Combining Chemistry and Physics in Ultracold Polar Molecules

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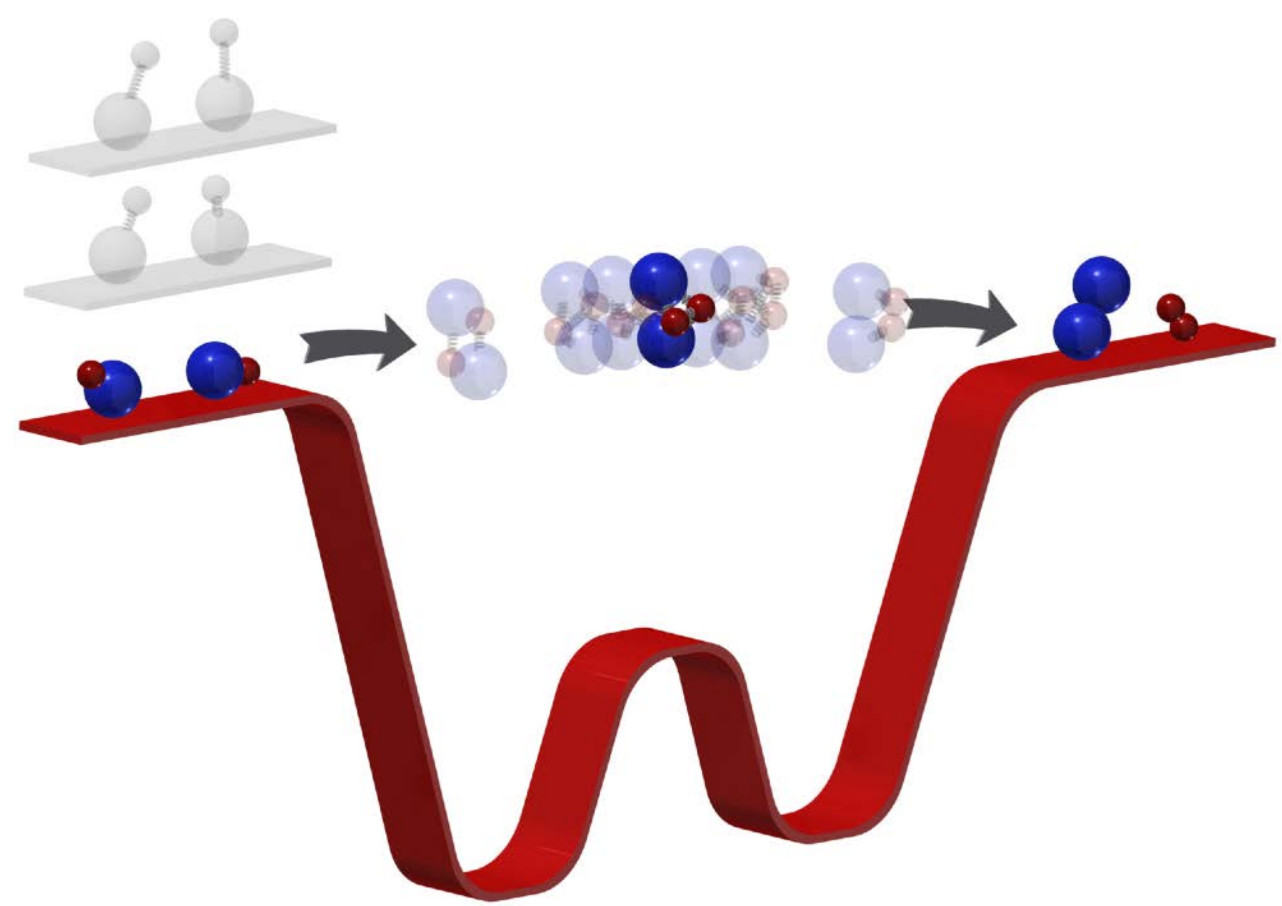
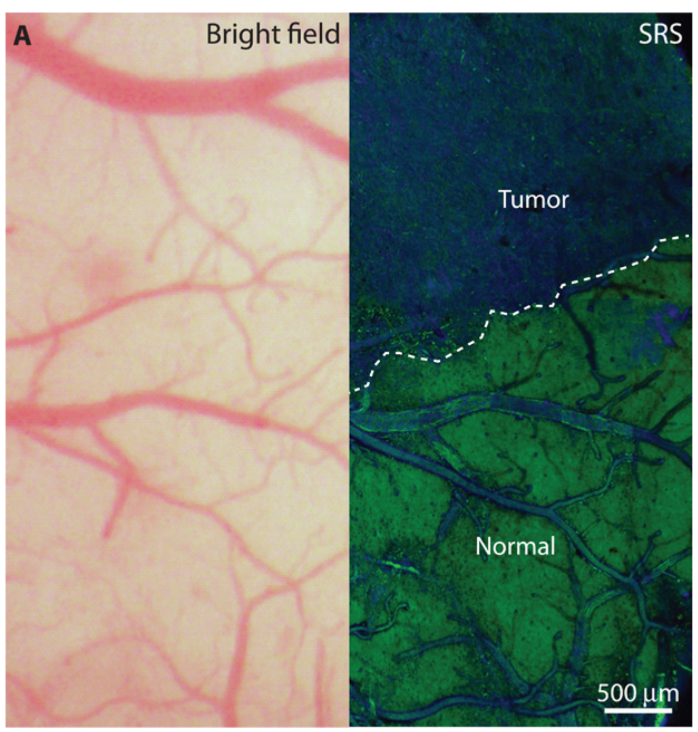
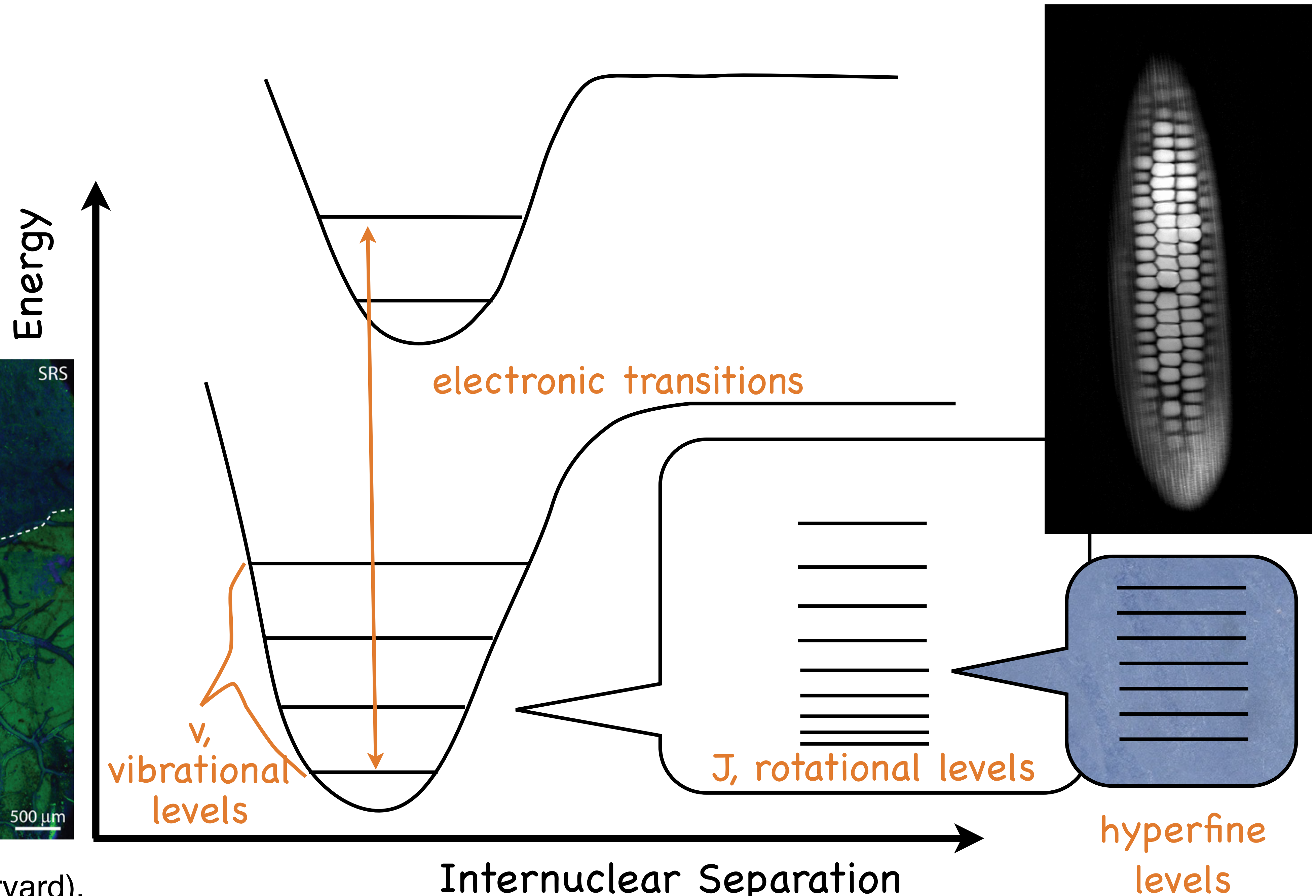


Quantum Science Seminar, May 21, 2020

Molecular Quantum Degrees of Freedom



Xie Group (formally at Harvard),
Sci. Transl. Med. 5, 201 (2013)

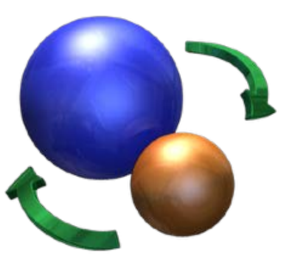


https://experiencetalk.files.wordpress.com/2014/04/corn-mri-scan.gif

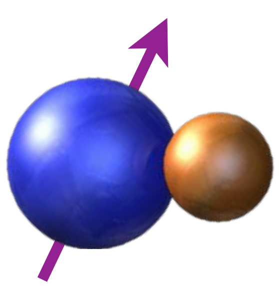
Molecular Quantum Resources

for quantum simulation and computation

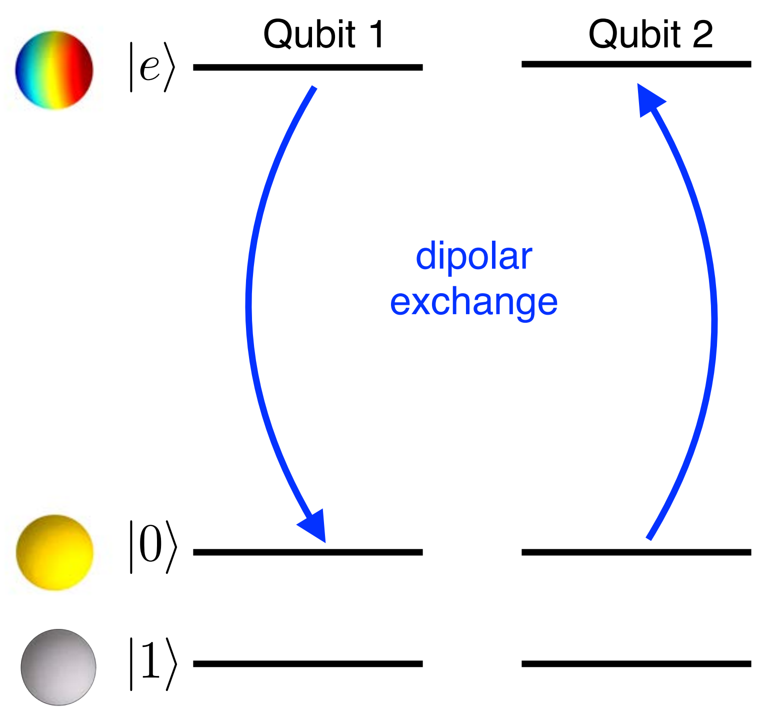
* larger variety of internal states for **storage** and **interaction**
* **intrinsic molecular couplings** between internal degrees of freedom

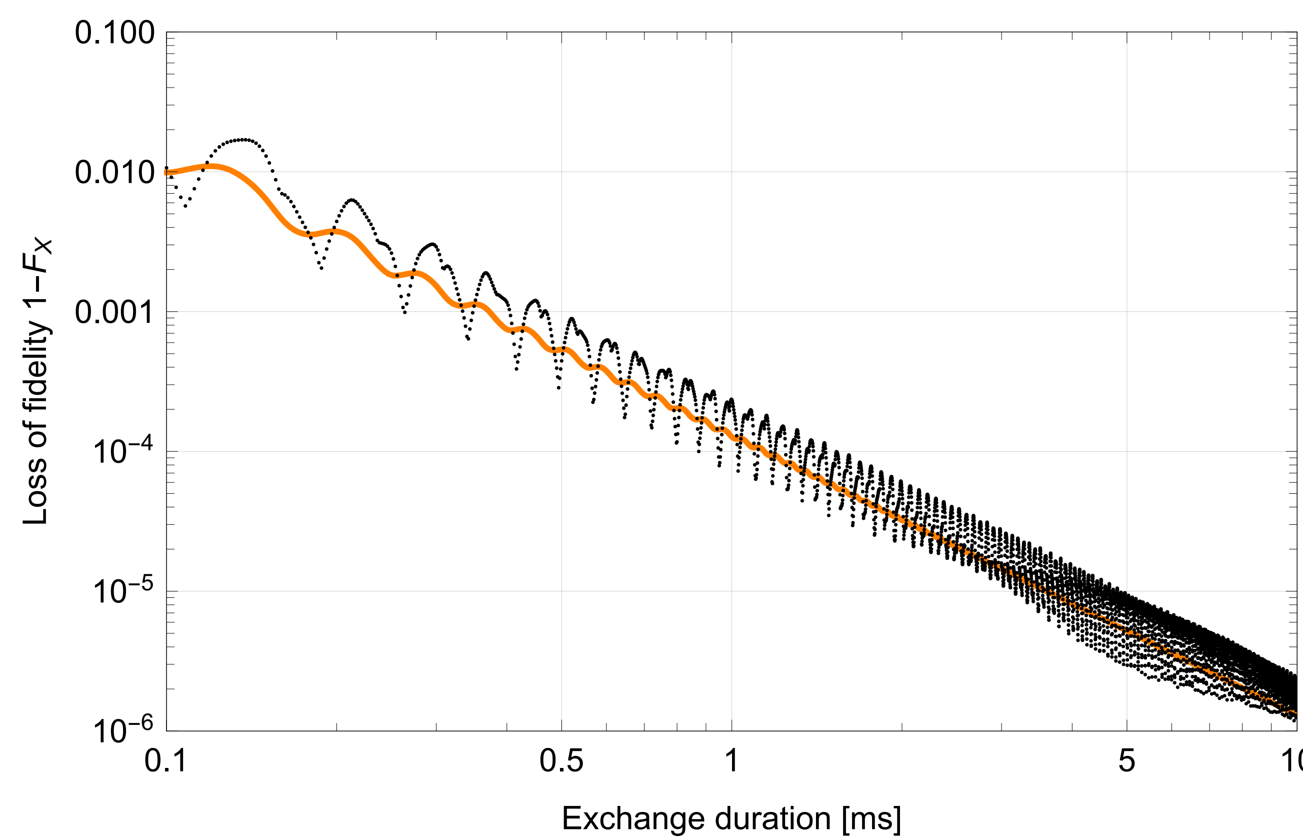


rotation



hyperfine





Ni, Rosenband, Grimes, Chemical Science **9**, 6830-6838 (2018)
Hudson and Campbell, PRA **98**, 040302 (2018)
DeMille, Yelin, Zoller, Demler, Lukin, Pupillo, Rey, Gorshkov, Friedrich, Herschbach, Kais,…

Gaining single particle control of molecules

Molecular assembly from atoms

Molecular ions

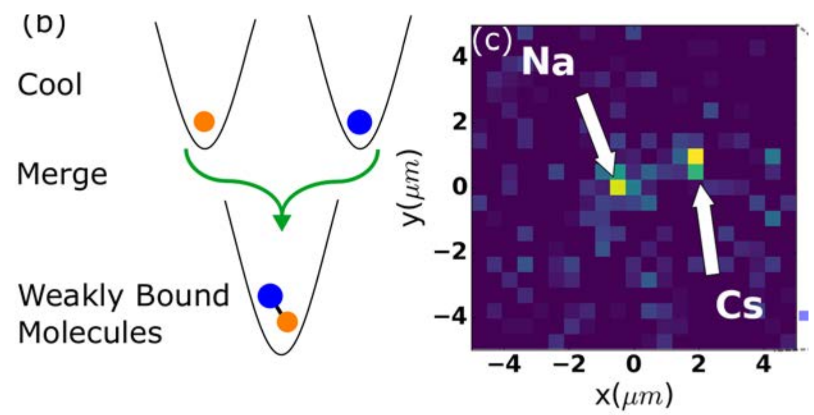
Laser-cooled molecules

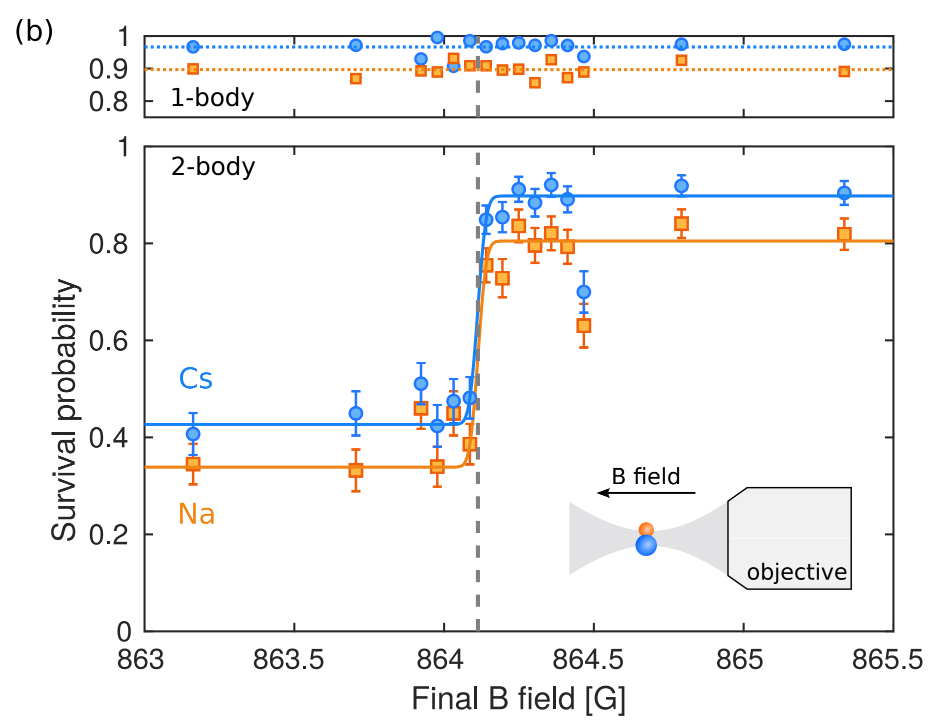
CaF molecule array

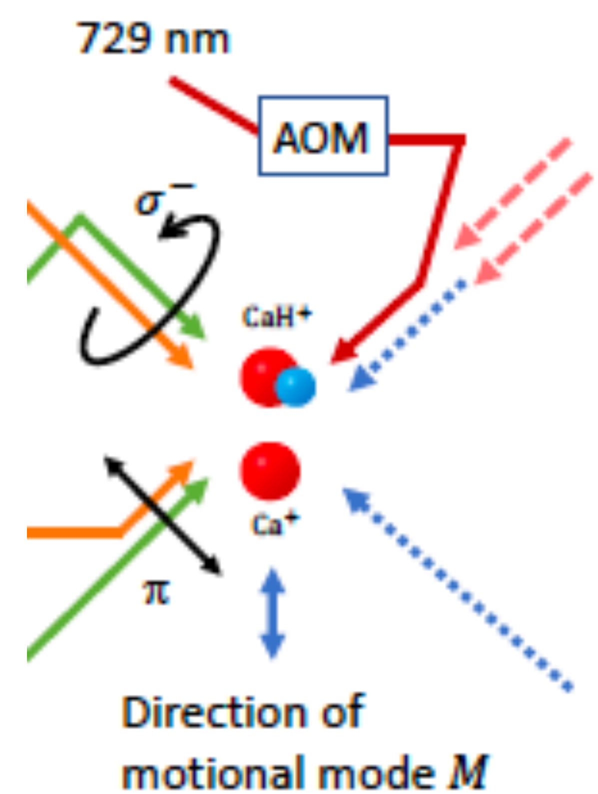
CUA Doyle/Ketterle/Ni Collaboration

Science 365, 1156 (2019)

