

# Modifying molecular scattering from flat and rough surfaces by ultrashort laser pulses

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**Batsheva de Rothschild Seminar on:**

**Laser Control of Chemical Reactions**

# Abstract

In recent years it has become possible to align molecules in free space using ultrashort laser pulses [1]. In this work, we explored theoretically a few schemes for controlling molecule-surface scattering processes, which are based on laser-induced molecular alignment [2].

In the first scheme, a single ultrashort non-resonant laser pulse is applied to a molecular beam of N<sub>2</sub> molecules hitting a flat surface, such as Ag(111) [3]. This pulse modifies the angular distribution of the incident molecules and causes the scattered molecules to rotate with a preferred sense of rotation (clockwise or counter-clockwise).

In the second scheme, two properly delayed laser pulses are applied to a molecular beam composed of two chemically close molecular species (isotopes, or nuclear-spin isomers). As the result of the double-pulse excitation, the two species are selectively scattered to different angles after the collision with the surface.

In the third scheme, a single laser pulse is applied to a molecular beam propagating normally to a corrugated surface, such as Pt(211), or LiF(001) [4]. The scattered molecules exhibit a correlation between their scattering angle and their direction of rotation.

These effects may shed light on the structure of solid surfaces, as well as provide new means for the analysis and separation of molecular mixtures.

[1] T. Seideman and E. Hamilton, *Adv. At. Mol. Opt. Phys.* **52**, 289 (2006); S. Fleischer, Y. Khodorkovsky, E. Gershnel, Y. Prior, and I. Sh. Averbukh, *Isr. J. Chem.* **52**, 414 (2012).

[2] Y. Khodorkovsky, J. R. Manson, and I. Sh. Averbukh, *Phys. Rev. A* **84**, 053420 (2011).

[3] M. E. M. Spruit, P. J. van den Hoek, E. W. Kuipers, F. H. Geuzebroek, and A. W. Kleyn, *Phys. Rev. B* **39**, 3915 (1989).

[4] J. C. Tully, *J. Chem. Phys.* **92**, 680 (1990); T. Kondo, H. S. Kato, T. Yamada, S. Yamamoto, M. Kawai, *J. Chem. Phys.* **122**, 244713 (2005).

# Interaction of a molecule with an ultrashort non-resonant laser pulse

Rigid rotor model + interaction potential:

induced dipole moment

polarizability anisotropy

$$V(\beta, t) = -\frac{1}{2} \overline{\boldsymbol{\mu}(\mathbf{E}) \cdot \mathbf{E}} = -\frac{1}{4} \mathcal{E}^2(t) (\Delta\alpha \cos^2 \beta + \alpha_{\perp})$$

$$\Delta\alpha = \alpha_{\parallel} - \alpha_{\perp} > 0$$

Induced dipole follows the electric field

$$\mu_{\parallel} = \alpha_{\parallel} E_{\parallel}$$

$$\mu_{\perp} = \alpha_{\perp} E_{\perp}$$

femtosecond laser pulse

$\mathbf{E}(t) = \mathbf{e}_p \mathcal{E}(t) \cos \omega t$

torque  $\propto -\frac{\partial V}{\partial \beta} \propto -\sin 2\beta$

The pulse is short compared to the rotational period:

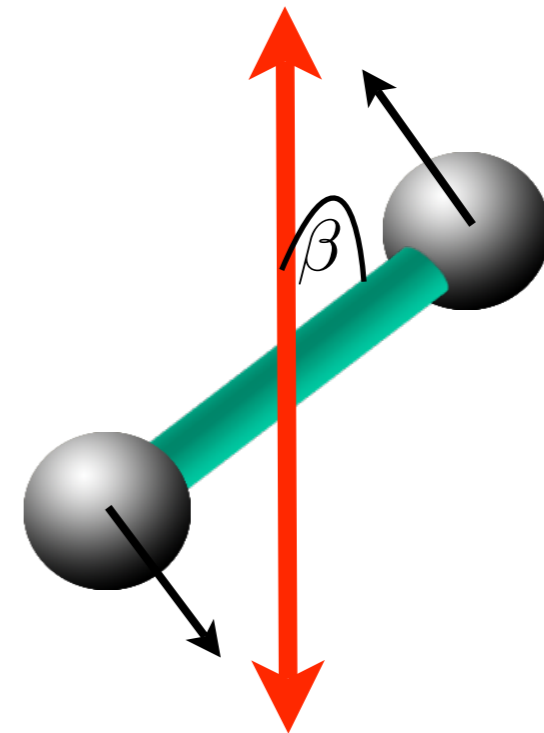
Pulse duration  $\approx 70$  fs  
 Rotational revival  
 time =  $1/(2Bc) = 8.3$  ps for  
 $^{14}\text{N}_2$

# The “kick” induced by the laser to the molecule

- Dimensionless pulse strength:

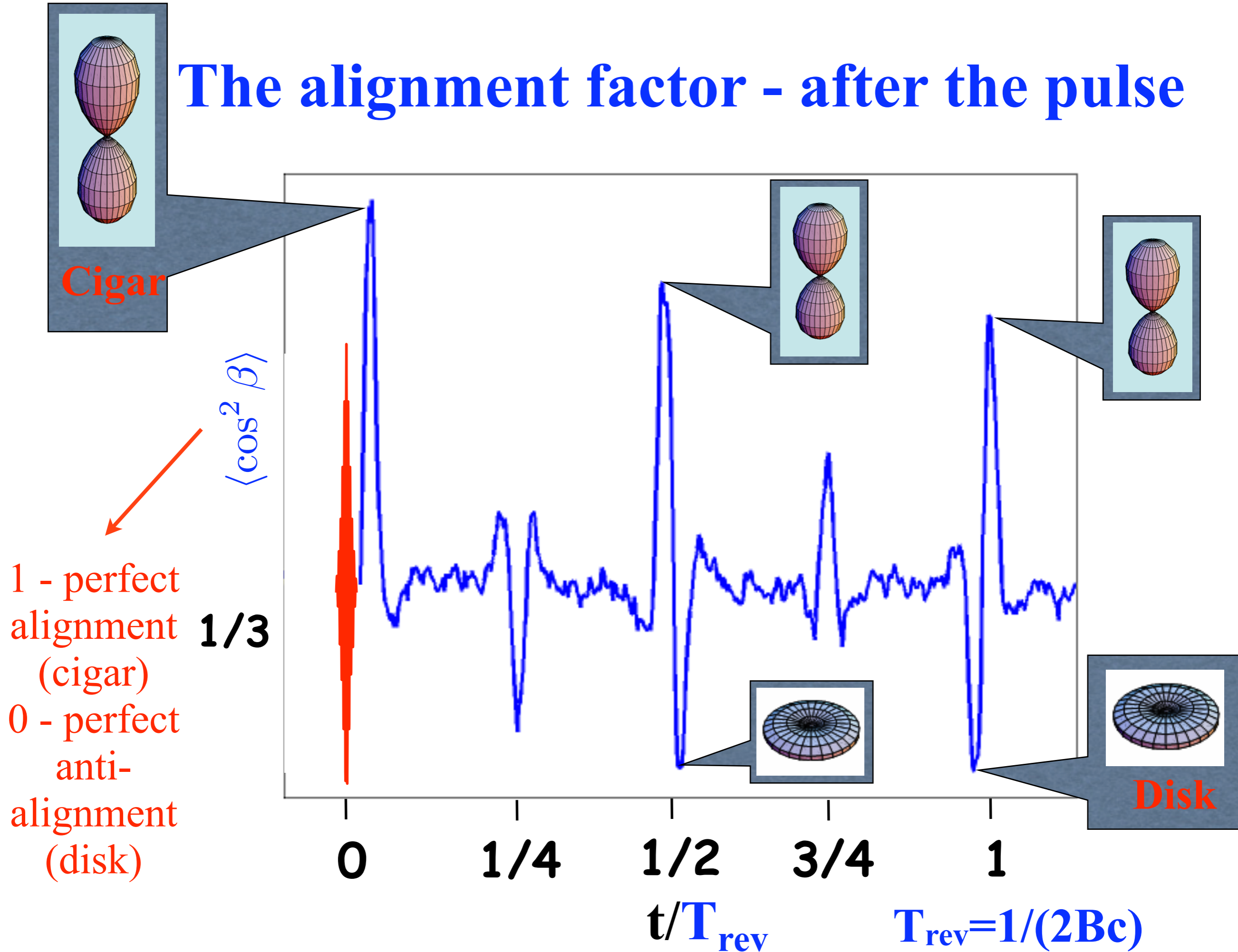
$$P = \frac{\Delta\alpha}{4\hbar} \int_{-\infty}^{\infty} \mathcal{E}^2(t) dt$$

- Classically: the molecule receives an angular momentum “kick” of  $\hbar P \sin 2\beta$

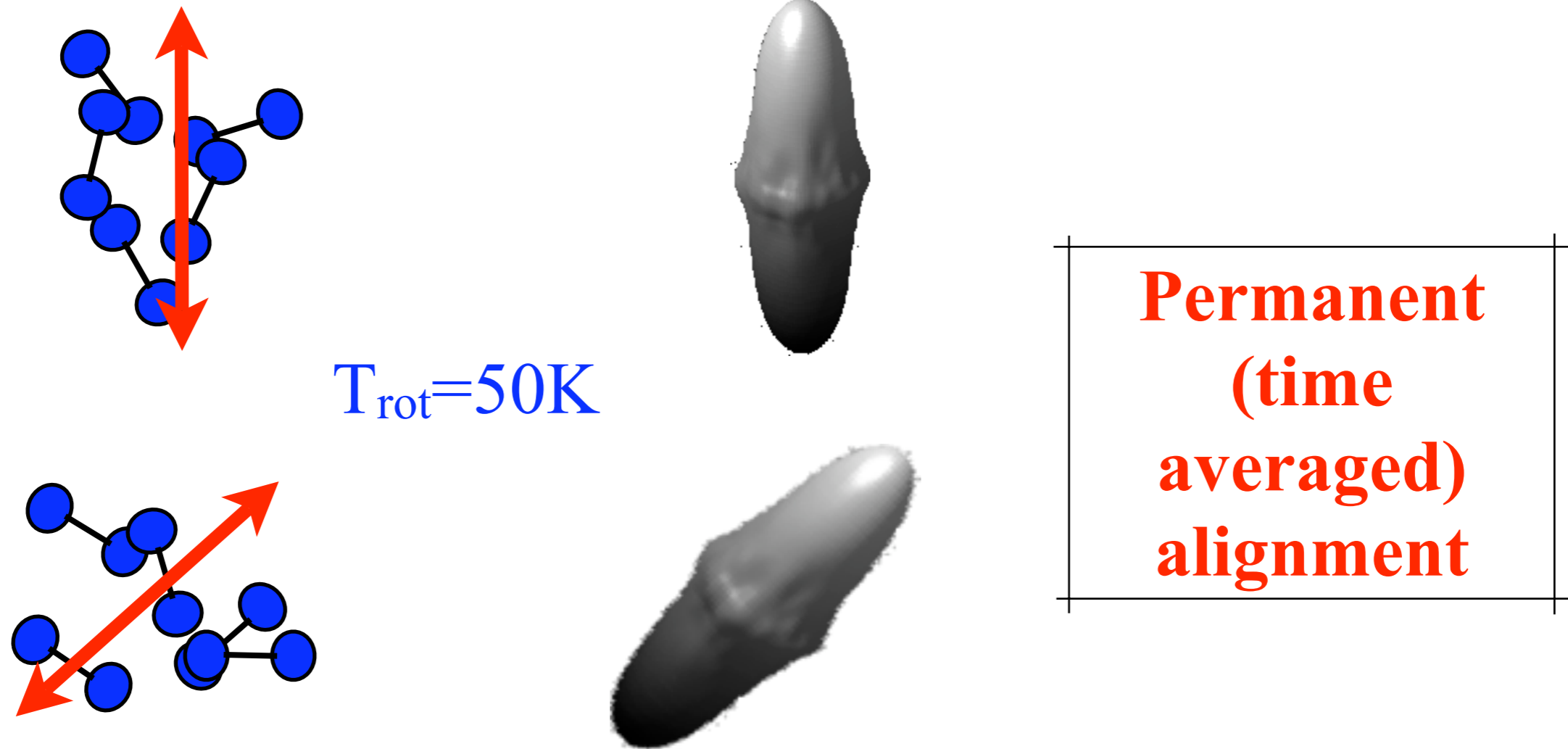


- Experimental parameters: a Gaussian shape pulse with  $I_{\max} = 3 \times 10^{13} \text{ W/cm}^2$ ,  $\Delta t = 70 \text{ fs}$ , for a nitrogen molecule  $\Rightarrow$   $P \sim 3$

# The alignment factor - after the pulse



# Time-averaged angular distribution



- The anisotropy of the “cigar” is smaller at higher rotational temperature, for the same pulse strength.

