

# Experimental and theoretical studies of molecular hydrogen ions in the low parts-per-trillion range: Doppler-free laser spectroscopy, QED, and the values of physical constants

Virtual Seminar on Precision Physics and  
Fundamental Symmetries, June 9, 2020

Jeroen Koelemeij (VU Amsterdam)

Jean-Philippe Karr (LKB Paris)



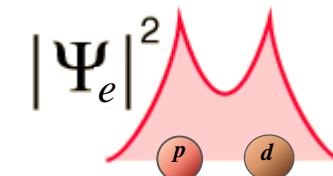
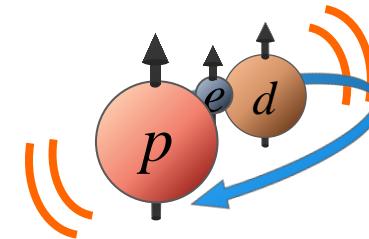
# Our interest in molecular hydrogen ions

- $\text{H}_2^+$ ,  $\text{HD}^+$ : simple three-body systems

Internal degrees of freedom:

- Electronic
- Vibrational
- Rotational
- Spin

} Direct dependence on  $m_p/m_e$  and  $m_d/m_e$

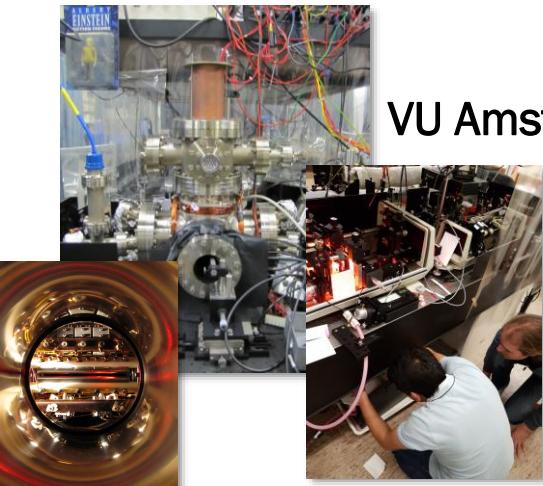


- Very accessible to theory (relativistic QM and QED)

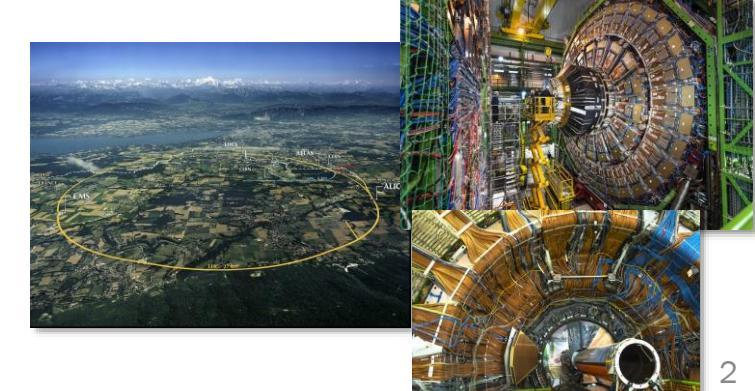
⇒ Presentation Jean-Philippe Karr

VU Amsterdam

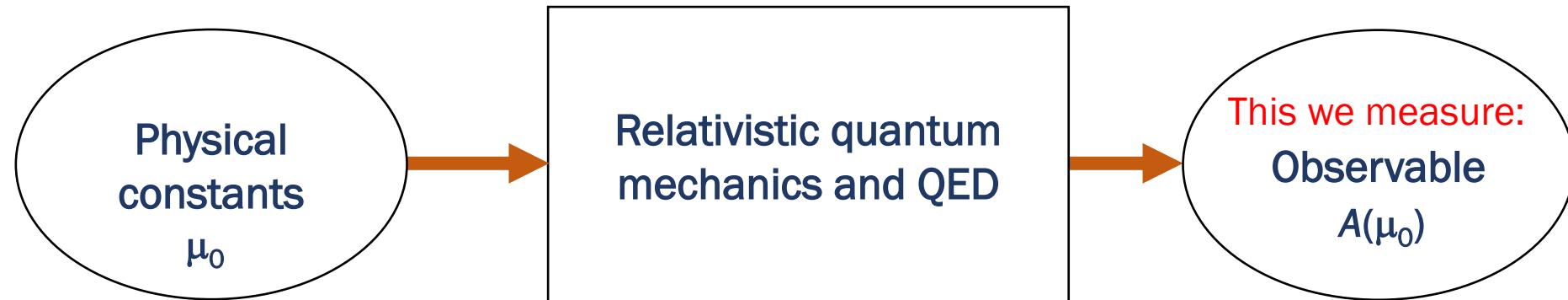
Tests of fundamental physical law  
and searches for new physics in a  
table-top experiment



LHC @CERN



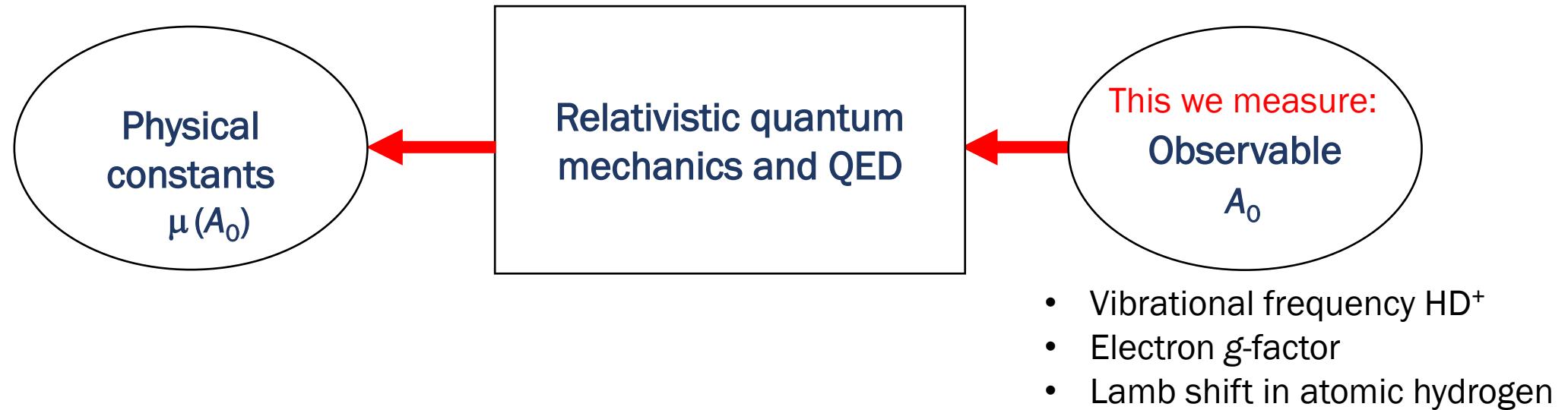
# Theory and fundamental constants



## Compare theory with experiment:

- Do we find agreement **also at the next digit of precision** and the **next level of complexity?**
- If so:
  - Adds to confidence in our theoretical framework
  - Rule out “new physics”
- If not:
  - **Breakdown of the existing theory?**
  - **Hitherto unrecognized phenomena (experimental or theoretical)?**

# Theory and fundamental constants

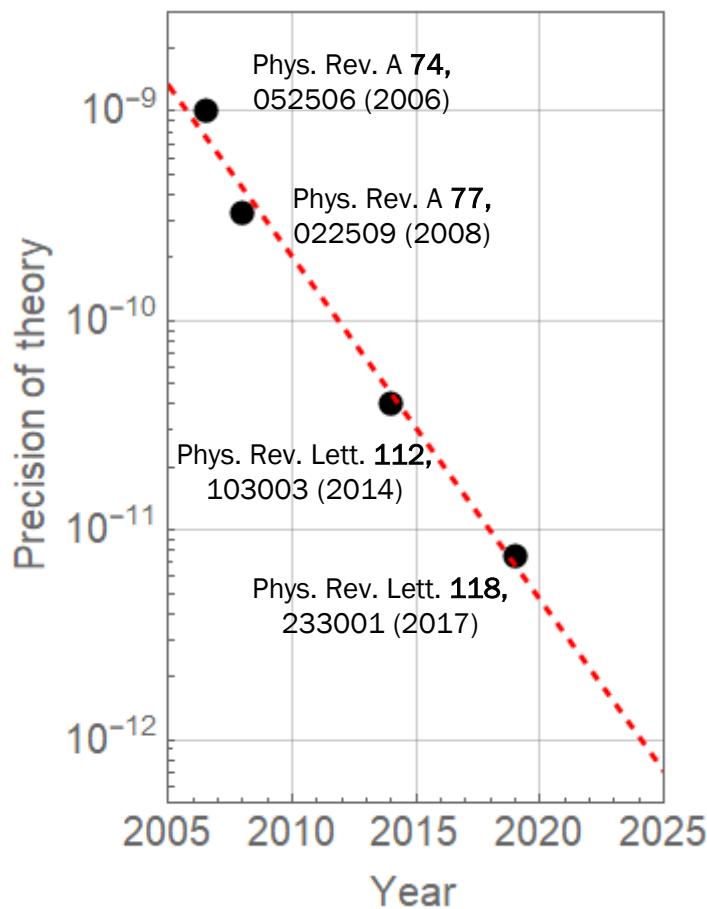


Old idea\*: use molecular theory to  
‘translate’ HD<sup>+</sup> vibrational frequency to  
new value of  $m_p/m_e$

\*W. H. Wing, W. E. Lamb, Jr. et al.,  
Phys. Rev. Lett. 36, 1488 (1976)

# Recent advances in theoretical precision

## Precision of rotational-vibrational level energies in HD<sup>+</sup>



- Impressive progress by our collaborators Karr and Hilico (LKB Paris) and Korobov (JINR Dubna, Russia)

