ORTHOMATIC AND THE AGE OF INTERSTELLAR DARK CLOUDS

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ABSTRACT

Interstellar dark clouds are the sites of star formation. Their main component, dihydrogen, exists under two states, ortho and para. H₂ is supposed to form in the ortho:para ratio (OPR) of 3:1 and to subsequently decay to almost pure para-H₂ (OPR ≤ 0.001). Only if the H₂ OPR is low enough, will deuteration enrichment, as observed in the cores of these clouds, be efficient. The second condition for strong deuteration enrichment is the local disappearance of CO, which freezes out onto grains in the core formation process. We show that this latter condition does not apply to DCO⁺, which, therefore, should be present all over the cloud. We find that an OPR ≥ 0.1 is necessary to prevent DCO⁺ large-scale apparition. We conclude that the inevitable decay of ortho-H₂ sets an upper limit of ~6 million years to the age of starless molecular clouds under usual conditions.

Key words: astrochemistry – evolution – ISM: abundances – ISM: clouds – ISM: molecules

1. INTRODUCTION

The low-mass star formation process is relatively well understood, however its first step details remain uncertain, especially regarding the question of time and age. Still much debated questions are how long it takes for a cloud to form from the diffuse atomic medium, how long a molecular cloud lives, and how long it takes to form a condensation that will evolve into a prestellar core that subsequently collapses to form a protostar. Today, much debate exists upon the lifetime of clouds, e.g., Hartmann et al. (2001) defending a short lifetime (one to a few million years) while Tassis & Mouschovias (2004) and Mouschovias et al. (2006) claim a typical age of 10 million years, but most arguments are either of limited statistical significance or model dependent (unknown magnetic field strength, small-scale turbulence rapid dissipation, etc.). Clues are needed and while the usual chemical age modeling is not satisfying (problem of unknown initial conditions), we present here a simple constraint based on basic chemistry: the absence of DCO⁺ in dark cloud envelopes can only be explained if the clouds are young enough and we propose to determine an upper limit for this age which is as much independent from the initial conditions as possible.

2. THE ABUNDANCE OF CO AND DCO⁺, AND THE DEUTERIUM CHEMISTRY

Dark clouds contain dust grains embedded in interstellar gas, itself mostly molecular as these clouds are self-shielded against our Galaxy’s UV background. These dark clouds are cold (typically 10 K, with cores as low as 7 K; Pagani et al. 2003, 2005), and deep inside, where the density reaches a few 10⁴ cm⁻³, the heavy species freeze out onto grains to form ices. Both these ices and the gas are subject to a rich chemistry. Recently, strong deuteration (deuterium enhancement with respect to hydrogen carriers: DCO⁺ versus HCO⁺, HDCO and D₂CO versus H₂CO, etc.) has been recognized as a useful tool to better understand both the chemistry itself and the star formation process (Bergin & Tafalla 2007; Ceccarelli et al. 2007).

H₂ is the main hydrogen reservoir in dark clouds, and similarly, HD is the main deuterium reservoir. Its relative abundance to H₂ is ~3 × 10⁻⁵ (Hébrard 2006; Linsky et al. 2006). Watson (1976) was the first to invoke chemical deuterium enrichment via the important reaction

H₃⁺ + HD → H₂D⁺ + H₂ + ΔE. (1)

ΔE = 232 K when all species (reactants and products) are in their ground state. In cold dark clouds, the forward reaction is strongly favorable, creating H₂D⁺/H₂⁺ ratios much larger than the original HD/H₂ ratio. If CO is abundant (X[CO] ≈ 1.5 × 10⁻⁴, where [X] denotes the relative abundance of a species with respect to H₂), H₃⁺ reacts five times more often with CO than with HD, and forms HCO⁺, strongly decreasing the abundance of H₂D⁺.

