Dynamical constraints and nuclear spin caused restrictions in $H^+ + H_2$, $H_3^+ + H_2$ and deuterated variants

Dieter Gerlich

Introduction

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Experimental techniques: beams and traps

Reactions: H^+ and $H_2^+ + H_2$

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Dynamically biased statistical model
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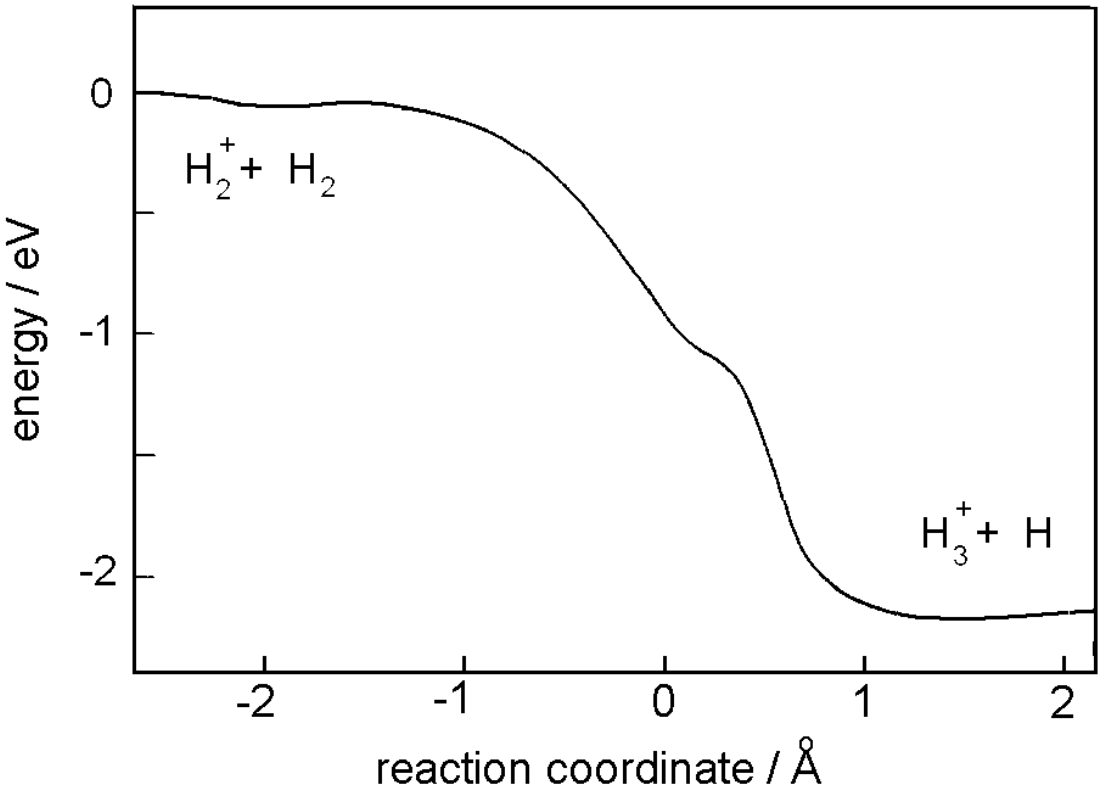
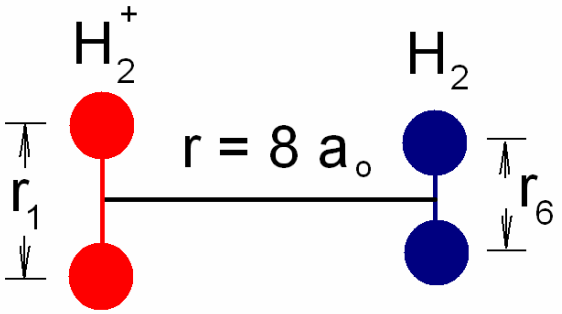
Outlook

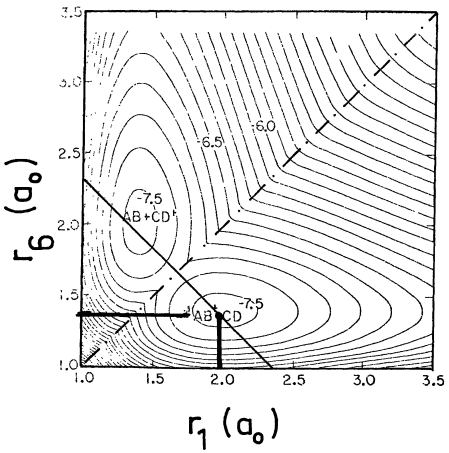
Reactions with hydrogen atoms, sub-K cooling of ions

H_4^+ surface

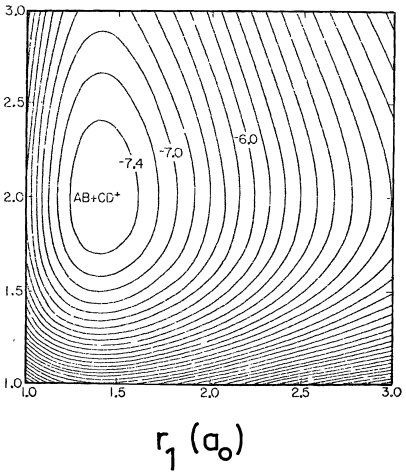


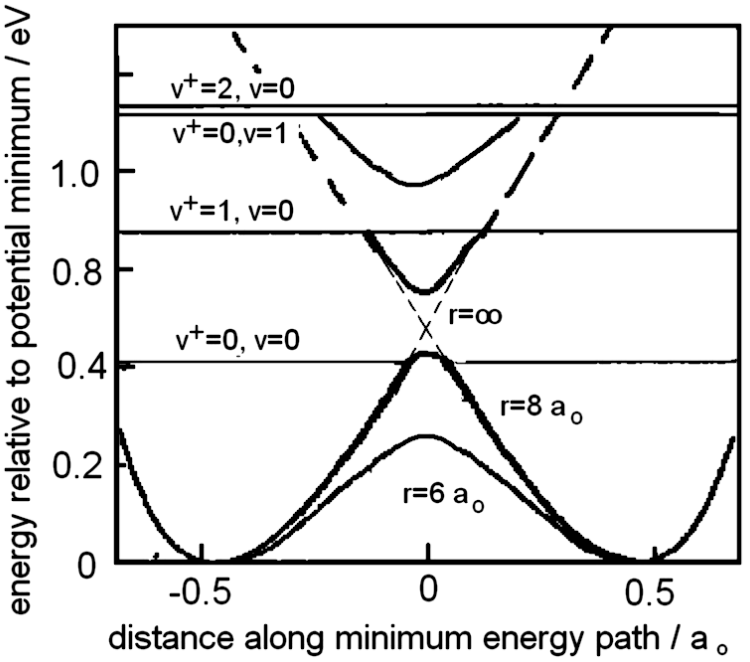


adiabatic



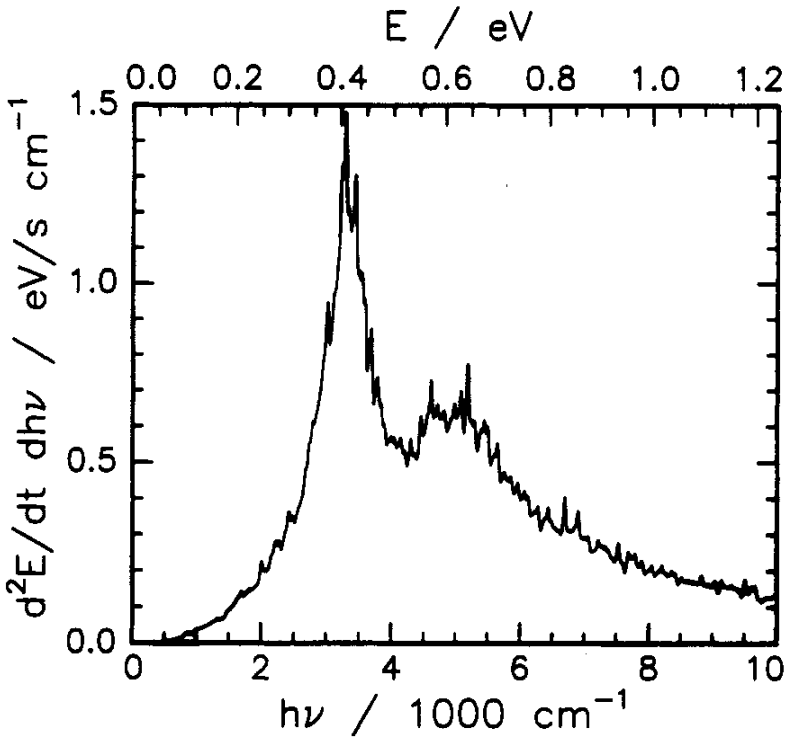
diabatic

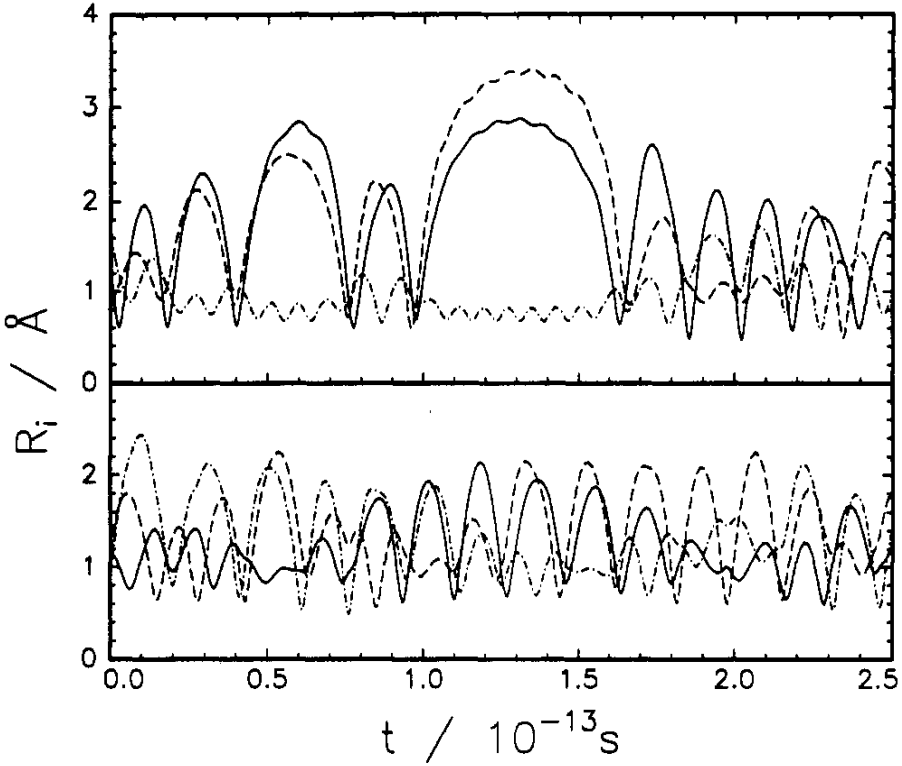




$H^+ + H_2$: Radiative association

$H^+ + H_2 \rightarrow H_3^+ + h\nu$
$H^+ + 2\,H_2 \rightarrow H_3^+ + H_2$
$H^+ + H_2 + He \rightarrow H_3^+ + He$



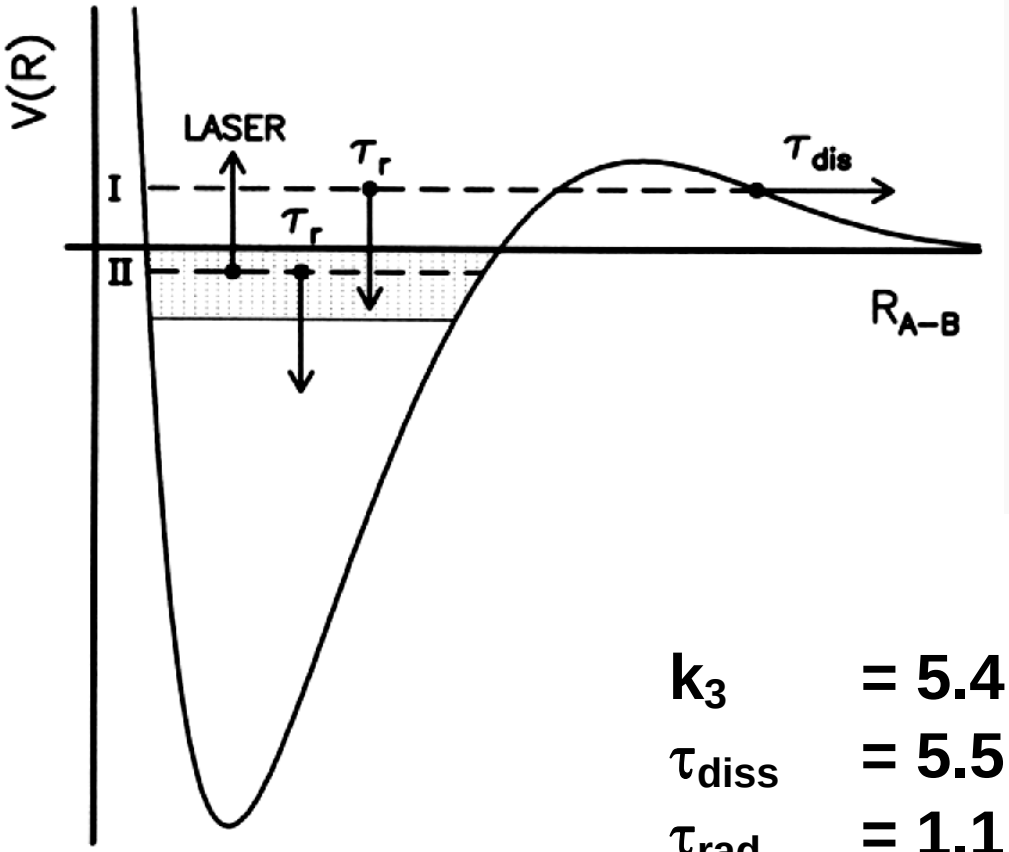


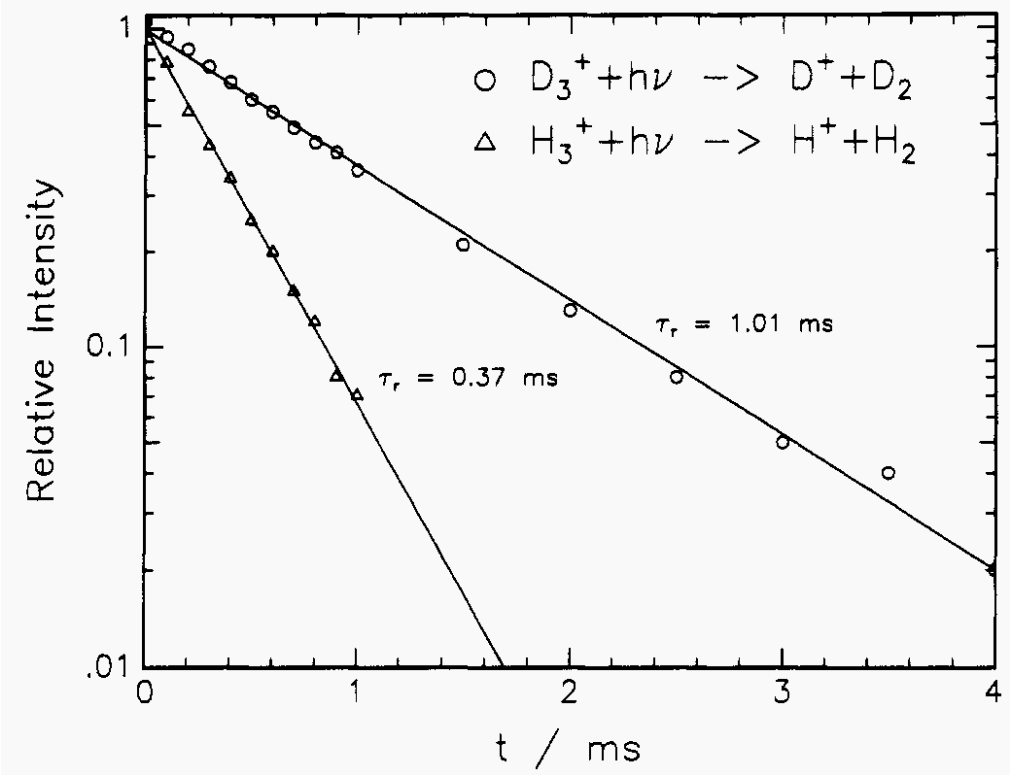
$$\tau_{dis} = (1.47 \times 10^{-14})(E + 4.9\ \text{eV}/E)^{1.9}\ \text{s}$$

D. Gerlich and S. Horning "Experimental Investigations of Radiative Association Processes as Related to Interstellar Chemistry" Chem. Rev. 92, 1509 (1992)

