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Modified rate equations revisited. A corrected treatment for diffusive reactions on grain surfaces

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Abstract. It is well known that the rate equations for diffusive reactions on grain surfaces can be inappropriate under certain circumstances because they do not take the discrete nature of grains into account. A previous modification of the rate equations developed by us to treat surface chemistry on grains more accurately contains an error in the probability of evaporation from grain surfaces. With the rate of evaporation handled correctly, we show for a simple system in which only O and H atoms accrete on grain surfaces and react to form H_2, OH, and O_2 that the modified rate method is in reasonable agreement with a corrected Monte Carlo approach through 20 K and in excellent agreement with a new master equation approach at 10 K.

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

1. Introduction

On grain surfaces such as amorphous ice and silicates, it is thought that the dominant mechanism for interstellar surface reactions such as the recombination of two hydrogen atoms to form molecular hydrogen is diffusive in nature (Tielens & Allamandola 1987; Hasegawa et al. 1992). In the diffusive, or Langmuir-Hinshelwood, mechanism, two reactants roam around a dust particle either by hopping over energy barriers or by quantum mechanical tunneling until they find one another. The temperature range over which diffusive chemistry is dominant depends upon the interplay among the rates of adsorption, diffusion, and evaporation, which in turn depend on the density and chemical composition of the gas, the specific surface reactants and the mechanism of diffusion, and the size and chemical nature of dust particles. Below a lower limit of temperature, diffusion, if it occurs by thermal hopping, is too slow to be of importance, while above an upper limit, evaporation will be so efficient that no surface chemistry can occur. Although the temperature range for diffusive formation of molecular hydrogen in dense interstellar clouds is not very well constrained and depends on a variety of uncertain factors, it is reasonably certain that the process can occur at temperatures around 10 K. It is also likely that other diffusive surface reactions, especially those involving atomic H, occur at this temperature.

Diffusive reactions on the two-dimensional surface of a dust particle can be handled by rate equations similar to those for gas-phase processes (Pickles & Williams 1977). Replacing the rate coefficients for gas-phase reactions, which consist of a thermal average of the product of relative velocity and collisional cross section, are rate coefficients that describe the rate of diffusional motion over the entire grain surface. For example, the formation rate of H_2 on grain surfaces is given by the equation (Caselli et al. 1998)

$$\frac{\mathrm{d}N(\mathrm{H}_2)}{\mathrm{d}t} = 0.5 k_{\mathrm{H,H}} N(\mathrm{H}) N(\mathrm{H}), \tag{1}$$

where N represents the average number of species per grain, and the rate coefficient $k_{\mathrm{H,H}}$ is the sum of inverse diffusion times (t_{s}) for sweeping over the entire grain via tunneling or thermal hopping:

$$k_{\mathrm{H,H}} = t_{\mathrm{s}}^{-1}(\mathrm{H}) + t_{\mathrm{s}}^{-1}(\mathrm{H}). \tag{2}$$

The inverse sweeping time t_{s}^{-1} for any species i moving classically over a grain is given by the equation

$$t_{\mathrm{s}}^{-1}(i) = N_{\mathrm{s}}^{-1} \nu_0(i) \exp\left(-E_{\mathrm{b}}(i)/T\right), \tag{3}$$

where N_{s} is the number of binding sites on a grain, $\nu_0(i)$ is the frequency of vibration of the adsorbed species, and $E_{\mathrm{b}}(i)$ is the energy barrier (K) against diffusion from one site to another (Hasegawa et al. 1992). The inverse sweeping time when tunneling is the dominant motion is given by the equation

$$t_{\mathrm{s}}^{-1}(i) = N_{\mathrm{s}}^{-1} \nu_0(i) \exp\left[-(2a/\hbar)(2mE_{\mathrm{b}}(i))^{1/2}\right], \tag{4}$$

