# 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)

Fundings :

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

# Deuterium Chemistry for ISM

$$D^+ + H_2 \rightarrow HD + H^+$$

represents the major source of HD in diffuse interstellar clouds
Dalgarno, Weisheit & Black, Ap.Lett., **14**,77 (1973)

A&A 430, 967–977 (2005)
DOI: 10.1051/0004-6361:20041589


Astronomy & Astrophysics

**Deuterated molecular hydrogen in the Galactic ISM**

**New observations along seven translucent sightlines**

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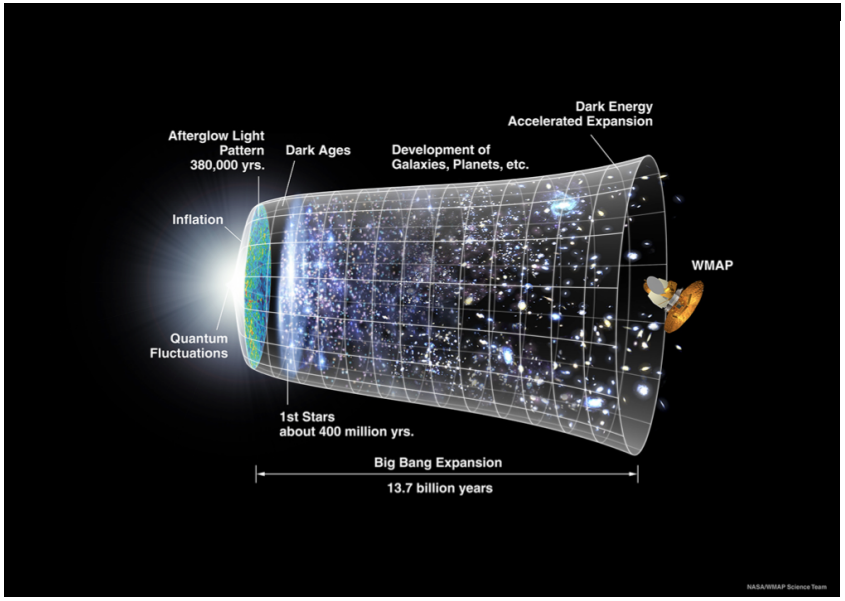
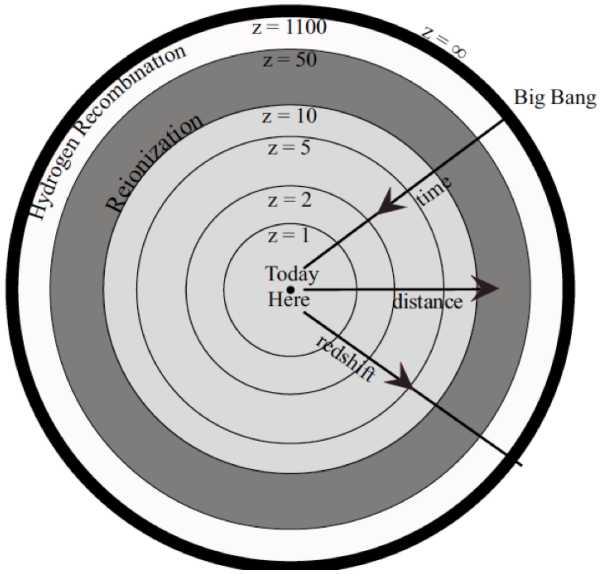
**Abstract.** We present column density measurements of the HD molecule in the interstellar gas toward 17 Galactic stars. The values for the seven most heavily reddened sightlines, with $E(B-V) = 0.38–0.72$, are derived from observations with the *Far Ultraviolet Spectroscopic Explorer* (*FUSE*). The other ten values are from a reanalysis of spectra obtained with *Copernicus*. In all cases, high-resolution ground-based observations of K I and/or the CH molecule were used to constrain the gas velocity structure and to correct for saturation effects. Comparisons of the column densities HD, CH, CN, and K I in these 17 sightlines indicate that HD is most tightly correlated with CH. Stringent lower limits to the interstellar D/H ratio, derived from the HD/2$H_2$ ratio, range from $3.7 \times 10^{-7}$ to $4.3 \times 10^{-6}$. Our results also suggest that the HD/$H_2$ ratio increases with the molecular fraction $f(H_2)$ and that the interstellar D/H ratio might be obtained from HD by probing clouds with $f(H_2) \sim 1$. Finally, we note an apparent relationship between the molecular fractions of hydrogen and deuterium.

$\Rightarrow$ a low temperature rate constant $k(T)$ is thus needed in order to get a correct estimation of $H_2$/HD ratio in the interstellar medium

# and for Primordial Universe




- just after the recombination era, atomic and molecular process 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 know ledg of their molecular abundance is required

# and for Primordial Universe

The Astrophysical Journal, 685:8–20, 2008 September 20


THE IMPACT OF HD COOLING ON THE FORMATION OF THE FIRST STARS

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*Received 2008 February 25; accepted 2008 May 23*

ABSTRACT

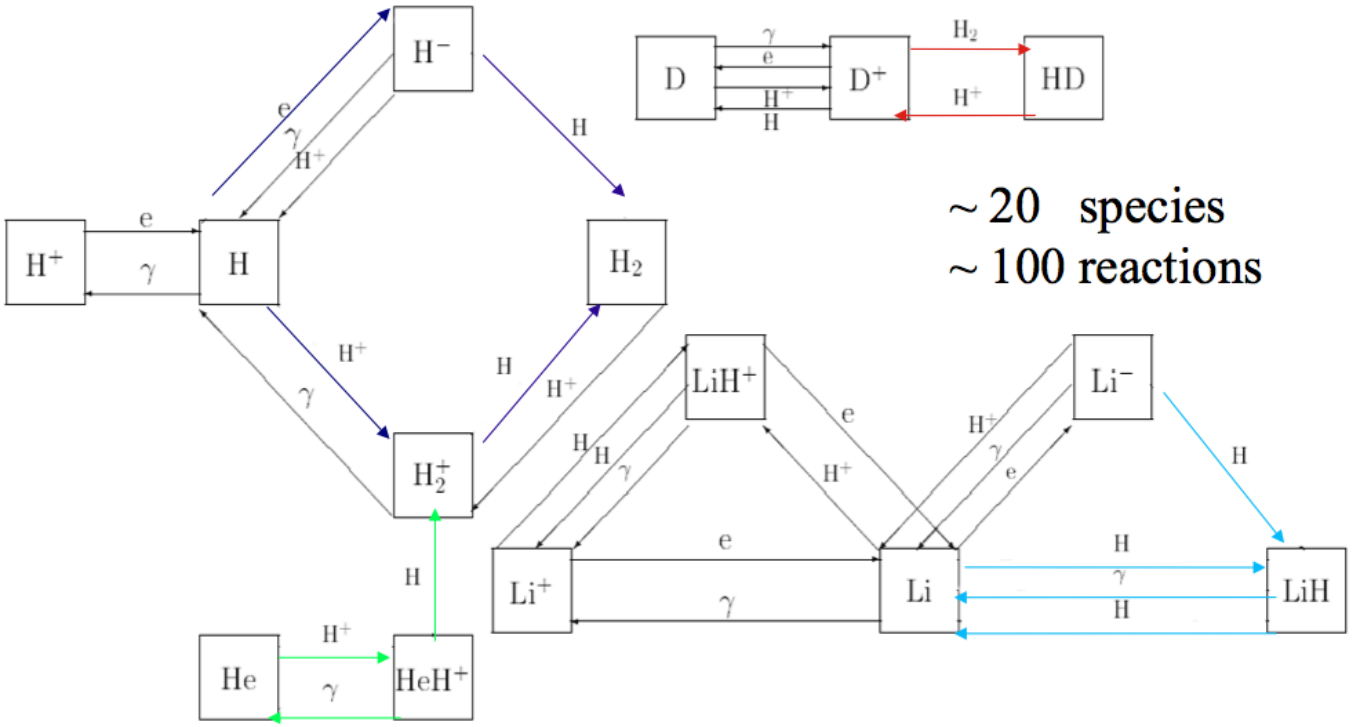
We use numerical simulations to investigate the importance of HD formation and cooling on the first generation of metal-free stars in a ΛCDM cosmology. We have implemented and tested non-equilibrium HD chemistry in an adaptive mesh refinement simulation code and applied it to two situations. (1) It is 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 $H_2$ cooling rate. This leads to a population of stars formed in halos with effective HD cooling that are less massive by a factor of ∼6 compared to halos dominated by $H_2$ 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 $H_2$), 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 $H_2$ cooling in the density range $10^2$–$10^6$ cm$^{-3}$, but above this density, the temperature rises and $H_2$ cooling dominates again. Because of this, the accretion rate on to the protostar is almost the same as in the $H_2$ 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: *n*-body simulations — stars: formation

