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ABSTRACT

The origin of CO and the external source of H_2O in the atmosphere of Titan is still a matter of debate. We investigated the chemical fractionation of oxygen isotopologues in order to give new constraints on the origin of oxygen species. We created a new chemical scheme and we developed a 1-D time-dependent photochemical model to compute the mole fraction profiles of various oxygen isotopologues. We show that the photochemical fractionation of oxygen isotopologues is quite low. Observations of $C^{18}O$ and $CO^{18}O$ are compatible with both an external origin or an internal origin of CO considering that the various sources of oxygen have a cometary $^{16}O/^{18}O$ ratio ($^{16}O/^{18}O \approx 500$). Improvement of the measurements of the $^{16}O/^{18}O$ ratio in both Enceladus' plumes and atmospheric CO_2 could give a valuable constraint on the origin of oxygen in Titan's atmosphere.

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1 Introduction

The atmosphere of Titan hosts a complex photochemistry producing hydro-carbons, nitriles, imines and oxygen compounds. Carbon monoxide is one of the most abundant molecules. It has been observed in many studies (see Serig-ano et al. (2016) for a recent review). However, its origin is still a matter of debate (Hörst et al., 2008; Bézard et al., 2012; Dobrijevic et al., 2014). Different scenarios have been proposed to explain its abundance but there are no definitive arguments to discriminate between an external origin of oxygen (micrometeorites, Enceladus' plumes) and an internal origin (outgassing of primordial CO from the surface). These two possible origins are supported by observations: the CAPS/Cassini instrument detected oxygen ions precipi-tating into Titan's atmosphere (Hartle et al., 2006) and the presence of ^{36}Ar detected by the GCMS/Huygens instrument (Niemann et al., 2010) shows that trapping of highly volatile gases, including possibly N_2 and CO, was possible during Titan's formation. In addition, the relative abundance of carbon diox-ide, which has also been detected in the atmosphere, is not well understood (Hörst et al., 2008; Krasnopolsky, 2009; Moreno et al., 2012; Dobrijevic et al., 2014; Lara et al., 2014).

In principle, the study of isotopic ratios can give valuable constraints on the formation and evolution of planetary atmospheres. In particular, it could help to discriminate between different physical and chemical processes that have been or are presently preponderant. In this context, the study of oxygen iso-topologues seems to be a promising step toward a better understanding of the origin and evolution of Titan's atmospheric composition. Several observations give some constraints on the ^{16}O/^{18}O ratio in Titan's atmosphere. The first estimation of ^{16}O/^{18}O ratio in the atmosphere of Titan was reported by Owen et al. (1999) using the James Clerk Maxwell Telescope with a preliminary value of 250 in CO (without error bars). From observations of submillimeter-wave rotational transitions of CO using the Submillimeter Array (SMA), Gurwell (2008) obtained a value of the ^{16}O/^{18}O ratio of 400 ± 41 (unpublished re-sult, value reported in Courtin et al. (2011). According to Serigano et al. (2016), Gurwell et al. (2011) obtained a value of 472 ± 104 with the same set of observations (unpublished result). Using high-resolution submillimetric observations performed with the SPIRE instrument on the Herschel satellite, Courtin et al. (2011) determined a ^{16}O/^{18}O ratio equal to 380 ± 60 in CO. Recently, from ALMA observations of CO, Serigano et al. (2016) obtained a ^{16}O/^{18}O ratio equal to 486 ± 22 and a ^{16}O/^{17}O ratio equal to 2917 ± 359. These latter results are in agreement with the terrestrial value of the ^{16}O/^{18}O ratio, which is 498.8 and the terrestrial value of ^{16}O/^{17}O ratio, which is 2680.0 (Lodders, 2003). Using the Cassini Composite Infrared Spectrometer (CIRS), Nixon et al. (2008) found a probable 3.5σ detection of CO^{18}O with the ra-tio $CO_2/CO^{18}O = 173 \pm 55$ leading to a ^{16}O/^{18}O ratio in CO_2 of 346 ± 110.

An update has been reported in Nixon et al. (2009), which revised the ratio upwards to 190 ± 71 (note that it encompasses the terrestrial value within error bars). If confirmed, these observations suggest that the $^{16}O/^{18}O$ ratio in CO_2 could be lower than in CO. This possible difference could be explained by chemical fractionation processes and/or could be the signature of several oxygen sources with different isotopic ratios.

In this paper, we present a new photochemical model to study the isotopic distribution between the various oxygen species to search for some additional constraints on the origin of oxygen in the atmosphere of Titan. In Section 2, we present the photochemical model and the chemical scheme with the different oxygen isotopologues and chemical and photolysis reactions that could lead to an isotopic fractionation. The main results are presented in Section 3. In Section 4, we discuss the sensitivity of the model to some parameters and the results of some previous models. The conclusions of this work are presented in Section 5.

2   Model

The model used in the present study is similar to the recent model of Dobrijevic et al. (2016), which couples ions and neutral species throughout the whole atmosphere (0-1500 km). Only additions and major modifications are outlined in the following.

2.1   Chemical model

The present model focuses on oxygen species and their isotopologues. Since we have to duplicate all reactions with isotopologues, computation time becomes huge when performing the uncertainty propagation model. So, we use a reduced chemical scheme for hydrocarbons and nitrogen species. It contains 71 species (47 neutrals and 24 ions) and 334 reactions (including photolysis processes). With this reduced scheme the densities of the major neutrals and ions are in a good agreement with our previous model and observations (see Dobrijevic et al. (2016) for comparison with various observations). Our reduced chemical scheme and the schematic diagrams highlighting the major production and loss pathways are given in appendix A.

The most noteworthy changes compared to Dobrijevic et al. (2016) are that we do not consider C_3H_x compounds, as well as most of the C_4H_x compounds and most of the complex nitriles. However, we always take into account the most important consumption reactions for all species present in our reduced

model. When a product of a reaction is not in our model, we consider it as a sink. In some cases we have to consider relatively complex species, which play non-negligible roles in the abundance of lighter species (like C_4H_4 for C_2H_2). Some large cations (like $C_3H_3^+$, $C_3H_5^+$, etc.) are considered as reservoirs in our model (i.e. end product species of our chemical scheme that have no chemical loss process). We then consider Dissociative Recombination (DR) of this non specific reservoir cation, with a rate constant equal to $1.0 \times 10^{-6}(T/300)^{-0.7}$ similar to the DR of $C_3H_3^+$, $C_3H_5^+$, etc, to reproduce the electron density as a function of altitude. We also introduced a H + neutral addition reaction to take into account the H + C_3H_x and H + $C_4H_x(x = 5 - 9)$ reactions which are not present in our reduced network and play a role at low altitude (with a mean altitude around 300 km, see appendix C) as an important sink for H atoms. The rate constant for this addition reaction has been adjusted to reproduce the H atom abundance given by our more complete model (Loison et al., 2015). For oxygenated compounds we do not consider HNO and HNCO. HNO is not considered in this study compared to our previous study (Dobrijevic et al., 2014) because this molecule leads almost exclusively to NO in Titan's atmosphere. Then, we considered that the $N(^2D)$ + H_2O reaction gives, apart from NH + OH, directly NO + H_2 instead of H + HNO. We have considered the NH_2 + NO and $N(^2D)$ + H_2CO reactions as loss pathways for NO and H_2CO. These reactions produce HNCO which is not considered here. This does not affect notably the oxygenated chemical network as the main consumption of HNCO leads to CO through photodissociation, being a small contribution to the total CO production (only 0.1% in the model Dobrijevic et al. (2014)). Anions are not taken into account in the present model since those with oxygen atoms are expected to have very low abundances particularly because oxygenated compounds have low Electron Affinities (Rienstra-Kiracofe et al., 2002). For all species in the present reduced model, the calculated abundances are very similar to the calculated ones with our more complete model (i.e. well within the error bars of the model results).

We have introduced several cations with the isotopologues of oxygen species. The effects of oxygenated cations are relatively minor, except for H_2CO as the DR of H_2COH^+ only partially gives back H_2CO (Hamberg et al., 2007). The list of oxygen species included (neutrals, ions and their isotopologues) is given in Table 1.

Some chemical reactions may induce isotopic fractionation. Among them, the most promising reactions are OH + CO, O + CO and HCO^+ + CO. The reaction OH + CO has been studied both theoretically (Chen and Marcus, 2005) and experimentally (Stevens et al., 1980; Rockmann et al., 1998; Feilberg et al., 2005) and shows some oxygen (and carbon) isotopic fractionation. Despite some disagreement between the various studies, all agree with the fact that the presence of ^{18}O slightly increases the rate constant with $k(OH+C^{18}O)=k(^{18}OH+CO)=1/0.985 \times k(OH+CO)$. The O + CO reaction

Table 1
List of the 28 oxygen species included in the model.

Neutral species	Ions
$O(^3P)$, $O(^1D)$, OH, H_2O, CO, HCO, H_2CO, CH_3O, CO_2, NO	H_3O^+, HCO^+, CH_2OH^+, NO^+
$^{18}O(^3P)$, $^{18}O(^1D)$, ^{18}OH, $H_2^{18}O$, $C^{18}O$, $HC^{18}O$, $H_2C^{18}O$, $CH_3^{18}O$, $CO^{18}O$, $N^{18}O$	$H_3^{18}O^+$, $HC^{18}O^+$, $CH_2^{18}OH^+$, $N^{18}O^+$

leads to CO_2 production with an activation barrier. This reaction plays a very minor role for CO_2 production in Titan's atmosphere as the rate constant is small, but it might lead to a $C^{18}O$ enrichment. We use the experimental data from Jaffe and Klein (1966); Simonaitis and Heicklen (1972); Inn (1974) and the Mahata and Bhattacharya (2009) theoretical model values from their study of CO_2 photodissociation. The last potentially important reaction for isotopic fractionation is the $CO + HCO^+$ reaction. This reaction has been measured over the temperature range 80-500K (Smith and Adams 1980) and recently revisited (Mladenovic and Roueff 2009). The production of CO through photodissociation shows no fractionation in our model. Indeed, CO is produced from H_2CO and HCO photodissociations, which occur mainly in the UV and in the visible range, where the solar flux is almost constant. Then, the Zero Point Energy (ZPE) effect on fractionation is negligible.