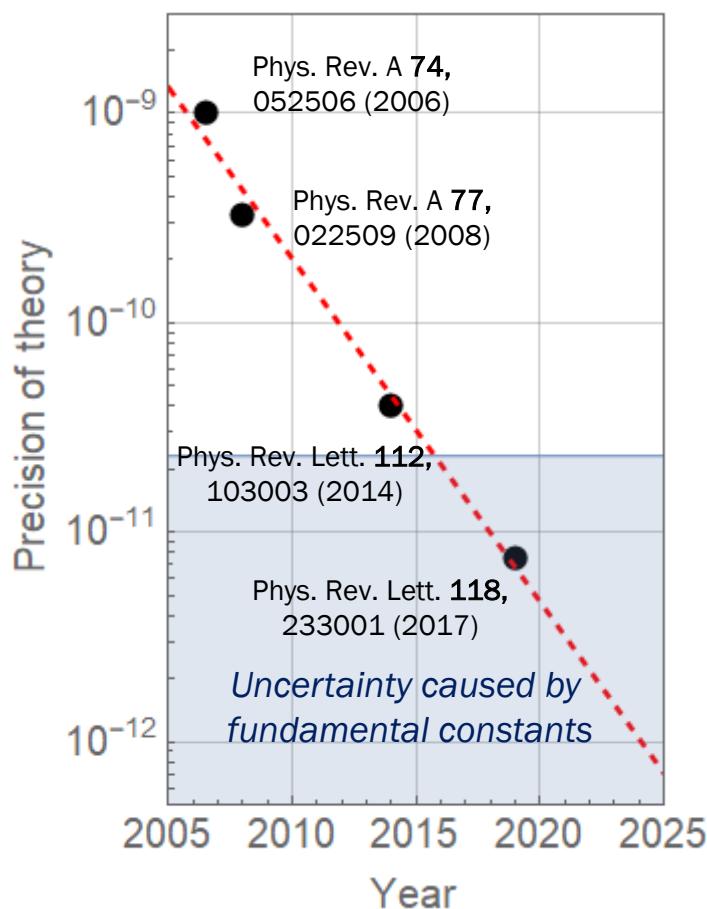


Second half of this talk

- Current precision 7-8 ppt

# Recent advances in theoretical precision

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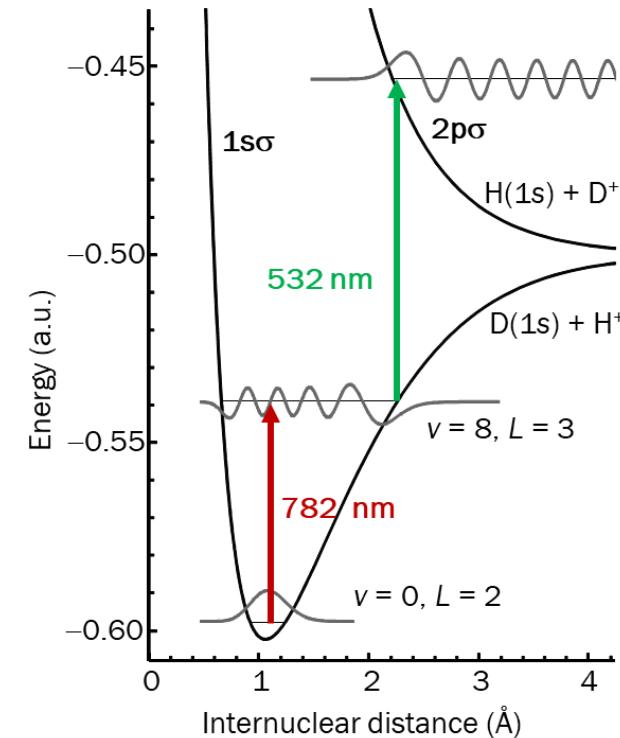


Second half of this talk

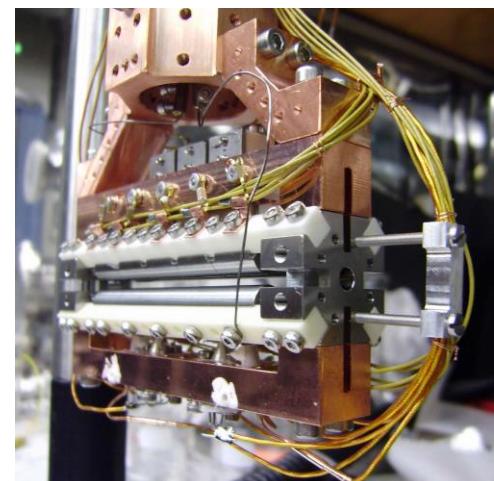
- Current precision 7-8 ppt
- Uncertainty no longer limited by precision of theory, but by the precision of the values of the fundamental constants!

# Matching theoretical precision with experimental precision

- Vibrational overtones of  $\text{HD}^+$  can be excited and detected using (N)IR lasers
- Natural line width of these overtones  $\sim 10 \text{ Hz} \Rightarrow$  resolution of  $10^{-14}$  possible
- **Requires reduction of Doppler broadening (thermal motion), pressure broadening, ...  $\Rightarrow$  ion traps**
- Foundation for present techniques laid by pioneering experiments at Düsseldorf (Schiller group):
  - Sympathetic cooling of molecular hydrogen ions through laser-cooled beryllium ions in an ion trap\*
  - Vibrational excitation of  $\text{HD}^+$  and REMPD detection ‡
  - Vibrational (NIR and IR) spectroscopy §,¶



J. Biesheuvel, J.-Ph. Karr, L. Hilico,  
K.S.E. Eikema, W. Ubachs, JK,  
*Nat. Commun.* 7, 10385 (2016)



\* P. Blythe, B. Roth, U. Fröhlich, H. Wenz, S. Schiller, *PRL* **95**, 183002 (2005).

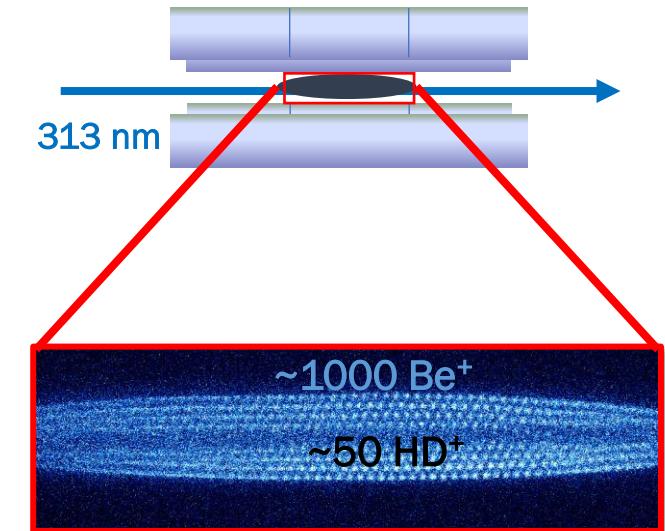
‡ B. Roth, J.C.J. Koelemeij, H. Daerr, S. Schiller, *PRA* **74**, 040501(R) (2006).

§ J.C.J. Koelemeij, B. Roth, A. Wicht, I. Ernsting, S. Schiller, *PRL* **98**, 173002 (2007),

¶ U. Bressel, A. Borodin, J. Shen, M. Hansen, I. Ernsting, S. Schiller, *PRL* **108** 183003 (2012).

# Laser cooling and REMPD spectroscopy

- Store beryllium atomic ions (these can be laser-cooled by a 313 nm laser)
- Embed HD<sup>+</sup> ions ⇒ **sympathetic cooling to 10 mK**
- We image 313 nm fluorescence on an EMCCD camera ⇒ count number of HD<sup>+</sup>

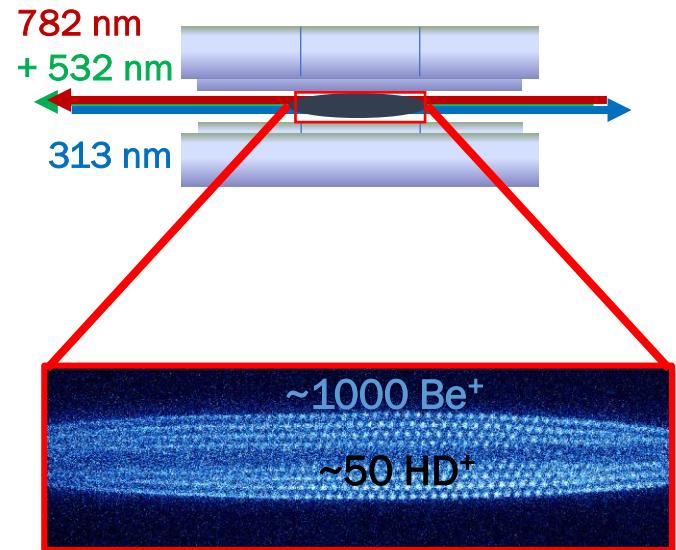
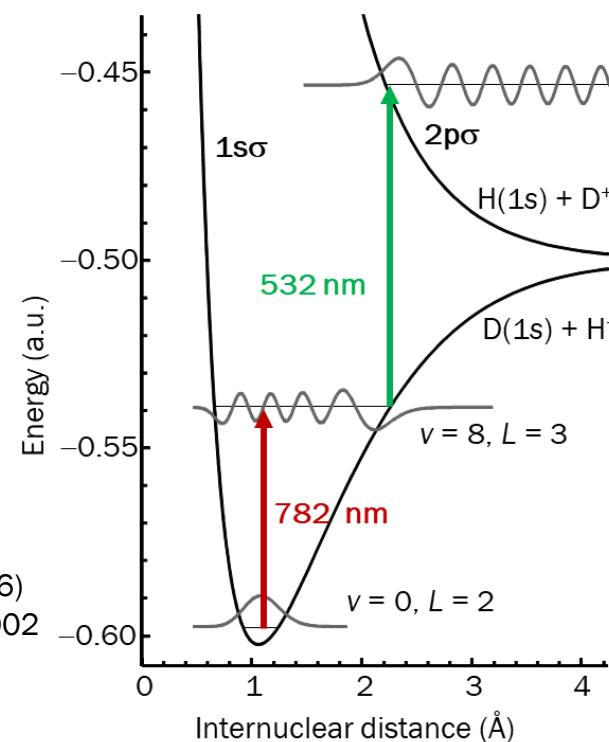


