Effects of initial condition and cloud density on the composition of the grain mantle

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ABSTRACT

The evolution of grain mantles in various interstellar environments is studied. We concentrate mainly on water, methanol and carbon dioxide, which constitute nearly 90 per cent of the grain mantle. We investigate how the production rates of these molecules depend on the relative gas-phase abundances of oxygen and carbon monoxide and constrain the relevant parameter space that reproduces these molecules close to the observed abundances. Allowing the accretion of only H, O and CO on the grains and using the Monte Carlo method, we follow the chemical processes for a few million years. We allow the formation of multilayers on the grains and incorporate the freeze-out effects of accreting O and CO. We find that the formation of these molecules depends on the initial conditions as well as on the average cloud density. Specifically, when the number density of accreting O is less than three times that of CO, methanol is always overproduced. Using the available reaction pathways it appears to be difficult to match the exact observed abundances of all three molecules simultaneously. Only in a narrow region of parameter space are all three molecules produced within the observed limits. Furthermore, we found that the incorporation of the freeze-outs of O and CO leads to an almost steady state on the grain surface. The mantle thickness grows anywhere between 60 and 500 layers in a period of two million years. In addition, we consider a case in which the gas number density changes with time owing to the gradual collapse of the molecular cloud and present the evolution of the composition of different species as a function of the radius of the collapsing cloud.

Key words: hydrodynamics – molecular processes – stars: protostars – ISM: abundances – ISM: molecules.

1 INTRODUCTION

The study of the chemical evolution of the interstellar medium (ISM) is recognized to be a challenging task. The ISM is a rich reservoir of complex molecules. So far, around 150 gas-phase molecules and around 20 molecular species on the grain surface have been detected in various regions of the ISM, especially in regions of star formation. In the last decade it has become well established that the gas-phase reactions alone cannot explain the molecular abundances in the ISM. The chemical reactions that occur on the interstellar dust grains are essential for explaining the formation of several molecules, especially hydrogenated species, including the simplest and most abundant molecule, H₂. Interstellar grains provide a surface on which the accreted species can meet and react. Therefore, an understanding of the formation of molecules on grain surfaces is of prime importance. In this paper, we follow the evolution of the grain mantle mainly as a function of the initial conditions. We concentrate only on water, methanol and carbon dioxide, as these molecules constitute nearly 90 per cent of the grain material in dense regions of the ISM. These molecules are detected on the grain surface as a result of their strong absorption bands arising out of multiple vibrational modes. Water is the most abundant species on grains in the dense ISM. It has an abundance of 10⁻⁴ with respect to the total hydrogen column density (Tielens et al. 1991). The ice band, at 3.07 μm (3280 cm⁻¹), is attributable to the O-H stretch mode of H₂O ice and was first discovered by Gillett & Forrest (1973) in Becklin & Neugebauer (1967, hereafter BN) objects. CO₂ is the second most abundant molecule in the ISM, with an abundance of around 20 per cent with respect to H₂O. However, this abundance can vary from cloud to cloud, and in clouds such as W 33A it could be even less than 5 per cent of the water abundance (Keane et al. 2001). Several strong CO₂ features are observed (de Graauw et al. 1996; Keane et al. 2001). Generally, it is found that the CO₂ correlates best with H₂O ice, suggesting that these molecules may have similar chemical histories. The next most abundant molecule is CO, which is a well-studied ice, with an abundance varying between 2 and 15 per cent of that of water and with a characteristic absorption...
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The number density of the molecule $n_i$ in a grain surface for a given pair of H atoms is the grain cross-section $\sigma_i$ (cm$^2$) times the velocity $v_i$ (cm s$^{-1}$). The next strongest feature is that the abundance is affected. In Section 2, we discuss the various physical processes that are involved during a gas–grain interaction. In Section 3, we describe the methodology of our calculations. In Section 4, we describe our model and the nature of the initial conditions. In Section 5, we present our results. Finally, in Section 6, we draw our conclusions.

2 MECHANISMS OF REACTIONS ON GRAIN SURFACES

There are four physical processes that are involved when gas-phase atoms/molecules interact with grains. The first step is ‘accretion’, that is, the landing of various species on a grain. In our case only H, O and CO are considered as accreting species onto the grain surface. The second step is ‘hopping’, through which the accreted species move around the grain. In the third step, the accreted species react to form various new species either through the Langmuir–Hinselwood (LH) mechanism or through the Eley–Rideal (ER) mechanism. In the LH scheme, the gas-phase species accreted onto a grain becomes equilibrated with the surface before it reacts with another atom/molecule, and in the ER reaction scheme, the incident gas-phase species collides directly with an adsorbed species on the surface and reacts with that species. In such a mechanism, the reactant does not generally become trapped at the surface and it is unlikely to be sensitive to the surface temperature (Farebrother et al. 2000). In our study, we take it that the reactions on a surface can occur through both LH and ER mechanisms. However, we assume that the molecules remain trapped after reactions owing to their high binding energy. The typical temperature of a dense cloud is $\sim$10 K, and at this temperature only hydrogen can desorb at a meaningful rate. All the other molecules stay on the grain until these grains are heated up. When the temperature of the grain is increased, these molecules desorb back into the gas phase according to their binding energy of desorption.