H_3^+ complex life time

$$(H_3^+)^* + h\nu \rightarrow H^+ + H_2$$





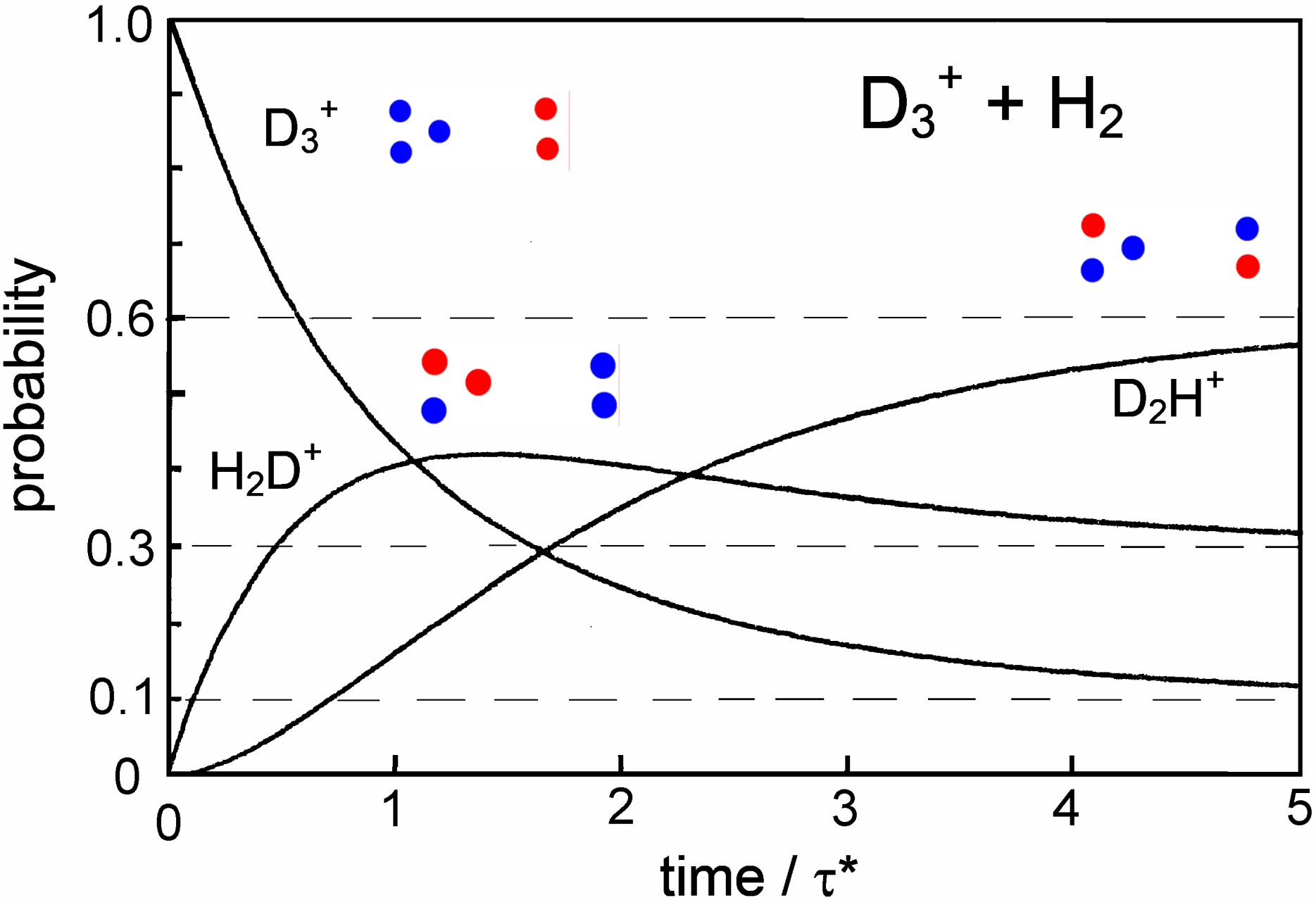
$k_3 = 5.4 \times 10^{-29}\ cm^3 s^{-1}$

$\tau_{diss} = 5.5 \times 10^{-11}\ s$

$\tau_{rad} = 1.1 \times 10^{-3}\ s$

D. Gerlich and S. Horning "Experimental Investigations of Radiative Association Processes as Related to Interstellar Chemistry" Chem. Rev. 92, 1509 (1992)

Simple scrambling model



Deuteration: thermal equilibrium?

$$H_3^+ + HD \leftrightarrow H_2D^+ + H_2$$

$$\sim \exp(232\ K / T)$$

Ramanlal & Tennyson	**2.6(+12)**
Adams & Smith (1981)	1.5(+9)
Sidhu et al. (1992)	7.1(+12)
Gerlich et al. (2002)	$H_2D^+ / H_3^+ = 12\ \%$

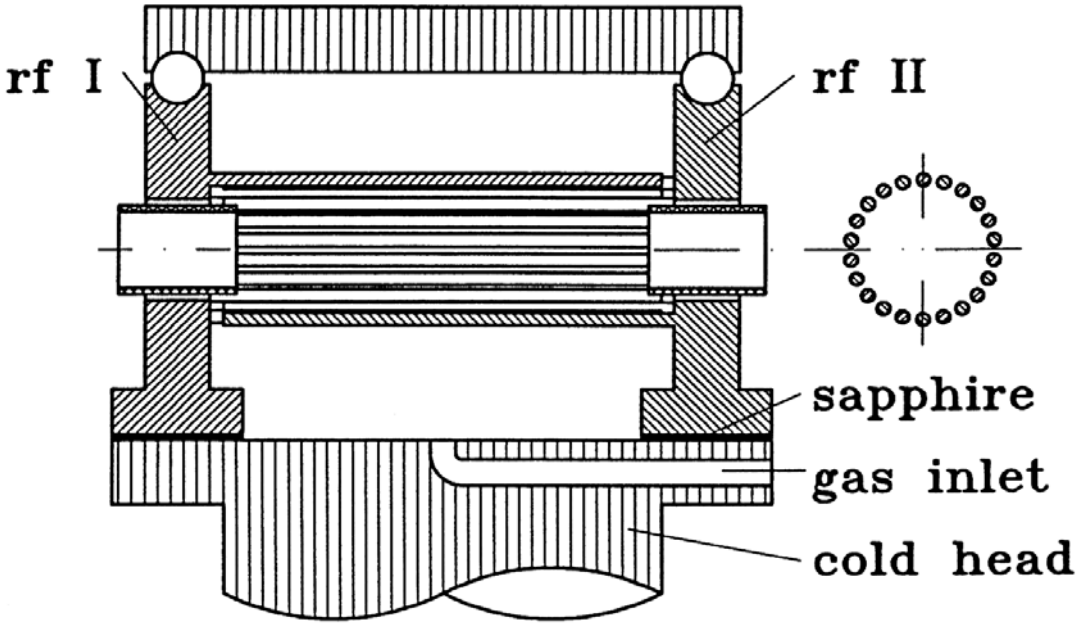
Ramanlal & Tennyson wrote in 2004:

trap experiment disagrees with calculations by

12 orders of magnitude

Ramanlal and J. Tennyson Monthly Notices of the Royal Astronomical Society , **354** (2004) 161
D. Gerlich, E. Herbst, and E. Roueff, Planetary and Space Science, **50** (2002) 1275

TV 22-pole trap



d = 1 mm
2 r_0 =10 mm

$r_0 = (n\text{-}1)\, d/2$
$2n = 22$

Effective potential V^*

$V^* = q^2 E_0^2 / 4m\Omega^2$

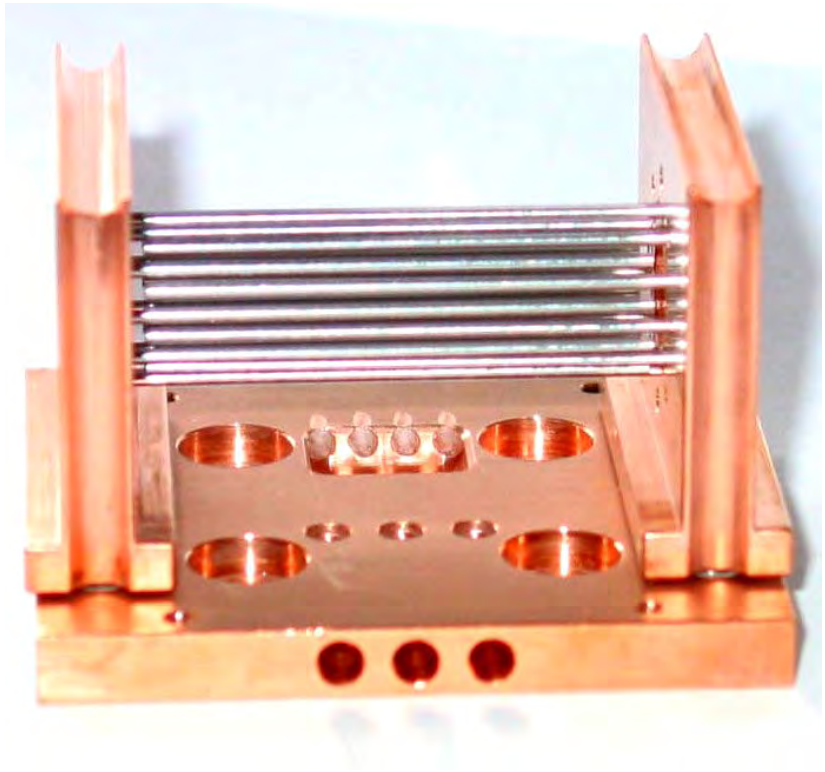
Adiabaticity parameter η

$\eta = 2\, q\, |\nabla E_0| \,/\, m\Omega^2$

parameters: q, m, E_0, Ω

scaling: $m\Omega^2$

$\eta \sim E_{max}^{(n-2)/(2n-2)} = E_{max}^{9/20}$



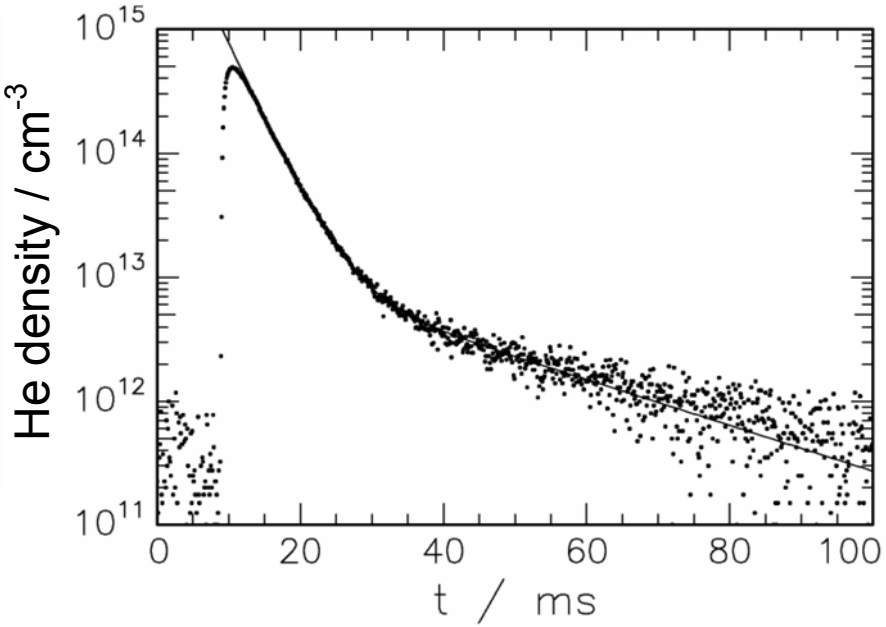
D. Gerlich Physica Scripta, **T59** (1995) 256

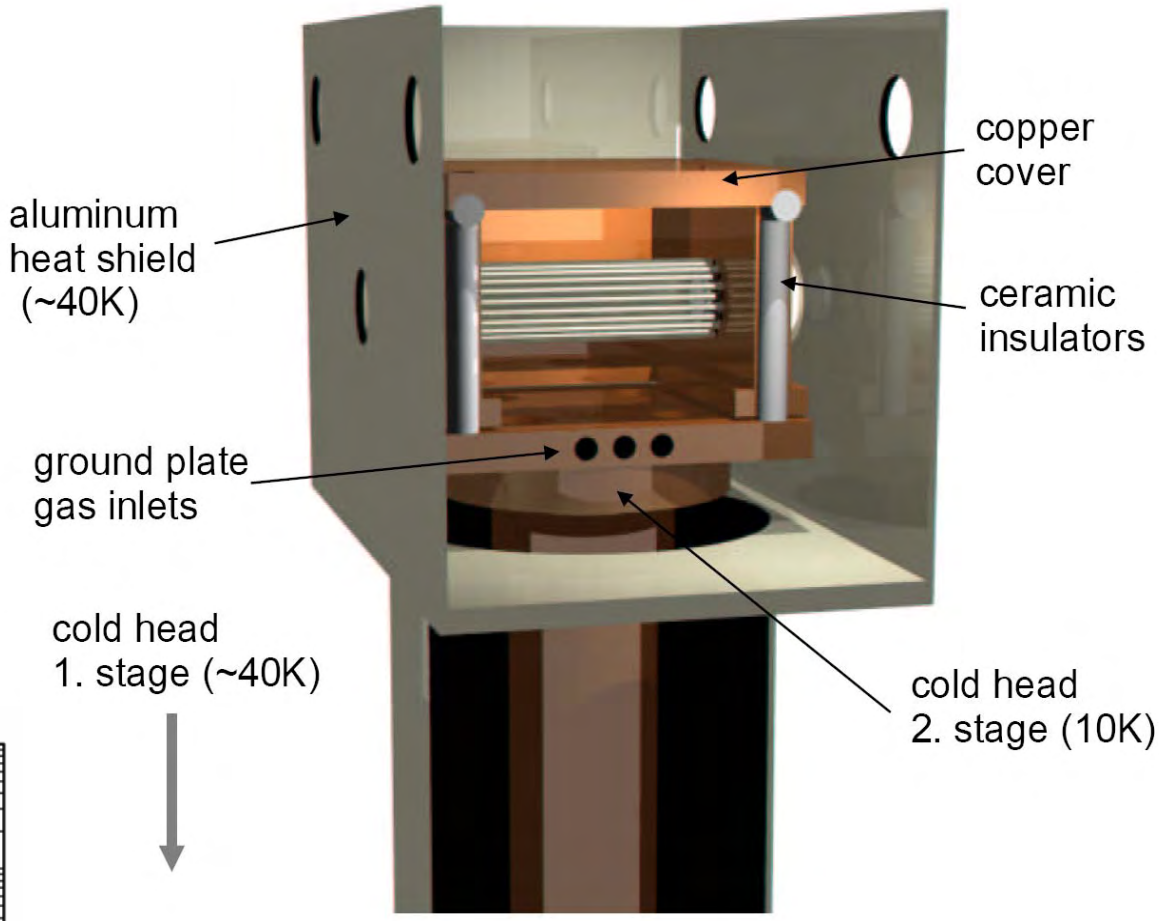
Buffer gas cooling in an rf trap

Dynamic traps such as Penning, storage rings, cone trap do not work

Paul trap does not work
η = const

Only way to cool efficiently internal degrees of freedom are
rf multielectrode traps