*Online material:* color figures

- HD is less abundant than $H_2$ ([D]/[H]$\simeq 2.10^{-5}$)
- but has a dipole moment ($\mu \simeq 8.3 \times 10^{-4}$Debyes) and thus its cooling can equal or surpass the $H_2$ cooling rate

# Chemical Network




Galli and Palla. Astron. Astrophys., **335**, 403, 1998

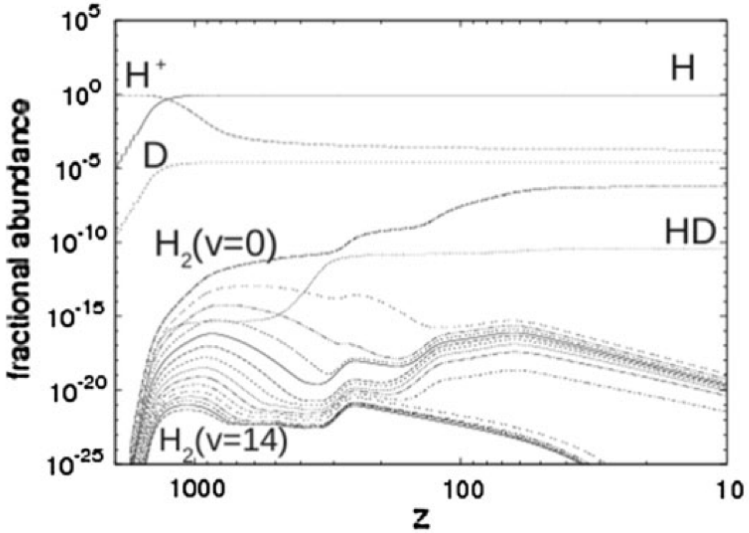
Kinetic equation :

$$\frac{dn_x}{dt} = k_x^{form}(T_m)n_j n_w - k^{dest}(T_m)_x n_x n_u - \xi_x^{dest}(T_r)n_x + \xi_x^{form}(T_r)n_z + \dots$$

# 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 $z$




Coppola et al. ApJ. Series, **193**, 7, 2011

- several order of magnitude for the abundance of $H_2^+$ in the photodissociation $H_2^+ + h\nu \rightarrow H + H^+$
Galli and Palla. Astron. Astrophys., **335**, 403, 1998

# State-to-State resolved kinetic

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

$$
\begin{aligned}
\frac{dn_{x,i}}{dt} &= k_{x,i}^{form}(T_m)n_{y,k}n_{w,l} - k^{dest}(T_m)_x n_{x,i}n_{u,m} \\
&- \xi_x^{dest}(T_r)n_{x,i} + \xi_x^{form}(T_r)n_{z,o} + \\
&+ \sum_{j\neq i} n_{x,j}[A_{x,ji} + B_{x,ji}J_{ji}(T_r) + C_{x,ji}(T_m)] \\
&- n_{x,i}\sum_{j\neq i}[A_{x,ij} + B_{x,ij}J_{ij}(T_r) + C_{x,ij}(T_m)]
\end{aligned}
$$

# State-to-State resolved kinetic

**FUTURE ISSUES**

- Major progress has been achieved by the inclusion of state-resolved chemical reaction rates for $H_2$ and $H_2^+$, which are formed out of equilibrium in highly excited vibrational levels and then decay radiatively to the fundamental state. It is desirable to extend this approach to other species like HD, $HD^+$, and $HeH^+$. Further improvement comes from recent fully-quantal ab initio calculations of reaction cross sections for He and Li chemistry specifically performed for applications to the early Universe. Extending these calculations to other species/processes is an obvious need. It is necessary to complement these theoretical studies with laboratory experiments, especially at sub–electron volt energies.

Galli and Palla, Annu. Rev. Astron. Astrophys., **51**, 163 (2013)

$\Rightarrow$ *state-resolved rate constant are required for early universe !*

$\Rightarrow$ *ab initio results at the state-of-the-art are very useful !*

# Experimental data for the HD formation

- First experimental study :

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 54, NUMBER 9 1 MAY 1971

**Investigation of Back-Scattering in the $D^+/H_2$ Reaction System***

M. G. Holliday,† J. T. Muckerman, and L. Friedman
*Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973*
(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 $H_2$ 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 $D^+ + H_2 \rightarrow H^+ + HD$ and $D^+ + H_2 \rightarrow HD^+ + H$ 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 :

THE ASTROPHYSICAL JOURNAL, **183**:L25–L26, 1973 July 1


MEASUREMENT OF THE RATE CONSTANT FOR THE REACTION $D^+ + H_2 \rightarrow HD + H^+$

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Aeronomy Laboratory, NOAA Environmental Research Laboratories, Boulder, Colorado
*Received 1973 May 3*

ABSTRACT

It has recently been pointed out that the reaction $D^+ + H_2 \rightarrow HD + H^+$ can lead to enhanced $HD/H_2$ ratios in the interstellar medium if the rate constant is sufficiently large. We have measured the rate constant and found it to be $1.0 \times 10^{-9}$ cm$^3$ s$^{-1}$, and independent of temperature from 80° to 278° K.

