

# Production of interstellar hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) on the surface of dust grains<sup>★</sup>

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## ABSTRACT

**Context.** The formation of water on the dust grains in the interstellar medium may proceed with hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) as an intermediate. Recently gas-phase  $\text{H}_2\text{O}_2$  has been detected in  $\rho$  Oph A with an abundance of  $\sim 10^{-10}$  relative to  $\text{H}_2$ .

**Aims.** We aim to reproduce the observed abundance of  $\text{H}_2\text{O}_2$  and other species detected in  $\rho$  Oph A quantitatively.

**Methods.** We make use of a chemical network that includes gas phase reactions, as well as processes on the grains. Desorption from the grain surface through chemical reaction is also included. We ran the model for a range of physical parameters.

**Results.** The abundance of  $\text{H}_2\text{O}_2$  can be best reproduced at  $\sim 6 \times 10^5$  yr, which is close to the dynamical age of  $\rho$  Oph A. The abundances of other species such as  $\text{H}_2\text{CO}$ ,  $\text{CH}_3\text{OH}$ , and  $\text{O}_2$  can also be reasonably reproduced at this time. In the early time, the gas-phase abundance of  $\text{H}_2\text{O}_2$  can be much higher than the currently detected value. We predict a gas phase abundance of  $\text{O}_2\text{H}$  at the same order of magnitude as  $\text{H}_2\text{O}_2$ , and an abundance on the order of  $10^{-8}$  for gas phase water in  $\rho$  Oph A. A few other species of interest are also discussed.

**Conclusions.** We demonstrate that  $\text{H}_2\text{O}_2$  can be produced on the dust grains and released into the gas phase through nonthermal desorption via surface exothermic reactions. The  $\text{H}_2\text{O}_2$  molecule on the grain is an important intermediate in the formation of water. That  $\text{H}_2\text{O}_2$  is overproduced in the gas phase for a range of physical conditions suggests that its destruction channel in the current gas phase network may be incomplete.

**Key words.** astrochemistry – ISM: abundances – ISM: molecules – ISM: clouds – stars: formation – molecular processes

## 1. Introduction

Oxygen is the most abundant “metal” element in the cosmos (Savage & Sembach 1996; Asplund et al. 2009). In the cold dense interstellar clouds, gas-phase chemical models predict that oxygen mainly resides in CO and  $\text{O}_2$  molecules (Herbst & Leung 1989; Millar & Herbst 1990; Wakelam et al. 2006). However, although CO is ubiquitously distributed in the interstellar medium,  $\text{O}_2$  is not. The latter is only detected very recently in  $\rho$  Oph A at a low abundance (relative to molecular hydrogen) of  $5 \times 10^{-8}$  (Larsson et al. 2007), and in Orion at an abundance of  $(0.3\text{--}7) \times 10^{-6}$  (Goldsmith et al. 2011). On the other hand, the observed water (gas or ice) abundance can be as high as  $10^{-4}$  (van Dishoeck 2004). Thus it seems that water, instead of  $\text{O}_2$ , is a main reservoir of oxygen in addition to CO. When only gas phase chemistry is included, the  $\text{H}_2\text{O}$  abundance can be on the order  $10^{-7}$  at most (see, for example, Bergin et al. 2000; Roberts & Herbst 2002) for typical dark cloud conditions. That  $\text{O}_2$  is overproduced and  $\text{H}_2\text{O}$  is underproduced in gas phase chemistry suggests that adsorption onto the grain surfaces and the reactions on the surfaces may play important roles.

On the grain surface,  $\text{H}_2\text{O}$  can form through successive additions of hydrogen atoms to an oxygen atom:



both of which are barrierless (Allen & Robinson 1977). It can also form via hydrogen addition to molecular oxygen:



Reaction (3) was assumed to have an activation barrier of 1200 K in Tielens & Hagen (1982). However, based on experimental results, Cuppen et al. (2010) have recently concluded that it is barrierless. Other possible formation pathways of water include the reaction between  $\text{H}_2$  and OH and the route with  $\text{O}_3$  as an intermediate (Tielens & Hagen 1982).

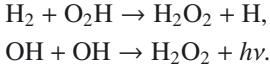
In the second route described above (Eqs. (3)–(5)), hydrogen peroxide ( $\text{HOOH}$ , also written as  $\text{H}_2\text{O}_2$ , which is adopted in this paper) appears as an intermediate product. Thus if this route is indeed important, a significant amount of  $\text{H}_2\text{O}_2$  might form on the grain, and its gas phase counterpart could also be detectable if effective desorption mechanisms exist.

In the current mainstream gas phase reaction networks for astrochemistry,  $\text{H}_2\text{O}_2$  is not efficiently formed in the gas phase.

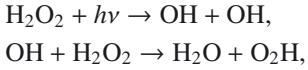
\* Appendices are available in electronic form at  
<http://www.aanda.org>

\*\* Member of the International Max Planck Research School (IMPRS) for Astronomy and Astrophysics at the Universities of Bonn and Cologne.

For example, in the 2009 version of the OSU network<sup>1</sup>, the only two reactions leading to the formation of H<sub>2</sub>O<sub>2</sub> are



The first one has a large activation barrier of 10<sup>4</sup> K, rendering it inactive at low temperatures. H<sub>2</sub>O<sub>2</sub> is mainly consumed by



the first of which is dissociation by cosmic-ray induced radiation. Other destruction channels by reacting with H and O are ineffective due to large activation barriers. At a temperature of 10 K and an H<sub>2</sub> density of 10<sup>4</sup> cm<sup>-3</sup>, the steady-state abundance of H<sub>2</sub>O<sub>2</sub> can be approximated by

$$X(\text{H}_2\text{O}_2) \simeq 10^3 X^2(\text{OH}) \simeq 5 \times 10^{-12}.$$

At a higher density, the abundance of H<sub>2</sub>O<sub>2</sub> will be even less because OH is less abundant in this case. With the UMIST RATE06 network the abundance of H<sub>2</sub>O<sub>2</sub> is essentially zero (Woodall et al. 2007). Thus if a substantial amount of H<sub>2</sub>O<sub>2</sub> can be detected in the interstellar medium, then it must have been synthesized on the dust grains, rather than in the gas phase. This would also provide information and constraints on the formation route of H<sub>2</sub>O.

It has indeed recently been detected (for the first time) in the  $\rho$  Oph A cloud by Bergman et al. (2011b), at an abundance of  $\sim 10^{-10}$ , which is well above what would be predicted by the gas phase chemistry, indicating that chemical processes on the grains are responsible for this detection. Why this molecule has not been detected in the past seems to be a puzzle and will be discussed later.

In the present work we aim at modeling the gas phase abundance of H<sub>2</sub>O<sub>2</sub> at a physical condition relevant to  $\rho$  Oph A, to demonstrate whether the grain chemistry is able to explain its observed abundance. The model is also required to give consistent abundances for other species detected earlier in this region. Also, ice and gas-phase abundance predictions for previously undetected species are made.

The remaining part of this paper is organized as follows. In Sect. 2 we describe the chemical model used in this work. In Sect. 3 we present the results of our modeling. The conclusions are in Sect. 4. Appendix A contains an explanation to a spike-like feature in the evolution curves of some species. The surface reaction network we use is listed in Appendix B, and the enthalpies of the surface species, which are needed in the chemical desorption mechanism (see Sect. 2) are listed in Appendix C.

## 2. Chemical model

For the gas phase chemistry, we use a subset of the UMIST RATE06 network<sup>2</sup> (Woodall et al. 2007). Species containing Fe, Na, Mg, and Cl are excluded. In total 284 gas phase species and 3075 gas phase reactions are included. The cosmic-ray ionization rate is taken to be the canonical value of 1.36  $\times 10^{-17}$  s<sup>-1</sup> (Woodall et al. 2007).

<sup>1</sup> [http://www.physics.ohio-state.edu/~eric/research\\_files/osu\\_01\\_2009](http://www.physics.ohio-state.edu/~eric/research_files/osu_01_2009)

<sup>2</sup> <http://udfa.net>

The surface chemical network is a combination of a selection of the reactions in Allen & Robinson (1977), Tielens & Hagen (1982), and Hasegawa et al. (1992), with the rates of a few reactions updated according to the recent experimental results and/or theoretical calculations. In total 56 surface species and 151 surface reactions are included (see Appendix B).

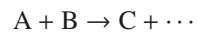
The binding energies of the surface species are either taken from Hasegawa & Herbst (1993) or estimated from the value of a similar species as in Garrod et al. (2008). These values are applicable to bare grains, i.e., grains without an ice mantle. A grain will be covered by ice (typically water) as adsorption and reaction proceeds, thus these values are not always appropriate. Ideally, they should be varied according to the real-time composition of the grain. The water ice mantle mainly affects the binding energies of species with a hydrogen bond, such as OH and H<sub>2</sub>O. The effect of this should be minor for our purpose, because most of the reactions involving a species with a hydrogen bond are primarily mediated by another reaction partner that does not have a hydrogen bond.

The barriers against surface diffusion are taken to be a fixed fraction of the binding energies. A range of values have been used for this fraction in the past, from 0.3 (Hasegawa et al. 1992) through 0.5 (Garrod et al. 2008) to 0.77 (Ruffle & Herbst 2000). We use a value of 0.77, based on the analysis of Katz et al. (1999). Because our model is mainly for a relatively high temperature ( $\sim 20$  K) in comparison with most of the previous models (predominantly for a temperature of  $\sim 10$  K), a low diffusion barrier for the surface species would lead to an unrealistic ice mantle composition. The effect of changing this parameter is discussed later. We allow H and H<sub>2</sub> on a dust grain to migrate through quantum tunneling or thermal hopping, depending on which is faster. All the heavier species are only allowed to move by thermal hopping. The quantum tunneling and thermal hopping rates are calculated using the formulation of Hasegawa et al. (1992). For calculating the quantum tunneling rates, we use a barrier width of 1 Å. The exact value of this width depends on the composition and structure of the surface, which has not been fully quantified.

About the activation barrier of reaction (3), as there is a big discrepancy between the value adopted in the past and the value proposed recently based on experiments (Cuppen et al. 2010), we adopt an intermediate value of 600 K. However, the effect of varying this parameter is also tested during the modeling, and will be discussed later. Reaction (5) has a barrier of 1400 K in Tielens & Hagen (1982), while in Cuppen et al. (2010) this reaction is barrierless. We choose to adopt the latter result in this case, because too high a barrier for it would result in building up too much H<sub>2</sub>O<sub>2</sub> on the grain surface.

Surface reactions with an activation barrier are allowed to proceed thermally or through quantum tunneling, depending on whichever is faster. The formula used to calculate the rates is also the same as in Hasegawa et al. (1992), and the reaction barriers are assumed to have a width of 1 Å, although different values are possible (Garrod & Pauly 2011).

