

Testing various assumptions for radiolysis, non-diffusive chemistry, and chemical desorption in cold cores

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ABSTRACT

Context. To study interstellar gas and grain chemistry, gas-phase astrochemical models have been developed since the early 1980s and gas-grain models since the 1990s. Each published model includes various assumptions mainly for surface processes.

Aims. In this paper, we compare recently added mechanisms for grain surface chemistry, namely, non-diffusive chemistry, radiolysis, and chemical desorption.

Methods. Several formalisms for these processes have been added to our astrochemical model Nautilus, and we tested them, comparing the predicted gas-phase and ice abundances. Our predictions are also compared to gas and ice observed compositions.

Results. Our main findings are that radiolysis itself does not influence the results. Non-diffusive chemistry can have an impact on the gas-phase and ice species, but it depends on the adopted formalism. In particular, the one of Shingledecker & Herbst (2018) changes the main reservoirs of the species in the ices, impacting the species in the gas-phase as well. The adopted formalism for chemical desorption can produce differences in the gas-phase by up to a factor of ten. Last, our standard model, without non-diffusive chemistry and with the chemical desorption from Fredon et al. (2021), produces the best results in relation to observed gas-phase abundances, while the ice observed agreement is unchanged.

Conclusions. The formalism for some grain surface processes are important even for gas-phase abundances. More experiments are needed to constrain their efficiency, however. For the chemical desorption, each formalism relies on an uncertain parameter, which is the fraction of the energy actually delivered to the products, that can be adjusted to reproduce the experiments.

Key words. Astrochemistry – ISM: abundances – ISM: molecules

1. Introduction

Carbon and heavier atoms are born in the centers of stars. At the end of their lives, stars spread their inner material into the interstellar medium (ISM), yielding at the same time the formation of interstellar dust refractory cores. In the diffuse medium, photodissociations by UV photons prevent the formation of molecules. Within large interstellar filaments, the material is organized as clouds (or clumps) of denser material.

Numerical models have been developed since the early 1980s to study interstellar gas and grain chemistry (Prasad & Huntress 1980; Graedel et al. 1982; Leung et al. 1984; Hasegawa et al. 1992; Hasegawa & Herbst 1993). If the gas-phase chemistry has been actively studied and improved over the past fifteen years thanks to a systematic review of gas-phase reactions (see Wakelam et al. 2015, and references therein), there is considerable room for improvement on the surface chemistry. Many modern astrochemical models have also been developed, such as Nautilus (Ruaud et al. 2016), MAGICKAL (Garrod & Pauly 2011), GRAINOBLE (Taquet et al. 2012), ROKKO (Furuya et al. 2015), MONACO (Vasyunin et al. 2017), and UCLCHEM (Holdship et al. 2017). Each of these models has different assumptions for grain surface chemistry, and they are constantly upgraded with new features. For example, Nautilus includes the desorption by sputtering induced by cosmic rays, based on experimental results, while the other models do not. In MAGICKAL, Garrod et al. (2022) includes a very large

number of new processes. In ROKKO, the distribution of binding energy has recently been added (Furuya 2024), which is used instead of relying on one single value. Except for Nautilus and UCLCHEM, the codes are not public, so it is difficult to assess the differences in their results. In Jiménez-Serra et al. (2025), we compared the ice composition obtained with some of these models in order to understand their prediction differences. We found major differences in all the ice species (H_2O , CO , CO_2 , CH_3OH , NH_3 , and CH_4). Again, given the complexity of these models, it was difficult to assess their origin, so some surface chemical pathways or the inclusion of non-diffusive chemistry were invoked.

Three major model modifications have occurred in the recent years. The chemical desorption has been found to be highly efficient at medium densities (about 10^4 cm^{-3} ; Wakelam et al. 2021). In this process, the energy released during an exothermic reaction at the surface of the grains can break the bonds of the products to the surface, resulting in their desorption (Garrod et al. 2007; Minissale et al. 2016; Cazaux et al. 2016; Oba et al. 2018). The fraction of desorbed molecules depends on the exothermicity of the reaction, the binding of the species to the surface, and the fraction of the energy remaining in the product. This last parameter is difficult to assess because of a lack of experimental results. The second modification is the new process of radiolysis, which is the chemical effect of cosmic rays in the ices. When a cosmic-ray particle collides with a grain, it can produce the dissociation of molecules and the pro-

duction of suprathermal species, which diffuse at high velocity, boosting the chemical reactions (Shingledecker & Herbst 2018; Shingledecker et al. 2018, 2019, 2020). The third modification is non-diffusive chemistry. This process has been introduced to mimic the fact that two species produced close to each other on the surface can react without diffusing (Jin & Garrod 2020; Shingledecker & Herbst 2018; Borshcheva et al. 2025).

Our goal with the work presented in this paper was to test the efficiency of these new surface processes using Nautilus, as the processes are treated differently in various models. The paper is organized as follows. The model is presented in Sect. 2 together with the different processes to test. The results of the different tests we made are given in Sect. 3. The different models are compared to gas and ice observations in Sect. 4, while we provide our conclusions in the final section.

2. Model presentation

2.1. General presentation

Nautilus is a three-phase gas-grain astrochemical model. It computes the molecular and atomic abundances of gas and ice as a function of time starting from an initial chemical composition. It has three phases, which means that in addition to the gas, it computes the chemistry at the surface (the four most external monolayers) of the grains as well as in the bulk (the rest of the ice below the surface). The diffusion at the surface is more efficient, so the species are more reactive than in the bulk. Both the species on the surface and the bulk are dissociated by direct and indirect UV photons. Compared to previous versions of Nautilus, the photo-rates in the ices have been updated with the latest values in the gas-phase from *kida.uva.2014* (Wakelam et al. 2015). The gas-phase network is *kida.uva.2024* (Wakelam et al. 2024).

The grain surface and bulk chemistry are computed using the rate equation approach. The species from the gas-phase remain at the surface of the grains, so they can diffuse and react upon encounters. Species from the surface can desorb due to temperatures breaking the bond linking them to the surface and through a number of nonthermal processes (global heating of the grains or sputtering by cosmic rays, chemical desorption). Species from the bulk can also be released in the gas phase by cosmic-ray sputtering. All the equations and details on the model can be found in Ruaud et al. (2016) and Wakelam et al. (2021) (see also Wakelam et al. 2024). As usually assumed, only one grain size made of silicates of $0.1\mu\text{m}$ is considered. The gas to dust mass ratio is 100.

2.2. Non-diffusive chemistry

To this version of Nautilus, we added the non-diffusive chemistry using two different methods. The Jin & Garrod (2020) formalism is computed by taking into account the rates of production of species by other processes. The rate of the reaction (in s^{-1}) between species A and B on the grains is computed via

$$R_{AB} = \frac{f}{N_S} (R_{\text{comp}}(A)N(B) + R_{\text{comp}}(B)N(A)), \quad (1)$$

where f is the probability of the reaction to occur assuming the competition between diffusion and reaction. The term N_S is the number of sites on one grain, while $N(B)$ and $N(A)$ are the number of species A and B on one grain. The expression of R_{comp} is more complicated. It is the rate of appearance of species A or B.

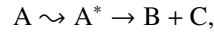
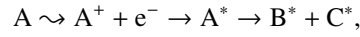
There is another formalism proposed by Shingledecker & Herbst (2018) where the rate of reaction is the diffusive rate (Hasegawa et al. 1992) and where the diffusion part is removed. Compared to the equation from Shingledecker & Herbst (2018), we slightly changed the expression to take into account the dilution of the species:

$$R_{AB} = f \left(\frac{\nu_A + \nu_B}{\max(N_{ab}, N_S)} \right) N(A)N(B), \quad (2)$$

where ν_A and ν_B are the vibrational frequencies of species A and B, and N_{ab} is the number of molecules in the bulk or the surface. In this work, we compare the two methods.

2.3. Radiolysis

Following Shingledecker et al. (2018), we included in Nautilus the radiolysis for all species. We considered the radiolysis processes



where the species with an asterisk are suprathermal species, which can react with thermal species without activation barriers or quenched by collision with the dust mantle. The radiolysis reactions are from Lu et al. (2025). The network involving suprathermal species has been constructed based on the *kida.uva.2024* grain network. For each reaction involving thermal species that has its suprathermal counterpart as a reactant, we duplicated this reaction, changed this reactant into its suprathermal counterpart, and removed the activation barrier. If both reactants have their suprathermal counterparts, we duplicated this reaction twice and modified only one species to be suprathermal in each duplication. These barrierless reactions, including both the diffusive and non-diffusive manner, are expected to be able to promote the formation of large molecules in the ice surface and bulk. In this work, we test the effect of this chemistry.