*Subject headings:* interstellar matter — molecules

I. INTRODUCTION

Recent observations of the abundance of HD in interstellar molecules (Spitzer *et al.* 1973) have led to a keen interest in possible isotopic fractionation processes which may occur. It has been brought to our attention by Dalgarno (private communication; also Dalgarno, Black, and Weisheit *et al.* 1973) and by Watson (private communication; also Watson 1973) that a potentially important process is the exothermic ion-molecule reaction

$$D^+ + H_2 \rightarrow HD + H^+ + 0.039\ \text{eV}, \qquad (1)$$

. . . but no temperature dependency of $k(T)$ available from this work

# Experimental data for the HD formation

- More recent experience :

PERGAMON

Planetary and Space Science 50 (2002) 1287 - 1297

Planetary and Space Science

www.elsevier.com/locate/pss

## Deuterium fractionation in gas-phase reactions measured in the laboratory

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*Department of Physics, Technische Universität Chemnitz, 09107 Chemnitz, Germany*

Received 21 January 2002; received in revised form 15 April 2002; accepted 17 June 2002

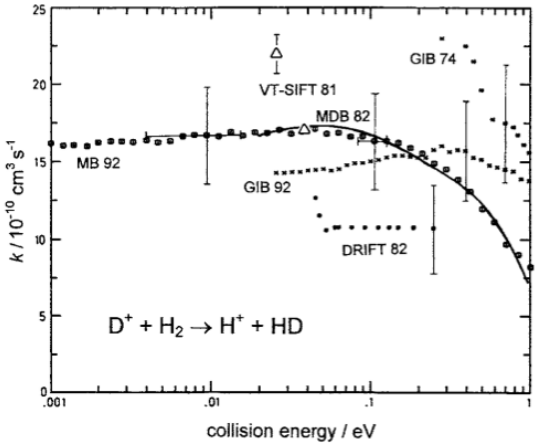
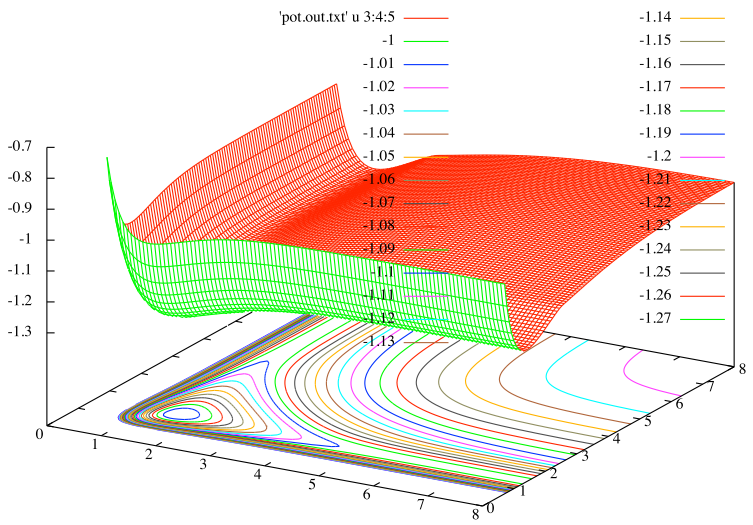
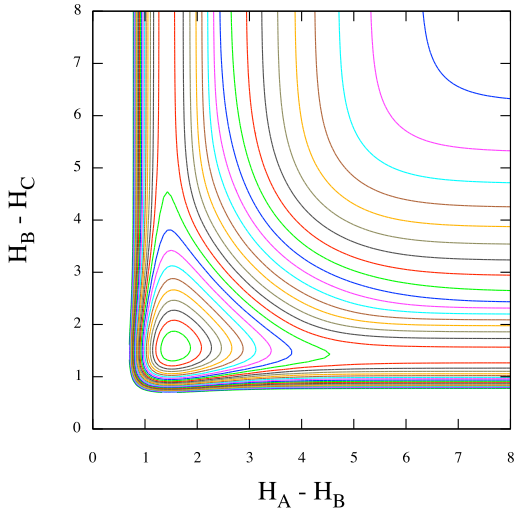



Fig. 1. Energy dependence of the rate coefficients for the exothermic proton–deuteron exchange $D^+ + H_2 \rightarrow H^+ + HD$ measured with different instruments (guided ion beam: GIB 74: Ochs and Teloy (1974), VT-SIFT 81: Henchman et al. (1981), DRIFT 82: Villinger et al. (1982), GIB 92 and MB 92: (Gerlich (1992)). The heavy line shows a rate coefficient, calculated with the MDB (most dynamically biased) statistical theory by Gerlich (1982). 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 $H_3^+$ PES of Velilla *et al.*
L. Velilla, B. Lepetit, A. Aguado, J.A. Beswick and M. Paniagua, J. Chem. Phys. 129, 084307 (2008)
Collinear Representation of the $H_3^+$ potential :



# Theoretical method : TIQM

Hyperspherical formulation of the close-coupling approach

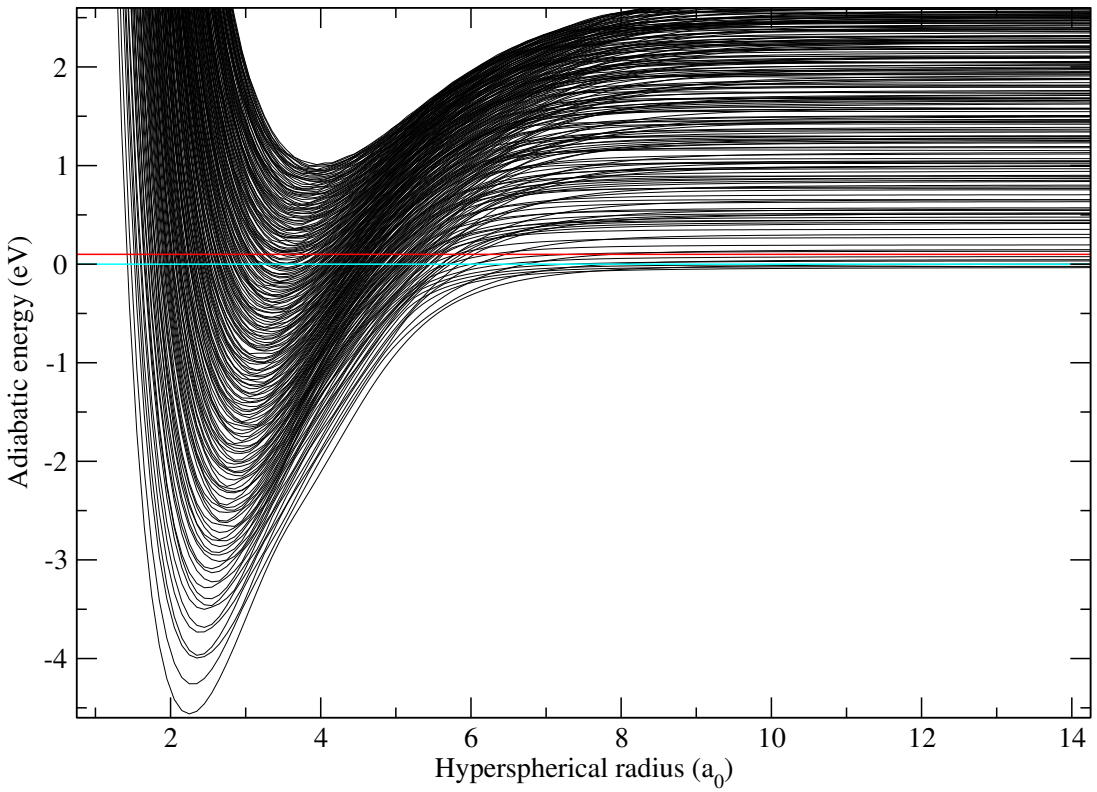
$$\sigma_{v'j',vj}(E) = \frac{\pi}{k_{vj}^2}\frac{1}{2j+1}\sum_{J\Omega'\Omega}(2J+1)\left|S^J_{v'j'\Omega',vj\Omega}(E)\right|^2$$

