Ortho-para transitions of molecular hydrogen in $H^+ + H_2$ collisions

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Consejo Superior de Investigaciones Científicas

Grenoble (France) May 2017

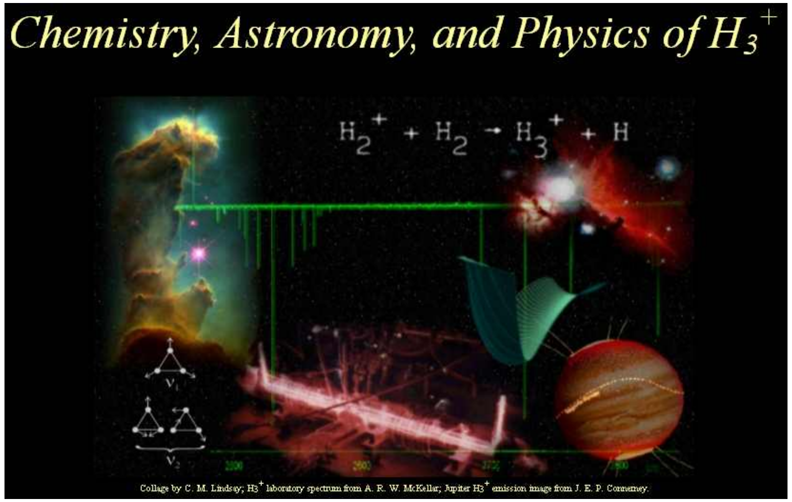
1. Introduction

2. Experiments and dynamics ($D^+ + H_2$, $H^+ + D_2$)

3. State-to-state study of $H^+ + H_2$

Importance of H_3^+

Almost an entire separate chapter on Chemistry, Physics and Astronomy



Chemistry, Astronomy, and Physics of H_3^+

Collage by C. M. Lindsay; H_3^+ laboratory spectrum from A. R. W. McKellar; Jupiter H_3^+ emission image from J. E. P. Connerney.

Most abundant ionic species in hydrogen plasmas.

Crucial role in first stages of stars formation

Largely investigated:

(i) Spectroscopy
(ii) PESs
(iii) Reactive scattering

Both k(T) and dynamics in terms of E

Chemical clock: The *o*-H_2(odd *j*) abundance is key to estimate the age of interstellar dark clouds which lead to form stars.

→ **Deuterium**

D/H ratio ~ $1.5 \cdot 10^{-5}$ in the vicinity of Solar System. This value is supposed to remain for HDO/H_2O, N_2D^+/N_2H^+ etc…

However ND_3 and CD_3OH have been detected at abundances 10^{10}, 10^{15} larger than expected.

Why? Grains depleted from newborn star at the center of the core.

Modelling the time for those species (D) to disappear gives age of the protostar.

→ **o-H_2**

o-H_2 can react with deuterated species removing D.
N_2D^+/N_2H^+ ratio increases when o-H_2 abundance decrease

Study of o-H_2 / p-H_2 ratio !!

o-H_2 conversion to p-H_2 via collisions:

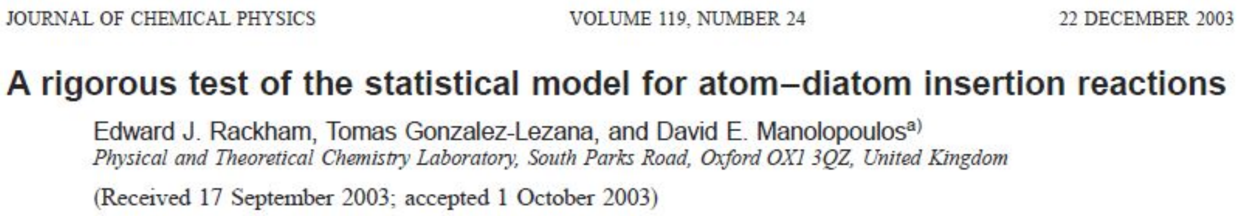
H^+ + o-H_2 → H^+ + p-H_2
H_3^+ + o-H_2 → H_3^+ + p-H_2

E. Roueff et al. *Rate Coefficients in Astrochemistry*
Kluwer Academ. Pub. 73-85 (1988)

"(...) *At low collisional energies, $H_2(j)$ collides with H^+ in a reactive process which proceeds through the strongly coupled intermediate complex H_3^+ which leads to a redistribution of the rotational states of H_2 without any selection rule on j and induces ortho-para transitions*"

H + H_2 ?

Formation of intermediate complex ⟷ Statistical methods for dynamics



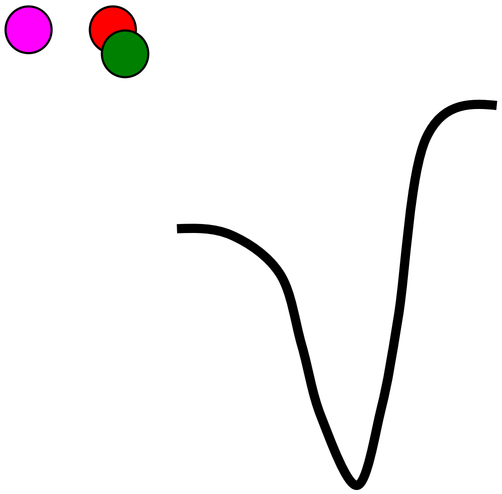
JOURNAL OF CHEMICAL PHYSICS VOLUME 119, NUMBER 24 22 DECEMBER 2003

A rigorous test of the statistical model for atom–diatom insertion reactions

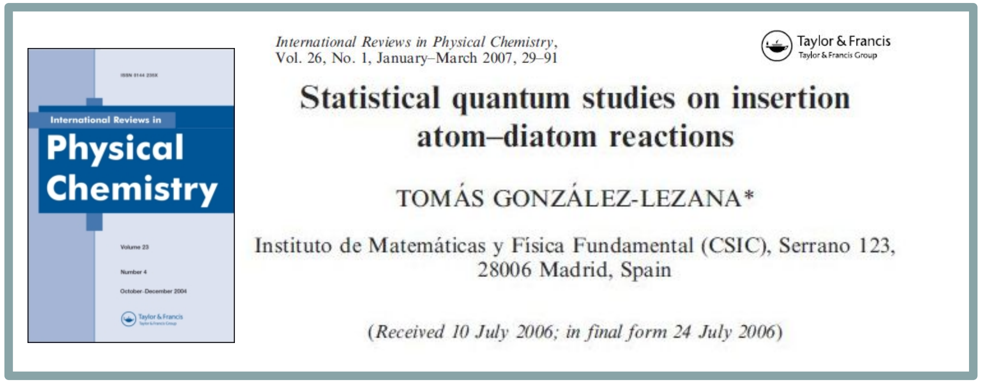
Edward J. Rackham, Tomas Gonzalez-Lezana, and David E. Manolopoulos[a)]
Physical and Theoretical Chemistry Laboratory, South Parks Road, Oxford OX1 3QZ, United Kingdom

(Received 17 September 2003; accepted 1 October 2003)

$$|S^J_{vjk,v'j'k'}(E)|^2 \cong \frac{p^J_{vjk}(E)\,p^J_{v'j'k'}(E)}{\sum_{v''j''k''} p^J_{v''j''k''}(E)}$$



QM calculation of probabilities
Ab initio PES



International Reviews in Physical Chemistry,
Vol. 26, No. 1, January–March 2007, 29–91

Taylor & Francis
Taylor & Francis Group

Statistical quantum studies on insertion atom–diatom reactions

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28006 Madrid, Spain

(Received 10 July 2006; in final form 24 July 2006)

A +BC → (ABC) → AB + C

2. Experiments and dynamics: ($D^+ + H_2$, $H^+ + D_2$)

What we know from Theory

- Indications of:

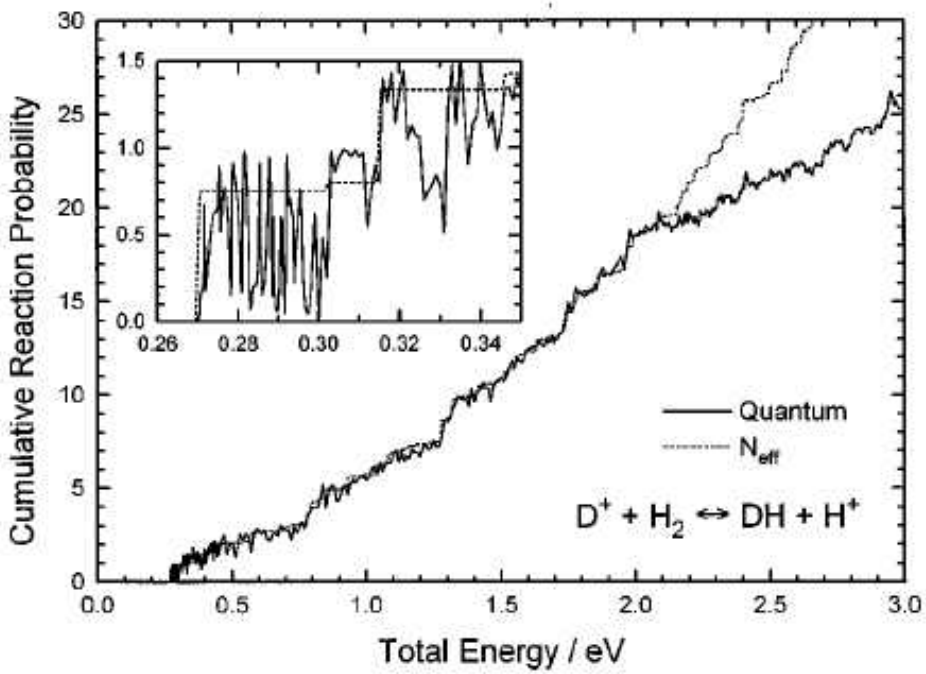
Short-lived complex formation
low energies (≤ 3 eV)

→

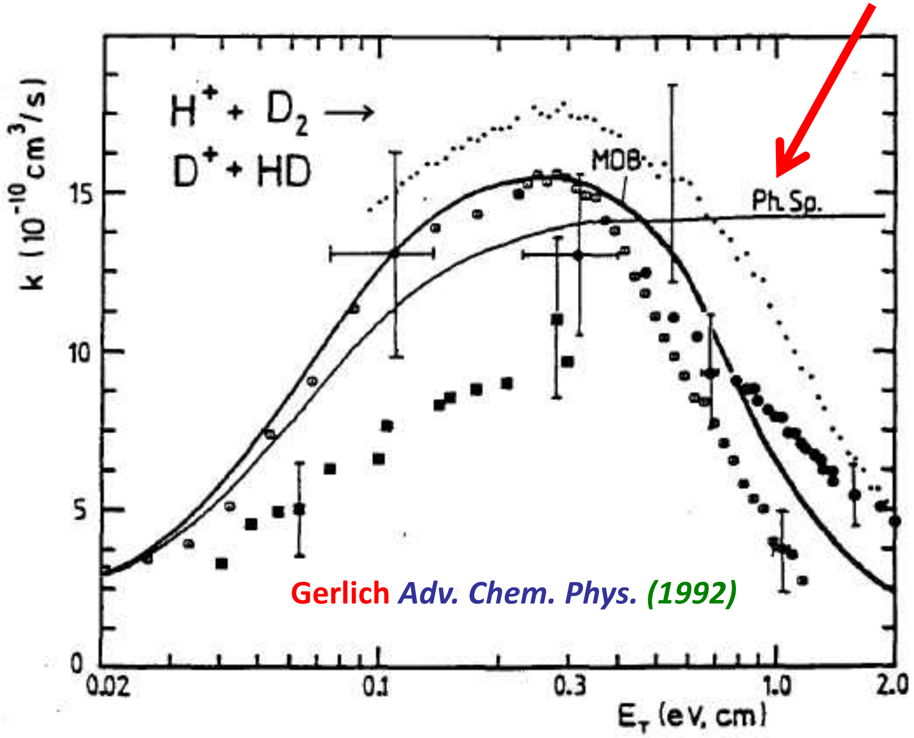
Direct impulsive mechanism
higher energies (≥ 4.5 eV)

Krenos (74); Schiler (85,87); Ichihara (00);