# Laser cooling and REMPD spectroscopy

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- Embed HD<sup>+</sup> ions ⇒ **sympathetic cooling to 10 mK**
- We image 313 nm fluorescence on an EMCCD camera ⇒ count number of HD<sup>+</sup>
- Now apply the lasers for vibrational excitation followed by state-selective dissociation
- Measure loss of HD<sup>+</sup> as a signature of successful vibrational excitation

First developed at Düsseldorf (group S. Schiller)

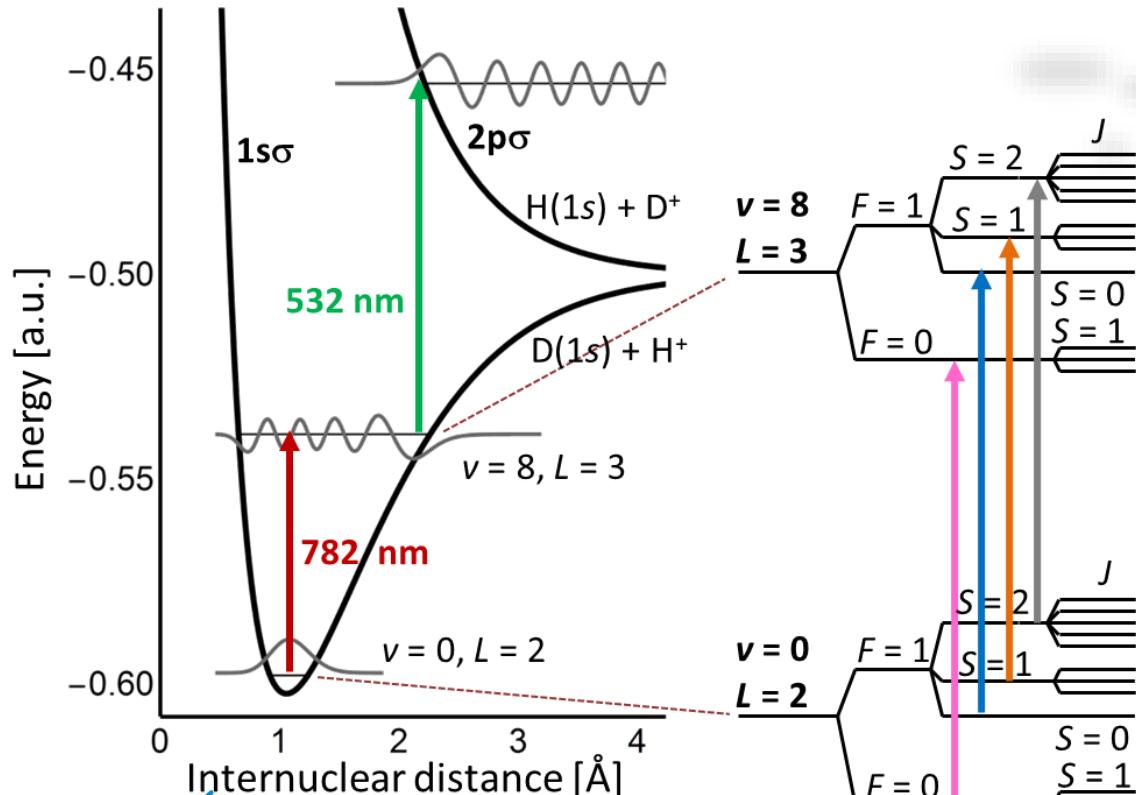
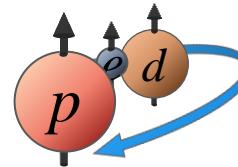
B. Roth, J.C.J. Koelemeij, H. Daerr, S. Schiller, PRA **74**, 040501(R) (2006)  
J.C.J. Koelemeij, B. Roth, A. Wicht, I. Ernsting, S. Schiller, PRL **98**, 173002



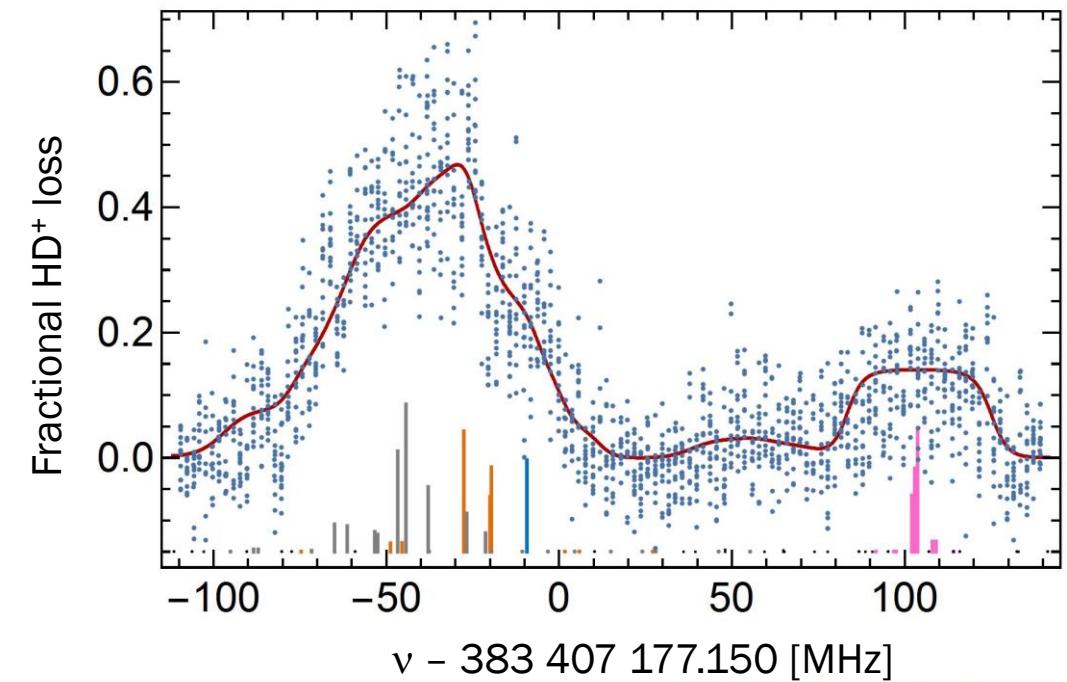
# Example of Doppler-broadened spectrum

VU 2016 ( $v=0 - v'=8$ )

J. Biesheuvel, J.-Ph. Karr, L. Hilico, K.S.E. Eikema,  
W. Ubachs, J.C.J. Koelemeij, Nat. Comm. 7, 10385



- Uncertainty 1.1 ppb
- Doppler-broadened spectrum with hyperfine complexity



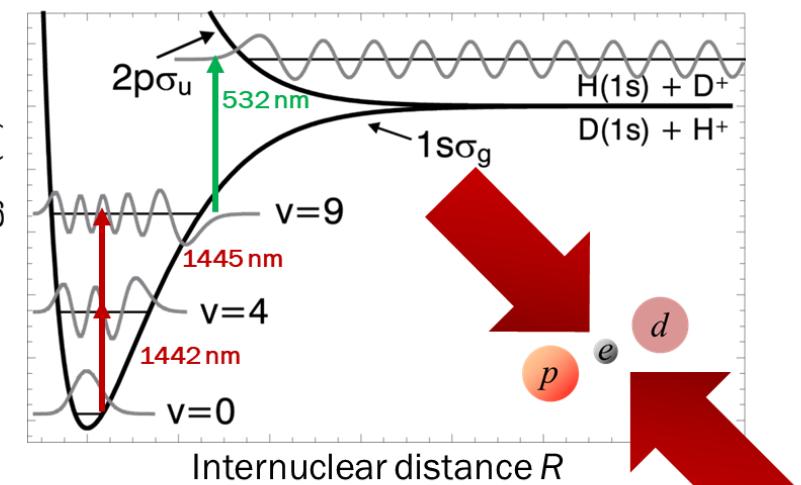
# Can we do better?

- Accuracy limit: Doppler broadening (despite cooling to 10 mK)
- 2013: proposed two-photon Doppler-free spectroscopy\*
- Effective wave vector 0.7 mm: can use our weakly confining linear rf trap ☺ (Lamb-Dicke regime)
- <2 kHz laser line width, frequency measurement <1 ppt (Cs clock, frequency comb laser)
- All set to improve uncertainty from ppb to ppt!