and the Differential Cross Section (DCS) :

$$\begin{aligned}\sigma_{v'j',vj}(\theta,E) &= \frac{1}{8\mu E_c(2j+1)}\times\sum_{\Omega'\Omega}\left|\sum_J(2J+1)\,d^J_{\Omega\Omega'}(\pi-\theta)\right.\\ &\times \left.\quad T^J_{v'j'\Omega',vj\Omega}(E)\quad\right|^2\end{aligned}$$

P. Honvault and J.-M. Launay, in Theory of Chemical Reaction Dynamics, edited by A. Lagana and G. Lendvay (Kluwer, Dordrecht, The Netherlands, 2004), Vol. 145, pp. 187215.

# 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 :

$$\mid S^J_{v'j'\Omega',vj\Omega}(E) \mid^2 \simeq \frac{p^J_{v'j'\Omega'}(E)p^J_{vj\Omega}(E)}{\sum_{v''j''\Omega''} p^J_{v''j''\Omega''}(E)}$$

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

$$\begin{aligned}\sigma^{SQM}_{v'j',vj}(\theta,E) &= \frac{1}{8\mu E_c(2j+1)} \times \sum_{\Omega'\Omega}\sum_{J}(2J+1)^2 \left[d^J_{\Omega\Omega'}(\pi-\theta)^2\right. \\ &+ \left. d^J_{\Omega\Omega'}(\theta)^2\right] \left|S^J_{v'j'\Omega',vj\Omega}(E)\right|^2\end{aligned}$$

# $J = 0$ Reaction Probability

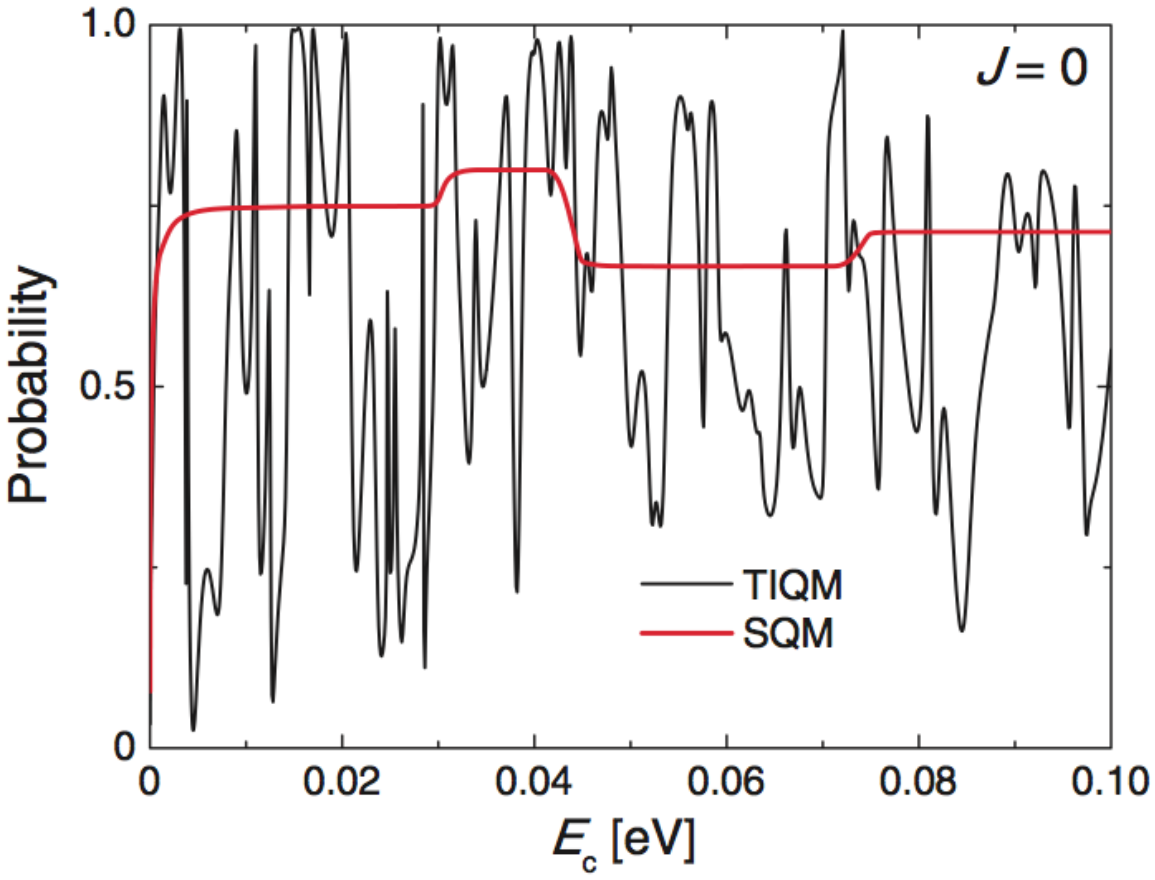
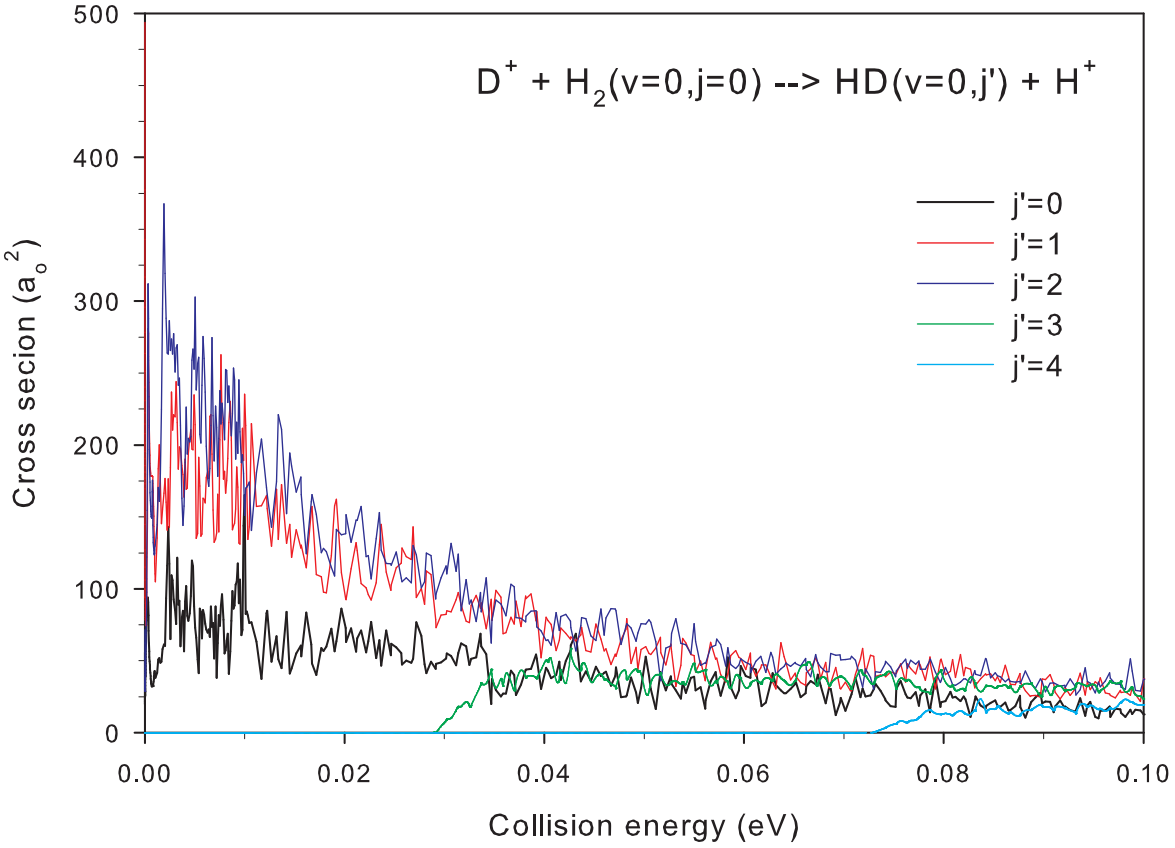


