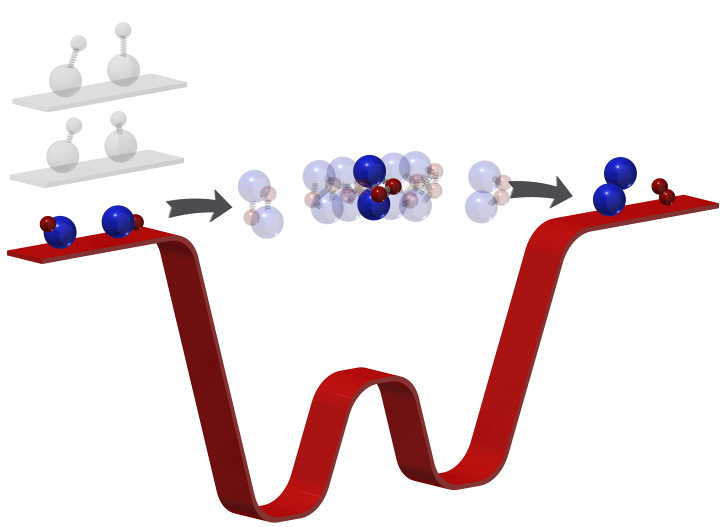
Precision test of statistical dynamics in molecular collisions and reactions

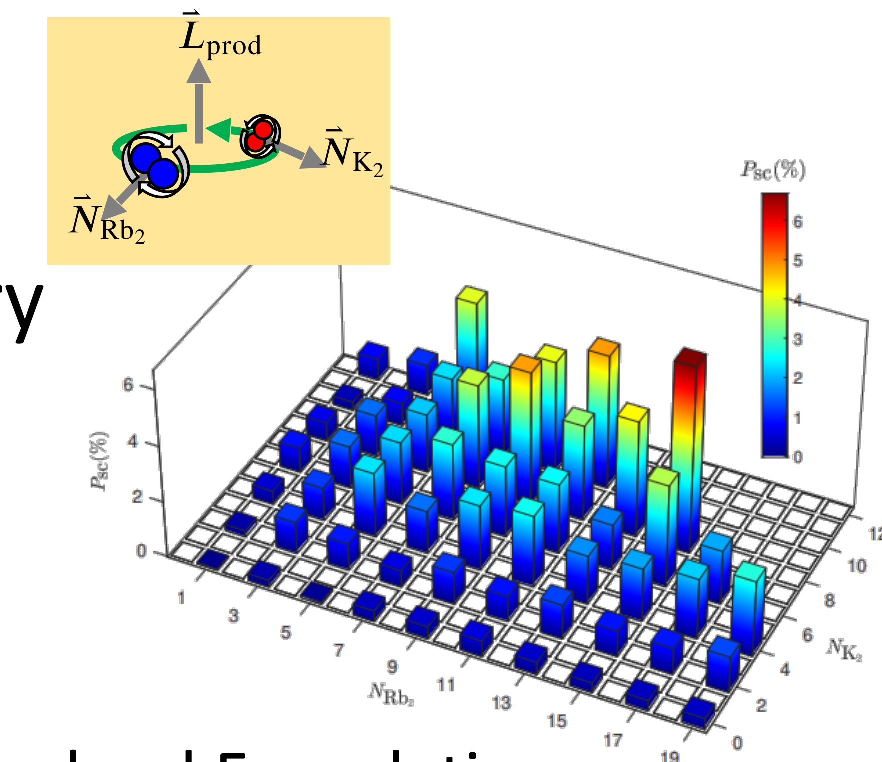


Kang-Kuen Ni

Department of Chemistry

and Chemical Biology

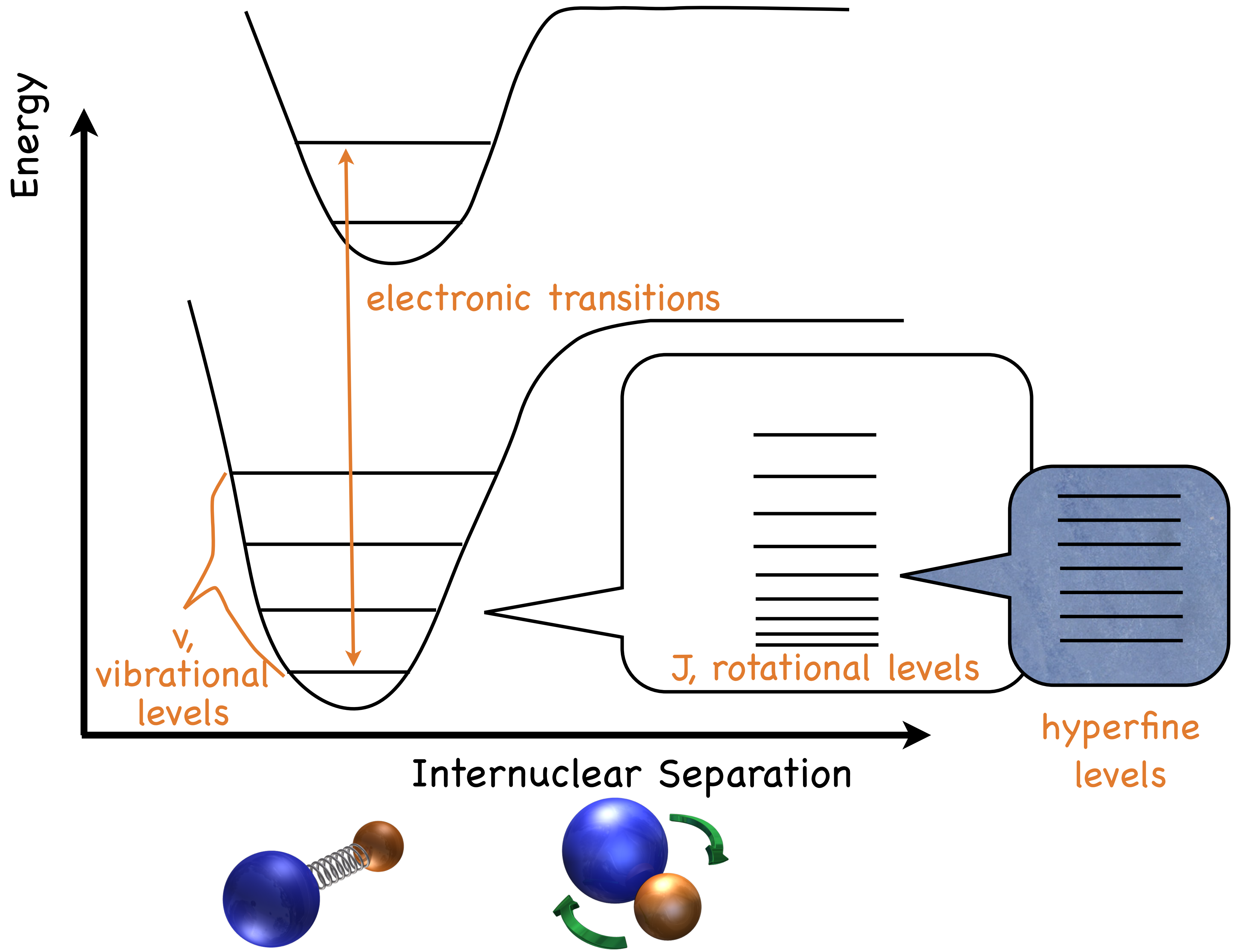
Harvard University



Funding: DOE-YIP, NSF-CUA, David and Lucile Packard Foundation

KITP Few-body Physics Conference, May 23 -26, 2022

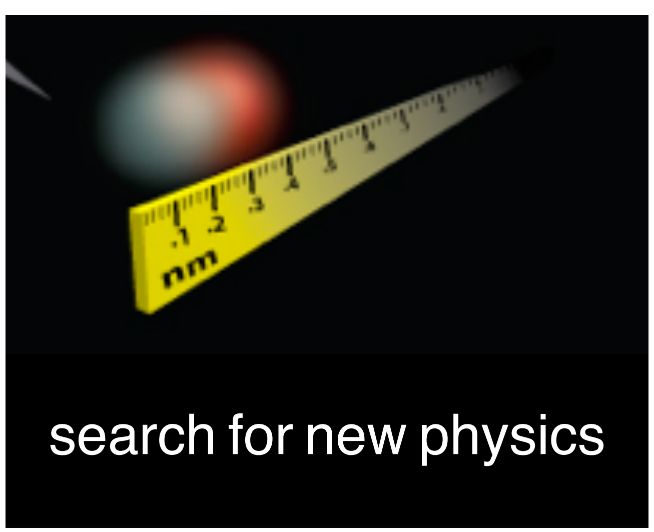
Molecular Quantum Degrees of Freedom

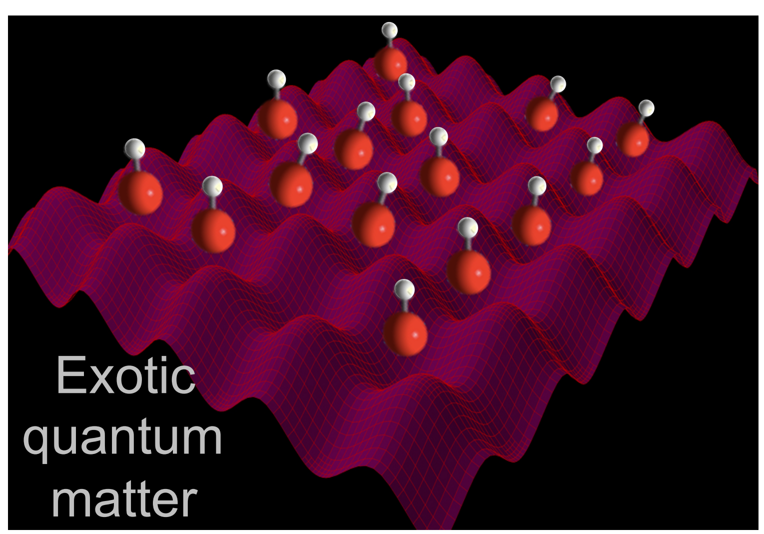


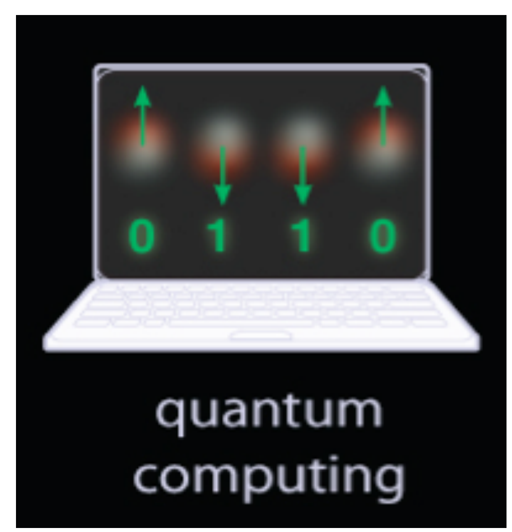
Quantum Control of Molecules

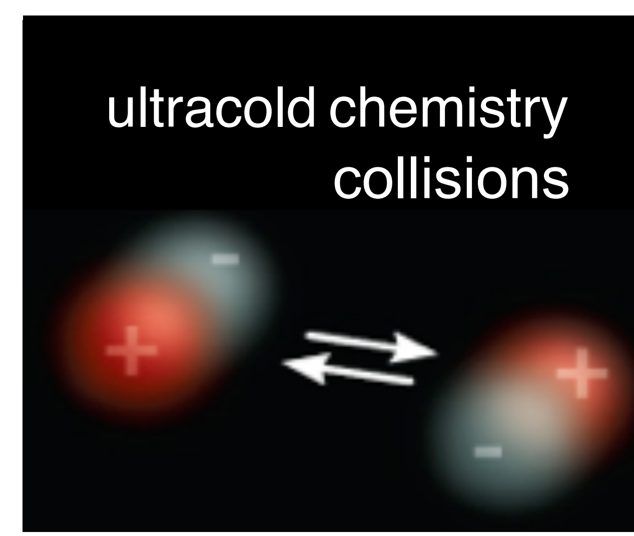
- cooling and trapping
- long interaction and probe time
- building complex system from the bottom up

Why Ultracold Molecules?









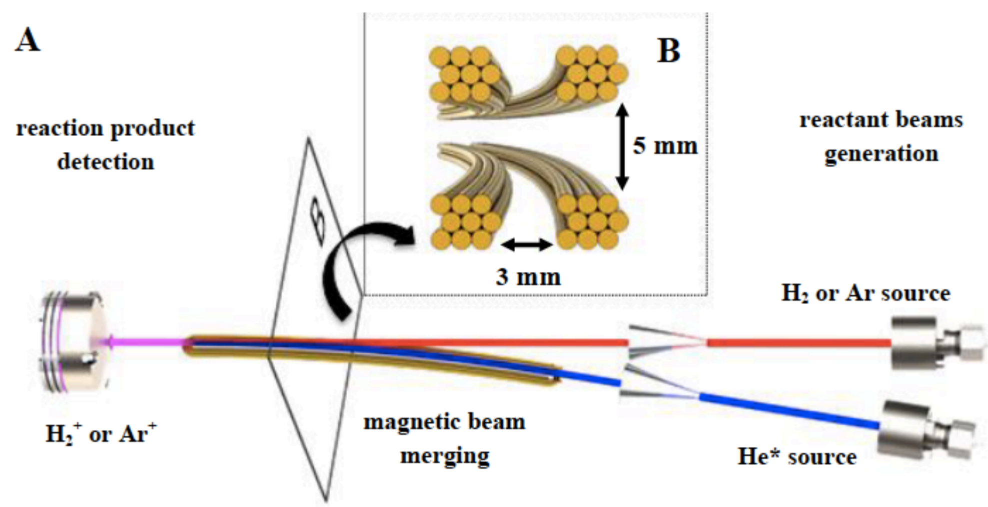
single-body physics

two- to many-body physics

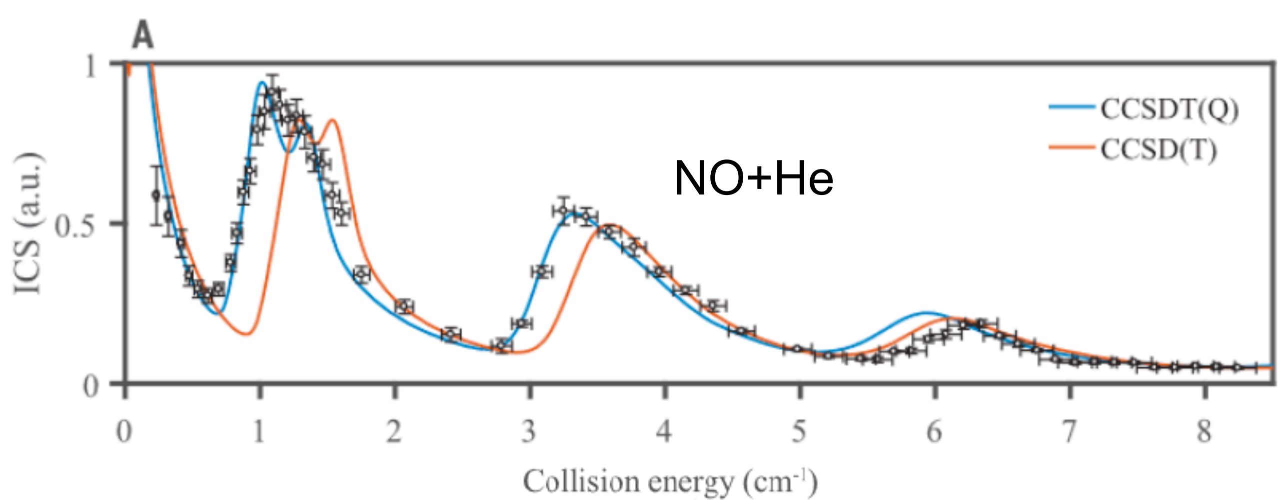
two- to few-body physics

Chemistry and Collisions with Cold Molecules

probing potential energy surfaces beyond “gold-standard” quantum chemistry calculation



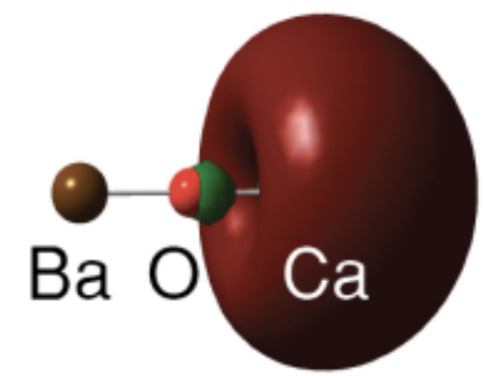
Narevicius (Wiezmann)
Nature Phys. 13, 35 (2017)