Harvard/MIT, Yale, Imperial, JILA…







NIST, arXiv:1912.05866 (2019)

PTB, NIST, Basel, UCLA,…

Liu, Hood, Yu et al., Science 360, 900 (2018)
Zhang, Yu, Cairncross et al., arXiv:2003.07850(2020)

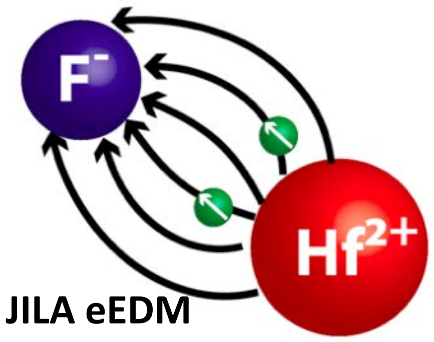
Harvard, Wuhan, Durham, Singapore,…

Fundamental Physics with Molecules

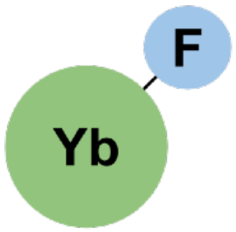
"Nature's high E-field laboratory"

- Searches for EDMs and other symmetry violations

- Bond distorts atomic orbitals
- Molecular symmetries cancel systematics

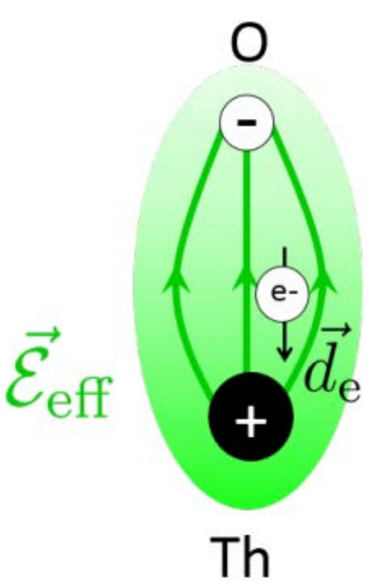


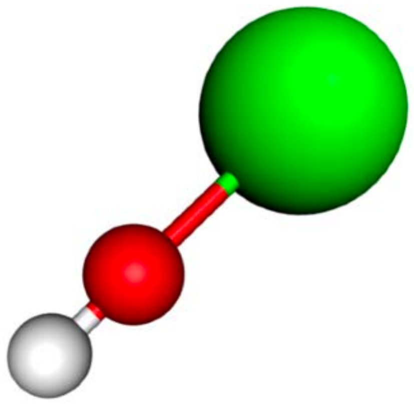
JILA eEDM molecular ions



Laser-cooled YbF (Imperial College)

ACME eEDM

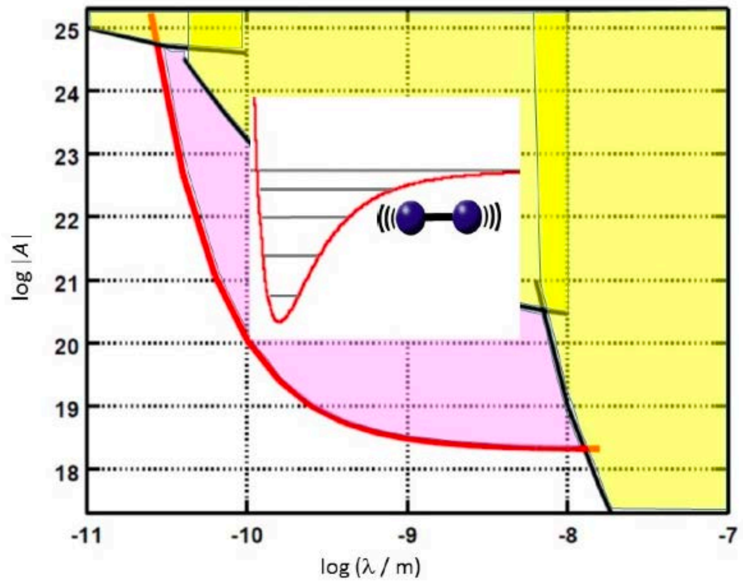




Future: laser-cooled YbOH (Hutzler, Doyle)

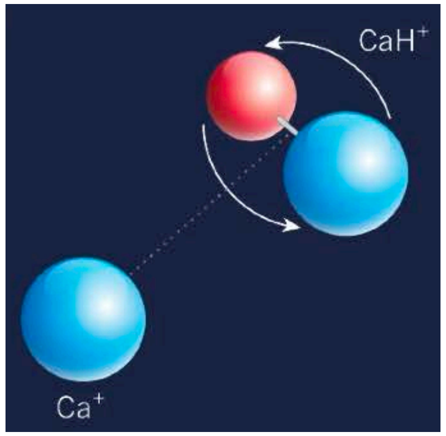
Bonded nuclei as "test masses"

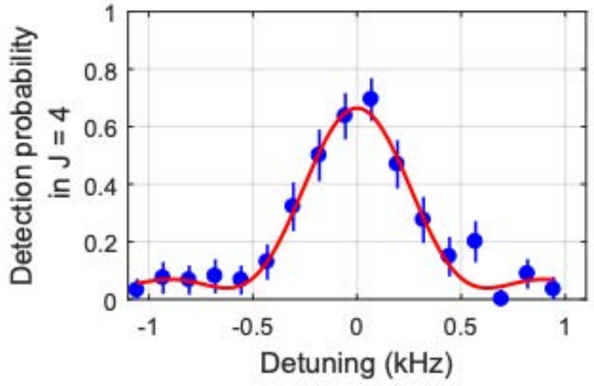
- Testing gravity at nanometer scales
- Ultracold Sr_2 – T. Zelevinsky, Columbia U



Testing precision theory

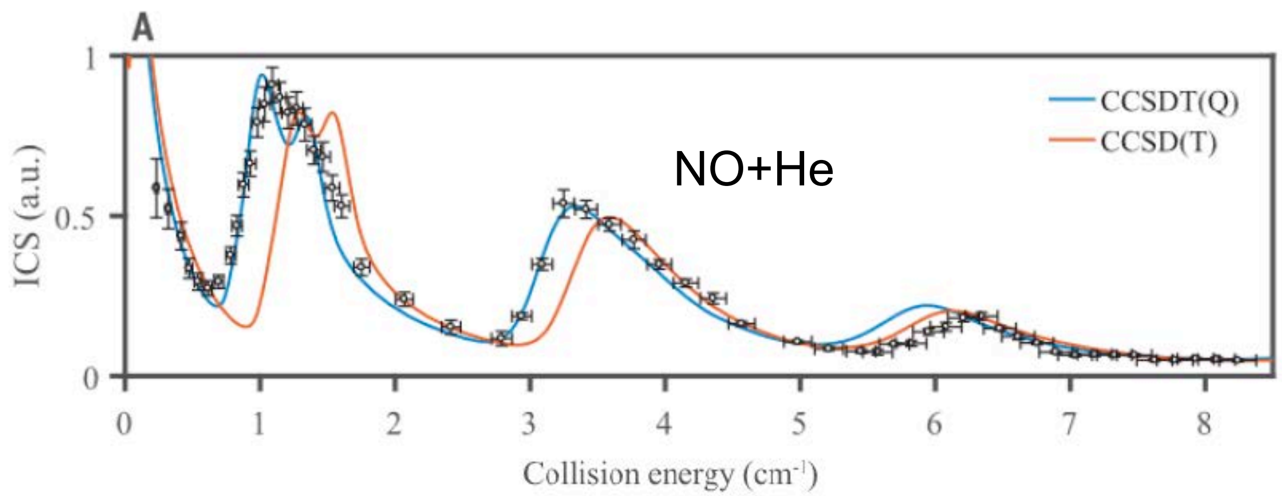
- High precision spectroscopy benchmarks theory
- CaH^+, NIST ion storage group
- HD^+, Vrije U. Amsterdam. Theory: C. Pachucki & co.





Cold Molecules for Chemistry

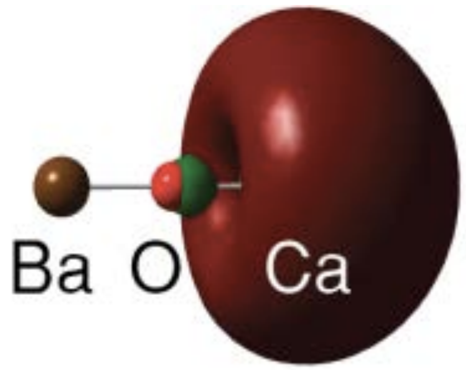
probing potential energy surfaces beyond "gold-standard" quantum chemistry calculation



van de Meerakker (Radboud)
Science 368, 626 (2020)

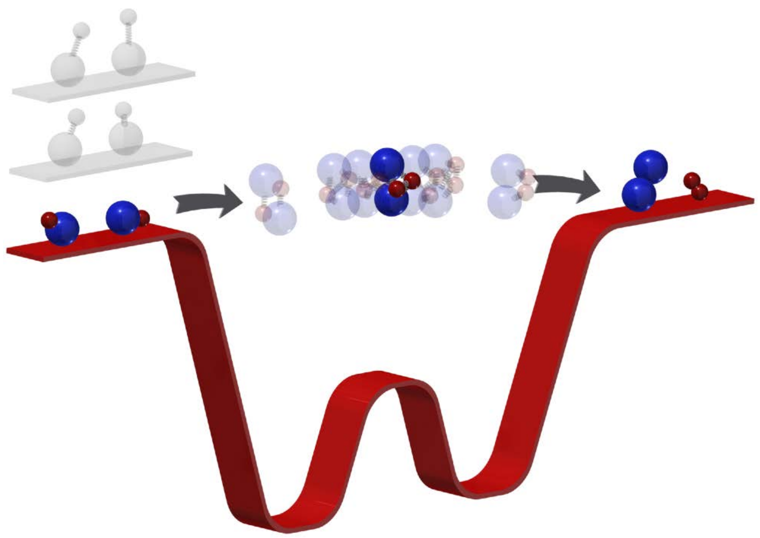
Narevicius (Wiezmann)
Nature Phys. 13, 35 (2017)

synthesizing new chemical species



Hudson (UCLA)
Science **357**, 1370 (2017)

Ye, Denschlag, Zelevinsky, Willitsch, Zare, …



Outline

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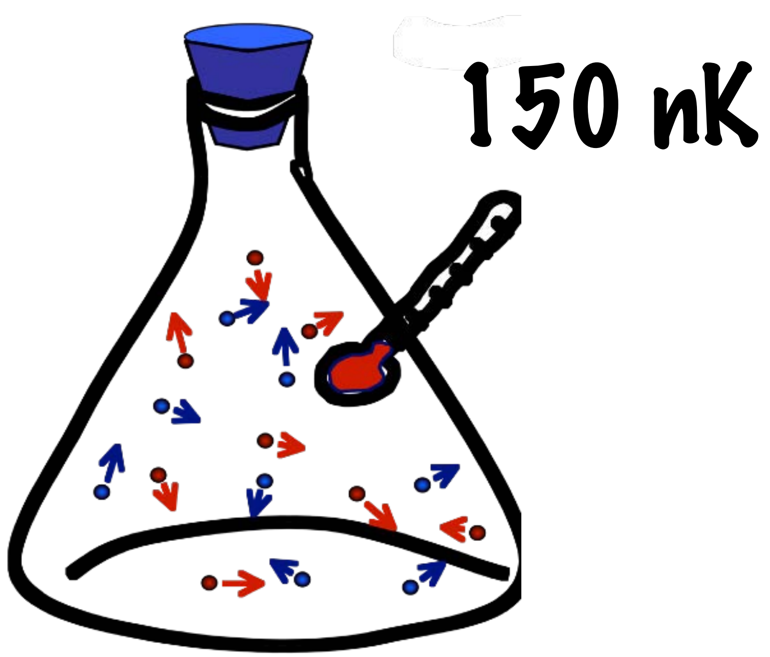
Associate Molecules from Ultracold Atoms



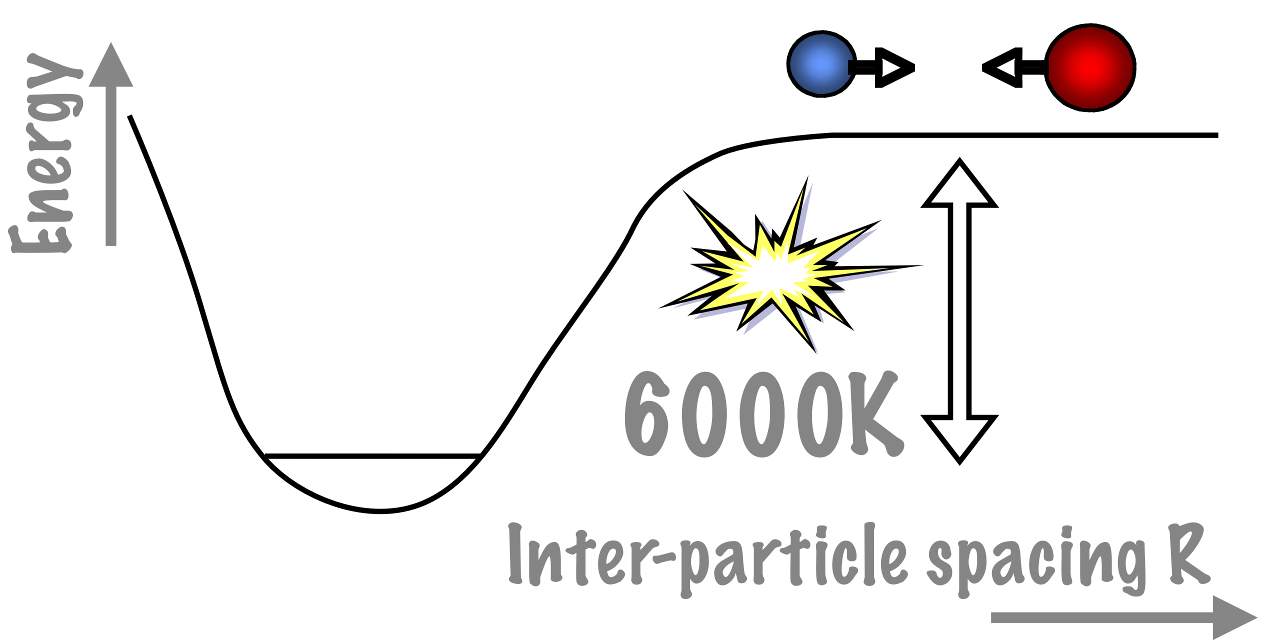
Two types of atoms

Rubidium (boson)

Potassium (fermion)

1K = 0.002 kCal/mol ~ 1 cm^{-1}

challenges: efficient molecule creation while staying cold



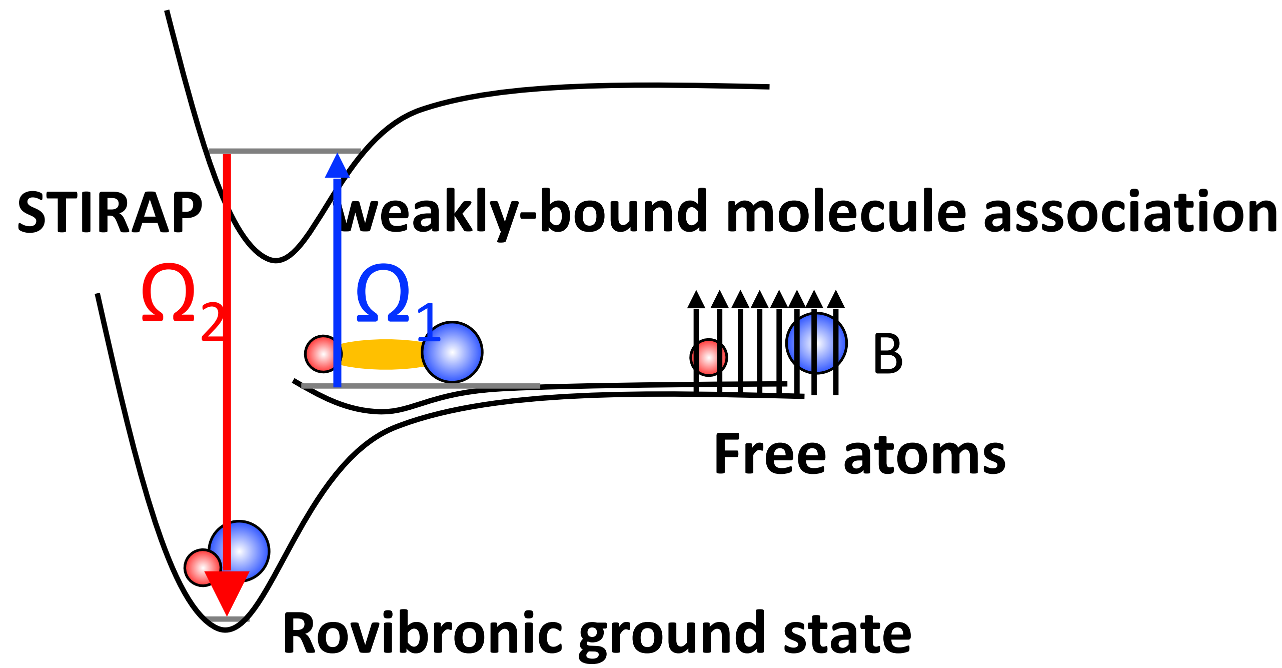
molecular bond length ~ a_0

average spacing of atoms in an ultracold gas ~10,000 a_0

Associate Molecules from Ultracold Atoms

2-step solution:

* bind atoms into weakly bound molecules through a Fano-Feshbach resonance, "Feshbach molecules" (this prepares them in a single quantum state)
* two-photon coherent transfer to ro-vibrational ground state (via STIRAP) stimulated photon takes away excess binding energy



Innsbruck and JILA (2008)

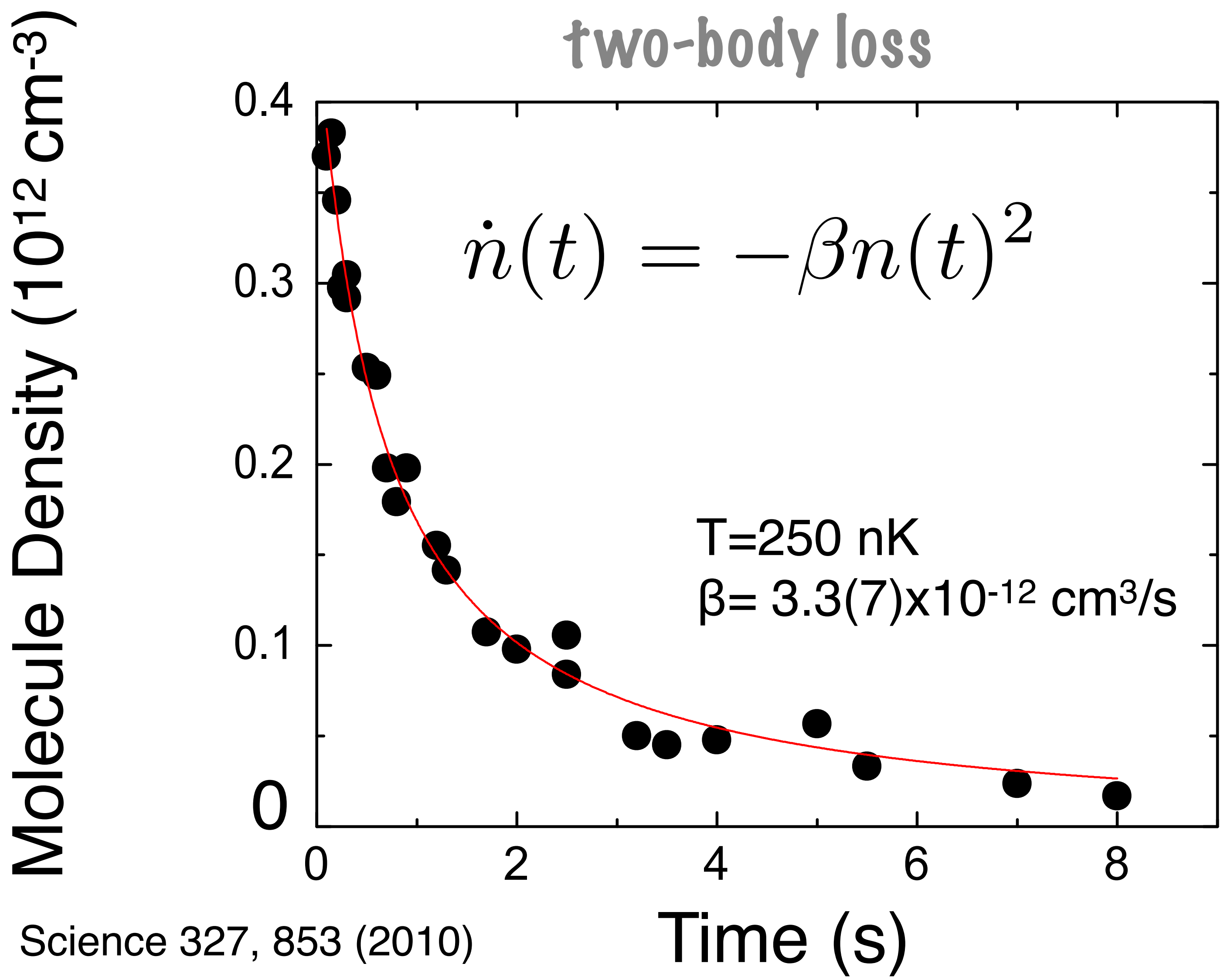
Durham, MIT, Hong Kong, MPQ, USTC, Harvard…

JILA KRb Experiment

trapped molecules in a single and lowest
hyperfine, rotational, vibrational, electronic ground state!

Science **322**, 231 (2008)

peak density= $10^{12}/cm^3$
temperature =200 nK

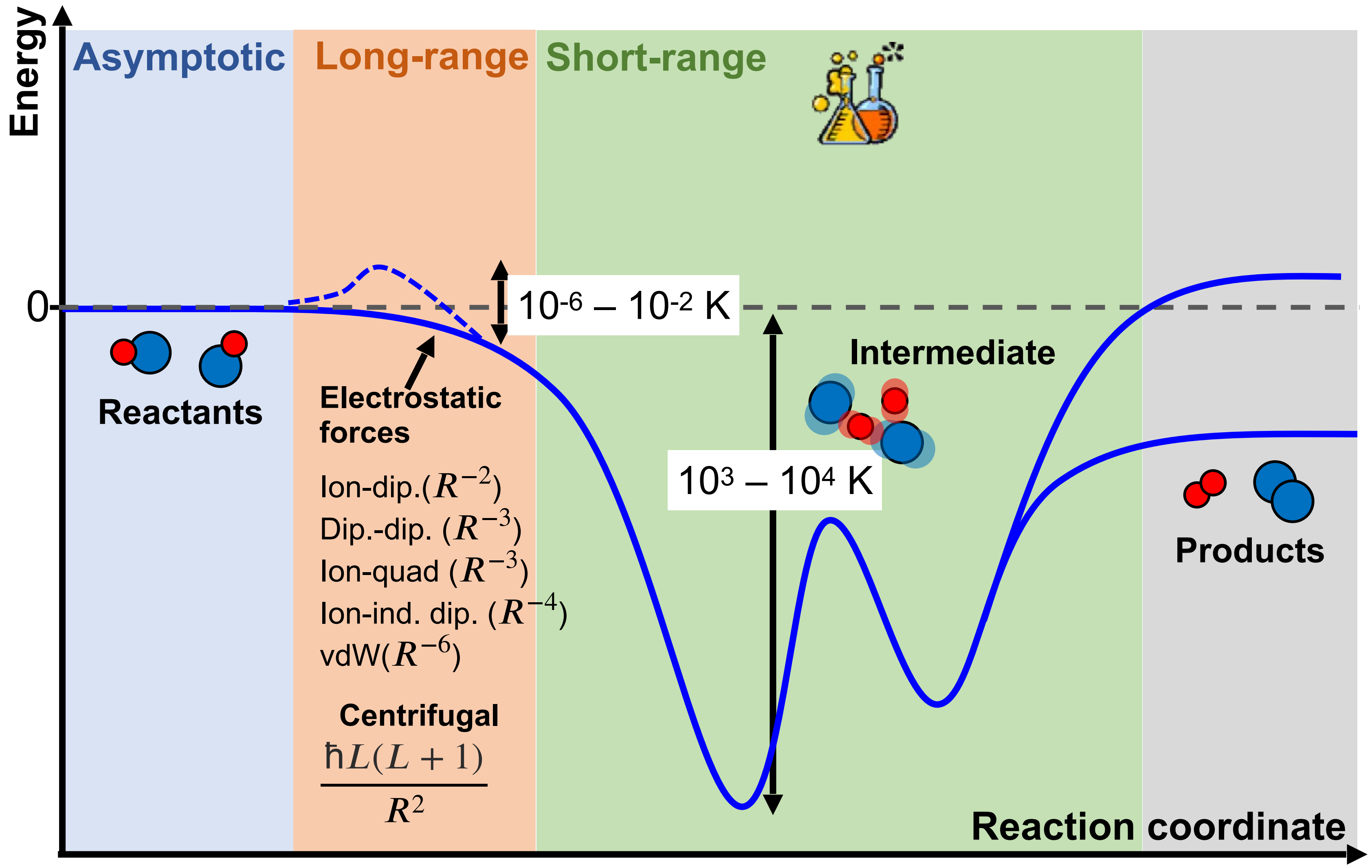


Science 327, 853 (2010)

Nature Physics 15, 523 (2019)

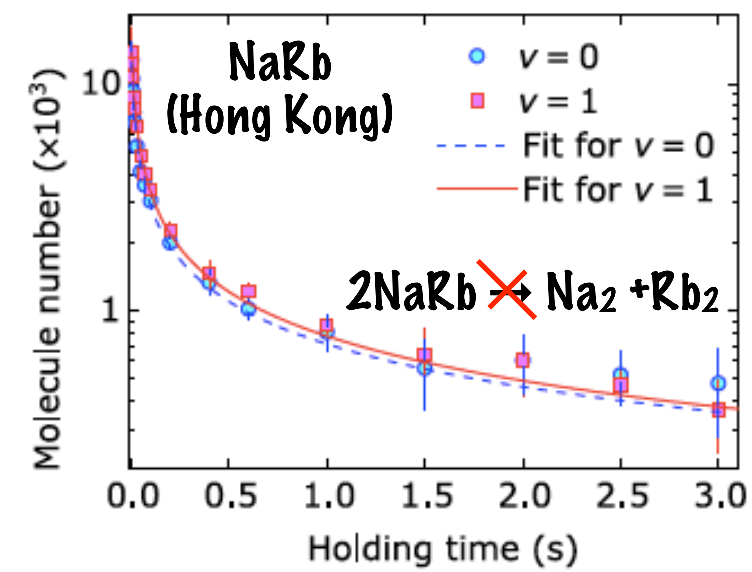
Quantum Degenerate KRb Gas, Science (2019)

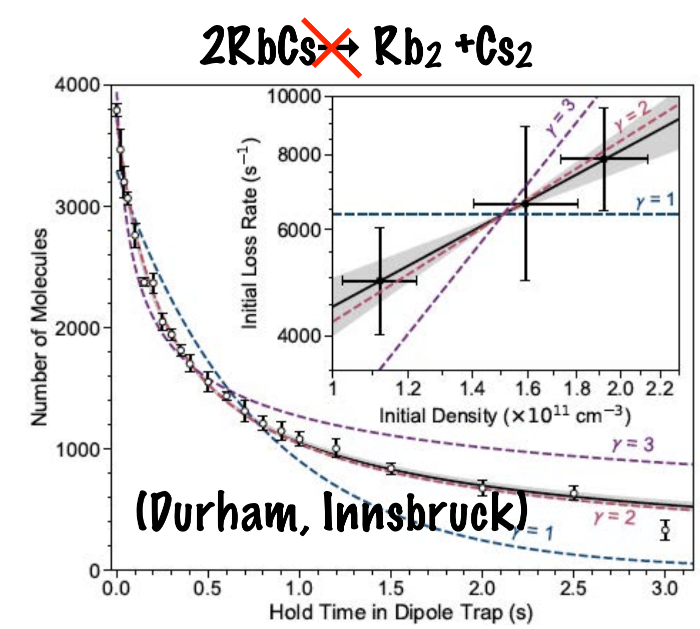
surprise #1: Ultracold Chemical Reaction?



direct detection needed

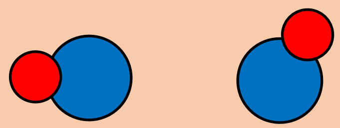
"non-reactive" species are also lossy



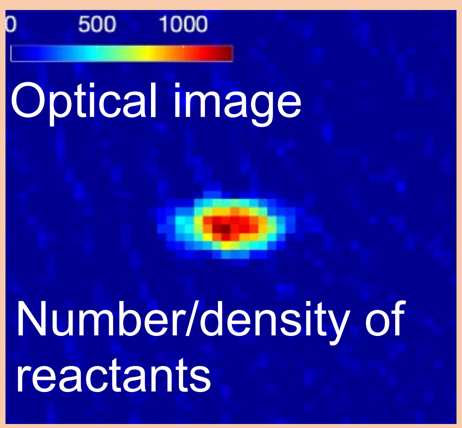


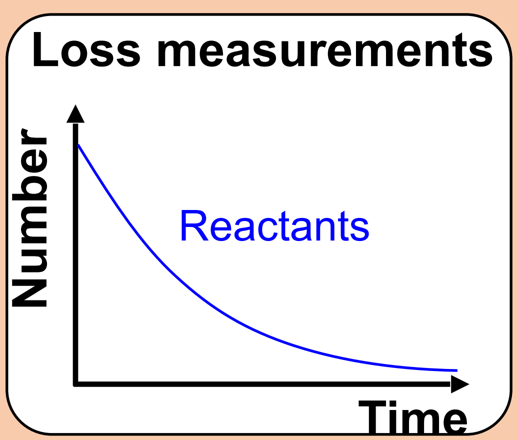
Probing the short-range and products: techniques

Long-range Imaging

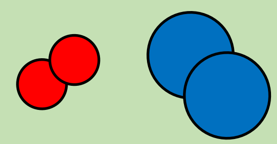


Reactants

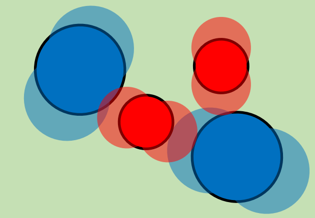




Short-range Ion spectrometry (Phys. Chem.)

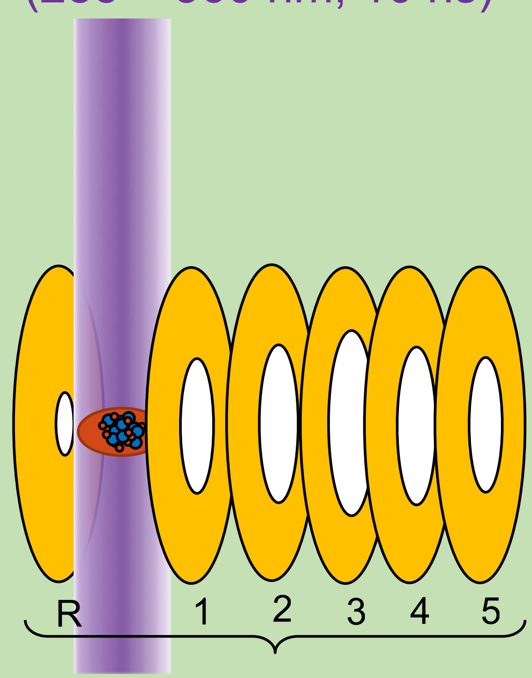


Products

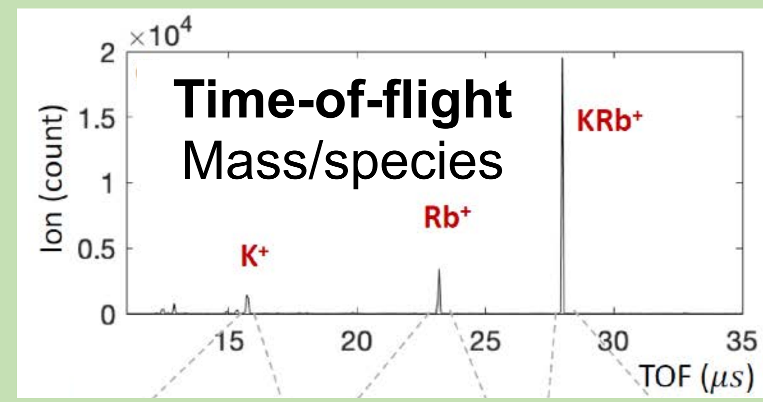


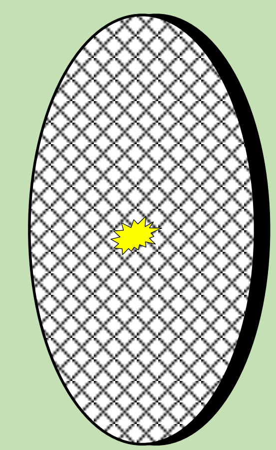
Intermediate complex

UV
(285 – 360 nm, 10 ns)



Electrostatic lens





MCP detector

Spatial distribution
Kinetic energy

Combining Physics and Chemistry tools

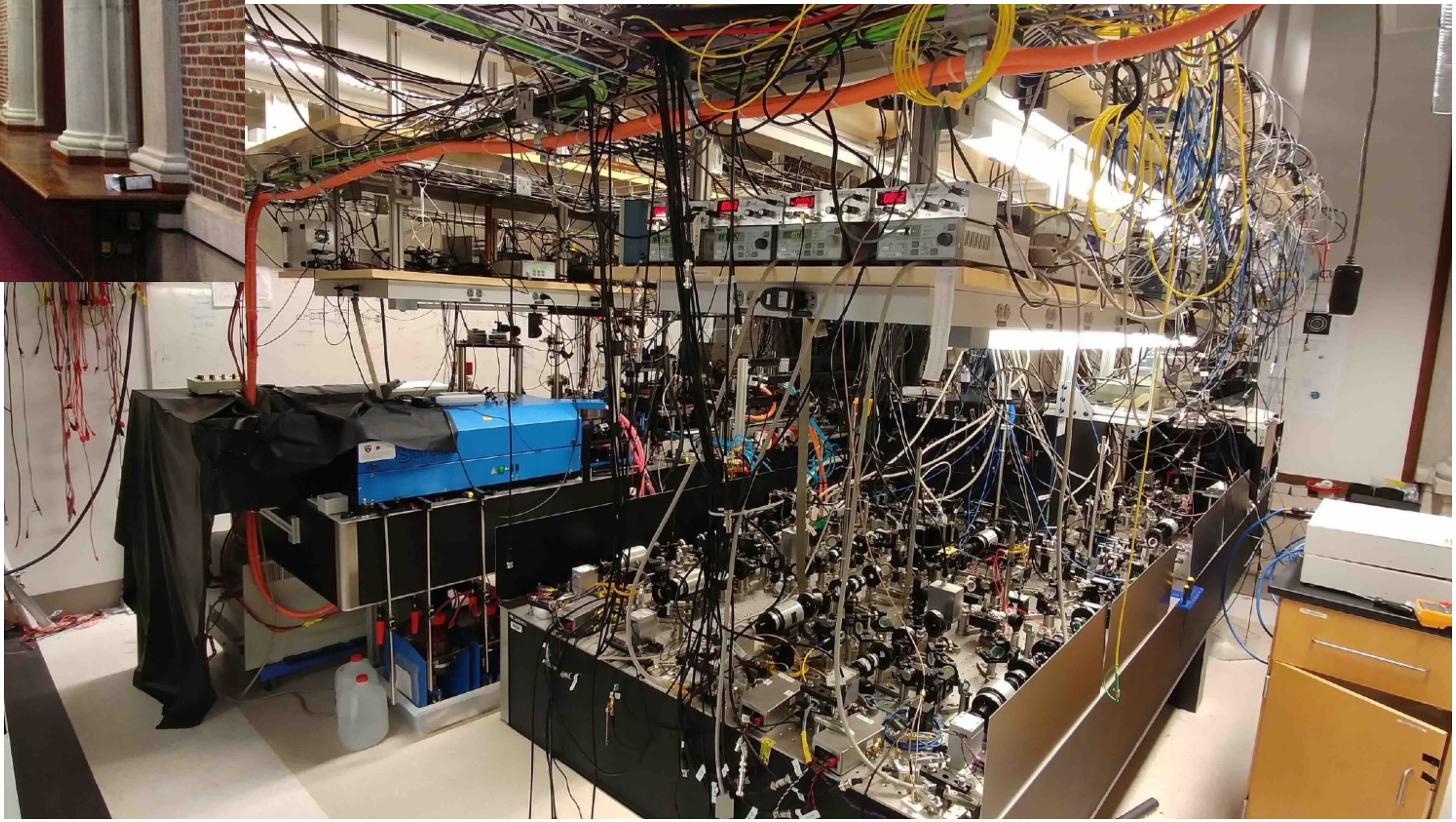
to probe ultracold chemical reactions

"The ultracold chemistry machine"
Y Liu *et al.*, *PCCP*, **22**(9), 4861 (2020)

