Ultracold Molecules for physics and chemistry

Probing sub-microKelvin chemistry

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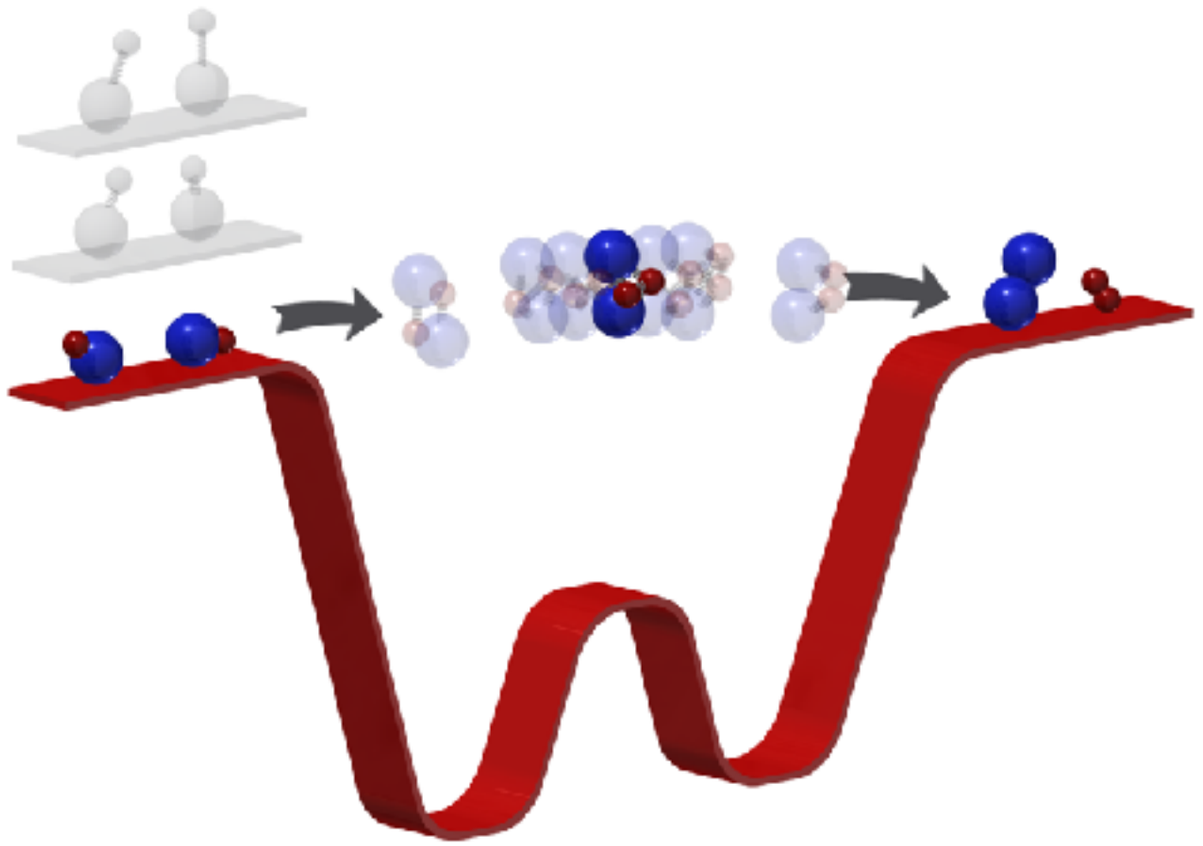
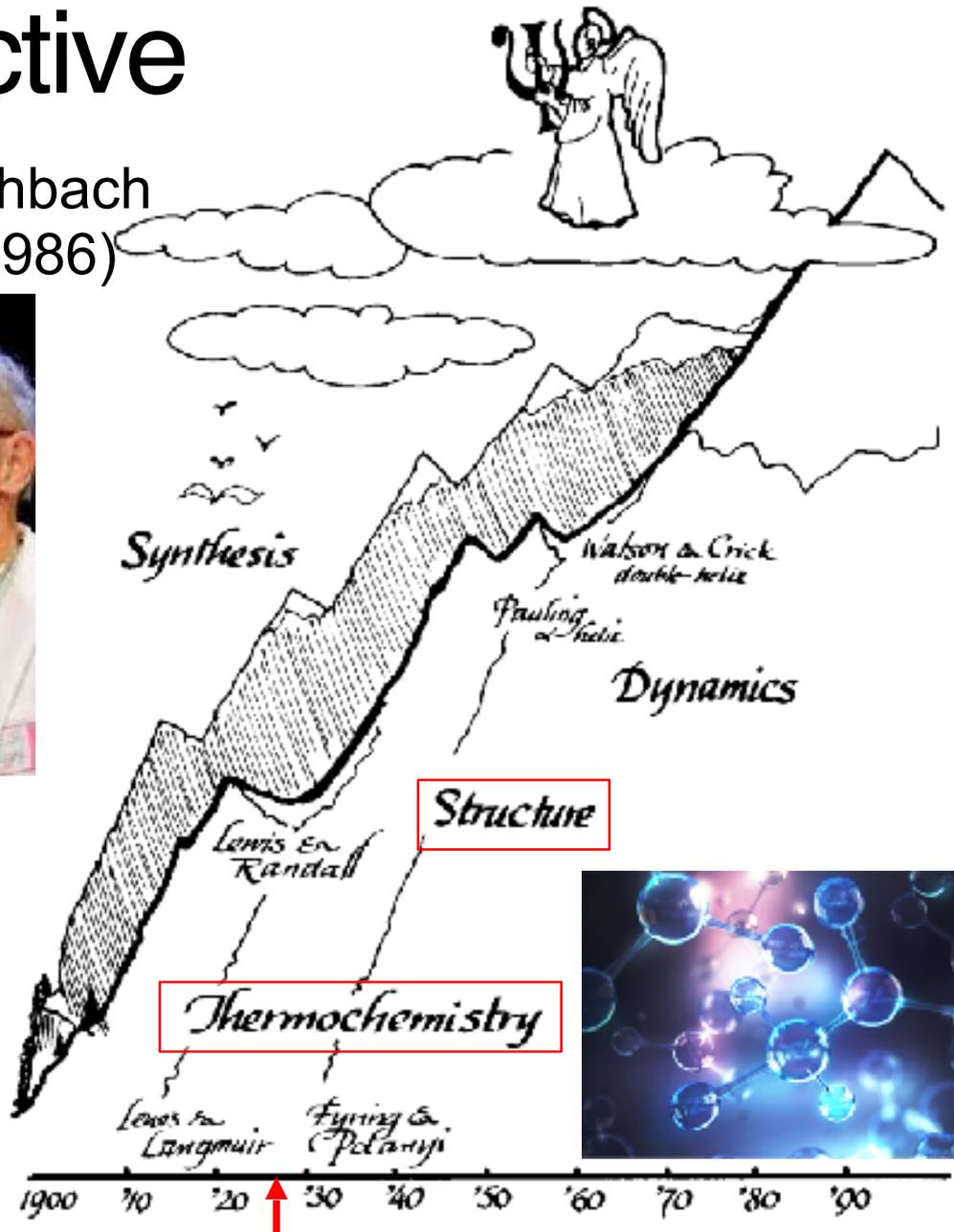
Harvard University



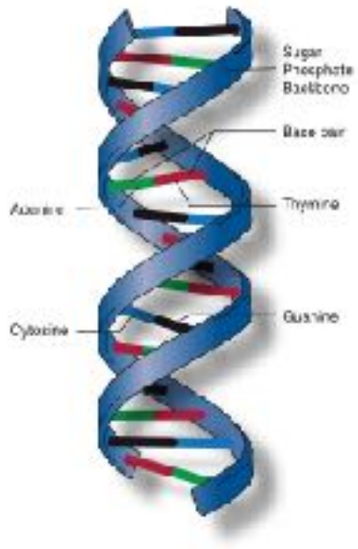
Boulder Summer School 2021

Historical perspective

Dudley R. Herschbach
Nobel Lecture (1986)



Quantum mechanics

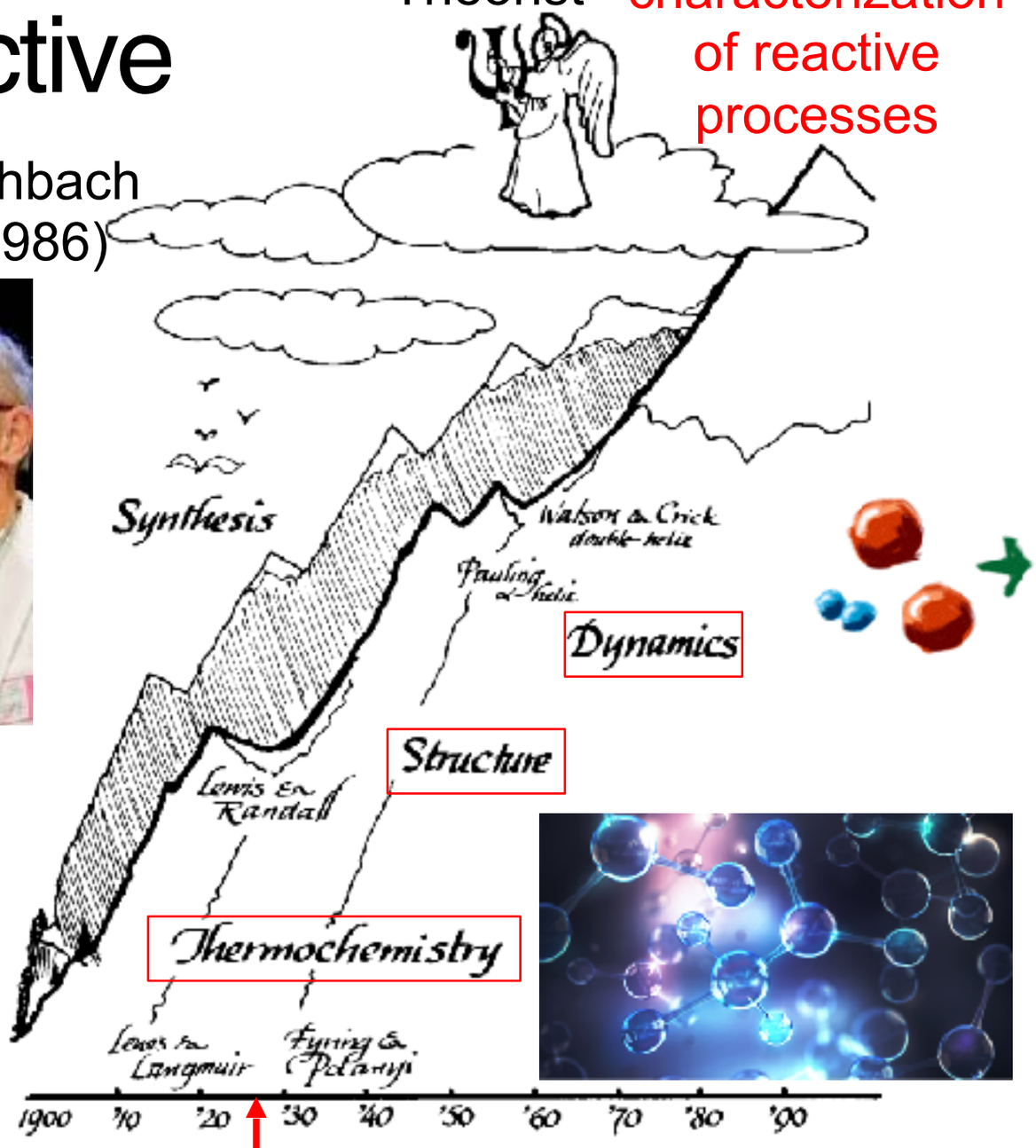


Historical perspective

Dudley R. Herschbach
Nobel Lecture (1986)

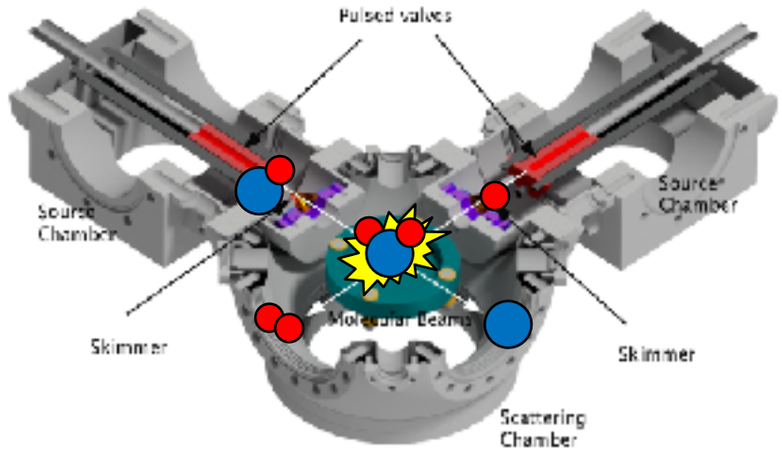
Theorist

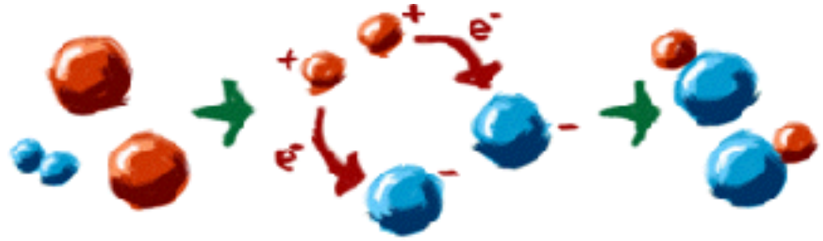
Complete characterization of reactive processes

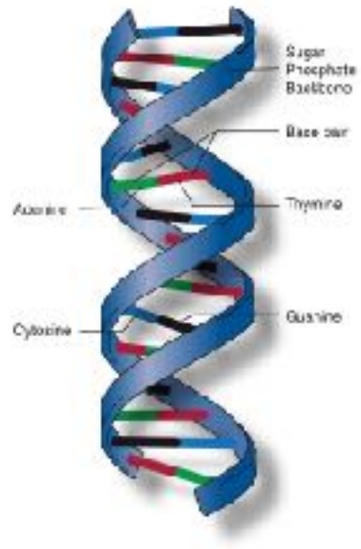


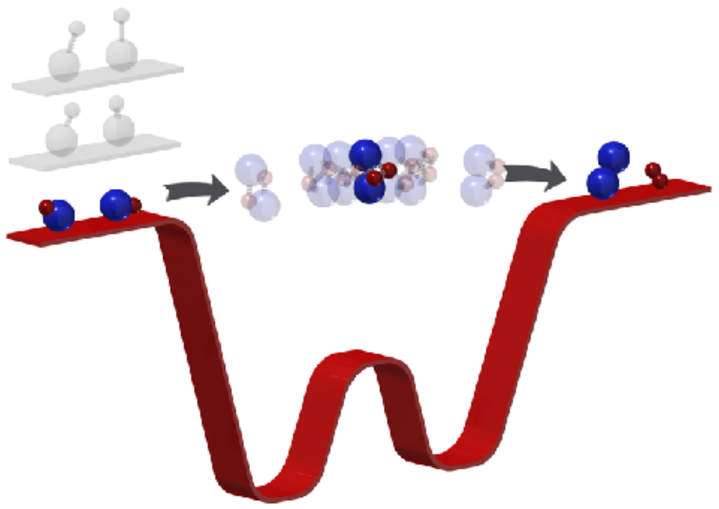
Quantum mechanics

Crossed molecular beams









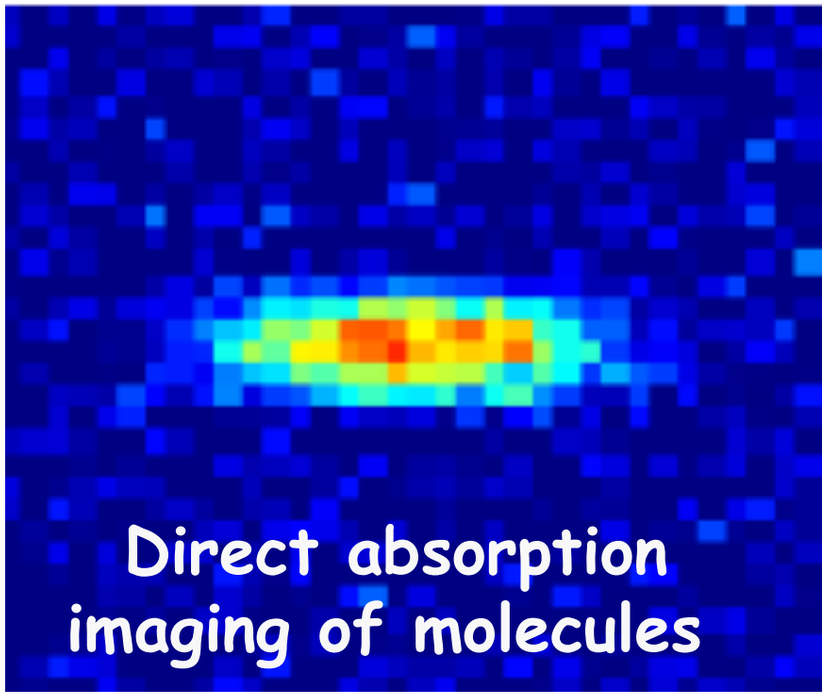
Outline

- 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
- Surprise 4 - control reaction product state via conserved nuclear spins
- Complete characterization of reactive process -
  mapping quantum states of correlated reaction product pairs

JILA KRb Experiment (2008-2010)

