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Chemical models of interstellar gas–grain processes – I. Modelling and the effect of accretion on gas abundances and mantle composition in dense clouds

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SUMMARY

We have developed a model to study the time-dependent gas–grain chemical interaction in dense, quiescent interstellar clouds. We describe the model and present results from the simplest form of this interaction: simple accretion of gas phase molecules on to dust grains in a static cloud. We show that gas phase evolution under accretion is non-trivial with respect to standard time-dependent models in which accretion is ignored. Substantial ice mantles consisting mostly of water and solid CO can coexist with a well-developed gas phase chemistry. By including accretion and considering the abundances time-dependently, prior to freeze-out, we show that on time-scales relevant to the age of the dark cloud TMC-1 good agreement with observations, compared to that from considering chemical equilibrium abundances, may be had. The model produces molecular mantles with $H_2O:NH_3 \approx 4:1$ in reasonable agreement with recent observations of the water ice feature in the Serpens cloud, but not with those of the Taurus ice features. It is suggested that the difference may be due to the different physical conditions in these clouds.

1 INTRODUCTION

It has long been realized that the most important chemical reaction occurring in the dense interstellar medium is the formation and desorption, by exothermic hydrogen atom reaction, of molecular hydrogen from the surfaces of dust grains (Hollenbach & Salpeter 1970, 1971). Whilst significant progress has been made in modelling the chemical abundances of the diffuse interstellar medium (van Dishoeck & Black 1988) (the abundance of CH^+ is a striking exception), there remain several open questions as to the important gas phase reaction pathways to many molecules, the possible role of the gas–grain interaction and the general dynamical processing in molecular clouds. Most theoretical models of dense cloud chemistry only include the presence of the grains, explicitly, to produce the requisite H_2 needed for the ion–molecule chemistry, driven by cosmic rays, and, implicitly, to provide the necessary extinction to attenuate the external interstellar radiation field.

Simple estimates of dense cloud evolution which allow for the collision and sticking of heavy gas phase species and grains, show that this component should freeze-out entirely on to the dust on a time-scale of $\sim 3 \times 10^9/n_H$ yr, where n_H is the hydrogen nuclei number density (e.g. Iglesias 1977; Williams 1987). This, for $n_H \geq 10^4$ cm^{-3}, is significantly less than the time-scales for chemical steady-state to be achieved ($\sim 10^7$ yr), and comparable with the time-scales for disruption of the reacting, accreting gas by dynamical events (e.g. shocks associated with star formation, supernovae, etc.). Iglesias (1977), in one of the first dense cloud chemistry models, showed explicitly that accretion on to the dust eventually dominates the evolution, and that total freeze-out is inevitable for non-zero sticking efficiency when no continuous desorption processes act to remove mantle material.

Observations of IR absorption spectra in a variety of astronomical sources show distinctive bands, corresponding most notably to H_2O ice at 3.08 μm and solid CO at 4.6 μm. The water ice feature is particularly prevalent, appearing in the IR spectra of molecular clouds (Whittet *et al.* 1983, 1988; Eiroa & Hodapp 1989), protostars (Tielens & Allamandola 1987a; Smith, Sellgren & Tokunaga 1988a) and in some oxygen-rich circumstellar outflows (Soifer *et al.* 1981; Smith, Sellgren & Tokunaga 1988b). In comets the molecular composition of ices in the nucleus will strongly affect the chemistry in the coma (Spinrad 1987; Tokunaga, Nagata & Smith 1987; Allamandola, Sandford & Valera

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1988). Observations of some of these sources indicate that the compositions of the molecular ices may include simple hydrocarbons such as alcohols, aldehydes, nitriles and ketones (Tielens & Allamandola 1987a; Smith *et al.* 1988a; Tielens *et al.* 1984; Lacy *et al.* 1984). These results are suggestive of the presence of a rather sophisticated solid-state chemistry.

Detailed quantum-mechanical calculations of the surface adsorption process appropriate to the interstellar medium (Leitch-Devlin & Williams 1985) indicate that, at the temperatures pertaining in dark clouds, the sticking of gas phase species on grains will be efficient. This result, coupled with the estimates of the freeze-out time-scale and the observational evidence for accretion, may represent a shortcoming of *pseudo*-time-dependent chemical calculations which ignore accretion (e.g. Leung, Herbst & Huebner 1984; Langer & Graedel 1989; Watt & Charnley 1985; Brown & Rice 1986; Herbst 1987; Millar, Leung & Herbst 1987). This may limit their applicability to studying dense cloud chemistry and we should require that the gas–grain interaction should be included as a fundamental feature of such models. Other works which have addressed this problem are those of Pickles & Williams (1977), who considered time-independent grain surface chemistry and the effect of the desorption of product molecules on the gas abundances. Similar calculations of this type are those of Millar (1982) and of Mann & Williams (1984) for the diffuse medium. Millar & Nejad (1985) carried out a limited time-dependent study of dense cloud accretion but ignored surface processing. They reproduced the earlier result of Iglesias (1977) and highlighted the probable shortcomings of *pseudo*-time-dependent studies which allow a chemical steady-state to develop. Tielens & Hagen (1982) considered a model in which the dense gas phase chemistry was in equilibrium and the grain chemistry was developed from a Monte Carlo simulation of the arrival rate of the various gas species on the surface. They considered detailed gas and solid phase chemistries and this was the most ambitious treatment until the work of d'Hendecourt, Allamandola & Greenberg (1985) who, for the first time, treated the quiescent gas–grain interaction in a fully time-dependent manner. This model is the most closely related to the one described in this paper. The main differences between this work and that of d'Hendecourt *et al.* are: we have ignored electron sticking on grains and thus a calculation of the evolution of the grain charge states; we have not included an explicit desorption mechanism; and we have considered a more limited surface reaction network. We shall treat these aspects in future papers. An important point, arising from the works of Millar & Nejad (1985) and of d'Hendecourt *et al.* (1985), is that accretion, surface reaction and any desorption process are all intrinsically time-dependent effects, they are not adequately treated by steady-state models.

The evidence then, both theoretically and observationally, is that gas phase species adhere to grains on a time-scale which is short compared to estimated cloud lifetimes. Although there exists the possibility that, in some regions, heavy molecular material may only be detectable by solid-state absorption studies (Williams 1985; Charnley & Williams 1989; Hartquist & Williams 1989), i.e. a highly depleted gas phase, the question naturally arises as to how this mantle material is returned to the gas phase. There are two, not mutually exclusive, solutions to this problem: continuous and/or sporadic (violent) desorption of mantle ices. The latter process is almost certainly efficient, occurring, for example, in star-forming regions where the ices are sublimed from warm grains and sputtered in shocks in non-quiescent chemical evolution (Charnley *et al.* 1988). The prospective mechanisms for the former remain contentious. These include thermal evaporation after thermal spike heating of small grains by high-energy photons (Allen & Robinson 1977), cosmic-ray desorption (Léger, Jura & Omont 1985; Watson & Salpeter 1972), removal of the entire mantle by explosions due to exothermic free radical reactions (Greenberg & Yencha 1973; Greenberg 1979), photodesorption by UV photons (d'Hendecourt *et al.* 1985; Watson & Salpeter 1972) and ejection after exothermic surface reaction, as in the case of H_2 (Allen & Robinson 1975, 1977; Watson & Salpeter 1972; Watson 1975). The relative efficiencies of some of these processes have been discussed by d'Hendecourt *et al.* (1985) who argued that the mantle explosion mechanism would be efficient at returning material continuously to the gas. They showed that complete accretion could be averted and a chemical steady-state attained after $\sim 10^7$ yr. The gas phase abundances were found to be strongly dependent on the assumed surface chemistry. These results, and those of Pickles & Williams (1977) and of Brown & Charnley (1990 and unpublished work) show that if desorption is highly efficient the gas phase chemistry can be considerably altered. This suggests that caution should be exercised in formulating possible surface reaction networks and in constraining desorption mechanisms.

