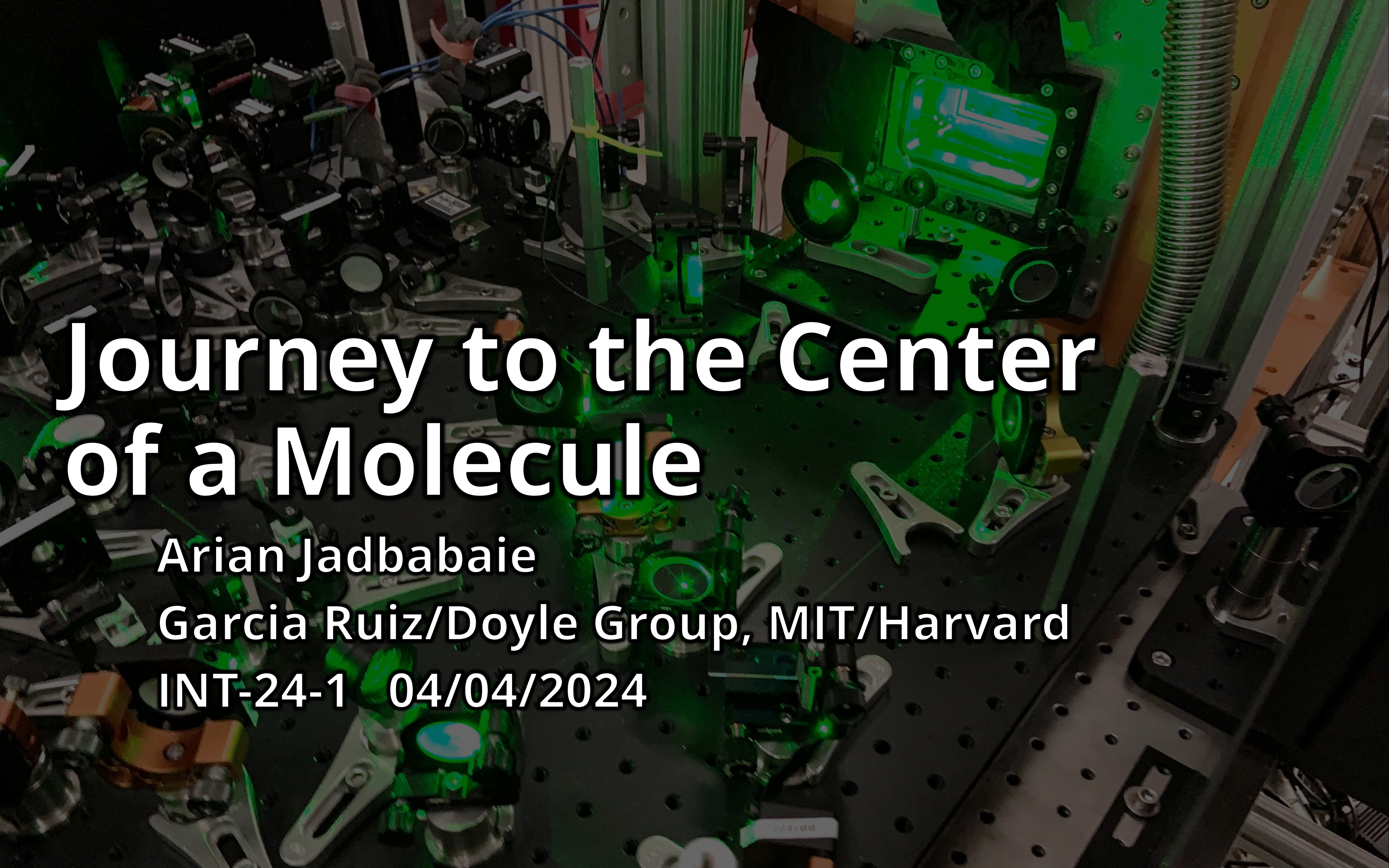
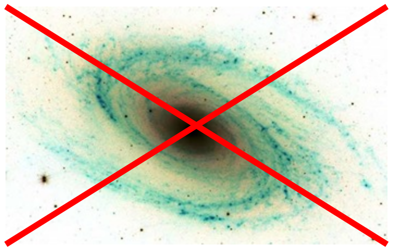


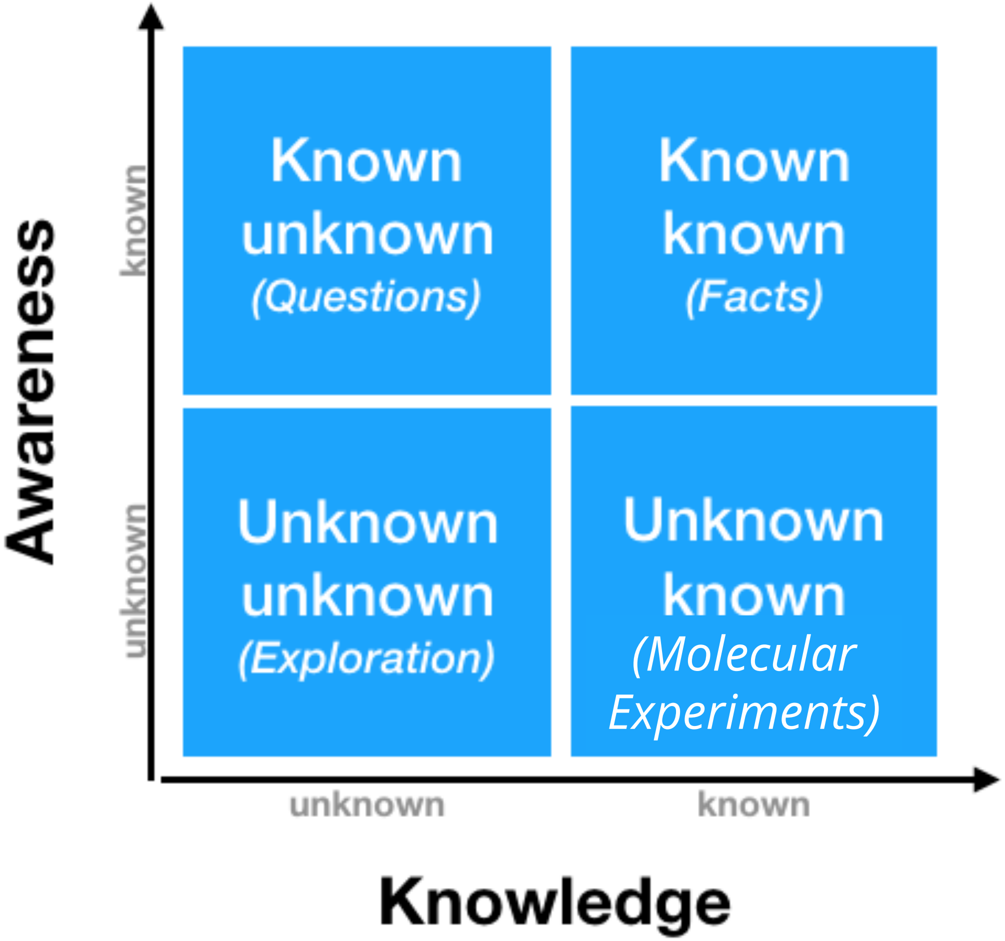
# Journey to the Center of a Molecule

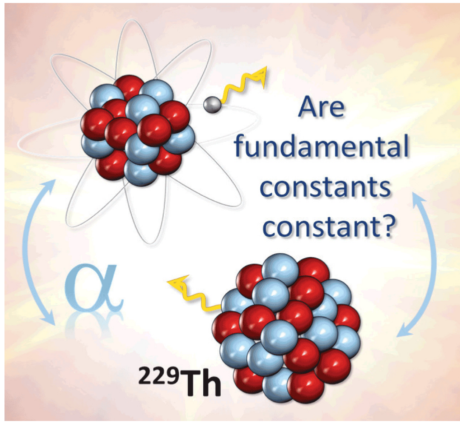
Arian Jadbabaie
Garcia Ruiz/Doyle Group, MIT/Harvard

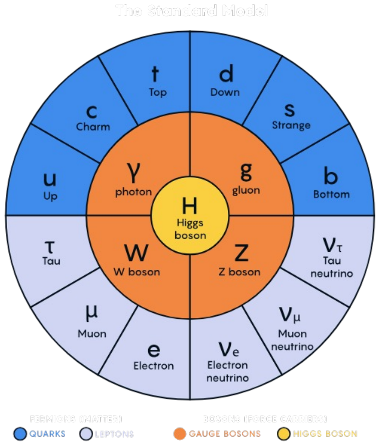
INT-24-1   04/04/2024

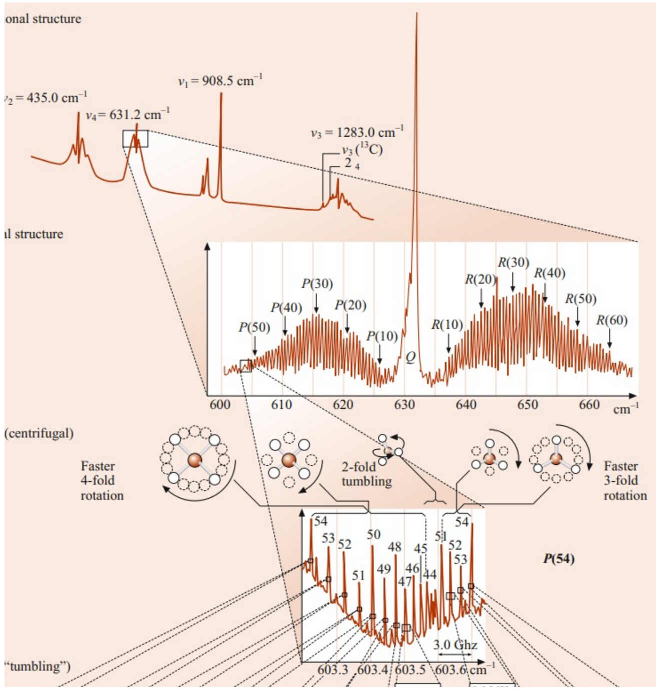
# Does nature violate fundamental symmetries?



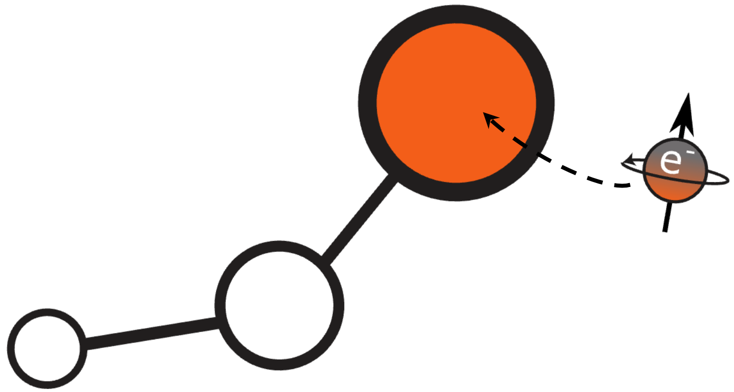


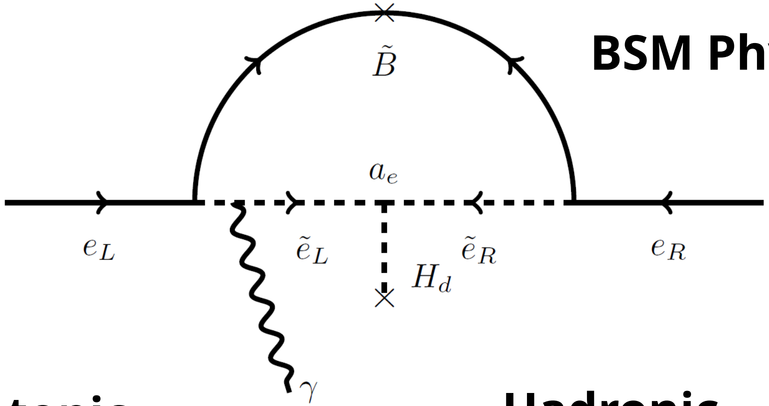



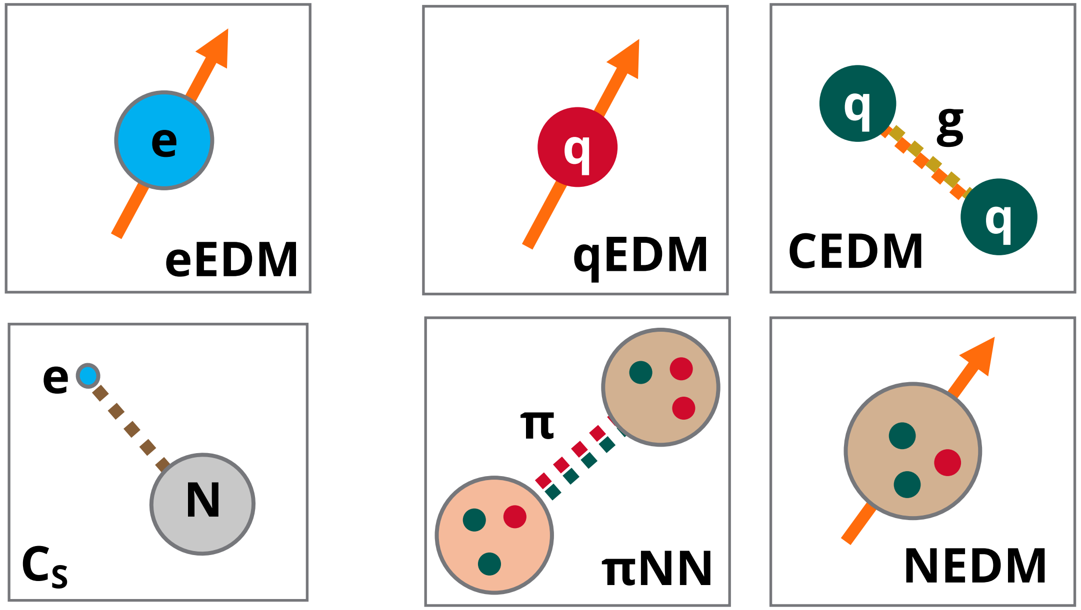
# The Center of the Molecule



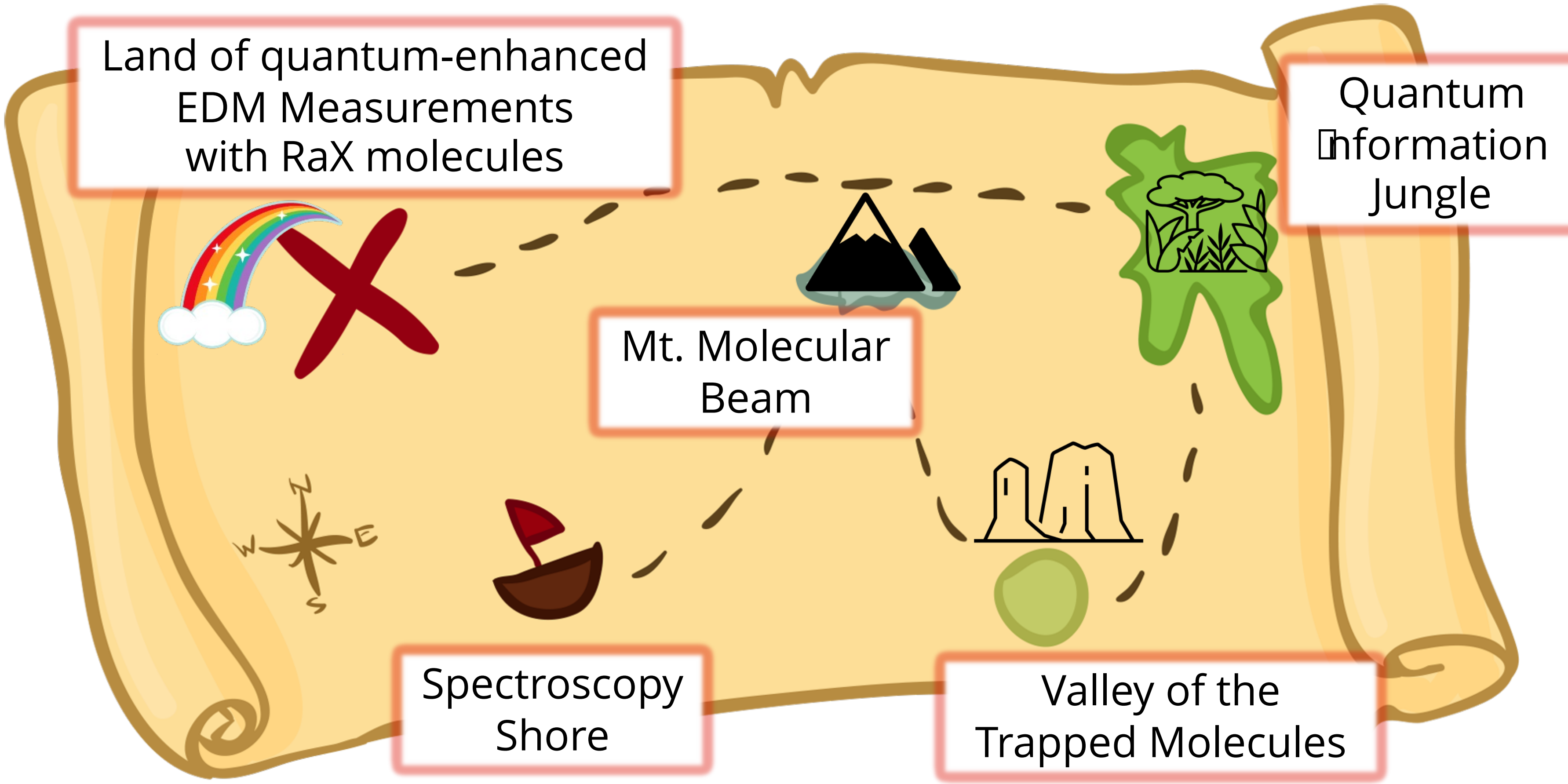

BSM Physics???




**Leptonic** **Hadronic**



# Where Are We Going?

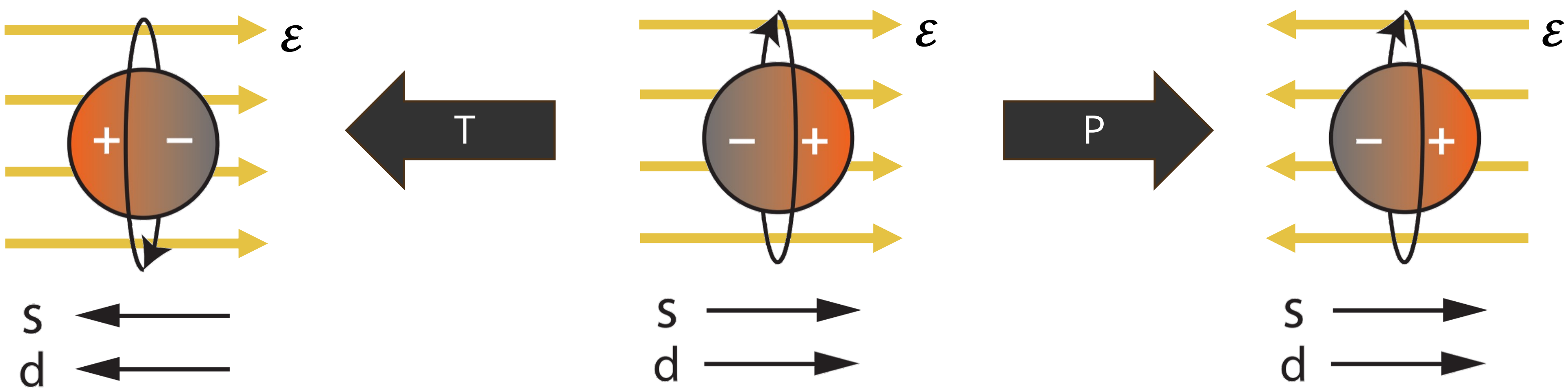


# Symmetry Violation and EDMs

- Permanent Electric Dipole Moments (EDMs) violate Parity (P) and Time-reversal (T) (=CP)

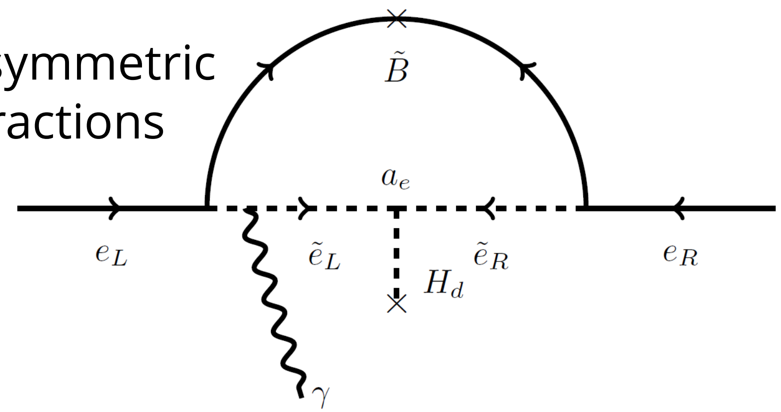
$$H_{EDM} = -\boldsymbol{d} \cdot \boldsymbol{\mathcal{E}} = -d\,\boldsymbol{S} \cdot \boldsymbol{\mathcal{E}}$$

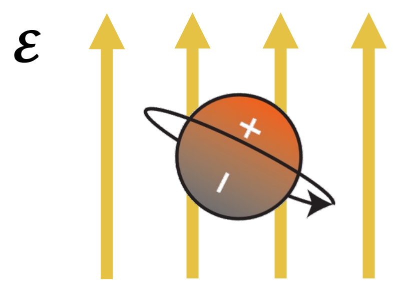
T-odd P-odd



# Probing High Energy Physics

Supersymmetric Interactions




EDM

$$H_{EDM} = -\boldsymbol{d_e} \cdot \boldsymbol{\mathcal{E}}$$

High Energy

New P,T-violating Physics

> TeV

$10^{12}$

Effective Field Theories

$10^{-3}$

< meV

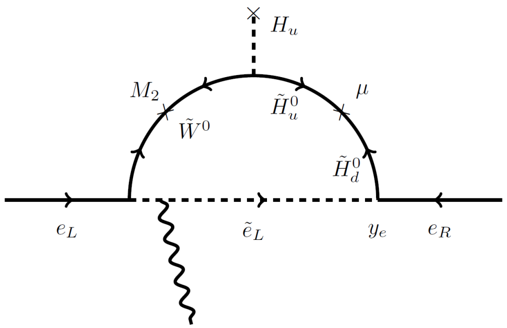
Atomic Observables

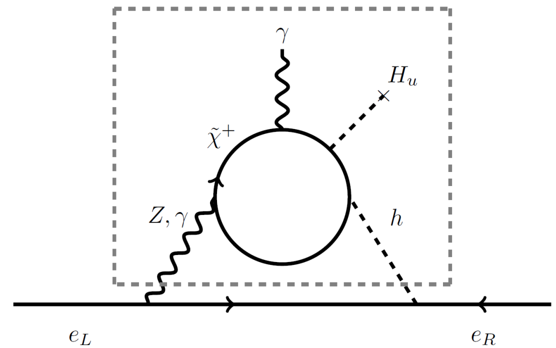
Low Energy

Cesarotti, C. et al. *J.H.E.P.*, 2019(5) (2019).

