vacuum to be  $n_v = 1$ . The factor of 2 accounts for the incoming and outgoing beams since the FTIR signal is measured in absorption–reflection–absorption mode. Equation (2) resulted in an average methanol-to-methane ratio of  $1.27 \pm 0.13$  to 1 (nominally 1.3 to 1), which is similar to the abundance ratios of these species as detected toward objects such as the low-mass protostars IRAS 03235 + 3004 and L1489 IRS (Graninger et al. 2016).

The density ( $\rho$ ) of the binary mixture, a parameter necessary to calculate the deposited dose of irradiation, was calculated based on the weighted average of the pure densities relative to the ratios (as determined from the derived column densities) of each component. The density of amorphous methanol and amorphous methane are  $1.01 \pm 0.03$  g cm<sup>-3</sup> and  $0.45 \pm 0.02$  g cm<sup>-3</sup>, respectively (Bouilloud et al. 2015, and references therein). Considering volume additivity, it yields to a density of  $0.76 \pm 0.02$  g cm<sup>-3</sup> for the methanol–methane ice mixture. Extracting the density of mixed ices following this technique has been demonstrated previously by Luna et al. (2012) as a reasonable approximation of the expected values.

The ice samples were monitored by a quadrupole massspectrometer (QMS; Extrel 5221) operating in residual gas analyzer mode (RGA) and by FTIR spectroscopy (Nicolet 6700) before and during the irradiation, and by RGA and PI-ReTOF-MS during the warm-up phase. The irradiation was

 Table 2

 Parameters of the VUV Generation in the Experiments

	Photoionization energy (eV)	10.49	10.25
	Wavelength (nm)	118.19	120.96
$\omega_1$	Wavelength (nm)—Nd:YAG laser #1	354.66	532.00
	Wavelength (nm)—Dye laser #1		606.948
ω <sub>2</sub>	Wavelength (nm)—Nd:YAG laser #2		532.00
	Wavelength (nm)—Dye laser #2		617.92
	Nonlinear medium	Xe	Kr
	Photon flux ( $\times 10^{13}$ photons s <sup>-1</sup> )	$2.6\pm0.5$	$3.1\pm0.6$

carried out using 5 keV electrons at  $(19 \pm 1)$  nA for 15 minutes at an angle of 70° relative to the surface normal of the substrate. Based on CASINO simulations (Drouin et al. 2007), this irradiation yields a dose of  $0.82 \pm 0.11$  eV per molecule of methanol and  $0.41 \pm 0.06$  eV per molecule of methane (Table 1).

After the irradiation, the sample was kept isothermal at  $(5.5 \pm 0.2)$  K for one hour until the beginning of the temperature programmed desorption (TPD) phase. The TPD phase warms up the sample from 5.5 to 300 K at a rate of 0.5 K per minute. During TPD, the subliming molecules are ionized by tunable VUV photons and mass-resolved by PI-ReTOF-MS (Jordan TOF Products, Inc.); the ions produced by the interaction with the VUV photons are detected by a multichannel plate in a dual chevron configuration and then amplified by a fast preamplifier (Ortec 9305) and shaped with a 100 MHz discriminator. The resulting spectrum is recorded by a personal-computer-based-multichannel scalar (FAST ComTec, P7888-1 E) with a bin width of 4 ns, triggered at 30 Hz (Quantum Composers, 9518). The ReTOF-MS produces 3600 sweeps per mass spectrum at every 1 K change in temperature. The VUV source produces pulsed (30 Hz) coherent VUV light  $(2\omega_1 - \omega_2)$ , which is used to softly ionize the molecules as they desorb from the ice into the gas phase, and it is comprised of two neodymium-doped yttrium aluminum garnet lasers (Nd:YAG-Spectra Physics, Models PRO-270-30 and PRO-250-30), two dye lasers (Sirah Lasertechnik, Models Cobra-Stretch, and Precision Scan); a pulsed rare gas jet is used as a nonlinear medium for the resonance enhanced VUV generation (Jones & Kaiser 2013). Since the source of VUV light is tunable, experiments can be carried out using photoionization energies to promote selective photoionization and detection of specific isomers synthesized in the ice. In the current work, VUV light with energies of 10.49 eV (118.19 nm) and 10.25 eV (120.96 nm) were exploited to separate the signal due to dimethyl ether (ionization energy (IE) = 10.02 eV from ethanol (IE = 10.48 eV). The main parameters used to generate the VUV photons are provided in Table 2. More details regarding the generation of 10.49 eV and 10.25 eV photons are described by (Bergantini et al. 2017). Table 3 provides an overview of the composition, thickness of the ices, and the VUV energies employed in each experiment.

