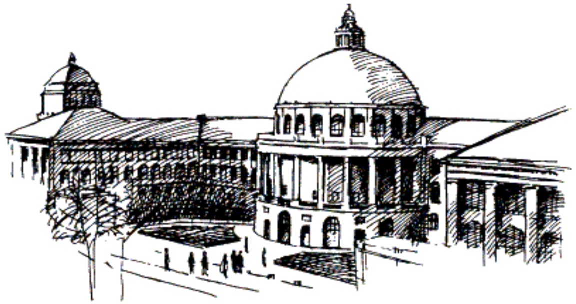
Precision measurements in Rydberg states of few-body atoms and molecules: H, He and H_2

PSI, Villigen, 9 October 2025



Frédéric Merkt
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Switzerland

I. Introduction

II. H-atom, the Rydberg constant and the proton-size puzzle
(Simon Scheidegger)

III. Molecules (H_2^+)
(Ioana Doran)

IV. He-atom, testing converged QED calculations
(Gloria Clausen)

V. Conclusions

Precision Rydberg spectroscopy in few-particle atoms and molecules

Precision measurements in H, H_2^+, He^+, He, H_2, ...

- electronic transitions
- fine structure
- hyperfine structure

Theory ⟷

- fundamental constants (R_∞,α,...)
- nuclear/particle properties
- fundamental interactions

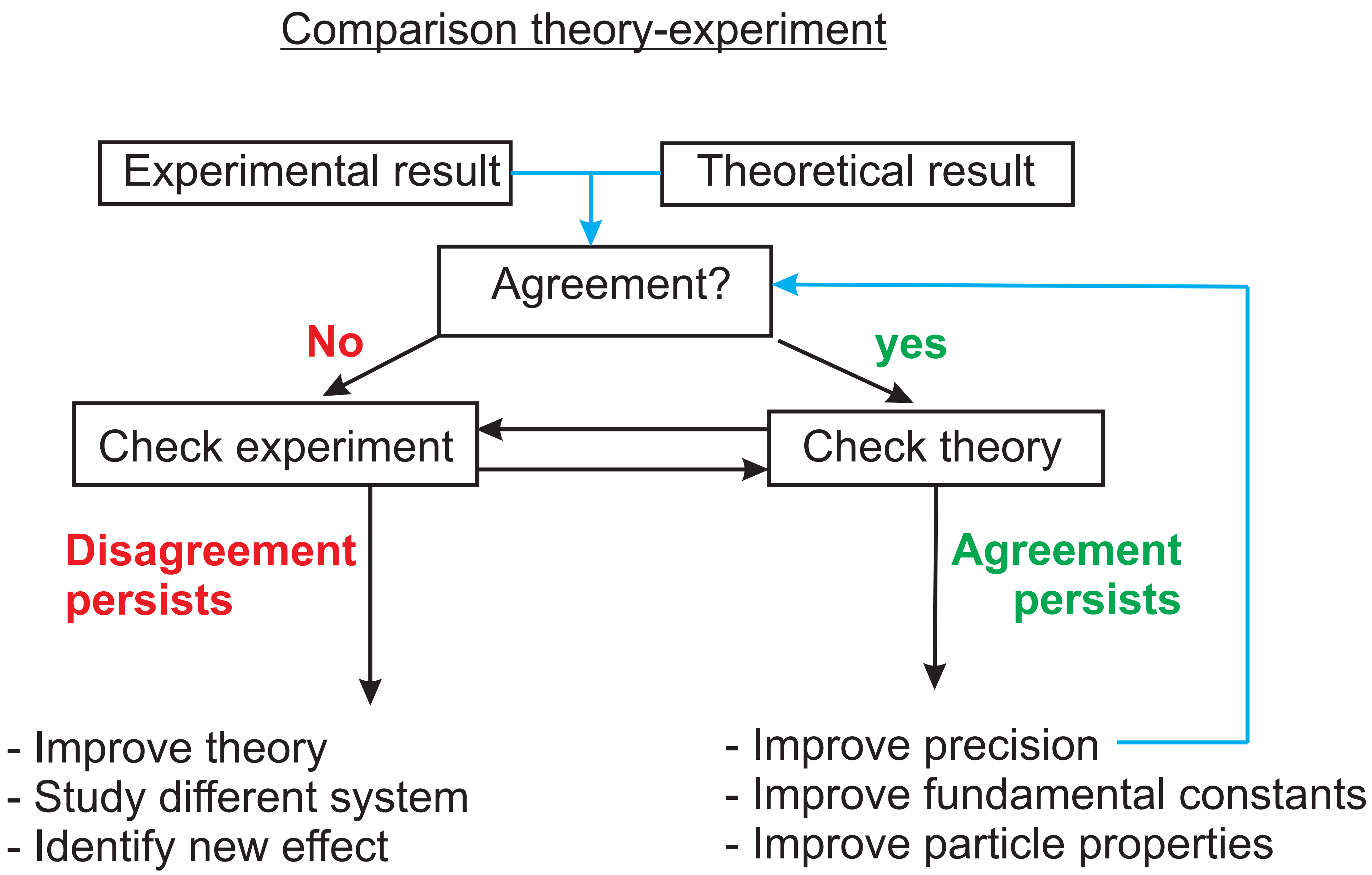
N-particle system —Rydberg-series extrapolation→ (*N*-1)-particle system

H — H^+ (proton radius r_p, Rydberg constant R_∞)

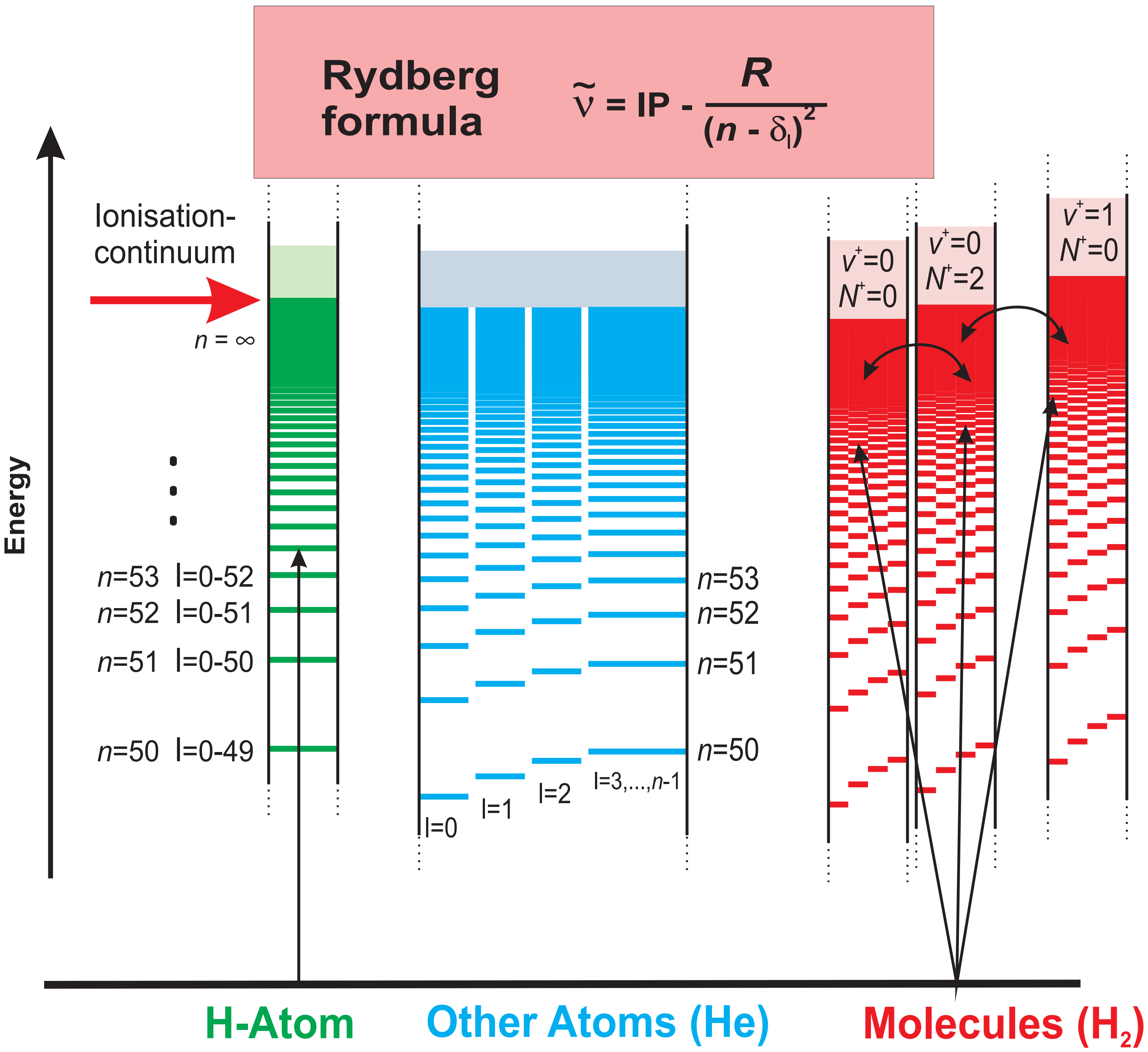
He — He^+ (electron binding energy, r_α, R_∞)

H_2 — H_2^+ (molecular effects; m_p/m_e, r_p, R_∞)

Physical constants and test of standard model of particle physics:
Delaunay et al., PRL **130**, 121801 (2023)
Tiesinga et al., Rev. Mod. Phys. **93**, 025010 (2021)


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

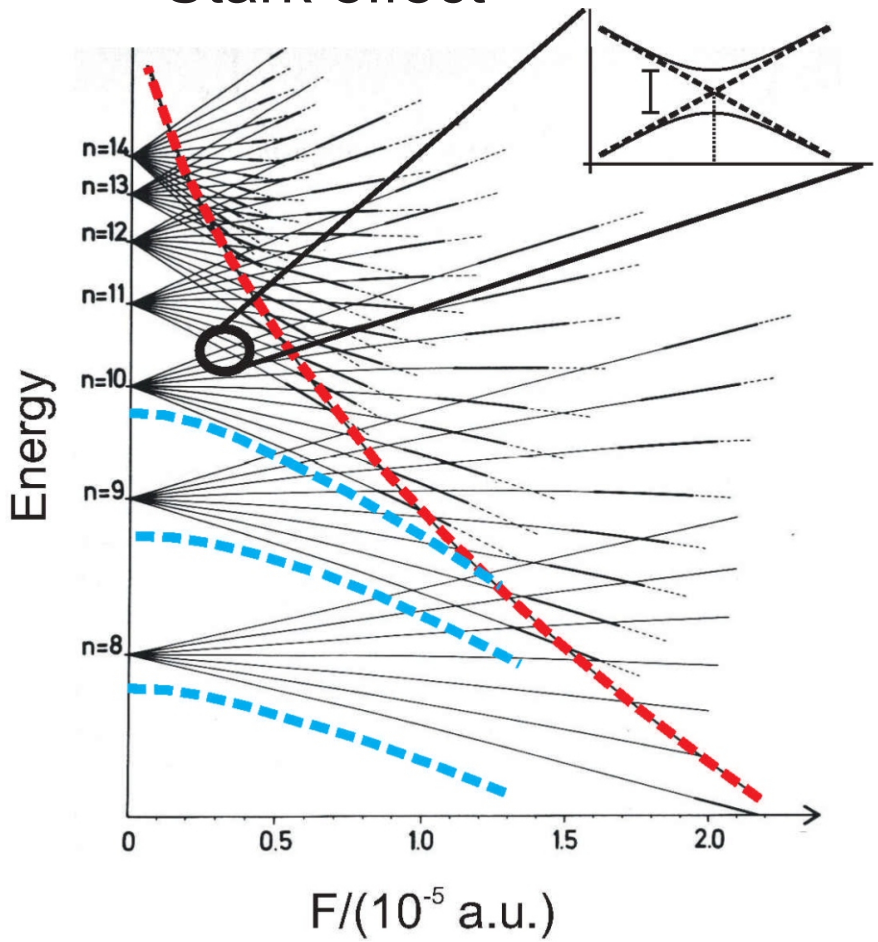
Atomic and molecular Rydberg states



Properties of Rydberg states

Property	n-dependence	n=100
Classical radius	$a_0\, n^2$	0.5 µm
Binding energy	$-R\, n^{-2}$	1.3 meV ~11 cm^{-1}
Ionisation field (V/cm)	$\propto n^{-4}$	2.5 V/cm
Radiative lifetime	$\propto n^3$	> 100 µs
Max. Induced dipole moment	$e a_0\, n^2$	30'000 Debye

Stark effect



Further properties:

Spacing between neighboring states of a series: $\propto n^3$

Resonant dipole-dipole interaction: $\propto n^4$

Polarisability: $\propto n^7$

Van der Waals interaction: $\propto n^{11}$

Rydberg states: From atoms to molecules

G. Herzberg

Atomic hydrogen

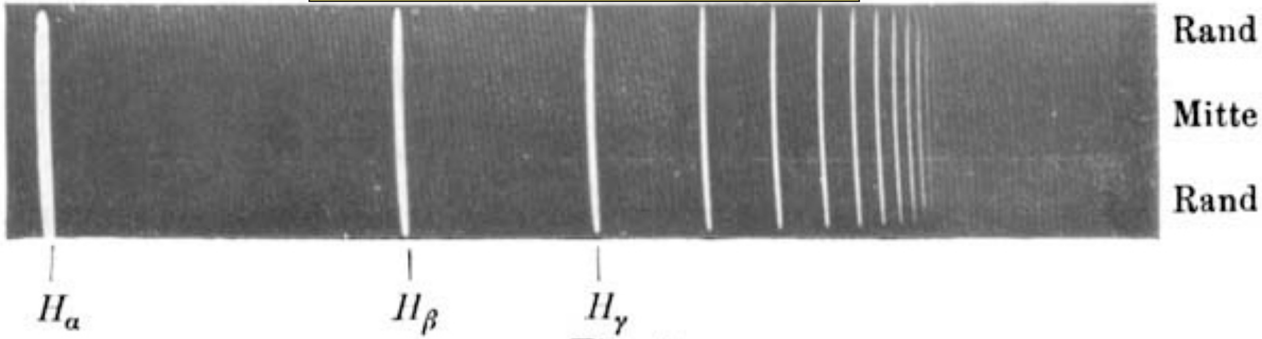
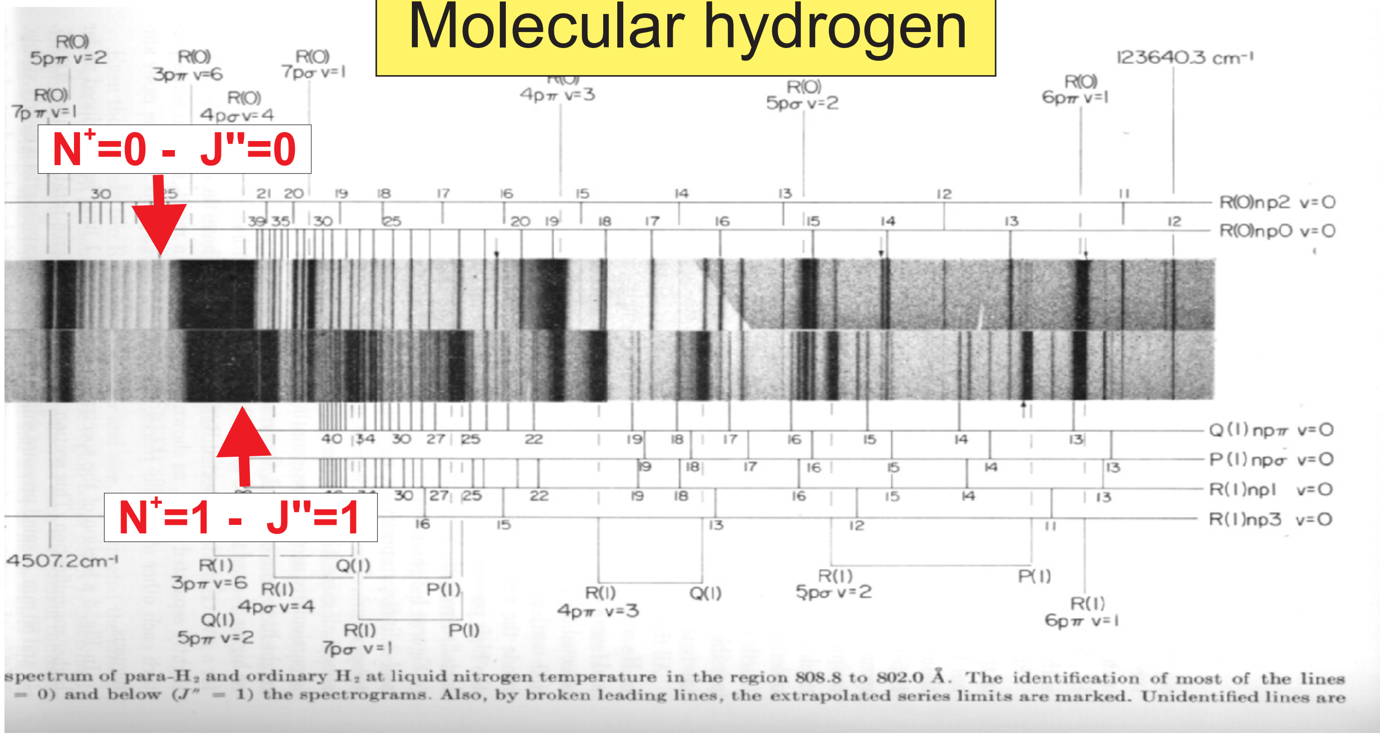


Fig. 4

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

Molecular hydrogen



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

Ab initio calculations in two-electron atoms

PHYSICAL REVIEW A **103**, 042809 (2021)

Complete $\alpha^7 m$ Lamb shift of helium triplet states

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(Received 1 March 2021; accepted 22 March 2021; published 5 April 2021)

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

α^2 α^4 α^5 α^6

TABLE VI. Breakdown of theoretical contributions to the ionization (centroid) energies of the $2\,^3S$ and $2\,^3P$ states of ^{4}He, in MHz. $R_\infty c = 3.289\,841\,960\,250\,8(64) \times 10^{15}$ Hz [33], $M/m_e = 7294.299\,541\,42\,(24)$ [33], $1/\alpha = 137.035\,999\,206\,(11)$ [34], $R = 1.678\,24\,(83)$ fm [15]. NS denotes the finite nuclear size correction; NP stands for the nuclear polarizability correction. The uncertainty of the theoretical α^2 contribution comes from the Rydberg constant; the uncertainty of the finite nuclear size correction comes from the nuclear radius.

	$(m/M)^0$	$(m/M)^1$	$(m/M)^2$	$(m/M)^3$	Sum
$2\,^3S$:					
α^2	−1 152 953 922.384 (2)	164 775.354	−30.620	0.006	−1 152 789 177.644 (2)
α^4	−57 629.312	4.284	−0.001		−57 625.029
α^5	3 999.431	−0.800			3 998.632
α^6	65.235	−0.030			65.205
α^7	−6.168 (1)				−6.168 (1)
α^8	0.158 (52)				0.158 (52)
NS	2.616 (3)				2.616 (3)
NP	−0.001				−0.001
Total					−1 152 842 742.231 (52)
Theory 2017 [17]					−1 152 842 741.4 (1.3)

(precision about 50 kHz)

Ab initio calculations in one-electron molecules

H_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

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

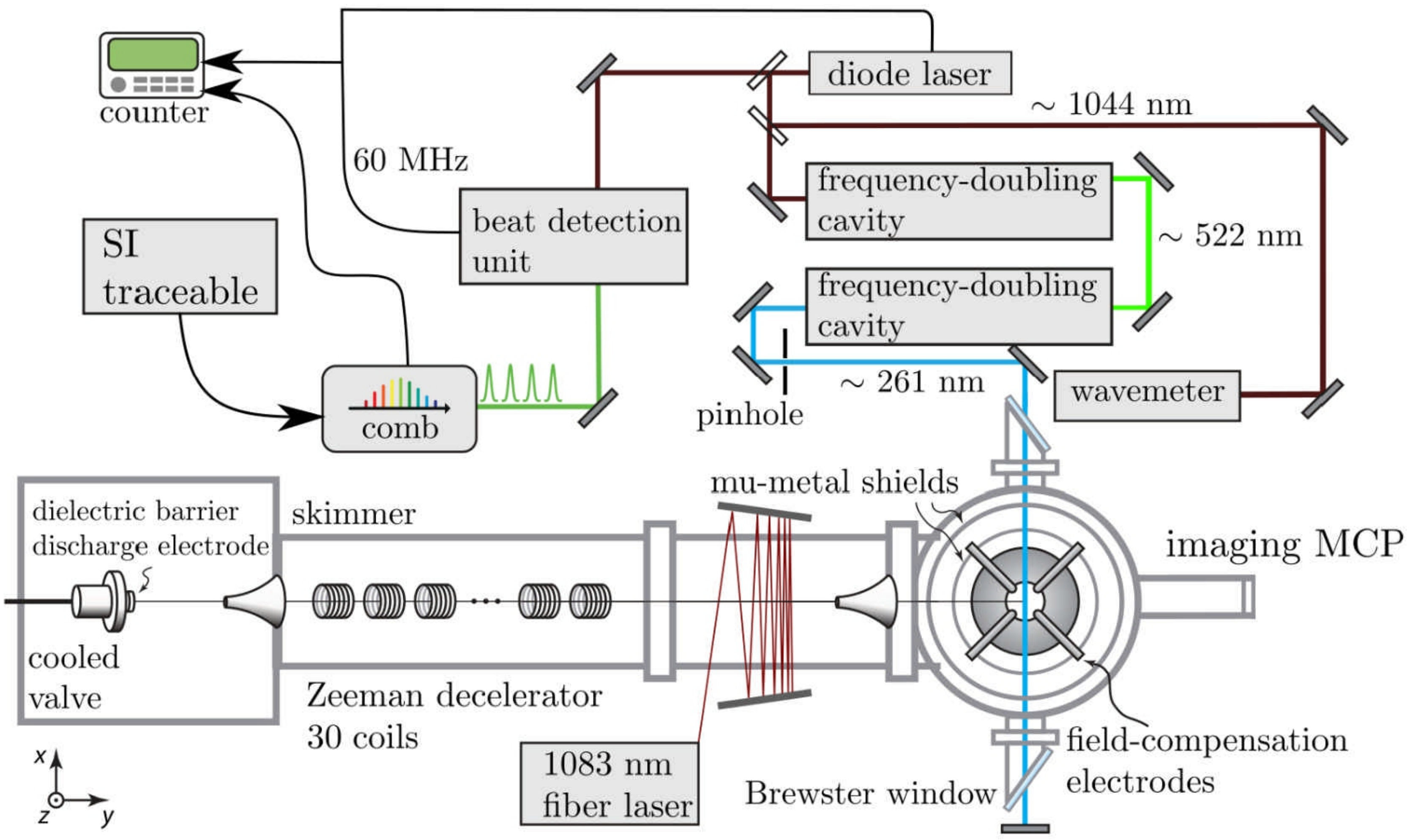
$$\nu(H_2^+) = \nu_0(H_2^+) + \frac{\Delta R_\infty}{R_\infty}\nu_0(H_2^+) + 2(R_\infty c) \times [-2.55528 \times 10^{-6}\Delta\mu_p - 8.117 \times 10^{-12}\Delta r_p],$$

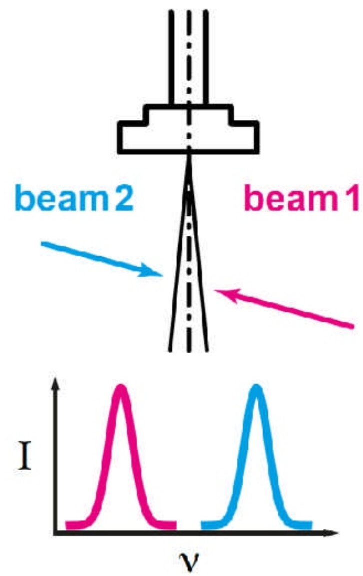
TABLE IV. Fundamental transition frequencies ν_{01} for H_2^+, D_2^+, and HD^+ molecular ions (in kHz). CODATA14 recommended values of constants. The first error is the theoretical uncertainty, the second error is due to the uncertainty in mass ratios.

