Optical methods in chemistry
or
Photon tools for chemical sciences

Session 9:

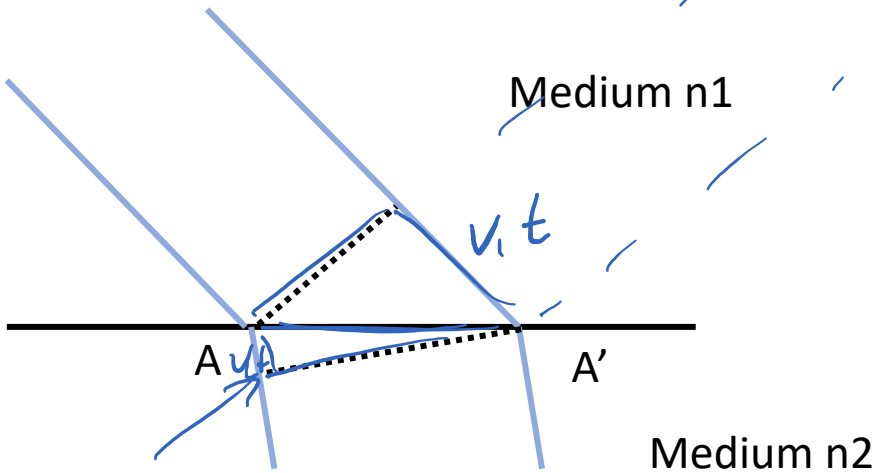
Course layout – contents overview and general structure

- 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



- Same time means same distance travelled, t= const
- From geometry: sin
- Relation:
- Results in Snell's law

Fermat's principle

$$\delta \int_A^B n_{(r)}\, ds = 0$$

→ straight lines

Optical media

$n = \frac{c_0}{c}$ ⇒ light inside media slower

missing reflected ray

Recap: Wave description of light

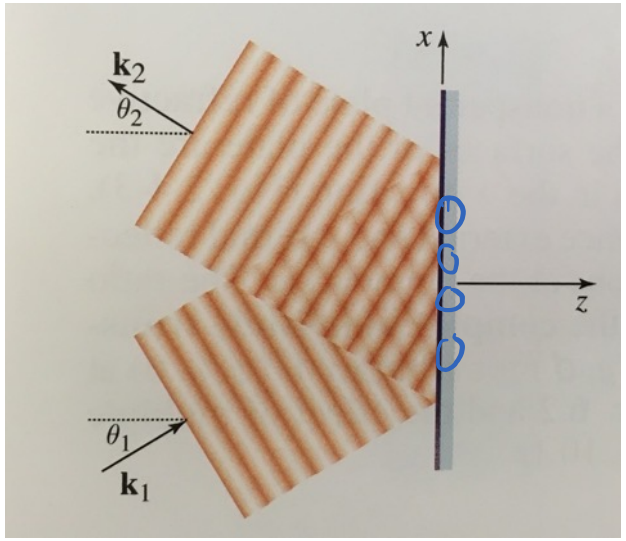
→ wave equation

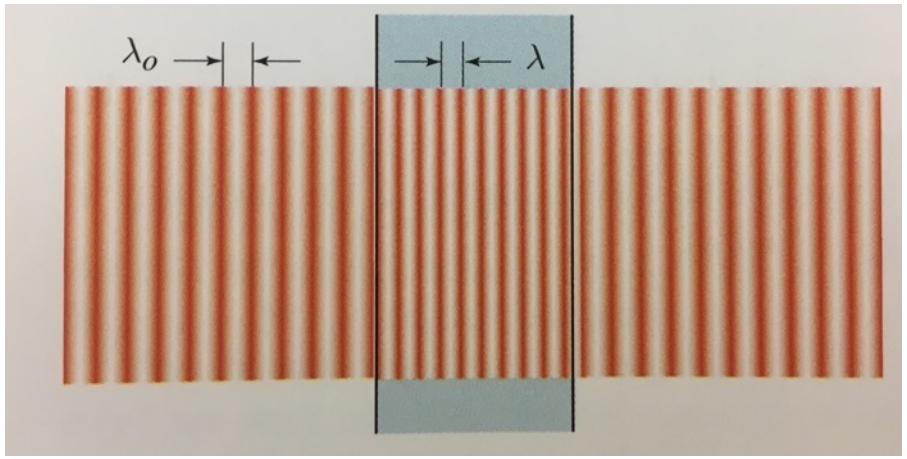
$$\nabla^2 u(\vec{r},t) - \frac{1}{c^2}\frac{\partial^2 u(\vec{r},t)}{\partial t^2} = 0$$

→ Monochromatic wave

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

→ wave number $k = \omega/c$



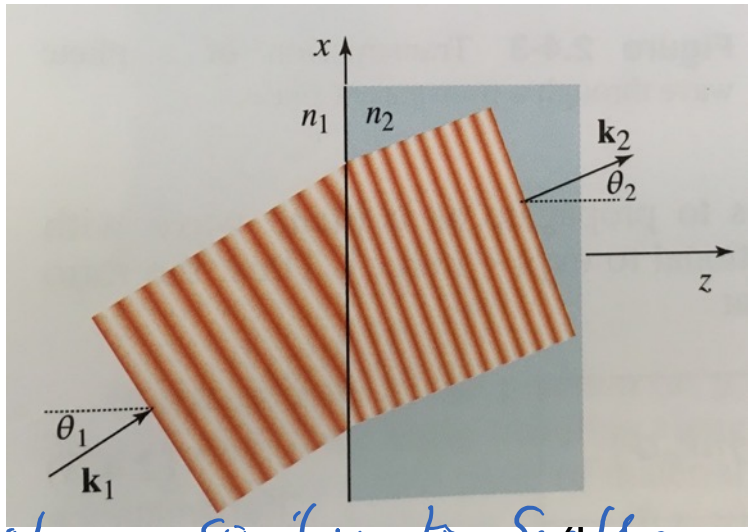


Phase matching

Speed → wavelength

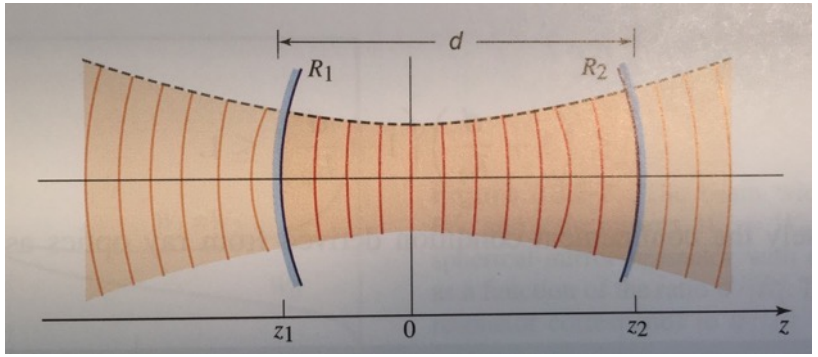
plane waves (but also spherical, paraxial, ...)

