Fundamental constants from hydrogen molecular ion spectroscopy

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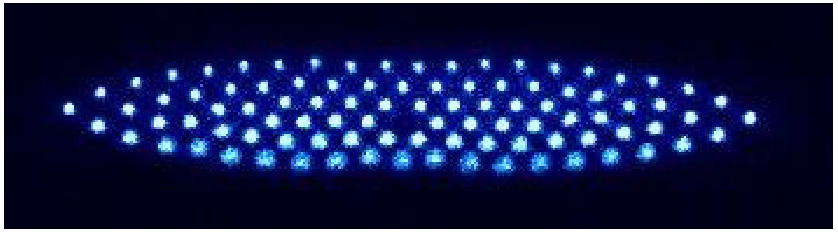
Université d'Evry – Val d'Essonne



Outline

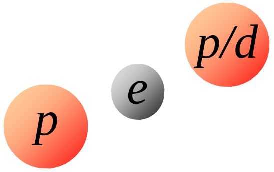
I. **Motivations**

II. **Theory** J.-Ph. Karr, M. Haidar, V. Korobov, X. Zhong

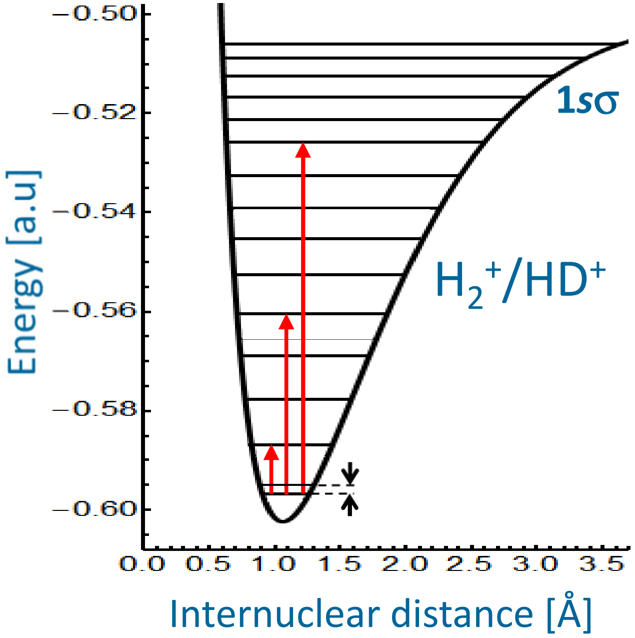
III. **Experiments** Th. Louvradoux, J. Schmidt, A. Mbardi, J. Heinrich, N. Sillitoe, A. Douillet, L. Hilico

Amsterdam S. Patra, M. Germann,
K. Eikema, W. Ubachs, J. Koelemeij

What is an hydrogen molecular ion ?



H_2^+ or HD^+



A calculable simple quantum system

having **many** very **narrow** transitions

with life times from 10’s of ms (HD+) to weeks (H_2^+)

Hydrogen molecular ions

Dependence of ro-vibrational transition frequencies on fundamental constants :

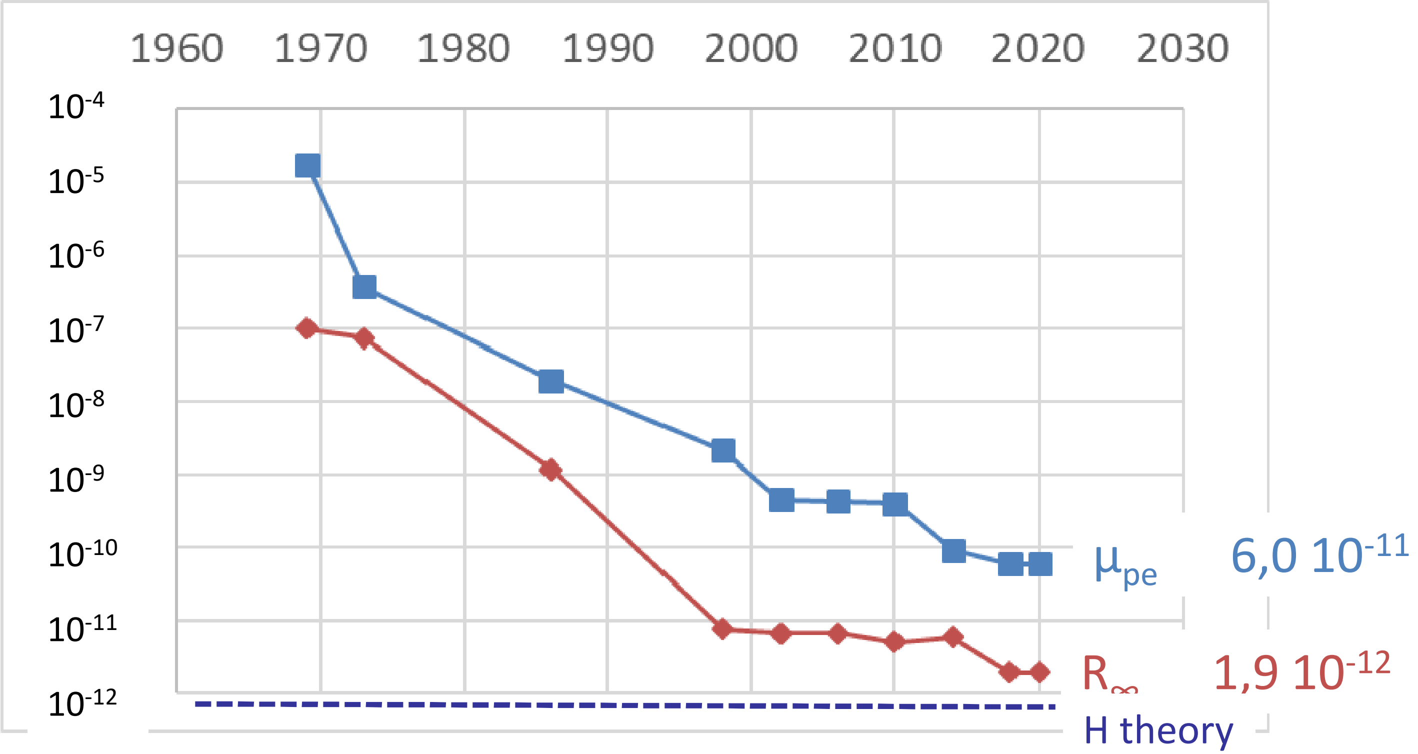
$$\nu = c\boxed{R_\infty}\left[\underbrace{\varepsilon_{nr}(\boxed{\mu_{ne}})}_{\text{Schrödinger}} + \underbrace{\alpha^2 F_{QED}(\alpha)}_{\text{Relativistic and QED corrections}} + \underbrace{\sum_n A_n^{fs}(\boxed{r_n}/a_0)^2}_{\text{Nuclear finite size correction}}\right]$$

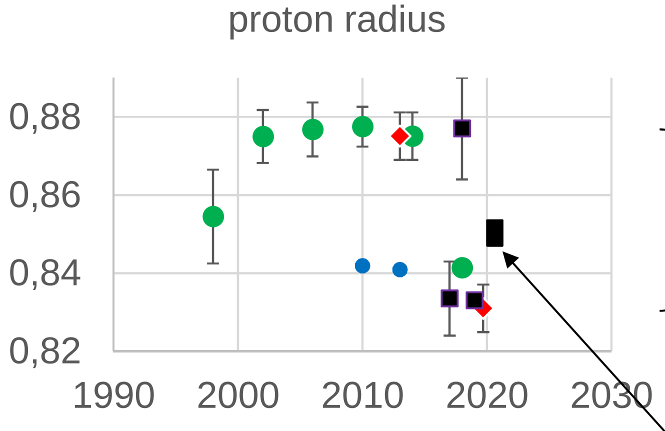
Vibrational: $\varepsilon_{nr} \propto \sqrt{m_e/m_r}$

Rotational: $\varepsilon_{nr} \propto m_e/m_r$

Different features and complementary w.r.t. atomic transitions

R_∞, μ_{pe} and r_p codata values





Codata
e^- scattering
μp spectroscopy
H spectroscopy

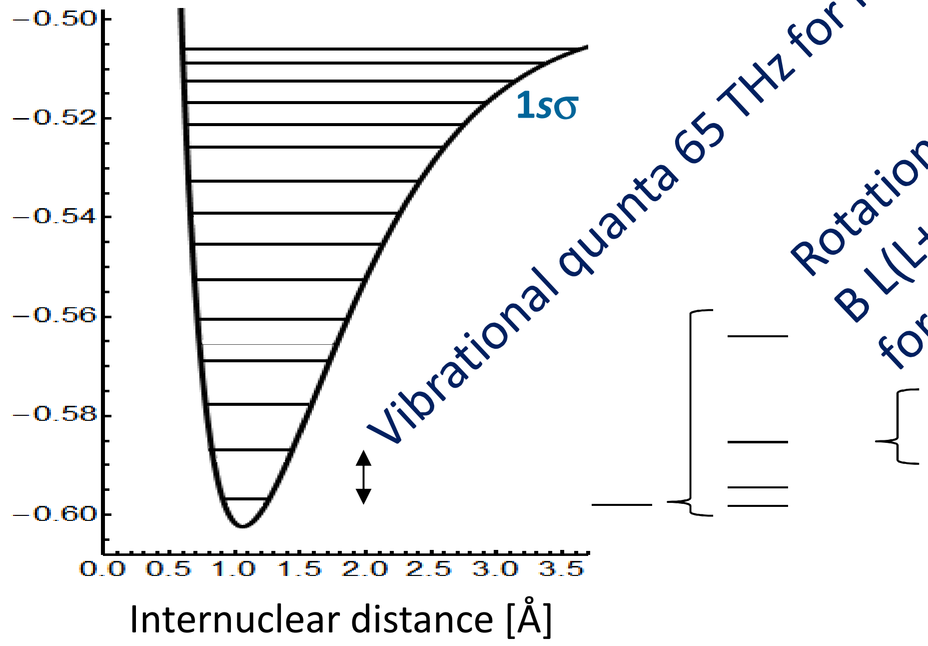
1S-3S H. Fleurbaey et al., PRL **120**, 183001 (2018)

Proton size puzzle

2S-4P A. Beyer et al.. Science **358**. 79 (2017)
H Lamb shift N. Bezginov et al., Science 365, 1007 (2020)

1S-3S A. Grinin et al., Science 370, 1061 (27-11-2020)

Hydrogen molecular ion spectroscopy



Vibrational quanta 65 THz for H_2^+

Rotational structure $B\,L(L+1)$, $2B \sim 1.4$ THz for HD^+

Hyperfine structure

HD^+

- Dipole allowed
    - Overtones vibrational v ⟶ v+p
    - Rotational transitions
- Doppler free two-photon transitions
- Quadrupole transitions
- Raman transitions

