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# $\text{H}_3^+$ recombination and bistability in the interstellar medium

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$\text{H}_3^+$  has recently been detected using infrared absorption towards several dense clouds. We have already shown that models of interstellar chemistry can exhibit several stable steady states, due to the nonlinear behaviour of chemical equations in which  $\text{H}_3^+$  plays a major role. We investigate the influence of various astrophysical parameters that control the evolution and the final state of the gas, such as the density, the cosmic-ray ionization rate, the elemental depletions, and the  $\text{H}_3^+$  dissociative recombination rate (which is a key reaction). We show that these parameters lead to bistability for a range of physical conditions appropriate to interstellar clouds and discuss more specifically their influence on the  $\text{H}_3^+$  abundance in dark clouds. Both steady-state and evolutionary aspects are discussed.

**Keywords:** interstellar molecules; astrochemistry; bistability

## 1. Introduction

In liquid as well as in gas-phase chemistry, the nonlinear behaviour of chemical systems has been extensively studied (see, for example, Scott 1991) and has been applied in many fields, such as in stratospheric chemical models (Fox *et al.* 1982). Indeed, the stationary state(s) of an open nonlinear chemical system (coupled to the external medium) can be far from local thermodynamic equilibrium (LTE) and may exhibit numerous instances of complex behaviour (Gray & Scott 1990). During the last decade, nonlinear chemical kinetics has become a major field of research with numerous applications.

As interstellar molecular clouds are obviously regions far from LTE, it is not surprising that nonlinear effects may occur in these environments, and the phenomenon of bistability in gas-phase chemical models of interstellar clouds is by now well known (Pineau des Forêts *et al.* 1992; Le Bourlot *et al.* 1993, 1995*a, b*; Lee *et al.* 1998). The aim of this paper is to explore the relevant range of parameters that may influence the conditions of bistability, paying particular attention to the role of the  $\text{H}_3^+$  dissociative recombination rate and also to the formation of  $\text{H}_3^+$ , which has recently been detected in infrared absorption against background protostars (Geballe & Oka 1996; McCall *et al.* 1998; Geballe *et al.* 1999; Geballe, this issue).

## 2. Chemistry in dark clouds: two chemical regimes

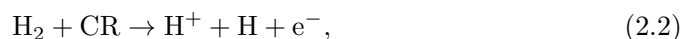
In interstellar molecular clouds, the fractional ionization is a crucial parameter, the origin of which is in the action of output energy that is injected through ultraviolet

radiation, X-rays, gamma rays and cosmic rays that ionize and dissociate the interstellar atoms and molecules. On the other hand, the chemical composition of the molecular gas depends on a complex ensemble of coupled ion–molecule, recombination, neutral–neutral and surface reactions. As the equations describing its chemical evolution are nonlinear, an interstellar cloud may thus be considered as an open dissipative system with continuous background energy sources permeating the medium. As a result of the nonlinearity of the chemical and thermal balance equations, models of quiescent dark clouds may present more than one steady-state solution. When these solutions overlap, the phenomenon is termed ‘bistability’.

The models presented here are restricted to the dark component of molecular clouds entirely shielded from external UV photons but include photodissociations and photoionizations induced by the secondary UV photons produced by cosmic rays (Gredel 1990). Therefore, ions are produced mainly by cosmic-ray (CR) ionization of  $\text{H}_2$ ,



or by dissociative ionization,



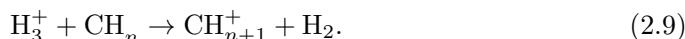
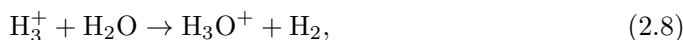
where the ionization rate  $\zeta$  is believed to be of the order of  $10^{-17} \text{ s}^{-1}$ . The branching ratio of the later reaction is approximately 0.05, according to Shah & Gilbody (1982). The production of  $\text{H}_2^+$  is followed rapidly by the formation of  $\text{H}_3^+$ :