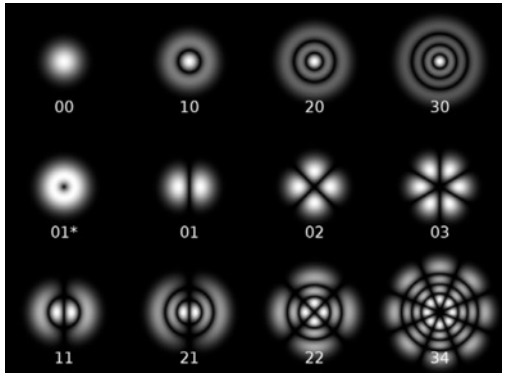
⇒ beams



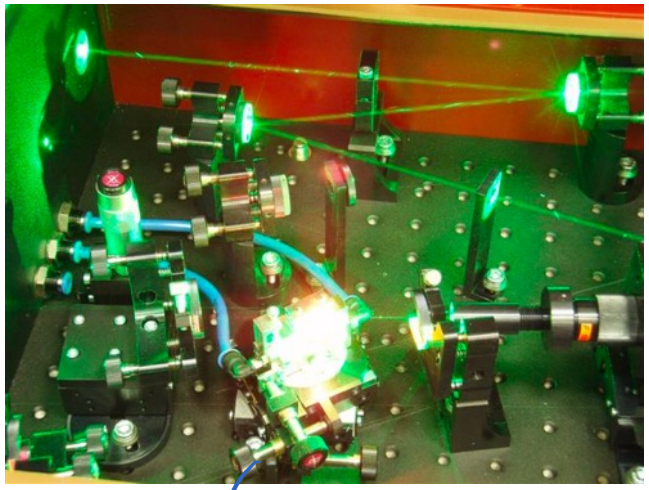
similar to Snell's

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

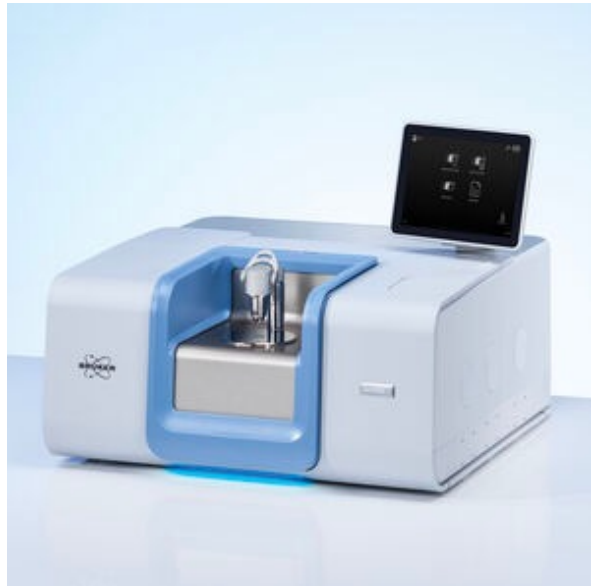




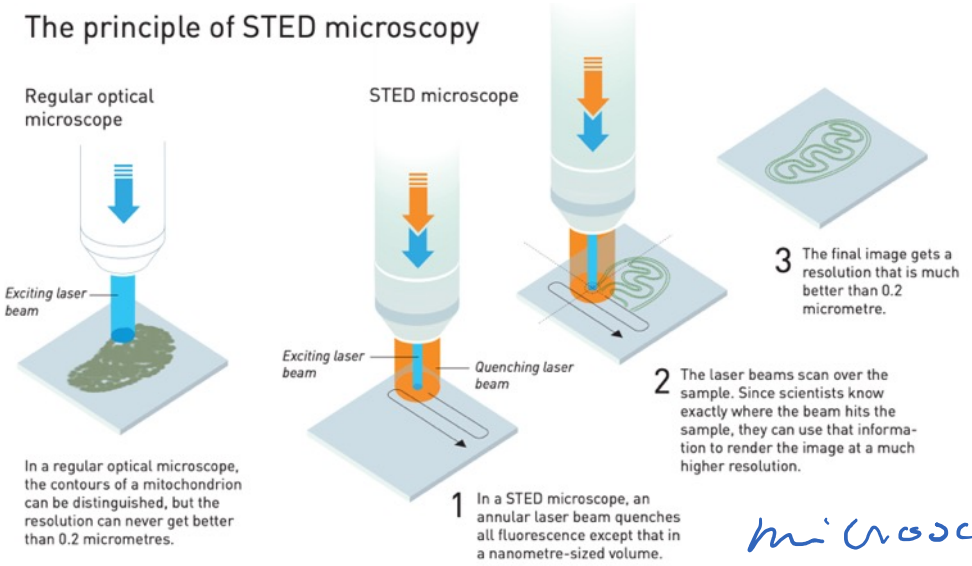
Beams & cavities



Lasers



Fourier Spectroscopy



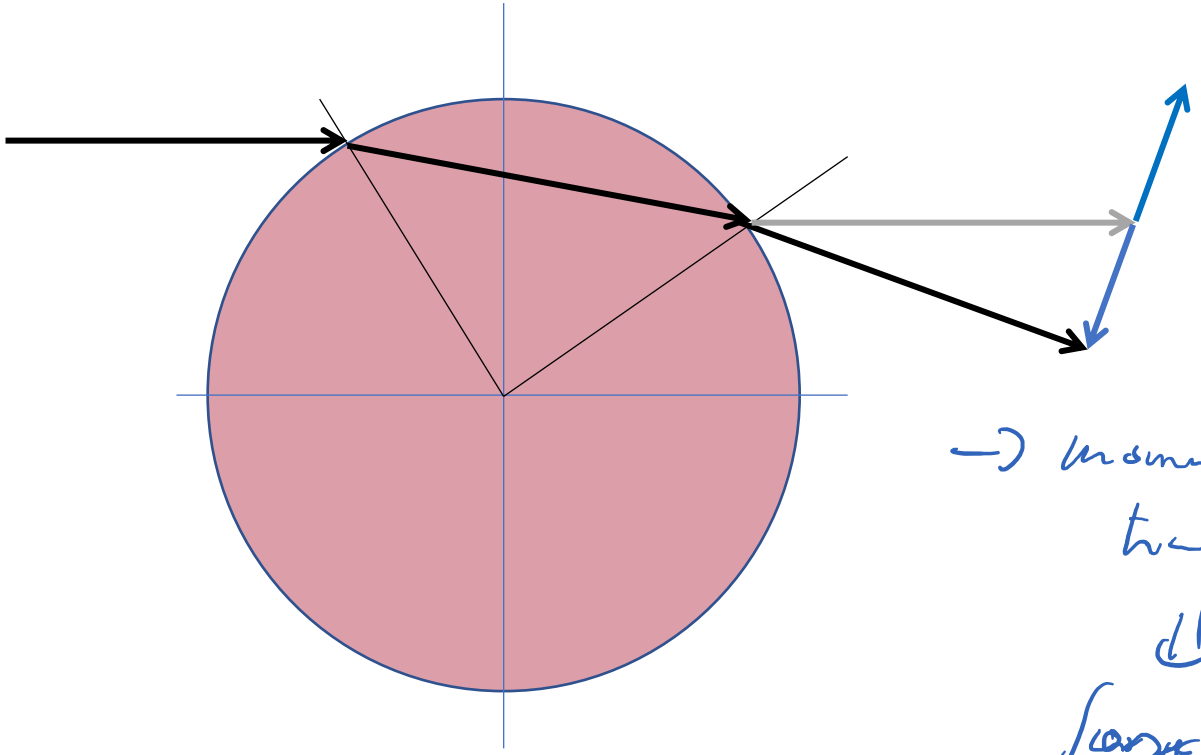
diffraction / interference

microscopy

Even

Even trapping of particles with photons (particle character)

Light → photon → particles



→ momentum through the sphere

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 large compared to wavelength

