The distribution of molecules in star-forming regions

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Abstract. A number of maps of low-mass star-forming regions have shown the molecule CS to be more widespread than NH_3, despite having a higher critical density in the transitions in question. In a previous paper a model was presented of unresolved clumps around the star-forming core. The clumps are transient and exhibit emission only from molecules that form quickly. In this paper it is shown how families of molecules can be found that ought to follow either the CS or NH_3 behaviour if mapped adequately in similar sources. The first family of early-time molecules, includes such species as CH_4, CH_3, H_2CO, H_2CS, HC_3N, CN and HCN. The second family of late-time molecules includes the species HCO^+, NO, OH, SO, N_2H^+, O_2, N_2 and OCN. The chemistry of these molecules is discussed.

Key words: ISM: clouds – ISM: molecules – ISM: structure – molecular processes

1. Introduction

Radio intensity maps of molecules in transitions with critical densities $n_{cr} \gtrsim 10^4$ cm^{-3} show emission mostly localised to ~ 0.1pc 'cores' that are known to be sites of star-formation. It is therefore reasonable to assume that this dense material is the consequence of the partial collapse of the more diffuse gas that surrounds it, traced, for example, in CO (J=1 $\rightarrow$ 0) emission. The molecules most commonly used to detect these cores are ammonia and carbon monosulphide (e.g. Benson & Myers 1989, Snell et al. 1984), and a puzzling discrepancy became apparent very early in these studies. Although CS should trace higher densities than NH_3 the surveys of Zhou et al. (1989), Myers et al. (1991) and Pastor et al. (1991) showed the CS (J=3 $\rightarrow$ 2, 2 $\rightarrow$ 1, and 1 $\rightarrow$ 0) emission to cover systematically wider areas than the NH_3 (1,1) inversion transition. The same conclusions for further sources were drawn by Juan et al. (1993), López et al. (1994) and Zinchenko et al. (1994). In addition, the CS linewidths were larger, and it was noted that there was a significant difference in the positions of the peaks of emission of CS and NH_3. However, the denser gas (traced in CS) should be more confined then the less dense gas (traced in NH_3).

The differences are not caused by the use of different instruments, and continue to appear whenever studies are made at similar angular resolution. Possible explanations for the anomaly may lie either in the effects of optical depth or of chemical differentiation. In the former case, Fuller (1988) proposed that a low density envelope would scatter photons from the core within, giving the impression of a wider emitting area, the effect occurring preferentially in CS since the NH_3 (1,1) population is distributed over all the hyperfine components. In the latter case, Taylor, Morata & Williams (1996; Paper 1) proposed a solution based on the differences in the chemistry of the two molecules, and furthermore using chemical models and an analysis of the excitation of CS in a particular source (L1524) came to the conclusion that the extended CS emission was due to unresolved clumps rather than homogeneous gas. In this model, the difference is due to the speed at which the molecules form, NH_3 only being present in observable amounts in longer-lasting clumps, perhaps only those that become star-forming cores. This model has the further advantages that it can continue to explain the observations when the CS lines are optically thin, and also the lack of coincidence of the molecular emission peaks and the larger CS linewidth.

In this paper we extend the work of Paper 1 to examine whether there are other potentially observable molecules that should show extended emission like CS, or more compact emission like ammonia, if this 'unresolved clump' model is correct. Although sulphur-containing molecules are some of the most useful in observing these regions, quantitative chemical modelling is hampered by the lack of information on the elemental depletion of sulphur; hence, we are especially interested in other signature molecules. The reliability of the chemistry that leads to these predictions is also discussed.

