Reversing the Arrow of Time Using **Polymer-Dye Interactions**

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ICOOPMA 2010 - Budapest

Acknowledgements

National Science Foundation

Wright-Patterson Air Force Base

Washington State University

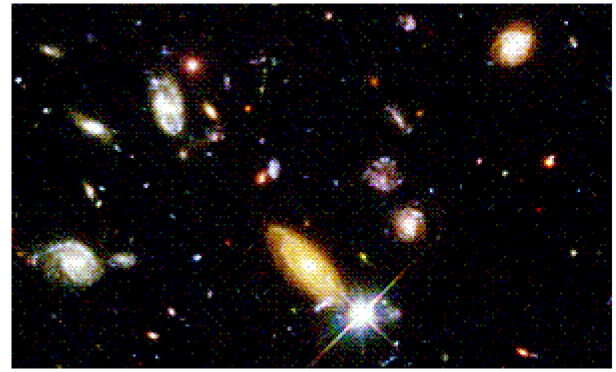
Where Are We?

Recreating Galileo's Experiments in Webster Hall



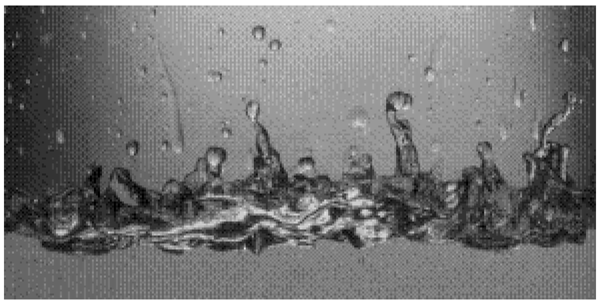

WASHINGTON STATE UNIVERSITY

Physics and Astronomy at WSU



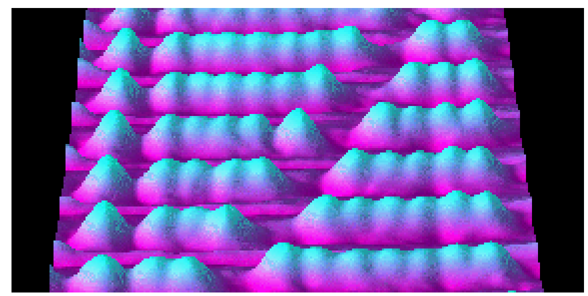
Astrophysics

LIGO (Hanford, WA) search for gravitational waves.
Hubble Space Telescope: galaxy formation studies.



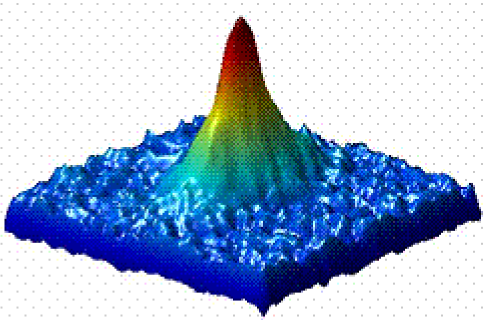
Matter Under Extreme Conditions

Institute for Shock Physics.
Studies of semiconductors and organic solids with diamond-anvil cells. Reduced-gravity acoustics on the "vomit comet."



Materials and Optical Physics

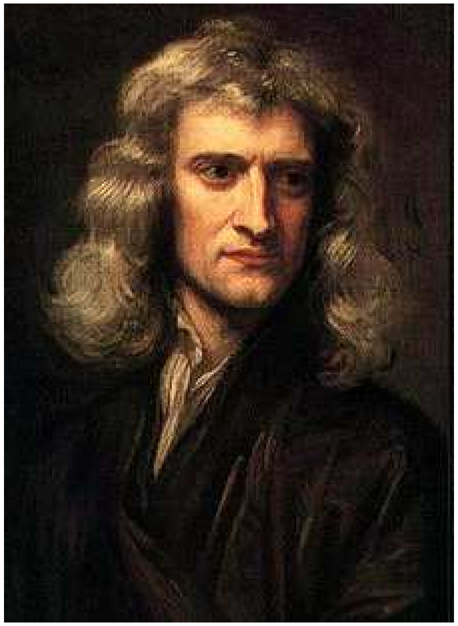
Femtosecond studies of ultrafast phenomena. Materials for energy applications. Nanostructures and biological materials. Nonlinear optics.



Novel States of Matter

Bose-Einstein condensation. Theory of cold quantum gases, many-body physics, chaos, and complexity. Gold Buckyballs.

Practical Problems Often Lead to Fundamental Science



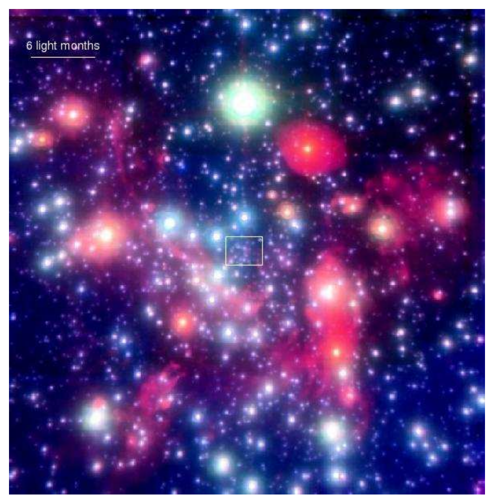
1643-1727

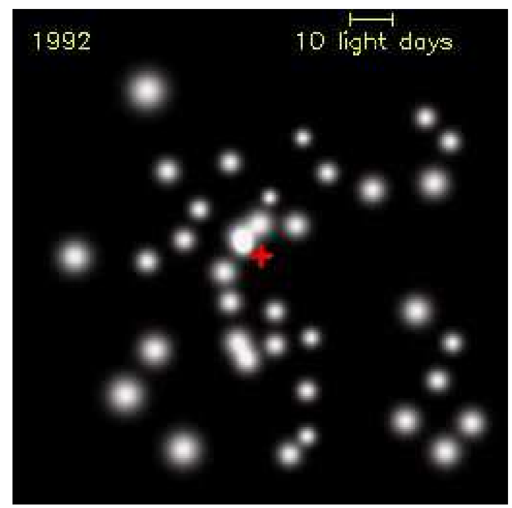
The Longitude Problem

“*Many thousands of lives had been lost at sea over the centuries due to the inability to determine an east-west position. This is the engrossing story of the clockmaker,* ***John "Longitude" Harrison****, who solved the problem that* ***Newton and Galileo had failed*** *to conquer*…” Amazon book review of Longitude