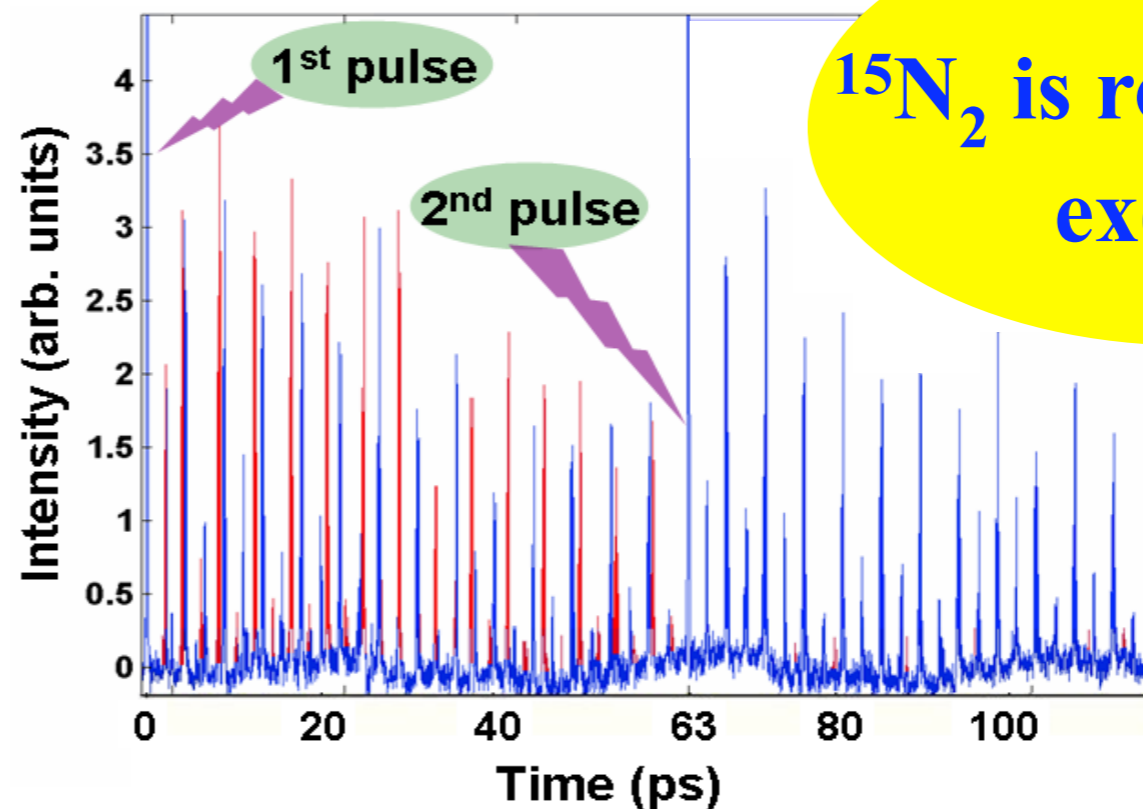
Y. Khodorkovsky, K. Kitano, H. Hasegawa, Y. Ohshima, I. Sh. Averbukh, Phys. Rev. A 83, 023423 (2011)

# Isotope-selective laser-induced molecular alignment

- A molecular mixture of **isotopes** is “kicked” by properly delayed two laser pulses. This pair of pulses excites one of the species, while leaving the other one unexcited and randomly oriented.

isotope mixture:

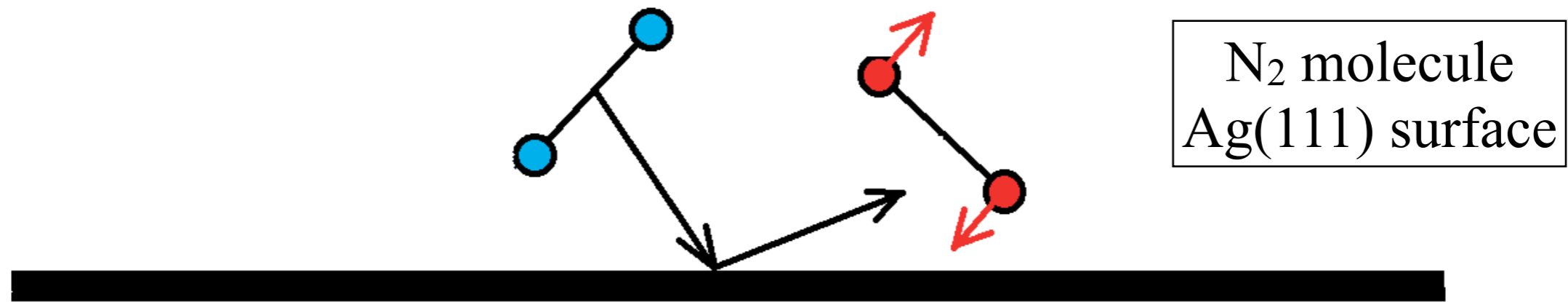
$^{14}\text{N}_2$  and  $^{15}\text{N}_2$



Measured by the time delayed degenerate four wave mixing technique - S. Fleischer, I. Sh. Averbukh, and Y. Prior, PRA **74**, 041403 (2006), PRL **99**, 093002 (2007).