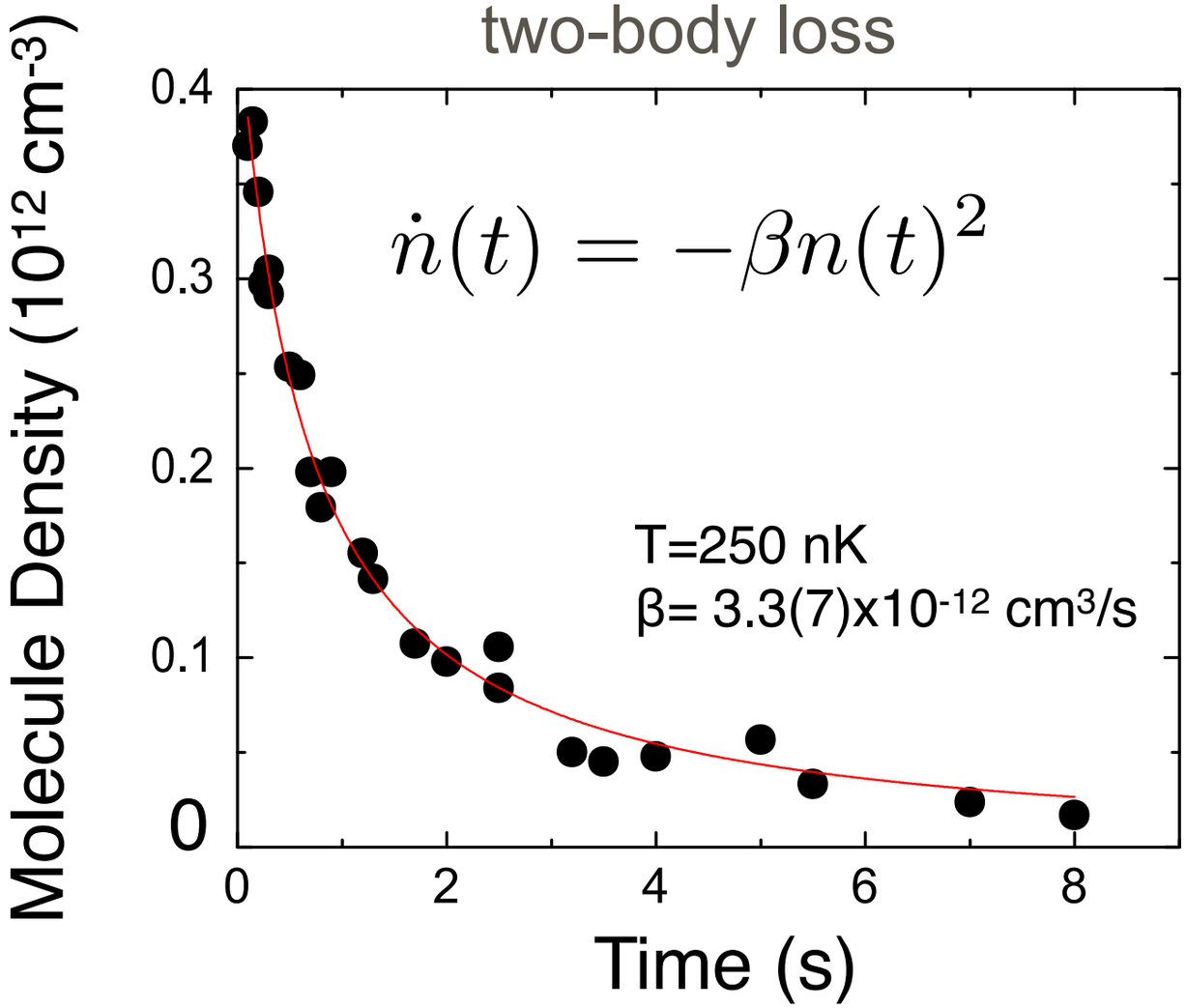
A trapped gas of molecules in a single and lowest hyperfine, rotational, vibrational, electronic ground state!

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)

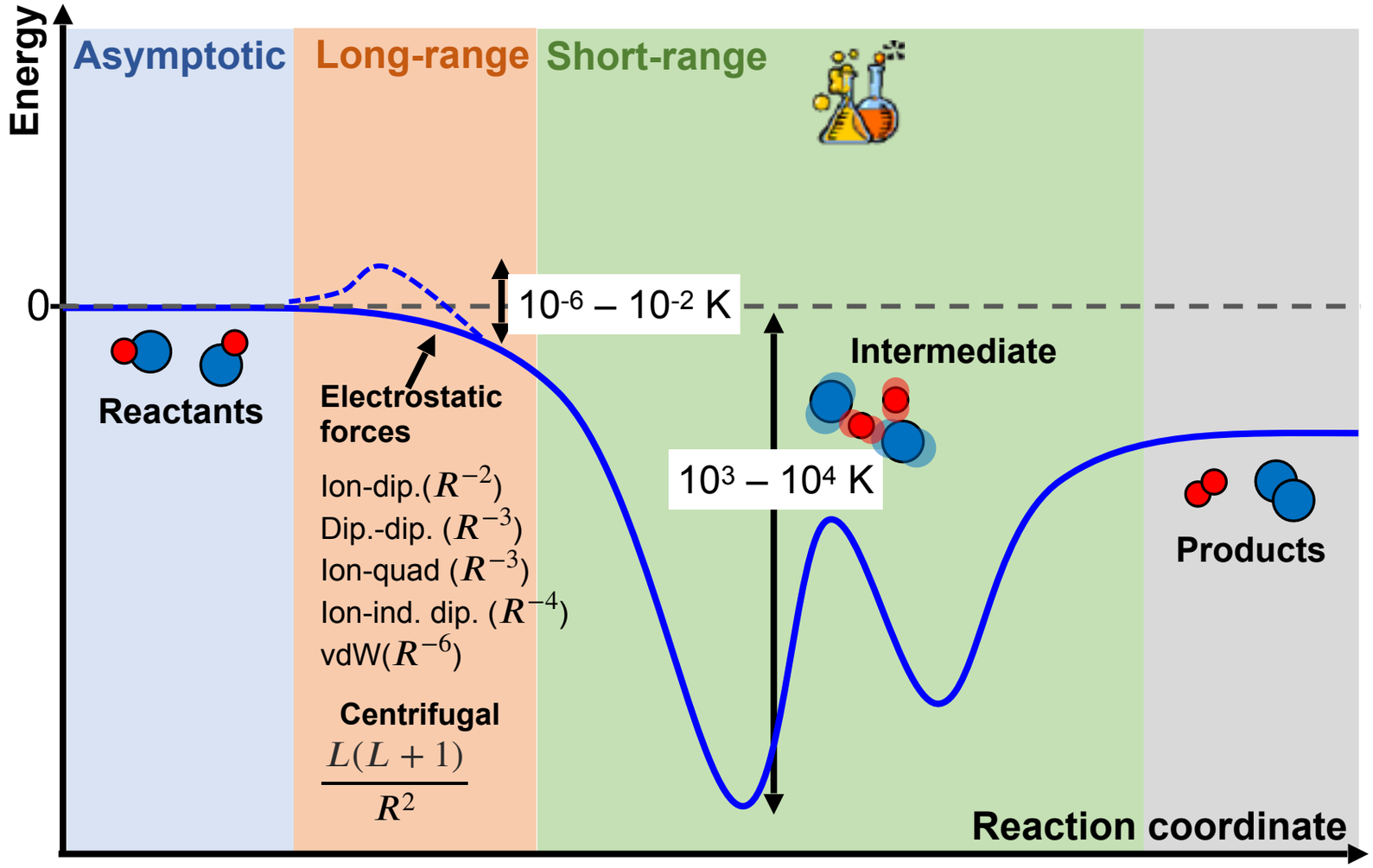
JILA KRb team 2003-2019

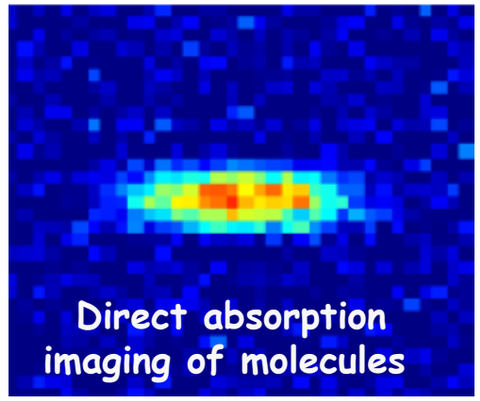
Quantum Degenerate KRb Gas,
Science **363**, 853 (2019)

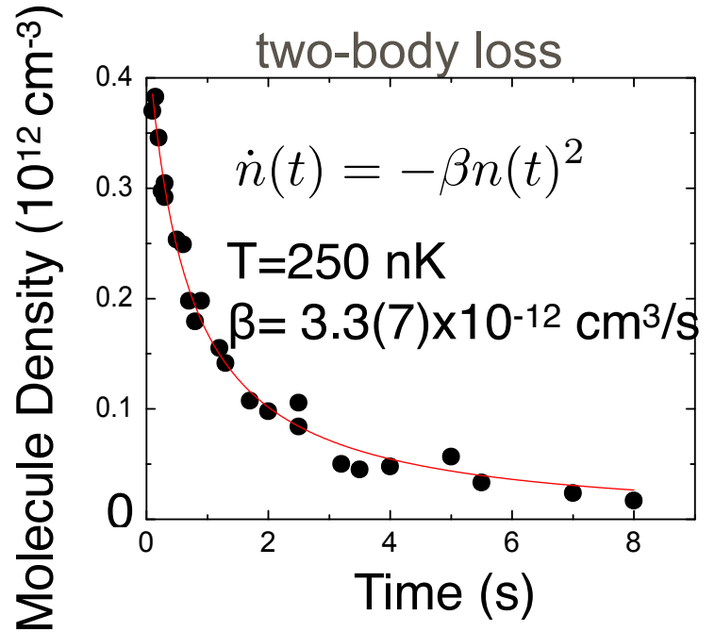
Nature Physics 15, 523-528 (2019)

Ultracold Chemical Reaction?

Ultracold Chemical Reaction?







direct detection needed

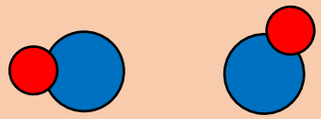
Ospelkaus, Ni,… Jin, Ye, Science, 327, 853 (2010)
Quéméner and Bohn, PRA 81 022702 (2010)
Idziaszek and Julienne, PRL 104, 113202 (2010)
Ni, Ospelkaus, … Ye, Jin, Nature 464, 1324 (2010)

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)

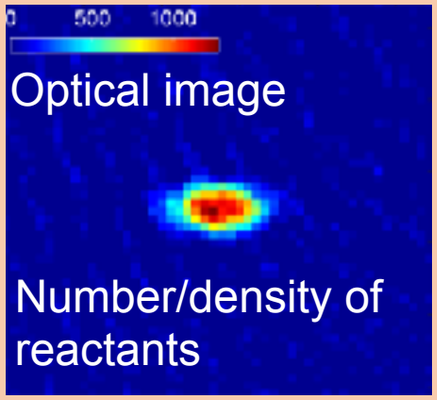
JILA, Innsbruck, Durham, MIT, Hong Kong, USTC, MPQ, Hannover, …

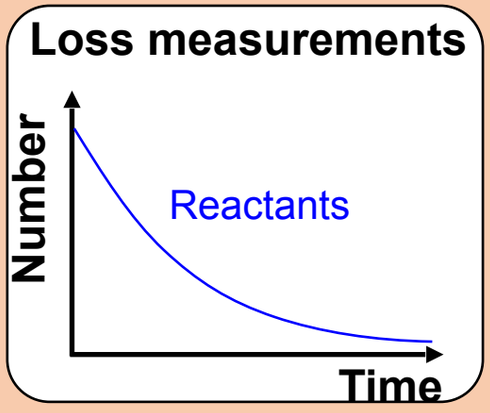
Probing the short-range and products: techniques

Long-range Imaging

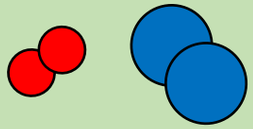


Reactants

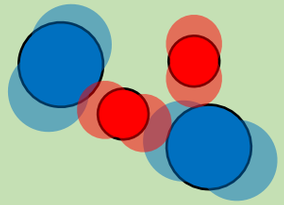




Short-range Ion spectrometry (Phys. Chem.)

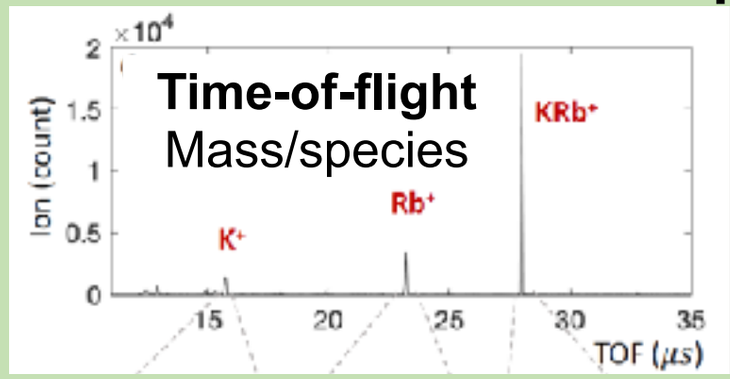


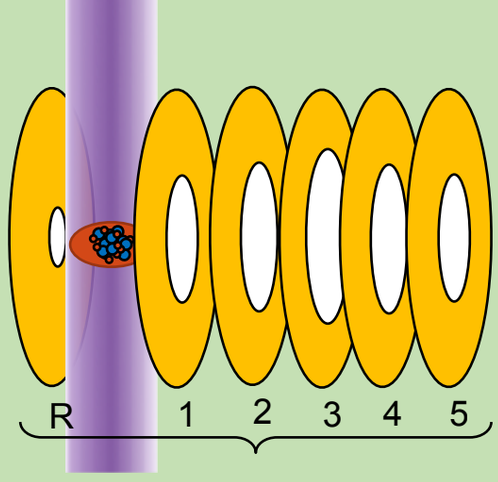
Products



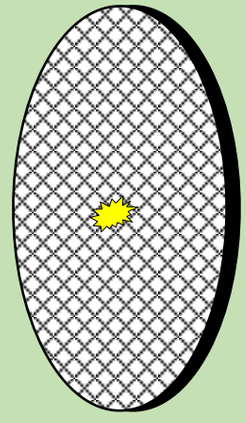
Intermediate complex

UV
(285 – 360 nm, 10 ns)