Düsseldorf Amsterdam

Düsseldorf

Amsterdam + Paris (th)

H_2^+

- No dipole allowed transitions
- Doppler free Two-photon transitions v ⟶ v+1
- Quadrupole transitions
- Raman transitions

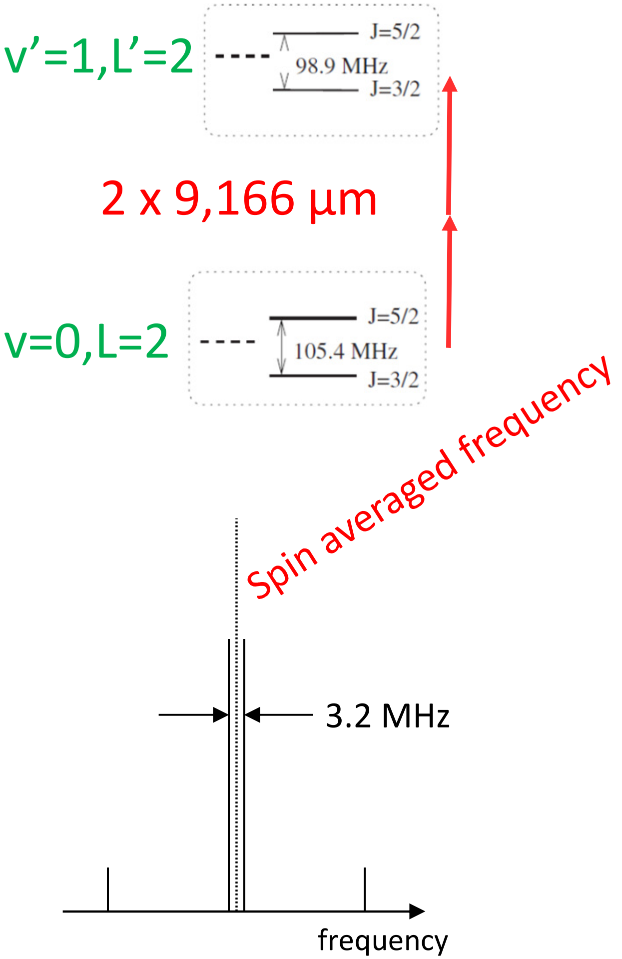
(Paris)

H_2^+ spectroscopy

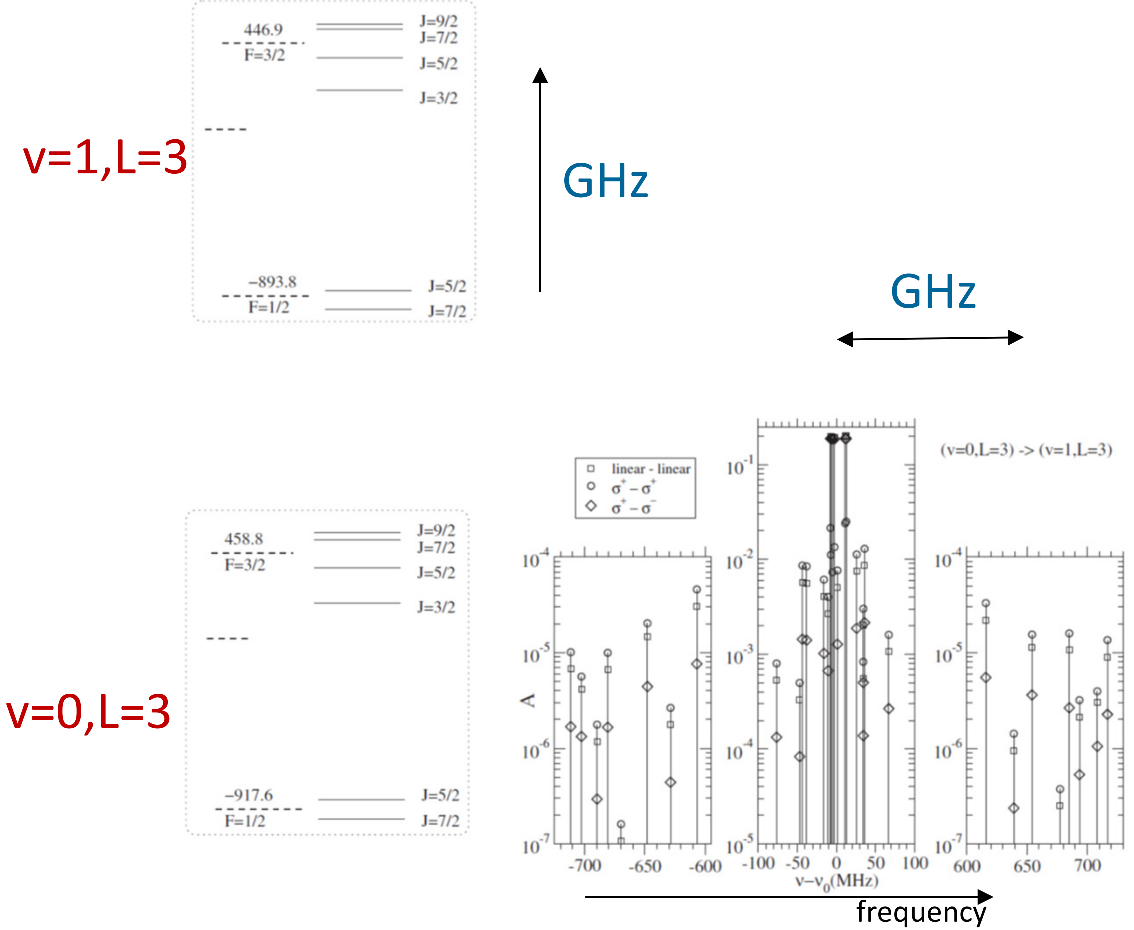
H_2^+ ½ ½ ½ ↑ ↑ ↑ p p e^-

total nuclear spin	total spin	total ang. mom.
I=0 (even L) para	F=1/2	L±1/2
I=1 (odd L) ortho	F=1/2, 3/2	L ±1/2 ±3/2

