# $H_2^+$ and $HD^+$ spectroscopy
# Status and perspectives


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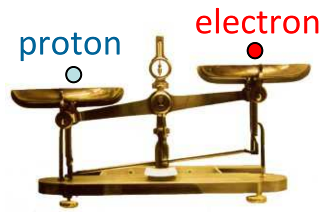
*Université d'Evry – Val d'Essonne*


*FFK, Budapest, 12 October 2015*

# Outline

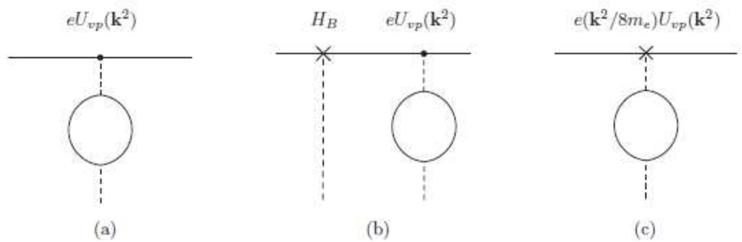
**I. Introduction**

$H_2^+$, $HD^+$ and fundamental constants



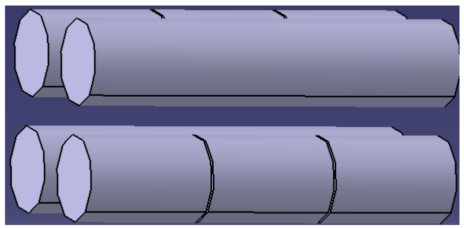

**II. Theory**

- Vacuum polarization at $m\alpha^7$ order




**III. Experiment**

- Results from Amsterdam: one-photon spectroscopy of $HD^+$
- Towards Doppler-free two-photon spectroscopy of $H_2^+$



# Hydrogen: from atoms to molecular ions

LKB ENS CNRS UPMC

- Laser spectroscopy of H and D atoms plays a major role in the fundamental constants adjustment.
  Rydberg constant $R_\infty$
  Proton and deuteron radii $r_p$ , $r_d$

- Molecular ions $H_2^+$, $HD^+$ : ro-vibrational transition frequencies are sensitive to the nuclear reduced mass.

Mass ratios $\boxed{\mu = \frac{m_p}{m_e}, \mu_{pd} = \frac{m_d}{m_p}}$ $\boxed{\nu_{vibr} \propto \frac{1}{\sqrt{\mu}} R_\infty c}$

An old idea... W.H. Wing, G.A. Ruff, W.E. Lamb Jr., J.J. Spezeski
Phys. Rev. Lett. **36**, 1488 (1976)

First experimental efforts : 1997 [H. Schnitzler PhD thesis, Düsseldorf]

S. Schiller (Düsseldorf) $HD^+$
L. Hilico (Paris) $H_2^+$
J.C.J. Koelemeij, W. Ubachs (Amsterdam) $HD^+$
T.-Y. Shi (Wuhan) $HD^+$

# Hydrogen molecular ions

- Three-body molecules are simple one-electron systems:
  high-accuracy predictions including high-order QED corrections are possible.

  Last published result: $\Delta\nu/\nu \approx 3\,10^{-11}$

  V.I. Korobov, L. Hilico, J.-Ph. Karr, PRL **112**, 103003 and PRA **89**, 032511 (2014).

  Recent progress: see "Theory" part

  … and V.I. Korobov's talk (Wednesday 11:00)

- Narrow ro-vibrational lines
  $H_2^+$ : one-photon ro-vibrational dipole transitions *strictly* forbidden $\Delta\nu \approx 10^{-7}$ Hz
  $HD^+$: one-photon transitions weakly allowed $\Delta\nu \approx 10$ Hz

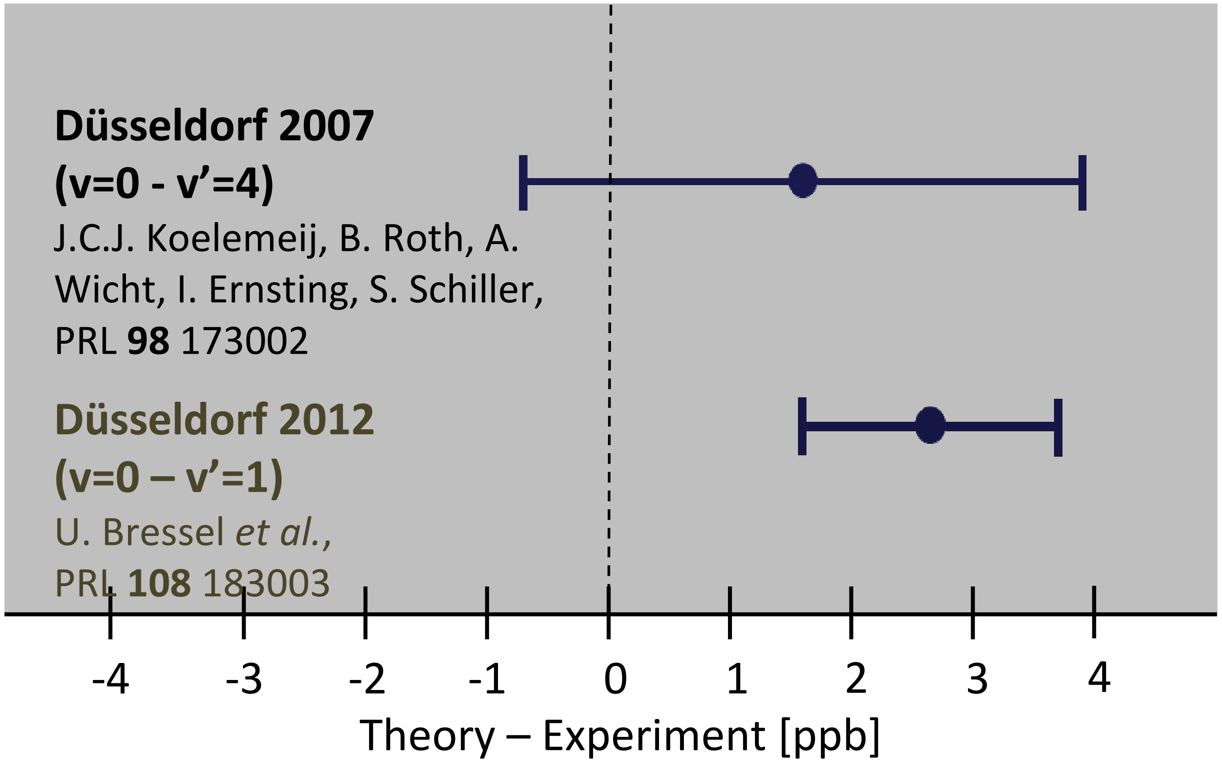
- High-accuracy experiments: same techniques as used in ion optical clocks
  Ion trap, laser cooling, ultra-stable lasers, frequency comb measurements

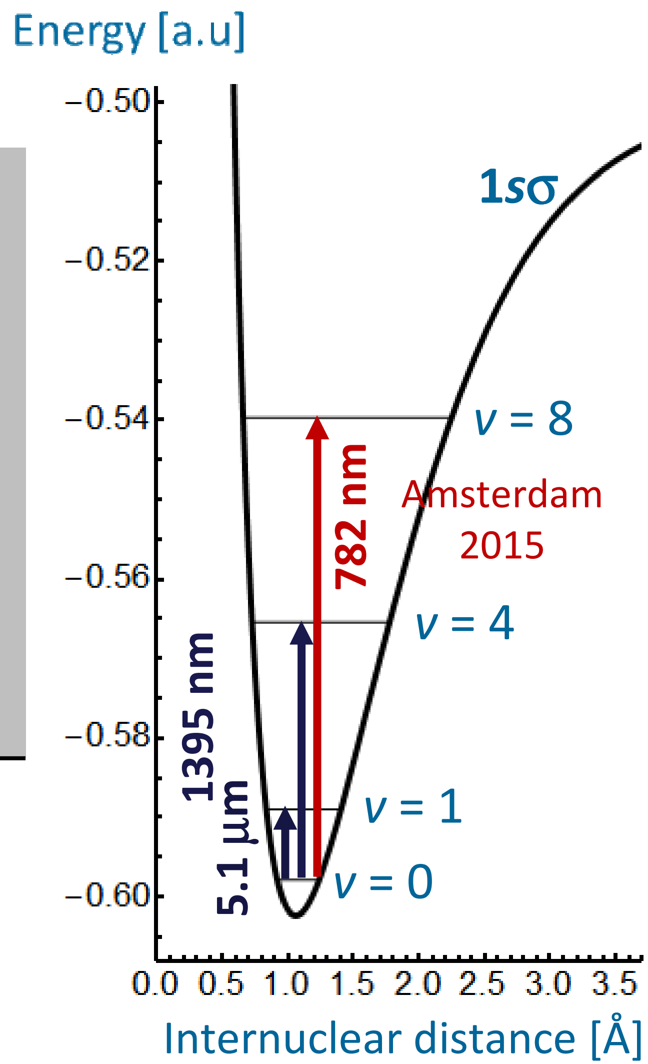
➡ A significantly improved determination of $\mu$ is achievable