Newton’s Law of Universal Gravitation

Describes the universe





Max-Planck-Institut für extraterrestrische Physik

Newton’s Laws

- Describe planets and galaxies
- Are time reversible

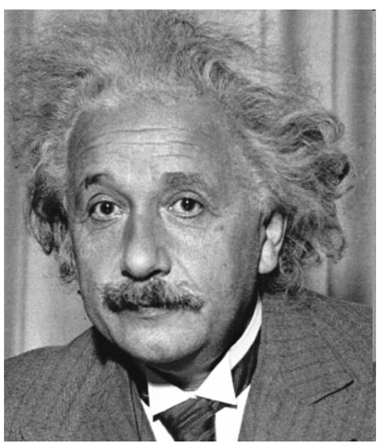
The Steam Engine

Steam Engine (2.0 - 0.2 kya)

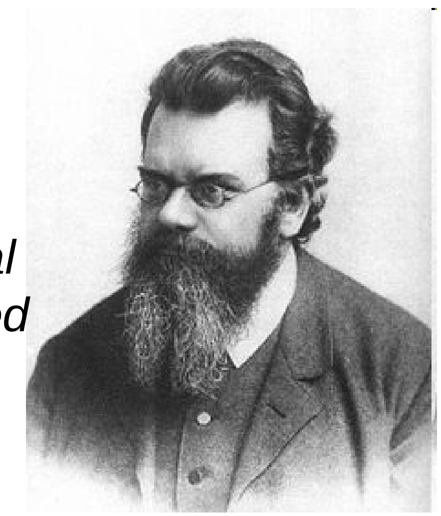
- Aeolipile [ee-ol-uh-pahyl] described by Hero of Alexandria (1 ad)
- Blasco de Garay (Barcelona,1543) powered a ship with a steam engine
- Carnot (1776-1832) Father of Thermodynamics

Thermodynamics

- Boltzmann (1844-1906) described the concept of entropy from a microscopic perspective - *irreversibility*

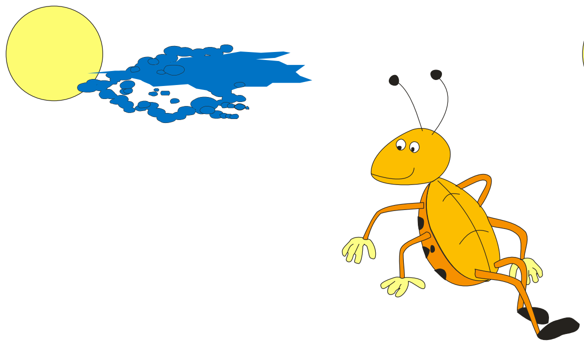


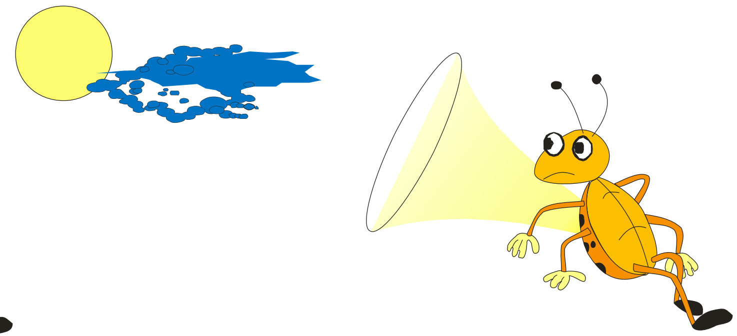
- *"It is the only physical theory of universal content concerning which I am convinced that, within the framework of the applicability of its basic concepts, it will never be overthrown." -- Einstein*



Entropy increases in irreversible processes

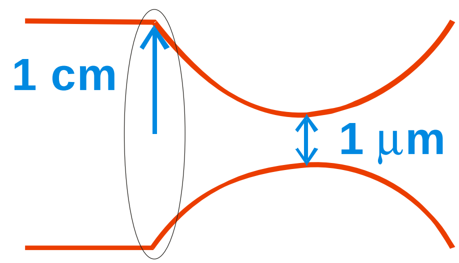
Irreversible Photodegradation

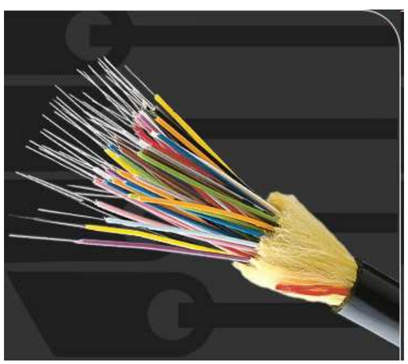


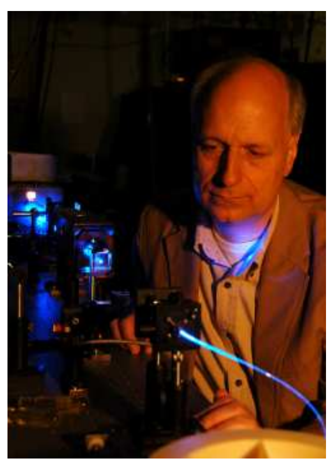


$I_{sun} = 1.4mW/cm^2$

$I_{focused} = 200MW/cm^2$







Single Mode Telecom Fiber

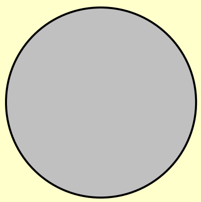
Core Size: $10\,\mu m$

Power: $10\,mW$

Intenisty: $13\,kW/cm^2$

Why Fiber Optics?

Electrons - Electronics	**Photons (light) - Photonics**
Copper Wire	Optical Fiber Core
0.1” diameter	0.0003” diameter
1,000 Telephone Conversations	**10,000,000,000 Telephone Conversations**



- Fibers provide high bandwidth transmission

Technological Challenges

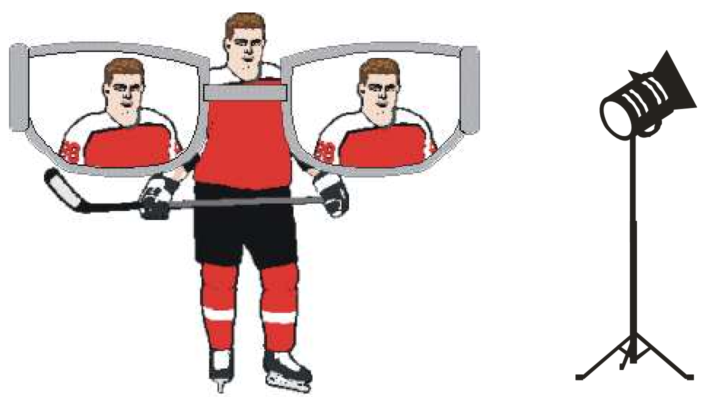
- Need waveguide-based optical switches to take advantage of bandwidth
- Need fiber lasers to power optical circuits
- Switches and light sources are based on high-intensity nonlinear optics