Chupp, T. E., et al. *Rev. Mod. Phys.* 91(1) (2019)

# EDM Energy Reach



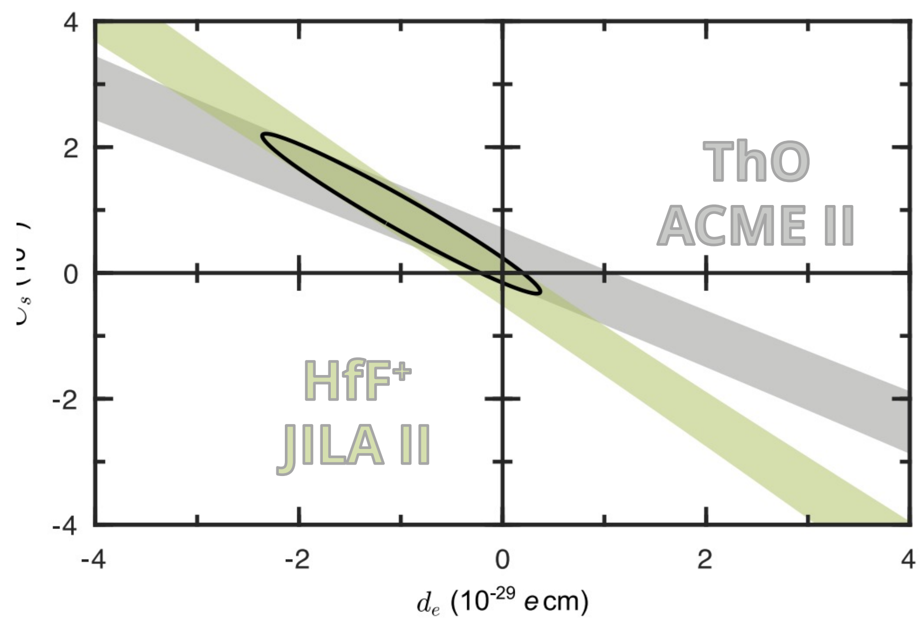




$$\sin\phi_{TV} \sim 1$$

$$g \sim g_{EW}$$

$$\frac{d_f}{e} \sim \sin\phi_{TV}\left(\frac{g^2}{16\pi^2}\right)^{\ell}\frac{m_f}{M_{NP}^2}$$

| Operator | Loop order | Mass reach |
|---|---|---|
| Electron EDM | 1 | $48\,\text{TeV}\sqrt{10^{-29}\,e\,\text{cm}/d_e^{\max}}$ |
| | 2 | $2\,\text{TeV}\sqrt{10^{-29}\,e\,\text{cm}/d_e^{\max}}$ |
| Up/down quark EDM | 1 | $130\,\text{TeV}\sqrt{10^{-29}\,e\,\text{cm}/d_q^{\max}}$ |
| | 2 | $13\,\text{TeV}\sqrt{10^{-29}\,e\,\text{cm}/d_q^{\max}}$ |
| Up-quark CEDM | 1 | $210\,\text{TeV}\sqrt{10^{-29}\,\text{cm}/\tilde{d}_u^{\max}}$ |
| | 2 | $20\,\text{TeV}\sqrt{10^{-29}\,\text{cm}/\tilde{d}_u^{\max}}$ |
| Down-quark CEDM | 1 | $290\,\text{TeV}\sqrt{10^{-29}\,\text{cm}/\tilde{d}_d^{\max}}$ |
| | 2 | $28\,\text{TeV}\sqrt{10^{-29}\,\text{cm}/\tilde{d}_d^{\max}}$ |
| Gluon CEDM | 2 ($\propto m_t$) | $22\,\text{TeV}\sqrt[3]{10^{-29}\,\text{cm}/(100\,\text{MeV})/\tilde{d}_G^{\max}}$ |
| | 2 | $260\,\text{TeV}\sqrt{10^{-29}\,\text{cm}/(100\,\text{MeV})/\tilde{d}_G^{\max}}$ |

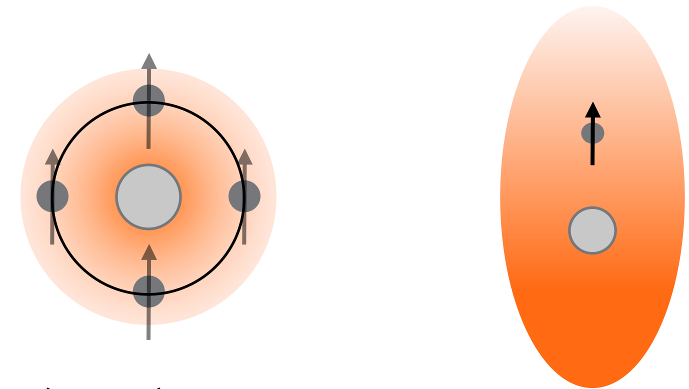



JILA: arXiv:2212.11841

Cesarotti, C. et al. *J.H.E.P.,* 2019(5) (2019) Chupp, T. E., et al. *Rev. Mod. Phys.* 91(1) (2019) 2022 EDM White Paper: arXiv:2203.08103

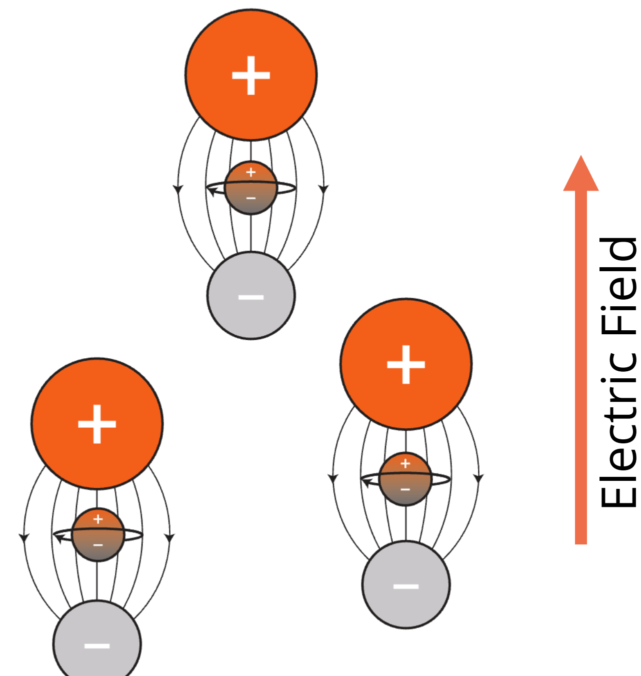
# Why Molecules?

- $H_{PTV}$ mixes opposite parity levels split by $\Delta$
- Atomic states: $\Delta{\sim}100\ \mathrm{THz}$
  - $\langle p_{1/2}|H_{PTV}|s_{1/2}\rangle$ suppressed
  - Polarization $\sim\mathcal{O}(10^{-3})$ possible
- Molecular states: $\Delta \lesssim 10\ \mathrm{GHz}$
  - Ligand field mixes $s, p, \ldots$
  - $|\psi_{mol}\rangle \approx \alpha|s_{1/2}\rangle + \beta|p_{1/2}\rangle$
  - Polarization $\sim\mathcal{O}(1)$ possible
  - "1000x" more sensitive



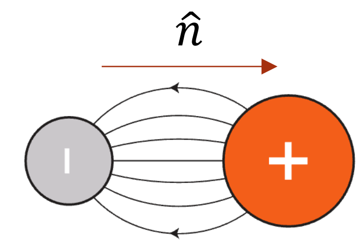
$\langle H_{PTV}\rangle = 0$

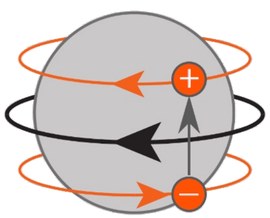
$\langle H_{PTV}\rangle \neq 0$



# Symmetry and Interactions

- Spherical tensor notation: $T_q^k(V)$ transforms under rotations like angular momenta
- Generic interaction: $T^k(J_i, J_j, \ldots) \cdot T^k(\hat{n})$



Nuclear Magnetic Quadrupole Moment

MOM shifts >kHz???

M1 (MDM)
$T^1(I) \cdot T^1(S)$
$T^2(I,S) \cdot T^2(n)$

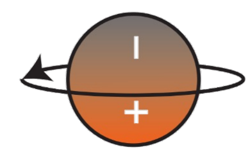
**M2 (MQM)**
$T^1(I^2,S) \cdot T^1(n)$

M3 (MOM)
$T^3(I) \cdot T^3(S)$
$T^2(I^3,S) \cdot T^2(n)$

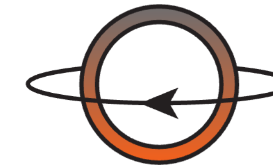
**E1 (EDM)**
$T^1(S) \cdot T^1(n)$
$T^1(I) \cdot T^1(n)$

E2 (EQM)
$T^2(I) \cdot T^2(n)$

**M3 (EOM)**
$T^3(I) \cdot T^3(n)$



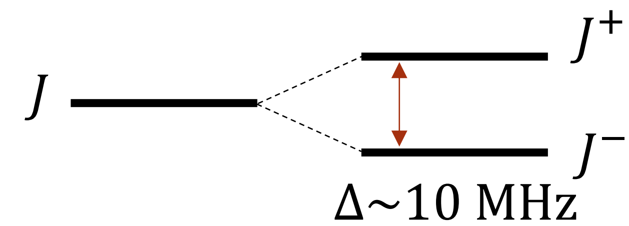
Electron EDM

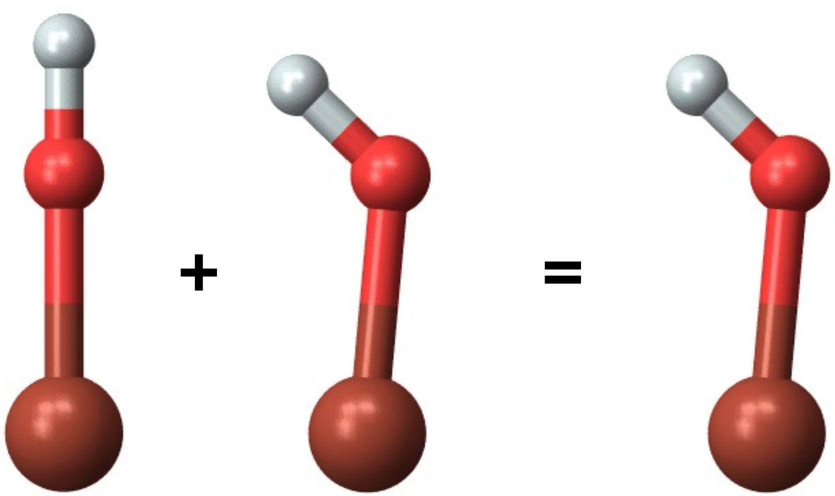


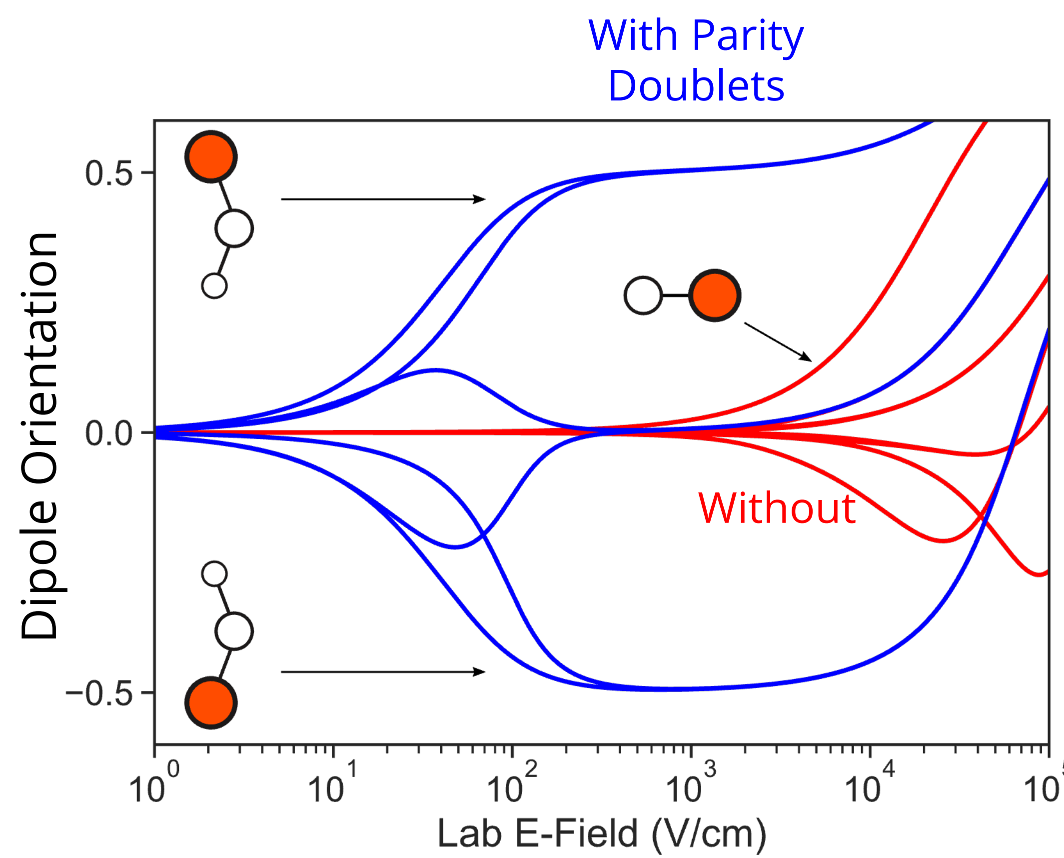
Schiff Moment

# Why Polyatomic Molecules?

- Generically support **parity doublets**
  - Ex: bending modes in triatomics
- Allows molecule orientation control

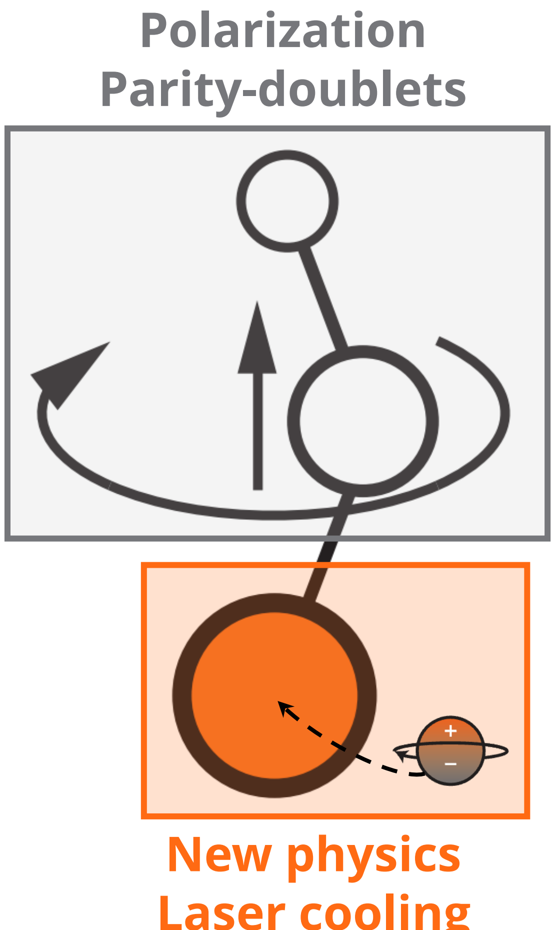


# Why Polyatomic Molecules?

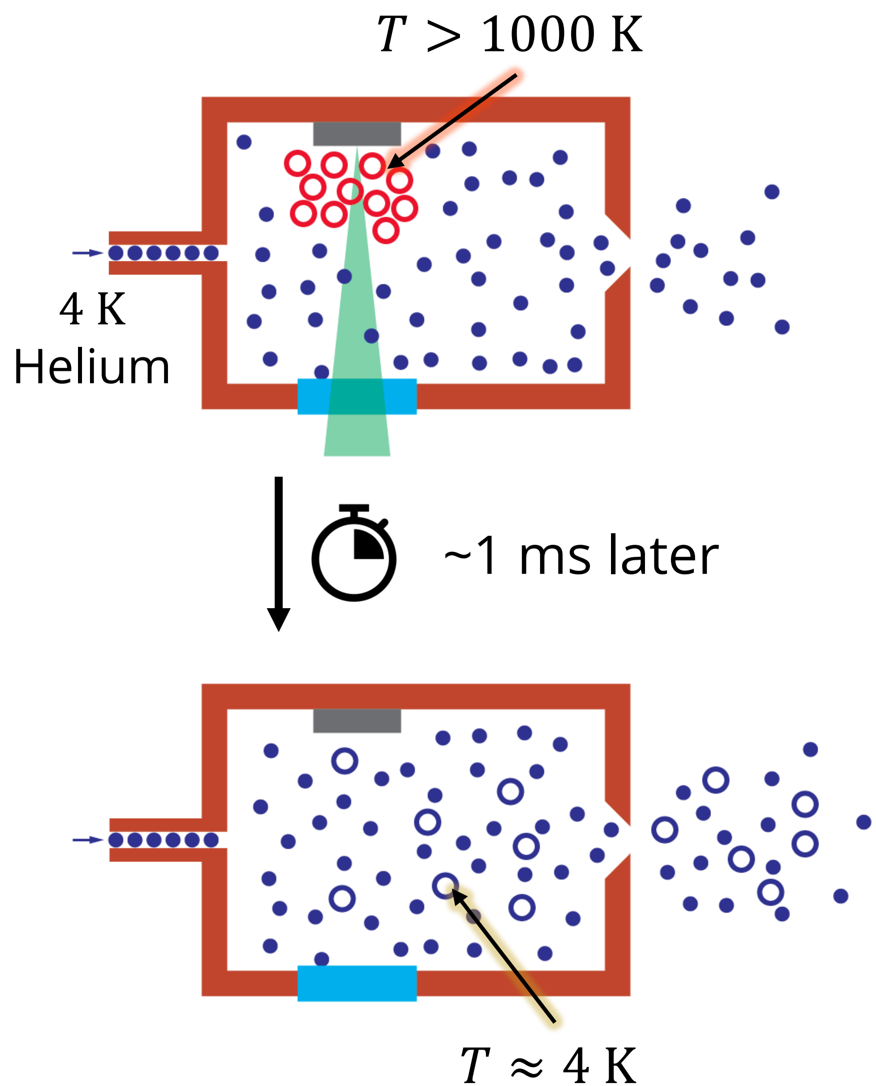
- Parity doublets from ligand rotation
- "Decoupled" metal center
  - Provides new physics sensitivity
  - Strong optical transitions useful for laser cooling and manipulation
- Rapid Progress
  - Harvard ($CaOH$, $CaOCH_3$, $SrOH$, $YbOH$, **RaX**)
  - MIT (**RaX**)
  - UCSB ($RaOH^+$, $RaOCH_3^+$)
  - MSU/FRIB ($RaOCH_3$)
  - Old Dominion ($LuOH^+$)
  - Groningen ($BaOH$)
  - Caltech ($YbOH$, $SrOH$, **RaOH**)



