Creation and quantum control of trapped molecular ions

Kia Boon Ng, TRIUMF

Fundamental Physics with Radioactive Molecules (INT 24-1)

27 March 2024

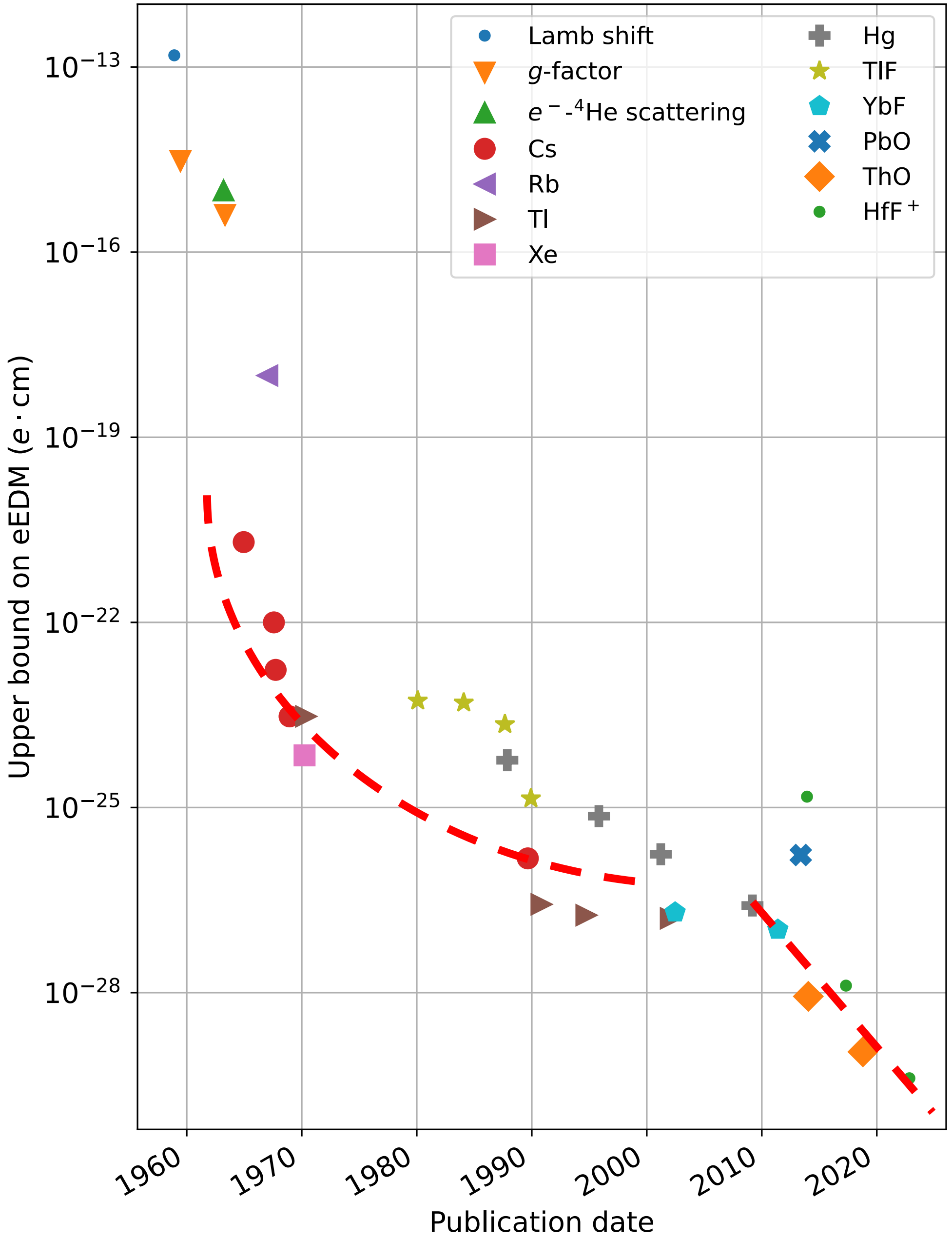
Overview

- Quick review
    - Molecules for EDMs
    - (Neutral) Molecules and molecular ions for interesting science

- Using molecular ions to measure an EDM
    - Quantum control of atoms and molecules
    - Collaborating with JILA for Schiff moment in $^{227}ThF^+$ @ TRIUMF
    - Complication from using molecular ions
    - Highly charged molecules & creation of CeF^{2+} as steppingstone to PaF^{3+}

Molecules for EDMs

- (Right) bound on eEDM vs publication date
- Why atoms (instead of bare)?
  - Sensitivity enhancement for certain types of EDM (e.g., eEDM, Schiff moment)
- Why (polar) molecules (instead of atoms)?
  - Polarization of electron cloud.
  - Molecules have rich(er) internal structure
    - Exploit to enhance measurement sensitivity.


Adapted from Paul Hess's thesis

Molecules for EDMs

- How exploit?

Stationary eigenstate insensitive to new physics

New physics embedded in states of good orientation

But eigenstates are states of good parity in absence of external fields

Apply external electric field to polarize

For experts in audience:

- E-field strength needs to overwhelm energy difference between parity states for good polarization
- $\Delta E_{\text{atom}} \sim 10$ THz
- $\Delta E_{\text{molecule}} \sim 10$ GHz → ~50% polarized in 10 kV/cm
- $\Delta E_{\text{molecule}+\Omega\text{ doubling}} \sim 10$ MHz
- $\Delta E_{\text{polyatomic}} \sim 10$ MHz

Fully polarized in 100 V/cm

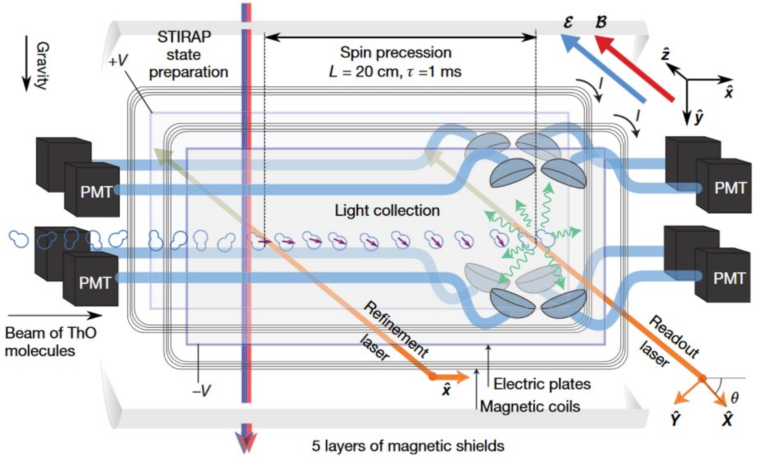
For younger audience:

- Spins don’t know where to point if no fields.
- Use fields to tell them where to point.
- Molecules have more atoms ⇒ peer pressure.
- More obedient, easier to orient.
- Oriented ⇒ sing like a choir.
- Not oriented ⇒ chatter in a restaurant.

(Quantumly controlled) Molecules:
Great for many things!

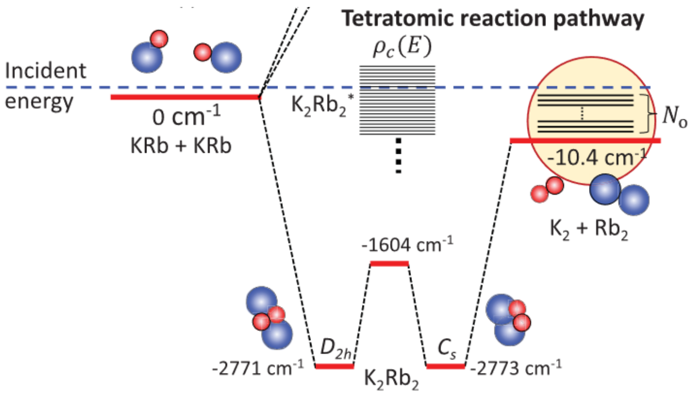
Non-exhaustive list!!!

Precision measurements of physics beyond the Standard Model



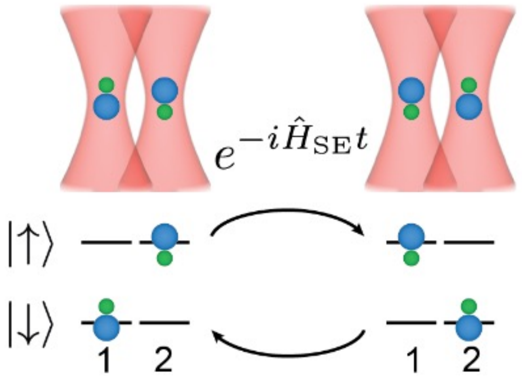
ACME collaboration

Probing intermediate complexes in chemical reactions



Ni group, Harvard

Quantum simulation and quantum computation



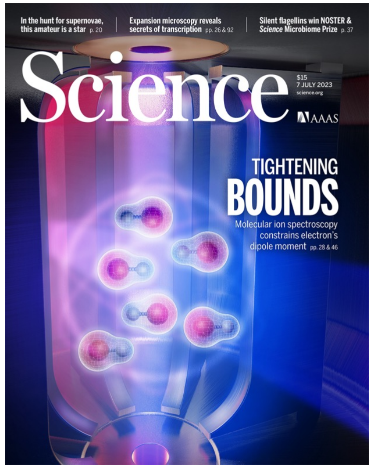
Cheuk group, Princeton

Quantum state control + Laser cooling Trapping *Not all molecules are laser coolable/trappable* + Entanglement

Molecular ions:
Advances on many fronts!

Non-exhaustive list!!!

Precision measurements of physics beyond the Standard Model



In the hunt for supernovae, this amateur is a star p. 20

Expansion microscopy reveals secrets of transcription pp. 26 & 92

Silent flagellins win NOSTER & *Science* Microbiome Prize p. 37

Science

$15
7 JULY 2023
science.org

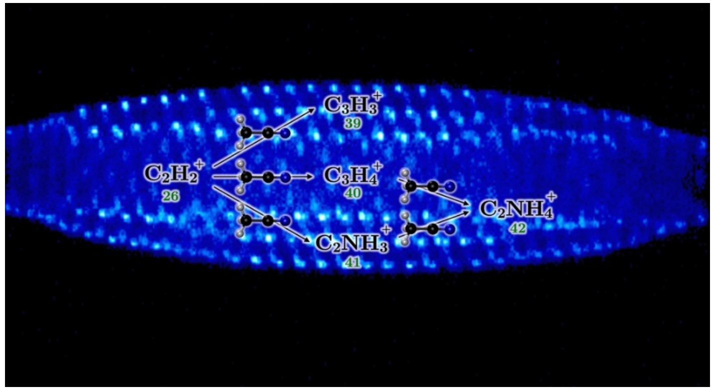
AAAS

TIGHTENING
BOUNDS

Molecular ion spectroscopy constrains electron's dipole moment pp. 28 & 46

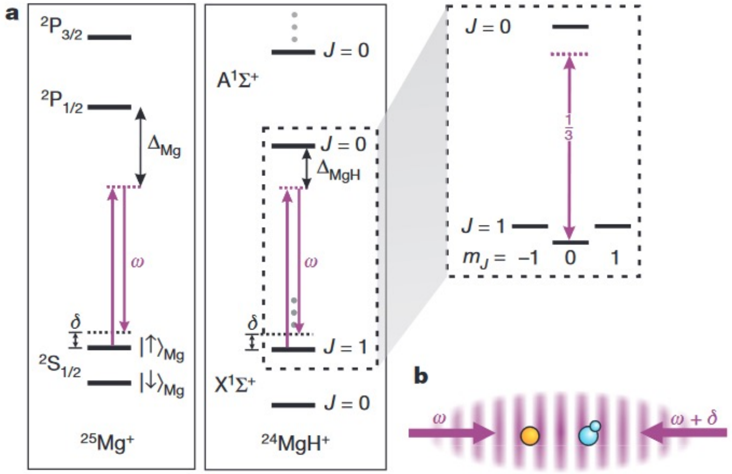
Cornell & Ye group, JILA

Probing chemical reactions to understand interstellar medium



Lewandowski group, JILA

Non-destructive state detection



Schmidt group, QUEST, PTB

Long trapping times
with (simple) ion traps

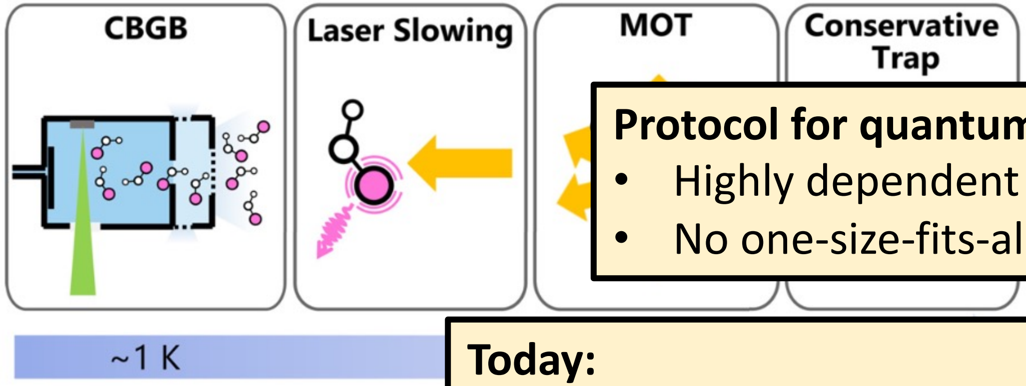
\+ Sympathetic cooling

\+ Quantum logic spectroscopy

Quantum control of molecules:
Two main classes

Non-exhaustive list!!!