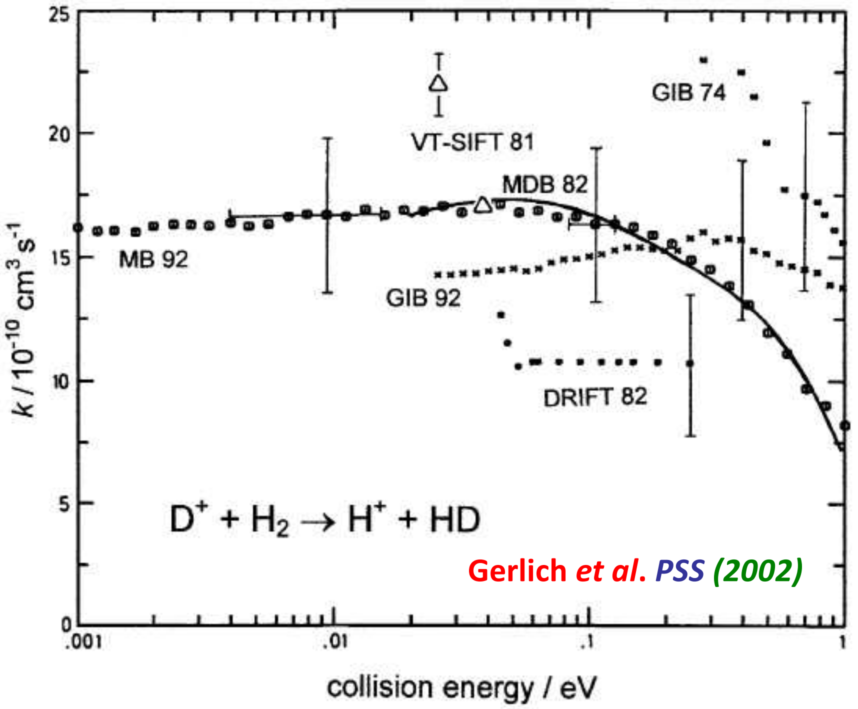
- Statistical approaches for *J*=0-CRP for:
  $D^+ + H_2$ at E < 2.1 eV Takayanagi (00)
  $H^+ + HD$: Kamisaka (02)



What we know from Experiment



Gerlich *Adv. Chem. Phys.* *(1992)*



Gerlich *et al*. *PSS* *(2002)*

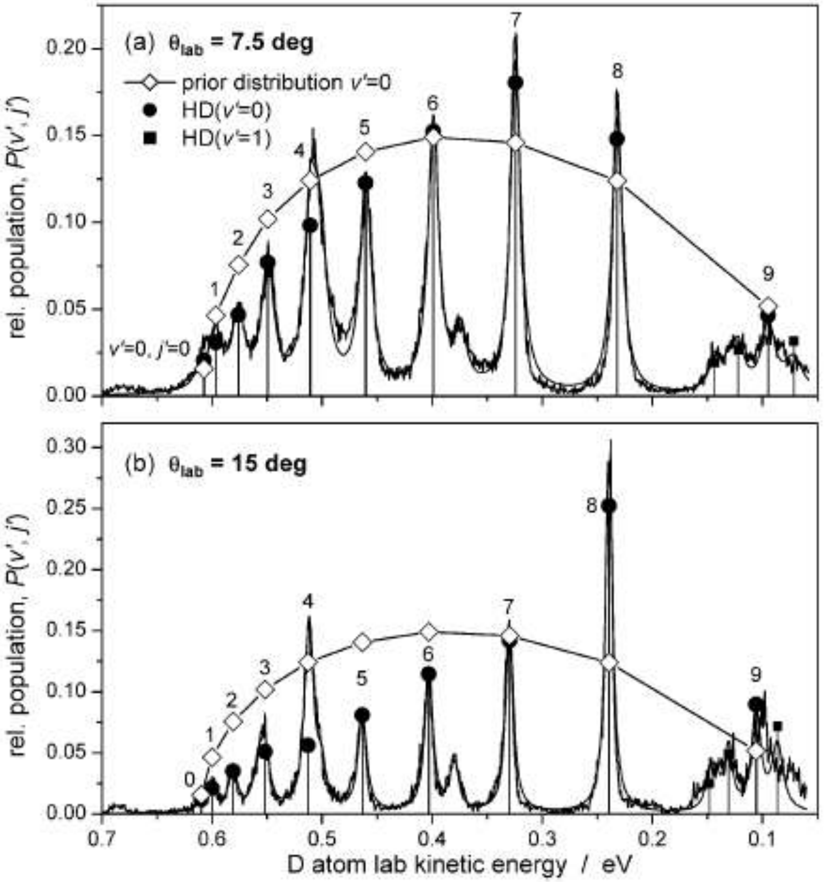
VT-SIFT: Variable Temp. Selected Ion Flow Tube **Henchman 81**
GIB: Guided Ion Beams **Ochs Teloy 74; Gerlich 92**
DRIFT: Drift Tube **Villinger 82**

Pioneering measurements of rate coefficients

Some differences with PST approach at large E

What we know from Experiment

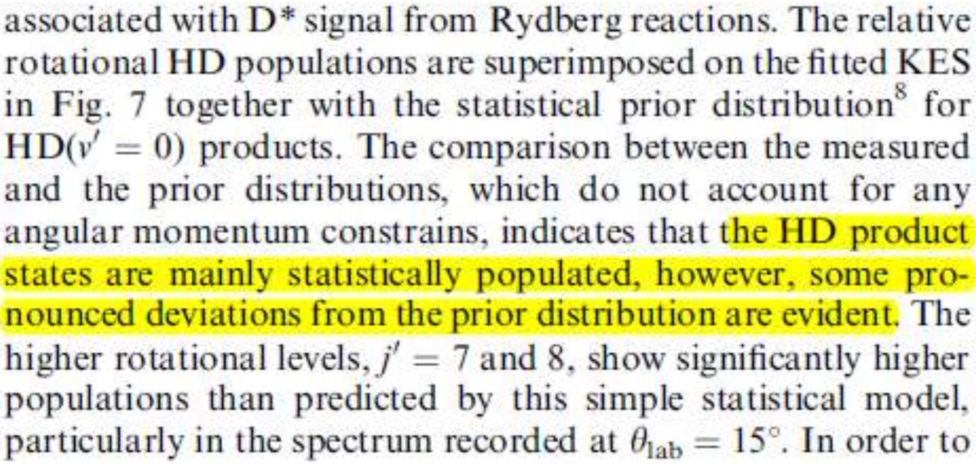
$H^{+}+D_{2} \rightarrow HD+D^{+}$



Wrede *et al.* *PCCP 7 1577 (2005)*

Rovibrationally resolved state distributions of HD are close to those from the ion-molecule reaction

Attempts to describe things statistically:

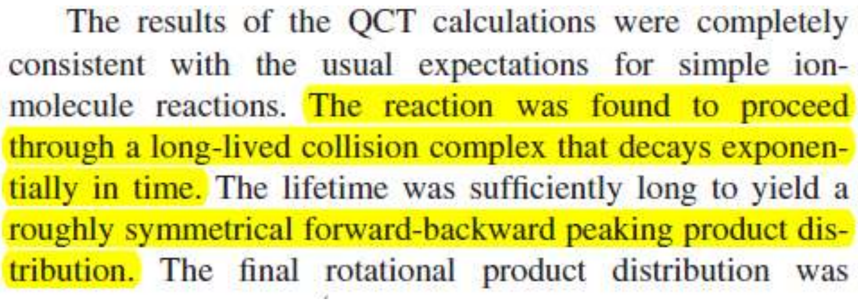


associated with D* signal from Rydberg reactions. The relative rotational HD populations are superimposed on the fitted KES in Fig. 7 together with the statistical prior distribution[8] for HD($v' = 0$) products. The comparison between the measured and the prior distributions, which do not account for any angular momentum constrains, indicates that the HD product states are mainly statistically populated, however, some pronounced deviations from the prior distribution are evident. The higher rotational levels, $j' = 7$ and 8, show significantly higher populations than predicted by this simple statistical model, particularly in the spectrum recorded at $\theta_{\mathrm{lab}} = 15°$. In order to

E. Wrede

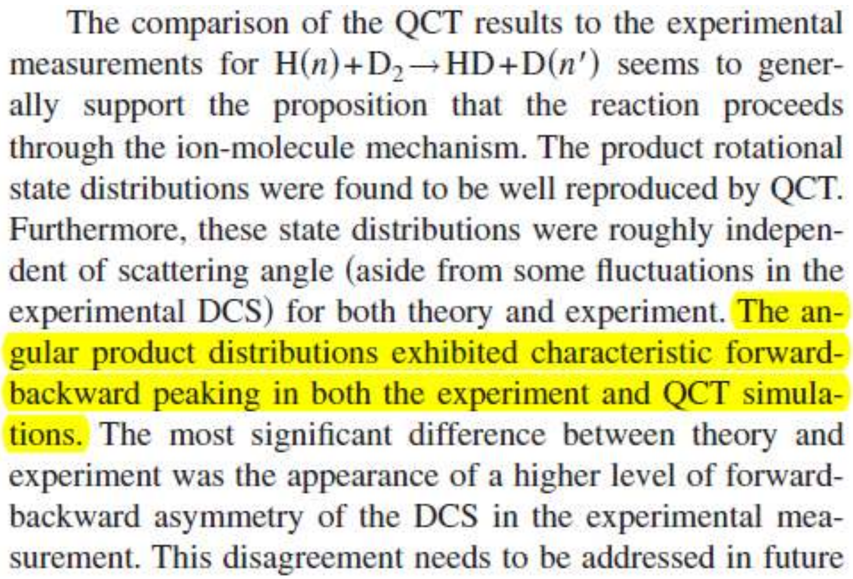
What we know from Experiment

Indications of a complex-forming dynamics from the QCT calculation:



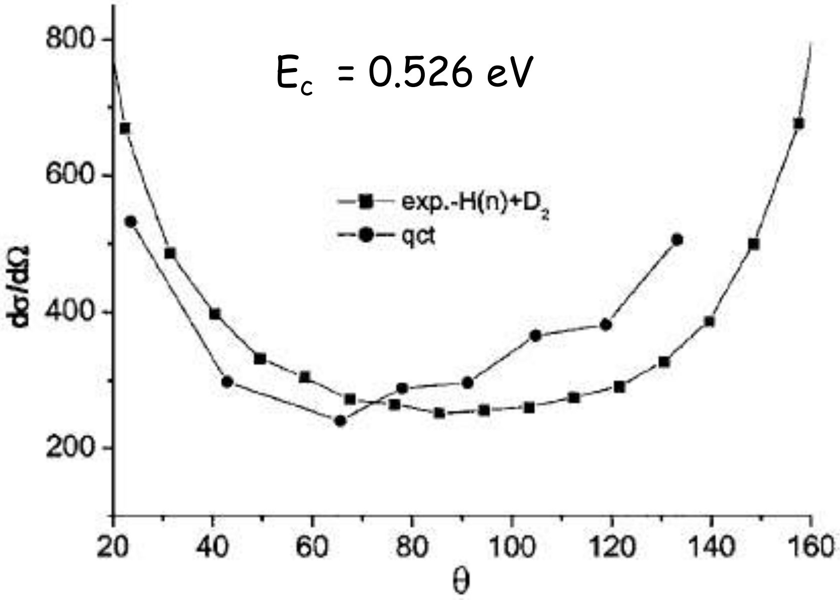
The results of the QCT calculations were completely consistent with the usual expectations for simple ion-molecule reactions. The reaction was found to proceed through a long-lived collision complex that decays exponentially in time. The lifetime was sufficiently long to yield a roughly symmetrical forward-backward peaking product distribution. The final rotational product distribution was

…and from the experiment:



The comparison of the QCT results to the experimental measurements for $H(n)+D_2 \rightarrow HD+D(n')$ seems to generally support the proposition that the reaction proceeds through the ion-molecule mechanism. The product rotational state distributions were found to be well reproduced by QCT. Furthermore, these state distributions were roughly independent of scattering angle (aside from some fluctuations in the experimental DCS) for both theory and experiment. The angular product distributions exhibited characteristic forward-backward peaking in both the experiment and QCT simulations. The most significant difference between theory and experiment was the appearance of a higher level of forward-backward asymmetry of the DCS in the experimental measurement. This disagreement needs to be addressed in future

$H^+ + D_2$



Song *et al.* *JCP* 123 074314 (2005)

