Molecular Dynamics RG

GIR Dinámica Molecular

Quantum Stereodynamics at cold energies.

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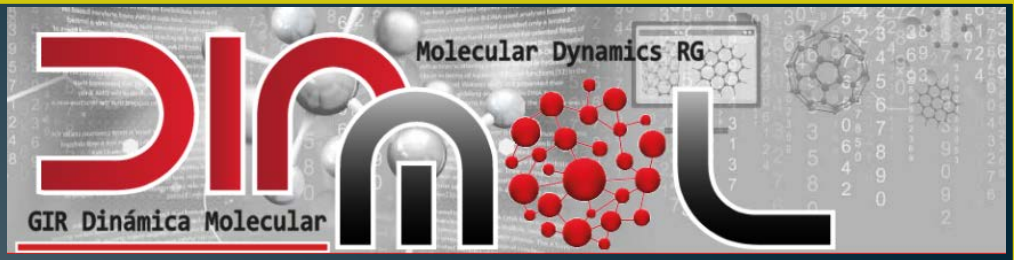
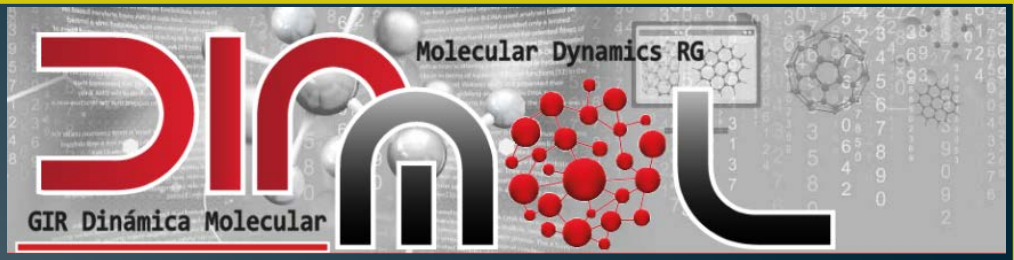
Credits



- Hua Guo (New Mexico)
- Naduvalath Balakrishnan (Nevada)
- James Croft (Dood-Walls Centre, New Zealand)
- F. Javier Aoiz(Universidad Complutense de Madrid)

Outline:



- Inelastic Collisions at Cold energies
- Stereodynamics. SARP Experiments
- Results: $D_2 + D_2$
- Results: $He + D_2$
- Conclusions

Aim: Reproduce Experimental Measurements

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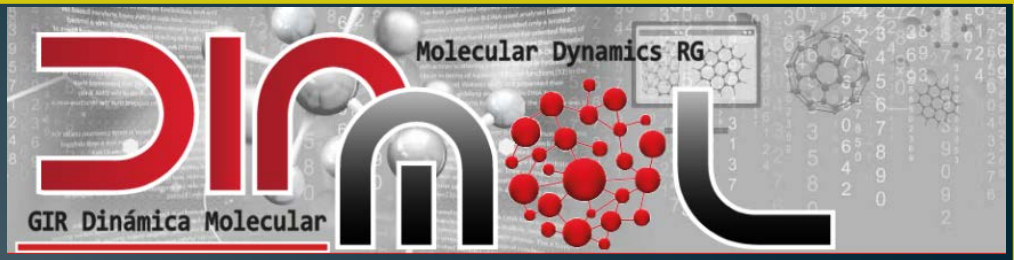

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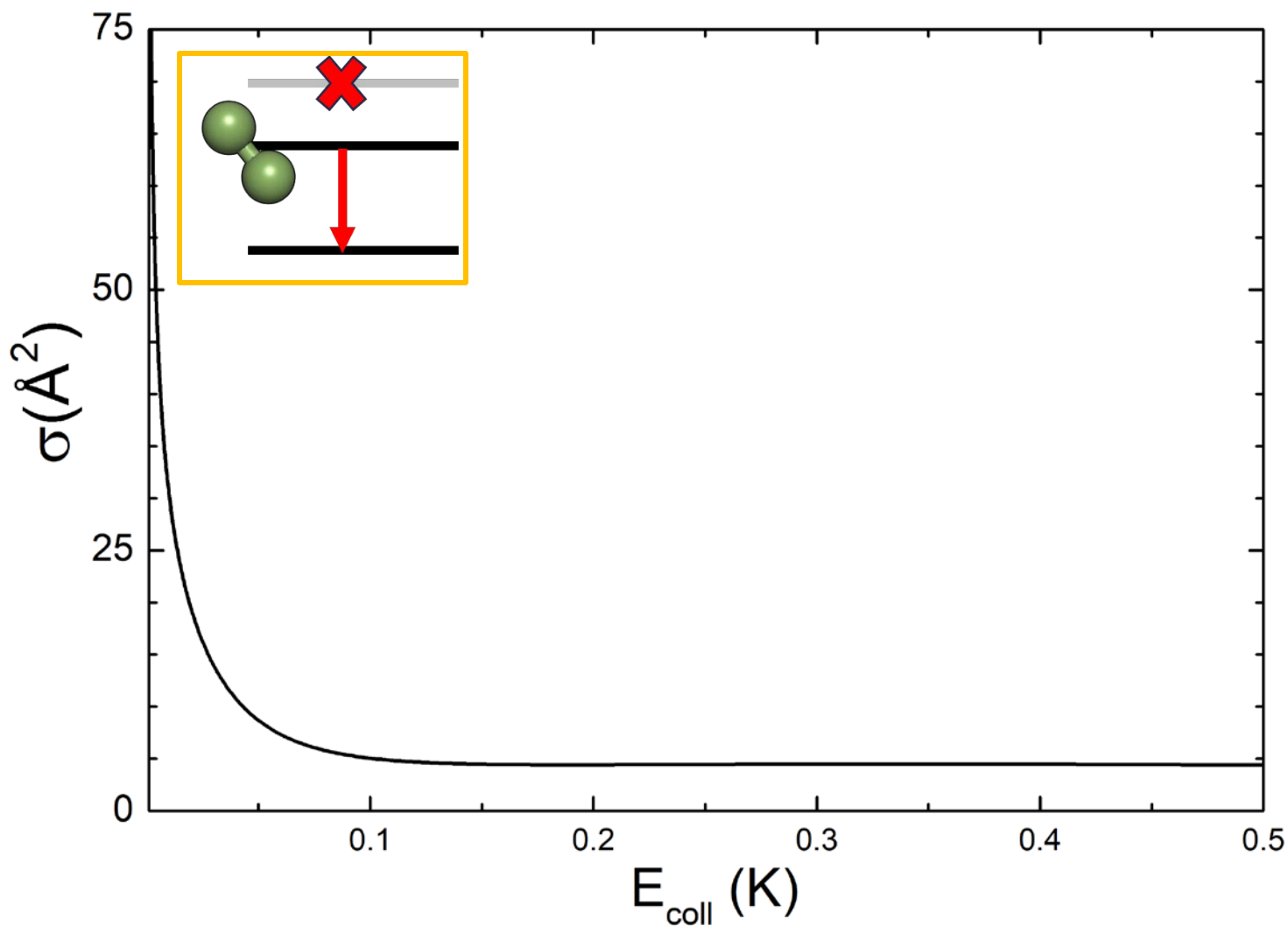

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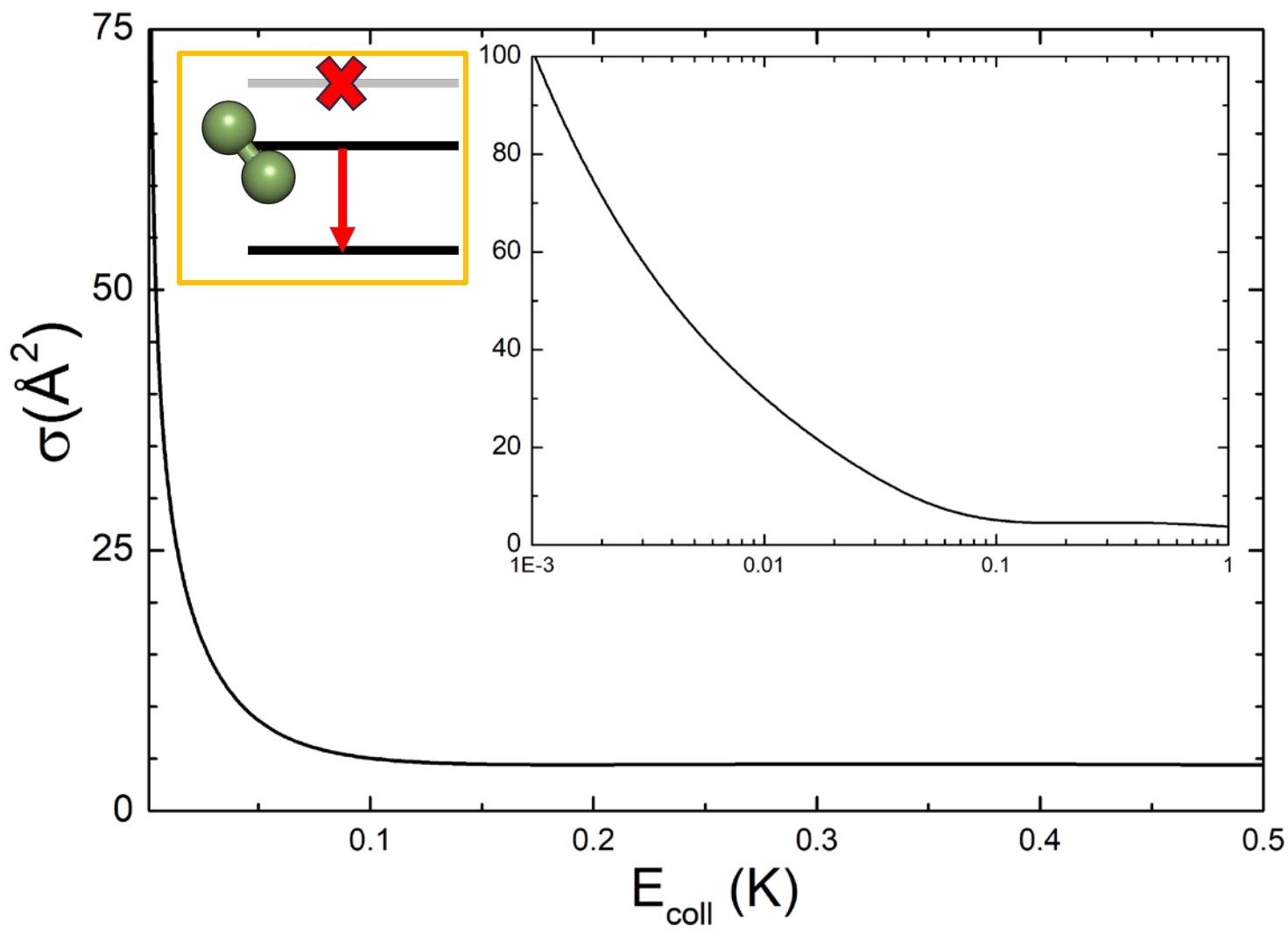

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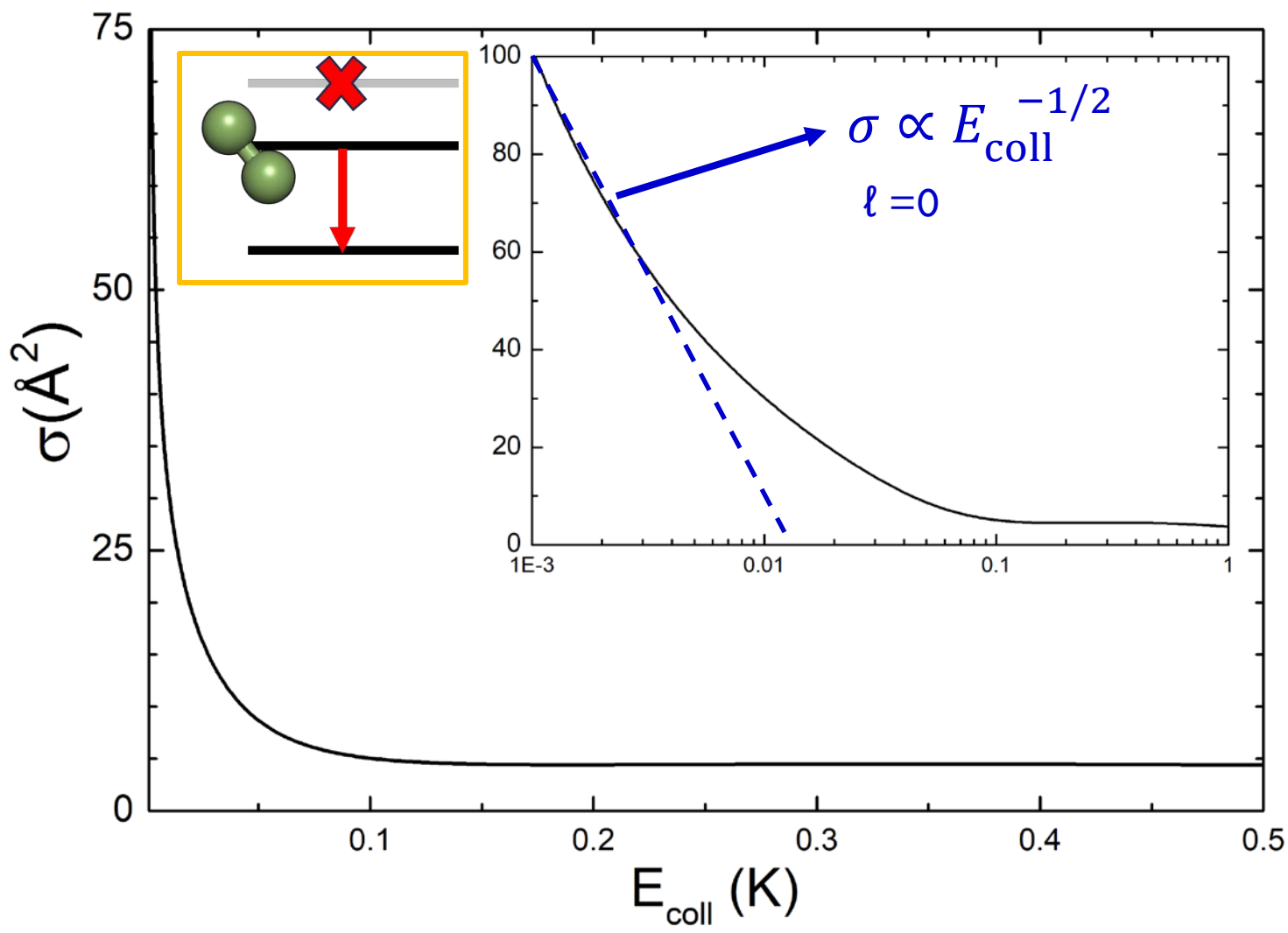

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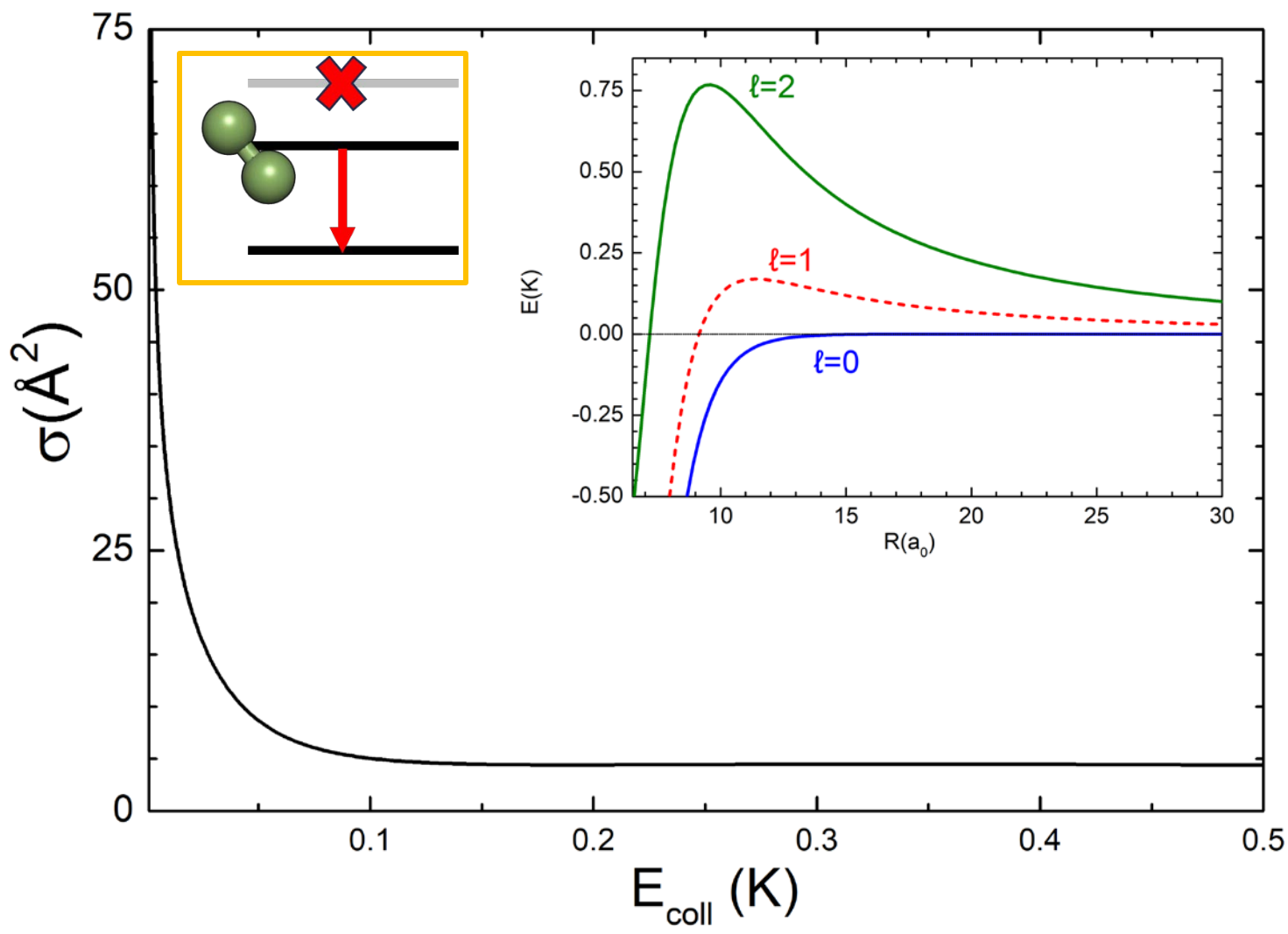

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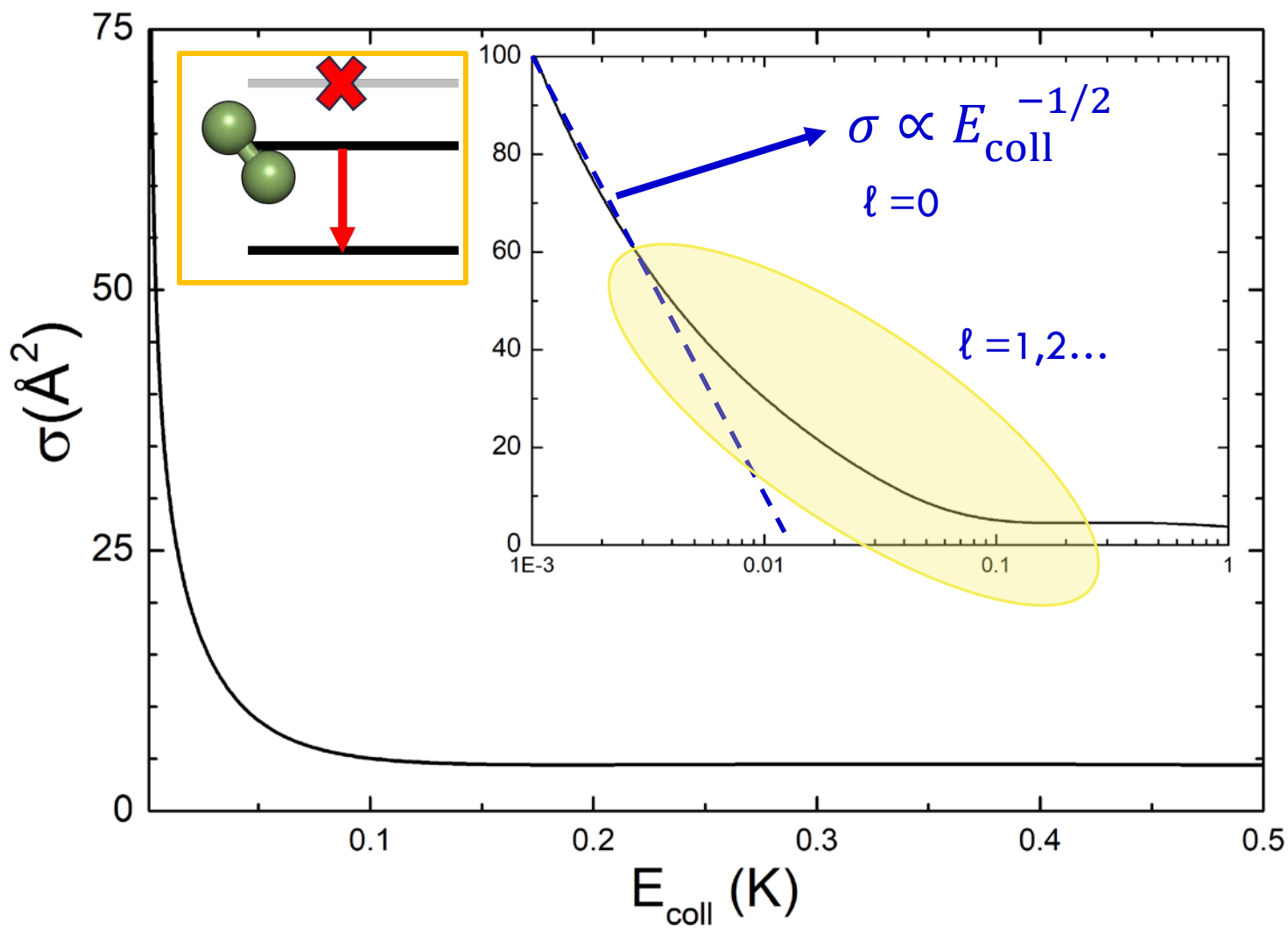

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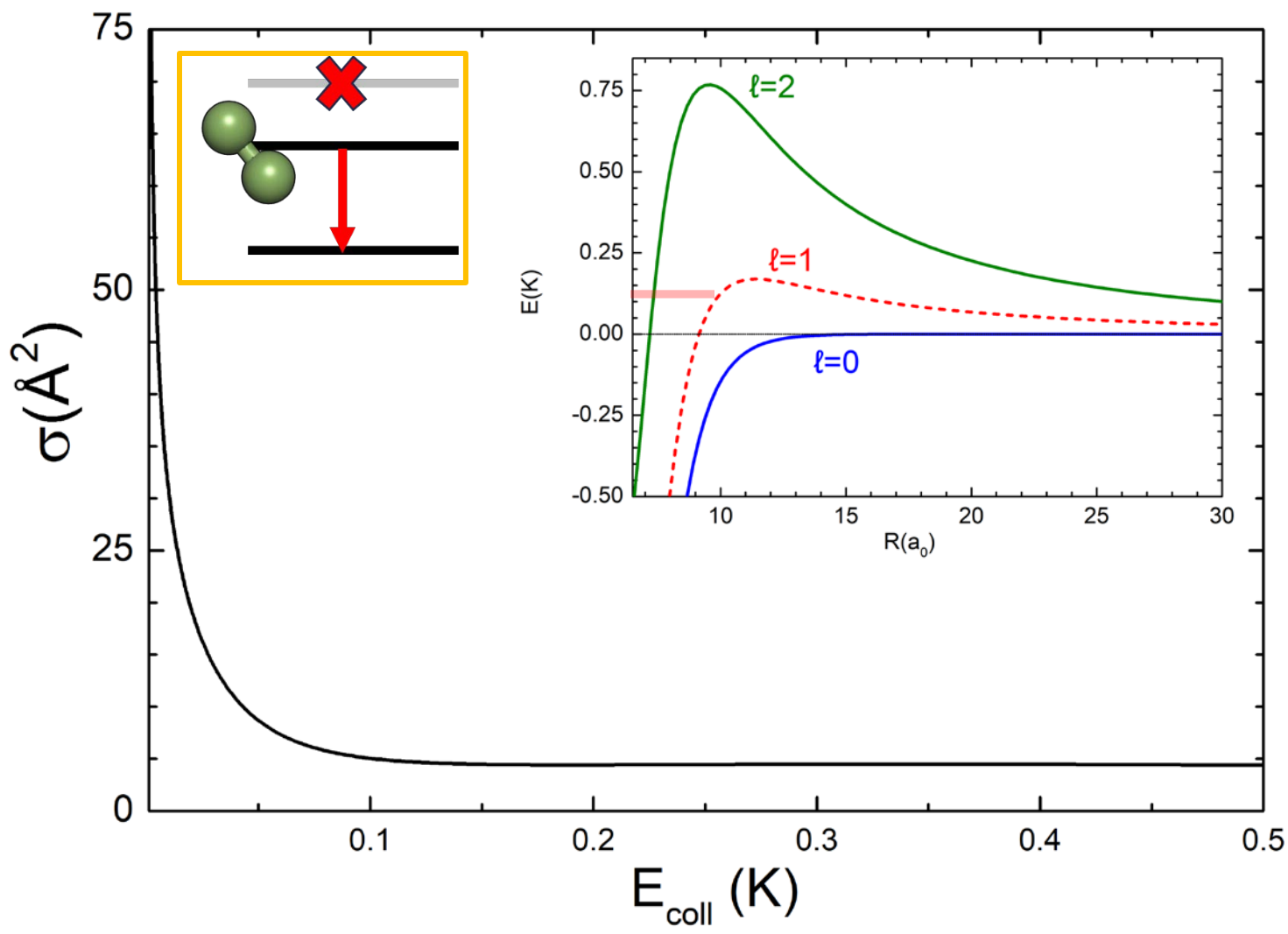

