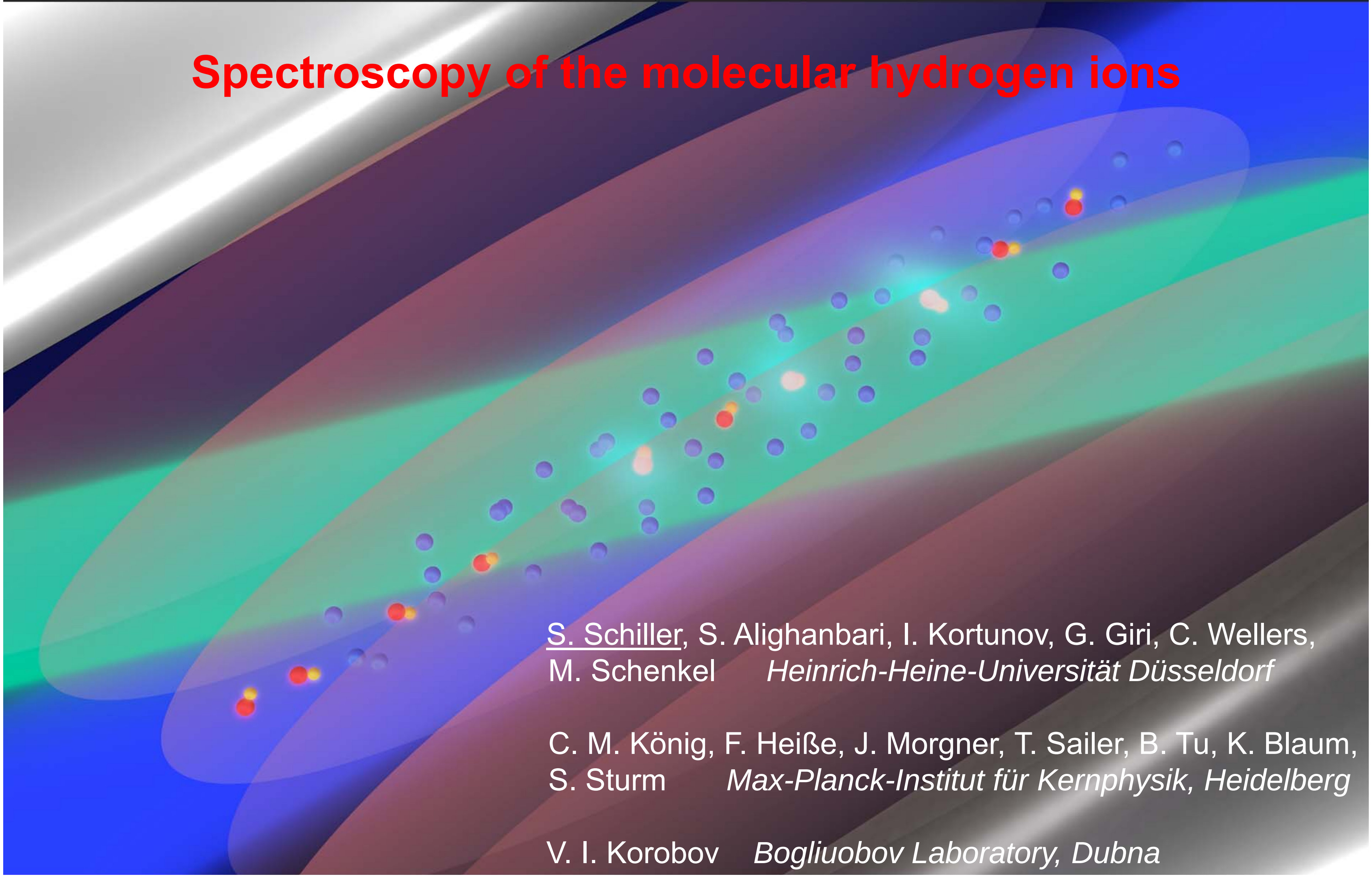
Spectroscopy of the molecular hydrogen ions



S. Schiller, S. Alighanbari, I. Kortunov, G. Giri, C. Wellers,
M. Schenkel *Heinrich-Heine-Universität Düsseldorf*

C. M. König, F. Heiße, J. Morgner, T. Sailer, B. Tu, K. Blaum,
S. Sturm *Max-Planck-Institut für Kernphysik, Heidelberg*

V. I. Korobov *Bogliuobov Laboratory, Dubna*

International STRONG-2020 Workshop on the Proton Charge Radius and related topics, Paris, June 20 - 23, 2022

Acknowledgements

Acknowledgments:

- Florin L. Constantin (CNRS, Villeneuve d'Ascq)
- Kenneth R. Brown (Duke University)

erc

- ERC European Union's Horizon 2020 grant: 786306, "PREMOL"
- DFG and NRW grants: INST-208/737-1 FUGG
  INST 208/774-1 FUGG
  INST 208/796-1 FUGG

DFG Deutsche Forschungsgemeinschaft

Nordrhein-Westfalen

- Scholarship of the Prof.-W.-Behmenburg-Schenkung

How can MHI spectroscopy contribute to nuclear physics?

- Introduction
- Basics on MHI spectroscopy and nuclear effects
- Precision MHI spectroscopy
- Current Results
- Ongoing Work
- Future opportunities

Introduction

Molecules and precision measurement of nuclear properties?

- Electric quadrupole moment of the deuteron

  From nuclear physics experiments and theory [1]: $Q_d = 0.2854^{+0.0038}_{-0.0017}\ \mathrm{fm}^2$

  From molecular deuterium spectroscopy and theory [2]: $Q_\mathrm{d} = 0.285\,699(15)_\mathrm{theo}(18)_\mathrm{exp}\ \mathrm{fm}^2$

  200 x more accurate!

- Ratios of magnetic moments of p, d, t

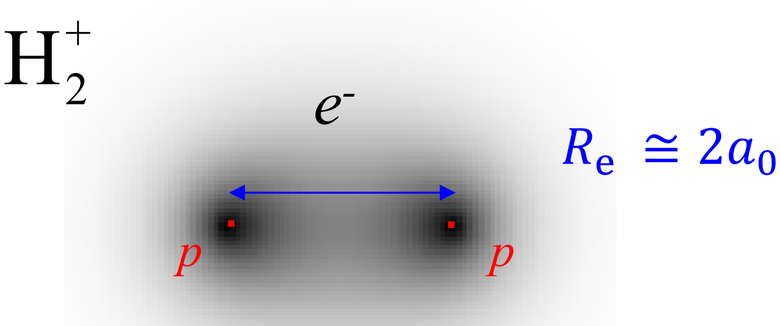
  From NMR of molecular hydrogen HD, HT and theory [3] *… fractional unc. (2-3) x 10^{-9}*

The molecular hydrogen ions (MHI):

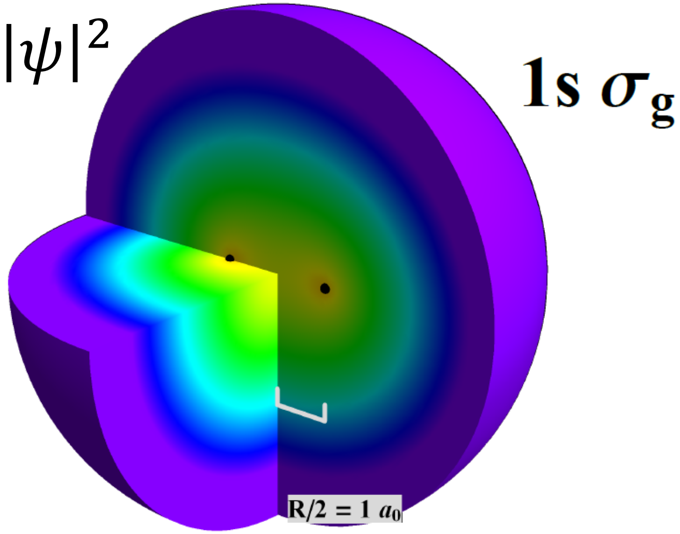
- Charge radii of proton, deuteron, triton
- Electric quadrupole moment of the deuteron Q_d
- Nuclear magnetic moments (shielded)
- *g*-factor of electron bound to two centers

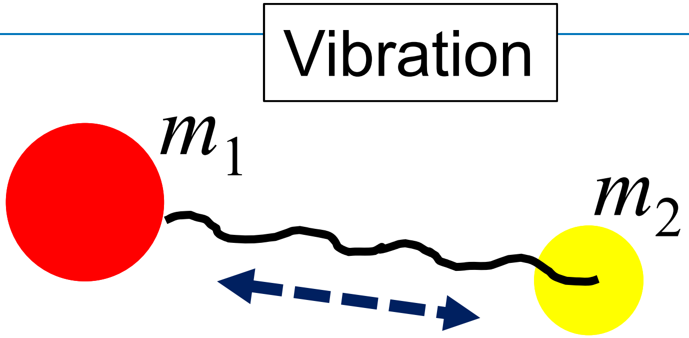
[1] Filin et al, PRC 103, 024313 (2021)
[2] Code and Ramsey, PRA 4, 1945 (1971)
Puchalski et al, PRL 125, 253001 (2020)
[3] CODATA 2018