We define the accretion rate $r_{\text{acc}}(i)$ of a given neutral species $i$, in units of s$^{-1}$, as

$$r_{\text{acc}}(i) = S_i \sigma_i v_i n_{i},$$

where $S_i$ is the sticking coefficient (taken as 1 for all three species), $v_i$ is the velocity (cm s$^{-1}$), $n_i$ is the number density of the $i$th species in the gas phase, and $\sigma_i$ is the grain cross-section (cm$^2$). Because we carried out our calculations for three different cloud densities and for different initial abundances we used many sets of accretion rates. Number densities for different clouds are taken from Stantcheva et al. (2002) and are listed in Table 1. The number density of hydrogen in the gas phase is denoted by $n_H$, and the number densities of O and CO with respect to the hydrogen number density are expressed as $n_O$ and $n_{CO}$ respectively.

The binding energy of the incoming species depends strongly on the species itself and on the way the interactions proceed. The incoming species might become trapped inside a shallow potential well at a physisorbed site. The interaction is mainly the result of mutually induced dipole moments. A strong covalent bond may also be formed through chemisorption. Recent studies have found

| Species | High (cm$^{-3}$) | Intermediate (cm$^{-3}$) | Low (cm$^{-3}$) |
|---------|----------------|-------------------------|----------------|
| H       | 1.10           | 1.15                    | 1.15           |
| O       | 7.0            | 0.75                    | 0.09           |
| CO      | 7.5            | 0.75                    | 0.075          |

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In this paper, we consider only thermal desorption. However, other than hydrogen and the hydrogen molecule, no species desorbs at 10 K. Other molecules can come out of the grain surface only when the grains are heated. Many types of desorption mechanisms are present in the literature. In a dense cloud, the most important is the impulsive heating of grains (Hasegawa & Herbst 1993) by cosmic rays. However, this mechanism is effective mainly for small molecules. Following Hasegawa & Herbst (1993), and assuming the binding energies of the species with water, we obtain time-scales for CO, O$_2$, H$_2$O, CH$_3$OH and CO$_2$ of $10^{14}$, $10^{14}$, $3 \times 10^{41}$, $2 \times 10^{19}$ s and $10^{22}$ s, respectively. Thus the cosmic ray-induced desorption mechanism is completely ineffective for H$_2$O, CH$_3$OH and CO$_2$, and weakly effective for CO and O$_2$ at much later times. In addition to this, Shen et al. (2004) argued that Hasegawa & Herbst (1993) overestimated the desorption rate resulting from cosmic ray heating. They assumed that the sublimation of volatile species such as CO occurs near 70 K, but it is not possible for a cosmic ray particle to heat a bigger grain (owing to dust accretion, the size of the grain in fact increases) up to such high temperature. Finally, Shen et al. (2004) concluded that the cosmic ray-induced ultraviolet field is about 10 times more efficient in depositing energy in the ice than direct cosmic ray energy deposition. So, if we scale our calculated time-scale of desorption accordingly, we can conclude that it is again ineffective for H$_2$O($\sim 3 \times 10^{40}$ s), CH$_3$OH($\sim 2 \times 10^{18}$ s) and CO$_2$(10$^{23}$ s). For CO and O$_2$ the desorption time scale is $\sim 10^{13}$ s $\sim 10^6$ yr, which is our simulation time-scale. So we can conclude that the inclusion of these desorption mechanisms will not significantly affect our results. Garrod, Wakelam & Herbst (2007) suggested a new type of desorption mechanism in which they used the exothermicity of the surface-addition reaction to desorb product molecules from the surface. They used this mechanism parametrically for the gas–grain interaction code and found that the maximum desorption owing to this mechanism is 10 per cent. It is important only at later times (after 3–4 million years). Therefore, we have not included this type of desorption in our computation. Along with the physical processes one also needs to know what reaction pathways can lead to the formation of these molecules. All the reaction pathways that are considered in our study are listed in Table 3. We assume that water is formed through H + O $\rightarrow$ OH,

### Table 2. Energy barriers in degrees kelvin. For all species $E_b = 0.3 E_D$ is used except for atomic hydrogen, for which $E_b = 0.2857 E_D$ is used.

