Astronomy
&
Astrophysics

Reduction of chemical networks

I. The case of molecular clouds

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Abstract. We present a new method to analyse and reduce chemical networks and apply this technique to the chemistry in molecular clouds. Using the technique, we investigated the possibility of reducing the number of chemical reactions and species in the UMIST 95 database simultaneously. In addition, we did the same reduction but with the "objective technique" in order to compare both methods. We found that it is possible to compute the abundance of carbon monoxide and fractional ionisation accurately with significantly reduced chemical networks in the case of pure gas-phase chemistry. For gas-grain chemistry involving surface reactions reduction is not worthwhile. Compared to the "objective technique" our reduction method is more effective but more time-consuming as well.

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

1. Introduction

Despite the significant growth of computer power over the last years, the modelling of the chemical evolution of protostellar cores and protoplanetary discs is still a challenging computational task. This is even more true if one aims at the simultaneous self-consistent modelling of the dynamical and chemical evolution of these systems.

The mathematical formulation of the chemical processes in space is realised by differential equations describing chemical kinetics. They contain terms for all chemical reactions expected to proceed efficiently in the interstellar medium (ISM). Along with abundances of all involved species, these terms depend on the rate coefficients that are summarised in special databases. The relevant astrochemical rate files, like the UMIST rate file or Ohio New Standard Model, comprise hundreds of species and thousands of reactions (Millar et al. 1991, 1997; Le Teuff et al. 2000; Terzieva & Herbst 1998; Aikawa & Herbst 1999). Of course, one can only wonder if these databases contain all the information about reactions needed to accurately reproduce observed abundances of interstellar molecules. The opposite question to ask is if all this information is always needed.

In many astronomically interesting situations it is enough to follow the evolution of a limited number of species only.

Intuitively, it seems to be apparent that to predict an abundance of N_2H^+, for example, one can afford computing C_{10} abundance with less accuracy or even ignore this molecule altogether. In most cases, though, modelling of the chemical evolution of a parcel of the interstellar gas under fixed conditions or in a limited predefined range of conditions is not very time-consuming, so one probably will not be eager to sacrifice any accuracy even for the sake of order of magnitude gain in computational speed. However, in the case of dynamical modelling with changing density, UV intensity, temperature etc., a reduced chemical network may help to distinguish between feasible and non-feasible problems or at least to ease the computational burden if parallel processors are in use. One possible application for reduced chemical networks would be the modelling of the evolution of magnetised protostellar clouds or protoplanetary accretion discs, when it is necessary to compute the fractional ionisation self-consistently. Another example of dynamically important species is carbon monoxide (CO) which under certain conditions can be the most important molecular coolant (see, for example, Glassgold & Langer 1973).

Several authors have already used reduced chemical networks, based on the above arguments, however, without presenting accurate mathematical considerations (e.g., Gerola & Glassgold 1978; Howe et al. 1994; El-Nawawy et al. 1997). Recently, Ruffle et al. (2002) (hereafter RRPHH) and Rae et al. (2002) (hereafter RBHPR) made a first attempt to reduce

astrochemical networks by so-called "objective reduction techniques", developed in combustion chemistry. They have shown that it is possible to quantify the reduction task by introducing a certain criterion that would allow in each particular case to indicate, abundances of which species must be followed in order to have a reasonable estimate for an abundance of a species under investigation. For static regions with physical conditions typical of diffuse clouds, they isolated the species set that contains tens instead of hundreds species. This reduction only introduces a factor of two uncertainty in predicted CO abundance. The same task has been solved for the fractional ionisation as well.

We perform a similar analysis of the UMIST 95 chemical reaction database in order to find if it is possible to reduce the number of species and/or reactions in the chemical networks used to calculate ionisation degree and carbon monoxide abundance under conditions typical of molecular clouds. Unlike RRPHH and RBHPR, we partly focus on the medium that is more advanced toward the formation of a star. This situation is more complicated from the chemical point of view. First, pre-stellar clouds are often shielded from the interstellar UV radiation field. Dissociating photons, being an additional chemical factor, in effect simplify the chemical network, as they prevent many complex species from being formed. Reactions on grain surfaces are another factor that cannot be ignored in dense clouds.

The paper is organised as follows. First, we describe our chemical model in Sect. 2. The species-based and reaction-based reduction methods are outlined in Sect. 3. Results of reductions obtained with both methods are presented in Sect. 4 (ionisation degree) and Sect. 5 (CO). These results are discussed in Sect. 6. A conclusion follows.

2. Chemical model

We take the rates for gas-phase reactions from the UMIST 95 rate file (Millar et al. 1997). In addition to gas-phase chemistry, gas-dust interaction and dust surface reactions are considered in some of the models. The rates at which surface reactions proceed and the very applicability of the rate approximation to surface chemistry still remain a subject of debate. This is why many authors prefer to neglect surface reactions altogether (for instance, see Aikawa & Herbst 1999; Bergin & Langer 1997; Bergin et al. 1995; Charnley et al. 2001). However, in the attempt to constrain the chemical network in a cold and dense molecular cloud core, taking into account gas-dust interactions seems to be unavoidable, as dust is now widely believed to play a crucial role in molecular cloud chemistry, serving both as a sink for frozen-out species and as a catalyst for the synthesis of complex molecules (see, however, Turner 2000). In this paper we seek not to reproduce any particular abundance pattern observed in molecular clouds, but rather to investigate the very possibility of reduction when surface reactions are present. This is why we did not try to incorporate any new ideas about surface chemistry.

Table 1. Model designations.

Notation	Meaning
DIFF	$n_H = 10^3$ cm^{-3}
DENS	$n_H = 10^7$ cm^{-3}
GAS	Gas-phase network (395×3864[a])
GAD	GAS with accretion and desorption (543×4593)
DUST	GAD with surface reactions (543×4785)
HM	"High metals"
LM	"Low metals"

[a]The network contains 395 species involved in 3864 reactions.

Table 2. Adopted elemental abundances.

Element	"High metals"	"Low metals"
He	9.75(−2)	9.75(−2)
C	7.86(−5)	7.86(−5)
N	2.47(−5)	2.47(−5)
O	1.80(−4)	1.80(−4)
S	9.14(−6)	9.14(−8)
Si	9.74(−7)	9.74(−9)
Na	2.25(−7)	2.25(−9)
Mg	1.09(−6)	1.09(−8)
Fe	2.74(−7)	2.74(−9)
P	2.16(−8)	2.16(−10)
Cl	1.00(−7)	1.00(−9)

2.1. Physical conditions and initial abundances

We solve equations of chemical kinetics for the range of fixed physical conditions, listed in Table 1, where model designations are given as well. Gas and dust temperatures are 10 K in all cases. No direct UV radiation is present, implying the conditions, typical of obscured regions, like cores of molecular clouds, where the visual extinction $A_V \geq 10$ mag. Dust grains are assumed to be silicate-like spheres with a constant size $a_d = 0.1$ μm, density $\rho_d = 3$ g cm^{-3}, and 10^6 surface sites for adsorption (Hasegawa et al. 1992). Dust is supposed to constitute 1% of the gas density by mass.

All abundances in the paper are given with respect to the number of hydrogen nuclei. We use "high metal" and "low metal" sets of initial abundances (e.g. Lee et al. 1998) quoted in Table 2. In the "high metal" set the standard solar elemental composition is corrected with a modest depletion of 2 for S and stronger depletions of 10 for Na, 50 for Si, 60 for Mg, and 110 for Fe. The "low metal" values contain additional depletion factors of 100 for each of these elements. The abundances of all elements but P and Cl are taken from Aikawa et al. (1996). For P and Cl we take values from Grevesse & Sauval (1998) and use the same depletion factors as for Fe. Hydrogen is assumed to be completely in molecular form initially. All other elements are present in atomic form at $t = 0$.

Below details of the adopted model of gas-dust interaction are provided.

2.2. Gas-grain interactions

2.2.1. Neutral accretion

The accretion rate $k_{ac}(i)$ of the ith species is given by

$$k_{ac}(i) = \pi a_d^2 v_{th}(i) n_d S,$$

where $v_{th}(i) = \sqrt{8kT_{gas}/\pi m_i}$ is the thermal velocity for the ith species, n_d is the number of dust grains per unit volume, T_{gas} is the gas temperature, m_i is the atomic mass of the ith species, and k is the Boltzmann constant. The sticking probability S is assumed to be 0.3 for all neutral species except for H, He, and H_2. The sticking coefficient of atomic hydrogen is estimated from Eq. (3.7) by Hollenbach & McKee (1979). Sticking probabilities for helium and molecular hydrogen are assumed to be zero.

