Astronomy
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Astrophysics

On the master equation approach to diffusive grain-surface chemistry: The H, O, CO system

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Abstract. We have used the master equation approach to study a moderately complex network of diffusive reactions occurring on the surfaces of interstellar dust particles. This network is meant to apply to dense clouds in which a large portion of the gas-phase carbon has already been converted to carbon monoxide. Hydrogen atoms, oxygen atoms, and CO molecules are allowed to accrete onto dust particles and their chemistry is followed. The stable molecules produced are oxygen, hydrogen, water, carbon dioxide (CO_2), formaldehyde (H_2CO), and methanol (CH_3OH). The surface abundances calculated via the master equation approach are in good agreement with those obtained via a Monte Carlo method but can differ considerably from those obtained with standard rate equations.

Key words. ISM: abundances – ISM: molecules – molecular processes

1. Introduction

Rate equations have been widely used in simulations of gas-phase processes in the interstellar medium (Le Teuff et al. 2000). Their application has also been extended to treat diffusive reactions on the surfaces of dust particles (Pickles & Williams 1977; Hasegawa et al. 1992). This approach, however, is valid only if the average number of reactive surface species per grain is large and the discrete nature of the system can be neglected. When this number becomes small, the rate equations may no longer constitute an accurate description of the chemical processes (Tielens & Hagen 1982); moreover, for species with surface populations less than one, it can become meaningless to use the rate equations (Charnley et al. 1997; Caselli et al. 1998).

This problem has spurred attempts to develop alternative methods for handling diffusive reactions on granular surfaces. One possible solution is to use Monte Carlo procedures to simulate the grain-surface chemistry. Different methods, based on Monte Carlo simulations, have already been employed for various grain surface networks (Tielens & Hagen 1982; Charnley et al. 1997; Charnley 2001; Caselli et al. 2002). These simulations were performed under the constraint that, during the evolution of the surface chemistry, the gas-phase abundances of all species stay constant – a requirement that cannot be met in complex gas-grain models, where it is essential that the

gas-phase and the grain-surface reactions run in a parallel mode during the calculations and that both adsorption onto and desorption from grain surfaces occur (Ruffle & Herbst 2000). It does not appear possible, however, to follow simultaneously the gas-phase chemistry with rate equations and the surface chemistry with a Monte Carlo approach. Although one can use the Monte Carlo method to simulate gas-phase reactions (Charnley 1998), a Monte Carlo solution for both gas-phase and grain-surface chemisty could be done only with an exceedingly large amount of computing time, and has not yet been attempted. Current gas-grain chemical models (e.g. Ruffle & Herbst 2000) use a semi-empirical modification of the standard rate equations for diffusive surface chemistry known as the "modified rate approach" (Caselli et al. 1998; Stantcheva et al. 2001; Caselli et al. 2002). Although this approach is efficient, its semi-empirical nature raises doubts of its suitability under all conditions.

Recently, two groups (Biham et al. 2001; Green et al. 2001) proposed a second stochastic approach to granular chemistry, known as the master equation treatment. In this approach, differential rate equations for species with a small surface abundance are replaced by differential equations in which one solves for the probability that a specific number of atoms or molecules of that species (0, 1, . . .) is present on a grain at any time. In general, the probabilities for each surface species are not independent and so an exact treatment requires the determination of joint probabilities (e.g., for 0 of species A, 1 of species B, etc.). Green et al. (2001) used the master equation method to study

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the simple O, H system; in this system O and H atoms, with fixed gas-phase abundances, are allowed to adsorb onto grains and react to produce the three molecules OH, O_2, and H_2 via diffusive processes. For this system, determination of the surface populations of the minor but important species H and O requires the calculation of two-body probabilities, while surface abundances of the diatomic species can be calculated from normal rate equations. The two-body probability approach to the simple O, H system can itself be simplified by a number of approximate methods (Green et al. 2001). One approximation, proposed by Biham et al. (2001) but not attempted by Green et al. (2001), reduces the two-body probability to independent probabilities for the individual species O and H. With this approach, the so-called "many-body" master equation reduces to separate master equations for the individual species. Although the approximation leads to a significantly smaller number of simultaneous differential equations to solve, its validity is not clear for systems with strong correlations between the surface abundances of the different minor species.

If one attempts to scale up the many-body master equation approach to model realistic complex networks of surface reactions, one can experience serious problems involving both computer time and memory, unless suitable approximations can be found. In order to learn more about the use of the method for larger systems, we have considered an intermediate system more complex than previously studied but not at the level of complexity needed for a complete network of surface reactions. In particular, we report here the use of the many-body master equation approach to solve a grain-surface chemical network in which gaseous H, O, and CO accrete onto grain surfaces and lead to the production of molecular hydrogen, formaldehyde, methanol, water, oxygen, and carbon dioxide (Caselli et al. 2002; see also Charnley et al. 1997). This system has previously been studied by the modified rate and Monte Carlo approaches (Caselli et al. 2002). We consider here a variety of different diffusive rates and temperatures to see how the master equation approach fares. As opposed to the previous treatments based on the master equation, we utilize a time-dependent approach designed eventually to be coupled with a time-dependent gas-phase chemistry, since the advantage of the direct solution of the master equation compared with the Monte Carlo realization is that the differential equations are easily coupled to rate equations for the gas-phase species.

The organization of the paper is as follows. In the next section, we discuss the chemical network of diffusive surface reactions and the different rates chosen. In Sect. 3, we write out the differential equations needed to model the methanol system via the master equation approach, while in Sect. 4 we present our results, and compare them with Monte Carlo and rate approaches. A general discussion is contained in Sect. 5. In addition, a detailed mathematical discussion of the master equation and Monte Carlo realizations to stochastic kinetics is contained in the Appendix.

2. The H, O, CO Network

In this network, three gas-phase species – H, O, and CO – are allowed to accrete onto a granular surface where they react via

Table 1. H, O, and CO gas-phase abundances (cm^{-3}) utilized.

Abundance n	Low	Intermediate	High
H	1.15	1.15	1.10
O	0.09	0.75	7.0
CO	0.075	0.75	7.5

diffusion to produce the stable molecules H_2, O_2, H_2O, H_2CO, CH_3OH, and CO_2, as well as reactive intermediate species. Of the ten reactions, nine are association reactions, in which a single product is formed. No gas-phase chemistry is allowed to occur and the gas-phase concentrations of the three species are assumed to remain constant despite accretion onto grains. This somewhat contradictory assumption permits the surface chemistry to occur only over a period sufficiently short that the abundances of the gas-phase species do not change dramatically.

The calculations were carried out for three different sets of gas-phase abundances of the accreting species, known respectively as the low, intermediate, and high density cases. All of these cases refer to dense clouds in which most of the atomic hydrogen has already been converted into molecular hydrogen, leaving only a small remnant in atomic form. Such conditions pertain when a significant amount of CO has been produced via gas-phase chemistry. The abundances $n(cm^{-3})$ of H, O, and CO shown in Table 1 were obtained from steady-state gas-phase models run at molecular hydrogen densities of 10^3, 10^4, and 10^5 cm^{-3}. In the low-density case, there is more atomic hydrogen than O and CO, and the chemistry will be seen to be strongly reductive, whereas in the high-density case, there is little atomic hydrogen around to react with CO.

