

# REDUCING AND ANALYZING CHEMICAL NETWORKS

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## Abstract

A new efficient method allowing the reduction of the number of species and reactions in chemical networks is outlined. We applied it to the UMIST 95 astrochemical database in order to find a subset of species and reactions governing the evolution of carbon monoxide under conditions, typical of dense molecular clouds. We succeeded in isolation of such a tiny set for the pure gas-phase chemistry which gives the reliable estimation of the CO abundances under a wide range of the gas temperatures, densities, and visual extinctions. We showed that the reduction is only modest when gas-grain interactions and surface reactions are taken into account.

**KEYWORDS:** *astrochemistry – stars: formation – molecular processes – ISM: molecules – ISM: abundances*

## 1. Introduction

Nowadays large progress is achieved in modelling of the chemical and dynamical evolution of various astrophysical environments, like protostellar cores or protoplanetary disks. Still the coupled self-consistent chemical and dynamical modelling of such objects is beyond the capabilities of modern computers. The main reason is that typical chemical networks used in astrophysical simulations contain hundreds of species involved in thousands of reactions. Their accurate handling together with hydrodynamical calculations requires enormous computational efforts.

However, in many cases only a few species are of the main interest for an astronomer. For instance, the most important species for the evolution of magnetized interstellar clouds are few dominant ions, as mainly their abundances regulate the ionization degree. Then it seems intuitively clear that one may neglect some of “exotic” species, like long carbon chains, in order to speed up the calculations and still have reasonable estimations on the degree of ionization.

Notwithstanding, the qualitative considerations of this kind require a rigorous mathematical analysis to be proven.

Ruffle et al. (2002) made a first attempt to apply such a method – objective technique developed in other scientific community – for the reduction of astrochemical networks. They were able to discriminate among about 200 species only 33 which are necessary to follow the evolution of CO abundances within accuracy of 30% at  $t > 10^5$  years in static translucent regions. In the paper of Rae et al. (2002) the same reduction technique has been applied to identification of reduced networks governing the fractional ionization in molecular clouds under a wide range of physical circumstances. It has been found that one has to keep about thirty species from the entire set of more than two hundred species in order to predict the ionization degree without significant errors.

In this paper, we introduce a new reaction-based method of reduction which allows to reduce *simultaneously* the number of species and reactions in chemical networks. Using this reduction technique, we perform an analysis of the UMIST 95 database of chemical reactions in order to select species and reactions that are needed for accurate estimations of carbon monoxide abundances under conditions of dense molecular clouds. Our special aim is to investigate the possibility to reduce the chemical networks when complicated gas-grain interactions and dust surface reactions are taken into account beside the common gas-phase reactions.

## 2. Chemical Model

The detailed description of our chemical model is given in the paper of Wiebe et al. (2002). Here, we briefly summarize its main features.

We take into account gas-phase reactions, gas-grain interactions, and dust surface reactions. The species set and gas-phase reaction rates are taken from the UMIST 95 database (Millar et al. 1997). Dust surface reactions are adopted from Hasegawa et al. (1992). The desorption energies of the surface species are taken or estimated from Hasegawa & Herbst (1993). The gas-grain interactions include the following physical processes: accretion of neutral species onto dust grains, their desorption due to the thermal evaporation and cosmic ray heating, and dissociative recombination of ions on grain surfaces.

Two chemical networks are investigated, namely, the pure gas-phase network consists of electron, 12 atoms, 137 molecules, and 245 ions (in total 395 species) involved in 3864 gas-phase reactions and the gas-grain network having additional 148 surface species, 729 gas-grain and 192 dust surface reactions.

The probability of species to stick on the dust surfaces is assumed to be 0.3 for all ions and all neutral species except for H, He, and H<sub>2</sub>. The sticking coefficient of the atomic hydrogen is estimated from the expression given in Hollenbach & McKee (1979), Equation (3.7). Sticking probabilities for helium and molecular hydrogen are assumed to be zero.

We consider the gas density  $n_{\text{H}} = 10^7 \text{ cm}^{-3}$  and fix gas and dust temperatures to 10 K. No photoprocessing by the interstellar UV radiation is assumed ( $A_{\text{V}} \geq 10$ ). Dust grains are considered as silicate-like spheres having a uniform size 0.1 micron, density  $3 \text{ g cm}^{-3}$ , and  $10^6$  surface sites for adsorption. Dust is assumed to constitute 1% of the gas density by mass.

We use well-known "high metal" and "low metal" initial abundances (see, for instance, Lee et al. 1998). The "high metal" means standard solar composition with a modest depletion of 2 for S and stronger depletions of  $\sim 10 - 100$  for Si and metal atoms. The "low metal" values contain additional depletion factors of 100 for each of these elements. The abundances of He, C, N, O, S, Si, Na, Mg, and Fe are taken from Aikawa et al. (1996). For P and Cl we take the values from Grevesse & Sauval (1998) and use the same depletion factors as for Fe. We suppose that only these atomic neutral species and molecular hydrogen are present at initial time  $t = 0$ .

