

Mass of Helium-4 from ${}^4\text{He}^+/\text{D}_2^+$, ${}^4\text{He}^+/\text{H}_2\text{D}^+$ and ${}^4\text{He}^+/\text{}^{12}\text{C}^{3+}$

Edmund G. Myers

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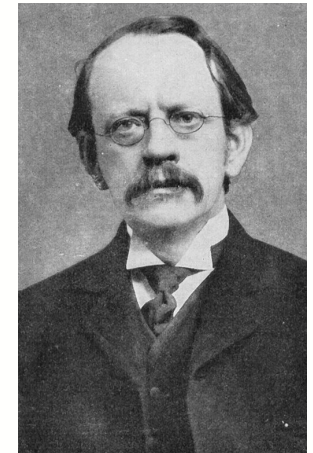
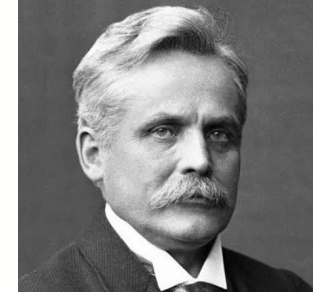
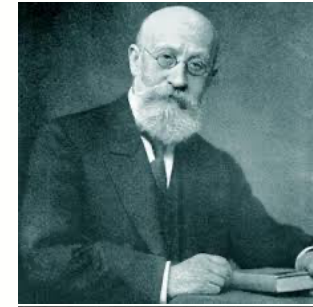
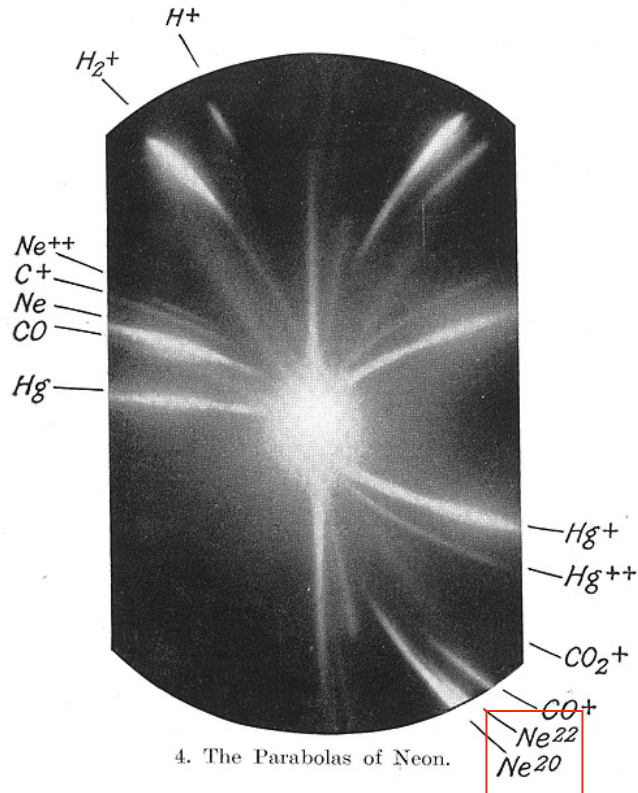
Team:

Moisés Medina Restrepo, Maria Fernandez Davila, Cristian Navarro

Support from US NSF and NIST

Early history of precision mass spec

- Eugen Goldstein 1886, Wilhelm Wien 1898: Canal (anode) rays
- J. J. Thompson (and F. W. Aston) 1913: **Separated** ^{20}Ne , ^{22}Ne



Early history of mass spec: Nuclear binding energy

F. W. Aston 1919: $4M[\text{H}] > M(^4\text{He})$, by 0.7%

$E = Mc^2 \rightarrow$ Binding energy: Nuclear fusion can power the Sun!

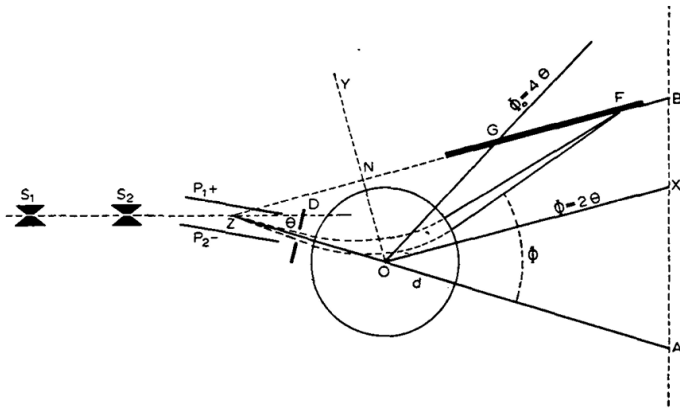


Fig.I. Diagram of mass spectrograph.



Focuses ions of **different energy** to same point

Obtain $M[e]$ from “ g -factor measurement” of ${}^4\text{He}^+$

- **Hydrogenlike ion:** Ratio of electron spin-flip (Zeeman) frequency f_{sf} to cyclotron frequency f_{c}

$$f_{\text{sf}}/f_{\text{c}} = (g_{\text{ion}}/2) (e/q)(m_{\text{ion}}/m_{\text{e}})$$

use g_{ion} from QED theory

- Best current “ g -factor” measurement of $M[e]$ uses ${}^{12}\text{C}^{5+}$: 2.8×10^{-11} , S. Sturm et al, Nature (2014)

Motivation for ${}^4\text{He}^+$ versus C^{5+} :

- Theory: Lower Z : Smaller relativistic, QED, and nuclear size corrections
- Experimental: Lower q : Smaller image-charge and ion-detector shifts

But need $M[{}^4\text{He}]$...

[HD⁺, H₂⁺ spectroscopy] + [QED theory + Penning trap $m_e/m_p, m_e/m_d$] Tests Angstrom-range “new force” between p, d, e

PHYSICAL REVIEW RESEARCH 3, L022028 (2021)

Letter

Three-body QED test and fifth-force constraint from vibrations and rotations of HD⁺

M. Germann,^{1,*} S. Patra^{1,†}, J.-Ph. Karr^{2,3}, L. Hilico^{2,3}, V. I. Korobov⁴, E. J. Salumbides,¹ K. S. E. Eikema¹,
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nature physics

Article

<https://doi.org/10.1038/s41567-023-02088-2>

Test of charged baryon interaction with high-resolution vibrational spectroscopy of molecular hydrogen ions

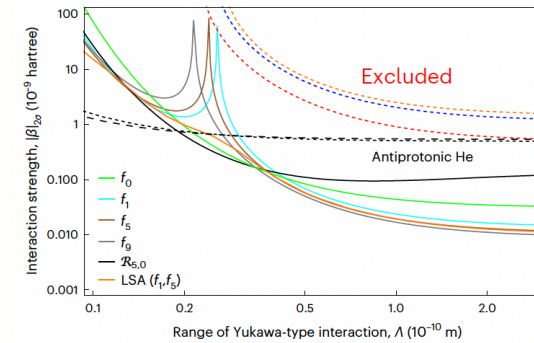
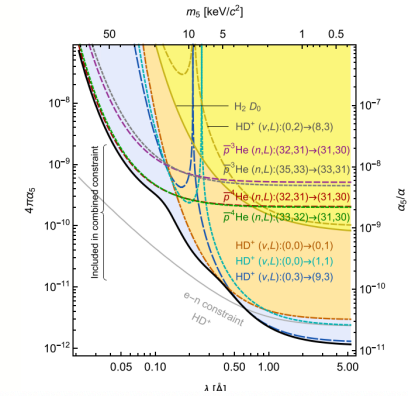
Received: 27 May 2022

S. Alighanbari¹, I. V. Kortunov, G. S. Giri² & S. Schiller¹ ✉

Accepted: 9 May 2023

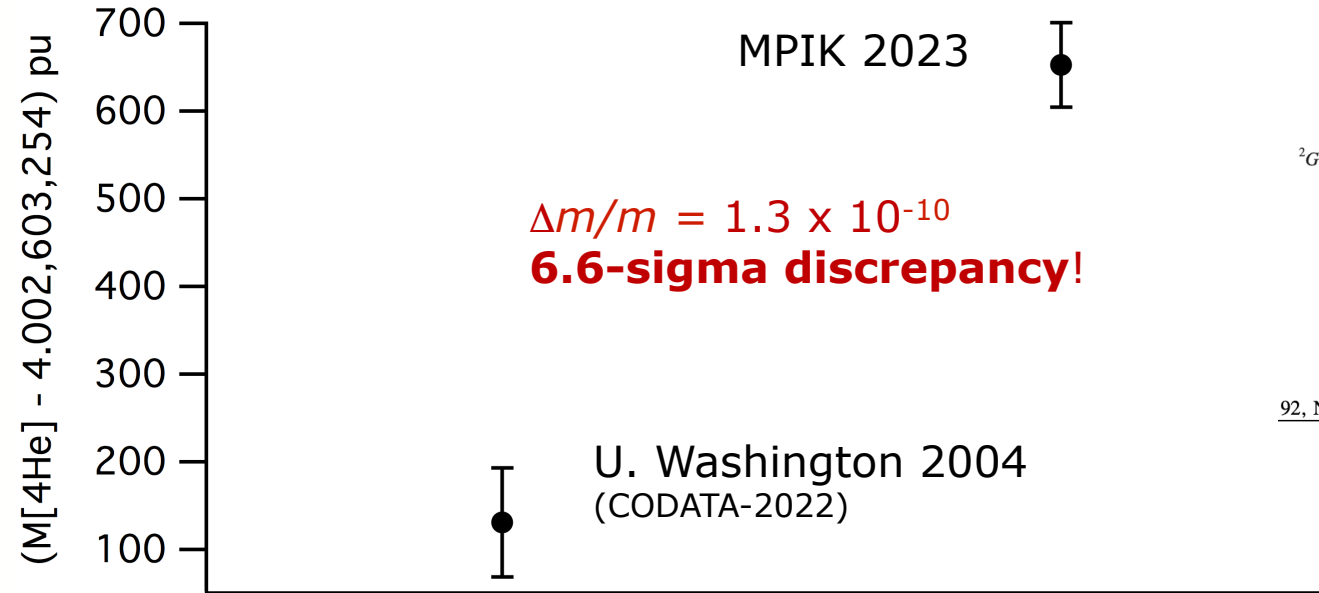
$$V_{\alpha_5, \lambda}(r) = \hbar c \alpha_5 A_1 A_2 \frac{e^{-r/\lambda}}{r}$$

M. GERMANN *et al.*



Limits on p - d coupling parameter vs range

Existing precision values for mass ^4He



Both measurements: $^4\text{He}^{2+} / ^{12}\text{C}^{6+}$

PHYSICAL REVIEW LETTERS **131**, 093201 (2023)

Penning-Trap Mass Measurement of Helium-4

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³Heidelberg University, Grabengasse 1, 69117 Heidelberg, Germany

92, NUMBER 22

PHYSICAL REVIEW LETTERS

week ending
4 JUNE 2004

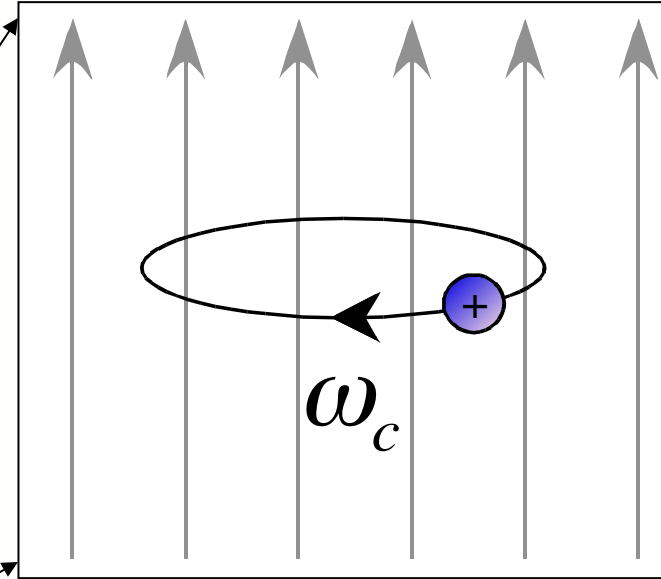
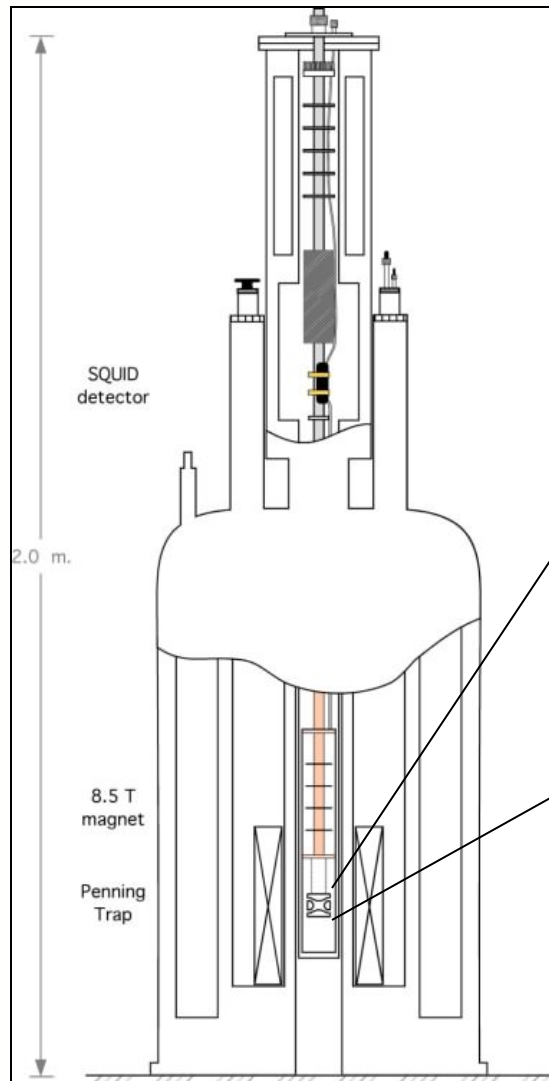
Ultraprecise Atomic Mass Measurement of the α Particle and ^4He