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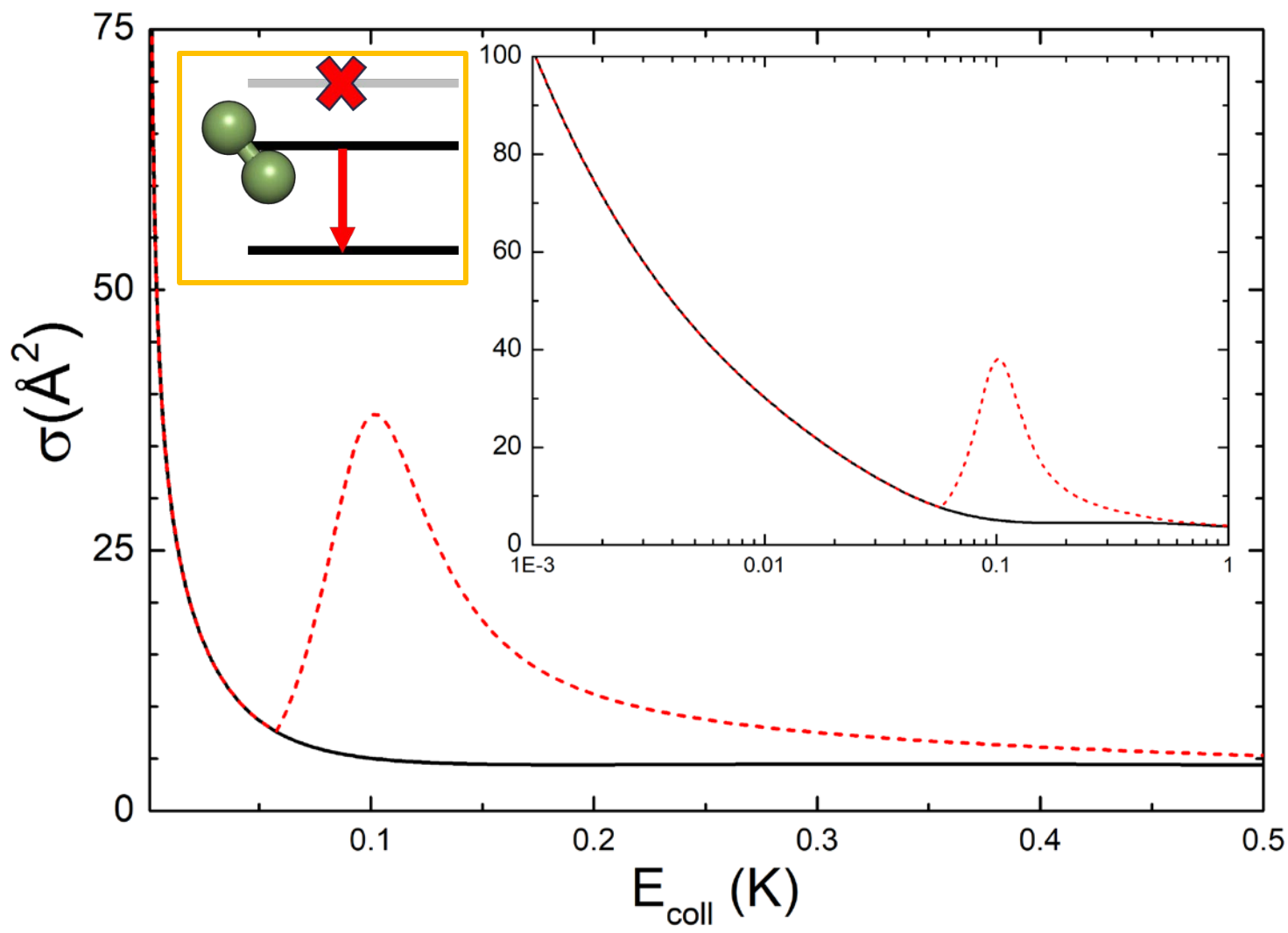

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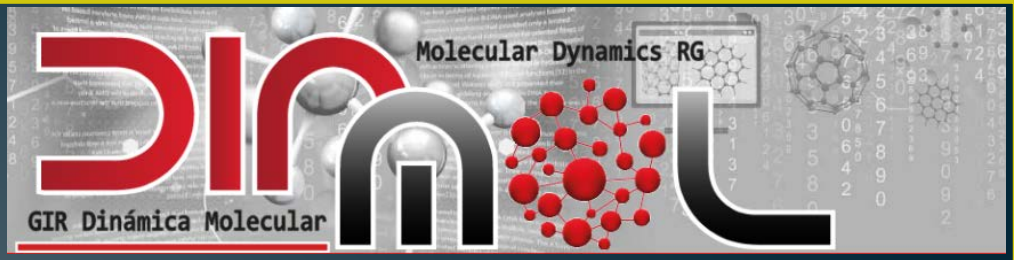

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- Can we talk about collision mechanisms?
- How could we define it? (Even quantify it?, measure it?)

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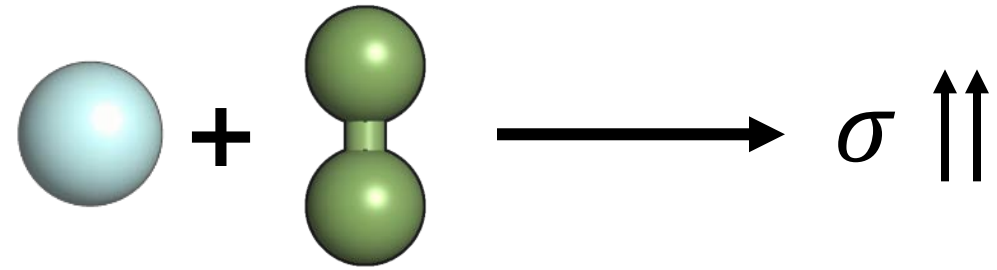

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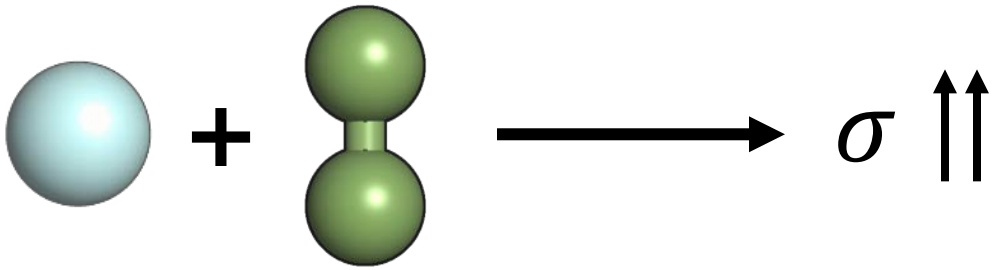

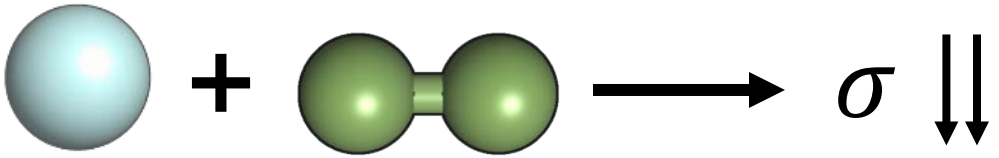

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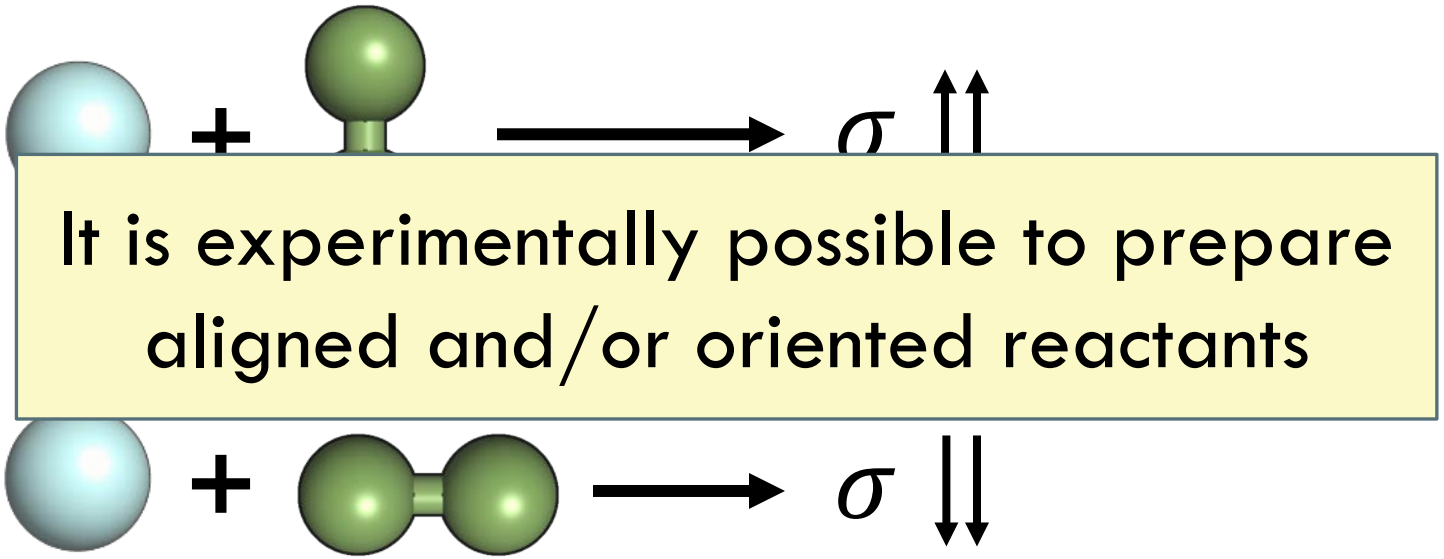

SARP Experiment

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Quantum-Controlled Collisions of H_2 Molecules

Nandini Mukherjee*

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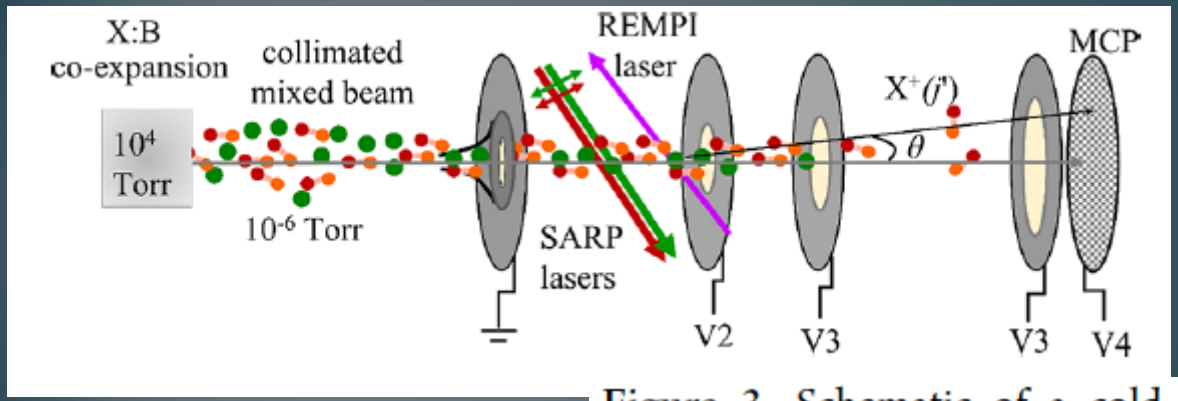
J. Phys. Chem. A 2023, 127, 418–438



co-expansion beam experiments for which using Optical Raman Pumping is possible to prepare a pure $|v\ j\ m=0\rangle$ state. m, determined regard to a laboratory frame (space-fixed).

Figure 3. Schematic of a cold scattering experiment within a co-expanded mixed supersonic beam containing the colliding partners (X and B). Polarized SARP laser beams (red and green) prepare the target molecule X (H_2, HD, or D_2) in a given rovibrational m eigenstate (v, j, m), where m refers to the projection of the rotational angular momentum j along the molecular beam direction. The colliding partner B (He, Ne, H_2, D_2, or HD) is left unprepared. The collision product is ionized state-selectively using REMPI with tunable vacuum ultraviolet pulses and detected on a multichannel plate (MCP) following a passage through the time-of-flight mass spectrometer, which is attached to the

SARP Experiment

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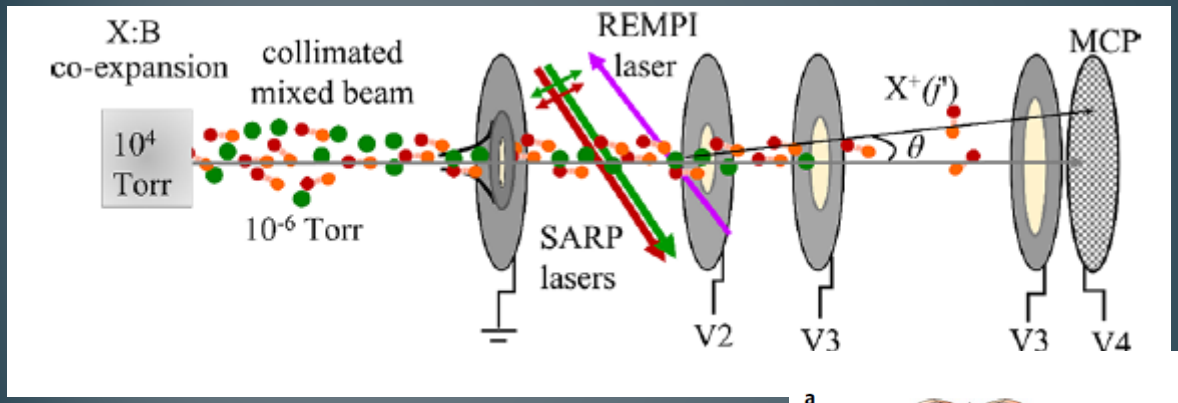

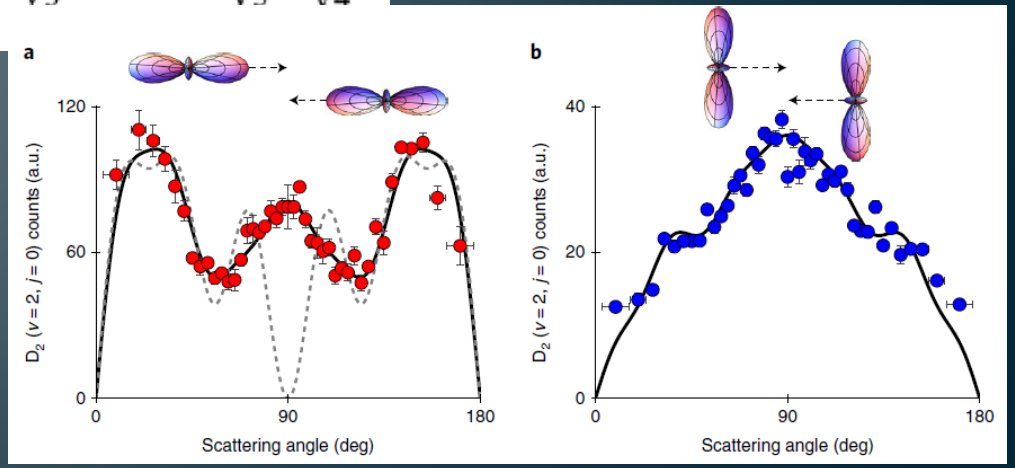

Zhou et al., Nature Chemistry, 14, 658–663 (2022)

SARP Experiment

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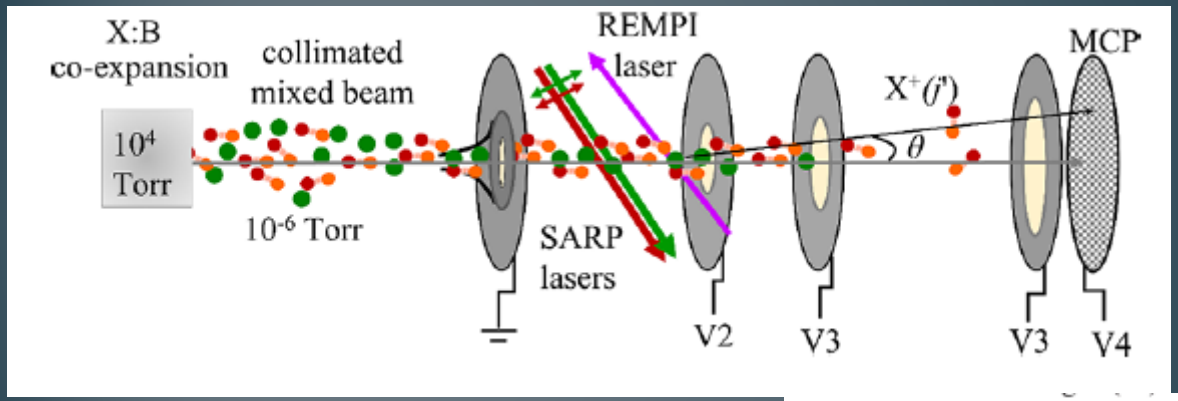

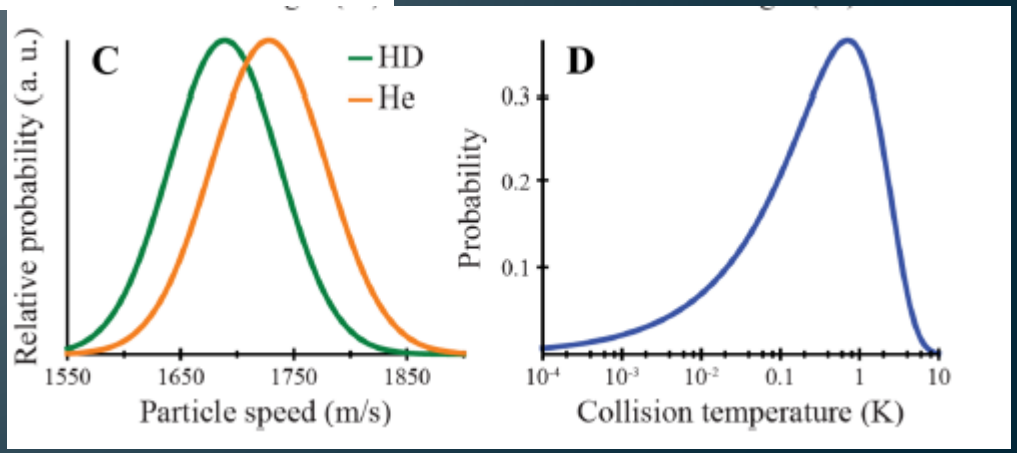

Perreault et al., J. Phys. Chem. Lett. 2022, 13, 10912−10917

SARP Experiment

RESEARCH

CHEMICAL PHYSICS

Quantum control of molecular collisions at 1 kelvin

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nature chemistry

ART

https://doi.org/10.1038/s41557-

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ARTICLES

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Quantum Controlled Cold Scattering Challenges Theory

William E. Perreault,† Haowen Zhou,† Nandini Mukherjee,* and Richard N. Zare*

RESEARCH

QUANTUM MECHANICS

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Very stringent test for calculations

SARP Experiment. 4 e^- systems

- $D_2 + D_2$
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SARP Experiment. 4 e^- systems

- $D_2 + D_2$
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- Conclusions:
  - For both systems they infere the presence of an intense $\ell=2$ resonance
  - For $D_2 + D_2$ only collisions between aligned-aligned molecules are relevant

SARP Experiment. 4 e^- systems

- $D_2 + D_2$
  - Inelastic collisions
  - 6D PES (probably rigid rotor also works)
  - No open-shell fragments
  - Very accurate PES
- $He + D_2$
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- But cold energies require very high accuracy
- And we need the machinery to make calculations for non-isotropic reactants

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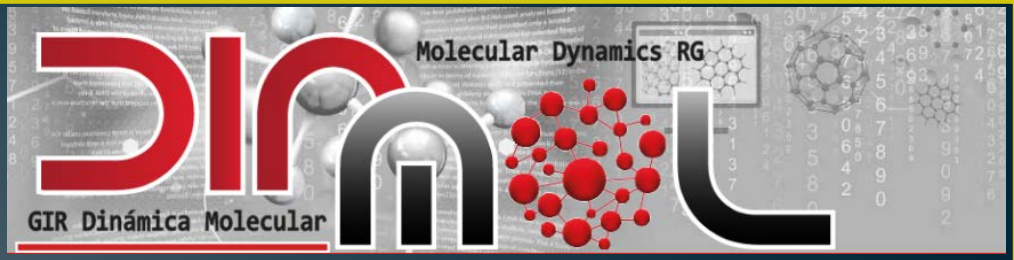

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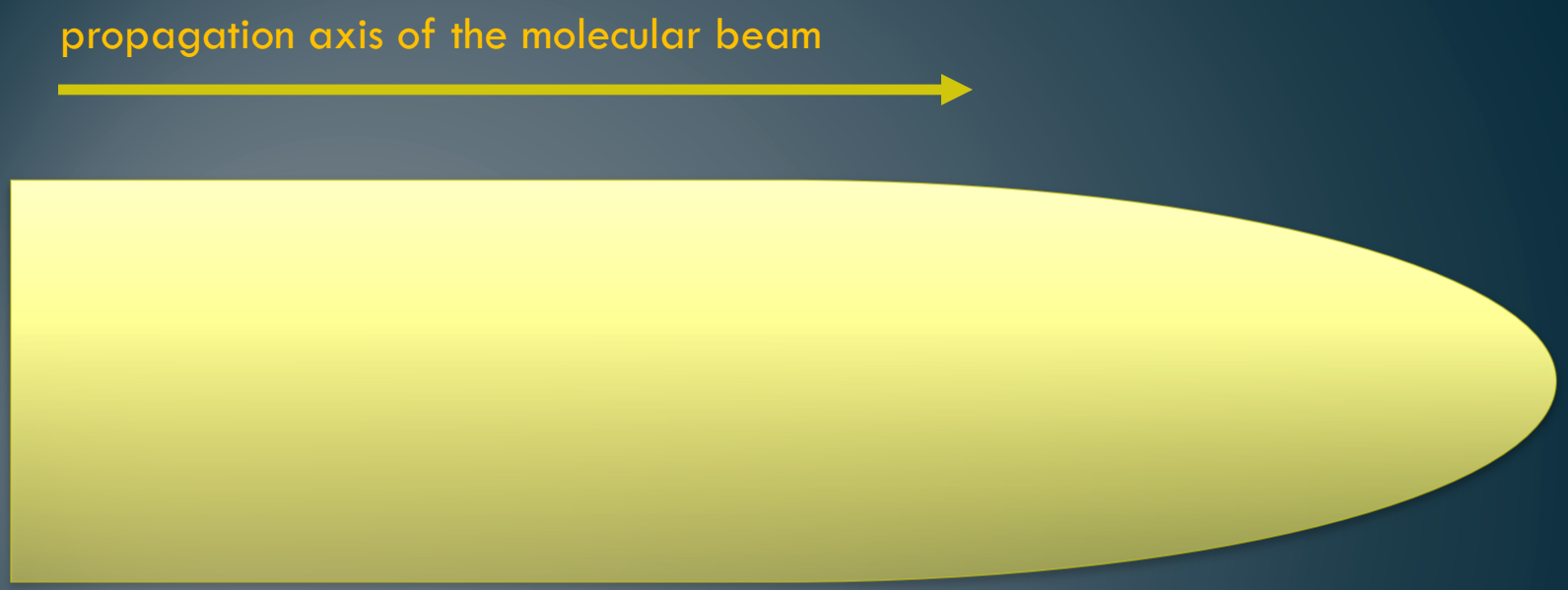

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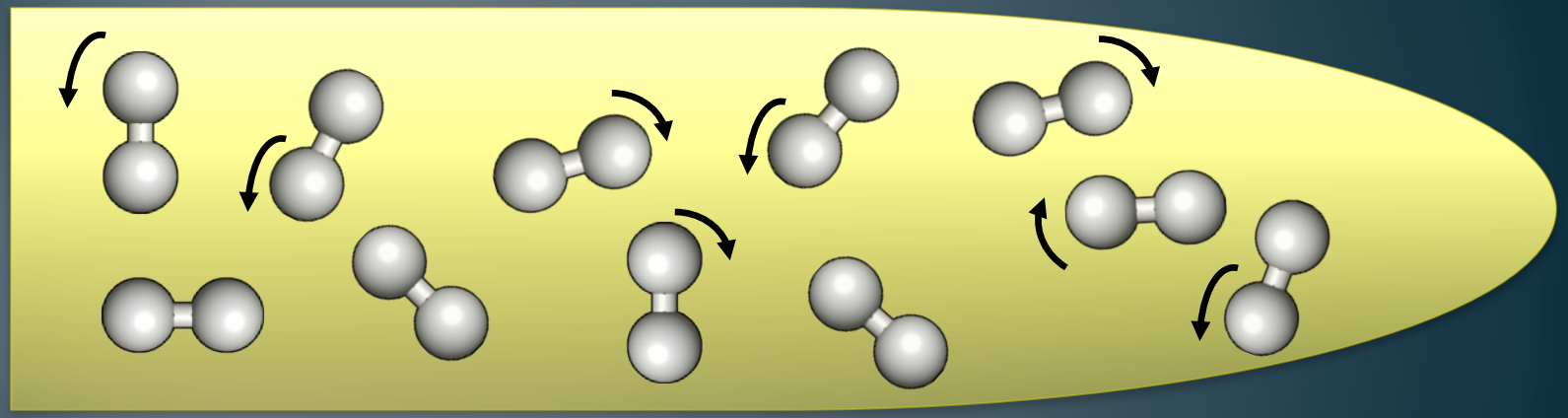
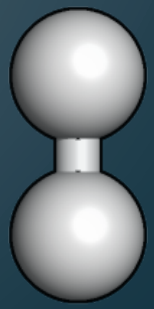
propagation axis of the molecular beam