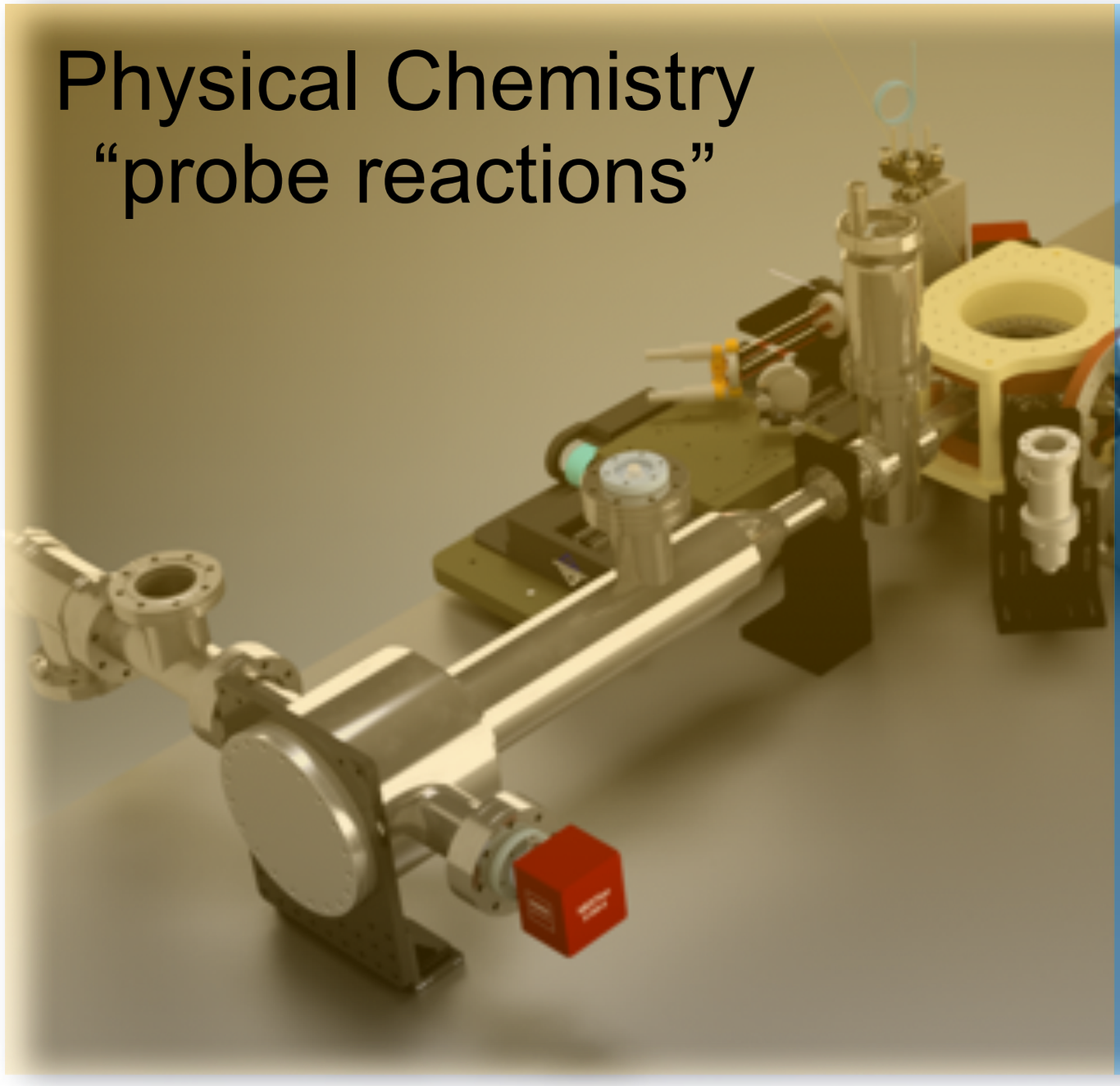
Electrostatic lens

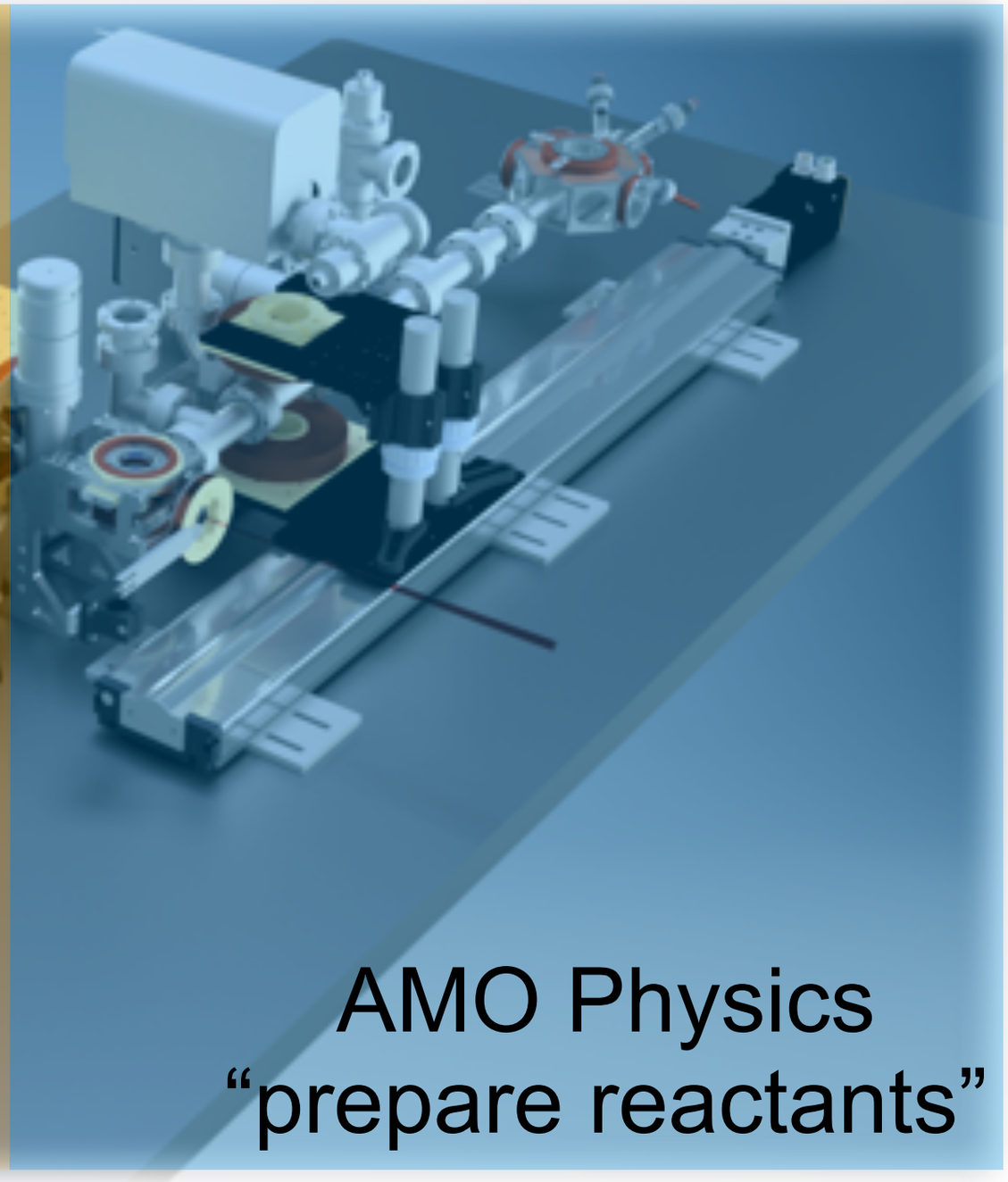


MCP detector

Spatial distribution
Kinetic energy

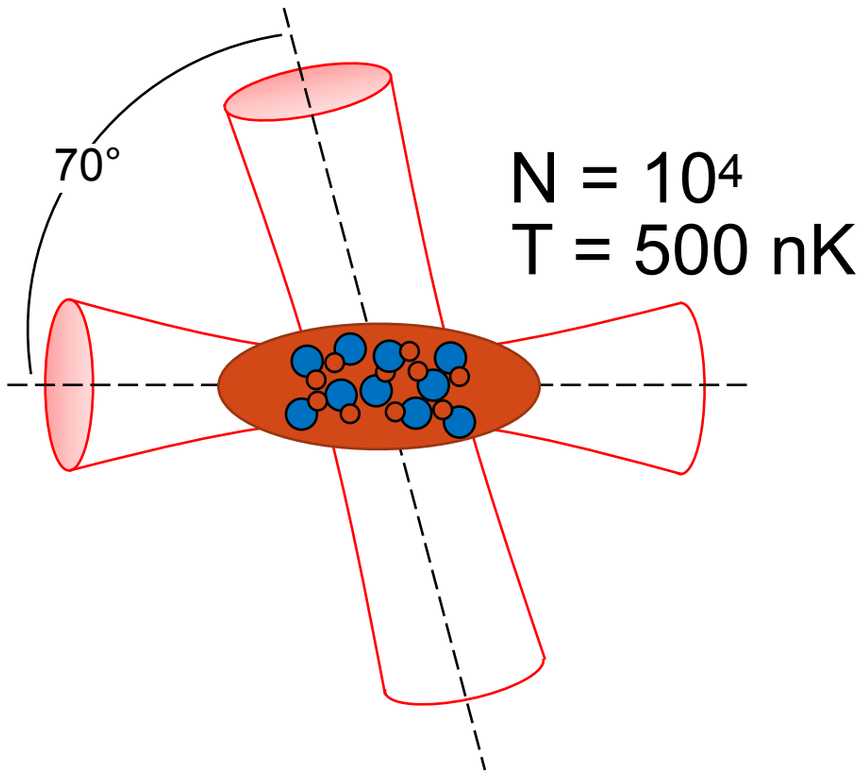
Combining Chemistry and Physics tools

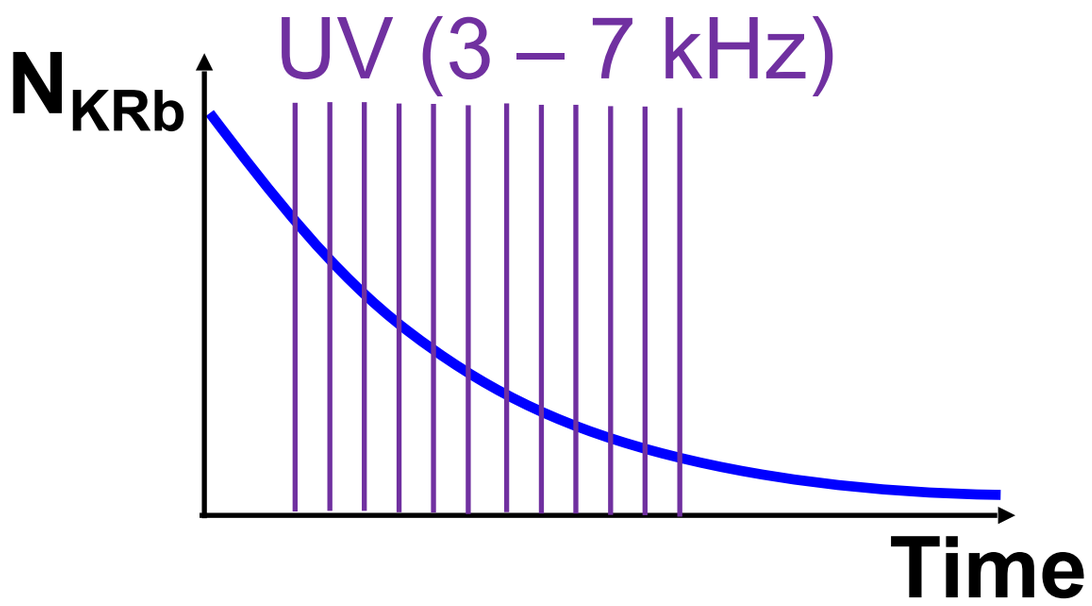




Phys. Chem. Chem. Phys. 22, 4861-4874 (2020)

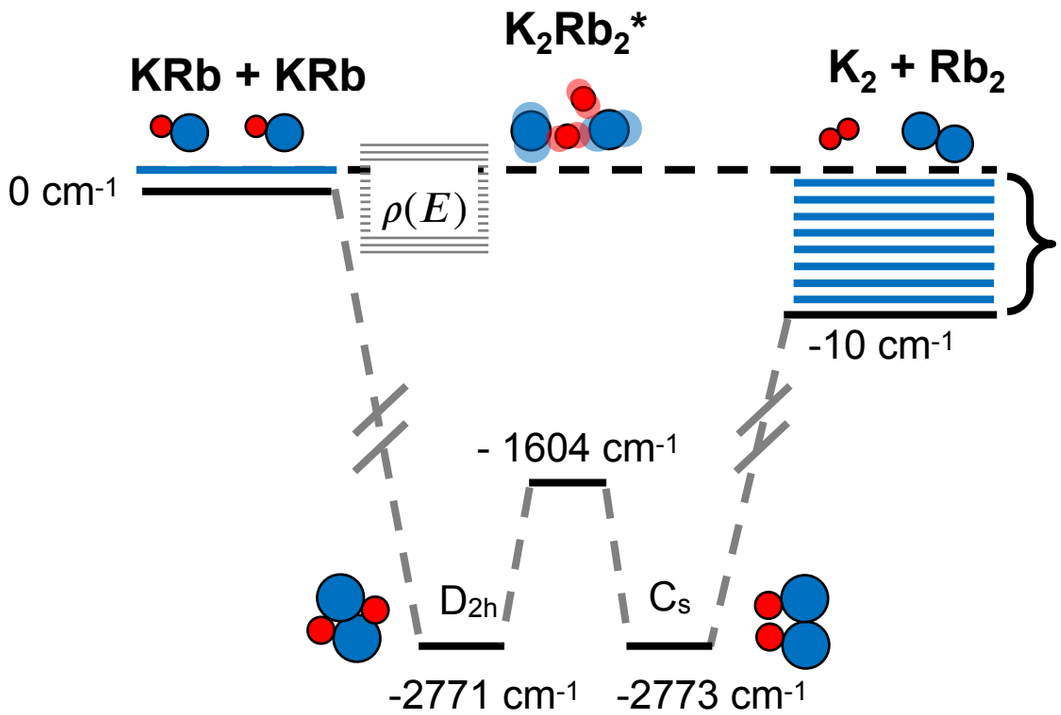
Probing the reaction

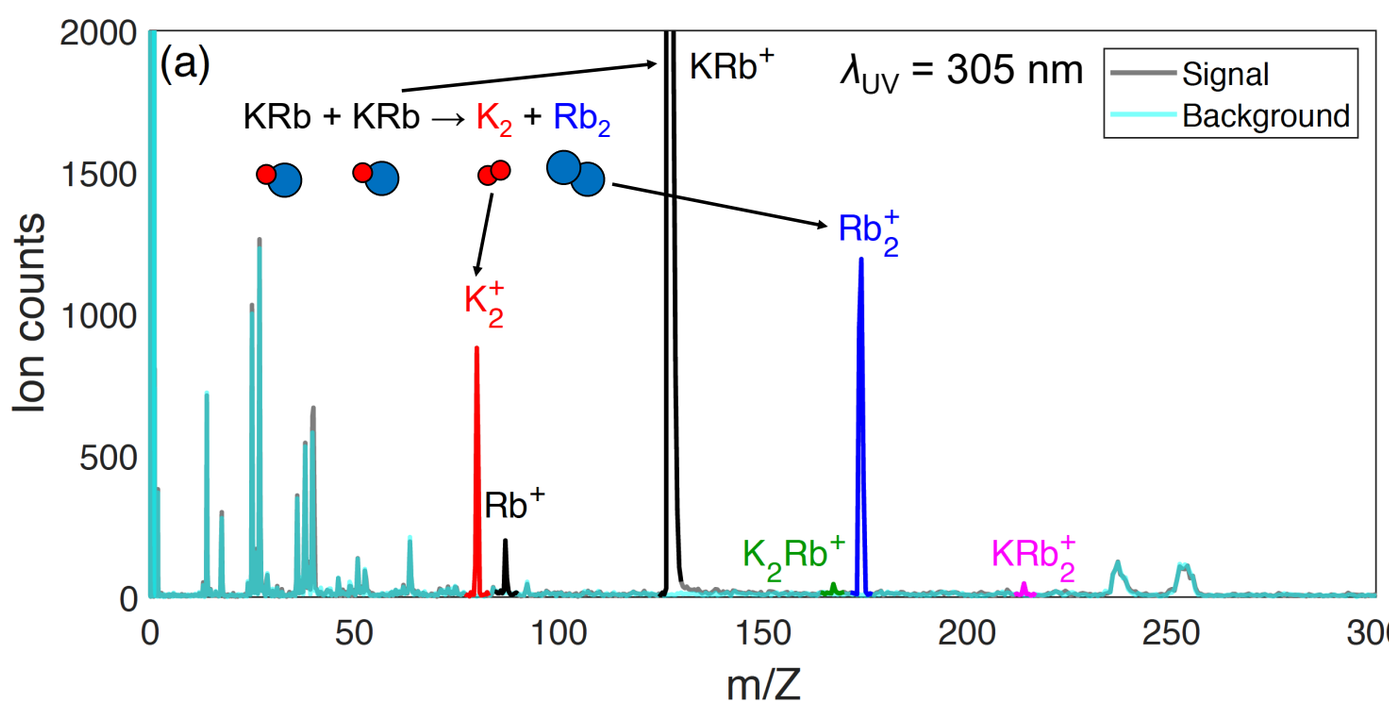




Product Detection

$$2KRb \rightarrow K_2Rb_2^* \rightarrow K_2 + Rb_2 + 10\ cm^{-1}$$

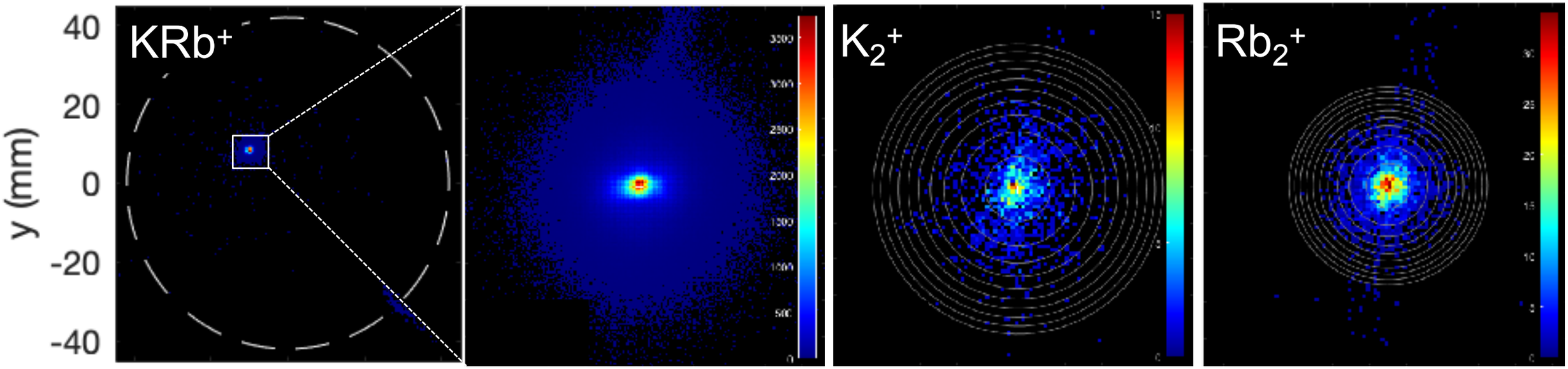




Byrd et al., PRA **82**, 010502 (2010)

Science **366**, 1111 (2019)