The surface reactions for the network are listed in Table 2 along with activation energies in K where appropriate. The activation energies E_a (K) are approximate only (Caselli et al. 2002). The total number of surface species is 12; this includes the highly reactive radicals OH, HCO, and H_3CO. The key reaction sequence in the network is the relatively slow hydrogenation of CO into methanol (CH_3OH) via H-atom addition reactions. Unambiguous laboratory evidence for this hydrogenation is not available (Hiraoka et al. 2000), but conditions in interstellar clouds are not those in the laboratory and the complete synthesis in Table 2 is by no means ruled out by experiments. Once produced, all stable species except H_2 remain on the grain surface; the evaporation of molecular hydrogen is included.

Whether one uses rate equations, the Monte Carlo approach, or the direct master equation method, it is necessary to utilize diffusion rate coefficients k for the reactive surface species (Hasegawa et al. 1992; Appendix). The rate coefficients here are in units of s^{-1}, as preferred by Caselli et al. (1998). These are the sum of the rates t_{diff}^{-1} (s^{-1}) of the reactive partners to traverse an entire grain, which is here assumed to contain 10^6 binding sites, multiplied by a factor κ that accounts for any non-zero chemical activation barrier (Hasegawa et al. 1992). The rates depend strongly on the barriers against diffusion E_b from site to site chosen, and whether diffusion occurs via thermal hopping or via quantum mechanical tunneling (Tielens & Hagen 1982).

Table 2. Surface reactions in the H, O, CO model.

Number	Reaction	E_a (K)
1	$H + H \longrightarrow H_2$	
2	$H + O \longrightarrow OH$	
3	$H + OH \longrightarrow H_2O$	
4	$H + CO \longrightarrow HCO$	2000
5	$H + HCO \longrightarrow H_2CO$	
6	$H + H_2CO \longrightarrow H_3CO$	2000
7	$H + H_3CO \longrightarrow CH_3OH$	
8	$O + O \longrightarrow O_2$	
9	$O + CO \longrightarrow CO_2$	1000
10	$O + HCO \longrightarrow CO_2 + H$	

Table 3. Energy barriers against diffusion (low values) and desorption energies (K).

Species	E_b (K)	E_D (K)
H	100	350
O	240	800
OH	378	1260
H_2	135	450
O_2	363	1210
H_2O	558	1860
CO	363	1210
HCO	453	1510
H_2CO	528	1760
CH_3O	651	2170
CH_3OH	618	2060
CO_2	750	2500

Table 4. Assorted rates for selected species at 10 K.

Species	k_{acc} (cm^3 s^{-1})	t_{evap}^{-1} (s^{-1})	t_{diff}^{-1} (s^{-1})
H	1.45(−5)	1.88(−3)	5.14(+4)[a]
O	3.62(−6)	2.03(−23)	4.24(−5)
CO	2.73(−6)		

[a] Quantum tunelling included.

In our calculation, we have considered three sets of barriers against diffusion. The first, which comes from the earlier astrochemical literature (Allen & Robinson 1977; Tielens & Hagen 1982; Hasegawa et al. 1992), contains rather low barriers and allows efficient tunneling for atomic H. The second and third are based on the recent experiments of Pirronello et al. (1997, 1999) as simulated by Katz et al. (1999), which show that atomic H moves much more slowly on olivine and amorphous carbon than previously assumed in the astrochemical literature. Two sets of barriers based on these experiments on olivine have been used (Ruffle & Herbst 2000) – one, designated "slow H", in which only the H atom barrier is raised, and the other, designated "slow", in which all other barriers are raised proportionately. In both sets of barriers, no tunneling is allowed, since no tunneling of H was detected in the laboratory. For our calculations here, the earlier astrochemical values are used principally because the slower diffusion rates cannot produce much formaldehyde and methanol in the small times considered, and so are not emphasized (Caselli et al. 2002). In our more complex gas-grain models, the slower rates have been used, and show that formaldehyde and methanol can be produced over long periods of time (Ruffle & Herbst 2000).

In addition to diffusive rates, the rates of adsorption and desorption must be included in our calculation (Hasegawa et al. 1992). Adsorption is assumed to occur at unit efficiency once a gas-phase species strikes a grain. We consider only thermal desorption (evaporation) and treat it as in previous models (see e.g. Caselli et al. 1998); the rates, exponentially dependent on the desorption energy E_D, are included for the accreting gas-phase species and for molecular hydrogen product. Heavy molecular species desorb too slowly for this process to be considered here. The small barriers against diffusion and the desorption energies for all species in the model are listed in Table 3.

Table 4 gives our values for the accretion rate coefficients k_{acc} (cm^3 s^{-1}) onto a grain, the evaporation rates t_{evap}^{-1} from the grain, and the diffusion rates for the species H, O, and CO at 10 K, unless they are vanishingly small. Calculations have been done mainly at this temperature, although temperatures up to 20 K have been considered.

3. Master equation for H, O, CO system

Of the three species – H, O, and CO – that accrete onto grain surfaces, the first two are very reactive and never build up large surface populations. On the other hand, CO reacts only slowly via reactions with activation energy and so can build up a large surface population under certain circumstances. In general, all surface species in our network can be classified as either major or minor species. The major ones correspond to the stable species that react slowly if at all (CO, H_2CO, CH_3OH, H_2O, O_2, H_2, CO_2) and can build up large abundances, while the minor ones are atoms and radicals likely to have a surface number, defined as the number of species per grain, at or below unity. We treat the minor species – H, O, OH, HCO, and H_3CO – probabilistically with corresponding surface numbers i_1, i_2, i_3, i_4, and i_5.

The first step in the master equation approach is to solve for the joint probability $P(i_1, i_2, i_3, i_4, i_5)$, defined as the probability that i_1, i_2, i_3, i_4, and i_5 numbers of minor species exist on the surface as a function of time. In the calculations discussed here, we start with the initial condition that the joint probability is unity for $P(0, 0, 0, 0, 0)$. Let X and Y be, respectively, the jth and kth reactive elements of the ordered set {H, O, OH, HCO, H_3CO}. Let Z represent any of the major

species. The time derivative of the five-body probability for each value of i_1, i_2, i_3, i_4, i_5 can then be written as (Appendix)

$$
\begin{aligned}
\frac{dP}{dt}(i_1, i_2, i_3, i_4, i_5) = \\
\sum_{\{X\}} k_{acc}(X) n(X) \Big[P(..., i_j - 1, ...) - P(..., i_j, ...) \Big] \\
+ \sum_{\{X\}} t_{evap}^{-1}(X) \Big[(i_j + 1) P(..., i_j + 1, ...) - i_j P(..., i_j, ...) \Big] \\
+ \sum_{\{X,Y\}} k_{X,Y} (i_j + 1)(i_k + 1) P(..., i_j + 1, ..., i_k + 1, ...) \\
- \sum_{\{X,Y\}} k_{X,Y} (i_j)(i_k) P(..., i_j, ..., i_k, ...) \\
+ \sum_{\{X\}} k_{X,X} \frac{(i_j + 2)(i_j + 1)}{2} P(..., i_j + 2, ...) \\
- \sum_{\{X\}} k_{X,X} \frac{i_j(i_j - 1)}{2} P(..., i_j, ...) \\
+ \sum_{\{X,Z\}} \langle N_Z \rangle k_{X,Z} \Big[(i_j + 1) P(..., i_j + 1, ...) \Big] \\
- \sum_{\{X,Z\}} \langle N_Z \rangle k_{X,Z} \Big[i_j P(..., i_j, ...) \Big],
\end{aligned}
\tag{1}
$$

where n stands for gas-phase concentration and $\langle N \rangle$ for surface abundance; i.e., the average number of atoms or molecules per grain of a species.