- 38% in ($v = 0, j = 0$)
- 36% in ($v = 0, j = 1$)
- 24% in ($v = 0, j = 2$)

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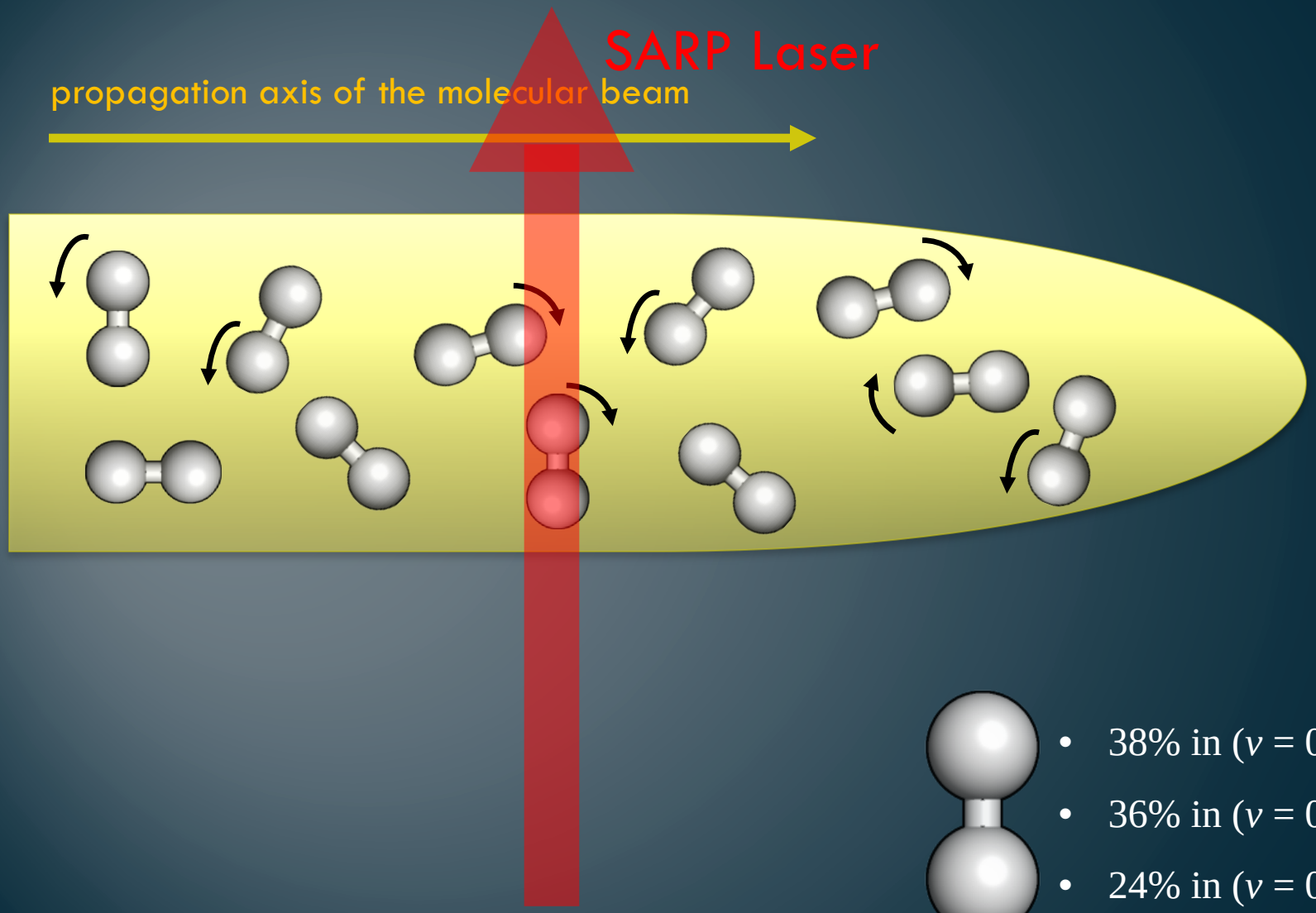

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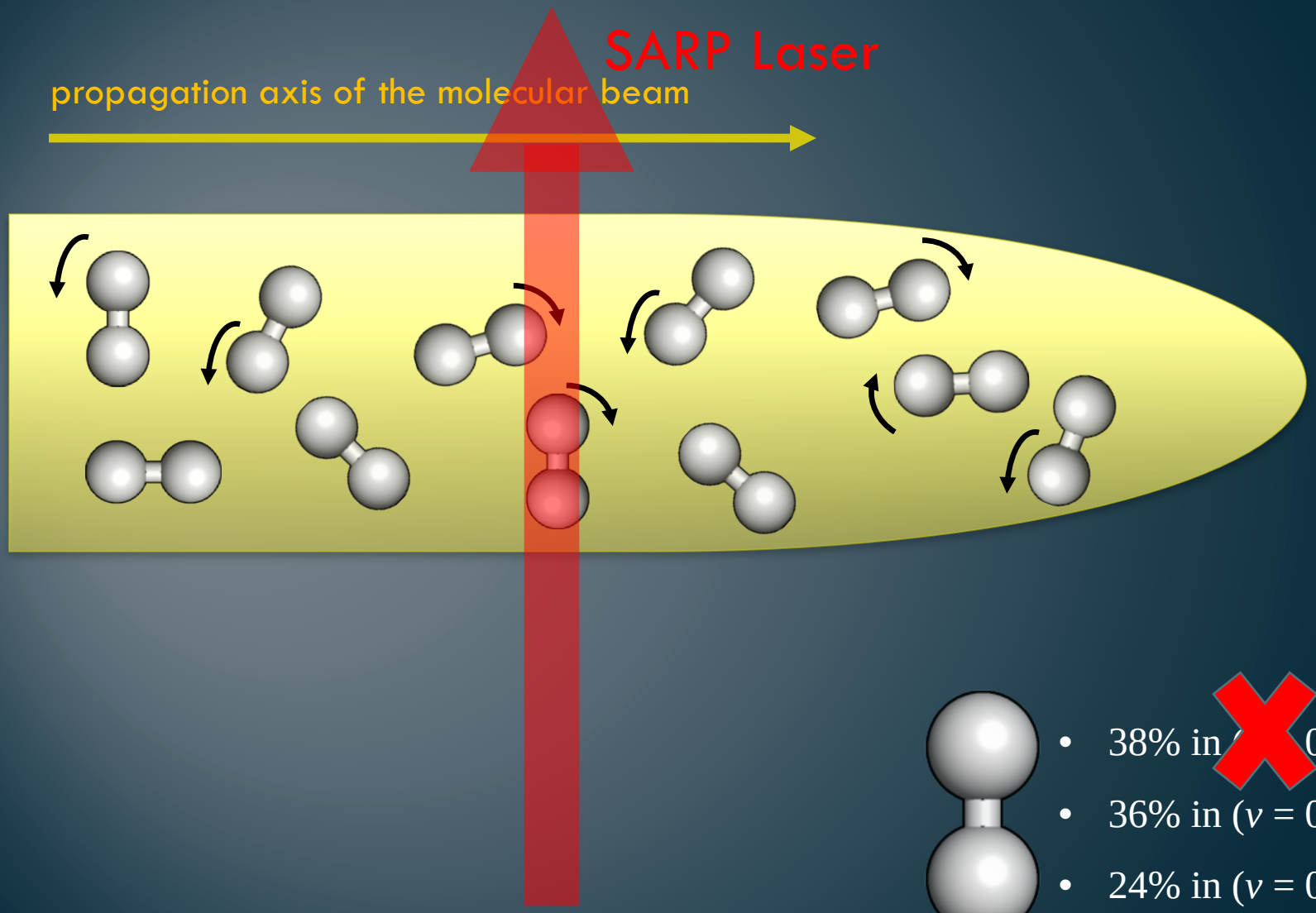

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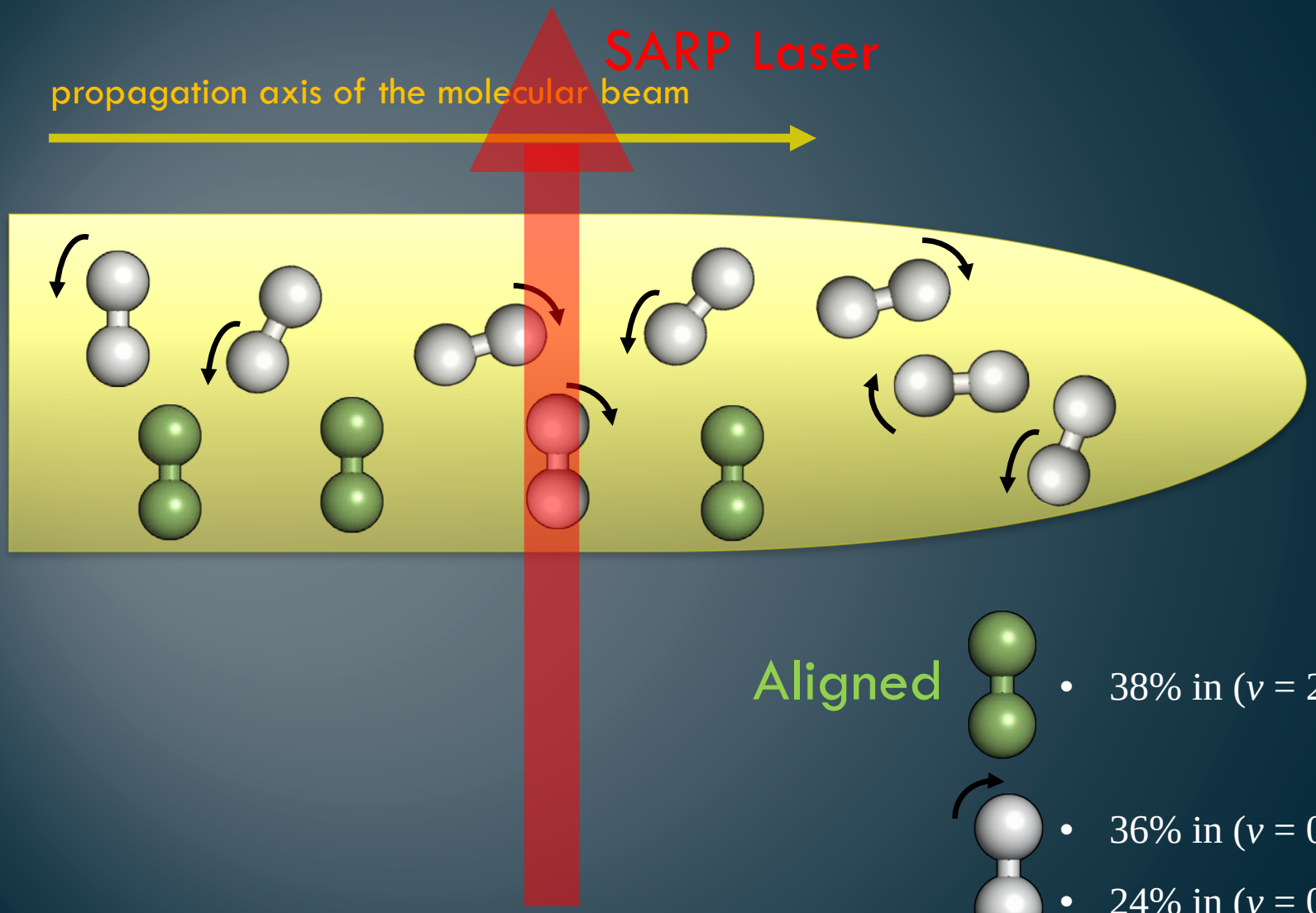

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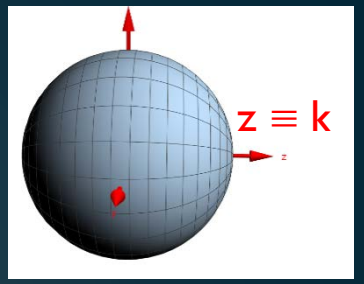
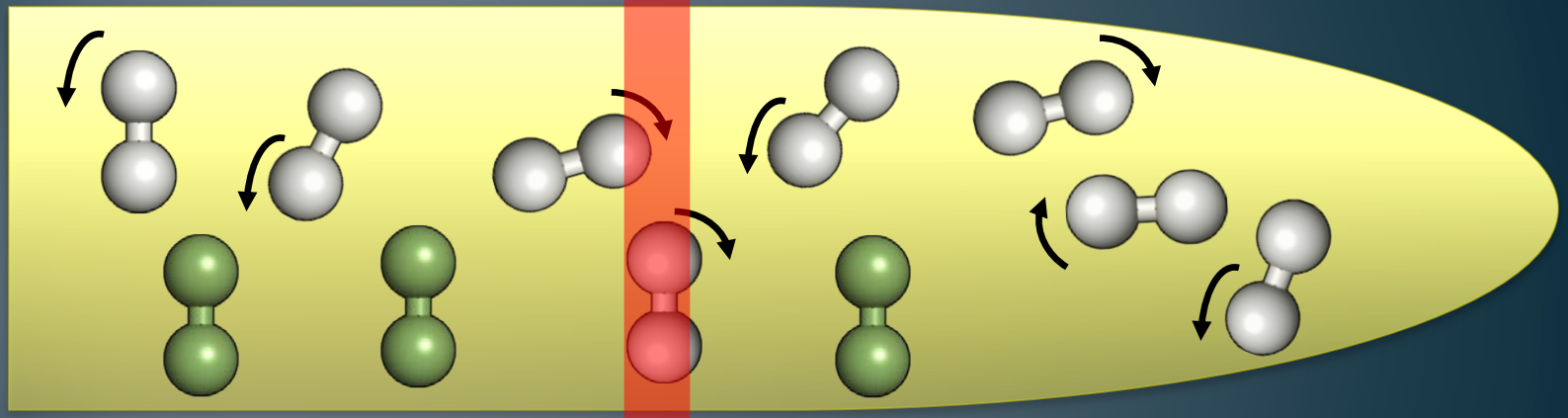
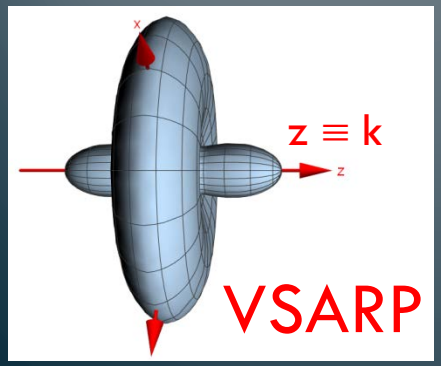


SARP Laser

propagation axis of the molecular beam





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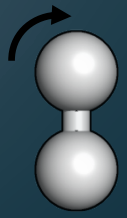

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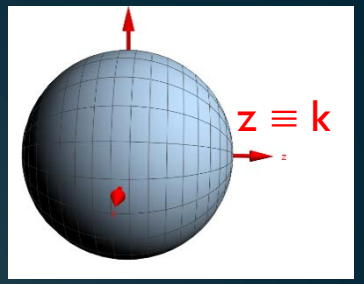

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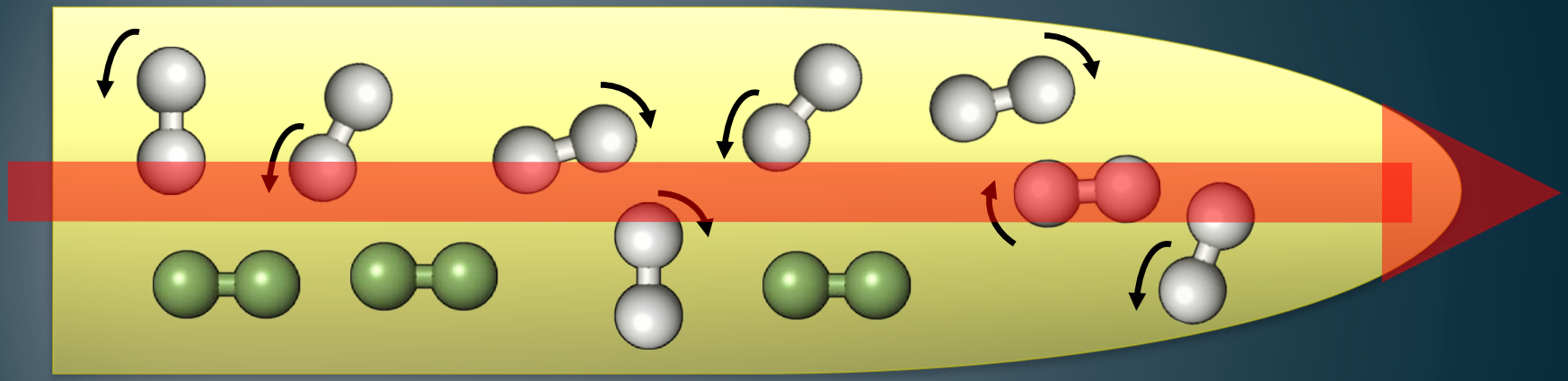

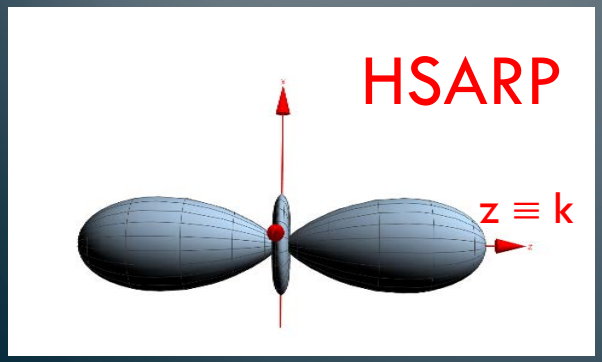

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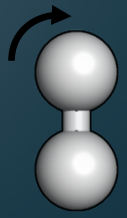

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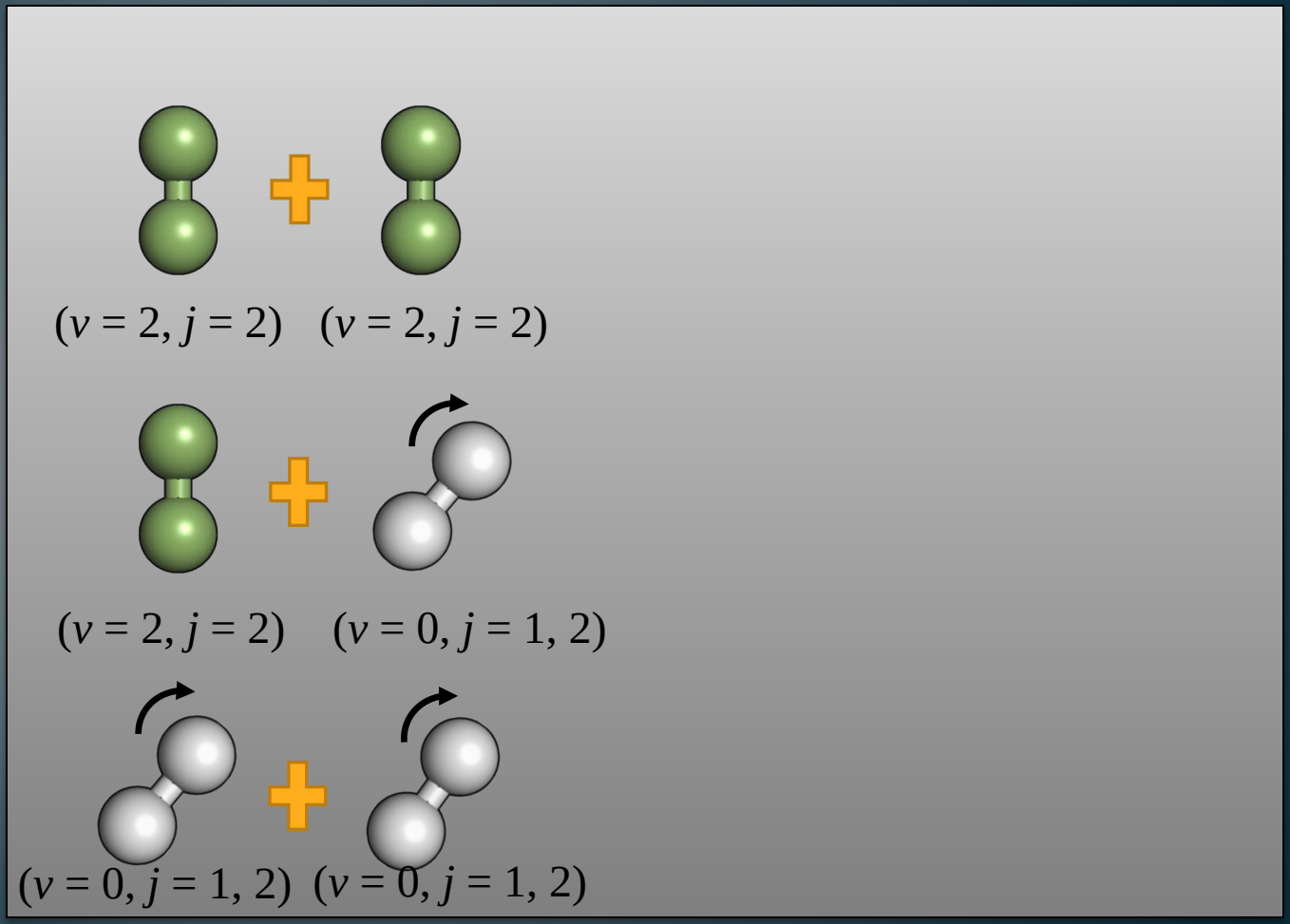

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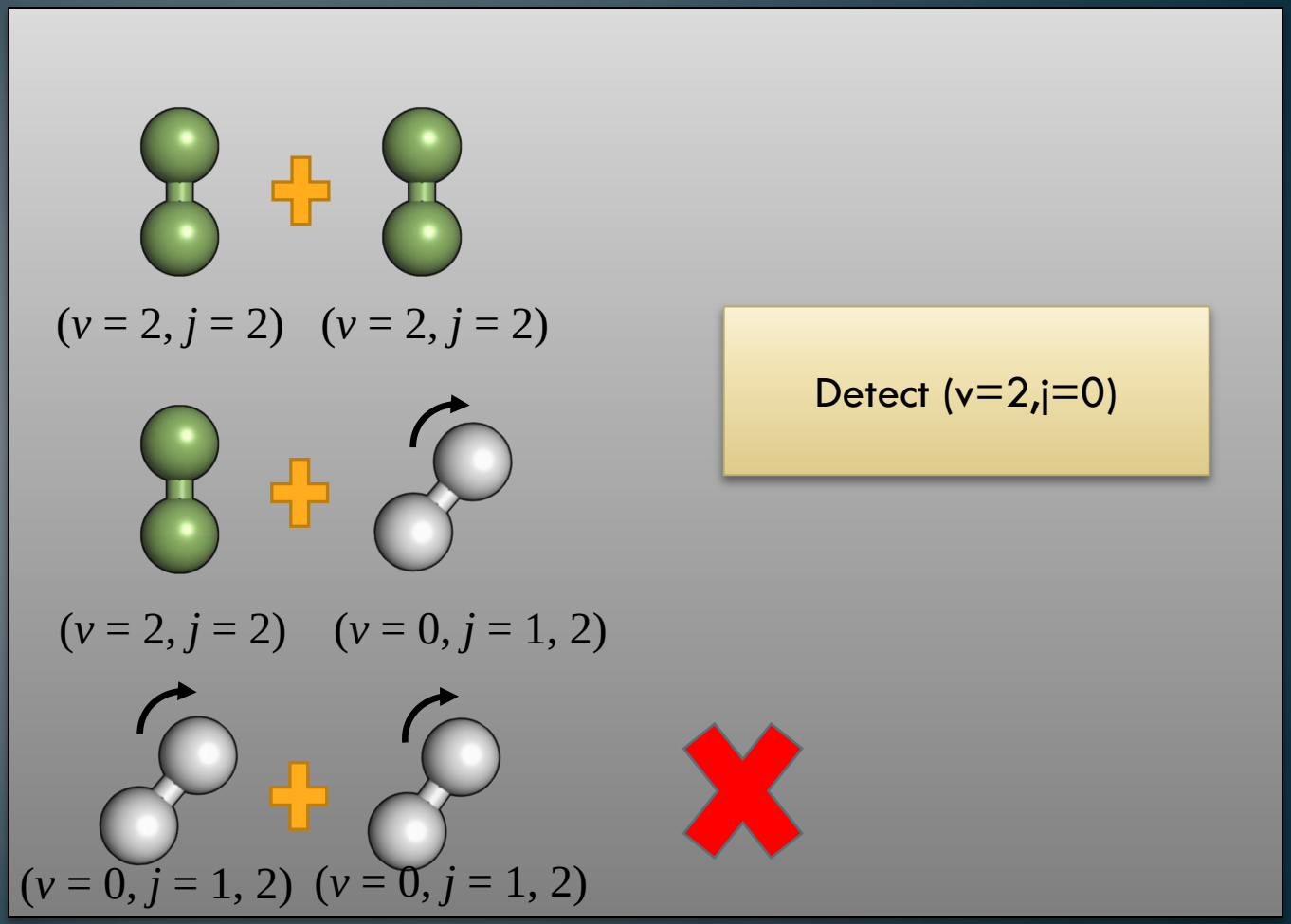

