# Optical methods in chemistry
# or
# Photon tools for chemical sciences

Session 9:

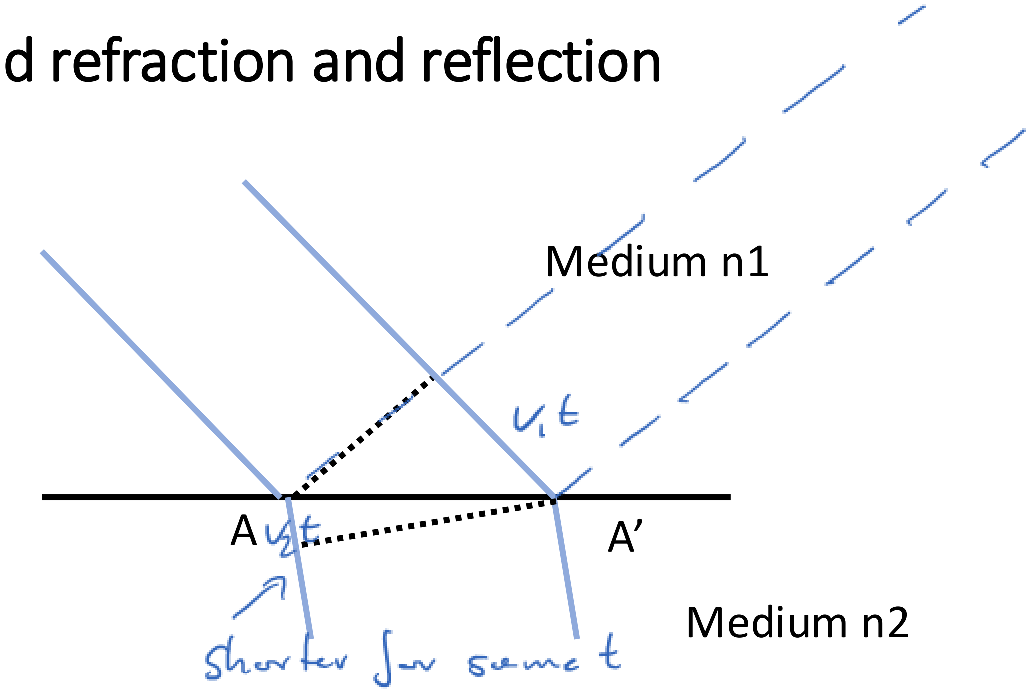
# Course layout – contents overview and general structure

- Introduction and ray optics
- Wave optics
- Beams
- From cavities to lasers
- More lasers and optical tweezers
- From diffraction and Fourier optics
- Microscopy
- Spectroscopy
- **Electromagnetic optics**
- Absorption, dispersion, and non-linear optics
- Ultrafast lasers
- Introduction to x-rays
- X-ray diffraction and spectroscopy
- Summary

Today: Going back to some basics.

Next week: Non-linear optics

# Recap: Ray optics and refraction and reflection




Fermat principle

$$\delta \int_A^O n(r)\, ds = 0$$

→ straight lines

Optical medium

$n = c_0/c$ → slower in medium

- Same time means same distance travelled, t= const
- From geometry: sin $\sin\theta_1 = \frac{v_1 t}{AA'}$ $\quad \sin\theta_2 = \frac{v_2 t}{AA'}$
- Relation: $\frac{\sin\theta_1}{\sin\theta_2} = \frac{n_2}{n_1}$
- Results in Snell's law $n_1 \sin\theta_1 = n_2 \sin\theta_2$

⇒ What is missing? ⇒ reflected ray!

# Recap: Wave description of light

wave equation

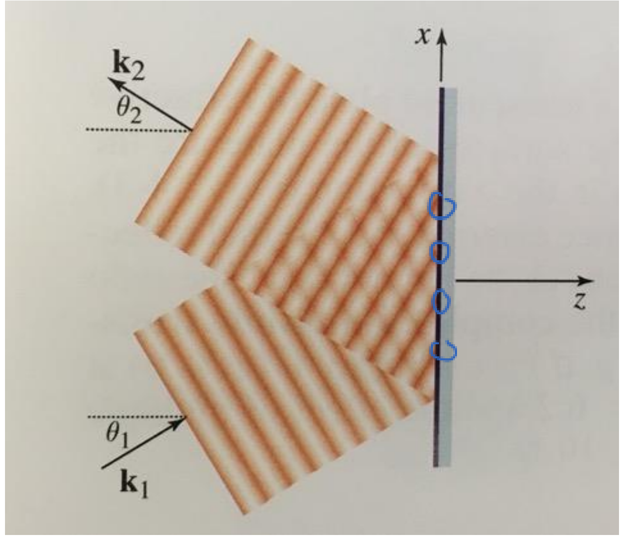
$$\nabla^2 u(\vec{r},t) - \frac{1}{c^2}\frac{\partial^2 u(\vec{r},t)}{\partial t^2} = 0$$

For monochromatic wave

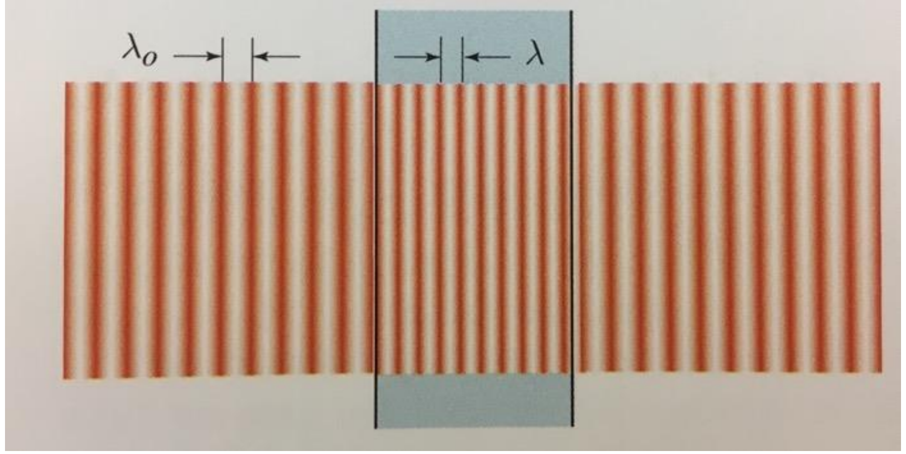
Helmholtz equation $\nabla^2 U + k^2 U = 0$

with wave number $k = \frac{2\pi\nu}{c} = \frac{\omega}{c}$

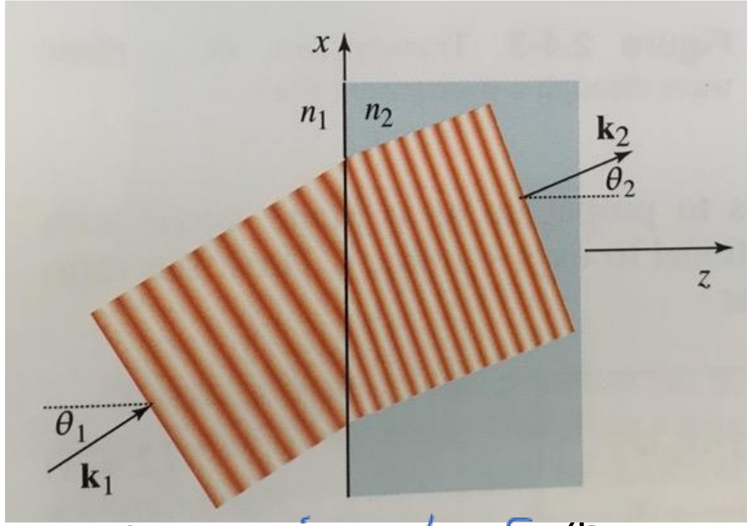
solution $u(\vec{r},t) = U(\vec{r})\exp[i\omega t]$