The first term on the right-hand side of Eq. (1) accounts for changes in the state of the surface on a particular grain due to accretion of species. In this particular case, the sum consists of two terms because the only accreting species with minor surface abundance are H and O. The second term describes the changes of the system due to evaporation, and the remaining terms take into account any changes due to surface reactions. These terms are subdivided into expressions for reaction between two distinct minor species (X, Y), for self-reaction (X, X), and for reaction between a minor and a major species (X, Z). Note that all of the terms refer to reactants; there is also one minor product – H atoms in reaction 10 of Table 2. To include the production of H in Eq. (1) requires a term which, when X and Y are equal to O and HCO, contains probability functions where three indices change. We have not included this term in Eq. (1) for simplicity, but it is of course included in our calculations. The average abundances of the major species are obtained from rate equations discussed below. It is easily shown that the total probability as a function of time is conserved at unity.

Because the abundances of minor species are low, joint probabilities with high numbers of these particles are very unlikely and therefore, the probabilities for such states can be neglected. In particular, we choose a set of parameters $\mathcal{N} = \{\mathcal{N}_1, \mathcal{N}_2, \mathcal{N}_3, \mathcal{N}_4, \mathcal{N}_5\}$ such that the only probabilities $P(..., i_j, ...)$ to be considered possess $i_j \leq \mathcal{N}_j, j \in \{1, 2, 3, 4, 5\}$. Specific

choices for the set $\mathcal{N}$ are discussed in the Results section. It is obvious that for the master equation method to be feasible, the set $\mathcal{N}$ must contain elements as small as possible.

Once the probabilities are determined by integration for a specific time, the average numbers of minor species, $\langle N_H \rangle$, $\langle N_O \rangle$, etc., as well as the correlation terms $\langle N_H N_O \rangle$, $\langle N_H N_{OH} \rangle$, etc., can be calculated from these probabilities; e.g.,

$$
\langle N_H \rangle = \sum_{i_1, i_2, i_3, i_4, i_5}^{\mathcal{N}} i_1 P(i_1, i_2, i_3, i_4, i_5).
\tag{2}
$$

Both average numbers and correlations are then used in the rate equations for the abundance of the major surface species, while the latter can also be used to test how independent or correlated the minor species are. In the rate equations for major species, shown below, the division of species into major and minor ones leads to the fact that correlations are only used for pairs of minor species:

$$
\begin{aligned}
\frac{d\langle N_{H_2} \rangle}{dt} &= -t_{evap}^{-1}(H_2) \langle N_{H_2} \rangle \\
&+ k_{H,H} \times 0.5 \times \langle N_H (N_H - 1) \rangle,
\end{aligned}
\tag{3}
$$

$$
\frac{d\langle N_{O_2} \rangle}{dt} = k_{O,O} \times 0.5 \times \langle N_O (N_O - 1) \rangle,
\tag{4}
$$

$$
\frac{d\langle N_{H_2O} \rangle}{dt} = k_{H,OH} \times \langle N_H N_{OH} \rangle,
\tag{5}
$$

$$
\begin{aligned}
\frac{d\langle N_{CO} \rangle}{dt} &= k_{acc}(CO) n(CO) \\
&- k_{H,CO} \langle N_{CO} \rangle \langle N_H \rangle - k_{O,CO} \langle N_{CO} \rangle \langle N_O \rangle
\end{aligned}
\tag{6}
$$

$$
\begin{aligned}
\frac{d\langle N_{H_2CO} \rangle}{dt} &= k_{H,HCO} \langle N_H N_{HCO} \rangle \\
&- k_{H,H_2CO} \langle N_{H_2CO} \rangle \langle N_H \rangle
\end{aligned}
\tag{7}
$$

$$
\frac{d\langle N_{CH_3OH} \rangle}{dt} = k_{H,H_3CO} \langle N_H N_{H_3CO} \rangle,
\tag{8}
$$

$$
\frac{d\langle N_{CO_2} \rangle}{dt} = k_{O,CO} \langle N_{CO} \rangle \langle N_O \rangle + k_{O,HCO} \langle N_O N_{HCO} \rangle.
\tag{9}
$$

3.1. Approximation of independent probabilities

Considering the large number of coupled differential equations for the many-body P required in the exact master equation approach, it is perhaps useful to consider whether the use of one-particle probability functions is adequate. This approach was suggested but not tested by Biham et al. (2001) for the simple O, H system, and leads to a different and somewhat simpler system of differential equations. The H, O, CO system reduces to the O, H system if no CO is allowed to accrete onto grains and the OH radical is treated as unreactive. Biham et al. (2001) used the notation $P_H(i)$ and $P_O(j)$ for the (independent) probabilities that i H atoms and j O atoms are on the surface, respectively.

For $X, Y \in \{H, O\}$, the equation for the probability that species X has i atoms is

$$
\begin{aligned}
\frac{\mathrm{d}P_X}{\mathrm{d}t}(i) =\ & k_{\mathrm{acc}}(X)n(X)[P_X(i-1) - P_X(i)] \\
& + t_{\mathrm{evap}}^{-1}(X)[(i+1)P_X(i+1) - iP_X(i)] \\
& + k_{X,X}\left[\frac{(i+2)(i+1)}{2}P_X(i+2) - \frac{i(i-1)}{2}P_X(i)\right] \\
& + k_{X,Y}\langle N_Y\rangle[(i+1)P_X(i+1) - iP_X(i)]
\end{aligned} \tag{10}
$$

with initial conditions: $P_H(0) = 1$ and $P_O(0) = 1$. Note that species X depends on species Y only through its average abundance.

The rate equations for the major species are in the form

$$
\begin{aligned}
\frac{\mathrm{d}\langle N_{\mathrm{OH}}\rangle}{\mathrm{d}t} &= k_{\mathrm{O,H}} \times \sum_{i_1=1}^{\infty} i_1 P_H(i_1) \times \sum_{i_2=1}^{\infty} i_2 P_O(i_2) \\
&= k_{\mathrm{O,H}} \times \langle N_H\rangle\langle N_O\rangle, \tag{11}
\end{aligned}
$$

$$
\begin{aligned}
\frac{\mathrm{d}\langle N_{\mathrm{H_2}}\rangle}{\mathrm{d}t} &= k_{\mathrm{H,H}} \times \sum_{i_1=2}^{\infty} \frac{i_1(i_1-1)}{2} P_H(i_1) \\
&= k_{\mathrm{H,H}} \times \frac{\langle N_H(N_H-1)\rangle}{2}, \tag{12}
\end{aligned}
$$

$$
\begin{aligned}
\frac{\mathrm{d}\langle N_{\mathrm{O_2}}\rangle}{\mathrm{d}t} &= k_{\mathrm{O,O}} \times \sum_{i_2=2}^{\infty} \frac{i_2(i_2-1)}{2} P_O(i_2) \\
&= k_{\mathrm{O,O}} \times \frac{\langle N_O(N_O-1)\rangle}{2}. \tag{13}
\end{aligned}
$$

For the production of OH, the average abundances of O and H appear as independent products rather than as a correlation, which would be the case if the minor (H, O) species were determined with a two-body probability function.

3.2. Implementation

The calculations were performed with the use of a Gear algorithm on a Cray SV1 computer. To enhance the performance, the equations were supplied by a subroutine which wrote them in an explicit form. Calculations were virtually all performed to a time of 1000 yr, which is rather short by astronomical scales, but is more than sufficient to allow the minor species to reach a steady-state condition and the major species to increase linearly with time. We have investigated how the needed computer time depends on the astronomical time scale and find that for the system studied, there is hardly any difference in computer time if the astronomical time is increased 100-fold. To increase the stability of the calculation, after every call of the equation-solving routine, the total sum of the many-body probabilities was evaluated and the amount by which it deviated from unity was added to the probability for the state with no minor species.