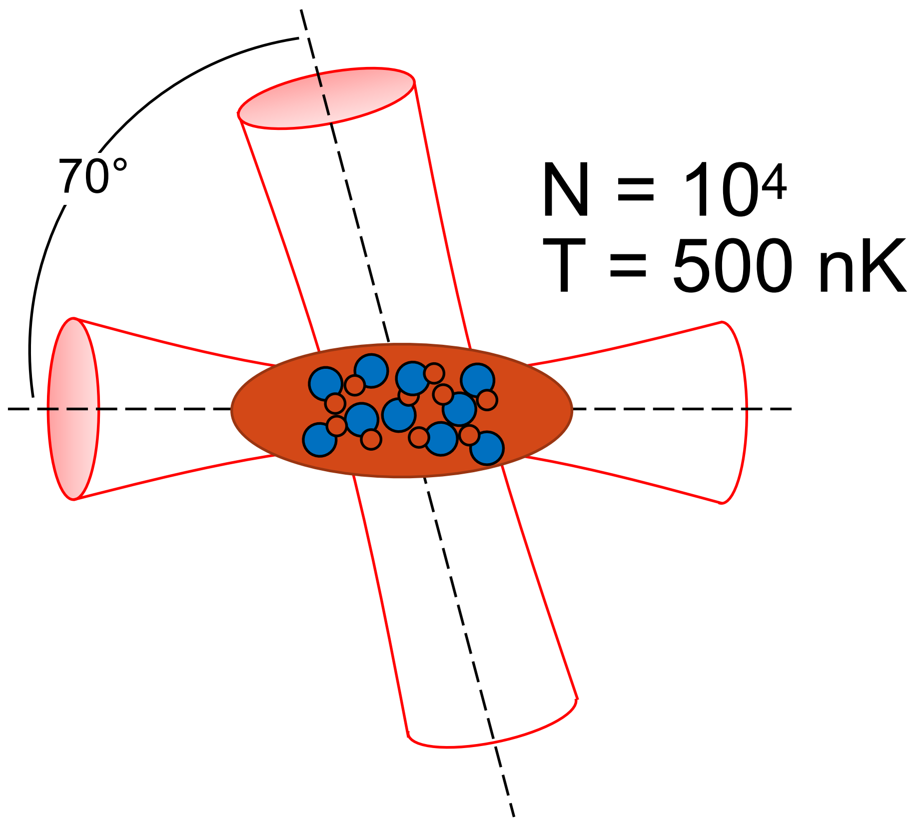
Harvard KRb lab

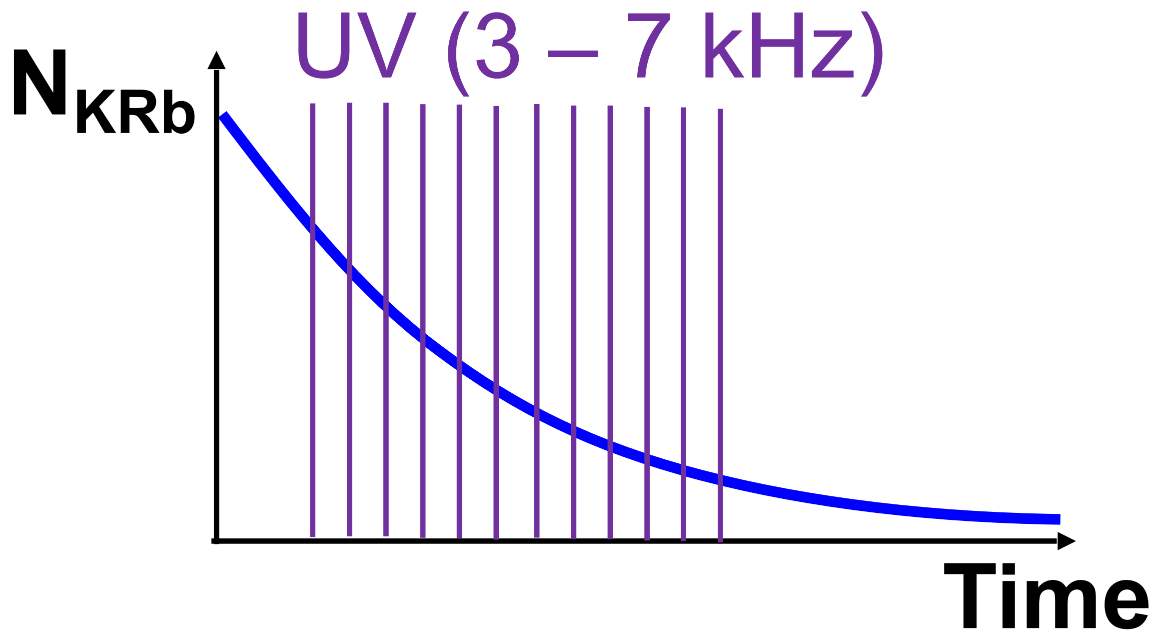
2014

2018

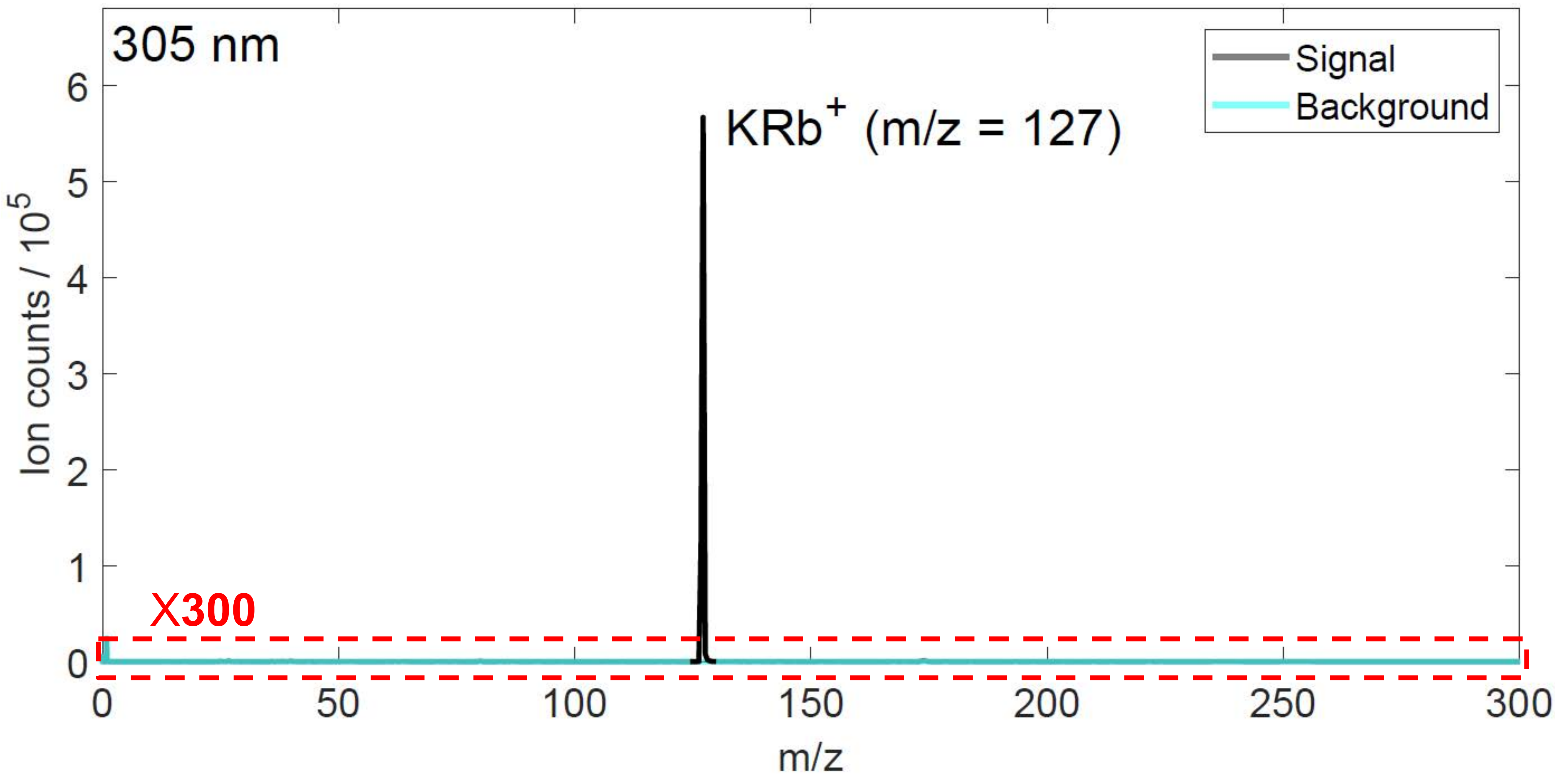


Probing the reaction





Species identification from mass spectrum



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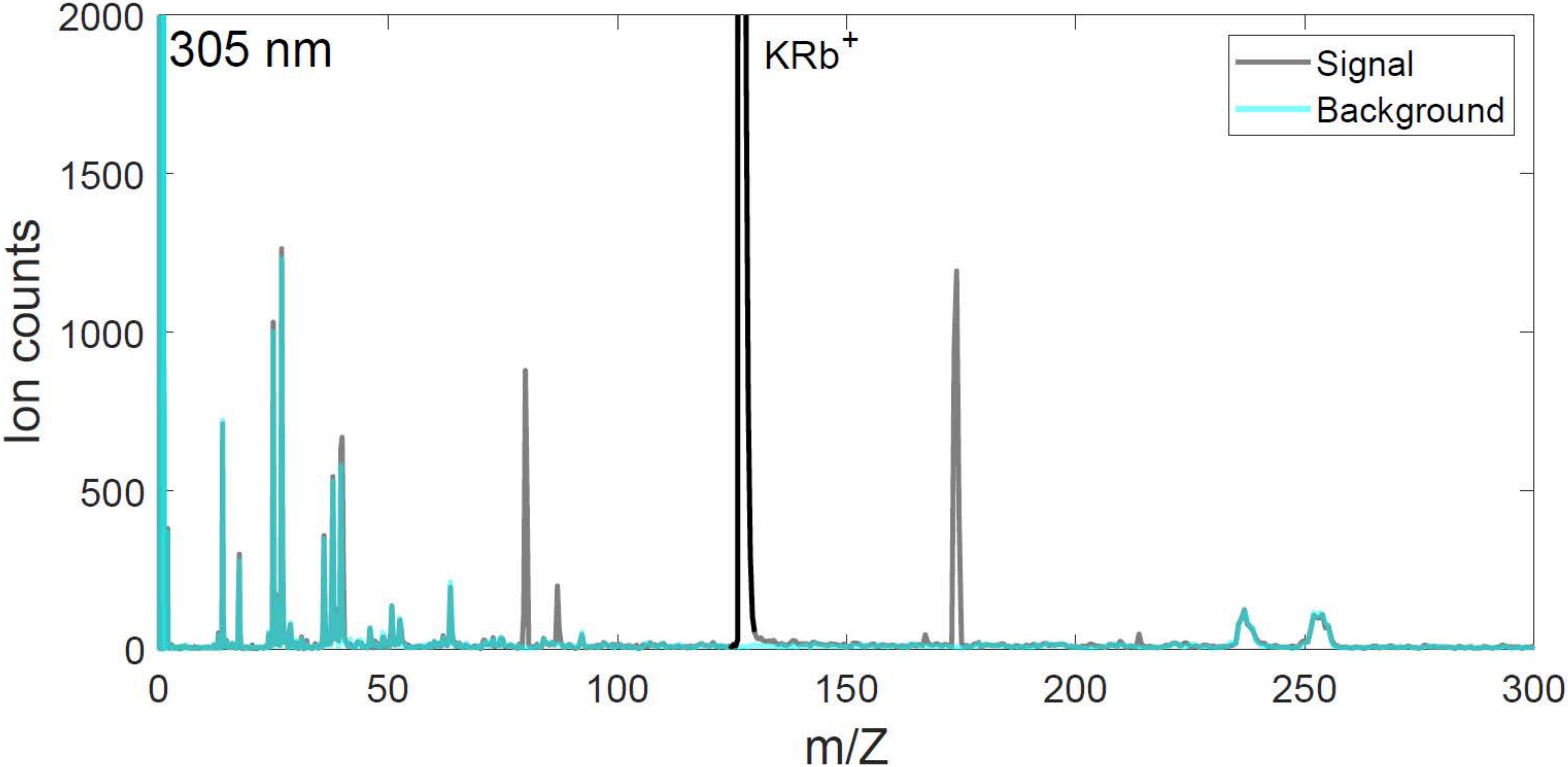

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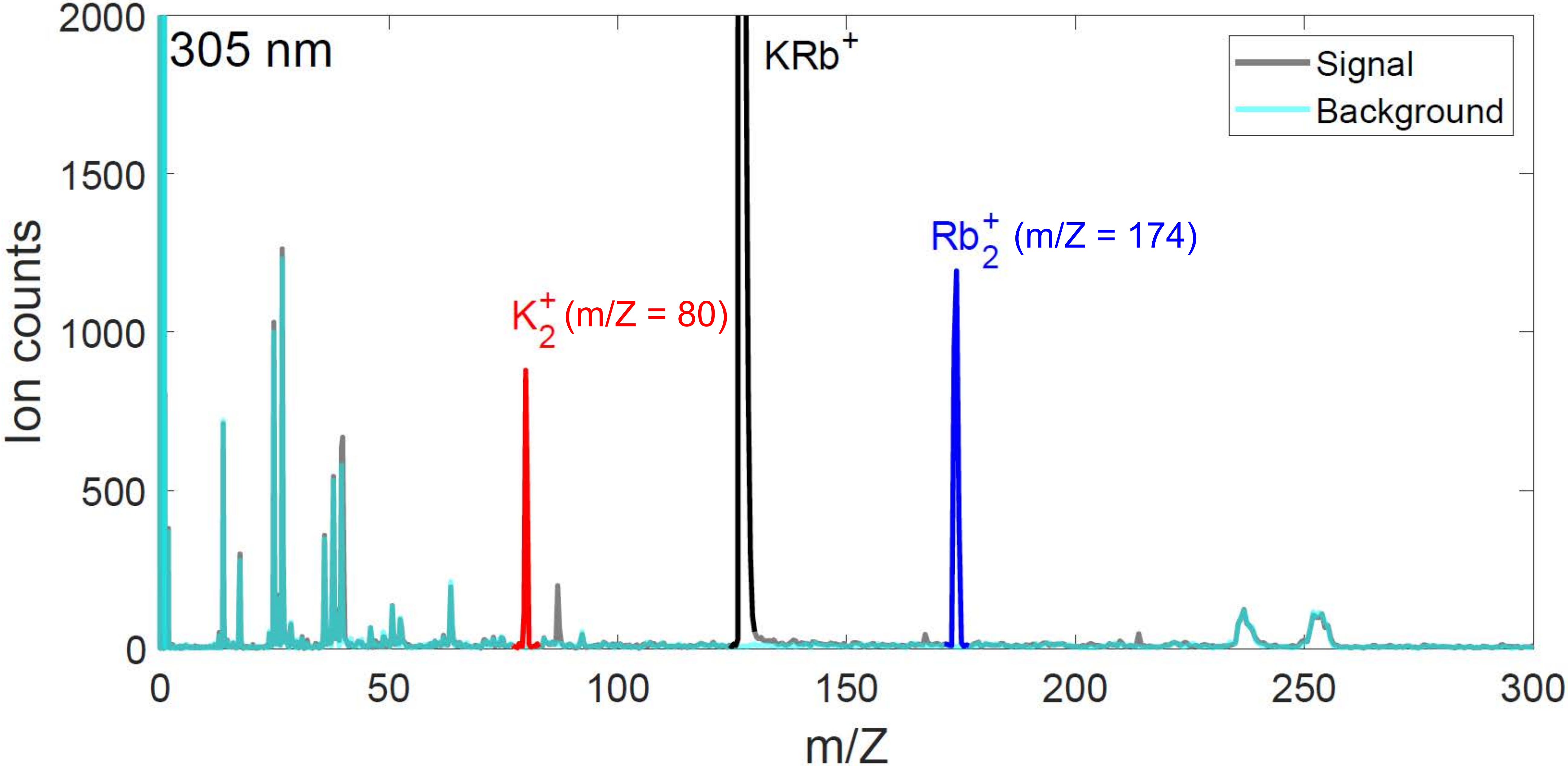
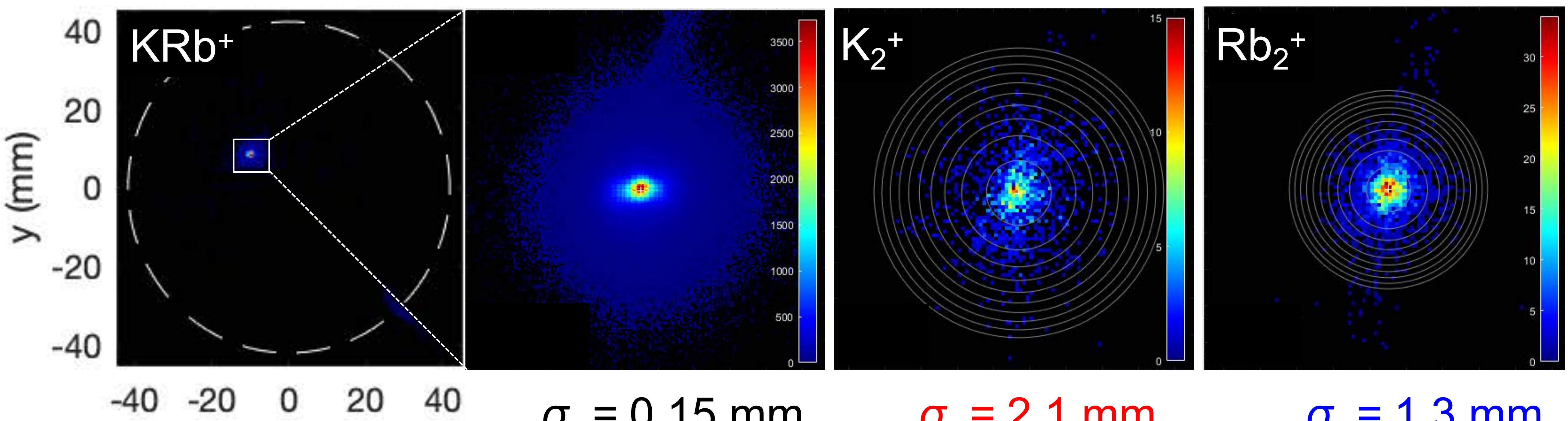