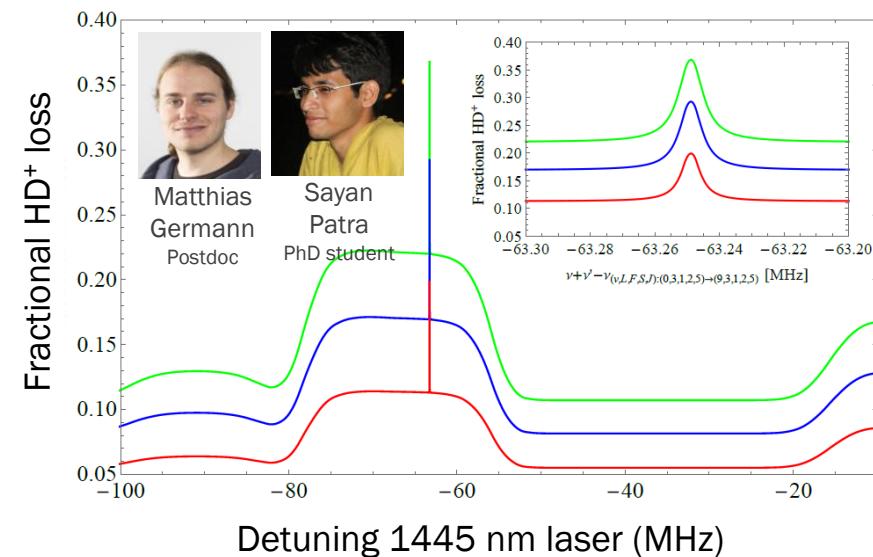
\*V.Q. Tran, J.-Ph. Karr, A. Douillet, J.C.J. Koelemeij, L. Hilico, Phys. Rev. A **88**, 033421 (2013)

\*\* S. Patra, PhD thesis VU Amsterdam, 2018

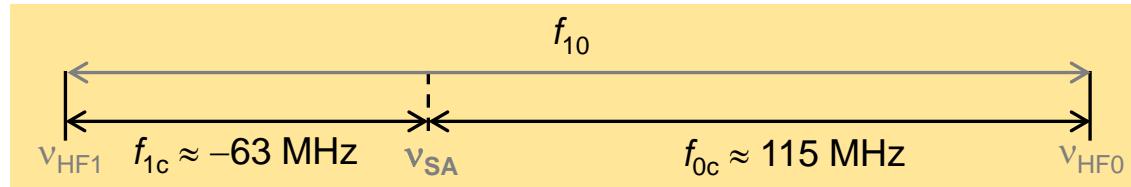
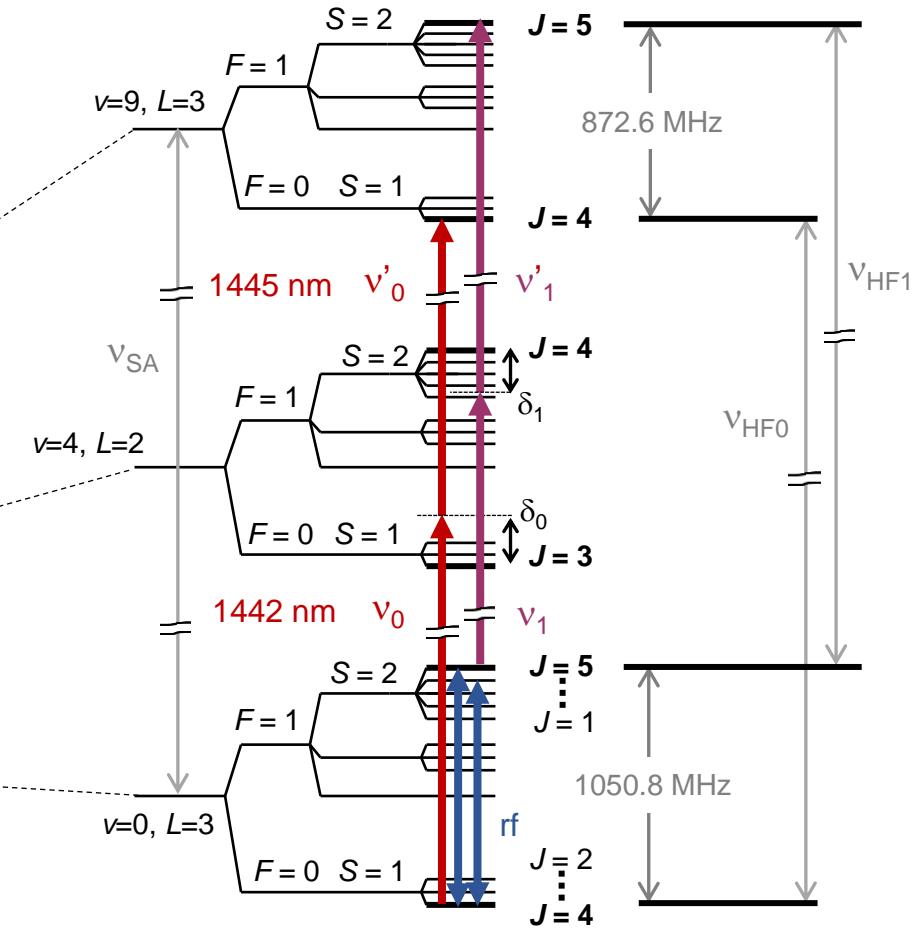
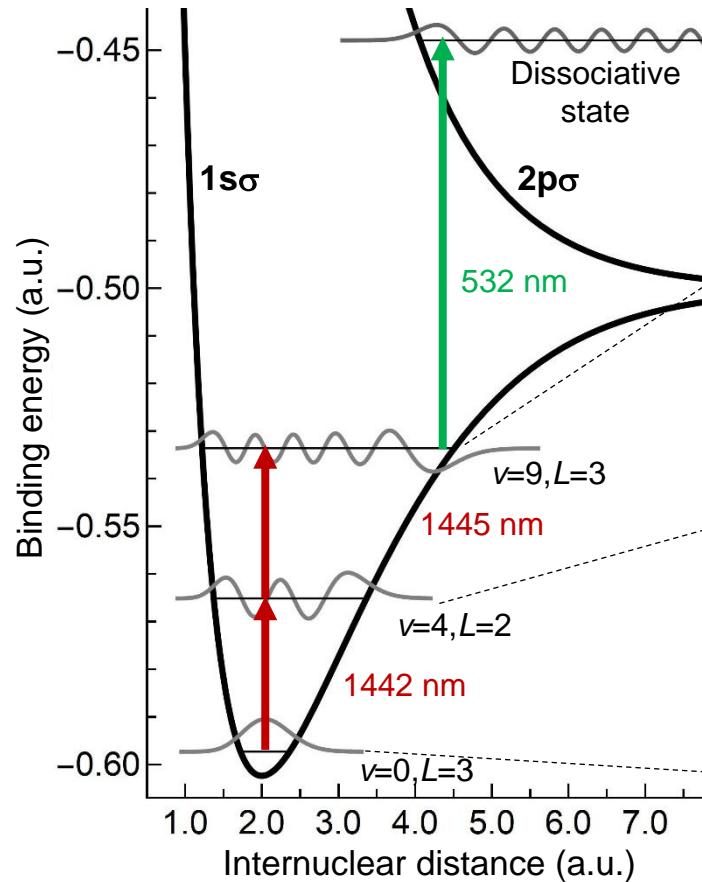
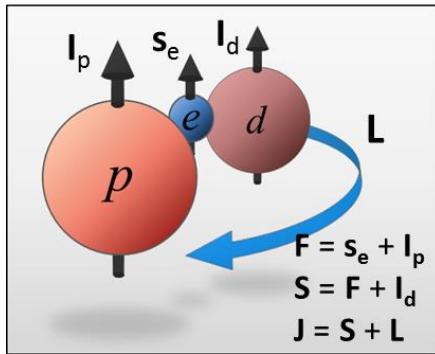
## Doppler-free two-photon spectroscopy (Lamb-Dicke regime)