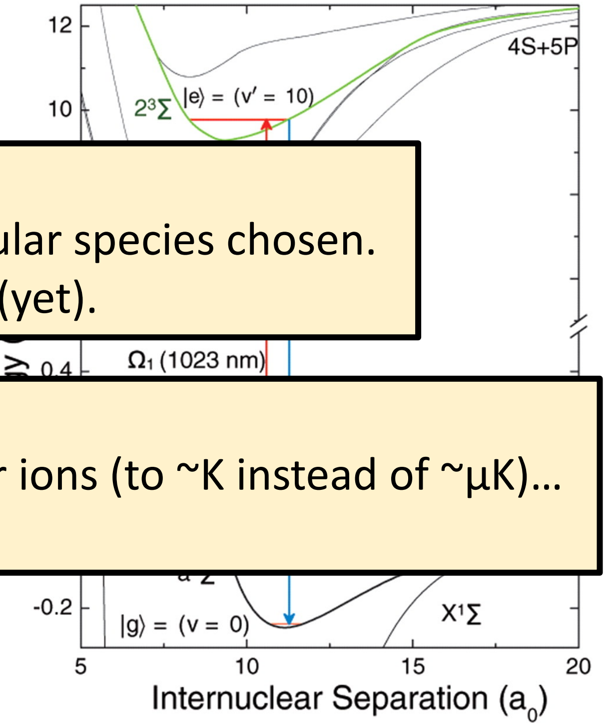
Direct cooling of molecules



1. Mak
2. Cool molecules

Doyle group, Harvard

Association of ultracold atoms



1. Make atoms
2. Cool atoms
3. Associate cooled atoms into molecules

Ye group, JILA

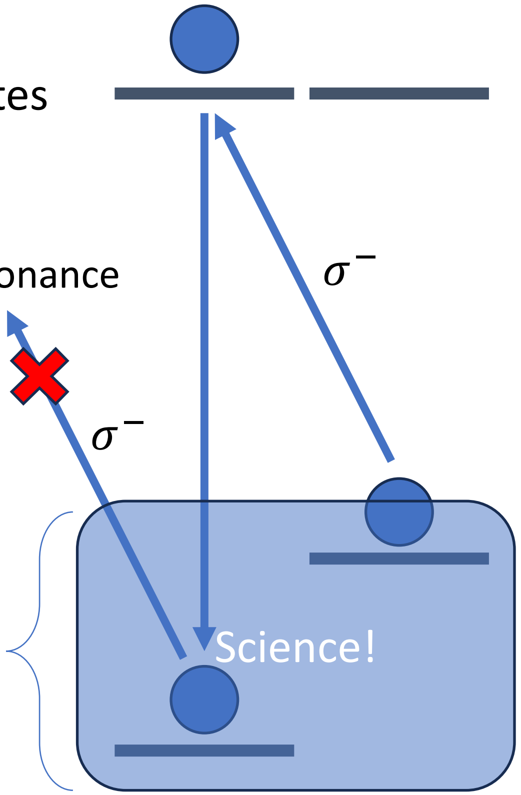
Protocol for quantum control:

- Highly dependent on molecular species chosen.
- No one-size-fits-all protocol (yet).

Today:

- Focus on direct cooling of molecular ions (to ~K instead of ~µK)…
- … with incoherent optical pumping.

Quantum control: simple atomic example



(Another set of)
Convenient excited states

No state on resonance

States of interest

Statistical distribution of population
Phase difference mapped to population difference

States of interest:

- Qubit states for quantum computation.
- Clock states for clock frequency measurements.
- Science states for precision measurements.

State preparation

- Reduce entropy / initialize into well defined state.
- Exploit selection rules, resonance, etc. for state selectivity.

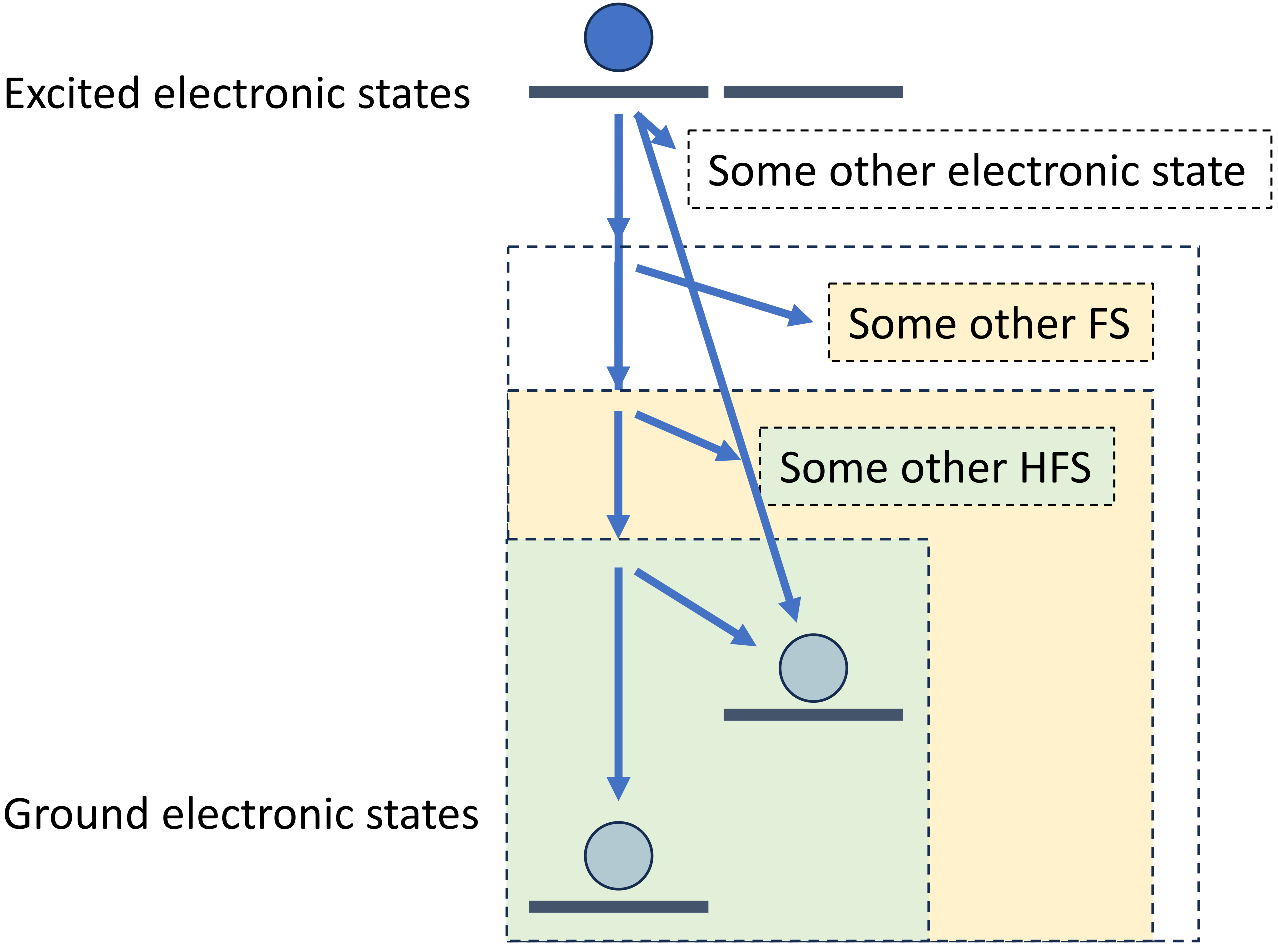
Science!

- Ramsey, Rabi, spin echo, etc.

State readout

- Exploit selection rules, resonance, etc., for state selectivity.

Quantum control: simple atomic example



For the case of incoherent optical pumping:

1. Branching ratio back to ground electronic state.
2. "Branching ratio" to various fine structure manifolds.
3. "Branching ratio" to various hyperfine manifolds.
4. "Clebsch-Gordon" overlap with spin states.

Typical tricks:

- Use selection rules to minimize losses.
- Repump losses back ($$$).

Quantum control: simple atomic example

- Probability of “good optical pumping” per cycle

$$P_{\text{cycle}} = P_{\text{electronic}} \times P_{\text{FS}} \times P_{\text{HFS}} \times P_{\text{spin}}$$

Probability of going to the desired electronic state

Probability of going to the desired fine structure manifold

- What about the losses then?
  - Leave them be
    - Fewer “useful” ions ⇒ degraded statistics.
    - “Useless” ions could form a source of decoherence.
    - Could decay down to “science state” and contaminate “science signal”.
  - Repump
    - More lasers/microwaves ⇒ $$$ and more cramped setup.
    - More components in the experiment ⇒ higher chance of something breaking.

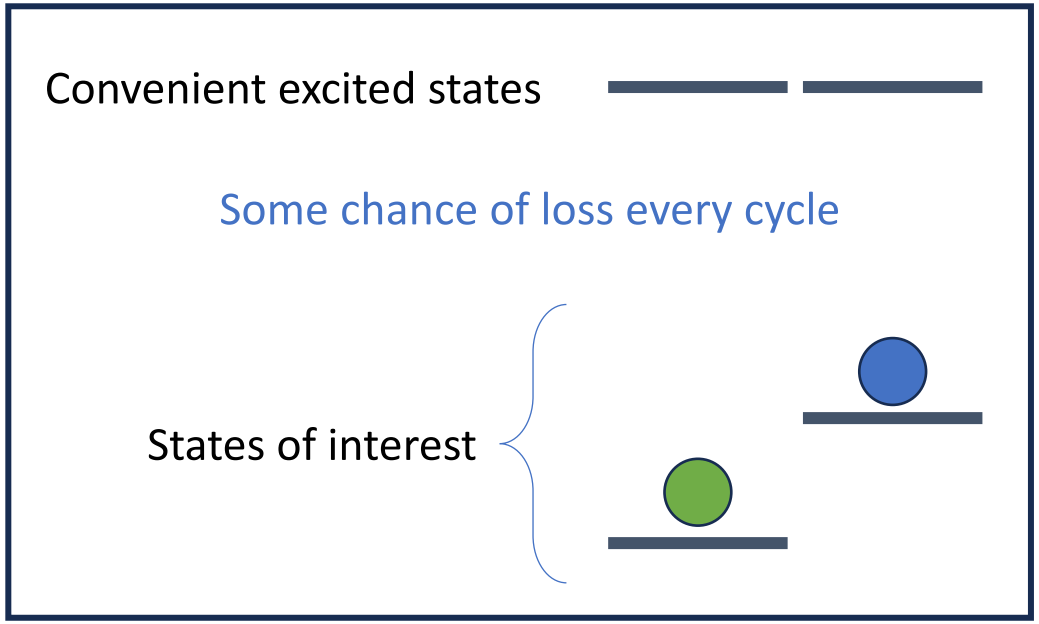
Quantum control: simple atomic example

- Probability of “good optical pumping” per cycle

$$P_{\text{cycle}} = P_{\text{electronic}} \times P_{\text{FS}} \times P_{\text{HFS}} \times P_{\text{spin}}$$

⇒ rich $$$

Small “Hilbert space”