Molecular hydrogen ions: basics



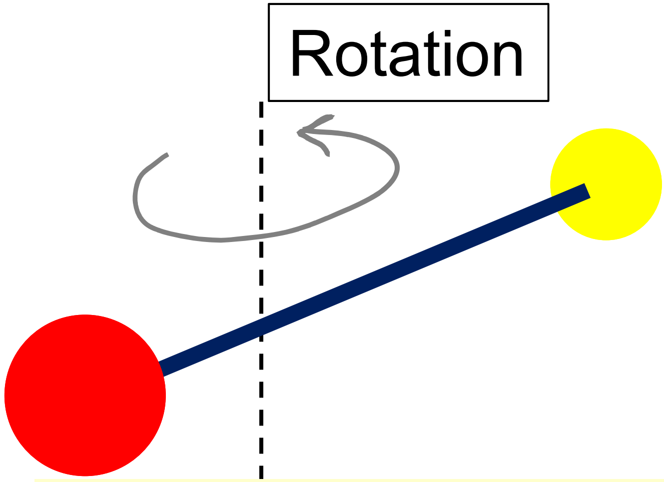
D_2^+, HD^+, T_2^+, HT^+, DT^+





$$f_{\rm vib} \propto cR_\infty\sqrt{m_e(1/m_1+1/m_2)}$$

+ relativity + QED + nuclear charge radii

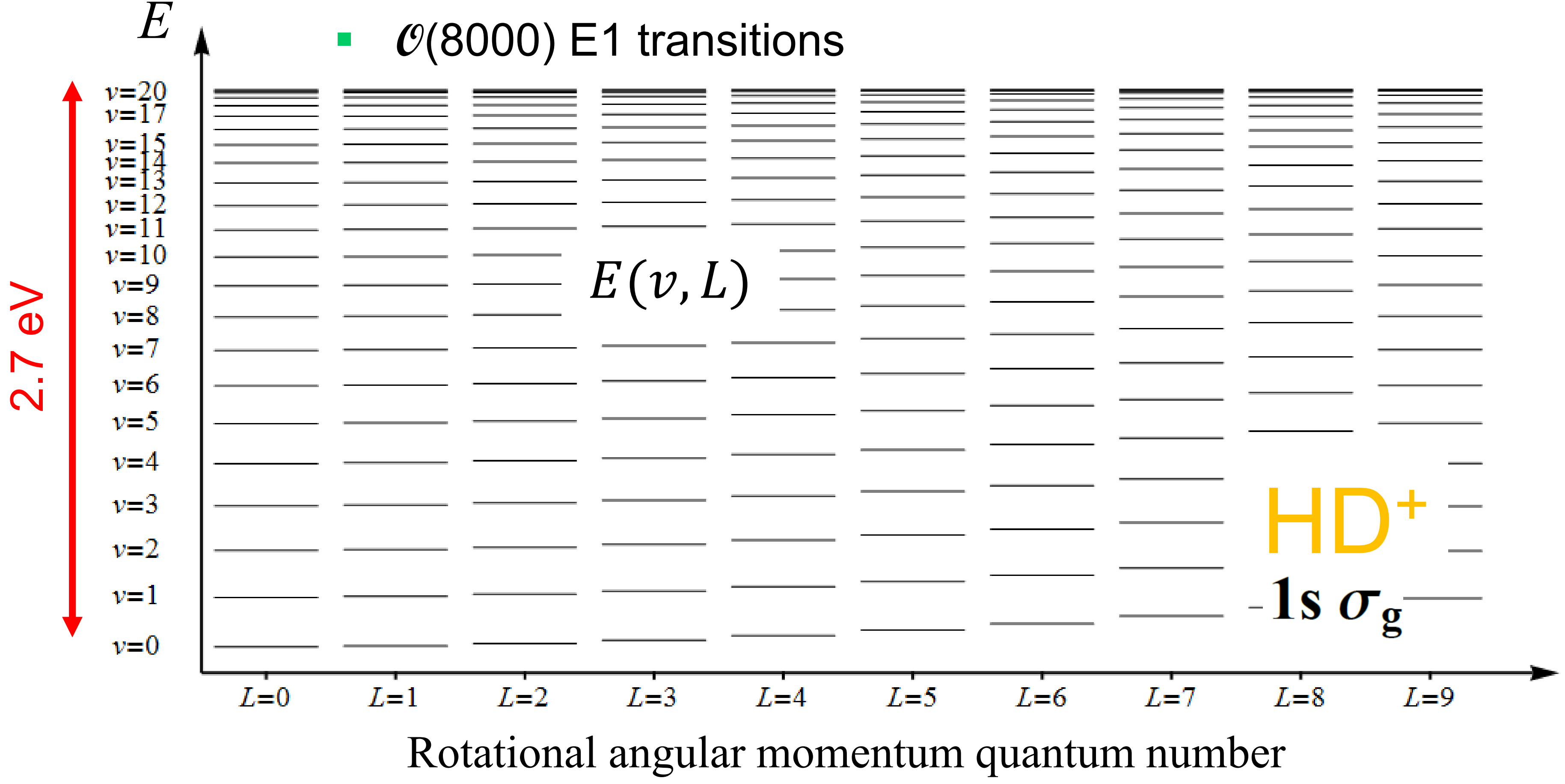


$$f_{\rm rot} \propto cR_\infty m_e(1/m_1+1/m_2)$$

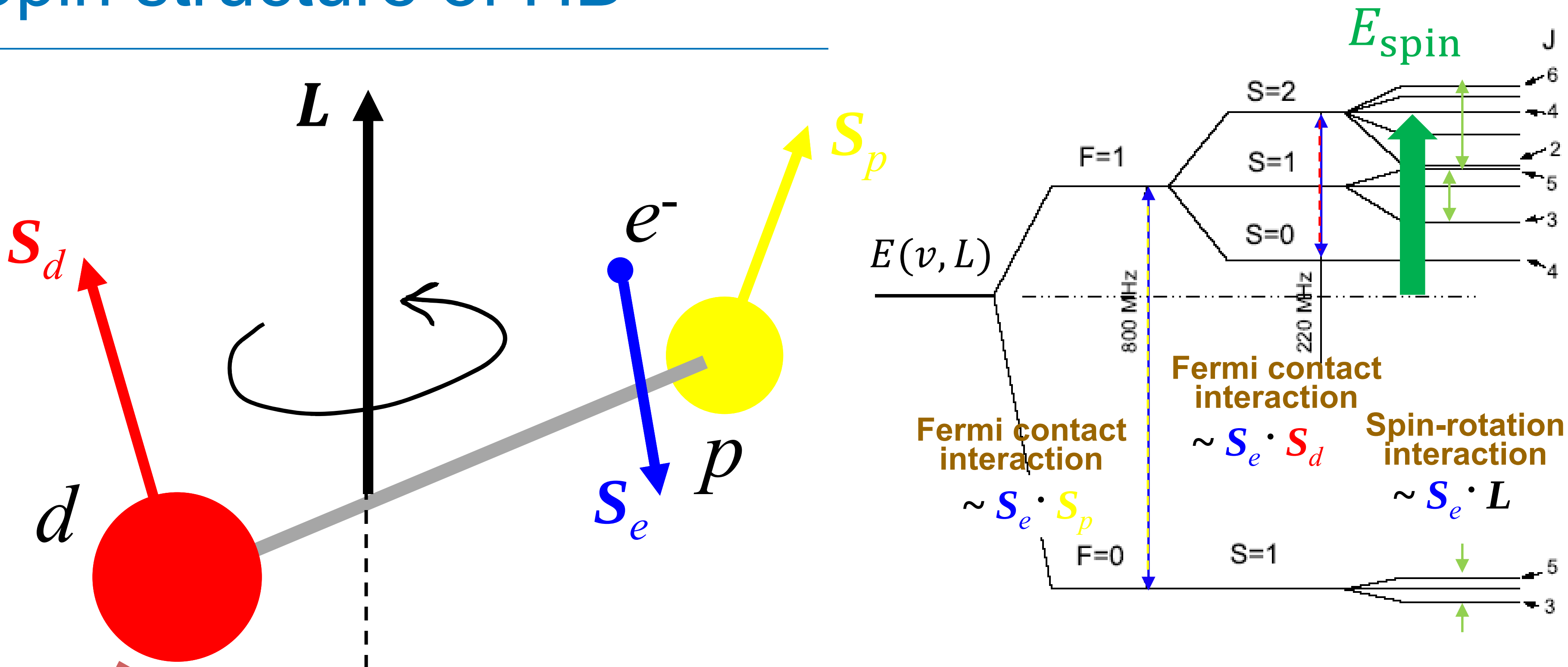
+ relativity + QED + nuclear charge radii

A rich rotation-vibration level structure

- 637 levels, 80% have spontaneous lifetimes ≥ 10 ms
- $\mathcal{O}(8000)$ E1 transitions



Spin structure of HD$^+$



Electric quadrupole moment

$$
\begin{aligned}
H^{\mathrm{spin}} = {} & E_1(\mathbf{S}_e\cdot\mathbf{L}) + E_2(\mathbf{S}_p\cdot\mathbf{L}) + E_3(\mathbf{S}_d\cdot\mathbf{L}) + E_4(\mathbf{S}_e\cdot\mathbf{S}_p) + E_5(\mathbf{S}_e\cdot\mathbf{S}_d) \\
& + 2E_6\Big(\mathbf{L}^2(\mathbf{S}_e\cdot\mathbf{S}_p) - 3(\mathbf{S}_p\cdot\mathbf{L})(\mathbf{S}_e\cdot\mathbf{L})\Big) \\
& + 2E_7\Big(\mathbf{L}^2(\mathbf{S}_e\cdot\mathbf{S}_d) - 3(\mathbf{S}_d\cdot\mathbf{L})(\mathbf{S}_e\cdot\mathbf{L})\Big) \\
& + 2E_8\Big(\mathbf{L}^2(\mathbf{S}_p\cdot\mathbf{S}_d) - 3(\mathbf{S}_p\cdot\mathbf{L})(\mathbf{S}_d\cdot\mathbf{L})\Big) \\
& + E_9\Big(\mathbf{L}^2\mathbf{S}_d^2 - \frac{3}{2}(\mathbf{S}_d\cdot\mathbf{L}) - 3(\mathbf{S}_d\cdot\mathbf{L})^2\Big)
\end{aligned}
$$

5.666 kHz

Bakalov, et al. PRL 97, 243001 (2006)
Korobov, et al., PRL 116, 053003 (2016)
Korobov et al PRA 102, 022804 (2020)
Karr et al PRA 102, 052827 (2020)

Theory of MHIs

$$E(v,L,FSJ) = E_{\text{non-relativistic}} + E_{\text{relativistic}} + E_{\text{QED}} + E_{\text{spin}}$$

Transition frequency: $f_{\text{spin-avg}}(vL, v'L') + f_{\text{spin}}(vLFSJ, v'L'F'S'J')$

[dominant dependencies only]

$$f_{\text{spin-avg}} \begin{cases} f_{\text{non-relativistic}}(R_\infty,\ m_e,\ m_p,\ m_d) \\ f_{\text{relativistic}}(\alpha,\ r_p,\ r_d) \qquad \text{relative size} \approx 2\times10^{-5} \\ f_{\text{QED}}(\alpha) \qquad \text{relative size} \approx 4\times10^{-6} \end{cases}$$

$$f_{\text{spin}} \qquad f_{\text{spin}}(g_e,\ g_p,\ g_d,\ Q_d) \qquad \text{relative size}\ \ \mathcal{O}(10^{-5})\ \ \text{[rotational trans.]}$$

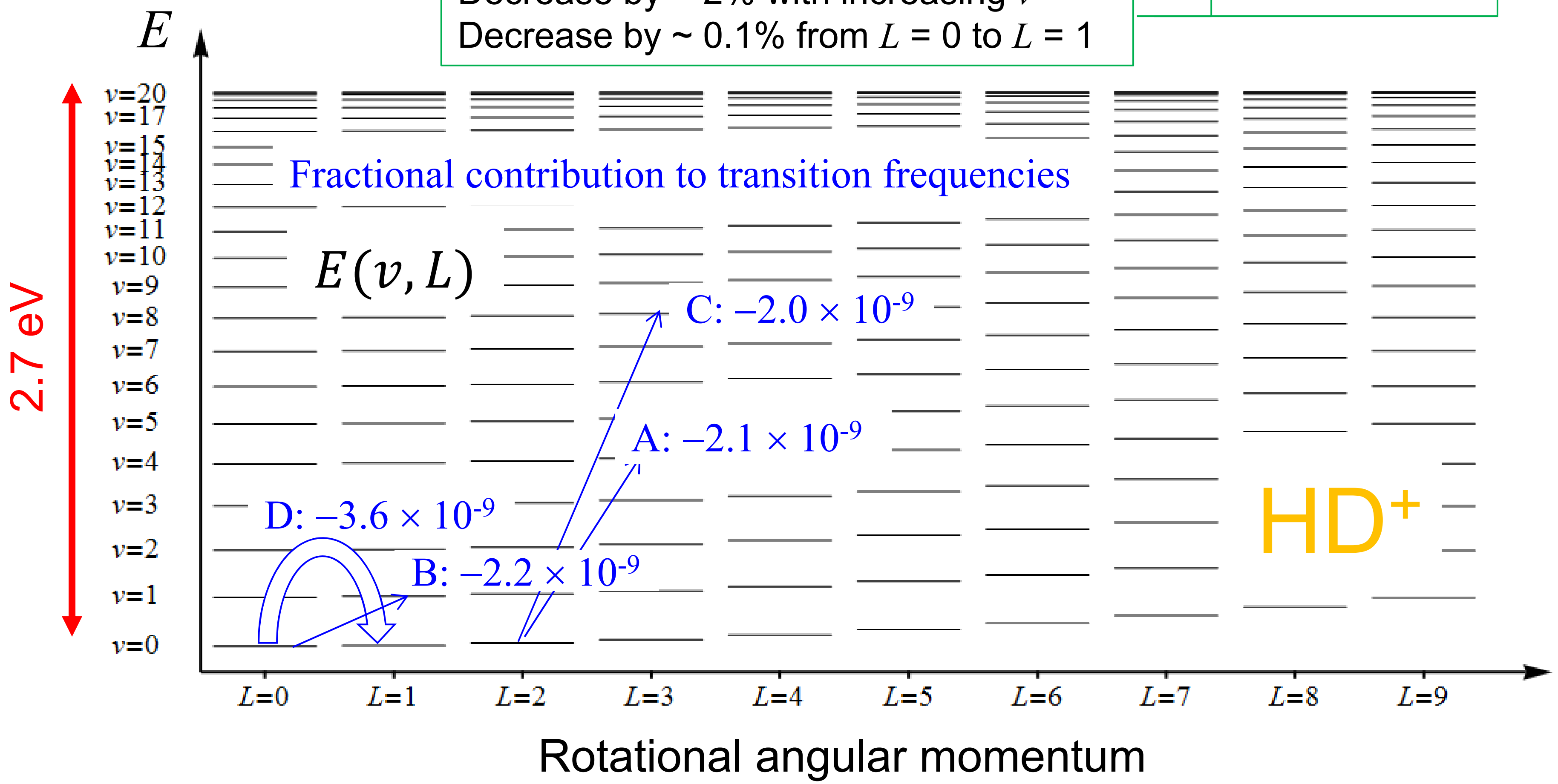
$$\mathcal{O}(10^{-7}\div10^{-8})\ \ \text{[vibrational trans.]}$$