2.4. Chemical desorption

We included in Nautilus the chemical desorption efficiency following Fredon et al. (2021). Two other formalisms are already present in Nautilus from Garrod et al. (2007) and Minissale et al. (2016) (see also Cazaux et al. 2016). All three methods depend on the fraction of the released energy that is dissipated to the grain surface. The first method is an adhoc formalism where the fraction of desorbing species (number of desorbing species when a single reaction takes place) is expressed as

$$\text{frac} = \frac{aP}{1 + aP}. \quad (3)$$

Here, a is the fraction of energy remaining in the product and P is $(1 - E_D/E_{\text{reac}})^{s-1}$. In the latter, E_D is the binding energy of the product, E_{reac} is the enthalpy of formation of the species, and s is 2 for diatomic molecules and $3N-5$ for more complex species (N being the number of atoms in the molecule). The parameter a is adjustable and suggested to be 0.01. For most if not all reactions, P is rather small so that frac is equal to a .

Table 1: Elemental abundances.

Species	Abundance	Reference
He	9×10^{-2}	1
N	6.2×10^{-5}	2
O	2.4×10^{-4}	3
C ⁺	1.7×10^{-4}	2
S ⁺	8×10^{-8}	4
Si ⁺	8×10^{-9}	4
Fe ⁺	3×10^{-9}	4
Na ⁺	2×10^{-9}	4
Mg ⁺	7×10^{-9}	4
P ⁺	2×10^{-10}	4
Cl ⁺	1×10^{-9}	4
F	6.68×10^{-9}	5

Notes. (1) See the discussion in Wakelam & Herbst (2008).
 (2) Jenkins (2009).
 (3) See the discussion in Hincelin et al. (2011).
 (4) Low metal abundance from Graedel et al. (1982).
 (5) Depleted value from Neufeld et al. (2005).

The second method (Cazaux et al. 2016) is based on experiments but only for very few and simple systems. The fraction of desorbing species is computed as

$$\text{frac} = \exp - \frac{E_D}{\epsilon E_{\text{reac}}/N}, \quad (4)$$

with N as the degree of freedom of the product. The term $\epsilon = \frac{(M-n)^2}{(M+m)^2}$, where m is the mass of the product and M is the effective mass of the surface, which is an unknown parameter for the water ices. Minissale et al. (2016) recommended using the M parameter of bare grains (120 amu) and divided the fraction by a factor of ten based on the experimental results.

The third method is from Fredon et al. (2021), and it is based on a comparison between rate equation models and Monte Carlo simulations. They defined the fraction of desorbing molecules as

$$\text{frac} = \theta \left(1 - \exp \left(- \frac{\chi \Delta E_{\text{react}} - E_D}{3E_D} \right) \right), \quad (5)$$

with χ as an empirical factor depending on the number of products (one or two). Note that for the two previous methods, only channels producing one species are considered, the other channels are set to zero desorption. The term f an empirical factor linked to where the species are on the surfaces. χ for two-produced species does not influence the results. For reactions producing only one species, we used the experimental results from Oba et al. (2018) to constrain χ . In the experiments, they found that H₂S formation via an H + HS reaction leads to a desorption of 60% of the product. Inverting Fredon's formula, we found an χ parameter of 0.08. We use this value in this work and make a comparison to the other two methods. This final formalism has been included in our standard model (see below). These are the three formalisms we tested.

2.5. Standard model and physical parameters

Our standard model is the version in Nautilus not including non-diffusive chemistry nor radiolysis and using the chemical desorption of Fredon et al. (2021). To simulate a cold core, we assumed the simple model in which the gas and grain temperature and H

density are constant with time to 10 K and $2 \times 10^4 \text{ cm}^{-3}$, respectively. The visual extinction is high (20) in simulated shielded regions. The cosmic-ray ionization rate ζ is $1 \times 10^{-16} \text{ s}^{-1}$. Note that we used a higher ζ compared to the typical values to get closer to the value found by Fuente et al. (2019). The initial conditions are atomic (neutral or ionic), except for H₂, which is molecular. The initial abundances are given in Table 1. All the abundances presented in this paper are with respect to the proton density.

3. Testing the various assumptions

We ran various models to test the processes described in Sects. 2.2 to 2.4. We found no influence of the radiolysis itself without non-diffusive chemistry. The suprathreshold species have such a low abundance and the dissociation rates are too low compared to the one induced by UV photons that reacting through normal diffusion mechanisms is not efficient. We therefore do not show any results of such models.

Our standard model is the one described in Sect. 2.5. Model 1 is our standard model with the non-diffusive chemistry by Jin & Garrod (2020). Model 2 is the same but with the non-diffusive chemistry by Shingledecker & Herbst (2018). Model 3 and 4 do not have any non-diffusive chemistry but the chemical desorption from Minissale et al. (2016) and Garrod et al. (2007), respectively. A summary of the models is given in Table 2.

3.1. Effect of the non-diffusive chemistry

In the following, we first compare our standard model (without non-diffusive chemistry) with Model 1 (non-diffusive chemistry by Jin & Garrod) and then Model 1 with Model 2 (non-diffusive chemistry by Shingledecker & Herbst). We focus on a number of gas-phase and ice molecules commonly observed in cold cores and then discuss the ice composition in general. The modeling results are shown in Figs. 1 and 2.

3.1.1. Gas-phase abundances

For the gas-phase species and the standard model compared to Model 1, the molecular abundances are not that different. The main difference is only a factor of a few. One exception is the complex organic molecule HCOOCH₃, which is enhanced by the non-diffusive chemistry by several orders of magnitude.

Comparing Models 1 and 2 (the two formalisms for non-diffusive chemistry), most molecules exhibit a strong difference of several orders of magnitude at the typical age of cold cores (10⁶ yrs), except for CO, HCO⁺, N₂H⁺, and CH₃OH. In nearly all cases, but N₂H⁺, Model 1 produces larger abundances. From a general point of view, in Model 2, the main reservoirs of species are shifted toward species that necessitate heavy precursors to diffuse (see also Sect. 3.1.3). The CS and SO abundances predicted by Model 2 are much smaller than the observed abundances (see Fig A.1). Note that we used an initial sulfur abundance of 8×10^{-8} , which is typically used in chemical models, but if we increase it to its cosmic value, the CS and SO abundances become closer to the observed values. The HCN_{ice} becomes a reservoir of nitrogen in Model 2, as abundant as NH_{3ice}. Carbon is mainly in HCOOCH_{3ice} and is more abundant than CO_{2ice} (see also Sect. 3.1.3). Note that both CH₃OCH₃ (not shown on the figure) and HCOOCH₃ are much more abundant in the gas-phase when using Model 2. The gas-phase molecules are produced by the chemical desorption at this density (see also Wakelam et al. 2021).

Table 2: Summary of the models.

Model	Description
Standard	without non-diffusive chemistry, Fredon et al. (2021) chemical desorption
Model 1	with non-diffusive chemistry from Jin & Garrod (2020), Fredon et al. (2021) chemical desorption
Model 2	with non-diffusive chemistry from Shingledecker & Herbst (2018), Fredon et al. (2021) chemical desorption
Model 3	without non-diffusive chemistry, Minissale et al. (2016) chemical desorption
Model 4	without non-diffusive chemistry, Garrod et al. (2006) chemical desorption

In Models 1 and 2, all molecules from the surface and the mantle can undergo non-diffusive chemistry. In Fig. 1, we overplot the abundances for these models with the non-diffusive chemistry only in the mantle. For Model 1, the results are only slightly changed. For Model 2, the impact is much stronger for CO, CS, HC₃N, c-CH₃H₂, and CH₃CN. Overall, the non-diffusive chemistry seems less efficient, and the molecular abundances are much higher if the non-diffusive chemistry is allowed only in the mantle. This also shows that the chemistry on the surface strongly influences the gas-phase molecular abundances.