# Molecular scattering from flat surface - the simplest model

Dumb-bell hitting a hard wall



- Analytical treatment is based on: conservation of energy, angular momentum and linear momentum parallel to the surface
- $E_{\text{trans}} + E_{\text{rot}} = \text{const.}$ ,  $P_{\text{parallel}} = \text{const.}$



# Velocities after a collision - result for 2D

- Final translational velocity:

$$V_f = \frac{-V_i \cos^2 \theta \pm 2v_i |\sin \theta|}{1 + \sin^2 \theta}$$

- Final rotational velocity:

$$v_f = \frac{v_i \cos^2 \theta \pm 2V_i |\sin \theta|}{1 + \sin^2 \theta}$$

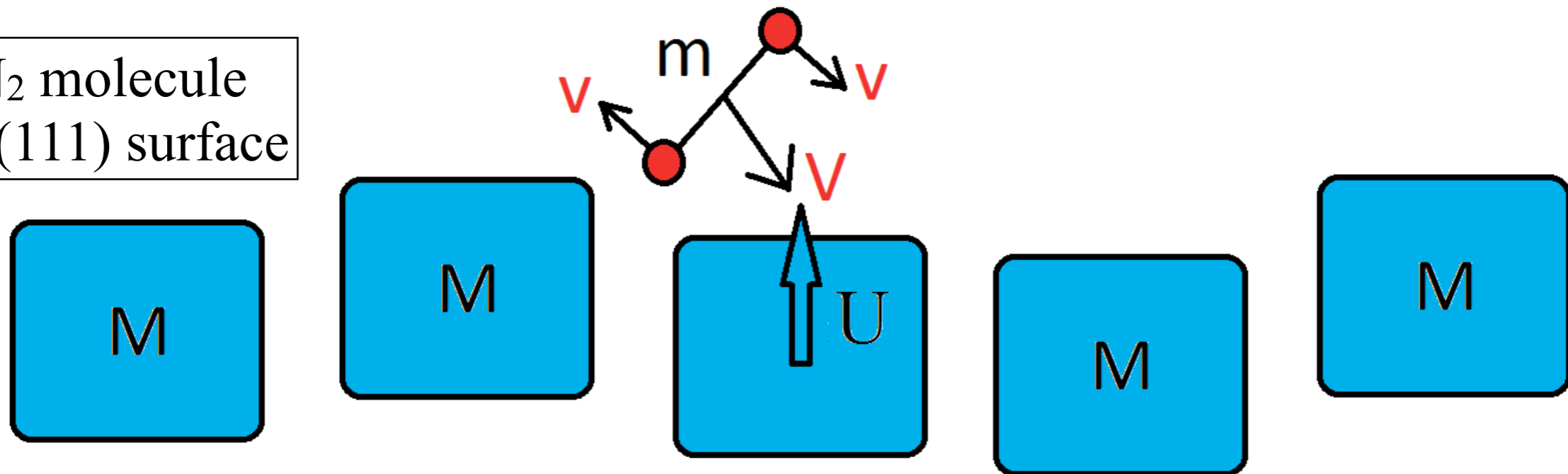
- $\theta$  - molecular orientation at the time of incidence

# Molecular scattering from flat surface - a simple account for surface motion

## Dumb-bell hitting a hard cube

- rigid dumb-bell molecule, flat frictionless cube
- the cube velocity  $U$  - thermal distribution with  $T_{\text{surf}}$
- $M$  is the mass of a surface atom, or a group of atoms;  
 $M \gg m$

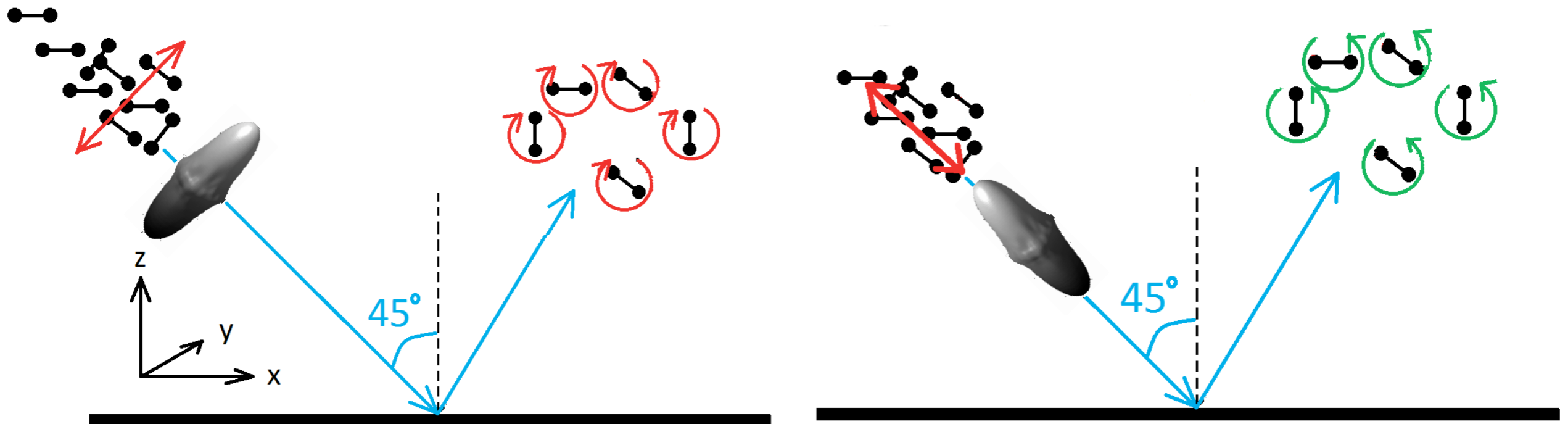
$\text{N}_2$  molecule  
Ag(111) surface



R. M. Logan and R. E. Stickney, J. Chem. Phys. 44, 195 (1966).  
J. D. Doll, J. Chem. Phys. 59, 1038 (1973).

# Inducing unidirectional rotation of molecules by laser pulse and surface scattering

- Before impinging on the surface, the molecules are “kicked” by a laser pulse polarized at an angle of  $\pm 45^\circ$  to the surface.
- On average, their angular distribution is cigar-shaped.
- After scattering, the molecules rotate with a specific sense (clockwise/counter-clockwise), as shown.

