

Time-dependent H₂ formation and protonation in diffuse clouds

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ABSTRACT

Aims. To demonstrate the time-approach to equilibrium of H₂-formation and protonation in models of diffuse or HI interstellar gas clouds previously published by the author.

Methods. The microscopic equations of H₂-formation and protonation are integrated numerically over time in such a manner that the overall structures evolve self-consistently under benign conditions.

Results. The equilibrium H₂ formation timescale in an HI cloud with $N(\text{H}) \approx 4 \times 10^{20} \text{ cm}^{-2}$ is $1\text{--}3 \times 10^7 \text{ yr}$, nearly independent of the assumed density or H₂ formation rate on grains, etc. Attempts to speed up the evolution of the H₂-fraction would require densities well beyond the range usually considered typical of diffuse gas. The calculations suggest that, under benign, quiescent conditions, H₂ in the diffuse ISM formation of H₂ is favored in larger regions having moderate density, consistent with the rather high mean kinetic temperatures measured in H₂, 70–80 K.

Formation of H₃⁺ is essentially complete when H₂-formation equilibrates but the final abundance of H₃⁺ appears more nearly at the very last instant. Chemistry in a weakly-molecular gas has particular properties so that the abundance patterns change appreciably as gas becomes more fully molecular, either in model sequences or with time in a single model. One manifestation of this is that the predicted abundance of H₃⁺ is much more weakly dependent on the cosmic-ray ionization rate when $n(\text{H}_2)/n(\text{H}) \lesssim 0.05$. In general, high abundances of H₃⁺ do not enhance the abundances of other species (e.g. HCO⁺) but late-time OH formation proceeds most vigorously in more diffuse regions having modest density, extinction and H₂ fraction and somewhat higher fractional ionization, suggesting that atypically high OH/H₂ abundance ratios might be found optically in diffuse clouds having modest extinction.

Key words. ISM: molecules – ISM: atoms – ISM: clouds

1. Introduction

The fact that individual HI/diffuse clouds have a substantial component of molecular hydrogen has been recognized observationally since the original *Copernicus* observations (Jura 1974; Spitzer 1978) and a quite high fraction of hydrogen in the nearby diffuse interstellar medium (ISM) overall is in molecular form (Savage et al. 1977; Liszt & Lucas 2002). More surprising perhaps is the recent discovery that this molecular component hosts a rich polyatomic chemistry with relatively large amounts of H₃⁺ (McCall et al. 2002) and a dozen other species including such ions as HCO⁺ (Lucas & Liszt 1996) and HOC⁺ (Liszt et al. 2004) and molecules as complex as C₃H₂ (Cox et al. 1988; Lucas & Liszt 2000), H₂CO (Liszt & Lucas 1995; Moore & Marscher 1995; Liszt et al. 2002) and NH₃ (Nash 1990; Liszt et al. 2002).

The presence of copious H₂ and relatively large amounts of H₃⁺ in HI clouds is supported theoretically when self-shielding (Lee et al. 1996) is included in equilibrium models of diffuse gas (Liszt & Lucas 2000; Liszt 2003) using empirically-determined H₂ formation rates (Jura 1974; Spitzer 1978; Gry et al. 2002); observed HD/H₂ ratios are also explained as long as the cosmic-ray ionization rate is taken large enough to support the inferred proton density in the presence of atomic-ion neutralization on small grains. However, formation of H₂ is a notoriously slow and supposedly rather fragile process. Moreover, it remains to be determined whether any such equilibrium is actually attained in the interstellar medium, which is the subject of this work.

Here we show the approach to equilibrium in the models discussed by Liszt & Lucas (2000), Liszt (2002) and

Liszt (2003): we present calculations of time-dependent H₂ and H₃⁺ formation in small, mostly-static gas parcels meant to represent typical diffuse “clouds”, like, for instance, the “standard” HI cloud of Spitzer (1978). As we discuss, the distinguishing characteristic of the chemistry in such clouds is that the H₂ formation process is unsaturated ($n(\text{H}_2) < n(\text{H})/2$). For this reason the equilibrium timescales for H₂ formation cannot be calculated from simple scaling arguments based on the local microscopic H₂ formation rate, nor are they shortened by self-shielding, or in many cases by assuming higher density or even a higher rate constant for H₂ formation on grains, etc. Furthermore the abundance of H₃⁺ does not always vary as might be expected from consideration of its equilibrium chemistry in more fully molecular gas.

Section 2 gives details of the methods used in the calculations, results of which are presented and discussed in Sects. 3 and 4.

2. Details of the calculations and microphysics

2.1. Framework and initial conditions

The calculations presented here build on a framework which was established in the work of Wolfire et al. (1995). Specifically, the two-phase model of heating and cooling developed by Wolfire et al. (1995) (see also Wolfire et al. 2003) was applied to small, uniformly illuminated spherical gas clots of constant density, intended to represent diffuse “clouds”; our model, however, uses the gas-phase abundances of Savage & Sembach (1996) which makes them a bit hotter. Assumption of a geometry is required

because the accumulation of H₂ and CO depends on shielding by dust and other molecules and is, therefore, strongly non-linear. We used the shielding factors calculated by Lee et al. (1996). Typical densities and column densities considered here, $n(\text{H}) = 32 \text{ cm}^{-3}$, $N(\text{H}) = 4 \times 10^{20} \text{ cm}^{-2}$ correspond to a Spitzer “standard cloud” (Spitzer 1978) having a dimension of a few pc and median reddening 0.05 mag over the face of the cloud. The central column density in such an HI cloud corresponds to the regime where the appearance of high H₂-fractions is first noted in the ISM.

In general, the hydrogen densities in our models (number or column) are assumed values. The temperature and thermal pressure follow from the details of the calculation, chiefly through the assumed gas-phase abundances of the dominant coolants carbon and oxygen, and the influence of the radiation field in heating the gas via the photoelectric effect on the same small grains which are so largely responsible for the overall charge balance. As shown in Fig. 9 of Liszt & Lucas (2000), a given value of the scaling factor (G_0) for the overall radiation field produces a roughly constant thermal pressure in the outer regions of our models, increasing somewhat with assumed density and decreasing slightly going inward from the cloud edge. The generally-accepted value for the thermal pressure of the ISM, $p/k \approx 2\text{--}3 \times 10^3 \text{ cm}^{-3} \text{ K}$ (Jenkins 2002; Jenkins & Tripp 2001) indeed applies to our typical model of the Spitzer “standard cloud” and the very densest models considered here have pressures a factor 2–3 times higher, as seems observationally to be the case as well.

The initial condition here is simply the equilibrium diffuse cloud model which would be calculated in the absence of any molecular chemistry, as is more typical in discussions of the overall structure of the diffuse ISM (Wolfire et al. 2003). That is, the initial model is equilibrated and self-consistent in terms of thermal and ionization equilibrium, but no molecule formation has occurred. Our models include the rudiments of molecular chemistry as discussed in several recent papers concerning questions of equilibrium CO, H₂, HD and H₃⁺ formation in diffuse gas (Liszt & Lucas 2000; Liszt 2002, 2003). Incorporation of the chemistry should not normally upset the basic microphysical balance (ionization, thermodynamic, etc.) in diffuse gas because such small fractions of oxygen and carbon are sequestered, although inclusion of OH and H₂ formation can affect some aspects of the distribution of charge among species.

Another effect mitigating the influence of H₂ formation in diffuse gas is the dominance of atomic-ion neutralization by small grains, substantially lowering the H⁺ and electron density which would otherwise obtain in the presence of cosmic-ray ionization of hydrogen (Wolfire et al. 1995; Liszt 2003). This effect is of the utmost importance in understanding the interplay between the cosmic ray ionization rate ζ_{H} (here taken as the rate per free H-nucleus) and abundance of H₃⁺ (Liszt 2003). Detailed calculation including grain charging (Draine & Sutin 1987; Weingartner & Draine 2001) is required if the heating rate is to be properly calculated according to the prescription of Bakes & Tielens (1994).

2.2. Formation of H₂

In this work we distinguish between the *formation* of H₂, which we consider to be a microscopic physical effect occurring on individual large grains and involving individual or paired H-atoms, and the *accumulation* of H₂ in the ISM, which is a macroscopic effect involving assumptions about cloud geometry, ISM topology, and so forth. The purpose of this work is to understand the

macroscopic aspects of the accumulation of H₂ in the ISM and we employ only the most standard, empirical, microscopic description of its formation.