# Experimental Methods

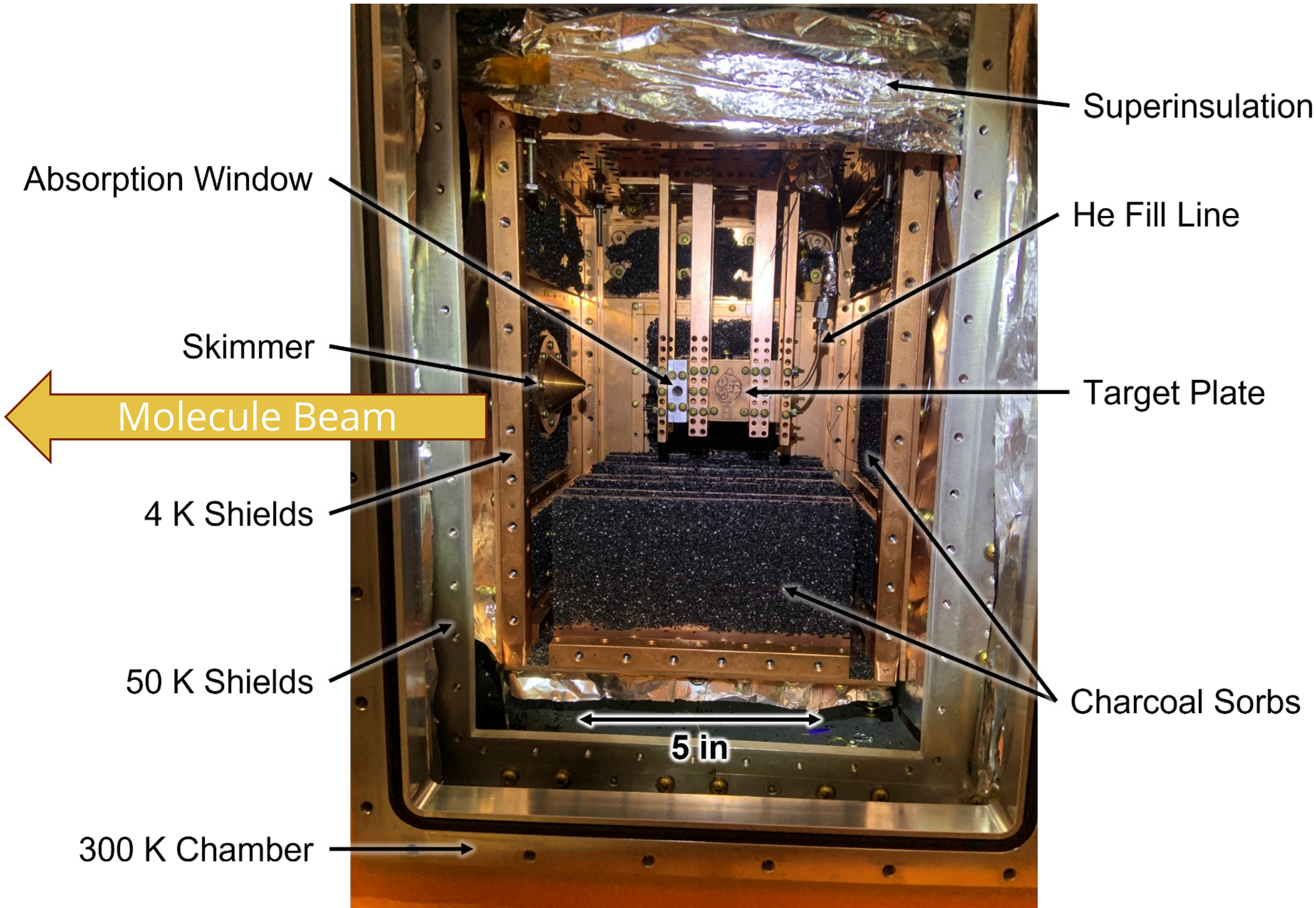
# Step 1: Making Cold Molecules

- Established technique:
  **Cryogenic Buffer Gas Cooling**
  - Broadly applicable
- Produces rotationally and translationally cold molecules
  - Vibrationally athermal
- Can extract species into a beam
  - 200 m/s velocity (or less)
  - Starting point for precision measurements, laser cooling, and trapping




Hutzler, Lu, Doyle, *Chem. Rev.* 2012, 112, 9, 4803−4827

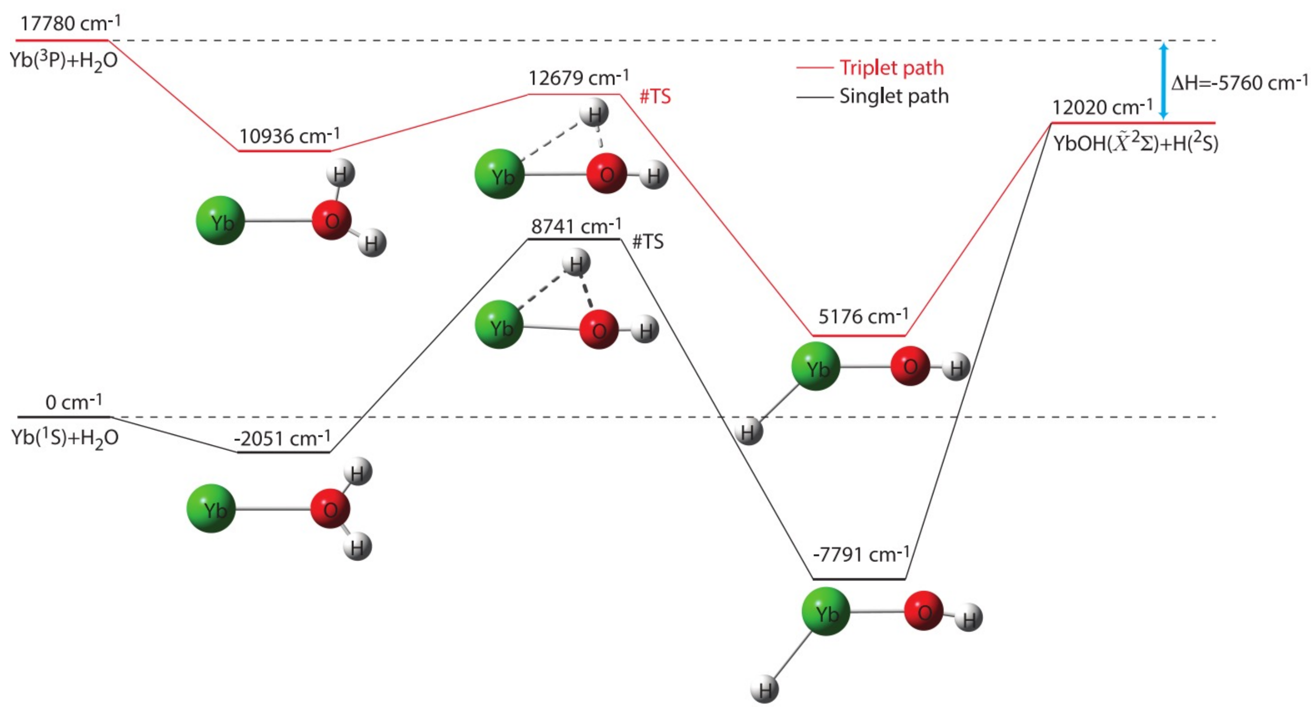
# Cryogenic Buffer Gas Beam Source



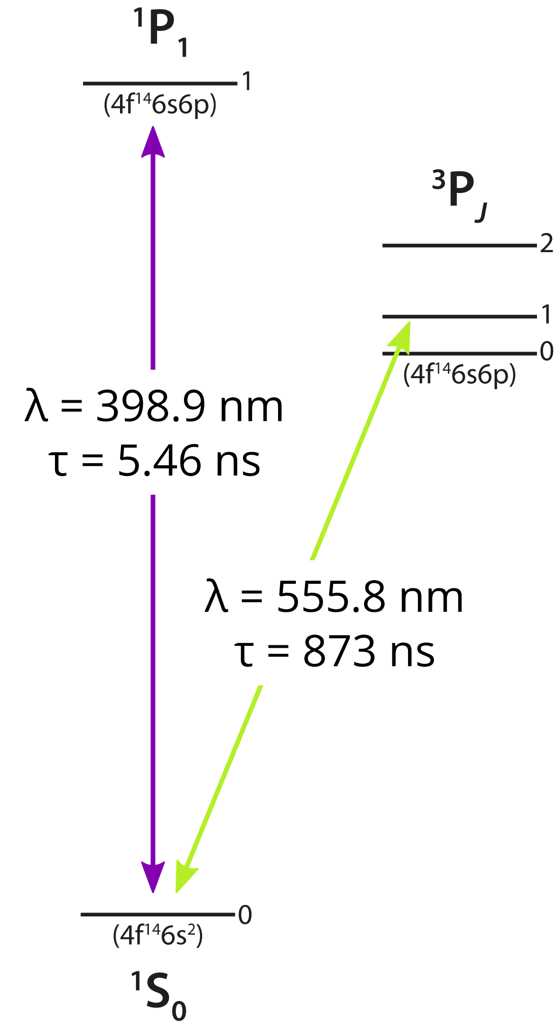

Nick Pilgram

# Chemical Enhancement

- Problem: Yb ($^1S_0$) + $H_2O$ do not react
- Solution: Excite to metastable $^3P_1$ state

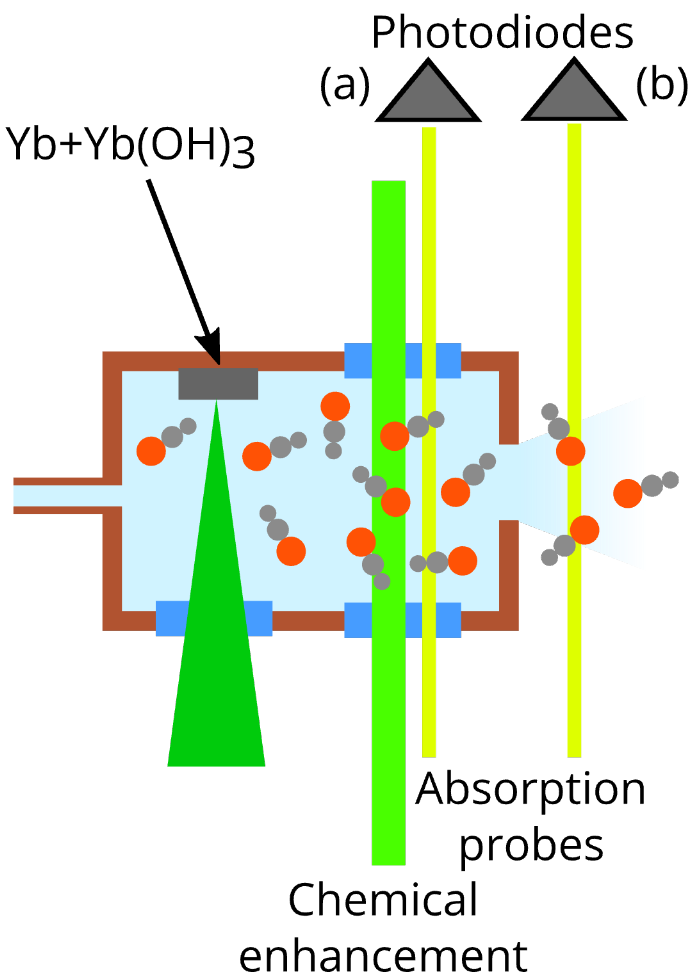


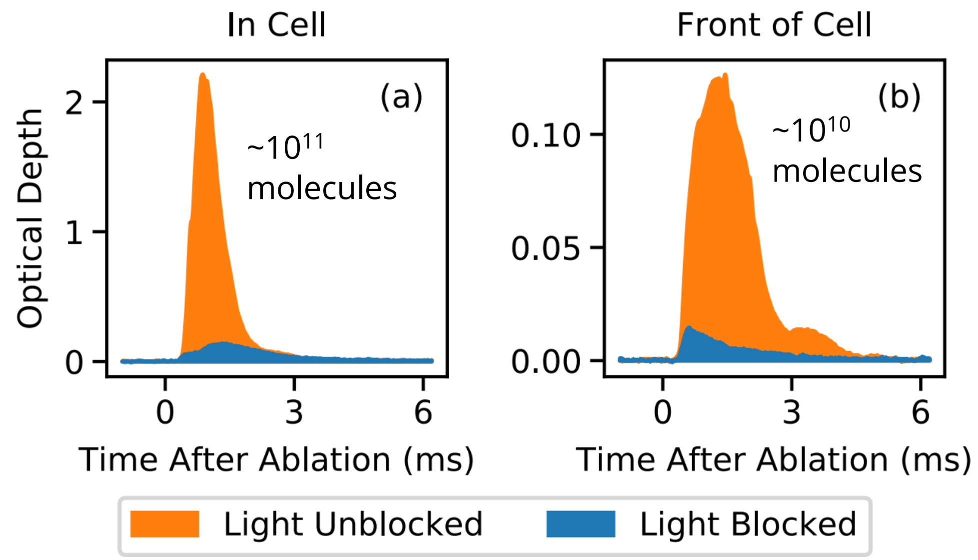

Ab initio calculations performed by Svetlana Kotochigova and Jacek Kłos




**Atomic Yb**

# YbOH Enhancement

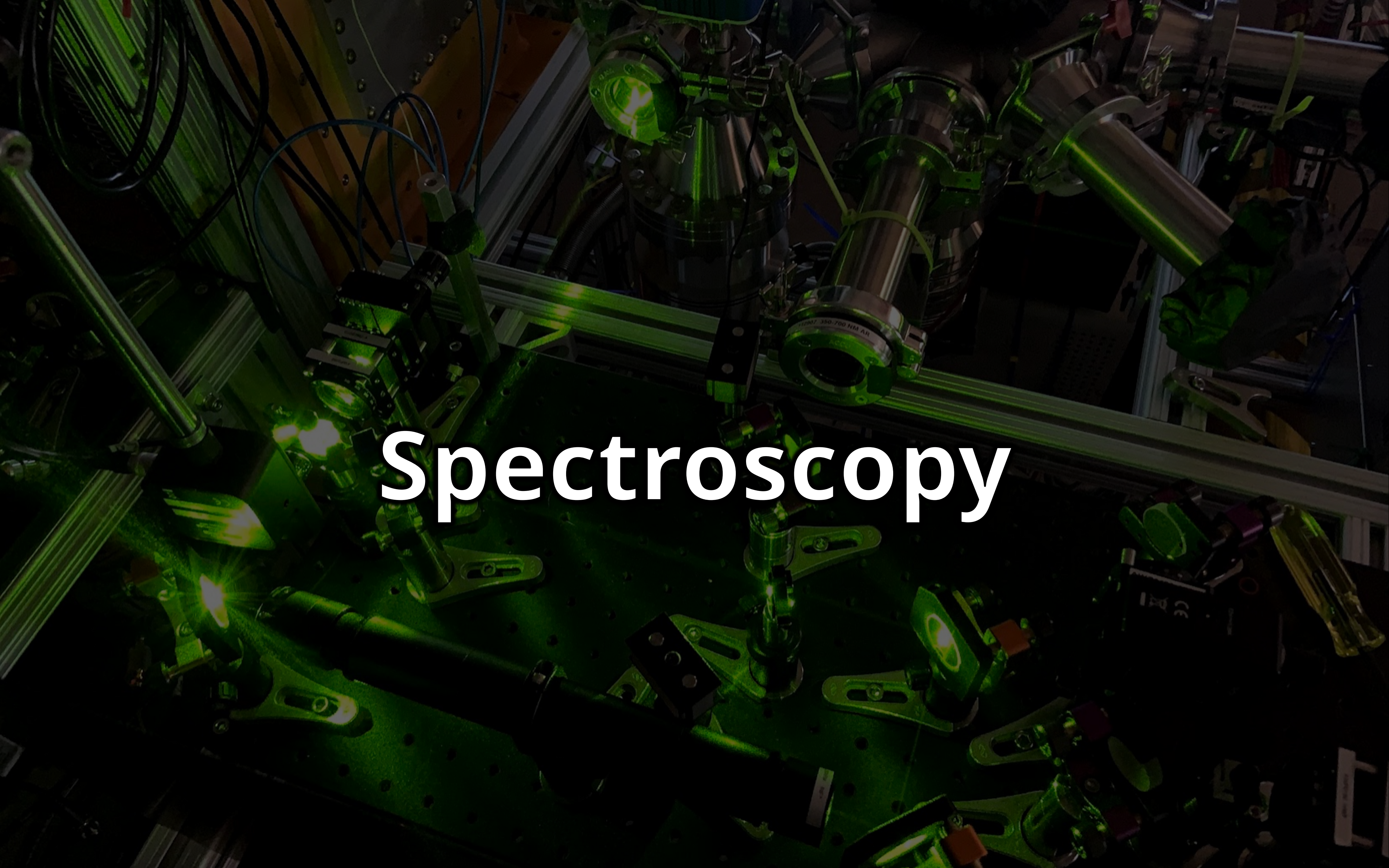



- Generic for M-O-R molecules (M=Ca, Sr, Ba, Yb, Ra)
- Enhancement of vibrational states
- Useful to disentangle congested spectra

**AJ** *et al* 2020 *New J. Phys.* 22 022002

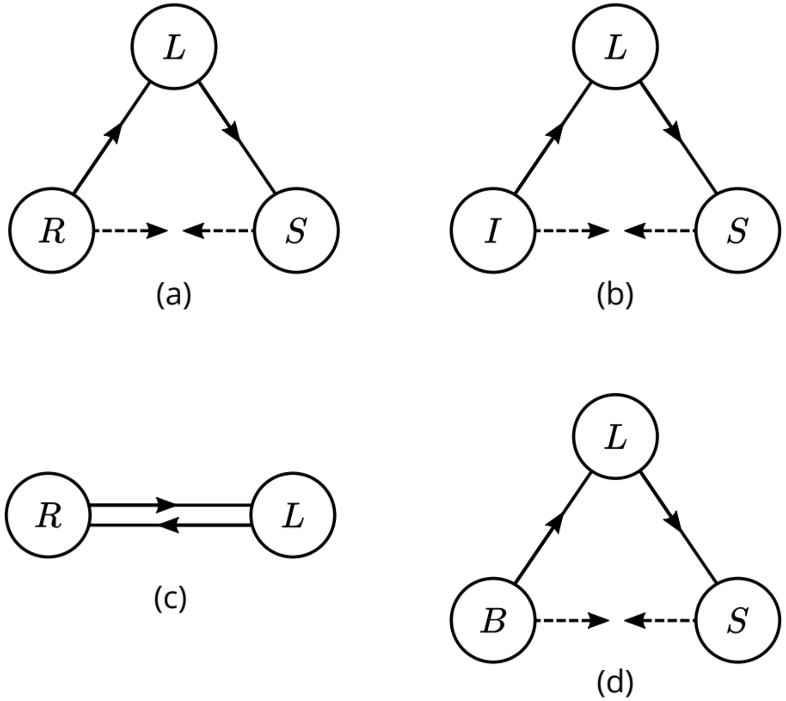
# Spectroscopy



# Aside on Effective Hamiltonians

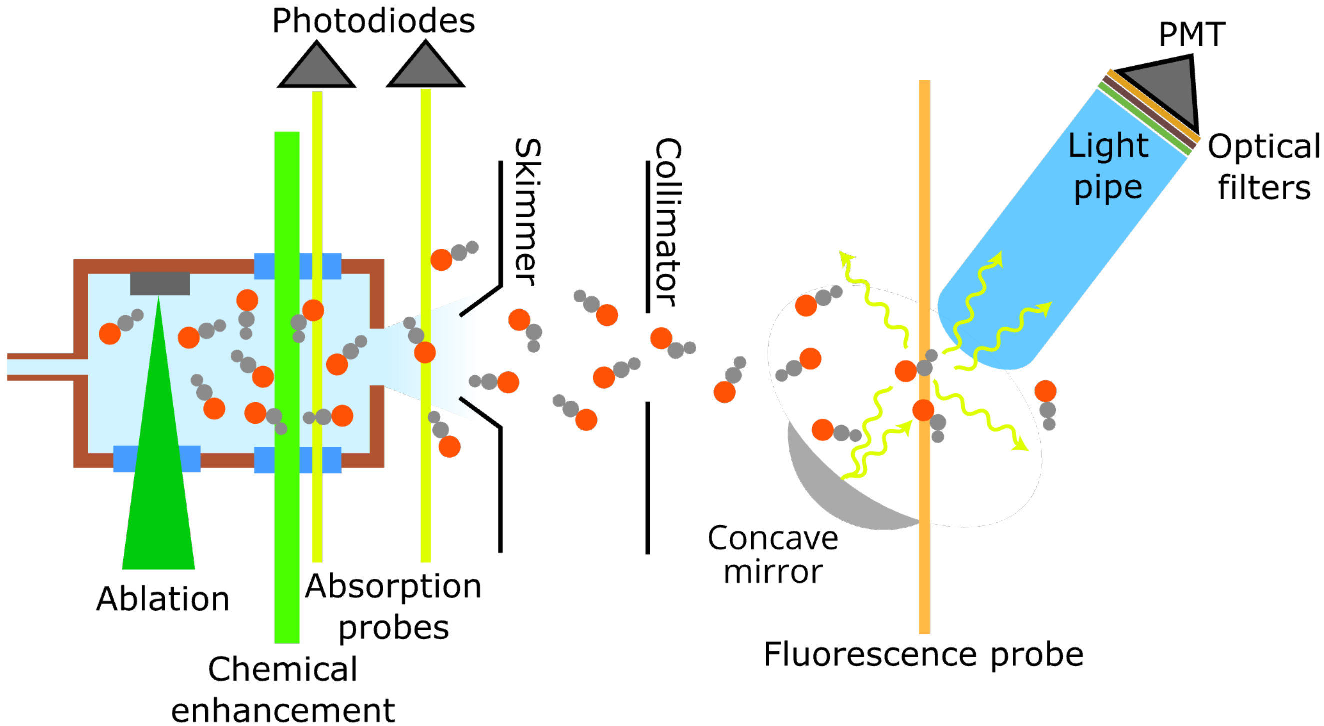
- **$L_{x,y}$, $L^2$** are not well defined in a molecule – integrate out