The reaction rate of a two-body surface reaction



is

$$[k_{\text{diff}}(\text{A}) + k_{\text{diff}}(\text{B})]N(\text{A})N(\text{B})/N_s,$$

if  $\text{A} \neq \text{B}$ . Here  $N_s$  is the number of reaction sites of a grain,  $k_{\text{diff}}(\text{A})$  and  $k_{\text{diff}}(\text{B})$  are the diffusion rates of A and B, and  $N(\text{A})$

and  $N(B)$  are the number of species A and B on a single grain. If  $A = B$ , then the reaction rate should be

$$k_{\text{diff}}(A)N(A)(N(A) - 1)/N_S.$$

With a number density of reaction sites being  $10^{15} \text{ cm}^{-2}$ , a dust grain with radius  $0.1 \mu\text{m}$  has an  $N_S$  of about  $10^6$ .

As we are mainly concerned with the gas phase abundances of several species, their desorption mechanism must be treated carefully, especially if they are mainly produced on the grains. Besides the normal thermal desorption, species can also get evaporated episodically when a cosmic-ray hits a grain. This is treated in the same manner as in [Hasegawa & Herbst \(1993\)](#). Furthermore, the nonthermal desorption mechanism via exothermic surface reactions (for brevity we call it “chemical desorption”) proposed by [Garrod et al. \(2006\)](#); see also [Watson & Salpeter 1972; Garrod et al. 2007; Cazaux et al. 2010](#)) is also included. Here the products of the exothermic reactions on the grain have a probability of being directly ejected into the gas phase. The rate of such a desorption mechanism depends on the exoergicity of the reaction, as well as on the desorption energy of the products. A parameter characterizing the efficiency of this mechanism (the “ $a$ ” parameter in [Garrod et al. 2007](#)) is introduced, which we take to be 0.1. The yield of chemical desorption is directly proportional to this “ $a$ ” parameter, although it is not well constrained. The value we adopt here gives a good match to the observational results. See Sect. 3.6 for further discussion. The exoergicities of these reactions are estimated from the enthalpies of the reactants and products in the same manner as in [Allen & Robinson \(1977\)](#), their Eqs. (3) and (4)), and the enthalpies of the species involved in these reactions are taken from [Binnewies & Milke \(1999\)](#), from the NIST chemistry web book<sup>3</sup>, or from some other sporadic sources (see Appendix C).

However, the desorption mechanisms described above are not always sufficient to provide enough gas phase abundances for some species, especially at late times. Even if a large amount of a species is produced on the grain and released into the gas phase at early times, it would later be accreted back to the grain surface. If at this later time its production is no longer active (due to the exhaustion of the precursor species), its gas phase abundance cannot be maintained. Dust sputtering ([Tielens et al. 1994](#)) and photodesorption ([Öberg et al. 2007](#)) might help release them to the gas phase, both of which should not be very important in a quiet cold dark cloud. Another possible mechanism is that cosmic-ray induced radiation can dissociate the species on the grain, and when the fragments recombine, the products can possibly be ejected into the gas phase directly because of the energy release of the reaction, as described before. We implement this mechanism in the same way as in [Ruffle & Herbst \(2001a\)](#) and [Garrod & Pauly \(2011\)](#); see also [Cuppen & Herbst 2007](#)), namely, the cosmic-ray induced photodissociation rates for the surface species are taken to be the same as in the gas phase. Several dissociation branches from [Garrod et al. \(2008\)](#), their Table 1) are included.

In our model the numbers of all the species on a single grain are solved with the hybrid moment equation (HME) approach ([Du & Parise 2011](#)). It has been shown in [Du & Parise \(2011\)](#) that the rate equation method can be inaccurate in some cases, and the HME approach provides a major improvement over the rate equation method. Since the HME approach is relatively new, in several cases we also benchmarked our HME results with the exact Monte Carlo method (similar to the one of [Vasyunin et al. 2009](#)) as in

[Du & Parise \(2011\)](#), and the agreement is satisfactory. It is impractical to run all the models with the Monte Carlo method because the run time would be too long.

At present the layered structure of the grain mantle is not incorporated into our model. Such a structure might be more realistic, and it is important for retaining some of the ice species. However, it is also possible that the interstellar dust grains may have an amorphous structure, which renders the layered structure an inaccurate description. On the other hand, particles landing on a grain are able to penetrate the interior by several to tens of layers, as demonstrated by experiments (see, e.g., [Ioppolo et al. 2010](#)), thus although a model neglecting the layered structure is not accurate, one that deactivates all the layers below the outermost surface does not reflect the whole reality either. In fact, for the H-addition reactions, whether the layered structure is taken into account only plays a minor role in determining the reaction rates in the accretion limit (i.e. when the accretion and evaporation processes are much slower than the reactions; [Garrod 2008](#)), because the species involved in these reactions never build up a full layer.

### 3. Results and discussions

#### 3.1. Modeling $\rho$ Oph A

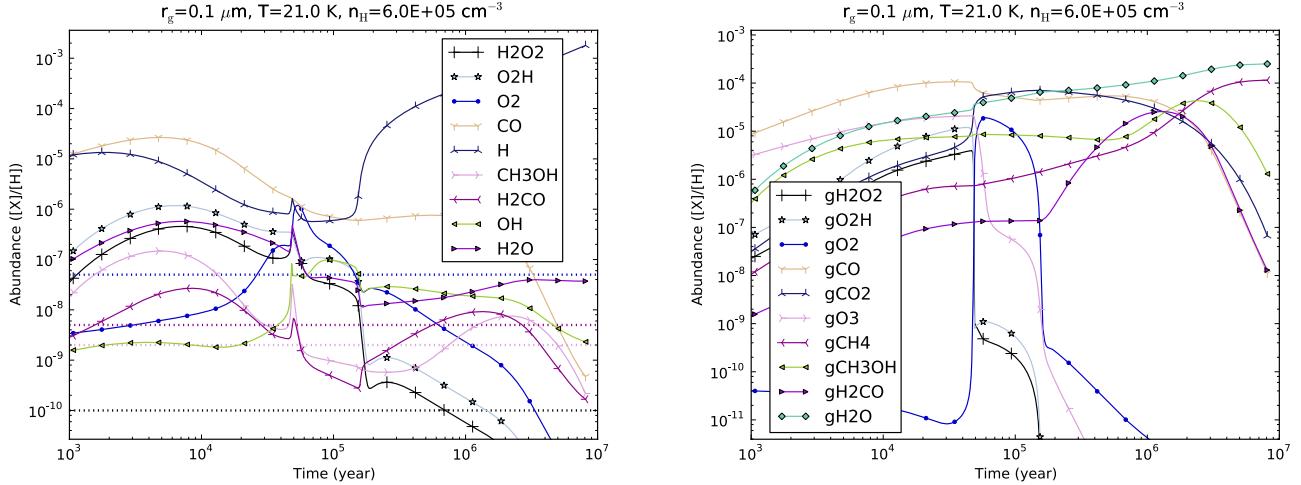
We ran the chemical model for the physical parameters that are appropriate for  $\rho$  Oph A, where H<sub>2</sub>O<sub>2</sub> has first been detected by [Bergman et al. \(2011b\)](#). In Fig. 1 we show the abundances of several species as a function of time. In this model, a temperature of 21 K and a hydrogen density of  $6 \times 10^5 \text{ cm}^{-3}$  have been assumed, which are determined for  $\rho$  Oph A observationally by [Bergman et al. \(2011a,b\)](#). The dust temperature and gas temperature are assumed to be the same. A fixed value of 15 for the visual extinction  $A_V$  has been adopted. We assume a canonical grain size of  $0.1 \mu\text{m}$  and a reaction site density of  $10^{15} \text{ cm}^{-2}$ . The dust-to-gas mass ratio is set to 0.01, and the dust grain material is assumed to have a mass density of  $2 \text{ g cm}^{-3}$ . We also assume that the ratio between the diffusion barrier and the binding energy is 0.77, which is at the higher end of the values used in the past, to give a reasonable ice composition. The initial condition is atomic except for H<sub>2</sub>. The elemental abundances are the same as in [Garrod & Pauly \(2011\)](#).

The observed abundance of gas phase H<sub>2</sub>O<sub>2</sub> is  $\sim 10^{-10}$  relative to H<sub>2</sub> ([Bergman et al. 2011b](#)). This value is best matched at a time of  $\sim 6 \times 10^5$  yr. In the early time, before about  $2 \times 10^5$  years, the gas phase H<sub>2</sub>O<sub>2</sub> abundance can be as high as  $\sim 5 \times 10^{-7}$ . At late times, the H<sub>2</sub>O<sub>2</sub> abundance decreases to a very low value, due to the exhaustion of O<sub>2</sub> on the grain and a full conversion of H<sub>2</sub>O<sub>2</sub> into H<sub>2</sub>O.

H<sub>2</sub>O<sub>2</sub> is mainly formed through reaction (4) on the grain, followed by immediate desorption of the product into the gas phase caused by the reaction heat. About 7% of the produced H<sub>2</sub>O<sub>2</sub> is released this way. Its gas phase abundance is determined by the adsorption and chemical desorption processes. The dissociation of gas phase H<sub>2</sub>O<sub>2</sub> by cosmic-ray-induced photons is unimportant in consuming it, compared to adsorption.

[Ioppolo et al. \(2008\)](#) modeled the abundance of H<sub>2</sub>O<sub>2</sub> ice briefly, giving a value of  $10^{-14}$ – $10^{-10}$  relative to molecular hydrogen, depending on which energy barriers of several relevant reactions were used. Our major goal is to model the gas phase H<sub>2</sub>O<sub>2</sub> abundance, rather than the H<sub>2</sub>O<sub>2</sub> ice. In our model results, the gas phase abundance of H<sub>2</sub>O<sub>2</sub> is much higher than its ice counterpart. The H<sub>2</sub>O<sub>2</sub> ice does not have a significant abundance in the later stage, being well below the upper limit (5.2% with

<sup>3</sup> <http://webbook.nist.gov/chemistry/>



**Fig. 1.** The time evolution of the abundances of selected species. A prefix “g” means a grain surface species (*right panel*), while a name without a prefix means a gas phase species (*left panel*). The dotted lines are the observed abundances (relative to H<sub>2</sub>) of O<sub>2</sub> (blue), H<sub>2</sub>CO (cyan), CH<sub>3</sub>OH (magenta), and H<sub>2</sub>O<sub>2</sub> (black), respectively, in the  $\rho$  Oph A source.

respect to H<sub>2</sub>O ice) given by Boudin et al. (1998), because it is constantly transformed into H<sub>2</sub>O by reacting with the accreted H atoms. However, by irradiating thin water ice film with low energy ions, Gomis et al. (2004) found that it is possible to obtain an H<sub>2</sub>O<sub>2</sub> to H<sub>2</sub>O ratio in the solid phase up to a few percent. This direct processing of the grain mantle by cosmic rays is not included in our model. The production of H<sub>2</sub>O<sub>2</sub> inside water ice in an O<sub>2</sub>-rich environment triggered by UV radiation (Shi et al. 2011) should also be of little importance here. We notice in Fig. 1 (right panel) that in the early stage (before  $\sim 5 \times 10^4$  yr) the H<sub>2</sub>O<sub>2</sub> ice can achieve a rather high abundance,  $\sim 5 \times 10^{-6}$  relative to H nucleus or  $\sim 10\%$  relative to H<sub>2</sub>O. During this early period the water formation on the grain mainly proceeds through reaction (5) with H<sub>2</sub>O<sub>2</sub> as an intermediate, which is responsible for about half of the final water ice repository on the grain mantle. In the later stage, reaction (2) takes over. In the results of Ioppolo et al. (2008, their Fig. 4), we do not see a similar feature (i.e. a high abundance of H<sub>2</sub>O<sub>2</sub> ice in the early stage). In our current model the layered structure of the grain mantle is not taken into account. It is possible that, if such a structure is considered, the inner layers with a relatively high H<sub>2</sub>O<sub>2</sub> content might be maintained, which would give a value of a few percent for the H<sub>2</sub>O<sub>2</sub>-to-H<sub>2</sub>O ratio in the solid phase.