High Intensity Nonlinear-Optical Phenomena

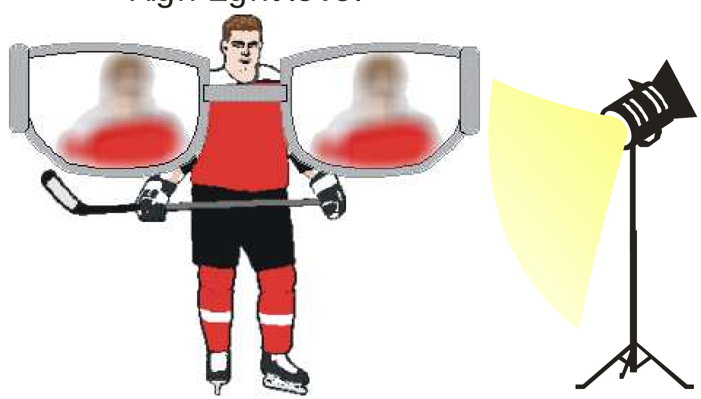
Light changes the optical properties of the material

Intensity Dependent Refractive Index

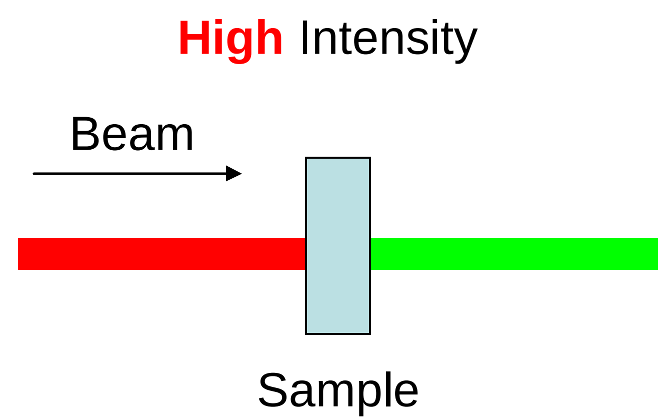
Low Light Level



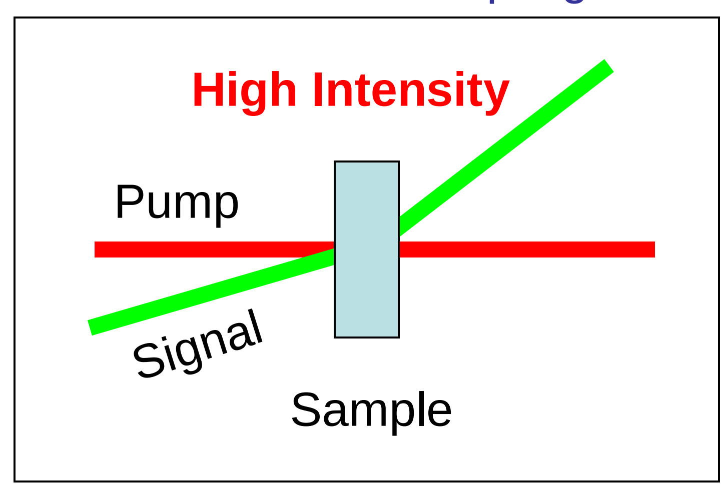
High Light level



Second Harmonic Generation



Two Beam Coupling



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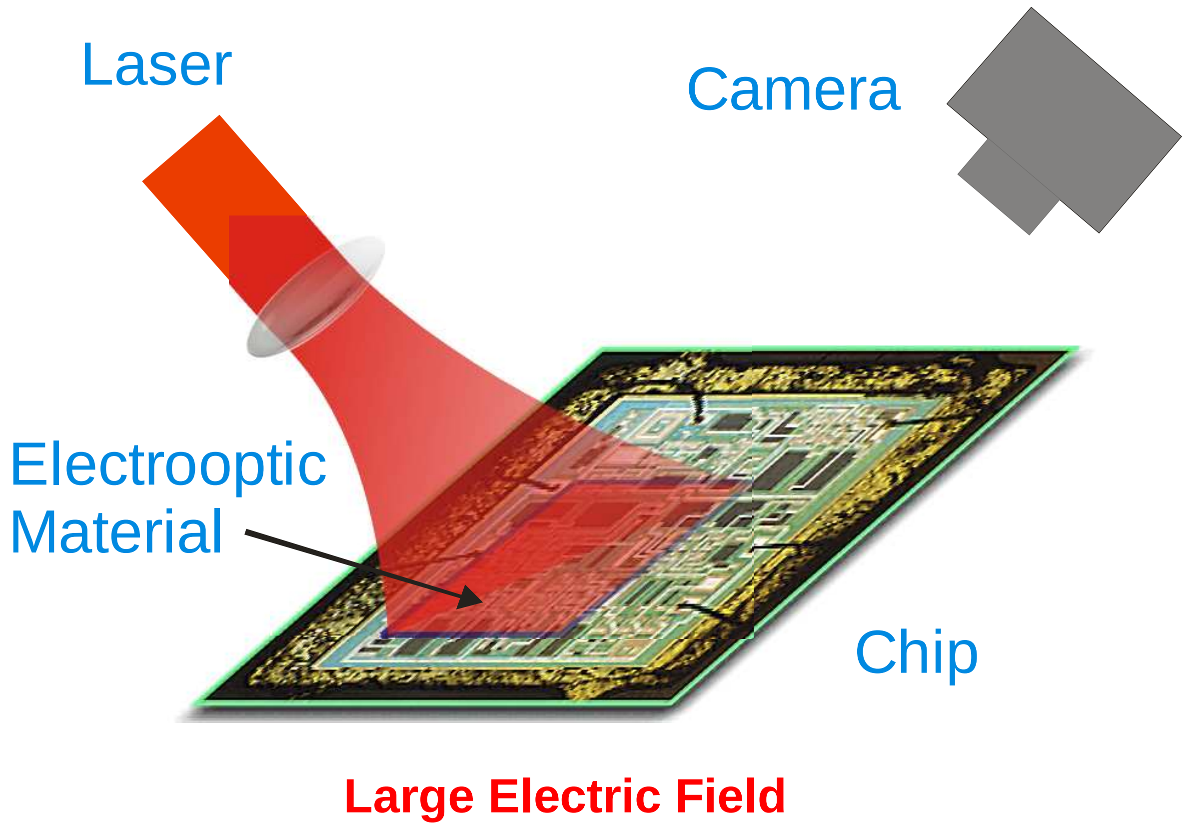
Some Applications of Nonlinear Optics