CODATA 2014: 9.5 $10^{-11}$ [ g-2 of bound electron in $C^{5+}$ ; S. Sturm et al., Nature 2014]

# Previous experimental results

## One-photon spectroscopy of HD⁺



# Determining $\mu$ : is it that simple ?

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What about the dependence on other F.C. ?

$H_2^+$ :
$$\nu_{(v,L)\to(v',L')} \approx cR_\infty \left[ A_{nr}\mu^{s_p} + B_{QED}(\cancel{\alpha}) + \frac{R_\infty^2}{\cancel{\alpha^2}} C_{fs}(r_p) \right] \qquad a_0 = \frac{\alpha}{4\pi R_\infty}$$

$HD^+$ :
$$\nu_{(v,L)\to(v',L')} \approx cR_\infty \left[ A_{nr}\mu^{s_p}\mu_{pd}^{s_d} + B_{QED}(\cancel{\alpha}) + \frac{R_\infty^2}{\cancel{\alpha^2}} C_{fs}(r_p, r_d) \right]$$

Ro-vibrational transitions: $s_p \approx -\frac{1}{2} \quad s_d \approx -\frac{1}{6}$

- Translating uncertainties on FC into uncertainties on transition frequencies

| Constant | With $r_p$ discr. | $H_2^+$ v=0→1 | $HD^+$ v=0→9 |
|---|---|---|---|
| $\mu$ | 9.5 $10^{-11}$ | 4.5 $10^{-11}$ | 3.3 $10^{-11}$ |
| $R_\infty$ | 3.2 $10^{-11}$ | 3.2 $10^{-11}$ | 3.2 $10^{-11}$ |
| $r_p$ | 3.9 $10^{-2}$ | 4.9 $10^{-11}$ | 2.3 $10^{-11}$ |
| $\mu_{pd}$ | 9.3 $10^{-11}$ | 0 | 1.1 $10^{-11}$ |
| $r_d$ | 1.2 $10^{-3}$ | 0 | 4.2 $10^{-12}$ |

# $H_2^+$, $HD^+$, and fundamental constants

- In the current situation, measurement of a *single* transition would not yield a fully trustworthy determination of $\mu$ .

- But combining *several* measurements in $H_2^+$ and $HD^+$ would constrain *several* constants ($\mu, R_\infty$ , $r_p$ …) and bring new data for solving the proton-radius puzzle.

- Key property : *all* ro-vibrational transitions are narrow (only 1S-2S in hydrogen atom), although they give partially redundant information.

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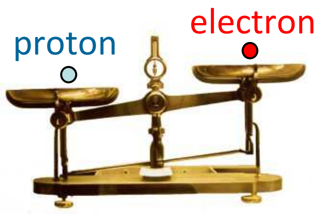


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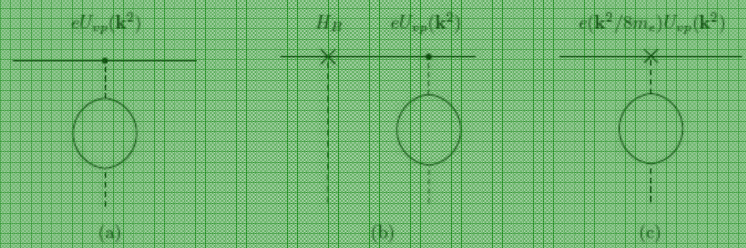


**Collaboration: V. Korobov (JINR, Dubna)**

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- Results from Amsterdam: one-photon spectroscopy of $HD^+$
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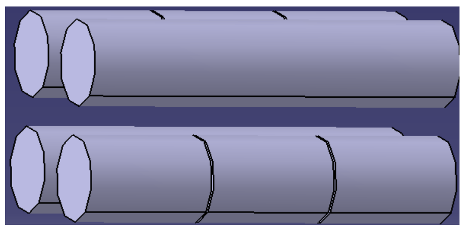

# Status of theory

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(v = 0, L=0) $\rightarrow$ (v'=1, L'=0) interval in MHz

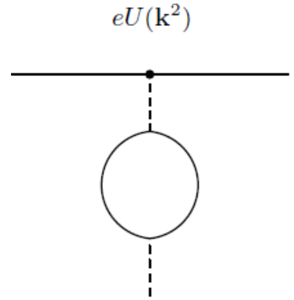
| | $H_2^+$ | $HD^+$ | |
|---|---|---|---|
| $\Delta E_{nr}$ | 65 687 511.0714 | 57 349 439.9733 | Full three-body calculation |
| $\Delta E_{\alpha^4}$ | 1091.0397 | 958.1510 | |
| $\Delta E_{\alpha^5}$ | −276.5450 | −242.1263 | |
| $\Delta E_{\alpha^6}$ | −1.9969 | −1.7481 | Adiabatic approximation |
| $\Delta E_{\alpha^7}$ | 0.138(2) | 0.120(2) | |
| $\Delta E_{\alpha^8}$ | 0.001(1) | 0.001(1) | |
| $\Delta E_{tot}$ | 65 688 323.708(2) | 57 350 154.371(2) | $3\ 10^{-11}$ |

*V.I. Korobov, L. Hilico, J.-Ph. Karr, PRL* ***112****, 103003 and PRA* ***89****, 032511 (2014)*

- Recent improvements
  - order $m\alpha^7$ : more accurate relativistic Bethe log. (one-loop self-energy)
  - order $m\alpha^8$ : two-loop corrections V.I. Korobov's talk
  - order $m\alpha^7$ : vacuum polarization (Uehling potential) this talk

# Uehling correction: leading orders ($m\alpha^5$, $m\alpha^6$)

$$U_{vp}(r) = -\frac{2}{3}\frac{Z\alpha}{\pi r}\int_1^\infty dt\, e^{-\frac{2r}{\alpha}t}\left(\frac{1}{t^2}+\frac{1}{2t^4}\right)\left(t^2-1\right)^{1/2}$$




$$\Delta E_a^{vp} = \langle nl | U_{vp} | nl \rangle \quad (1)$$

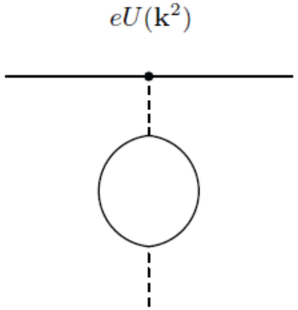
H(nS) $$\Delta E_a^{vp} = \frac{\alpha(Z\alpha)^4}{\pi n^3}\left[\underbrace{-\frac{4}{15}+\frac{5\pi}{48}(Z\alpha)}_{\propto\, |\psi(0)|^2} - \frac{2}{7}\left(1+\frac{1}{5n^2}\right)(Z\alpha)^2 + \frac{7\pi}{768}\left(7+\frac{5}{n^2}\right)(Z\alpha)^3\right]$$

HMI $$\Delta E_a^{vp(5)} = -\frac{4\alpha^3}{15}\left\langle Z_1\delta(\mathbf{r}_1)+Z_2\delta(\mathbf{r}_2)\right\rangle \qquad \Delta E_a^{vp(6)} = -\frac{5\pi\alpha^4}{48}\left\langle Z_1^2\delta(\mathbf{r}_1)+Z_2^2\delta(\mathbf{r}_2)\right\rangle$$

V.I. Korobov, PRA **74**, 052506 (2006)

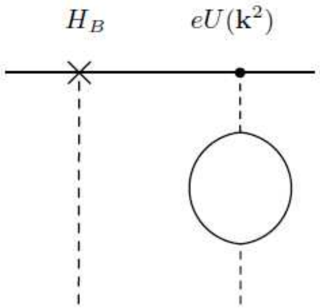
For higher-order terms, direct calculation of (1) is required.

