

The importance of the ortho:para H₂ ratio for the deuteration of molecules during pre-protostellar collapse

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ABSTRACT

Context. We have studied the evolution of molecular gas during the early stages of protostellar collapse, when the freeze-out of “heavy” species on to grains occurs.

Aims. In addition to studying the freeze-out of “heavy” species on to grains, we wished to compute the variation of the population densities of the different nuclear spin states of ‘tracer’ molecular ions, such as H₂D⁺ and D₂H⁺, which are currently observed only in their ortho and para forms, respectively.

Methods. Chemical processes which determine the relative populations of the nuclear spin states of molecules and molecular ions were included explicitly. Nuclear spin-changing reactions have received much less attention in the literature than those leading to deuteration; but, in fact, the former processes are as significant as the latter and often involve the same reactants. A “free-fall” model of gravitational collapse was adopted.

Results. We found that the ortho:para ratios of some species, e.g. H₂D⁺, vary considerably as the density increases. Because the dynamical timescale is much shorter than some of the chemical timescales, there can be large departures of the predictions of the free-fall model from the steady-state solution at the same density and temperature. In the case of H₂, it seems unlikely that the steady state value of the ortho:para ratio is attained before protostellar collapse from the progenitor molecular cloud commences. Values of the ortho:para H₂ ratio much higher than in steady state, which would prevail in “young” molecular clouds, are found to be inconsistent with high levels of deuteration of the gas. The internal energy of ortho-H₂ acts as a reservoir of chemical energy which inhibits the deuteration of H₃⁺ and hence of other species, such as N₂H⁺ and NH₃.

Conclusions. The principal conclusion is that the degree of deuteration of molecular ions and molecules is sensitive to the ortho:para H₂ ratio and hence to the chemical and thermal history of the precursor molecular cloud.

Key words. astrochemistry – stars: formation – ISM: molecules – submillimeter

1. Introduction

Studies of the early stages of protostellar collapse are presently at the leading edge of research in astronomy. These studies have been driven mainly by new observations, which suggest that, during an initial, approximately isothermal phase of the collapse process, molecular species containing the heavy elements, notably carbon and oxygen, are removed from the gas phase by “freeze-out” on to the surfaces of grains (Bacmann et al. 2002; Tafalla et al. 2004). Nitrogen-bearing species, specifically N₂H⁺ and NH₃, subsist longer (Bergin & Langer 1997; Belloche & André 2004) but eventually freeze out also. There remains a gas which is “fully depleted”, in the sense that only hydrogen-bearing species and helium remain.

In conditions under which CO is heavily depleted from the gas phase, H⁺ and H₃⁺ become the principal ions. The abundance of H⁺ is controlled by its recombination with electrons

on the surfaces of negatively charged grains: two-body recombination in the gas phase is a radiative process and hence slow. Indeed, the relative abundance of H⁺ and H₃⁺ during collapse depends on the surface area of negatively charged grains, per unit volume of gas, which is available for the recombination of H⁺ ions. If the rate of coagulation of the grains is insufficiently rapid, compared with the rate of collapse of the protostellar core, the grain surface area remains high and the H⁺ ions are more effectively neutralized; H₃⁺ becomes the dominant ion.

Observations have shown, and calculations have confirmed, that the abundances of the singly and multiply deuterated forms of H₃⁺ can attain exceptionally high values under conditions of extreme heavy element depletion (Caselli et al. 2003; Ceccarelli et al. 2004; Vastel et al. 2004; Walmsley et al. 2004; Ceccarelli & Dominik 2005). Furthermore, these high degrees of deuteration can propagate to the residual nitrogen-bearing species, such as N₂H⁺ and NH₃. The deuterated

isotopes of NH₃ have been detected with fractional abundances which are many orders of magnitude higher than would be anticipated on the basis of the D:H elemental abundance ratio, which is of the order of 10⁻⁵. The related reaction networks have been considered in detail by several authors (Roberts et al. 2003, 2004; Roueff et al. 2005). Deuteration occurs in deuteron-proton exchange reactions with the deuterated forms of H₃⁺. The analogous proton exchange reactions modify the relative population densities of the different possible nuclear spin states of molecules and molecular ions, such as NH₃ and H₃⁺ itself. These processes have received much less attention in the literature but are, in fact, as significant as deuteration. Observations of ortho and para forms could provide information on the physical conditions in the core during collapse. Moreover, when only one of the possible nuclear spin states of a species is observed, which is usually the case, calculations of the relative population densities provide a means of estimating the total number density of the species.

The ortho:para ratio of species such as H₃⁺ and H₂D⁺ are dependent on the ortho:para H₂ ratio and vary with the gas density in the course of the gravitational collapse. Furthermore, the degree of deuteration of H₃⁺ depends on the density of ortho-H₂, through the reaction ortho-H₂D⁺(ortho-H₂, HD)H₃⁺, which is the reverse of the process of deuteration of H₃⁺ (cf. Pineau des Forêts et al. 1991; Gerlich et al. 2002). The analogous reactions involving para-H₂ and para-H₂D⁺ are endothermic and slow at low gas temperatures. However, para-H₂D⁺ is converted into ortho-H₂D⁺ in the reaction para-H₂D⁺(ortho-H₂, para-H₂)ortho-H₂D⁺, which is exothermic. Thus, as the assumed value of the initial abundance of ortho-H₂ (equivalently, the initial ortho:para H₂ ratio) increases, both ortho- and para-H₂D⁺ are converted back to H₃⁺. Consequently, the initial degrees of deuteration, not only of H₃⁺, but also of nitrogen-bearing species such as N₂H⁺ and NH₃, fall to low values, as H₂D⁺ is the main agent of their deuteration. It should be clear from these comments that the initial value of the ortho:para H₂ ratio is critical to the composition of the collapsing gas, particularly to its level of deuteration. Indeed, the high levels of deuteration which are observed in some protostellar cores impose constraints on the initial ortho:para H₂ ratio.