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

Macroscopic wave

charges / electrons

re-radiate → scatter

resonant

non-resonant

em "moves" electrons → polarization

electrons → re-radiate "scatter"

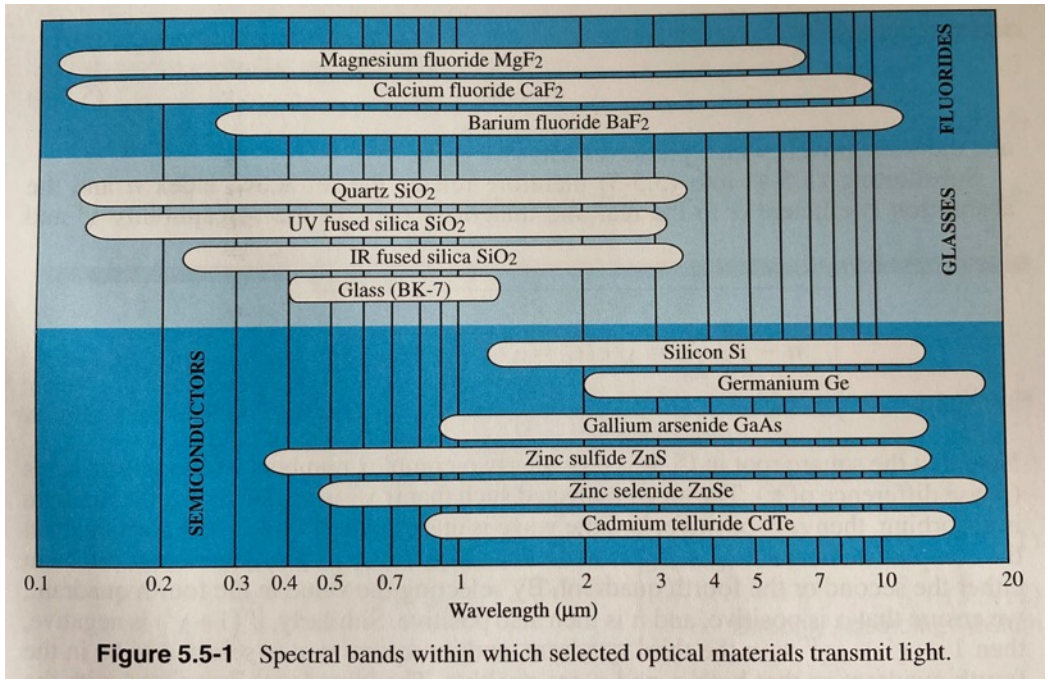


Figure 5.5-1 Spectral bands within which selected optical materials transmit light.

What is "transparent" things depends on

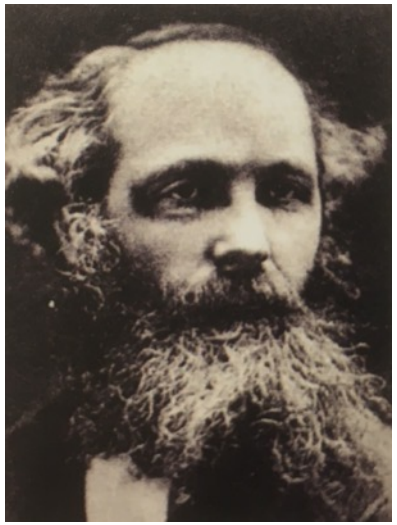
the photon energy / ν

or λ

⇒ the details of material matters energy bands, charge conductivity

Welcome to EM description of light!