Reflection ↓ phase matching



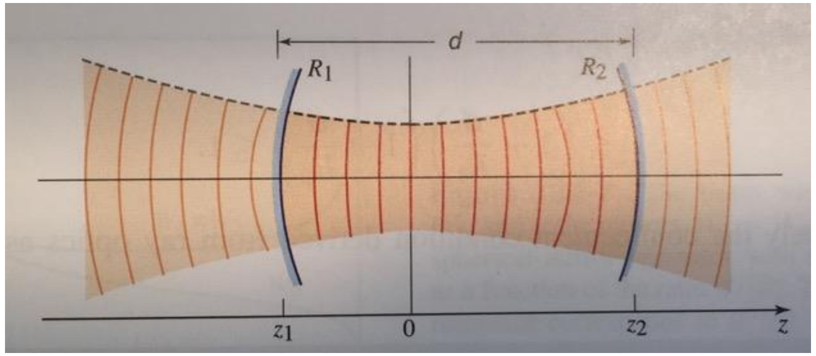

Speed → wavelength / ω

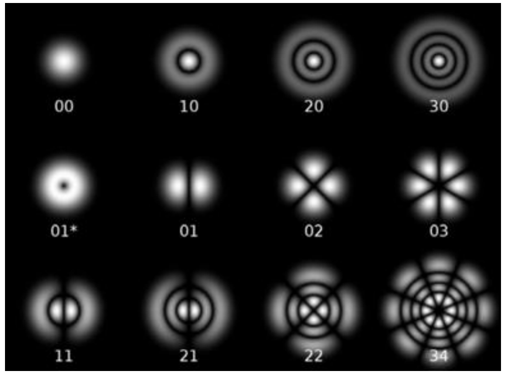



↳ similar to Snell

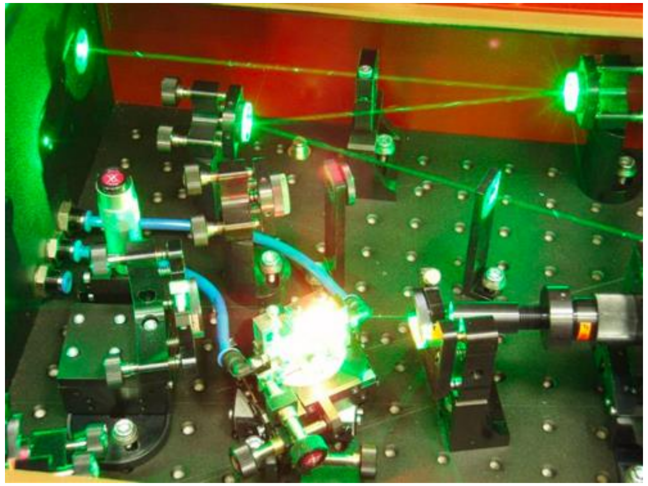
here: plane wave but also for spherical, paraxial approx ⇒ beams

