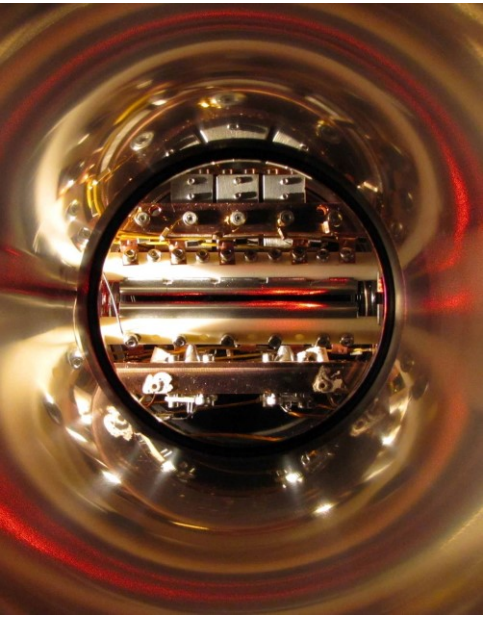

Solving a 9σ discrepancy between hyperfine theory and experiment in HD^+ trapped ions

Jeroen Koelemeij

Vrije Universiteit Amsterdam

Schloß Bückeburg, September 28, 2023

ECTI

7th European Conference on Trapped Ions

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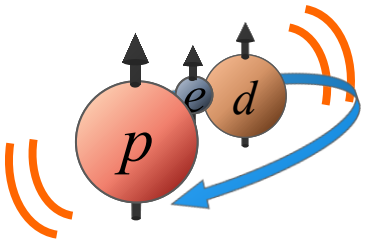
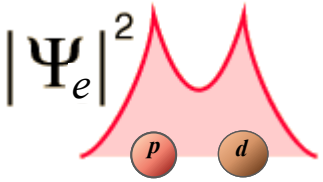
Our interest in molecular hydrogen ions

- H_2^+, 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) and to experiment!
  - Relative uncertainty theoretical vibrational level energies **~20 ppt**

    Of which <**10 ppt** due to QED theory*

    CODATA-18 m_p/m_e largest contributor (**~15 ppt**)
  - Rotational & vibrational spectroscopy: **1.5 – 15 ppt**

    Amsterdam/Paris *Science* **369**, 1238 (2020)

    Düsseldorf *Nature* **581**, 152 (2020), *Nat. Phys.* **17**, 569 (2021), *Nat. Phys.* ***19***, 1263 (2023)

*Korobov, Hlico, Karr *PRL* **118**, 233001 (2017)
Korobov & Karr, *PRA* **104**, 032806 (2021)

⇒ Determination of m_p/m_e with ~20 ppt uncertainty

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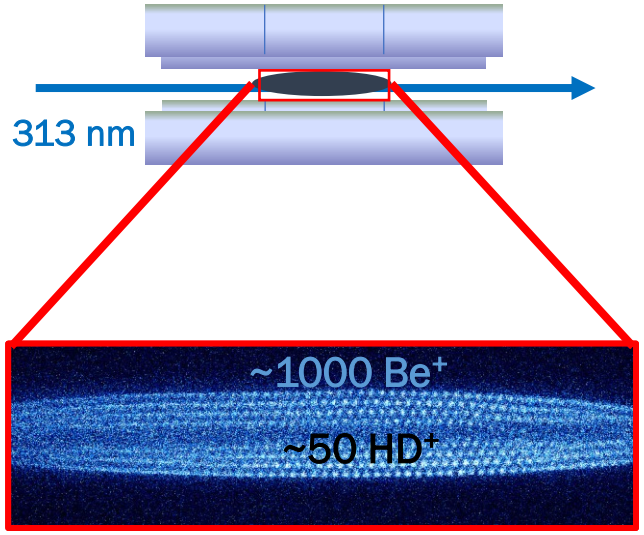
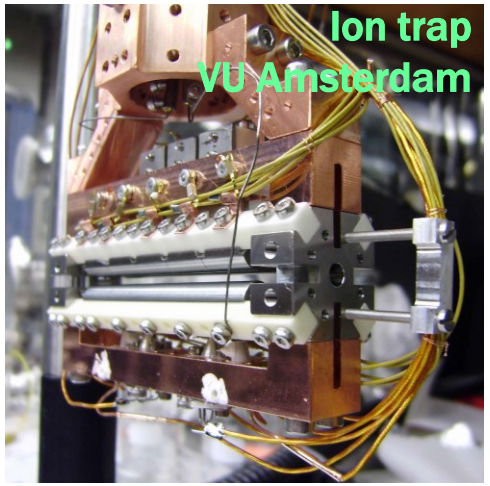
Amsterdam HD^+ spectroscopy setup

- RF ion trap with large ensembles of Be^+ ions, laser-cooled by a 313 nm laser
- Embed HD^+ ions ⇒ **sympathetic cooling to 10 mK**
- We image 313 nm fluorescence on an EMCCD camera ⇒ count number of HD^+
- Spectroscopy via resonance enhanced multiphoton dissociation (REMPD)*

- Large trap, weak confinement
  ⇒ not in the optical Lamb-Dicke regime
- Doppler broadening to ~10 MHz (that's 24 000 ppt…)
- Unpaired electron in HD^+: Zeeman effect 3 400 ppt/G…)





*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)

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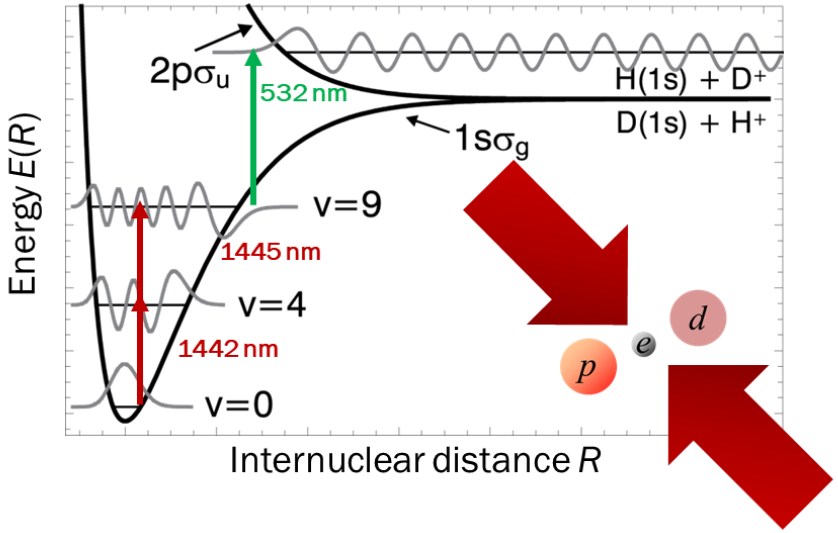
Two-photon spectroscopy

- 2013: proposed two-photon Doppler-free spectroscopy*
- Effective wave vector 0.7 mm: can use our weakly confining rf trap ☺ (Lamb-Dicke regime)
- <2 kHz laser line width (natural line width ~10 Hz)
- Frequency measurement uncertainty <1 ppt (Cs clock, frequency comb laser)

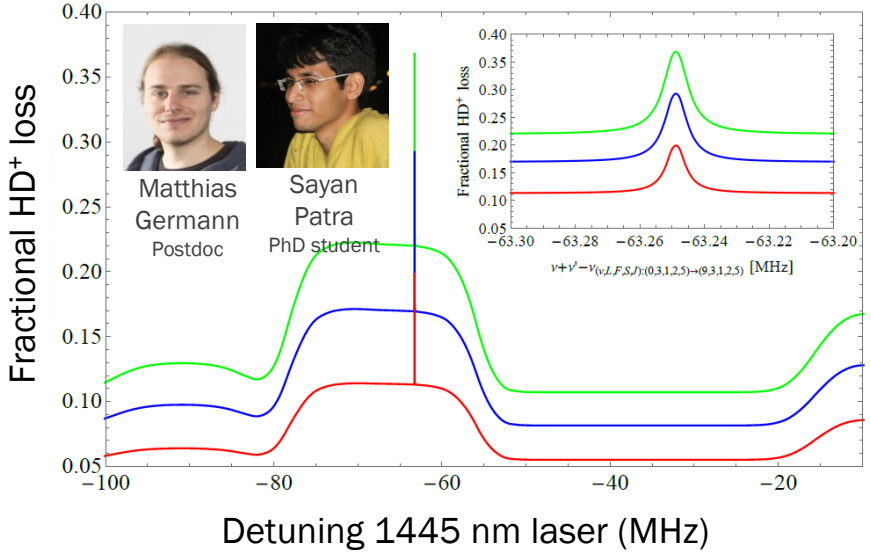
*V.Q. Tran, J.-Ph. Karr, A. Douillet, J.C.J. Koelemeij, L. Hilico, Phys. Rev. A **88,** 033421 (2013)

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

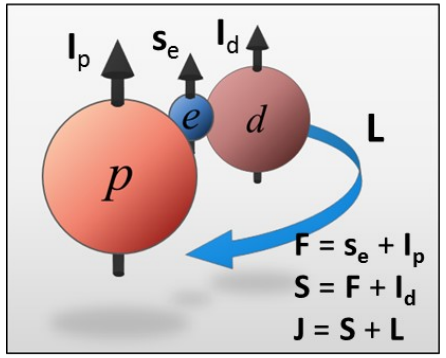
Doppler-free two-photon spectroscopy (Lamb-Dicke regime)

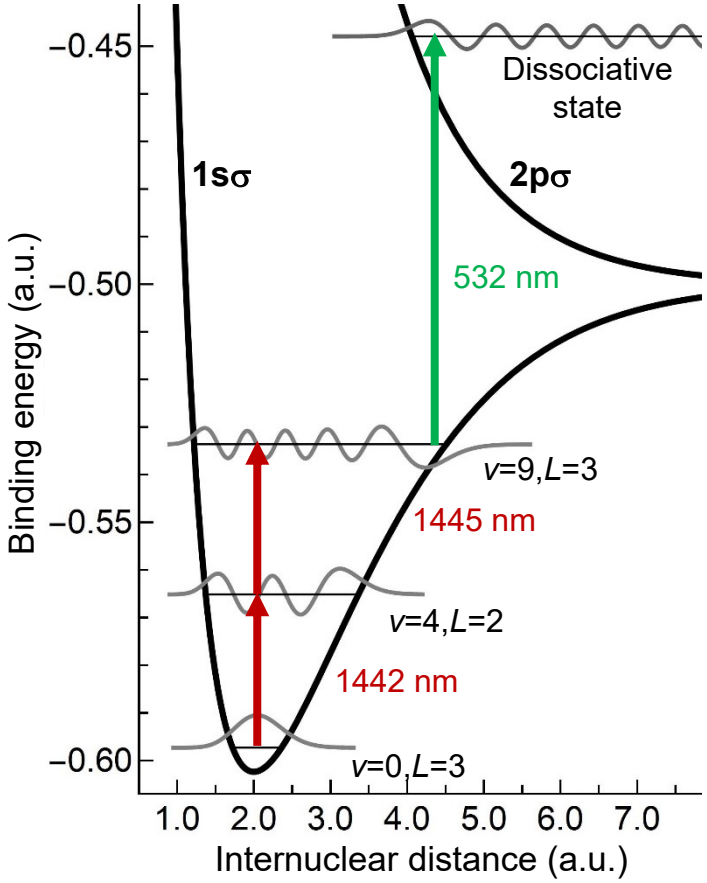


Simulated spectra*,**



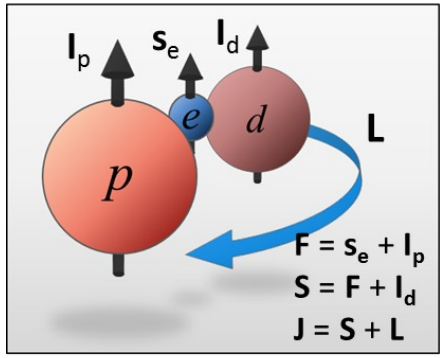
Hyperfine structure...