	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)

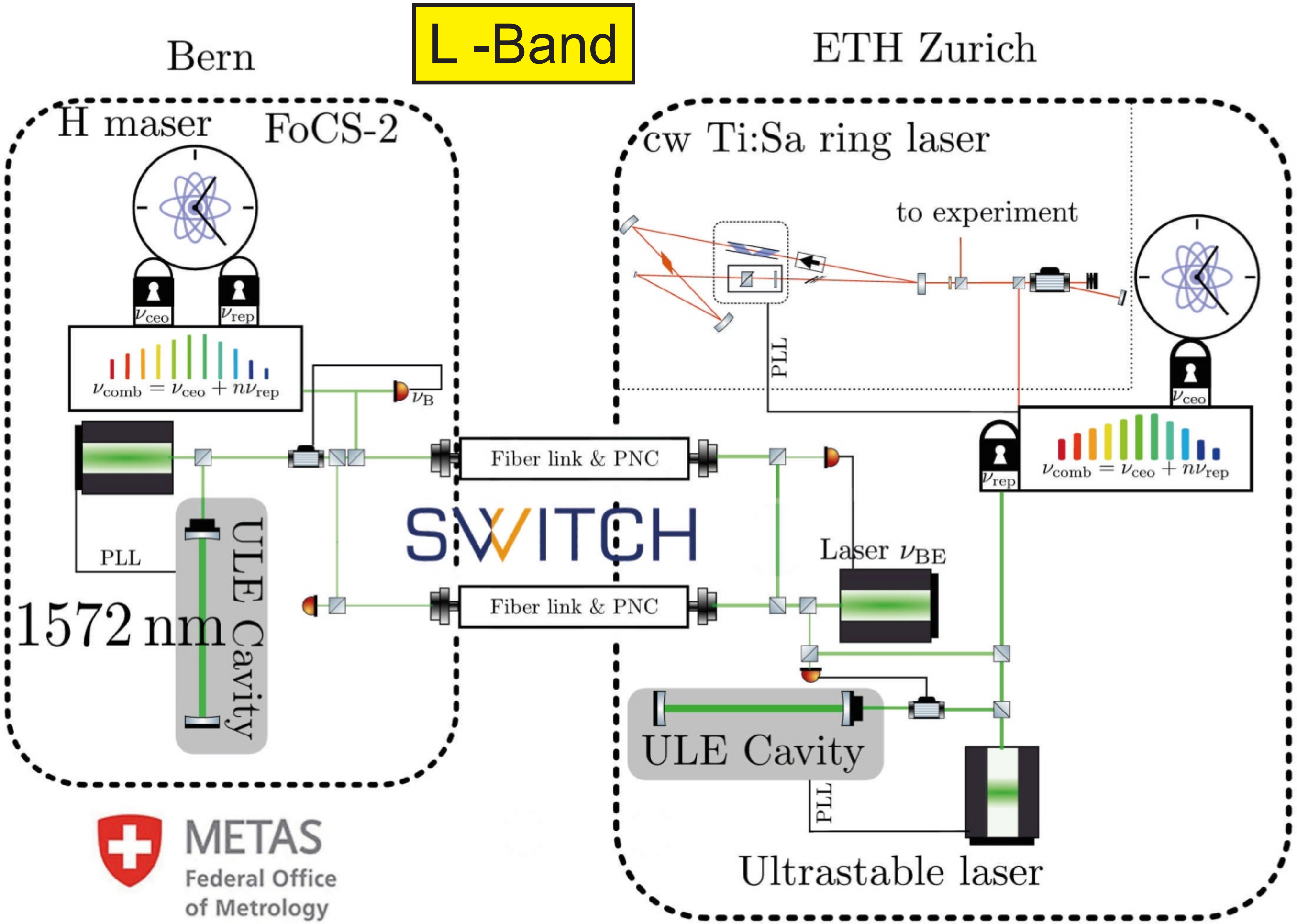
Generic experimental setup

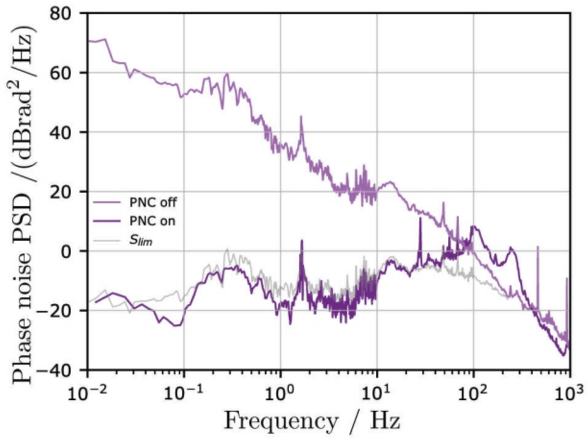
- supersonic beams (cryogenic valves)
- control of electric and magnetic fields
- Doppler-shift compensation
- SI-traceable frequency calibration





Laser-Frequency Calibration beyond Rb:GPS Standard





Link instability
4.7×10^{-16} at 1s
3.8×10^{-19} at 2000s

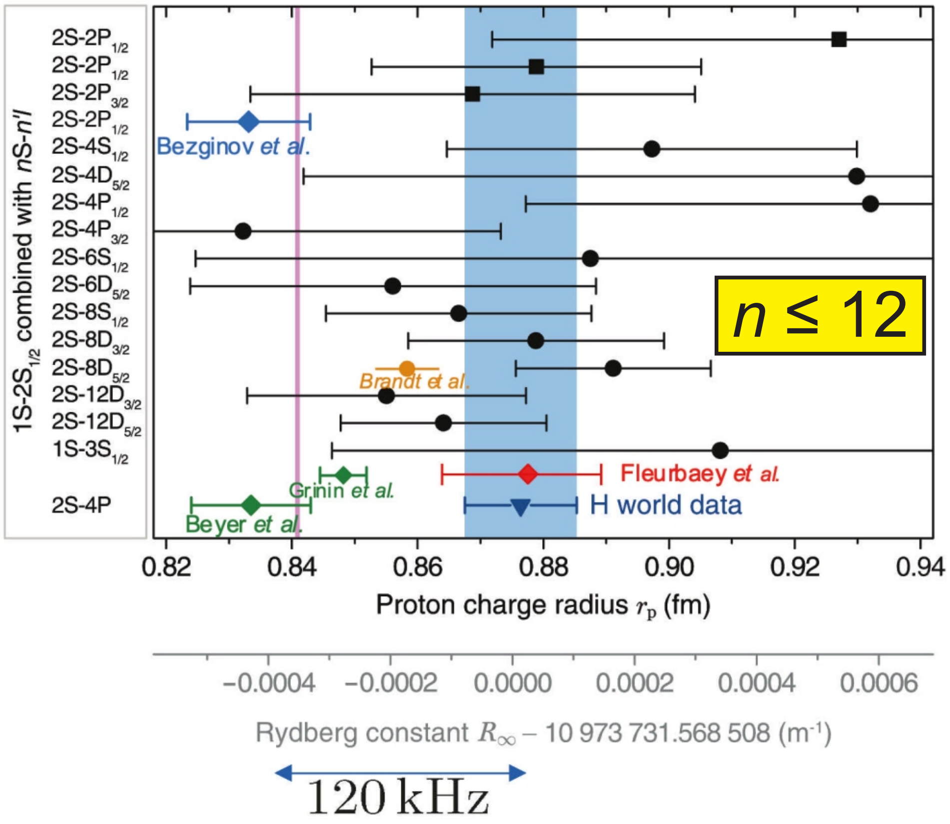
D. Husmann *et al.*, Opt.Express **29**, 24592-24605 (2021)

SI-traceable frequency calibration
Outside commercial C-Band (1530-1565 nm)

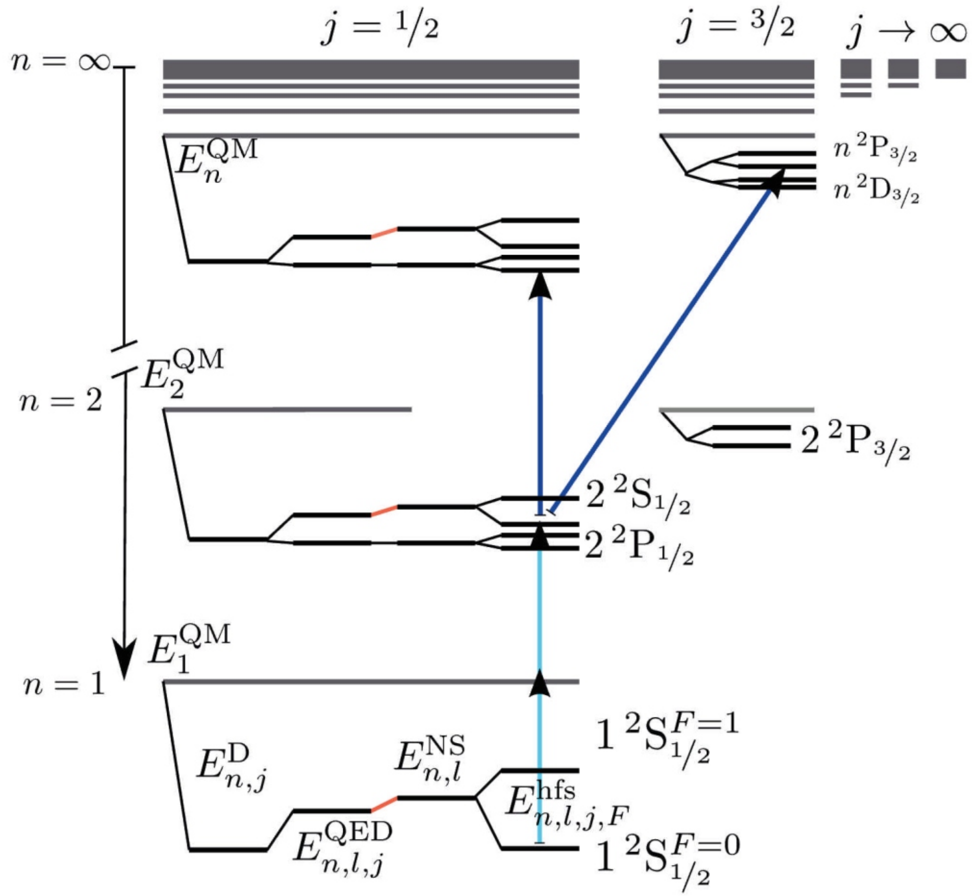
II. H-atom Rydberg states, the Rydberg constant and the proton-size puzzle

$$E_{n,l,j,f}(R_\infty, r_\mathrm{p}, \ldots) = E_n^{\mathrm{QM}} + E_{n,j}^{\mathrm{D}} + E_{n,l,j}^{\mathrm{QED}} + E_{n,l,j,f}^{\mathrm{hfs}} + E_{n,l}^{\mathrm{NS}}$$

$$R_\infty = 10\,973\,731.568\,160(21)\ \mathrm{m}^{-1}$$
$$r_\mathrm{p} = 0.8414(19)\ \mathrm{fm}$$



Tiesinga et al., J. Phys. Chem. Ref. Data **50**, 033105 (2021)
Eqs. (7) - (41)



adapted from A. Beyer *et al.*, Science **358**, 79 (2017)
R. Pohl *et al.*, Nature **466**, 213-216 (2010)
A. Grinin *et al.*, Science **370**, 1061 (2020)
A. D. Brandt *et al.*, Phys. Rev. Lett. **128**, 023001 (2022)
H. Fleurbaey *et al.*, Phys. Rev. Lett. **120**, 183001 (2018)
N. Bezginov *et al.*, Science **365**, 1007 (2019)

H-atom Rydberg States and the Rydberg Constant

Rydberg constant from high-*n* measurements using circular states ($m=l=n-1$)

(a) D. Kleppner's group, 1990-2002: transitions between circular states of H at $n \approx 30$

→ Sensitivity: $2R_\infty/27000$

J. C. De Vries, A precision millimeter-wave measurement of the Rydberg frequency, PhD thesis, MIT, 2002

cR_∞ = 3 289 841 960 306(69) kHz
cR_∞ = 3 289 841 960 368(16) kHz (CODATA 1998)
cR_∞ = 3 289 841 960 250.8(6.4) kHz (CODATA 2018)

(b) G. Raithel's group, ongoing: transitions between circular Rydberg states of Rb

A. Ramos et al., Phys. Rev. A **96**, 032513 (2017)

(c) U. D. Jentschura and D. C. Yost: Proposed measurement with *n=18* circular Rydberg states of H.

Phys. Rev. A **108**, 062822 (2023)

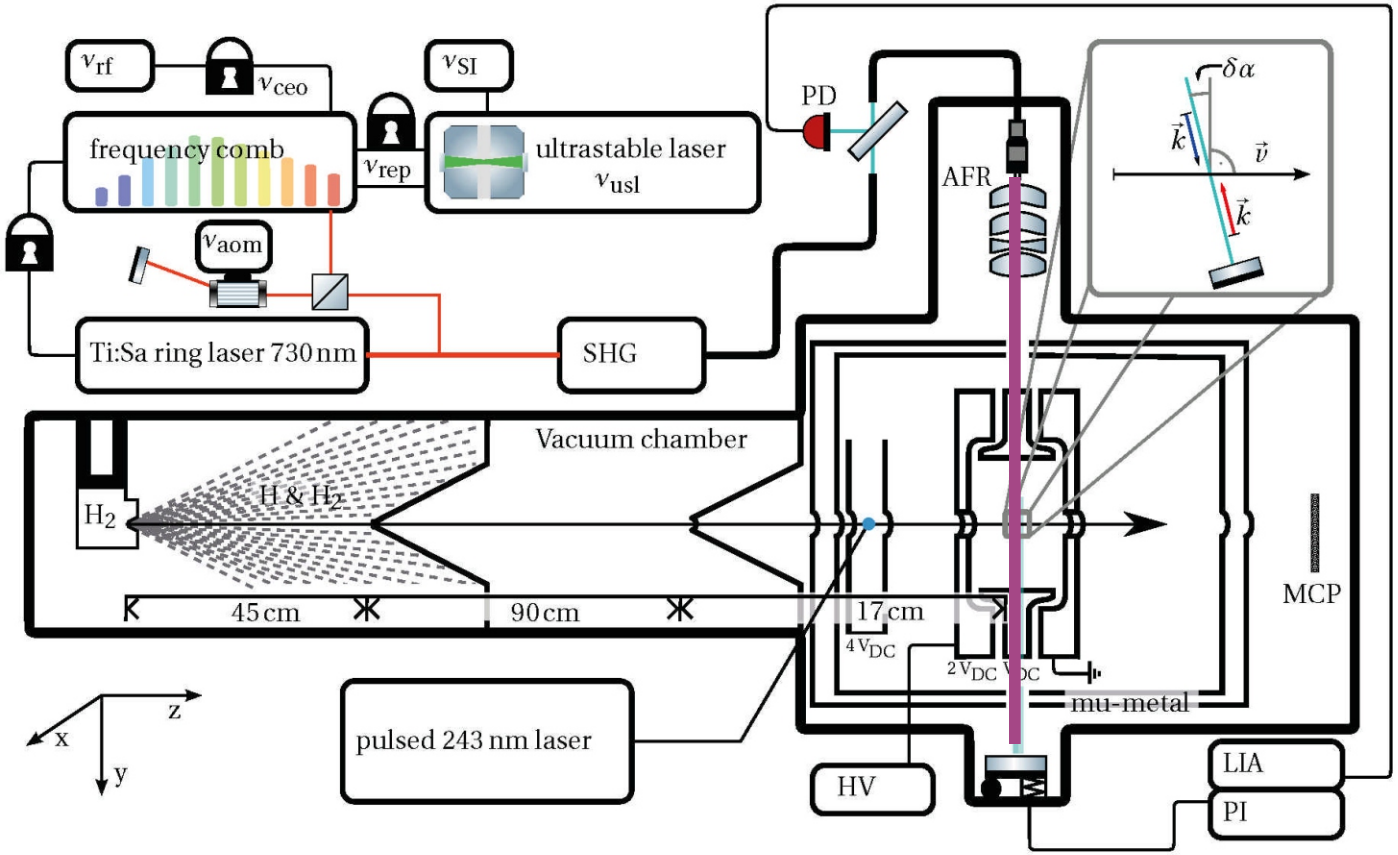
Here: Rydberg constant from $m_l \geq 1$ Rydberg states ($2 \leq n \leq \infty$) → Sensitivity: $R_\infty/4$

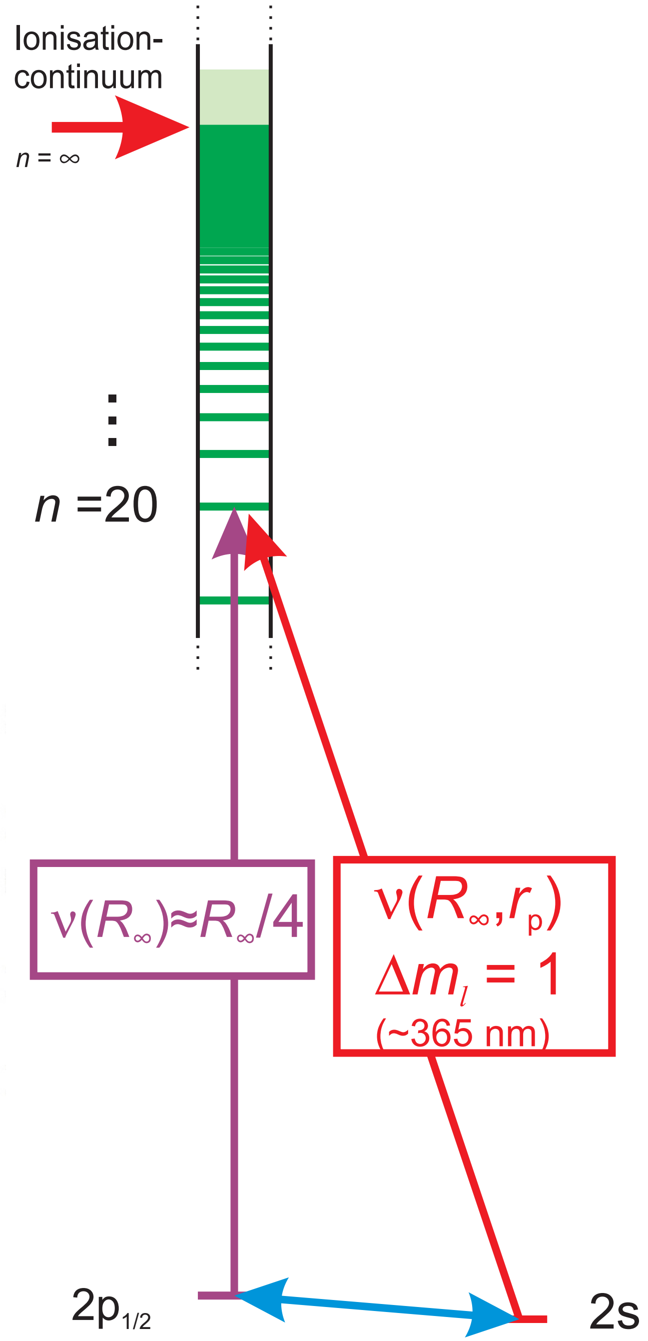
Experimental approach

Supersonic beam of metastable H (2s)

Overcome the stray-field problem: Apply fields intentionally and resolve the Stark states

Transitions to high-*n* Rydberg states with $m_l \geq 1$ (r_p insensitive)

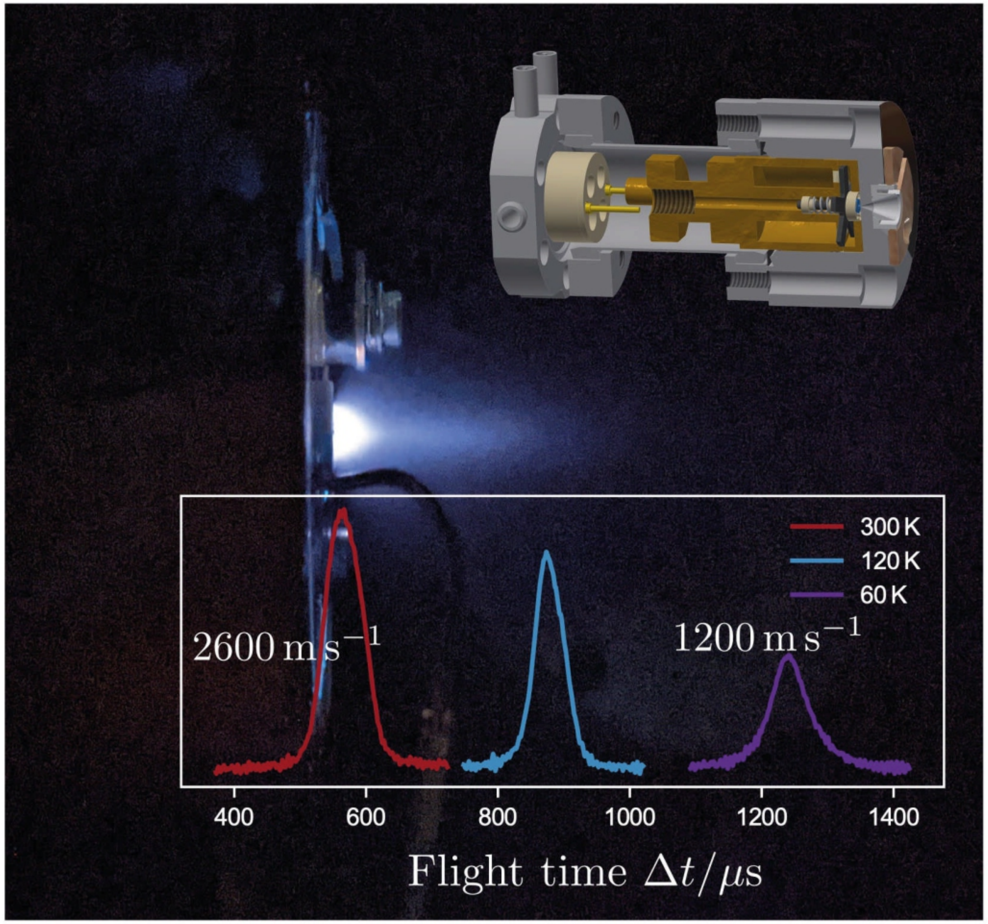




ν = 909.8717(32) MHz

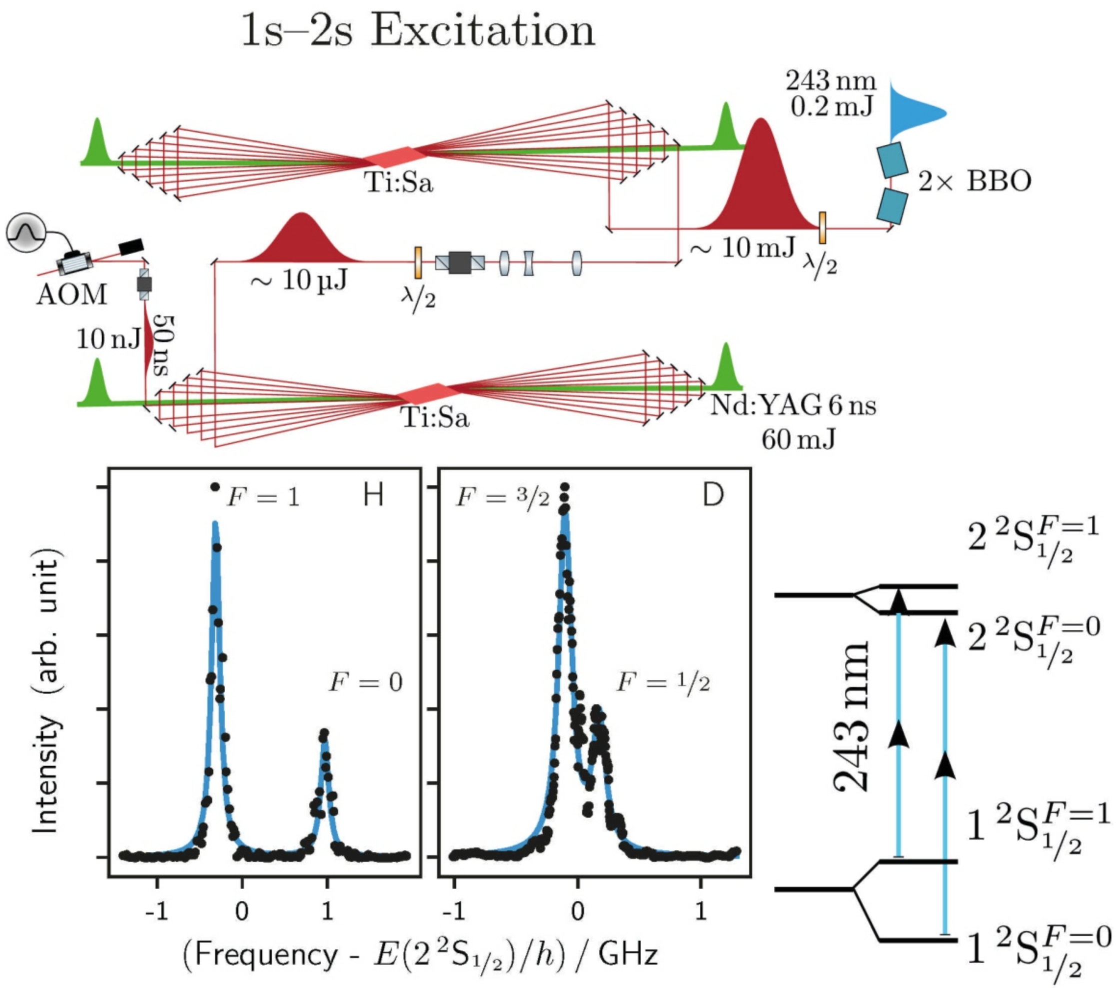
Bezginov et al., Science **365**, 1007 (2019)