- light as em wave
- em wave description is needed to properly treat light (→ polarization, beam splitting, ...)



James Maxwell
1831 - 1879

coupled differential equations

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

→ time varying electric field

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

→ (solenoidal) time varying magnetic field

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

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

→ also satisfy

Familiar wave equation:

$$\nabla^2 u - \frac{1}{c_0} \frac{\partial^2 u}{\partial t^2} = 0$$

in vacuum

$$c_0 = \frac{1}{\sqrt{\varepsilon_0 \mu_0}}$$

ε_0 – dielectric permittivity

μ_0 – magnetic permeability

$c_0 = 3 \cdot 10^8 \frac{m}{sec}$ (in vacuum)

Maxwell equation in medium

dielectric → dielectric medium → no free charges

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

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

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

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

Need two additional vector fields

D → electric flux density (displacement)

B → magnetic flux density (displacement)

$$\mathcal{D} = \epsilon_0 \mathcal{E} + \mathcal{P}$$

$$\mathcal{B} = \mu_0 \mathcal{H} + \mu_0 \mathcal{M}$$

P → polarization density

M → magnetization density

D ~ E → relates ext field response of medium

P → Polarization density → $\sum$ electric dipole moment induced by ext field

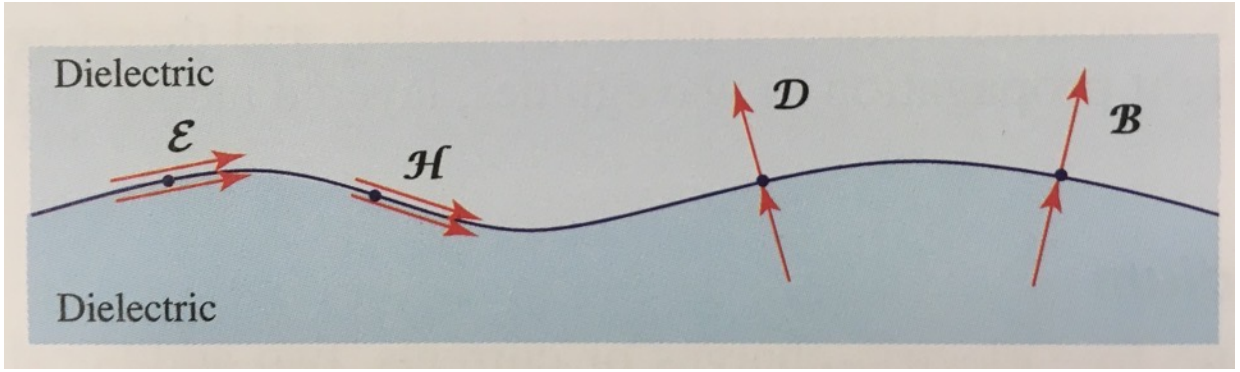
ε_0 → electric permittivity → "resistance" to building field

(Magnetic field analogous)

P, M → response of the medium to ext. field.

Boundary conditions at interfaces

Two dielectric media



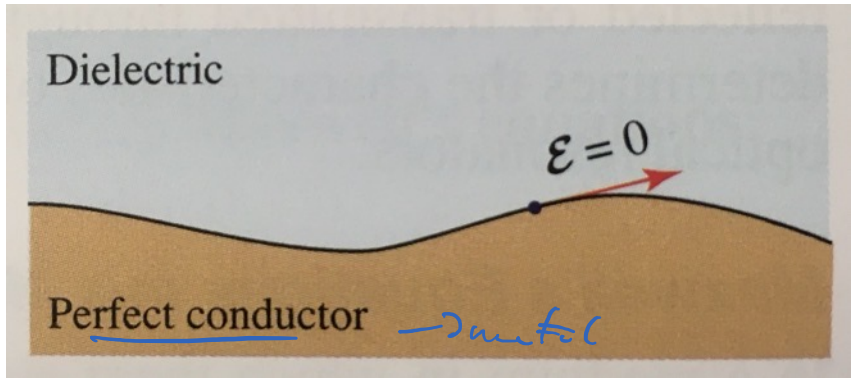
Charge cannot move (relocate)

→ tangential components of the fields are the same

→ $E_{\parallel}$ and $H_{\parallel}$ → tangential components continuous

→ for D, B, normal components are continuous

Dielectric and conducting media

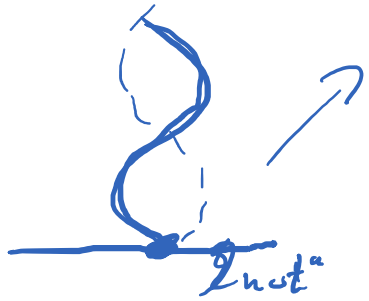


↳ charge is mobile

⇒ no field can be build

tangential $E_{\parallel} = 0$

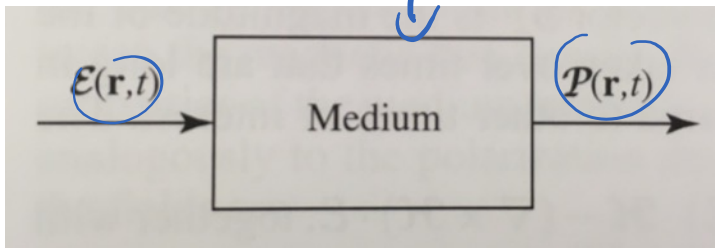
Comment



reflected light phase shifted by π

Electromagnetic waves in dielectric media

General



interpretation → output response

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

instantaneous, no r, no directional

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

$\mathcal{M}$ Scalar response

Simplifies to

$$\mathcal{P} = \epsilon_0 \chi \mathcal{E},$$

→ electric Susceptibility

χ - Scalar

$\mathcal{E} - [\chi] \rightarrow \mathcal{P}$

$\mathcal{E} = \epsilon_0 (1 + \chi)$

ϵ dielectric constant

$$\frac{\mathcal{E}}{\mathcal{E}_0} = 1 + \chi$$

relative permittivity

This leads to the following Maxwell and wave equations wave equations

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

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

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

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

ε – dielectric constant (↪ electric permittivity)

