Reaction rates of ultra-cold $^6Li_2$ dimers

Quantum state dependent chemistry

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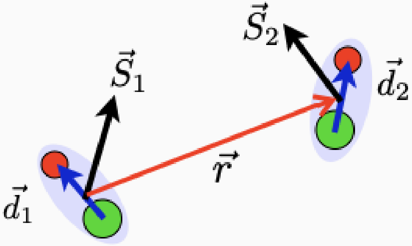
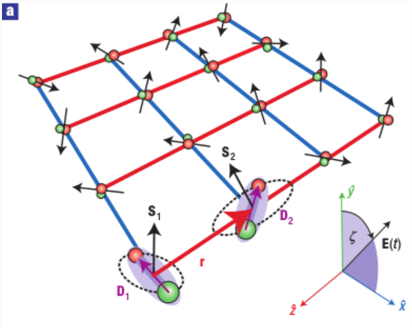
Background and Motivation

Micheli et al. [2006] A toolbox for lattice-spin models with polar molecules





Reaction Channels

Two possibilities for homonuclear alkali dimers:

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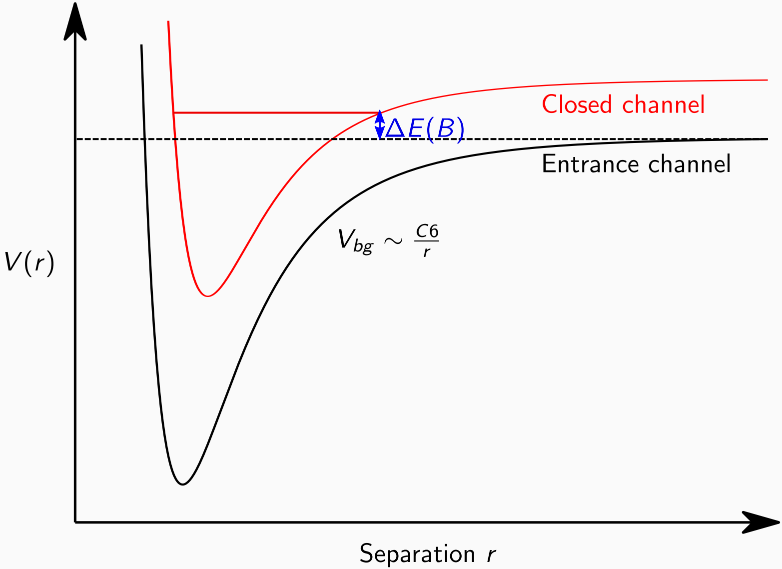
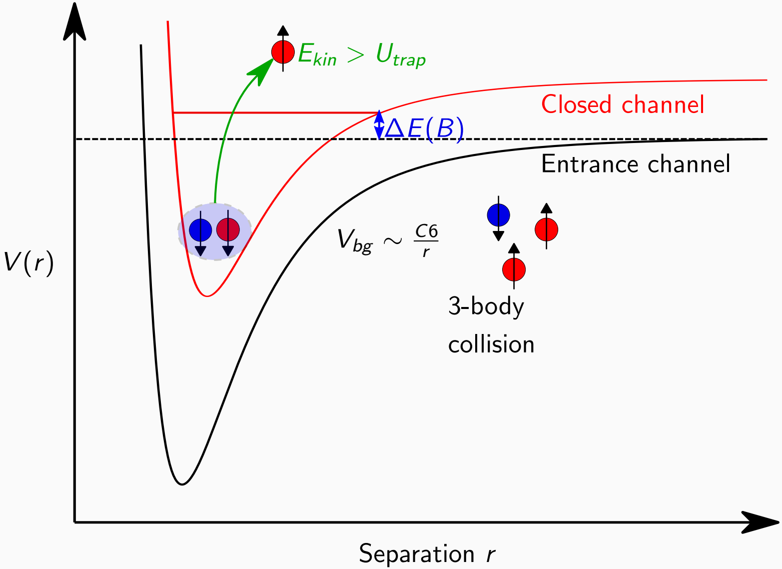
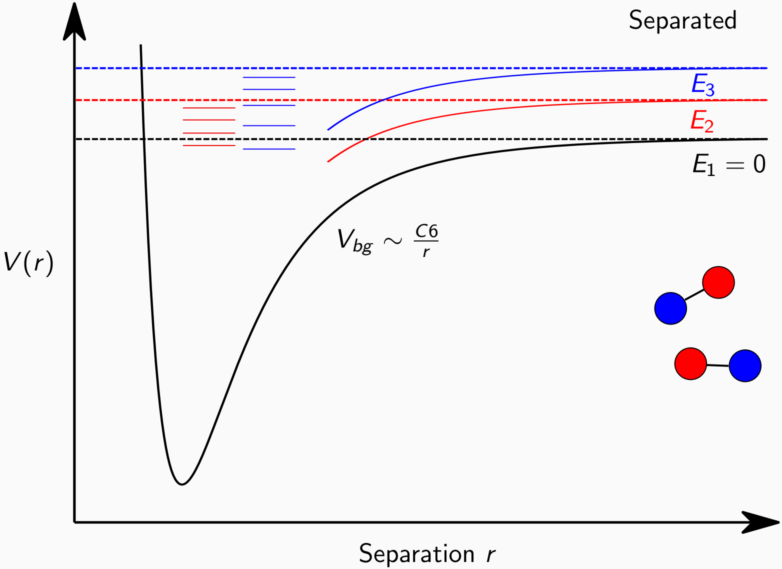
$\implies$ Trimer Formation expected to dominate