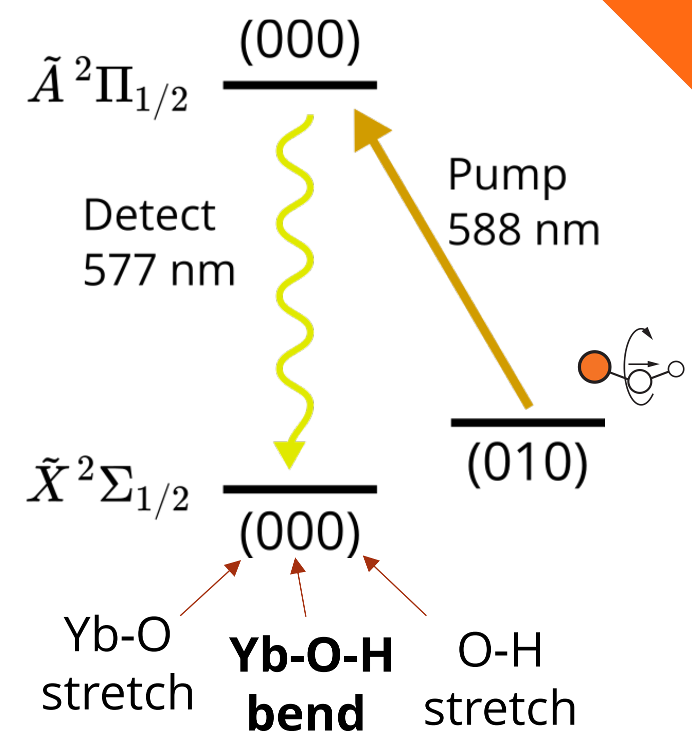
1. Construct $H_{\text{eff}} = f(\boldsymbol{\mathcal{E}}, \boldsymbol{\mathcal{B}})$
   a. Choose basis (Hund's cases)
   b. Calculate matrix elements $\langle i|H_{\text{eff}}|j\rangle$ using angular momentum algebra
2. Diagonalize $H_{\text{eff}}|\psi_i\rangle = E_i|\psi_i\rangle$
3. Calculate observables $\langle\psi_i|\hat{\mathcal{O}}|\psi_j\rangle = \mathcal{O}_{ij}(\boldsymbol{\mathcal{E}}, \boldsymbol{\mathcal{B}})$
4. Use structure as input for simulations and fits

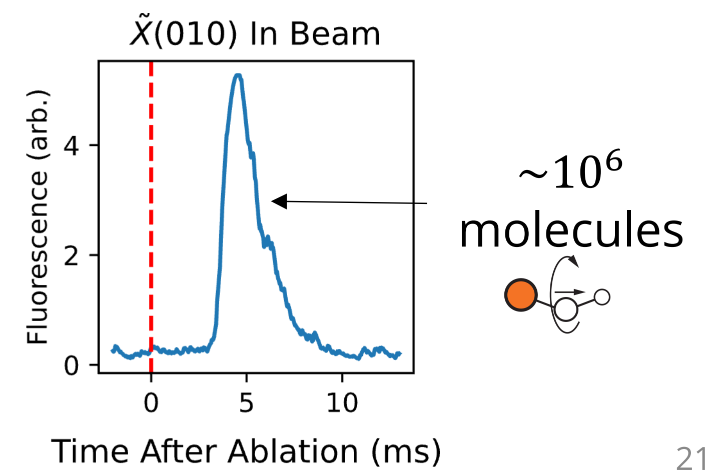



# Probing the Science State

- Drive forbidden X(010) – A(000) line
  - ~0.05% branching, known excited state



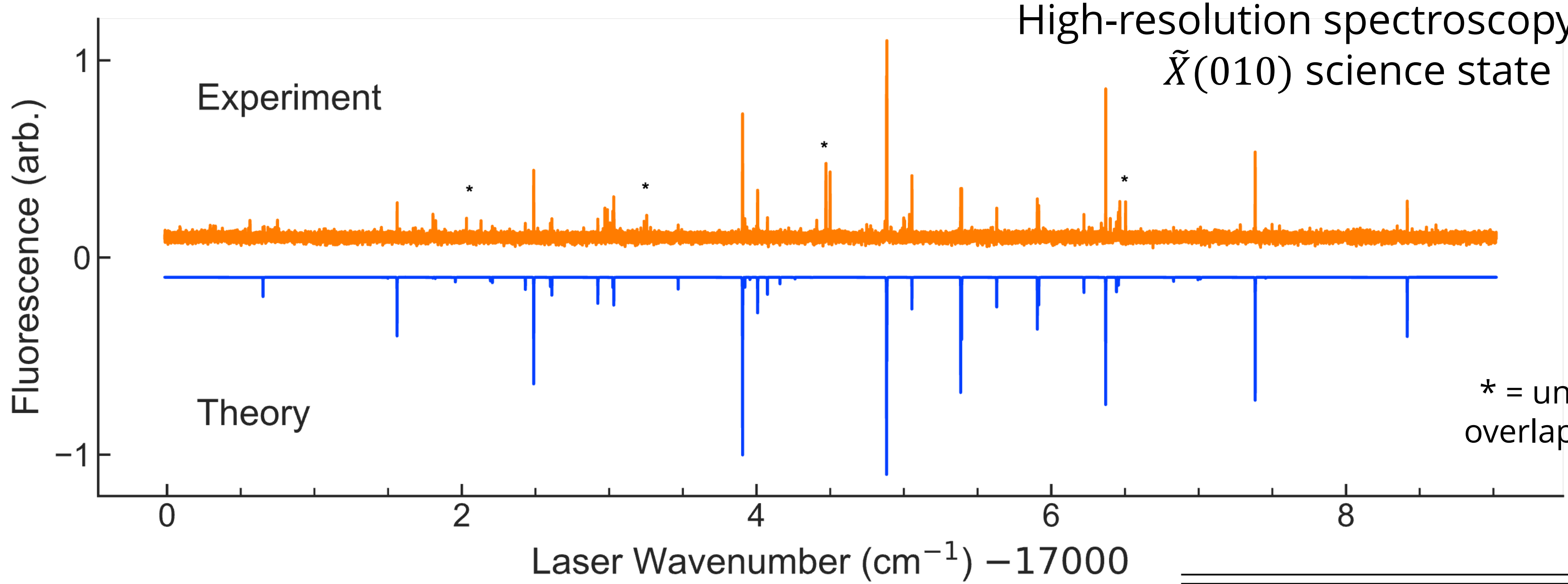




**AJ** et al, New Journal of Physics 25 (7), 073014.

# Science State Spectrum

High-resolution spectroscopy of the $\tilde{X}(010)$ science state




* = unassigned, overlapping band

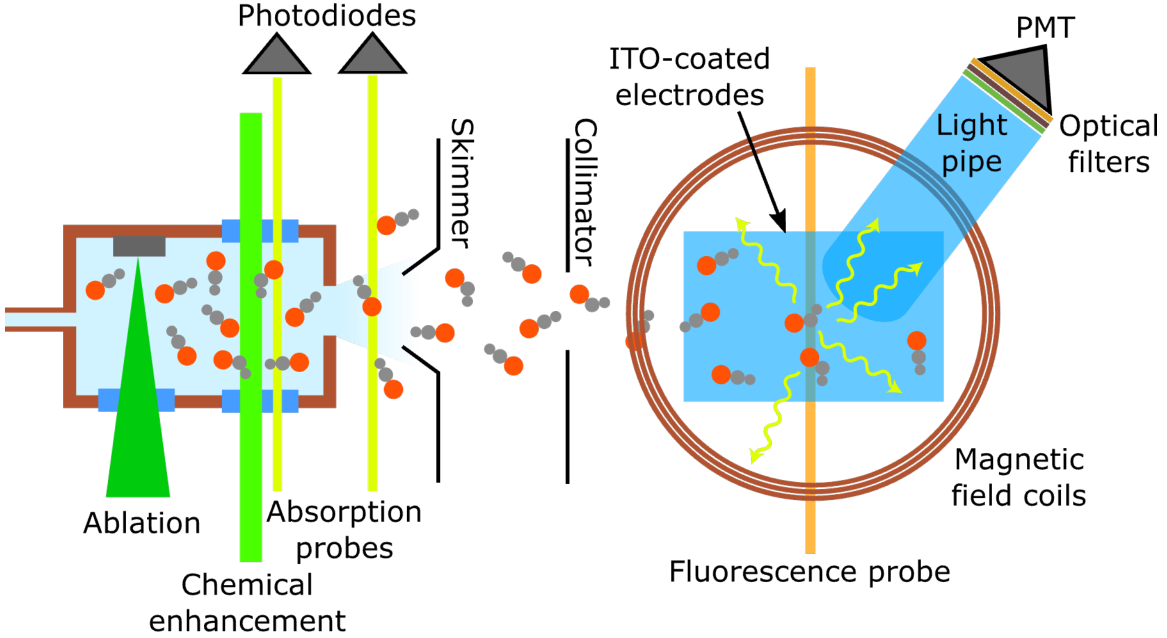
| Parameter | $\tilde{X}(010)$ |
|---|---|
| $T_0/\mathrm{cm}^{-1}$ | 319.90901(6) |
| $B$/MHz | 7328.64(15) |
| $\gamma$/MHz | -88.7(9) |
| $\gamma_G$/MHz | 16(2) |
| $q_G$/MHz | -12.0(2) |
| $p_G$/MHz | -11(1) |

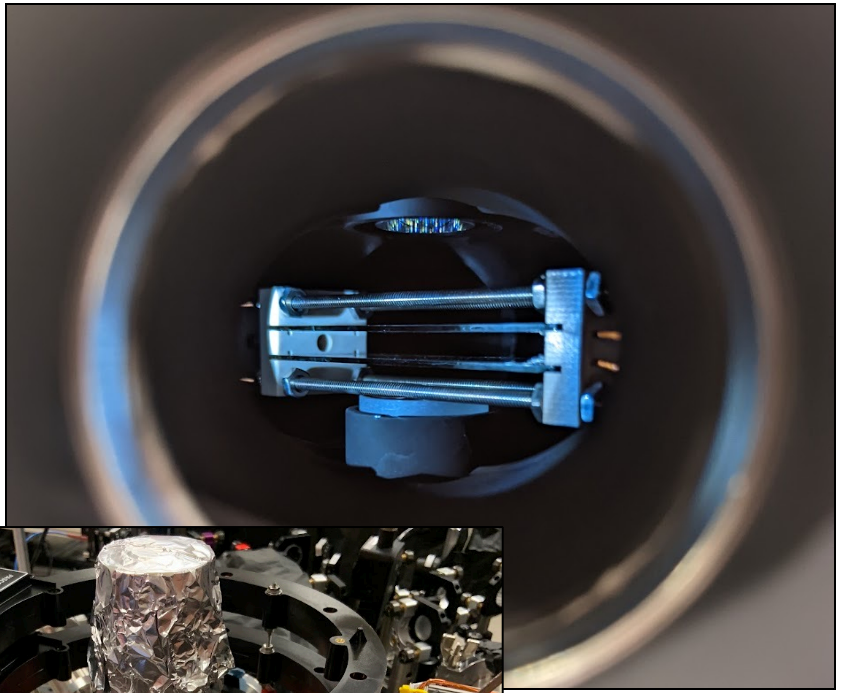
$$H_{\tilde{X}(010)} = B(\vec{N}^2 - \ell^2) + \gamma(\vec{N}\cdot\vec{S} - N_z S_z) + \gamma_G N_z S_z + \frac{p_G}{2}\left(N_+S_+e^{-i2\phi} + N_-S_-e^{i2\phi}\right) - \frac{q_G}{2}\left(N_+^2e^{-i2\phi} + N_-^2e^{i2\phi}\right).$$

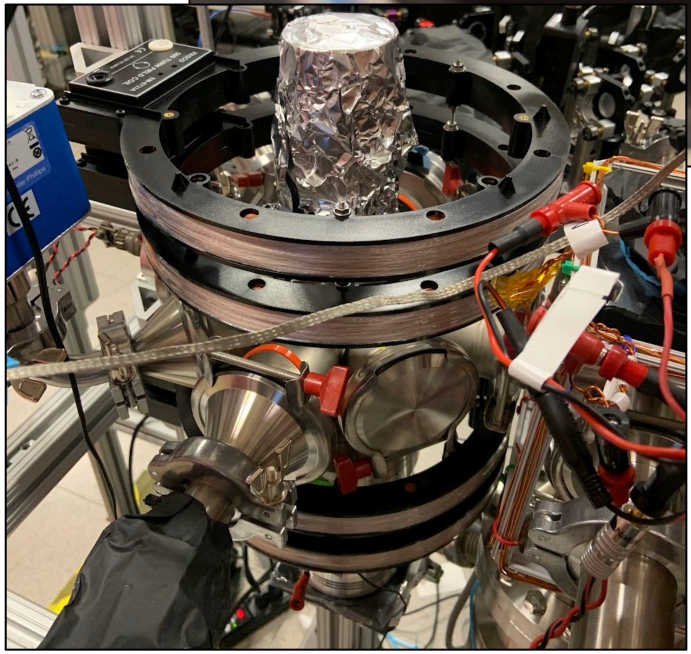
**AJ** et al, New Journal of Physics 25 (7), 073014.

# Electric and Magnetic Tuning

$$E = 0 - 250\ \mathrm{V/cm}$$
$$B = 0 - 80\ \mathrm{G}$$

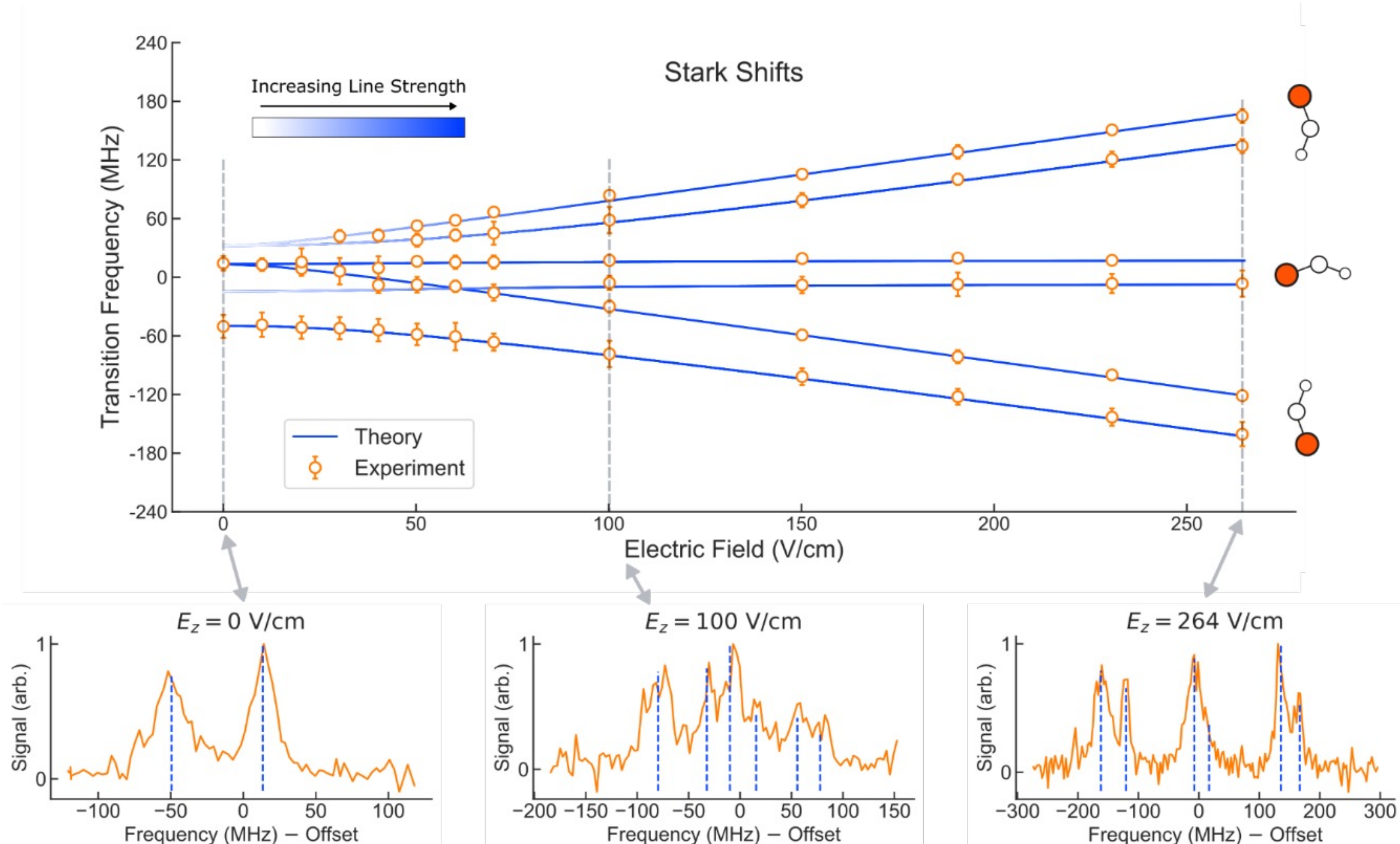




# Electric Field Shifts

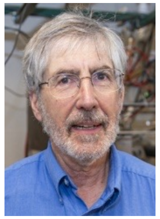
$$D_{\text{mol}} = 2.16(2)\ \text{D}$$




Molecular orientation control

# YbOH Summary

## What do we need to know?

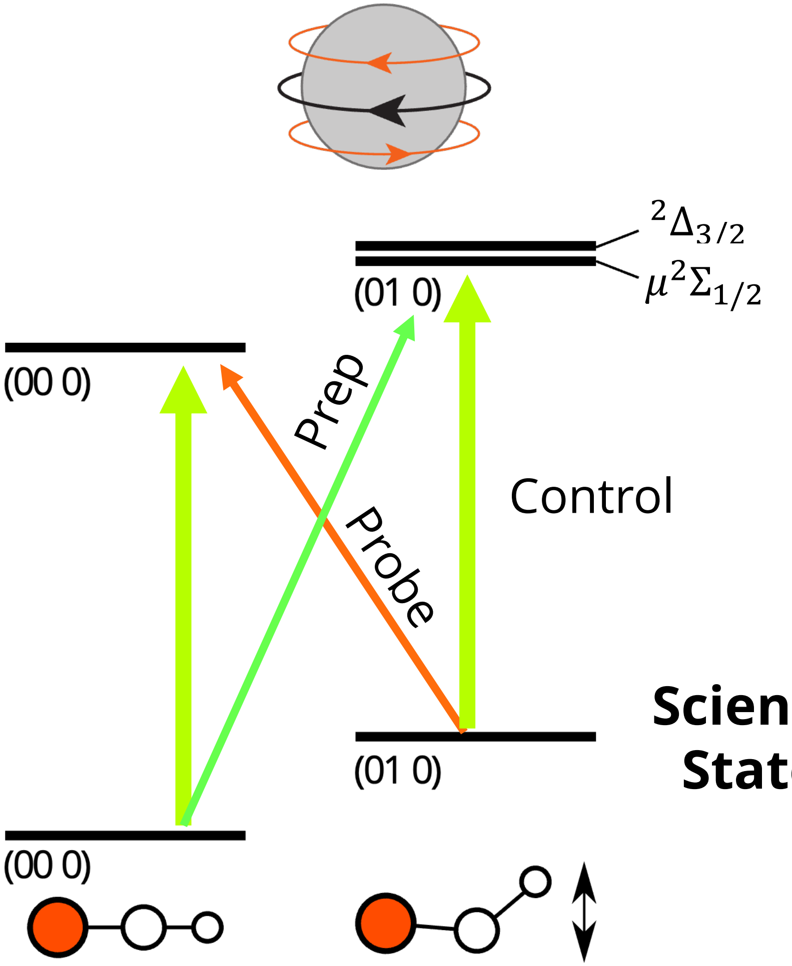


Tim Steimle

- X(000) structure ✓
- A(000) structure ✓
- X(010) science state: structure, field shifts ✓
- A(010) lines for science control, preparation ✓
- Optional: laser cooling ?