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

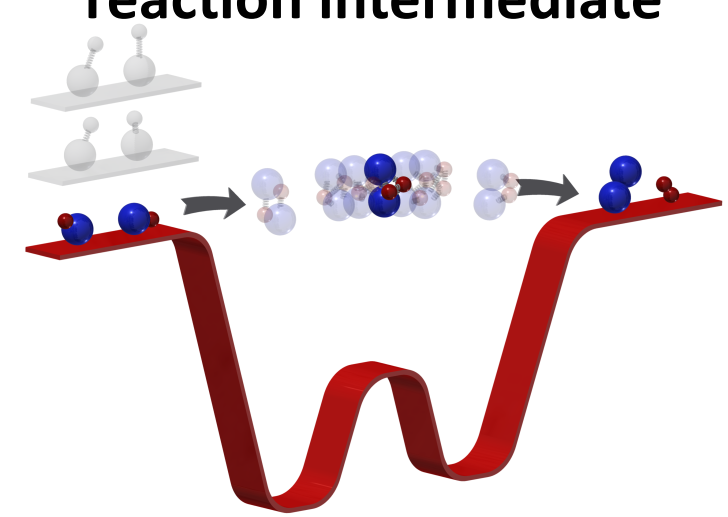
Other work: Ye, Denschlag, Zelevinsky, Willitsch, Zare, …

synthesizing new chemical species



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

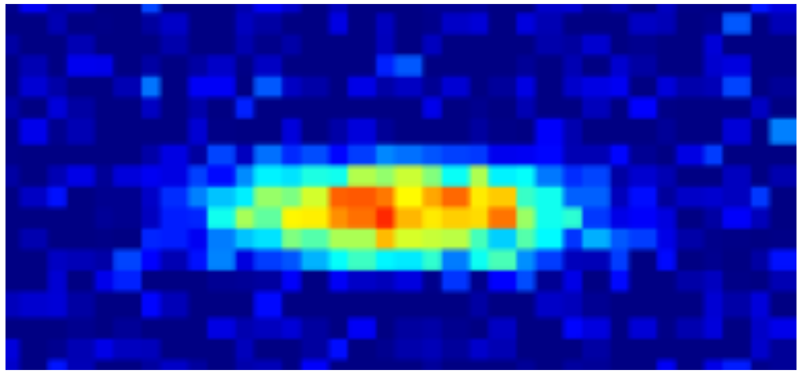
Direct detection of reaction intermediate



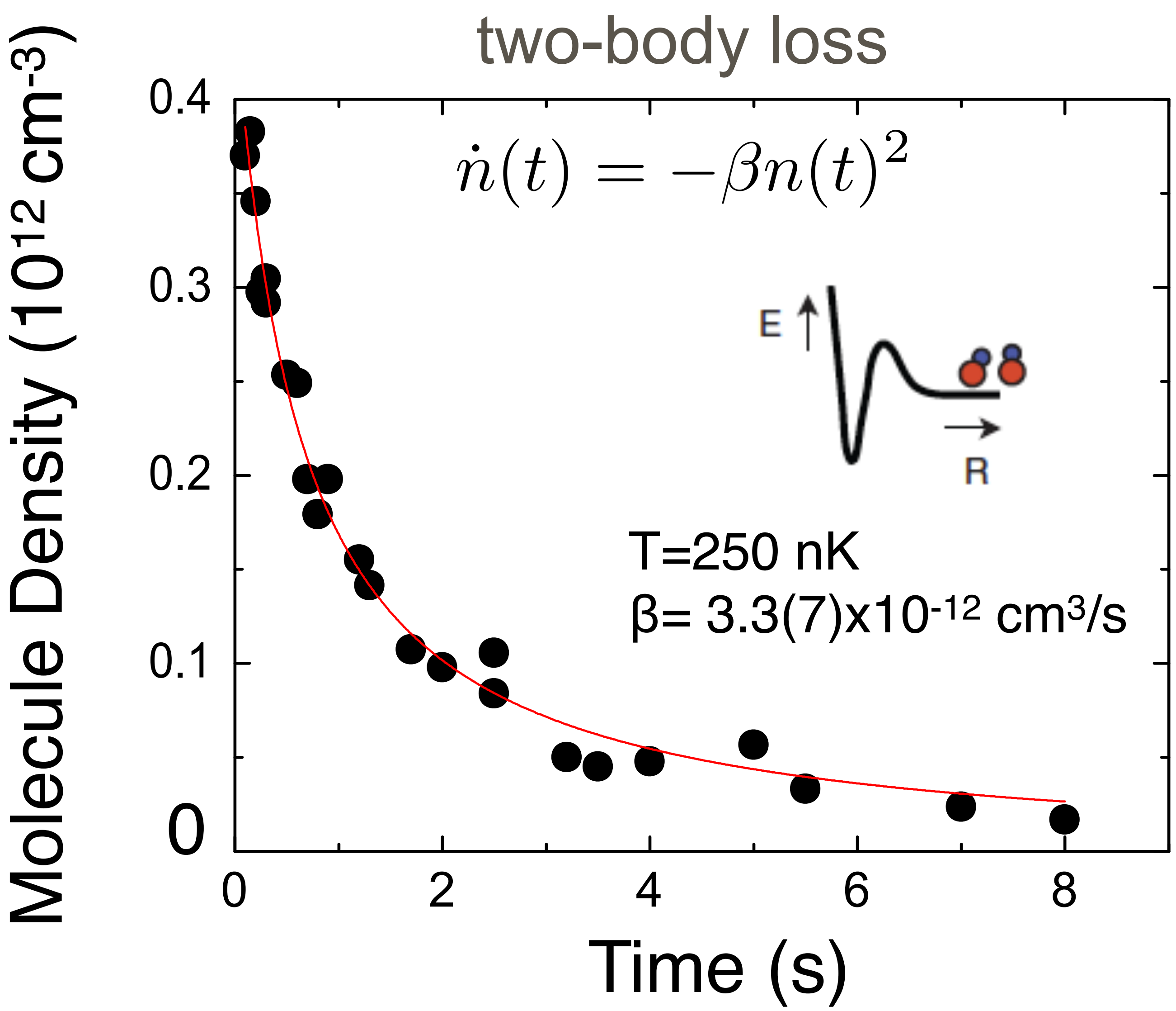
Hu, Liu, et al. (Harvard),
Science **366**, 1111 (2019)

JILA KRb Experiment (2008-2010)

A trapped *gas* of molecules in a single and lowest hyperfine, rotational, vibrational, electronic ground state!

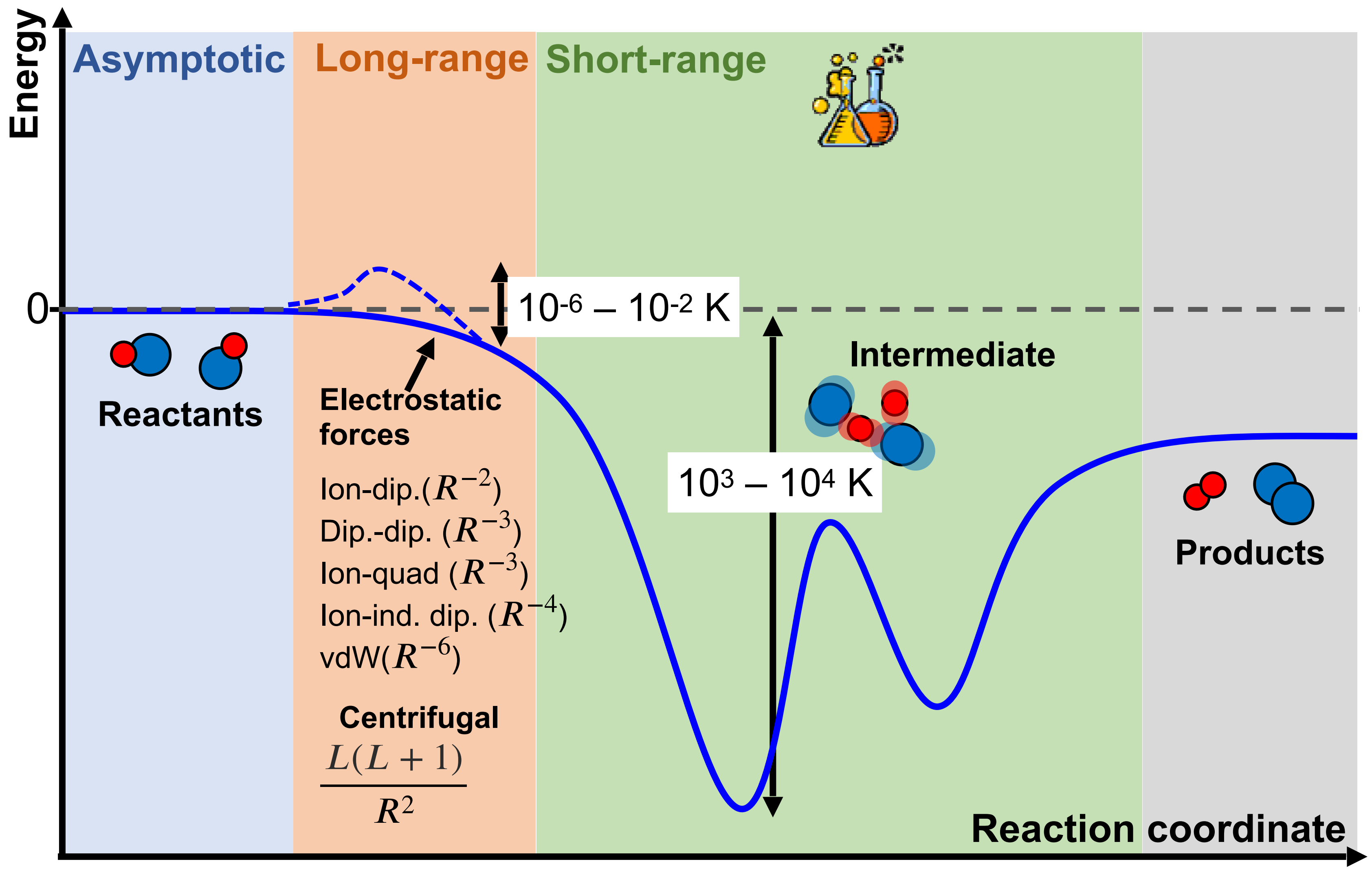


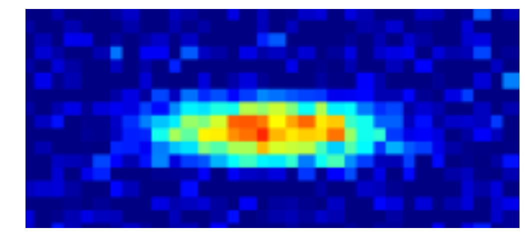
peak density = $10^{12}/cm^3$
temperature = 200 nK

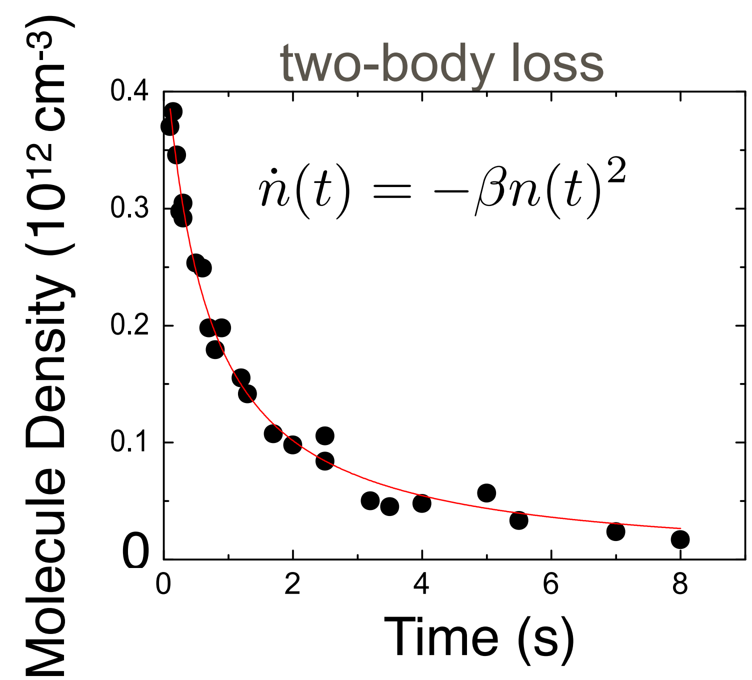


Ni, Ospelkaus et al., Science **322**, 231 (2008)
Wang *et al.*, PRA **81**, 061404 (2010)
Ospelkaus, Ni et al., Science **327**, 853 (2010)
Innsbruck, Durham, MIT, Hong Kong, USTC, MPQ, Hannover, …

Ultracold Chemical Reaction?





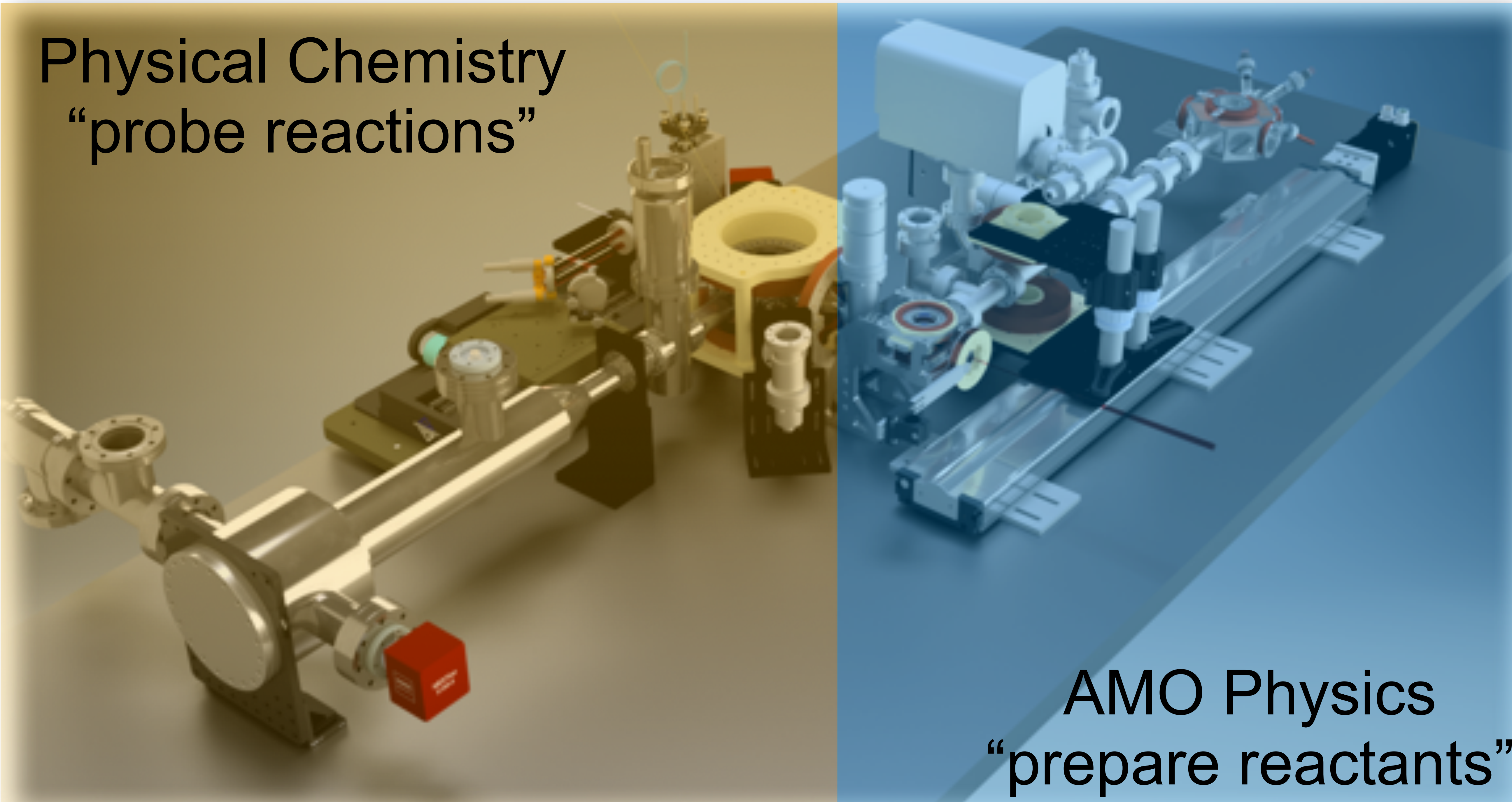


Direct detection needed

Idziaszek and Julienne, PRL 104, 113202 (2010)
Quéméner and Bohn, PRA 81 022702 (2010)
Ospelkaus, Ni,… Jin, Ye, Science, 327, 853 (2010)
Ni, Ospelkaus, … Ye, Jin, Nature 464, 1324 (2010)