Once H₂D⁺ is formed, it can be enriched in deuterium by reacting with HD again to form D₂H⁺ as first recognized by Roberts et al. (2003):

H₂D⁺ + HD → D₂H⁺ + H₂ + 187 K (2)

D₂H⁺ + HD → D⁺ + H₂ + 234 K. (3)

These two reactions are again favorable in the forward direction at low temperatures because of their exothermicity. Then, these H₂D⁺ isotopologues can easily transfer their deuterons to other species:

CO + H₂D⁺ → \( \frac{2}{3} \) HCO⁺ + \( \frac{1}{3} \) DCO⁺ + \( \frac{1}{3} \) H₂ + \( \frac{2}{3} \) HD (4)

CO + D₂H⁺ → \( \frac{1}{3} \) HCO⁺ + \( \frac{2}{3} \) DCO⁺ + \( \frac{1}{3} \) HD + \( \frac{2}{3} \) D₂ (5)

CO + D⁺ → DCO⁺ + D₂ (6)

N₂ + H₂D⁺ → \( \frac{2}{3} \) N₂H⁺ + \( \frac{1}{3} \) N₂D⁺ + \( \frac{1}{3} \) H₂ + \( \frac{2}{3} \) HD (7)

N₂ + D₂H⁺ → \( \frac{1}{3} \) N₂H⁺ + \( \frac{2}{3} \) N₂D⁺ + \( \frac{1}{3} \) HD + \( \frac{2}{3} \) D₂ (8)

N₂ + D⁺ → N₂D⁺ + D₂. (9)
When CO is abundant, H$_2$D$^+$ is much less abundant as noted above and also reacts with CO preferentially, quenching all the other deuteration paths. CO also reacts with species like N$_2$H$^+$ and N$_2$D$^+$ to destroy them:

$$\text{N}_2\text{H}^+ + \text{CO} \rightarrow \text{HCO}^+ + \text{N}_2$$ (10)

$$\text{N}_2\text{D}^+ + \text{CO} \rightarrow \text{DCO}^+ + \text{N}_2.$$ (11)

The strong correlation between CO freezeout onto grains and deuteration (e.g., Crapsi et al. 2005) confirms the chemical models (e.g., Roberts et al. 2003) as sketched above and has led to the conclusion that CO freezeout was necessary for strong deuteration to occur. There is however one exception to this statement: the deuteration of CO itself can form DCO$^+$. In first approximation, if H$_3^+$ is mainly destroyed by CO, $X[\text{H}_2\text{D}^+]$ varies like $X[\text{CO}]^{-1}$, whereas the production of DCO$^+$ is proportional to $X[\text{CO}]$ and $X[\text{H}_2\text{D}^+]$ (Reaction (4)). Thus, the dependency upon $X[\text{CO}]$ cancels out and $X[\text{DCO}^+]$ should remain approximately constant. Figure 1 shows the abundance of $X[\text{DCO}^+]$, $X[\text{H}_3\text{D}^+]$ isotopologues, and $X[N_2\text{D}^+]$ as a function of $X[\text{CO}]$ in a steady-state chemical model. The $X[\text{H}_3\text{D}^+]$ isotopologues is the sum of the abundances of all three deuterated H$_3^+$ isotopologues, which represent altogether the main deuteration partners of species like CO and N$_2$. The model is the same as in Pagani et al. (2009) but CO now runs from an undepleted relative abundance of $1.5 \times 10^{-4}$ down to a depletion by a factor of 300 ($X[\text{CO}] = 5 \times 10^{-7}$), for a cloud density of $10^4$ cm$^{-3}$ at 10 K. When $X[\text{CO}]$ starts to drop, $X[\text{H}_3\text{D}^+]$ isotopologues increases faster than proportional (indicated by the $-1$ slope) because the D$_2$H$^+$ abundance depends both on the destruction of H$_3^+$ by CO and on the destruction of H$_2$D$^+$ by CO, and the D$_2$H$^+$ abundance depends also on the destruction of D$_2$H$^+$ by CO. This explains that at the beginning, $X[\text{DCO}^+]$ increases: the deuteration capabilities increase faster than $X[\text{CO}]$ decreases. While $X[\text{CO}]$ keeps decreasing, the deuteration capabilities reach saturation and $X[\text{DCO}^+]$ becomes proportional to $X[\text{CO}]$ (traced by the $+1$ slope). $X[N_2\text{D}^+]$, a representative gas-phase deuteration species, follows the deuteration capabilities of the cloud, as expected. It is clear that DCO$^+$ has a behavior different from the other deuteration species, with an abundance varying only by $\pm 50\%$ while the CO abundance drops by a factor of 30, and most importantly by reaching its maximum abundance when CO is high and deuteration capabilities are down. Therefore, one would expect DCO$^+$ to be present everywhere in the cloud. It is not the case. Indeed, DCO$^+$ is, as the other deuteration species, only detected in the depleted prestellar cores on extents similar to NH$_3$ (Butner et al. 1995; Juvela et al. 2002) and nowhere else. This can only be explained if a high H$_2$ ortho:para ratio (OPR) is present. Indeed the H$_2$ OPR is an important controller of the cold cloud deuteration chemistry, as already discussed in Pineau des Forêts et al. (1991), Flower et al. (2006), and Pagani et al. (1992, 2009).