2.2   High resolution photolysis rates

The list of photolysis processes is given in appendix A. In our previous model, we used low resolution cross sections ($\Delta\lambda = 1$ nm) for all the photolysis processes except for N_2. In the present study, we introduce high resolution cross sections for several oxygen species, which are presented in appendix B. The photolysis rates of oxygen species and their isotopologues are presented in Figure 1. Except for CO_2, the relative differences between the photolysis rates of the lighter species and their isotopologues are very low in our model. In particular, the relative difference between the photolysis rates of the HCO isotopologues is null because we consider that the cross section of $HC^{18}O$ is the same as the HCO one (see appendix B). Indeed, HCO is very efficiently photodissociated in the visible range, where the solar flux is constant. As a consequence, we consider that there is no ZPE effect for HCO.
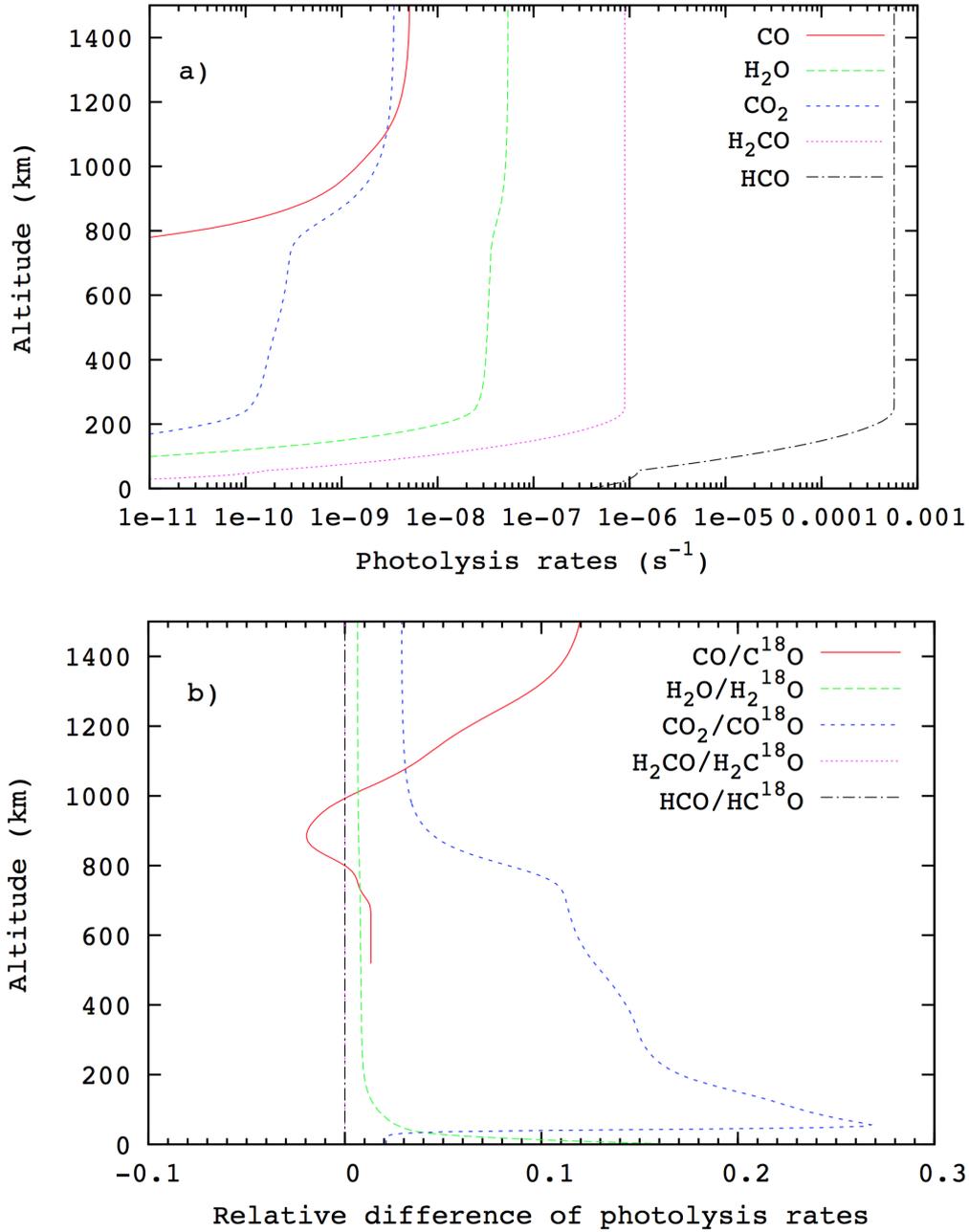
Fig. 1. a) Photolysis rates of the main neutral oxygen species in the model as a function of altitude. b) Relative difference of the photolysis rates for the two isotopologues of each compound.

2.3 Boundary conditions for oxygen species

Dobrijevic et al. (2014) discussed in detail the origin of oxygen species observed in Titan's atmosphere. They showed that several sources of oxygen species are possible and that different values of several parameters can give model

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results in agreement with observations. In the following, we do not consider this extensive set of parameters. Only two main scenarios are considered: (1) CO is continuously outgassed from the surface, (2) CO is only produced by the supply of external oxygen atoms from Enceladus' plumes and micrometeorites.

In the following, we present the isotopic ratio of oxygen species that are considered in the boundary conditions of our model. At the top of the atmosphere, oxygen could come from Enceladus' plumes or micrometeorites (in the form of OH and/or H_2O) (Hörst et al., 2008). Cassidy and Johnson (2010) simulated the evolution of the water molecules vented from Enceladus' south pole. They showed that this might be a significant source of oxygen atoms to Titan's upper atmosphere with a neutral O flux of $1 - 5 \times 10^{24}$ s^{-1} (see also Hartle et al. (2006) and Sittler et al. (2009) concerning the possible source of O in Titan's upper atmosphere). From INMS/Cassini, Waite et al. (2009) derived a measurement of the $^{16}O/^{18}O$ ratio in the Enceladus' plumes equal to 476^{+50}_{-76}. Bockelée-Morvan et al. (2012) measured the $^{16}O/^{18}O$ ratio in H_2O in the Oort-cloud comet C/2009 P1 (Garradd) using the Herschel HIFI instrument. They found a value of 523 ± 32, which is in agreement with the results obtained by Biver et al. (2007) for 4 comets using the Odin satellite (508 ± 33, 530 ± 60 (twice) and 550 ± 75). Using the Ultraviolet-Visual Echelle Spectrograph (UVES) of the Very Large Telescope (VLT), Hutsemékers et al. (2008) found $^{16}O/^{18}O = 425 \pm 55$ in OH in the Oort-Cloud comet C/2002 T7 (LINEAR). Measurements obtained from the neutral mass spectrometer on the Giotto space probe gave the $^{16}O/^{18}O$ ratio in H_3O^+ ion in comet 1P/Halley and allowed Eberhardt et al. (1995) to derive the $^{16}O/^{18}O$ ratio in $H_2O =$ 493 ± 36. Most of these data are in agreement with the terrestrial value of the $^{16}O/^{18}O$ ratio. As a consequence, the $^{16}O/^{18}O$ ratio in micrometeorites is likely to be terrestrial. At the lower boundary, CO might be outgassed from the surface. The latest measurements from ALMA observations favor a cometary $^{16}O/^{18}O$ ratio for CO (Serigano et al., 2016). However, when considering an internal origin for CO, we also investigated various values of this ratio.

So, we have investigated various values as boundary conditions for the $^{16}O/^{18}O$ ratio in O(^{3}P) (i.e. the Enceladus' plumes source), in H_2O (micrometeorite source) and in CO (internal source).

2.4   Vapor pressure

We assume that the vapor pressure expressions of oxygen species that condense in the lower atmosphere (i.e. H_2O, CO_2 and H_2CO) are identical to the ones of their respective isotopologues. Van Hook (1968) studied the vapor pressure isotope effects of H_2O over liquid and ice. In particular, he found that the ratio between the vapor pressure of H_2O and $H_2^{18}O$ is equal to 1.0165 at 233

K. Such a difference is very low compared to many other uncertainties in the model, especially in the chemistry. Moreover, since H_2O is produced in the stratosphere and diffuses vertically down to the condensation level, this slight difference in the vapor pressure only leads to a slight difference in the level of condensation and has no noticeable incidence on the results of our model.

3 Results

3.1 Internal source of CO

In our internal model, we consider that CO is continuously outgassed from the surface, so the mole fraction of CO at the lower boundary (surface) is fixed to 5.1×10^{-5} to be in agreement with observations (see Dobrijevic et al. (2014)) and we first consider that the $^{16}O/^{18}O$ ratio is the same as in comets. At the upper boundary (top of the atmosphere: 1500 km), the flux of $O(^3P)$ from Enceladus' plumes is 1.6×10^6 cm^{-2}s^{-1} (Hörst et al., 2008; Dobrijevic et al., 2014) and the flux of water from micrometeorites is 1.0×10^6 cm^{-2}s^{-1}. This value is twice the flux of water used in Dobrijevic et al. (2016). In the present model, the integrated photodissociation rate of H_2O over the atmosphere is twice the value inferred in Dobrijevic et al. (2016) because of the use of the high resolution solar flux and absorption cross sections. As a consequence, the water flux required to compensate this photolytic loss is two times greater. For these two fluxes, we consider in our nominal model that the $^{16}O/^{18}O$ ratio is the same as in comets.

