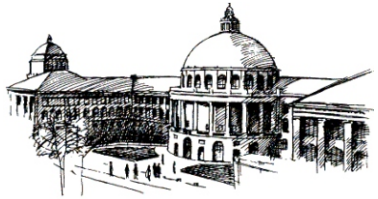


Dutch Astrochemistry Network Meeting
Leiden, 28. November 2018

Quantum Effects in Ion-Neutral Reactions at Low Temperatures

Frédéric Merkt, Physical Chemistry, ETH Zurich
Department of Physics and Astronomy, VU Amsterdam

Introduction

Part I. The $H_2^+ + H_2 \longrightarrow H_3^+ + H$ reaction (Katharina Höveler, Pitt Allmendinger, Johannes Deiglmayr)

Part II. The $H^+ + H \longrightarrow H_2^+ + h\nu$ association reaction (Maximilian Beyer)

Conclusions

Cold hydrogen ion chemistry

H_2 and H_2^+ are the simplest molecules.

They are ideal for studies of quantum effects in ion-neutral chemistry

Hydrogen is the most abundant element in the universe

$$T_{\mathrm{VLT}} = \frac{\hbar^4}{k_B \mu^2 q^2 \alpha}.$$

$H^+ + H$: 100 mK

$Mg^+ + Na$: < 100 μK

Troe, Nikitin and coworkers,
JCP **122**, 184311 (2005)

In dense clouds (H_2 from grains):

$$H_2 \xrightarrow{\text{cosmic rays}} H_2^+ + e^-$$

$$H_2^+ + H_2 \longrightarrow H_3^+ + H$$

Fast (Langevin)

$$H_3^+ + X \longrightarrow HX^+ + H_2$$

(X=C,N,O,...)

Herbst, E., & Klemperer, W. 1973,
"The Formation and Depletion of Molecules in Dense Interstellar Clouds," ApJ, 185, 505-533

In early universe:

$$H^- + H \longrightarrow H_2 + e^-$$

Dalgarno and others

$$H^+ + H \longrightarrow H_2^+ + h\nu$$

Slow

Bates and coworokers

T. Oka, Chem. Rev. 13, 8738 (2013)

CHEMICAL REVIEWS

Review

pubs.acs.org/CR

Interstellar H_3^+

Takeshi Oka

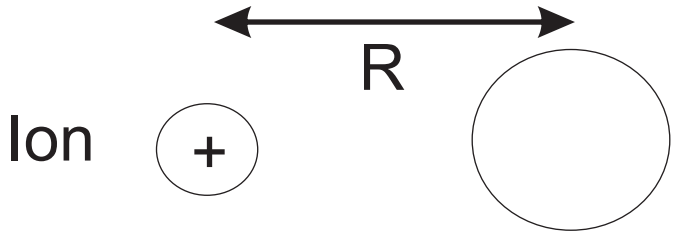
Department of Chemistry and Department of Astronomy and Astrophysics, The Enrico Fermi Institute, University of Chicago, 5801 South Ellis Avenue, Chicago, Illinois 60637, United States

2.2.1. $H_2 + H_2^+ \rightarrow H_3^+ + H$, the Langevin Rate. The chemistry of interstellar H_3^+ is extremely simple. H_3^+ is produced by cosmic ray ionization of H_2 to H_2^+ followed by the proton-hop reaction in eq 1. This reaction is very efficient with a high exothermicity of 1.74 eV, the difference between the proton affinity of H_2 (4.39 eV) and H (2.65 eV), and a high Langevin cross section on the order of a few 100−1000 Å^2 in interstellar space depending on the temperature. When H_2 and H_2^+ approach at a distance of r, the positive charge on H_2^+ with the Coulomb field of e/r^2 polarizes H_2 and induces a dipole moment $d = \alpha e/r^2$, where α is the polarizability of H_2. This leads to the attractive charge-induced dipole potential,[63] $V_L = -de/2r^2 = -\alpha e^2/2r^4$, the Langevin potential. The motion of a

dx.doi.org/10.1021/cr400266w | *Chem. Rev.* 2013, 113, 8738−8761

Ion-neutral reactions at low temperature - Langevin capture

Langevin capture cross sections and rate coefficients

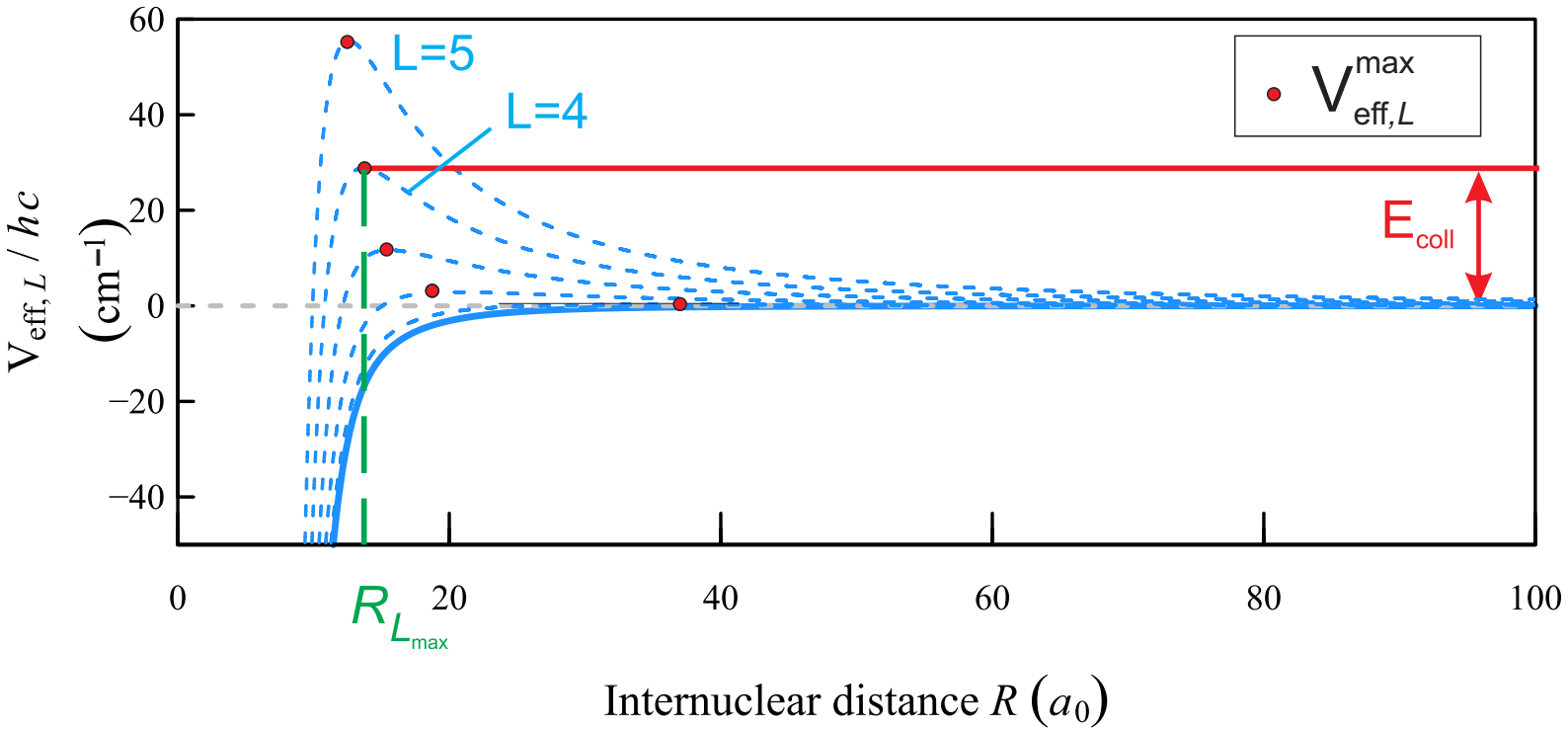


Polarizable neutral atom or molecule

$$E_{coll} = \mu v_{rel}^2/2 + L^2/(2\mu R^2) + V(R),$$

$$T_{VLT} = V_{eff,L=1}^{max}/(2k_B)$$

with $V(R) = -\alpha E^2/2 = -(4\pi\varepsilon_0\alpha')(e/(4\pi\varepsilon_0 R^2))^2/2 = -\alpha' e^2/(8\pi\varepsilon_0 R^4)$



Rate coefficient

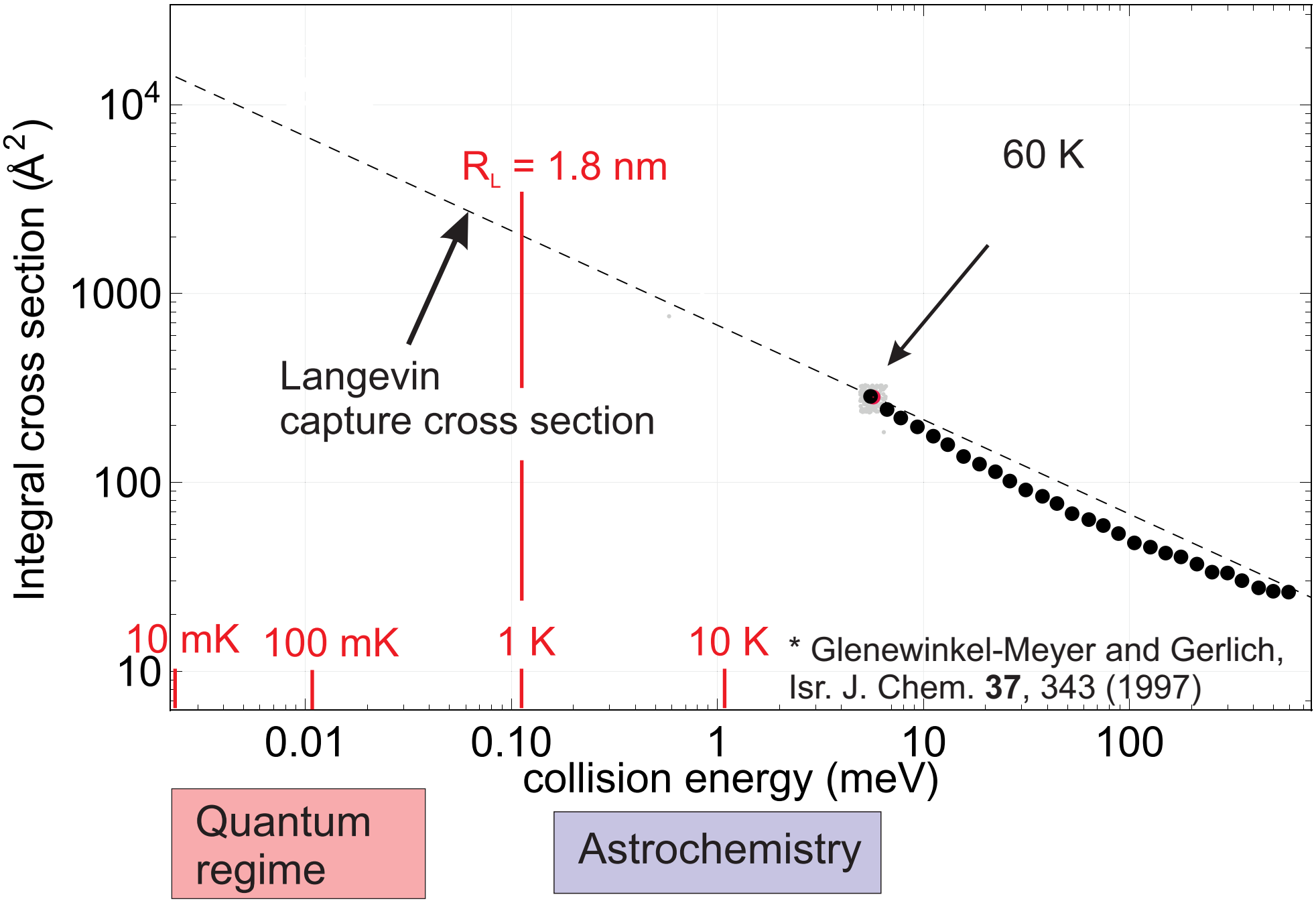
$$k_L = \sigma_L v_{rel} = \left(\pi\alpha' e^2/(\varepsilon_0\mu)\right)^{1/2}$$