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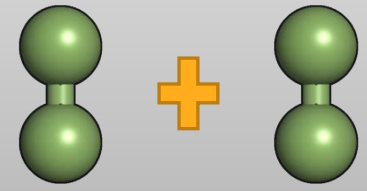
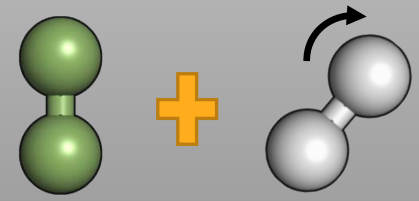


$(v = 2, j = 2)$ $(v = 2, j = 2)$

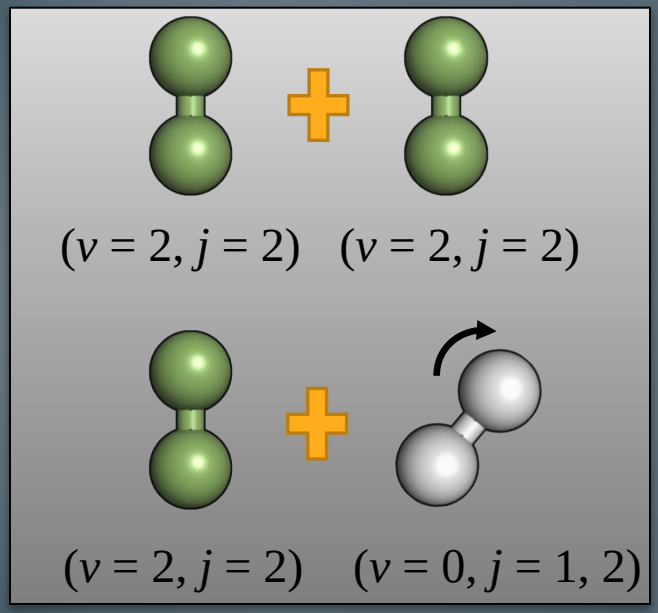
4-vector correlations (k-j_1-j_2-k')

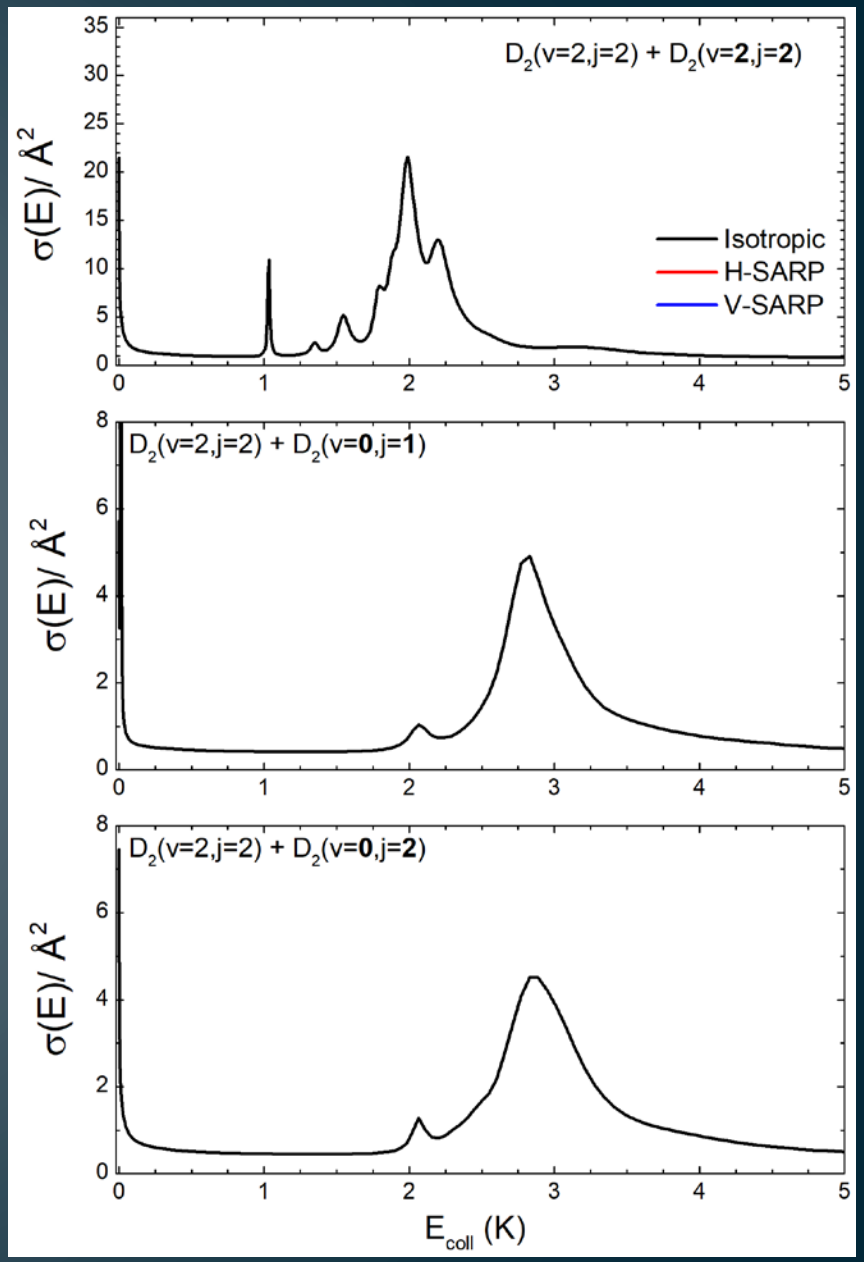


$(v = 2, j = 2)$ $(v = 0, j = 1, 2)$

3-vector correlations (k-j_1-k')

$D_2 + D_2$ collisions





Jambrina, Croft, Zuo, Guo, Balakrishnan, Aoiz Phys. Rev. Lett., **130,** 033002 (2023)

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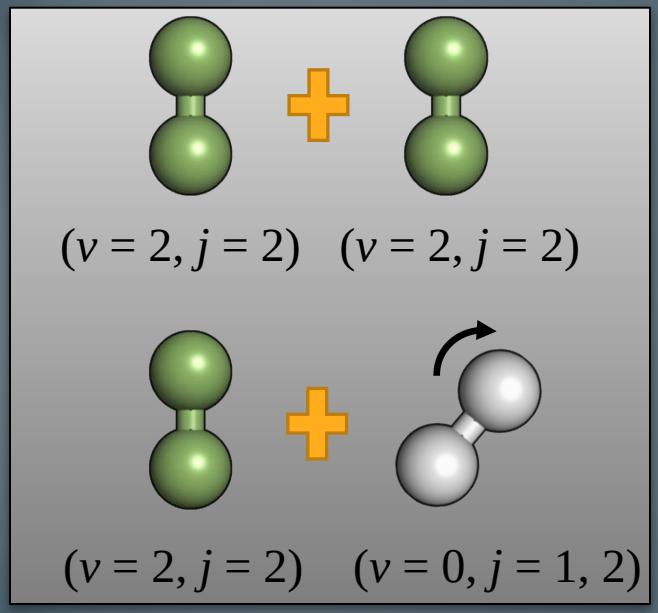

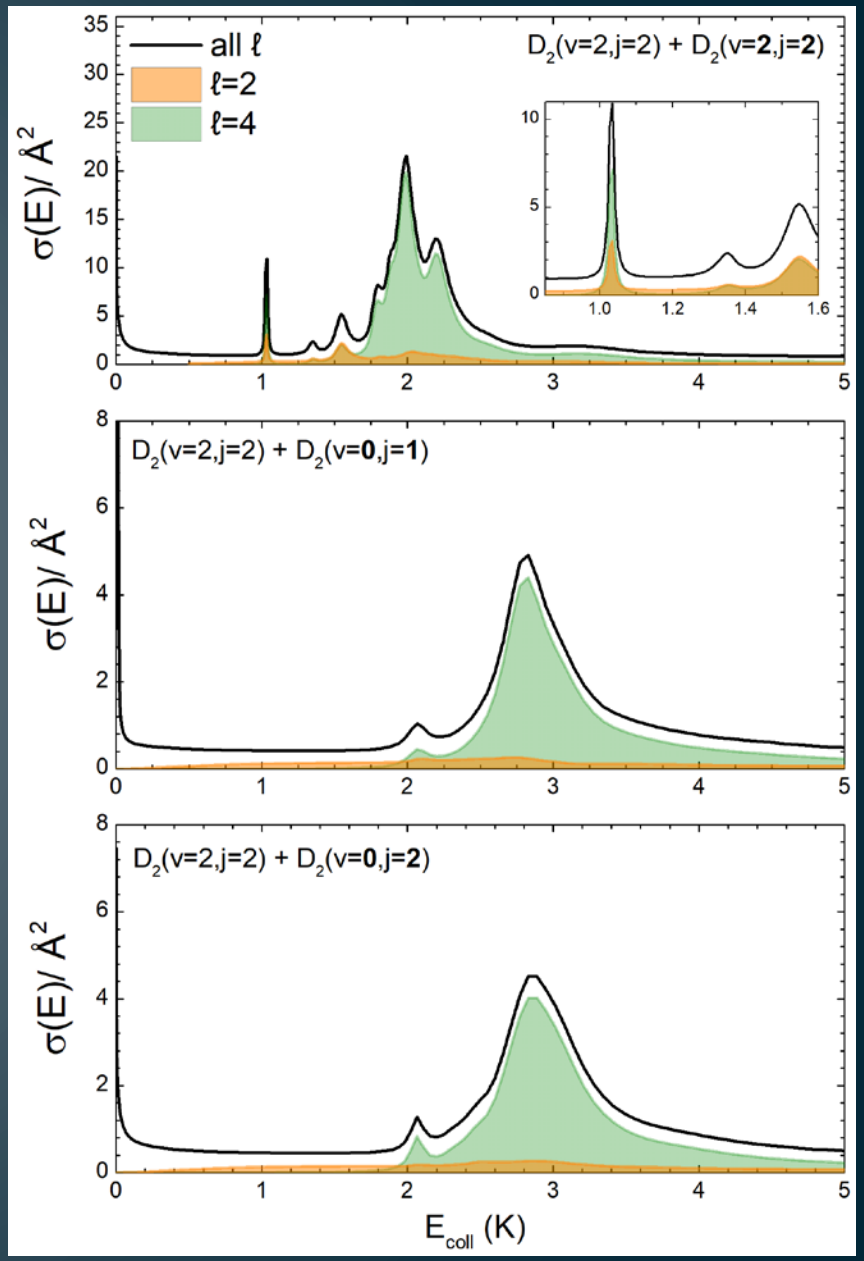

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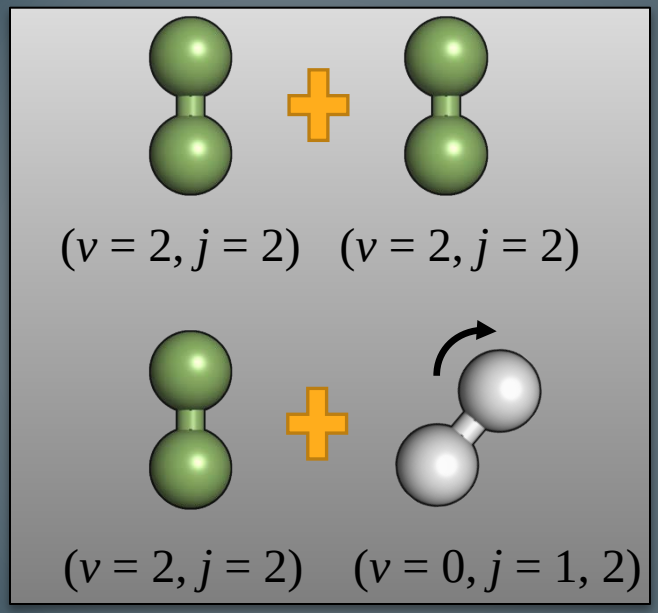

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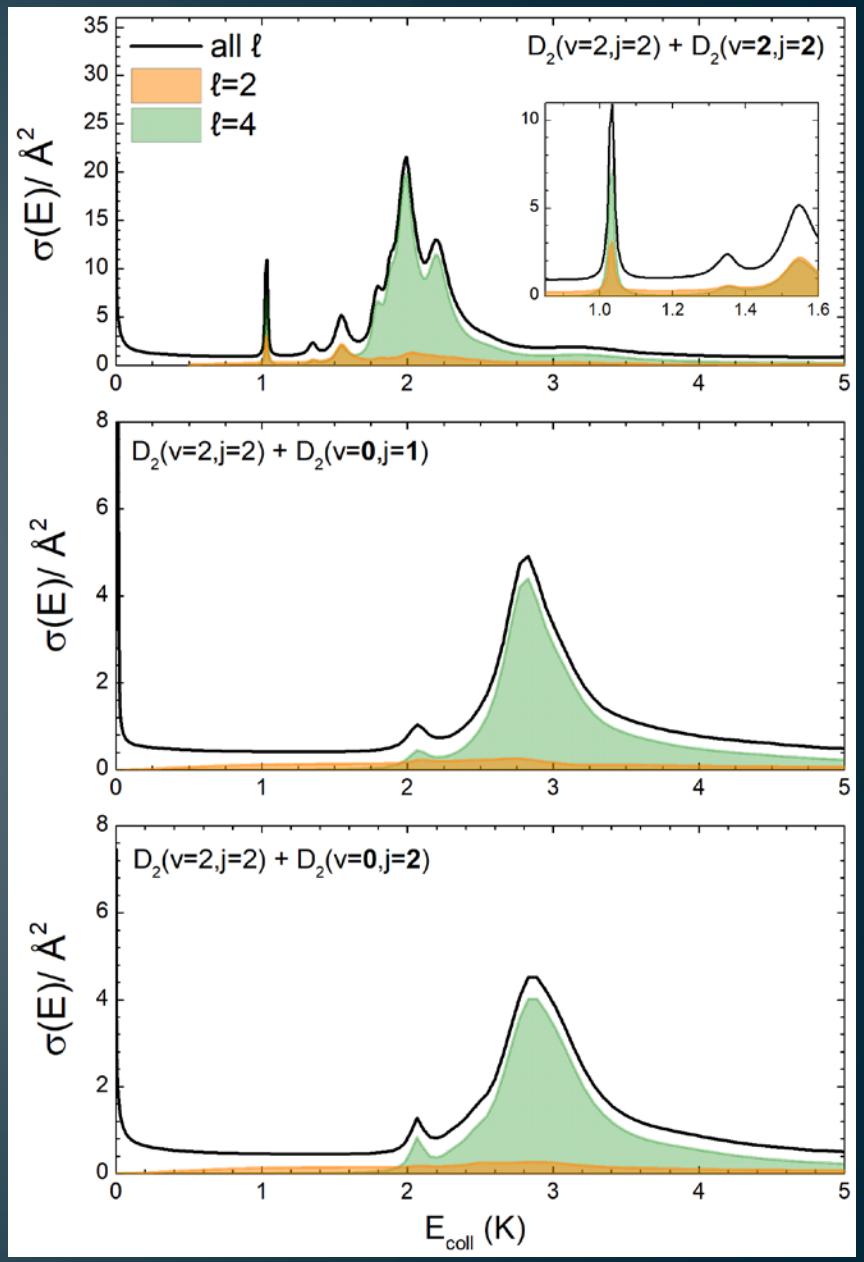
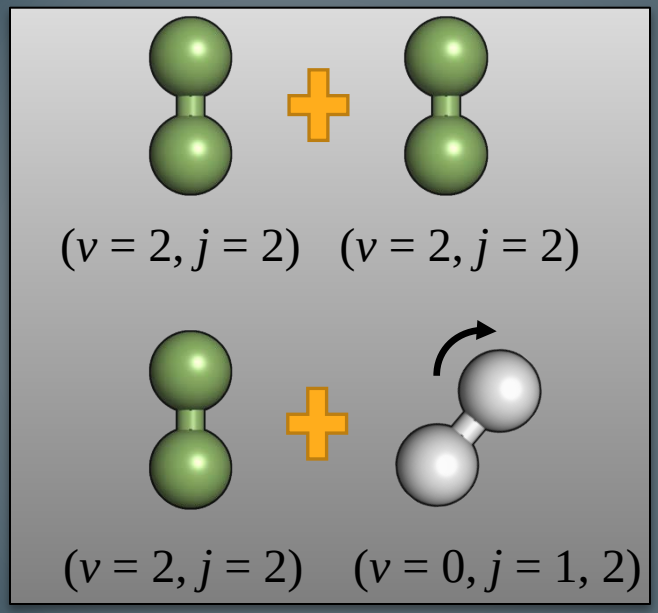
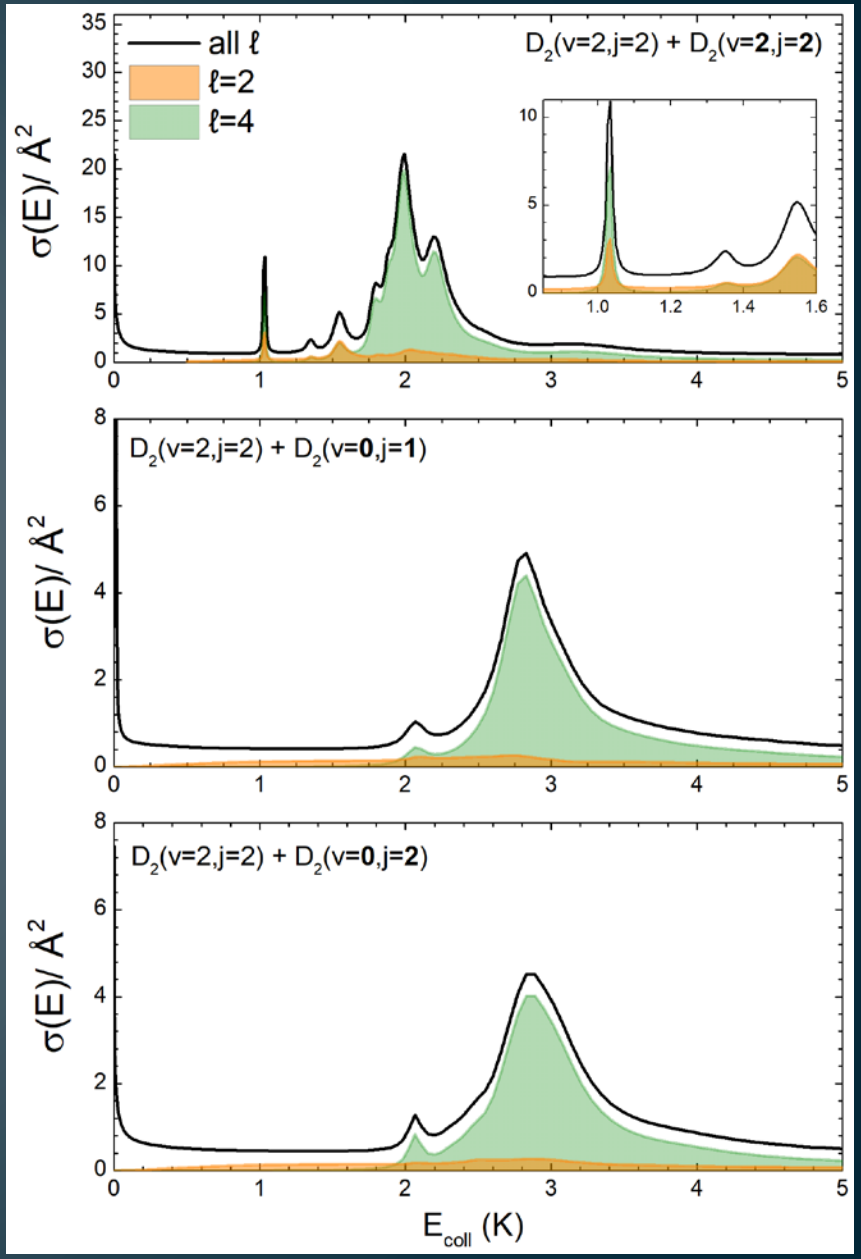


Jambrina, Croft, Zuo, Guo, Balakrishnan, Aoiz Phys. Rev. Lett., **130,** 033002 (2023)

D_2 + D_2 collisions



~~ℓ=2~~ ℓ=4



Jambrina, Croft, Zuo, Guo, Balakrishnan, Aoiz Phys. Rev. Lett., **130,** 033002 (2023)

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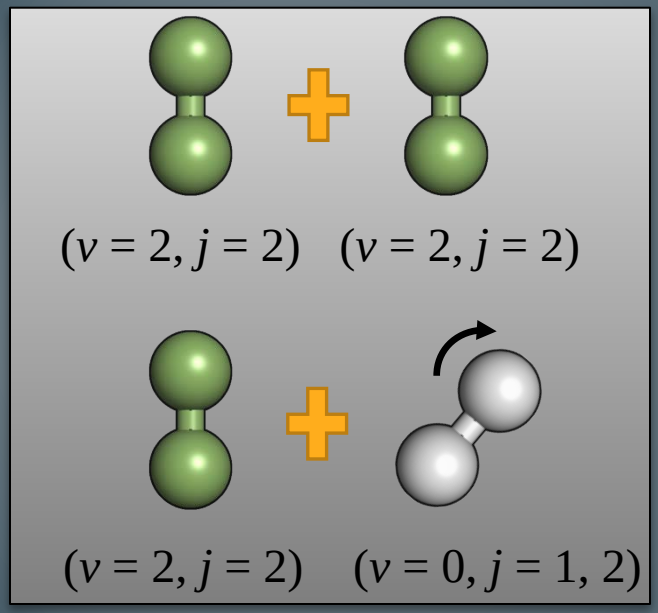

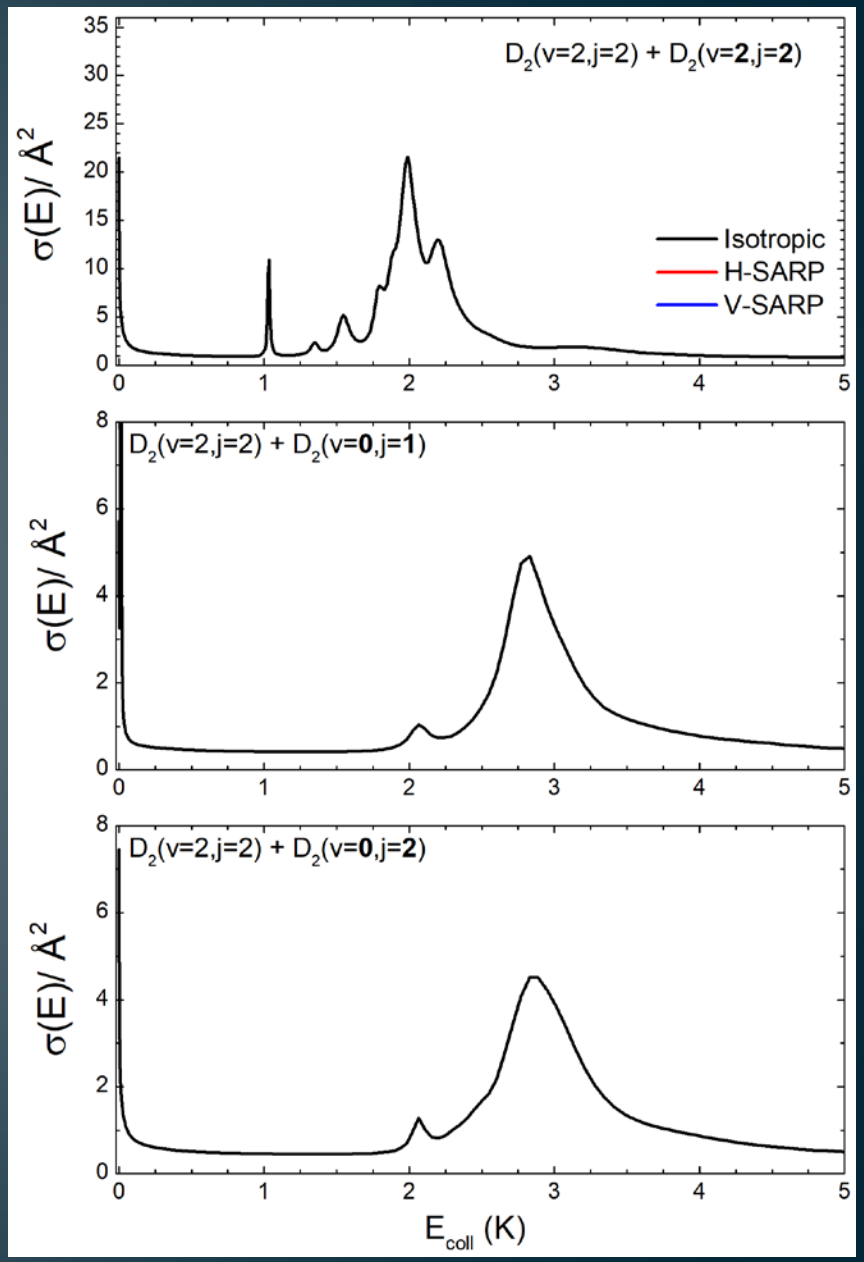

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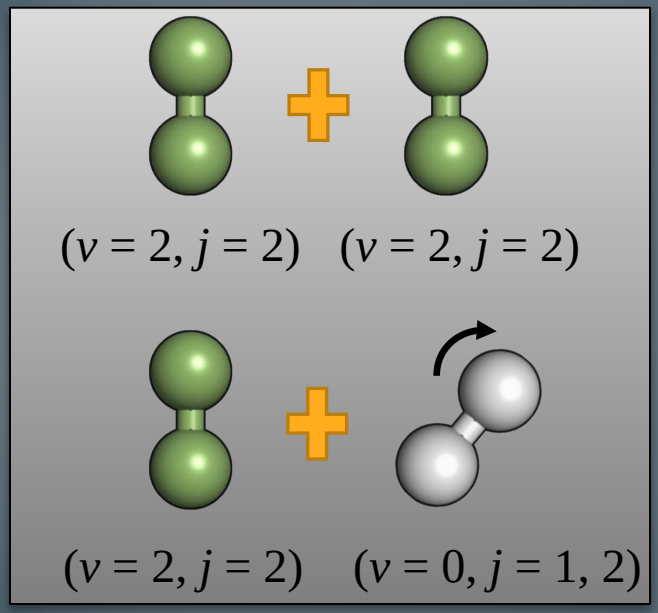