| Species | Silicate | H | H$_2$ | O | O$_2$ | OH | H$_2$O | CO | HCO | H$_2$CO | H$_3$CO | CH$_3$OH | CO$_2$ |
|---------|----------|---|------|---|------|----|-------|----|-----|--------|--------|--------|-------|
| H       | 350      | 350 | 45   | 350 | 45   | 350 | 650   | 350 | 350 | 350    | 350    | 350    | 350  |
| H$_2$   | 450      | 30  | 23   | 30  | 30   | 30  | 440   | 450 | 450 | 450    | 450    | 450    | 450  |
| O       | 800      | 480 | 55   | 480 | 55   | 55  | 650   | 800 | 450 | 450    | 450    | 450    | 450  |
| O$_2$   | 1210     | 69  | 69   | 69  | 69   | 1000| 1210  | 1210| 1210| 1210   | 1210   | 1210   | 1210 |
| OH      | 1260     | 1260| 240  | 240 | 240  | 240 | 240   | 240 | 240 | 240    | 240    | 240    | 240  |
| H$_2$O  | 1860     | 390 | 390  | 390 | 390  | 390 | 5640  | 1860| 1860| 1860   | 1860   | 1860   | 1860 |
| CH$_3$OH| 2060     | 2060| 2060 | 2060| 2060 | 2060| 2060  | 2060| 2060| 2060   | 2060   | 2060   | 2060 |
| CO      | 2500     | 2500| 2500 | 2500| 2500 | 2500| 2500  | 2500| 2500| 2500   | 2500   | 2500   | 2500 |

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Table 3. Surface reactions in the H, O and CO models.

| Number | Reactions | $E_d$(K) |
|--------|-----------|----------|
| 1      | H + H $\rightarrow$ H$_2$ |       |
| 2      | H + O $\rightarrow$ OH   |       |
| 3      | H + OH $\rightarrow$ H$_2$O | 2000 |
| 4      | H + CO $\rightarrow$ HCO |       |
| 5      | H + HCO $\rightarrow$ H$_2$CO | 2000 |
| 6      | H + H$_2$CO $\rightarrow$ H$_3$CO | 2000 |
| 7      | H + H$_3$CO $\rightarrow$ CH$_3$OH |       |
| 8      | O + O $\rightarrow$ O$_2$ |       |
| 9      | O + CO $\rightarrow$ CO$_2$ | 1000 |
| 10     | O + HCO $\rightarrow$ CO$_2$ + H |       |
H + OH → H$_2$O (reactions 2 and 3) (Hasegawa et al. 1992; Stantcheva et al. 2002). Recently, Ioppolo et al. (2008) suggested the formation of water through a H + O$_2$ channel, in which O$_2$ is converted to H$_2$O via H$_2$O$_2$. However, considering that water is the most abundant species on a grain surface and that there is very little observed O$_2$ and H$_2$O$_2$, we have not considered this pathway. Methanol formation through hydrogenation has been studied by three groups (Hiraoka et al. 2002; Watanbe & Kouchi 2002; Fuchs et al. 2009). Hiraoka et al. (2002) observed only formaldehyde formation, whereas Watanbe & Kouchi (2002) found efficient methanol production also. These two groups presented these apparently contradictory results in a series of papers, and the discrepancy was attributed mainly to the use of different experimental conditions, especially regarding H-atom flux. Fuchs et al. (2009) found that the formation mechanism of formaldehyde and methanol does not fundamentally change with varying flux and concluded that the surface hydrogenation of CO can safely be used to explain the majority of the methanol formed in the ISM. We have also considered methanol formation through successive hydrogenation of CO through reactions 4, 5, 6 and 7. Among these, reactions 4 and 6 have an activation barrier of 2000 K. O$_2$ is formed through reaction 9. Finally, CO$_2$ is formed through reactions 9 and 10 (Stantcheva et al. 2002).

3 PROCEDURE

We used a continuous-time random-walk Monte Carlo method to study the evolution of the grain mantle. For the sake of simplicity, we take all grains to be square-shaped and assume that each site has four nearest neighbours, as in an fcc[100] plane. In order to mimic the spherical grain structure, we assume a periodic boundary condition; that is, a species that leaves the simulation grid from one boundary re-enters from the opposite boundary. In an earlier section, we discussed all the steps that occur on a grain surface and we implement these steps in the following way. In the first step, we drop atoms/molecules after every 1/$\tau_{rec}$ s. Because we are considering three different species we have three different accretion rates for each species, depending on the number densities. Typically, for a cloud of intermediate number density and a classical grain they are 1.2 × 10$^5$ s (order of a day), 7.5 × 10$^3$ s (order of a month) and 8.75 × 10$^2$ s (order of a week) for H, O and CO, respectively, at the beginning. The location of the accreting site of the grain is determined by a random number generator. This pair would place the incoming species at the (j, k)th site of the grain, where j and k are the nearest integers obtained using the Integer function: $j = \text{int}(nR_i + 0.5)$ and $k = \text{int}(nR_j + 0.5)$. Here, $n = \sqrt{s}$, where s is the number of sites on the grain. We have considered a grain having 50 × 50 numbers of sites. It was found by Chang et al. (2005) that when the size of the simulated surface is at least 50 × 50 there is no size effect. We then scaled the result for classical grains (~10$^6$ sites). When considering the grain-mantle formation in a multilayer regime, there are two possible scenarios, depending on whether the site is already occupied or not. If the site is not occupied, then the accreted species can sit on the surface of the bare silicate grain at the randomly generated (j, k)th location. However, if the site is occupied then either a reaction between the incoming and the stationary species will occur, provided the reaction is permitted (ER mechanism), forming a new molecule, or the incoming species will diffuse through the grain according to the binding energy with the stationary species. In the second step, all the accreted species are allowed to hop. We choose 1/$\tau_{hopp}$, the hopping time of hydrogen, as the minimum time step and advance the global time by this time step. The hopping times of H, O and CO with the silicate surface at 10 K are 7.5 × 10$^{-7}$, 0.02 and 6000 s, respectively. Because the CO hopping time is much longer than that of O and of H, we have not considered the hopping of CO.