We first checked that our internal model is in agreement with our previous model and observations. Results are shown in Figure 2 and the mole fraction of water is in quite good agreement with the observation of Moreno et al. (2012). We note however that the use of high resolution solar flux and absorption cross sections have a noticeable effect on the water abundance profile in the lower atmosphere. For a detailed discussion on the disagreement between the observations of Moreno et al. (2012) and Cottini et al. (2012) for H_2O and the disagreement between the model and observations for CO_2, see Dobrijevic et al. (2014) and Lara et al. (2014). The main chemical production and loss processes for the various species are presented in appendix C together with all the integrated column rates. The $^{16}O/^{18}O$ ratio in the different oxygen species depends on the altitude according to the hydrostatic equilibrium and molecular diffusion. In particular, above the homopause (located around 900 km for CH_4 in the present model), these physical processes lead to a depletion of ^{18}O compounds compared to ^{16}O compounds that exceeds the small contribution of photodissociations and/or chemical reactions in the fractionation of isotopologues. In the troposphere, some species condense (like CO_2

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and H_2O) and their isotopologue ratio then remains constant. In the middle atmosphere, around 600 km, the calculated $^{16}O/^{18}O$ ratios in H_2O, CO and CO_2 are 497, 500 and 484 respectively. So, there is a slight photochemical fractionation for CO_2 since we should expect a $^{16}O/^{18}O$ ratio equal to 500 for this species too. This small isotopic CO_2 fractionation comes mainly from the OH + CO reaction. There is also a small contribution from CO_2 photodissociation. The nominal value of $CO_2/CO^{18}O$ ratio we obtained (242) is different from the nominal value inferred by Nixon et al. (2009) (190 ± 71). However, the uncertainty on this value is large and any conclusion may be premature. Since CO_2 is produced mainly through the OH + CO reaction, and since we do not find any isotope fractionation in CO, a low value of the $CO_2/CO^{18}O$ ratio (if confirmed) would suggest that the $^{16}O/^{18}O$ ratio in OH (and consequently in H_2O) is not cometary or that there is a photochemical fractionation that is not considered in our model (or also that there are some observational issues). In conclusion, additional observations of both CO_2 and $CO^{18}O$ would be valuable to better constrain the model.

CO and $C^{18}O$ are the main reservoirs of oxygen isotopologues in Titan's atmosphere. Although the $CO + HCO^+$ reaction is characterized by large fluxes, HCO^+ is involved in reactions leading ultimately back to CO. So, the $CO + HCO^+$ reaction does not lead to any isotopic $C^{18}O$ fractionation, but instead it controls the $HCO^+/HC^{18}O^+$ ratio. Since there is no efficient fractionation in CO in our model, this indicates that the current observed value of $^{16}O/^{18}O$ in CO corresponds to the $CO/C^{18}O$ ratio continuously outgassed by the surface. Fractionation could occur during outgassing but it might be quite low. Indeed, $C^{18}O$ could be slightly more abundant in clathrates than $C^{16}O$ but outgassing might slightly favor $C^{16}O$ (Hesse and Harrison, 1981; Clark and Fritz, 1997). These two processes induce a fractionation around 1%. As a consequence, a cometary $^{16}O/^{18}O$ ratio is expected in primordial CO, which is compatible with observations and our model.

The abundance profiles of the other neutral oxygen species included in our model are shown in Figure 3. The only other oxygenated molecule relatively abundant in the ionosphere is H_2CO (H_2CO is produced mainly through the O + CH_3 reaction with a minor contribution of OH + CH_3, which are among the most important reactions involving oxygen species in Titan's atmosphere). All the oxygen species have abundances that strongly decrease in the stratosphere with decreasing altitude. The species which is the subject of the most important fractionation by photochemical processes in the ionosphere is NO. At the lower boundary of the ionosphere (around 800 km), the $^{16}O/^{18}O$ ratio in NO is equal to 544 (see Table 2). The chemical production of NO (N($_2$D) + H_2O and N + OH) as well as its loss (N + NO and CH_2 + NO) are thought to be the same for ^{16}O and ^{18}O compounds leading to no fractionation. Moreover, NO photodissociation is a very minor destruction process. At high altitude $N^{18}O$ is depleted as diffusion is controlled by the mass and this depletion propagates

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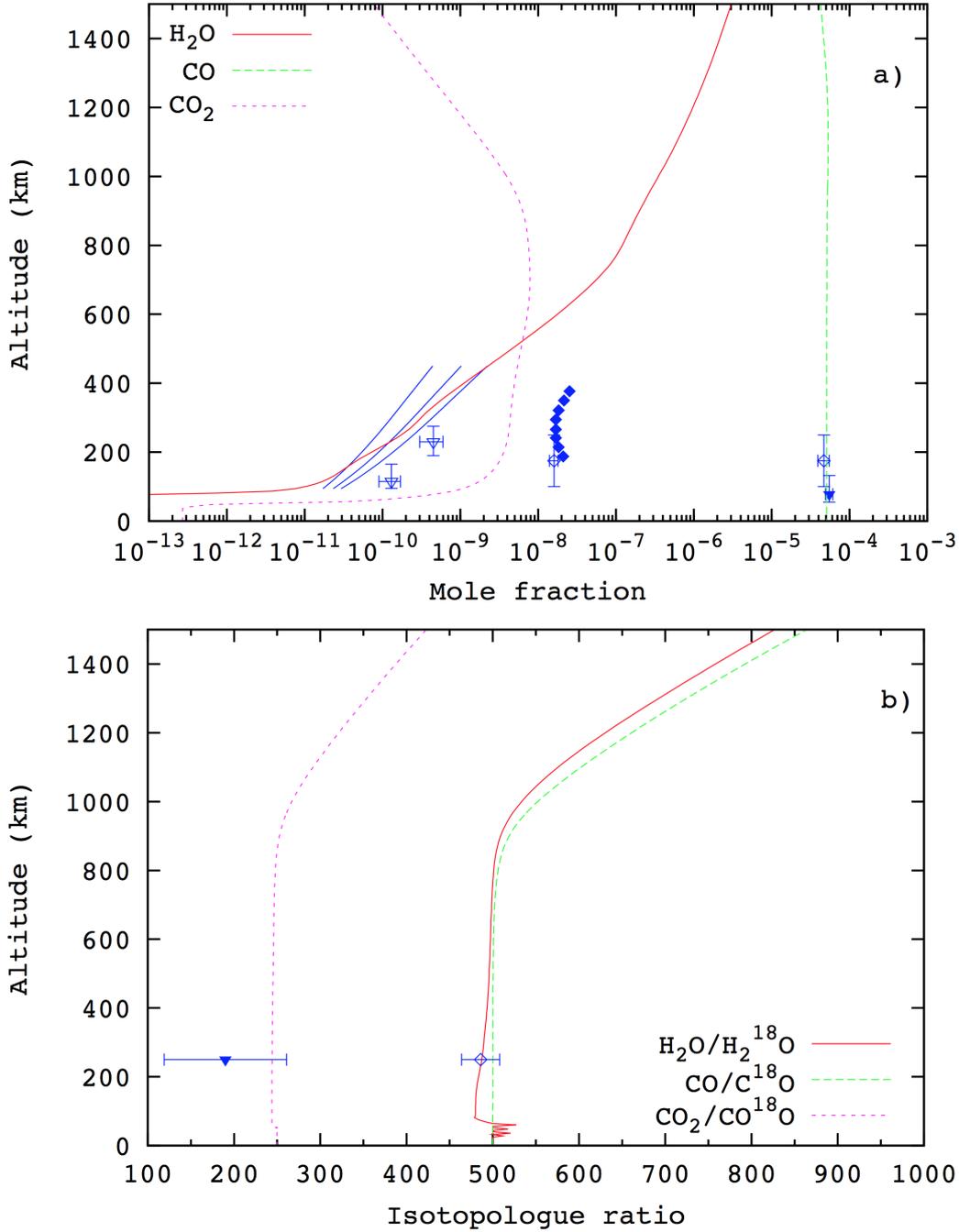
Fig. 2. a) Mole fraction profile of H_2O (solid line), CO (long dashed line) and CO_2 (short dashed line) as a function of altitude in the nominal model (internal CO, $O(^3P)$ from Enceladus' plumes and H_2O from micrometeorites). Observations (in blue) of Moreno et al. (2012) (solid lines for mean and 1-sigma uncertainty), Cottini et al. (2012) (triangles) for H_2O, observations of CO and CO_2 from de Kok et al. (2007) (diamond) and CO observation of Teanby et al. (2010) (triangle) are shown for comparison. b) $H_2O/H_2^{18}O$, $CO/C^{18}O$ and $CO_2/CO^{18}O$ as a function of altitude. Values inferred from observations of Serigano et al. (2016) and Nixon et al. (2009) are given for CO (diamond) and CO_2 (triangle). Due to very low abundances, numerical fluctuations appear in the lower troposphere.

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in the stratosphere. The fractionation in H_2CO, is quite low since the $^{16}O/^{18}O$ ratio in H_2CO is equal to 485 at 800 km. The photodissociation of H_2CO is slightly different from the one of $H_2C^{18}O$ in our model, which induces some fractionation and finally leads to a small enrichment in $H_2C^{18}O$. Below 500 km, the main source of H_2CO is the $O(^3P)$ + CH_3 reaction, $O(^3P)$ atoms coming at this altitude mainly from the photodissociation of CO_2. Then, the change in the $H_2CO/H_2C^{18}O$ profile (and in some other species) comes from fractionation of CO_2 by photodissociation. This fractionation has no, or very little effect on HCO because at this altitude HCO is produced mostly by the H + CO reaction rather than the photodissociation of H_2CO. For that reason, the $HCO/HC^{18}O$ ratio is equal to $CO/C^{18}O$. The depletion of ^{18}O species at 800 km and 500 km is due to the fact that $H_2^{18}O$ and $CO^{18}O$ are less photodissociated than H_2O and CO_2 respectively (cross sections of these species are slightly displaced for the isotopologues), leading to depletion in $^{18}O(^1D)$ and $^{18}O(^3P)$ which are produced by the photodissociation of both H_2O and CO_2. The relative importance of these photolyses change as a function of altitude, then the $^{16}O(^1D)/^{18}O(^1D)$ and $^{16}O(^3P)/^{18}O(^3P)$ ratios have slightly different values at different altitudes.