4. Results

Unless we state that slow H or slow rates are being used, the results below are for the fast rates discussed in Sect. 2. The fast diffusion rates are emphasized both because they allow the rapid production of methanol and because they cause a larger discrepancy between the results of the standard rate equations

Table 5. Abundances and correlations for the H, O system.

| Average	Exact	Approx.
$\langle N_H\rangle$	6.24(−03)	5.69(−03)
$\langle N_O\rangle$	1.82(−01)	1.23(−08)
$\langle N_H\rangle\langle N_O\rangle$	1.14(−03)	7.00(−11)
$\langle N_H N_O\rangle$	4.80(−11)	−

and more exact methods. Unless stated to the contrary, the temperature is fixed at 10 K.

## 4.1. Check of the independence approximation

Before proceeding to our main results, it is interesting to check the validity of the suggestion by Biham et al. (2001) that independent probabilities be utilized. We have used the simple O, H system for a comparison among the following five methods: the Monte Carlo approach (Charnley 2001; Appendix), the master equation approach, the approximation to the master equation approach of Biham et al. (2001), the rate equation approach, and the modified rate equation approach (Stantcheva et al. 2001). Calculations were performed at a fixed concentration of gas-phase atomic oxygen (1 cm^{-3}) and a variable concentration of gas-phase atomic hydrogen. No desorption of the products was allowed. In the master equation calculations, the maximum allowed numbers $\{\mathcal{N}_i\}$ for H and O were never larger than 5.

Figures 1–3 show the mole fractions of the three diatomic molecules, calculated by the various approaches as functions of the gas-phase atomic hydrogen abundance. For the range of conditions investigated, the exact master equation (Exact ME) and the Monte Carlo simulation (Appendix) show excellent agreement for all three species. The independent probability approximation of Biham et al. (2001) (Approx. ME) follows the inaccurate results of the rate equations for O$_2$, is in good agreement with the exact approaches for H$_2$, and is in tolerable agreement for OH except at very low gas-phase H concentrations, where it approaches the inaccurate rate equation results. In general, the semi-empirical modified rate equation approach outperforms the independent probability approximation. Biham (private communication) has reported better success with the approximation for slower diffusion rates, so one should not rule it out for all situations.

Another test of whether or not an approximation based on independent probabilities is useful is to compare various correlations and averages computed with both the exact and the approximate master equation approaches. In Table 5, we list the average surface abundances and correlations for the atomic H and O when $n(H) = n(O) = 1$ cm^{-3}. We can see that the values calculated with both approaches are in mixed agreement, just as Figs. 1–3 suggest. For example, while the hydrogen surface abundance is almost identical in both cases, the oxygen abundances differ from each other by almost seven orders of magnitude. Moreover, the correlation $\langle N_H N_O\rangle$ is nowhere near the product of the individual averages when calculated by the exact approach.
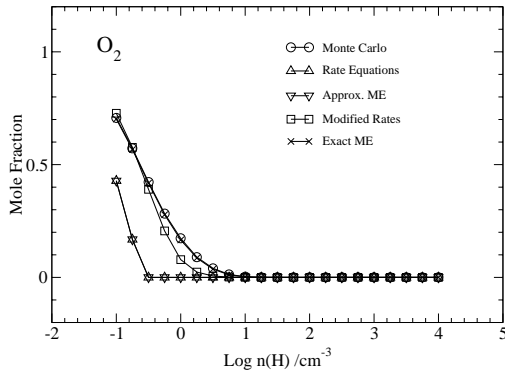
Fig. 1. H, O system. Mole fraction of surface molecular oxygen determined via various methods plotted vs. the gas-phase concentration of H for a 10 K system.
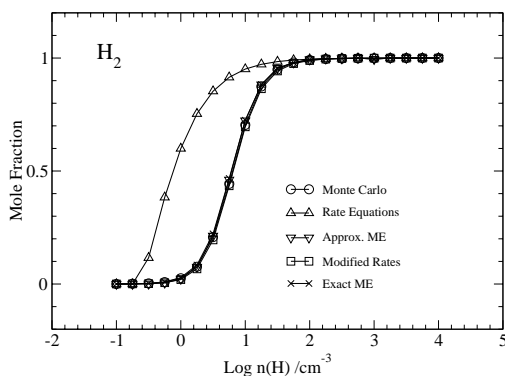
Fig. 2. H, O system. Mole fraction of surface molecular hydrogen determined via various methods plotted vs. the gas-phase concentration of H for a 10 K system.
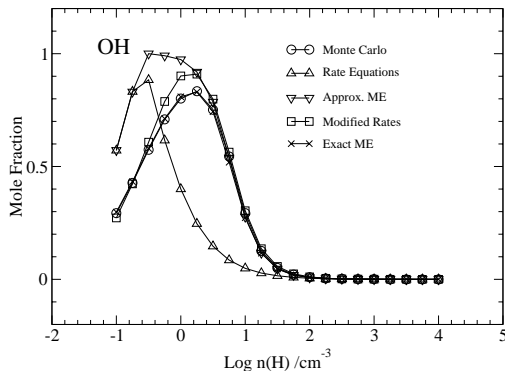
Fig. 3. H, O system. Mole fraction of surface OH determined via various methods plotted vs. the gas-phase concentration of H for a 10 K system.

4.2. H, O, CO system

For this system, we performed calculations at the three densities shown in Table 1 using the simple rate equation, Monte Carlo, and master equation methods. For the master equation calculations, the set of minimum $\mathcal{N}_i$'s which must be used is {2, 2, 1, 1, 1}, since it is necessary to consider at least two atoms of H and O on the surface for the production of H_2 and O_2, respectively. Calculations were first performed with this minimal cutoff for the five minor species, and the results checked

by comparison with the Monte Carlo method, and by increasing the $\mathcal{N}_i$'s. In general, one can get a picture of what cutoff is needed for each species by looking at the average number of each minor species calculated at a given cutoff, or even the number obtained via the rate equation method. If this number approaches unity, then a higher cut-off is needed, and if it exceeds unity, then it is reasonable to treat the species as a major one not requiring inclusion in the many-body probability P.

Because the steady-state criterion leads to the fact that the surface abundances of O and OH in all three density cases are approximately equal, we raised the cut-off of OH from 1 to 2 leading to $\mathcal{N}_i$'s of {2, 2, 2, 1, 1}, which should produce more accurate results. In the case of high density, however, the O and OH abundances are sufficiently high (see the detailed discussion below) that we also tried the case {2, 3, 3, 1, 1}. Any further increase of $\mathcal{N}_i$'s led to an increase in the computing time without changing the results significantly. After the following discussion, we turn to analogous calculations with slow diffusion rates, where the cutoff problem is more severe.

The calculated surface populations at 10 K for low, medium, and high density are shown, respectively, in Tables 6–8 for a time of 10^3 yr. In addition to the individual populations, the total number of surface species is shown, as is the CPU time utilized for the calculation. It can be seen that at most one monolayer is built up during the time of the calculation. With the normal assumptions, one monolayer of material corresponds to a fractional abundance with respect to the total gas density of 10^{-6}. It is to be remembered that only major species can be detected on grain surfaces (or in subsequent evaporation into the gas during star formation) so that inaccuracies in minor species need not pose a critical problem.

