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Letter to the Editor

A network for interstellar CO – The first application of objective reduction techniques in astrochemistry

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Abstract. A reduced network for CO production and removal, obtained via the use of objective techniques, is shown to produce reliable results over a wide range of physical conditions. Our analysis indicates that reactions involving species with long carbon chains are important in governing the CO abundance in some translucent regions.

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

1. Introduction

A typical database for interstellar chemistry includes thousands of reactions occurring among hundreds of species (e.g. Millar et al. 1997; Terzieva & Herbst 1998). Usually only a handful of these species are under consideration in the interpretation of observations aimed at unveiling the dynamics and structure in a molecular cloud. In such a situation the use of a complete database can be unnecessarily time-consuming and computationally expensive. However, the identification of a reduced network that can be used to give reliable results for the evolving abundances of the species of prime importance can be fraught with difficulty. Even very experienced astrochemists can occasionally be surprised by the complexity of seemingly simple results. The realization in recent years that whole classes of reactions may proceed at much higher rates than previously thought (e.g. Sims & Smith 1995) is just one of the potential causes of complexity in determining reduced networks.

Here we introduce into astrochemistry the use of a set of objective techniques, developed in another community (Tomlin et al. 1992, 1997), for network reduction. We identify a reduced network for the calculation of CO abundances in static cold molecular clouds, clumps and dense cores, under a large variety of physical circumstances. We focus on CO in this first application of the techniques because it is the most abundant molecule other than H_2 and because the chemistry that controls its abundance is central to the chemistry of many other species. The central role of CO results, to some degree, from its part in establishing the availability of carbon in reactive species, which participate in the formation of many of the other observationally most interesting species.

Section 2 briefly summarizes the objective techniques employed and the full network from which the reduced network for CO was obtained. In Sect. 3 we describe several different ranges of parameters over which the application of the objective techniques yields a separate reduced network. Section 3 also contains some illustrative intermediate results obtained in the network reduction for one case, as well as a table listing all reactions appearing in all of the reduced networks. All of the reduced networks applicable in restricted regimes must be combined to form a reduced network of general utility. Results from the combined reduced network are compared with results from the full network for the evolution of the CO abundance. Section 4 concludes the paper.

2. The reduction techniques and the initial large network

The principles behind the network reduction techniques are described by Tomlin et al. (1992, 1997). The code used is called KINALC. We designate the number density of species i by $n(i)$, the *net* production or removal rate per unit volume of species j by $f(j)$, and the larger of the formation and removal rates per unit volume of species j by $g(j)$.

The first step in the reduction process is the specification of the species whose abundances are *important*. In addition to these species we shall assume that there are *necessary* species, i.e. those that are not of interest but whose abundances must be calculated in order to obtain reasonable results for the important species.

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The determination of the species that are necessary proceeds in a step-by-step process that begins with the calculation of

$$B_i \equiv \sum_{j=1}^{N'} \left(\frac{n(i)}{g(j)} \frac{\partial f(j)}{\partial n(i)} \right)^2 \qquad (1)$$

for all species (i.e. all choices of i). The summation is over N' species, already previously recognized to be important or necessary. B_i is clearly a measure of the sensitivity of the net formation rates per unit volume per unit time of the important and necessary species to the abundance of species i. If the difference between the smallest value of a B_i obtained for one of the N' species and the largest value of a B_i for any species not already deemed important or necessary is large, then the identification of necessary species is complete. Otherwise, the species previously not belonging to the set of identified important and necessary species with the largest B_i is added to that set, and B_i's are calculated for the new set of identified important and necessary species.

Once the final set of important and necessary species has been identified, a network consisting of all reactions involving these species with one another that do not produce species outside the final set is constructed. Subsequent analysis is restricted to this intermediate network. The rate coefficient of reaction k in the intermediate network is signified by α_k. The quantities

$$F_{ik} \equiv \frac{\alpha_k}{g(i)} \frac{\partial f(i)}{\partial \alpha_k} \qquad (2)$$

are calculated. The decision of whether a reaction must be retained in the reduced network is guided by an analysis of the eigenvalues and eigenvectors of the product of a matrix having components F_{ik} and its transpose; the details of this analysis are described by Tomlin et al. (1992, 1997).