The effect of mantle removal can have a profound effect on observed gas phase abundances. In the hot core component of Orion, the observation of enhanced abundances of ammonia (Pauls *et al.* 1983), methanol (Menten *et al.* 1986) and other fully hydrogenated species (Blake *et al.* 1987) is strong evidence that molecular mantles have been sublimed from grains warmed by nearby star-forming activity. The high NH_3 abundance cannot be explained by gas phase chemistry alone. Furthermore, the presence of enhanced abundances of deuterated molecules such as HDO (Moore, Langer & Huguenin 1986; Henkel *et al.* 1987; Olofsson 1984) and NH_2D (Walmsley *et al.* 1987) is indicative of the importance of deuterium fractionation reactions on grain surfaces (Tielens 1983). The basic model described in this paper has recently been extended to treat hot core gas–grain chemistry (Brown, Charnley & Millar 1988a,b) and also the associated fractionation effects (Brown & Millar 1989).

Surface catalysis may provide several of the observed large, complex molecules which may be difficult to produce solely by gas phase reactions. Ethanol (CH_3CH_2OH), ethyl cyanide (CH_3CH_2CN) and vinyl cyanide (CH_2CHCN) are possible candidates whose abundances may be wholly or at least partly dependent on grain chemistry (Millar *et al.* 1988; Brown 1989). Also, since H_2O and CH_3OH are observed to be the major constituents of protostellar ices (Tielens & Allamandola 1987a), their release into the gas in star-forming regions may drive the production of more complex oxygen-bearing species, making hitherto relatively inefficient gas phase pathways more attractive. Processing of this kind may be responsible for the anomalously large, but spatially confined, abundances of such molecules as dimethyl ether (CH_3OCH_3), methanol, formaldehyde and methyl formate

($HCOOCH_3$) in the Orion compact ridge source (Millar, Herbst & Charnley 1990), and is more efficient at forming these species than, say, the interaction of any oxygen-rich wind with the ambient gas (Blake *et al.* 1987). The effect on the gas phase evolution of complex hydrocarbons due to the desorption of volatile surface-catalysed methane will be described in Paper II (Brown & Charnley 1990).

Theoretical models of this kind should then interact strongly with observations of gas phase species and the IR spectra of interstellar ices, and also with the laboratory studies of ice analogues (e.g. d'Hendecourt 1984). This is necessary to place constraints on model parameters, to provide input on the important surface processes, and to assess the relative importance of the gas–grain interaction in a variety of astronomical sources. In this paper we describe a time-dependent model of gas and grain chemistries in quiescent, dense molecular clouds. In Section 2 we give a general description of the basic model and the important processes included. In Section 3 we discuss the values of the main physical and chemical parameters required by the model. Illustrative calculations of gas phase evolution and mantle growth in a dense cloud are given in Section 4. In Section 5 we apply the simplest version of the model to interpret the observed gas phase abundances of the dark cloud TMC-1 in the context of a continuously accreting region. Conclusions and points raised from these studies are discussed in Section 6.

2 THE GAS–GRAIN INTERACTION IN QUIESCENT CLOUDS

The basic theoretical considerations relevant to formulating the general problem have been given by several authors (Hollenbach & Salpeter 1971; Williams 1968; Hollenbach, Werner & Salpeter 1971), here we give the analysis relevant to this model. The equations governing the gas and solid phase chemical evolution of the heavy atoms and molecules (i.e. containing C, O, N, S and P) are

$$\dot{f}_i = -\lambda_i f_i + G_i + d_g \sum_j \sum_m \varepsilon_{jm}\gamma_{jm}R_jR_m + d_g R_i \sum_p \xi_p \tag{1a}$$

$$d_g\dot{R}_i = +\lambda_i f_i + d_g \sum_j \sum_m (1-\varepsilon_{jm})\gamma_{jm}R_jR_m - d_g R_i \sum_p \xi_p, \tag{1b}$$

where dots denote time derivatives and where f_i is the gas phase fractional abundance of the ith chemical species and R_i is the grain surface population of i. As gas phase ions are only neutralized and ejected by the (negative) grains they do not reside on the grains ($\dot{R}_{i^+}=0$), and for them only the first two terms in equation (1a) are relevant. The accretion rate λ_i is found from the gas–grain collision rate, assuming a Maxwellian velocity distribution for the gas. The quantities d_g and n_H are the dust to gas number density ratio and the total hydrogen nucleon density; they are related by $d_g = n_g/n_H$, where n_g is the dust number density. The second term in equation (1a), G_i, denotes the net production of i by gas phase chemistry and may include contributions from ion–neutral and neutral–neutral reactions, electron recombinations, photoprocesses and cosmic ray ionizations (e.g. Duley & Williams 1984). The third term in equation (1a) represents the rate of production of gas phase species by grain surface reactions. The quantity γ_{jm} is the surface reaction rate ($\sim s^{-1}$) of the formation of i from species j and m. The product of any given surface reaction may be retained in the mantle or, if the reaction is exothermic and the surface binding energy of the product is exceeded, it may be desorbed into the gas (*cf.* H_2). This process, if viable, will be most likely for saturated volatiles such as CH_4 and H_2S. We include this process by defining an ejection efficiency, ε_{jm}, for each surface reaction such that $0 \le \varepsilon_{jm} \le 1$ and the case $\varepsilon_{jm}=0$ corresponds to no ejection of products (i.e. 100 per cent retention on the mantle). The fourth term in equation (1a) corresponds to the ejection of surface species i induced by a variety of continuous processes. We denote the pth process by ξ_p and identify these with desorption via photoprocesses, grain explosions, cosmic rays and grain heating. Appropriate rates for these processes, ξ_p, have been summarized by d'Hendecourt *et al.* (1985) and by Tielens & Allamandola (1987b). The term with the subscript is non-zero when i is a neutral species and its ion, i^+ say, exists in the gas. It corresponds to the instantaneous neutralization of i^+ on collision with negatively charged dust grains. In fact, some gas phase ions do not have corresponding neutrals (e.g. H_3O^+). For these species we have assumed dissociative recombination with the grains. This means that for some neutrals additional source terms will appear in equation (1a). The three terms in the surface rate equation (1b) for i are, respectively: the direct accretion of gas phase material, chemical reactions on the mantle with possible ejection and desorption by non-chemical processes. In the present paper we have set $\varepsilon_{im}=0$ and $\xi_p=0$ for all processes p, corresponding to the neglect of any continuous recycling of material between gas and dust. We shall relax this constraint in future papers (Brown & Charnley 1990).