Molecular hydrogen forms on grains, at a rate which is still not well determined. It is believed (and assumed here) that the ortho:para ratio of the hydrogen molecules which are formed and released into the gas phase is the statistical value of 3:1. Subsequent proton-exchange reactions with H⁺ and H₃⁺ interconvert ortho- and para-H₂. However, at low temperatures, the timescales associated with these reactions are large, owing to the low degree of ionization of the gas; this is particularly true of para to ortho conversion, which is endothermic. As we shall see below, it is certainly *not* clear that the ortho:para H₂ ratio at the commencement of gravitational collapse of the molecular gas has attained its value in steady state; and it is almost certainly higher than its value in thermal (Boltzmann) equilibrium. At low temperatures, ortho-H₂ is formed principally by H-atom recombination on the surfaces of grains, rather than through proton-exchange reactions with para-H₂ in the gas phase. Accordingly, we have treated the initial ortho:para H₂ ratio as a parameter, which we have varied

between its upper limit of 3 and its lower limit, taken to be the ratio of the populations of the $J = 1$ and $J = 0$ rotational states in thermal equilibrium at kinetic temperature T . A high fractional abundance of ortho-H₂ constitutes a major source of (internal) energy in molecular gas at low kinetic temperatures ($T \approx 10$ K): the lowest state of ortho-H₂, $J = 1$, lies approximately 170 K above the ground state of para-H₂, $J = 0$; this energy becomes available in proton-exchange reactions with ortho-H₂.

In Sect. 2, we outline the model of gravitational collapse which we have employed and consider the processes which influence the ortho:para ratios (more generally, the relative populations of the possible nuclear spin states of a given molecule or molecular ion). Section 3 contains the results of the calculations of the fractional abundances of the ions and of the relative populations of the nuclear spin states. Particular attention is paid to the influence of the initial value of the ortho:para H₂ ratio. Also, we compare the results of the calculations, following the gravitational collapse, with the values which are predicted, assuming that the medium has time to attain a steady state. The possible effects of grain coagulation are considered. In Sect. 4, we summarize our results and make our concluding remarks.

2. The model

Following the procedures and conclusions of our previous paper (Flower et al. 2005), we consider the evolution of a contracting sphere of gas and dust and apply the equations appropriate to free-fall, homologous, isothermal collapse. The timescale for free-fall collapse is

$$\tau_{\text{ff}} = \left[\frac{3\pi}{32G\rho_0} \right]^{\frac{1}{2}} \quad (1)$$

where ρ_0 is the initial mass per unit volume. For an initial gas density of $n_{\text{H}} = n(\text{H}) + 2n(\text{H}_2) = 10^4 \text{ cm}^{-3}$, the free-fall time is of the order of 10⁵ yr. The (constant) temperature was $T = 10$ K. These values of n_{H} and T are typical of those prevailing in dark molecular clouds, from which protostars form, through gravitational contraction.

The initial composition was taken to be that of a molecular gas in static equilibrium, with the elemental abundances and depletions as specified in Table 1 of Flower et al. (2005). The value of the dust:gas mass ratio was 0.0094. The chemical reaction set was a composite of our previous studies (Walmsley et al. 2004; Flower et al. 2004, 2005). It comprises reactions involving species containing H, He, C, N, O and S and distinguishes the nuclear spin states of H₃⁺ and its deuterated isotopes, in addition to those of H₂⁺ and H₂ (see Sect. 2.1 below). Following the discussion in Sect. 4.4 of Flower et al. (2005), we have continued to adopt a grain sticking coefficient $S(\text{N}) = 0.1$ for atomic nitrogen, and, with a view to internal consistency, we have taken $S(\text{O}) = 0.1$ also. For all other atomic and molecular species, $S = 1.0$. The rate of cosmic ray ionization of hydrogen was taken to be $\zeta = 1 \times 10^{-17} \text{ s}^{-1}$, as in our previous paper.

The initial grain radius was taken to be $a_{\text{g}} = 0.05 \mu\text{m}$. As shown in our previous paper (Flower et al. 2005), this

value of a_g yields approximately the same grain opacity, $n_g \pi a_g^2$ (where n_g is the grain number density), as the grain size distribution of Mathis et al. (1977), with limits of $0.01 \leq a_g \leq 0.3 \mu\text{m}$.

The validity of assuming static equilibrium, particularly for the ortho:para H₂ ratio, will be considered below. In view of the importance of the ortho:para H₂ ratio – which becomes apparent from the results presented in Sect. 3 – we have varied its initial value between the statistical ratio of 3 and the ratio of 3.6×10^{-7} , which corresponds to Boltzmann equilibrium (Eq. (2) below) at $T = 10$ K.

2.1. Nuclear spin statistics

In the calculations reported below, the abundances not only of the chemical species but also of their individual nuclear spin states have been determined, where applicable. The cases of interest here involve molecules or molecular ions comprising two or more protons, such as H₂. Fermi-Dirac statistics require that the nuclear wave function should be asymmetric under exchange of identical protons, and this restriction associates states of given nuclear spin symmetry with states of appropriate rotational symmetry. Thus, in the case of H₂, states with total nuclear spin $I = 0$ (para-H₂) are associated with rotational states with even values of the rotational quantum number, J ; states with $I = 1$ (ortho-H₂) are associated with odd J . Transitions between states of differing nuclear spin, $I = 0$ and $I = 1$ in this example, are induced by proton-exchange reactions with H⁺ and H₃⁺. (Although HCO⁺ is initially the most abundant ion which might undergo proton exchange with H₂, the measurement by Huntress (1977) of the rate coefficient at $T = 300$ K for the reaction HCO⁺(D₂, HD)DCO⁺ suggests that the analogous reaction with H₂ is probably too slow to be significant.) In view of the importance of H₂ in the chemistry of molecular clouds, it might be anticipated that its ortho:para ratio would influence the analogous ratios in other molecules and molecular ions.

In order to provide a framework for the interpretation of the numerical results which will be presented in the following section, we shall establish first the values of the relative populations of the nuclear spin states of a number of key species, in static equilibrium, on the basis of an analysis which is necessarily statistical in nature.