The rate of production of ions (in  $\text{s}^{-1}$ ) by cosmic rays is constant and, thus, independent of the value of the density of the medium; the rate of their ultimate removal, by dissociative recombination, is then proportional to the electron density. It follows that as the density decreases, the fractional ionization of the gas tends to rise, and also the fractional abundance of ions such as  $\text{H}^+$ , while the rise in the electron density causes a decrease in the  $\text{H}_3^+$  fractional abundance, owing to its enhanced rate of dissociative recombination. This process occurs until a point is reached at which saturated molecules such as  $\text{H}_2\text{O}$ ,  $\text{O}_2$ , or  $\text{CH}_n$  are predominantly destroyed through charge transfer reactions with  $\text{H}^+$ :



On the other hand, at higher densities,  $\text{H}_3^+$  remains the key ion, and sequences of protonation reactions yield oxygen- and carbon-bearing molecular ions:



Dissociative recombination reactions with electrons then produce neutral species such as  $\text{CH}_n$  and  $\text{H}_2\text{O}$  (see the review by Herbst in this issue for more details on the

chemistry of  $\text{H}_3^+$ ). The interesting point is that these two regimes—corresponding, respectively, to a ‘high ionization phase’ (HIP) and a ‘low ionization phase’ (LIP)—can be at work simultaneously in dark clouds.

As we will see in the following section, the range of bistability depends on many physical parameters. Not only the density and the  $\text{H}_3^+$  recombination rate have an influence on the fractional ionization of the quiescent medium, but also the cosmic-ray ionization rate  $\zeta$ , the elemental depletion (for example the metallicity, the sulphur elemental abundance or the [C/O] ratio), and the gas-phase and grain-surface reaction rates.

### 3. Chemical models: the bistability

In dark clouds, the ionization of the medium is driven by cosmic rays and we take a conservative value of the cosmic-ray ionization rate of the  $\text{H}_2$  molecule,  $\zeta = 2 \times 10^{-17} \text{ s}^{-1}$ . We consider a set of 95 chemical species including H, C, O, N and S with a maximum number of six atoms and a representative metal M coupled through 900 chemical reactions (described in Le Bourlot *et al.* (1995*b*) and references cited therein). We use the latest storage-ring results (Larsson *et al.* 1993; Sundström *et al.* 1994) for the temperature dependence and product branching fraction of the dissociative recombination rate coefficient of  $\text{H}_3^+$  with electrons. Specifically, the formula derived for the overall rate coefficient  $k$  is  $1.15 \times 10^{-7} (T(\text{K})/300)^{-0.65} \text{ cm}^3 \text{ s}^{-1}$  with a product fraction of 0.75 for the  $3\text{H}$  channel and 0.25 for the  $\text{H}_2 + \text{H}$  channel. Two different numerical methods can be used to solve the chemical equations involved, as follows.

**Steady-state models**, in which stationary abundances and temperatures are calculated as functions of one physical parameter (density, ionization rate, etc.), which is done using a Newton–Raphson scheme.

**Time-dependent models**, in which the time evolution of the chemical abundances and temperatures is followed for a given set of physical parameters and for a given set of initial conditions (abundances at  $t = 0$ ). A Gear solver is then required to solve the stiff equations.

Figure 1*a* illustrates the first numerical approach and shows the steady-state solutions for different values of the density, all the other parameters being fixed. Each dot corresponds to *one* solution of the steady-state coupled equations. The curve displayed by all the solutions is a typical hysteresis curve of the chemical solutions when density is taken as a ‘control parameter’. At a given density, there are up to three equilibrium solutions of the chemical rate equations. Two branches of stable solutions corresponding to the HIP and to the LIP are connected by a branch of unstable solutions, with intermediate values, between two critical points. We see that the range of densities in which bistability occurs is quite compatible with the current values deduced for the interstellar medium from observations. In fact, the physical parameters (temperature, cosmic ionization rate, depletions, etc.) for which bistable solutions are found are consistent with the range of values expected from the observations.