The nuclear charge radii contribution to transition frequencies

- $E_{\text{relativistic}}(v,L) \ni E_{\text{nuc}}^{(2)}(v,L)$
- Can be precisely computed *ab initio*

$$E_{\text{nuc}}^{(2)} = \frac{2\pi}{3}\left(\frac{r_{\text{p}}^2}{a_0^2}\langle\delta(\boldsymbol{r}_{\text{e,p}})\rangle + \frac{r_{\text{d}}^2}{a_0^2}\langle\delta(\boldsymbol{r}_{\text{e,d}})\rangle\right)$$

Decrease by ~ 2% with increasing v
Decrease by ~ 0.1% from L = 0 to L = 1



Aznabayev, Bekbaev, Korobov PRA 99, 012501 (2019)

Ab-initio theory: dependence on fundamental constants

Rotational transition

Korobov, et al., PRL 118, 233001 (2017)

$$f^{\mathrm{(theor)}}_{\mathrm{spin-avg}} = 1{,}314{,}925{,}752{,}896(18)_{\mathrm{theor,QED}}\ \mathrm{Hz}$$

$$u_{r,\mathrm{theor,QED}} = 1.4 \times 10^{-11}$$

$$+\left(2.5\ \Delta R_{\infty,\mathrm{r}} - 60\ \Delta M_{\mathrm{\mu e,r}} - 2.9\ \Delta r_{\mathrm{p,r}} - 1.1\ \Delta r_{\mathrm{d,r}}\right)\ \mathrm{Hz}$$

$$M_{\mathrm{\mu e}} = \left(m_{\mathrm{d}}^{-1} + m_{\mathrm{d}}^{-1}\right)^{-1} / m_{\mathrm{e}}$$

with the normalized deviations ΔX_r of the constants from their nominal values:

$$\Delta X_{\mathrm{r}} = \frac{X - X_{\mathrm{CODATA18}}}{u_{\mathrm{CODATA18}}\,(X)}$$

Vibrational transition

$$f^{\mathrm{(theor)}}_{\mathrm{spin-avg}} = 58{,}605\ 052\ 163.9(5)_{\mathrm{theor,QED}}\ \mathrm{kHz}$$

$$u_{r,\mathrm{theor.QED}} = 0.8 \times 10^{-11}$$

$$+\left(0.11\ \Delta R_{\infty,\mathrm{r}} - 1.3\ \Delta M_{\mathrm{\mu e,r}} - 0.078\ \Delta r_{\mathrm{p,r}} - 0.030\ \Delta r_{\mathrm{d},r}\right)\ \mathrm{kHz}$$

- Today‘s QED uncertainty is too large by a factor ~10 to permit a competitive determination of the charge radii

Ab-initio theory: dependence on fundamental constants

Rotational transition

Korobov, et al., PRL 118, 233001 (2017)

$$f^{(\mathrm{theor})}_{\mathrm{spin-avg}} = 1{,}314{,}925{,}752{,}896(18)_{\mathrm{theor,QED}}\ \mathrm{Hz}$$

$$u_{r,\mathrm{theor.QED}} = 1.4 \times 10^{-11}$$

$$+\left(2.5\ \Delta R_{\infty,\mathrm{r}} - 60\ \Delta M_{\mathrm{\mu e,r}} - 2.9\ \Delta r_{\mathrm{p,r}} - 1.1\ \Delta r_{\mathrm{d,r}}\right)\ \mathrm{Hz}$$

$$M_{\mathrm{\mu e}} = \left(m_{\mathrm{d}}^{-1} + m_{\mathrm{d}}^{-1}\right)^{-1} / m_{\mathrm{e}}$$

with the normalized deviations ΔX_r of the constants from their nominal values:

$$\Delta X_{\mathrm{r}} = \frac{X - X_{\mathrm{CODATA18}}}{u_{\mathrm{CODATA18}}\,(X)}$$

$$f^{(\mathrm{theor})}_{\mathrm{spin-avg}} = 1{,}314{,}925{,}752{,}896(18)_{\mathrm{theor,QED}}\ (61)_{\mathrm{CODATA18}}\ \mathrm{Hz}$$

$$u_{r,\mathrm{CODATA18}} = 4.6 \times 10^{-11}$$

- Additionally, we need to also measure $m_{\mathrm{p}}/m_{\mathrm{e}}$ and $m_{\mathrm{d}}/m_{\mathrm{p}}$ more precisely than CODATA18

An ambitious program

Analysis of Karr et al *PRA **94**, 050501(R) (2016)*

Assumptions:

- Reduce QED theory unc. by factor ~3 to 3x10^{-12} for vibrational and rot. transitions
- Measure 3 transitions on HD^+, 2 on H_2^+
- Achieve experimental accuracy 1x10^{-12} on all 5 transitions
- HFS contribution not considered, but controllable [*]

$\rightarrow$ Obtain $u_\mathrm{r}(r_\mathrm{p})$ = 0.8%, $u_\mathrm{r}(r_\mathrm{d})$ = 0.3%, $u_\mathrm{r}(R_\infty) \approx 9\times10^{-12}$

Compare with CODATA2018: 0.22% 0.035%

- 2 vibrational, 1 rotational transition in HD^+? Yes
- 2 transitions on H_2^+? Future
- Experimental uncertainty improvement? Near-future [**]
- QED theory uncertainty reduction? Already achieved for H-atom, must be extended to MHI

[**] Ultimatetly, 10^{-17} should be feasible:
Schiller et al. PRL 113, 023004 (2014) Karr, J. Mol. Spectrosc. 300, 37 (2014)

[*] Alighanbari et al., Nature 581, 152 (2020)
Schiller and Korobov PRA 98, 022511 (2018)

Impact of HFS

Transition frequency: $f_{\text{spin-avg}}(vL, v'L') + f_{\text{spin}}(vLFSJ, v'L'F'S'J')$

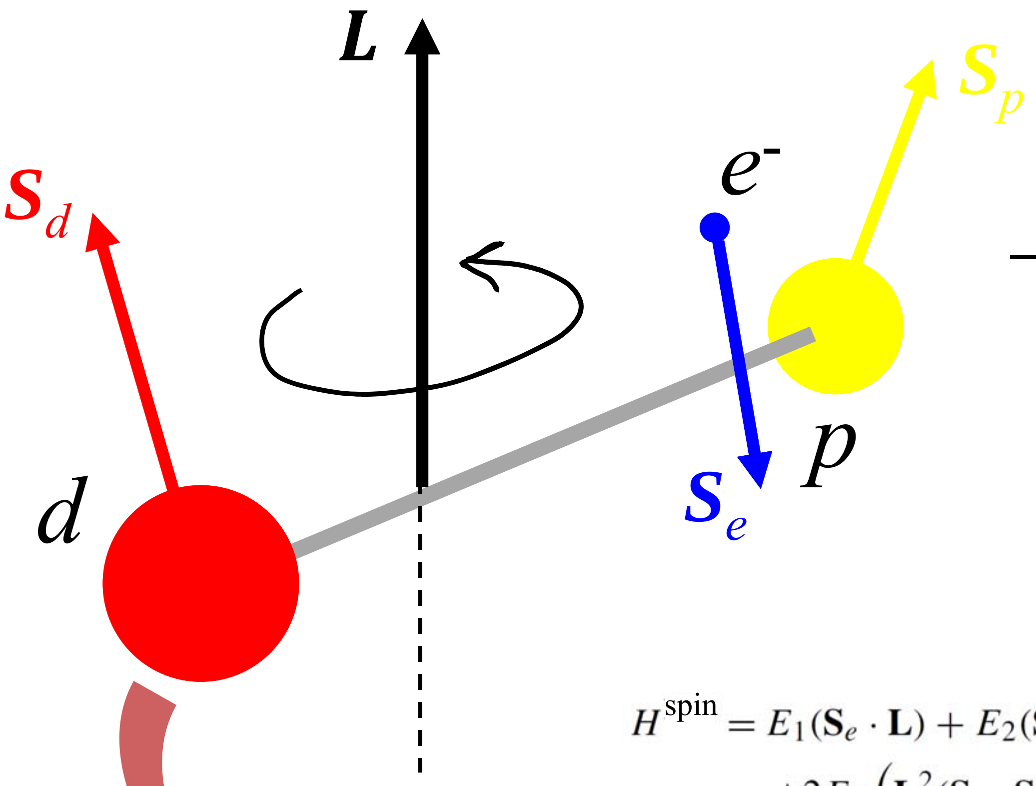
$(u)_{r_p,\text{CODATA18}} \approx 0.7\ \text{kHz}$ @ 250 THz

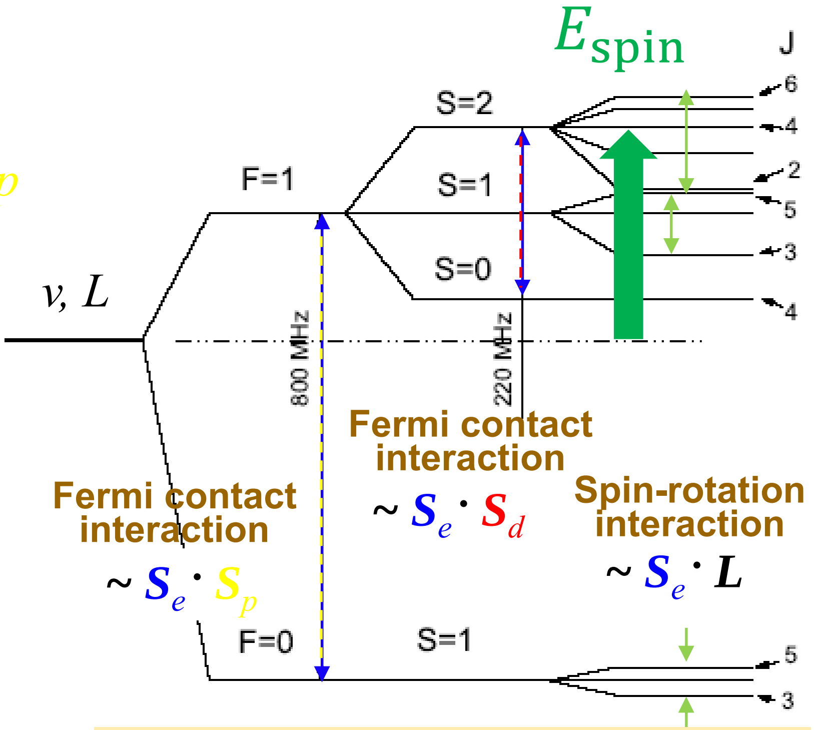
$u \approx \mathcal{O}(10^4\ \text{kHz}) \times u_r(f_{\text{spin}})$
$\approx (0.2 – 1.4)\ \text{kHz}$

- HFS theory [*] has reached a level where $u_r(f_{\text{spin}})$ for selected individual components is sufficiently low for competitiveness
- Measurement of two, more or all HFS components i can effectively suppress the uncertainty even further, also to a negligible level (reason: $f_{\text{spin,i}}$ are correlated, arising from the same hamiltonian) [**]

[*] Korobov et al PRA 102, 022804 (2020), Karr et al PRA 102, 052827 (2020)
[**] Schiller and Korobov, PRA 98, 022511 (2018)

Spin structure of HD^+





Fermi contact interaction $\sim \boldsymbol{S}_e \cdot \boldsymbol{S}_p$

Fermi contact interaction $\sim \boldsymbol{S}_e \cdot \boldsymbol{S}_d$

Spin-rotation interaction $\sim \boldsymbol{S}_e \cdot \boldsymbol{L}$

$$
\begin{aligned}
H^{\text{spin}} = {} & E_1(\mathbf{S}_e \cdot \mathbf{L}) + E_2(\mathbf{S}_p \cdot \\
& +2E_6\Big(\mathbf{L}^2(\mathbf{S}_e \cdot \mathbf{S}_p) - \\
& +2E_7\Big(\mathbf{L}^2(\mathbf{S}_e \cdot \mathbf{S}_d) - \\
& +2E_8\Big(\mathbf{L}^2(\mathbf{S}_p \cdot \mathbf{S}_d) - \\
& +E_9\Big(\mathbf{L}^2\mathbf{S}_d^2 - \frac{3}{2}(\mathbf{S}_d \cdot
\end{aligned}
$$

Electric quadrupole moment

5.666 kHz

Individual HFS components have a contribution of up to

$$f_{\text{spin}} \ni 3\,E_9$$

Since $u(f_{\text{spin}}) = \mathcal{O}(1\text{ kHz})$, high accuracy for E_9 can only be obtained with a tailored approach

Precision spectroscopy of MHI

Goal I: Achieve highest possible accuracy

Requires:
- Doppler-free spectroscopy
- Long observation times
- Control of systematics
- Resolve hyperfine structure

Today: $\approx 3\times10^{-12}$ uncertainty (in HD^+ [1,2])

Goal II: Measure several transitions,
and at least 2 isotopologues

[1] this work.
[2] Germann, M. et al. *Phys. Rev. Research* **3**, L022028 (2021).