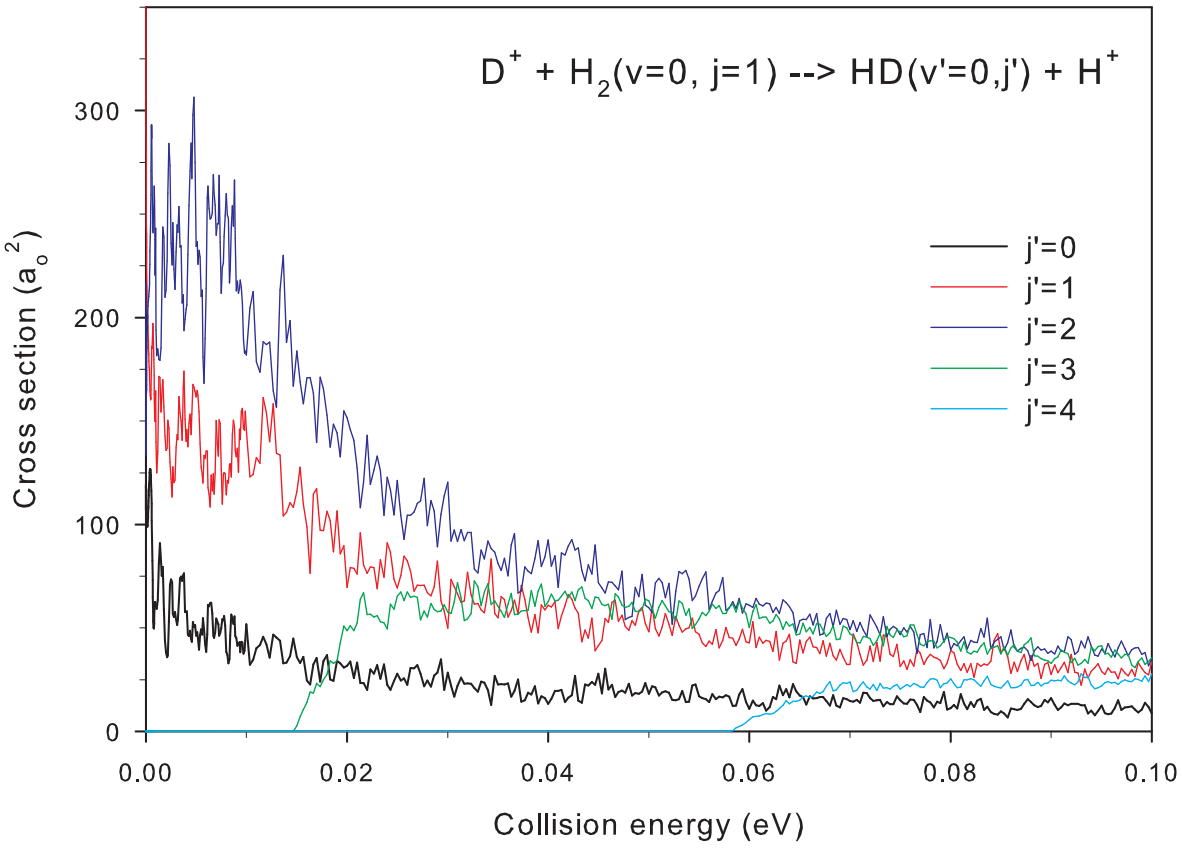

FIG. 1. Reaction probabilities for the $D^+ + H_2(v = 0, j = 0) \rightarrow H^+ + HD$ reaction at $J = 0$. TIQM results (black line) are compared with statistical predictions (red line).