That is, the volume formation rate of H₂ is expressed as $dn(\text{H}_2)/dt = n(\text{H}) n(\text{HI}) R_G \langle v_T \rangle = 3 \times 10^{-18} \text{ cm}^3 \text{ s}^{-1} n(\text{H}) n(\text{HI}) \sqrt{T_K}$ (Spitzer 1978) where the factor $n(\text{H})$ (the total density of H-nuclei) represents a constant number of large H₂-forming grains per H-nucleus in the gas; $n(\text{HI})$ is the density of atomic hydrogen (after protons, H⁺ ions, and H₂, etc. are reckoned) and the thermal velocity and/or kinetic temperature terms correspond to the speed at which H-atoms move through the gas, possibly encountering large grains. The rate constant R_G nominally includes a sticking coefficient.

The inferred rate in the diffuse ISM has been remarkably steady over the last 25 years (Jura 1974; Spitzer 1978; Gry et al. 2002) and use of this simple formulation, combined with the modern shielding coefficients, accounts extremely well for the observations of H₂ in diffuse lines of sight (Liszt & Lucas 2000). As discussed in Sect. 3 (see Fig. 4) varying the assumed value of R_G by factors of a few has appreciable effect upon the amount of H₂ which is produced but the equilibrium time scale changes little. As an aside we note that the gas-phase formation of H₂ via H⁺, which could account for some of the very low molecular fractions seen along lines of sight having low extinction (Liszt 2002), is included in the present calculations as well but without much effect.

2.3. Solving the H₂-accumulation problem

The equilibrium solutions for the radial distributions of CO, H₂ and H₃⁺ described in our earlier papers were achieved through what is essentially a relaxation method. An initially atomic sphere is divided into a substantial number (typically 100) of thin radial shells and the molecular densities are calculated for each, working inward, self-consistently accounting for the shielding which accrues from each configuration. Each time a quasi-equilibrium state is reached for the entire structure (that is, when the calculation has successively converged in each shell), the calculation starts anew at the outermost shell (whose H₂-abundance was, after all, calculated in at least partial ignorance of the conditions interior to it) and the process is repeated until the whole structure varies sufficiently little between iterations. The process is not particularly difficult or unstable and convergence is rapid, typically requiring only a few seconds on a recent laptop computer. Note that the thermal and charge balance, etc. are continually updated during the calculation.

The time-dependent calculations basically just wrap the equilibrium solver in an outer loop which allows the entire structure to evolve self-consistently over short times. The time step, which initially cannot be as large as even 1000 years in most cases, is examined and lengthened by a factor of $\sqrt{2}$ whenever the structure changes sufficiently little between time steps. The full time-dependent calculation *is* somewhat tedious, typically requiring several hours per model and much exercising of the tiny (but assertive) fan on the author’s laptop computer in cases of high H₂-fraction.

2.4. Elementary analytic considerations of the time-dependent solutions for H₂

Although the real solution to the time-dependent accumulation problem is strongly non-linear and can only be achieved globally over an entire geometrical construct, several important aspects

of the problem may be understood with reference to a simple parametric treatment of purely local behaviour.

Accordingly, the local rate of accumulation of molecular hydrogen may be written

$$dn(\text{H}_2)/dt = -n(\text{H}_2)\Gamma_{\text{H}_2} + R_G n(\text{H})n(\text{HI})\sqrt{T_K} \quad (1)$$

where Γ_{H_2} is the rate of H₂ destruction (mostly by cosmic rays and ultra-violet photons, although interaction of He⁺ and H₂ is included in the numerical calculation), T_K is the kinetic temperature (calculated in the models) and $R_G = 3 \times 10^{-18} \text{ cm}^3 \text{ s}^{-1}$ (see Sect. 2.2). After rewriting $n(\text{HI}) = n(\text{H}) - 2n(\text{H}_2)$ (for the present purposes; all forms of hydrogen are considered in the numerical models) the solution is

$$n(\text{H}_2)|_t = b/a + (n(\text{H}_2)|_{t=0} - b/a)e^{-at} \quad (2)$$

where $a = \Gamma_{\text{H}_2} + 2R_G n(\text{H})\sqrt{T_K}$, $b = R_G n(\text{H})^2\sqrt{T_K}$.

The time constant in the problem is $1/a$, where a is a linear combination of the per-particle formation and destruction rates, observing the conservation of H-nuclei, and is therefore relatively short in weakly-shielded gas. The rate of accumulation of H₂ takes on its highest value $dn(\text{H}_2)/dt = b$ at time 0 and the equilibrium solution $n(\text{H}_2)|_{t \rightarrow \infty} = b/a$ may be thought of as the result of accumulation at the maximum rate over a period of time $1/a$. Thus, self-shielding (lowering Γ_{H_2}) cannot increase the rate at which H₂ forms or speed up the accumulation of H₂, it only increases the final amount of H₂ by allowing the accumulation process to work longer. By lengthening the time-scale, self-shielding may also provide a buffer against sudden change once equilibrium is attained.

Increasing the microscopic formation rate constant or density will hasten the pace at which H₂ accumulates but even so, global equilibria are not generally achieved more rapidly in cases where the H₂ fraction would otherwise be small, as discussed in Sect. 3 (see Fig. 4); it only happens that more H₂ is made (which requires somewhat more time). Maintenance of high equilibrium H₂-fractions requires $\Gamma_{\text{H}_2} \lesssim R_G n(\text{H})\sqrt{T_K}$, which is roughly equivalent to reducing the photodestruction rate (of order 10^{-10} s^{-1} in free space) to insignificance i.e. $\Gamma_{\text{H}_2} \approx \zeta_{\text{H}}$.

2.5. Weak vs. slow processes

Indeed, the situations which equilibrate most rapidly are those for which the H₂ abundance is smallest, which exemplifies the fact that even processes like H₂ formation or cosmic-ray ionization – which seem weak because they have low rates – may equilibrate quickly when not called upon to do very much; the time constant is then determined by the overall destruction rate, which may be high. It is for this reason that formation of H₃⁺ – a much higher-order process which after all requires formation of H₂, cosmic ray ionization of H₂ and further interaction of H₂⁺ and H₂ (see Sect. 4.2) – is essentially complete as soon as H₂ accumulation equilibrates: one need not wait for a further period $1/\zeta_{\text{H}}$.

2.6. The cosmic-ray ionization rate ζ_{H}

The evolution of the H₂ fraction is largely independent of the assumed value of ζ_{H} in our models but the standard cosmic-ray ionization rate assumed in the models in this work is $\zeta_{\text{H}} = 10^{-16} \text{ s}^{-1}$ (the cosmic-ray destruction rate per H₂ is slightly more than $2\zeta_{\text{H}}$). This is approximately one order of magnitude larger than what is often used in calculations of cosmic-ray ionization of the ISM (Wolfire et al. 1995) especially for dense dark cloud

chemistry and is about that which is needed to explain the overall abundance of H₃⁺ (see Sect. 4). The equilibrium H₃⁺ concentration is nearly proportional to ζ_{H} in our models having larger H₂ fractions (see Fig. 5) owing to the intervention of small-grain neutralization of protons: the formation can be pushed harder without unduly increasing the electron density and recombination rate for H₃⁺. However, for reasons discussed in Sect. 4, the concentration of H₃⁺ is more weakly dependent on ζ_{H} in regions of small H₂-fraction or when ζ_{H} is very large.

2.7. Heating by cosmic rays and H₂-formation

The current assumption is that the diffuse ISM is heated by the photoelectric effect on small grains in both the warm phase (where X-rays make a larger contribution) and cool phase. The heating rate as a function of density in partly-shielded gas is shown in Fig. 3 of Wolfire et al. (1995) based on the work of Bakes & Tielens (1994). As may be seen from that figure, the cosmic ray heating rate is roughly 1.2 dex below that of the photoelectric effect in diffuse gas and 2–2.5 dex lower in cool gas, for $\zeta_{\text{H}} = 10^{-17} \text{ s}^{-1}$. Thus the higher cosmic-ray ionization rates considered here may imply a substantial contribution to the heating of the warm gas by cosmic rays, harkening back to the very earliest discussions of two-phase equilibrium, before the role of diffuse X-ray heating was incorporated (Goldsmith et al. 1969). The highest cosmic-ray rates considered here still do not produce dominant heating effects in the cool neutral gas, but much higher ionization rates $\zeta_{\text{H}} \gtrsim 10^{-15} \text{ s}^{-1}$ were recently suggested by Le Petit et al. (2004) for the line of sight to ζ Persei.