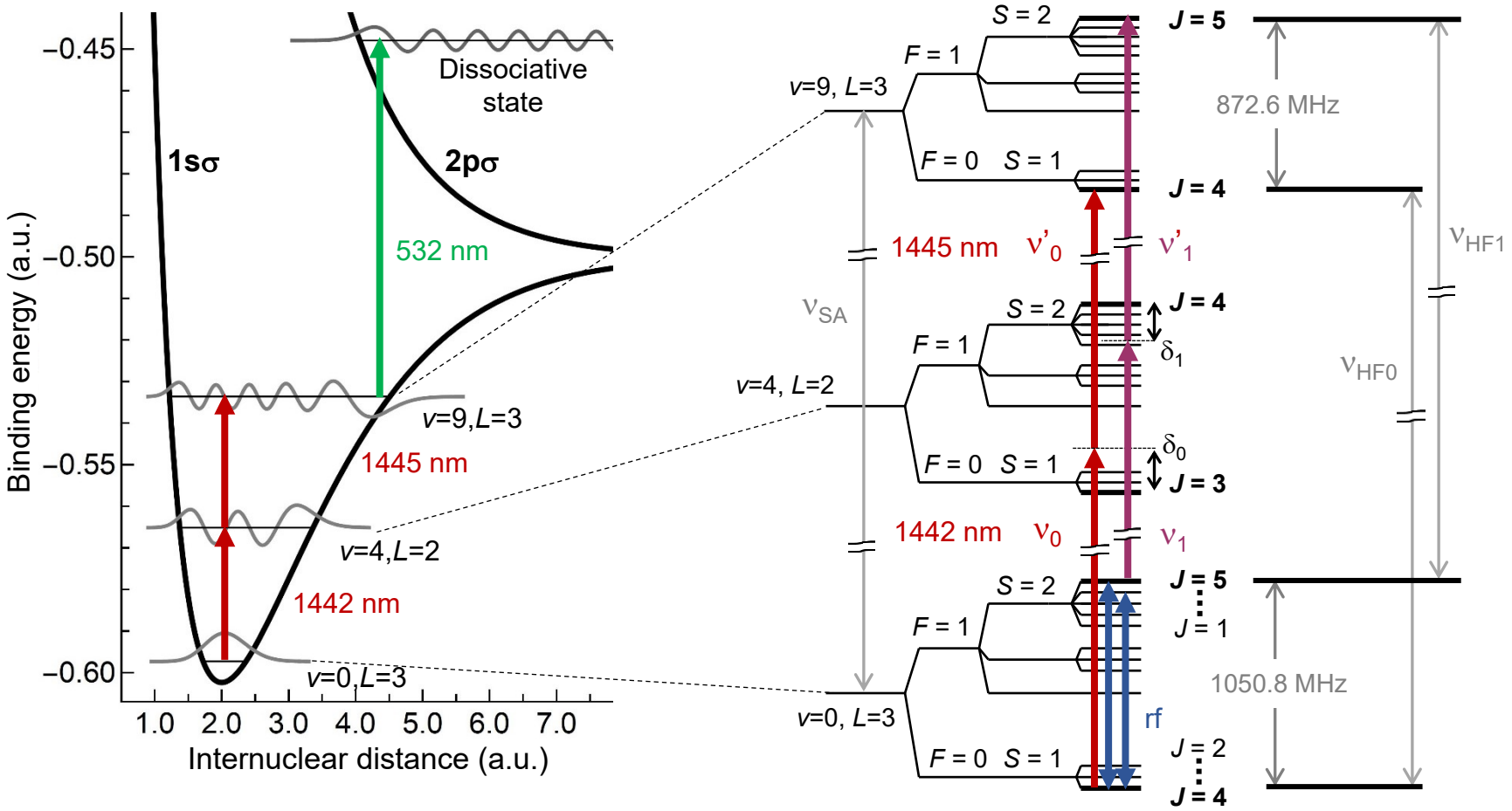


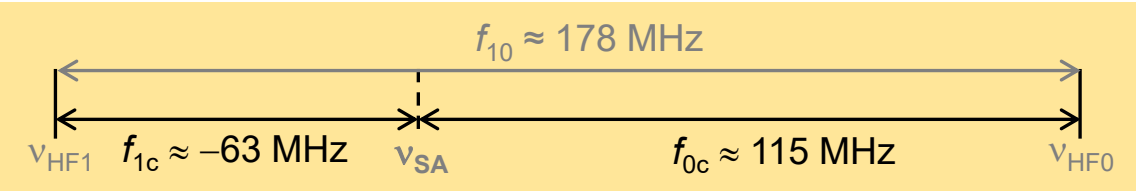
v

Hyperfine structure...



Homologous initial and final spin states: **near-cancellation of Zeeman effect ☺**

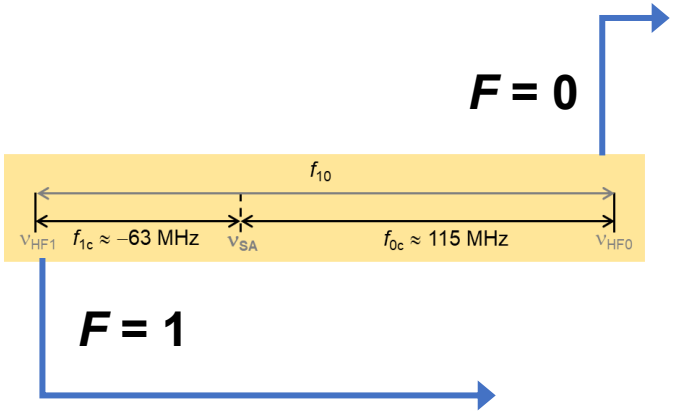


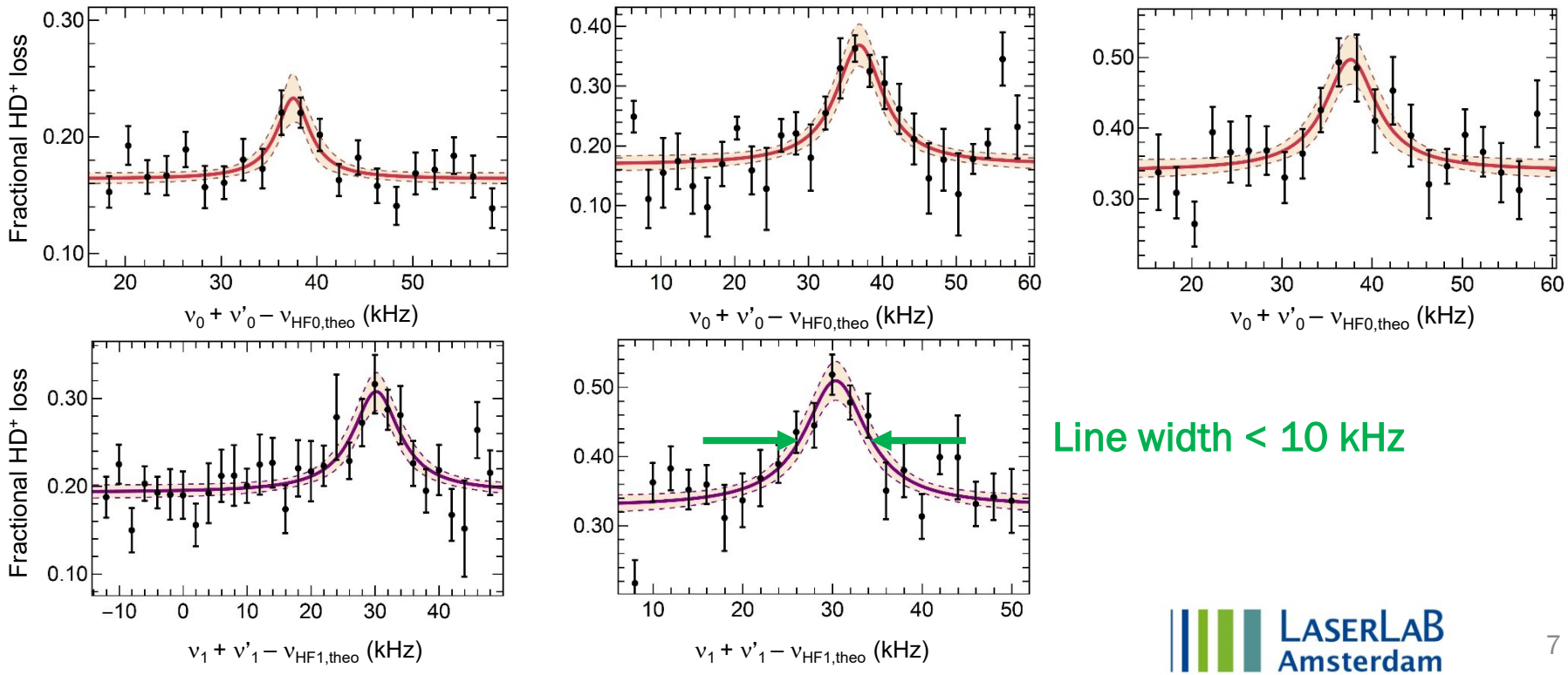


Doppler-free laser spectroscopy - results

- First observation of Doppler-free optical transitions in HD^+ (v=0 – v'=9)
- Spin-averaged transition frequency measured with **1.6 kHz uncertainty (3.9 ppt)**
  - 0.6 kHz (1.5 ppt) pure experimental uncertainty, 1.6 kHz due to theoretical hyperfine structure correction

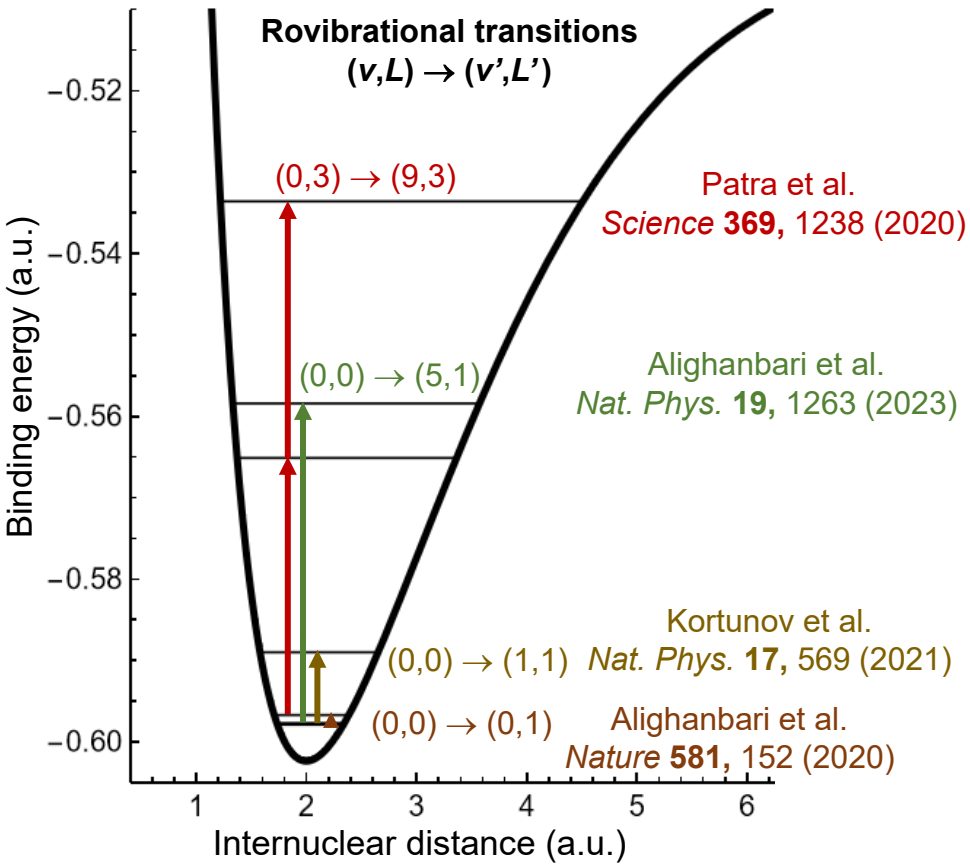
* S. Patra, M. Germann, J.-Ph. Karr, M. Haidar, L. Hilico, V.I. Korobov, F.M.J. Cozijn, K.S.E. Eikema, W. Ubachs, J.C.J. Koelemeij, *Science* **369**, 1238 (2020)