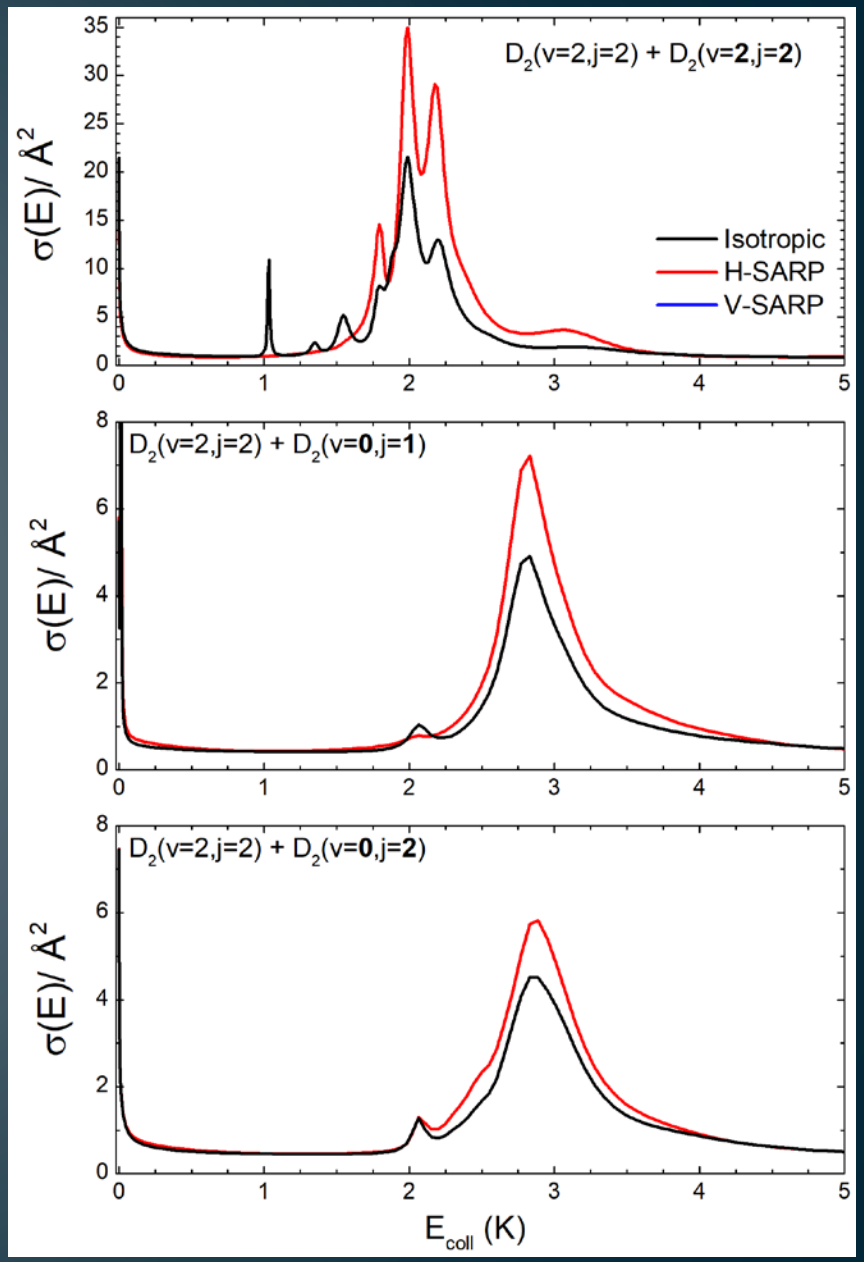

Jambrina, Croft, Zuo, Guo, Balakrishnan, Aoiz Phys. Rev. Lett., **130,** 033002 (2023)

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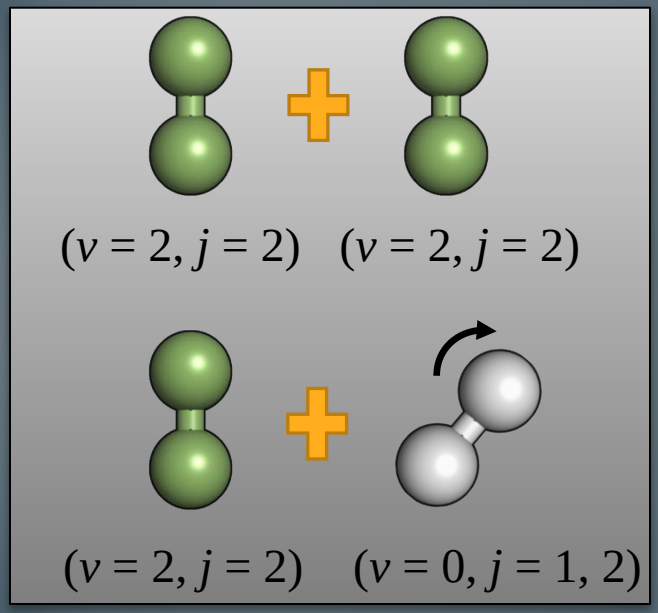

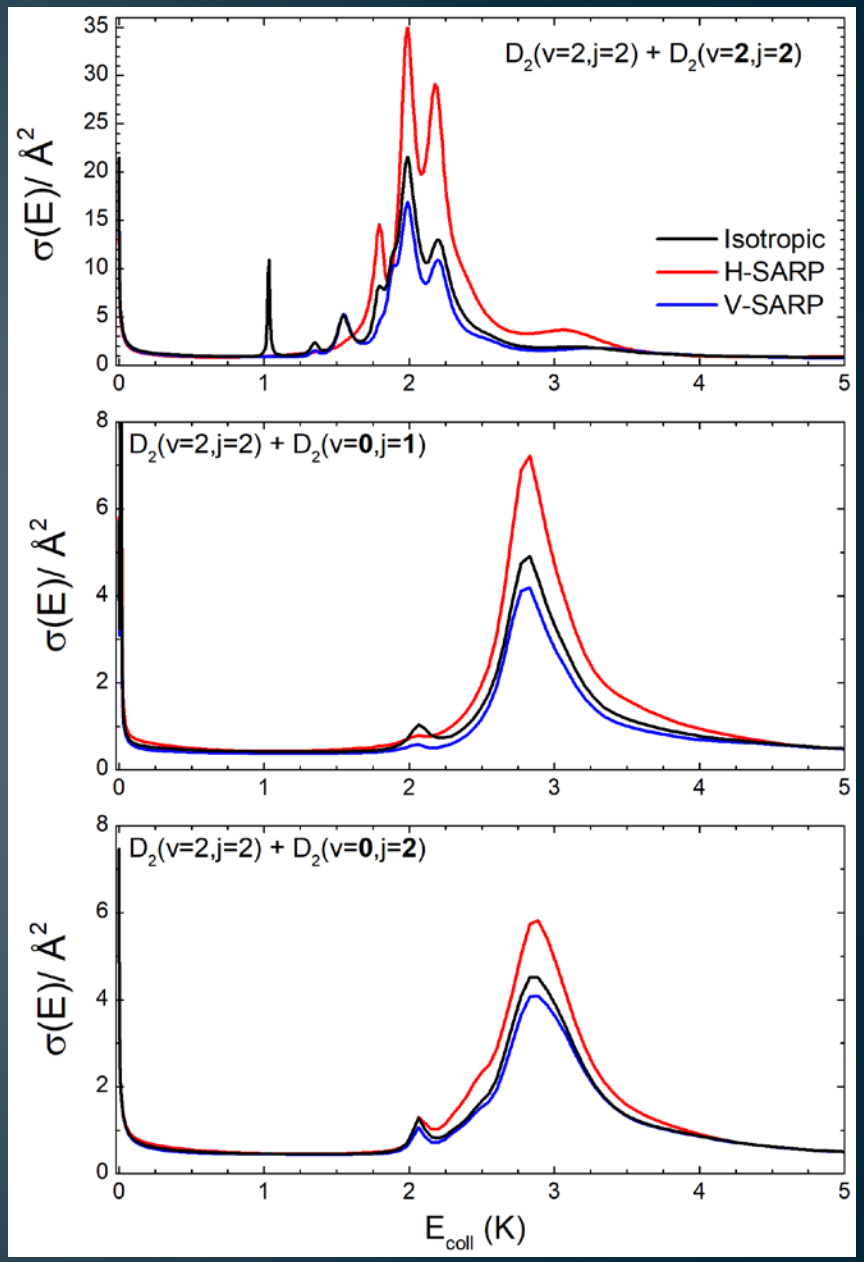

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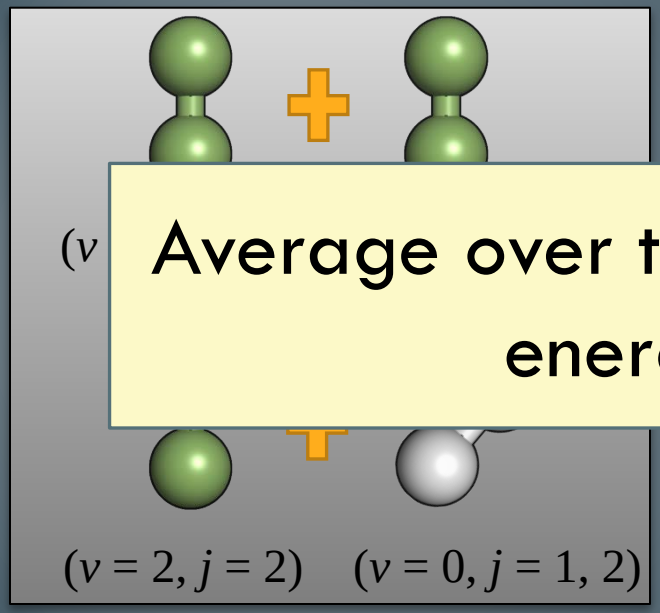
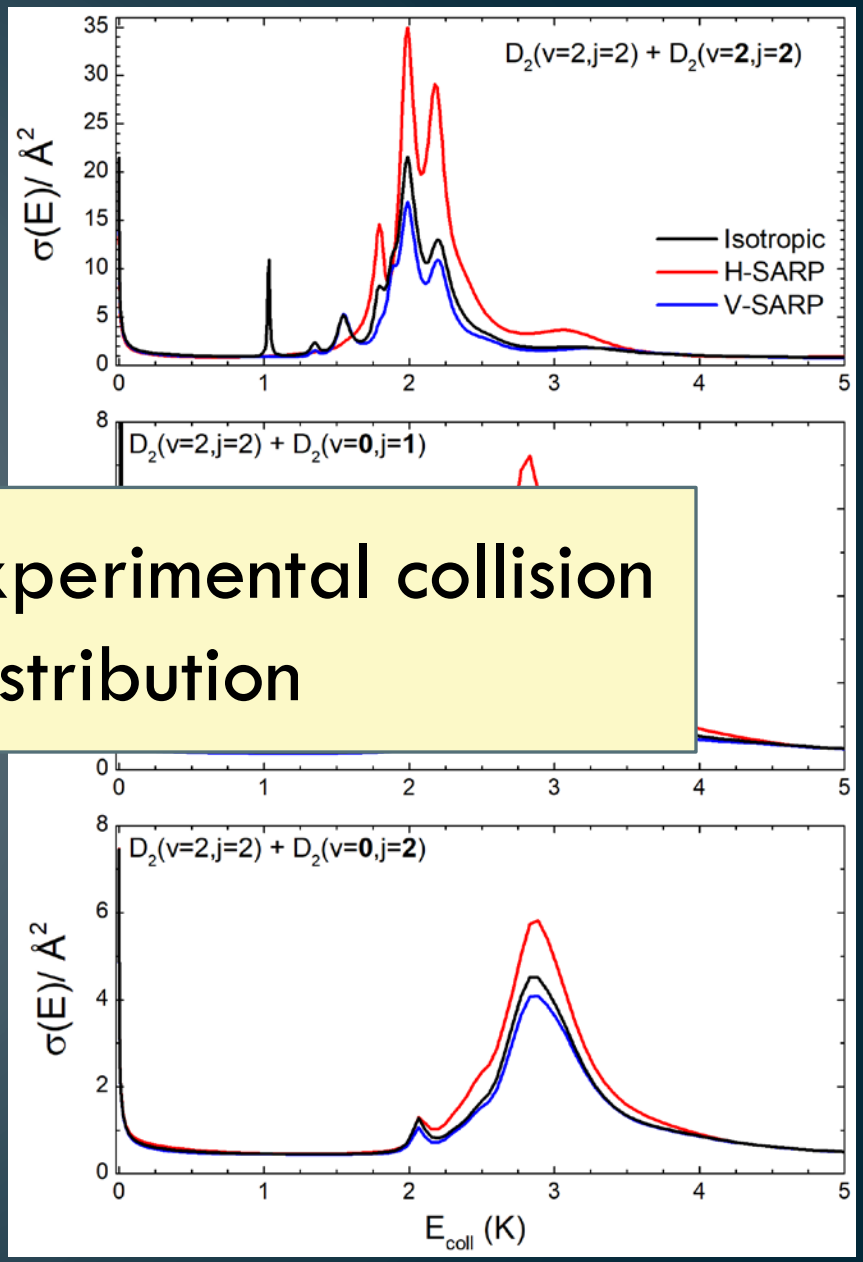


Average over the Experimental collision energy distribution



Jambrina, Croft, Zuo, Guo, Balakrishnan, Aoiz Phys. Rev. Lett., **130,** 033002 (2023)

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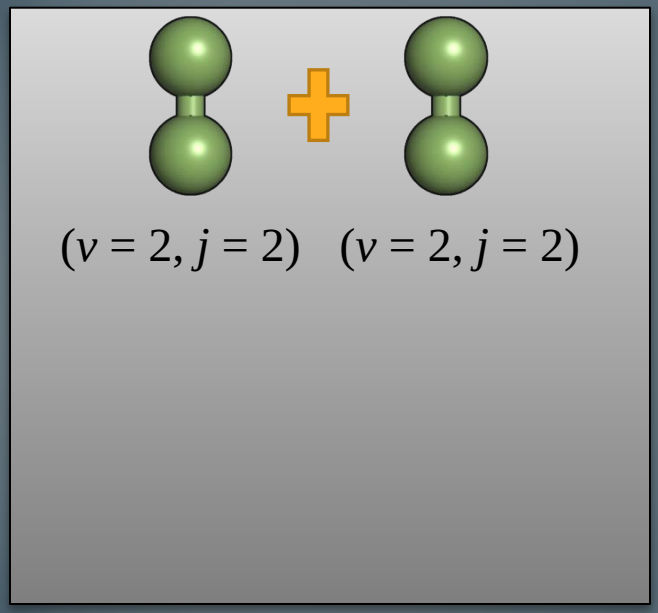

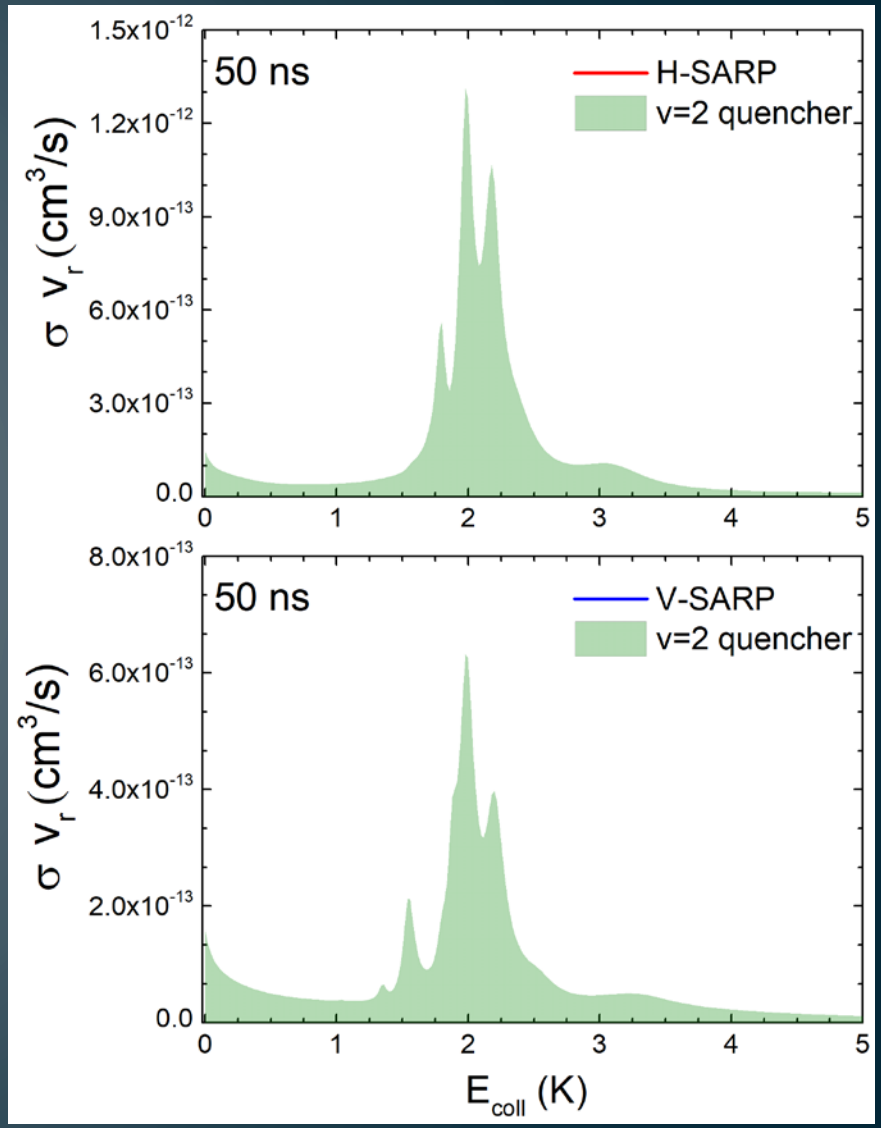

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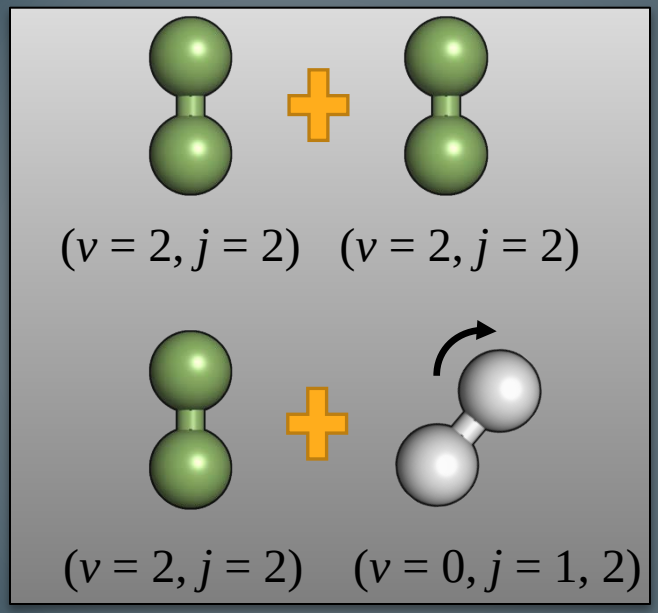

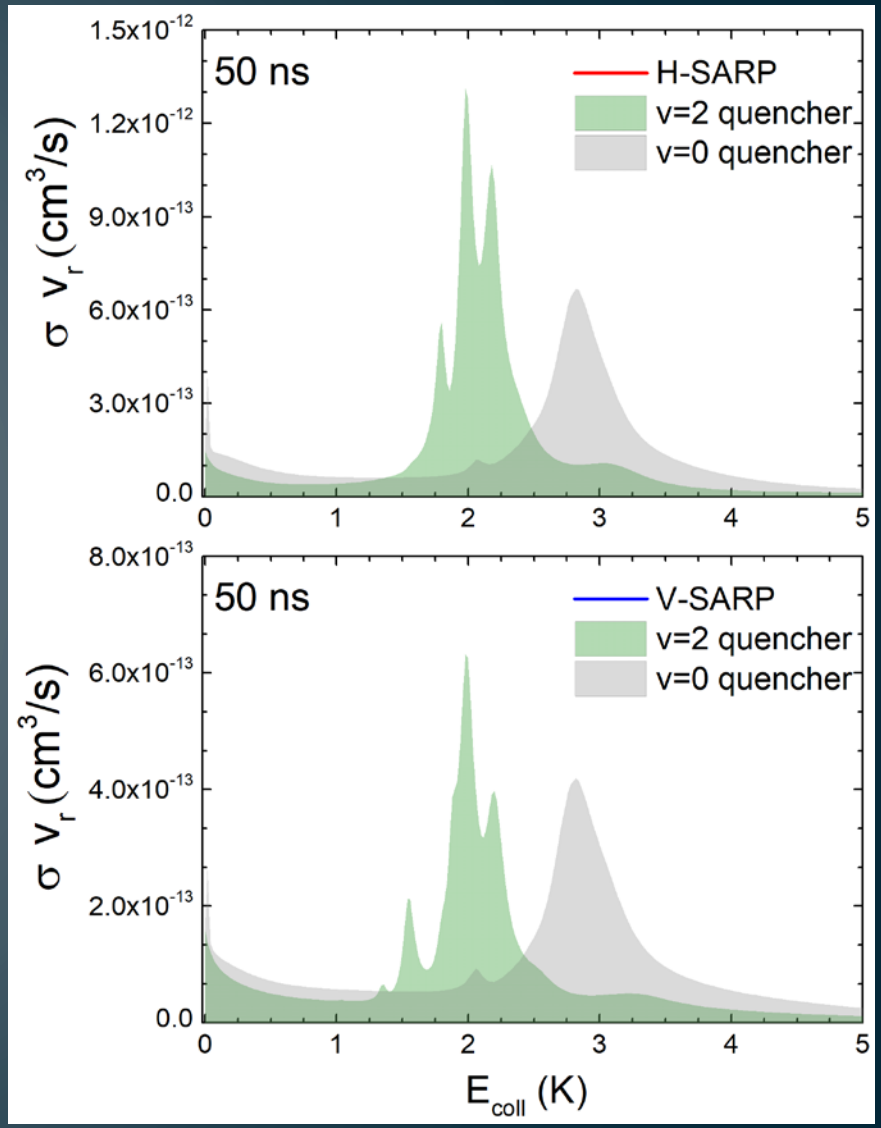

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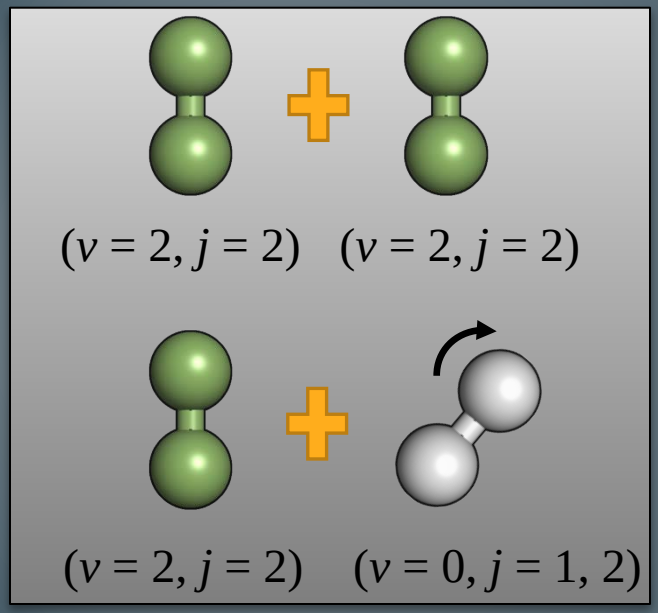

