Quantum dynamics study of rate constant for a reactive collision of astrophysical interest: the D$^+$ + H$_2$ reaction

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Collaborators/Fundings

Collaborators:
- P. Honvault (ICB, Dijon, France)
- T. Gonzalez-Lezana (CSIC, Madrid, Spain)

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in a collaborative proposal with F. Lique* and A. Faure (2012-2014)
Deuterium Chemistry for ISM

\[ \text{D}^+ + \text{H}_2 \rightarrow \text{HD} + \text{H}^+ \]

represents the major source of HD in diffuse interstellar clouds


\[ \Rightarrow \text{a low temperature rate constant } k(T) \text{ is thus needed in order to} \\
\text{get a correct estimation of H}_2/\text{HD ratio in the interstellar medium} \]
and for Primordial Universe

- just after the recombination era, atomic and molecular processes occur and play a role in the formation of first stars
- first structures are efficiently formed thanks to the molecular cooling of proto-molecular clouds
- $H_2$ and HD are the most efficient cooling molecules thus an accurate knowledge of their molecular abundance is required
and for Primordial Universe

THE IMPACT OF HD COOLING ON THE FORMATION OF THE FIRST STARS
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ABSTRACT
We use numerical simulations to investigate the importance of HD formation and cooling on the first generation of metal-free stars in a \( \Lambda \)CDM cosmology. We have implemented and tested non-equilibrium HD chemistry in an adaptive mesh refinement simulation code and applied it to two situations. (1) It is first applied to the formation of \( 10^5 - 10^6 M_\odot \) halos which form in the absence of any ionizing source (“unperturbed” halos). We show, in agreement with previous work, that HD cooling is of only marginal importance for most halos; however, we find that for the lowest mass halos, with masses a few times \( 10^5 M_\odot \), HD cooling can equal or surpass the \( \text{H}_2 \) cooling rate. This leads to a population of stars formed in halos with effective HD cooling that are less massive by a factor of \( \sim 6 \) compared to halos dominated by \( \text{H}_2 \) cooling. (2) In the second part of the paper, we ionize the halos in order to explore the impact of HD cooling in the presence of an ample population of free electrons. This leads to cooler temperatures (due to the electron-catalyzed production of \( \text{H}_2 \)), implying somewhat lower resulting protostellar mass. Adding HD chemistry changes this by lowering the temperature further, to the level of the CMB. We find that HD cooling dominates over \( \text{H}_2 \) cooling in the density range \( 10^5 - 10^6 \text{ cm}^{-3} \), but above this density, the temperature rises and \( \text{H}_2 \) cooling dominates again. Because of this, the accretion rate on to the protostar is almost the same as in the \( \text{H}_2 \) case (at least for accreted masses below \( 50-100 M_\odot \)); therefore we argue that HD cooling in ionized halos will probably not result in a population of significantly lower mass stars.

Subject headings: cosmology: theory — galaxies: formation — galaxies: high-redshift — methods: \( \eta \)-body simulations — stars: formation

Online material: color figures

- HD is less abundant than \( \text{H}_2 \) \( ([D]/[H] \sim 2.10^{-5}) \)
- but has a dipole moment \( (\mu \sim 8.3 \times 10^{-4}\text{ Debyes}) \) and thus its cooling can equal or surpass the \( \text{H}_2 \) cooling rate

Kinetic equation:

\[
\frac{dn_x}{dt} = k_{x}^{\text{form}}(T_m)n_j n_w - k_{x}^{\text{dest}}(T_m)x n_x n_u - \xi_{x}^{\text{dest}}(T_r)n_x + \xi_{x}^{\text{form}}(T_r)n_z + \ldots
\]
Non-LTE effect

In many studies, molecular level populations are assumed to follow a Maxwell-Boltzmann law (LTE) but ...  