- Second Harmonic Generation
  - Light sources, high density storage, tunable lasers

High Intensity

Some Applications of Nonlinear Optics

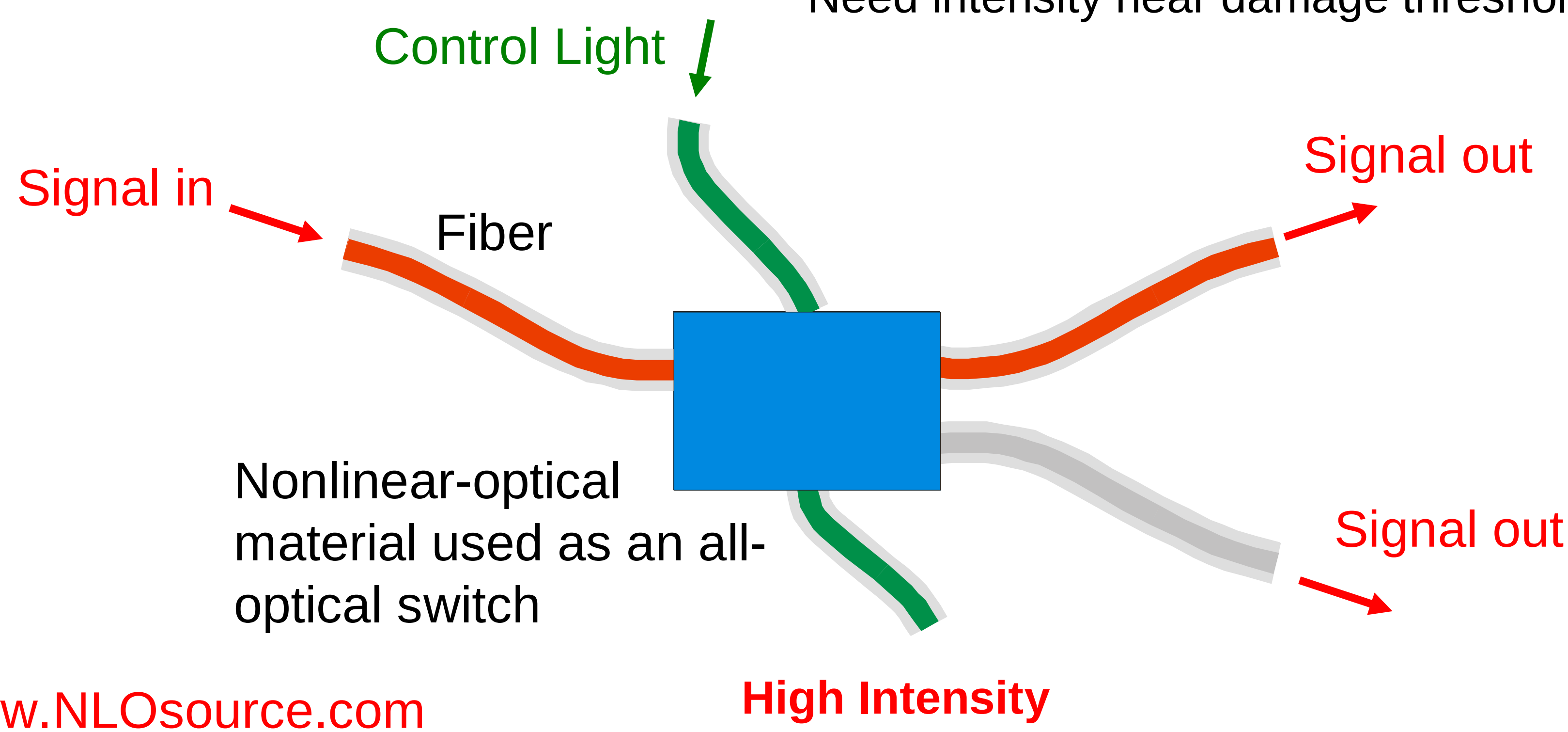
- Second Harmonic Generation
  - Light sources, high density storage
- Electrooptic Effect
  - Electro-optical switching, circuit testing



Some Applications of Nonlinear Optics

- Second Harmonic Generation
  - Light sources, high density storage
- Electrooptic Effect
  - Electro-optical switching, circuit testing
- All-Optical Switching

Need intensity near damage threshold



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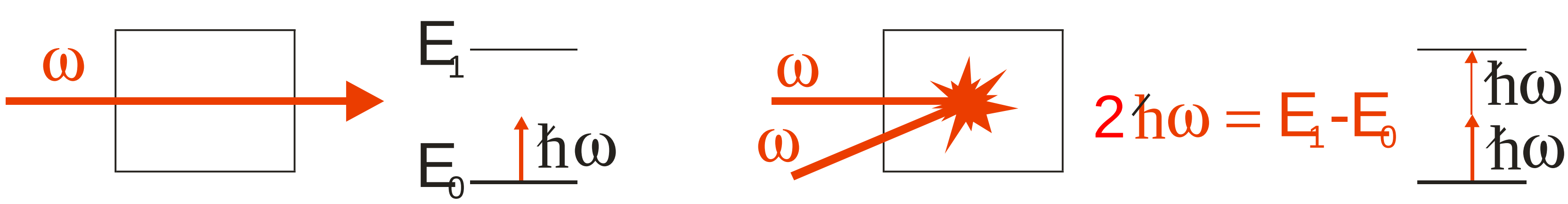
Some Applications of Nonlinear Optics

- Second Harmonic Generation
  - Light sources, high density storage
- Electrooptic Effect
  - Electro-optical switching, circuit testing
- All-Optical Switching
- Self-Focusing
  - Solitons for information transmission
- Two-Photon Absorption
  - Cancer Therapies, 3D photolithography, eye protection



$2\hbar\omega = E_1 - E_0$

High Intensity

www.NLOsource.com

First Observation of Second Harmonic Generation

VOLUME 7, NUMBER 4 PHYSICAL REVIEW LETTERS AUGUST 15, 1961

GENERATION OF OPTICAL HARMONICS*

P. A. Franken, A. E. Hill, C. W. Peters, and G. Weinreich
The Harrison M. Randall Laboratory of Physics, The University of Michigan, Ann Arbor, Michigan
(Received July 21, 1961)