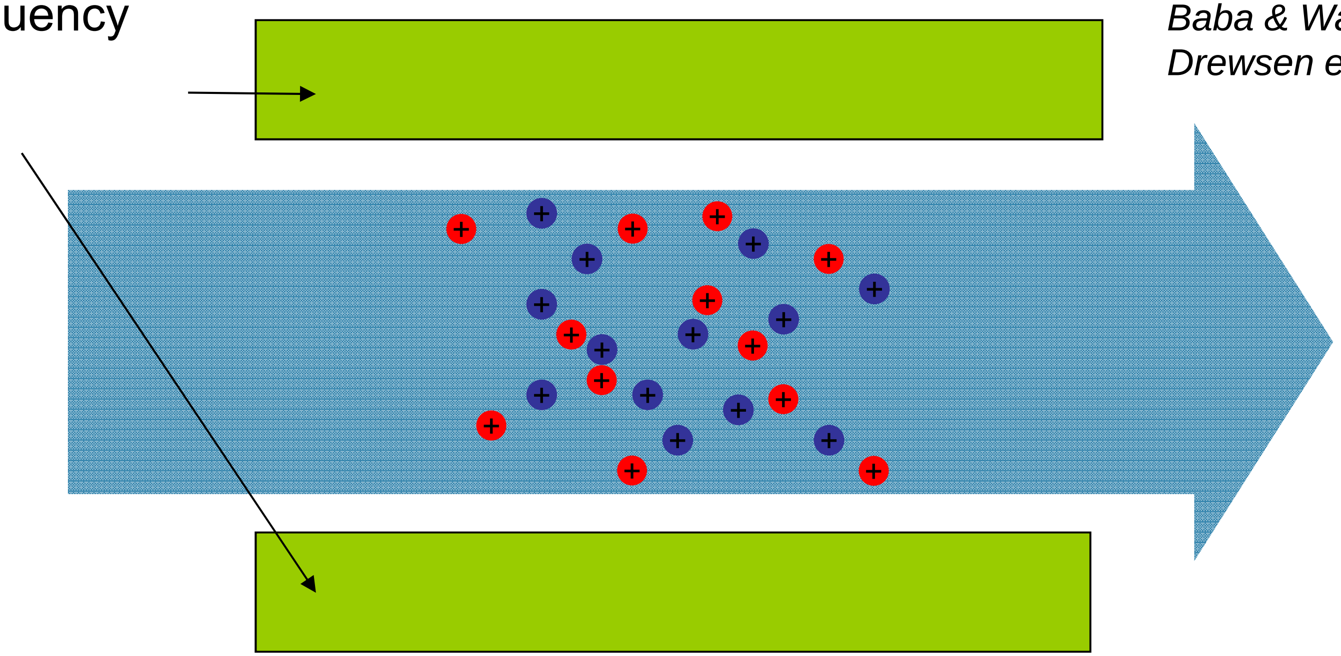
Sympathetic cooling of charged particles

- Efficient, since Coulomb force is long-range
- General method: independent of nature of particle (only charge and mass relevant)
- Final state: Coulomb „crystal“ (cluster) (particles on sites, well-separated)

First experiments:

Penning trap: *Drullinger et al. 1980*
Larson et al. 1986

Paul trap: *Diedrich et al. 1987*
Waki et al 1992
Raizen et al 1992
Baba & Waki 1996
Drewsen et al. 1999



Linear radiofrequency trap

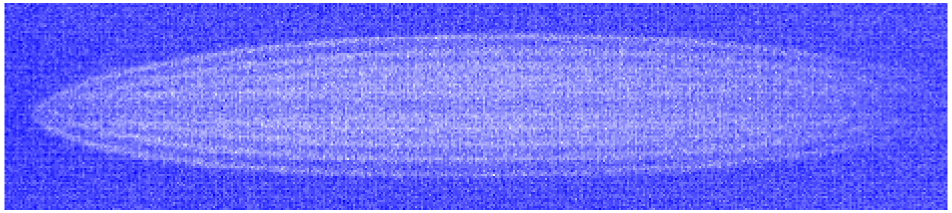
Cooling laser beam

Experimental Techniques

- ✓ Trapping and sympathetic cooling [1]
- ✓ Detection of REMPD by in-situ measurement of remaining molecular ions [2]
- ✓ Rotational laser cooling [3]
- ✓ Adressing of individual hyperfine components via long-wavelength spectroscopy [4]
- ✓ Novel c.w. narrow-linewidth and comb-referenced laser sources [5]
- ✓ Achievement of Dicke condition and detection of carrier transitions [6]
- ✓ Determining composite frequencies [7]
- ✓ Controlled experiments on single molecular hydrogen ions [8]
- ✓ 313 nm beryllium cooling lasers [9]

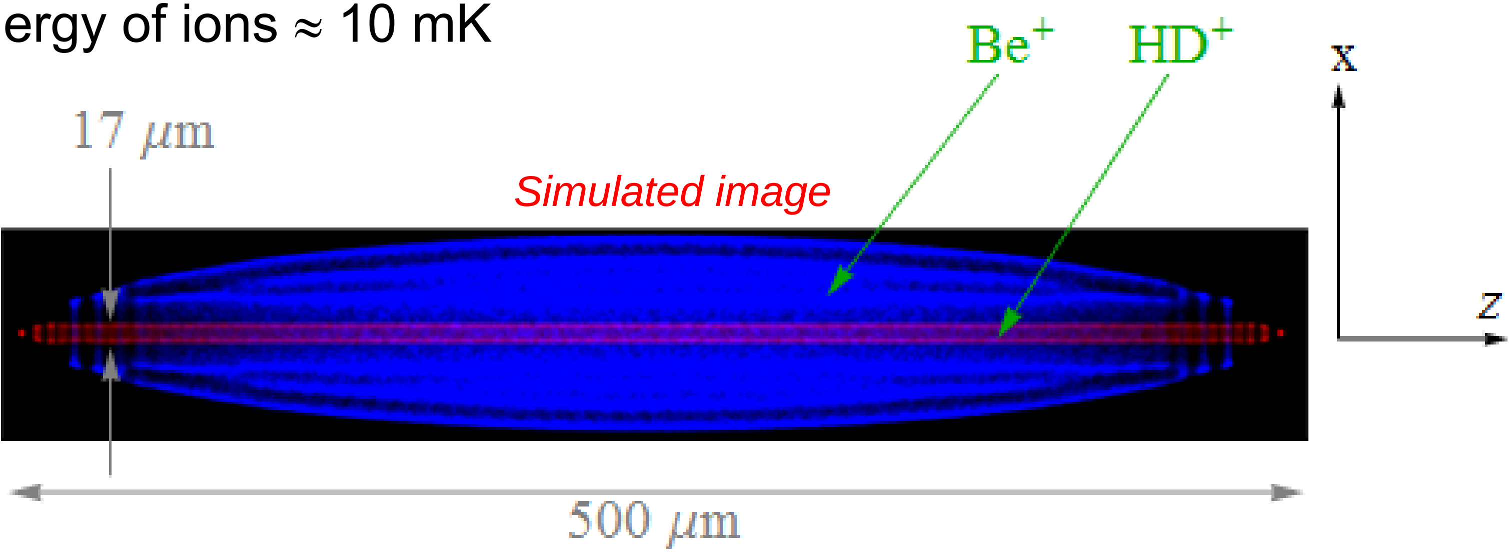
[1] Roth et al. DOI: 10.1109/EQEC.2003.1314167; Blythe et al., PRL 95,183002 (2005)
[2] Roth et al. PRA 74, 040501(R) 2006
[3] Schneider et al., Nat. Phys. 6, 275 (2010)
[4] Bressel et al., PRL 108, 183003 (2012)
[5] Bressel et al., Opt. Lett. 37, 918 (2012); Kortunov et al., Nat. Phys. 17, 569 (2021)
[6] Alighanbari et al, Nature Phys. 14, 555 (2018); Kortunov et al., Nat. Phys. 17, 569 (2021)
[7] Alighanbari et al. Nature 581, 152 (2020)
[8] C. Wellers, subm. [9] Schnitzler et al., Appl. Opt. 41, 7000 (2000); Vasilyev et al. Appl. Phys. 103, 27 (2011)

Two-species ion cluster: Be^+ / HD^+



Be^+ Coulomb cluster with sympathetically cooled HD^+ [1]

Kinetic energy of ions ≈ 10 mK



Simulated image

MD Simulation: 2000 Be^+, 200 HD^+, T = 30 mK

[1] *Blythe et al., PRL 95,183002 (2005)*

Precision measurements on sympathetically cooled MHI

HHU Düsseldorf:

Rotational transition f_0
Alighanbari et al. *Nature* **581**, 152 (2020).

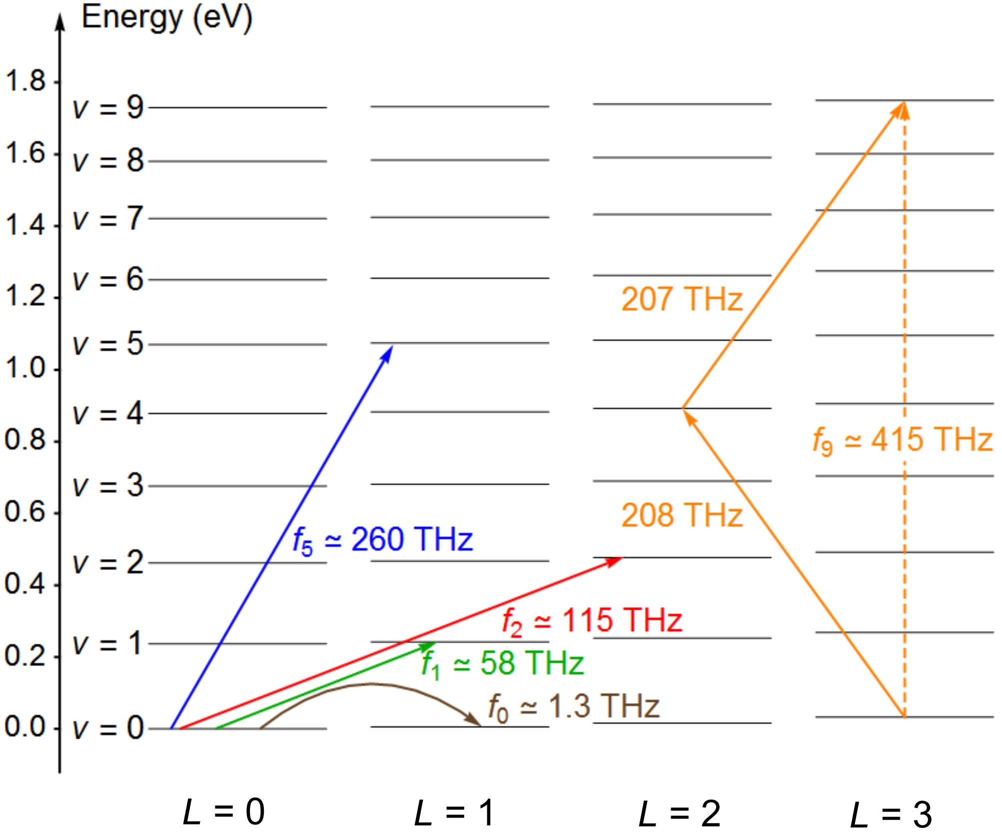
Vibrational transition f_1
Kortunov, et al. *Nat. Phys.* **17**, 569 (2021).