It is generally observed that the hopping time-scale is many orders of magnitude smaller than the accretion time-scale. Therefore, once one H or O lands on a grain surface, it can scan the grain very efficiently and react almost instantaneously as a result of the thermal hopping. Tunnelling also enables the mobility of hydrogen atoms and is much faster than hopping. Therefore, the inclusion of tunnelling means that the scanning can proceed even faster. However, as the accretion time-scale is not altered, there will be no major differences in our results. In an earlier paper Das et al. 2008b, we did not find any major difference between the results obtained with the hydrogen tunnelling and the hydrogen hopping. Pirronello et al. (1997a,b, 1999) did not find any experimental evidence of tunnelling either. However, many models, for example Cazaux et al. (2008), still use tunnelling for the mobility of hydrogen atoms.

In an fcc[100] plane there are four directions in which to hop. We generate random numbers for the four nearest neighbours of the diffusing species to decide the direction (n, l) in which to hop. Here we are considering all situations with the Markov chain Monte Carlo method, which is a random-walk process in which the walker will often move back and cover a place covered previously. So by considering this we automatically include the back-diffusion probability noted by Chang et al. (2005). Once again, there are two possibilities. If the site is occupied then either the species will react when the reaction is permitted or it will wait until the next hopping time. If the neighbouring site is vacant and there are no species just beneath that site then it can roll down on the (n, l)th grid until it touches some species or the bare grain surface. If the reaction between the species and the diffusing species is permitted, a new species is formed, and if not, then it can sit on the top of that species. From Table 2, it can be seen that some species are very weakly bound with the other surface species, for example O with O$_2$. Because the hopping probability is higher than that of evaporation, it is most likely that the species will drop down from the top of the weak binding species rather than evaporating from there. Finally, the species are desorbed back into the gas phase. This is also done by generating random numbers. Actually, after each hopping we generated a random number to decide if the species will hop or desorb. We have evolved our system up to a few million years, which is the typical life time of a molecular cloud.

In Das et al. (2008b), the simulations were restricted to the monolayer regime. Therefore, it was not possible to study the evolution and composition of the grain mantle with time. In this paper, we use binding energies not just between the different species with the bare olivine substrate but also with ice and with the other adsorbed species. In fact, we consider all possible binding energies to describe the system. Moreover, we also consider the freeze-out of O and CO from the gas phase. These are the major improvements with respect to our previous model. Cuppen & Herbst (2007) and Cuppen et al. (2009) also considered the formation of grain mantles. However, Cuppen & Herbst (2007) restricted themselves to the formation of water, and Cuppen et al. (2009) restricted themselves to the formation of methanol. They did not study the variation as a function of initial abundances. We have extended the study of the grain mantle by incorporating all the major grain-surface species, namely H$_2$O, CH$_3$OH and CO$_2$ and CO, which constitute nearly 90 per cent of the grain mantle composition, and we have studied the variation of the abundances with respect to the initial conditions and cloud densities.

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4 MODEL

In our calculation, only three gas-phase species, namely H, O and CO, are allowed to accrete on a silicate grain surface. In total, on a grain surface, 10 chemical reactions are considered, which can occur among these three constituents via thermal hopping. H$_2$, O$_2$, H$_2$O, H$_2$CO, CH$_3$OH and CO$_2$, as well as reactive intermediate species are formed. No gas-phase chemistry is considered, and only the initial gas-phase concentrations of CO and O are varied from model to model, while the hydrogen concentration is assumed to be constant. This will decrease the accretion rate of O and CO species with time. In other words, the freeze-out effect of these two molecules is taken into account. Because of this effect, the accretion rates of these molecules decrease and the number of these species on the grain surface will also decrease. This will, in turn, result in a decrease in the formation rate of molecules that use them.