#### 3. Results

# 3.1. Infrared Spectroscopy

Figure 1 depicts the infrared spectrum of methanol ( $CH_3OH$ ) and methane ( $CH_4$ ) before and after the irradiation by energetic electrons at 5.5 K. The FTIR spectrum of the isotopically labeled

 Table 3

 Ice Composition, Thickness, and Photoionization Energies

 Exploited in the Experiments

Ice sample	Composition	Thickness (nm)	VUV energy (eV)
CH <sub>3</sub> OH/CH <sub>4</sub>	$1.27\pm0.13{:}1$	$620\pm20$	10.49
CD <sub>3</sub> OD/CH <sub>4</sub>			10.49
CH <sub>3</sub> OH/CD <sub>4</sub>			10.49
CD <sub>3</sub> OD/CH <sub>4</sub>			10.25
CH <sub>3</sub> OH/CD <sub>4</sub>			10.25

ice mixtures (CD<sub>3</sub>OD/CH<sub>4</sub> and CH<sub>3</sub>OH/CD<sub>4</sub>) are presented in the Appendix. The newly formed infrared absorptions detected after the irradiation of the samples can be seen at 1191 cm<sup>-1</sup>, 1492 cm<sup>-1</sup>, 1712 cm<sup>-1</sup>, 1725 cm<sup>-1</sup>, and 2136 cm<sup>-1</sup> (Figure 1). Since the carbonyl group (C = O) [1725 cm<sup>-1</sup>] and the carboxyl functional group (COOH) [1712 cm<sup>-1</sup>] from several different species may contribute to those infrared bands (Bennett et al. 2007; Maity et al. 2015) and hence the absorptions are not unique, more sensitive techniques are needed to confirm the presence of specific COMs in the sample, as FTIR alone cannot do so. The assignments of the IR bands are presented in Table 4.

# 3.2. Photoionization Reflectron Time-of-flight Mass Spectrometry (PI-ReTOF-MS)

Here we present the results observed by highly sensitive tunable PI-ReTOF-MS collected during the TPD phase of the experiment. The first experiment consisted of the irradiation of a methanol and methane mixture (CH<sub>3</sub>OH/CH<sub>4</sub>) with subsequent PI-ReTOF-MS collected utilizing photoionization energy of 10.49 eV. This sample was used as a benchmark, so the mass shifts caused by the isotopically labeled molecules in subsequent experiments could be determined. This reference experiment reveals signals of ions up to m/z = 91 as shown in Figure 2(a). Figures 2(b) and (c) reveal the PI-ReTOF-MS spectrum from the isotopically labeled D4-methanol-methane ices in the experiments in which the desorbing species were photoionized at 10.49 eV and at 10.25 eV, respectively. Figures 2(d) and (e) exhibit the spectrum from the isotopically labeled methanol-D4-methane ices photoionized at 10.49 eV and at 10.25 eV, respectively. The TPD profiles of the individual masses as function of temperature from the reference experiment are compiled in the Appendix. Also, in Figure 2, is possible to note sublimation events occurring very early in the TPD. The analysis of the TPD profiles and of the mass shifts reveal that these ions are related to the sublimation of weakly bond methane found in the surface of the ice, and because these signals were also present in the blank experiments, they were considered artifacts in our spectrum.

## 3.2.1. Ethanol and Dimethyl Ether Detection

First of all, ion signal at m/z = 46 (C<sub>2</sub>H<sub>6</sub>O<sup>+</sup>) could be observed in the CH<sub>3</sub>OH/CH<sub>4</sub> system upon photoionization of the subliming molecules at 10.49 eV (Figure 2(a)). This finding alone reveals that C<sub>2</sub>H<sub>6</sub>O isomer(s) are formed in the CH<sub>3</sub>OH/CH<sub>4</sub> ice upon interaction with energetic electrons. In order to elucidate the reaction mechanisms, we are combining isotopic labeling with selective photoionization of distinct isotopologues of ethanol and dimethyl ether. The synthetic approach is compiled in Figure 3. In principle, methane (CH<sub>4</sub>) can decompose through interaction with energetic electrons via



Figure 1. Infrared spectra of the CH<sub>3</sub>OH/CH<sub>4</sub> ice of 620  $\pm$  20 nm of thickness before (black line) and after irradiation (red line) dose of 0.82  $\pm$  0.11 eV per molecule of methanol and 0.41  $\pm$  0.06 eV per molecule of methane.

two channels (reaction (R5) and reaction (R6)) involving simple carbon-hydrogen rupture to the methyl radical and atomic hydrogen (R5) and also via molecular hydrogen elimination to form singlet carbene (R6; Kaiser & Roessler 1998; Bennett et al. 2006). Both processes are highly endoergic by 4.4 eV and 4.7 eV (calculated from data available from the National Institute of Standards and Technology—NIST), respectively. This energy has to be imparted by the energetic electrons via inelastic energy loss to the methane molecules. In perdeuterated methane, these pathways lead to the formation of  $CD_3 + D$  and  $CD_2(a^1A_1) + D_2$ , respectively.

$$CH_4 \rightarrow CH_3 + H \ 427 kJ \ mol^{-1} 4.4 \ eV,$$
 (R5)

$$CH_4 \rightarrow CH_2(a^1A_1) + H_2 456 \text{ kJ mol}^{-1}4.7 \text{ eV}.$$
 (R6)