Ultracold Collisions- Atoms




$E_{kin} > U_{trap}$
Closed channel
$\Delta E(B)$
Entrance channel
$V_{bg} \sim \frac{C6}{r}$
$V(r)$
3-body
collision
Separation r

Ultracold Collisions- Molecules



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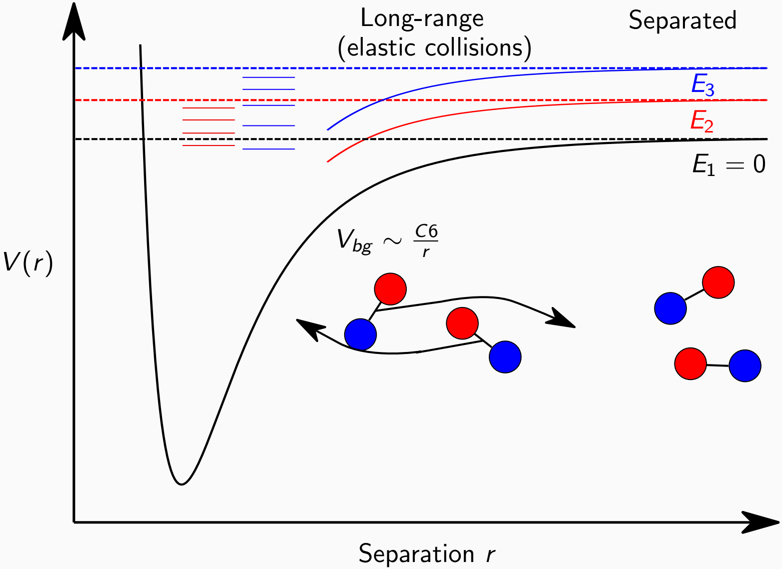

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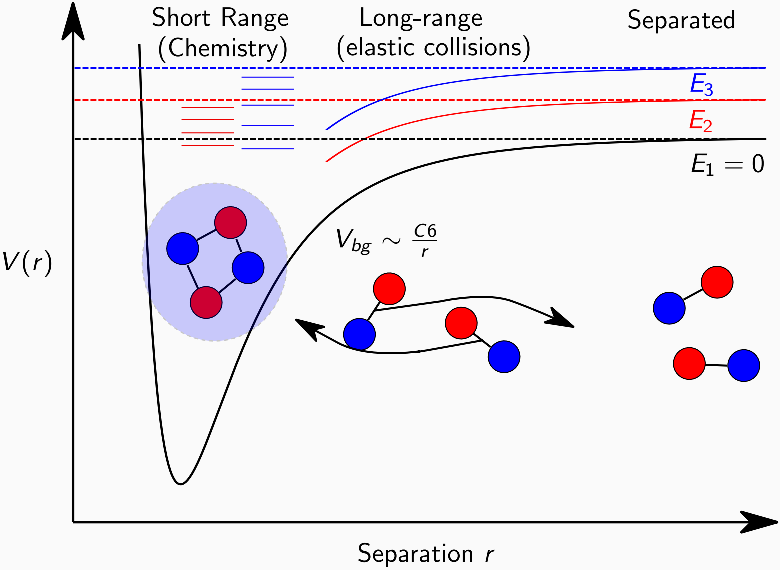
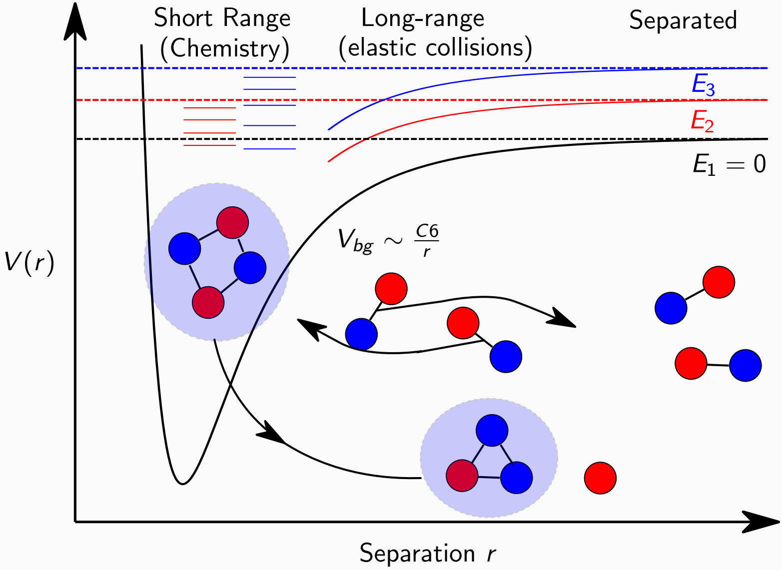
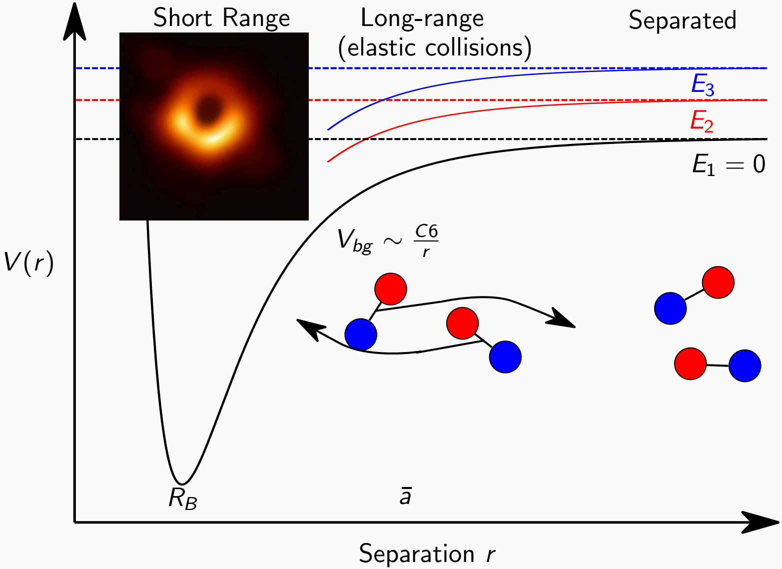