2.1.1. H₂

We assume that ortho- and para-H₂ are formed (on grains) in the statistical ratio of 3:1, i.e. the ratio of the corresponding values of $(2I + 1)$. Subsequent radiative cascade leads to the $J = 1$ ($I = 1$) and $J = 0$ ($I = 0$) levels of the ground vibrational state, which are separated by 170.5 K. The rates of cosmic ray dissociation and ionization of H₂ are taken to be independent of the total nuclear spin, I . At the low temperature which we consider ($T = 10$ K), proton-exchange reactions convert ortho-H₂

to para-H₂; the reverse reaction is insufficiently rapid at low T for the ortho:para ratio to attain its Boltzmann value,

$$\frac{n(J = 1)}{n(J = 0)} = 9 \exp\left(\frac{-170.5}{T}\right) \quad (2)$$

where the factor of 9 corresponds to the ratio of the statistical weights, $(2I + 1)(2J + 1)$, of these ortho ($J = 1$) and para ($J = 0$) levels. At $n_{\text{H}} = 10^4 \text{ cm}^{-3}$, the steady-state value of $n(J = 1)/n(J = 0)$ is 2.7×10^{-3} , which is much larger than the value of this ratio (3.6×10^{-7}) in Boltzmann equilibrium at $T = 10$ K. In other words, at low temperatures, ortho-H₂ is formed principally by H-atom recombination on the surfaces of grains, rather than from para-H₂ in the gas phase, through proton-exchange reactions with H⁺ and H₃⁺. At a higher temperature of $T = 30$ K, the steady-state value of $n(J = 1)/n(J = 0)$ (3.3×10^{-2}) is much closer to its value in Boltzmann equilibrium at this temperature (3.1×10^{-2} ; cf. Fig. 1), as would be expected.

2.1.2. H₂⁺

H₂⁺ is formed through cosmic ray ionization of H₂, and hence the rates of production of ortho- and para-H₂⁺ are proportional to the number densities of ortho- and para-H₂, respectively. Both ortho- and para-H₂⁺ are destroyed by para-H₂, which is the much more abundant of the two forms of H₂, at equal rates, yielding H₃⁺. It follows that the ortho:para ratio of H₂⁺ is essentially the same as that of H₂.

2.1.3. H₃⁺

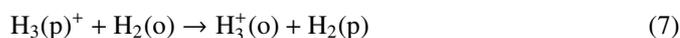
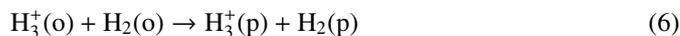
Para-H₃⁺ forms principally from para-H₂⁺ and para-H₂, which are the more abundant forms of H₂⁺ and H₂, respectively,



whereas ortho-H₃⁺ is produced from either ortho-H₂⁺ and para-H₂ or para-H₂⁺ and ortho-H₂,



with the same total rate coefficient ($2.1 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$). Recalling that the ortho:para ratio of H₂⁺ is essentially the same as that of H₂, we conclude that the ortho:para H₃⁺ ratio expected from considerations of its formation and destruction alone is the same as the ortho:para H₂ ratio. However, proton-exchange reactions of H₃⁺ with H₂ modify the ortho:para H₃⁺ ratio. The proton-exchange reactions of the lowest energy states of ortho- and para-H₃⁺ with para-H₂ are both endoergic, by 137.6 K and 203.4 K, respectively, and consequently negligible at $T = 10$ K. On the other hand, the reverse reactions with ortho-H₂



are exoergic and would yield a ratio of ortho:para H₃⁺ of 4:1, as may be seen from the following argument.

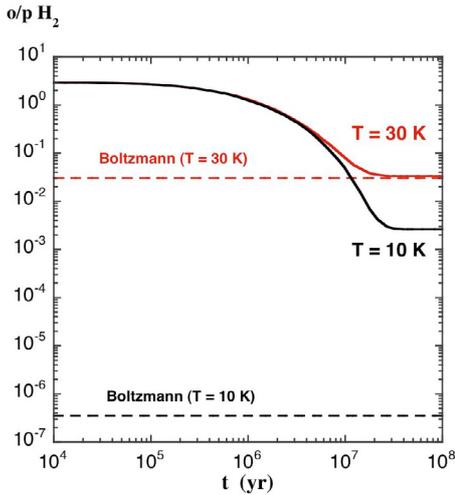


Fig. 1. The ratio of abundances of ortho- and para-H₂ as a function of time, t , from an assumed initial value of 3 through to the attainment of steady state. A constant gas density of $n_{\text{H}} = 10^4 \text{ cm}^{-3}$ and temperatures $T = 10 \text{ K}$ and $T = 30 \text{ K}$ were adopted. The ortho:para ratios in Boltzmann equilibrium are shown for both values of T .

The statistical weight of the lowest level of para-H₃⁺ is 2, and that of ortho-H₃⁺ is 4. The rate coefficient for a reaction is taken proportional to the ratio of the combined (by multiplication) statistical weight of the products to that of the reactants. Thus, the rate coefficient for the reaction (7) is taken to be 4 times larger than for reaction (6).

In equilibrium, the population densities of ortho- and para-H₃⁺ are found to be comparable, i.e. the proton-exchange reactions with ortho-H₂ dominate. As a consequence, the ortho:para H₃⁺ ratio depends on the density of ortho-H₂ and hence on ortho:para H₂ ratio.

3. Results

3.1. Initial abundances

The elemental abundances and their initial repartition between the gas and the solid phases were taken from Table 1 of Flower et al. (2005); the value of the dust:gas mass ratio was 0.0094. The chemical composition of the gas, in steady state, was determined by running a time-dependent calculation, at a constant density $n_{\text{H}} = 10^4 \text{ cm}^{-3}$ and kinetic temperature $T = 10 \text{ K}$, neglecting any further freeze-out on to the grains, until the fractional abundances became constant. Under these conditions, the steady-state value of the ortho:para H₂ ratio is 2.7×10^{-3} .

Flower & Pineau des Forêts (1990) and Pineau des Forêts et al. (1991) studied the isobaric thermal and chemical evolution of interstellar clouds, from initially atomic to finally molecular gas which had attained a steady state; the values of the gas pressure which they considered were similar to the initial value adopted here ($n_{\text{H}}T = 10^5 \text{ cm}^{-3} \text{ K}$). Their studies showed that the timescale for establishing the steady-state value of the ortho:para H₂ ratio is particularly large, in excess of 10^7 yr . At time $t \approx 10^6 \text{ yr}$, the formation of H₂ on grains gives rise to a local maximum of the ortho:para ratio, which approaches the statistical value of 3:1 associated with the

formation process. The ortho:para ratio subsequently falls towards its steady-state value, which is reached at $t \approx 10^7 \text{ yr}$; the steady-state value of the ratio exceeds that in Boltzmann equilibrium (Eq. (2)). Thus, during the time interval $10^6 \lesssim t \lesssim 10^7 \text{ yr}$, the ortho:para H₂ ratio in the molecular gas remains larger than its final, steady-state value.

