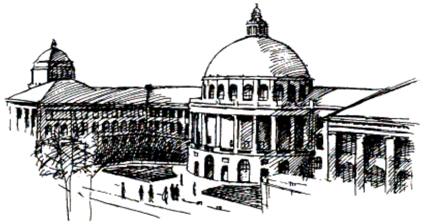
Precision spectroscopy in molecular hydrogen and helium

PS, Kolloquium, 24 September 2020



F. Merkt, Physical Chemistry Laboratory, ETH Zurich

Introduction

I.a*: Precision measurement of the dissociation energy (D_0) of H_2

I.b*: Constraint on a global energy shift between para- and ortho-H_2

II*: He_2 and and He_2^+ and pressure standards

Conclusions

* Work by Maximilian Beyer and Nicolas Hölsch, in collaboration with
the groups of Wim Ubachs, VU Amsterdam and Christian Jungen, CNRS, Orsay

* Work by Paul Jansen and Luca Semeria

Financial support:

- ❖ Swiss National Science Foundation
- ❖ ERC advanced-grant program

LaserLaB Amsterdam

VU Vrije Universiteit Amsterdam

Cunfeng Cheng
Joël Hussels
Edcel Salumbides
Wim Ubachs

Robert Altmann
Kjeld Eikema

Christian Jungen
(CNRS, Orsay)

Precision measurements at low energies

Determination of fundamental constants and particle properties, test of standard model of particle physics at low energies

a) Particle physics: precision measurements on neutrons, positronium, muonic hydrogen, antihydrogen, ... (in CH: PSI, CERN)

b) Atomic physics: precision measurements in H-atom, He$^+$ ion, He atom, ...

- electronic transitions
- fine structure
- hyperfine structure

$\xleftrightarrow{\text{Theory}}$

- fundamental constants $(R,\alpha,\ldots)$
- nuclear/particle properties
- fundamental interactions

c) Molecular physics: precision spectroscopy in molecules

- electronic transitions
- fine, hyperfine structures
- rotational, vivrational structure
- permanent dipole moments

$\xleftrightarrow{\text{Theory}}$

- molecule structure
- reactivity, dynamics
- nuclear properties
- fundamental constants

The H atom and muonic hydrogen

Electronic structure (Lyman, Balmer, ...): QM

Fine structure: relativistic QM, QED

Lamb shift: QED

Nuclear-size effects, hyperfine structure

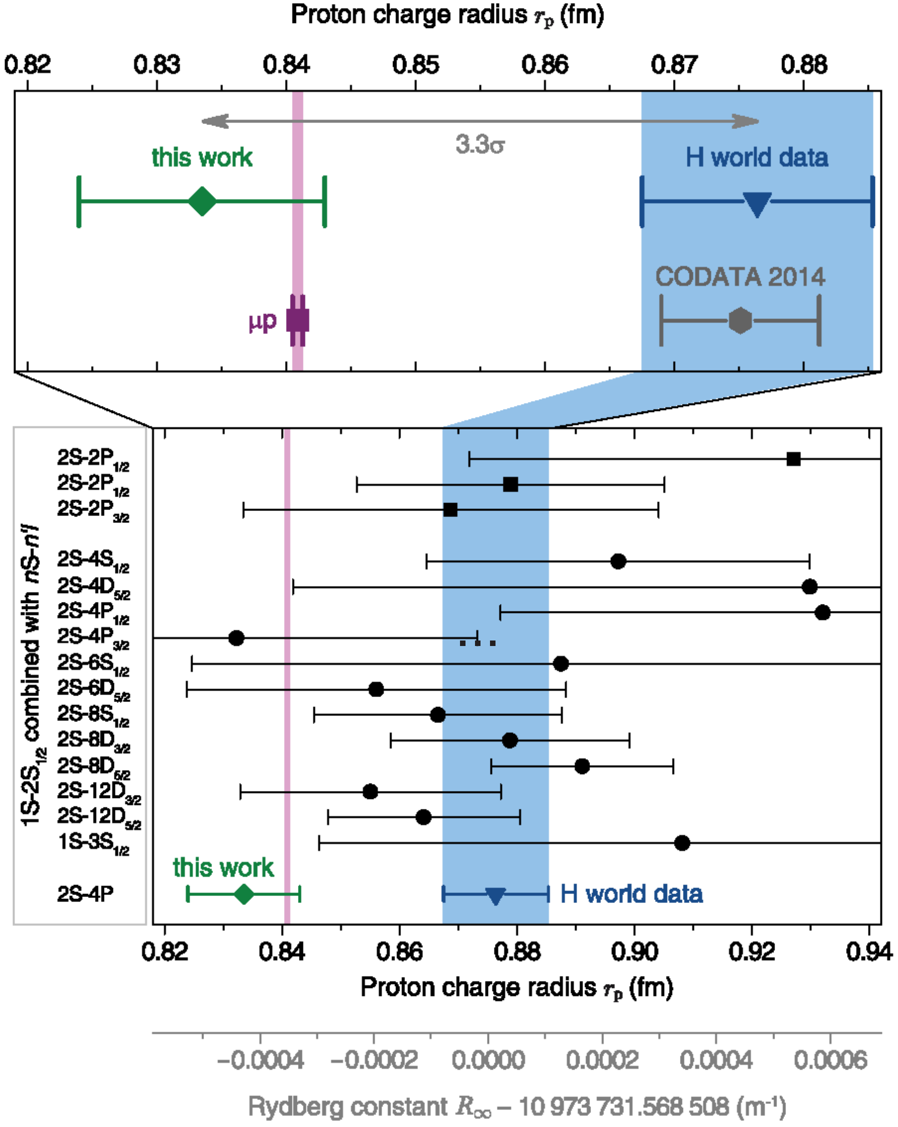
Experimental H spectra (world data) ⟷ *R*, α, m_p/m_e, magnetic moments, proton radius, ...

RESEARCH ARTICLE

ATOMIC PHYSICS

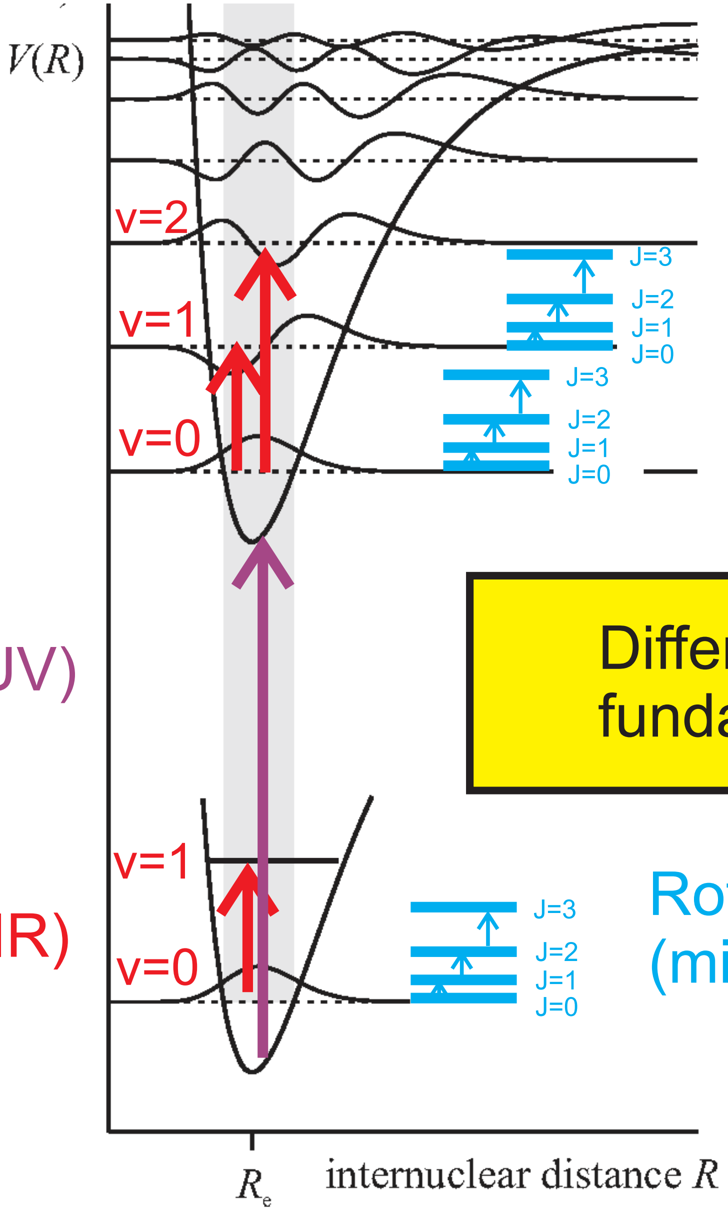
The Rydberg constant and proton size from atomic hydrogen

Axel Beyer,[1] Lothar Maisenbacher,[1*] Arthur Matveev,[1] Randolf Pohl,[1†] Ksenia Khabarova,[2,3] Alexey Grinin,[1] Tobias Lamour,[1] Dylan C. Yost,[1‡] Theodor W. Hänsch,[1,4] Nikolai Kolachevsky,[2,3] Thomas Udem[1,4]



R. Pohl, A. Antognini et al., Nature, **466**,213 (2010)
Beyer et al., Science, **358**, 79 (2017)

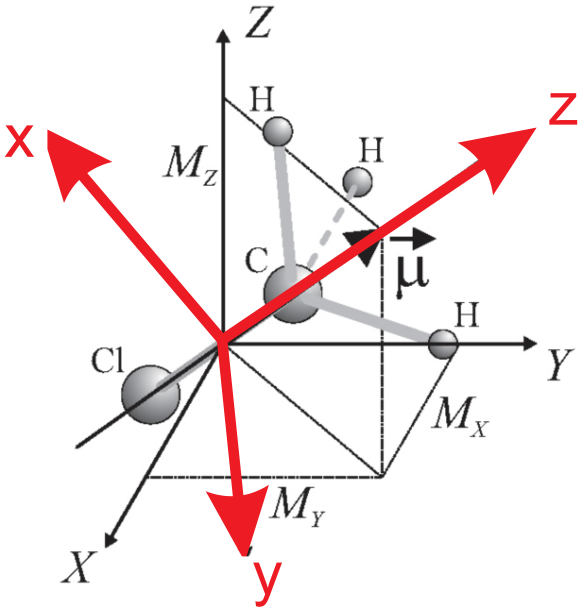
Molecular spectra have electronic, vibrational, rotational, spin-orbit and hyperfine structures



Electronic transitions (UV)

Vibrational transitions (IR)

Rotational tansitions (microwaves- mm-waves)



Different dependence on fundamental constants

Handbook of high-resolution spectroscopy, Eds. M. Quack and FM, Wiley, 2011

Atoms and Molecules for precision measurments in the gas phase

Atoms	Molecules
About 115 elements (2900 nuclides)	Uncountable number of molecules
Only few isotopes per element	Many iso(topo)mers per chemical formula
Simple energy-level structure	Complex energy-level structure
Excited states usually accessible and well-known	Excited states usually not easily accessible or poorly known
Can be laser cooled (at least some)	Cannot in general be laser cooled
Overseeable set of general rules and principles	Each molecules requires special treatment
Space-fixed axis system suffices	Internal axis sytem and degrees of freedom (orientation, alignment, ...)

What are the relevant molecules in physics?
What are the relevant temperature ranges?

Molecular gases near quantum degeneracy
- phase diagrams
- quantum simulation
- many-body long-range interactions

$T < 1$ mK

RbCs,...
LiSr, ...
$BaCl^{(+)}$, ...
Rydberg molecules

Metrology
- fundamental constants and their possible evolution
- fundamental physics with molecules (EDM, parity violation in chiral molecules, QED in molecules)

$T < 1$ K

CH_3OH, HD^+
YbF, PbO,
H_2, CHClFBr,..

Chemical reactions at low temperature
- Astrophysics
- Quantum aspects of chemical reactivity

$T < 10$ K

H_3, H_3^+, H_2^-, HeH,
$CH^{(+/-)}$, $OH^{(+/-)}$, $NH^{(+/-)}$,
CH_3, CH_5^+,CH_3OH,...

Engineering of quantum systems, hybrid quantum systems

$T < 1$ K

C_{60},
H_2,
C-nanotubes,...

Few-electron atoms and molecules

1-electron: H, He^+, Li^{2+},..., ps, ... H_2^+, ...
2-electron: H^-, He, Li^+, ... H_2, HeH^+, He_2^{2+},H_3^+ ...
3-electron: Li, Be+, ... HeH, He_2^+, ...

Highly accurate first-principles calculations are possible

Comparison with experimental results has the potential of:

in case of agreement
- reducing uncertainties of fundamental constants (R, α)
- reducing uncertainties of particle properties (nuclear masses, electric and magnetic moments, charge radii, ...)

in case of disagreement
- discovering new effects

On the accuracy of ab initio calculations in small molecular systems

Two-electron molecules (100 MHz) - Situation in 1995

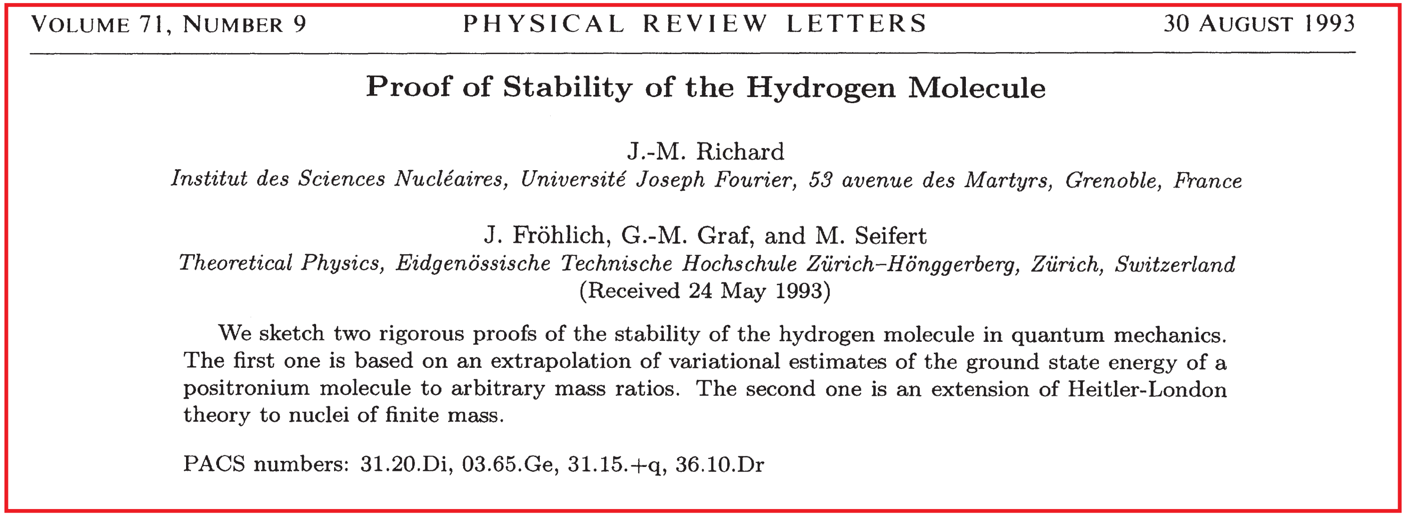
All values in cm^{-1}

From: Wolniewicz, JCP 99, 1851 (1993); JCP 103, 1792 (1995)

	Born-Oppenheimer energy with zero point energy	Adiabatic correction	Nonadiabatic correction	Nonrelativistic energy
H_2	36112.593	+5.7711	+0.4339	36118.798
HD	36401.9332	+4.2509	+0.3267	36406.511
D_2	36746.1623	+2.7725	+0.1563	36749.091

Relativistic and QED corrections

	α^2	α^3	α^4	α^5	Total energy
H_2	-0.533	-0.196			36118.069
HD	-0.531	-0.197	?		36405.783
D_2	-0.529	-0.199			36748.363



VOLUME 71, NUMBER 9 PHYSICAL REVIEW LETTERS 30 AUGUST 1993

Proof of Stability of the Hydrogen Molecule

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(Received 24 May 1993)

We sketch two rigorous proofs of the stability of the hydrogen molecule in quantum mechanics. The first one is based on an extrapolation of variational estimates of the ground state energy of a positronium molecule to arbitrary mass ratios. The second one is an extension of Heitler-London theory to nuclei of finite mass.

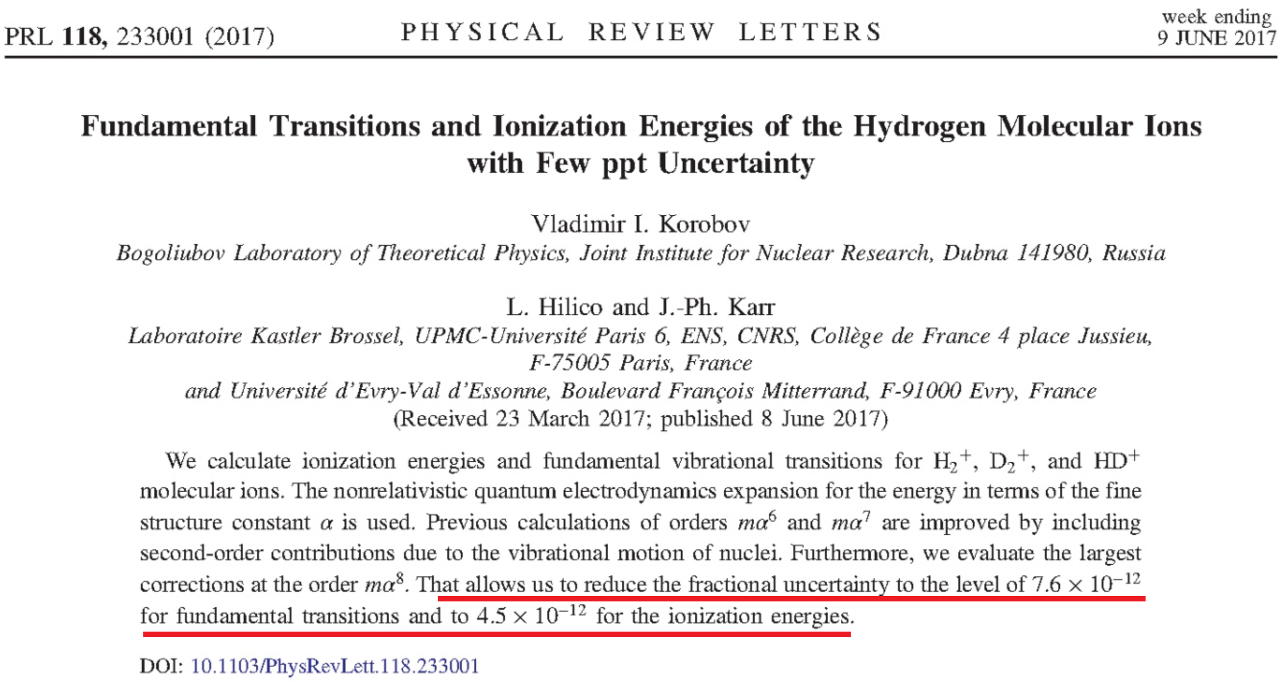
PACS numbers: 31.20.Di, 03.65.Ge, 31.15.+q, 36.10.Dr

H. Primas and U. Müller-Herold
Elementare Quantenchemie
(Teubner Verlag, Stuttgart, 1984)

Accuracy of ab initio calculations for one-electron molecules

H_2^+, HD^+, D_2^+

(2-3 kHz)



PRL **118,** 233001 (2017) PHYSICAL REVIEW LETTERS week ending 9 JUNE 2017

Fundamental Transitions and Ionization Energies of the Hydrogen Molecular Ions with Few ppt Uncertainty

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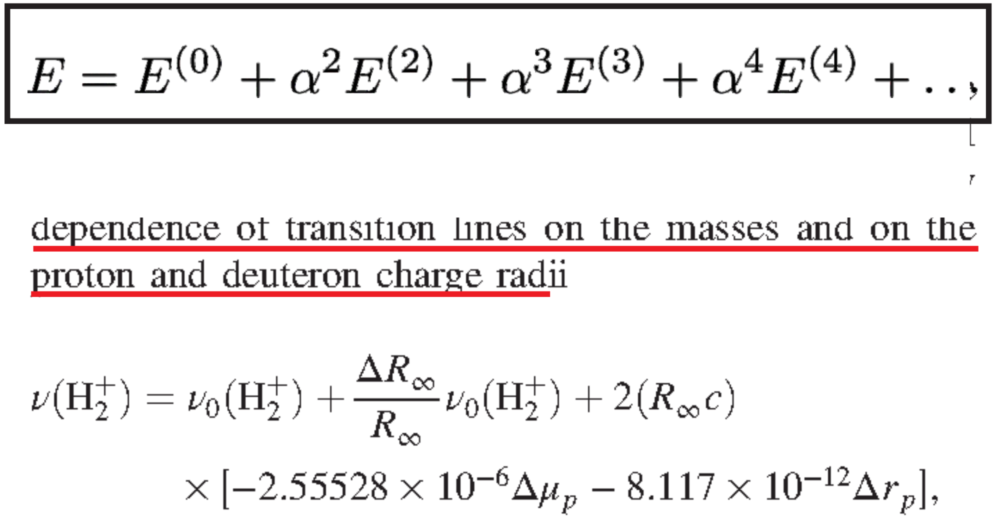
(Received 23 March 2017; published 8 June 2017)

We calculate ionization energies and fundamental vibrational transitions for H_2^+, D_2^+, and HD^+ molecular ions. The nonrelativistic quantum electrodynamics expansion for the energy in terms of the fine structure constant α is used. Previous calculations of orders $m\alpha^6$ and $m\alpha^7$ are improved by including second-order contributions due to the vibrational motion of nuclei. Furthermore, we evaluate the largest corrections at the order $m\alpha^8$. That allows us to reduce the fractional uncertainty to the level of 7.6×10^{-12} for fundamental transitions and to 4.5×10^{-12} for the ionization energies.

DOI: 10.1103/PhysRevLett.118.233001



$$E = E^{(0)} + \alpha^2 E^{(2)} + \alpha^3 E^{(3)} + \alpha^4 E^{(4)} + \ldots,$$

dependence of transition lines on the masses and on the proton and deuteron charge radii

$$\nu(\mathrm{H}_2^+) = \nu_0(\mathrm{H}_2^+) + \frac{\Delta R_\infty}{R_\infty}\nu_0(\mathrm{H}_2^+) + 2(R_\infty c) \times [-2.55528 \times 10^{-6}\Delta\mu_p - 8.117 \times 10^{-12}\Delta r_p],$$

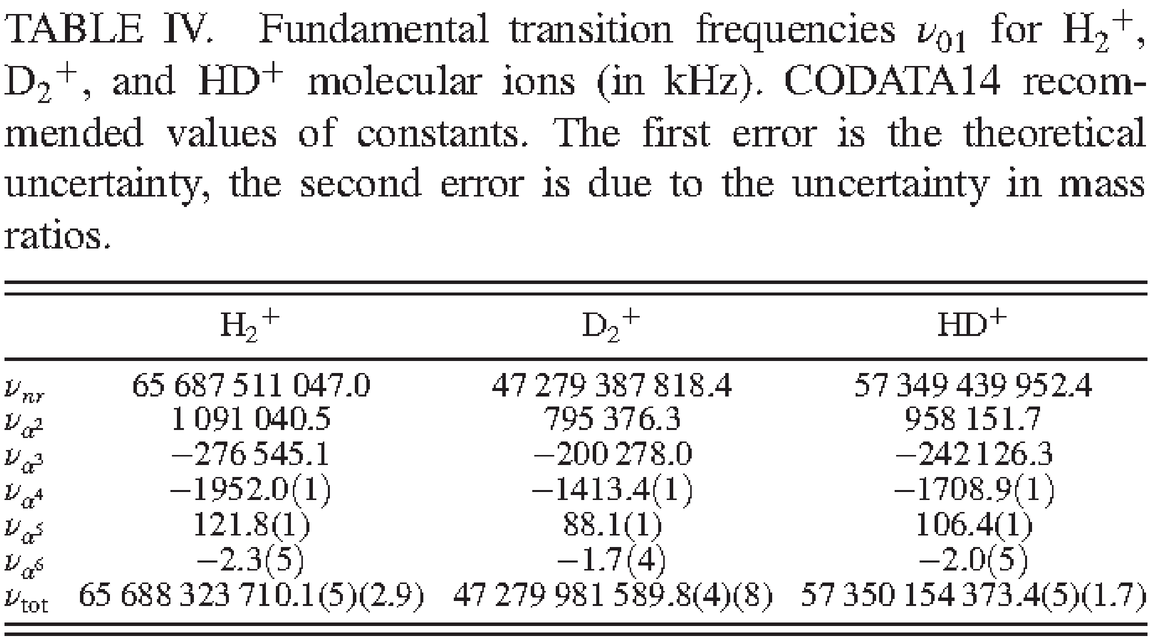


TABLE IV. Fundamental transition frequencies ν_{01} for H_2^+, D_2^+, and HD^+ molecular ions (in kHz). CODATA14 recommended values of constants. The first error is the theoretical uncertainty, the second error is due to the uncertainty in mass ratios.

	H_2^+	D_2^+	HD^+
ν_{nr}	65 687 511 047.0	47 279 387 818.4	57 349 439 952.4
ν_{α^2}	1 091 040.5	795 376.3	958 151.7
ν_{α^3}	−276 545.1	−200 278.0	−242 126.3
ν_{α^4}	−1952.0(1)	−1413.4(1)	−1708.9(1)
ν_{α^5}	121.8(1)	88.1(1)	106.4(1)
ν_{α^6}	−2.3(5)	−1.7(4)	−2.0(5)
ν_{tot}	65 688 323 710.1(5)(2.9)	47 279 981 589.8(4)(8)	57 350 154 373.4(5)(1.7)

Limitations: Proton charge radius, fundamental constants, theory?