2.2.2. Dissociative recombination on grain surfaces

Following Umebayashi & Nakano (1980), we suppose that all grains have unit negative charge and thus can act as electron donors in the same reactions of dissociative recombination that occur in the gas phase. The rate coefficient for reactions of dissociative recombination on grain surfaces is given by

$$k_{dr}(i) = \sum_j \alpha_j \pi a_d^2 v_{th}(i) n_d C_{ion}, \tag{1}$$

where

$$C_{ion} = S \left(1 + \frac{1.671 \times 10^{-3}}{a_d T_d} \right) \tag{2}$$

with a_d and T_d being the dust size and temperature, respectively (Rawlings et al. 1992). Here the summation is over different recombination channels; the quantity α_j denotes the probability of a particular channel. Sticking probability S is 0.3 for all ions. Products of these reactions are assumed to return to the gas-phase immediately.

2.2.3. Desorption from grain surfaces

The two desorption processes taken into account in our model are thermal evaporation and cosmic ray induced desorption.

The thermal evaporation rate $k_{th}(i)$ of the ith surface species is

$$k_{th}(i) = \nu_0 \exp(-T_D(i)/T_d), \tag{3}$$

where T_d is the dust temperature, $kT_D(i)$ is the binding energy for physical adsorption of the ith species to the dust surface, ν_0 is the characteristic vibrational frequency for the adsorbed species (Eq. (3) from Hasegawa et al. 1992).

The cosmic ray desorption rate $k_{cr}(i)$ of the ith surface species can be estimated as

$$k_{cr}(i) = 3.16 \times 10^{-19} \nu_0 \exp(-T_D(i)/70\,K). \tag{4}$$

The values of T_D for most species are taken from Hasegawa & Herbst (1993). There are some species in the UMIST 95 database for which desorption energies are not given in that paper. For these species, T_D is interpolated from values of chemically identical species or estimated as

$$T_D = 50 A_i, \tag{5}$$

with A_i being the corresponding atomic number, which is a good approximation for species from Table 4 of Hasegawa & Herbst (1993).

2.2.4. Surface reactions

The surface reactions as well as their rates are taken from Hasegawa et al. (1992) with the appropriate correction for different densities. Activation energy of 1000 K is adopted for O + CO surface reaction (Hasegawa & Herbst 1993).

2.3. Chemical networks

Three chemical networks are considered. The first one is the pure gas-phase network GAS. It consists of electrons, 12 atoms, 137 molecules, and 245 ions (395 species in total) involved in 3864 gas-phase reactions. The gas-grain network GAD is supplemented by 148 surface species and 729 gas-grain interaction processes (accretion, desorption, and surface ion recombination). The gas-grain network DUST contains 192 additional surface reactions. These networks form the basis of our investigations. In the rest of the text we refer to them as "full" networks. Equations of chemical kinetics are solved with the standard DVODE solver. Adopted solver parameters are given in the appendix.

3. Reduction methods

To reduce the number of species and/or reactions in a chemical network, one has to provide a mathematical method designed to estimate the significance of particular species or reactions to the evolution of the species under consideration. In this paper we elaborate two such methods that are outlined in this section.

3.1. Species-based reduction

This technique is derived from the method used by RRPHH and RBHPR. They have shown that it is possible to reduce the number of species in a chemical network in order to compute abundances of *selected* species with a reasonable accuracy. The species-based reduction technique is based on the strategy to specify *important* species and then to select from the entire set only *necessary* species, that must be included in the chemical network in order to compute abundances of important species with a reasonable accuracy.

Initially, the reduced species set consists of N_0 important species only. For each species in the entire set we compute the value

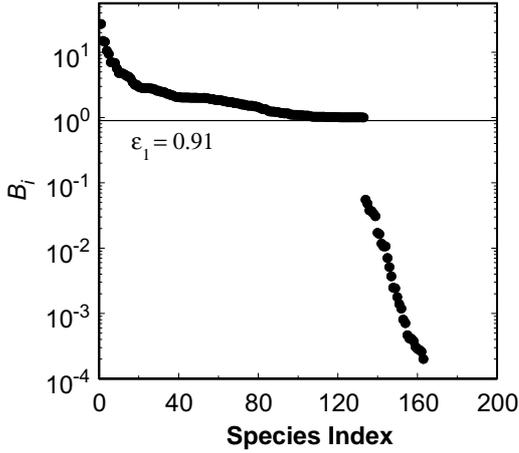$$B_i = \sum_{j=1,N_0} \left(\frac{n_i}{g_j} \frac{\partial f_j}{\partial n_i} \right)^2, \tag{6}$$

Fig. 1. Representative B values for the HM-GAS-DIFF model computed at $t = 10^7$ years. Important species are Mg^+ and S^+. The value of the cut-off parameter ϵ_1 is indicated.

where n_i is the abundance of ith species,

$$f_j = \sum_{lm} k_{lm} n_l n_m - n_j \sum_l k_{jl} n_l = G_j - L_j \qquad (7)$$

is the net rate of the jth species abundance change which can be expressed as the difference between net gain G_j and loss L_j rates, and

$$g_j = \max(G_j, L_j). \qquad (8)$$

With these definitions, the quantity

$$\frac{n_i}{g_j} \frac{\partial f_j}{\partial n_i} \qquad (9)$$

is the total rate of the abundance change of species j due to those reactions that involve species i only. The B_i is a measure of the sensitivity of the selected species abundances to the abundance of the ith species. As RRPHH noted, in this set of B_i values there is a clear boundary between "needed" and "not-so-needed" species. This is illustrated in Fig. 1, where representative B_i values and a cut-off threshold ϵ_1 are shown. We select only those species from the entire set that have B_i above a boundary value, that is

$$B_i \geq \epsilon_1. \qquad (10)$$

They are added to the reduced set if they are not there already, and B calculation is repeated with the expanded species set. The process goes on until at some step no species are added to the reduced set. The entire network then consists of these species and of only those reactions that involve the selected species. Normally, the resultant reduced set is a combination of several intermediate sets constructed at different times to account for "early" chemistry, "late" chemistry etc. But it turned out that the set reduced at the last time step ($t = 10^7$ years) works quite well at earlier times as well.

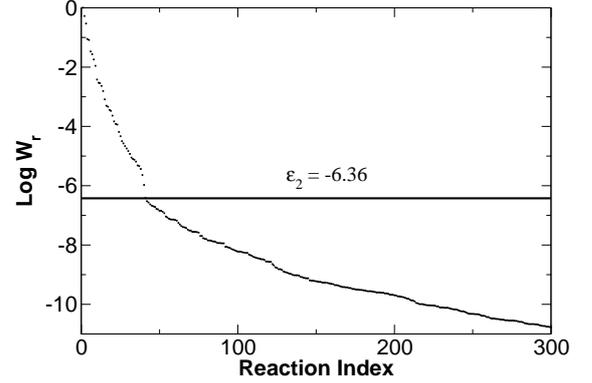It should be kept in mind that this method represents only the first part of the algorithm proposed by RRPHH.

Fig. 2. Representative w_r values for the HM-GAS-DENS model computed at $t = 10^7$ years. An important species is CO. The value of the cut-off parameter ϵ_2 is indicated.

3.2. Reaction-based reduction

This new method allows to select only those species and reactions from the entire network that are *necessary* to compute abundances of *important* species with a reasonable accuracy. Unlike the species-based reduction technique, where the number of reactions is decreased only as a by-product of the lower number of species, in this method the numbers of unnecessary species and ineffective reactions are reduced *simultaneously*. In addition to the significantly shortened computational time, this could be useful if one aims at key destruction and formation pathways for important species, where a smaller number of chemical reactions makes the analysis easier.

The basic idea of the reaction-based reduction is to search for the production and destruction reactions, most important for the evolution of an important species, and to determine their relative significance. This is done via the analysis how sensitive the net formation (or loss) rate of a given species is to the presence of particular reactions at a certain physical time.

At the beginning, the chemical model is computed with the full network in order to obtain abundances of all species from the network during the entire evolutionary time span.

Second, the *important* species are specified. Further, the algorithm estimates the weights of all species w_s and reactions w_r in order to quantify their importance for the evolution of the species under investigation by the following iterative process.

At the first iteration, weights of important species are set to 1 and weights of all other species are set to 0. At the ith iteration all possible formation and destruction pathways of the current species s_i are found and their significance values w_r^i are specified as

$$w_r^i(j) = \max \left\{ w_r^{i-1}(j), \ \frac{k_j n_{r_1}(j) n_{r_2}(j)}{\displaystyle\sum_{l=1, N_r(i)} k_l n_{r_1}(l) n_{r_2}(l)} w_s(i) \right\}. \qquad (11)$$

Here k_j is the rate of the jth reaction, $n_{r_1}(j)$ and $n_{r_2}(j)$ are the abundances of the first $r_1(j)$ and second $r_2(j)$ reactants in the jth reaction, respectively, $N_r(i)$ is the number of reactions, in which s_i is a reactant or a product, and $w_s(i)$ is the weight of the species s_i.