Not in gen 1…

Also accomplished for $^{173}$YbOH ✓

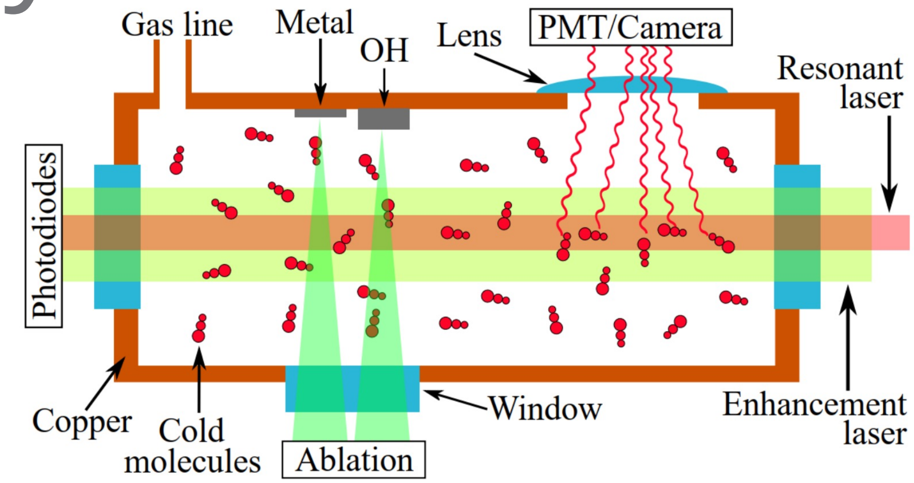


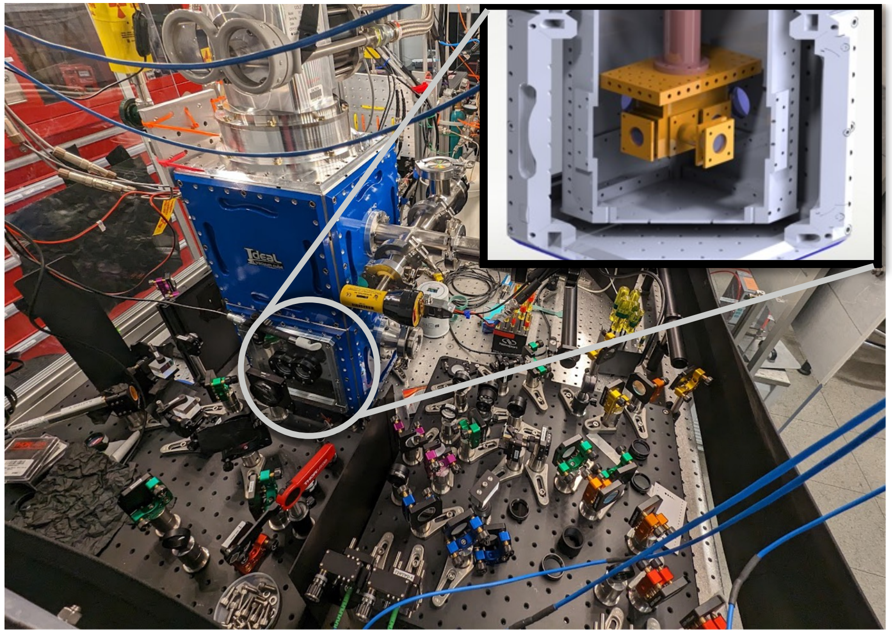

**AJ**, Thesis, Caltech (2023)

Y. Takahashi, C. Zhang, **AJ**, N.R. Hutzler, Physical Review Letters 131 (18), 183003

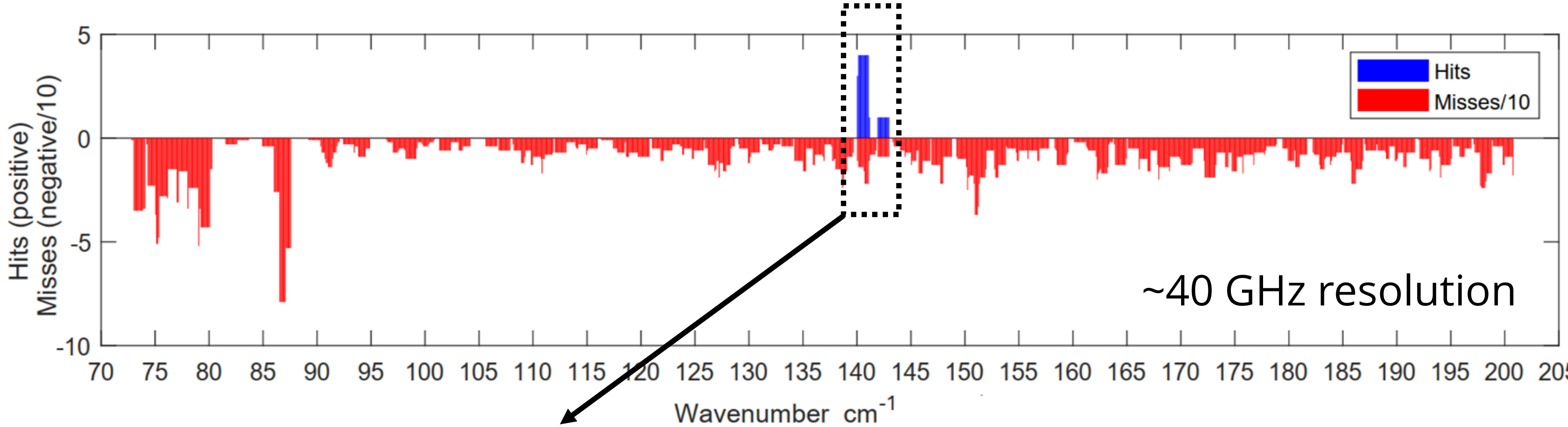
# $^{226}$RaOH Spectroscopy

- Octupole deformation: 100-1000x enhancement
- RaOH expected to be laser coolable
- Challenge: radioactive, limited quantity, unknown spectra
- “Minifridge”: tabletop, closed buffer gas cell for trace/radioactive species

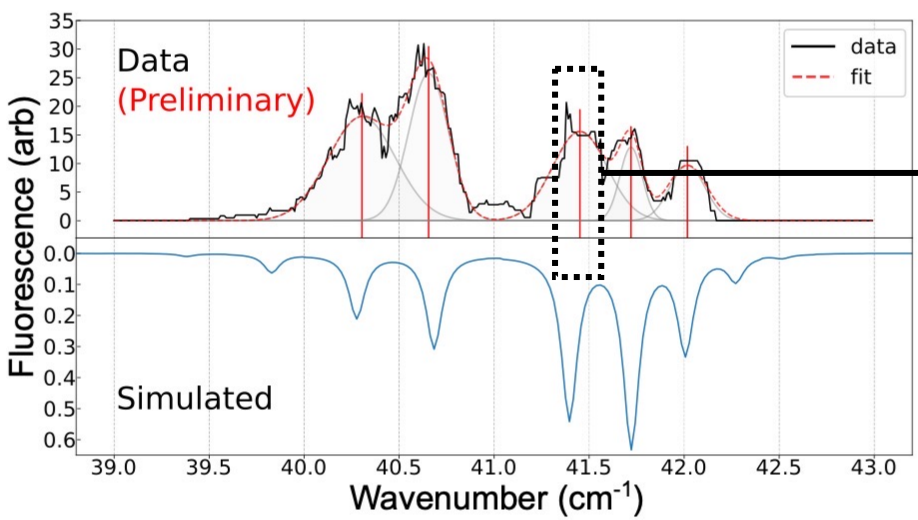


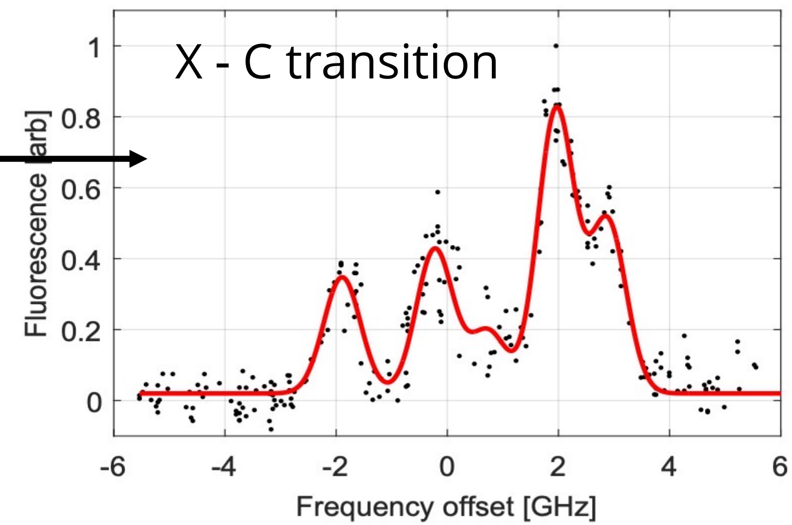
# Preliminary $^{226}$RaOH Results





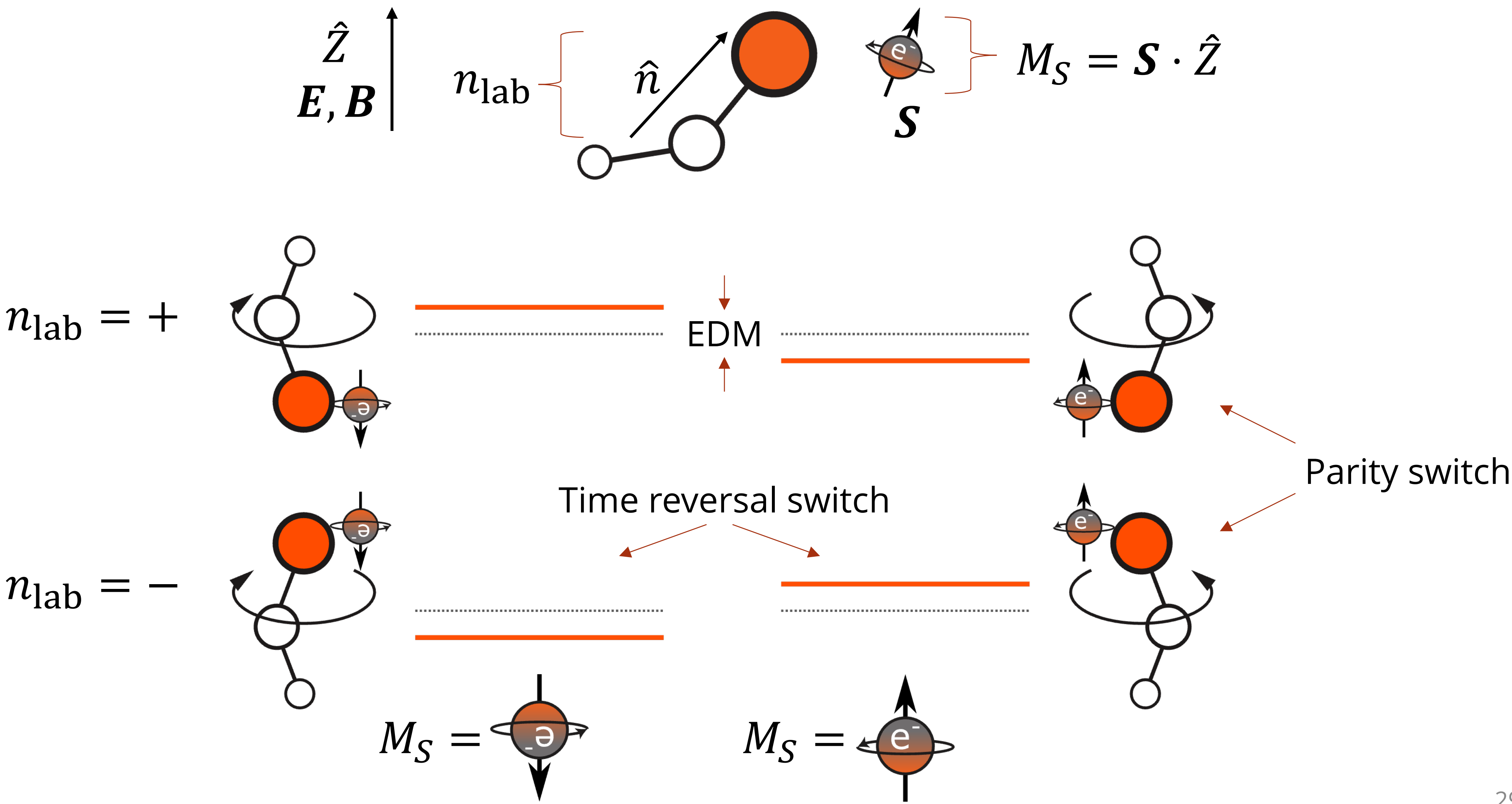

~3 GHz resolution




~100 MHz resolution

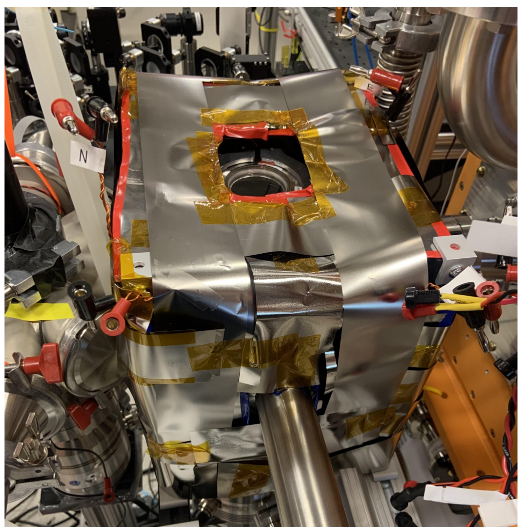
# Measurement

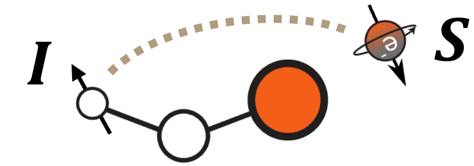
# EDM Energy Shifts



# State Prep and Hyperfine

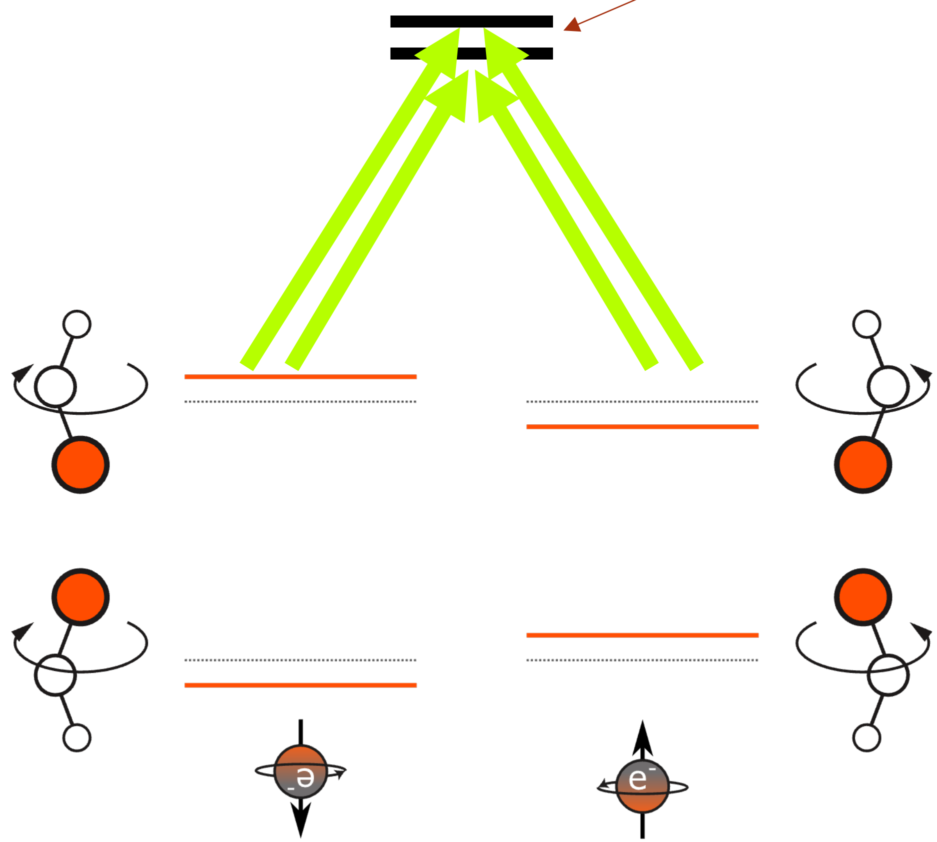
## Issues with Coherent Population Trapping (CPT)






Unresolved hyperfine structure:

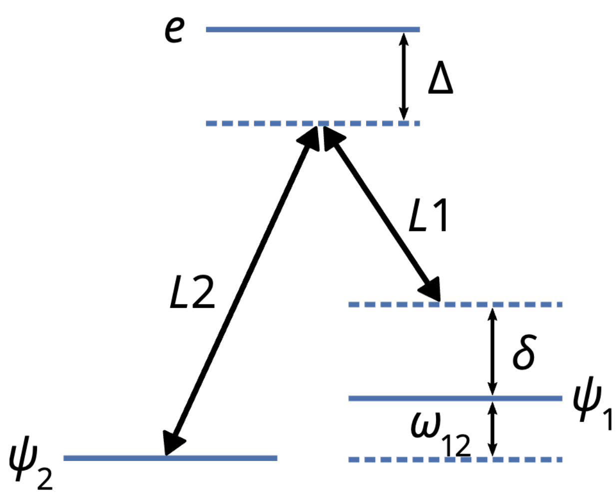
$|\uparrow\downarrow\rangle \pm |\downarrow\uparrow\rangle$




Interference means no dark superpositions

**Solution: Narrow linewidth schemes**

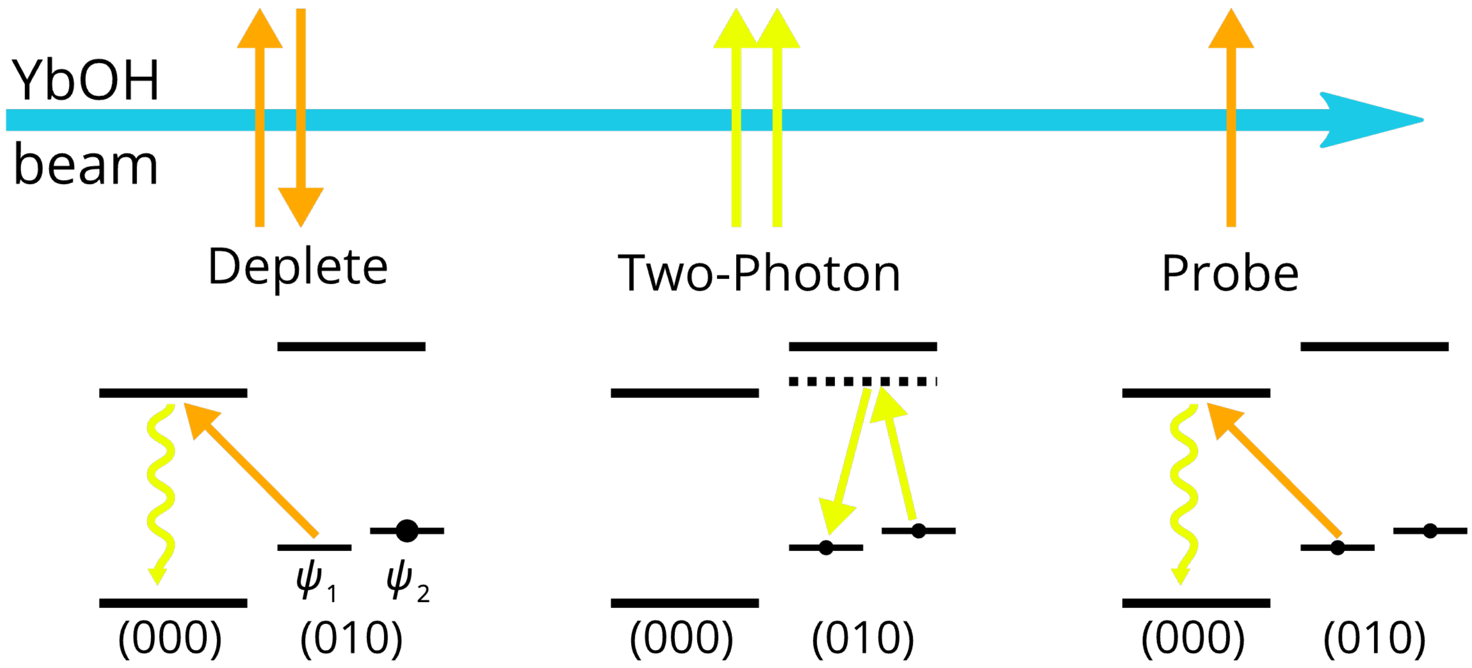
# Two-Photon Transitions



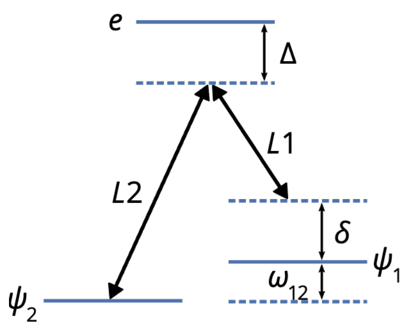

$\delta = 0 \rightarrow$ Two-Photon Resonance

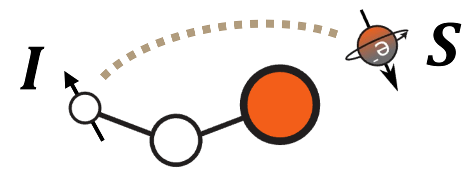
$\Delta = 0 \rightarrow$ Coherent Population Trapping (CPT)