2. Model

If the telescope beam includes a number of unresolved clumps then the difference in emission may be due to the differences in the physical, and hence chemical, evolution between them. We proposed in Paper 1 that all clumps had collapsed from a relatively diffuse state, in which only hydrogen is predominantly molecular. As the gas collapses, a large amount of free carbon is available to form molecules such as CS, before the carbon is swallowed up in CO. These 'early-time' carbon-based molecules (like CS) exhibit a peak in fractional abundance (=

$n(X)/n_H$, where $n(X)$ is the number density per unit volume of the molecule X and n_H is the number density of hydrogen nuclei) before falling off at later times. Other molecules may simply achieve their maximum abundance at the same time as the peak of the early-time molecules and then remain at constant abundance (being in chemical equilibrium), but some termed 'late-time' only peak in abundance at significantly later times due to bottlenecks in the their formation routes caused by low reaction rates. Ammonia is an example of this latter type since the reactions involved in its formation

$$N^+ + H_2 \rightarrow NH^+ + H \tag{1}$$

$$NH_3^+ + H_2 \rightarrow NH_4^+ + H \tag{2}$$
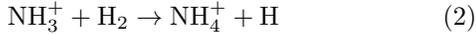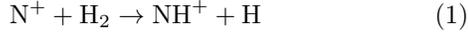
appear to be considerably slower at 10K than other comparable reactions. Only cores that are stable upon the initial collapse will be detectable in these molecules. Other cores, perhaps dispersed quickly because they are too small or are not in pressure equilibrium with the external medium, will not be detectable in "late-time" species.

Our chemical model is described in detail in Paper 1; the important points are reiterated here. In a single point calculation chemical abundances are followed from initial conditions typical of a diffuse cloud ($n_H = 10^3$ cm^{-3}, visual extinction $A_V = 0.5$) through a free-fall collapse (increasing n_H and A_V) until $n_H = 5 \times 10^4$ cm^{-3} and $A_V \sim 7$, after which both of these parameters are kept constant. The formula used for this collapse is given in Rawlings et al. (1992), and includes a scaling parameter 'B' that we have normally taken to be unity. This description is intended to represent the relaxation to an equilibrium state in magnetohydrodynamic numerical collapse models, which in those simulations is followed by a longer phase in which magnetic support for the core is slowly removed by ambipolar diffusion so that the core can then collapse further to form a star. The formation of a number of such clumps may be the result of the fragmentary collapse of a larger scale ($\sim$ 1pc) cloud. Observational evidence for such clumps comes from the small scale structure of core D in TMC-1 (Langer et al. 1996), and from the clumpy emission seen ahead of bow shocks in a number of sources (Taylor & Williams 1996).

The observations pertinent to Paper 1 could only be explained if the effective freezeout parameter, FR, was low. This parameter accounts for the efficiency of adsorption of gas molecules onto dust grain surfaces and for the grain size distribution (which affects the surface area available for gas species to stick to), and its low value may be an indication of effective *desorption* rather than inefficient sticking. There are a number of methods of desorption, described e.g. in Williams & Taylor (1996), and amongst the more recent to be considered are desorption due to the heat emitted from the exothermic formation of molecular hydrogen on the grain surface (Willacy, Williams & Duley 1994), and the desorption of CO by transfer of energy from the O-H vibration at 3.1 μm (Dzegilenko & Herbst 1995). As in Paper 1 we normally take FR=0.01, and we also use the same elemental abundances. However, the chemical data

has been updated, and also extended, by increasing the carbon chain chemistry to include species as complex as HC$_3$N (there are now 138 gas phase species and 1996 reactions), and the revised UMIST ratefile has also been used (Millar, Farquhar & Willacy 1997).

3. Results and chemistry

The present paper aims to establish whether there are potentially observable molecules that belong to the CS and NH$_3$ 'families' of early and late time formation. Fig. 1 shows the fractional abundances of a number of relevant species as a function of time, the associated changes in the n_H and A_V values are shown in Fig. 4 of Paper 1. Fig. 1a details the C$^+$/C/CO conversion that takes place as free carbon is converted into CO; this transition takes place as the gas reaches its final density and as it occurs a number of carbon based molecules achieve peaks in their abundance (most of these peaks being rather more pronounced than CS) – these are the *early-time* molecules. These peaks occur at $t \sim 1.6 \times 10^6$yr. A number of the other molecules achieve their maximum abundance (usually their equilibrium chemical abundance) at least 3×10^5yr later – these are the *late-time* molecules. The actual time of the peak of the early-time molecules is not particularly relevant since this is just the free-fall time, these molecules form immediately when the gas is dense and opaque – in this sense they are *dynamically* led, whereas the late-time species occur at a subsequent time dictated by a *chemical* timescale.