Methanol (CH<sub>3</sub>OH) and formaldehyde (H<sub>2</sub>CO) are also detected in the  $\rho$  Oph A SM1 core (Bergman et al. 2011a), at an abundance of  $\sim 2 \times 10^{-9}$  and  $\sim 5 \times 10^{-9}$ , respectively. Their abundances are also reproduced very well at a time of  $\sim 6 \times 10^5$  yr in our model. At early times, both CH<sub>3</sub>OH and H<sub>2</sub>CO have a high abundance. Their abundances also have a peak in the period between  $2 \times 10^5$  yr to  $10^7$  yr. In our current network, CH<sub>3</sub>OH is mainly formed on the grains, and mainly through the addition of H atom to CH<sub>2</sub>OH, while the latter is mainly produced from the reaction between C and OH to form HOC followed by successive H additions. Thus the abundance of CH<sub>3</sub>OH decreases at very late times due to the depletion of atomic C (which is mainly in CH<sub>4</sub> ice in the late stage). The normal formation channel through successive hydrogenation of CO is important at around  $5 \times 10^5$ – $2 \times 10^6$  yr. The gas phase H<sub>2</sub>CO mainly forms in the gas phase in the early stage ( $< 10^5$  yr), and mainly through the reaction CH<sub>3</sub> + O  $\rightarrow$  H<sub>2</sub>CO + H. Later it is mainly formed through successive hydrogenation of CO on the grain surface followed by chemical desorption. The abundance of methanol

and formaldehyde ice relative to water ice can be as high as  $\sim 20\%$  at their peaks at a time of  $\sim 2 \times 10^6$  yr, but falls to a very low value in the late times. The late-time abundances are consistent with the upper limit derived for quiescent environment and low-mass young stellar objects in Gibb et al. (2004). However, in Pontoppidan et al. (2004) a much higher abundance of CH<sub>3</sub>OH ice is observed along the line-of-sight of SVS4 (a dense cluster of pre-main sequence stars), which is close to a class 0 protostar, and this is consistent with the peak abundances in our model.

From Fig. 1 (left panel) it can be seen that the abundance of gaseous O<sub>2</sub> at an intermediate time of  $6 \times 10^5$  year is  $\sim 6 \times 10^{-9}$ , which is within one order of magnitude of the observed abundances of  $5 \times 10^{-8}$  for O<sub>2</sub> (Larsson et al. 2007). The late-time abundance of O<sub>2</sub> drops to a very low value, while its observed abundance is best matched at a time of  $\sim 2 \times 10^5$  yr. We notice that during the period  $\sim (0.6\text{--}2) \times 10^5$  yr, the abundance of O<sub>2</sub> ice has a prominent bump, reaching a peak abundance of  $\sim 10^{-5}$  relative to H<sub>2</sub>. At the same time, the gas phase O<sub>2</sub> also reaches an abundance of  $\sim (1\text{--}5) \times 10^{-7}$ . These values can be compared with the recent detection of gas phase O<sub>2</sub> at an abundance of  $(0.3\text{--}7) \times 10^{-6}$  in Orion by Herschel (Goldsmith et al. 2011). Warm-up of the dust grain at this stage may release a large amount of O<sub>2</sub> molecule into the gas phase.

As a precursor of H<sub>2</sub>O<sub>2</sub>, O<sub>2</sub>H mainly forms from the reaction between O and OH on the grain, which does not have a barrier according to Hasegawa et al. (1992). The ratio between the gas phase O<sub>2</sub>H and H<sub>2</sub>O<sub>2</sub> is almost constant throughout the evolution, being approximately 3. Thus in our current network, the gas phase O<sub>2</sub>H also has a remarkable abundance, which might be detectable in the future.

Except at very early times, the grain mantle is mainly composed of water ice. The abundances of CO and CO<sub>2</sub> are comparable at an intermediate time of  $(0.3\text{--}1) \times 10^6$  yr, being about 40–60% of water ice. This is in rough agreement with the ice composition for intermediate-mass YSOs (Gibb et al. 2004) (see also Öberg et al. 2011), and is also in line with the suggestion of An et al. (2011) that CO<sub>2</sub> ice is mixed with CH<sub>3</sub>OH ice (the latter is about 10% of the former in our model). Water ice mainly forms from reaction (5) in the early time, and from reaction (2) in the late time. The gas phase formation route of water only plays a minor role. In contrast, the CO ice mantle is mainly from

accretion of CO molecules formed in the gas phase. For the CO<sub>2</sub> ice, it is mainly accreted from its gas phase counterpart in the early time, and its abundance is increased further through the reaction OH + CO → CO<sub>2</sub> + H in the late stage. At late times ( $>3 \times 10^6$  yr), most of the carbon resides in the form of CH<sub>4</sub> ice, with the latter about half of the water ice. However, as far as we know, such a high abundance of CH<sub>4</sub> ice (see also Garrod & Pauly 2011) has not been observed in the interstellar medium.

The gas phase CO is heavily depleted, with an abundance  $\sim 10^{-6}$  relative to the H nucleus or  $\sim 1\%$  relative to its ice counterpart, at an intermediate time ( $10^5$ – $10^6$  yr). Its abundance is mainly determined by the balance between the adsorption and cosmic-ray induced evaporation processes. At late times the CO ice abundance drops to a very low value. This is because CO is continuously hydrogenated into H<sub>2</sub>CO or CH<sub>3</sub>OH, and the dissociation of CH<sub>3</sub>OH by cosmic-ray induced photons produces CH<sub>3</sub>, which quickly becomes CH<sub>4</sub> by hydrogenation. Taking the layered structure of grain mantle into account can retain a fair amount of CO ice.

The abundance of gas phase H<sub>2</sub>O in the intermediate to late time is on the order  $10^{-8}$ . At these times, its grain surface production route (2) followed by chemical desorption and the gas phase production route H<sub>3</sub>O<sup>+</sup> + e<sup>-</sup> → H<sub>2</sub>O + H plays a similarly important role. H<sub>3</sub>O<sup>+</sup> itself is mainly formed from successive protonation of atomic oxygen at this stage.

The hydroxyl radical (OH) has an abundance  $\sim 10^{-8}$ – $10^{-9}$  in the gas phase at the intermediate-to-late times. These values are comparable to the observed abundance of  $\sim(0.5\text{--}1)\times 10^{-8}$  in the envelope around the high-mass star-forming region W3 IRS 5 obtained with HIFI onboard *Herschel* (Wampfler et al. 2011). The physical condition in this source is different from  $\rho$  Oph A. However, since OH is readily produced and recycled in the gas phase by the reactions H<sub>3</sub>O<sup>+</sup> + e<sup>-</sup> → OH + 2H and H<sub>3</sub><sup>+</sup> + OH → H<sub>2</sub>O<sup>+</sup> + H<sub>2</sub>, grain processes will not play a dominant role in determining its abundance, especially when the temperature is not too low. However, Goicoechea et al. (2006) detected a much higher abundance  $(0.5\text{--}1)\times 10^{-6}$  of OH in the Orion KL outflows, which seems to require other formation pathways (e.g. shock destruction of H<sub>2</sub>O ice).

A relatively high abundance ( $\sim 10^{-7}$  and  $\sim 10^{-5}$ ) of gas phase and grain surface ozone (O<sub>3</sub>) is also obtained for  $t \lesssim 10^5$  yr. However, these values should be treated with caution, because the chemistry of O<sub>3</sub> is very incomplete in our current model: neither the OSU gas phase network nor the UMIST RATE06 network includes it. Possible gas phase destruction pathways involving atomic O and S (according to the NIST chemistry web book; see footnote 3) may lower its gas phase abundance significantly, but its ice mantle abundance should not be severely affected.

The abundance of atomic hydrogen in the gas phase is quite high at late times as seen from Fig. 1, which seems to be at odds with the usual results. In many gas phase chemical models, the abundance of atomic hydrogen in the gas phase is determined by the balance between its adsorption onto the dust grains and the dissociation of H<sub>2</sub> molecules by cosmic rays. The adsorption process is thought to have a sticking coefficient close to unity, and evaporation is assumed not to occur (which is appropriate at low temperatures). In such a framework it can be found that the gas phase atomic hydrogen will always have a fixed density on the order of 1 cm<sup>-3</sup>. However, in our case with a temperature of 21 K, evaporation is very fast and cannot be neglected. Furthermore, the dissociation of ice mantle by cosmic-ray induced photons generates atomic hydrogen, which enhances its gas phase abundance significantly in the late stage.

We note that, at a time of about  $5 \times 10^4$  years, the abundances of several species change very quickly, and the abundances of some other species show a spike-like feature. At first sight this may resemble an erroneous behavior caused by the differential equation solver, so we ran the model with the same parameters using a Monte Carlo code (also used for benchmark purpose in Du & Parise 2011), which is free of such problems, and it turns out that these features are genuine. A semi-quantitative explanation of this feature is in Appendix A.

### 3.2. Chemical age versus dynamical time scale

As noted before, the time of the closest agreement between our modeling results and the observational results of Bergman et al. (2011a,b) is at  $\sim 6 \times 10^5$  year. Interestingly, this time scale is quite close to those derived in André et al. (2007, their Table 7). For example, the evolution time scale for  $\rho$  Oph A as estimated to be three times the free-fall time is  $(0.5\text{--}2)\times 10^5$  years, which is close to the statistically estimated age, while the collisional time scale of  $5.5 \times 10^5$  years and the cross time scale of  $8 \times 10^5$  years are also within the same order of magnitude.