We now discuss the rates and parameters appearing in the equations. The accretion rate is given by

$$\lambda_i = a^2 d_g n_H (8\pi\mathscr{R}T)^{1/2}\left[1+\frac{Z_i e^2\pi}{4kTa}\right] S_i M_i^{-1/2}, \tag{2}$$

where S_i is the sticking efficiency, a is the grain radius, assumed constant and spherical, $\mathscr{R}$ is the gas constant, T is the gas temperature, k is the Boltzmann constant, e is the electron charge and M_i is the molecular weight in atomic mass units. In deriving equation (2) we have assumed a Maxwellian distribution of gas velocities, and that the gas phase ions and the dust grains have electric charges of $+Z_ie$ and $-e$, respectively. For the conditions in dense clouds, $Z_i=1$ for ions and of course $Z_i=0$ for neutrals. We have not followed the evolution of the grain charge between positive, negative and neutral states. We have not treated the evolution of the dark cloud from a diffuse state where the grains would be expected to be positively charged. We assume initially that all the grains have a charge of $-e$ and ignore electron sticking to the dust. This is an uncertain process; however, theoretical and experimental studies (Umebayashi & Nakano 1980; Lander & Morrison 1964) suggest that the sticking efficiency is close to unity. Adopting $d_g \approx 10^{-13}$, $n_H \approx 10^4$ cm^{-3}, and noting that in dark clouds the fractional ionization, although not well determined, is about 10^{-8}, yields ion, electron and grain number densities of n_i, $n_e \approx 10^{-4}$ cm^{-3} and $n_g \approx 10^{-9}$ cm^{-3}. Given that the thermal velocity of electrons, and hence the accretion rate, will be greater than that of the ions, our approximation that the grains form a large reservoir of negative collision partners will be reasonable. Since $n_e \gg n_g$, we would not expect inclusion of electron sticking to affect the results. We note, however, that at substantially higher densities ($\geq 10^7$ cm^{-3}) the grains can carry a significant fraction of the negative charge. Under these conditions a full treatment of multiply charged grain states is necessary (Havnes, Hartquist & Pilipp 1987).

The value of the sticking efficiency was taken as a free parameter in some of our models. It is a function of the nature of the grain surface and thus of the nature of the molecule-surface binding. It is also dependent on the extent of surface coverage, grain temperature and the possible presence of sites of enhanced binding (due to chemical bond formation). Quantum-mechanical calculations by Leitch-Devlin & Williams (1985) show that, for chemisorption, $S_i \approx 1$, although it may vary with time during the evolution of a dense cloud (Jones & Williams 1985). We take S_i to be constant and equal to unity for all heavy neutral molecules and atoms, unless otherwise stated. For lighter hydrogen atoms we used $S_i = \frac{1}{3}$ throughout and $S_i = 0$ for $i = H_2$, He, and e^-.

The surface reaction rate, γ_{jm}, was calculated from (Duley & Williams 1984)

$$\gamma_{jm} = \frac{L}{4\pi a^2 \tau_\gamma}, \tag{3}$$

where L is the average spacing between surface binding sites and $\tau_\gamma = 1/v_\gamma$, where v_γ is the mean relative velocity of the two reactants on the surface. This implicitly assumes that there is no reaction barrier (i.e. the reaction is instantaneous), and thus that the surface chemistry is diffusion-controlled. We assumed a simple equally spaced lattice of binding sites. We have treated the grain surface as chemically inert, and only consider heterogeneous catalysis of physisorbed species. Due to the absence of any specific details as to the nature of the grain surface (e.g. the presence of defects), its amorphous state, and the possible presence of enhanced binding sites, we have not attempted to include these in the present model.

The surface reaction rates are governed by the processes which allow adsorbed species to explore the grain surface and hence by their associated characteristic time-scales, τ_γ. Two processes can cause migration of adsorbed species; thermal hopping out of, and quantum tunnelling through, surface potential barriers. Simple estimates show that the rate of tunnelling is several orders of magnitude faster than that of hopping, at typical interstellar grain temperatures. Due to the low mass and high abundance of H atoms the predominant surface reactions should be hydrogenation of heavy atoms and radicals (Leitch-Devlin & Williams 1984). These reactions are generally assumed to be activationless, thus, when the surface barriers separating reactive species are overcome/penetrated, the reaction proceeds instantaneously. This simple scenario leads to complete hydrogenation of accreted mantle species such as C and the C–H radicals to methane and of N and the N–H radicals to ammonia. However, observations (Tielens & Allamandola 1987a; Smith *et al.* 1988a) and experiments on laboratory ice analogues (d'Hendecourt 1984; Allamandola *et al.* 1988) suggest that, whilst hydrogenation to water is important and predominant, the mantle chemistry is probably more complex than that presented here and in other theoretical models. In particular, ammonia is not observed as a major component of the ices in a number of sources. The model can treat surface reactions between heavy neutral species; however, due to the uncertainty in these, and in the competitiveness of their rates compared to H atom reactions, we have neglected them. Possible schemes are discussed by Brown (1990) and by Millar *et al.* (1988).

The efficiency of ejection/retention of a surface reaction product, ε_{jm}, depends on its binding energy and the energy released in the reaction. It may also depend upon the depth of the reaction in the ice mantle; depth effects are clearly unimportant on the surface but deeper in the mantle it may depend upon the diffusion of the product through the icy mantle (Sandford & Allamandola 1988). Given these uncertainties we have taken ε_{jm} to be a free parameter of the model, constant in time, which must be constrained by exemplary calculations and comparison with observation.

3 THE CHEMICAL MODEL

The considerations of the previous section have allowed us to construct easily adaptable models of gas–grain chemistry. In this section we give an elementary description of the modelling and the numerical values selected of the theoretical parameters important for dense cloud models.

The basic gas phase chemistry incorporates 1468 reactions between 152 species containing C, O, N, H and a representative metal, Mg. The general features of this chemistry in dense clouds, neglecting grain effects, are described by Charnley *et al.* (in preparation). Due to the innate time-dependence of the accretion process (and any continuous desorption of grain-catalysed material) it is necessary to follow the evolving gas phase chemistry since, as shown in Section 4, accretion affects gas phase abundances in other, more subtle ways, than in the simple removal of a given species from the gas.

The physical conditions and parameters used in the basic model are summarized in Table 1. As is usual with such *pseudo*-time-dependent calculations we have ignored any physical evolution of cloud density and temperature. A more realistic approach could be to initiate the calculation from a

Table 1. Parameters used in the basic gas–grain model.

Temperature, $T = T_{grain}$	10 K
Total hydrogen density, n_H	3×10^4 cm^{-3}
Visual extinction, A_V	5.0 mags.
Cosmic ray ionisation rate, ζ	1.3×10^{-17}
Grain radius, a	0.15 μm
Density of grains, d_g (relative to H nuclei)	3.5×10^{-13}
Surface reaction rate, γ	8800 s^{-1}
Sticking coefficient, S ($^1/_3$ for H atoms)	1.0

Initial depletion of elements
(relative to solar abundances):

carbon	0.5
nitrogen	1.0
oxygen	0.8
magnesium	0.0002

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collapse from a diffuse state (Charnley *et al.* 1988; Brown, Charnley & Millar 1988a,b). We assume that initially all heavy elements are present as atoms and that all the hydrogen is molecular, except for 1 per cent present in atomic form. The range of elemental depletions we have considered are also given in Table 1. We have assumed that only large grains accrete mantles and have ignored processes involving small grains. In determining the surface rates, γ_{jm}, we have modelled the surface as a uniformly spaced lattice of binding sites (i.e. potential wells) separated by a distance $L=10^{-8}$ cm. For H atom tunnelling times of $\approx 10^{-11}$ s (Duley & Williams 1984), this gives $\gamma_{j\mathrm{H}} \approx 8800\ \mathrm{s}^{-1}$ for the grain radius of Table 1.