H-Atom Source



$T_{\parallel} \approx 12\,\mathrm{mK}$

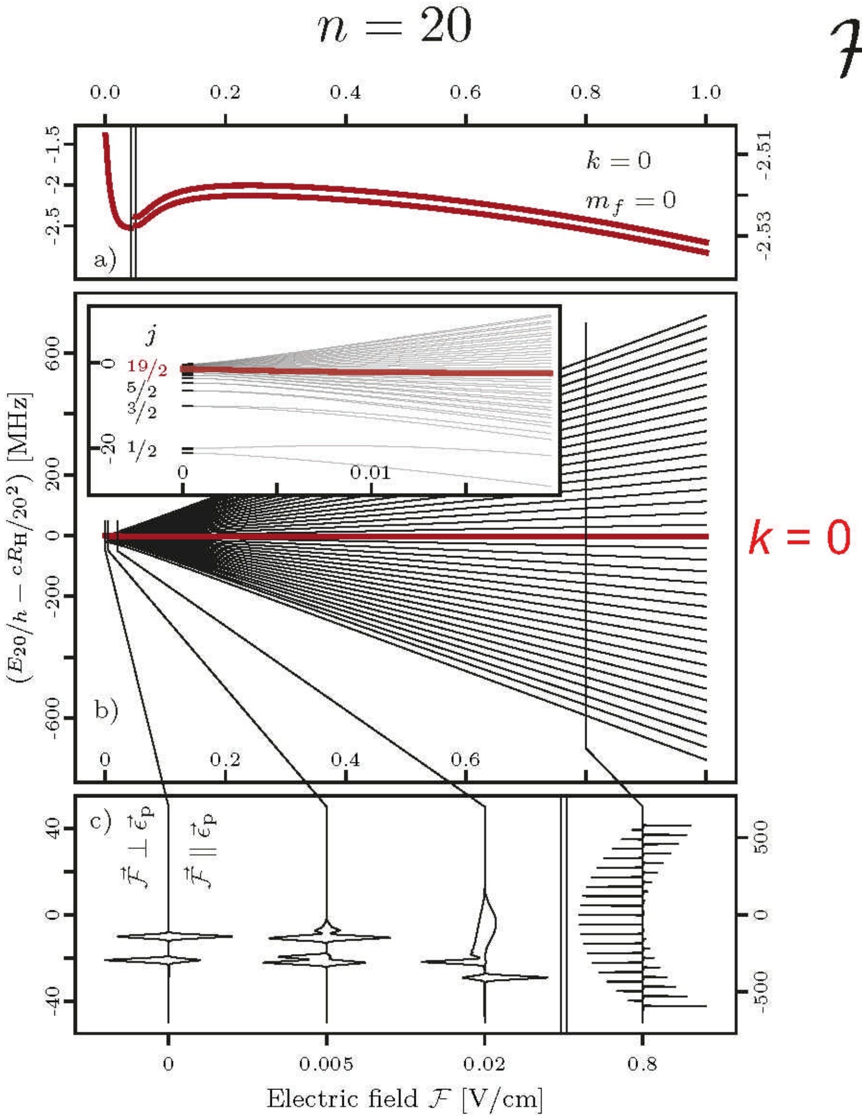
$T_{\perp} \approx 10\,\mu\mathrm{K}$

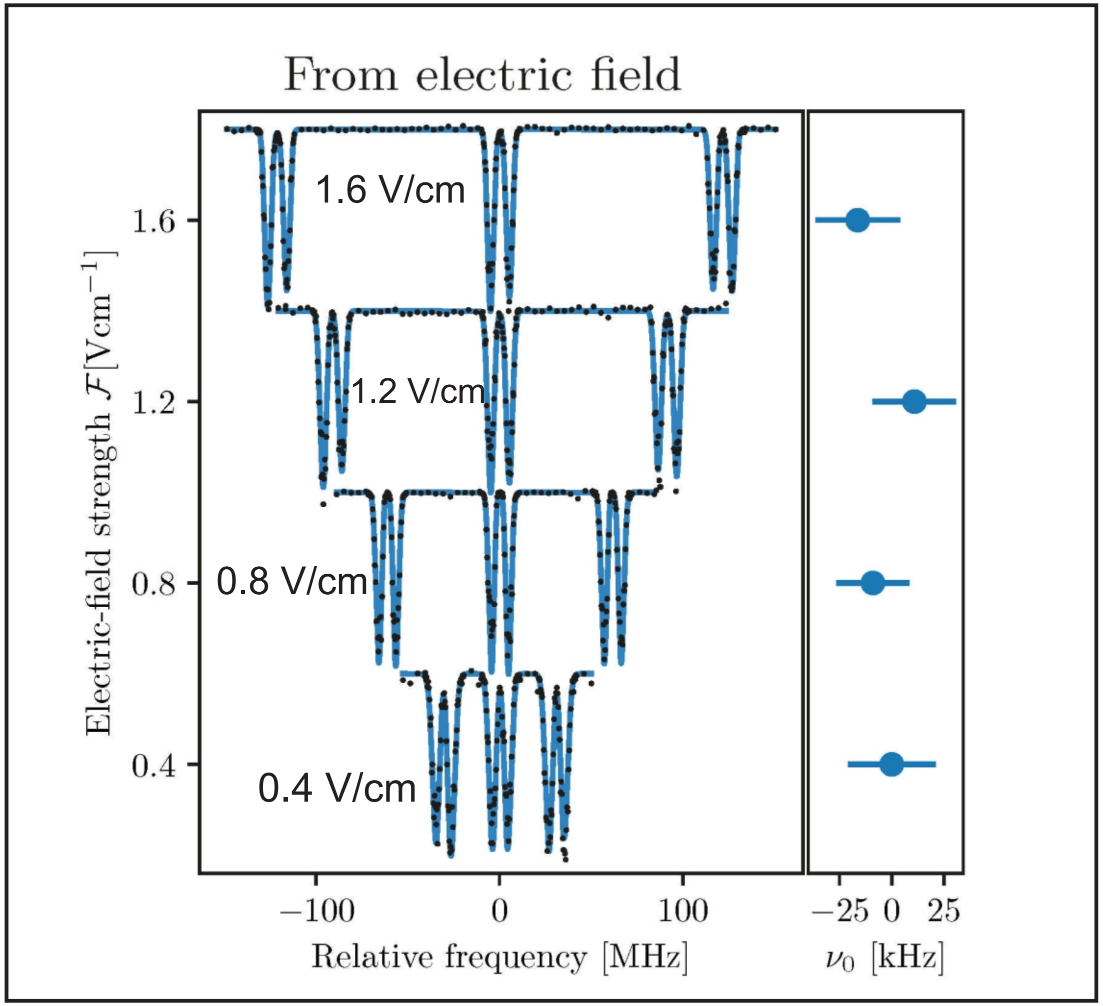


S. Scheidegger *et al.*, J. Phys. B **55**, 155002 (2022)

Interaction with a Static Electric Field

$$\mathcal{H} = \mathcal{H}^{\text{Atom}} + e\mathcal{F}z$$





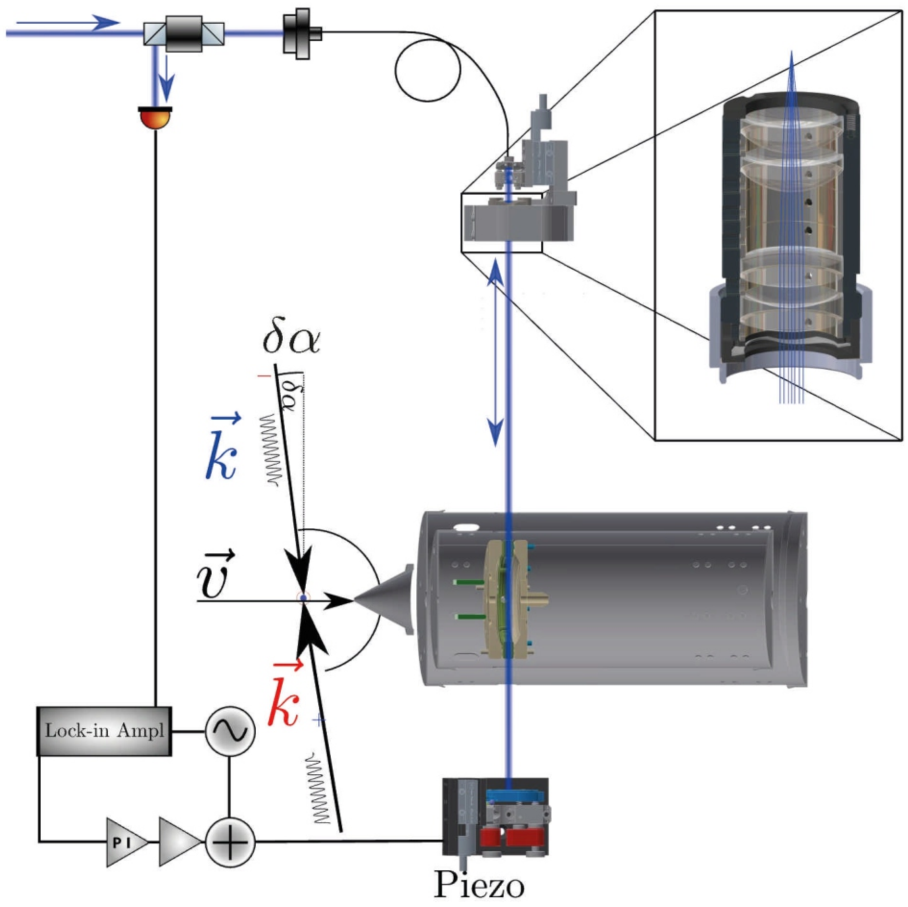
k = 0 Stark states: field insensitive to first order

k = ± 2 Stark states: field calibration

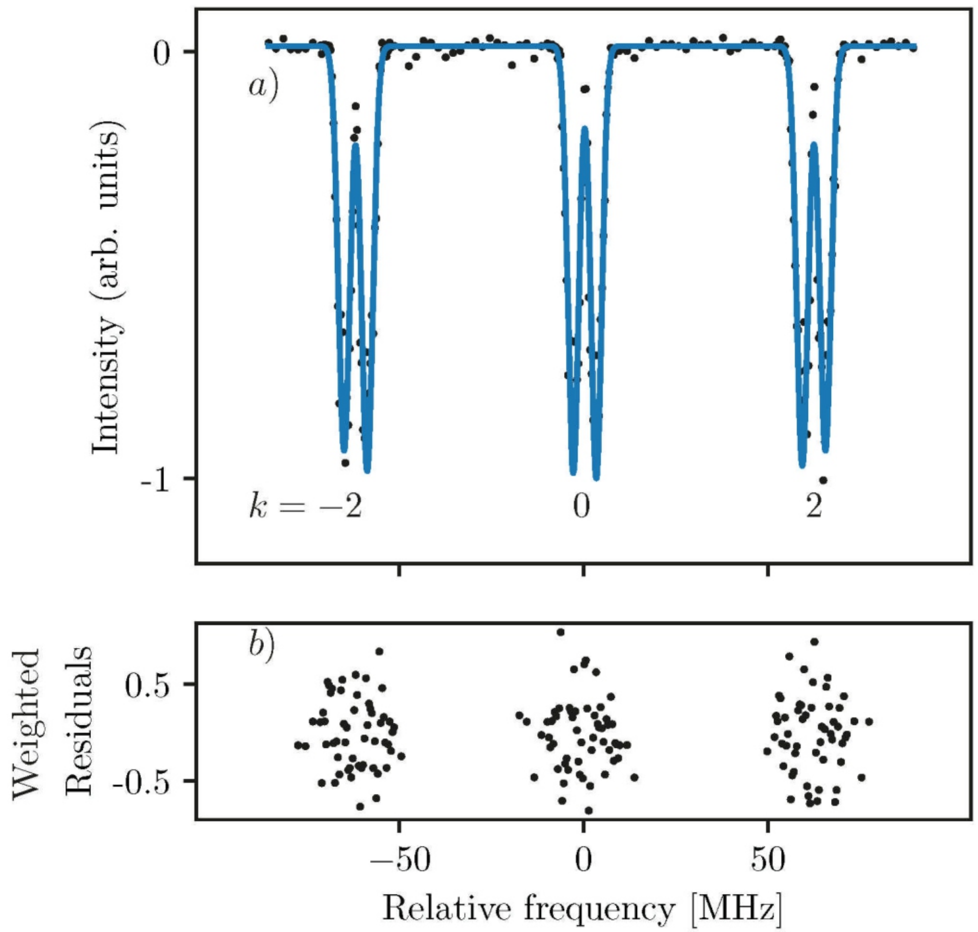
Scheidegger et al., PRA **108**, 042803 (2023)

Doppler-shift cancellation: Retroreflection at ~365 nm

$$\nu_\mathrm{D} = \vec{v} \cdot \vec{k}/(2\pi) \approx \frac{v}{\lambda}\sin(\delta\alpha)$$



FWHM $\leq$ 4 MHz

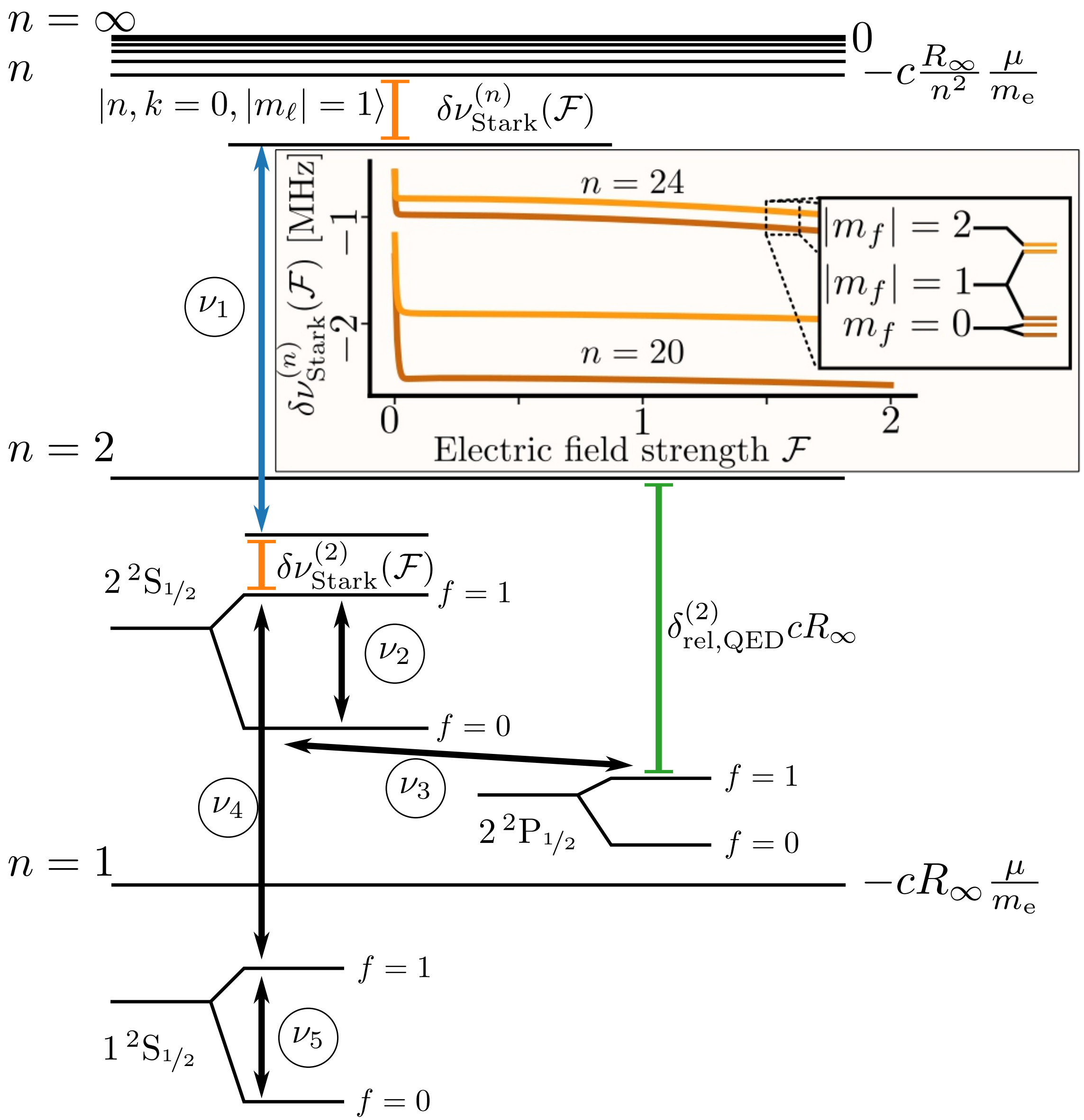


Beyer *et al.*, Opt. Express **24**, 17470 (2016)
Wirthl *et al.*, Opt. Express **29**, 7024 (2021)

S. Scheidegger, FM, PRL **132**, 113001 (2024)

The Ionisation Energy of H(1s, f=0)

$$\nu_{\mathrm{i}}^{1\mathrm{S}(0)} = \nu_1 + \nu_4 + \nu_5 + \delta\nu_{\mathrm{Stark}}^{(n)}(\mathcal{F}) + \delta\nu_{\mathrm{Stark}}^{(2)}(\mathcal{F}) + c\frac{R_\infty}{n^2}\frac{\mu}{m_\mathrm{e}}$$



Rydberg constant:

$$cR_\infty\left[\left(\frac{1}{4} - \frac{1}{n^2}\right)\frac{\mu}{m_\mathrm{e}} + \delta_{\mathrm{rel,QED}}^{(2)}\right] =$$

$$\nu_1 + \nu_2 + \nu_3 + \delta\nu_{\mathrm{Stark}}^{(n)}(\mathcal{F}) + \delta\nu_{\mathrm{Stark}}^{(2)}(\mathcal{F})$$

ν_1: This work
ν_2: Bullis et al., PRL **130**, 203001(2023)
ν_3: Bezginov et al., Science **365**, 1007 (2019)
ν_4: Parthey et al., PRL **107**, 203001 (2011)
ν_5: Essen et al., Nature **229**, 110 (1971)

S. Scheidegger, FM, PRL **132**, 113001 (2024)

The Ionisation Energy of H(1s, f=0)

550 measurements over 8 months, blinded

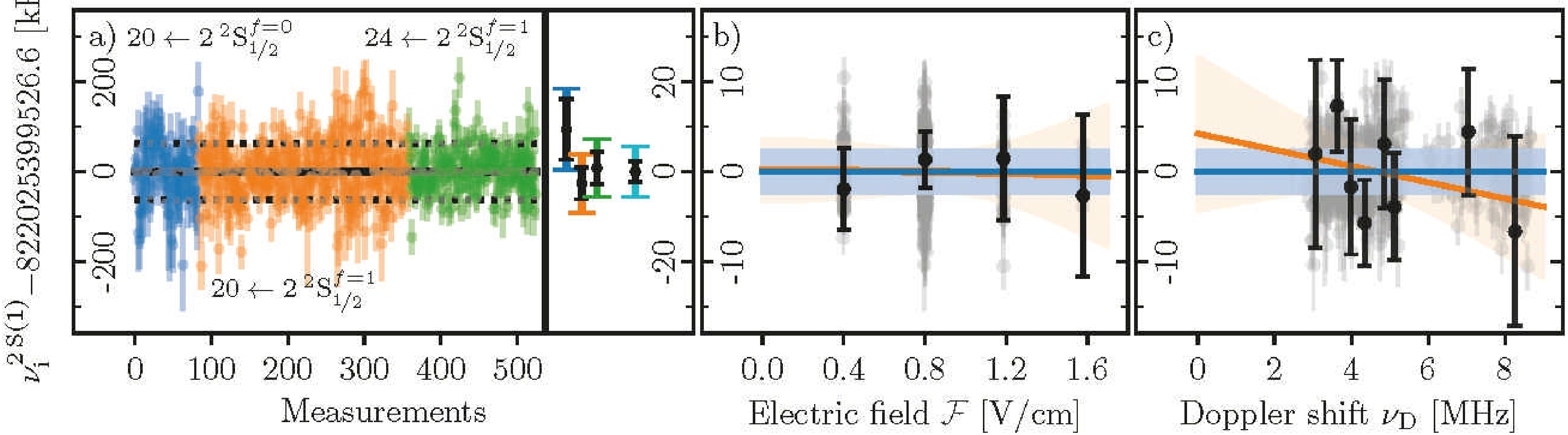


TABLE I. Corrections and uncertainties considered in the determination of the ionization frequency of H(2S(1)). All values and uncertainties are reported in kHz.