Figure 1*b* illustrates the second approach and shows the time-dependent evolution of the degree of ionization starting from slightly different initial conditions

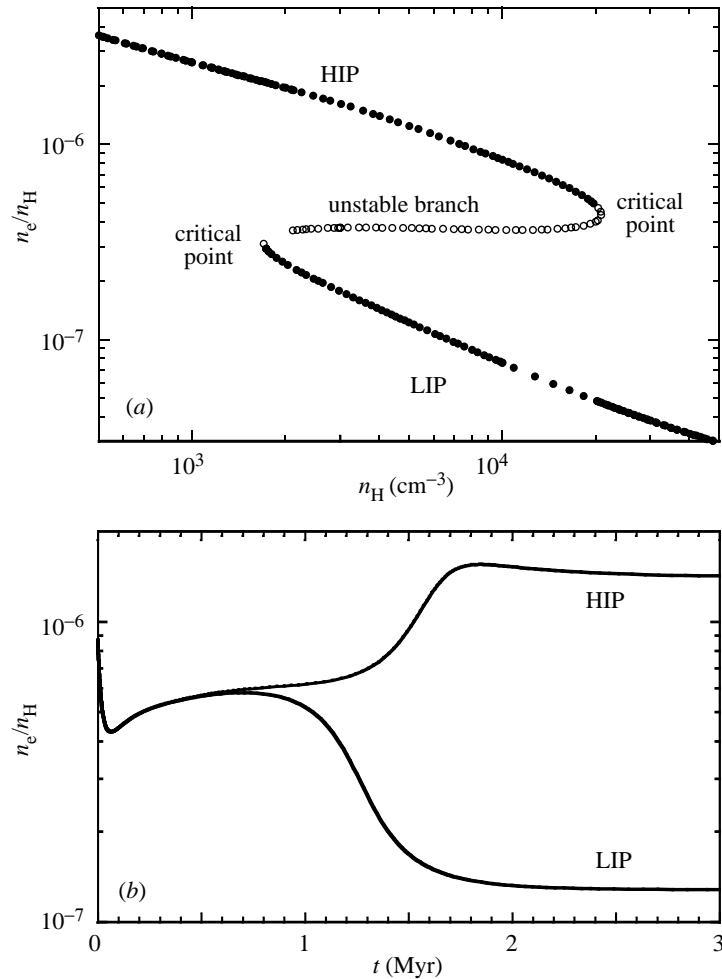


Figure 1. (a) Steady-state solutions of the fractional ionization as a function of the density  $n_H$ . The physical conditions are fixed as follows:  $\zeta = 2 \times 10^{-17} \text{ s}^{-1}$ ,  $[\text{C}/\text{H}] = 1.45 \times 10^{-4}$ ,  $[\text{O}/\text{H}] = 7.1 \times 10^{-4}$ ,  $[\text{N}/\text{H}] = 1.12 \times 10^{-4}$ ,  $[\text{S}/\text{H}] = 1.85 \times 10^{-5}$ . (b) Time evolution of the fractional ionization for two slightly different initial conditions, the same physical conditions as in part (a) and a fixed density  $n_H = 5 \times 10^3 \text{ cm}^{-3}$ . The two final steady-state solutions (at  $t = 3 \text{ Myr}$ ) correspond to the two HIP and LIP points at  $n_H = 5 \times 10^3 \text{ cm}^{-3}$  in part (a).

but keeping the same set of physical parameters (for example, the proton density  $n_H = n(\text{H}) + 2n(\text{H}_2)$  is fixed to  $5 \times 10^3 \text{ cm}^{-3}$ ). After *ca.*  $10^6$  years, the trajectories split and converge towards two different solutions. The upper curve corresponds to the HIP solutions with  $n_e/n_H \approx 10^{-6}$ , whereas the lower curve corresponds to the LIP solutions at  $n_e/n_H \approx 10^{-7}$ .