In our models there is a modest contribution to the heating due to H₂ formation, comparable to that arising from heating by cosmic-ray ionization of HI. The volume heating rate due to the latter is $\zeta_{\text{H}} n(\text{HI})\langle E_{\text{cr}} \rangle$ where $\langle E_{\text{cr}} \rangle \approx 8 \text{ eV}$ is the energy available for heating after the primary ionization. The equivalent rate for H₂-formation is $R_G n(\text{H})n(\text{HI})\sqrt{T_K}\langle E_{\text{H}_2} \rangle$ where $\langle E_{\text{H}_2} \rangle$ represents that fraction of the heat of formation of H₂ which is available to heat the gas. The heating rates for the two processes are very nearly equal under typical conditions, $\zeta_{\text{H}} = 10^{-16} \text{ s}^{-1}$, $T_K = 80 \text{ K}$, $n(\text{H}) = 32 \text{ cm}^{-3}$ and $\langle E_{\text{H}_2} \rangle = 1.5 \text{ eV}$.

2.8. The recombination rate of H₃⁺ and other chemical reactions

The chemical rate constants used in our models have been taken from the UMIST database (Le Teuff et al. 2000) (see <http://www.rate99.co.uk>) including, for consistency with the results of Liszt (2003), the rate constant for e + H₃⁺ recombination $\alpha(T_K) = 4 \times 10^{-6}/\sqrt{T_K} \text{ cm}^3 \text{ s}^{-1}$. This rate has been measured many times, including, most recently and probably accurately, by McCall et al. (2003). Their measured values, at 23 K and 300 K, are 70% of those used in our work.

3. Time-dependent H₂ accumulation in diffuse clouds

3.1. Evolutionary effect of varying column density

Figure 1 shows the evolution of the H₂ and H₃⁺ densities in a series of models, each having the same uniform total density of hydrogen $n(\text{H}) = 32 \text{ cm}^{-3}$ threaded by a cosmic ray flux yielding $\zeta_{\text{H}} = 10^{-16} \text{ s}^{-1}$. The central column density of hydrogen across the clouds $N(\text{H})$ (from edge to edge) varies from 0.5 to $16 \times 10^{20} \text{ cm}^{-2}$, as indicated at the right hand side of each

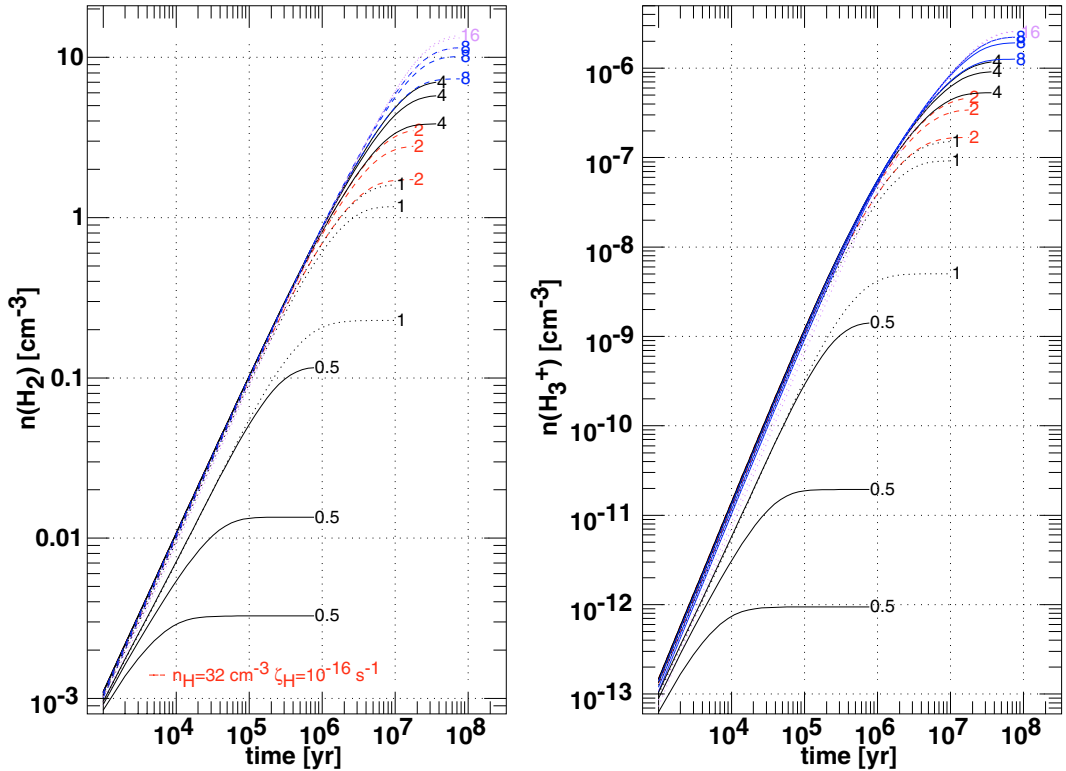


Fig. 1. Density of molecular hydrogen $n(H_2)$ (left) and H_3^+ (right) as functions of time within spherical, uniformly illuminated, initially atomic gas spheres of constant density of H-nuclei $n(H) = 32 \text{ cm}^{-3}$, threaded by a cosmic ray flux yielding a primary ionization rate per H-atom $\zeta_H = 10^{-16} \text{ s}^{-1}$. Three curves corresponding to shells at fractional radii 0, 1/3 and 2/3 from the center are shown for each of a series of models with differing central column density of hydrogen $0.5 \times 10^{20} \text{ cm}^{-2} \leq N(H) \leq 16 \times 10^{20} \text{ cm}^{-2}$. The physical size of the models in pc and their central (edge-to-edge) column density in units of 10^{20} cm^{-2} are equal and shown at the right of each curve.

curve. The physical size of the models (diameter) in pc is, coincidentally, equal to the column density as labelled in units of 10^{20} cm^{-2} . Three curves are shown for each model, corresponding to the shells centered at fractional radii 0, 1/3 and 2/3 from the center. These curves separate at larger times when the outermost regions have reached equilibrium. For a sphere, the median line of sight occurs at a fractional impact parameter of 2/3 where the column density traversed is 3/4 that at the center. The median line of sight through the model with central column density $4 \times 10^{20} \text{ cm}^{-2}$, $3 \times 10^{20} \text{ cm}^{-2}$ corresponds exactly to the standard HI cloud of Spitzer (1978).

For the optically-thinnest model there is a large radial gradient in the H_2 density and a wide disparity between the times required to reach equilibrium (10^4 – 10^6 yr). The fact that such appreciable (easily detectable) amounts of H_2 form in as little as 10^4 yr demonstrates why it is so hard to find lines of sight having measurable reddening which are devoid of H_2 . For $N(H)$ as large as $16 \times 10^{20} \text{ cm}^{-2}$ the H_2 accumulation process is thoroughly saturated ($n(H_2) \rightarrow n(H)/2$) when equilibrium is reached at very large times approaching 10^8 yr. Models in which the equilibrium H_2 -distribution is more uniform also evolve more uniformly, as illustrated in Fig. 2 which shows (at top) the time-dependent evolution of the radial variation of $n(H_2)$ in the model resembling a “standard” HI cloud. The H_2 -density is remarkably constant for fractional radii of 90% or more for most of the first 1 – 3×10^6 yr, after which a more molecular core develops, as well as a very thin (actually, unresolved) transition layer into a more nearly atomic envelope.