Line width < 10 kHz

HD^+ and fundamental particle mass ratios



- Transition frequencies depend on nuclear reduced-to-electron mass ratio:

$$\mu_r = \frac{m_\mathrm{p} m_\mathrm{d}}{m_\mathrm{p} + m_\mathrm{d}} / m_\mathrm{e}$$

- Several transitions have been measured, but all contain hyperfine shifts ~100 MHz – how to correct for hfs?
  - Note: not enough experimental data to reconstruct hfs – must rely on theory…

Removing hyperfine structure

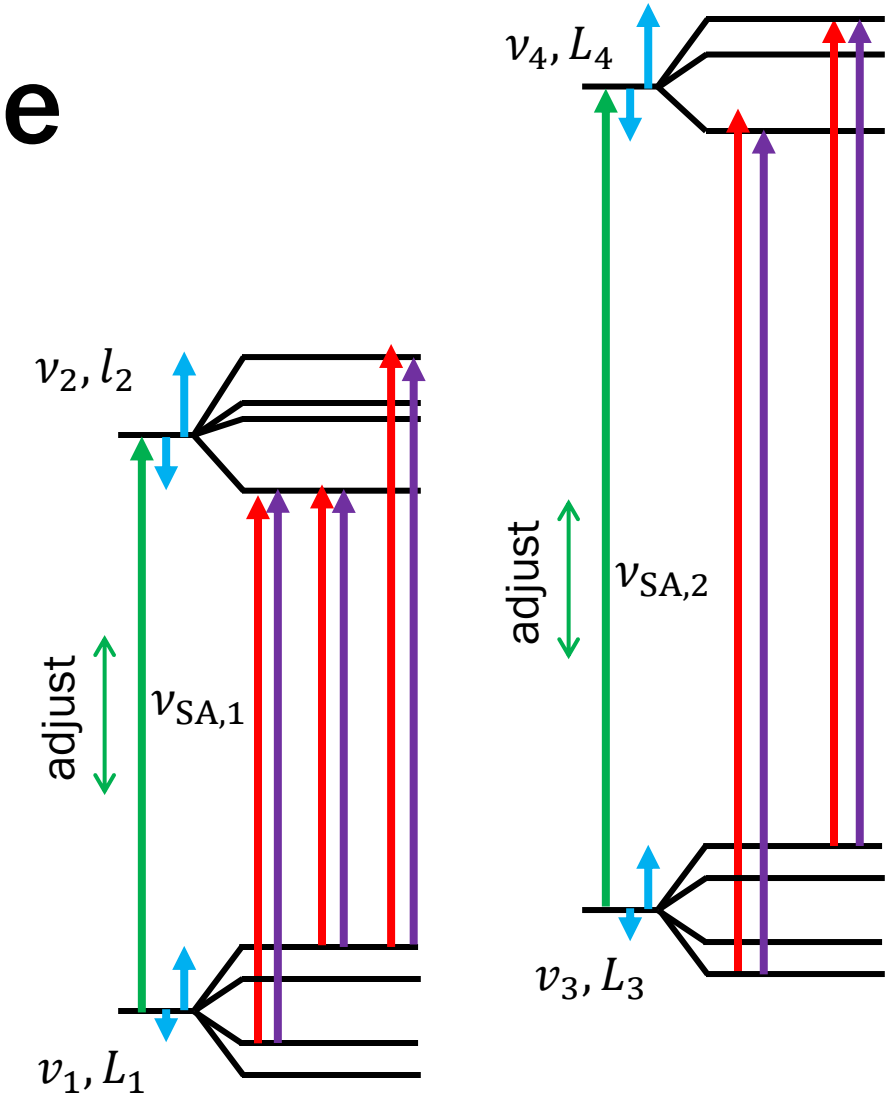
For a given rovibrational transition $v_1, L_1 \rightarrow v_2, L_2$:

- Experimental values: $\nu^i_{\text{exp}} \quad (i = 1,2,\ldots,N)$
- Theoretical predictions: $\nu^i_{\text{theo}} = \nu_{\text{SA}} + \nu^i_{\text{hfs}}$
- Obtain ν_{SA} by weighted least-squares adjustment of N equations*,**:

Contains information on m_p, m_d, m_e, μ_r !

$$\nu^i_{\text{exp}} \doteq \nu_{\text{SA}} + \nu^i_{\text{hfs}}$$

  - Note: simplified picture, actual adjustment is more involved**
- Uncertainty of theory values ν^i_{hfs} strongly correlated:
  - Spin-spin interactions developed from same QED framework
  - Same hyperfine uncertainties for different rovibrational states
- Mandatory to include all HD^+ data in a single adjustment**!
  - Adjust $\nu_{\text{SA},1}, \nu_{\text{SA},2}, \nu_{\text{SA},3}, \ldots$
  - Correlations included in input covariance matrix



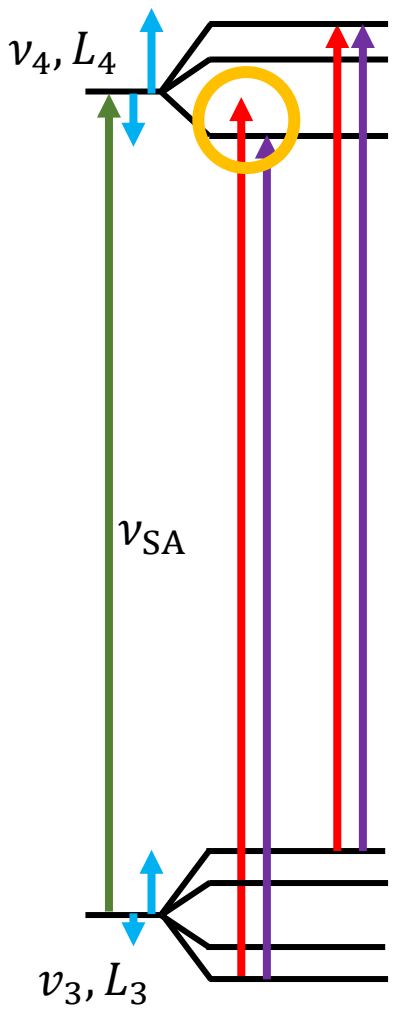
* J.C.J. Koelemeij *Mol. Phys.* **120** , e2058637 (2022).

** J.-Ph. Karr & J.C.J. Koelemeij *Mol. Phys* (2023). DOI: 10.1080/00268976.2023.2216081

Hyperfine discrepancies

- After adjustment: deviations of up to 7.1σ for two rotational L = 0 - 1 lines and for the two v = 0 - 9 lines*
  - 4 out of 10 lines deviate
  - Unclear whether problem lies in theory or experiment
  - Absorb deviations by increasing all uncertainty margins by 3.6 (expansion factor)
    - Reduce tension to below 2σ
  - Other recent approach: composite frequency approach & omission of 'problematic' lines from analysis**
- Least-squares + expansion factor pros and cons:
  - ☹ Uncertainty of final results increased ⇒ smaller scientific impact
  - ☺ Larger uncertainty reduces 'shock' by the time discrepancies are resolved
  - ☺ Agnostic to human perception & untested hypotheses (i.e. avoids human bias)

AFTER adjustment of ν_{SA}



*J.-Ph. Karr & J.C.J. Koelemeij *Mol. Phys* (2023). DOI: 10.1080/00268976.2023.2216081
Alighanbari et al. *Nat. Phys.* **19, 1263 (2023)

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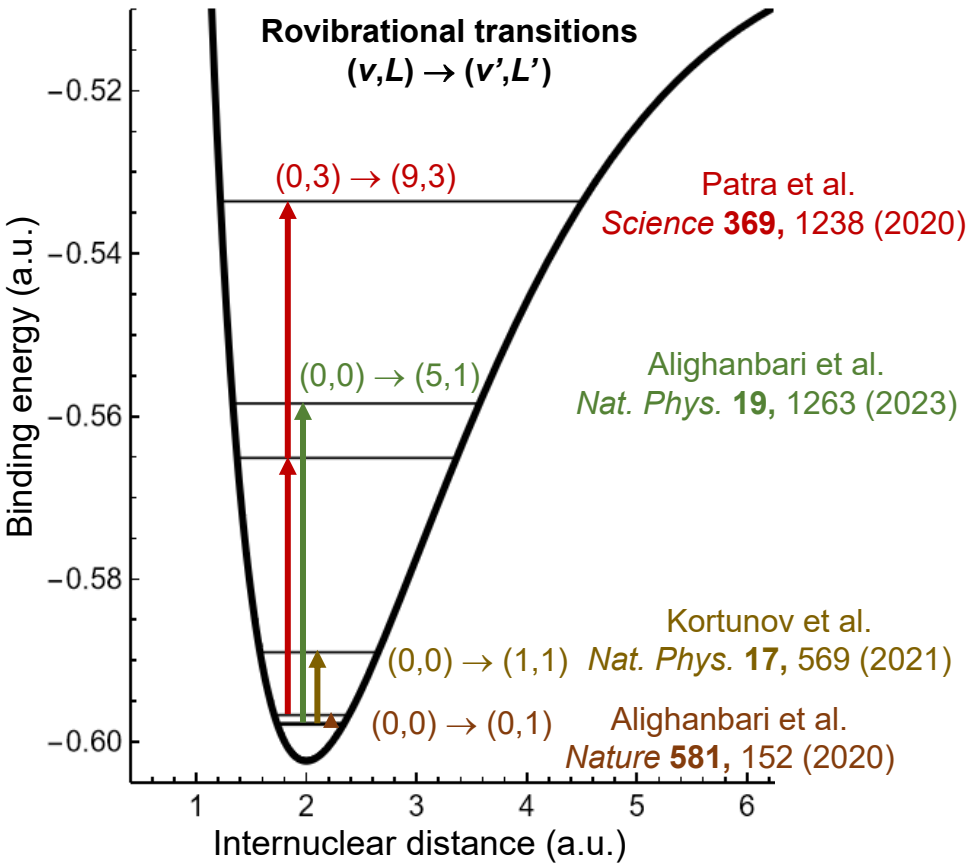
HD^+ and fundamental particle mass ratios

Karr & Koelemeij, *Mol. Phys.* (2023) DOI: 10.1080/00268976.2023.2216081



- Frequencies depend on nuclear reduced-to-electron mass ratio:

$$\mu_r = \frac{m_\mathrm{p} m_\mathrm{d}}{m_\mathrm{p}+m_\mathrm{d}} / m_\mathrm{e}$$

- Determined all spin-averaged frequencies ν_SA except v = 0 - 5 (not available at the time)
- Determine μ_r (another LSQ adjustment) and compare with value from Penning trap measurements*

$$\mu_r(\mathrm{HD}^+) = 1{,}223.899\,228\,719(26) \quad (21\text{ ppt})$$

$$\mu_r(\mathrm{Penning}) = 1{,}223.899\,228\,646(37) \quad (30\text{ ppt})$$

Note: expansion factor HD^+ hfs is not the limiting factor

- Combine with recent Penning trap measurements* of A_r(p), A_r(d), A_r(e), and m_d/m_p