3.1. Early-time molecules

Initially, most of the carbon is in the form of C$^+$, and this can react with H$_2$ by hydrogen abstraction to form ions such as CH$_5^+$ which may recombine to produce molecules such as CH$_3$ and CH$_4$. Since oxygen is predominantly atomic, formaldehyde can be formed via

$$O + CH_3 \rightarrow H_2CO + H \,. \tag{3}$$
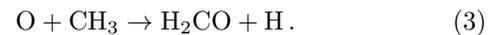
These hydrocarbons can also react with nitrogen atoms,

$$N + CH \rightarrow CN + H \tag{4}$$

$$N + CH_2 \rightarrow HCN + H \,. \tag{5}$$
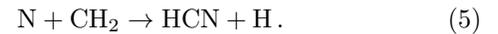
Sulphur is in the form S$^+$, so that H$_2$CS can also be formed

$$CH_4 \xrightarrow{S^+} H_3CS^+ \xrightarrow{e^-} H_2CS \,. \tag{6}$$

Further reaction of C$^+$ with CH$_4$ leads to the C$_2$H$_3^+$ and C$_2$H$_4^+$ ions which recombine to give the important acetylene molecule, which is the precursor to a number of carbon-chain molecules,

$$C + C_2H_2 \rightarrow C_3H + H \tag{7}$$

$$N + C_3H \rightarrow C_3N + H \tag{8}$$
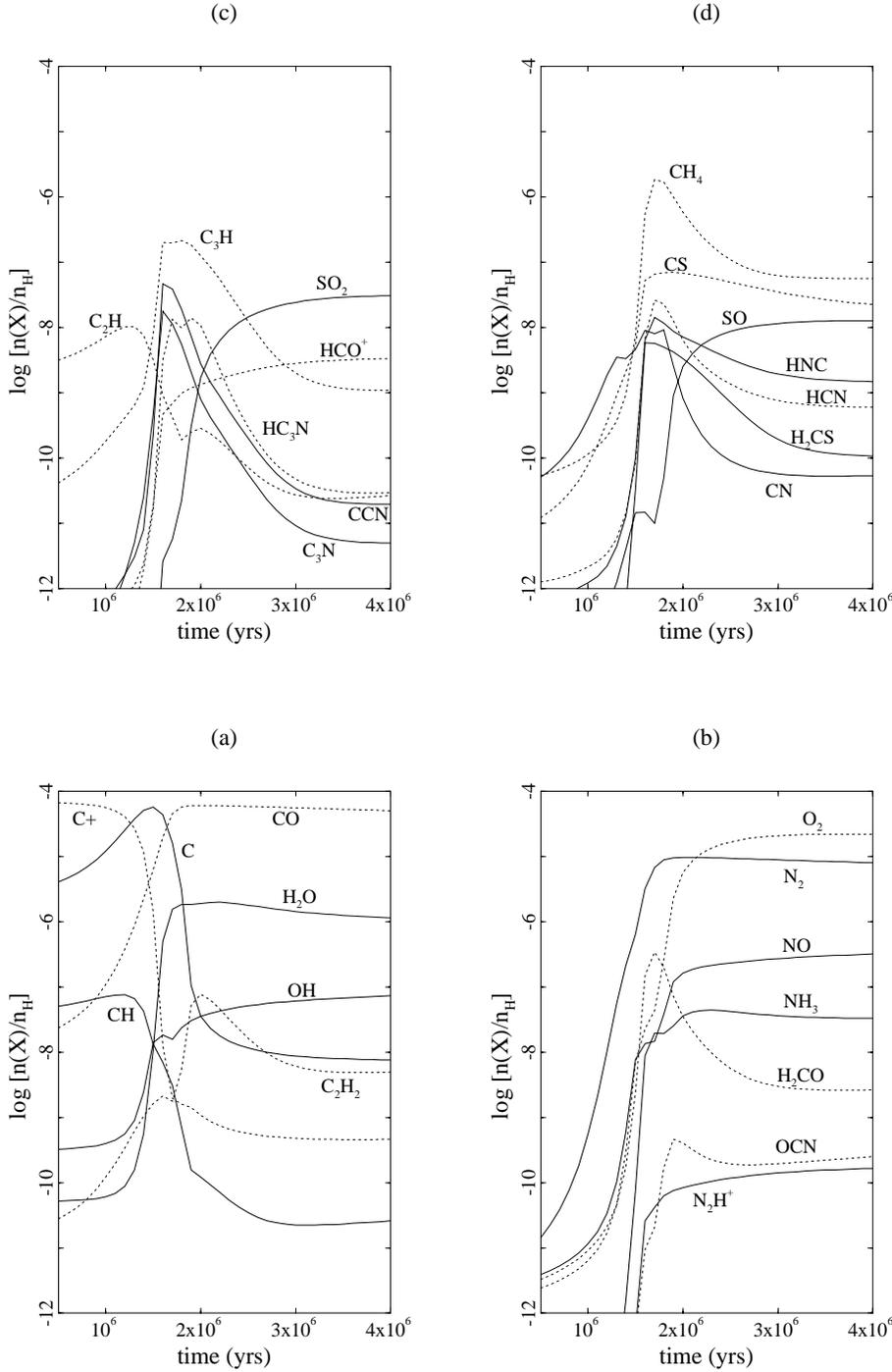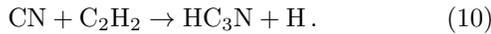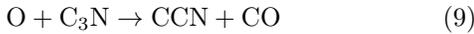
(c)