T. Gonzalez-Lezana, Y. Scribano and P. Honvault, J.Chem.Phys. **139**, 054301 (2013)

# Integrated cross sections $\sigma(E)$



# Integrated cross sections $\sigma(E)$



# ICS : TIQM vs SQM

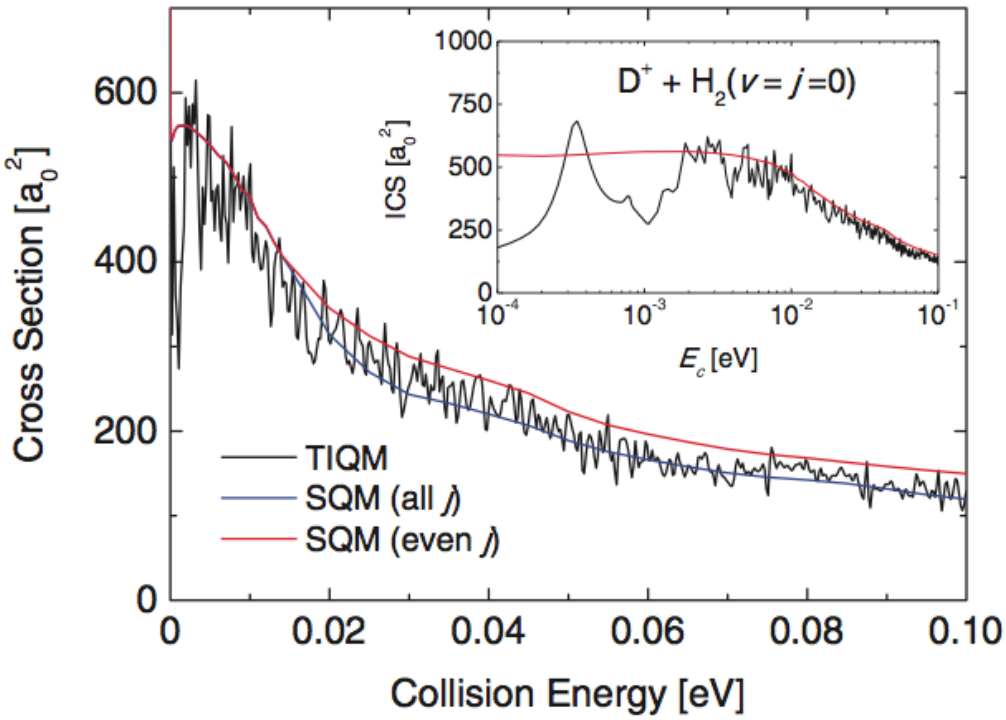



FIG. 2. Integral cross sections for the $D^+ + H_2(v = 0, j = 0) \rightarrow H^+ + HD$ reaction. TIQM results (black line) are compared with statistical predictions in which only even (red lines)/all (blue lines) rotational states of $H_2(v = 0, j)$ are taken into account. The inset displays the same results on a log scale for the sake of clarity at the low energy regime. See text for details.

# ICS : TIQM vs SQM

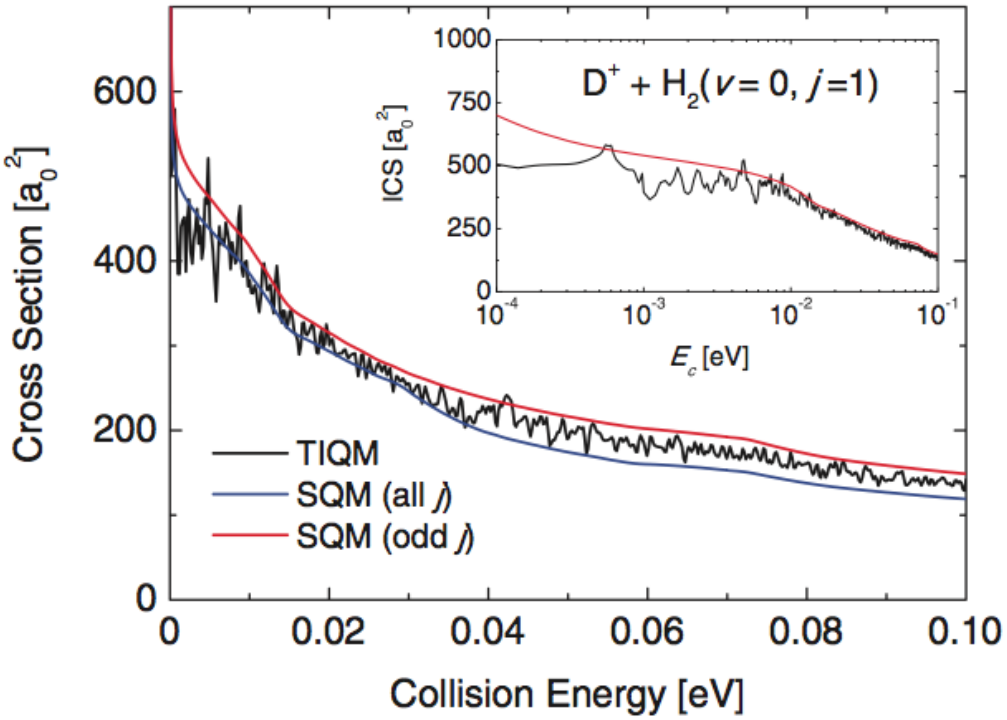



FIG. 3. Same as Fig. 2 for $D^+ + H_2(v = 0, j = 1) \rightarrow H^+ + HD$ reaction. SQM results are in this case for odd (red lines)/all (blue lines) rotational $H_2(v = 0, j)$ states.