As described in the previous section, the chemical properties are very different for the two steady-state conditions. In the HIP, chemical processes are mainly driven by charge-transfer processes with protons and carbon ions.  $\text{H}_3^+$  is then predominantly destroyed by electrons, and saturated molecules undergo dissociative charge transfer, which favours the occurrence of neutral carbon and unsaturated carbon

molecules. This is a new solution that reproduces some striking observations, e.g. the presence of atomic carbon in dark clouds such as TMC-1 (Schilke *et al.* 1995). In the LIP, the chemistry is dominated by proton transfer and  $\text{H}_3^+$  is destroyed by abundant neutrals such as O and CO. Saturated molecules are efficiently formed from the dissociative recombination processes. Most of the species are affected by bistability with differences in their abundances that can reach several orders of magnitude.

The evolution of a molecular cloud to equilibrium may be represented in different ways. In figure 2*a*, the evolution from a given set of initial conditions is displayed as a ‘phase portrait’, projected on the  $(\text{C}_2\text{H}, \text{O}_2)$ -plane. The stable equilibrium solutions are the HIP or the LIP fixed points. States that are initially very close to but on opposite sides of the separatrix evolve to very different equilibrium compositions. Enhanced fractional abundances of organic molecules, such as  $\text{C}_2\text{H}$ , are associated with a relatively high abundance of atomic carbon, which occurs in the HIP. Note that the apparent crossing of trajectories in the lower right of figure 2*a* is a projection effect.

The fractional abundance of  $\text{C}_2\text{H}$  is plotted as a function of time in figure 2*b*. Solutions evolving from the initial conditions to the left in figure 2*a* are plotted as full curves, and those from the initial conditions to the right as broken curves. As the evolutionary time becomes large, either the high-ionization phase or the low-ionization phase-equilibrium solution is attained, depending on the initial conditions; these solutions differ by an order of magnitude in the fractional abundance of  $\text{C}_2\text{H}$ . The closer the initial composition to the separatrix, the longer is the time required to attain equilibrium.

#### 4. The importance of the chemical data

We have seen that bistability can be obtained for a range of astrophysical parameters that are relevant to dark-cloud interstellar chemistry, i.e.

- (i) low temperatures (10–15 K);
- (ii) densities between  $10^3$  and  $10^4 \text{ cm}^{-3}$ ; and
- (iii) standard cosmic-ray ionization rate.

The phenomenon of bistability does not depend on the size of the chemical networks. We have used chemical models of various sizes, from a few hundred chemical reactions to the UMIST database (Millar *et al.* 1997), or the chemical models developed by Herbst and co-workers (Bettens *et al.* 1995), which involve about 400 species linked by more than 4000 reactions. Moreover, one has to keep in mind that for interstellar chemical studies relevant to dark clouds, these reaction-rate coefficients should be known at the very low temperatures of the molecular interstellar clouds. Despite the numerous efforts undertaken to improve our knowledge of these chemical data, it is clear that a certain range of inaccuracy is still present in the chemical reaction-rate coefficients. This concerns the actual value of the reaction-rate coefficients, their temperature dependence, the branching ratios of the reactions involving complex species, etc. We may then consider that the reaction-rate coefficients can also play the role of control parameters in the kinetic chemical equations.