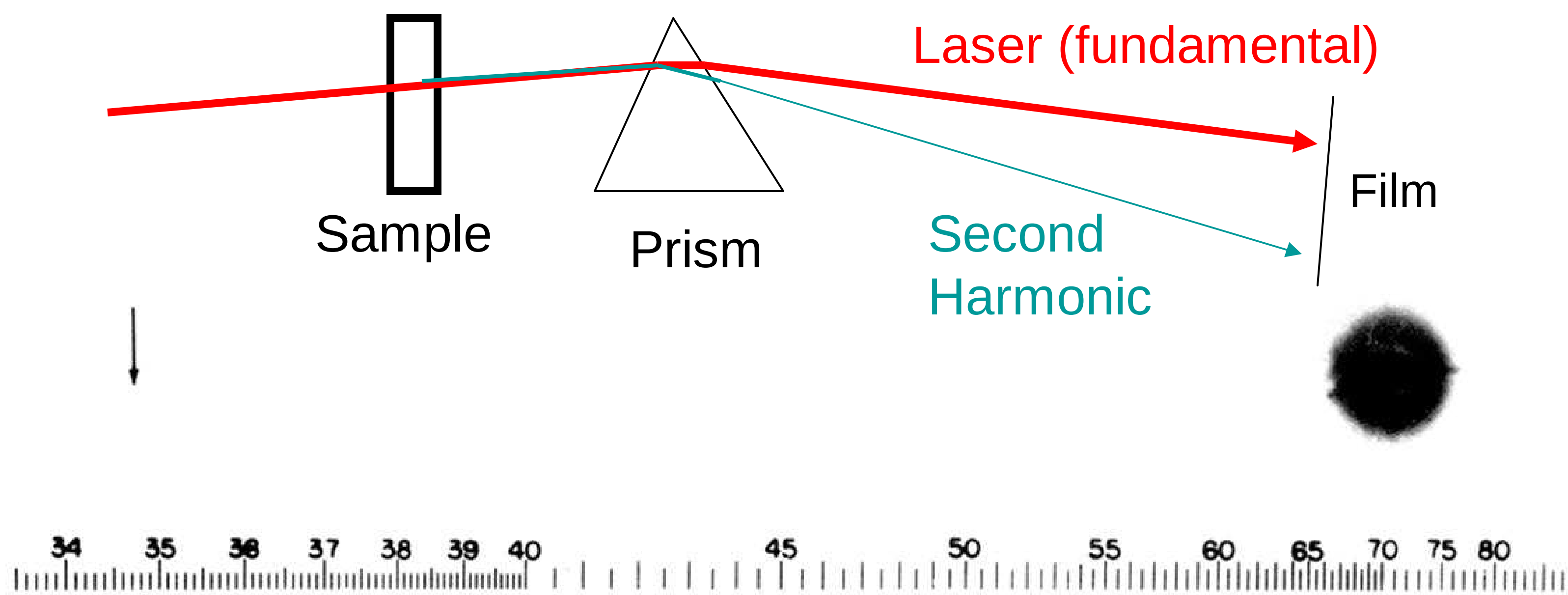
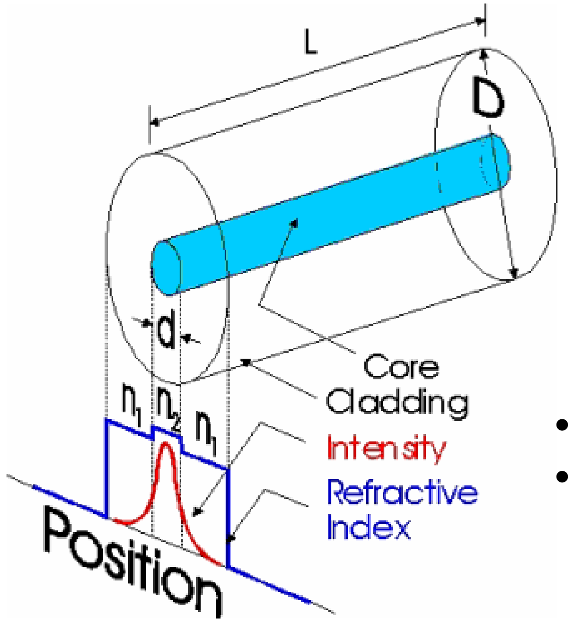


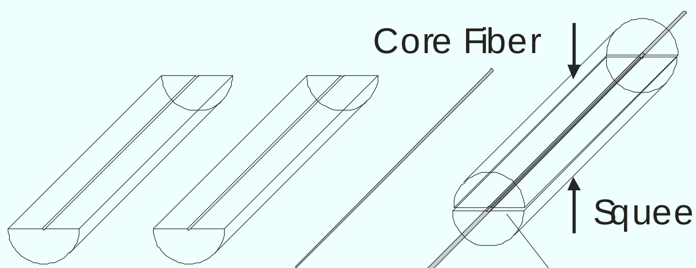
FIG. 1. A direct reproduction of the first plate in which there was an indication of second harmonic. The wavelength scale is in units of 100 A. The arrow at 3472 A indicates the small but dense image produced by the second harmonic. The image of the primary beam at 6943 A is very large due to halation.

Single-Mode Polymer Optical Fiber



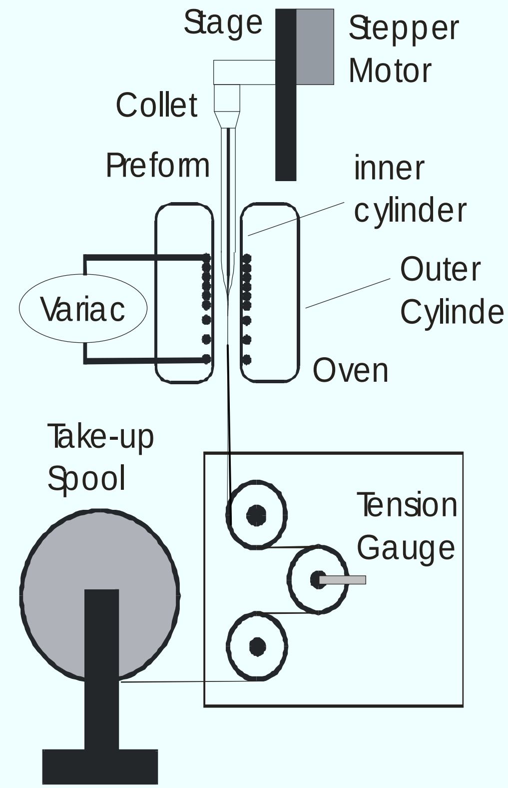
- High Intensity
- Long Distances

Making a Preform



D. W. Garvey, K. Zimmerman, P. Young, J. Tostenrude, J. S. Townsend, M. Lobel, M. Dayton, R. Wittorf, M. G. Kuzyk, J. Sunick, and C. W. Dirk, J. Opt. Soc. Am. B **13**, 2017 (1996).