We consider conditions that are representative of a dense cloud. In these clouds, most of the atomic hydrogen is converted into molecular hydrogen, and atomic carbon into CO via gas-phase chemistry. Therefore, we have considered the accretion of CO instead of atomic carbon. The abundances (cm$^{-3}$) of H, O and CO are shown in Table 1. These values were obtained from steady-state gas-phase model runs at total hydrogen number densities ($n_h$) of $10^3$, $10^4$ and $10^5$ cm$^{-3}$, taken from Stantcheva et al. (2002). We designate them as `low', `intermediate' and `high' density cases. Furthermore, we varied the initial abundances of O ($n_o$) and CO (n$_{CO}$) for the intermediate-density case to see the effects. We showed earlier that methanol and water can be efficiently formed in clouds of intermediate density (Das et al. 2008b). We scanned the entire parameter space to find favourable conditions for the production of water, methanol and carbon dioxide. We varied the O abundance between $7 \times 10^{-5}$ and $7 \times 10^{-4}$ and CO between $7.5 \times 10^{-4}$ and $1.5 \times 10^{-4}$ with respect to the total hydrogen. The Submillimeter Wave Astronomy Satellite (SWAS) findings of very low H$_2$O and O$_2$ give rise to a serious concern over the gas-phase O abundance. Gas- and solid-state molecules can account for about 55 per cent of the oxygen (Bergin et al. 2000). Therefore, the remaining atomic oxygen is in the gas phase, as has been found towards a few sources (Caux et al. 1999; Lis et al. 2001 and references therein). Another possibility is that there is a higher depletion of atomic oxygen onto the dust grain. Bergin et al. (2000) found that, using a C/O > 0.9, they could reproduce the SWAS observations of H$_2$O and O$_2$ abundance in star-forming cores. We have chosen a lower limit of O abundance such that we have the C/O ratio close to 1. An atomic oxygen abundance as high as $7 \times 10^{-4}$ is used to mimic the conditions in the solar neighbourhood. We chose the CO initial abundance on the basis of various available studies (Jørgensen, Schöier & van Dishoeck 2002; Wilson & Rood 1994). We consider the grain temperature to be 10 K. At this temperature, only H, O and H$_2$ have mobility, and CO is almost immobile; we therefore neglected the hopping of CO, thereby reducing the computational time. We present in this paper a few selected results from our many model runs.

5 RESULTS

We found that the formation of water, methanol and carbon dioxide on a grain surface strongly depends on the initial gas-phase abundances of O and CO and on the cloud density. The initial abundance and cloud density dictate the relative accretion rates of O and CO, thereby controlling the formation of these molecules.

5.1 Variation of abundance as a result of initial abundance

In Figs 1(a)–(l), we show the variation of abundances of selected species as a function of time for different initial conditions and for an intermediate cloud density (i.e. the total hydrogen number density is $10^4$ cm$^{-3}$). We vary the gas-phase atomic abundance between $7 \times 10^{-5}$ and $7 \times 10^{-4}$ and the CO abundance between $7 \times 10^{-5}$ and $1.5 \times 10^{-4}$ with respect to the total hydrogen number density. Table 4 summarizes the abundances of these molecules after two million years. In Fig. 1(a), the initial O abundance of $7 \times 10^{-5}$ and CO abundance of $7.5 \times 10^{-5}$ were used. We find that under this condition there is more methanol than water. The reason is that the accretion rate of CO is a little higher (7 per cent) than that of O and is used mainly to form methanol and CO$_2$, whereas O is utilized to form water, O$_2$ and CO$_2$. The next most abundant molecule is CO$_2$. It is formed mainly through reaction number 10 in Table 3. We find that at around $2 \times 10^6$ yr, the rate of formation of these molecules slowed down significantly; this is because we have considered the freeze-out effects of CO and O. As the number densities of these two species decrease in the gas phase, their accretion rates also decrease, which results in a decrease in the rate of formation of other molecules. When O and CO are heavily depleted from the gas phase, we obtain a near steady state on the grain surface. In Figs 1(b) and (c), we have decreased the initial CO abundance by a factor of half and one-fifth, respectively, for a fixed O abundance, which results in a decrease in methanol and an increase in water abundance. Water accounts for nearly 60 and 80 per cent of the grain mantle, respectively. The methanol abundance is 52 and 20 per cent with respect to water, and the CO$_2$ abundance is 9 and 3 per cent, respectively (Table 4).

At this stage, it is pertinent to ask how close these results are to the observed values. We find that in almost all cases methanol is overestimated and CO$_2$ is underestimated (Keane et al. 2001). In Fig. 1(d), we increase the abundance of O. The net effect is a decrease of methanol and a small increase in the abundance of molecular oxygen. Once again, if we compare this set with the observed value (Keane et al. 2001), we find that the abundances of water and CO$_2$ are close to observed values. However, the methanol is overproduced. In Fig. 1(e), we decreased the abundance CO by half, which results in a further reduction of methanol. For this case, the abundances of methanol and water are in close agreement with the observed values in GL 7009S. However, the abundance of CO$_2$ is nearly half of the observed abundance. In Fig. 1(f), the CO$_2$ abundance is one-fifth, and ~90 per cent of the grain mantle is made up of water. This is understandable because, with this initial condition, the accretion rate of O is nearly one order of magnitude greater than the accretion rate of CO. Next we increase the initial O abundance by a factor of five (Fig. 1g). Once again, the water is the most abundant species, methanol and CO$_2$ are within the observed limits, but a substantial increase in the abundance of molecular oxygen is seen. Thus a high abundance of molecular oxygen could be found in an oxygen-rich environment. In Figs 1(h) and (f), results are shown for half and one-fifth CO abundance. The abundance of CO in most cases is very low. This is because CO in a grain is rapidly converted into methanol and CO$_2$. Finally, we increased the O abundance 10 times and found substantial increases in molecular oxygen abundance (Figs 1, j, k and l).

