Gas-grain chemical models of star-forming molecular clouds as constrained by ISO and SWAS observations

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Abstract. We have investigated the gaseous and solid state molecular composition of dense interstellar material that periodically experiences processing in the shock waves associated with ongoing star formation. Our motivation is to confront these models with the stringent abundance constraints on CO\textsubscript{2}, H\textsubscript{2}O and O\textsubscript{2}, in both gas and solid phases, that have been set by ISO and SWAS. We also compare our results with the chemical composition of dark molecular clouds as determined by ground-based telescopes. Beginning with the simplest possible model needed to study molecular cloud gas-grain chemistry, we only include additional processes where they are clearly required to satisfy one or more of the ISO-SWAS constraints. When CO, N\textsubscript{2} and atoms of N, C and S are efficiently desorbed from grains, a chemical quasi-steady-state develops after about one million years. We find that accretion of CO\textsubscript{2} and H\textsubscript{2}O cannot explain the [CO\textsubscript{2}/H\textsubscript{2}O] ice ISO observations; as with previous models, accretion and reaction of oxygen atoms are necessary although a high O atom abundance can still be derived from the CO that remains in the gas. The observational constraints on solid and gaseous molecular oxygen are both met in this model. However, we find that we cannot explain the lowest H\textsubscript{2}O abundances seen by SWAS or the highest atomic carbon abundances found in molecular clouds; additional chemical processes are required and possible candidates are given. One prediction of models of this type is that there should be some regions of molecular clouds which contain high gas phase abundances of H\textsubscript{2}O, O\textsubscript{2} and NO. A further consequence, we find, is that interstellar grain mantles could be rich in NH\textsubscript{2}OH and NO\textsubscript{2}. The search for these regions, as well as NH\textsubscript{2}OH and NO\textsubscript{2} in ices and in hot cores, is an important further test of this scenario. The model can give good agreement with observations of simple molecules in dark molecular clouds such as TMC-1 and L134N. Despite the fact that S atoms are assumed to be continuously desorbed from grain surfaces, we find that the sulphur chemistry independently experiences an “accretion catastrophe”. The S-bearing molecular abundances cease to lie within the observed range after about $3 \times 10^6$ years and this indicates that there may be at least two efficient surface desorption mechanisms operating in dark clouds – one quasi-continuous and the other operating more sporadically on this time-scale. We suggest that mantle removal on short time-scales is mediated by clump dynamics, and by the effects of star formation on longer time-scales. The applicability of this type of dynamical-chemical model for molecular cloud evolution is discussed and comparison is made with other models of dark cloud chemistry.

Key words. molecular abundances – astrochemistry – molecular processes

1. Introduction

Recent measurements by the space-based observatories ISO (Kessler et al. 1996) and SWAS (Melnick et al. 2000a) are placing stringent constraints on the relative abundances and the physical conditions under which the most abundant heavy molecules are found in molecular clouds: CO, CO\textsubscript{2}, H\textsubscript{2}O and O\textsubscript{2}. Gaseous water is found to have high abundances in star-forming regions ($\sim 10^{-5} - 10^{-4}$ relative to molecular hydrogen) that are consistent with ice mantle evaporation or hydrogenation of atomic oxygen in shocked gas (Gensheimer et al. 1996; van Dishoeck & Helmich 1996; Harwit et al. 1998). In contrast, although water ice is ubiquitous and abundant in lines of sight though cold molecular clouds, SWAS observations indicate a gas phase abundance in the range $\sim 10^{-9} - 10^{-8}$ (Snell et al. 2000), significantly below values expected from current models of ion-molecule chemistry in steady-state (Lee et al. 1996; Millar et al. 1997).

Solid molecular oxygen has been unsuccessfully searched for by ISO (Vandenbussche et al. 1999) and the upper limits are [O\textsubscript{2}/H\textsubscript{2}O] ice $< 0.2$. If water abundances of $\sim 10^{-5}$ typically result from mantle evaporation (Gensheimer et al. 1996) then this corresponds to a gas
phase abundance limit of \( \frac{O_2}{H_2} < 2 \times 10^{-6} \) in protostellar cores. However, the SWAS limits on \( O_2 \) in many sources indicate a column density ratio of \( \frac{N(O_2)}{N(C^{18}O)} < 2 - 17 \) (Goldsmith et al. 2000); this translates to limits of \( \frac{O_2}{H_2} < (5 - 9) \times 10^{-7} \) in the molecular oxygen abundance. These \( O_2 \) limits place severe constraints on interstellar chemistry models. These predict that dense molecular gas \( \rho(H_2) \sim 10^4 \text{ cm}^{-3} \) should evolve \( O_2 \) abundances in excess of \( 10^{-5} \) after a few times \( 10^8 \) years (e.g. Brown & Charnley 1990; Bergin et al. 1996; Bergin & Langer 1997), and also that \( O_2 \) can be a significant component of the mantles (Tielens & Hagen 1982; d’Hendecourt et al. 1985). There is clearly a severe discrepancy between the model predictions and observations.

ISO has also demonstrated that solid \( CO_2 \) is a major component of interstellar grain mantles (de Graauw et al. 1996) and that, in protostellar cores, the gas phase abundance is much less than expected from thermal evaporation of these ices in the innermost “hot core” region. The low abundance of gaseous \( CO_2 \) found by ISO, and of \( O_2 \) found by SWAS, may be due to the mantles being sputtered in strong shock waves where both \( CO_2 \) and \( O_2 \) are destroyed in endoergic gas phase reactions (Charnley & Kaufman 2000). The \( [CO_2/H_2O]_{\text{ice}} \) ratios for many high-mass sources, as well as the field star Elias 16, lie within a range of values \( \approx 15 - 20\% \) (Gibb et al. 2000). Recently, in lines of sight towards low mass protostars up to 40% \( CO_2 \) relative to \( H_2O \) have been measured (Nummelin et al. 2001). Furthermore, toward high-mass protostars much of the \( CO_2 \) ice is not intimately mixed with the \( H_2O \)-dominated polar ice phase, but rather exists in a separate phase which shows the spectroscopic signature of thermally processed ice (Ehrenfreund et al. 1998a). For many lines of sight it can be excluded that \( CO_2 \) is contained in the \( CO \)-dominated apolar phase (Ehrenfreund et al. 1998b), because even a small contribution of \( CO_2 \) would significantly broaden the \( CO \) profile and this is not observed (Ehrenfreund et al. 1997). The \( CO_2 \) observations are difficult to reconcile with grain-surface pathways which produce \( CO_2 \) from \( CO \) by oxygen atom addition reactions, mediated by UV photolysis or radiolysis (Tielens & Hagen 1982; Allamandola et al. 1997; Moore & Hudson 1998), and indicates little enhancement in solid \( CO_2 \) by “energetic processing” as one goes from from cold molecular clouds to the more active environment of a young protostar. An important finding is that the \( CO_2 \) fraction appears to be largely independent of the amount of \( CO \) present in the ice (polar or apolar); this trend is apparent in observations towards background field stars and towards massive protostars. The simplest interpretation is that, since protostars gravitationally condense out of molecular clouds, the grain mantle [\( CO_2/H_2O \)]_{\text{ice}} ratios in their natal cores reflect that set in the parent cloud. The presence of higher methanol ice fractions in massive protostellar cores does however indicate that some solid state reactions do proceed more efficiently near protostars (Charnley 1997a; Gibb et al. 2000).