Verifying the product signal: *KE* distribution

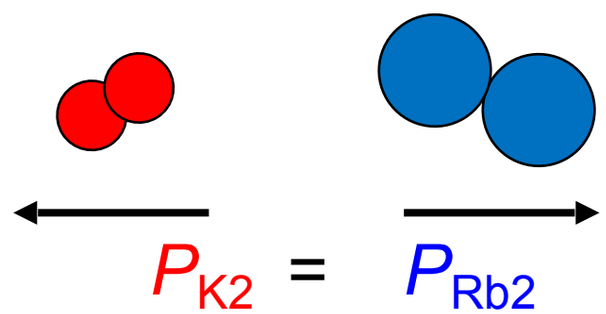


σ_r = 0.15 mm
KE = 0.15 cm^{-1}

σ_r = 2.1 mm
KE = 1.9 cm^{-1}

σ_r = 1.3 mm
KE = 0.87 cm^{-1}

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



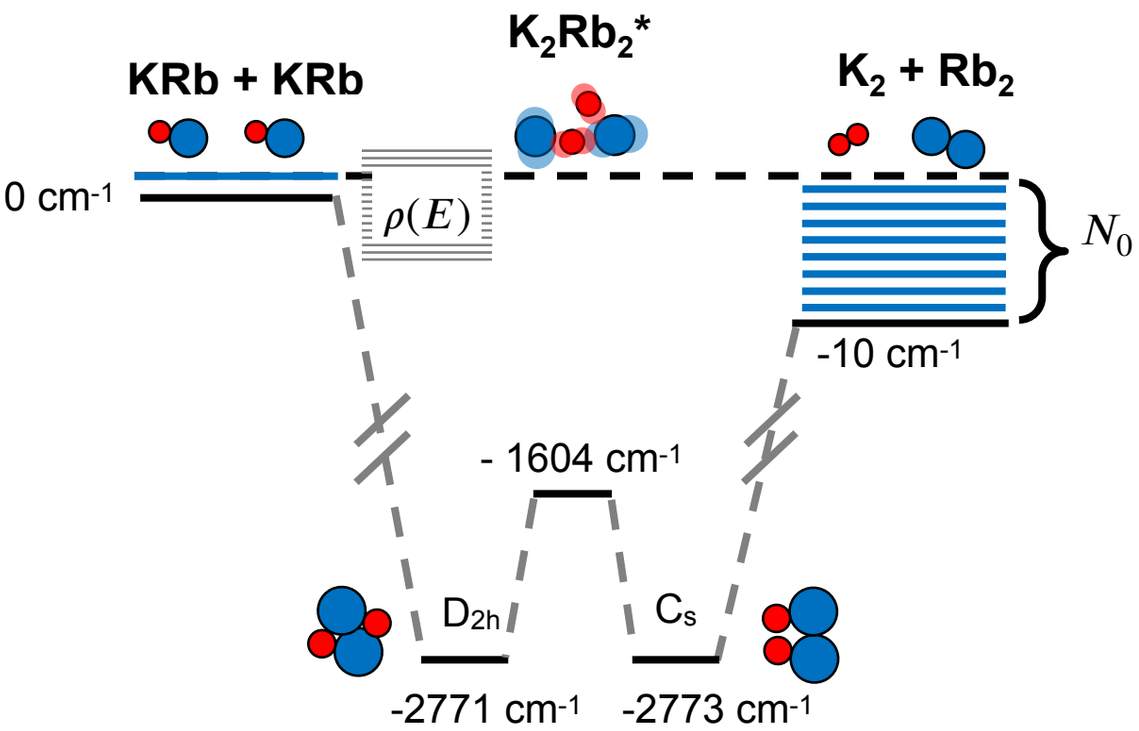
$$P_{K2} = P_{Rb2}$$

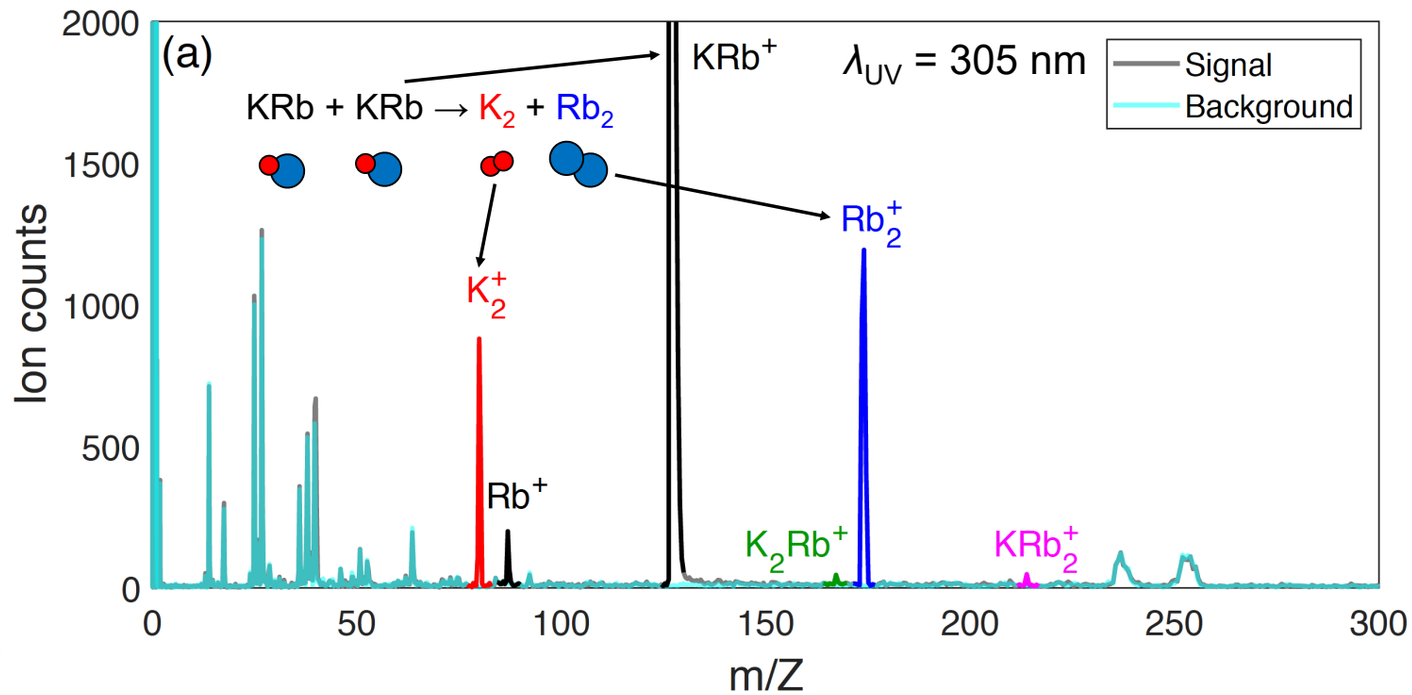
$$\frac{KE_{Rb2}}{KE_{K2}} = \frac{m_{K2}}{m_{Rb2}} = 0.46$$

Surprise #1: ultracold chemical reaction!

Surprise #2: Reaction Complex Detection

$$2KRb \rightarrow K_2Rb_2^* \rightarrow K_2 + Rb_2 + 10\ cm^{-1}$$



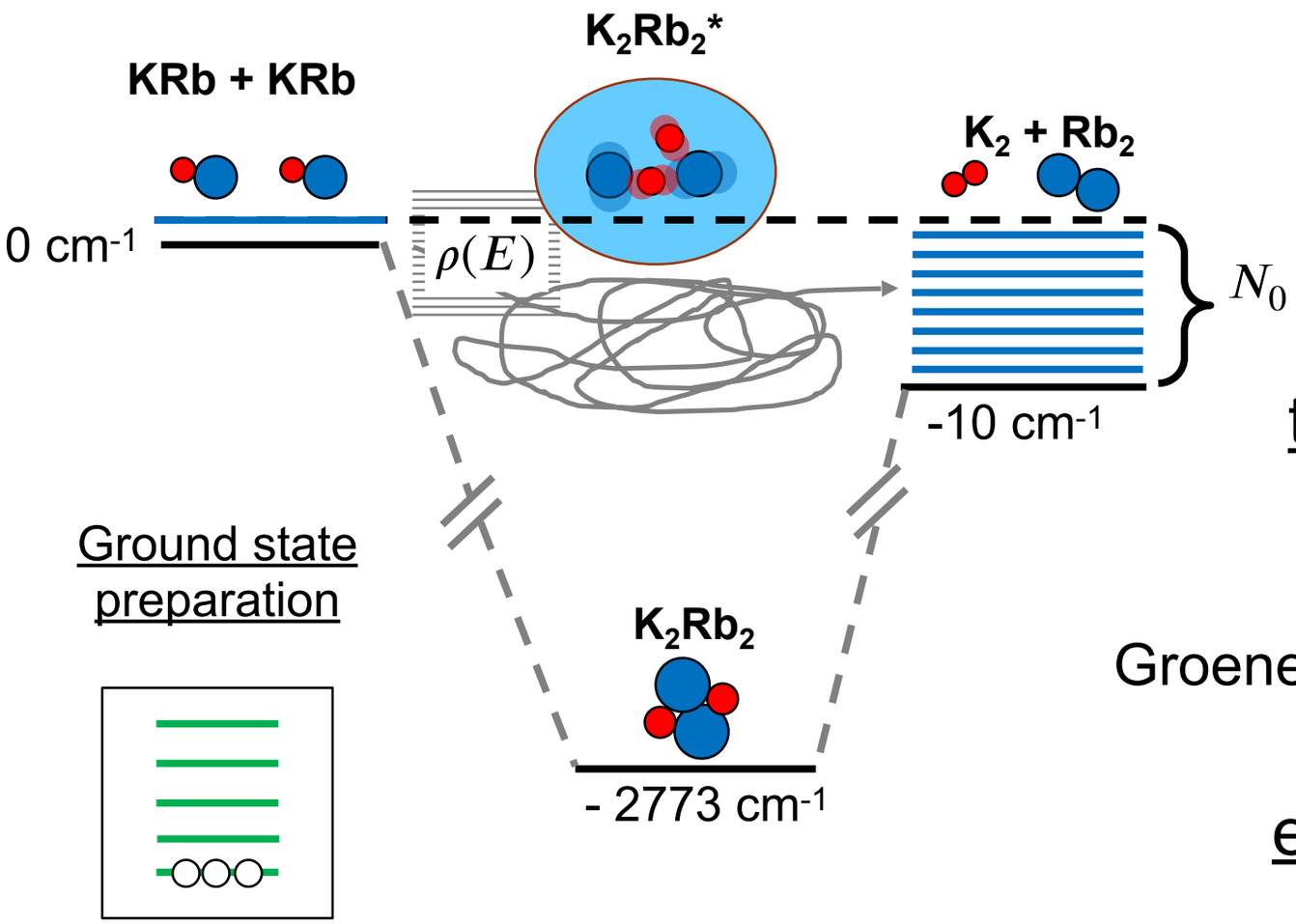


Byrd et al., PRA **82**, 010502 (2010)

Science **366**, 1111 (2019)

The long-lived intermediate complex

>> ps



Ground state preparation

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): $\tau_c = 0.3\ \mu s$

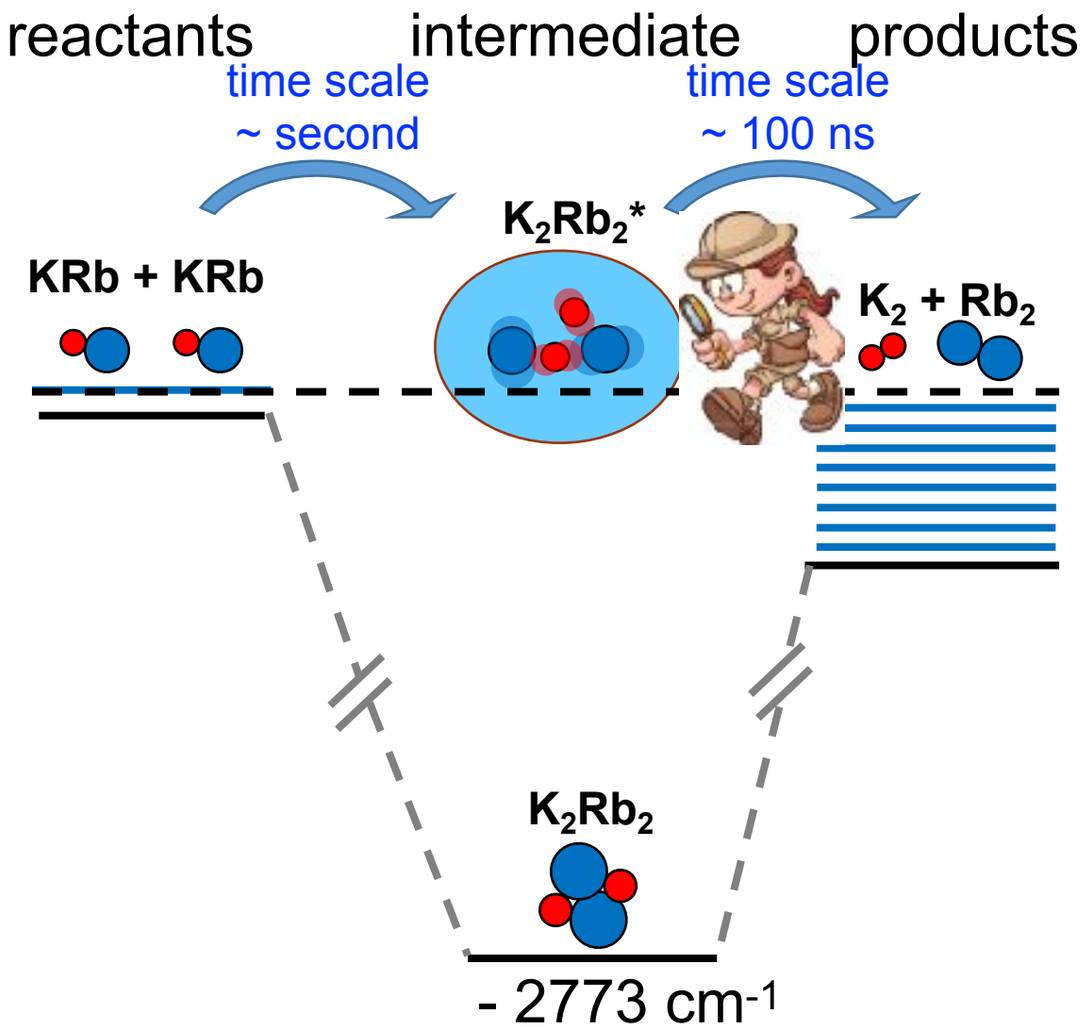
experiment estimated lifetime

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

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

lifetime of the transient intermediate

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



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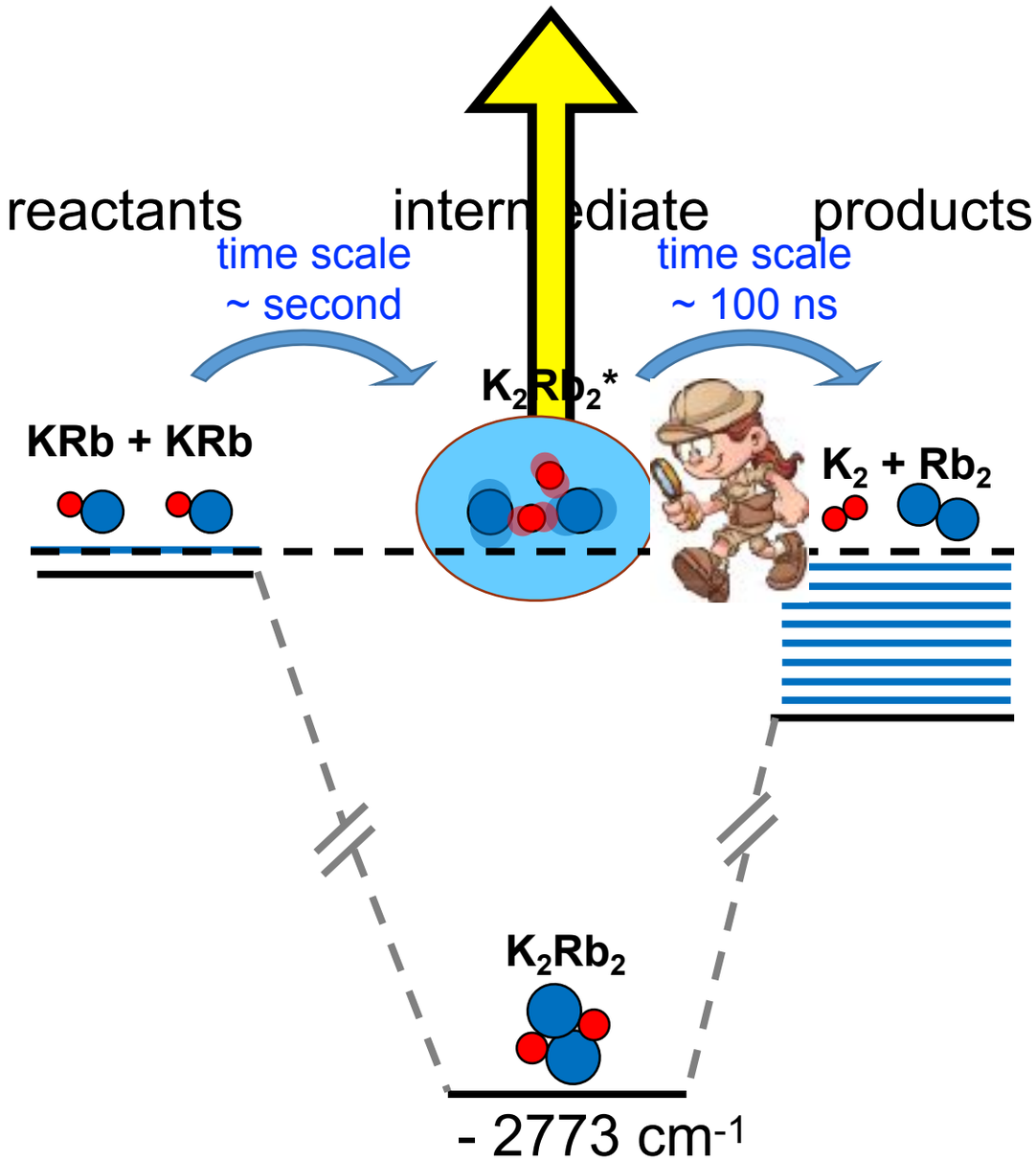
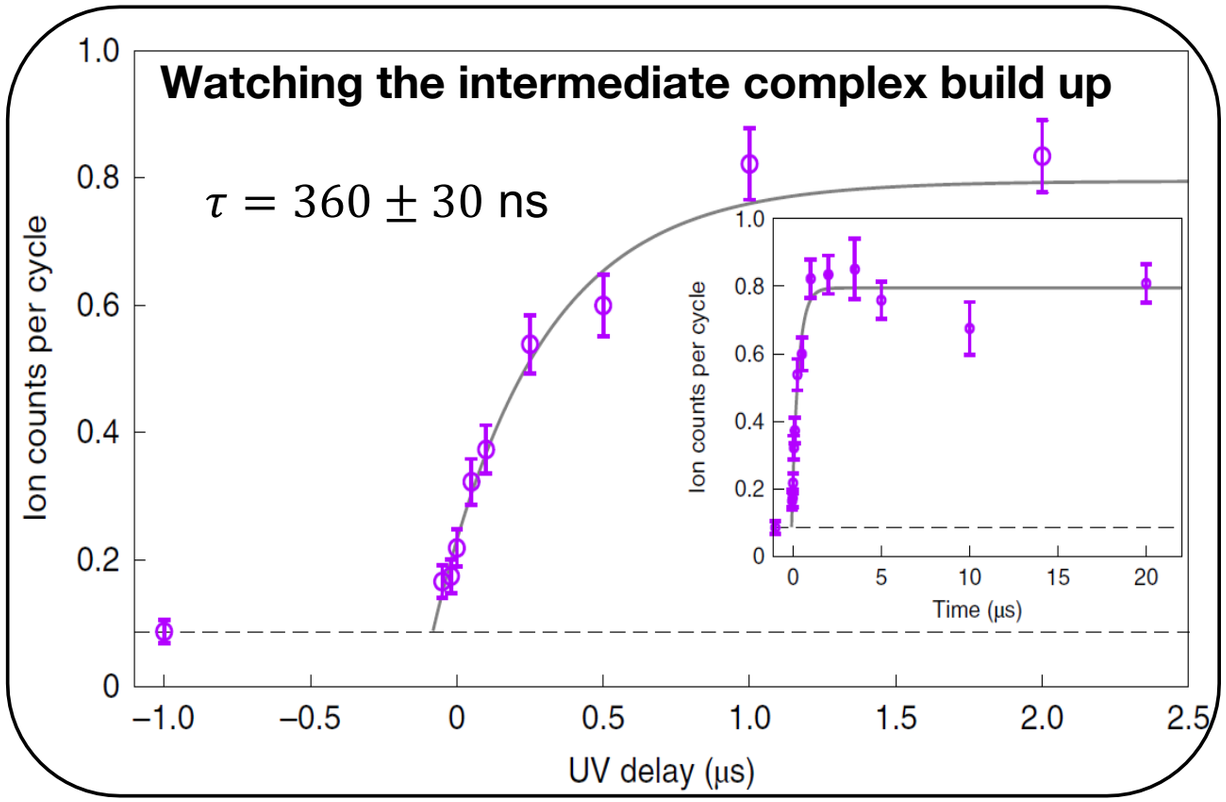
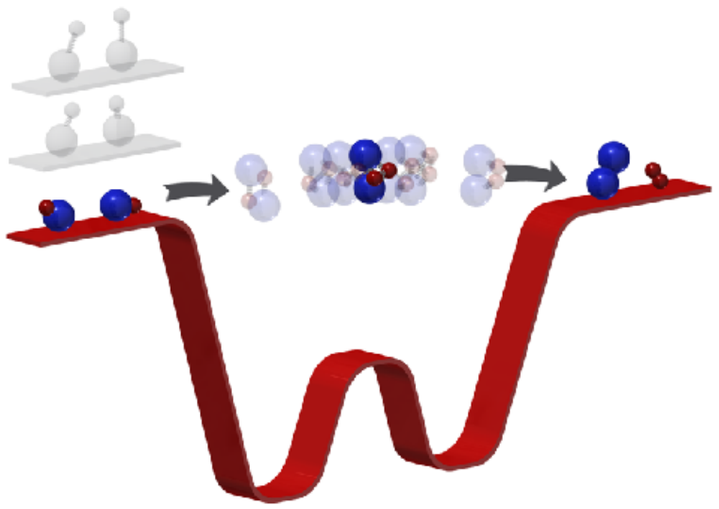