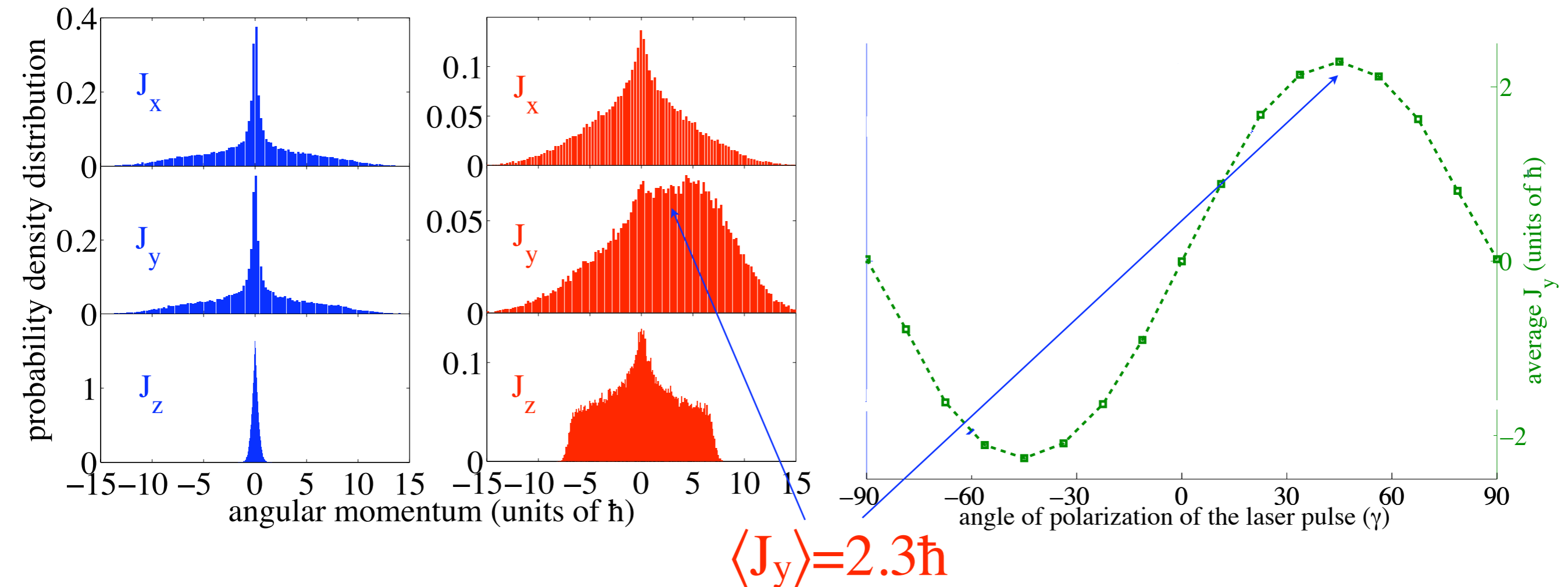


# Inducing unidirectional rotation of molecules by laser pulse and surface scattering

Results of Monte Carlo simulations with  $5 \times 10^4$   $\text{N}_2$  molecules, incident at 350 m/sec on an Ag(111) surface.  $T_{\text{rot}}=1\text{K}$ ,  $P=10$ ,  $T_{\text{surf}}=300\text{K}$ .

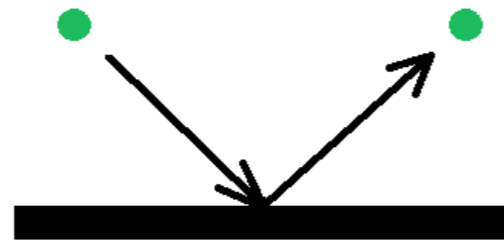
Distribution of the angular momenta of the scattered molecules (**without** and **with** laser pulse at  $+45^\circ$  to the surface)

Average  $J_y$  as a function of the laser polarization direction



# Isotope-selective molecule-surface scattering

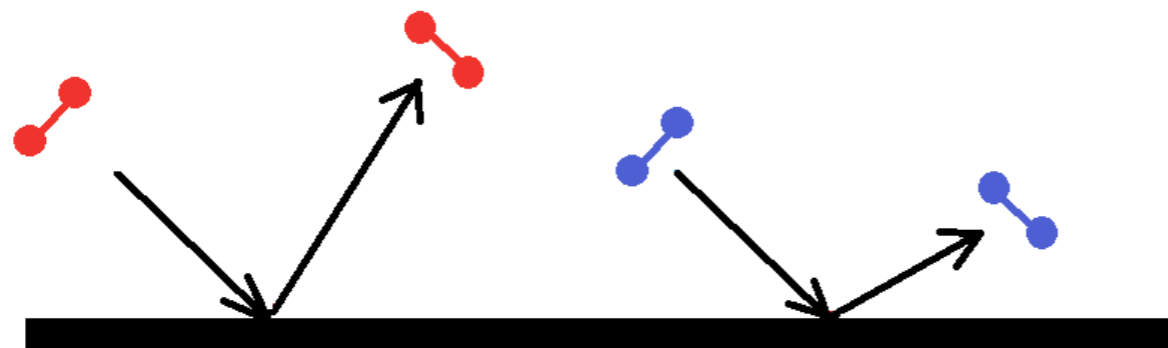
- Scattering of atoms:



$$E_{\text{trans}} = \text{const.}$$

$$P_{\text{parallel}} = \text{const.}$$

- Scattering of molecules:



rotationally hot  
molecules

rotationally cold  
molecules

$E_{\text{rot}} \rightarrow E_{\text{trans}}$

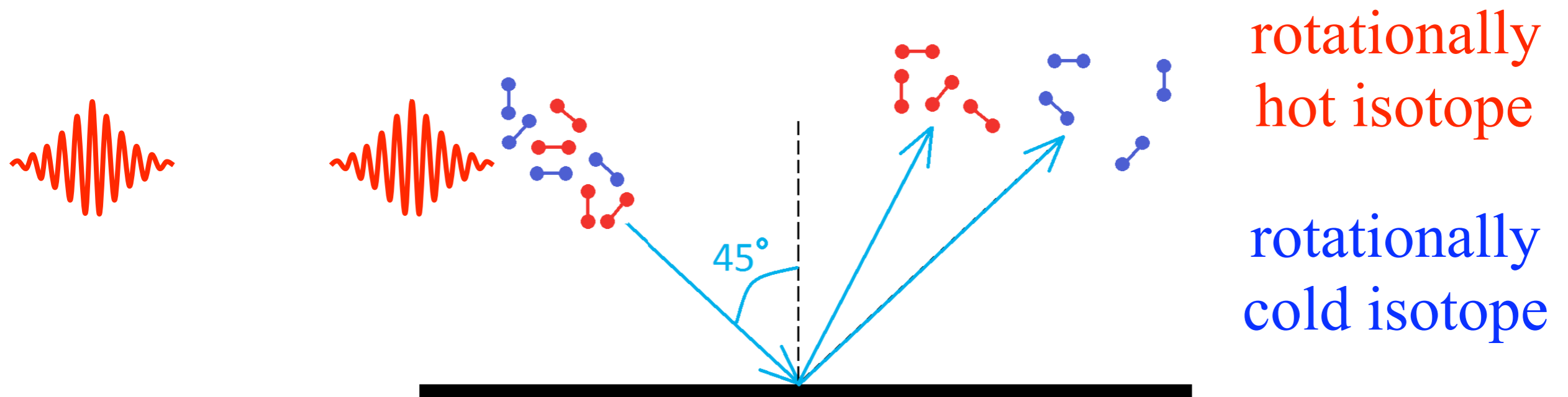
$E_{\text{trans}} \rightarrow E_{\text{rot}}$