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where a is the tunneling length and m is the mass of the adsorbate (Tielens & Hagen 1982; Hasegawa et al. 1992). In addition to chemical terms, the rate equations for surface species contain terms for accretion from the gas and desorption into the gas. Accretion terms are of the form $k_{\rm acc}(i)n(i)$ for species i where $n(i)$ is the gas-phase concentration of i and

$$k_{\rm acc}(i) = v_{\rm i}\sigma; \tag{5}$$

here $v_{\rm i}$ is the speed of the gas-phase species and σ is the cross section of the grain. Thermal evaporation terms are of the form $t_{\rm evap}^{-1}(i)N(i)$, where $N(i)$ is the average number of species of type i per grain, and

$$t_{\rm evap}^{-1}(i) = \nu_0(i)\exp\left(-E_{\rm D}(i)/T\right). \tag{6}$$

Here $E_{\rm D}$ is the energy needed for evaporation, which on well-characterized surfaces is significantly greater than the barrier against diffusion (Tielens & Allamandola 1987). Non-thermal desorption can also be included (Hasegawa & Herbst 1993). The rate equations can be written in terms of concentrations of grain species per unit volume rather than in terms of average numbers of species per grain (Hasegawa et al. 1992).

The concept of an average number of species on a grain surface is adequate if the average is large enough that the distinction between integers and non-integers is unimportant. Once the average number becomes small, however, and especially if the number falls significantly below unity, the concept of an average becomes less meaningful, as was recognized by Allen & Robinson (1977) and Tielens & Hagen (1982). The latter authors developed a Monte Carlo procedure adequate for the so-called "accretion" limit, in which successive reactive species that land on a grain will react with one another if migration is more rapid than evaporation. To construct a Monte Carlo code in the accretion limit, one follows individual species as they adsorb onto grains and then determines their chance of evaporation or reaction. If neither of these options is highly probable, large numbers of reactive species will build up on grain surfaces and the rate equations will become adequate as long as there is some diffusion to cause reaction. If, however, diffusion occurs so slowly that reactions are very inefficient, there is the possibility that another mechanism for surface chemistry – the so-called Eley-Rideal mechanism – will become dominant. Here gas-phase species strike rather stationary adsorbed atoms and molecules to form products.

Although, in principle, one might be able to construct a gas-grain chemical code for interstellar clouds in which the diffusive grain surface reactions are handled by switching between rate equations and the Monte Carlo approach, depending on the abundances of reactive species on grains, it has heretofore proven unfeasible to use even the simple Monte Carlo approach of Tielens & Hagen (1982) in a complex model of interstellar chemistry, both because of the long computer times needed and because of the difficulty of integrating a Monte Carlo approach for grains with standard rate equations for the gas. Charnley (1998) has shown how one can use a detailed stochastic treatment for gas-phase chemistry but has not shown how to extend it to surface processes. His method is based on the Gillespie (1976) approach to the stochastic master equation. Several years ago, we developed a simple procedure in which the rate equations could be modified so that the results would approach the Monte Carlo result in the accretion limit (Caselli et al. 1998). The modified rate method was compared with a Monte Carlo approach based on that of Tielens & Hagen (1982) for several simple systems, most notably a system with fixed abundances of O and H atoms in the gas in which adsorption on grains leads to surface reactions to produce the three diatomic molecules H_2, OH, and O_2.

The essence of the semi-empirical modified rate approach is to reduce the diffusion rate of fast-moving atoms, if necessary, to the larger of their accretion and evaporation rates. The idea behind this approach is to reduce the probability of reaction of an atom striking a grain with one reactive species on it to at most unity during an accretion interval. One cannot just slow the diffusion rate to the accretion rate because, if evaporation is much more rapid than accretion, slowing the diffusion rate to the accretion rate results in no reaction at all. The importance of the modification depends on how much the diffusive rate of a particular atom exceeds its accretion and evaporation rates. Although, in principle, the slowing of the diffusion rate should be performed for all reactive species, Caselli et al. (1998) only used the approach for atomic H since at 10 K, the sole temperature considered, only H can diffuse sufficiently rapidly to require a strong correction. They also added two other modifications: (i) a correction to account for the fact that one H atom can evaporate before another lands, and (ii) a totally empirical correction to increase the rate of formation of OH. The modified rate method, when compared with the Monte Carlo approach at 10 K for the simple O, H system (and for other simple systems), proved adequate. The approach was then used for a variety of complex gas-grain models of quiescent interstellar cores (Shalabiea et al. 1998).