Table 3. Reductions made for ionisation degree in a diffuse cloud.

Model	Important species	Reduced network	Speed gain
Species-based reduction			
HM-GAS-DIFF	S^+	123×1583	~ 25
HM-GAS-DIFF	S^+, Mg^+	126×1619	~ 20
LM-GAS-DIFF	H_3^+	282×2539	~ 4
LM-GAS-DIFF	H_3^+, HCO^+	309×3177	~ 3
Reaction-based reduction			
HM-GAS-DIFF	e^-	58×111	550
LM-GAS-DIFF	e^-	73×169	490
HM-DUST-DIFF	e^-	210×683	15
LM-DUST-DIFF	e^-	357×1648	2

Consequently, a new set of species, which are found at that iteration to be *necessary* for the evolution of the important species and which were not considered at previous iterations, is formed. Their weights w_s are estimated as the maximum possible values of the weights w_r of the reactions they are involved in. Then these species are added to the set of necessary species, and the last two steps are repeated. This process is performed for several stages during the computational time.

The iterations are stopped when all species and all time moments are considered. Then one obtains a reduced chemical network from the full network by choosing only those reactions, that have weights w_r exceeding a pre-defined cut-off threshold ϵ_2

$$\log w_r \geq \epsilon_2. \tag{12}$$

The typical w_r values and cut-off parameter ϵ_2 are shown in Fig. 2. The value of this cut-off is chosen to satisfy the requested accuracy requirement. In our calculations the maximum allowed error is set to 30%. If there is a difference greater than 30% in abundances of the important species computed with the full and reduced networks for any particular time step, the cut-off is readjusted to a new, smaller value, and the last step is repeated.

4. Ionisation degree

We use the two reduction techniques described in the previous section to build the reduced chemical networks that could be used for the computation of the ionisation degree in molecular clouds. All the models are first computed with the full chemical networks. Then we apply the reduction techniques and compare the ionisation degree computed with the full and reduced networks. The results of the reduction together with relevant computational speed gains are summarised in Tables 3–5.

4.1. Diffuse cloud

This case corresponds to the cloud at the initial stage of the protostellar collapse ($n_H = 10^3$ cm^{-3}). For pure gas-phase chemistry and high initial metal abundances (HM-GAS-DIFF), the
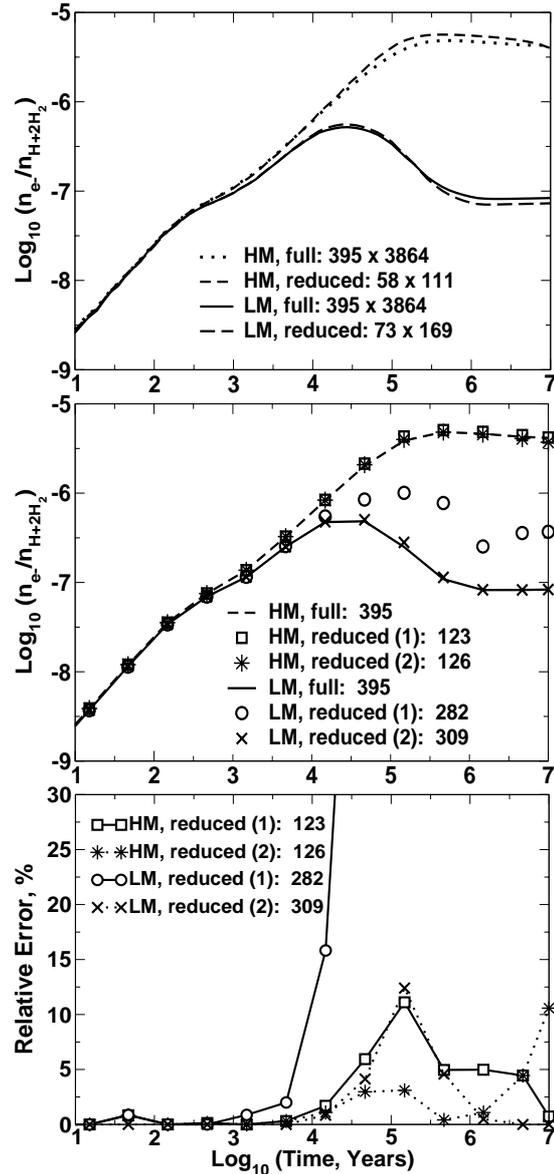

Fig. 3. Ionisation degree (top and middle panels) and relative errors (bottom panel) in a diffuse cloud, computed with the full and reduced networks for pure gas-phase chemistry (HM-GAS-DIFF and LM-GAS-DIFF models). *Top* panel reproduces results of the reaction-based reduction. Indicated are the "exact" solutions for high (dotted line) and low (solid line) metallicities as well as the solution for the reduced species sets (HM – dashed line, LM – long-dashed line). *Middle* and *bottom* panels illustrate the results of the species-based reduction. Shown are the "exact" solutions (HM – dashed line, LM – solid line) and the solutions for various reduced sets (see text).

dominant ions during most of the 10^7 years are S^+ and Mg^+. We found that it is sufficient to consider only these ions as important species in the species-based reduction method. Taking sulphur to be the only important species, we can reduce the number of species from 395 to 123 and achieve a computational speed gain of a factor of about 25 with uncertainty of $\sim 15\%$ at $t \sim 10^5$ years (see Fig. 3, middle and bottom panels, squares). If we consider both ionised magnesium and ionised sulphur to be important species, the number of species in the reduced set

is 126, and the accuracy is better than 5% during the entire evolution (see Fig. 3, middle and bottom panels, stars). The computational gain is almost the same (see Table 3). Note that metals other than magnesium (i.e., sodium and iron) are almost equally important for the ionisation degree. But as they enter the chemical network in a similar way, it is sufficient to designate magnesium to be an important species in order to include in the reduced set all the species that are needed to compute abundances of Na and Fe as well.

With the reaction-based reduction technique, we choose electrons to be the only important species. In this case the number of necessary species is 58, which is more than two times smaller compared to the species-based reduction. Additionally, the number of chemical reactions is reduced from 3864 to 111 (see Fig. 3, top panel). The achieved computational time gain is of the order of 500, while the resulting uncertainties are by definition smaller than 30% during all 10^7 years of the evolution (see Table 3). It should be recalled that the accuracy is preset in the reaction-based reduction, so in all figures we only show relative errors for the species-based technique.

The small number of necessary reactions in the reduced network can be explained by the fact that in this case the chemistry is governed by a rather restricted set of ionisation-recombination processes. Such a set is easily extracted from the entire network by the reaction-based selection algorithm. The fundamental reactions during the entire evolution time are the ionisation of molecular hydrogen and helium by cosmic rays and ionisation of carbon and sulphur by cosmic ray induced UV photons. These ions rapidly react with abundant molecules by efficient ion-molecule reactions, forming complex molecular ions, like HCO^+. In turn, these molecular ions transfer charge to metal atoms. As metal ions are less chemically active, they become the most abundant charged species, regulating the fractional ionisation (Oppenheimer & Dalgarno 1974).

The situation is more complicated from the chemical point of view when the initial metallicity is low. In the absence of abundant metals, the role of electron suppliers goes to H_3^+, HCO^+, and C^+, involved in a rich chemistry. Even though H_3^+ is the dominant ion, it alone does not determine the ionisation degree with enough accuracy which is illustrated in Fig. 3 (middle and bottom panels, circles). When this ion only is considered to be an important species in the species-based reduction, errors are negligible only at earlier times when the chemistry is relatively simple. However, after 10^4 years the errors grow significantly, exceeding a factor of 3 at the end of the computation. To account for later chemistry, one has to take into account another important ion, HCO^+. When these two species are designated as important, errors do not exceed 15% during the entire computational time (crosses in middle and bottom panels in Fig. 3). However, due to the complicated chemical connections of the two ions, the species set reduction is only modest in this case. Less than one hundred species can be excluded from the set with a reduction of the computational time by a factor of 3 only (see Table 3).

Not all the reactions involving these ions are important, though. With the reaction-based reduction method, we succeed in isolating a three time smaller set of 73 species involved in 169 reactions which are needed to follow the evolution of the

ionisation degree in this case. It decreases the time, needed for the computation, by a factor of 500 (see Table 3). The slightly larger number of the necessary species and reactions in this case compared to the case of high metal initial abundances can be explained by more diverse chemistry involving interactions of complex species. The accuracy of the computed ionisation degree is again better than 30%.