RRKM (from Tijs Karman)

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





Outline

- Total quantum control of molecules from association of atoms
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- Surprise 2 - reactions play out in “slow motion”
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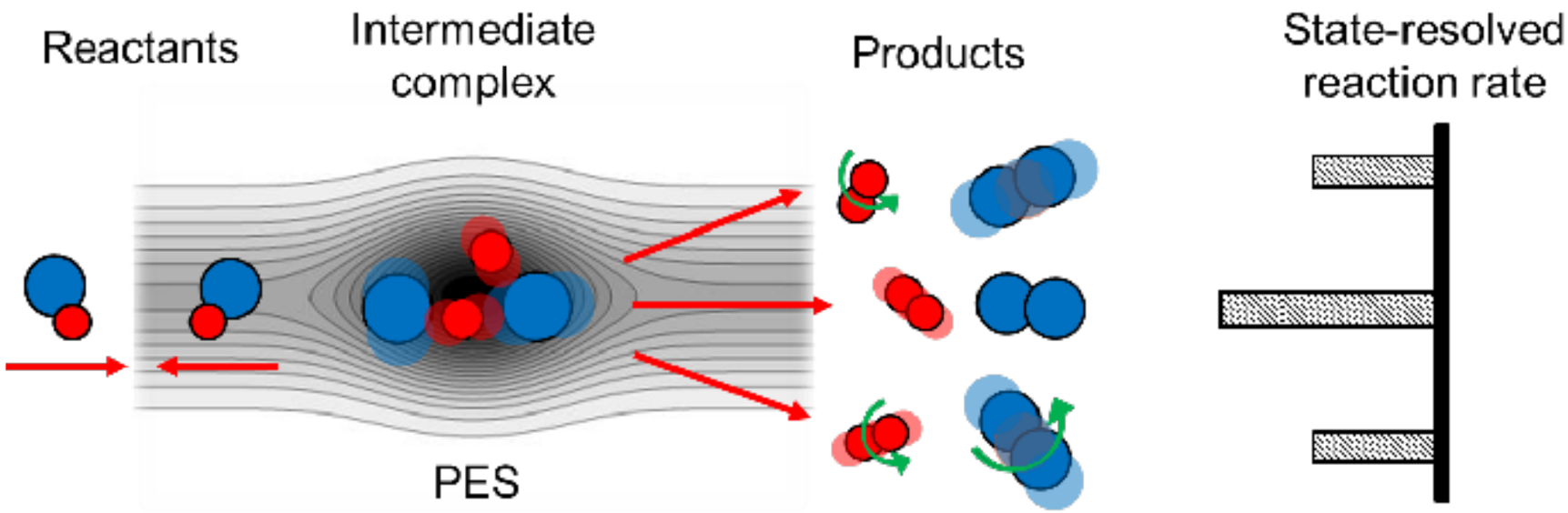
- Complete characterization of reactive process -
  mapping quantum states of correlated reaction product pairs

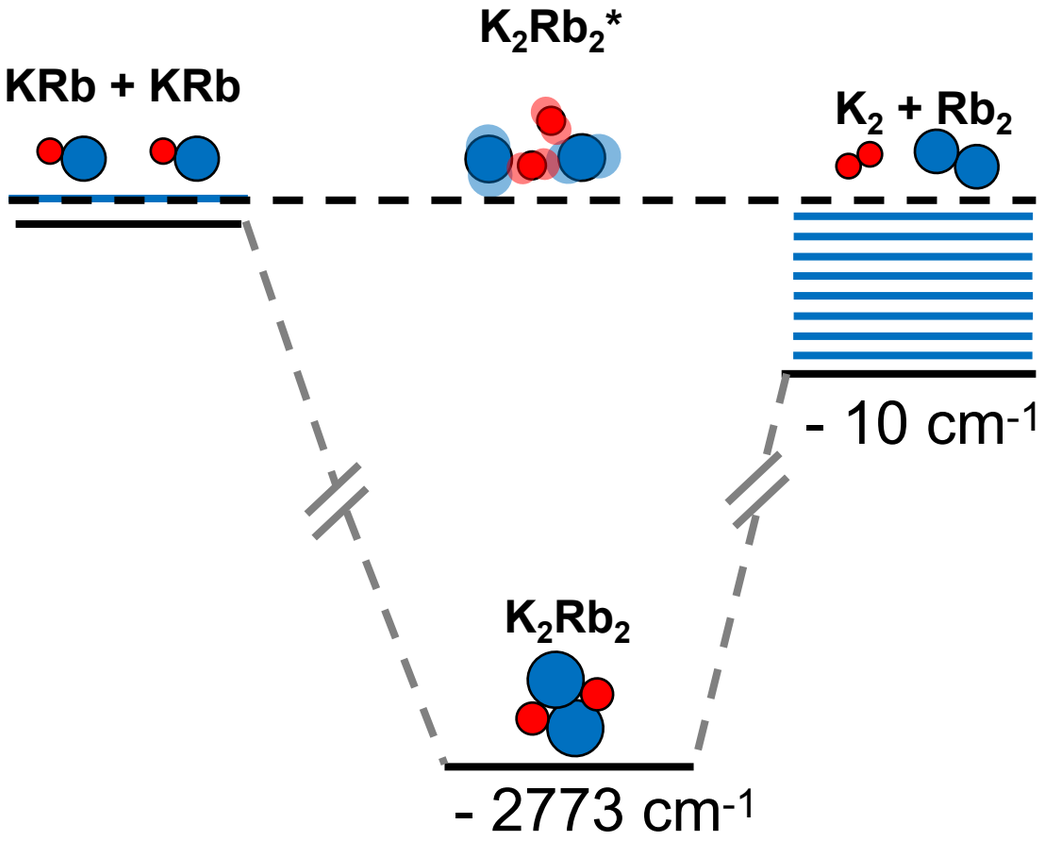
Chemical Reaction: a scattering problem



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

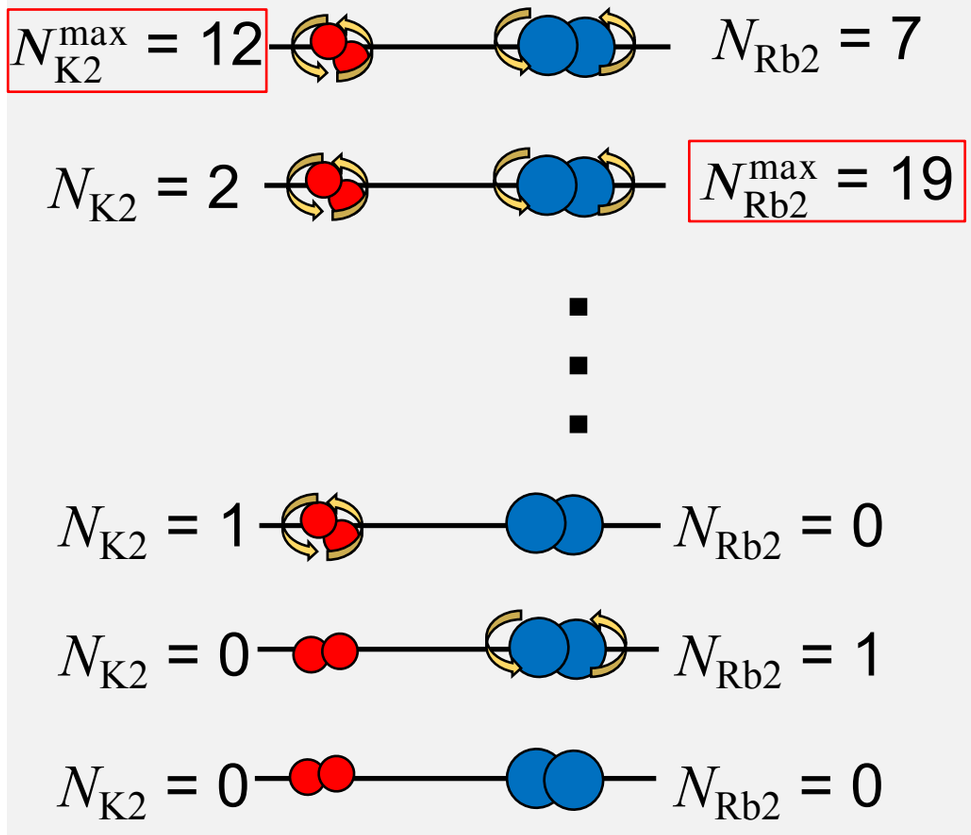
Possible quantum states of the products



No vibrational excitation

$(v_{K2} = v_{Rb2} = 0)$

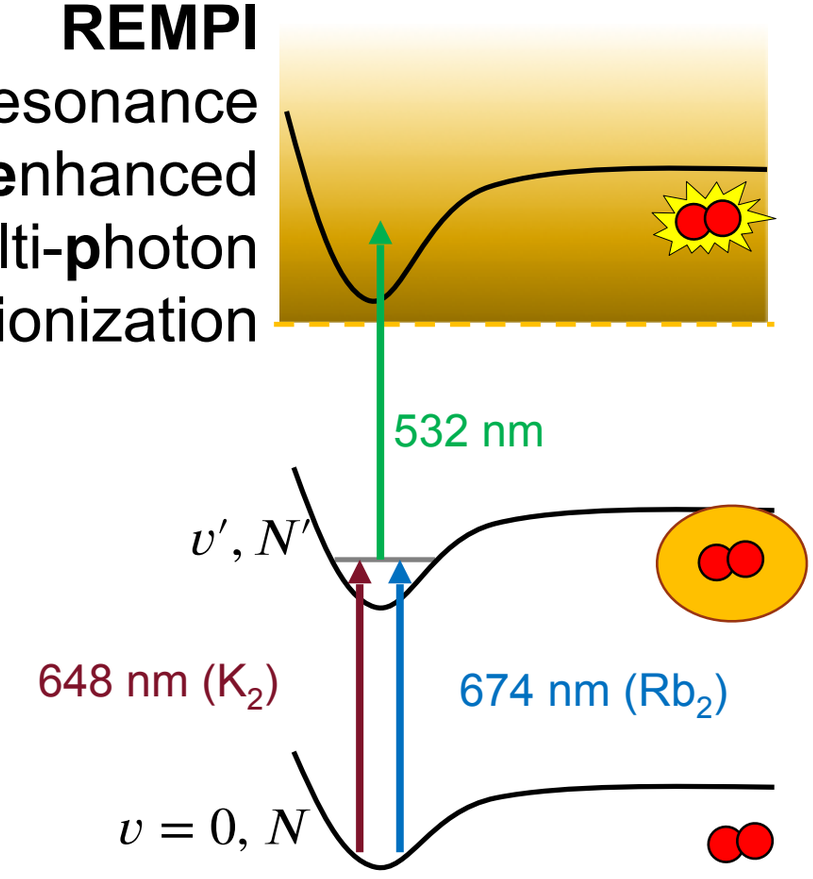
Rotational excitation

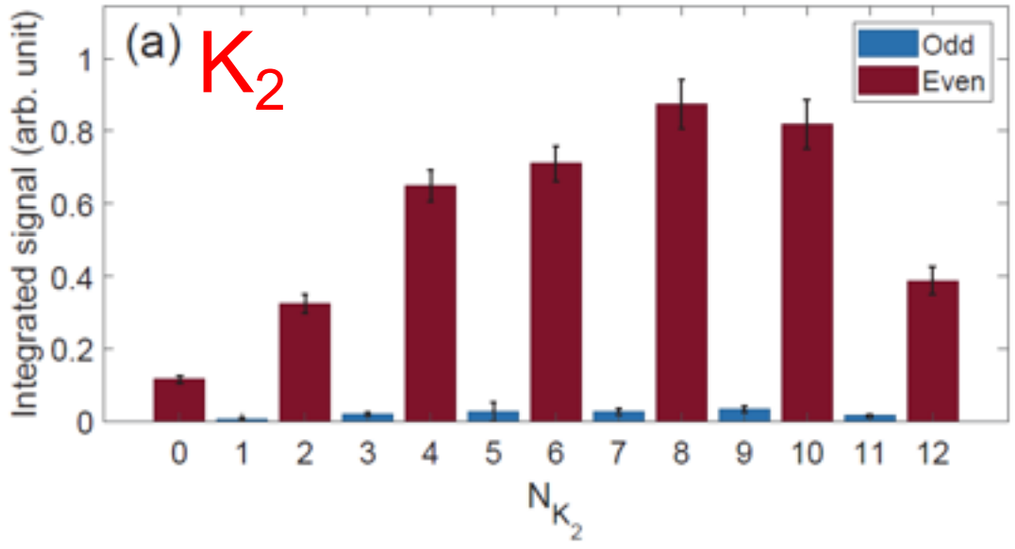


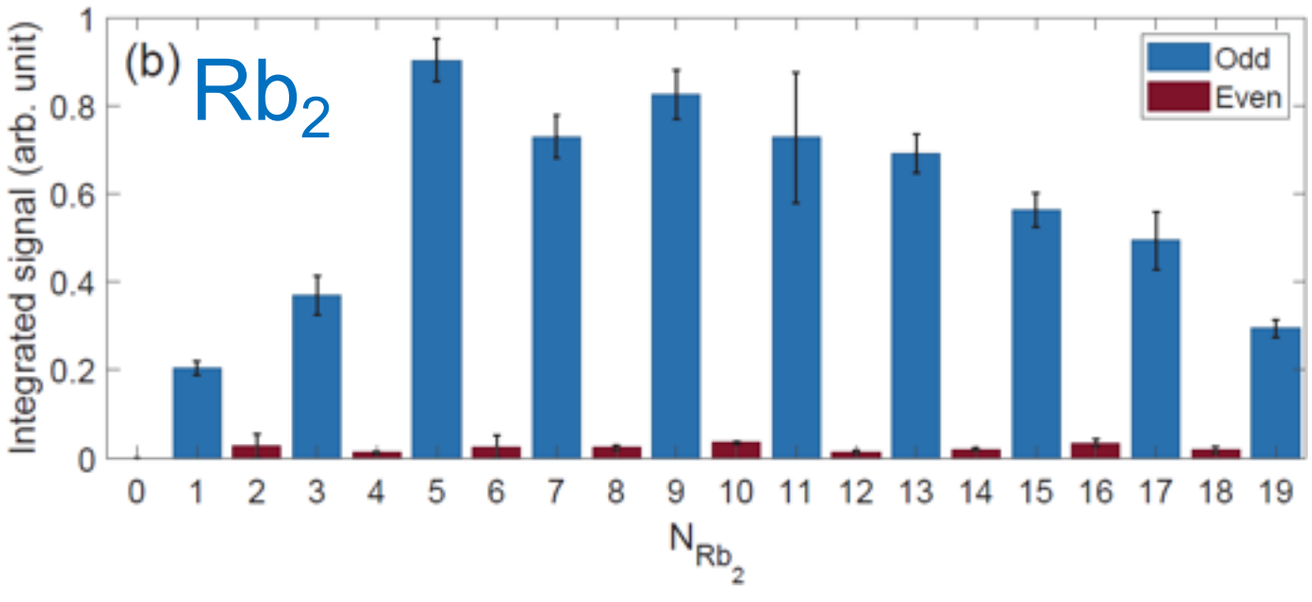
Rotational state distributions of K_2 and Rb_2

Strong parity preference → Nuclear spin conservation!