Clearly, self-shielding is important only at somewhat later times. In some models with moderate density, $n(H_2)$ behaves as

a single power-law from center to edge, as illustrated in Fig. 2 at bottom which shows the equilibrium solutions for $n(H_2) = 32 \text{ cm}^{-3}$ corresponding to the models used in Fig. 1. However this is not a general feature of the equilibrium solutions. Figure 2 also illustrates the effect of finite resolution on the structure of the atomic envelope, which fractionally is substantially larger with higher resolution. The results in Fig. 1 are not affected by the illustrated doubling of the number of radial shells.

As shown in Fig. 1, even a standard HI cloud model has a very substantial fraction of molecular hydrogen in its interior. This of course is borne out observationally (Jura 1974) as molecular fractions of 25–45% are derived for even the diffuse ISM observed in *uv*/optical absorption lines of H_2 and CH (Savage et al. 1977; Liszt & Lucas 2002). Less obvious, however, is that the conditions so favourable to H_2 may actually work for as long as the calculations require to reach equilibrium in Fig. 1, i.e. for times as long as 10^8 yr.

3.2. Evolutionary effect of varying number density

It seems natural to inquire in what ways the evolution might be hastened. Shown in Fig. 3 are results for series of models of different number density $8 \text{ cm}^{-3} \leq n(H) \leq 128 \text{ cm}^{-3}$ at column densities $N(H) = 2$ – $16 \times 10^{20} \text{ cm}^{-2}$. At least for moderate column densities, as shown at the left in Fig. 3, increasing the number density within the range expected for diffuse gas has surprisingly little effect on the time required for the models to reach equilibrium: the increased rate of accumulation is compensated by the tendency to produce more H_2 , making the equilibrium

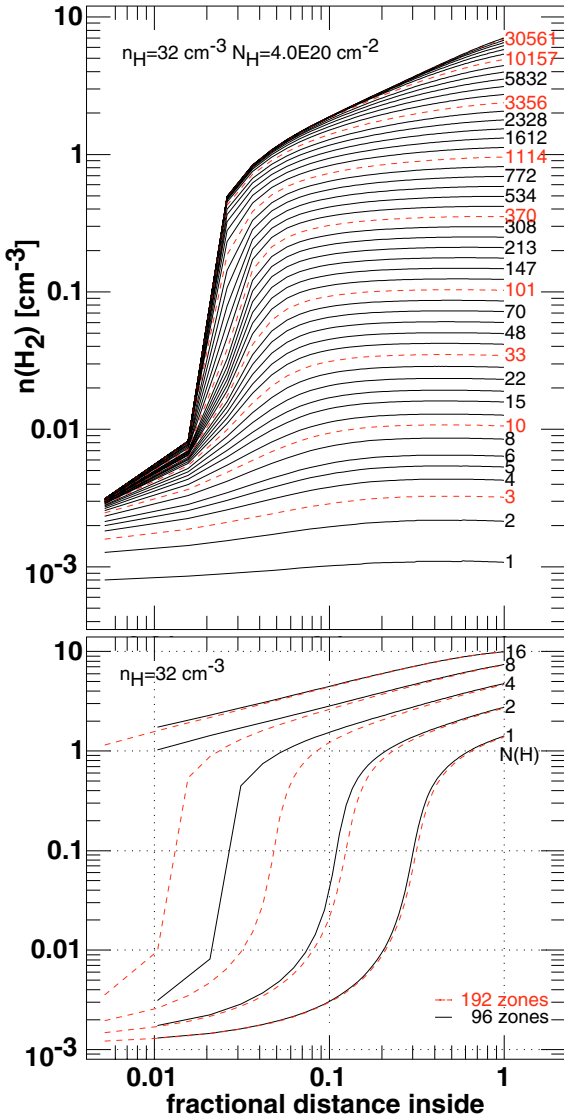


Fig. 2. Radial and secular variation of molecular hydrogen density within models illustrated in Fig. 1. *Top:* time evolution of $n(\text{H}_2)$ for $n(\text{H}) = 32 \text{ cm}^{-3}$, $N(\text{H}) = 4 \times 10^{20} \text{ cm}^{-2}$. Labels at right give the elapsed time in units of 1000 yr. *Bottom:* radial variation in equilibrium for $n(\text{H}) = 32 \text{ cm}^{-3}$ and $N(\text{H}) = 1, 2, 4, 8, 16 \times 10^{20} \text{ cm}^{-2}$, for calculations employing 96 and 192 radial zones.

timescale about constant over a wide range of density for the standard HI cloud column density.

Only when very high H₂ fractions are attained at a given density does increasing the density shorten the equilibrium time (i.e. Fig. 3 at right, or for the two very highest densities at left). With reference to Fig. 3, note that, although the local accumulation rate initially varies as $n(\text{H}_2)^2 \sqrt{T_K} \propto n(\text{H})^{3/2}$ in thermal pressure equilibrium, the total amount of H₂ produced within a model at any time is much less dependent on density because the more tenuous models are larger, varying as $1/n(\text{H})$. Obviously, all models in which the H₂ accumulation saturates at high molecular fractions produce the same $N(\text{H}_2)$ if they have the same $N(\text{H})$, so less dense models having the same $N(\text{H}_2)$ then make more H₂ molecules overall because they are larger.

3.3. Does size matter?

Physically larger clouds tend to produce more H₂ in both series of models just discussed. Those in Fig. 1 with larger column density $N(\text{H})$ are physically larger and have higher internal molecular number density, so, at fixed number density, physically larger regions of higher column density are responsible for the very great bulk of the accumulation of H₂. In Fig. 3, molecular number densities are higher in clouds of higher $n(\text{H})$, but usually not by such large amounts as to compensate for the very large differences in volume. That is, the model volumes vary by a factor $(128/8)^3 \approx 4000$ whereas $n(\text{H}_2)$ varies by factors of 100–500 for the models with $N(\text{H}) = 4\text{--}16 \times 10^{20} \text{ cm}^{-2}$. Over a substantial range in $N(\text{H})$, it is expected that the bulk of the molecules will form in (again) physically larger regions, but of lower density.

So is the bulk of the interstellar H₂ really formed in large tenuous regions, or in more compact, denser ones? Observationally, the mean column density-weighted kinetic temperature inferred for H₂-forming diffuse gas is 70–80 K (Savage et al. 1977; Shull et al. 2004), which, for typical interstellar thermal pressures, implies densities like those of the standard HI cloud¹. Attempts to form the observed H₂ more rapidly in regions of high density must account for these high kinetic temperatures; perhaps it is relevant that Jenkins & Tripp (2001) found a small but pervasive fraction of material at much higher than normal thermal pressure in typical diffuse clouds probed in the fine-structure excitation of CI. This high-pressure component is generally ignored in calculation of the mean thermal pressure in the ISM, but would approximately double it.

3.4. Changes in formation and dissociation rate constants

The empirically-inferred microscopic formation rate of molecular hydrogen formation has changed remarkably little since H₂ was first observed in the ISM (Jura 1974; Spitzer 1978; Gry et al. 2002). Figure 4 shows the effects of changing the assumed H₂ formation rate constant R_G in some of the models illustrated in Fig. 1. Although the H₂ column and number densities increase faster than linearly with changes in R_G at late times, the timescale may only be shortened after the molecular fraction approaches its maximum possible value.

As noted in Sect. 2.4, high molecular fractions may only accrue in cases where the free-space photodissociation rate of H₂ is attenuated (by dust and self-shielding) to the point where it is no more than competitive with cosmic-ray induced destruction rates. It follows that natural variations in the ambient interstellar radiation field (ISRF) may encourage or discourage H₂ accumulation, but only modestly and at late times when equilibrium is approached. Shown in Fig. 5 at left are results for a lower-density model ($n(\text{H}) = 8 \text{ cm}^{-3}$) at $N(\text{H}) = 4 \times 10^{20} \text{ cm}^{-2}$, with the ISRF lowered by factors of 2 and 4. Clearly the H₂ accumulation process may be enhanced by making the material sufficiently dark, but only at the expense of incurring very long equilibrium times. Note that the darker models actually form and accumulate somewhat less H₂ at smaller times because they are substantially cooler; lower photoelectric heating rates accompany lower photoionization rates for molecules. Clouds in very locally darker regions would have to be overpressured in order to compensate for this sluggishness, but in the ISM a tendency to higher thermal pressure at higher density seems a real effect.