$$= \pi R_L^2 v_{rel}$$

$$\sigma_L \sim E_{coll}^{-1/2}$$

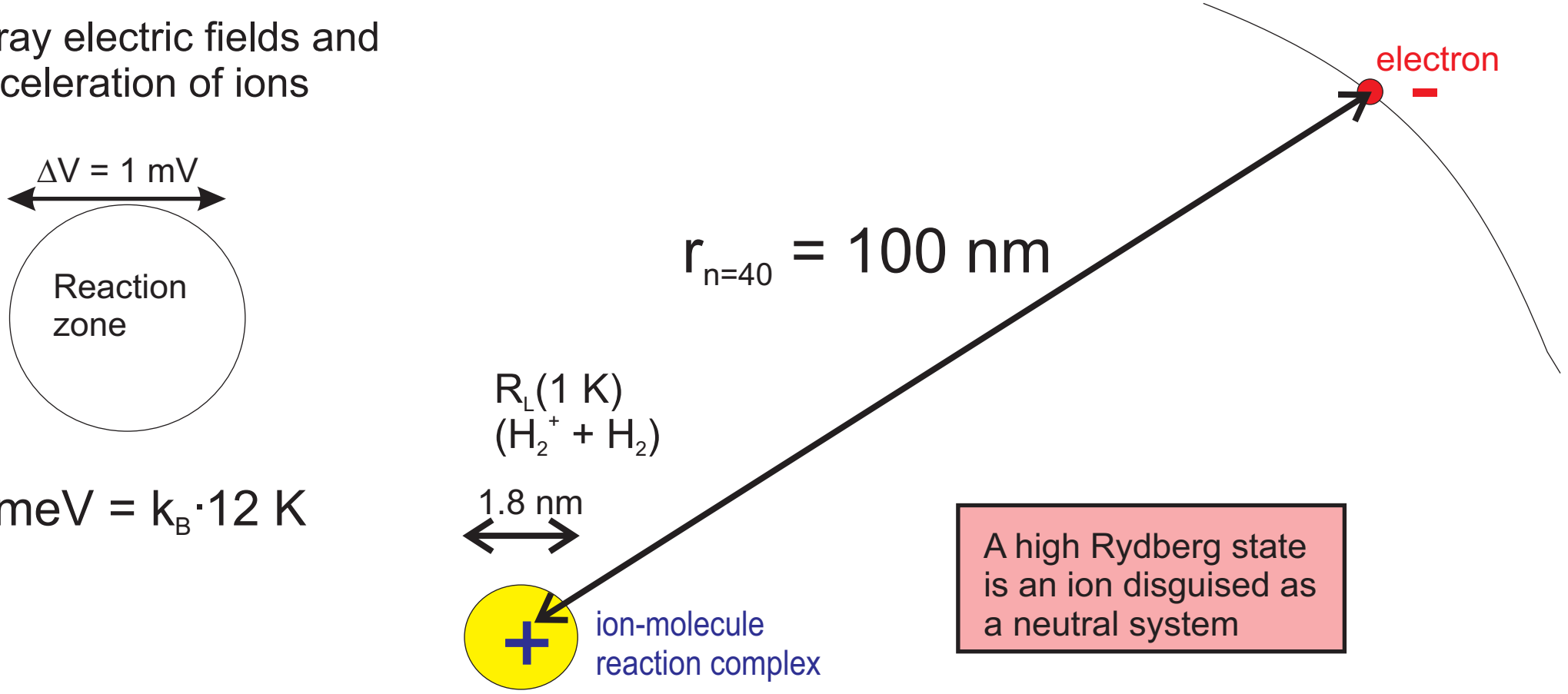
P. M. Langevin,
Une formule fondamentale de théorie cinétique,
Ann. Chim. Phys.,
Serie 8 (T5), 245 (1905)

The $H_2^+ + H_2 \longrightarrow H_3^+ + H$ reaction



Ion-molecule reaction within the orbit of a Rydberg electron

Stray electric fields and acceleration of ions



1 meV = k_B·12 K

A high Rydberg state is an ion disguised as a neutral system

S. T. Pratt, J. L. Dehmer, P. M. Dehmer and W. A. Chupka, J. Chem. Phys. 101 , 882 (1994)
D. Dai, C. C. Wang, G. Wu, S. A. Harich, H. Song, M. Hayes, R. T. Skodje, X. Wang, D. Gerlich and X. Yang, Phys. Rev. Lett. 95 013201 (2005).
M. Matsuzawa, Phys. Rev. A 82 , 054701 (2010)

What happens at 0 K?

s-wave capture

Quantum Langevin model for exoergic ion-molecule reactions and inelastic processes

Bo Gao*
Department of Physics and Astronomy, Mailstop 111, University of Toledo, Toledo, Ohio 43606, USA
(Dated: January 31, 2011)

We presents a fully quantal version of the Langevin model for the total rate of exoergic ion-molecule reactions or inelastic processes. The model, which is derived from a rigorous multichannel quantum-defect formulation of bimolecular processes, agrees with the classical Langevin model at sufficiently high temperatures. It also gives the first analytic description of ion-molecule reactions and inelastic processes in the ultracold regime where the quantum nature of the relative motion between the reactants becomes important.

PACS numbers: 34.10.−x,03.65.Nk,34.50.Cx,34.50.Lf

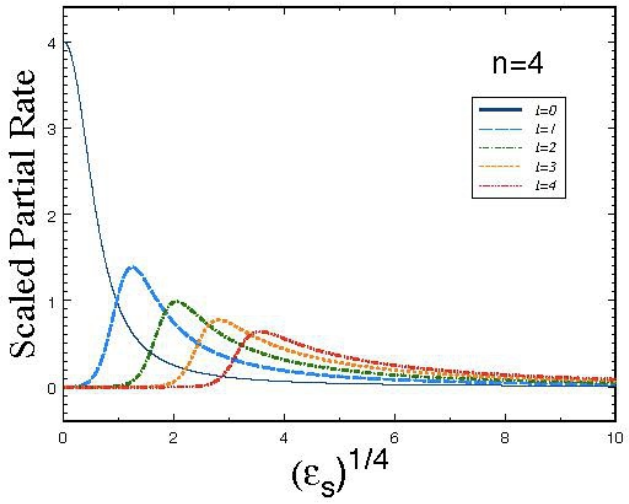


FIG. 1. (color online) The scaled partial rates $\mathcal{W}_l^{(n)}(\epsilon_s)$ for $n = 4$, corresponding to $-1/R^4$ type of interaction in the entrance channel.

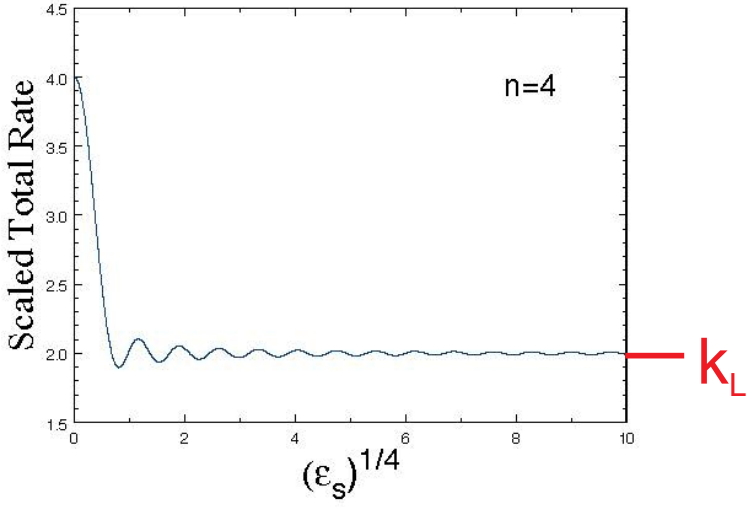


FIG. 2. (color online) The scaled total rate $\mathcal{W}^{(n)}(\epsilon_s)$ for $n = 4$, corresponding to $-1/R^4$ type of interaction in the entrance channel.

Generalized multichannel quantum defect theory for a -1/R^4 potential

Universal behavior of scattering in the 0 K limit

What happens at 0 K?