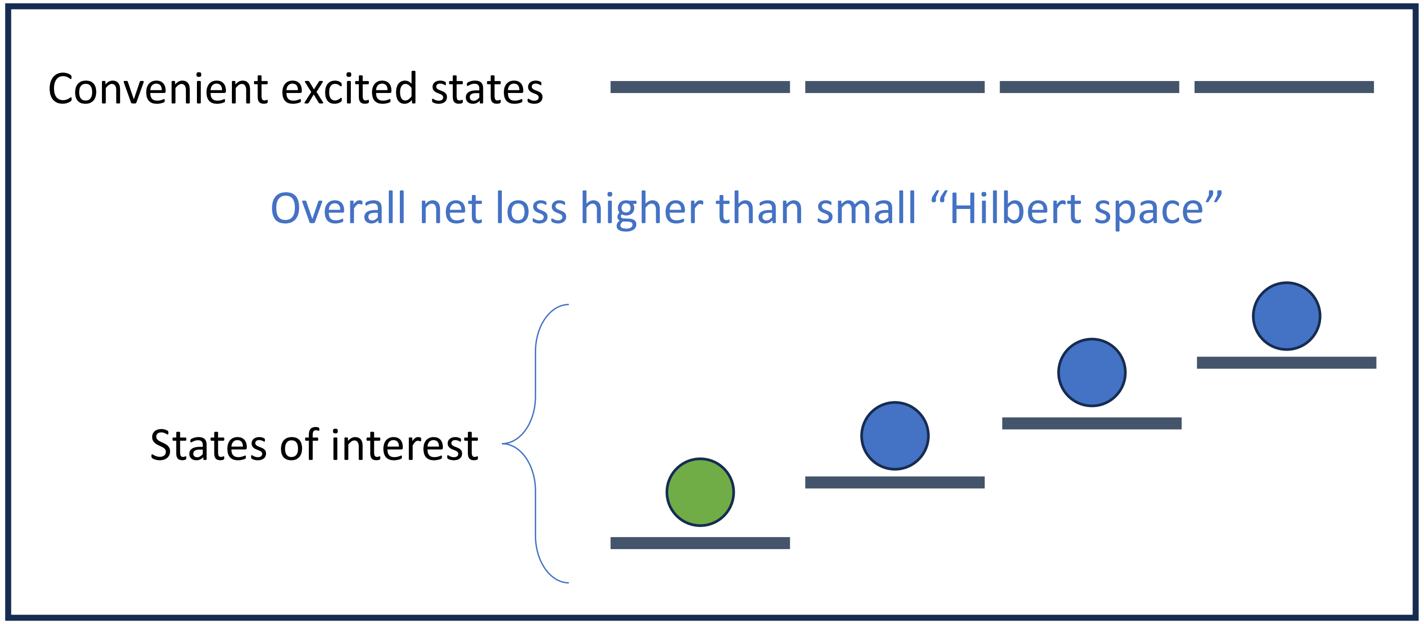


Convenient excited states

Some chance of loss every cycle

States of interest

Big “Hilbert space” ⇒ more lasers (& hardworking students+postdocs)



Convenient excited states

Overall net loss higher than small “Hilbert space”

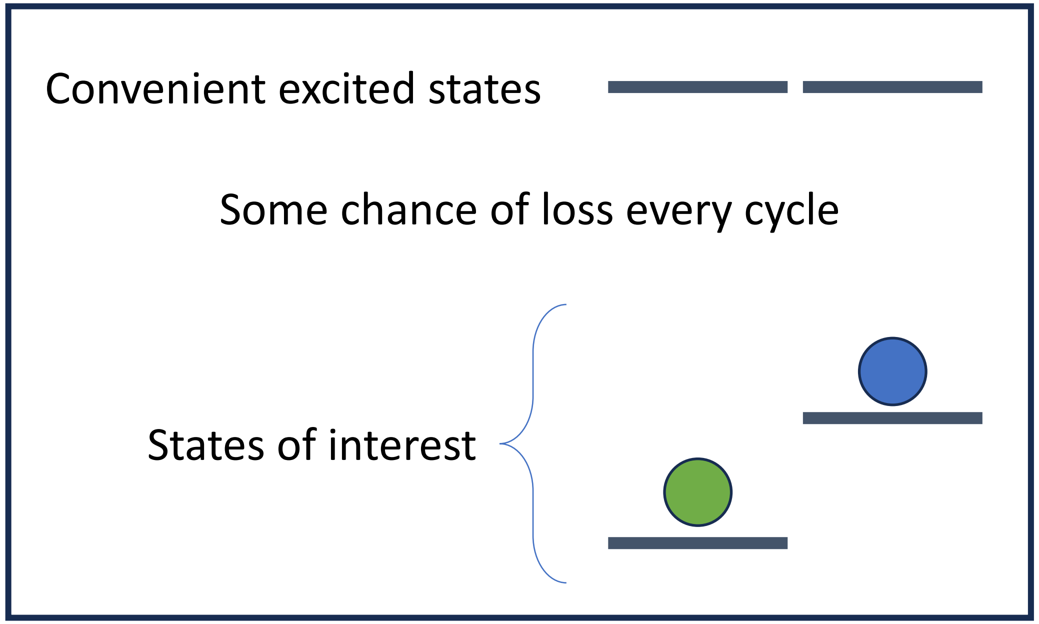
States of interest

Quantum control: molecule

- Probability of “good optical pumping” per cycle

$$P_{\text{cycle}} = P_{\text{electronic}} \times P_{\text{FS}} \times P_{\text{HFS}} \times P_{\text{spin}} \times P_{\text{vibrational}} \times P_{\text{rotational}}$$

Small “Hilbert space”

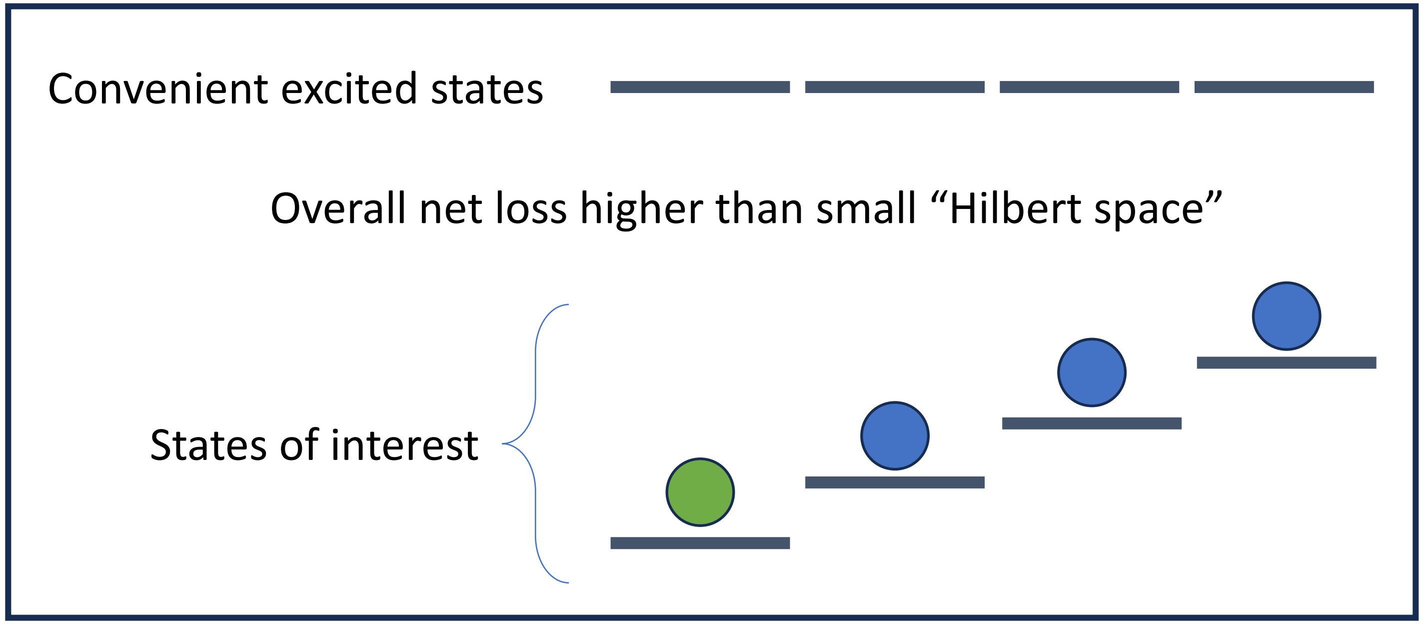


Convenient excited states

Some chance of loss every cycle

States of interest

Big “Hilbert space” ⇒ more lasers (& hardworking students+postdocs)



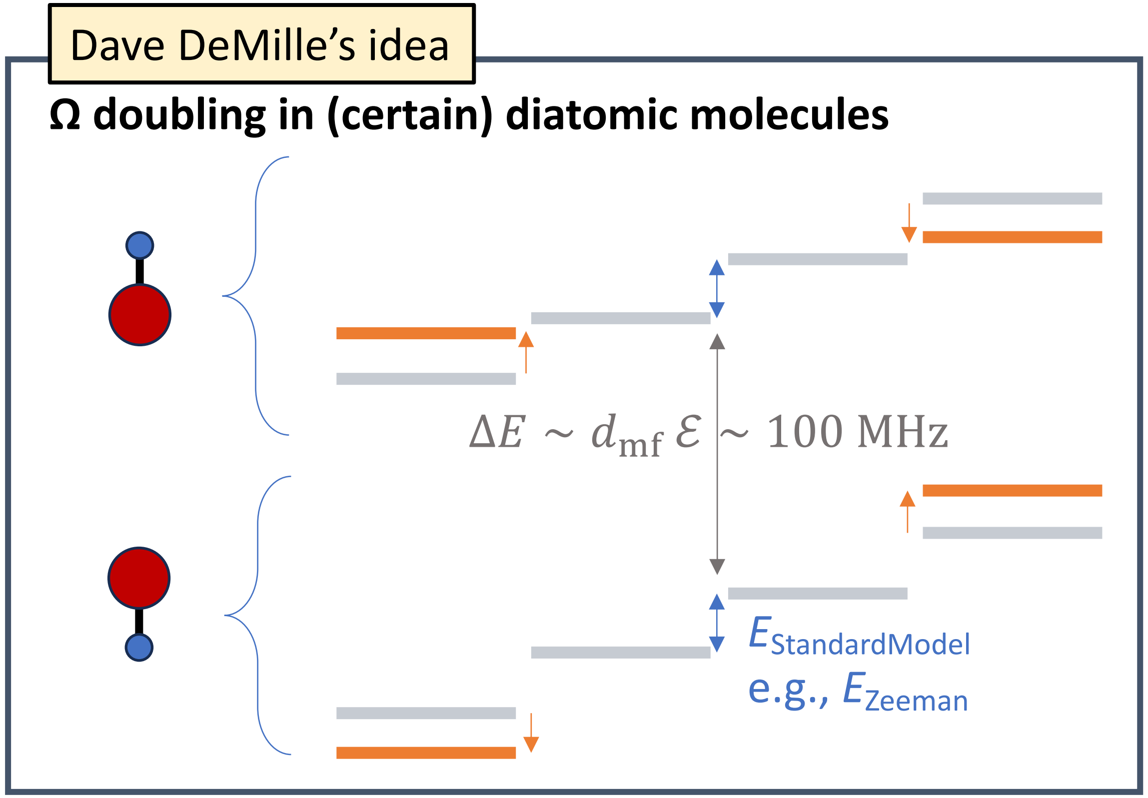
Convenient excited states

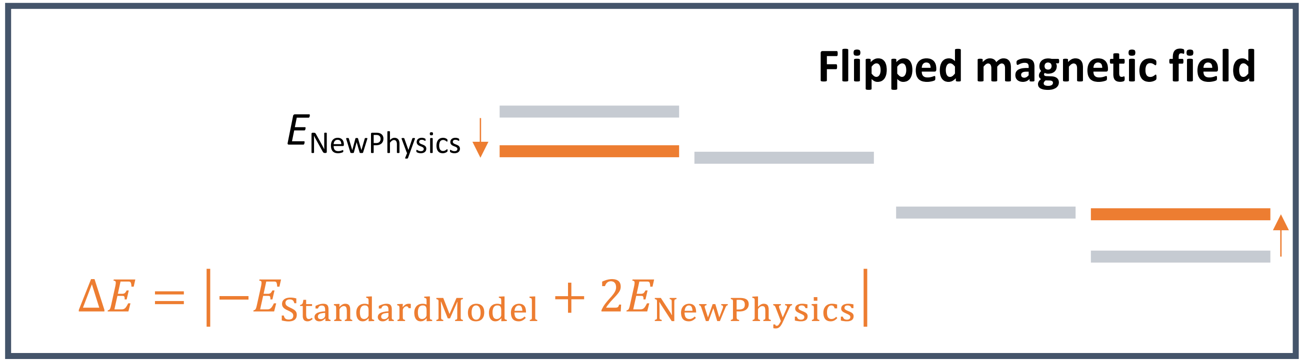
Overall net loss higher than small “Hilbert space”

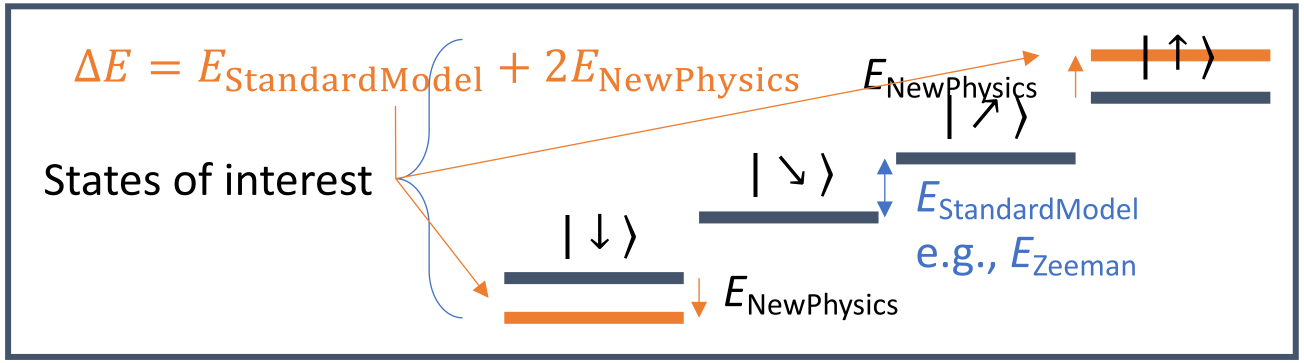
States of interest

Brief discourse on suppressing systematics

- New physics effects ∝ projection of spin (onto inter-nuclear axis)
  - Electron spin for electron's EDM.
  - Nuclear spin for nuclear EDM, e.g., Schiff moment.