Likewise, the methanol molecule (CH<sub>3</sub>OH) can undergo unimolecular decomposition and can lose atomic hydrogen either from the methyl group (reaction ( $\mathbb{R}^7$ )) and also from the hydroxyl group (reaction ( $\mathbb{R}^8$ )) leading in strongly endoergic processes by 4.3 eV and 4.5 eV (calculated from data available from NIST) to the formation of the hydroxymethyl radical (CH<sub>2</sub>OH) and methoxy radical (CH<sub>3</sub>O), respectively.

$$CH_3OH \rightarrow CH_2OH + H412kJ \text{ mol}^{-1} 4.3 \text{ eV}, \qquad (R7)$$

$$CH_3OH \rightarrow CH_3O + H \ 438 \ kJ \ mol^{-1} \ 4.5 \ eV.$$
 (R8)

In principle, two kinds of barrierless elementary reactions are open: radical-radical reactions between the methyl radical (CH<sub>3</sub>) and the hydroxymethyl (CH<sub>2</sub>OH) as well as methoxy radical (CH<sub>3</sub>O; reactions (R9) and (R10), respectively) and also carbene (CH<sub>2</sub>( $a^{1}A_{1}$ )) insertions into the carbon-hydrogen and into the carbon-oxygen bonds of methanol, along with insertion into the oxygen-hydrogen bond of methanol. These pathways can lead to ethanol (R11) as well as dimethyl ether (R12), respectively.

$$\begin{array}{l} \mbox{CH}_2\mbox{OH} + \mbox{CH}_3 \rightarrow \mbox{CH}_3\mbox{CH}_2\mbox{OH} \\ \mbox{-371 kJ mol}^{-1} - 3.8 \ \mbox{eV}, \end{array} \tag{R9}$$

$$CH_3OH + CH_2(a^lA_l) \rightarrow CH_3CH_2OH$$
  
-457 kJ mol<sup>-1</sup> - 4.7 eV, (R11)

$$CH_3OH + CH_2(a^{l}A_{l}) \rightarrow CH_3OCH_3$$
  
-407 kJ mol<sup>-1</sup> - 4.2 eV. (R12)

These reactions are highly excergic by up to 4.7 eV (calculated from data available from NIST). Since multiple reactions can lead to the same products, it is crucial to exploit isotopic labeling as demonstrated in Figure 3. Here, the products of the carbene insertion pathways as well as the radical-radical recombination mechanisms are compiled for the  $CH_3OH/CD_4$  and CD<sub>3</sub>OD/CH<sub>4</sub>ices. In detail, CD<sub>2</sub> reaction with CH<sub>3</sub>OH via insertion can form D2-substitued ethanol and dimethyl ether (m/z=48); on the other hand, CD<sub>3</sub> radical reaction with CH<sub>2</sub>OH/CH<sub>3</sub>O can lead to D3-substitued ethanol and dimethyl ether (m/z = 49). Therefore, insertion (CD<sub>2</sub>) and radical-radical recombination (CD<sub>3</sub>) pathways can lead to distinct mass-to-charge ratios of the ionized products. The same strategy holds for the CD<sub>3</sub>OD/CH<sub>4</sub>ices. Here, a CH<sub>2</sub> reaction with CD<sub>3</sub>OD via insertion can form D4-substitued ethanol and dimethyl ether (m/z = 50); on the other hand, a  $CH_3$  radical reaction with  $CD_2OD/CD_3O$  can lead to D3-substitued ethanol and dimethyl ether (m/z = 49). Consequently, insertion (CH<sub>2</sub>) and radical-radical recombination (CH<sub>3</sub>) pathways can also lead to distinct mass-to-charge ratios of the ionized products, i.e., m/z = 50 versus 49.

What are the experimental findings? The temperature programmed desorption (TPD) profiles of ethanol and dimethyl ether are shown in Figure 4. Figures 4(a) and (c) show the signal from radical-radical recombination both at m/z = 49, whereas Figures 4(b) and (d) reveal insertion products from CH<sub>2</sub> and CD<sub>2</sub> reactions at m/z = 50 and 48, respectively. The data taken at photoionization energy of 10.49 eV can be seen in the top of Figure 4; data recorded at 10.25 eV is shown at the bottom. These findings so far reveal the clear existence of two distinct pathways: carbene insertion versus methyl radical reactions. However, we

 Table 4

 Infrared Absorption Features Recorded before Irradiation of Methanol/Methane Ices at 5.5 K