Statistical adiabatic-channel approach
Quantum capture

THE JOURNAL OF CHEMICAL PHYSICS 122, 184311 (2005)

Rates of complex formation in collisions of rotationally excited homonuclear diatoms with ions at very low temperatures: Application to hydrogen isotopes and hydrogen-containing ions[a)]

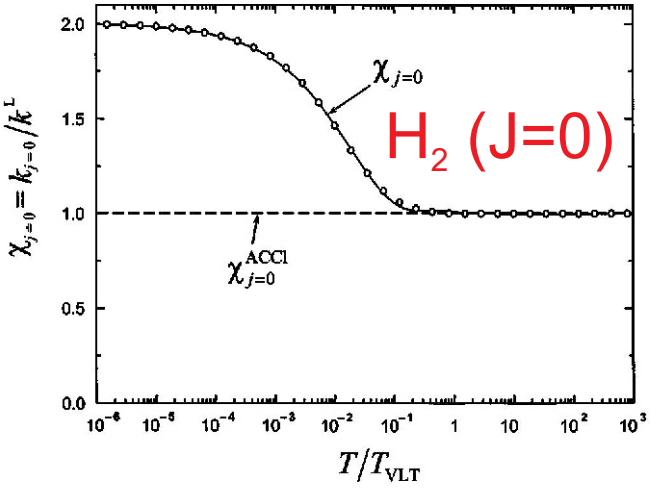
E. I. Dashevskaya
Department of Chemistry, Technion—Israel Institute of Technology, Haifa 32000, Israel and Max-Planck-Institut für Biophysikalische Chemie, Am Fassberg, D-37077 Goettingen, Germany

I. Litvin
Department of Chemistry, Technion—Israel Institute of Technology, Haifa 32000, Israel and Institut für Physikalische Chemie der Universität Goettingen, Tammannstrasse 6, D-37077 Goettingen, Germany

E. E. Nikitin
Department of Chemistry, Technion—Israel Institute of Technology, Haifa 32000, Israel and Max-Planck-Institut für Biophysikalische Chemie, Am Fassberg, D-37077 Goettingen, Germany

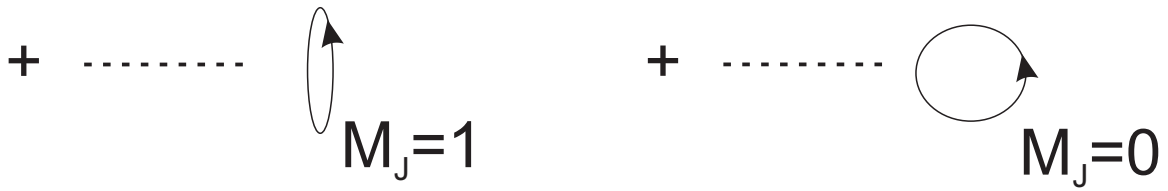
J. Troe
Max-Planck-Institut für Biophysikalische Chemie, Am Fassberg, D-37077 Goettingen, Germany and Institut für Physikalische Chemie der Universität Goettingen, Tammannstrasse 6, D-37077 Goettingen, Germany

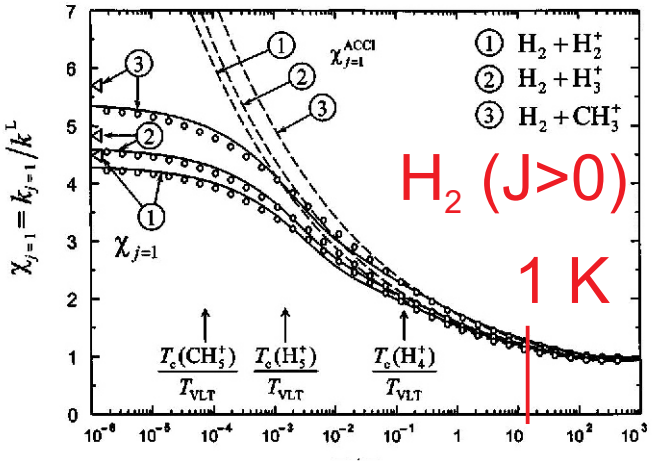
(Received 14 December 2004; accepted 21 February 2005; published online 10 May 2005)



Para H_2 (J=0): Pure Langevin

Ortho H_2 (J=1): Ion-quadrupole interaction

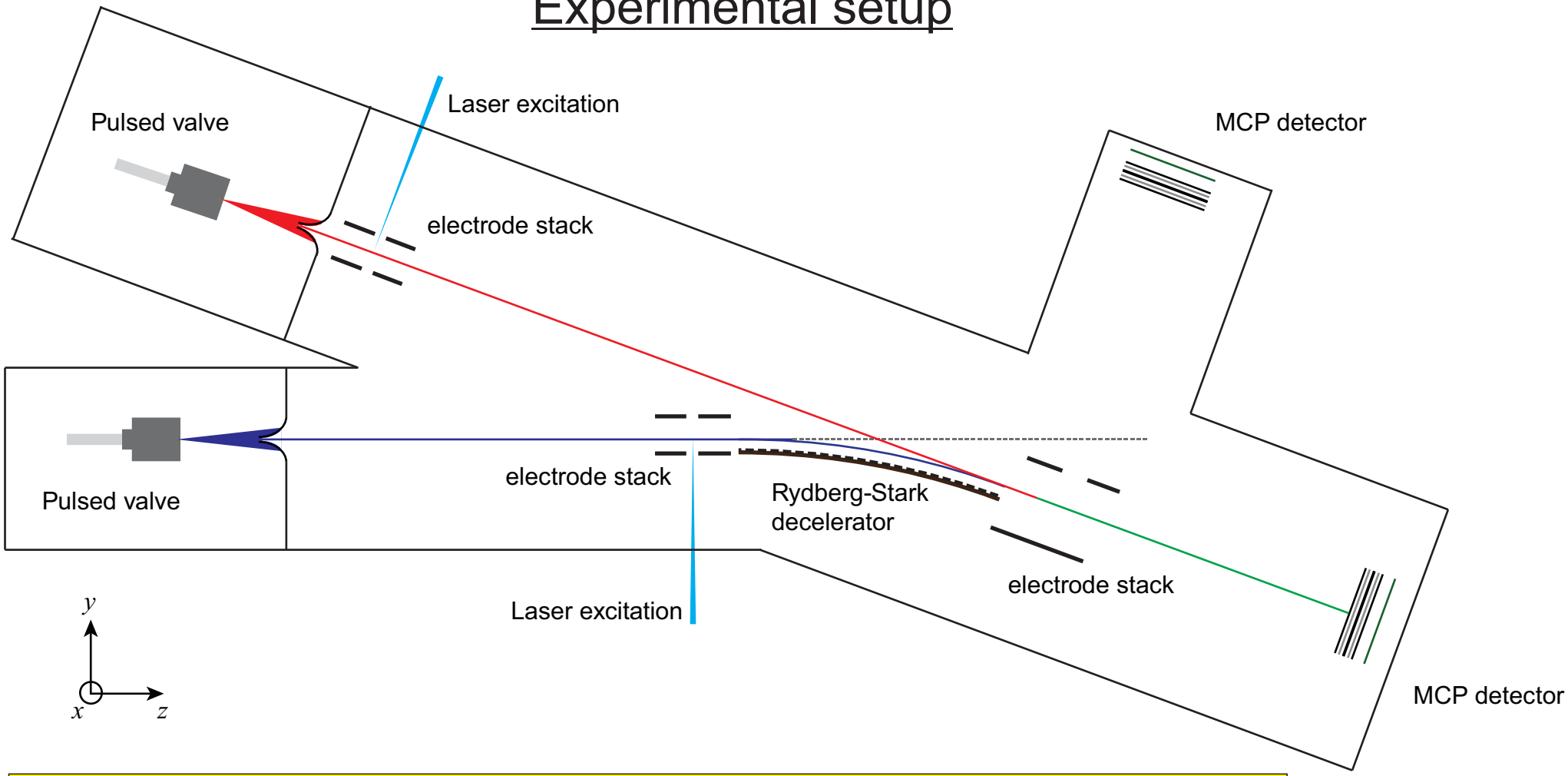




$$T_{VLT} = \frac{\hbar^4}{k_B \mu^2 q^2 \alpha}$$

Theory advanced; no experiments

Experimental setup



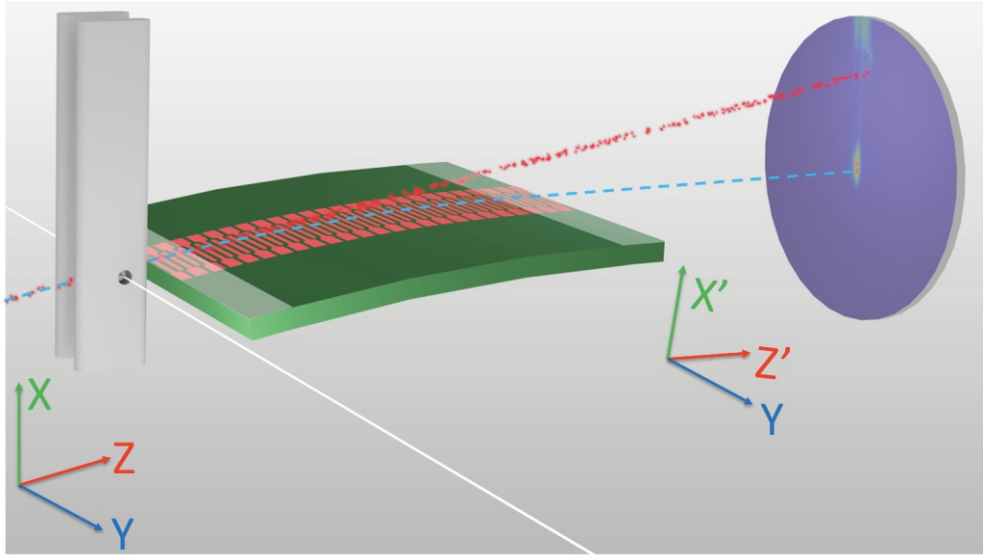
Formation of H_3^+ at
6 meV collision energy
$v(H_2)$ = 2400 m/s
$v(H_2^*)$ = 1600 m/s

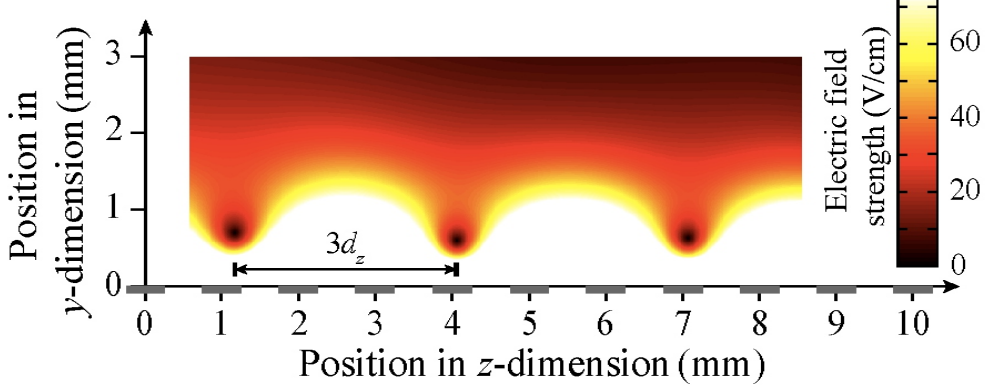
Formation of H_3^+ at
0.1 meV collision energy
$v(H_2)$ = 1540 m/s
$v(H_2^*)$ =1600 m/s

Allmendinger et al. ChemPhysChem 17, 3596 (2016)

