THE D/H RATIO IN MOLECULAR CLOUDS

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1. ABSTRACT

This paper summarizes our understanding of the dominant D-reservoirs in molecular clouds and suggests possible direct determinations of the D-abundance. It is concluded that rotational HD lines from shock regions provide the best way to determine the gas phase D-abundance. In cold dense cores, the dominant gas phase D-reservoir is likely to be atomic D, because of expected inefficient HD formation on grain surfaces. The gas phase D-abundance derived from observations of dense cores is $\approx 5 \times 10^{-6}/n_4$ (with n_4 the total density in units of 10^4 cm^{-3}). A large fraction of the D ($\approx 50\%$) may be locked up in deuterated molecules in grain mantles. A small fraction ($\approx 2\%$) may be locked up in the photolyzed residues of such grain mantles. PAHs will also be deuterated (PADs), containing $\approx 1\%$ of the D. Finally, it is likely that all of these processes have contributed to the D-enrichment observed in solar system materials.

2. INTRODUCTION

The elemental D-abundance and its gradient in the galaxy has important implications for our understanding of the origin and early evolution of the universe; ie., is the universe closed by exotic dark matter or by white dwarfs resulting from an early epoch of star formation[1]. Furthermore, various components enriched in D have been isolated from carbonaceous meteorites and interplanetary dust particles[2]. This D-fractionation probably reflects an ancestry dating back to molecular clouds. Past studies on the D-abundance in molecular clouds have relied on measuring trace species and relating their abundance back to the dominant D-reservoir. However, because of the zero-point energy difference, abundances of deuterated species are very susceptible to fractionation effects and thus sensitive to the local physical conditions. A reliable determination of the D-abundance requires a direct study of the dominant D-reservoirs.

3. DEUTERIUM IN WARM DENSE CLOUDS

In warm dense media, such as PDRs and shocks, the deuterium chemistry is dominated by neutral-neutral reactions, in particular, D + H$_2$ --> H + HD. The conversion of D into HD by this reaction is much faster than the shock cooling time ($\tau \approx N(H_2)/[n_o v_s]$) and all D should be in the form of HD in this shock (Fig. 1). Likewise, although previously neglected, this neutral reaction is much faster than grain surface formation in PDRs (Fig. 1). However, in PDRs, photodestruction quickly reverts the HD back into D and, unlike shocks, D is the dominant reservoir.
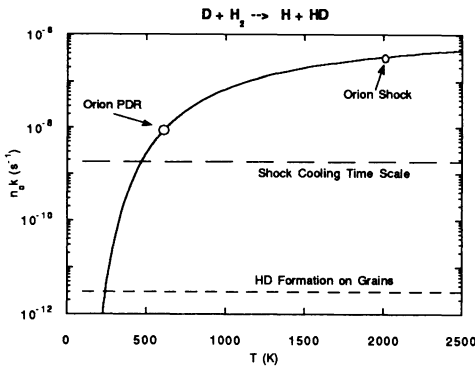
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Fig. 1: The rate of D-HD conversion in warm gas for an H_2 density of $n_0=10^5$ cm^{-3}. Also indicated are the conditions characteristic for the Orion shock (derived from the 2μm vibrotational H_2 lines) and the Orion Bar PDR (derived from the rotational H_2 lines).
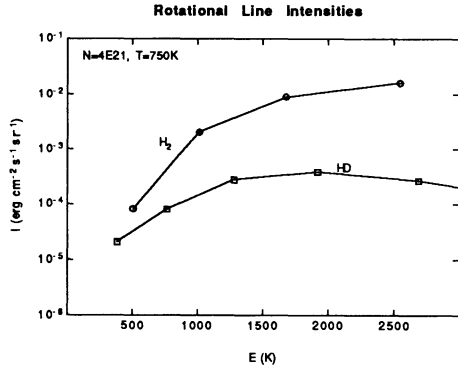
Fig. 2: Predicted intensities of rotational H_2 and HD lines for the Orion shock as a function of their excitation energy. The assumed column density and temperature are characteristic for the observed CO and pure rotational H_2 lines, gas downstream from that observed in the 2μm H_2 lines.

Since all D is in the form of HD and the gas is warm, shocks present an excelent probe of the total gas phase deuterium abundance (Fig. 2). Although line-to-continuum forms somewhat a problem for the HD lines, these lines are measurable with present day techniques. Careful selection of HD and H_2 lines from similar excitation energies will allow a direct estimate of the HD/H_2 ratio, circumventing the rather uncertain aspects of shock theory. Although the figures are geared towards the Orion shock, any strong shock (≈ 35 km/s) will do and this may present the best oppertunity to measure the elemental D gradient in the galaxy.