$\Delta \gg 10\ \mathrm{MHz} \rightarrow$ Detuned Raman Transitions



# Two-Photon Physics

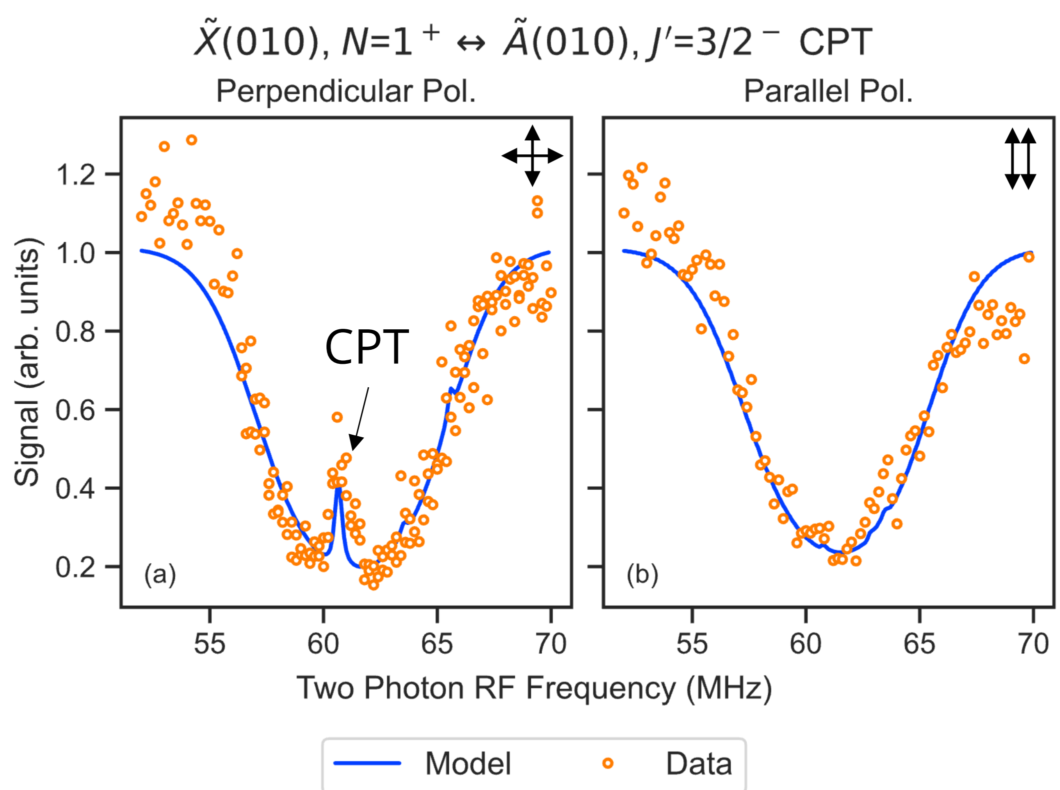


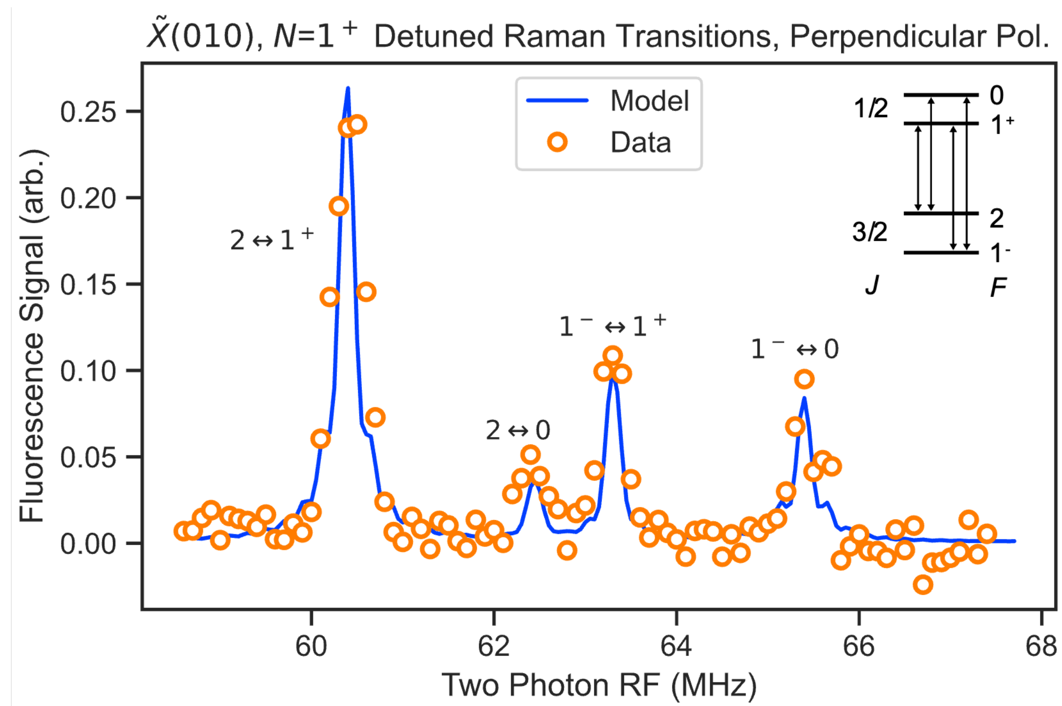




Hyperfine parameters:
$b_F = 4.07(18)$ MHz
$c = 3.49(38)$ MHz

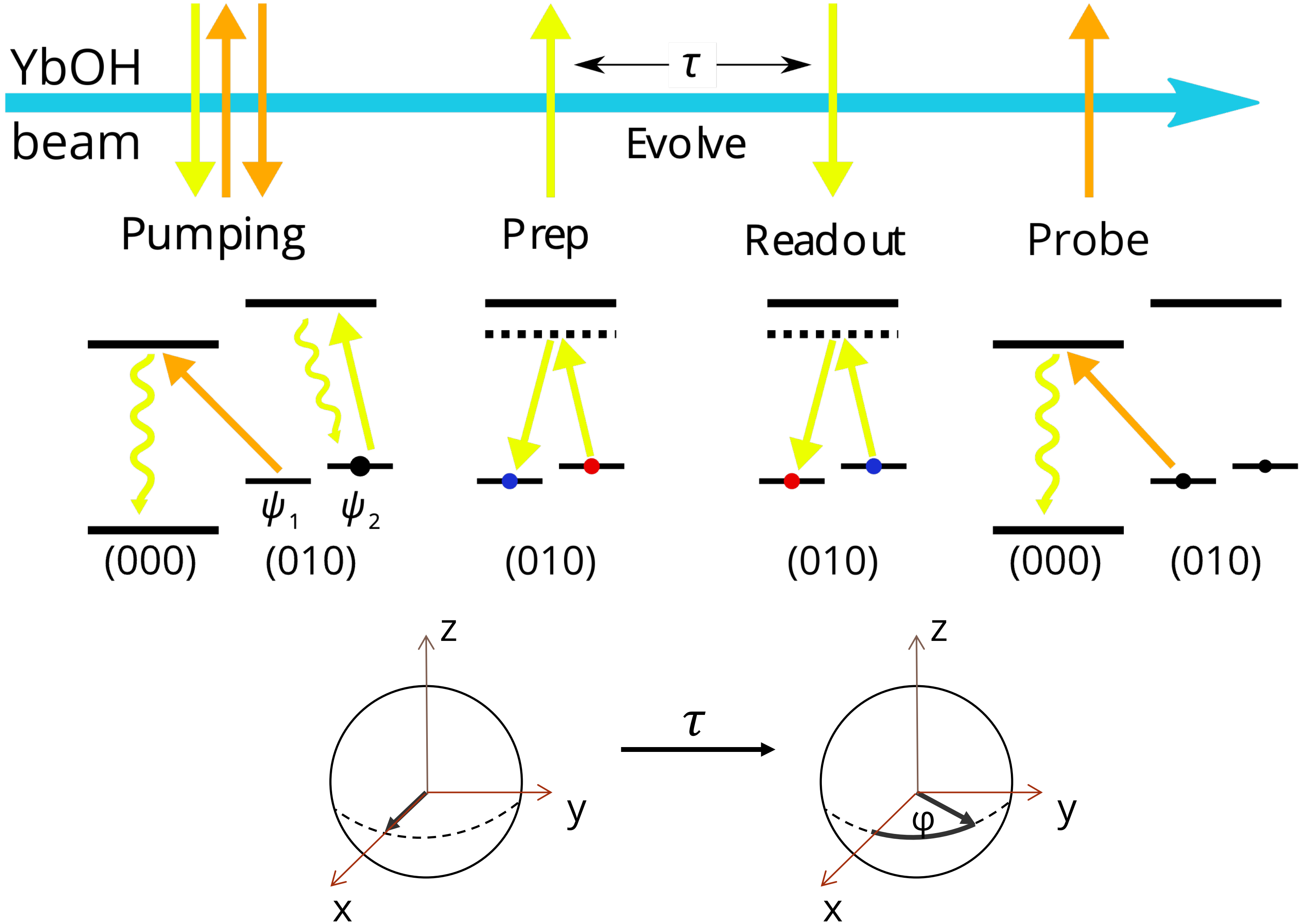
$\Delta = 0$

$\Delta = 1\ \mathrm{GHz}\times 2\pi$

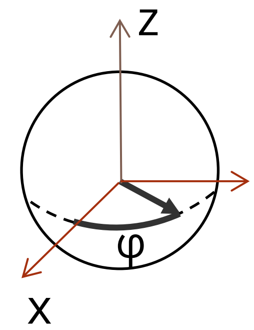


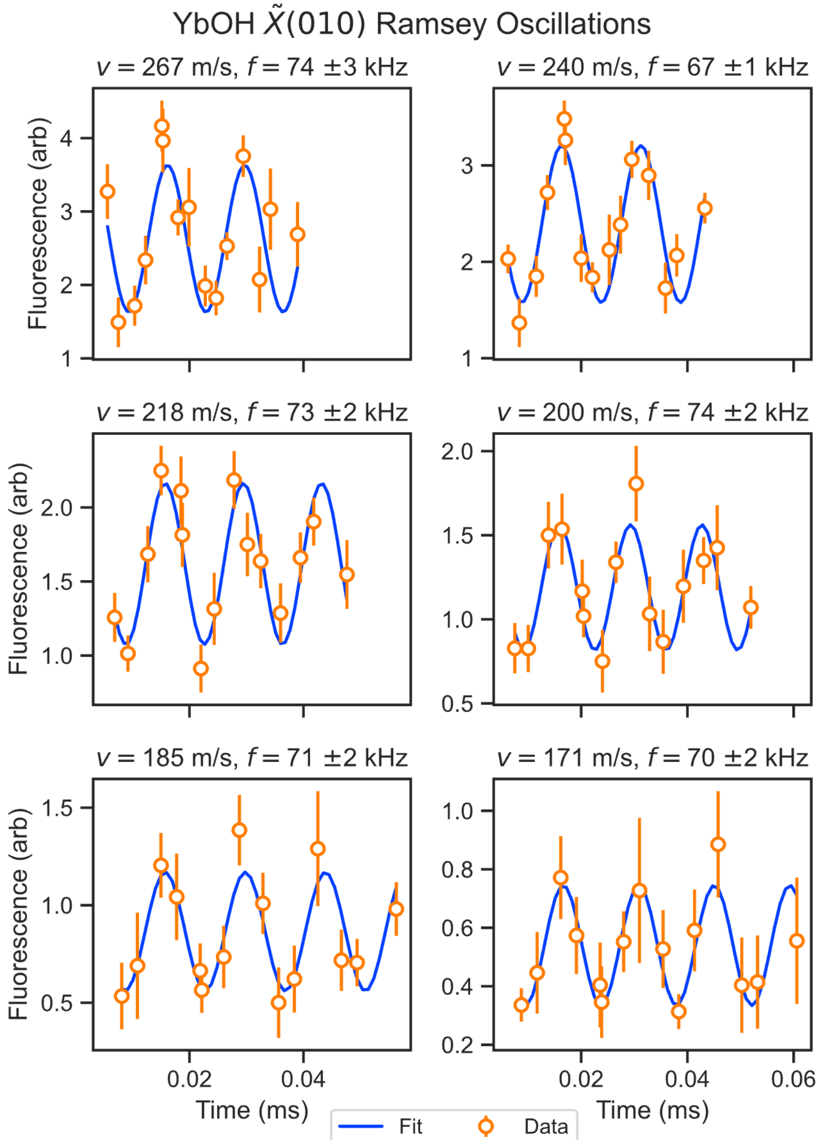



# Ramsey Interferometry



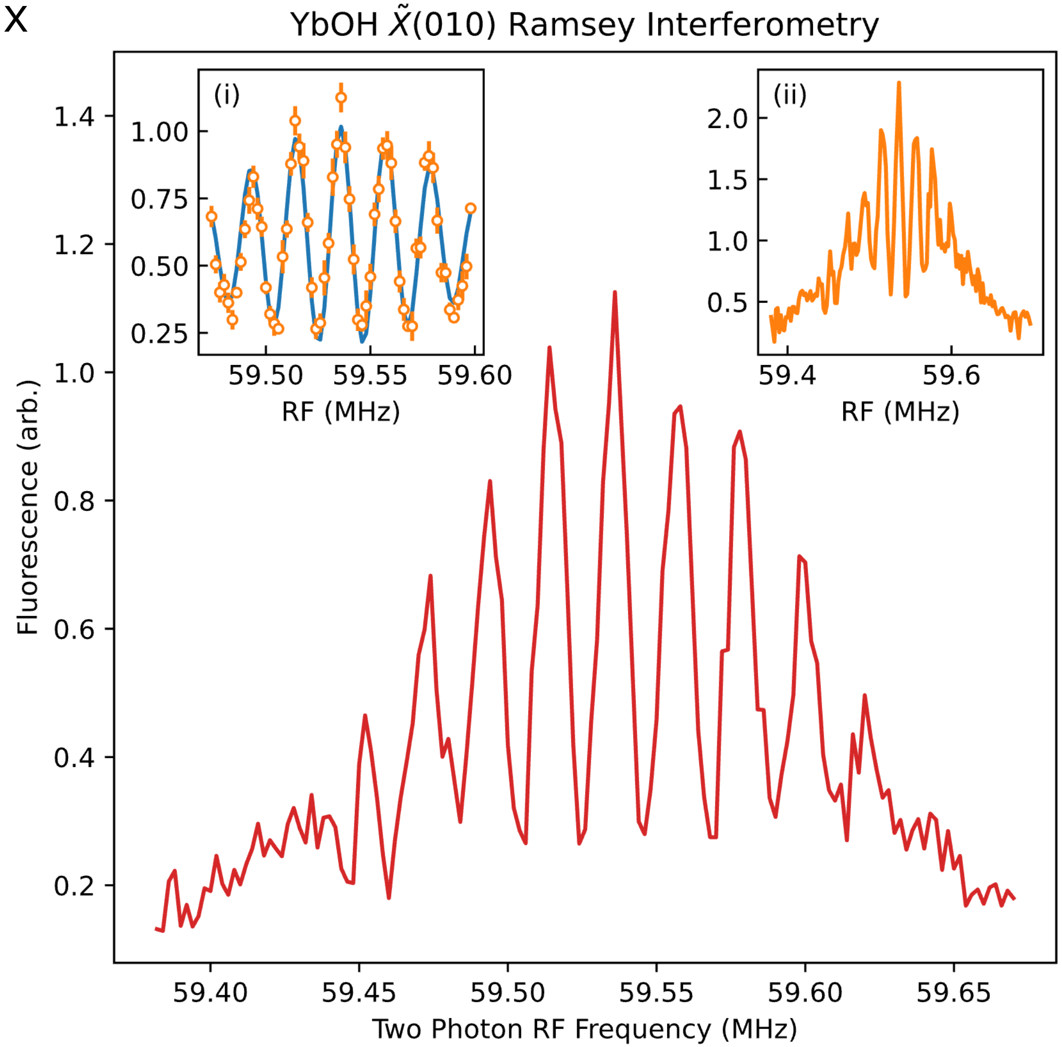
# Ramsey Results



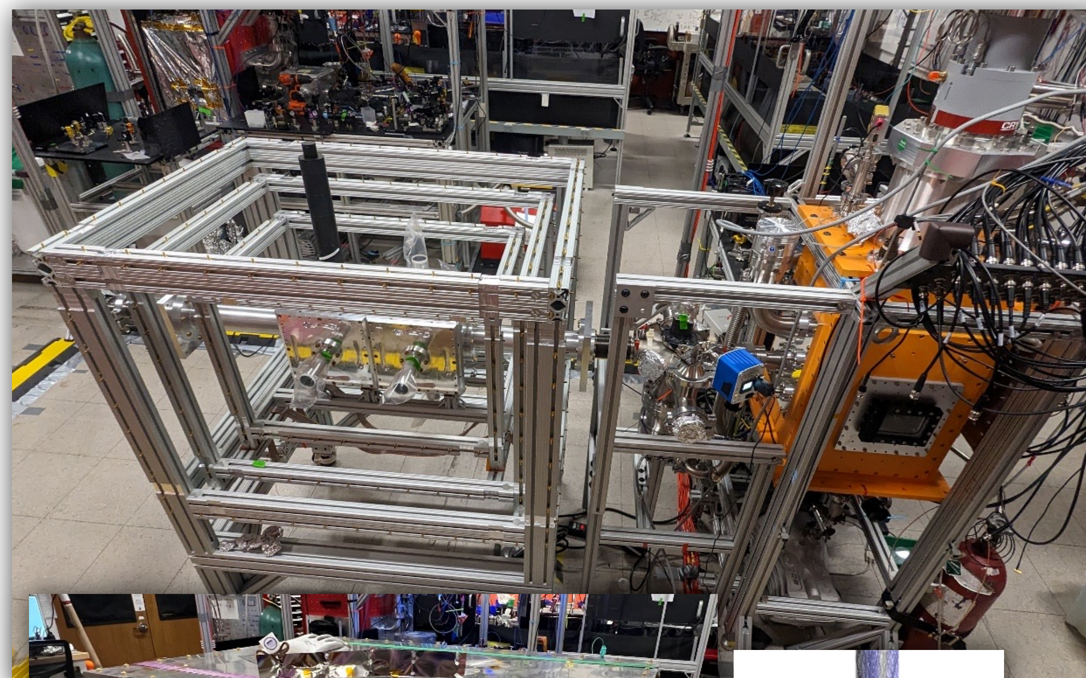



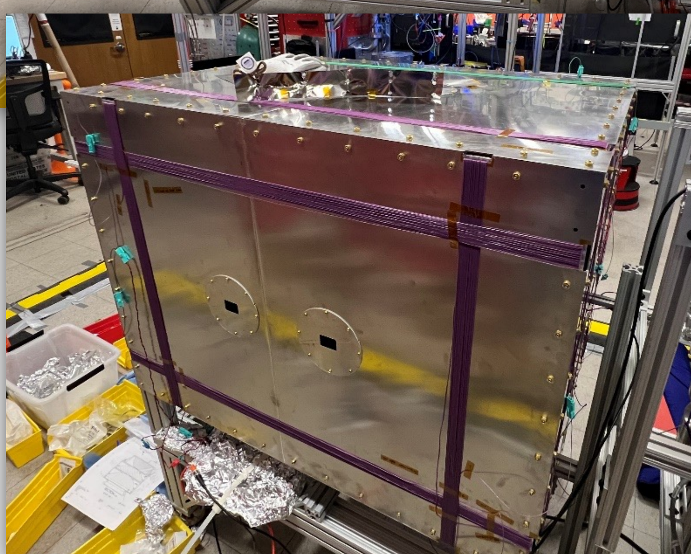

Fast YbOH

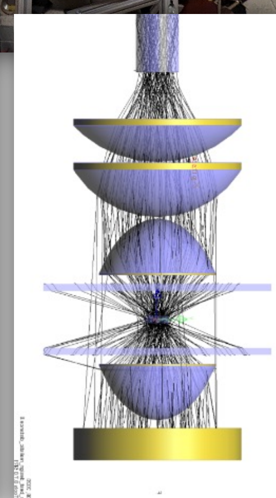
Slow YbOH

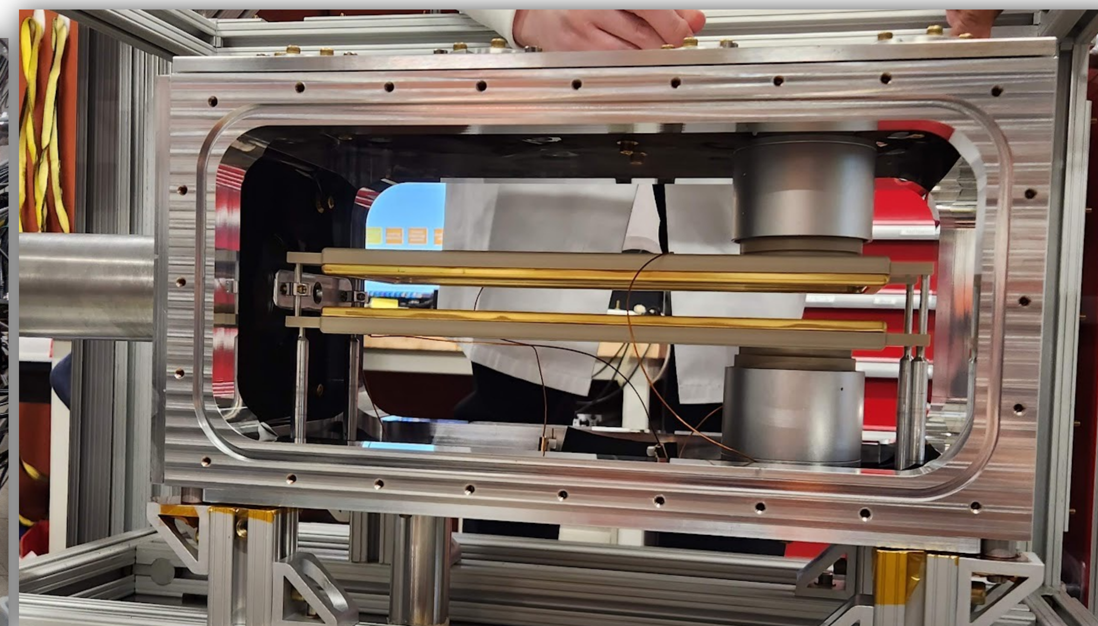


# MQM Science Chamber









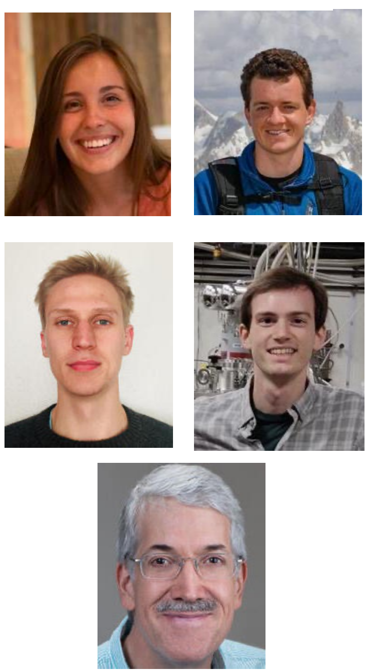
20 cm

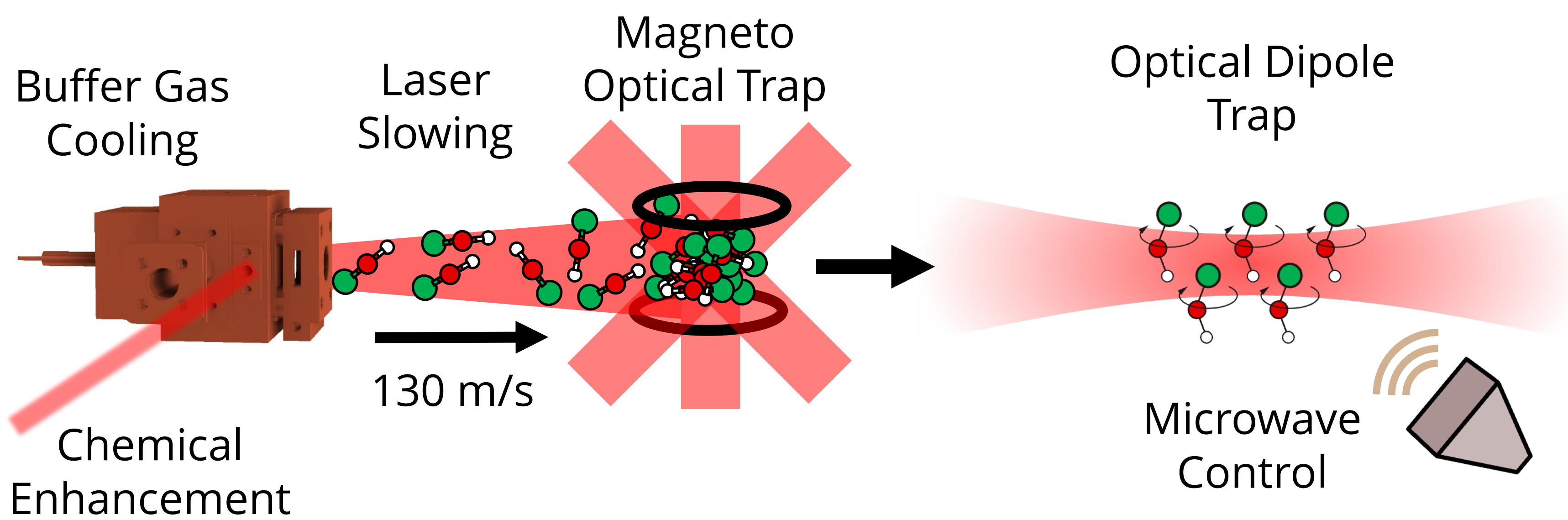
Harish Ramachandran | Yi Zeng | Chi Zhang | Chandler Conn | Daniel Grass | Yuiki Takahashi