The method described so far must for the most general case be applied for a number of time points in each of a variety of scenarios in which initial chemical conditions, elemental abundances and the evolution of physical conditions vary. The *combined reduced network* includes all reactions identified in the construction of all of the specific reduced networks.

For the study of the astrochemistry of CO, we have begun with the full gas-phase network of the Ohio State New Standard Model (e.g. Lee et al. 1996; Terzieva & Herbst 1998; Ruffle & Herbst 2000). The only surface reactions included are those leading to the neutralization of ions after which immediate return of the reaction products to the gas phase is assumed. The elemental abundances were taken to be the standard ones ("low metals") assumed in the previous work of the Ohio State group and are appropriate for dense cores. The H_2 number density was a specified constant rather than calculated; all hydrogen was assumed to be in molecular hydrogen initially (i.e. $n(H_2) = 0.5\ n_H$, where n_H is the hydrogen nuclei number density), and at all subsequent times the fraction of elemental hydrogen in other species was found to be small. The only other species present initially are He, O, N, e, C^+, S^+, Na^+, Mg^+, Si^+, Fe^+, Cl^+ and P^+.

Table 1. An example of a well-defined group of species.

Species			log B_i	Species			log B_i
1	H_2	*	0.85	14	CH_3^+	*	0.28
2	O	*	0.70	15	OH^+	*	0.28
3	C	*	0.62	16	CH^+	*	0.28
4	e	*	0.56	17	HCO^+	*	0.20
5	H_3O^+	*	0.48	18	H_2O^+	*	0.19
6	CO	*	0.45	19	H_2O	*	0.09
7	H_3^+	*	0.42	20	C^+	*	0.08
8	He^+	*	0.39	21	CH_2	*	0.06
9	H_2^+	*	0.30	22	O_2	*	0.02
10	OH	*	0.30	23	CH_4	*	–0.65
11	CH_5^+	*	0.30	24	HNC		–1.90
12	He	*	0.30	25	HCN		–1.92
13	CH_2^+	*	0.30				

Table 2. The ranges of valid conditions for the five species groups.

Range	n_H $(\mathrm{cm}^{-}3)$	A_V (mag)
1	2×10^4	3.5–10
	1×10^5	2.0–10
2	5×10^2	5.0–10
	1×10^3	4.0–10
	2×10^4	2.5–3.5
	1×10^5	2.0
3	5×10^2	3.5–4.0
	1×10^3	3.0–3.5
	2×10^4	1.0–2.0
	1×10^5	0.5–1.5
4	5×10^2	2.5–3.0
	1×10^3	2.0–2.5
5	5×10^2	0.5–2.5
	1×10^3	0.5–2.0
	2×10^4	0.5–1.0

3. Individual reduced networks

In all cases we assumed CO to be the only important species. For each case described in this section we assumed $n(H_2)$ to be constant in time (t) and adopted a temperature of 10 K.

Table 1 lists the logs of the largest B_i's calculated for $t = 10^5$ yr, $n(H_2) = 10^4$ cm^{-3} and for a visual extinction, A_V, of 10, under the assumption that any species indicated with an asterisk is important or necessary. A clear jump in the values occurs between the species CH_4 and HNC. Similar analyses were carried out for different times for these values of $n(H_2)$ and A_V.

As stated in the previous section, we analysed the eigenvalues and eigenvectors of the product of the matrix with elements F_{ik} and its transpose in the identification of a reduced network. Once a potential reduced network was found for an individual case, we used it to generate time dependent results for the CO abundance. A reduced network was accepted as reliable only if its results were

Table 3. The reduced reaction network.