(d)

(a)

(b)
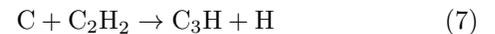
Fig. 1a–d. Chemical fractional abundances (relative to H nuclei) as a function of time for a free-fall collapse model halted at density $n_H=5\times10^4$ cm^{-3}. Initially $n_H=1\times10^3$ cm^{-3} and $A_V=0.5$. Freeze-out parameter FR=0.01

$$O + C_3N \rightarrow CCN + CO \qquad (9)$$

$$CN + C_2H_2 \rightarrow HC_3N + H. \qquad (10)$$

3.2. Late-time molecules

Ammonia does not achieve its maximum fraction until $t > 2 \times 10^6$ yr, mostly because the slight endothermicity (equivalent to 85K) of reaction 1 slows the NH$_3$ formation. Oxygen atoms cannot be ionised by UV photons in these regions, and oxygen atom reaction with H$_2$ is endothermic. Thus, when the clump has collapsed to the extent that molecules are not photodissociated, it is still necessary to wait for sufficient time to elapse for oxygen to be ionised by cosmic rays before hydrogenating reactions can take place. H$_3^+$ can react with O, but the formation of this molecule also requires cosmic-ray ionisation (of H$_2$). Thus, OH is a late-time molecule;

$$O \stackrel{c.r.}{\rightarrow} O^+ \stackrel{H_2}{\rightarrow} OH^+ \stackrel{H_2}{\rightarrow} H_2O^+ \stackrel{e^-}{\rightarrow} OH. \qquad (11)$$

Table 1. List of late-time molecules, along with the factor increase in their fractional abundance at their own peak compared with their abundance at the CS family peak time of $t = 1.65 \times 10^6$ yr. For some of these molecules the late time peak occurs at times even later than those shown in Fig. 1

Molecule	Factor Increase
OH	7
O_2	565
SO	333
NH_3	3
NO	32
N_2	2
HCO^+	7
OCN	52
C_2H_2	36