# EDM "Pathfinder"

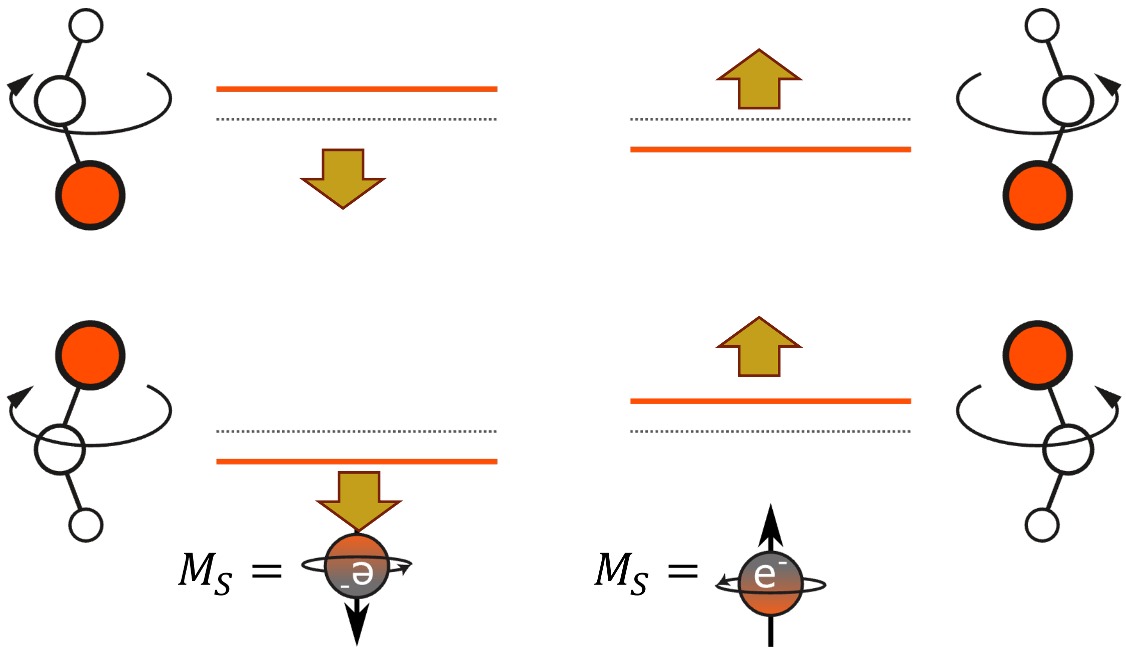
- Collaboration with CaOH group at Harvard
  - Iso-electronic to SrOH, YbOH, RaOH
- Microwave linewidth << Hyperfine splitting (~MHz)

CaOH Team





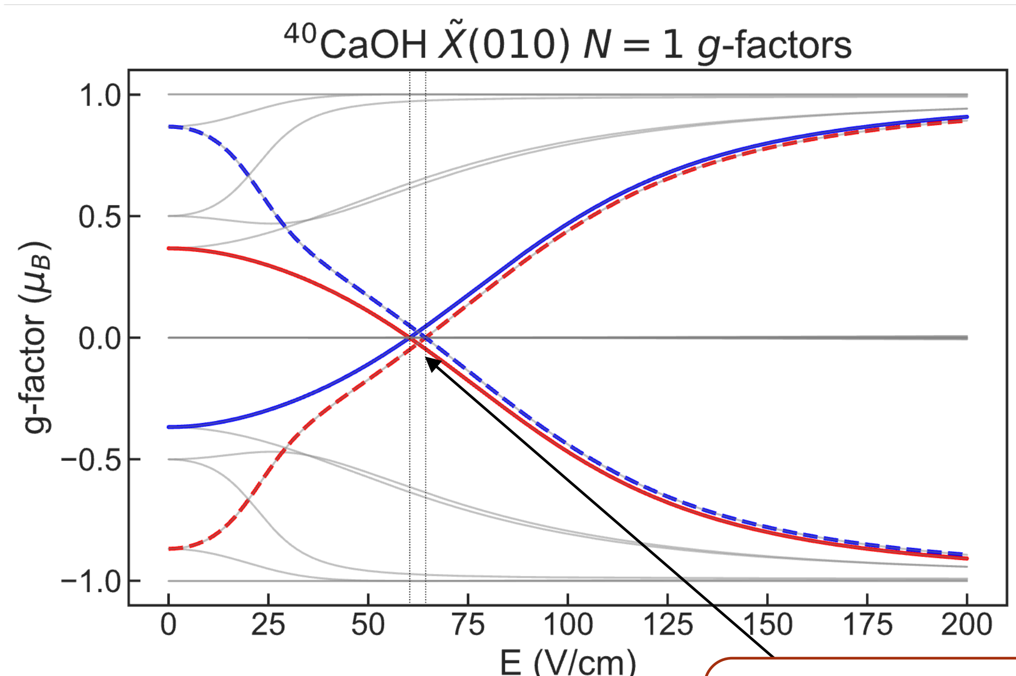
# Problem: Magnetic Sensitivity

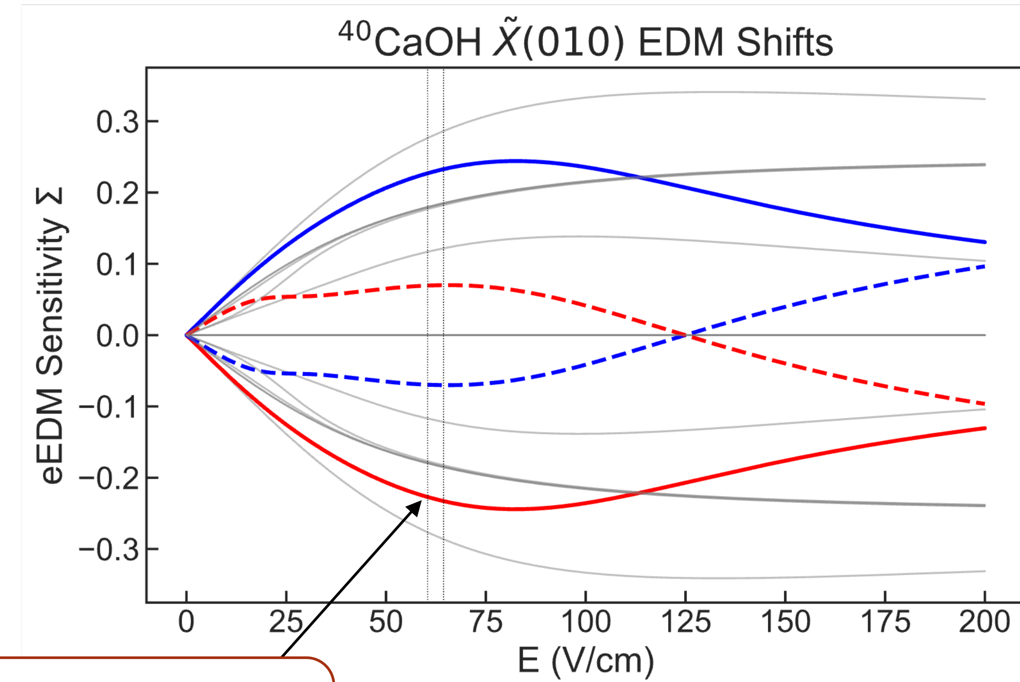



- Magnetic shifts are also T-odd
- Generic issue for laser-coolable molecules with unpaired electrons

# Solution: Zero *g*-Factor States

- Use E-field and parity doublets to engineer magnetically insensitive EDM states

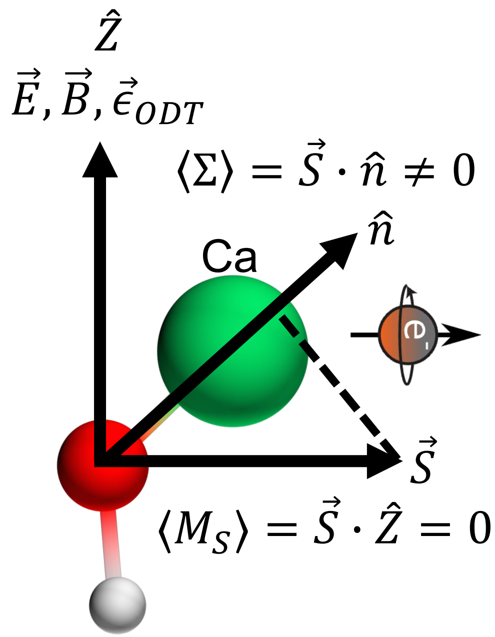


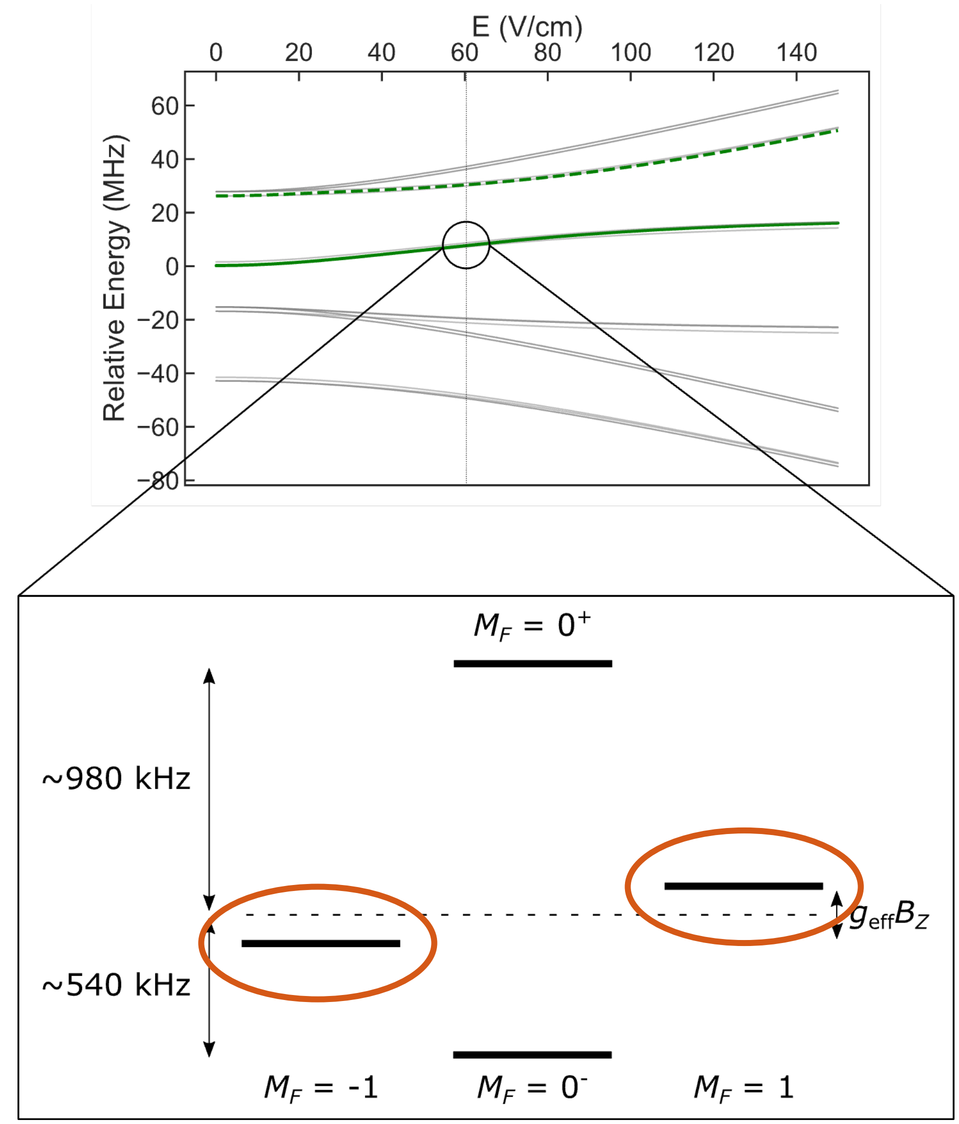




Magnetically insensitive…
…and eEDM sensitive!

L. Anderegg, N.B. Vilas, C. Hallas, P. Robichaud, **AJ**, J.M. Doyle, N.R. Hutzler, Science 382 (6671), 665-668

# Intuition

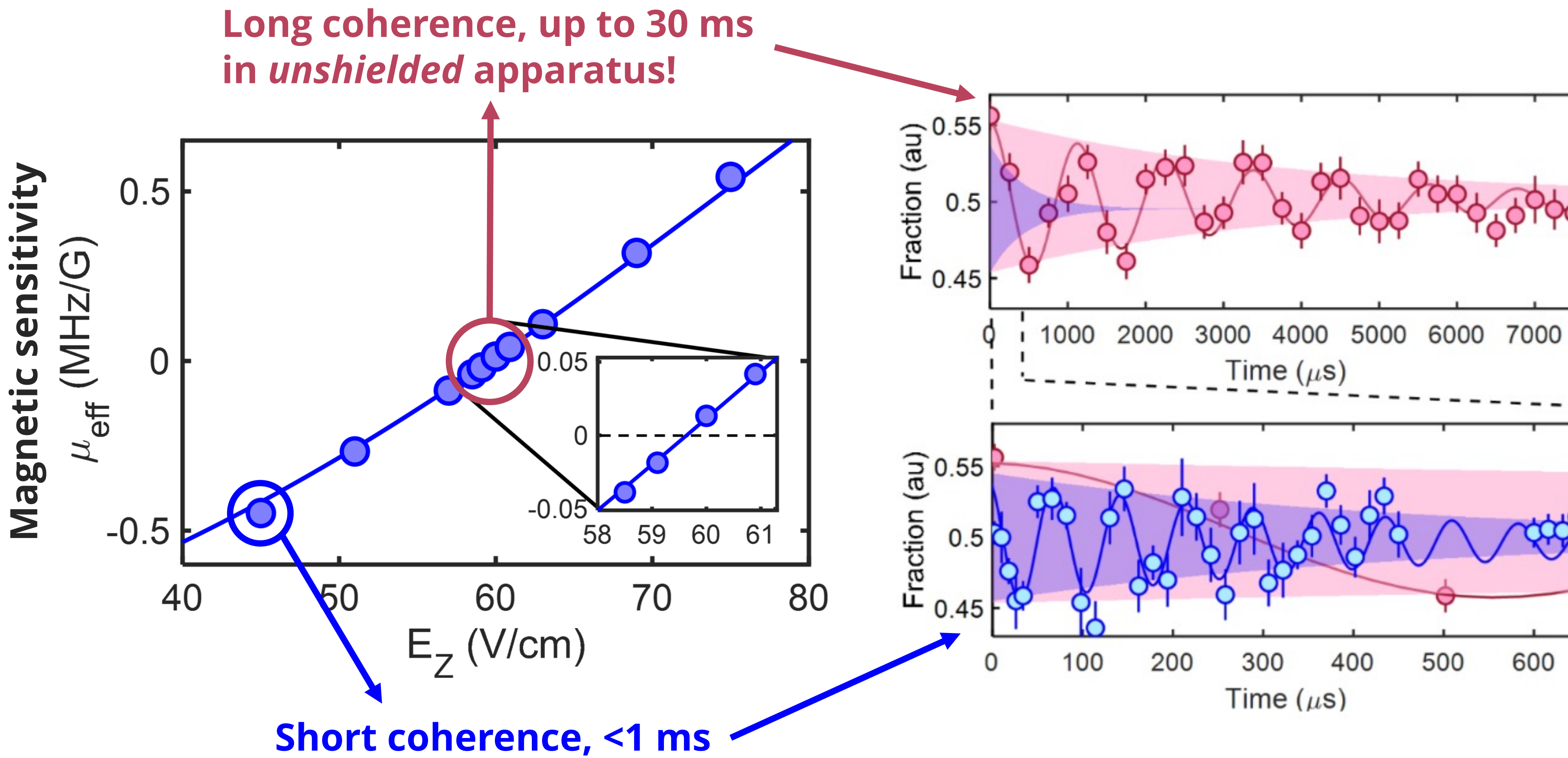



- Generic avoided level crossings from spin-rotation
- $g_{\text{eff}} \lesssim 10^{-3} \mu_B$