4th overtone transition f_5 this work

E2 transition f_2 this work

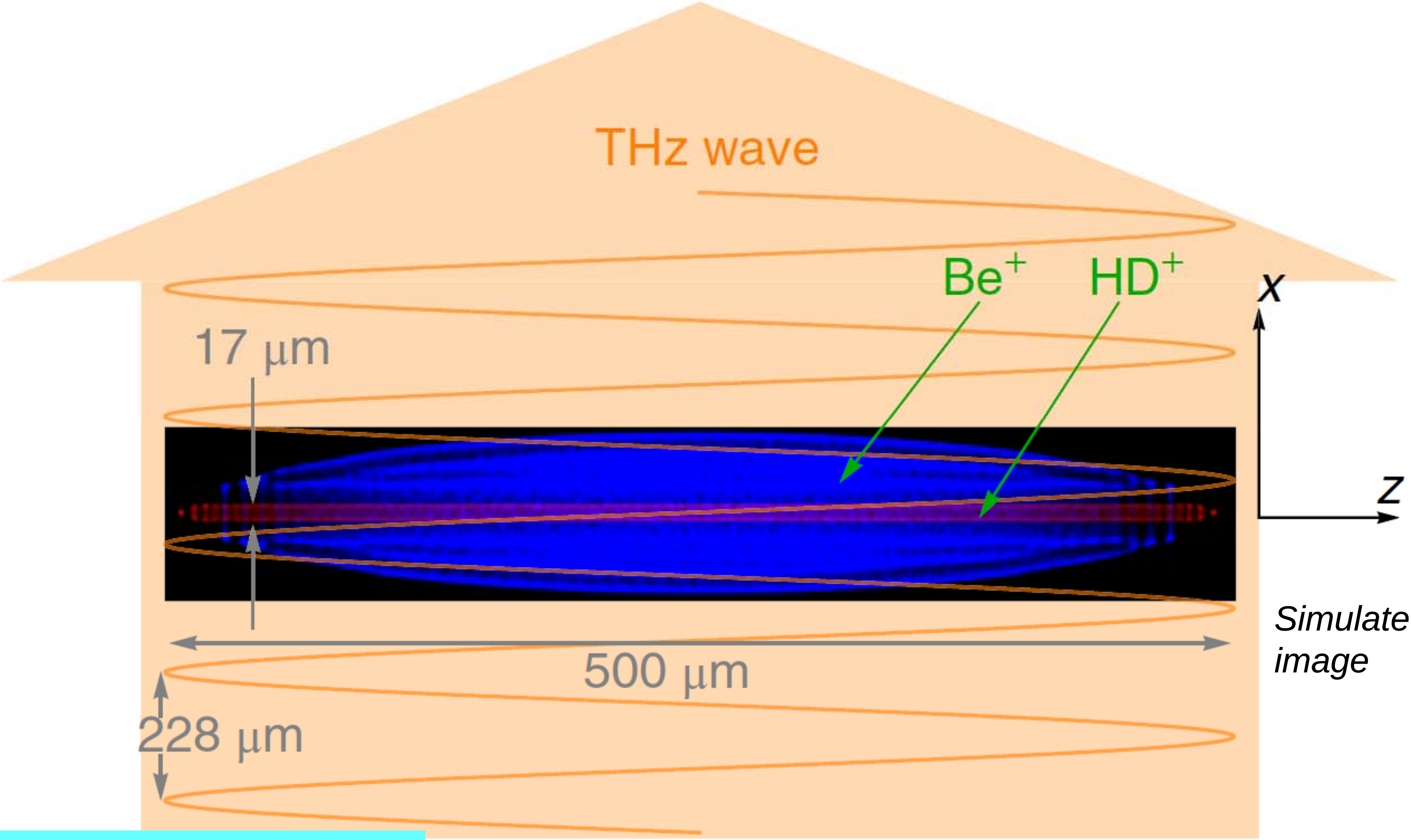
VU Amsterdam:

Two-photon transition f_9
Patra et al. *Science* 369, 1238 (2020).



TICTES: Trapped ion cluster transverse excitation spectroscopy

S. Alighanbari et al, Nature Phys. 14, 555 (2018)



Simulated image

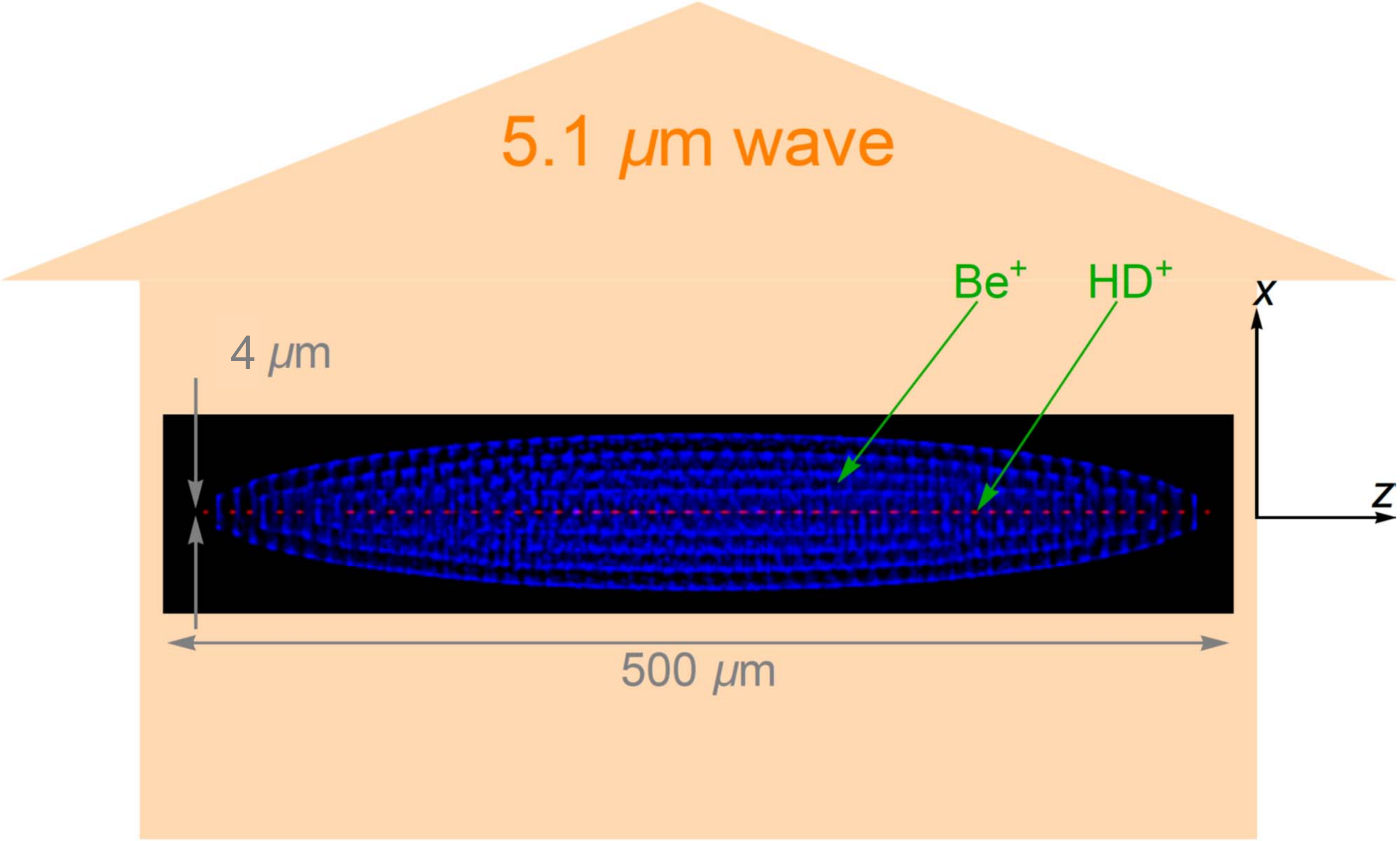
$\Delta x \approx 8\ \mu\text{m}$ @ 12 mK

$\rightarrow \Delta x \ll \lambda_{\text{rot}}/2\pi$

→ Spectroscopy in the Dicke regime

TICTES: Spectroscopy with short wavelength

Kortunov et al., Nat. Phys. 17, 569 (2021)



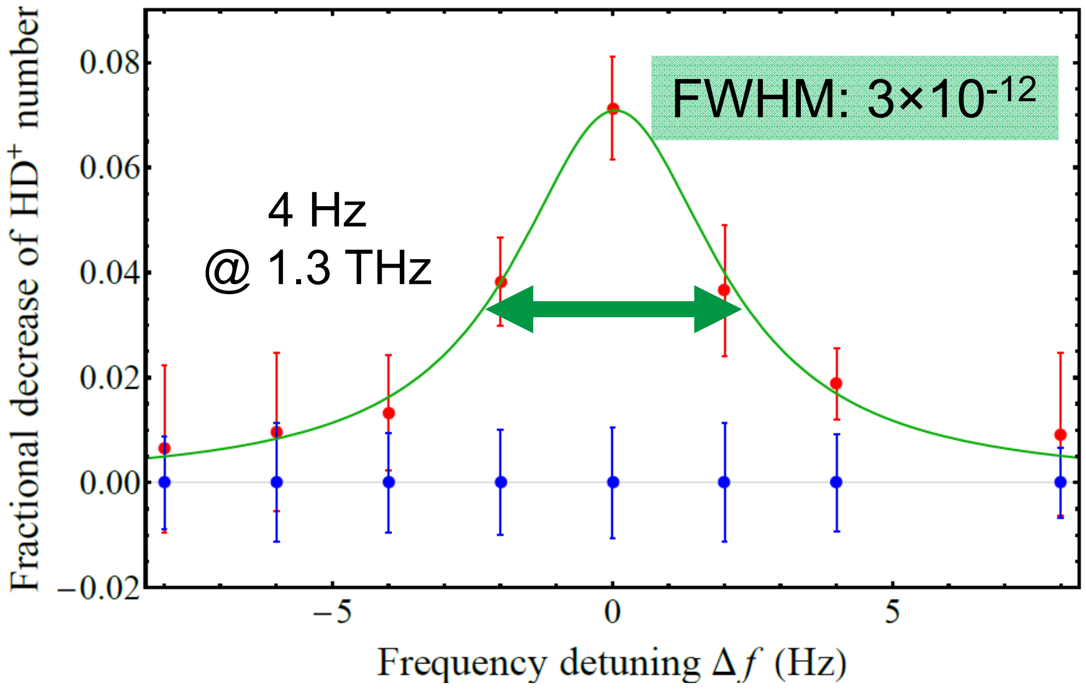
→ Spectroscopy with resolved carrier

MD Simulation: 2000 Be^+, 50 HD^+, T = 10 mK

Doppler-free one-photon rotational spectroscopy

- Fundamental rotational transition, $f = 1.3$ THz

Alighanbari et al. Nature Phys. 14, 555 (2018)
Alighanbari et al. Nature 581, 152 (2020)



FWHM: 3×10^{-12}

4 Hz
@ 1.3 THz

10^4 times higher resolution than conventional rotational spectroscopy of neutrals or ions

- Spectroscopy source:
frequency multiplier,
referenced to H-maser

Schiller et al., Appl. Phys. B 95, 55 (2009)

