Astronomy
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Astrophysics

Dark cloud chemistry in initially H-rich regions

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Abstract. The chemistry in dark regions of dense cores is explored as a function of the initial abundance ratio of H to H_2, on the assumption that some cores form on a timescale and are younger than the time required for the H:H_2 ratio to attain its equilibrium value. Observational diagnostics of non-equilibrium values of the initial H:H_2 ratio are identified. In initially H-rich material, the abundances of OH, NH_3, CN, and HNC are for some time higher than they are in initially H-poor material. In initially H-poor regions, the abundances of CO, species containing multiple carbon atoms in each molecule, and CS are larger for an (observationally significant) period than in initially H-rich material.

Key words. ISM: clouds – ISM: molecules – astrochemistry – molecular processes

1. Introduction

The assumption that almost all hydrogen is initially in H_2 is made so routinely by researchers modelling the chemistry of dark interstellar clouds that it is not usually stated explicitly. However, interferometric observations of HI 21 cm self-absorption towards the dense core L134 show that the hydrogen atom number density in its coldest parts is more than one order of magnitude higher than expected in a dark region in which cosmic rays induce ionisation at a rate of 10^{-17} s^{-1} and an H/H_2 equilibrium obtains (van der Werf et al. 1988). L134 may have existed in its present state for a time shorter than that required for H to be converted to H_2 and formed from material in which a considerable fraction of the hydrogen was atomic. Jura (1974) has argued that ultraviolet data for H_2 and H obtained with Copernicus observations indicate that at about 100 K the timescale to convert atomic hydrogen to molecules H_2 is roughly $10^9 \times (1 \text{ cm}^{-3}/n_t)$ years if H_2 removal can be neglected; where n_t is the total number density of hydrogen nuclei. The dark regions of L134 would have to have been in their present state for less than a time of about 10^6 years for conversion of H to H_2 to have failed to establish an equilibrium H:H_2 ratio.

A number of researchers (e.g. Elmegreen 1999; Hartmann et al. 2001) consider many of the translucent clumps detected in CO maps (e.g. Williams et al. 1995) to be transient. Falle & Hartquist (2002) have suggested that the clumps form by the excitation of slow-mode waves due to the non-linear steepening of fast-mode waves having modest associated density

fluctuations. If they are correct, the clump formation time is only a couple or several tenths of the GMC total extent divided by the typical clump-to-clump relative speed. Thus, the formation time of a clump would be about 10^7 years. At densities that are appropriate for typical translucent clumps, the H:H_2 equilibrium in dark regions requires about 10^7 years. Hence the H:H_2 ratio in a clump may plausibly exceed the equilibrium value. Falle & Hartquist (2002) have proposed that the mechanism involving slow-mode excitation operates within clumps to form dense cores. The dense core formation timescale would be comparable to the clump extent divided by the internal clump velocity dispersion, which is around 10^6 years. The formation time of L134 may therefore have been rather less than the time required for the H:H_2 ratio to reach its equilibrium value.

HI has been observed towards other dark cores although in most cases there is potential confusion with foreground material. The importance of the contribution of envelope/halo material to the observed total column densities was emphasised in the multi-layered inhomogeneous cloud models of TMC1 developed by Lee et al. (1996), although observations of CI towards TMC1 by Schilke et al. (1995) suggest that significant atomic abundances may be present deep within the cloud. The microstructure in Core D of TMC-1 may indicate that that dense core formed in a time much less than 10^6 years. Many of the fragments in Core D are too small to be bound gravitationally, and have sound crossing times of only 10^5 years or less (Peng et al. 1998). One would expect the microstructure to dissipate on a time comparable to a fragment's sound crossing time. As the microstructure may be a remnant of Core D's formation, the birth of Core D may have occurred only 10^5 years ago. Hartquist et al. (2001) were able to construct a chemical

model consistent with such youth and in harmony with a variety of measurements of the chemical abundances in Core D. In that study a low initial H:H$_2$ ratio was assumed.

Various other studies have considered models with variable initial H:H$_2$ ratios (e.g. the gas-grain models of Ruffle & Herbst 2000), but none have emphasised the chemical distinctions between the H-rich and the H-poor initial conditions. As a number of considerations support the conjecture that the H:H$_2$ ratio may not have attained its equilibrium value, in this paper we investigate the effects of the initial H:H$_2$ ratio on a chemical model for dark, dense core conditions with a view to identifying observationally detectable diagnostics of non-equilibrium initial conditions. In Sect. 2 we describe the model and our assumptions, and in Sect. 3 we give the model results. We give our conclusions in Sect. 4.