¹ Note that the surveys from which these mean temperatures are derived have somewhat low sample mean H₂-fractions, 0.17–0.18.

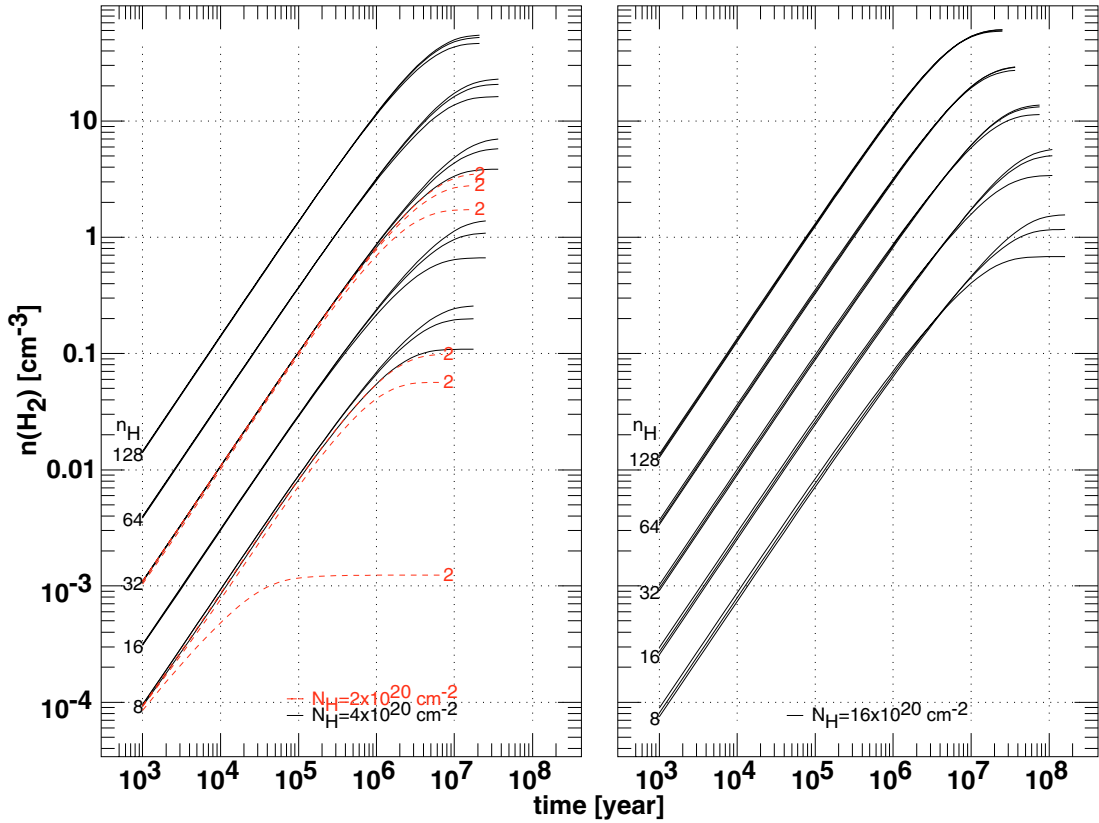


Fig. 3. Density of molecular hydrogen $n(\text{H}_2)$ as a function of time within spherical, uniformly illuminated, initially atomic gas spheres of differing density of H-nuclei $n(\text{H}) = 8\text{--}128\text{ cm}^{-3}$ (as shown at the left of each family of curves), threaded by a cosmic ray flux yielding a primary ionization rate per H-atom $\zeta_{\text{H}} = 10^{-16}\text{ s}^{-1}$. *At right*, all models have a central column density $N(\text{H}) = 16 \times 10^{20}\text{ cm}^{-2}$ (from edge to edge); *at left*, results are interspersed for $N(\text{H}) = 2$ (dashed; red in appropriate media) and $4 \times 10^{20}\text{ cm}^{-2}$. As in Fig. 1, three curves are shown for each model, corresponding to fractional radii 0, 1/3 and 2/3 from the cloud center.

Figure 5 at right shows the effect of varying the primary cosmic ray ionization rate by factors of three about the standard value $\zeta_{\text{H}} = 10^{-16}\text{ s}^{-1}$. Such variations have little effect on the equilibrium H₂ densities in standard HI clouds as long as they are not so large as to upset the thermal balance (which can occur for $\zeta_{\text{H}} \gtrsim 10^{-15}\text{ pc}$). The more complicated behaviour of H₃⁺ is discussed in Sect. 4.

4. H₃⁺ and other trace species

4.1. Evolution of $n(\text{H}_3^+)$

In the ISM there is a general increase in $N(\text{H}_3^+)$ with reddening corresponding to $N(\text{H}_3^+) = 8 \times 10^{14}\text{ cm}^{-2}$ over 6 mag, or to $N(\text{H}_3^+)/N(\text{H}) \approx 2.3 \times 10^{-8}$ for the standard gas-reddening ratio $N(\text{H})/E_{B-V} = 5.8 \times 10^{21}\text{ cm}^{-2}\text{ mag}^{-1}$ (see Fig. 14 of McCall et al. 2002).

As discussed previously (Liszt 2003) or as shown in the figures here, $n(\text{H}_3^+)$ concentrations comparable to those required can be produced in equilibrium models of diffuse clouds of moderate number and column density for cosmic ray ionization rates ζ_{H} at or somewhat above 10^{-16} s^{-1} (see Fig. 5 at right). Such models of H₃⁺ in diffuse gas have the added virtue that the HD/H₂ ratios observed in diffuse clouds – which are very sensitive to the actual proton density – are also reproduced.

As shown in the figures, the H₃⁺ fraction is sensitive to the same effects which increase the concentration of H₂, and in some circumstances to the cosmic ray ionization rate as well (Fig. 5 here). There are some more subtle effects which are less obvious

in the figures: in models which achieve large H₂-fractions, the electron density is lower by a factor of (typically) about two at late times because the gas cannot sustain high proton densities when most of the hydrogen is molecular.

Although the H₃⁺ fraction equilibrates on very much the same final timescale as that of H₂, the problem of timescales is somewhat more critical for H₃⁺ because its time derivative is much steeper; the final concentration occurs more nearly at only the final moments of the calculation. Conversely, the H₃⁺ fraction would deteriorate more rapidly should conditions suddenly become less hospitable. Of course this effect is mitigated slightly when the H₃⁺ fraction is calculated with respect to H₂ (instead of $n(\text{H})$) but in most cases the lines of sight with known $N(\text{H}_3^+)$ are not accessible to direct measurement of $N(\text{H}_2)$ or even $N(\text{HI})$. Note that H₃⁺ is also more centrally concentrated than H₂, but the effect is really strong only in models within which there are larger radial gradients in $n(\text{H}_2)$.

4.2. Effect of changing ζ_{H}

The presence of high cosmic ray ionization rates in diffuse gas has been inferred from very elementary analysis of the H₃⁺ abundance which treats it like an atomic ion (McCall et al. 2002). Assuming – as is true of dark, dense molecular gas – that every primary ionization of H₂ leads to an H₃⁺ ion and that H₃⁺ ions are destroyed by electron recombination with a rate