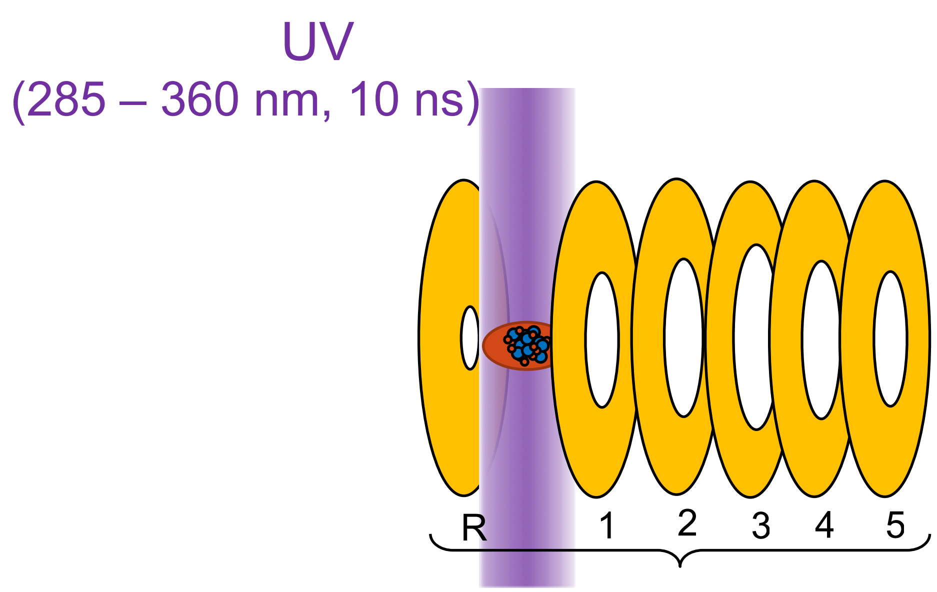
Guo et al., PRX 8, 041044 (2018)
Ye et al., Sci. Adv. (2018)
Gregory et al., Nat. Commun. (2019)
Nesbitt, Chem. Rev. 122, 9, 5062 (2012)

Combining Chemistry and Physics tools



Phys. Chem. Chem. Phys. 22, 4861-4874 (2020)

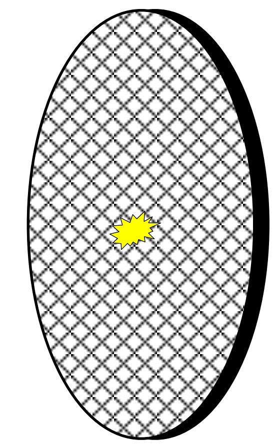
Probing the reaction via ion spectrometry



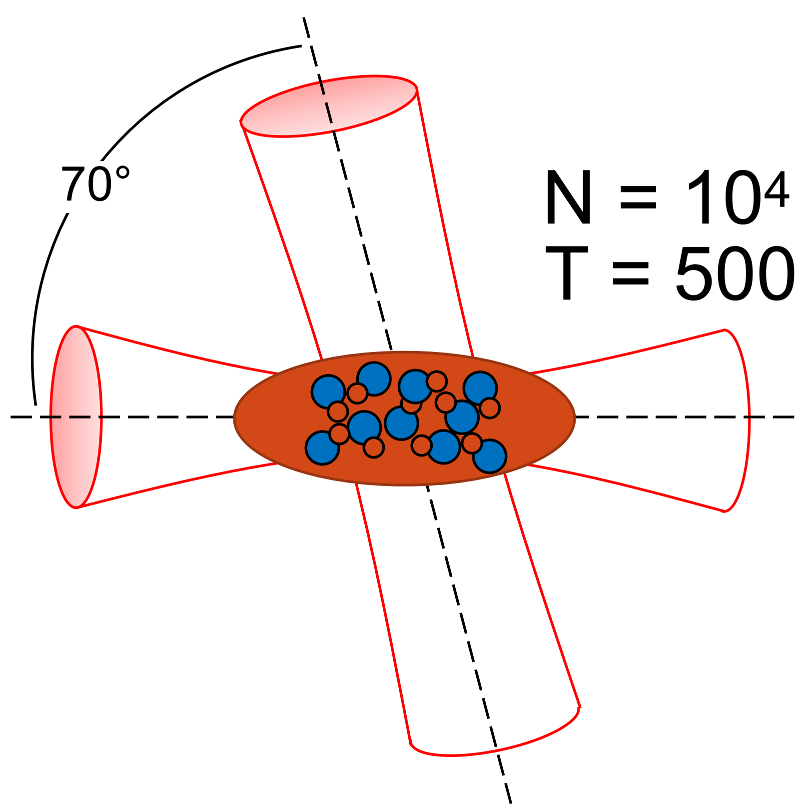
Electrostatic lens

Time-of-flight
Mass/species

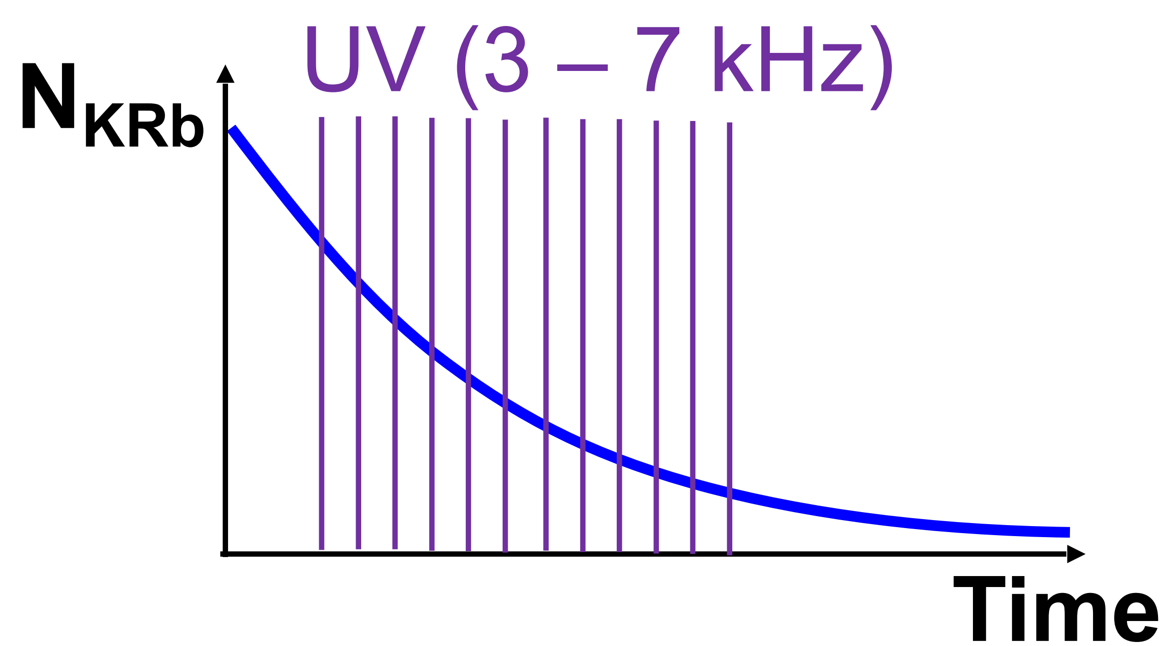
Spatial distribution
Kinetic energy



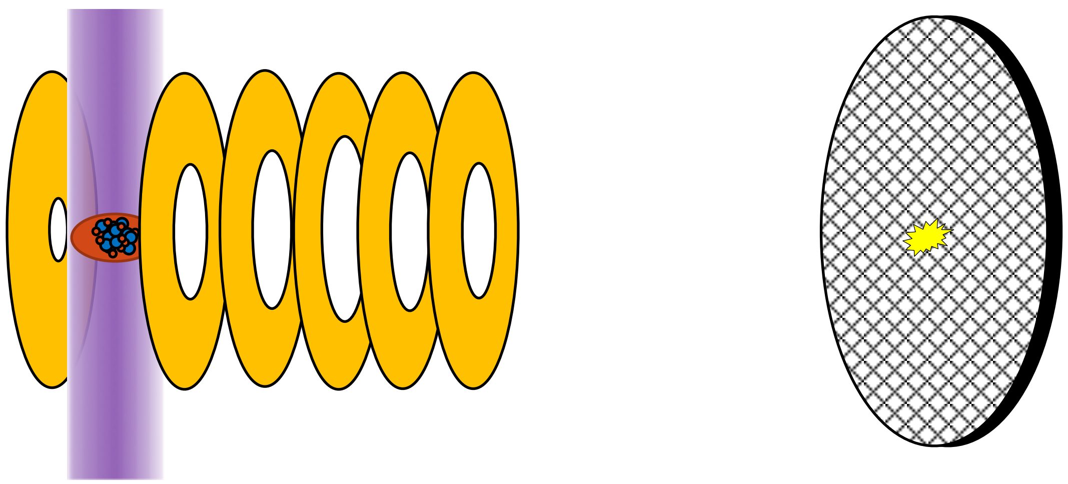
MCP
detector

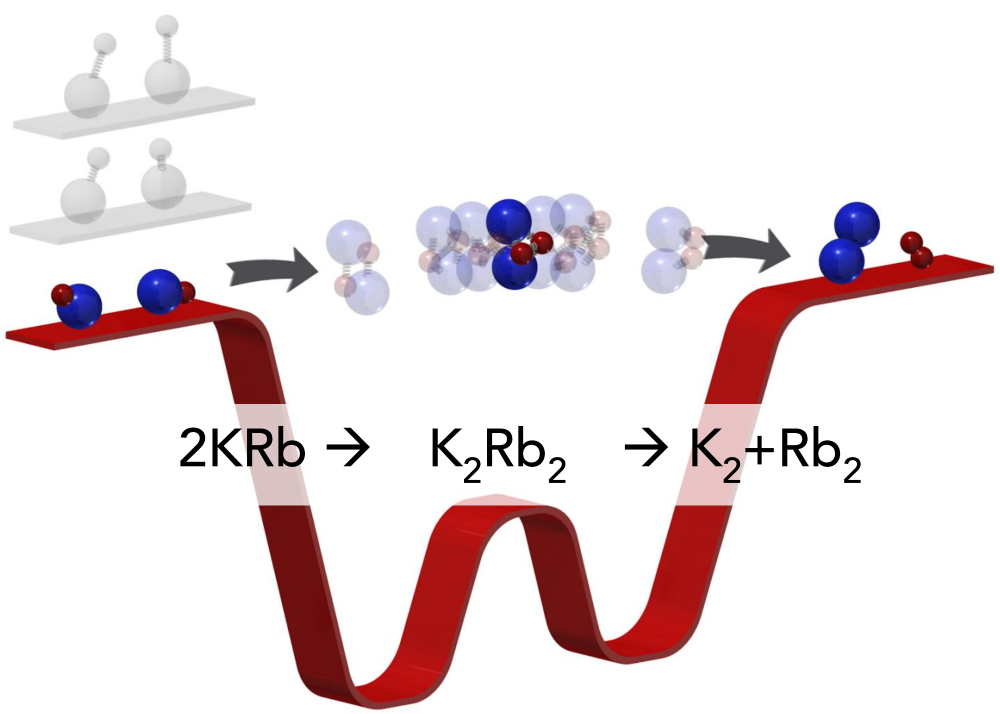


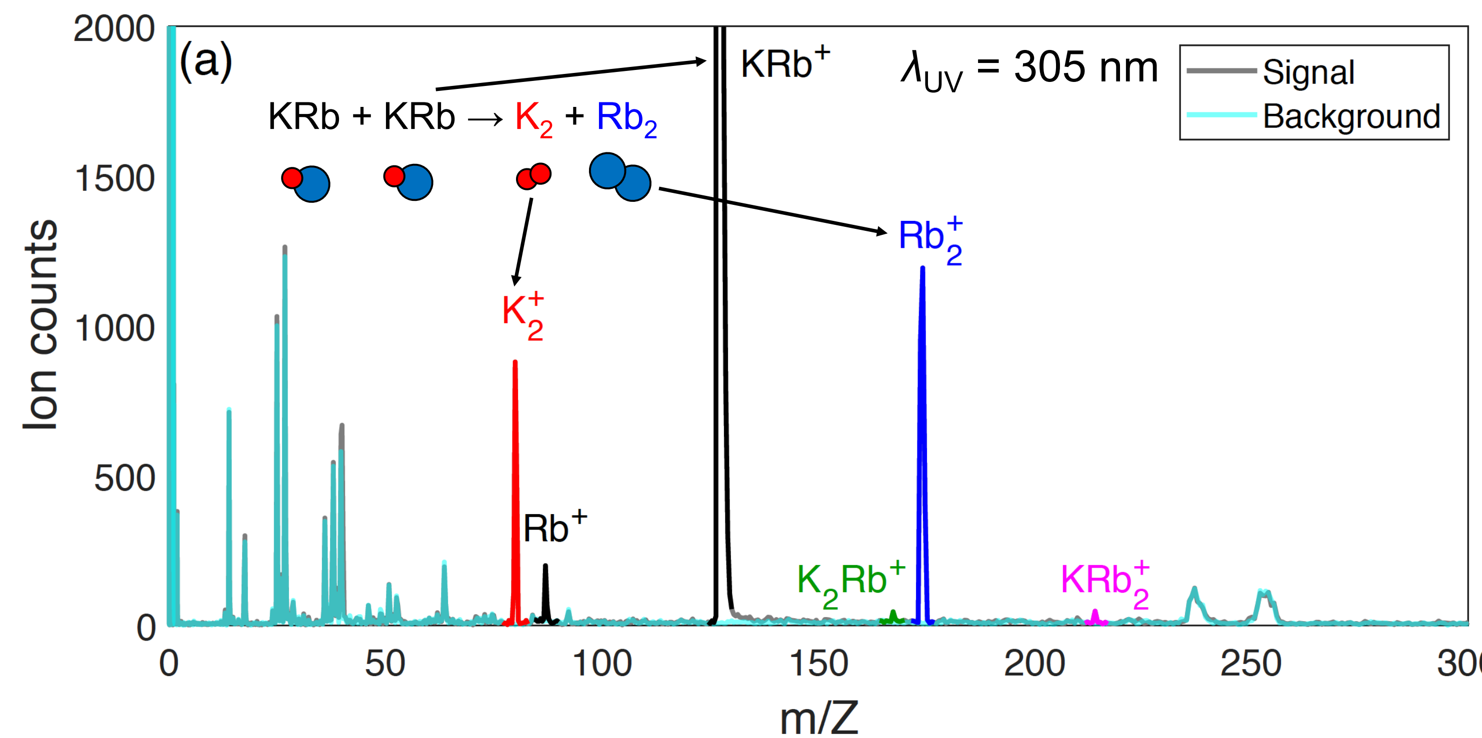
$N = 10^4$
$T = 500$ nK



Product Detection via mass spectrometry

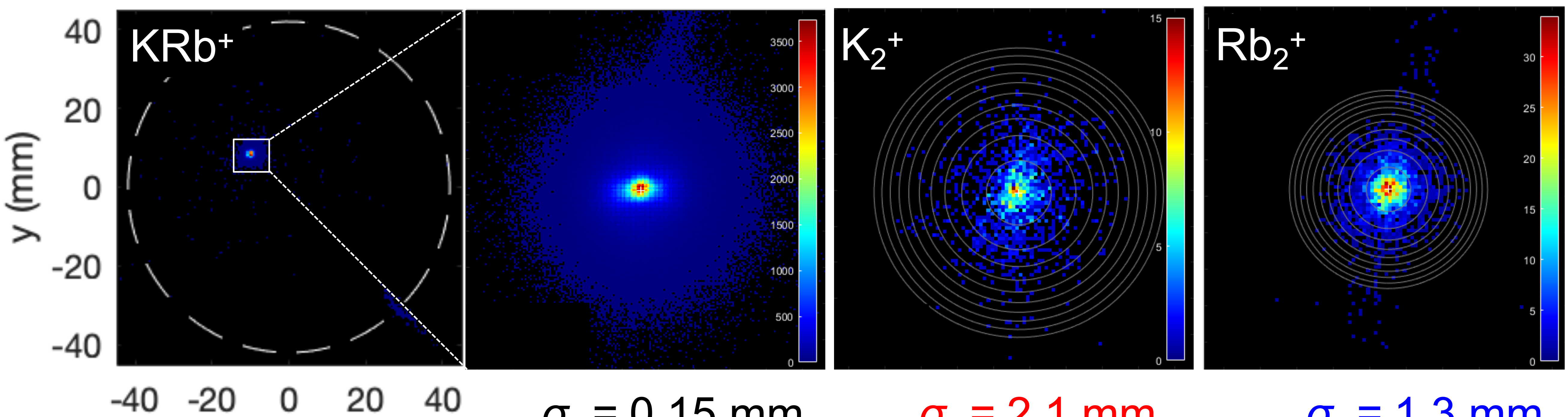






Science **366**, 1111 (2019)

