Chemistry in Star-Forming Regions: Making Complex Modelling Feasible

D. Wiebe[1], D. Semenov[2], Th. Henning[3]

[1]Institute of Astronomy of the RAS
48, Pyatnitskaya str., Moscow 119017, Russia
[2]Astrophysical Institute and University Observatory
Schillergäßchen 2-3, 07745 Jena, Germany
[3]Max Planck Institute for Astronomy
Königstuhl 17, 69117 Heidelberg, Germany
E-mail: `dwiebe@inasan.rssi.ru`

Abstract

In this paper we discuss possible ways to reduce the chemical reaction network for the situations when the accurate abundances are only needed for a limited number of species to compute, for example, such dynamically important factors as the ionisation degree or molecular cooling. We show that it is possible to reduce the number of reactions and species so that the computational time in some astrophysically interesting situations will be reduced by orders of magnitude without appreciable loss of accuracy. For example, to model magnetised dark clouds, self-consistently estimating the ionisation degree with the UMIST 95 database, one only needs to retain about 100 of 395 species with the computational time cut by a factor of a hundred. In the case of dynamical modelling with changing density, extinction, UV-intensity, temperature etc., the reduced chemical network may help to distinguish between feasible and non-feasible tasks.
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1. Introduction

One of the main problems of the star formation studies is the absence of easily detectable emission from molecular hydrogen, which is the most abundant molecule in molecular clouds that are sites of star formation. Gas motion in star-forming clouds, pre-stellar, protostellar, and young stellar objects (YSO) is essentially motion of H_2 molecules. Yet we have to infer this motion observing far less abundant species.

Molecular diagnostics has now developed into effective tool for the investigation of interstellar clouds. It allows to determine physical conditions in the ISM, may help to elucidate the evolutionary state of different objects (through

the concept of chemical clock), and even sheds some light on the problem of life origins (through observations of complex organic molecules). However, species that are used as tracers for the study of the star formation are not necessarily well mixed with molecular hydrogen and thus with bulk gas. To relate observed distributions of trace molecules to that of molecular hydrogen, the modelling of the chemical evolution of the region under investigation seems to be inevitable.

There are more than 120 species that are known now to exist in the ISM. As they do not form a closed chemical system, one has to assume that many other chemical species are present there that are not (yet) observable. A typical chemical network used in the modelling of the ISM, like the UMIST 95 database (Millar et al. 1997), consists of hundreds of species and thousands of reactions. Differential equations of chemical kinetics that describe time-dependent molecule production and destruction rates are usually stiff and require special methods of solution, implemented, e.g., in LSODE and DVODE packages. Solving of these equations is a demanding computational task even for the fixed relevant physical conditions (density, temperature, extinction, etc.). But interferometric observations that are now becoming abundant allow not only to determine the chemical composition of a particular object but also reveal its detailed chemical structure. To confront these data with theoretical predictions one has to model the chemical evolution at least in several points across the object with the physical conditions that vary, in general, not only in space but also in time.

One way to do this is to place the chemical model over the pre-computed dynamical model. However, it is sometimes necessary to model the chemical and dynamical evolution of the ISM self-consistently in order to take into account a feedback that chemistry has on dynamics either through heating and cooling processes that depend on abundances of certain molecules or through chemically determined ionisation degree (Ciolek & Mouschovias 1993). This makes the situation more complicated.

Even in the case of a static cloud or a cloud with the pre-defined dynamics, modelling of its detailed chemical structure is very time-consuming, if one recalls the number of parameters that can be varied. It seems to be clear that self-consistent coupling of the full-fledged chemical model to the (more or less) full-fledged dynamical model is next to impossible, even with ever-increasing computational power.

2. Motivation and Reduction Model

While one can only guess if the chosen chemical network contains all the needed species and all the needed reactions, the natural question to ask is if we really need all this information. To compare results of chemical modelling with observational data one usually needs to compute abundances of a few selected molecules (like CO, NH_3, CS, HCN, etc.) without spending much computational time on the accurate predictions about, say, complex carbon chains. To model thermal balance in a cloud self-consistently it is in most situations enough to have accurate abundances of CO which is a major molecular coolant in interstellar clouds (Glassgold & Langer 1973). Ionisation degree is determined not by the entire species set but only by a few dominant ions that are involved in a handful of chemical reactions. Intuitively, it seems obvious that in such cases the number of species and reactions can be significantly reduced. However, for now attempts to use abridged chemical networks have been mainly based on a more or less qualitative arguments, without accurate mathematical consideration (e.g. Gerola & Glassgold 1980; Shematovich et al. 1997; Desch & Mouschovias 2001).