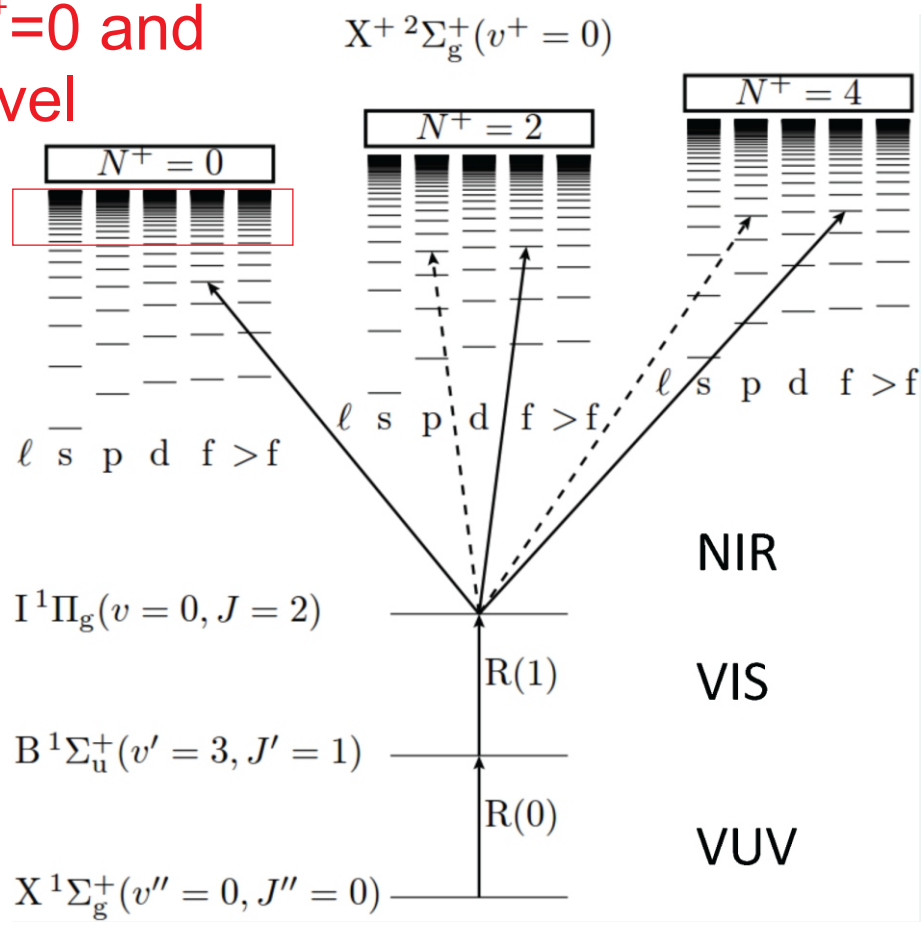
Rydberg-Stark decelerator and deflector

Moving traps for low-field-seeking Stark states
Dipole:





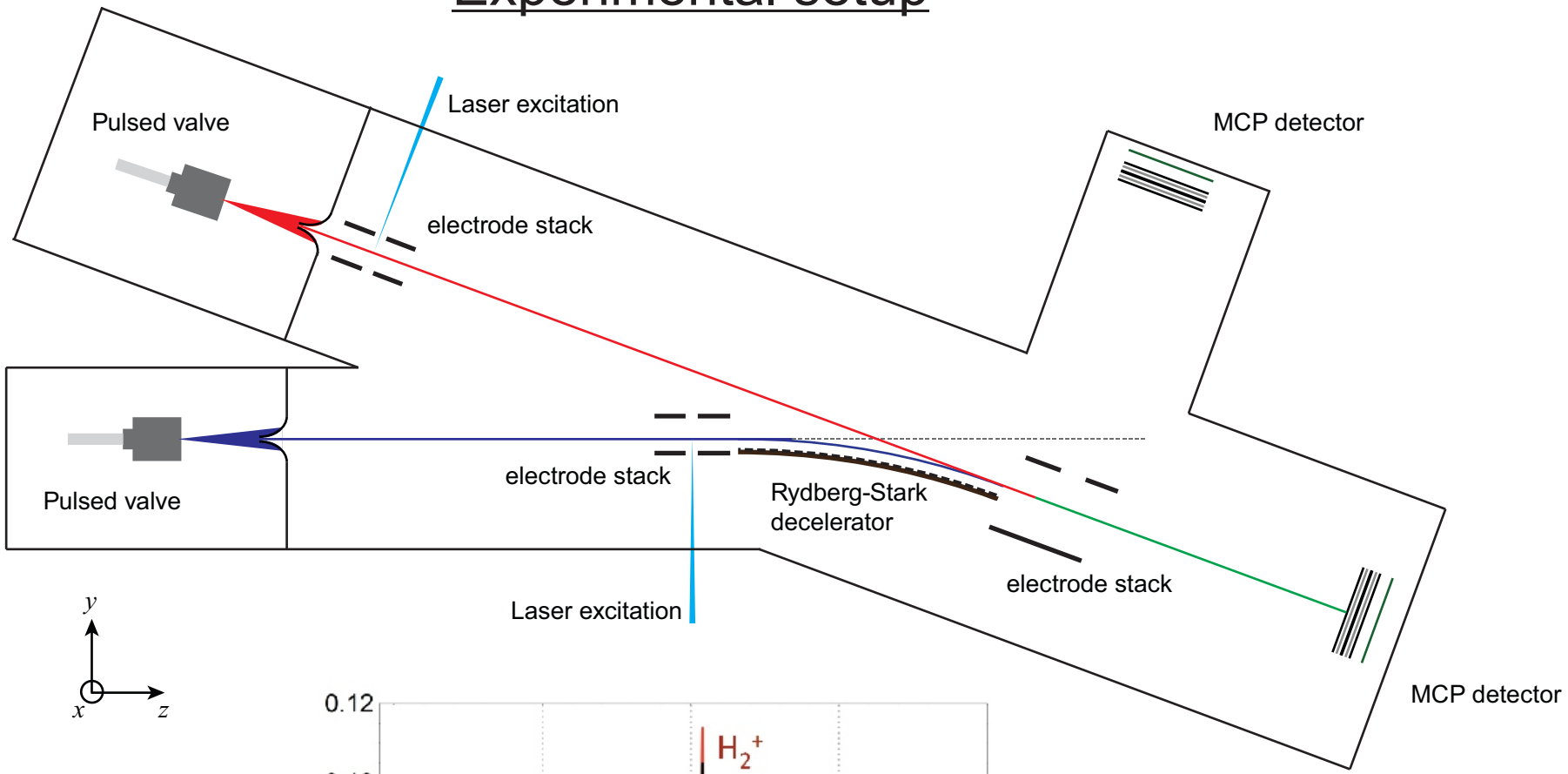
H_2^+ in v^+=0 and
N^+=0 level

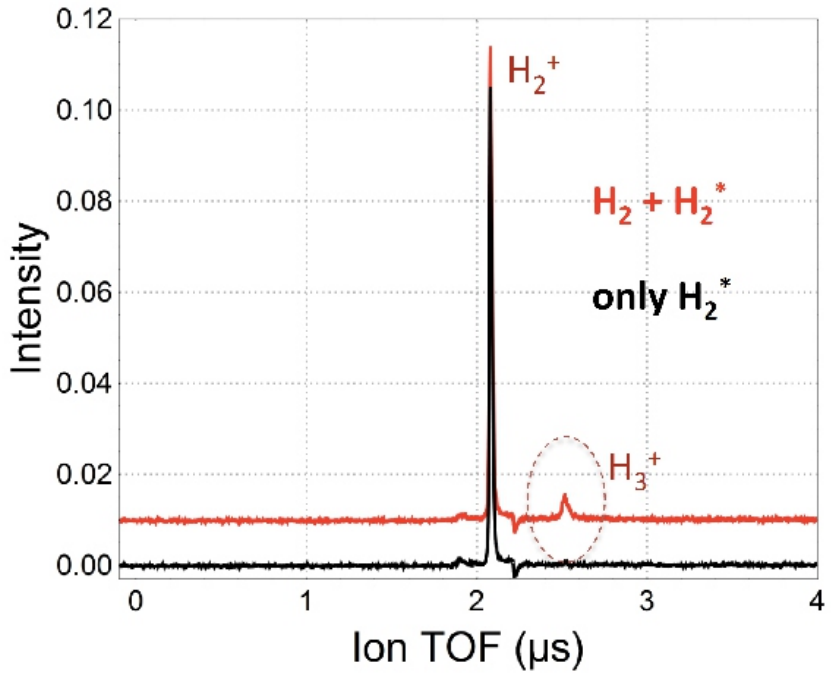


50 electrodes on a printed circuit board
Length: 50 mm
Amplitude of applied potentials: 40-80 V
Deflection angle: 10°

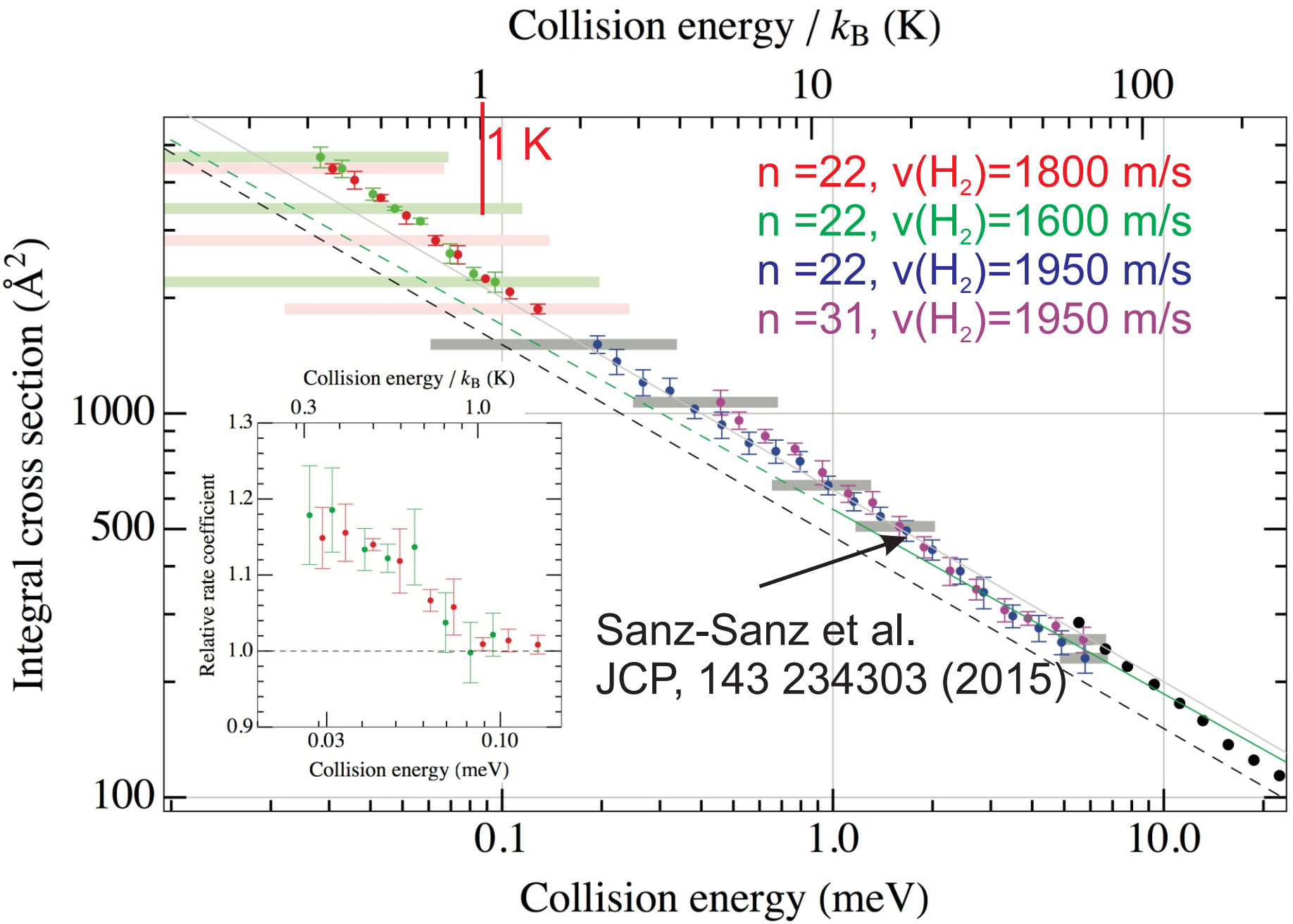
Deceleration: Hogan et al., Phys. Rev. Lett. **108**, 063008 (2012)
Deflection: Allmendinger et al., Phys. Rev. A **90**, 043403 (2014)
For polar molecules: Meek, Conrad and Meijer, Science **324**, 1699 (2009)