sub K:
cold pulsed effusive beam

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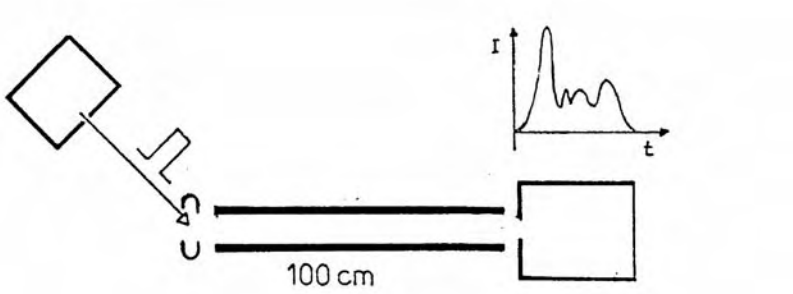
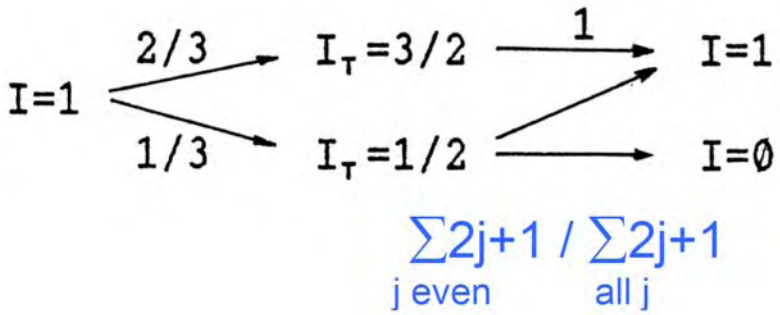
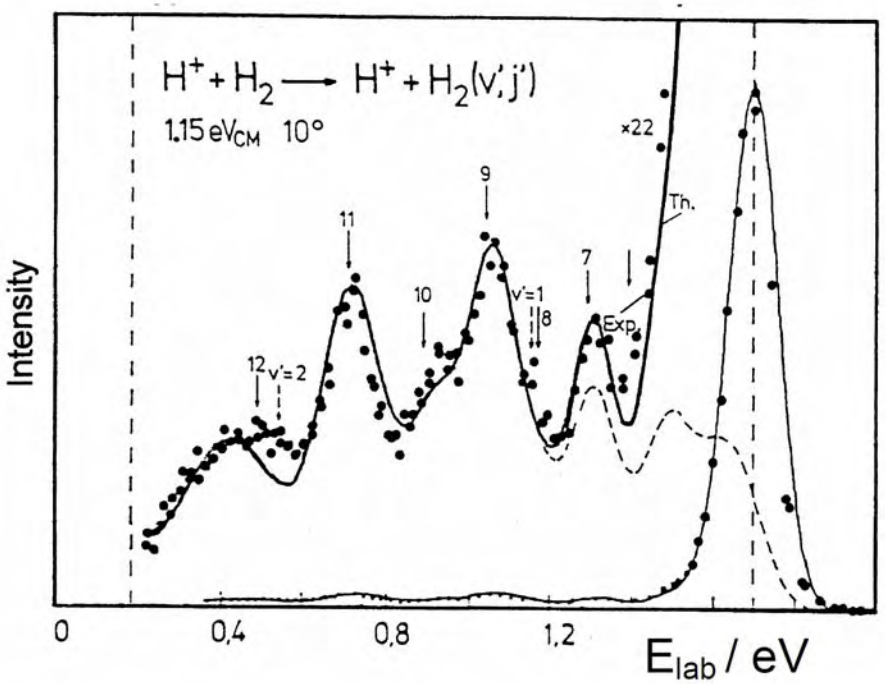
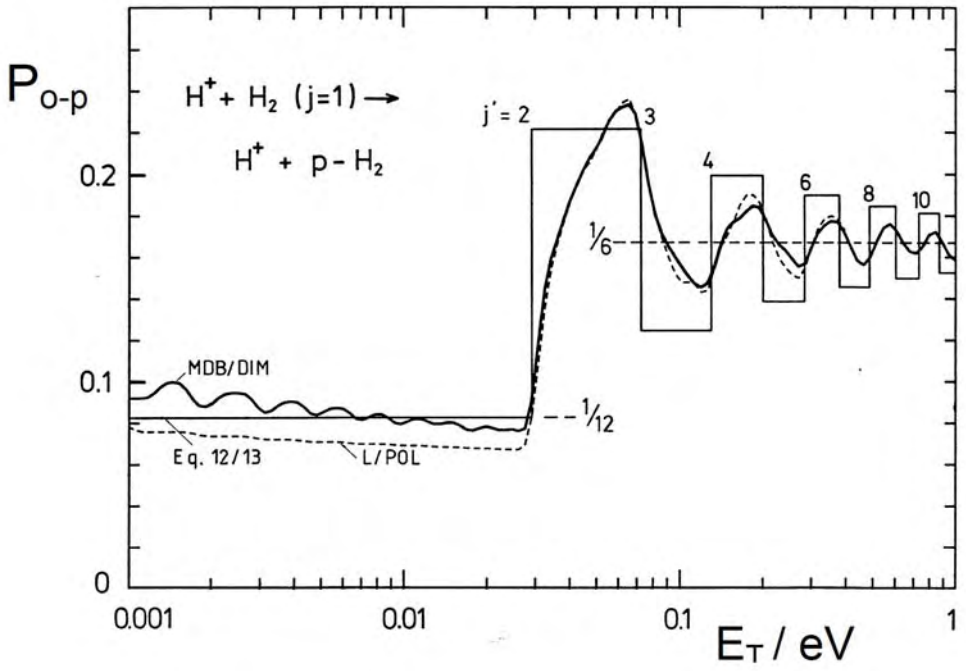
Ortho para transitions in reactive $H^+ + H_2(j)$ collisions









$$k(T) = \int dg\ f(g,T) \sum P(v,j,T)\ \sigma_{vj \to v'j'}$$

$H^+ + H_2$ statistical theory

$$\sigma^E_{jv\to j'v'} = \frac{\pi}{k^2(2j+1)} \sum_{\Pi=0}^{1} \sum_{J=0}^{J_m} \frac{2J+1}{N^{JE\Pi}} \sum_{l=|J-j|}^{J+j} P^{JE\Pi}_{ljv} \times \sum_{l'=|J-j|}^{J+j'} P^{JE\Pi}_{l'j'v'} g_{jj'}$$

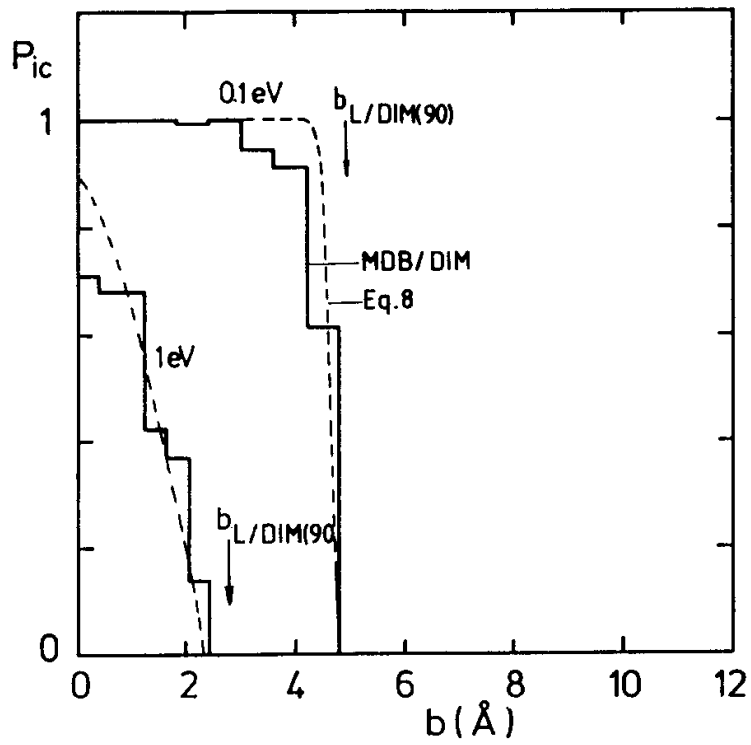
$$k^2 = 2\mu E_T/\hbar^2$$

$$N^{JE\Pi} = \sum_{v=0}^{v_m} \sum_{j=0}^{j_m} \sum_{l=|J-j|}^{J+j} P^{JE\Pi}_{ljv} g_{jj'}$$

CNS: $g_{jj'} = \begin{cases} 3 & \text{if } j' \text{ odd} \\ 1 & \text{if } j' \text{ even} \end{cases}$

FNS: $g_{jj'} = \begin{cases} 5 & \text{if } j \text{ and } j' \text{ are odd} \\ 1 & \text{else} \end{cases}$

$$P_{ic} = A(E,E_T,\mu)\cdot f(l,E_T,\mu)$$

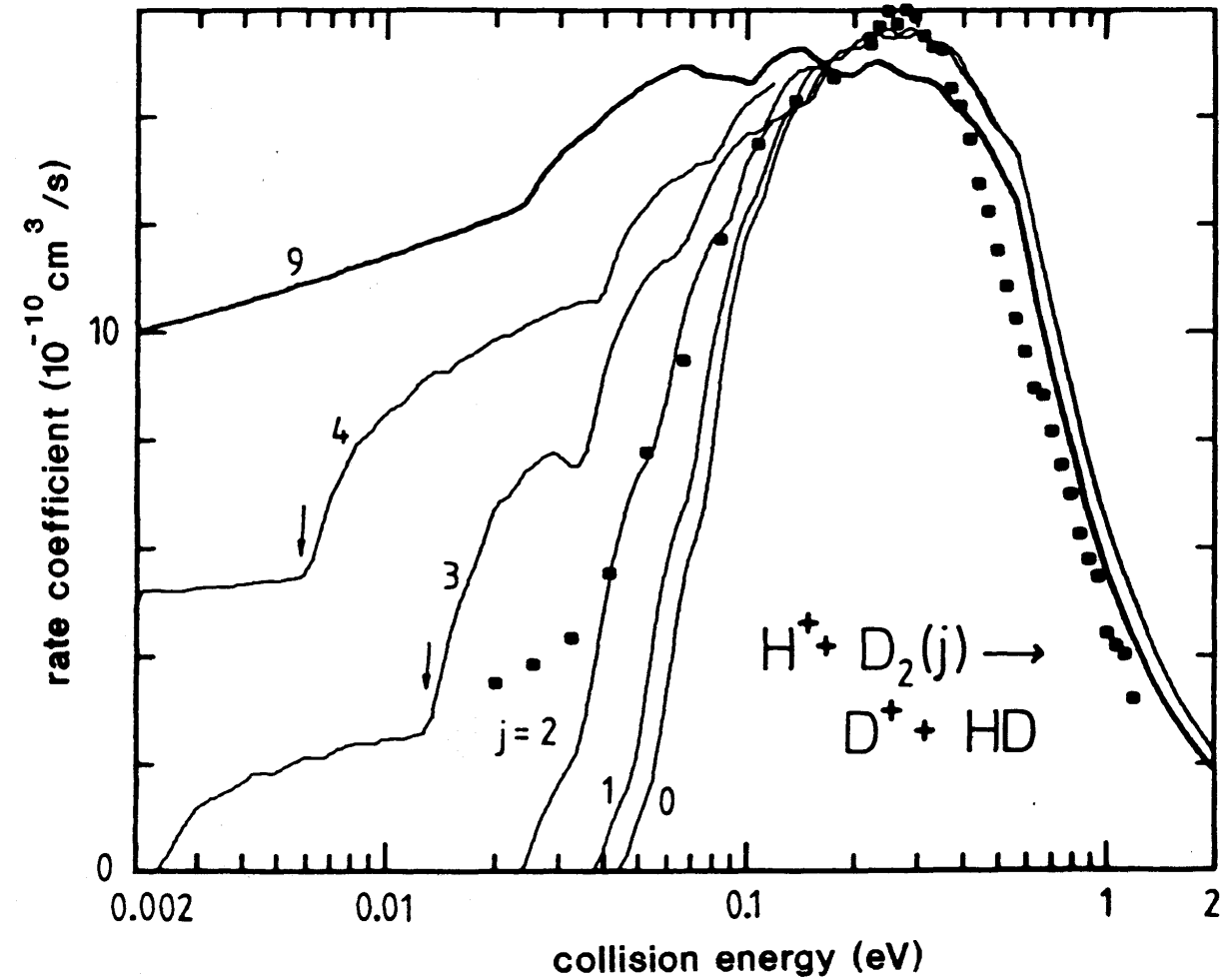


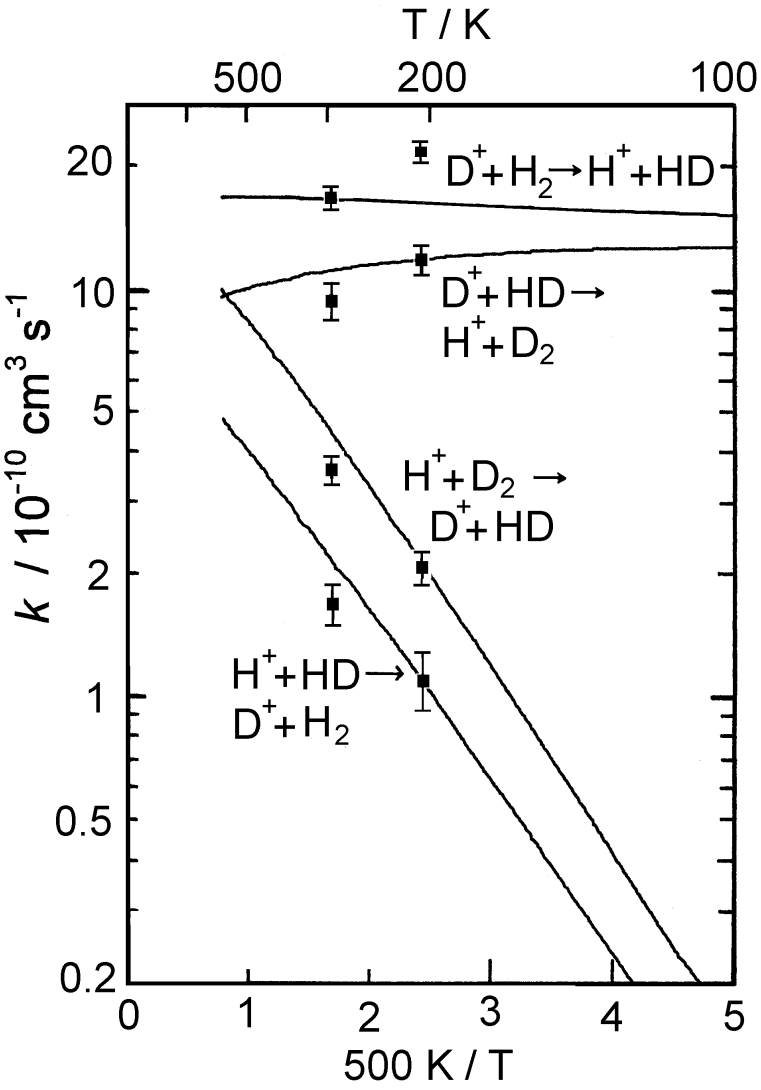
$$n(ortho)/n(para) = 9.35\cdot\exp(-169.4\,K/T)$$

$$P_0(v',j') = \frac{1}{\Sigma P_0}(2j'+1)g_{jj'}\cdot E'^{1/2}_T$$

D. Gerlich "Ortho para transitions in slow $H^+ + H_2$ collisions"
J. Chem. Phys. **92** (1990) 2377

$H^+ + D_2(j)$ statistical theory



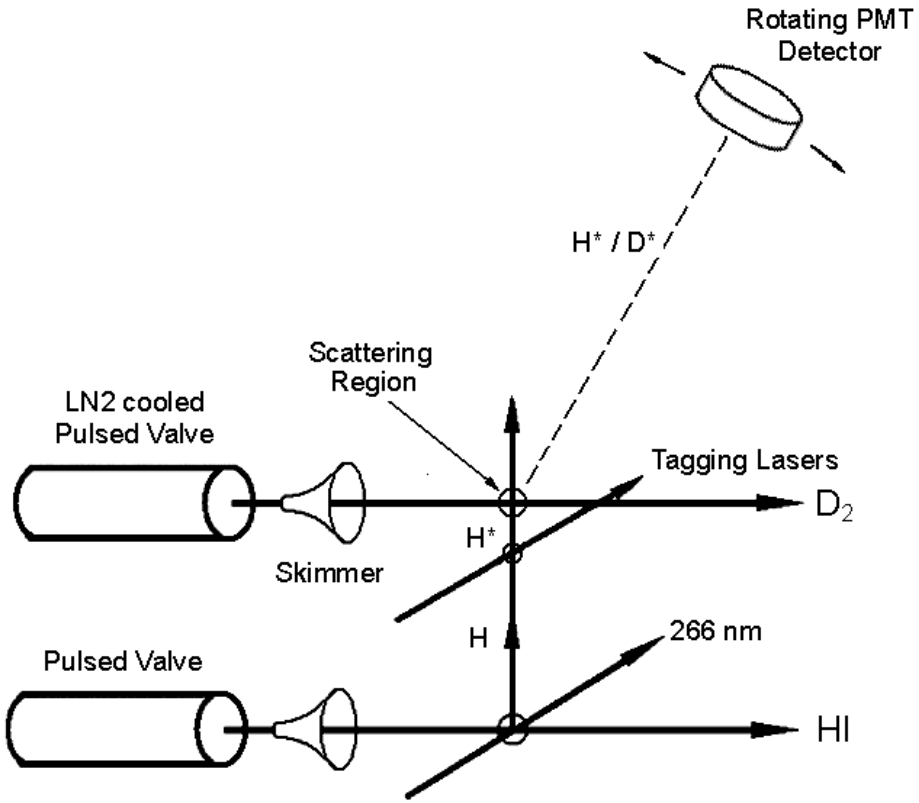


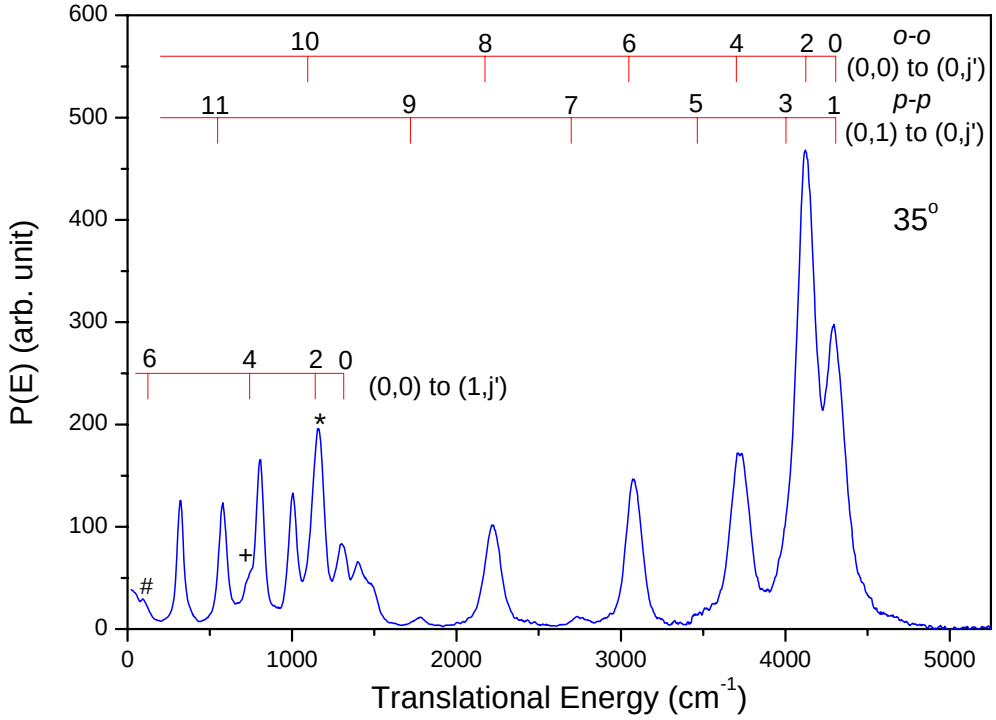
D. Gerlich "Calculations of reactive cross sections and rate coefficients for isotopic variants of the H+ + H2 - system in the energy range 2 meV - 1.8 eV", in SASP edited by W. Lindinger et al., 304 (1982)