Inclusion of accretion and desorption processes as well as surface reactions into these models does not lead to any noticeable changes, primarily, because the density is too low to produce significant ice mantles. Results of the species-based method show that it is possible to use the same reduced set in HM-GAS-DIFF, HM-GAD-DIFF, and HM-DUST-DIFF models without significant loss of accuracy. The same is true for the low metallicity models. However, applying the reaction-based approach to the gas-grain chemical network including surface reactions (DUST-DIFF), we found only moderate reduction as nearly half of the species have to be retained in the reduced network. The reason is that the surface reactions have very high rates compared to the gas-phase reactions and due to the selectivity of the reaction-based method many of them are designated to remain in the reduced network. This leads to the larger number of chemical species and reactions in such a network compared to the pure gas-phase case and, consequently, to the smaller computational time gains, which are about a factor of ten in this case (see Table 3).

4.2. Dense cloud

4.2.1. Gas-phase chemistry

When no gas-dust interaction is taken into account, the case of a dense cloud ($n_H = 10^7$ cm^{-3}) at high metallicity is qualitatively similar to the low-density case. Metals are again the dominant ions. To compute their abundances (and hence the ionisation degree) with better than 50% mean accuracy one needs to include sodium only to the list of important species in the case of the species-based reduction. The reduced set contains 72 species and provides two orders of magnitude gain in computational speed. To further improve accuracy we add sulphur to the list of important species. With the reduced set of 121 species we obtain errors less than 10% during the entire computational time. The reaction-based technique gives similar results and produces a reduced network consisting of 131 species and 313 reactions with the same computational gain. The difference between the high- and low-metallicity cases is smaller for a dense cloud than for a diffuse cloud. In a denser environment such chemically active ions as H_3^+ and HCO^+ are less abundant, and metal ions dominate the ionisation degree both in high- and low-metallicity cases. As a result of this similarity, in a dense cloud for the high and low metallicities the reduced species sets are nearly the same both for the species- and reaction-based approaches, with similar errors and computational gains (see Table 4).

Table 4. Reductions made for the ionisation degree in a dense cloud with pure gas-phase chemistry.

Model	Important species	Reduced network	Speed gain
	Species-based reduction		
HM-GAS-DENS	Na$^+$	72×568	~100
HM-GAS-DENS	Na$^+$, S$^+$	121×1560	~30
LM-GAS-DENS	Na$^+$	71×567	~100
LM-GAS-DENS	Na$^+$, S$^+$	132×1717	~25
	Reaction-based reduction		
HM-GAS-DENS	e$^-$	131×313	130
LM-GAS-DENS	e$^-$	157×386	55

4.3. Gas-grain chemistry

The situation changes drastically, when gas-grain interactions are taken into account. In the high-metallicity case, at early stages of the evolution, the dominant ions are the same as in the diffuse medium, i.e., metals. However, after 10^4 years their depletion becomes important, and the dominant ions are H$_3^+$, HCO$^+$, and N$_2$H$^+$. The straightforward use of the species-based criterion under such conditions leads to the significant loss of accuracy at this time. The problem is that this criterion is based on the selection of species whose *abundances* are needed to compute the abundance of an important species. But the depletion case is not that simple. Abundances of mantle species with high desorption energies are definitely not important and do not have to be computed with any accuracy. Based on the formal criterion (10), these species are to be excluded from the reduced set. However, this leads to the exclusion of the corresponding accretion reactions from the network, and counterparts of the excluded mantle species remain in the gas phase, significantly altering its chemistry.

With the species-based reduction method we investigated the GAD-DENS model, i.e., the model in which accretion and desorption processes are taken into account in addition to gas-phase chemistry. As we have no formal way to select species whose *absence* in the gas phase is important to compute the ionisation degree, we choose to check two artificial possibilities. First, we add surface metals to the reduced network as they are primary contributors to the electron abundance in the gas phase. Second, we allow all the selected neutral species to stick to dust grains, reasoning that if their gas phase abundances are deemed important then their depletion is important as well. Results are shown in Fig. 4 (middle and bottom panels). When only metal depletion (with a handful of other species selected automatically) is taken into account the errors are quite large, sometimes reaching 50%. To decrease errors, depletion of all selected neutral species is needed. In the latter case, the approximate solution differs from the "exact" one by as much as 20% but later on the difference is much smaller dropping to just a few per cent at $t = 10^7$ years (see Table 5).

The ambiguity of the previous selection procedure is not an issue in the reaction-based approach which is specifically designed to find necessary formation and destruction pathways
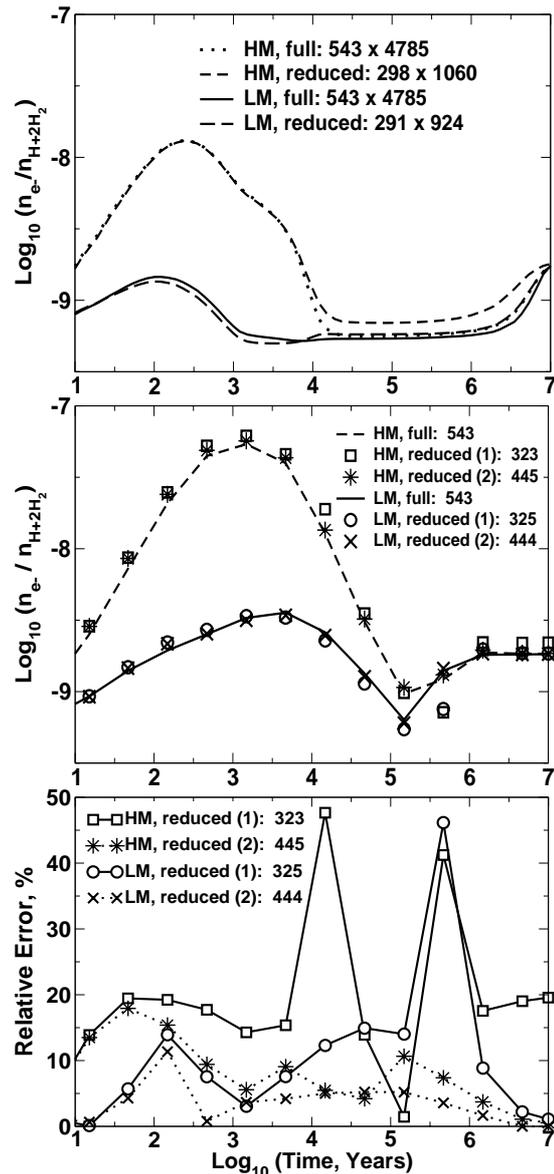

Fig. 4. Ionisation degree (top and middle panels) and relative errors (bottom panel) in a dense cloud, computed with the full and reduced networks for gas-phase chemistry including accretion and desorption processes and dust surface reactions. *Top* panel reproduces results of the reaction-based reduction for the DUST-DENS model. Indicated are the "exact" solutions for high (dotted line) and low (solid line) metallicities as well as the solution for the reduced species sets (HM – dashed line, LM – long-dashed line). *Middle* and *bottom* panels illustrate results of the species-based reduction for the GAD-DENS model. Shown are the "exact" solutions (HM – dashed line, LM – solid line) and the solutions for various reduced sets (see text).

rather than necessary species. As it was mentioned above, this method of reduction treats gas-grain interactions and surface reactions equally with gas-phase reactions. Thus, one does not have to worry about which surface species to keep in a reduced set in order to estimate the abundances of important species. Therefore, this method works much better in the reduction of chemical networks involving complicated processes like gas-grains interactions and surface reactions. With the

Table 5. Reductions made for the ionisation degree in a dense cloud with gas-grain chemistry included.

Model	Important species	Reduced network	Speed gain
Species-based reduction			
HM-GAD-DENS	H_3^+, surface metals	323×3201	~6
HM-GAD-DENS	H_3^+, all surface	445×3445	~2
LM-GAD-DENS	H_3^+, surface metals	325×2933	~4
LM-GAD-DENS	H_3^+, all surface	444×3171	~2.5
Reaction-based reduction			
HM-DUST-DENS	e^-	298×1060	8
LM-DUST-DENS	e^-	291×924	7

reaction-based technique, we reduced the number of species and reactions in the gas-grain chemical network involving surface reactions (DUST-DENS). We were able to remove about half of the species from the full gas-grain network and to reduce the number of reactions by a factor of 5 (see Fig. 4, top panel). The reduction speeds up the computation by a factor of 8 only (see Table 5). At times, earlier than about 10^4 years, the ionisation degree is calculated with an accuracy better than 10%. At $t > 10^4$ years, the uncertainties grow but remain less than 30%. The reason is that it is more difficult to follow the evolution of the ionisation degree with the reduced network, since the importance of the complicated gas-grain interactions and surface reactions is raising up. In the low-metallicity case (LM-GAD-DENS), which is more complex from the chemical point of view, the reaction-based approach produces a reduced network that consists of 291 species and 924 reactions and predicts an ionisation degree with a requested accuracy of 30% during the entire evolutionary time. It accelerates the computations by a factor of 7 (see Table 5).