R. S. Van Dyck, Jr., S. L. Zafonte, S. Van Liew, D. B. Pinegar, and P. B. Schwinberg
Department of Physics, University of Washington, Seattle, Washington 98195-1560, USA

Penning Trap: Measures Cyclotron Frequency Ratio (CFR)

FSU Trap
8.5 Tesla

*Transferred
from MIT
in 2003*



$$\omega_c = \frac{B}{(m/q)}$$

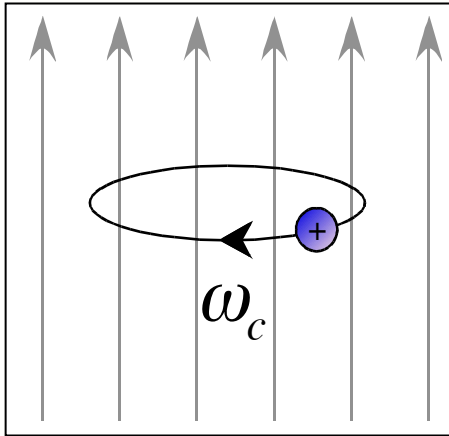


$$R = \frac{\omega_{c0}}{\omega_{c1}} = \frac{q_0 m_1}{q_1 m_0}$$

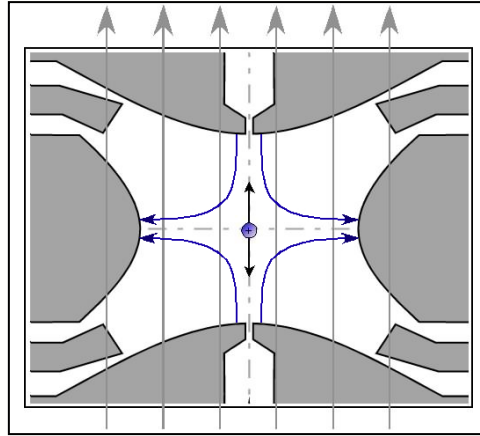
For "atomic mass" in u, need to (ultimately)
reference to ^{12}C

Penning trap: Three normal modes

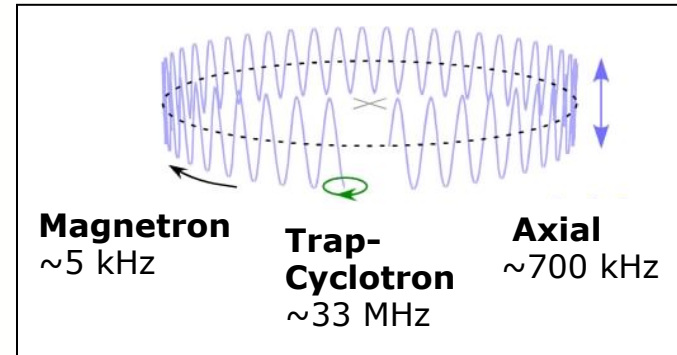
Uniform B -field



Quadrupole Potential



3 Normal Modes

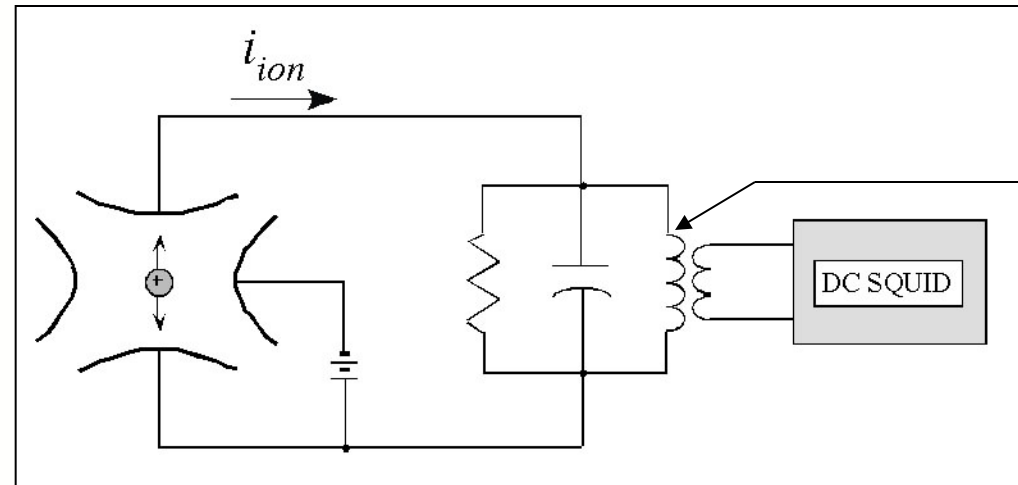


$$\omega_c^2 = \omega_{ct}^2 + \omega_z^2 + \omega_m^2$$

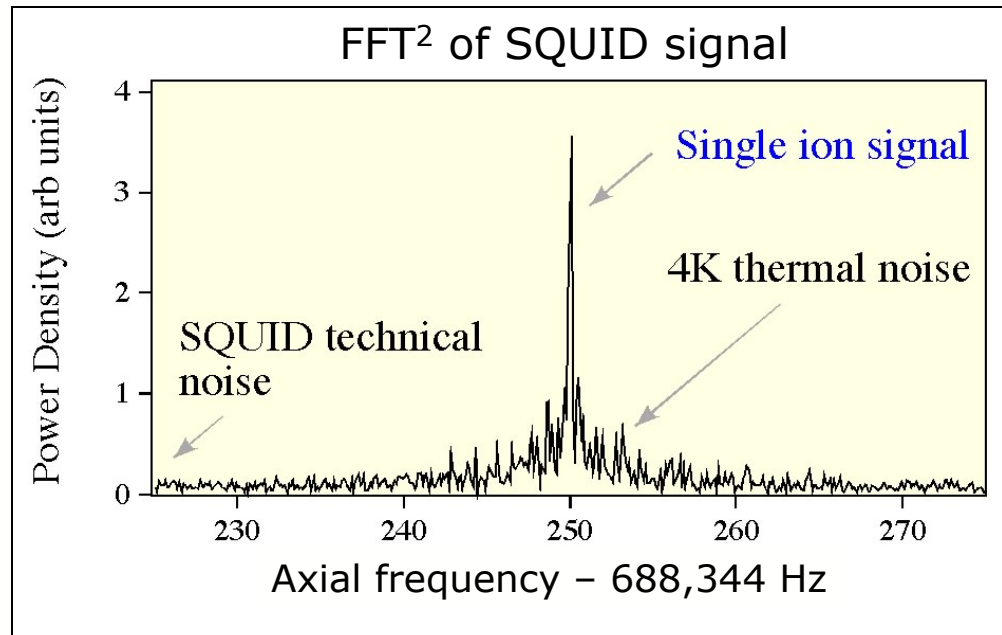
Relates the "true" cyclotron frequency ω_c to the *measurable* **trap-cyclotron frequency** ω_{ct} , **axial frequency** ω_z , and **magnetron frequency** ω_m .

(Even if electrodes are tilted or deformed elliptically: "Invariance Theorem", *L S Brown and G Gabrielse, PRA 1982*)

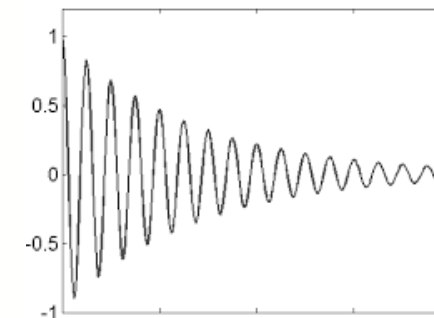
Image current detection (and cooling) of Axial Motion



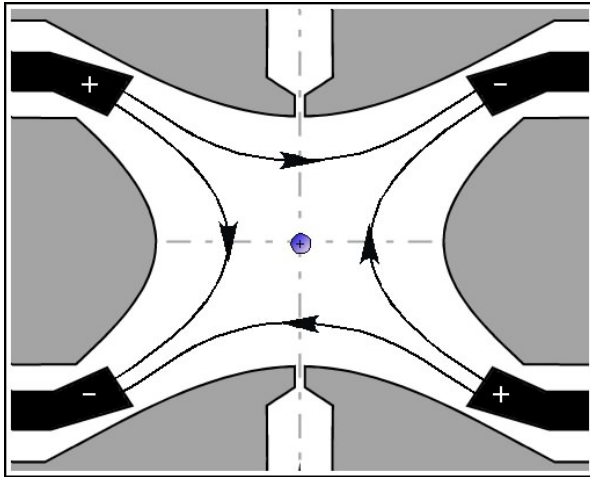
Superconducting self-resonant inductor ($Q \sim 34,000$)