3.1.2. Ice abundances

We compared our standard model with Model 1 for the ices, and the main differences are for CO_{2ice} and HCOOCH_{3ice}, which are produced much more by non-diffusive chemistry (see Fig. 2). The main difference between the model with and without non-diffusive chemistry from Jin & Garrod (Model 1) concerns the formation of heavy molecules that are not formed by simple hydrogenation as expected. The abundance of other hydrogenated species, such as CH_{4ice} and H₂O_{ice}, and the one of CO_{ice} are decreased in the non-diffusive model because HCOOCH_{3ice} takes a significant fraction of the carbon (see also Sect. 3.1.3).

In Table 3 we list the molecules that present the largest difference between our standard model and Model 1 at 10⁶ yr. The difference was computed as $\log(X_{\text{standard model}}) - \log(X_{\text{Model 1}})$, which means that a difference of -2 in the abundance in Model 1 is two orders of magnitude higher than in the abundance with Model 1. The minimal difference considered in the table is two orders of magnitude. All of these species are produced more with the non-diffusive chemistry, as they require heavy precursors to form. For instance, all sulfur-bearing species require sulfur to diffuse, which has a heavy binding energy of 2600 K (Wakelam et al. 2017). Some of these species are enhanced by 29 orders of magnitude or more. Among these six species, two have an abundance of about 10⁻⁹ at 10⁶ yr (H₂S_{3ice} and NHCHO_{ice}) with Model 1. NH₂CH₂SH_{ice} has an abundance of 10⁻¹¹, while NH₂CHS_{ice} and NH₂CH₂S_{ice} have an abundance of about 10⁻¹³. Last, S_{3ice} has a very small abundance of 10⁻¹⁹. Among the species without sulfur, we found a number of complex organic molecules. HCOOCH_{3ice} shows an increase of more than seven orders of magnitude, starting from an abundance of 10⁻¹² with the standard model to an abundance of more than 10⁻⁵ with Model 1. This molecule is formed by the non-diffusive chemistry between HCO_{ice} and CH₃O_{ice}. CH₃OCH_{3ice} starts by the non-diffusive reaction between O_{ice} and C_{2ice} to form CCO_{ice}, followed by the successive hydrogenation. It has a high abundance of 3×10^{-6} . CH₃OCH_{2ice}, CH₃CHO_{ice}, H₂CCO_{ice}, and CH₃CO_{ice} are formed during this process. HOCO_{ice} and HCOOH_{ice} are also linked starting from the non-diffusive reaction between OH_{ice} and CO_{ice}.

In Fig. 2 we also plot the ice composition if the non-diffusive chemistry is only allowed in the mantle. In contrast to the gas-phase molecules, the effect here is less obvious. The main effect

Table 3: Difference between the standard model and Model 1.

Molecule	diff	Molecule	diff
NH ₂ CH ₂ SH _{ice}	-29.8	HOCO _{ice}	-4.6
H ₂ S _{3ice}	-29.2	CH ₃ OCH _{3ice}	-4.0
NH ₂ CHS _{ice}	-29.0	HCOOH _{ice}	-3.7
NH ₂ CH ₂ S _{ice}	-29.0	CH ₃ OCH _{2ice}	-3.2
S _{3ice}	-21.7	CH ₃ CHO _{ice}	-3.2
NHCHO _{ice}	-20.0	CS _{2ice}	-3.0
S _{4ice}	-19.8	CH ₃ NCO _{ice}	-2.6
S _{5ice}	-17.8	HSSH _{ice}	-2.5
S _{6ice}	-15.7	HSS _{ice}	-2.3
S _{7ice}	-13.7	H ₂ CCO _{ice}	-2.1
S _{8ice}	-11.7	H ₂ C ₃ O _{ice}	-2.1
HCOOCH _{3ice}	-7.2	CH ₃ CO _{ice}	-2.0
CH ₃ CH ₂ OH _{ice}	-5.7		

is on CO_{ice}, CO_{2ice}, CH₃OH_{ice}, CH_{4ice}, and HCOOCH_{3ice}. The main effect is a decrease of these molecule abundances at late times ($> 3 \times 10^6$ yr). The reason for this decrease is a less efficient formation of these species in favor of CO_{2ice}.

Comparing Models 1 and 2 in Fig. 2, except for water and NH₃, all species abundances are changed at 10⁶ yrs. CO_{ice}, CH₃OH_{ice}, and CH_{4ice} are produced much less in Model 2. CO_{2ice} is less decreased but still less abundant in Model 2, while HCN_{ice} and HCOOCH_{3ice} are produced more and become reservoirs of N and C. In this model, HCN_{ice} is produced by the non-diffusive reaction between H_{ice} and CN_{ice}, while CN_{ice} is enhanced in Model 2 by the UV induced photo-dissociation of HOCN_{ice} and HOCN_{ice} by the non-diffusive reaction between N_{ice} and HCO_{ice}. HCOOCH_{3ice} is formed by the non-diffusive reaction between HCO_{ice} and CH₃O_{ice}.

Regarding the ice composition in general, we list in Table 4 the difference ($\log(X_{\text{Model 2}}) - \log(X_{\text{Model 1}})$) between molecular abundances up to 10¹² orders of magnitude. For all of these species, Model 1 predicts higher abundances than Model 2. The differences between the two models is extremely high for many species. Interestingly, the atomic abundance of S, C, and O are strongly decreased in Model 2. The abundance of many intermediate radicals, such as CH_{3ice}, CH_{2ice}, CH_{ice}, NH_{2ice}, and NH_{ice}, is also decreased in Model 2. This is due to a more efficient molecular formation in Model 2.

3.1.3. Reservoirs

Table 5 presents the main reservoirs for the different families of molecules (O-, C-, N, and S-bearing species) at 10⁶ yr. The percentages represent the fraction of the molecules in each element times 100.

The main reservoirs change from one model to the other, except for H₂O_{ice} and NH_{3ice}, which are the main reservoirs of oxygen and nitrogen, respectively. Most of the reservoirs are on the grains, except for CO, S, and CS. For O- and C-bearing