# So far we have done well: Fourier optics, beam optics, lasers…



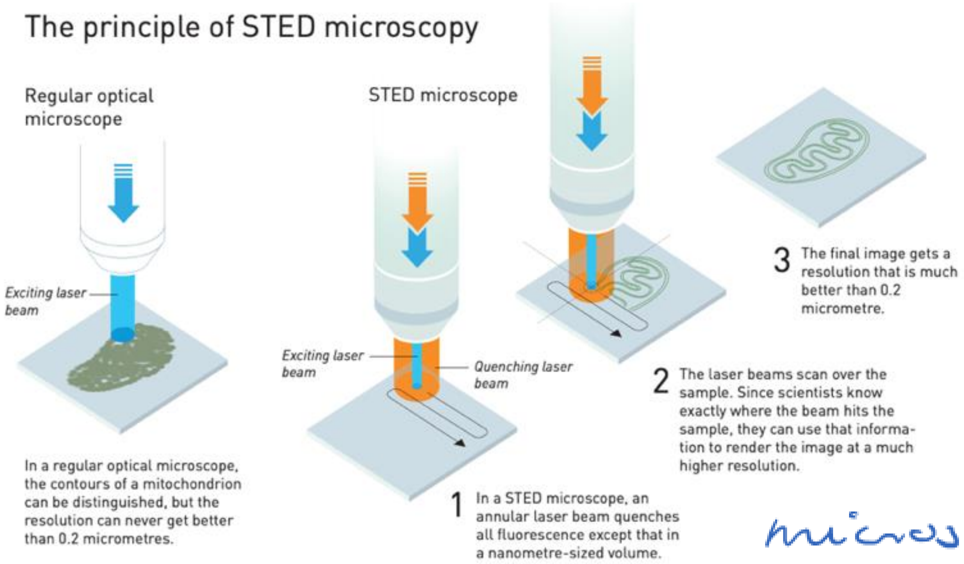




beams + cavities



Lasers

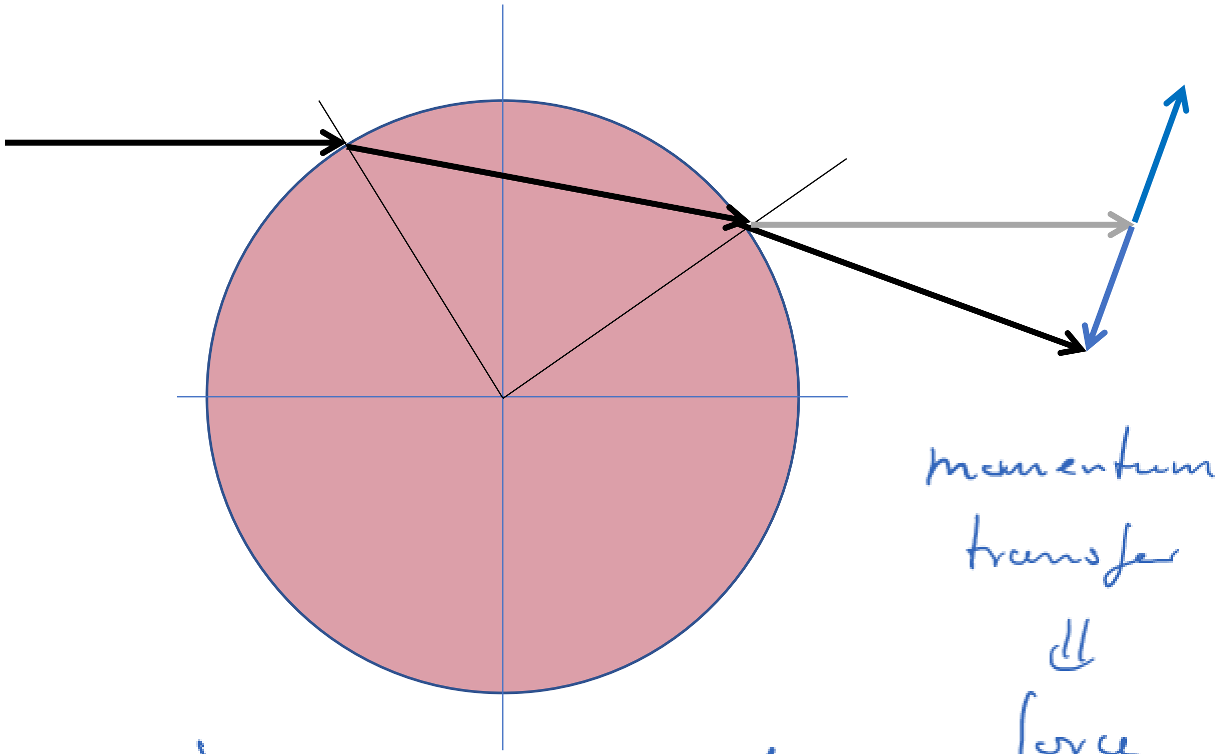
FTIR




microscopy

# Even trapping of particles with photons (particle character)

Light → Photon → Particle   $\vec{p} = \hbar \vec{k}$ ⟷ momentum



momentum transfer

⇓

force

refraction

gradient force on particle

Some boundary conditions:

- Optically thicker sample in optically thinner medium
- Transparent sample, i.e., negligible scattering and reflection compared to transmission

Process:

- Rays are refracted, leading to momentum change
- Action equals reaction, sphere is pushed …………wards
- With equal illumination there is……

BUT particle is larger than $\lambda$

Clearly!

# But we are missing something: details of interaction with matter!

microscopic wave

charges/ electrons

re-radiate/ scatter

resonant/ non-resonant

em-wave "moves" electrons
→ polarization

electrons re-radiate
→ scattering

"transparency" strongly depends on energy/ $\lambda$

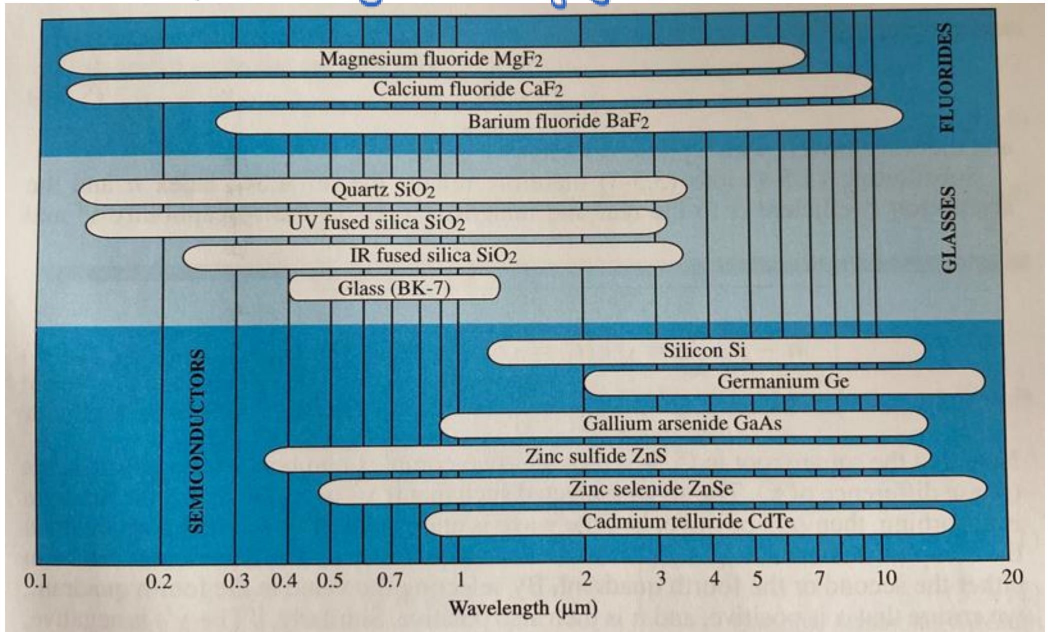
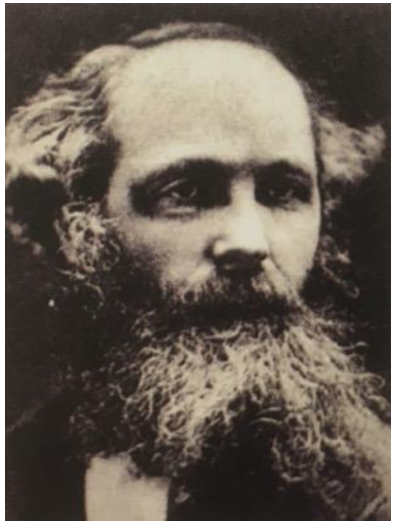



**Figure 5.5-1** Spectral bands within which selected optical materials transmit light.

⇒ details of materials matter, i.e., energy levels, charge (or electron) mobility, etc

## Welcome to EM description of light!

- light is an em wave
- em wave description is needed to properly treat polarization, beam splitting, interaction with matter



James Maxwell
1831 - 1879

Note:
$\times$ – curl
$\nabla$ – divergence

$$\nabla \times \mathcal{H} = \epsilon_o \frac{\partial \mathcal{E}}{\partial t}$$
→ time-varying electric field

$$\nabla \times \mathcal{E} = -\mu_o \frac{\partial \mathcal{H}}{\partial t}$$
→ related time-varying magnetic field

$$\nabla \cdot \mathcal{E} = 0$$

$$\nabla \cdot \mathcal{H} = 0,$$

also satisfies

$$\nabla^2 u - \frac{1}{c_o^2} \frac{\partial^2 u}{\partial t^2} = 0$$

Familiar wave equation: in vacuum

$$c_o = \frac{1}{\sqrt{\varepsilon_o \mu_o}}$$

$\varepsilon_o$ – dielectric permittivity
$\mu_o$ – magnetic permeability

$c_o \simeq 3 \cdot 10^8$ m/sec (in vacuum)

# Maxwell equation in dielectric medium

dielectric → no free charges

$$\nabla \times \mathcal{H} = \frac{\partial \mathcal{D}}{\partial t}$$

$$\nabla \times \mathcal{E} = -\frac{\partial \mathcal{B}}{\partial t}$$

$$\nabla \cdot \mathcal{D} = 0$$

$$\nabla \cdot \mathcal{B} = 0.$$

→ Additional vector fields are needed

D – electric flux density (displacement)