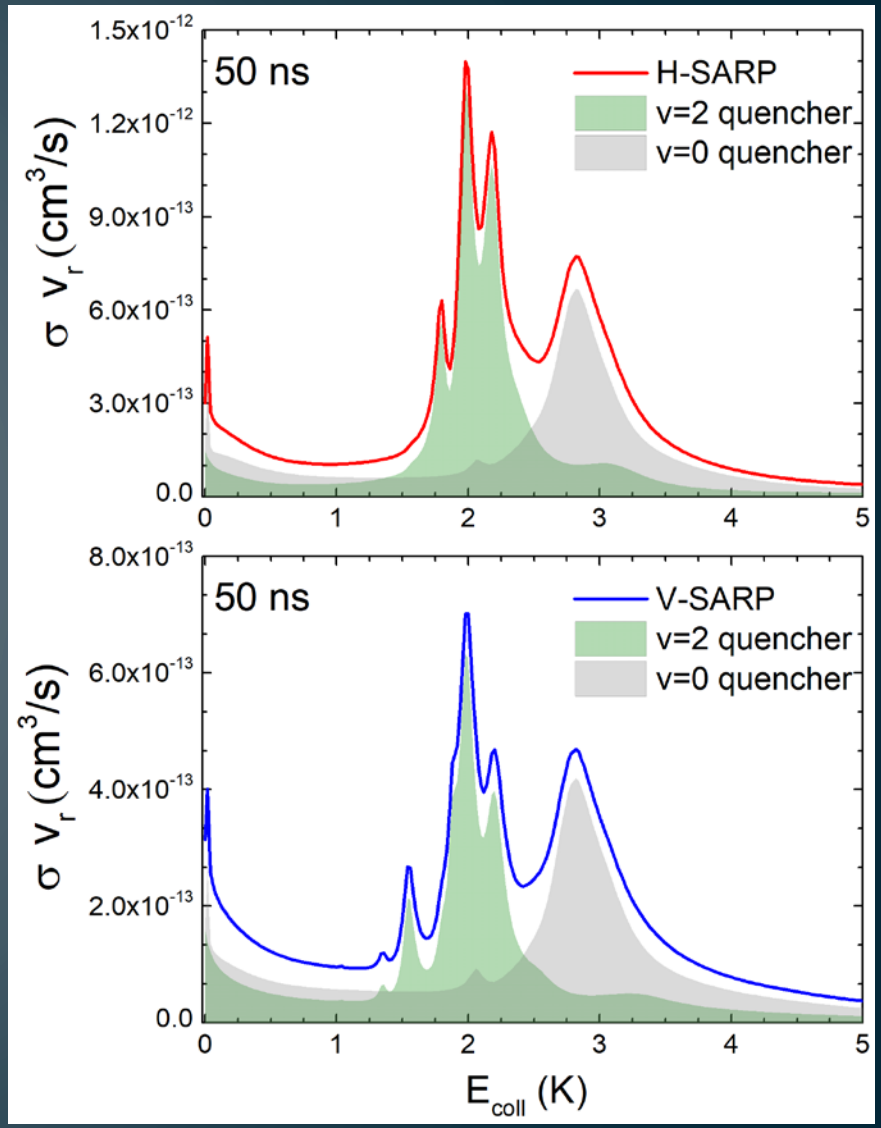

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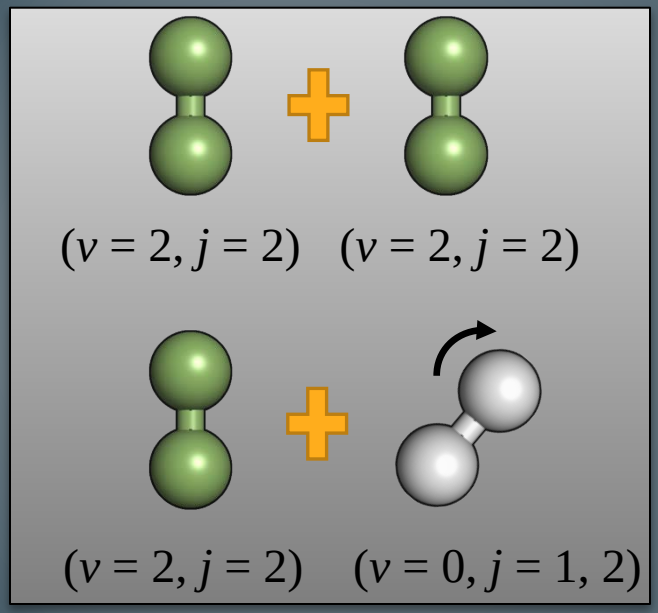

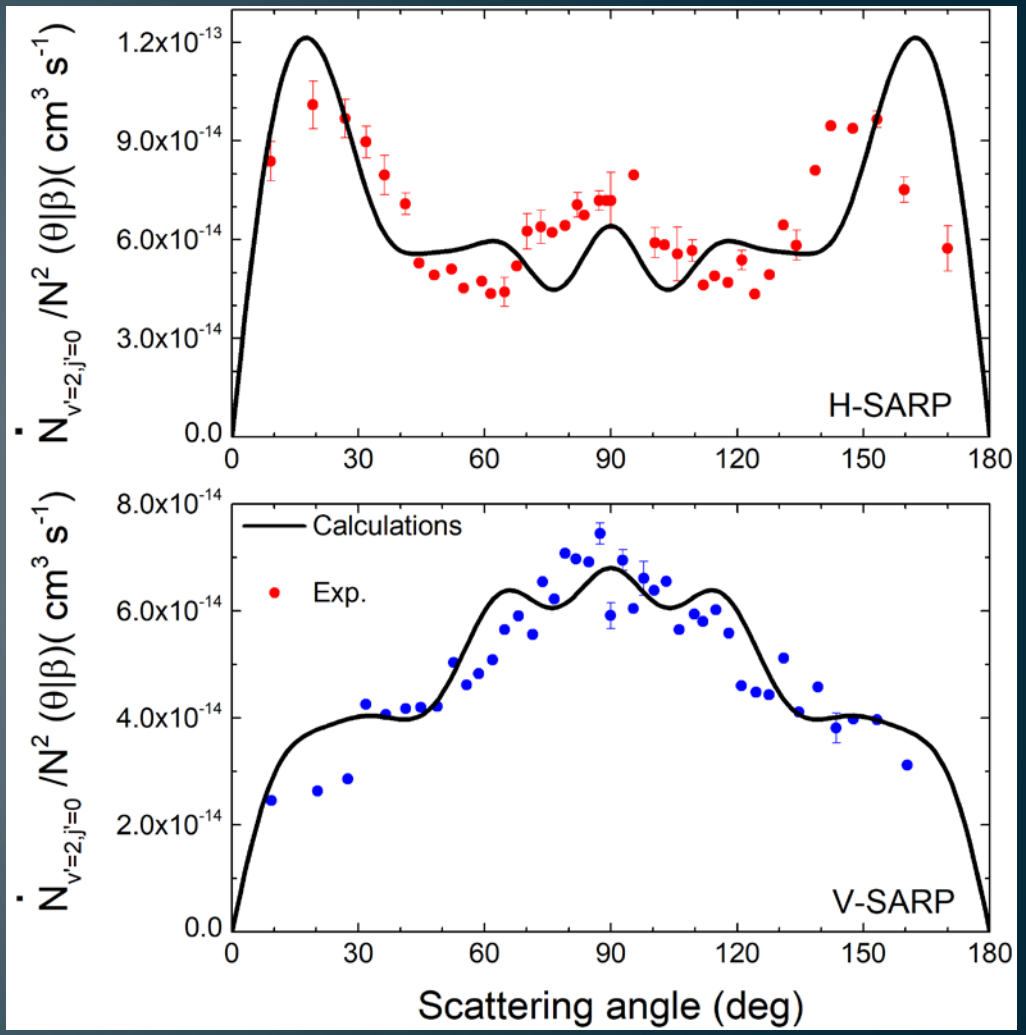

Experiments: Zhou, Perreault, Mukherjee, Zare,Nat. Chem. **14**, 658 (2022).

Jambrina, Croft, Zuo, Guo, Balakrishnan, Aoiz Phys. Rev. Lett., **130**, 033002 (2023)

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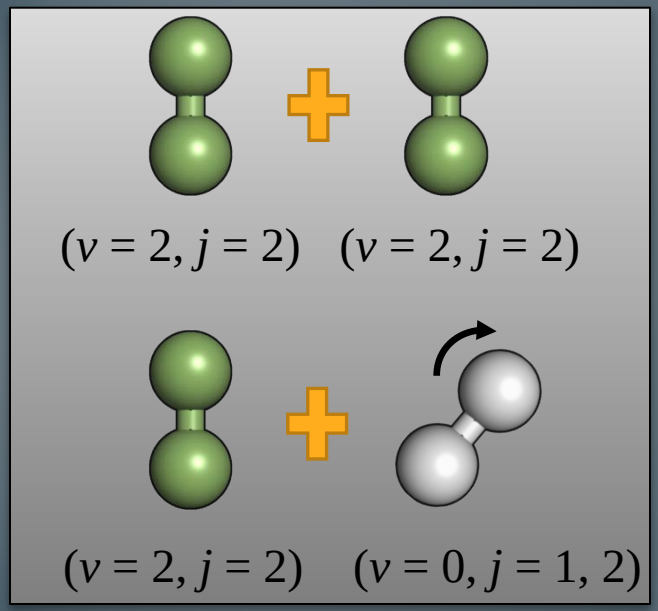

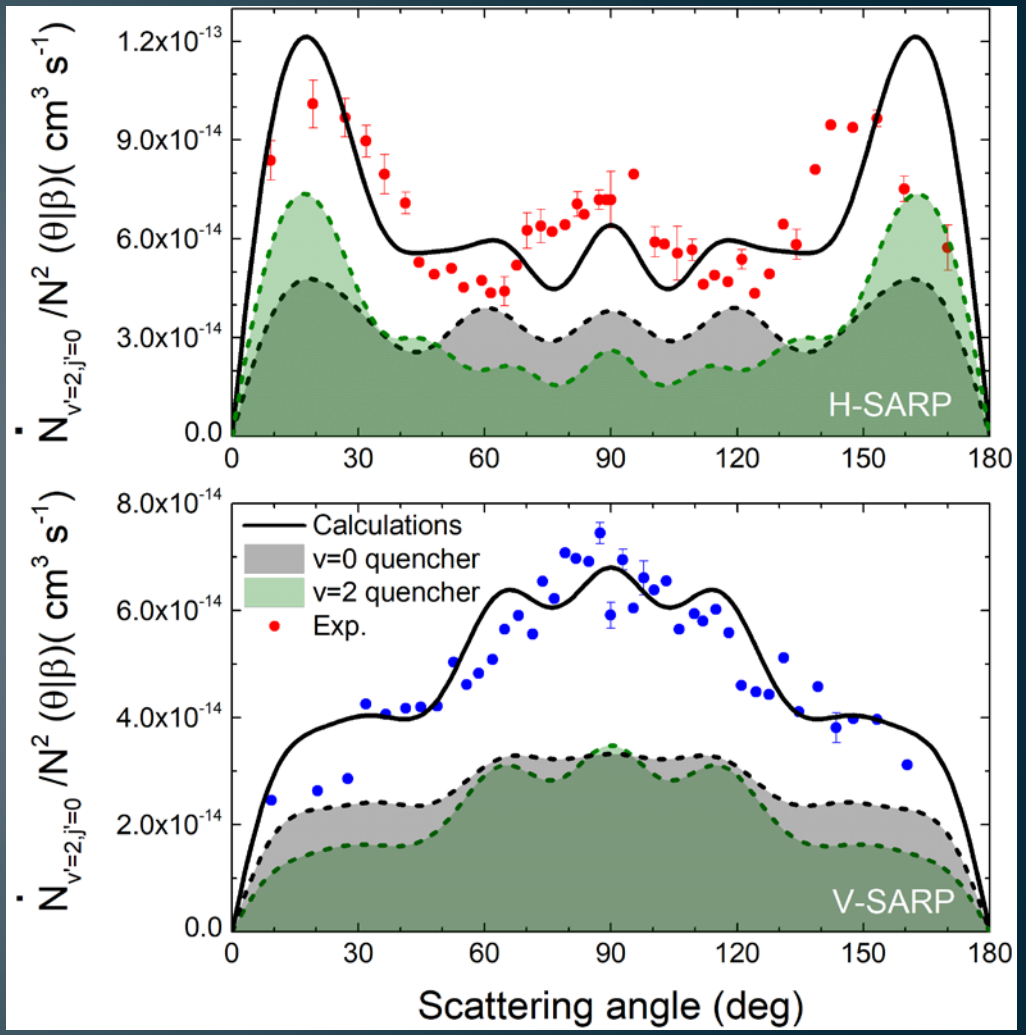

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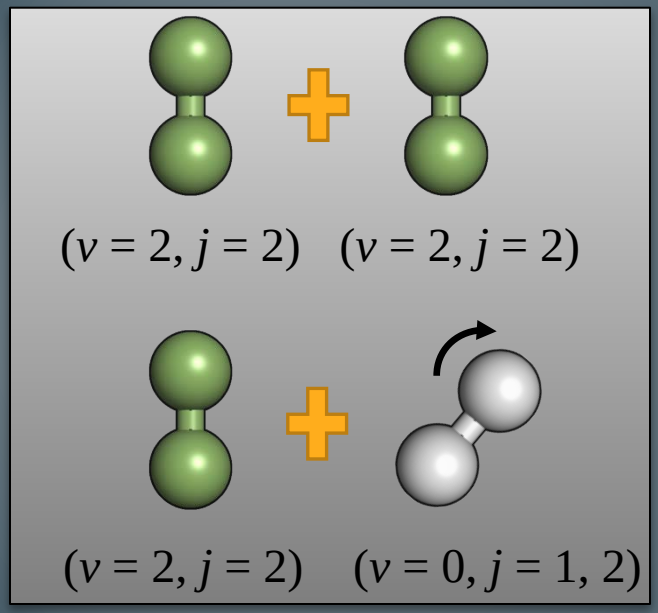

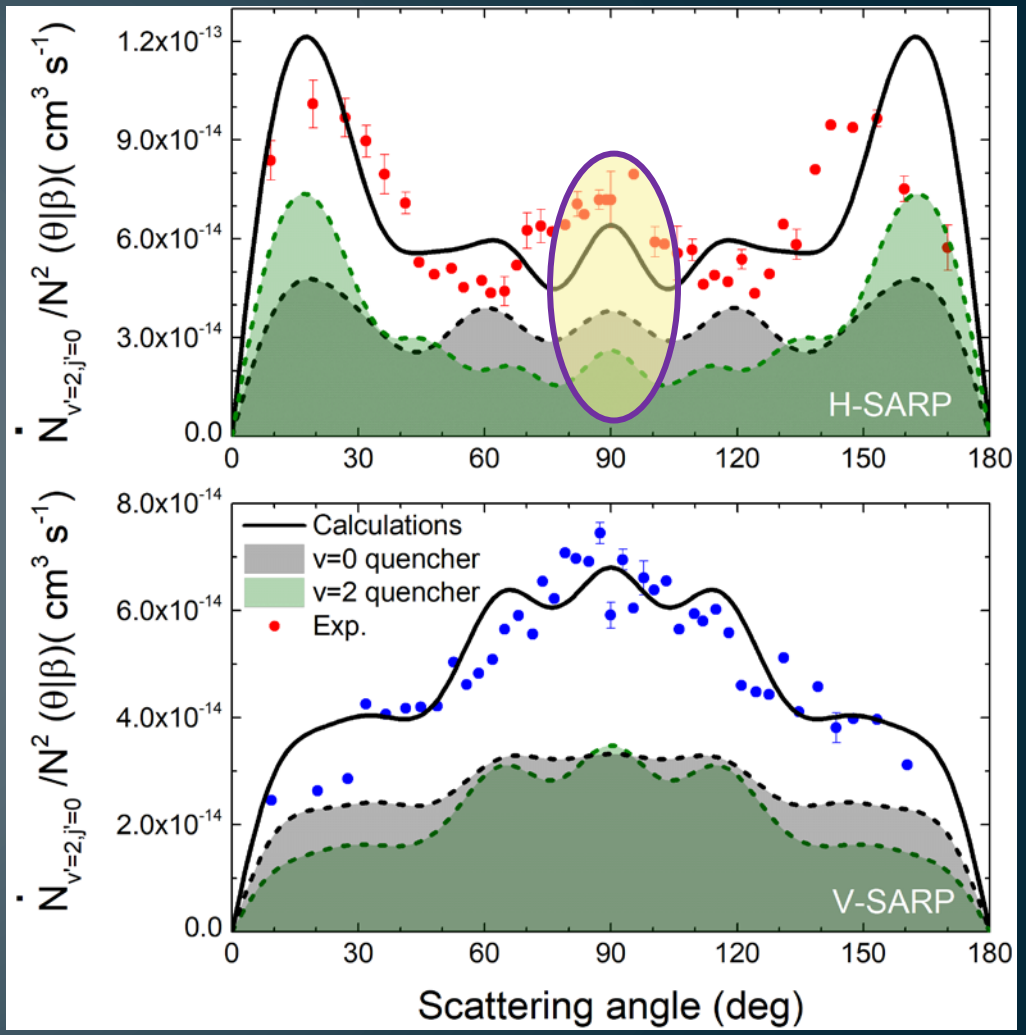

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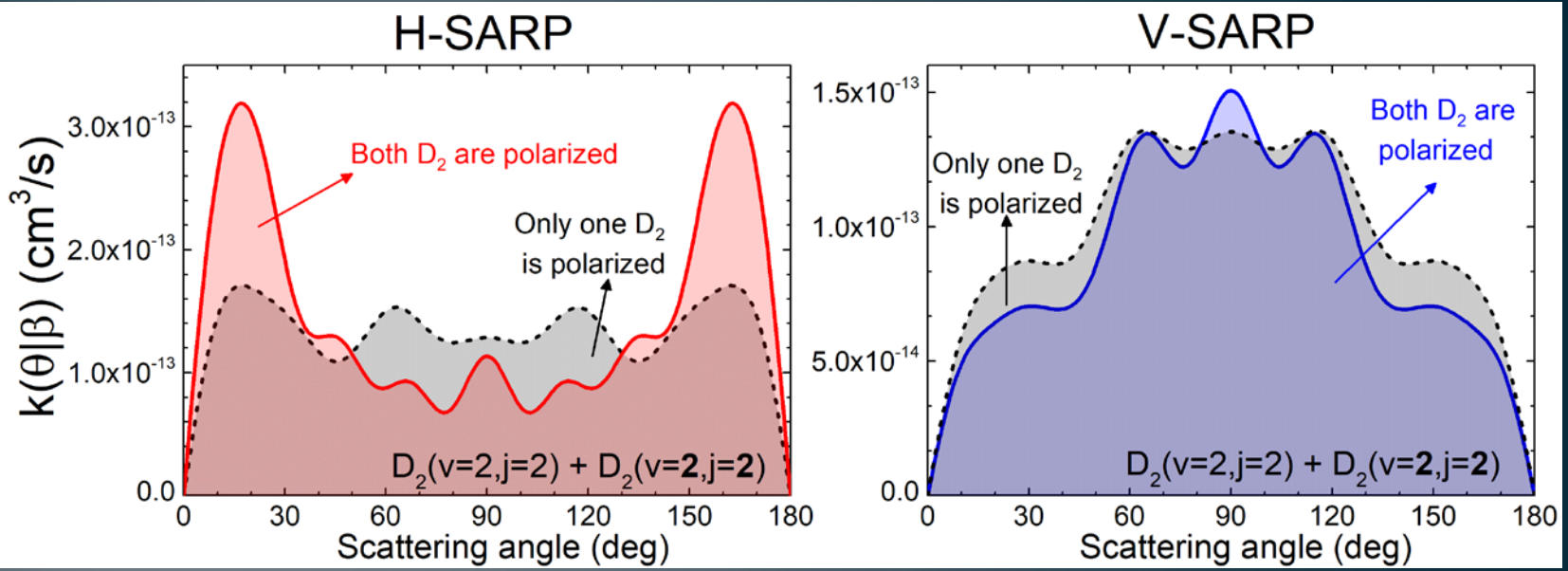
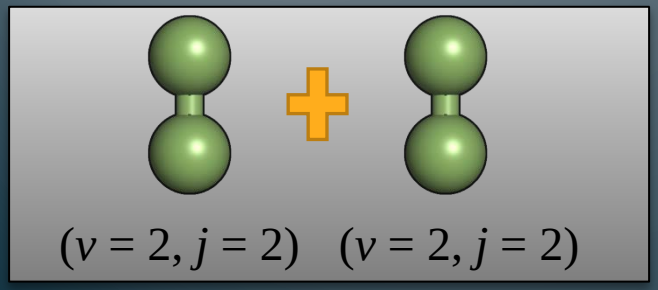
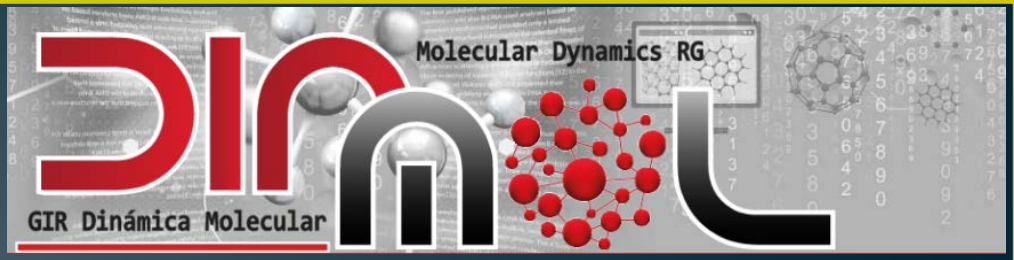




Jambrina, Croft, Zuo, Guo, Balakrishnan, Aoiz Phys. Rev. Lett., **130,** 033002 (2023)

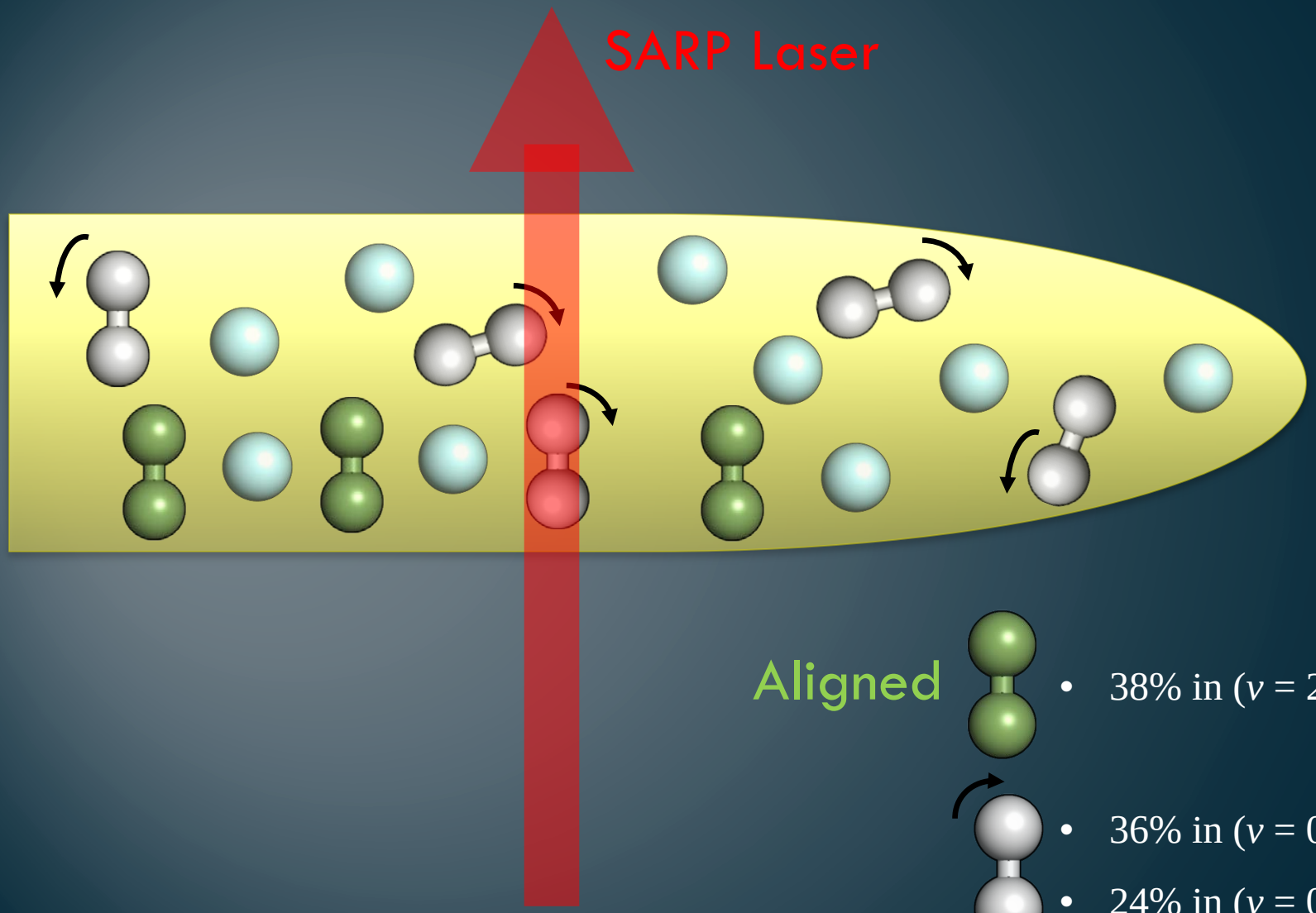
Outline:



- Inelastic Collisions at Cold energies
- Stereodynamics. SARP Experiments
- Results: $D_2 + D_2$
- Results: $He + D_2$
- Conclusions