Even L, I=0



Odd L, I=1



HD$^+$ spectroscopy

½ 1 ½

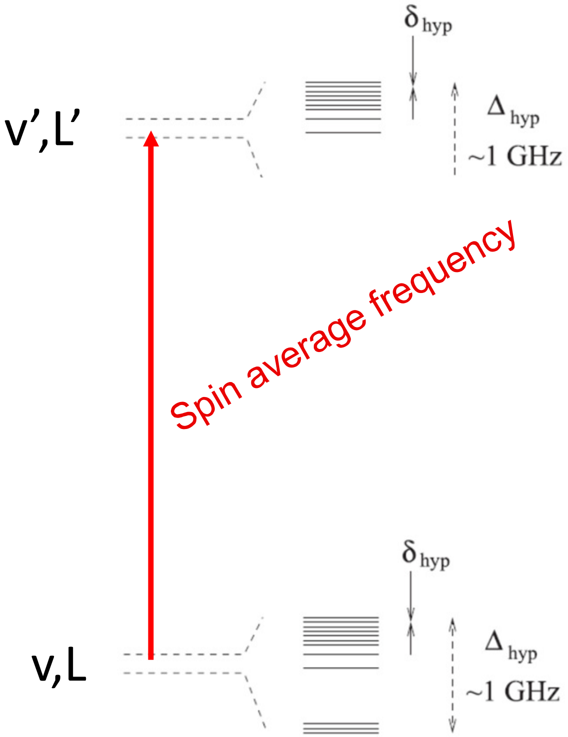
HD$^+$ ↑ ↑ ↑

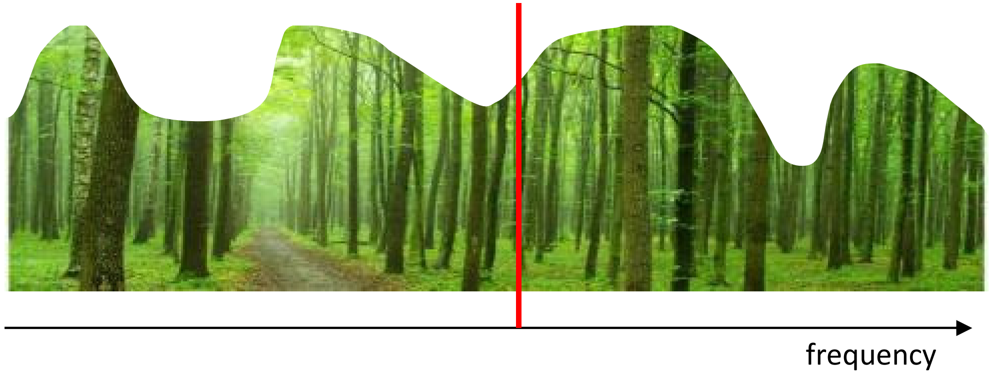
p d e$^-$

$F = S_e + I_p = 0 \quad 1$

$S = F + I_d = 1 \quad 0,1,2$

$J = L+S = L \quad L\pm1,\ L\pm2$

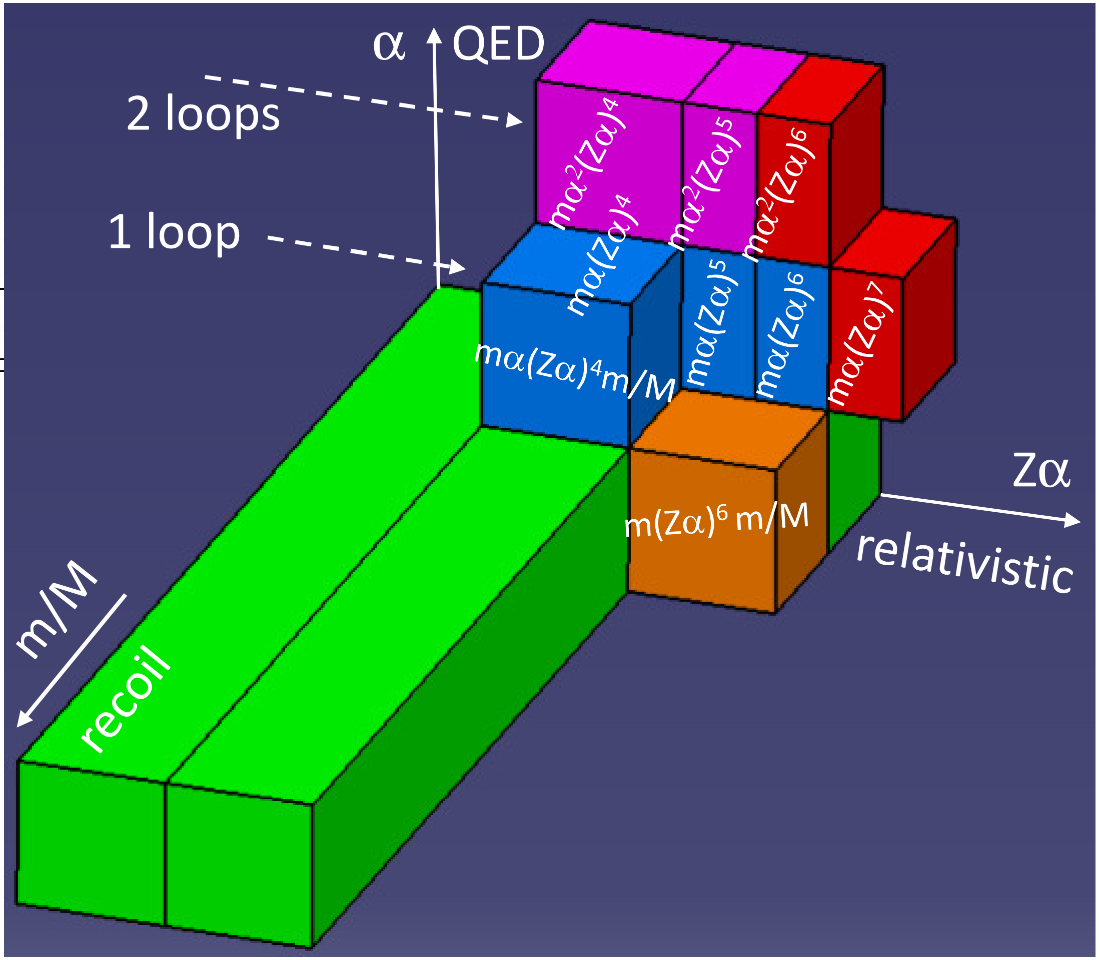


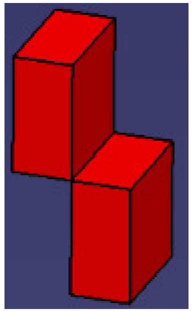


Hydrogen molecular ions: status of theory

3 small parameters, m_e/m_p, $Z\alpha$ and α

H_2^+	
ν_{nr}	65 687 511 047.0
$\nu\ \alpha^4$	1 091 040.5
$\nu\ \alpha^5$	−276 545.1
$\nu\ \alpha^6$	−1 952.0(1)
$\nu\ \alpha^7$	121.8(1)
$\nu\ \alpha^8$	−2.3(**5**)
ν_{tot}	65 688 323 710.1(5)

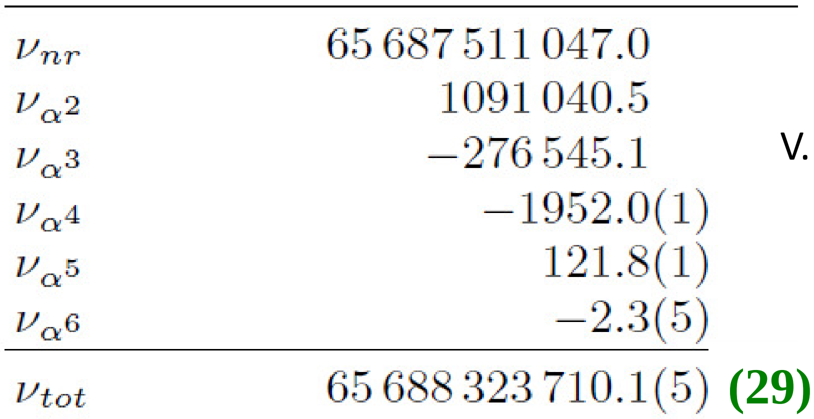




terms limiting the accuracy to **7.6 10^{-12}** on spin averaged transition frequencies

Hydrogen molecular ions: status of theory

H_2^+ (v = 0, L=0) $\longrightarrow$ (v'=1, L'=0) interval in kHz



ν_{nr}	65 687 511 047.0
ν_{α^2}	1091 040.5
ν_{α^3}	−276 545.1
ν_{α^4}	−1952.0(1)
ν_{α^5}	121.8(1)
ν_{α^6}	−2.3(5)
ν_{tot}	65 688 323 710.1(5)

(29)(18)(11)
(13)

V.I. Korobov, L. Hilico, J.-Ph. Karr,
PRL **118**, 233001 (2017)

- (5) Theoretical uncertainty = **7.6 10^{-12}**
- (29) CODATA 2014 uncertainty on 9.5 10^{-11}
- (18) CODATA 2018 6.0 10^{-11}
- (13) uncertainty due to new μ_{pe} with 4.3 10^{-11}
- (11) Discrepancies on R_∞ and r_p between CODATA 2014 and μp + H(1S-2S)

F. Heiße et al.,
Phys. Rev. Lett. **119**, 033001 (2017)

HD$^+$ Hyperfine structure

- Recent progress in HD$^+$ spectroscopy

  - Pure rotational transition in HD$^+$ (S. Schiller, Düsseldorf) Alighanbari *et al.*, *Nature 581, 152* (2020)
    v=0, L=0→L=1, resolution 2 Hz at 1.4 THz, all hyperfine components

  - Doppler free two-photon vibrational overtone in HD$^+$ (J. Koelemeij, Amsterdam)
    v=0,L=3 → v=4,L=2 → v=9,L=3, resolution ~ kHz at 415 THz, 2 hyperfine components
    Patra *et al*, *Science* 369, 1238, (2020)

- Progress on hyperfine structure

$$
\begin{aligned}
H_{\rm eff} = {} & \overset{\sim 30\text{ MHz}}{\underline{E_1}}(\mathbf{L}\cdot\mathbf{s}_e) + E_2(\mathbf{L}\cdot\mathbf{I}_p) + E_3(\mathbf{L}\cdot\mathbf{I}_d) + \overset{\sim 900\text{ MHz}}{\underline{E_4}}(\mathbf{I}_p\cdot\mathbf{s}_e) + \overset{\sim 140\text{ MHz}}{\underline{E_5}}(\mathbf{I}_d\cdot\mathbf{s}_e) + E_6\{2\mathbf{L}^2(\mathbf{I}_p\cdot\mathbf{s}_e) - 3[(\mathbf{L}\cdot\mathbf{I}_p)(\mathbf{L}\cdot\mathbf{s}_e) + (\mathbf{L}\cdot\mathbf{s}_e)(\mathbf{L}\cdot\mathbf{I}_p)]\} \\
& + E_7\{2\mathbf{L}^2(\mathbf{I}_d\cdot\mathbf{s}_e) - 3[(\mathbf{L}\cdot\mathbf{I}_d)(\mathbf{L}\cdot\mathbf{s}_e) + (\mathbf{L}\cdot\mathbf{s}_e)(\mathbf{L}\cdot\mathbf{I}_d)]\} + E_8\{2\mathbf{L}^2(\mathbf{I}_p\cdot\mathbf{I}_d) - 3[(\mathbf{L}\cdot\mathbf{I}_p)(\mathbf{L}\cdot\mathbf{I}_d) + (\mathbf{L}\cdot\mathbf{I}_p)(\mathbf{L}\cdot\mathbf{I}_d)]\} \\
& + E_9\{2\mathbf{L}^2\mathbf{I}_d^2 - \tfrac{3}{2}(\mathbf{L}\cdot\mathbf{I}_d) - 3(\mathbf{L}\cdot\mathbf{I}_d)^2\}, \qquad (1)
\end{aligned}
$$

th/exp agreement

0.8 kHz in H$_2^+$, Jefferts 1969

8 kHz in HD$^+$, Patra 2020

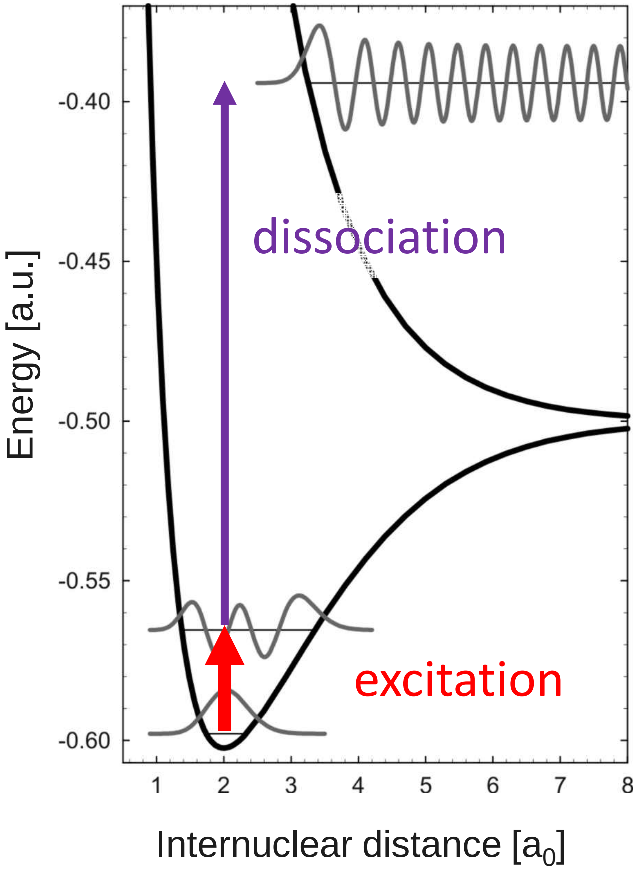
J.-Ph. Karr & al., Phys. Rev. A 102, 052827 (2020)

The experimental method

Resonance Enhanced MultiPhoton Dissociation (**REMPD**) spectroscopy

on **sympathetically cooled**

trapped hydrogen molecular ions



- H_2^+ (v=0,L=2)→(v=1,L=2) (LKB Paris)

  REMPI ionisation

  Doppler free 2 photon excitation at 9.166 µm

  32.7 THz: $10^{-12} \leftrightarrow$ 33 Hz

  Dissociation at 213 nm

- HD^+ (v=0,L=3)→(v=9,L=3) (Amsterdam)