In Fig. 1 is plotted the ratio of ortho- to para-H₂ as a function of time, t , at a constant gas density of $n_{\text{H}} = 10^4 \text{ cm}^{-3}$ and kinetic temperatures $T = 10 \text{ K}$ and $T = 30 \text{ K}$; the initial value was taken to be 3, corresponding to the statistical ratio associated with the formation of H₂ on grains. Figure 1 shows that the time required for the ratio of ortho- to para-H₂ to attain its steady-state value (2.7×10^{-3} at $T = 10 \text{ K}$ and 3.3×10^{-2} at $T = 30 \text{ K}$) is approximately $3 \times 10^7 \text{ yr}$; this time is comparable with a recent determination, by Tassis & Mouschovias (2004), of the lifetimes of molecular clouds ($\approx 10^7 \text{ yr}$). (We note that Hartmann et al. (2001) estimated the ages of clouds in the solar vicinity as being of the order of 10^6 yr .) We conclude that it is probable that the ortho:para H₂ ratio does not reach its steady-state value before protostellar collapse begins. Accordingly, we have varied the initial value of the ortho:para H₂ ratio between the statistical value of 3 and 3.6×10^{-7} , corresponding to Boltzmann equilibrium at $T = 10 \text{ K}$. It transpires that the initial value of this ratio is critical not only to the populations of the nuclear spin states of H₃⁺ and its deuterated isotopes but, perhaps more significantly, also to the degree of deuteration of H₃⁺ (cf. Pineau des Forêts et al. 1991).

We see from Fig. 1 that, for $T = 30 \text{ K}$, the ortho:para H₂ ratio in steady-state is close to its value in thermodynamic equilibrium, whereas this is not the case for $T = 10 \text{ K}$. At low temperatures, the direct formation of ortho-H₂ on grains is more rapid than the endoergic proton-exchange reactions of H⁺ and H₃⁺ with para-H₂. The value of the kinetic temperature, T_{cr} , below which the steady-state value of the ortho:para ratio exceeds its value in Boltzmann equilibrium may be estimated by equating these two rates of formation of ortho-H₂. Noting that ortho- and para-H₂ are assumed to form, on grains, in the statistical ratio of 3:1, and equating the total rate of formation of H₂ to the rate of its destruction by cosmic rays, we obtain $T_{\text{cr}} \approx 20 \text{ K}$ for the parameters adopted in the present calculations. In general, when $T \lesssim T_{\text{cr}}$, the initial ortho:para H₂ ratio depends on the thermal history of the core.

3.2. Depletion during collapse

In Fig. 2, we show the fractional abundances of CO and selected isotopes of H₃⁺ as functions of the gas density, n_{H} , for our “reference” model of collapse. We note that density is related to age through the equation for free-fall collapse.

The tracer molecule, CO, is already significantly depleted (through freeze-out) by the time that $n_{\text{H}} = 3 \times 10^4 \text{ cm}^{-3}$, whereas the fractional abundances of H₂D⁺ and D₃⁺ increase until much higher densities, $n_{\text{H}} > 3 \times 10^5 \text{ cm}^{-3}$, corresponding to later times. It is clear that, in this model, deuterium fractionation occurs at densities for which CO is practically completely depleted (as is N₂ also). In order to achieve high levels of deuterium fractionation in molecules such as NH₃, it is

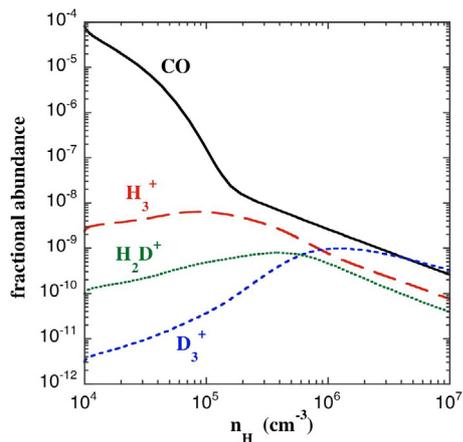


Fig. 2. The fractional abundances of CO and selected isotopes of H₃⁺ as functions of the gas density, n_{H} , for a constant kinetic temperature, $T = 10$ K (our “reference” model of collapse). The initial value of the ortho:para H₂ ratio is 2.7×10^{-3} .

necessary to minimize the difference between the critical densities (or the corresponding times) at which (i) heavy species, such as CO and N₂, have frozen out, and (ii) deuterium fractionation, through reactions with H₂D⁺ and the other deuterated forms of H₃⁺, has begun.

3.3. Steady-state vs. free-fall

In our previous paper (Flower et al. 2005, Fig. 6), we compared the fractional abundances of H⁺, H₃⁺ and e⁻, in steady-state and as predicted by the free-fall model, for densities $2 \times 10^5 \leq n_{\text{H}} \leq 2 \times 10^7 \text{ cm}^{-3}$. The comparison was made in the limit of complete heavy element depletion. At times which are sufficiently large for steady state to be attained, essentially all the species containing elements heavier than He are frozen on to the grains. The agreement between the two calculations was found to be good, for the species listed above; but the deuterated isotopes of H₃⁺ were not included in the collapse model, and neither were the various possible nuclear spin modifications. We are now in a position to make such comparisons in considerably more detail. However, for reasons which will now be given, we have chosen to make the comparison in a somewhat different way from that followed in our previous paper.