2. The model and assumptions

The chemical model is similar to that employed by Rawlings & Yates (2001); the chemistry is limited to species containing the elements, H, He, C, N, O, S and Na and has been updated and expanded to include a more fully descriptive chemistry of the commonly observed tracers H$_2$CO, N$_2$H$^+$, HNC, HC$_3$N and C$_2$S. Most of the reaction network and the rate coefficients are drawn from the UMIST rate file databases (Millar et al. 1991; Millar et al. 1997). The chemical network consists of some 1627 reactions between 108 gas-phase chemical species.

For all models, the total number density of the hydrogen nuclei, n_t, is 1×10^4 cm^{-3}, the temperature is 10 K, and the cosmic ray induced ionisation rate is 1.3×10^{-17} s^{-1}. No radiation other than that arising as a consequence of cosmic ray induced ionisation was included. Specifically, the photodissociation of H$_2$ was completely suppressed.

Grains were assumed to have little influence on the chemistry. H$_2$ was assumed to form due to surface catalysis at a rate 1.32×10^{-17} cm^{-3} s^{-1} $(n_t/\mathrm{cm}^{-3})(n(\mathrm{H})/\mathrm{cm}^{-3})$, where $n(\mathrm{H})$ is the number density of atomic hydrogen. In some models, Na$^+$ (the representative metal ion) and S$^+$ were allowed to freeze out of the gas phase at the standard rate (e.g. Rawlings et al. 1992), while in others the chemistry was purely gas-phase, with no gas-grain interactions included. Except for providing sites for neutralization of ions, grains were taken to play no other chemical roles. The calculations were performed as a straightforward integration of the chemistry in a static gas – no dynamical flows or variations in density were considered.

In models A and C, initially $n(\mathrm{H})/n_t \ll 1$, while in models B and D, initially $n(\mathrm{H})/n_t = 1/3$, so that $n(\mathrm{H}) = n(\mathrm{H}_2)$. Models C and D are those in which Na$^+$ and S$^+$ were allowed to freeze-out. Initially, Na and S were assumed to be fully ionized. Other than these two elements, and hydrogen, all elements were initially in neutral atomic form.

3. Results

In our discussions we highlight 19 species of interest, which were selected on the basis of: (a) whether they have appreciable and potentially observable abundances, and (b) whether they

demonstrate significant differences between the H-poor and the H-rich models in the time interval of 2×10^4 to 10^6 years.

Panels a, c and e of Fig. 1 and panels g and i of Fig. 2 show the ratios of number densities for model A and model B for the selected species as functions of time. Panels b, d and f of Fig. 1 and panels h and j of Fig. 2 give the logarithm of the fractional abundances of these species for model A, the low atomic H case. Figures 3 and 4 gives the results for the models (C and D) which include the freeze-out of Na$^+$ and S$^+$.

Panels a, c and e of Fig. 3 and panels g and i of Fig. 4 show the ratios for model C and model D for the selected species (as in Figs. 1 and 2). Panels b, d and f of Fig. 3 and panels h and j of Fig. 4 give the logarithm of the fractional abundances for model C.

Firstly, it should be noted that even in the H-rich models significant conversion of H to H$_2$ is assumed to have already occurred (H:H$_2$ = 1:1). This results in similar H$_3^+$ abundances (differing by 50% or less in models A and B) and is consistent with the fact that H$_3^+$ is observed even in diffuse clouds. It is also consistent with models of deuterium fractionation (e.g. Roberts & Miller 2000) which seem to require a high H$_2$ abundance to explain the observed abundances of deuterated species in TMC1.

However, in general, the results for models in which initially $n(\mathrm{H})/n_t = 1/3$ differ strikingly from those of similar models in which initially $n(\mathrm{H})/n_\mathrm{H} \ll 1$. Some differences remain substantial for a good fraction of a million years. We discuss here the conclusions of a detailed analysis of the model results. This analysis shows that the chemistry in H-rich models differs in several significant ways from that in conventional H-poor models.