  ⇒ HD^+ will improve uncertainty of A_r(e) from 29 ppt to 18 ppt

- HD^+ helps improve $u_r(m_p/m_e)$ from 60 ppt to 18 ppt

HD^+ also sensitive to R_∞, r_p, r_d …

Heiße et al. *PRL* **119,** 033001 (2017); *PRA* **100**, 022518 (2019)
Rau et al., *Nature* **585,** 43 (2020)
Sturm et al., *Nature* **506,** 467 (2014)
Fink & Myers *PRL* **127,** 243001 (2021)

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(Graph taken from Antognini et al., arXiv:2210.16929v1)

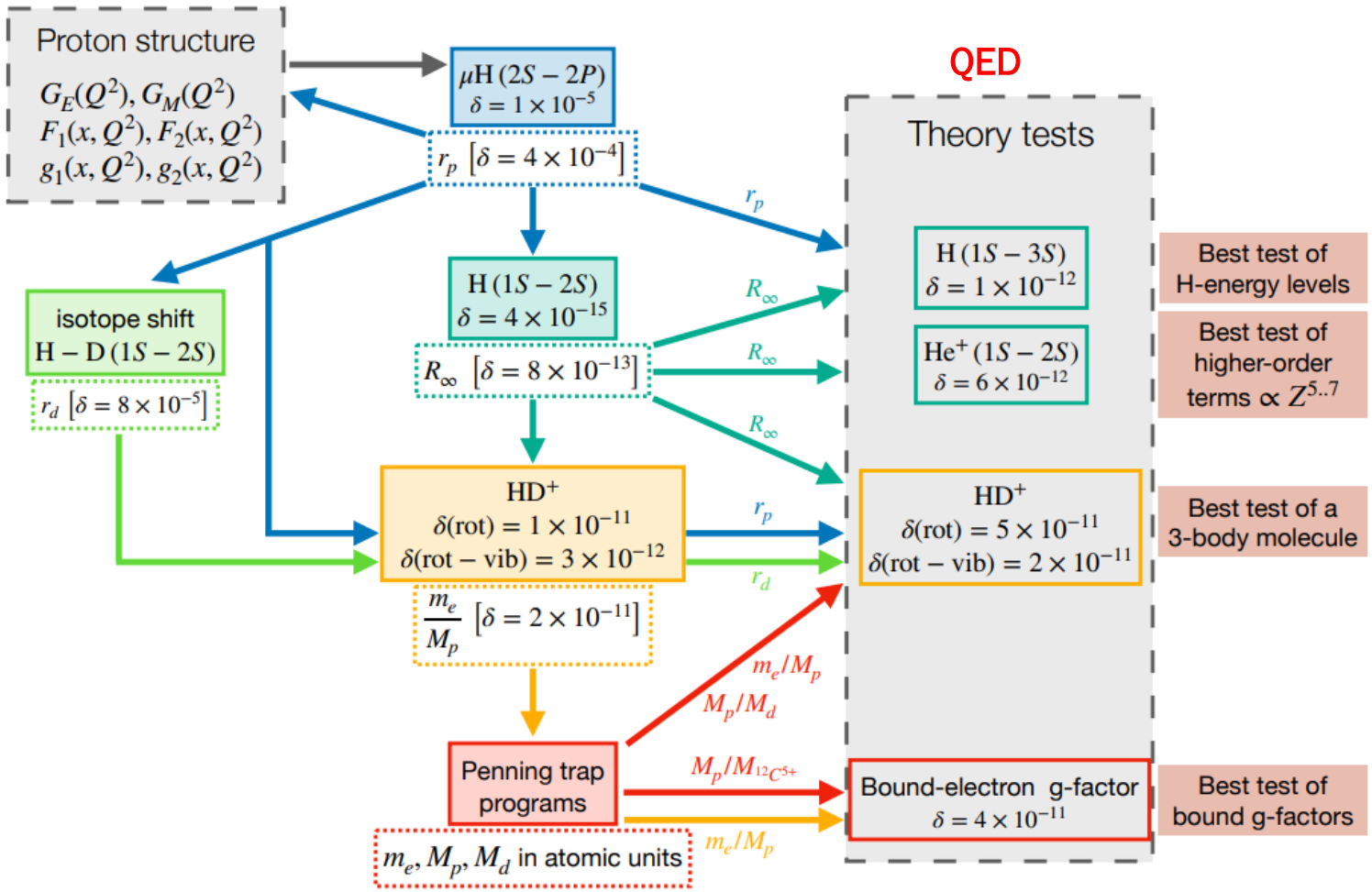
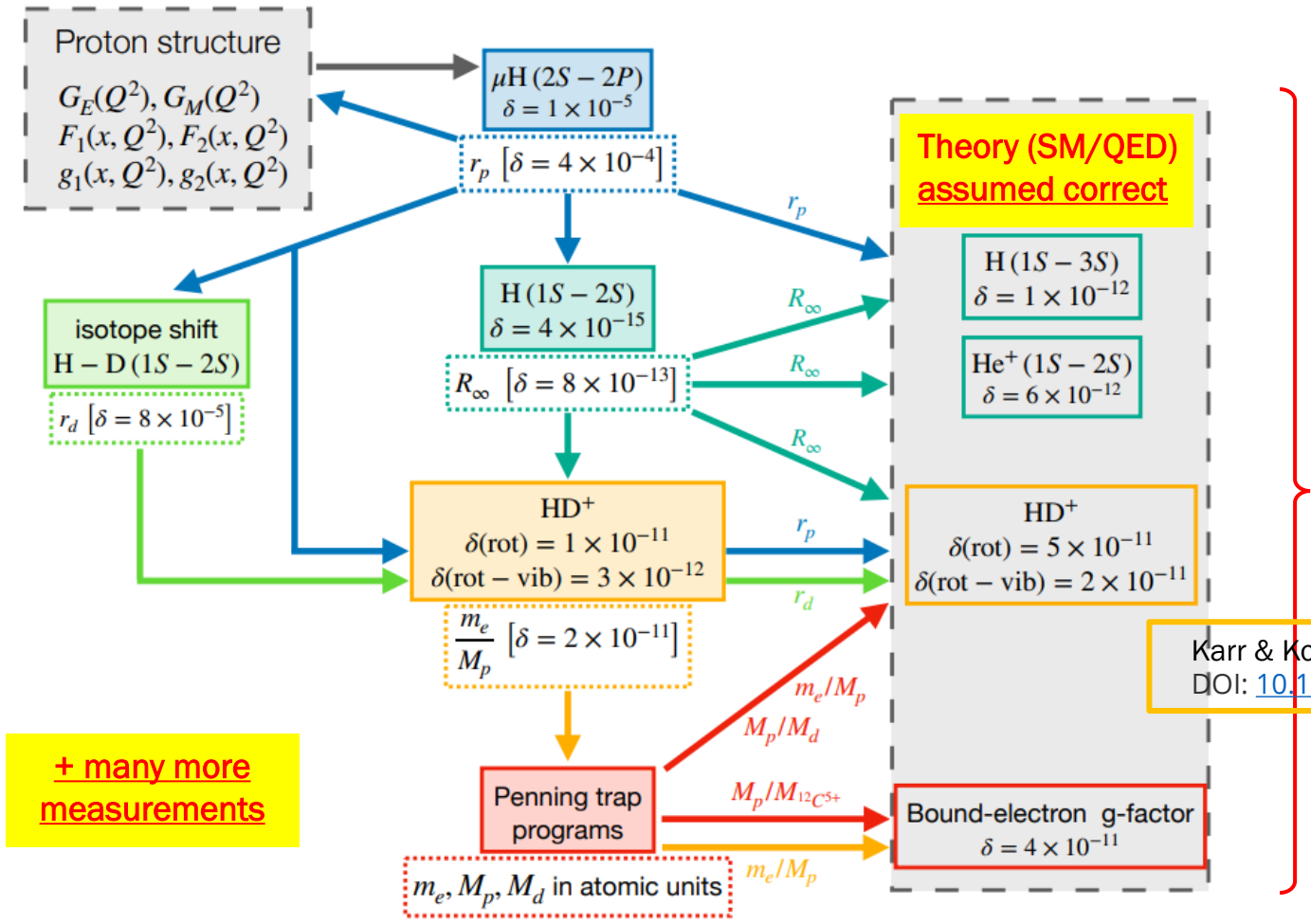


FIG. 2. Interplay of experiments to improve fundamental constants and bound-state QED tests.

Values of fundamental constants (CODATA)

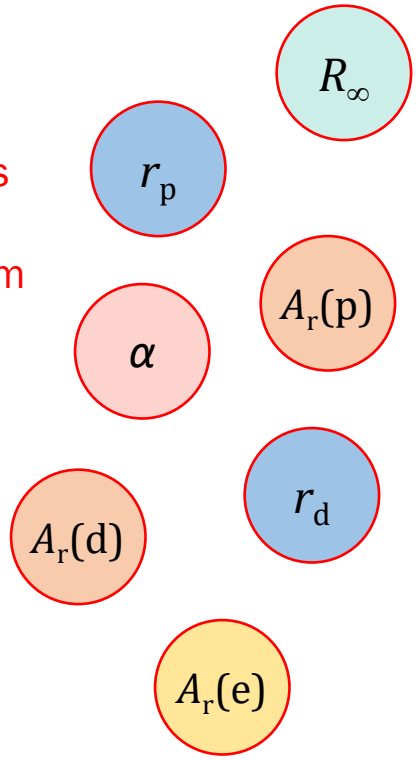


+ many more measurements

Least-squares adjustment of fundamental physical constants

(i.e. adjust constants for optimum match of theory to experiment)