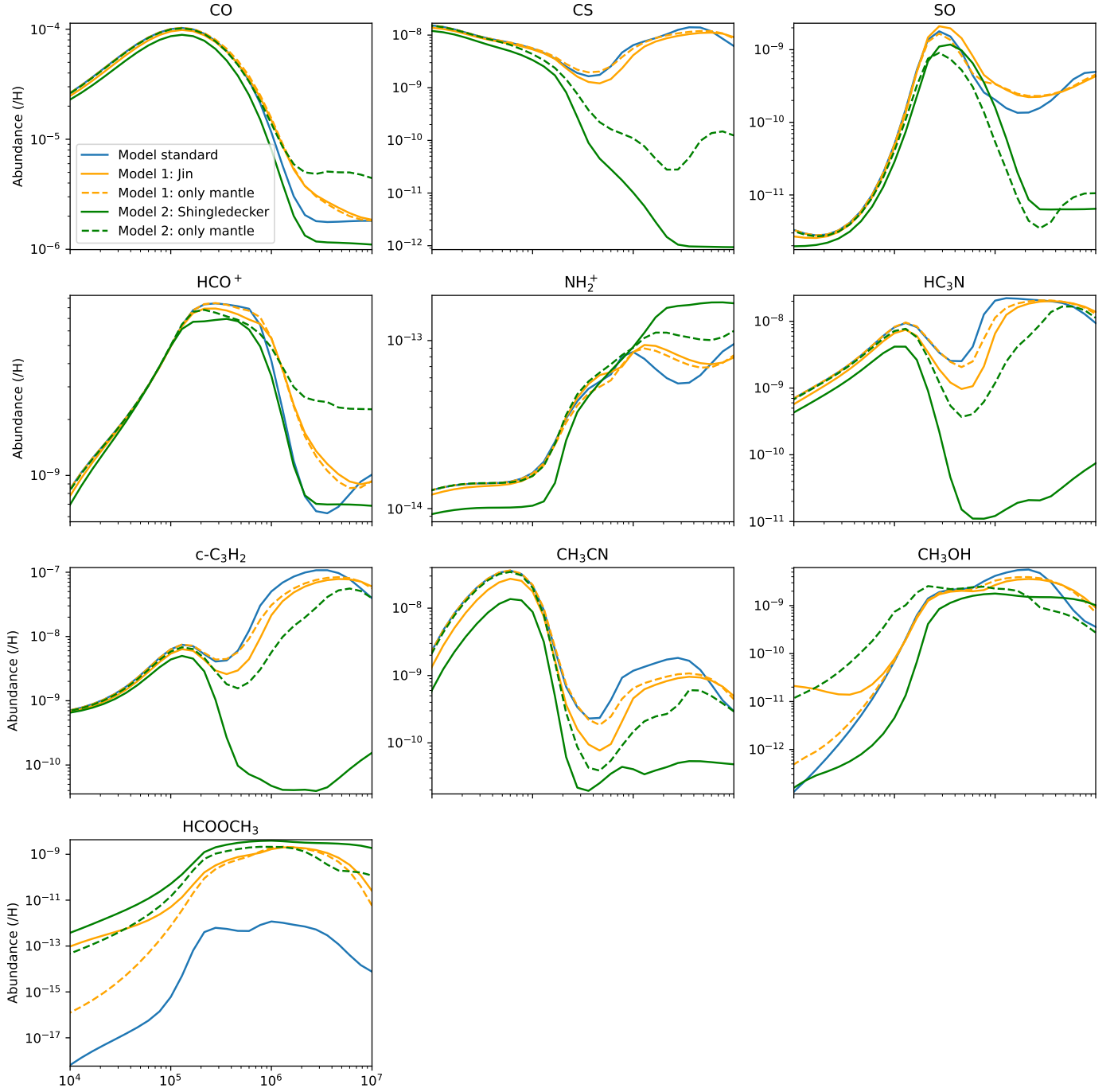


Fig. 1: Abundances as a function of time using our standard model (without non-diffusive chemistry), Model 1, and Model 2 for a selection of gas-phase species.

species, one new species appears in Models 1 and 2, which is $\text{HCOOCH}_{3\text{ice}}$, as already stated in the previous sections. The $\text{H}_2\text{CO}_{\text{ice}}$ molecule important in the standard model is not a reservoir in the two other models. For N-bearing species, we have the same molecules, $\text{NH}_{3\text{ice}}$ and $\text{N}_{2\text{ice}}$, as for the main ones. HCN_{ice} is also an important molecule for all models, although it has not been detected in ices (McClure et al. 2023). $\text{CH}_3\text{NH}_{2\text{ice}}$ is also expected to contain a significant amount of nitrogen in all models. Some elements are still expected to be abundant in the gas-phase despite the cloud age: CO and atomic sulfur for all models and CS for Model 1. Sulfur is expected to mostly be in the gas phase for the standard model and in Model 1, whereas

it is expected to be in the second reservoir in Model 2. $\text{H}_2\text{S}_{\text{ice}}$ is only predicted to be a reservoir in the standard model. In Model 2, the formation of $\text{H}_2\text{S}_{3\text{ice}}$ is extremely efficient. Even though it is not a reservoir in Model 1, its abundance is still high – much higher than in the standard model. It should be noted that we do not claim that $\text{H}_2\text{S}_{3\text{ice}}$ is the reservoir of sulfur on grains because its chemistry is too uncertain. However, we can suggest that non-diffusive chemistry could produce heavy S-bearing molecules. Shingledecker et al. (2020) predicts that $\text{S}_{8\text{ice}}$ is the reservoir of sulfur instead of $\text{H}_2\text{S}_{3\text{ice}}$. When comparing our standard model with Model 2, the $\text{S}_{8\text{ice}}$ abundance is increased by more than two orders of magnitude in Model 2, but it still

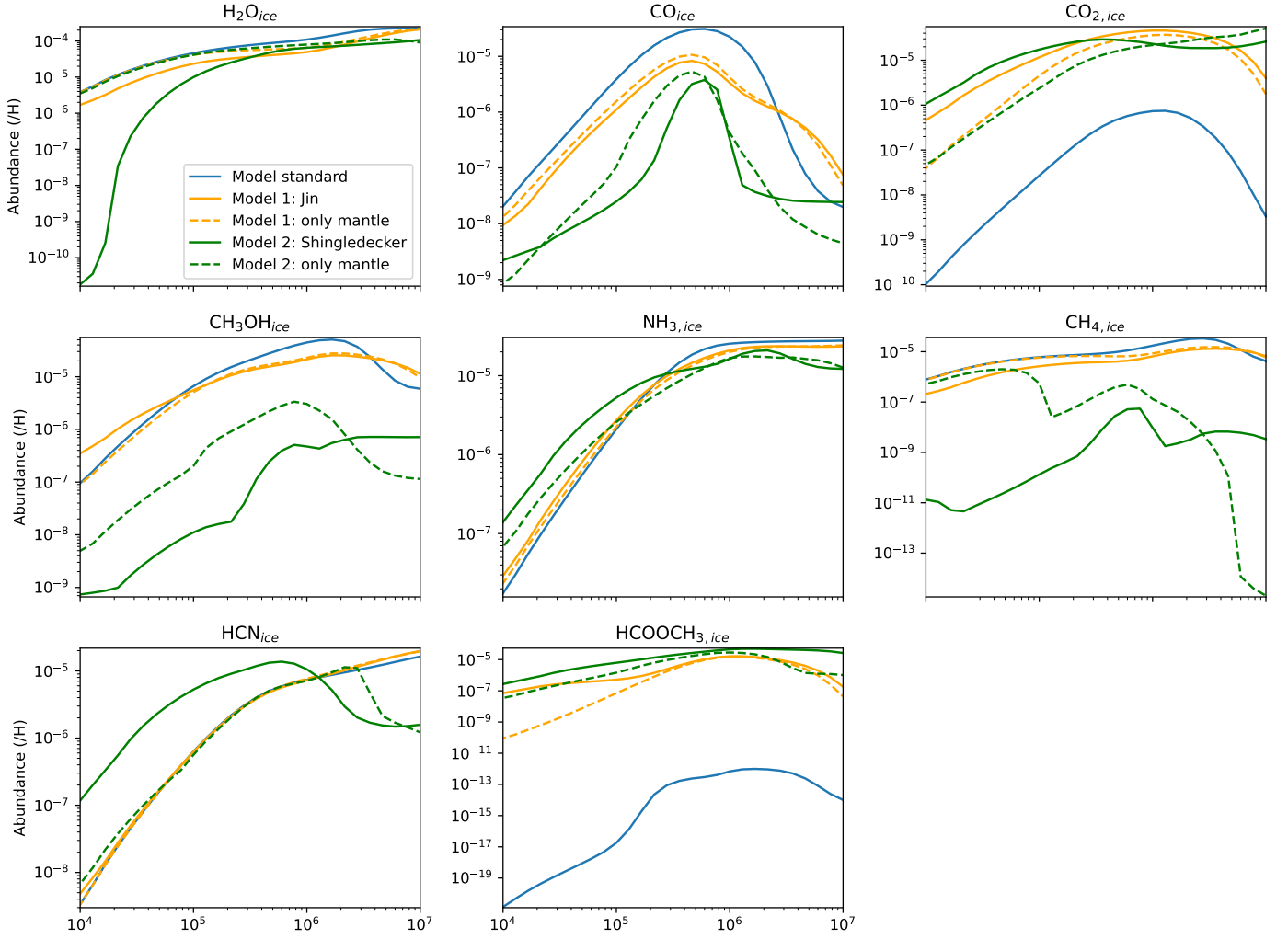


Fig. 2: Abundances as a function of time using our standard model (without non-diffusive chemistry), Model 1, and Model 2 for the main ice constituents.

Table 4: Difference between Models 1 and 2.

Molecule	diff	Molecule	diff
S_{ice}	-20.1	CH_{2ice}	-12.8
C_{ice}	-16.8	CH_{ice}	-12.7
HCS_{ice}	-15.0	C_6H_{3ice}	-12.7
S_{3ice}	-13.8	O_{ice}	-12.6
CH_{3ice}	-13.6	NH_{2ice}	-12.5
OH_{ice}	-13.3	C_3H_{5ice}	-12.4
C_4H_{3ice}	-13.3	$NH_2CH_2S_{ice}$	-12.3
CH_2SH_{ice}	-13.1	NH_{ice}	-12.1
C_8H_{3ice}	-13.0	CH_2CCH_{ice}	-12.1
S_{4ice}	-12.8		

negligible. Shingledecker et al. (2020) also allowed non-diffuse chemistry only for radicals and suprathreshold species, while we used it for all reactions. However, this may not explain the difference, as it would probably decrease the efficiency of this process. The difference between the two predictions is probably due to different chemical networks. First, Shingledecker et al. (2020) do not include H_2S_{3ice} . It includes, however, the reaction $H_2S_{2ice} + H_{ice} \rightarrow HS_{ice} + H_2S_{ice}$, which probably efficiently destroys H_2S_{2ice} . In our model, this reaction is not included, and reac-

tions $H_2S_{ice} + HS_{ice}$, $H_2S_{2ice} + S_{ice}$, $H_2S_{2ice} + HS_{ice}$, and $H_{2ice} + HS_{ice}$ produce H_2S_{3ice} . Except for direct and indirect photo-dissociations, no reaction destroys H_2S_{3ice} , so it becomes a reservoir, preventing the formation of larger $S_{n,ice}$.