Comparison of top (DUST) and middle (GAD) panels in Fig. 4 shows that there is a difference between the evolution of ionisation degree in the case of gas-grain chemistry with and without surface reactions. When surface reactions are accounted for, fractional ionisation drops to 10^{-9} in $t \sim 10^4$ years. In the case of gas-phase chemistry with accretion and desorption it reaches the same equilibrium value later, after 10^5 years. Also, the maximum value of the ionisation degree is higher in the latter case. Thus, we conclude that surface reactions are important for the accurate estimation of the fractional ionisation in dense molecular clouds at late stages of their evolution.

To conclude this section, we emphasise that the reaction-based technique is more suitable for the reduction of gas-phase or gas-grain chemical networks if one intends to follow the evolution of the ionisation degree in diffuse or dense molecular clouds with a relatively small number of chemical species and reactions and a reasonable accuracy than it is the case for the species-based scheme.

5. Carbon monoxide

Essentially the same scheme of reduction, as in the previous section, is utilised for CO as well. First, the chemical model is computed with one of the full chemical networks. Its results are used to select key species needed to predict the CO abundance. Then the validity of a reduced network is checked by comparing the abundances obtained with the full and reduced networks for the entire evolutionary time. In all cases, we assumed that the CO molecule is the only important species. Results of the reduction and relevant computational speed gains are presented in Tables 6–9.

5.1. Diffuse cloud

In the case of pure gas-phase chemistry in a diffuse cloud (at the gas density $n_H = 10^3$ cm^{-3}, GAS-DIFF) the main processes, relevant to the evolution of carbon monoxide, are its destruction by cosmic rays or by cosmic ray induced photons and its production through the neutral-neutral reactions of oxygen with carbon atoms and various light carbon-bearing molecules, dissociative recombination of HCO$^+$, and destruction of H$_2$CO by CR-induced photons. Since metals as well as S, Si, P, and Cl do not affect the evolution of CO abundances directly, it is natural to expect that there should not be large differences between the high- and low- metallicity cases.

In the absence of gas-grain interactions the evolution of CO is comparatively simple – during almost the entire evolutionary time its abundance is steadily approaching the equilibrium value of about 10^{-4} which is reached at ~10^6 years (see Fig. 5, top and middle panels).

With the species-based reduction, of all 395 species we select only 36 species in the high-metallicity case and 27 species in the case of low metal abundances (see Fig. 5, middle panel). Due to the small size of these reduced networks, time needed to solve the relevant ODE system is negligible, less than a few seconds (see Table 6). At early evolutionary phase ($t \sim 10^3$–10^4 years) the uncertainties of the CO abundance can reach 50% for high metallicity and 80% for low metallicity. Later, when the equilibrium abundance is reached, error drops to about 20% (see Fig. 5, bottom panel). The reason for the high uncertainty at early times is that such rare species as CH$_3$CO$^+$ and CH$_2$CO, which are not recognised by the species-based algorithm to be necessary species, are in fact important at the early evolutionary phase for the accurate estimation of the CO abundance.

Applying the reaction-based reduction, we are able to follow the evolution of the CO abundance for 10^7 years with an accuracy better than 30%. However, the price to pay for this is a significant number of species to be held in the corresponding reduced networks. One needs to keep 158 and 95 species in the reduced networks for high and low metallicities, respectively (see Fig. 5, top panel). The relevant computational speed gain is a factor of 50 for the HM case and about 200 for the LM case (see Table 6). It can be seen from Fig. 5 (top and middle panels), that the CO abundances in the case of high- and low-metallicities do behave similarly. Nevertheless, from the chemical point of view the case of low initial abundances of metals
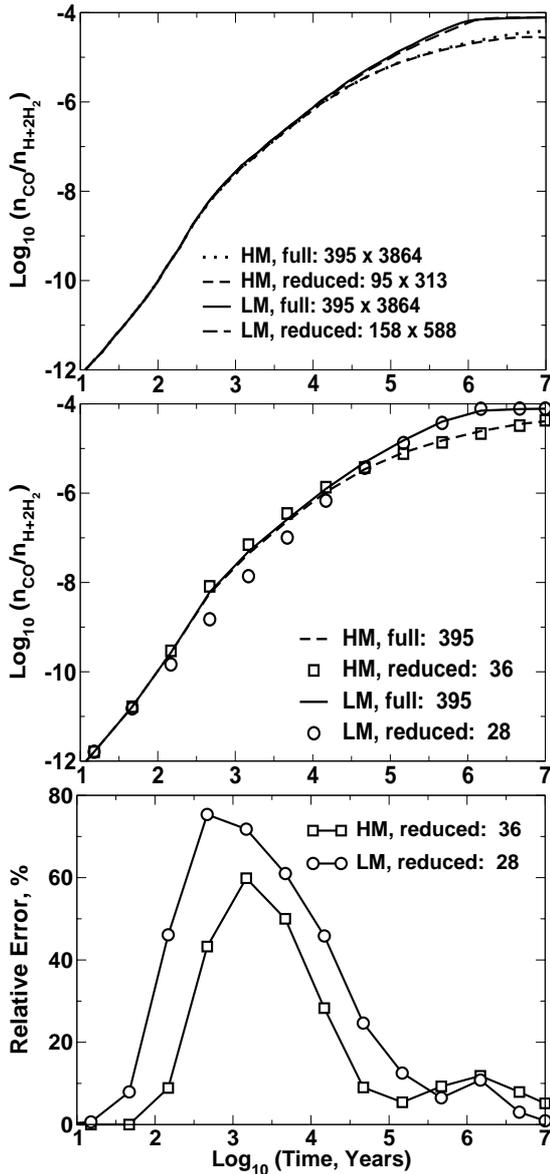
Fig. 5. The CO abundances (top and middle panels) and relative errors (bottom panel) in a diffuse cloud, computed with the full and reduced species set for pure gas-phase chemistry (GAS-DIFF model). *Top* panel reproduces results of the reaction-based reduction. Indicated are the "exact" solutions (HM – dotted line, LM – solid line) and the solution for the case when CO is considered to be the only important species (HM – dashed line, LM – long-dashed line). The *middle* and *bottom* panels illustrate results of the species-based reduction. Shown are the "exact" solutions (HM – dashed line, LM – solid line) and the solution for the case when CO is an important species (HM – open squares, LM – open circles).

is somewhat simpler in comparison with the high metallicity case and implies smaller number of species and reactions to be kept in the reduced network.

Inclusion of accretion-desorption processes and surface reactions does not affect the chemistry in a diffuse cloud significantly. As we already mentioned in Sect. 4.1, the gas-grain interactions are not efficient at such low density ($n_H = 10^3$ cm^{-3}) since the typical rate of collisions between dust grains and gas

Table 6. Reductions made for CO in a diffuse cloud.

Model	Important species	Reduced network	Speed gain
Species-based reduction			
HM-GAS-DIFF	CO	36×240	>100
LM-GAS-DIFF	CO	28×182	>100
HM-GAD-DIFF	CO	37×242	>100
LM-GAD-DIFF	CO	27×173	>100
Reaction-based reduction			
HM-GAS-DIFF	CO	158×588	50
LM-GAS-DIFF	CO	95×313	240
HM-DUST-DIFF	CO	298×1293	8
LM-DUST-DIFF	CO	306×1310	5

species is far too low. Using the species-based approach, we found that it is enough to retain only 37 species for the high metal initial abundances and 27 species in the LM case (see Table 6). These are almost the same numbers as in the case of pure gas-phase chemistry. In fact, one can use the same reduced sets of species and reactions in the GAS-DIFF, GAD-DIFF, and DUST-DIFF models (separately for each metallicity set). However, uncertainties in the computed CO abundances in all cases exceed 50% at $t \sim 10^3$–10^4 years.

It is not that easy to remove these uncertainties. The application of the reaction-based method allows to cut the entire 543 species set by a factor of 2 in this case (see Table 6). It is more than two times the number of species found to be necessary for the correct reproduction of CO abundances in the case of pure gas-phase chemistry. Consequently, it speeds up the calculations by a factor of 5 only. The reason is, as noted in the previous section, that the reaction-based algorithm tends to keep some surface reactions in the reduced networks. Obviously, it leads to the larger number of species to be retained in the relevant reduced networks compared to the case of pure gas-phase chemistry.

5.2. Dense cloud

5.2.1. Gas-phase chemistry

In a dense molecular cloud ($n_H = 10^7$ cm^{-3}) the main processes leading to the production and destruction of CO molecules in the case of pure gas-phase chemistry (GAS-DENS) are the same as in a diffuse cloud, but with one important change. At such high density, the role of chemical reactions involving abundant species like C, O, CH, and CH$_2$, becomes even more important. Therefore, we may expect that in this case the chemistry relevant to the evolution of carbon monoxide is even simpler than in the diffuse cloud (GAS-DIFF). It implies a smaller set of necessary species.