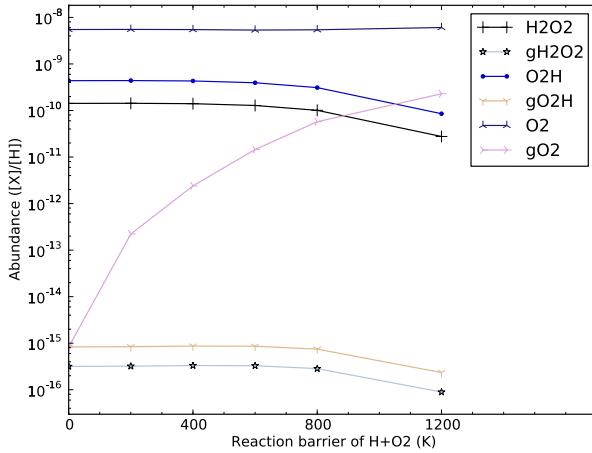
It is important to define the starting point when talking about age. In the chemical evolution model described above, the whole system starts to evolve from a simple initial state where all the elements except for hydrogen are in atomic form, and the grains are bare. How relevant is such an initial condition when we talk about the dynamical evolution of a cloud condensation? At a density of  $\sim 10^3$  cm<sup>-3</sup>, a temperature of  $\sim 20$  K, and a visual extinction of 2, which are typical of diffuse or translucent molecular clouds, a chemical model starting from an atomic initial condition (except for H<sub>2</sub>) reaches steady state for most of the species in several  $10^3$  years. Because such a time scale is much shorter than the dynamical time scale of a cloud, it should not make much difference for a time-dependent model (i.e. one in which temperature and density etc. vary with time) to use either atomic or molecular initial conditions. For a time-independent cloud model (such as the one we are using) with constant physical conditions, adopting an atomic initial condition and a high density is equivalent to assuming that the cloud was compressed from the diffuse interstellar medium very quickly. Converging flows in the interstellar medium might play such a role, although this seems unlikely in  $\rho$  Oph A because only a very small velocity gradient was observed (André et al. 2007).

However, the time of best match and the predicted abundances may also be very dependent on the value adopted for some of the modeling parameters that are not very well constrained. It is necessary to see how the results would be changed if these parameters are varied.

### 3.3. Effects of changing the energy barrier of the surface reaction H + O<sub>2</sub> → HO<sub>2</sub>

The activation barrier of reaction (3) was set to 1200 K in Tielens & Hagen (1982), which was taken from the theoretical calculation by Melius & Blint (1979) for the gas phase case. Cuppen et al. (2010) conclude that this reaction has a negligible barrier. We choose to use an intermediate value for the energy barrier of reaction (3), namely, 600 K for the modeling. Here we study how the uncertainties in this parameter would affect the abundances of several species of interest.

In Fig. 2 the abundances of several species at the best-match time ( $6 \times 10^5$  yr) are plotted as a function of the activation energy barrier of reaction (3). The temperature and density are fixed



**Fig. 2.** Dependence of the abundances of several species at the best-match time ( $6 \times 10^5$  yr) on the reaction barrier of reaction (3), with density fixed to  $6 \times 10^5$  cm $^{-3}$  and temperature fixed to 21 K.

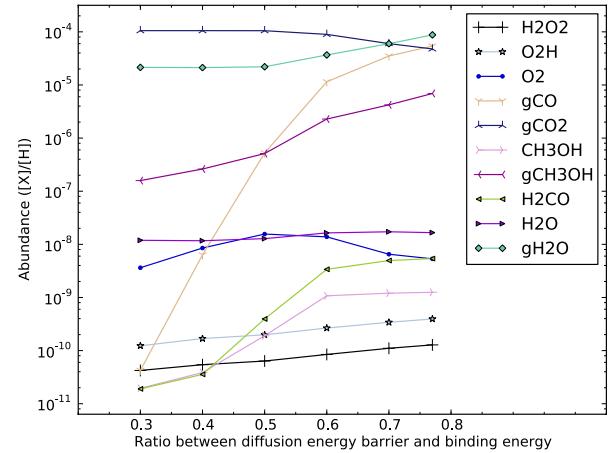
at 21 K and  $6 \times 10^5$  cm $^{-3}$ , and the ratio between the diffusion energy barrier and the binding energy is set to 0.77.

The abundance of gas phase O<sub>2</sub> is not affected by changing the energy barrier of reaction (3) because its abundance is mainly determined by the gas phase production process O + OH → O<sub>2</sub> + H and adsorption. However, the abundance of grain surface O<sub>2</sub> increases by five orders of magnitude as the barrier changes from 0 to 1200 K, because reaction (3) is one of the main reactions for the consumption of grain O<sub>2</sub>. However, even with a barrier of 1200 K for reaction (3), the abundance of O<sub>2</sub> on the grain at a late stage is too low to be detected. Although the rate coefficient of reaction (3) is reduced by six orders of magnitude when its barrier changes from 0 to 1200 K, the abundance of O<sub>2</sub>H on the grain does not change significantly. The reason is that when reaction (3) becomes slower, more O<sub>2</sub> will build up on the grain, compensating for the effect of increasing the barrier of reaction (3). The abundance of gas phase H<sub>2</sub>O<sub>2</sub> does not change much either, as its abundance is mainly determined by accretion onto the grain, and production by hydrogenation of O<sub>2</sub>H followed by partial chemical desorption.

### 3.4. Effects of changing the diffusion energy barriers

The diffusion energy barrier of a species on the grain determines how fast it can migrate on the grain, so it basically determines the pace of the grain chemistry. Usually it is set to a fixed fraction (here we denote it by  $\eta$ ) of the binding energy of each species. The latter determines how fast a species evaporates into the gas phase. However, this parameter might depend on the material and morphology of the dust grain, as well as on the property of the adsorbate itself, so it is very uncertain. Values in the range of 0.3–0.77 have been adopted in the literature. We mainly used 0.77 for our modeling. Here we investigate how different values of  $\eta$  would affect the abundances of several species of interest.

In Fig. 3 we plot the abundances of several species at the time of best match ( $6 \times 10^5$  yr) as a function of the ratio between the diffusion barrier and binding energy ( $\eta$ ). Changing this parameter has a strong effect on the abundances of some species. For example, the abundance of CO<sub>2</sub> ice is reduced with a higher  $\eta$ . This is because at the time of concern it mainly forms through



**Fig. 3.** Dependence of the abundances of several species at the best-match time ( $6 \times 10^5$  yr) on the ratio between the diffusion and desorption energy, with density fixed to  $6 \times 10^5$  cm $^{-3}$  and temperature fixed to 21 K.

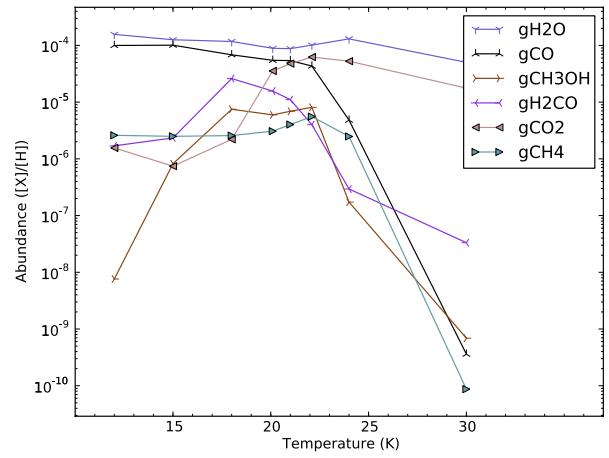
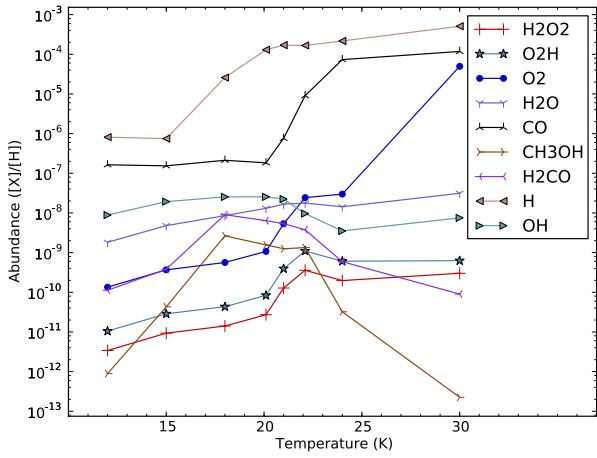
the reaction OH + CO → CO<sub>2</sub> + H, which requires the migration of two relatively heavy species. With a low diffusion energy and a moderate temperature (~20 K), OH and CO can thermally hop quite fast, leading to a high abundance of CO<sub>2</sub>, which is not observed. However, if a lower temperature (~10 K) is adopted, the problem becomes the opposite: the mobilities of OH and CO are so low that it is difficult for them to meet each other to form enough CO<sub>2</sub> ice, and some intricate mechanisms (e.g. three body reaction) have to be introduced to account for this (Garrod & Pauly 2011).

The abundance of H<sub>2</sub>O ice increases as  $\eta$  increases. At this stage it is mainly formed by hydrogenation of OH. As the mobility of atomic hydrogen on the grain is not greatly affected by the value of the diffusion energy barrier because it is allowed to migrate through quantum tunneling, the reaction rate of H + OH → H<sub>2</sub>O is not significantly affected by  $\eta$ ; however, a larger  $\eta$  leaves more OH available for water because a lower amount of it is consumed in forming CO<sub>2</sub>. This is also the reason for a higher CO (and species dependent on it such as H<sub>2</sub>CO and CH<sub>3</sub>OH) ice abundance when  $\eta$  is larger. The abundances of gas phase H<sub>2</sub>O<sub>2</sub> and O<sub>2</sub>H also increase for larger  $\eta$ , albeit only mildly.

### 3.5. Dependence on the temperature and density

The physical conditions (temperature and density) of  $\rho$  Oph A are determined by non-LTE radiative transfer modeling (Bergman et al. 2011a), which is usually subject to uncertainties from many aspects, such as the excitation condition, source geometry, beam filling factor, etc. In this section we study how the uncertainties in the temperature and density of the system would affect the abundances of several species in our model. In Figs. 4 and 6 we plot the abundances of several species at the time of best match ( $6 \times 10^5$  yr) as a function of temperature and density.