B – magnetic flux density (displacement)

$$\mathcal{D} = \epsilon_o \mathcal{E} + \mathcal{P}$$ → polarization density

$$\mathcal{B} = \mu_o \mathcal{H} + \mu_o \mathcal{M}$$ → magnetization density

$D \sim \mathcal{E}$ ⇒ relates ext. field to response of media

P – Polarization density → Σ electric dipole moments induced by ext. field

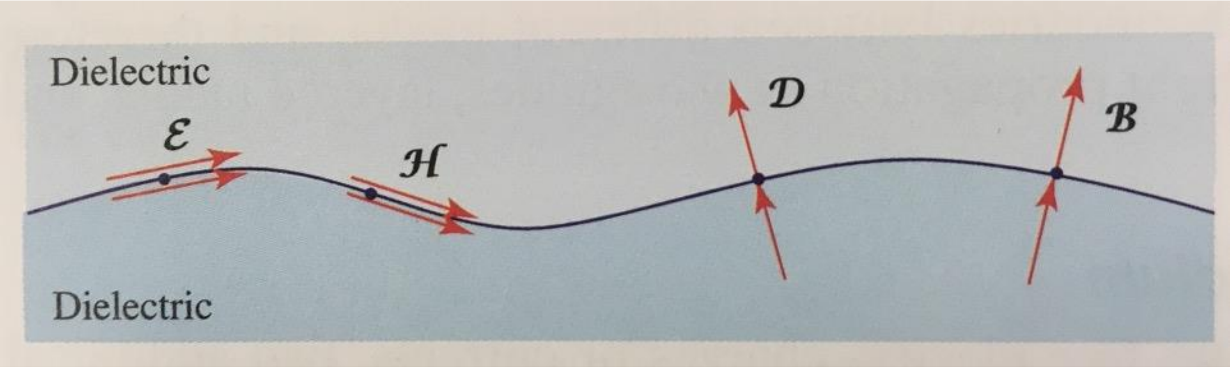
$\varepsilon_0$ electric permittivity → "resistance" to building field

Magnetic field → analogue

P, M → response of media to ext fields

# Boundary conditions at interfaces

**Two dielectric media**



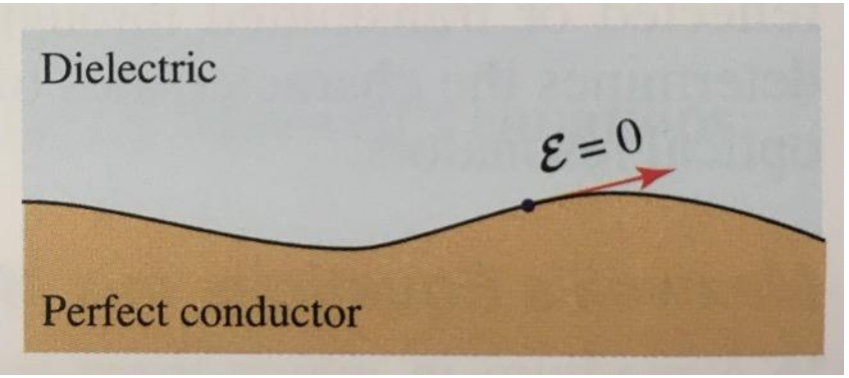

Charge can <u>not</u> move (relocate)

⇒ tangential component of field are the same

$\mathcal{E}_\parallel$ and $\mathcal{H}_\parallel$ → tangential components continuous

⇒ for D, B normal component continuous

**Dielectric and conducting media**

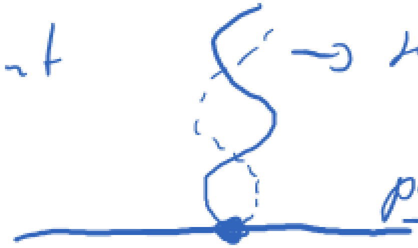



↳ charge is mobile

⇒ no field can be built

tangential $\mathcal{E}_\parallel = 0$

Comment



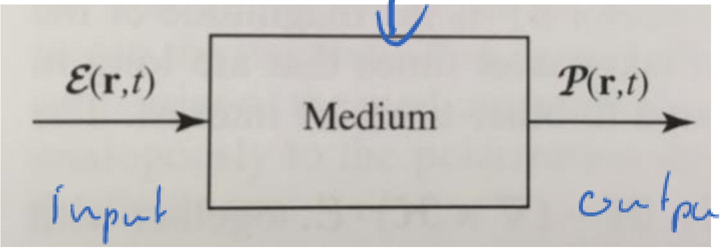
→ reflected light is phase <u>shifted</u>!

"Knot"

# Electromagnetic waves in dielectric media

General

interpretation → output response




in response to an electric field $\mathcal{E}$
media creates a polarization

"instantaneous" "no $\vec{r}$" "no direction"

But stick with linear, nondispersive, homogenous, and isotropic media right now: $\mathcal{E} \to \boxed{M} \to P$

simplify to

$$\boxed{\mathcal{P} = \epsilon_o \chi \mathcal{E},}$$

→ electric susceptibility

$\chi$ scalar

$\mathcal{E} \to \boxed{\chi} \to P$

$D = \varepsilon \mathcal{E}$ / $\varepsilon = \varepsilon_0 (1+\chi)$

$\varepsilon = \varepsilon_0 (1 + \chi)$

dielectric constant

" electric permittivity

# This leads to the following Maxwell and wave equations wave equations

$$\nabla \times \mathcal{H} = \epsilon \frac{\partial \mathcal{E}}{\partial t}$$

$$\nabla \times \mathcal{E} = -\mu \frac{\partial \mathcal{H}}{\partial t}$$

$$\nabla \cdot \mathcal{E} = 0$$

$$\nabla \cdot \mathcal{H} = 0.$$

$\varepsilon$ – dielectric constant (electric permittivity)

$\mu$ – magnetic permeability

back to wave equation

$$\nabla^2 u - \frac{1}{c^2}\frac{\partial^2 u}{\partial t^2} = 0 \quad \Big| \text{ in medium}$$