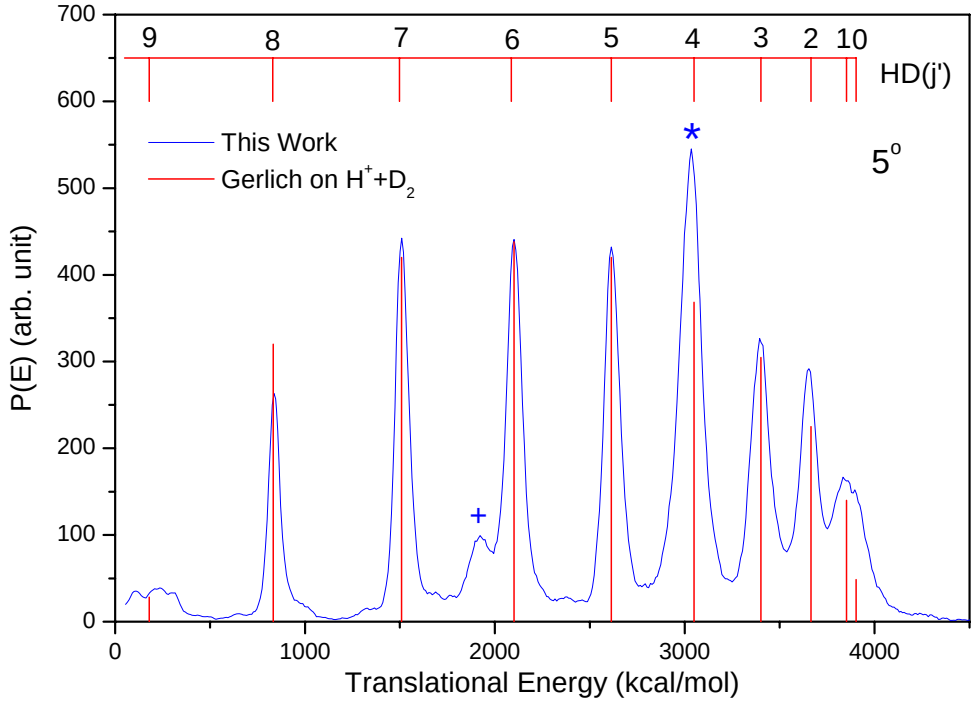
Rotational-State Resolved Scattering of Rydberg H^*-Atoms with D_2

$H^* + D_2 \rightarrow D^* + HD$

$H^+ + D_2 \rightarrow D^+ + HD$







Xueming Yang, Dalian Institute of Chemical Physics

H_3^+: internal exitation

ionization

$H_2 + e^- \rightarrow H_2^{+*} + 2\ e^-$

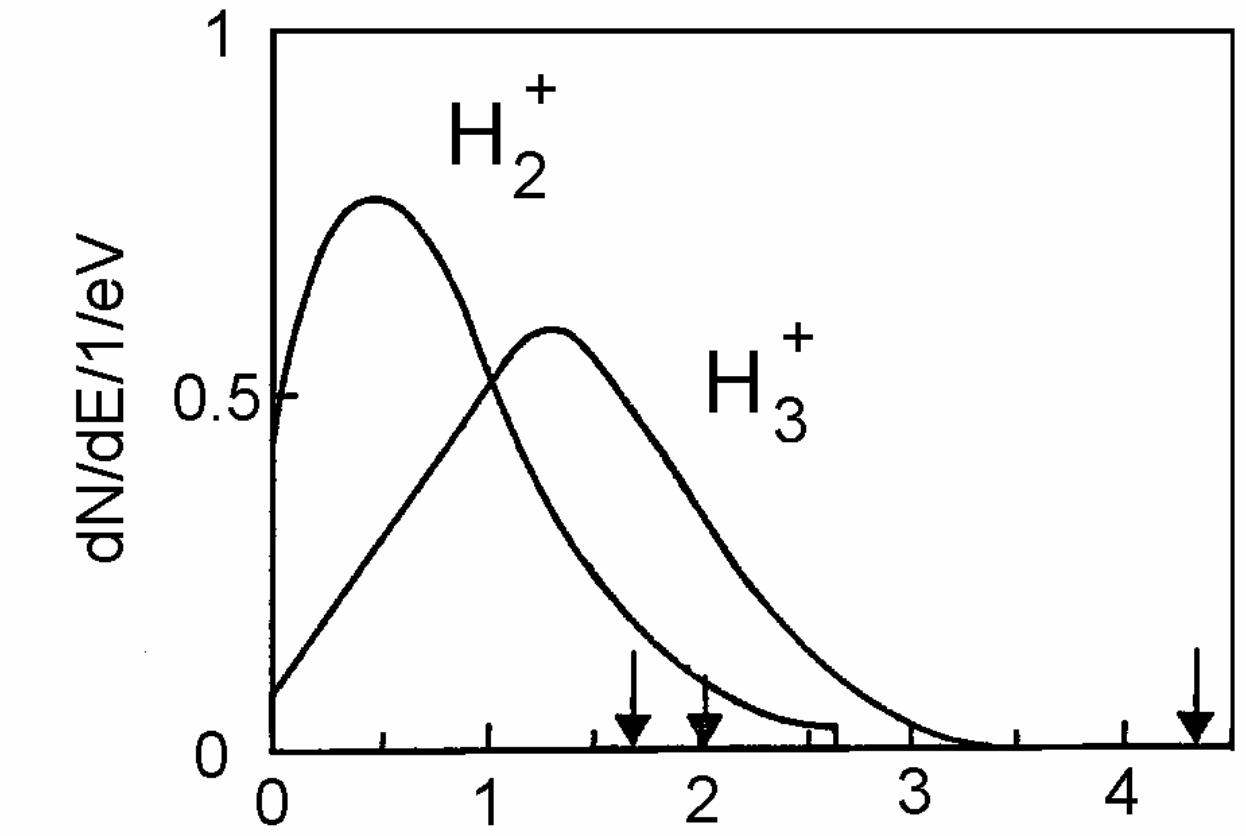
relaxation, reaction

$H_2 + H_2 \rightarrow H_2^+ + H_2$

$\rightarrow H_3^{+*} + H$

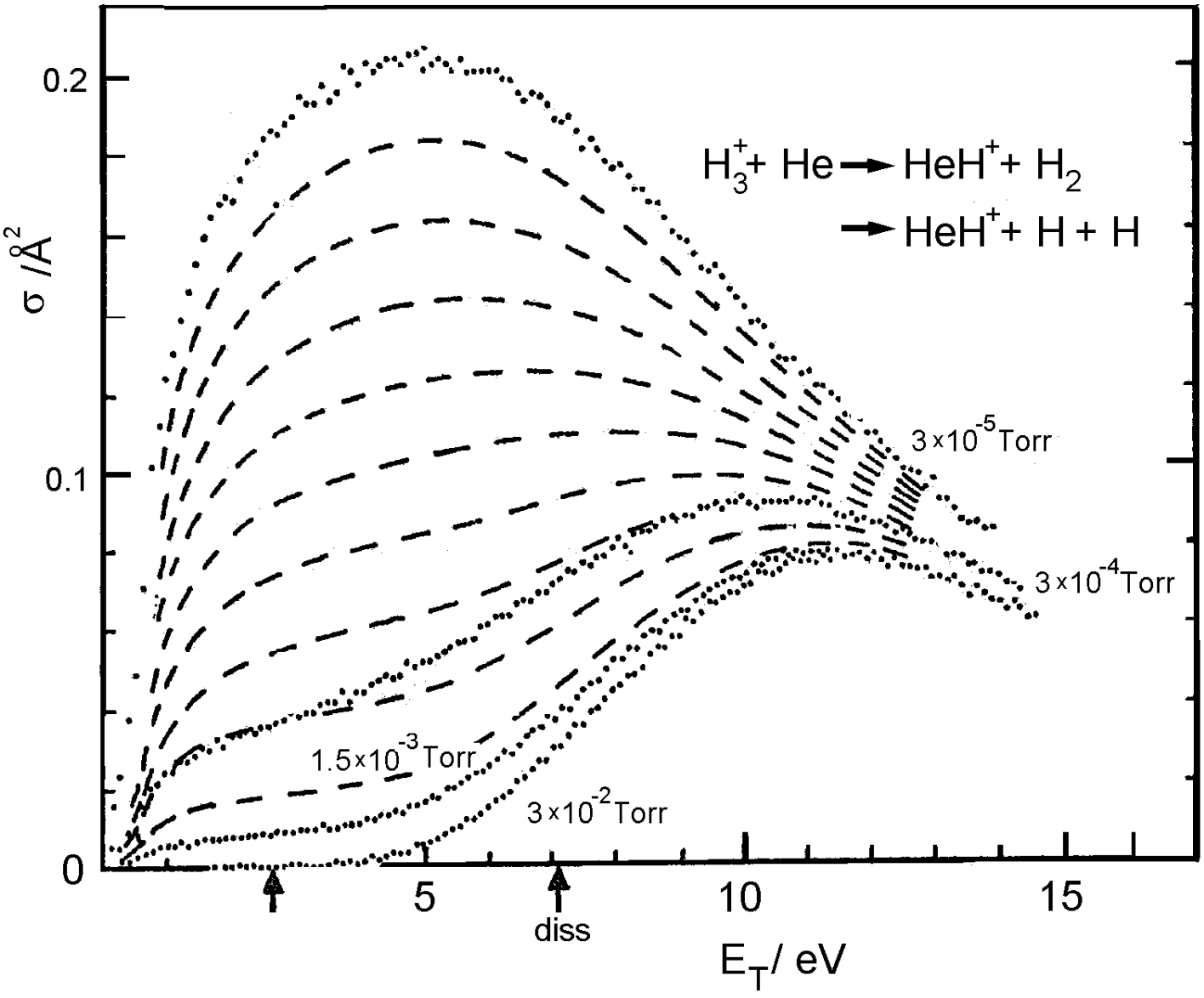
relaxation

$H_3^{+*} + H_2 \rightarrow H_3^+ + H_2$



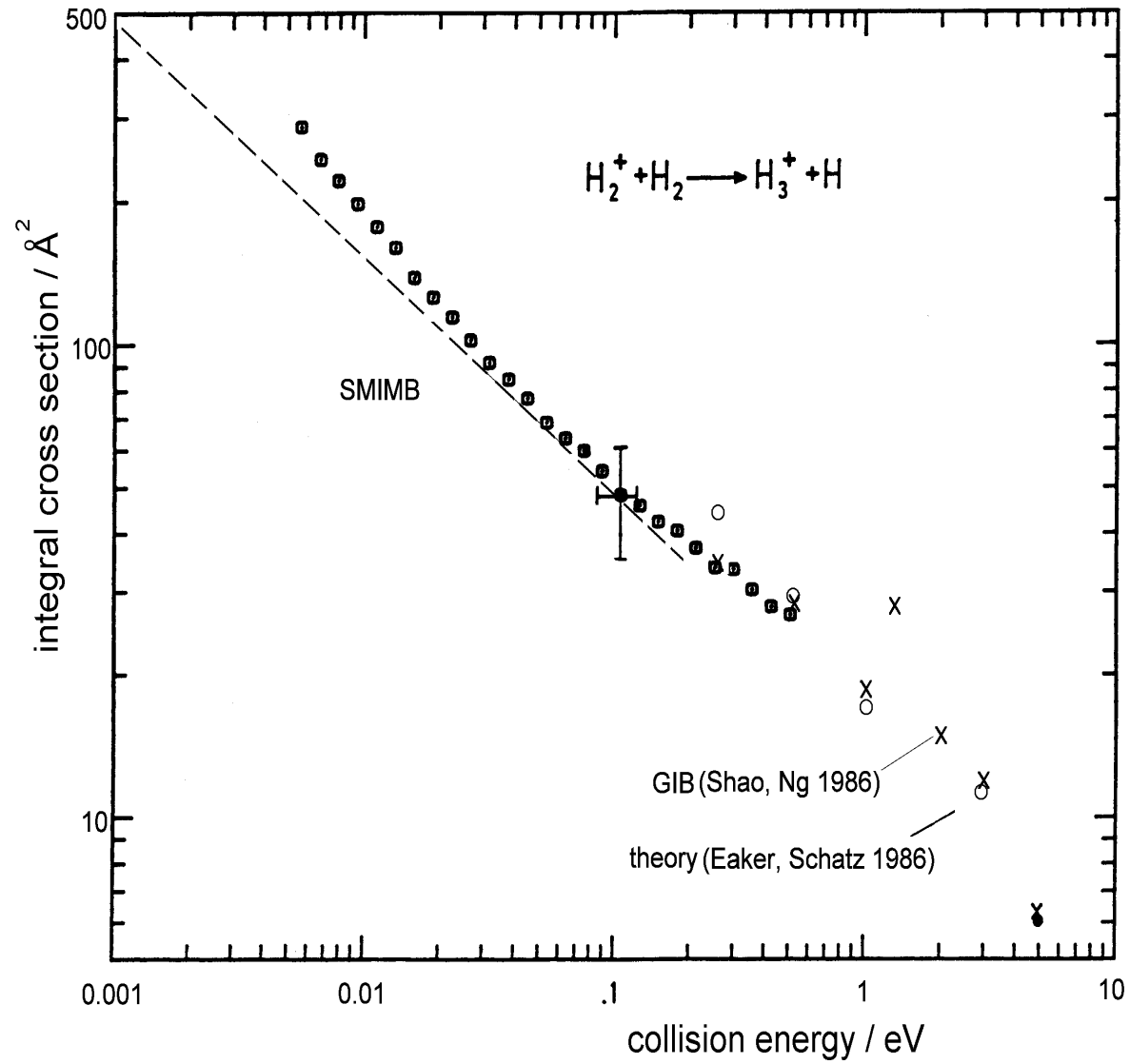
high rotational states
ortho-para ratio

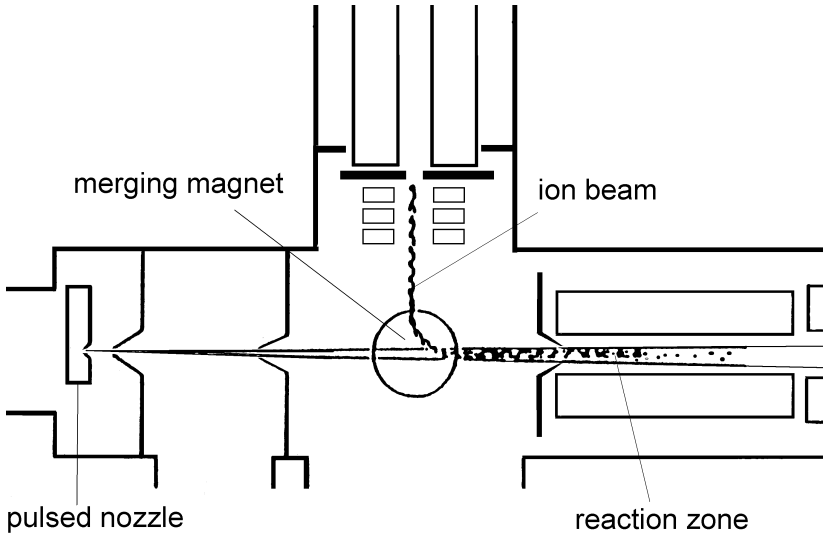
Internal excitation of H_3^+



W. Beyer Dipl. Thesis Freiburg 1976

$H_2^+ + H_2 \rightarrow H_3^+ + H$: merged beam results





$k_L = 2 \times 10^{-9} cm^3 s^{-1}$

charge transfer

$D_2(v=0)^+ + H_2 \rightarrow H_2^+ + D_2$

$\sigma \sim 20$ Å^2

T. Glenewinkel-Meyer, D. Gerlich, "Single and Merged Beam Studies of the Reaction H2+ + H2 → H3+ + H", Israel Journal of Chemistry, 37 (1997) 343

Decay probabilities o/p-H_2^+ + o/p-H_2 → o/p-H_3^+ + H

Oka group (Table III b from Cordonnier et al. 2000)