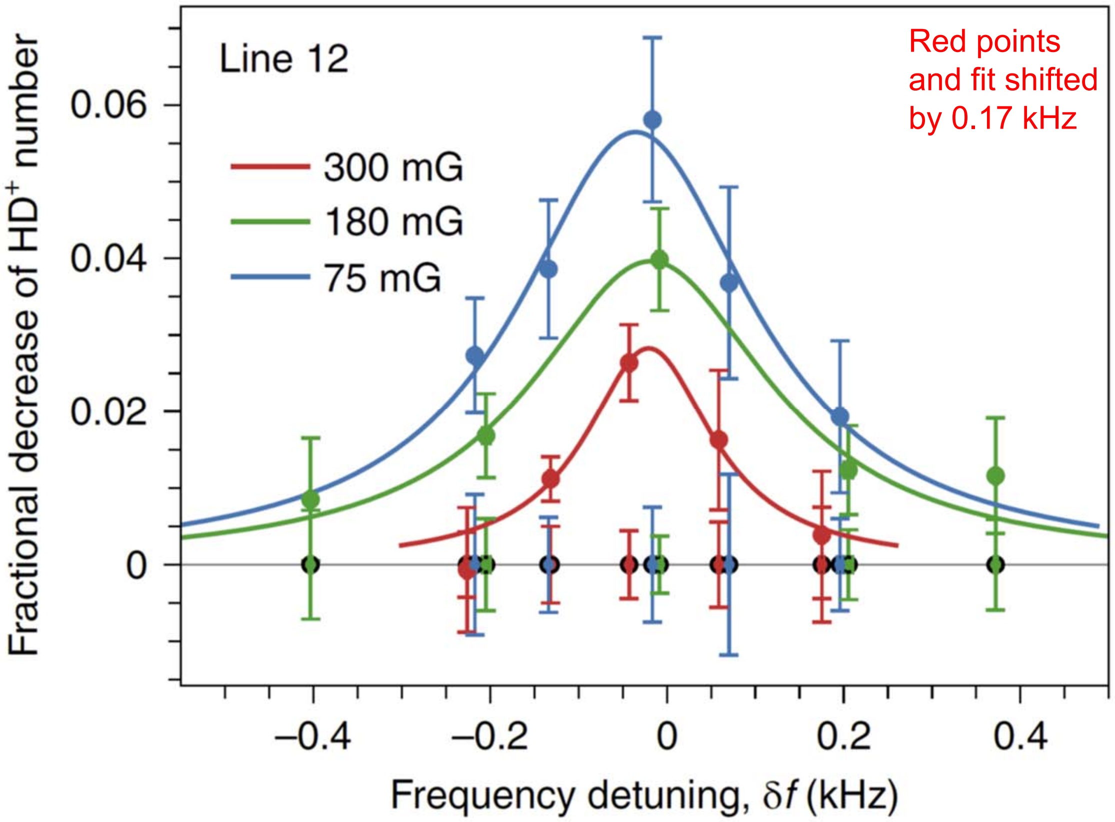
- Experimental resolution better than theory uncertainty of the spin-averaged frequency, 1.4×10^{-11}
- > 100 × better than theory uncertainty of spin frequency
- Can resolve Zeeman splittings

Also: *Chou et al. Science 367, 1458 (2020): 500 Hz FWHM*

Doppler-free one-photon vibrational spectroscopy

Kortunov et al., Nat. Phys. 17, 569 (2021)

- Fundamental vibrational transition, λ = 5.1 µm, f = 59 THz
- Fractional linewidth as small as 3×10^{-12}

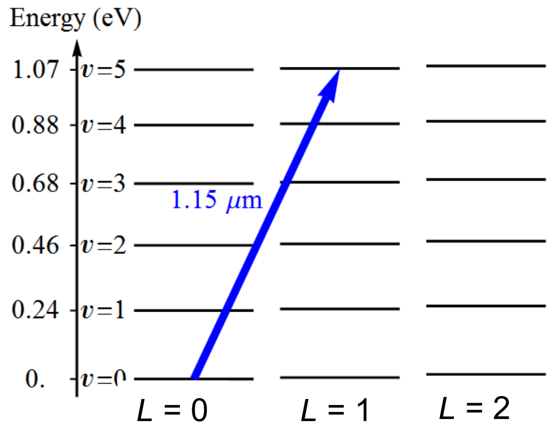


10^4 times higher resolution than best previous one-photon vibrational spectroscopy of molecular ions*

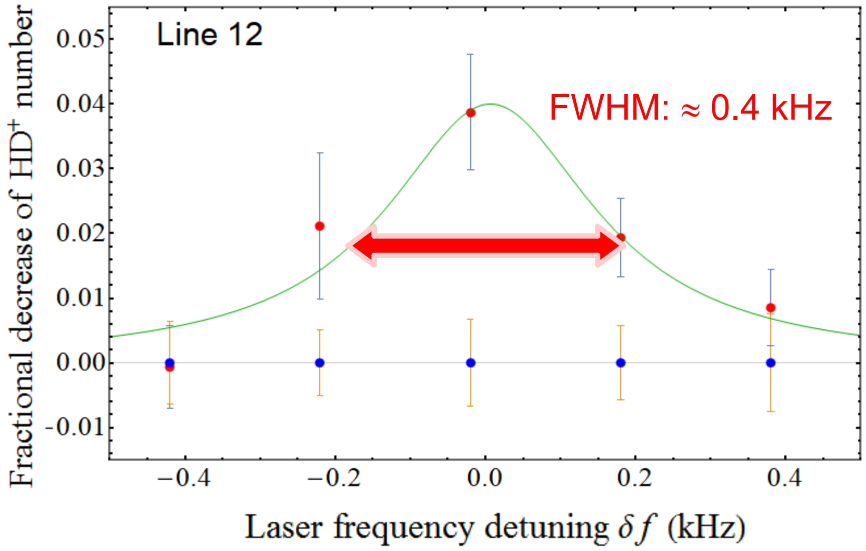
- Experimental resolution better than theory uncertainty of the spin-averaged frequency, 0.9×10^{-11}
- 2 × better than theory uncertainty of spin frequency
- Can resolve Zeeman splittings

Bressel et al, PRL 108, 183003 (2012)

Surprise!



(v,N): (0,0) → (5,1) @ 1.15 µm



Q factor: 6×10^{11}

Not predicted by simple model!
Possible explanation: “transient Dicke regime”

- Occasional time intervals of restricted transverse motion give rise to narrow carrier line
- Other intervals give rise to a spectrally broad background.

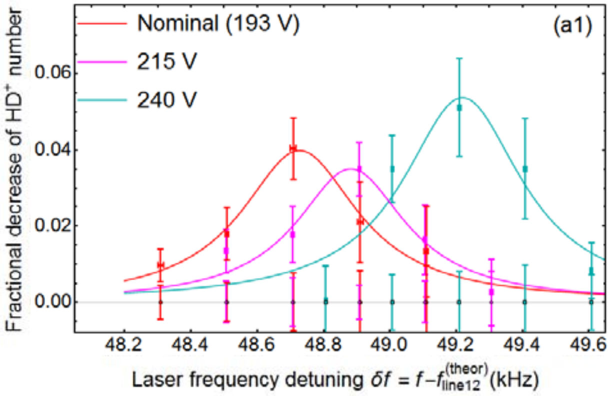
- The highest Q-factor for any molecular ion spectroscopy to date:
  - 2 × larger than in the fundamental rotational and vibrational transitions [1,2].
  - 12 × larger than two-photon transition [3].
  - 100 × larger compared to best single molecular ion spectroscopy [4].
- Close to the best resolution achieved on ultracold neutral molecules [5].

[1] Alighanbari, S. et al. *Nature* 581, 152 (2020).
[2] Kortunov, I.V. et al. *Nat. Phys.* 17, 569 (2021).
[3] Patra, S. et al. *Science* 369, 1238 (2021).
[4] Chou, C.W. et al. *Science* 367, 1458 (2020).
[5] Kondov, S.S. et al. *Nat. Phys.* 15, 1118 (2019).

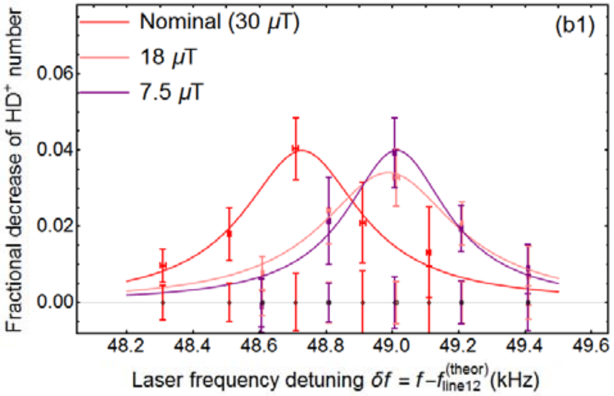
Systematic effects on the 4th overtone transition

One HFS component (line 12):

Trap-induced shift

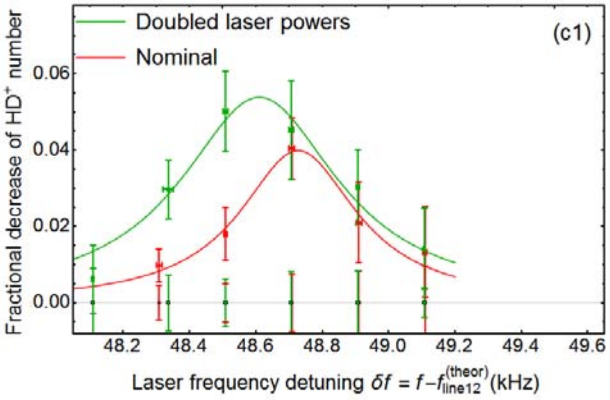


DC Zeeman shift

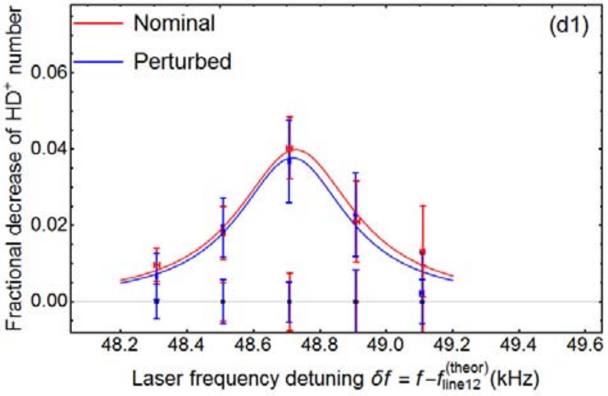


Physical effect	$f^{(\text{exp})}_{\text{line12}} - f^{(\text{exp,nom})}_{\text{line12}}$
Statistics	0.00(21)
Trap field	−0.89(70)
d.c. Zeeman	0.33(19)
a.c. Stark	−0.12(35)
d.c. Stark	0.00(21)
Maser offset	1.46
Recoil	−49.58
Total	**−48.46(86)**

AC Stark shift (light shift)



DC Stark shift



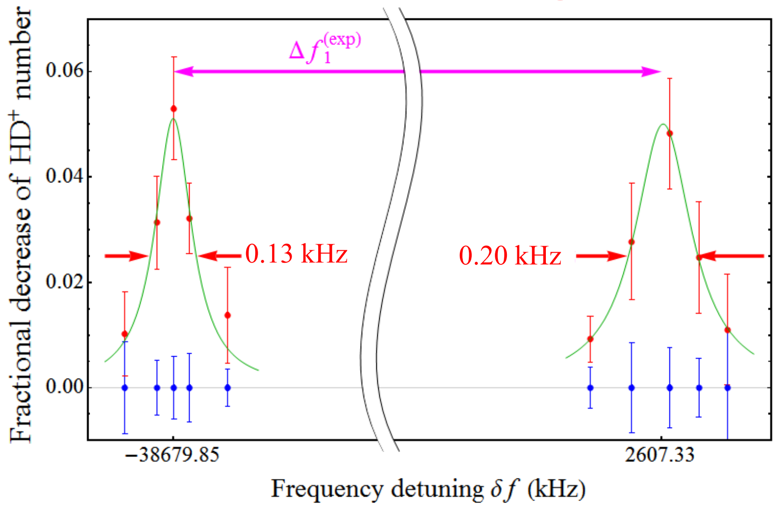
Similar for line 21

HFS

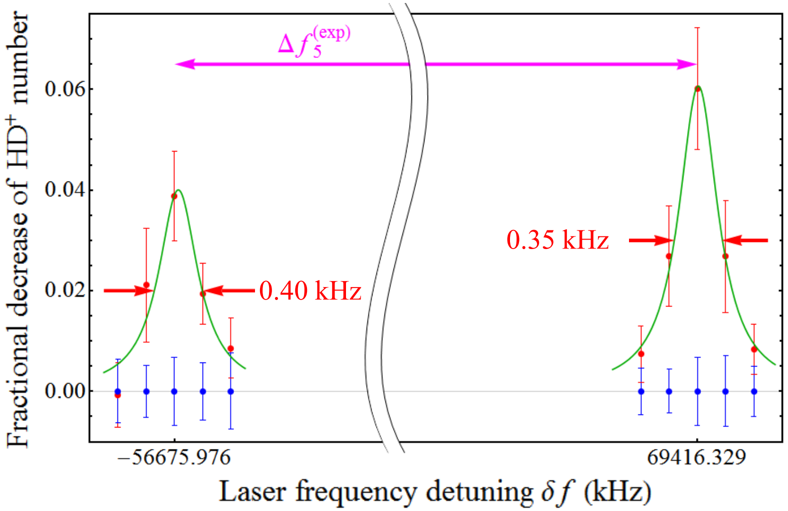
Kortunov, I.V. et al. *Nat. Phys.* **17**, 569 (2021).