$$E_{\text{trans}} + E_{\text{rot}} = \text{const.}$$

$$P_{\text{parallel}} = \text{const.}$$

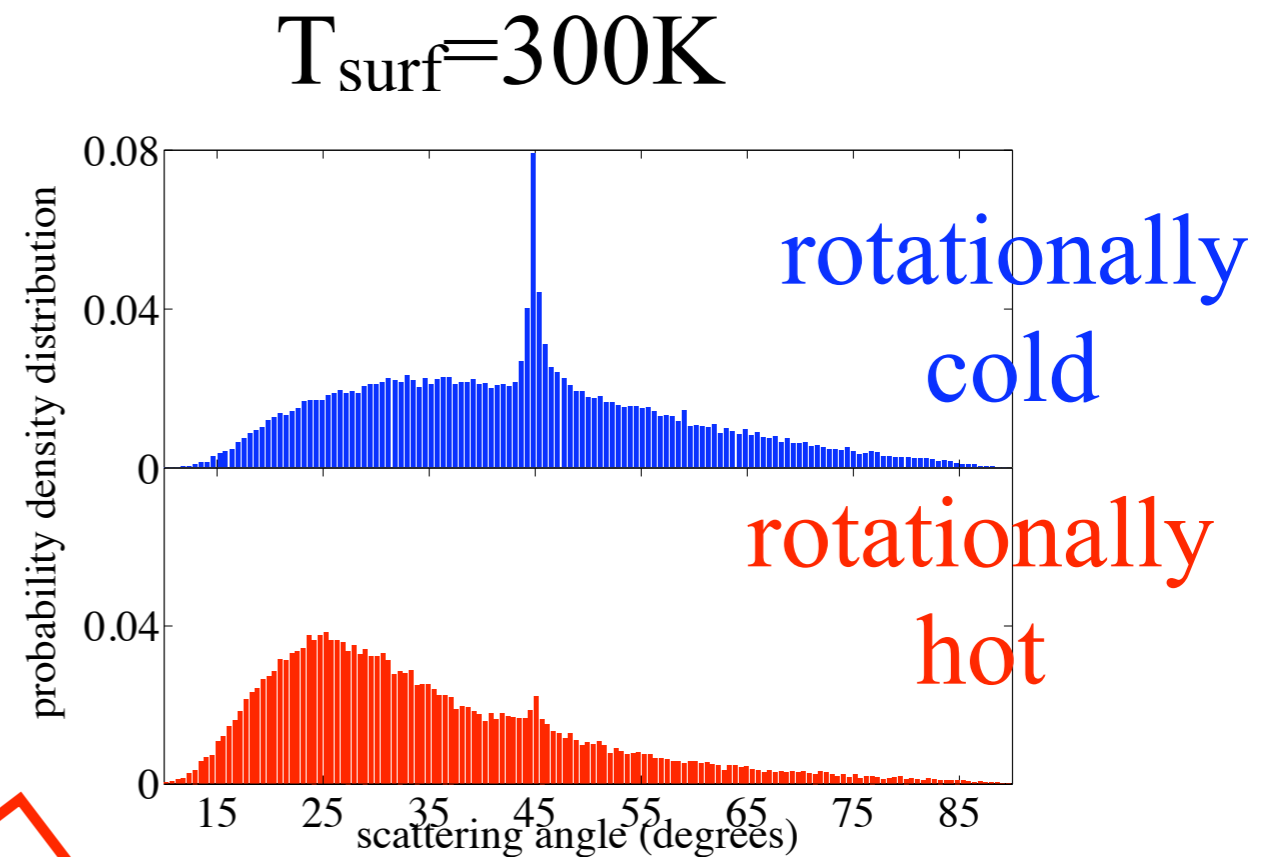
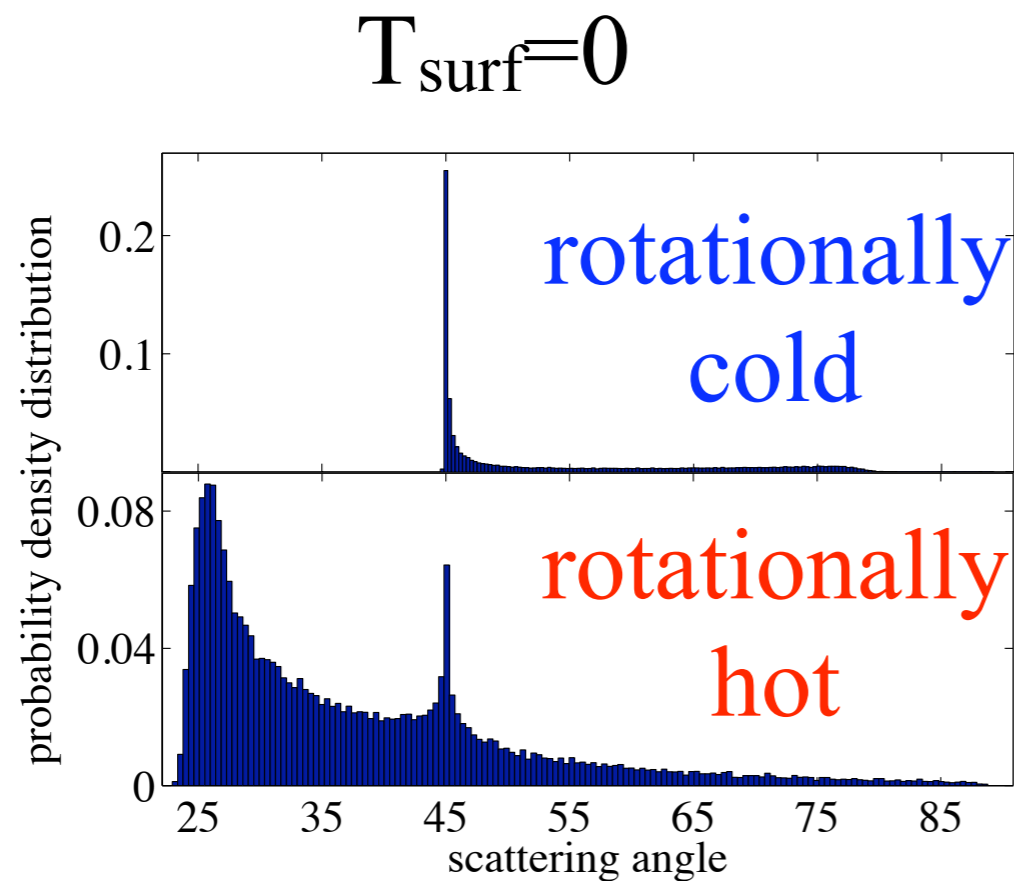
# Isotope-selective molecule-surface scattering