The high abundances of many carbon-bearing molecular species seen in models A and C at early times relative to those of models B and D arise from the importance of the reaction

$$\mathrm{CH} + \mathrm{H} \to \mathrm{C} + \mathrm{H}_2$$
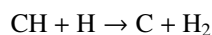
which provides an effective loss route for CH when atomic hydrogen is abundant. Some molecules bearing multiple carbon atoms become more abundant at times of a couple of hundred thousand years in models B and D than they are in models A and C; this is a consequence of the "early time" peak (e.g. Millar 1990) of the abundances of such species occurring later in models B and D than in models A and C.

At early times OH is more abundant in the initially H-rich models (e.g. B and D). OH is formed primarily through the radiative association
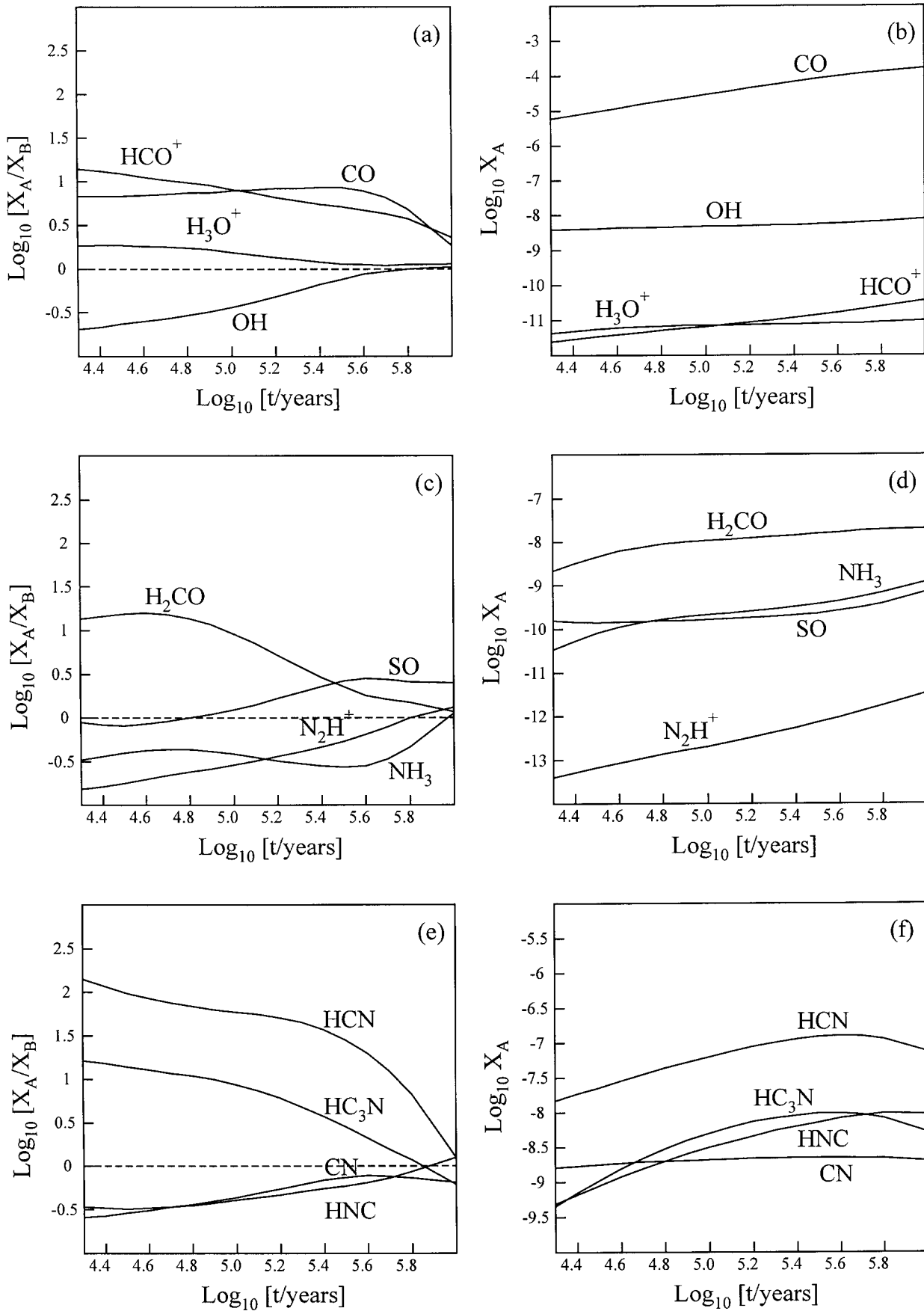