### 3. Reaction-based Reduction Technique

The new method of reaction-based reduction allows us to select from the entire network only those species and reactions that are *necessary* to compute abundances of chosen (*important*) species with a reasonable accuracy.

The basic idea of this reduction technique is to search for the production and destruction reactions, critical for the evolution of the important species, and determine their relative importance. It can be done by the analysis of the sensitivity of the net formation (or loss) rate of given species in respect to the presence of particular reactions at a certain time.

Below we briefly outline the algorithm of our reduction approach.

First, one runs the chemical model with the full network for certain physical conditions in order to obtain abundances of all species in the network during the entire evolutionary time.

Then, important species for which reduction will be made, are specified. The algorithm estimates weights of all species  $w_{\text{s}}$  and reactions  $w_{\text{r}}$  in order to quantify their significance for the evolution of the important species at a particular time moment by the following iterative process:

1. During the first iteration, weights of important species are set to 1 and weights of all other species and all reactions are set to 0;
2. For the iteration  $i$  and the current species  $s_i$  all relevant formation and destruction reactions are found and their weights  $w_r^i$  are specified as

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

Here  $k_j$  is the rate of  $j$ th 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  $j$ th reaction, respectively,  $N_r(i)$  is the amount of the reactions having  $s_i$  as a reactant or a product, and  $w_s(i)$  is the weight of the species  $s_i$ ;

3. Consequently, a new set of species, those found at that iteration to be related to the evolution of the important species and not considered in 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.

The iterations are finished when all species and all time steps are passed. Then one easily obtains a reduced chemical network from the full network by choosing only those reactions, that have weights above a predefined cut-off threshold.

We assume that if there is a difference greater than 30% in abundances of the important species computed with the full and reduced networks for any time moment, then the cut-off is readjusted to a new, smaller value, and the last step is repeated. Utilizing this rather strong selection criterion for the reduced networks, we preserve ourself from introducing severe computational errors in abundances of the important species.

#### 4. Chemistry of Carbon Monoxide

We follow the approach described in the previous section to build the gas-phase and gas-grain reduced networks for CO. The carbon monoxide is chosen as the only important species to be used with the reaction-based reduction technique.

In the case of the purely gas-phase chemistry in a dense cloud the main chemical processes for the evolution of CO are the following. At very early

evolutionary stages,  $t < 10^2$  years, key formation processes are the neutral-neutral reactions of oxygen with various light carbon-bearing molecules, like CH and CH<sub>2</sub>. Later, CO is formed due to destruction of OCS, H<sub>2</sub>CO, and CO<sub>2</sub> by the cosmic ray induced UV photons. The removal of CO during the entire evolutionary time is controlled by the cosmic ray ionization and destruction due to the cosmic ray induced UV photons.

The evolution of carbon monoxide under such circumstances is shown in Figure 1 (left panel). As can be clearly seen, in the absence of the gas-grain interactions the evolution of CO is rather simple – its abundance is rapidly increasing till the chemical equilibrium value of about  $10^{-4}$  (in respect to the amount of hydrogen nuclei) is reached at  $\sim 3 \cdot 10^3$  years. The rest (and most!) of the evolutionary time the abundance of carbon monoxide remains almost a constant. Remarkably, there is no difference between the high and low metallicity cases.

Applying our reduction approach, we found that one may keep from the entire set of 395 species and 3864 reactions only 8 species involved in 9 reactions in order to accurate estimation CO abundances for all  $10^7$  years of the evolution. The corresponding reduced network is given in Table 1. The size of this network is so small that the computational time which is needed to solve the relevant system of the ordinary differential equations (ODE) is negligible, less than a second. Still the uncertainties of the resulting abundances do not exceed 15% during the entire evolutionary time.

This extraordinary result demonstrates the power of our reduction technique and explains why there is no difference between the high and low metallicity cases. The reason is that the evolution of these 8 necessary species (see Table 1) depends only on the total amount of H, C, and O available in the gas phase at  $t = 0$ . As the initial abundances of these atoms are exactly the same for both metallicities, it leads to the nearly identical values of CO abundances for all  $0 - 10^7$  years.

It is interesting to examine if such extremely small amount of necessary species and reactions is caused by merely favorable circumstances or it is due to the nature of the CO chemistry itself. In the latter case, the relevant reduced network must reproduce accurately the abundances of carbon monoxide in a range of the physical conditions.

We discovered that this network is functional within accuracy of 50% under the following circumstances:

$$10^4 \text{ cm}^{-3} \leq n_{\text{H}} \leq 10^{10} \text{ cm}^{-3}, T \leq 250 \text{ K}, A_{\text{V}} \geq 1$$

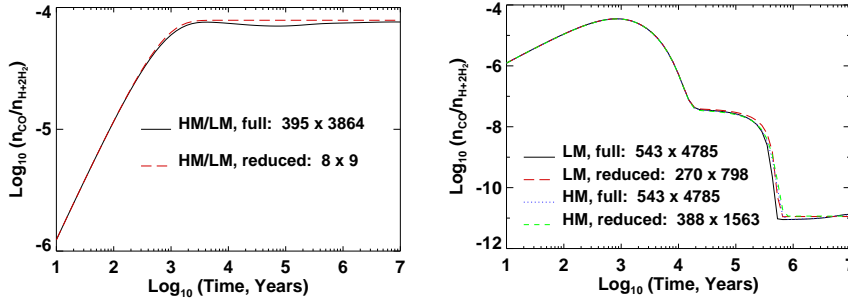


Figure 1: The evolution of CO in a dense cloud computed with the full and reduced networks in the case of the purely gas-phase chemistry (**left panel**) and the gas-grain chemistry involving the surface reactions (**right panel**). The “HM” and “LM” mean high and low metallicity cases, respectively. The sizes of the chemical networks are indicated as “ $N_1 \times N_2$ ”, where  $N_1$  is the number of chemical species and  $N_2$  is the number of reactions.

