Two-photon optical shielding of collisions between ultracold polar molecules

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Ultracold polar molecules

- **Two alkalis**: KRb, RbCs, NaRb, NaK, NaCs
- In their **absolute ground state**

- **Anisotropic** and **long-range** interactions
- Quantum **simulation, ultracold chemistry**, ...

Website of JILA
BUT: limited lifetime

For all molecules!

\[ \text{KRb} + \text{KRb} \rightarrow \text{K}_2 + \text{Rb}_2 \] (exoenergetic)

\[ \text{NaK} + \text{NaK} \rightarrow \text{Na}_2 + \text{K}_2 \] (endoenergetic)

PRL 116, 205303 (2016)
BUT: limited lifetime

For all molecules!

- KRb + KRb $\rightarrow$ $K_2 + Rb_2$ (exothermic)
- NaK + NaK $\rightarrow$ $Na_2 + K_2$ (endothermic)

What is the origin of losses?

- Sticky collisions?
- Photoexcitation of complex by trapping light?

PRL 116, 205303 (2016)
Idea: preventing molecules from getting close to each other and starting a reaction

=> Shielding
Blue shielding: principle

= Engineer repulsive long-range interactions
Blue shielding : principle

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Blue shielding: principle

= Engineer repulsive long-range interactions

\[ E(R) = \begin{cases} \text{repulsive energy} & \text{for } R \leq R_C \\ \text{attractive energy} & \text{for } R > R_C \end{cases} \]

\[ E(R) = \begin{cases} M + M + 1 \text{ photon} & \text{for } R \leq R_C \\ M + M^* & \text{for } R > R_C \end{cases} \]
Blue shielding: principle

= Engineer repulsive long-range interactions
• **Static electric field**

Rotational-level mixing creates repulsive van der Waals interaction

JILA team: Science *370*, 1324 (2020)  
Nature *588*, 289 (2020)
• **Static electric field**

Rotational-level mixing creates repulsive van der Waals interaction

JILA team: Science **370**, 1324 (2020)
Nature **588**, 289 (2020)

• **Microwave (MW) field**

With respect to purely rotational transition

MIT/Harward: Science **373**, 779 (2021)
Garching: Nature **607**, 677 (2022)
Cornell: arxiv:2303.16845 (2023)
• **Optical field**

Frequency close to $D_2$ transition of alkali atoms

**Deteriorated by spontaneous emission**

Na$_2$: PRA 51, 1446 (1995)
• **Optical field**

Frequency close to \( D_2 \) transition of alkali atoms

Deteriorated by spontaneous emission

Quasi-forbidden transitions in bialkali molecules

Transition \( X^1\Sigma^+ (v_x = 0, j_x = 0) \rightarrow b^3\Pi_{0+} (v_b = 0, j_b = 1) \)

Theory for NaRb: PRL **125**, 153202 (2020)

Na\(_2\): PRA **51**, 1446 (1995)
$X \rightarrow b$ transition in NaRb

$X(j_x = 0) + X(j_x = 0), n = 0$

$X(j_x = 0) + b(j_b = 1), n = -1$

$X(j_x = 1) + b(j_b = 0), n = -1$

$\Delta = 100$ MHz

$\Omega = 10$ MHz

Linear pola.

Incoming channel
X \rightarrow b \text{ tranition in NaRb}

\[ X(j_x = 0) + X(j_x = 0), n = 0 \]

\[ X(j_x = 0) + b(j_b = 1), n = -1 \]

\[ X(j_x = 1) + b(j_b = 0), n = -1 \]

\[ \Delta = 100 \text{ MHz} \]
\[ \Omega = 10 \text{ MHz} \]

Linear pola.

BUT : 1 molecule photon scattering
Idea: applying optical fields without spontaneous emission

=> 2-photon transition
2-photon transition (1 molecule)

\[ |q\rangle \quad \text{\(\hbar \Delta\)} \quad |g_1\rangle \]

\[ \text{\(\Omega_1\)} \quad \text{\(\hbar \delta\)} \quad \text{\(\Omega_2\)} \quad |g_2\rangle \]
2-photon transition (1 molecule)

\[ |q\rangle = |b, j_b = 1\rangle \]

\[ |g_1\rangle = |X, j_X = 0\rangle \]

\[ |g_2\rangle \]

\[ \Omega_1 \]

\[ \Omega_2 \]

\[ \hbar \Delta \]

\[ \hbar \delta \]
2-photon transition (1 molecule)

\[ |q\rangle = |b, j_b = 1\rangle \]
\[ |g_1\rangle = |X, j_x = 0\rangle \]
\[ |g_2\rangle = |X, j_x = 2\rangle \]
\[ \hbar \delta \]
\[ \hbar \Delta \]
\[ \Omega_1 \]
\[ \Omega_2 \]