REMPI
Resonance
enhanced
multi-**p**hoton
ionization





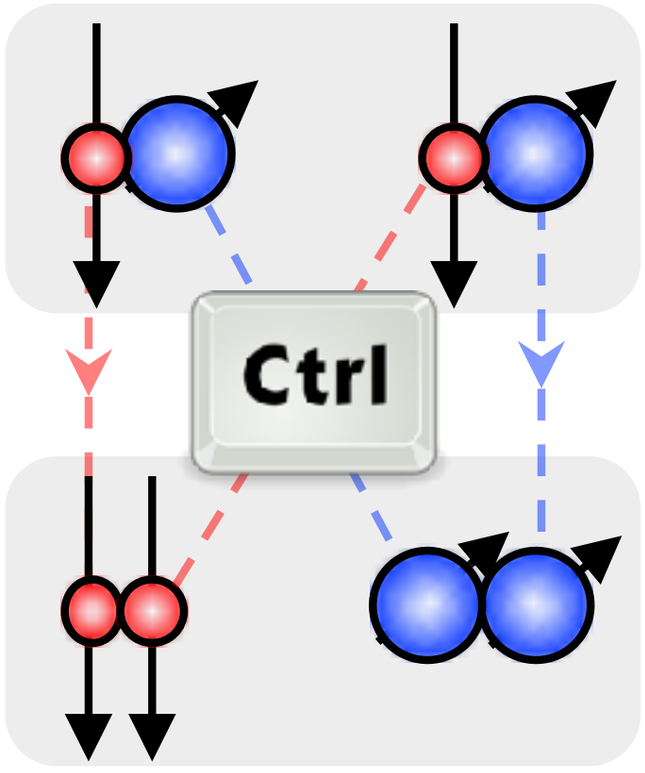


Hu, Liu et. al, Nature Chemistry **13**, 435-440 (2021)

Rotational state distributions of K_2 and Rb_2

Strong parity preference → Nuclear spin conservation!

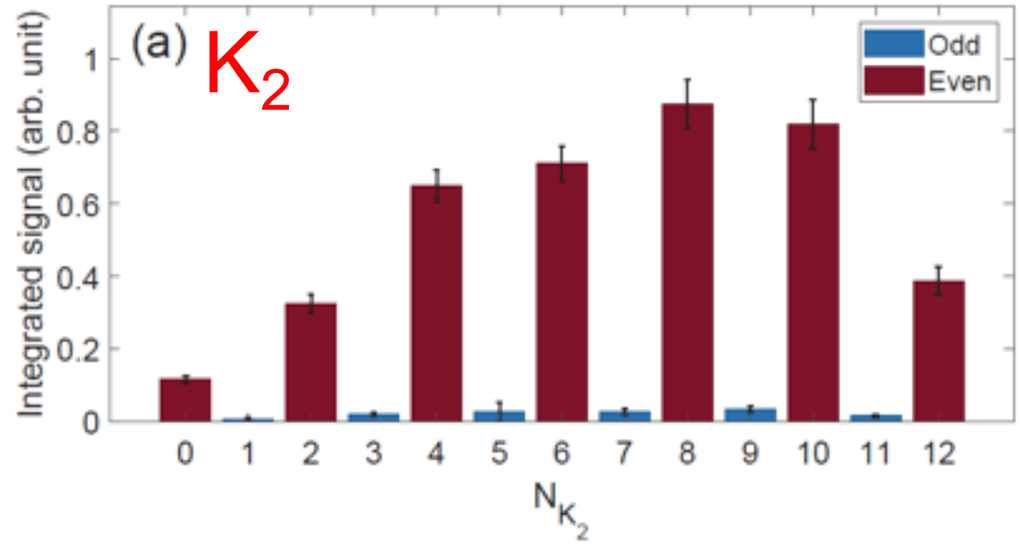
Reactants:

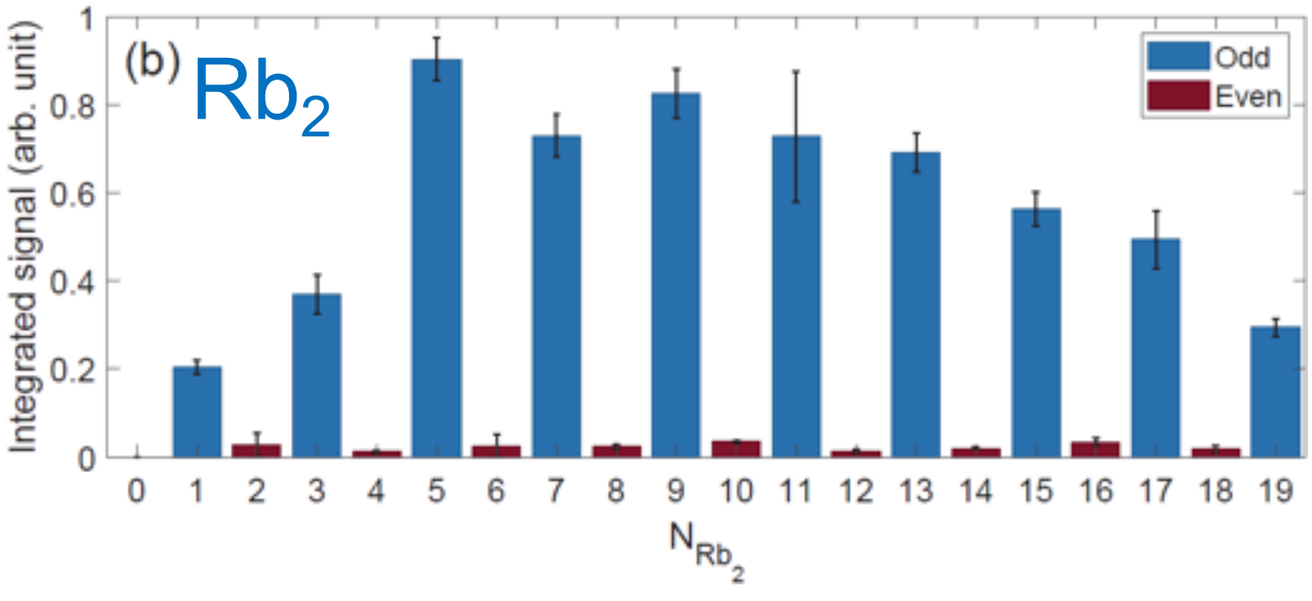


Products:

Nuclear statistics: Bosonic nuclei Fermionic nuclei

Allowed rotations: $N_{K2} = even$ $N_{Rb_2} = odd$

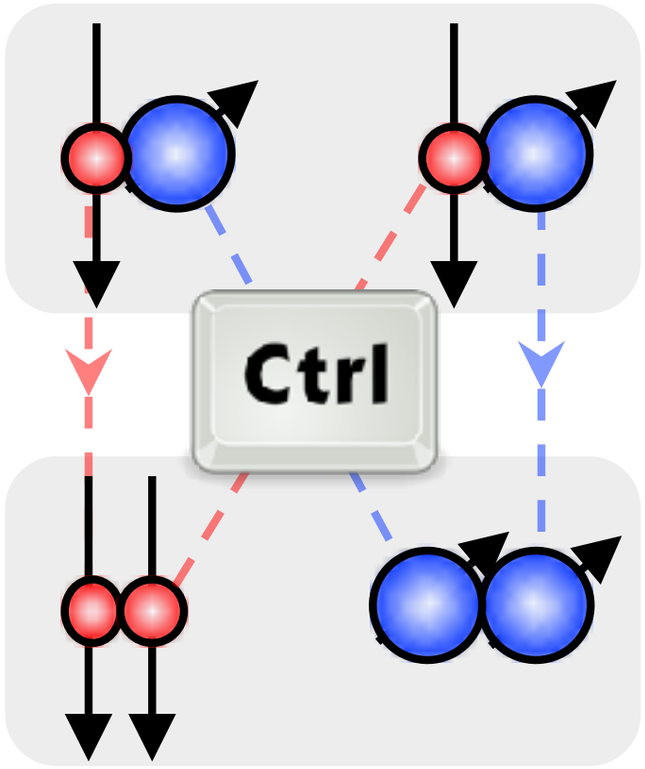




Rotational state distributions of K_2 and Rb_2

Strong parity preference → Nuclear spin conservation!

Reactants:



Products:

Nuclear statistics: Bosonic nuclei Fermionic nuclei

Allowed rotations: $N_{K2} = even$ $N_{Rb_2} = odd$

Adjust input spin state:

$$\alpha \left| \quad \right\rangle + \beta \left| \quad \right\rangle + \gamma \left| \quad \right\rangle$$

to control output rotation state:

$$N_{K_2} = \begin{cases} even \\ odd \end{cases} \qquad N_{Rb_2} = \begin{cases} odd \\ even \end{cases}$$

Continuous control of product population

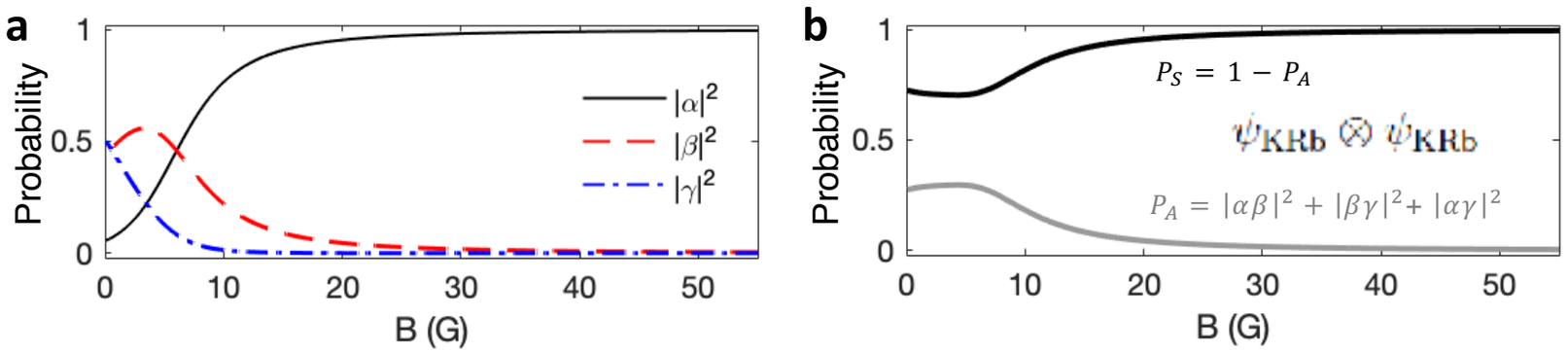
$$\alpha \left| \uparrow\downarrow \right\rangle + \beta \left| \downarrow\downarrow \right\rangle + \gamma \left| \uparrow\uparrow \right\rangle$$

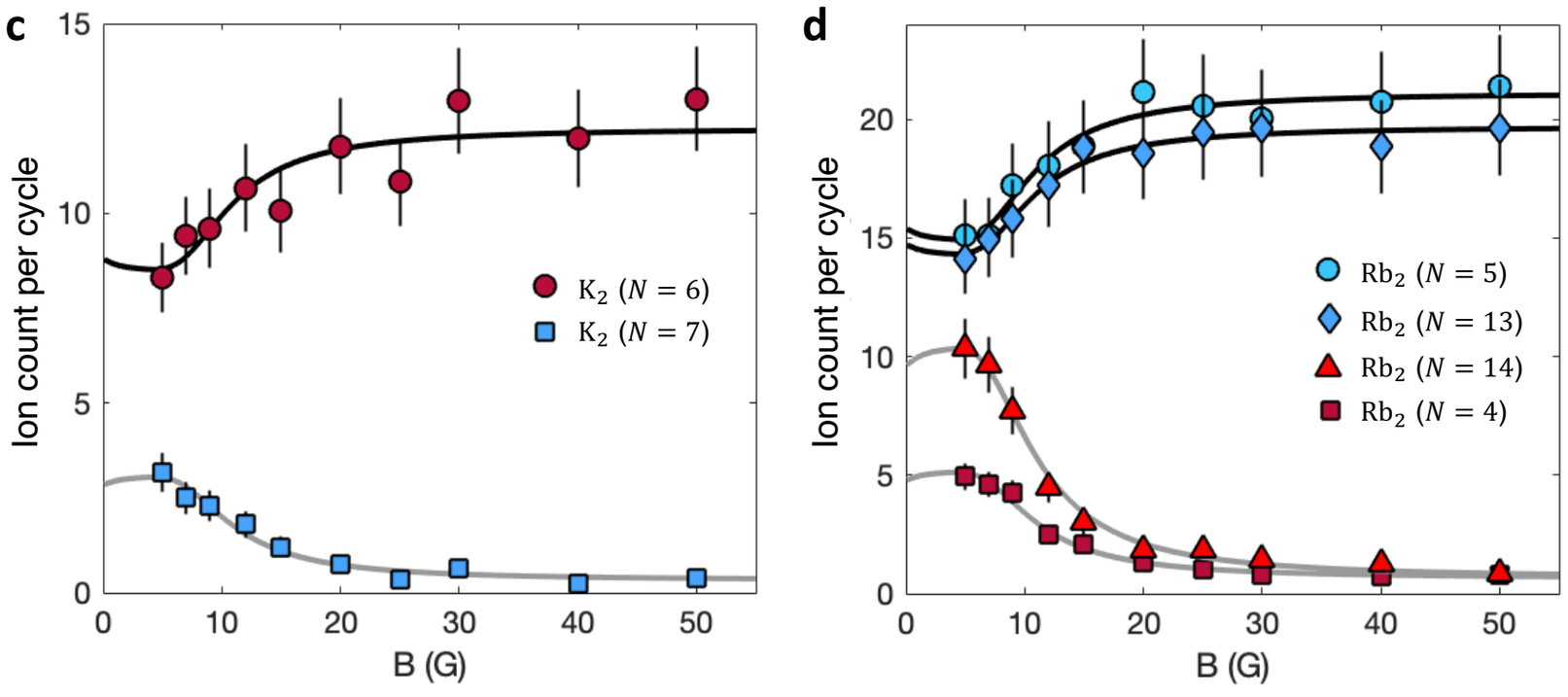
antisymmetric spin state

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

symmetric spin state

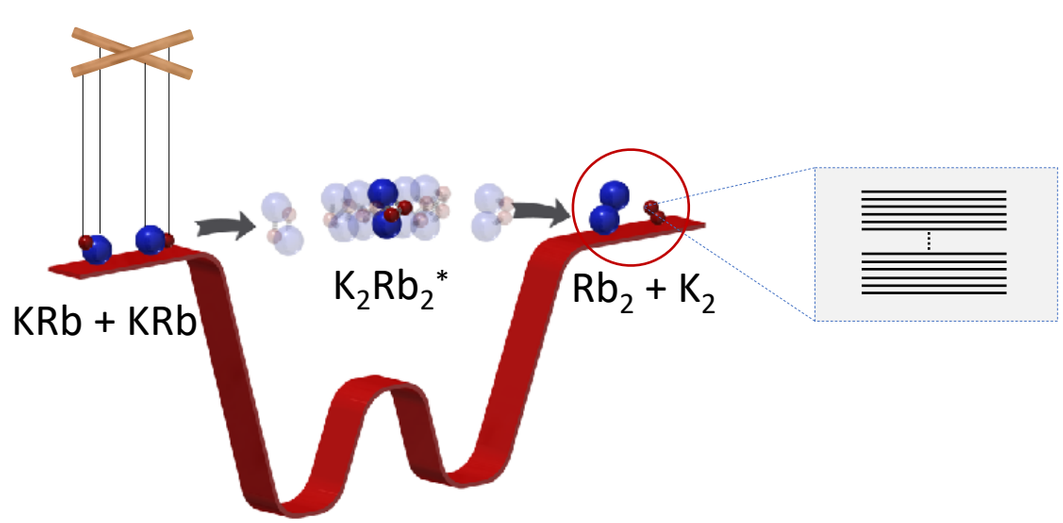
$$P_S = 1 - P_A$$





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

Surprise#4: despite a long-lived complex, we can control the product rotational state parity via the nuclear spin of the reactants