Experimental setup



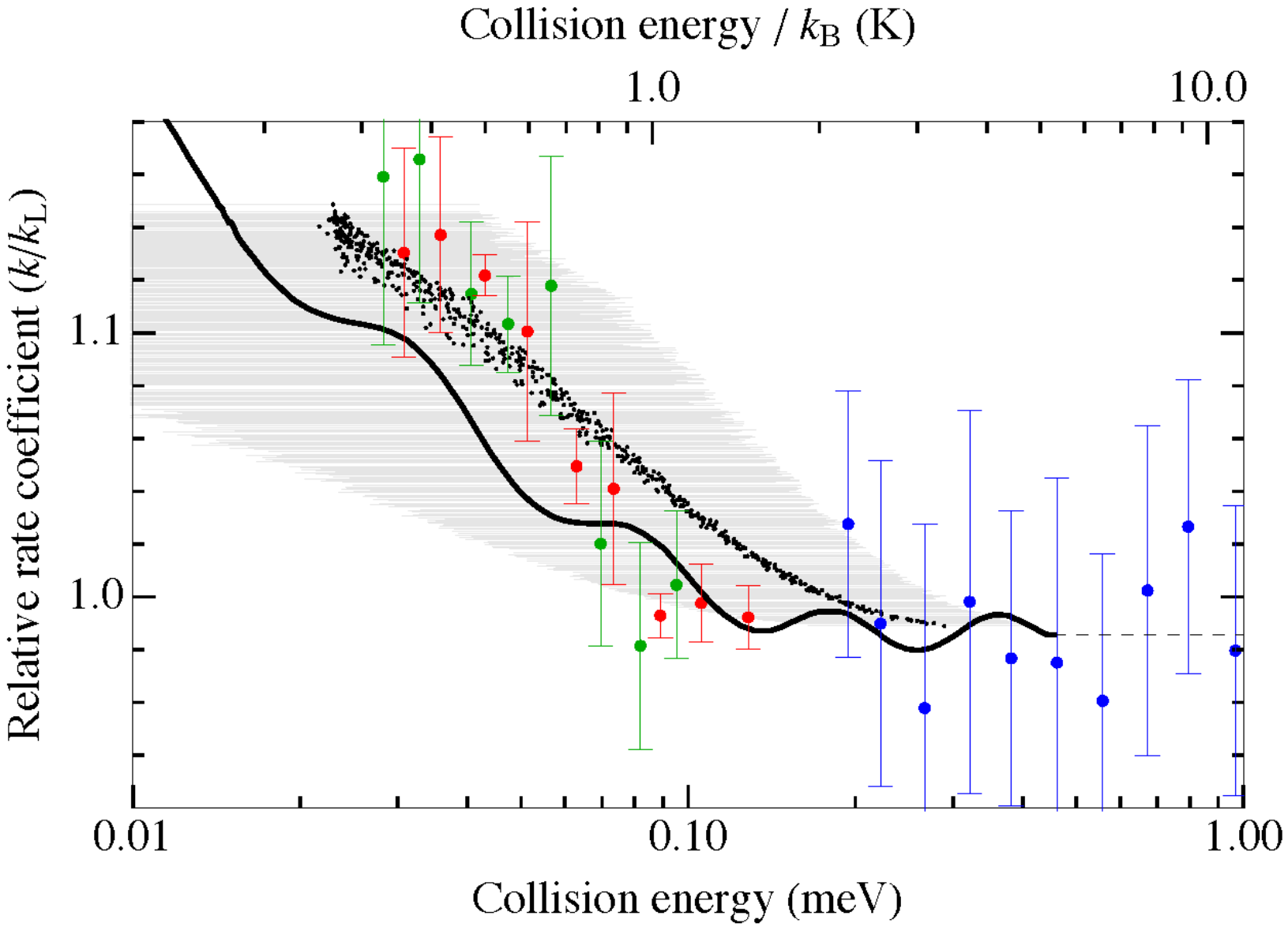


Relative integral cross section as function of collision energy



Allmendinger *et al.*, ChemPhysChem **17**, 3596 (2016), J. Chem. Phys. **145**, 244316 (2016)

Low-T behavior, comparison of experiment and theory



Allmendinger et al., J. Chem. Phys. **145**, 244316 (2016)

Dashevskaya, Litvin, Nikitin and Troe, J. Chem. Phys. **145**, 244315 (2016)

Conclusions (part I):

Equivalence of an ion-molecule reaction and a reaction within a Rydberg-electron orbit

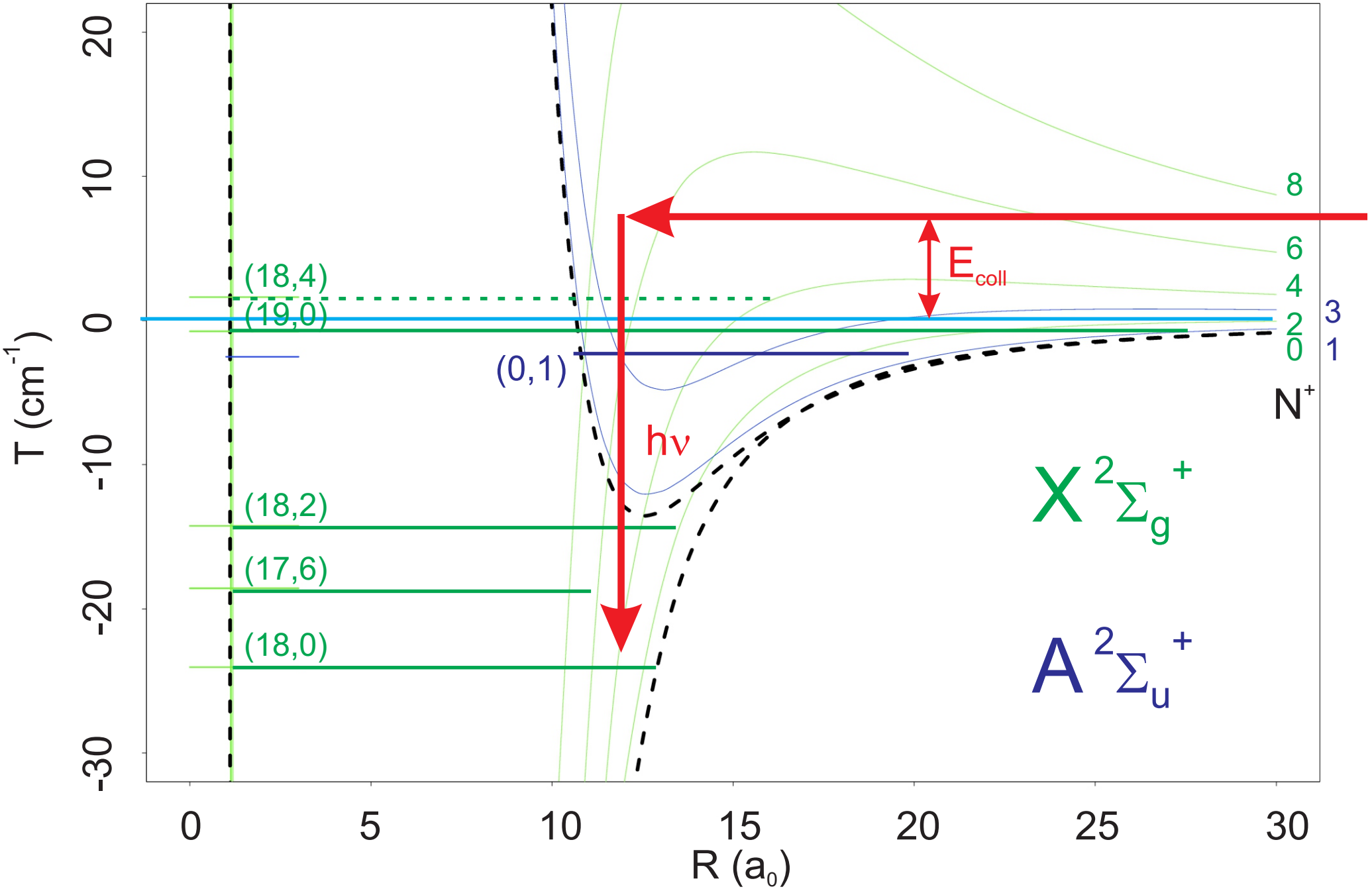
Measurements of relative cross sections from k_B ▪ 60 K down to below k_B ▪ 1 K

No resonances («Langevin» capture)