The modified rate approach has proven to be controversial since it is semi-empirical in nature and since it cannot be tested for complex systems. In addition, it is no longer clear how necessary it is because recent experiments by Pirronello et al. (1997, 1999) on the low-temperature formation of H_2 on olivine and amorphous carbon as simulated by Katz et al. (1999) show that H atoms travel much more slowly than astrochemists had anticipated. For example, Hasegawa et al. (1992) and Caselli et al. (1998) derived a value of 5.1×10^4 s^{-1} for the rate of diffusion of H over an entire grain of 10^6 binding sites and a radius of 0.1 μm at 10 K, a rate achieved by quantum mechanical tunneling. These authors also used values of 1.9×10^{-3} s^{-1} for the evaporation rate $t_{\rm evap}^{-1}({\rm H})$ and $1.4 \times 10^{-5} n({\rm H})$ s^{-1} for the accretion rate $t_{\rm acc}^{-1}({\rm H})$, where $n({\rm H})$ is the gas-phase concentration of atomic hydrogen. At all densities considered, the diffusion rate of H exceeds its evaporation and accretion rates, so that it is necessary to slow the rate of diffusion. Katz et al. (1999) found, however, that even on olivine, a form of polycrystalline silicate to which H is weakly bound, the rate of diffusion at 10 K is slower than the rates of evaporation and accretion, so that the artificial slowing of H is not required on grains with 10^6 binding sites. This slow diffusion found by Katz et al. (1999) has not been universally accepted, and other experiments are being constructed to confirm the results and to extend them to unstudied surfaces such as amorphous ice. Ruffle & Herbst (2000) and Ruffle & Herbst (2001) generalized the result of Katz et al. (1999) to construct gas-grain chemical models of quiescent interstellar cores at assorted temperatures and densities, and found not surprisingly that the modifications of Caselli et al. (1998) were hardly needed at all. Work by Biham et al. (2001) indicates that on smaller grains with fewer binding sites, the rate equations still need to be corrected, at least for H_2 production, since the surface population of H becomes smaller, or put another way, the diffusion rate of H over an entire grain becomes larger compared with its accretion and evaporation rates per grain.

Most recently, the master equation approach to diffusive surface chemistry has been revitalized by several groups (Green et al. 2001; Biham et al. 2001) In this treatment one replaces rate equations such as Eq. (1) with a set of analogous equations that yield the probability that the number of atoms or molecules of a species on a grain is a specific value. In the accretion limit, one can reduce the number of these equations to a manageable size, although it is currently unclear whether one can solve for independent probabilities of specific species or whether the probabilities must be coupled. Applying the method to the simple O, H system of Caselli et al. (1998), Green et al. (2001) showed, among other things, that the Monte Carlo approach used by Caselli et al. (1998) as a test for their modified rate method was itself in error. This point had also been made by David Hollenbach (private communication) and Ofer Biham (private communication; see also Biham et al. 2001; Green et al. 2001).

The purpose of this paper is two-fold. First, we report results of a corrected Monte Carlo approach, which, when applied to the simple O, H system, is in excellent agreement with the master-equation results of Green et al. (2001) at 10 K. Secondly, we show that the modified rate method, when used in a more coherent manner than before, is in reasonable agreement with the more accurate Monte Carlo approach over the temperature range 6–20 K.

2. Model

The simple O, H system, to which we will be referring throughout the paper, is defined as follows. The gas phase consists of oxygen atoms with a fixed concentration $n(\mathrm{O}) = 1\ \mathrm{cm}^{-3}$ and a concentration of hydrogen atoms $n(\mathrm{H})$ ranging from 0.1–$10^4\ \mathrm{cm}^{-3}$. The gas-phase atoms are assumed to remain at their initial concentrations for the duration of the calculation. The atoms stick to the grains with 100% efficiency and react to form the three molecules H_2, OH, and O_2, none of which is allowed to evaporate (despite the fact that in reality, the great majority of the molecular hydrogen does evaporate). The surface reactions are diffusive in nature and the diffusion rates are the large ones used by Hasegawa et al. (1992) and Caselli et al. (1998) for grains with 10^6 binding sites. The rates/rate coefficients for diffusion, accretion, and evaporation used for the calculations at 10, 15, and 20 K are given in Table 1 along with the parameters from which the rates are generated. The rapid rates of diffusion are chosen not because we believe the results of Katz et al. (1999) to be incorrect but because (a) the larger rates lead to a greater problem for the rate method and (b) the results of Katz et al. (1999) may not apply for icy surfaces. With the rates in Table 1, the accretion limit pertains because the average surface populations of H and O atoms are much less than unity.