For the present we only consider activationless surface hydrogenation reactions, in particular the following simple network:

$$O + H \rightarrow OH \tag{4a}$$

$$OH + H \rightarrow H_2O \tag{4b}$$

$$N + H \rightarrow NH \tag{4c}$$

$$NH + H \rightarrow NH_2 \tag{4d}$$

$$NH_2 + H \rightarrow NH_3 \tag{4e}$$

$$C + H \rightarrow CH \tag{4f}$$

$$CH + H \rightarrow CH_2 \tag{4g}$$

$$CH_2 + H \rightarrow CH_3 \tag{4h}$$

$$CH_3 + H \rightarrow CH_4. \tag{4i}$$

Due to the uncertainty in the ability of H atoms to overcome the barrier to both steps of

$$CO \xrightarrow{H} HCO \xrightarrow{H} H_2CO \tag{5}$$

at low temperature (d'Hendecourt *et al.* 1985), we have ignored any reaction involving CO, and all carbon monoxide is thus present in the mantle directly from accretion. The sequence (5) may, however, be important, leading to the formation of formaldehyde and methanol, if the reaction barriers can be overcome. All the reactions (4a)–(4i) were assumed to proceed with the same rate coefficient $\gamma \equiv \gamma_{j\mathrm{H}}$, where we have identified the surface reactant m with R_H, the surface population of hydrogen atoms.

The differential equations describing the coupled gas–grain chemistries were integrated using a stiff ODE-solver (Hindmarsh 1974) and employing a code-writer (Nejad 1986).

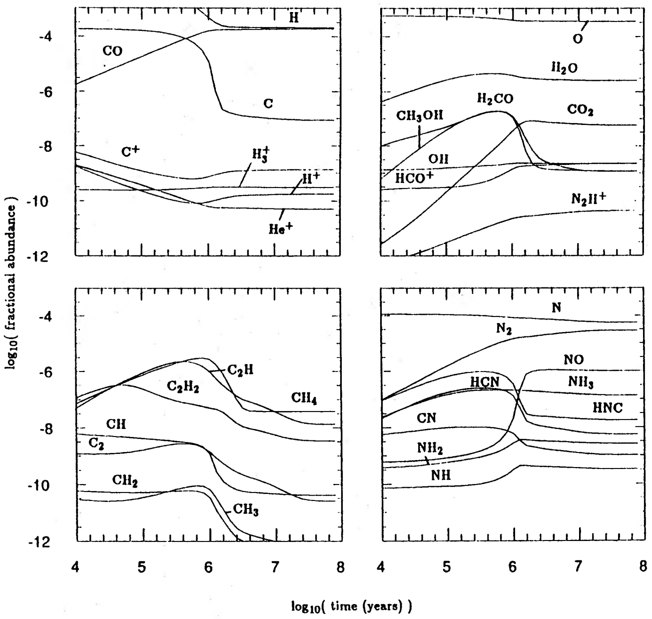

Figure 1. Evolution of the chemical fractional abundances with no accretion on to the dust. This corresponds to $S_i = 0$ in equation (2).

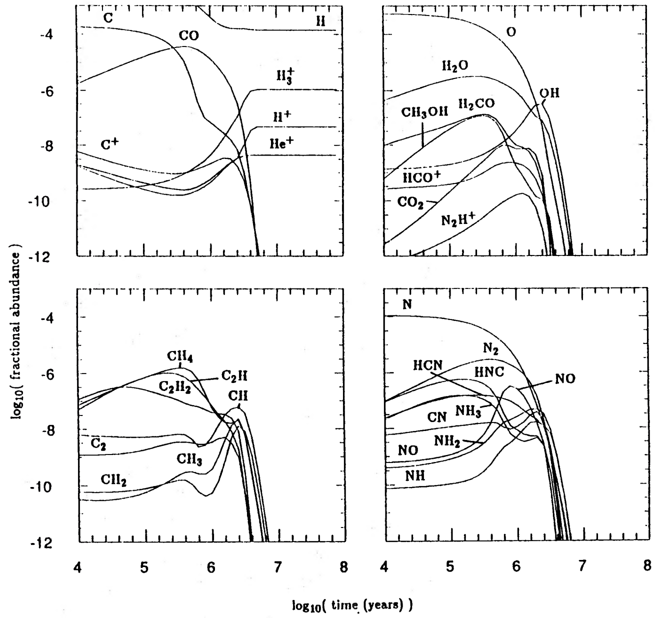

Figure 2. Evolution of the chemical fractional abundances with accretion on to the dust. This corresponds to $S_i = 1$ in equation (2).

4 DENSE CLOUD MODEL CALCULATIONS

Fig. 1 shows the chemical evolution of the gas phase for a model calculation in which accretion on to the dust has been neglected. As is usual with this treatment of dense cloud chemistry, a chemical steady-state is attained after about 10^7 yr. Observed molecular abundances are usually compared to those at chemical equilibrium. Doubts as to the applicability of this approach from the point of view of the shorter time-scales associated with accretion, dynamics, and some chemical reaction pathways, have been raised by several authors, as discussed in Section 1. Fig. 2 is as Fig. 1 except that accretion of gas phase species is allowed to proceed unabated by any desorption process. The accretion time is marginally longer than the quoted value of $\sim 3 \times 10^9 / n_\mathrm{H}$ yr (Iglesias 1977) due to our assumption that only the large grains accrete mantles and so present a lower total available surface area. It is clear from Figs 1 and 2 that, for the simple accretion scenario, one must consider the time-dependence of the model abundances when comparing the results with observations. A chemical steady-state is never attained and so there is no obvious time at which to make the comparison. We describe our approach to interpreting the abundances in Section 5.

An important result for the gas phase chemistry in an accreting region is that the evolution of several species is significantly different. Gas phase abundances do not simply follow what would have been their evolutionary path, neglecting accretion, and then simply fall off as accretion begins to dominate. In fact, when accretion becomes important the abundances of many species may evolve in a non-trivial manner. At a given time the abundance of a particular species can be orders of magnitude *larger* than that when accretion is neglected. In Figs 1 and 2 this behaviour is most apparent for the radicals CH, CH_2, CH_3, NH, NH_2 and OH. The chemical reason for this behaviour is that these species are destroyed in neutral–neutral reactions with light species, specifically carbon and oxygen atoms, which have faster removal rates from the gas. Their destruction becomes inhibited as the cloud evolves until ultimately they too freeze-out on to the grains.

In simple accretion models one is limited to considering the chemistry at times when substantial quantities of heavy molecular material remains in the gas phase. In models in which accretion is neglected, after several million years, most of the lower abundance element (C or O) is locked up in CO and the chemistry at later times is strongly influenced by whether C or O remains free (Watt 1985). Under accretion this conversion is not completed. The gas never evolves to a state where a large overabundance of C or O atoms exists, and the accretion-limited model abundances, which one then compares with observation, are less sensitive to the initial C:O ratio. At these early times, for reasonable variations from the solar C:O ratio, the difference between the abundances of C and O atoms will be only a factor of a few. At steady-state this difference is typically orders of magnitude and suggests that, precluding very peculiar values, the C:O ratio may only be a critical model parameter for chemistry in clouds in which CO formation is complete and which have (or have almost) reached a chemical steady-state. Accretion naturally limits the abundances of some molecules which are significantly overabundant at steady-state in non-accretion models. Two examples are NO and CN. For oxygen-rich chemistries (e.g. C:O = solar) NO has a large abundance $\sim 10^{-6}$ (Fig. 1; Langer & Graedel 1987) although it is not observed in dark clouds, only in the GMC Sgr B2 (Irvine, Goldsmith & Hjalmarson 1987). For carbon-rich C:O ratios (≥ 1) CN has a particularly large steady-state abundance (Langer & Graedel 1989; Charnley *et al.*, in preparation). The effect of accretion is to keep these abundances lower at times, $\sim 10^6$ yr, which are consistent with the estimated ages of some dense condensations (e.g. TMC-1).