$C + CRP \rightarrow C^+ + e$	1–3	$He + CR \rightarrow He^+ + e$	1–5	$O + CR \rightarrow O^+ + e$	12
$CO + CRP \rightarrow C + O$	12	$H_2 + CR \rightarrow H + H$	1–4	$H_2 + CR \rightarrow H^+ + H + e$	1–5
$H_2 + CR \rightarrow H_2^+ + e$	1–5	$O_2 + CRP \rightarrow O + O$	12	$CH_4 + CRP \rightarrow CH_2 + H_2$	1
$H + CR \rightarrow H^+ + e$	2–5	$C_2H_2 + CRP \rightarrow C_2H + H$	2	$C_2H_2 + CRP \rightarrow C_2H_2^+ + e$	2
$C^+ + O_2 \rightarrow O^+ + CO$	12	$C^+ + H_2O \rightarrow HCO^+ + H$	12	$He^+ + CO \rightarrow C^+ + O + He$	1–5
$H^+ + CH_4 \rightarrow CH_3^+ + H_2$	1	$H^+ + H_2O \rightarrow H_2O^+ + H$	12	$He^+ + CH_4 \rightarrow CH^+ + H_2 + H + He$	1
$O^+ + H_2 \rightarrow OH^+ + H$	12	$CH^+ + H_2 \rightarrow CH_2^+ + H$	1–5	$H_2^+ + H_2 \rightarrow H_3^+ + H$	1–5
$OH^+ + H_2 \rightarrow H_2O^+ + H$	1–3	$CH_2^+ + H_2 \rightarrow CH_3^+ + H$	1–5	$H_2O^+ + H_2 \rightarrow H_3O^+ + H$	1–3
$H_3^+ + C \rightarrow CH^+ + H_2$	1–3	$H_3^+ + O \rightarrow OH^+ + H_2$	1–3	$HCO^+ + H_2O \rightarrow H_3O^+ + CO$	12
$H_3^+ + CH_4 \rightarrow CH_5^+ + H_2$	1	$H_3^+ + CO \rightarrow HCO^+ + H_2$	1235	$CH_5^+ + CO \rightarrow HCO^+ + CH_4$	1
$CH_5^+ + O \rightarrow H_3O^+ + CH_2$	12	$CH_5^+ + C \rightarrow CH^+ + CH_4$	1	$C^+ + O_2\ (+ H_2) \rightarrow HCO^+ + O + H$	23
$C^+ + CH \rightarrow CH^+ + C$	2–5	$C^+ + CH \rightarrow C_2^+ + H$	2–5	$C^+ + OH\ (+ H_2) \rightarrow HCO^+ + H + H$	235
$C^+ + CH_2 \rightarrow C_2H^+ + H$	2–5	$C^+ + CH_2 \rightarrow CH_2^+ + C$	2–5	$H^+ + CH \rightarrow CH^+ + H$	2–5
$H^+ + OH \rightarrow OH^+ + H$	23	$H^+ + C_2H_2 \rightarrow C_2H^+ + H_2$	2	$He^+ + H_2 \rightarrow H^+ + H + He$	2–5
$H^+ + C_2H_2 \rightarrow C_2H_2^+ + H$	2	$He^+ + H_2 \rightarrow H_2^+ + He$	2–5	$He^+ + OH \rightarrow O^+ + H + He$	2
$He^+ + O_2 \rightarrow O^+ + O + He$	2	$C_2^+ + H_2 \rightarrow C_2H^+ + H$	2–5	$He^+ + H_2O \rightarrow H^+ + OH + He$	2
$H_2^+ + H \rightarrow H^+ + H_2$	2–5	$C_2H^+ + H_2 \rightarrow C_2H_2^+ + H$	2–5	$H_3^+ + CH \rightarrow CH_2^+ + H_2$	2
$H_3^+ + C_2H \rightarrow C_2H_2^+ + H_2$	2	$H_3^+ + H_2O \rightarrow H_3O^+ + H_2$	2	$HCO^+ + CH \rightarrow CH_2^+ + CO$	2
$HCO^+ + C \rightarrow CH^+ + CO$	2	$C_2H_2^+ + C \rightarrow C_2H_2 + C^+$	2	$CH_3^+ + C \rightarrow C_2H^+ + H_2$	23