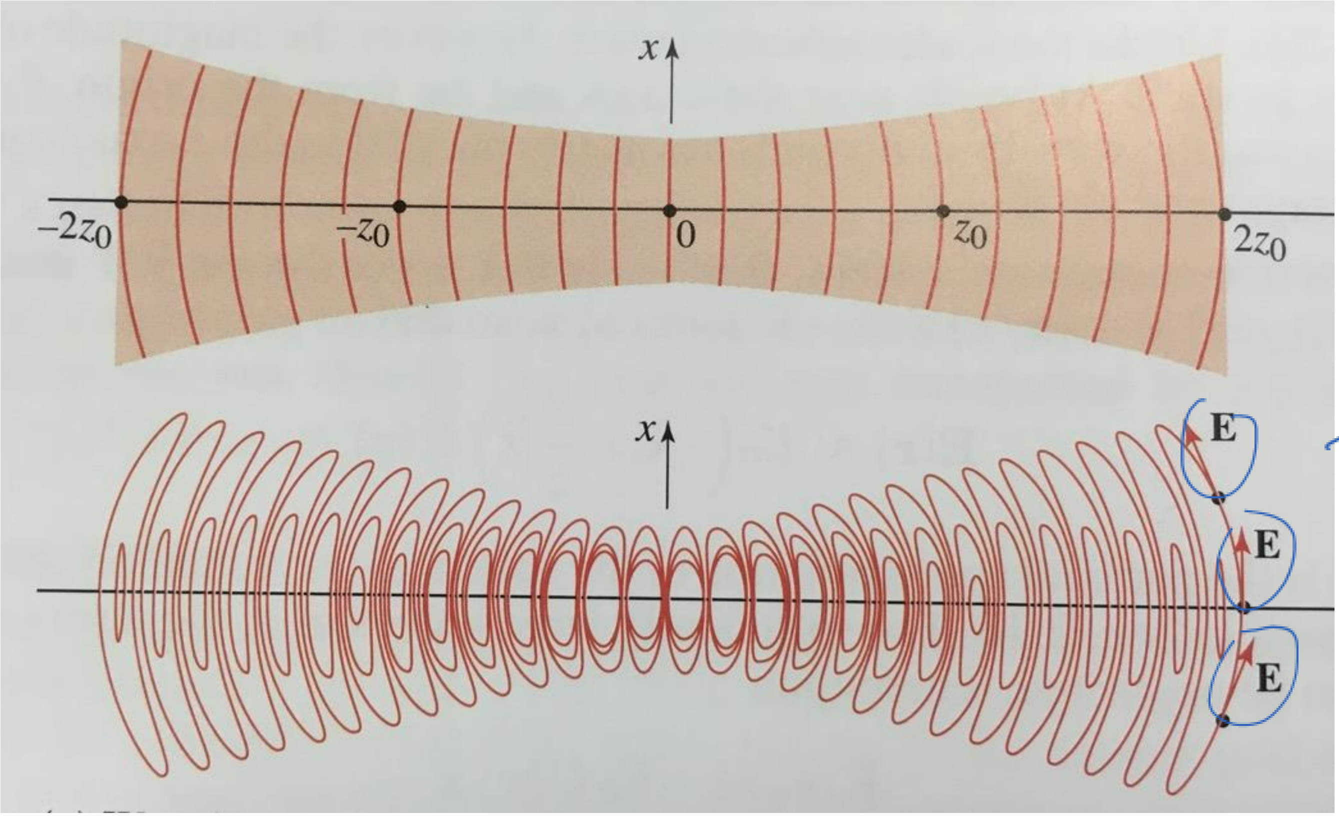
$$c = \frac{1}{\sqrt{\varepsilon \mu}}$$

define $n = c_0/c = \sqrt{\frac{\varepsilon}{\varepsilon_0}\frac{\mu}{\mu_0}}$ = <u>refractive index!</u>

non – magnetic materials

$$n = \sqrt{\frac{\varepsilon}{\varepsilon_0}} = \sqrt{1 + \chi}$$

## A note on wavefronts




→ electric field lines

⇓

previous discussions remain the same

# Back to optical tweezers: Now small particles compared to wavelength

Lorentz force on dipole

polarizability

$$\mathbf{F} = (\mathbf{p}\cdot\nabla)\mathbf{E} + \frac{d\mathbf{p}}{dt}\times\mathbf{B} \qquad \mathbf{p} = \alpha\mathbf{E} \leftarrow \text{field}$$

induced dipole of a sphere

vector math

$$= \alpha\left[(\mathbf{E}\cdot\nabla)\mathbf{E} + \frac{d\mathbf{E}}{dt}\times\mathbf{B}\right]$$

$$= \alpha\left[\frac{1}{2}\nabla E^2 + \frac{d}{dt}(\mathbf{E}\times\mathbf{B})\right]$$

$$= \frac{1}{2}\alpha\nabla E^2$$

Poynting vector

$\frac{d}{dt} \sim 0$

Force $\sim \nabla E^2 \sim \underline{\underline{\nabla I}}$

→ Look at forces in terms of e-dynamics

→ treat forces for scattering, reflection, etc properly

→ assume particle as a dipole → point dipole

response to external field

# Trapping condition in e-m description

288 OPTICS LETTERS / Vol. 11, No. 5 / May 1986

## Observation of a single-beam gradient force optical trap for dielectric particles

Nobel tweezers

A. Ashkin, J. M. Dziedzic, J. E. Bjorkholm, and Steven Chu
AT&T Bell Laboratories, Holmdel, New Jersey 07733

Nobel cooling

**Gradient force** **Scattering force**

$$\mathbf{F} = \frac{1}{2}\alpha\nabla E^2 = \frac{2\pi n_0 r^3}{c}\left(\frac{m^2-1}{m^2+2}\right)\nabla I(\mathbf{r}) \quad > \quad \mathbf{F}_{\mathrm{scat}}(\mathbf{r}) = \frac{8\pi n_0 k^4 r^6}{3c}\left(\frac{m^2-1}{m^2+2}\right)^2 I(\mathbf{r})\hat{z}$$