  Electron impact ionisation

  Doppler free 2 photon excitation

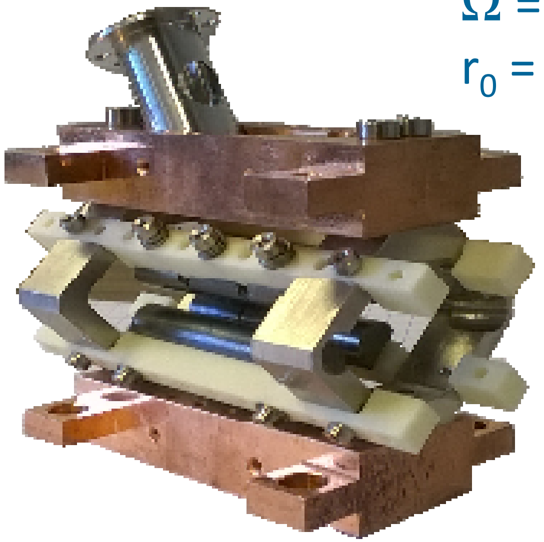
  at 1.442 and 1.445 µm

  200 THz: $10^{-12} \leftrightarrow$ 200 Hz

  Dissociation at 532 nm

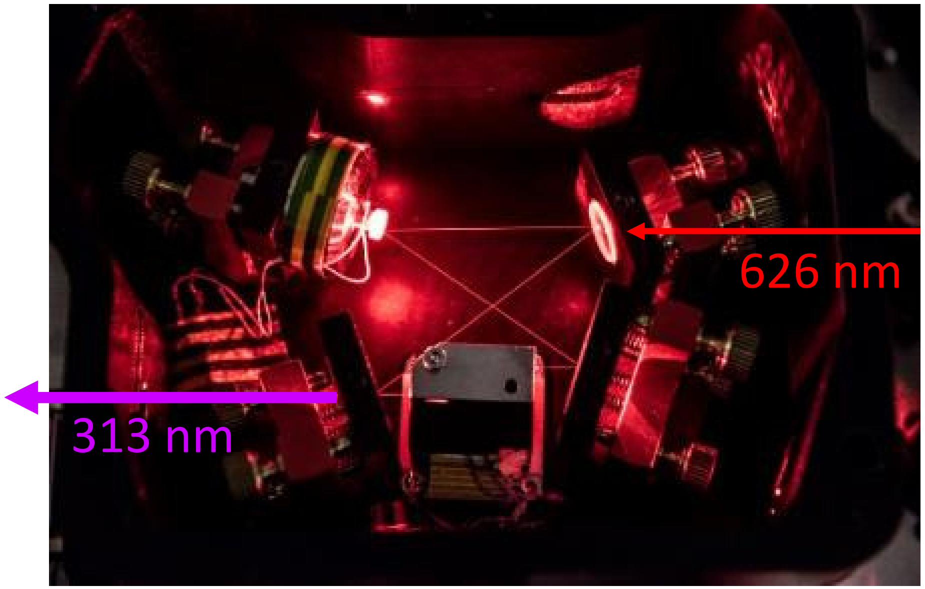
Signal : fraction molecular ion loss

The tools: ion trap and ion clouds

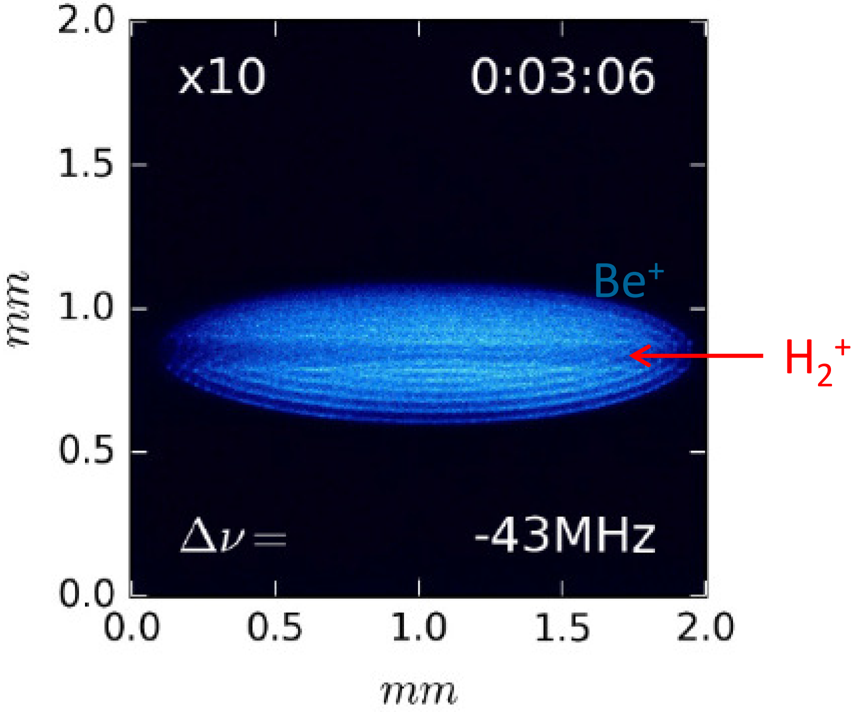


$\Omega = 2\pi \times 13$ MHz, 200-550 V

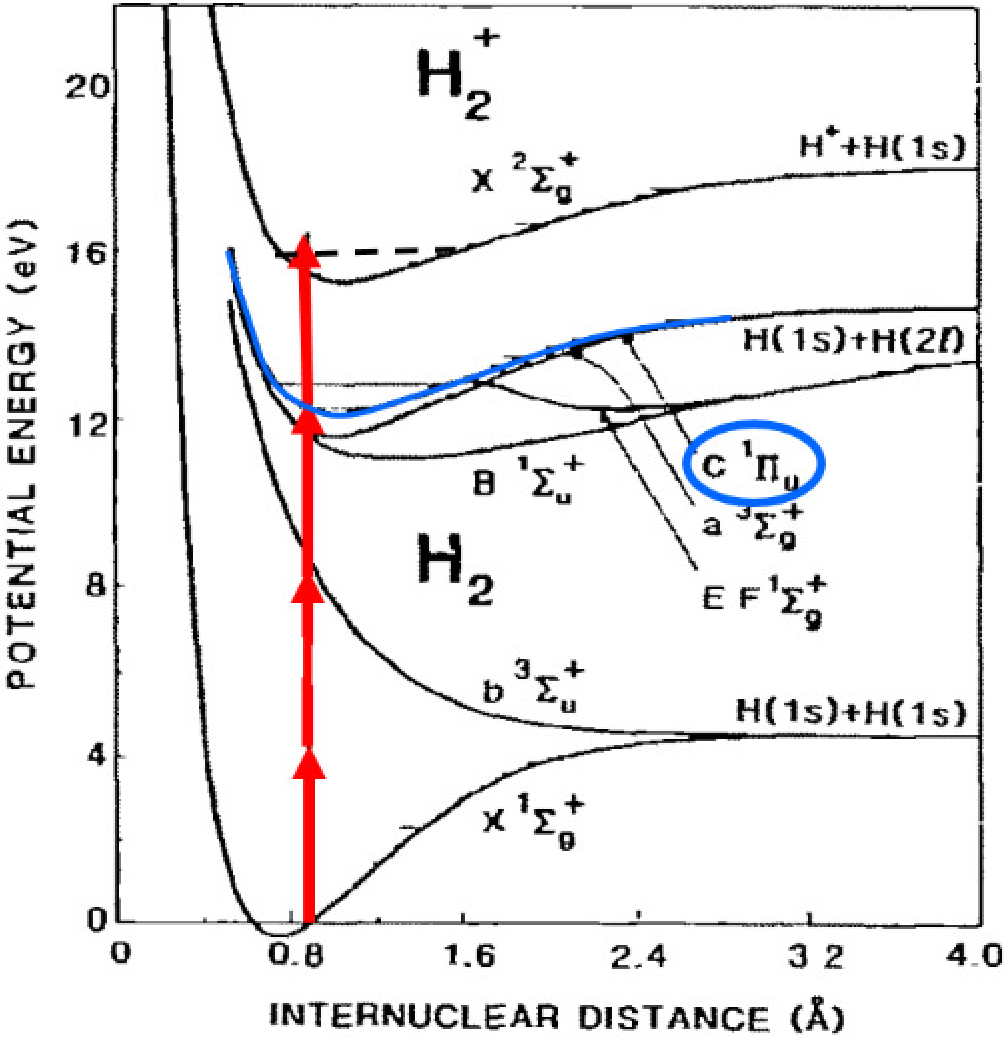
$r_0 = 3.5$ mm



Be$^+$/H$_2^+$ ion crystal



REMPI H_2^+ ion source

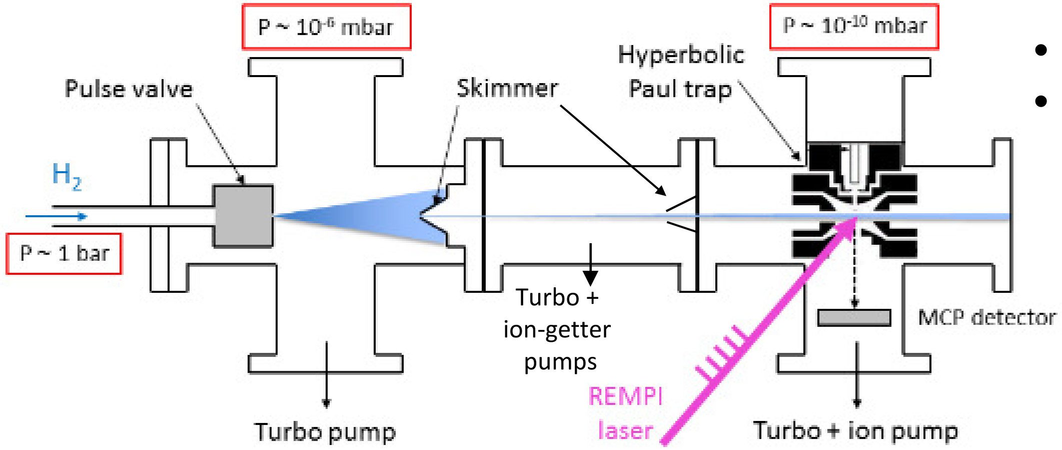


- 3+1 REMPI at 303 nm
- 4 mJ, 7 ns, 20 Hz
- waist ~ 10 µm

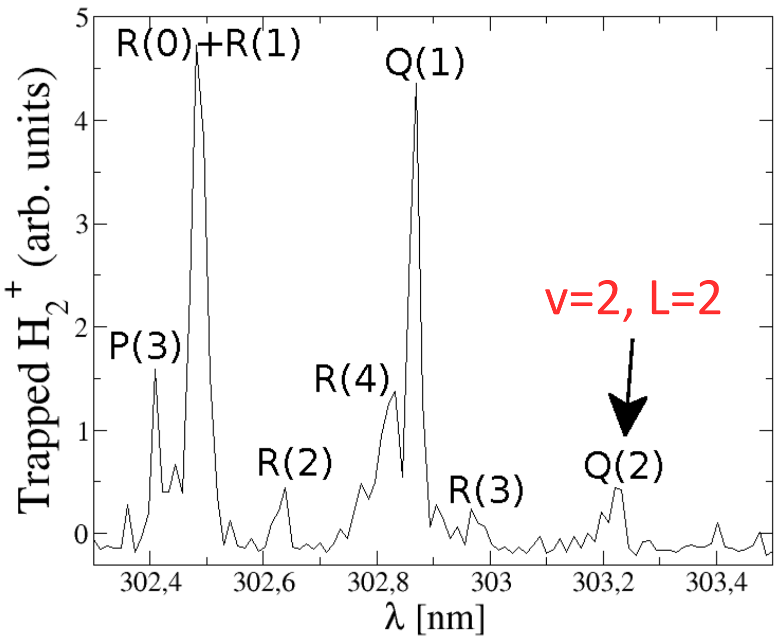
Vibrational selectivity 90 %
Rotational selectivity 99 %