The results of reduction for this case are shown in Fig. 6. The CO abundance increases rapidly at early evolutionary stages ($t \lesssim 10^3$ years). Later, when the chemical equilibrium is reached, it remains constant around 10^{-4}.
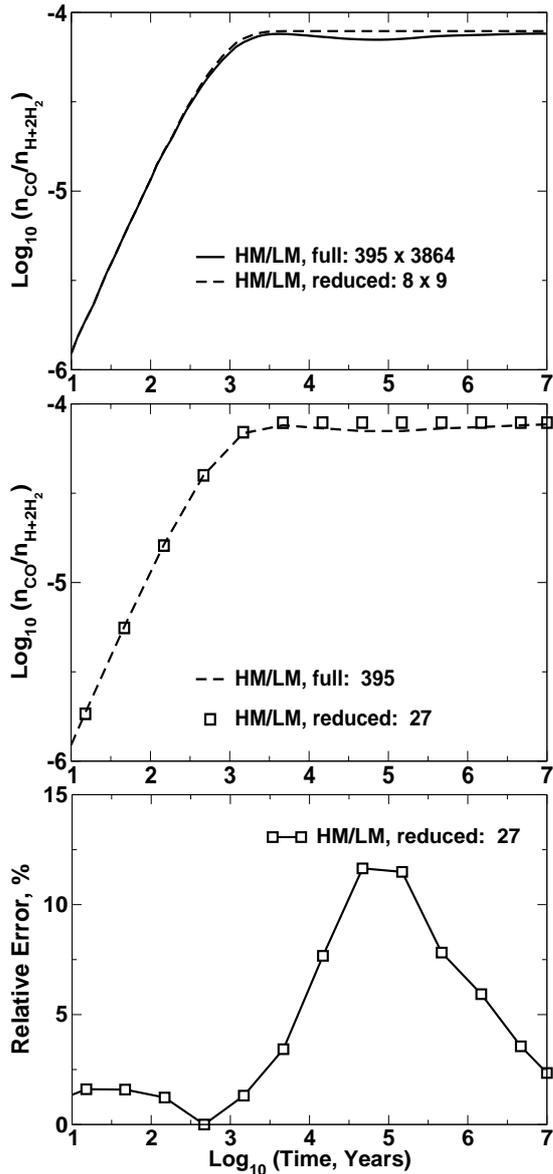
Fig. 6. Same as in Fig. 5 but for a dense cloud (GAS-DENS).

Using the species-based reduction technique, we succeeded in the isolation of a small set of 27 species allowing us to follow the evolution of CO with a very good accuracy <15% for all 10^7 years for both the high- and low-metallicity case (see Fig. 6, middle and bottom panels). Again, the computational time is negligibly small, less than a second (see Table 7).

But even this 27 species set contains excessive information. Applying the reaction-based reduction approach, we revealed that in reality there are only 8 species involved in 9 reactions which are necessary for the accurate estimation of CO abundances during the entire evolutionary time (see Fig. 6, top panel). The relevant reduced network is given in Table 8. The uncertainties of computed CO abundances do not exceed 15% for all 10^7 years of the evolution. This remarkable result, showing the power of the reaction-based technique, explains why there is no difference between the cases of high and low

metals in a dense cloud: metals are completely excluded from this network.

In the medium with the atomic initial composition (except for molecular hydrogen) reactions start from the dissociation of H_2 molecules by cosmic ray particles and from their radiative association with atomic carbon. The latter reaction leads to CH_2 formation. This molecule reacts with atomic H and C leading to CH and C_2H. These three molecules (CH, CH_2, and C_2H) associate with atomic oxygen finally producing the CO molecule. These processes are balanced by destruction of CO and CH by CR-induced photons. In this way, the key reaction pathways can be isolated for which high-quality experimental reaction rate measurements have to be provided for an accurate modelling. It may seem to be somewhat surprising that the reduced network does not contain HCO^+, at variance with the diffuse cloud case. Note, however, that the maximum value of the HCO^+ abundance reached in the high-density model ($\sim 10^{-10}$) is two orders of magnitude less than in the diffuse cloud model. Given the correspondingly low electron abundance, this prevents effective CO synthesis in dissociative recombination of HCO^+. Proton transfer reactions of CO with H_2^+ and H_3^+ that would transform CO to HCO^+ are also nearly quenched due to low abundances of these ions. Thus, while CO is definitely an important species for HCO^+ in a dense medium, the opposite is not true.

Going somewhat out of the scope of the present paper, we mention briefly that this network proved to be valid under a much wider range of conditions that are described here. Calculations that will be presented in a subsequent paper show that it can be used for estimating the CO abundance not only in dark dense clouds, but in a translucent ($A_V > 1$ mag) medium as well. It gives less than 50% error at $10^4 < n_H < 10^{10}$ cm^{-3} and $T < 250$ K and can be used in a denser medium as well ($n_H < 10^{12}$ cm^{-3}) provided $T \sim 200$–250 K and $A_V > 5$ mag, conditions being typical of hot cores or protoplanetary discs.

The accuracy of this network is also insensitive to the variation of the adopted C/O ratio (0.43) within a factor of a few. The value of this ratio would be critical, though, in the attempt to construct a reduced network for carbon or oxygen separately. If carbon is less abundant than oxygen (as in the adopted abundance sets), all C atoms are locked in CO molecules, and the reduction is rather effective. In fact, it is possible to construct a single network of a few tens of species that reproduces abundances of C, O, and CO simultaneously with less than 100% uncertainty. If the C/O ratio is greater than 1, extra carbon is available for producing long carbon chains, and the effective reduction (with C as an important species) is not possible.

5.2.2. Gas-grain chemistry

The situation is no longer trivial when gas-grain interactions and surface reactions are taken into account (GAD-DENS and DUST-DENS). The influence of these processes on the evolution of abundances is twofold. First, the freeze-out of the gas-phase CO leads to the activation of certain chemical reaction chains that are suppressed in the presence of CO. Second, the presence of CO in icy mantles can drive some surface reactions

Table 7. Reductions made for CO in a dense cloud with pure gas-phase chemistry.

Model	Important species	Reduced network	Speed gain
Species-based reduction			
HM-GAS-DENS	CO	27×133	>100
LM-GAS-DENS	CO	27×152	>100
Reaction-based reduction			
HM-GAS-DENS	CO	8×9	$>10^4$
LM-GAS-DENS	CO	8×9	$>10^4$

Table 8. The reduced gas-phase network for CO chemistry in a dense cloud obtained with the reaction-based method.

	Reactions		
1 $H + CH_2$	$\rightarrow$	$CH + H_2$	
2 $H_2 + C$	$\rightarrow$	$CH_2 + PHOTON$	
3 $C + CH_2$	$\rightarrow$	$C_2H + H$	
4 $O + CH$	$\rightarrow$	$CO + H$	
5 $O + CH_2$	$\rightarrow$	$CO + H + H$	
6 $O + C_2H$	$\rightarrow$	$CO + CH$	
7 $H_2 + CRP^a$	$\rightarrow$	$H + H$	
8 $CH + CRPHOT^b$	$\rightarrow$	$C + H$	
9 $CO + CRPHOT$	$\rightarrow$	$C + O$	

[a] Cosmic ray particle.
[b] CRP-induced photon.

that may eventually result in the formation of complex organic species.

In the absence of surface reactions the evolution of carbon monoxide is simple (see Fig. 7, middle panel). First, its abundance grows steadily, at $t \lesssim 5 \times 10^3$ years reaching a value of $\sim 5 \times 10^{-5}$. Then the gas-grain interaction becomes important, and the CO molecules heavily deplete from the gas phase, forming significant mantles. The chemical equilibrium is reached at 10^5 years with the gas-phase CO abundance of a few times 10^{-8}.

The species-based reduction technique isolates two sets to be used in the high- and low-metallicity cases of the GAD-DENS model. But in fact these sets are very similar to each other, and one can use the same set containing about 30 species with high- and low- initial metallicities both in pure gas-phase models and with accretion/desorption taken into account. The resulting uncertainties are smaller than 10% for both metallicity cases (see Fig. 7, bottom panel). Again, the computational time which is necessary to compute the evolution of CO is negligibly small.

The evolution of carbon monoxide in the situation, when surface reactions are considered, is shown in Fig. 7, top panel. The gas-phase CO abundance increases at early times and reaches the value of $\sim 10^{-4}$ at $t \sim 10^3$ years. Then, the depletion of CO becomes efficient. At $t \sim 10^4–10^6$ years the gas-phase CO abundance is determined by the balance between accretion

Table 9. Reductions made for CO in a dense cloud with gas-grain chemistry included.