PHYSICAL REVIEW LETTERS **122,** 103003 (2019)

Nonadiabatic QED Correction to the Dissociation Energy of the Hydrogen Molecule

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(Received 7 December 2018; published 15 March 2019)

The quantum electrodynamic correction to the energy of the hydrogen molecule has been evaluated without expansion in the electron-proton mass ratio. The obtained results significantly improve the accuracy of theoretical predictions reaching the level of 1 MHz for the dissociation energy, in very good agreement with the parallel measurement [Hölsch *et al.*, Phys. Rev. Lett. **122**, 103002 (2019)]. Molecular hydrogen has thus become a cornerstone of ultraprecise quantum chemistry, which opens perspectives for determination of fundamental physical constants from its spectra.

H_2, HD, ...
(about 1 MHz)

[33] is independent of the Rydberg constant, but depends on the proton charge radius through

$$\frac{E(\mathrm{H}_2,\mathrm{IP})}{E(\mathrm{H},2S\text{-}1S)} = 1.512 - 1.4\cdot 10^{-10}\, r_p^2/\mathrm{fm}^2\,. \qquad (27)$$

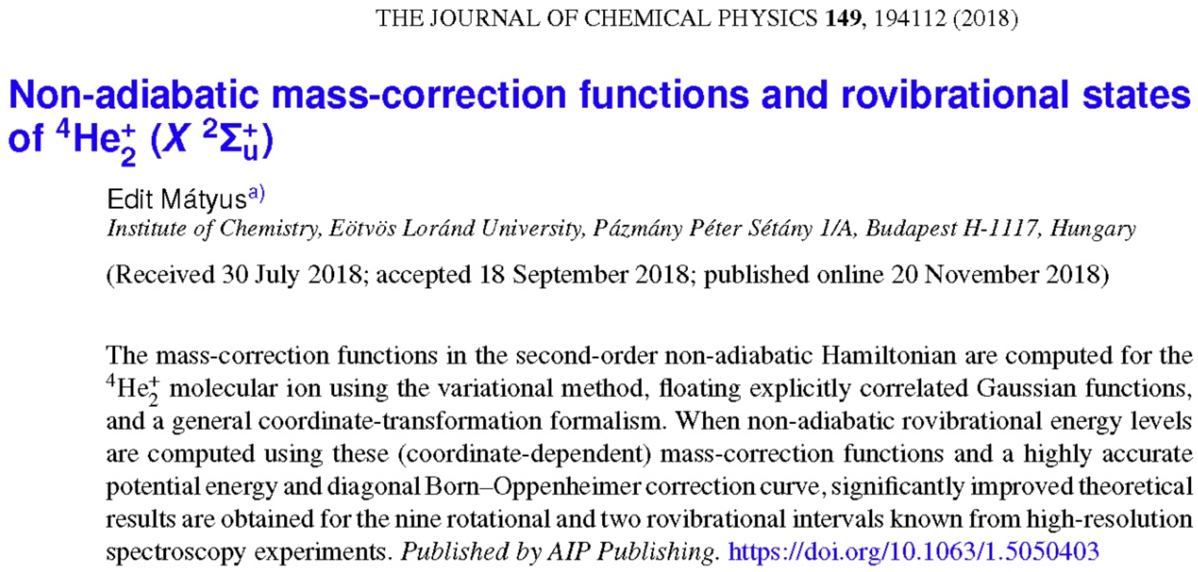
TABLE III. Theoretical predictions for the dissociation energy budget for the ground level of H_2. $E^{(6)}_{\mathrm{sec}}$ is a second order correction due to relativistic BO potential; E_{FS} is the finite nuclear size correction with $r_p = 0.84087(39)$ [28] . All the energy entries are given in cm^{-1}.

Contribution	$D_{0,0}$	$D_{0,1}$	$(0,1) \to (0,0)$	Remarks & References
$E^{(2)}$	36 118.797 746 10(3)	36 000.312 485 66(2)	118.485 260 44(4)	naJC; [10], [29]
$E^{(4)}$	−0.531 215 6(5)	−0.533 799 2(5)	0.002 583 55(2)	naECG; [12], this work
$E^{(5)}$	−0.194 910 43(15)	−0.193 887 7(11)	−0.001 022 7(11)	naECG; [14], this work
$E^{(6)}$	−0.002 067(6)	−0.002 058(6)	−0.000 008 9	BO; [17]
$E^{(6)}_{\mathrm{sec}}$	0.000 009 2	0.000 009 1	0.000 000 1	BO; this work
$E^{(7)}$	0.000 101(25)	0.000 101(25)	0.000 000 5(1)	BO; [14, 17]
$E^{(4)}_{\mathrm{FS}}$	−0.000 031	−0.000 031	−0.000 000 2	BO; [14, 17]
Total	36 118.069 632(26)	35 999.582 820(26)	118.486 812 7(11)	

Three-electron molecules

He_2^+

(about 10 MHz)



THE JOURNAL OF CHEMICAL PHYSICS **149**, 194112 (2018)

Non-adiabatic mass-correction functions and rovibrational states of $^4He_2^+$ ($X\ ^2\Sigma_u^+$)

Edit Mátyus[a)]
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(Received 30 July 2018; accepted 18 September 2018; published online 20 November 2018)

The mass-correction functions in the second-order non-adiabatic Hamiltonian are computed for the $^4He_2^+$ molecular ion using the variational method, floating explicitly correlated Gaussian functions, and a general coordinate-transformation formalism. When non-adiabatic rovibrational energy levels are computed using these (coordinate-dependent) mass-correction functions and a highly accurate potential energy and diagonal Born–Oppenheimer correction curve, significantly improved theoretical results are obtained for the nine rotational and two rovibrational intervals known from high-resolution spectroscopy experiments. *Published by AIP Publishing.* https://doi.org/10.1063/1.5050403

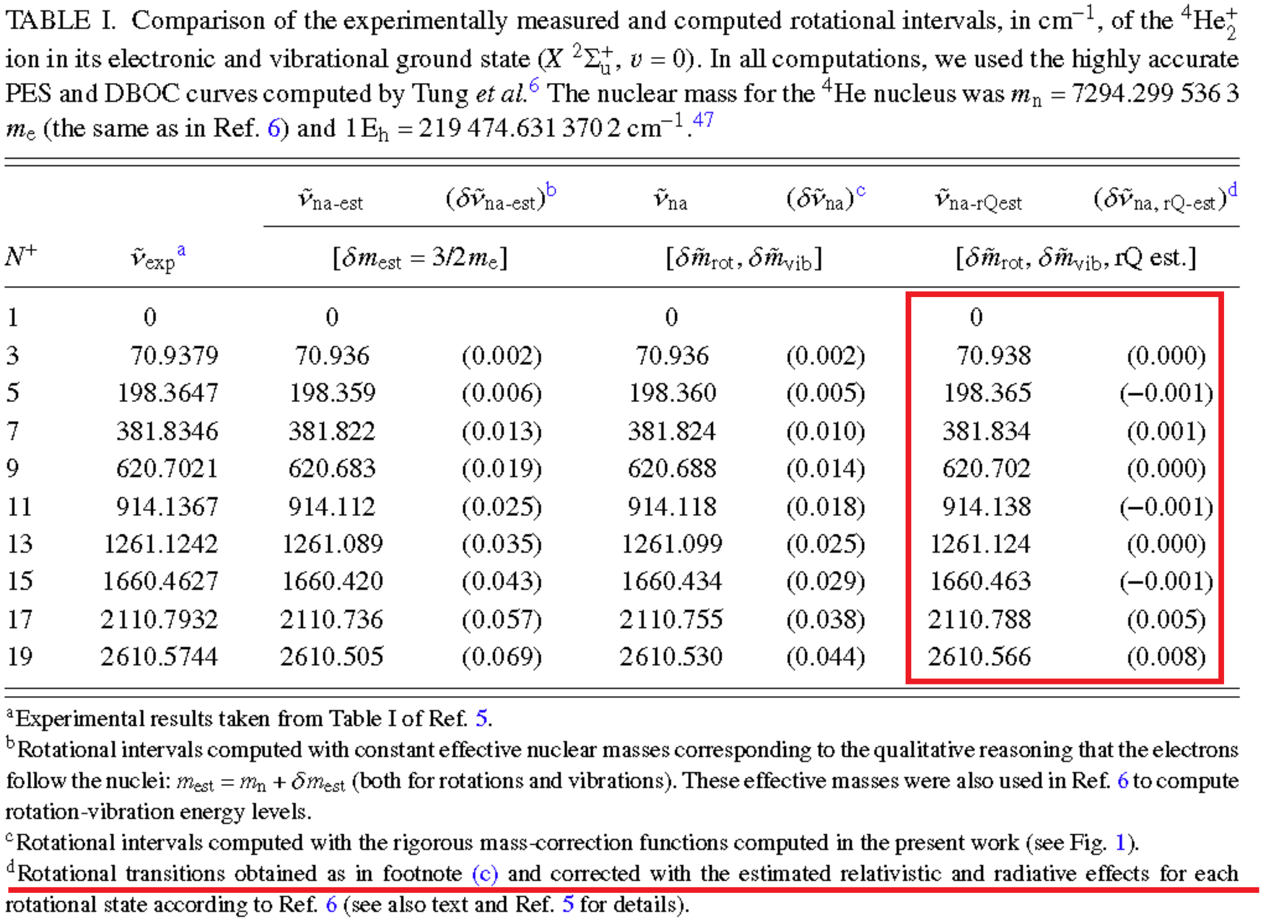


TABLE I. Comparison of the experimentally measured and computed rotational intervals, in cm^{-1}, of the $^4He_2^+$ ion in its electronic and vibrational ground state ($X\ ^2\Sigma_u^+$, $v = 0$). In all computations, we used the highly accurate PES and DBOC curves computed by Tung *et al.*[6] The nuclear mass for the ^4He nucleus was $m_n = 7294.299\,536\,3\ m_e$ (the same as in Ref. 6) and $1\ E_h = 219\,474.631\,370\,2\ cm^{-1}$.[47]

		$\tilde{\nu}_{\text{na-est}}$	$(\delta\tilde{\nu}_{\text{na-est}})$[b]	$\tilde{\nu}_{\text{na}}$	$(\delta\tilde{\nu}_{\text{na}})$[c]	$\tilde{\nu}_{\text{na-rQest}}$	$(\delta\tilde{\nu}_{\text{na, rQ-est}})$[d]
N^+	$\tilde{\nu}_{\text{exp}}$[a]	$[\delta m_{\text{est}} = 3/2 m_e]$		$[\delta\tilde{m}_{\text{rot}}, \delta\tilde{m}_{\text{vib}}]$		$[\delta\tilde{m}_{\text{rot}}, \delta\tilde{m}_{\text{vib}}, \text{rQ est.}]$	
1	0	0		0		0	
3	70.9379	70.936	(0.002)	70.936	(0.002)	70.938	(0.000)
5	198.3647	198.359	(0.006)	198.360	(0.005)	198.365	(−0.001)
7	381.8346	381.822	(0.013)	381.824	(0.010)	381.834	(0.001)
9	620.7021	620.683	(0.019)	620.688	(0.014)	620.702	(0.000)
11	914.1367	914.112	(0.025)	914.118	(0.018)	914.138	(−0.001)
13	1261.1242	1261.089	(0.035)	1261.099	(0.025)	1261.124	(0.000)
15	1660.4627	1660.420	(0.043)	1660.434	(0.029)	1660.463	(−0.001)
17	2110.7932	2110.736	(0.057)	2110.755	(0.038)	2110.788	(0.005)
19	2610.5744	2610.505	(0.069)	2610.530	(0.044)	2610.566	(0.008)

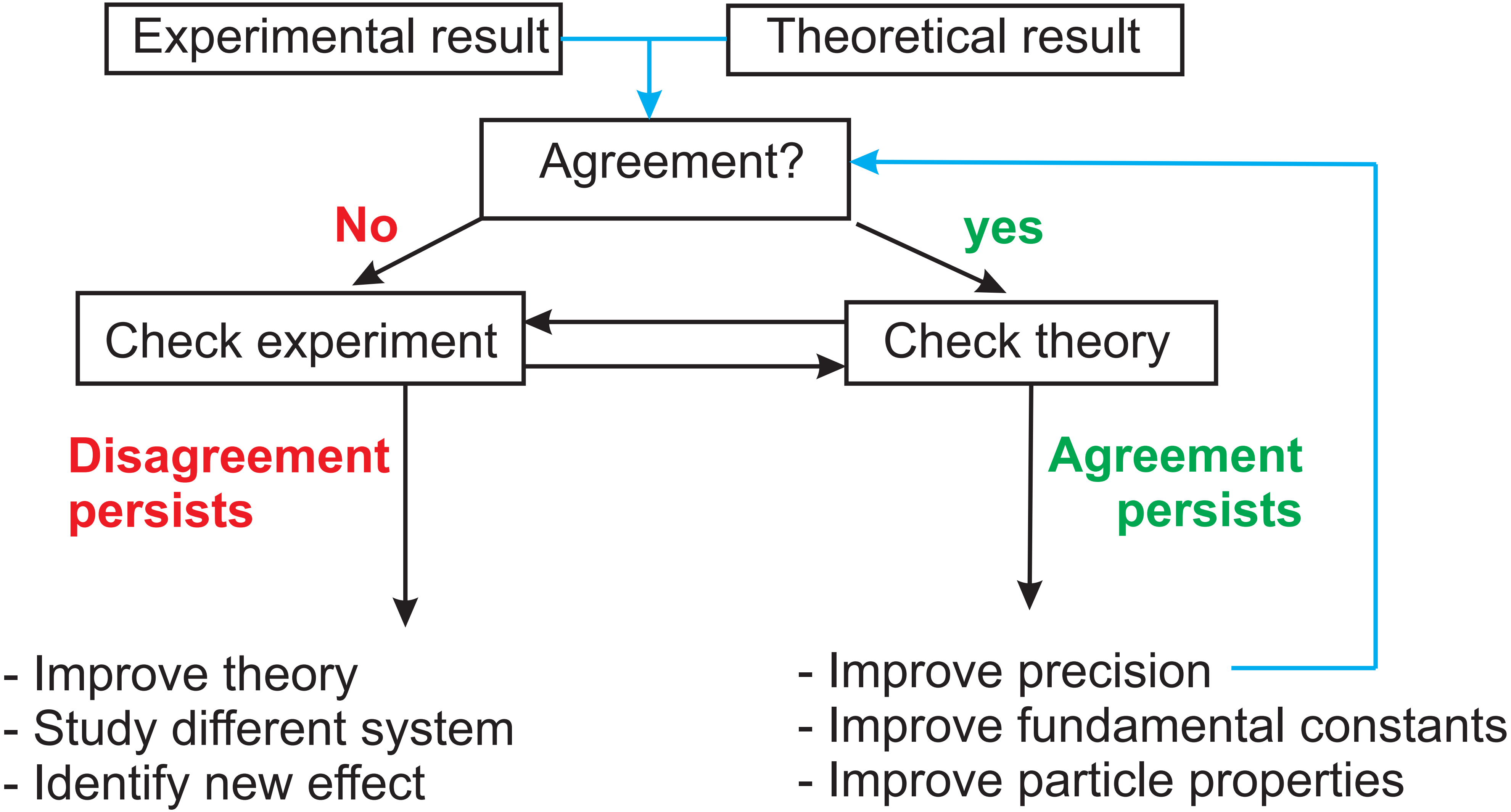
[a] Experimental results taken from Table I of Ref. 5.

[b] Rotational intervals computed with constant effective nuclear masses corresponding to the qualitative reasoning that the electrons follow the nuclei: $m_{\text{est}} = m_n + \delta m_{\text{est}}$ (both for rotations and vibrations). These effective masses were also used in Ref. 6 to compute rotation-vibration energy levels.

[c] Rotational intervals computed with the rigorous mass-correction functions computed in the present work (see Fig. 1).

[d] Rotational transitions obtained as in footnote (c) and corrected with the estimated relativistic and radiative effects for each rotational state according to Ref. 6 (see also text and Ref. 5 for details).

Comparison theory-experiment



Experimental result

Theoretical result

Agreement?

No

yes

Check experiment

Check theory

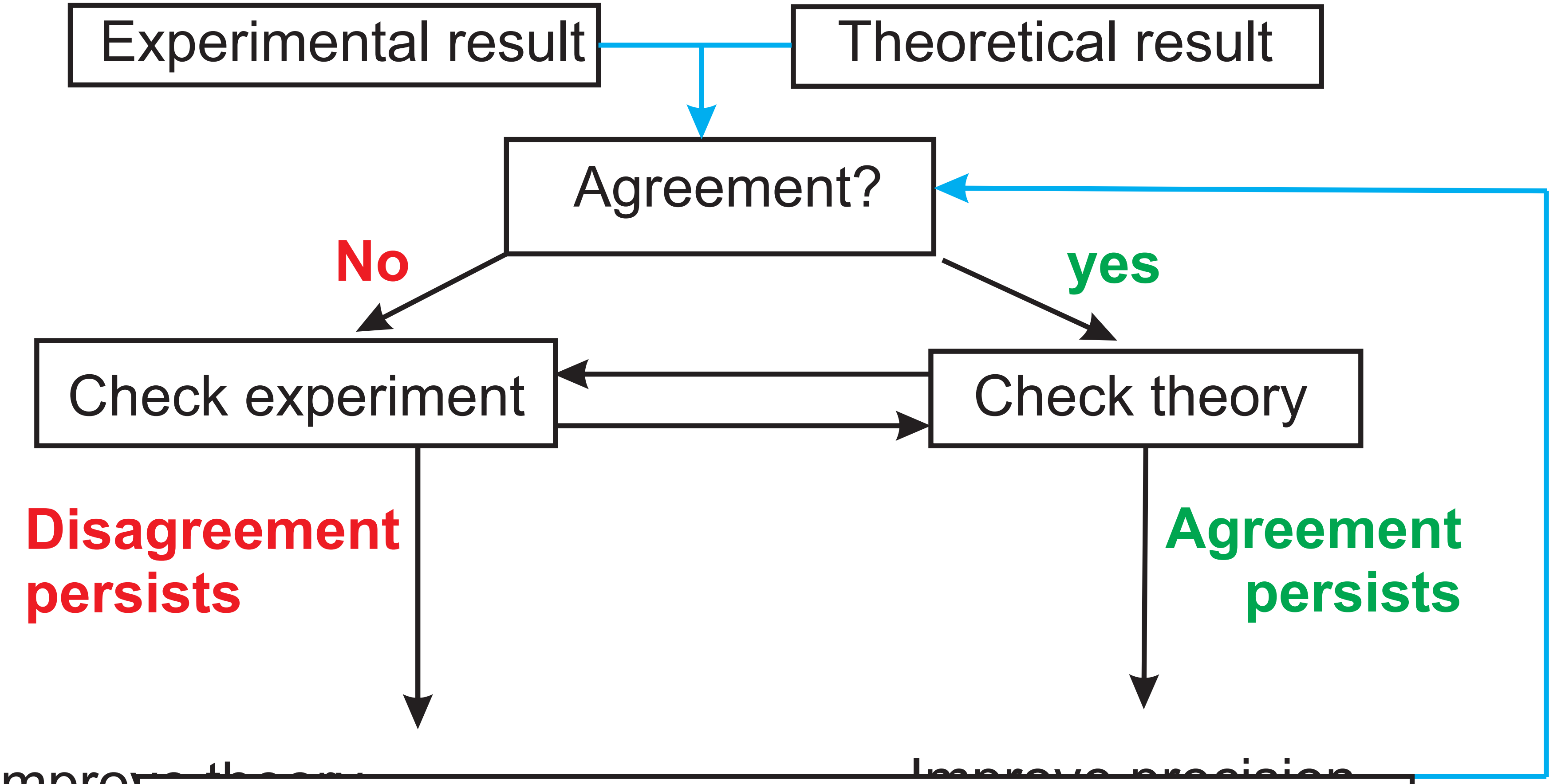
Disagreement persists

Agreement persists

- Improve theory
- Study different system
- Identify new effect

- Improve precision
- Improve fundamental constants
- Improve particle properties

Comparison theory-experiment



Experimental result

Theoretical result

Agreement?

No

yes

Check experiment

Check theory

Disagreement persists

Agreement persists

- Impro
- Study
- Identif

Improve precision

al constants

perties

But: - Uncertainties are difficult to estimate
and tend to be underestimated
- Agreement may be accidental
(error compensation)

The problems of spectroscopic experiments on small molecules

H_2^+, H_2, He_2, He_2^+

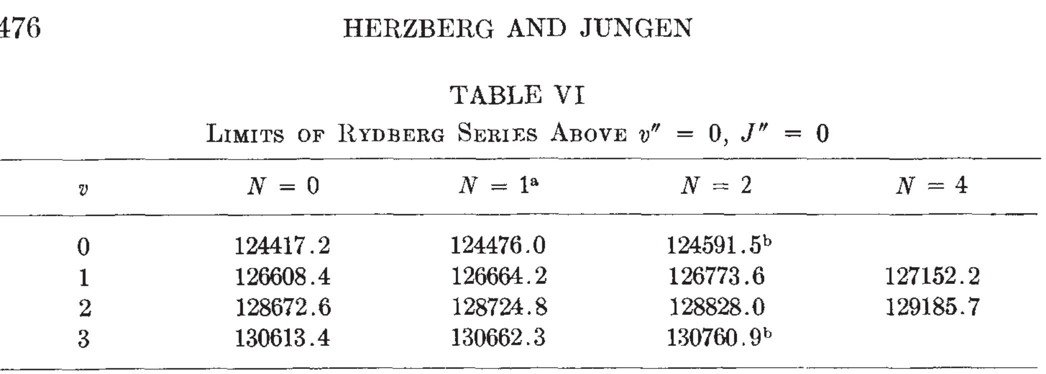
No permanent electric dipole moment

No pure rotational spectrum

No vibrational spectrum

Electronic spectrum

Rydberg states: From atoms to molecules



476 HERZBERG AND JUNGEN

TABLE VI

LIMITS OF RYDBERG SERIES ABOVE $v'' = 0$, $J'' = 0$

v	$N = 0$	$N = 1^a$	$N = 2$	$N = 4$
0	124417.2	124476.0	124591.5^b	
1	126608.4	126664.2	126773.6	127152.2
2	128672.6	128724.8	128828.0	129185.7
3	130613.4	130662.3	130760.9^b	

(Precision: about 30 GHz)

G. Herzberg

Atomic hydrogen

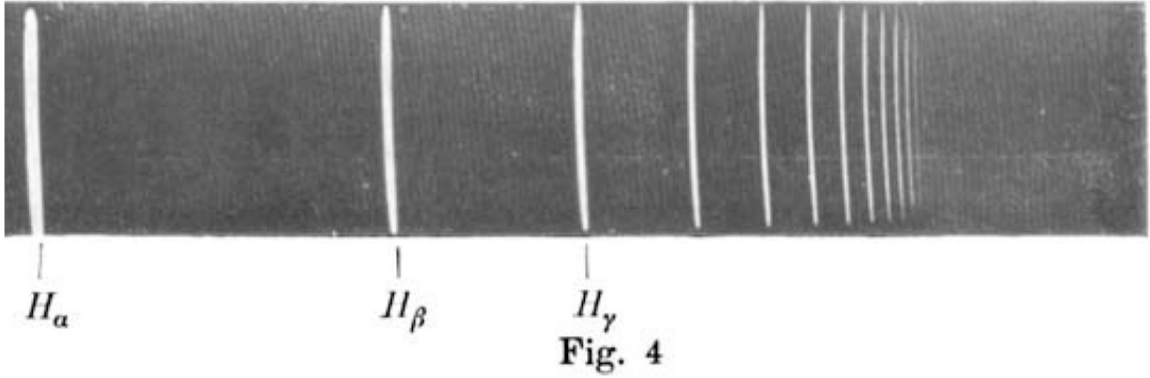
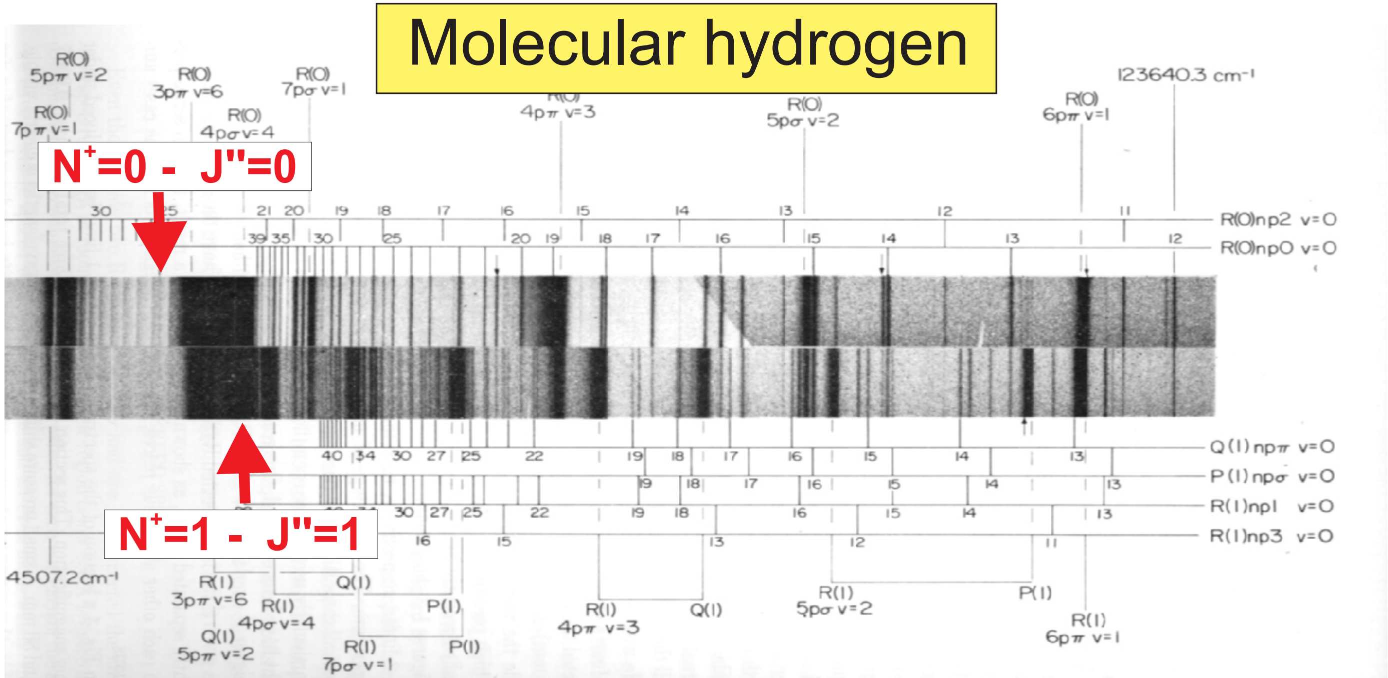