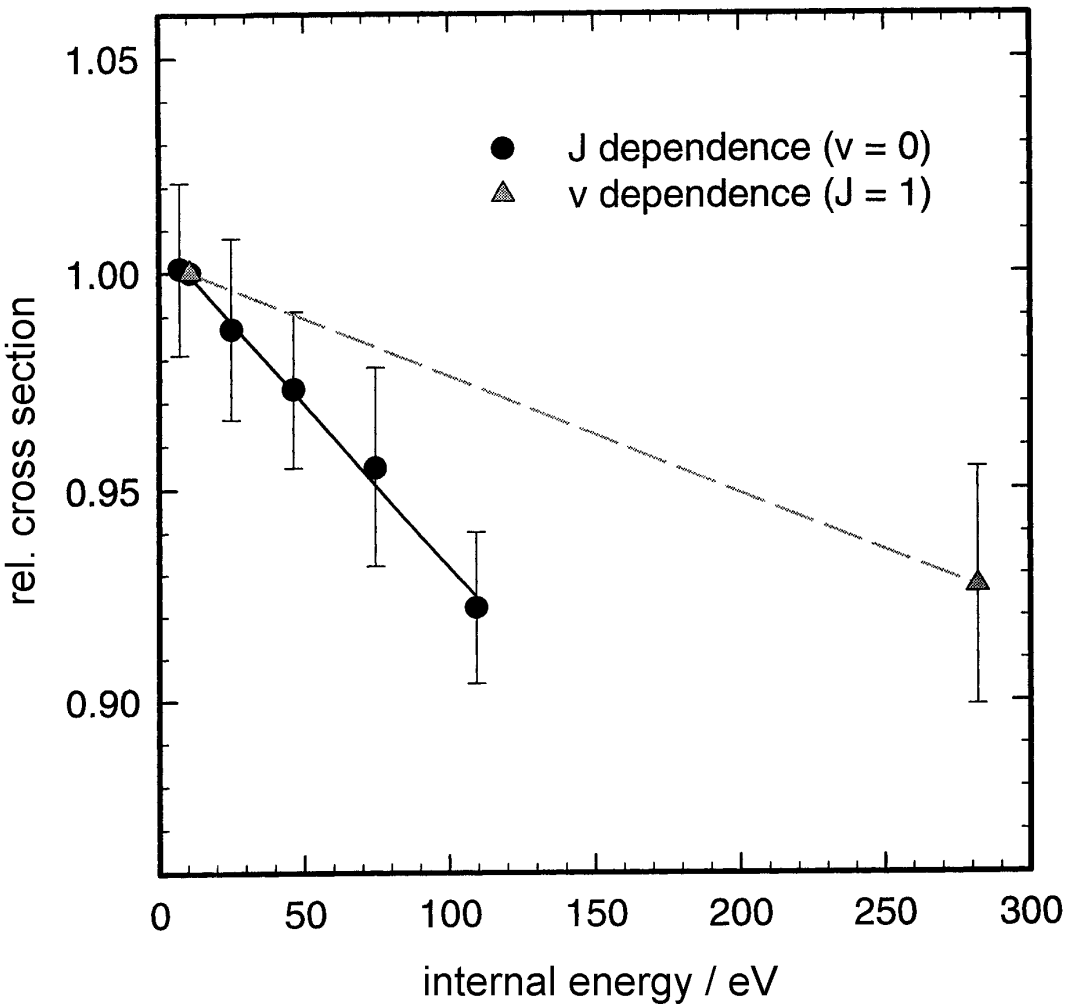
	o	p
oo	2/3	1/3
op	1/3	2/3
po	1/3	2/3
pp	0	1

Gerlich (2004)

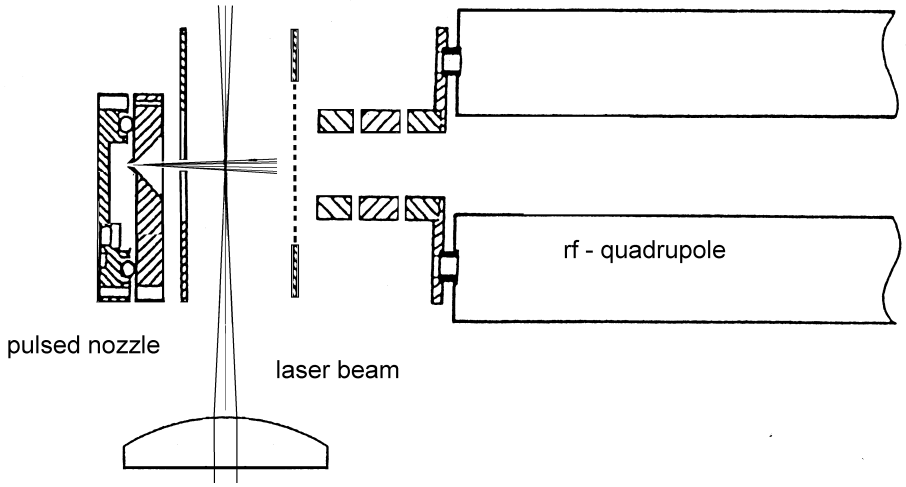
	o	p
oo	13/18	15/18
op	1/2	1/2
po	1/2	1/2
pp	0	1

Cordonnier, Uy,Dickson, Kerr, Zhang, Oka, J. Chem. Phys. **113 (**2000), 3181.
Gerlich, in: Book of abstracts XIV SASP, ed. P. Casavechia, La Thuile, Italy, (2004) 1

$H_2(j)^+ + H_2 \rightarrow H_3^+ + H$



state selective preparation using REMPI



T. Glenewinkel-Meyer, D. Gerlich, "Single and Merged Beam Studies of the Reaction H2+ + H2 → H3+ + H", Israel Journal of Chemistry, 37 (1997) 343

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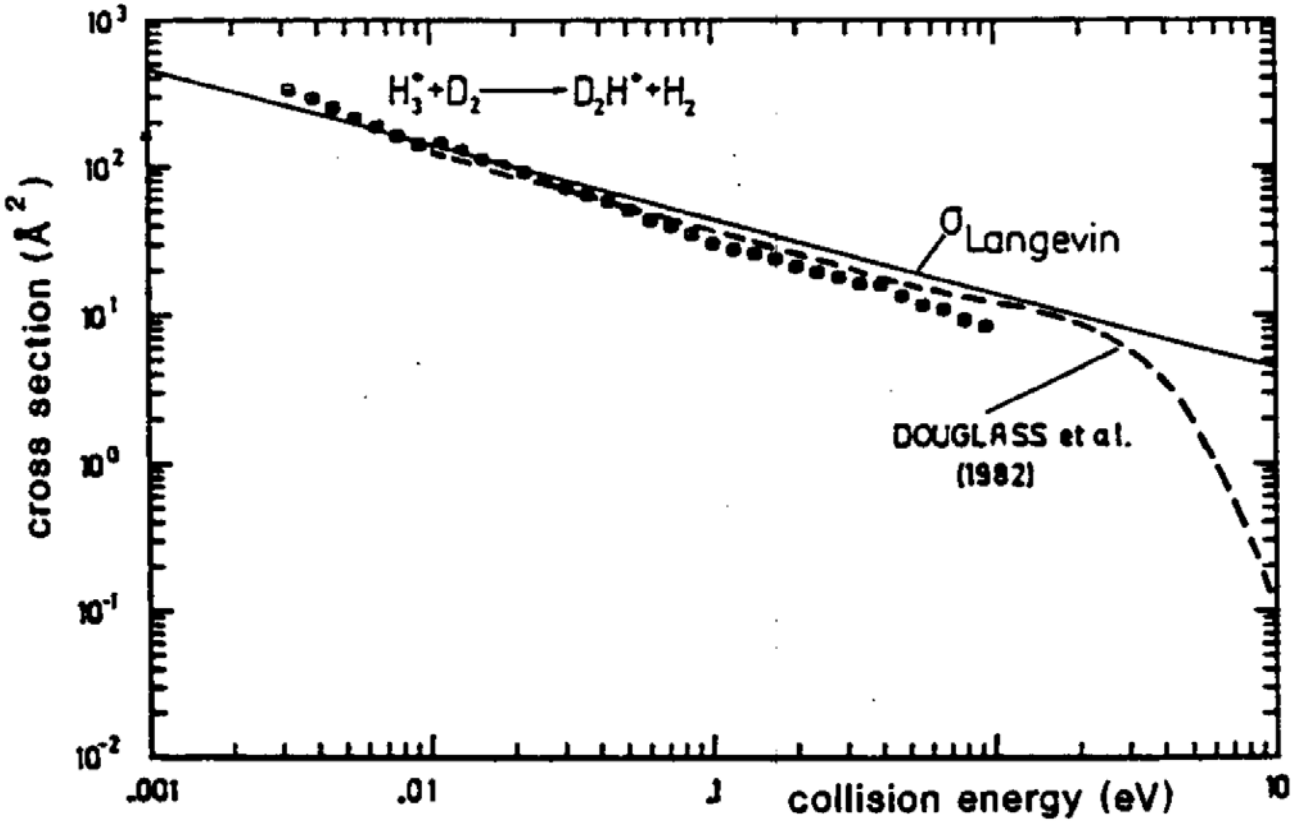
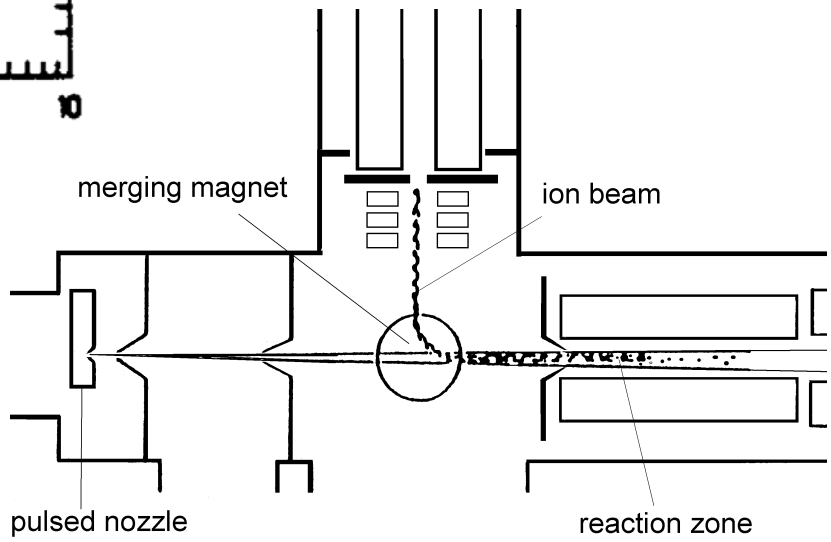
$H_3^+ + D_2$ merged beams





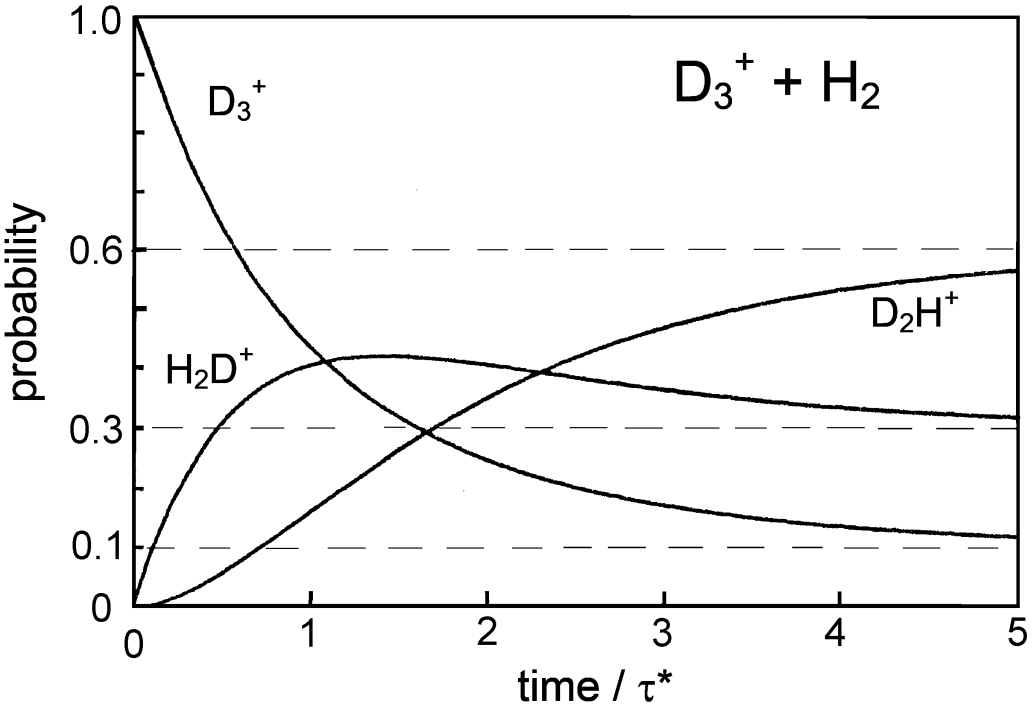
D. Gerlich "Inhomogeneous Electrical Radio Frequency Fields: A Versatile Tool for the Study of Processes with Slow Ions"
Adv. in Chem. Phys. LXXXII (1992)

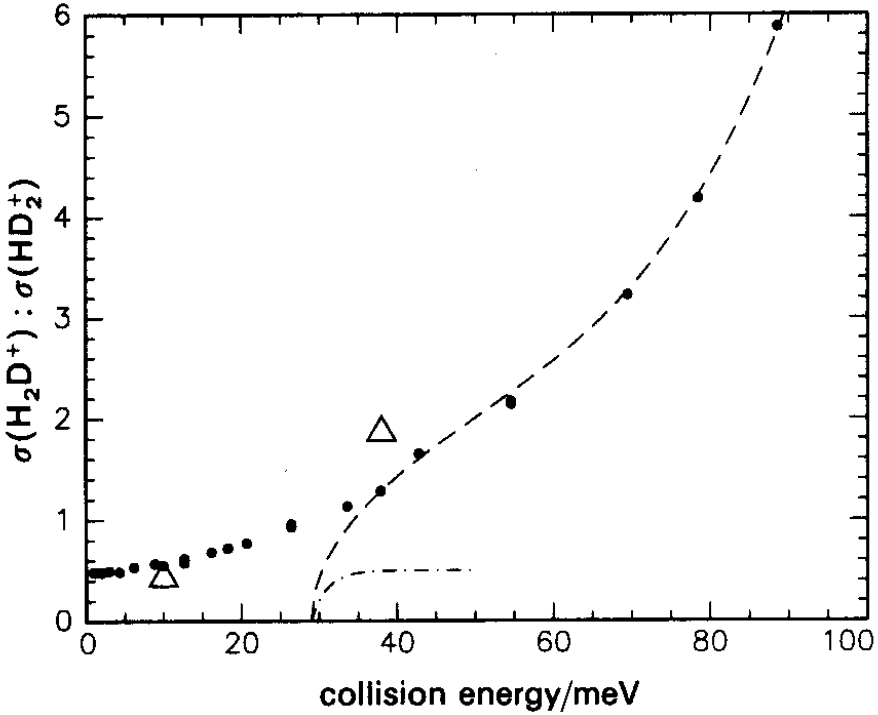
D - H scrambling

$D_3^+ + H_2 \rightarrow D_3^+ + H_2$

$\rightarrow H_2D^+ + D_2$ - 29 meV

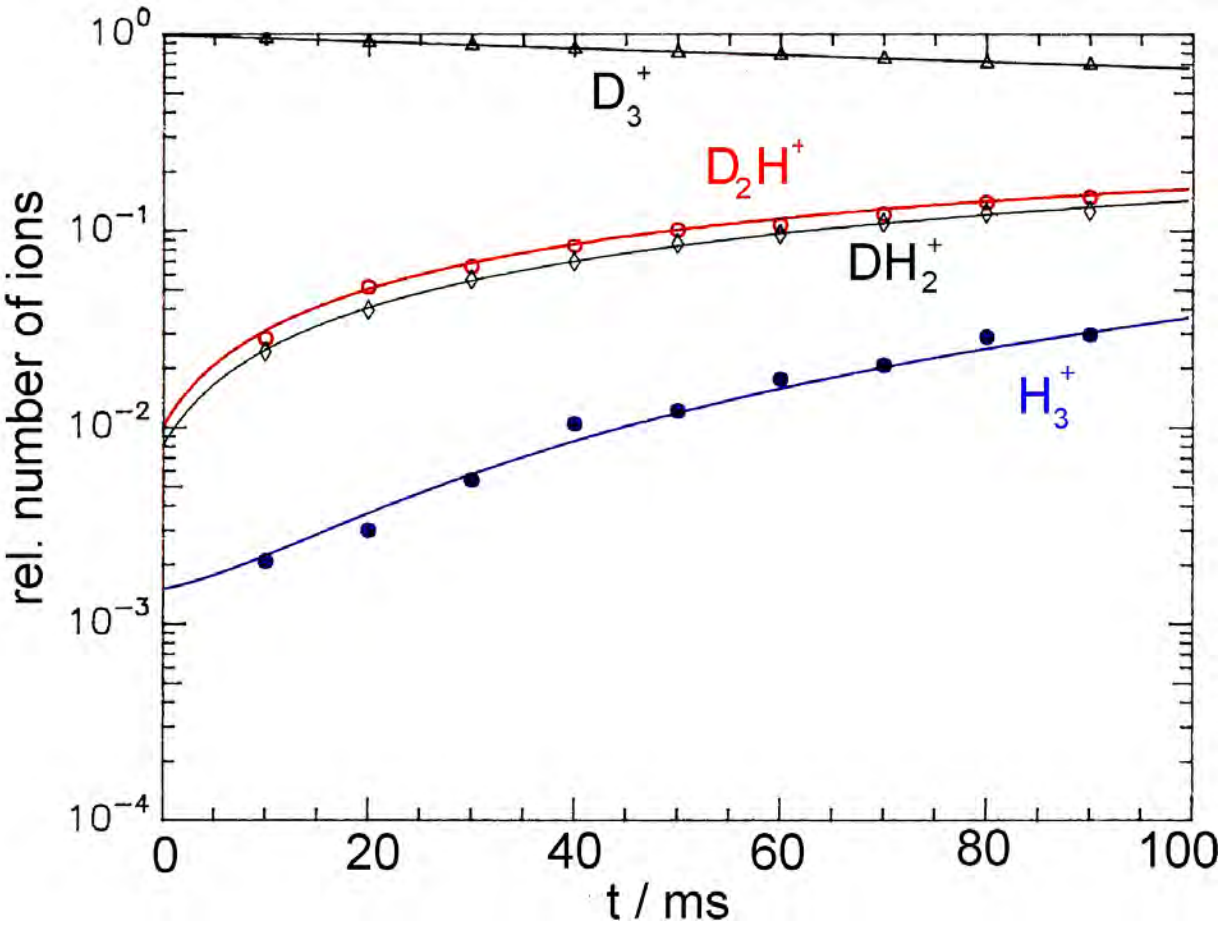
$\rightarrow HD_2^+ + HD$ - 20 meV





D. Gerlich “Experimental Investigation of Ion-Molecule Reactions Relevant to Interstellar Chemistry”
J. Chem. Soc. Faraday Trans., 89 (13), 2199-2208, (1993)