The mantle evolution corresponding to the gas phase accretion of Fig. 2 is shown in Fig. 3. For this case the mantle grows steadily and a substantial mantle is formed after about 10^5 yr. For the limited hydrogenation scheme we have employed, the only significant difference in the mantle evolution depend upon the initial fraction of hydrogen in atomic form. If the initial fractional abundance of H is greater than about 10^{-3} then the entire mantle is hydrogenated rapidly. All O atoms arriving are hydrogenated to H_2O in less than 10^4 yr. Alternatively, if initially all the hydrogen is molecular, then at times less than 10^5 yr the mantle comprises mostly of accreted atoms and radicals. It is not until sufficient atomic H has been released from H_2, by gas phase reactions, and subsequently accreted, that the simple surface chemistry can proceed to completion. This is illustrated in Fig. 3 by the broken curves. The final mantle composition is relatively insensitive to the initial atomic H abundance. The possibility of the, albeit short-lived, presence of atoms and radicals on grain surfaces may have consequences for surface reactions between heavy species. Some neutral–neutral reactions may become more favourable than when rapid hydrogenation reactions are predominant (Pickles & Williams 1977; Brown 1990). A zero H atom abundance would not, however, be consistent with collapse from a diffuse atomic phase since there would always be sufficient numbers of H atoms to hydrogenate the accreted species, assuming that H atom reactions are not inhibited by the structure of the surface (Smoluchowski 1981, 1983). However, in cycling models of dense clouds it may be possible to have a gas of molecular hydrogen and a large fraction of the heavy species present as atoms due to the action of young stars embedded in the cloud (Charnley *et al.* 1988).

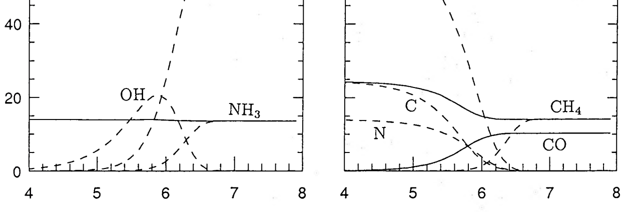

Figure 3. Mantle evolution corresponding to the model of Fig. 2. The full curves are for the case of an initial H atom fractional abundance of 0.01. The broken curves are for the case where all the hydrogen is initially in molecular form. The broken curve for CO lies under the solid one.

The amount of H_2O ice on the mantles deposited solely by accretion is ~2 per cent. This is not sufficient to account for the strength of the 3.08 μm feature in Taurus (Tielens & Hagen 1982) and we find that surface chemistry is essential to reproduce the copious amounts of water ice observed in many objects. Our results support earlier estimates of Jones & Williams (1984) that reactions (4a) and (4b) should be efficient and that at least 70 per cent of the H_2O formed should be retained on the surface. We note that the ices seen on some oxygen-rich circumstellar outflows are quite likely formed purely by accretion in the inner dense regions of the flow, where gaseous H_2O is by far the most abundant heavy molecule (Jura & Morris 1985; Smith *et al.* 1988b).

Solid CO is present on the dust solely by accretion of gas phase CO since no subsequent processing of CO on the mantle was considered. At a model time of 5×10^5 yr, the gas phase ratio of C:CO is ~0.1, and the fraction of total available CO in solid form is 46 per cent. Both these theoretical results are in accord with two observational results of the carbon budget in dense clouds. First, observations of fine-structure transitions of neutral atomic carbon, in a variety of dark clouds, show that the C abundance is very large, perhaps comparable to that of CO (Phillips & Huggins 1981; Jaffe *et al.* 1985; Keene *et al.* 1985; Zmuidzinas *et al.* 1988). Typical abundance ratio values are C:CO ≈ 0.1–0.01. Secondly, Whittet *et al.* (1983) found that, in some lines-of-sight in Taurus, almost 50 per cent of the observed CO was in solid form. Explanation of the gas phase C:CO observation constitutes a major problem for chemical models and has been reviewed by Blake *et al.* (1987). If a chemical equilibrium is allowed to develop (*cf.* Fig. 1) then it is impossible to reproduce this result. By comparing Figs 1 and 2 one may observe that acceptable values of the C:CO ratio occur, at similar times, even when accretion is neglected. However, only by including accretion can one explain the C:CO ratio and the presence of solid CO. If our model is accurate then it predicts that neutral carbon should be abundant in Taurus along lines-of-sight with CO ices. Other authors have also suggested that consideration of these 'early times' may resolve the C:CO problem (Leung, Herbst & Huebner 1984) and other problems associated with reproducing complex hydrocarbon abundances (Herbst & Leung 1989). However, one should be cautious in correlating a high C abundance with a young chemical and dynamical age. In a dynamically evolving cloud, accretion, and the associated gas phase chemistry, may be disrupted by star formation (Williams & Hartquist 1984). If this disruption occurs on the time-scale of the accretion time, and most of the heavy elements are reduced to atoms by the effects of stellar winds, then quiescent chemical evolution such as that in Fig. 2 may be regarded as just a phase in the cloud evolution. Such a model is described by Charnley *et al.* (1988) and can account for the existence of a 'young' chemistry in a more dynamically mature object.

The model tends to produce solid CH_4 at about 15 per cent of the mantle composition. Solid methane is not observed to be a major mantle constituent in molecular clouds. Tielens & Allamandola (1987a) infer that the CH_4:H_2O solid ratio towards some protostars is $\leq 0.005-0.05$, in contrast to our theoretical result of ≈ 0.25. It is likely that the missing methane is due to accreted C–H radicals and C atoms taking part in reactions, mediated perhaps by photons or cosmic rays, producing other hydrocarbon molecules (e.g. CH_3OH), and leading possibly to the long wavelength 'hydrocarbon' wing on the 3.08-μm feature seen in many sources (e.g. Knacke 1988; Smith *et al.* 1988a). The reaction pathways to these species are unknown. A further possibility is that most of the volatile methane is desorbed, either on formation or by grain heating due to cosmic rays (Léger *et al.* 1985).

The computed abundance of solid ammonia is about 14 per cent of the mantle. Observations of a weak shoulder on the 3.08-μm feature at 2.97 μm have been attributed to the N–H stretching mode in NH_3. Knacke *et al.* (1982) fitted this feature towards the BN object with an ice mantle H_2O:NH_3 ratio of (4 ± 0.5):1, a result which, incidentally, our model reproduces (*cf.* Fig. 3). However, more recent observations have shown that this result is in doubt (Knacke & McCorkle 1987; Knacke 1988) and that in many objects the solid NH_3:H_2O ratio is ≤ 0.1 (Tielens & Allamandola 1987a), compared to our result of 0.23. Recent observations by Smith *et al.* (1988a) towards BN and GL989 found NH_3:H_2O $<0.01-0.02$ and have raised questions concerning the presence of significant amounts of ammonia in interstellar ices. These studies refer to ices seen towards protostars; the model results presented here should be more applicable to mantle evolution in regions of moderate density and extinction. Ices have been detected in three such molecular clouds. In Taurus (Whittet *et al.* 1983), Serpens (Eiroa & Hodapp 1989) and in Barnard 5 (Charnley, Whittet & Williams 1990). The results of van de Bult, Greenberg & Whittet (1985), for Taurus, support the protostellar observations that ammonia is not present in the mantle in significant quantities. They found that H_2O:$NH_3 = 9$:1 was more appropriate to fit the water ice feature. However, in the Serpens cloud, Eiroa & Hodapp (1989) have shown that the best fit to the 3.08-μm feature is for H_2O:$NH_3 = 3$:1. This latter result is more in accord with our model calculations. We discuss this difference in mantle composition below. As discussed in Section 1, ammonia can be efficiently synthesized on grains (by reactions 4c, d and e), as evidenced by the large gas phase abundances in the Orion hot core, believed to be sublimed from grain mantles.