Fig. 4

G. Herzberg, Ann. Phys. 84, 565 (1927)

Molecular hydrogen



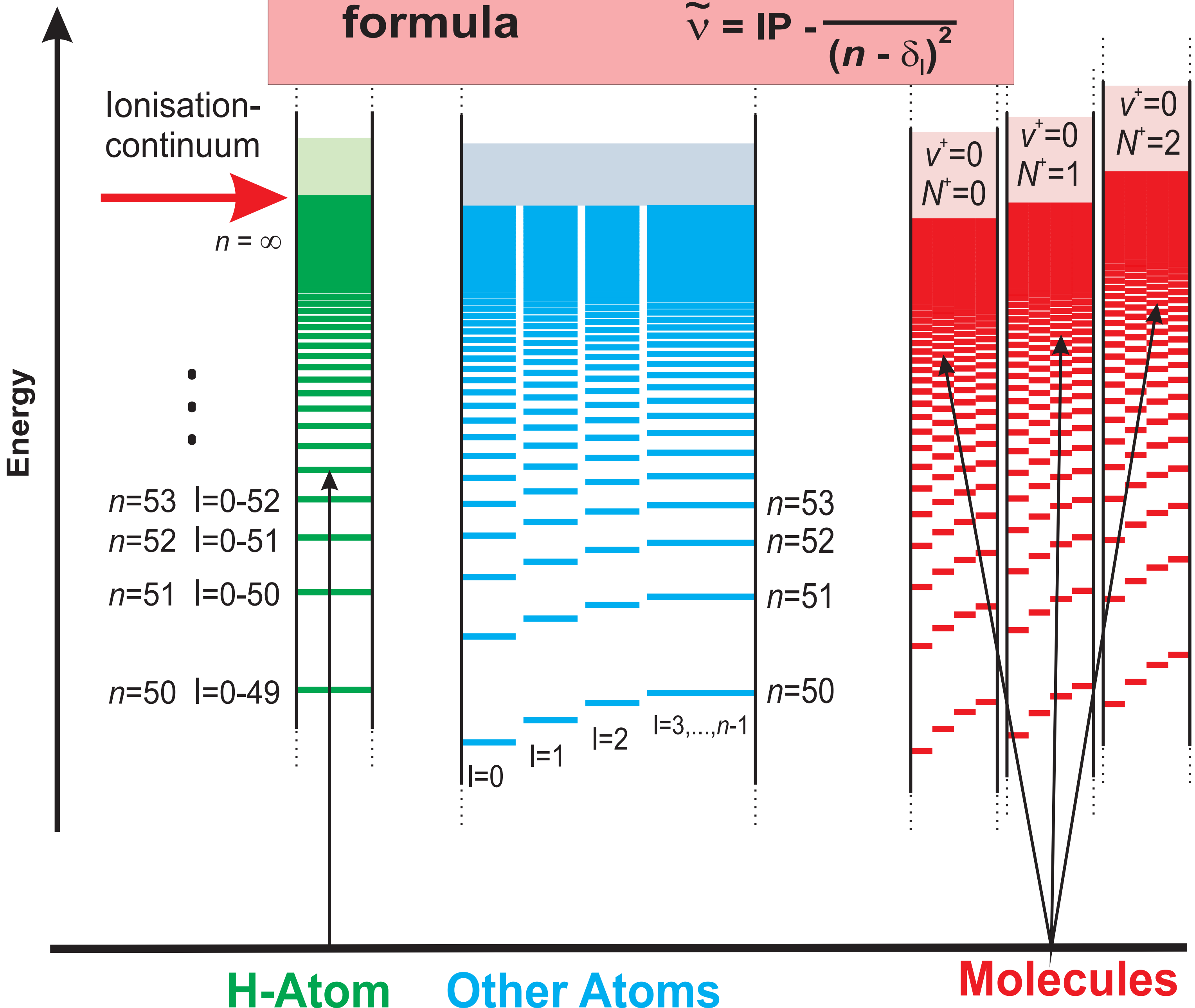
spectrum of para-H_2 and ordinary H_2 at liquid nitrogen temperature in the region 808.8 to 802.0 Å. The identification of most of the lines
= 0) and below ($J'' = 1$) the spectrograms. Also, by broken leading lines, the extrapolated series limits are marked. Unidentified lines are

G. Herzberg and Ch. Jungen, J. Mol. Spec. 41, 425 (1972)

Atomic and molecular Rydberg states

Rydberg formula

$$\tilde{\nu} = IP - \frac{R}{(n - \delta_l)^2}$$

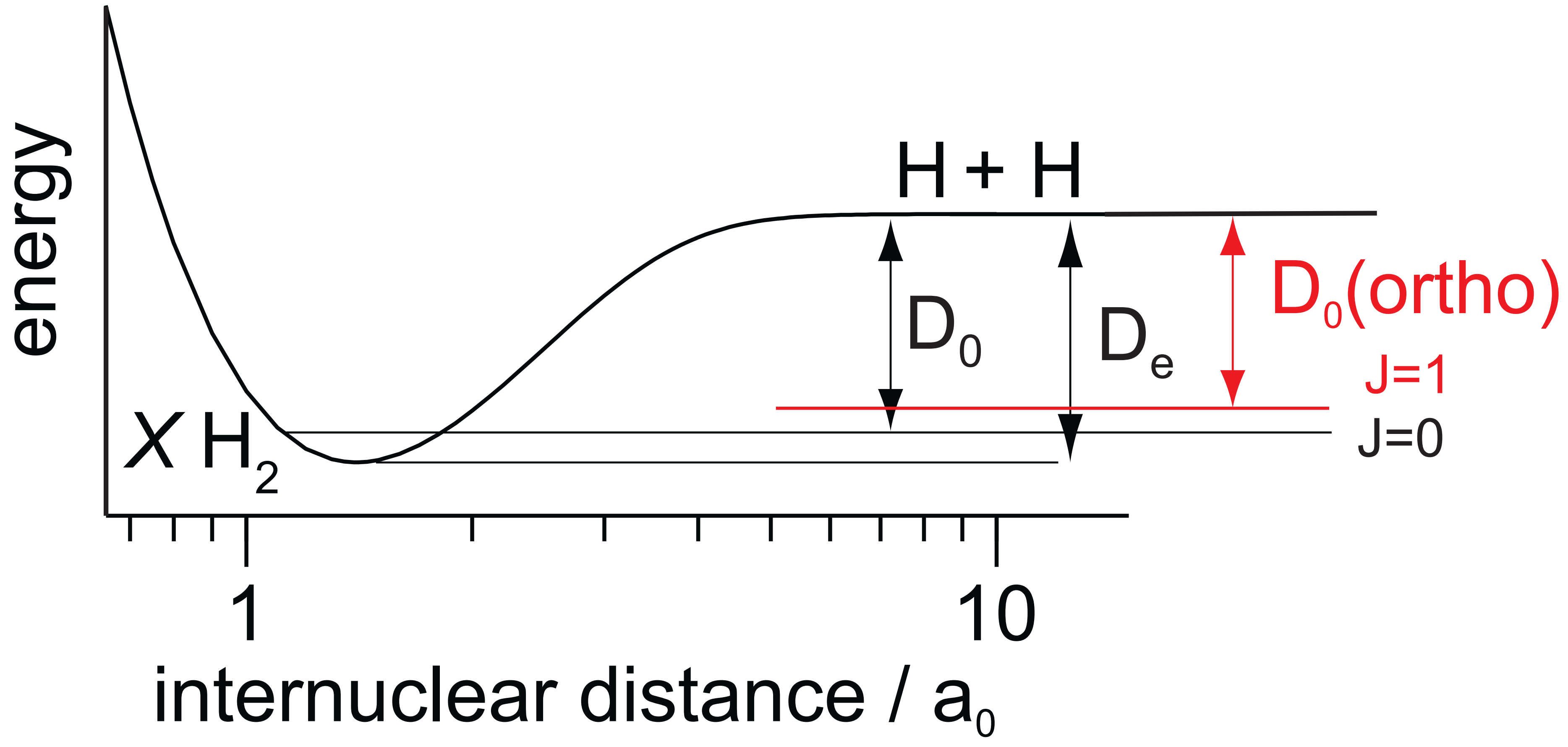


- Cold samples
- Supersonic beams
- cw lasers
- frequency combs
- ultrahigh vacuum
- resonant multi-photon excitation

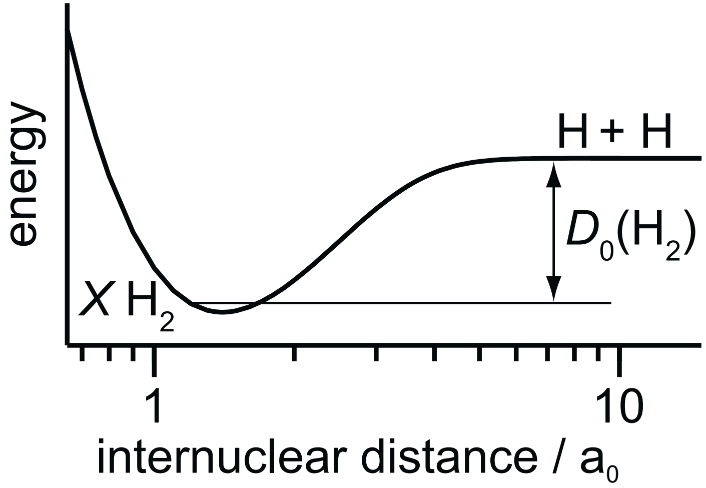
II. The dissociation energy of H_2

D_0: Minimal energy required to break a molecule in its energetic ground state into two fragment, both in the energetic ground state

D_e: Energy difference between the dissociation limit and the minimum energy of the Born-Oppenheimer potential function



Dissociation energy of the hydrogen molecule



$D_0(H_2)$	Year	Experiment	Theory
Langmuir	1912	130 kJ/mol (5.6 eV)	
Bohr	1913		60 kJ/mol (2.6 eV)
Witmer	1926	4.34(20) eV	
Heitler and London	1927		2.9 eV

1927 The "Spin-Valenz-Methode" (valence-bond theory)

$$\Psi(\vec{q}_1, m_1, \vec{q}_2, m_2) = \boxed{\Phi(\vec{q}_1, \vec{q}_2)} \cdot \boxed{\chi(m_1, m_2)}$$

$$\boxed{\chi = 2^{-1/2}\{\alpha \otimes \beta - \beta \otimes \alpha\}} \qquad \boxed{\Phi(\vec{q}_1, \vec{q}_2) = (2+2S^2)^{-1/2}\{\varphi_1(\vec{q}_1)\varphi_2(\vec{q}_2) + \varphi_2(\vec{q}_1)\varphi_1(\vec{q}_2)\}}$$

Heitler and London, Z. Phys. **44**, 455 (1927)

Dissociation energy of the hydrogen molecule

$D_0(H_2)$ / cm^{-1}	Year	Experiment	Theory
James and Coolidge	1933		35924(105)
Beutler	1935	36116(6)	
Kolos and Roothaan	1960		36112.9
Herzberg and Monfils	1960	36113.0(3)	
Kolos and Wolniewicz	1965		36117.3
Kolos and Wolniewicz	1968		36117.4
Herzberg	1970	36117.3(10)	
Stwalley	1970	36118.6(5)	
⋮	⋮		
Wolniewicz	1995		36118.069
Eyler and coworkers	2004	36118.062(10)	
Rydberg spectroscopy	2009	36118.06962(37)	
Pachucki, Jeziorski and coworkers	2010		36118.0695(10)

Experiment: J. Liu, E. J. J. Salumbides, U. Hollenstein, J. C. J. Koelemeij, K. S. E. Eikema, W. Ubachs, and F. Merkt, J. Chem. Phys. **130**, 174306 (2009)

Theory: K. Piszczatowski, G. Lach, M. Przybytek J. Komasa, K. Pachucki and B. Jeziorski, JCTC **5**. 3039 (2009)

Principle of earlier measurements

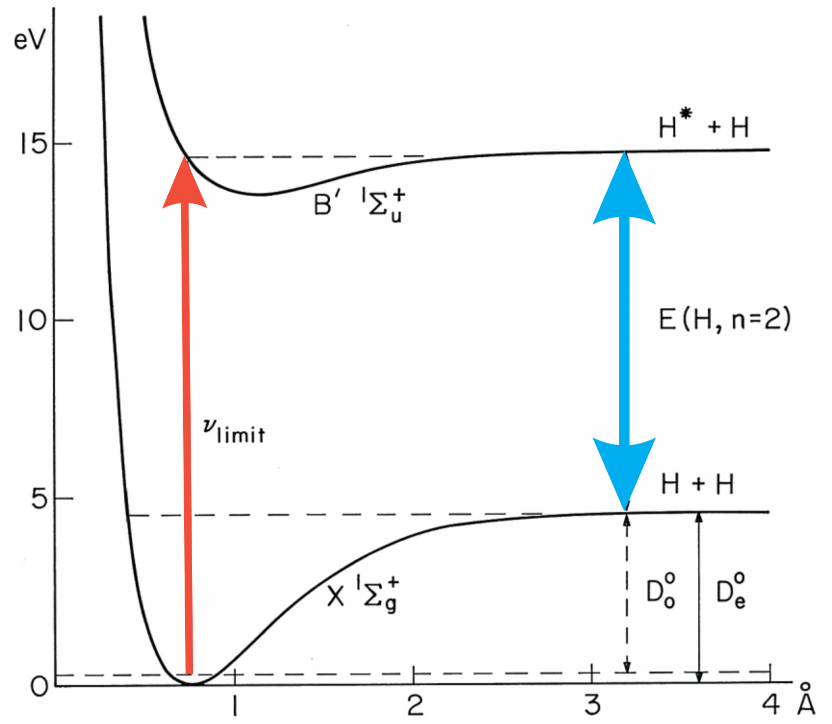
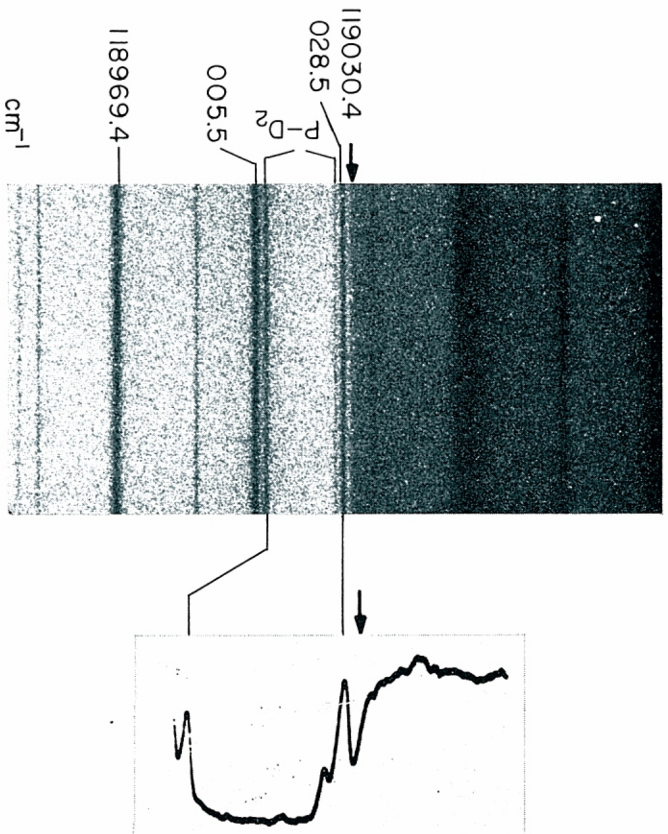
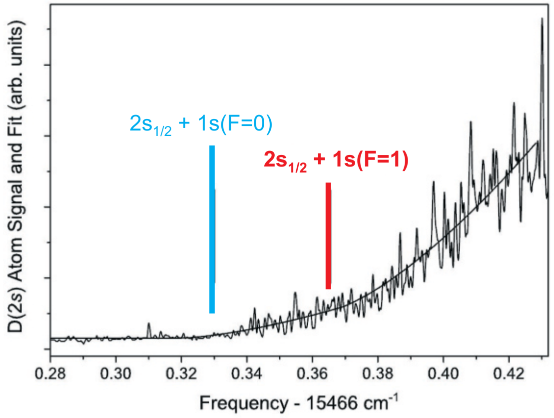


Fig. 2.
Potential functions of the ground state ($X^1\Sigma_g^+$) and the second excited state ($B'\ ^1\Sigma_u^+$) of H_2 showing the relation between the absorption limit and the dissocation energy in the ground state: $D_0^0 = \nu_{\text{limit}} - E(\text{H}, n = 2)$.

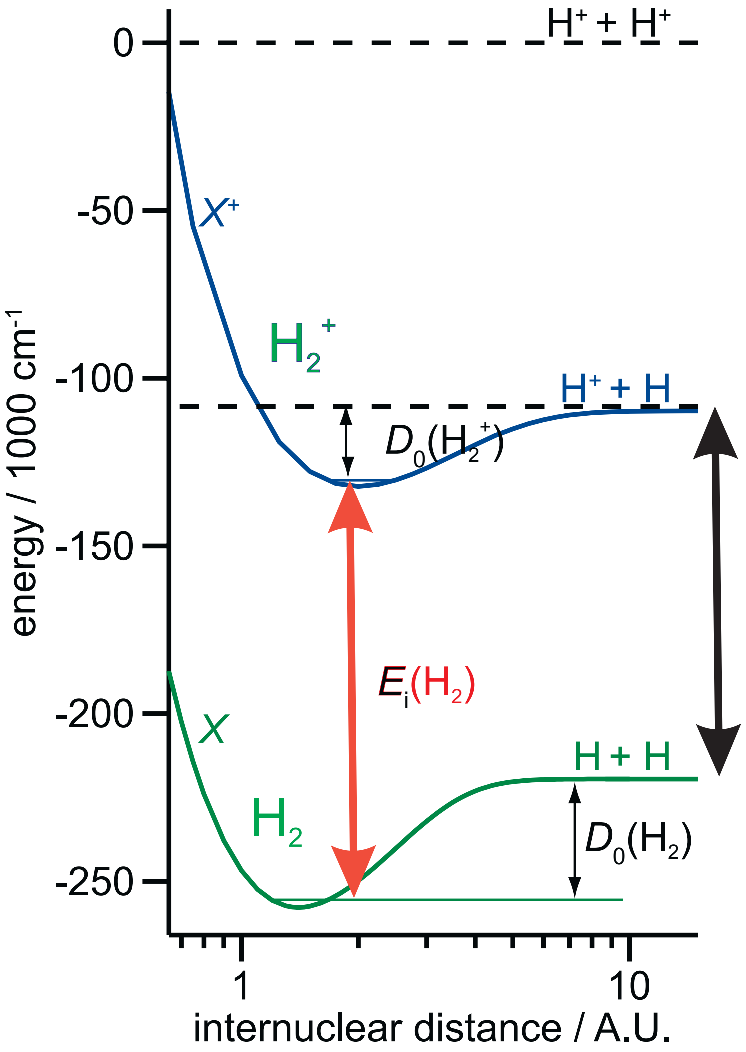


G. Herzberg, Nobel lecture 1971



Eyler and cowokers PRL **92**, 203003 (2004)]

Ionization and dissociation energy of H_2



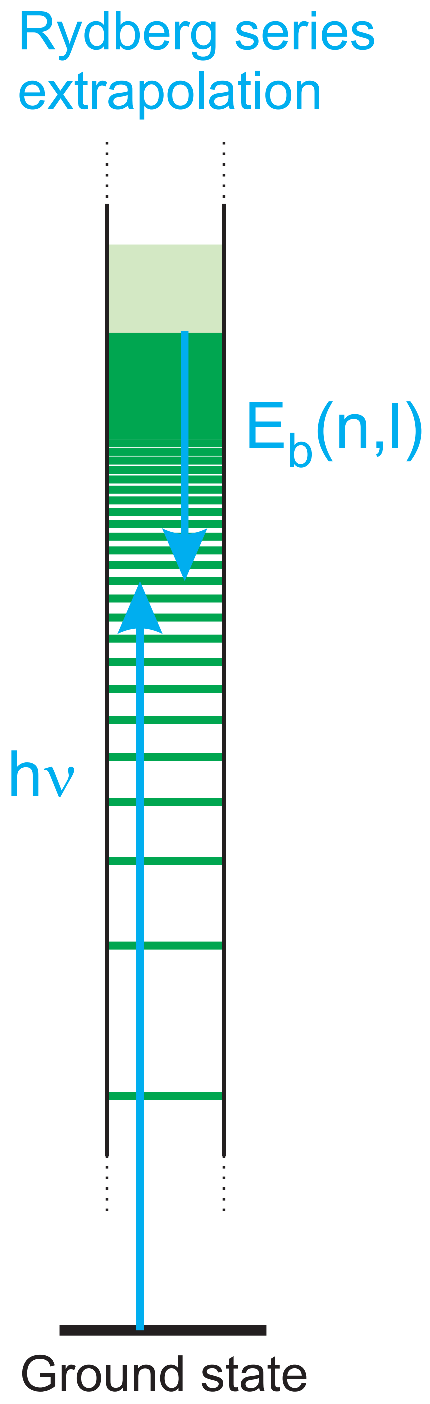
$$D_o(H_2) = E_I(H_2) + D_o^+(H_2^+) - E_I(H)$$

$D_o^+(H_2^+)$: 21'379.350'249'6(6) cm^{-1}

$E_I(H)$ = 109'678.771'743'07(10) cm^{-1}

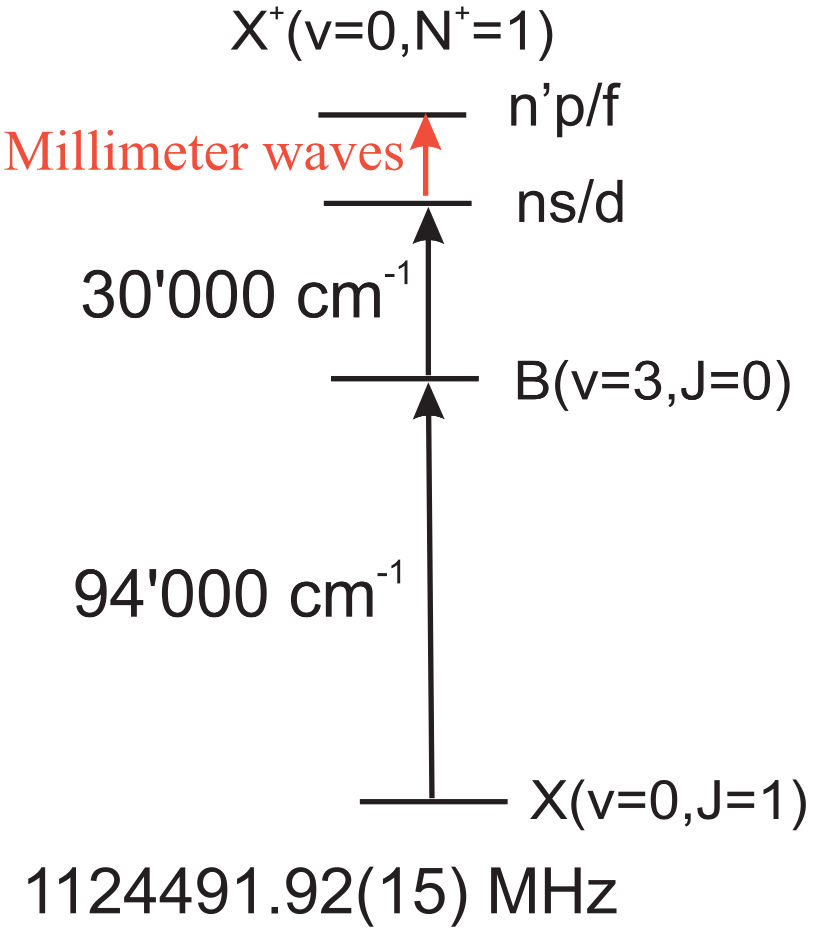
Measure ionization energy of H_2

CODATA 2014/18



Rydberg-state binding energy by millimeter-wave spectroscopy

$$E_b(54p1) = 37.509'013'0(30)\ \mathrm{cm}^{-1} = 1'124'491.92(10)\ \mathrm{MHz}$$