Model	Important species	Reduced network	Speed gain
Species-based reduction			
HM-GAD-DENS	CO	31×148	>100
LM-GAD-DENS	CO	29×133	>100
Reaction-based reduction			
HM-DUST-DENS	CO	388×1563	3
LM-DUST-DENS	CO	270×798	16

and desorption processes. Its value is almost the same as the equilibrium CO abundance in the GAD-DENS model, i.e., a few times 10^{-8}. After 10^6 years surface re-processing of CO takes over. It is converted to other species, mainly, CO_2. At this stage the accretion of CO is no more balanced by its desorption, and after some time the new, much lower equilibrium value $\sim 10^{-11}$ is established. Note that this behaviour is at least partially caused by our simplified treatment of the gas-dust interactions. We adopt the Hasegawa & Herbst (1993) value for CO binding energy which is estimated for a SiO_2 surface. In reality, after the CO mantle is formed, the binding energy of CO and other molecules may become smaller, so that desorption is still competitive with surface re-processing.

With the reaction-based reduction, we are able to select sets of 388 species and 1563 reactions for the high-metallicity case and 270 species and 798 reactions for the low-metallicity case. The relevant computational gains are only about 3 and 16, respectively (see Table 9). The error of the predicted CO abundances is less than 10% during the entire evolutionary time. The number of species which are needed to estimate the CO abundance accurately in the high-metallicity case is again $\sim 50\%$ larger compared to the low-metallicity case. Reduced networks with smaller number of species are not usable in the calculations in this case. The reason is that the relevant ODE systems are so stiff for the DVODE solver that the computational times are much larger compared to the case of the full chemical network.

Concluding this section, we emphasise that if surface reactions are considered in a chemical network, then its reduction for carbon monoxide is of no practical use as the relevant computational speed gains are too small. However, if accretion and desorption of species are taken into account as the only gas-grain processes, then it is possible to find a few tens in half a thousand species which must be kept in a reduced network in order to follow the evolution of CO without significant ($\gtrsim 50–100\%$) errors.

6. Discussion

The purpose of the present paper is to check whether a typical astrochemical database contains redundant information that can be ignored in certain calculations regarding interstellar chemistry. The primary incentive for our work is the long time
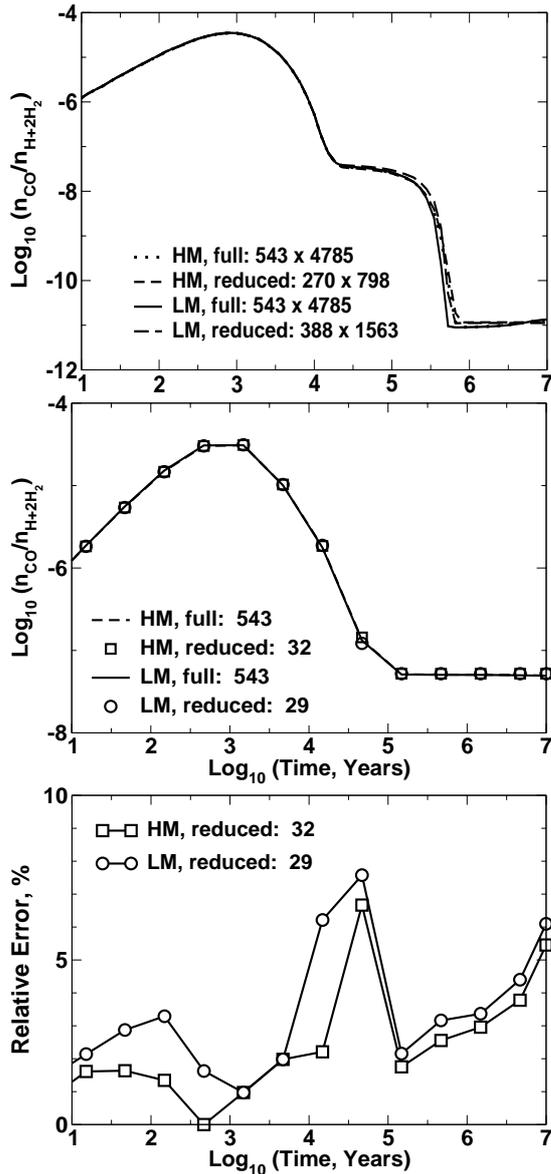
Fig. 7. Same as in Fig. 6 but for the DUST-DENS (*top* panel) and GAD-DENS (*middle* and *bottom* panels) models.

usually needed to complete a more or less detailed model of interstellar chemistry in dynamically evolving media. In many cases the evolution of only a few or even one species are of the main interest for an astronomer. The notable example is the degree of ionisation in dense interstellar clouds which is regulated by the abundances of a few dominant ions. It has been shown by many authors that in this case the relevant chemistry is governed by a rather restricted set of chemical processes (e.g. Oppenheimer & Dalgarno 1974; Ciolek & Mouschovias 1995).

Of course, one needs a mathematically rigorous way to "extract" only those species and reactions from the entire network that are needed to reproduce the evolution of a species under investigation within a reasonable numerical accuracy (say, <100%). Such a reduction would decrease the number of species in the network and, hence, the relevant computational time. Using the DVODE solver, we found that this time is proportional to roughly the third power of the number of

the involved chemical species. Thus, by decreasing the number of species in the model by just a factor of two, one can obtain an order of magnitude computational speed gain! Besides, the reduction would help to understand the role of a particular chemical compound or reaction for the evolution of an important species. However, one must bear in mind that the cost of the reduction is that the relevant reduced network has a certain range of applicability, i.e. it gives reliable estimates on the abundances of an important species for a specific range of the gas temperature, density, etc.

The first mathematically proven reduction of astrochemical networks is made by RRPHH. Their intention was to isolate a set of species and reactions which are needed to follow the evolution of the CO abundance within the 30% accuracy. They considered physical conditions, typical of translucent regions, i.e., $n_H = 500-10^5$ cm^{-3}, $T = 10$ K, $A_V = 0.5-5$ mag, with "low metal" initial abundances. They discriminated 69 necessary species participating in 241 reactions from the Ohio New Standard Model, including reactions of dissociative recombination on dust grains. They found that it is possible to decrease further the number of necessary species and reactions to 33 and 116, respectively, by the artificial modification of the network. It consisted in exclusion of all reactions involving carbon chains longer than $C_2H_2^+$ and in introduction instead of few synthetic reactions to correctly predict the abundances of shorter carbon chains.

The same method was applied by RBHPR in order to identify reduced networks that predict the degree of ionisation in interstellar clouds with less than 30% uncertainty under a wide range of physical conditions. They reduced two networks, namely, a "full" network of 218 species and 2747 reactions and a "large" network of 79 species and 1026 reactions. In the "full" network metals beside sodium were excluded, whereas the "large" network in addition excluded nitrogen and most species having more than two nuclei heavier than hydrogen. High and low metal initial abundances were used. They considered the following physical conditions: $T = 20$ K, $n_H = 500-10^5$ cm^{-3}, $A_V = 1-10$ mag. The small combined reduced network having 28 species and 71 reactions was found for the case of low metallicity. In the high metallicity case similar network of 29 species and 65 reactions was isolated with the artificially simplified sulphur chemistry.

We analysed the possibility of reducing the number of species and reactions in the UMIST 95 database by two different methods that we refer to as species-based and reaction-based techniques. Our primary goal is to compare the efficiency of these techniques under physical conditions typical of dark regions. We study the applicability of both methods in the case, when the complicated gas-grain interactions and the surface reactions are taken into account. Having in mind possible applications, we tried to make these methods as automatic as possible. Unlike RRPHH and RBHPR, we did not apply artificial modifications to the reduced networks. While such modifications can be useful in certain cases, usually it is not a trivial task and can be fraught with difficulties when a wide range of physical conditions is considered. Thus, we left the reduction entirely to the reduction techniques.

Both techniques proved to be efficient enough to reduce significantly gas-phase chemical networks needed to compute the ionisation degree or CO abundance in diffuse and dense molecular clouds with a reasonable accuracy of <30%. If the accretion-desorption processes and surface reactions are accounted for, the reduction becomes less effective since the relevant chemistry is too complicated. Even though the number of chemical reactions in the reduced networks could be decreased by a few times, making their analysis easier, the computational speed gains are too small in these models to make this reduction of particular interest for chemo-dynamical modelling. Though, at least for the ionisation degree, the situation may be alleviated by the fact that at high densities when depletion is effective, grain charging processes are more important for the fractional ionisation than the chemistry.