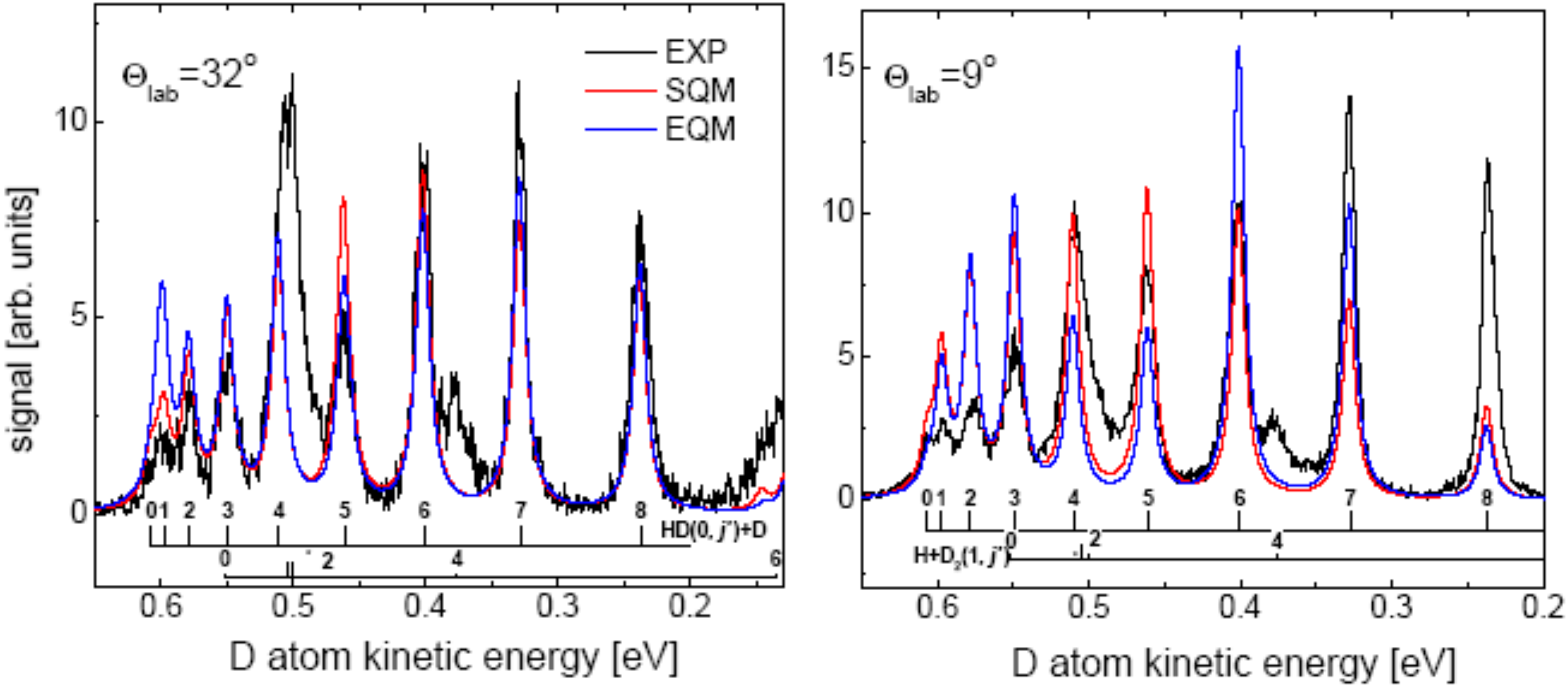
R.T. Skodje

X. Yang

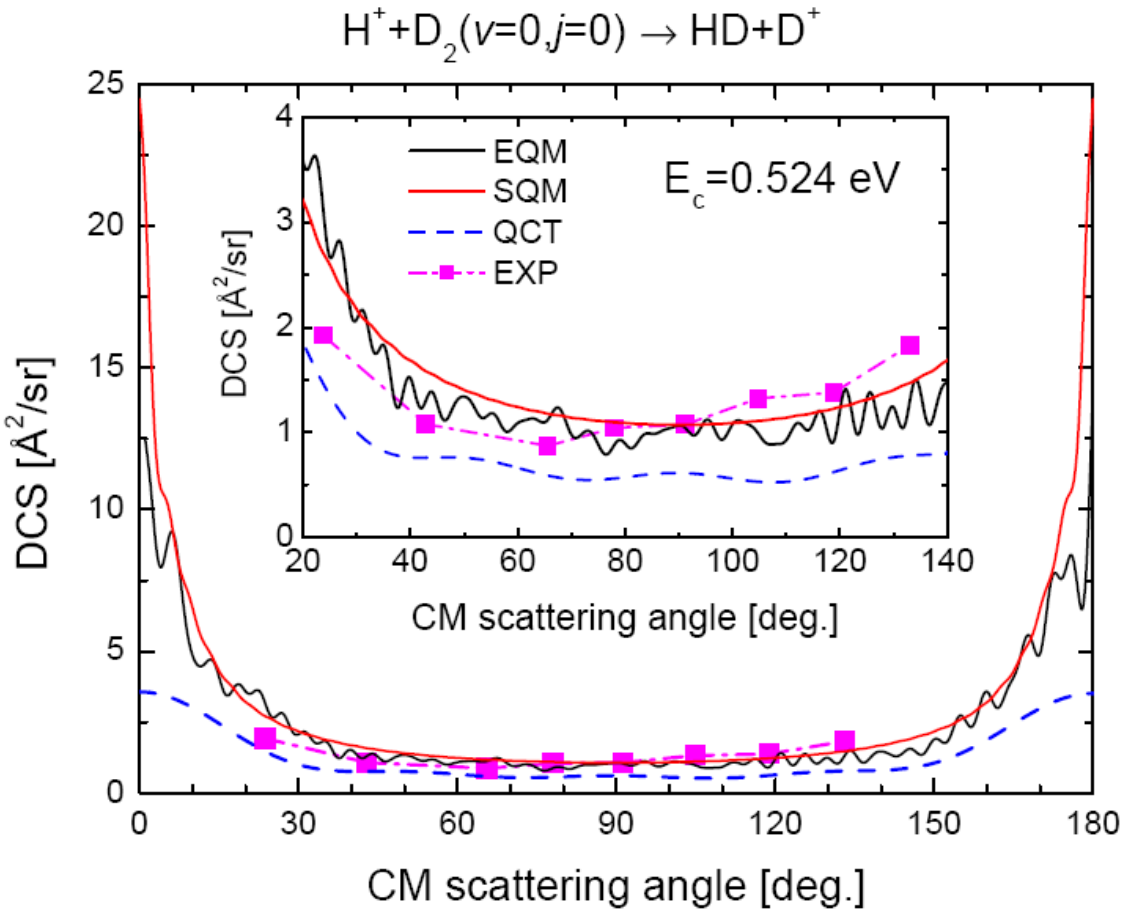
$H^+ + D_2(v=0, j=0) \rightarrow D^+ + DH$

Carmona-Novillo *et al.* *JCP* *(2008)*

$E_c = 0.526$ eV

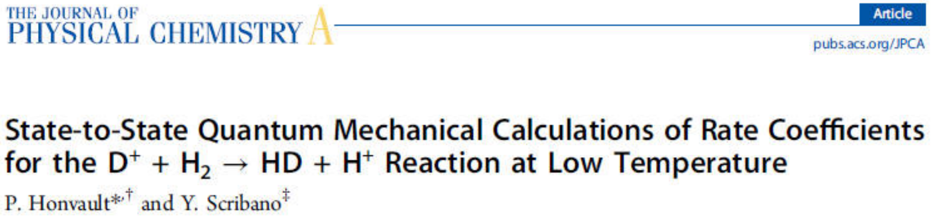


Better agreement between theory and experiment at sideways scattering (Θ_{lab}=52º) than at backward scattering (Θ_{lab}=9º)



Agreement with and exact TIQM result except at the strict forward/backward peaks

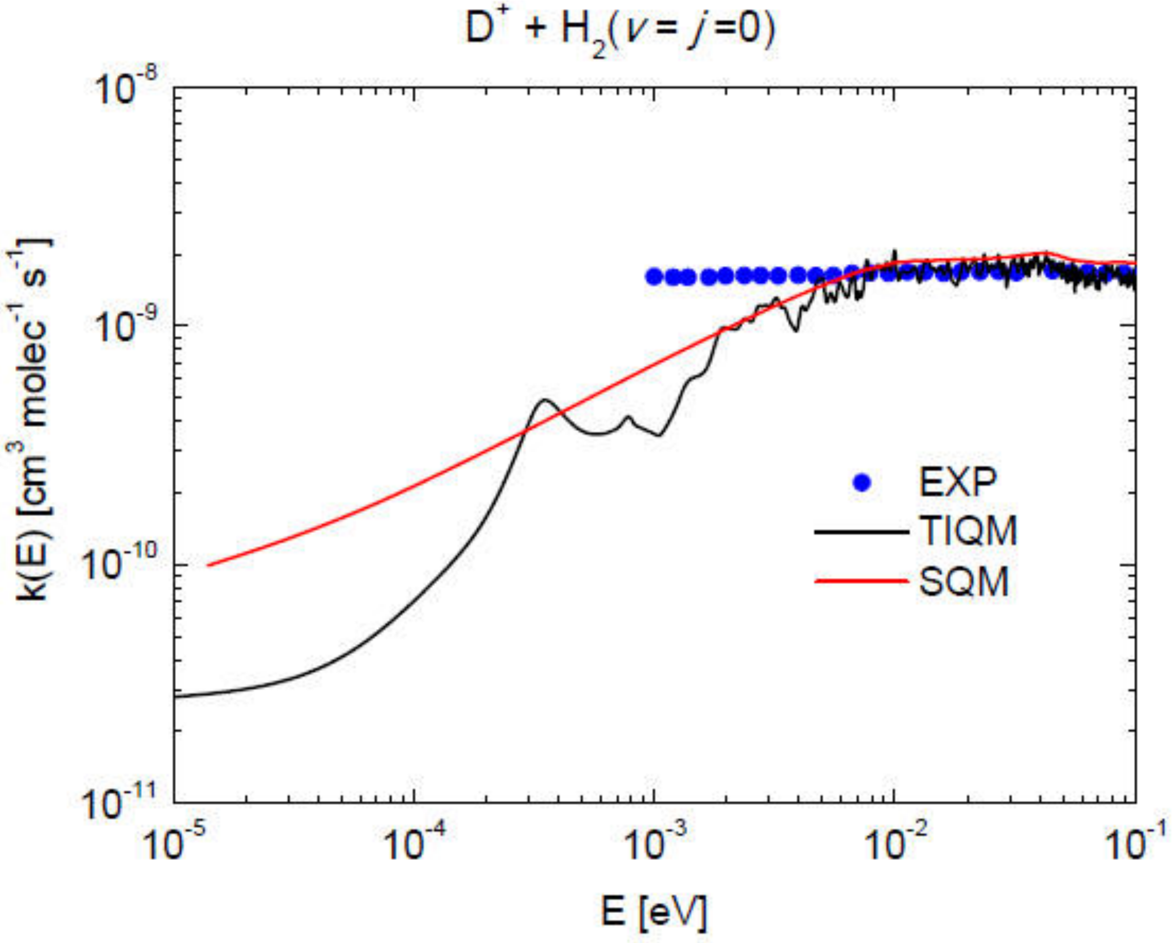
Failure of the QCT approach ↔ QM effects



THE JOURNAL OF PHYSICAL CHEMISTRY A
Article
pubs.acs.org/JPCA

State-to-State Quantum Mechanical Calculations of Rate Coefficients for the $D^+ + H_2 \rightarrow HD + H^+$ Reaction at Low Temperature