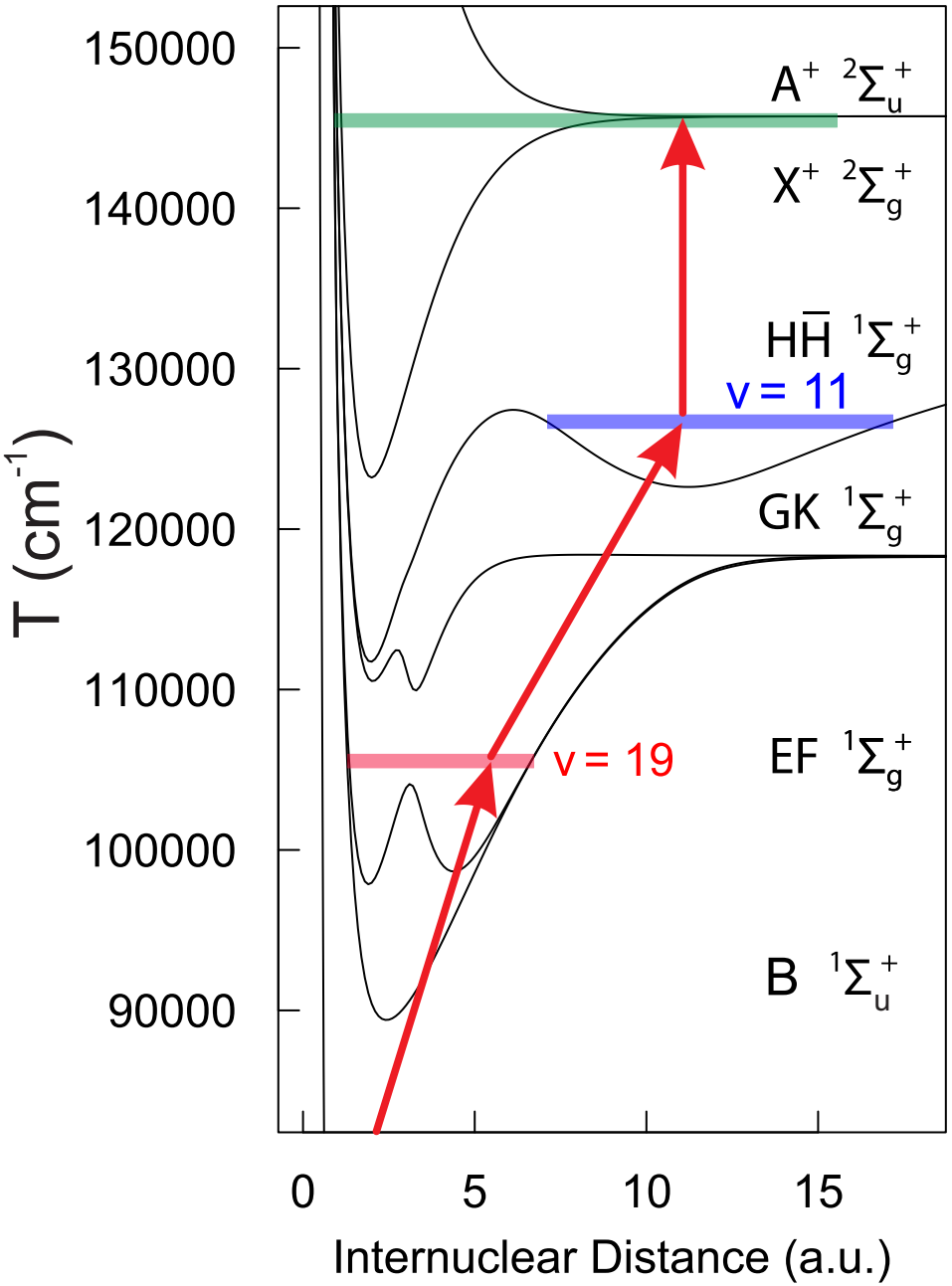
Observation of a deviation from classical Langevin capture below 1 K

Good agreement with predictions of Dashevskaya et al. (JCP **145**, 244315 (2016)). Deviation from 75% contribution of ortho H_2 (J=1, with quadrupole) to the neutral beam.

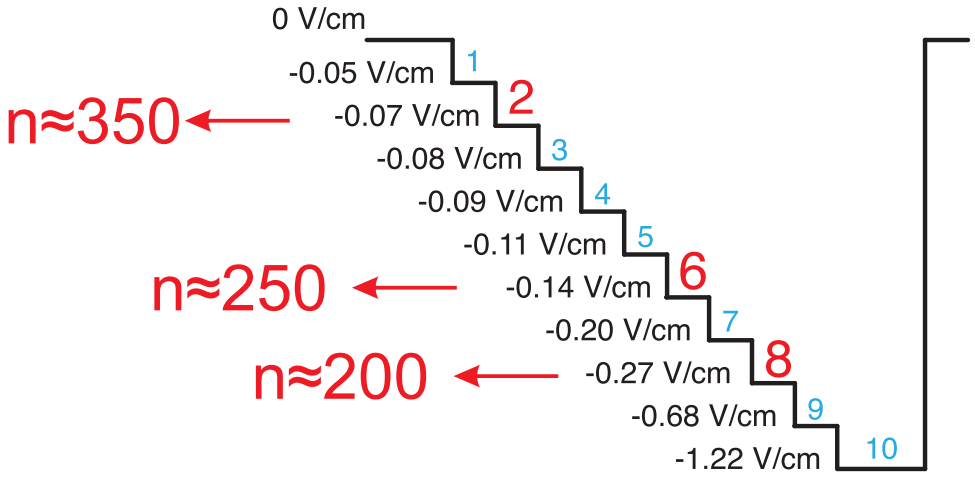
Part II. H_2^+ association / dissociation ($H_2^+ \longleftrightarrow H^+ + H$)



PFI-ZEKE photoelectron spectroscopy of H_2 near the dissociative ionization threshold

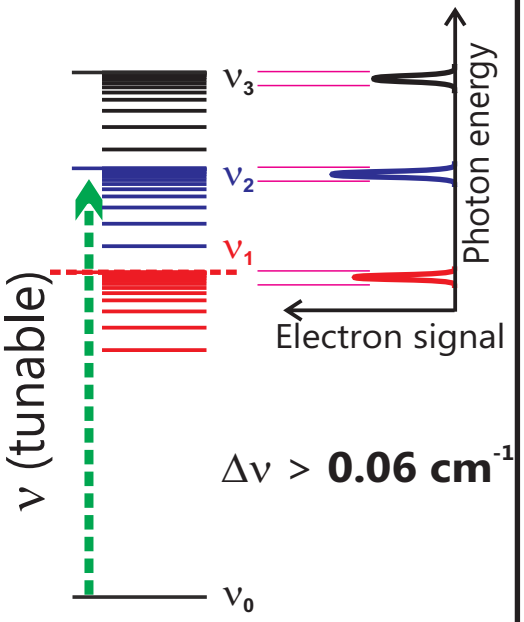


Field-ionization pulse sequence



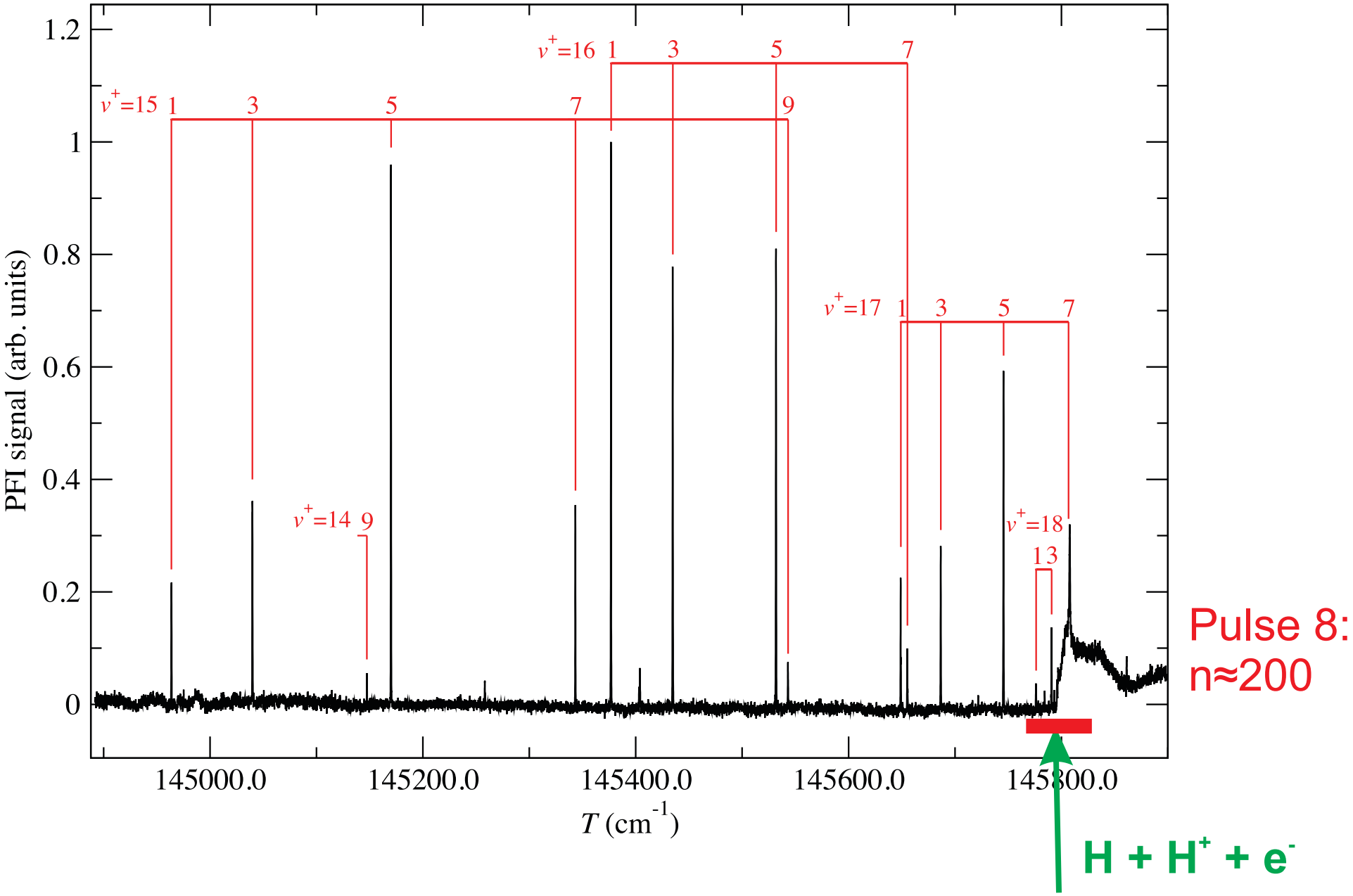
Pulsed-field ionisation

PFI-ZEKE photoelectron spectroscopy



Reiser et al. CPL **152**, 119 (1988)

The photoelectron spectrum of ortho H_2 from $H\bar{H}$(v=11,N=3)



First complete calculation of shape resonances in H_2^+

Dissociation energies
Resonance widths

v^+	N^+		BO	AD	NA	NArel	NArelrad	Exp
18	4	$E_{\rm res}$	-1.991	-1.879	-1.876	-1.879	-1.878	-1.84(4)
		Γ	0.259 (0.002)	0.206 (0.002)	0.193 (0.001)	0.194 (0.001)		0.21(7)
17	7	$E_{\rm res}$	-11.699	-11.210	-11.094	-11.104	-11.104	-11.08(6)
		Γ	0.232 (0.001)	0.177 (0.001)	0.162 (0.001)	0.163 (0.001)		0.56(8)

all values in cm^{-1}

NA corrections with R-dependent reduced masses
(see R. Jaquet, M. Kohma, Mol. Phys., 2018)

Bound levels of A $^2\Sigma_u^+$ state:
v=0, N=0,1,2
v=1, N=0

Beyer and Merkt, Phys. Rev. Lett. **116**, 093001 (2016)
J. Mol. Spectrosc. **330**, 147 (2016)
J. Phys. B **50**, 154005 (2017)

Half-collision approach to $H^+ + H$ radiative association

1) Measurement of the positions and widths of the shape resonances of H_2^+ and D_2^+

2) Full *ab initio* quantum-chemical calculations of the resonance positions and widths

3) Validation of the calculations

4) --> scattering phase shifts for individual partial waves η_N in X^+ and A^+ states

5) --> elastic-scattering cross sections

$$\sigma_{\mathrm{el}} = \frac{4\pi}{k^2} \sum_{N^+=0}^{\infty} \left[\omega_{X^+}^{\pm} \sin^2(\eta_{N^+}^{X^+}) + \omega_{A^+}^{\pm} \sin^2(\eta_{N^+}^{A^+}) \right]$$

6) Determination of radiative-association cross sections and rate constants

$$\sigma(f, v'', N''; i, k, N') = \frac{4\pi^2\alpha^3}{3\mu E} (E_{\mathrm{coll}} - E_{v'',N''})^3 S_{N'',N'} \left| M_{N'',N'}^{fi} \right|^2$$

Einstein A coeff.