μ – magnetic permeability

back to wave equation

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

$$c = \frac{1}{\sqrt{\varepsilon \mu}} \quad \text{in media}$$

define refractive index

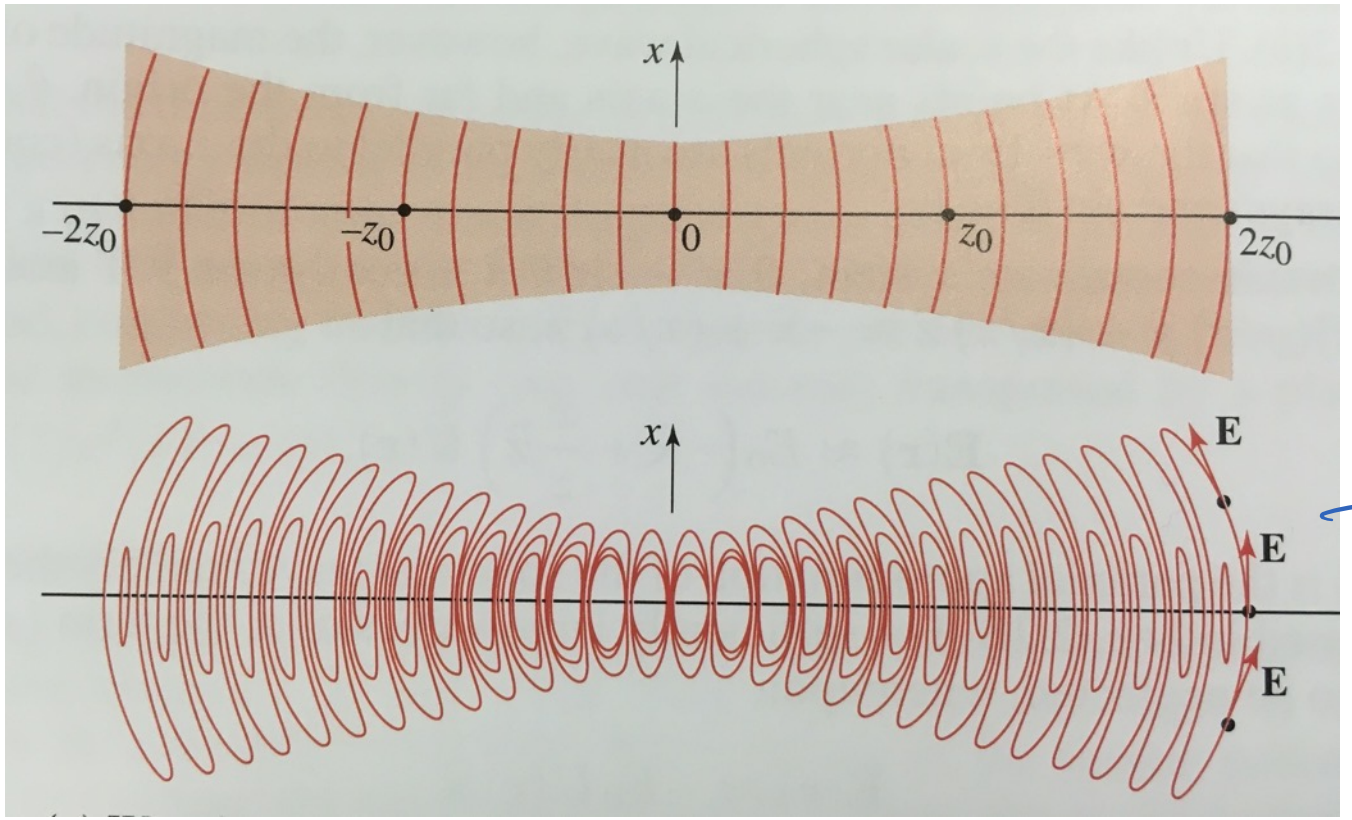
$$n = \frac{c_0}{c} = \sqrt{\frac{\varepsilon}{\varepsilon_0} \frac{\mu}{\mu_0}} = \text{refractive index}$$

non-magnetic materials $n = \sqrt{\frac{\varepsilon}{\varepsilon_0}} = \sqrt{1 + \chi}$ (χ susceptibility)

Homework

Familiarize yourself with this link of e-dynamics

A note on wavefronts



→ electric field lines

Previous concept stay the same!

Back to optical tweezers: Now small particles compared to wavelength

Lorentz force on dipole

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

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

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

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

polarizability of sphere

induced dipole of sphere

Poynting vector

$d/dt = 0$

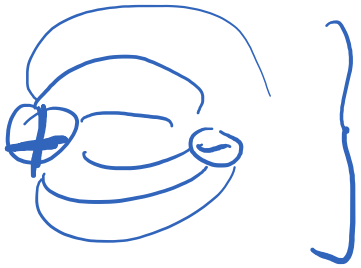
Force ~ ∇E^2 — ∇I

→ look at forces in in terms of e-dyn

→ treat forces for scattering, reflection, etc properly

→ assume particle as a dipole

→ point dipole → Lorentz force



response to ext 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

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

Model pole for tweezers

Model pole for cooling

Gradient force

$$\mathbf{F} = \frac{1}{2}\alpha \nabla E^2 = \frac{2\pi n_0 r^3}{c}\left(\frac{m^2-1}{m^2+2}\right)\nabla I(\mathbf{r})$$