$$\mathrm{O} + \mathrm{H} \to \mathrm{OH} + h\nu$$
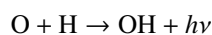
a reaction not normally considered to be important in models of dark cloud chemistry, but which dominates OH formation in dense H-rich environments. The higher OH abundance leads to the rapid initiation of the nitrogen chemistry by
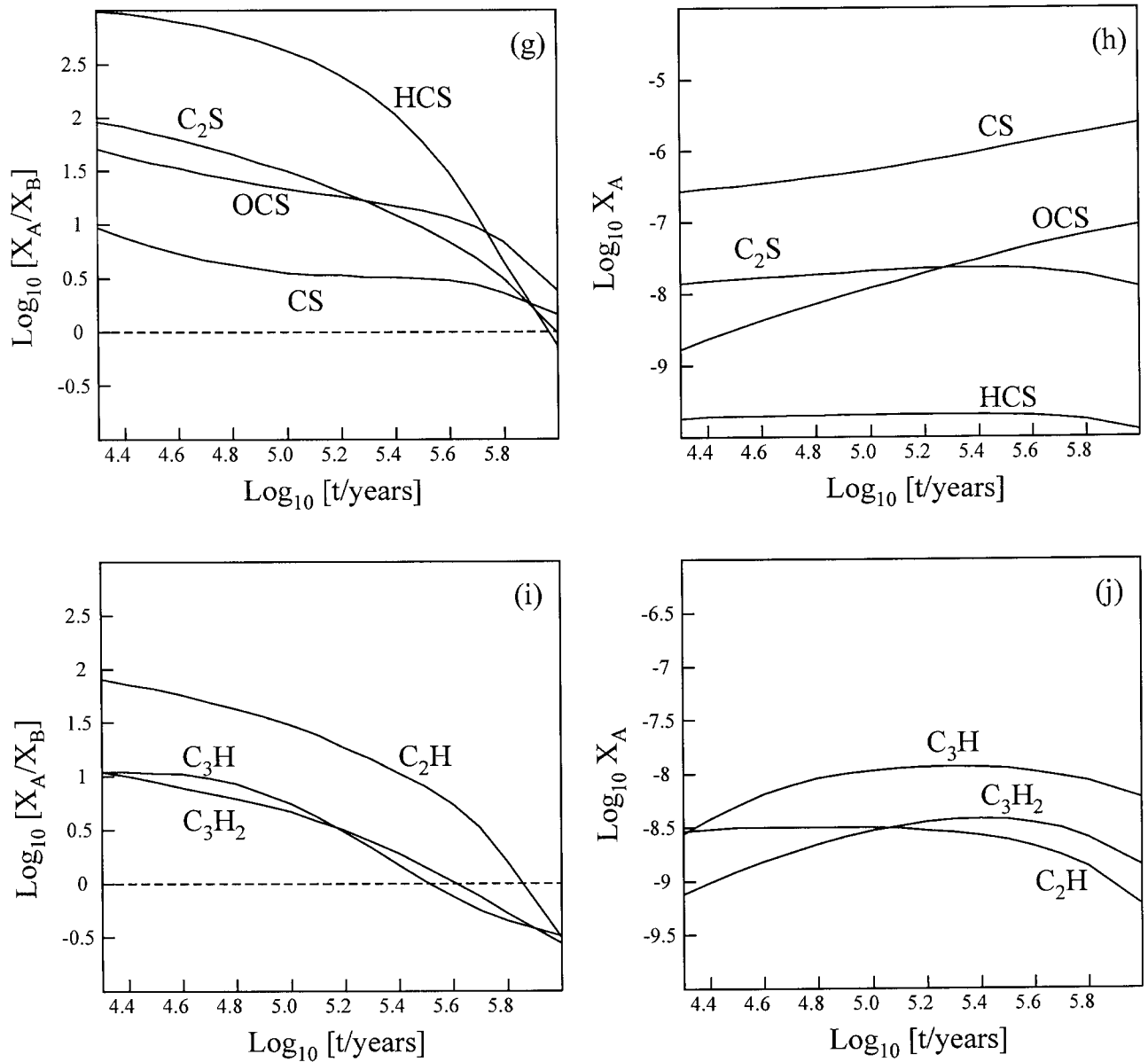
$$\mathrm{N} + \mathrm{OH} \to \mathrm{NO} + \mathrm{H}.$$

The reactions

$$\mathrm{NO} + \mathrm{C} \to \mathrm{CN} + \mathrm{O}$$
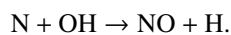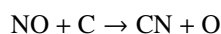
Fig. 1. Results for models A and B. Panels **a)**, **c)** and **e)** display the abundances of selected species for model A divided by the abundances for model B. Panels **b)**, **d)** and **f)** give the logarithmic fractional abundances of these species for model A.