# $m\alpha^7$ order (and higher)




a) First-order contribution (leading-order terms subtracted)

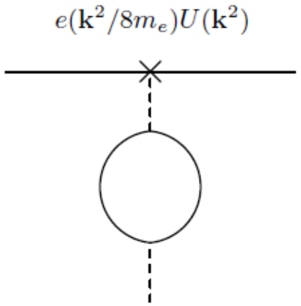
$$\Delta E_a^{(7+)} = \langle \psi_0 | U_{vp} | \psi_0 \rangle - \Delta E_{vp}^{(5)} - \Delta E_{vp}^{(6)}$$




b) Relativistic correction to the wave function

$$\Delta E_b^{(7+)} = 2 \left\langle \Big( H_B - \langle H_B \rangle \Big) (E_0 - H)^{-1} \Big( U_{vp} - \langle U_{vp} \rangle \Big) \right\rangle + \frac{3\alpha^4}{16} \pi \, \langle \psi_0 | Z_1^2 \delta(\mathbf{r_1}) + Z_2^2 \delta(\mathbf{r_2}) | \psi_0 \rangle$$

Spurious $m\alpha^6$-order term subtracted




c) Modification of vertex function (Darwin term)

$$\Delta E_c^{(7+)} = \langle \psi_0 | H_{vp}^{(7)} | \psi_0 \rangle - \frac{3\alpha^4}{16} \pi \, \langle \psi_0 | Z_1^2 \delta(\mathbf{r_1}) + Z_2^2 \delta(\mathbf{r_2}) | \psi_0 \rangle$$

Result for H(nS) $\Delta E_U^{(7)} = \dfrac{\alpha (Z\alpha)^6}{\pi n^3} \left\{ V_{60}(nS) + V_{61} \ln\left(\alpha^{-2}\right) \right\}; V_{61} = -\dfrac{2}{15}.$

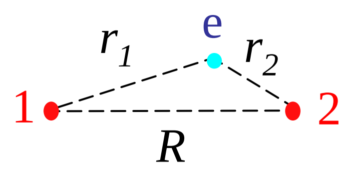
P.J. Mohr, PRL **34**, 1050 (1975); PRA **26**, 2338 (1982)

V.G. Ivanov and S.G. Karshenboim, Yad. Phys. **60**, 333 (1997) [Phys. Atom. Nuclei **60**, 270 (1997)]

# 1. Adiabatic approximation

- Clamped nuclei : electron in a two-center potential

$$V(r) = -\frac{Z_1}{r_1} - \frac{Z_2}{r_2}$$




- Exponential variational expansion

For $\sigma_g$ electronic states : $\psi_0(\mathbf{r_1}, \mathbf{r_2}) = \sum_{i=1}^{N} C_i \left( e^{-\alpha_i r_1 - \beta_i r_2} + e^{-\alpha_i r_2 - \beta_i r_1} \right)$

- Numerical integration using approximate form of Uehling potential

L.W. Fullerton and G.A. Rinker Jr., PRA **13**, 1283 (1976)

$\longrightarrow$ **Effective potential curve** $\Delta E_{vp}^{(7+)}(R)$

$\longrightarrow$ Averaging over ro-vibrational w.f. yields $\Delta E_{vp}^{(7+)}(v, L)$

# 2. Exact three-body approach

➢ First calculation of a high-order QED correction in three-body framework
Provides a test of the two-center approximation.

- Full three-body Hamiltonian

- Exponential variational expansion

$$F(r_1, r_2, r_{12}) = \sum_{n=1}^{N} \left( C_n \,\mathrm{Re}\left( e^{-\alpha_n r_1 - \beta_n r_2 - \gamma_n r_{12}} \right) + D_n \,\mathrm{Im}\left( e^{-\alpha_n r_1 - \beta_n r_2 - \gamma_n r_{12}} \right) \right)$$

- Analytical integration: matrix elements of the Uehling potential in exponential basis set are known in analytical form.

J.-Ph. Karr and L. Hilico, PRA **87**, 012506 (2013)

# Results (nonlogarithmic term)

| | $H_2^+$ 2-center | $H_2^+$ 3-body | $HD^+$ 2-center | $HD^+$ 3-body |
|---|---|---|---|---|
| $v=0, L=0$ | -28.35 | -31.64 | -28.38 | -32.69 |
| $v=1, L=0$ | -27.93 | -30.67 | -28.01 | -31.04 |
| *trans.* | 0.42 | 0.97 | 0.37 | 0.75 |

**Unit: kHz**

2-center calculation : J.-Ph. Karr, L. Hilico, V.I. Korobov, PRA **90**, 062516 (2014).

- Discrepancy: ~ 3.3 (4.3) kHz for $H_2^+$ ($HD^+$) ground states

- Second-order contribution in the adiabatic approximation:

$$\Delta E_b = 2 \sum_{exc.\sigma_g} \frac{\langle \psi_0 | H_B | \psi_n \rangle \langle \psi_n | U_{vp} | \psi_0 \rangle}{E_0 - E_n}$$

The contribution from ***vibrational excitations*** is missing!
Numerical evaluation : ~ -4.6 kHz for v=0.

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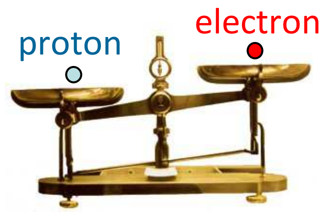


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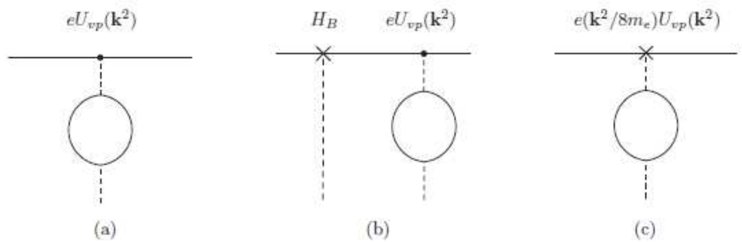


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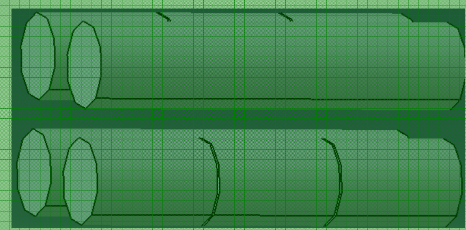
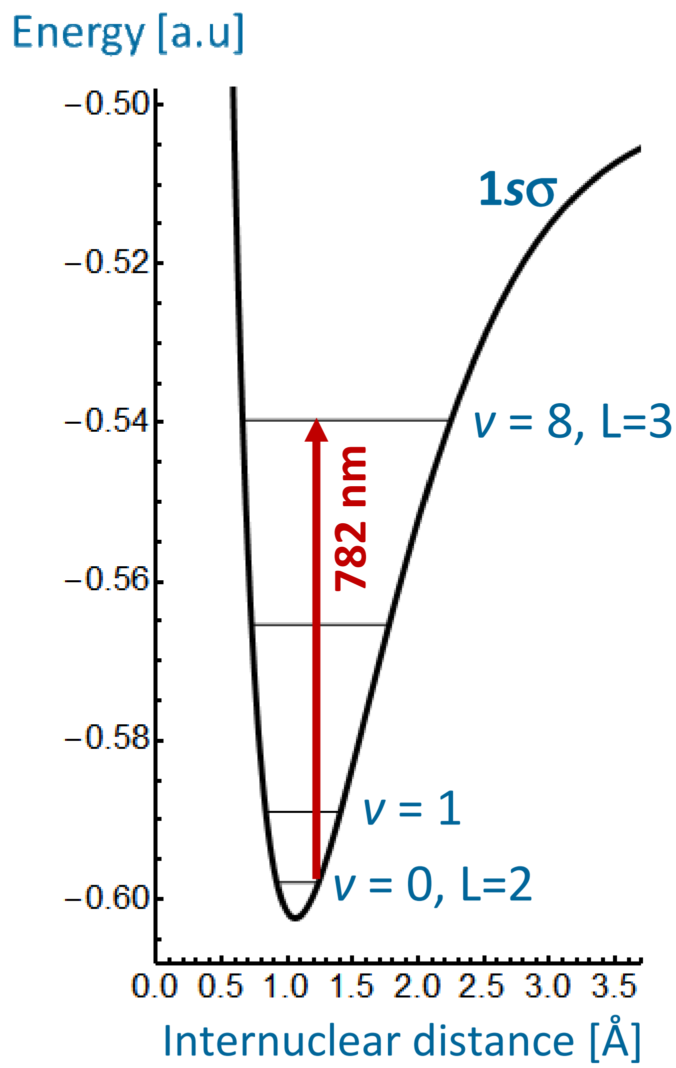