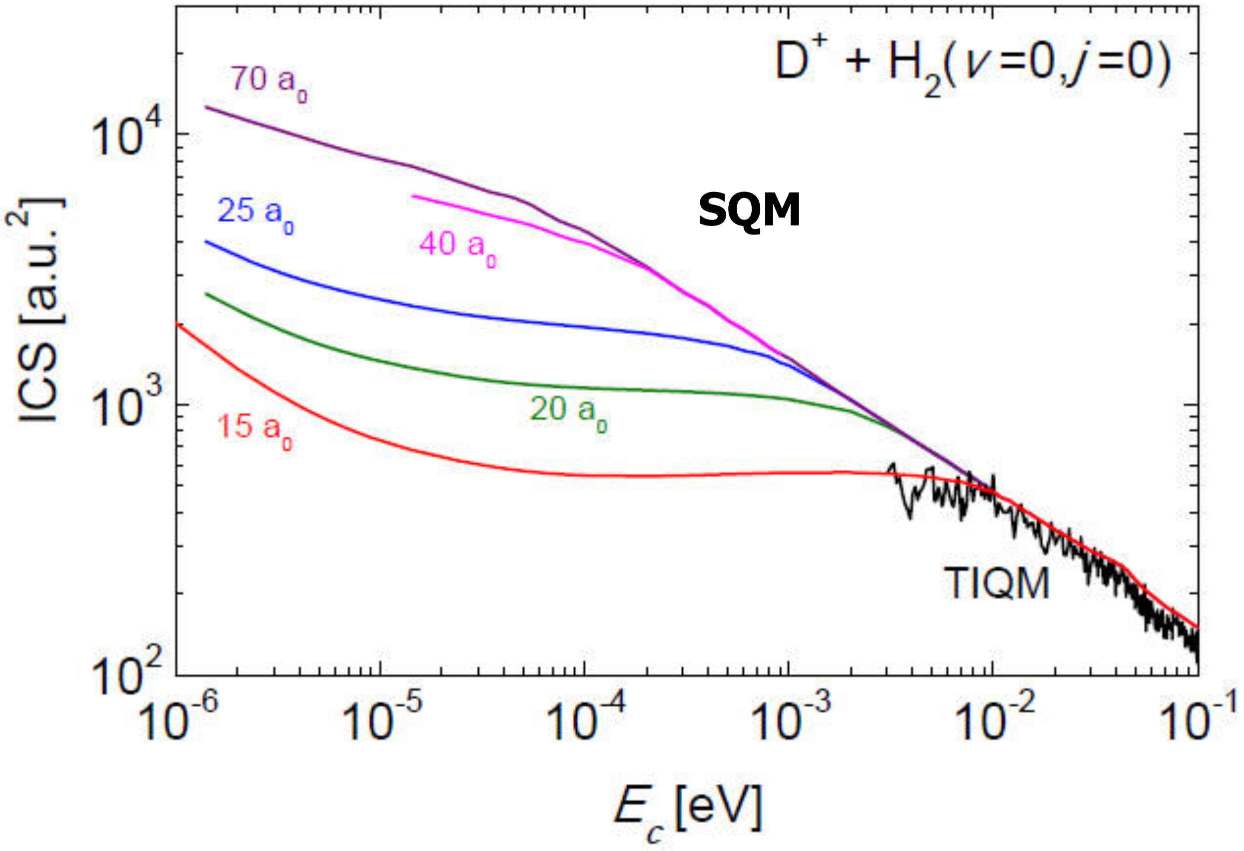
P. Honvault*,† and Y. Scribano‡



TIQM rate coefficients decrease as E decreases

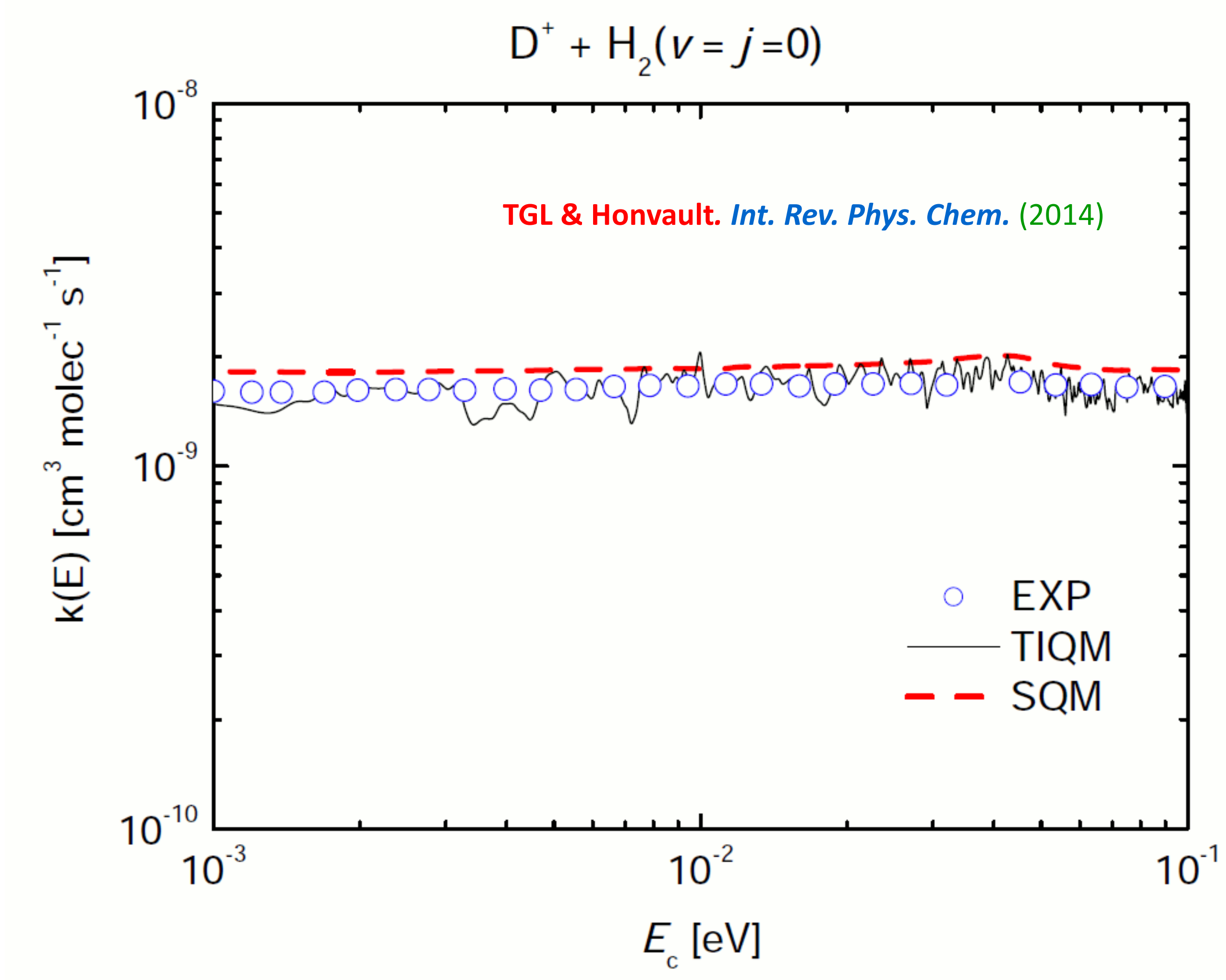
SQM results agree with TIQM; same discrepancies with EXP

TGL, Scribano & Honvault. *J. Phys. Chem. A* (2014)

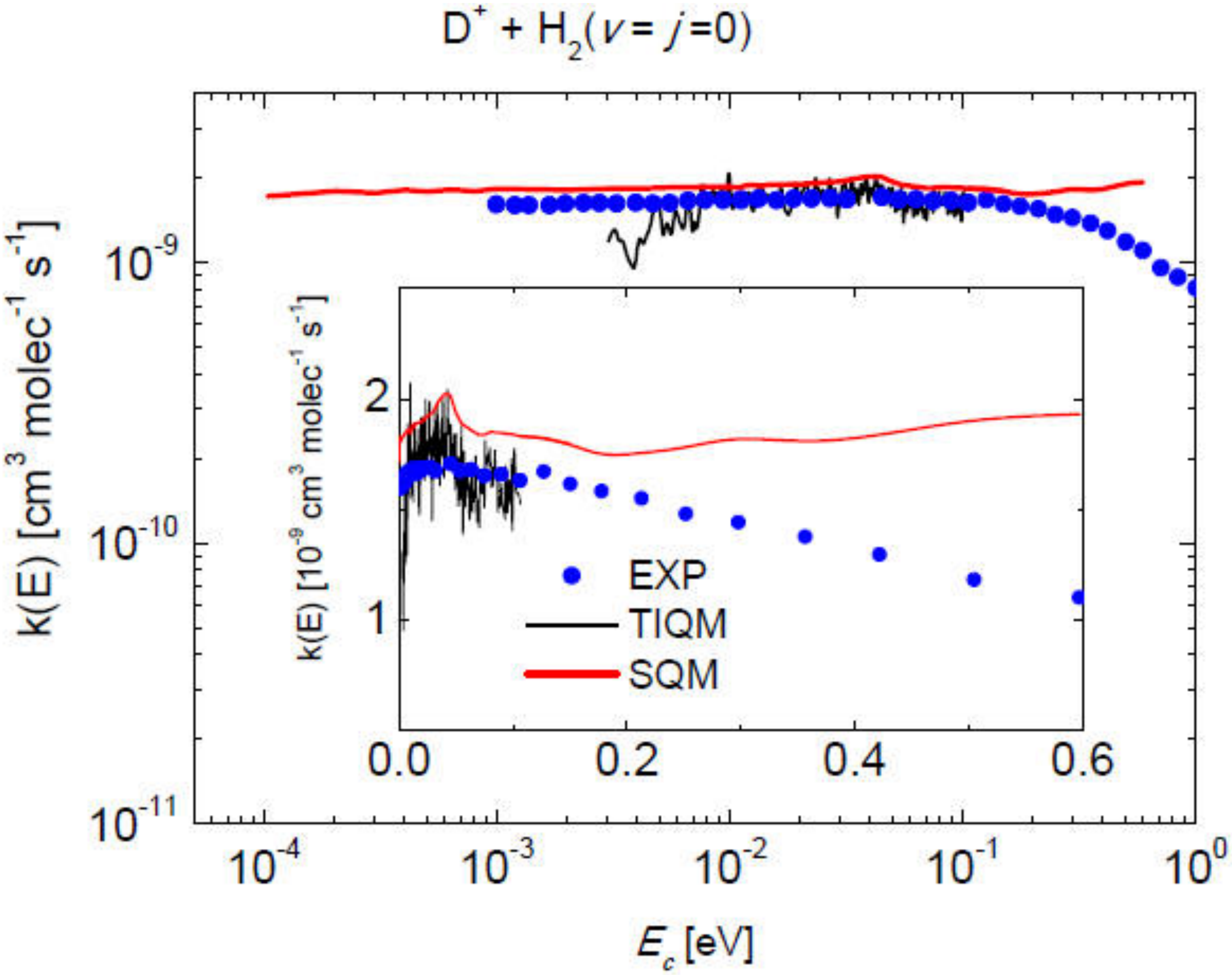


R_{max} consistent with ρ_{max} of the TIQM is only valid for $E_c \sim 10^{-2}$ eV

R_{max} 25 a_0 $E_c \sim 10^{-3}$ eV
R_{max} 40 a_0 $E_c \sim 2 \cdot 10^{-4}$ eV
R_{max} 70 a_0 $E_c \sim 10^{-4}$ eV