Laboratory experiments of ice irradiation seem to indicate that the final products of ice chemistry are spread among several products rather than in a single reservoir, as predicted by Model 2 for carbon and sulfur and by Model 1 for sulfur. For instance, for sulfur the irradiation of H_2S ices by Herath et al. (2025) preferably produces $H_2S_{n,ice}$, with $n=2-8$ and S_{8ice} between 5 and 20% of sulfur each. Note, however, that H_2S_{2ice} is the major product in the experiment not predicted by our models. For carbon, Mejía et al. (2024) irradiated a mixture of CO , H_2O , and CH_3OH ices. They found that the produced carbon species were distributed among a large number of molecules, including CO_2 and H_2CO , but also among a variety of complex organic molecules (including possibly $HCOOCH_3$). Our model predictions seem to be, qualitatively, not in strong disagreement with these experiments, but they tend to predict major reservoirs, while findings based on experiments tend to report that the elements are spread over a larger number of molecules.

Interestingly, except for NH_{3ice} , all reservoirs of nitrogen are not detected or not detectable. McClure et al. (2023) lists three upper limits: 8.5% for H_2S_{ice} , 5% for HCN_{ice} , and 1%

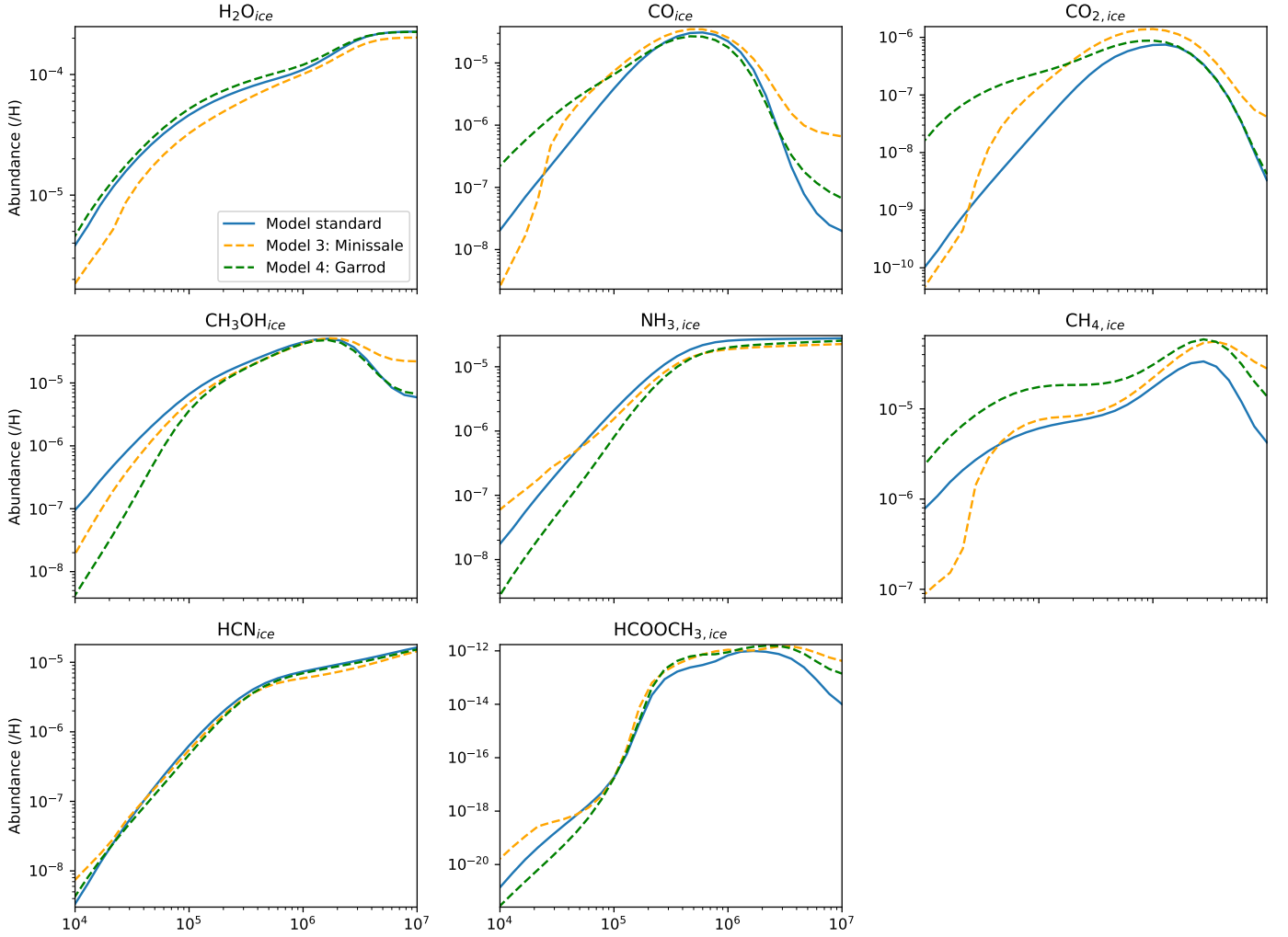


Fig. 3: Abundances as a function of time using our standard model (without non-diffusive chemistry), Model 3, and Model 4 for a selection of gas-phase species.

Table 5: Main reservoirs for the standard model and Models 1 and 2.

Element	O		C		N		S	
Model	Molecule	%	Molecule	%	Molecule	%	Molecule	%
Standard	H ₂ O _{ice}	41	CH ₃ OH _{ice}	26	NH ₃ _{ice}	40	S	31
	CH ₃ OH _{ice}	18	H ₂ CO _{ice}	22	N ₂ _{ice}	16	HS _{ice}	16
	H ₂ CO _{ice}	16	CH ₄ _{ice}	12	HCN _{ice}	12	H ₂ S _{ice}	16
	CO _{ice}	9	CO _{ice}	13	CH ₃ NH ₂ _{ice}	3	NS _{ice}	9
	CO	5	HCN _{ice}	4				
Model 1	H ₂ O _{ice}	20	CO ₂ _{ice}	26	NH ₃ _{ice}	32	S	65
	CO ₂ _{ice}	37	CH ₃ OH _{ice}	12	N ₂ _{ice}	32	CS	5
	HCOOCH ₃ _{ice}	13	HCOOCH ₃ _{ice}	18	HCN _{ice}	11		
	CH ₃ OH _{ice}	8	CO	9	CH ₃ NH ₂ _{ice}	5		
Model 2	HCOOCH ₃ _{ice}	37	HCOOCH ₃ _{ice}	64	NH ₃ _{ice}	26	H ₂ S ₃ _{ice}	75
	H ₂ O _{ice}	27	CO ₂ _{ice}	32	N ₂ _{ice}	20	S	6
	CO ₂ _{ice}	19	HCN _{ice}	7	HCN _{ice}	16		
	CO	6			CH ₃ NH ₂ _{ice}	9		

for CH₃CN_{ice}. The upper limit for the first molecule is not in agreement with the standard model. The upper limit for HCN_{ice} is only in agreement with the standard model. The upper limit on CH₃CN_{ice} is compatible with all models.