These \( O_2 \) and \( CO_2 \) observations present challenges to the simplest gas and solid phase chemical models. As \( O_2 \) is destroyed in the reaction

\[
C^0 + O_2 \rightarrow CO + O
\]  

(1)

the low gas phase abundance implied by SWAS can be seen to be related to the problem of explaining the high \( C^0/CO \) ratios (\( \approx 0.01 - 0.1 \)) in molecular clouds - a problem almost 20 years old (see for example Phillips & Huggins 1981). Simple chemical models show that \( C^0 \) is almost entirely incorporated in \( CO \) after several hundred thousand years and that the \( O_2 \) abundance subsequently climbs above the SWAS limits after this time (see above). Hence, explanation of the low \( O_2 \) abundances would appear to rely on freezing atomic carbon from \( CO \) and thereby keeping the cloud chemistry looking relatively “young”. Previous explanations have relied upon photodissociation of \( CO \) – either by cosmic-ray-induced photons (Prasad & Tarafdar 1983), or in models of turbulent clouds where gas parcels are periodically cycled out close to the cloud surface to experience higher UV fluxes before being returned to the denser inner core (Boland & de Jong 1980; Xie et al. 1995). Other scenarios to elevate the \( C^0/CO \) ratio appeal to the dynamical effects of periodic shock waves (Williams & Hartquist 1984), produced by each generation of stars in a cloud (Norman & Silk 1980), or to astrochemical bistability (Le Bourlot et al. 1993).

We are motivated to reconsider dynamical-chemical models of dense cloud chemistry in light of the ISO \( CO_2 \) data. Detailed chemical models of a shock-regulated chemistry (Charnley et al. 1988a,b; Nejad et al. 1990; Nejad & Williams 1992; Bergin et al. 1998, 1999) show that gas-grain cycling can lead to grain mantles in which all the \( CO_2 \) and most of the \( H_2O \) were formed in postshock gas and subsequently condensed out after an accretion time, given approximately by \( t_{\text{acc}} \sim 3 \times 10^5/\text{Myr} \). The large water abundance formed promptly in the postshock gas \( \sim 10^{-4} \) decays by accretion on to dust and by erosion in ion-molecule reactions until it reaches the abundance attainable solely by ion-molecule reactions, typically \( \sim 10^{-7} \). Protonation of \( H_2O \) to \( H_3O^+ \) produces \( OH \) upon electron dissociative recombination. Hence, large gas phase \( OH \) abundances can be expected within \( t_{\text{acc}} \) and this can lead to enhanced gas phase production of \( CO_2 \) and \( O_2 \) in

\[
CO + OH \rightarrow CO_2 + H
\]  

(2)

\[
O + OH \rightarrow O_2 + H
\]  

(3)

which then freeze out, along with the remnant postshock \( H_2O \), to form the grain mantles. Dynamically-regulated models thus directly link \( H_2O \) and \( CO_2 \) formation and co-deposition as ices. They also possess an intrinsic time-scale, \( t_{\text{acc}} \) which can naturally limit the evolution of the accreted \( CO_2/H_2O \) ratio in the mantles. As \( t_{\text{acc}} \) depends on quantities that should not vary dramatically from cloud to cloud these models may in principle account quantitatively for the similarity in many sources.
of the [CO$_2$/H$_2$O]$_{\text{ice}}$ ratios found by ISO, as well as the fact that CO and CO$_2$ mantle fractions seem to be independent (see above). Allowing accretion onto dust grains may also be expected to lower the gas phase O$_2$ abundance and may also raise the C$^0$/CO ratio to within the observed range.

In this paper we present model calculations designed to test this idea quantitatively. These models are most applicable to molecular clouds where low mass star formation occurs. We investigate if all the gas and solid phase constraints imposed by the ISO and SWAS measurements, as well as by ground-based observations, can be met in these models.

2. The reference chemical model

Our approach is to first develop a reference model for the long-term evolution of the gas-grain chemistry in molecular cloud material that is evolving from some postshock state. We initially make the simplest assumptions concerning the most uncertain model parameters, and then investigate the changes necessary to meet the observational constraints.

For each neutral species $i$, the gas and grain-surface abundances relative to H$_2$ obey the coupled differential equations.

\[
\dot{y}_i = n_H G_i - \lambda_i y_i + \xi_i g_i \quad \text{(4)}
\]

\[
\dot{g}_i = \lambda_i y_i - \xi_i g_i \quad \text{(5)}
\]

where $y_i$ and $g_i$ are, respectively, the abundance of molecule $i$ in the gas phase and resident on grain surfaces. $G_i$ is net production/loss of $i$ in gas phase chemical reactions, $\lambda_i$ is the accretion rate and $\xi_i$ is the surface desorption rate (e.g. Brown & Charnley 1990).

The chemical model described by the above equations is solved as an initial-value problem for a given chemical network. The initial conditions, $y_i(0)$, are consistent with cold postshock gas (see 2.2 below). The accretion time-scale in dark clouds is short compared to most other time-scales of interest (e.g. the ambipolar diffusion time and the star formation rate, or cycle/shock time) which are all $\gtrsim 10^6$ yr. Given the cold temperatures (10 K) and modest densities ($n_H \sim 10^4$ cm$^{-3}$) of most molecular cloud material, this would lead to loss of the entire heavy component of the gas phase unless some process acts to desorb heavy neutral atoms and molecules from grain surfaces and maintain the gas phase chemistry for longer than $t_{\text{acc}}$. The gas-grain chemical evolution on timescales of $t > t_{\text{acc}}$ reaches a quasi-steady-state determined by the values adopted for the (nonthermal) rates of surface desorption $\xi_i$ (Charnley 1997b). Several mechanisms have been proposed to provide a significant rate for $\xi_i$ on cold grains (see Léger et al. 1985; Willacy & Williams 1993; Willacy & Millar 1998; Markwick et al. 2000). These include chemical explosion of UV-photolyzed mantles and thermal evaporation mediated by cosmic ray impacts. In this work we calculate the chemical compositions with the $\xi_i$ essentially a parameter of the models, although we do appeal to the known binding properties of the major species in deciding on the relative values of $\xi_i$.