# $HD^+$ spectroscopy in Amsterdam

J. Bisheuvel, K.S.E Eikema,
W. Ubachs, J.C.J. Koelemeij
*LaserLaB, Amsterdam VU*

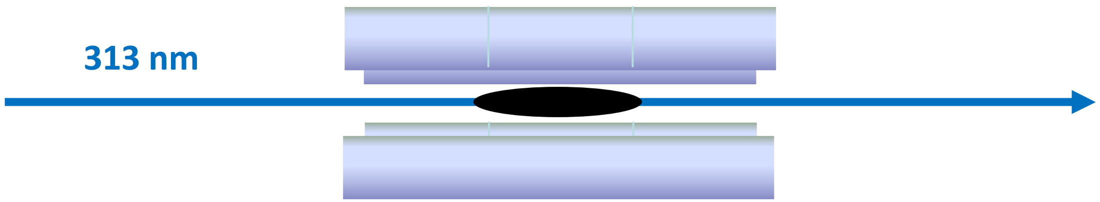
J.P.K., L. Hilico
*LKB, Paris*
(systematic shifts, MD simulations)

J. Biesheuvel, J.-Ph. Karr, L. Hilico,
K.S.E. Eikema, W. Ubachs,
J.C.J. Koelemeij (submitted)

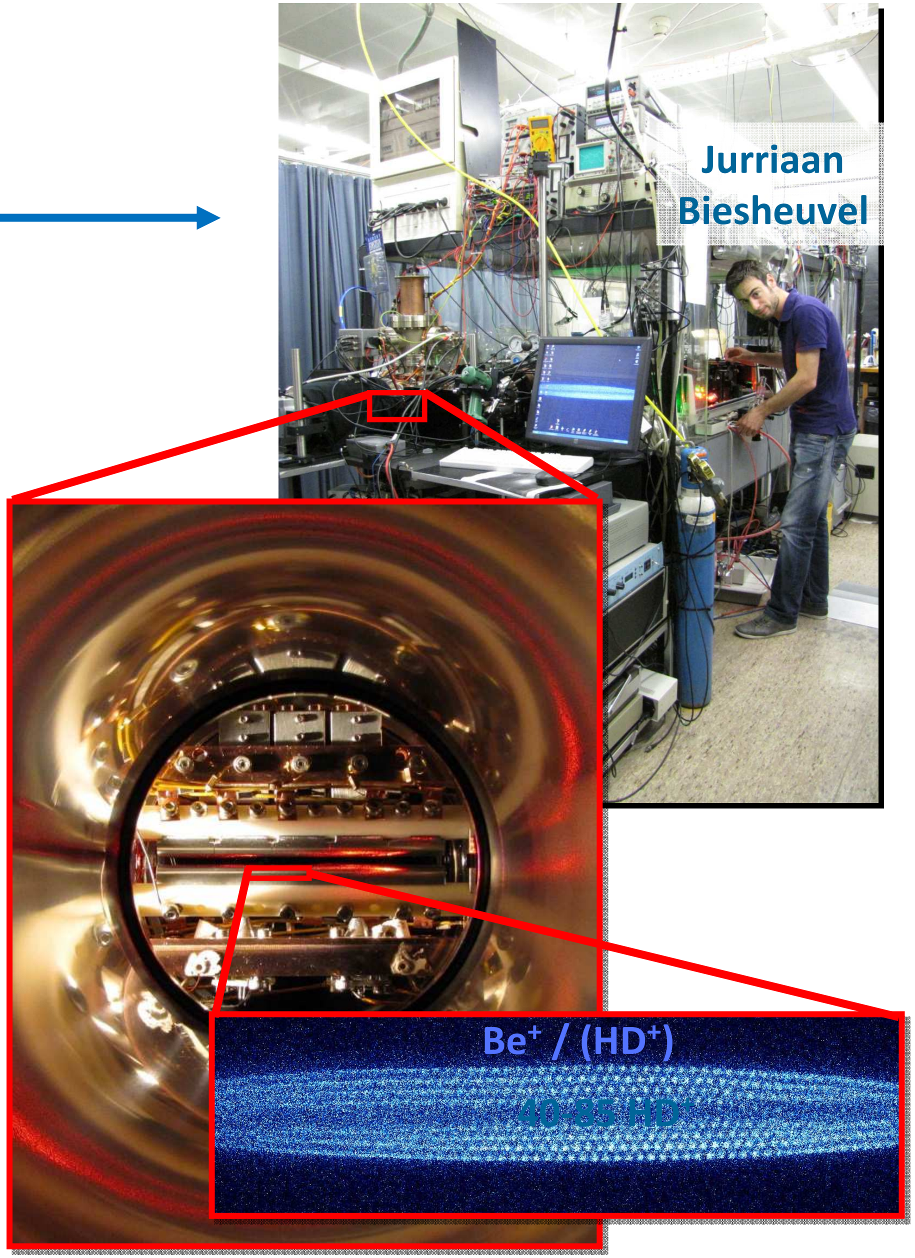


# Experimental methods

**Linear RF trap**

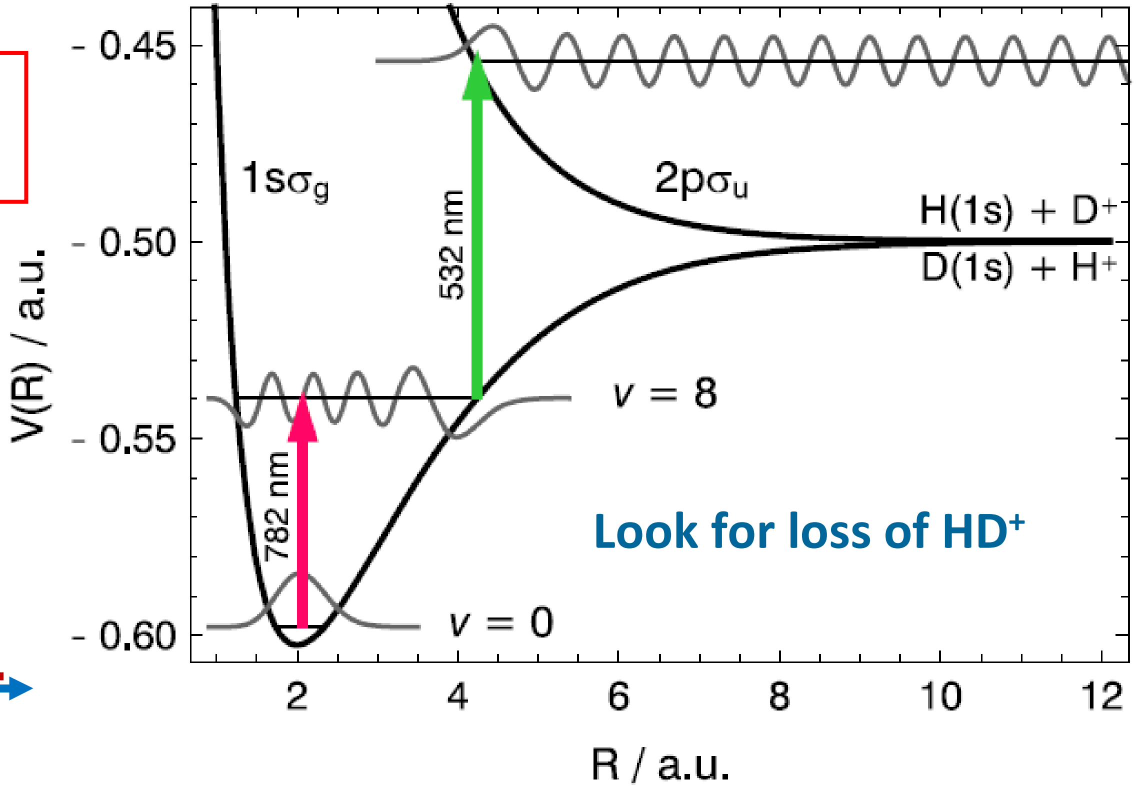


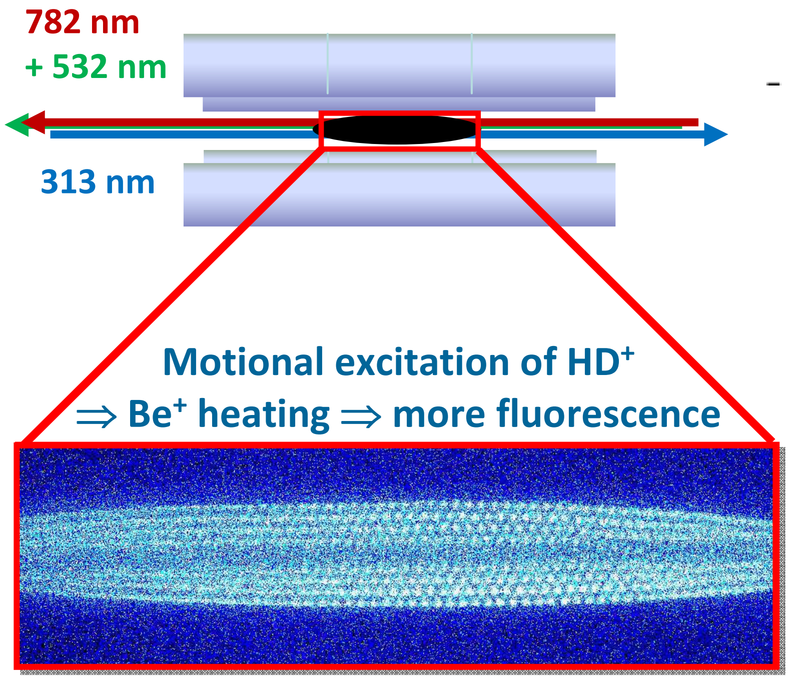

- Laser-cooled $Be^{+}$ ions (313 nm)
- Weakly confining ($\omega_{Be+} = 2\pi\times0.3$ MHz)