		$\Delta\nu$	σ_{stat}	σ_{syst}
$\delta\nu_{D^{(1)}}$		0	2.4	0
$\delta\nu_{D^{(2)}}$		4.5	0	0.12
$\delta\nu_{\mathcal{F}^2}$		0	1.6	0
$\delta\nu_{ac-Stark}^{(TR)}$ [38]		-2.2	0	1.1
Zeeman shifts		0	0	0.56
Pressure shifts		0	0	0.05
Recoil shift	$(n = 20)$	-1458.8	0	0
	$(n = 24)$	-1467.8	0	0

$$\nu(20 \leftarrow 2S(0)) = 813\,805\,449\,014.0(7.4)_{\rm stat}(1.8)_{\rm syst}\ {\rm kHz}$$

$$\nu(20 \leftarrow 2S(1)) = 813\,805\,271\,445.1(4.5)_{\rm stat}(1.8)_{\rm syst}\ {\rm kHz}$$

$$\nu(24 \leftarrow 2S(1)) = 816\,316\,977\,250.3(4.6)_{\rm stat}(1.8)_{\rm syst}\ {\rm kHz}$$

This work:

$$\nu_{\rm i}(1S(0)) = 3\,288\,087\,922\,407.2(3.7)_{\rm stat}(1.8)_{\rm syst}\ {\rm kHz}$$

CODATA2018:

$$\nu_{\rm i}(1S(0)) = 3\,288\,087\,922\,416.2(3.0)_{R_\infty, r_p}(1.6)_{\rm calc}\ {\rm kHz}$$

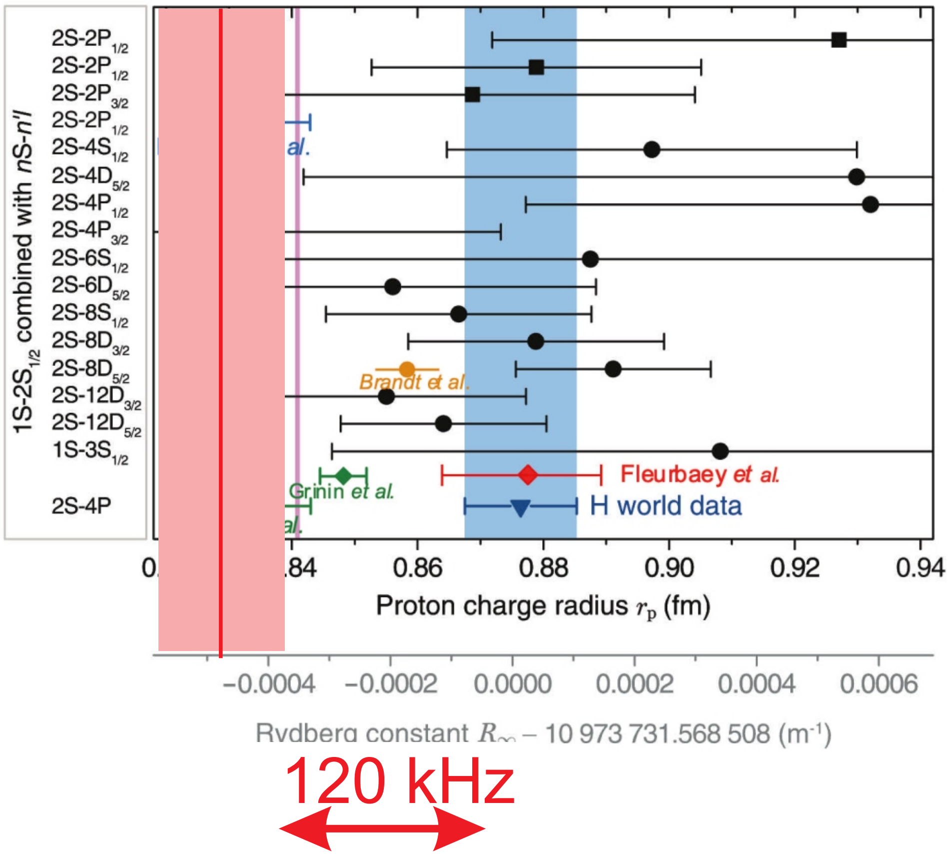
The Rydberg constant and the proton radius

$$cR_\infty = 3\,289\,841\,960\,204(15)_{\text{stat}}(7)_{\text{syst}}(13)_{\text{2S-2P}}\ \text{kHz} \quad \text{(this work)}$$

$$cR_\infty = 3\,289\,841\,960\,306(69)\ \text{kHz} \quad \text{(MIT, de Fries 2001)}$$

$$cR_\infty = 3\,289\,841\,960\,364(16)\ \text{kHz} \quad \text{(CODATA2010)}$$

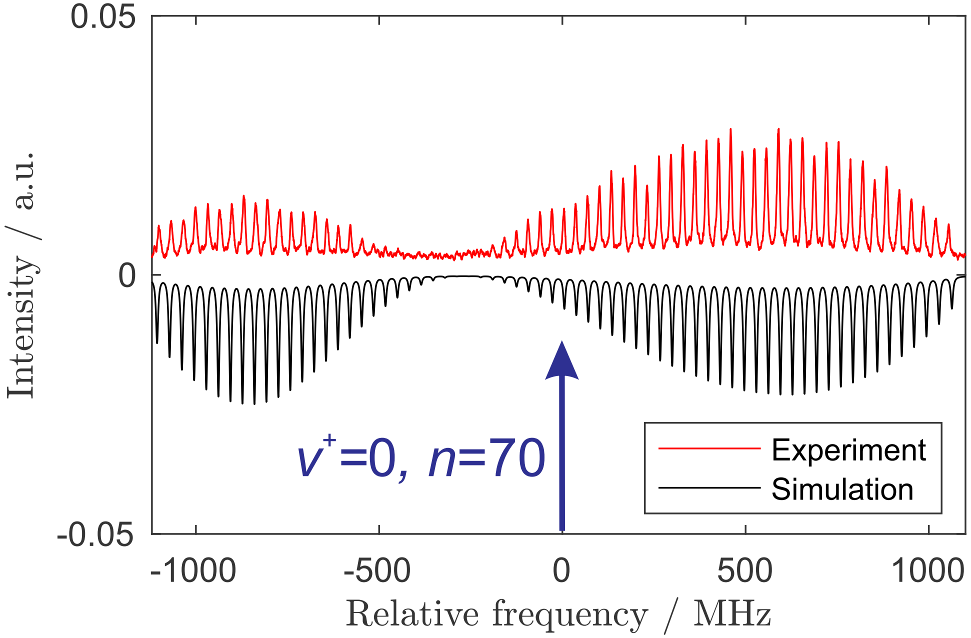
$$cR_\infty = 3\,289\,841\,960\,250.8(6.4)\ \text{kHz} \quad \text{(CODATA2018)}$$

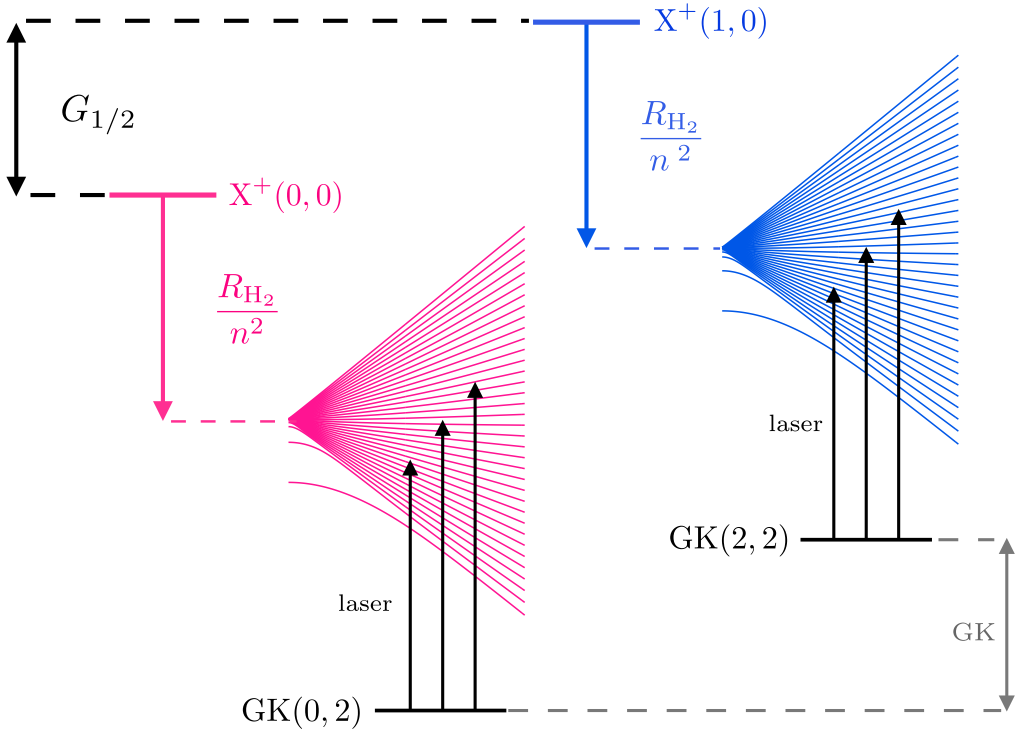


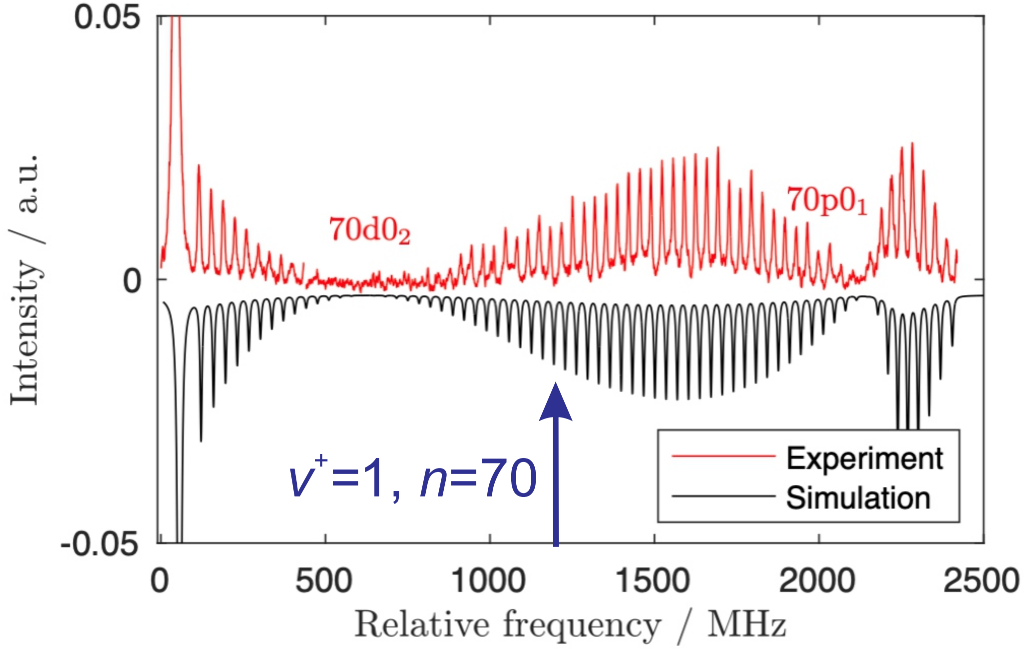
[2] Tiesinga et al., Rev. Mod. Phys. **93**, 025010 (2021)
[3] Mohr et al., Rev. Mod. Phys. **84**, 1527 (2012)
[20] Beyer et al., Science 358, 79 (2017)
[21] Fleurbaey et al., PRL 120, 183001 (2018)
[22] Bezginov et al., Science 365, 1007 (2019)
[23] Grinin et al., Science 370, 1061 (2020)
[24] Brandt et al., PRL 128, 023001 (2022)
[25] de Vries, PhD thesis, MIT (2001)

S. Scheidegger, FM, PRL **132**, 113001 (2024)

III. The fundamental vibrational interval of H_2^+







$$\nu(v^+ = 1) - \nu(v^+ = 0):$$

Exp.: 65 688 323.34(15)$_{stat}$(36)$_{syst}$ MHz
2 191.126 614(5)$_{stat}$(12)$_{syst}$ cm^{-1}
2191.2(2) cm^{-1} [2]

Theor.: 65 688 323.7101(5)(29) MHz [1]
2191.126 626 344(17)(100) cm^{-1}

[1] V. I. Korobov et al., PRL **118**, 233001 (2017)
[2] G. Herzberg and C. Jungen, JMS **41**, 425 (1972)

Doran, Hölsch, Beyer, FM, PRL**132**, 073001 (2024)

IV. The ionization energy of triplet metastable He

$$E(\alpha, \frac{m}{M}, R_\infty, r_{\mathrm{He}^{2+}}) = \underbrace{\alpha^2 E^{(2)}(\frac{m}{M})}_{\text{non-relativistic energy}} + \underbrace{\alpha^4 E^{(4)}(\frac{m}{M})}_{\text{relativistic correction}} + \underbrace{\alpha^5 E^{(5)}(\frac{m}{M})}_{\text{leading Lamb-shift correction}} + \underbrace{\alpha^6 E^{(6)}(\frac{m}{M})}_{\text{higher-order QED correction}} + \ldots + \underbrace{E_{NS}(r_{\mathrm{He}^{2+}})}_{\text{nuclear-size contribution}}$$

$R_\infty c = 3.289\,841\,960\,250\,8(64) \cdot 10^{15}$ Hz [2] $1/\alpha = 137.035\,999\,206(11)$ [4]

$M/m_e = 7294.299\,541\,42(24)$ [2] $r_{\mathrm{He}^{2+}} = 1.678\,24(83)$ fm [3]

In MHz	$(m/M)^0$	$(m/M)^1$	$(m/M)^2$	$(m/M)^3$	Sum
$2\,^3S$:					
α^2	−1 152 953 922.384 (2)	164 775.354	−30.620	0.006	−1 152 789 177.644 (2)
α^4	−57 629.312	4.284	−0.001		−57 625.029
α^5	3 999.431	−0.800			3 998.632
α^6	65.235	−0.030			65.205
α^7	−6.168 (1)				−6.168 (1)
α^8	0.158 (52)				0.158 (52)
NS	2.616 (3)				2.616 (3)
NP	−0.001				−0.001
Total					−1 152 842 742.231 (52)

Complete $\alpha^7 m$ Lamb shift of helium triplet states[1]

Vojtěch Patkóš,[1] Vladimir A. Yerokhin,[2] and Krzysztof Pachucki[3]

We have derived the complete formula for the $\alpha^7\, m$ contribution to energy levels of an arbitrary triplet state of the helium atom, performed numerical calculations for the $2\,^3S$ and $2\,^3P$ states, and thus improved the theoretical accuracy of ionization energies of these states by more than an order of magnitude. Using the nuclear charge radius extracted from the muonic helium Lamb shift, we obtain the theoretical prediction in excellent agreement with the measured $2\,^3S - 2\,^3P$ transition energy [X. Zheng *et al.*, Phys. Rev. Lett. **119**, 263002 (2017)]. At the same time, we observe significant discrepancies with experiments for the $2\,^3S - 3\,^3D$ and $2\,^3P - 3\,^3D$ transitions.

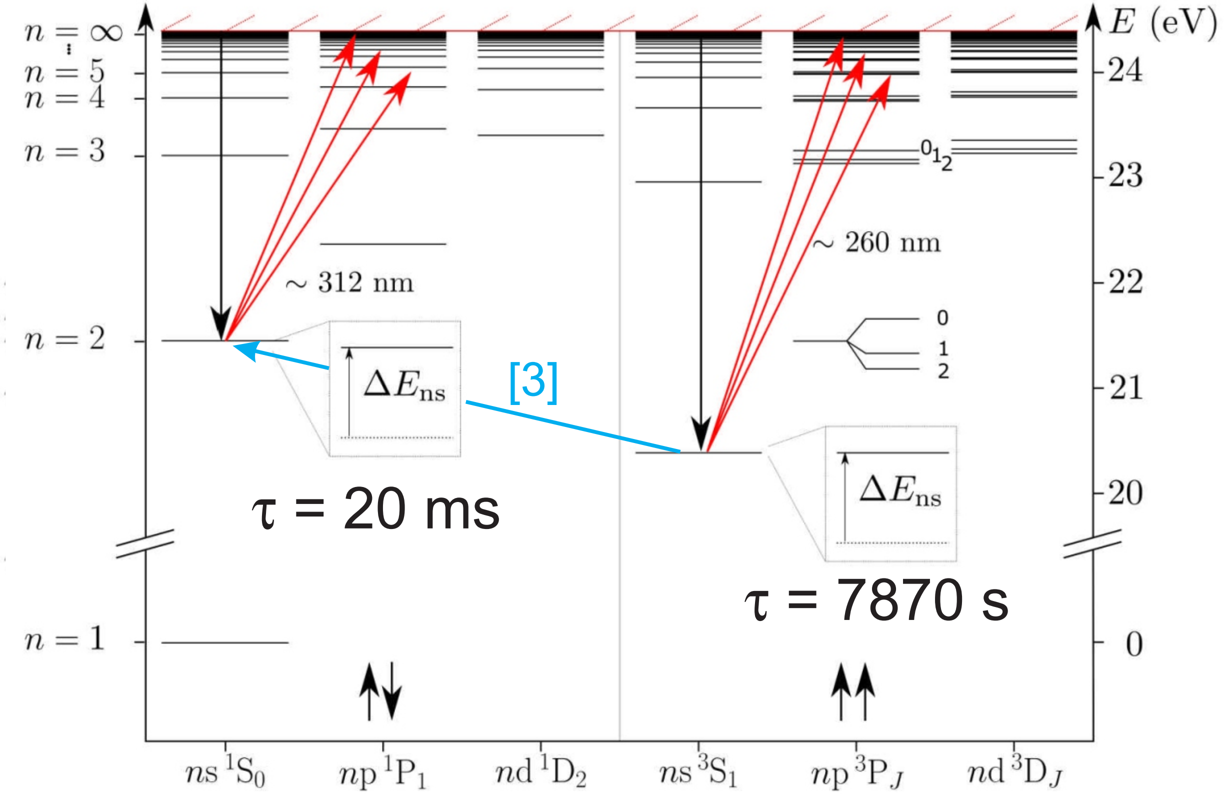
$$E_{\mathrm{I}}((1\mathrm{s})^1(2\mathrm{s})^1\,2\,^3\mathrm{S}_1)/h = 1152\,842\,742.231(52)\ \mathrm{MHz}$$

$4 * 10^{-11}$ fractional uncertainty

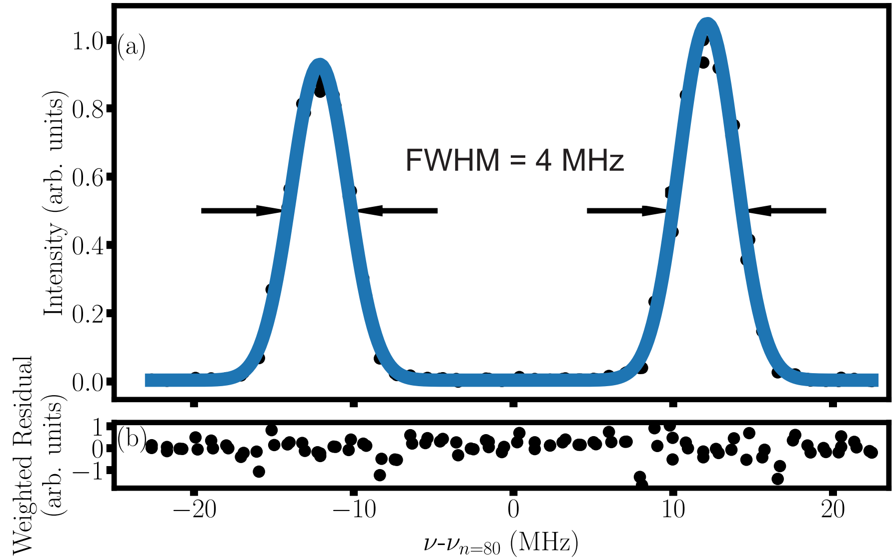
[1] Patkóš *et al.*, PRA **103**, 042809 (2021)
[2] E. Tiesinga, P. J. Mohr, D. B. Newell, and B. N. Taylor, Fundamental Physical Constants from NIST (2018)
[3] J. J. Krauth *et al.*, Nature (London) **589**, 527 (2021)
[4] L. Morel, Z. Yao, P. Cladé, and S. Guellati-Khélifa, Nature (London) **588**, 61 (2020)