⇒

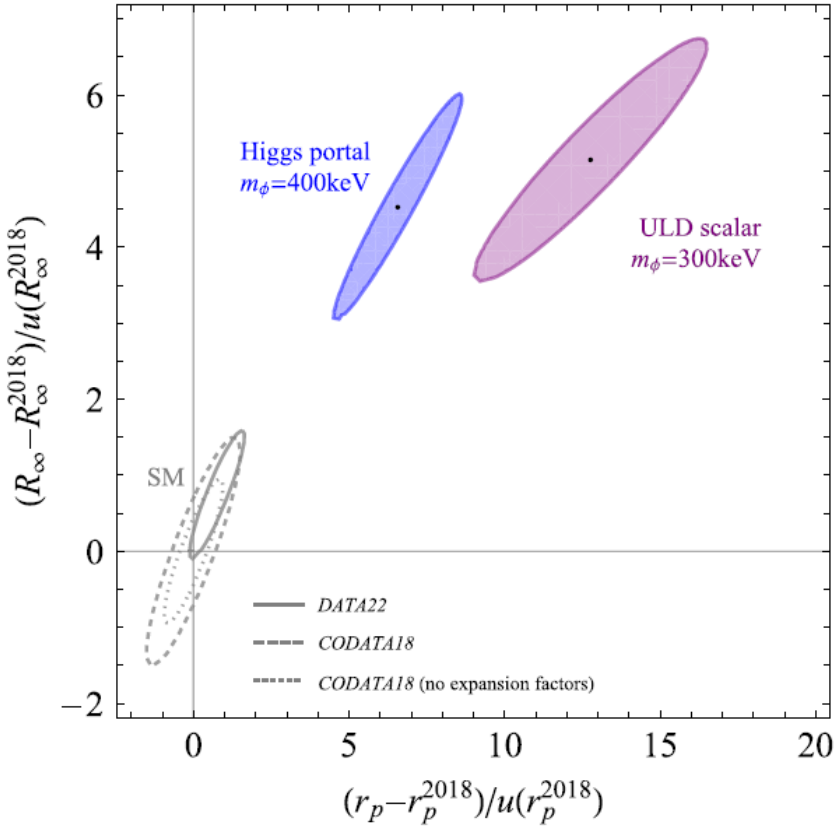


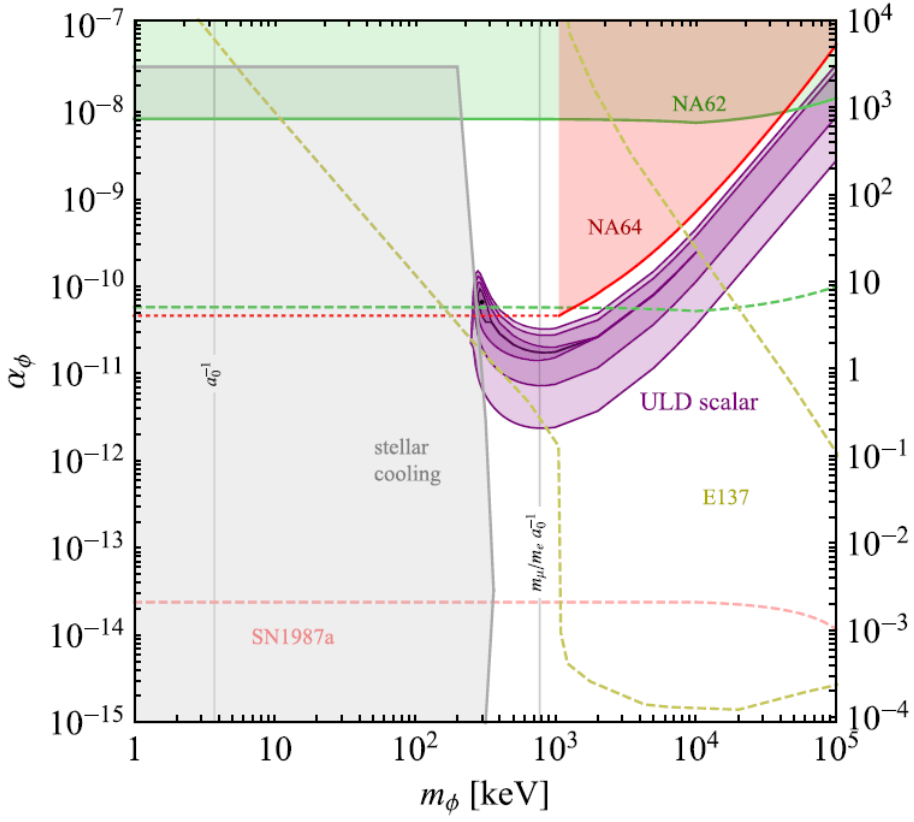
Karr & Koelemeij, *Mol. Phys.* (2023)
DOI: 10.1080/00268976.2023.2216081

If tension between input datum and adjusted constants: increase uncertainty by 'expansion factor' to reduce tension to 2σ

Fundamental constants & new physics

- … but if SM/QED theory were incomplete, discrepancies could be due to new physics
- Do we get a better match if we extend the theory with 'new' particles/forces?
  Delaunay, Karr, Kitahara, Koelemeij, Soreq & Zupan *Phys. Rev. Lett.* **130,** 121801 (2023)

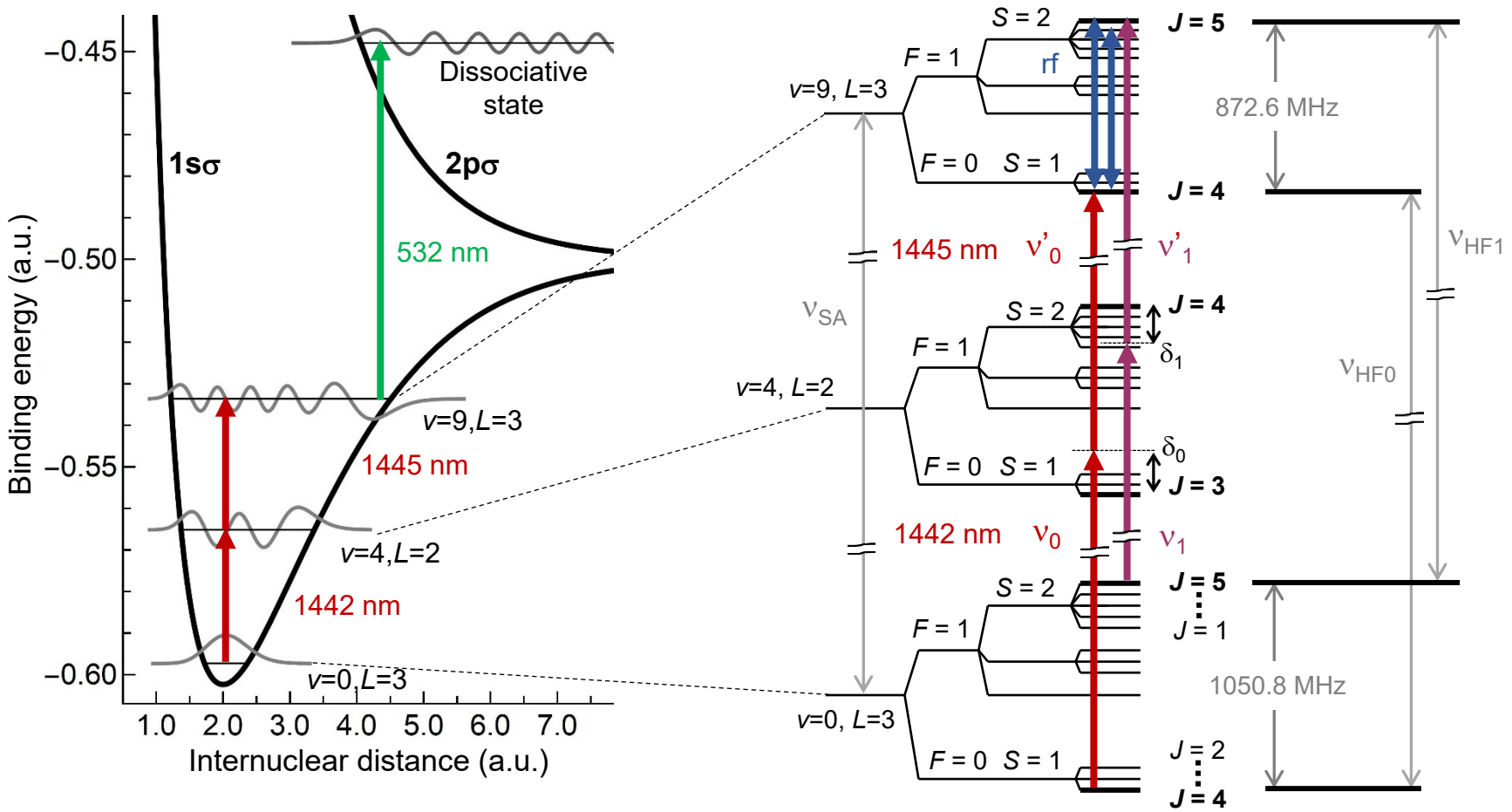


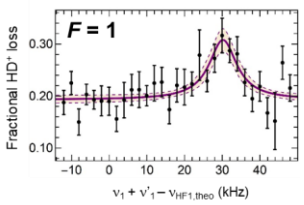


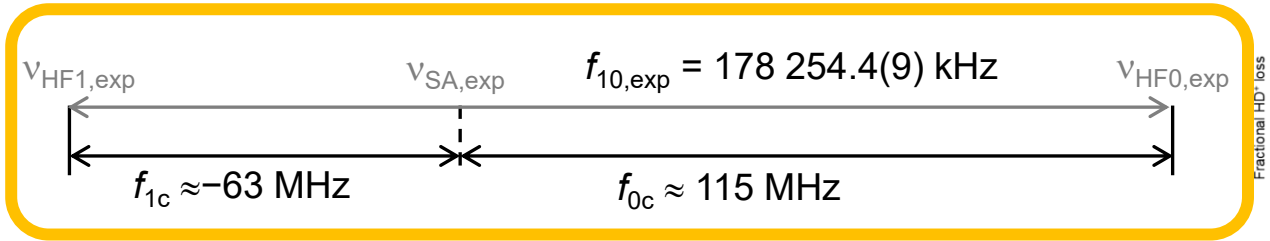
A new particle??

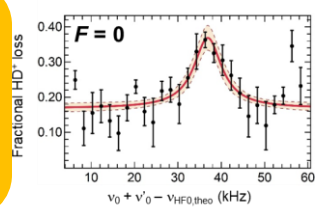
Well, historically most tensions disappear in the next CODATA adjustment without invoking new physics…

Back to Amsterdam...









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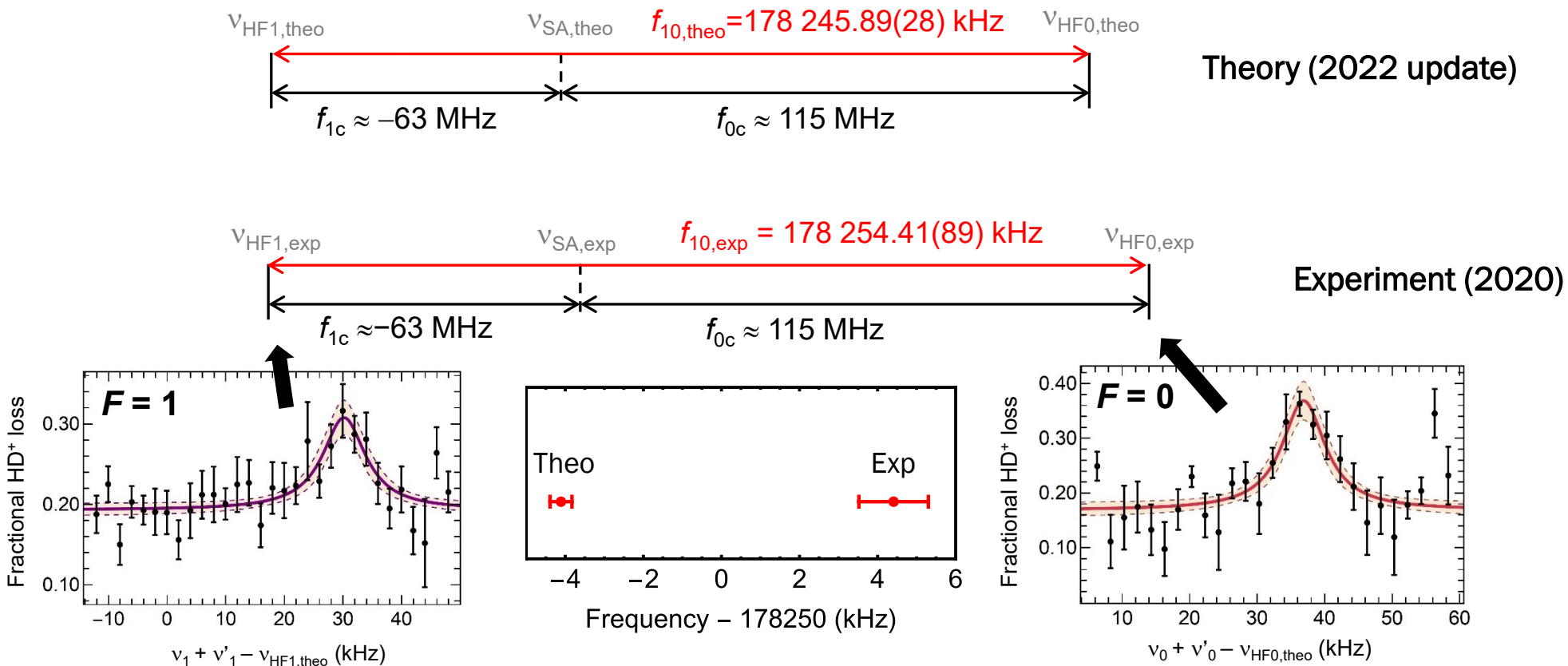
Hyperfine anomaly??