This work

Fundamental vibrational @ 5.1 µm



4th overtone @ 1.15 µm



$$\Delta f_1^{(\mathrm{exp})} = 41294.06\ (32)\ \mathrm{kHz}$$
$$\Delta f_1^{(\mathrm{theor})} = 41293.81\ (44)\ \mathrm{kHz}$$
$$0.25\ (54)\ \mathrm{kHz}$$

$$\Delta f_5^{(\mathrm{exp})} = 126092.6\ (1.2)\ \mathrm{kHz}$$
$$\Delta f_5^{(\mathrm{theor})} = 126092.0\ (2.1)\ \mathrm{kHz}$$
$$0.6\ (2.4)\ \mathrm{kHz}$$

HFS agrees at 0.5 kHz level

HFS theory: Bakalov, D. et al. PRL 97, 243001 (2006).
Haidar, M. et al. PRA 101, 022501 (2020).

Spin-averaged frequency

Extract the spin-averaged frequency:

$$f^{(\mathrm{exp})}_{\mathrm{spin-avg}} = b_{12}\left(f^{(\mathrm{exp})}_{\mathrm{line12}} - f^{(\mathrm{theor})}_{\mathrm{spin,12}}\right) + (1 - b_{12})(f^{(\mathrm{exp})}_{\mathrm{line21}} - f^{(\mathrm{theor})}_{\mathrm{spin,21}})$$

Experiment + HFS theory:

$$f^{(\mathrm{exp})}_{\mathrm{spin-avg}} = 259\,762\,971\,051.1(7)_{\mathrm{exp}}(3)_{\mathrm{theor,spin}}\ \mathrm{kHz}$$

$$u^{(\mathrm{exp})}_{\mathrm{r,tot}} = 2.9 \times 10^{-12}$$

Experiment - theory agree at 2.1 x 10^{-11} level

Prediction (QED, no HFS)

$$f^{(\mathrm{theor})}_{\mathrm{spin-avg}} = 259\,762\,971\,051.0(2.1)_{\mathrm{theor,QED}}(5.1)_{\mathrm{CODATA2018}}\ \mathrm{kHz}$$

$$u^{(\mathrm{theor})}_{\mathrm{r,tot}} = 2.1 \times 10^{-11}$$

Proton charge radius contribution:

-73.0(3)$_{\mathrm{CODATA2018}}$ kHz

Deuteron charge radius contribution:

-465.9(3)$_{\mathrm{CODATA2018}}$ kHz

Prediction based on CODATA 2014:

- Fundamental masses:	-17.7 kHz smaller
- Nuclear radii and Rydberg constant:	-3.6 kHz smaller
- Total:	-21.3 kHz smaller

Experiment - theory agreement is consistent with CODATA2018 adjustment

Some conclusions

- The HD$^+$ data available so far (4 transitions) do not allow to extract (r_p, r_d) with anywhere competitive accuracy
  (*reasons*: theory unc. level, exp. unc. level, sensitivities of frequencies)
- Assuming CODATA values of R_∞, r_p, r_d, the data does allow to deduce

$$\frac{m_p m_d/(m_\mathrm{p}+m_\mathrm{d})}{m_e} = 1223.899\,228\,730(22)$$

2 times smaller uncertainty than CODATA2018

- The HFS of the rotational transition was measured with exp. uncertainties ≈ 0.07 kHz [1]; comparison with HFS theory shows partial agreement and partial disagreement at level of 5 σ = 1.1 kHz for one splitting [*]
- A fit of the E_9 coefficient to the spin frequency yields Q_d with ~ 2% uncertainty, consistent with the more precise literature value [1]
- Tests of fundamental physics

[1] Alighanbari et al. Nature 581, 152 (2020)
[*] status: 2/2022

What now?

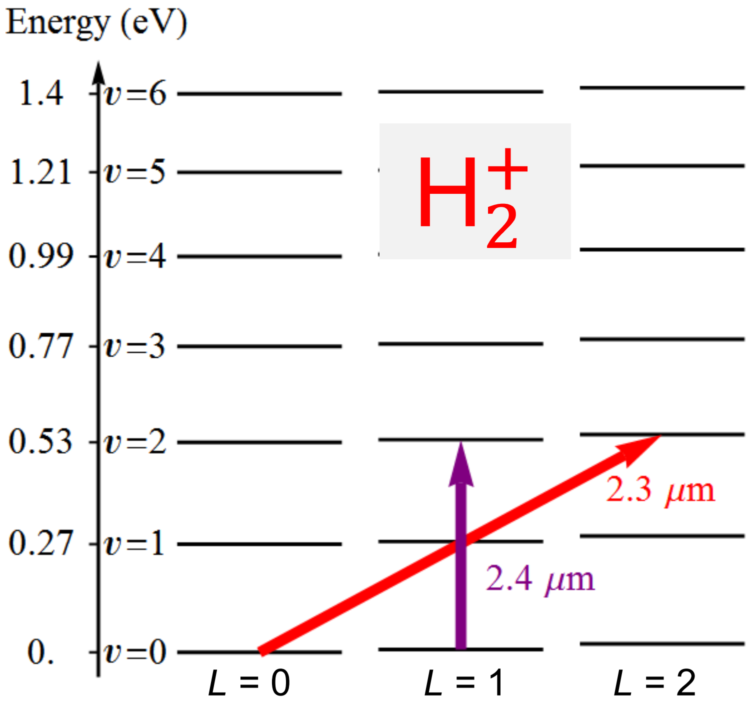
Towards spectroscopy of H_2^+, D_2^+

- H_2^+ → determine m_p/m_e
- D_2^+ → determine m_d/m_e

… and eventually R_∞, r_p, r_d

A flexible approach:

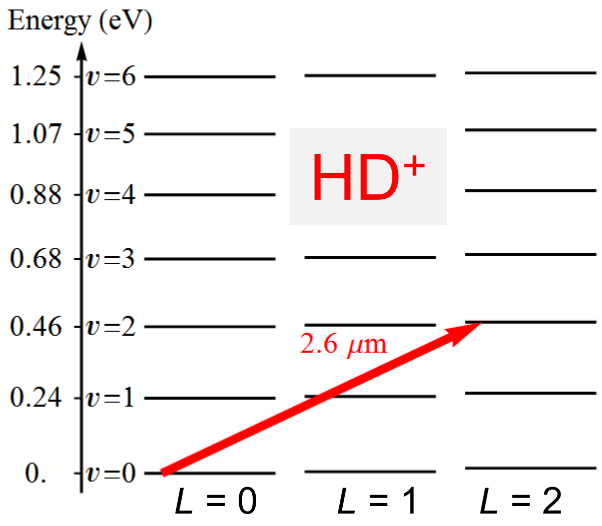
Electric quadrupole (E2) transitions



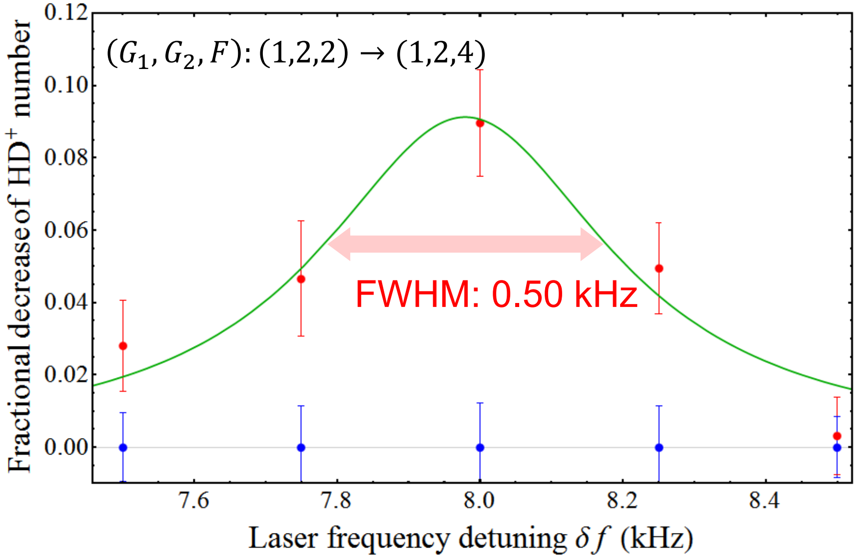
Schiller et al. *Phys. Rev. Lett.* 113, 023004 (2014).
Karr, J.-P. *J. Mol. Spectrosc.* 300, 37 (2014)
Korobov, V.I. et al. *Phys. Rev. A* 97, 032505 (2018).
Danev, P. et al. *Phys. Rev. A* 103, 012805 (2021).

A test experiment: E2 spectroscopy on HD^+ *

- E2 transitions can be observed both in axial propagation (with Doppler-broadening) and by TICTES (no Doppler broadening)



TICTES



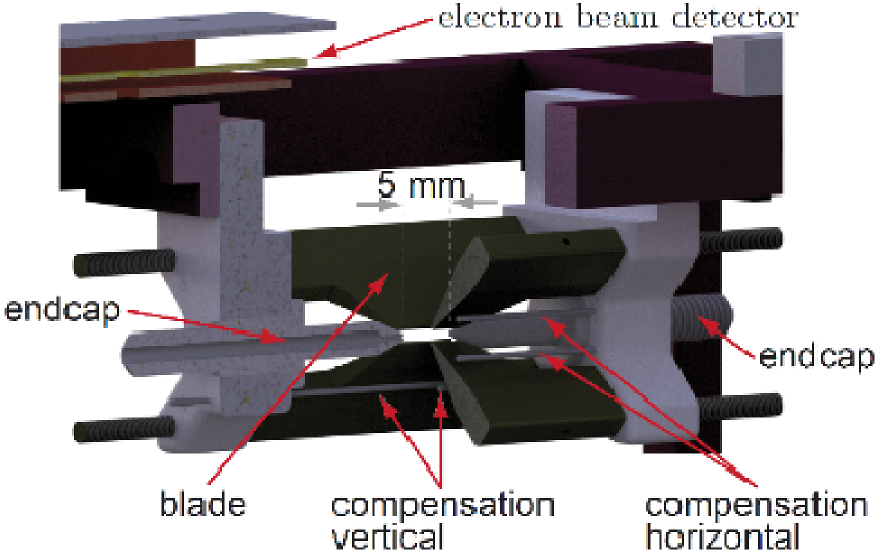
Q factor: 2.3×10^{11}

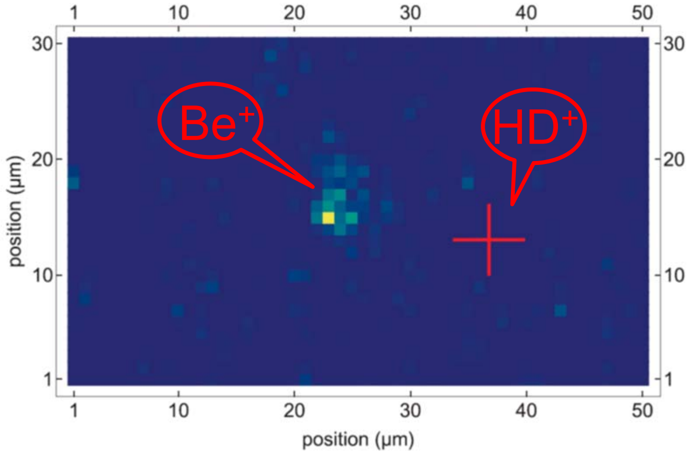
A factor 40 000 improvement, compared to the only previous demonstration of E2 spectroscopy of molecular ions, Germann, M., et al. *Nat. Phys.* **10**, 820 (2014)