$D_3^+ + p - H_2$ in a T-variable trap

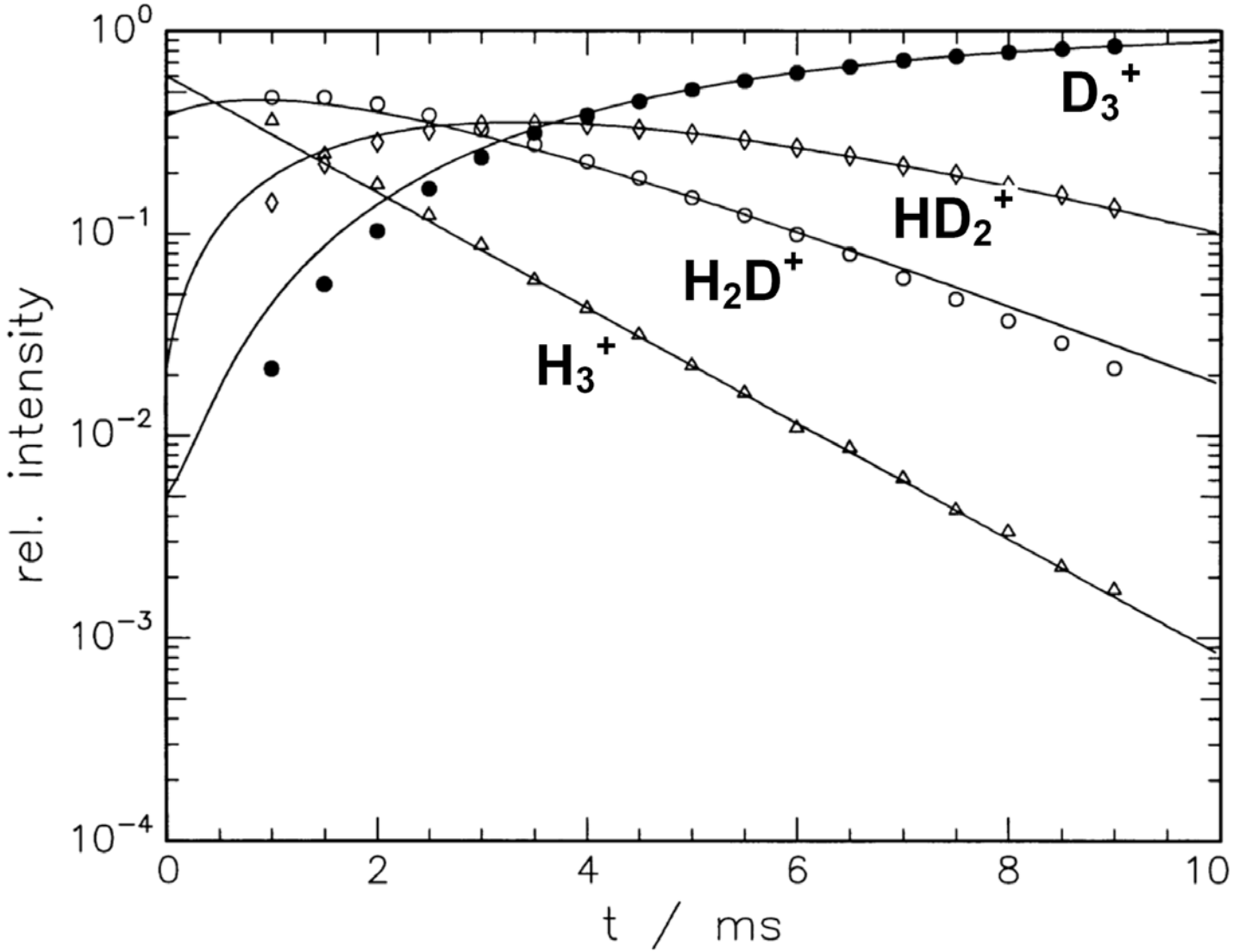


$k / 10^{-11}$ cm^3s^{-1}

m/*u*	300 K	15 K
6→5	**90**	**4**
6→4	**70**	**0.8**
5→4	50	0.5
5→3	70	0.7
4→3	90	0.9

Sequential deuteration of H_3^+

[HD]=1.8×10^{12}cm^{-3} T = 10 K



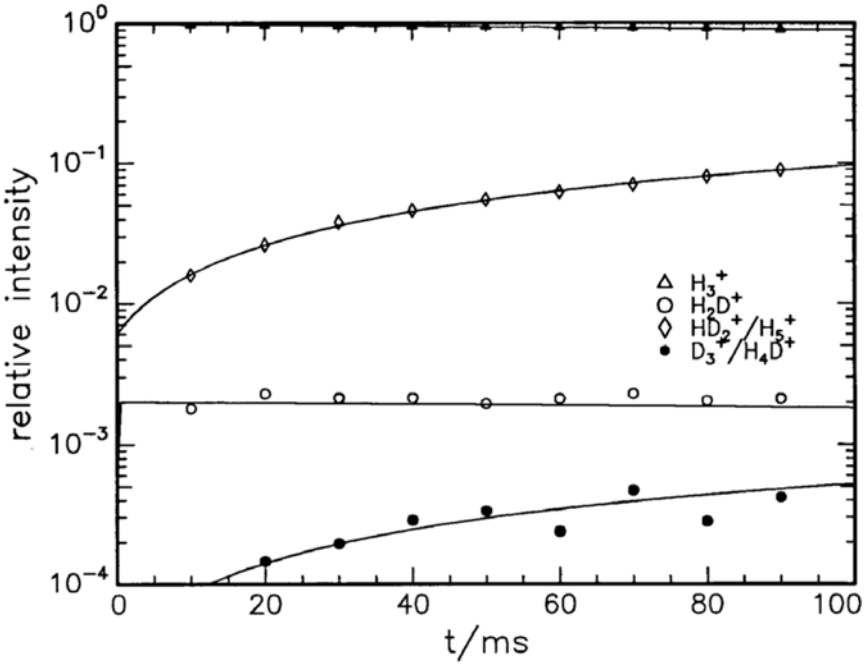
$k(H_3^+ \rightarrow H_2D^+)$= 3.5×10^{-10}cm^3/s

$k(H_2D^+ \rightarrow HD_2^+)$= 2.6×10^{-10}cm^3/s

$k(HD_2^+ \rightarrow D_3^+)$= 2.0×10^{-10}cm^3/s

D. Gerlich, E. Herbst, and E. Roueff, Planetary and Space Science, **50** (2002) 1275

H_2D^+ / H_3^+ equilibrium in 22PT



H_3^+ 90%

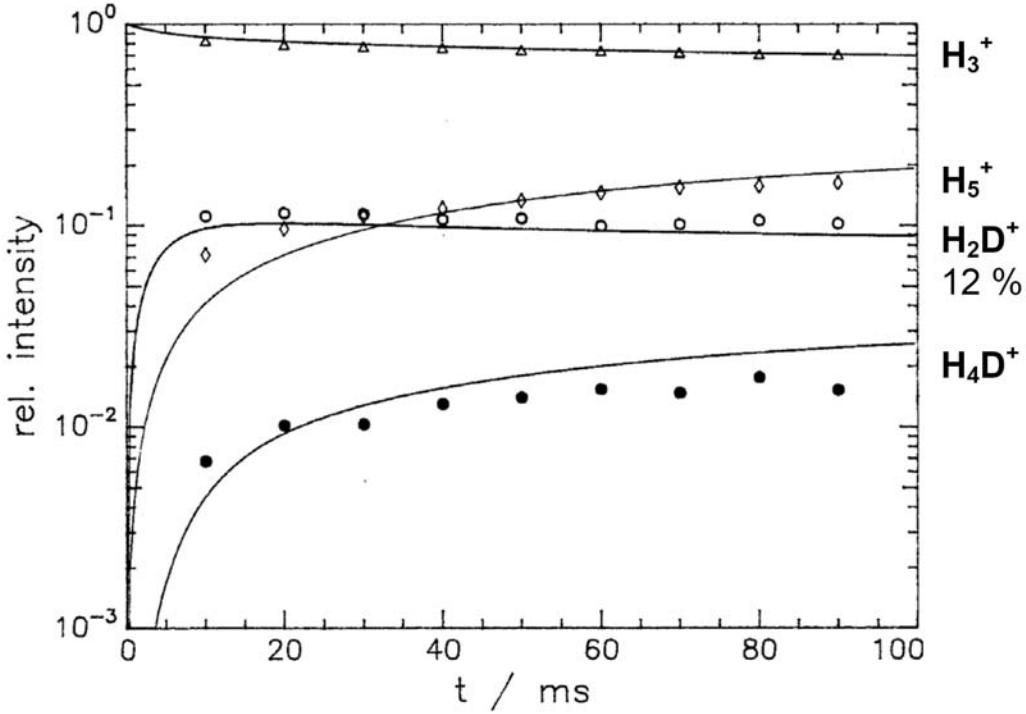
H_5^+ 9.8%

H_2D^+ 0.2%

H_4D^+

n-H_2

$[H_2] = 1.4 \times 10^{14}$ cm^{-3}



p-H_2

$[H_2] = 1 \times 10^{14}$ cm^{-3}

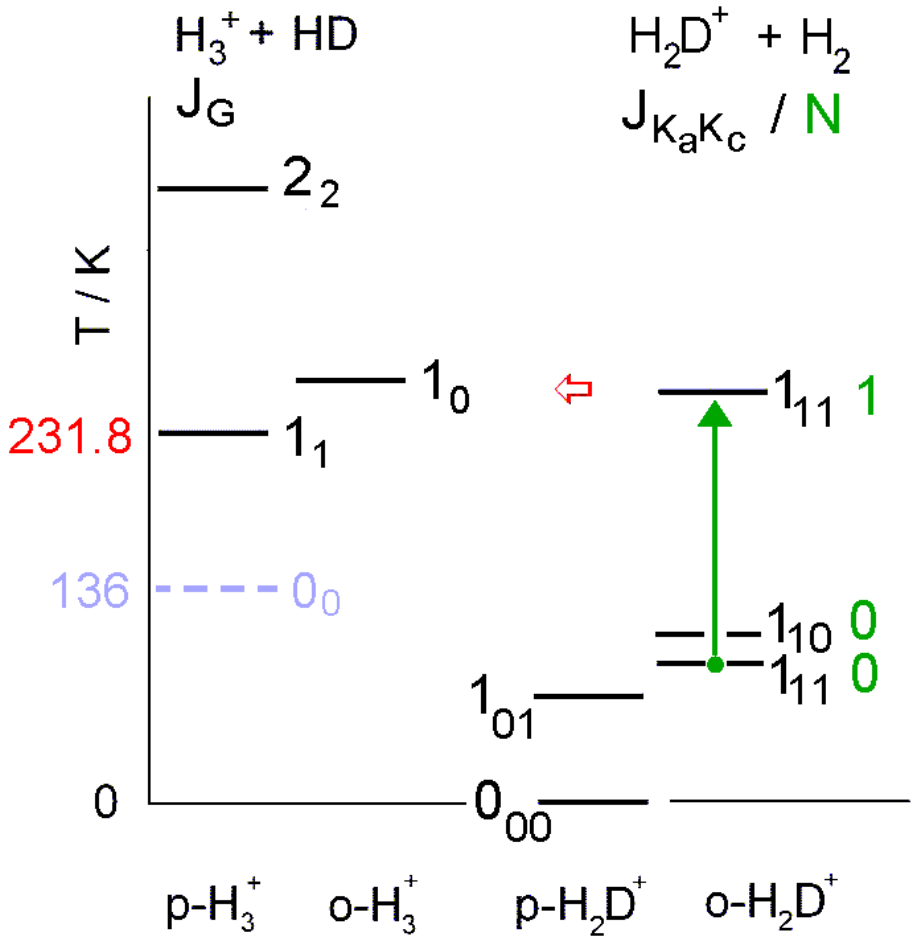
D. Gerlich, E. Herbst, and E. Roueff, Planetary and Space Science, **50** (2002) 1275

Deuteration $H_3^+ + HD \leftrightarrow H_2D^+ + H_2$: equilibrium constant *K*?

$K \sim \exp(231.8\ K / T)$

T (K)	Adams and Smith	Herbst	Ramanlal
80	4.5 (±1.3)	5.9	6.82
200	2.4 (±0.7)	2.6	1.52
295	2.0 (±0.6)	2.1 [a]	1.07 [a]
[a] The theoretical value is actually at 300 K.			

Ramanlal & Tennyson	**2.6(+12)**
Adams & Smith (1981)	1.5(+9)
Sidhu et al. (1992)	7.1(+12)
Gerlich et al. (2002)	**n-H_2 6** **p-H_2 500**
T_{22PT} 10 K, $T_{p\text{-}H2\ Gen}$ 12.5K	**600**

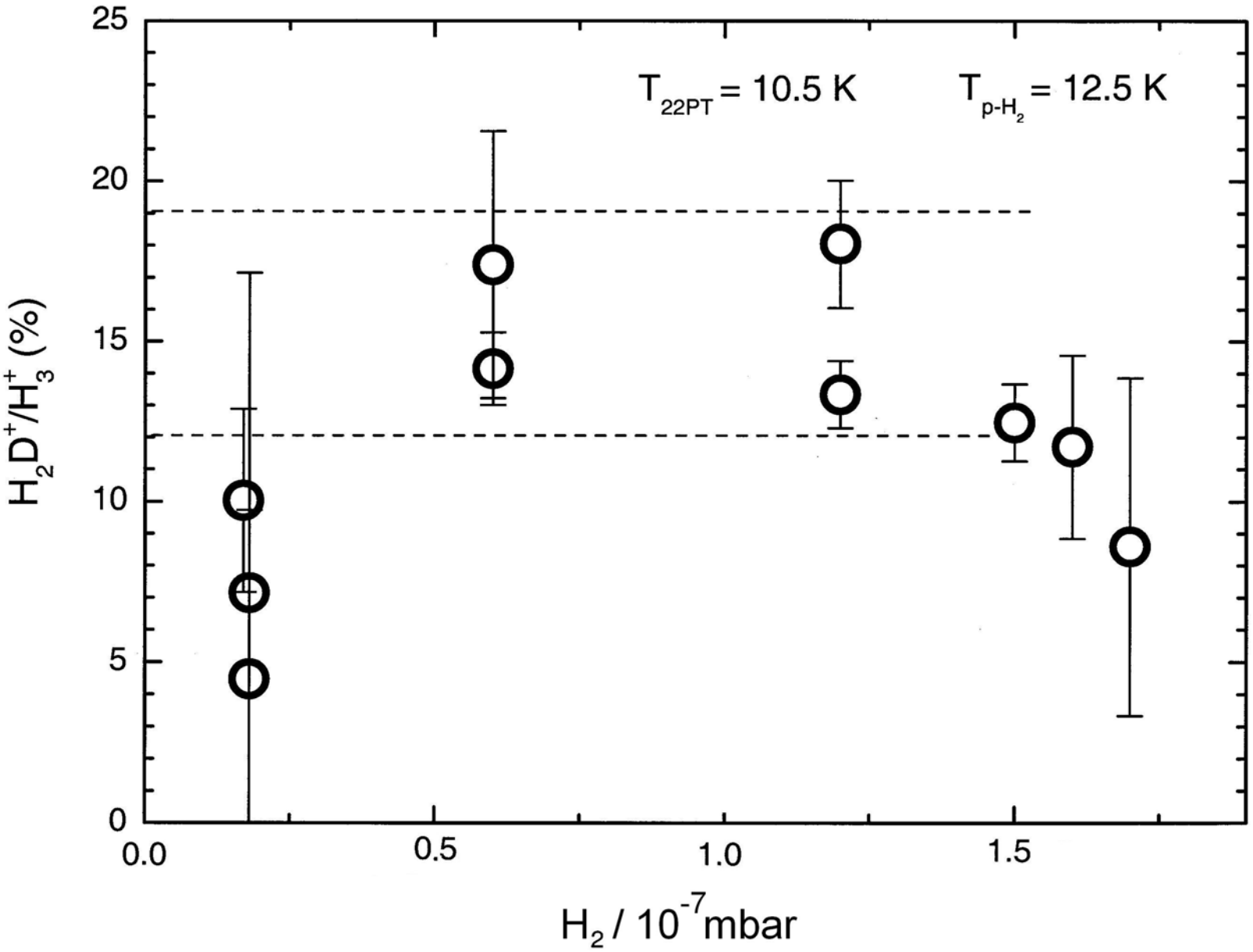


Ramanlal & Tennyson wrote in 2004:
trap experiment disagrees with calculations by
12 orders of magnitude

role of o-H_2 (N=1)
state specific $k_i(T)$
method overtone LIR

Ramanlal and J. Tennyson Monthly Notices of the Royal Astronomical Society , **354** (2004) 161
D. Gerlich, E. Herbst, and E. Roueff, Planetary and Space Science, **50** (2002) 1275