## Simulated spectra\*, \*\*

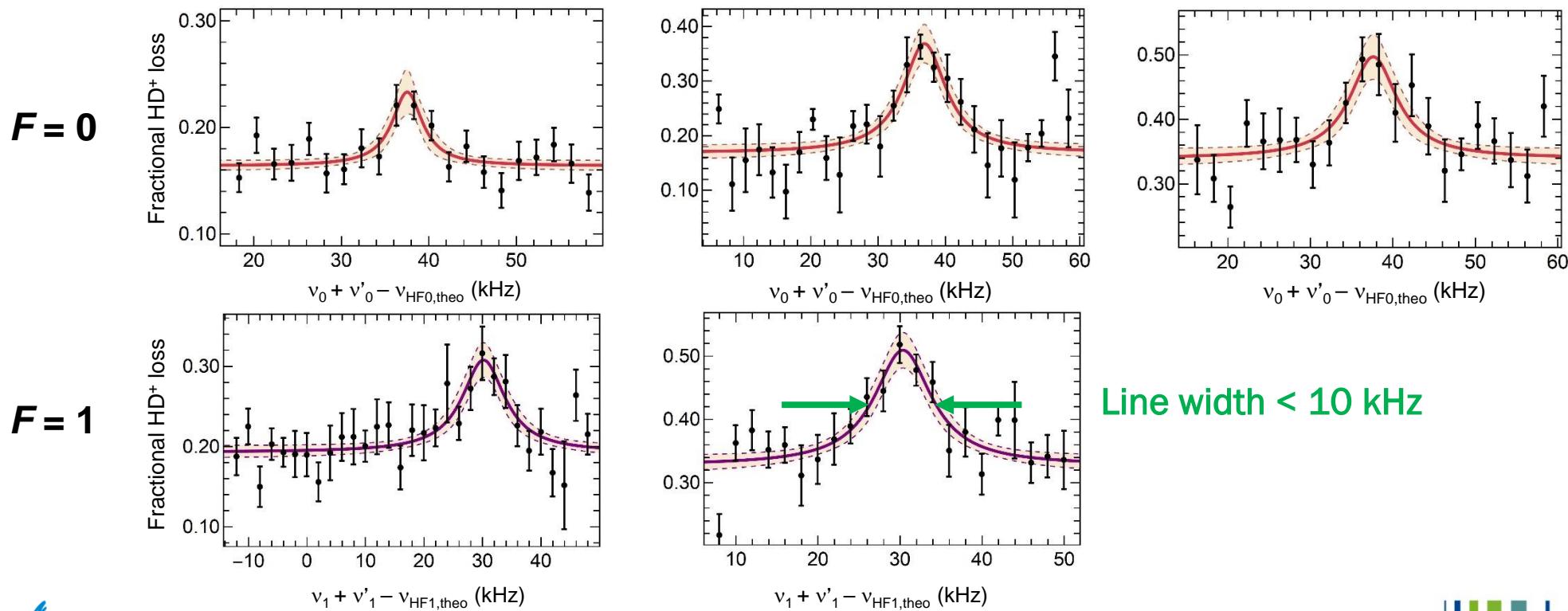


# Hyperfine structure – target transitions



# Our 2018 – 2019 results

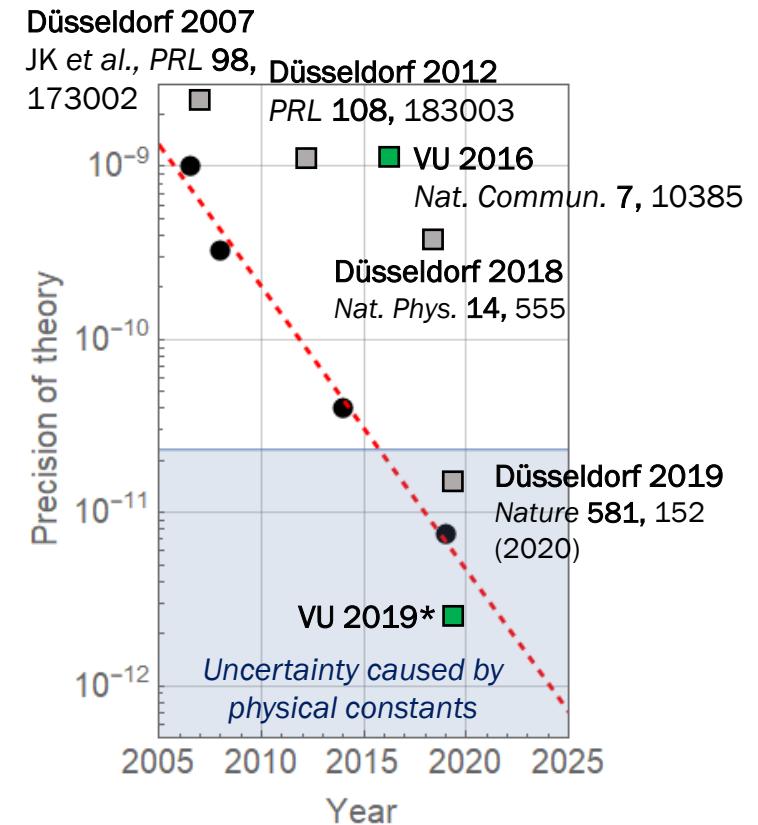
- First observation of Doppler-free optical transitions in HD<sup>+</sup> ( $v=0$  –  $v'=9$ ) !
- Frequency measurement with **1.2 kHz uncertainty (2.9 ppt)**



Line width < 10 kHz

# Implications

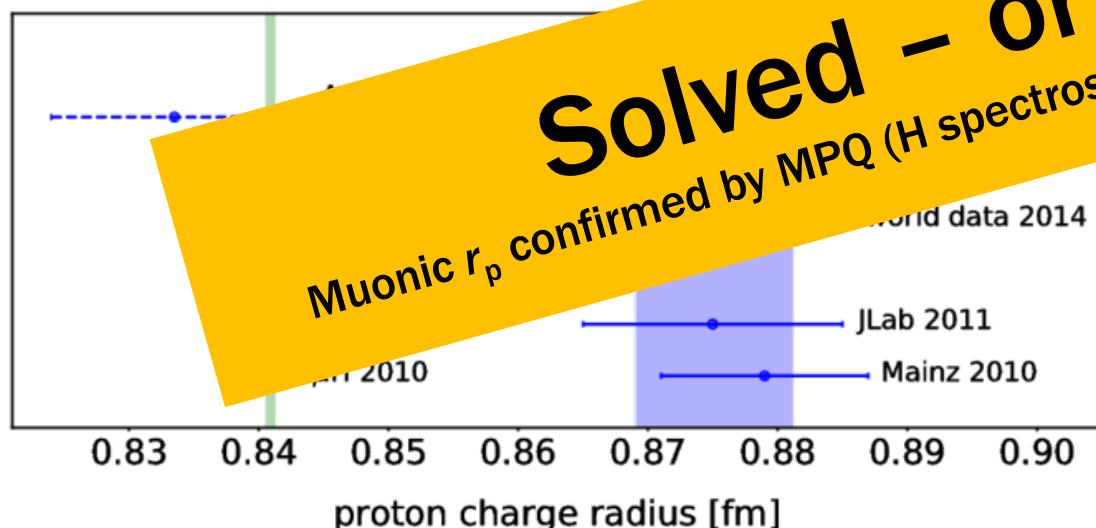
- Latest result in the quest for ever higher precision
- For the first time, accuracy of experiment exceeds that of theory
- We have deeply entered the regime where uncertainties of physical constants dominate the theoretical uncertainty
- We can say something about their values – and about two ‘big issues’ in contemporary physics...



\* S. Patra, M. Germann, J.-Ph. Karr, M. Haidar, L. Hilico, V.I. Korobov, F.M.J. Cozijn, K.S.E. Eikema, W. Ubachs, J.C.J. Koelemeij (forthcoming)

# Big issue 1: the ‘proton radius puzzle’

- Measurements in muonic hydrogen:  
Proton charge radius 5.6 $\sigma$  smaller than CODATA literature value  
(R. Pohl et al., Nature 466, 213 (2010))
- Affects also Rydberg constant (at similar level)
- Subject of VU FOM Program ‘The m...’



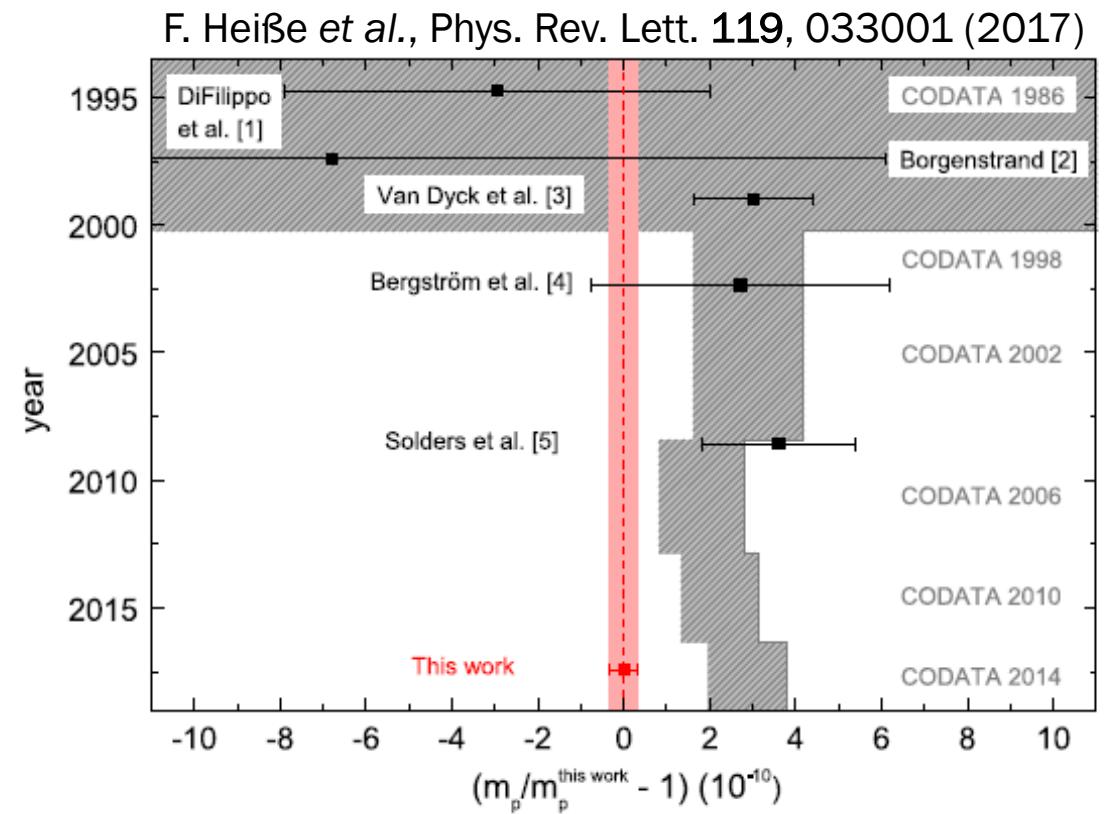
## List of unsolved problems in physics

From Wikipedia, the free encyclopedia

- Proton radius puzzle: What is the electric charge radius of the proton?