Table 1. Accretion, sweeping and evaporation rates of H and O atoms.

Temperature	Species	k_{acc} ($\mathrm{cm}^3\ \mathrm{s}^{-1}$)	t_{s}^{-1} (s^{-1})	t_{evap}^{-1} (s^{-1})
10 K	H . . .	1.45×10^{-5}	5.14×10^{4}	1.88×10^{-3}
	O . . .	3.61×10^{-6}	4.24×10^{-5}	2.03×10^{-23}
15 K	H . . .	1.77×10^{-5}	5.51×10^{4}	2.19×10^{2}
	O . . .	4.43×10^{-6}	1.27×10^{-1}	7.74×10^{-12}
20 K	H . . .	2.04×10^{-5}	7.13×10^{4}	7.47×10^{4}
	O . . .	5.11×10^{-6}	6.91×10^{0}	4.78×10^{-6}

Note: $t_{\mathrm{acc}}^{-1}(i) = k_{\mathrm{acc}}(i)n(i)$.
For H, $E_{\mathrm{D}} = 350$ K, $E_{\mathrm{b}} = 100$ K, and $a = 1$ Å.
For O, $E_{\mathrm{D}} = 800$ K, and $E_{\mathrm{b}} = 240$ K.

Calculations were undertaken with the standard rate method, a simplified modifed rate method, and a corrected Monte Carlo approach. The actual rate equations used to study the system are given in Caselli et al. (1998). The surface abundances were obtained when the rate of growth of the three molecules on the surface is linear with time so that the mole fractions of the three are constant.

In formulating their Monte Carlo approach, Caselli et al. (1998) assumed that the probability of one atom to remain on a grain until a second arrives is given by the exponential relation $\exp(-x)$, where x is the ratio between the rate of evaporation and the total rate of accretion. This equation does not pertain to the interstellar situation because it is based on the assumption that the interval between successive atoms' accreting onto a given grain is fixed, when, in reality, it is random. If one takes this randomness into account and integrates over all times, the correct probability is $1/(1+x)$, which is the same as $\exp(-x)$ only for small x. In actuality, the latter expression is itself an approximation because it represents the probability that 2 *or more* atoms are on a grain at the same time, although this point is picayune in the accretion limit. For large x, there is a significant difference between

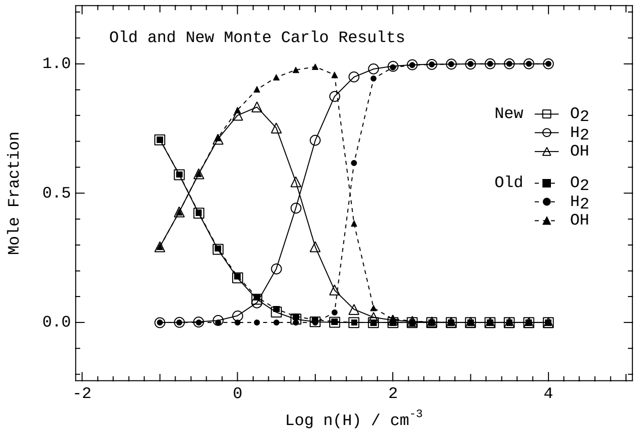

Fig. 1. Mole fractions of surface O_2, H_2 and OH vs. gas-phase number density of atomic hydrogen, $n(\mathrm{H})$, calculated with the old and corrected Monte Carlo approaches.

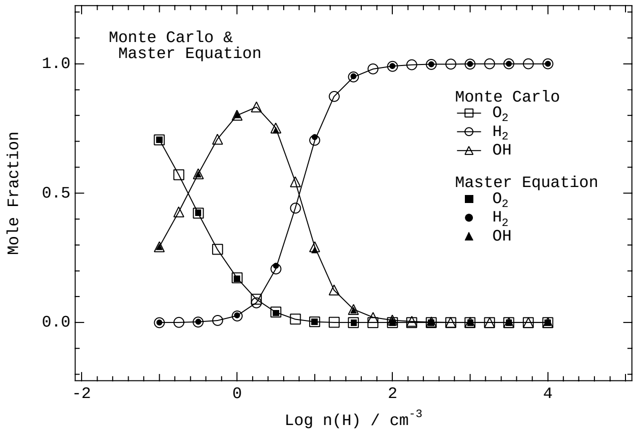

Fig. 2. Mole fractions of surface O_2, H_2 and OH vs. gas-phase number density of atomic hydrogen, $n(\mathrm{H})$; shown are the corrected Monte Carlo results and the master equation results of Green et al. (2001).