3. THE ROLE OF ORTHO-H$_2$

H$_2$ has two different possible nuclear spin states due to the proton spin of $\frac{1}{2}$: parallel (ortho, $I = 1$, weight 2$\frac{1}{2} + 1 = 3$) and anti-parallel (para, $I = 0$, weight 1). The ortho state corresponds to the odd rotational levels ($J = 1, 3, 5, \ldots$), the para state to the even levels. The first ortho state ($J = 1$) is 170 K above the ground ($J = 0$) para state. The ortho–para exchange is possible neither via radiative processes, nor via inelastic collisions. It can occur in the gas phase and on the surface of dust grains (Le Bourlot 2000). The conversion rate on a solid surface is however highly uncertain (Watanabe et al. 2010; Chehrouri et al. 2011) and it is most probable that this is mainly realized by gas-phase chemical reactions with H$^+$ or H$_2^+$ ions (Dalgarno et al. 1973; Flower & Watt 1984; Le Bourlot 1991; Flower et al. 2006). The importance of ortho-H$_2$ in the deuteration process was first studied by Pineau des Forêts et al. (1991) and Pagani et al. (1992), and later on, Flower et al. (2006) revealed its importance as a deuteration regulator. However, they considered the consequences of the OPR evolution only for the prestellar core formation itself. In a study of L183 main prestellar core, Pagani et al. (2009) noted that the H$_2$ OPR evolution timescale required by the observed N$_2$D$^+/N_2$H$^+$ ratio was on the order of the free-fall time. They also noted that the OPR had to drop below 0.01 for N$_2$D$^+$ to become detectable.

The H$_2$ OPR value is not easily accessible. H$_2$ does not emit in cold dark clouds and is seen only in shocked regions, especially protostar outflows, or in absorption in UV in low-extinction regions. The energy release from the H$_2$ formation reaction, assumed to be 1.5 eV in the equipartition hypothesis, is large enough to populate many levels of both ortho and para species: it is hence generally accepted, though not certain, that the OPR is 3:1 when H$_2$ forms on grains. Once released in the gas phase, H$_2$ tends to relax toward its thermal equilibrium state but never reaches it because at trace abundance levels, ortho-H$_2$ destruction is compensated by fresh H$_2$ formed onto grains from residual H and from destruction of ions such as H$_3^+$ and H$_2$D$^+$ that can release an ortho-H$_2$ (Le Bourlot 1991; Flower et al. 2006). It is therefore necessary to model the chemical evolution of the H$_2$ OPR to understand the evolution of dark clouds. Once H$_2$ is formed, it can react with H$^+$ and H$_2^+$ to exchange states (Le Bourlot 1991; Flower et al. 2006). For example,

$$o\text{-H}_2 + H^+ \rightarrow p\text{-H}_2 + H^+ + \Delta E.$$ (12)