Short Range
(Chemistry)
Long-range
(elastic collisions)
Separated
E_3
E_2
$E_1 = 0$
$V_{bg} \sim \frac{C6}{r}$
$V(r)$
Separation r

Ultracold Collisions- Molecules



Universal Reaction Rates- Summary

Described in Quéméner and Julienne [2012], Ultracold Molecules Under Control!

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$$\bar{a} = \frac{2\pi}{\Gamma(1/4)^2}\left(\frac{2\mu C_6}{\hbar^2}\right)^{1/4}$$

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$$\bar{a} = \frac{2\pi}{\Gamma(1/4)^2}\left(\frac{2\mu C_6}{\hbar^2}\right)^{1/4}$$

- Unitary limit

$$\beta_{\mathrm{u}} = g\frac{4\pi\hbar}{\mu}\bar{a} \approx 7.1\times 10^{-10}\mathrm{cm}^3/\mathrm{s}$$

$\Longrightarrow$ Unless there are deviations from this rate, there is very little you can learn about the reactions

Dimer-dimer collisions:

- Ospelkaus et al. [2010]: KRb
  Universal + state-dependent (Pauli suppression)

Literature Review

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- Hudson et al. [2008]: RbCs+Cs & RbCs+Rb
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- Deiglmayr et al. [2011]: LiCs + Cs
- Yang et al. [2019]: NaK + K $\Rightarrow$ Magnetically tunable resonances

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Experimental Questions

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2. Do we observe non-universal reaction rates?

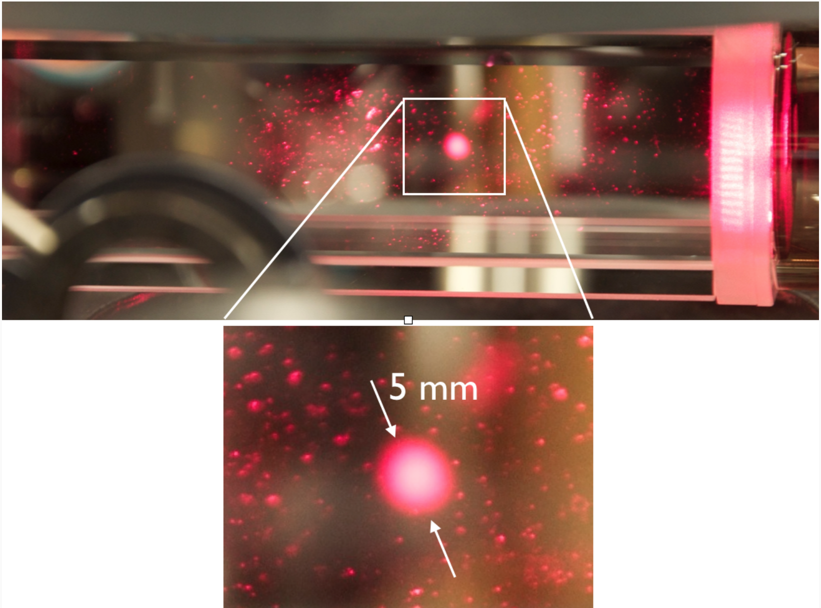
Experimental Questions

1. Is the triplet ground state stable?
2. Do we observe non-universal reaction rates?
3. Is there a magnetic field dependence?