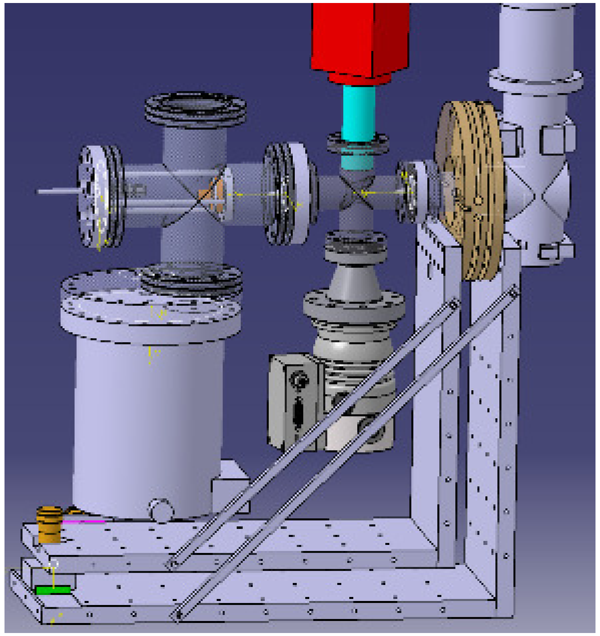
Vu Tran, PhD thesis

REMPI H_2^+ ion source

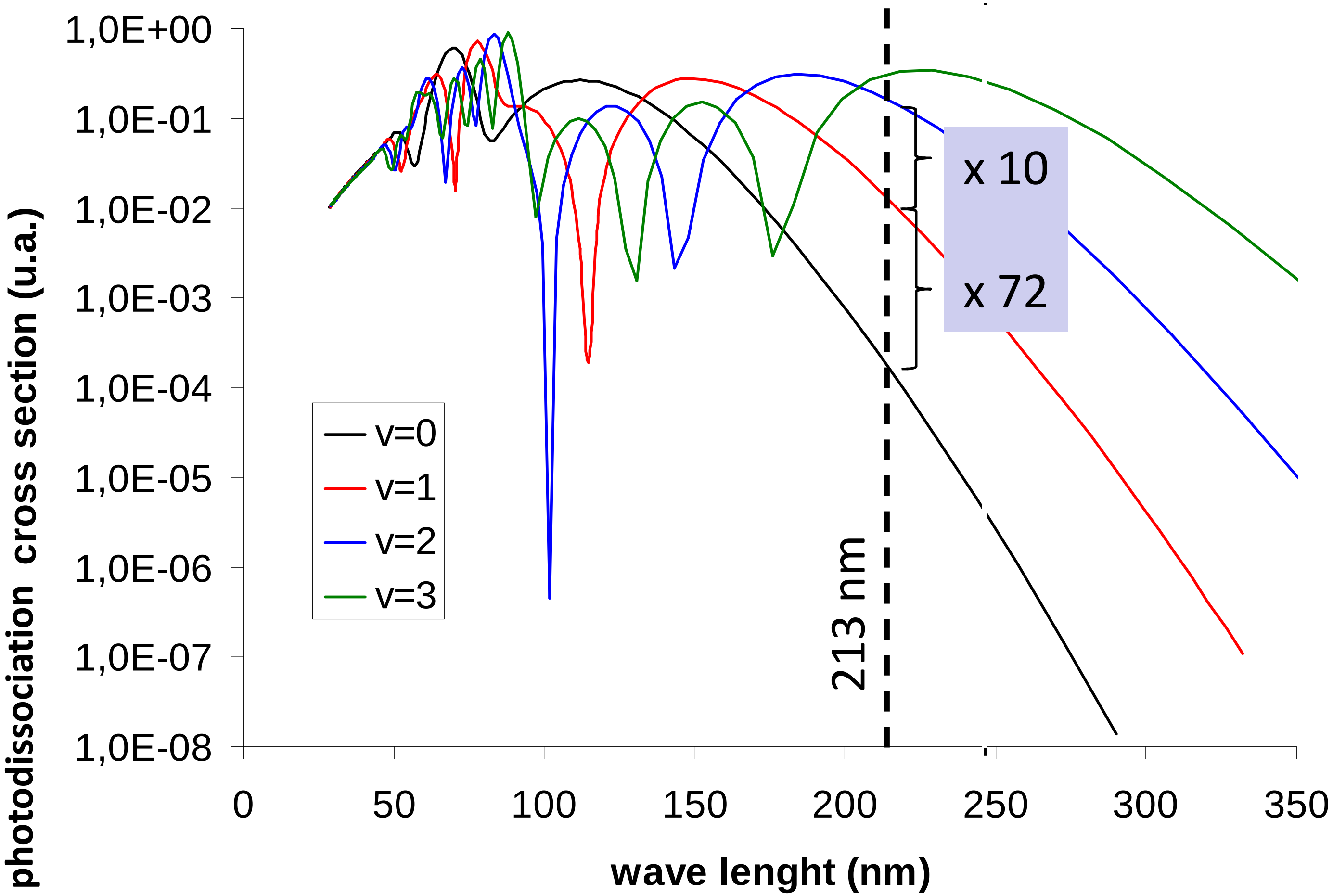


- Worked out on the old hyperbolic trap
- Now implemented on the linear trap



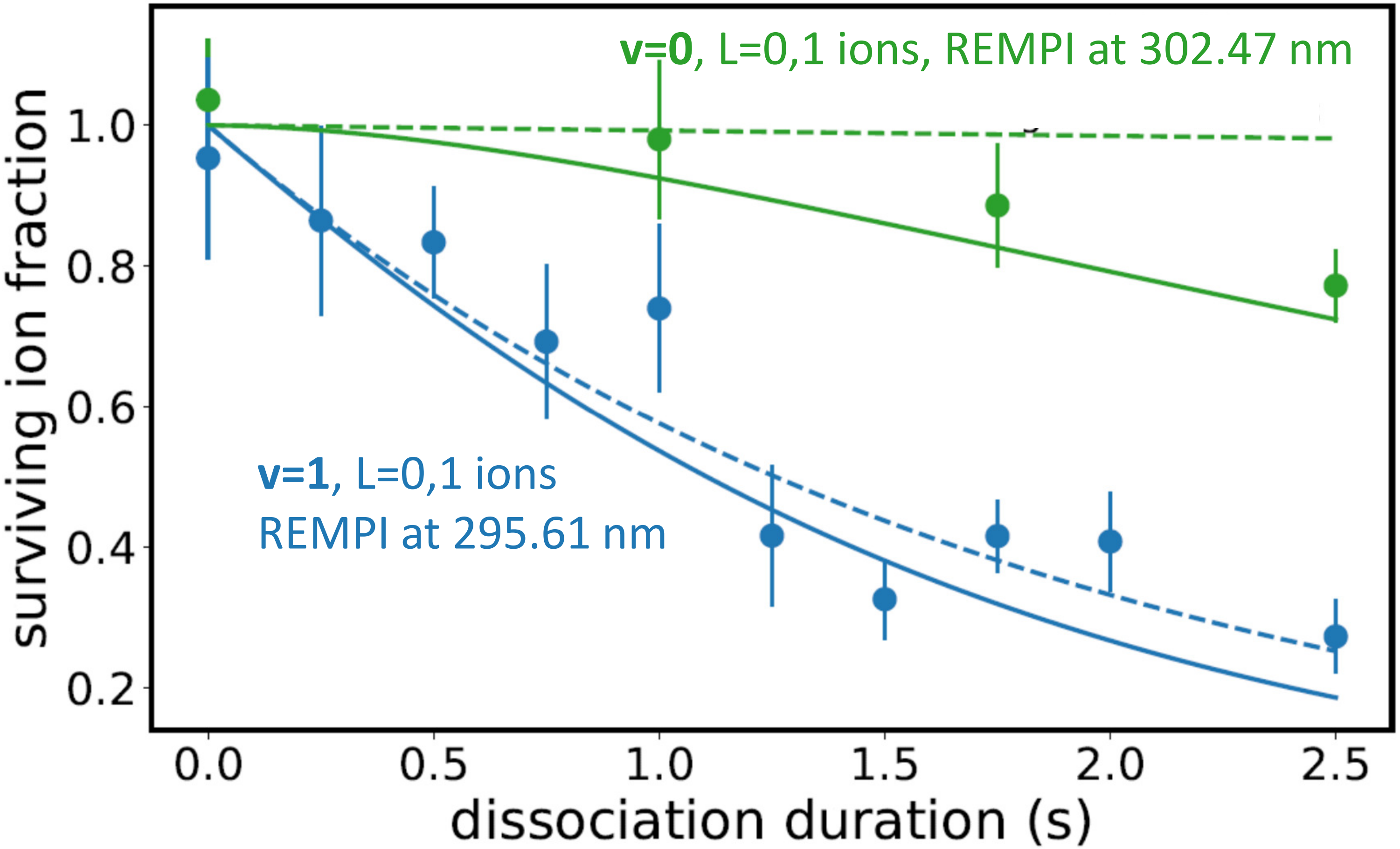


H_2^+ photodissociation



Photodiss. of state selected H_2^+ ions

213 nm at max power



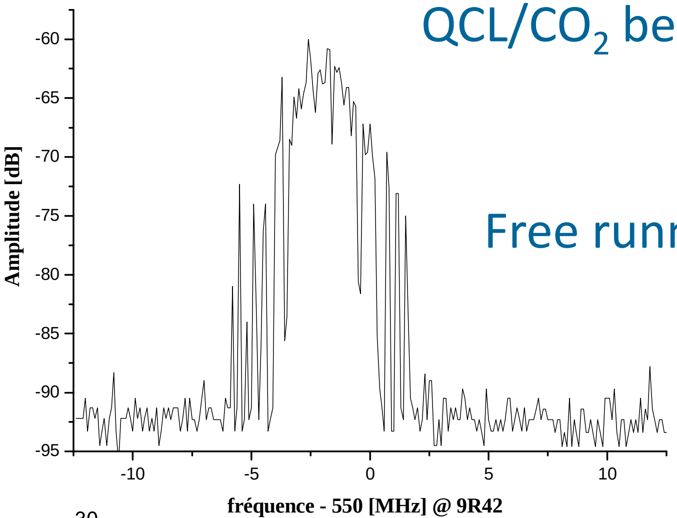
Add. loss due to
UV induced
pressure increase