Hu, Liu, et al., *Science* **366**, 1111 (2019)

Verifying the product signal: *KE* distribution

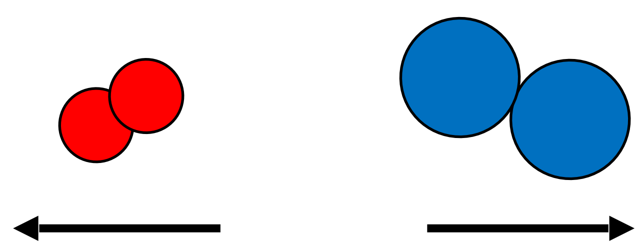


σ_r = 0.15 mm
KE = 0.15 cm^{-1}

σ_r = 2.1 mm
KE = 1.9 cm^{-1}

σ_r = 1.3 mm
KE = 0.87 cm^{-1}

$$\frac{0.87\ \text{cm}^{-1}}{1.9\ \text{cm}^{-1}} = 0.46$$



$$P_{K2} = P_{Rb2}$$

$$\frac{KE_{Rb2}}{KE_{K2}} = \frac{m_{Rb2}}{m_{K2}} = 0.46$$

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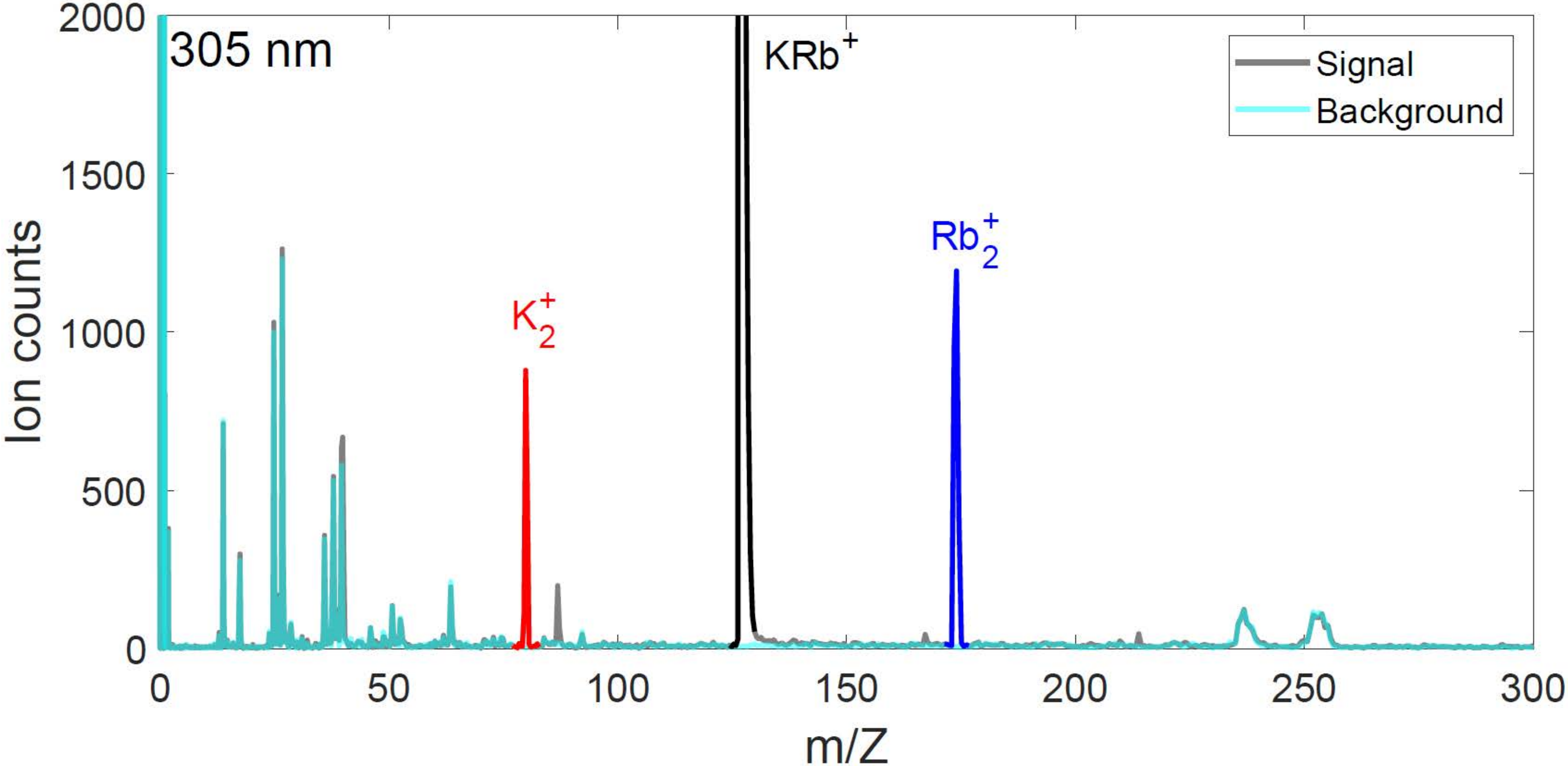
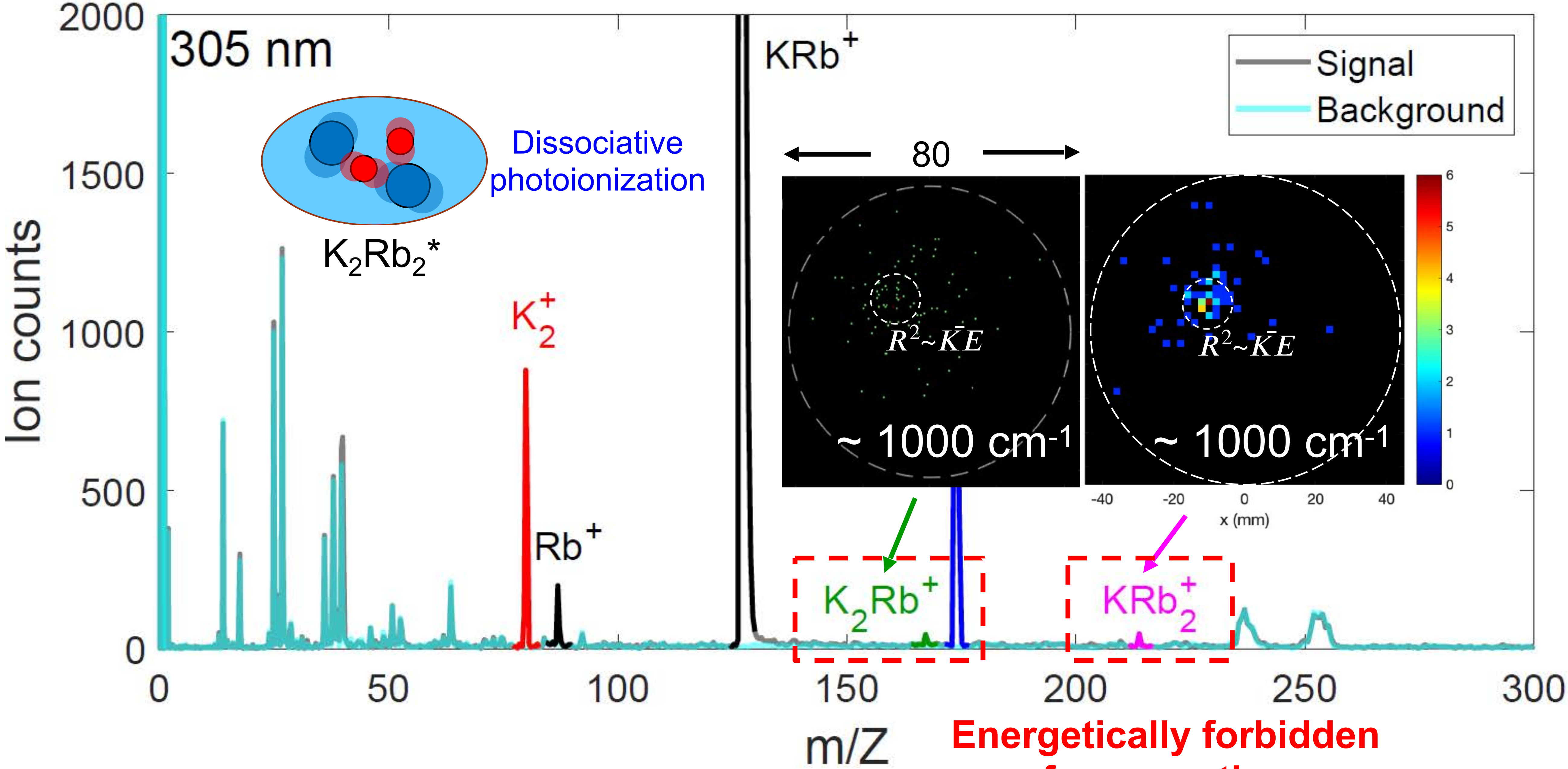
Species identification from mass spectrum



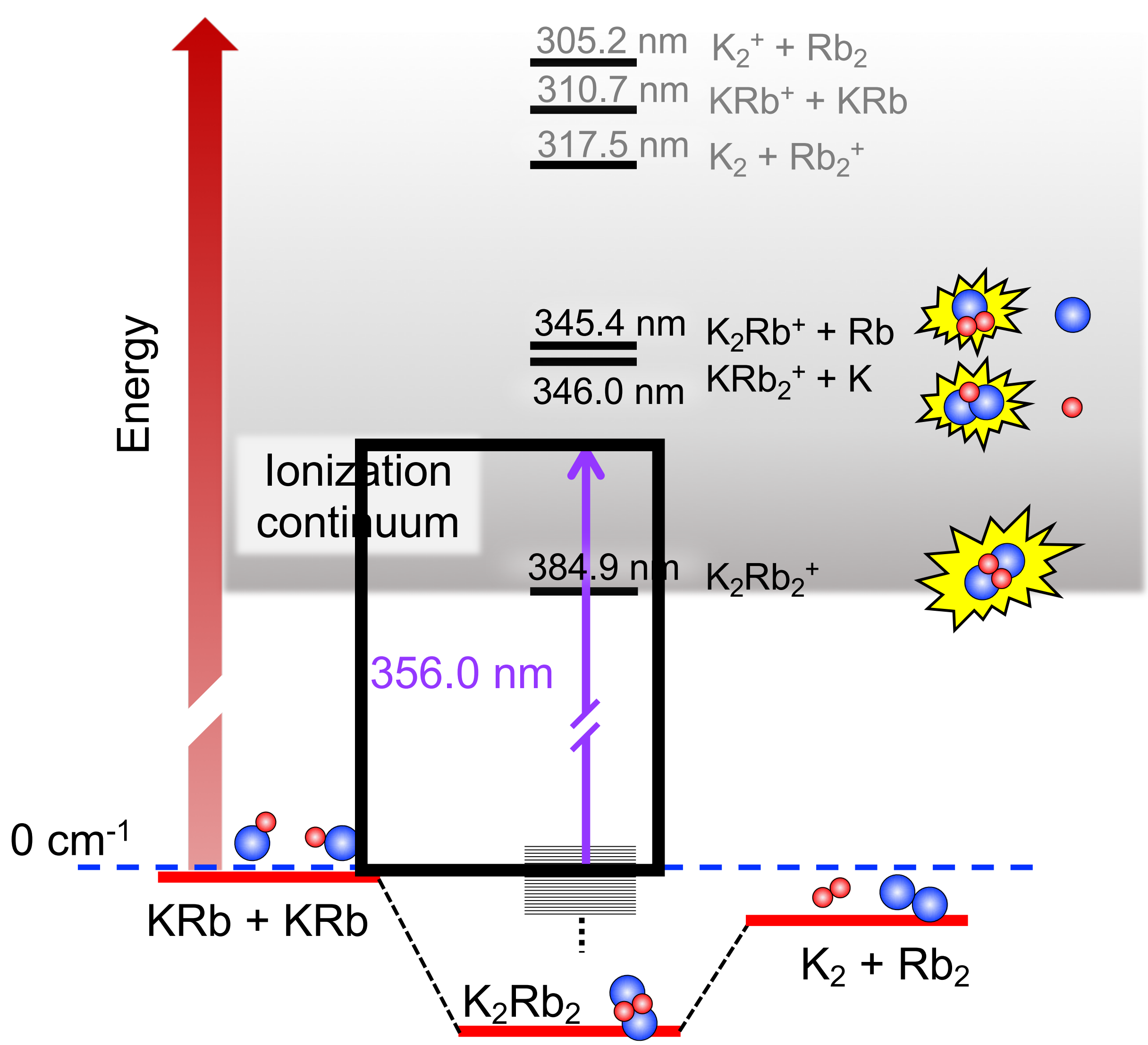
surprise #2: seeing transient intermediate?



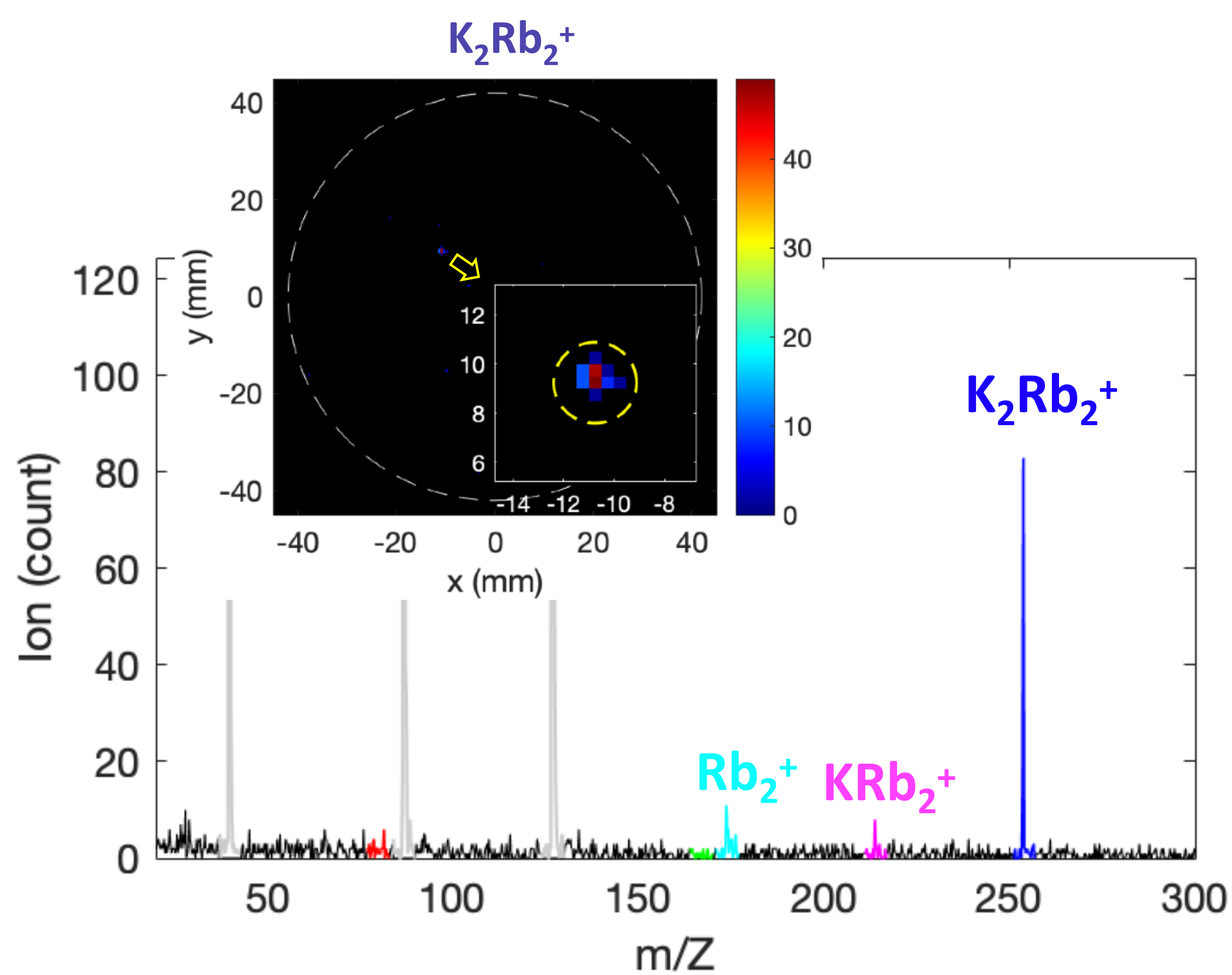
Energetically forbidden from reaction

Origin of the triatomic species is the transient intermediate

Calculation by Olivier Dulieu and Romain Vexiau (Orsay)



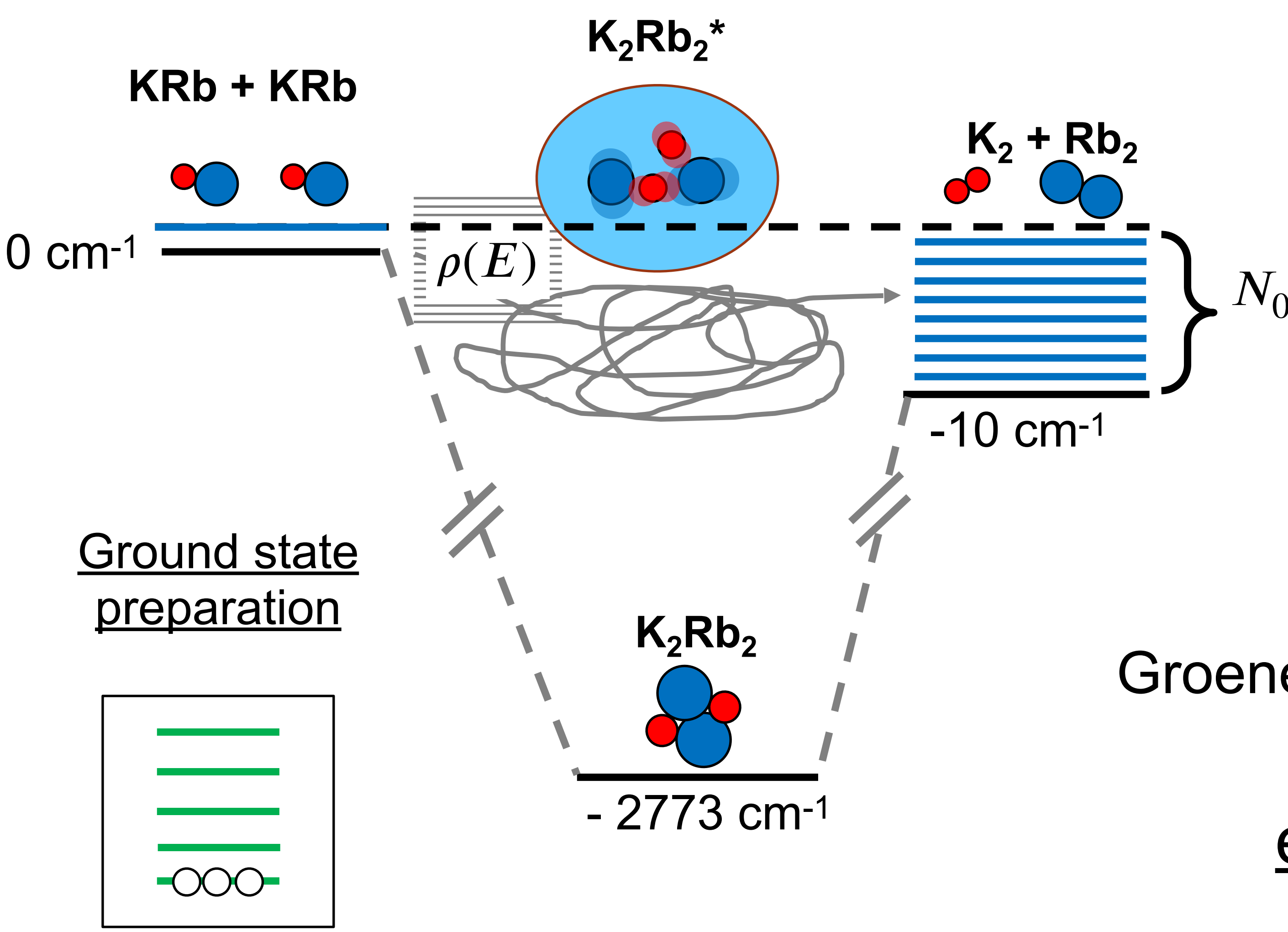
356 nm Photoionization



Hu, Liu, et al., *Science* **366**, 1111 (2019)