The free-fall collapse is initiated at a density $n_{\text{H}} = 10^4 \text{ cm}^{-3}$ and for a given repartition of the elements between the gas and solid phases (cf. Sect. 3.1 above). In the course of the free-fall collapse, atoms and molecules continue to freeze on to the grains, on a timescale which is comparable with the free-fall time. Thus, the degree of depletion of the heavy elements from the gas phase increases with time and hence with the density of the medium. When comparing the “collapse” model with the “steady-state” solution, we adopt the composition of the gas at a given density on the collapse profile and then compute the corresponding steady-state solution, at a time $t > 10^8$ yr, keeping constant both the density and the degree of depletion of the gas. This procedure ensures that the comparison reflects departures of the free-fall model from steady state for *all* times

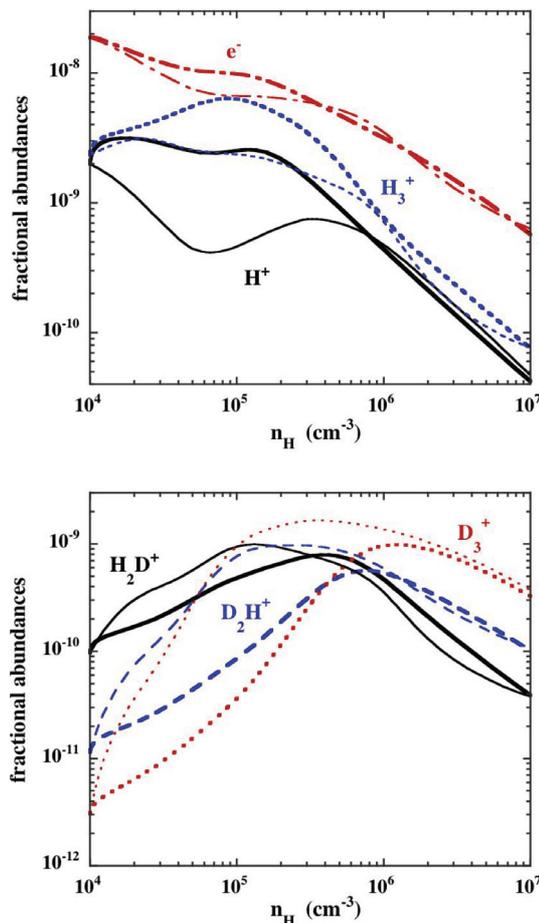


Fig. 3. The fractional abundances, relative to n_{H} , of **a)** H⁺ (full curve), H₃⁺ (broken curve) and e⁻ (chain curve), and **b)** H₂D⁺ (full curve), D₂H⁺ (long-dashed curve) and D₃⁺ (short-dashed curve), as functions of n_{H} . The bold curves are the predictions of the free-fall model, the light curves are the corresponding results in steady-state.

(densities), including those which fall short of the “complete depletion” limit.

3.3.1. Fractional abundances of ions

First, we compare the abundances of H⁺ and H₃⁺, computed in steady-state and following the free-fall collapse: see Fig. 3a. In the present calculations, the deuterated isotopes of H₃⁺ and their nuclear spin modifications have been included in the calculations. For the purposes of this first comparison, we sum the fractional abundances of ortho- and para-H₃⁺. Reactions leading to the deuteration of heavy species (those containing elements heavier than He, specifically NH₃ and N₂H⁺) have not been included explicitly in the present model. Nonetheless, qualitative conclusions regarding the degrees of deuteration of such species can still be drawn, in so far as the deuterated isotopes of H₃⁺ are primarily responsible for the deuterium fractionation of heavy molecules. We note that the abundances of the deuterated isotopes of H₃⁺ are determined mainly by reactions such as H₃⁺(HD, H₂)H₂D⁺, which determine the degree of deuteration of H₃⁺, and not by reactions with heavy molecules, such as CO, whose fractional abundances become rapidly much

smaller than that of HD, owing to freeze-out. Comparison calculations have shown that, at densities $n_{\text{H}} \gtrsim 10^5 \text{ cm}^{-3}$, at which the fractional abundances of the deuterated isotopes of H₃⁺ become significant (cf. Fig. 2), the reactions with CO have no effect on their fractional abundances.

The results of the two calculations (steady-state and free-fall collapse) are in agreement for densities $n_{\text{H}} \gtrsim 10^6 \text{ cm}^{-3}$, for which complete freeze-out has effectively occurred. At lower densities, $n_{\text{H}} \approx 10^5 \text{ cm}^{-3}$, the steady-state solutions underestimate the fractional abundances of both H⁺ and H₃⁺ – the former by approximately a factor of 5. Protons are removed by charge transfer reactions with neutral species whose ionization potentials are less than that of atomic hydrogen. As the heavy neutrals freeze on to the grains, the fractional abundance of H⁺ begins to increase, and ultimately the steady-state solution merges with the results of the collapse model. The timescale for establishing ionization equilibrium is small (of the order of 1000 yr, for $n_{\text{H}} = 10^4 \text{ cm}^{-3}$) compared with the equilibrium timescale of the chemistry as a whole (Walmsley et al. 2004). Consequently, the free electron density calculated by the collapse model exceeds the steady-state value by no more than about 50% over the entire range of density, n_{H} .

The reason that the steady-state solution underestimates the fractional abundance of H₃⁺ in the vicinity of $n_{\text{H}} = 10^5 \text{ cm}^{-3}$ may be seen by referring to Fig. 3b, where the fractional abundances of the deuterated isotopes of H₃⁺ are plotted. In essence, the steady-state solutions overestimate the degree of deuteration of H₃⁺ at intermediate densities. The level of agreement between the steady-state and free-fall collapse calculations deteriorates as the degree of deuteration of H₃⁺ increases, i.e. in the sense H₂D⁺, D₂H⁺, D₃⁺; see Fig. 3b. The differences between the steady-state abundances of these species, and those calculated following the free-fall collapse, are significant in the context of the deuteration of molecules such as NH₃, for which deuteron-transfer and proton-deuteron exchange reactions with the deuterated isotopes of H₃⁺ are crucially important. We note that the analogous proton-transfer and proton-exchange reactions with H₃⁺, H₂D⁺ and D₂H⁺ contribute to ortho-para conversion in NH₃. It follows that the issues of the degree of deuteration of NH₃, on the one hand, and the relative population densities of its ortho and para nuclear spin states, on the other hand, are inter-related (cf. Pineau des Forêts et al. 1991).