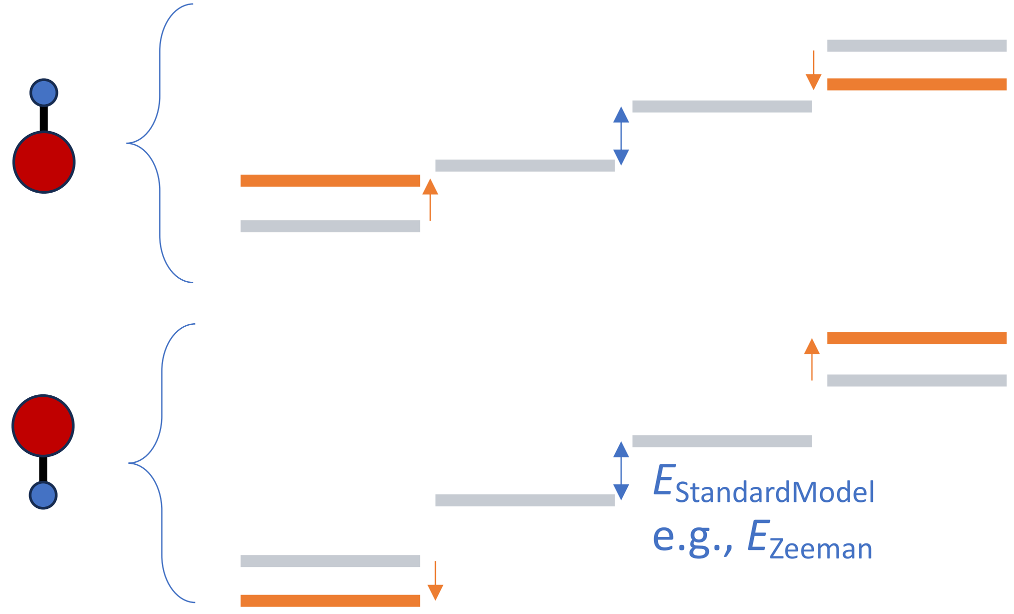


Brief discourse on suppressing systematics

- Pick a molecule that is sensitive to your favorite EDM
  - Unpaired electron spin for electron's EDM.
  - Non-zero nuclear spin for nuclear EDM, e.g., Schiff moment.

Dave DeMille's idea

Ω doubling in (certain) diatomic molecules



- Better if molecule comes with in-built systematics-rejection mechanism
  - Ω doubling co-magnetometry (left), and reduced magnetic field sensitivity with $^3\Delta_1$ e.g. **^{180}HfF$^+$ (JILA)**, **^{232}ThO (ACME)**, ^{232}ThF$^+$ (JILA).
  - Field insensitive clock transition, e.g. ^{174}YbAg (Vutha group, Toronto).
  - States engineered to be field insensitive (magic E-field), e.g. ^{173}YbOH (Hutzler group, Caltech).

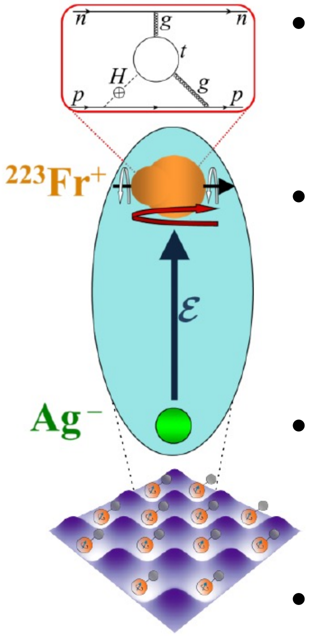
Dave DeMille’s talk last week;
Timo Fleig’s talk yesterday!

Talk to Rane Simpson!

RadMol collaboration

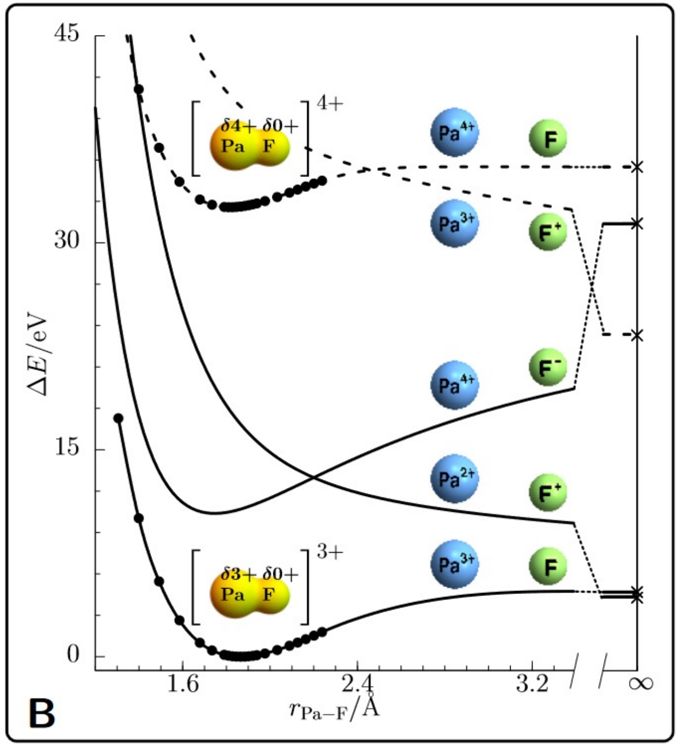
Collaborative effort!!!

Ultracold molecular francium-silver



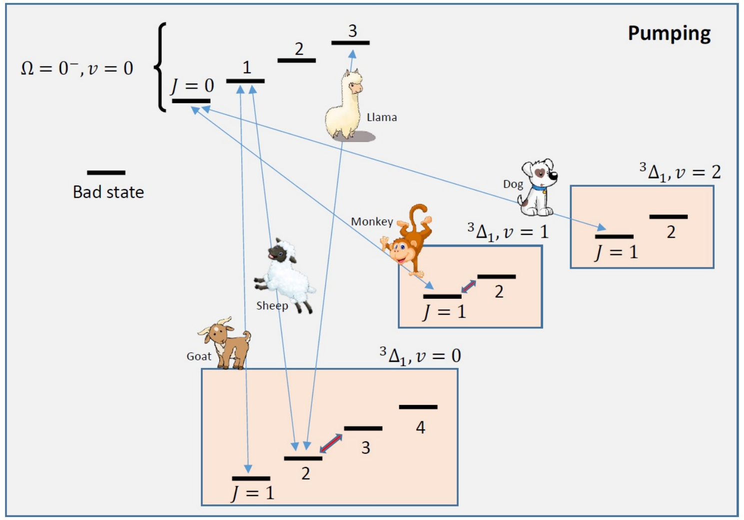
- Cool atomic Fr and Ag (separately).
- Associating ultracold atoms to form molecule.
- Molecules trapped optically.
- Measure science!

Towards highly charged molecules



Zülch et al., arXiv:2203.10333

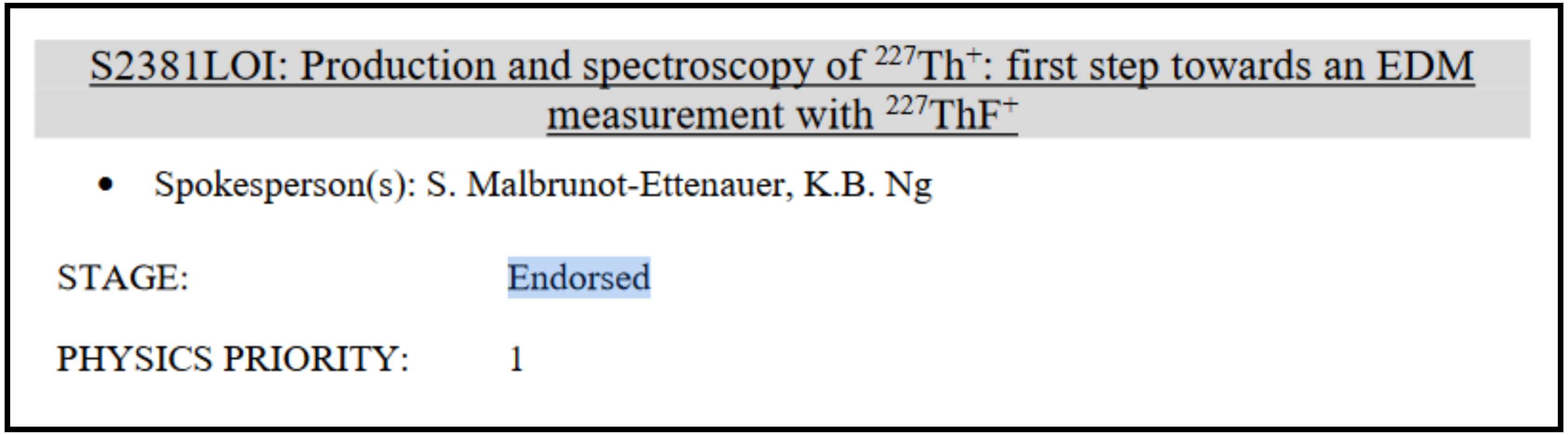
Spectroscopy of ionic molecules



- (Above) optical pumping scheme.
- Spectroscopy to learn about internal structure for quantum control.

^{227}ThF^{+}: JILA + TRIUMF

- Collaboration with JILA's Gen. III eEDM experiment using ^{232}ThF^{+} [1-4].
- Beam development ongoing at TRIUMF.



S2381LOI: Production and spectroscopy of ^{227}Th^{+}: first step towards an EDM measurement with ^{227}ThF^{+}

- Spokesperson(s): S. Malbrunot-Ettenauer, K.B. Ng

STAGE: Endorsed

PHYSICS PRIORITY: 1

[1] Zhou, et al., JMS, 358 (2019) 1-16.
[2] Gresh, et al., JMS, 319 (2016), 1-9.
[3] Ng, et al., PRA 105 (2022) 022823.
[4] Ng, PhD thesis

^{227}ThF^{+}: some properties

- Nuclear spin of Th-227: 1/2 [1,2]
  - Nonzero nuclear spin ⇒ Schiff moment!
  - Smallest nonzero spin ⇒ small Hilbert space!
- Octupole deformation of Th-227 [1-4]
  - Enhancement of Schiff moment ⇒ easier to measure!
- Chemically similar to ^{232}ThF^{+}
  - Spectroscopy already performed by JILA group [5-8] ⇒ less work!
- Science state = ground electronic state [6]
  - Coherence time not limited to natural decay lifetime ⇒ more precise measurement!

[1] Hammond et al., PRC 65 , 064315 (2002)
[2] Müller et al., PRC 55, 2267 (1997)
[3] Liang et al., PRC 51, 1199 (1995)
[4] Flambaum, private communication
[5] Zhou, et al., JMS, 358 (2019) 1-16.
[6] Gresh, et al., JMS, 319 (2016), 1-9.
[7] Ng, et al., PRA 105 (2022) 022823.
[8] Ng, PhD thesis

^{227}ThF^{+}: science goals

- Springboard TRIUMF directly to quantum control stage
  - Preparation into and control of individual quantum states.
  - Quantum-enabled two-state detection [1], etc.

- Co-develop techniques
  - Many protocols yet to be fully optimized, but only one setup at JILA.

- Compare measurement results with JILA's ^{232}ThF^{+}
  - Global analysis.
  - Systematics cross check.