Verifying the product signal: *KE* distribution

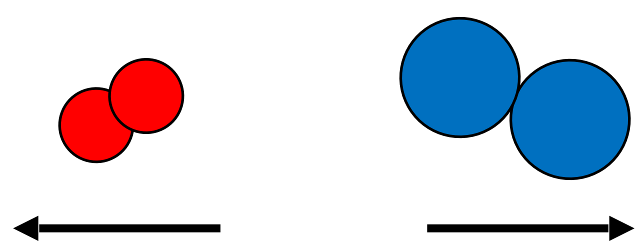


σ_r = 0.15 mm
KE = 0.15 cm^{-1}

σ_r = 2.1 mm
KE = 1.9 cm^{-1}

σ_r = 1.3 mm
KE = 0.87 cm^{-1}

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

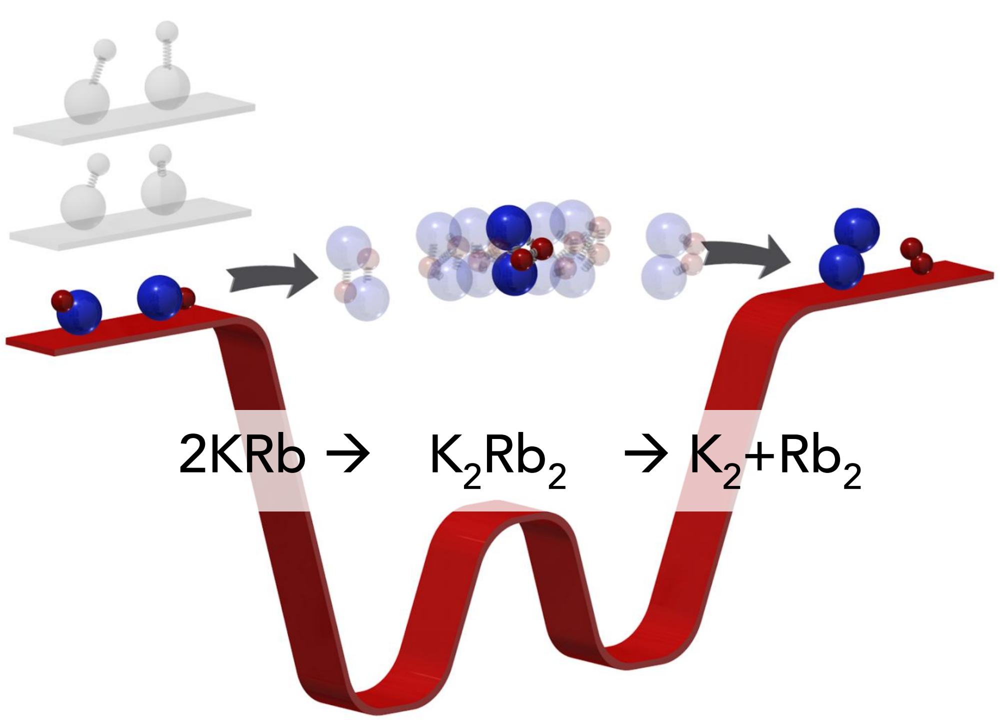


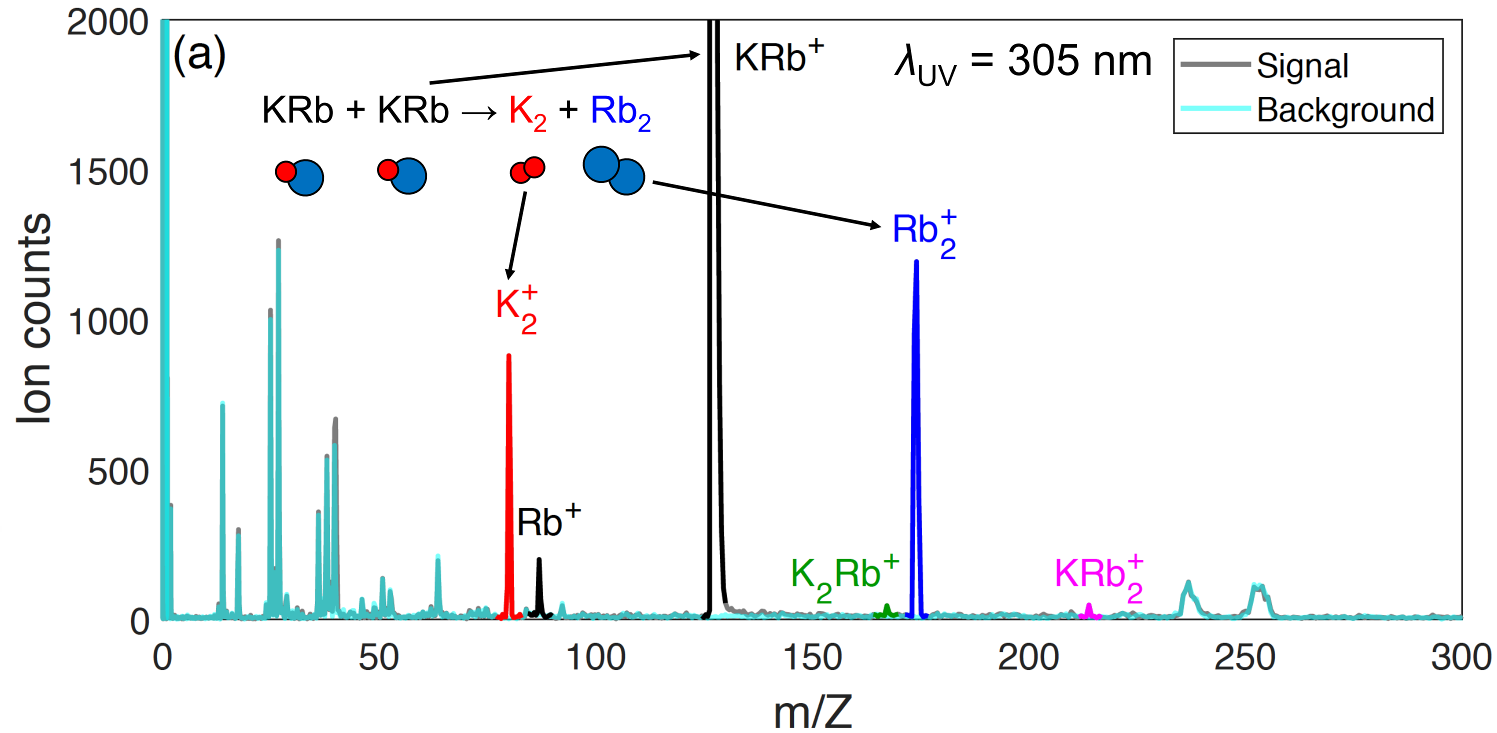
$$P_{K2} = P_{Rb2}$$

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

Surprise #1: ultracold chemical reaction!

Surprise #2: Reaction Complex Detection

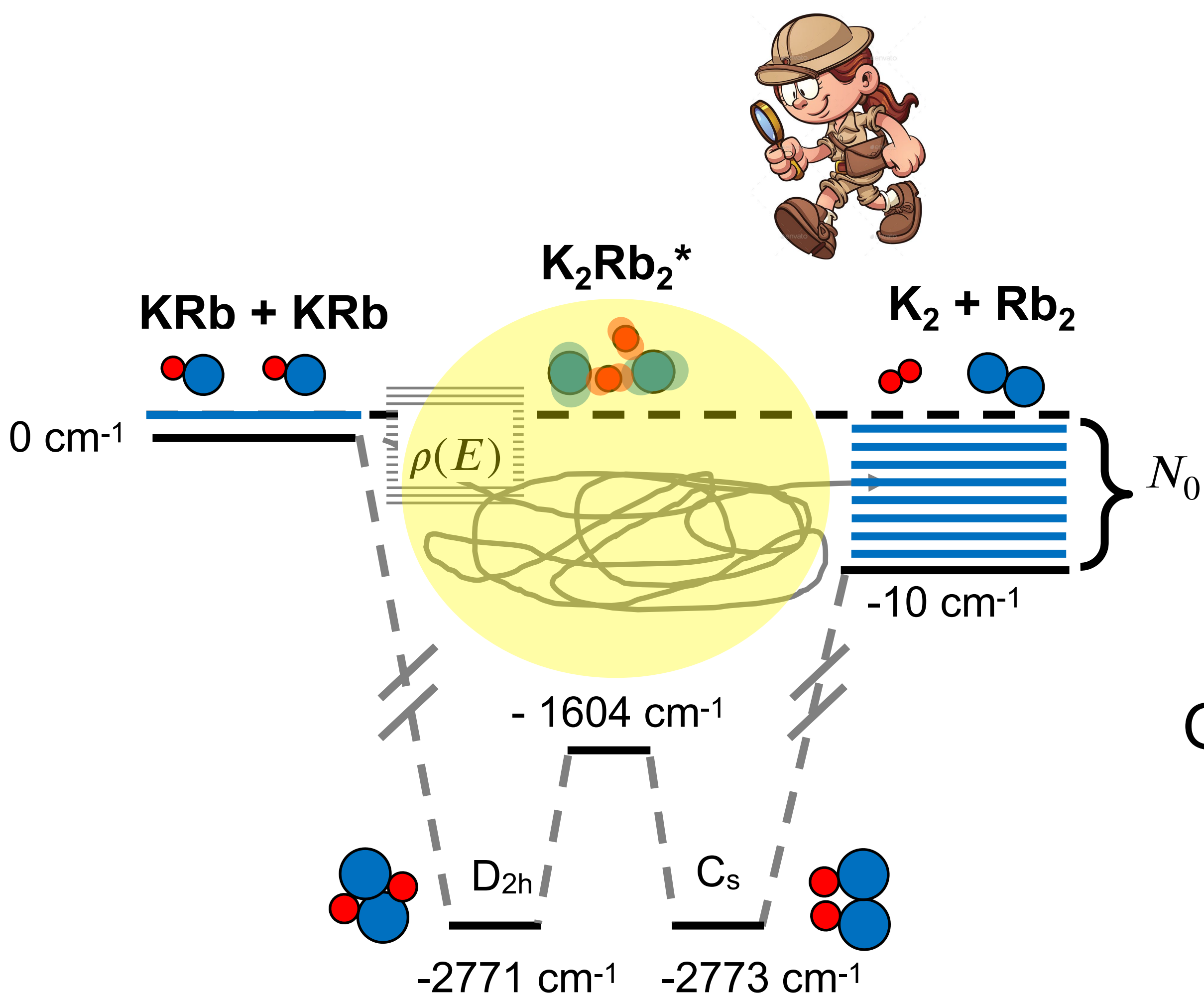




Science **366**, 1111 (2019)

The long-lived intermediate complex

>> ps



Rice-Ramsperger-Kassel-Marcus
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): $\tau_c \sim 0.1\ \mu s$

experiment estimated lifetime

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

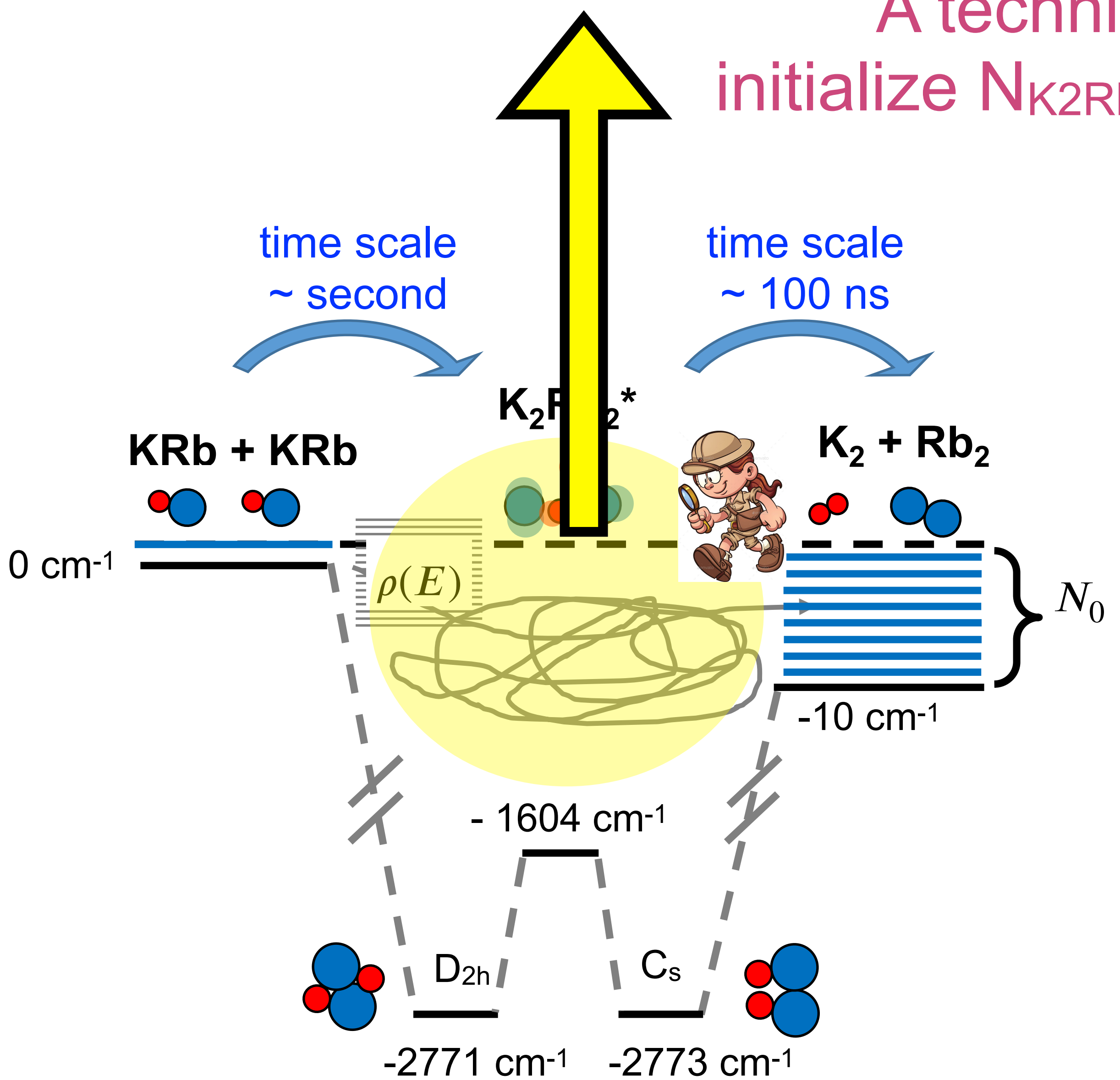
$\sigma(K_2Rb_2^* \rightarrow K_2Rb_2^+) \sim 10^{-17} - 10^{-18}\ cm^2$

Reaction coordinate PES,
Byrd et al., PRA **82**, 010502 (2010)