Measure the phase of a *ring-down* of the *pulsed* axial motion

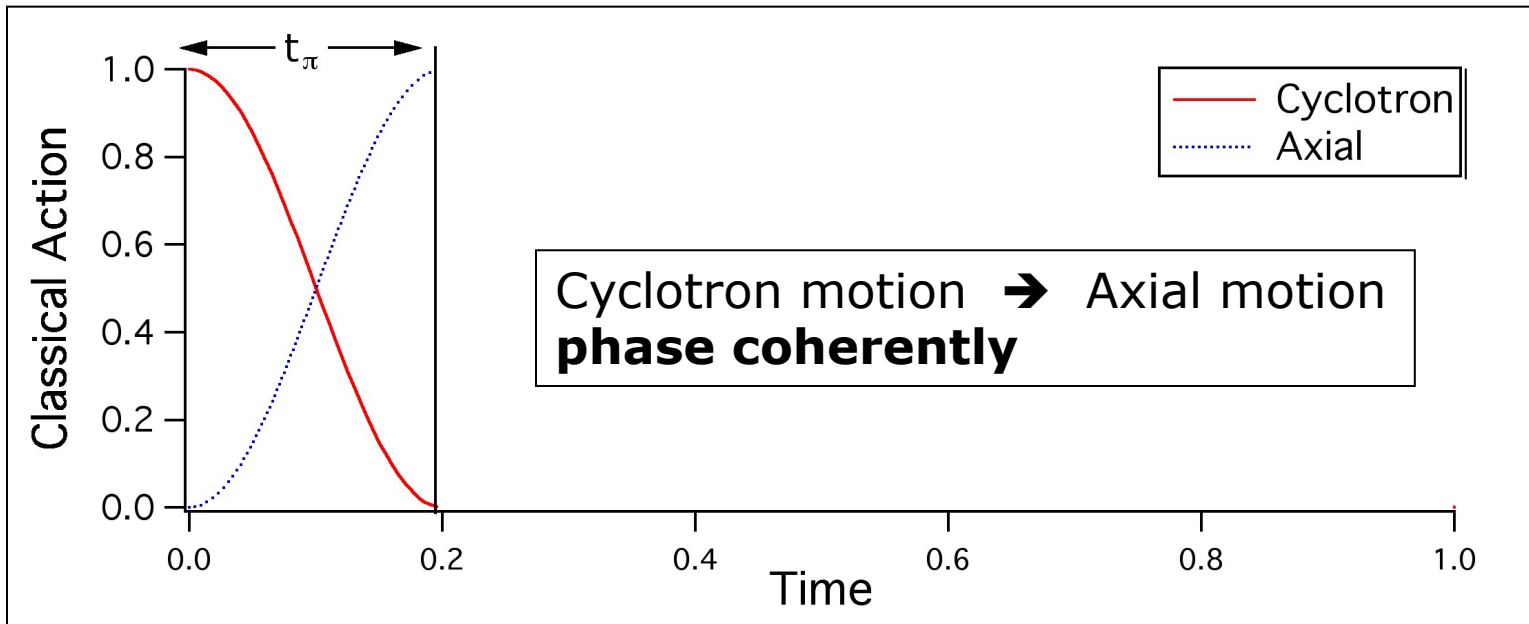


Detecting (and cooling) Cyclotron Motion



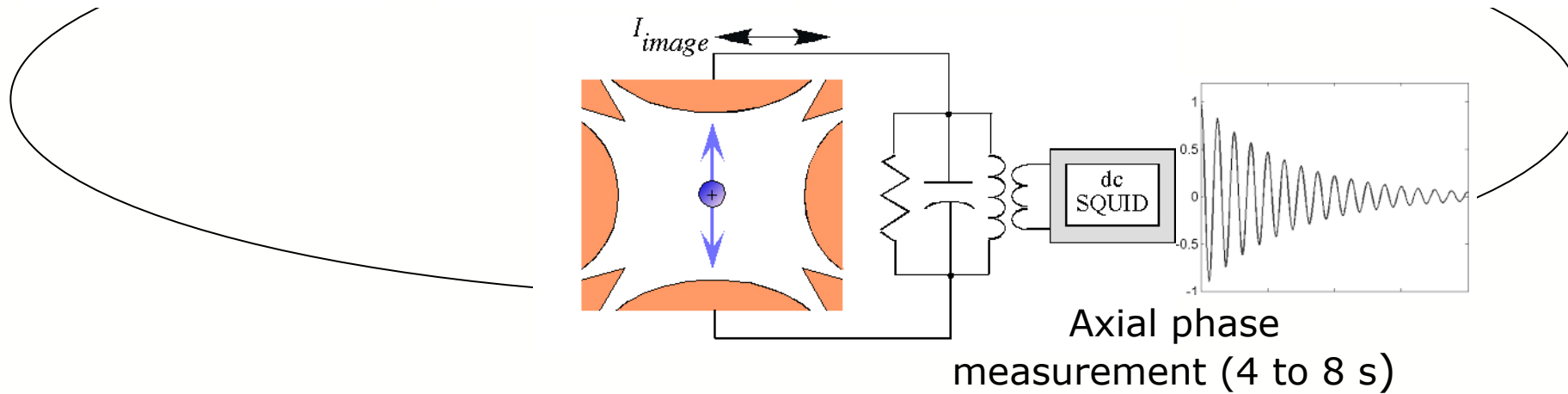
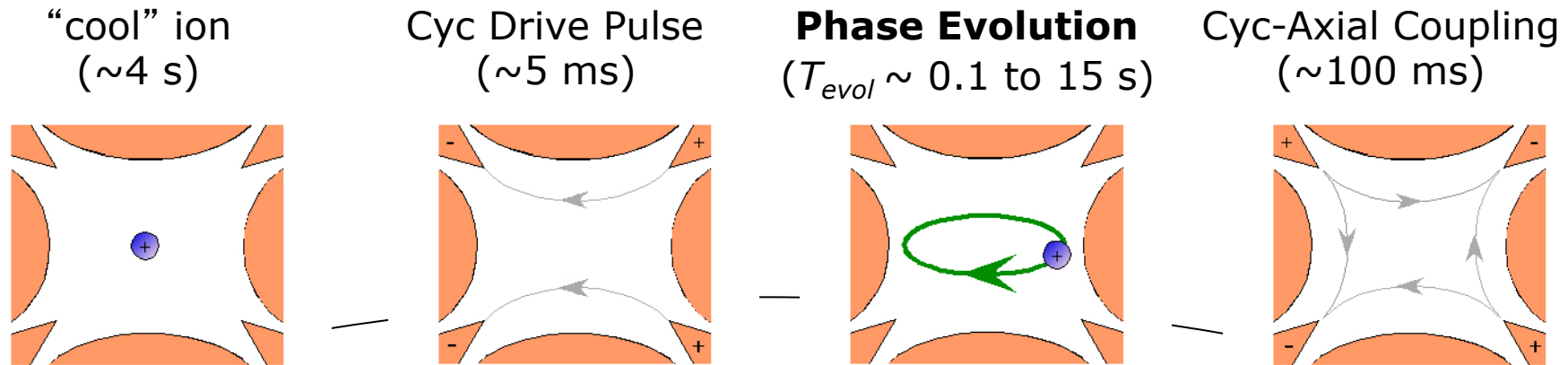
Tilted, quadrupole, electric field at $\omega_{CC} = \omega_{CT} - \omega_Z$
couples the axial and cyclotron modes

Cornell, ..Pritchard, PRA 1990

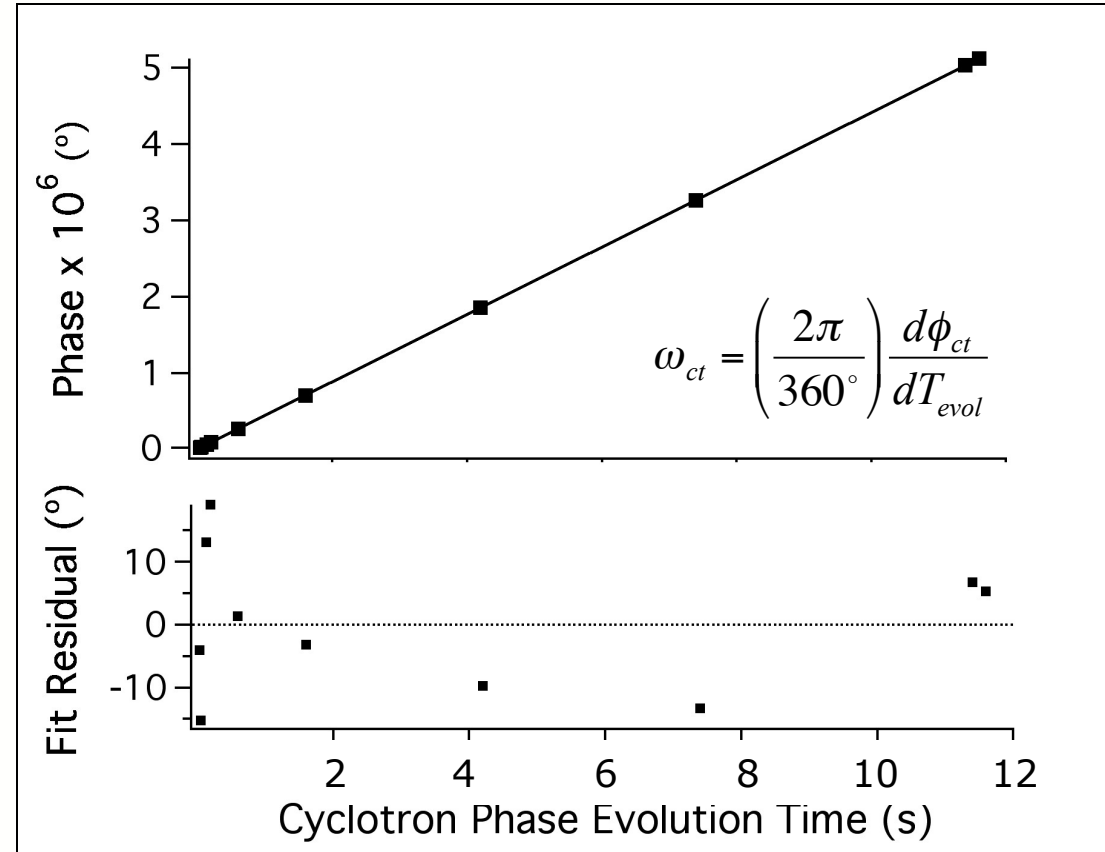


Measuring Trap-Cyclotron Frequency

“Pulse and Phase Technique” (PnP)

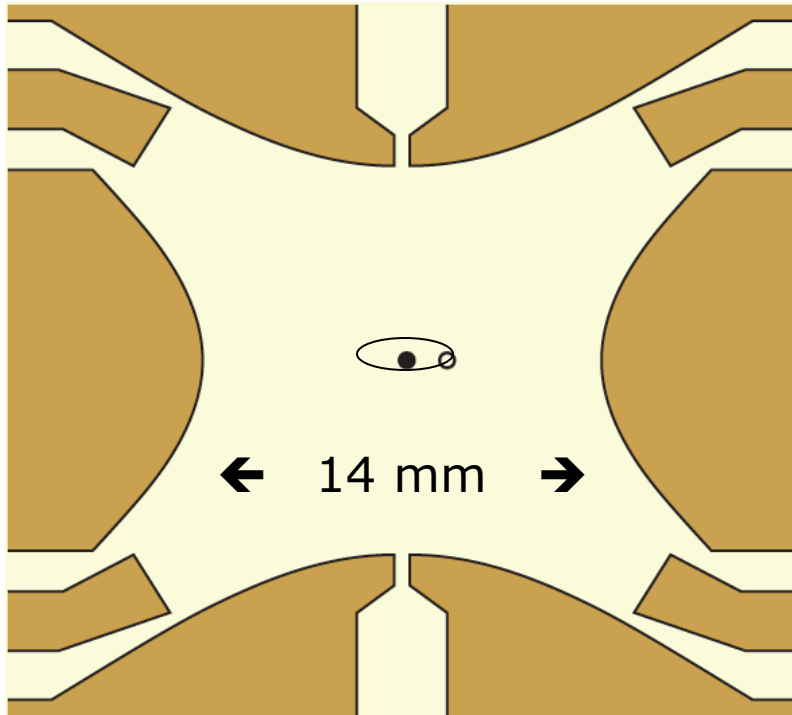


Measuring Trap-Cyclotron Frequency



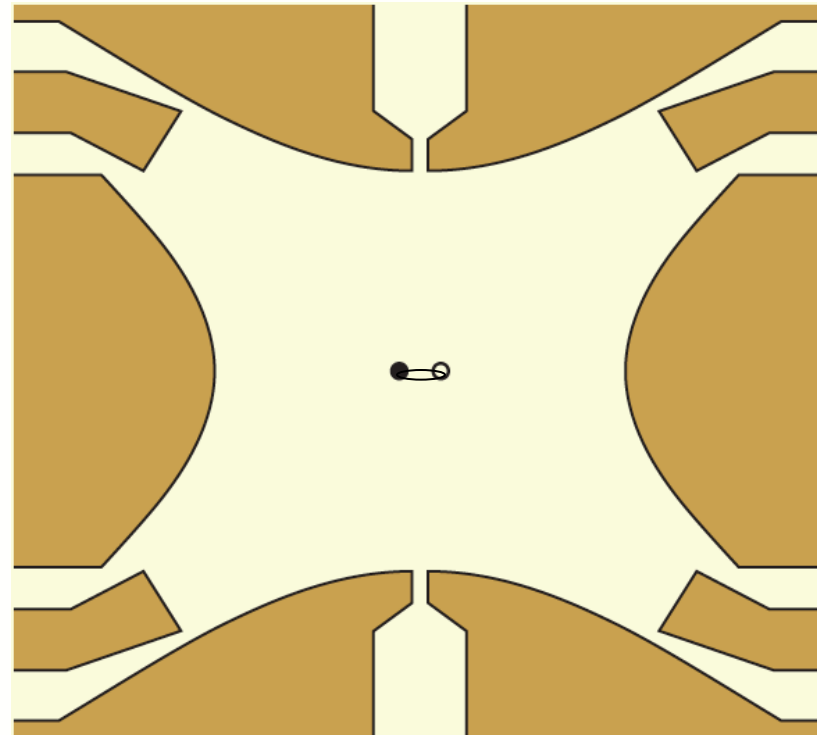
***B*-field variation: Two, Two-Ion Techniques**