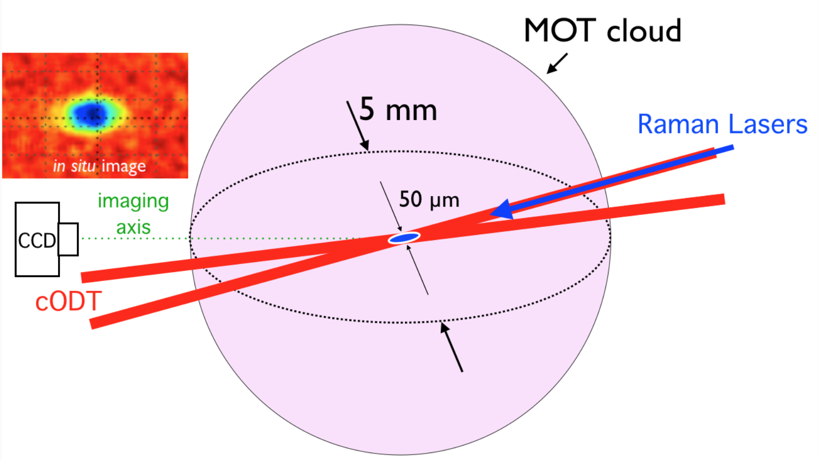
Making Cold Li2 molecules

Li MOT

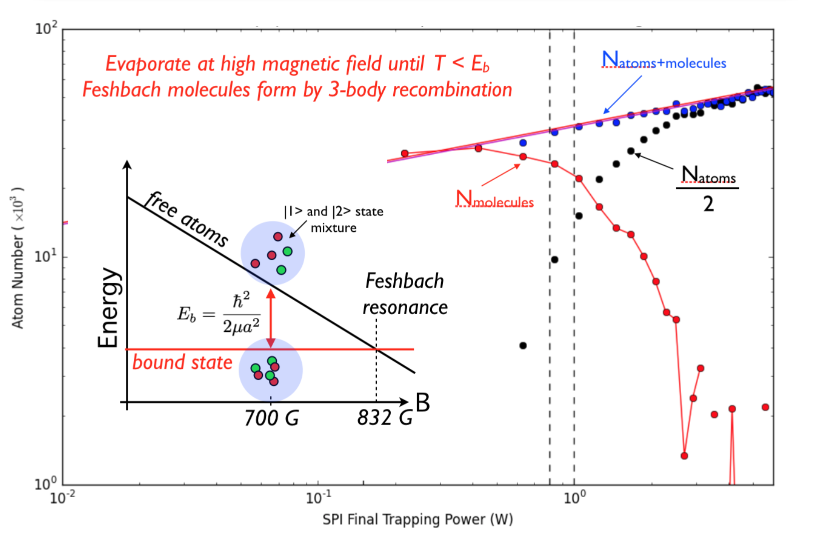
$\sim$ 10 million atoms at $\sim$ 10mK



Crossed Optical Diple Trap (cODT)

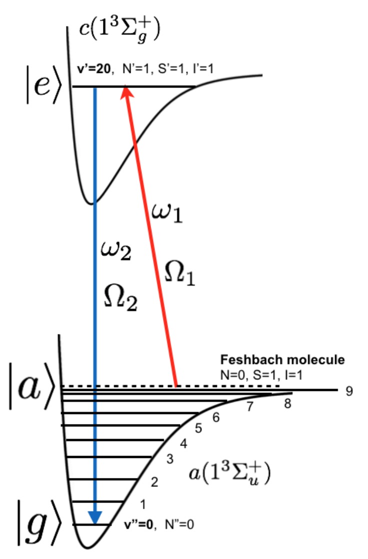


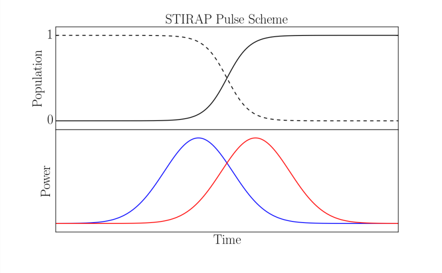
Feshbach molecules



Transfer to the ground state: STIRAP

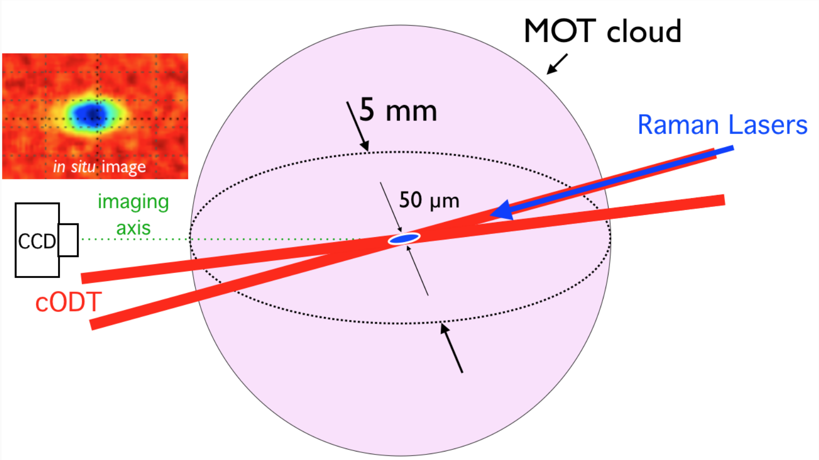
Stimulated Raman Adiabatic Passage (STIRAP)



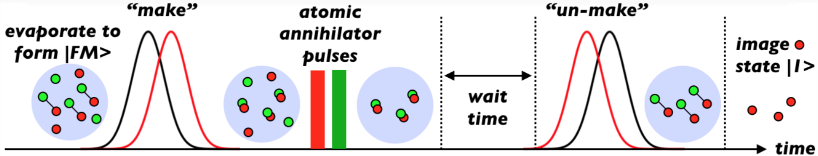


$$\left|a^0\right\rangle = \frac{\Omega_1\left|g\right\rangle - \Omega_2\left|a\right\rangle}{\sqrt{\Omega_1^2 + \Omega_2^2}}$$