Apparently, temperature plays a much more drastic role than density. This is intuitively easy to understand because temperature enters the calculation of rates exponentially for the surface reactions. The general trend is that when the temperature is either too low or too high, the grain surface chemistry tends



**Fig. 4.** Dependence of the abundances of several species at the time of best match ( $6 \times 10^5$  yr) on temperature, with density fixed to  $6 \times 10^5$  cm<sup>-3</sup>. Left panel: gas phase species; right panel: surface species.

to be inactive or unimportant. In the former case the mobilities of species other than atomic hydrogen (which migrates through quantum tunneling in our present model) are low, while in the latter case the surface abundances of many species are low due to elevated evaporation rates.

As can be seen in Fig. 4, the abundance of CO ice starts to decrease at a temperature of around 20 K. This value can be estimated as the temperature at which the gas phase and grain surface abundance of CO are equal (see also Tielens & Hagen 1982), when only the adsorption and evaporation processes are taken into account (see also Hollenbach et al. 2009):

$$T_{\text{evap}} = E_D / \ln \left[ \frac{\nu}{n_H R_G \pi r^2} \frac{1}{\sqrt{8kT_{\text{gas}}/\pi m}} \right] \approx E_D / \left\{ 60 + \ln \left[ \left( \frac{10^5 \text{ cm}^{-3}}{n_H} \right) \left( \frac{20 \text{ K}}{T_{\text{gas}}} \right)^{1/2} \left( \frac{m}{28 \text{ au}} \right)^{1/2} \right] \right\}, \quad (6)$$

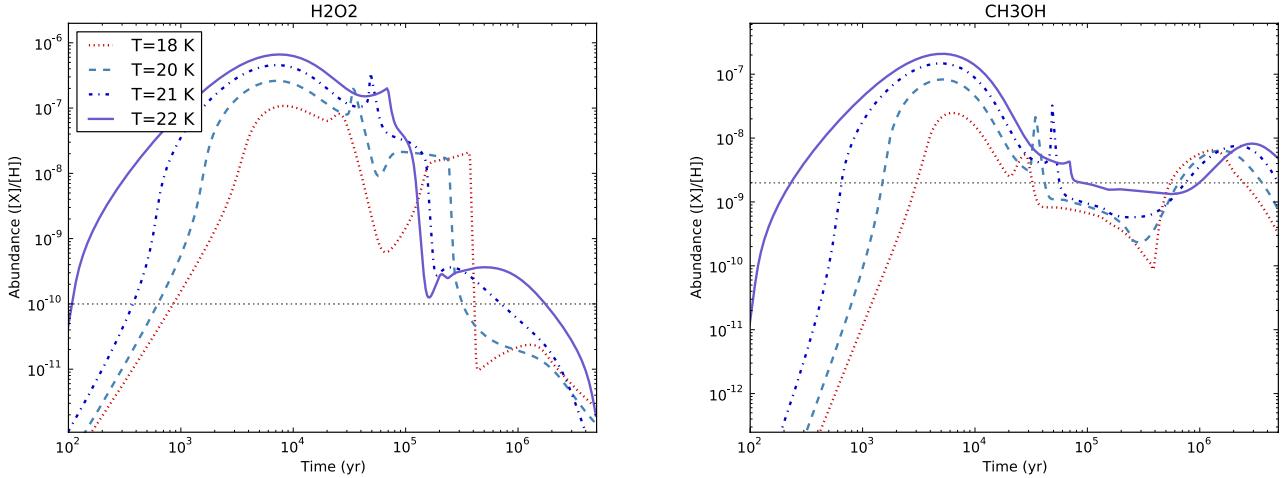
where  $E_D$  is the evaporation energy barrier of a species on the grain surface,  $\nu$  the vibrational frequency of a species on the grain,  $R_G$  the dust-to-gas number ratio,  $r$  the grain radius, while  $m$  is the molecular mass of the species being considered. A typical value of  $10^{12}$  s<sup>-1</sup> for  $\nu$ , a dust grain radius of  $0.1 \mu\text{m}$ , and a dust-to-gas ratio of  $2.8 \times 10^{-12}$  have been adopted in deriving the number 60. Since the logarithmic part in this equation is usually small for a typical gas density and temperature, the evaporation temperature can be approximated simply by  $T_{\text{evap}} \approx E_D/60$ . For CO, a canonical value of  $E_D$  is 1210 K (Allen & Robinson 1977), which gives an evaporation temperature of 20 K, while for water, an  $E_D$  of 1860 K (Hasegawa & Herbst 1993) on bare graphite grains gives an evaporation temperature of  $\sim 30$  K. In Garrod & Herbst (2006) a much higher desorption energy of 5700 K for water is used (appropriate for water ice), which gives an evaporation temperature of  $\sim 95$  K, close to the observed evaporation temperature of water in envelopes surrounding protostars (Maret et al. 2002). The evaporation temperature of CH<sub>4</sub> ice is close to that of CO ice. The evaporation time scale at the evaporation temperature can be estimated to be roughly  $\nu^{-1} \exp(E_D/T_{\text{evap}}) \approx 10^{-12} e^{60} \text{ s} \approx 3.6 \times 10^6$  yr. For higher temperature, the evaporation will be much faster.

The abundance of CO<sub>2</sub> ice initially increases with increasing temperature. This is because it mainly forms from the reaction CO + OH → CO<sub>2</sub> + H with a barrier of 80 K, and an increase

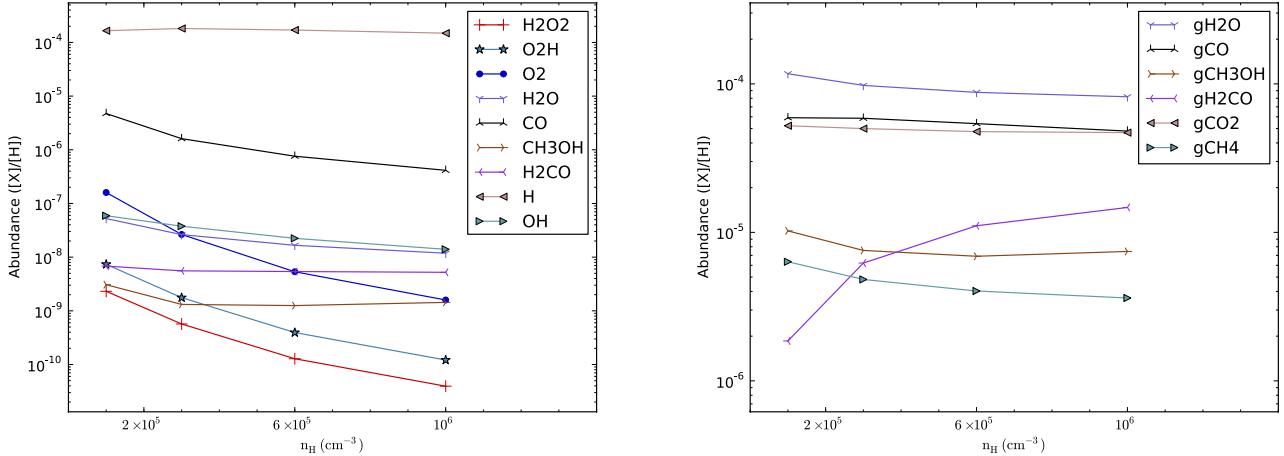
in temperature greatly enhances the mobility of the reacting species, as well as the probability of overcoming the reaction barrier. But when temperature increases more, the abundance of CO ice becomes so low that the CO<sub>2</sub> abundance also drops. The evaporation temperature of CO<sub>2</sub> is about 40 K, so evaporation is not responsible for the decline in CO<sub>2</sub> ice abundance seen in Fig. 4. A similar trend is seen in other species, such as H<sub>2</sub>CO ice, CH<sub>3</sub>OH ice, as well as gas phase H<sub>2</sub>O<sub>2</sub>, CH<sub>3</sub>OH, H<sub>2</sub>CO, and H<sub>2</sub>O. On the other hand, for species efficiently produced in the gas phase, e.g. O<sub>2</sub>, its abundance increases with temperature owing to the faster evaporation at a higher temperature.

The abundances of gas phase H<sub>2</sub>O<sub>2</sub>, CH<sub>3</sub>OH, CO, and O<sub>2</sub> have a sensitive dependence on temperature at around 21–24 K as seen from Fig. 4. For example, changing the temperature from 20 K to 22 K increases the abundance of H<sub>2</sub>O<sub>2</sub> at a given time ( $6 \times 10^5$  yr) by about one order of magnitude. This rather small change of 2 K in temperature is normally below the accuracy of the kinetic temperature as determined from observational data. The dependence of the evolution curves of H<sub>2</sub>O<sub>2</sub> and CH<sub>3</sub>OH on temperature can be seen more clearly in Fig. 5. Changing the temperature not only shifts the evolution curves horizontally, it also changes their shapes significantly. We can see that, although for CH<sub>3</sub>OH it is possible to match the observed abundance at multiple stages, for H<sub>2</sub>O<sub>2</sub> the best match is only possible at  $3 \times 10^5$ – $10^6$  yr (if we ignore the match in the very early stage).

Regarding the density dependence, Fig. 6 shows that the abundances of the gas phase species at  $6 \times 10^5$  yr generally decrease with increasing density, because the accretion of molecules onto the dust grains is faster for a higher density. This does not necessarily mean that the abundances of the surface species always increase with density. For example, the abundances of CH<sub>4</sub> ice and CH<sub>3</sub>OH ice decrease with higher density, while the abundance of H<sub>2</sub>CO ice has the opposite trend. One important factor is the time when we look at the system. In Fig. 7 we plot the abundances of H<sub>2</sub>CO ice and CH<sub>3</sub>OH ice as a function of time for different densities, while the temperature is fixed at 21 K. It can be seen that at a given time, the abundances of H<sub>2</sub>CO ice or CH<sub>3</sub>OH ice can either increase or decrease when the density is increased. We note that the evolution curves of these species have a quasi-oscillatory feature. For the same species, the evolution curves have a similar shape for



**Fig. 5.** The abundances of gas phase  $\text{H}_2\text{O}_2$  and  $\text{CH}_3\text{OH}$  as a function of time for different temperatures. The density is fixed to  $6 \times 10^5 \text{ cm}^{-3}$ . The horizontal dotted lines mark the observed abundances of the corresponding species.