Densities of oxygen ions are shown in Figure 4. The main oxygen ion in our model is CH_2OH^+, which is about 100 times lower than the most abundant ion in the ionosphere ($HCNH^+$). CH_2OH^+ cannot be detected in INMS/Cassini data because of the presence of a contribution from C_2H_6 in the mass spectrum at the mass 31 amu. Like NO, NO^+ is the species with the largest photochemical fractionation. This is due to the fact that NO^+ is formed through charge exchange between CH_3^+, CH_4^+ and NO so that the fractionation of NO and NO^+ are similar.

The most important chemical pathways for ^{16}O and ^{18}O oxygenated compounds are presented in Figure 5. It highlights which compounds are subject to a photochemical fractionation. In order to confirm this scheme, we computed the isotopic ratios of all the oxygen compounds when changing the $CO/C^{18}O$ ratio at the lower boundary of our model. The evolution of the isotopologue ratios for several compounds as a function of the primordial $CO/C^{18}O$ ratio (from 300 to 700) at the lower boundary is shown in Figure 6. Results are given at 250 km of altitude, a region where sub-millimeter and infrared observations are available. The observational values (and their error bars) of Serigano et al. (2016) for CO and Nixon et al. (2008) for CO_2 are also depicted. Given the observational error bars, our model is currently in agreement with data but future observations of $CO^{18}O$ would be interesting to take this comparison further. We see that the $HCO^+/HC^{18}O^+$ and $H_2CO/H_2C^{18}O$ ratios are strongly affected by the $CO/C^{18}O$ ratio (the $HCO^+/HC^{18}O^+$ ratio is almost equal to $CO^+/C^{18}O^+$ ratio). The $CO_2/CO^{18}O$ ratio is noticeably affected. We also note that the evolution of the $H_2CO/H_2C^{18}O$ ratio is fully correlated to the $CH_2OH^+/CH_2^{18}OH^+$ ratio, $NO/N^{18}O$ is fully correlated to $NO^+/N^{18}O^+$ and
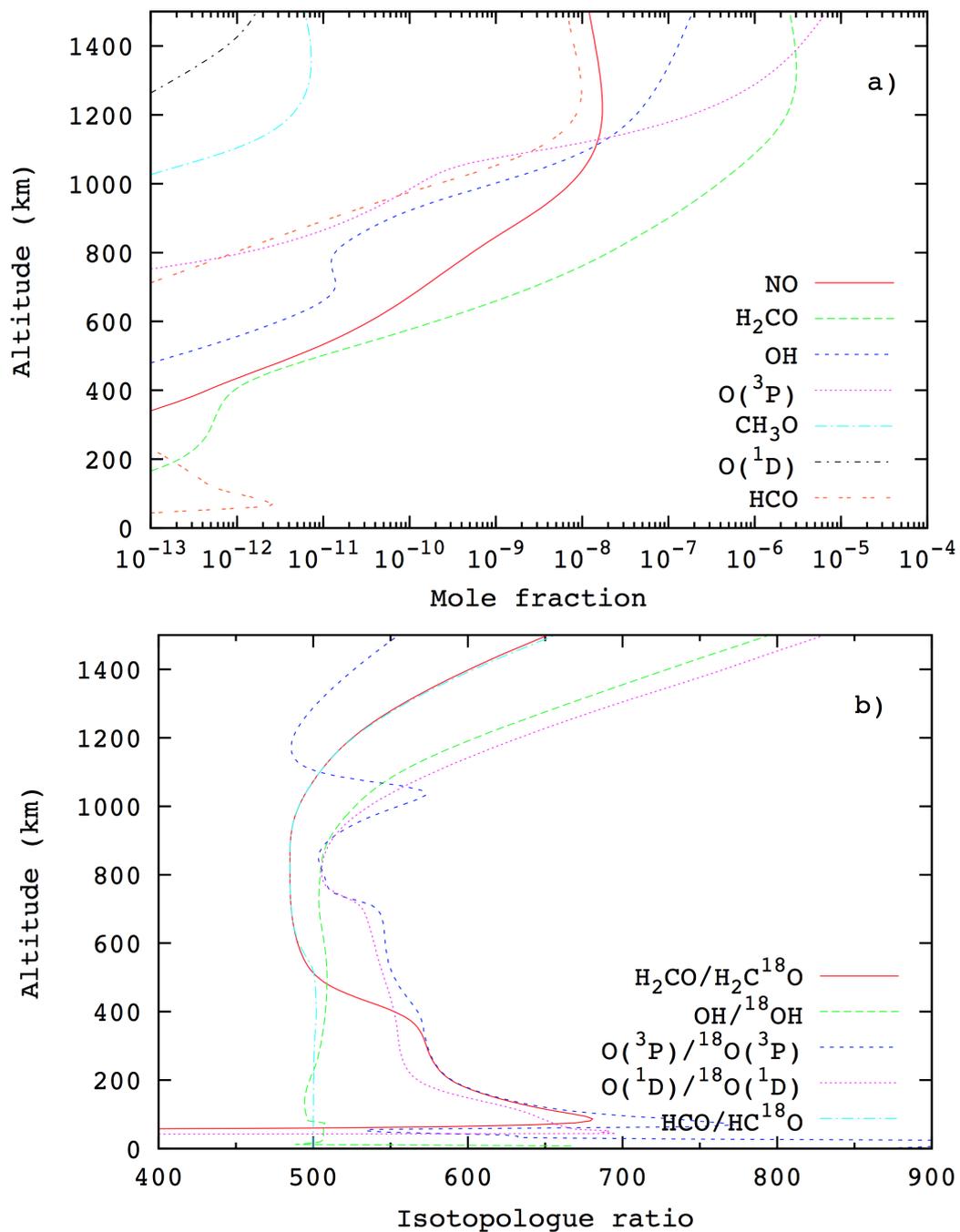
Fig. 3. a) Mole fraction profiles of neutral oxygen species as a function of altitude in the nominal model. b) isotopologue ratio of some neutral species as a function of altitude. Due to very low abundances, numerical fluctuations appear in the lower troposphere.
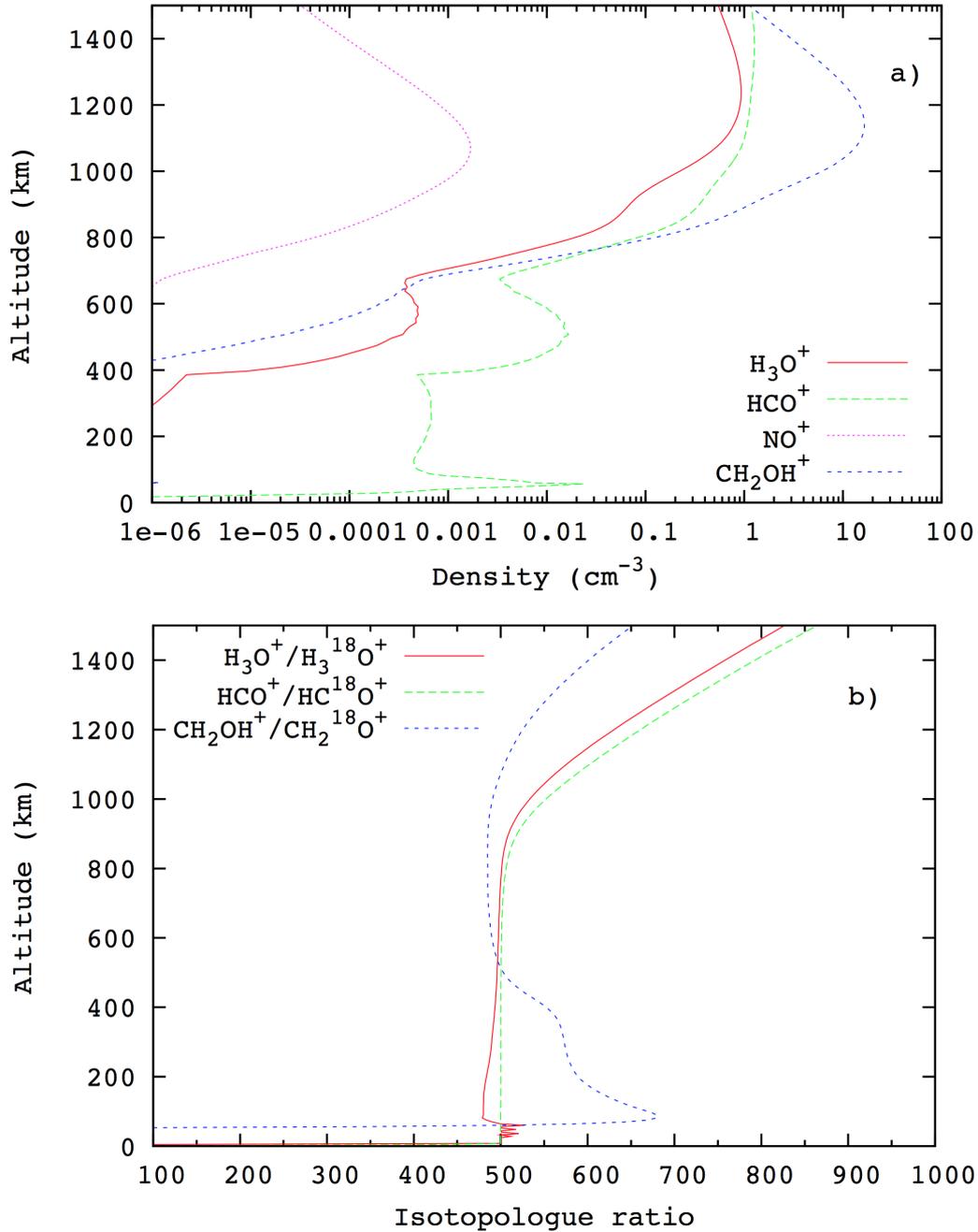
Fig. 4. a) density profiles of oxygen ions as a function of altitude in the nominal model. b) isotopologue ratio of some ions as a function of altitude. Due to very low abundances, numerical fluctuations appear in the lower troposphere.

$H_2O/H_2^{18}O$ to $H_3O^+/H_3^{18}O^+$. All these behaviours are in agreement with the simple chemical scheme shown in Figure 5.