Two-photon transition laser at 9,17 µm

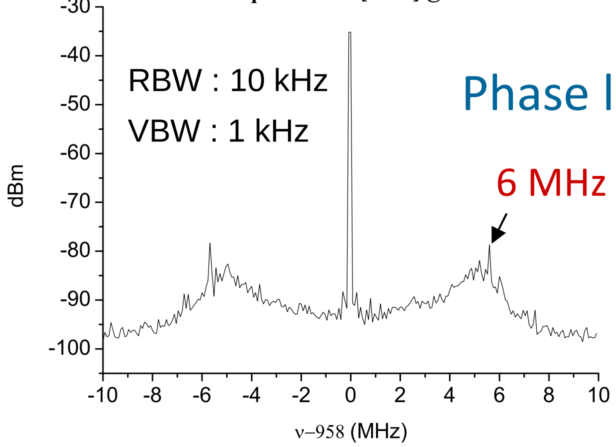
- Quantum cascade laser phase locked to a ultrastable CO_2 laser stabilized to HCOOH (kHz uncertainty)

Alpes Laser DFB
T = 80 K
100 mW cw

QCL/CO_2 beat notes

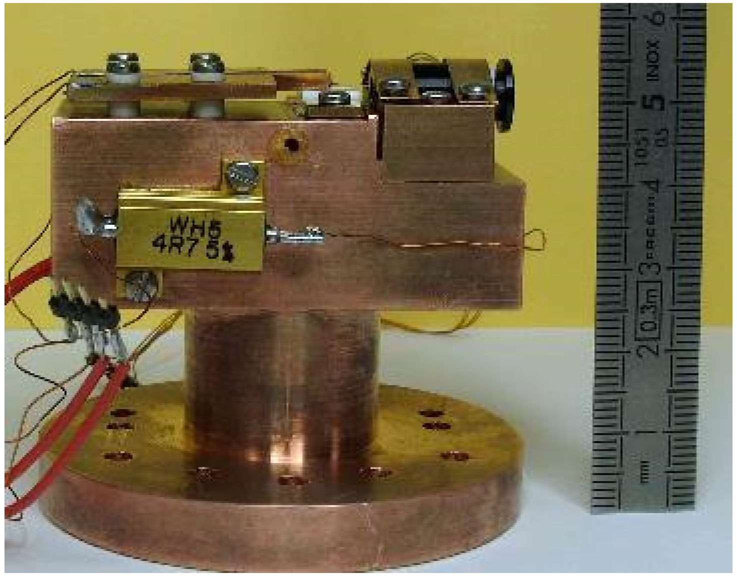


Free running QCL



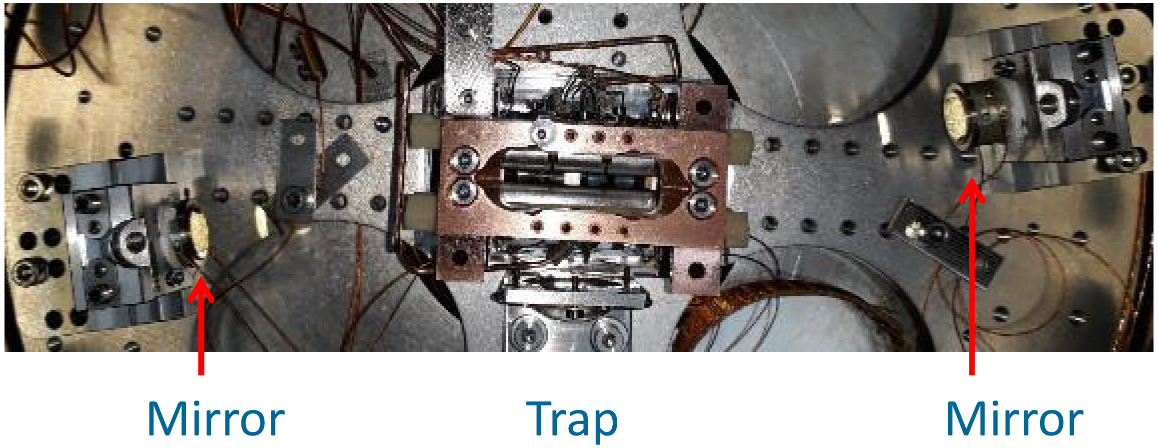
Phase locked QCL

6 MHz loop bandwidth



F. Bielsa & al, Optics Letters **32**, 1641-1643 (2007)
F. Bielsa & al, Journal of Molecular Spectroscopy 247, 41-46 (2008)

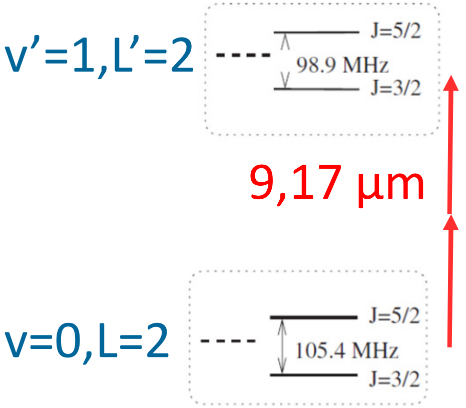
In vacuum enhancement cavity

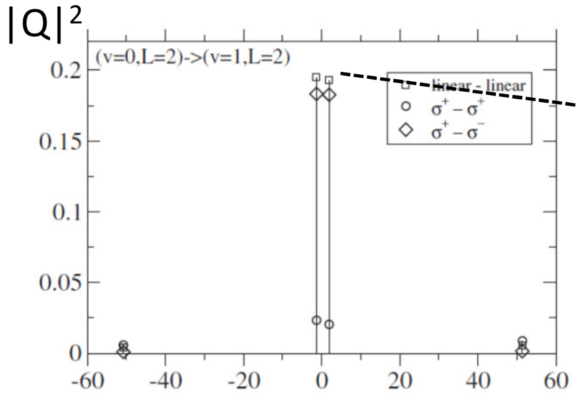


High reflectivity mirrors 99.8 %
Finesse ~ 1000, Enhancement factor ~ **200**
Beam waist 300 µm, Rc = 10 cm, L = 17 cm
Input power ~ 30 mW

Two-photon transition probability

$$\Gamma_{vv'} = \left(\frac{4\pi a_0^3}{\hbar c}\right)^2 \frac{4I^2}{\Gamma_f}(1+\epsilon)^4 \left|Q_{vv'}\left(\frac{E_v+E_{v'}}{2}\right)\right|^2$$





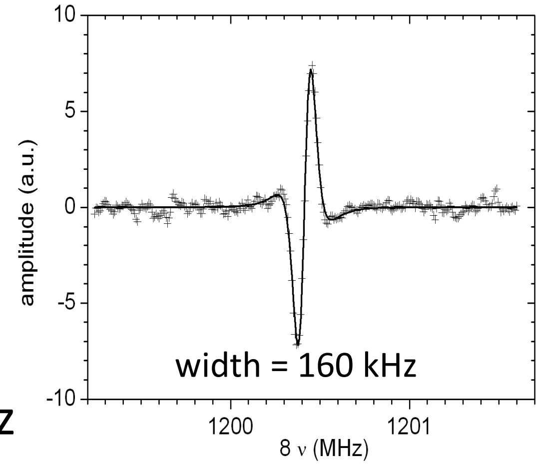
Γ_{01} = **77** /s
with
$\Gamma_f = 2\pi \times 10$ kHz

9.17 µm frequency control

Present situation

- QCL phase locked to a CO_2 (9R(42) line)
- CO_2 laser locked to HCOOH saturated absorption, 1 kHz