the two expressions such that the formation of e.g. H_2 is much more likely with the correct, non-exponential expression. The effect of the change in expression on the O, H system is shown in Fig. 1, where the mole fraction of H_2 is plotted vs. $n(\mathrm{H})$ for Monte Carlo calculations with the old and new expressions. It can immediately be seen that the formation of molecular hydrogen at relatively low gas-phase abundances of atomic hydrogen is more efficient with the correct approach. In Fig. 2, the mole fractions for the three molecules are plotted vs. $n(\mathrm{H})$ with the corrected Monte Carlo approach and the new master equation approach (Green et al. 2001). The agreement is excellent.

The mistake in the original Monte Carlo formulation led to a mistake in the second of the three modifications of Caselli et al. (1998) – that the rate of H_2 formation has to be multiplied by a factor of $y \exp(-y)$, in the evaporative limit ($y > 1$) where y is the ratio of the evaporation rate of H atoms to the accretion rate of H atoms. Instead, it is better to eliminate this correction entirely because, if we neglect the presence of atomic O (so that $y = x$), solution of the modified rate equation for the production rate of molecular hydrogen in the evaporative limit shows it to be equal to the rate of accretion of H atoms divided by x. The physical meaning of this result is that after one accretion time, the probability of an H atom remaining on the grain to react with the next is $1/x$, an expression equal to that of the Monte Carlo approach when $x \gg 1$. To derive this result, substitute the average surface abundance of atomic H

$$N(\mathrm{H}) = \frac{t_{\mathrm{acc}}^{-1}(\mathrm{H})}{t_{\mathrm{evap}}^{-1}(\mathrm{H})} \tag{7}$$

obtained from a steady-state solution of the modified rate equation for the H abundance in the evaporative limit (see Eqs. (4) and (15) of Caselli et al. 1998) into Eq. (1) with the modified value for $k_{\mathrm{H,H}}$:

$$k_{\mathrm{H,H}} = t_{\mathrm{evap}}^{-1}(\mathrm{H}) + t_{\mathrm{evap}}^{-1}(\mathrm{H}). \tag{8}$$

In addition to elimination of the second correction, we eliminate the third correction of Caselli et al. (1998), which is totally empirical, and replace it with a correction for atomic O analogous to that for H; namely, that the rate of diffusion of O is lowered to the larger of its accretion and evaporation rates, if necessary. This modification becomes especially important at temperatures higher than 10 K.

3. Results

In Figs. 3, 4, and 5, we compare the calculated mole fractions of O_2, H_2, and OH obtained as a function of $n(\mathrm{H})$ for the corrected Monte Carlo, original rate, and modified rate methods at 10 K, 15 K, and 20 K, respectively. A quick glance at all three figures shows that the modified rate method is in much better agreement with the Monte Carlo approach than is the unmodified (original) rate method. The agreement between the modified rate and Monte Carlo approaches is not perfect, however. Discrepancies in the mole fraction plots show up especially at higher temperatures and low atomic hydrogen abundances in the gas. For example, at 20 K and $n(\mathrm{H}) = 1.0$ cm^{-3}, the mole fraction of O_2 is 0.3 in the Monte Carlo calculation and less than 0.1 in the modified rate method, a considerable disagreement. The disagreement can become greater when the mole fraction of a species becomes very low, although this can be masked in the mole fraction plots. In Fig. 6, we compare production rates per year for O_2 at 20 K as a function of $n(\mathrm{H})$ between the Monte Carlo (with uncertainties obtained by varying the initial random numbers) and modified rate approaches. The dispersion in the Monte Carlo values is larger than the expected statistical error because the numbers used are not truly random. Although the uncertainties in the Monte Carlo approach can be large even when a supercomputer is run for hours, they do not cover the differences between the two approaches in this figure except at very small production rates. (The differences at high $n(\mathrm{H})$ in Fig. 5 for OH and H_2 are due to poor statistics, however.) Thus, although the modified rate method is a