	*			,	
Assignment	Position (cm <sup>-1</sup> )			Carrier	References
	CH <sub>3</sub> OH/CH <sub>4</sub>	$\rm CH_3OH/CD_4$	$CD_3OD/CH_4$		
ν <sub>11</sub> (CH <sub>3</sub> OH)	1036	1033	977	CH <sub>3</sub> rock	(Maity et al. 2015)
ν <sub>7</sub> (CH <sub>3</sub> OH)	1126	1126	898	CH <sub>3</sub> rock	(Maity et al. 2015)
ν <sub>4</sub> (CH <sub>4</sub> )	1300	990	1300	deg. str	(Kaiser & Roessler 1998)
ν <sub>6</sub> (CH <sub>3</sub> OH)	1421	1420	1062	O-H bend	(Maity et al. 2015)
ν <sub>7</sub> (CH <sub>3</sub> OH)	1447	1445	1095	CH <sub>3</sub> wagging	(Bennett et al. 2007)
ν <sub>10</sub> (CH <sub>3</sub> OH)	1460	1460	1117	C-H asym. bend	(Maity et al. 2015)
ν <sub>4</sub> (CH <sub>3</sub> OH)	1475	1476	1123	C-H asym. bend	(Maity et al. 2015)
2v <sub>8</sub> (CH <sub>3</sub> OH)	2051	2050	1673	Overtone	(Maity et al. 2015)
$\nu_6 + \nu_{11}$ (CH <sub>3</sub> OH)	2521	2514	1928	Combination	(Maity et al. 2015)
2v <sub>4</sub> (CH <sub>4</sub> )	2591	1974	2565	Overtone	(Kaiser & Roessler 1998),(Bennett et al. 2006)
ν <sub>3</sub> (CH <sub>3</sub> OH)	2826	2826	2069	CH <sub>3</sub> str.	(Bennett et al. 2007)
ν <sub>1</sub> (CH <sub>4</sub> )	2902	2088	3004	sym. str.	(Kaiser & Roessler 1998), (Bennett et al. 2006)
ν <sub>9</sub> (CH <sub>3</sub> OH)	2950	2950	2215	C–H sym. str.	(Bennett et al. 2007)
ν <sub>2</sub> (CH <sub>3</sub> OH)	2981	2980	2242	C–H asym. str.	(Maity et al. 2015)
ν <sub>3</sub> (CH <sub>4</sub> )	3005	2247	3005	deg. str.	(Kaiser & Roessler 1998), (Bennett et al. 2006)
ν <sub>1</sub> (CH <sub>3</sub> OH)	3242	3262	2435	O–H str.	(Maity et al. 2015)
$\nu_1 + \nu_4 (CH_4)$	4200	3088	4003	Combination	(Kaiser & Roessler 1998)
$\nu_3 + \nu_4  (\text{CH}_4)$	4297	3234	4098	Combination	(Bennett et al. 2006)
$\nu_2/\nu_3 + \nu_4/\nu_6/\nu_{10}$ (CH <sub>3</sub> OH)	4393	4394	4190	Combination	(Maity et al. 2015)
$\nu_2 + \nu_3 ({\rm CH_4})$	4527	4473	4323	Combination	(Kaiser & Roessler 1998)

have not disclosed the nature of the product isomers yet. Here, ionizing the subliming products with tunable VUV light helps to discriminate the product isomers. VUV light at 10.49 eV ionizes both the ethanol and the dimethyl ether isomers, whereas 10.25 eV photons only ionize the dimethyl ether isomer. A close look at the TPD profiles recorded at 10.25 eV-the ionization energy where solely dimethyl ether can be ionized-(Figure 4) reveals that this molecule is clearly detected in both the CH<sub>3</sub>OH/CD<sub>4</sub> and CD<sub>3</sub>OD/CH<sub>4</sub> ices. Recall that at 10.49 eV, both ethanol and dimethyl ether can be ionized. However, since the photoionization cross-section of dimethyl ether is known for 10.49 eV and 10.25 eV ( $8.16 \times 10^{-18}$  cm<sup>2</sup> and  $6.15 \times 10^{-18}$  cm<sup>2</sup>, respectively; Cool et al. 2005), we can scale the ion counts recorded at 10.25 eV for dimethyl ether to determine what is expected at 10.49 eV, and subtract this contribution from the TPD profiles recorded at 10.49 eV. The difference represents the remaining contribution for the ethanol isomer (Figure 4). In other words, the inserts represent the sole, remaining signal from ethanol obtained from the subtraction of the scaled signal at 10.25 eV from the signal at 10.49 eV. Therefore, we can conclude that ethanol is also formed in the CH<sub>3</sub>OH/CD<sub>4</sub> and CD<sub>3</sub>OD/CH<sub>4</sub> ices via insertion and radical-radical recombination. In summary, Figures 3 and 4 reveal the strategy and detection, respectively, of both  $C_2H_6O$ isomers-dimethyl ether and ethanol; furthermore, we disclosed qualitatively that each isomer can be formed via carbene insertion and also via radical-radical recombination. Note that the central position of the dimethyl ether second sublimation event changes

from 134.3  $\pm$  0.2 K in the CD<sub>3</sub>OH/CH<sub>4</sub> system to 136.7  $\pm$  0.5 K in the CH<sub>3</sub>OH/CD<sub>4</sub> system, which could account for the slight difference in the TPD profiles of Figures 4(a)–(b) (top) in comparison with Figures 4(c)–(d) (top). Also, note that the shoulder seen in the 150 K—170 K range in Figures 4(c) and (d) (top) is probably related to a fragment of m/z = 60 and m/z = 61 (see the Appendix), but because these events occur outside of the sublimation interval of ethanol, it is not expected that they would interfere with the quantitative calculations.