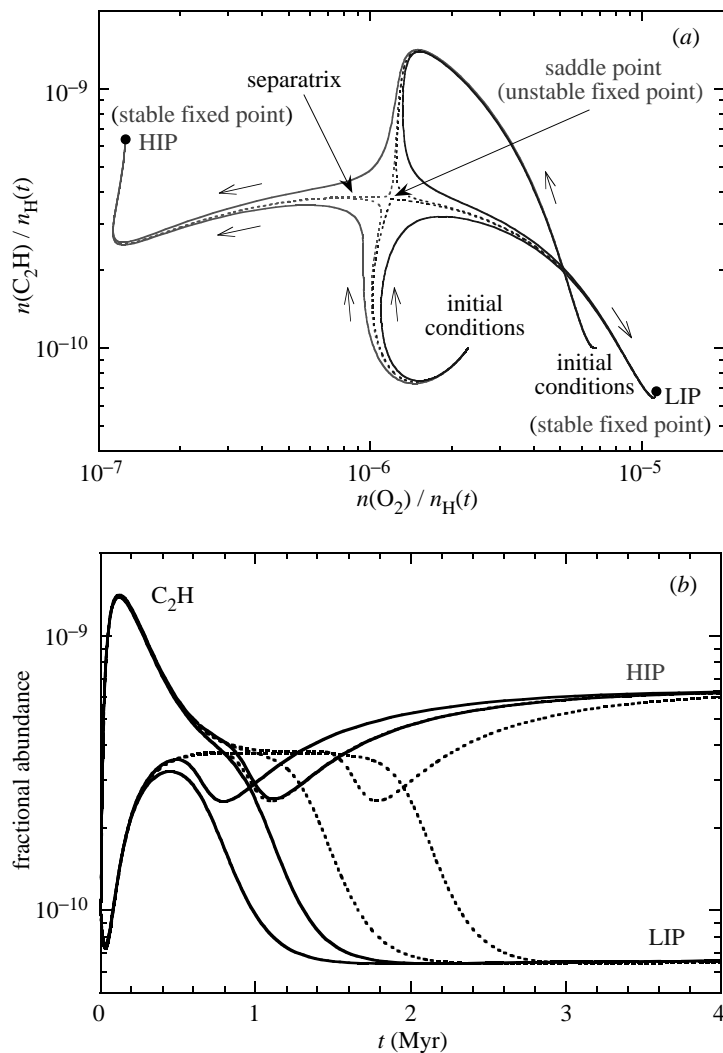


Figure 2. (a) Phase portrait of the model with control parameters:  $\zeta = 2 \times 10^{-17} \text{ s}^{-1}$  and  $n_{\text{H}} = 10^4 \text{ cm}^{-3}$ , projected on the  $(\text{C}_2\text{H}, \text{O}_2)$ -plane. Three fixed points are apparent, two stable ones corresponding to the HIP and LIP, respectively, and an unstable saddle point on the separatrix between the two basins of attraction. The crossing of the trajectories is a projection effect. (b) Evolution with time of the relative abundance of  $\text{C}_2\text{H}$  for the same model as in part (a). Eight evolution curves are displayed, each one corresponding to one trajectory in part (a), i.e. to different initial conditions. Note that the initial abundance of  $\text{C}_2\text{H}$  is the same in all cases:  $10^{-10} n_{\text{H}}$ .

(a) *Dependence on all chemical reactions*

We perform a random variation by a factor of less than two of the reaction-rate coefficients of *all* the chemical reactions included in our network. More than 1000 runs have been performed in the steady-state approximation and we display the corresponding results in figure 3.