$X^+(v=0,N^+=1)$

n’p/f

Millimeter waves

ns/d

30'000 cm^{-1}

B(v=3,J=0)

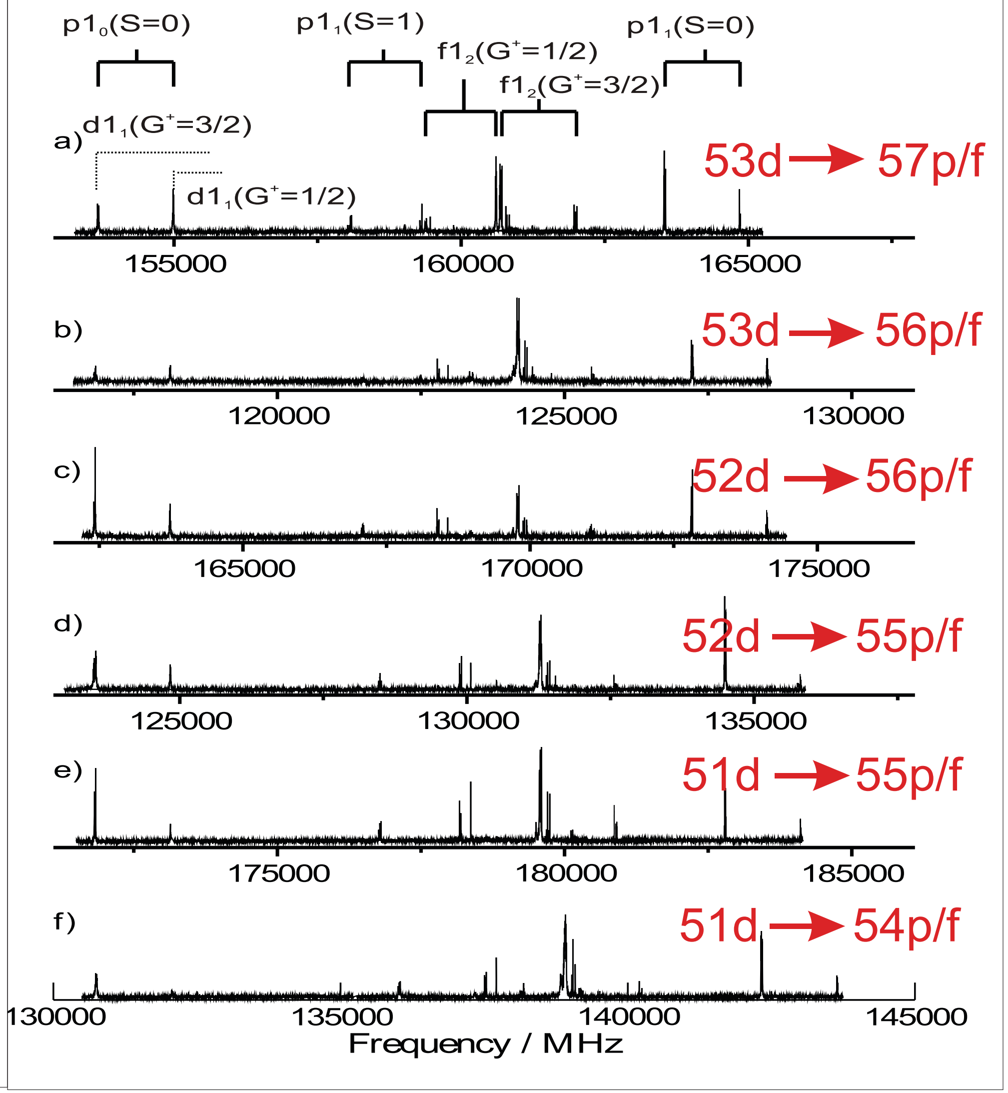
94'000 cm^{-1}

X(v=0,J=1)

1124491.92(15) MHz

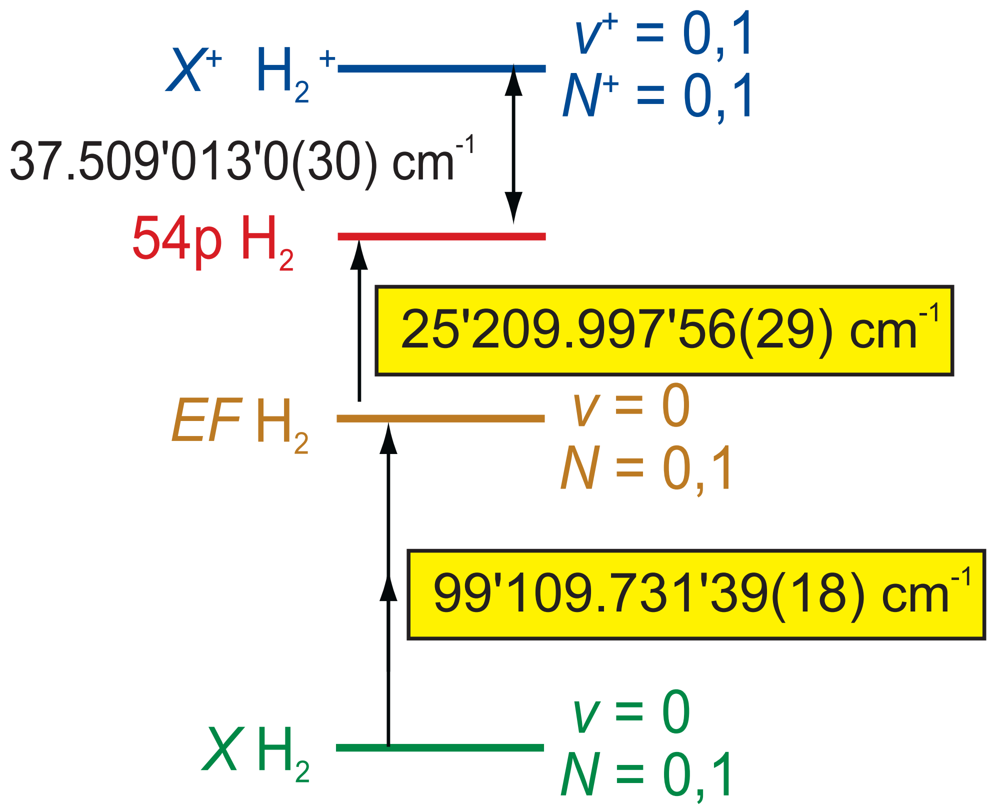
Gerade states

Metastable series: $nd(N^+=1,N=1) \longrightarrow np/nf$



Osterwalder, Wüest, FM, Jungen, JCP **121**, 11810 (2004)
Sprecher, Jungen, FM, JCP **140**, 104303 (2014)

2009 determination of the ionization and dissociation energies of H_2



X^+ H_2^+ $v^+ = 0,1$ $N^+ = 0,1$

37.509'013'0(30) cm^{-1}

54p H_2

25'209.997'56(29) cm^{-1}

EF H_2 $v = 0$ $N = 0,1$

99'109.731'39(18) cm^{-1}

X H_2 $v = 0$ $N = 0,1$

Pulsed lasers

Calibaration with I_2 lines

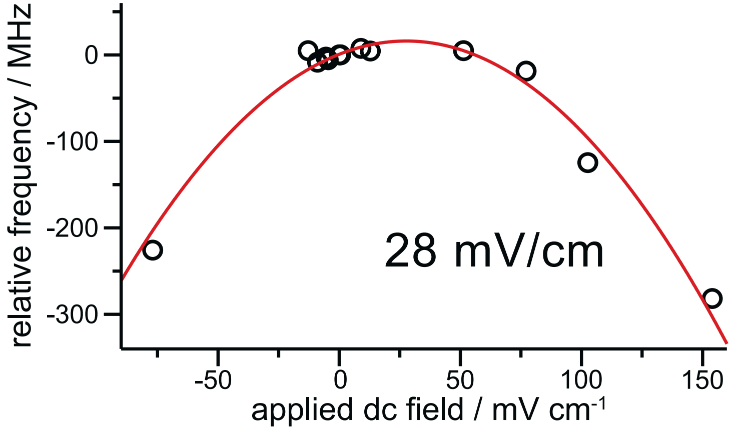
Zurich: single-photon,
Doppler-limited

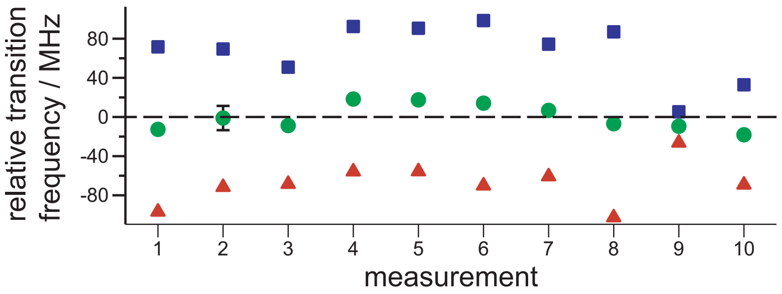
$\Delta\nu = 10$ MHz

Amsterdam: two-photon,
Doppler-free

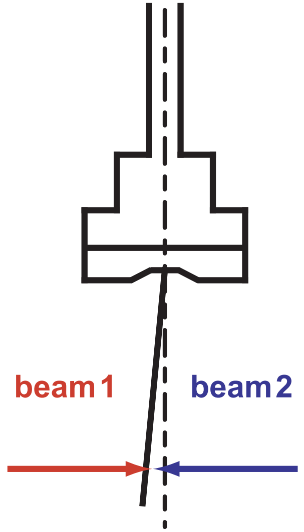
$\Delta\nu = 6$ MHz

dc Stark shift (15.4±2.4 MHz)





EF (v=0,N=1) → 54p(v^+=0,N^+=1)



Observations:

Precision of theory and experiment improve by a factor of 10 every 10 years

Agreement between theory and experiment at a given time does not imply agreement at later times

Despite disagreement, nobody really doubted the validity of quantum mechanics

Uncertainties are often underestimated by theorists and experimentalists

New aspects since 2010:

Effect of proton charge radius on D_0: 930 kHz [1]

Proton-charge-radius puzzle: 4.5 % discrepancy $\longrightarrow$ 43 kHz precision needed in D_0

[1] M. Puchalski, J. Komasa, P. Czachorowski and K. Pachucki, Phys. Rev. Lett. **117**, 263002 (2016)

New calculation of the dissociation energy of H_2

	2010 [1]	**2017** [2]
Born-Oppenheimer energy	36112.5928	36112.59**7**3158
Adiabatic correction	+5.7711	+5.770**9**817(3)
Non-adiabatic correction	+0.4339	+0.434**0**331(1)
Relativistic correction (α^2)	-0.5319	-0.53**3**121(1)
Radiative correction (α^3)	-0.1948	-0.1948(2)
(α^4)	-0.0016	-0.002**0**67(6)
(α^5)	---	0.00012(6)
Total (Theory) (Para-H_2)	36118.0695(10)	36118.06**7**8(6)
Experiment (Para-H_2)	36118.06962(37)	?

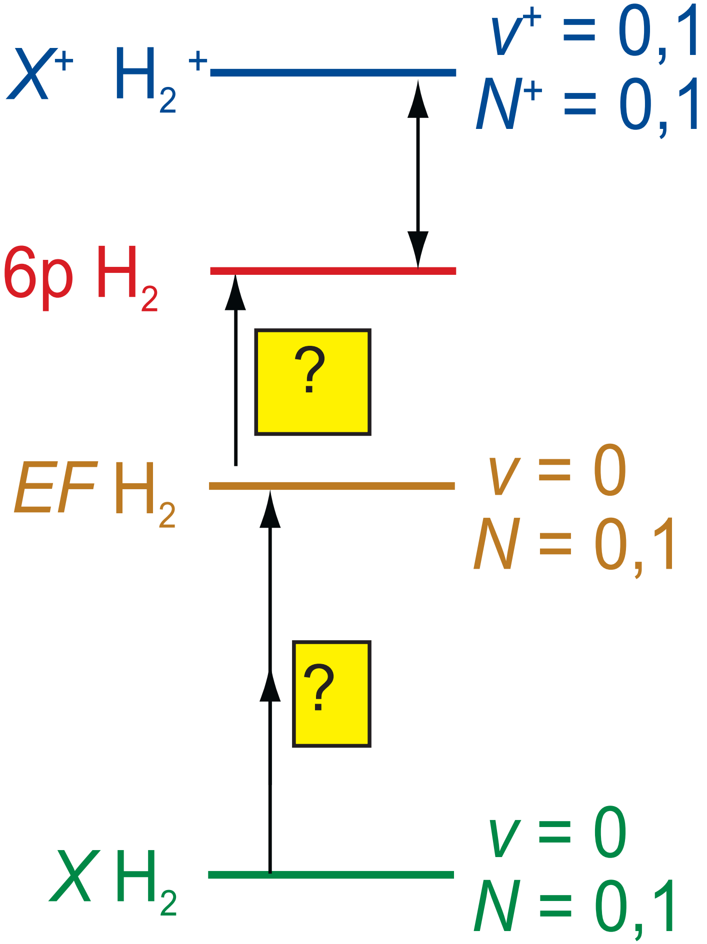
«Agreement between theory and experiment was accidental»

[1] K. Piszczatowski, G. Lach, M. Przybytek J. Komasa, K. Pachucki and B. Jeziorski, JCTC **5**. 3039 (2009)

[2] M. Puchalski, J. Komasa and K. Pachucki, Phys. Rev. A **95**, 052506 (2017)

2018-19: Repetition of the 2009 experiment

Frequency combs, cw lasers
Calibration: Rb GPS standard



X^+ $H_2{}^+$ $v^+ = 0,1$ $N^+ = 0,1$

56p H_2

?

EF H_2 $v = 0$ $N = 0,1$

?

X H_2 $v = 0$ $N = 0,1$

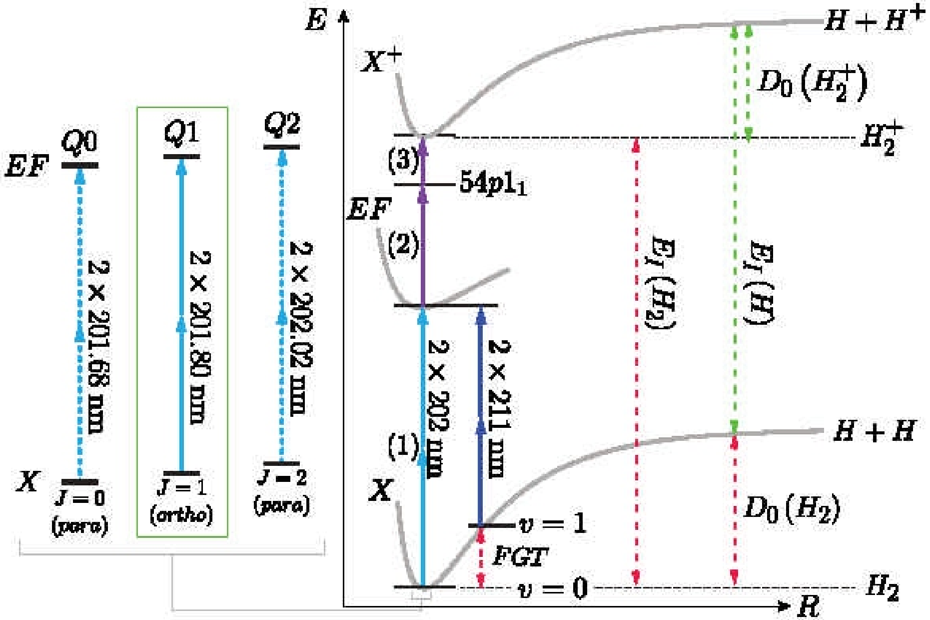
E_b(56p1)= 34.881'112'0(30) cm^{-1}
= 1'045'709.43(10) MHz

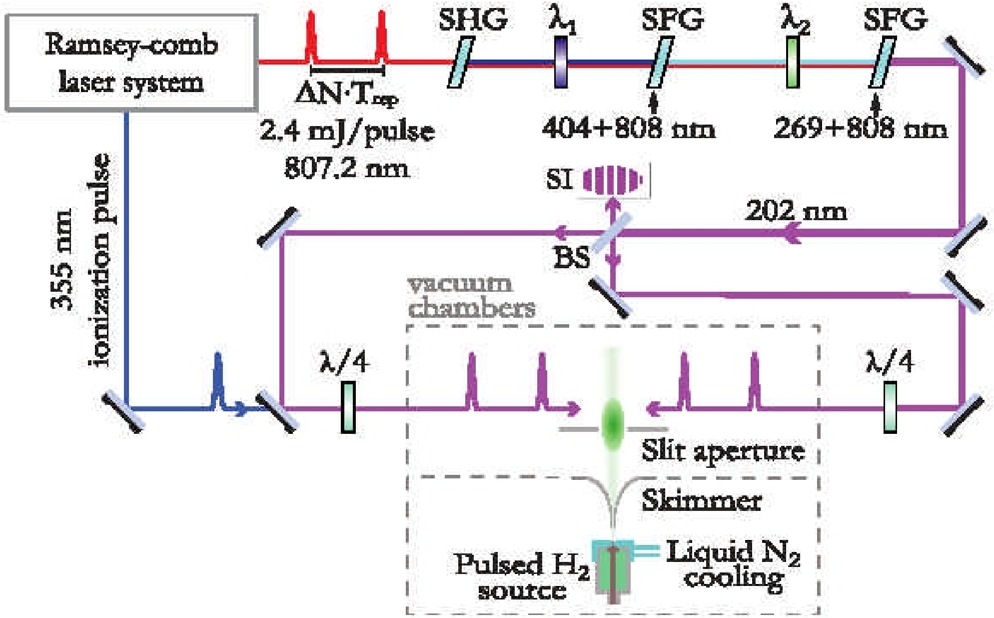
$\Delta\nu = 100$ kHz

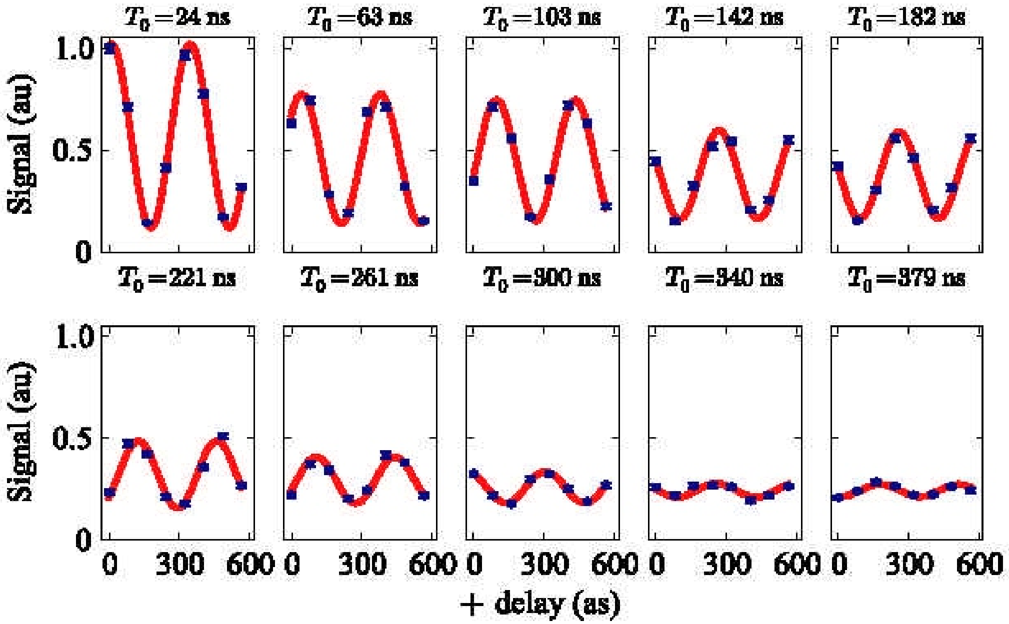
Zurich: single-photon,
Doppler-limited

Amsterdam: Ramsey-comb,
two-photon, Doppler-free

Amsterdam experiment:

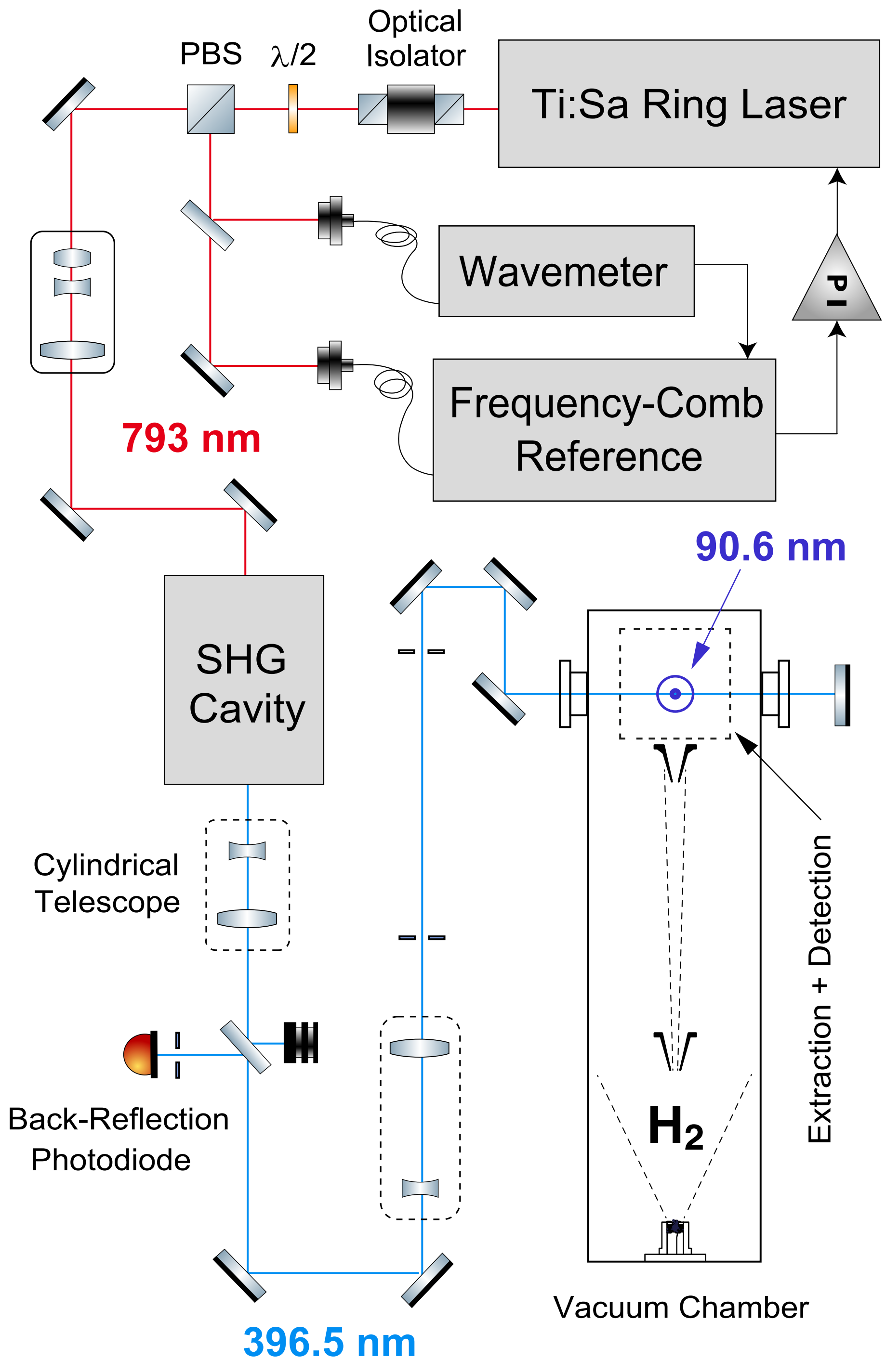


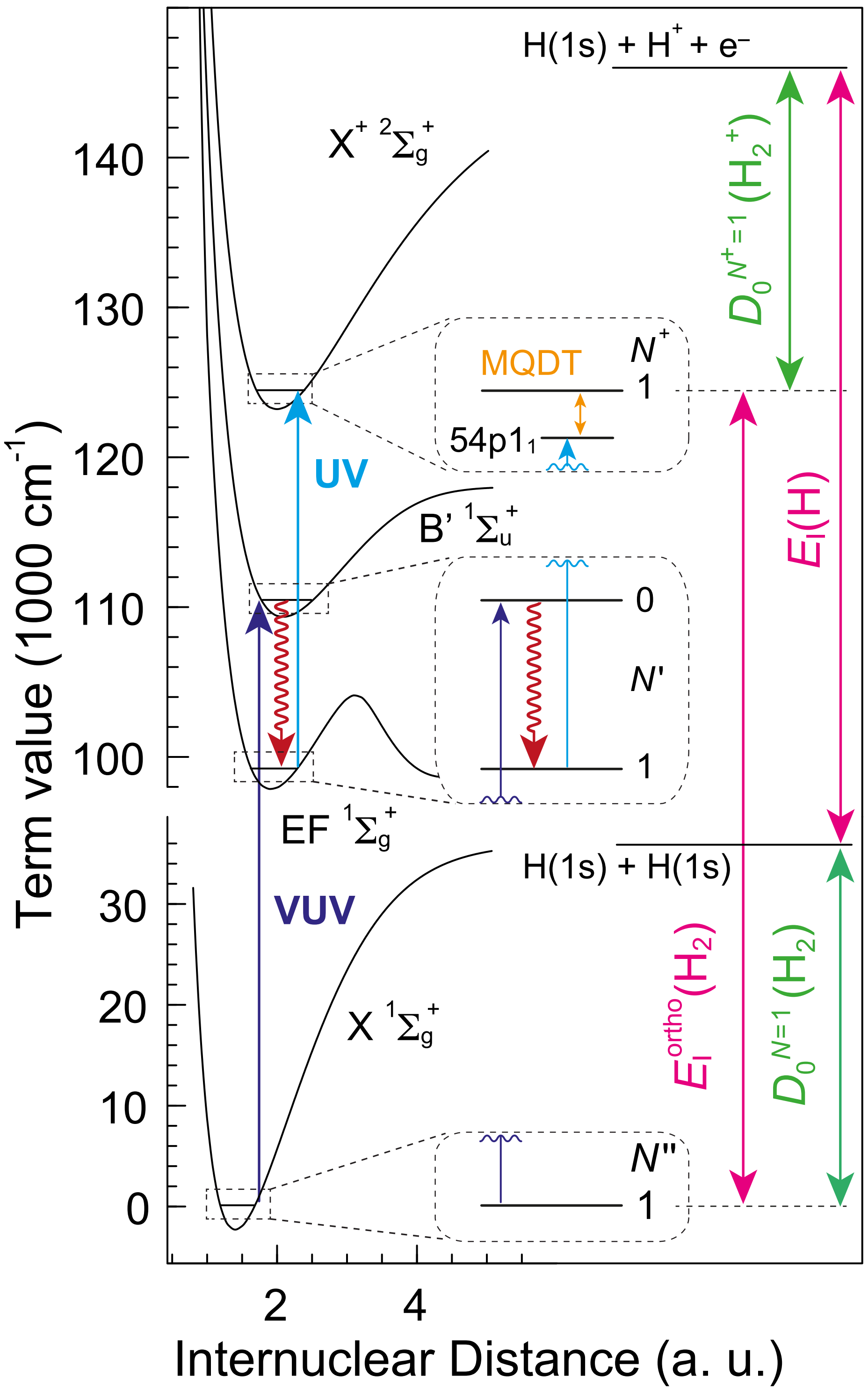


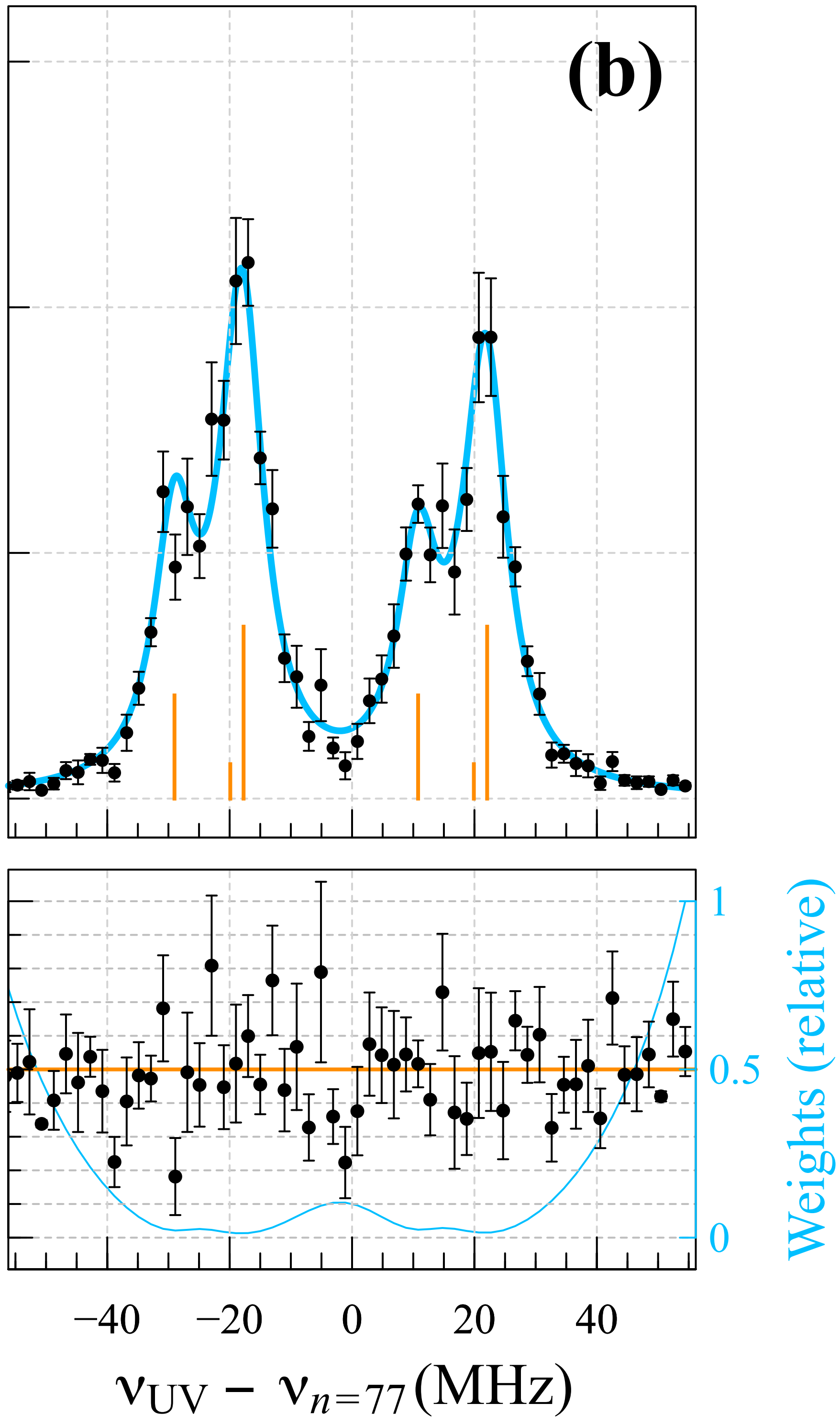


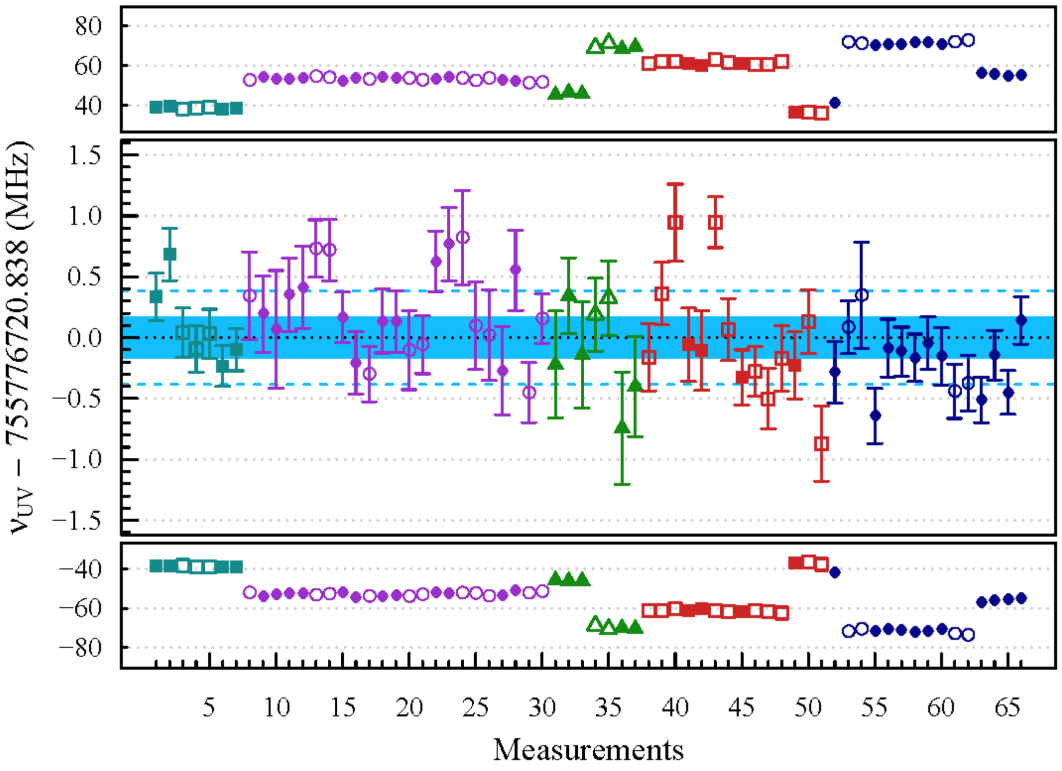
Altmann et al., PRL 120, 043204 (2018)

Zurich experiment:









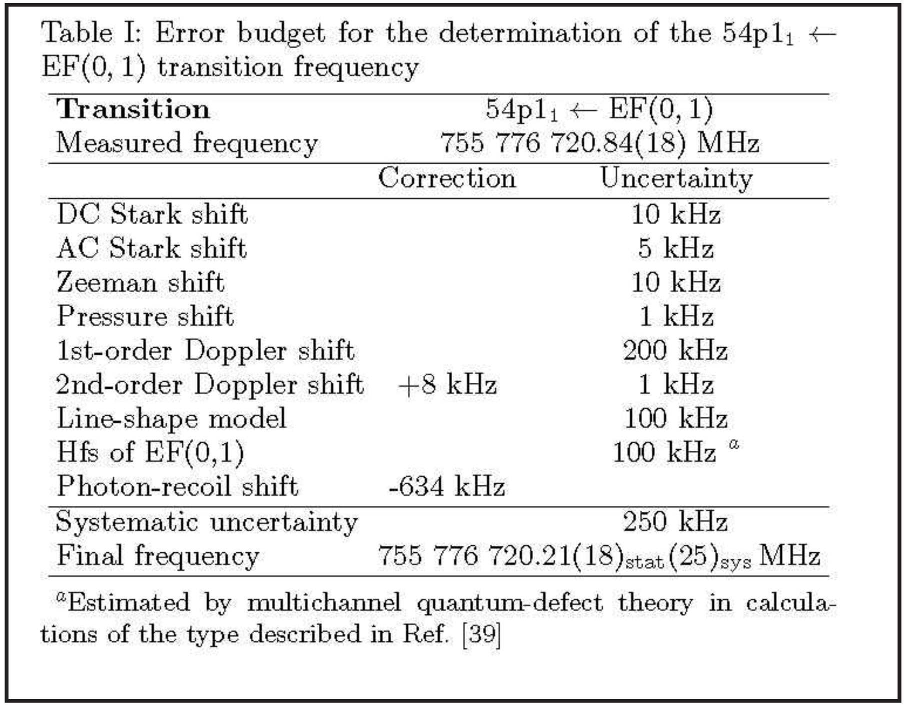


Table I: Error budget for the determination of the $54p1_1 \leftarrow$ EF(0, 1) transition frequency

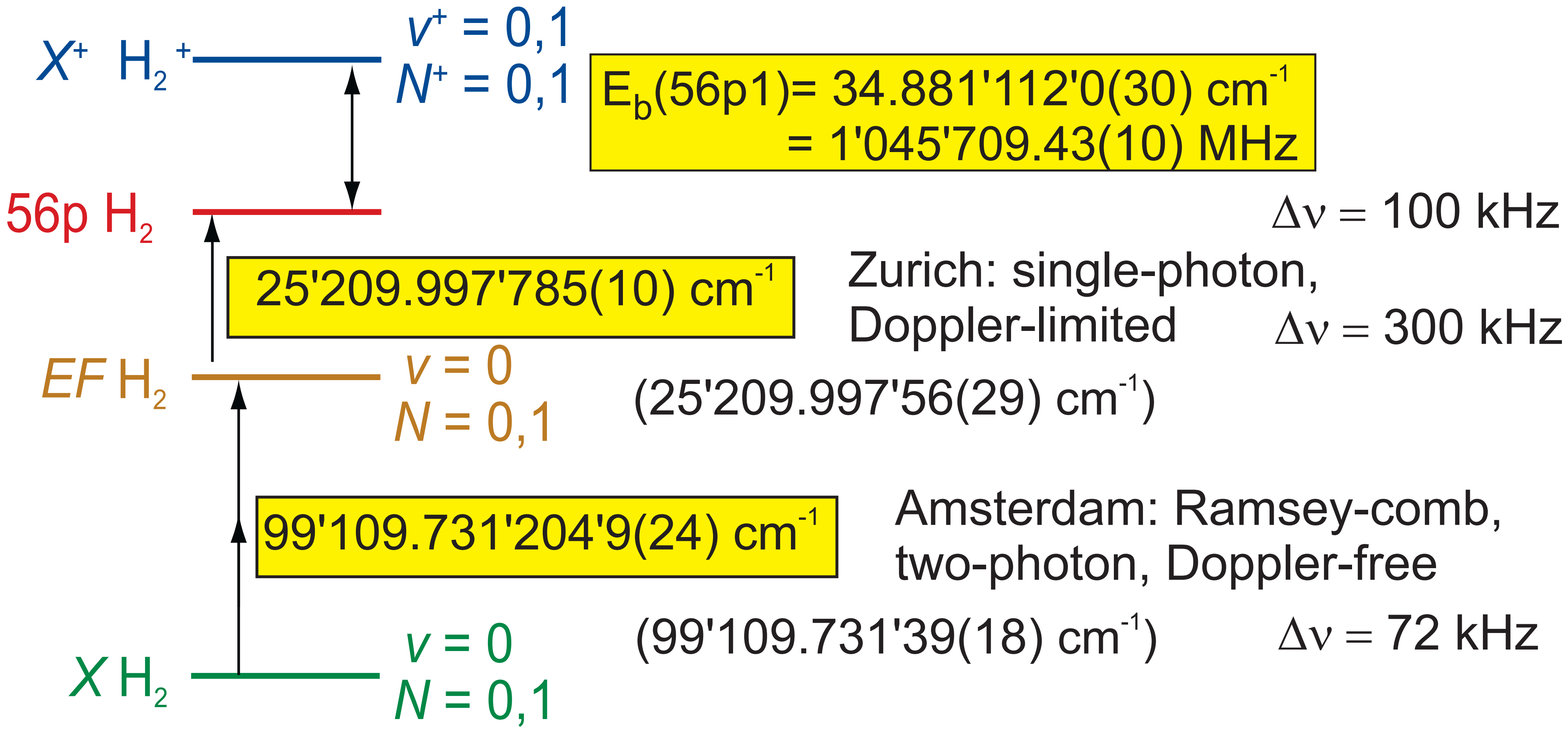
Transition	$54p1_1 \leftarrow$ EF(0, 1)	
Measured frequency	755 776 720.84(18) MHz	
	Correction	Uncertainty
DC Stark shift		10 kHz
AC Stark shift		5 kHz
Zeeman shift		10 kHz
Pressure shift		1 kHz
1st-order Doppler shift		200 kHz
2nd-order Doppler shift	+8 kHz	1 kHz
Line-shape model		100 kHz
Hfs of EF(0,1)		100 kHz [a]
Photon-recoil shift	-634 kHz	
Systematic uncertainty		250 kHz
Final frequency	755 776 720.21(18)$_{\mathrm{stat}}$(25)$_{\mathrm{sys}}$ MHz	

[a] Estimated by multichannel quantum-defect theory in calculations of the type described in Ref. [39]

Hoelsch et al., Phys. Rev. Lett. **122**, 013001 (2019)

2018-19: Repetition of the 2009 experiment

Frequency combs, cw lasers
Calibration: Rb GPS standard



E_b(56p1)= 34.881'112'0(30) cm^{-1}
= 1'045'709.43(10) MHz

$\Delta\nu = 100$ kHz

25'209.997'785(10) cm^{-1}

Zurich: single-photon,
Doppler-limited

$\Delta\nu = 300$ kHz

(25'209.997'56(29) cm^{-1})

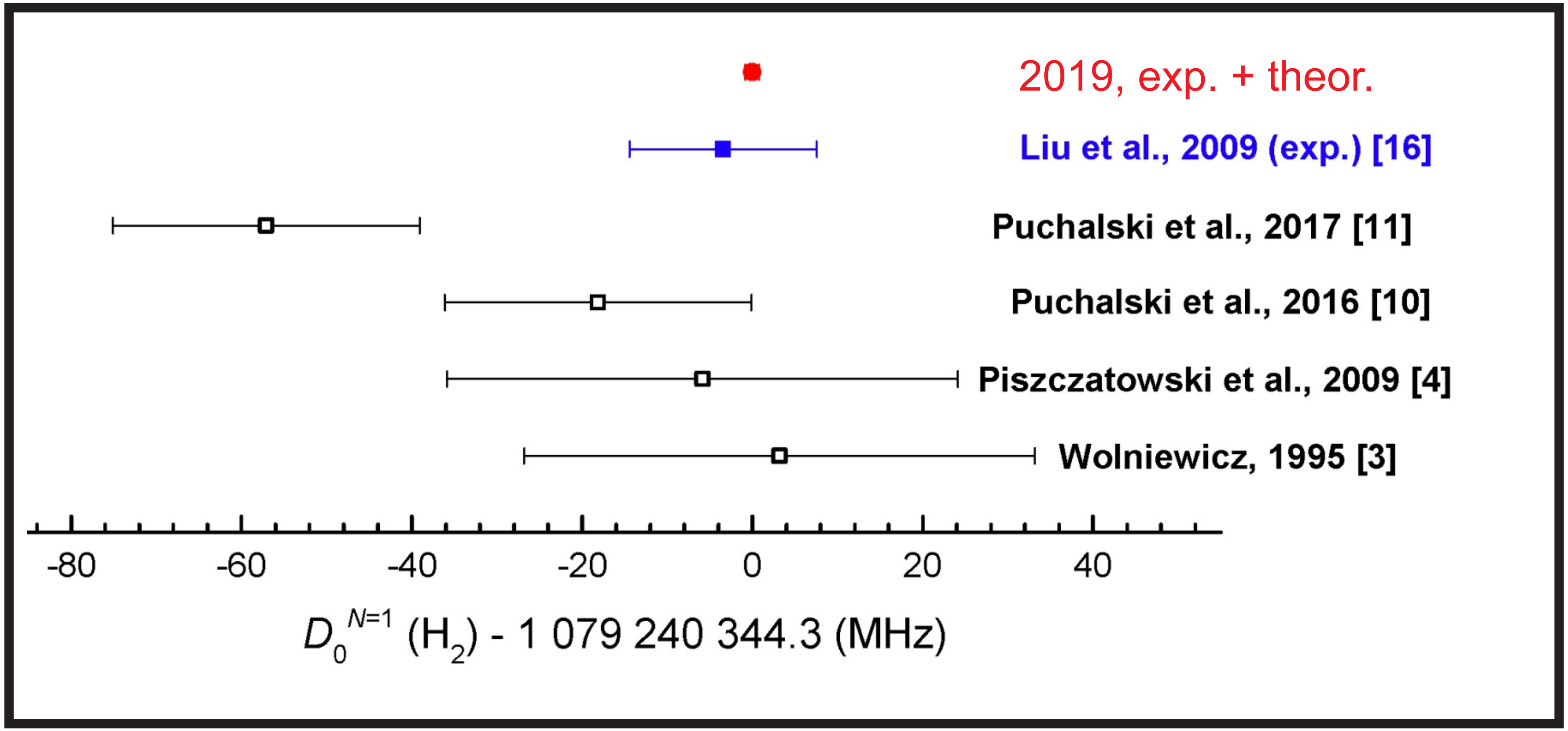
99'109.731'204'9(24) cm^{-1}

Amsterdam: Ramsey-comb,
two-photon, Doppler-free

(99'109.731'39(18) cm^{-1})

$\Delta\nu = 72$ kHz

The dissociation energy of H_2 (in cm^{-1}): 2009 vs 2019



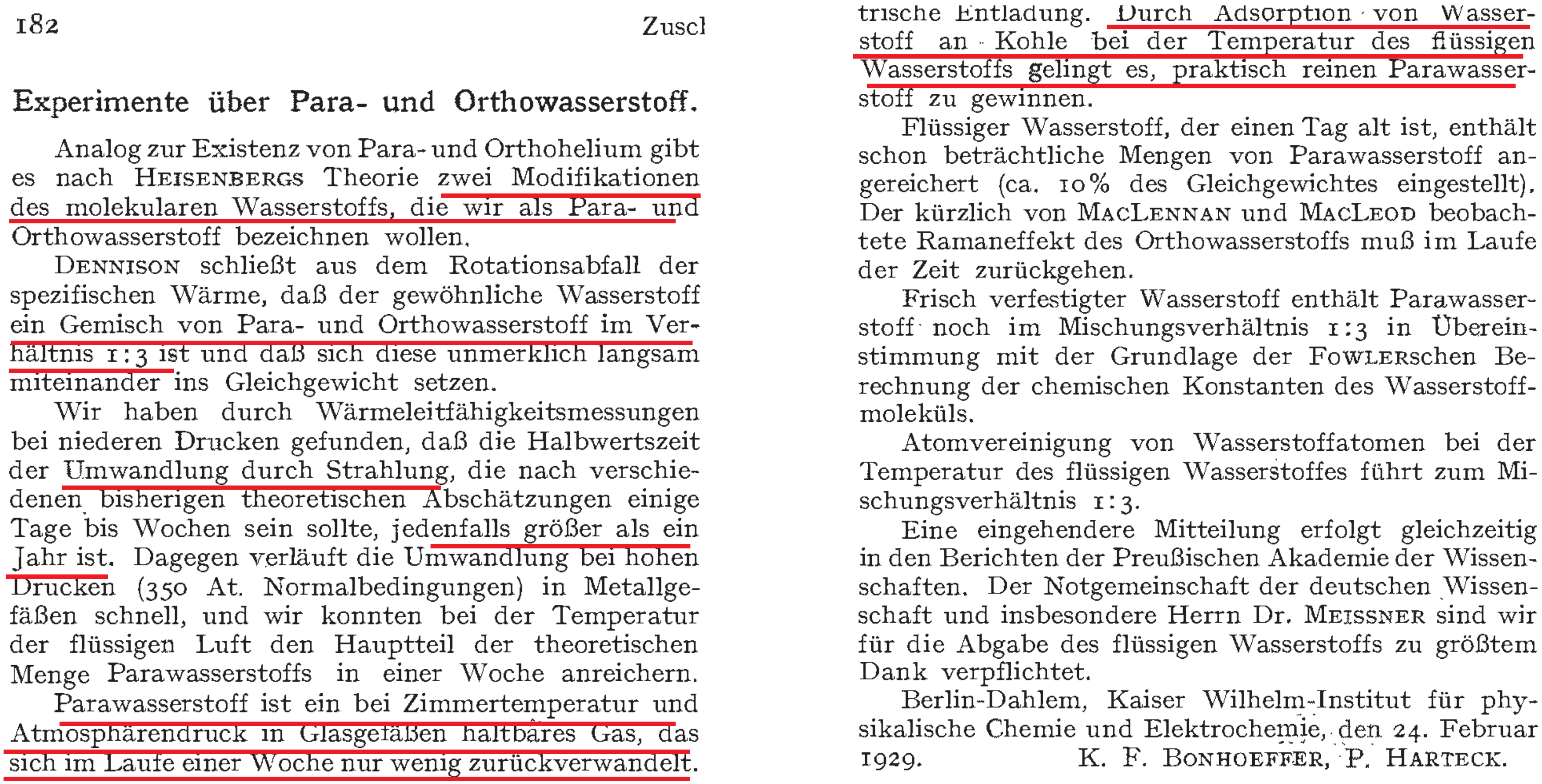
2019:

Pre-Born-Oppenheimer calculations:
M. Puchalski, J. Komasa, P. Czachorowski and K. Pachucki, PRL, 123, 103003 (2019)
36'118.069'632(26) cm^{-1} (uncertainty 780 kHz)

Experiment:
Hoelsch et al., Phys. Rev. Lett. **122**, 013001 (2019)
36'118.069'647(11) cm^{-1} (uncertainty 330 kHz)

Para- and ortho-H_2

Energy-level structures of para- and ortho-H_2 have never been connected. Global shift?



Experimente über Para- und Orthowasserstoff.

Analog zur Existenz von Para- und Orthohelium gibt es nach Heisenbergs Theorie zwei Modifikationen des molekularen Wasserstoffs, die wir als Para- und Orthowasserstoff bezeichnen wollen.

Dennison schließt aus dem Rotationsabfall der spezifischen Wärme, daß der gewöhnliche Wasserstoff ein Gemisch von Para- und Orthowasserstoff im Verhältnis 1:3 ist und daß sich diese unmerklich langsam miteinander ins Gleichgewicht setzen.

Wir haben durch Wärmeleitfähigkeitsmessungen bei niederen Drucken gefunden, daß die Halbwertszeit der Umwandlung durch Strahlung, die nach verschiedenen bisherigen theoretischen Abschätzungen einige Tage bis Wochen sein sollte, jedenfalls größer als ein Jahr ist. Dagegen verläuft die Umwandlung bei hohen Drucken (350 At. Normalbedingungen) in Metallgefäßen schnell, und wir konnten bei der Temperatur der flüssigen Luft den Hauptteil der theoretischen Menge Parawasserstoffs in einer Woche anreichern.