Procedure



MOT cloud
5 mm
Raman Lasers
in situ image
imaging axis
CCD
50 μm
cODT



evaporate to form |FM>
"make"
atomic annihilator pulses
wait time
"un-make"
image state |I>
time

STIRAP Lineshape

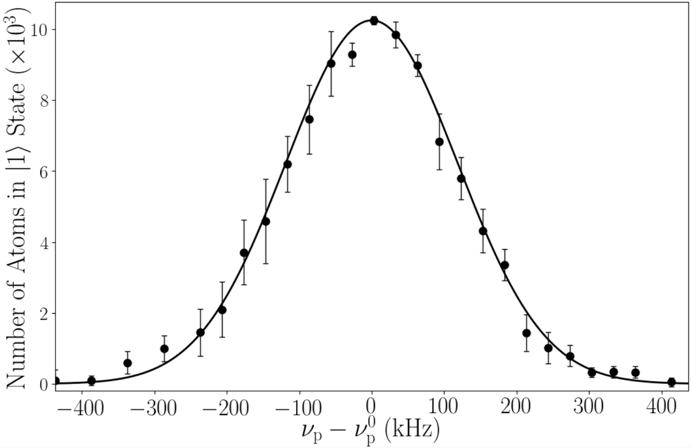


Figure 1: Feshbach molecule number after a forward and reverse STIRAP sequence to the $v'' = 9$ level as a function of the probe laser's frequency. The stokes laser's frequency is fixed close to the resonance of the $|g\rangle - |a\rangle$

Modeling Ultracold Reactions

Cloud Density

Assuming a thermal cloud:

$$n(\mathbf{r}, t) = n_{\mathrm{peak}}(t) e^{-x^2/2\sigma_x^2} e^{-y^2/2\sigma_y^2} e^{-z^2/2\sigma_z^2} \tag{1}$$

Cloud Density

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$$\int n(\mathbf{r}, t) d\mathbf{r} = \int \left(n_{\mathrm{peak}}(t) e^{-x^2/2\sigma_x^2} \, e^{-y^2/2\sigma_y^2} \, e^{-z^2/2\sigma_z^2} \right) d\mathbf{r} = N(t) \quad (1)$$

$$\Rightarrow n_{\mathrm{peak}}(t) = \frac{N(t)}{(2\pi)^{3/2}\sigma_x\sigma_y\sigma_z}. \quad (2)$$

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$$\frac{1}{2} k_B T = \frac{1}{2} m\omega_i^2\sigma_i^2 \quad (3)$$

$$\sigma_i = \frac{1}{\omega_i}\sqrt{\frac{k_B T}{m}} \quad (4)$$

Reaction Rate Model

$$n_{\mathrm{peak}}(t) = N(t)\frac{\omega_x\omega_y\omega_z m^{3/2}}{(2\pi k_B T)^{3/2}} \tag{5}$$

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$$\dot{n} = \cancel{-\alpha n(t)} - \beta n^2(t) - \cancel{\gamma n^3(t)} \tag{6}$$

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which reduces to (two-body losses)

$$n(t) = \frac{n_0}{1 + \beta n_0 t} \tag{7}$$

Results

State-dependence of Reaction Rate

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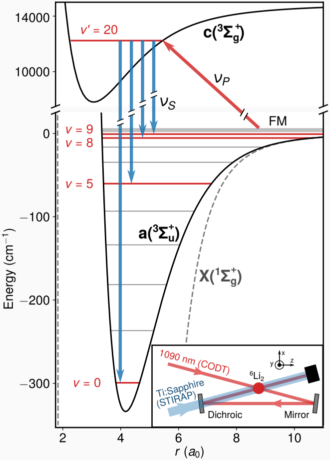
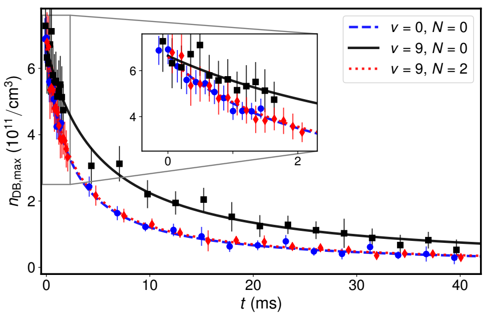
Accessible states



Lifetimes comparison



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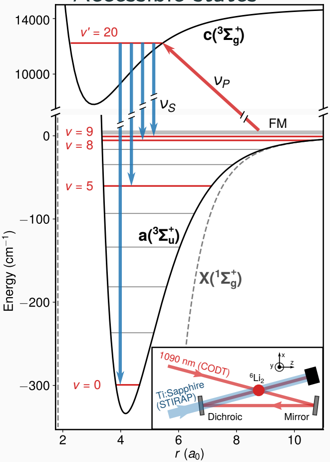

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v_g	N_g	E_b (GHz)	β $(10^{-10}\mathrm{cm}^3/\mathrm{s})$
0	0	8974.77	8.5 ± 2.1
5	0	1807.13	7.4 ± 1.8
8	0	164.31	7.3 ± 1.9
9	0	24.38	3.9 ± 1.2
9	2	16.39	7.1 ± 1.8