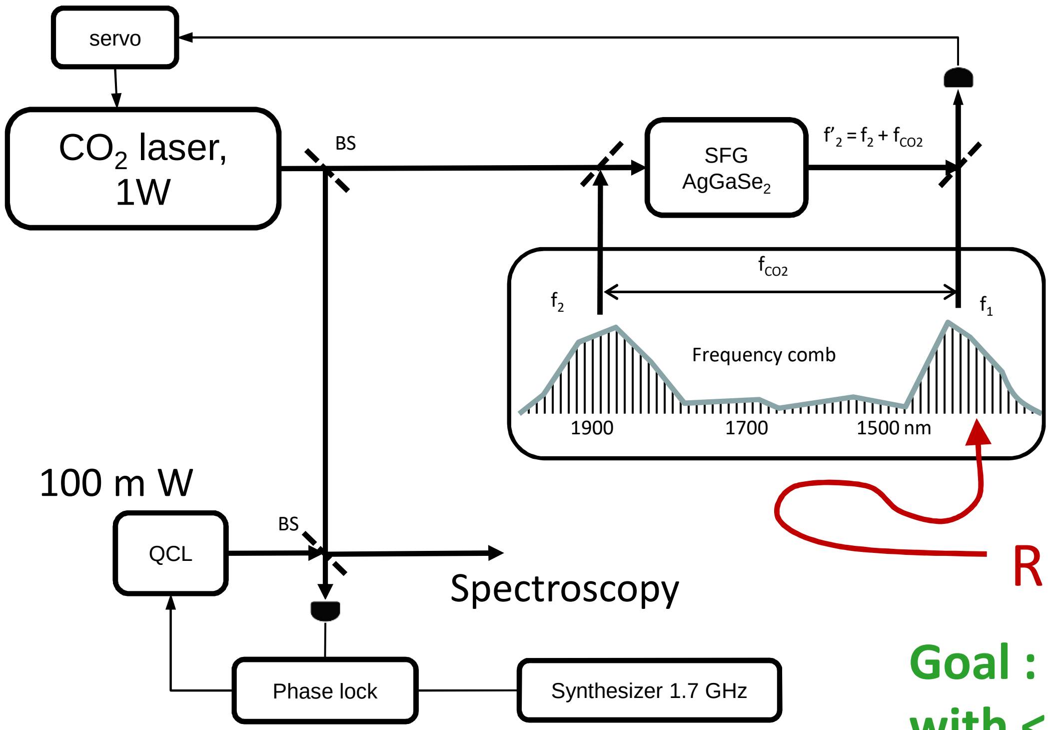
>> 33 Hz



Next step

- Frequency control against a SI referenced frequency comb

ANR HYMPE grant, 2019-2023



SFG in $AgGaSe_2$

$1890 + 9166 \rightarrow 1567$ nm

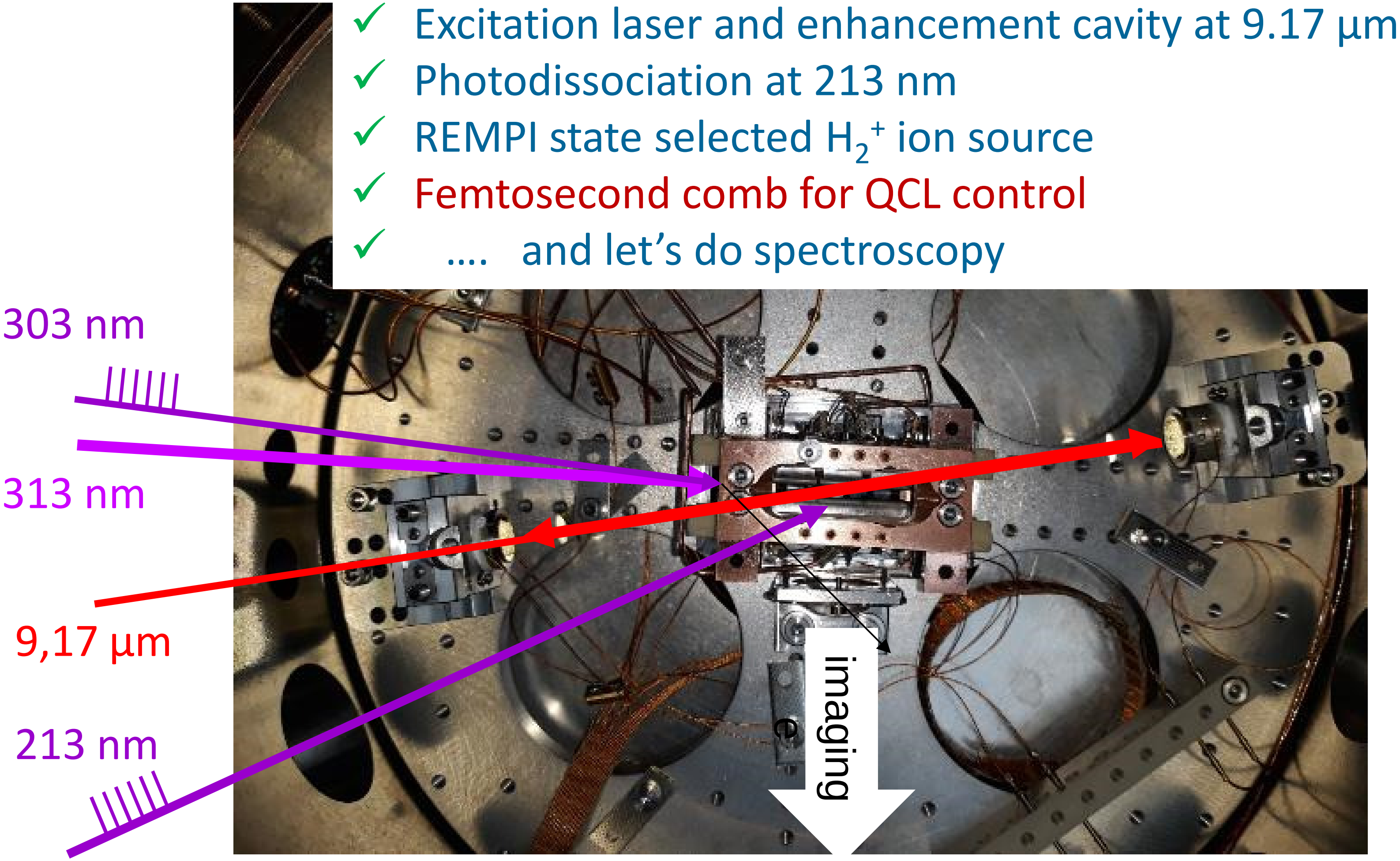
A. Amy Klein, B. Darquié, LPL, Villetaneuse

REFIMEVE+ network, 1542 nm

Goal : MIR frequency synthesis with < 10^{-12} stability at 1 .. 10 s

H_2^+ spectroscopy summary

- ✓ Ion trapping, sympathetic cooling and counting
- ✓ Excitation laser and enhancement cavity at 9.17 µm
- ✓ Photodissociation at 213 nm
- ✓ REMPI state selected H_2^+ ion source
- ✓ Femtosecond comb for QCL control
- ✓ …. and let's do spectroscopy



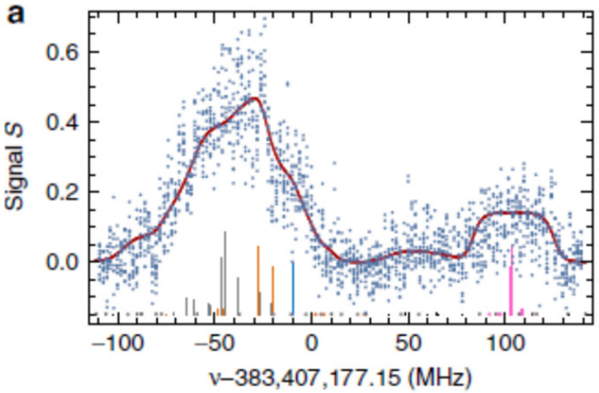
HD^+ project in Amsterdam

The HD$^+$ project in Amsterdam

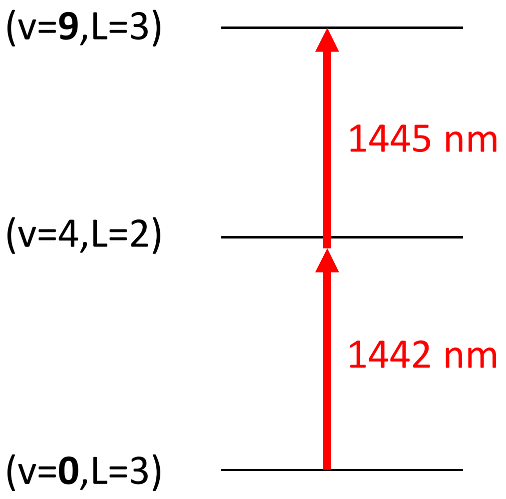
W. Ubachs, J. Koelemeij group

- (v=0,L=2)→(v=8,L=3) vibration overtone at 782 nm
  Doppler broadened, resolution 1 ppb (10^{-9})

J. Biesheuvel et al., Nature 7, 10385 (2016)



- (v=0,L=2)→(v=9,L=2) **Doppler free** quasi-degenerate **two-photon** transition in an **effective Lamb regime**



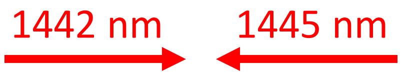
(v=**9**,L=3)

1445 nm

(v=4,L=2)

1442 nm

(v=**0**,L=3)



1442 nm

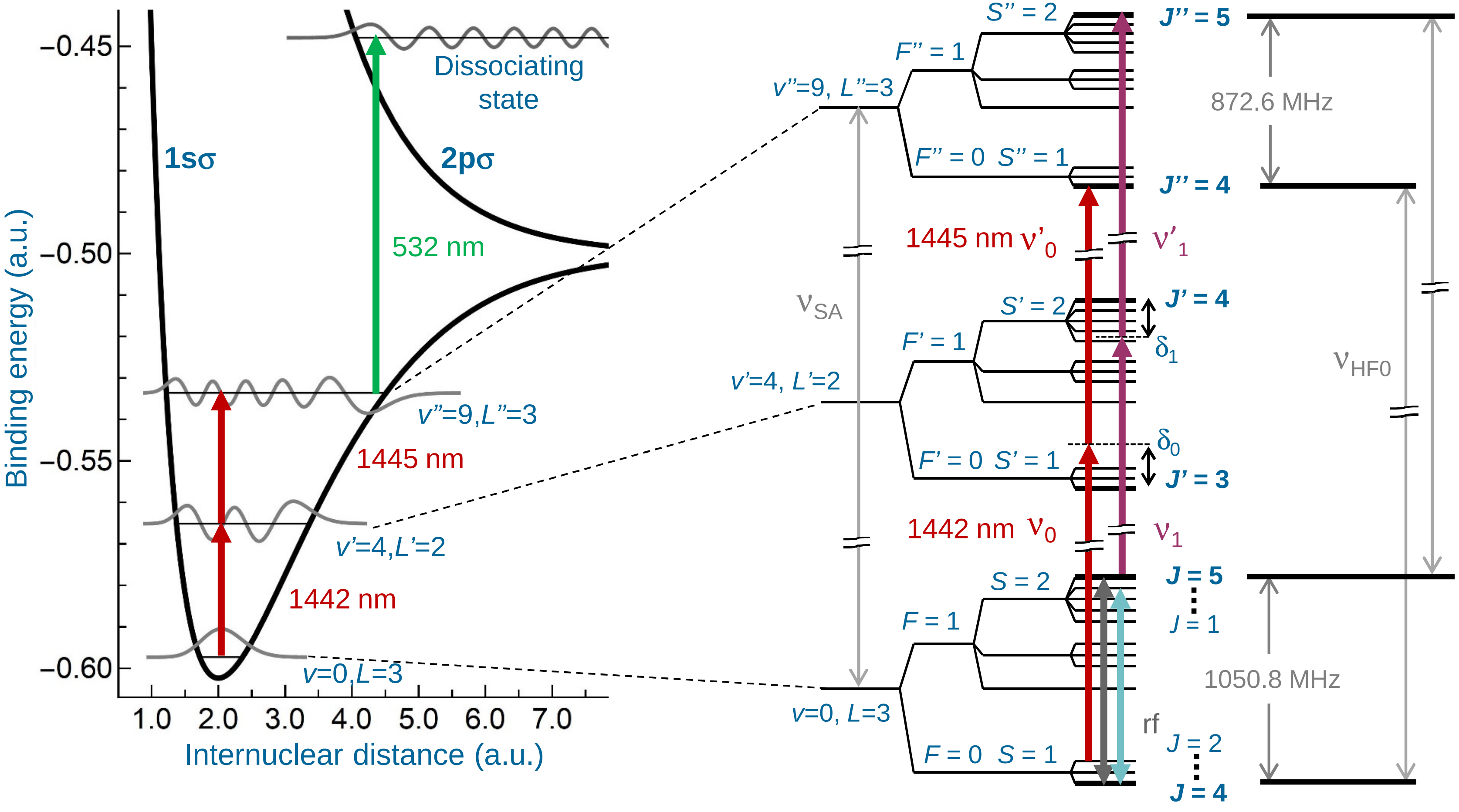
1445 nm

λ_{eff} = (1/1.442 - 1/1.445)$^{-1}$
= 700 µm >>> HD$^+$ displacement
in the trap

Theory: V. Q. Tran &al., Phys. Rev A **88**, 033421 (2013)