2.1. Gas-grain processes

We now discuss the numerical values and assumptions underlying our reference model.

2.1.1. Accretion

The accretion rate of a gas phase neutral on to dust grains is

\[
\lambda_i = 1.45 \times 10^4 \left(\frac{T}{M_i}\right)^{0.5} < \pi a^2 n_{\text{gr}} > \quad \text{(6)}
\]

where $T$ is the gas temperature, $n_{\text{gr}}$ is the grain number density, $a$ is the average grain radius, $k$ is the Boltzmann constant, and $M_i$ is the molecular weight of $i$. Unit sticking efficiency is assumed. In dark clouds, negatively-charged grains dominate the dust distribution and their density is approximately equal to $n_{\text{gr}}$ (Umebayashi & Nakano 1990); hence ions of charge Ze are depleted at a rate given by Eq. (6) multiplied by the factor $(1 + Ze^2/akT)$. It is assumed that when electrons and atomic ions collide with grains of opposite charge the grain is neutralised and the atoms ejected. For typical values of $n_{\text{gr}}$ and $a$, one has

\[
\lambda_i = 4.55 \times 10^{-18} n_H \left(\frac{T}{M_i}\right)^{0.5} \text{ s}^{-1}. \quad \text{(7)}
\]

2.1.2. Desorption

We assume that species with physiosorption binding energies of $E_B \geq 1200$ K are retained in the mantle (Tielens & Allamandola 1987; Sandford & Allamandola 1993; Hasegawa & Herbst 1993) – this is sufficient to partition the gas-grain chemistry such that accreted O$_2$ and CO$_2$ molecules are retained on dust. For the species with $E_B < 1200$ K we specify their desorption rates as follows. We assume that He atoms, H$_2$ and N$_2$ molecules effectively do not stick to the grains. For helium and hydrogen this is consistent with many previous models. Based on N$_2$H$^+$ measurements, N$_2$ is the dominant form of nitrogen in molecular gas and appears to suffer little depletion in dark clouds (Womack et al. 1992). Due to their relative volatilities, one expects that CO will be preferentially retained on dust relative to N$_2$. Both theory and observations support this view but also the stronger view that N$_2$ simply does not condense on to 10 K dust grains for particle densities less than about $n_{\text{gr}} < 10^7$ cm$^{-3}$; Charnley 1997b, the high abundances of N$_2$D$^+$ in the core of the L1544 cloud ($n_{\text{gr}} \sim 10^6$ cm$^{-3}$; Caselli & Walmsley 1999) and the enhanced D/H ratios of NH$_2$D and NH$_2$D$_2$ found in the dark cloud L134N ($n_{\text{gr}} \sim 10^4$ cm$^{-3}$; Téné et al. 2000; Roberts & Millar 2000; Rodgers & Charnley 2001a;
Millar et al. 2000). On the other hand, CO ice is observed in lines of sight to field stars where gas:solid ratios as high as 2:1 are found.

We adopt a CO mantle fraction of 15% as typical and use a finite value for \( \xi_{\text{CO}} \) determined as follows. For non-zero \( \xi_{\text{CO}} \), the chemistry will reach a steady-state where the accretion of CO will balance the desorption, i.e., \( \lambda_{\text{CO}} y_{\text{CO}} = \xi_{\text{CO}} g_{\text{CO}} \). If the total abundance of carbon monoxide in both the solid and gas phase is represented by \( Y_{\text{CO}}(= n_{\text{CO}} + g_{\text{CO}}) \), it follows that at quasi-steady-state the fraction of CO in the gas is given by

\[
y_{\text{CO}} = \frac{1}{1 + \frac{\lambda_{\text{CO}}}{\xi_{\text{CO}}}}.
\]

Hence, setting \( \xi_{\text{CO}} = 5.667 \lambda_{\text{CO}} \) ensures that 15% of the CO freezes out.

### 2.1.3. Grain-surface reactions

We are ignorant of the true physical processes leading to nonzero \( \xi_i \) and determining the appropriate \( \xi_i \) for heavy atoms is even more problematic. Based on their physiosorption binding energies (\approx 800 K; Tielens & Allamandola 1987) any desorption mechanism that can keep all the N\(_2\) in the gas should also keep these heavy atoms off the dust grains. The situation is different for atomic hydrogen as it can scan the surface and find any available reaction partners (e.g. either another H atom, if available, or a surface radical like O or OH) at a faster rate than that of any plausible \( \xi_H \). Such surface hydrogenation reactions lead to grain mantles comprising of the more strongly-bound hydrides: H\(_2\)O, NH\(_3\), CH\(_4\) and H\(_2\)S (e.g. Tielens & Allamandola 1987).

In the reference model, we initially neglect surface reactions and implicitly assume that, as they scan the surface by slow thermal hopping, heavy atoms are more likely to be desorbed than undergo reaction. This allows us to quantify the extent to which mantle composition could be solely attributable to accreted molecules. We also found it necessary to compute models in which this assumption was relaxed and in which oxygen atoms were allowed to be selectively accreted and reacted to form water. We did not attempt an explicit treatise of grain surface chemical kinetics but assumed that all O and OH accreted are rapidly converted to water (Charnley et al. 1988b).

### 2.2. Gas phase chemistry

The shocks are assumed to be associated with ongoing star formation (Norman & Silk 1980; Charnley et al. 1988a; Bergin et al. 1998, 1999). In the Norman-Silk picture, the physical evolution of clumpy molecular clouds is regulated by the formation of low-mass stars within them. Protostars form from the clumps and strong protostellar winds drive shocks into the surrounding medium and generate wind-blown bubbles that eventually fragment, coalesce, and form the next generation of dense clumps. In this scenario, gas and dust are continuously cycled between the clumps and a more diffuse interclump medium and hence the chemical evolution of much of the cloud gas has been influenced by the dynamical effects of star formation (Charnley et al. 1988a). Molecules undergo continuous chemical “cycling” between gas and dust regulated by star formation activity. More recently, Liseau & Olofsson (1999) proposed that ISO-LWS water observations of \( \rho \) Oph could be explained in a model where most of the molecular gas had been shocked and the water condensed out as ice.