Parawasserstoff ist ein bei Zimmertemperatur und Atmosphärendruck in Glasgefäßen haltbares Gas, das sich im Laufe einer Woche nur wenig zurückverwandelt.

trische Entladung. Durch Adsorption von Wasserstoff an Kohle bei der Temperatur des flüssigen Wasserstoffs gelingt es, praktisch reinen Parawasserstoff zu gewinnen.

Flüssiger Wasserstoff, der einen Tag alt ist, enthält schon beträchtliche Mengen von Parawasserstoff angereichert (ca. 10% des Gleichgewichtes eingestellt). Der kürzlich von MacLennan und MacLeod beobachtete Ramaneffekt des Orthowasserstoffs muß im Laufe der Zeit zurückgehen.

Frisch verfestigter Wasserstoff enthält Parawasserstoff noch im Mischungsverhältnis 1:3 in Übereinstimmung mit der Grundlage der Fowlerschen Berechnung der chemischen Konstanten des Wasserstoffmoleküls.

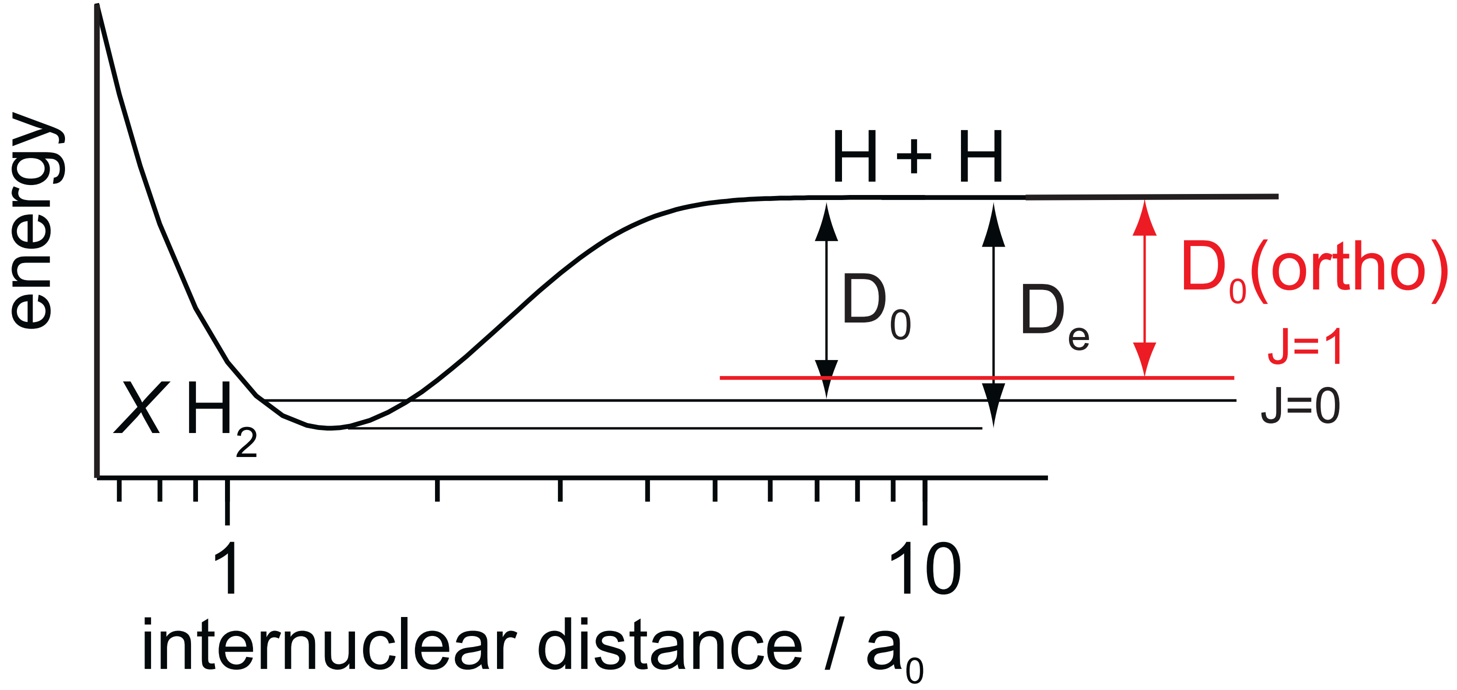
Atomvereinigung von Wasserstoffatomen bei der Temperatur des flüssigen Wasserstoffes führt zum Mischungsverhältnis 1:3.

Eine eingehendere Mitteilung erfolgt gleichzeitig in den Berichten der Preußischen Akademie der Wissenschaften. Der Notgemeinschaft der deutschen Wissenschaft und insbesondere Herrn Dr. Meissner sind wir für die Abgabe des flüssigen Wasserstoffs zu größtem Dank verpflichtet.

Berlin-Dahlem, Kaiser Wilhelm-Institut für physikalische Chemie und Elektrochemie, den 24. Februar 1929. K. F. Bonhoeffer, P. Harteck.

Bonhoeffer and Harteck, Naturwissenschaften **17**, 182 (1929)

The (J=1) - (J=0) ortho-para interval



D_0(para-H_2): (1) = 36 118.069 605(31) cm^{-1}
D_0(ortho-H_2) (2) = 35 999.582 834(26) cm^{-1}
Ortho-para interval [a]: (1)-(2) = 118.486 771(50) cm^{-1}
Theory [b]: 118.486 812 7(11) cm^{-1} (without global shift)

Global shift [a]: 0.000041(52) cm^{-1} = 1.2(1.5) MHz

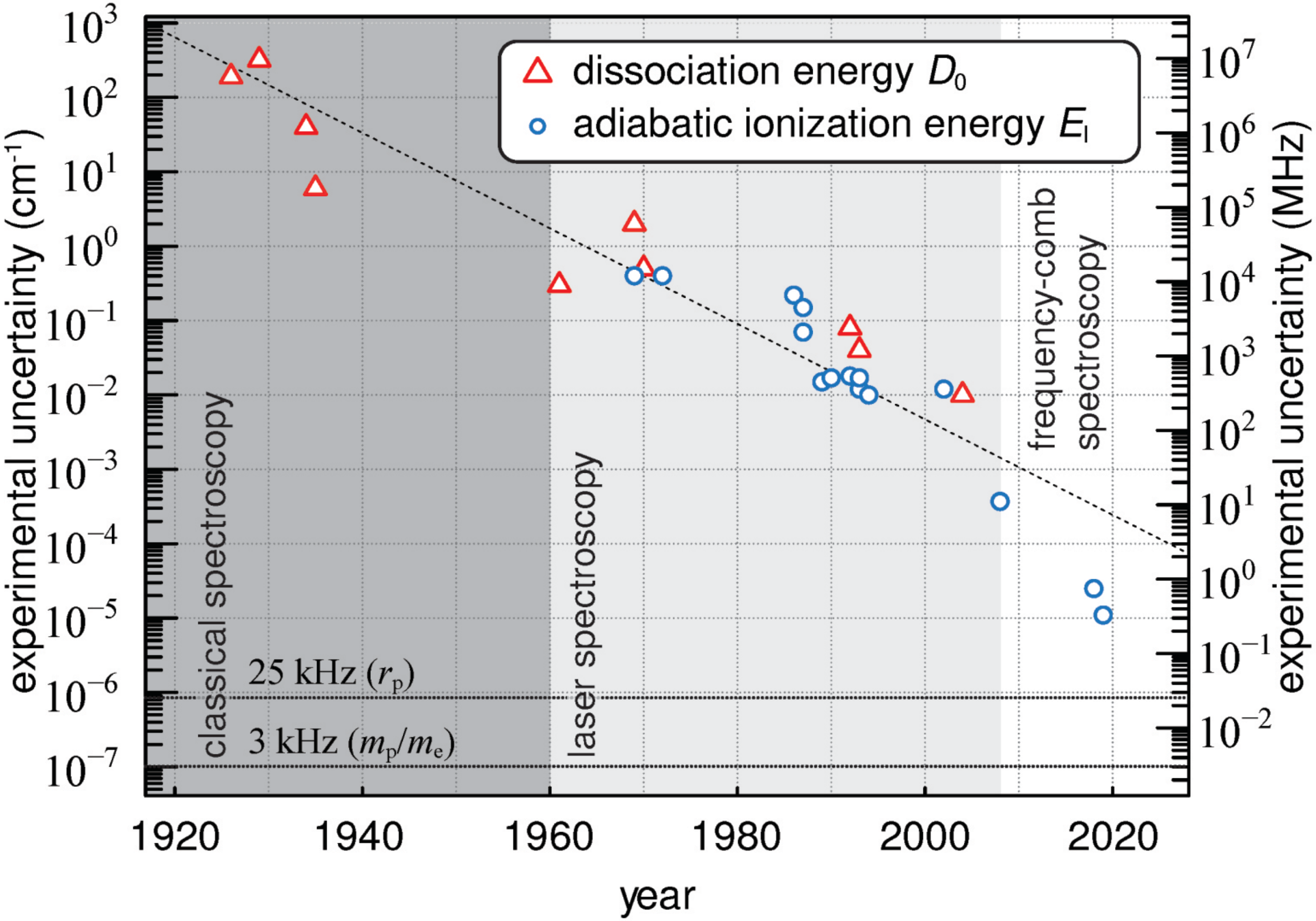
[a] Beyer et al., PRL **123**, 163002 (2019)
[b] Puchalski et al., PRL **122**, 103003 (2019)

Conclusions

Experimental determination of dissociation energy of H_2 with uncertainty of 330 kHz. Calculations tested to unprecedented level

Energy level structure of ortho and para H_2 have been connected for the first time

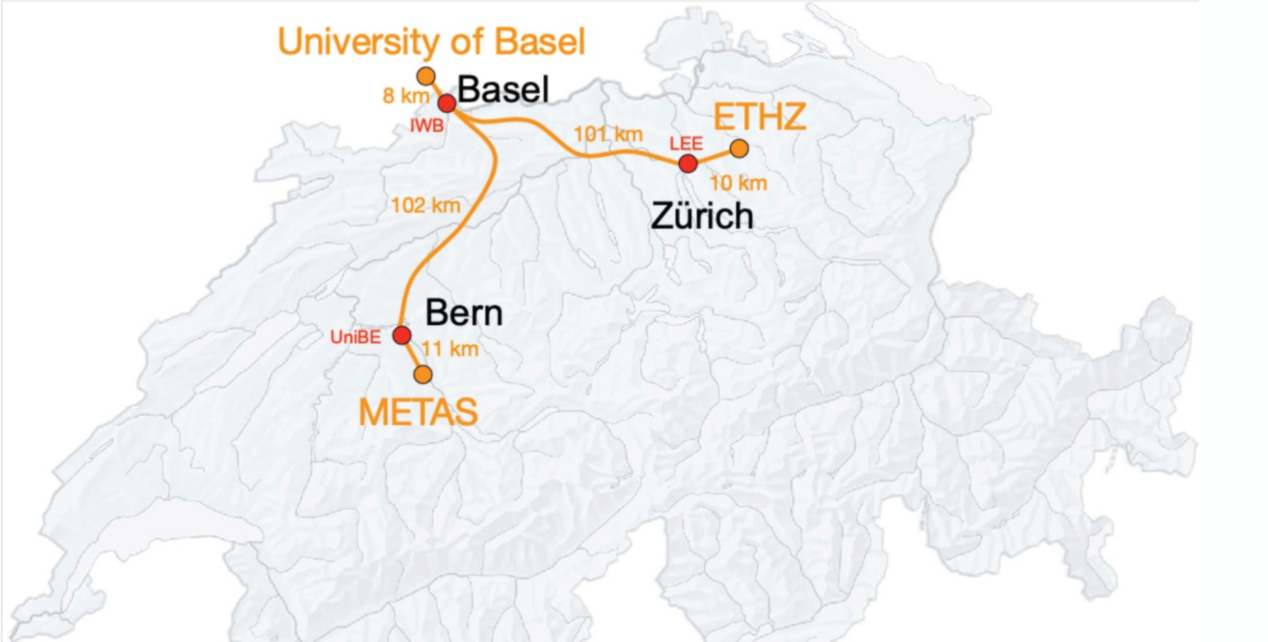
Limitations: Transit time of molecules through laser field, Doppler effect, Rb clock GPS reference

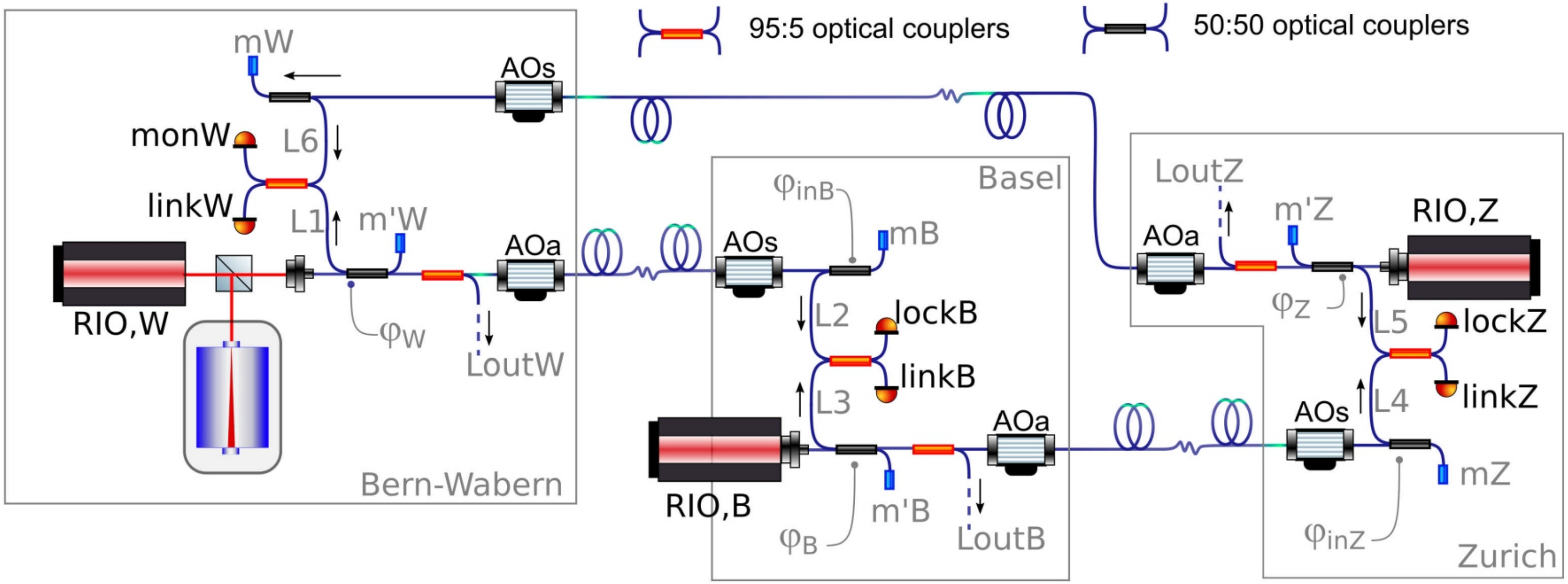


Next steps: Connection to METAS Cs primary frequency standard

(Sinergia project involving METAS, SWITCH, Unibas, ETH)

Closed-loop distribution of Cs primary frequency standard from METAS via a fiber network (Switch)



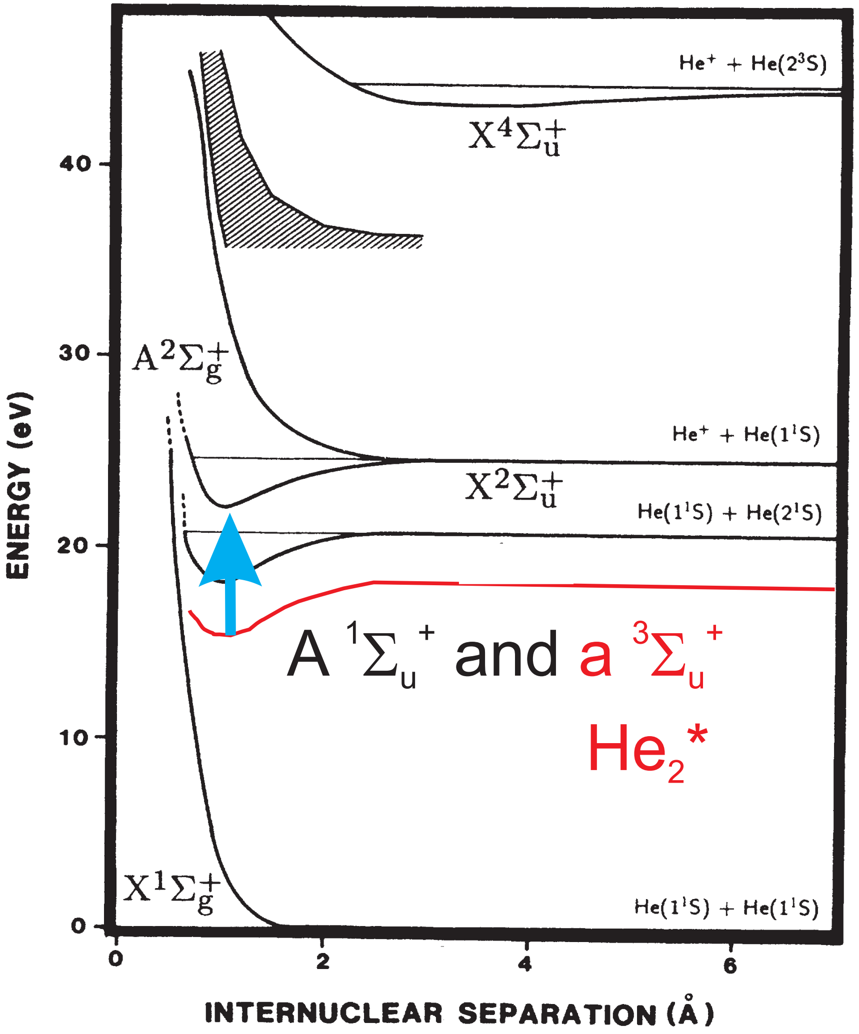


Spectroscopy of He_2 and He_2^+ using cold Zeeman-decelerated metastable He_2

Potential energy functions of He_2 and He_2^+

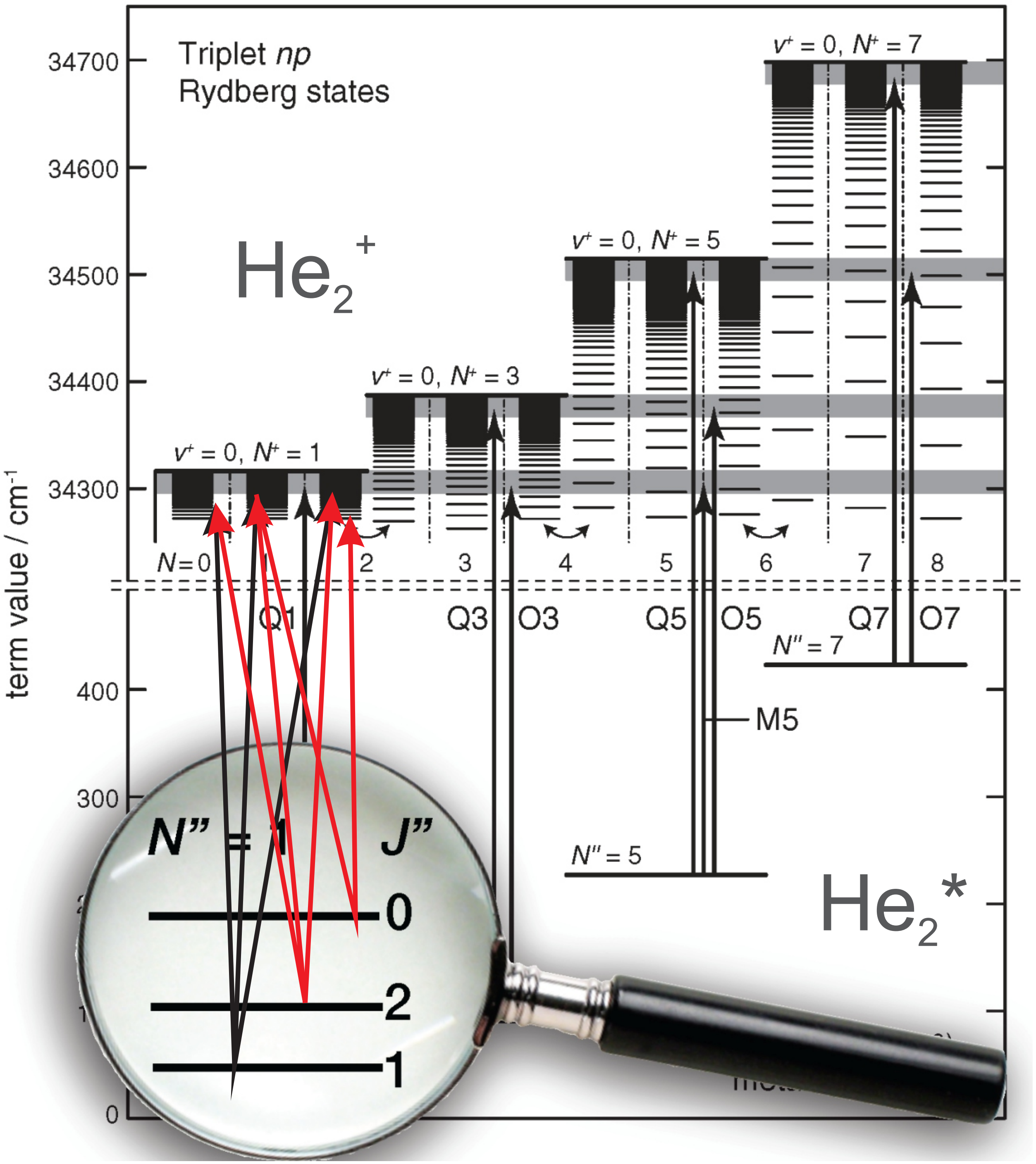
Slow beams of cold molecules:

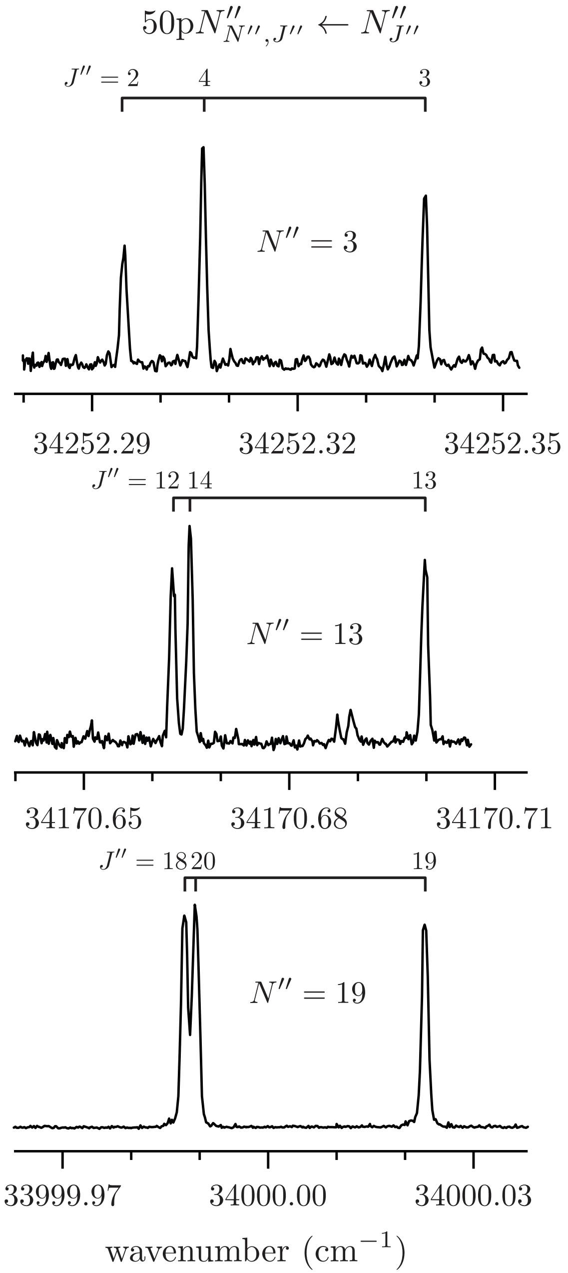
- long transit times through radiation fields
- reduction of Doppler broadening



Hill, PRA 40, 5006 (1989)