With the large diffusion rates, the minor species (H, O, OH, HCO, and CH_3O) all have exceedingly low abundances (<1 per grain), a situation known as the "accretion limit". Such abundances are not capable of being determined accurately by the Monte Carlo method, which yields integers only. Occasionally we have run the simulations several times and averaged the results, so that non-integers can be obtained. In the accretion limit, the rate equations should not reliably yield accurate answers for the stable species, and it is easy to see from the tables that such can be the case here. Concerning the more accurate methods, the minimal master equation method (designated 22111; note that the commas have been removed) takes about as little CPU time as the rate equation approach and never yields results more than a factor of two different from the Monte Carlo approach for species which can be compared. The latter method is significantly more computer intensive. The master equation calculation with cutoffs 22211 is typically even better, but at the expense of a factor of three in computer time. For the high density case, the oxygen atom abundance is 0.5, and increasing the cutoffs to 23311 improves the agreement with the Monte Carlo method but, again, at the expense of increased computer time. We conclude that under these physical conditions, the minimal master equation method is a fast and reliable appoach for the H, O, CO system. Although the results for the modified rate method were not presented, this approach typically does better than the simple rate method but worse than the other approaches.

Table 6. Calculated populations for surface species at low density and 10^3 yr.

Species	Rate eq.	Monte Carlo	Master Eq. 22111	Master Eq. 22211
Total	1.69(+04)	1.65(+04)	1.63(+04)	1.65(+04)
Total (monolayers)	1.68(−02)	1.65(−02)	1.63(−02)	1.65(−02)
H	1.21(−05)	1.00(+00)	7.96(−03)	7.96(−03)
O	5.21(−07)	0.00(+00)	1.92(−02)	1.90(−02)
OH	5.21(−07)	0.00(+00)	1.86(−02)	1.93(−02)
H_2	1.11(+02)	2.00(+00)	1.94(+00)	1.94(+00)
O_2	3.64(−07)	1.70(+02)	1.62(+02)	1.62(+02)
H_2O	1.03(+04)	9.90(+03)	9.65(+03)	9.86(+03)
CO	1.51(+02)	0.00(+00)	2.81(−02)	2.81(−02)
HCO	3.28(−07)	0.00(+00)	1.22(−02)	1.22(−02)
H_2CO	1.55(+02)	0.00(+00)	2.82(−02)	2.83(−02)
H_3CO	3.28(−07)	0.00(+00)	1.23(−02)	1.23(−02)
CH_3OH	6.17(+03)	6.40(+03)	6.28(+03)	6.39(+03)
CO_2	2.24(−07)	9.00(+01)	8.95(+01)	8.95(+01)
CPU (s)	0.5	11	1	3

Table 7. Calculated populations for surface species at intermediate density and 10^3 yr.

Species	Rate eq.	Monte Carlo	Master Eq. 22111	Master Eq. 22211
Total	1.50(+05)	1.34(+05)	1.25(+05)	1.33(+05)
Total (monolayers)	1.50(−01)	1.34(−01)	1.25(−01)	1.33(−01)
H	5.41(−06)	1.00(+00)	3.01(−03)	2.88(−03)
O	9.75(−06)	0.00(+00)	1.35(−01)	1.36(−01)
OH	9.75(−06)	0.00(+00)	1.11(−01)	1.35(−01)
H_2	2.20(+01)	5.00(−01)	7.32(−01)	7.01(−01)
O_2	1.12(−04)	9.40(+03)	8.92(+03)	9.03(+03)
H_2O	8.57(+04)	6.02(+04)	5.18(+04)	5.93(+04)
CO	3.39(+03)	1.00(+00)	7.43(−01)	7.76(−01)
HCO	7.36(−06)	0.00(+00)	1.14(−01)	1.14(−01)
H_2CO	3.47(+03)	1.00(+00)	6.18(−01)	7.11(−01)
H_3CO	7.36(−06)	0.00(+00)	1.21(−01)	1.22(−01)
CH_3OH	5.79(+04)	5.79(+04)	5.79(+04)	5.81(+04)
CO_2	8.23(−05)	6.60(+03)	6.64(+03)	6.64(+03)
CPU (s)	1	13	1	3

Table 8. Calculated populations for surface species at high density and 10^3 yr.

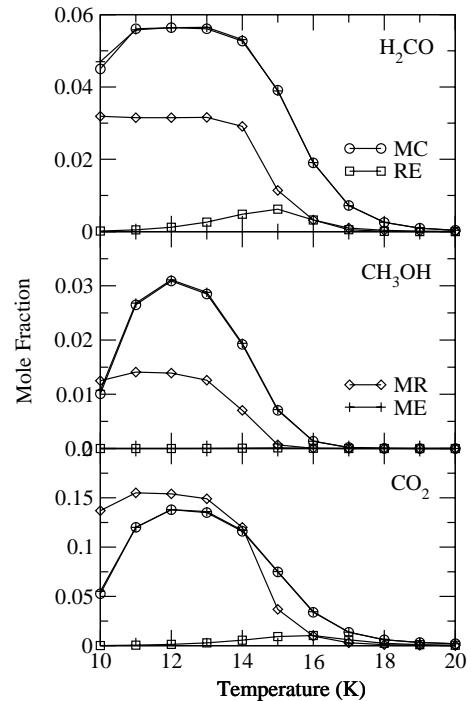| Species	Rate eq.	Monte Carlo	Master Eq. 22111	Master Eq. 22211	Master Eq. 23311
Total	1.17(+06)	1.11(+06)	9.20(+05)	9.63(+05)	1.09(+06)
Total (monolayers)	1.17(+00)	1.11(+00)	9.20(−01)	9.63(−01)	1.09(+00)
H	3.42(−10)	0.00(+00)	1.30(−08)	1.09(−08)	8.29(−09)
O	4.52(−01)	1.00(+00)	4.90(−01)	5.06(−01)	5.76(−01)
OH	4.52(−01)	1.00(+00)	2.60(−01)	4.05(−01)	5.97(−01)
H_2	8.79(−8)	0.00(+00)	2.90(−06)	2.50(−06)	1.89(−06)
O_2	2.74(+05)	2.81(+05)	1.80(+05)	1.91(+05)	2.68(+05)
H_2O	2.51(+05)	1.79(+05)	1.00(+05)	1.33(+05)	1.71(+05)
CO	6.47(+05)	5.28(+05)	4.80(+05)	4.93(+05)	5.23(+05)
HCO	6.71(−04)	0.00(+00)	2.10(−01)	1.88(−01)	1.53(−01)
H_2CO	1.86(+02)	5.01(+04)	6.40(+04)	5.98(+04)	5.12(+04)
H_3CO	3.96(−07)	0.00(+00)	5.30(−02)	4.54(−02)	3.62(−02)
CH_3OH	7.33(−02)	1.10(+04)	1.90(+04)	1.56(+04)	1.17(+04)
CO_2	2.04(+02)	5.82(+04)	7.90(+04)	7.15(+04)	6.01(+04)
CPU (s)	1	30	1	3	10
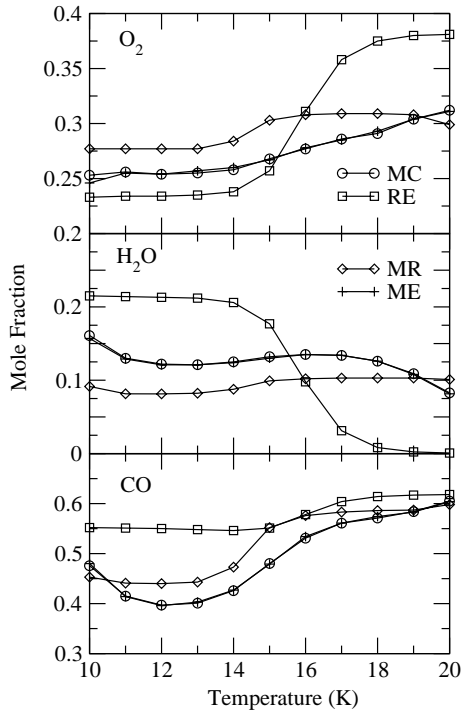
Fig. 4. The mole fractions of surface O_2, H_2O, and CO after 1000 yr for high density conditions plotted vs. temperature (K).