$\Delta E = 170$ K is the energy released as H$_2$ goes from $J = 1$ to $J = 0$ levels. The reverse endothermic reaction is thus difficult to obtain in a cloud at 10 K and ortho-H$_2$ slowly decreases to low abundance levels ($\approx 10^{-3}$ to $10^{-4}$). Similarly, in Reaction (1), except for HD, all the species have ortho and para states and $\Delta E$ therefore depends on fact in the considered initial and final states. If only para states are involved in the products, $\Delta E$ is
maximal ($\Delta E = 232$ K with para-H$_2$ and $265$ K with ortho-H$_2$), HD being always in its ground state, $J = 0$, but if both products are in their ortho ground state while the reactants are in their lowest state, para-H$_2$ ground state and HD ($J = 0$), $\Delta E$ becomes negative and the reaction is slightly endothermic (H$_2$D$^+$ lowest ortho state is $87$ K above the para ground state, and the total required energy is $25$ K). Similarly, while the reverse reaction is impossible in a $10$ K cloud with both para reactants, it becomes rapid with ortho-H$_2$D$^+$ and ortho-H$_2$ even at $10$ K, as this channel is slightly exothermic ($\Delta E = 25$ K) to produce para-H$_2^+$. A few such channels are opened with ortho-H$_2$ allowing the efficient destruction of the H$_2^+$ deuterated isotopologues. Ortho-H$_2$ is thus an important chemical poison to deuteriation in dark clouds. Its abundance is therefore critical to control the deuteration enhancement (Flower et al. 2006; Pagani et al. 2009). Because DCO$^+$ is not observed everywhere in the clouds outside the depleted cores where it is detected (Butner et al. 1995; Juvela et al. 2002) while its abundance should be maximal, this sets a minimum level for the abundance of ortho-H$_2$. In turn, this minimum level gives rise to an upper limit to the age of the cloud, as ortho-H$_2$ abundance must eventually decrease to low levels as implied by Reaction (12), and in order to explain the deuteration enhancements seen in the depleted cores, which, in some cold cores, can become huge (amplification up to $10^{12}$; Lis et al. 2002; van der Tak et al. 2002; Parise et al. 2004).