# ICS : TIQM vs SQM

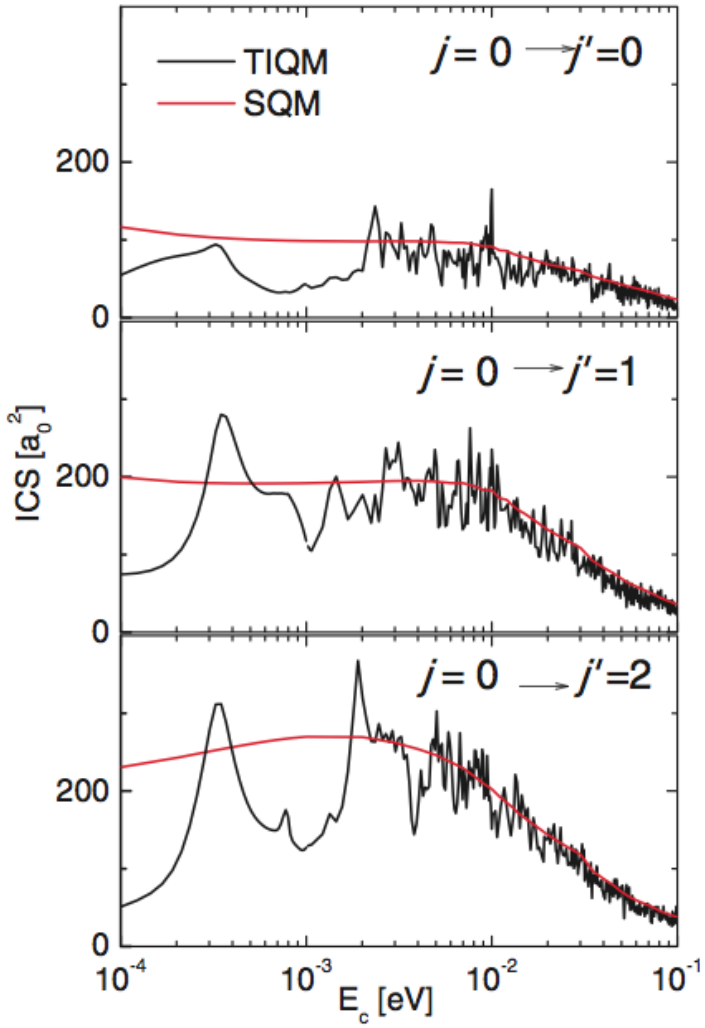
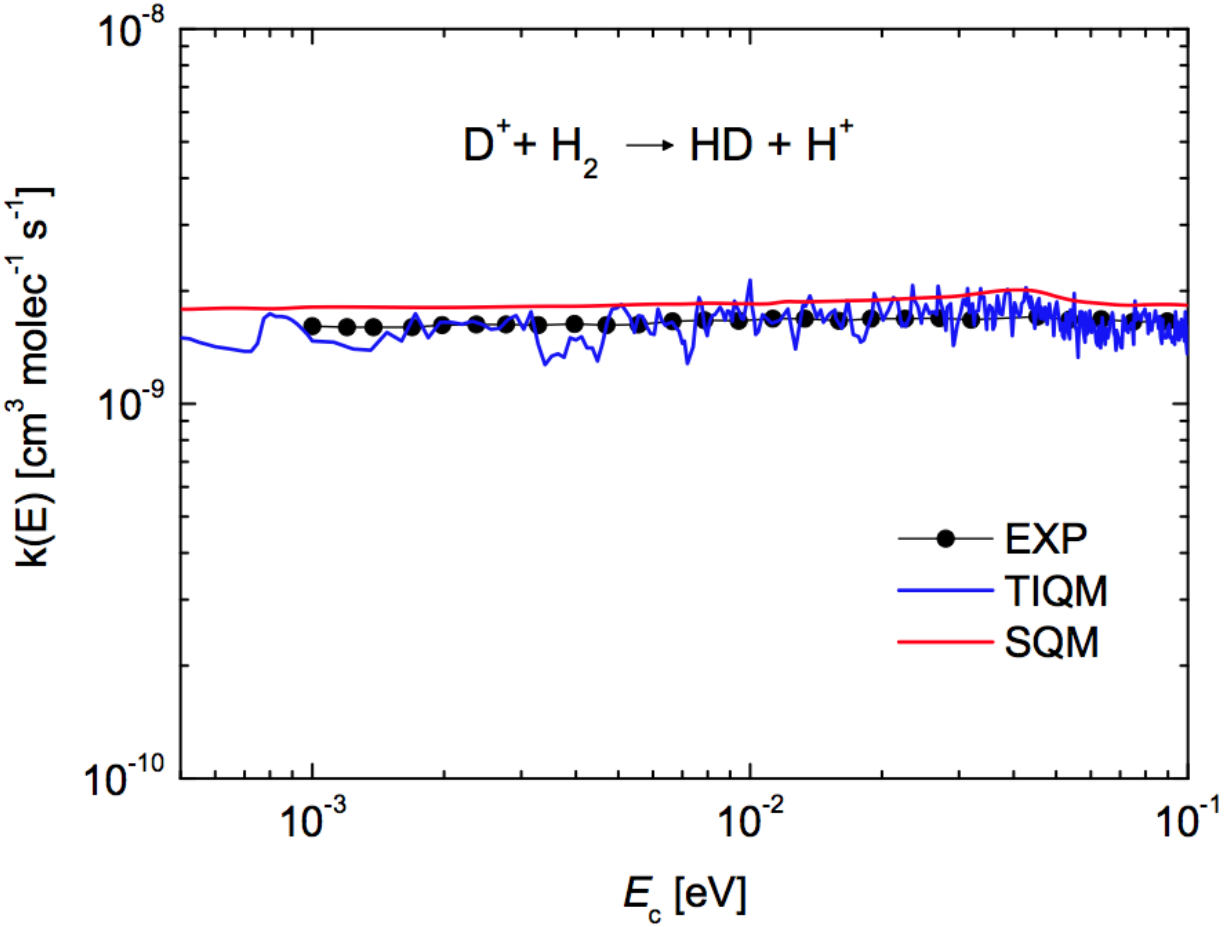



FIG. 4. State-to-state rate coefficients in terms of $E_c$ for the $D^+ + H_2(v = 0, j = 0) \rightarrow H^+ + HD(v' = 0, j' = 0 - 2)$ reaction.

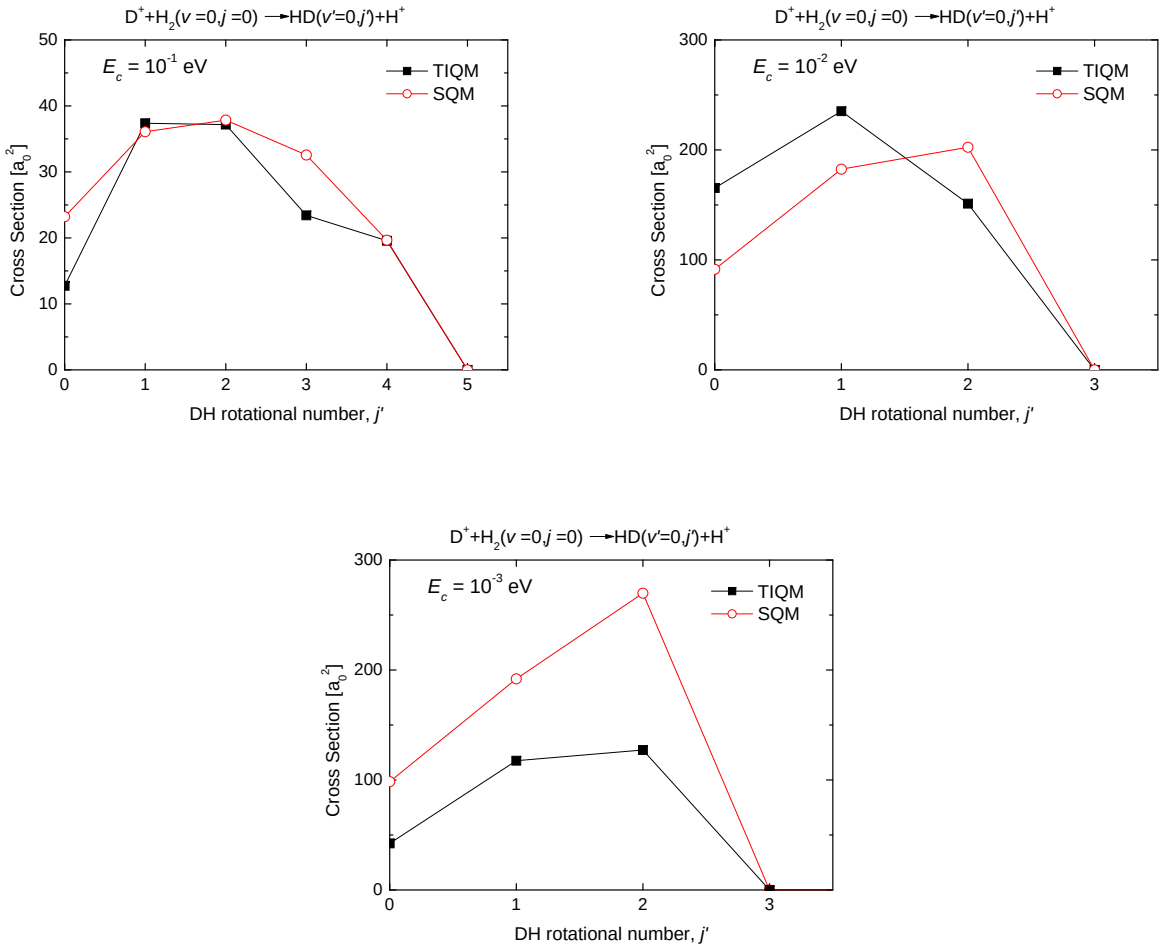
# Energy-Rate constant $k(E)$




P. Honvault and Y. Scribano, J.Phys.Chem. A **117**, 9778 (2013)

- Very good agreement with experimental data of D. Gerlich
- Only a slight decrease when we go to low collisional energy