4. DEUTERIUM IN COLD DENSE CLOUDS

In recent years it has been realized that D-fractionation is more complex than previously thought since both D and HD may be important reservoirs[3,4]. The atomic D abundance can be directly and reliably determined from observations. The atomic H and D abundances are governed by very similar reactions; ie., formation by dissociative recombination of molecular ions (HCO$^+$ and DCO$^+$), and destruction by accretion and reaction on grain surfaces (Fig. 3). The atomic D/H abundance ratio in reflects therefore directly that of these gas phase ions. The DCO$^+$/HCO$^+$ ratio is observed to be about 0.05 in dark clouds[5,6]. Thus, the atomic D/H ratio is ≈ 0.05, much larger than the deuterium cosmic abundance. Now, the H abundance is essentially a balance between cosmic ray ionization of H_2 and accretion on grain surfaces and is ≈ 1 cm^{-3}. Thus, the fraction of the deuterium in the form of atomic D is about $0.5/n_4$, assuming an elemental D abundance of 10^{-5}.

The HD abundance is much more difficult to estimate. Generally, it has been assumed that HD is efficiently formed on grain surfaces, which implies then: HD/D$\approx 4n_4$ (Fig. 3). In that case, most of the deuterium would be in HD in dense cores. However, the atomic H abundance is very low in dense dark clouds (≈ 1 cm^{-3}) and the H accretion rate on grains is less than that of the heavier species (ie., O, CO). Almost all accreted H and D will then
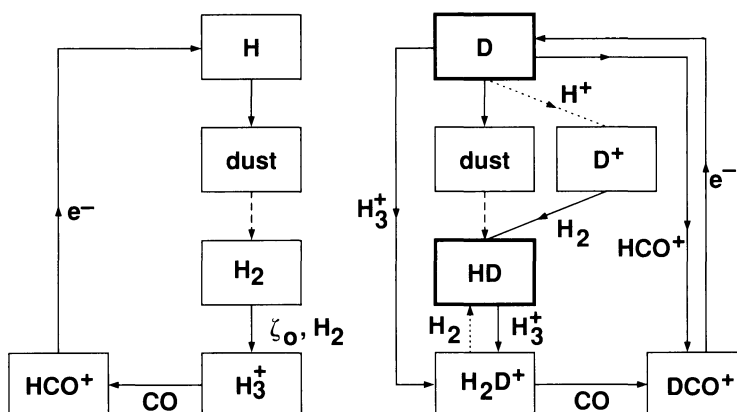
THE GAS PHASE D/HD RATIO

Fig. 3: A schematic view of the important reactions involved in the exchange between the two important gas phase reservoirs of deuterium, D and HD.

react to form H_2O, HDO, etc (see below) and HD formation is inefficient[7]. Gas phase formation of HD is also inefficient (Fig. 3) and leads to HD/D$\approx 10^{-2}$ H^+/H_3^+. Although somewhat depending on the details of the chemistry, the HD/D ratio in that case is $\approx 10^{-1}$-10^{-2} and D is the dominant reservoir. In warm gas (T>25K), HD is the important reservoir since H_2D^+ will be channeled to HD rather than DCO^+ (Fig. 3).

   Thus, in summary, HD formation on grain surfaces is probably inefficient and D is the main gas phase reservoir in dense cores. The total D-abundance in the gas phase is then estimated to be $\approx 4 \times 10^{-6}$. This is less than the generally accepted elemental deuterium abundance ($\approx 10^{-5}$) and, thus, some of the D may well be in the solid state.

5.   DEUTERATED GRAIN MANTLES

The atomic D/H ratio in the gas phase is much larger than the elemental D abundance, leading to large D-fractionation in grain mantles[7]. Moreover, since the activation barrier for abstraction of a D-atom is larger than for H abstraction by the zero-point energy difference, D abstraction from a deuterated molecule has very low probability. As a result, the abundance of some deuterated molecules such as HDCO and D_2CO can be considerably enhanced over the gas phase D/H ratio. The recent observations of the high $D_2CO/HDCO$ relative to the $HDCO/H_2CO$ ratio in Orion lends some support for this scheme[8].