One ion centered.
Second ion "parked" in
2 mm radius cyclotron orbit



Alternating

Both ions in **0.4 mm** radius
magnetron orbit,
coupled by Coulomb interaction



Simultaneous

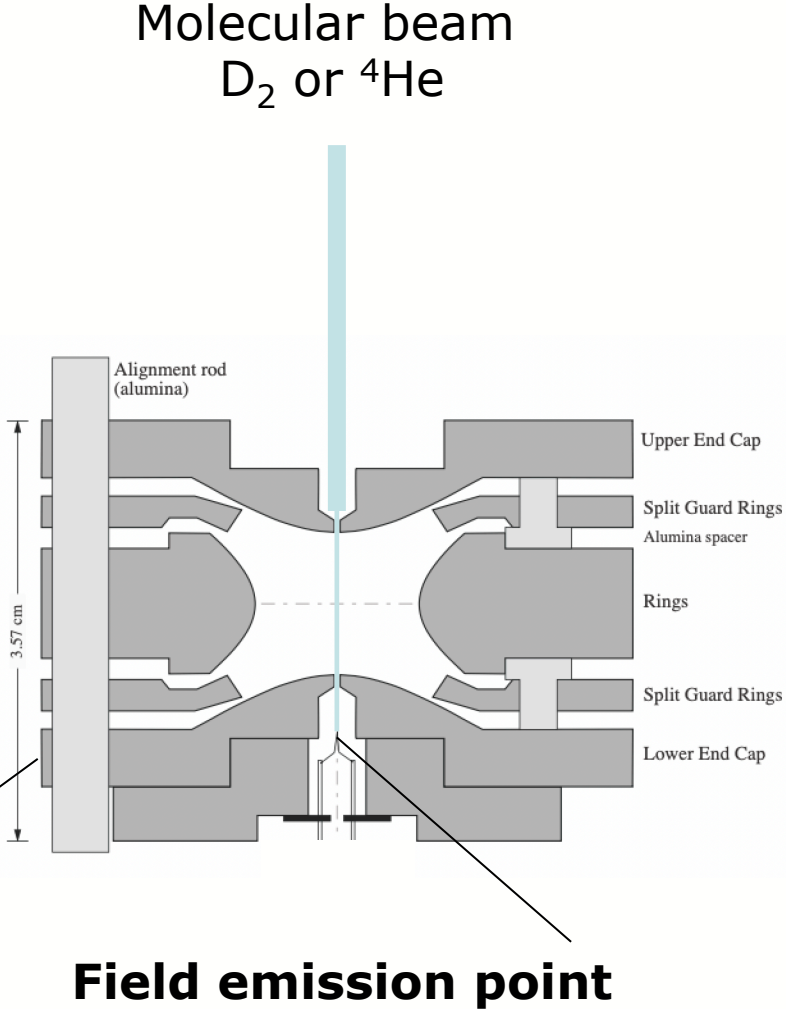
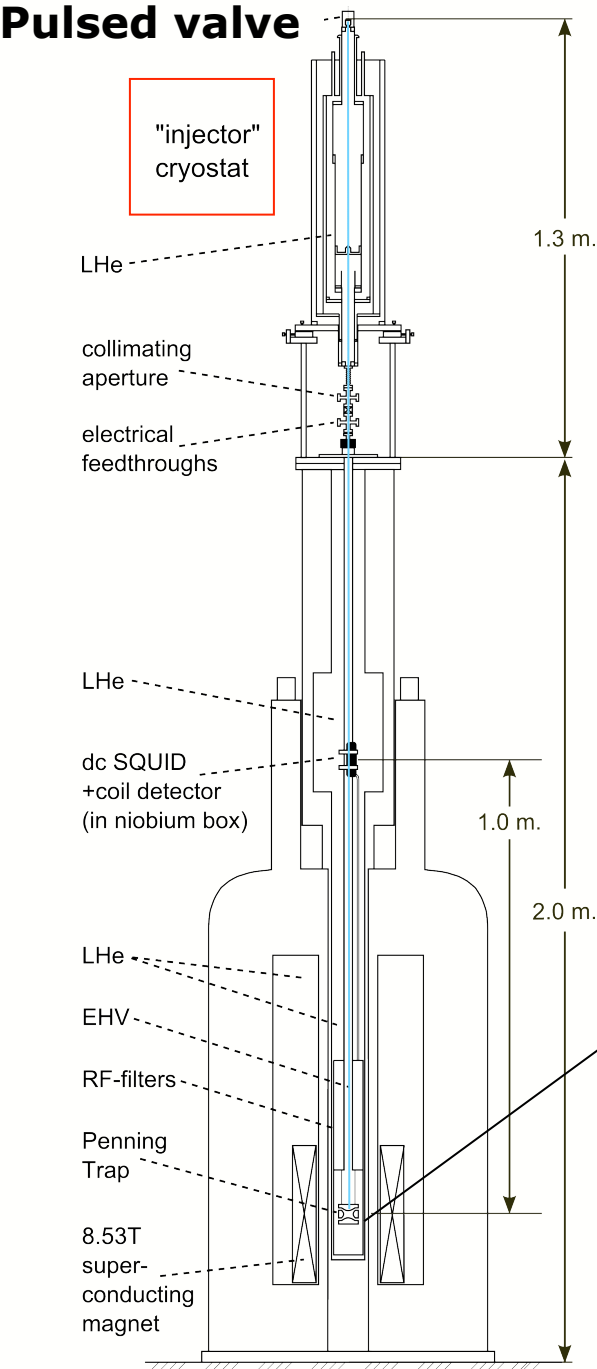
For $M[{}^4\text{He}]$ we only used *Alternating*

Rainville,
Thompson,
Pritchard,
Science 2004

Molecular beam injector for in-trap ion making

Hydrogen and helium are poorly cryo-pumped

Reduce gas load into trap volume by injecting a pulsed, pre-collimated molecular beam



${}^4\text{He}^+/\text{D}_2^+$ and ${}^4\text{He}^+/\text{H}_2\text{D}^+$

Why use molecular ions as references?

With ion pairs with similar m/q but different q (and m) there are additional systematics:

- Initial cyclotron energy
- Ion-detector interaction
- Image charges in electrodes
- Ion-ion interaction

Need molecules to get same q and similar m/q

Problems with Molecular ions: Stored Energy and Polarizability Shifts

(Binding energies usually known to sufficient accuracy)

If **no Electric Dipole**: Stored Ro-vibrational energy (H_2^+ , etc.) $\Delta m = \Delta E/c^2$

If **Electric Dipole**: Polarizability shifts the cyclotron frequency ($\mathbf{E} = \mathbf{V} \times \mathbf{B}$ causes Stark shift)

$$\Delta\omega_c/\omega_c = -\alpha_{xx} B^2/m, \quad \alpha_{xx} \text{ polarizability transverse to } B\text{-field}$$

${}^4\text{He}^+/\text{D}_2^+$

Previous work with H_2^+

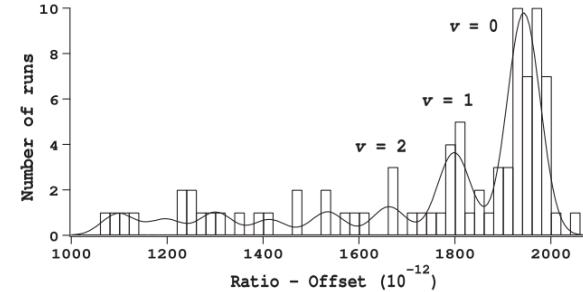
PHYSICAL REVIEW LETTERS **124**, 013001 (2020)

ation

Deuteron-to-Proton Mass Ratio from the Cyclotron Frequency Ratio of H_2^+ to D^+ with H_2^+ in a Resolved Vibrational State

David J. Fink and Edmund G. Myers

Department of Physics, Florida State University, Tallahassee, Florida 32306-4350, USA



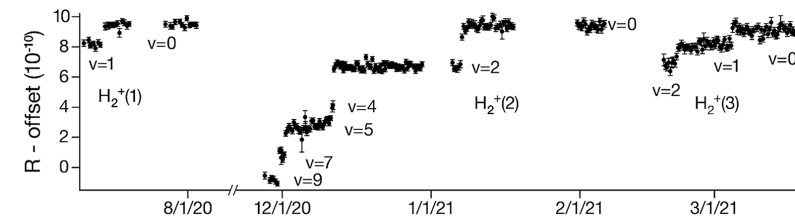
PHYSICAL REVIEW LETTERS **127**, 243001 (2021)

on

Deuteron-to-Proton Mass Ratio from Simultaneous Measurement of the Cyclotron Frequencies of H_2^+ and D^+

David J. Fink  and Edmund G. Myers 

Department of Physics, Florida State University, Tallahassee, Florida 32306-4350, USA

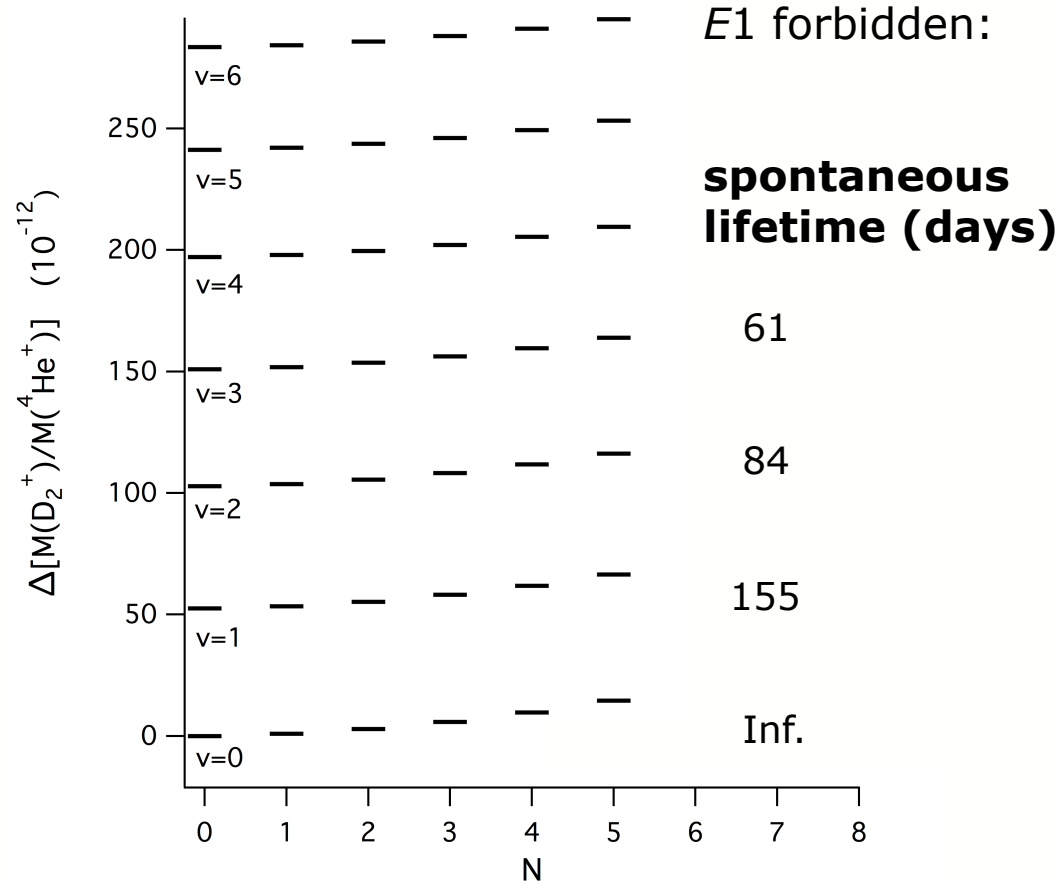


Tracked spontaneous vibrational decay $v=9$ to $v=0$ over 50 days!

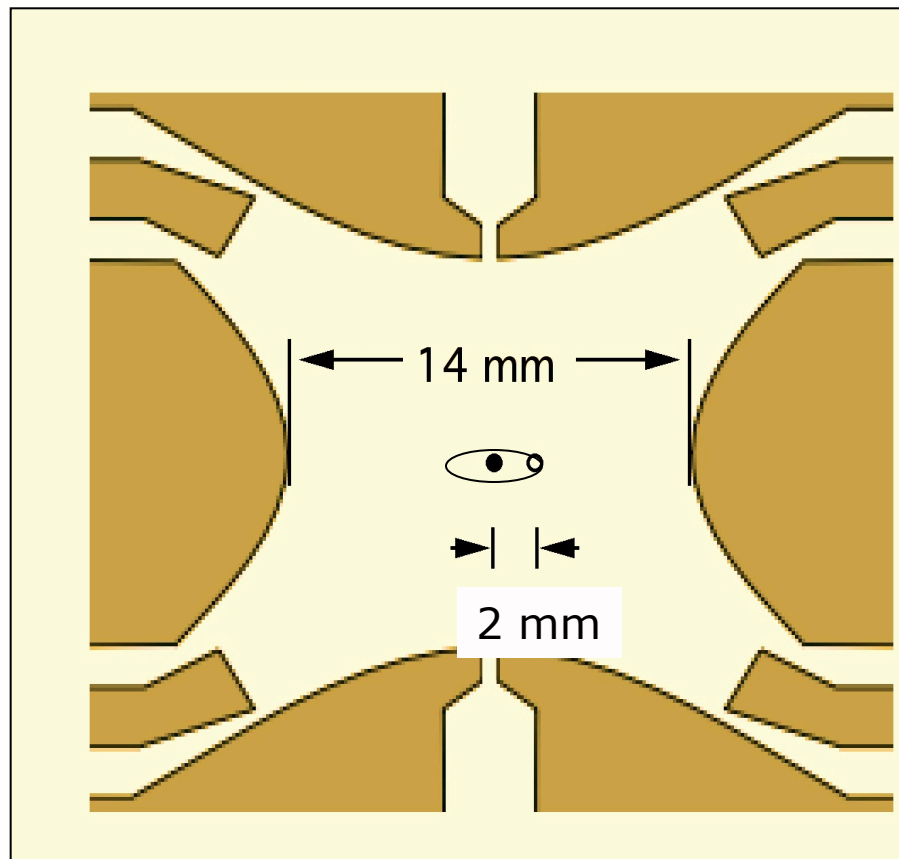
D₂⁺ Ro-vibrational energy levels

Shift to He⁺/D₂⁺ CFR due to D₂⁺ ro-vibrational energy

**D₂⁺ Vibrational spacing
~ 5 x 10⁻¹¹ in mass**



Stark-quenching speeds-up D_2^+ vibrational decay



H_2^+ in $\rho_c = 2 \text{ mm}$, $B = 8.5 \text{ T}$:

$$\mathbf{E} = \mathbf{v} \times \mathbf{B}$$

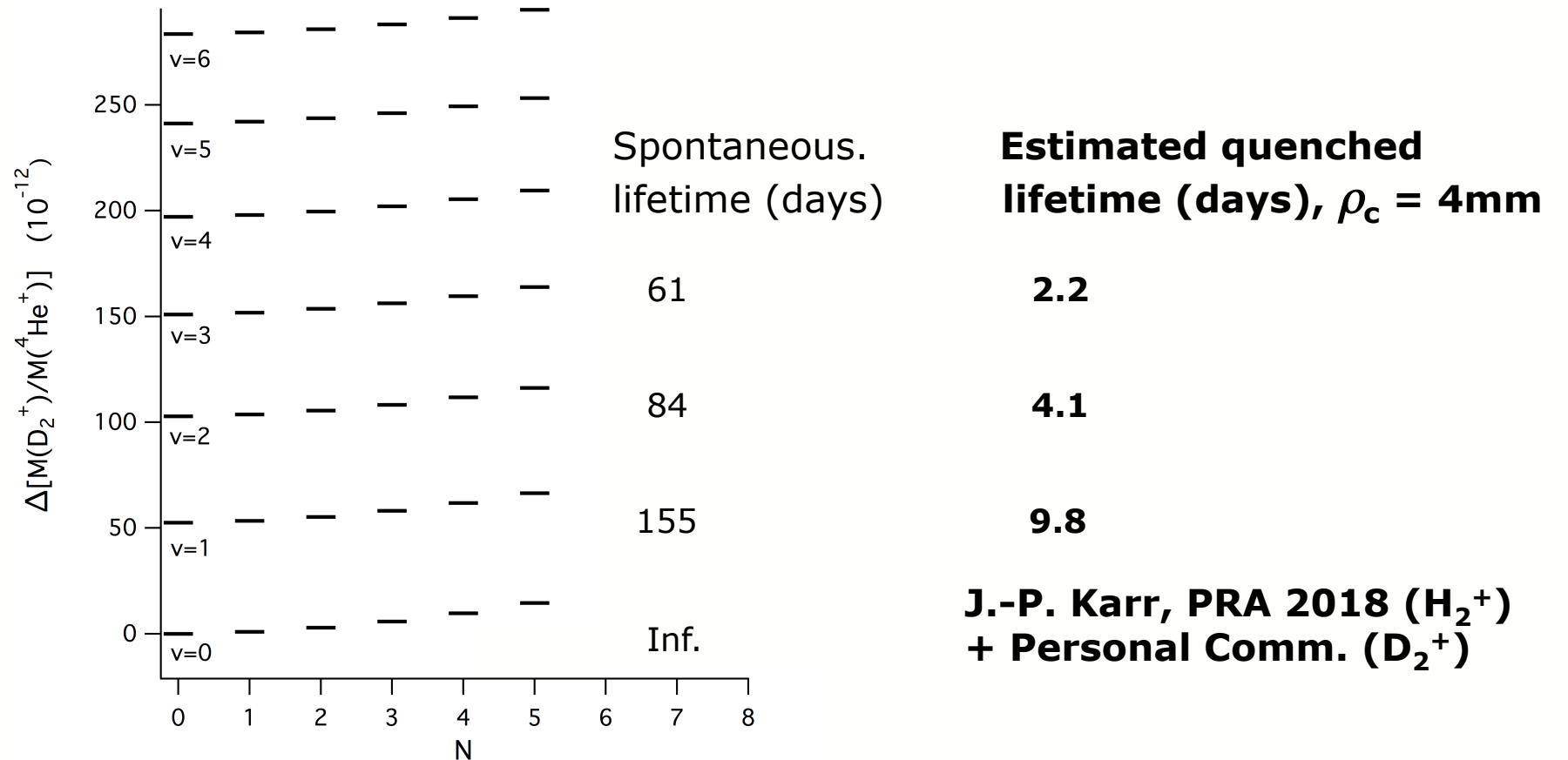
$$\rightarrow \mathbf{E} = 70 \text{ kV/cm}$$

Induces electric dipole:
shortens lifetime of vibrational levels

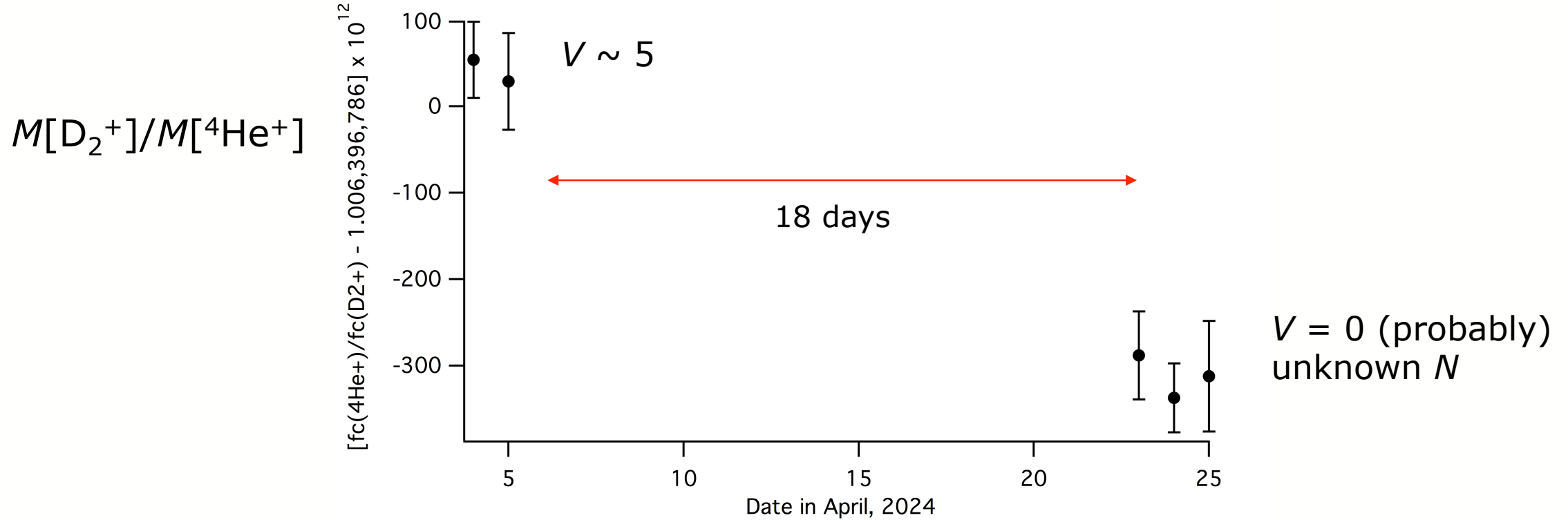
For D_2^+ , $\rho_c = 4.2 \text{ mm}$

$$\rightarrow \mathbf{E} = 79 \text{ kV/cm}$$

D₂⁺ Ro-vibrational energy levels



Stark-Quenching of D_2^+ in $\rho_c = 4.2$ mm

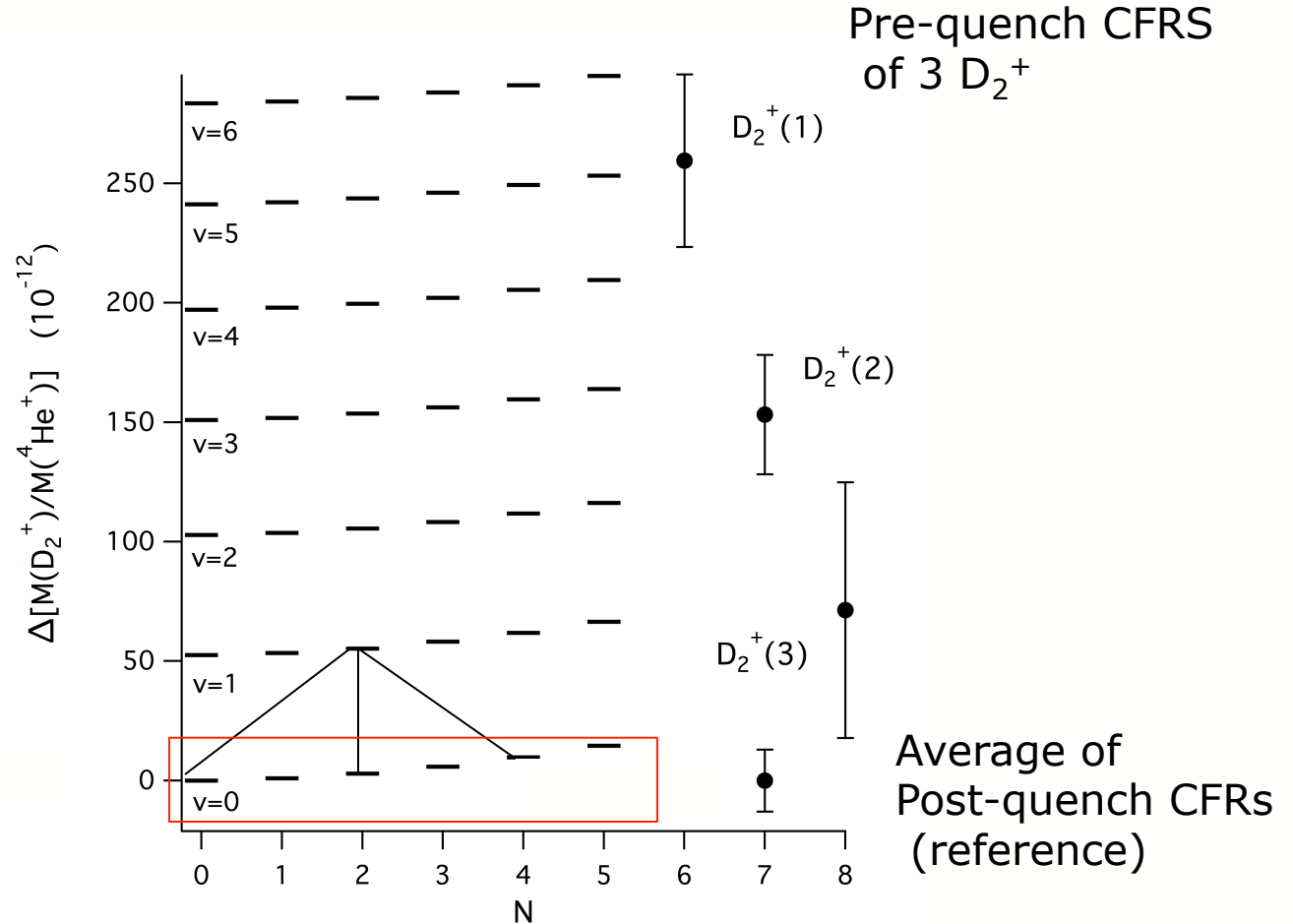


Used 3 D_2^+ : Modeled rotational energy in $v=0$

Estimate average rotational energy in $v=0$

- Use pre-quench CFR measurements to estimate v_{init}
- Assume a Boltzmann distribution over N in v_{init} , corresponding to parent D_2 at 300 K
- Estimate final rotational distribution in $v=0$ by modelling cascade from a given initial v_{init} to $v=0$
- Obtained CFR corrections of **9.5, 6.9, 5.1 $\times 10^{-12}$** for $D_2^+ = 1, 2, 3$ (with **100%** uncertainty)

(Polarizability shifts $< 10^{-12}$)



${}^4\text{He}^+/\text{H}_2\text{D}^+$

- **The third D_2^+ died by becoming H_2D^+ !** ($\text{D}_2^+ + \text{H}_2 \rightarrow \text{H}_2\text{D}^+ + \text{D}$)

Fortunately:

- H_2D^+ has longer lifetime in the trap than D_2^+ ! (>160 hours)
- *E1* decays to vibrational ground ro-vibrational state!
- Binding energy from Born-Oppenheimer for H_3^+ + zero-point energy
Pavenello, Adomowicz JCP (2003) Ramanlal, Polyansky, Tennyson, Astron. Astrophys. (2003)

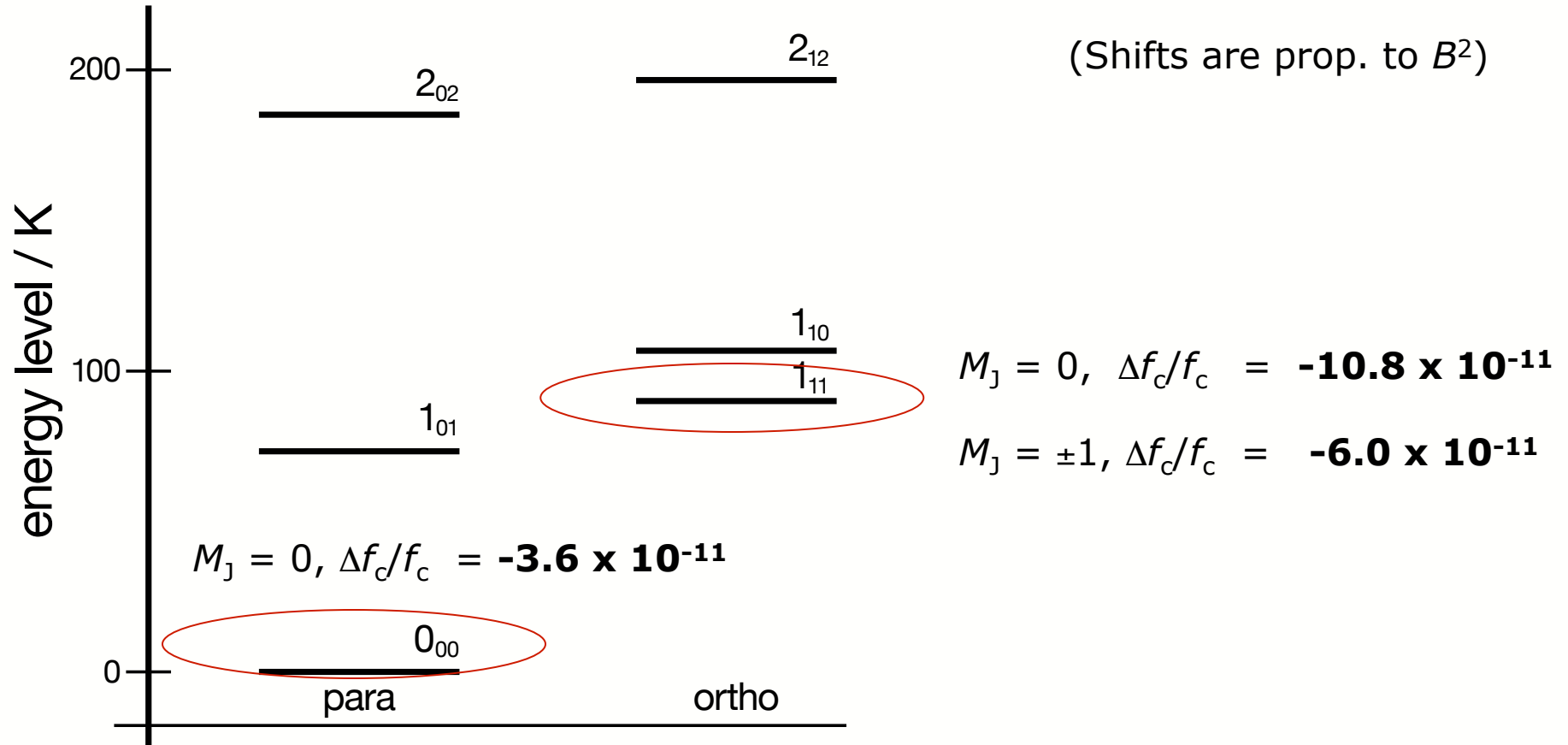
Unfortunately:

- Two ground rotational states, Ortho (proton spin = 1), Para (proton spin = 0)
- **Significant, state-dependent polarizability**

H₂D⁺ Polarizability Shifts as fraction of CFR

Rotational levels of
H₂D⁺ vibrational
Groundstate

Notation: \mathbf{J}_{KaKc}



Energies and A -values for polarizability calculation from
J. Tennyson et al, ExoMol Line list, MNRAS **519**, 6333 (2023).

$M[{}^4\text{He}]$ from the three D_2^+ and one H_2D^+

$$M[\text{D}_2^+(0,0)]/M[{}^4\text{He}^+] =$$

1.006 396 785 720 (14)(10)(7) (19)
 Fit Sys Rot Total

$$M[\text{H}_2\text{D}^+(0_{00})]/M[{}^4\text{He}^+] =$$

1.006 783 656 787 (11)(10)(43) (46)
 Fit Sys Pol Total

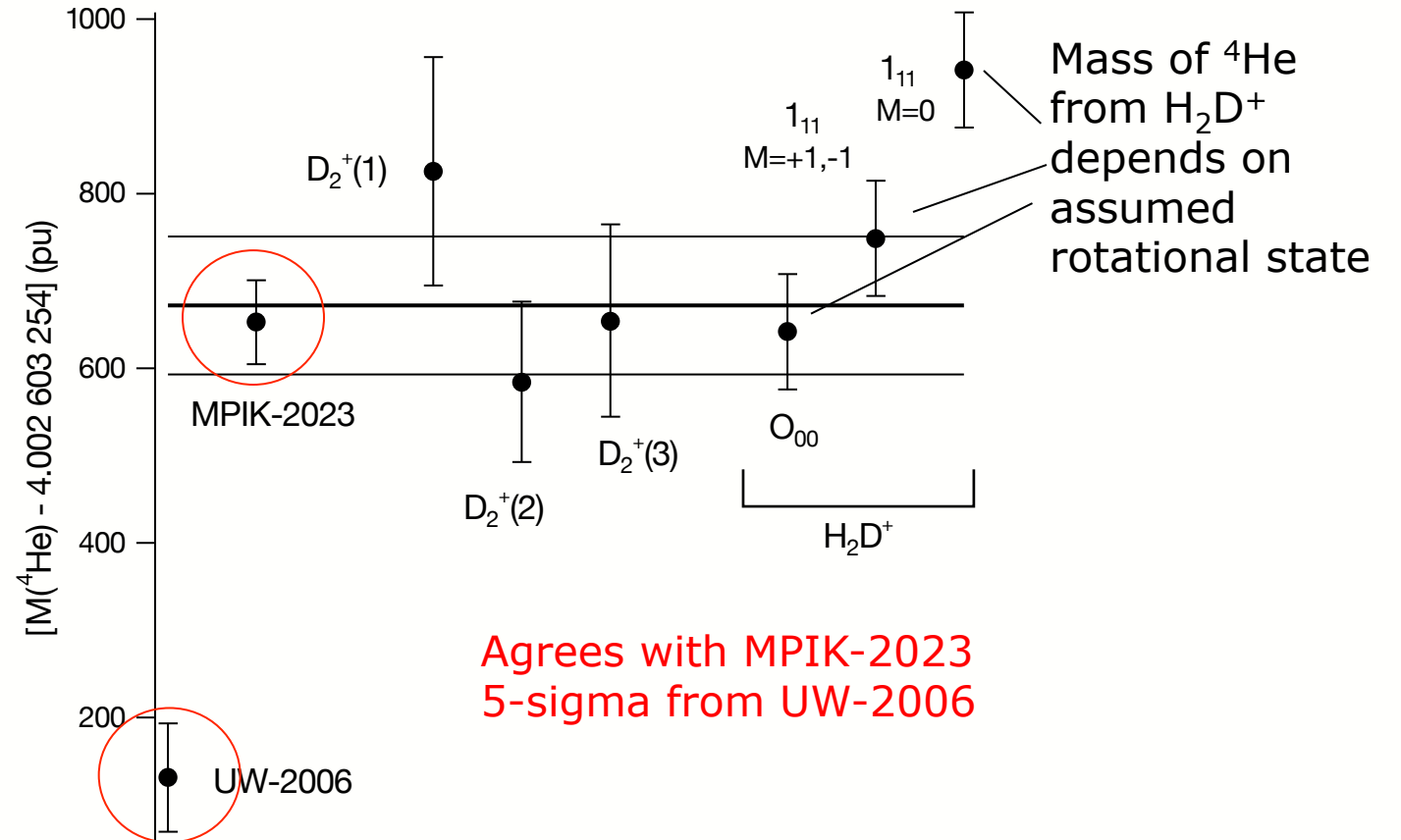
Assume CODATA-22 values for $M[p]$, $M[d]$, $M[e]$ (mainly from MPIK)

Final result:

Combines values from D_2^+ ,
 de-weights contribution from H_2D^+

$M[{}^4\text{He}] = 4.002\,603\,254\,672(79)$
 (2×10^{-11})

"Model dependent"



$M[{}^4\text{He}]$ from ${}^4\text{He}^+/\text{C}^{3+}$

- C^{3+} is difficult to make and isolate in our trap (\sim day)
- Short C^{3+} lifetime \sim 24 hours (\sim 4 runs) at trap center: we made 11 C^{3+}

- **Different q, m**
- Closer in m/q than ${}^4\text{He}^+/\text{D}_2^+$, ${}^4\text{He}^+/\text{H}_2\text{D}^+$!

Amplitude-dependent frequency shifts due to Trap Imperfections and Special Relativity

Electric

$$\Phi(\vec{r}) = \frac{V_r}{2} \sum_{n=2}^{even} C_n \left(\frac{r}{d}\right)^n P_n(\cos\theta)$$

$$\frac{\Delta\omega_z}{\omega_z} = \frac{1}{4} \frac{B_2}{B_0} \left(\rho_m^2 + \frac{\omega_c}{\omega_m} \rho_c^2 \right) + \frac{3}{8} \frac{B_4}{B_0} \left(z^2 \rho_m^2 - \rho_m^4 + \frac{\omega_c}{\omega_m} z^2 \rho_c^2 - \frac{\omega_c}{\omega_m} \rho_c^4 - \frac{\omega_c}{\omega_m} 2\rho_c^2 \rho_m^2 \right)$$

$$\frac{\Delta\omega_{ct}}{\omega_{ct}} = \frac{1}{2} \frac{B_2}{B_0} (z^2 - \rho_c^2 - \rho_m^2) + \frac{3}{8} \frac{B_4}{B_0} (z^4 - 4z^2 \rho_c^2 + \rho_c^4 - 4z^2 \rho_m^2 + 4\rho_c^2 \rho_m^2 + \rho_m^4)$$

Magnetic

$$\Psi(\vec{r}) = - \sum_{n=0}^{\infty} \frac{B_n}{n+1} r^{n+1} P_{n+1}(\cos\theta)$$

$$\frac{\Delta\omega_z}{\omega_z} = \frac{3}{4} \frac{C_4}{d^2} (z^2 - 2\rho_c^2 - 2\rho_m^2) + \frac{15}{16} \frac{C_6}{d^4} (z^4 - 6z^2 \rho_c^2 + 3\rho_c^4 - 6z^2 \rho_m^2 + 12\rho_c^2 \rho_m^2 + 3\rho_m^4)$$

$$\frac{\Delta\omega_{ct}}{\omega_{ct}} = -\frac{3}{2} \frac{\omega_m}{\omega_c} \frac{C_4}{d^2} (2z^2 - \rho_c^2 - 2\rho_m^2) - \frac{15}{8} \frac{\omega_m}{\omega_c} \frac{C_6}{d^4} (3z^4 - 6z^2 \rho_c^2 + \rho_c^4 - 12z^2 \rho_m^2 + 6\rho_c^2 \rho_m^2 + 3\rho_m^4)$$

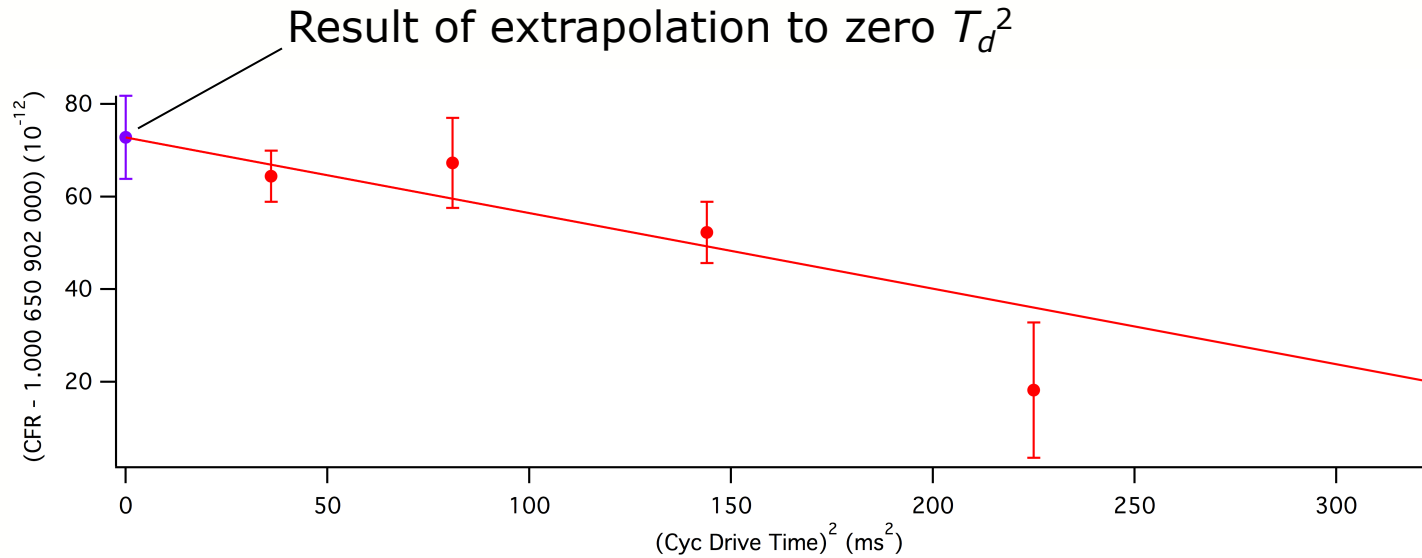
J.K. Thompson, S. Rainville, PhD 2003

Special Relativity

$$\frac{\Delta\omega_c}{\omega_c} = -\frac{\omega_c^2}{2c^2} \rho_c^2$$

Remove main relativistic shift: CFR versus ρ_c^2

ρ_c is proportional to Cyclotron Drive Time T_d $\Delta R/R = (-1/2c^2)[(\rho_{c1}\omega_{c1})^2 - (\rho_{c2}\omega_{c2})^2] \propto T_d^2$



CFR (from fit) = $f_c(\text{C}^{3+})/f_c(\text{}^4\text{He}^+) = 1.000\ 650\ 902\ 073\ 3(88)$

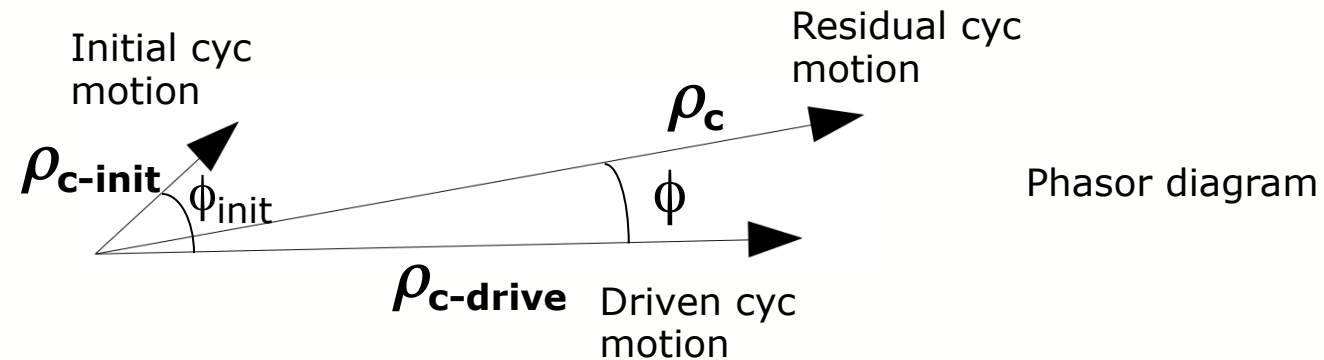
Uncertainty includes: Statistical, main relativistic shift,
and trap imperfection and ion-ion shifts proportional to ρ_c^2

Other Systematic Corrections

TABLE I. Systematic corrections and uncertainties to the $f_c(\text{C}^{3+})/f_c(\text{He}^+)$ CFR. Units are 10^{-12} .