We essentially consider one postshock “cycle” – with the assumptions we make for the \( \xi_i \) (see 2.1.3.) we do not require further shocks to occur on the order of \( t_{\text{acc}} \) to avert the “accretion catastrophe” (but see 3.2.2. below). We also ignore several of the more esoteric ingredients of some previous cycling models, such as injection of amorphous carbon from dust and the mixing of high abundances of ionized material (Charnley et al. 1988b). Our model therefore most closely resembles that of Bergin and co-workers.

The physical conditions of the reference model are summarised in Table 1. We assume that the shocked gas cools to reach a final hydrogen nucleon density, \( n_H \), of \( 2 \times 10^4 \) cm\(^{-3} \), consistent with compression of an interclump medium by a C-type MHD shock of speed \( 15 \) km s\(^{-1} \) for magnetic field strengths and ionization levels typical of preshock molecular gas of density \( \sim 10^3 \) cm\(^{-3} \) (M. J. Kaufman, private communication). As shock cooling times, \( t_{\text{cool}} \), are very short compared to all other relevant time-scales (e.g. \( t_{\text{acc}} \)) we simply prescribe the postshock abundances of the major species at \( t = 0 \) in the calculation and adopt a fixed gas temperature of 10 K. Thus, our calculation actually starts to follow the chemistry after about \( t_{\text{cool}} \) years postshock.

### Table 1. Physical conditions in the reference model.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>10 K</td>
</tr>
<tr>
<td>Hydrogen number density</td>
<td>( n_H ) 2 \times 10^4 \text{ cm}^{-3}</td>
</tr>
<tr>
<td>Visual extinction</td>
<td>( A_V ) 15 mag</td>
</tr>
<tr>
<td>Cosmic ray ionization rate</td>
<td>( \zeta ) 1.3 \times 10^{-17} \text{ s}^{-1}</td>
</tr>
<tr>
<td>Sticking coefficients</td>
<td>( S_i ) 1(^a)</td>
</tr>
<tr>
<td>Desorption rates</td>
<td>( \xi_i ) 0(^b)</td>
</tr>
<tr>
<td>Prasad-Tarafdar photons?</td>
<td>( \beta ) No</td>
</tr>
</tbody>
</table>

Note. \(^a\) except for H\(_2\), He, N\(_2\),and atomic C, O, S, N for which \( S_i = 0 \neq \xi_{\text{CO}} \).

The chemical model is based on the UMIST RATE95 database (Millar et al. 1997) with additions from Rodgers & Charnley (2001b). We consider models both with and without the effects of cosmic ray-induced photochemistry (Prasad & Tarafdar 1983). Table 2 lists the initial chemical abundances. We assume that the preshock gas contained relatively high abundances of atomic oxygen and nitrogen, but that all C atoms were incorporated in CO. This latter assumption allows us to avoid making any additional
assumptions concerning the preshock $C/CO$ ratio, a quantity we are attempting to reproduce, and correspondingly we have no $O_2$ initially present in the model. It turns out that, for the long-term evolution in the quasi-steady-state, the precise details of the shock chemistry are washed out.

Detailed C-shock models (Pineau des Forêts et al. 1993) show that by the time the neutral gas has cooled to preshock values almost all the initial atomic sulphur is contained in $H_2S$. Thereafter, most of the sulphur coexists as atomic S, $H_2S$ and SO2. These calculations, however, consider higher preshock densities than adopted here and so, for simplicity, at $t = 0$ we place all the elemental S in $H_2S$. Other S-bearing molecules – SO, SO$_2$, CS – are ignored at $t = 0$, however we find in any case that they can attain their typical dark cloud abundances after $\sim 10^4$ years. The sulphur chemistry presents one of the major difficulties for this scenario and this is discussed where appropriate below. Finally, we ignore any injection of metal atoms by sputtering of refractory grain material.

We first describe the modifications that are needed to the reference model in order to satisfy the constraints on the most abundant species; we then summarise the results for the nitrogen and sulphur chemistries.

### 3.1. CHO-containing molecules

Figure 1 shows the long-term variation of the fractional abundances and mantle composition of the major CHO-bearing species. At times $t_{\text{cool}} \leq t \leq t_{\text{acc}}$ the gas phase is dominated by the products of shock chemistry. Clearly, our assumptions concerning the relative desorption efficiencies of the volatiles allow a quasi-steady-state chemistry to persist for long times $t > t_{\text{acc}}$ (but see Sect. 3.2.2 below). It is most likely, therefore, that observed molecular cloud gas will be in this quasi-steady-state regime.

#### 3.1.1. The reference model

From Fig. 1a we can immediately see that accretion of molecular oxygen lowers $y_{\text{gas}}(O_2)$ to $\sim 10^{-6}$ from values of $\sim 10^{-5}$ when accretion is neglected (e.g. Bergin et al. 2000). This allows the SWAS $O_2$ constraints for the dark clouds TMC-1 and L134N to be marginally satisfied for $t > t_{\text{acc}}$. However the constraints on most other sources cannot be satisfied at any time: for $t \lesssim 10^6$ years, we find that although the ISO limits on $[O_2/H_2O]_{\text{ice}}$ can be satisfied, the SWAS limits on gaseous $O_2$ cannot; for $t > 10^6$ years the converse is true. The ice mantle compositions in TMC-1 and L134N are unknown but imposing the ISO constraint of $[O_2/H_2O]_{\text{ice}} < 20\%$ means that we cannot simultaneously satisfy both gas and solid constraints. The $H_2O$ condensed is not all that formed in the shock since, within $t_{\text{acc}}$, OH is produced by chemical “erosion” in ion-molecule reactions. The calculated solid $CO_2/H_2O$ ratio is about 10% and never approaches the target range of 15–40% found by ISO. Furthermore, the gaseous water abundance in the quasi-steady-state is $\sim 3 \times 10^{-7}$, much higher than the SWAS limits. We therefore need to modify the assumptions used in our model. In the quasi-steady-state atomic oxygen is produced in the reaction

$$He^+ + CO \rightarrow C^+ + O + He \quad (9)$$

and is subsequently incorporated in $O_2$ and $H_2O$. Hence, as we must retain a significant fraction of the available CO in the gas; accretion and reaction of atomic oxygen on grains appears to be indicated.