In dressed basis \{ |\tilde{g}_1\rangle, |\tilde{g}_2\rangle, |\tilde{q}\rangle \}:

\[
H^I = \hbar \begin{pmatrix}
0 & 0 & \Omega_1/2 \\
0 & \delta & \Omega_2/2 \\
\Omega_1/2 & \Omega_2/2 & \Delta
\end{pmatrix}
\]
2-photon transition (1 molecule)

|\( q \rangle = |b, j_b = 1 \rangle\)

\[ \Omega_1 \]

\[ \Omega_2 \]

|\( g_2 \rangle = |X, j_X = 2 \rangle\)

\[ g_1 \rangle = |X, j_X = 0 \rangle\]

\[ \hbar \Delta \]

In dressed basis \( \{|\tilde{g}_1\rangle, |\tilde{g}_2\rangle, |\tilde{q}\rangle\}\)

\[
H^I = \hbar \begin{pmatrix}
0 & 0 & \Omega_1/2 \\
0 & \delta & \Omega_2/2 \\
\Omega_1/2 & \Omega_2/2 & \Delta
\end{pmatrix}
\]

Adiabatic elimination of \( |\tilde{q}\rangle\)

\[ \Delta \gg \Omega_1, \Omega_2, \Gamma_q \]

\[ H^I_{\text{eff}} = \hbar \begin{pmatrix}
0 & -\Omega_{\text{eff}}/2 \\
-\Omega_{\text{eff}}/2 & \Delta_{\text{eff}}/2
\end{pmatrix}
\]

\[ \Delta_{\text{eff}} = \delta + \frac{\sqrt{\Omega_1^2 - \Omega_2^2}}{4\Delta} \]; \[ \Omega_{\text{eff}} = \frac{\Omega_1 \Omega_2}{2\Delta} \] with \( \delta = 0 \)

04/07/2023

M. Lepers
2 photons & 2 molecules

\[ H = T + H_1 + H_2 + V(R) + H_f + H_{m-f} \]

Relative kinetic energy

Molecules 1 & 2

molecule-molecule

fields

molecules-fields

\[ T = T_R + \frac{\hbar^2 L^2}{2\mu R^2} \]

\[ H_i = B_0 J_i^2 \]

\[ V(R) = V_{dd}(R) = \text{dipole-dipole} \]

\[ H_{m-f} = \text{molec. 1 & 2} \]

– fields 1 & 2
2 photons & 2 molecules

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- Relative kinetic energy
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\[ T = T_R + \frac{\hbar^2 \mathbf{L}^2}{2\mu R^2} \]

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\[ \text{– fields 1 & 2} \]

\[ H_{LR}(R) = \frac{\hbar^2 \mathbf{L}^2}{2\mu R^2} + B_0 (\mathbf{J}_1^2 + \mathbf{J}_2^2) + V_{dd}(R) \]

Diagonalization for each \( R \gtrsim 50 \) a.u.

\[ V_{LR}(R); |\psi\rangle = \sum_m \chi_m(R) |m\rangle \]

\[ \Omega_{\text{eff}}(R) \propto \sum_{m,p} \chi_m(R) \chi_p(R) \langle m || T^{(2)} || p \rangle \]
Lab-frame, fully uncoupled basis: $|j_i, m_i, j_k, m_k, \ell, m_\ell\rangle$
Basis sets \( \{ |m\rangle \} \)

**Lab-frame, fully uncoupled basis:** \( |j_i, m_i, j_k, m_k, \ell, m_\ell\rangle \)

To better account for symmetries, **fully-coupled** basis

\[ [\hat{j}_i, \hat{j}_k], j_{ik}, \ell, J, M \rangle^{(\pm)} \]

- \( \hat{J} = \hat{j}_{ik} + \hat{L} = (\hat{j}_1 + \hat{j}_2) + \hat{L} \) = total angular momentum of the complex (without HFS). \( M \) associated to its **z-projection**
- \( \ell \) = partial wave
- \( [j_i, j_k] = \) permutation
- \( (\pm) = \) inversion of all coordinates
Basis sets \(\{|m\}\}\)

**Lab-frame, fully uncoupled basis:** \(|j_i, m_i, j_k, m_k, \ell, m_\ell\rangle\)

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- \((\pm)\) = inversion of all coordinates

Initial collision channel = 2 ultracold ground-state bosonic molecules

\(|m_1\rangle = |[[0,0], 0,0,0,0\rangle^{(\pm)}\]

![Potential energy graph]

-554000 / \(R^6\)

-0.2
-0.15
-0.1
-0.05
0
0.05

Potential energy (cm\(^{-1}\))