3.3.2. Relative population densities of nuclear spin states

In Fig. 4 are compared the relative populations of the two lowest nuclear spin states of H₃⁺, H₂D⁺, D₂H⁺ and D₃⁺. In each case, the ortho:para H₂ ratio (specifically, the ratio $n(J=1):n(J=0)$) is plotted, for reference. We see from Fig. 4 that there are large discrepancies between the predictions of the free-fall collapse model and the equivalent steady-state calculations. The ortho:para H₃⁺ and H₂D⁺ ratios are correlated with that of H₂, owing to the importance of proton exchange with H₂. Thus, the underestimation (in steady-state) of the ortho:para H₂ ratio results in the ortho:para H₃⁺ and H₂D⁺ ratios being

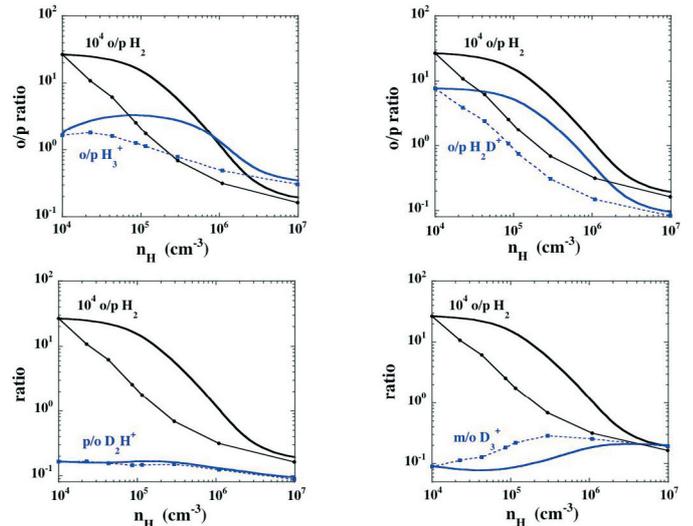


Fig. 4. The relative abundances of the two lowest nuclear spin states (in the sense of energetically higher:lower) of H₃⁺, H₂D⁺, D₂H⁺ and D₃⁺ as functions of n_{H} , as predicted by the free-fall model (bold curves). The corresponding values in steady-state are shown as the light curves joining the symbols (full circles for H₂, full squares for the other species).

underestimated also – by more than an order of magnitude in the case of H₂D⁺ at $n_{\text{H}} = 10^5 \text{ cm}^{-3}$. (We note that the ortho:para H₂D⁺ ratio is initially large (at $n_{\text{H}} = 10^4 \text{ cm}^{-3}$), owing to proton-exchange reactions with ortho-H₂, which are statistically favourable to the production of ortho-H₂D⁺ (Walmsley et al. 2004).)

In steady state, the relative value of the population densities of the meta and ortho nuclear spin states of D₃⁺ is determined principally by deuteron exchange reactions with HD, which favour energetically the production of ortho-D₃⁺ (specifically, the ground state of the ion; the first excited state is the lowest state of meta symmetry). However, as noted in Appendix B of Flower et al. (2004), the reaction meta-D₃⁺(ortho-H₂, HD)ortho-D₂H⁺, which is endoergic by only 18 K, removes meta-D₃⁺, even at low T . Whilst this reaction is of secondary importance *in steady state* at $n_{\text{H}} = 10^5 \text{ cm}^{-3}$, owing to the decrease in the ortho:para H₂ ratio with increasing n_{H} , it dominates the removal of meta-D₃⁺ in the free-fall model at $n_{\text{H}} = 10^5 \text{ cm}^{-3}$, for which the ortho:para H₂ ratio is much higher than in steady state (see Fig. 4). As a consequence, the meta:ortho D₃⁺ ratio is lower at $n_{\text{H}} = 10^5 \text{ cm}^{-3}$ in the free-fall model than in steady state at the same density.

3.4. Dependence on the initial ortho:para H₂ ratio

The ortho:para H₂ ratio is important in establishing the relative populations of the nuclear spin states of a number of species, as the discussion in Sect. 2 should have made clear. Furthermore, the initial value of this ratio proves to be critical to the degree of deuteration of H₃⁺ during free-fall collapse. For the purposes of the illustrations which follow, grain coagulation has been neglected.

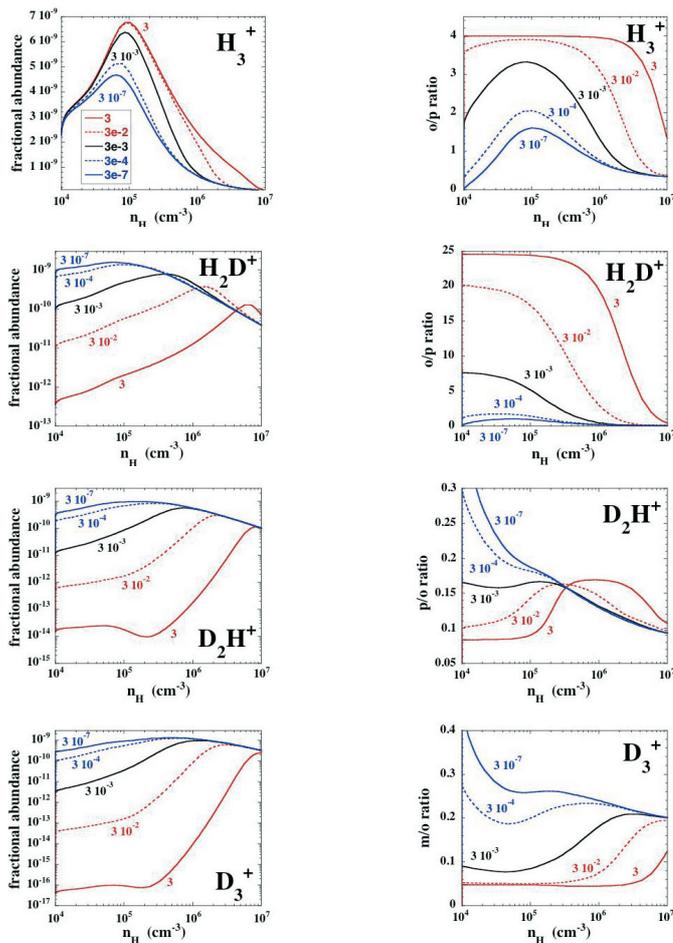


Fig. 5. The fractional abundances, relative to $n_{\text{H}} \approx n(\text{H}) + 2n(\text{H}_2)$, of H_3^+ , H_2D^+ , D_2H^+ and D_3^+ as functions of the gas density, n_{H} , at a constant temperature $T = 10$ K. Results are shown for five values of the ortho:para H_2 ratio, between the statistical value of 3 and 3.6×10^{-7} , the ratio in Boltzmann equilibrium at $T = 10$ K. The computed values of the relative populations of nuclear spin states of the same species are also shown, in the sense of the population of the energetically higher state divided by that of the lower.