- Load $HD^{+}$ by e-impact ionization, sympathetic cooling to ~10 mK
- Typically 750 $Be^{+}$, 40 - 85 $HD^{+}$



# Experimental methods

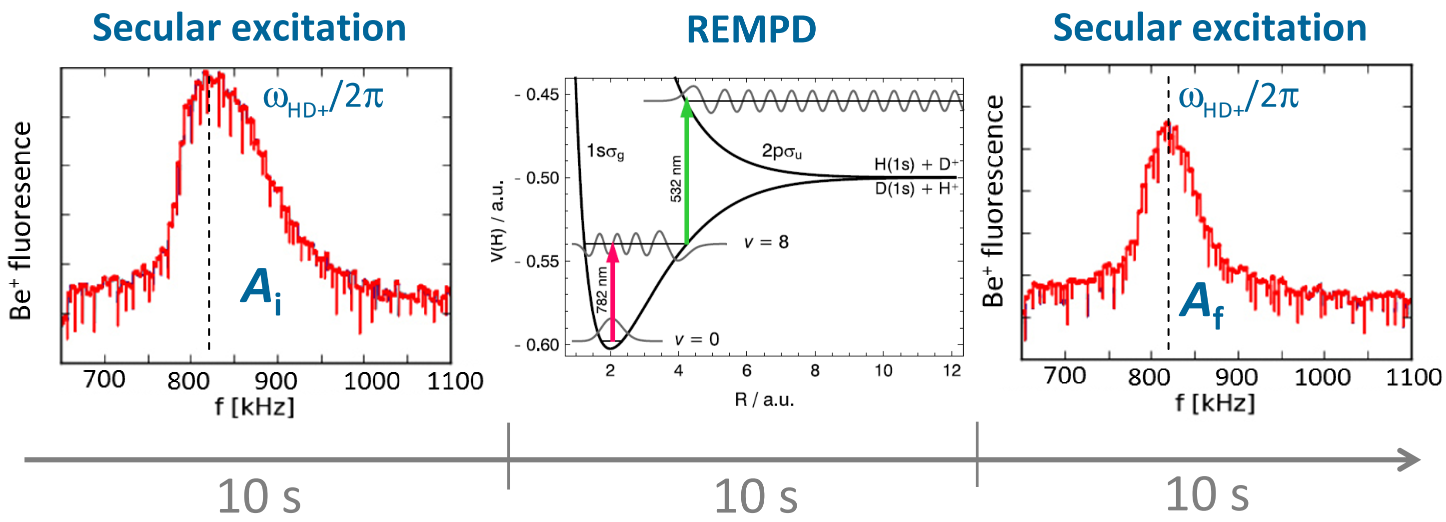
**R**esonance **E**nhanced **M**ulti-**P**hoton **D**issociation (REMPD)



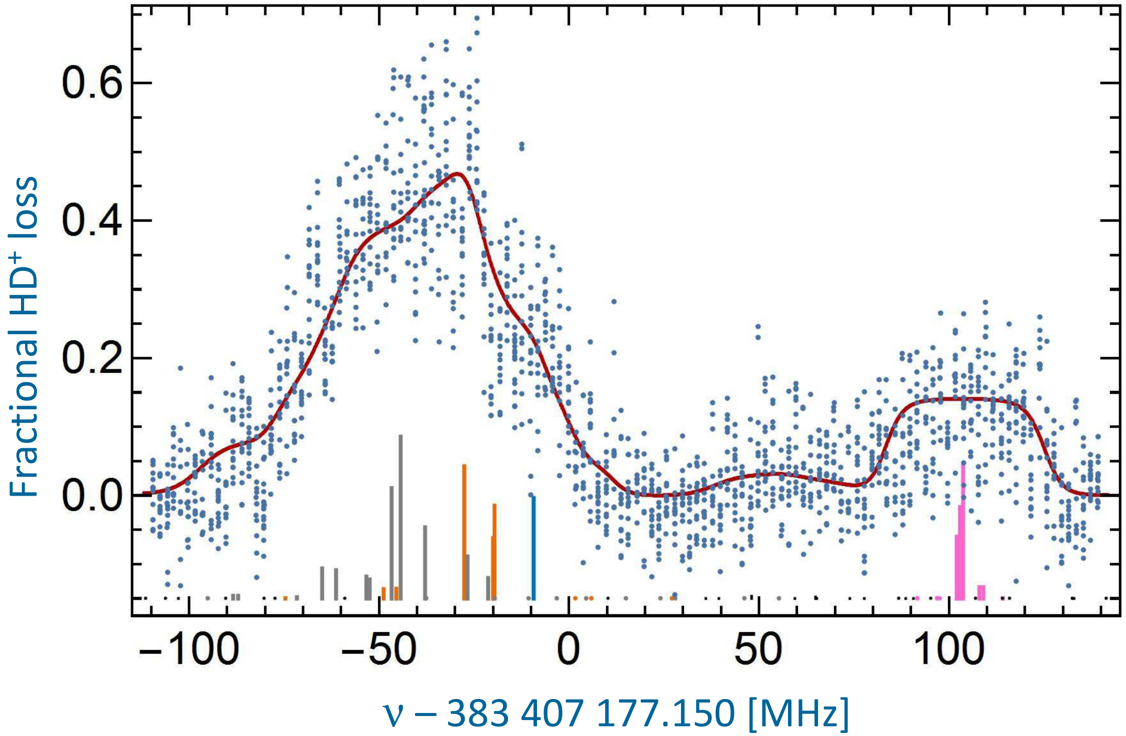

$\Rightarrow$ ***Measure of the number of $HD^+$***

# Experimental sequence




Signal = fractional loss of ions $(A_f - A_i)/A_i$

# Data and analysis




1772 data points

Data analysis: Rate equation model with all time-dependent effects realistically included:

- REMPD (Doppler-broadened line shape)
- Background collisions (e.g. $HD^+ + H_2 \longrightarrow H_2D^+ + H$ )
- Population recycling by BBR

➡ Fitting of the “hyperfine-less” frequency with 0.85 ppb (0.33 MHz) uncertainty

# Uncertainty budget and result

| Origin | Shift | Uncertainty | |
|---|---|---|---|
| | (MHz) | (MHz) | (p.p.b) |
| Resolution (statistical fit error) | 0 | 0.33 | 0.85 |
| Doppler effect due to chemistry | -0.25* | 0.25 | 0.66 |
| Ignoring population L=6 in rate equations | 0 | 0.032 | 0.083 |
| Doppler effect due to micromotion | -0.055* | 0.020 | 0.052 |
| Frequency measurement | 0 | 0.010 | 0.026 |
| BBR temperature | 0 | 0.005 | 0.013 |
| Zeeman effect | -0.0169 | 0.003 | 0.008 |
| Stark effect | -0.0013 | 0.0001 | 0.0004 |
| Electric-quadrupole shift | 0† | 0.0001 | 0.0003 |
| 2nd-order Doppler effect | 0† | 0.000005 | 0.00001 |
| Total | -0.0182 | 0.41 | 1.1 |

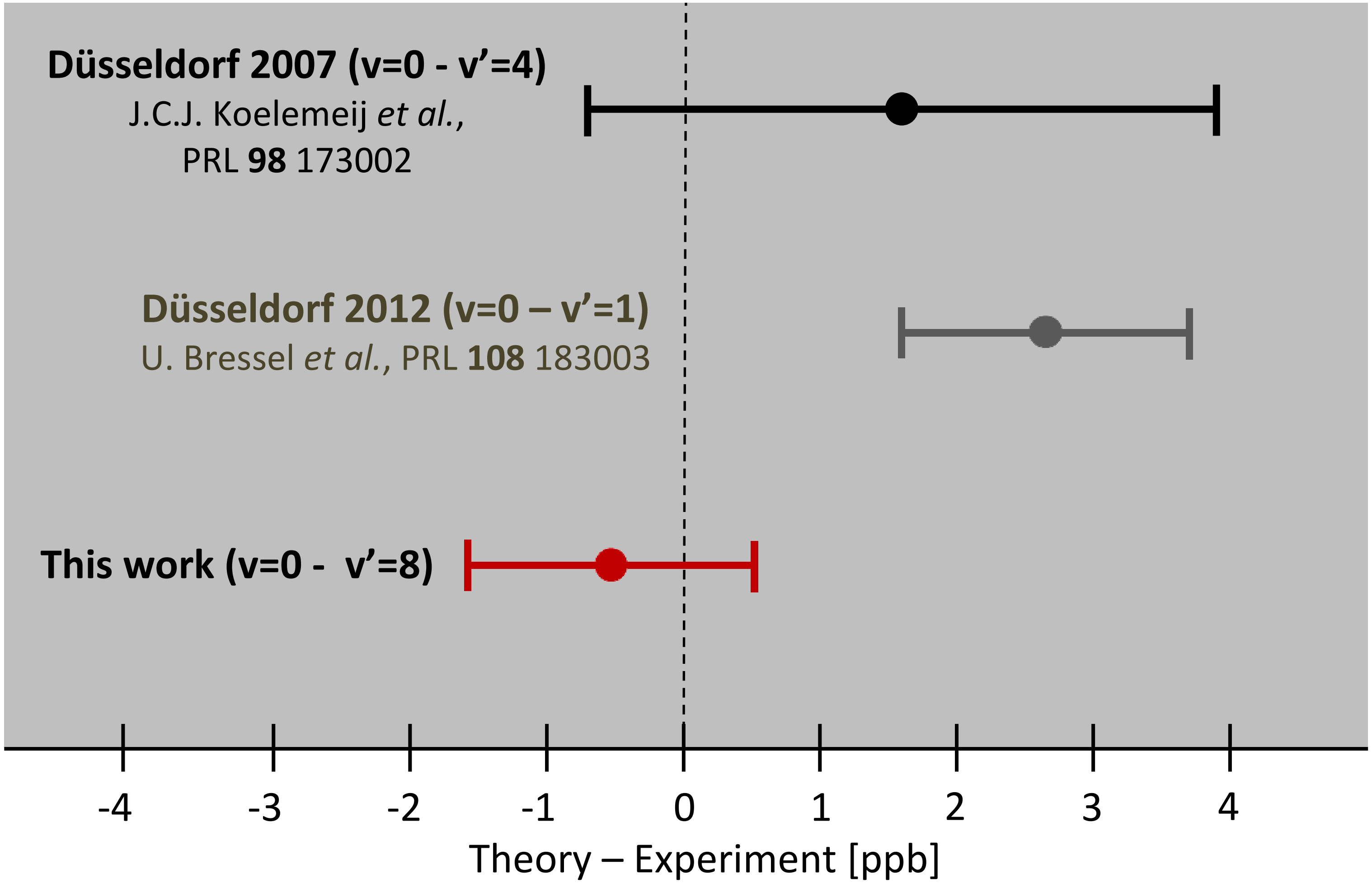
**Experiment:** **383 407 177.38(41) MHz**
**Theory:** **383 407 177.150(15) MHz**

# Doppler effect due to chemistry

- Photodissociation of $HD^+$, and observed reactions with background $H_2$, produces **hot ions** (2000 to 5000 K !) which will exchange energy with the laser-cooled ion crystal.
- Realistic MD simulations reveal **non-Maxwell-Boltzmann distributions.**
- Combined with saturation effects and overlapping lines : **significant line shift**
- Precise knowledge of the velocity distribution during REMPD would require determining the **thermalization time** (huge simulation effort).
- **Upper/lower limits** on the thermalization time lead to limits on the line shift.

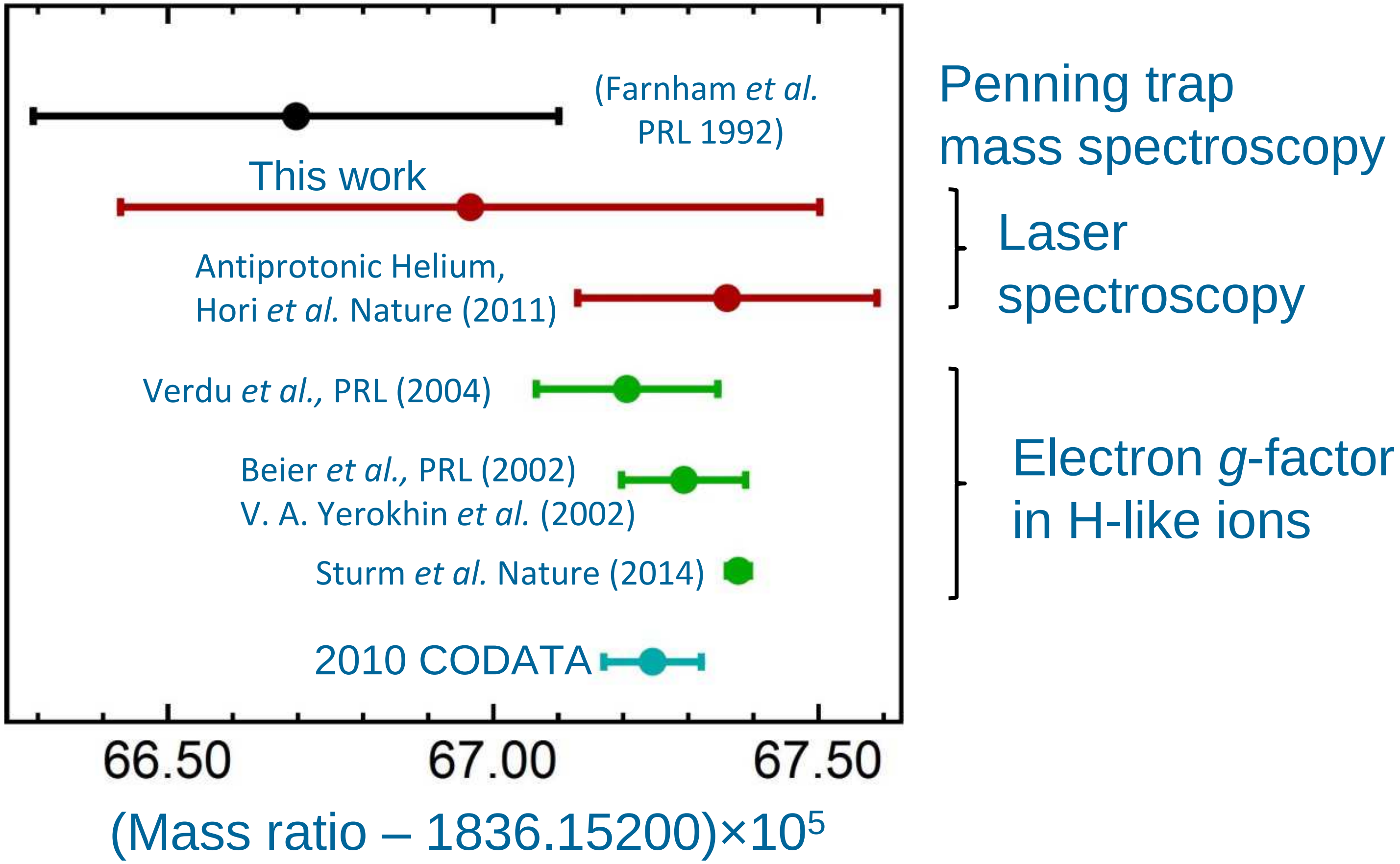
**Effect on line position ~ -0.25(25) MHz**