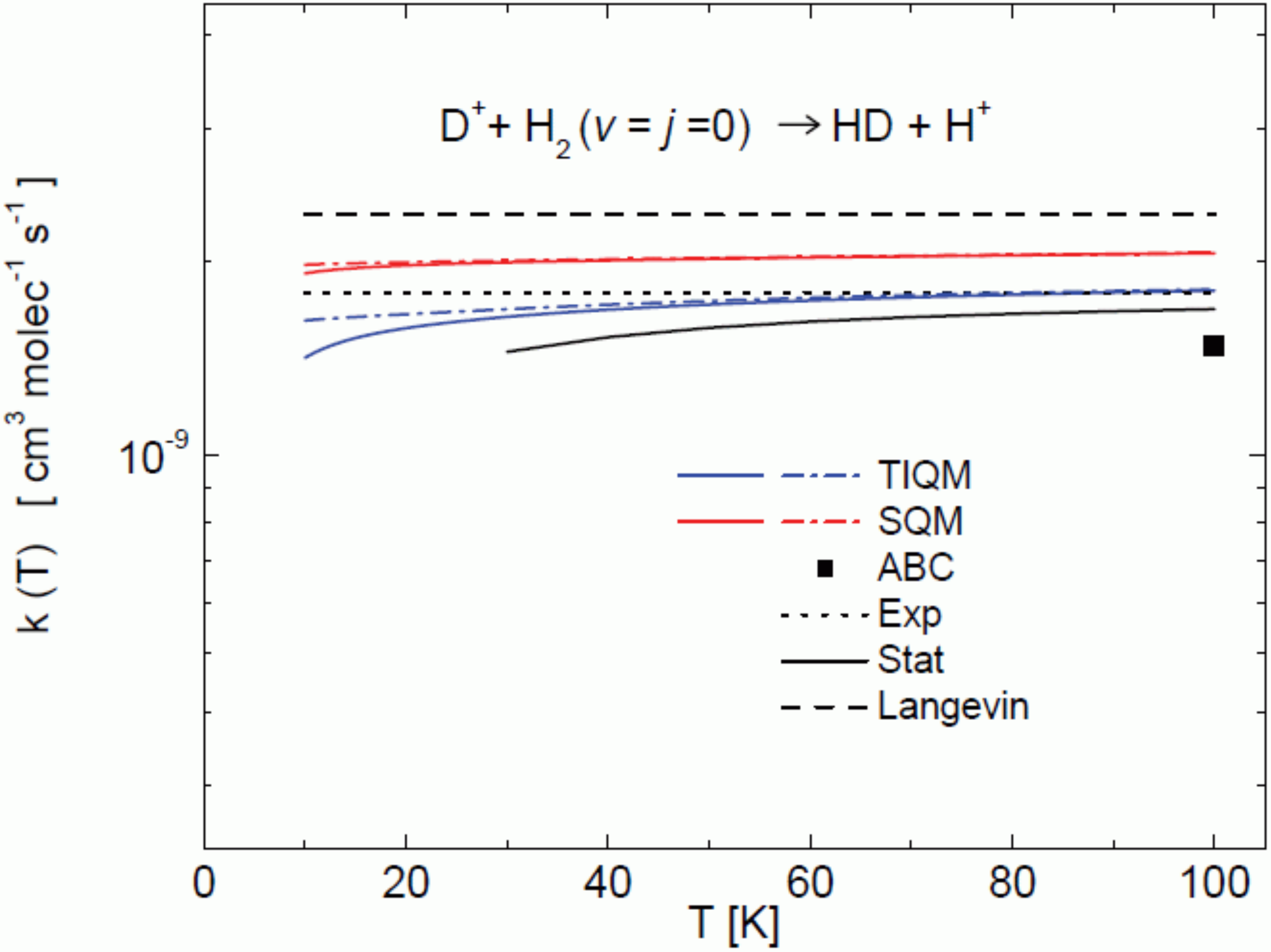


Actual EXP vs Theory comparison with limits of validity for SQM and TIQM

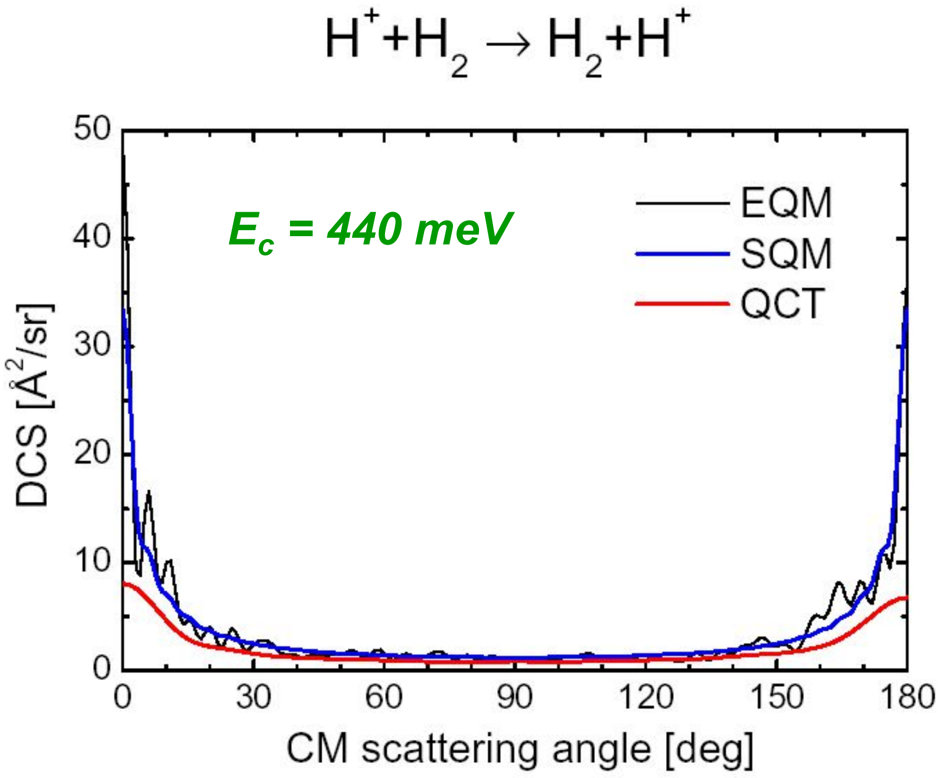


SQM slightly differs from EXP beyond 0.2 eV

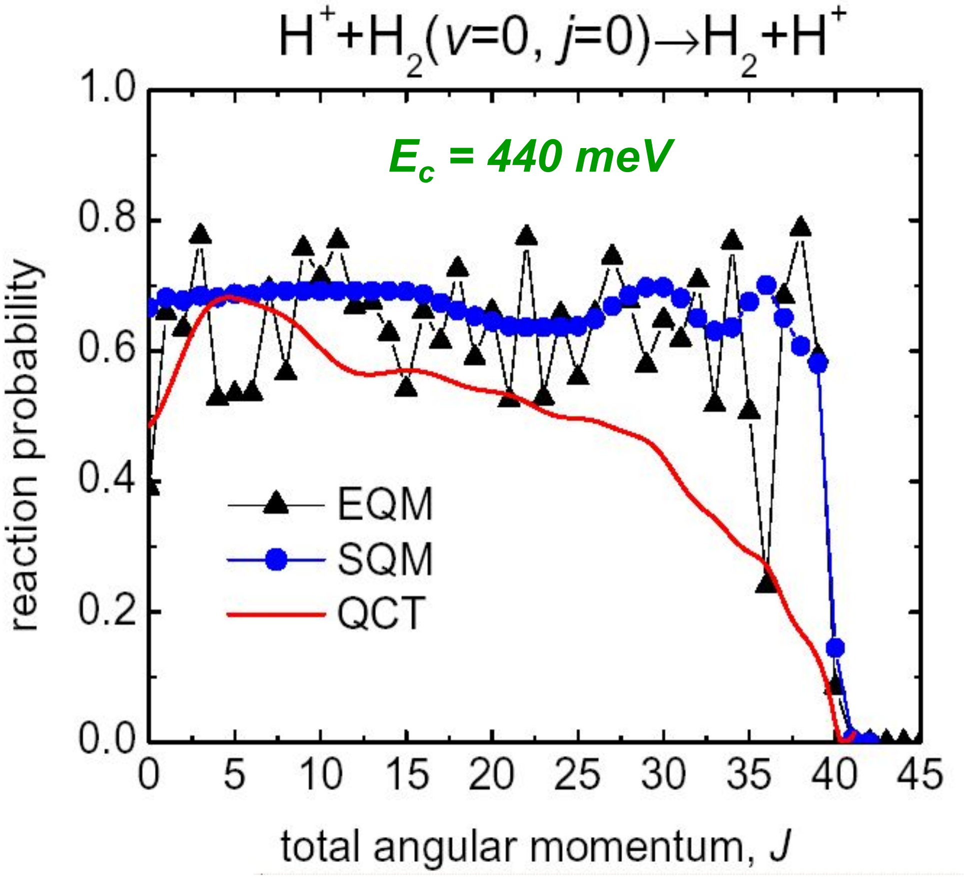
TIQM shows the correct trend as E_c increases


$D^+ + H_2(v = j = 0) \rightarrow HD + H^+$
k (T) [cm^3 molec^{-1} s^{-1}]
10^{-9}
0
20
40
60
80
100
T [K]
TIQM
SQM
■ ABC
Exp
Stat
Langevin

3. State-to-state study of $H^+ + H_2$



TGL *et al*. *JCP* 125, 094314 *(2006)*

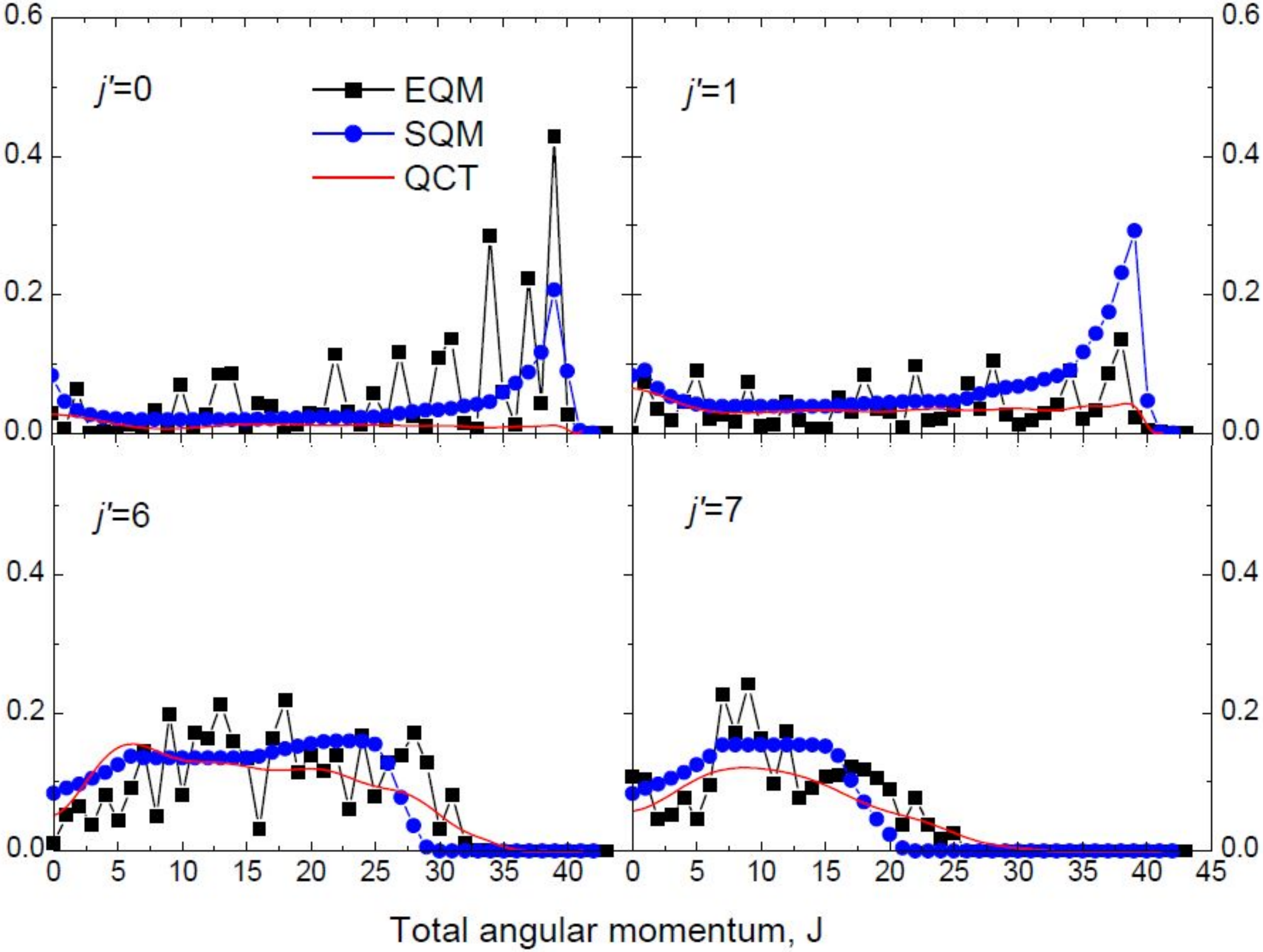


Good agreement (forward/backward peaks!)