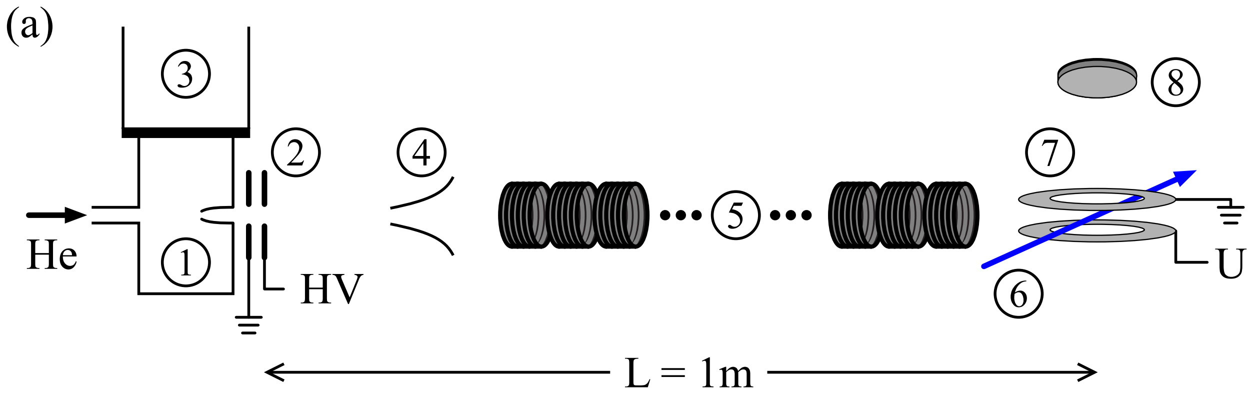
Fine structure of Rydberg spectra

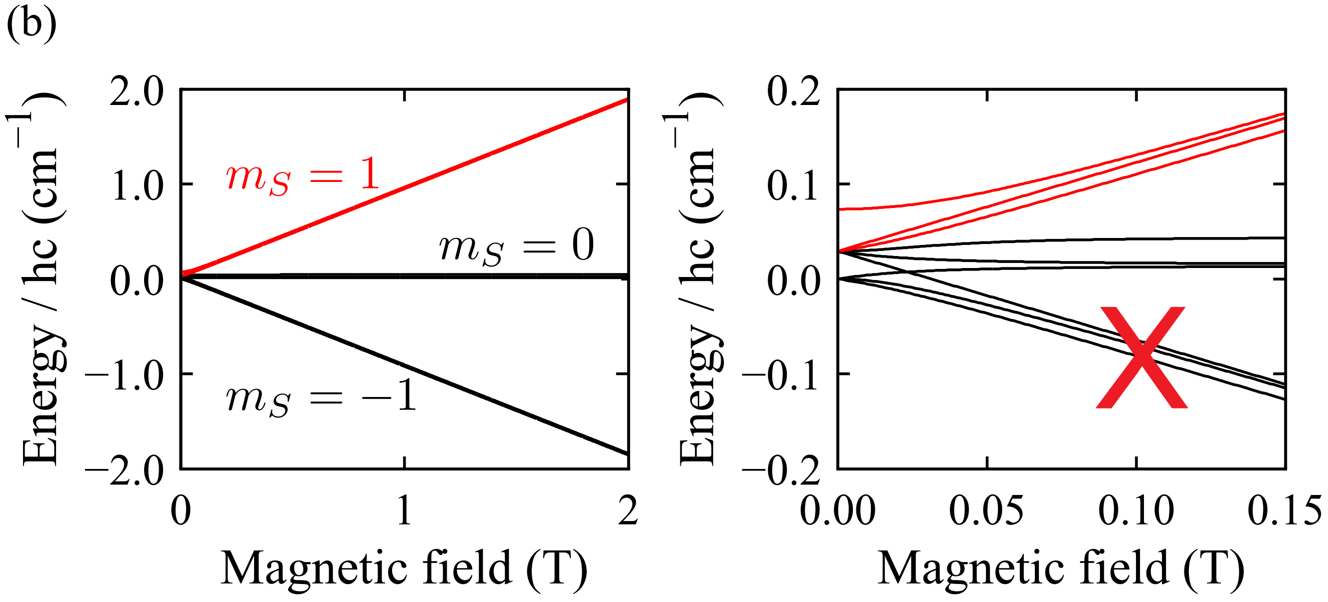


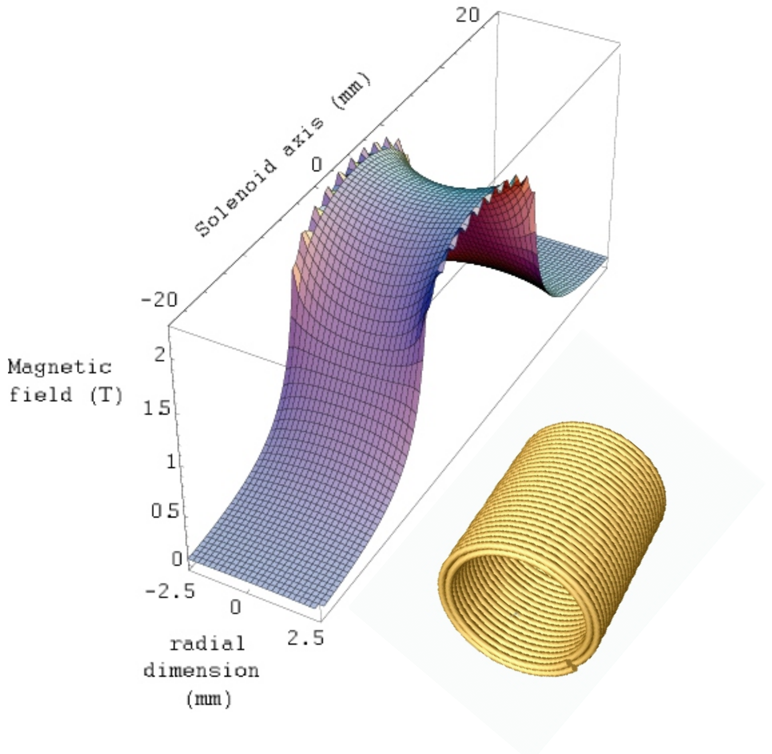


FWHM = 15 MHz

Multistage Zeeman deceleration of paramagnetic samples



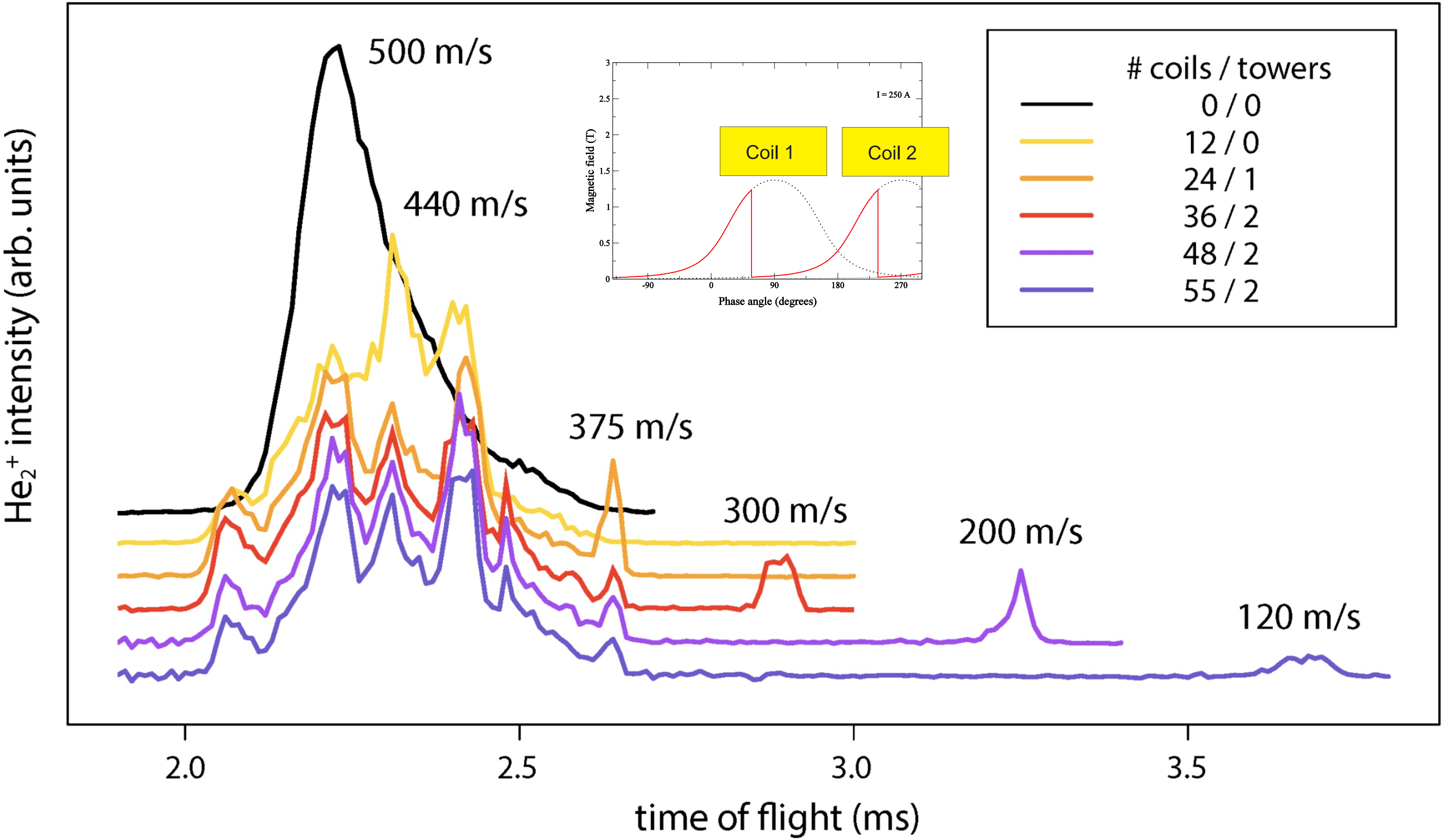




Coils:
Length 7.3 mm
Diameter 7 mm
64 windings
300 Amperes
B_{max}=2.2 Tesla
E_{Zeeman}=1.2 cm^{-1}

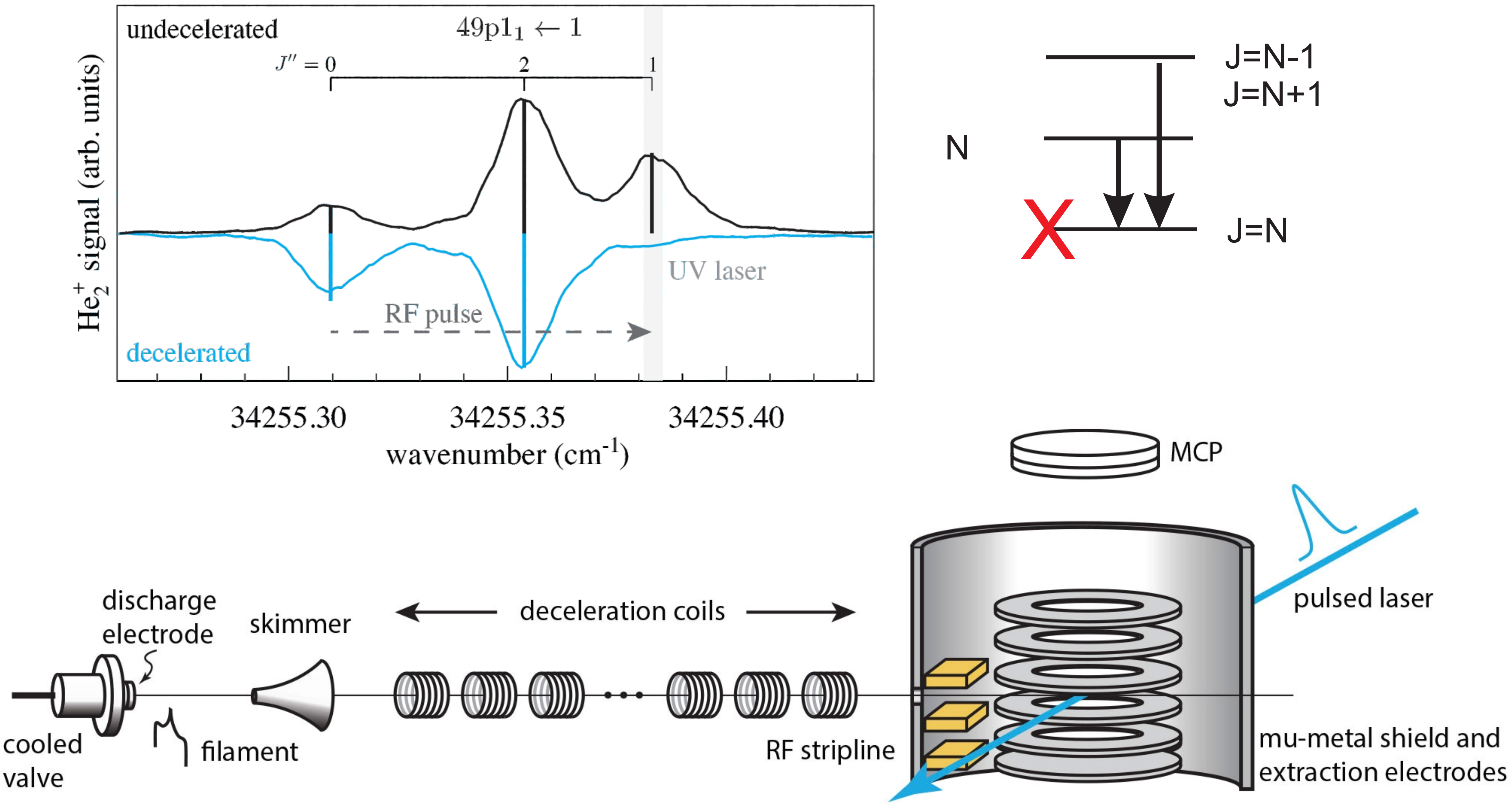
Vanhaecke et al., Phys. Rev. A **75**, 031402 (2007)
Motsch et al., Phys. Rev. A **89**, 043420 (2014)

Deceleration from 500 m/s to 120 m/s with 55 stages



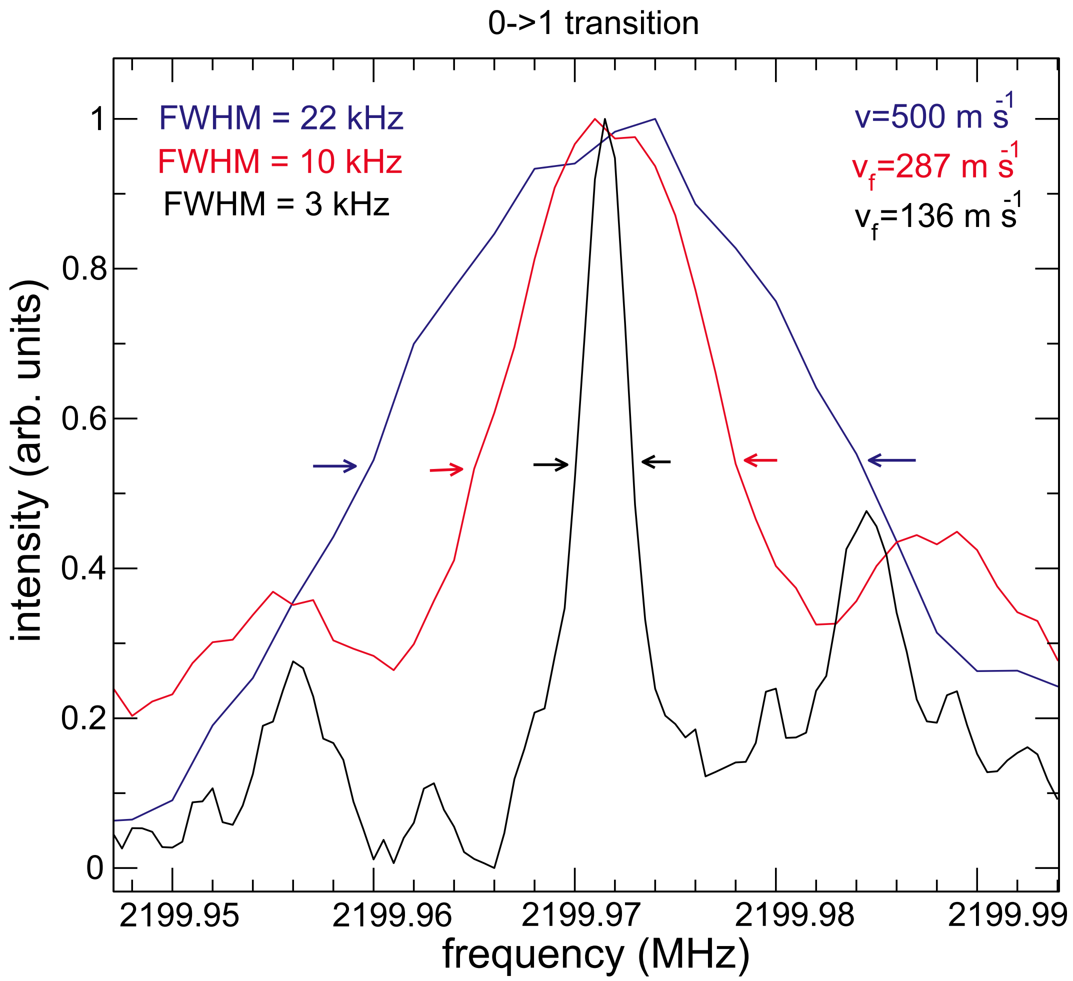
Motsch et al., Phys. Rev. A **89**, 043420 (2014)

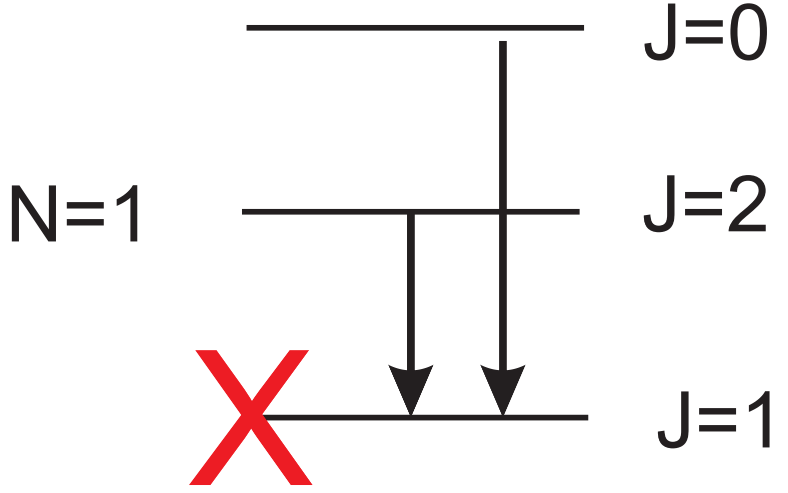
Principle of measurement of spin-rotation fine structure of a $^3\Sigma_u^+$ (v=0,N) state



Microwave measurements of spin-rotation fine structure of He_2^*

$a\ {}^3\Sigma_u^+$ (v=0,N=1)





2199.97147(29) MHz

Uncertainty: 290 Hz

Zeeman splitting: 11 mGauss

Semeria et al., PRA **98**, 062518 (2018)

Determination of ionization energy of He_2 and rotational structure of He_2^+

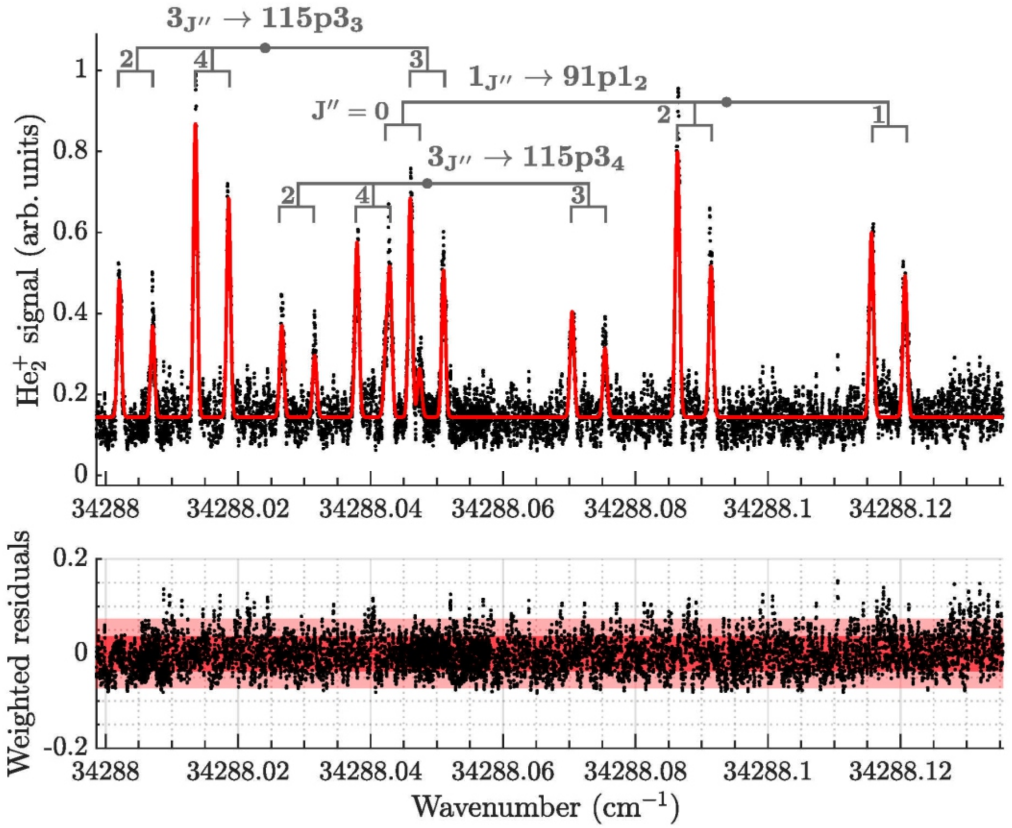
Ionization energy of metastable He_2

$E_I/(hc) = 34'301.207002(23)_{stat}(37)_{syst}\ cm^{-1}$

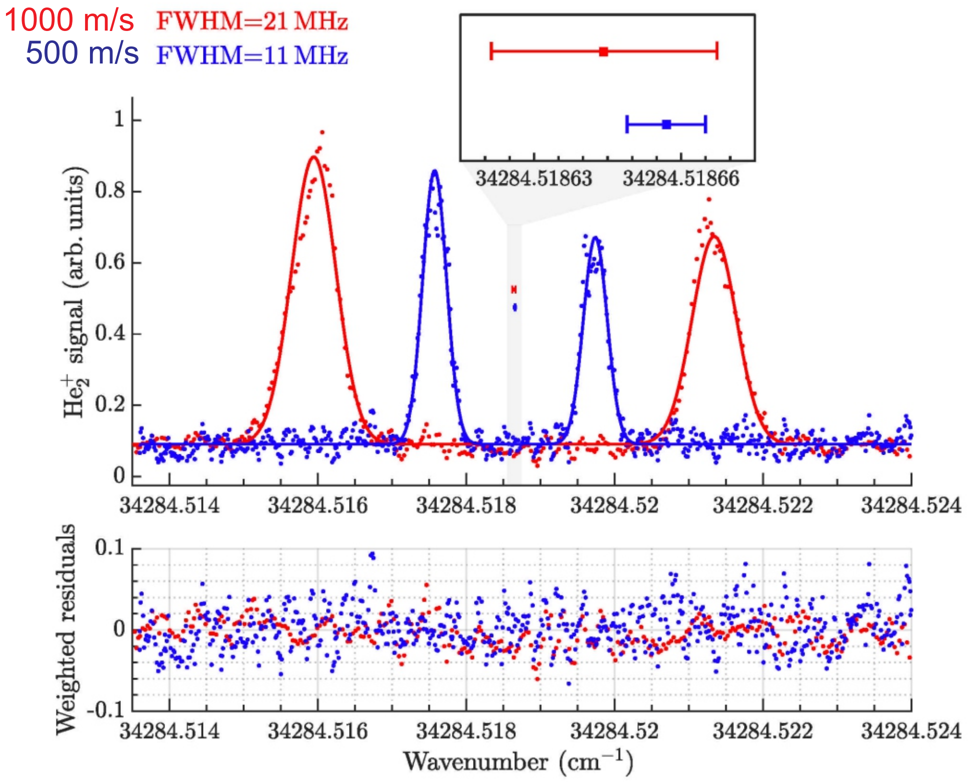
First rotational interval of He_2^+

$\Delta E(N=3-N=1)/(hc) = 70.937589(23)_{stat}(60)_{syst}\ cm^{-1}$

(Improved value of the polarizability of He and pressure standard)



$1_2 \rightarrow 81p1_2$



Semeria et al., PRL 124, 213001 (2020)

Conclusions:

Precision measurements in molecules as alternative to precision measurements in atoms

Dissociation energy of H_2:

- Most precise thermochemical determination ever performed
- ortho-para H_2 energy levels connected within 1.5 MHz
- Theory and experiment evolve hand in hand with continuous surprises