#### 3.1.2. O atom accretion and reaction

Figure 2 shows that reduction of O atoms to water on grains lowers the gas phase $O_2$ abundance to $\sim 10^{-7}$ and hence comparable with the most stringent SWAS limits. This process also lowers the solid $O_2$ mantle fraction below the ISO limit, but at the expense of moving the solid $CO_2/H_2O$ ratio even further out of the desired range at $t \gg t_{\text{acc}}$. This discrepancy could be resolved if some of

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$y_i(0)$</th>
<th>Molecule</th>
<th>$y_i(0)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_2O$</td>
<td>$4.0 \times 10^{-5}$</td>
<td>CO</td>
<td>$1.0 \times 10^{-2}$</td>
</tr>
<tr>
<td>$N_2$</td>
<td>$2.0 \times 10^{-5}$</td>
<td>NH$_3$</td>
<td>$5.0 \times 10^{-6}$</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>0</td>
<td>$H_2S$</td>
<td>$5.0 \times 10^{-8}$</td>
</tr>
<tr>
<td>O$_2$</td>
<td>0</td>
<td>metals</td>
<td>0</td>
</tr>
<tr>
<td>He</td>
<td>0.14</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3. Results

In analysing the model results, we impose the constraints from ISO and SWAS on gaseous and solid $CO_2$, $H_2O$ and $O_2$, as well as those available for other relevant species. These are summarised in Table 3 for a dark cloud (TMC-1), a region of low mass star formation ($\rho$ Oph) and, for sake of completeness, a region of massive star formation (OMC-1). We take the solid $O_2$ limits of Vandenbussche et al. (1999) to be generally applicable to all sources.

Vandenbussche et al. (1999) derived an upper limit of 50% and 100% of solid $O_2$ relative to CO ice toward the protostellar sources R CrA IRS2 and NGC 7538 IRS9, corresponding to an abundance of $30 \times 10^{-6}$ and $15 \times 10^{-6}$ relative to hydrogen, respectively. R CrA is located in the Corona Australis complex, which, like Taurus, appears cold in nature. Toward IRS2 the amount of apolar CO relative to water ice is more than 50%, the highest value ever measured (Chiar et al. 1998). These sources represented the best targets in which to search for solid molecular oxygen. These considerations indicate that the abundance of solid $O_2$ in dense clouds accounts for less than 6% of the total oxygen budget in the interstellar medium.
Table 3. Observed constraints in representative sources.

<table>
<thead>
<tr>
<th>Species</th>
<th>TMC-1</th>
<th>ρ Oph A</th>
<th>OMC-1</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>gas</td>
<td>ice⁵</td>
<td></td>
</tr>
<tr>
<td>H₂O</td>
<td>7 × 10⁻⁸</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>OH</td>
<td>10⁻⁷</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O₂</td>
<td>&lt;3.2 × 10⁻⁶</td>
<td>&lt;20</td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>8 × 10⁻⁵</td>
<td>19</td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>...</td>
<td>37</td>
<td></td>
</tr>
<tr>
<td>C⁰</td>
<td>&gt;1 × 10⁻⁵</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note:

a Gas phase abundances are relative to H₂; ice abundances are scaled relative to H₂O being 100%.

b Ice mantles are not observed in TMC-1. We approximate from the Taurus source Elias 18 which has nearly the same right ascension and declination (Nummelin et al. 2001).

c Data are for the sightline to the low-mass protostar Elias 29 (Boogert et al. 2000).

d Solid O₂ abundance limits are for NGC 7538 IRS9 (Vandenbussche et al. 1999) and are assumed to also be appropriate for these sources.

e The entry for ρ Oph is based on C⁰/CO ∼ 0.1 in a sample of molecular clouds (Zmuidzinas et al. 1986). The value given for OMC-1 is for the Orion Bar (Tauber et al. 1995).

f Data are for the source Orion IRc2, measured from ISO spectra (Boogert 2001; Wright 2001).

Gas phase water abundances are from Snell et al. (2000) and (for OMC-1) from Melnick et al. (2000b). Gas phase O₂ from Goldsmith et al. (2000) with C¹⁸O/H₂ = 2 × 10⁻⁷.

TMC-1: OH (Harju et al. 2000); CO (Ohishi et al. 1992); C⁰ (Schilke et al. 1995); CO₂: not observed.

ρ Oph: OH from Heiles (1968) and assuming N(H₂) = 10²² cm⁻²; CO, CO₂ (Boogert et al. 2000); C⁰ (Zmuidzinas et al. 1986).

OMC-1: OH from Baud & Wouterloot (1980); gas phase CO from Blake et al. (1987); C⁰ (Tauber et al. 1995; Phillips & Huggins 1981); CO₂ (Boonman et al. 1999).

3.1.3. Effect of Prasad-Tarafdar photons

As we expect that cosmic-ray-induced photochemistry will tend to lower gas phase abundances of H₂O, while elevating that of C (Gredel et al. 1989), we have considered its effect in a model. Figure 3 shows that the C abundance is more in line with the lower end of the C/CO ratios in the accreted O atoms also react with CO to produce CO₂ (e.g. Tielens & Hagen 1982). In this model there is improved agreement with the OH observations. Nevertheless, the H₂O abundance remains too high relative to the constraints of Table 3 and the model still cannot produce a large atomic carbon abundance.
molecular clouds and that the $O_2$ abundance is also reduced in the quasi-steady-state.

The gaseous $H_2O$ abundances in the quasi-steady-state of Fig. 3 are comparable to the SWAS limit in TMC-1 and below the higher published limits set in some other sources observed (B335, L134N). However, we cannot approach the very low limits of $\sim 2-10 \times 10^{-9}$ found in most of the sources. As we cannot justifiably reduce the $H_2O$ production of atomic O in the quasi-steady-state by further lowering the CO abundance, it appears that either the SWAS limits have to be revised upwards by a factor of about 10-100, or, in the context of this model, the postshock evolution must occur at densities 10-100 times higher. High-density accretion of shock-formed $H_2O$ has been invoked close to protostars (Molinari et al. 1999). A third possibility is that, even if it is correct, this model is not applicable to all the SWAS sources, such as those containing photodissociation regions (PDRs) (see Spaans & van Dishoeck 2000).

3.2. An optimal model

It appears that this simple model can come close to satisfying the abundance constraints of Table 3 over a significant fraction of the age of cold molecular clouds – dark clouds in which low-mass stars form. We adopt the model of Fig. 3 as the optimal one and now discuss some of the other predictions concerning the nitrogen and sulphur chemistries which follow from this scenario. Figures 4 and 5 show the gas and solid state chemistries of N and S.