Intermolecular distance (a.u.)
## Selection rules

| Quant. nber   | Dipole-dipole          | Raman       |
|---------------|------------------------|-------------|
| \([\Delta j_i, \Delta j_k]\) | \([\pm 1, \pm 1]; [\mp 1, \pm 1]\) | \([0, \pm 2]\) |
| \(\Delta \ell\) | 0 or \(\pm 2^*\) | 0           |
| \(\Delta J\) | 0*                     | 0 or \(\pm 1\) or \(\pm 2^*\) |
| \(\Delta M\) | 0                      | 0, if = polarizations |
| parity       | \(\pm \leftrightarrow \pm\) or \(\mp \leftrightarrow \mp\) | \(\pm \leftrightarrow \pm\) or \(\mp \leftrightarrow \mp\) |

* 0 \(\leftrightarrow\) 0, and 1/2 \(\leftrightarrow\) 1/2 for \(\Delta J\)
### Selection rules

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| $\Delta \ell$ | 0 or $\pm 2^*$ | 0 |
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| $\Delta M$ | 0 | 0, if = polarizations |
| parity | $\pm \leftrightarrow \pm \text{ or } \mp \leftrightarrow \mp$ | $\pm \leftrightarrow \pm \text{ or } \mp \leftrightarrow \mp$ |

* $0 \leftrightarrow 0$, and $1/2 \leftrightarrow 1/2$ for $\Delta J$

\[
|m_1\rangle = |[j_X = 0, j_X = 0], j_{ik} = 0, \ell = 0, J = 0, M = 0\rangle^{(+)}
\]

\[
|[1, 1], 0 \text{ or } 2, 2, 2, 0\rangle^{(+)}
\]

\[
|[1, 3], 0 \text{ or } 2, 2, 2, 0\rangle^{(+)}
\]

\[
|m_2\rangle = |[0, 2], 2, 0, 2, 0\rangle^{(+)}
\]
Results for NaK
Long-range potential energy curves

\[ \text{Potential energy (cm}^{-1}\text{)} \]

\[ \text{Intermolecular distance (a.u.)} \]

- \( [j_X = 0, j_X = 2]^{(+)} \)
- \( [j_X = 1, j_X = 1]^{(+)} \)
- \( [j_X = 0, j_X = 1]^{(-)} \)
- \( [j_X = 0, j_X = 0]^{(+)} \)

2nd-order dipole-dipole \( \propto R^{-6} \)

Resonant dipole-dipole \( \propto R^{-3} \)
**Long-range potential energy curves**

**\[ \Delta_{\text{eff}} = 70 \text{ MHz} \]**

![Graph showing potential energy curves with labels and equations]

**Equations:**

- **A':**
  \[ D + \frac{17.29}{2\mu R^2} + \frac{1.045 \times 10^6}{R^6} \text{ (in a.u.)} \]

- **B':**
  \[ D + \frac{6.668}{2\mu R^2} + \frac{2.711 \times 10^5}{R^6} \text{ (in a.u.)} \]
Long-range potential energy curves

\[ \Delta_{\text{eff}} = 70 \text{ MHz} \]

\[ \Delta_{\text{MW}} = 70 \text{ MHz} \]

\[ A': D + \frac{17,29}{2\mu R^2} + \frac{1,045 \times 10^6}{R^6} \text{ (in a.u.)} \]

\[ B': D + \frac{6,668}{2\mu R^2} + \frac{2,711 \times 10^5}{R^6} \text{ (in a.u.)} \]

PRL 125, 163402 (2018)
### Eigenvector components at $R_C$

| Basis vector $|m_1\rangle = |[0, 0], 0, 0, 0, 0\rangle^{(+)}$ | Potential curve $|g_1\rangle = \text{init.}$ | $R_C = 240$ a.u. $\Delta_{\text{eff}} = 70$ MHz | $R_C = 170$ a.u. $\Delta_{\text{eff}} = 500$ MHz |
|---|---|---|---|
| $|m_1\rangle = |[0, 0], 0, 0, 0, 0\rangle^{(+)}$ | $|g_1\rangle = \text{init.}$ | 99.95 % | 98.61 % |

| Basis vector $|m_2\rangle = |[0, 2], 2, 0, 2, 0\rangle^{(+)}$ | Potential curve $|g_2\rangle$ | $R_C = 240$ a.u. $\Delta_{\text{eff}} = 70$ MHz | $R_C = 170$ a.u. $\Delta_{\text{eff}} = 500$ MHz |
|---|---|---|---|
| $|m_2\rangle = |[0, 2], 2, 0, 2, 0\rangle^{(+)}$ | $|g_2\rangle = A'$ | 10.90 % | 16.16 % |
| | $|g_2\rangle = B'$ | 9.80 % | 32.11 % |
| | $|g_2\rangle = C'$ | 78.88 % | 49.26 % |
\[ \Delta_{\text{eff}} = 8 \text{ MHz} \text{ and } \Omega_{\text{eff}} = 11 \text{ MHz} \]