   Due to the mass difference, the IR active modes involving deuterium will be shifted by $\approx \sqrt{2}$ from those of the hydrogenated species - typically to the 4.5-4.8μm and 13-15μm region, both completely opaque due to telluric CO_2. Direct detection of deuterated grain mantle molecules has therefore to await space borne missions (ISO). Such observations will be crucial to determine the total D-abundance in molecular clouds. Of course, they will also be important in determining the composition of interstellar grain mantles, testing grain chemistry schemes, as well as testing the importance of grain mantles for the gas phase

composition of hot molecular cloud cores. In the absence of direct measurements, the fraction of D in grain mantles can be guestimated from observations of hot cores. If the molecules in hot cores result from evaporation of grain mantles[9] and if we assume that accretion was complete prior to the formation of the protostar, the observed D-fractionation ($HDO/H_2O \approx 1\%$) in hot cores implies that $\approx 50\%$ of all the D was in grain mantles. Finally, this D-fractionation is expected to be passed on to the organic residue formed by UV photolysis of these grain mantles. Since $\approx 3 \times 10^{-5}$ of the H is observed to be in these organic grain mantles (via the 3.4μm band) in the diffuse interstellar medium, $\approx 2\%$ of the D is expected to be locked up in this dust component. Although this estimate may be somewhat on the low side due to preferential loss of H over D by photolysis, organic grain mantles seem to be a rather unimportant sink for D.

6. DEUTERATED PAHS

Two different chemical pathways may play a role in the deuteration of PAHS: 1) Small PAHs (<25 C-atoms) highly excited by an UV photon will preferentially "cool" by loss of a peripheral H-atom rather than IR emission[10]. The resulting radical may react with atomic D rather than atomic H. Due to the zero-point energy difference, the ratio of the fission rates of H to D is ≈ 3 and fractionation can occur this way. In steady state, the fraction, f_D, of peripheral D relative to H is then given by $f_D \approx 3 [n_D/n_H]$. In PDRs - the prime emission zones of the IR emission features - the atomic D/H abundance ranges from $\approx 10^{-5}$ at the surface to $\approx 10^{-3}$ at an A_v of 5 (H_2 goes molecular before HD). Thus, fractionation due to this process, although substantial, is too small to be observable. Inside dense clouds, the UV field due to cosmic ray excitation of H_2 is still large enough to drive the PAD/PAH abundance to steady state. Now, of course, n_D/n_H is much larger (≈ 0.05, §4) and every small PAH is expected to have 1 or 2 of its peripheral H's replaced by a D.

2) Proton transfer or isotope exchange reactions ($PAH + H_2D^+ \rightarrow PAD + H_3^+$ and $PAH^+ + HD$ (D) $\rightarrow PAD^+ + H_2$ (H)) can also lead to D-fractionation of PAHs inside dense cores. Assuming typical abundances for the coreactants and realizing that $PAH^+/PAH \approx 10^{-4}$, the D-fractionation timescale $\approx 3 \times 10^6/n_4$ yrs for both reactions. Thus, over the timescale of a dense core every PAH would acquire ≈ 1 peripheral D-atom. Consequently, in a dense core, about 1% of the elemental D could be locked up in PADs. Note that, while the e-sticking coefficient for small PAHs (<50 C-atoms) is small ($\approx 10^{-4}$-10^{-2}), larger PAHs will predominantly (90%) be negatively charged. These timescales are then 10 times longer and PADs are correspondigly less important. Finally, once the small PADs find themselves in a UV bright region (ie., IR emission zone), they will quickly equilibrate with the local atomic D/H ratio and only PAHs in the 25-50 C-atom range may retain the D-signature of dense cores.

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QUESTIONS AND ANSWERS

C.M.Walmsley: Why do you think HD is not formed efficiently on grains?

A.G.G.M.Tielens: When the gas density is higher than $\sim 10^4 cm^{-3}$, the accretion rate of heavy molecules (such as CO, O_2 and O) is larger than of atomic H. In that case, all accreted H atoms will go into hydrogenating these heavy molecules rather than form H_2, forming an icy grain mantle (ie.,H_2O, H_2CO, CH_3OH).

M.Gray: Do you think molecules of Buckminster-Fullerene type could hold a significant of D?

A.G.G.M.Tielens: Buckminster-Fullerene (C_{60}) itself does not have any H and thus will not (directly) fractionate. However, partially closed fullerenes are probably hydrogenated in the ISM. They are expected to behave like PAHs and could thus D_- fractionate as well.