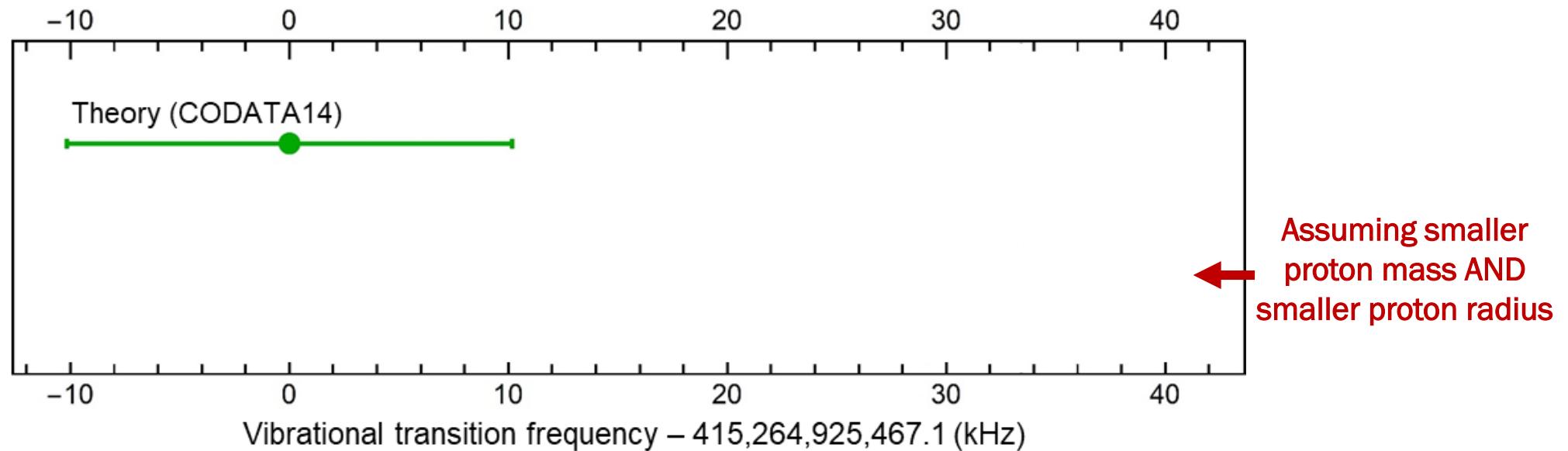
# Big issue 2: the ‘proton mass puzzle’

- ‘Proton mass puzzle’ (2017): Improved value of proton atomic mass measured at MPIK Heidelberg\* is  $3\sigma$  smaller than CODATA literature value – what is going on?
- This also shifts HD<sup>+</sup> theoretical predictions by almost  $3\sigma$  !

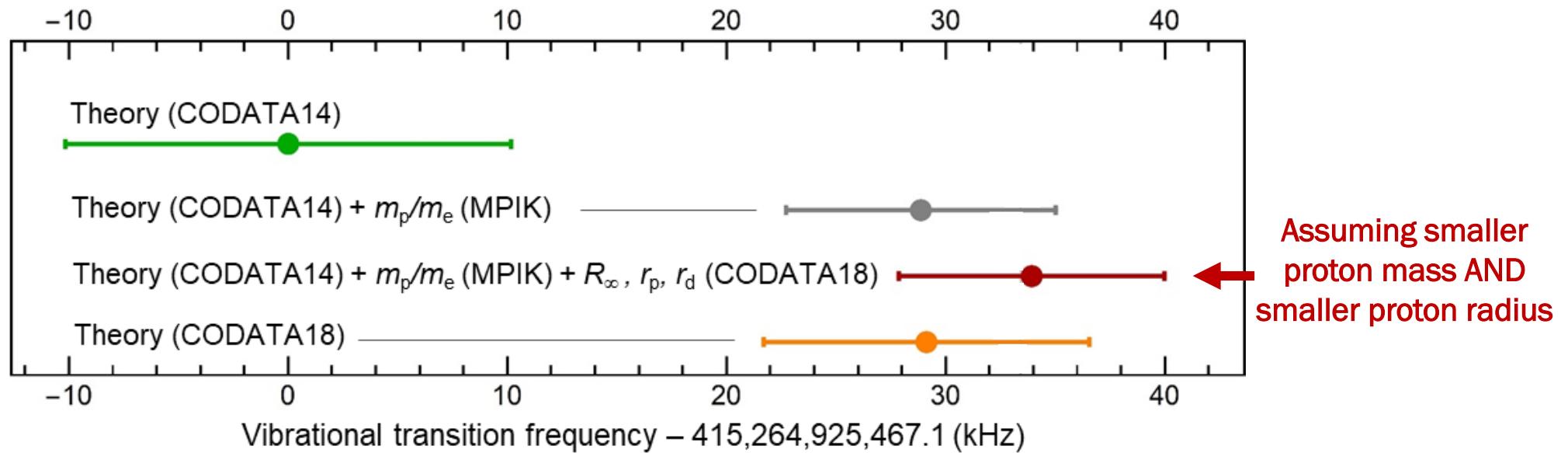


\*F. Heiße et al., Phys. Rev. Lett. **119**, 033001 (2017);  
Phys. Rev. A **100**, 022518 (2019)

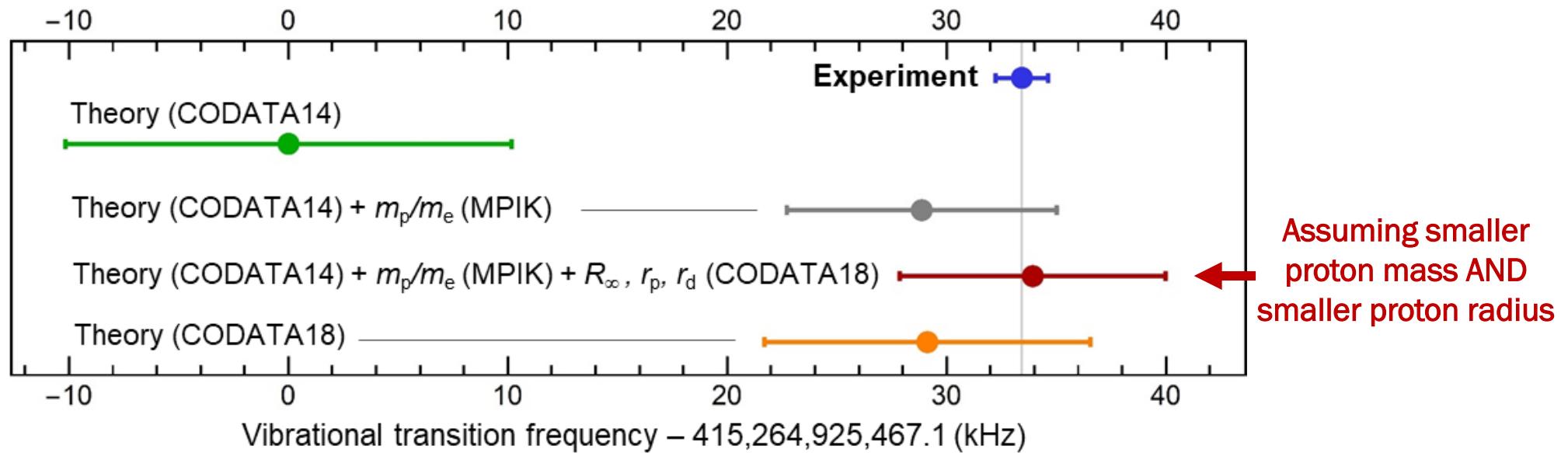
# Impact on theoretical vibrational frequency



# Impact on theoretical vibrational frequency

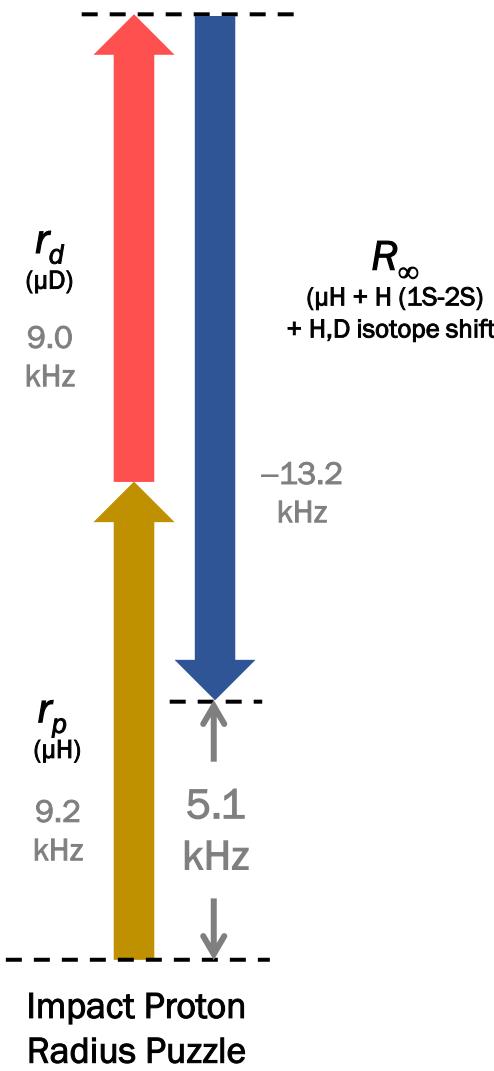
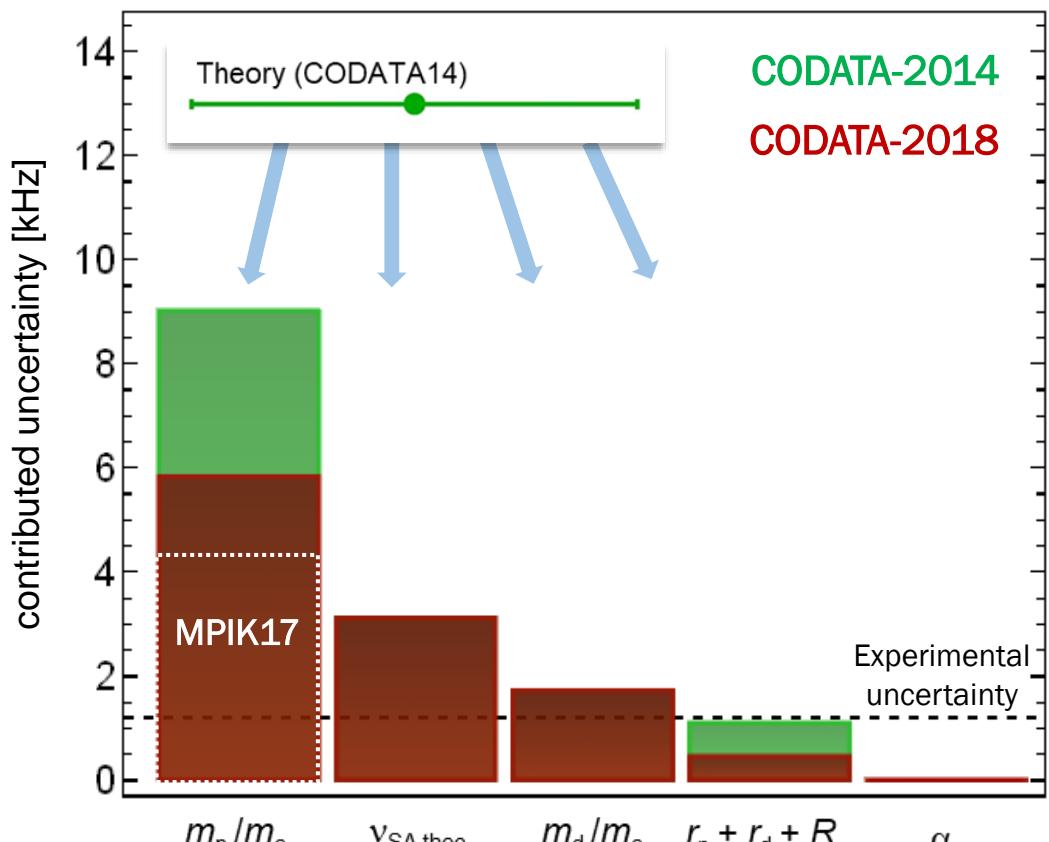


