Survival of Rotational Alignment in Molecule-Surface Scattering

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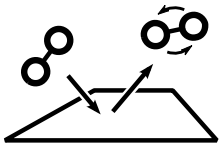
Summary

H_2 is rotationally aligned by laser excitation into the $j = 3$ rotational state. The aligned molecules are then scattered from a Si(100) surface, and the survival of the alignment is measured using a second laser. The survivals are measured for two different planes of initial alignment.

Introduction

Chemical dynamics:

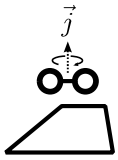
- *What are the trajectories taken by atoms as they rearrange to form products from reactants?*
- *What is the role played by each degree of freedom?*
  - Rotational scattering:
    - *How does molecular rotation affect the outcome of a scattering event?*
    - *How does scattering affect a molecule's rotational motion?*



Rotational Alignment

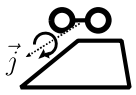
Angular momentum $\vec{j}$ is a **vector**:

- magnitude: speed of rotation
- direction: axis of rotation



← **Helicopter**: axis perpendicular to surface

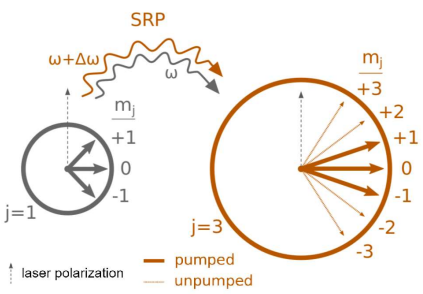
axis parallel to surface: **Cartwheel** ↴

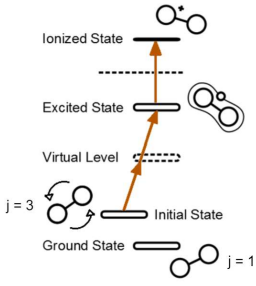


Optical Preparation / Detection of Alignment

Alignment preparation:

- $j = 1 \rightarrow 3$ stimulated Raman pumping (SRP)
- $\Delta m_j = 0$ selection rule
  ⇒ uneven m_j distribution in $j = 3$ ⇒ aligment



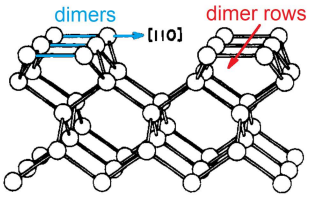


Alignment detection:

- (2+1) REMPI
- $\Delta m_j = 0$ selection rule now works in reverse:
  - varation in signal with laser polarization measures alignment

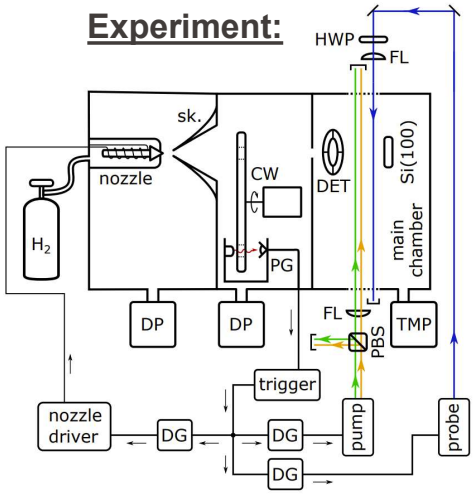
System: H_2 / Si(100)

- (100) surface of silicon reconstructs into rows of dimers [1]
- H_2 unreactive at Si(100):
  sticking probability less than 10^{-8} for $T_S < 550K$ [2]
- H_2 rotationally cold on desorption [3]:
  ⇒ rotational corrugation in molecule-surface potential



[1]

Experiment:



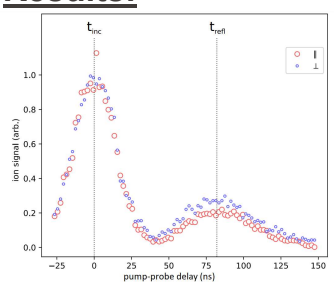
- Incident molecular alignment (helicopter or cartwheel) controlled by pump laser polarizer (PBS).
- Scattered alignment measured by detecting change in REMPI ionization with rotation of probe laser polarization, controlled by half-wave plate (HWP)

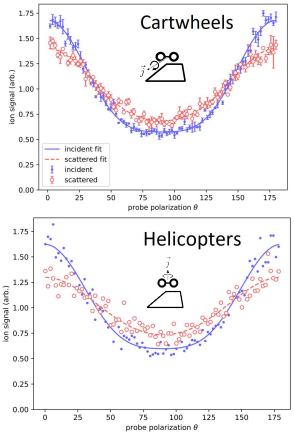
Results:

Monitoring probe ionization with pump-probe delay shows:

- t_{inc}: rotationally excited molecules coming towards the surface, then
- t_{refl}: rot. exc. molecules scattering off the surface

Disparate scattered peak heights at different HWP angles indicate modification of alignment.





Both cartwheels and helicopters show measurable decrease in modulation of ionization vs. polarization curve upon scattering, indicating signifcant coupling of angular momentum between molecule and surface.

Can quantify by looking at survival of modulation at cos2θ (b_2) and cos4θ (b_4):

survival ratios	b_2	b_4
Helicopters	55±1%	-15±10%
Cartwheels	65±2%	33±5%

References

[1] R. E. Schlier and H. E. Farnsworth, J. Chem. Phys. 30, 917-926 (1959)
[2] R Bratu et al., Chem. Phys. Lett. 251 1-7 (1996)
[3] Kolasinski et al., J. Chem. Phys. 96, 3995-4006 (1992)
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