So, we can formulate the following task: to reduce the number of species and reactions into a subset that is necessary in a particular situation using mathematically proven arguments that will ensure reliability of the reduced network. Ruffle et al. (2002) and Rae et al. (2002) made the first attempt of this kind found in the astronomical literature. They used methods developed in different branches of science to reduce networks used in modelling of combustion processes. They show that it is possible to isolate species and reactions governing the CO abundance and the ionisation degree at the conditions typical of diffuse illuminated clouds. Their reduced network for CO contains 33 species involved in 116 reactions and is valid for $n_{\rm H} \sim 10^3$ cm^{-3} and $A_{\rm v} = 4 - 10$.

In this paper we present a similar approach to the chemical network reduction and check it for a wider range of physical conditions. We utilise two methods that we refer to as species-based reduction and reaction-based reduction. With these two methods we built reduced networks needed to compute electron and CO abundances for the conditions typical of diffuse ($n_{\rm H} \sim 10^3$ cm^{-3}) and dense ($n_{\rm H} \sim 10^7$ cm^{-3}) molecular clouds. We assume no photoprocessing by interstellar UV photons, implying obscured regions with $\rm A_V > 10$. We consider both purely gas-phase chemistry and gas-phase chemistry coupled to the surface chemistry with two different sets of initial abundances usually referred to as high and low metallicities (e.g. Lee et al. 1998).

We use the UMIST 95 rate file for the gas-phase reactions. Rates for surface

reactions are taken from Hasegawa et al. (1992) and Hasegawa & Herbst (1993). As surface chemistry is included here for illustration purposes only, the rate equation approach is used to model these reactions, even though its validity is now questioned. Gas-phase network consists of 395 species (including electrons) taking part in 3864 reactions. All 148 neutral species but helium and molecular hydrogen are allowed to stick to dust grains where they are involved in 192 surface reactions. Gas-dust connection is realized through accretion and desorption processes. Desorption energies are taken from Hasegawa & Herbst (1993) or interpolated from their data.

The species-based reduction rests upon the first part of the Ruffle et al. (2002) technique and consists of choosing species that are important in a particular context and then selecting from the entire network only those species that are necessary to compute abundances of important species with reasonable accuracy. The analysis is based on sensitivities B_i defined in Ruffle et al. (2002) as

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

where n_i is the abundance of ith species, N' is the current number of important and necessary species,

$$f_j = G_j - L_j$$

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

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

With these definitions, the quantity in parentheses gives the normalised rate of jth species abundance change due to those reactions only that involve ith species. B_i value thus gives a measure of the relative importance of the ith species. The important feature of B_i values pointed out by Ruffle et al. (2002) is the clear cutoff between species with large B_i and small B_i. Before the first step the reduced set contains only important species. Then B_i values are computed for all species from the full network, and those of them, having B_i above the cut-off threshold, are added to the reduced network, and the process starts over. If after the current iteration no new species are added to the reduced network, the process stops.

In the reaction-based method analysis starts from reactions that govern the abundance of important species. All reactions in the entire network are assigned weights according to the influence they have on the abundance of an important

species. Then, only those reactions are selected that have weights above some cut-off parameter that is selected on the basis of the requested accuracy. Only those species are included in the reduced network that participate in selected reactions. Details on the algorithm of the reaction-based reduction are given in Semenov et al. (2003).

3. Ionisation Degree

To build the reduced chemical network that could be used to compute ionisation fraction in molecular clouds we adopted the following approach. First, the model was computed with the full chemical species set. Then, with the abundances of all species corresponding to $t = 0 - 10^7$ years, we estimated which of them are needed to estimate the abundances of dominant ions. Finally, we checked the reduced networks by comparing the ionisation degrees computed with the full and reduced networks.

In a purely gas-phase chemistry case, at $n_{\rm H} = 10^3$ cm^{-3} and high initial metal abundances, the dominant ions during most of the computational time are S^+ and Mg^+. By considering only ionised sulphur as an important species in species-based approach we can reduce the number of species from 395 to 123 and to achieve the computational speed gain of order of 25, but at the expense of $\sim$ 20% uncertainty at times approaching 10^7 years. If we consider both dominant ions to be important species, the number of species in the reduced set is 126, and the computational gain is almost the same with the uncertainty less than 10%. With the reaction-based reduction technique, we choose electron to be the only important species. In this case the number of necessary chemical reactions can be reduced from 3864 to 111 and the number of species from 395 to 58. The computational gain exceeds 500.