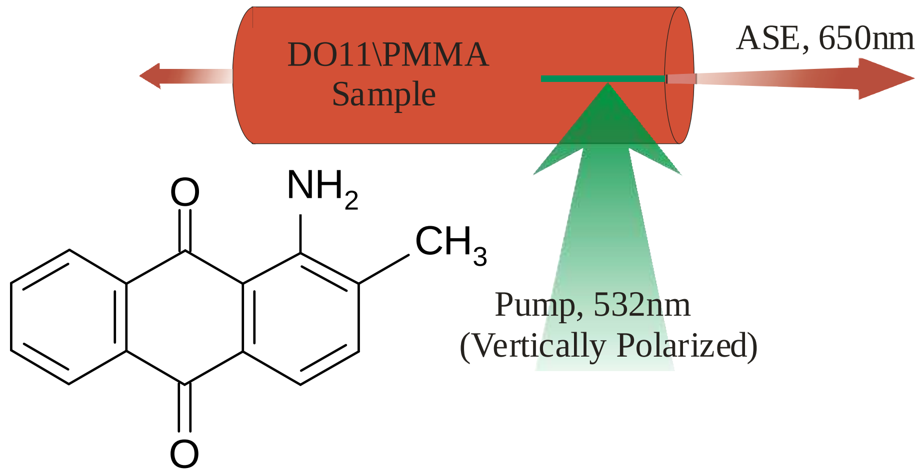
Drawing a Fiber



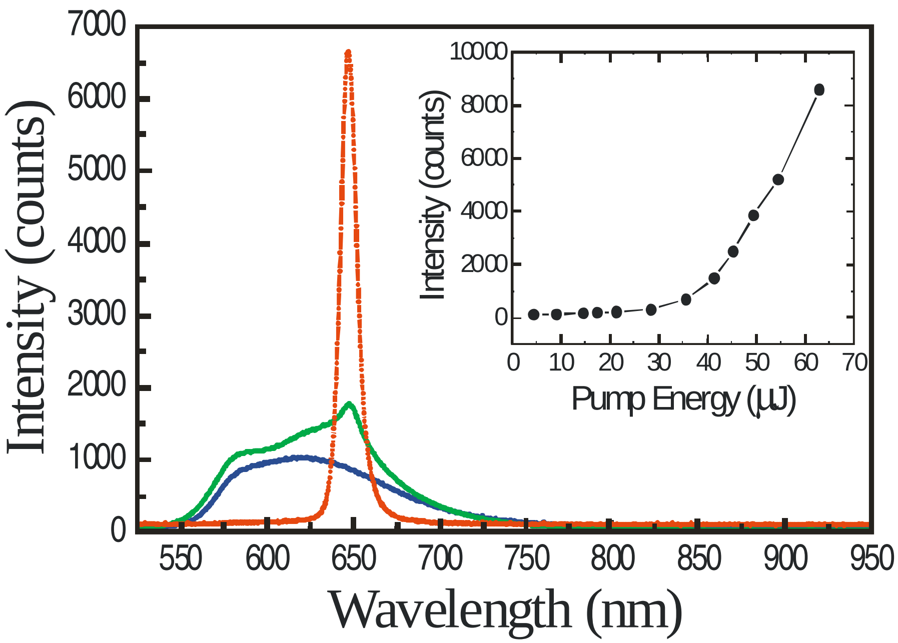
→ Can make all-optical switches/logic

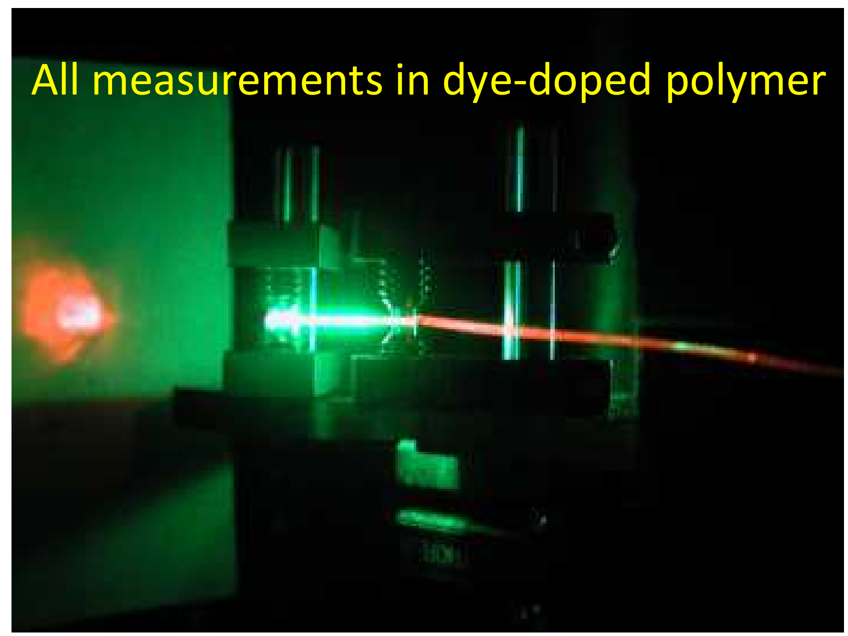
M. G. Kuzyk, U. C. Paek, and C. W. Dirk, "Dye-Doped Polymer Fibers for Nonlinear Optics," Appl. Phys. Lett. **59**, 902 (1991).