We found that the reaction-based technique is more effective compared to the species-based technique (see Tables 3–5). The number of reactions is at least three times smaller for the reaction-based reduction than for the species-based reduction which is natural to expect as reaction rates are not discriminated in the latter method. But the number of species is also smaller for the reaction-based technique in most models. When the gas-dust interaction is taken into account, the reaction-based technique is even more effective than the species-based technique, as it provides the simultaneous reduction of the number of species and reactions and proper treatment of the gas-grain processes. Unfortunately, it is impossible to compare our results for the ionisation degree directly with the results of RBHPR. One reason is that they considered moderate values of visual extinction $A_V = 1-10$ mag, typical of translucent clouds, whereas we dealt with obscured regions, where $A_V > 10$ mag. Another issue is that RBHPR started the reduction from a somewhat smaller "full" network of 218 species and 2747 reactions, while we considered the network of 395 species involved in 3864 reactions. Nonetheless, the resulting reduced networks have comparable sizes, namely, 29 species and 65 reactions (RBHPR, see Table 4) and 58 species and 111 reactions (this work, Table 3) in the case of high metals. In the low metallicity case the reduced network by RBHPR has 28 species involved in 71 reactions, compared to our network of 73 species and 169 reactions.

In the case of reduction made for CO, the situation is a bit more diverse. In a diffuse cloud with pure gas-phase chemistry, the species-based reduction technique overcomes the reaction-based method, but at the expense of higher uncertainties (see Table 6 and Fig. 5). In a dense cloud with pure gas-phase chemistry, the reaction-based technique allows us to extract the reduced network which is very small (Table 8) but still functional under a very wide range of physical conditions. This network is smaller than the one found by RRPHH, though it has been extracted from the larger full network. Also, it has a wider range of applicability.

The next question to ask is how to apply these methods in dynamical calculations. One can envisage two different strategies to pursue this goal. One way is to reduce the number of species and reactions at the outset and then to use the reduced network during the entire computational time. Another strategy

would be to perform the network analysis in the "real-time" mode, during the dynamical evolution.

The first strategy is obviously more cost-effective as it does not add any overhead to the computational time. The reduced network must be prepared in advance and checked against the range of physical conditions that are expected in the dynamical model. Of course, this check is only possible under simplified conditions (otherwise it makes no sense). For example, if the range of densities (temperatures) is expected in the model, one may check that the reduced network is valid at its upper and lower boundaries, hoping that it is valid as well for any densities (temperatures) in between. Of our two techniques, the reaction-based approach works in this mode, as to construct the reduced network the abundances during the entire evolutionary time are analysed. The resultant network accounts for both the early and later chemistry.

The second method seems to be more robust. After the ability of the reduction technique to remove the excessive information from the chemical network is checked, one can perform the reduction, for example, at each dynamical time step or even less often. The full chemical network must be taken into account every time, with current abundances, temperature, density, etc. One may want to identify not only species that can be ignored but species with quasi-stationary abundances as well. Our species-based reduction technique is well suited to be used at a given t with the current values of parameters because, as we mentioned above, the sharp jump in B_i values allow to distinguish necessary and unnecessary species clearly. Usually, there is no clear boundary between needed and unneeded reactions (see Fig. 2), so one has to readjust cut-off threshold several times before optimal reduction is found. Thus, in some cases, the reaction-based method is more time-consuming than the species-based approach which is critical if the method is to be invoked from the dynamical code more than once.

Neither method guarantees that the same accuracy, as found in test cases, is preserved during the real computations. With the first method one cannot be sure that conditions, under which the reduced network is not valid, are never met in the dynamical model. The second method properly takes into account the current conditions but is more sensitive to the history of abundance changes. Consider the ionisation degree in the dense cloud when freeze-out is taken into account (high-metallicity case). One of the dominant ions at later times is N_2H^+. As a necessary species, it is included in the network at the time when metal depletion becomes important (late stages). However, the abundance of this ion cannot be followed with any accuracy as it is absent in early-time reduced networks, and its entire previous evolution is lost. So, both strategies must be applied with care, taking into account possible uncertainties.

We note in passing that the decreased accuracy of the reduced networks may not be such an issue. Many reactions in the UMIST 95 have poorly measured or estimated rates, with typical uncertainties $\lesssim 25-100\%$ or more (Millar et al. 1997). This introduces unknown global errors in the modelled species abundances. On the other hand, modern observations usually provide column densities of abundant species with uncertainties of few tens of percents. Therefore, at nearly all

astrophysically important situations accuracy of ~50% seems to be quite appropriate.

7. Conclusions

We developed a robust method to reduce simultaneously the number of species and reactions in chemical networks. The straightforward application for such reduced chemical networks would be the modelling of the evolution of magnetised protostellar clouds or protoplanetary discs, when it is necessary to compute the fractional ionisation self-consistently with dynamical processes.

Investigating the applicability of this reduction approach, we considered the conditions of diffuse and dense molecular clouds and utilised the UMIST 95 database of chemical reaction rates. For the sake of comparison, we performed the same reduction with the objective reduction technique. The new reaction-based way of reduction proved to be more efficient and accurate but more time-consuming as well.

It is found that the number of species and reactions that are needed to follow the evolution of the CO abundance or the ionisation degree can be greatly decreased in the case of pure gas-phase chemistry, implying computational speed gains of more than a few hundred. For instance, to follow accurately (with <15% uncertainty) the evolution of the CO abundance in a dense cloud, it is enough to retain only 8 species involved in 9 reactions in the chemical network. However, as soon as the gas-grain interactions and surface chemistry are taken into account, reduction is modest and corresponding acceleration factors are around 10.

Appendix A: Adopted input parameters

We use the standard DVODE package designed to solve systems of ordinary differential equations. The relevant input parameters adopted in our computations are the following:

– absolute error $\epsilon_{abs} = 2.20 \times 10^{-16}$;
– relative error $\epsilon_{rel} = 10^{-8}$;
– Jacobian computed by the solver (internally).

We found that the relative error $\epsilon_{rel} = 10^{-8}$ is enough to give reliable estimations of the abundances of the species.

We use the g77 compiler and SuSe Linux 7.3 installed on the Pentium IV 2 GHz, 1 GB RAM PC as well as Compaq Visual Fortran 6.5 compiler on Pentium III, 850 MHz, 256 MB RAM PC. The typical time necessary to run a model is only a few minutes in the case of gas-phase chemistry and can reach half an hour if the gas-grain interactions are taken into account.

References

Aikawa, Y., & Herbst, E. 1999, ApJ, 526, 314
Aikawa, Y., Miyama, S. M., Nakano, T., & Umebayashi, T. 1996, ApJ, 467, 684
Bergin, E. A., & Langer, W. D. 1997, ApJ, 486, 316
Bergin, E. A., Langer, W. D., & Goldsmith, P. F. 1995, ApJ, 441, 222
Brown, P. D., & Charnley, S. B. 1990, MNRAS, 244, 432
Charnley , S. B., Rodgers, S. D., & Ehrenfreund, P. 2001, A&A, 378, 1024
Ciolek, G. E., & Mouschovias, T. Ch. 1995, ApJ, 454, 194
El-Nawawy, M. S., Howe, D. A., & Millar, T. J. 1997, MNRAS, 292, 481
Gerola, H., & Glassgold, A. E. 1978, ApJS, 37, 1
Glassgold, A. E., & Langer, W. D. 1973, ApJ, 179, 147
Hasegawa, T. I., Herbst, E., & Leung, C. M. 1992, ApJS, 82, 167
Hasegawa, T. I., & Herbst, E. 1993, MNRAS, 263, 589
Hollenbach, D., & McKee, C. F. 1979, ApJS, 41, 555
Howe, D. A., Hartquist, T. W., & Williams, D. A. 1994, MNRAS, 271, 811
Lee, H.-H., Roueff, E., Pineau des Forêts, G., Shalabiea, O. M., et al. 1998, A&A, 334, 1047
Le Teuff, Y. H., Millar, T. J., & Markwick, A. J. 2000, A&AS, 146, 157
Millar, T. J., Rawlings, J. M. C., Bennett, A., Brown, P. D., & Charnley, S. B. 1991, A&AS, 87, 585
Millar, T. J., Farquhar, P. R. A., & Willacy, K. 1997, A&AS, 121, 139
Oppenheimer, M., & Dalgarno, A. 1974, ApJ, 192, 29
Rae, J. G. L., Bell, N., Hartquist, T. W., Pilling, M. J., & Ruffle, D. P. 2002, A&A, 383, 738 (RBHPR)
Rawlings, J. M. C., Hartquist, T. W., Menten, K. M., & Williams, D. A. 1992, MNRAS, 255, 471
Ruffle, D. P., Rae, J. G. L., Pilling, M. J., Hartquist, T. W., & Herbst, E. 2002, A&A, 381, L13 (RRPHH)
Grevesse, N., & Sauval, A. J. 1998, Space Sci. Rev., 85, 161
Terzieva, R., & Herbst, E. 1998, ApJ, 501, 207
Turner, B. E. 2000, ApJ, 542, 837
Umebayashi, T., & Nakano, T. 1980, PASJ, 32, 405