# Impact on theoretical vibrational frequency

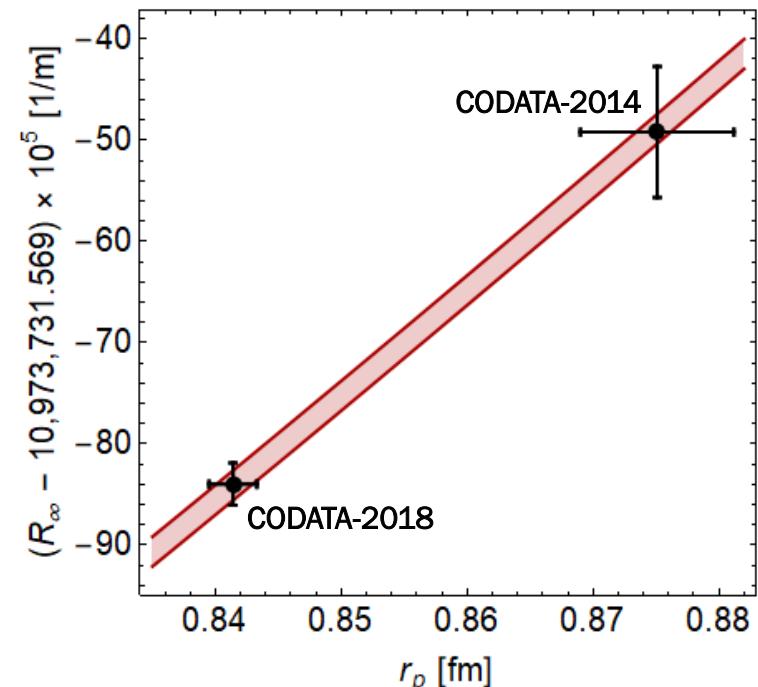


# Influence of physical constants

## Breaking down the theoretical error bar

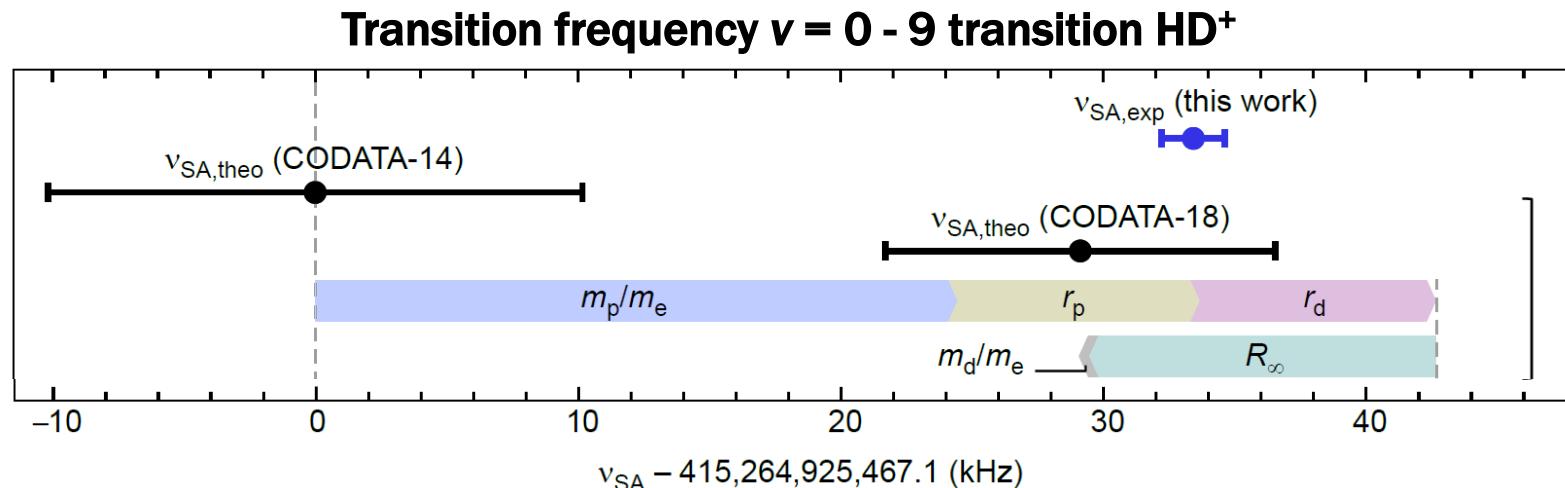


**H (1S-2S)\* : constrains  $r_p$ ,  $R_\infty$**   
see e.g. Horbatsch & Hessels,  
*PRA 93, 022513 (2016)*



\* C. G. Parthey et al., *PRL 107, 203001 (2011)*

# Agreement theory & experiment



**Now, what conclusions can we draw? Typically (in our field\*, \*\*) one claims:**

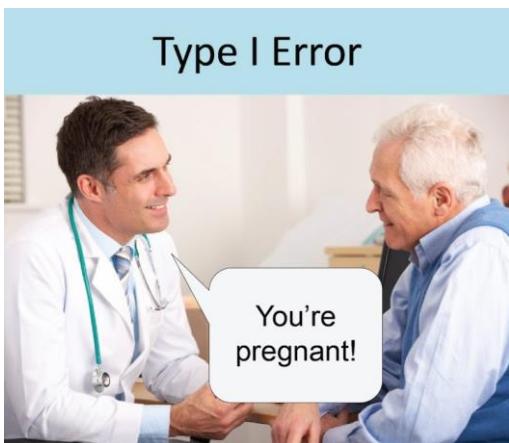
1. Theory (including QED) is successfully tested
2. Adjust value of  $m_p/m_e$  so as to match theory to experiment
3. Improved constraint on “new physics” (e.g. Yukawa-type fifth forces)

# Testing theory

- Essentially a **hypothesis test**
- Theory:  $f\left(\frac{m_p}{m_e}, \frac{m_d}{m_p}, R_\infty, r_p, r_d, \alpha\right) \approx f\left(\frac{m_p}{m_e}\right)$
- **Test statistic:**  $\Delta/\sigma \equiv \left(f_{\text{exp}} - f\left(\frac{m_p}{m_e}\right)\right)/\sigma$
- Three ingredients, one equation  $\Rightarrow$  we can test only one ingredient  $\Rightarrow$  we **must** make assumptions for other two ingredients:
  - Fix  $\frac{m_p}{m_e}$  to CODATA value, assuming it is correct
  - Assume  $f_{\text{exp}}$  is correctly determined
- Test theory: must allow for a possible deviation  $\zeta$ , i.e.  $f\left(\frac{m_p}{m_e}\right) \rightarrow f\left(\frac{m_p}{m_e}\right) + \zeta$ 
  - **Null hypothesis: theory is correct**  $H_0: \zeta = 0$
  - **Alternative hypothesis: theory is incorrect**  $H_1: |\zeta| > 0$

# Hypothesis test outcomes

Test outcome \ Reality	Negative reality: $\zeta = 0$ $H_0$ is true ( $H_1$ is false)	Positive reality: $ \zeta  > 0$ $H_0$ is false ( $H_1$ is true)
Test outcome negative: " $H_0$ is true, $H_1$ is false"	True negative	False negative (Type II error)
Test outcome positive: " $H_0$ is false, $H_1$ is true"	False positive (Type I error)	True positive



# Hypothesis test outcomes

Test outcome	Negative reality: $\zeta = 0$ $H_0$ is true ( $H_1$ is false)	Positive reality: $ \zeta  > 0$ $H_0$ is false ( $H_1$ is true)
Test outcome negative: " $H_0$ is true, $H_1$ is false"	True negative Likelihood $1 - \alpha$	False negative (Type II error) Likelihood $\beta$
Test outcome positive: " $H_0$ is false, $H_1$ is true"	False positive (Type I error) Likelihood $\alpha$	True positive Likelihood $1 - \beta$