- Our measured hyperfine interval is actually much larger than theoretically predicted!
  - 4σ discrepancy in 2020
  - 9σ discrepancy after 2022 theory update (Haidar et al. *PRA* **106,** 042815 (2022))



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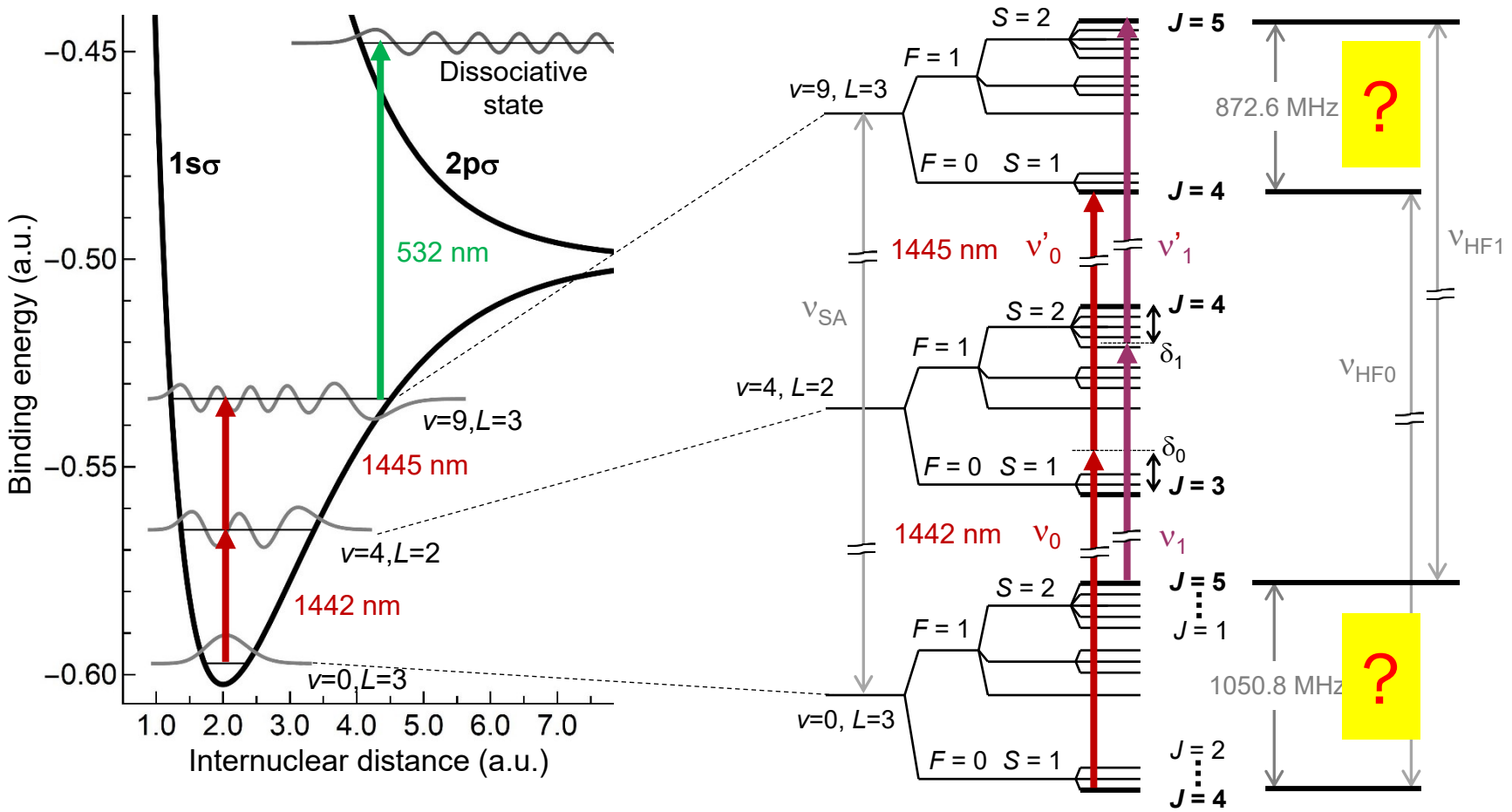
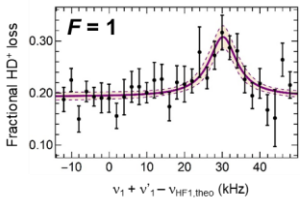
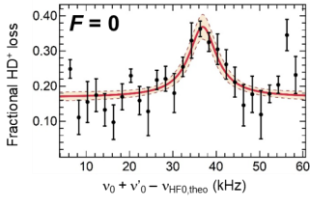
What is going on?





$\nu_{HF1,exp}$ $\nu_{SA,exp}$ $f_{10,exp}$ = 178 254.4(9) kHz $\nu_{HF0,exp}$

$f_{1c} \approx -63$ MHz $f_{0c} \approx 115$ MHz



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The plot thickens…

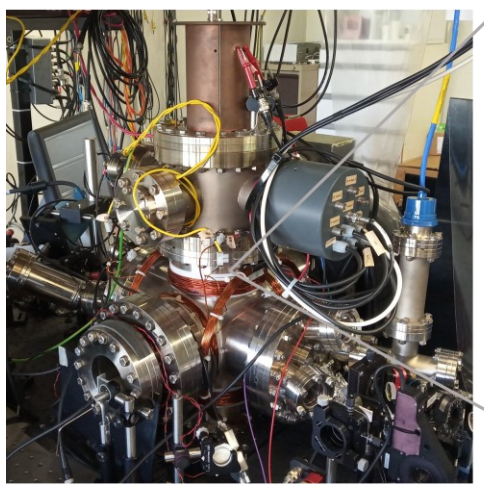
- Remarkably, the hfs of H_2^+ (same theory!) agrees perfectly with direct hfs measurements (rf spin flip spectroscopy, K. B. Jefferts *PRL* 1969, theory: Korobov, JK, Hilico, Karr, *PRL* 2016)
- So, in H_2^+ there is agreement at the 1 kHz level
- … but in HD^+ the disagreement seems to be >>1 kHz
- Muonic <u>hydrogen</u> 2*S* hyperfine splitting: experiment and theory in agreement
- Muonic <u>deuterium</u> 2*S* hyperfine splitting: 5σ discrepancy!
  - See e.g. M. Kalinowski, *PRA* **99,** 030501(R) (2019)
    Kalinowski, Pachucki, Yerokhin, *PRA* **98,** 062513 (2018)

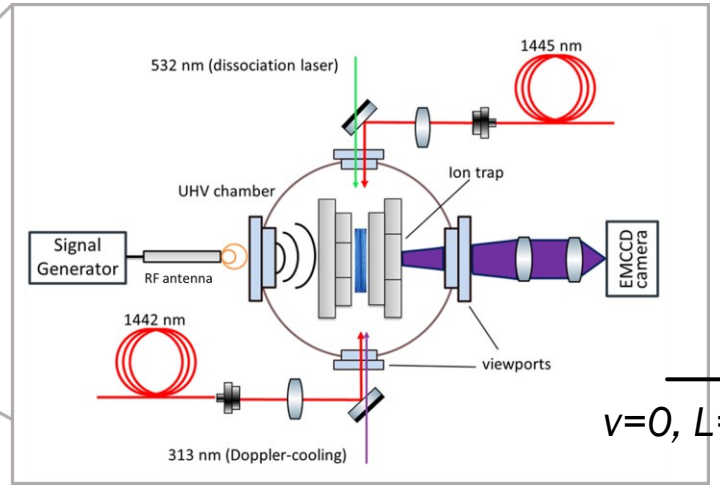
Proton ✓ **Deuteron** ✗

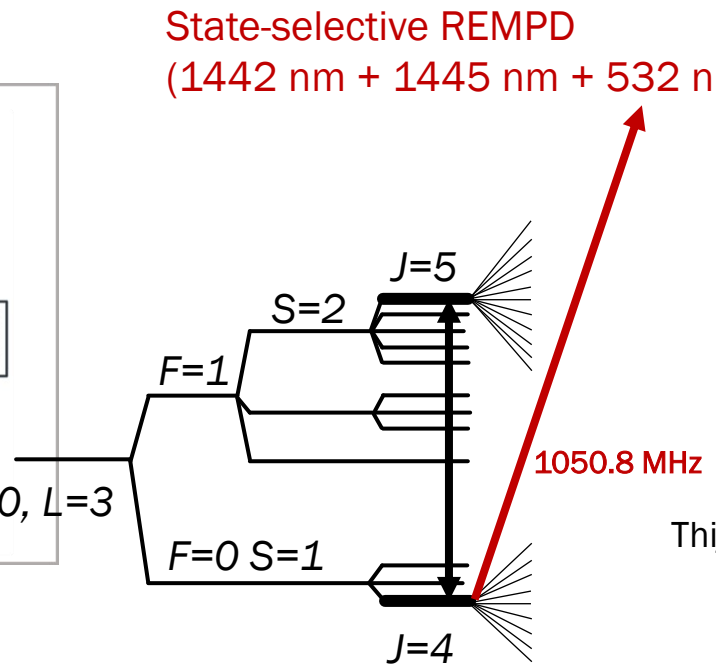
^{4}He, ^{6}Li, and ^{7}Li. We note, however, that the spin-dependent part of the nuclear polarizability is not well understood, which is reflected in the recently observed 5σ discrepancy between the theoretical prediction [30] and the experimental measurement [8] of the 2*S* hyperfine splitting in muonic deuterium. In general, to reduce the uncertainty further and

Hyperfine spectroscopy

- Measure hyperfine splittings in v=0, L=3 and v=9, L=3 directly (RF spin-flip spectroscopy) to verify the experimental value of the 178 MHz ‘anomalous’ interval
  - Work performed under financial assistance award NIST PMG 60NANB21D184
- RF excitation: only 532 nm laser on, other lasers off
- Target uncertainty ~0.1 kHz







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Thijmen Klijn Velderman
(PhD student)

Roya Ahemeh
(PhD student)