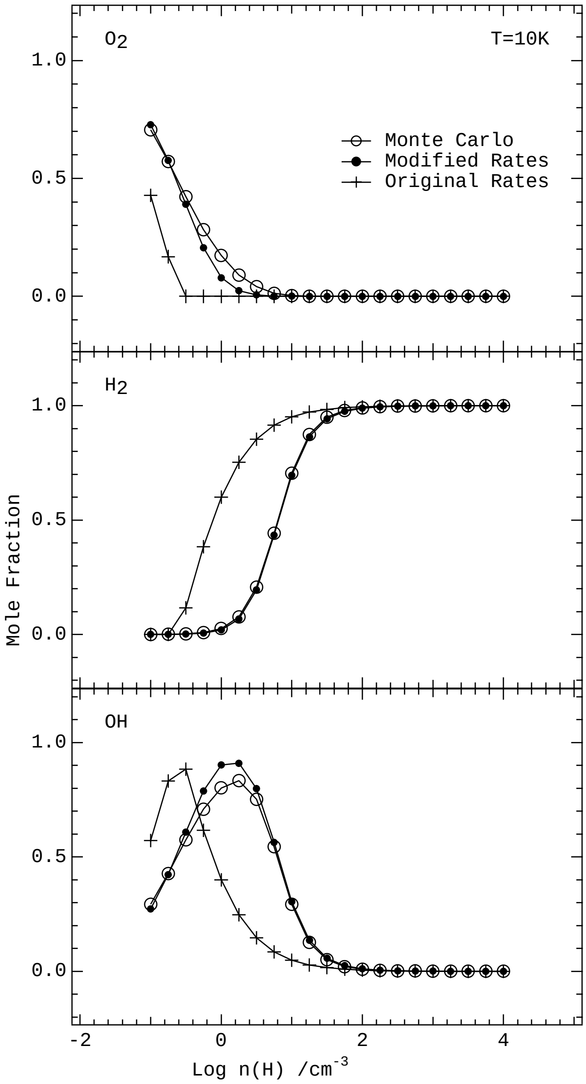

Fig. 3. Mole fraction vs. the gas-phase atomic hydrogen abundance computed via the original rate method, the modified rate method, and the corrected Monte Carlo method for **a)** O_2, **b)** H_2 and **c)** OH at 10 K.

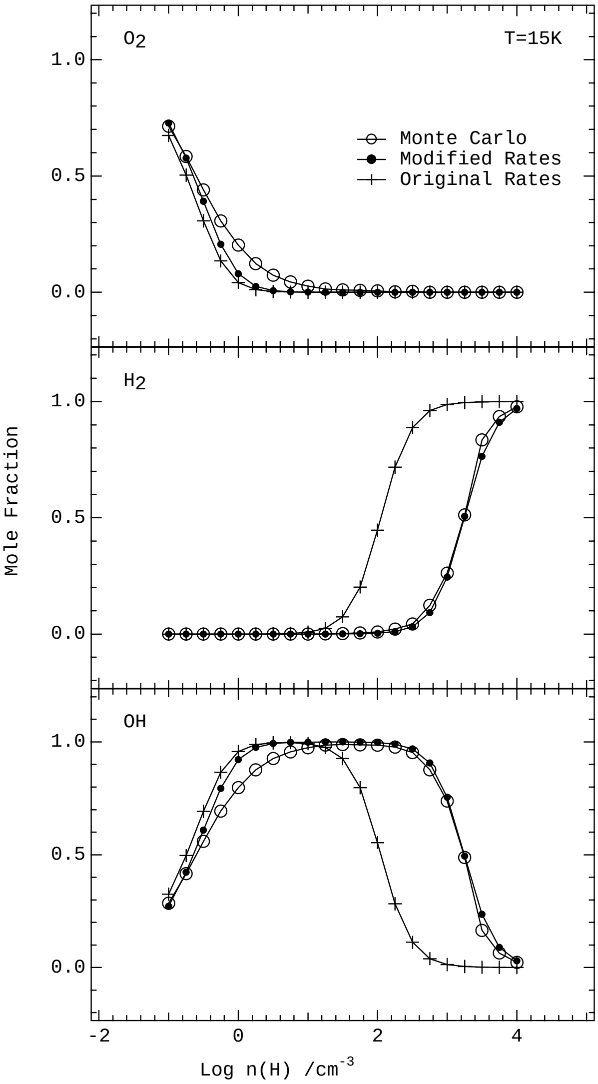

Fig. 4. The same as Fig. 3 but for 15 K.

simple and improved alternative to the use of unmodified rates in gas-grain models, it can still lead to significant discrepancies for certain regions of parameter space.