Aim: Reproduce Experimental Measurements

He + D_2 (v=2,j=2) collisions

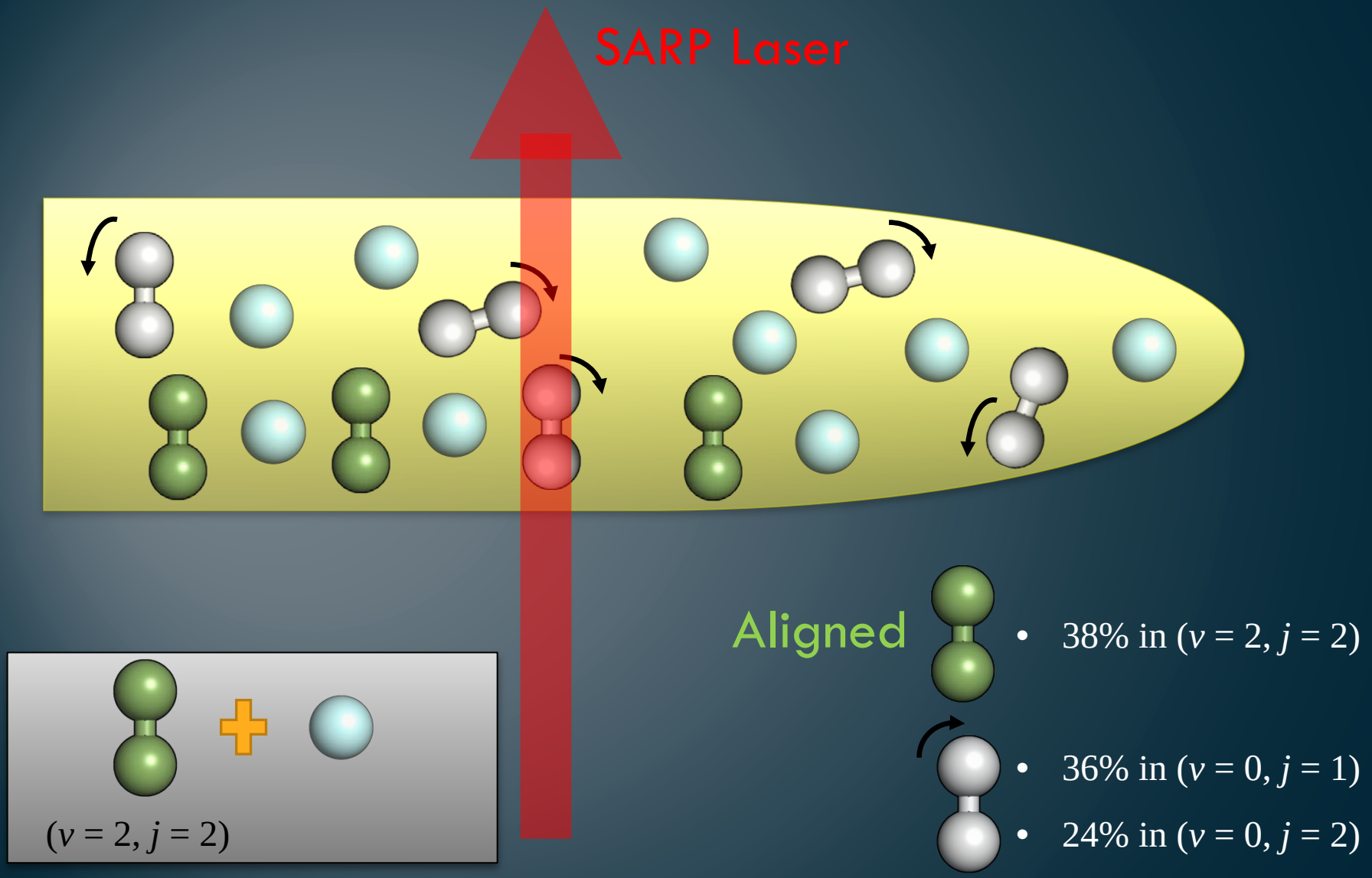


Aligned

- 38% in (v = 2, j = 2)

- 36% in (v = 0, j = 1)
- 24% in (v = 0, j = 2)

He + D_2 (v=2,j=2) collisions



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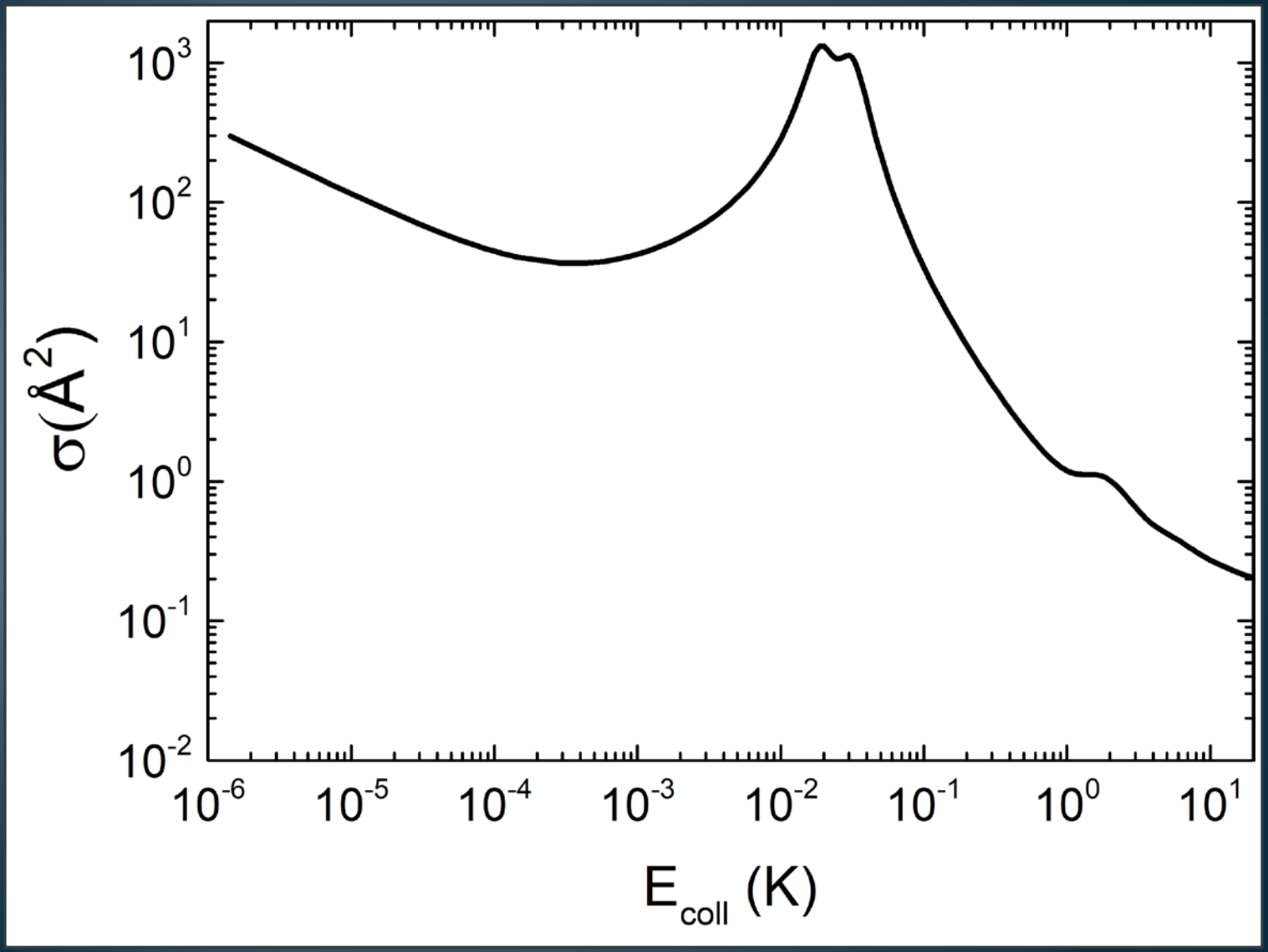

Jambrina, Morita, Croft, Aoiz, Balakrishnan, JPC Lett. **13**, 4064 (2022)

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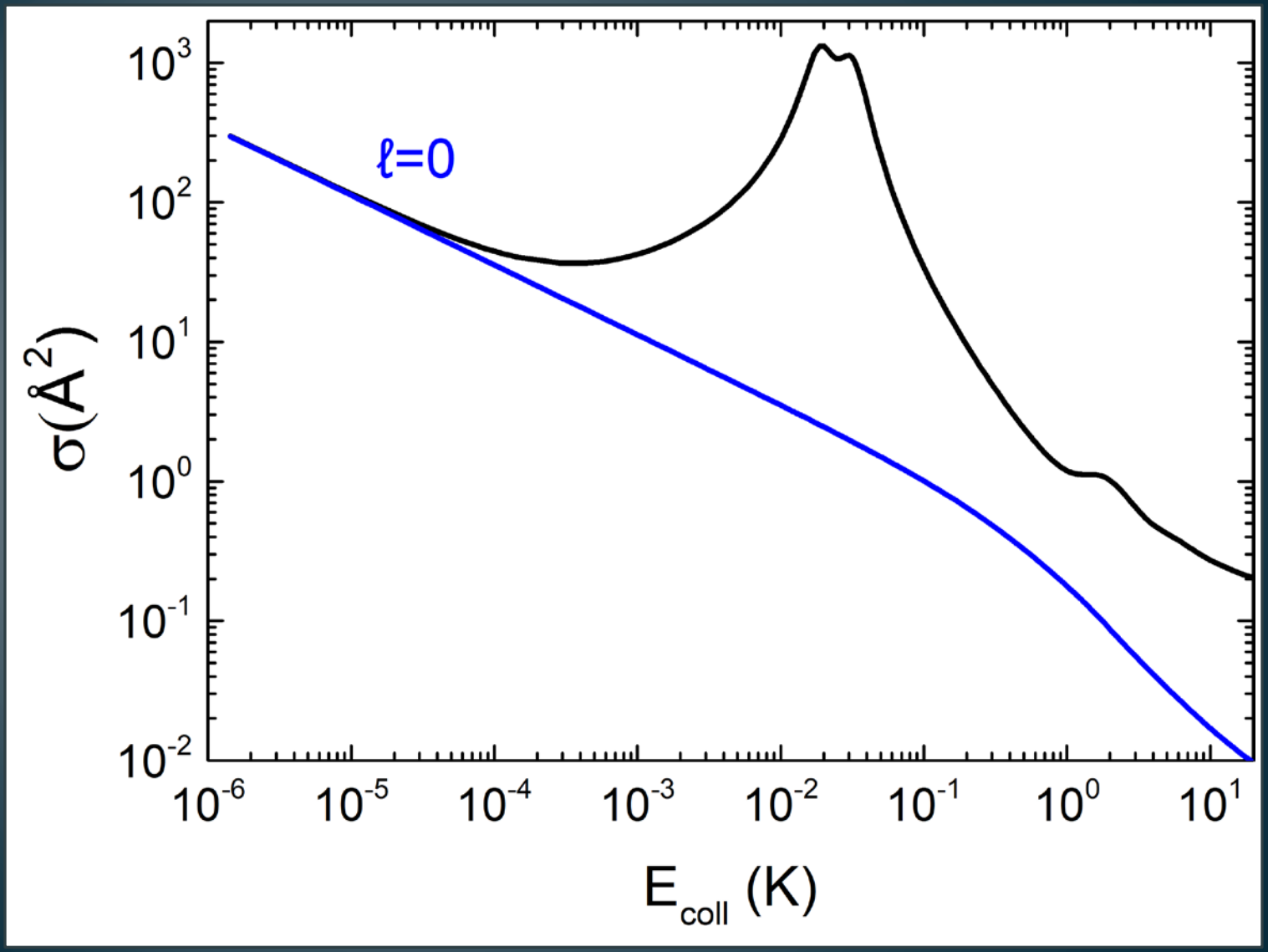

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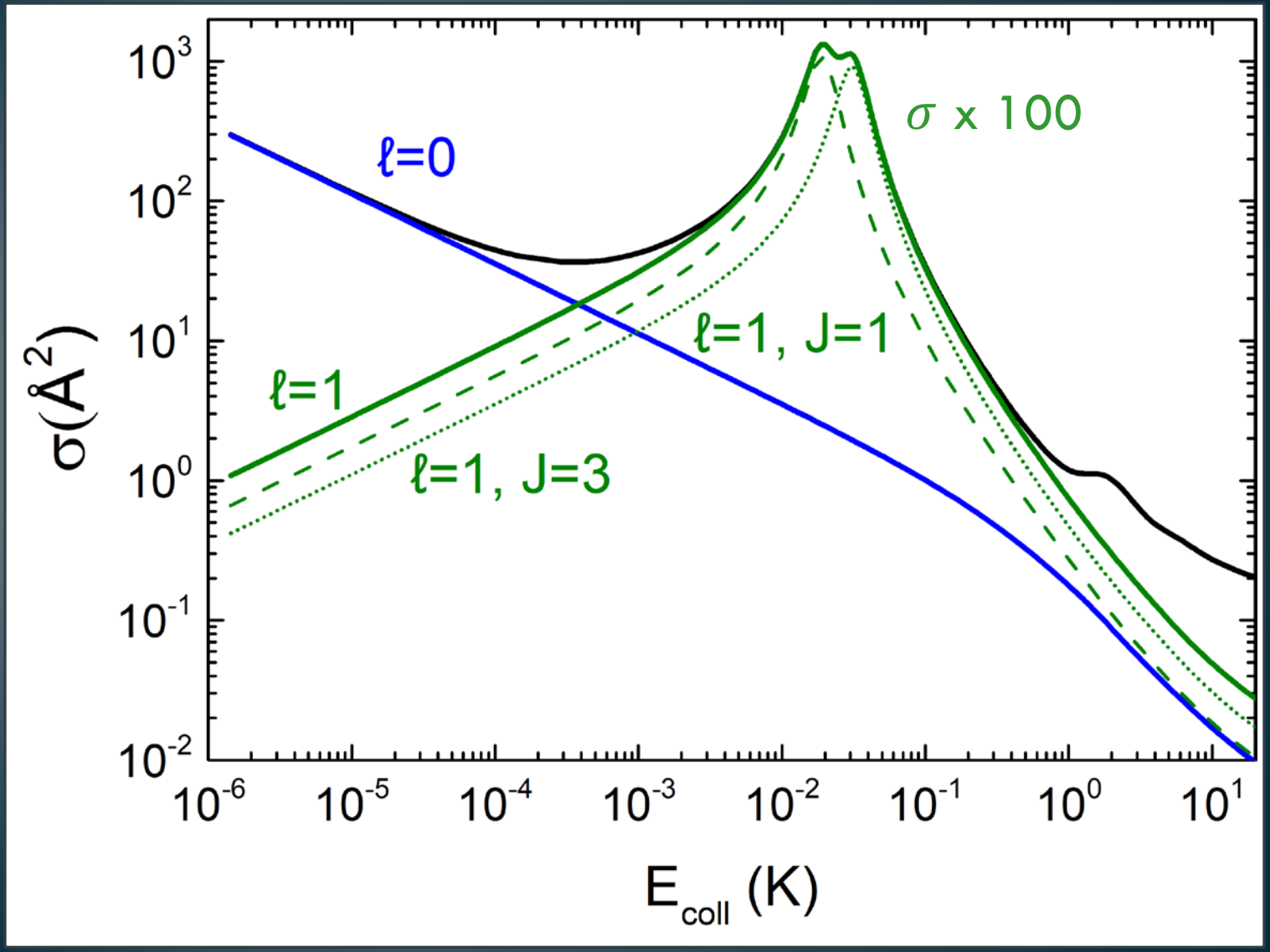

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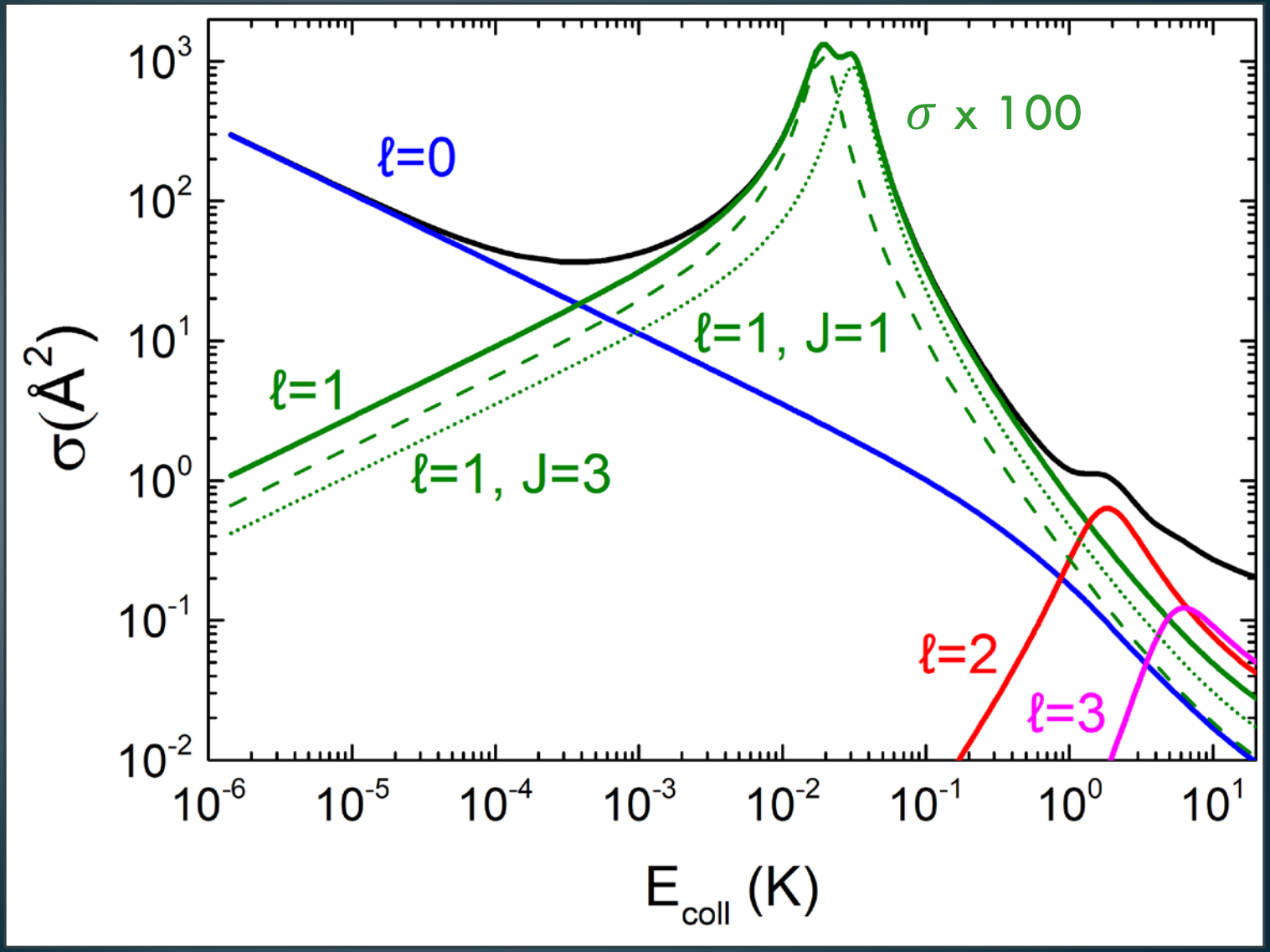

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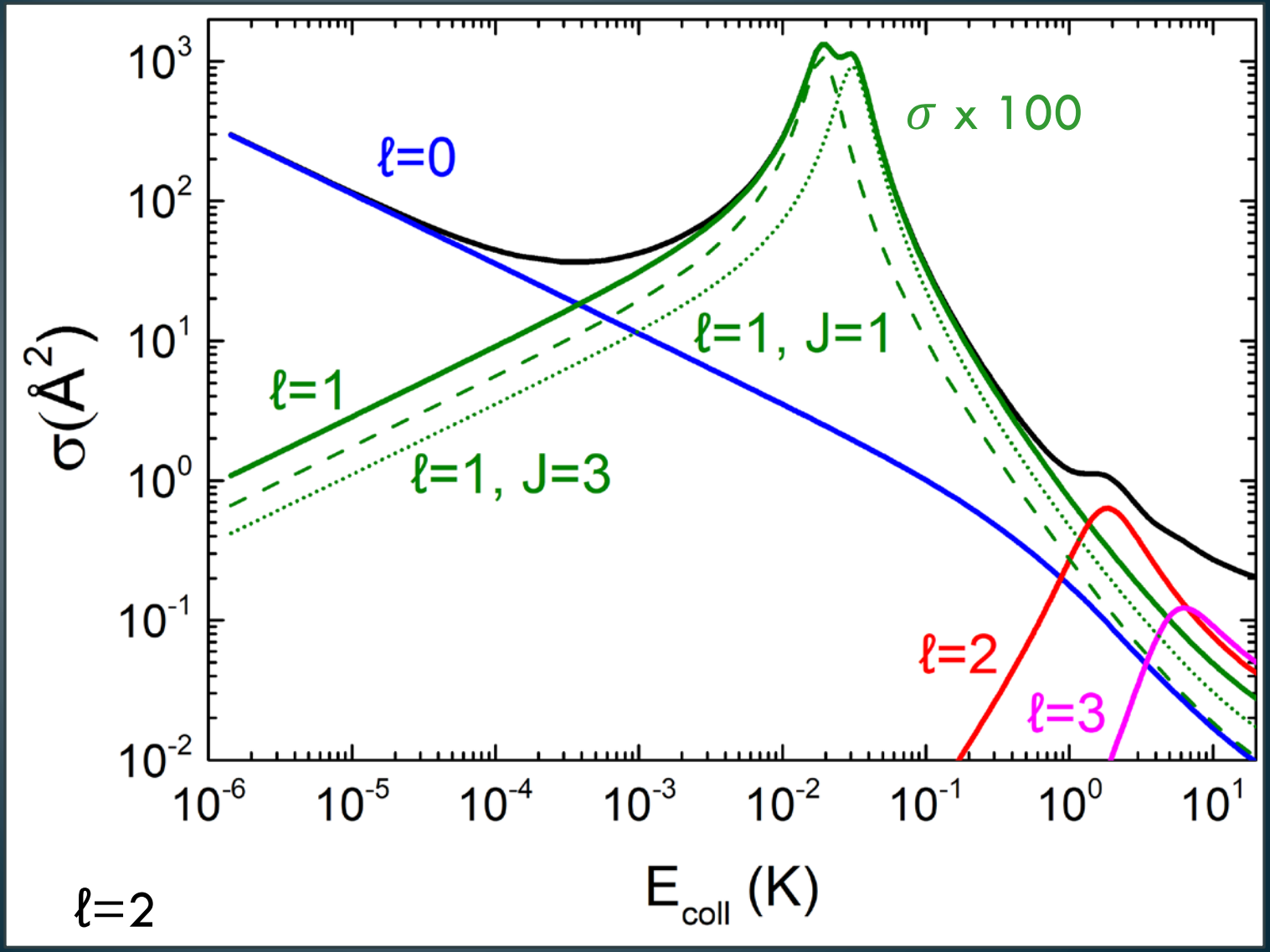

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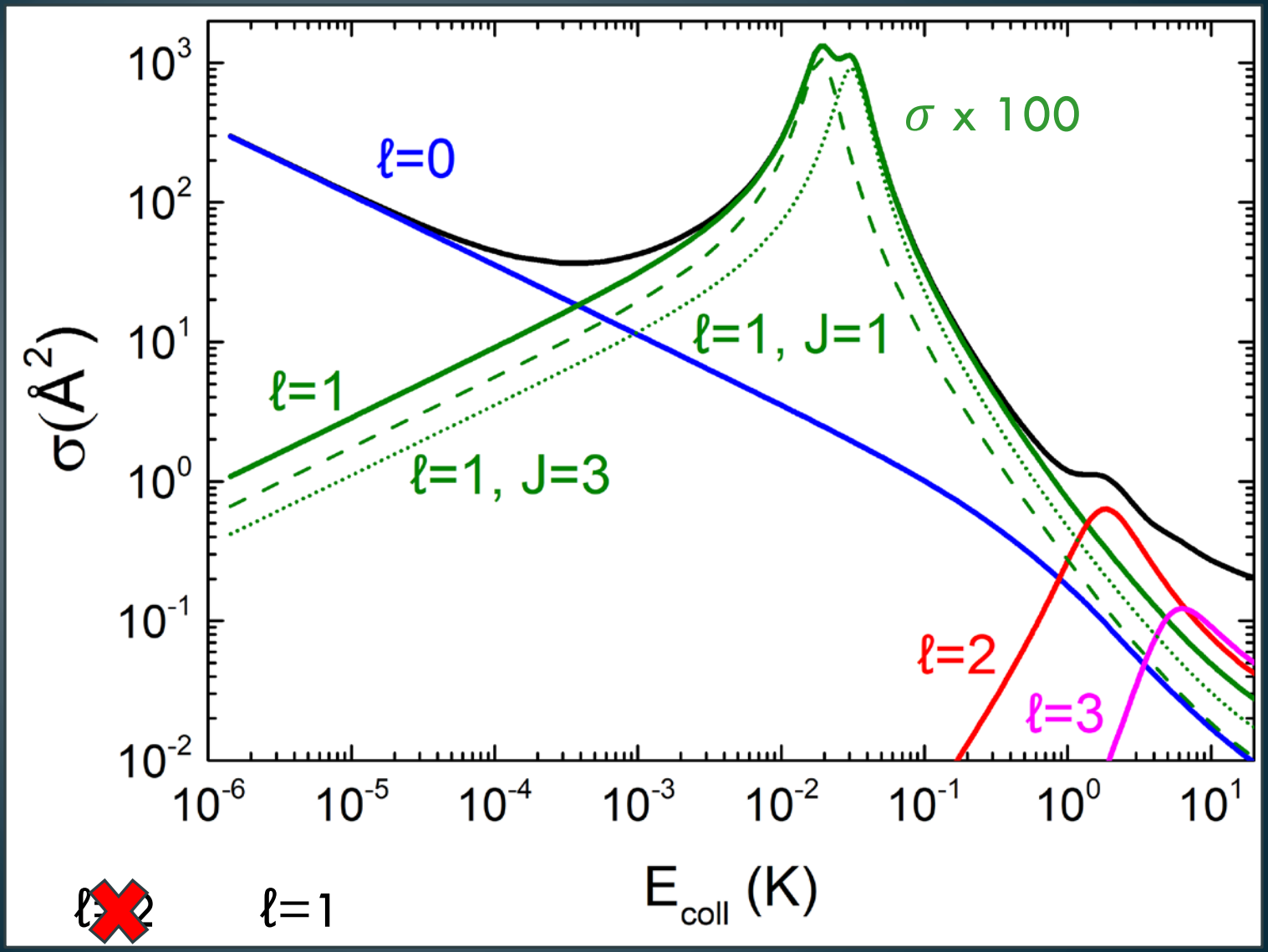