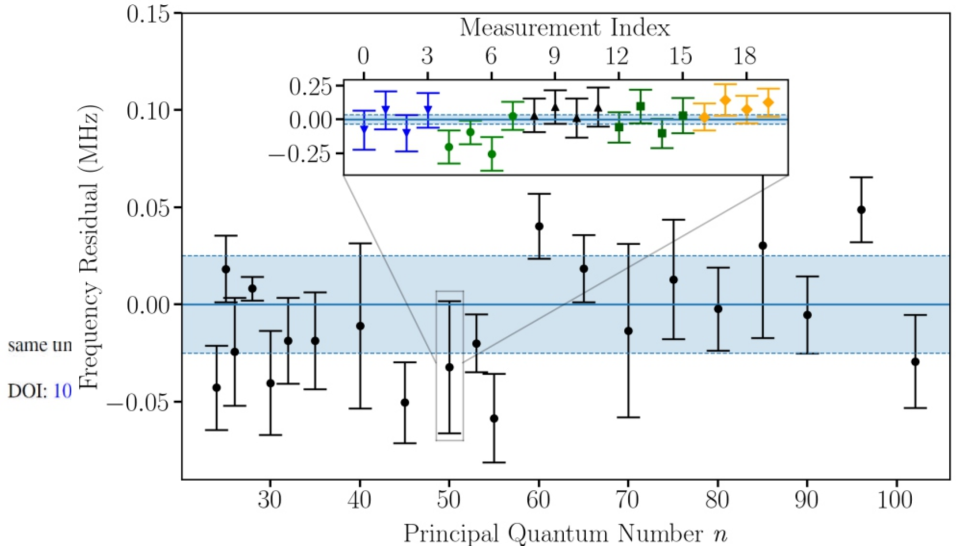
Ionization energy of ^{4}He (1s2s $^1S_0$)

$$E_{n,\ell} = E_I - \frac{hcR_{He}}{(n - \delta(n,\ell))^2}$$



1s2s $^1S_0$ ⟶ 1s50p $^1P_1$



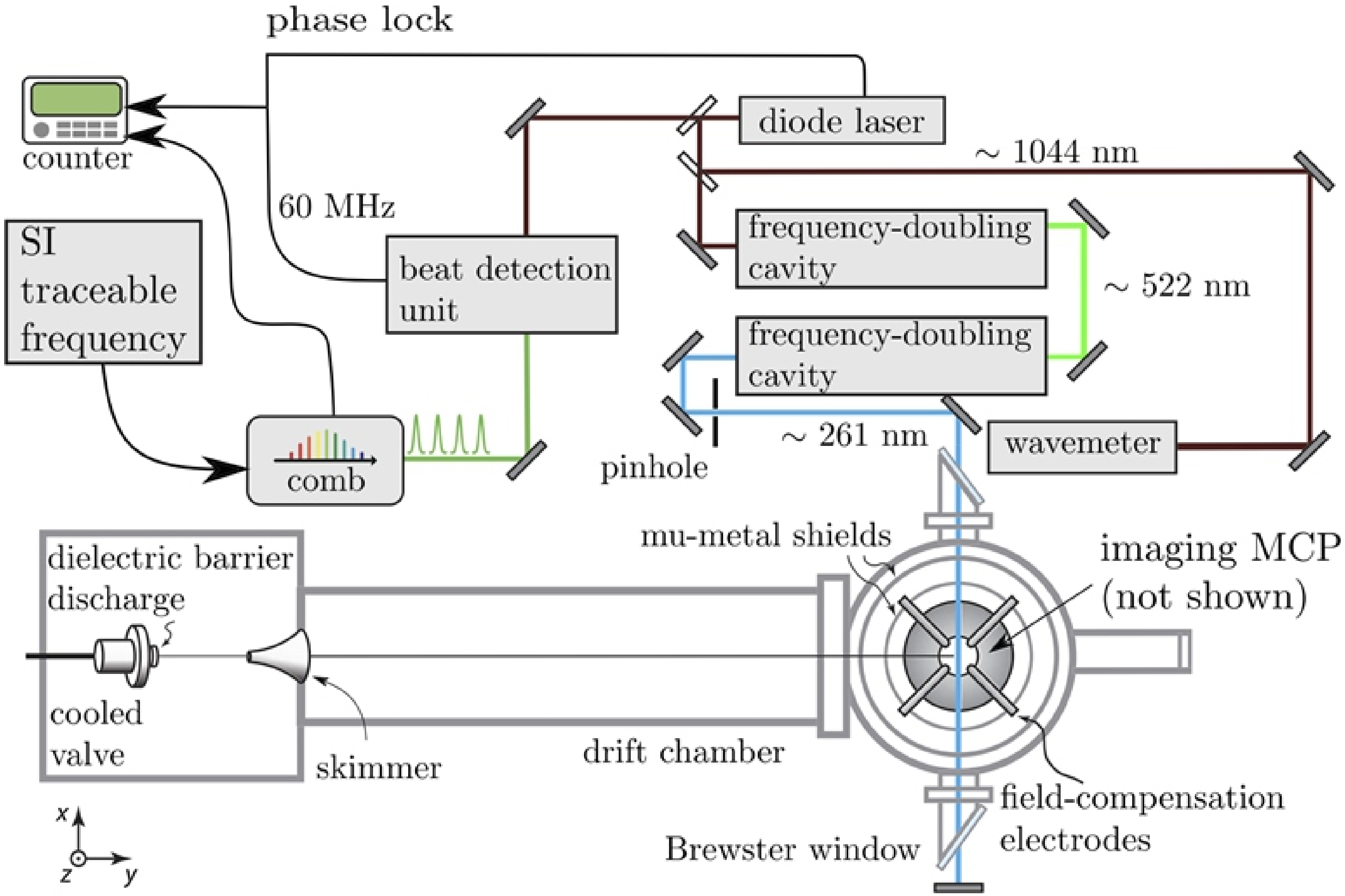


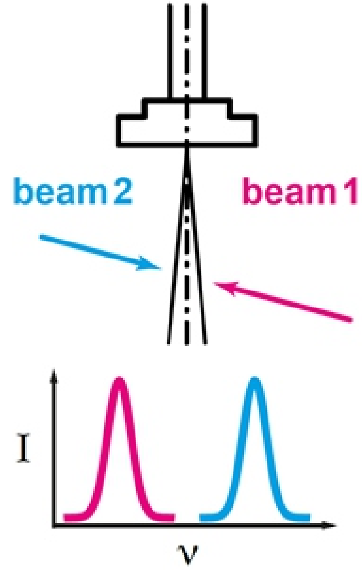
	Experiment[2,3]	Theory[1]	$\Delta E_I/h$
$2\,^3S_1$	1 152 842 742.637(32)	1 152 842 742.231(52)	0.406(61)

7σ

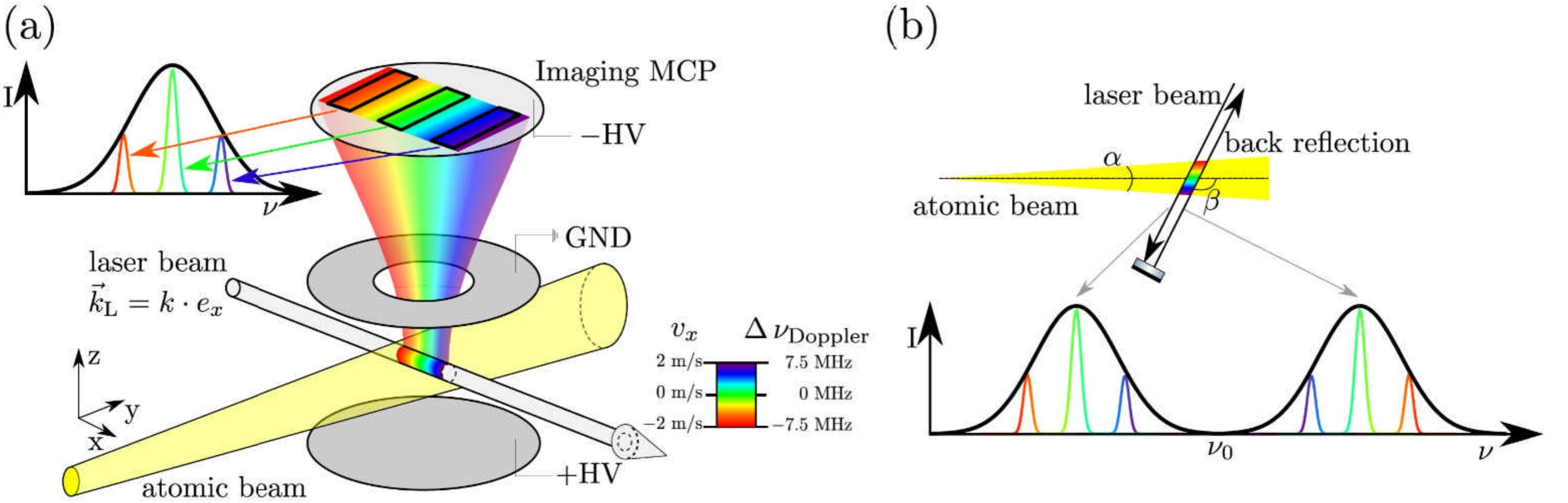
[1] Patkóš *et al.*, PRA **103**, 042809 (2021)
[2] Clausen *et al.*, PRL **127**, 093001 (2021)
[3] Rengelink *et al.*, Nat. Phys. **14**, 1132 (2018)

Experimental setup $2\,^3S_1 \rightarrow n\,^3P_J$ measurements





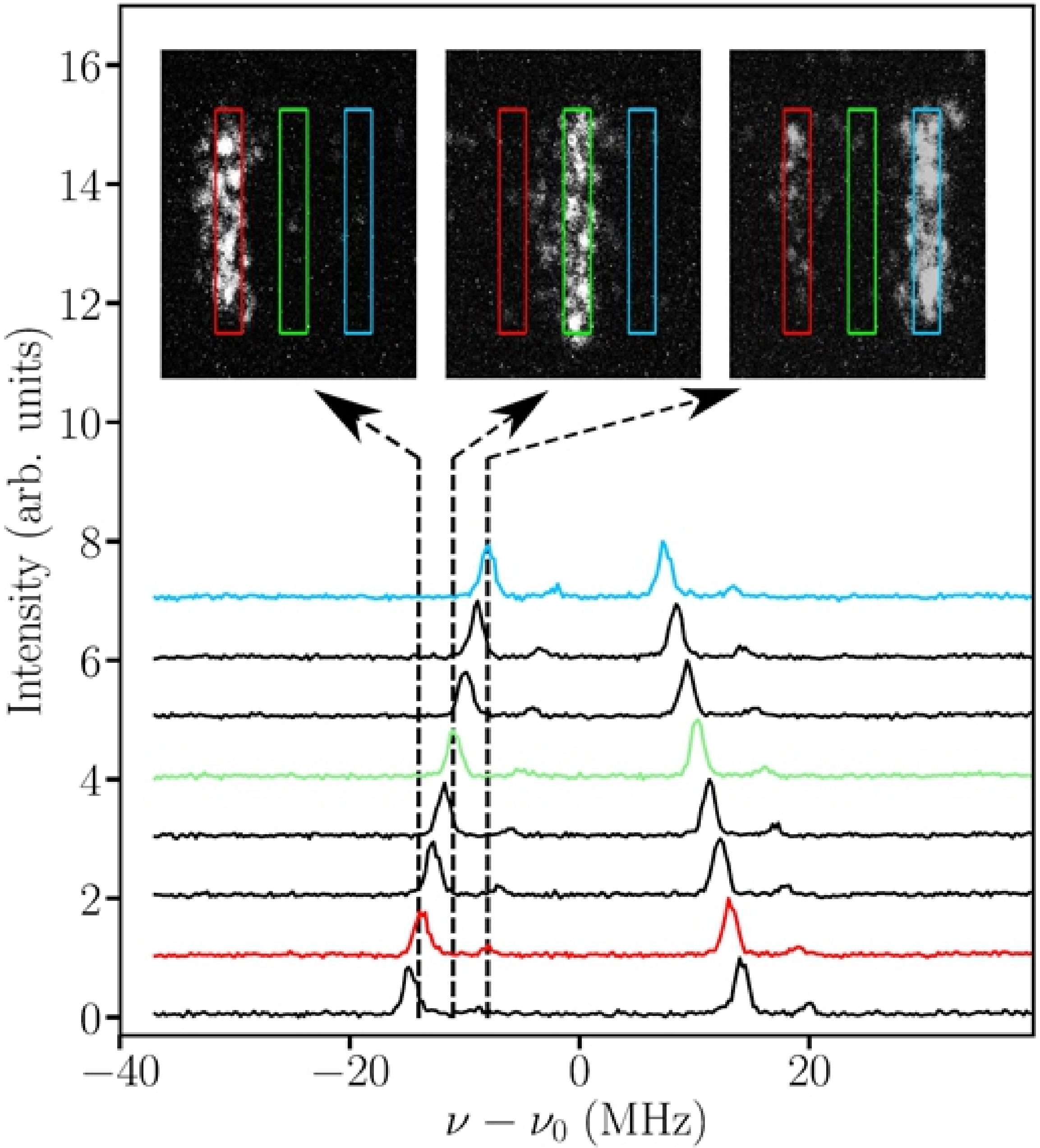
Imaging-assisted sub-Doppler single-photon spectroscopy



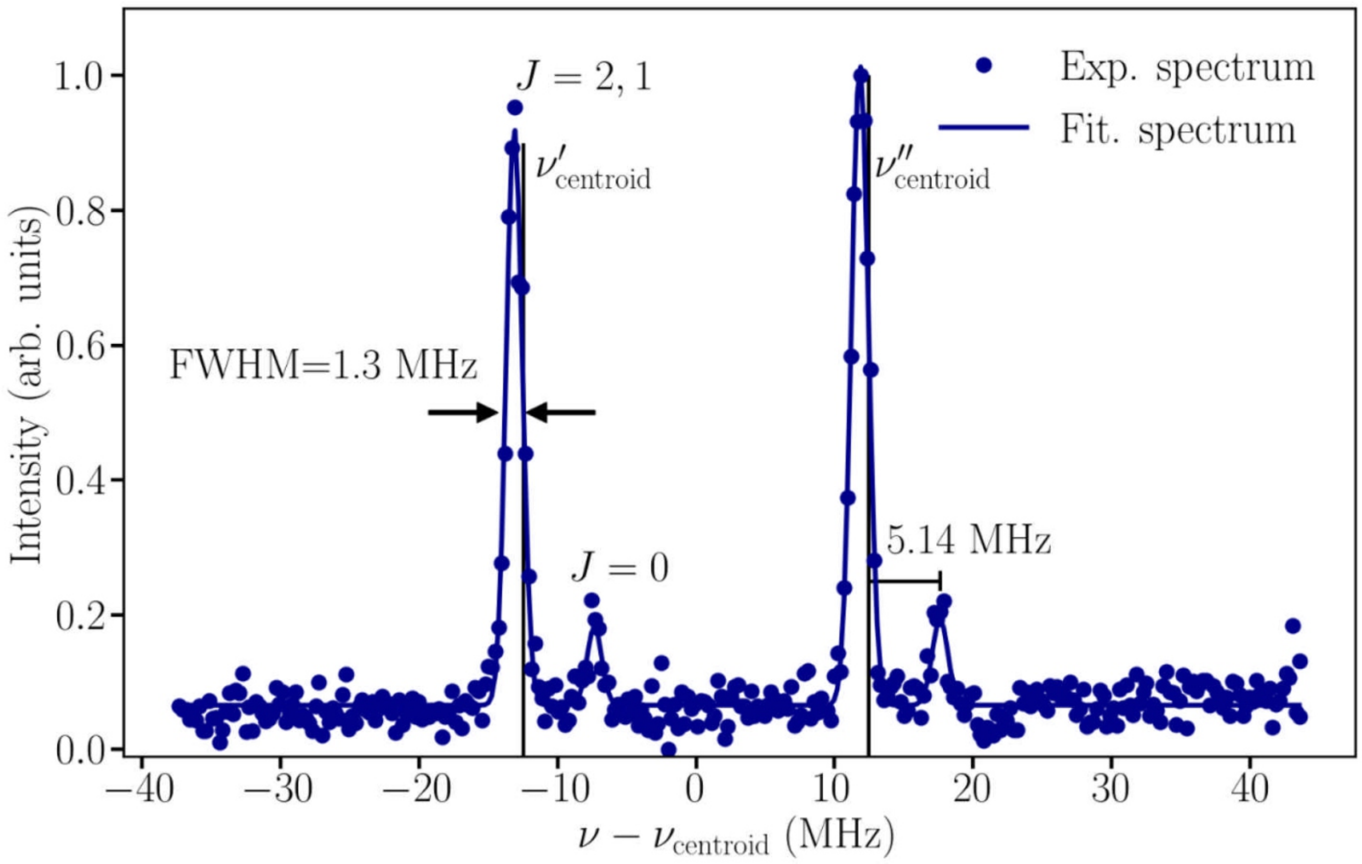
Clausen et al., PRL **131**, 103001 (2023)

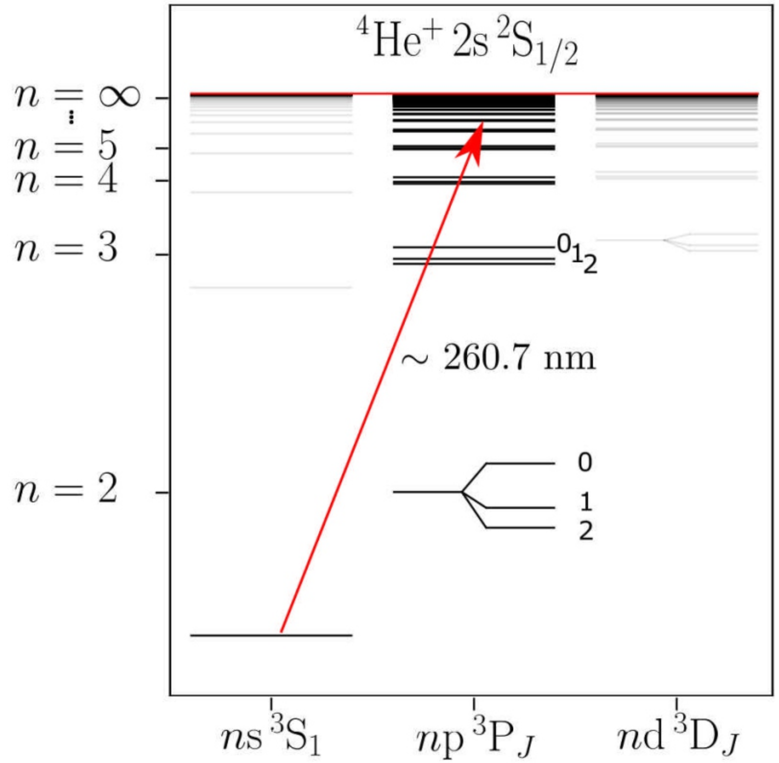
Image acquisition with microchannel-plate detector and CCD camera

$1s2s\ ^3S_1 \longrightarrow 1s33p\ ^3P_{0\text{-}2}$



Assignment of 2 $^3S_1 \rightarrow$ 33 ^3P_J spectrum





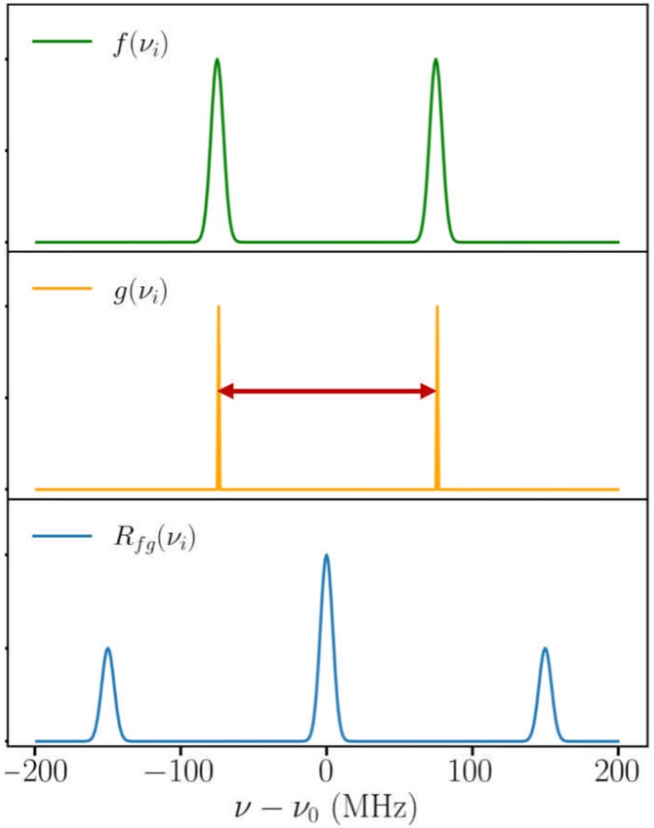
$$n = 33: \ \nu_{\text{centroid}} = 1149\,809\,632.350(150)_{\text{sys}}(25)_{\text{stat}}\ \text{MHz}$$

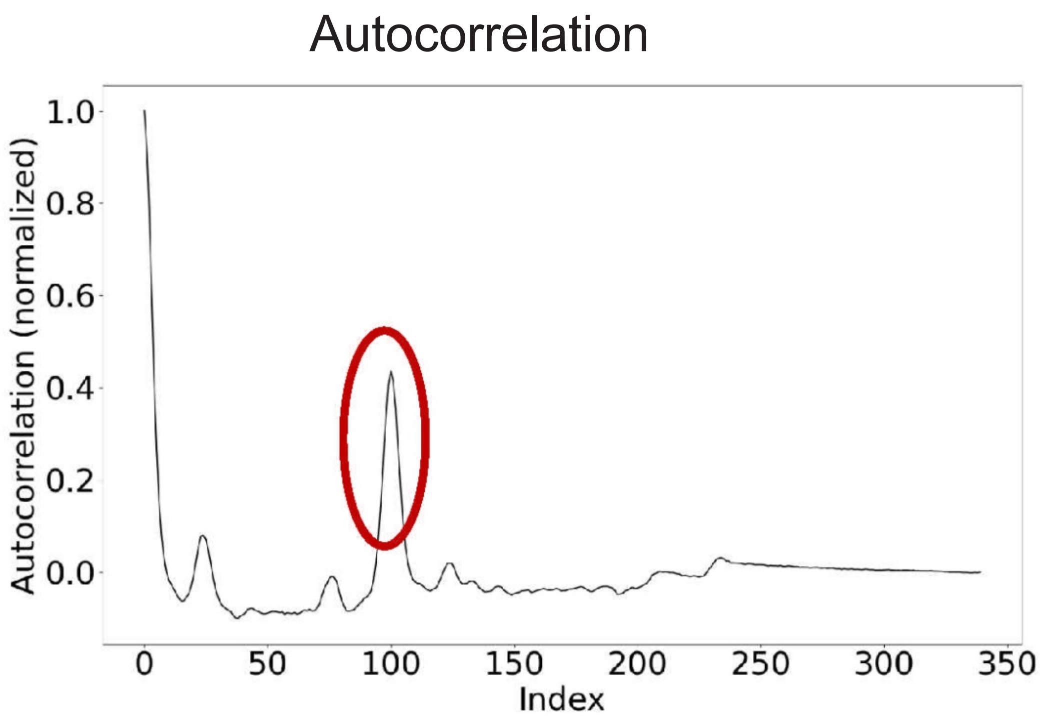
Clausen et al., PRL **131**, 103001 (2023)

Autocorrelation and circular cross correlation

$$R_{fg}(k) = \sum_{i=0}^{N-1} f(i)g(i+k)_{\mathrm{mod\,N}}.$$

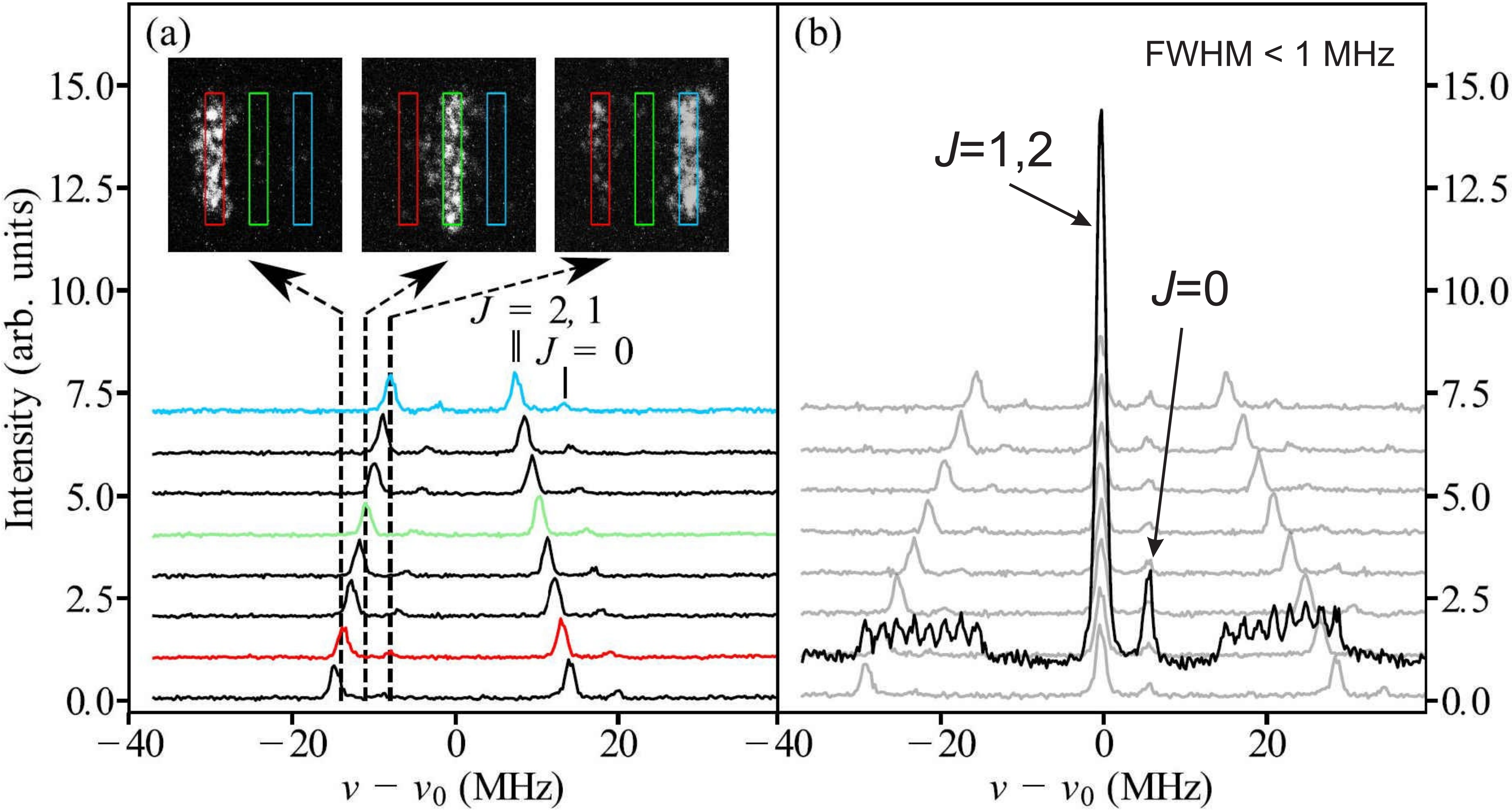
$f(i)$ →spectrum with frequencies(N data points)
$g(i)$ →test function with 2 Dirac delta distributions with distance found from autocorrelation spectrum