The long-lived intermediate complex

>> ps



Byrd, Montgomery, Cote
PRA **82**, 010502 (2010)

RRKM theory

$$\tau_c = \frac{h\,\rho(E)}{N_0}$$

theory estimated lifetimes

Bohn et al.(2013): $\tau_c = 3\ \mu s$

Groenenboom et al. (2019): $\tau_c = 0.3\ \mu s$

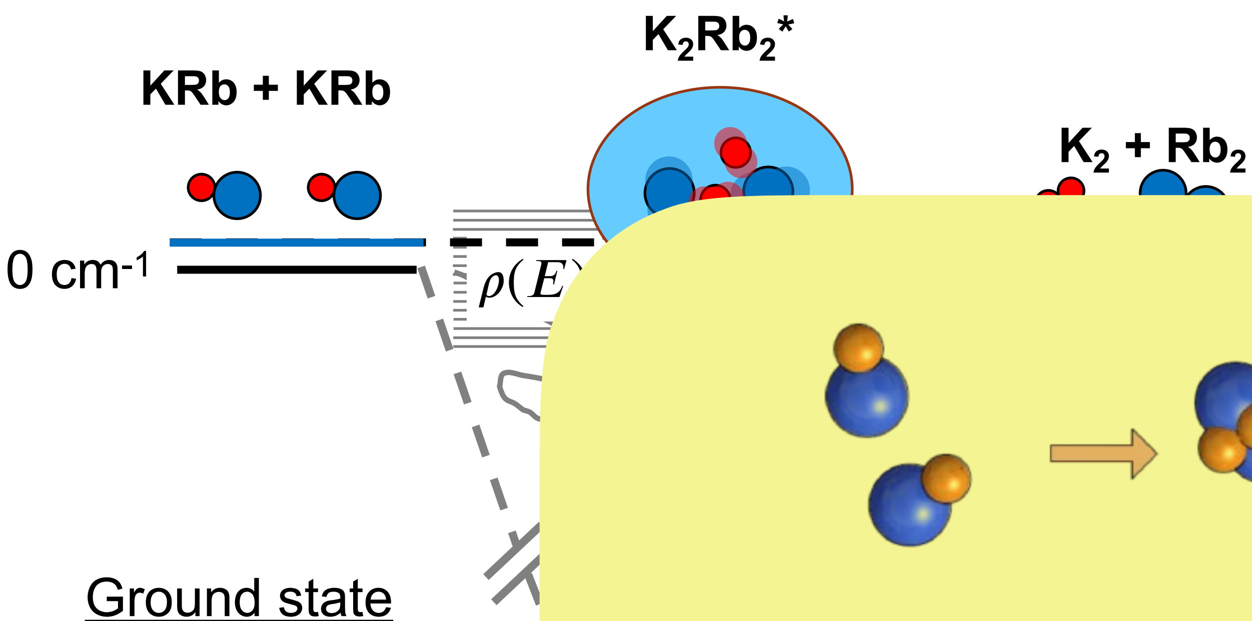
experiment estimated lifetime

$\tau_c \sim 0.35 - 3\ \mu s$

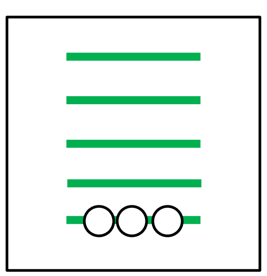
$\sigma(K_2Rb_2^* \rightarrow K_2Rb_2^+) \sim 10^{-17} - 10^{-18}\ cm^2$

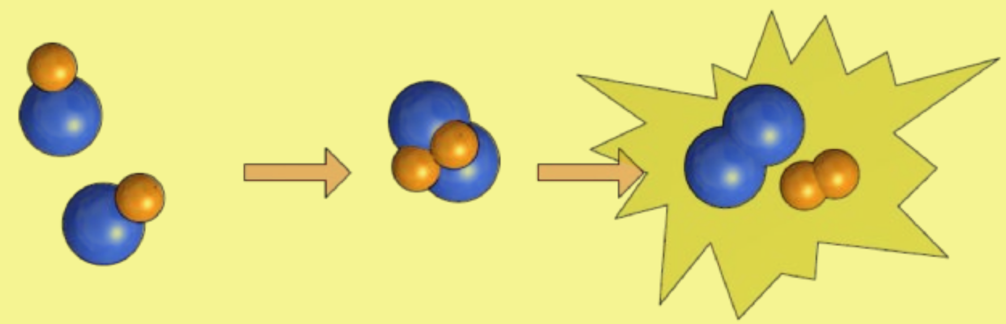
The long-lived intermediate complex

>> ps



Ground state preparation





ultracold reaction prolongs the "transient" nature of the intermediate complex

RRKM theory

$\tau = \frac{h\,\rho(E)}{}$

times

$= 3\ \mu s$

$= 0.3\ \mu s$

ed lifetime

$\tau_c \sim 0.35\ - 3\ \mu s$

$\sigma(K_2Rb_2^* \rightarrow K_2Rb_2^+) \sim 10^{-17} - 10^{-18}\ cm^2$

Byrd, Montgomery, Cote
PRA **82**, 010502 (2010)

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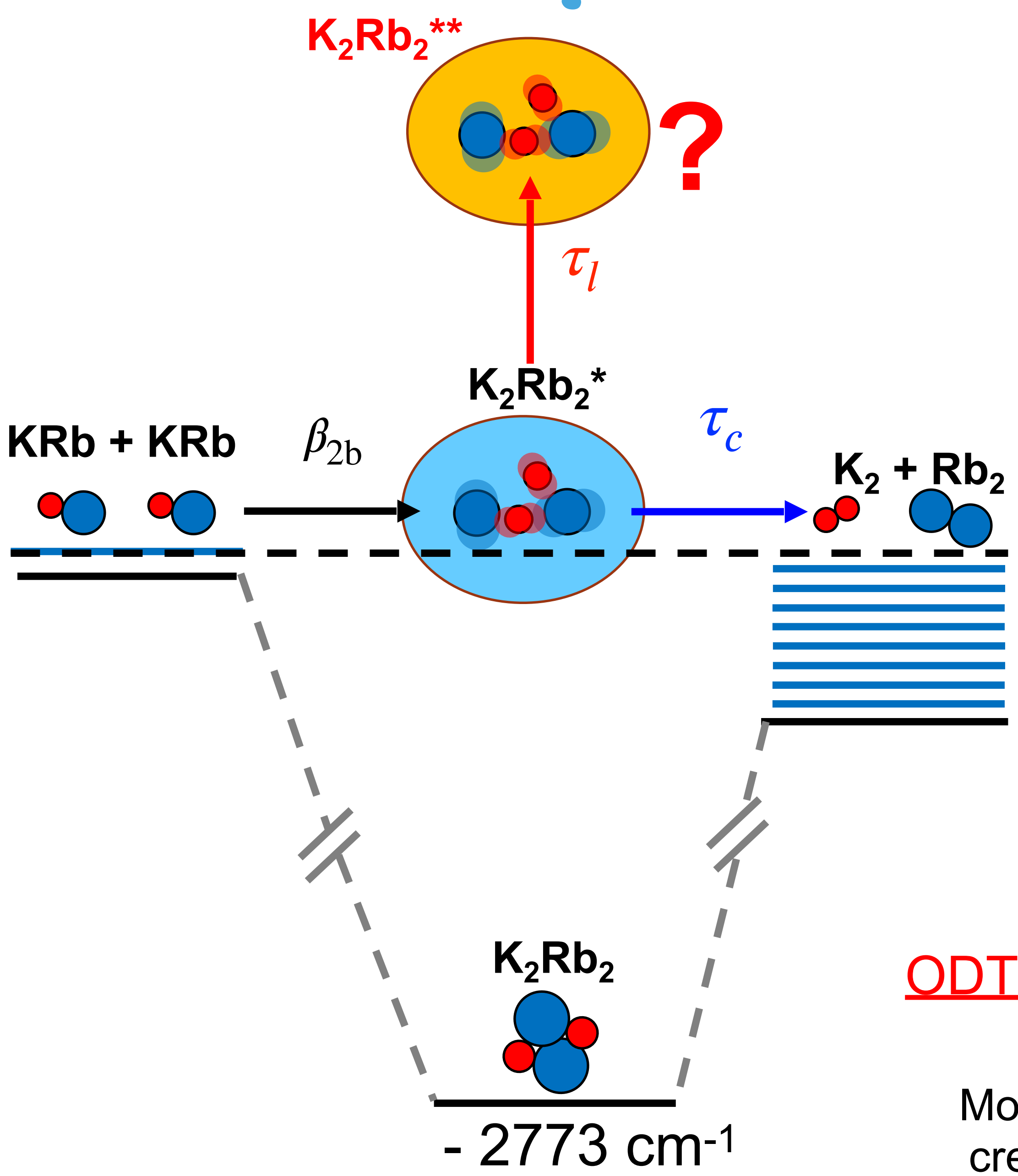
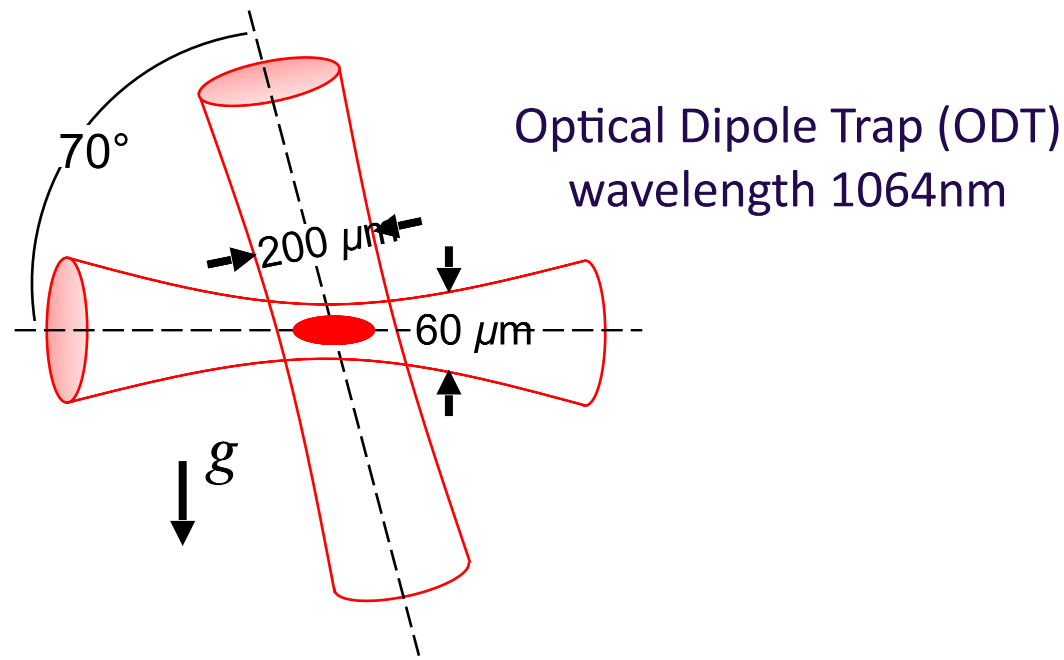
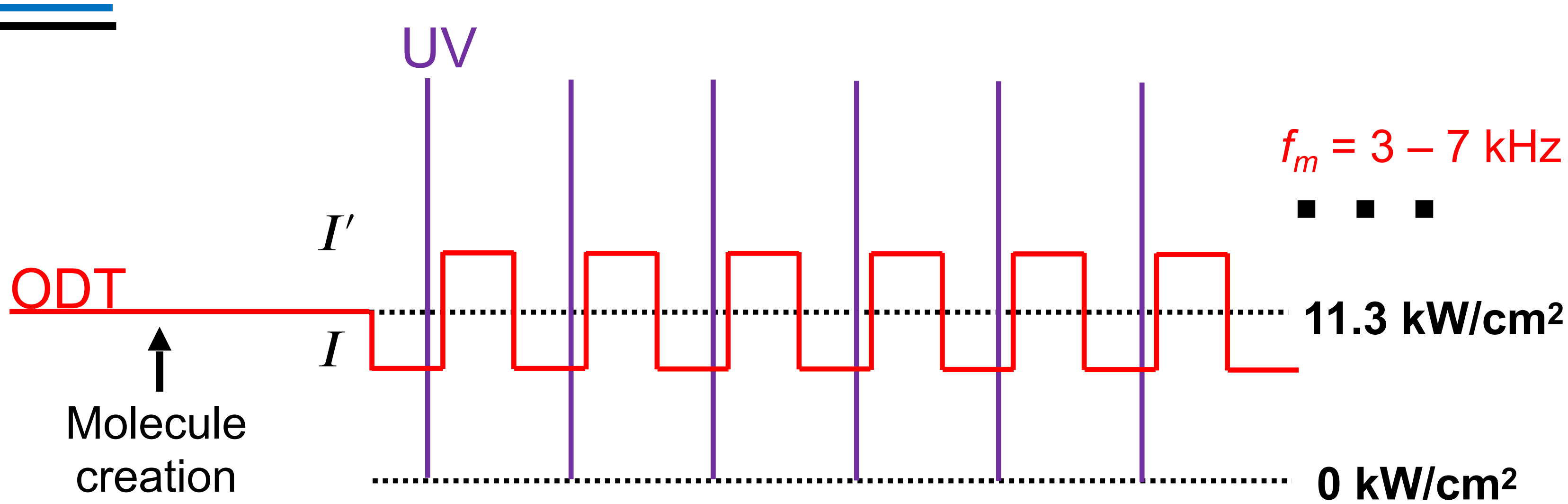
* surprise 4 - control reaction product state via nuclear spins