L. Anderegg, N.B. Vilas, C. Hallas, P. Robichaud, **AJ**, J.M. Doyle, N.R. Hutzler, Science 382 (6671), 665-668

# Engineering Coherence

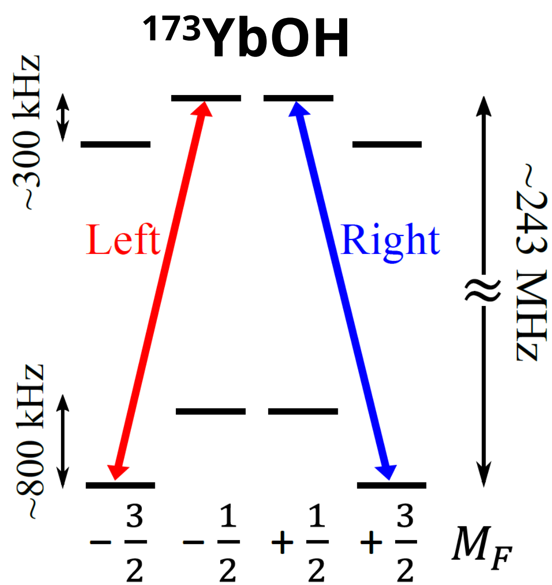


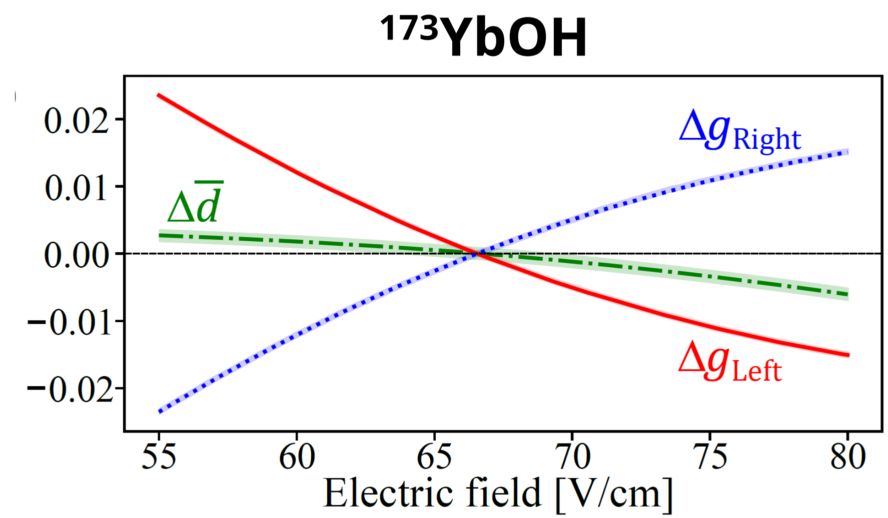

L. Anderegg, N.B. Vilas, C. Hallas, P. Robichaud, **AJ**, J.M. Doyle, N.R. Hutzler, Science 382 (6671), 665-668

# State Engineering Possibilities


- Field-insensitive transitions
  - Low E,B sensitivity, high PTV sensitivity
  - Generic to many molecules of interest (diatomic and polyatomic)

| Species | $I$ | $\mathcal{E}$/(V/cm) | $\lvert\Delta\bar{P}_{CPV}\rvert$/% | $\lvert\Delta g\rvert$ | $\lvert\Delta\bar{d}\rvert$ |
|---|---|---|---|---|---|
| $^{225}$RaF | ½ | 10,215 | 44 (NSM) | $1\times10^{-1}$ | 0 |
| $^{225}$RaF | ½ | 24,568 | 43 (NSM) | $5\times10^{-3}$ | 0 |
| | | 24,576 | 43 (NSM) | 0 | $6\times10^{-3}$ |




Y. Takahashi, C. Zhang, **AJ**, N.R. Hutzler, Physical Review Letters 131 (18), 183003

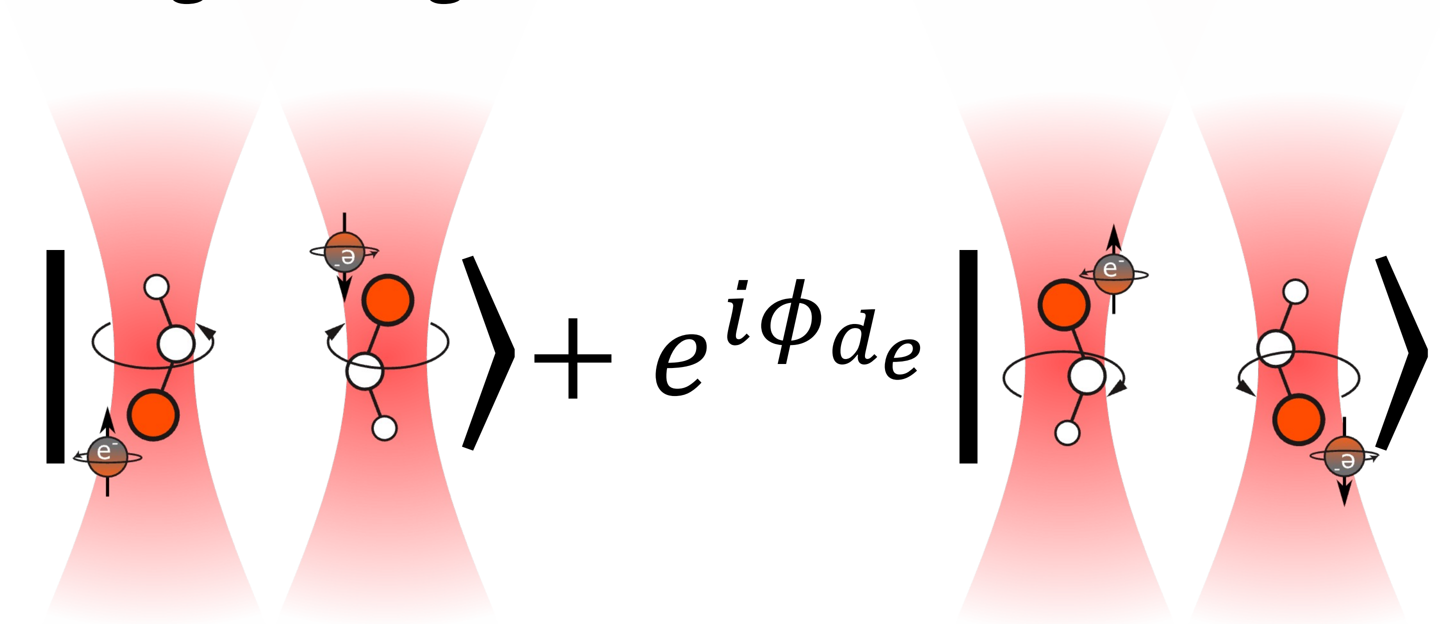
# Entanglement Possibilities

**Quantum-Enhanced Metrology for Molecular Symmetry Violation Using Decoherence-Free Subspaces**

Chi Zhang,* Phelan Yu, Arian Jadbabaie, and Nicholas R. Hutzler
*California Institute of Technology, Division of Physics, Mathematics, and Astronomy, Pasadena, California 91125, USA*

Chi Zhang

- AC polarization of molecular dipole moment
- Heisenberg scaling without additional noise

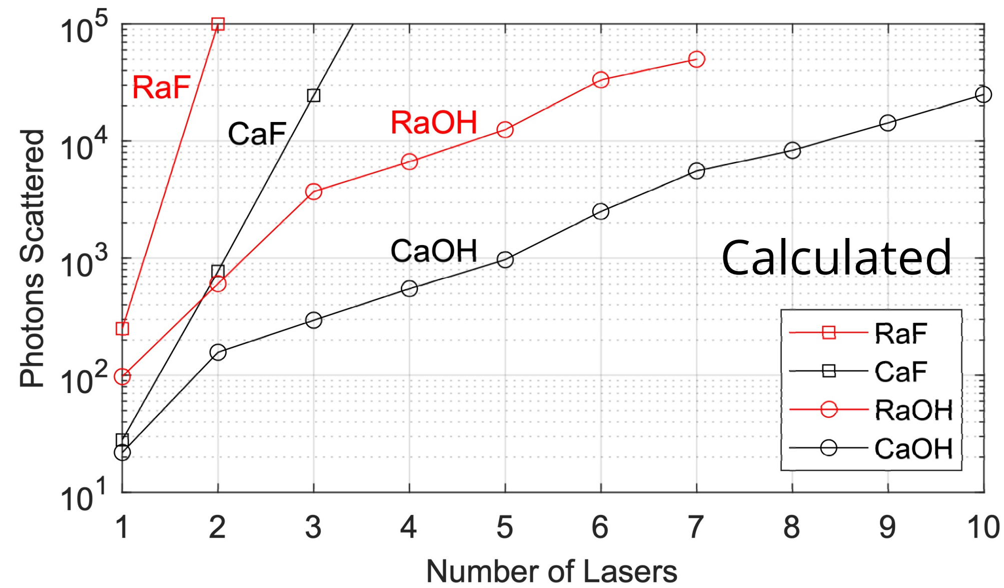


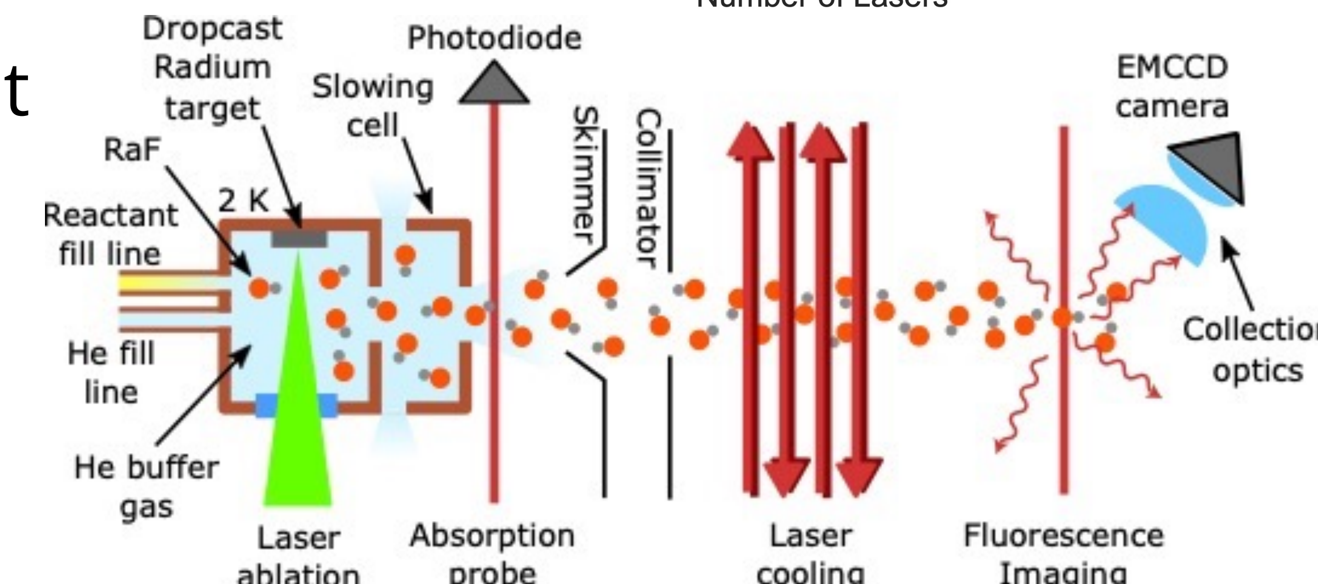

C Zhang, P Yu, **AJ**, NR Hutzler, Physical Review Letters 131 (19), 193602

# New Horizons: RaX

# $^{226}$RaX Experiment

- RaF and RaOH predicted to be laser coolable
- Building lab at Harvard
  - Laser cool RaF
  - Explore RaOH
- Making beams with drop-cast $^{226}$Ra target
  - 10 µCi initially
  - 1 mCi possible?
- Need to be efficient

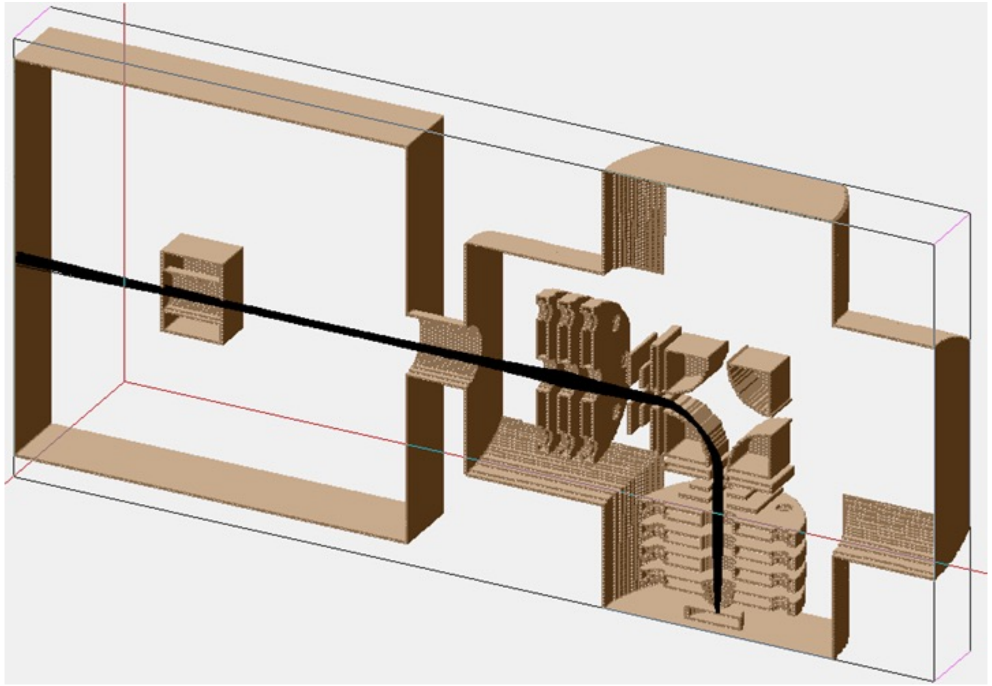



Zhang C, Hutzler NR, Cheng L. J Chem Theory Comput. 19.13 (2023)

# $^{225}$RaF Prospects

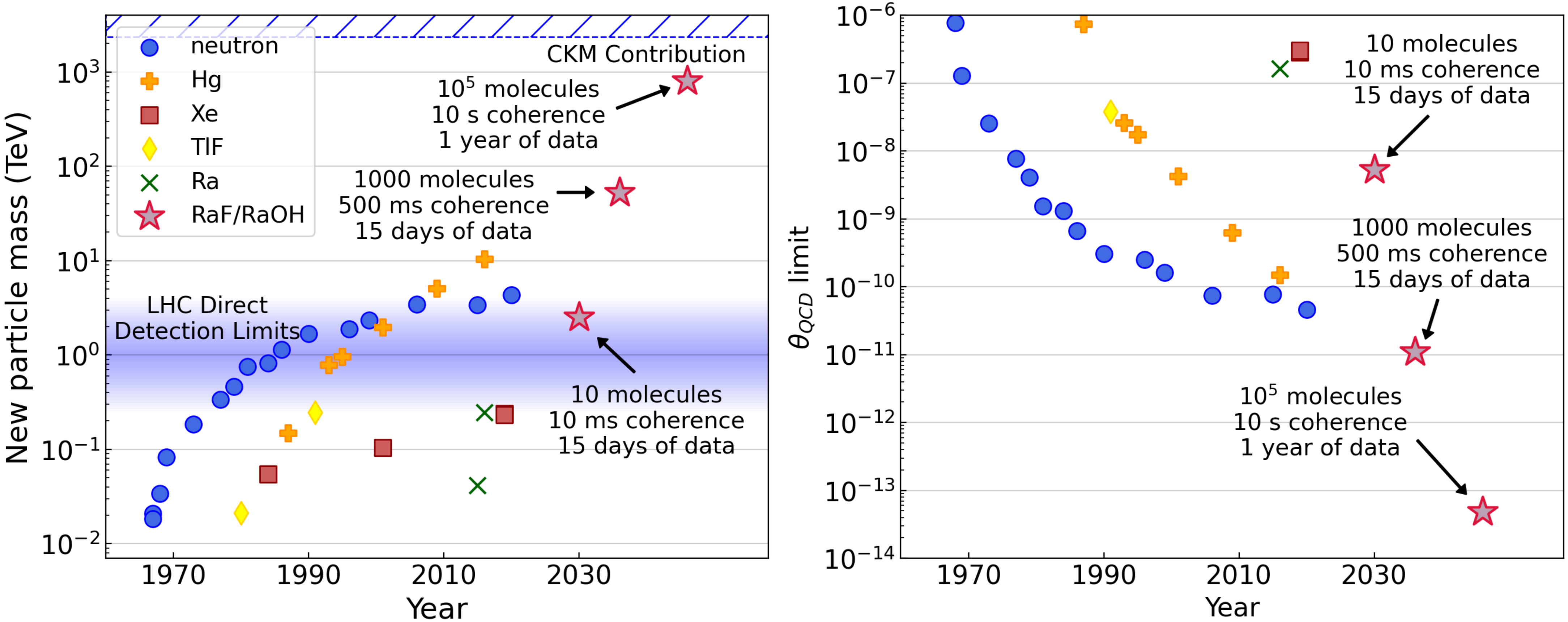
- $^{225}RaF^{+}$ produced at facilities as fast (≥keV) beams
  - Thermalize to 300K in RFQ
  - Neutralization with Na creates heating
- Use cryogenic buffer gas cell to simultaneously neutralize ions and cool?
  - Optimal neutralization species? Rydberg?
  - Theory guidance?
- ”Recombination” chemistry of $Ra^{+}$ and $F^{-}$ (or $OH^{-}$)?



# $^{225}$RaX Energy Reach

Subject to caveats!

Hadronic EDM Limits



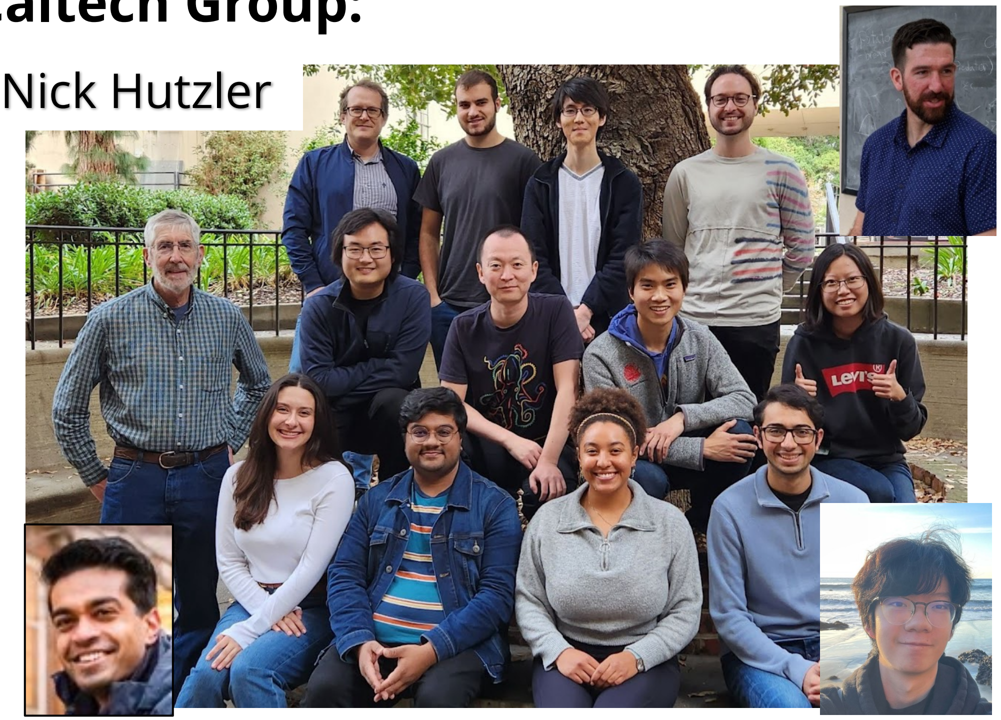

Chupp, T. E., et al. *Rev. Mod. Phys.* 91(1) (2019)
2022 EDM White Paper: arXiv:2203.08103
Engel, J., Ramsey-Musolf, M. J. & van Kolck, U., Prog. Part. Nucl. Phys. 71, 21–74 (2013).

Limits compiled by A. Jayich

# Thank You

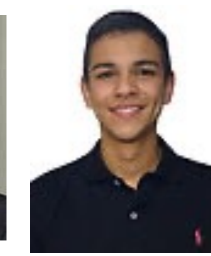
## Caltech Group:

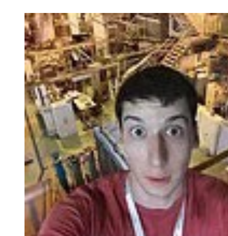
Nick Hutzler



NIST

## MIT/Harvard:





**Collaborations:**

PolyEDM:
Tim Steimle – ASU→Caltech
Doyle Group – Harvard
Amar Vutha – UToronto

PEDM

Chemical Enhancement:
Svetlana Kotochigova and Jacek Kłos – Temple University

Others:
Lan Cheng – Johns Hopkins
Michael Heaven – Emory University
Colan Linton – University of New Brunswick
Anastasia Borschevsky – University of Groningen

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GORDON AND BETTY MOORE FOUNDATION
FRIB
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ALFRED P. SLOAN FOUNDATION
NIST
NSF

# Extra Slides