These differences in the amount of solid NH_3 predicted and the amount observed could be reconciled in a number of possible ways. It has been argued that the non-detection of ammonia is due to much of the available nitrogen being locked up in molecular rather than atomic form (e.g. Knacke 1988). N_2 is relatively inert and has a low binding energy on H_2O ice (Tielens & Allamandola 1987a). With the gas phase chemistry for N_2 used in the present model it does not seem possible to lock up even more N in N_2, starting from atomic initial conditions. Furthermore, the time-scale for $N \rightarrow N_2$ conversion is about $\sim 6 \times 10^6$ yr (Fig. 1; Langer & Graedel 1987), longer than the assumed time-scale for accretion. Thus we find that in the present model a significant amount of the nitrogen will always be in atomic form.

In real dark clouds some continuous recycling of the gas and dust may in fact be occurring, although perhaps not efficiently enough to offset accretion and establish a gas–grain chemical equilibrium (d'Hendecourt *et al.* 1985). In the case of NH_3, the mantle abundance could be reduced by the effects of heavy cosmic ray impacts (Léger, Jura & Omont 1985). Léger *et al.* have suggested that cosmic ray interaction with interstellar ices may be responsible for large quantities of gas phase ammonia, and this may account for the variations in the ammonia abundance seen between several sources (Irvine *et al.* 1987).

It is possible that the chemical history of ice mantles is such that ammonia, formed rapidly on the surface, is subsequently processed into other species. Ammonia absorbs photons over a larger frequency range and has a lower photoabsorption threshold than other abundant mantle molecules (Allamandola *et al.* 1988). It may therefore be preferentially destroyed by the weak flux of UV photons present in molecular clouds. These photons originate in the external ambient medium, from the cosmic ray ionization of H_2 (Prasad & Tarafdar 1983), or from the effects of local star formation (Norman & Silk 1980). The first of these is only significant in clouds with low to moderate extinction, typically $A_V \leq 7$ (Tielens & Allamandola 1987b). Tentative evidence for photolytic processing of ammonia in mantles is suggested by the 3-μm observations of the Taurus and Serpens clouds described above. The visual extinction is relatively low along many lines-of-sight through the Taurus cloud (Whittet *et al.* 1983); in addition, if the cloud is clumpy, the UV flux could be locally enhanced in some regions. In the Serpens cloud, Eiroa & Hodapp (1989) conclude that there is little UV penetrating this object or present from internal sources. This may mean mantle photolysis is inhibited in Serpens, but that some processing has occurred in Taurus.

In this scenario the question of the eventual fate of the photolysed NH_3 remains open. It is unlikely that the UV flux is sufficiently strong to evaporate the tightly bound NH_3 molecules; the presence of the more volatile CO in the Taurus mantles supports this. The N–H radical photoproducts would be expected to remain on the dust where they take part in subsequent reactions. One would expect that the N–H stretch feature at 2.97 μm should persist in any product molecule containing this bond. Allamandola *et al.* (1988) have shown that photolysis and heating of laboratory ice analogues can convert NH_3 into species containing the cyanogen group (—C≡N or C≡N—). In other photolysis experiments, d'Hendecourt *et al.* (1986) found that N_2O, NO and NO_2 could be produced from ammonia dissociation. Some observational evidence for the presence of a species, labelled XCN, in the spectra of the protostar W33A exists (Lacy *et al.* 1984), but the corresponding strong absorption at 4.62 μm is not evident in dense cloud spectra. If solid NH_3 is destroyed preferentially by photolysis then, on the basis of the laboratory experiments, the above four species appear to be the most likely product molecules, whose appearance could account for the absence of the 2.97-μm feature.

If this proposition should prove to be correct then it suggests that the UV fluxes in Serpens from H_2 ionization and star formation are insufficient to affect the accreted molecular ices. It suggests that the presence of solid ammonia may be correlated with A_V. High-resolution studies of the 3-μm feature, such as those carried out for protostars (Smith *et al.* 1988a), are required to confirm whether or not ammonia is a major mantle constituent in some molecular clouds.

5 ACCRETION CHEMISTRY IN TAURUS (TMC-1)

In this section we apply the simple accretion model to interpret the observed gas phase abundances of a specific molecular source, the dark cloud TMC-1 in Taurus. This object is a small, quiescent low-mass ($\sim 1 M_\odot$) condensation in Heiles Cloud 2, about 115 pc from the Sun. The kinetic temperature as deduced from CO and NH_3 observations (Allen & Knapp 1978; Tölle *et al.* 1981) is about 10 K. The visual extinction is estimated from star counts (Sherwood & Wilson 1981) and CO studies to lie in the range $A_V \sim 5$–7.5 mag. The total hydrogen nuclei density is assumed to be $n_H = 3 \times 10^4$ cm^{-3}, although there is evidence for clumping and spatial abundance gradients in several molecules (Olano, Walmsley & Wilson 1988).

Important for interpreting our model results are the various estimates of the age of the Taurus cloud which have been made. Cohen & Kuhi (1979) estimate an age of $\sim 6 \times 10^6$ yr from the age and distribution of stellar types. Heyer (1988) estimates the lifetime of the dense core regions to be $\sim 4 \times 10^6$ yr. For TMC-1, Olano *et al.* find a lower limit to the dynamical age to be $\geq 2 \times 10^5$ yr.

Molecular ices are not observed in TMC-1 due to the lack of background sources, although they are widely observed in other lines-of-sight in Taurus (Whittet *et al.* 1988). We thus make no attempt to discuss the grain mantle composition and concentrate on the effect of accretion on the gas phase chemical evolution. Previous chemical modelling studies appropriate to TMC-1 are those of Millar & Freeman (1984), Herbst & Leung (1986, 1989) and Millar & Nejad (1985). Of these the latter included the effect of grain accretion but did not attempt to interpret the observed abundances in this context.

The basic chemical model of Section 3 is appropriate for an elementary study of the chemistry in TMC-1. The chemical scheme was based on that of Millar & Freeman (1984), and was constructed from the UMIST reaction database (Bennett 1988). Physical parameters for the modelling were as for the standard dark cloud of Section 3 (Table 1).