#### 3.2.2. Ethanol and Dimethyl Ether Quantification

Having identified both ethanol and dimethyl ether qualitatively, it is of fundamental importance to quantify the ethanol-todimethyl ether branching ratios (BR), so that this information can be compared with the relative abundance ratio of these two isomers detected toward star-forming regions; this will determine the feasibility of the reaction mechanisms that are being suggested to take place in our ices. Here, the normalized PI-ReTOF-MS counts (Figure 4) were exploited to calculate the branching ratios of each mechanism (Bergantini et al. 2017) (Equation (3)):

$$BR\frac{ETH}{DME} - \frac{\int AdA_{ETH}}{\int AdA_{DME}} \frac{\sigma_{DME}}{\sigma_{ETH}},$$
(3)

where ETH and DME define ethanol and dimethyl ether, respectively; the term  $\int A \ dA_x$  corresponds to the integrated ion



Figure 2. PI-ReTOF-MS data of the irradiated ices as a function of the temperature and mass-to-charge ratio of the ionized species in the (a)  $CH_3OH/CH_4$  ice photoionized at 10.49 eV; (b)  $CD_3OD/CH_4$  ice photoionized at 10.49 eV; (c)  $CD_3OD/CH_4$  ice photoionized at 10.25 eV; (d)  $CH_3OH/CD_4$  ice photoionized at 10.49 eV; (e)  $CH_3OH/CD_4$  ice photoionized at 10.25 eV.

 Table 5

 Branching Ratios of Isotopologues of Ethanol vs. Dimethyl Ether in the CD<sub>3</sub>OD/CH<sub>4</sub> System

Mechanism	m/z	Isotopologue	Structure	Branching Ratio (Ethanol/Dimethyl Ether)
CH <sub>2</sub> Insertion	50	Ethanol-d4		(1.00 ± 0.18):1
		Dimethyl ether-d4		
Radical–Radical	49	Ethanol-d3		(1.88 ± 0.21):1
		Dimethyl ether-d3	р. – н р. – с. – о. – н ј – н р. – н	

counts, and  $\sigma_x$  is the photoionization cross-section of a given species at a given VUV energy (with x = ETH or DME). A photoionization cross-section of  $0.75 \times 10^{-18} \text{ cm}^2$  at 10.49 eV was adopted for ethanol (Person & Nicole 1971) and of  $8.16 \times 10^{-18} \text{ cm}^2$  for dimethyl ether (Cool et al. 2005). For clarity, the branching ratios of ethanol over dimethyl ether

calculated from the  $CD_3OD/CH_4$  experiments are compiled in Table 5; branching ratios extracted from the  $CH_3OH/CD_4$  experiments are shown in Table 6.

As can be noted from Figure 3, the probability of forming ethanol through  $CH_2$  insertion in the  $CD_3OD/CH_4$  experiment is higher (4 to 1) than the probability of forming



Figure 3. Reaction mechanisms leading to the formation of ethanol and dimethyl ether via processing of methanol/methane ices. Top: carbene insertion; bottom: radical-radical reactions. The left-hand side depicts the reactions occurring in the  $CD_3OD/CH_4$  ice, whereas the right-hand side compiles reactions in the  $CH_3OH/CD_4$  ice.

Mechanism	m/z	Isotopologue	Structure	Branching Ratio (Ethanol/Dimethyl Ether)
CD <sub>2</sub> Insertion	48	Ethanol-d2		(1.39 ± 0.07):1
		Dimethyl ether-d2		
Radical–Radical	49	Ethanol-d3		(4.54 ± 0.29):1
		Dimethyl ether-d3		

 Table 6

 Branching Ratios of Isotopologues of Ethanol vs. Dimethyl Ether in the  $CH_3OH/CD_4$  System

dimethyl ether via the same mechanism considering the availability of three C–D bonds plus one C–O bond for CH<sub>2</sub> insertion leading to ethanol formation, versus only one O–D bond for CH<sub>2</sub> insertion leading to dimethyl ether. However, the ethanol-to-dimethyl ether branching ratio measured in this specific mechanism is  $(1.00 \pm 0.18)$  to 1 (Table 5), revealing that the formation of dimethyl ether through this mechanism is

favored. A small favorability to produce dimethyl ether also applies for the other mechanism—radical–radical recombination —in which the probability of forming ethanol is 3 to 1 if compared to dimethyl ether (see Figure 3), since the cleavage of any of the D–C bonds of the methyl group of methanol will generate the CD<sub>2</sub>OD radical, leading to ethanol upon reaction with the CH<sub>3</sub>radical, while only the cleavage of the O–D bond



**Figure 4.** Temperature programmed desorption (TPD) profiles of ethanol and dimethyl ether. Figures 4(a) and (c) show the signal from radical-radical recombination, Figures 4(b) and (d) from CH<sub>2</sub> and CD<sub>2</sub> insertion, respectively. Top: data taken at a photoionization energy of 10.49 eV. Bottom: data taken at a photoionization energy of 10.25 eV. The inserts represent the sole signal from ethanol obtained from the subtraction of the scaled signal at 10.25 eV from the signal at 10.49 eV. The asterisks in panels (c) and (d) mark the sublimation of a possible fragment from m/z = 62.