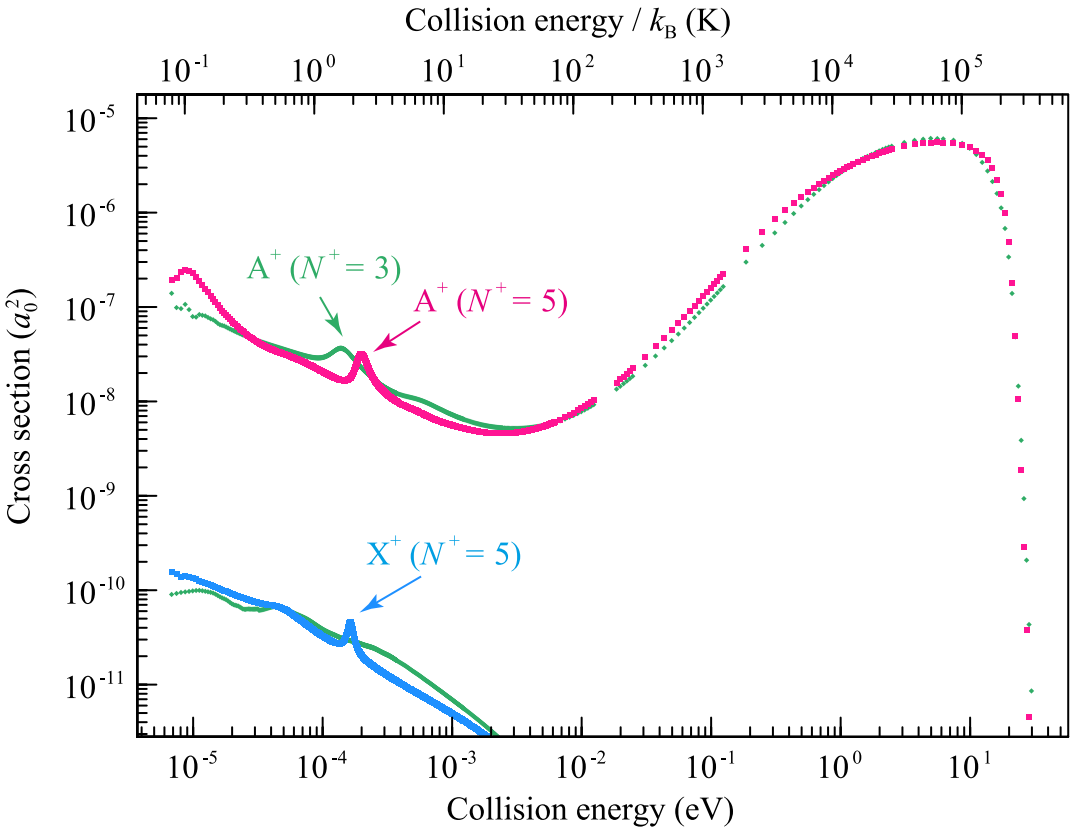
$$\sigma_i(E_{\mathrm{coll}}) = \sum_{N'} \sum_{v''} \sum_{N''} p_{N',i} \sigma(f, v'', N''; i, k, N')$$

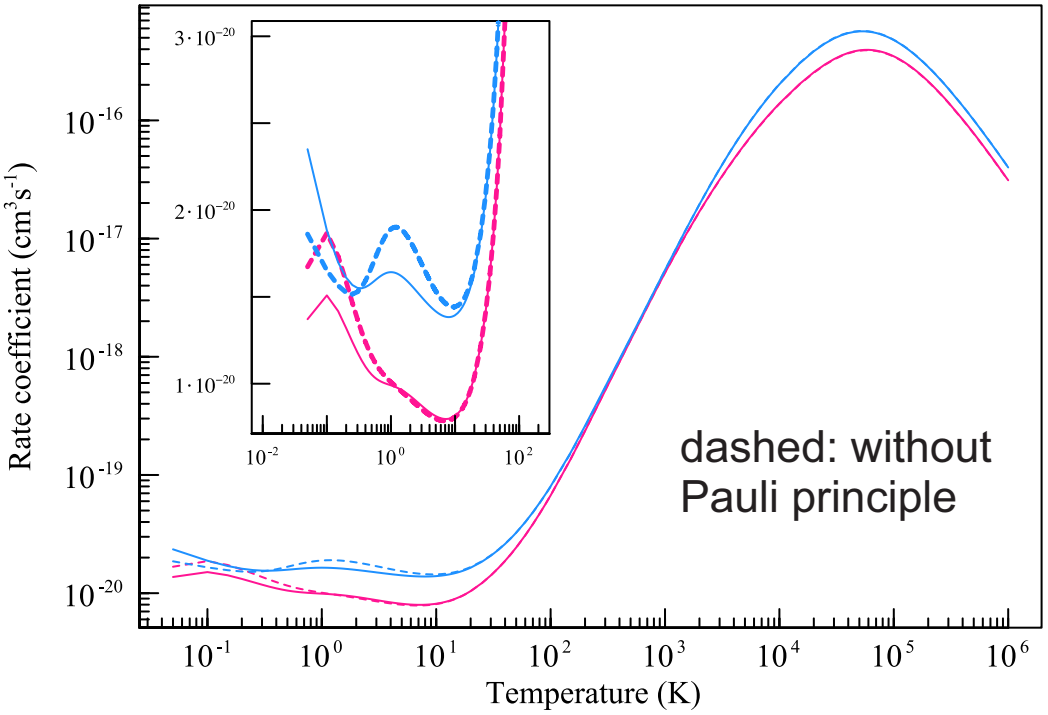
Sum over possible transitions

$$\alpha(T) = \left(\frac{8}{\pi\mu}\right)^{1/2} \left(\frac{1}{k_{\mathrm{B}}T}\right)^{3/2} \int_0^{\infty} \mathrm{d}\, E_{\mathrm{coll}} \sigma(E_{\mathrm{coll}}) E_{\mathrm{coll}} \exp\left[-E_{\mathrm{coll}}/k_{\mathrm{B}}T\right]$$

Thermal average

Radiative association cross sections and thermal rate coefficients





D_2^+ A$^+$ state

D_2^+ X$^+$ state

H_2^+ X$^+$ and A$^+$ state

TABLE III. Probabilities p_i for approaching in a given partial wave N' in the vibrational continuum of state $i = \{X^+, A^+\}$ for H_2^+ and D_2^+.

N'	state	H_2^+	D_2^+
even	X^+	1/4	2/3
	A^+	3/4	1/3
odd	X^+	3/4	1/3
	A^+	1/4	2/3

M. Beyer, FM, Phys. Rev. X **8**, 031085 (2018)

Conclusions

Molecular hydrogen is a model system to study fundamental aspects of molecules and of chemical reactivity

Rydberg atoms and molecules are ions disguised as neutral molecules

Observation and full calculation of shape resonances of H_2^+
Full quantum treatment of $H + H^+$ association reaction.

Study of the reaction $H_2^+ + H_2 \longrightarrow H_3^+ + H$ at low collision energies

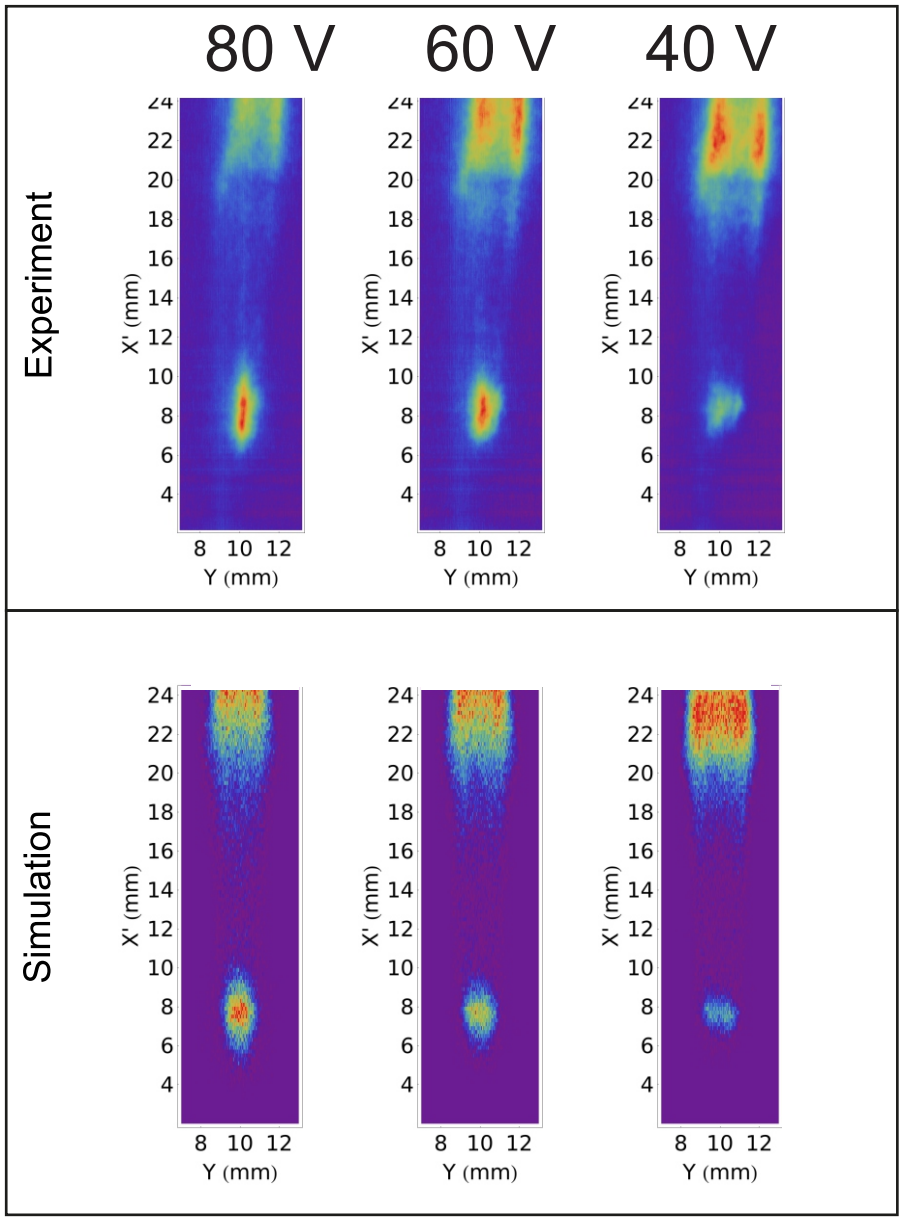
Observation of onset of quantum capture below 1 K