Source	Correction	Uncertainty
Initial thermal energy	-4.9	0.7
Ion-detector interaction	-15.8	1.2
Image charge	5.6	0.1
Trap anharmonicities	0.0	0.4
Ion-ion interaction	-0.3	<0.1
Average ion position	-0.5	0.4
Trap heating	-2.1	0.7
Total	-17.9	1.7

Initial thermal cyclotron motion affects radius of cyclotron motion during PnP

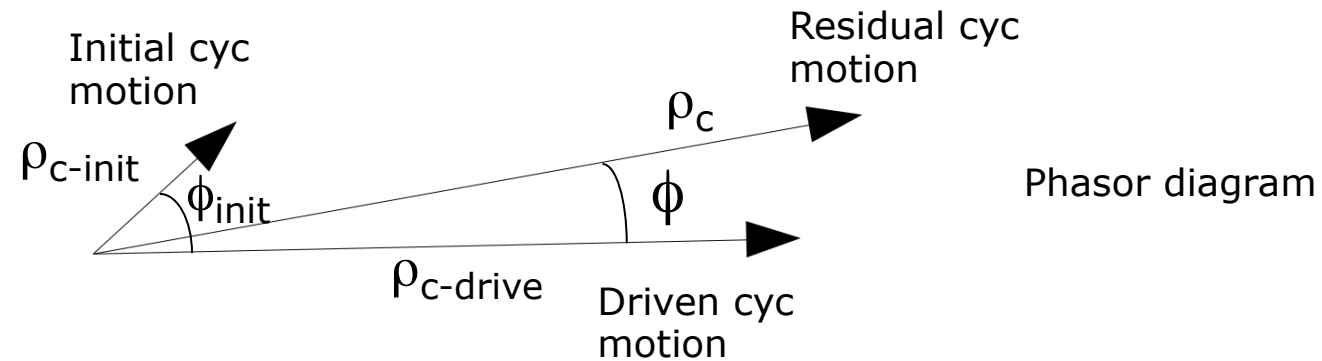


$$\rho_c^2 = \rho_{c-drive}^2 + 2 \rho_{c-drive} \rho_{c-init} \cos(\phi_{init}) + \rho_{c-init}^2$$

Can relate to cyclotron temperature T_c and axial temperature T_z :

$$(\omega_{ct} \rho_{c-init})^2 / 2m = E_{c_init} = k_B T_c = (\omega_{ct} / \omega_z) k_B T_z, \quad T_z = 4.2 \text{ K}$$

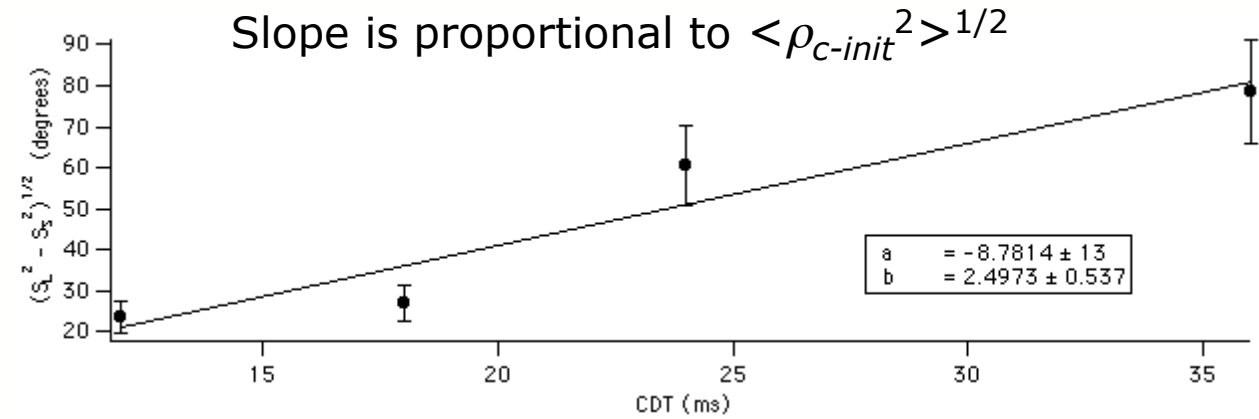
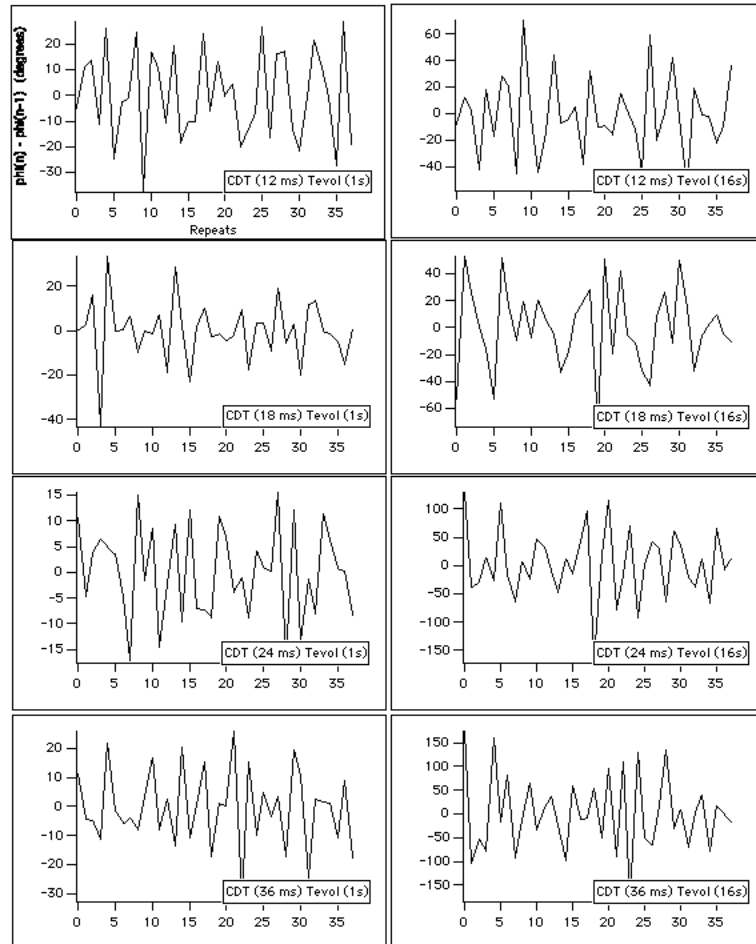
Initial thermal cyclotron motion affects radius of cyclotron motion during PnP



$$\rho_c^2 = \rho_{c-drive}^2 + 2 \rho_{c-drive} \rho_{c-init} \cos(\phi_{init}) + \rho_{c-init}^2$$

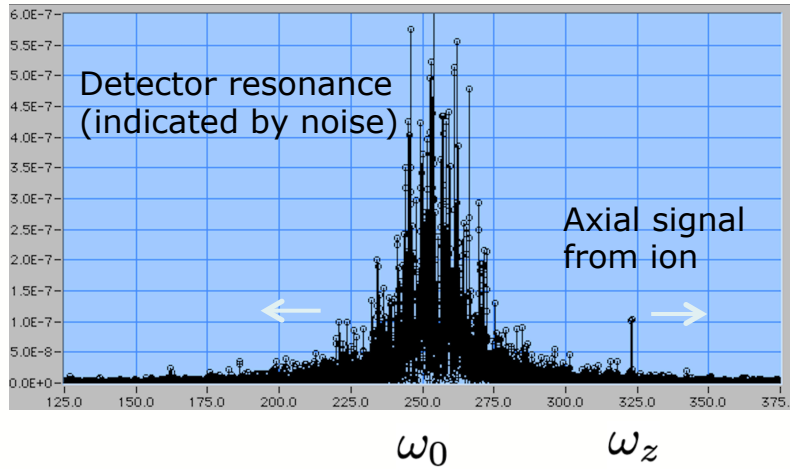
- Obtain ρ_{c-init} **directly** by measuring contribution to **relativistic noise on f_c**

Initial cyclotron energy from contribution to Phase Noise from Relativistic Frequency Noise



- Measure Phase fluctuations for long and short PnP phase evolution times to get frequency noise
- Vary Cyc. Drive Time to separate rel. frequency noise from *B*-field variation

Ion-detector interaction



Ion axial frequency and detector resonance repel each other

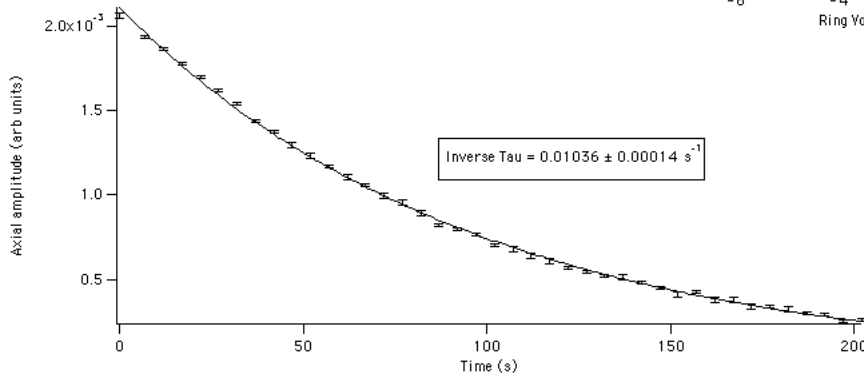
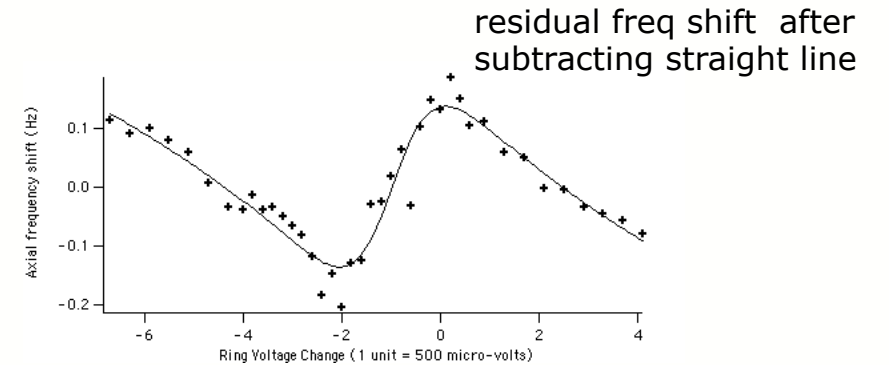
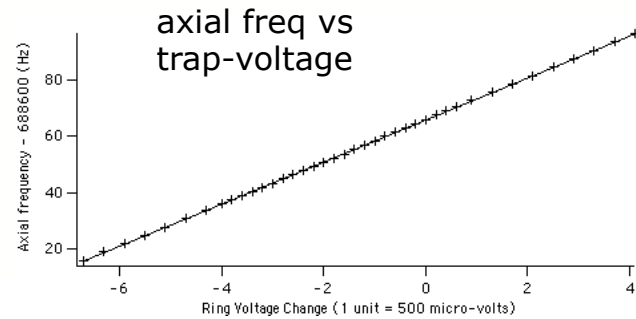
Shift to axial frequency:

$$\Delta\omega_z = \frac{(\gamma_0\gamma_z/4)(\omega_z - \omega_0)}{[(\omega_z - \omega_0)^2 + (\gamma_0/2)^2]}$$