(hydroxyl group) will generate the CD<sub>3</sub>O radical needed for dimethyl ether formation. However, the ethanol to dimethyl ether branching ratio measured in this case is  $(1.88 \pm 0.21)$  to 1 (Table 5). On the  $CH_3OH/CD_4$  experiment, the  $CD_2$  insertion mechanism yields to a branching ratio of ethanol to dimethyl ether of  $(1.39 \pm 0.07)$  to 1 (Table 6), again revealing that dimethyl ether formation is favored, while the radical-radical recombination resulted in a branching ratio of  $(4.54 \pm 0.29)$  to 1, which is close to the expected statistical value. Finally, summing up the ion counts of the dimethyl ether and ethanol species formed via insertion and radical-radical recombination, the processing of the methanol-methane ices results in overall ethanol-to-dimethyl ether branching ratio of  $(2.33 \pm 0.14)$  to 1, which is slightly below the statistical value expected from the two reaction mechanisms analyzed here, meaning that dimethyl ether production is favored in methanol-methane ices when compared to ethanol production. Note that other processes (such as H/D substitution, impurities in the isotopologue samples, presence of undesirable fragments, etc.) may take place in any experiment, which could theoretically influence the final results even in the most controlled environments. Despite that, the results presented here are the best results so far regarding the mechanisms of formation of C<sub>2</sub>H<sub>6</sub>O isomers in model ices.

To aid the implementation of our experimental findings into astrochemical models development incorporating non-equilibrium processing of interstellar ices, we also provide production rates of the ethanol and dimethyl ether isomers. Here, the production rate of both  $C_2H_6O$  isomers was calculated using the methodology described in detail in our previous work (Bergantini et al. 2017), in which calibration experiments exploiting neat and doped ices established a quantitative correlation between the number of PI-ReTOF-MS ion counts and the number of ethanol and dimethyl ether molecules synthesized within the ice. Here, for ethanol, the production rate was determined to be  $0.45 \pm 0.15$  molecules  $eV^{-1}$ , and for dimethyl ether  $0.24 \pm 0.07$  molecules  $eV^{-1}$ . Compared to production rates in water–methane experiments (Bergantini et al. 2017), these values are one and two orders of magnitude higher, respectively, confirming our aforementioned conclusion that the processed methanol–methane ice mixtures are more efficient in the synthesis of  $C_2H_6O$  isomers.

# 3.3. Formation of $C_2H_6O_2$ Isomers

The ion signal detected at m/z = 62 represents the most intense signal measured in the CH<sub>3</sub>OH/CH<sub>4</sub> system. The stable species for the ion signal at m/z = 62 are ethylene glycol (HOCH<sub>2</sub>CH<sub>2</sub>OH—*IE* = 10.16 eV), dimethyl peroxide (CH<sub>3</sub>OOCH<sub>3</sub>—*IE* = 9.1 eV), and methoxymethanol (CH<sub>3</sub>OCH<sub>2</sub>OH). Comparing our data with calibration experiments performed with ethylene glycol in methanol ices (Maity et al. 2015), the main sublimation event at 200 K is in excellent agreement with the sublimation profile of methanol–ethylene glycol samples from the ethylene glycol molecule; sublimation events observed at 113 K and 162 K

may be related to dimethyl peroxide and methoxymethanol, respectively, as observed by Maity et al. (2015), and by Boamah et al. (2014). Note that at atmospheric pressure, the boiling points of dimethyl peroxide is 293 K and of methoxymethanol 356 K compared to the boiling point 470 K of ethylene glycol. This trend follows an increase in boiling point with an enhanced polarity of the molecule from dimethyl peroxide via methoxymethanol to ethylene glycol. Therefore, even at ultra-high vacuum conditions, this polarity sequence expects that dimethyl peroxide sublimes before methoxymethanol. Consequently, we may assign the sublimation events at 113 K and 162 K to dimethyl peroxide and methoxymethanol, respectively. Note that a signal of similar intensity at m/z = 62 was also detected in the CH<sub>3</sub>OH/CD<sub>4</sub> experiments, but shifting to m/z = 68 in the CD<sub>3</sub>OD/CH<sub>4</sub> experiment (Figure 5). We suggest that ethylene glycol (HOCH<sub>2</sub>CH<sub>2</sub>OH) is formed via dimerization of hydroxymethyl radicals (CH<sub>2</sub>OH; reaction (R13)), dimethyl peroxide (CH<sub>3</sub>OOCH<sub>3</sub>) is formed from recombination of methoxy radicals (CH<sub>3</sub>O; Maity et al. 2014, 2015) (R14) and methoxymethanol (CH<sub>3</sub>OCH<sub>2</sub>OH) can be formed from the reaction between methoxy (CH<sub>3</sub>O) and hydroxymethyl (CH<sub>2</sub>OH) radicals (R15; Harris et al. 1995).