We have performed some calculations for temperatures in the range 6–9 K and found that agreement among the modified rate and Monte Carlo approaches is good until, at the lowest H gas densities and 6 K, the accretion limit no longer pertains for the slow-moving O atoms and our Monte Carlo method fails. Given the fast (and temperature-independent) tunneling rates which dominate H diffusion, molecular hydrogen is made efficiently even at 6 K at most gas-phase densities considered. In fact, the slowing of the evaporation of H as temperature is lowered improves the likelihood of H_2 formation.

4. Summary and conclusions

The use of rate equations to describe the diffusive chemistry occurring on the surfaces of interstellar grains can be inaccurate because the number of reactive species on any individual grain can be very small. In such a situation, known as the accretion limit, the probability of reaction has less to do with the rate of diffusion than with the order in which species are adsorbed onto a grain. The only rigorous alternative to rate equations so far presented – the master equation approach (Biham et al. 2001; Green et al. 2001) – has not yet been generalized to complex systems nor will such a generalization prove simple unless the correlations between the probability distributions P calculated for different surface species such as O and H can be safely neglected (see Eqs. (25)–(30) of Biham et al. 2001). A simplified Monte Carlo approach (Tielens & Hagen 1982) works reasonably well for the surface chemistry of simple systems in the accretion limit.

We have used our version of the Monte Carlo approach of Tielens & Hagen, which it has been necessary to correct, to test a simplified version of the modified rate approach of Caselli et al. (1998) in the accretion limit for a reduced system in which only O and H atoms with fixed abundances are present in the gas. These atoms land on grains

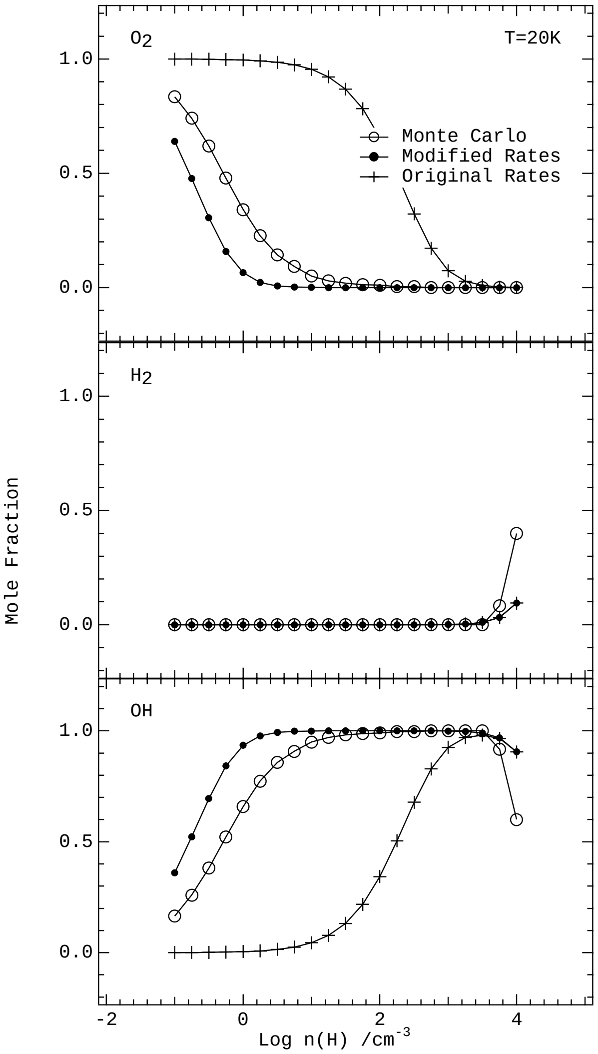

Fig. 5. The same as Fig. 3 but for 20 K.