A number of other molecules then follow from OH,

$$O + OH \rightarrow O_2 + H \tag{12}$$

$$CN + O_2 \rightarrow OCN + O \tag{13}$$

$$N + OH \rightarrow NO + H \tag{14}$$

$$N + NO \rightarrow N_2 + O \tag{15}$$

$$S + OH \rightarrow SO + H. \tag{16}$$
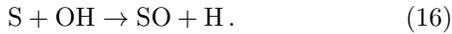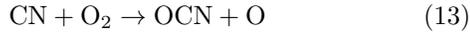
NO can also be formed from via reaction of O with NH_2, but NH_2 (which forms during the NH_3 production) is itself a late-time molecule. SO is also formed by reaction of the molecules HS and O_2, and again both of these molecules are late time (HS being late time because the reaction of S^+ with H_2 is endothermic and therefore slow at low temperature). HCO^+ is an important ion that forms late, mostly through the reaction of H_3^+ with CO.

Table 1 gives the enhancements in abundance of these late-time molecules over their values at the time of the CS peak. Note that ammonia has one of the smallest enhancements. The larger this factor the greater the chance that the molecule will be seen in long-lived cores.

4. Discussion

4.1. Observability

A complication of this analysis is that it is not enough to argue that NH_3 family molecules will cover smaller areas of the sky than CS family molecules. We have postulated in Paper 1 that this is the case for NH_3 only by assuming that it is at such an abundance that it is undetectable in the CS clumps, and this may not be the case for other molecules of the NH_3 family. What can be said, however, is that at similar angular resolution

Table 2. Transitions of relevant early- and late-time molecules with the estimated line strength relative to the CS (J=1-0) line intensity, at the time of reaching maximum abundance. Calculations have been made assuming LTE, T_{ex}=10 K and a line width ΔV=1 km s^{-1}

Molecule	Transition	ν (GHz)	$\dfrac{T_{mb}}{T_{mb}(CS)}$	Time (yrs)
HCN	$J=1 \rightarrow 0$	88.6	0.9	1.7×10^6
	$J=2 \rightarrow 1$	177.2	1.1	
H_2CS	$J_{K-1,K+1}=3_{12} \rightarrow 2_{11}$	104.6	0.1	1.6×10^6
	$J_{K-1,K+1}=4_{14} \rightarrow 3_{13}$	135.3	0.1	
H_2CO	$J_{K-1,K+1}=2_{12} \rightarrow 1_{11}$	140.8	1.4	1.7×10^6
	$J_{K-1,K+1}=2_{02} \rightarrow 1_{01}$	145.6	1.4	
	$J_{K-1,K+1}=2_{11} \rightarrow 1_{10}$	150.5	1.3	
	$J_{K-1,K+1}=3_{03} \rightarrow 2_{02}$	218.2	1.2	
	$J_{K-1,K+1}=3_{22} \rightarrow 2_{21}$	218.5	1.2	
HC_3N	$J=10 \rightarrow 9$	91.0	0.3	1.9×10^6
	$J=11 \rightarrow 10$	100.1	0.2	
	$J=12 \rightarrow 11$	109.2	0.2	
HCO^+	$J=1 \rightarrow 0$	89.2	0.5	4.0×10^6
	$J=3 \rightarrow 2$	267.6	0.1	
SO	$J_K=3_2 \rightarrow 2_1$	99.3	0.6	3.9×10^6
NO	$^2\Pi_{1/2}, J=3/2 \rightarrow 1/2$ F=5/2$\rightarrow$3/2	150.5	0.1	4.0×10^6

molecules of the NH_3 family should show a much steeper decrease in intensity from peak, i.e. a smaller half-power contour. In order to sample fully the area a resolution of $\sim 1'$ is preferable for mapping purposes, though higher resolution would be required to resolve most of the individual clumps. On the other hand, the excitation conditions for particular transitions are important, so for example a member of the CS family will not appear widespread compared with NH_3 if the transition n_{cr} is so high that it is only significantly excited in the densest of cores (e.g. CS(J=5 $\rightarrow$ 4)). Mappings of molecules in low-mass star-forming regions on the $10'$ scale are rare in the literature, so this discussion is concerned more with potential observability. In Table 2 we show line information concerning transitions, frequencies and estimated line strengths for the most relevant molecules discussed.