>

Scattering force

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

gradient intensity

particle is moved to area of highest intensity

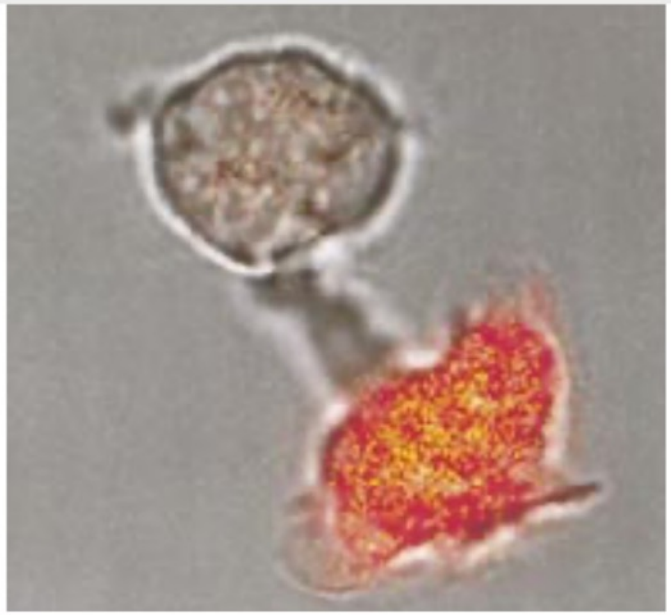
against gradient

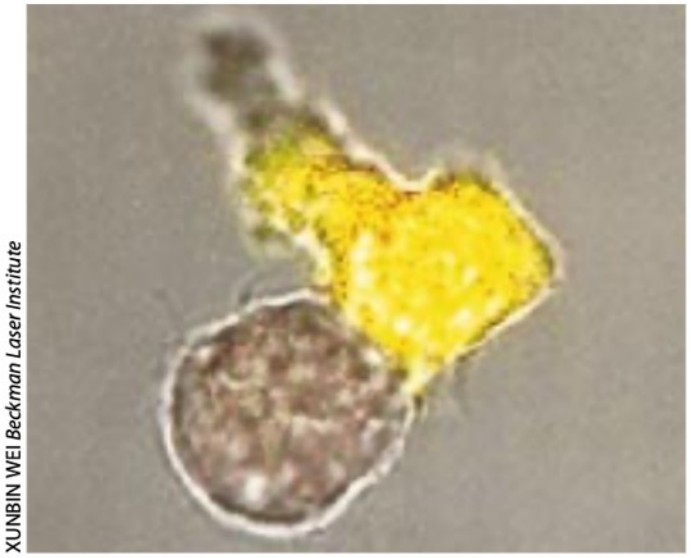
α, induced dipole of sphere

n_o, refractive index and $m=n_1/n_o$ relative index.

⟹ particle trapped slightly out of focus

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

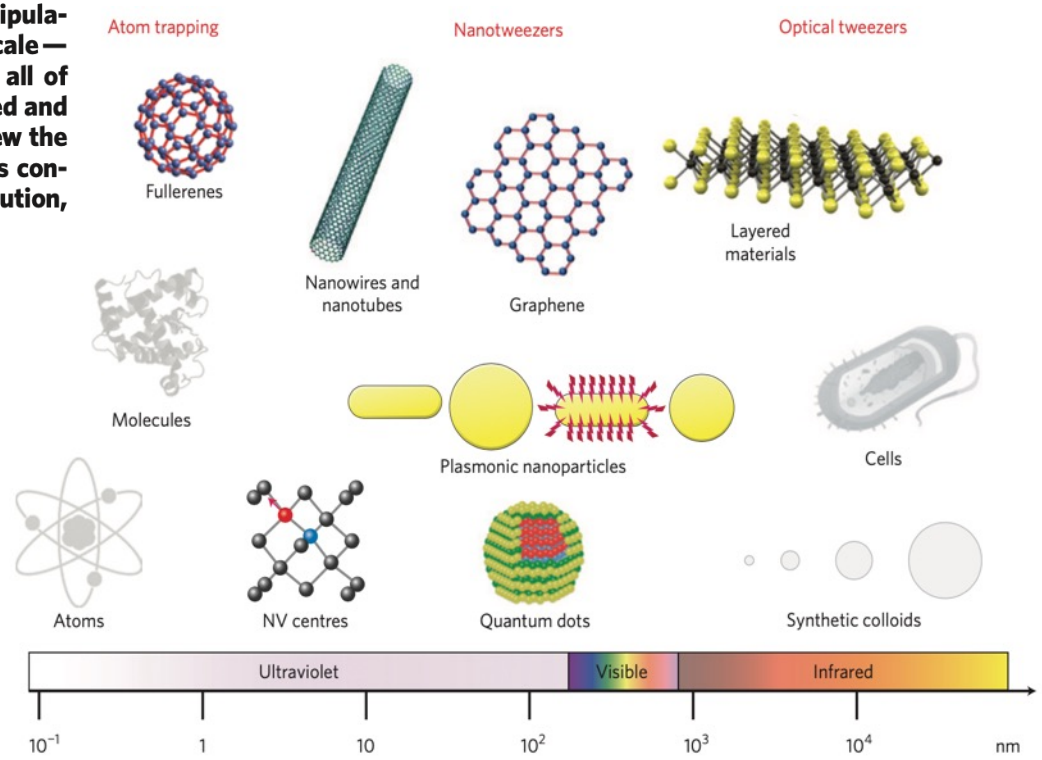
REVIEW ARTICLE

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]*

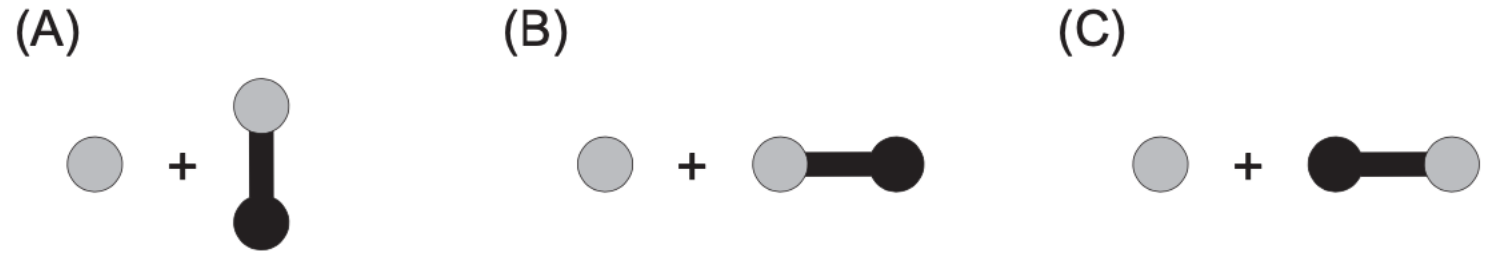
Optical trapping and manipulation of micrometre-sized particles was first reported in 1970. Since then, it has been successfully implemented in two size ranges: the subnanometre scale, where light–matter mechanical coupling enables cooling of atoms, ions and molecules, and the micrometre scale, where 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**