Fig. 2. Results for models A and B. Panels **g)** and **i)** display the abundances of selected species for model A divided by the abundances for model B. Panels **h)** and **j)** give the logarithmic fractional abundances of these species for model A.
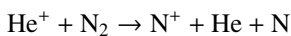
and

$$NO + N \rightarrow N_2 + O$$
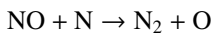
then follow. At early times He^+ is more abundant in the initially H-rich models, as a consequence of the lower CO abundances leading to less rapid removal of He^+ by

$$He^+ + CO \rightarrow He + C^+ + O.$$
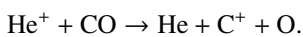
In the initially H-rich models, the reaction

$$He^+ + N_2 \rightarrow N^+ + He + N$$

drives the formation of NH_3 through the hydrogen abstraction sequence initiated by N^+, followed by the dissociative recombination of NH_4^+, much more rapidly than in the initially H-poor models. This is actually a rather surprising and important

result as NH_3 and other nitrogen-rich molecules are traditionally thought of as "late time" species whose abundances peak in well-evolved and, consequently, H-poor environments. Our results suggest that such simple categorisations may not be appropriate and that the abundances of these species may be determined as much by the initial conditions as by the age of the cloud.

The general distinction between the enhancement of carbon-bearing species in the H-poor models and the enhancement of nitrogen-bearing species in the H-rich models is clearly seen in the cases of the isomers HCN and HNC. HCN is formed by
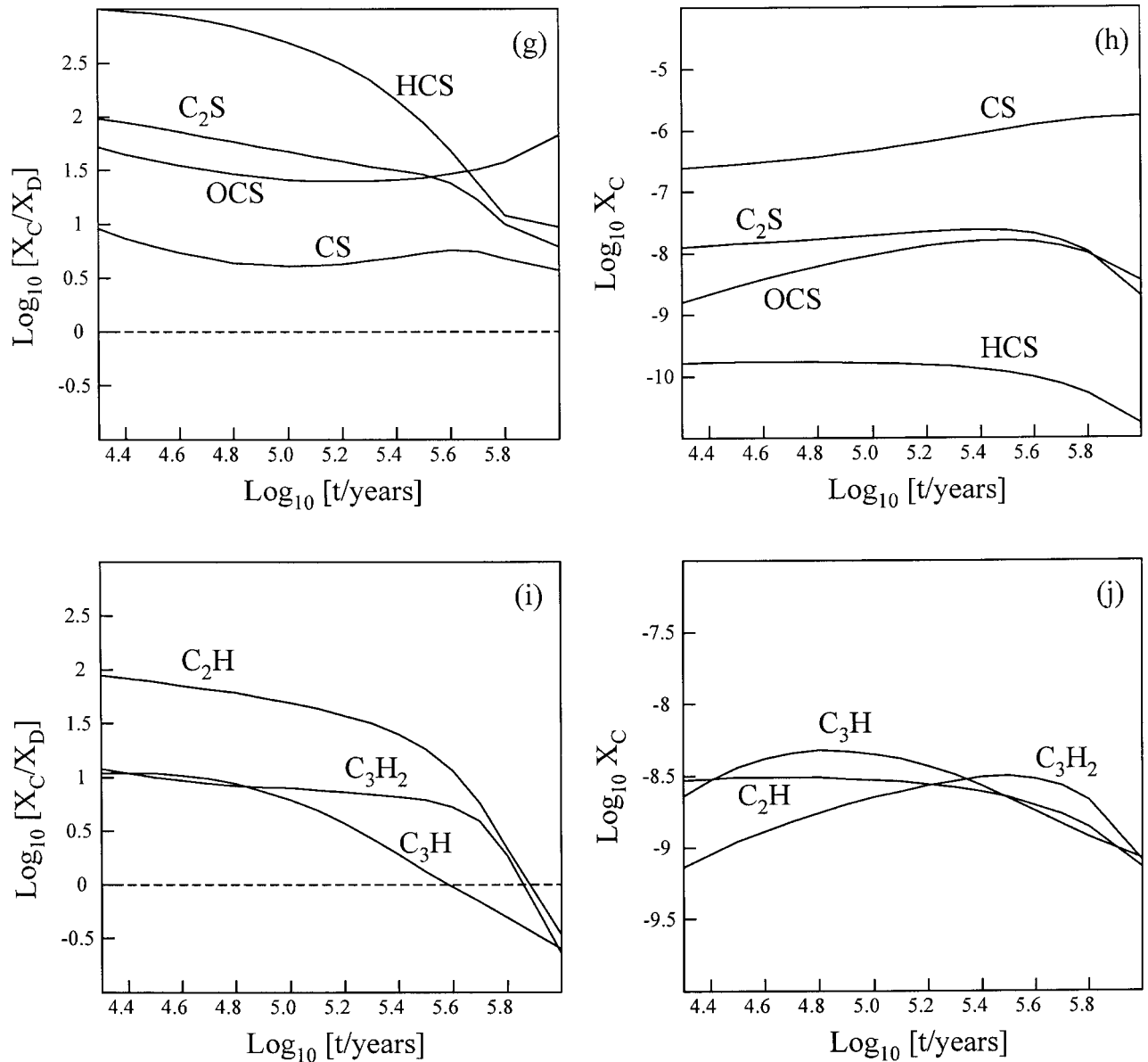
$$N + CH_2 \rightarrow HCN + H$$