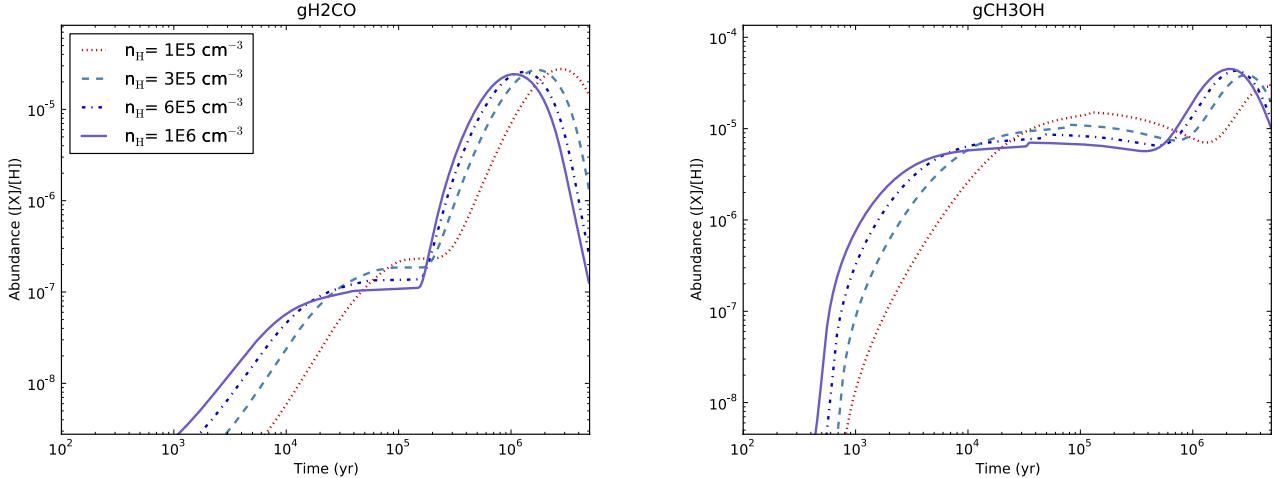
**Fig. 6.** Dependence of the abundances of several species at the time of best match ( $6 \times 10^5 \text{ yr}$ ) on  $n_{\text{H}}$ , with temperature fixed to 21 K. *Left panel:* gas phase species; *right panel:* surface species.

different densities, except that with a lower density the evolution is slower and thus the curves are shifted toward the right.

### 3.6. Discussions and limits of the model

It can be seen from Figs. 1, 6, and 5 that  $\text{H}_2\text{O}_2$  can be produced with a rather high abundance at certain evolutionary stages or with certain physical parameters, which is frequently higher than the currently observed value (Bergman et al. 2011b), especially in the early-to-intermediate times ( $\sim 10^3$ – $10^5 \text{ yr}$ ). One natural question to ask is why  $\text{H}_2\text{O}_2$  has not been commonly detected in the interstellar medium. One possibility is that its spectral lines have been overlooked in the past. Another simple explanation would be that it is overproduced in our model, because in the past the chemistry of  $\text{H}_2\text{O}_2$  (as well as  $\text{O}_2\text{H}$  and  $\text{O}_3$ , etc.) may not have been studied in detail in the astrochemistry context (especially the destruction reactions in the gas phase), so that its destruction routes might be incomplete. For example, there is no reaction in which  $\text{H}_2\text{O}_2$  is destroyed by reacting with  $\text{H}_3^+$  in the current mainstream gas phase chemical networks. As a rough estimate, if we take the rate of destruction by such a reaction to

be the same as the rate of the reaction  $\text{H}_3^+ + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{H}_2$ , then the abundance of gas phase  $\text{H}_2\text{O}_2$  can be reduced by about one order of magnitude. Further theoretical/experimental studies of the  $\text{H}_2\text{O}_2$  chemistry would thus be very helpful, given that it has been detected recently and it plays a potentially important role in the grain chemistry of water. A third possibility is that the rarity of  $\text{H}_2\text{O}_2$  might be an age effect. From Fig. 5 we notice that the abundance of  $\text{H}_2\text{O}_2$  is only very high in a relatively early stage (before  $\sim 5 \times 10^5 \text{ yr}$ ). If for certain reasons most of these cloud cores that are being observationally studied are older than this (due to some selection effects), then the  $\text{H}_2\text{O}_2$  abundance in these objects would be too low to detect. Basically, at least three physical parameters are relevant, namely age, density, and temperature. A probability distribution of these three parameters of the cloud cores would help to give the detection probability of  $\text{H}_2\text{O}_2$  (and any other molecules). Thus  $\rho$  Oph A may be considered special in the sense that it has a relatively high density ( $\sim 10^6 \text{ cm}^{-3}$ ) and temperature (20–30 K), while most dark clouds with a high density ( $\gtrsim 10^4 \text{ cm}^{-3}$ ) tend to be very cold ( $\lesssim 15 \text{ K}$ ) (Bergin & Tafalla 2007). An inhomogeneous physical condition would make the situation more complex, which may require a



**Fig. 7.** The abundances of H<sub>2</sub>CO and CH<sub>3</sub>OH ice as a function of time for different densities. The temperature is fixed to 21 K.

self-consistent dynamical-chemical model. However, a thorough study of these possibilities has to be left to future work.

On the other hand, although CH<sub>3</sub>OH has been studied quite extensively in the past, we notice that the gas phase reactions associated with it contain some important (although not decisive) differences between the OSU09 network and the UMIST RATE06 network. For example, the reaction between CH and CH<sub>3</sub>OH to form CH<sub>3</sub> and H<sub>2</sub>CO has a rate  $2.49 \times 10^{-10}(T/300)^{-1.93}$  in the UMIST RATE06 network, but it does not exist in the OSU09 network. One possible problem is that the temperature of cold interstellar medium (at most several tens of Kelvins) is out of the indicated valid range for many reactions in RATE06, and it is not clear how to extrapolate these reaction rates correctly, although we have closely followed the instructions in [Woodall et al. \(2007\)](#). In our modeling we have been using the RATE06 network.

The energy barriers for the hydrogenation of CO and H<sub>2</sub>CO on the grain are both taken to be 2500 K. [Woon \(2002\)](#) calculated the barrier heights of these two reactions, giving a value of  $\sim 2740$  K and 3100 K in the case three water molecules are present, with zero-point energy corrections added. If these values are adopted, then the observed abundances of H<sub>2</sub>CO and CH<sub>3</sub>OH can only be reproduced within one order of magnitude at best. However, [Goumans \(2011\)](#) gives a lower barrier height ( $\sim 2200$  K) for the hydrogenation of H<sub>2</sub>CO, which would give better agreement with the observational results than if [Woon \(2002\)](#) were used in our model.

The chemical desorption is very important for the abundances of the gas phase H<sub>2</sub>O<sub>2</sub> and CH<sub>3</sub>OH. However, the efficiency of this mechanism (the “*a*” parameter in [Garrod et al. 2007](#)) is uncertain. [Garrod & Pauly \(2011\)](#) adopt a low value of 0.01 for it, to avoid overproduction of some gas phase species ([Garrod et al. 2007](#)). We use a value of 0.1 in our study, and the abundances of H<sub>2</sub>CO and CH<sub>3</sub>OH are not overproduced, except possibly in the early stages of the evolution. We note that the temperature and density of major concern in our study is around 20 K and  $6 \times 10^5$  cm<sup>-3</sup>, while in [Garrod et al. \(2007\)](#) the temperature is set to 10 K and density to  $2 \times 10^4$  cm<sup>-3</sup>. As a test we ran our model with the latter physical condition, and in this case CH<sub>3</sub>OH and H<sub>2</sub>CO are indeed overproduced by about one order of magnitude. Thus it seems that the efficiency of chemical desorption depends on the temperature of the dust grain, in the sense that at higher temperature the probability that the product

of a surface exothermic reaction gets ejected to the gas phase is higher. However, a detailed study of this possibility is beyond the scope of the present paper.

Regarding the formation of water ice, [Bergin et al. \(1998\)](#) propose an interesting mechanism in which water is first formed in the high-temperature shocked gas, and then gets adsorbed onto the dust grains in the post-shock phase. This mechanism may act as an alternative or supplement to the grain chemistry route. It is not our aim here to discuss to what extent this mechanism contributes to the water ice budget. However, we point out that even with a temperature 1000–2000 K, the amount of H<sub>2</sub>O<sub>2</sub> produced in a pure gas phase chemistry (using the UMIST RATE06 network) is still much lower than the detected level.

#### 4. Conclusions

- With a gas-grain chemical model that properly takes the desorption of grain surface species by the heat released by chemical reactions into account, we reproduced the observed abundances of H<sub>2</sub>O<sub>2</sub> in  $\rho$  Oph A at a time of  $\sim 6 \times 10^5$  yr. The solid phase H<sub>2</sub>O<sub>2</sub> abundance is very low at this stage. However, a H<sub>2</sub>O<sub>2</sub> to H<sub>2</sub>O ratio of a few percent might be obtained in the solid phase if the layered structure of grain mantle is considered.
- The abundances of other species such as H<sub>2</sub>CO, CH<sub>3</sub>OH, and O<sub>2</sub> detected in the same object can also be reasonably reproduced at a time of  $\sim 6 \times 10^5$  yr. Such a time scale is consistent with the evolution time scale estimated through dynamical considerations.
- The O<sub>2</sub>H radical is a precursor of H<sub>2</sub>O<sub>2</sub> on the dust grain, and we predict that it has a gas-phase abundance with the same order-of-magnitude of H<sub>2</sub>O<sub>2</sub> and should thus be detectable. Observational searches for it are under way.
- For physical conditions relevant to  $\rho$  Oph A, water is mainly in solid form, being the dominant grain mantle material. Its gas phase abundance is only on the order of 10<sup>-8</sup> according to our model.
- We note that the abundance of gas-phase H<sub>2</sub>O<sub>2</sub> in our model results can be much higher than the current observed level for a range of physical conditions. This may suggest that its gas-phase destroying channels are incomplete. Due to the potentially important role played by H<sub>2</sub>O<sub>2</sub> in the formation

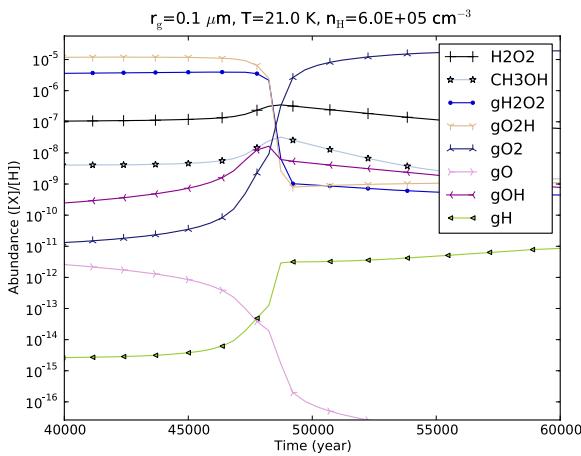
of water, its reaction network needs to be studied more thoroughly in the future.

Other uncertainties in our modeling include the ratio between the diffusion energy barrier to the binding energy of a species on the grain surface, the activation energy barriers of certain key reactions, and the efficiency of the chemical desorption mechanism. In the present work we mainly make use of their canonical values or of values that give good matches to the observational results, and we also vary them to see the effects on the resulting abundances, which are significant in many cases.