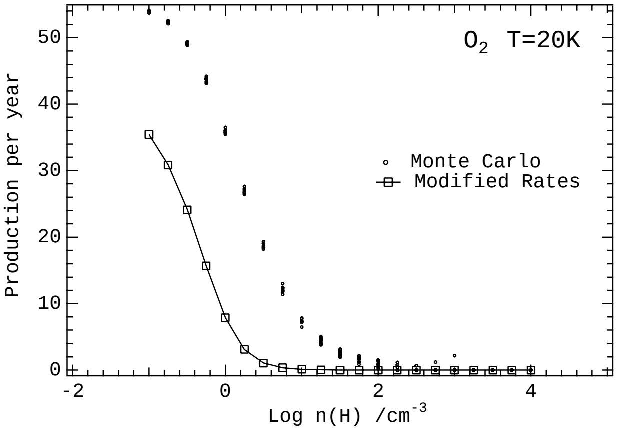

Fig. 6. Yearly production of molecular oxygen at $T = 20$ K plotted vs. $n(\mathrm{H})$.

and either evaporate or react to form the three diatomic molecules H_2, O_2, and OH, the mole fractions of which are independent of time after an initial period. At 10 K, the Monte Carlo approach is in excellent agreement with the rigorous master equation method (Green et al. 2001).

In our modified rate approach, the form of the diffusive rate laws is preserved, but the rate coefficients for diffusion of each atom over an entire grain are slowed to the greater of the accretion and evaporation rates for that atom, when the diffusion rate exceeds these two quantities. This simple modification has the advantage that it can be generalized without difficulty to a large set of reactions in a complex gas-grain model, but has the disadvantage that it is semi-empirical and can only be tested by comparison with a more accurate approach. The current approach differs from that of Caselli et al. (1998) by reducing the number of modifications, a reduction which became more apparent when the error in the Monte Carlo program used to test the modified rate approach was corrected.

For the simple O, H system, the modified rate method comes much closer to the Monte Carlo results than does the regular rate method over the temperature range 10–20 K with the rapid diffusive rates used by Hasegawa et al. (1992), which may pertain on icy surfaces. Still, there are some regions of parameter space (high temperature, low atomic hydrogen gas-phase abundance) where discrepancies exist. Some of the discrepancies can be reduced if we lower surface diffusion rates to the overall accretion rate, when it exceeds the evaporation rate, rather than to individual accretion rates. If the diffusive rates used are based on the smaller values measured by Katz et al. (1999) for H on cold silicon and amorphous carbon, there is little need for any rate modifications with the grain size utilized since the diffusive rates are rarely if ever significantly greater than the accretion and evaporation rates under interstellar conditions. As shown by Biham et al. (2001), however, the use of smaller grains than considered here changes the situation so that the normal rate equations can once again be inaccurate.

Unless generalizations of the master equation approach prove to be achievable for large systems, the modified rate method, despite its obvious shortcomings, may continue to be the best practical aproach to diffusive surface chemistry. In addition to planned testing of generalized master equation approaches, we are therefore extending the method reported here to include surface reactions with activation energy such as the reactions

$$\mathrm{H} + \mathrm{CO} \longrightarrow \mathrm{HCO}, \tag{9}$$

$$\mathrm{H} + \mathrm{H_2CO} \longrightarrow \mathrm{H_3CO}, \tag{10}$$

which are important in the surface synthesis of methanol. Previous attempts to include such processes in a modified rate treatment with large diffusive rates (Herbst 2000; van der Tak et al. 2000) suffer from being tested against our former, incorrect Monte Carlo approach. Finally, the rate equations also have the advantage that it is facile to generalize them to incorporate the Eley-Rideal mechanism for surface chemistry, which can be important for surfaces such as graphite where the binding of adsorbates is thought to be strong enough so that no diffusive motion occurs at interstellar temperatures (Farebrother et al. 2000).

Of course, it must be remembered that interstellar surfaces, especially after some ice is formed, are likely to be impure and to consist of materials with different binding capabilities for adsorbates. The consequence is undoubtedly that the sharp temperature dependences often obtained for a pure surface (e.g. see Table 1) are likely to be smoothed out no matter what other assumptions are made.

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