- strong non-LTE effect have been shown for H$_2$(v) in the early universe at low $z$


- several order of magnitude for the abundance of H$_2^+$ in the photodissociation $H_2^+ + h\nu \rightarrow H + H^+$

State-to-State resolved kinetic

The population of a molecule should be solved self-consistently:

\[
\frac{dn_{x,i}}{dt} = k^{\text{form}}_{x,i}(T_m)n_{y,k}n_{w,l} - k^{\text{dest}}_{x,n_x,i}n_{u,m} \\
- \xi^{\text{dest}}_x(T_r)n_{x,i} + \xi^{\text{form}}_x(T_r)n_{z,o} + \\
+ \sum_{j \neq i} n_{x,j}[A_{x,ji} + B_{x,ji}J_{ji}(T_r) + C_{x,ji}(T_m)] \\
- n_{x,i} \sum_{j \neq i} [A_{x,ij} + B_{x,ij}J_{ij}(T_r) + C_{x,ij}(T_m)]
\]
State-to-State resolved kinetic

⇒ state-resolved rate constant are required for early universe!
⇒ ab initio results at the state-of-the-art are very useful!
Experimental data for the HD formation

• First experimental study:

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Investigation of Back-Scattering in the D+/H2 Reaction System*

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(Received 22 December 1970)

A collision chamber designed for efficient collection of product ions was used to determine the extent of back scattering in the reactions of D+ and H2 to form H+ and HD+. No significant amount of back scattering in the laboratory system was detected.

• singles cross section values:

We also determined absolute cross sections (in the absence of a repeller field) at a laboratory energy of 7.8 eV (3.9 eV c.m.) for the reactions D+ + H2 → H+ + HD and D+ + H2 → HD+ + H using the procedure described in our previous paper. The values obtained were 0.26 Å² and 0.57 Å² for H+ and HD+ formation, re-

...but experimental data obtained at room temperature thus not really useful for astrochemical models
Experimental data for the HD formation

• Second experimental study of $k(T)$ at 80 K:

...but no temperature dependency of $k(T)$ available from this work
Experimental data for the HD formation

- More recent experience:

Deuterium fractionation in gas-phase reactions measured in the laboratory
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Fig. 1. Energy dependence of the rate coefficients for the exothermic proton-deuterium exchange D⁺ + H₂ → H⁺ + HD measured with different instruments (guided ion beam: GIB 74: Ochs and Tielby (1974), VT-SIFT 81: Henchman et al. (1981), DRIFT 82: Villinger et al. (1982), GIB 92 and MB 92: Gerlich (1992)). The heavy line shows a rate coefficient, calculated with the MDB (most dynamically biased) statistical theory by Gerlich (1992). Errors of the various experiments are indicated schematically as bars or crosses.
First Principles calculations

In both dynamical approaches (TIQM/SQM) we have used the recent accurate $\text{H}_3^+$ PES of Velilla et al.
Collinear Representation of the $\text{H}_3^+$ potential:
Hyperspherical formulation of the close-coupling approach

\[
\sigma_{v'j',vj}(E) = \frac{\pi}{k_{v'j}^2} \frac{1}{2j + 1} \sum_{J\Omega'\Omega} (2J + 1) \left| S^J_{v'j'\Omega',vj\Omega}(E) \right|^2
\]

and the Differential Cross Section (DCS) :

\[
\sigma_{v'j',vj}(\theta, E) = \frac{1}{8\mu E_c(2j + 1)} \times \sum_{\Omega'\Omega} \left| \sum_J (2J + 1) d^J_{\Omega\Omega'}(\pi - \theta) \right|^2 
\times T^J_{v'j'\Omega',vj\Omega}(E)
\]

Adiabatic channels

- For $J = 0$, more than 200 channels
- For $J \neq 0$, more than 1930 channels
Theoretical method : SQM