and

$$N + CH_3 \rightarrow HCN + H_2$$
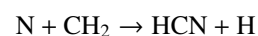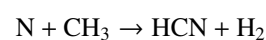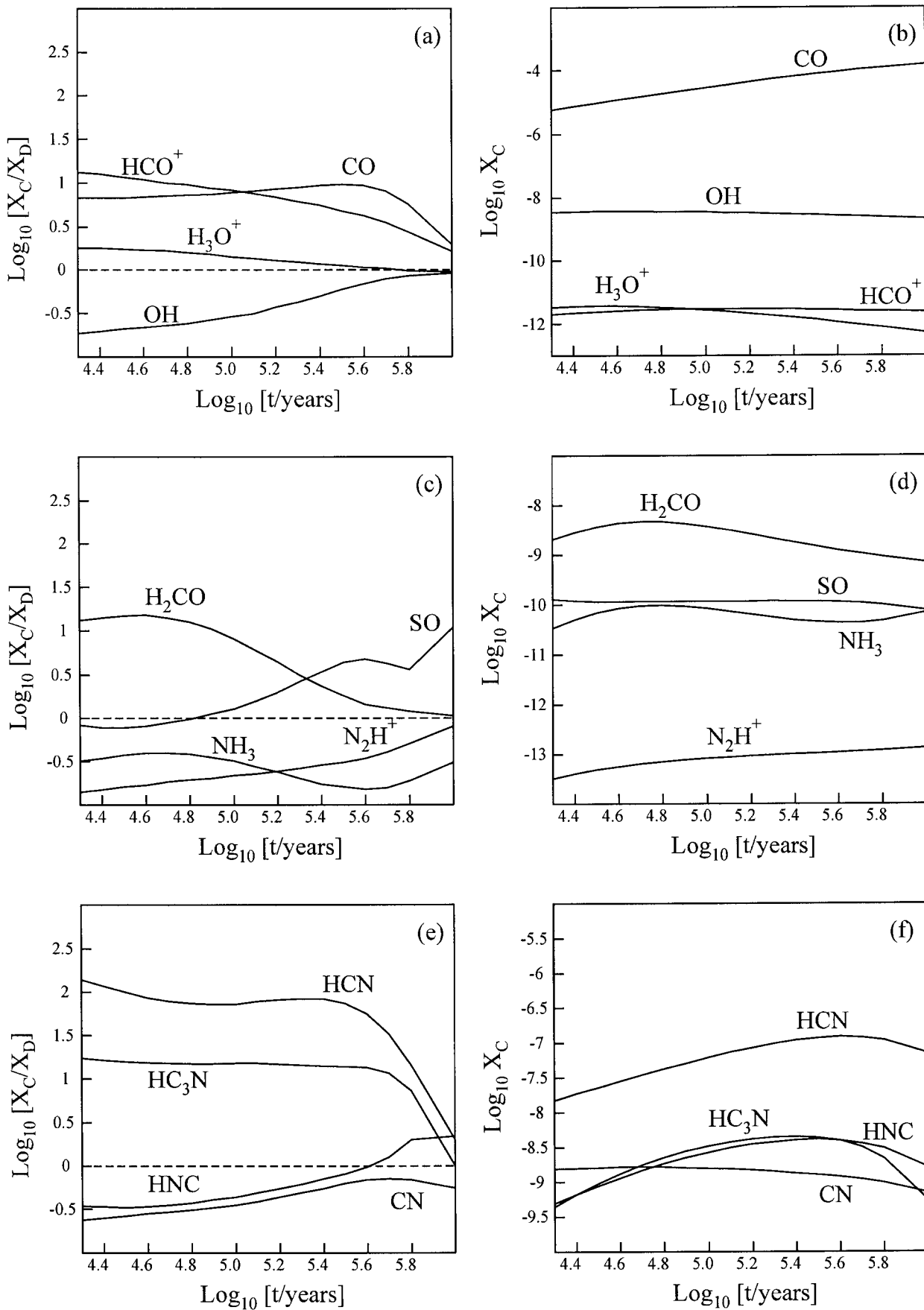
Fig. 3. Results for models C and D. Panels **a)**, **c)** and **e)** display the abundances of selected species for model C divided by the abundances for model D. Panels **b)**, **d)** and **f)** give the logarithmic fractional abundances of these species for model C.