4.2. Early-time molecules

HCN (J=1 $\rightarrow$ 0) was mapped in two cores in high-mass star-forming regions by Zinchenko et al. (1994), and those authors remark that the spatial extent follows CS rather than ammonia, as predicted here. The molecule is easily observable in low-mass sources as well (e.g van Dishoeck et al. 1995). We anticipate that CN will follow the same distribution.

H_2CO is now widely observed since it appears to be a good indicator of infall due to collapse (e.g. Myers et al. 1995). Its emission appears widespread in diffuse clouds (Turner 1994), which may not be star-forming, but mappings of star-forming cores would probably be better in transitions like $2_{12} - 1_{11}$ (rather than at cm wavelengths) which is at a high enough

frequency ($\sim$ 141 GHz) that the required resolution can be achieved.

H_2CS is clearly observable (e.g. Minh et al. 1991) and mapping would be possible. Like H_2CO, however, there has been speculation that this molecule is formed on grains rather than in the gas, which could affect our conclusions.

We predict a number of carbon chains to be members of the CS family, most prominently C_3N, HC_3N, and C_3H. Although their abundances are probably inflated in our models since the chemical network for species with four or more carbon atoms is incomplete, their early-time behaviour should not be affected. The original impetus to this work came from our analysis (Howe, Taylor & Williams 1996) of observations of HC_3N and NH_3 (together with CCS and C_4H) in TMC-1 by Hirahara et al. (1992). This exceptionally rich source shows at least five distinct cores, the carbon chains and ammonia showing intensity peaks in different cores. We interpreted this spatial difference as being due to sequential time evolution. By associating C_3H with C_4H there does not seem to be any doubt that all three of these molecules could be mapped in other star-forming regions. CCS appears well suited to core observation and, although not included in these models, is also early-time. HC_5N ought to follow the distribution of HC_3N, and was mapped in four sources by Benson & Myers (1983), however the maps were not extensive and the comparison with NH_3 is indeterminate. Our models predict CCN to belong to the CS family, but the molecule is yet to be observed.

4.3. Late-time molecules

HCO^+ is another commonly used tracer of infall, though again maps are rare. However, Butner, Lada, & Loren (1995) do show the coverage of DCO^+ in a number of sources previously mapped in CS/NH_3, and it is apparent that for the most part this molecule is closer to ammonia than CS. Assuming that HCO^+ follows DCO^+ then these observations are consistent with our prediction that HCO^+ is a late-time molecule. Since we presume the late-time molecules to emit from far fewer clumps than the early time molecules (perhaps only one clump), it follows that their peaks of emission ought to coincide. In this respect it is encouraging that HCO^+ has been observed in L1251 by Sato et al. (1994) and the emission is smaller than, but coincident with, the NH_3 mapped by Morata et al. (1997).

The molecule SO has been mapped by Chernin, Masson, & Fuller (1994) in a number of low to intermediate-mass sources. The 3_2–2_1 emission is quiescent (rather than being associated with molecular outflows) and seems to be compact, although none of the sources appear to coincide with those of the CS/NH_3 surveys. An understanding of the behaviour of SO is impeded by lack of information on the elemental depletion of sulphur. However, a comparison with CS would be very interesting.

Emission from NO at $\sim$ 150GHz is clearly detectable (e.g Gerin, Viala & Casoli 1993) and maps ought to be possible at the required resolution, though none appear to exist at present. OCN peaks at 1.9×10^6yr in our model and so can be classed as late-time, but has not been observed. A number of archetypal late-time molecules (O_2, N_2, C_2H_2) are unfortunately not observed in emission because of their lack of dipole moment. The chemistry of C_2H_2 is unusual in that it exhibits an early-time peak due to formation through C^+ and CH_4, but experiences a larger late-time peak because its main destruction paths through C and C^+ are reduced as these species are removed from the gas-phase.