It implies physical conditions, typical of dense and translucent interstellar clouds and “hot cores” of molecular clouds. Thus one may use essentially the same tiny set of species and reactions in order to follow the evolution of CO in the case of the purely gas-phase chemistry in a very wide range of conditions. Compared to the similar network obtained by Ruffle et al. (2002), that has 33 species involved in 116 reactions and is valid for  $n_{\text{H}} \sim 10^3 \text{ cm}^{-3}$ ,  $A_{\text{V}} = 4-10$ , and  $t > 10^5$  years our network is much smaller and still is applicable under a much wider range of the physical circumstances.

The situation is more complicated from the chemical point of view when the gas-grain interactions and the dust surface reactions are taken into account. The accretion of species onto the grain surfaces is efficient at high gas density,  $n_{\text{H}} = 10^7 \text{ cm}^{-3}$ , leading to significant amount of mantle material. Then the quantum tunneling of H and  $\text{H}_2$  and thermal hopping of other atoms and light molecules drive the rich surface chemistry, which results in production of heavier species, mostly complex organic molecules. Occasional impulse heating of the dust grains by the energetic cosmic ray particles returns some of the surface species back to the gas phase. All these processes alter the gas-phase chemistry in a high degree.

The evolution of carbon monoxide in this case is shown in Figure 1 (right

Table 1: Reduced network for CO (DENS model)

1 $\text{H} + \text{CH}_2 \rightarrow \text{CH} + \text{H}_2$	6 $\text{O} + \text{C}_2\text{H} \rightarrow \text{CO} + \text{CH}$
2 $\text{H}_2 + \text{C} \rightarrow \text{CH}_2 + \text{PHOTON}$	7 $\text{H}_2 + \text{CRP}^{\text{a}} \rightarrow \text{H} + \text{H}$
3 $\text{C} + \text{CH}_2 \rightarrow \text{C}_2\text{H} + \text{H}$	8 $\text{CH} + \text{CRPHOT}^{\text{b}} \rightarrow \text{C} + \text{H}$
4 $\text{O} + \text{CH} \rightarrow \text{CO} + \text{H}$	9 $\text{CO} + \text{CRPHOT} \rightarrow \text{C} + \text{O}$
5 $\text{O} + \text{CH}_2 \rightarrow \text{CO} + \text{H} + \text{H}$	

<sup>a</sup>“CRP” is an abbreviation for “cosmic ray particle”,

<sup>b</sup>“CRPHOT” means “CRP-induced UV photon”

panel). The abundance of the gas-phase CO is increasing at early evolutionary times, till the maximum value of  $n_{\text{CO}}/n_{\text{H}} \sim 10^{-4}$  is reached at  $t \sim 10^3$  years. Then, accretion of CO molecules onto the grains becomes efficient and its abundance in the gas phase is decreasing. The bump on the curve at  $t \sim 10^4 - 10^6$  years is due to the influence of the surface reactions as they become quite important at these times. Finally, the equilibrium value  $n_{\text{CO}}/n_{\text{H}} \approx 10^{-11}$  is reached after about  $10^6$  years of evolution. Again, as in the previous case, there is no difference between the high and low metallicities.

Our method of reduction is able to select two 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 speed gains are only about factors of 3 and 15 for the former and latter cases, respectively. The accuracy of the predicted CO abundances is better than 15% during the entire evolutionary time.

The number of necessary species and reactions is high due to perplexity of the chemical processes in this model. Indeed, the selectivity criterion of the reduction method recognizes many of the surface reactions to be important, so they remain in the reduced chemical network. Consequently, it leads to larger amount of necessary reactions and species compared to the case of the purely gas-phase chemistry.

There is a large ( $> 50\%$ ) difference between the number of the species found to be necessary in the high metallicity case compared to the low metallicity case. The reason is that the reduced networks with smaller amounts of species cannot be used in the calculations because the relevant ODE systems are too stiff to be solved in reasonable time. This is a common situation when the surface reactions are taken into account as they have far too high kinetic rates compared to the gas-phase chemical reactions.

## 5. Conclusions

We have developed a robust technique to reduce the amount of species and reactions in the chemical networks. It is shown that by utilizing this method the size of the gas-phase chemical network used to compute CO abundances in the dense clouds can be significantly reduced. We have found that such reduction is of no practical use when the gas-grain interactions and the surface chemistry are taken into account since the relevant computational time gains are about factors a few only.

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