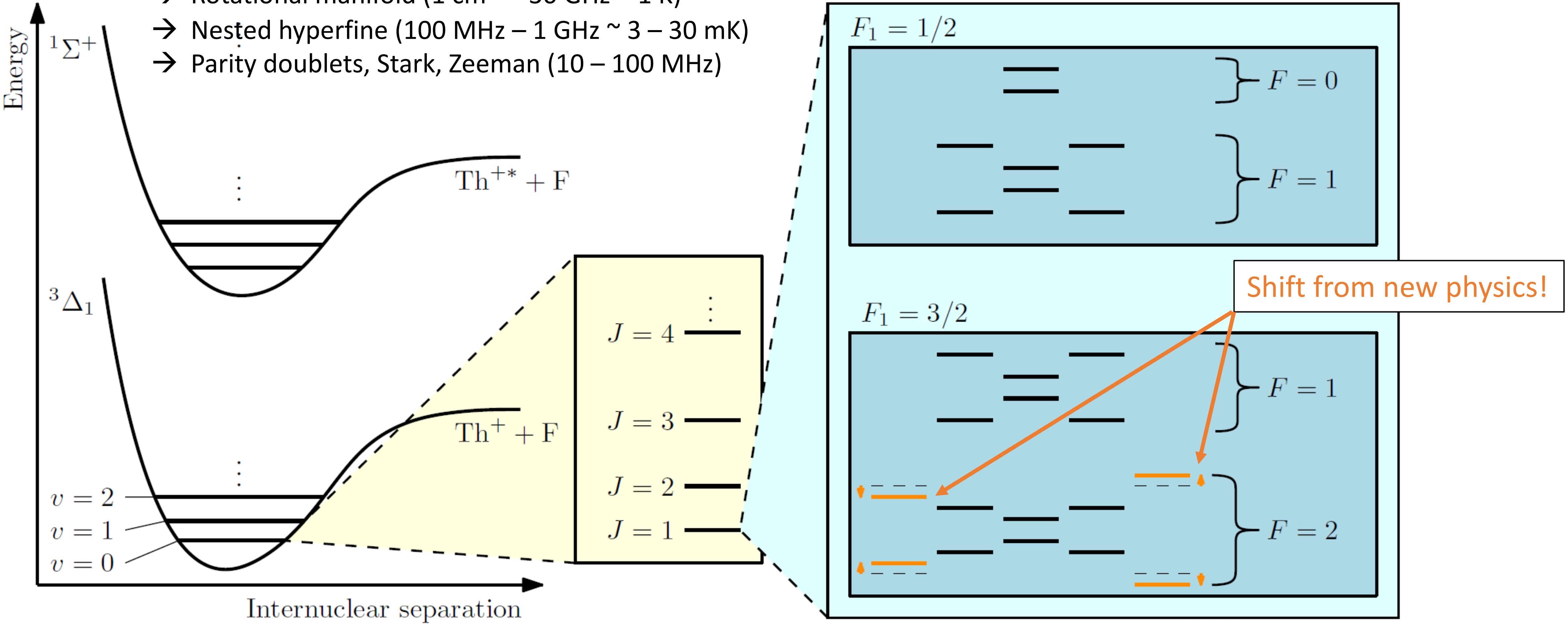
- Steppingstone to quantum control of radioactive molecular ions
  - Discover new effects in context of quantum control.

[1] Zhou et al., Phys. Rev. Lett. 124, 053201 (2020); a collaboration with Tanya Zelevinsky.

Energy landscape in a molecule like ^{227}ThF$^+$

Electronic level (1000 cm^{-1} ~ 1400 K ~ 0.1 eV)
→ Vibrational manifold (600 cm^{-1} ~ 800 K)
→ Rotational manifold (1 cm^{-1} ~ 30 GHz ~ 1 K)
→ Nested hyperfine (100 MHz – 1 GHz ~ 3 – 30 mK)
→ Parity doublets, Stark, Zeeman (10 – 100 MHz)

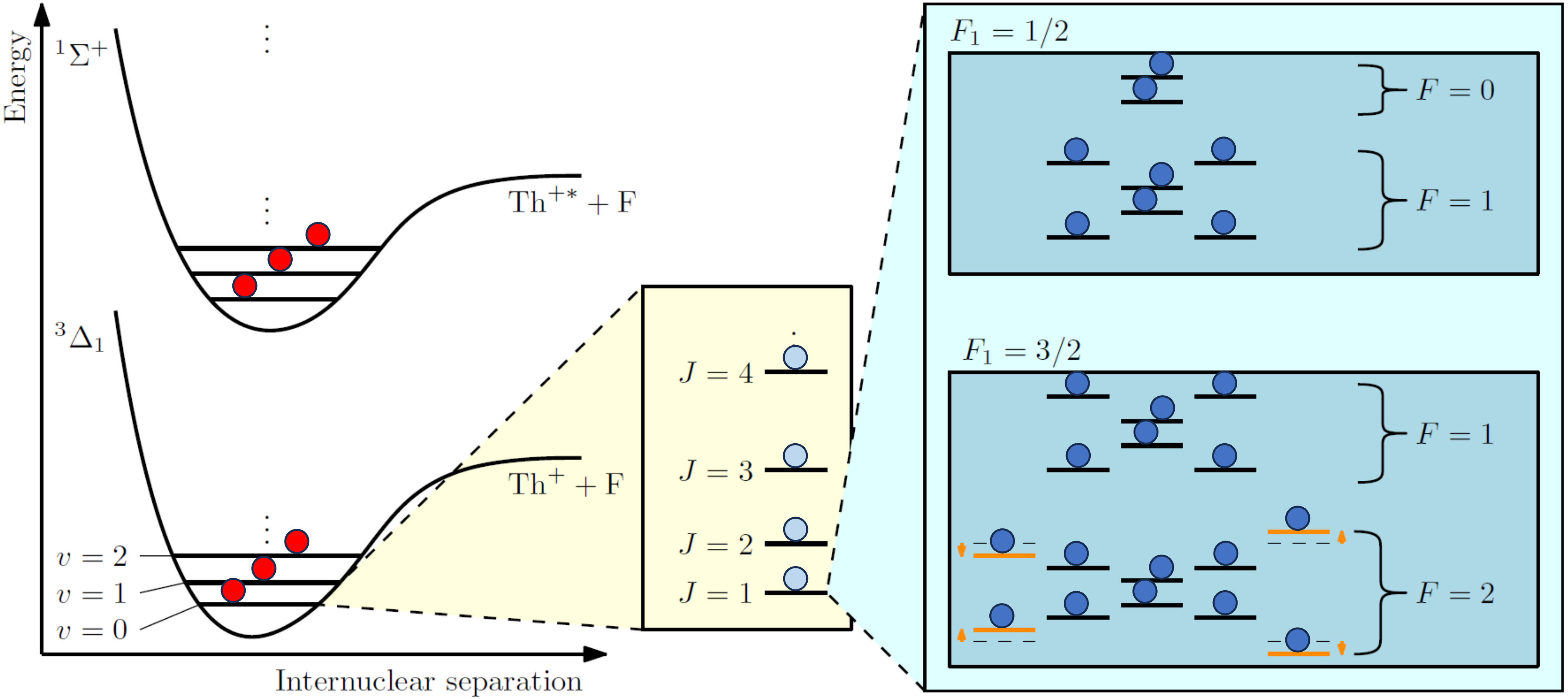
Ions typically produced/cooled to ~10 K
⇒ distributed across multiple *J* (and finer structures).



State preparation

Multi-step entropy reduction process:

1. Ions created ~1000 K.
2. Cryogenics (~10 K).
3. Optical pumping for rotational cooling.
4. More optical pumping to usher population around.



Optical pumping

- Use lasers and microwaves to move population around
  - Entropy of system carried away by emitted photons.
  - Transitions chosen to exploit selection rules for net cooling.
- Excited states can decay into unwanted states
  - Use repump lasers to bring back lost population.
- Typical number of lasers ~ 10

Scheme developed at JILA for ThF$^+$

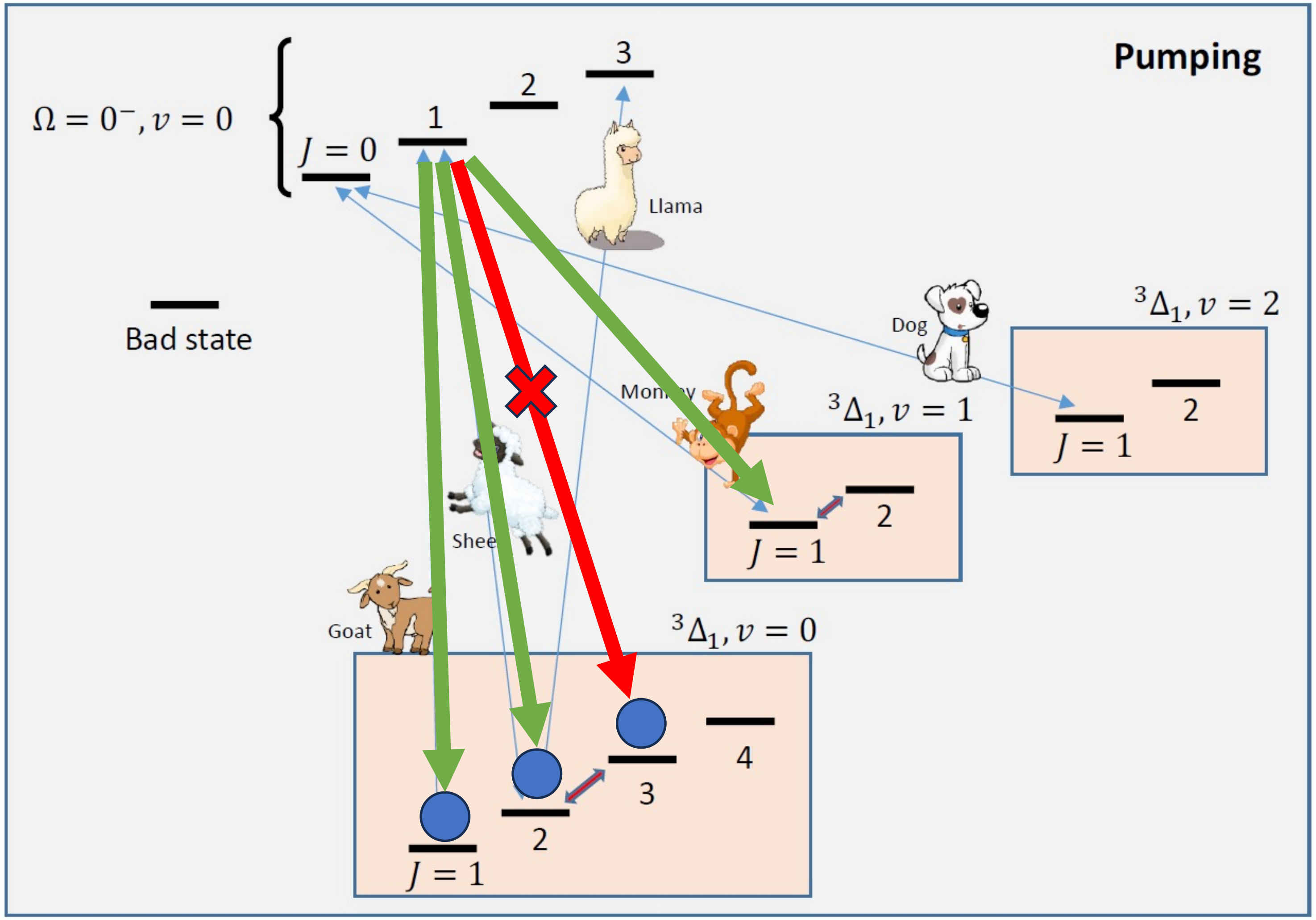
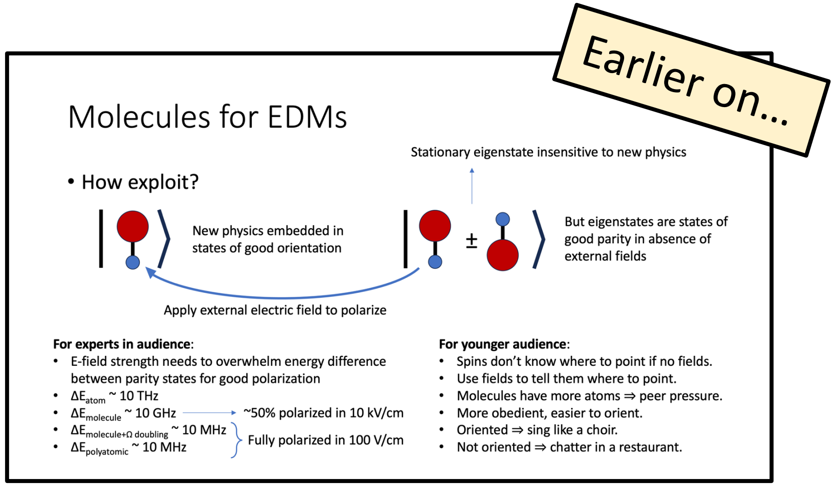


Figure from Ng, PhD thesis

Complication from using molecular ions

- Molecular ions are nice
  - Molecules: easily polarizable!
  - Ions: easily trapped!
- Molecular ions are not that straightforward
  - Polarizing E-field must rotate to keep ions confined
    - Fast compared to typical motion in ion trap.
    - Adiabatic compared to typical energy scales in molecule.
  - Spectroscopy performed in rotating frame
    - Non–inertial-frame coupling terms
      - Typically absent in experiments with neutral molecules.
      - Care required when porting quantum control techniques from neutral molecular systems.