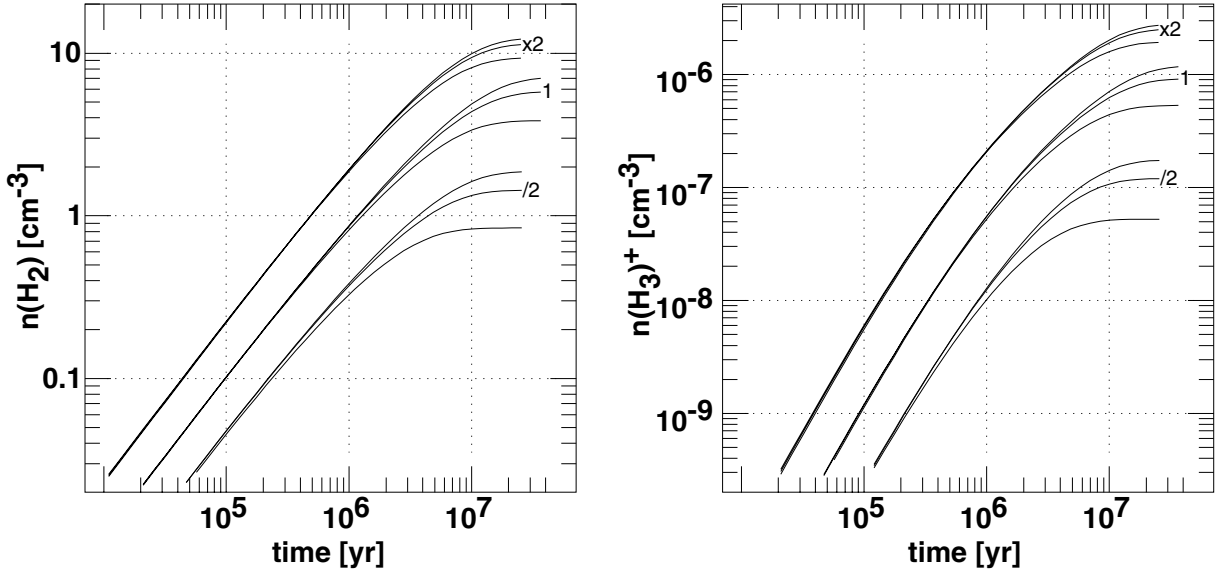


Fig. 4. Similar to Fig. 1, for models having $n(\text{H}) = 32 \text{ cm}^{-3}$, $N(\text{H}) = 4 \times 10^{20} \text{ cm}^{-2}$ and primary cosmic ray ionization rate $\zeta_{\text{H}} = 10^{-16} \text{ s}^{-1}$, with the rate constant for H₂ formation scaled by factors of 2 about the standard value.

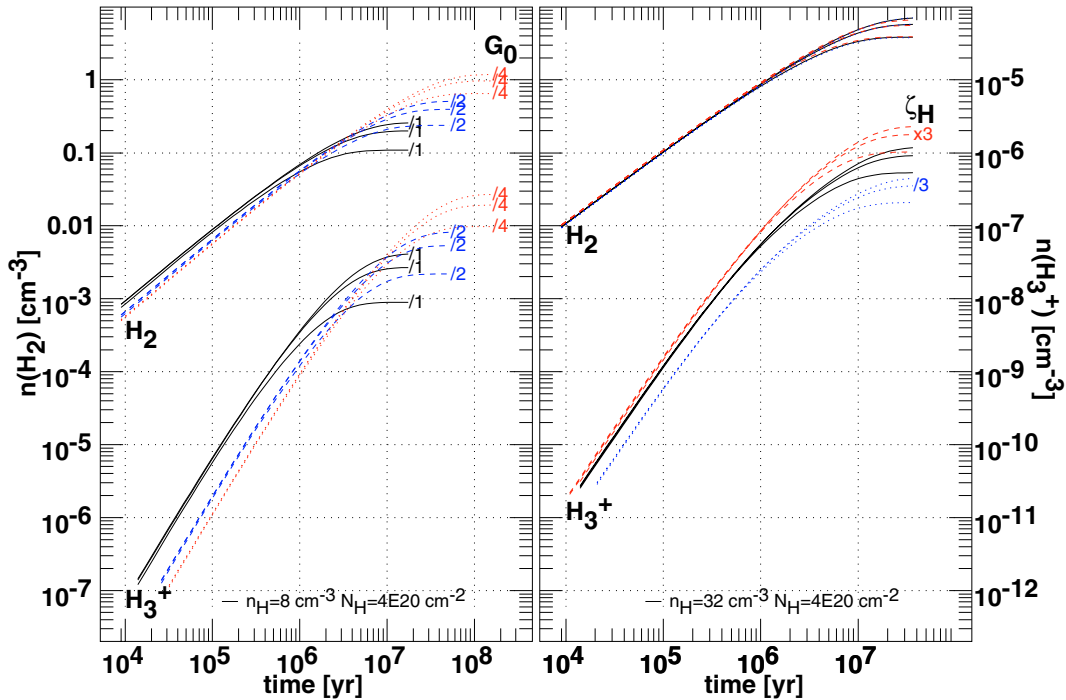


Fig. 5. H₂ and H₃⁺ densities calculated for varying strengths of the interstellar radiation field (*left*) and cosmic ray primary ionization rate ζ_{H} (*right*): the scale for $n(\text{H}_2)$ is given at far left, that for $n(\text{H}_3^+)$ at far right. In the panel at left the scaling parameter G_0 is taken as 1, 1/2 and 1/4; at right ζ_{H} varies by factors of 3, 1 and 1/3 about the standard model value $\zeta_{\text{H}} = 10^{-16} \text{ s}^{-1}$. As in Fig. 1, three curves are shown for each model, at fractional radii 0, 1/3, and 2/3 from the center. The models in both panels have $N(\text{H}) = 4 \times 10^{20} \text{ cm}^{-2}$ but the model at left has lower number density $n(\text{H}) = 8 \text{ cm}^{-3}$. Note that $n(\text{H}_3^+)$ is relatively insensitive to changes in ζ_{H} at early times when $n(\text{H}_2)$ is small, as discussed in Sect. 4 of the text.

constant α_e , there follows a simple, formal expression for the H₃⁺ density:

$$n(\text{H}_3^+) \approx 2\zeta_{\text{H}}n(\text{H}_2)/(\alpha_e n(e)). \quad (3)$$

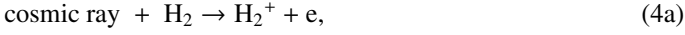
The discrepancy between observation and the values of $n(\text{H}_3^+)$ which result from putting typical values for ζ_{H} , $n(e)$, etc. in this expression is sufficient to suggest that $\zeta_{\text{H}} \gg 10^{-17} \text{ s}^{-1}$. Nonetheless, Eq. (3) is only a formal, very approximate solution for $n(\text{H}_3^+)$ because of the implicit dependences of $n(e)$ and α_e

upon the physical effects of ionization and heating (respectively) denoted by ζ_{H} , and because of other, less obvious assumptions made about the molecular chemistry. Furthermore, the obvious changes in the H₃⁺/H₂ ratio with time show that such considerations might at best apply only at very late times (e.g. Fig. 5 at right).

Figure 5 at right exhibits the further surprising result that the H₃⁺ abundance is largely independent of the cosmic ray ionization rate at early times when the H₂ abundance is small. This

occurs because formation of H₃⁺ is a multistep process with a resultant inverse dependence on the electron density which may be much faster than linear (as suggested by Eq. (3)), combined with the tendency (suppressed but not eliminated by neutralization of atomic ions on small grains) for the ionization fraction to increase with ζ_{H} .

In a somewhat simplified form neglecting chemical reactions of H₂⁺ and H₃⁺ with neutral atoms etc. (appropriate in diffuse gas), and the complexities of grain neutralization, the main steps involved in forming and destroying H₃⁺ and its immediate antecedent H₂⁺ are:



So, whenever the recombination described in reaction 4b dominates over the protonation in reaction 4c, the abundance of H₂⁺ will be inversely proportional to $n(\text{e})$ and $n(\text{H}_3^+) \propto n(\text{H}_2) n(\text{H}_2^+)/n(\text{e}) \propto \zeta_{\text{H}}/n(\text{e})^2$. Calculating the ionization balance in an atomic gas according to the prescription in Spitzer (1978) indeed yields $n(\text{e}) \propto \sqrt{\zeta_{\text{H}}}$ for $\zeta_{\text{H}} \geq 10^{-17} \text{ s}^{-1}$ under conditions typical of HI clouds.

For the model of a typical HI cloud shown at right in Fig. 5, such considerations are apparently sufficient to remove much of the dependence on ζ_{H} from the H₃⁺ density at early times. To ascertain the conditions under which this effect is important, note that the recombination coefficient of H₂⁺ is $\alpha = 4 \times 10^{-6} / \sqrt{T_{\text{K}}} \text{ cm}^3 \text{ s}^{-1}$ and reaction 4c proceeds with a rate constant $k = 2.08 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ in the UMIST database, see Le Teuff et al. (2000) or <http://www.rate99.co.uk>. Thus for $T_{\text{K}} = 100 \text{ K}$ and taking $n(\text{e})$ as a small multiple (2×) of the gas-phase abundance of carbon, $n(\text{C}^+) \approx 1.4 \times 10^{-4} n(\text{H})$, it follows that recombination dominates and the functional dependence of $n(\text{H}_3^+)$ upon ζ_{H} is weakened for $n(\text{H}_2)/n(\text{H}) \lesssim 0.05$, with higher H₂ concentrations required for higher $n(\text{e})$ and/or ζ_{H} . In Fig. 5 at right, this is case for the first $1\text{--}2 \times 10^6 \text{ yr}$.