The long-lived intermediate complex

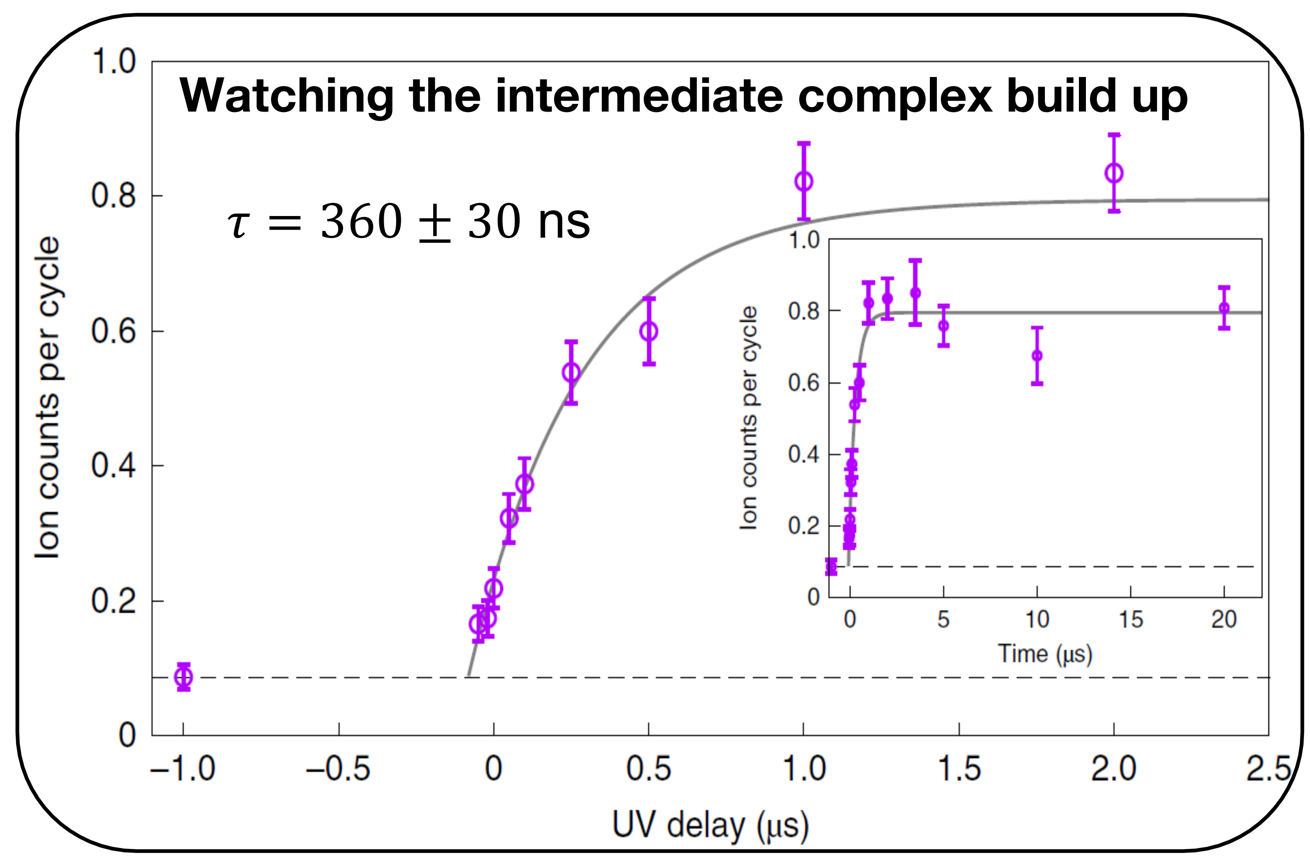
A technical challenge:
initialize N_{K2Rb2} at t=0 to <100 ns

>> ps

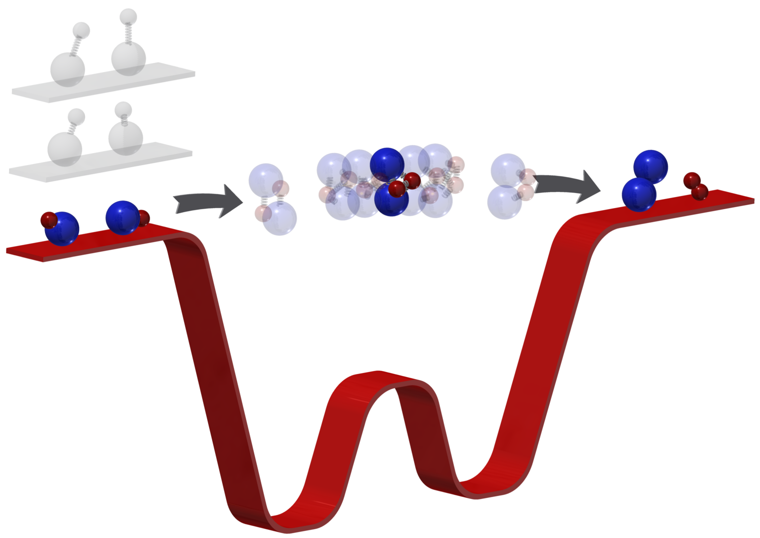


RRKM (from Tijs Karman)

$$\tau_c^{\mathrm{RRKM}} = \mathbf{170(60)}\ \mathrm{ns}$$



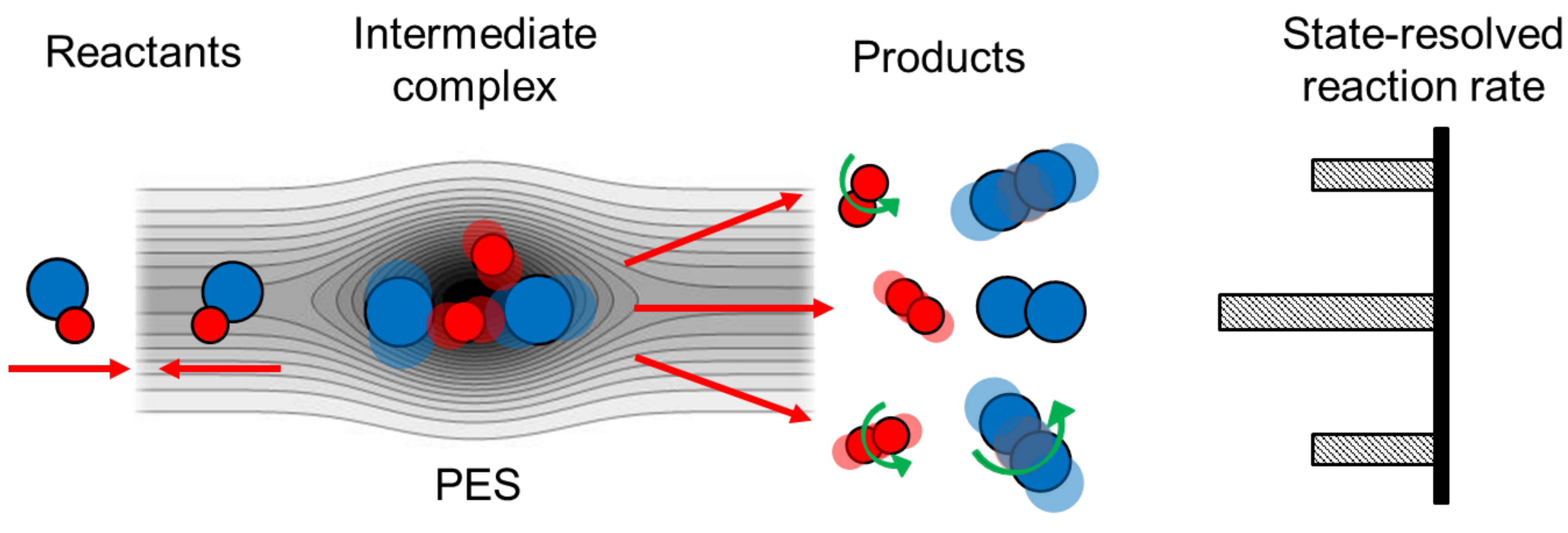
Liu*, Hu* et al., Nature Physics **16**, 1132 (2020)
Related work for RbCs + RbCs (Durham), PRL 124, 163402 (2020)



Outline

* Total quantum control of molecules from association of atoms
* Surprise 1 - chemical reactions at ultralow temperatures
* Surprise 2 - reactions play out in “slow motion”
    * Surprise 3 - steering reactions with light
* Complete characterization of reactive process - mapping quantum states of correlated reaction product pairs
    * Surprise 4 - control reaction product parity state
* More surprises - long-lived atom-molecule complexes

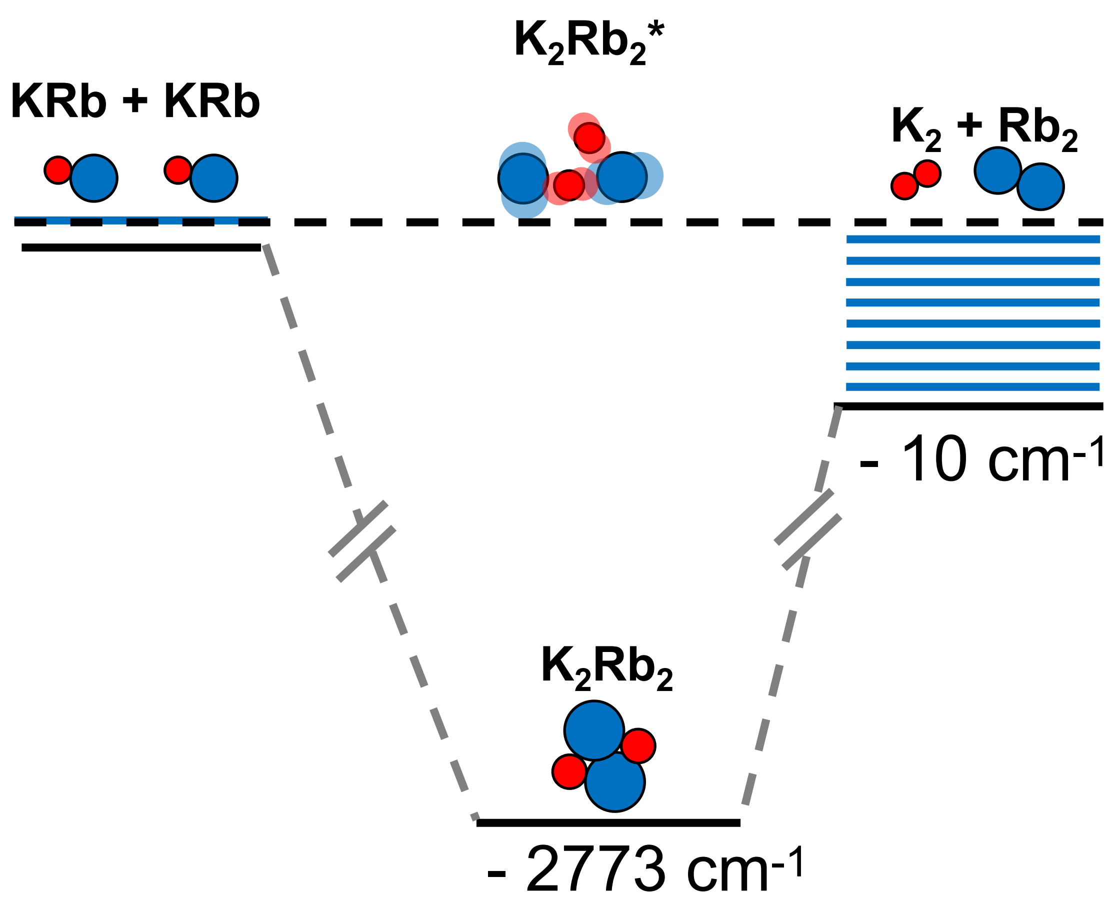
Chemical Reaction: a scattering problem

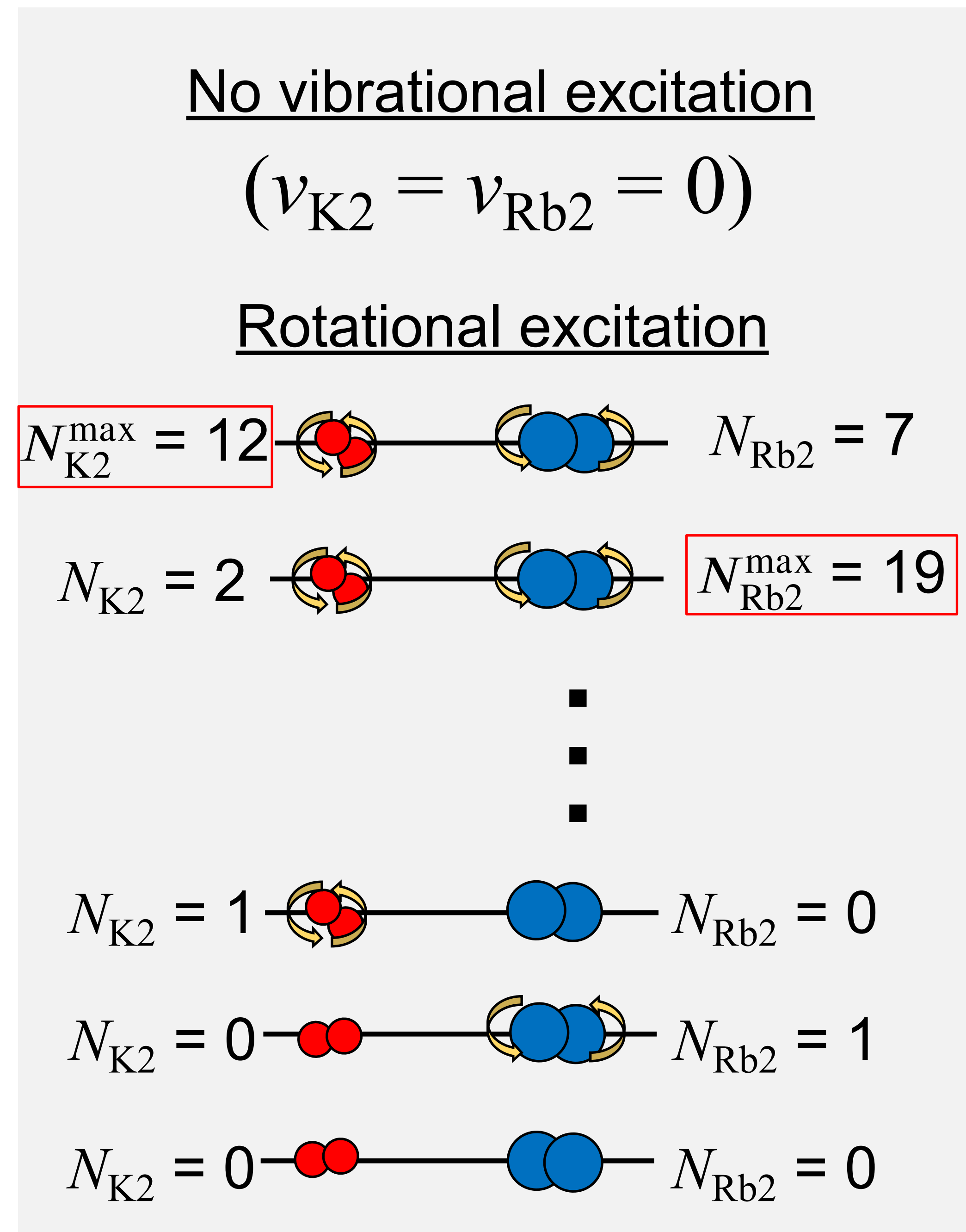


State-of-the-art theory cannot exactly predict the quantum state distribution for reactions involving 4 heavy atoms

but the observation of a long-lived complex suggests a statistical product state distribution