Earlier on...

Molecules for EDMs

- How exploit?

For experts in audience:
- E-field strength needs to overwhelm energy difference between parity states for good polarization
- ΔE_{atom} ~ 10 THz
- $\Delta E_{molecule}$ ~ 10 GHz → ~50% polarized in 10 kV/cm
- $\Delta E_{molecule+\Omega\ doubling}$ ~ 10 MHz
- $\Delta E_{polyatomic}$ ~ 10 MHz

Fully polarized in 100 V/cm

For younger audience:
- Spins don’t know where to point if no fields.
- Use fields to tell them where to point.
- Molecules have more atoms ⇒ peer pressure.
- More obedient, easier to orient.
- Oriented ⇒ sing like a choir.
- Not oriented ⇒ chatter in a restaurant.

Non–inertial-frame coupling: boon & bane

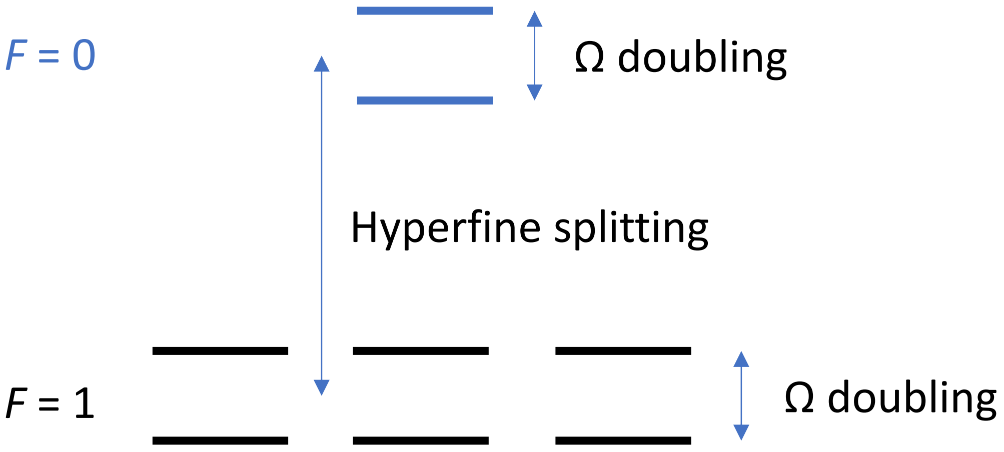
- No field
  - F is a good quantum number.
    - Hyperfine from fluorine / heavy metal
  - Plot assumes $E_{\mathrm{HFS}} >> E_{\Omega}$.

- Eigenstates
  - States of good parity:

$$|\pm\rangle = |\Omega\rangle \pm |-\Omega\rangle$$

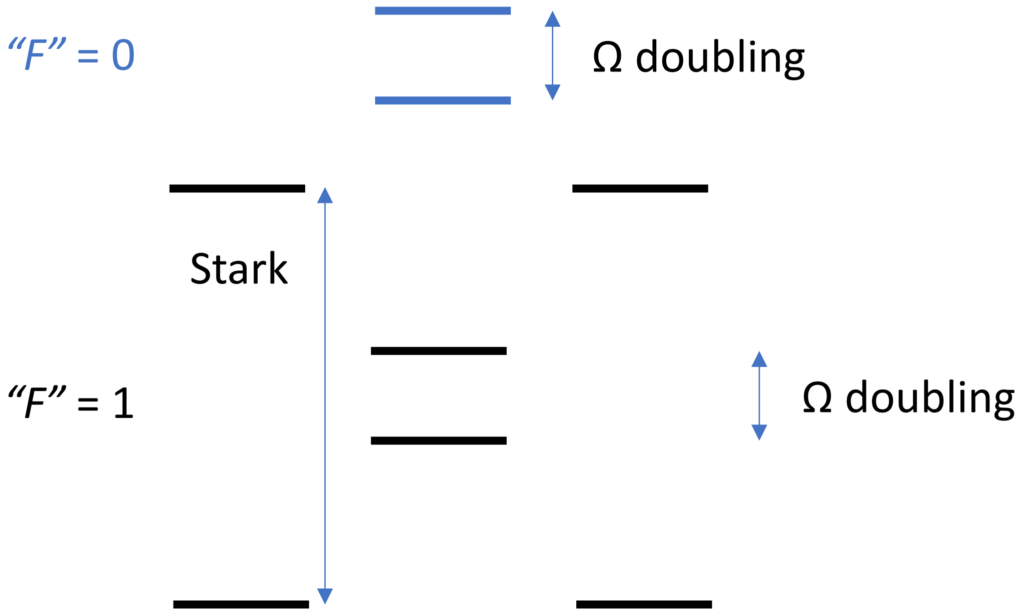
Parity

“Orientation” / “polarization”



Non–inertial-frame coupling: boon & bane

- With E-field
  - F is an asymptotic quantum number.
- Eigenstates
  - States of good orientation in when $E_{\text{Stark}} >> E_{\Omega}$.



“F” = 0

Ω doubling

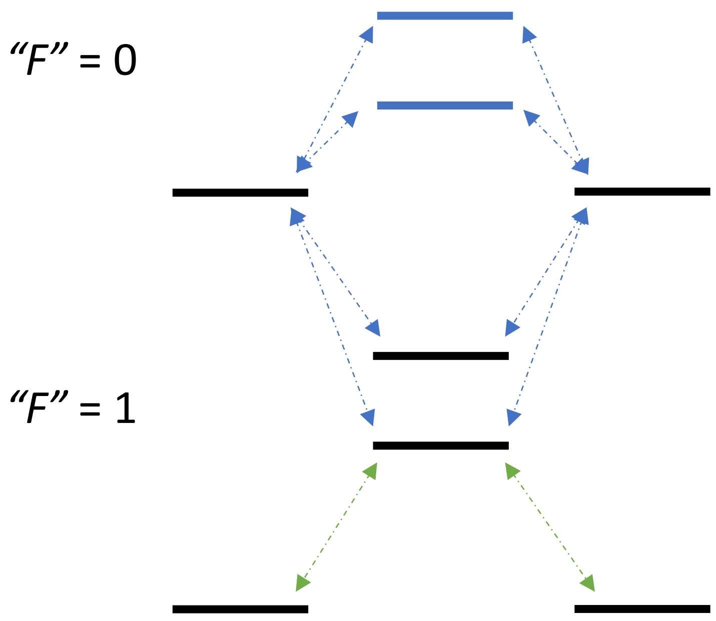
Stark

“F” = 1

Ω doubling

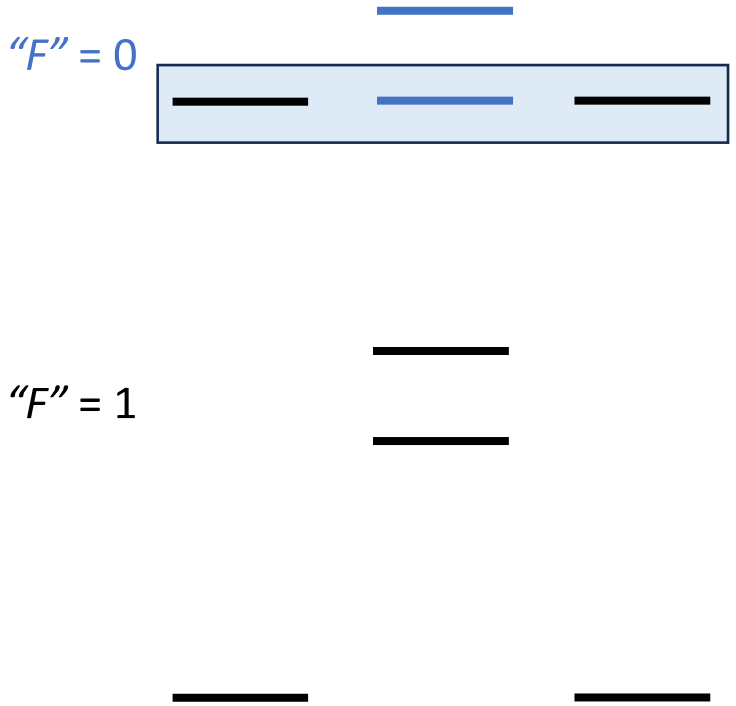
Non–inertial-frame coupling: boon & bane

- Non–inertial-frame coupling
  - $H_{NIF} \sim \hbar\omega_{\mathrm{rot}} F_x$.
  - Couples states of neighboring m_F.
- Degeneracy lifted by coupling (Δ).
- Magnitude of coupling effect
  - Sum of all possible $2m_F$-order perturbations.
  - $\Delta \sim \omega_\Omega \left(\frac{\omega_{\mathrm{rot}}}{\omega_{\mathrm{Stark}}}\right)^{2m_F}$.



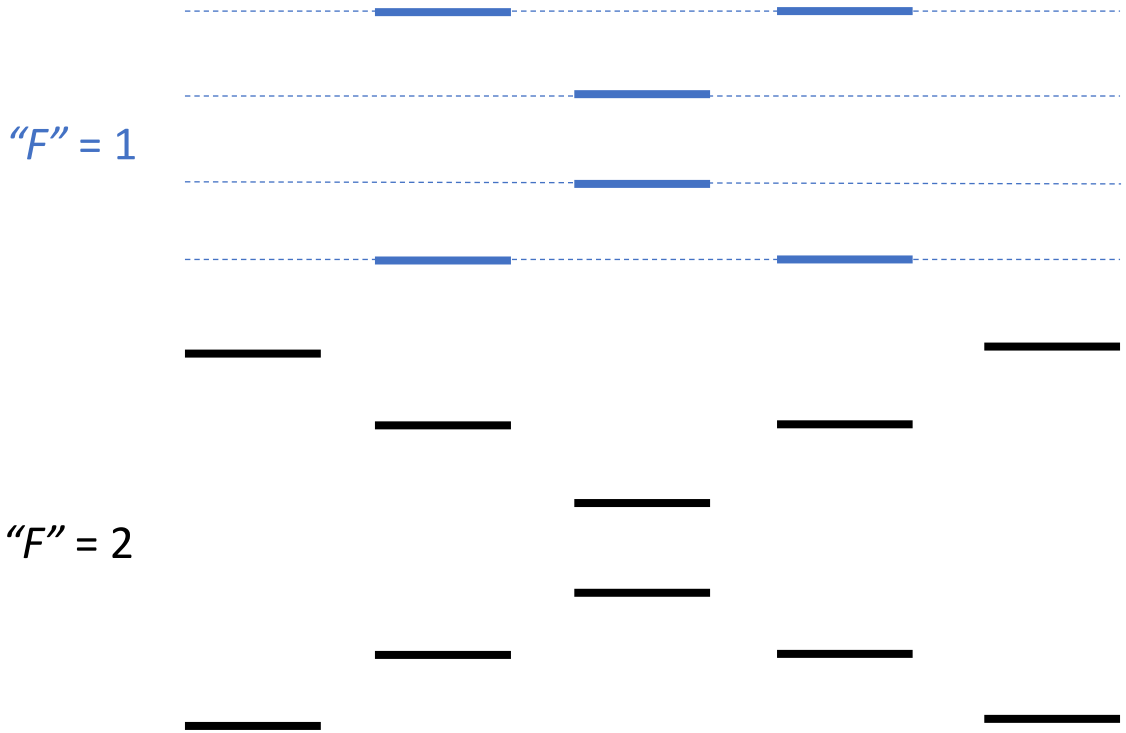
Non–inertial-frame coupling: boon & bane

- Non–inertial-frame coupling
  - $H_{NIF} \sim \hbar\omega_{\mathrm{rot}}F_x$.
  - Couples states of neighboring m_F.
- Hyperfine crossing
  - Stretched states are strongly mixed with each other…
  - … and also with unstretched states.