3.2.1. Nitrogen chemistry

Accretion of gas phase ammonia results in a solid $NH_3/H_2O$ ratio of $\sim 2\%$, significantly less than the observed values of 10-30\% (Lacy et al. 1998; Chiar et al. 2000; Gibb et al. 2000). We can increase the amount of $NH_3$ on the grains if we assume that, like O atoms, N atoms also accrete onto grains and undergo hydrogenation. When we include this process in our model, the solid $NH_3/H_2O$ ratio rises to $\sim 10\%$, in line with the lower end of the observed range. However, a recent paper by Dartois & d’Hendecourt (2001) analyzed ground-based observations and claims that $NH_3$ is never more abundant than 5\% relative to $H_2O$ ice.

In general, we find that the chemistry of other N-bearing molecules is insensitive to the Prasad-Tarafdar photon field. This is due to the fact that most such species are formed from reactions initiated by $NH_3$. For example, HCN and HNC are formed by the reaction

$$C + NH_3 \rightarrow HCNH^+ + H$$

followed by dissociative recombination. This reaction has traditionally been assumed to form $H_2NC^+$, in order to account for the observed HNC/HCN ratio of $\gtrsim 1$ in dark clouds, but recent work by Talbi & Herbst (1998) showed that the favoured product is the $HCNH^+$ isomer. Our gas phase chemistry cannot reproduce the observed HNC/HCN ratio, principally because CN radicals – which are also produced in dissociative recombination of $HCNH^+$ – are recycled into HCN but not HNC by reaction with $NH_3$. In the ices, we predict HCN abundances of $\sim 1\%$, and a HNC/HCN ratio of $\approx 0.5$. In high-mass protostars an upper limit of HCN has been estimated to be
\begin{align}
N + \text{OH} & \rightarrow \text{NO} + \text{H} \\
& \quad \text{(11)}
\end{align}

followed by accretion, raises the possibility that interstellar ice mantles could contain other molecules derived from the large amount of NO that can be accreted (\sim 10\%). We have shown above that these models still require simple reduction and oxidation reactions to occur on grains and so we might expect the accreted NO to be converted to HNO, NH$_2$OH and NO$_2$. Both NH$_2$OH and NO$_2$ are unknown in the interstellar medium but both HNO and N$_2$O are detected towards star-forming regions (Ziurys et al. 1994a,b). The HNO abundances are found to be \sim 10^{-10} and are reasonably consistent with “early-time” formation in purely gas phase chemical models with atomic initial conditions. Our model would predict HNO abundances resulting from mantle evaporation of \sim 10^{-6}, unless the accreted NO is in fact mainly distributed amongst solid NH$_2$OH and NO$_2$. If most accreted NO is oxidised and reduced, then a search for hydroxylamine and nitrogen dioxide in interstellar ices and in hot core gas would appear to be worthwhile.

3.2.2. Sulphur chemistry

Figure 4b shows that the model predicts that the S-component of the ices should comprise a total mantle fraction of less than 0.1\%. The dominant molecules should be H$_2$S, SO$_2$ and molecules derived from oxidation and reduction of accreted CS: OCS, H$_2$CS and CH$_3$SH. At present, the only sulphur-bearing molecule observed in the ice phase is OCS (Palumbo et al. 1997). Abundances are less than about 2\% relative to water ice; oxidation of the peak CS abundance in Fig. 5 is consistent with this limit. To obtain higher mantle fractions of sulphuric ices in this model would require that either S atoms be allowed to accrete and react, for example with CO to form OCS, or that the S-depletion in the gas is less that we assumed, leading to more CS molecules being accreted.

Figure 5 shows the gas phase chemical evolution of the S-bearing molecules and illustrates that the sulphur chemistry raises the most serious problems for these gas-grain models of molecular clouds. The S chemistry never attains a quasi-steady-state and all the gas phase species are frozen out after \sim 6 \times 10^6 years. This is despite the the fact that S atoms themselves do not stick to grains (this effect was also noted by Bergin & Langer 1997). The reason for this behaviour is that for $t < t_{\text{acc}}$ there is so much OH in the gas that most of the atomic S broken out of H$_2$S is rapidly converted to SO$_2$ in the sequences

\begin{align}
\text{S} + \text{OH} & \rightarrow \text{SO} + \text{H} \\
\text{SH} & \rightarrow \text{SO} + \text{H}_2
\end{align}

and thereafter accreted onto the dust grains. For $t > t_{\text{acc}}$ the remaining S in the gas forms CS and this is also removed by accretion. The chemical evolution of Fig. 5 is largely independent whether or not an internally-generated radiation field is considered. When it is, the higher abundances of atomic carbon present means that more CS is formed at the expense of SO, i.e.

\begin{align}
\text{C} + \text{SO} & \rightarrow \text{CS} + \text{O}.
\end{align}

Unlike the carbon and nitrogen chemistry there is no major volatile form of molecular sulphur that can persist in the gas phase as it would need a formation efficiency comparable to that of CO and N$_2$. For example, injecting
S\textsubscript{2} instead of H\textsubscript{2}S produces the same result, even if both atomic S and S\textsubscript{2} are not allowed to stick. Simply imposing the condition that CS not stick to grains would be contrary to the observation in fact it does (e.g. Kuiper et al. 1996). However, a modest CS desorption rate could retain a sulphur gas phase at these densities and be overwhelmed at higher densities (\(\sim 10^5\text{ cm}^{-3}\)) where there is evidence for depletion. As each of the above processes have measured reaction rate coefficients (Le Teuff et al. 2000), the model chemistry in Fig. 5 is quite robust. Thus, consideration of the S chemistry leads us to consider three alternative explanations if these models actually apply to molecular clouds.

- CS and/or SO\textsubscript{2} are nonthermally desorbed from 10 K grains in dark clouds. If this is correct then we may expect that molecules of greater volatility than CS and SO\textsubscript{2} will also be desorbed into the gas phase. In principle, this conclusion leads to a further refinement of the partitioning between gas and dust. However, this would almost certainly require that O\textsubscript{2} also be desorbed and so lead to its abundance being in violation of the SWAS constraints for \(t > t_{\text{acc}}\); we therefore discount this alternative;
- there is an unknown form of molecular sulphur in dark clouds that is the major carrier of elemental S; this molecule is volatile and can be formed efficiently in the gas;
- cloud material is shocked every \(\sim 3 \times 10^6\) years and the S chemistry replenished – this is basically the view taken in the models of Charnley et al. (1988b), except that here this mechanism is needed to prevent an “accretion catastrophe” only in the sulphur chemistry.