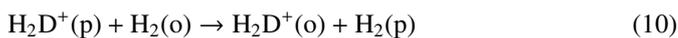
In Fig. 5 are shown both the fractional abundances and the relative populations of the nuclear spin states of H_3^+ , H_2D^+ , D_2H^+ and D_3^+ . It is apparent from this figure that the fractional abundances of H_2D^+ and more highly deuterated isotopes of H_3^+ are strongly dependent on the initial ortho:para H_2 ratio – whose value is varied between 3 and 3.6×10^{-7} (the ratio in Boltzmann equilibrium at $T = 10$ K) – even at densities as high as $n_{\text{H}} = 10^6 \text{ cm}^{-3}$. This dependence arises from the reactions



and

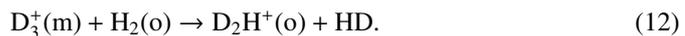
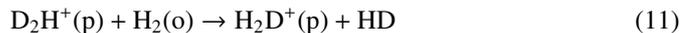


which remove directly ortho- H_2D^+ and indirectly para- H_2D^+ , which is converted into ortho- H_2D^+ by the proton-exchange reaction



which occurs, once again, with ortho- H_2 . Reactions (8) and (9) are the reverse of the reactions of ortho- and para- H_3^+ with HD, which are responsible for the deuteration of H_3^+ ; as the initial ortho:para H_2 ratio increases, the deuteration of H_3^+ is inhibited effectively by these reverse reactions.

From Fig. 5, we see that the populations of the energetically higher nuclear spin states (i.e. the ortho states) of H_3^+ and H_2D^+ increase, relative to the lower (para) states, as the ortho:para H_2 ratio rises, whereas it is the *lower* states of the multiply-deuterated isotopes, D_2H^+ and D_3^+ , which become relatively more populated. Proton-exchange reactions, such as (10) and the analogous reaction involving H_3^+ , are enabled by the internal excitation energy (170 K) of ortho- H_2 , which acts as a reservoir of chemical energy. The net effect is the transfer of population to the excited (ortho) states of H_2D^+ and H_3^+ . In the case of H_2D^+ , essentially all of the population is in the ortho state at low gas densities and high ortho:para H_2 ratios. On the other hand, the excited nuclear spin states of the multiply-deuterated species, D_2H^+ and D_3^+ , are *removed* preferentially by ortho- H_2 in the reactions



Reaction (11) is exothermic, and reaction (12) is endothermic, but by only 18 K. (The corresponding reactions of ortho- H_2 with ortho- D_2H^+ and ortho- D_3^+ are less energetically favourable, as the reacting ion is in its ground state.)

In Fig. 6 are plotted the fractional abundances of ortho- H_2D^+ and para- D_2H^+ as functions of the gas density, n_{H} , in the course of the collapse. Both these species have been observed in protostellar cores, with fractional abundances of the order of 10^{-10} (Caselli et al. 2003; Vastel et al. 2004); the fractional abundances of ortho- H_2D^+ in L1544 (Caselli et al. 2003) and IRAS 16293E (Vastel et al. 2004), and the fractional abundance of para- D_2H^+ in IRAS 16293E, deduced from the observations of Vastel et al. (2004), are indicated. The ortho:para H_2 ratio which is inferred from the observations is sensitive to the gas density. In the case of IRAS 16293E, if one adopts a density of $4 \times 10^6 \text{ cm}^{-3}$ (cf. Lis et al. 2002), all models with an initial ortho:para H_2 ratio below 3 are consistent with the observations. For the lower density of L1544 ($6 \times 10^5 \leq n_{\text{H}} \leq 2 \times 10^6 \text{ cm}^{-3}$), the data suggest an initial ortho:para ratio which is within an order of magnitude of its steady-state value of 2.7×10^{-3} at $n_{\text{H}} = 10^4 \text{ cm}^{-3}$. More definitive conclusions must await not only further observations but also the introduction of temperature and density gradients into the models of the cores.

3.5. Influence of coagulation

The coagulation of grains in the course of the collapse was considered in our previous paper (Flower et al. 2005). The critical velocity, below which two colliding grains of radius a_{g} are assumed to coagulate, was taken to be

$$v_{\text{crit}} \propto a_{\text{g}}^{-\frac{5}{6}}$$

following Chokshi et al. (1993). In the extreme cases which we considered, the constant of proportionality was taken equal

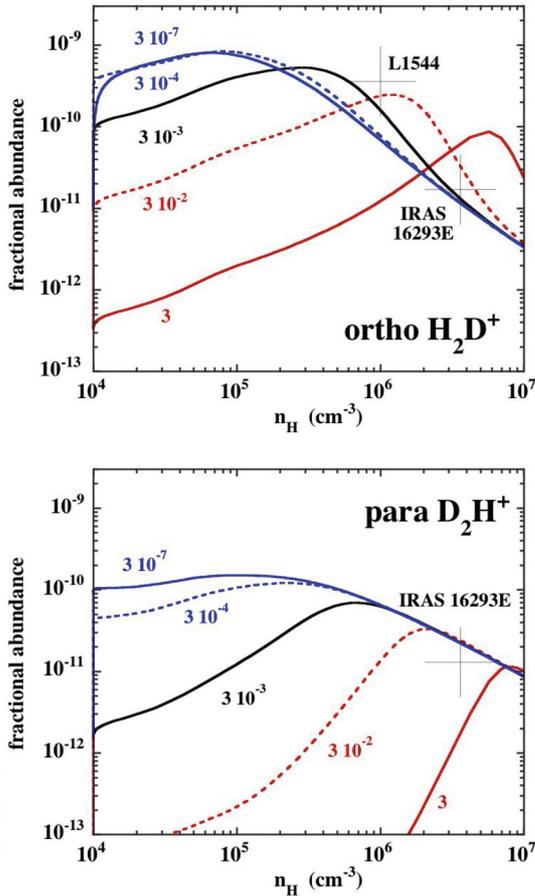


Fig. 6. The fractional abundances, relative to $n_{\text{H}} \approx n(\text{H}) + 2n(\text{H}_2)$, of ortho- H_2D^+ and para- D_2H^+ as functions of the gas density, n_{H} , at a constant temperature $T = 10$ K. Results are shown for five initial (i.e. at $n_{\text{H}} = 10^4 \text{ cm}^{-3}$) values of the ortho:para H_2 ratio, between the statistical value of 3 and 3.6×10^{-7} , the ratio in Boltzmann equilibrium at $T = 10$ K. The fractional abundance of ortho- H_2D^+ in L1544 (Caselli et al. 2003) and IRAS 16293E (Vastel et al. 2004), and the fractional abundance of para- D_2H^+ in IRAS 16293E (Vastel et al. 2004), are indicated, as are the densities believed to prevail in these cores.