Non–inertial-frame coupling: boon & bane

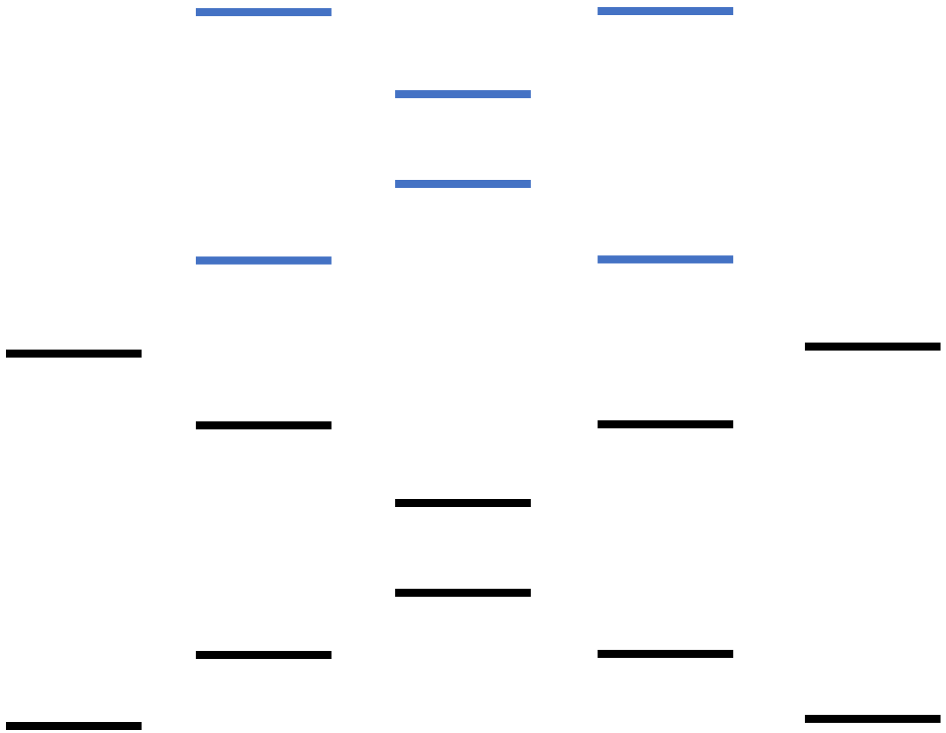
- Non–inertial-frame coupling
  - $H_{NIF} \sim \hbar\omega_{\mathrm{rot}} F_x$.
  - Couples states of neighboring m_F.
- Hyperfine crossing
  - Stretched states are strongly mixed with each other…
  - … and also with unstretched states.
  - More hyperfine crossings in larger Hilbert spaces.



Non–inertial-frame coupling: boon & bane

- Constraints
  - Avoid hyperfine crossings.
  - States of good orientation.

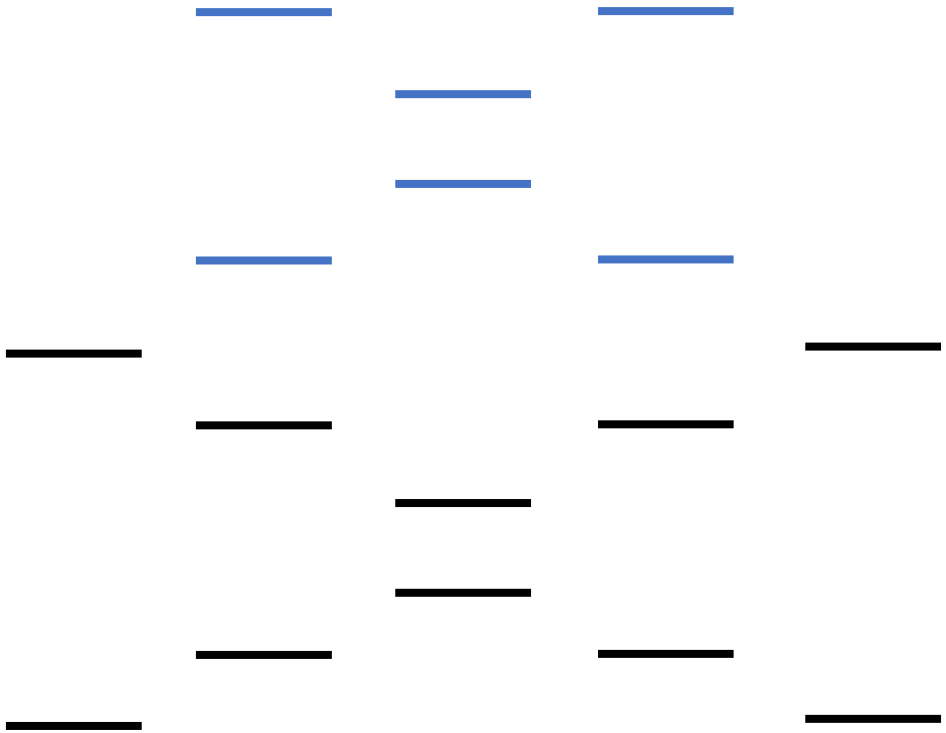
- Require
  - Careful/smart choice of E-field strength.
  - Choice depends on
    - Molecular dipole moment;
    - Ω doubling;
    - Hyperfine splitting;
    - Size of "Hilbert space", etc.
  - No guarantee that sweet spot exists.



Non–inertial-frame coupling: boon & bane

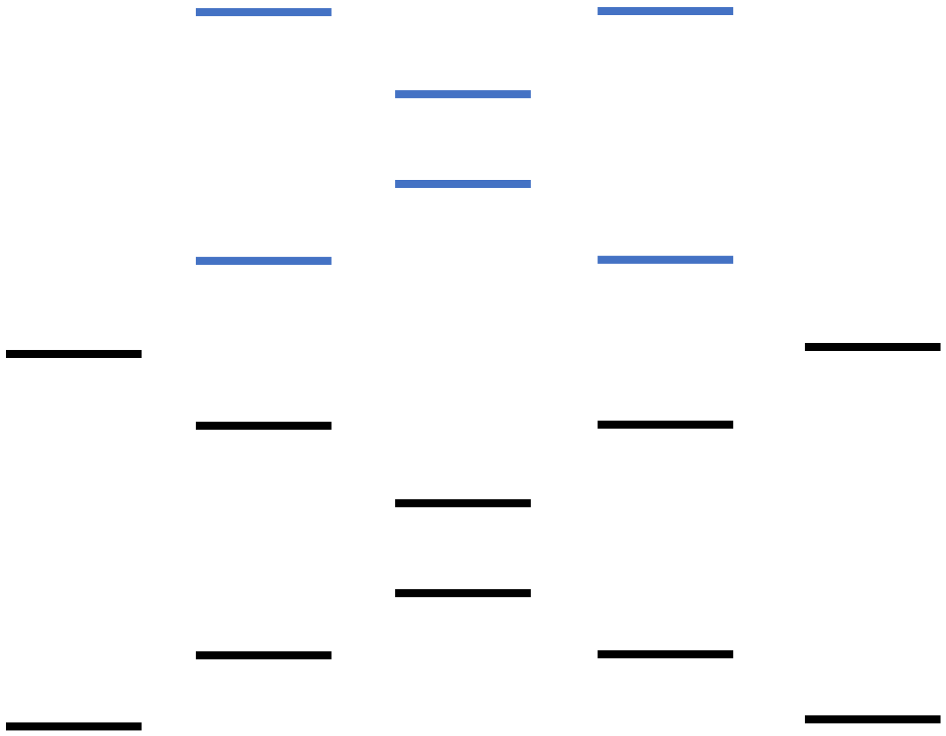
- Use coupling as a resource
  - Ramp to low E-field…
  - … for a substantial coupling between “science states”…
  - … but with “science states” far enough from hyperfine crossing…
  - … for negligible coupling of “science states” with “unstretched states”.

- Effect π/2 pulses
  - Between stretched “science states”…
  - … that would otherwise require multiphoton laser coupling.



Non–inertial-frame coupling: boon & bane

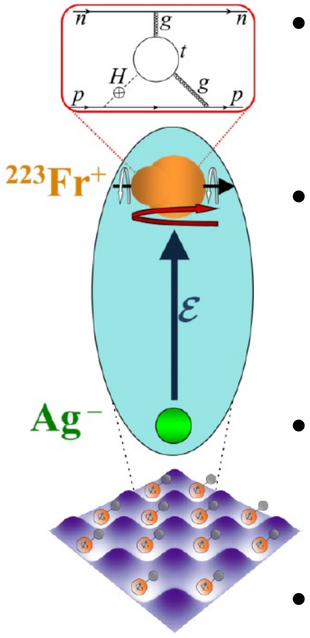
- Magnitude of coupling effect:
  - $\Delta \sim \omega_\Omega \left(\frac{\omega_{\mathrm{rot}}}{\omega_{\mathrm{Stark}}}\right)^{2m_F}.$
- Effect of coupling more severe for less-stretched states
  - Fully mixed under typical experimental parameters.
  - Renders many protocols involving use of unstretched states much less effective.
  - Opportunity for new protocols to be discovered!



RadMol collaboration

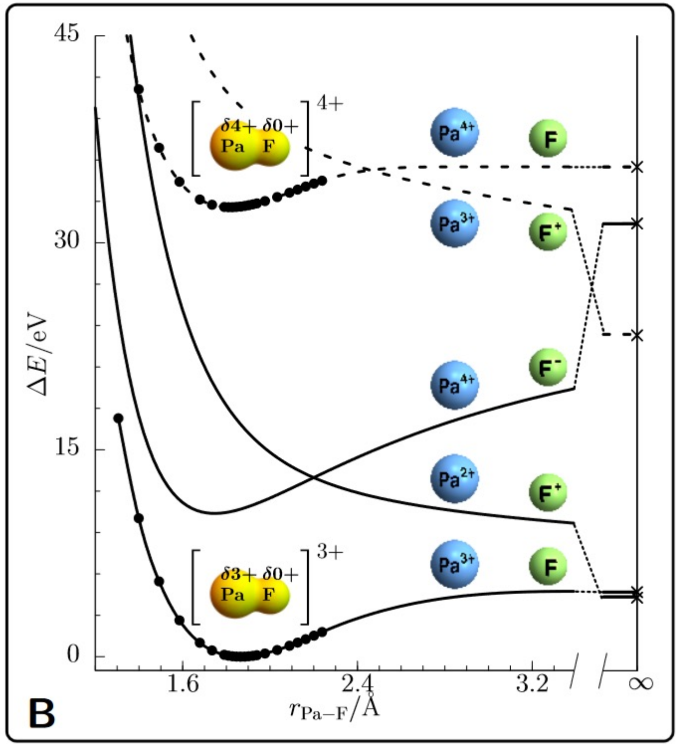
Collaborative effort!!!

Ultracold molecular francium-silver



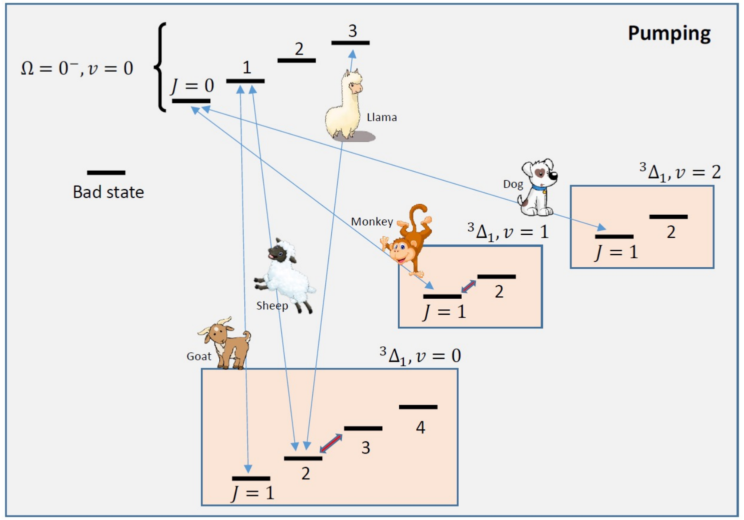
- Cool atomic Fr and Ag (separately).
- Associating ultracold atoms to form molecule.
- Molecules trapped optically.
- Measure science!

Towards highly charged molecules



Zülch et al., arXiv:2203.10333

Spectroscopy of ionic molecules



- (Above) optical pumping scheme.
- Spectroscopy to learn about internal structure for quantum control.

Highly charged molecules: motivation

[1] Spevak et al., PRC 56, 1357 (1997)
[2] Flambaum et al., PRA 101, 042504 (2020)
[3] Zülch et al., arXiv:2203.10333

- Case study: ^{229}PaF^{3+}
  - ^{229}Pa promises huge enhancements to effects of Schiff moment [1,2].
  - ^{229}PaF^{3+} calculated to be stable and have desirable properties [3].