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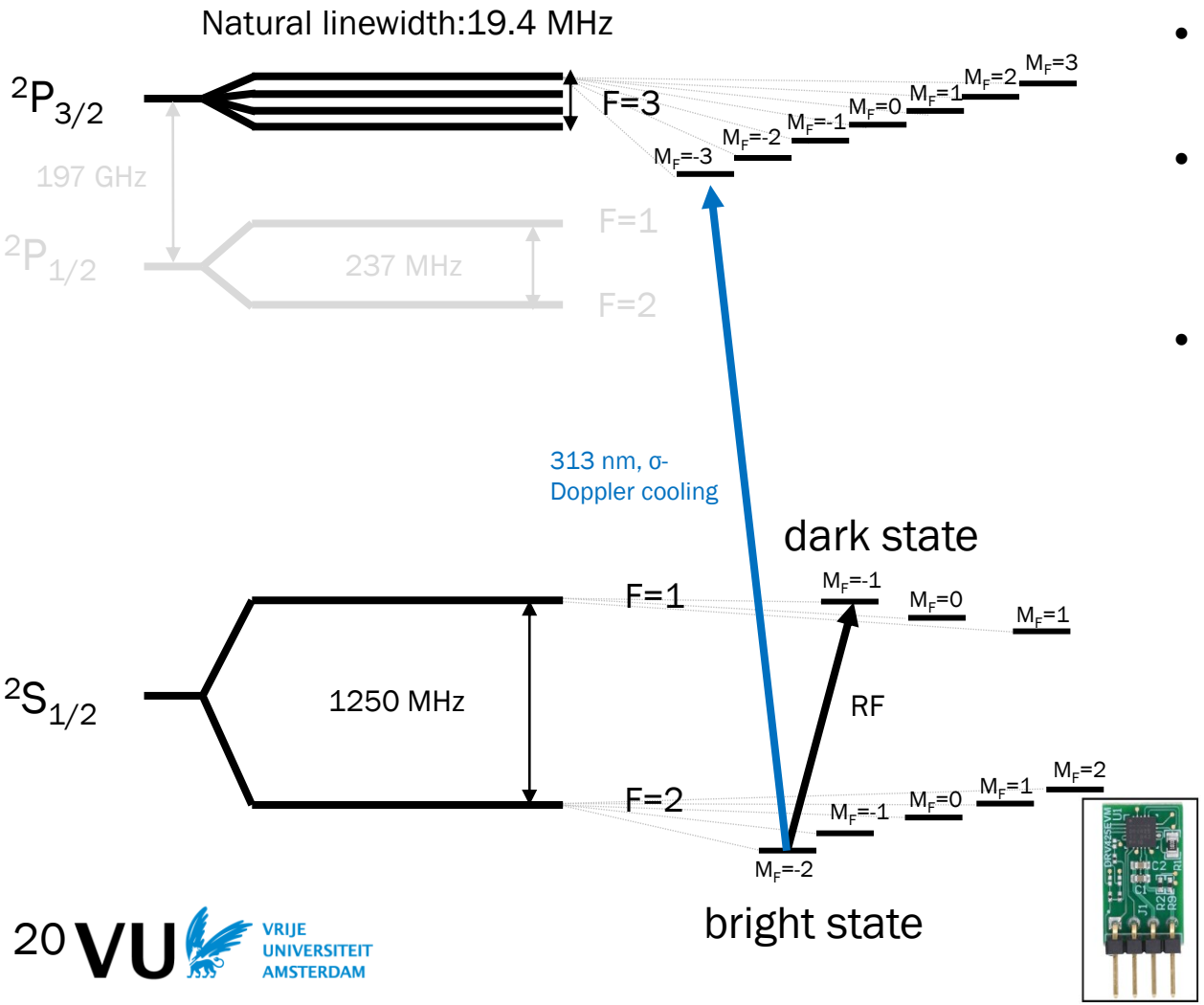
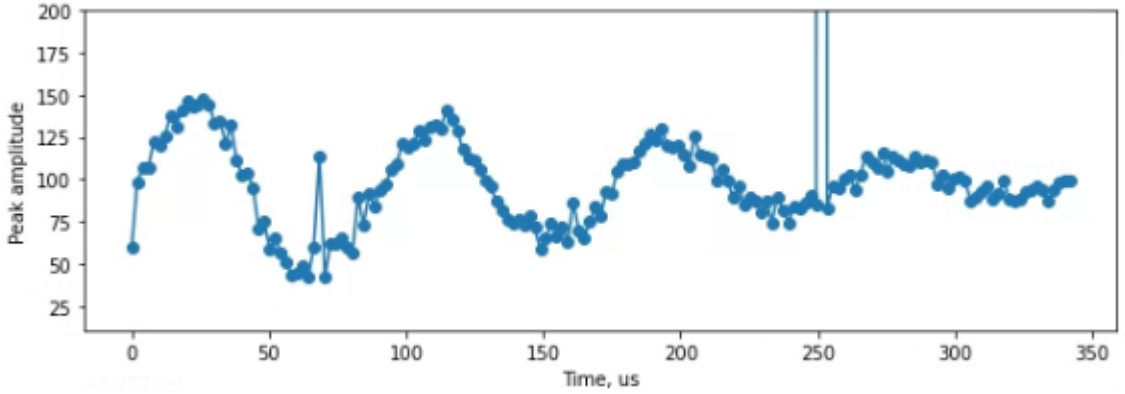
Challenge 1: Zeeman shifts

$^9Be^+$ (I=3/2)



- Unshielded ion trap with modest (~1 G) bias field
- HD^+, Be^+ unpaired electron, Zeeman shifts ~1 MHz/G (broadening > 30 kHz)
- Bias field calibration using Be^+ hyperfine spin-flips and known Be^+ Zeeman effect [Wineland et al., *PRL* **50**, 628 (1983)]
  - Uncertainty 1 mG, long-term variations: 10-20 mG
- RF field amplitude and state of polarization determined from Be^+ as well (RF Rabi flopping on σ/π transitions)

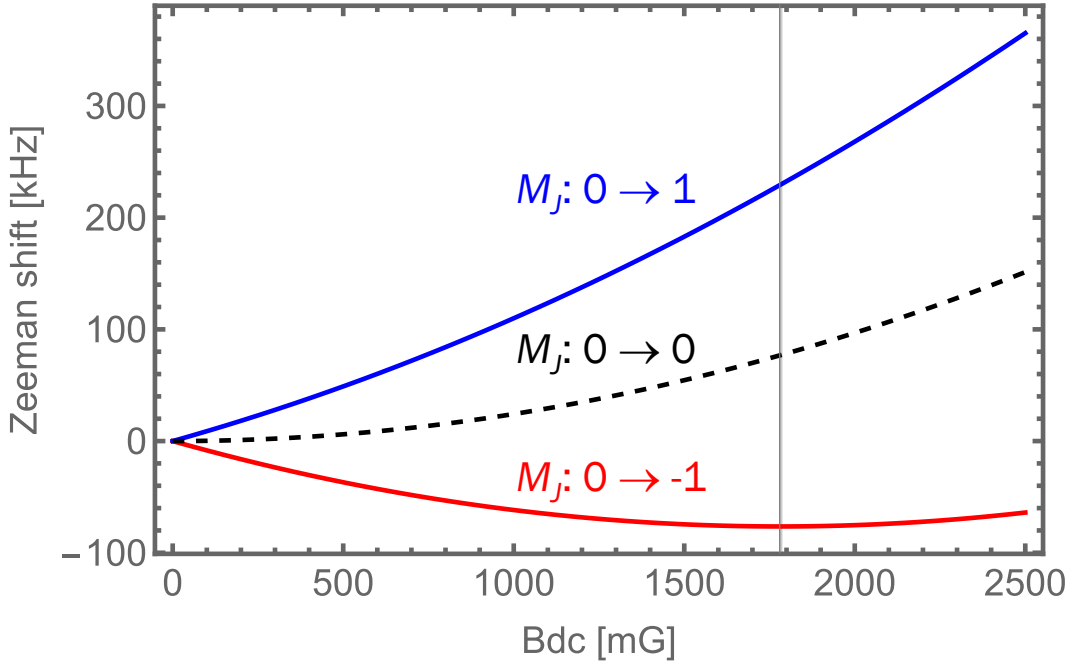


Fluxgate magnetic field sensors: ~10 mG rms noise due to 50 Hz, 830 Hz (turbo pump), switching power supplies…

Challenge 1: Zeeman shifts

- *B*-field instability 10 – 20 mG ⇒ ~20 kHz of Zeeman shift/broadening
  - To be implemented: *B*-field stabilization (~30 dB suppression of noise below 1 kHz)
- Or: resolve field-insensitive transitions $FSJM_J$: $125M_J = 0 \rightarrow 014M_J = 0,-1$
  - Line widths <0.2 kHz

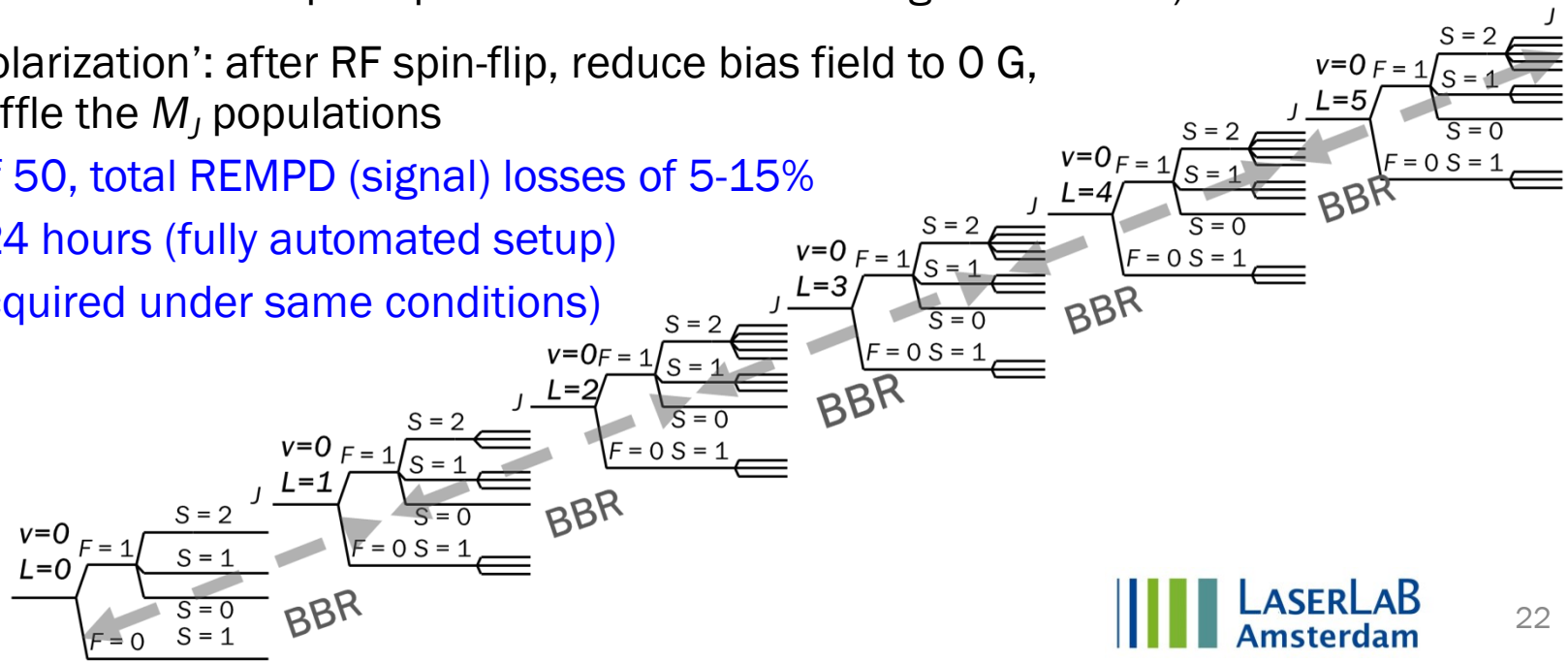
Sjard ter Huurne
(BSc student)



However...

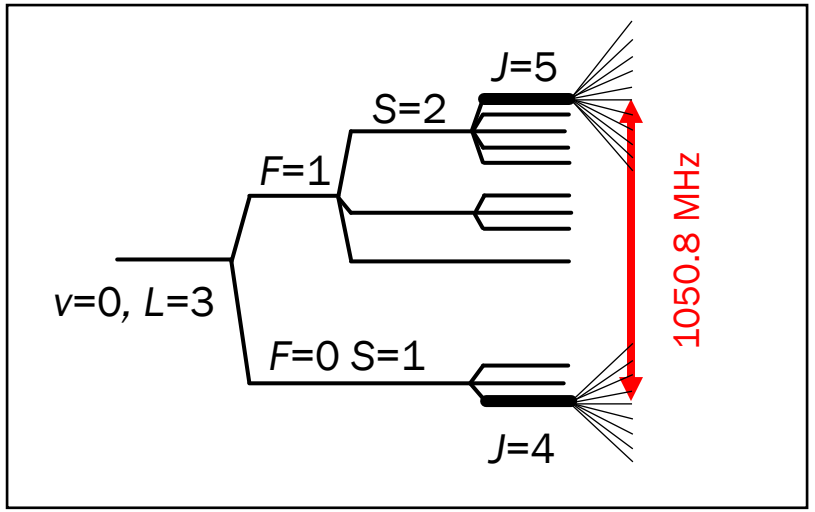
Challenge 2: Quantum statistics

- 50-100 HD^+ ions in trap
- Room-temperature BBR: population distributed over lowest 6 rotational states/384 magnetic substates
- So most times <u>our trap contains exactly 0 HD^+ ions</u> in the v=0, L=3, FSJ=125, M_J=0 target state
- Solution:
  - Rely on BBR recycling (repeated 50 ms RF spin-flips + 50 ms REMPD during 30 seconds)
  - Use periodic 'Majorana depolarization': after RF spin-flip, reduce bias field to 0 G, and let noisy AC fields reshuffle the M_J populations
  - Increases SNR by a factor of 50, total REMPD (signal) losses of 5-15%
  - Acquire single spectrum in 24 hours (fully automated setup)
  - Combine up to 4 spectra (acquired under same conditions)