# Comparison with theory



# First determination of $\mu$ from molecular vibrations

$\mu$ =1836.1526695(53)  (2.9 ppb)



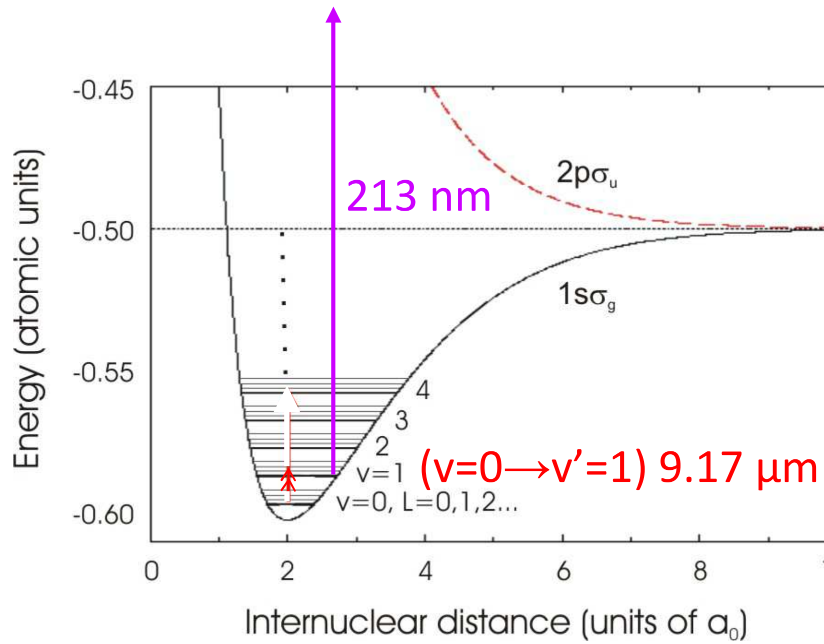

- Other outcome: constraints on deviations from Coulomb law

See W. Ubachs' talk

# The $H_2^+$ experiment in Paris

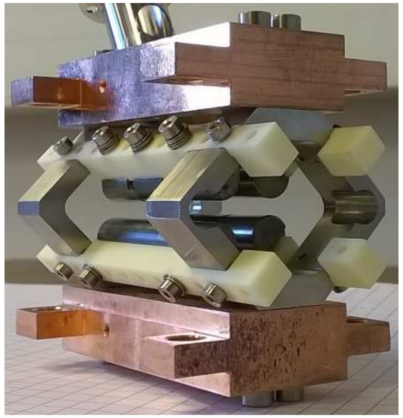
J. Heinrich, N. Sillitoe,
A. Douillet, JPK, L. Hilico
*LKB, Paris*

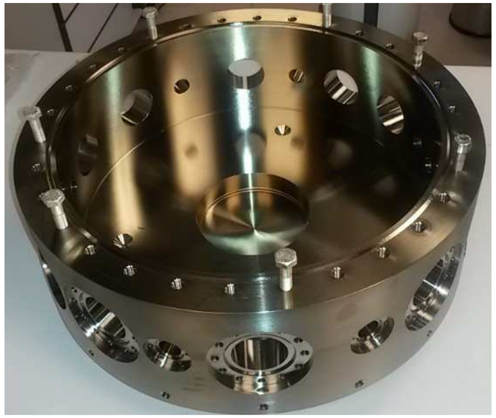
Eliminate Doppler broadening:
**Doppler-free two-photon transition**

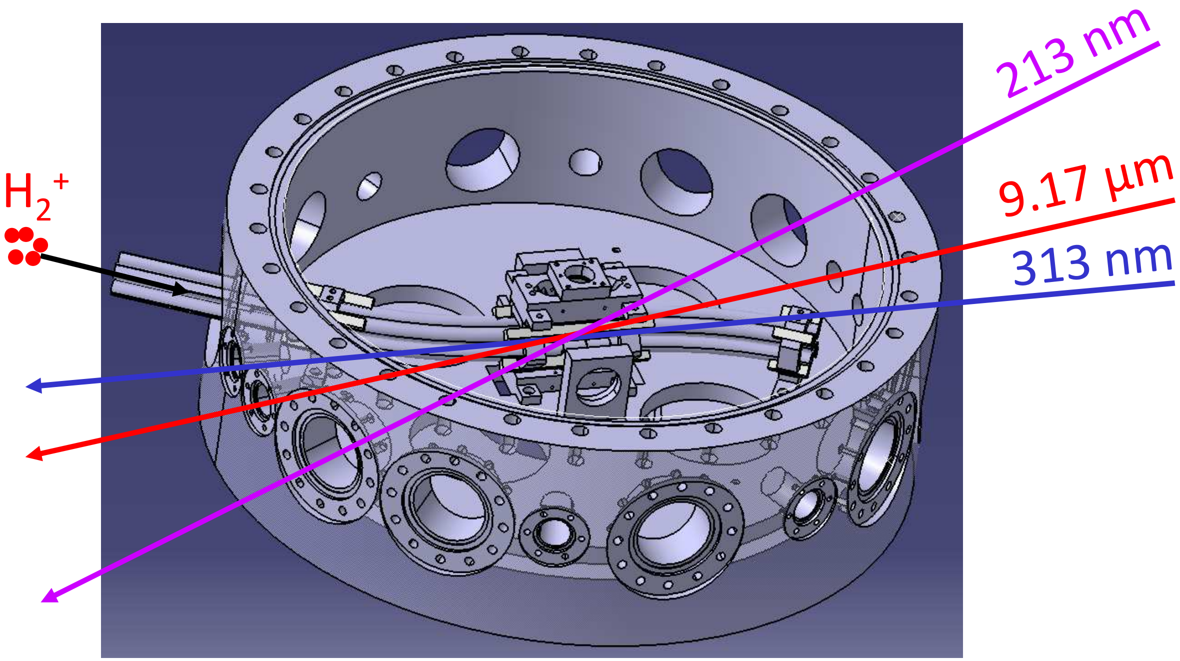



- Linear rf ion trap, sympathetic cooling by laser-cooled $Be^+$
- Ultra-stable Quantum Cascade Laser (QCL) at 9.17 µm
  In-vacuum enhancement cavity for the two-photon transition
- Loading of $H_2^+$ by $e^-$ impact ionization: insufficient !
  Long-lived states ⟶ not enough population in (v=0,L=2)
  Production in selected state by **resonant multiphoton ionization** (**REMPI**)