- New opportunities to implement quantum control
  - Branching out from “plain old” stable neutral/singly charged atoms.

Radioactive – e.g., radium: Fan et al., PRL 122, 223001 (2019)

See, e.g., white paper arXiv:2302.02165

Highly charged ions – see, e.g., review article Kozlov et al., Rev. Mod. Phys. 90(4) 045005 (2018)

Molecules – see, e.g., review article Augenbraun et al., AAAMOP 72, 89-182 (2023)

Highly charged molecules: non-trivial

- In principle
  - Can it even exist: Coulomb explosion
    - No guarantee that highly charged molecule is stable.
    - Calculations can help determine feasibility, e.g., [1].

  - Can we control it: excited states for optical pumping/cycling as source of loss
    - Excited states can lie above dissociation threshold
    - ⇒ molecules can dissociate from optical pumping/cycling, e.g., [2].

[1] Zülch et al., arXiv:2203.10333
[2] Sun et al., PRR 5, 043070 (2023)

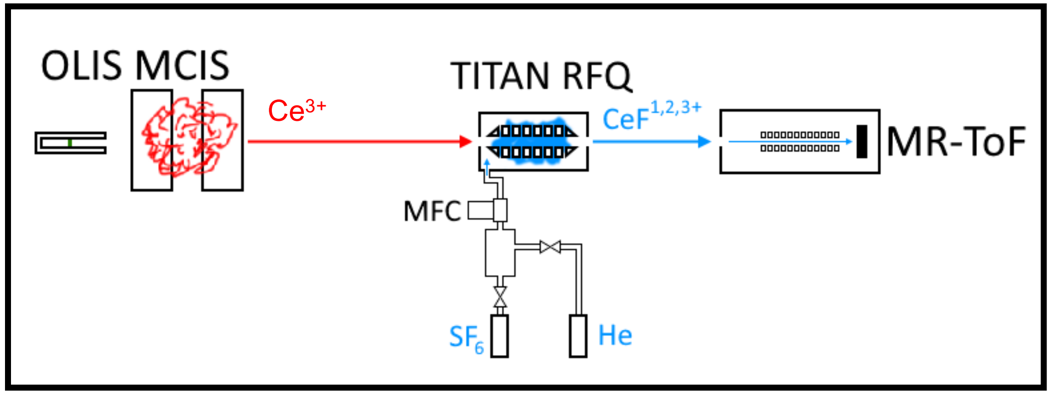
Highly charged molecules: non-trivial

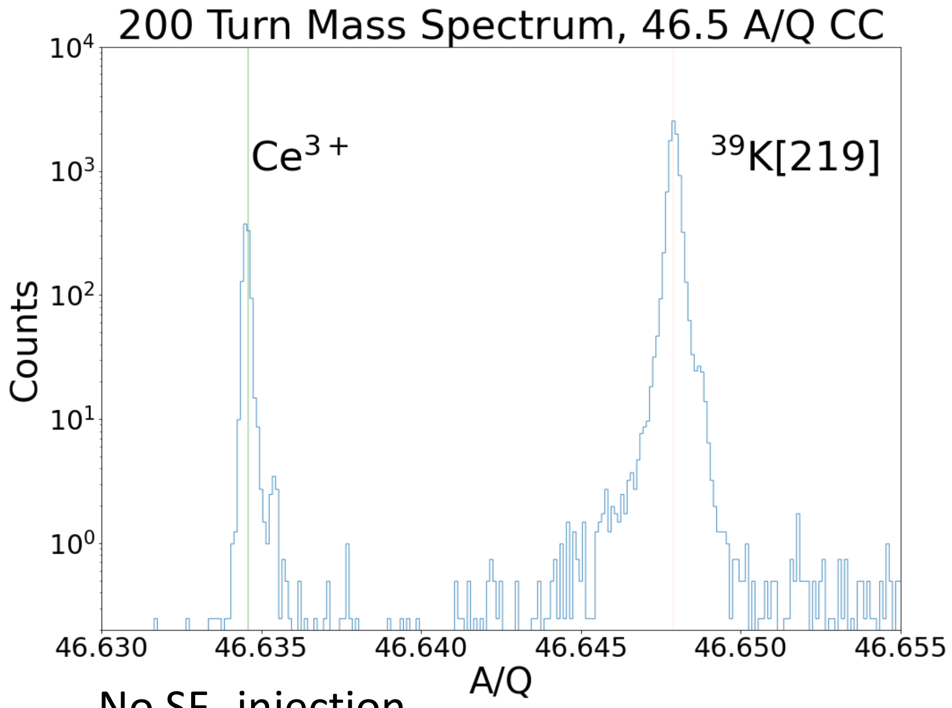
- In practice
  - Can we create it?
    - Need to / can we isolate reaction pathways?
    - Yield and efficiency.
  - Can we tame it?
    - Purity, both for external and internal degrees of freedom.
    - State manipulation schemes: do they exist / are we smart enough?

Highly charged molecules: CeF^{2+}

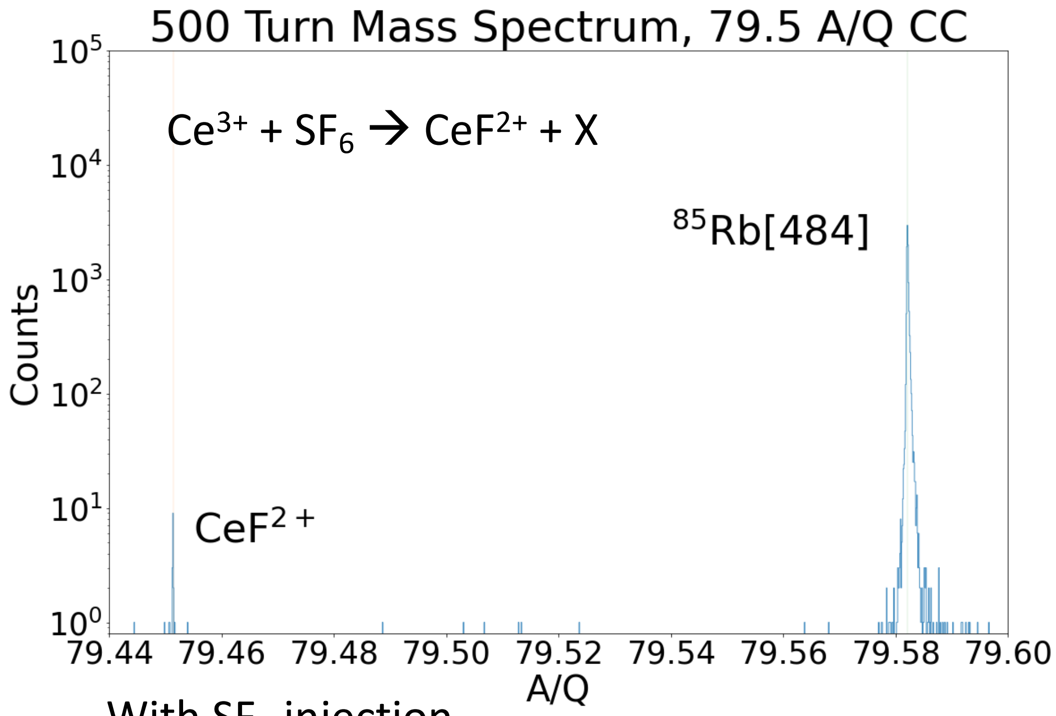
Talk to Rane Simpson!

- Collaboration with Robert Berger
  - Manuscript in preparation.





No SF_6 injection



With SF_6 injection

Acknowledgements

Accelerator @ TRIUMF

- Jon Aoki
- Carla Babcock
- Ferran Boix Pamies
- Alexander Gottberg
- Peter Kunz
- Jens Lassen
- Ruohong Li
- Dave Neilson
- Navid Noori
- Aaron Schmidt

Life Sciences @ TRIUMF

- Joe Huser
- Valery Radchenko
- Hua Yang

Theory

- Robert Berger
- Lan Cheng
- Victor Flambaum
- Marianna Safronova
- Carsten Zülch

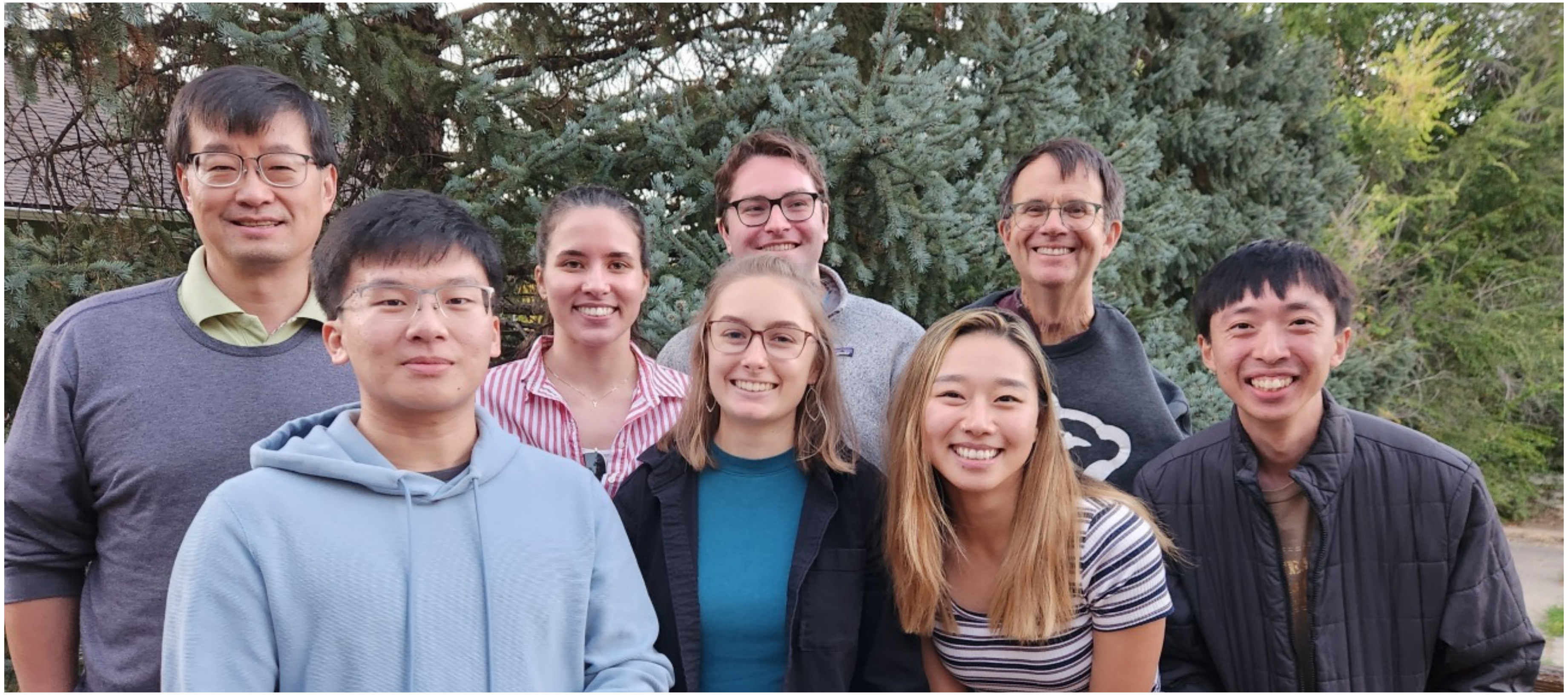
Wisdom

- Friedhelm Ames
- John Behr
- Greg Hackman
- Eric Cornell

And many others…

JILA eEDM group

Ex-postdoc Yan Zhou will also be at INT during Weeks 5-6



PIs: Eric Cornell, Jun Ye
Graduate students: Sun Yool Park, Anzhou Wang, Addison Hartman, Patricia Hector
Undergraduate: Rohan Kompella
Ex-graduate students: Trevor Wright, Kia Boon Ng

RadMol

Local team:

- PI: Stephan Malbrunot
- Research scientist: Christopher Charles
- Experimental officer: Andrea Teigelhoefer
- Graduate students: Louis Croquette, Rane Simpson
- Postdoc: Kia Boon Ng

TRIUMF

THE UNIVERSITY OF CHICAGO

University of Colorado Boulder

McGill

UNIVERSITY OF TORONTO

UNIVERSITY OF WATERLOO

UBC

University of Manitoba

uOttawa

THE UNIVERSITY OF EDINBURGH

Philipps Universität Marburg

UNIVERSITY OF DELAWARE

JOHNS HOPKINS UNIVERSITY

UNSW THE UNIVERSITY OF NEW SOUTH WALES

[Space for more!]

Massachusetts Institute of Technology