$$CH_2OH + CH_2OH \rightarrow HOCH_2CH_2OH,$$
 (R13)

$$CH_3O + CH_3O \rightarrow CH_3OOCH_3,$$
 (R14)

$$CH_3O + CH_2OH \rightarrow CH_3OCH_2OH.$$
 (R15)

## 4. Astrophysical Implications

Our study unveiled the formation mechanisms of two COMs detected in the ISM: ethanol (CH<sub>3</sub>CH<sub>2</sub>OH) and dimethyl ether (CH<sub>3</sub>OCH<sub>3</sub>), as a consequence to the processing of methanolmethane ices submitted to doses equivalent to  $(10 \pm 3)$  million years of exposition to cosmic rays inside a typical molecular cloud (Yeghikyan 2011). The results obtained with the use of isotopic ice mixtures and tunable PI-ReTOF-MS revealed that both formation mechanisms, radical-radical recombination and carbene insertion, are participating in the synthesis of  $C_2H_6O$ isomers in our system, although radical-radical formation was found to be more efficient regarding the absolute yield of molecules. In principle, ethanol and dimethyl ether could be either synthesized within the ices during exposure to ionizing radiation at 5 K or during the annealing phase involving thermal (equilibrium) chemistry. If they were formed via the thermal equilibrium process, this pathway would be connected with temperature-dependent equilibrium constants  $K_{eq}$  between the two isomers according to Equation (4):

$$K_{\rm eq} = e^{(-\Delta_r G \circ / \rm{RT})}.$$
 (4)

Where  $\Delta_r G^\circ$  is the Gibbs free energy, *R* is the ideal gas constant (in units of kJ K<sup>-1</sup> mol<sup>-1</sup>), and *T* is the temperature (K). With the  $\Delta_r G^\circ$  of ethanol–dimethyl ether being equal to 107 kJ mol<sup>-1</sup> (Ramond et al. 2000; DePuy et al. 1984), at thermodynamic equilibrium, ethanol-to-dimethyl ether branching ratios of  $3.4 \times 10^{-280}$  at 20 K and  $5.4 \times 10^{-38}$  at 150 K would be expected, when in fact the experimentally derived branching ratio of  $(2.33 \pm 0.14)$ :1 (ethanol-dimethyl ether) reveal that these isomers were *not* formed under thermal equilibrium conditions, but through non-equilibrium processes within the ices at ultra-low temperatures. The ethanol-to-dimethyl ether branching ratio of  $(2.33 \pm 0.14)$  to 1 agrees within the same order of magnitude with relative abundances of these two species as observed toward



**Figure 5.** Temperature programmed desorption (TPD) profiles of  $C_2H_6O_2$  isomers from CH<sub>3</sub>OH/CH<sub>4</sub> (a) and CH<sub>3</sub>OH/CD<sub>4</sub> experiments (b). Figure 5(c) shows the signal at m/z = 68 from the CD<sub>3</sub>OD/CH<sub>4</sub> experiment, corresponding to  $C_2D_6O_2$  isomers. The sublimation events observed at 113 K and 162 K are related to dimethyl peroxide (CH<sub>3</sub>OOCH<sub>3</sub>) and methoxymethanol (CH<sub>3</sub>OCH<sub>2</sub>OH), respectively (Maity et al. 2015). The dip at 195 K (b) was caused by a dip in the VUV signal.

several star-forming regions such as W51 e2, G34.3+0.2 (Lykke et al. 2015), G31.41+0.31 (Rivilla et al. 2017), Sgr B2N, Sgr B2M (Requena-Torres et al. 2006), NGC 7129 FIRS2 (Fuente et al. 2014), NGC 1333 IRAS 2A, NGC 1333 IRAS 4A (Taquet et al. 2015), and Orion KL (White et al. 2003). This result is especially relevant when compared to our previous study on water-methane ices (Bergantini et al. 2017), which resulted in an overproduction of ethanol over dimethyl ether, despite the fact that the relative abundance of ethanol in star-forming regions is not higher than the abundance of dimethyl ether in most sources (see references above). The results presented in this work led to the conclusion that methanol is the most important precursor of C<sub>2</sub>H<sub>6</sub>O isomers in the ISM, although alternative processes, including formation pathways involving water-rich ices in the presence of hydrocarbons are also possible, even though the production of dimethyl ether in these ices seems to be considerably less efficient, as demonstrated by Bergantini et al. (2017). However, our experimental results are not sufficient to explain why the high abundance of dimethyl ether when compared to ethanol in high-mass star-forming regions such as NGC 6334 IRS 1, G24.78, W3(H2O), and W33A (Bishop et al. 2007), making clear that additional energetic and non-energetic effects that may be participating in chemical transformation of the interstellar medium, such as UV photolysis, heavy ion bombardment, and H-atom addition (Chuang et al. 2017), deserve to be investigated in future studies.