Fig. 4. Results for models C and D. Panels **g)** and **i)** display the abundances of selected species for model C divided by the abundances for model D. Panels **h)** and **j)** give the logarithmic fractional abundances of these species for model C.

and so behaves like a carbon-bearing species, being enhanced in the H-poor models.

By contrast, HNC is formed from NH_2, a product of the dissociative recombination of NH_3^+,
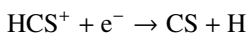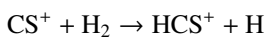
$$C + NH_2 \rightarrow HNC + H$$
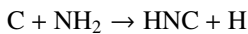
so that, like NH_3, HNC is enhanced in the H-rich models.

In the initially H-poor models, we also see that the higher abundances of CH at early times allows the initiation of the sulphur chemistry by

$$S^+ + CH \rightarrow CS^+ + H$$

followed by

$$CS^+ + H_2 \rightarrow HCS^+ + H$$

$$HCS^+ + e^- \rightarrow CS + H$$
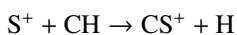
more quickly than in the initially H-rich models.

4. Conclusions

The chemistry in dark regions of a dense core depends markedly on the initial $H:H_2$ abundance ratio if the core formed and has been in its present state for a time shorter than that required for the H to H_2 abundance ratio to reach its equilibrium value. The main chemical pathways in the reaction network in H-rich and H-poor cases are found to be different. Abundances of commonly observed molecular tracers can differ by more than one order of magnitude between initially H-rich and H-poor cases, for evolutionary times approaching one million years. Simple hydrocarbons and HCN and HCS are more abundant in H-poor cases, while NH_3 and OH are enhanced in H-rich cases. The general result of this paper is, therefore, that the interpretation of molecular observations of interstellar clouds must take account of the initial H-atom abundance which may not have achieved a chemical steady-state.

Recent laboratory and theoretical results (e.g. Biham et al. 2001) suggest that the conversion rate of H to H_2 may actually be slower than previously believed, in which case the likelihood of detecting cores in non-equilibrium states will be increased. Indeed it may be possible to use the ratios of the abundances of some of the common tracer molecules that we have discussed in this paper to diagnose the initial $H:H_2$ ratio and the chemical youth of dense cores.

One possible application of these results is to the chemical differentiation along the TMC-1 ridge. At Core B the abundance ratios of CS and long-chained carbon molecules to ammonia are much lower than at Core D (e.g. Hirahara et al. 1992). A number of explanations have been offered for these differences (e.g. Howe et al. 1996; Markwick et al. 2000). On the basis of the results in this paper, we speculate that Core B formed from initially H-rich material while Core D was initially H-poor, though how this contiguity of H-rich and H-poor material arose is unclear.

As noted in Sect. 1, L134 is an example of a molecular cloud in which an unusually high fraction of atomic hydrogen is currently observed. This anomaly should be revealed in the chemistry of this cloud. It is consistent with the conclusions of the present work that in L134 the abundance of C_3H_2 is relatively low and that of N_2H^+ is relatively high (Benson et al. 1998), whilst that of NH_3 is at least at the canonical value (Benson & Myers 1989).

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