In conclusion, considering that the external $O(^3P)$ and H_2O fluxes, and the internal CO outgassed from the surface, all have a $^{16}O/^{18}O$ ratio equal to 500, our model is consistent with current observations of the two $CO/C^{18}O$ and
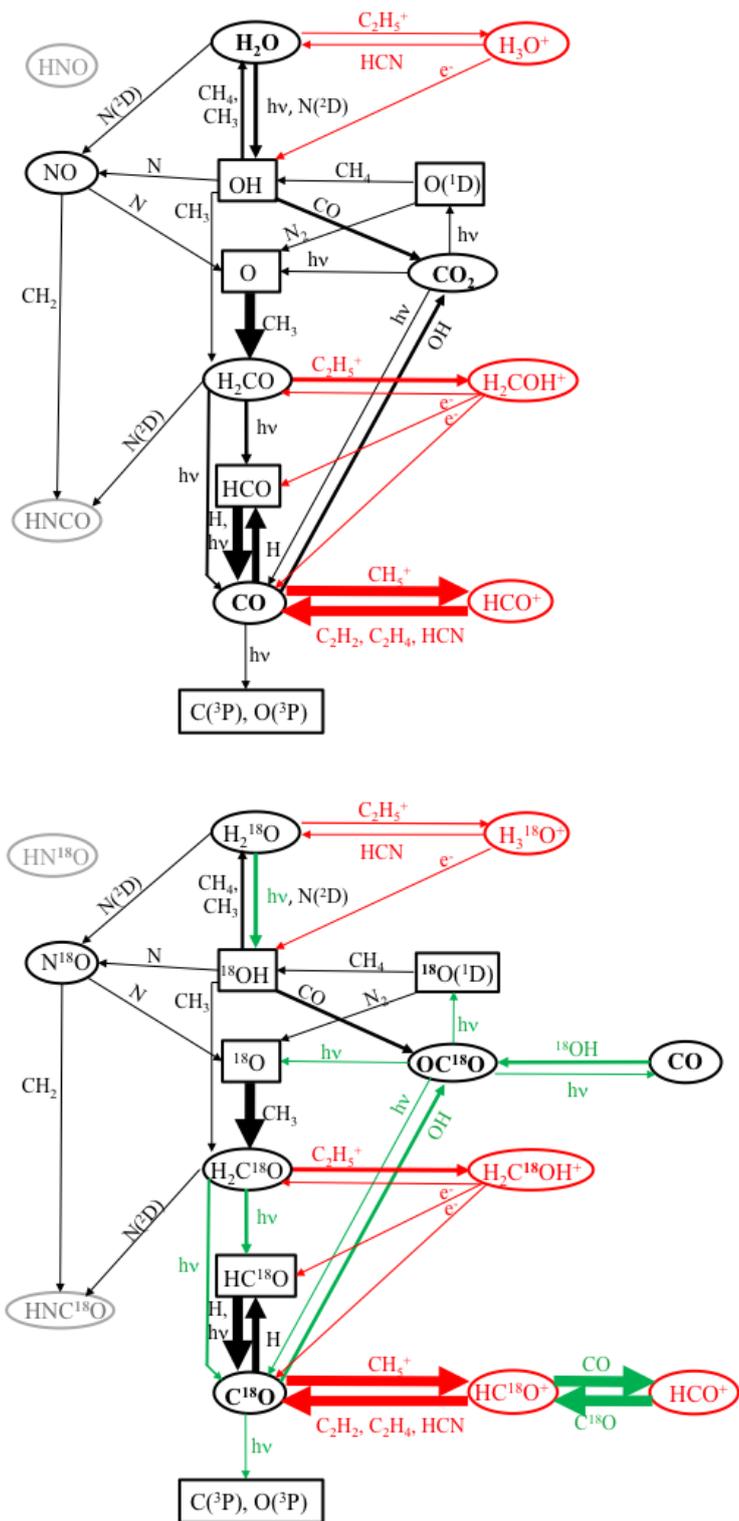
Fig. 5. Schematic diagram highlighting the important pathways for the chemistry of ^{16}O and ^{18}O containing compounds. The thickness of each arrow represents the integrated total production. The use of red as a color corresponds to ionic chemistry. Species in gray are not considered in this study. Compounds that have been detected are highlighted in bold. Processes in green correspond to reactions which may induce some fractionation.

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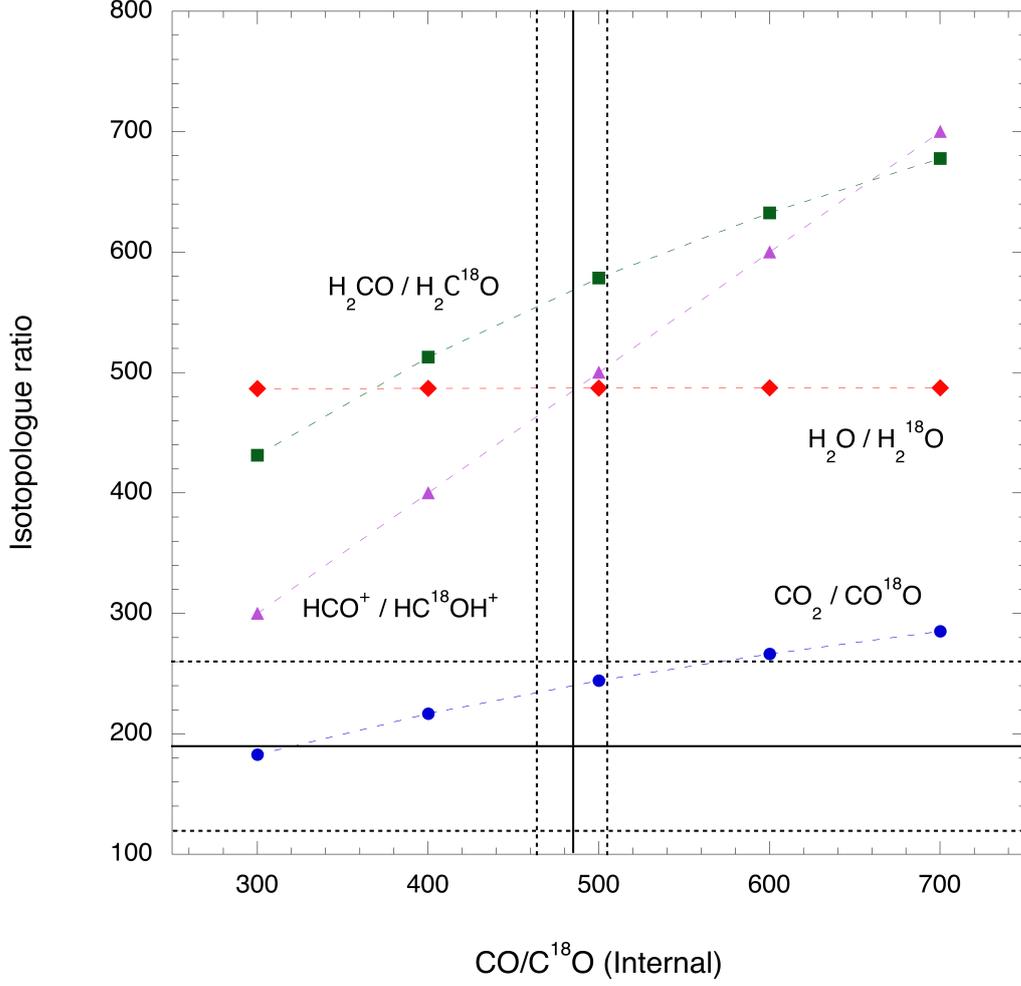
Fig. 6. The $CO_2/CO^{18}O$ (blue disk), $H_2CO/H_2C^{18}O$ (red diamond), $H_2O/H_2^{18}O$ (green square) and $HCO^+/HC^{18}O^+$ (purple triangle) ratios at 250 km of altitude (region where observations are available) as a function of the $CO/C^{18}O$ ratio fixed at the lower boundary. Note that the $CH_2OH^+/CH_2^{18}OH^+$ ratio has the same evolution as $H_2CO/H_2C^{18}O$. Horizontal line: $CO_2/CO^{18}O$ value from Nixon et al. (2009). Vertical line: $CO/C^{18}O$ value from Serigano et al. (2016). Black dashed lines represent error bars of observations.

$CO_2/CO^{18}O$ ratios.

3.2 External source of CO

We have also investigated the production of oxygen compounds (CO, CO_2,...) through an external supply of oxygen via micrometeorites (in the form of H_2O) and Enceladus' plumes (in the form of $O(^3P)$). The integration time needed to obtain a CO mole fraction of about 4.5×10^{-5} is equal to 10^{16}s (317×10^6 years). At this time, the mole fractions of the major oxygen species

are identical to the ones obtained with the internal scenario (see Dobrijevic et al. (2014) for details). This confirms that different scenarios give the same profiles of CO and CO_2.

Although values derived from Waite et al. (2009) for the $^{16}O/^{18}O$ ratio in the Enceladus' plumes range from 400 to 526, we have investigated larger variations of this ratio. We first consider that the $^{16}O/^{18}O$ ratio in H_2O from micrometeorites is constant and equal to 500 (see section 4.2 for a study of this parameter). Results are shown in Figure 7. The most striking results are the following: (1) the evolution of the $CO/C^{18}O$ and $H_2CO/H_2C^{18}O$ ratios are strongly correlated with the external $O(^3P)/^{18}O(^3P)$ flux from Enceladus, (2) as a consequence, the evolution of $CO_2/CO^{18}O$ and the $HCO^+/HC^{18}O^+$ ratios are similar to the internal case since they are correlated to the $CO/C^{18}O$ ratio.

In conclusion, considering that the external H_2O and $O(^3P)/^{18}O(^3P)$ fluxes both have a $^{16}O/^{18}O$ ratio equal to 500, our model is consistent with current observations of both $CO/C^{18}O$ and $CO_2/CO^{18}O$ ratios. The $CO_2/CO^{18}O$ ratio that has been measured (Nixon et al., 2008) does not seem to be required to constrain the origin of CO. It is of course important to lower the uncertainty on this ratio by future measurements to validate the present model but our model seems to indicate that it might be irrelevant for discriminating an external origin from an internal origin of CO. The only neutral species highly dependent on the $^{16}O/^{18}O$ ratio from Enceladus is H_2CO. However, the abundance of H_2CO in Titan's atmosphere is relatively low in our model and has never been detected from infrared observations in the lower atmosphere. It should be noted that the relative H_2CO abundance in the upper atmosphere is only 1/10 of the one of HNC which has been detected through microwave spectroscopy (Moreno et al., 2011; Cordiner et al., 2014).