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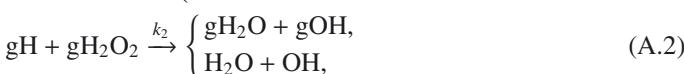
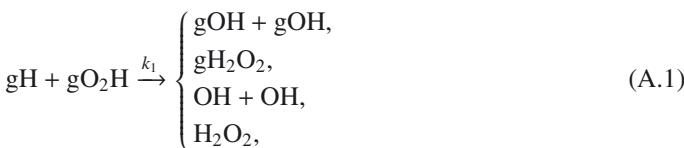


**Fig. A.1.** A zoom-in plot of Fig. 1 (with several species removed and several added), focusing on the spike-like feature (though nothing looks like a spike anymore). The abundance of gH has been multiplied by a factor of 10<sup>12</sup> (to make the plot look more compact).

## Appendix A: An explanation of the spike-like features in the evolution curves

In Fig. 1 we note that at a time of  $\sim 5 \times 10^4$  yr a spike-like feature appears in the evolution curves of some species (e.g. gas phase H<sub>2</sub>O<sub>2</sub> and CH<sub>3</sub>OH), while the abundances of some other species (e.g. H<sub>2</sub>O<sub>2</sub> and O<sub>2</sub> on the grain) change very rapidly at the same time. These features might appear to be caused by faults in the program for solving the set of differential equations. However, after solving the same problem with the Monte Carlo method, which is immune to such numerical instabilities, we find that these features are still present, indicating that they are genuine. How could a smooth ordinary differential equation system generate such an almost-singular feature? In Fig. A.1 we make a zoom-in of Fig. 1 (with several species added and several species removed). It can be seen that, although the time scale of the spike-like feature is relatively short, the evolution is always smooth (except the discreteness caused by the finite sampling of the curve). Then what determines the appearance of such a feature?

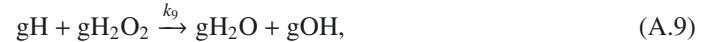
Because atomic hydrogen is central to the surface chemistry, we first look at the most important reactions governing its abundance on the grain. The main reactions consuming atomic hydrogen on the grains are (in the following a species name preceded by a “g” means a species on the grain, otherwise it is in the gas phase),



while others such as the reactions with gO<sub>3</sub> and gCH<sub>2</sub>OH are relatively unimportant in the early times. It is mainly produced by



As the abundance of atomic H in the gas phase and the abundance of gCO and gH<sub>2</sub>O change relatively smoothly, they can be viewed as constant on a short time scale. The main reactions for the consumption and production of gOH are



From the above reaction list we may write the evolution equation of gH and gOH as<sup>4</sup>

$$\begin{aligned} \partial_t gH = & -k_1 gH gO_2H - k_2 gH gH_2O_2 \\ & + k_3 H + k_4 gOH gCO + k_5 gH_2O, \end{aligned} \quad (A.11)$$

$$\partial_t gOH = -k_6 gO gOH - k_7 gCO gOH$$

$$+ 2k_8 gH gO_2H + k_9 gH gH_2O_2 + k_{10} gH_2O, \quad (A.12)$$

or in a more succinct form

$$\partial_t gH = \kappa_1 gH + \kappa_2 gOH + b_1,$$

$$\partial_t gOH = \kappa_3 gH + \kappa_4 gOH + b_2, \quad (A.13)$$

where

$$\kappa_1 = -k_1 gO_2H - k_2 gH_2O_2,$$

$$\kappa_2 = k_4 gCO,$$

$$\kappa_3 = 2k_8 gO_2H + k_9 gH_2O_2,$$

$$\kappa_4 = -k_6 gO - k_7 gCO,$$

$$b_1 = k_3 H + k_5 gH_2O,$$

$$b_2 = k_{10} gH_2O.$$

If we view  $\kappa_1-\kappa_4$ , as well as  $b_1$  and  $b_2$ , as constants (of course they are not), then Eq. (A.13) can be solved exactly; the solution contains an exponential part and a constant part. The amplitude of the exponential part will be inversely proportional to the determinant of the coefficient matrix

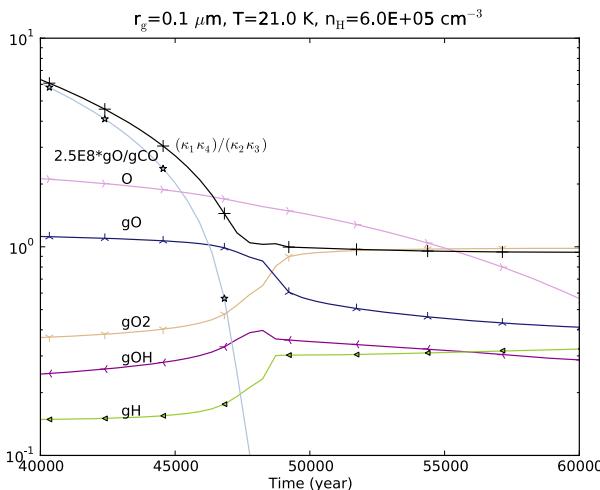
$$\det(\kappa) = \begin{pmatrix} \kappa_1 & \kappa_2 \\ \kappa_3 & \kappa_4 \end{pmatrix}.$$

Since  $\kappa_1-\kappa_4$  are not really constant in our problem, we expect that when they become such that  $\det(\kappa)$  is close to zero, a spike-like or jump-like behavior would appear. Namely, we require

$$\begin{aligned} \frac{\kappa_1 \kappa_4}{\kappa_2 \kappa_3} &= \frac{(k_1 gO_2H + k_2 gH_2O_2)(k_6 gO + k_7 gCO)}{(k_4 gCO)(2k_8 gO_2H + k_9 gH_2O_2)} \\ &\simeq \frac{gO_2H/gH_2O_2 + 1}{1.2gO_2H/gH_2O_2 + 1} \times (2.5 \times 10^8 gO/gCO + 1) \\ &\simeq 1. \end{aligned} \quad (A.14)$$

The actual value of the parameters have been inserted in the second line of the above equation. These parameters depend on the physical conditions.

<sup>4</sup> Here for brevity we use the name of a species to denote its average population on a single grain; for example, if gCO = 100, it means on average there are 100 CO molecules on a single grain.



**Fig. A.2.** The ratio  $(\kappa_1 \kappa_4)/(\kappa_2 \kappa_3)$  and the value of  $2.5 \times 10^8 \times gO/gCO$  as a function of time. They are to scale. The abundances of several other species are plotted only for reference (not to scale).

To satisfy this condition (at least approximately),  $gO/gCO$  should be very small. In Fig. A.2 the ratio  $(\kappa_1 \kappa_4)/(\kappa_2 \kappa_3)$  and the value of  $2.5 \times 10^8 gO/gCO$  are plotted as a function of time. The abundances of O, gO, gO<sub>2</sub>, gH, and gOH are also plotted for reference (not to scale). It can be seen that the  $(\kappa_1 \kappa_4)/(\kappa_2 \kappa_3)$  ratio does decrease, and it approaches a value of unity before the time of the spike/jump feature, and the  $gO/gCO$  ratio drops to a very low value monotonically.

The above mathematical argument can also be understood intuitively. When the  $gO$  abundance is so low that reaction (A.6) can be neglected,  $gOH$  is only destroyed by reaction (A.7). Each time a  $gOH$  radical is consumed, one  $gH$  is created (if we neglect the desorption process), and this  $gH$  will quickly react with  $gH_2O_2$  or  $gO_2H$  to create one or two  $gOHs$ . There will then be a net gain in the  $gOH$  abundance, leading to its fast growth, and the  $gH$  abundance will increase accordingly. Thus we see that reaction (A.8) is crucial in that it produced two  $gOH$  radicals by consuming only one  $gH$ .

Therefore for such a spike-like feature to occur, the abundance of  $gO$  must decrease to a low value such that the reaction between  $gOH$  and  $gO$  becomes unimportant for consuming

$gOH$ . Namely, we require  $[gO] \lesssim [gCO]$   $k_7/k_6 \simeq 5 \times 10^{-13}$ . The abundances of atomic oxygen in the gas phase and on the grain surface are related by  $O/gO \simeq k_{evap}(gO)/k_{ad}(O) \simeq 3 \times 10^6$ , so equivalently we require  $[O] < 1.5 \times 10^{-6}$  (i.e., about a factor of 200 less than the initial O abundance) at the time of the spike-like feature. Atomic oxygen is mainly consumed on the grain surface by reacting with another  $gO$  to form  $gO_2$  (for  $t \lesssim 10^3$  yr) or by reacting with  $gOH$  to form  $gO_2H$ . Only the latter is relevant here. As the abundance of  $gOH$  does not change much before the spike-like feature, the time scale for the consumption of atomic oxygen can be estimated to be  $\ln 200 \times (O/gO)/(k_6 gOH) \simeq 10^5$  yr, which is on the same order of magnitude as the time of occurrence of the spike-like feature.

The time scale for the endurance of the spike-like feature itself can be estimated to be the time scale for the exhaustion of  $gO_2H$  or  $gH_2O_2$  (so that Eqs. (A.11) and (A.12) do not hold anymore) by reacting with  $gH$ , which is

$$1/(k_1 gH) \simeq 10^3 \text{ yr},$$

where the  $gH$  population (the average number of atomic H on a single grain) is taken to be a median value ( $10^{-14}$ ) during the rapidly varying period. That equation (A.14) seems to hold after this period (see Fig. A.2) does not mean that  $gH$  will keep increasing rapidly, simply because the premise of our argument, namely Eqs. (A.11) and (A.12) are not a good description of the evolution of  $gH$  and  $gOH$  anymore.

As the abundance of H on the grain increases, almost all the  $O_3$  on the grain are converted into  $O_2$  and OH.  $O_2$  molecules on the grain are then consumed by the slower reaction  $gH + gO_2 \rightarrow gO_2H$ , with a time scale  $\sim 10^5$  yr. This explains the prominent peak in the evolution curve of  $gO_2$  (see Fig. 1).

Would the spike-like feature have any practical significance (especially observationally)? Ideally, such a short-time feature may be used to constrain the age of a dense cloud, by distinguishing the abundances of certain species between their early-time values (before the spike-like feature) and late-time values (after the spike-like feature). However, due to its dependence on the reaction network being used, which usually contains a lot of uncertainties and is subject to change when new experiments are carried out, the question whether this feature is really relevant for the study of interstellar medium can only be answered by future investigations.