$CH_3^+ + C \rightarrow C_2H_2^+ + H$	23	$H^+ + C_2 \rightarrow C_2^+ + H$	3–5	$He^+ + C_2 \rightarrow C^+ + C + He$	45
$H^+ + C_2H \rightarrow C_2H^+ + H$	34	$H^+ + C_2H \rightarrow C_2^+ + H_2$	34	$C_2^+ + O\ (+ H_2) \rightarrow HCO^+ + C + H$	5
$CH^+ + H \rightarrow C^+ + H_2$	5	$CH^+ + O \rightarrow CO + H^+$	5	$C_2H_2^+ + O \rightarrow HCO^+ + CH$	5
$CH_2^+ + O \rightarrow HCO^+ + H$	5	$CH_3^+ + O \rightarrow HCO^+ + H_2$	5	$C^+ + H_2 \rightarrow CH_2^+$	1–5
$CH_3^+ + H_2 \rightarrow CH_5^+$	12	$O + CH \rightarrow HCO^+ + e$	25	$C + O_2 \rightarrow CO + O$	1–3
$O + OH \rightarrow O_2 + H$	1–3	$O + CH_2 \rightarrow CO + H + H$	1–5	$O + CH_2 \rightarrow CO + H_2$	1–5
$O + C_2 \rightarrow CO + C$	2–5	$O + CH \rightarrow CO + H$	23	$C_2H + O_2 \rightarrow H + CO + CO$	2
$O + C_2H \rightarrow CO + CH$	23	$C + H_2 \rightarrow CH_2$	1–4	$H + O \rightarrow OH$	5
$H_3^+ + e \rightarrow H + H + H$	1–5	$HCO^+ + e \rightarrow CO + H$	1235	$CH_3^+ + e \rightarrow H_2 + C + H$	1–5
$CH_3^+ + e \rightarrow CH_2 + H$	1–5	$H_3O^+ + e \rightarrow OH + H + H$	1–3	$H_3O^+ + e \rightarrow H_2O + H$	12
$H_3O^+ + e \rightarrow OH + H_2$	1–3	$H_3^+ + e \rightarrow H_2 + H$	2–5	$C_2H_2^+ + e \rightarrow C_2 + H + H$	2–5
$C_2H_2^+ + e \rightarrow CH + CH$	2–5	$C_2H_2^+ + e \rightarrow C_2H + H$	2–5	$CH_3^+ + e \rightarrow CH + H + H$	2–5
$CH_3^+ + e \rightarrow CH + H_2$	2–5	$C_2H^+ + e \rightarrow C_2 + H$	5	$CH_5^+ + e \rightarrow CH + H_2 + H_2$	2
$CH_2^+ + e \rightarrow C + H + H$	45	$C_2^+ + e \rightarrow C + C$	5	$CH_5^+ + e \rightarrow CH_2 + H_2 + H$	2
$C_2H^+ + e \rightarrow CH + C$	5	$CH_2^+ + e \rightarrow C + H_2$	5	$C^+ + C_2H\ (+ e) \rightarrow C + C_2H$	2–5
$CH_2^+ + e \rightarrow CH + H$	5	$C^+ + e \rightarrow C$	2–5	$H^+ + e \rightarrow H$	5
$He^+ + e \rightarrow He$	5	$C + PHOT \rightarrow C^+ + e$	3–5	$C_2 + PHOT \rightarrow C_2^+ + e$	3–5
$CO + PHOT \rightarrow C + O$	3–5	$O_2 + PHOT \rightarrow O + O$	3	$C_2H_2 + PHOT \rightarrow C_2H + H$	34
$C_2H + PHOT \rightarrow C_2 + H$	3–5	$H_3^+ + PHOT \rightarrow H^+ + H_2$	3–5	$C_2 + PHOT \rightarrow C + C$	45
$H_2 + PHOT \rightarrow H + H$	45	$CH_2 + PHOT \rightarrow CH_2^+ + e$	45		