Ionization energy + fine structure of He_2 and rotational structure of He_2^+

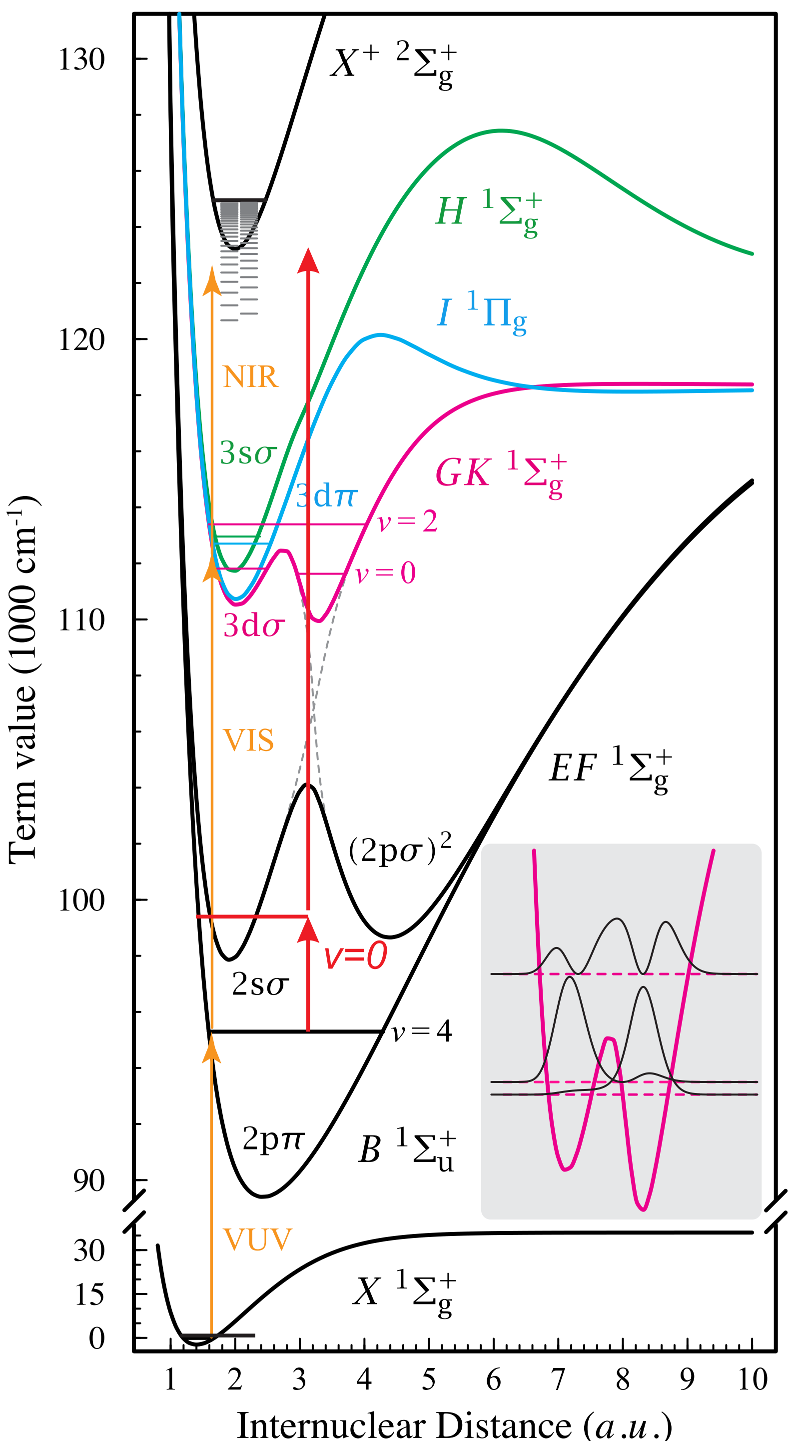
First precision measurements in 3,4-electron molecules

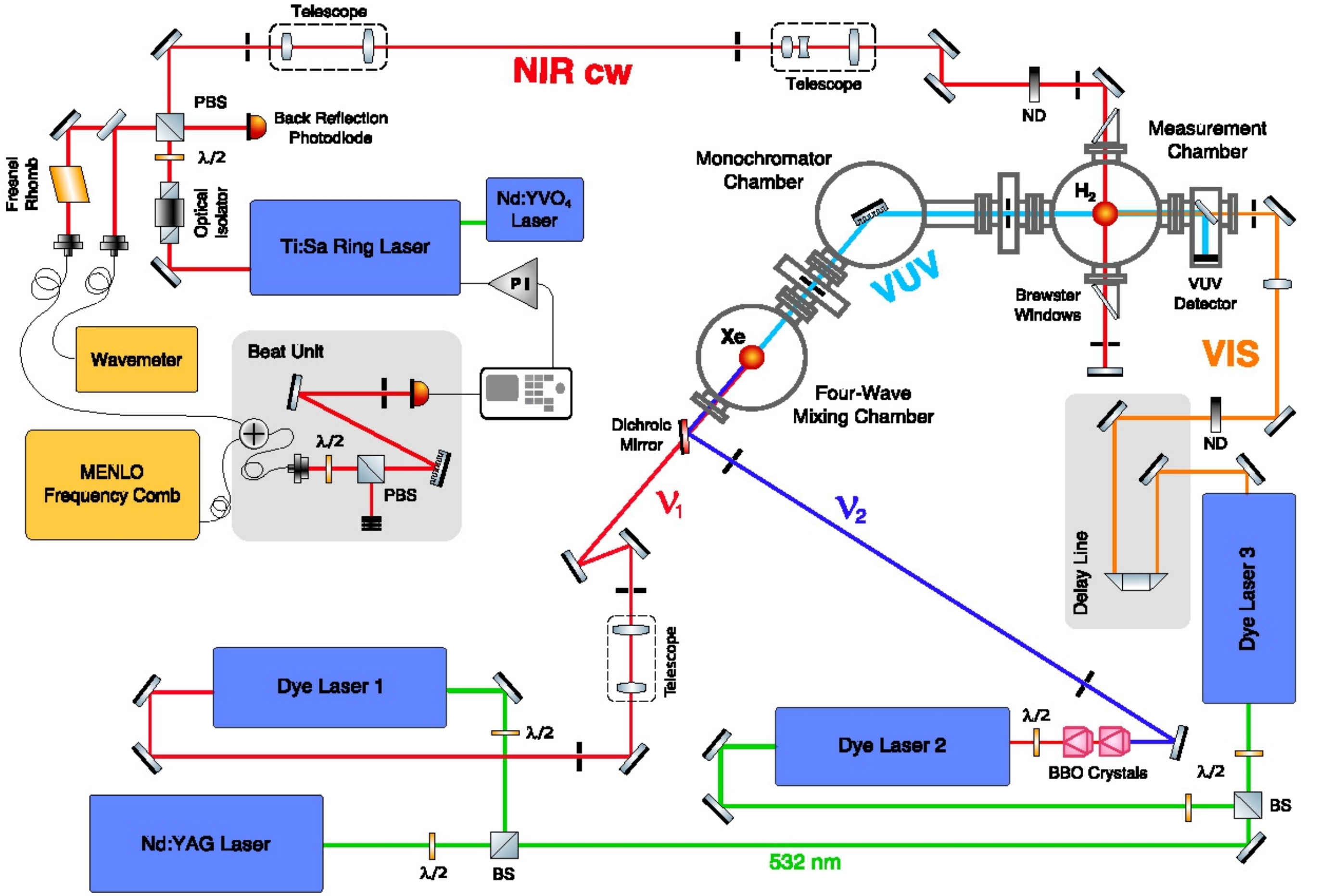
Possible route towards a pressure standard

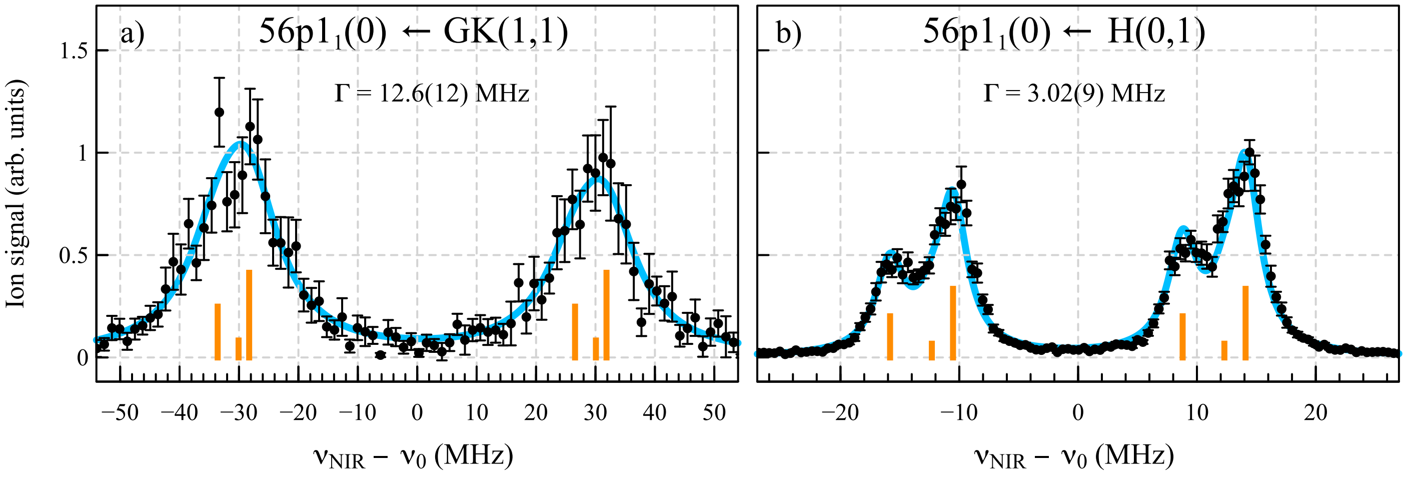
Financial support: **Swiss National Science Foundation, ERC advanced Grant Program**

Collaborations: Prof. W. Ubachs, Amsterdam and Dr. Ch. Jungen (Orsay)

Experiment (H_2)

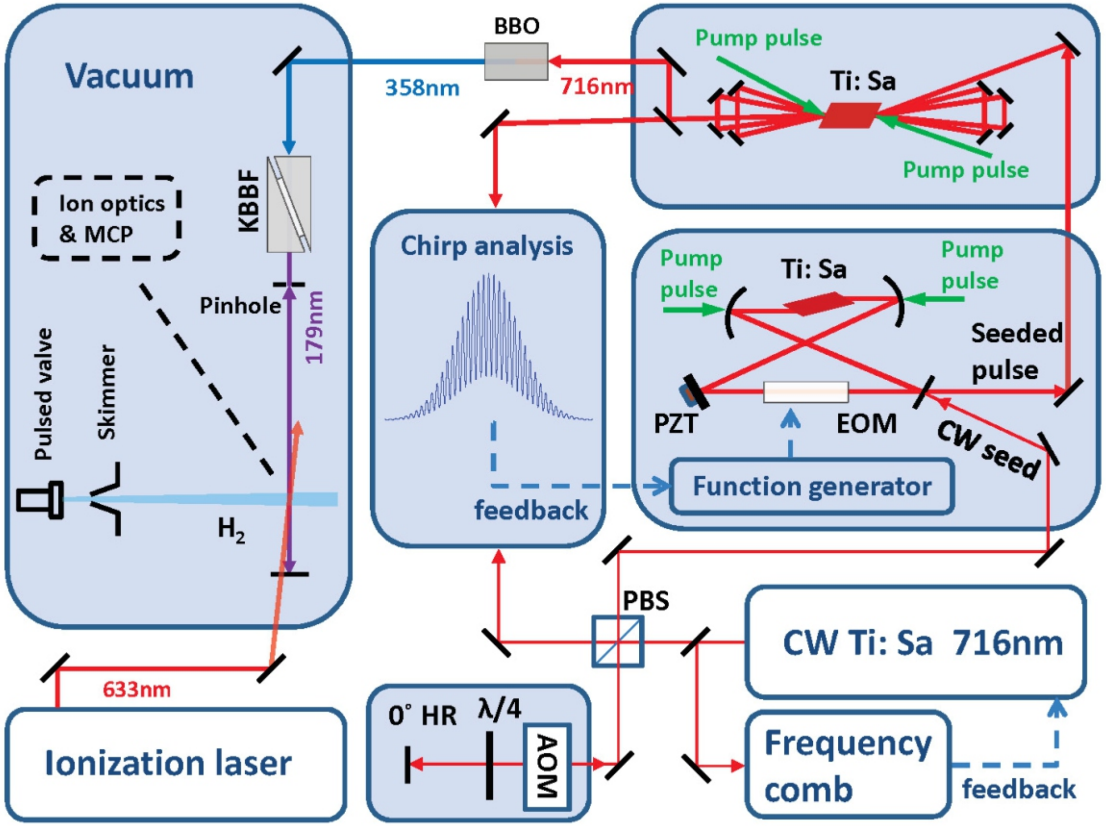


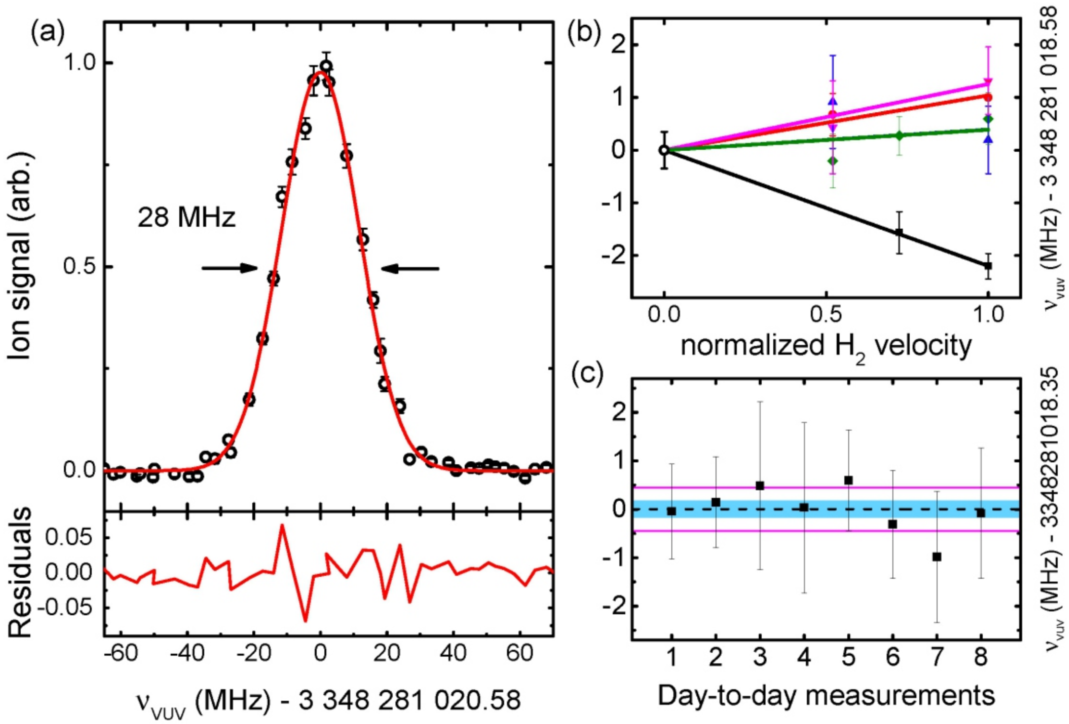




Result of Amsterdam experiment:

X(v=0,N=1) - GK(v=1,N=1): $\nu = 3\ 348\ 281\ 018.35(49)_{\text{stat}}(43)_{\text{sys}}$ MHz





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Transition frequencies and their uncertainties

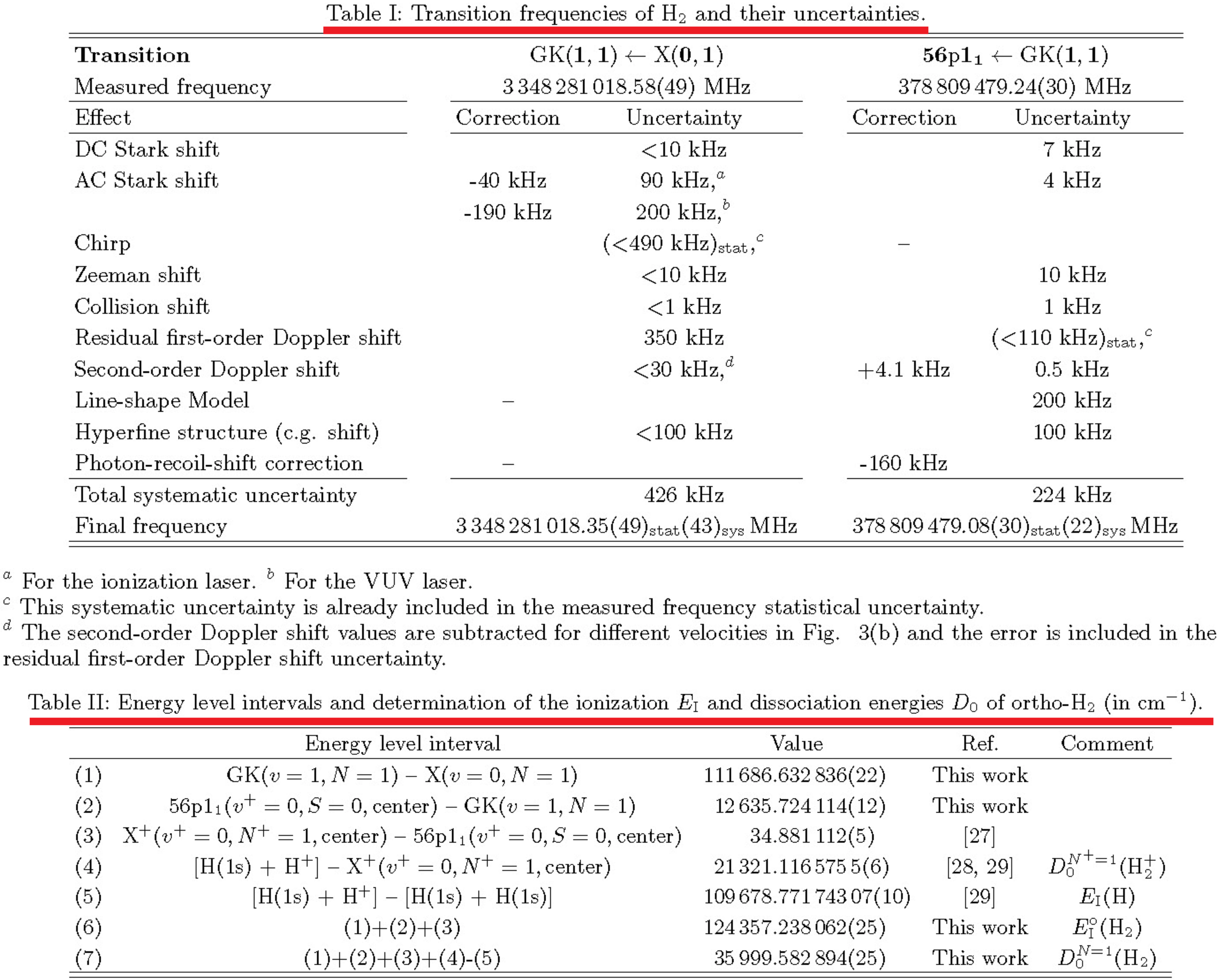

Table I: Transition frequencies of H_2 and their uncertainties.

Transition	$\mathbf{GK(1,1)} \leftarrow \mathbf{X(0,1)}$		$\mathbf{56p1_1} \leftarrow \mathbf{GK(1,1)}$	
Measured frequency	3 348 281 018.58(49) MHz		378 809 479.24(30) MHz	
Effect	Correction	Uncertainty	Correction	Uncertainty
DC Stark shift		<10 kHz		7 kHz
AC Stark shift	-40 kHz	90 kHz,[a]		4 kHz
	-190 kHz	200 kHz,[b]		
Chirp		(<490 kHz)$_{\mathrm{stat}}$,[c]	–	
Zeeman shift		<10 kHz		10 kHz
Collision shift		<1 kHz		1 kHz
Residual first-order Doppler shift		350 kHz		(<110 kHz)$_{\mathrm{stat}}$,[c]
Second-order Doppler shift		<30 kHz,[d]	+4.1 kHz	0.5 kHz
Line-shape Model	–			200 kHz
Hyperfine structure (c.g. shift)		<100 kHz		100 kHz
Photon-recoil-shift correction	–		-160 kHz	
Total systematic uncertainty		426 kHz		224 kHz
Final frequency	3 348 281 018.35(49)$_{\mathrm{stat}}$(43)$_{\mathrm{sys}}$ MHz		378 809 479.08(30)$_{\mathrm{stat}}$(22)$_{\mathrm{sys}}$ MHz	

[a] For the ionization laser. [b] For the VUV laser.

[c] This systematic uncertainty is already included in the measured frequency statistical uncertainty.

[d] The second-order Doppler shift values are subtracted for different velocities in Fig. 3(b) and the error is included in the residual first-order Doppler shift uncertainty.

Table II: Energy level intervals and determination of the ionization E_{I} and dissociation energies D_0 of ortho-H_2 (in cm^{-1}).

	Energy level interval	Value	Ref.	Comment
(1)	$\mathrm{GK}(v=1, N=1) - \mathrm{X}(v=0, N=1)$	111 686.632 836(22)	This work	
(2)	$56\mathrm{p}1_1(v^+=0, S=0, \mathrm{center}) - \mathrm{GK}(v=1, N=1)$	12 635.724 114(12)	This work	
(3)	$\mathrm{X}^+(v^+=0, N^+=1, \mathrm{center}) - 56\mathrm{p}1_1(v^+=0, S=0, \mathrm{center})$	34.881 112(5)	[27]	
(4)	$[\mathrm{H}(1\mathrm{s}) + \mathrm{H}^+] - \mathrm{X}^+(v^+=0, N^+=1, \mathrm{center})$	21 321.116 575 5(6)	[28, 29]	$D_0^{N^+=1}(\mathrm{H}_2^+)$
(5)	$[\mathrm{H}(1\mathrm{s}) + \mathrm{H}^+] - [\mathrm{H}(1\mathrm{s}) + \mathrm{H}(1\mathrm{s})]$	109 678.771 743 07(10)	[29]	$E_{\mathrm{I}}(\mathrm{H})$
(6)	(1)+(2)+(3)	124 357.238 062(25)	This work	$E_{\mathrm{I}}^{\mathrm{o}}(\mathrm{H}_2)$
(7)	(1)+(2)+(3)+(4)-(5)	35 999.582 894(25)	This work	$D_0^{N=1}(\mathrm{H}_2)$

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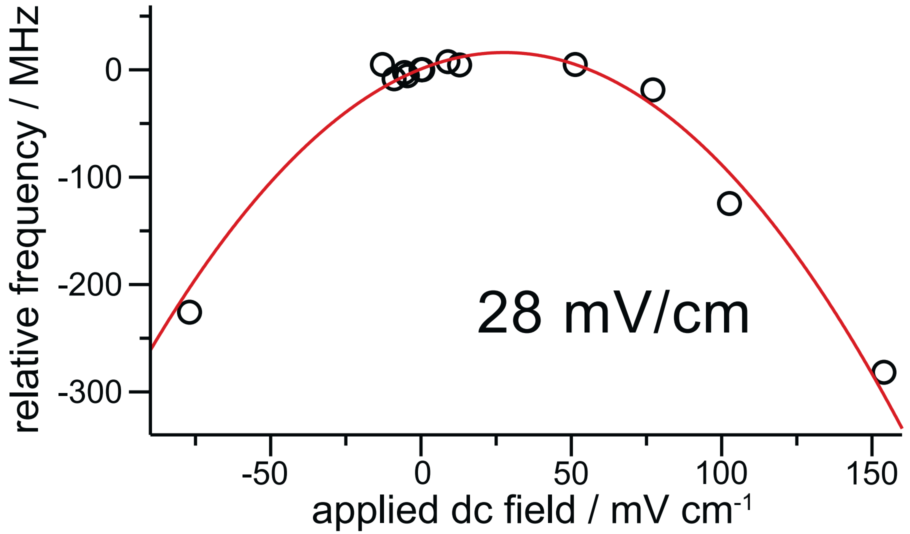
Absolute wave number measurements in H_2

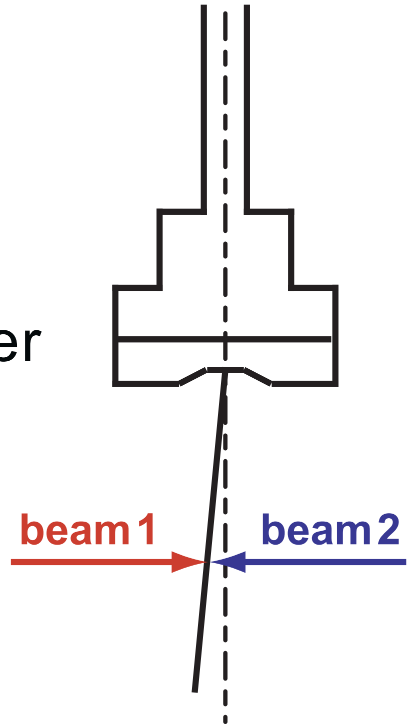
Sources of experimental errors

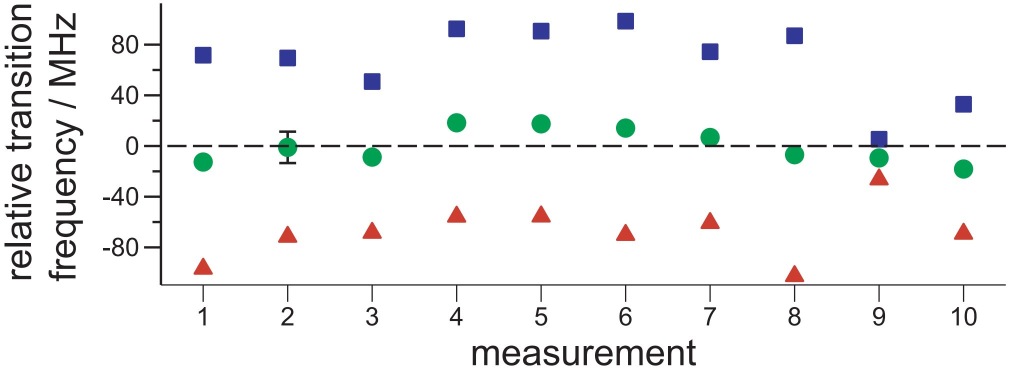
- dc Stark shift (15.4±2.4 MHz)



- ac Stark shift (0.0±4.4 MHz)
- shift induced by H_2^+ ions (0.0±5.2 MHz)
- frequency shift in the Ti:Sa amplifier (typically -8±1 MHz)

- elimiminate Doppler shift by using counter-propagating laser beams:





EF (v=0,N=1) → 56p (v^+=0,N^+=1)