Fig. 5. The mole fractions of surface H_2CO, CH_3OH, and CO_2 after 1000 yr for high density conditions plotted vs. temperature (K).

The tabulated results are all for a temperature of 10 K. We have also done calculations for high density at temperatures through 20 K. The results are plotted for major species in Figs. 4 and 5 in terms of mole fractions vs. temperature. Cutoffs of 23311 have been used. Although the major species have surface abundances that increase linearly with time, the mole fractions remain constant. Results are shown for the Monte Carlo (MC), master equation (ME), simple rate equation (RE), and modified rate equation (MR) approaches. An analogous plot based on the Monte Carlo method is shown in Caselli et al. (2002) and is in good agreement with the present results. The Monte Carlo and master equation results are essentially identical, while the rate equation results are at best in mixed agreement with the two exact approaches. The modified rate method is significantly better than the simple rate approach but still can show factor of 2 or greater disagreement with the Monte Carlo and master equation methods.

Generally speaking, the results show that under the high density conditions considered here, the production of methanol is reasonably efficient only at the lower temperatures considered. Its efficiency at 10 K appears to peak at intermediate densities (see Table 7). The mole fraction of CO_2 also decreases strongly at the higher temperatures, while O_2 and CO tend generally to increase with increasing temperatures.

4.3. Slow diffusion rates for the H, O, CO system

As the diffusion rates are lowered, the abundances of surface oxygen atoms and OH radicals increase dramatically and the need for a more detailed treatment than the rate equation approach lessens. Indeed, as the average abundance of a minor species becomes greater than unity, it becomes difficult for the many-body master equation treatment to converge, so that it is best to remove those species from the many-body probability Eq. (1) and compute them via equations similar to Eq. (3). In Tables 9 and 10 we plot results at low and high densities obtained with the "slow" (M2) diffusion rates of Ruffle & Herbst (2000) using the rate equation, Monte Carlo, and master equation methods. For low density, we report results for both the minimal cutoff case and for a calculation, designated 2xx11 in which O and OH are not treated probabilistically. For high density, we can only perform the latter calculation since the surface abundances for O and OH are very large.

For the slow rates, it can be seen that little chemistry occurs except for the formation of water and, at high densities, OH. (Any H_2 formed has desorbed.) Nevertheless, the simple rate equation approach agrees surprisingly well with the 2xx11 reduced master equation approach. This occurs despite the fact that the average H atom abundance is less than unity, presumably because the abundances of its reactive partners O and OH exceed unity. The Monte Carlo method is also in fine agreement for major species although it once again is more computer intensive; it cannot really be compared with the other methods for minor species given the large statistical uncertainties in the small numbers. For low density, the minimal cutoff master equation approach is unreliable, as is to be expected when the O abundance exceeds unity. For high density, the O atom abundance is so large that a calculation with astronomical significance should include the Eley-Rideal mechanism of surface chemistry, in which gas-phase species collide reactively with nearly stationary species on grain surfaces.

Table 9. Calculated populations for surface species with "slow" diffusion rates at low density and 10^3 yr.

Species	Rate eq.	Monte Carlo	Master Eq. 22111	Master Eq. 2xx11
Total	1.68(+04)	1.69(+04)	6.98(+03)	1.68(+04)
Total (monolayers)	1.68(−02)	1.69(−02)	6.98(−03)	1.68(−02)
H	8.22(−02)	0.00(+00)	8.43(−02)	8.15(−02)
O	3.75(+00)	3.00(+00)	7.86(−01)	3.79(+00)
OH	3.75(+00)	5.00(+00)	1.81(−01)	3.79(+00)
H_2	1.71(−07)	0.00(+00)	1.60(−07)	1.50(−07)
O_2	8.84(−10)	0.00(+00)	2.66(−11)	9.00(−10)
H_2O	1.03(+04)	1.03(+04)	5.05(+02)	1.03(+04)
CO	6.47(+03)	6.59(+03)	6.47(+03)	6.47(+03)
HCO	1.15(−04)	0.00(+00)	3.93(−05)	7.38(−05)
H_2CO	1.58(−01)	0.00(+00)	5.49(−02)	9.96(−02)
H_3CO	2.76(−09)	0.00(+00)	3.27(−10)	1.11(−09)
CH_3OH	2.52(−06)	0.00(+00)	3.04(−07)	1.00(−06)
CO_2	1.36(−14)	0.00(+00)	1.24(−15)	8.77(−15)
CPU (s)	0.4	12	1.2	0.2

Table 10. Calculated populations for surface species with "slow" diffusion rates at high density and 10^3 yr.

Species	Rate eq.	Monte Carlo	Master Eq. 2xx11
Total	1.45(+06)	1.45(+06)	1.45(+06)
Total (monolayers)	1.45(+00)	1.45(+00)	1.45(+00)
H	2.33(−05)	0.00(+00)	2.33(−05)
O	4.50(+05)	4.51(+05)	4.50(+05)
OH	1.97(+05)	1.97(+05)	1.97(+05)
H_2	1.38(−14)	0.00(+00)	1.38(−14)
O_2	4.25(+00)	4.00(+00)	4.25(+00)
H_2O	1.52(+05)	1.52(+05)	1.52(+05)
CO	6.47(+05)	6.48(+05)	6.47(+05)
HCO	5.04(−03)	0.00(+00)	5.01(−03)
H_2CO	3.88(−03)	0.00(+00)	3.87(−03)
H_3CO	2.94(−11)	0.00(+00)	2.93(−11)
CH_3OH	2.19(−11)	0.00(+00)	2.17(−11)
CO_2	4.75(−08)	0.00(+00)	4.73(−08)
CPU (s)	0.6	27	0.6

5. Discussion

We have shown that a moderately complex network of chemical reactions that occur diffusively on the surfaces of dust particles can be studied successfully by a master equation approach previously used only for significantly simpler systems (Biham et al. 2001; Green et al. 2001). It is important to use an "exact" method such as the master equation approach or its Monte Carlo realization when there is a very low surface abundance of reactive species, since the rate equation method may be inaccurate, and the semi-empirical modified rate equation method may not be entirely correct either. The advantage of the master equation approach to the Monte Carlo method is that the former involves the solution of simultaneous differential equations. It is therefore facile to consider the gas-phase chemistry occurring simultaneously, because gas-phase abundances are also determined by solving simultaneous differential equations. Moreover, it is possible to determine when the master equation method must be used for all minor species, and when it is

acceptable to use the simpler and faster rate equation approach to diffusive surface chemistry. Specifically, when the abundances of reactive species on grain surfaces begin to exceed unity, there may be no need to use the more detailed approach, as can easily be tested. Calculations reported here show instances where even if the average atomic hydrogen surface abundance is below unity, the simple rate equation method works well if the O and OH abundances are high. Finally, for the system studied here, the master equation approach is actually faster than its Monte Carlo analog.