3.3. Global comparison with dark cloud observations

We make a comparison between our optimal model and that of observed chemical abundances in dark clouds since it is only in these sources that we can come close to the SWAS H\textsubscript{2}O constraints. As noted in Sect. 3.2.1, the chemical age of “quiescent” molecular cloud material in dynamical-chemical models of this type is most likely to lie in the quasi-steady-state regime (i.e. \(t_{\text{age}} > t_{\text{acc}}\)). An approximate upper limit for the postshock chemical age of the cloud is set by the termination of the S chemistry. The CS abundance of about \(10^{-9} - 10^{-8}\) observed in many dark clouds (e.g. Linke & Goldsmith 1980) implies \(t_{\text{age}} \lesssim 3 \times 10^6\) years.

Table 4 shows such a comparison at two times in the model of Figs. 3–5. The aim of Table 4 is simply to show

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**Fig. 4.** Gas-grain chemical evolution of the principal N-bearing species in the model of Fig. 3: a) gas phase abundances, b) solid mantle fractions, including those of S-bearing molecules.

**Fig. 5.** Gas phase chemical evolution of the principal S-bearing species in the model of Fig. 3.
that reasonable agreement can be had in the quasi-steady-state when CO and N$_2$ are mostly retained in the gas (see also Millar & Nejad 1985), prior to termination of the S chemistry, and with the parameter adjustments necessary to satisfy the ISO-SWAS constraints. The observed gas phase abundances are for the well-studied sources TMC-1 and L134N (Ohishi et al. 1992; Ohishi & Kaifu 1998; Pratap et al. 1997; Dickens et al. 2000). These two clouds have similar physical conditions but exhibit large differences in the relative abundances of particular species. The particular model times chosen are those when the constraint of the non-detection of SO$_2$ in these clouds is first met. However, this model cannot give a robust explanation of the SWAS H$_2$O limits; in TMC-1, better agreement can be had by considering slightly later times just after the onset of the quasi-steady-state regime. The model also cannot reproduce the highest neutral carbon abundances found in dark clouds – an additional mechanism is required. Although TMC-1 does exhibit strong spatial abundance gradients, involving anomalously high concentrations of carbon-chain molecules, the abundances of many other species are similar to those found elsewhere. Despite the problem with the CN-HCN-HNC ratios (see 3.2.1), the most severe problems lie in the abundances of the carbon chains, e.g. CH$_3$CCH and HC$_5$N.

We conclude that while this model can be adjusted to give reasonable global agreement with the observations of dark clouds, specifically through desorption of CO and N$_2$, other dynamical-chemical models give much more convincing explanations of the molecular abundances and spatial gradients (Markwick et al. 2000).

4. Conclusions and discussion

We have investigated the possibility that molecular cloud chemistry is regulated by periodic shock waves. Our approach to modelling this scenario has been to develop the simplest possible gas-grain model. We only include additional processes where they are clearly required to avoid violating one or more of the ISO-SWAS constraints relevant to dark clouds.

Our principal conclusions from the chemical modelling are:

- Direct accretion of CO$_2$ and O$_2$ from the gas cannot satisfy the ISO limits. Relative to the water ice abundance, the model produces too little CO$_2$ ice and tends to overproduce O$_2$ ice at later times. The problem with gaseous overproduction of O$_2$ is simply transferred to the solid state.

- We find that accretion and reduction of oxygen atoms to water solves the problem of large [O$_2$/H$_2$O]$_{\text{ice}}$ ratios but cannot increase the amount of solid CO$_2$ unless some oxygen atoms also react with CO ices. Thus, our initial conjecture that the ISO [CO$_2$/H$_2$O]$_{\text{ice}}$ ratios could be set in the gas is not supported by these results. Accretion of O atoms also reduces the efficiency of gaseous O$_2$ production and lowers the O$_2$ abundance below the SWAS limits for most of the sources observed thus far.

- Inclusion of Prasad-Tarafdar photons increases the atomic carbon abundance to give modest agreement with observations. We cannot form atomic carbon abundances of $\sim 10^{-5}$ and an additional mechanism appears to be necessary.

- To be consistent with gas phase observations of OH, O$_2$ and H$_2$O in dark clouds, we require that these clouds be chemically older than an accretion time of about a few $\times 10^5$ years. Nevertheless, the periodically-shocked scenario requires that there should be regions of some cold molecular clouds that maintain high abundances of OH, O$_2$ and H$_2$O, for around a few $\times 10^5$ years. These regions should be most easily detectable through ground-based observations of enhanced NO and SO$_2$ emission.

- The model can best match the H$_2$O abundance limits for the dark clouds TMC-1 and L134N, but fails to reach the lowest values set by SWAS. For other sources, additional destruction processes for water would appear to be necessary (e.g. Bergin et al. 2000; Spaans & van Dishoeck 2000).

- We are able to obtain reasonable agreement with the observed dark cloud abundances of many compounds when CO and N$_2$ are retained in the gas. However, the model abundances of many others, particularly the hydrocarbons at C$_3$ and higher, are not in good agreement with observation. The mantle composition predicted by this model is quite similar to that of many previous models and requires the same processes (accretion, H additions, CO oxidation) to form them.

One interesting prediction of this model is that N-O bonded compounds could be more abundant than ammonia in interstellar ices: both NH$_2$OH and NO$_2$ may be detectable in ices and in hot molecular cores. The IR transition of NO$_2$ falls at 6.19 $\mu$m, making a solid state detection rather difficult because of the nearby H$_2$O bending mode. Halfen et al. (2001) have recently determined an upper limit of $1.6 \times 10^{-8}$ for NO$_2$ in the massive Sgr B2(N) core. Observations of hot cores in regions of low-mass star formation, where this model is most relevant, are needed.

- The sulphur chemistry raises the most severe problem for this scenario as it cannot be sustained against accretion for longer than $\sim 3 \times 10^6$ years. Even though S atoms are assumed not to stick to the grains, chemical reactions incorporate them into molecules which do stick.

In conclusion, we find that our modelling can generally reproduce the gas phase abundances of dark clouds, if their chemical ages are older than $\sim 6 \times 10^5$ years. It is only in these sources that the model can come close to the SWAS H$_2$O limits. The atomic carbon abundances we calculate are still too low, as are those of the carbon chain molecules. For other regions of star-formation (see Table 3) the postshock chemistry models cannot match
Table 4. Comparison of theory with the observed abundances in TMC-1 (“cyanopolyyne peak”) and L134N (position “N”).