$\alpha$ : significance level

$1 - \beta$ : power

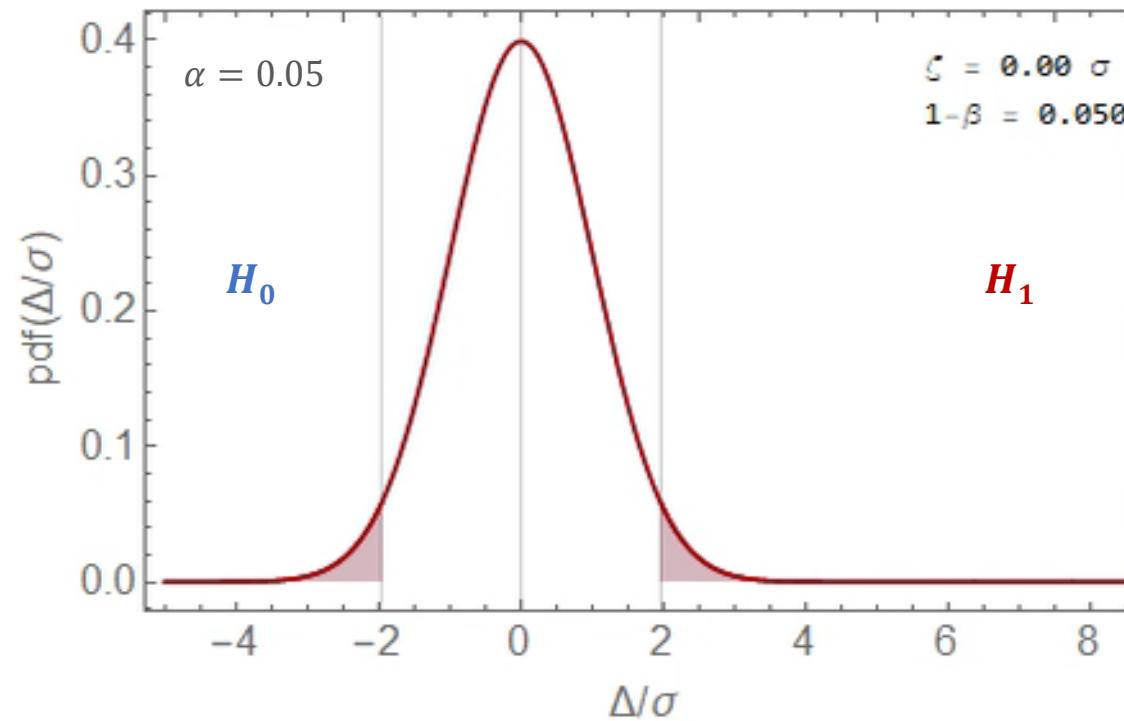
$1 - \alpha$

Confidence level if  
 $H_0$  is accepted

$1 - \beta$

Confidence level if  
 $H_1$  is accepted

# Significance level vs power



Need a fairly large deviation  $\zeta$  to achieve acceptable power

# If theory is found to be correct, we ...

- **Can claim** that “theory was successfully tested with a relative precision of  $\sigma/f$ , at a confidence level of  $1 - \alpha$ ”), and **conclude** that  $\zeta = 0$
- **Can rule out/constrain** “beyond-theory” effects  $\zeta$ , at confidence level  $1 - \beta$
- **Cannot** conclude that  $\zeta = 0$  **and** use this knowledge to adjust  $m_p/m_e$  to a new value, i.e.

$H_0$  accepted

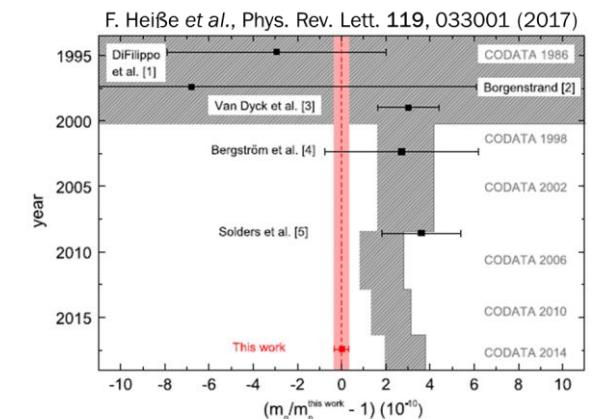
$$f\left(\frac{m_p}{m_e}\right) + \cancel{\zeta} = f\left(\frac{m_p}{m_e}\right) = f_{\text{exp}},$$

as this violates the assumptions of the test  
– and thereby invalidates it!



# How do we determine $m_p/m_e$ then?

- We **assume** theory is correct (no test!) and **adjust**  $m_p/m_e$  to a new value
- We assume **CODATA-18** constants in  $f\left(\frac{m_p}{m_e}, \frac{m_d}{m_p}, R_\infty, r_p, r_d, \alpha\right)$ , except for  $m_d/m_p$  \*
- Find excellent agreement\*\* with the “anomalous”  $m_p/m_e$  MPIK-17 !
- Improve uncertainty  $m_p/m_e$  to **21 ppt**
  - CODATA-2018: 60 ppt
  - Penning trap, MPIK-2019: 43 ppt
  - HD<sup>+</sup> THz spectroscopy†, Düsseldorf-2020: 20 ppt
- Combine with Düsseldorf result  $\Rightarrow$  18 ppt (theoretical errors are correlated!)



2020 marks the year in which:

- Spectroscopy of HD<sup>+</sup> finally surpasses *ab initio* theory in precision
- Molecules confirm anomalies seen in measurements of atoms and single particles
- Molecular spectroscopy provides particle mass ratios with precision comparable to the best Penning-trap measurements

\* Fink & Myers, *Phys. Rev. Lett.* **124**, 013001 (2020)

\*\* S. Patra et al. (forthcoming)

† Alighanbari et al., *Nature* **581**, 152 (2020)

# Outlook/fifth forces

- Constraint on Yukawa-type fifth forces\*

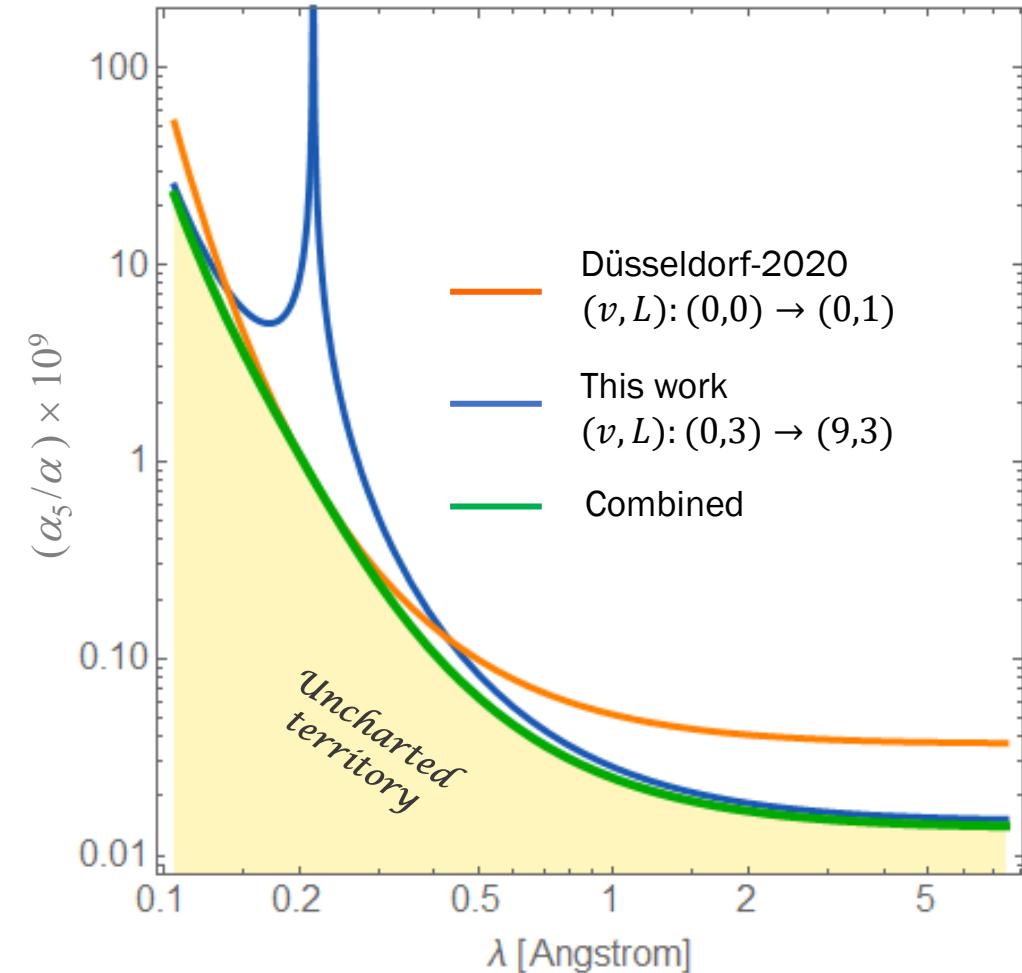
$$V_5(r, \lambda) = \alpha_5 N_1 N_2 \frac{e^{-r/\lambda}}{r} \equiv \alpha_5 \mathcal{V}(r, \lambda)$$

Range of the force  
Coupling constant  
Number of nucleons H,D

- Constraint concerns alternative hypothesis  $H_1$ , so must use **power of the test**

⇒ for 95% C.L. we must use  **$3.6\sigma$**  threshold, not  $2\sigma$  (i.e. previous HD<sup>+</sup> constraints were over-constraining)

- Refined method:** combines multiple data into one constraint





# Thank you!

## VU team Amsterdam

- Sayan Patra (former PhD student)
- Matthias Germann (former postdoc)
- Frank Cozijn (former MSc student)
- Kjeld Eikema
- Wim Ubachs

## External collaborators

- Vladimir Korobov (Dubna, Russia)
- LKB team Paris – **up next!**