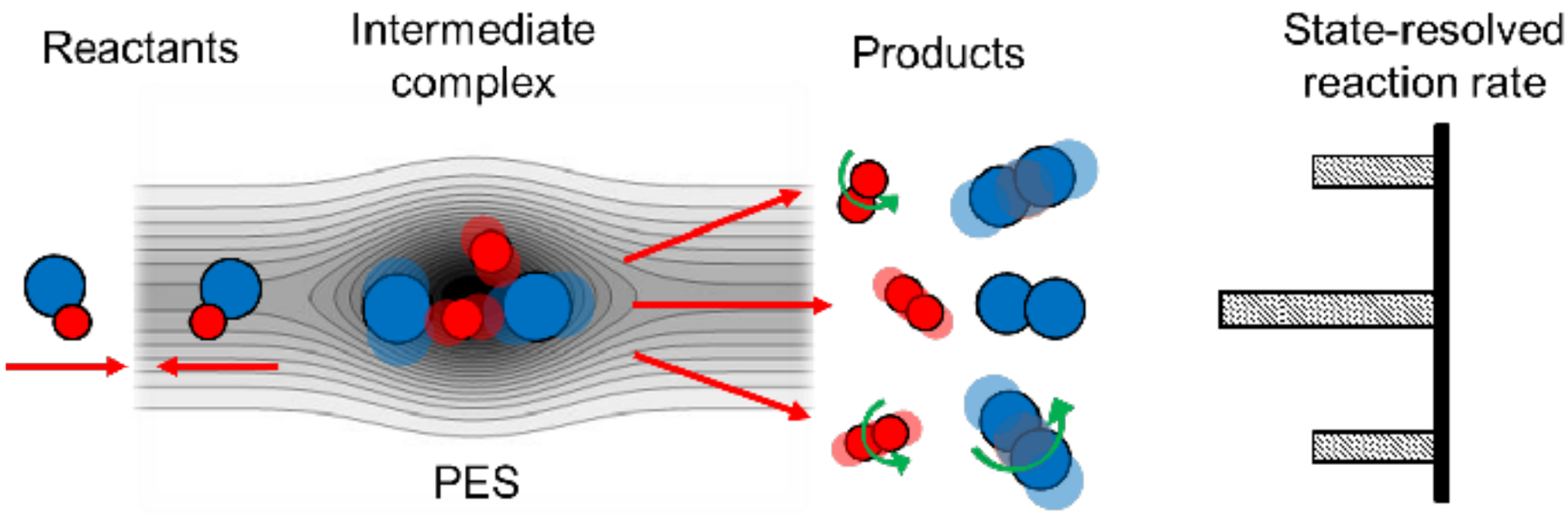


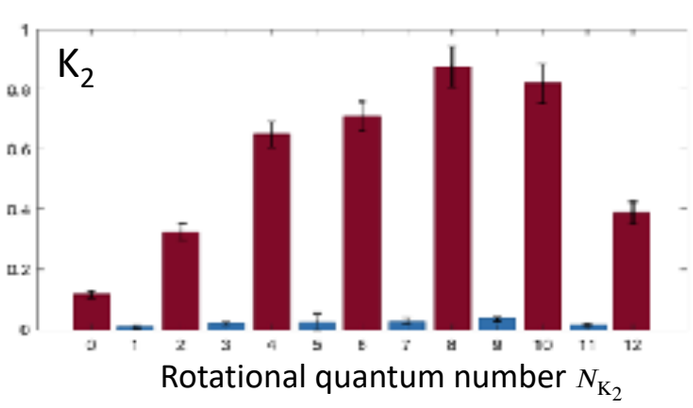
Future direction:

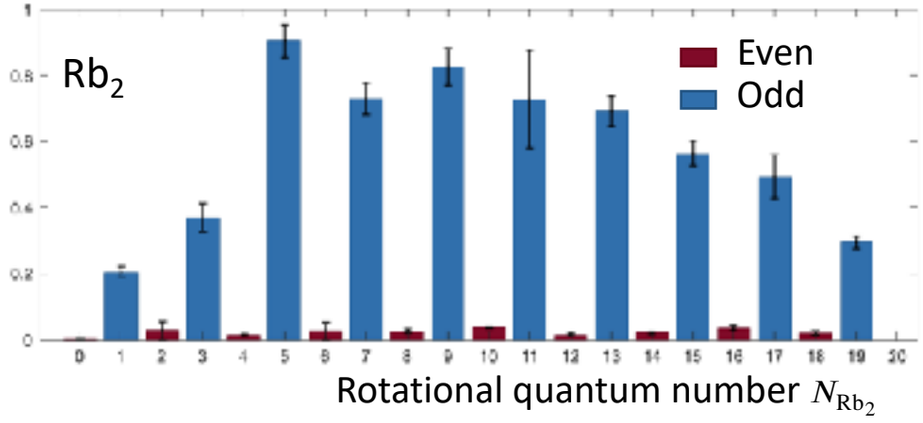
Quantum entanglement between rotational states of products

$$\psi^{\mathrm{R}}_{\mathrm{products}} = \sqrt{P_S}\ |\mathrm{even}, \mathrm{odd}\rangle + \sqrt{P_A}\ |\mathrm{odd}, \mathrm{even}\rangle.$$

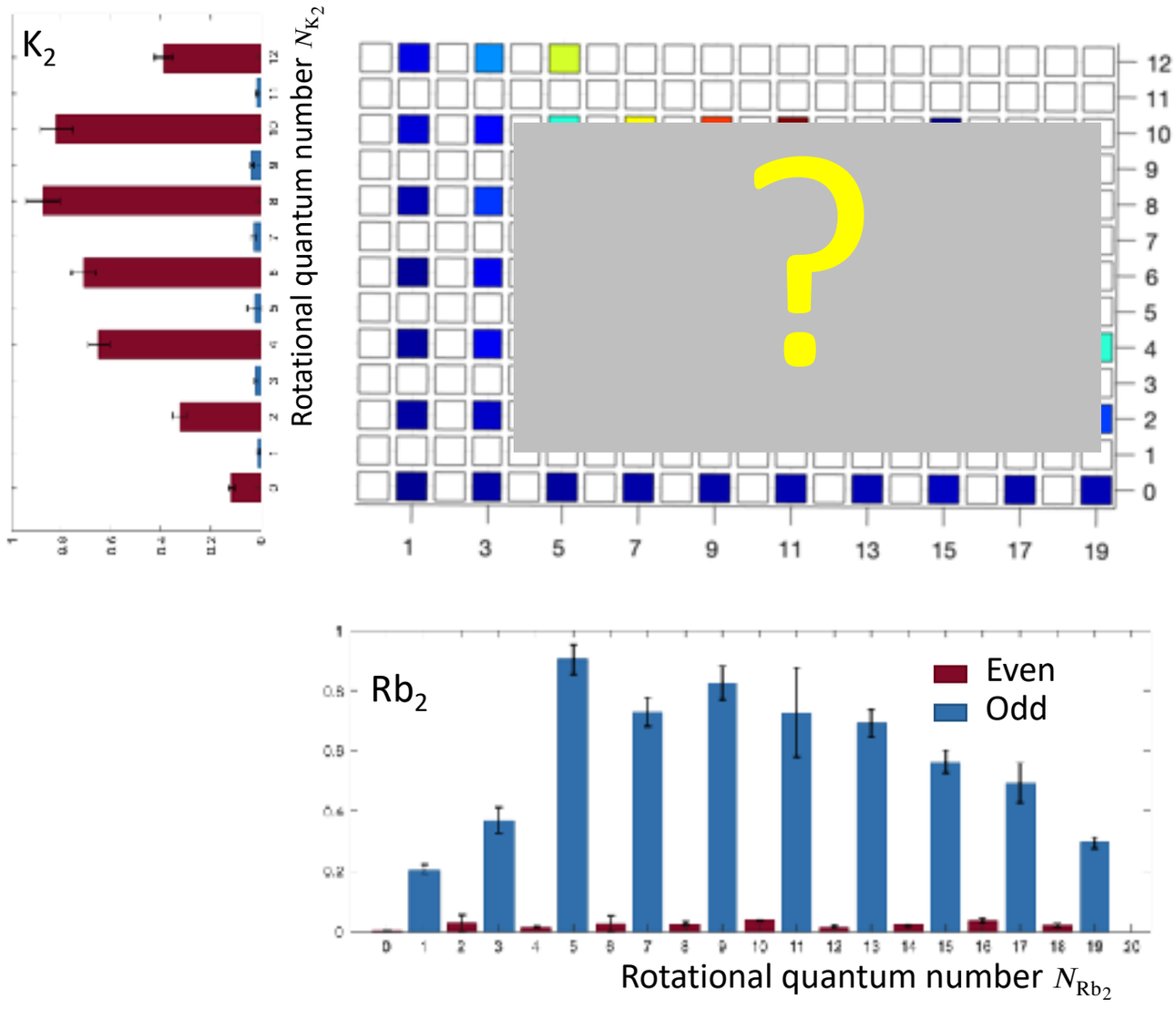
Chemical Reaction: a scattering problem





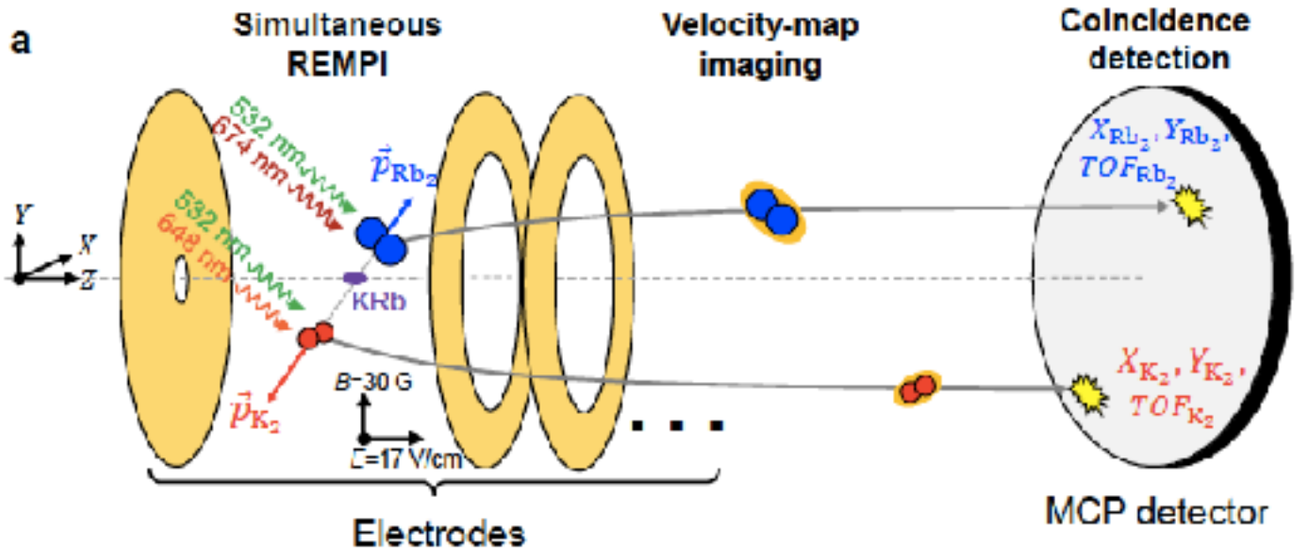


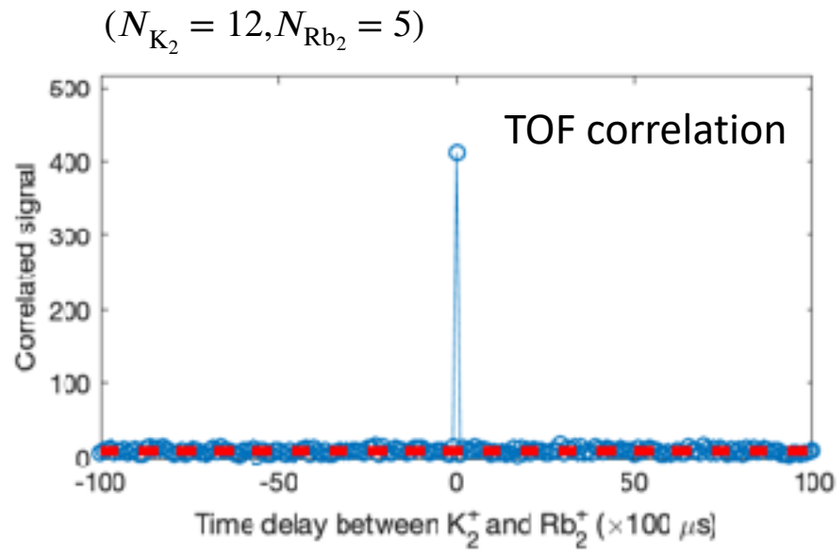
Complete product state mapping



Need simultaneous detection on K_2 and Rb_2 products that are formed from a single event

Coincidence detection

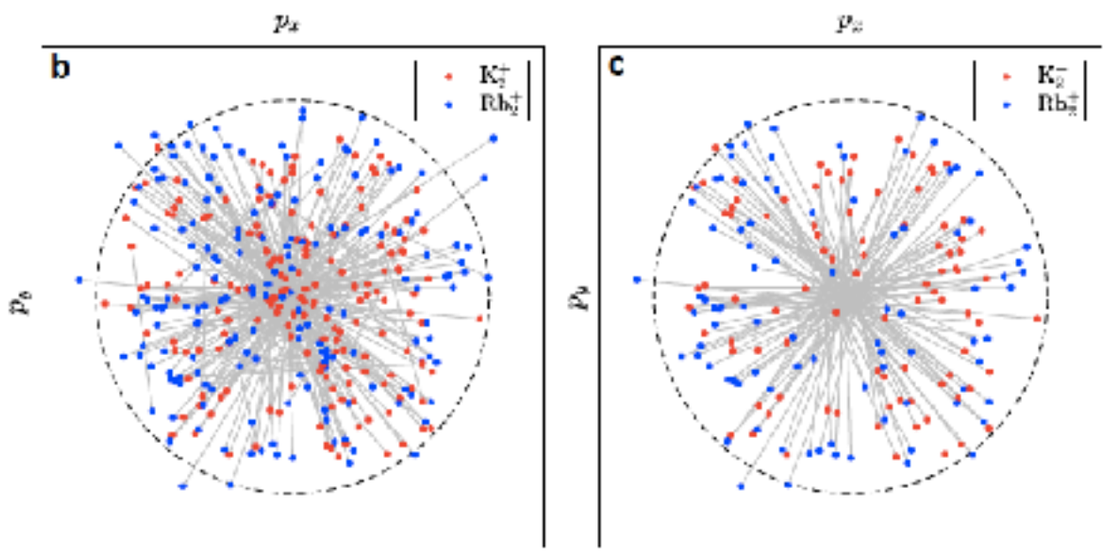




Momentum conservation constrains:

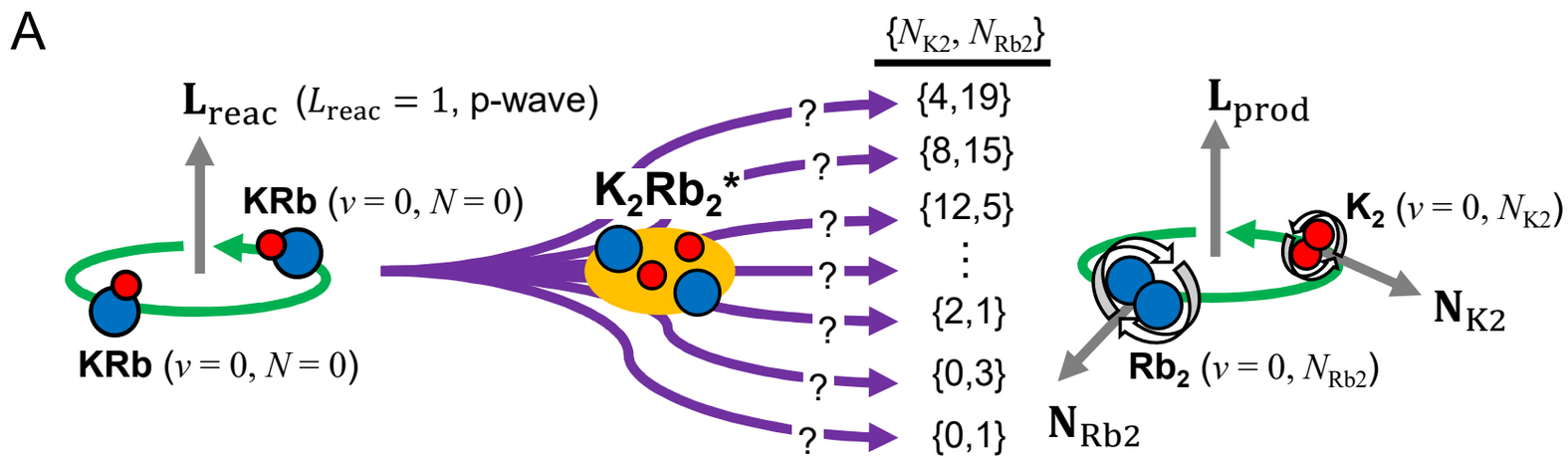
$$\vec{P}_{K_2} + \vec{P}_{Rb_2} = \vec{P}_{KRb} + \vec{P}_{KRb} \to 0$$