Note: CR indicates a cosmic ray. CRP represents a photon produced as a consequence of cosmic ray ionization, whilst PHOT is short for a photon of external origin. A reaction which includes a species in parentheses is one of the artificial three-body reactions described in the sixth paragraph of Sect. 3.

accurate within thirty percent of those of the full network in the individual case under consideration, for 10^5 yr and later.

Once an individual reduced network was identified for a particular case, its range of reliability was tested through its application to cases with other values of $n(H_2)$ and A_V. Comparisons of its results for CO in these cases were made to the CO results of the full network for the same cases. Agreement between the individual reduced network and full network results within thirty percent was required at all times ($\geq 10^5$ yr) for a case to be included in the range for which the individual reduced network was deemed reliable. Table 2 indicates each range over which a single individual reduced network was found to be valid.

Tables 3 and 4 comprise a list of all reactions found to be important in any of the individual networks obtained for fixed n_H and A_V cases. In Table 3 a column indicates for what ranges of cases any particular reaction must be included in the individual reduced networks. Thus, one can easily identify the reactions of the individual reduced network for the $n_H = 2 \times 10^4$ cm^{-3}, $A_V = 10$ case and other cases in the same range of validity.

For the most part Table 4 includes reactions involving more complicated species. When calculating the B_i's for cases in range 3 we found that many large hydrocarbons and long carbon chain species (e.g. C_9H^+) appeared to be necessary species. In an attempt to minimize the size of the combined reduced network we removed all hydrocarbon and carbon chain species larger than $C_2H_2^+$ and assumed that $e + C^+ + C_2H \rightarrow C + C_2H$ produces C at the same rate per unit volume as the reaction $C^+ + C_2H \rightarrow C_3^+ + H$ produces C_3^+. Thus, not even C_3^+ appears in the artificially *modified combined reduced network.* One other alteration was included in the modified combined network.

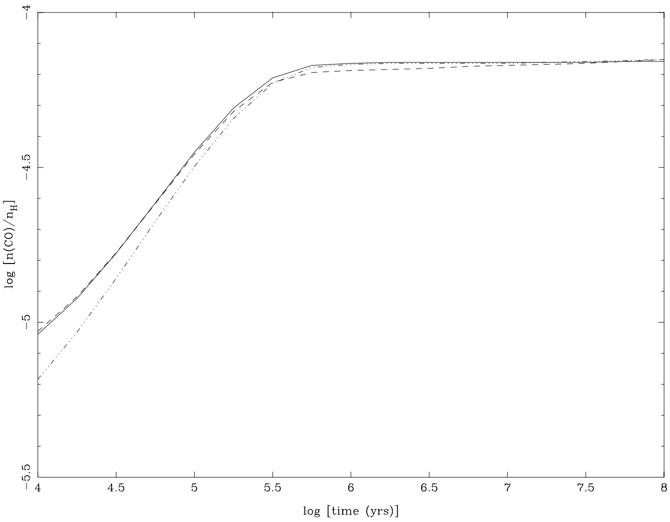

Fig. 1. Comparison of CO abundance as a function of time obtained using the full network (solid line), the combined reduced network (dashed line) and the modified combined reduced network (dot-dash line) for $n_{\rm H} = 2 \times 10^4$, $A_V = 3$.

Any reaction producing CO^+ was assumed instead to generate HCO^+ at the same rate per unit volume by an artificial three-body reaction.

Table 4 lists the reactions removed from the combined reduced network to form the modified version that appears in Table 3. The unmodified combined reduced network contains 69 species and 241 reactions, and the modified combined reduced network contains 33 species taking part in 116 reactions. We note that the modified combined reduced network is accurate to only a factor of about two for a few limited cases: $n_{\rm H} = 10^3$ cm^{-3}, $A_V = 4$, and $n_{\rm H} = 500$ cm^{-3}, $A_V = 4$–10.

4. Conclusions

Figure 1 shows values of the CO fractional abundance, with respect to hydrogen nuclei, as a function of time given by the use of the full network, the combined reduced network and the modified reduced network, for $n_{\rm H} = 2 \times 10^4$ cm^{-3}, $A_V = 3$. The good agreement shown in the figure together with the agreement found in comparisons described earlier establishes the utility of the combined reduced network for many studies.

We have succeeded in the isolation of reduced networks governing the CO abundance in static regions. Rather surprisingly, long chain carbon-bearing molecules play a major role in the chemistry of CO in some regions as a consequence of their overall high abundance making them sinks for C^+, which would otherwise enter reactions initiating CO formation. Nevertheless, these complex species can be excluded under most conditions through the use of an artificial reaction. In future work we will identify reduced networks that give reliable results for the CO abundance in dynamically evolving regions and regions with differing depletions.

Table 4. Reactions removed from the combined reduced network.