The main parameters varied in this study were the accretion rates, λ_i, which were altered via the sticking efficiency. The variation of S_i simulates the variation of the total grain surface area available for sticking. We performed the analysis in terms of the S_i for the standard grain parameters of Table 1. Values of the sticking efficiency used were 0, 0.10, 0.50, 0.80 and 1.00. As unabated accretion ultimately removes the entire heavy atom component on to the dust, we need to compare the model results with observation in a time-dependent manner. We computed the quantity

$$D_i(t) = \log_{10}(f_i^{\text{theory}}) - \log_{10}(f_i^{\text{obsvn}}), \tag{5}$$

where f_i^{theory} and f_i^{obsvn} are the model and observed abundance of the ith species. We then examine how the $D_i(t)$ vary over times relevant to the estimated ages of the Taurus region and TMC-1, prior to complete freeze-out of the gas on to the dust. The times we consider lie in the range $\approx (8\text{–}60) \times 10^5$ yr. This method of comparison thus consists of examining the $D_i(t)$ at several 'snapshots' in the cloud evolution. Ideally one would wish to find $D_i(t_{\text{age}}) = 0$, for all observed i, where t_{age} is the chemical age of TMC-1. This, however, is not the case. Table 2 gives the observed fractional abundances in TMC-1 of 25 molecules included for comparison in the present study. It should be noted that many of the molecular abundances are accurate to no better to an order of magnitude (e.g. Irvine *et al.* 1987), and that many of our model rate coefficients and reaction pathways are unknown or not well-

Table 2. Observed chemical abundances in TMC-1.

Chemical Species	Fractional Abundance
HCO^+	4.0(-09)
CO	4.0(-05)
CH	1.0(-08)
CH_3OH	2.0(-09)
CH_3CN	5.0(-10)
CH_2CO	5.0(-11)
HC_3N	3.0(-09)
HC_5N	1.5(-09)
H_3C_4N	2.5(-10)
C_3H_4	3.0(-09)
C_5H_4	1.0(-09)
C_2H	2.5(-08)
C_3H	2.5(-09)
C_4H	1.0(-08)
C_3N	5.0(-10)
C_3O	5.0(-11)
C_2	2.5(-08)
H_2CO	1.0(-08)
OH	1.5(-07)
N_2H^+	2.5(-10)
NH_3	1.0(-08)
HCN	1.0(-08)
HNC	1.0(-08)
CN	1.5(-08)

determined. A further source of uncertainty is that the set of $D_i(t)$ we consider at any time limits us to performing a global analysis of the abundances. That is, we implicitly assume that all the molecules observed in TMC-1 exist and evolve in a very similar physical and chemical environment. In fact large abundance gradients between NH_3, C_4H and HC_7N exist (Olano *et al.* 1988), and may be indicative of chemical evolution in a clumpy non-homogeneous medium. Also, within the physically similar dark cloud L134N there is evidence for a gradient in the gas phase C:O ratio (Swade 1989). Thus we only interpret the abundances in the context of continuous accretion and do not consider the effects of non-homogeneities in density, temperature and elemental depletion. The above caveats should be borne in mind when comparing chemical model abundances with observation. Following the analysis of Millar & Freeman (1984), we shall regard a factor of 5 difference as reasonable agreement between observation and theory, that is $|D_i(t)| \leq 0.7$.

An example of the evolution of the $D_i(t)$ for our model of TMC-1 is shown in Fig. 4. For many of the molecules the agreement is within an order of magnitude for most of the relevant time ($10^{5.9}$–$10^{6.3}$ yr), before accretion begins to dominate. However, for several others (H_3C_4N, HC_5N, C_3O) the agreement is never particularly good. It is clear that those in good agreement are simple species whose gas phase chemistry is quite well understood. Those in poor agreement reflect deficiencies in the gas phase network. These species are usually large molecules whose formation routes and associated rates are not well understood. Also, since we have had to terminate our networks at some points (e.g. HC_5N for the cyanopolyynes) further errors have been introduced.

For each value of the sticking efficiency (i.e. accretion rate) it is possible to find a time, t_{opt} say, at which the number of species in agreement (within these prescribed limits) is a maximum. A summary of the agreement at each of these optimal times as a function of sticking efficiency is shown in Table 3. It may be seen that, for model times appropriate to TMC-1, the abundances of many species are in good agreement. The optimal times for all values of the accretion rate used lie in the range $\approx(1\text{–}4)\times10^6$ yr. Employing this global method of analysis yields acceptable agreement for 17 of the 25 species considered. The case corresponding to $S_i=0$ yields the poorer agreement at the t_{opt} of 3.2×10^6 yr. The agreement is even worse for the steady-state abundances of the larger species when this model is allowed to evolve to a chemical equilibrium (not shown).

Other studies of the chemical evolution of TMC-1 (Herbst & Leung 1989) have endeavoured to interpret the complex hydrocarbon abundances by considering earlier times, similar to those of our optimal fits. The abundances at steady-state do not reflect those observed, unless one chooses a high C:O ratio. This result, and the need to consider times prior to freeze-out, suggests that TMC-1 is not in chemical equilibrium. Even the early time abundances of Herbst & Leung (1989) cannot be fine-tuned to give agreement with the complex hydrocarbon (cyanopolyyne) abundances. In Paper II we shall model the chemistry of TMC-1 in greater detail and consider the effects of grain-catalysis and desorption of carbon-bearing species, specifically methane. Here we have simply shown that inclusion of grain accretion leads to acceptable agreement, at least as good as that from equilibrium models, without fine-tuning elemental abundances, at times consistent with estimates of the dynamical age of the cloud, and prior to complete removal of the gas phase.

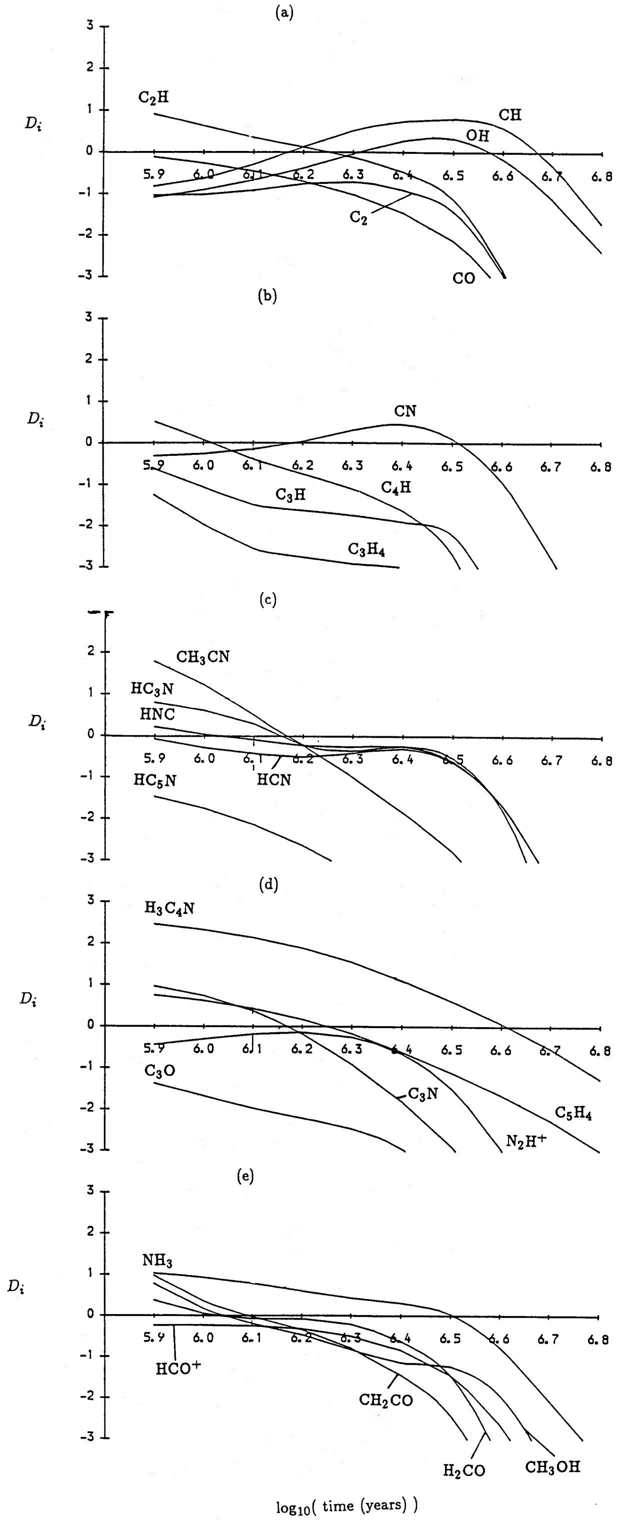

Figure 4. Evolution of the logarithmic differences, $D_i(t)$ (equation 5) for the accretion chemistry model of TMC-1 ($S_i=1$).