- After exciting the molecular mixture by two properly delayed laser pulses, one of the isotopes is rotationally **hot**, and the other one is rotationally **cold**.
- The rotationally **hot** molecules have a large probability to transfer  $E_{\text{rot}}$  to  $E_{\text{trans}}$  during the collision, and to be scattered to the angles closer to the surface normal.



# Isotope-selective molecule-surface scattering

Results of Monte Carlo simulations with  $5 \times 10^4$   $\text{N}_2$  molecules, incident at 350 m/sec on Ag(111) surface.  $T_{\text{rot}}=1\text{K}$ ,  $P_1=P_2=5$ .



$<1\%$  vs  $69\%$  of the molecules are scattered towards  $\alpha_{\text{scat}} < 45^\circ$

Cooling the surface enhances the effect!

$52\%$  vs  $77\%$  of the molecules are scattered towards  $\alpha_{\text{scat}} < 45^\circ$

# Molecular scattering from rough surface - the washboard model<sup>1</sup> (corrugated surface)

- On top of the hard cube model for a flat surface we add:

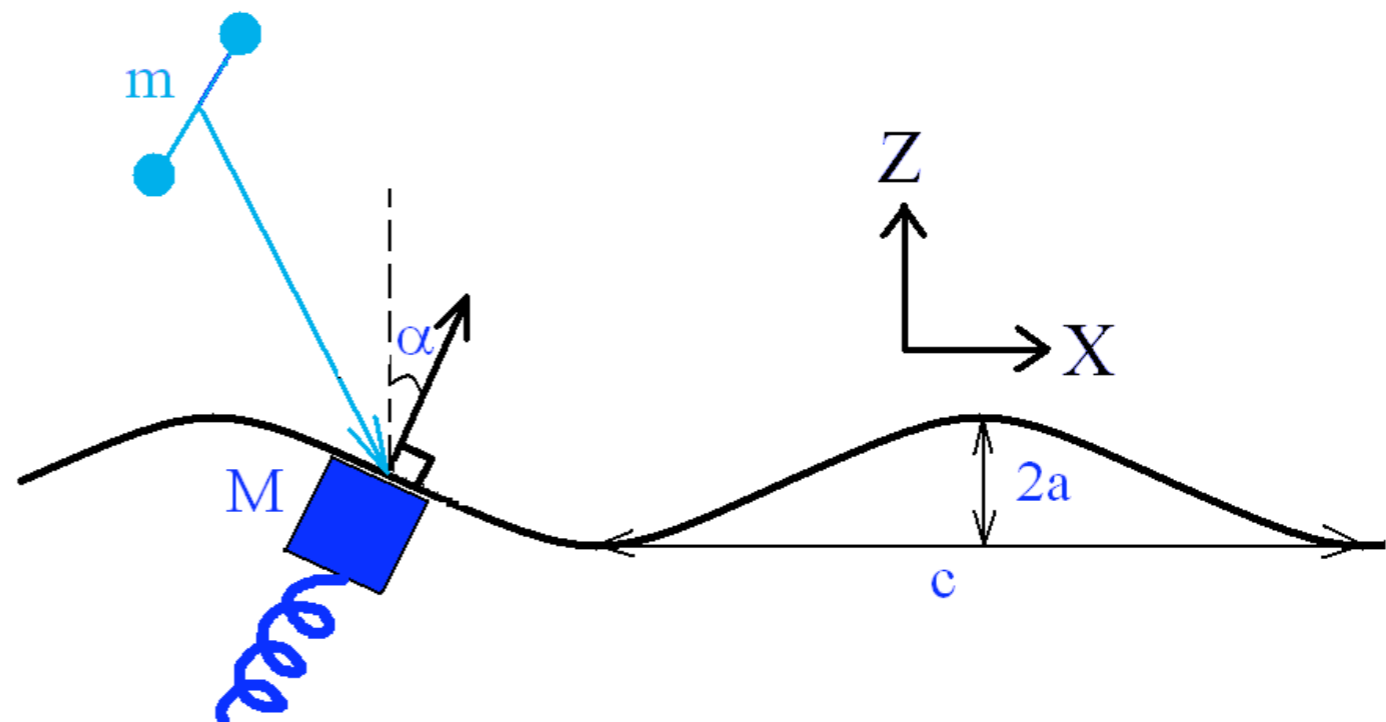
- A one-dimensional sinusoidal corrugation:  $Z(X) = a \cos\left(\frac{2\pi X}{c}\right)$