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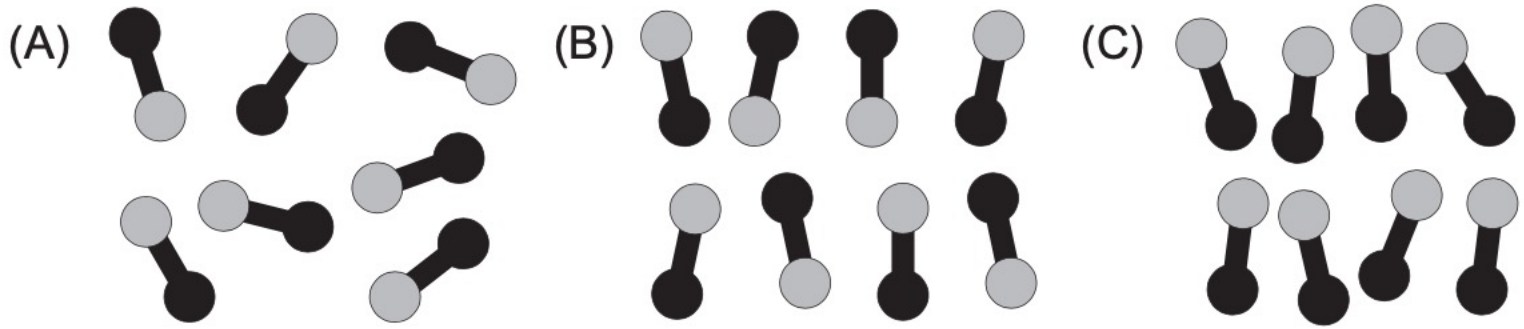
Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada

Laser alignment of molecules



Unaligned align ↑↓ orient ↑↑

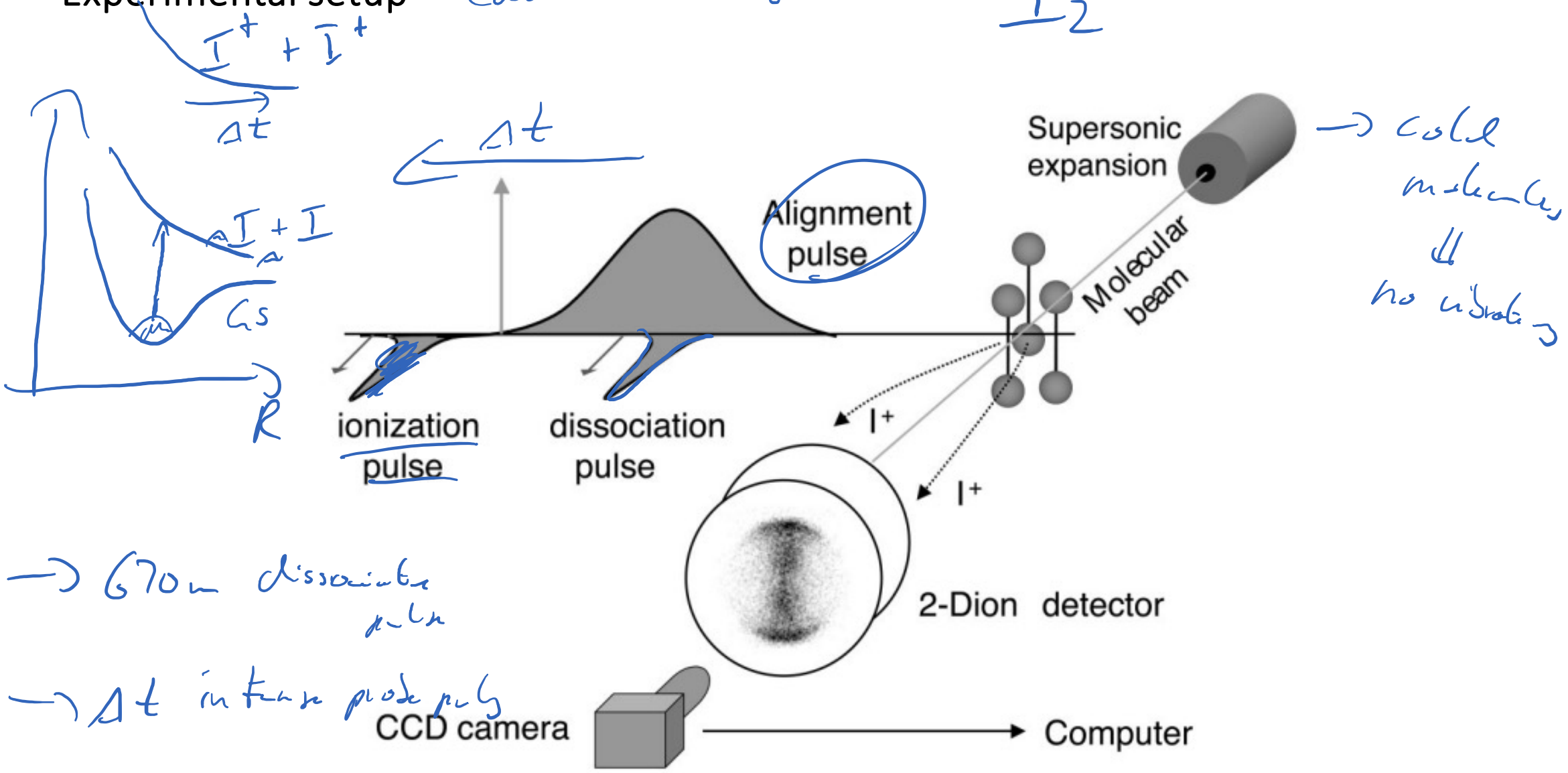
Approach Molecule → Dipole (polarizable, homonuclear, non-rigid)

Describe potential energy in field ($U_{pot} = -\frac{1}{2} \varepsilon \alpha \varepsilon$, α: molecular polarizability (tensor))