Nature 607, 677 (2022)
$\Delta_{\text{eff}} = 2 \text{ MHz and } \Omega_{\text{eff}} = 1 \text{ MHz}$
Conclusion

➢ Possibility of two-photon optical shielding
➢ No spontaneous emission or photon scattering
➢ « Mapping » on one-photon shielding
➢ Applicable to other molecules than NaK
➢ Possible use of other electronically excited states (A, B)

➢ Full scattering calculations

Phys. Rev. Research, accepted (2023)
Conclusion

➢ Possibility of two-photon optical shielding
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➢ Applicable to other molecules than NaK
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Phys. Rev. Research, accepted (2023)

Thank you!
Electronically-excited PECs

![Graph showing potential energy vs. intermolecular distance for different transitions.]

- $[i_X = 0, j_b = 2]^{(-)}$
- $[i_X = 2, j_b = 0]^{(-)}$
- $[i_X = 1, j_b = 1]^{(-)}$
- $[i_X = 0, j_b = 1]^{(-)}$

Potential energy (cm$^{-1}$) vs. Intermolecular distance (a.u.).
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| Basis vector | Potential curve | $R_C = 240$ a.u. $\Delta_{\text{eff}} = 70$ MHz | $R_C = 170$ a.u. $\Delta_{\text{eff}} = 500$ MHz |
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| | $|g_2\rangle = B'$ | 9.80 % | 32.11 % |
| | $|g_2\rangle = C'$ | 78.88 % | 49.26 % |
| $[[X, 0, b, 1], 1, 0, 1, 1]^{(-)}$ | $|q\rangle = I$ | 33.06 % | 33.17 % |
| | $|q\rangle = K$ | 16.74 % | 16.68 % |
Scheme of energy levels

\[ \Delta_{\text{eff}} = \delta + \frac{\Omega_1^2 - \Omega_2^2}{4\Delta} \]

\[ \Omega_{\text{eff}}(R) = \frac{\Omega_1(R)\Omega_2(R)}{2\Delta(R)} \]
Blue shielding: principle

= Engineer repulsive long-range interactions
## Molecular data

| Species     | $C_6^{es}$ (a.u.) | PDM$_X$ (a.u.) | PDM$_b$ (a.u.) | TDM$_{X\rightarrow b}$ (a.u.) | $B_{(X)}$ (cm$^{-1}$) | $B_{(b)}$ (cm$^{-1}$) |
|-------------|-------------------|----------------|----------------|-------------------------------|-----------------------|-----------------------|
| $^7\text{Li}^{23}\text{Na}$ | 3333.6            | 0.2228         | 0.645          | 0.0082                        | 0.374                 | 0.387                 |
| $^6\text{Li}^{39}\text{K}$   | 6096.8            | 1.410          | 1.810          | 0.0216                        | 0.256                 | 0.274                 |
| $^7\text{Li}^{87}\text{Rb}$  | 7268              | 1.645          | 2.214          | 0.1149                        | 0.215                 | 0.231                 |
| $^7\text{Li}^{133}\text{Cs}$ | 9263              | 2.201          | 2.709          | 0.1327                        | 0.187                 | 0.204                 |
| $^{23}\text{Na}^{39}\text{K}$| 7088.1            | 1.095          | 1.220          | 0.0456                        | 0.0950                | 0.0951                |
| $^{23}\text{Na}^{87}\text{Rb}$| 8374.6            | 1.304          | 1.735          | 0.1918                        | 0.0697                | 0.0700                |
| $^{23}\text{Na}^{133}\text{Cs}$| 10642             | 1.845          | 2.369          | 0.4204                        | 0.0579                | 0.0600                |
| $^{39}\text{K}^{87}\text{Rb}$ | 12610.1           | 0.2423         | 0.491          | 0.1353                        | 0.0378                | 0.0387                |
| $^{39}\text{K}^{133}\text{Cs}$| 15481.9           | 0.7237         | 1.282          | 0.2342                        | 0.0304                | 0.0320                |
| $^{37}\text{Rb}^{133}\text{Cs}$| 17839.4           | 0.4903         | 0.840          | 0.2697                        | 0.0164                | 0.0170                |
NaRb with shielding and trapping lights
X → b transition in NaRb

\[ k_{el} (cm^3/s) \]

\[ k_{in} (cm^3/s) \]

\[ k_{re} (cm^3/s) \]

\[ \gamma = \frac{k_{el}}{k_{in} + k_{re}} \]
X → b transition in NaRb

**BUT : 1 molecule photon scattering**