The dispersion of the solutions covers more than two orders of magnitude. The



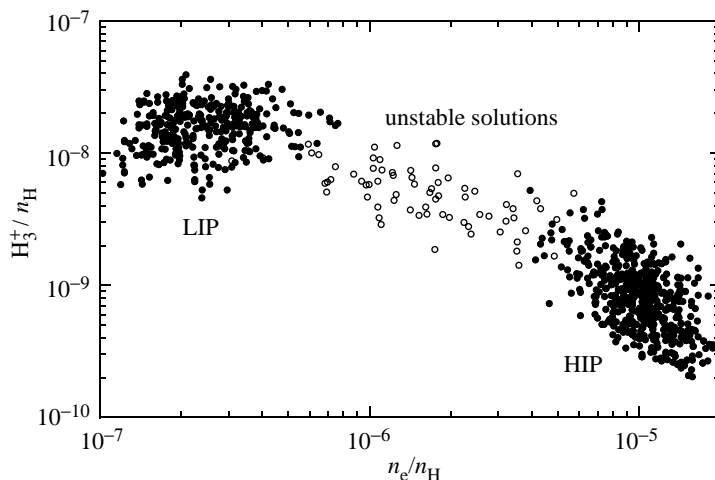


Figure 3. Steady-state solutions of the fractional abundance of  $H_3^+$  versus fractional ionization when all reaction-rate coefficients are varied randomly by at most a factor of 2.

interpretation of such an occurrence is, however, clear from the previous statements: we just span different types of solutions when varying reaction-rate coefficients. Consequently, the three different groups of solutions displayed on figure 3 are just referring to the HIP, LIP and unstable solutions in between as shown. The dispersion of the results inside one group of solutions may reach a factor of a few. So, we have shown that caution has to be kept in mind when comparing observations with numeric interstellar models.

#### (b) Dependence on the recombination of $H_3^+$

The dissociative recombination reaction of  $H_3^+$  is the subject of a lingering controversy (Dalgarno 1994) that is not yet over and has been extensively discussed in the present issue. The values of the rate coefficient range typically between  $2 \times 10^{-8}$  (Smith & Španel 1993) and  $2 \times 10^{-7}$  at 300 K (Larsson, this issue). From the measured temperature dependence  $T^{-0.65}$  (Sundström *et al.* 1994), we infer values between  $2 \times 10^{-7}$  and  $1.8 \times 10^{-6}$  at 10 K. It is then interesting to test the influence of the range of values on chemical interstellar models.

Figure 4 shows the ionization fraction for typical interstellar conditions when this rate coefficient is used as a control parameter. We see that we again recover a hysteresis curve, and bistable solutions are obtained for values at 300 K typically between  $3 \times 10^{-7}$  and  $7 \times 10^{-8} \text{ cm}^{-3} \text{ s}^{-1}$ , the critical range of values determined from present experimental studies. We note that HIP solutions are favoured by the larger values of the reaction-rate coefficient. Again, all variables show this same behaviour.

The variations may attain up to four orders of magnitude for C/CO and less than two orders of magnitude for the ionization degree. Depending on the values of the dissociative recombination of  $H_3^+$ , one or several solutions may be found.

We emphasize here the crucial importance of solving the remaining discrepancies between experiments and of understanding the theoretical mechanism involved in this reaction.



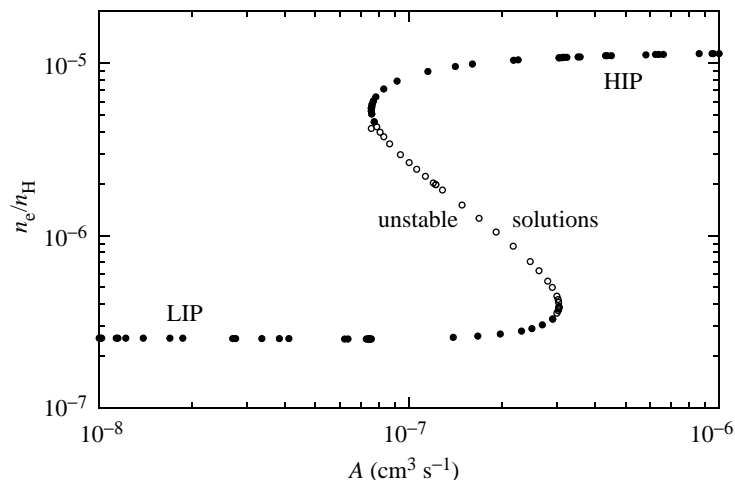


Figure 4. Steady-state solutions of the ionization fraction when the dissociative recombination reaction-rate coefficient of  $\text{H}_3^+$  is varied. The physical parameters are the same as in the previous figures. ( $k_e(\text{H}_3^+) = A(T/300)^{-0.65}$ .)