3.3   Propagation of chemical uncertainties

The propagation of chemical uncertainties in the photochemical model of Titan has been investigated by Dobrijevic et al. (2014) and Dobrijevic et al. (2016) for neutral oxygen chemistry and the coupled ion-neutral chemistry, respectively. Associated to a global sensitivity analysis, these studies allow us to identify the key reactions that mainly contribute to the uncertainties in the model results'. In the present paper, we only present the uncertainties on the various oxygen species. The propagation of uncertainties is presented for the case of an internal source of CO.

The methodology we used to estimate the uncertainties on the photolysis rates for the different isotopologues is the following. Five species that include ^{18}O atoms are photodissociated in our model. Absorption cross sections of the
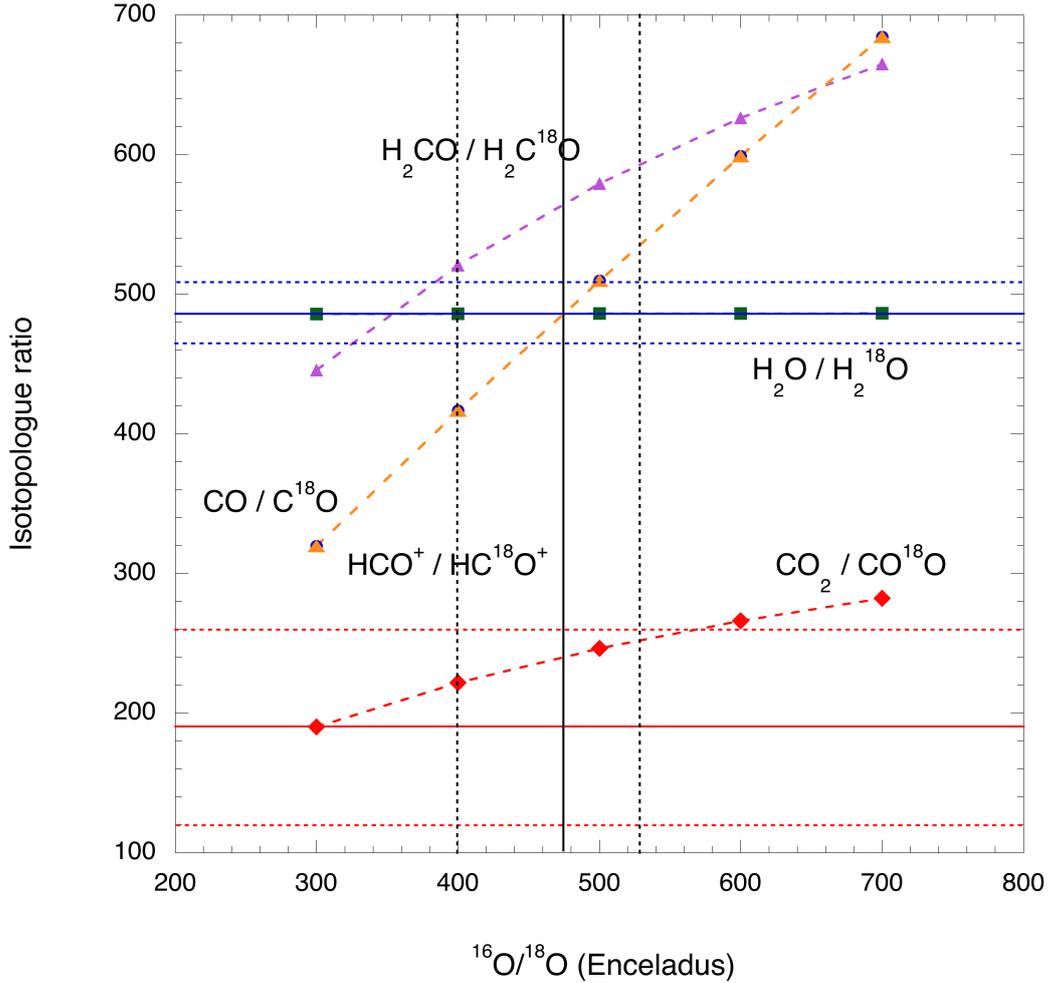
Fig. 7. The CO/C^{18}O (blue circle), CO$_2$/CO^{18}O (red diamond), H$_2$CO/H$_2$C^{18}O (purple triangle), H$_2$O/H$_2$^{18}O (green square) and HCO$^+$/HC^{18}O$^+$ (orange triangle) ratios at 250 km of altitude (region where observations are available) as a function of the ^{16}O/^{18}O ratio in the external flux of O(^{3}P) at the higher boundary. Blue horizontal line: CO/C^{18}O value from Serigano et al. (2016) (which overlap the H$_2$O/H$_2$^{18}O ratios). Red horizontal line: CO$_2$/CO^{18}O value from Nixon et al. (2009). Black vertical line: ^{16}O/^{18}O value from Waite et al. (2009). Dashed lines represent error bars of observations.

various light oxygenated compounds studied here are relatively well known at room temperature (various studies are available). Considering uncertainties on the various measurements and also that most of the experiments have been performed at room temperature, we consider that the uncertainties on the absorption cross section values are equal to 20%. This arbitrary uncertainty should be a good approximation for closed shell molecules and for HCO. We consider that the uncertainties on branching ratios are of the same order of magnitude for the oxygenated compounds studied here. Due to the Zero Point Energy (ZPE) effect (Liang et al., 2004) the absorption of heavy isotopologues (containing one ^{18}O atom) is systematically shifted to the blue due to the larger

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reduced mass. So, the difference in absorption between the light and the heavy isotopes could be considered as known. It does not depend on the uncertainties on the experimental measurements. Moreover, we can consider that the branching ratios for the photodissociation of both isomers are identical. The photodissociations of CO_2 and $CO^{18}O$ are fairly well known (Schmidt et al., 2013), and both $H_2C^{18}O$ and $HC^{18}O$ are photodissociated in the visible part of the spectrum. In this case, as the solar flux is relatively constant, the spectral shift induced by the ZPE effect does not lead to an important difference in the photolysis rates for the respective isotopologues. Consequently, for these systems we fixed the $J^{16}O/J^{18}O$ ratio (where $J^{16}O$ is the photolysis rate of the light isotopologue (for instance CO) and $J^{18}O$ is the photolysis rate of the heavy isotopologue (for instance $C^{18}O$)). The fixed value corresponds to the nominal model. So, it means that at the end of the Monte-Carlo procedure, the distribution of $J^{18}O$ values has the same shape as the one of $J^{16}O$ but shifted by a constant value given by the nominal $J^{16}O/J^{18}O$ ratio. For H_2O, which absorbs below 200 nm and should show a relatively strong ZPE effect, we used the calculated ZPE effect in the nominal model (20 cm^{-1}) and we performed an additional run with a ZPE effect of 40 cm^{-1} leading to a very similar result. We conclude then that the uncertainty on $H_2^{18}O$ photodissociation is similar to the uncertainty on H_2O photodissociation.

For the reactions involving the other isotopologues, we consider that for all the reactions the $k^{16}O/k^{18}O$ ratio stays constant for each Monte-Carlo run ($k^{16}O$ is the constant rate of the reaction that includes only ^{16}O atoms and $k^{18}O$ is the constant rate of similar reactions including one ^{18}O atom). We considered that only a few reactions have a $k^{16}O/k^{18}O$ ratio different than 1 (see appendix A).

Results for the internal source of CO are summarized in Table 2. We see that due to uncertainties on the rate constants and photolysis rates, the uncertainties on some $XO/X^{18}O$ ratios in the atmosphere are quite important. This is particularly noticeable for $H_2CO/H_2C^{18}O$ in the lower atmosphere (where the abundance is low), $NO/N^{18}O$ and $CH_2OH^+/CH_2^{18}OH^+$. In the ionosphere, the uncertainty on the $H_2O/H_2^{18}O$ ratio (and consequently on the $H_3O^+/H_3^{18}O^+$ ratio) is also noticeable. In the ionosphere, the origin of water is a mix between diffusion from micrometeorite deposition around 750 km, and a minor contribution from oxygen reactions (due to the $O(^3P)$ flux at the upper boundary of the model). The uncertainty on the $H_2O/H_2^{18}O$ ratio is due to cycling processes involving H_2O and $H_2^{18}O$ photodissociations associated to reformation of H_2O and $H_2^{18}O$ (through the reactions of OH with CH_3 and CH_4) in competition with net water loss through the OH + CO reaction (see Dobrijevic et al. (2014)). The other compounds that present high uncertainties in the lower atmosphere are H_2CO and NO for neutrals and the four oxygen ions included in our model. Figure 8 illustrates the distributions of $H_2O/H_2^{18}O$ and $CH_2OH^+/CH_2^{18}OH^+$ profiles generated by our Monte-Carlo procedure.

The chemical uncertainties on the ^{16}O/^{18}O ratios are quite low for CO and CO_2, the two compounds for which we have measurements. It can be noted that the uncertainties in the calculated $CO_2/CO^{18}O$ ratio is much lower than the uncertainty on the observation.

Table 2
Nominal and mean ^{16}O/^{18}O ratios and their 1-σ uncertainty for all oxygen species in the model at two altitudes. Ratio values of $CO_2/CO^{18}O$ and $CO/C^{18}O$ inferred from observations from Nixon et al. (2009) and Serigano et al. (2016) respectively are also given for comparison.