Detector damping rate

Ion damping rate on resonance

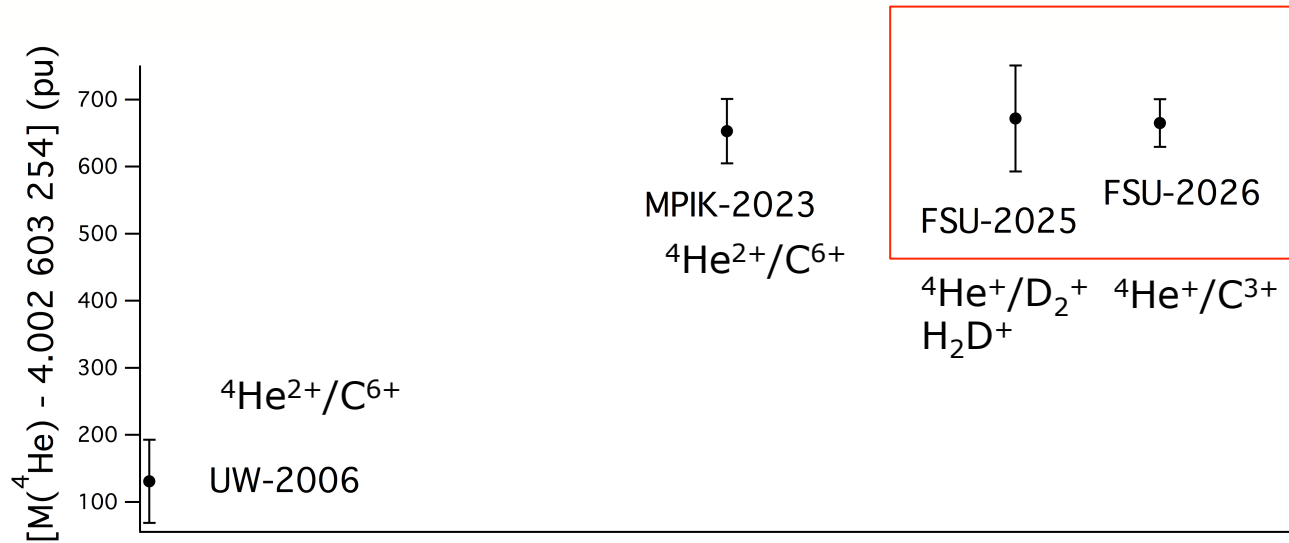
Try to measure shift directly:



Instead, measure decay rate of axial signal to

$$\gamma_z(\omega_z) = \frac{\gamma_z(\gamma_0/2)^2}{[(\omega_z - \omega_0)^2 + (\gamma_0/2)^2]}$$

Final Results for $M[{}^4\text{He}]$



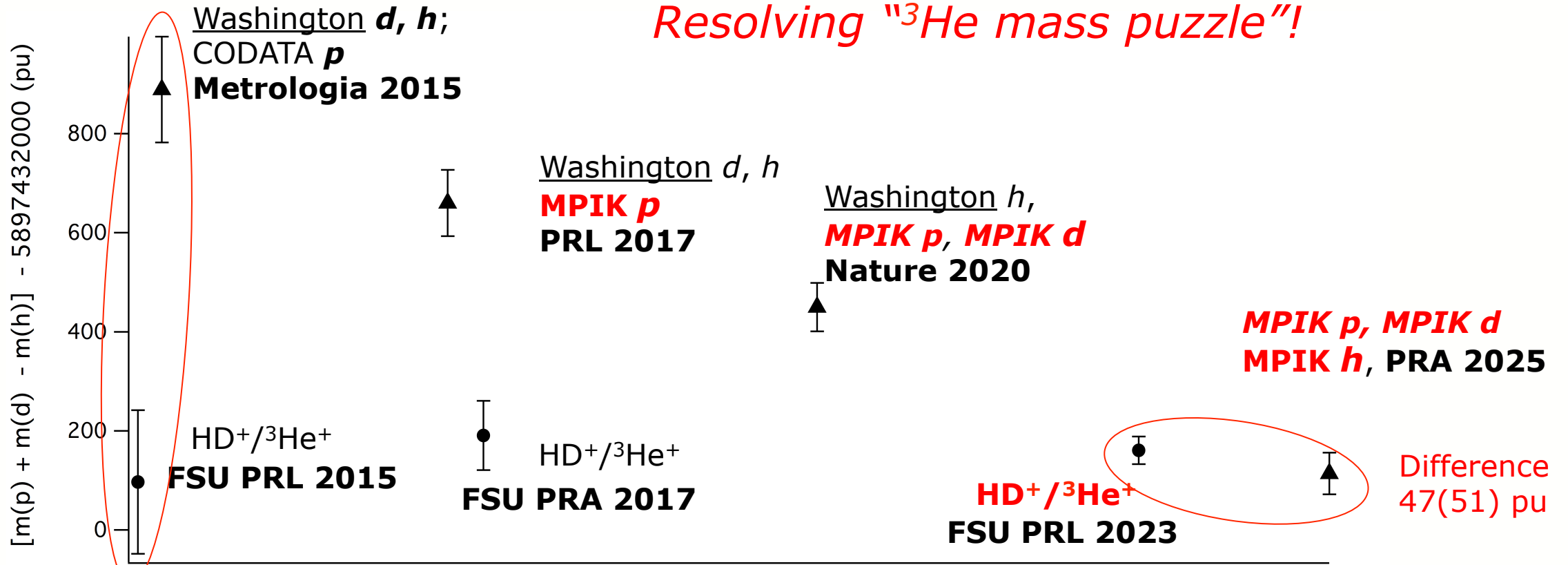
${}^4\text{He}^+/\text{C}^{3+}$ analysis
was completed blind

Source	Reference ion(s)	$M[{}^4\text{He}]$ (u)
UW 2006 [20]	C^{6+}	4.002 603 254 131(62)
LIONTRAP 2023 [22]	C^{6+}	4.002 603 254 653(48)
FSU 2025 [18]	D_2^+ , H_2D^+	4.002 603 254 672(79)
This work	C^{3+}	4.002 603 254 665(36)

9×10^{-12}

$$m_p + m_d - m_h \text{ (2024)}$$

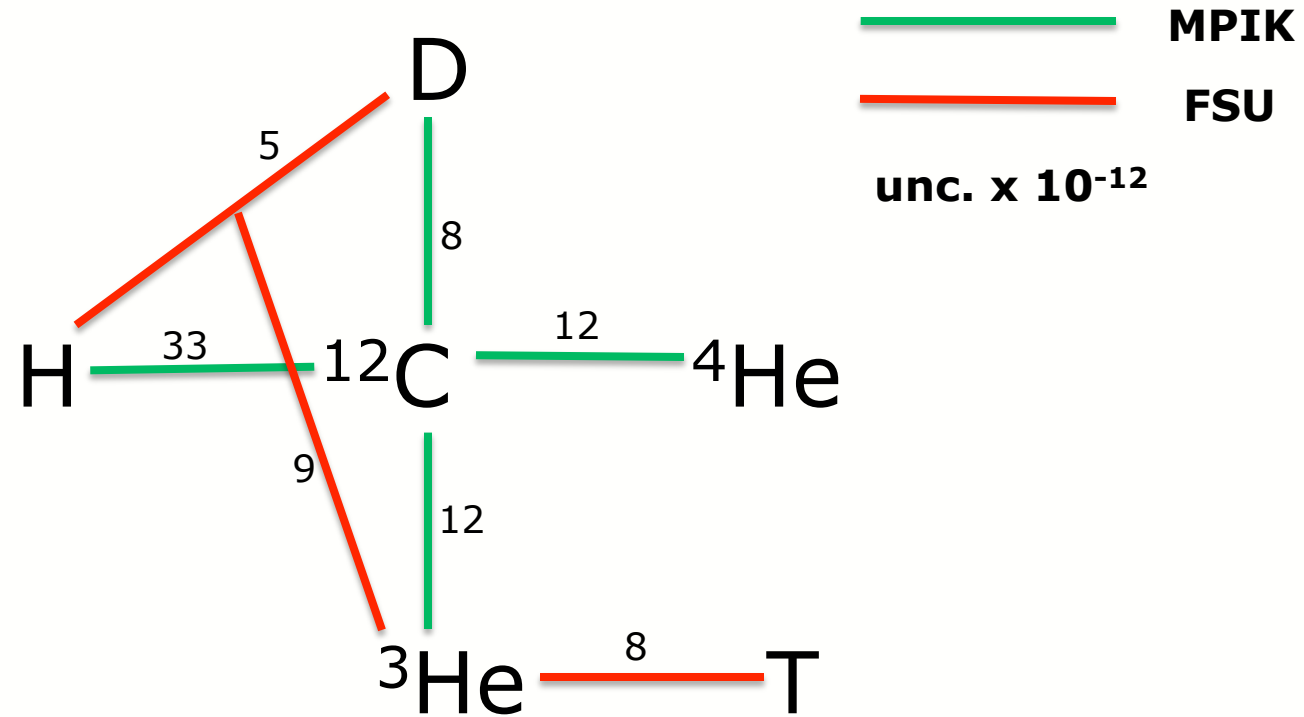
Resolving "³He mass puzzle"!



- UW m_p, m_d, m_h disagree individually with MPIK
- FSU $m_p + m_d - m_h$ FSU agrees with MPIK
- FSU m_d/m_p also agrees with MPIK

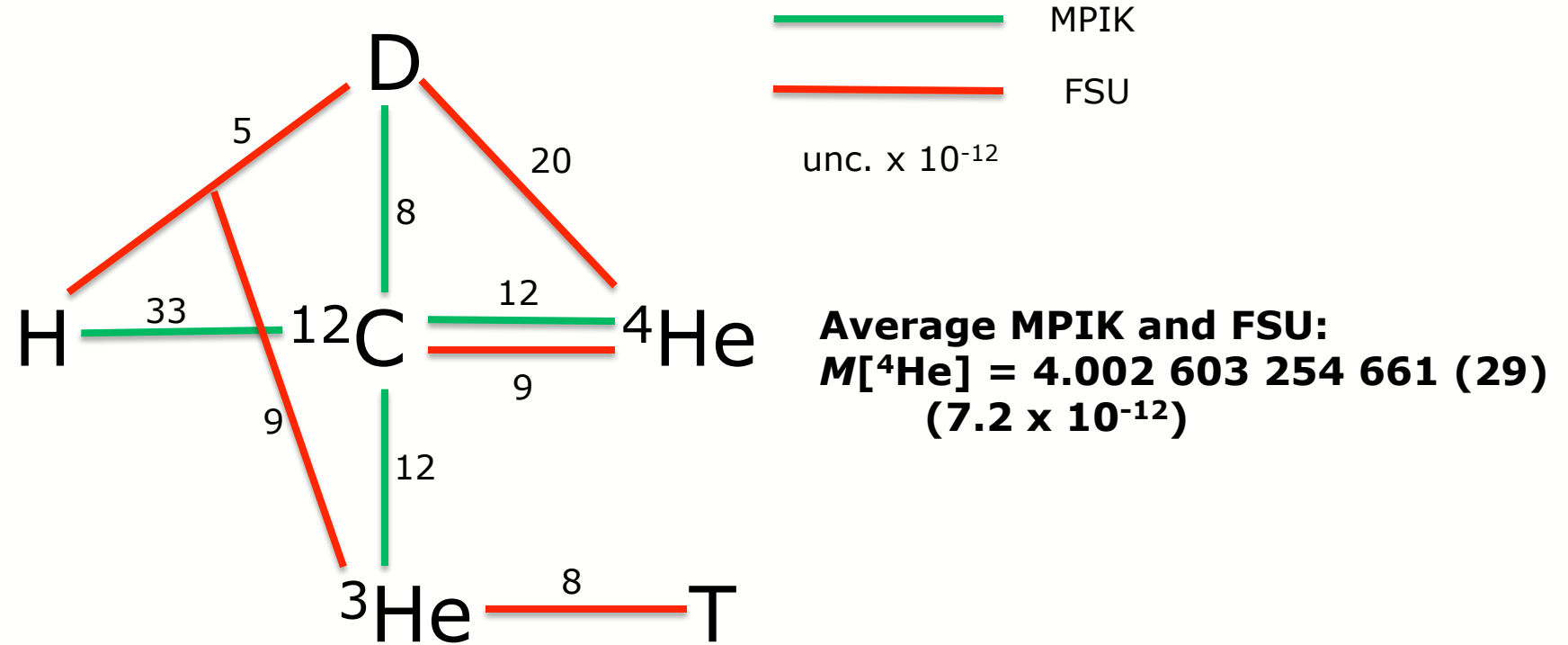
***O. Bezrodnova et al,
PSAS-2024, Zurich
PRA 2025***

MPIK and FSU Light Ion Results 2024



- FSU ($m_p + m_d - m_h$) from $HD^+ / {}^3He^+$ (" 3He puzzle") agrees with MPIK m_p, m_d, m_h
- FSU ($m_d - 2m_p$) from H_2^+ / D^+ agrees with MPIK m_p, m_d

MPIK and FSU Light Ion Results 2026



- FSU ($m_p + m_d - m_h$) from $\text{HD}^+ / {}^3\text{He}^+$ (" ${}^3\text{He}$ puzzle") agrees with MPIK m_p, m_d, m_h
- FSU ($m_d - 2m_p$) from $\text{H}_2^+ / \text{D}^+$ agrees with MPIK m_p, m_d
- **First direct check of MPIK masses vs ${}^{12}\text{C}$**

Thank you for your attention!