Amplified Spontaneous Emission in a Polymer Fiber



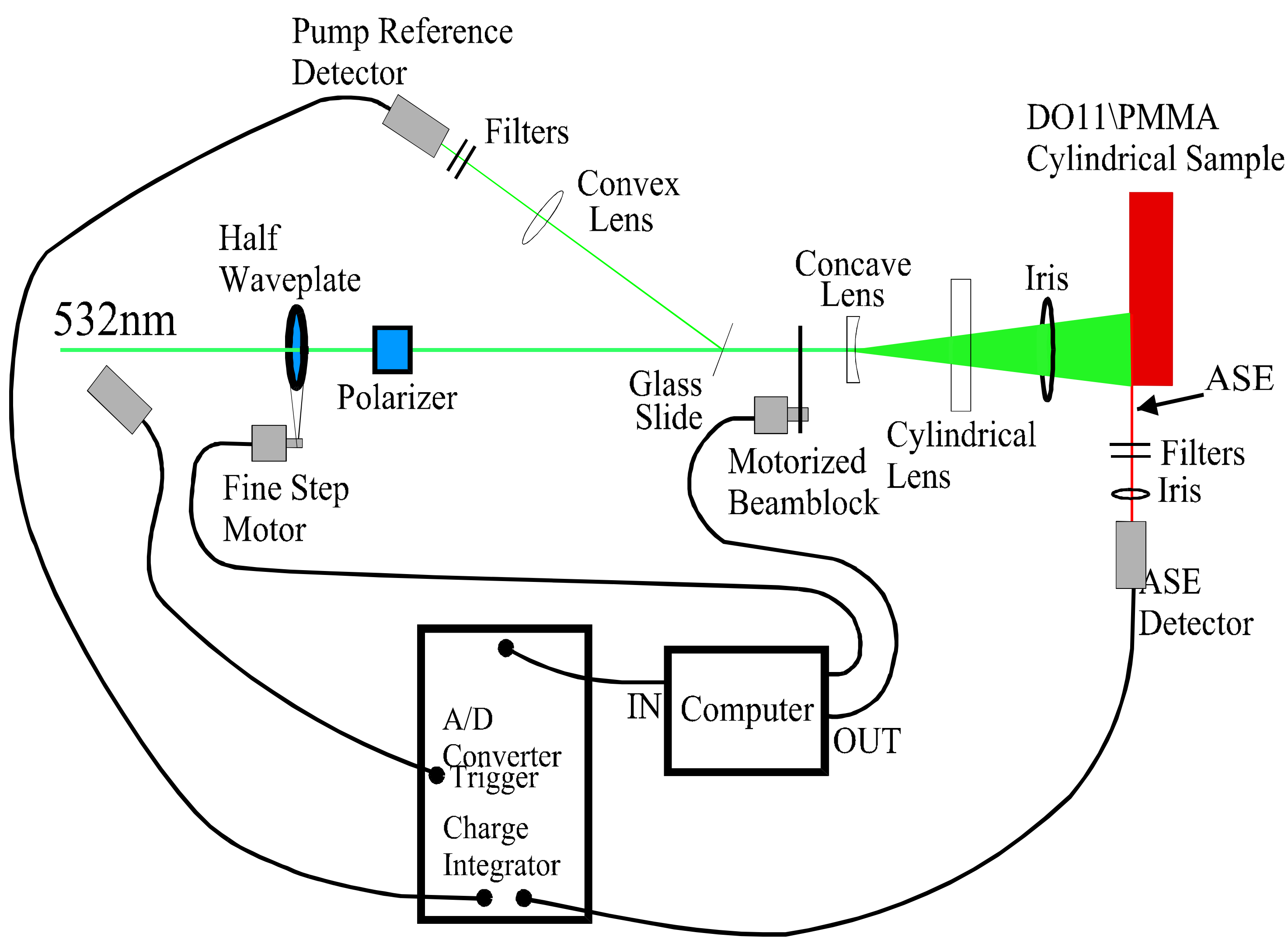
Transition from Fluorescence to ASE



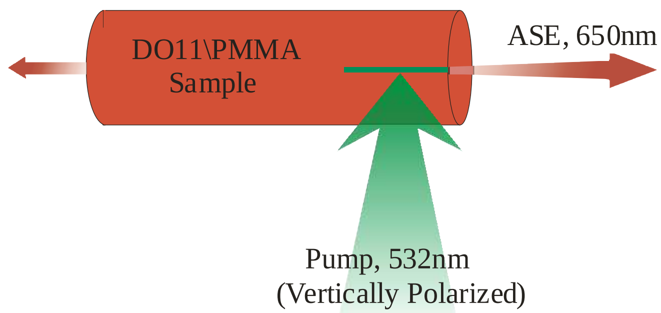


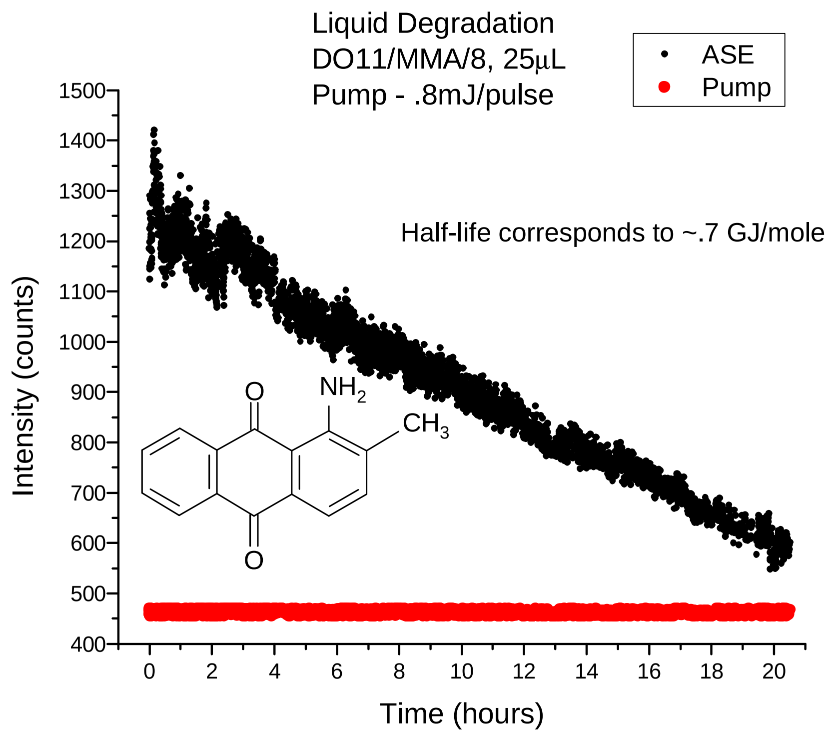
B. Howell and M. G. Kuzyk, Journal of the Optical Society of America B **19** (8) 1790 (2002).