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

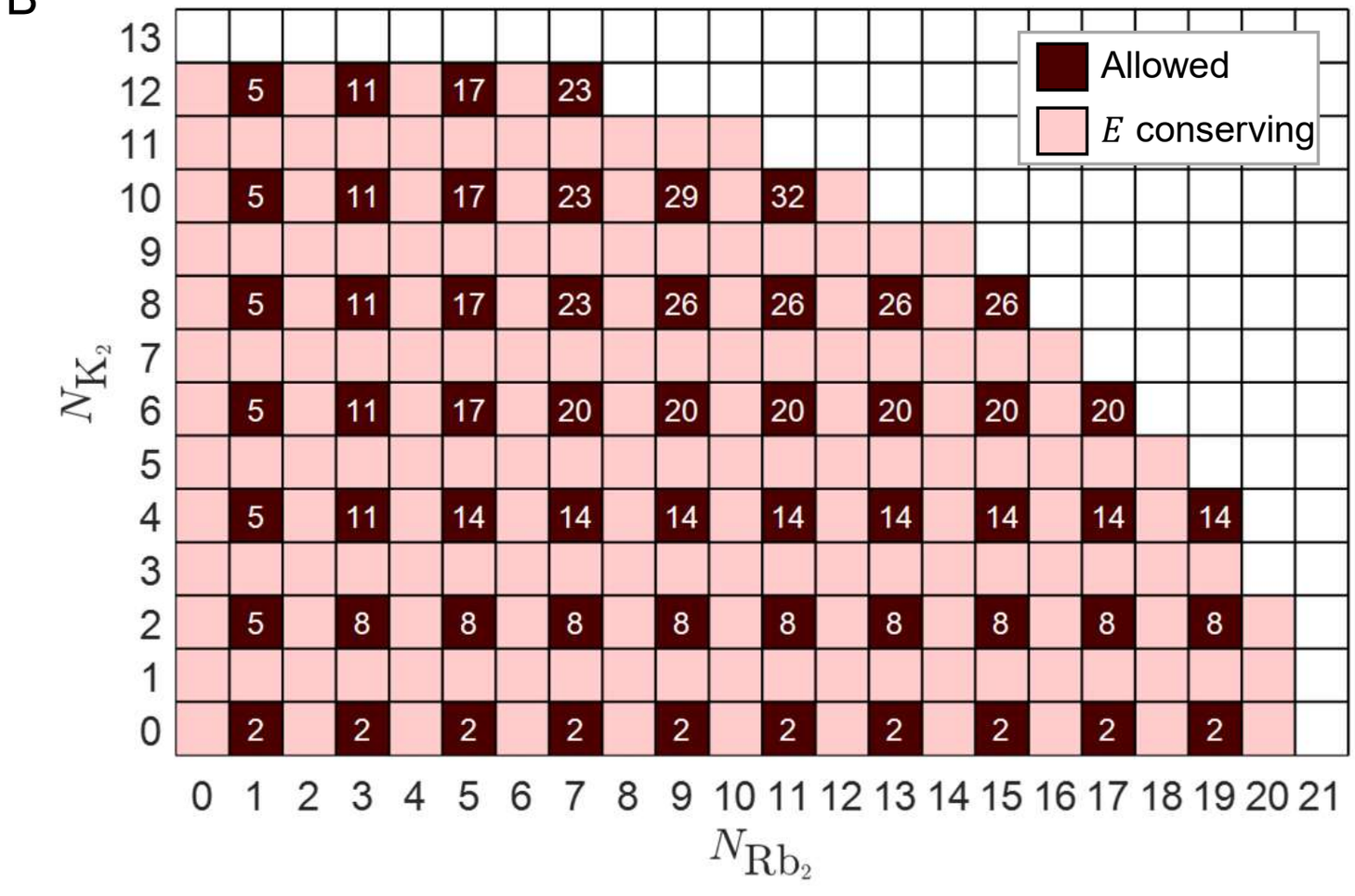


Non-trivial statistical distribution

A

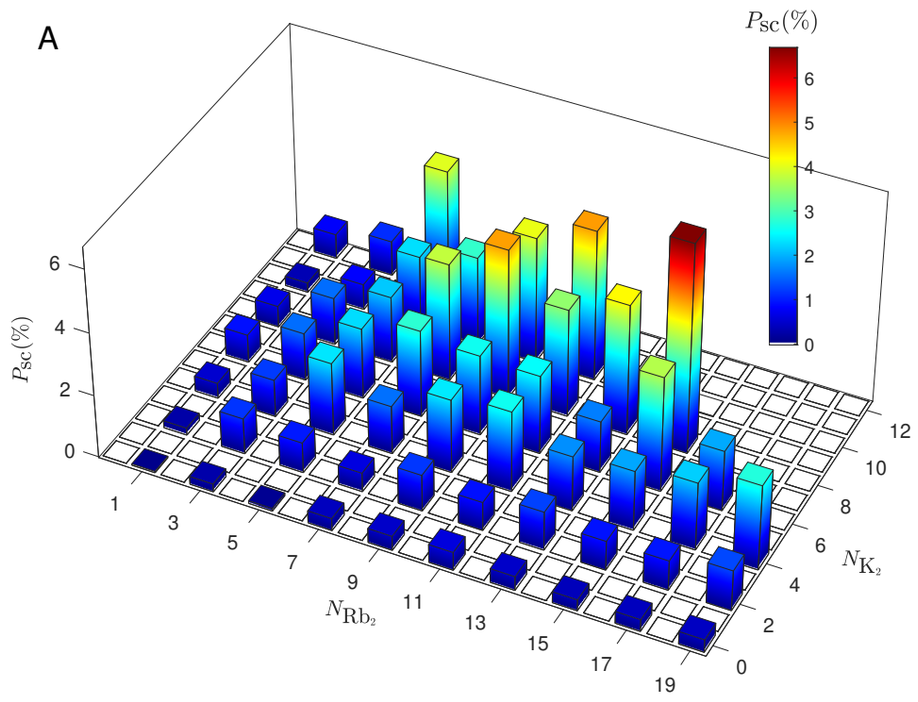


B



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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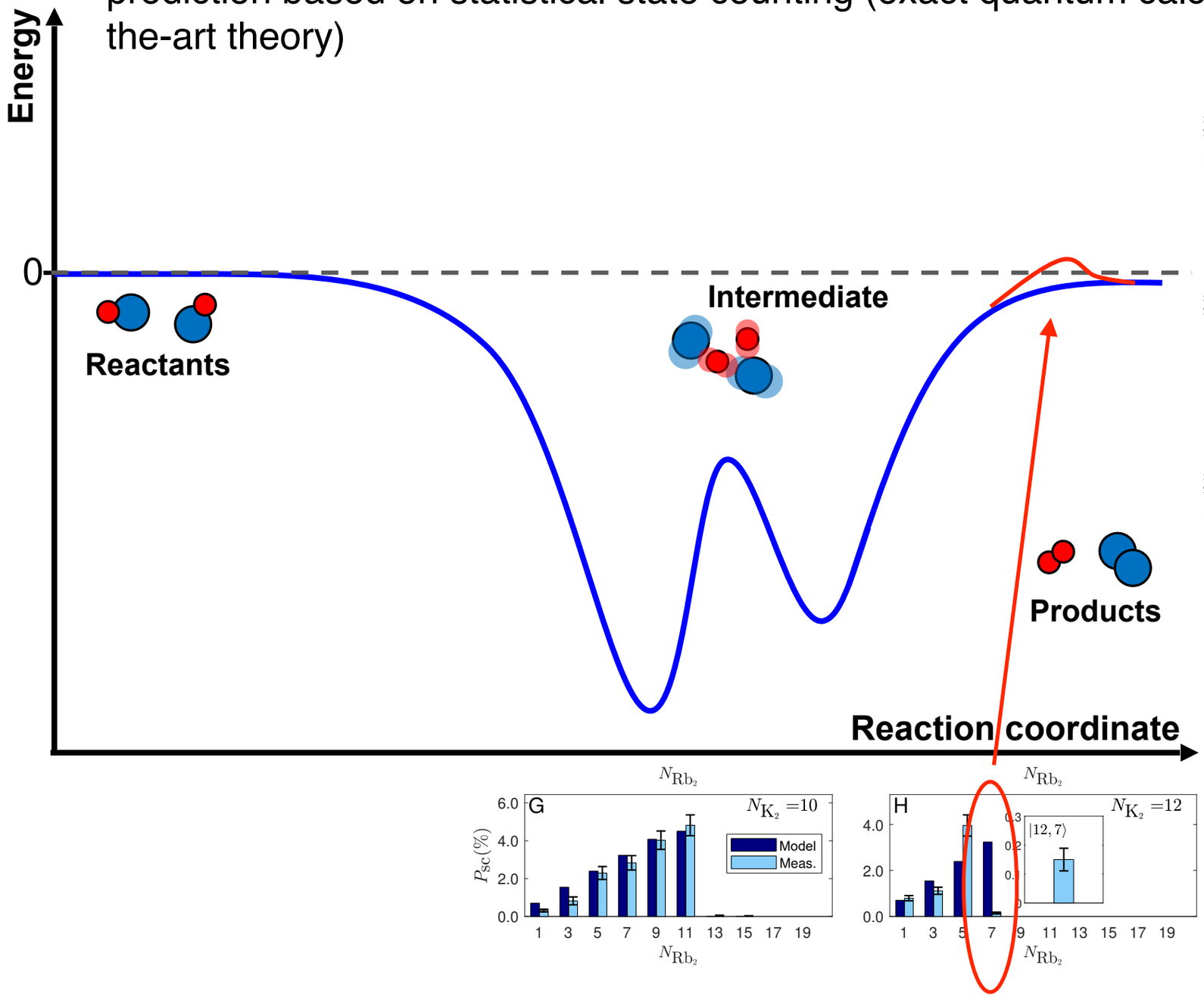
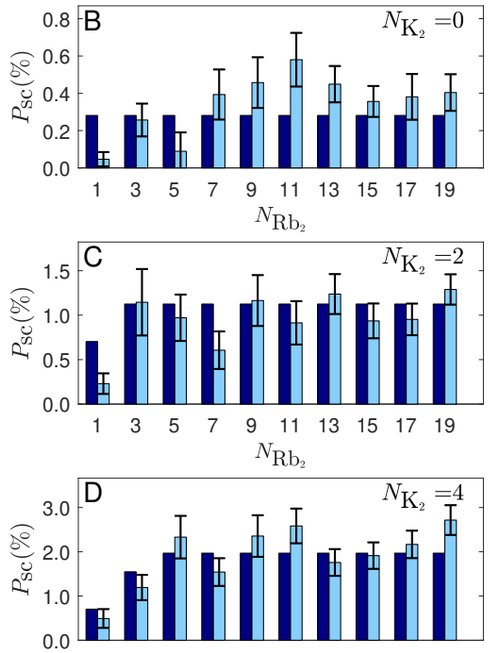


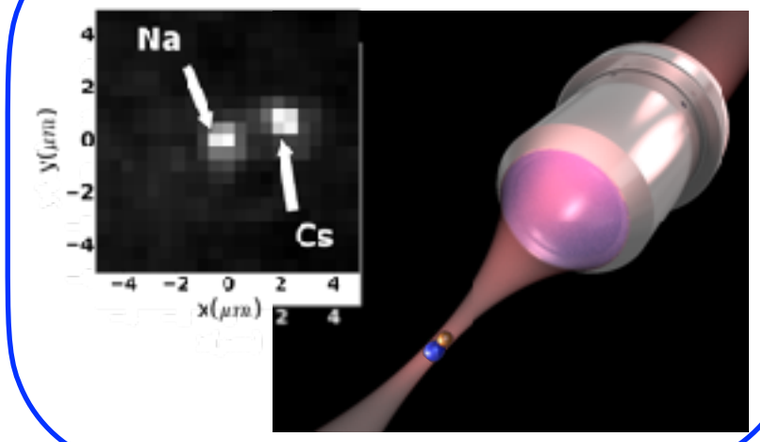


Yu Liu*, Ming-Guang Hu*, Matthew A. Nichols, D. Yang, D. Xie, H. Guo, Kang-Kuen Ni, Nature **593**, 379-384 (2021)

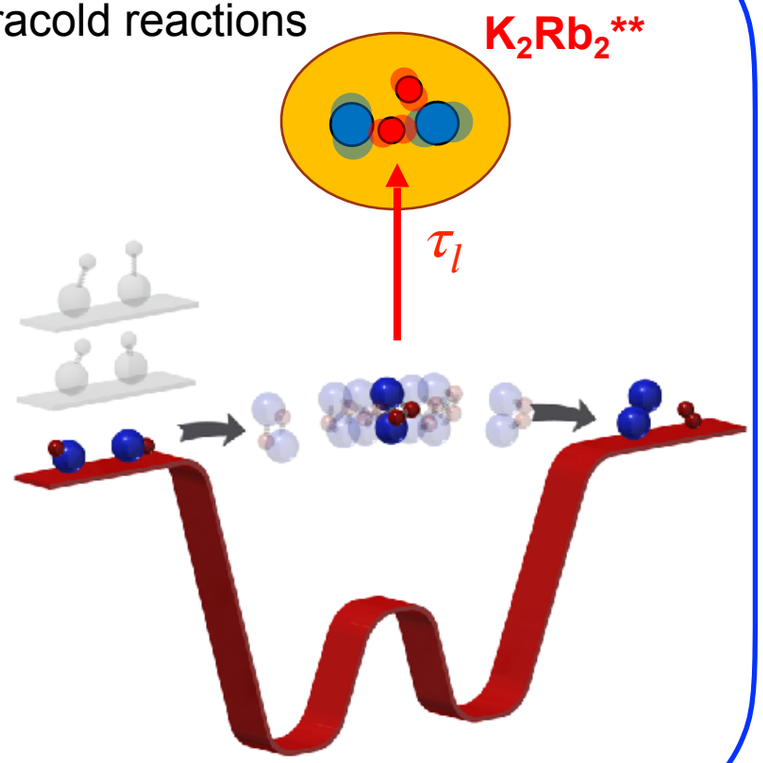
Summary and Outlook

- Quantum control of molecules is essential for “quantum sciences with molecules”
- We built fully control individually molecular qubit and will harness intrinsic molecular properties for quantum simulations and computations
- We brought chemistry and physics tools together to completely characterize a reactive process at a “ultra cold” temperature
- We will leverage our understanding of chemical reactions for future quantum science applications

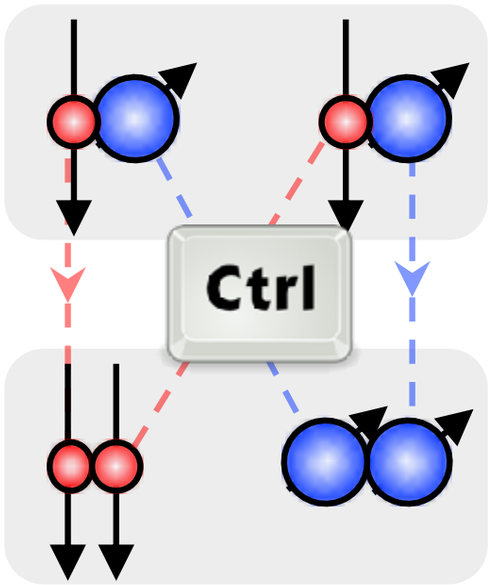
Building molecules atom-by-atom



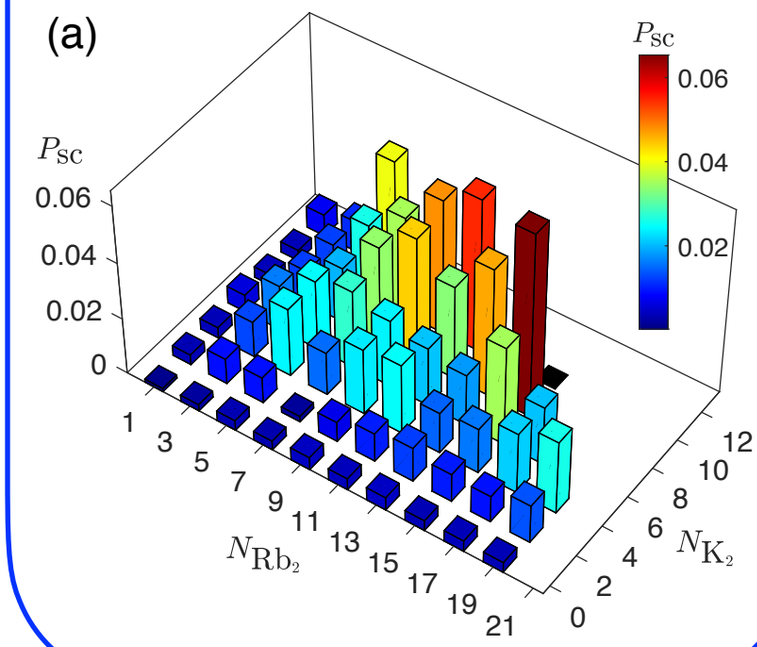
Observation and steering ultracold reactions



Control of reaction product quantum states

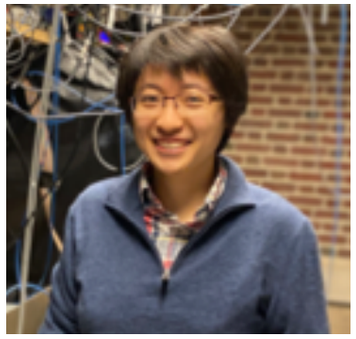


Complete characterization of bimolecular reactions



Acknowledgments

Current members



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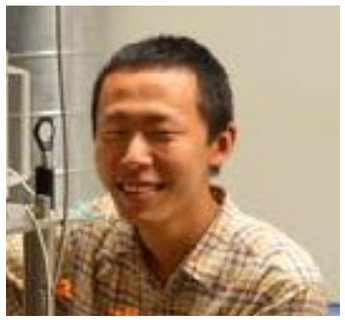

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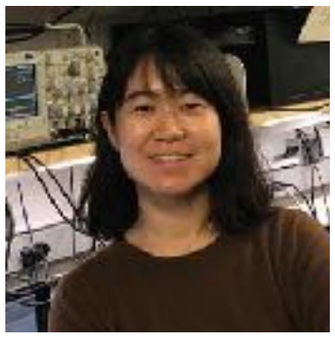

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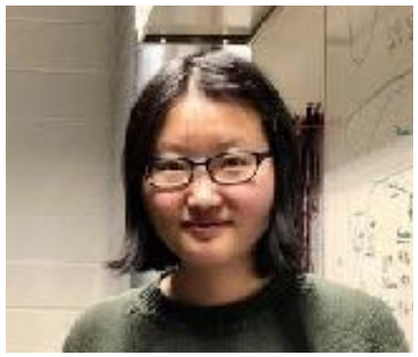

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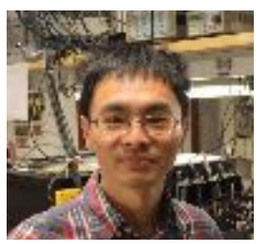

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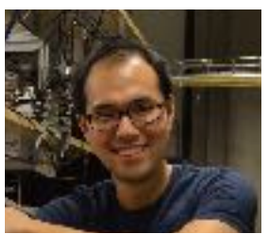

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