# Ion trap and vacuum vessel

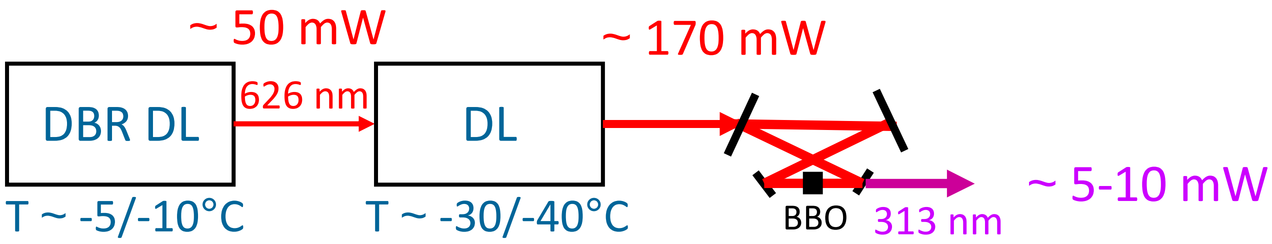






# 313 nm lasers for Be$^+$ cooling

- **Low-cost sources** for Doppler cooling



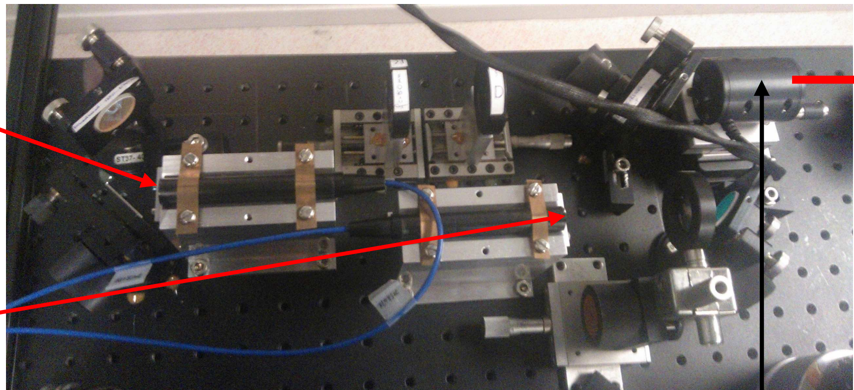

✓ Master and slave lasers mounted and operated
✓ DBR DL locked on $I_2$ saturated absorption line @ 626.26 nm
✓ Compact SHG cavity design by Amsterdam group (F. Cozijn, J. Koelemeij)

- **High-power source** for Raman sideband cooling

GBAR talk

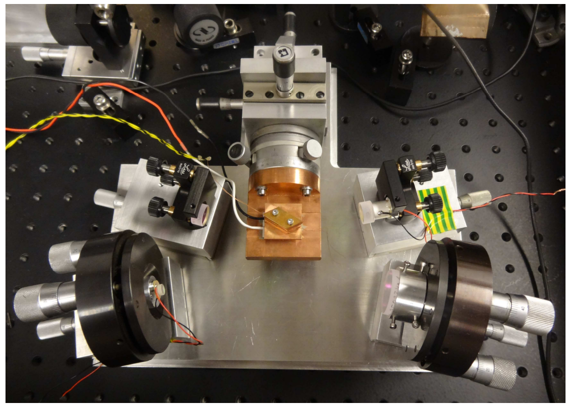
Fiber laser
1550 nm
4-5 W

Fiber laser
1051 nm
4-5 W



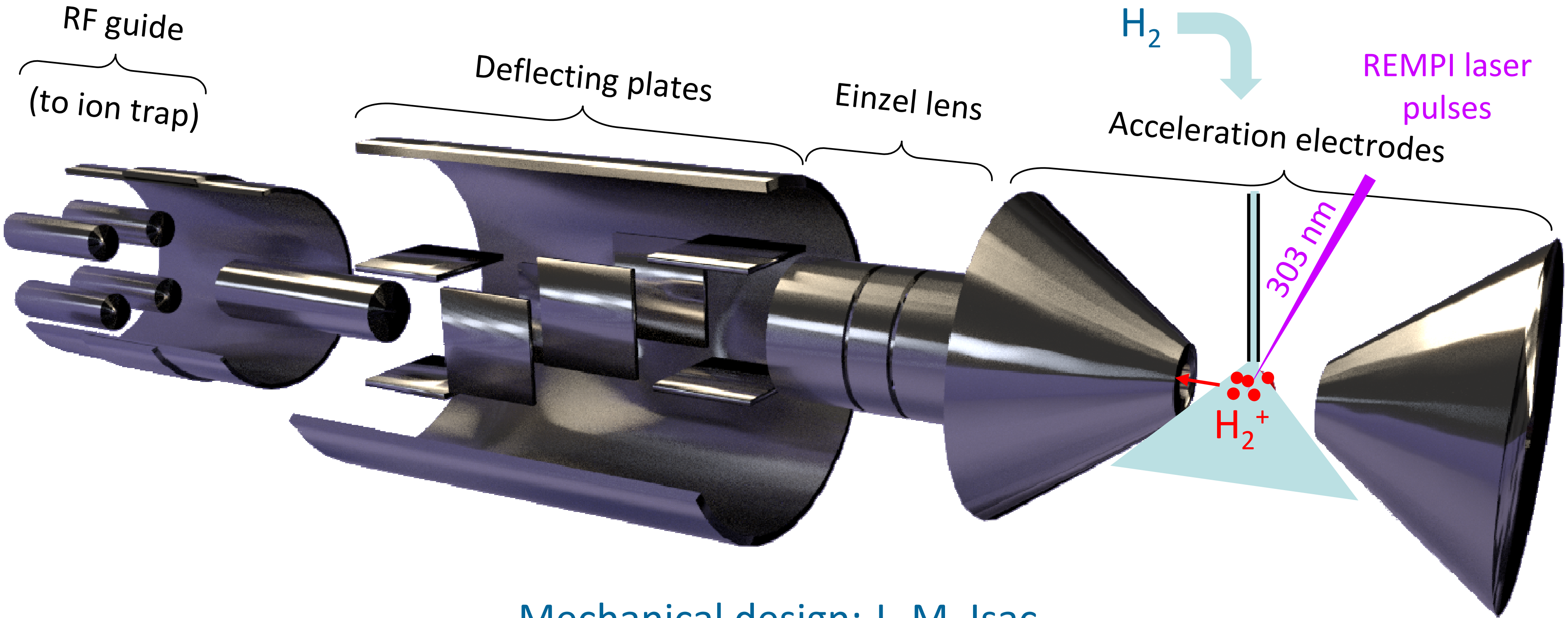
626 nm
2 W

PPLN crystal in oven



SHG cavity

# $H_2^+$ ion source




Mechanical design: J.-M. Isac

- Fabrication in progress
- Other option to be tested: in-situ creation with pulsed $H_2$ beam
- Ion injection from an external source is useful to “simulate” GBAR!

# Expected performances

- Linewidth
  - limited by the spectral width of the laser source (no Doppler broadening) i.e. currently ~ **2-3 kHz**
- Signal-to-noise ratio
  - The number of ions could be higher than in $HD^+$ experiment
  - REMPI creates 90% of the ions in the desired ro-vibrational state
- Frequency measurement
  - current setup $HCOOH/CO_2$ “secondary” standard, accuracy limit ~ **1 kHz ($3\ 10^{-11}$)**
  - to be implemented: frequency comb measurements in the 9 µm range

# Conclusions

- The vacuum polarization (Uehling) $m\alpha^7$-order correction has been calculated. Comparison of 2-center and 3-body approaches questions the accuracy of the adiabatic approach.

- Measurement of the (0,2) $\rightarrow$ (8,3) one-photon transition in $HD^+$ by the Amsterdam group.
  - agreement with theory at the 1 ppb level
  - determination of $\mu$ with 2.9 ppb accuracy

- Doppler-free two-photon spectroscopy is being prepared
  - (0,2) $\rightarrow$ (1,2) in $H_2^+$ (Paris)
  - (0,3) $\rightarrow$ (9,3) in $HD^+$ (Amsterdam) with non-degenerate photons

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

- Combined measurements in $H_2^+$ and $HD^+$ can lead to improve the determination of several fundamental constants : $\mu$ , $R_\infty$ , $r_p$ ...

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