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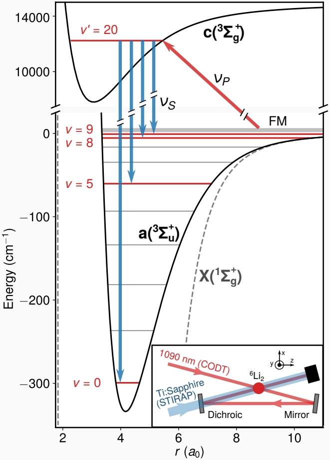

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9	0	24.38	3.9 ± 1.2
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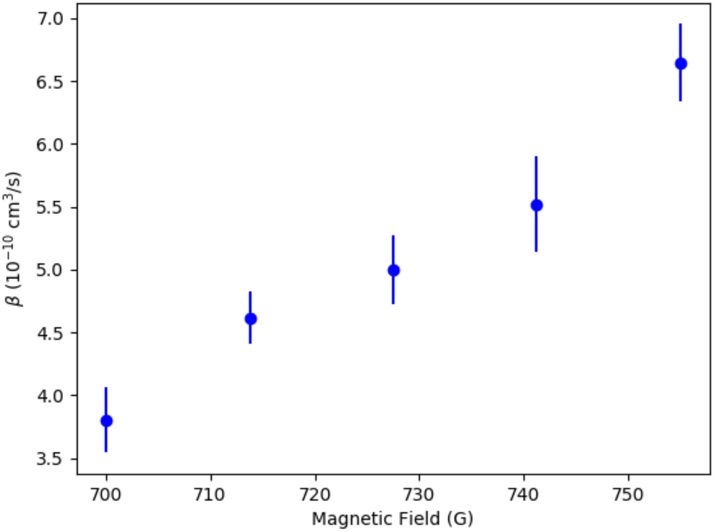
Quenching for high vibrational states was predicted "many years ago" [Stwalley, 2004]

Magnetic Field Dependence of Reaction Rate



Conclusion

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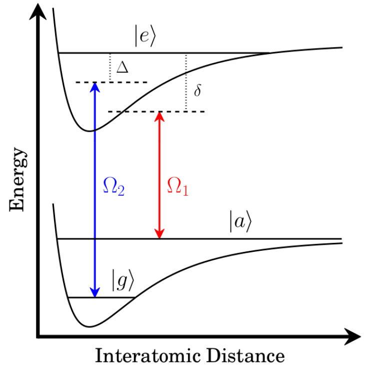
- Strong evidence for observation of trimer formation: $v'' = 0$ molecules should stable against other loss mechanisms
- Observed universal reaction rates, except for the $|v'' = 9, N = 0\rangle$ state
- Magnetic field dependent reaction rates, below universal limit

Questions?

Dark State



$$H(t) = \frac{\hbar}{2}\begin{bmatrix} 0 & \Omega_1(t) & 0 \\ \Omega_1(t) & 2\Delta & \Omega_2(t) \\ 0 & \Omega_2(t) & 2\delta \end{bmatrix}$$

Eigenstates at two photon resonance $\hbar(\omega_2 - \omega_1) = E_a - E_g$:

$$\left|a^0\right\rangle = \frac{\Omega_1\left|g\right\rangle - \Omega_2\left|a\right\rangle}{\sqrt{\Omega_1^2 + \Omega_2^2}}$$

Alternatively:

$$\left|a^0\right\rangle = \cos\theta|a\rangle - \sin\theta|g\rangle$$

Mixing angle: $\tan\theta = \frac{\Omega_1}{\Omega_2}$

Modeling Lifetimes 1

The decay of ground state molecules can be described by integrating the density distributions over the entire volume:

$$\dot{N}(t) = -\alpha N(t) - \beta \int_{-\infty}^{\infty} n^2(\boldsymbol{r}, t) d^3\boldsymbol{r} - \gamma \int_{-\infty}^{\infty} n^3(\boldsymbol{r}, t) d^3\boldsymbol{r} \tag{8}$$

Assuming Maxwell-Boltzmann statistics ($n(\boldsymbol{r}, t) \sim$ Gaussian):

$$\begin{aligned} \dot{N}(t) &= -\alpha N(t) - \frac{\beta}{8\pi^{3/2}\sigma_x\sigma_y\sigma_z} N^2(t) - \frac{\gamma}{24\sqrt{3}\pi^3\sigma_x^2\sigma_y^2\sigma_z^2} N^3(t) \\ &= -\underbrace{\alpha' N(t)}_{\text{one}-\text{body}} - \underbrace{\beta' N^2(t)}_{\text{two}-\text{body}} - \underbrace{\gamma' N^3(t)}_{\text{three}-\text{body}} \end{aligned} \tag{9}$$

Modeling Lifetimes 2

We determine α',β' and γ' by fitting our data to this model. Then we extract β,the reaction rate constant for two body collisions, measured in $\text{cm}^3\ \text{s}^{-1}$):