Possible quantum states of the products

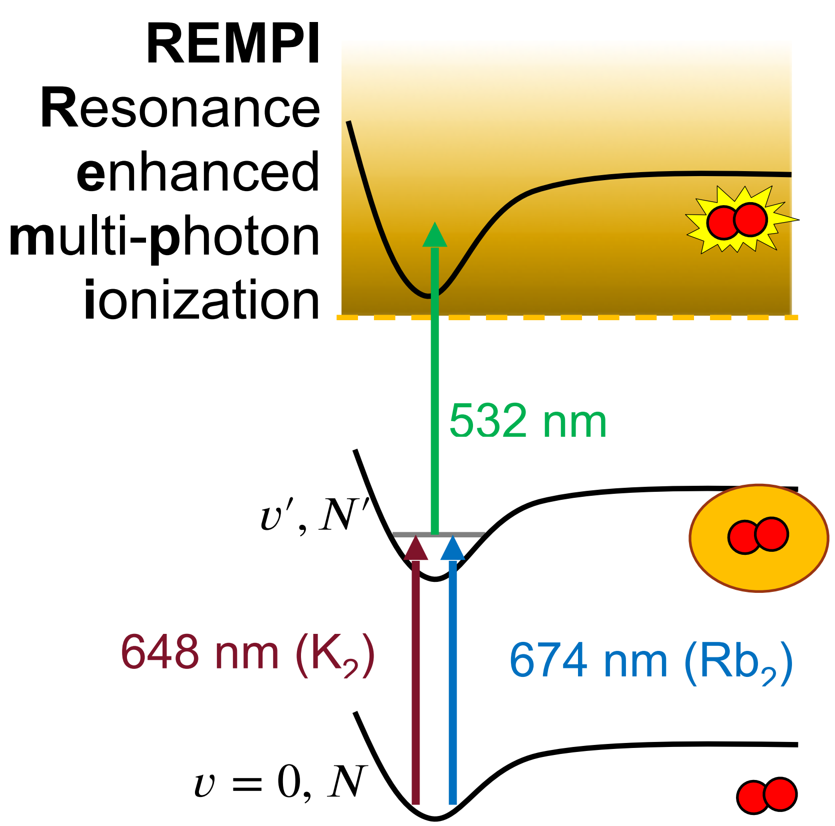


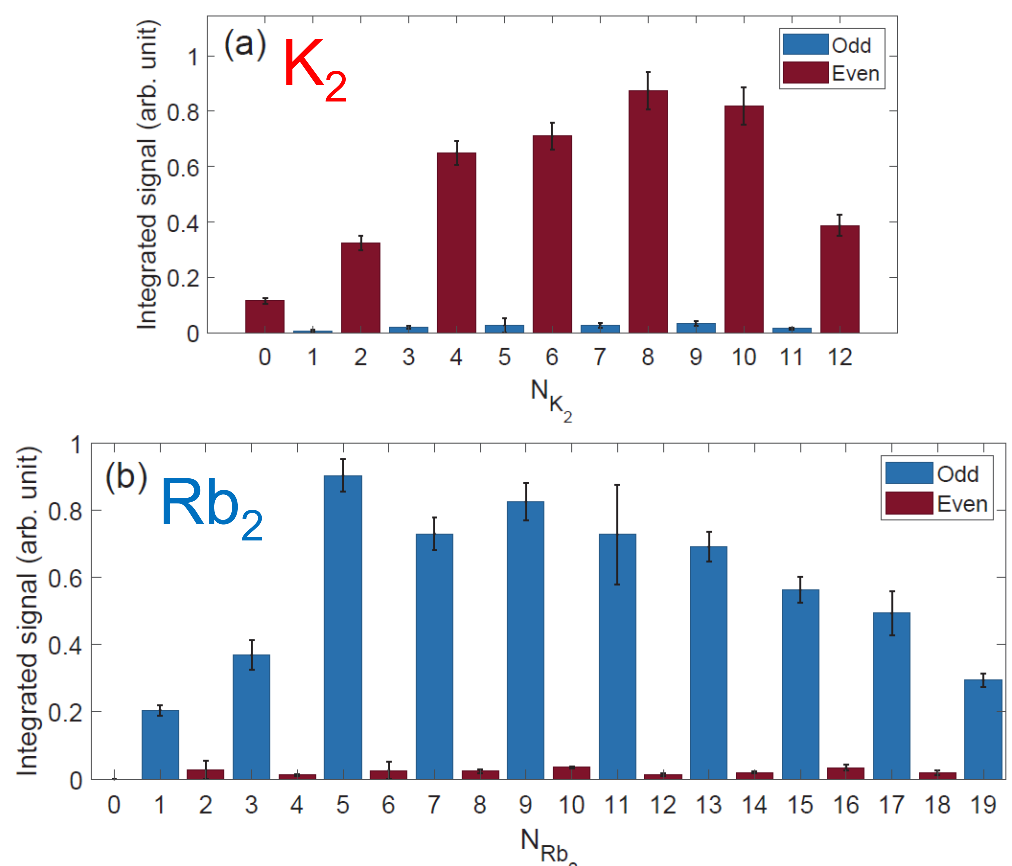


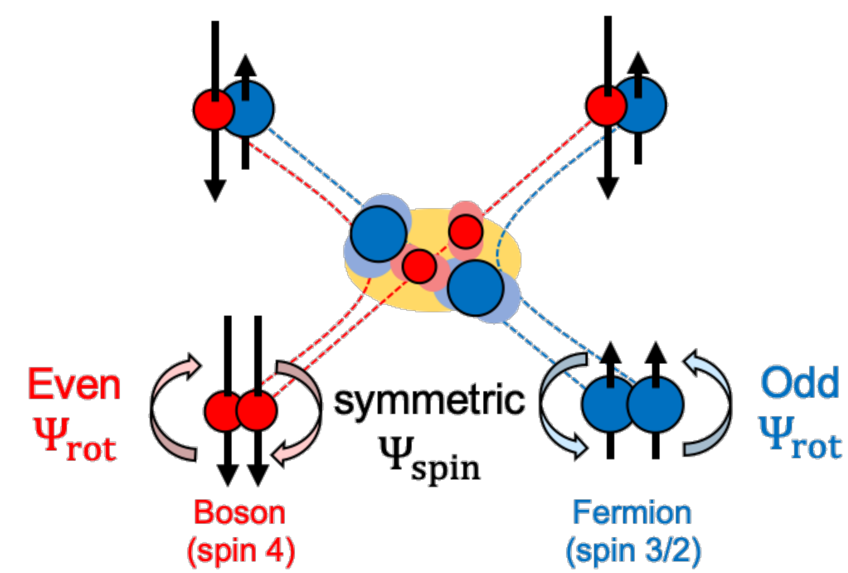
1K = 0.002 kCal/mol ~ 1 cm^{-1}

Rotational state distributions of K_2 and Rb_2

Strong parity preference → Nuclear spin conservation!

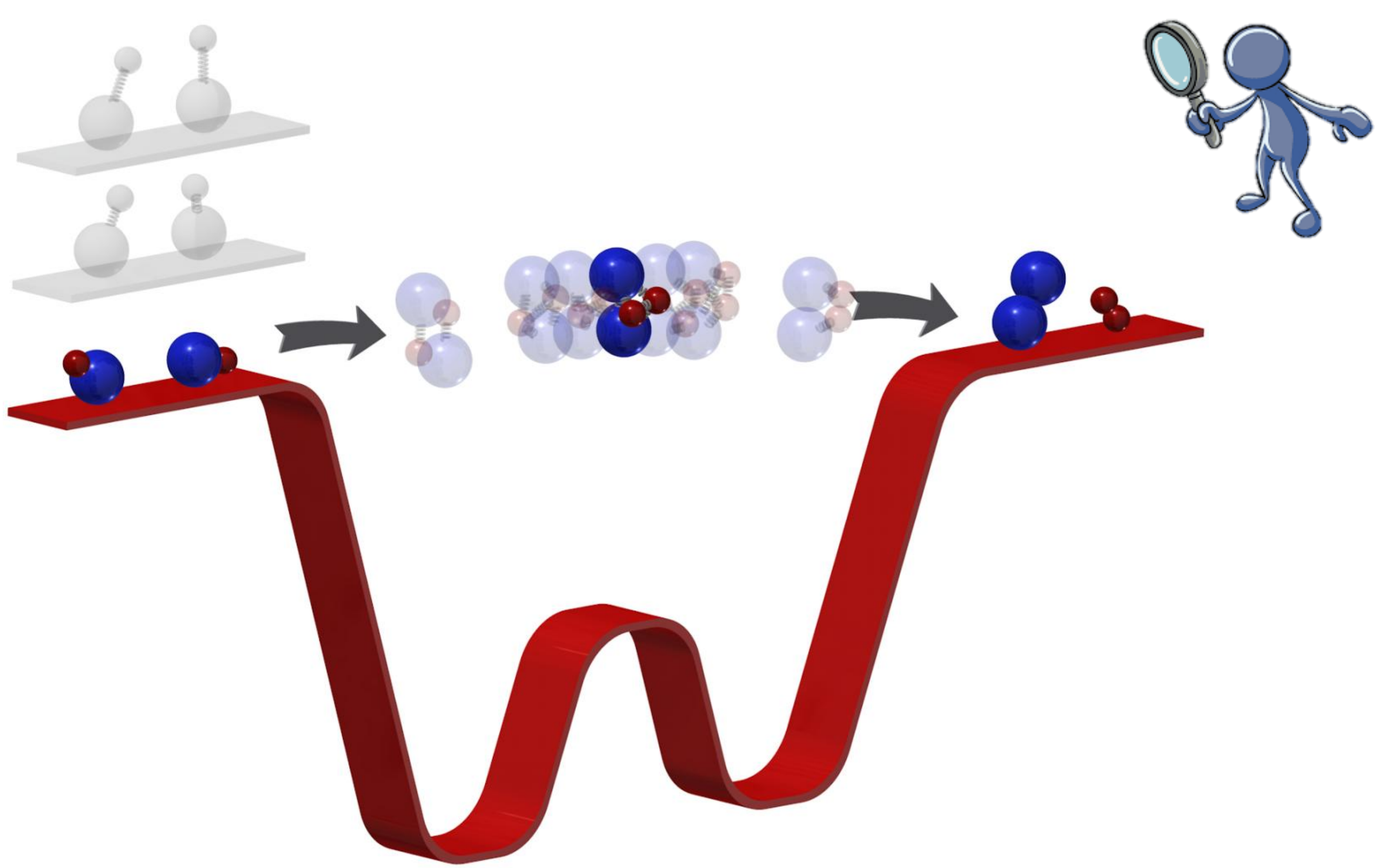




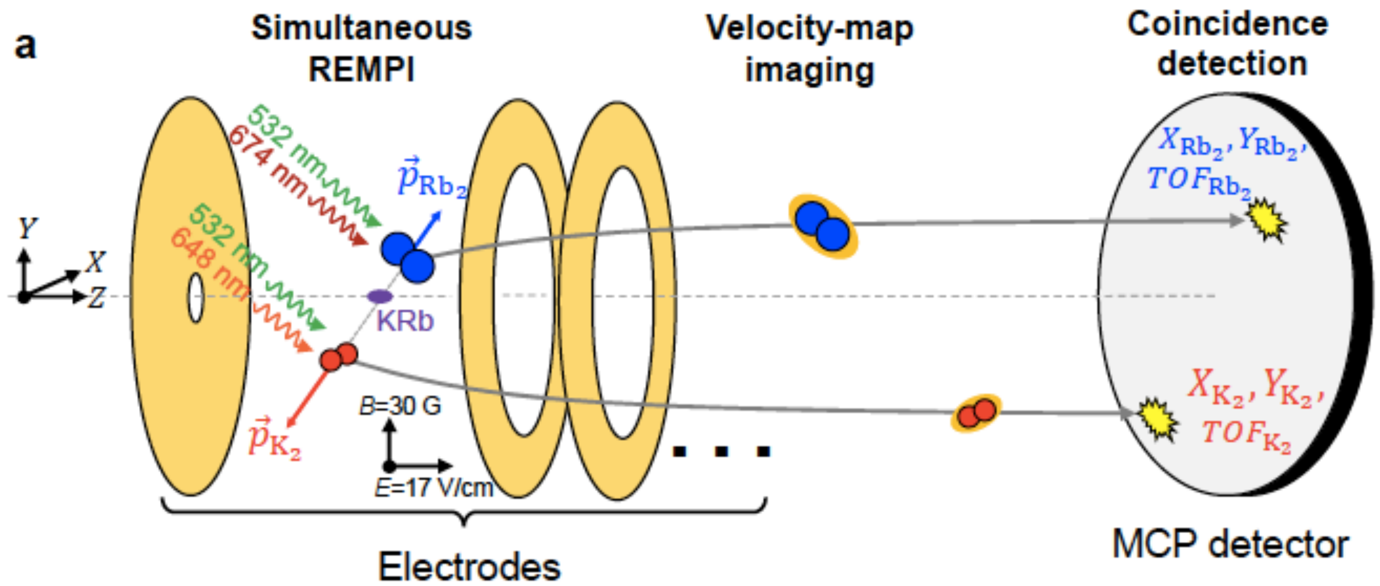


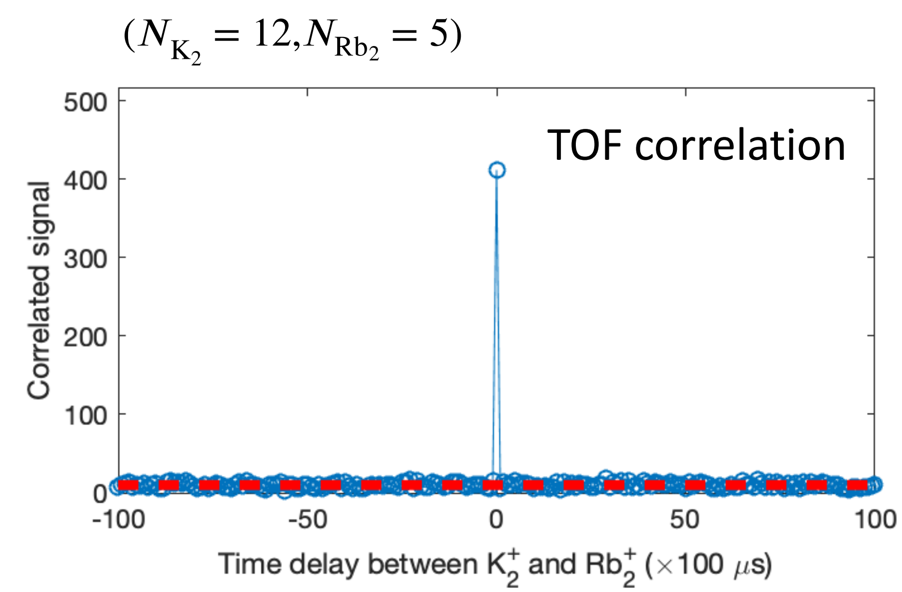
Hu, Liu et. al, Nature Chemistry **13**, 435-440 (2021)

Resolve products from individual reaction events?