With all of these advantages, one might conclude that it should be facile to implement the master equation approach in current complex gas-grain models of interstellar clouds. But this optimism is misplaced. If the master equation method discussed in this paper is to be extended to still larger systems of reactions, such as that used in current gas-grain chemical models (Ruffle & Herbst 2000), some method must be found to reduce the number of simultaneous equations neccessary. Let us consider the extent of the problem. The minimal-cutoff

(22111) master-equation approach for fast diffusion rates requires the solution of $3 \times 3 \times 2 \times 2 \times 2 = 72$ simultaneous differential equations to fully determine the many-body P, excluding the additional coupled equations for the major species. As one increases the number of minor species, the number of simultaneous equations to be solved increases dramatically. Suppose, we wish to consider the chemistry of deuterium fractionation in the H, O, CO network discussed here. Such an extension requires the following new minor species: D, OD, DCO, H_2DCO, HD_2CO, D_3CO, making a total of 11 such species. The deuterium fractionation in this model was treated successfully by the Monte Carlo method (Caselli et al. 2002). Assuming that minimal cutoffs of 1 are needed for all these additional species with the exception of D, we calculate that a total number of 6912 simultaneous equations is needed for the many-body probability function P. This compares unfavorably with the total of 652 equations used for both the gas-phase and surface chemistry in our most complex models. It is difficult to even load the variables for such a calculation onto most computers, and the computer time necessary is virtually prohibitive. Even if only D is treated stochastically and OD, DCO, etc. are treated via rate equations, the computer time increases by a factor larger than 10 compared with the H, O, CO system.

Given the importance of developing approximation methods, we have investigated a simple such approximation: the idea that the many-body probability can be approximated as the product of individual, independent probabilities. We have seen that, even for the simple O, H system, the approximation of independent probabilities is not a reliable approach to the solution of the many-body master equation if one assumes fast diffusion rates. Although we did not report the results here, our extension of the independent probability approach to the more complex H, O, CO system has also met with failure. We are currently studying other approximation methods. One rather promising approach at this time is to limit the total number of equations by limiting the total number of reactive species on a grain surface. We hope to report results with this method in the near future.

Appendix A:

A.1. Kinetics of chemically reacting system

Let us consider an interstellar gas consisting of K different atomic and molecular species labelled by $\alpha_i, i = 1, ..., K \geq 1$ in a fixed physical volume V with concentration n_{α_i}. Each particle of species α_i is characterized by mass m_i, velocity c_i, and a set z_i of internal quantum states. The chemical species in the gas can interact through $m = 1, ..., M \geq 1$ chemical reactions of the type:

$$m: \alpha_i(c_i, z_i) + \alpha_j(c_j, z_j) \rightarrow \alpha_k(c_k, z_k) + \alpha_l(c_l, z_l). \quad (A.1)$$
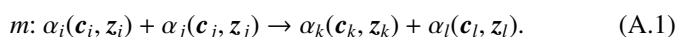
The probability that reaction (A.1) occurs at a specific relative velocity with products scattered in a certain direction is related to

$$g_{ij}d\sigma_m = g_{ij} \frac{d\sigma_m(g_{ij}, \Omega)}{d\Omega} d\Omega, \quad (A.2)$$

where $d\sigma_m$ is the reactive differential scattering cross-section, $g_{ij} = |c_i - c_j|$ is a relative velocity, and Ω is a solid scattering angle. The differential cross section depends on the interaction potential of the particles involved and can be calculated by methods of quantum mechanics or measured in laboratory experiments (Light et al. 1969).

In astrochemical problems, interstellar gases are usually considered under the assumption of local thermal equilibrium. This requires that reactive collisions occur less frequently than elastic and inelastic processes so that a temperature can be maintained. At thermal equilibrium, the distribution of possible molecular speeds is given in three dimensions by the Maxwellian distribution function $f_\alpha^{(M)}$. It is then possible to obtain the conventional rate equations of chemical kinetics (Light et al. 1969):

$$\frac{d}{dt}n_{\alpha_i}(t) = \sum_m [n_{\alpha_k}n_{\alpha_l}q_{\alpha_k, \alpha_l} - n_{\alpha_i}n_{\alpha_j}q_{\alpha_i, \alpha_j}], \quad (A.3)$$

where the functions $q_{..}$ are kinetic rate coefficients for the forward (with cross section indicated by $\rightarrow$) and backward (with cross section indicated by $\leftarrow$) directions of chemical reaction (A.1):

$$q_{\alpha_k, \alpha_l} = \int dc_k\, dc_l g_{kl}\, d\sigma_{m\leftarrow} f_{\alpha_k}^{(M)}(c_k) f_{\alpha_l}^{(M)}(c_l)$$
$$q_{\alpha_i, \alpha_j} = \int dc_i\, dc_j g_{ij}\, d\sigma_{m\rightarrow} f_{\alpha_i}^{(M)}(c_i) f_{\alpha_j}^{(M)}(c_j). \quad (A.4)$$

A.2. Stochastic approach to a chemically reacting system

Chemical kinetics in a rarefied interstellar gas can be formulated as a stochastic evolution of an ensemble of atoms and molecules. A stochastic approach is based on the relationship between two basic ways of describing the chemically reacting and evolving gas: (i) the Liouville dynamic equation and corresponding kinetic equations (Smith 1969) and (ii) the stochastic laws, describing a random process and its stochastic Kolmogorov equation equivalent (Gillespie 1976; Marov et al. 1997). For a space-uniform gas, the changes in the state of the gas caused by instant collisions can be considered to be jump-like Markovian processes (Marov et al. 1997), after which the state of the system does not contain the memory of how the state was reached.

In a stochastic treatment, the evolution of the reacting system is governed by the so-called chemical master equation (Gillespie 1982; van Kampen 1992):

$$\frac{\partial \phi(N, t)}{\partial t} = \sum_{m=1}^{M} [a_m(N^m)\phi(N^m, t) - a_m(N)\phi(N, t)], \quad (A.5)$$

which is linear with respect to the probability density $\phi(\mathbf{N}, t)$ that a system is described by state $\mathbf{N}$ at time t. The parameters in the equation are defined below:

a) The state of the system is characterized by

$$\mathbf{N}(t) = \{N_1(t), ..., N_K(t)\}, \tag{A.6}$$

where the atomic and molecular populations $N_i(t)$ for each species i are random integer variables in the considered gas volume V at time t;

b) The state of the system realized after an instant change of molecular populations in accordance with the stoichiometric scheme of reaction m is given by

$$\begin{aligned} \mathbf{N}^m = \{..., N_i - 1, ..., \\ N_j - 1, ..., N_k + 1, ..., N_l + 1, ...\}; \end{aligned} \tag{A.7}$$

c) The probability that a certain reaction m will take place in an infinitesimal time interval $[t, t + \mathrm{d}t]$ is given by the expression $a_m(\mathbf{N})\mathrm{d}t$, where $a_m(\mathbf{N})$ is independent of $\mathrm{d}t$ and is equal to:

$$a_m(\mathbf{N}) = V^{-1}h_{ij}q_m. \tag{A.8}$$

Here, q_m is the rate coefficient for reaction m, and h_{ij} is a combinatorial factor equal to the number of possible pairs of reacting molecules, or N_iN_j, for $\alpha_i \neq \alpha_j$, and $N_i(N_i-1)/2$ for $\alpha_i = \alpha_j$.

The function $a_m(\mathbf{N})$ depends on the specific chemical channel m, the current gas state $\mathbf{N} = \mathbf{N}(t)$, and the gas temperature and volume. This function, usually called the propensity function (Gillespie 1976), refers to processes that lead away from state $\mathbf{N}$. The function $a_m(\mathbf{N}^m)$ depends on the state of the gas $\mathbf{N}^m$, and refers to processes that lead to state $\mathbf{N}$.