- Depends on $\sigma_{x,y,z} = \sqrt{\frac{k_B T}{m}} \frac{1}{\omega_{x,y,z}} \rightarrow$ *we need accurate measurements of temperature T and trap frequencies* $\omega_{x,y,z}$.
- For Thomas-Fermi statistics, $n(\boldsymbol{r}, t)$ has a different form, yielding:

$$\dot{N}(t) = -\alpha N(t) - \beta \frac{15^{2/5}(aN(t))^{7/5}}{14\pi a^2 \left(\frac{\hbar}{m\bar{\omega}}\right)^{6/5}} - \gamma \frac{5^{4/5}(aN(t))^{9/5}}{56\sqrt[5]{3}\pi^2 a^3 \left(\frac{\hbar}{m\bar{\omega}}\right)^{12/5}} \quad (10)$$

Proof of two-body losses

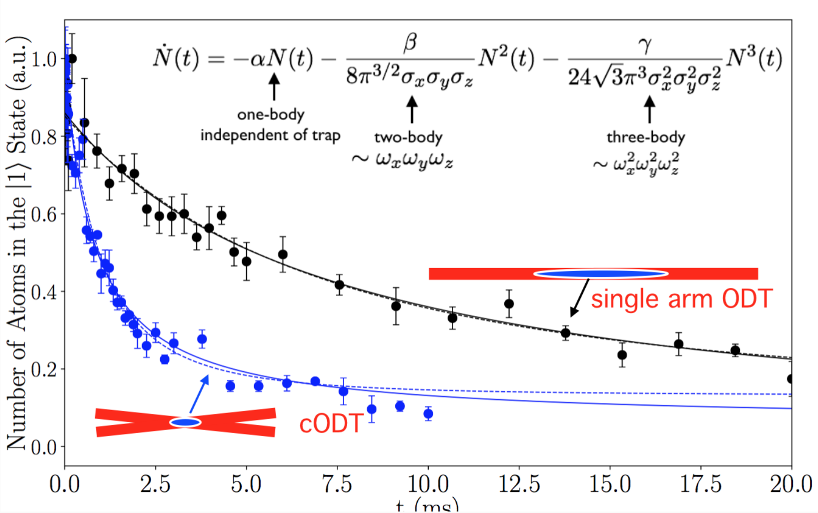


Figure 2: Comparison of lifetimes for a single arm ODT and CODT.

Matching the trap frequencies

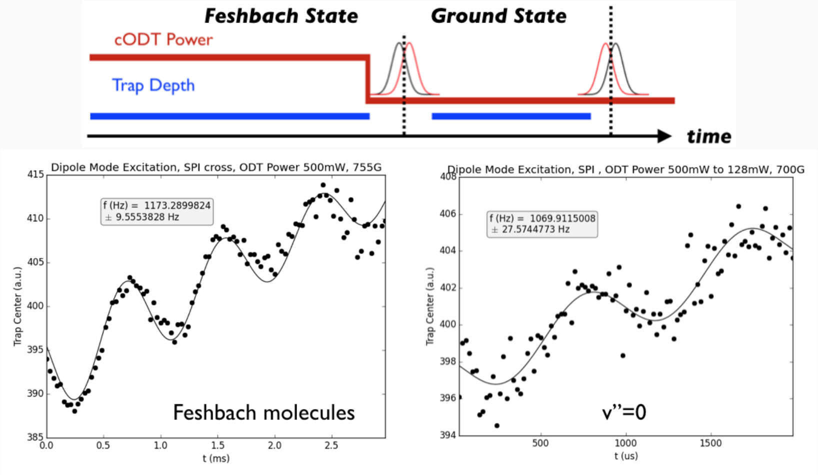


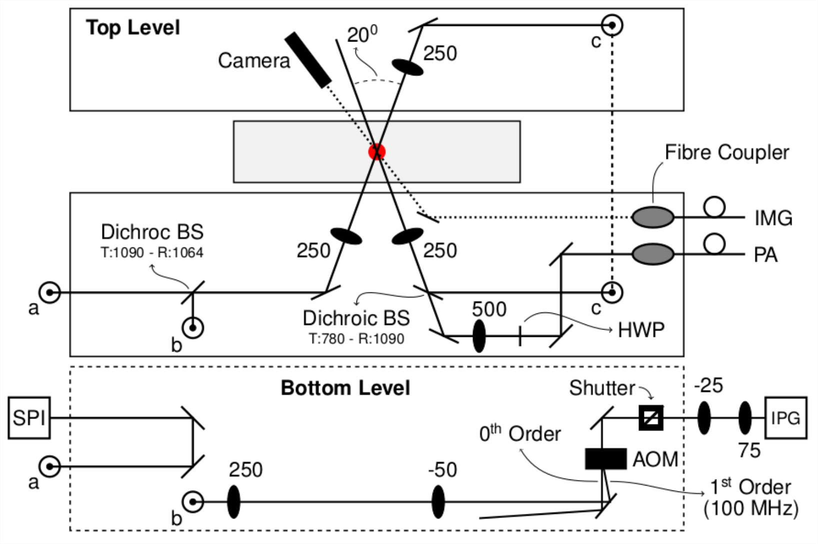
Figure 3: ODT Power 3:1

Binding Energies

Table 1: Energy differences between the initial state $|\mathrm{FM}\rangle$ and the DBM state $|g\rangle = |v_g, N_g\rangle$ as well as two-body loss coefficients for each DBM state. For every $|g\rangle$ state, $m_N = 0$, $m_S = -1$ and $m_I = 1$. The $|\mathrm{FM}\rangle \to |e\rangle$ transition frequency $\nu_\mathrm{P} = 366861.2522$ GHz was also magnetic field independent. .