Coincidence detection

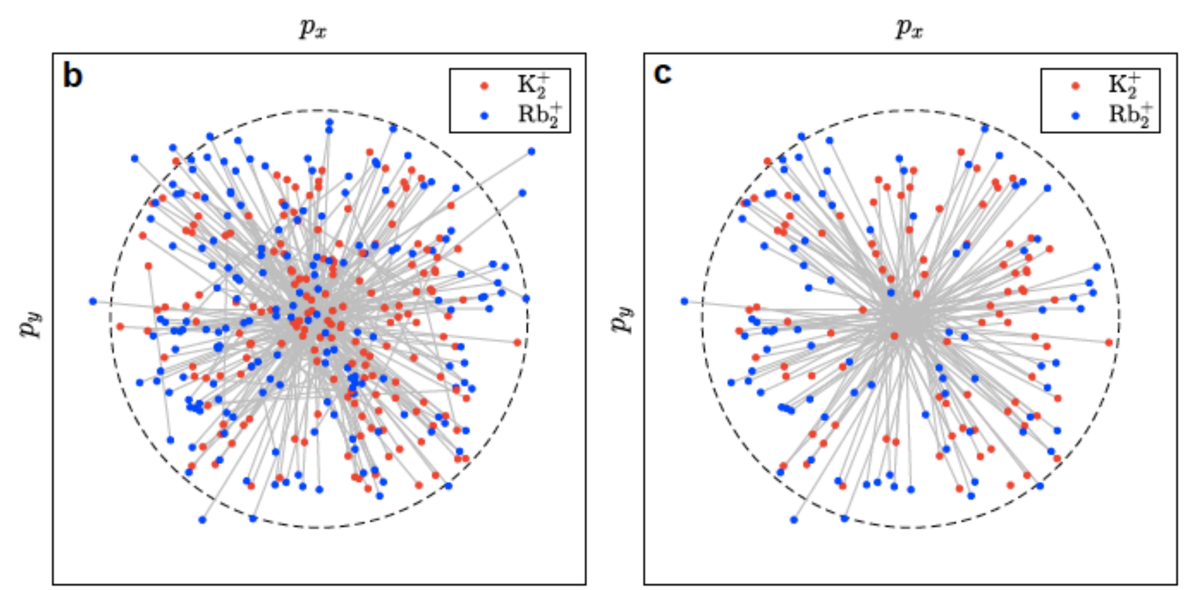




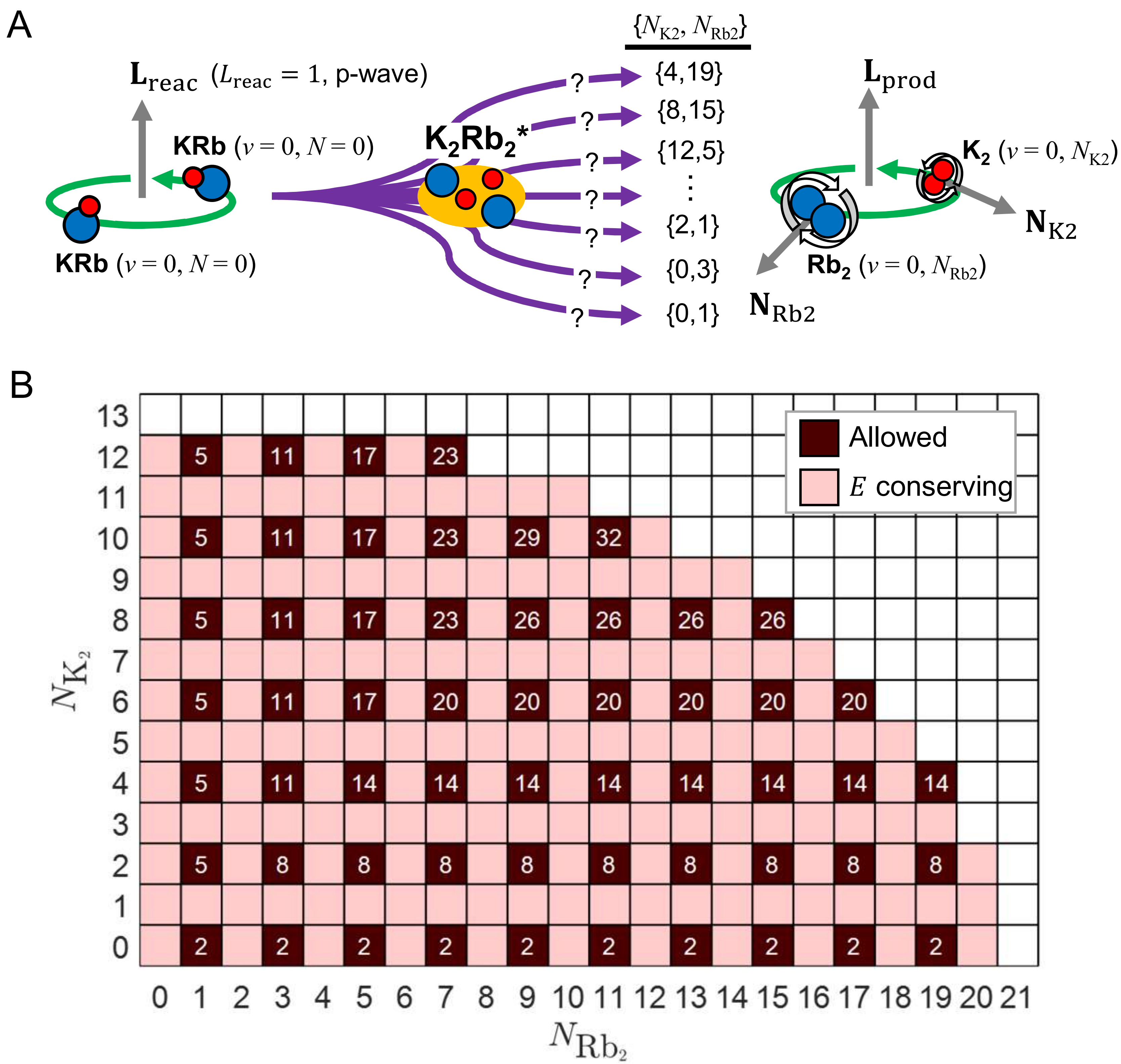
Momentum conservation constrains:

$$\vec{P}_{K_2} + \vec{P}_{Rb_2} = \vec{P}_{KRb} + \vec{P}_{KRb} \to 0$$

- Z momentum – TOF information filter
- X, Y momentum – X, Y spatial information filter

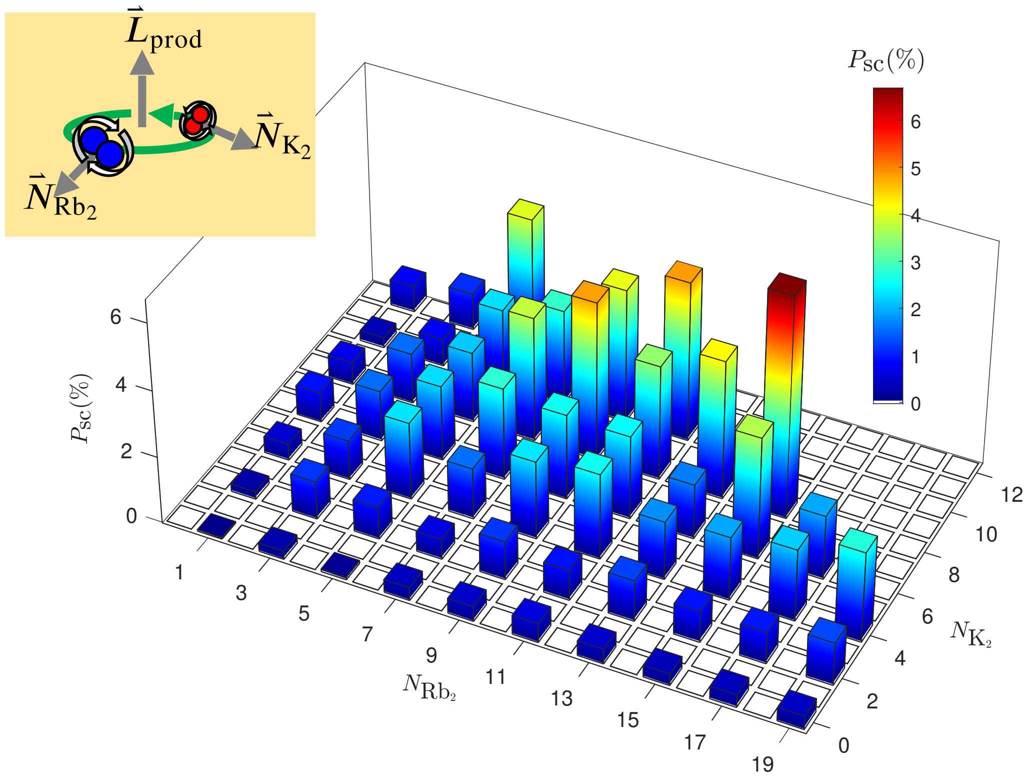


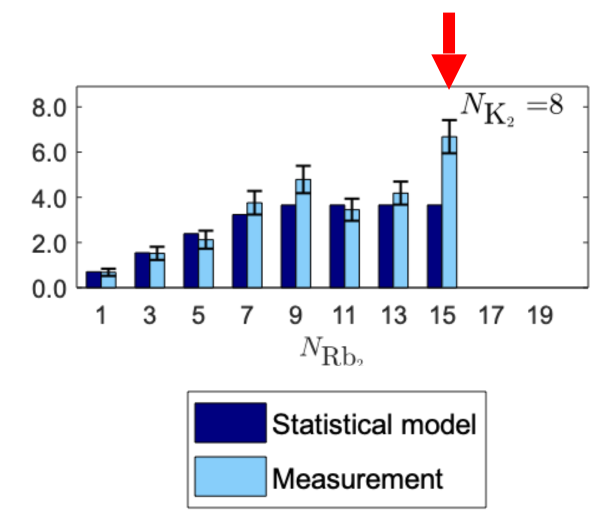
Non-trivial statistical distribution



Complete Characterization of a Chemical Reaction

- Full quantum state outcome measured for the molecule+molecule reaction. Our analysis (likelihood ratio test) shows that after removing 7 deviating channels, the data matches the prediction based on statistical state counting (exact quantum calculation is beyond the state-of-the-art theory)





Yu Liu*, Ming-Guang Hu*, Matthew A. Nichols, D. Yang, D. Xie, H. Guo, Kang-Kuen Ni, Nature **593**, 379-384 (2021)

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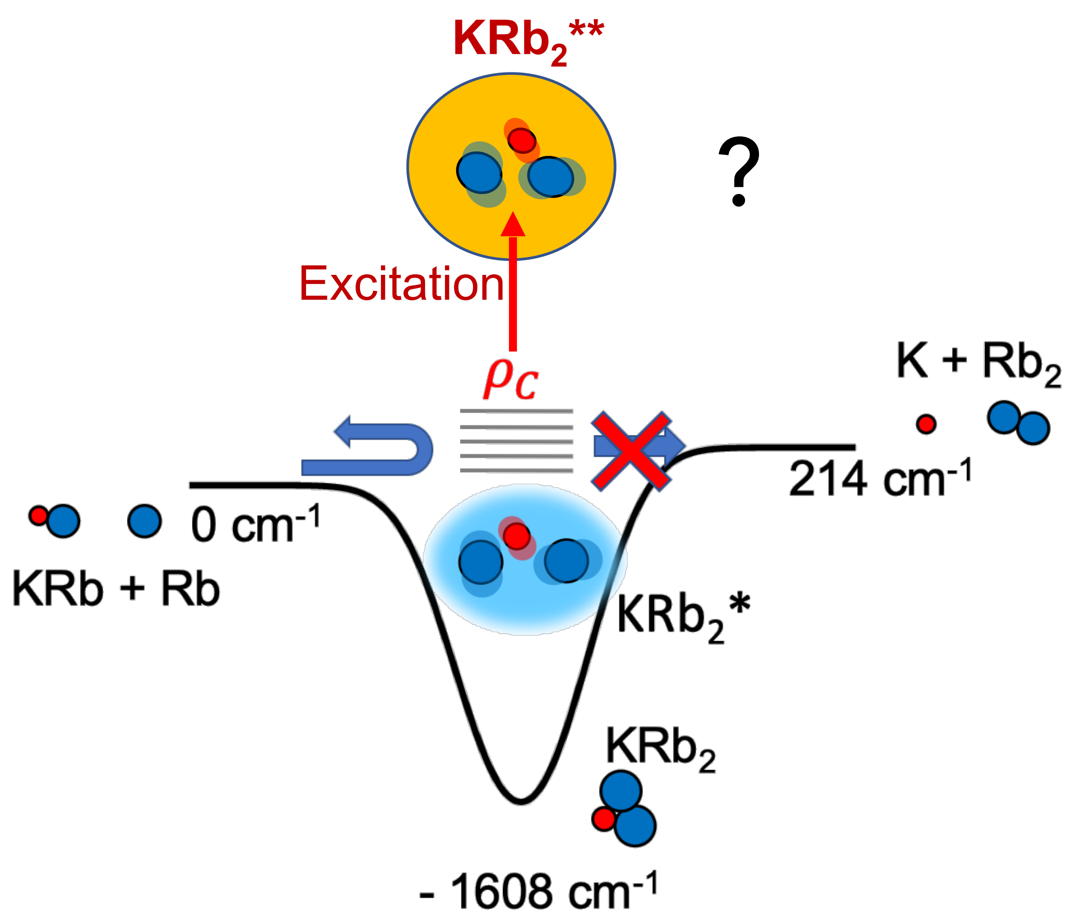
What's Next?

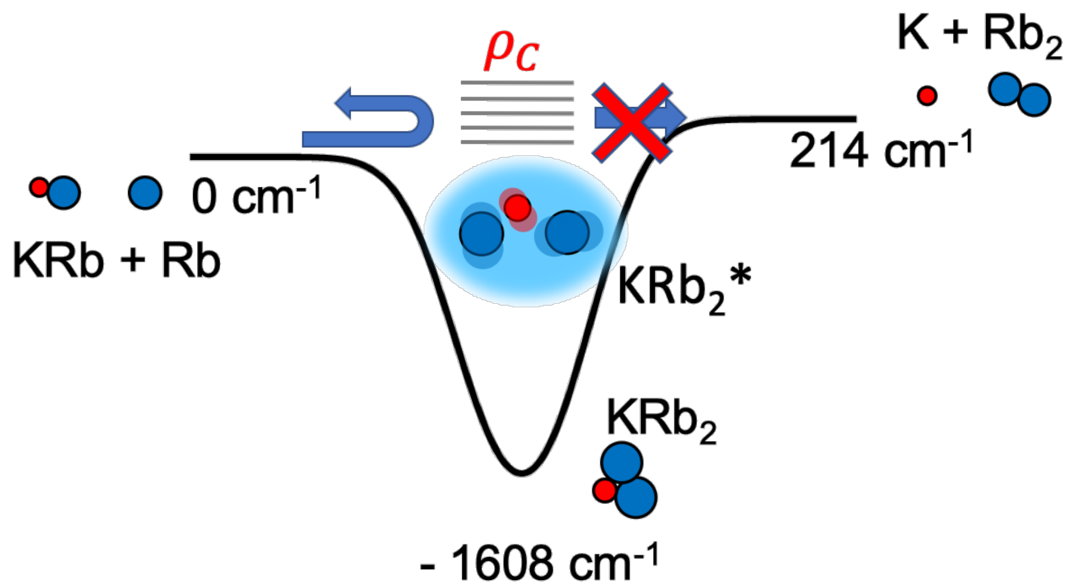
"more tractable" atom-molecule reactions/collisions

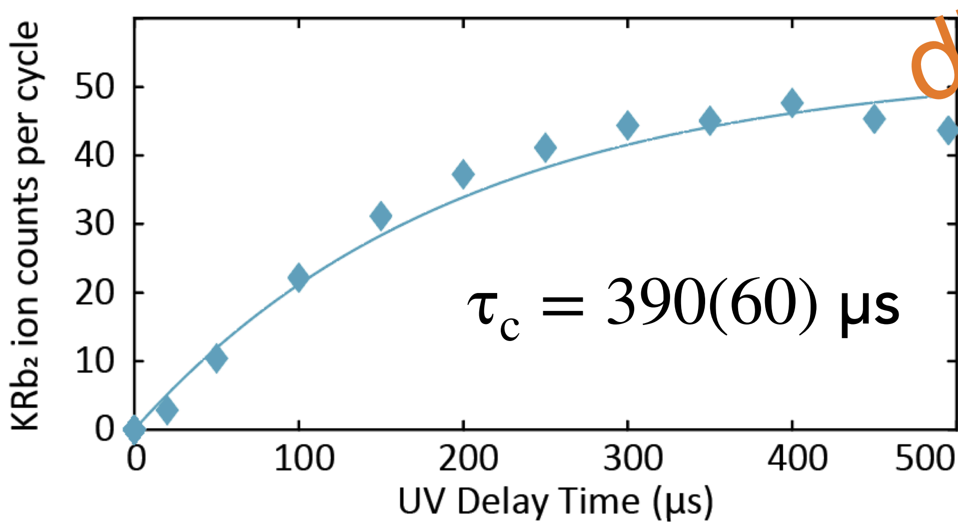


* KRb+Rb reaction is energetically forbidden
* Long-lived complex?
* Photo-excitation of complexes?
* KRb+K reaction is energetically allowed

Exp vs RRKM predicted complex lifetime

$$\tau_{\mathrm{RRKM}} = \frac{h\,\rho_C}{N_0}$$





M. Nichols, Y.-X. Liu, L. Zhu et al., PRX 12, 011029 (2022)

	Measurement	RRKM prediction
KRb + KRb [1]	360(30) ns	170(60) ns
RbCs + RbCs [2]	0.53 ms	0.25 ms

[1] Liu*, Hu*, et al., Nature Physics (2020)
[2] Gregory et al, PRL 124, 163402 (2020)

KRb + Rb

RRKM prediction
1 ns [3]
270 ns [4]

differs by 10^5!!?