gradient intensity

$\Downarrow$

particle is moved to area of highest intensity $\Longrightarrow$

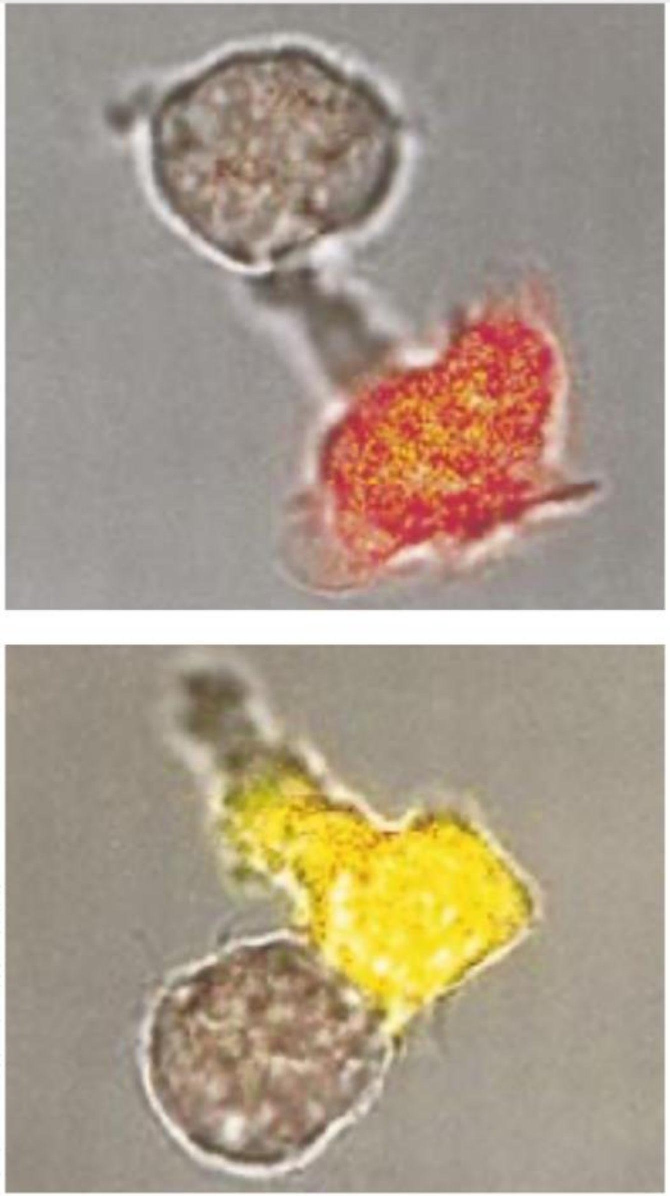
against gradient

$\Downarrow$

particle slightly out of focus

$\alpha$, induced dipole of sphere
$n_o$, refractive index and $m=n_1/n_o$ relative index.

# Optical tweezers in biology (example, Scientific American)



XUNBIN WEI *Beckman Laser Institute*

# Laser Scissors and Tweezers

*Researchers are using lasers to grasp single cells and tinier components in vises of light while delicately altering the held structures. These lasers offer new ways to investigate and manipulate cells*

by Michael W. Berns

**POLARITY OF *T* CELLS is borne out in studies made possible by laser tweezers. *B* cells, which provoke calcium release by *T* cells, were carefully positioned alongside *T* cells using tweezers. Positioning of the *B* cell at one end of a quiescent *T* cell elicited no change; a fluorescent red stain in the *T* cell remained red (*top*). But when the *B* cell touched the other end of the *T* cell, calcium was released, signaled by yellow fluorescence (*bottom*).**

Ref: Scientific American, April 1998, page 62 onwards

# Optical tweezers on the nanoscale

nature nanotechnology

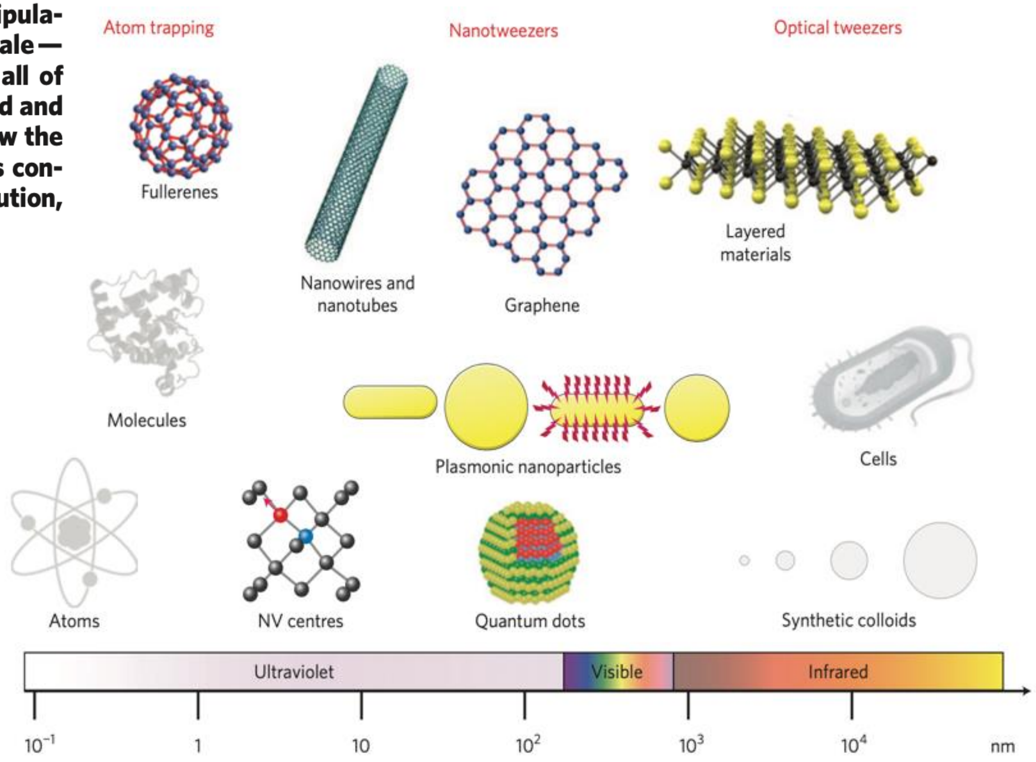
REVIEW ARTICLE

PUBLISHED ONLINE: 7 NOVEMBER 2013 | DOI: 10.1038/NNANO.2013.208

# Optical trapping and manipulation of nanostructures

Onofrio M. Maragò[1]*, Philip H. Jones[2], Pietro G. Gucciardi[1], Giovanni Volpe[3] and Andrea C. Ferrari[4]*

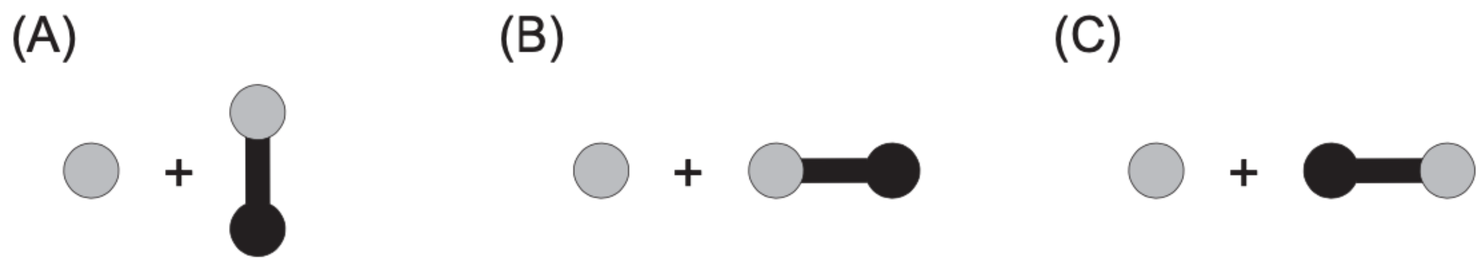
**Optical trapping and manipulation of micrometre-sized particles was first reported in 1970. Since then, it has been successfully implemented in two size ranges: the subnanometre scale, where light–matter mechanical coupling enables cooling of atoms, ions and molecules, and the micrometre scale, where the momentum transfer resulting from light scattering allows manipulation of microscopic objects such as cells. But it has been difficult to apply these techniques to the intermediate — nanoscale — range that includes structures such as quantum dots, nanowires, nanotubes, graphene and two-dimensional crystals, all of crucial importance for nanomaterials-based applications. Recently, however, several new approaches have been developed and demonstrated for trapping plasmonic nanoparticles, semiconductor nanowires and carbon nanostructures. Here we review the state-of-the-art in optical trapping at the nanoscale, with an emphasis on some of the most promising advances, such as controlled manipulation and assembly of individual and multiple nanostructures, force measurement with femtonewton resolution, and biosensors.**



# More on chemistry:

**Stereochemistry:** Study of the relative spatial arrangement of atoms that form the structure of molecules and their manipulation.