to either 0 or 0.4 (with v_{crit} in cm s^{-1} and a_{g} in cm), corresponding, respectively, to no coagulation or a critical velocity for coagulation which is consistent with the measurements of Poppe & Blum (1997). The discussion so far has been concerned exclusively with the limit of no coagulation; now we shall compare with results obtained on including coagulation, with $v_{\text{crit}} = 0.4 a_{\text{g}}^{-\frac{5}{6}}$; see Fig. 7.

In Figs. 7a and 7b are compared the results of calculations, with and without coagulation, of the fractional abundances of H^+ , H_3^+ and its isotopes, and of the free electrons. From these figures, it is apparent that the main effect of coagulation is that, at high densities, H^+ becomes the principal ion; this is because the rate of recombination of H^+ with electrons on the surfaces of (negatively charged) grains decreases with decreasing grain surface area and hence with the degree of coagulation (cf. Flower et al. 2005). To the higher density of H^+ there correspond lower values of the ortho:para ratios of H_2 , H_3^+ and H_2D^+ , as may be seen from Figs. 7c and 7d.

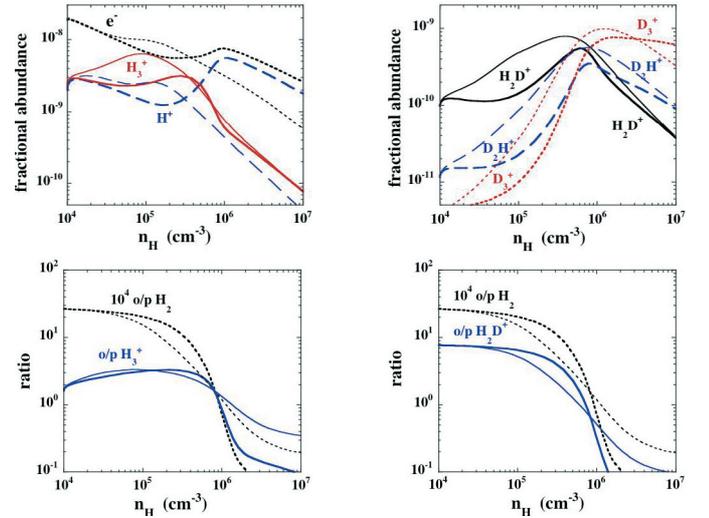


Fig. 7. The fractional abundances of **a)** H_3^+ and **b)** its isotopes, as functions of n_{H} , as predicted by the free-fall model including (bold curves) and excluding (corresponding light curves) coagulation; see Sect. 3.5. The fractional abundances of H^+ and of the free electrons are also plotted in panel **a)**. The ortho:para ratios of H_2 , H_3^+ and H_2D^+ are displayed in panels **c)** and **d)**.

In effect, the excited (ortho) states are more rapidly depopulated when the density of H^+ is higher, and so the ortho:para ratios decrease towards their values in Boltzmann equilibrium: $9 \exp(-170.5/T)$ for the ortho:para H_2 ratio; $2 \exp(-32.9/T)$ for the ortho:para H_3^+ ratio; and $9 \exp(-86.4/T)$ for the ortho:para H_2D^+ ratio.

4. Concluding remarks

We have studied the population densities of molecules and molecular ions during the early stages of protostellar collapse, including H_3^+ and its deuterated isotopes, in their various nuclear spin states. The results of a free-fall simulation were compared with the corresponding steady-state calculation, for densities in the range $10^4 \leq n_{\text{H}} \leq 10^7 \text{ cm}^{-3}$. Calculations at this level of detail are required because current observations of the deuterated isotopes of H_3^+ (H_2D^+ , D_2H^+) relate to *specific nuclear spin states*. The simulations show that there can be large discrepancies between the “free-fall” and “steady-state” results during the early stages of collapse.

In general, the computed population densities of the different nuclear spin states of molecules and molecular ions differ considerably from their values in Boltzmann equilibrium. A striking and important example is H_2 , for which the ratio of population densities $n(J = 1):n(J = 0)$, computed in steady state in Boltzmann equilibrium by 4 orders of magnitude. Furthermore, the value of the ortho:para H_2 ratio computed following the isothermal free-fall collapse exceeds the steady-state value by more than an order of magnitude at $n_{\text{H}} = 10^5 \text{ cm}^{-3}$. It is this overabundance which underlies the importance of ortho- H_2 in inducing population transfer between the different

nuclear spin states of molecular ions, such H₃⁺ and H₂D⁺, at low temperatures.

In view of the long timescales associated with the processes involved, it seems unlikely that the ortho:para H₂ ratio will reach its steady-state value prior to the commencement of gravitational collapse. Present observations of the protostellar cores L1544 (Caselli et al. 2003) and IRAS 16293E (Vastel et al. 2004) are consistent with this statement; but the uncertainties in the observations and the limitations of the current model are such that definitive conclusions cannot be drawn. Our calculations show that values of the ortho:para H₂ ratio higher than in steady state lead to a reduction in the degree of deuteration of H₃⁺. As H₂D⁺ and D₂H⁺ are the main agents of deuteration of other species, such as N₂H⁺ and NH₃, a decrease in the level of deuteration of H₃⁺ implies lower levels of deuteration of these other species. High values of the ortho:para H₂ ratio will occur earlier in the lifetime of the progenitor molecular cloud. Thus, one of the predictions of the present study is that protostars forming in “young” ($t \lesssim 10^6$ yr) molecular clouds should *not* display high levels of deuteration, owing to the higher prevailing values of the ortho:para H₂ ratio.

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