4. THE CHEMICAL MODEL

To address these questions, we used the deuteration network from Roueff et al. (2005, 2007) in which we have included the ortho–para chemistry as described in Pagani et al. (2009), based itself on the work by Walmsley et al. (2004), Flower et al. (2006), and the new rate coefficients of Hugo et al. (2009). We have also included analytical approximations of the spin-state-dependent dissociative recombination rates of H$_2^+$ isotopologues from the tables in Pagani et al. (2009). The deuteration network includes all simple species (up to six atoms) based on C, N, O, and S with up to five deuterium substitutions (CD$_2$). For those reactions with a small endothermicity ($E/k_B < 600$ K), we have corrected the endothermy when the reaction with ortho-H$_2$ was involved (e.g., CD + H$_2$ $\rightarrow$ CH + HD) is endothermic with para-H$_2$ and exothermic with ortho-H$_2$). For all reactions with rare species producing H$_2$ (e.g., HCN$^+$ + H $\rightarrow$ CN$^+$ + H$_2$), we have always assumed that H$_2$ is released in its para form, the most favorable energetically (similarly, only ortho-D$_2$ is considered in similar reactions with deuterated species). This does not noticeably accelerate the decay of ortho-H$_2$. We checked that after, e.g., $10^5$ yr the para-H$_2$ production rate is $99.9\%$ dominated by reactions of ortho-H$_2$ with H$_2^+$ and H$.^+$ Our model is not aimed at reproducing accurately a given cloud, but it allows to follow the evolution of the H$_2$ OPR in a molecule-rich gas. We have computed the chemical evolution of a cloud of constant density ($n$(H$_2$) = $10^4$ cm$^{-3}$), constant temperature ($10$ K), average grain radius of $0.1 \mu$m, and cosmic ionization rate of $1 \times 10^{-17}$ s$^{-1}$, which represent the usual conditions met in starless dark clouds. We have started with all species being atomic except H which is considered to be already entirely converted to H$_2$ and D to HD, and we have considered different OPR starting ratios from $3$ down to $3 \times 10^{-3}$ to account for the possibility of H$_2$ production OPR below $3$. Figure 2 shows the evolution of DCO$^+$ and ortho-H$_2$ with time. We have traced the detectability limit of DCO$^+$ for a cloud with an H$_2$ column density of $10^{22}$ cm$^{-2}$, considering that a DCO$^+$ $J:1\rightarrow0$ line with a width of $0.5$ km s$^{-1}$ and an intensity of $0.1$ K would be easily detectable with present-day radio telescopes. With the RADEX non-LTE radiative transfer model (van der Tak et al. 2007), we find that a DCO$^+$ column density of $\sim 2 \times 10^{11}$ cm$^{-2}$ is detectable, equivalent to a relative abundance to H$_2$ of $\sim 2 \times 10^{-11}$. Figure 2 shows that for any initial H$_2$ OPR below $0.1$, DCO$^+$ should be detected throughout the cloud in less than $3 \times 10^5$ yr. For an initial OPR = $0.1$, the DCO$^+$ becomes marginally detectable around $5 \times 10^5$ yr, disappears, and finally becomes clearly detectable after $2$ Myr. For OPR > $0.1$, it takes $3$–$6$ million yr to become detectable, i.e., when the H$_2$ OPR drops below $0.03$. Compared to the H$_2$ OPR drop from $3 \rightarrow 0.01$ in depleted cores which takes less than $2 \times 10^5$ yr to happen (Pagani et al. 2009), the difference is twofold: as density increases during the prestellar core formation, (1) the chemistry accelerates, and (2) depletion sets in and H$^+$ is no more destroyed by the other species which have now disappeared from the gas phase (H$_2^+$ also becomes more abundant but to a lesser extent). H$^+$ can even become the dominant ion. The higher abundance of H$^+$ and H$_2^+$ and the accelerated chemistry provoke the rapid decline of ortho-H$_2$.

On the same figure, we also trace the abundance of the sum of the deuterated H$_2^+$ isotopologues in the case H$_2$ OPR = $3$. It shows that under $1$ Myr, deuteriation is dominated by the carbon chemistry (CH$_3$D$^+$, C$_2$HD$^+$, etc.) which is not dependent upon the ortho-H$_2$ abundance due to exothermicities close to $400$ K. It is only beyond $1$ Myr that the H$_2^+$ deuteration network takes.
over when ortho-H₂ starts to be negligible. If ortho-H₂ is low since the beginning, the H² isotopeologue contribution to the abundance of DCO⁺ is important from the start which explains the disappearance of the dip between 1 and ∼3 Myr.

The model is also sensitive to two other initial conditions: the abundance of metals and the cosmic ray ionization rate. Metals, especially alkali and alkaline earth metals like Ca, Na, and K, and others like Fe, have a direct influence on the electronic equilibrium of the chemical model which in turn changes the dissociative recombination efficiency for DCO⁺ and therefore its abundance. For standard ζ (1 × 10⁻¹⁷ s⁻¹) and H₂ OPR (3), we have varied their abundance from 3.4 × 10⁻⁸ to 1.3 × 10⁻⁷. For the lowest abundance (50% of the default one), DCO⁺ becomes detectable much earlier (2 × 10⁵ yr) than in the standard case, drops below the detectability limit when ortho-H₂ starts to be negligible. If ortho-H₂ is low since the beginning, the H² isotopeologue contribution to the abundance of DCO⁺ is important from the start which explains the disappearance of the dip between 1 and ∼3 Myr.

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