Isotopologue ratio	Model				Observation
	Altitude: 200 km		Altitude: 800 km		
	Nominal	Monte-Carlo	Nominal	Monte-Carlo	
$CO/C^{18}O$	500	500 ± 0	505	505 ± 0	486 ± 22 (200-275 km)
$H_2O/H_2^{18}O$	483	483 ± 11	500	501 ± 20	
$CO_2/CO^{18}O$	243	244 ± 3	247	248 ± 2	190 ± 71 (100-150 km)
$H_2CO/H_2C^{18}O$	589	568 ± 94	484	485 ± 16	
$HCO/HC^{18}O$	500	500 ± 0	484	485 ± 16	
$CH_3O/CH_3^{18}O$	567	569 ± 8	505	506 ± 19	
$NO/N^{18}O$	519	519 ± 72	536	544 ± 88	
$OH/^{18}OH$	497	497 ± 11	504	505 ± 67	
$O(^3P)/^{18}O(^3P)$	589	567 ± 97	507	507 ± 2	
$O(^1D)/^{18}O(^1D)$	567	569 ± 8	505	506 ± 19	
$HCO^+/HC^{18}O^+$	500	500 ± 0	505	505 ± 0	
$CH_2OH^+/CH_2^{18}OH^+$	589	568 ± 94	484	485 ± 16	
$NO^+/N^{18}O^+$	519	519 ± 72	536	544 ± 88	
$H_3O^+/H_3^{18}O^+$	483	483 ± 11	500	501 ± 20	

Another way to present the results of our uncertainty propagation procedure is to present scatterplots of a species and its isotopologue. Figure 9 shows the scatterplots of H_2O and H_2CO mole fractions and their respective isotopologues at different altitudes. With the exception of a few points (obtained from about 10% of the runs), most of the points are gathered in a relatively narrow range of values. They also show that there is a strong correlation between the mole fraction value of a species and its isotopologue and that uncertainty on model results are about the same for the lighter isotopologue than the heavier one. As a consequence, if our procedure does not underestimate the uncertainty on the rate constants for the higher isotopologues, it would be more efficient, in order to reduce the model uncertainties, to improve the pre-
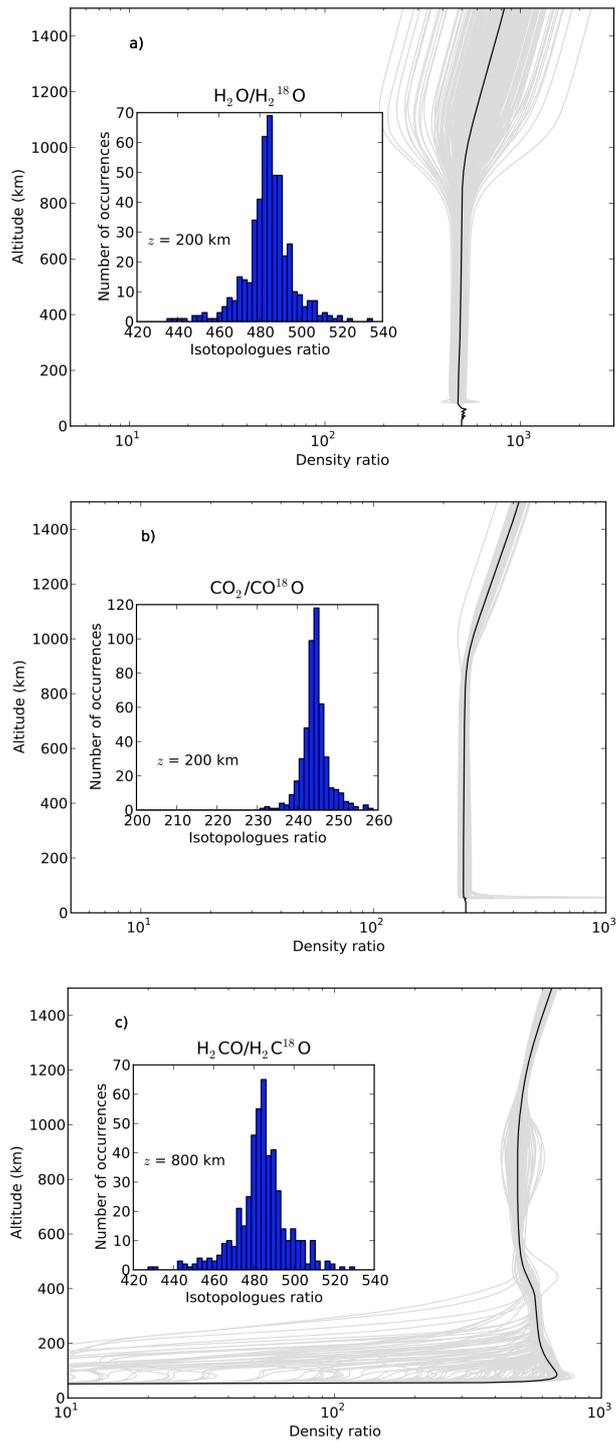
Fig. 8. Ratio profiles generated by the Monte-Carlo method and histogram at a given altitude. a) $H_2O/H_2{}^{18}O$ at $z = 200$ km. b) $CO_2/CO^{18}O$ at $z = 200$ km. c) $H_2CO/H_2C^{18}O$ at $z = 800$ km. Dark line: nominal profile. Grey lines: Monte-Carlo profiles.

cision of the key reactions involving the lighter species; i.e. the key reactions presented in Dobrijevic et al. (2014).
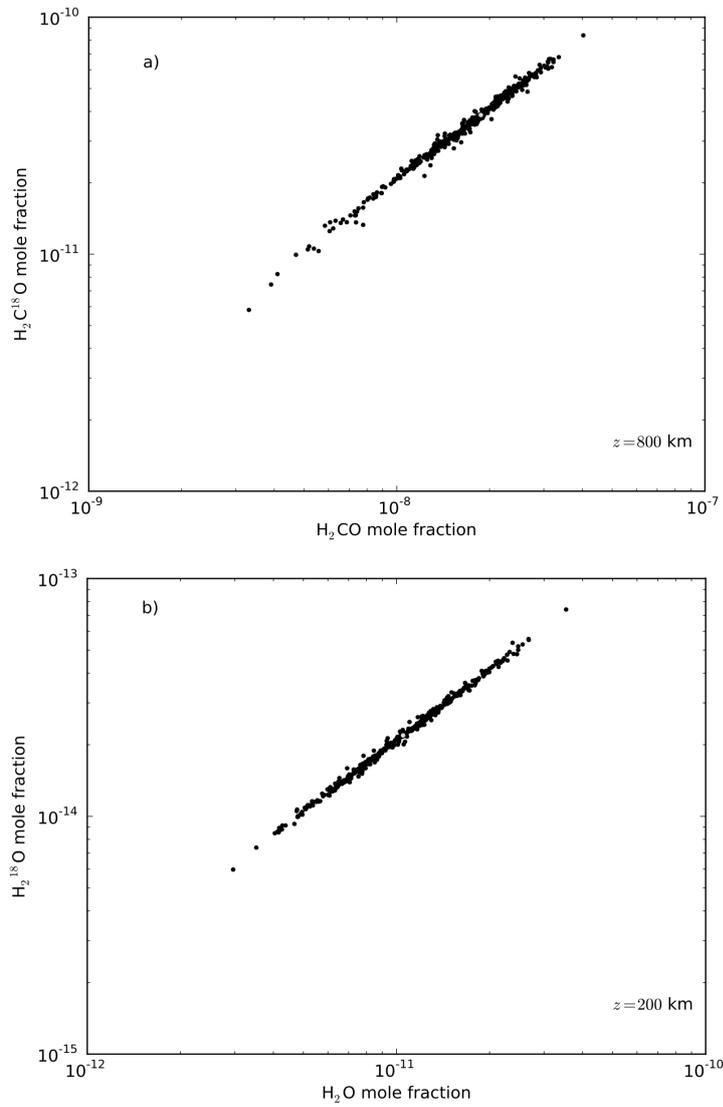
Fig. 9. a) Scatterplot of H_2CO and $H_2C^{18}O$ mole fractions at 800 km. b) Scatterplot of H_2O and $H_2^{18}O$ mole fractions at 200 km. Black points correspond to the 480 mole fractions generated by our uncertainty propagation procedure. Grey point correspond to our nominal results.

4 Discussion

4.1 Photochemical fractionation of ^{17}O species

Recent ALMA observations of CO (Serigano et al., 2016) give a $^{16}O/^{17}O$ ratio equal to 2917 ± 359, in agreement with the terrestrial value, which is 2680.0 (Lodders, 2003). We did not perform calculations considering the photodissociation and chemistry of ^{17}O compounds, but we think that the $^{16}O/^{17}O$ ratio will follow the same trend as the $^{16}O/^{18}O$ one, the fractionation processes being of a similar amplitude. So, we do not expect a large fractionation effect for ^{17}O compounds.

4.2 Sensitivity to micrometeorite composition

We added several species in the micrometeorites flux (such as O_2, CO, CO_2 with relative abundances corresponding to their cometary composition) to check their putative role in the chemistry. In particular, the O_2 molecule has been recently detected in the coma of comet 67P/Churyumov-Gerasimenko (Bieler et al., 2015) with an average abundance O_2 (relative to H_2O) equal to $3.80 \pm 0.85\%$. We have investigated the effect of such abundance in micrometeorites on the $^{16}O/^{18}O$ ratio of various oxygenated compounds in Titan's atmosphere. We have built a chemical network describing the photodissociation and reactivity of O_2 and $O^{18}O$ (chemical scheme presented in appendix A). However, despite the different photodissociation efficiencies of O_2 and $O^{18}O$ (Yoshino et al., 1989), the $O_2/O^{18}O$ input does not have any effect on oxygen compounds fractionation. This is due to the fact that $O_2/O^{18}O$ is quickly consumed in Titan's atmosphere (through photodissociation and reaction with CH_3) and are transformed into $CO/C^{18}O$ (and a small fraction into $H_2O/HO^{18}O$). As there is no efficient O_2 production, there is no O_2 recycling and then no possibility of oxygen fractionation. Potential O_2 input from micrometeorites leads only to a small increase of the abundances of oxygen compounds. So, we do not consider O_2 and $O^{18}O$ in our nominal model. Similarly, the addition of cometary CO and CO_2 in micrometeorites has no significant effect on the abundance of the main oxygen species, nor on their isotopic ratio.