H_2D^+ / H_3^+ equilibrium in 22PT



Plasil, Glosik, Gerlich, 2004

Ortho-para conversion in $H_3^+ + H_2$ collisions

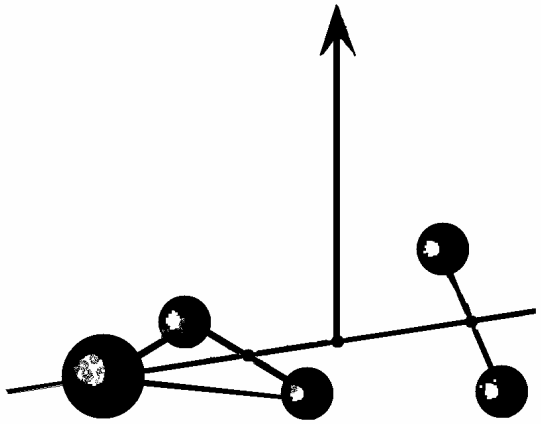
Cordonnier et al. (2000) Table III b

	oo	op	po	pp
oo	37/60	1/12	7/30	1/15
op	1/4	1/4	1/2	0
po	7/30	1/6	7/15	2/15
pp	1/5	0	2/5	2/5

Gerlich (2004) (high energy limit)

	oo	op	po	pp
oo	5/7	1/21	1/7	2/21
op	3/7	1/7	3/7	0
po	3/7	2/21	3/7	1/21
pp	3/7	0	1/7	3/7

$o/p\text{-}H_3^+ + o/p\text{-}H_2 \rightarrow o/p\text{-}H_3^+ + o/p\text{-}H_2$



dynamical constraints

(i) total nuclear spin $\boldsymbol{I}$ is conserved

(ii) $P_C \sim (2\,\boldsymbol{I} + 1)$

(iii) at high energies:

P_{decay} ~ statistical weight of the products: $[o\text{-}H_2] / [p\text{-}H_2] = 3 / 1$

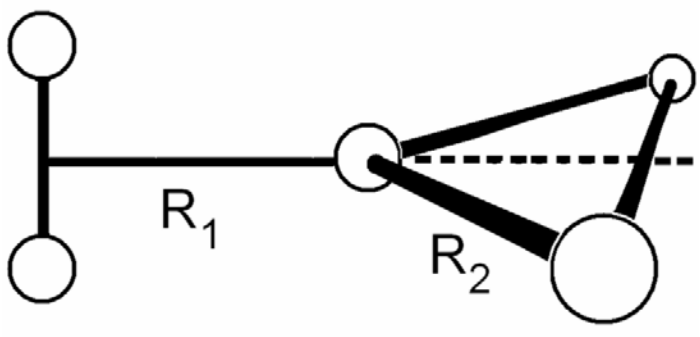
$[o\text{-}H_3^+] / [p\text{-}H_3^+] = 1 / 1$

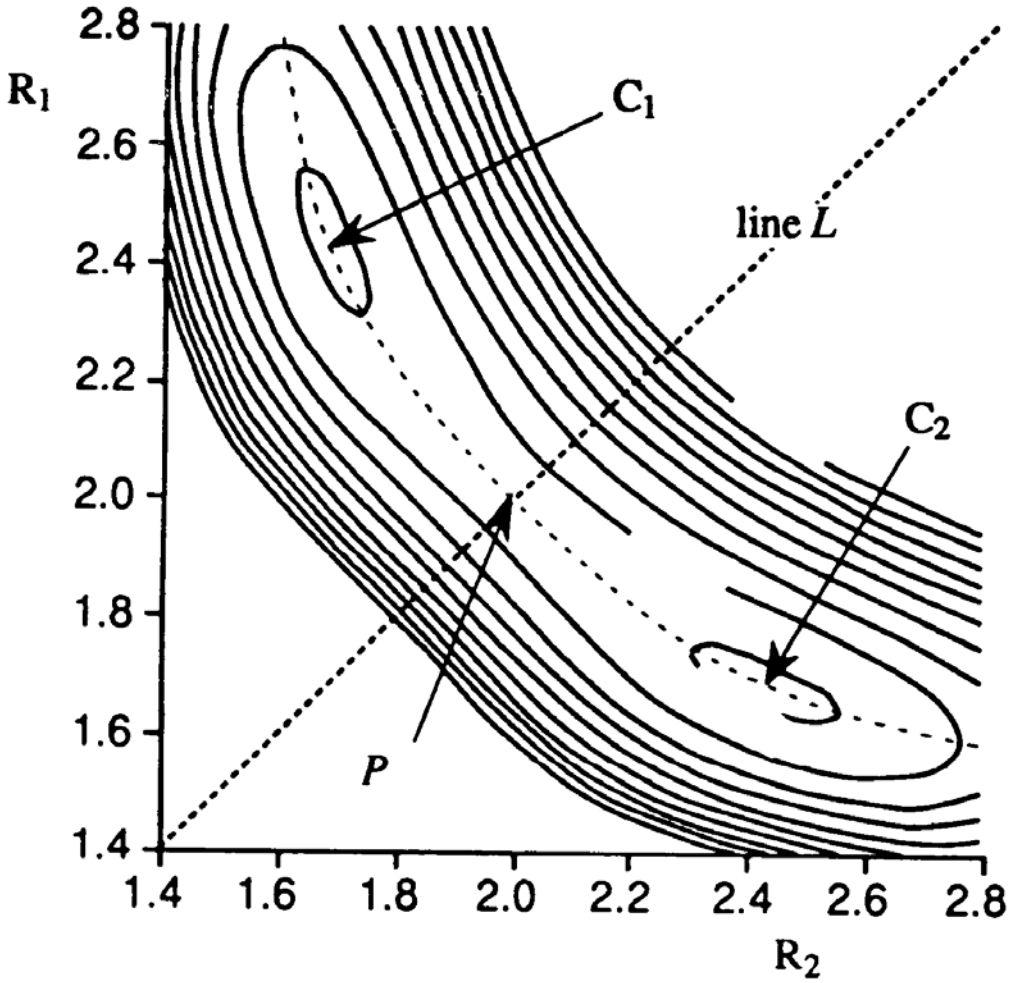
(iii)´ at low energies:

P_{decay} from **phase space theory (counting accessible states)**

Cordonnier, Uy, Dickson, Kerr, Zhang, Oka, J. Chem. Phys. **113** (2000), 3181.
D. Gerlich, Symposium in Atomic, Cluster and Surface Physics, La Thuile, Italy, 1 (2004)

PES H_5^+: proton transfer





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Dieter Gerlich

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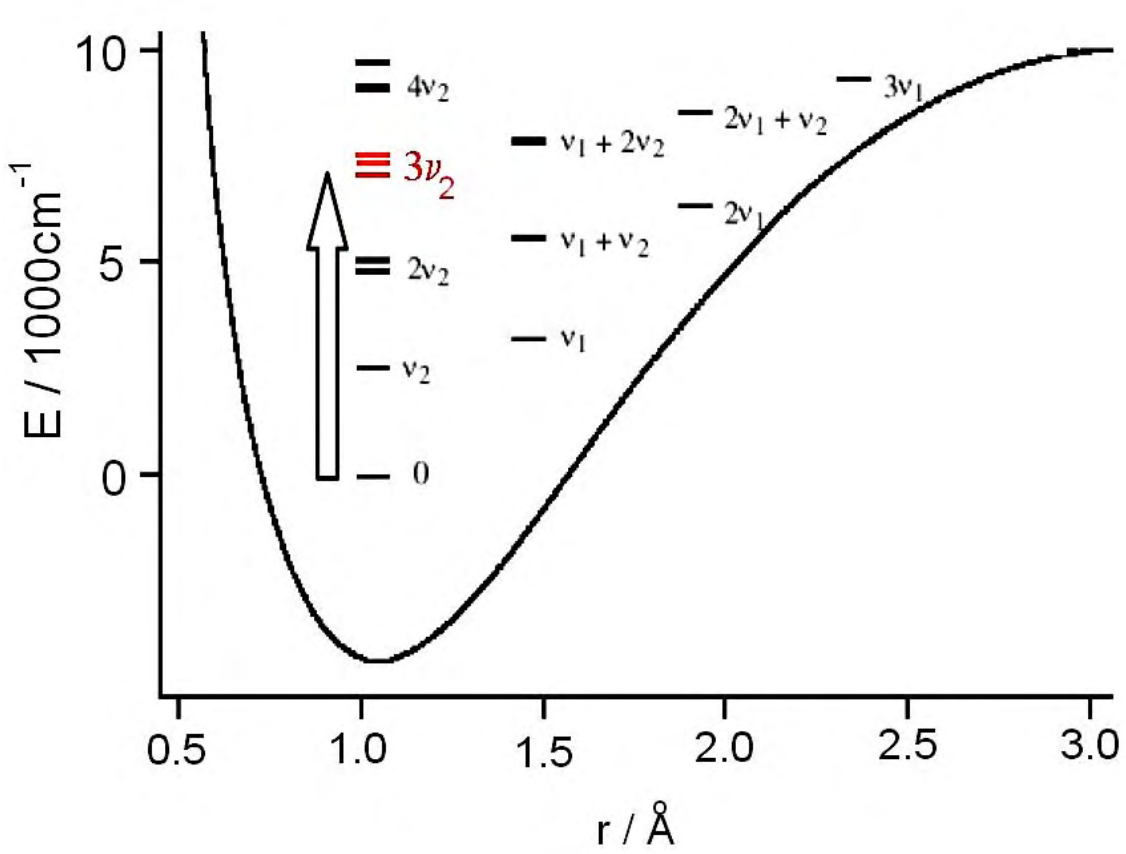
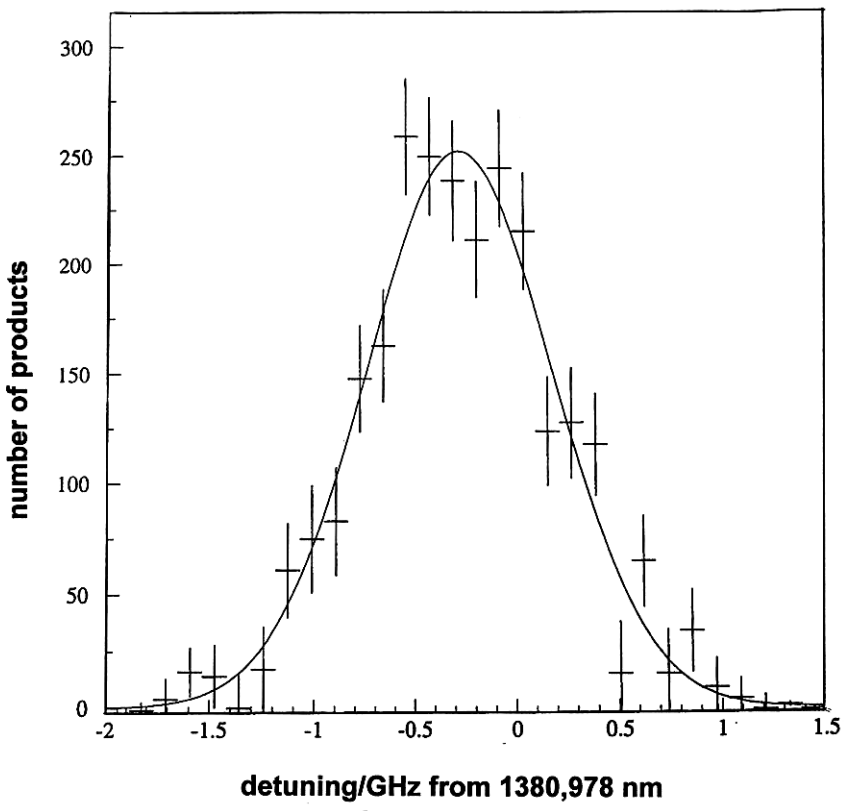
Overtone probing of H_3^+ states

$$H_3^+(v=0) \quad + \quad h\nu \Rightarrow \quad H_3^+(v_2=3)$$

$$H_3^+(v>1) \quad + \quad Ar \Rightarrow \quad ArH^+ \quad + \quad H_2$$





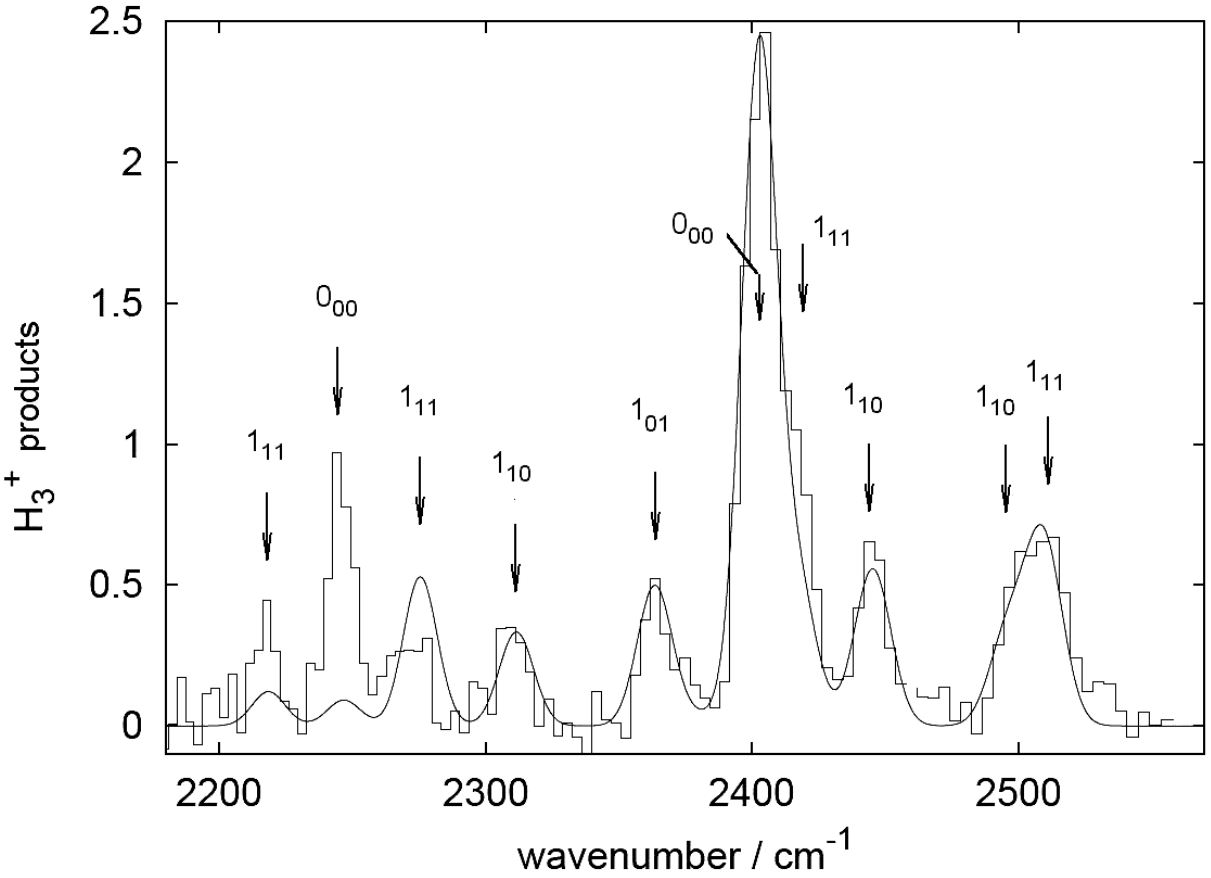
GIF Project e- + H3+ TSR and 22PT (MPIK HD

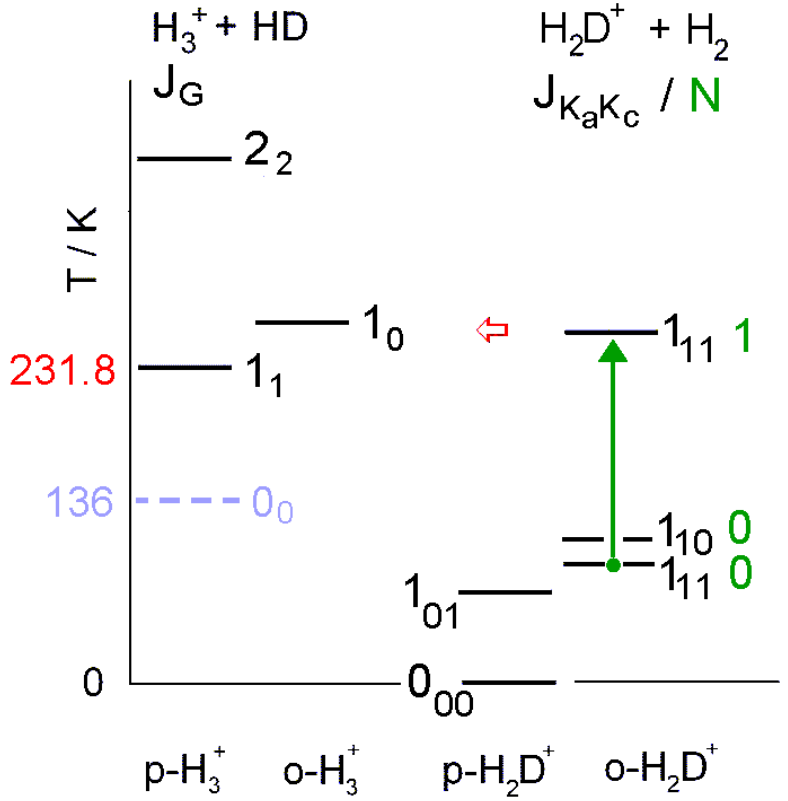
J. Mikosch, H. Kreckel, R. Plasil, D. Gerlich, J. Glosik, D. Schwalm, A. Wolf, J. Chem. Phys., 121, 11030 - 11037 (2004)