Consequences of the long-lived complex



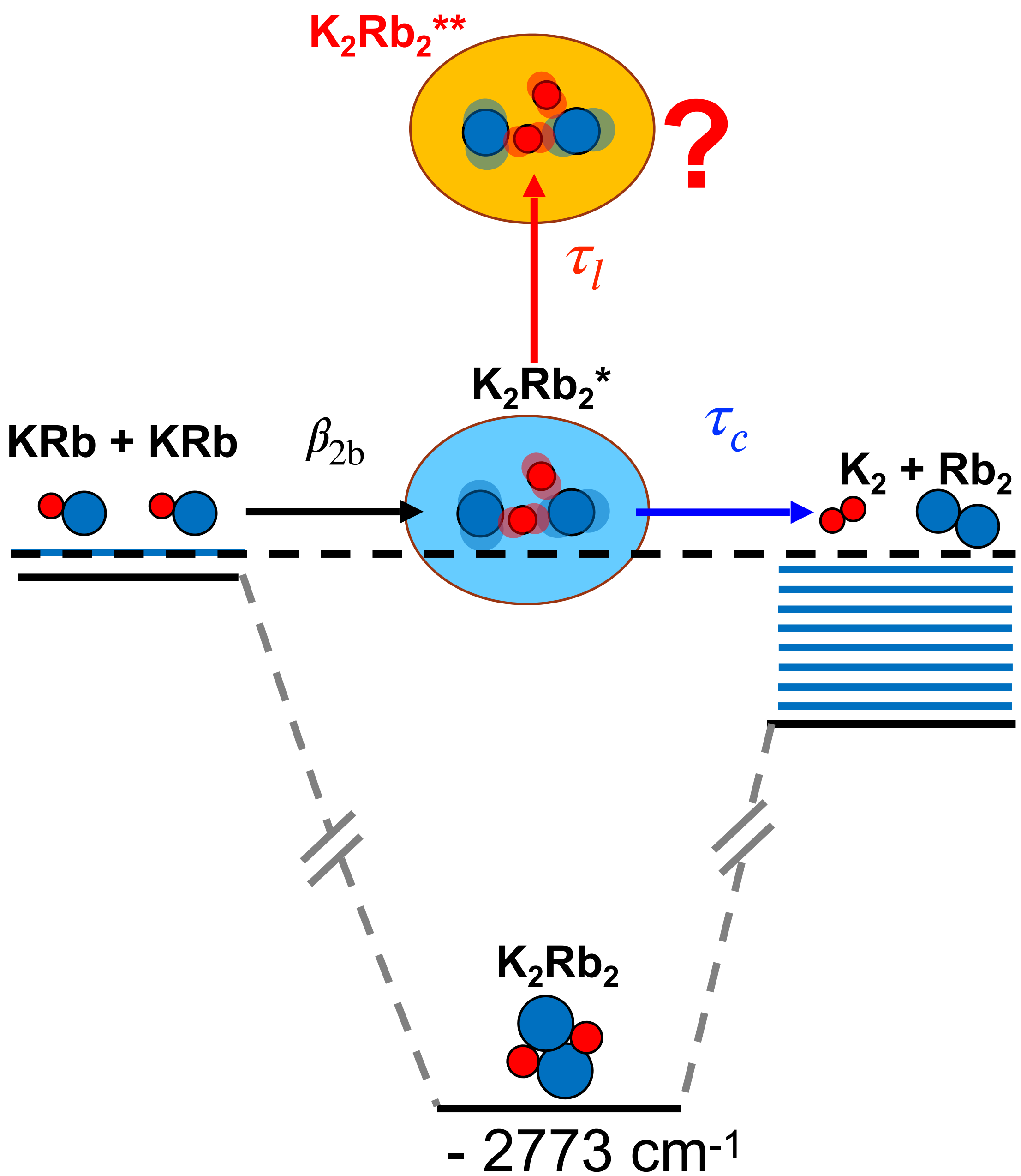


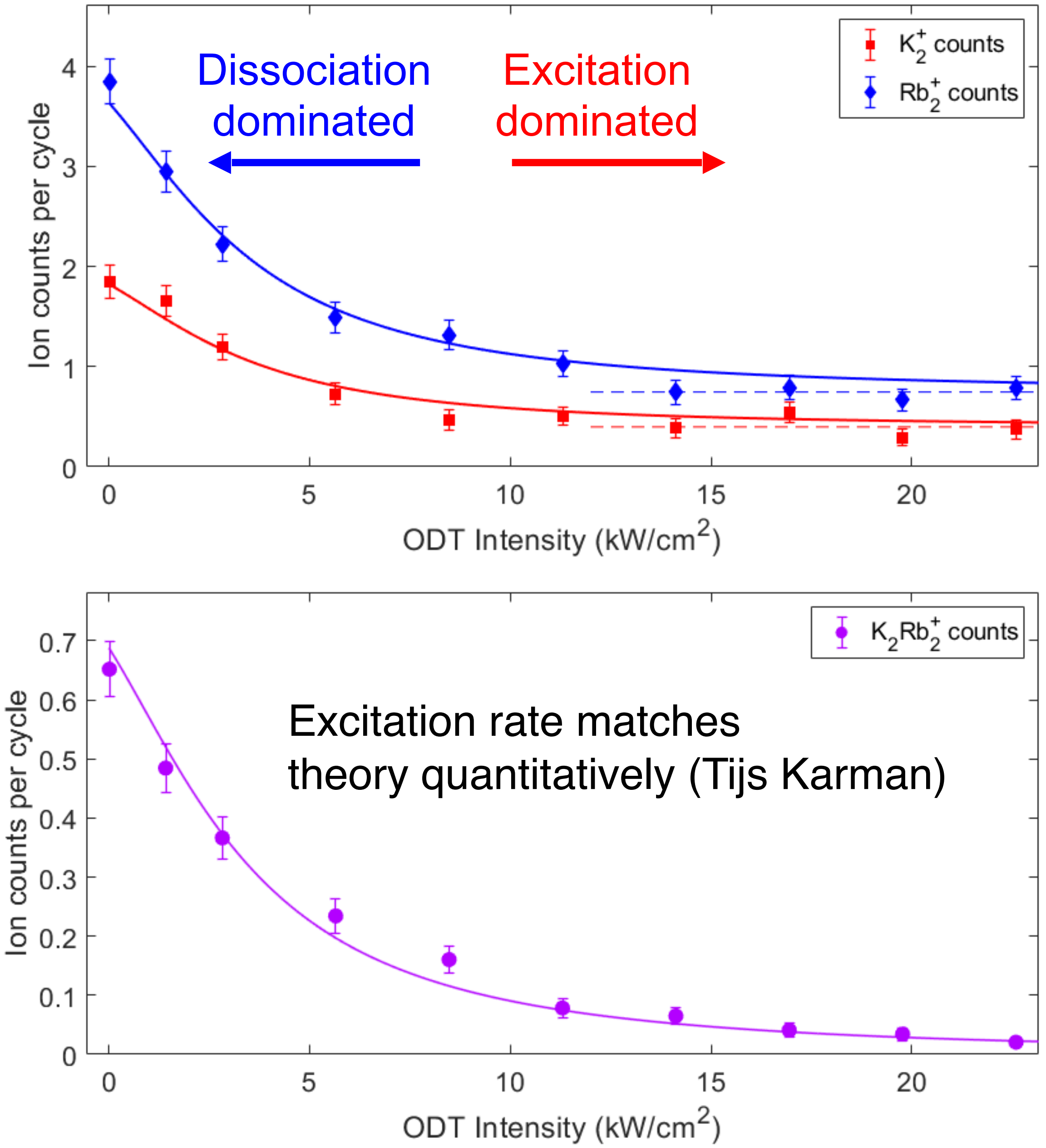


Theory: Christianen et al. PRL 123, 123402 (2019)

Liu, Hu, Nichols, Karman…..Ni, arXiv:2002.05140v2 (2020)
Related exp work in RbCs: Gregory…Cornish, PRL 124, 163402 (2020)

surprise#3: Photo-excitation of $K_2Rb_2^*$



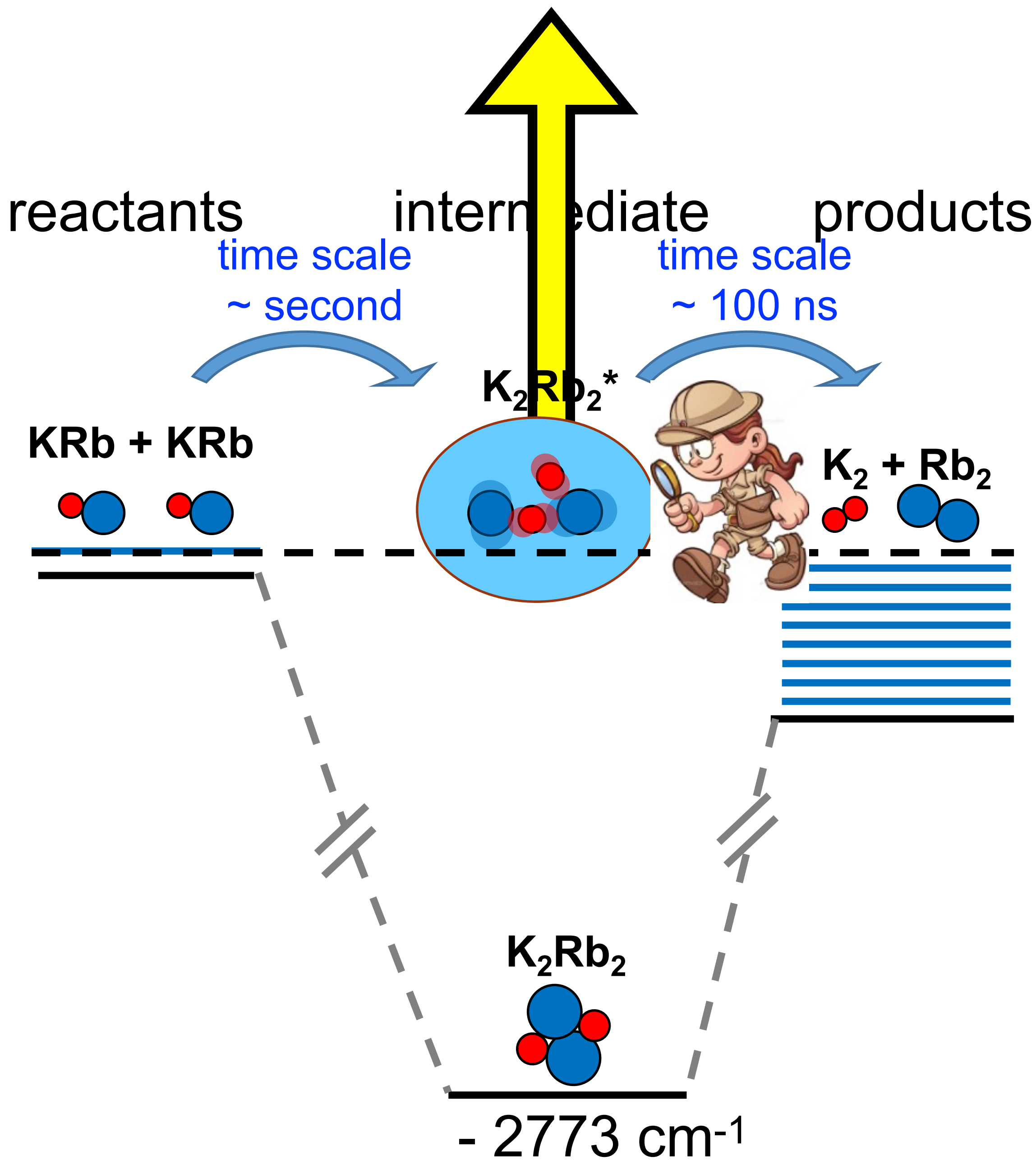


Theory: Christianen et al. PRL 123, 123402 (2019)

Liu, Hu, Nichols, Karman…..Ni, arXiv:2002.05140v2 (2020)
Related exp work in RbCs: Gregory…Cornish, PRL 124, 163402 (2020)

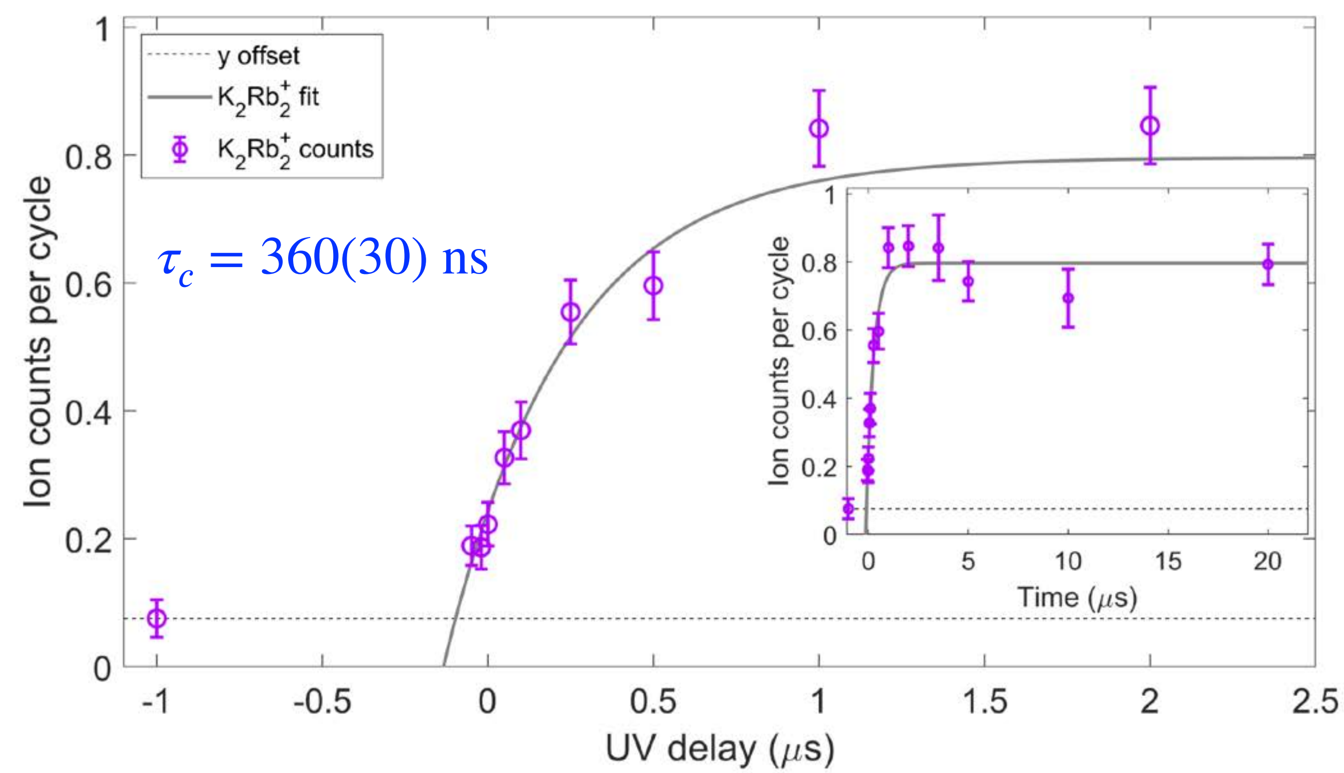
lifetime of the transient intermediate

A technical challenge:
initialize N_{K2Rb2} at t=0 to <100 ns



RRKM (from Tijs Karman)

$$\tau_c^{\mathrm{RRKM}} = h\,\rho_c / N_0$$
$$\rho_c = 2.6 \pm 0.6\ \mu\mathrm{K}^{-1}$$
$$N_0 = 745$$
$$\tau_c^{\mathrm{RRKM}} = \mathbf{170(60)}\ \mathrm{ns}$$

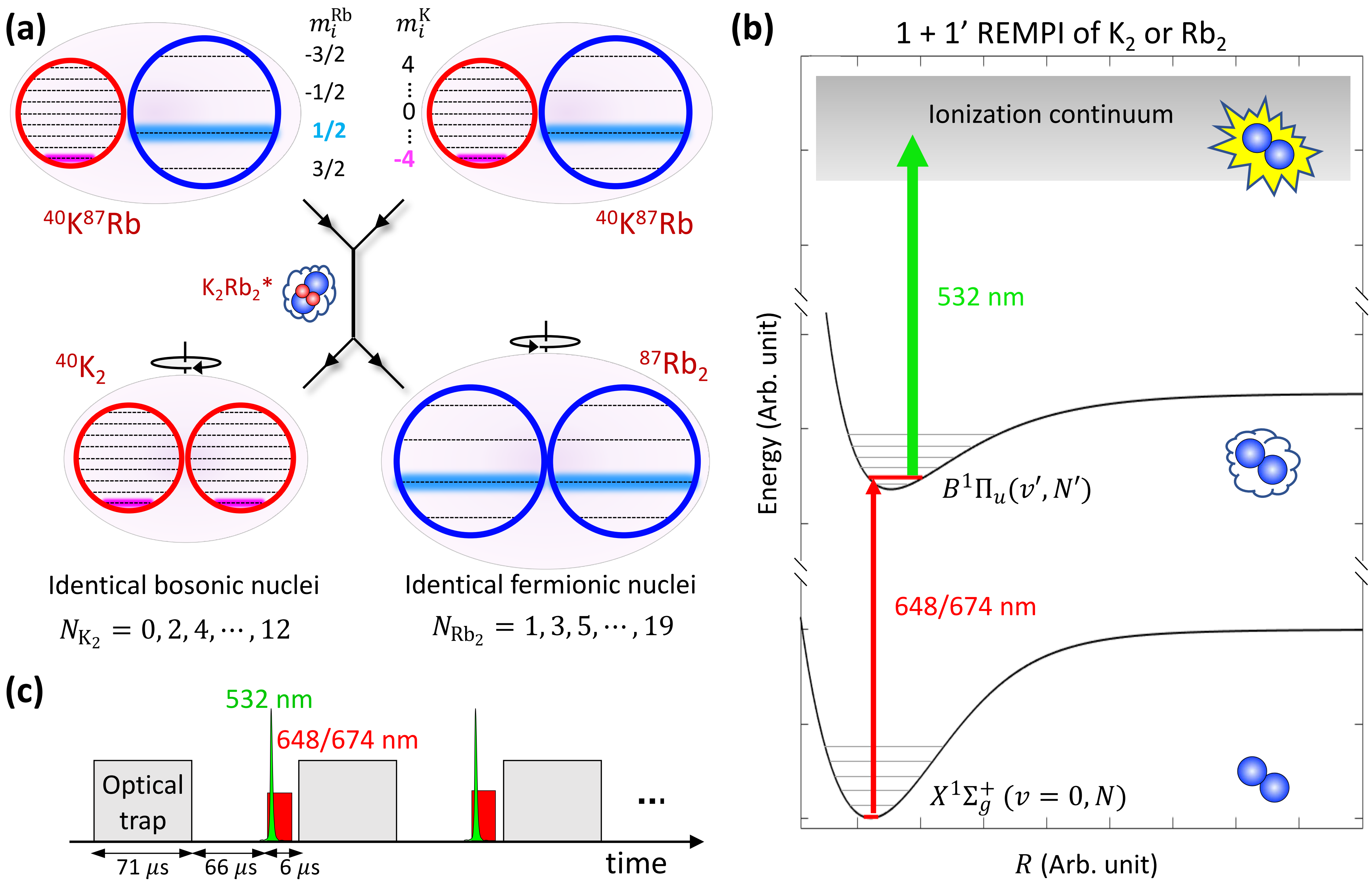


Outline

* Total quantum control of molecules
  * Make molecules from atoms with total control
* surprise 1 - chemical reactions at ultralow temperatures $2KRb \rightarrow K_2 + Rb_2$
* surprise 2 - reactions play out in "slow motion" Observed transient intermediate
* surprise 3 - steering reactions with light intermediate liftime ~360ns
* surprise 4 - control reaction product state via nuclear spins

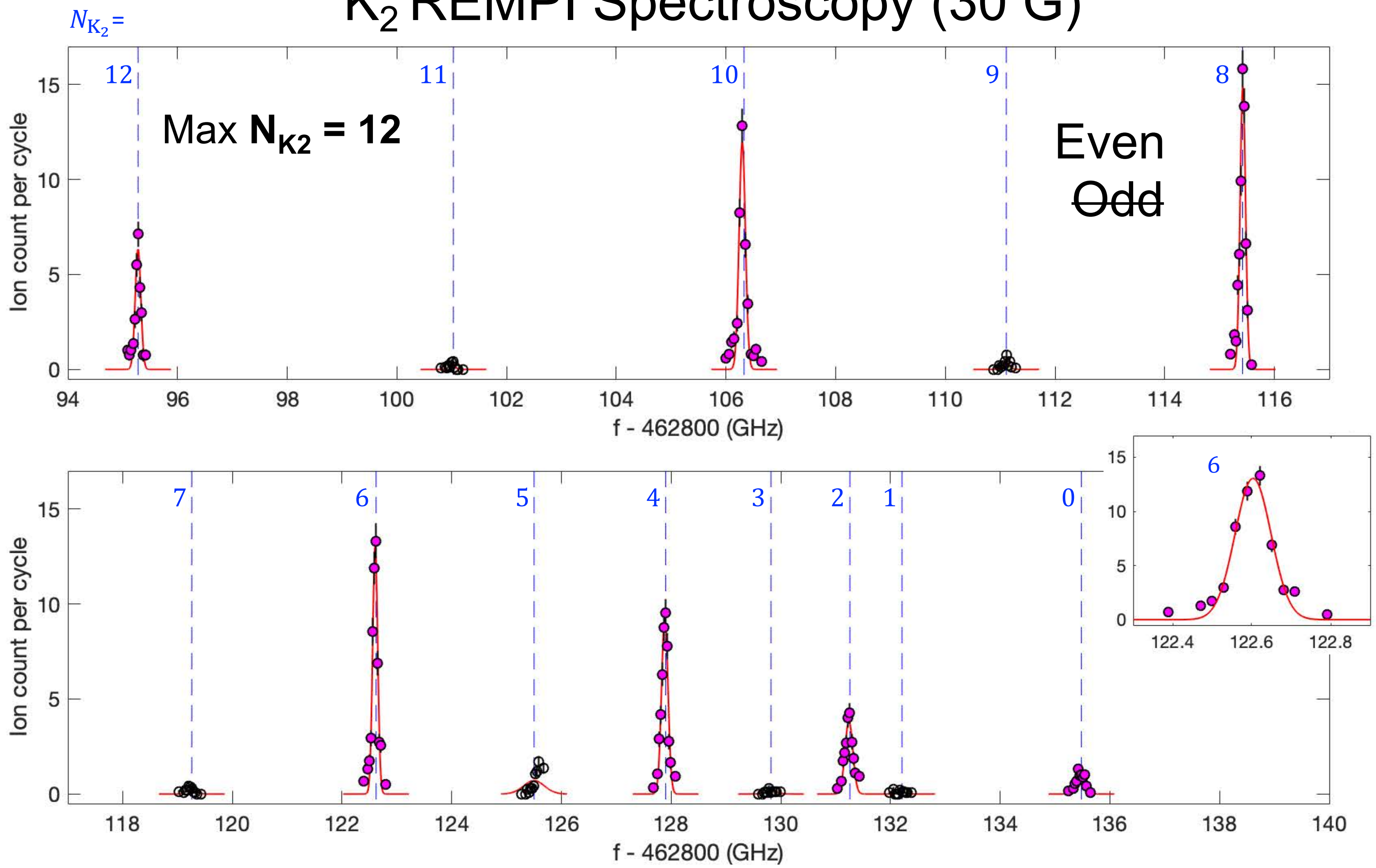
Can we control the quantum state of the reaction outcome?