3.2. Results comparing various chemical desorption formalisms

Using the same species as in the previous sections, we compared the model results of our standard model (following Fredon et al. 2021) with the two other chemical desorption formalisms:

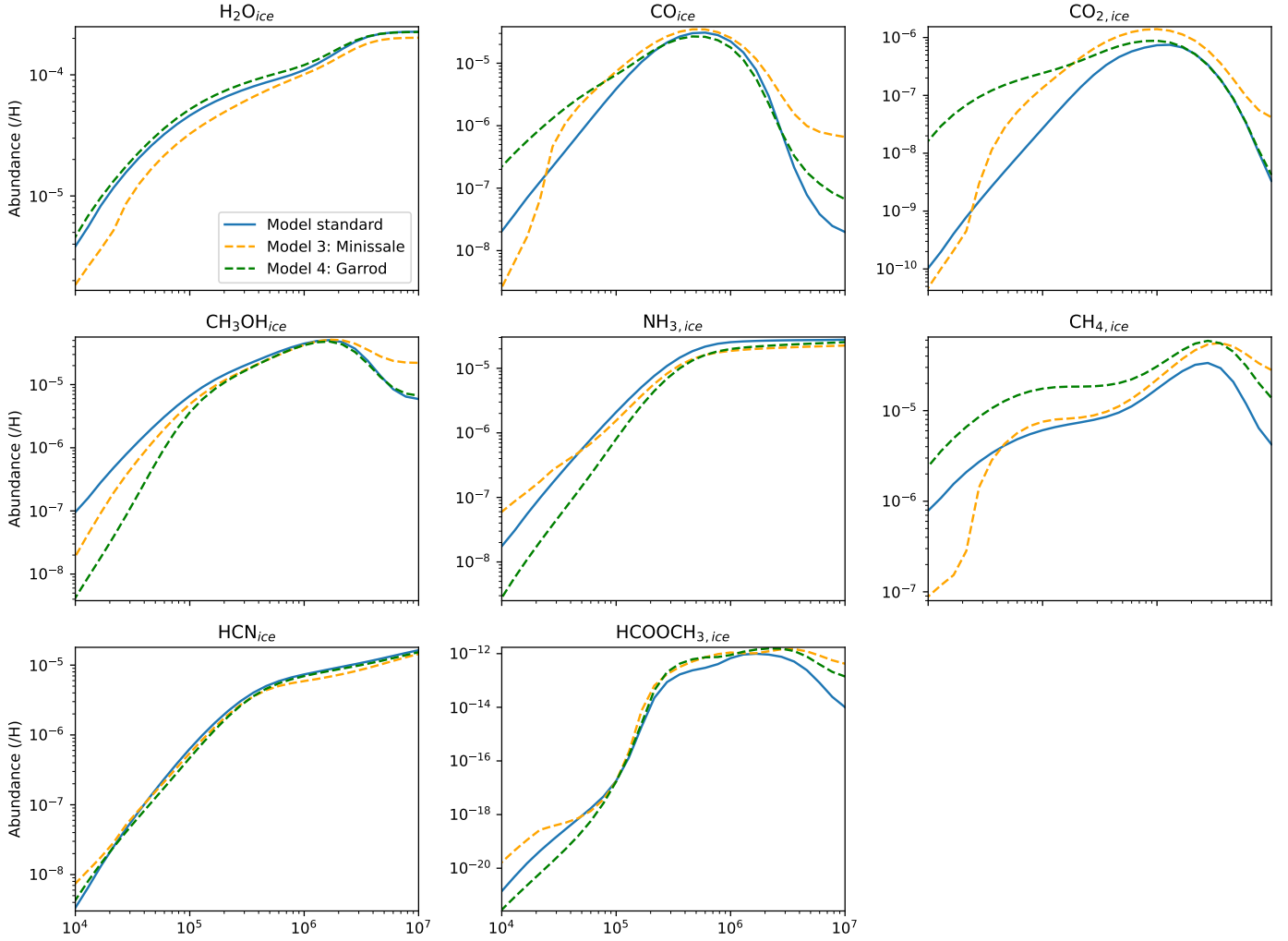


Fig. 4: Abundances as a function of time using our standard model (without non-diffusive chemistry), Model 3, and Model 4 for the main ice constituents.

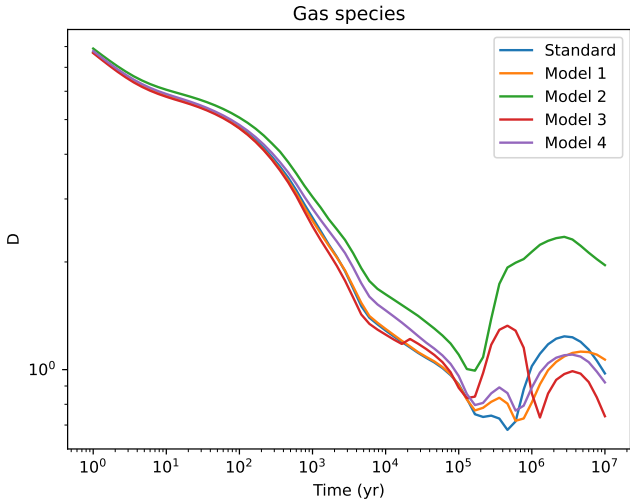


Fig. 5: Distance of disagreement for gas-phase molecules and all models as a function of time.

Model 3 for Minissale et al. (2016) and Model 4 for Garrod et al. (2007). Figs 3 and 4 show the results for the three models. As

expected, the ice composition is not influenced much by the formalism of chemical desorption compared to the gas-phase abundances. Interestingly, some species not formed on the grains, such as SO, CS, HC_3N , and $\text{c-C}_3\text{H}_2$, show differences up to one order of magnitude.

CS is produced by the gas-phase reaction between H and HCS, and HCS by the reaction between C and H_2S . HCS is more abundant in the standard model because C is more abundant. At 10^6 yr, C is produced by the abstraction reaction between H and CH. CH is produced on the grains by the reaction between C and H, which is followed by chemical desorption. Chemical desorption is more efficient in the standard model ($\text{frac} = 0.28$), with Model 4 following next in efficiency ($\text{frac} = 0.09$) and then Model 3 ($\text{frac} = 0.08$).

SO is produced more in Model 3, while it is similar in the two other models. Tracing back its formation in the gas phase, it starts by the formation of H_2O in the ices followed by chemical desorption of the product. While the desorption is negligible for the standard model and Model 4, it is 24% in Model 3. This last ratio is a direct result of the experiments conducted by Minissale et al. (2016). H_2O reacts in the gas phase with H_3^+ to form H_3O^+ and subsequently forms OH, and OH reacts with S to form SO.

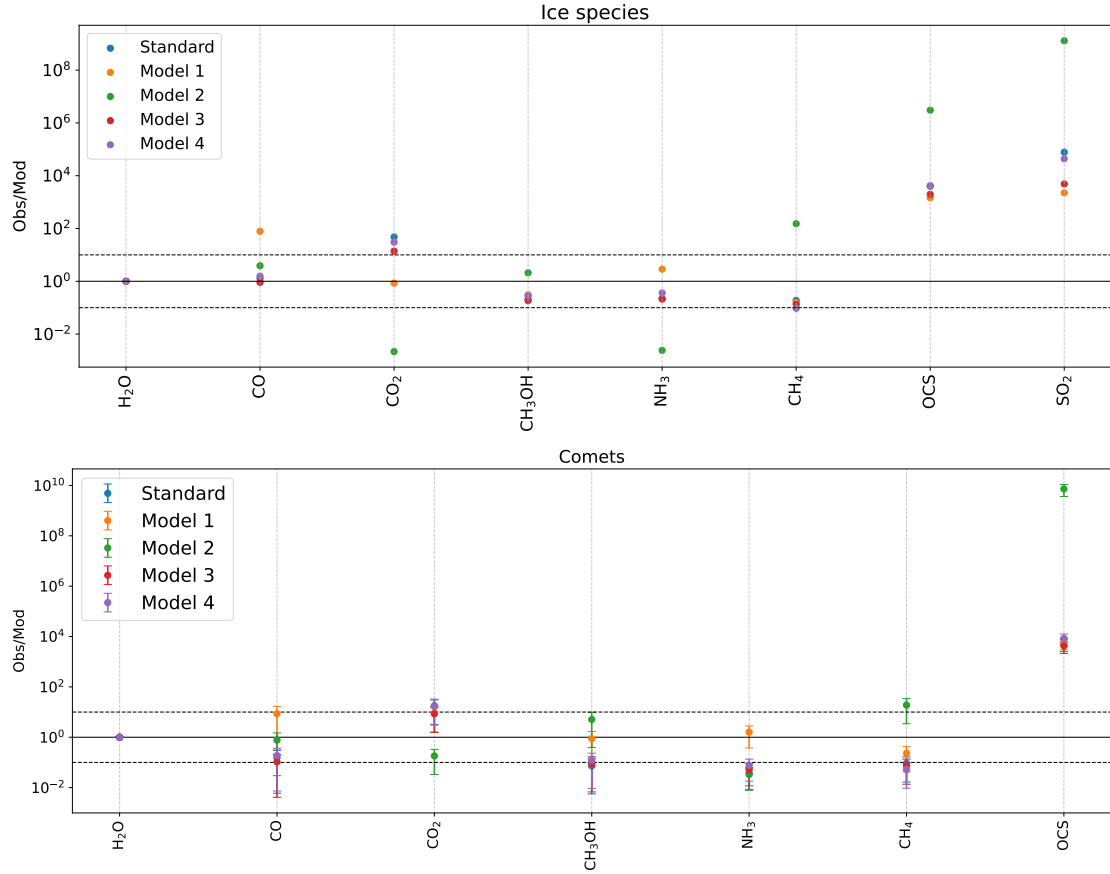


Fig. 6: Ratio between observed and modeled abundances for all ice species and in comets at the best D.