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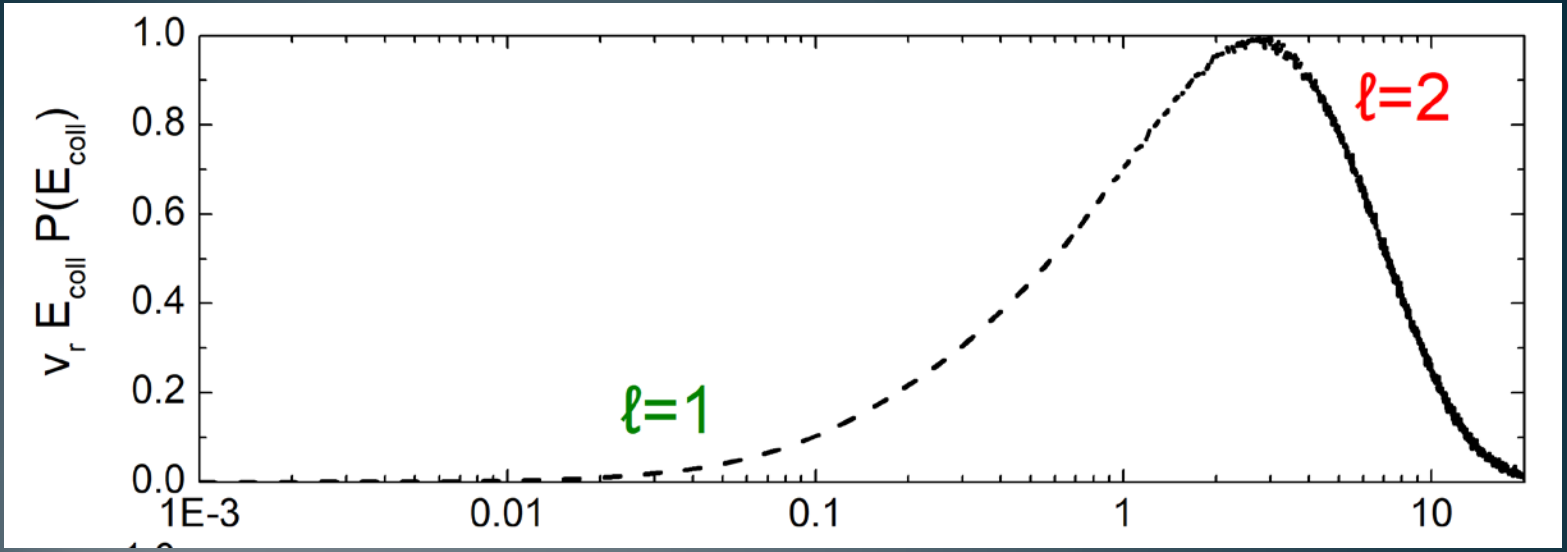

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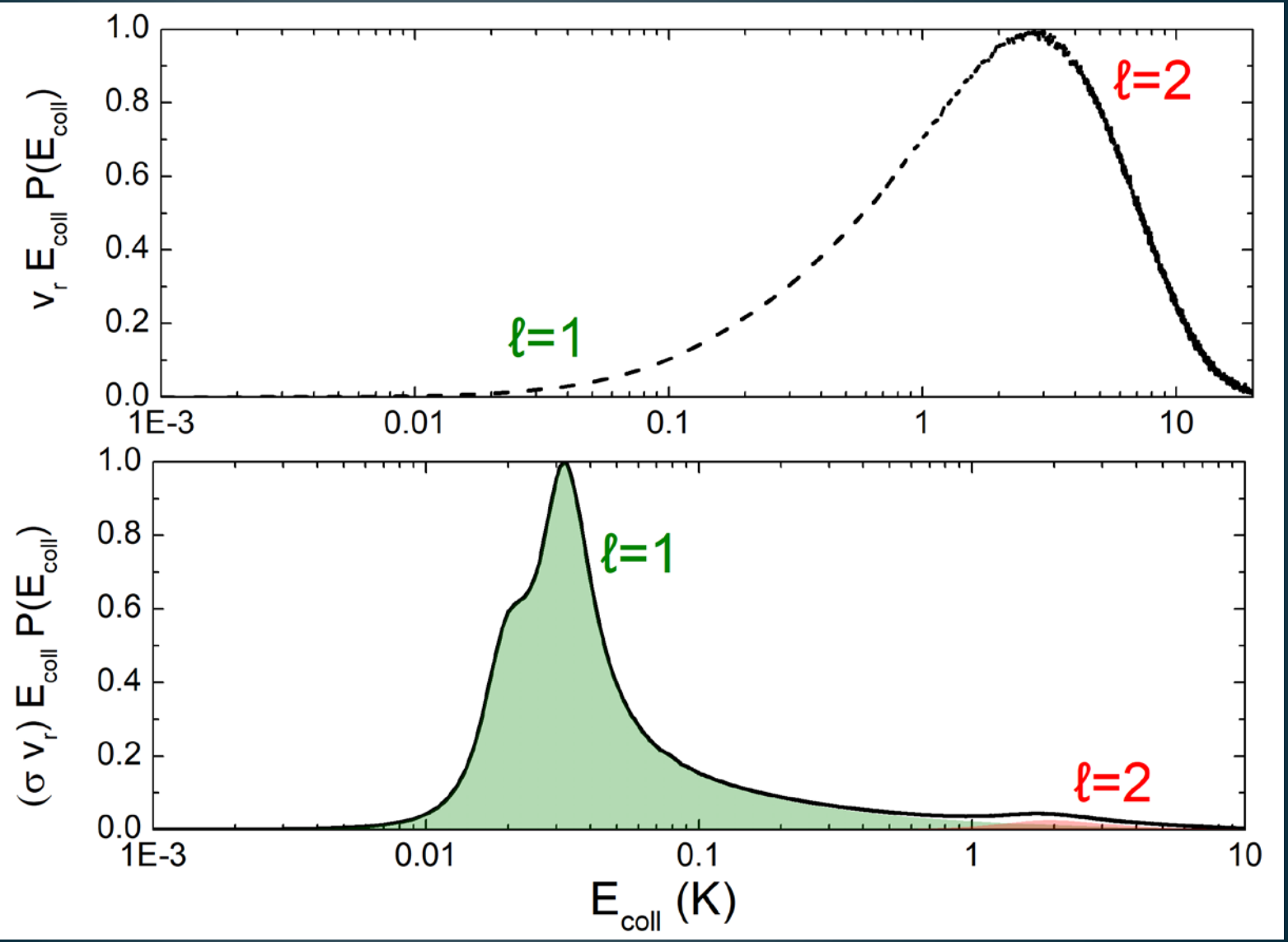

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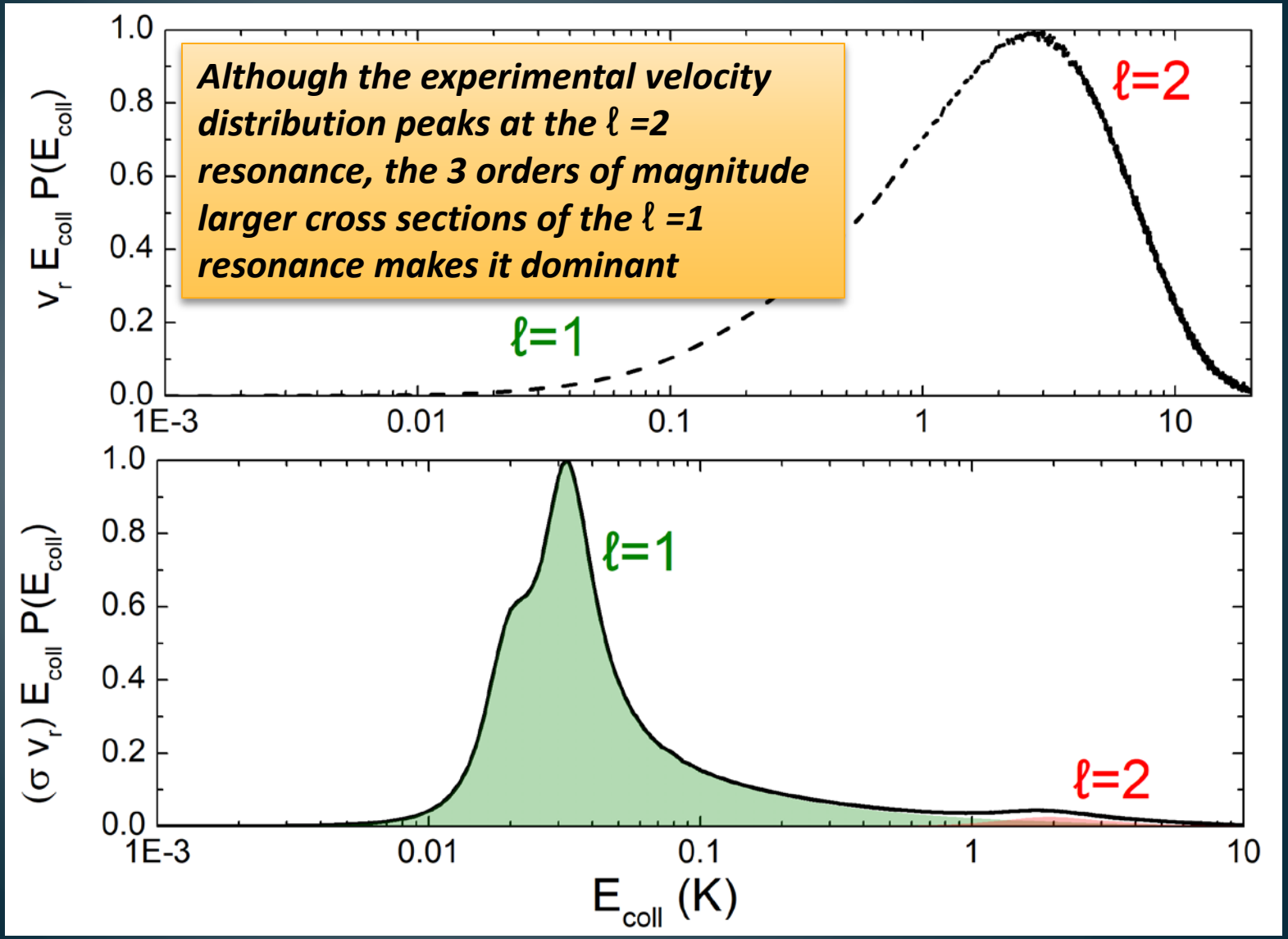

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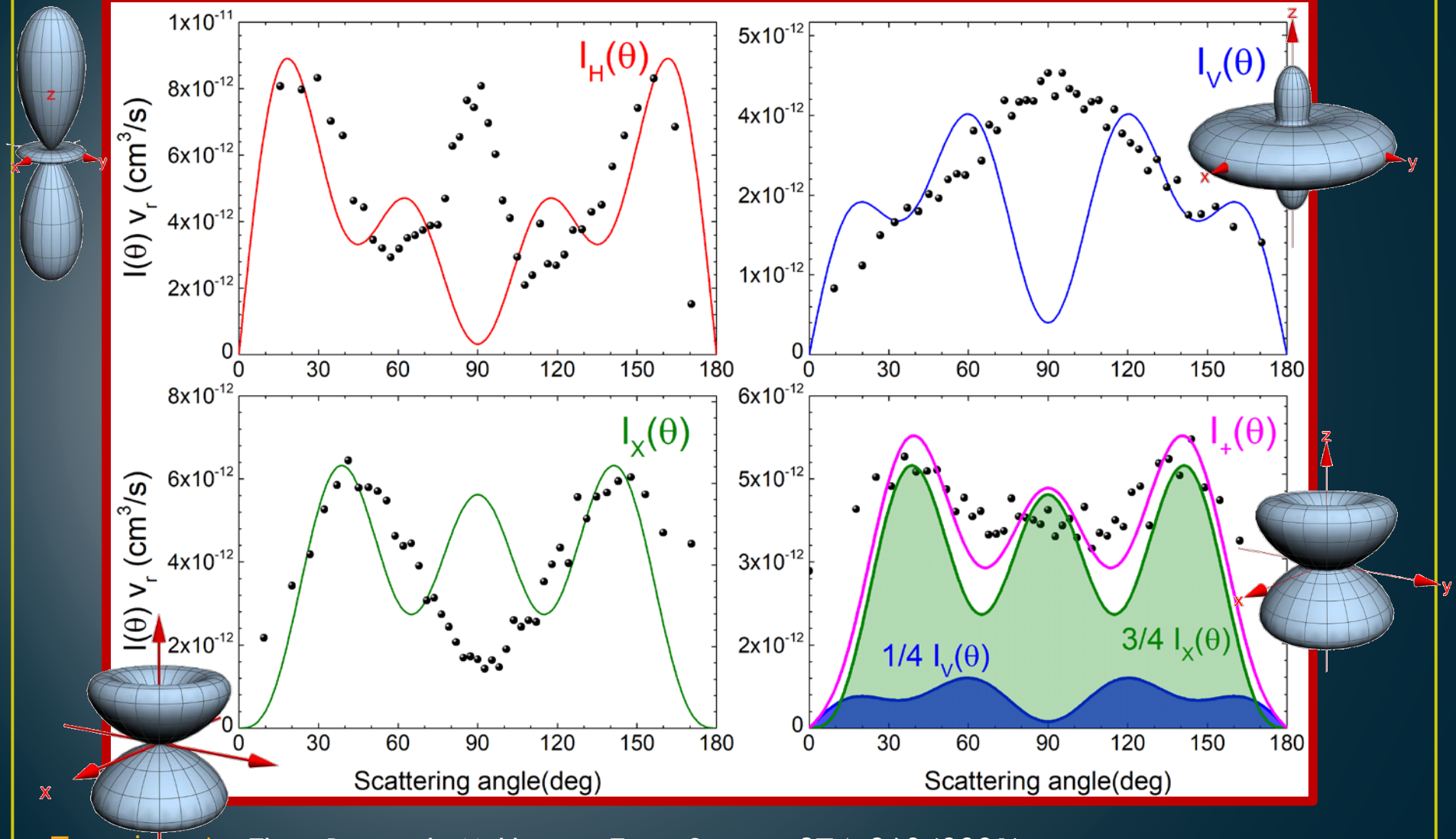

Experiments: Zhou, Perreault, Mukherjee, Zare. Science. 374. 960 (2021)
Jambrina, Morita, Croft, Aoiz, Balakrishnan, JPC Lett. **13**, 4064 (2022)

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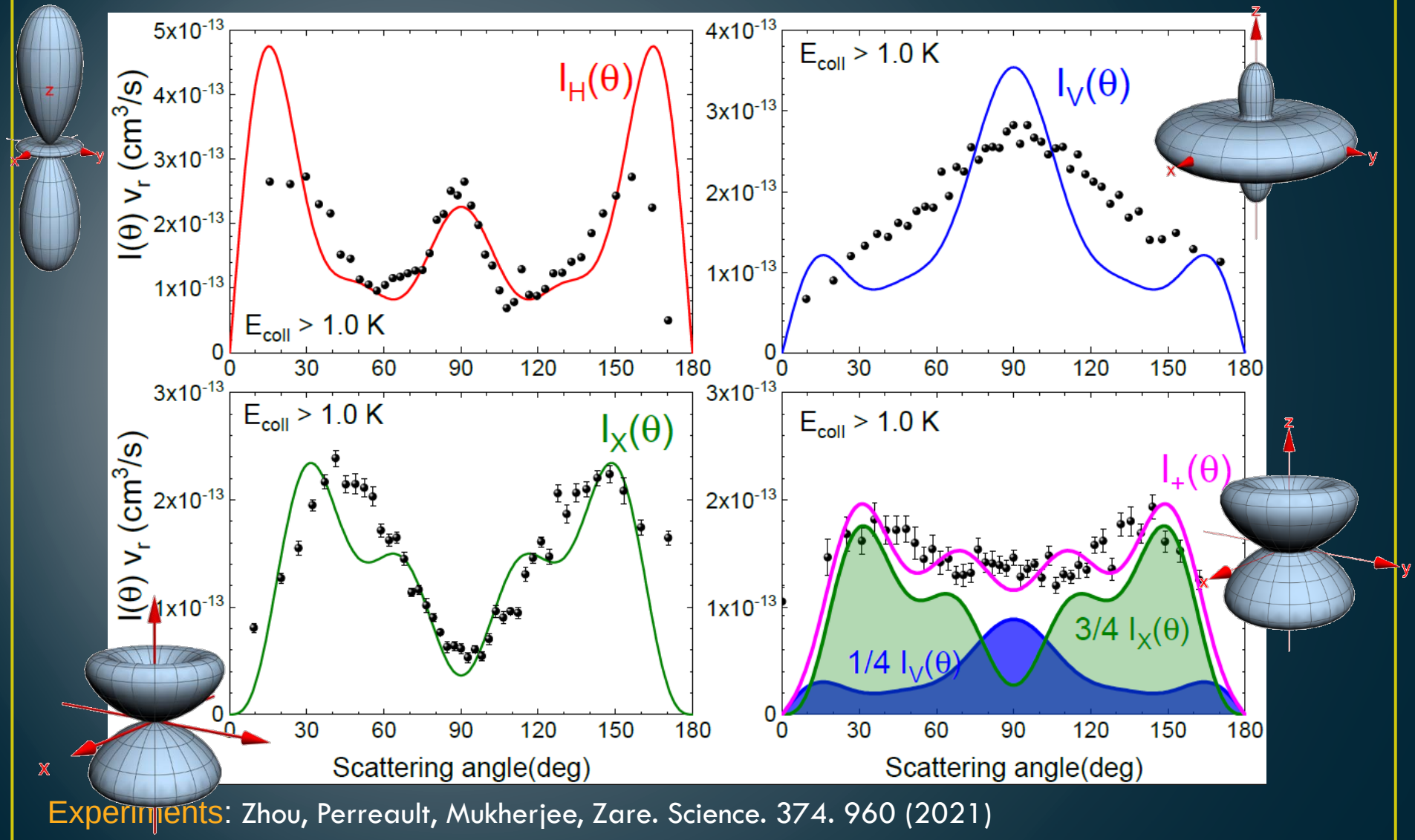

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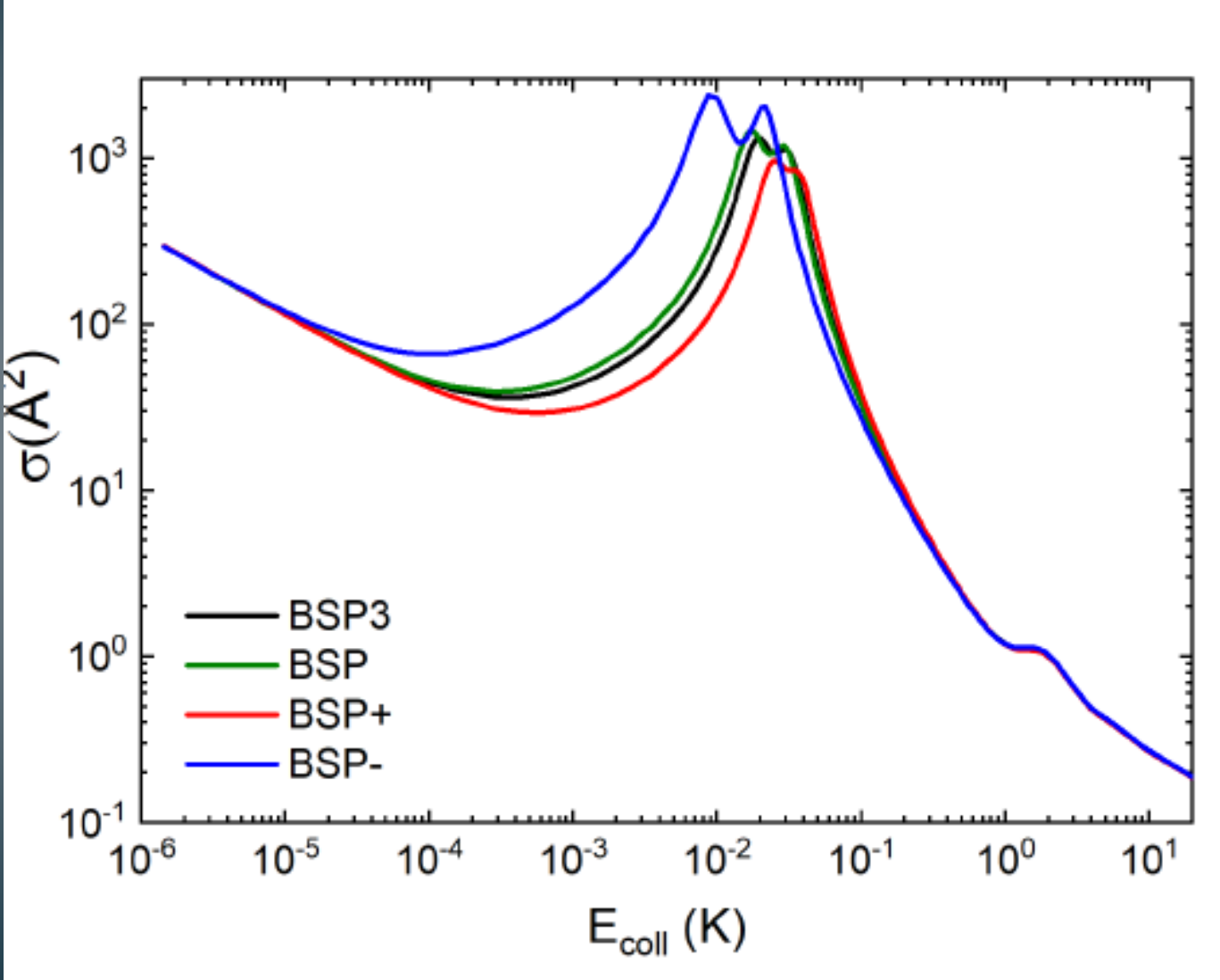
Possible sources of discrepancy

- Theory side
- Scattering Calculations are wrong
  - Tested with different codes (different people). Similar results
- What about the formalism?
  - It worked for other experiments.
- What about the PES?

Problems with the PES ??



Possible sources of discrepancy

- Theory side
- Scattering Calculations are wrong
  - Tested with different codes (different people). Similar results
- What about the formalism?
  - It worked for other experiments.
- What about the PES? Unlikely
- Experimental side
- Something related to the velocity distribution?

Possible sources of discrepancy

- Theory side
  - Scattering Calculations are wrong
    - Tested with different codes (different people). Similar results
  - W
    - I
  - W
- Experimental side
  - Something related to the velocity distribution?

Perhaps we are not calculated what they are measuring

CONCLUSIONS

- The shape of the DCS changes dramatically with the alignment of the intermolecular axis.
- Experimental results can be simulated from first principles for inelastic collisions.
- Contribution of theory is important for the interpretation of the experimental results.
- No agreement for He + D_2. More calcs/expt are needed

More information

$He + D_2$:

P. G. Jambrina et al. J. Phys. Chem. Lett. 2022, 13, 4064–4072

$D_2 + D_2$:

P. G. Jambrina et al. Phys. Rev. Lett. 2023, 130, 033002

Funding

PID2020-113147-GA-I00

Fundación Salamanca City of Culture and Knowledge
(programme for attracting scientific talent to Salamanca)


Muito Obrigado !!!

$$F_{m'_A m'_B m_A m_B}(\theta) = \frac{\sqrt{(1+\delta_{v_A v_B}\delta_{j_A j_B})(1+\delta_{v'_A v'_B}\delta_{j'_A j'_B})}}{2ik} \times \sum_J (2J+1) d^J_{m'_A+m'_B, m_A+m_B}(\theta) \times S^J_{m'_A m'_B m_A m_B}(E), \quad (4)$$

$$d\sigma(\theta|\beta,\alpha) = \sum_{k_A=0}^{2j_A} \sum_{q_A} \sum_{k_B=0}^{2j_B} \sum_{q_B} (2k_A+1)(2k_B+1) \times \left[U_{q_A,q_B}^{(k_A,k_B)}(\theta)\right]^* a_{q_A}^{(k_A)} a_{q_B}^{(k_B)},$$

$$a_q^{(k)} = C_{kq}(\beta,\alpha) A_0^{(k)} = C_{kq}(\beta,\alpha) \langle j_A 0, k0 | j_A 0 \rangle,$$

$$
\begin{aligned}
U^{(k_A,k_B)}_{q_A,q_B}(\theta) = & \frac{1}{(2j_A+1)(2j_B+1)} \\
& \times \sum_{\substack{m'_A,m'_B \\ m_A,m_B}} F_{m'_A m'_B m_A m_B}(\theta) F^*_{m'_A m'_B (m_A+q_A)(m_B+q_B)}(\theta) \\
& \times \langle j_A m_A, k_A q_A | j_A (m_A+q_A) \rangle \\
& \times \langle j_B m_B, k_B q_B | j_B (m_B+q_B) \rangle . \qquad (6)
\end{aligned}
$$