6 CONCLUSIONS AND DISCUSSION

We have developed a model to study the time-dependent gas–grain chemical interaction in dense, quiescent inter-

Table 3. Summary of the $D_i(t_{\text{opt}})$ for various values of the sticking coefficient.

S_i	0.0	0.1	0.3	0.6	0.8	1.0
t_{opt}	3.2×10^6	4.0×10^6	4.0×10^6	2.0×10^6	1.3×10^6	1.3×10^6
Species						
CO	0.64	0.24	-0.55	-0.61	-0.46	-0.73
C_2	-2.05	-1.74	-0.95	-0.82	-0.91	-0.75
OH	-1.82	-1.38	-0.51	-0.48	-0.67	-0.38
CH	-2.24	-1.47	0.04	0.03	-0.29	0.10
C_2H	0.62	0.40	0.11	0.16	0.35	0.13
C_3H	-1.15	-1.47	-1.57	-1.58	-1.50	-1.62
C_4H	-0.56	-0.71	-0.85	-0.72	-0.39	-0.68
C_3H_2	-5.86	-4.89	-3.59	-3.59	-3.59	-3.58
C_3H_4	-3.24	-3.04	-2.78	-2.73	-2.56	-2.74
CN	-0.96	-0.69	-0.01	-0.01	-0.14	0.03
HCN	0.07	-0.24	-0.50	-0.49	-0.42	-0.50
HNC	0.38	0.20	-0.16	-0.19	-0.09	-0.23
CH_3CN	-0.13	-0.28	-0.35	-0.32	0.50	0.11
HC_3N	0.78	0.55	-0.28	-0.12	0.29	-0.18
HC_5N	-2.64	-3.19	-3.73	-2.87	-2.14	-2.40
C_3N	1.31	0.90	-0.20	-0.03	0.38	-0.16
C_3O	-1.39	-1.69	-2.17	-2.15	-1.97	-2.20
H_3C_4N	2.97	2.41	1.63	1.94	2.15	1.89
C_5H_4	1.13	0.51	-0.18	0.21	0.43	0.18
N_2H^+	-0.87	-0.48	-0.08	-0.11	-0.18	-0.16
NH_3	1.24	1.05	0.61	0.63	0.79	0.63
HCO^+	-0.31	-0.22	-0.26	-0.28	-0.24	-0.33
CH_3OH	-0.15	-0.10	-0.45	-0.41	-0.19	-0.44
H_2CO	-0.57	-0.50	-0.05	-0.06	-0.07	-0.09
CH_2CO	0.72	0.53	-0.16	-0.22	-0.02	-0.36
A	13	15	19	19	19	19
B	9	13	17	17	17	17

The last two entries in each column (labelled A and B) indicate the number of species for which agreement is obtained within factors of 10 and 5, respectively.

stellar clouds. The model admits a large degree of flexibility in the grain surface and gas phase chemistries which may be studied, as well as in the treatment of possible surface desorption mechanisms. For the simplest form of the model, that of simple accretion, we have demonstrated that the gas phase chemistry evolves in a non-trivial manner. In particular, for quiescent gas, the accretion rate is $\propto M_i^{-1/2}$ (equation 2) and so lighter species are removed from the gas more rapidly. Atomic oxygen and carbon are depleted sufficiently quickly that the O–H, C–H and N–H radicals they destroy can *increase* by orders of magnitude close to the accretion time. These 'radical peaks' are entirely dissimilar from chemical evolution in an accretion-free scanario. Accretion chemistry is qualitatively different from that which occurs at the 'early times' of standard *pseudo*-time-dependent models, in which accretion is ignored.

Under accretion a fully developed molecular chemistry can coexist with substantial ice mantles. In particular, the observation that, in some lines-of-sight, almost 50 per cent of the CO is in solid form, and the high gas phase C:CO ratio may be interpreted as being due to accretion in a *chemically* young region. For the particular case of TMC-1 we have shown that, for times within its estimated dynamical age and prior to complete accretion, the observed abundances are consistent with the chemistry of a continuously accreting region. The model results are as good as those from the 'early-times' of *pseudo*-time-dependent models and suggest that it may be more appropriate to consider the abundances in dense clouds in the context of accretion, and that ultimately a chemical steady-state may never be attained. In the accretion scenario the model abundances, which one compares with observation, are less sensitive to the initial C:O ratio than the steady-state abundances of non-accretion models. Observational constraints on the gas phase CO abundance imply that much interstellar carbon is in solid form (Knacke 1988), and so accretion should be a fundamental feature of any chemical model. Our present treatment of the chemistry of many of the more complex species is uncertain. In Paper II we examine the effect of accretion in a more comprehensive chemical model, in which more pathways to the higher hydrocarbons are considered (e.g. Herbst & Leung 1989). A comparison of the abundances at 'early-times', with and without accretion effects and grain catalysis, may be instructive and lead to better agreement with observation.

Surface hydrogenation of O and OH are necessary to explain the strength of the water ice feature in the Taurus molecular cloud. The presence of solid CO in Taurus, and in the Serpens cloud, can be understood in the context of purely accreted gas phase CO. The model produces an $H_2O:NH_3$ mantle composition similar to that inferred for Serpens but inconsistent with that inferred for Taurus or towards some protostars. This difference is interpreted as being due to the relative importance of photolytic mantle processing in these objects, the solid ammonia in Taurus having been significantly destroyed by photoabsorption. It is suggested that the presence of solid ammonia in molecular clouds may be related to extinction.

The inferred chemical composition of ices seen towards protostars (Tielens & Allamandola 1987a) cannot be reproduced by the simple surface chemistry in the present model. The model can treat the formation of water ice and solid CO quite well, and an extension of it has been able to offer a quantitative explanation of the nitrogen chemistry in the Orion 'hot core' component. Efficient surface processes, which may lead to large amounts of solid methanol and ethanol and other simple organic molecules, are much more uncertain. Brown, Charnley & Millar (1988a) showed that in collapsing, accreting gas, the large quantities of species whose abundances peak on the order of the accretion time (e.g. CH_3OH and CH_3CN) could be stored in the mantles of the dense core. However, it is unlikely that this process could reproduce observed mantle compositions of $H_2O:CH_3OH \approx 3:1$. The production of CH_3OH in protostellar mantles may involve reaction of H with CO and H_2CO and it is likely that protostellar mantles have been subjected to more sophisticated processing than that of simple activationless hydrogenation. Solid state astrochemical models now require knowledge of the reactions (and associated rates) between heavy neutral species, perhaps mediated by UV photons and/or cosmic rays.

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