[*] Schiller and Korobov, PRA 98, 022511 (2018)

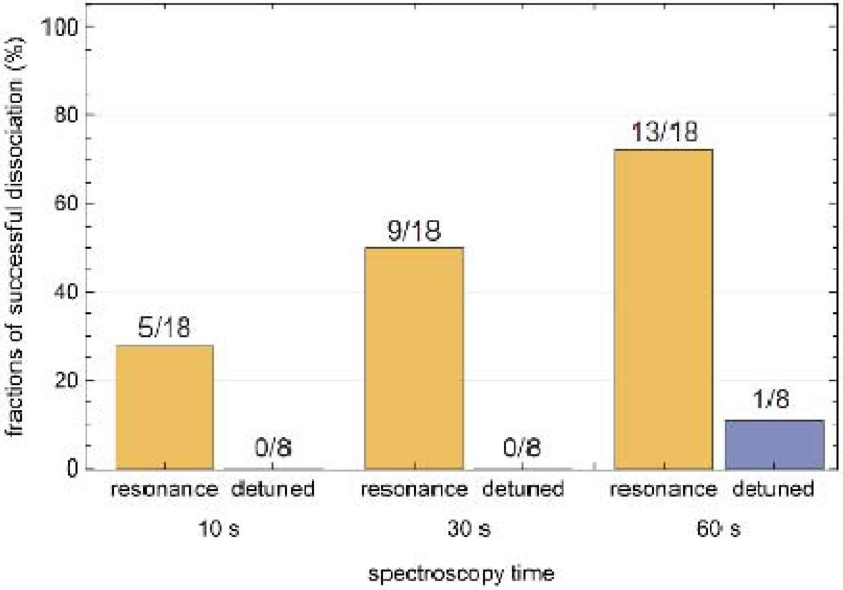
Towards precision spectroscopy of a single MHI

- Tightly confining trap





First vibrational excitation of single molecular hydrogen ions



Goal: remeasure transitions with aiming for higher accuracy

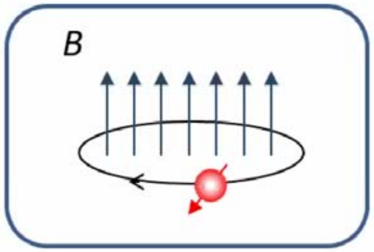
Wellers, C. et al. *Mol. Phys.* e2001599 (2021).

Precision spectroscopy of MHI in a Penning trap

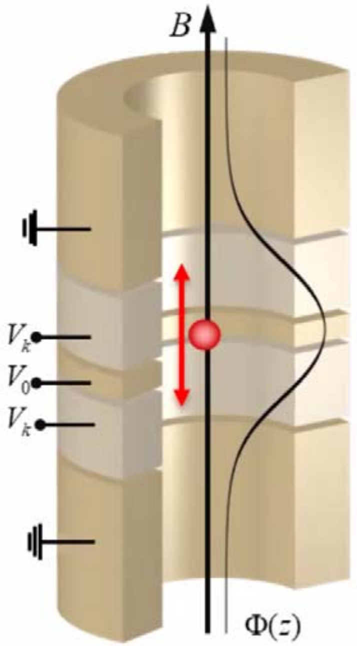
C. M. König, F. Heiße, J. Morgner, T. Sailer, B. Tu, K. Blaum, S. Schiller, S. Sturm

- Penning traps are powerful tools for mass spectroscopy and g-factor measurements
- Here, for the first time, quantum spectroscopy of molecular ions

Simultaneous cyclotron frequency measurement



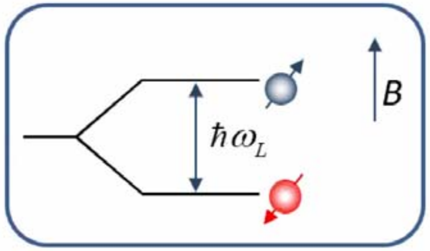
$$\omega_c = \frac{q}{m} B$$



radial confinement: $\vec{B} = B_0 \hat{z}$

axial confinement: $\Phi(\rho, z) = V_0 c_2 \left(z^2 - \frac{\rho^2}{2} \right)$

Determination of energy splitting between spin-states



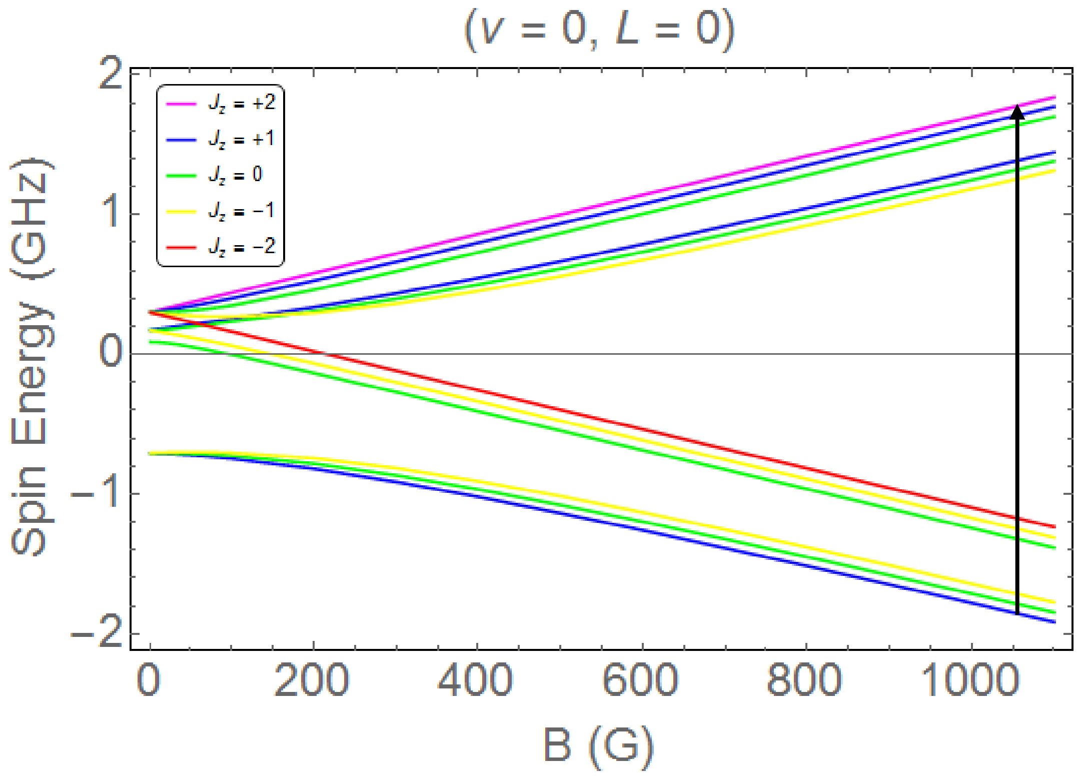
$$\omega_L = \frac{\mu\, g}{\hbar} B$$

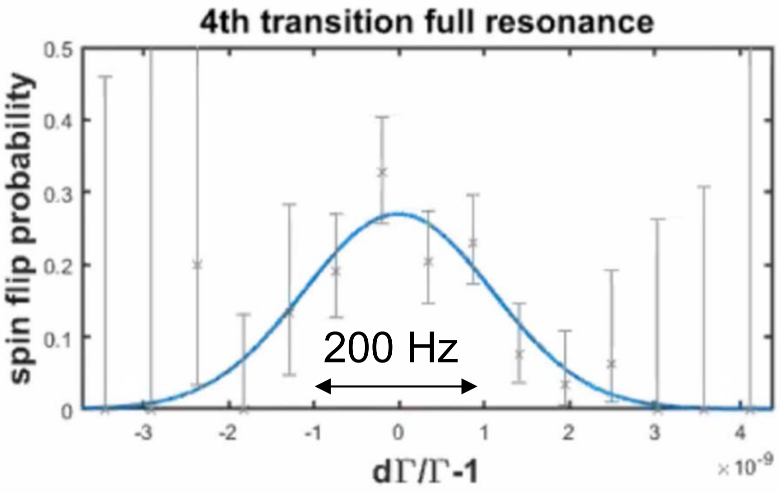
Figure credit:
A. Kaiser, MPI-K Heidelberg

First study

C. König et al, PSAS 2022

- Electron spin resonance in strong field





- Measurement of 6 strong transitions @ 110 GHz
- Extract g_e, E_4, E_5 with expected unc.s, resp., of few x 10^{-10}, 0.1 kHz, 0.1 kHz
- Comparison with HFS theory, where $u(E_4)$ = 0.9 kHz, $u(E_5) = 0.08$ kHz
- Comparison with future theory for bound g-factor (*)

(*) R. Hegstrom, PRA 19, 17 (1979), Karr, PRA 104, 032822 (2021)

Outlook - I

- ESR & Radiofrequency spectroscopy of HD^+ or D_2^+ could lead to independent determination of Q_d.
  - In Penning trap, given an experimental accuracy of 1 Hz (*) $\rightarrow u_\mathrm{r}(Q_\mathrm{d}) = 0.5 \times 10^{-4}$ ($\rightarrow$ improved HFS theory for E_9 desirable!)
  - RF spectroscopy could also be performed in RF trap
- Rotational or vibrational spectroscopy are also suitable [1]. Again, ~ 1 Hz uncertainty required.

- Vibrational laser spectroscopy of MHI in Penning trap

Challenging!

(*) e.g. König et al. Nature (2022) 10.1038/s41586-022-04761-7

[1] Danev et al. PRA 103, 012805 (2021)

Outlook - II

Triton charge radius?

- Interesting because it is a three-nucleon system (I_t=1/2; Q_t = 0)
- Charge radius experimentally known to 3%: r_t = 1.598(40) fm
- Recent theoretical calculation in agreement: 1.62(3) fm
  Vanasse PRC ***95****, 024002 (2017)*
- Exp.l uncertainty substantially larger than for r_p (0.22%) and r_d (0.035%); future improved calculation cannot be compared to experiment
  → Improved measurement worthwhile?
- Some properties of the triton are in principle accessible via spectroscopy of molecules (HT, DT, …, HT^+, ….)
- On the triton-containing neutral molecular hydrogen gas a series of experiments have been made over the years (no radius determination)
- MHI spectroscopy should be able to deliver an uncertainty $u_r(r_t) \approx 0.5\%$ (*)

(*) *Estimate analogous to Karr et al. PRA 94, 050501(R) (2016)*

Summary

- The spectroscopy of molecular hydrogen ions represents the link between the spectroscopy of the H-atom and the mass spectroscopy of simplest nuclei
- Established result: possibility of determining of certain mass ratios with competitive accuracy
- Such determinations profit very much, at present, from the charge radius determinations performed by ***other*** means
- We can expect more high-precision measurements to come in in the near future
- **Important**: push the QED calculations for this family of particles

Future:

- an independent accurate determination of the deuteron quadrupole moment
- a more accurate measurement of the triton charge radius
- a test of CPT symmetry by vibrational spectroscopy of H_2^+ vs. anti-H_2^+