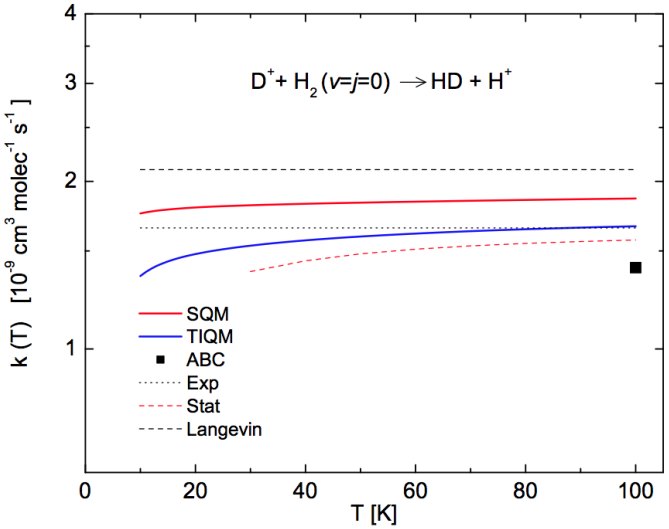
# Rotational distribution




SQM calculations provides a reasonably good counterpart for the TIQM rotational distribution

# Temperature-Rate constant $k(T)$

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




T. Gonzalez-Lezana, Y. Scribano and P. Honvault, J. Phys. Chem. A, 2014, 118 (33), pp 6416-6424

An Analytical formula was fitted for KIDA

# How to get the convergence ?

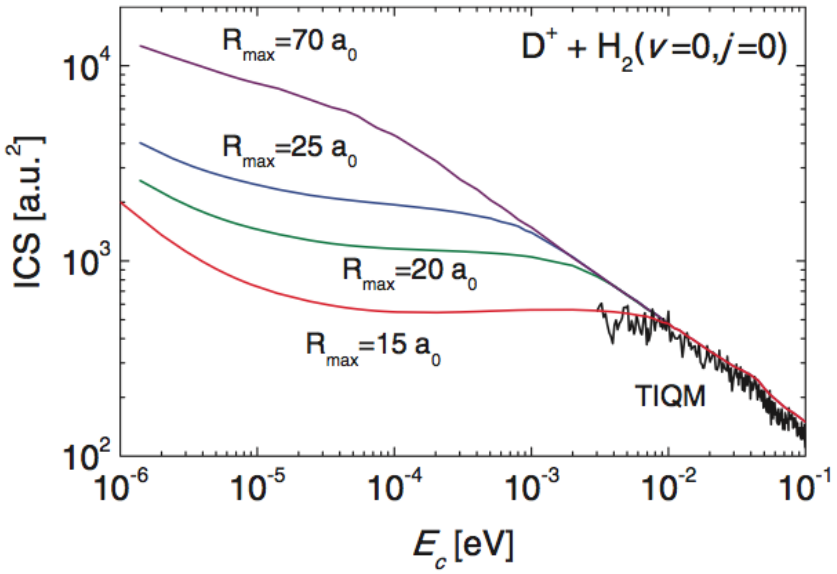



FIG. 9. Convergence test of the cross sections for $D^+ + H(v = 0, j = 0)$ obtained with the SQM approach for different values of $R_{max}$. TIQM results[49] are shown for comparison.

T. Gonzalez-Lezana, P. Honvault and Y. Scribano, J.Chem.Phys. **139**, 054301 (2013)

- 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)

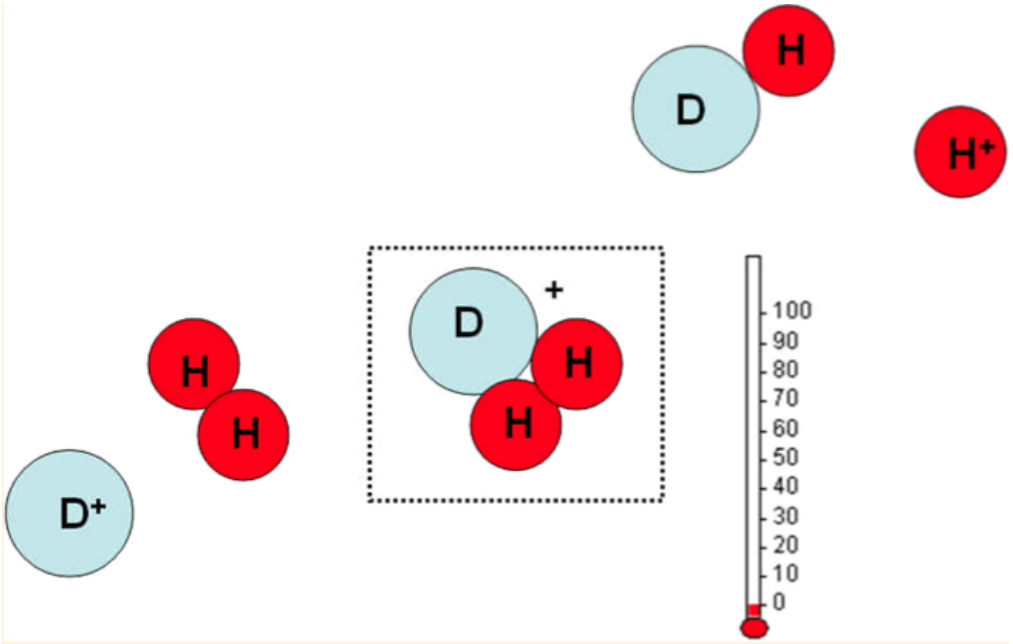
# Perspectives

- Perform the complementary study of $HD+H^+ \rightarrow D^+ + H_2$ (TIQM/SQM)
- Investigate the role of vibrationally excited $H_2(v)$ and $HD(v')$ in the rate constant (SQM/TIQM)
- Calculations for higher temperature than 100 K for early universe application but ...

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

- use of more efficient methods for such higher collisional energy range (such as TDWP method).
  see $HeH^+$+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 !