From a general point of view, the higher abundances of the C molecules (HC_3N , $\text{c-C}_3\text{H}_2$, and CH_3CN) in the standard model traces back to the larger carbon abundance in the gas phase that is followed by a series of reactions in the gas phase or at the surface of the grains. HC_3N and CH_3CN chemistry are related to the CN molecule, which is more abundant in the standard model, with Model 4 having the second-highest abundance. $\text{c-C}_3\text{H}_2$ is formed by a series of ion-neutral reactions, which starts from C. CH_3CHO is also formed in the gas-phase through $\text{O} + \text{C}_2\text{H}_5 \rightarrow \text{H} + \text{CH}_3\text{CHO}$. Again C_2H_5 is more abundant in the standard model and in Model 4.

4. Comparison with observations

To test the various hypotheses presented above, we compared the model results to the observed abundances listed in Appendix A. To define the best agreement, we computed the difference between observed and modeled abundances as a function of time, also called the distance of disagreement D:

$$D(t) = \frac{1}{N_i} \sum_i |\log(X_{\text{obs},i}) - \log(X_{\text{mod},i})|. \quad (6)$$

Figure 5 shows the distance of disagreement for all models (standard to Model 4). Model 2 (with non-diffusive chemistry from Shingledecker & Herbst 2018) gives the poorest agreement among the models, while the standard model gives the best at 5×10^5 yr. Model 3 and Model 1 also give good agreement, though at a slightly later point. This means that neither the non-diffusive chemistry in Model 2 nor the chemical desorption in Model 3

improves the agreement between the observation and the model. The best distance of disagreement D for the standard model is 0.7, which means that the mean difference between the observed and modeled abundances is a factor of five. Figure B.1 shows the ratio between the observed and modeled abundances for the best times of all five models. The species whose abundance is larger than a factor of ten for all models are C_3O , C_4H_2 , C_6H_2 , CN, H_2CN , C_5N , HCS^+ , and CCS.

We performed the same work for the ice species as observed by McClure et al. (2023) with JWST. The distance of disagreement values are shown in Fig. B.2. All models but Model 2 show a similar agreement for a similar time, with Models 1 and 3 being slightly better: D is 1.3 (meaning a mean difference by a factor of 20) and has a time of 4×10^5 yr. Overall, the agreement is not very good, but Model 2 clearly provides the worst agreement with the observations. Figure 6 (upper panel) shows the ratio between observed and modeled abundances for ice species at the best time of each model. The worst agreement for Model 2 comes from an underestimation of the abundance of $\text{CH}_{4\text{ice}}$, OCS_{ice} , and $\text{SO}_{2\text{ice}}$, while $\text{CO}_{2\text{ice}}$ and $\text{NH}_{3\text{ice}}$ are overestimated. $\text{CO}_{2\text{ice}}$ are underestimated by the models, except in Model 1. As noted by Clément et al. (2023), CO_2 formation needs the diffusion of CO or O in the surfaces and has to overcome an activation barrier. The non-diffusion chemistry in Model 1 is then efficient to form $\text{CO}_{2\text{ice}}$, while Model 2 is too efficient. $\text{NH}_{3\text{ice}}$ is too efficiently produced by Model 2, while $\text{CH}_{4\text{ice}}$, OCS_{ice} , and $\text{SO}_{2\text{ice}}$ are not produced enough. Methanol, $\text{NH}_{3\text{ice}}$, and $\text{CH}_{4\text{ice}}$ are well reproduced by the other models. Using the higher elemental abundance of sulfur, the overall D values are slightly better for the standard model and Model 1. The agreement for

OCS_{ice} is better but still highly underproduced by the models, while the CH_{4ice} abundance is underproduced by Model 2.

We also compared our model to observations in comets. For this, we used the review paper by Mumma & Charnley (2011). In Fig. B.3 we plot the distance of disagreement for comets, while in Fig. 6 (lower panel) we plot the ratio between modeled abundances with respect to water with the observed ones in comets. The vertical bars represent the variations among comets. The first striking result is that the overall agreement is very similar to interstellar ices but with a worse agreement with Model 2, while Model 1 has a slightly better agreement. As can be seen in Fig. 6, the main species not reproduced by the models in OCS, which are underestimated by the models. Using the higher sulfur elemental abundance does not improve the agreement for OCS, while it does not change much for the other species.

The CO_{ice} over the water ratio is also overpredicted by all models as well as the CH_{4ice} over the water ratio. Model 2 also underestimates OCS_{ice}. SO_{2ice} was not observed or detected in comets. This again shows that the ratio of the molecules over water is very similar in comets and interstellar ices.

5. Summary and conclusions

We have examined the differences of the model predictions produced by various assumptions on the radiolysis with and without non-diffusive chemistry, the diffusive chemistry itself, and the chemical desorption. Several formalism have been tested for the non-diffusive chemistry and chemical desorption. The following conclusions can be drawn from our work:

- Radiolysis without non-diffusive chemistry has no impact on the model predictions.
- Non-diffusive chemistry from Jin & Garrod (2020) has an effect of only a factor of a few for gas-phase observed molecules in cold cores when compared to our model without non-diffusive chemistry. Only heavy species, such as complex organic molecules, are produced more by the non-diffusive chemistry.
- When comparing the two formalisms of non-diffusive chemistry, we found strong differences. The one of Shingledecker & Herbst (2018) changes the main reservoirs of the species in the ices, impacting the species in the gas-phase as well. The main reservoirs become H₂S_{3ice} for S and HCOOCH_{3ice} for C. For N, both NH_{3ice} and N_{2ice} remain the main reservoirs in all models.
- Allowing non-diffusive chemistry in the mantle only significantly reduces the formation of molecules in Model 2 with the formalism of Shingledecker & Herbst (2018).
- Model 2 represents a very fast bulk chemistry capturing qualitatively experimental results, but it predicts major reservoirs of carbon and sulfur, while the experiments show that the elements are spread over a large number of molecules.
- From comparison of the three formalisms for chemical desorption, we found almost no differences for the ice species. The difference in the gas-phase can be up to a factor of ten.
- We also compared the results of our models with gas-phase and ice observations in cold cores. Our standard model (without non-diffusive chemistry and the chemical desorption by Fredon et al. 2021) gives the best agreement with the gas-phase observed abundances in TMC-1 CP within a factor of five between observed and modeled abundances at 5×10^5 yr, while Model 3 (no non-diffusive chemistry and chemical desorption by Minissale et al. 2016) and Model 1 (non-diffusive chemistry by Jin & Garrod 2020 and chemical desorption by Fredon et al. 2021) also show a good agreement.

For ice species and species observed in comets, it was impossible to discriminate among Models 1, 3, and 4, while Model 2 strongly disagrees with the observations, especially for S-bearing species. Using a higher elemental abundance of sulfur does not improve the agreement.

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Appendix A: Observed abundances

In Fig. A.1 we display the observed abundances listed in Agúndez & Wakelam (2013) and those computed by Xue et al. (2025) in TMC-1 (CP) assuming a H_2 column density of $2 \times 10^{22} \text{ cm}^{-2}$. Some molecules are present in both of them and, except for a small number of them, they give similar abundances. For such cases, we selected the abundance from Xue et al. (2025) because it is a self-consistent calculation while the other reference is a list of molecules obtained by various studies.