**Example**:




**Need**: Control and manipulation of molecules

Following pages based on Stapelfeldt group work (Aarhus) as well as

REVIEWS OF MODERN PHYSICS, VOLUME 75, APRIL 2003

***Colloquium*: Aligning molecules with strong laser pulses**


Henrik Stapelfeldt

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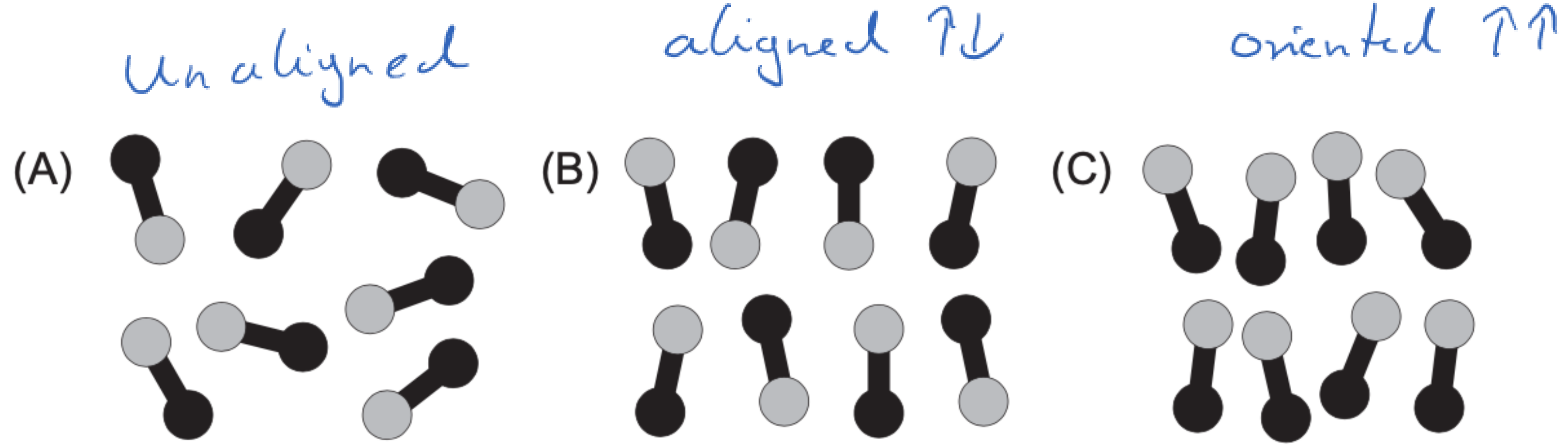
Tamar Seideman

*Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada*

# Laser alignment of molecules




Approach: Molecule → Dipole

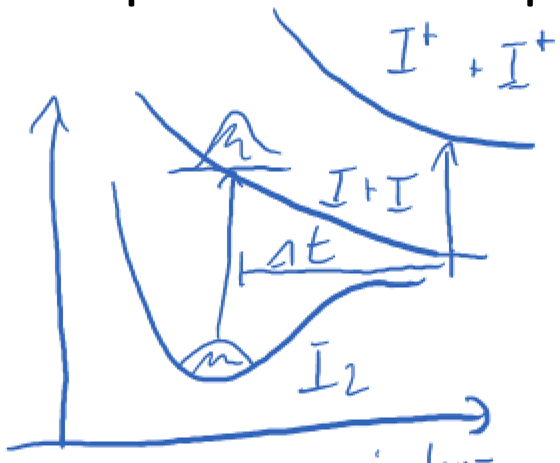
Describe potential energy in field $\quad U_{pol} = -\frac{1}{2} \mathcal{E} \alpha \mathcal{E}$

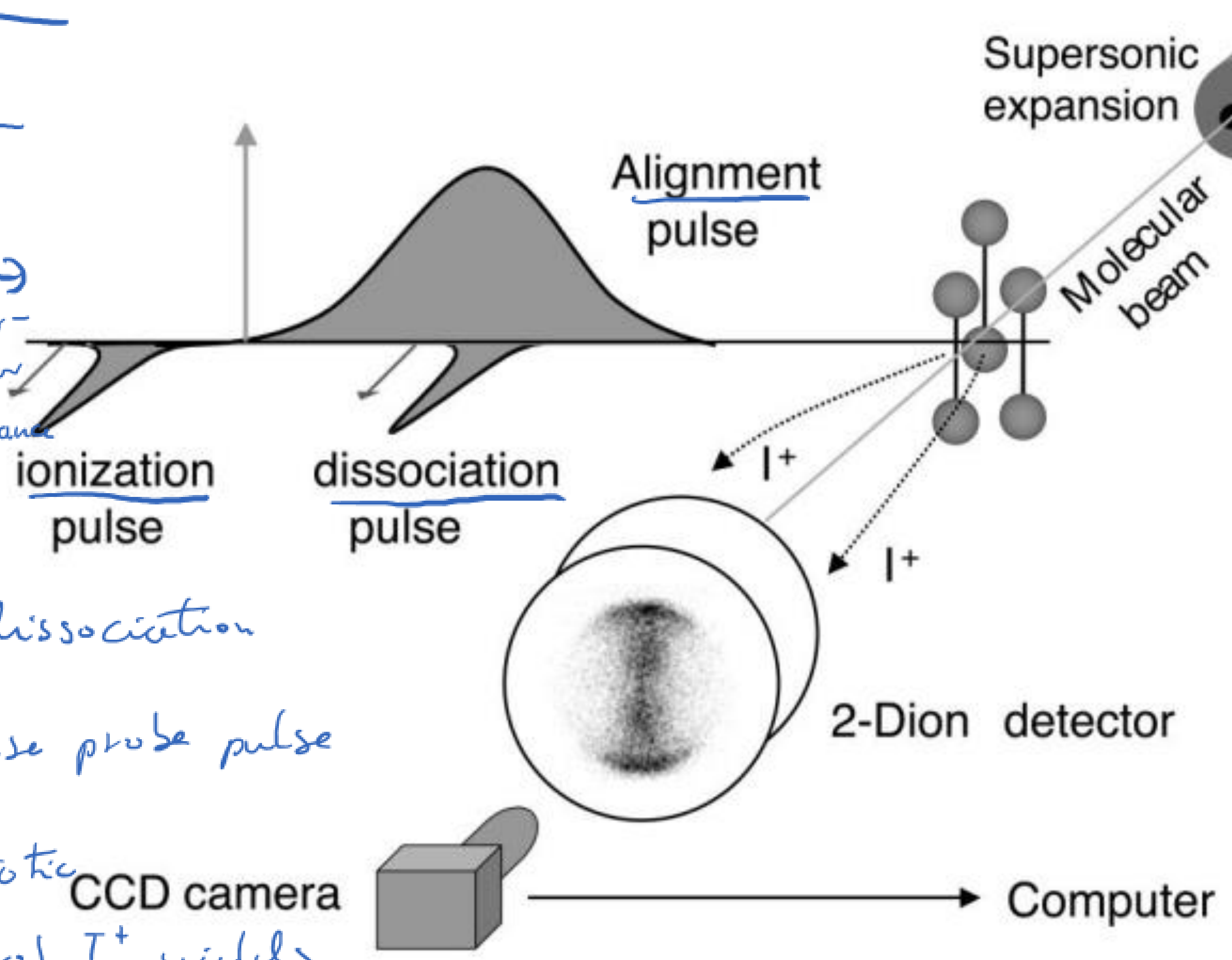
$\Downarrow$ $\quad\quad$ ↑ molecular polarizability (tensor)