4.4. Chemistry

A glance at the chemical equations in Sect. 3 confirms that neutral-neutral reactions are surprisingly important, although much of interstellar chemistry is based on ion-molecule chemistry. It is important to confirm that these neutral-neutral reactions proceed at 10K; in fact, most of these reactions have only been studied at room temperature, if they have been studied at all. The CS family chemistry, in particular, depends on efficient neutral-neutral reactions. For the NH_3 family, the removal of these predominant pathways will probably lead to even slower formation.

Certain neutral-neutral reactions have indeed been studied at low temperatures. The reaction of CN with C_2H_2 (reaction 10) has been examined by Sims et al. (1993), and of CN with O_2 (reaction 13) by Rowe, Canosa, & Sims (1993). Gerin et al. (1992) show that N with OH (reaction 14) proceeds with a negligible barrier. The reaction C + C_2H_2 (reaction 7) was studied recently by Kaiser et al. (1997) and found to proceed, and also in the correct ratio of cylic to linear C_3H product. The reaction of O with OH is thought to have a barrier of $\sim$ 30K, low enough to be a significant barrier in cold clouds. For the schemes used here, OH reactions are based on the assumption that atom-radical reactions can in fact proceed without barrier, given the evidence above (cf. Herbst et al. 1994).

The initial condition of the gas that is adopted in these studies has been typical of fairly diffuse interstellar material, and we have further assumed that most of the carbon is in the form of C^+. We have, however, also explored the consequences of starting with significant quantities of carbon in CO. The results are not greatly different from those illustrated in Fig. 1. This is because the photodissociation of CO before the collapse dominates (at $\sim 1 \times 10^6$ yr) always ensures enough free carbon to drive the carbon chemistry, as described in Sect. 3.

The initial condition also sets the sulphur abundance at about 1% of its cosmic value. This is clearly incorrect under the near-diffuse conditions at the start of the collapse; in diffuse clouds sulphur is observed to have a relative abundance close to the cosmic value. However, in calculations that we have made using higher values of the sulphur relative abundance, sulphur-bearing molecules are found to have abundances that are much too high when compared to the observed values. Evidently, these calculations are telling us that sulphur is being heavily depleted *during* the collapse process. The physical mechanism by which this depletion occurs is unknown, and is currently a topic of study by us. Until this mechanism is understood, we have chosen to adopt a (low) fractional abundance of sulphur that is necessary

to give approximately the abundances of the S-bearing family of molecules.

As mentioned earlier (Sect. 3), the dynamical and chemical timescales control the appearance of early and late families of molecules. In this simple model, the dynamical timescale is controlled by the scaling parameter, B (Sect. 2). The value of B has been set equal to unity in the calculations reported here. We have, however, also explored the consequences of a slow collapse (B=0.1). In this case, the early time abundance peaks are suppressed. These peaks are a consequence of the cloud having attained a high density before the gas can respond chemically. With the slower collapse, represented by B=0.1, the chemical timescale is shorter than the dynamical timescale, so these peaks are smoothed out. The arguments of Paper 1 and of Howe et al. (1996) therefore suggest that collapses as slow as those modelled by B=0.1 are excluded.

5. Summary

A plausible explanation for the anomalously widespread emission of CS compared with NH_3 in low-mass star-forming regions is the formation (in the collapse process) of many clumps of dense gas, only some of which go on to form stars or at any rate persist for a long enough time to be visible in 'late-time' molecules such as NH_3, but all of which may be observable in 'early-time' molecules such as CS. Here, models of this collapse process are used to predict which other molecules will fall into each of the CS and NH_3 families, and which will be suitable for study at the appropriate resolution, if they have not already been mapped. HCN, H_2CO, H_2CS, C_3N, HC_3N, and C_2H are found to fall into the CS family, whilst HCO^+, SO, NO, OH, N_2H^+ and OCN are in the ammonia family. The reliability of the neutral-neutral chemistry that is predominantly responsible for their the formation is also considered.

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