### 5. Deuteration in interstellar clouds

A number of deuterated molecules are found in cold dense clouds with a much greater abundance than the actual D-to-H ratio would imply at first sight. Such an enhancement in heavy molecular isotopomers comes from chemical fractionation processes. The deuteron exchange between HD and  $\text{H}_3^+$  occurs preferentially in the forward direction due to the respective values in the zero point energies:



An exothermicity of *ca.* 220 K is obtained for the reaction when one takes into account the additional rotational energy coming from Fermi statistics, because the  $0_{00}$  state of  $\text{H}_3^+$  is forbidden. Such an energy (20 meV) is significant in interstellar physical conditions and the subsequent reactions of  $\text{H}_2\text{D}^+$  with CO,  $\text{N}_2$ , HCN, etc., produce  $\text{DCO}^+$ ,  $\text{N}_2\text{D}^+$ ,  $\text{HCND}^+$ , etc., ions. These observed enhancements in cold dark clouds are an additional manifestation of the role of ion–molecule reactions.

We have shown the link between  $\text{H}_3^+$  and  $\text{H}_2\text{D}^+$  and, in figure 5*a, b*, we show the steady-state abundances of both ions as a function of density for a set of interstellar depletions and cosmic ionization rates. Figure 5*c* displays the ratio of the abundances of  $\text{H}_3^+$  and  $\text{H}_2\text{D}^+$ .

The dissociative recombination of  $\text{H}_2\text{D}^+$  and the branching ratios have been measured in the ion storage-ring experiment (Larsson, this issue). The three-body dissociation channel is predominant with a 73% probability, whereas the channels leading to  $\text{H}_2$  and HD occur with a probability of 7% and 20%, respectively.

We infer that deuteration is more likely to occur for LIP solutions. Indeed, deuterated molecules are predominantly found in dense dark clouds (Caselli *et al.* 1998; Gerin *et al.* 1997; Roueff *et al.* 2000; Tiné *et al.* 2000), where such conditions are fulfilled. Let us note, however, that deuterated molecules are also found in dense hot cores (Hatchell *et al.* 1998) and in star-forming regions, where evaporation from grains is probably taking place, a mechanism that is not considered in the models discussed here.