Reaction	
$C_n + CRP \rightarrow C_{n-1} + C$	n3,5
$C^+ + C_nH_m \rightarrow C_{n+1}H^+_{m-1} + H$	m1 n2–6,8; m2 n2,3
$C^+ + C_n \rightarrow C^+_{n+1}$	n3–9;
$H^+ + C_nH_m \rightarrow C_nH^+_m + H$	m0 n3–9; m1 n3–6,8
$H^+ + C_nH_m \rightarrow C_nH^+_{m-1} + H_2$	m1 n3–6,8; m2 n3
$H_2 + C_nH^+_m \rightarrow C_nH^+_{m+1} + H$	m0 n3–9; m1 n3,4,6,8
$H_2 + C_nH^+_m \rightarrow C_nH^+_{m+2}$	m0 n6; m1 n3; m2 n2
$H^+_3 + C_nH_m \rightarrow C_nH^+_{m+1} + H_2$	m0 n3; m1 n3
$HCO^+ + C_nH_m \rightarrow C_nH^+_{m+1} + CO$	m0 n3; m1 n3
$H_3O^+ + C_nH_m \rightarrow C_nH^+_{m+1} + H_2O$	m0 n3; m1 n3
$O + C_nH^+_m \rightarrow HCO^+ + C_{n-1}H_{m-1}$	m2 n4; m3 n3
$O + C_nH_m \rightarrow CO + C_{n-1}H_m$	m0 n4,6,8; m1 n3,4
$C_nH^+_m + e \rightarrow C_{n-1}H_m + C$	m0 n3,4,6,8–10; m1 n3,5–7,9; m2 n3
$C_nH^+_m + e \rightarrow C_n + H_m$	m1 n3-7,9; m2 n3,4,6,8
$C_nH^+_m + e \rightarrow C_{n-2}H_m + C_2$	m0 n4–10; m1 n4; m2 n3
$C_nH^+_m + e \rightarrow C_nH_{m-1} + H$	m2 n3,4,6,8; m3 n3
$C_nH^+_m + e \rightarrow C_nH_{m-2} + 2H$	m2 n3,6; m4 n2
$C_nH^+_m + e \rightarrow C_nH_{m-2} + H_2$	m3 n3,4; m4 n2
$C_n + PHOT \rightarrow C_{n-1} + C$	n3,4
$C_nH_m + PHOT \rightarrow C_nH_{m-1} + H$	m1 n3,4; m2 n3
$C_nH_m + PHOT \rightarrow C_{n-2}H_m + C_2$	m0 n4,5; m1 n4
$C_3H_2 + PHOT \rightarrow C_3 + H_2$	
$C^+_7 + e \rightarrow C_4 + C_3$	
$C_3H^+_3 + e \rightarrow C_2H_2 + CH$	
$C + C_2H_2 \rightarrow C_3H + H$	
$C_4H^+_2 + H \rightarrow C_4H^+_3$	
$C_3H_2 + C^+ \rightarrow C^+_4 + H_2$	
$C_3H^+_2 + H \rightarrow C_3H^+ + H_2$	
$C_2H^+_2 + C \rightarrow C^+_3 + H_2$	
$C_2H^+_2 + C \rightarrow C_3H^+ + H$	
$He^+ + C_3H \rightarrow C^+_3 + H + He$	
$He^+ + C_3 \rightarrow C^+ + C_2 + He$	
$He^+ + C_3 \rightarrow C^+_2 + C + He$	

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References

Lee, H.-H., Bettens, R. P. A., & Herbst, E. 1996, A&AS, 119, 111

Millar, T. J., Farquhar, P. R. A., & Willacy, K. 1997, A&AS, 121, 139

Ruffle, D. P., & Herbst, E. 2000, MNRAS, 319, 837

Sims, I. R., & Smith, I. W. M. 1995, Ann. Rev. Phys. Chem., 46, 109

Terzieva, R., & Herbst, E. 1998, ApJ, 501, 207

Tomlin, A. S., Turányi, T., & Pilling, M. J. 1997, in Low Temperature Combustion and Autoignition, ed. M. J. Pilling (Elsevier, Amsterdam), 293

Tomlin, A. S., Pilling, M. J., Turányi, T., Merkin, J. H., & Brindley, J. 1992, Comb. & Flame, 91, 107