4.3. Influence of H₃⁺ on other trace molecule abundances

In general the surprisingly high abundance of H₃⁺ in diffuse gas should not alter significantly the patterns of abundance of other trace species under the quiescent conditions discussed here, and it will certainly not by itself explain such outstanding mysteries as the high abundances of CH⁺, NH, HCO⁺, etc. For the former, the reaction $\text{C} + \text{H}_3^+ \rightarrow \text{CH}^+ + \text{H}_2$ is exothermic but not particularly fast and the fraction of gas-phase carbon which is neutral is very small in diffuse gas, typically below 1%: this forms only minuscule amounts of CH⁺ (more CH⁺ might be formed by the reaction of C with H₂⁺). For NH (Crawford & Williams 1997; Meyer & Roth 1991), the reaction of N and H₃⁺ is endothermic. For HCO⁺, which in dark clouds is formed via the reaction $\text{H}_3^+ + \text{CO} \rightarrow \text{HCO}^+ + \text{H}_2$, the amounts of both H₃⁺ and CO are too small in diffuse clouds to sustain HCO⁺ against its recombination to CO, $\text{HCO}^+ + \text{e} \rightarrow \text{CO} + \text{H}_2$. CO can form from HCO⁺ in quiescent diffuse gas (Liszt & Lucas 2000), but not the other way around.

One species for which H₃⁺ might make a difference is OH, because both the reactions $\text{O} + \text{H}_3^+ \rightarrow \text{OH}^+ + \text{H}_2$ (rate constant $k_1 = 8 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$) and $\text{O}^+ + \text{H}_2 \rightarrow \text{OH}^+ + \text{H}$ (rate constant $k_2 = 1.7 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$) are exothermic. Figure 6 shows the time evolution of the volume formation rate of OH⁺ through both routes (shown are $k_1 n(\text{O})n(\text{H}_3^+)$ and $k_2 n(\text{O}^+)n(\text{H}_2)$) in three

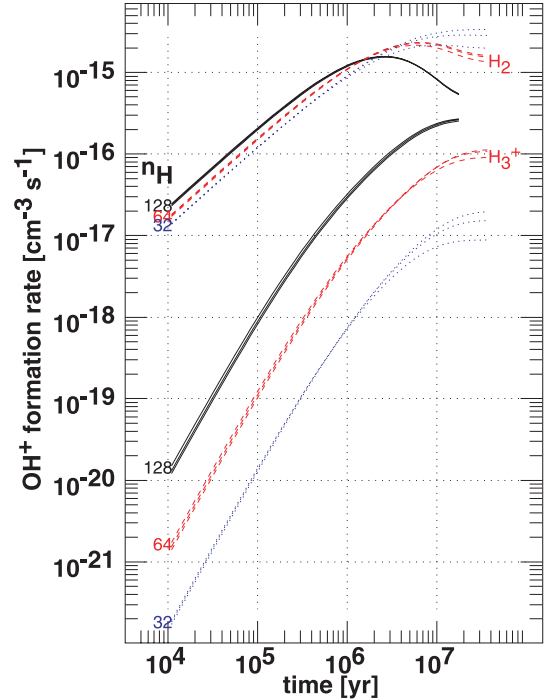


Fig. 6. OH⁺ volume formation rates due to reaction of O⁺ + H₂ (upper family of curves) and O + H₃⁺ (lower family) in the presence of a high primary cosmic ray ionization rate $\zeta_{\text{H}} = 3 \times 10^{-16} \text{ s}^{-1}$. Results are shown at the usual three fractional radii within models of diameter 4.05 pc having $n(\text{H}) = 32 \text{ cm}^{-3}$, 64 cm^{-3} and 128 cm^{-3} , so that $N(\text{H}) = 4 \times 10^{20} \text{ cm}^{-2}$, $8 \times 10^{20} \text{ cm}^{-2}$ and $16 \times 10^{20} \text{ cm}^{-2}$, respectively.

models threaded by a high cosmic ray flux, $\zeta_{\text{H}} = 3 \times 10^{-16} \text{ s}^{-1}$, at three densities $n(\text{H}) = 32 \text{ cm}^{-3}$, 64 cm^{-3} and 128 cm^{-3} . The cloud diameter is held fixed so that $N(\text{H}) = 4 \times 10^{20} \text{ cm}^{-2}$, $8 \times 10^{20} \text{ cm}^{-2}$ and $16 \times 10^{20} \text{ cm}^{-2}$, respectively, purposely driving the highest density gas to very high H₂ fractions and H₃⁺ abundances at late times.

As shown in Fig. 6, the reaction of O and H₃⁺ is never a dominant source of OH⁺. The figure does show, however, the effect of ionization balance on the OH formation rate (see also Sect. 2.3 of Liszt 2003): at later times the first step toward OH formation occurs more vigorously in the more tenuous models because their higher ionization levels (both overall and in oxygen) more than compensate for lower H₂ fractions. In the models with larger H₂ fractions, the proton density declines at late times because a more nearly molecular gas cannot sustain a high proton density and the O⁺/O ratio also declines, due partly to its rapid charge exchange reaction with hydrogen and because of its rapid reaction with H₂. The cosmic-ray ionization alone, even at the high rates assumed here, cannot support high ionization fractions in atomic hydrogen or oxygen in the presence of PAH and high H₂ concentrations.

The next (necessary) step toward OH formation, $\text{OH}^+ + \text{H}_2 \rightarrow \text{OH}_2^+ + \text{H}$ will dominate over recombination of the OH⁺ ion for H₂-fractions as small as 2% at diffuse cloud temperatures. Thus, the thinner models will actually form OH more rapidly (not just OH⁺), as the H₂ accumulation process equilibrates². Chemical effects like those shown in Fig. 6 undoubtedly contribute to the appearance of radio frequency

² At early times, the formation of OH in less dense clouds will be seriously impeded by their larger e/H₂ ratios and the denser models may make more OH. As with H₃⁺ itself, high OH abundances only appear at the conclusion of the H₂ accumulation process.

OH emission in the envelopes of dark clouds well outside the most strongly molecular regions (see Wannier et al. 1993; and Fig. 6 of Liszt & Lucas 1996). In the current context we expect/predict that regions of higher than normal OH abundance should be found optically in diffuse clouds having modest extinction and H₂ fractions.

5. Summary and discussion

5.1. Summary

We showed the approach to equilibrium under benign conditions for some recently-published models (Liszt & Lucas 2000; Liszt 2002, 2003), calculating the time-dependent H₂ and H₃⁺ formation in pc-size, otherwise largely static gas parcels meant to represent typical quiescent diffuse “clouds”. We pointed out that self-shielding does not hasten the formation or accumulation of H₂, although it may foster the production of *more* H₂ over longer times. Because the H₂ formation process in diffuse gas is incomplete, timescales can in general not be deduced from simple scaling arguments based on the local H₂ formation rate. The equilibrium H₂ formation timescale in an HI cloud having a column density $N(\text{H}) \approx 4 \times 10^{20} \text{ cm}^{-2}$ is $1-3 \times 10^7$ yr, nearly independent of the assumed density or H₂ formation rate on grains, etc. Under the benign conditions described here, the bulk of the H₂ formation in the diffuse ISM actually occurs under diffuse conditions in physically larger regions of moderate density; that is, there is little apparent advantage in hypothesizing a process which forms H₂ in denser clumps, if the density remains within the range inferred for quiescent diffuse gas.

Other species reach equilibrium essentially as soon as H₂ does, even when they involve higher-order and/or very “slow” processes (like cosmic ray ionization of H₂) but their equilibrium abundances appear more nearly at just the last minute; it is more critical for explaining H₃⁺ that conditions equilibrate than, say, for H₂ itself. This is also relevant because the chemistry of a weakly-molecular gas – which could be either a model of low density or one of higher density at early time – behaves in various particular ways. For instance, the predicted abundance of H₃⁺ is less strongly dependent on the cosmic-ray ionization rate when $n(\text{H}_2)/n(\text{H}) \lesssim 0.05$.