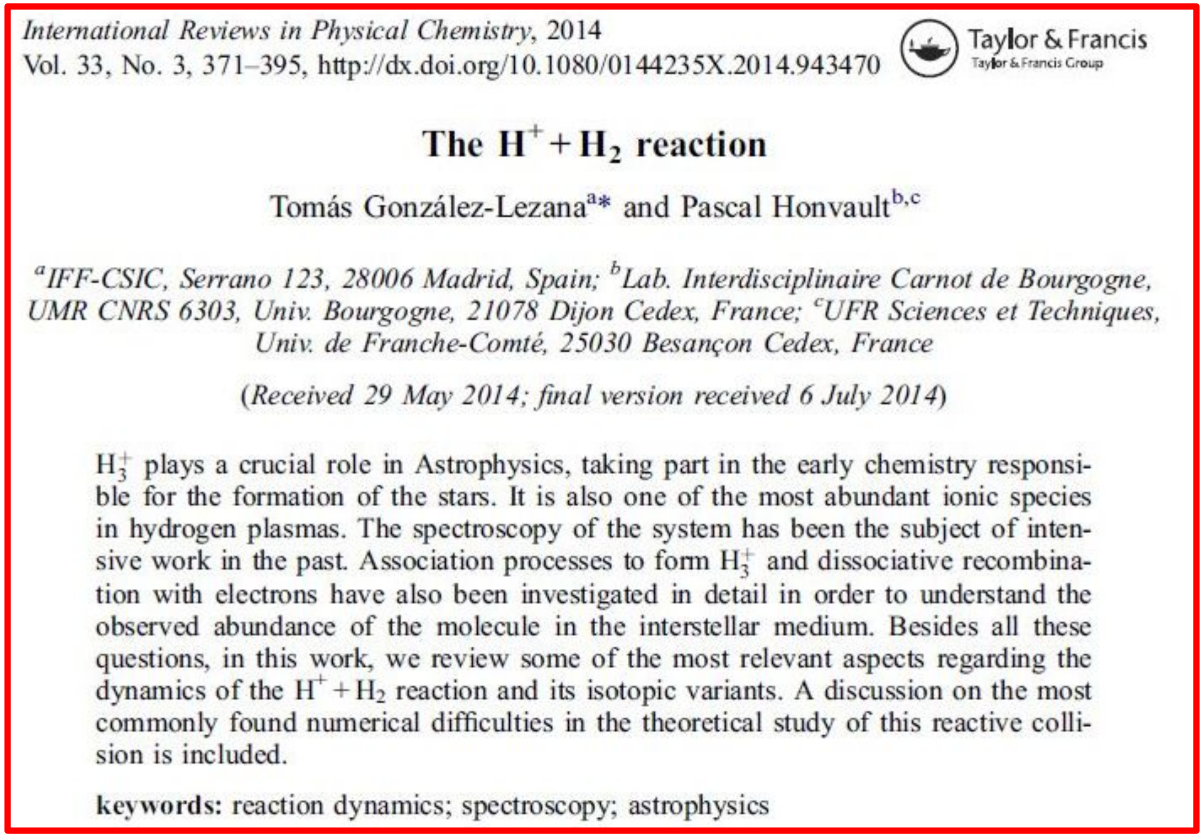
QCT failure as J increases

No oscillations in SQM result

$H^+ + H_2(v = 0, j = 0)$



TGL *et al*. *JCP* 125, 094314 *(2006)*



International Reviews in Physical Chemistry, 2014
Vol. 33, No. 3, 371–395, http://dx.doi.org/10.1080/0144235X.2014.943470

The $H^+ + H_2$ reaction

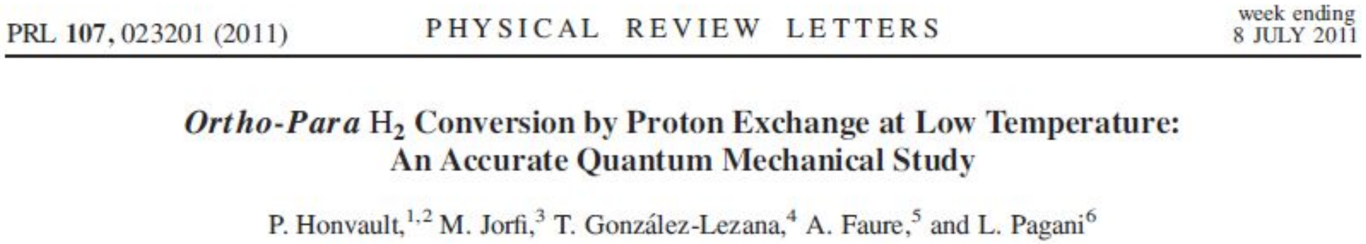
Tomás González-Lezana[a]* and Pascal Honvault[b,c]

[a]*IFF-CSIC, Serrano 123, 28006 Madrid, Spain;* [b]*Lab. Interdisciplinaire Carnot de Bourgogne, UMR CNRS 6303, Univ. Bourgogne, 21078 Dijon Cedex, France;* [c]*UFR Sciences et Techniques, Univ. de Franche-Comté, 25030 Besançon Cedex, France*

(*Received 29 May 2014; final version received 6 July 2014*)

H_3^+ plays a crucial role in Astrophysics, taking part in the early chemistry responsible for the formation of the stars. It is also one of the most abundant ionic species in hydrogen plasmas. The spectroscopy of the system has been the subject of intensive work in the past. Association processes to form H_3^+ and dissociative recombination with electrons have also been investigated in detail in order to understand the observed abundance of the molecule in the interstellar medium. Besides all these questions, in this work, we review some of the most relevant aspects regarding the dynamics of the $H^+ + H_2$ reaction and its isotopic variants. A discussion on the most commonly found numerical difficulties in the theoretical study of this reactive collision is included.

keywords: reaction dynamics; spectroscopy; astrophysics



PRL **107,** 023201 (2011) PHYSICAL REVIEW LETTERS week ending 8 JULY 2011

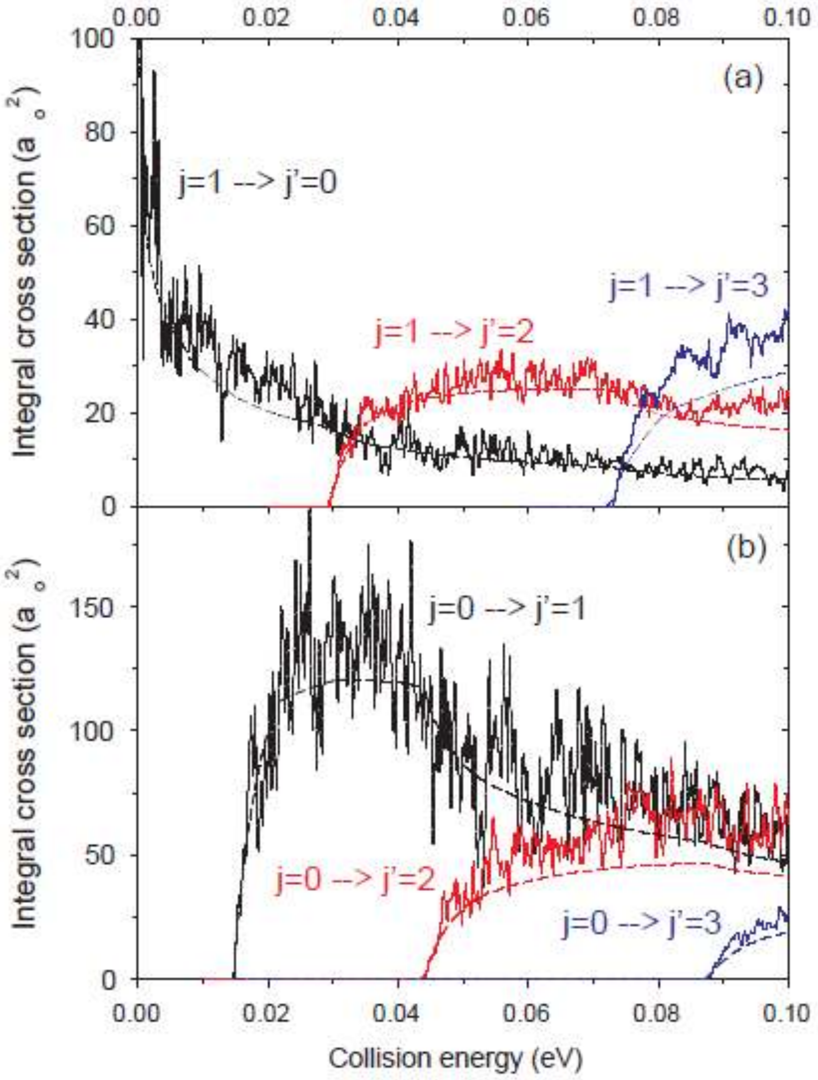
Ortho-Para **H_2 Conversion by Proton Exchange at Low Temperature: An Accurate Quantum Mechanical Study**

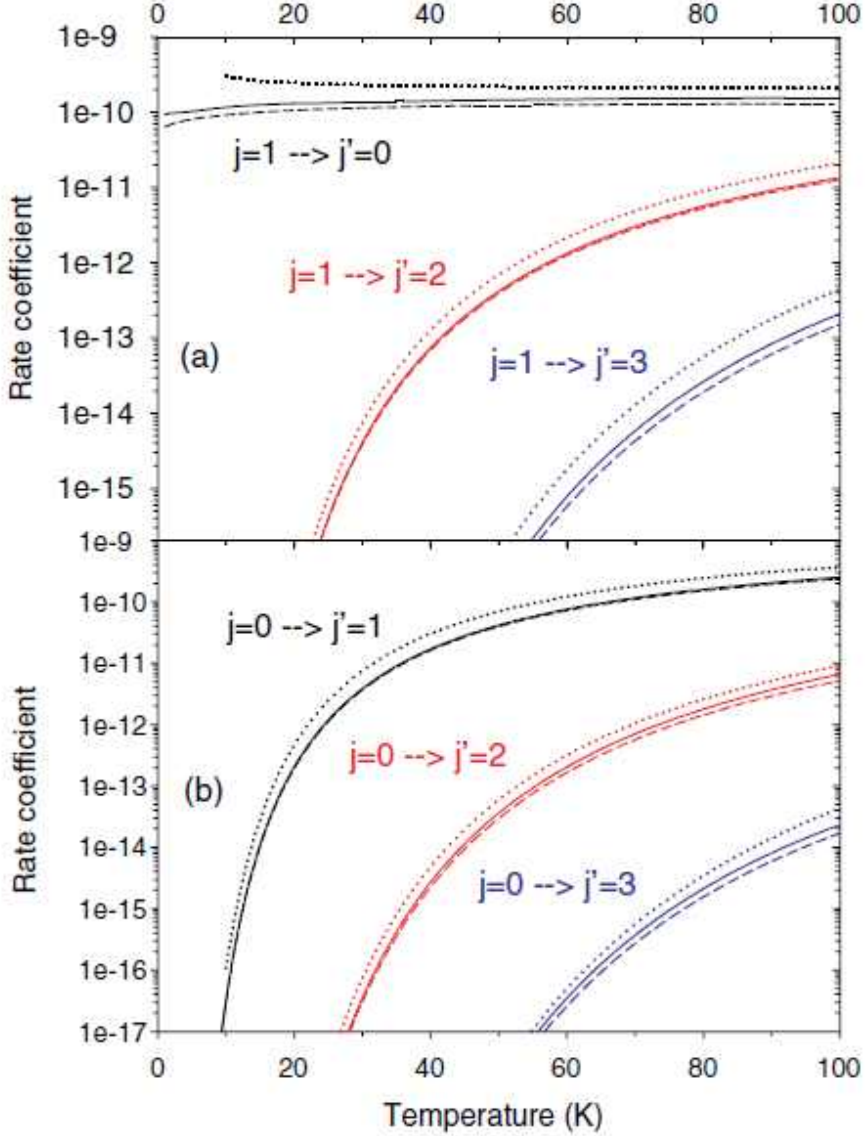
P. Honvault,[1,2] M. Jorfi,[3] T. González-Lezana,[4] A. Faure,[5] and L. Pagani[6]