In Fig. 2, a cross-sectional view of the mantle structure after one million years is shown. An O abundance of $1.05 \times 10^{-4}$ and a CO abundance of $1.5 \times 10^{-3}$ were used in the simulation. In this case, water forms about 85 per cent of the grain mantle, methanol about 13 per cent and CO$_2$ about 3 per cent of water. The total number of
Fig. 1. Time variation of major grain-surface species for different initial abundances of CO and O. Chosen CO abundances are $7.5 \times 10^{-5}$ (first column), $3.75 \times 10^{-5}$ (second column) and $1.5 \times 10^{-5}$ (third column).

The number of mono-layers formed is 85. The species having less than 1 per cent surface coverage are not shown in the figure.

In Figs 3 and 4, we show the variation of the final mantle abundance of selected species as a function of the initial abundance of gas phases O and CO. This figure is analogous to Fig. 1. In Fig. 1 we showed results as a function of time, and in these two figures we have plotted abundances of selected species as a function of accreted gas-phase O and CO abundances. In Fig. 3, each column represents a fixed value of CO: $7.5 \times 10^{-5}$ (first column), $3.75 \times 10^{-5}$ (second column) and $1.5 \times 10^{-5}$ (third column) with respect to the total hydrogen number density, and initial gas-phase O abundances ranging from $7 \times 10^{-5}$ to $7 \times 10^{-4}$ with respect to the total hydrogen number density. The purpose of this plot is to gain an idea of how absolute abundance changes with initial conditions. With increasing gas-phase O, the production of oxygenated species such as H$_2$O, O$_2$ and CO$_2$ increases, whereas the production of methanol decreases. Grain-phase CO also less populated with the increase in initial gas phase O as CO are mostly converted to CO$_2$. O$_2$ and CO$_2$ also increase with the increase in the gas-phase O and CO abundances.

5.1.1 Grain-mantle thickness

In Fig. 5, we show the time evolution of the number of mono-layers for initial gas phases of CO = $7.5 \times 10^{-5}$, $3.75 \times 10^{-5}$ and $1.5 \times 10^{-5}$ and for the various values of gas-phase O noted on the right-hand side of the box. It is found that the mantle thickness is a function of initial gas-phase abundance and that the thickness varies between 60 and 500 mono-layers. For higher initial abundances, the accretion rate is high, which results in greater grain-mantle thickness because now the grain has more matter to process.

5.1.2 Parameter space and zone of interest

By varying the initial abundances of O and CO we find that in almost all cases water is the most abundant species. The next most abundant
species is methanol, which is generally contrary to the various observational results. The next most abundant species is CO$_2$, which is generally close to the observed values. This prompted us to run our code for a wide set of parameters to ascertain the parameter space in which these molecules are produced in the observed range. The results are presented in Figs 6(a), (b) and (c). We plot water, methanol and CO$_2$ coverages on the grain mantle as a function of initial abundances of O and CO and mark the zone in which these molecules are within the observed limit. We call this the favourable zone. Thus, the favourable zone excludes abundances that are overproduced or underproduced with respect to the observed limit. Observed limits are selected using Keane et al. (2001). To find out the favourable zone we considered those cases for which at least 80 mono-layers are formed, water abundance is around 10$^{-3}$, methanol abundance is between 2 and 30 per cent of the solid-state water, and CO$_2$ abundance is between 2 and 20 per cent of the solid-state water. We find that the water abundance is close to the observed value when the CO abundance is less than 5 × 10$^{-5}$ and O is between 3.5 × 10$^{-5}$ and 7 × 10$^{-4}$. Methanol is close to the observed value when CO$_2$ abundance is between 7.5 × 10$^{-6}$ and 1.5 × 10$^{-4}$ and O is between 3.5 × 10$^{-5}$ and 7 × 10$^{-4}$. Similarly, with CO$_2$, this zone for CO is between 1.5 × 10$^{-5}$ and 7.5 × 10$^{-5}$ and O between 3.5 × 10$^{-5}$ and 7 × 10$^{-4}$. In Fig. 6(d), we have superimposed favourable zones from all three species to see whether there is any region that is common to all three favourable zones. It can clearly be seen that only in a very narrow region of the parameter space could the observed abundances be roughly reproduced.