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Observed TMC-1 $7.6 \times 10^5$ yr</th>
<th>Theory</th>
<th>Observed L134N $7.0 \times 10^5$ yr</th>
<th>Theory</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
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<td>H$_2$O</td>
<td>&lt;7.0 (−8)</td>
<td>2.4 (−7)</td>
<td>&lt;3.0 (−7)</td>
<td>2.7 (−7)</td>
<td>(1)</td>
</tr>
<tr>
<td>OH</td>
<td>1.0 (−7)</td>
<td>2.2 (−7)</td>
<td>7.5 (−8)</td>
<td>2.5 (−7)</td>
<td>(2), (3)</td>
</tr>
<tr>
<td>O$_2$</td>
<td>&lt;3.2 (−6)</td>
<td>7.8 (−7)</td>
<td>&lt;3.4 (−6)</td>
<td>1.1 (−6)</td>
<td>(4)</td>
</tr>
<tr>
<td>C$_6^+$</td>
<td>&gt;1.0 (−5)</td>
<td>3.8 (−7)</td>
<td>&gt;1.0 (−6)</td>
<td>3.0 (−7)</td>
<td>(5), (8)</td>
</tr>
<tr>
<td>H$_2$CO</td>
<td>2.0 (−8)</td>
<td>4.8 (−8)</td>
<td>2.0 (−8)</td>
<td>4.3 (−8)</td>
<td>(3)</td>
</tr>
<tr>
<td>C$_2$H</td>
<td>7.2 (−9)</td>
<td>5.9 (−9)</td>
<td>4.0 (−9)</td>
<td>4.6 (−9)</td>
<td>(6), (3)</td>
</tr>
<tr>
<td>C$_2$</td>
<td>5.0 (−8)</td>
<td>1.6 (−8)</td>
<td>–</td>
<td>1.2 (−8)</td>
<td>(3)</td>
</tr>
<tr>
<td>HCO$^+$</td>
<td>9.2 (−9)</td>
<td>6.0 (−9)</td>
<td>1.2 (−8)</td>
<td>6.6 (−9)</td>
<td>(6), (7)</td>
</tr>
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<td>CH$_3$OH</td>
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<td>3.7 (−9)</td>
<td>2.7 (−10)</td>
<td>(6), (7)</td>
</tr>
<tr>
<td>CH$_3$CCH</td>
<td>8.0 (−9)</td>
<td>4.3 (−12)</td>
<td>&lt;1.2 (−9)</td>
<td>4.1 (−12)</td>
<td>(6), (3)</td>
</tr>
<tr>
<td>C$_3$H$_2$</td>
<td>1.0 (−8)</td>
<td>4.5 (−8)</td>
<td>2.0 (−9)</td>
<td>3.7 (−8)</td>
<td>(3)</td>
</tr>
<tr>
<td>C$_4$H</td>
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<td>–</td>
<td>3.2 (−8)</td>
<td>(3)</td>
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<td>C$_4$H</td>
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<td>5.6 (−8)</td>
<td>1.0 (−9)</td>
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<td>(3)</td>
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<td>9.1 (−8)</td>
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<td>(3)</td>
</tr>
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<td>CH$_3$CN</td>
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<td>(3)</td>
</tr>
<tr>
<td>NO</td>
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<td>6.0 (−8)</td>
<td>3.7 (−7)</td>
<td>(3)</td>
</tr>
<tr>
<td>CS</td>
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<td>9.0 (−9)</td>
<td>(6), (7)</td>
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<td>1.7 (−11)</td>
<td>6.0 (−11)</td>
<td>1.5 (−11)</td>
<td>(3)</td>
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<td>SO</td>
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<td>H$_2$CS</td>
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<td>3.6 (−10)</td>
<td>6.0 (−10)</td>
<td>2.9 (−10)</td>
<td>(3)</td>
</tr>
</tbody>
</table>

References: – (1) Snell et al. (2000); (2) Harju et al. (2000); (3) Ohishi et al. (1992); (4) Goldsmith et al. (2000); (5) Schilke et al. (1995); (6) Pratap et al. (1997); (7) Dickens et al. (2000); (8) Stark et al. (1996).

the much lower H$_2$O abundances observed and additional mechanisms to depress H$_2$O and increase C$^+$ are required (e.g. Charnley et al. 1988b; Le Bourlot et al. 1993; Xie et al. 1995; Spaans & van Dishoeck 2000; Bergin et al. 2000).

Models of this type predict that there should be some regions of molecular clouds which contain high abundances of H$_2$O, O$_2$ and NO. The search for these regions would be a good test of the importance of this scenario for star-forming molecular clouds. This scenario has been proposed to explain the dynamical state of the ρ Oph star-forming region (Liseau & Olofsson 1999) and so molecular maps of this region, such as exist for TMC-1 and L134N (Pratap et al. 1997; Dickens et al. 2000), would be very useful.

Although continuous desorption of CO and N$_2$ can maintain gas phase chemistry for long times, as originally shown by Millar & Nejad (1985), the collapse of the S chemistry in these models indicates that there may be two efficient surface desorption mechanisms operating in dark clouds – one quasi-continuous and the other more sporadic. This second mechanism is required to replenish the gas phase sulphur on a time-scale of ~3 × 10$^6$ years or less. This is of the order of the period between successive shocks suggested by Charnley et al. (1988b). More recent dynamical-chemical models of dark cloud chemistry of Markwick et al. (2000) suggests a shorter replenishment time-scale, due to MHD motions in clumpy media. If clump dynamics drives mantle removal then the replenishment time-scale could be as short as a few × 10$^4$ years (Dickens et al. 2001). These models give better quantitative agreement with the observed molecular abundances in TMC-1 than found here. Furthermore, it is unclear if models such as that presented here could explain the observed
spatial abundance gradients seen in TMC-1. Gradients of complex molecule abundances and deuterium fractionation ratios also appear to be better matched in the models of Markwick et al. (Markwick et al. 2000, 2001a,b). These considerations fit into the overall picture of star-formation regulating the physics and chemistry of clumpy molecular clouds, as proposed by Norman & Silk (1980). Star formation probably turns over (recycles) the cloud material on a time-scale of $\sim 1 - 5 \times 10^8$ yr, and in this case mantle removal may be by energetic shock waves. However, the gas-grain cycling, driven on short time-scales by clump motions themselves, may be responsible for keeping the most abundant, and most volatile, molecules (CO and N$_2$) off grains and sustaining dense cloud chemistry between periods of star-formation activity.

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