EQM ——

SQM – – –

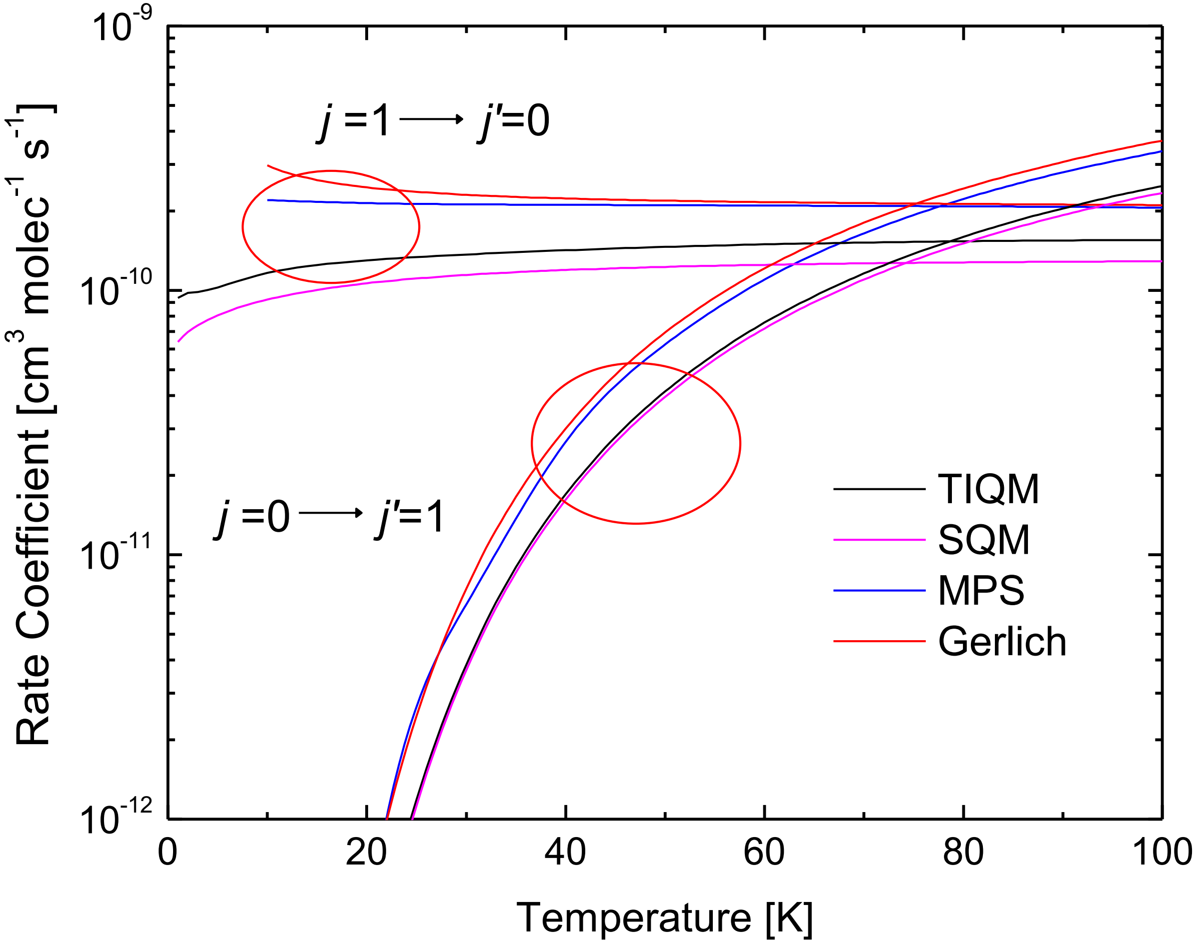
Prev. ········





Numerous narrow resonances (even for the ICS!)

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



MPS: Grozdanov & McCarroll *JPCA (2012)*

Langevin type + Isotropic Mean Potential

Permutation symmetry of three protons

Still different behaviour at low T

Still far from the TIQM rates

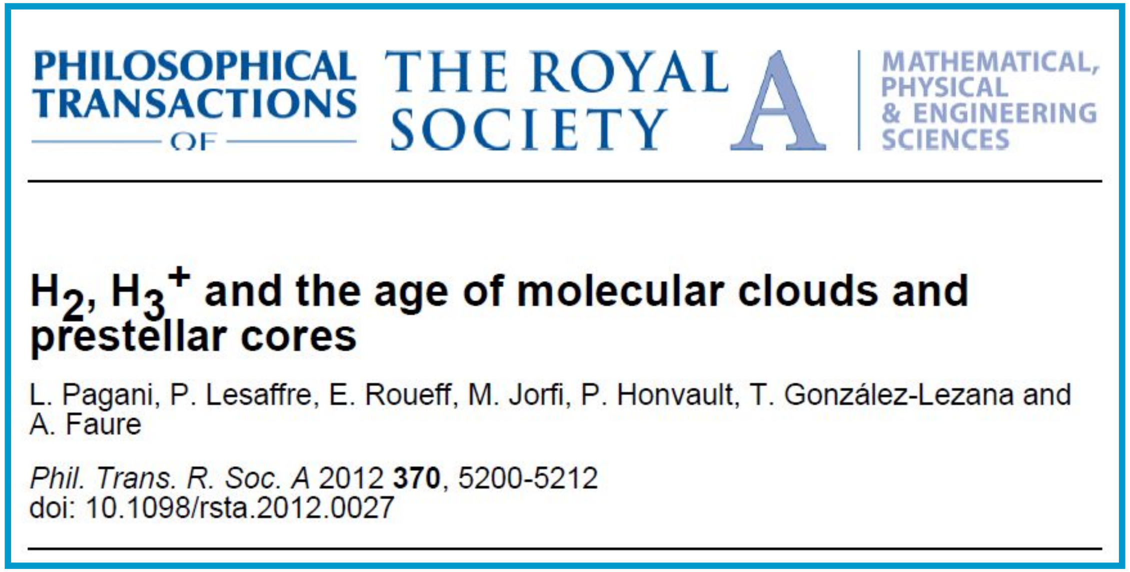
Chemical clock: The *o*-H_2(odd *j*) abundance is crucial to estimate the age of interstellar dark clouds which lead to form stars.

A&A 551, A38 (2013)
DOI: 10.1051/0004-6361/201117161

Astronomy & Astrophysics

Ortho-H_2 and the age of prestellar cores★

L. Pagani[1], P. Lesaffre[2], M. Jorfi[3], P. Honvault[4,5], T. González-Lezana[6], and A. Faure[7]



PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A
MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

H_2, H_3^+ and the age of molecular clouds and prestellar cores

L. Pagani, P. Lesaffre, E. Roueff, M. Jorfi, P. Honvault, T. González-Lezana and A. Faure

Phil. Trans. R. Soc. A 2012 **370**, 5200-5212
doi: 10.1098/rsta.2012.0027

Monthly Notices
of the
ROYAL ASTRONOMICAL SOCIETY

MNRAS **467,** 1294–1299 (2017)
Advance Access publication 2017 January 22

doi:10.1093/mnras/stx192

Rovibrational transitions of H_2 by collision with H^+ at high temperature

T. González-Lezana[1]★ and P. Honvault[2,3]★

[1] *Instituto de Física Fundamental (IFF-CSIC), Serrano 123, E-28006 Madrid, Spain*
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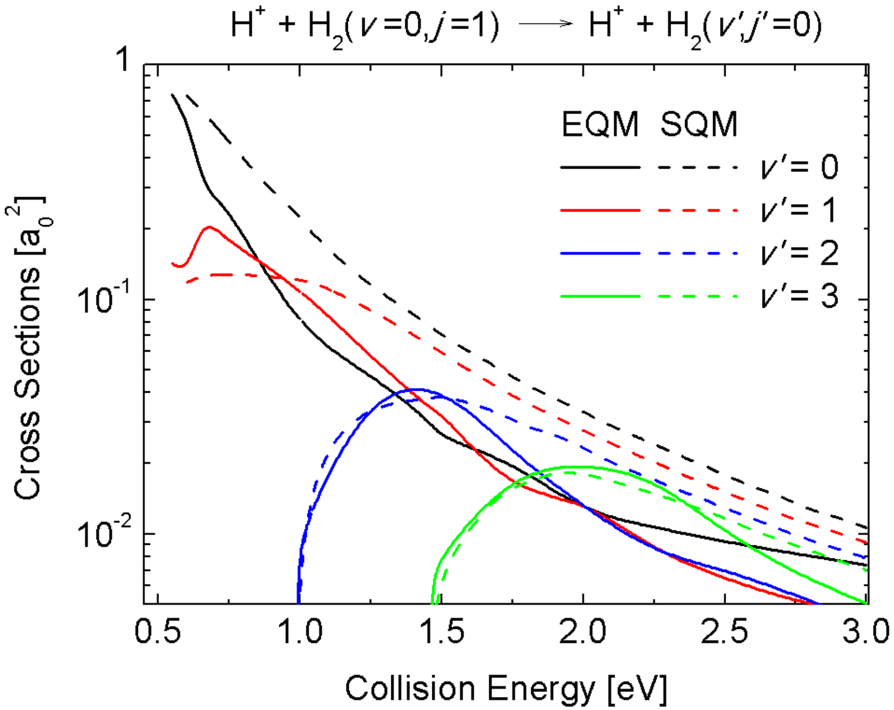
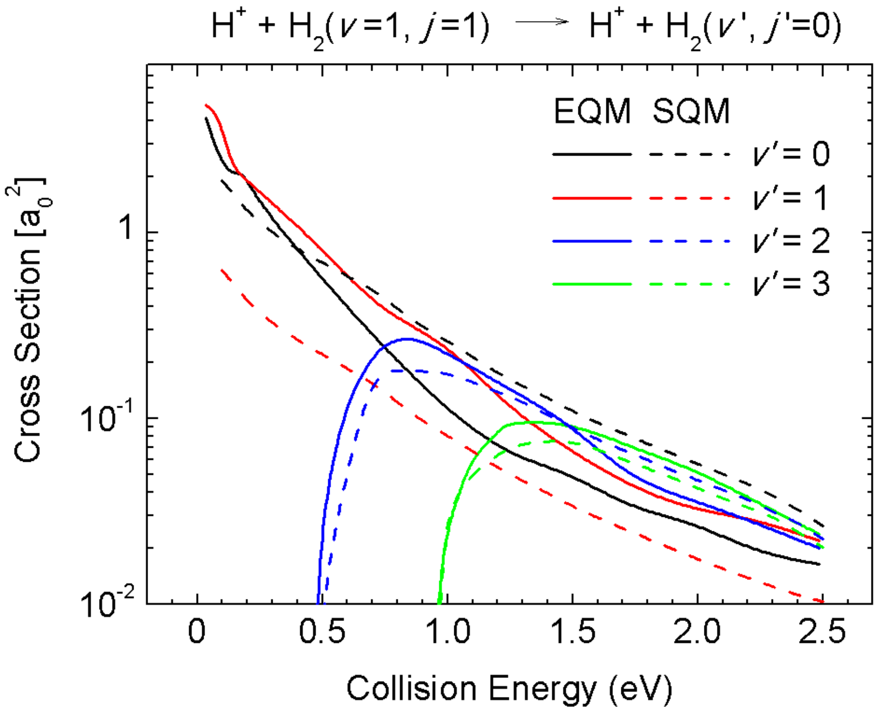
Accepted 2017 January 19. Received 2017 January 16; in original form 2016 November 16





Monthly Notices of the ROYAL ASTRONOMICAL SOCIETY

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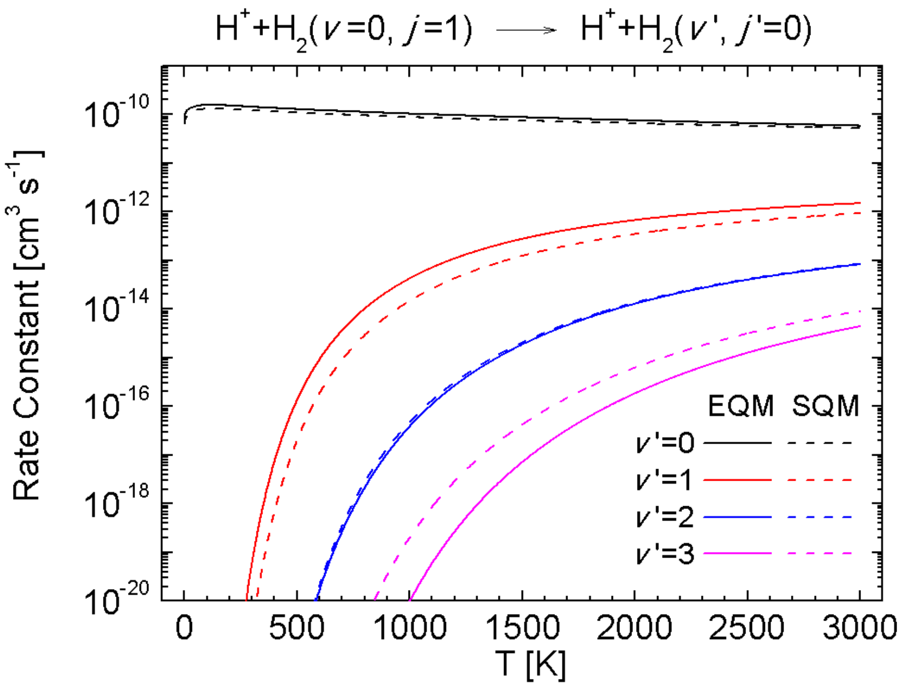