Doppler-free single-photon spectroscopy

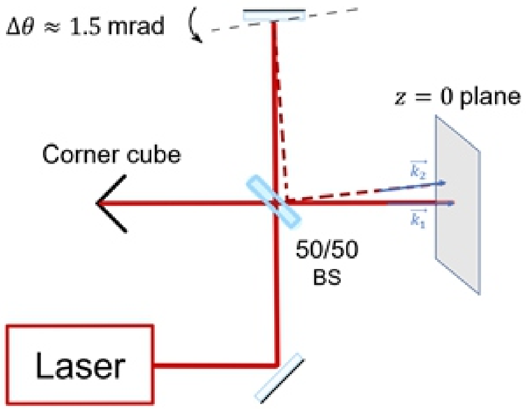
$2\,^3S_1 \longrightarrow 33\,^3P_J$ (J = 0-2) cross-correlation spectra

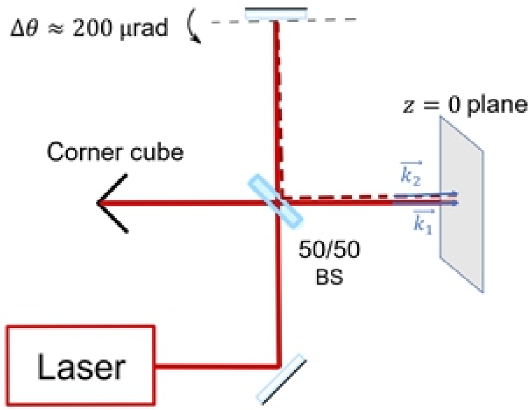


Sub-Doppler spectra Cross-correlated spectra

Clausen et al., PRL **131**, 103001 (2023)

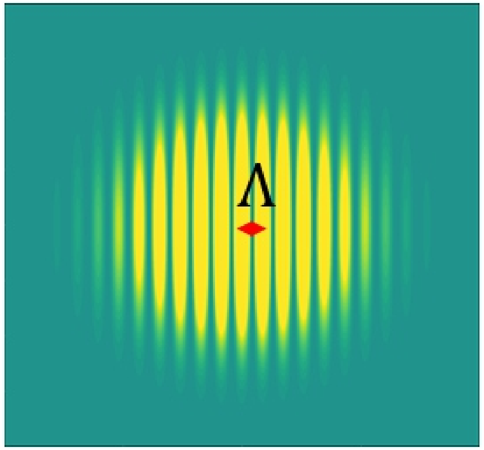
Interferometric retroreflection alignment at 261 nm



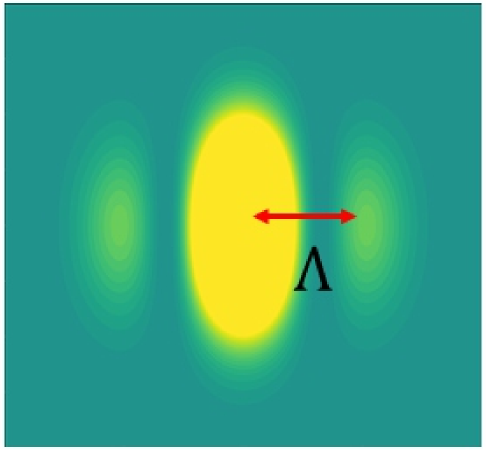


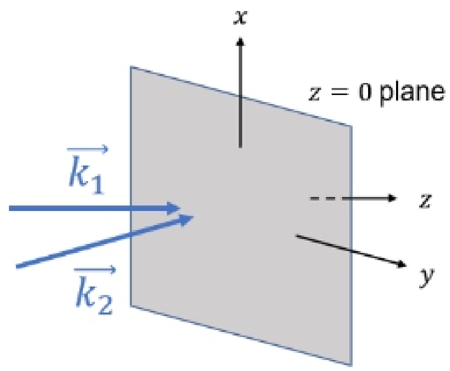
- Interference pattern encodes value of the tilt angle $\Delta\theta$
- Fringe distance $\Lambda = \dfrac{\lambda}{\sin(\Delta\theta)}$
- $\overrightarrow{k_1}$: wavevector of the reference beam (Corner cube)
- $\overrightarrow{k_2}$: wavevector of the tilted retro-reflected beam

$\Delta\theta = 1.5$ mrad



$\Delta\theta = 200$ µrad

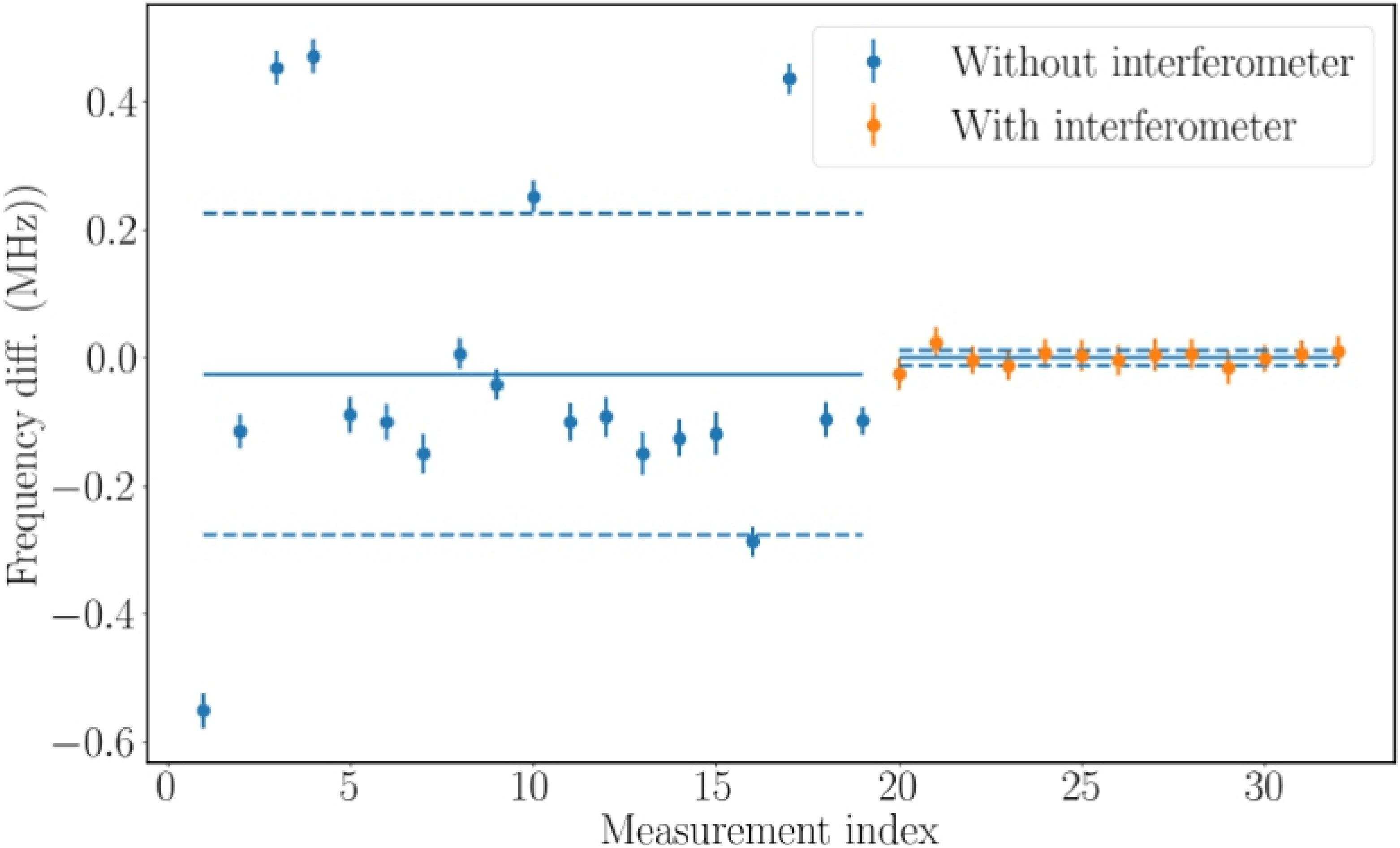




Müller et al., Opt. Lett. **30**, 3323 (2005)

Improvement of centroid frequency determination

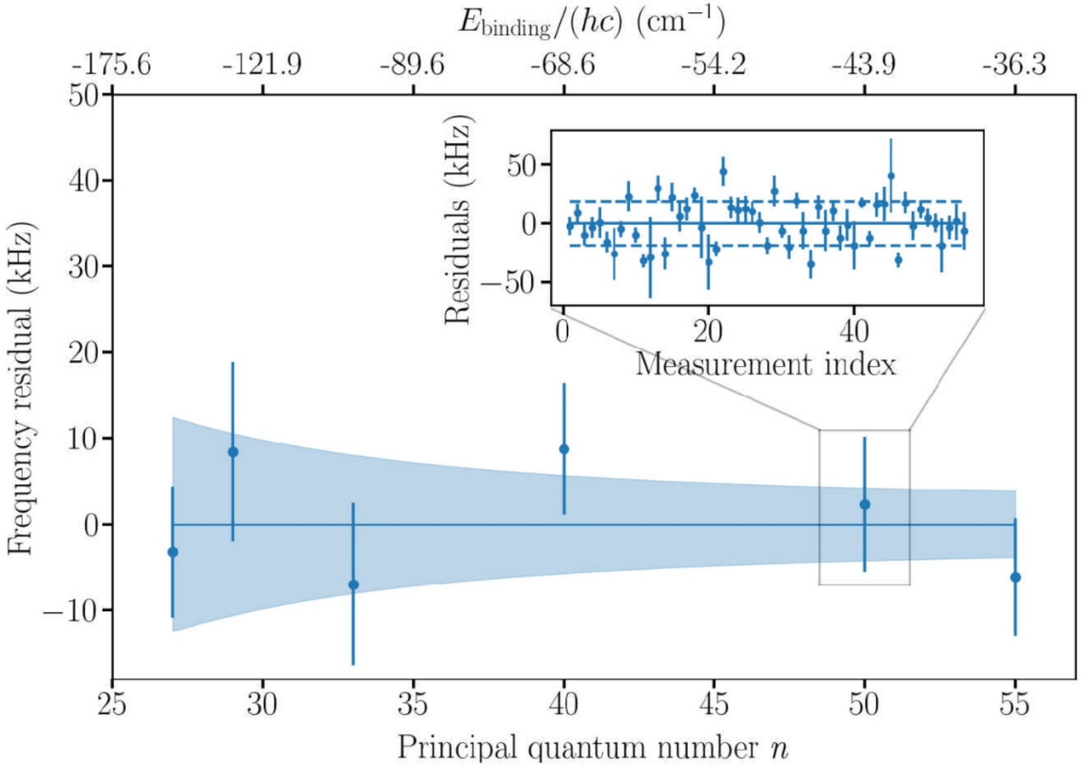
$2\ ^3S_1 \rightarrow 33\ ^3P_J$



$$\nu_{\mathrm{centroid}}(n = 33) = 1149809632.361(4)_{\mathrm{stat}}(5)_{\mathrm{syst}} \text{ MHz}$$

Ionization energy of ^{4}He 2 $^3S_1$ state

Rydberg-series extrapolation



$$E_{n,l} = E_I(2\,^3S_1) - \frac{hcR_{He}}{(n-\delta(n,l))^2}$$

[1]Patkóš *et al.*, Phys. Rev. A **103,** 042809 (2021),
[2]Clausen *et al.*, Phys. Rev. Lett. **127,** 093001 (2021)

Overview of systematic shifts and uncertainties. All values in kHz.

Source	$\Delta\nu$	σ_{stat}	σ_{sys}
1st-order Doppler shift [a]	0	7.5 to 17	0
Photon-recoil shift [b]	731.3 to 735.7	0	0
Post-selection shift [c]	−2.5 to −2	0	0.4
ac- Stark shift	2.2		1.1
Zeeman shift	0	0	0.1
Pressure shift	0	0	0.1
dc-Stark shift ($n = 55$) [b]	−7.6	0	0.6
2nd-order Doppler shift [c]	−7.5 to −1.5	0	0.2
Sum	n.a.	n.a.	2.5 [d]

	$E_I/h\ (2\,^3S_1)$ / (MHz)
This measurement (2024)	1 152 842 742.7082(55)$_{stat}$(25)$_{sys}$
Patkóš *et al.*[1] (2021)	1152 842 742.231(52)
Clausen *et al.*[2] (2021)	1152 842 742.640(32)

9σ

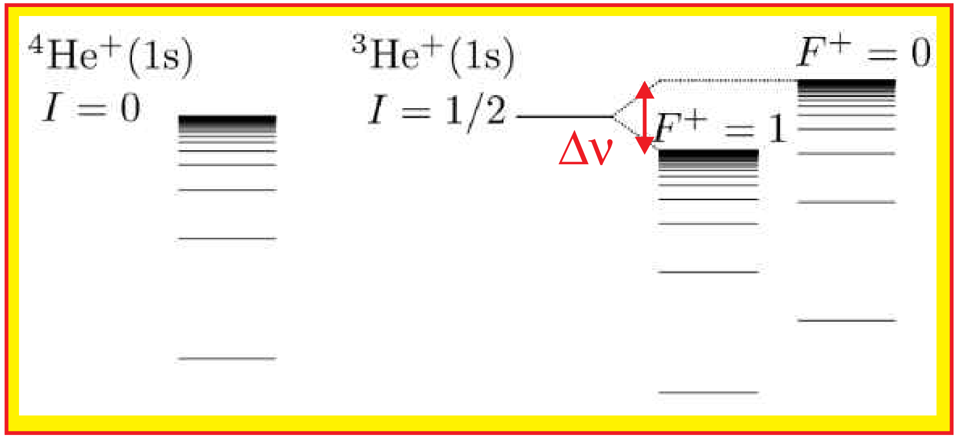
Deviation (exp - calc): 477(52) kHz

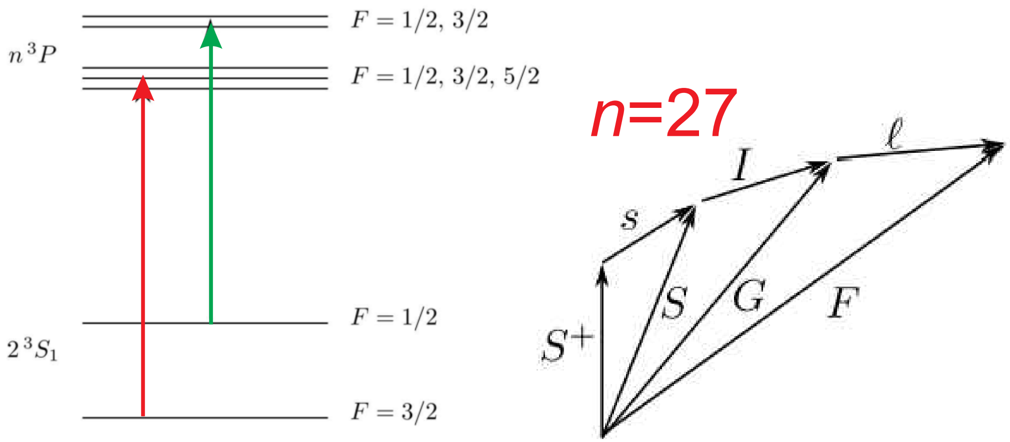
G. Clausen *et al.*, PRA 111, 012817 (2025)

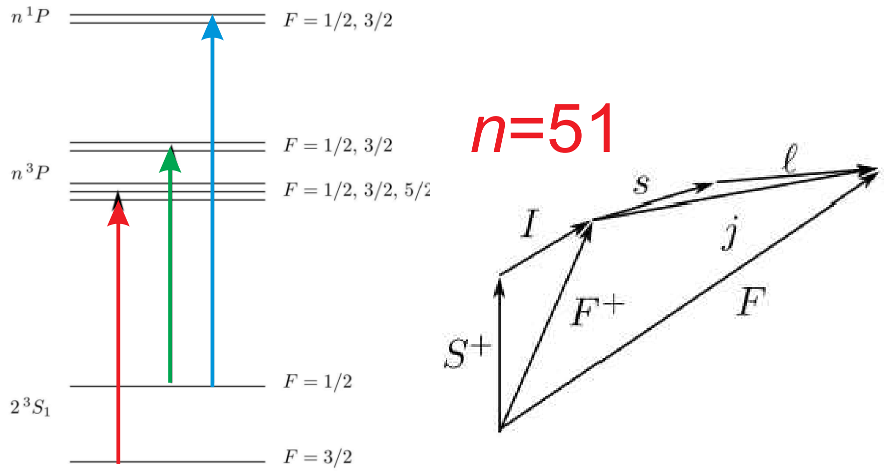
*n*p Rydberg series and ionization energy of ^{3}He

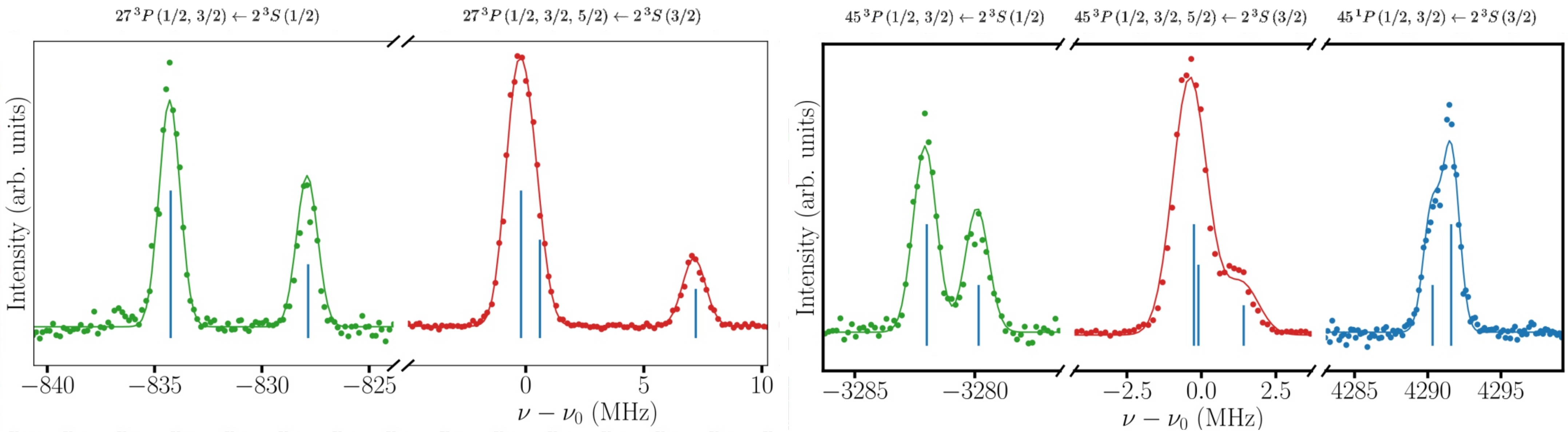
$\Delta\nu$ = 8 665 649 865.77(26)$_{stat}$(1)$_{sys}$ Hz

(Schneider et al., Nature 524 (London) 606, 878 (2022))









^{3}He: Rydberg-series extrapolation with hyperfine-split ionic levels (1)-(6):

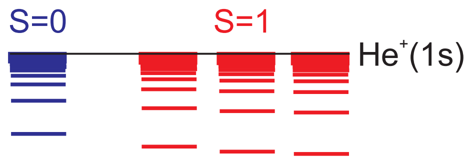
a) Hyperfine structure too weak to affect close-coupling quantum defects

b) Hyperfine structure splits the ionic levels: more channels

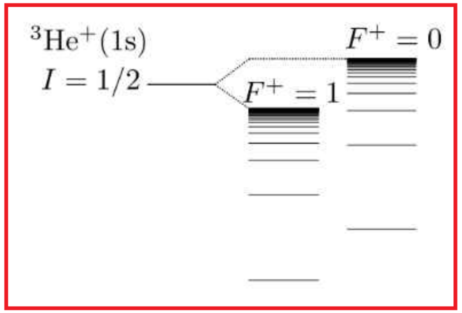
c) Use Fano´s angular-momentum frame-transformation method (MQDT)

For He:

^{4}He (1s)(*n*p)

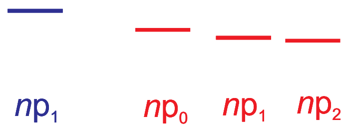


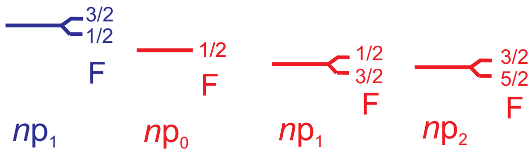
^{3}He (1s)(*n*p)



$(S^+I)F^+(ls)jF$

LS





LSJ(I)F

Four series
- One series limit
- Four quantum defects

$\delta_{0,1}$ $\delta_{1,0}$ $\delta_{1,1}$ $\delta_{1,2}$

Seven series
- Two series limits
- Four quantum defects

$\delta_{0,1}$ $\delta_{1,0}$ $\delta_{1,1}$ $\delta_{1,2}$

(1) U. Fano, Phys. Rev. A **2**, 353 (1970) J. Sun and K. T. Lu, J. Phys. B **21**, 1957 (1988): general
(2) V. Vassen, W. Hogervorst, Phys. Rev. A **39**, 4615 (1989): ^{3}He (1s)(*np*)
(3) H. J. Wörner, U. Hollenstein, F. Merkt, Phys. Rev. A **68**, 032510 (2003): ^{83}Kr $(4p)^5(nl)$
(4) A. Osterwalder, A. Wüest, F. Merkt and Ch. Jungen, J. Chem. Phys. **121**, 11810 (2004): H_2 $(1s\sigma_g)(nl)$
(5) N. Chen, L. Li,1, W. Huie, M. Zhao, I. Vetter, C. H. Greene, and J. P. Covey: Phys. Rev. A **105**, 052438 (2022), ^{171}Yb (1s)(*nl*)

Early important contribution: (6) M. Aymar, Phys. Rep. **110**, 163 (1984) Ca - Ba (*n*s)(*n´l*)