Attempts to form increased amounts of H₃⁺ may be thwarted at very high assumed values of ζ_{H} both because the fractional ionization increases and because the H₂-fraction declines as cosmic-ray ionization overtakes photodissociation as the main H₂-destruction mechanism. Assuming $\zeta_{\text{H}} \gg 10^{-16} \text{ s}^{-1}$ will also change the thermal balance in the diffuse ISM as a whole as cosmic-ray ionization becomes the dominant heating process in both warm and cold neutral diffuse gas. Although observations of both HD and H₃⁺ seem to indicate an enhanced low-level source of hydrogen ionization, it is important to ascertain whether it is indeed a cosmic-ray related process which is responsible (or some other form of very hard radiation) and whether any related effects occur in other phases of the interstellar medium, either in the warm or dark gas.

The presence of relatively high H₃⁺ abundances per se probably does not have strong effects on the chemistry of other trace species whose abundances are puzzling (CH⁺, NH, HCO⁺ etc.) or on those of species like OH which are generally considered to be better understood. However, in considering competition between OH formation paths through H₂ and H₃⁺, we showed that late-time OH formation proceeds most vigorously in more diffuse regions having modest density, extinction and H₂ fraction and somewhat higher fractional ionization, suggesting that high

OH abundances might be found optically in diffuse clouds having modest extinction.

5.2. Lifetimes of diffuse clouds and their H₂

In this work we modelled the formation and accumulation of H₂ under conditions like those which are inferred from observations of the H₂ and related neutral gas species themselves; temperatures from H₂ (Savage et al. 1977; Shull et al. 2004) and mean thermal pressures (densities) from CI (Jenkins & Tripp 2001). Although modest amounts of H₂ form quickly enough that molecule-free sightlines are relatively rare, the observed high mean molecular fractions of 25–40% (Savage et al. 1977; Liszt & Lucas 2002) are achieved only over timescales of 10⁷ yr or longer, when starting from scratch.

H₂ aside, timescales for thermal, ionization, chemical etc. equilibrium are short (Spitzer 1978; Wolfire et al. 2003; Rawlings et al. 2002) and diffuse gas is not normally thought of as having much longevity in any particular form. The HI cloud spectrum evolves under the continual influences of cloud-cloud collisions, evaporation, passage of supernova blast waves and stellar wind shocks etc. (Chieze & Lazareff 1980) and in a 3-phase model of the diffuse ISM, gas in any particular volume element turns over on timescales shorter than 10⁶ yr according to McKee & Ostriker (1977).

How then are high H₂ fractions and short diffuse gas lifetimes to be reconciled? This question has never really been considered when the overall structure of the diffuse ISM is modelled, but there are several alternatives. 1) The long equilibrium timescales under diffuse neutral conditions provide, in reverse, some resilience which might help pre-existing H₂ to weather the changes which occur. 2) Dark clouds have haloes (Wannier et al. 1993; Bensch 2006) and it has been suggested that the molecules supposedly seen in diffuse clouds are actually located around and exchanging material with dark clouds (Federman & Allen 1991); this may be true in some cases, but complex trace molecules are also seen along sightlines which are quite well separated from the nearest dark material (Liszt et al. 2002). 3) Perhaps most promisingly, turnover within diffuse neutral gas due to turbulence, rapidly cycling material through a very dense phase, may provide for much faster formation of H₂ and trace species (Glover & Mac Low 2005; Falgarone et al. 2005), establishing high molecular fractions from scratch on short timescales. The small fraction of neutral material which is observed to exist at very high pressure within diffuse clouds (Jenkins & Tripp 2001) and other aspects of small-scale structure in diffuse gas (Deshpande 2000) may perhaps also be understood in such terms.

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References

- Bakes, E. L. O., & Tielens, A. G. G. M. 1994, ApJ, 427, 822
- Bensch, F. 2006, A&A, 448, 1043
- Chieze, J. P., & Lazareff, B. 1980, A&A, 91, 290
- Cox, P., Güsten, R., & Henkel, C. 1988, A&A, 206, 108
- Crawford, I. A., & Williams, D. A. 1997, MNRAS, 291, L53
- Deshpande, A. A. 2000, MNRAS, 317, 199
- Draine, B. T., & Sutin, B. 1987, ApJ, 320, 803
- Falgarone, E., Pineau Des Forêts, G., Hily-Blant, P., & Schilke, P. 2005, in IAU Symp., ed. D. Lis, G. Blake, & E. Herbst, 105

- Federman, S. R., & Allen, M. 1991, *ApJ*, 375, 157
Glover, S. C. O., & Mac Low, M.-M. 2005, in *IAU Symp.*, ed. D. C. Lis, G. A. Blake, & E. Herbst, 160
Goldsmith, D. W., Habing, H. J., & Field, G. B. 1969, *ApJ*, 158, 173
Gry, C., Boulanger, F., Nehmé, C., et al. 2002, *A&A*, 391, 675
Jenkins, E. B. 2002, *ApJ*, 580, 938
Jenkins, E. B., & Tripp, T. M. 2001, *ApJS*, 137, 297
Jura, M. 1974, *ApJ*, 191, 375
Le Petit, F., Roueff, E., & Herbst, E. 2004, *A&A*, 417, 993
Le Teuff, Y. H., Millar, T. J., & Markwick, A. J. 2000, *A&AS*, 146, 157
Lee, H. H., Herbst, E., Pineau Des Forets, G., Roueff, E., & Le Bourlot, J. 1996, *A&A*, 311, 690
Liszt, H. 2002, *A&A*, 389, 393
Liszt, H. 2003, *A&A*, 398, 621
Liszt, H. S., & Lucas, R. 1995, *A&A*, 299, 847
Liszt, H. S., & Lucas, R. 1996, *A&A*, 314, 917
Liszt, H. S., & Lucas, R. 2000, *A&A*, 355, 333
Liszt, H., & Lucas, R. 2002, *A&A*, 391, 693
Liszt, H., Lucas, R., & Pety, J. 2002, *A&A*, 448, 253
Liszt, H., Lucas, R., & Black, J. H. 2004, *A&A*, 428, 117
Lucas, R., & Liszt, H. S. 1996, *A&A*, 307, 237
Lucas, R., & Liszt, H. S. 2000, *A&A*, 358, 1069
McCall, B. J., Hinkle, K. H., Geballe, T. R., et al. 2002, *ApJ*, 567, 391
McCall, B. J., Huneycutt, A. J., Saykally, R. J., et al. 2003, *Nature*, 422, 500
McKee, C. F., & Ostriker, J. P. 1977, *ApJ*, 218, 148
Meyer, D. M., & Roth, K. C. 1991, *ApJ*, 376, L49
Moore, E. M., & Marscher, A. P. 1995, *ApJ*, 452, 671
Nash, A. G. 1990, *ApJS*, 72, 303
Rawlings, J. M. C., Hartquist, T. W., Williams, D. A., & Falle, S. A. E. G. 2002, *A&A*, 391, 681
Savage, B. D., & Sembach, K. R. 1996, *ARA&A*, 34, 279
Savage, B. D., Drake, J. F., Budich, W., & Bohlin, R. C. 1977, *ApJ*, 216, 291
Shull, J. M., Anderson, K., Tumlinson, J., & FUSE Science Team. 2004, *Am. Astron. Soc. Meeting*, 204
Spitzer, L. 1978, *Physical processes in the interstellar medium* (New York: Wiley-Interscience), 333
Wannier, P. G., Andersson, B.-G., Federman, S. R., et al. 1993, *ApJ*, 407, 163
Weingartner, J. C., & Draine, B. T. 2001, *ApJS*, 134, 263
Wolfire, M. G., Hollenbach, D., McKee, C. F., Tielens, A. G. G. M., & Bakes, E. L. O. 1995, *ApJ*, 443, 152
Wolfire, M. G., McKee, C. F., Hollenbach, D., & Tielens, A. G. G. M. 2003, *ApJ*, 587, 278