v_g	N_g	$\nu_\mathrm{S} - \nu_\mathrm{P}$ (GHz)	β $(\mathrm{cm}^3/\mathrm{s})$
0	0	8974.7701	$(8.5 \pm 2.1) \times 10^{-10}$
0	2	8919.0313	-
2	0	5442.3258	-
5	0	1807.1250	$(7.4 \pm 1.8) \times 10^{-10}$
6	0	1037.5121	-
7	0	491.9990	-
8	0	164.3079	$(7.3 \pm 1.9) \times 10^{-10}$
9	0	24.3832	$(3.9 \pm 1.2) \times 10^{-10}$
9	2	16.3854	$(7.1 \pm 1.8) \times 10^{-10}$

Apparatus



Top Level
Camera
20⁰
250
c
Fibre Coupler
IMG
PA
Dichroc BS
T:1090 - R:1064
250
250
a
b
Dichroic BS
T:780 - R:1090
500
c
HWP
Bottom Level
Shutter
-25
SPI
IPG
0th Order
AOM
75
a
250
-50
1st Order
(100 MHz)
b

References

J. Deiglmayr, M. Repp, R. Wester, O. Dulieu, and M. Weidemüller. Inelastic collisions of ultracold polar lics molecules with caesium atoms in an optical dipole trap. *Physical Chemistry Chemical Physics*, 13(42): 19101–19105, 2011.

B. Drews, M. Deiß, K. Jachymski, Z. Idziaszek, and J. H. Denschlag. Inelastic collisions of ultracold triplet rb 2 molecules in the rovibrational ground state. *Nature communications*, 8:14854, 2017.

M. Guo, X. Ye, J. He, M. L. González-Martínez, R. Vexiau, G. Quéméner, and D. Wang. Dipolar collisions of ultracold ground-state bosonic molecules. *Phys. Rev. X*, 8:041044, Dec 2018. doi: 10.1103/PhysRevX.8.041044. URL https://link.aps.org/doi/10.1103/PhysRevX.8.041044.

E. R. Hudson, N. B. Gilfoy, S. Kotochigova, J. M. Sage, and D. DeMille. Inelastic collisions of ultracold heteronuclear molecules in an optical trap. *Phys. Rev. Lett.*, 100:203201, May 2008. doi: 10.1103/PhysRevLett.100.203201. URL https://link.aps.org/doi/10.1103/PhysRevLett.100.203201.

A. Micheli, G. Brennen, and P. Zoller. A toolbox for lattice-spin models with polar molecules. *Nature Physics*, 2(5):341, 2006.

S. Ospelkaus, K.-K. Ni, D. Wang, M. H. G. de Miranda, B. Neyenhuis, G. Quéméner, P. S. Julienne, J. L. Bohn, D. S. Jin, and J. Ye. Quantum-state controlled chemical reactions of ultracold potassium-rubidium molecules. *Science*, 327(5967):853–857, 2010. doi: 10.1126/science.1184121.

G. Quéméner and P. S. Julienne. Ultracold molecules under control. *Chemical Reviews*, 112(9):4949–5011, 2012. ISSN 00092665. doi: 10.1021/cr300092g.

T. M. Rvachov, H. Son, A. T. Sommer, S. Ebadi, J. J. Park, M. W. Zwierlein, W. Ketterle, and A. O. Jamison. Long-Lived Ultracold Molecules with Electric and Magnetic Dipole Moments. *Phys. Rev. Lett.*, 119(14):1–5, 2017. ISSN 10797114. doi: 10.1103/PhysRevLett.119.143001.

W. C. Stwalley. Collisions and reactions of ultracold molecules. *Canadian Journal of Chemistry*, 82(6):709–712, 2004. doi: 10.1139/v04-035. URL `https://doi.org/10.1139/v04-035`.

T. Takekoshi, L. Reichsöllner, A. Schindewolf, J. M. Hutson, C. R. Le Sueur, O. Dulieu, F. Ferlaino, R. Grimm, and H.-C. Nägerl. Ultracold dense samples of dipolar rbcs molecules in the rovibrational and hyperfine ground state. *Phys. Rev. Lett.*, 113:205301, Nov 2014. doi: 10.1103/PhysRevLett.113.205301. URL `https://link.aps.org/doi/10.1103/PhysRevLett.113.205301`.

H. Yang, D.-C. Zhang, L. Liu, Y.-X. Liu, J. Nan, B. Zhao, and J.-W. Pan. Observation of magnetically tunable Feshbach resonances in ultracold 23 Na 40 K + 40 K collisions Downloaded from. Technical report, 2019. URL `http://science.sciencemag.org/`.

References v

X. Ye, M. Guo, M. L. González-Martínez, G. Quéméner, and D. Wang. Collisions of ultracold 23na87rb molecules with controlled chemical reactivities. *Science*, 4(1), 2018. doi: 10.1126/sciadv.aaq0083.

N. Zahzam, T. Vogt, M. Mudrich, D. Comparat, and P. Pillet. Atom-molecule collisions in an optically trapped gas. *Phys. Rev. Lett.*, 96:023202, Jan 2006. doi: 10.1103/PhysRevLett.96.023202. URL https://link.aps.org/doi/10.1103/PhysRevLett.96.023202.

Beamer Theme Acknowledgement

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