We have also investigated the role of the uncertainty on the $H_2O/H_2^{18}O$ ratio coming from micrometeorites. Regarding the values published in the literature (see section 2.3), the $^{16}O/^{18}O$ ratio in micrometeorites ranges from 370 to 626 (in H_2O). In Figure 10 we show the results we obtained varying this ratio in the influx of H_2O and keeping the external $^{16}O/^{18}O$ ratio constant and equal to

500. CO and CO_2 show little variations as a function of $^{16}O/^{18}O$ ratio in H_2O. However, measurements are not compatible with a $H_2O/H_2^{18}O$ ratio greater than 600. A more precise determination of the $CO_2/CO^{18}O$ ratio would give a valuable constraint on the $H_2O/H_2^{18}O$ ratio in micrometeorites. As mentioned before, the $H_2CO/H_2C^{18}O$ ratio shows strong variations with the $H_2O/H_2^{18}O$ ratio. We obtain the same results when considering an internal source of CO.
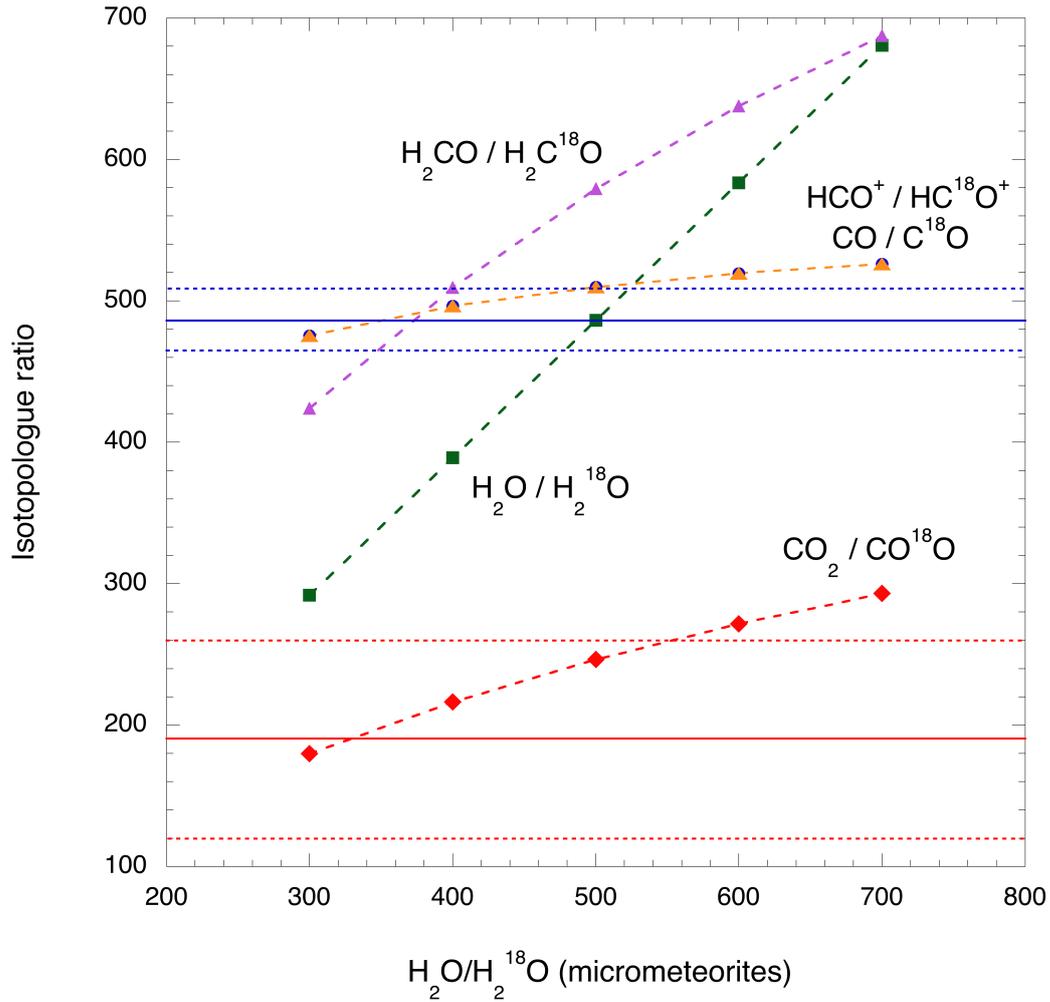
Fig. 10. The $CO/C^{18}O$ (blue circle), $CO_2/CO^{18}O$ (red diamond), $H_2CO/H_2C^{18}O$ (purple triangle), $H_2O/H_2^{18}O$ (green square) and $HCO^+/HC^{18}O^+$ (orange triangle) ratios at 250 km of altitude (region where observations are available) as a function of the $H_2O/HO^{18}O$ ratio in the micrometeorite flux of H_2O around 750 km. Blue horizontal line: $CO/C^{18}O$ value from Serigano et al. (2016). Red horizontal line: $CO_2/CO^{18}O$ value from Nixon et al. (2009).

4.3   Sensitivity to $H_2^{18}O$ absorption cross section

To our knowledge, the photodissociation cross section of $H_2^{18}O$ has not been measured, in contrast to $C^{18}O$ and $CO^{18}O$. We estimate it from the H_2O photodissociation cross section using the ZPE effect (Liang et al., 2004) which is a rough approximation. The ZPE effect shifts the absorption of $H_2^{18}O$ to the blue, a shift equal to the difference of the ZPE of the ground vibrational states of H_2O and $H_2^{18}O$ calculated to be equal to 20 cm^{-1}. As the ZPE effect is a rough approximation we varied the shift of the $H_2^{18}O$ absorption to see if the value of the shift is critical. Using a shift of 40 cm^{-1} leads to very similar results. The photodissociation is the main loss, along with condensation, of water in Titan's atmosphere, and the difference between H_2O and $H_2^{18}O$ photodissociation seems too small to induce a strong enrichment. However, uncertainty on the $H_2^{18}O$ photodissociation may be underestimated using ZPE effect and experimental measurements will be of great help to improve this point.

4.4   Comparison with previous photochemical models

Wong et al. (2002) developed a photochemical model to explain the preliminary value of $^{16}O/^{18}O$ in CO obtained by Owen et al. (1999), which was about half of the cometary value. Due to the low dilution of $C^{18}O$ with time inferred from their model, they inferred that a strong initial $C^{18}O$ enrichment of 3.23 is required to be compatible with these observations. In fact, due to the recent observations of oxygen species (especially H_2O) and the new determination of isotopic ratios in CO and CO_2 (which are compatible with a cometary $^{16}O/^{18}O$ ratio), the model of Wong et al. (2002) would rather suggest that there was a low or no $C^{18}O$ enrichment at all 4.6 Gyr ago.

Recently, Lara et al. (2014) proposed that a time-variable Enceladus source could explain the discrepancy of the relative H_2O and CO_2 profiles between the photochemical models and observations. According to the present work, the isotopic ratio in CO and CO_2 requires a cometary $^{16}O/^{18}O$ ratio influx (in $O(^3P)$ from Enceladus' plumes or in CO from the surface, and in H_2O from micrometeorites). Unfortunately, the measurement of the oxygen isotopic ratio in Enceladus' plumes (Waite et al., 2009) does not give an additional constraint to test this hypothesis.

5 Conclusion

We have developed a photochemical model of oxygen isotopologues to bring some new theoretical constraints on the origin of oxygen species in Titan's atmosphere. Our model gives satisfactory results concerning the main oxygen species and their isotopologues. In particular, the current isotopic fractionation observed in CO and CO_2 can either be explained by an internal source of CO or by an external source of oxygen atoms from Enceladus' plumes, both with a micrometeoritic influx of water, assuming that all these sources have a cometary $^{16}O/^{18}O$ ratio.

If the origin of CO is external (reaching its present concentration after 3.17×10^8 years of accumulation), CO is produced from a set of reactions that begins with the reaction $O(^3P) + CH_3$, the contribution from $OH + CH_3$ being almost negligible (1/50 of the $O(^3P) + CH_3$). Our results suggest that the $^{16}O/^{18}O$ ratio in CO is then mainly controlled by the $^{16}O/^{18}O$ ratio in $O(^3P)$. Measurements of the oxygen isotopic ratio in Enceladus' plumes is in agreement with this statement. In order to give more reliable conclusions on the origin of oxygen, it would be very helpful to determine the origin of the discrepancies between the various measurements of H_2O abundances in the stratosphere (CIRS and Herschel observations) and to lower the uncertainty on the measured $CO_2/CO^{18}O$ ratio. New measurements, even at low spatial resolution, are necessary to move this work forward. In particular, according to Dobrijevic et al. (2014) and the present work, the detection of new oxygen species in Titan's atmosphere would provide valuable constraints for photochemical models.

Clearly, our study shows that oxygen fractionation is low in Titan's atmosphere. In the higher atmosphere, above the homopause, oxygen fractionation is controlled by molecular diffusion. Photochemical fractionation, the most efficient fractionation process in Titan's atmosphere apart from molecular diffusion, is only efficient in the lower stratosphere. The main species subject to this fractionation, taking chemical uncertainties into account, are H_2CO, H_2O, NO and some oxygen ions like CH_2OH^+. The most efficient reaction is the OH + CO reaction. The CO + HCO^+ reaction involves high flux but as HCO^+ is involved in reactions leading ultimately back to CO, this reaction does not lead to any isotopic $C^{18}O$ fractionation, but instead controls the $HCO^+/HC^{18}O^+$ ratio.

Differences in photolysis between ^{16}O and ^{18}O compounds are small in our model. However, in some cases, such as H_2O photolysis, the effect may not be negligible. So, precise photodissociation cross sections of $H_2^{18}O$ are needed to lower the uncertainties in the modeled $H_2O/H_2^{18}O$ fractionation.

A List of reactions

B Cross sections and branching ratios of the oxygen species and their isotopologues considered in the present paper

C Integrated production and loss rates for the nominal internal model of CO

Acknowledgements

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