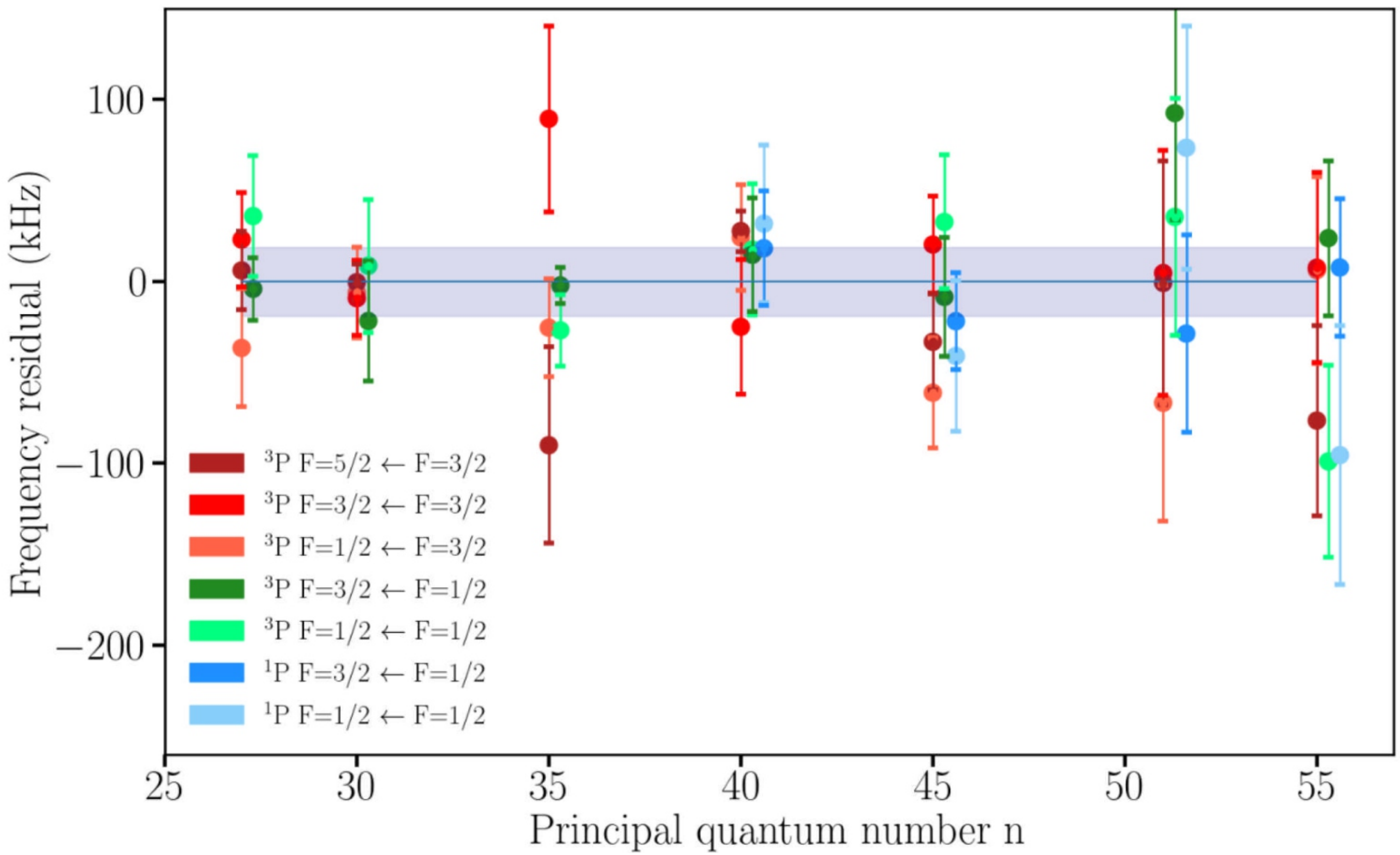
Ionization frequencies, isotope shift and nuclear square radii

$$E_\mathrm{I}(^4\mathrm{He})/h = 1\,152\,842\,742.7082(55)_\mathrm{stat}(25)_\mathrm{sys}\ \mathrm{kHz}$$

$$E_\mathrm{I}(^3\mathrm{He})/h = 1\,152\,788\,844.6154(77)_\mathrm{stat}(25)_\mathrm{sys}\ \mathrm{kHz}$$

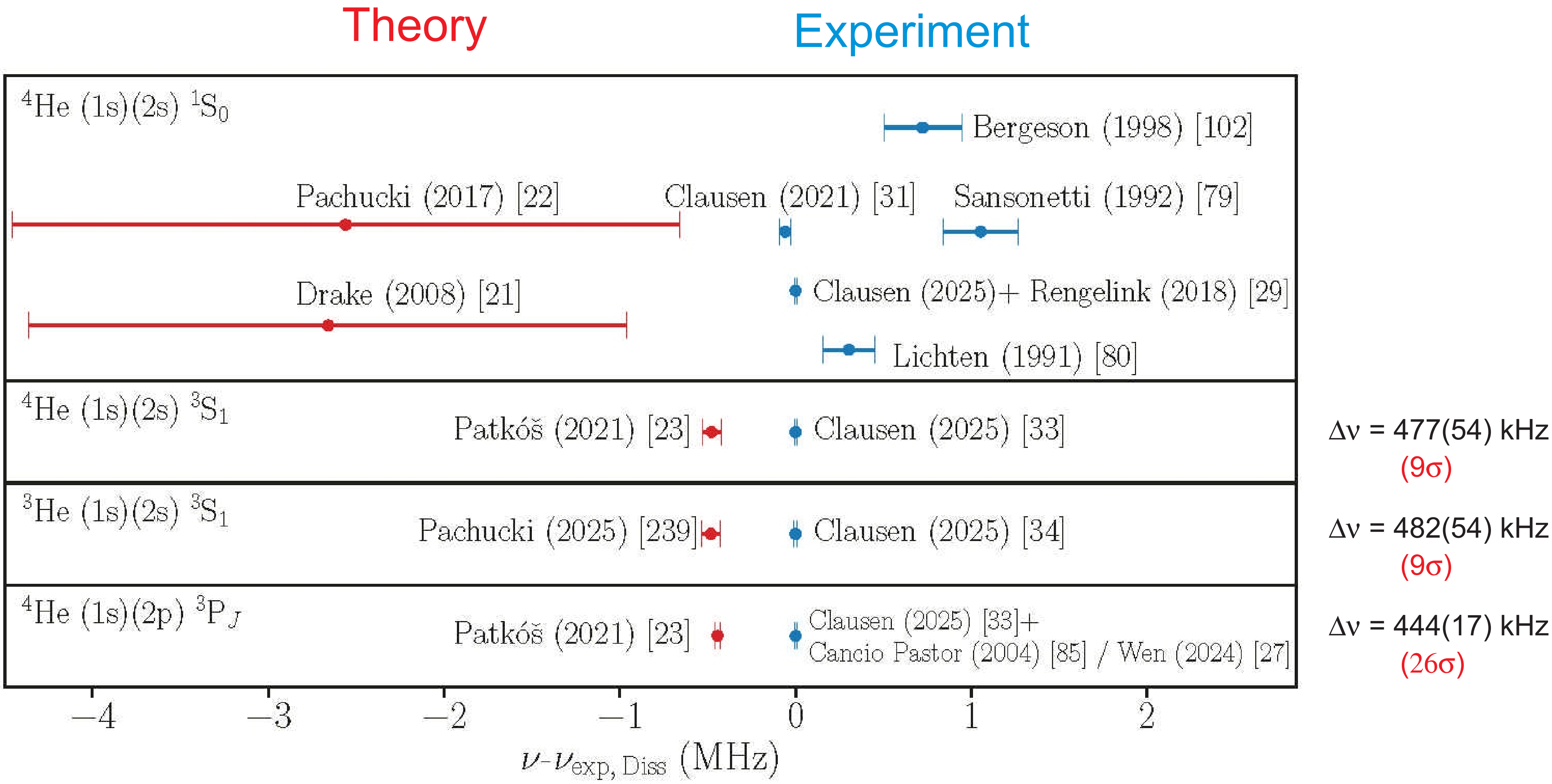
$$\Delta E_\mathrm{I} = 53\,898.093(9)_\mathrm{stat}\ \mathrm{kHz}$$

$$\Delta r^2 = 1.060(10)\ \mathrm{fm}^2$$



G. Clausen, FM, PRL **134**, 223001 (2025)

Ionization energies of He (1s)(2s) and (1s)(2p) states



Agreement between experiment and theory for the (1s)(2s) $^3S_1$ ⟶ (1s)(2p) ^3P_J transitions is accidental

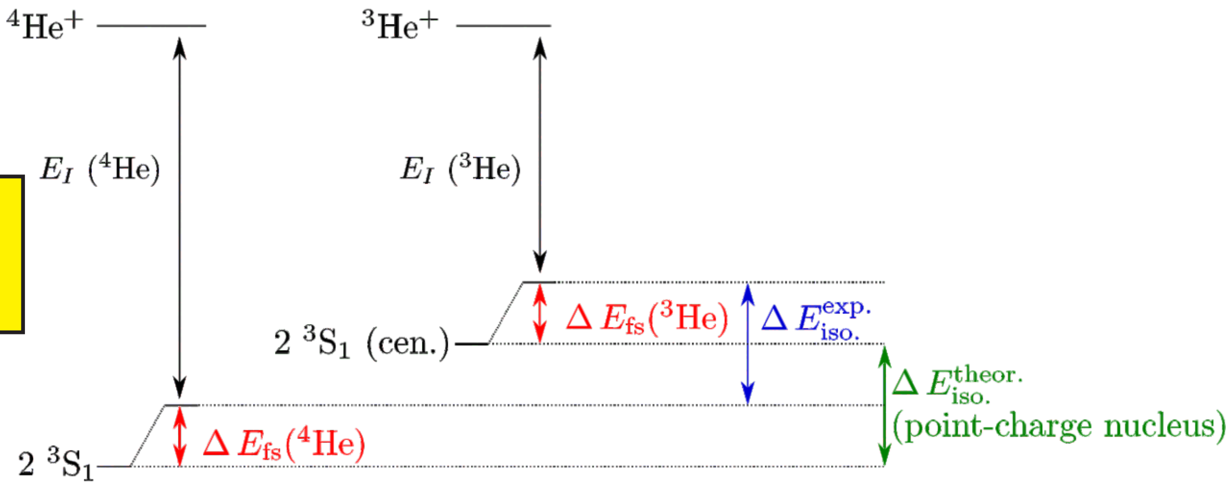
A possible error in the calculations cannot be from a mass-dependent term nor from a finite-nuclear-size effect

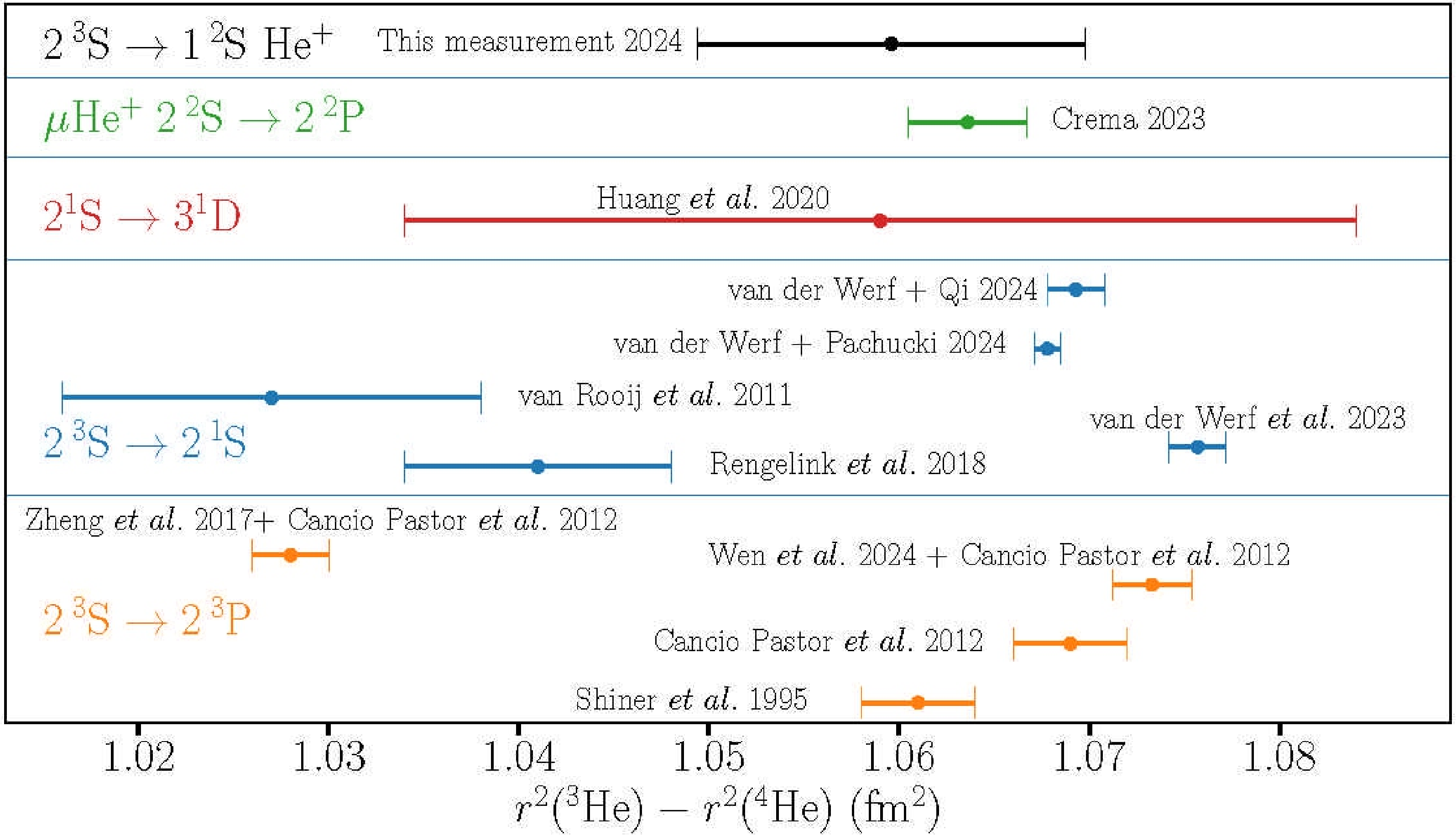
G. Clausen, FM, PRL, **134**, 223001 (2025)

Nuclear radii

$\Delta E_I/h = 53\,898.084(8)_{stat}$ kHz
$r^2(^3He) - r^2(^4He) = 1.060(10)$ fm^2

$\Delta E_{iso} - \Delta E^{theor.}_{iso.}$(point charge)$= C(r_h^2 - r_\alpha^2)$





Conclusions:

H atom:

- Method to determine the Rydberg constant independently of r_p
- Proton puzzle: New value in favor of the r_p value from muonic hydrogen

H_2^+ ion:

- First precision measurement of the fundamental vibrational interval

He atom:

- Method to measure Doppler-free single-photon spectra
- Large discrepancy between theory and experiment in the ionization energies of $2\ ^3S_1$ and $2\ ^3P_J$ states. Agreement with the nuclear charge radii from muonic helium and from He spectroscopy

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

H-atom Rydberg States and the Rydberg Constant

Rydberg constant from high-n measurements using circular states ($m=l=n-1$)

(a) D. Kleppner's group, 1990-2002: transitions between circular states of H at $n \approx 30$

$\longrightarrow$ Sensitivity: $2R_\infty/27000$

J. C. De Vries, A precision millimeter-wave measurement of the Rydberg frequency, PhD thesis, MIT, 2002

cR_∞ = 3 289 841 960 306(69) kHz
cR_∞ = 3 289 841 960 368(16) kHz (CODATA 1998)
cR_∞ = 3 289 841 960 250.8(6.4) kHz (CODATA 2018)

(b) G. Raithel's group, ongoing: transitions between circular Rydberg states of Rb

A. Ramos et al., Phys. Rev. A **96**, 032513 (2017)

(c) U. D. Jentschura and D. C. Yost: Proposed measurement with $n=18$ circular Rydberg states of H.

Phys. Rev. A **108**, 062822 (2023)

Rydberg constant from $m_l \geq 1$ Rydberg states ($2 \leq n \leq \infty$) $\longrightarrow$ Sensitivity: $R_\infty/4$

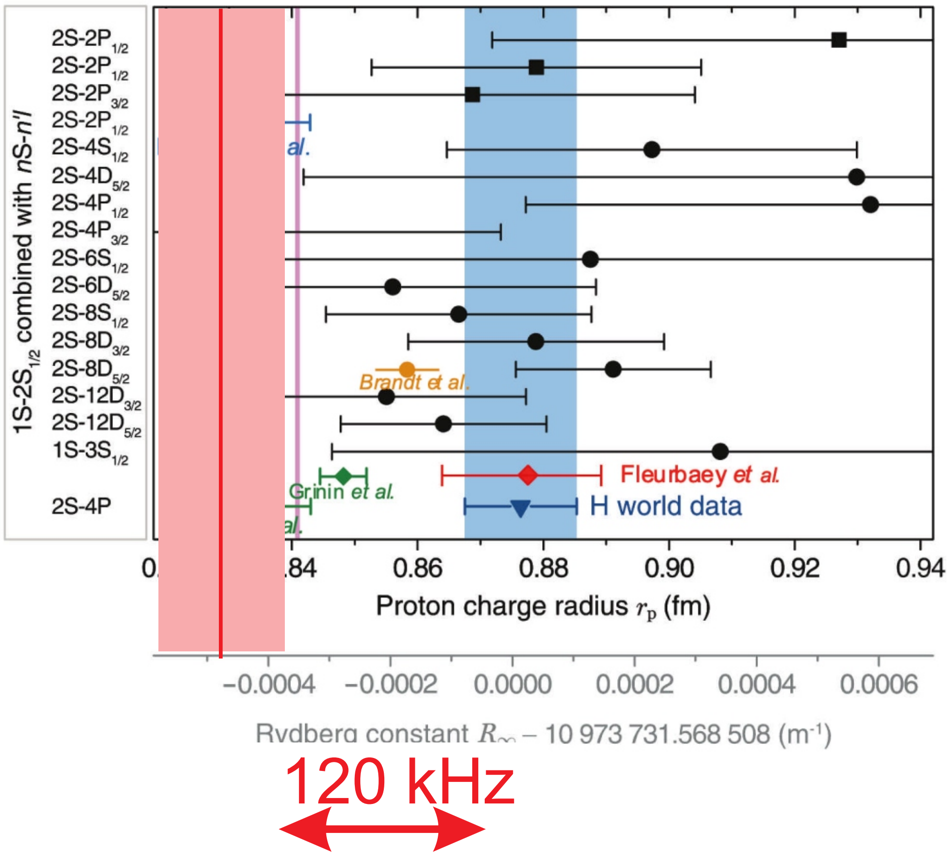
The Rydberg constant and the proton radius

$$cR_\infty = 3\,289\,841\,960\,204(15)_{\rm stat}(7)_{\rm syst}(13)_{\rm 2S-2P}\ \rm kHz \quad (this\ work)$$

$$cR_\infty = 3\,289\,841\,960\,306(69)\ \rm kHz \quad (MIT, de\ Fries\ 2001)$$

$$cR_\infty = 3\,289\,841\,960\,364(16)\ \rm kHz \quad (CODATA2010)$$

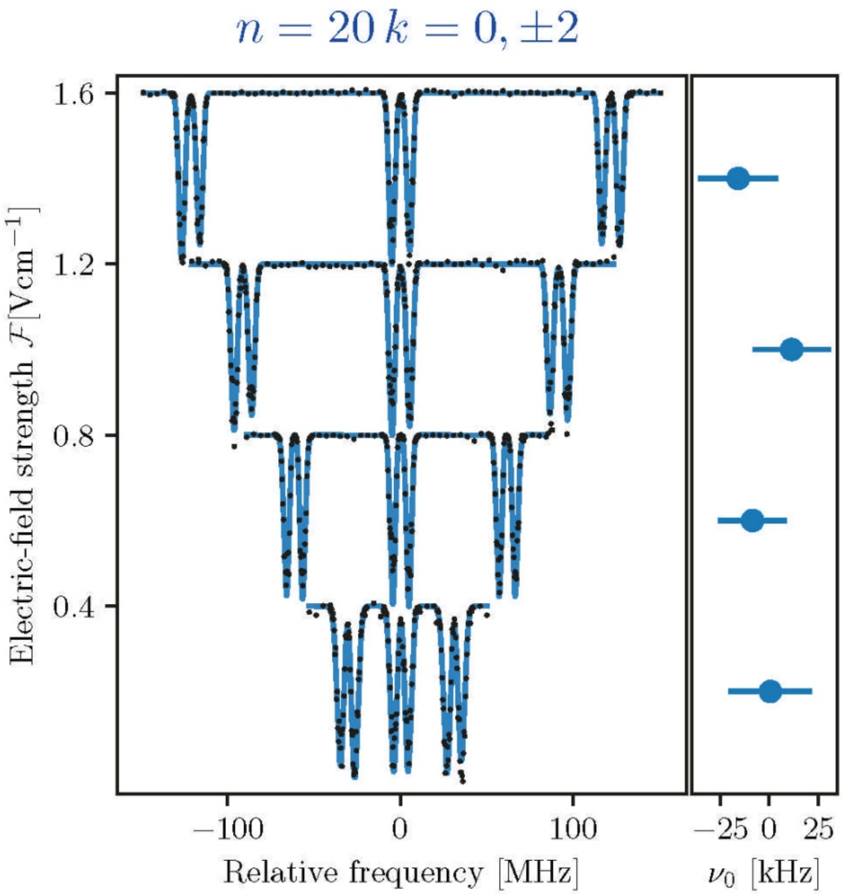
$$cR_\infty = 3\,289\,841\,960\,250.8(6.4)\ \rm kHz \quad (CODATA2018)$$



[2] Tiesinga et al., Rev. Mod. Phys. **93**, 025010 (2021)
[3] Mohr et al., Rev. Mod. Phys. **84**, 1527 (2012)
[20] Beyer et al., Science 358, 79 (2017)
[21] Fleurbaey et al., PRL 120, 183001 (2018)
[22] Bezginov et al., Science 365, 1007 (2019)
[23] Grinin et al., Science 370, 1061 (2020)
[24] Brandt et al., PRL 128, 023001 (2022)
[25] de Vries, PhD thesis, MIT (2001)

S. Scheidegger, FM, PRL **132**, 113001 (2024)

Compensating Stark Shifts



No residual shifts from electric field observed

	$0.4\,\mathrm{V\,cm^{-1}}$	$0.8\,\mathrm{V\,cm^{-1}}$	$1.2\,\mathrm{V\,cm^{-1}}$	$1.6\,\mathrm{V\,cm^{-1}}$
ν_0/kHz	0(21)	-9(17)	10(20)	-16(20)
$\mathcal{F}$/Vcm^{-1}	0.4005(4)	0.7992(3)	1.1876(4)	1.5794(3)

From lineshape broadening of $|20, \pm 2, 1\rangle_\mathrm{S}$

Electric-field gradient

$\frac{\partial \mathcal{F}}{\partial z} \approx 12(3)\,\mathrm{mV\,cm^{-2}} \;\rightarrow\; \delta\nu_\mathrm{S} \leq 150\,\mathrm{Hz}$

Scheidegger et al., PRA **108**, 042803 (2023)

Theoretical contributions to the ionization energies of ^{4}He

Table 8.2: Theoretical contributions in order α to the calculated ionization energies of the $(1s)(2s)\,^3S_1$, $(1s)(2p)\,^3P_J$ and $(1s)(3d)\,^3D_J$ centroid states in ^{4}He, as reported in Refs. 23, 202. Finite nuclear size and nuclear polarizability contributions are marked as NS and NP, respectively, and singlet-triplet mixing of the $J = 2$ (1s)(3d) states is labeled as Mix. All values are given in MHz.