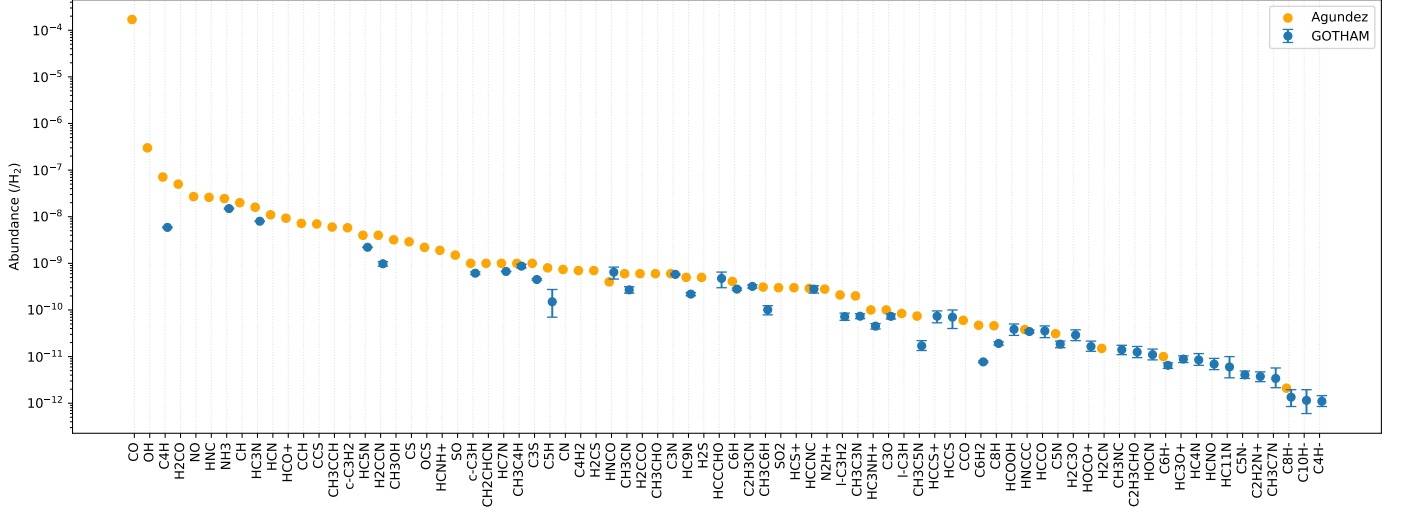


Fig. A.1: Observed abundances in the gas-phase in TMC-1 (CP) listed in Agúndez & Wakelam (2013) and Xue et al. (2025).

Appendix B: Comparison between observations and models

Figure B.1 shows the ratio between the observed abundances (see Appendix A) and the modeled abundances for all 5 models (see Table 2). The time of the best D is used as a reference to obtain the modeled abundance for each model. Figs. B.2 and B.3 show the distance of disagreement for ice species and comets as a function of time.

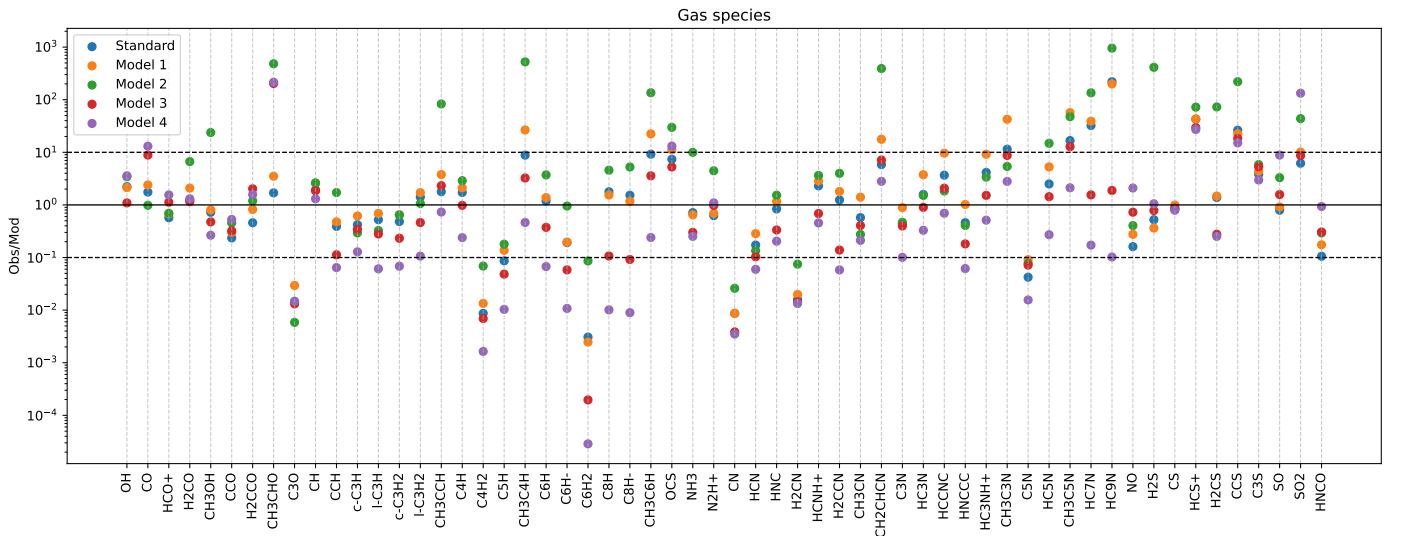


Fig. B.1: Comparison between observed and modeled abundances for all observed molecules in the gas phase at the best time.

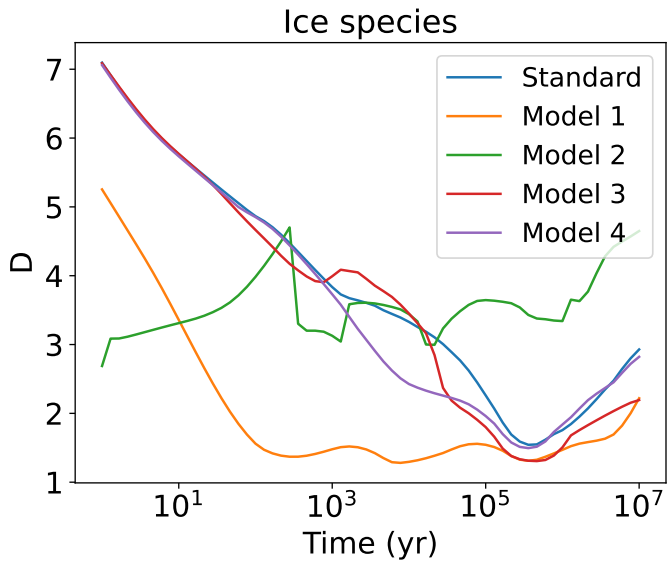


Fig. B.2: Distance of disagreement for ice species.

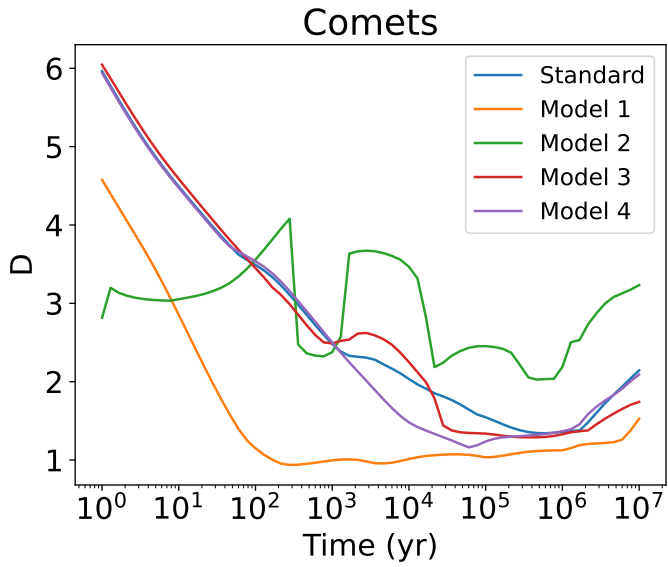


Fig. B.3: Distance of disagreement for species observed in comets.