⇓

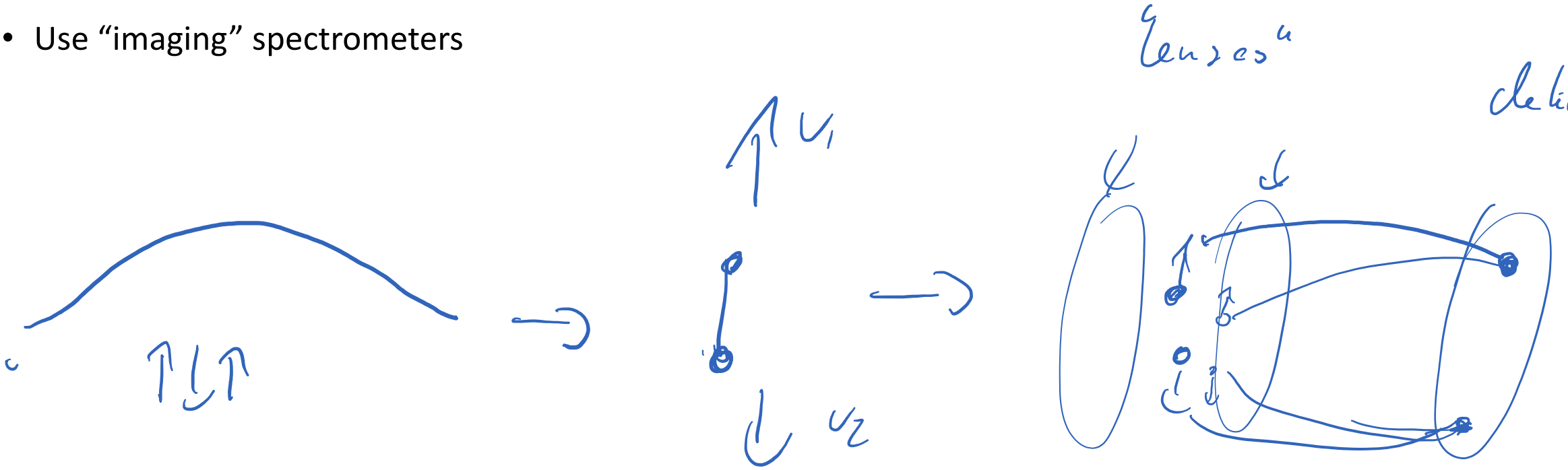
Minimize potential energy through alignment

Experimental setup



Detection scheme: Coulomb explosion imaging

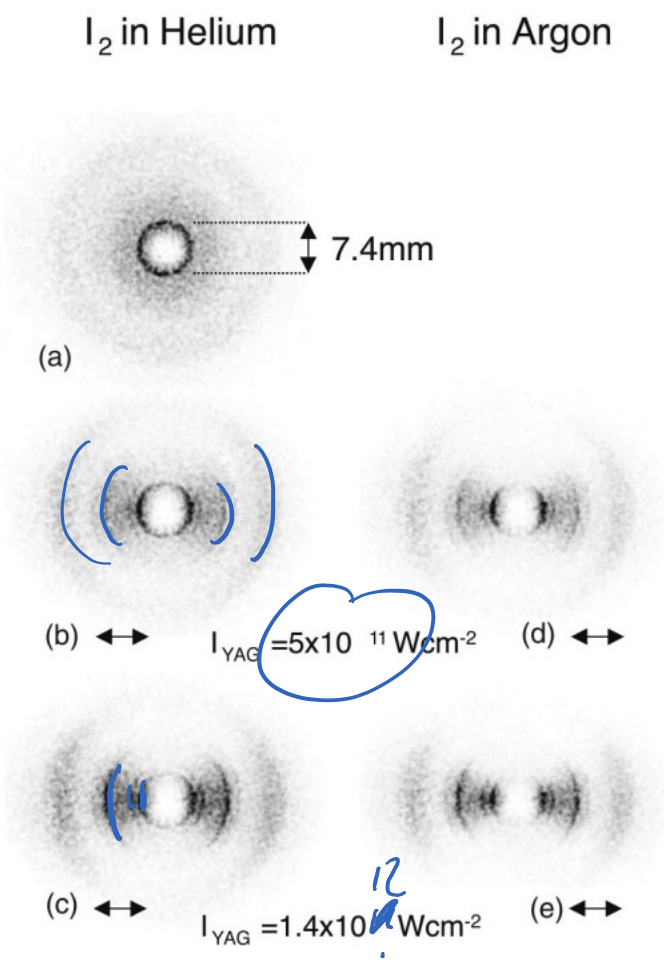
- Fragment whole molecule through sudden ionization
- Use ionization laser pulse shorter than alignment pulse
- Use “imaging” spectrometers



VMI (velocity map imaging spectrometer)

lens focus ions with same velocity on detector

Some data examples



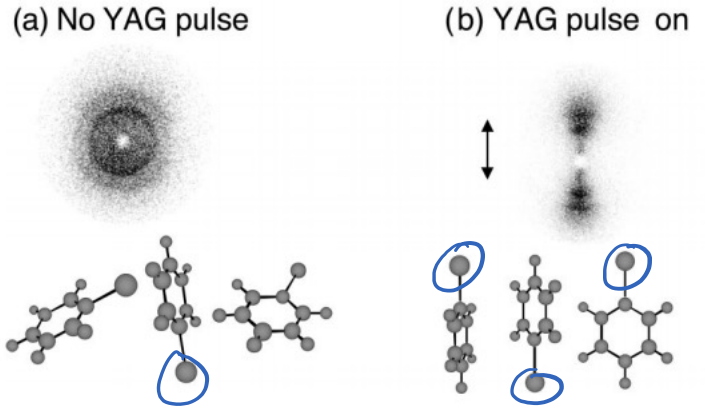


FIG. 9. Ion images of I^+ recorded when iodobenzene is irradiated by a circularly polarized, 100-fs, 8×10^{13} W/cm^2, 800-nm pulse. (a) No alignment field. (b) In the presence of a linearly polarized (vertical) alignment field with intensity 1.2×10^{12} W/cm^2. The spatial orientation of the molecules is illustrated below the two images.

Final note: There is also impulsive alignment

The end.