LIR spectrum of H_2D^+ (Δv_2 or Δv_3 = 1)

$H_2D^+ + H_2 + hv \rightarrow H_3^+$

$[H_2] = 7 \times 10^{10} cm^{-3}$ T = (25 ± 5) K



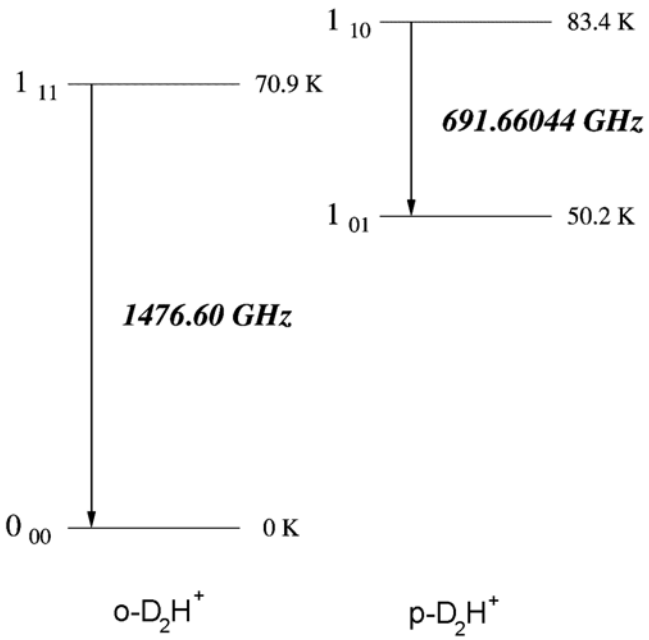


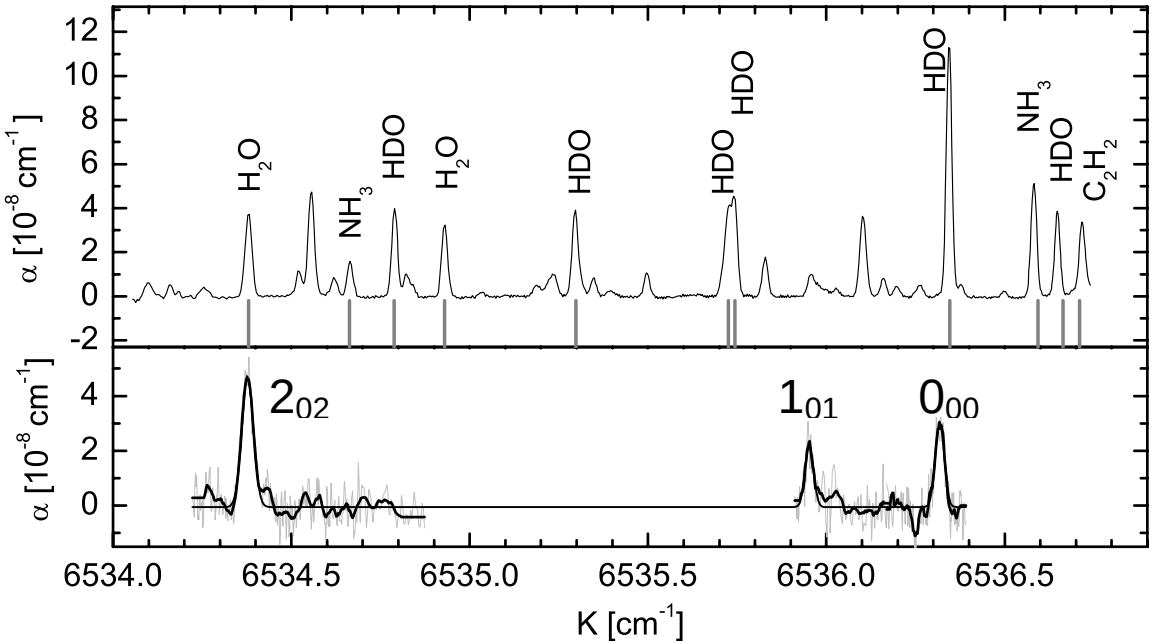
n- H_2 : o : p = 0.75 : 1

"p"- H_2 : o : p = 0.20 : 1

Schlemmer, Asvany, Hugo, Gerlich, Astrochemistry, IAU Symposium 231, 2005

Overtone detection of D_2H^+ (0_{00})





Doppler width

discharge 250 K
trap 9 K

Transition

calc. 6536.301
measured 6536.319

Hlavenka, Plasil, Bano, Korolov, Gerlich, Ramanlal, Tennyson, Glosik (2005) submitted

Laser induced reactions in a trap

H_3^+ LIR

- finite sample of ions (~1000)
- Population: P(J,G), P(2)... P(J), ...
- Pumping J to excited state
- reaction

$$H_3^* + Ar \rightarrow ArH + H$$

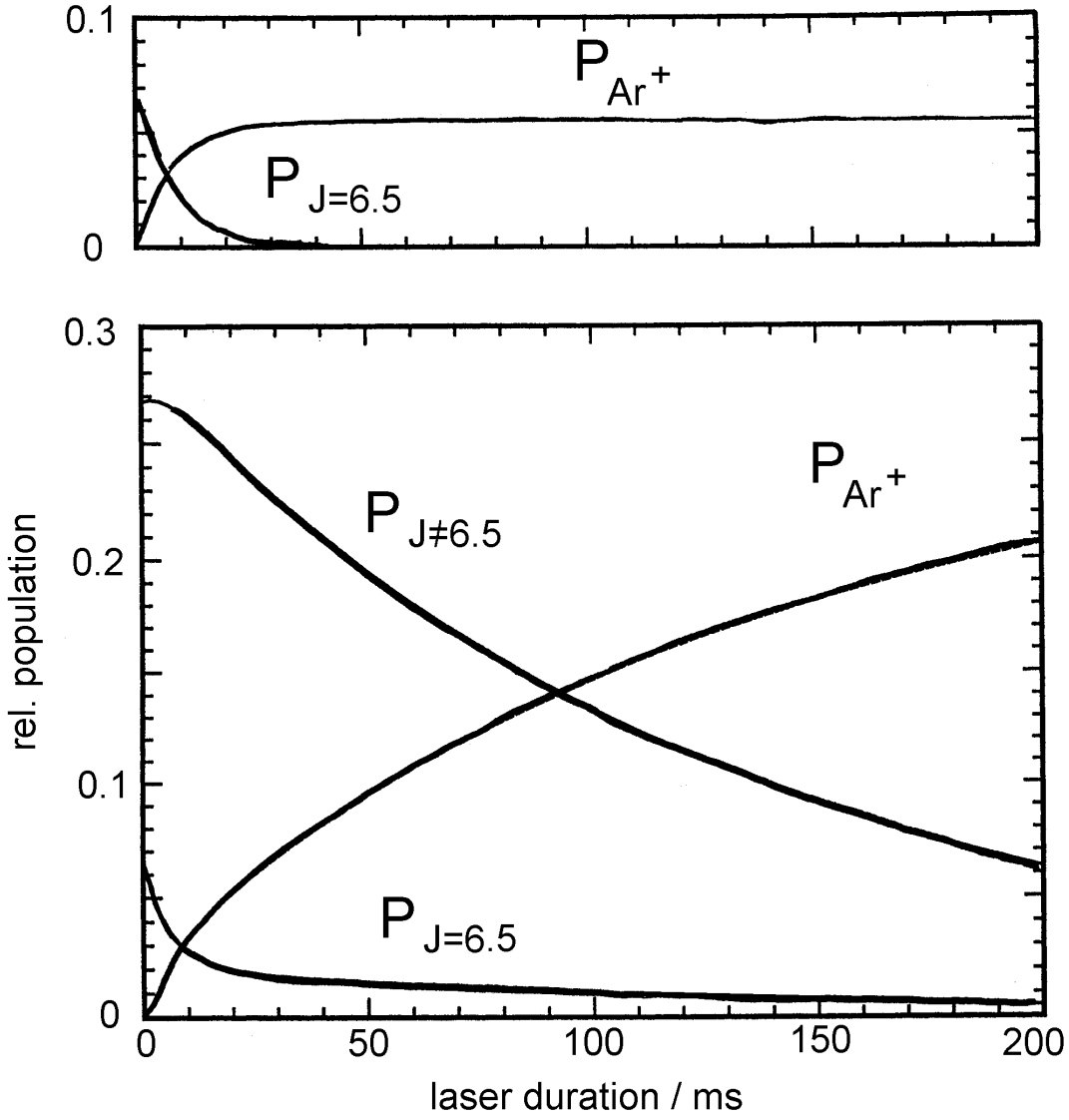
- P(J) → 0 ("hole burning")
- relaxation

$$J' \rightarrow J$$

rate coefficients

laser excitation
relaxation: radiative, collisions,..
reaction
....
IR excitation

$N_2^{+*} + Ar \rightarrow Ar^+ + N_2$



S. Schlemmer, T. Kuhn, E. Lescop, and D. Gerlich, "Laser excited N_2^+ in a 22-Pole trap"
Int. J. Mass Spectrom. Ion Proc. **185** (1999) 589

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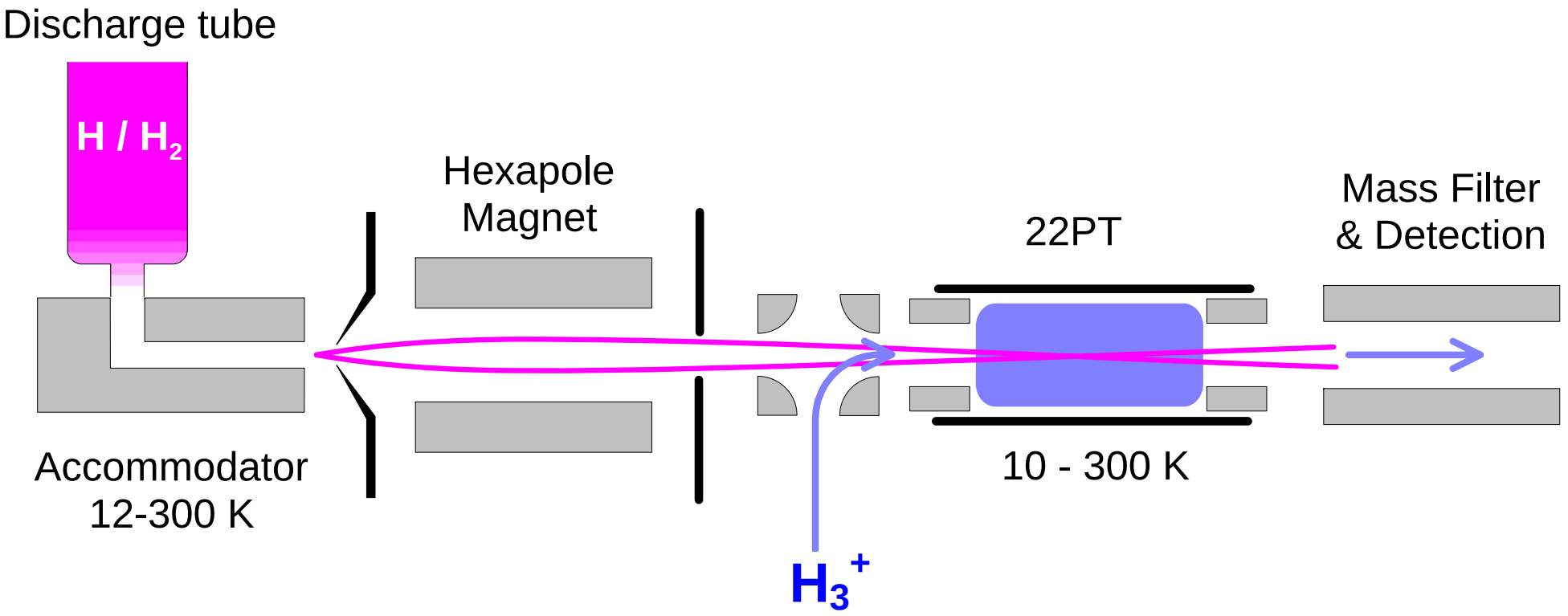
Atomic Beam 22-Pole Ion Trap (AB-22PT)

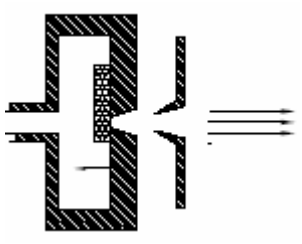


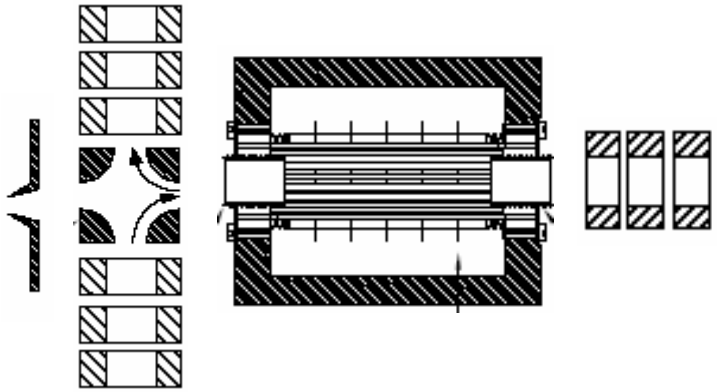
H_3^+ + H: ortho para transitions

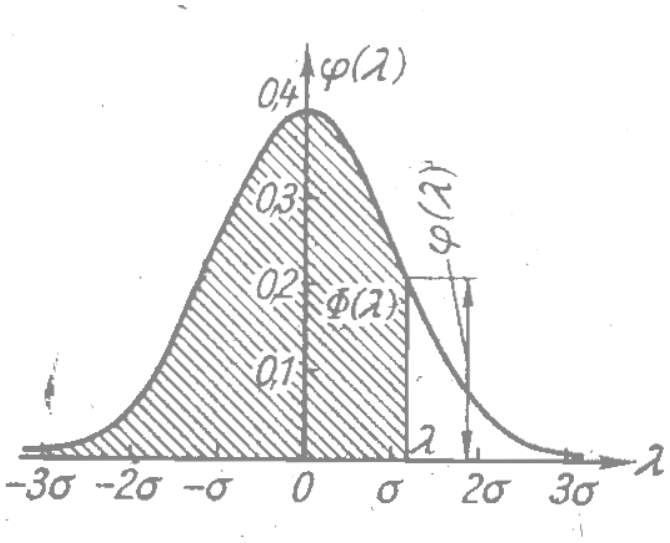
H_3^+ + D: deuteration

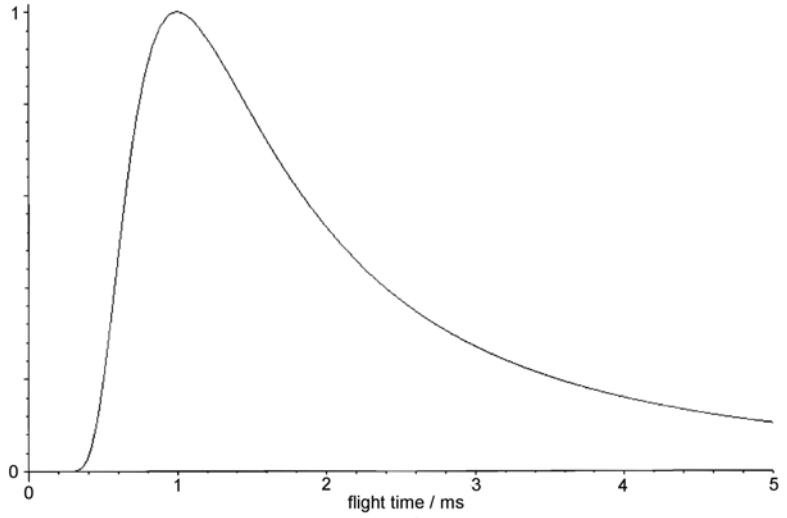
Combination: pulsed effusive beam with 22PT

Effusive source
T=4 K for He









Velocity distribution
largest probability for [0,dv]

Time distribution of the density
Chopped beam

TECHNISCHE UNIVERSITÄT CHEMNITZ | FAKULTÄT FÜR NATURWISSENSCHAFTEN

Gasentladungs- und Ionenphysik

DFG FG *Laboratory Astrophysics*

4K-22PT	**J. Glosik**, R. Plasil, F. Windisch
$H_3^+(J,K) + e^-$	D. Zajfmann, A. Wolf, H. Krekel, TSR Heidelberg
AB-22PT + H-beam	**A. Luca,** G. Borodi, C. Mogo
22PT-spectroscopy	**J. Maier,** Basel
Beam-Trap **astrochemistry**	**M. Smith** THE UNIVERSITY OF ARIZONA TUCSON ARIZONA
TV-22PT	**S. Schlemmer,** O. Asvany **(Köln, Leiden)**