Minimize potential energy through alignment

Example: $I_2$ photo dissociation

# Experimental setup




→ Cold molecules

→ 670 nm dissociation

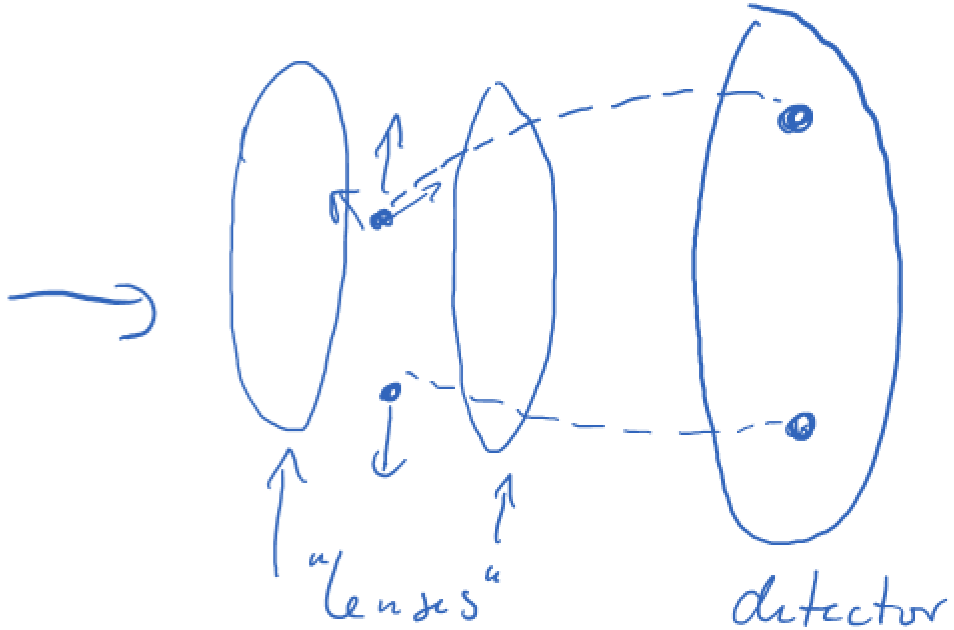
→ $\Delta t$ intense probe pulse

⇒ asymptotic speed of $I^+$ yields internuclear separation

# Detection scheme: Coulomb explosion imaging

VMI → velocity map imaging with electrostatic lens

- Fragment whole molecule through sudden ionization
- Use ionization laser pulse shorter than alignment pulse
- Use "imaging" spectrometers

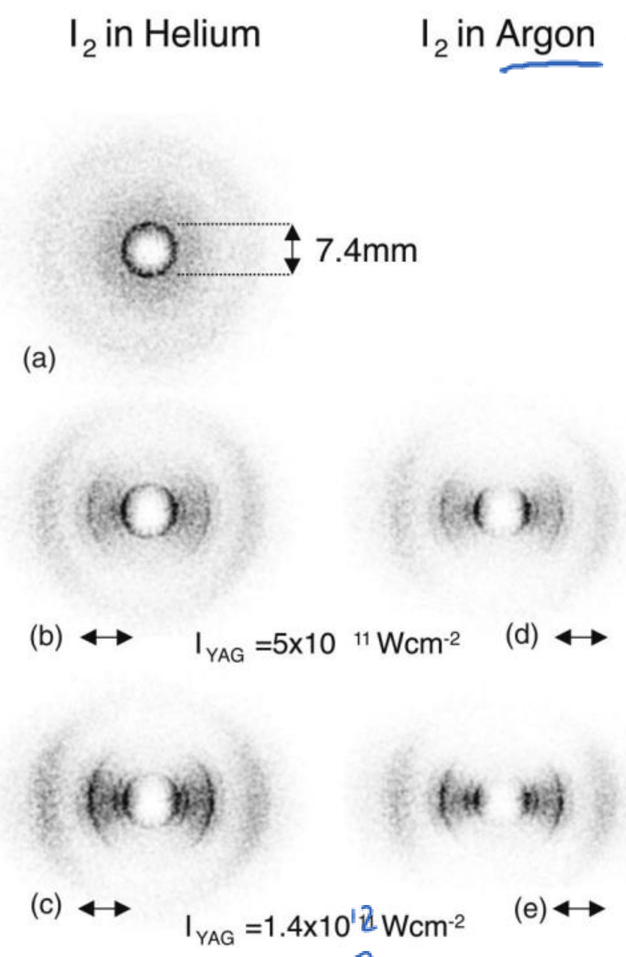

VMI → lens focuses ions with same velocities on detector

# Some data examples

no laser

laser on

more laser




→ Ar mass closer to I → lower rotational velocity

more alignment

12 ↳ paper text & figure

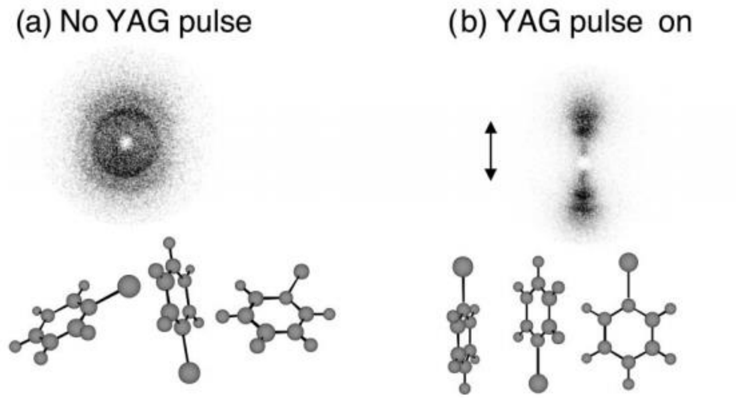



FIG. 9. Ion images of $I^+$ recorded when iodobenzene is irradiated by a circularly polarized, 100-fs, $8\times10^{13}$-W/cm$^2$, 800-nm pulse. (a) No alignment field. (b) In the presence of a linearly polarized (vertical) alignment field with intensity $1.2\times10^{12}$ W/cm$^2$. The spatial orientation of the molecules is illustrated below the two images.

## Final note: There is also impulsive alignment

The end.