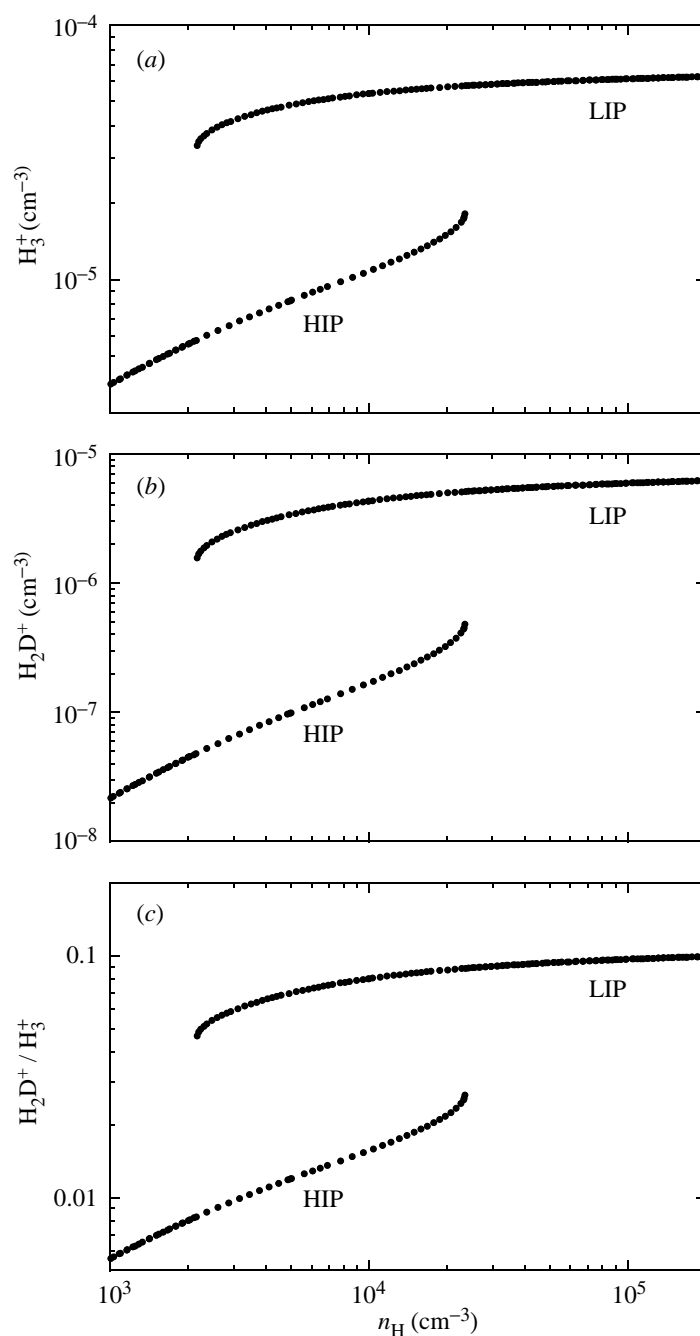


Figure 5. (a) Steady-state solutions of the  $\text{H}_3^+$  abundance for a range of densities between 300 and  $10^5 \text{ cm}^{-3}$ . The unstable solutions have not been calculated. (b) Steady-state solutions of the  $\text{H}_2\text{D}^+$  abundance for the same conditions as in part (a). (c) Steady-state solutions of the  $\text{H}_2\text{D}^+$ -to- $\text{H}_3^+$  ratio for the same conditions as in parts (a) and (b).

## 6. Conclusion

We have shown that the interstellar medium may be considered as an *open* dynamical system interacting with the external world via cosmic rays. The nonlinear character of the chemical equations may then be probed via the occurrence of bistability. Multiple steady-state solutions can be found numerically for physical conditions that are in the range of those available in cold dark interstellar clouds. Moreover, the actual values of the reaction-rate coefficients are decisive to settle the conditions of bistability. Amongst those, the dissociative recombination of  $\text{H}_3^+$  plays a pivotal role. We find that, for typical interstellar densities, temperature or elemental depletions, the present gap between experimental results is crucial to the development of bistable solutions. The two stable solutions have very different chemical properties: the LIP solution has a low ionization fraction and favours stable saturated molecules ( $\text{O}_2$ ,  $\text{H}_2\text{O}$ , etc.) and molecular ions ( $\text{HCO}^+$ ,  $\text{N}_2\text{H}^+$ , etc.) as well as high abundances of deuterated isotopomers, corresponding to the *standard* solution described in numerous chemical models (see, for example, Bettens *et al.* 1995); whereas the HIP solution corresponds to a much larger ionization fraction, enhancing radicals and atomic ions, and represents a new solution of the chemical equations. The consequences of such a theoretical finding have yet to be demonstrated. Some chemical puzzles may be explained by the HIP solution: the large C/CO fraction observed in dense clouds, the non-detection of  $\text{O}_2$  in molecular clouds, and perhaps the low abundances of  $\text{H}_3^+$  found in some dense clouds. However, other processes that are not taken into account are at work here, such as grain-surface reactions, coupling between two different cells of gas, the role of the magnetic field, etc. Moreover, the observations display large chemical variations over very small spatial scales. Perhaps new statistical methods should be used to perform observational analyses. Finally, we stress that a manifestation of nonlinearity in the interstellar medium should be considered as quite plausible despite the fact that, until now, it has raised more questions than answers.

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