The HD$^+$ project in Amsterdam

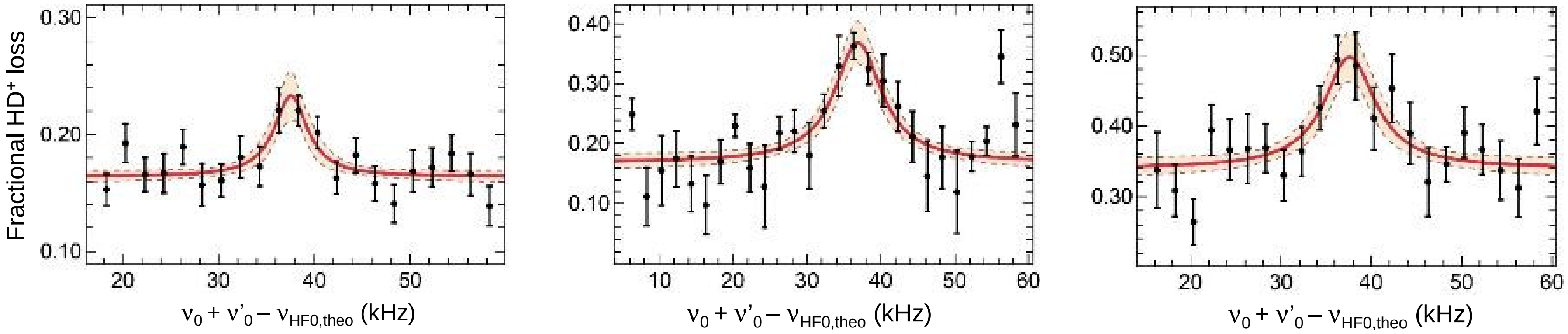
- Transition: (v, L, F, S, J): $(0,3,1,2,5) \rightarrow (9,3,1,2,5)$ (Transition frequency: ~415 THz)
- $(0,3,0,1,4) \rightarrow (9,3,0,1,4)$



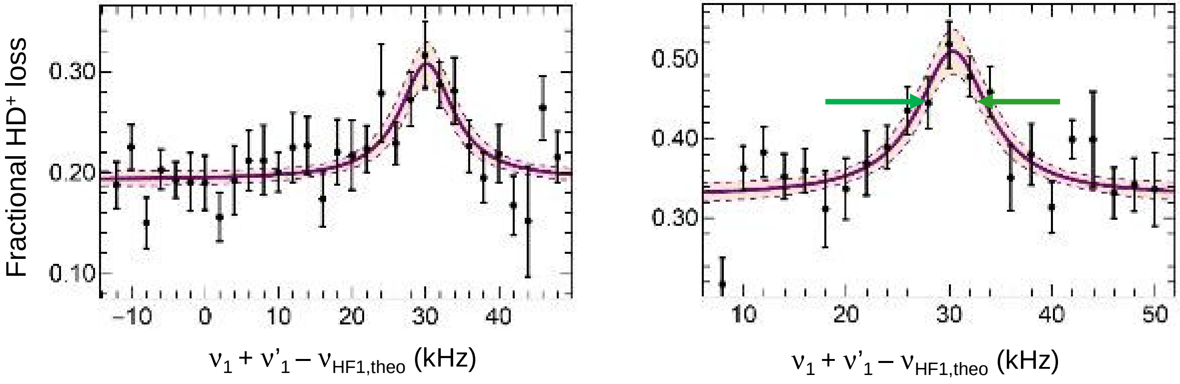
The HD$^+$ project in Amsterdam

S. Patra, … J.C.J. Koelemeij, Science 369, 1238 (2020)

(v, L, F, S, J): $(0,3,0,1,4) \rightarrow (9,3,0,1,4)$



(v, L, F, S, J): $(0,3,1,2,5) \rightarrow (9,3,1,2,5)$



Linewidth < 10 kHz

$Q_{exp} = 2.\ 10^{10}$

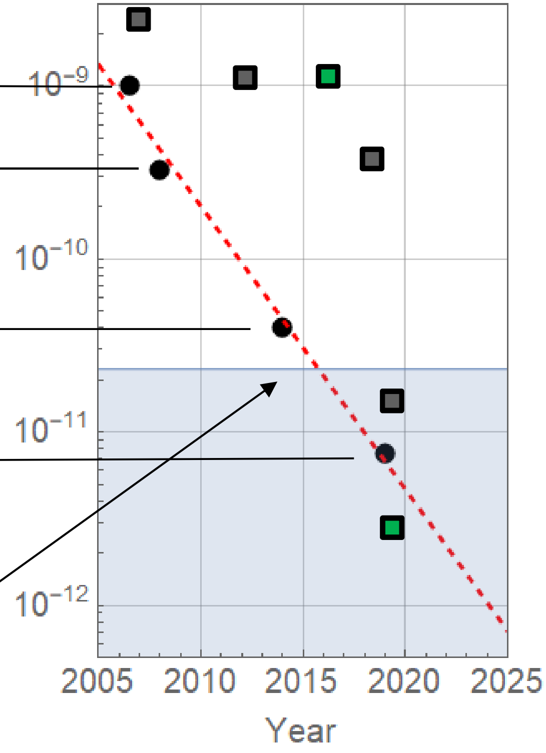
- Frequency measurement with **1.2 kHz uncertainty (2.9 ppt)**
  - **0.4 kHz** purely experimental uncertainty
  - **1.1 kHz** due to theoretical hyperfine structure correction

Precision on transition frequencies

Theory

Paris + Dubna

Experiments



Phys. Rev. A **74,** 052506 (2006)

Phys. Rev. A **77,** 022509 (2008)

Phys. Rev. Lett. **112,**103003 (2014)

Phys. Rev. Lett. **118,** 233001 (2017)

Düsseldorf 2007 JK *et al., PRL* **98,** 173002

Düsseldorf 2012 *PRL* **108,** 183003

Amsterdam 2016 *Nat. Commun.* **7,** 10385

Düsseldorf 2018 *Nat. Phys.* **14,** 555

Düsseldorf 2019 *Nature* **581,** 152 (2020)

Amsterdam 2019 *Science* **369,** 1238 (2020)

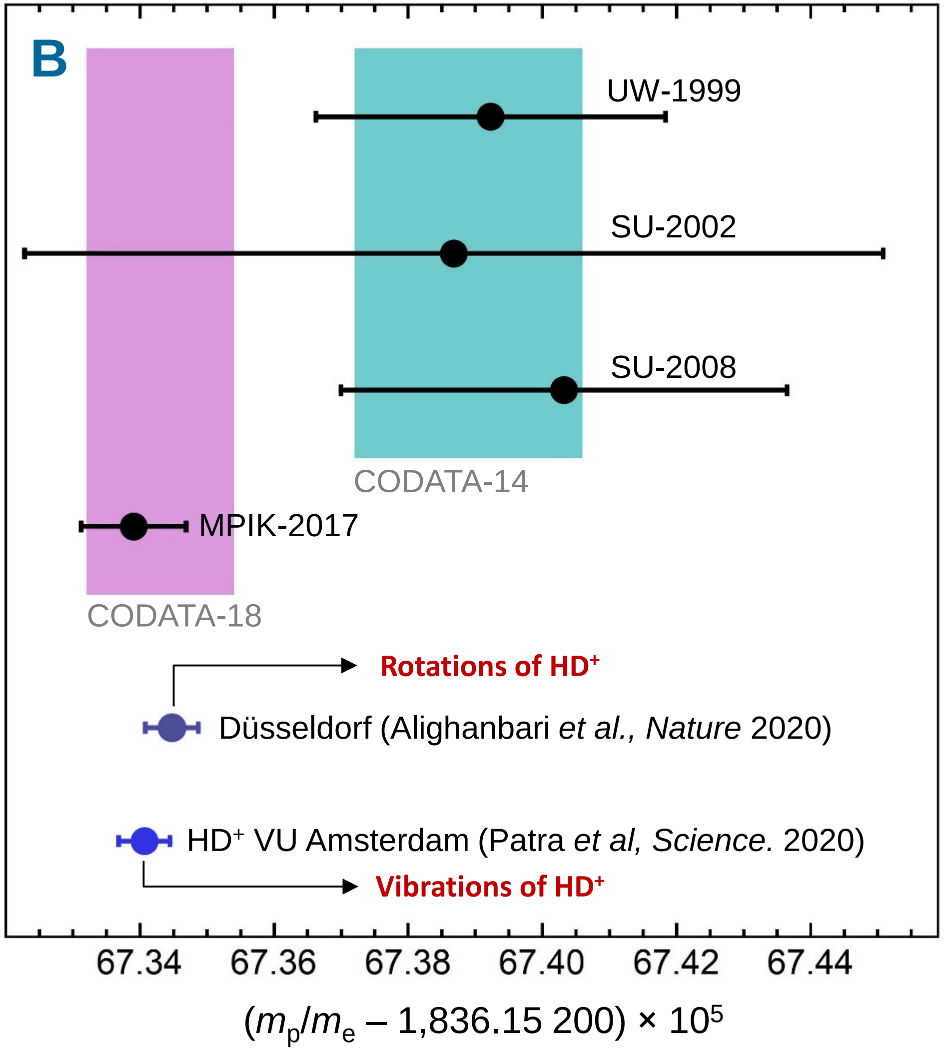
Uncertainty caused by fundamental constant, mainly m_p/m_e

Proton to electron mass ratio from HD$^+$

$$m_p/m_e = 1{,}836.152\ 673\ 43(11)$$

÷ 2.9

$$m_p/m_e = 1{,}836.152\ 673\ 406(38)$$



Perspectives

Short term

- Improve frequency synthesis stability below 100 Hz

  REFIMEVE+ in France, VSL in the Netherlands
- Observe other transitions, e.g. $v=0 \rightarrow v=1$ in H_2^+, in D_2^+
- Perform « molecular » fundamental adjustment
- Actively contribute to CODATA input
- Standard model test and search for new physics beyond SM

Mid term

- Improve theory down to 10^{-12}
- Prepare experiments for quantum logic spectroscopy (QLS)

Long term

- Spectroscopy at the $10^{-16..-17}$ accuracy level
- Variation of fundamental constants

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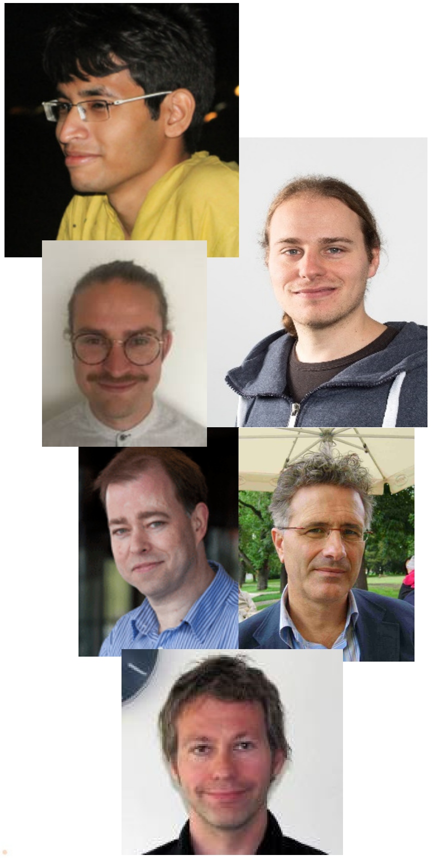

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