In terms of the energetics involved, the bond cleavage of methane to produce carbene (CH<sub>2</sub>) in its electronically excited singlet state  $(a^{1}A_{1})$  requires 495 kJ mol<sup>-1</sup> (5.13 eV), and the generation of the triplet electronic ground state (X<sup>3</sup>B<sub>1</sub>) of carbene requires 461 kJ mol<sup>-1</sup> (4.78 eV). The formation of methyl radical (CH<sub>3</sub>) from methane needs (436 kJ mol<sup>-1</sup>; 4.52 eV), the production of hydroxymethyl radical (CH<sub>2</sub>OH) from methanol is endothermic by 412 kJ mol<sup>-1</sup> (4.27 eV), and the generation of the methoxy radical (CH<sub>3</sub>O) from methanol requires 438 kJ mol<sup>-1</sup> (4.53 eV).

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dictate the necessity of a cosmic-ray induced non-equilibrium chemistry to lead to the formation of the detected species, with the excess of energy in our system being incorporated by the impinging electrons. Considering that singlet carbene has a lifetime of less than a few seconds (Tomioka et al. 2001) and recalling that the ice samples were kept at 5.5 K for 3600 s prior to the TPD, during which singlet carbenes would have relaxed to their triplet ground state, we can conclude that the detected carbene insertion products can only be formed at 5.5 K during the irradiation, but not during the TPD phase up of the samples, since no singlet carbene would be present anymore. Finally, given the high intensity of the signal at m/z = 62 in our experiments and the fact that methanol ice is abundant in some sources in the ISM (Dartois et al. 1999), our results suggest that so-far undetected C<sub>2</sub>H<sub>6</sub>O<sub>2</sub> isomers dimethyl peroxide  $(CH_3OOCH_3)$  and methoxymethanol  $(CH_3OCH_2OH)$  are likely to be present in methanol-rich star-forming regions as well.

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#### Appendix

The infrared spectrum of the  $CH_3OH/CD_4$  ice mixture at 5.5 K before and after irradiation by 5 keV electrons can be seen in Figure 6. Figure 7 shows the infrared spectrum of the



Figure 6. Infrared spectrum of the  $CH_3OH/CD_4$  ice before (black line) and after (red line) irradiation.



Figure 7. Infrared spectrum of the CD<sub>3</sub>OD/CH<sub>4</sub> ice before (black line) and after (red line) irradiation.



Figure 8. Sublimation profiles of individual mass-to-charge signals detected by PI-ReTOF-MS during the TPD phase of the irradiated  $CH_3OH/CH_4$  ice.

 $CD_3OD/CH_4$  ice before and after irradiation by 5 keV electrons at 5.5 K. The assignment of the infrared bands observed before irradiation in Figures 6 and 7 is available in



**Figure 9.** Sublimation profile collected from the irradiated  $CH_3OH/CH_4$  ice using RGA (QMS) during the TPD phase of the experiment. From top to bottom, the signals are from methane (CH<sub>4</sub>), methanol (CH<sub>3</sub>OH), and C<sub>2</sub>H<sub>6</sub>O isomers (ethanol and dimethyl ether). The signal from C<sub>2</sub>H<sub>6</sub>O<sub>2</sub> isomers is within the background noise.

Table 4. The individual TPD profiles of the masses-to-charge detected after irradiation of the CH<sub>3</sub>OH/CH<sub>4</sub> ice, which served as reference for the isotopically labeled experiments, can be seen in Figure 8. Quadrupole mass spectrometry (QMS) operating in the residual gas analyzer mode (RGA) can be used in tandem with the PI-ReTOF-MS to detect products that sublime into the gas phase to compare the sensitivity of these techniques, and also to detect species that present high ionization energies, such as methane (IE = 12.61 eV) and methanol (10.84 eV), which is above the photon energies used in our experiments. However, RGA has some disadvantages compared to PI-ReTOF-MS, especially with regard to fragmentation of the detected molecules and low sensitivity if compared to PI-ReTOF-MS. As shown in the RGA spectrum from the irradiated CH<sub>3</sub>OH/CH<sub>4</sub> ice represented in Figure 9, no information regarding the new species formed within the ice can be extracted using RGA, except for a weak signal from m/z = 46 (C<sub>2</sub>H<sub>6</sub>O isomers). The RGA signal from  $C_2H_6O_2$  isomers (m/z = 62) and its fragments-which was the strongest signal in the PI-ReTOF-MS-is not distinguishable from the background noise. Additionally, upon analysis of the RGA spectrum, no new products other than C<sub>2</sub>H<sub>6</sub>O isomers could be detected.

## **ORCID** iDs

Alexandre Bergantini <sup>®</sup> https://orcid.org/0000-0003-2279-166X Ralf I. Kaiser <sup>®</sup> https://orcid.org/0000-0002-7233-7206

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