Surprise #4: yes, via nuclear spins

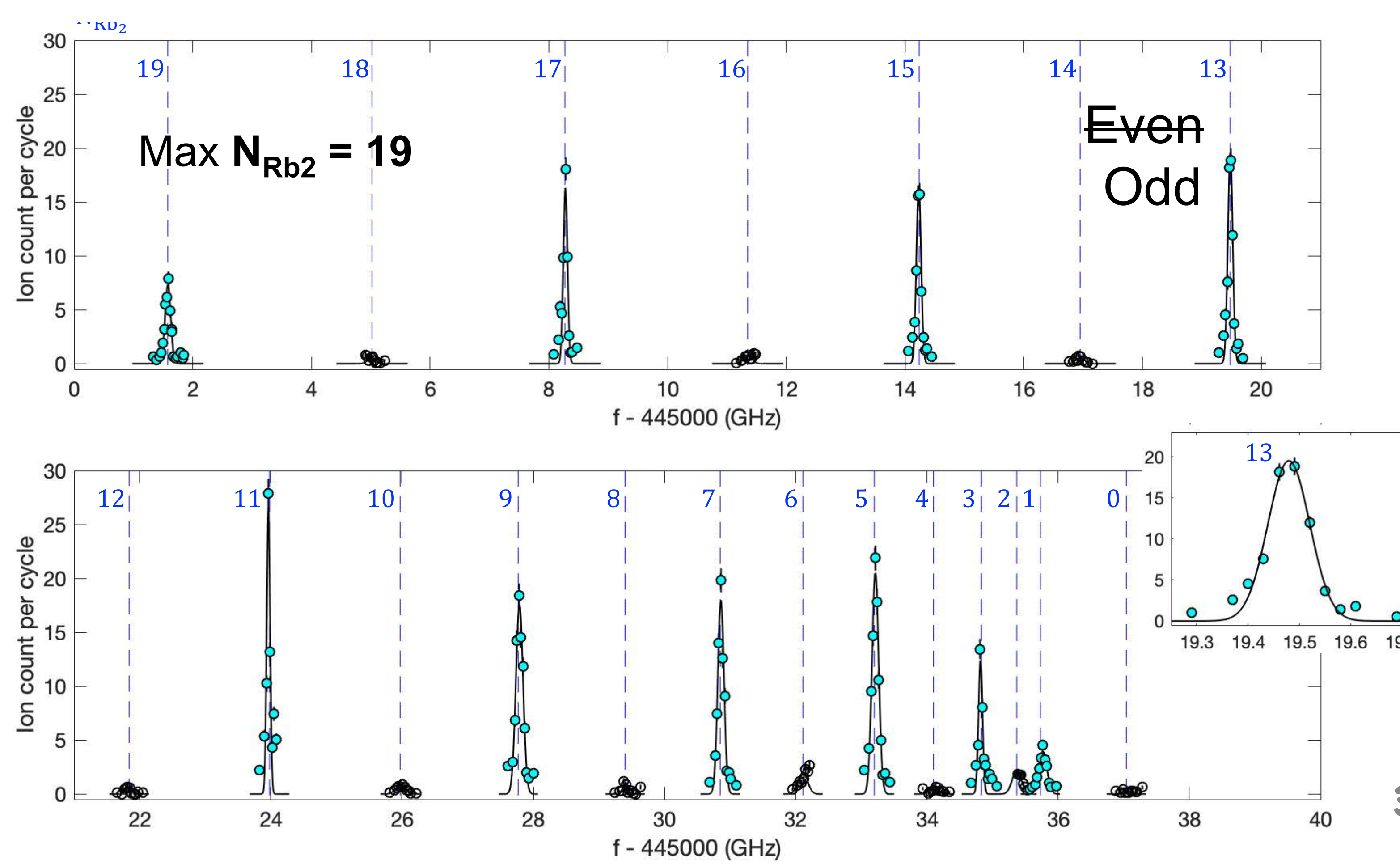


Hu, Liu, Nichols, Zhu, Quemener, Dulieu, Ni, arXiv:2005.10820 (2020)

K_2 REMPI Spectroscopy (30 G)



Rb_2 REMPI Spectroscopy (30 G)



Resolving Product Rotation states

Strong parity selection → nuclear spin conservation

Product state control via nuclear spin conservation

$i_\mathrm{K}\ \ i_\mathrm{Rb}\ m_i^\mathrm{K} m_i^\mathrm{Rb}$

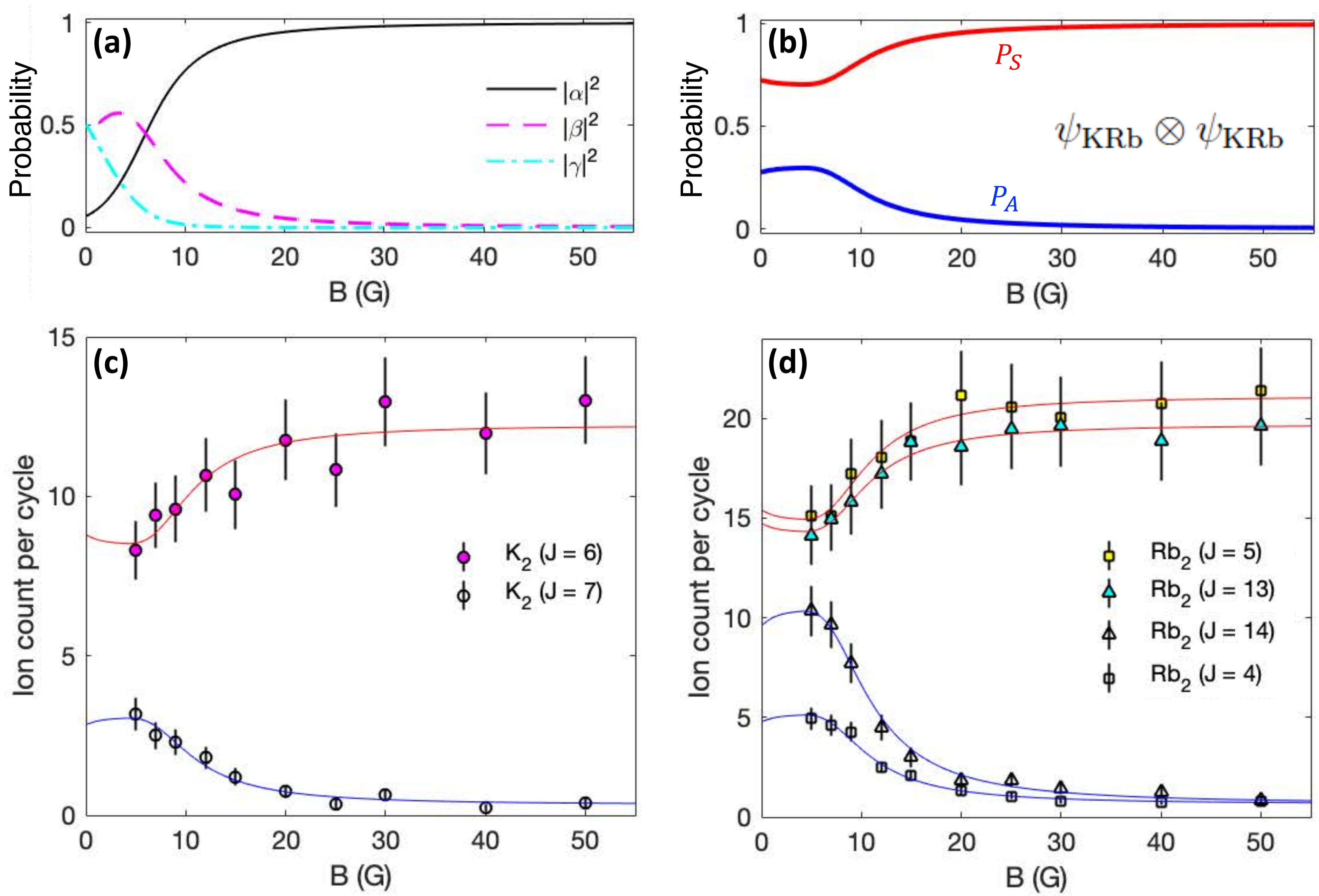
$$\psi_\mathrm{KRb} = \alpha\left|4, \frac{3}{2}, -4, \frac{1}{2}\right\rangle + \beta\left|4, \frac{3}{2}, -3, -\frac{1}{2}\right\rangle + \gamma\left|4, \frac{3}{2}, -2, -\frac{3}{2}\right\rangle$$

antisymmetric spin state

$$P_A = |\alpha\beta|^2 + |\alpha\gamma|^2 + |\beta\gamma|^2$$

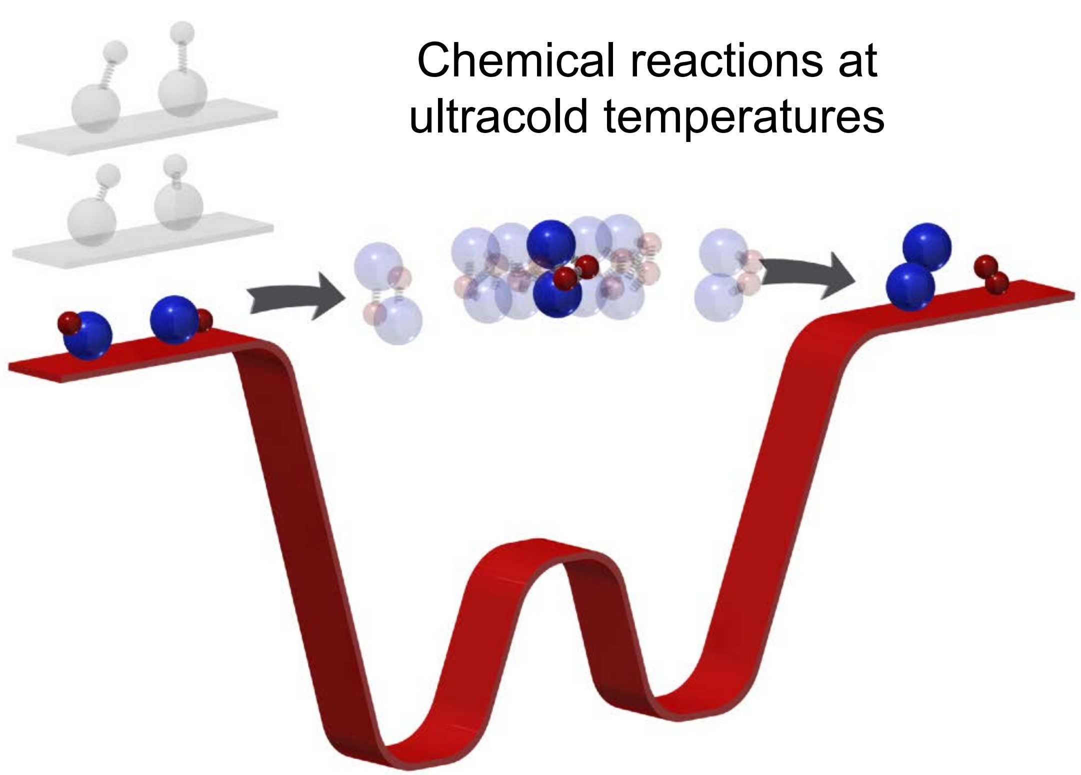
symmetric spin state

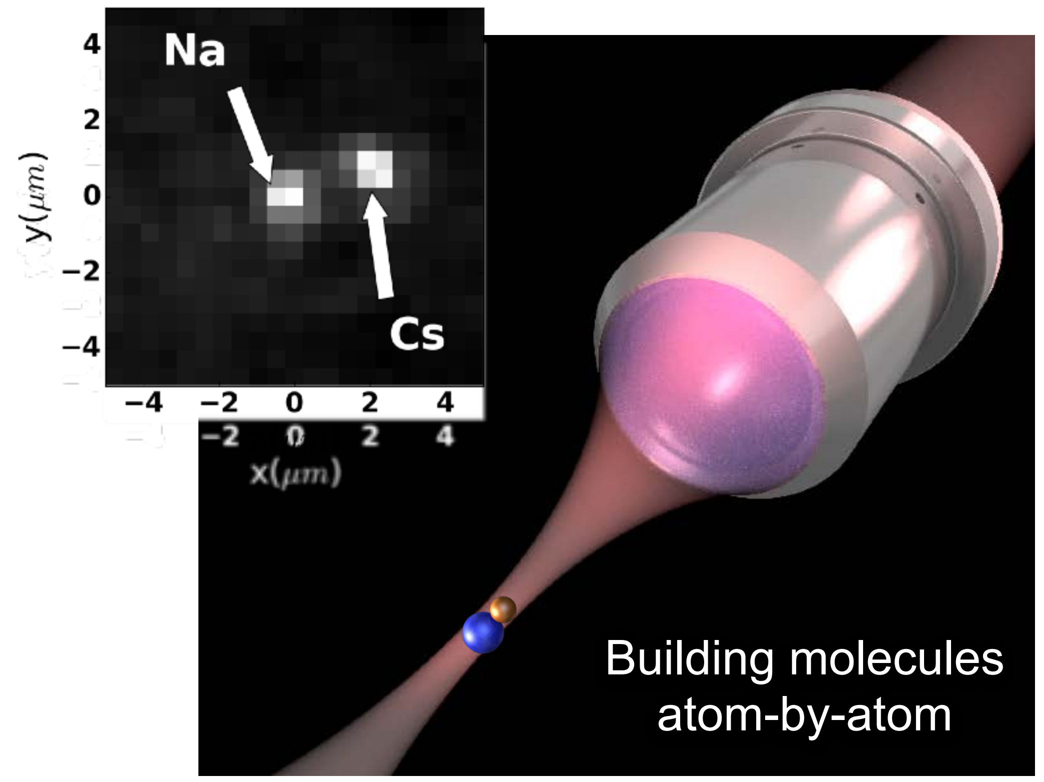
$$P_S = 1 - P_A.$$



Summary and Outlook

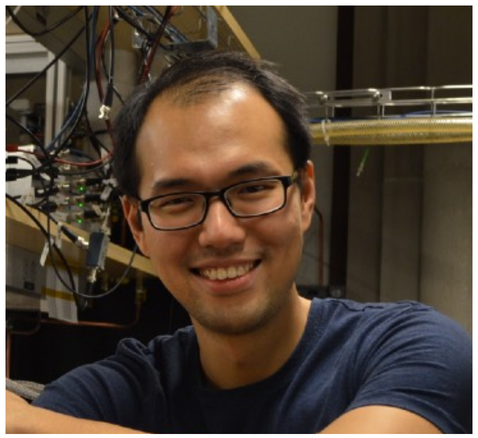
* We bring physics and chemistry tools together to make molecules and to study ultracold reactions
* Ultralow temperature prolongs the transient nature of intermediate complex and allows for a new handle to steer reaction away from its ground-state pathway
* Despite the existence of a long-lived complex, we demonstrate quantum state control of reaction product by taking advantage of nuclear spin conservation in ultracold reactions
* Direct observation offers many opportunities to gain microscopic picture of molecules transforming from one species to another and for checking quantum entanglement in reactions





Thank you

Acknowledgments



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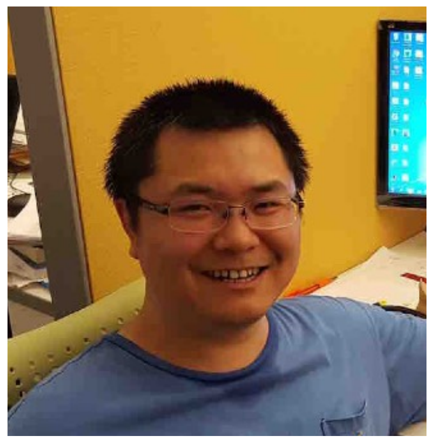

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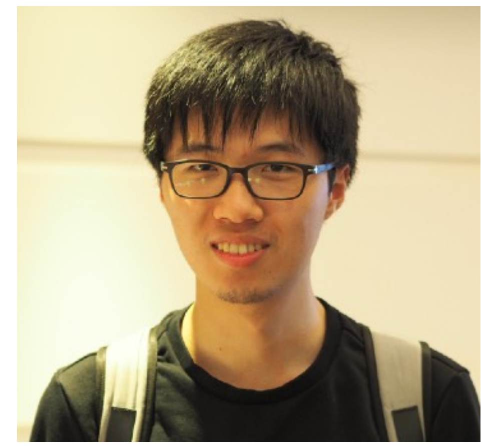

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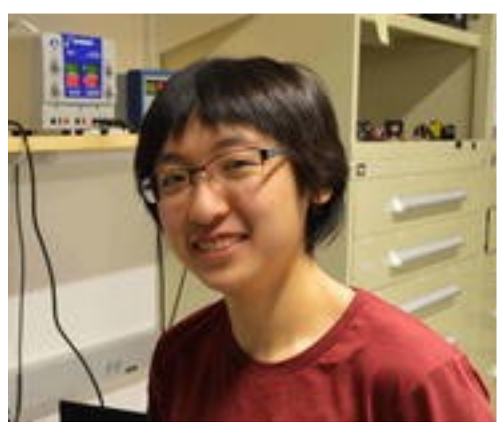

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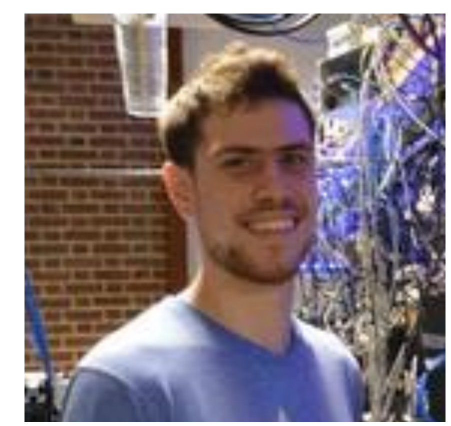

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Funding: DOE YIP, NSF, Packard fellowship, Dreyfus award, AFOSR
Past: Beckman foundation, ARO, Sloan fellowship

Past members:
Dr. Nick Hutzler => Caltech
Lee Liu, PhD => JILA
Dr. David Grimes => MIT
Dr. Yen-Wei Lin
Dr. Jon Hood => Purdue