## Appendix B: The surface reaction network used in this work

**Table B.1.** Surface network used in this work.

Num	Reaction	Branching ratio	Energy barrier (K)	Reference
1	H + H → H <sub>2</sub>	1.0	0.0	HHL92
2	H + O → OH	1.0	0.0	ICet10
3	H + O <sub>2</sub> → O <sub>2</sub> H	1.0	600.0	Estimated
4	H + O <sub>3</sub> → O <sub>2</sub> + OH	1.0	200.0	Estimated
5	H + OH → H <sub>2</sub> O	1.0	0.0	ICet10
6	H + O <sub>2</sub> H → H <sub>2</sub> O <sub>2</sub>	0.38	0.0	CIRL10
7	H + O <sub>2</sub> H → OH + OH	0.62	0.0	CIRL10
8	H + H <sub>2</sub> O <sub>2</sub> → H <sub>2</sub> O + OH	1.0	0.0	ICet08
9	H + CO → HCO	0.5	2500.0	GWH08
10	H + HCO → H <sub>2</sub> CO	1.0	0.0	FCet09
11	H + H <sub>2</sub> CO → CH <sub>3</sub> O	0.5	2500.0	RH00
12	H + H <sub>2</sub> CO → HCO + H <sub>2</sub>	0.5	3000.0	G11
13	H + CH <sub>3</sub> O → CH <sub>3</sub> OH	1.0	0.0	FCet09
14	H + CH <sub>3</sub> OH → CH <sub>3</sub> OH	1.0	0.0	GWH08
15	H + HCOO → HCOOH	1.0	0.0	AR77
16	H + C → CH	1.0	0.0	AR77
17	H + CH → CH <sub>2</sub>	1.0	0.0	AR77
18	H + CH <sub>2</sub> → CH <sub>3</sub>	1.0	0.0	AR77
19	H + CH <sub>3</sub> → CH <sub>4</sub>	1.0	0.0	AR77
20	H + N → NH	1.0	0.0	AR77
21	H + NH → NH <sub>2</sub>	1.0	0.0	AR77
22	H + NH <sub>2</sub> → NH <sub>3</sub>	1.0	0.0	AR77
23	H + S → HS	1.0	0.0	HHL92
24	H + HS → H <sub>2</sub> S	1.0	0.0	HHL92
25	H + H <sub>2</sub> S → HS + H <sub>2</sub>	1.0	860.0	TH82
26	H + CS → HCS	1.0	0.0	HHL92
27	C + S → CS	1.0	0.0	HHL92
28	O + S → SO	1.0	0.0	HHL92
29	O + SO → SO <sub>2</sub>	1.0	0.0	HHL92
30	O + CS → OCS	1.0	0.0	HHL92
31	H + CN → HCN	1.0	0.0	AR77
32	H + NO → HNO	1.0	0.0	AR77
33	H + NO <sub>2</sub> → HNO <sub>2</sub>	1.0	0.0	AR77
34	H + NO <sub>3</sub> → HNO <sub>3</sub>	1.0	0.0	AR77
35	H + N <sub>2</sub> H → N <sub>2</sub> H <sub>2</sub>	1.0	0.0	AR77
36	H + N <sub>2</sub> H <sub>2</sub> → N <sub>2</sub> H + H <sub>2</sub>	1.0	650.0	HHL92
37	H + NHCO → NH <sub>2</sub> CO	1.0	0.0	AR77
38	H + NH <sub>2</sub> CO → NH <sub>2</sub> CHO	1.0	0.0	AR77
39	N + HCO → NHCO	1.0	0.0	AR77
40	CH + CH → C <sub>2</sub> H <sub>2</sub>	1.0	0.0	HHL92
41	O + O → O <sub>2</sub>	1.0	0.0	AR77
42	O + O <sub>2</sub> → O <sub>3</sub>	1.0	0.0	ABet04
43	O + CO → CO <sub>2</sub>	1.0	1580.0	GMet08
44	O + HCO → HCOO	0.5	0.0	GMet08
45	O + HCO → CO <sub>2</sub> + H	0.5	0.0	GMet08
46	O + N → NO	1.0	0.0	AR77
47	O + NO → NO <sub>2</sub>	1.0	0.0	AR77
48	O + NO <sub>2</sub> → NO <sub>3</sub>	1.0	0.0	AR77
49	O + CN → OCN	1.0	0.0	AR77
50	C + N → CN	1.0	0.0	AR77
51	N + N → N <sub>2</sub>	1.0	0.0	AR77
52	N + NH → N <sub>2</sub> H	1.0	0.0	AR77
53	H <sub>2</sub> + OH → H <sub>2</sub> O + H	1.0	2100.0	ABet04
54	OH + CO → CO <sub>2</sub> + H	1.0	80.0	RH01
55	H + C <sub>2</sub> → C <sub>2</sub> H	1.0	0.0	HHL92
56	H + N <sub>2</sub> → N <sub>2</sub> H	1.0	1200.0	HHL92
57	H + C <sub>2</sub> H → C <sub>2</sub> H <sub>2</sub>	1.0	0.0	HHL92
58	H + HOC → CHO	1.0	0.0	HHL92
59	C + OH → HOC	0.5	0.0	HHL92

**Table B.1.** continued.

Num	Reaction	Branching ratio	Energy barrier (K)	Reference
60	$C + OH \rightarrow CO + H$	0.5	0.0	HHL92
61	$CH + OH \rightarrow CHOH$	1.0	0.0	HHL92
62	$H + CHOH \rightarrow CH_2OH$	1.0	0.0	HHL92
63	$OH + OH \rightarrow H_2O_2$	1.0	0.0	HHL92
64	$OH + CH_2 \rightarrow CH_2OH$	1.0	0.0	HHL92
65	$C + C \rightarrow C_2$	1.0	0.0	HHL92
66	$C + O_2 \rightarrow CO + O$	1.0	0.0	HHL92
67	$O + CH \rightarrow HCO$	1.0	0.0	HHL92
68	$O + OH \rightarrow O_2H$	1.0	0.0	HHL92
69	$O + CH_2 \rightarrow H_2CO$	1.0	0.0	HHL92
70	$O + CH_3 \rightarrow CH_2OH$	1.0	0.0	HHL92
71	$C + O \rightarrow CO$	1.0	0.0	HHL92
72	$C + CH \rightarrow C_2H$	1.0	0.0	HHL92
73	$C + NH \rightarrow HNC$	1.0	0.0	HHL92
74	$C + CH_2 \rightarrow C_2H_2$	1.0	0.0	HHL92
75	$C + NH_2 \rightarrow HNC + H$	1.0	0.0	HHL92
76	$N + CH \rightarrow HCN$	1.0	0.0	HHL92
77	$N + NH_2 \rightarrow N_2H_2$	1.0	0.0	HHL92
78	$O + NH \rightarrow HNO$	1.0	0.0	HHL92

**Notes.** The photodissociation reactions induced by cosmic rays and the chemical desorption reactions are not included here.

**References.** HHL92: [Hasegawa et al. \(1992\)](#); ICet10: [Ioppolo et al. \(2010\)](#); CIRL10: [Cuppen et al. \(2010\)](#); ICet08: [Ioppolo et al. \(2008\)](#); G11: [Goumans \(2011\)](#); FCet09: [Fuchs et al. \(2009\)](#); GWH08: [Garrod et al. \(2008\)](#); AR77: [Allen & Robinson \(1977\)](#); TH82: [Tielens & Hagen \(1982\)](#); GMet08: [Goumans et al. \(2008\)](#); ABet04: [Atkinson et al. \(2004\)](#); RH00: [Ruffle & Herbst \(2000\)](#); RH01: [Ruffle & Herbst \(2001b\)](#).

## Appendix C: The enthalpies of the surface species

**Table C.1.** Enthalpies of the surface species considered in this work that are used to calculate the exoergicities of the surface reactions.

Num	Species	Enthalpy (kJ/mol)	Reference
1	C	716.7	NIST Webbook
2	CH	594.1	BM02, p238
3	CH <sub>2</sub>	386.4	BM02, p240
4	CH <sub>3</sub>	145.7	BM02, p241
5	CH <sub>3</sub> O	17.0	NIST Webbook
6	CH <sub>2</sub> OH	-9.0	NIST Webbook
7	CH <sub>3</sub> OH	-201.2	BM02, p241
8	CH <sub>4</sub>	-74.9	BM02, p241
9	CN	435.1	BM02, p247
10	CO	-110.5	BM02, p251
11	CO <sub>2</sub>	-393.5	BM02, p251
12	CS	280.3	BM02, p253
13	H	218.0	BM02, p558
14	H <sub>2</sub>	0.0	BM02, p568
15	H <sub>2</sub> CO	-115.9	BM02, p240
16	H <sub>2</sub> O	-241.8	BM02, p571
17	H <sub>2</sub> O <sub>2</sub>	-135.8	BM02, p572
18	H <sub>2</sub> S	-20.5	BM02, p574
19	HCN	135.1	BM02, p239
20	HNC	135.1	Estimated
21	HCO	43.5	BM02, p239
22	HCOO	-386.8	BM02, p240 Url1
23	HCOOH	-378.6	BM02, p240
24	HCS	296.2	K98
25	HNO	99.6	BM02, p563
26	HNO <sub>2</sub>	-78.8	BM02, p563
27	HNO <sub>3</sub>	-134.3	BM02, p563
28	HS	139.3	BM02, p567
29	N	472.7	BM02, p693
30	N <sub>2</sub>	0.0	BM02, p699
31	N <sub>2</sub> H	245.2	VS91
32	N <sub>2</sub> H <sub>2</sub>	213.0	BM02, p570
33	NH	376.6	BM02, p563
34	NH <sub>2</sub>	190.4	BM02, p570
35	NH <sub>2</sub> CHO	-186.0	NIST Webbook
36	NH <sub>2</sub> CO	-13.1	NCet10
37	NH <sub>3</sub>	-45.9	BM02, p577
38	NHCO	-101.7	BM02, p239
39	NO	90.3	BM02, p695
40	NO <sub>2</sub>	33.1	BM02, p695
41	NO <sub>3</sub>	71.1	BM02, p695
42	O	249.2	BM02, p733
43	O <sub>2</sub>	0.0	BM02, p741
44	O <sub>2</sub> H	2.1	BM02, p567
45	O <sub>3</sub>	142.7	BM02, p752
46	OCN	159.4	BM02, p248
47	OCS	-138.4	BM02, p251
48	OH	39.0	BM02, p566
49	S	277.0	BM02, p811
50	SO	5.0	BM02, p736
51	SO <sub>2</sub>	-296.8	BM02, p743
52	C <sub>2</sub>	837.74	NIST Webbook
53	C <sub>2</sub> H	476.98	NIST Webbook
54	C <sub>2</sub> H <sub>2</sub>	226.73	NIST Webbook

**References.** BM02: Binnewies & Milke (1999); NIST Webbook: <http://webbook.nist.gov/chemistry/>; NCet10: Nagy et al. (2010); K98: Kaiser et al. (1998); VS91: Vandooren et al. (1991); Url1: <http://chem.engr.utc.edu/webres/331f/teams-98/chp/Boiler%20DC/tstd007.htm>