	$(1s)(2s)\,^3S_1$	$(1s)(2p)\,^3P_J$	$(1s)(3d)\,^3D_J$
α^2	−1 152 789 177.644(2)	−876 116 438.795(2)	−366 019 135.854
α^4	−57 625.029	11 447.932	−827.104
α^5	3 998.632	−1 235.346	−16.699
α^6	65.205	−21.835	0.119
α^7	−6.168(1)	2.280(1)	0.023(23)[a]
α^8	0.158(52)[a]	−0.048(16)[a]	
NS	2.616(3)	−0.799(1)	−0.009
NP	−0.001	0.000	
Mix			−8.322(3)
Tot.	−1 152 842 742.231(52)	−876 106 246.611(16)	366 019 987.846(23)

[a] Only the leading contributions of this term was reported and used to estimate the uncertainty.

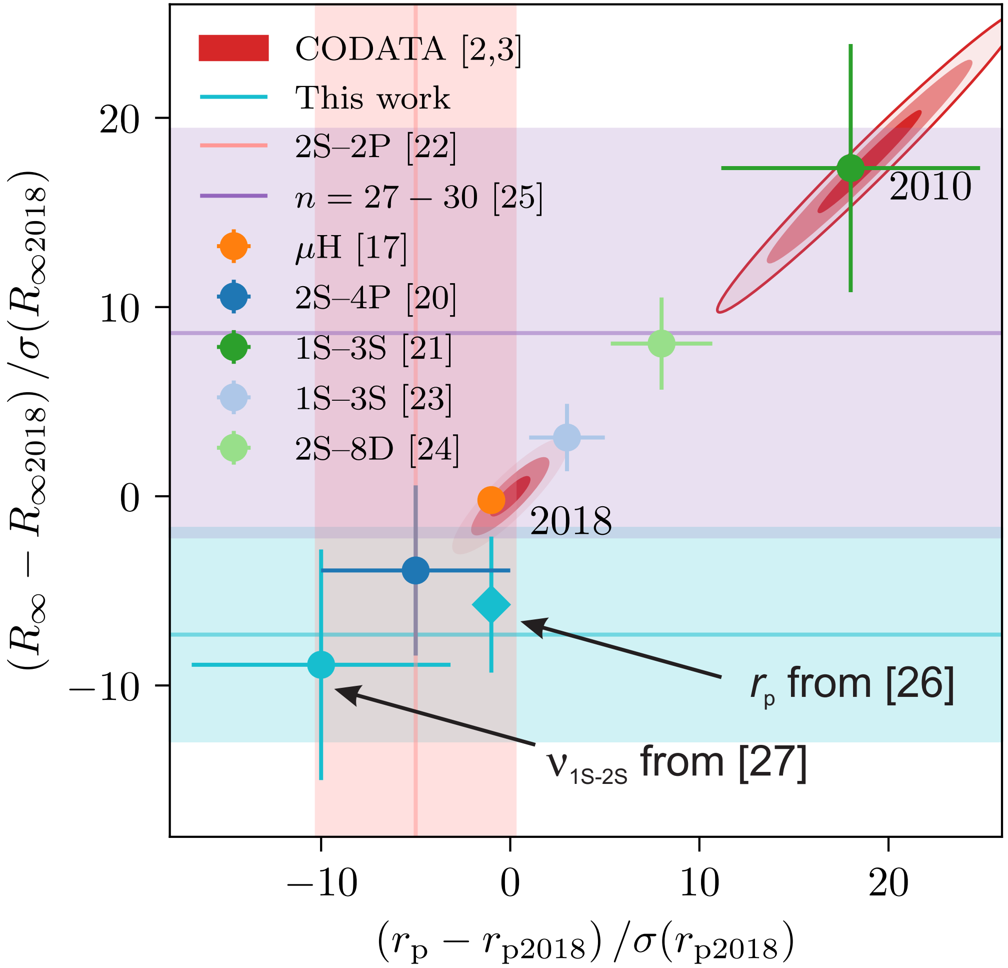
The Rydberg Constant and the Proton Radius

$$cR_\infty = 3\,289\,841\,960\,204(15)_{\rm stat}(7)_{\rm syst}(13)_{\rm 2S-2P}\,\text{kHz} \quad \text{(this work)}$$

$$cR_\infty = 3\,289\,841\,960\,306(69)\,\text{kHz} \quad \text{(MIT, de Fries 2001)}$$

$$cR_\infty = 3\,289\,841\,960\,364(16)\,\text{kHz} \quad \text{(CODATA2010)}$$

$$cR_\infty = 3\,289\,841\,960\,250.8(6.4)\,\text{kHz} \quad \text{(CODATA2018)}$$

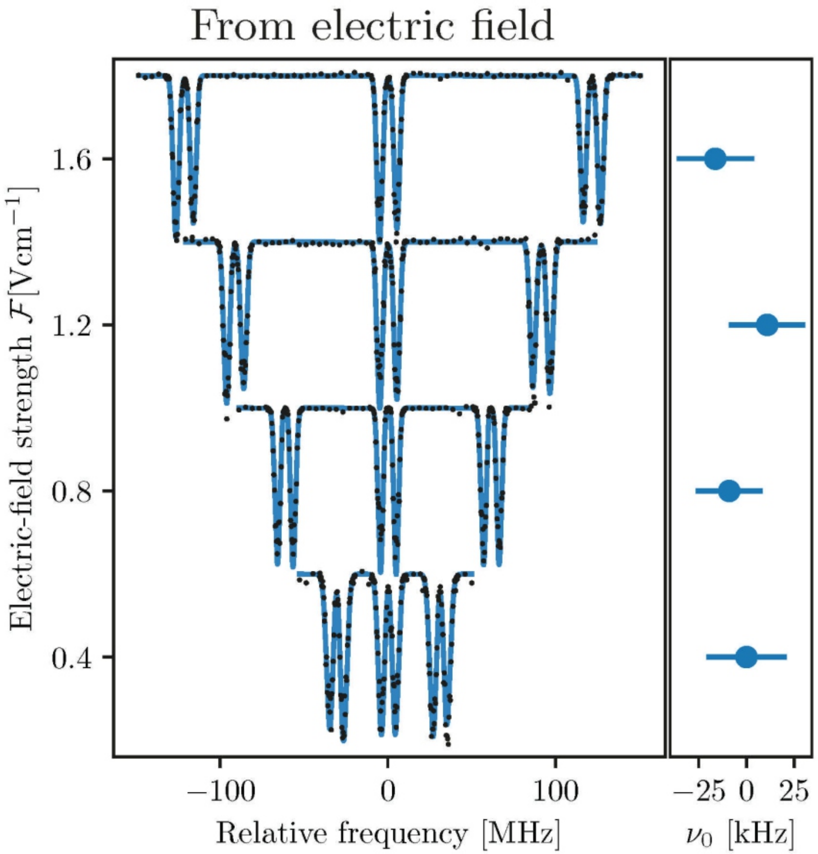


with r_p from µH [276 : 3 289 841 960 214(22) kHz
wth 1s-2s frequency [27] : 3 289 841 960 194(40) kHz

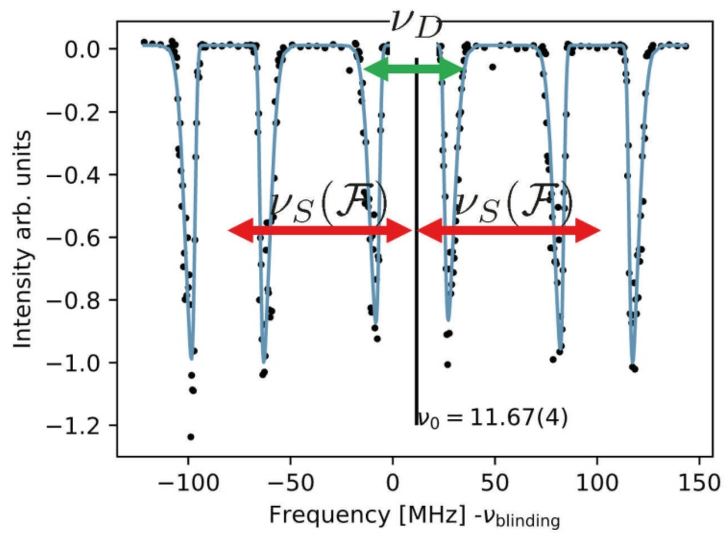
[2] Tiesinga et al., Rev. Mod. Phys. **93**, 025010 (2021)
[3] Mohr et al., Rev. Mod. Phys. **84**, 1527 (2012)
[20] Beyer et al., Science 358, 79 (2017)
[21] Fleurbaey et al., PRL 120, 183001 (2018)
[22] Bezginov et al., Science 365, 1007 (2019)
[23] Grinin et al., Science 370, 1061 (2020)
[24] Brandt et al., PRL 128, 023001 (2022)
[25] de Fries, PhD thesis, MIT (2001)
[26] Pohl et al., Nature 466, 213 (2010)
[27] Parthey et al., PRL **107**, 203001 (2011)

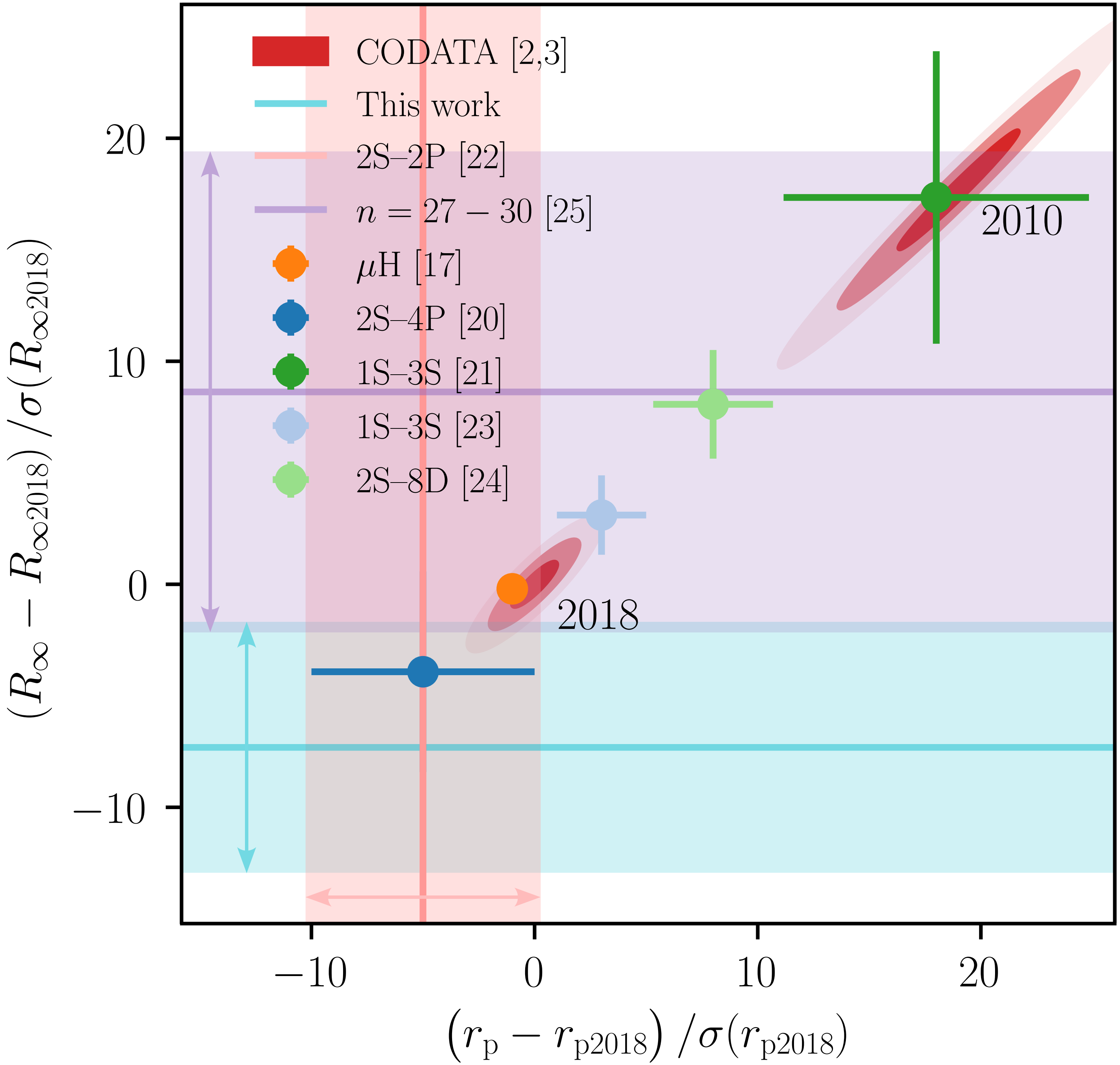
S. Scheidegger, FM, PRL **132**, 113001 (2024)

Lineshapes



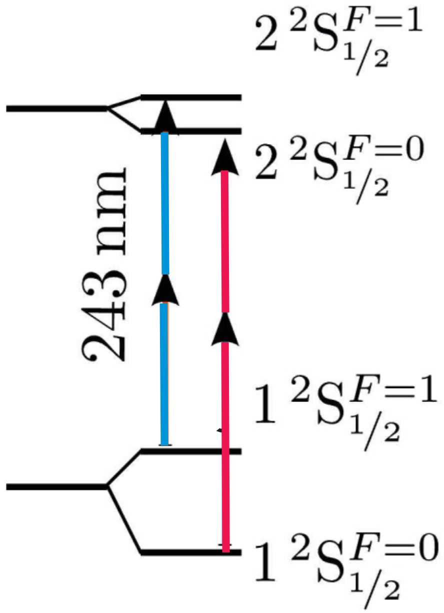
$$I_0 \exp\left(-\frac{(\nu-\nu_0 \mp \nu_D - \nu_S(\mathcal{F},k))^2}{2(\sigma_D^2 + k\sigma_S^2)}\right)\left(1+\mathrm{erf}\left(\frac{\gamma_D(\nu - \ldots)}{\sqrt{2}\sigma_D}\right)\right)$$

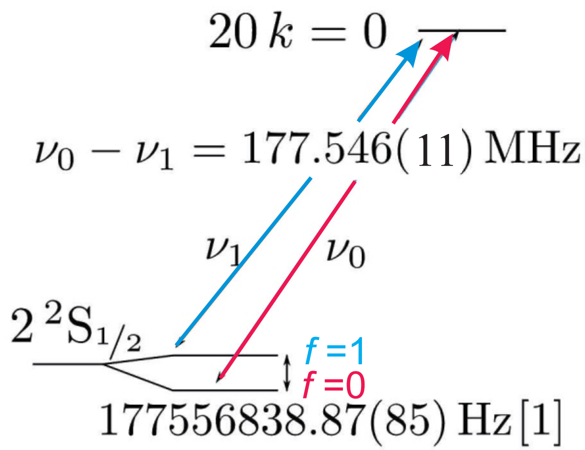


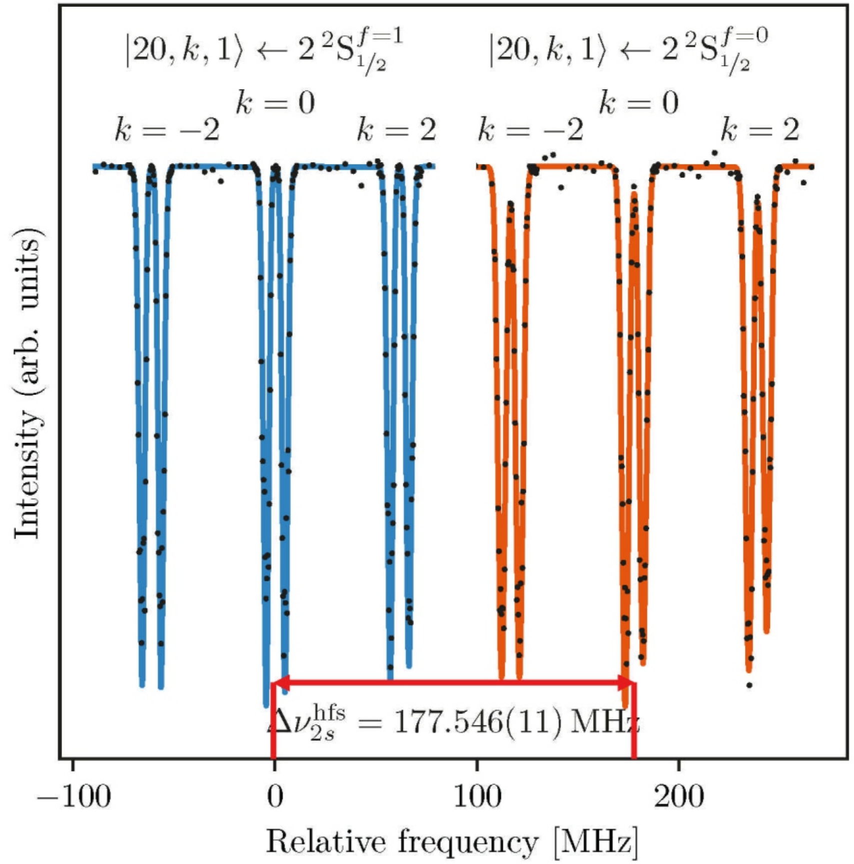


CODATA [2,3]
This work
2S–2P [22]
$n = 27 - 30$ [25]
μH [17]
2S–4P [20]
1S–3S [21]
1S–3S [23]
2S–8D [24]
2010
2018
20
10
0
−10
−10
0
10
20
$(R_\infty - R_{\infty 2018}) / \sigma(R_{\infty 2018})$
$(r_p - r_{p2018}) / \sigma(r_{p2018})$

2s Hyperfine Splitting







[1] R. G. Bullis *et al.*,, PRL **130**,203001 (2023)

Statistically limited

Scheidegger et al., PRA **108**, 042803 (2023)

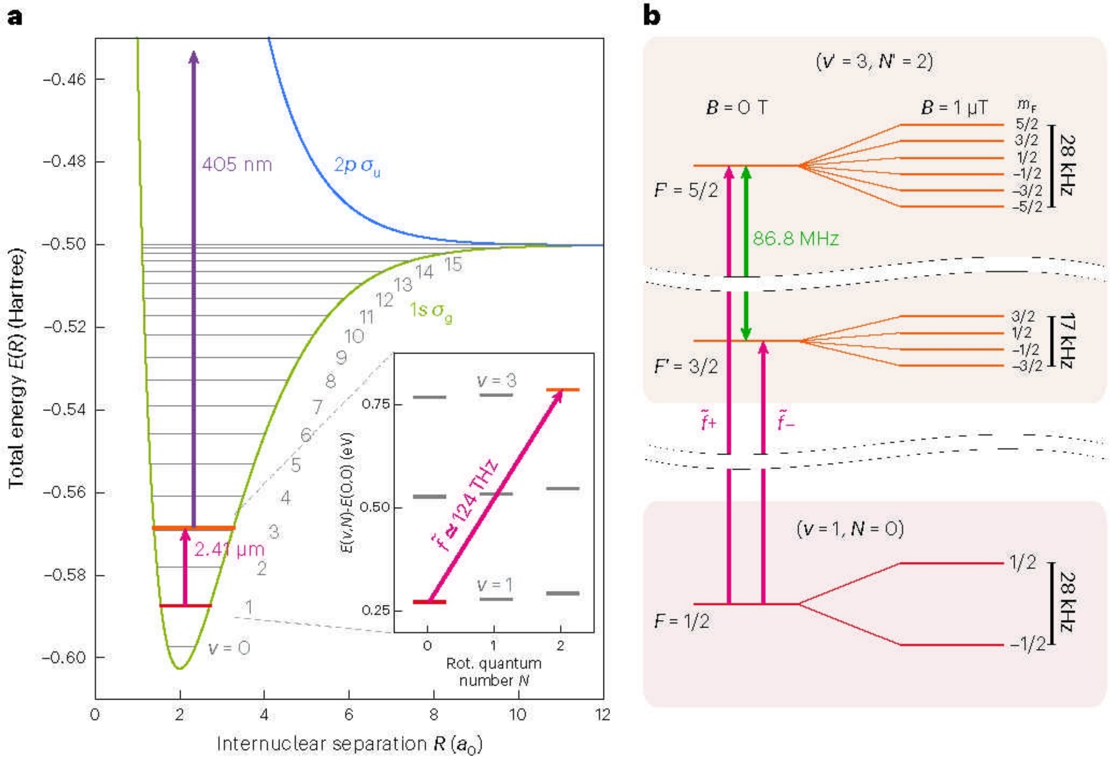
Precision spectroscopy in H_2^+

nature physics

Article https://doi.org/10.1038/s41567-023-02320-z

Laser spectroscopy of a rovibrational transition in the molecular hydrogen ion H_2^+

Schenkel, Alighanbari and Schiller,
Nature Physics **20,** 383–388 (2024)

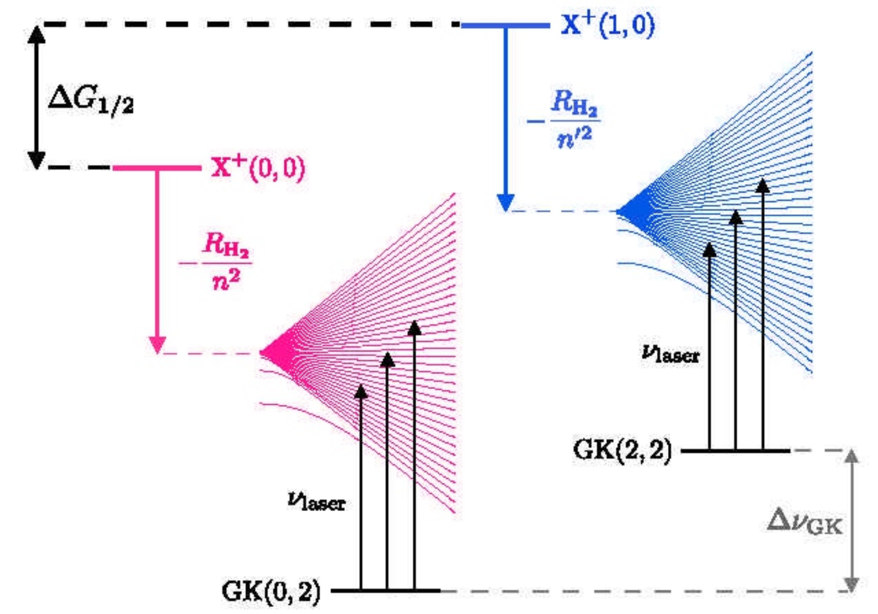


Exp.: 124'487'032.7(1.5) MHz
Th.: 124'487'032.45(6) MHz
(Korobov et al., PRL **118**, 233001 (2017))

PHYSICAL REVIEW LETTERS **132,** 073001 (2024)

Zero-Quantum-Defect Method and the Fundamental Vibrational Interval of H_2^+

I. Doran,[1] N. Hölsch,[1] M. Beyer,[2] and F. Merkt[1,3,4,*]



Exp.: 65 688 323.3(5) MHz
Th.: 65 688 323.7101(5)(29) MHz
(Korobov et al., **PRL** 118, 233001 (2017))