Maximal angle between the local normal and the Z-axis:

$$\alpha_{\max} = \arctan(2\pi a/c)$$

- The size of the molecule is much smaller than the corrugation wavelength

Pt(211) or  
LiF(001)  
surface

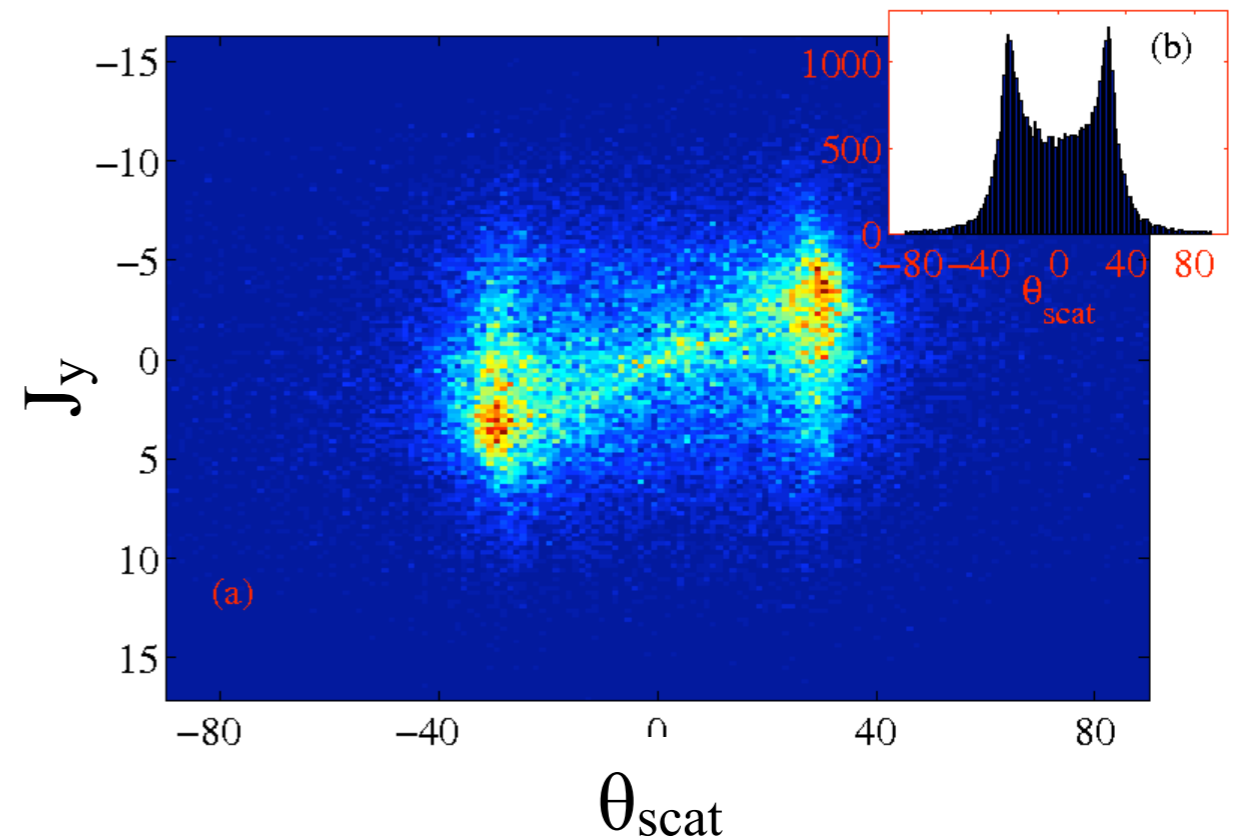
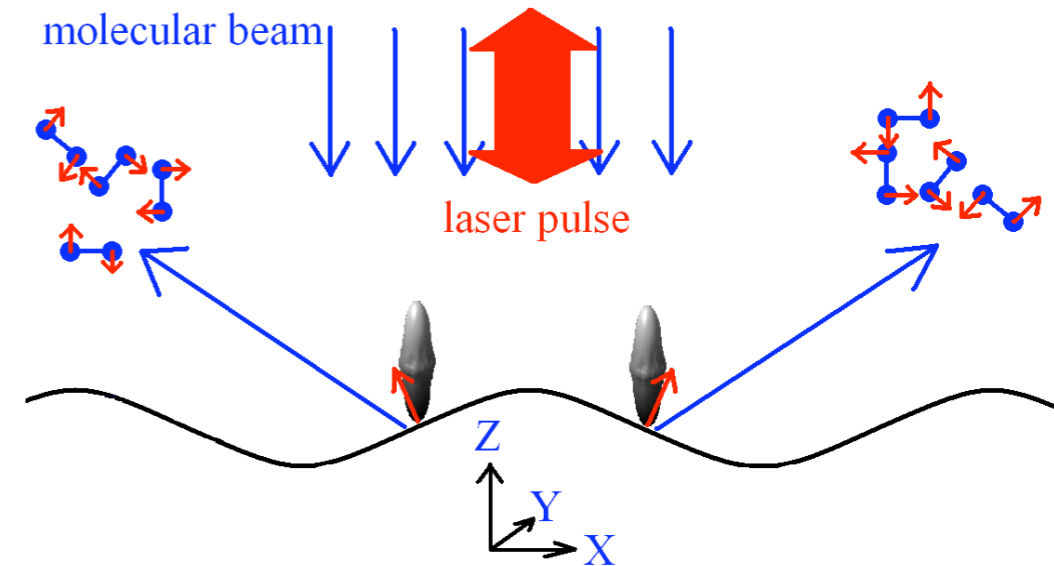


<sup>1</sup>J. C. Tully, J. Chem. Phys. **92**, 680 (1990)



# Correlation between the scattering angle and the sense of rotation

- The molecules are propagating normally to the corrugated surface ( $\alpha_{\max}=20^\circ$ ), and are “kicked” by a laser pulse with  $P=10$  (polarized along the thick red arrow).
- (a) Two dimensional distribution of the scattered molecules. Molecules scattered towards **positive angles**, have, on average, **negative  $J_y$** , and vice versa.
- (b) Distribution from (a) integrated over the angular momentum. “Rainbow” scattering.



# Conclusions

- **Unidirectional rotation** of molecules can be induced by pre-aligning them by a laser pulse before they scatter from a solid surface
- Two laser pulses can direct **different molecular isotopes, or nuclear spin isomers** to different angles after the surface scattering process
- Scattering of pre-aligned molecules from a corrugated surface leads to a **correlation** between the scattering angle and the sense of rotation