Because $\mathbf{N}(t)$ refers to a Markovian jump-like random process, the time distribution between collisions is given by an exponential law:

$$P\{\tau(\mathbf{N} \to \mathbf{N}') \leq \tau\} = 1 - \exp(-a_0(\mathbf{N})\tau), \tag{A.9}$$

where a_0, the total reaction probability, is defined by

$$a_0(\mathbf{N}) = \sum_{m=1}^{M} a_m(\mathbf{N}). \tag{A.10}$$

Expressions (A.6)–(A.10) give an exact definition of the random state of the system $\mathbf{N}(t)$ describing a chemically reacting gas within a stochastic framework. How do we describe a system of reactions on the surface of a dust particle?

It is well known that the random nature of interstellar grain surface chemistry, as well as the accretion and desorption processes leading to grain mantle growth, necessarily involves a stochastic framework (Tielens & Hagen 1982; Tielens & Charnley 1997; Herbst 2000; Charnley 2001). The stochastic treatment of grain surface chemistry can be formulated in terms of the master equation approach. To do this, the surface should be represented by a lattice or a monolayer – each lattice point corresponds to a surface site. A lattice point can assume a number of distinct values that stand for various adsorbed molecules (with zero for a free site). The monolayer, together with all its

site populations, is considered as a state vector $\mathbf{N}$ for the surface reacting system. Each surface reaction changes the monolayer population vector in accordance with the reaction stoichiometry. The evolution of this surface reacting system over time is described by a chemical master equation – Eq. (A.5). Since there are a large number of reactive sites on interstellar dust particles, additional assumptions are normally made for stochastic theories – that all sites are identical, that one need only follow the number of particles of a given species on the entire grain, and that the distribution of particles on a grain is random.

In astrochemical environments at very low temperatures ($\sim$10 K), light atoms are the major mobile species on grain surfaces. Atoms migrate mainly by thermal hopping from site to site with a timescale

$$\tau_{\mathrm{h}}^{\alpha} = \nu^{-1} \exp(E_{\mathrm{D}}^{\alpha}/kT_{\mathrm{d}}),$$

where E_{D}^{α} is the energy barrier for surface diffusion for atomic species α, T_{d} is the surface temperature, and ν is the vibrational frequency of the particle in the lattice binding site ($\sim$10^{12} s^{-1}). Light hydrogen atoms can also migrate by quantum mechanical tunneling, with a characteristic timescale $\tau_{\mathrm{H}} \sim 10^{-12}$ s. Migration on the surface leads to reactions with other light migrating atoms or heavy and relatively static molecules and radicals with reactive transition probabilities

$$a_m(\mathbf{N}) = h'_{ij} \times p_m \times (\tau_{\alpha}^{-1} + \tau_{\beta}^{-1}), \tag{A.11}$$

where the τ^{-1} factors are for the two reacting species and can be either for surface hopping or tunneling. The factor p_m is unity unless there is an activation energy barrier E_m. This factor is then equal to the Arrhenius factor $\exp(-E_m/kT_{\mathrm{d}})$ or, for the case of quantum mechanical tunneling through the potential barrier of height E_m and width L_m, is equal to $\exp(-4\pi L_m(2\mu E_m)^{0.5}/h)$, where μ is the reduced mass. The prime in the combinatorial factor h'_{ij} means that there is a denominator with the actual number of sites on a grain. The denominator converts the rate of diffusion from one site to another into the rate of diffusion t_{diff}^{-1} over the equivalent of an entire grain. As suggested by Charnley (2001), the surface chemical network should be extended by interpreting the accretion and desorption processes as additional reactions responsible for the chemical coupling between gas-phase and grain mantle fractions of the interstellar gas.

A.3. Methods for solving the chemical master equation

A.3.1. Monte Carlo algorithms

These algorithms are based on the fact that the probability of generating the stochastic "trajectory" with a Monte Carlo algorithm is exactly the probability that would come out of the solution of the corresponding master equation.

To accomplish this, the homogeneous Markovian process $\mathbf{N}(t)$ is replaced by an equivalent uniform Markovian chain. An exact realization for the Markovian chain on a discrete time grid is as follows. We choose a time interval $\triangle t$ and determine times $t_1 = 1\triangle t$, $t_2 = 2\triangle t$, ..., $t_{\delta} = \delta\triangle t$, for which we will store the values of $\mathbf{N}_1 = \mathbf{N}(t_1)$, $\mathbf{N}_2 = \mathbf{N}(t_2), ..., \mathbf{N}_{\delta} = \mathbf{N}(t_{\delta})$,

respectively. To determine the state $N_{\delta+1}$ of a dust particle, we perform the following steps:

a) we determine randomly: (1) which reaction will occur during the transition via (A.10) and (A.11), and (2) in accordance with the probability distribution (A.9), the time τ that has elapsed from the previous transition. This can be done using the *direct simulation* or *first reaction* methods (Gillespie 1976; Lukken et al. 1998; Charnley 1998, 2001), the former of which is used here. Then, we update the species' populations, and advance the transition time counter as $T^{(s)} = T^{(s-1)} + \tau$;

b) if the transition time counter satisfies the following condition:

$$t_{\delta+1} \leq T^{(s)} < t_{\delta+2},$$

it means that we have stepped over the next point on the time grid. In such a case, we assign a value to $N_{\delta+1}$ that is equal to the current state. If the inequality does not hold, we repeat the operations from step a).

We repeat the whole procedure until the time counter reaches a fixed time T_{final}.

Algorithmic steps (a)–(b) represent the exact Monte-Carlo procedure for solving the chemical master equation. One realization for the Markovian chain $N_1, N_2, N_3, \ldots,$ gives only one possible evolution of the system. Thus, it is important that the procedure be repeated and many trajectory realizations be obtained. Due to the linearity of the chemical master Eq. (A.5) and, consequently, of analogous Monte-Carlo algorithms for its solution, the evolution can be calculated by averaging through trajectory realizations of the random process $N(t)$.

A.3.2. Direct solution

For surface chemistry, one natural way to deal with the stochastic approach is to create one probability variable for each possible state of the reacting chemical system under study. If the system can be contained within a limited set of possible states so that the number of molecules of each species is limited by some fixed value $\bar{N}_i$ during the system evalution – $N_i(t) \leq \bar{N}_i$ – it is useful to adopt as a representation of the state probability distribution $\phi(N, t)$ a set of many-body probabilities P for specific numbers of molecules for the species being considered. By substituting this set into the chemical master equation, we can obtain a set of coupled differential equations for the time derivative of the detailed probabilities of all possible states – $\frac{d}{dt}P(i_1, ...i_N)$.

Such a set of differential equations is used in this paper, but with a caveat. For surface chemistry, it is normally not necessary to include all species in the model in the realization of the master equation. Generally, only a few reactive species have surface abundances so low that a stochastic treament is necessary. All other molecules can be described by a deterministic approach with coventional rate equations. These two (stochastic and deterministic) subsets of the system are coupled through the combinatorial factors

$$\bar{h}_{ij} = \langle N_j \rangle \sum_{i=1}^{\bar{N}_i} i P(..., i, ...) \qquad (A.12)$$

where $\langle N_j \rangle$ is a mean molecular population for the deterministic j species and the $P(..., i, ...)$ are probabilities for the stochastic i species. This division allows us to combine the direct solution of the chemical master equation for stochastic species with simple or modified rate equations for deterministic species to produce realistic grain-surface chemical networks.

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