5.1.3 Effect of the activation energy

We performed another exercise by increasing the activation energy of methanol formation to check whether this could reduce methanol formation. We increased the activation barrier energy by factors of 1.5, 2 and 2.5 with respect to the activation energy barrier used by several authors. An increase in activation energy up to two times has almost no effect on methanol production. However, when the activation energy is 5000 K (2.5 times higher) we find a dramatic reduction in methanol formation (Table 5). This also reduces CO$_2$ production, because the efficient formation route for CO$_2$ in our method is found to be reaction number 10 of Table 3. Under this condition, a lot of unused CO remains on the grain and an enhanced production of CO is observed.

5.2 Variation of abundance with cloud density

In Fig. 7, we plot the abundance of selected species as functions of time for various cloud densities for the initial abundance shown in Table 1, and we tabulate the results in Table 6. In the low-density case, only water and methanol are produced efficiently and their abundances are also not close to the observed limit. In the intermediate case, the most abundant species is methanol rather than water. A reasonably high amount of CO remains on the grain and an enhanced production of CO is observed.

5.3 Collapsing cloud

In a realistic molecular cloud, the density will change with time as a result of the gradual collapse of the cloud. To understand how the abundances of various species change with density we now consider a cloud that collapses over time. However, because the coupling of the grain chemistry and the gas chemistry in the presence
of a collapsing cloud is a very difficult task we make certain simplifications: we use the radial density distribution from Das et al. (2008a), where a spherically symmetric, self-gravitating, isothermal, collapsing cloud was considered. Initially this cloud is assumed to have a negligible mass. The outer boundary is at 1 parsec and the inner boundary is at \(10^{-4}\) parsec. The matter that crosses the inner boundary is assumed to form the core. Matter is injected at a constant rate at the outer boundary. In Das et al. (2008a), the cloud was divided into 100 logarithmically equally spaced grids. Here, we consider only five shells, each containing 20 grids. We take the volume average of the number densities in each shell to give an average density. We take the initial number density of various species to be same as for \(10^3\) cm\(^{-3}\) (low density, Table 1). The time evolution of the number density for a collapsing cloud is shown in Fig. 8(a). The system is evolved with time as a result of collapse and incorporating the freeze-out and desorption effects. The abundances of a few selected species are shown in Fig. 8(b), where the five data points from the five shells can be seen. Methanol varies between 60 and 100 per cent of water, a signature we observed when the cloud density was varied. Thus methanol is always overproduced. Deep inside the cloud, the methanol abundance begins to drop owing to the unavailability of H atoms. CO\(_2\) is produced within the observed limit between the outer and middle shells. As we go deep inside the cloud, however, CO\(_2\) is heavily produced. Very little O\(_2\) is produced up to the middle shells, but a substantial amount of O\(_2\) is produced deep inside the cloud. We found that, as the density increases, the H atoms are rapidly used up owing to the hydrogenation reaction. As a result, \(\text{H}_2\text{O}\) and \(\text{CH}_3\text{OH}\) are produced very efficiently in the outer shells. In the process, as the cloud collapses, the relative numbers of CO and O increase with respect to the H atom. This then favours the formation of CO\(_2\) and O\(_2\) in the inner shells. These results resemble the abundances we obtained by varying the cloud density. Thus once again we can conclude that the final abundances of the interstellar species are strongly dependent on the relative initial abundances of their constituents.

5.4 Comparison with previous works

In Das et al. (2008b), the formation of water and methanol in a mono-layer on grain surfaces was studied, neglecting the freeze-out effects of gas-phase species. In the present paper, we study the evolution of the mantle up to several tens of layers in the presence of freeze-out effects. We also identify the parameter space in which the produced water, methanol and carbon dioxide are comparable to the values observed.
We compared our results with those obtained from the rate equation method of Hasegawa et al. (1992) and display the results in Fig. 9, where ‘(m)’ denotes the Monte Carlo method and ‘(r)’ the rate equation method. We found that the difference between the Monte Carlo method and the rate equation method is negligible for H$_2$O and CH$_3$OH. However, for the species with smaller abundances, the differences are significant. For instance, our production of CO$_2$ on grains via reaction 10 of Table 3 is more efficient (than that via reaction 9), when HCO is a reactant. In the rate equation method, it is likely that CO$_2$ would be estimated incorrectly owing to the very low abundance of HCO on the grain. This is reflected in Fig. 9. Discrepancies in other species can be similarly explained. The species with higher abundances are not affected because the rate equation method is valid in this regime. In this regard we can compare our results with various previous works. Stantcheva et al. (2004) considered a gas–grain coupled network to study the chemical evolution of a static molecular cloud. As with our approach, their model also seems to be efficient for the production of methanol. The major differences from our results are that at the end we obtain significant amounts of solid CO and CO$_2$, whereas their results show virtually no solid CO and little solid CO$_2$. In Ruffle & Herbst (2000), a complete network of surface reactions was considered to study the quiescent source in front of the field star Elias 16. These authors were able to reproduce the CO abundances and upper limit to the methanol abundances by considering much lower diffusion rates than the diffusion rates used here. However, none of their models was able to produce significant amounts of CO$_2$.