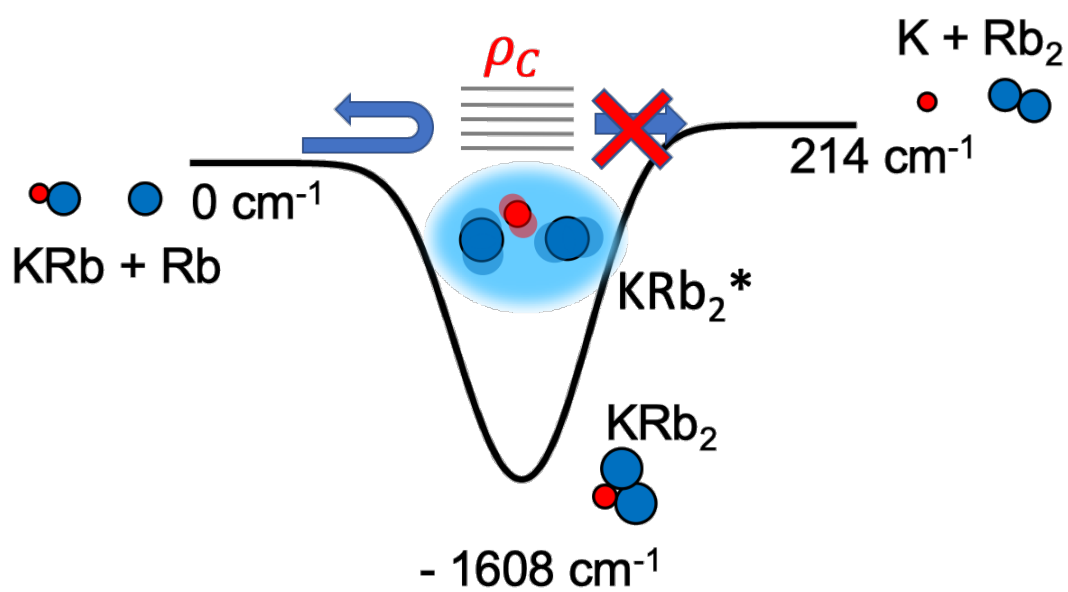
[3] Private Communication with Tijs Karman & Christianen, et al, Phys. Rev. A 100, 032708 (2019)
[4] Mayle, et al, Phys. Rev. A 85, 062712 (2012)

Other systems	Measurement*	RRKM prediction
NaK + NaK (bonson, fermion)	>0.35 ms, >2.6 ms	6 μs, 18 μs
NaRb + NaRb	>1.2 ms	13 μs

Bause et al., PRR 3, 033013 (2021)
Gersema et al. PRL 127, 163401 (2021)

What could explain the x10^5 difference?

$$\tau_{\mathrm{RRKM}} = \frac{h\,\rho_C}{N_0}$$



RRKM assumption

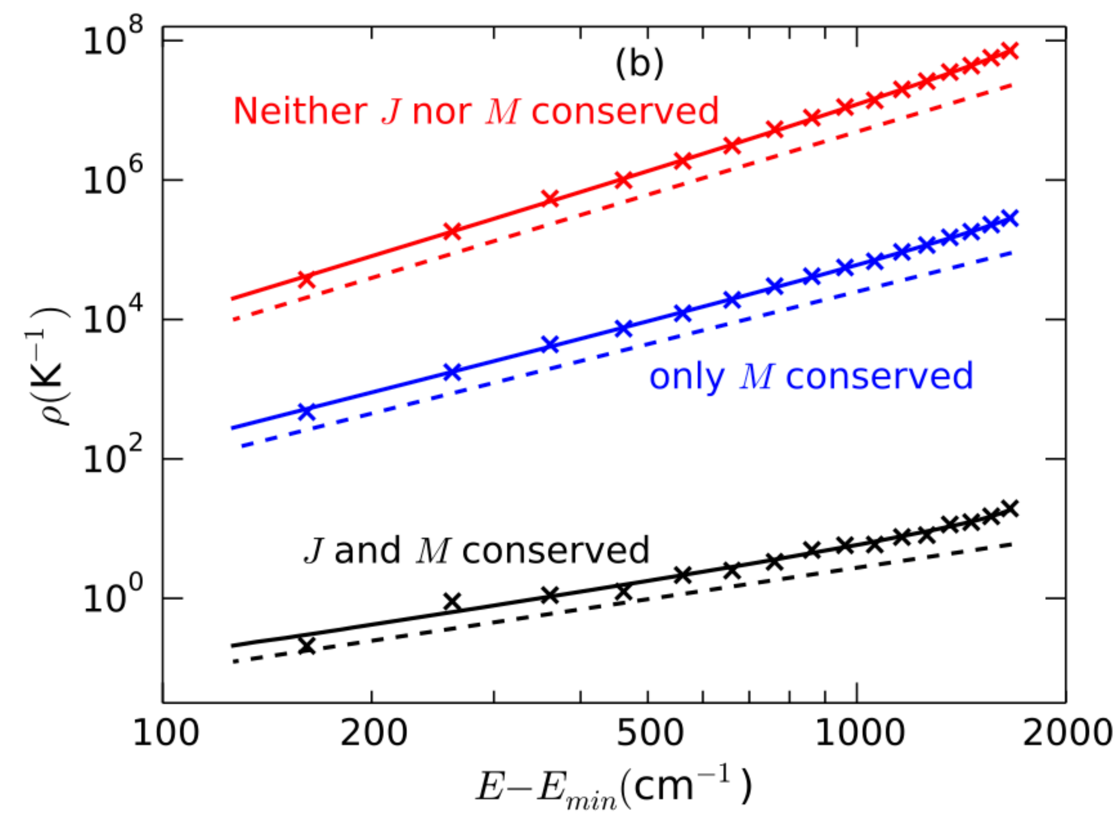
- DOS large

breaks down?

Croft et al. arXiv:2111.09956

RRKM holds but

- Angular momentum is not conserved?

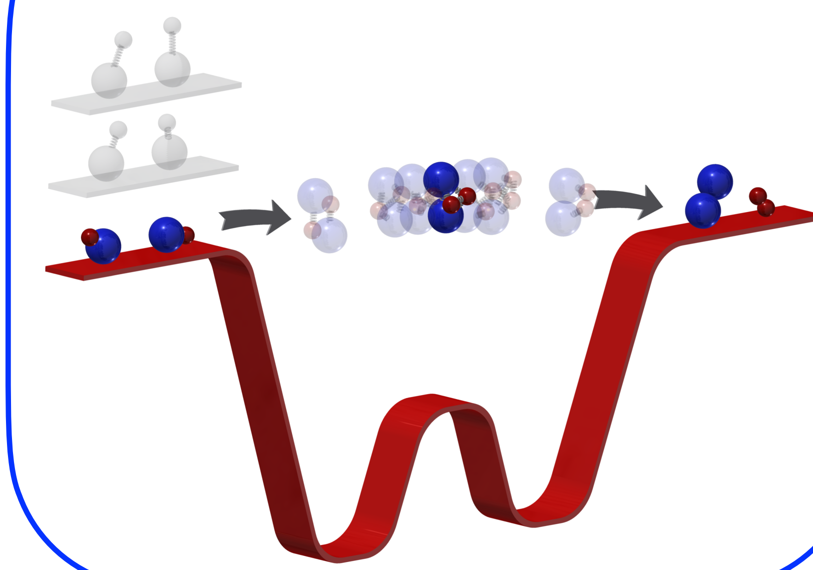


Christianen, et al, Phys. Rev. A 100, 032708 (2019)
Also: Frye, et al, NJP 23 125008 (2021)

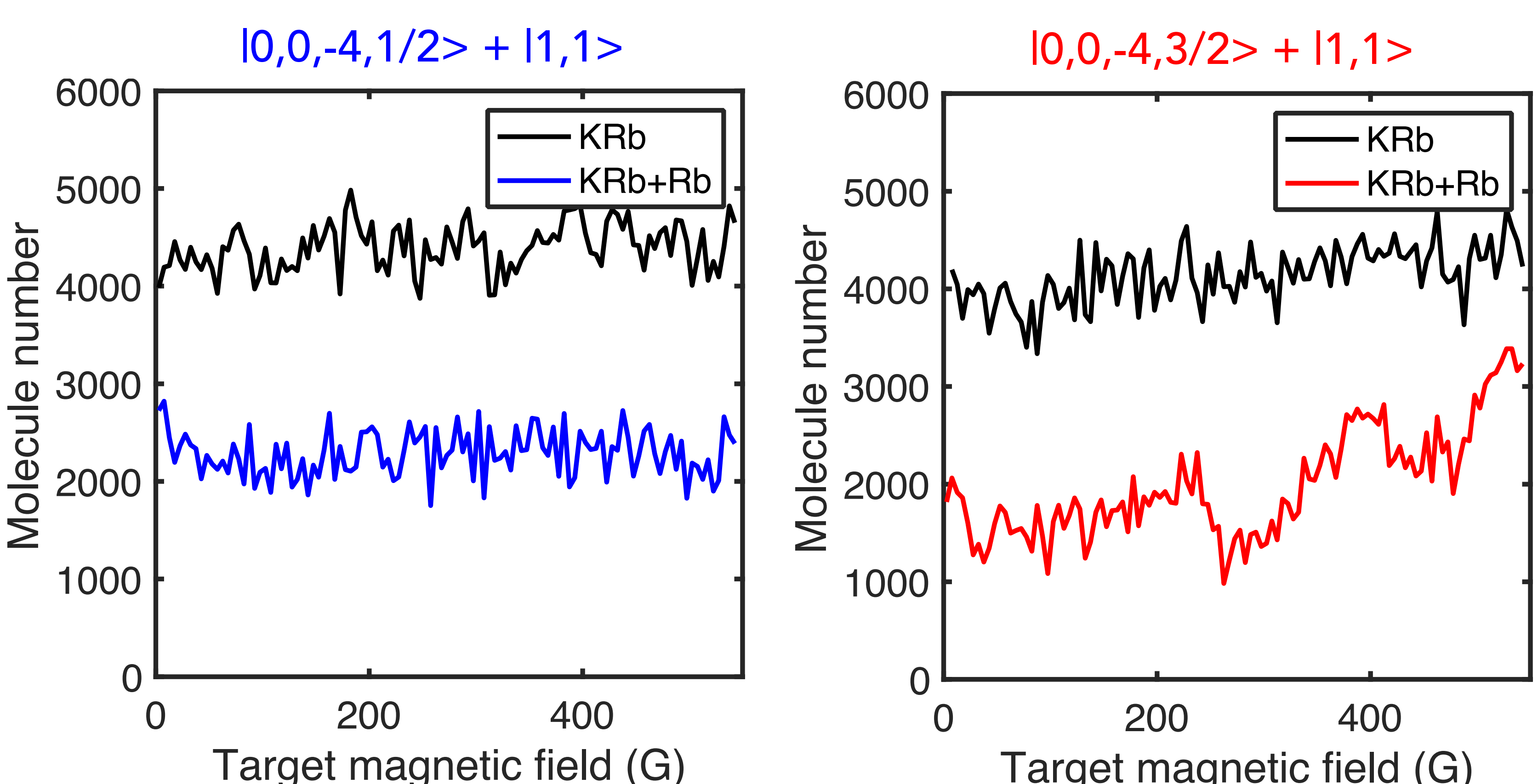
Summary and Outlook

* We brought chemistry and physics tools together to completely characterize a molecule-molecule reactive process with full state-to-state details
* We now turn our attentions to atom-molecule reactions/collisions where exact quantum calculations are more tractable, but new questions arise

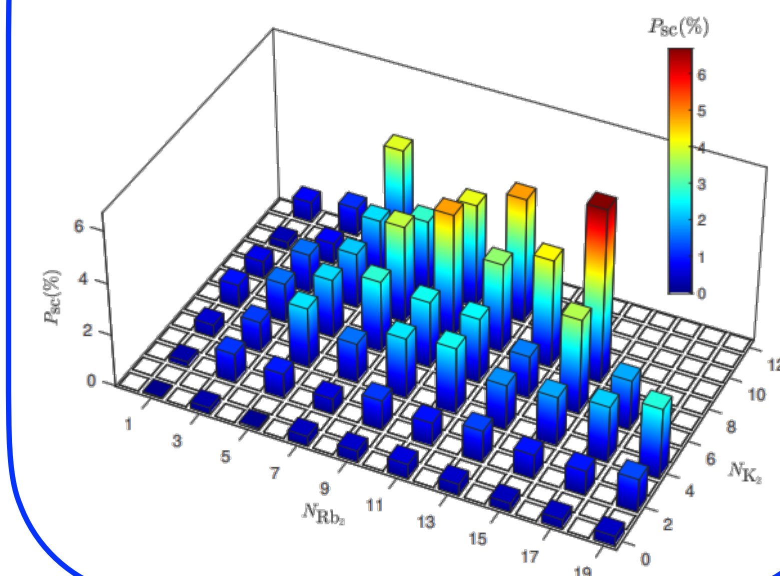
Observation of ultracold reactions



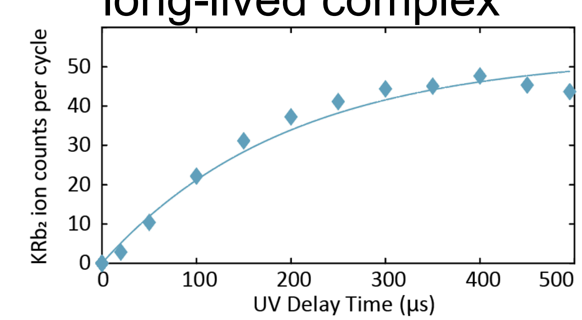
Magnetic field dependent atom-molecule loss *(preliminary)*



Complete characterization of bimolecular reactions



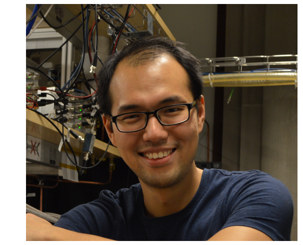
Orders of magnitude too long-lived complex



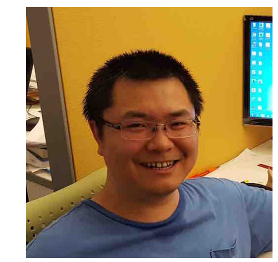
Acknowledgments

Thank you!

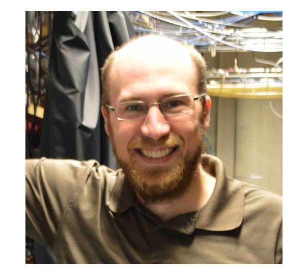
KRb Alumni



Yu Liu, PhD
=> NIST Boulder



Dr. Ming-Guang Hu
=> QuEra Computing



Dr. David Grimes
=> MIT

Dr. Matt Nichols
=> Apple

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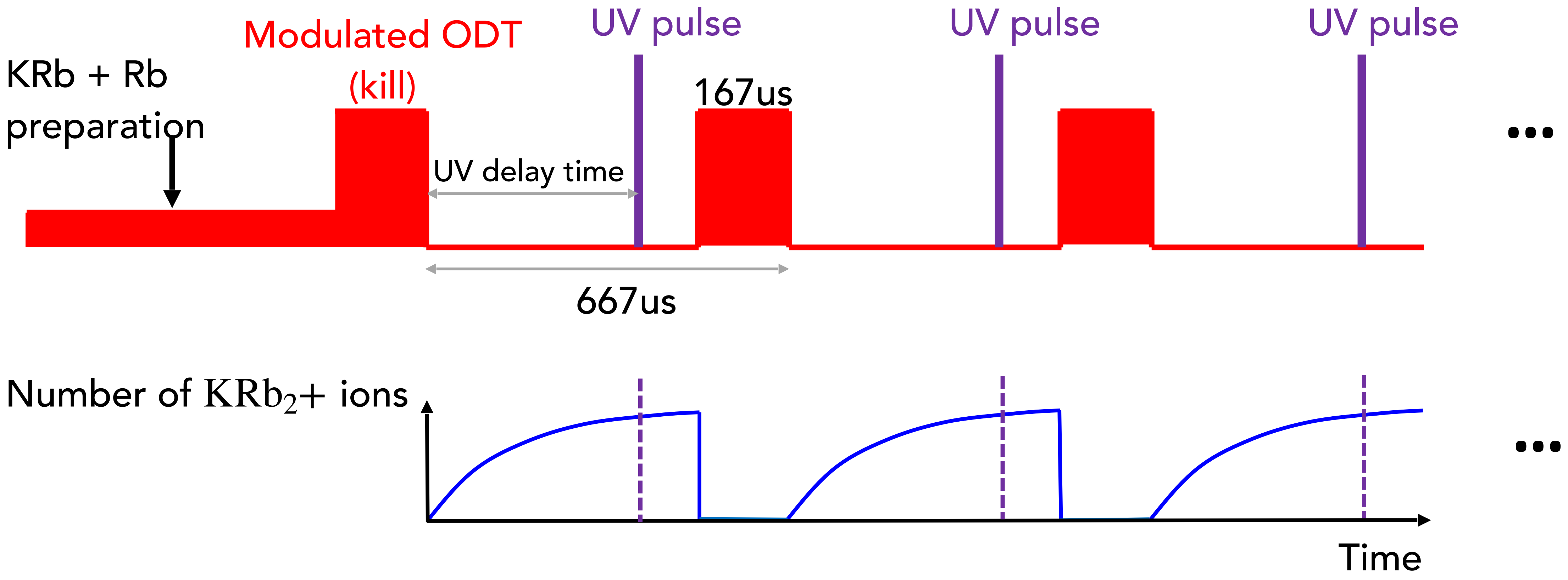
Past: Beckman foundation, ARO, Sloan fellowship


Modulated ODT
(kill)
UV pulse
UV pulse
UV pulse
KRb + Rb
preparation
167us
UV delay time
667us
Number of KRb$_2$+ ions
Time