Assumption of a complex-forming dynamics of the process in which the state-to-state probability can be expressed as:

\[
|S_{v'j'\Omega',vj\Omega}(E)|^2 \approx \frac{p_{v'j'\Omega'}^J(E)p_{vj\Omega}^J(E)}{\sum_{v''j''\Omega''}p_{v''j''\Omega''}^J(E)}
\]

which can be used to determine the ICS \(\sigma_{v'j',vj}(E)\). The DCS are approximated by:

\[
\sigma_{v'j',vj}^{SQM}(\theta, E) = \frac{1}{8\mu E_c(2j + 1)} \times \sum_{\Omega'\Omega} \sum_{J} (2J + 1)^2 \left[ d_{\Omega\Omega'}^J(\pi - \theta)^2 + d_{\Omega\Omega'}^J(\theta)^2 \right] |S_{v'j'\Omega',vj\Omega}(E)|^2
\]
$J = 0$ Reaction Probability

FIG. 1. Reaction probabilities for the $\text{D}^+ + \text{H}_2(v = 0, j = 0) \rightarrow \text{H}^+ + \text{HD}$ reaction at $J = 0$. TIQM results (black line) are compared with statistical predictions (red line).

Integrated cross sections $\sigma(E)$

$D^+ + H_2(v=0,j=0) \rightarrow HD(v=0,j') + H^+$

Cross section ($a_0^2$) vs. Collision energy (eV)
Integrated cross sections $\sigma(E)$

$D^+ + H_2(v=0, j=1) \rightarrow HD(v'=0, j') + H^+$

[Graph showing the integrated cross sections for different values of $j'$]
FIG. 2. Integral cross sections for the $\text{D}^+ + \text{H}_2(\nu = 0, j = 0) \rightarrow \text{H}^+ + \text{HD}$ reaction. TIQM results (black line) are compared with statistical predictions in which only even (red lines)/all (blue lines) rotational states of $\text{H}_2(\nu = 0, j)$ are taken into account. The inset displays the same results on a log scale for the sake of clarity at the low energy regime. See text for details.
FIG. 3. Same as Fig. 2 for $D^+ + H_2(v = 0, j = 1) \rightarrow H^+ + HD$ reaction. SQM results are in this case for odd (red lines)/all (blue lines) rotational $H_2(v = 0, j)$ states.
FIG. 4. State-to-state rate coefficients in terms of $E_c$ for the $D^+ + H_2(v = 0, j = 0) \rightarrow H^+ + HD(v' = 0, j' = 0 - 2)$ reaction.
Energy-Rate constant $k(E)$


- Very good agreement with experimental data of D. Gerlich
- Only a slight decrease when we go to low collisional energy
SQM calculations provides a reasonably good counterpart for the TIQM rotational distribution.
Temperature-Rate constant $k(T)$

$$k(T) = \frac{1}{k_B T} \left( \frac{8}{\pi \mu k_B T} \right)^{1/2} \int_0^\infty \sigma(E_c) e^{-E_c/k_B T} E_c dE_c$$


An Analytical formula was fitted for KIDA
For low temperature (less than 10 K) the propagation should be done until a large asymptotic matching distance

or use a more efficient propagation scheme (see Launay and Lara development of HYP3D)
Perspectives

- Perform the complementary study of $\text{HD}+\text{H}^+ \rightarrow \text{D}^++\text{H}_2$ (TIQM/SQM)
- Investigate the role of vibrationally excited $\text{H}_2(v)$ and $\text{HD}(v')$ in the rate constant (SQM/TIQM)
- Calculations for higher temperature than 100 K for early universe application but ... 

$$D^+ + H_2 \rightarrow HD + H^+$$
$$\rightarrow HD^+ + H \text{(charge transfer)}$$

- use of more efficient methods for such higher collisional energy range (such as TDWP method).
  see $\text{HeH}^++\text{H}$ reaction, DeFazio, 2014
- use the state-to-state rate constant in a chemical model to evaluate the HD abundance for low temperature
Aknowledgements

Thank you for your attention!