While comparing our results with other multilayer methods, we note that Cuppen & Herbst (2007) studied the formation of water on grain surfaces for diffuse, translucent and dense clouds. The most striking difference of Cuppen & Herbst (2007) from the present work is that they did not include methanol formation at all. In our case, the H atom is partially used up to form methanol. Furthermore, in the absence of a few important species on the grain, such
as methanol, carbon monoxide etc., they always found that water dominates the grain mantle. By contrast, we found that, for C/O ≥ 1, methanol is produced more than water. Recently, Cuppen et al. (2009) studied the surface formation of CH$_3$OH and H$_2$CO from precursor CO using the continuous-time, random-walk Monte Carlo method. They found the formation of both species to be very efficient, and the efficiency to depend mainly on the grain temperature and the abundance ratio of H and CO in the gas phase. They also found that the freeze-out of CO favours more complete hydrogenation of CO to form CH$_3$OH. We indeed found that the methanol is formed very efficiently. However, in most cases formaldehyde in our case is less than 1 per cent, while it is somewhat higher in Cuppen et al. (2009). Another difference from Cuppen et al. (2009) is that we have considered the accretion of O also on the grain surface and thus we find that some fraction of the mantle is covered with O$_2$ and CO$_2$. Through varying the initial cloud composition (by changing the initial gas-phase O and CO), we found that in a narrow region of parameter space (Fig. 6d) our model produces H$_2$O, CO$_2$ and CH$_3$OH within the observed limits. In other regions of the parameter space we have an anti-correlation between the production of CH$_3$OH and CO$_2$ and that of H$_2$O.

6 CONCLUSIONS

In this paper we have carried out numerical simulations using a continuous-time random-walk Monte Carlo method to investigate the formation of water, methanol and CO$_2$ as a function of the cloud density and the initial abundances of CO and O. We found that when the accretion rate of CO is higher than that of O, methanol is the most abundant species on the grain surface. With an increase in the accretion rate of O over CO, the methanol abundance gradually decreases. When the accretion rate of O is 1.4 times that of CO, the water abundance is more than that of methanol; that is, a crossover is seen. One has to increase O/CO by a factor of 3 to obtain a methanol abundance that is ∼30 per cent, the maximum abundance of methanol seen in molecular clouds (Keane et al. 2001). When the accretion rate of O is increased further, methanol starts to be reduced, and this trend continues. When we increase the ratio O/CO by a factor of more than 10, although water is the most abundant molecule on the grain surface, we observe a surge in O$_2$ abundance. We scanned the entire parameter space and found that in the clouds having O/CO < 3, methanol is overproduced. This criterion is true only when there is no depletion, because we have more O than CO to start with. Once the accretion process sets in, the gas-phase species will be depleted onto the grain and we will have clouds with
different C/O ratios. For cloud conditions in which the C/O ratio is less than 0.33, water is found to be produced very efficiently on the grain surface. We concede that matching CO\(_2\) abundance with the observational results still remains a problem. We found that CO\(_2\) is mainly formed through reaction no. 10 in Table 3; that is, it requires HCO to form. Therefore, conditions that lead to a decrease in methanol formation also decrease the formation of CO\(_2\). We have also checked the effects of increasing the activation barrier energy for methanol formation, but the result is not improved as far as matching with observed abundances is concerned. We also failed to match with observed abundances by changing the cloud density only. However, when we superimpose the favourable formation zones of H\(_2\)O, CH\(_3\)OH and CO\(_2\) we do obtain a narrow region in which all these molecules are produced within the observed limits. To have a more realistic estimation of the abundances of various interstellar species in the different regions of the molecular cloud, we also considered a collapsing cloud and coupled the time evolution of the density distribution with our Monte Carlo approach to the grain chemistry. We noticed that throughout the cloud CH\(_3\)OH is always overproduced. Deep inside the cloud CO\(_2\) and O\(_2\) are

Table 6. Relative abundances of the ice species in different regions of the interstellar cloud.

| Species | Low  | Intermediate | High |
|---------|------|--------------|------|
| H\(_2\)O | 100  | 100          | 100  |
| CO      | 0.7  | 3            | 160  |
| H\(_2\)CO | 0.02 | 0.2          | 13   |
| CH\(_3\)OH | 68   | 116          | 146  |
| CO\(_2\) | 2.5  | 23           | 143  |
| O\(_2\) | 0.5  | 5            | 96   |

Figure 7. Time evolution of selected species for various cloud densities.

Figure 8. Time evolution of (a) gas number density and (b) final abundances of selected species in different regions of a collapsing cloud.
Figure 9. Comparison of results from Monte Carlo simulation (m) and rate equation (r) methods.

heavily produced, whereas at the outer edge their production gradually decreases.

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