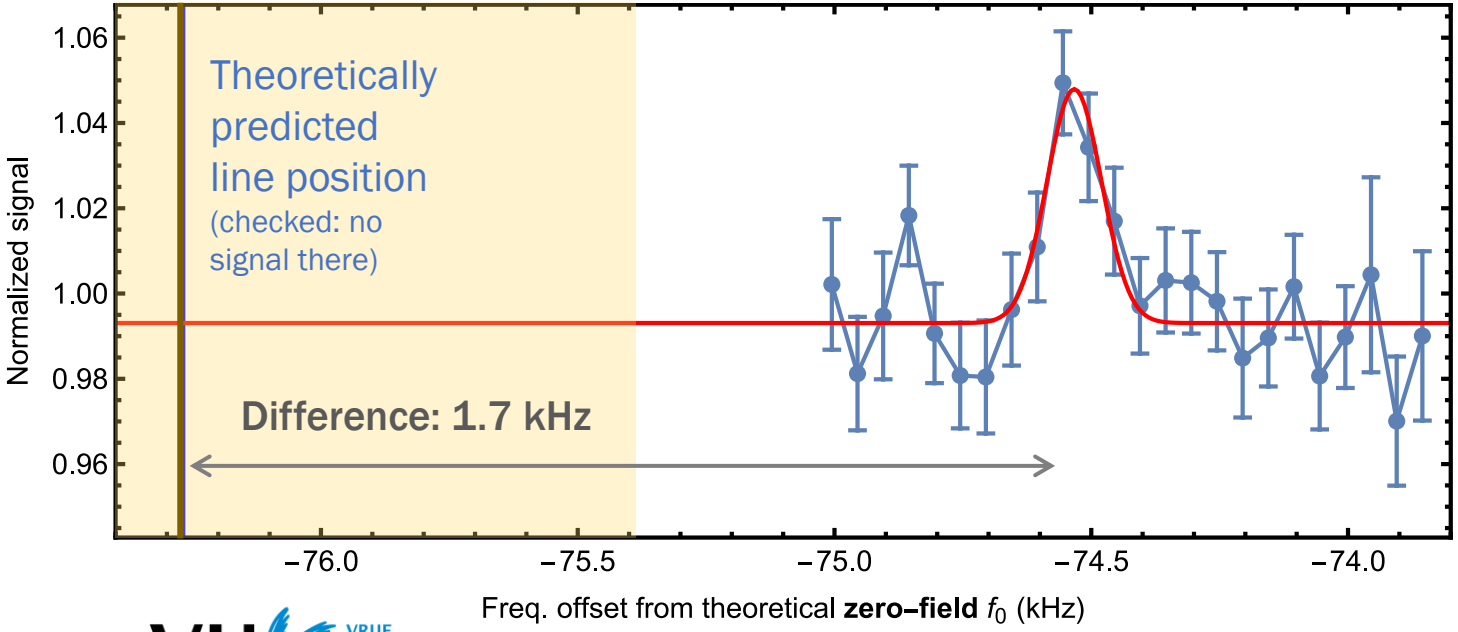


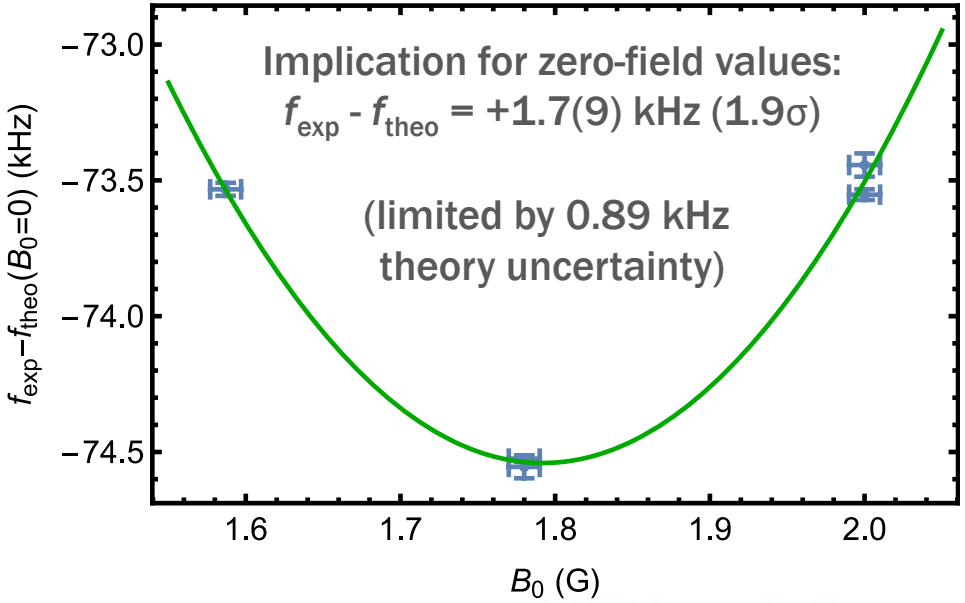
Preliminary results

- Improved calculation Zeeman effect (J.-Ph. Karr, preliminary)
- Measure M_J: 0 → −1 spin-flip transitions at various static fields
- Fit theoretical Zeeman shift + offset frequency + offset B-field
  - f_{off} = 1.73(4) kHz, B_{off} = −10(5) mG [consistent with long-term stability of B-field]



M_J: 0 → −1 transition, static field B_0 = 1.78 G





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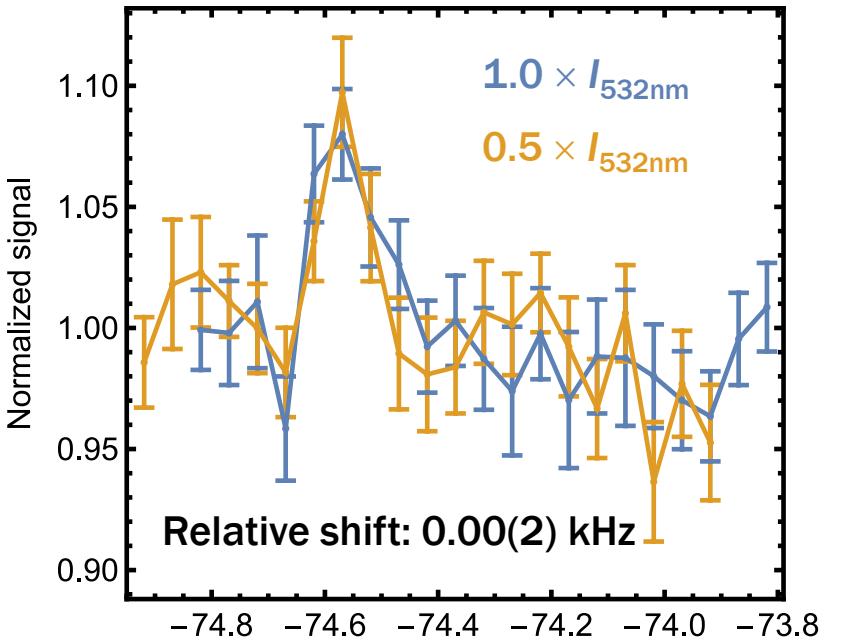
Systematic effects (work in progress)



***v*=0, *L*=3 *FSJ*: 125 – 014 transition:**
f_{exp} - f_{theo} = +1.7(9) kHz (1.9σ)

(limited by 0.89 kHz theory uncertainty)

- Target uncertainty: 0.1 kHz (or 0.1 ppm)
- AC-Stark shifts due to lasers: expected to be <1 Hz
  - No detectable shift when reducing 532 nm laser intensity by 50%
  - Other lasers (1442 nm, 1445 nm) expected to have similar small shifts
- AC-Zeeman shifts: expected to be <50 Hz
  - Including trap rf field: *B*-fields from electrode currents don't cancel out (trap geometry/connections)
  - Magnetic component BBR field (cf. Barrett group, *PRA* **98,** 032514 (2018))
- Quadrupole shifts: expected to be negligible
  - cf. work by Barrett group, *PRA* **99,** 022515 (2019); Bakalov & Schiller, Appl. Phys. B **114,**:213–230 (2014)
- Motional effects (2nd-order Doppler), space charge effects, magnetic field of spin-polarized Be^+ ensemble: expected to be negligible

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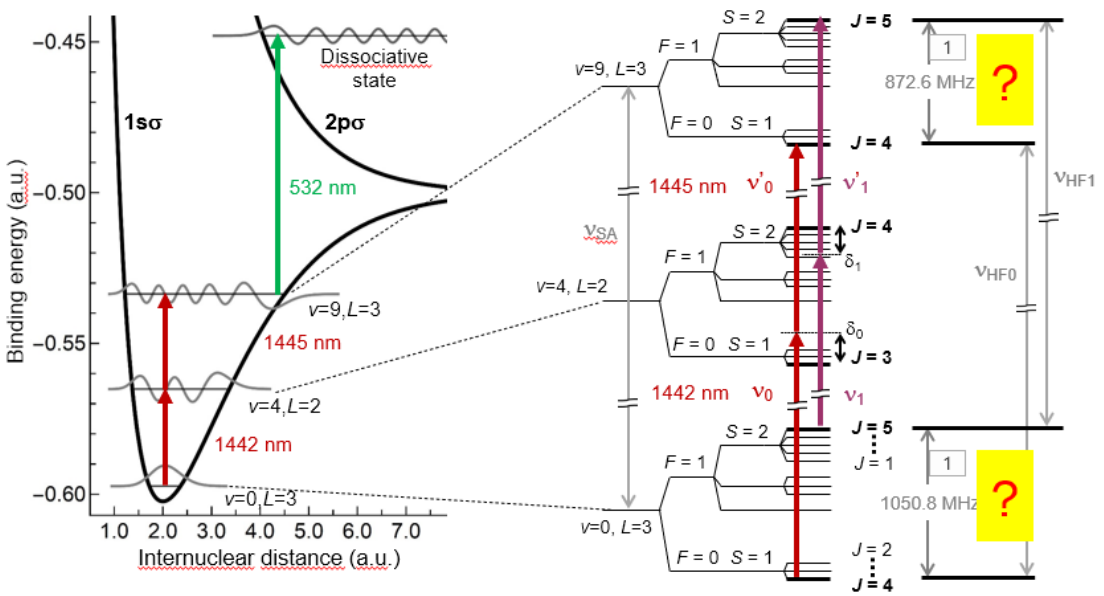
Conclusion & outlook

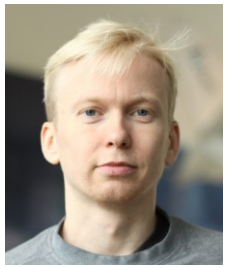


- Measure hfs in both v=0, *L*=3 and *v*=9, *L*=3
- Evaluation of systematic shifts and uncertainty
  - Field-free RF spin flips: test theory prediction 178 MHz interval
  - Recreate conditions two-photon spectroscopy: test experimental 178 MHz interval
- Measure multiple hyperfine lines to identify origin of 1.9σ offset: p, d, or molecular rotation?
  - Fermi contact interaction (p-e, d-e) or spin-orbit interaction
- Hint towards a possible explanation:
  - +1.7 kHz deviation in *v*=0, *L*=3 requires $f_{exp} - f_{theo}$ = –6.8 kHz in *v*=9 to reconcile 8.5 kHz discrepancy…

    … sign opposite to shift *v*=0 ⇒ missing vibrational effect in the hyperfine theory?
  - OR find extraordinarily large <u>vibrational- and spin-dependent</u> systematic shift that was overlooked in the two-photon spectroscopy?

Thank you!

Questions: j.c.j.koelemeij@vu.nl



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