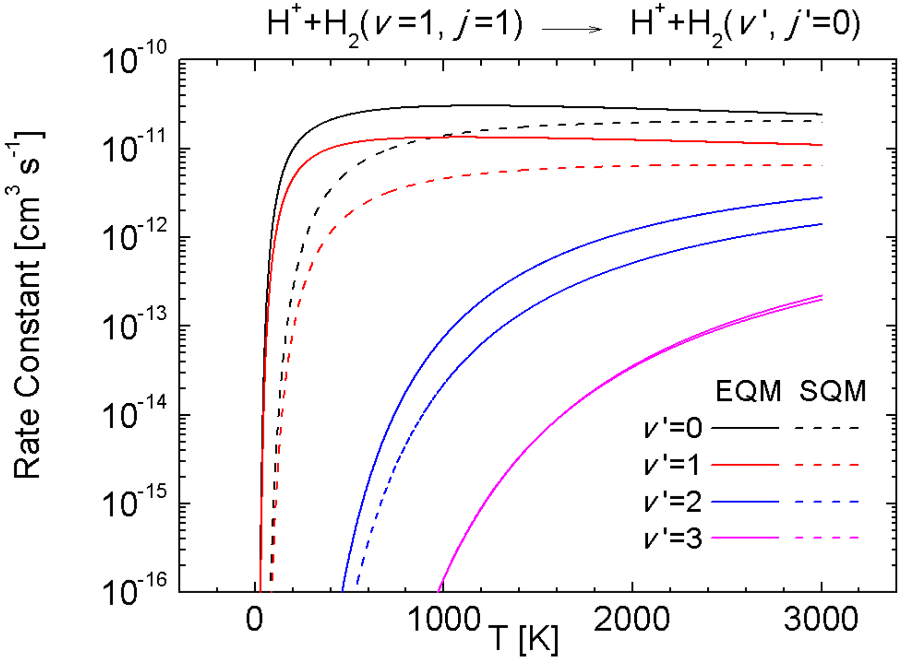

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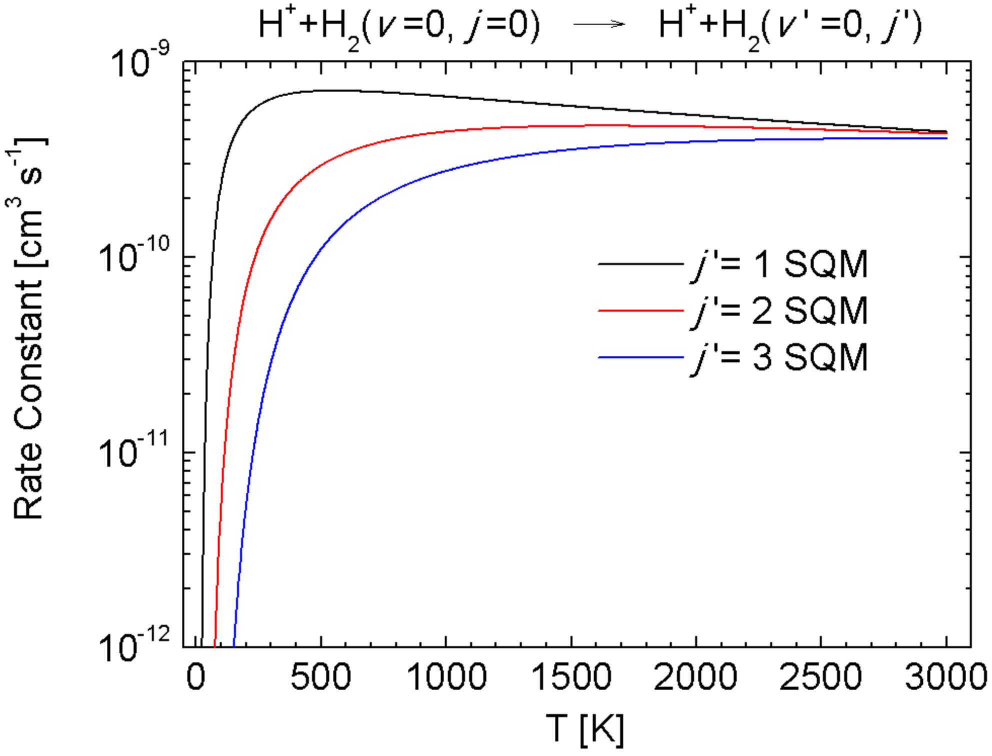
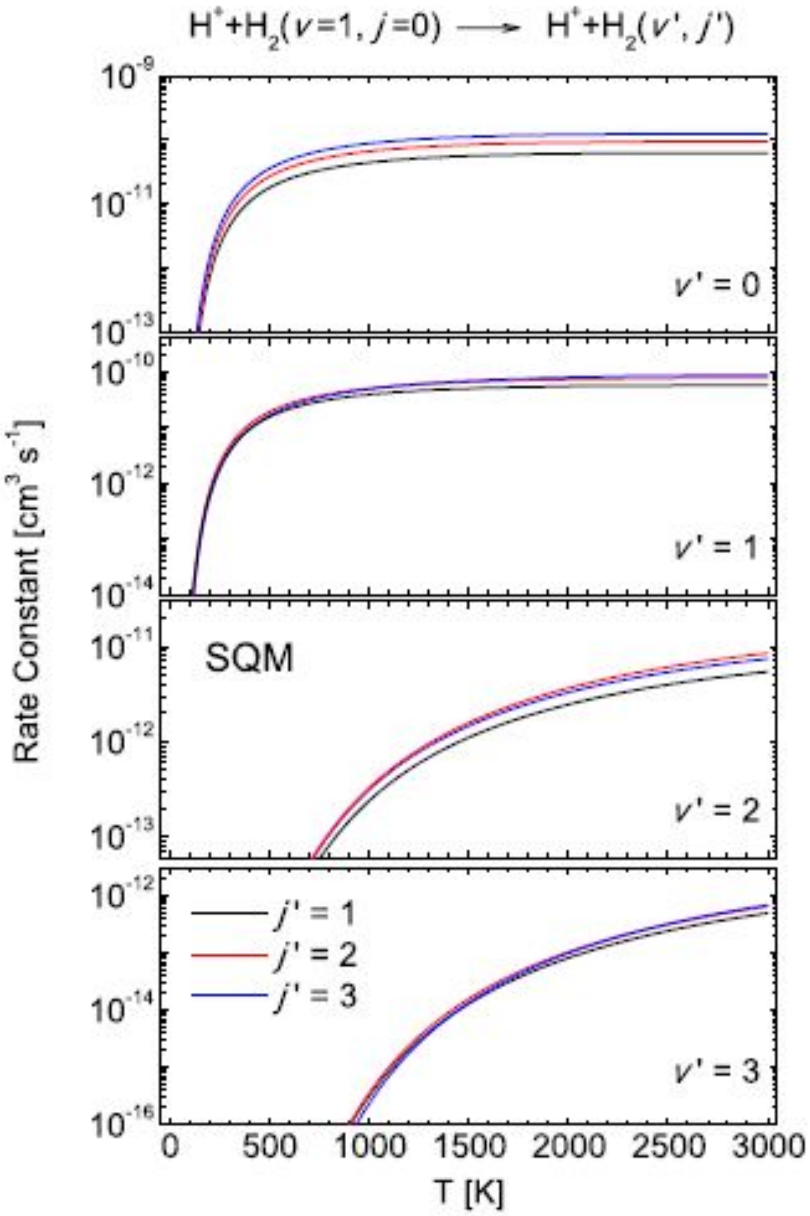
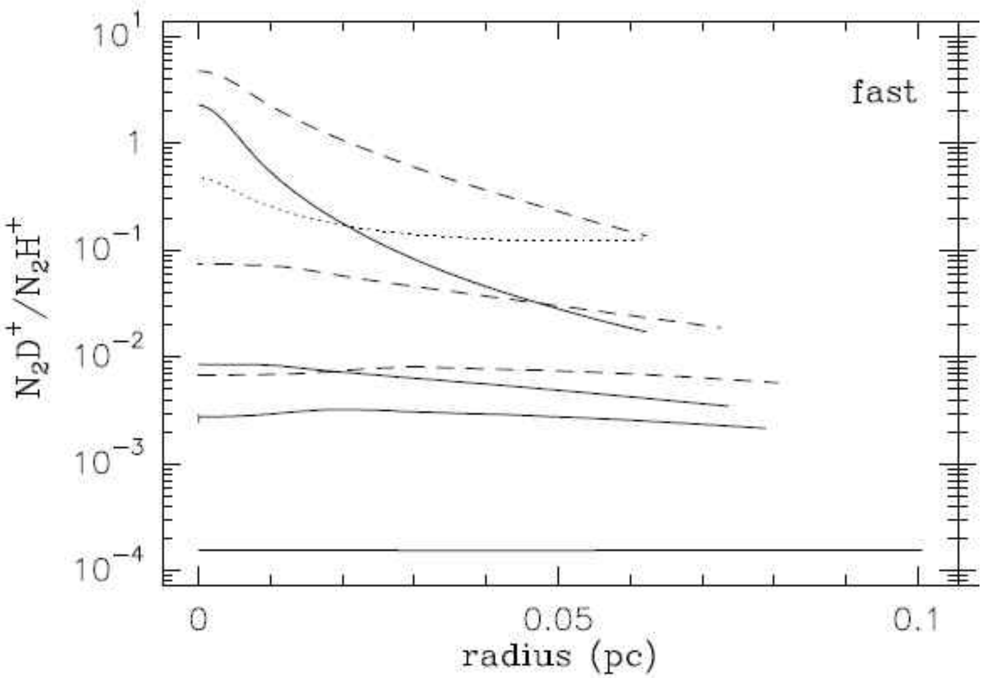




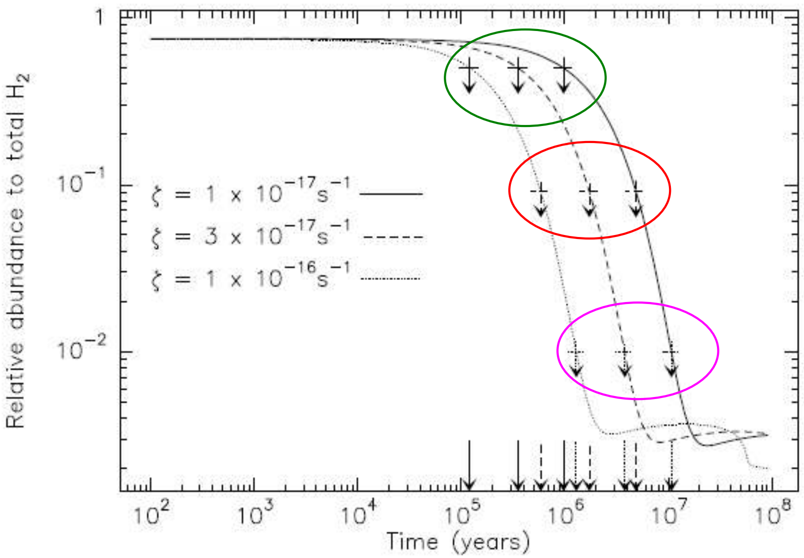
Pagani, Lesaffre, Honvault, Jorfi, TGL, Faure, *A&A* *(2012)*



Deuteration acceleration:

—— With old rates

- - - - With new rates



o-H_2 abundance variation with time for 3 values of cosmic ray ionization rate.

Arrows: OPR = 1, 0.1, 0.01

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Consejo Superior de Investigaciones Científicas

O. Roncero
E. Carmona-Novillo

P.G. Jambrina
F. J. Aoiz, L. Bañares

Durham University

E. Wrede
A. Trottier

uB Université de Bourgogne

Université de Rennes 1

LAOG

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um2 Université Montpellier 2 Sciences et Techniques

P. Honvault

J.-M. Launay

A. Faure

L. Pagani

Y. Scribano