The low metallicity case is more complicated from the chemical point of view since in the absence of abundant metals the role of dominant electron suppliers goes to complex species involved in a more diverse chemistry. At this low density gas-dust connections are not important again. In the diffuse cloud case, the dominant ion is H_3^+ most of the time, however it alone does not determine the ionisation degree with enough accuracy. Errors are negligible at earlier times when the chemistry is relatively simple, however, after 10^4 years the error grows significantly, exceeding a factor of 3 at the end of 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 entire computational time in the case of species-based

approach. However, due to the perplexed chemical connections of the two ions, the species set reduction is only modest in this case. About one hundred species can be excluded from the set with the reduction of the computational time by a factor of 3 (if errors like 200% cannot be afforded). The reaction-based algorithm is better suited for such situation. From the complicated chemistry involving H_3^+ and HCO^+ it is able to isolate 169 most important reactions, simultaneously reducing the number of species to 73. The speed gain in this case approaches 500, as in the high metallicity case.

Inclusion of accretion and desorption processes, as well as surface reactions, into the diffuse cloud model does not lead to any noticeable changes, primarily because the density is so low that it prevents the effective gas-grain interactions.

When no gas-dust interaction is taken into account, the case of dense cloud ($n_{\rm H} = 10^7$ cm^{-3}) at high metallicity is qualitatively similar to the low-density case. The difference between high and low metallicity cases is much smaller for a dense cloud than for a diffuse cloud. In a denser environment, such chemically active ions as H_3^+ and HCO^+ are much 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 reduced species sets are nearly the same both for high and low metallicity, with similar errors and computational gains.

The situation changes drastically, when gas-dust connection is taken into account. In high metallicity case, at early stages of the evolution the dominant ions are the same as in diffuse medium, i.e., metals. However, after 10^4 years the metal depletion becomes important, and the dominant ions are H_3^+ and HCO^+. Basically, a dense cloud at high metallicity with accretion and desorption processes behaves similarly to the low metallicity diffuse cloud.

In the low metallicity case, which is more diverse from the chemical point of view, difference between initial and final stages of the cloud evolution (separated by the moment when depletion takes over) is so prominent that the reduced network estimated from the final abundances is not valid at earlier phase, at $t < 10^4$ years, leading to a factor of 2 errors, even though it still predicts later abundances with much better accuracy (less than 20%). In order to take the two different stages into account, we build the reduced set for two times, $t \sim 10^3$ years and 10^7 years, and then use the combined set during the entire time span.

The addition of surface chemistry changes the evolution of the ionisation degree somewhat, but in the absence of effective desorption mechanisms these changes are not strong enough to affect the list of necessary species, so that it is possible to use the same reduced sets as in the case when only accretion and desorption are taken into account, with similar accuracy and computational

gain. Both methods are able to remove about two hundred species from the entire network with the gas-grain interaction (remember that the full network consists of 542 species in this case). This reduction provides the decrease of the computational time by a factor of a few. The greatest speed gain (~ 8) in the model with surface reactions included is achieved with the reaction-based technique due to its ability to remove not only excessive species but excessive reactions as well.

4. Carbon Monoxide

Reduction results for CO are more impressive if no surface chemistry is taken into account. For both metallicities and both cloud densities, the reduced set consists of no more than 35 species and provides accuracy better than 20%. Even though we build reduced sets for each of the considered models separately, it is possible to use a common reduced set for all of them with error less than 100%. This is true both in the case of the purely gas-phase chemistry and in the case when accretion and desorption processes are taken into account. The resulting speed gain is very large. In fact, while it takes about 5 minutes to run the full model, with the reduced network time needed to compute the CO abundance is lost in technical operations (like input/output etc.).

The reduction is most effective in a dense cloud. The reaction-based method shows that 8 species and 9 reactions completely determine the CO abundance when only gas-phase reactions are taken into account (for more details see Semenov et al., 2003).

The situation changes drastically again if surface reactions are switched on. In this case the species-based reduction is less effective. The reduced set contains about 340 species and produces overabundance of CO at later times, when depletion becomes important. The species-based reduction has the disadvantage of not being able to include properly surface molecules. To obtain reasonable results one has to add manually surface species that serve as sinks for surface CO, that is, CO_2 and HCO. The computational gain is only about 2. When surface reactions are taken into account, reaction-based reduction provides modest computational gain, too, though somewhat larger than species-based reduction, with more controllable accuracy and without the need of manual corrections. The speed gain is only about 3 in the high metallicity case, but reaches 16 in the low metallicity case.

So, the species-based reduction is an effective tool for constructing limited chemical networks in situations that do not involve surface chemistry. When

surface reactions are taken into account, species-based reduction is not that effective and reliable. The reaction-based method gives more impressive results.

5. Conclusions

We show that purely gas-phase chemical networks can be significantly reduced to compute electron and CO abundances in dark clouds. The computational gain varies from a few tens up to the point where the computational time needed for chemical modelling is lost in service operations. If the surface chemistry is included, both methods are only able to accelerate the computation by a factor of a few.

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