The two reactions exhibit opposite behaviors of low-temperature quantum reactivity (Langevin vs. resonance dominated)

Arolla, March 2018

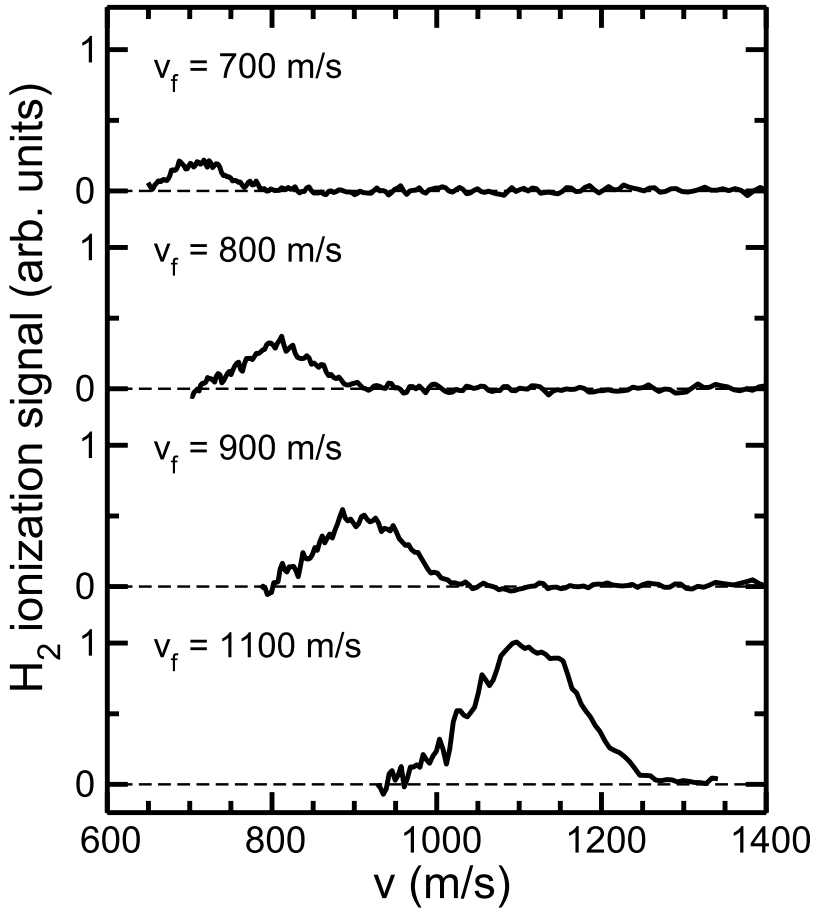
Financial support: Swiss National Science Foundation, ERC advanced Grant Program

Deflection



300 mK 150 mK 75 mK

Deceleration



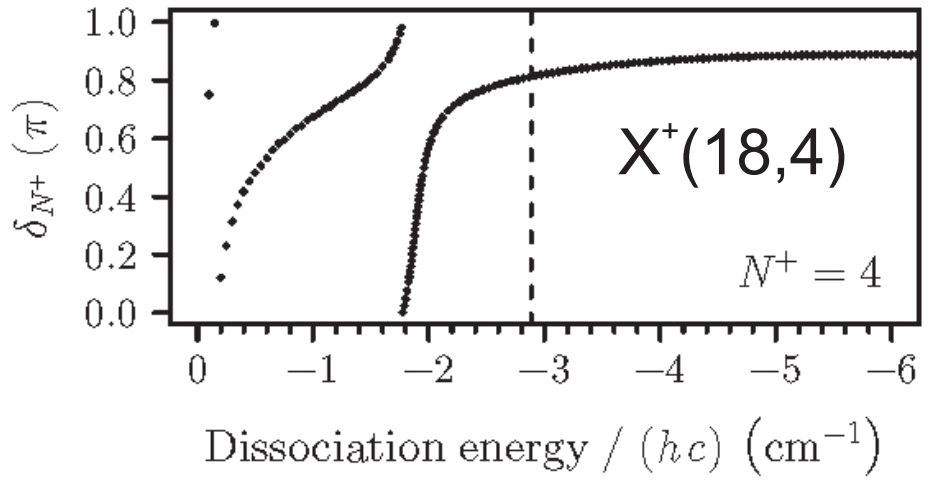
H_2, n=30 Rydberg-Stark states

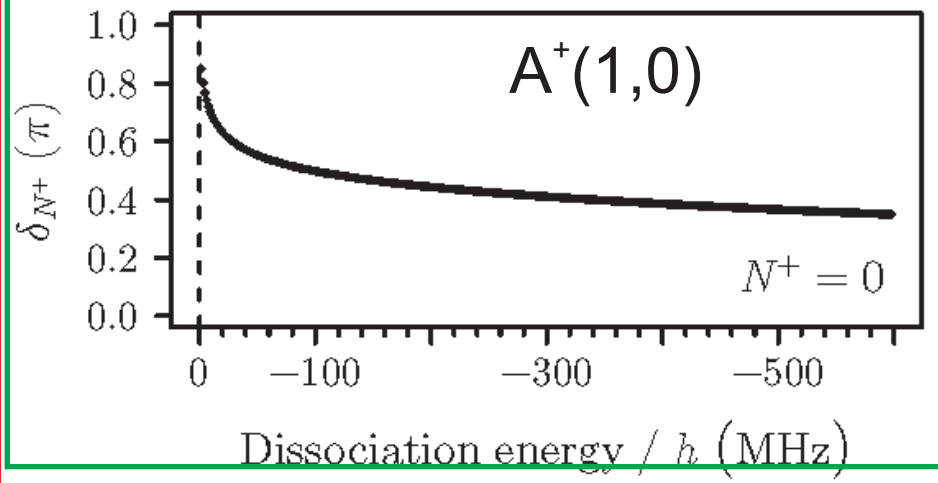
Initial velocity: 1280 m/s

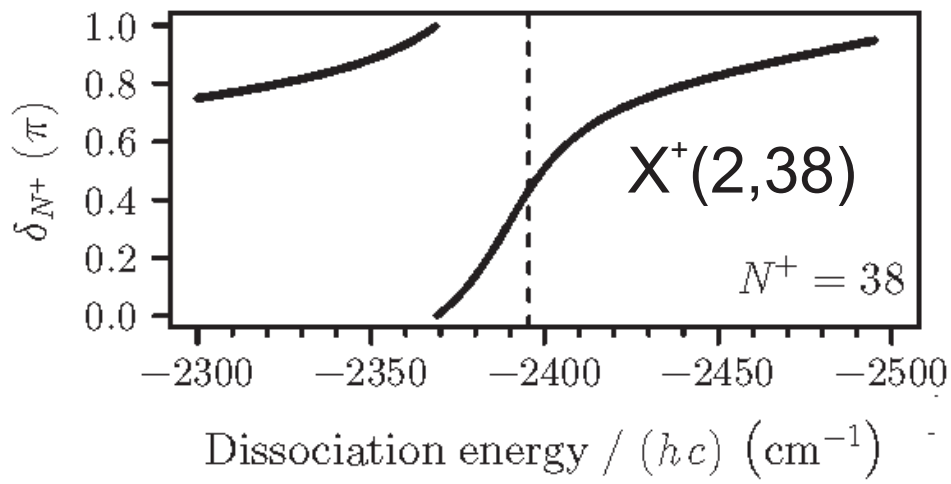
Allmendinger et al. Phys. Rev. A **90**, 043403 (2014)

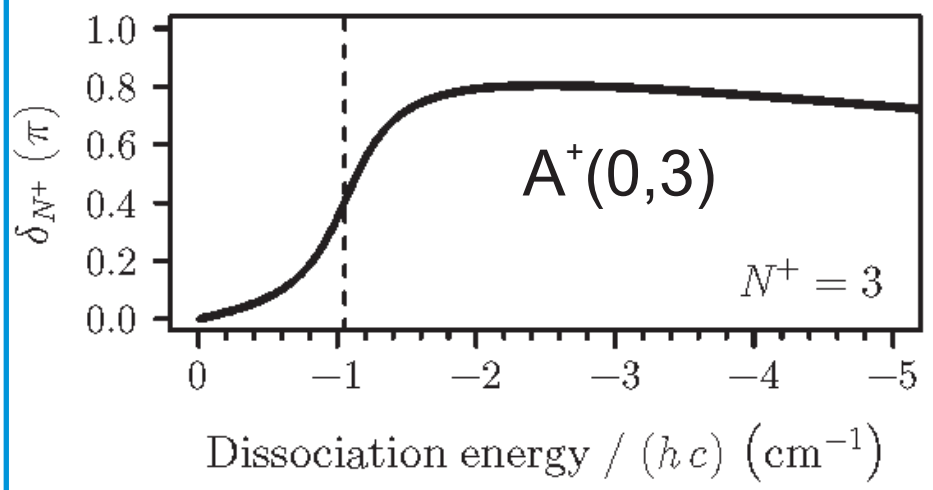
Scattering phase shift $\delta(N^+)$ modulo π as a function of the fragments kinetic energy

s-wave scattering









Orbiting resonances

$\Delta\delta(N^+) = \pi$ Shape resonances

$\Delta\delta(N^+) < \pi$

Half-collision approach to $H^+ + H$ radiative association

1) Measurement of the positions and widths of the shape resonances of H_2^+ and D_2^+

2) Full *ab initio* quantum-chemical calculations of the resonance positions and widths

3) Validation of the calculations

4) --> scattering phase shifts for individual partial waves η_N in X^+ and A^+ states

5) --> elastic-scattering cross sections

$$\sigma_{\mathrm{el}} = \frac{4\pi}{k^2} \sum_{N^+=0}^{\infty} \left[\omega_{X^+}^{\pm} \sin^2(\eta_{N^+}^{X^+}) + \omega_{A^+}^{\pm} \sin^2(\eta_{N^+}^{A^+}) \right]$$

6) Determination of radiative-association cross sections and rate constants

$$\sigma(f, v'', N''; i, k, N') = \frac{4\pi^2\alpha^3}{3\mu E} (E_{\mathrm{coll}} - E_{v'',N''})^3 S_{N'',N'} \left| M_{N'',N'}^{fi} \right|^2$$

Einstein A coeff.

$$\sigma_i(E_{\mathrm{coll}}) = \sum_{N'} \sum_{v''} \sum_{N''} p_{N',i} \sigma(f, v'', N''; i, k, N')$$

Sum over possible transitions

$$\alpha(T) = \left(\frac{8}{\pi\mu}\right)^{1/2} \left(\frac{1}{k_{\mathrm{B}}T}\right)^{3/2} \int_0^{\infty} \mathrm{d}\, E_{\mathrm{coll}} \sigma(E_{\mathrm{coll}}) E_{\mathrm{coll}} \exp\left[-E_{\mathrm{coll}}/k_{\mathrm{B}}T\right]$$

Thermal average