ASE Detection Setup



Amplified Spontaneous Emission (ASE) of DO11 dye in MMA liquid solution

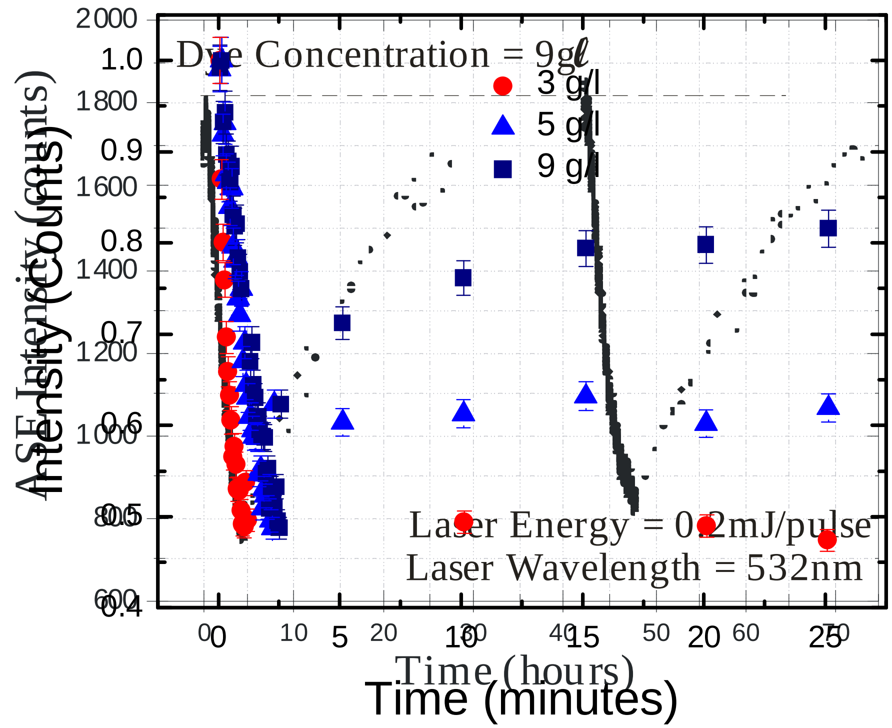




- No recovery in MMA monomer

B. F. Howell and Mark G. Kuzyk, Appl. Phys. Lett. **85**, 1901 (2004)

ASE of DO11 dye in PMMA polymer

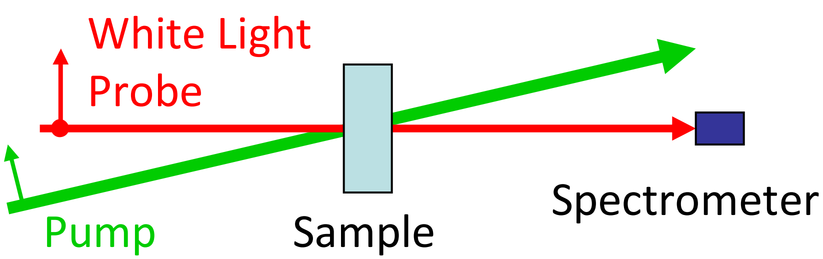


- Degradation is reversible
- Efficiency gets better upon cycling
- Degradation is slower upon cycling
- Depends on concentration
- Polymer plays a critical role in recovery

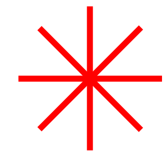
N. B. Embaye, S. K. Ramini, and M. G. Kuzyk, J. Chem. Phys. **129**, 054504 (2008).

B. Howell and M. G. Kuzyk, Journal of the Optical Society of America B **19** (8), 1790 (2002).

Time-Dependent Optical Absorption

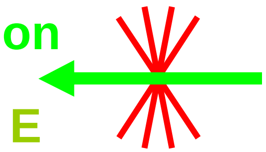


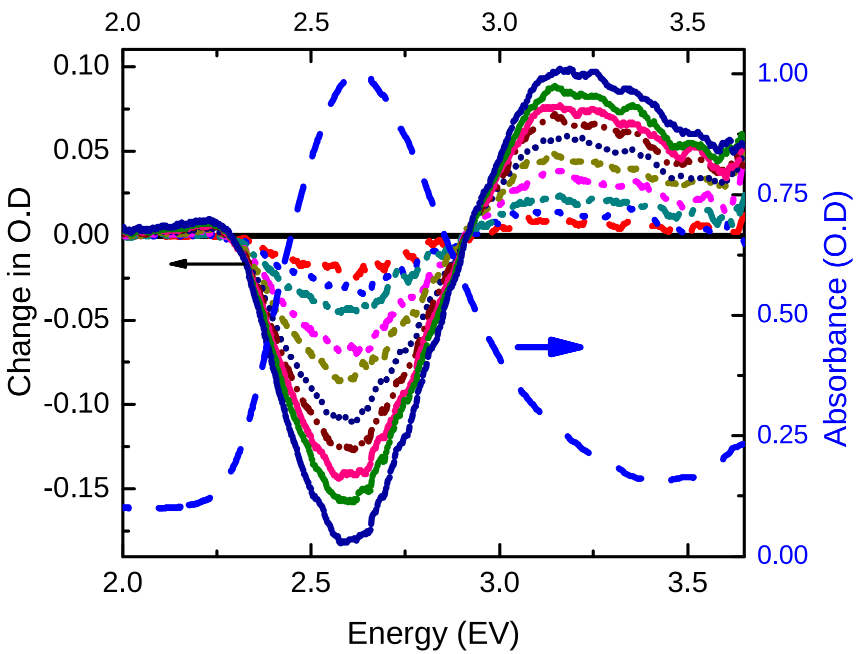
What about molecular reorientational mechanisms?

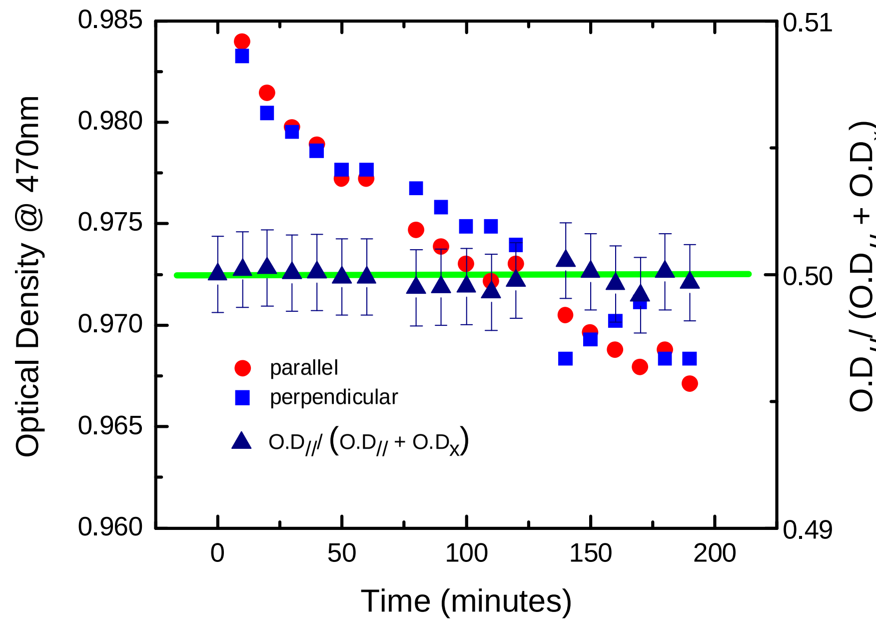


Pump Polarization

Should lead to dichroism.





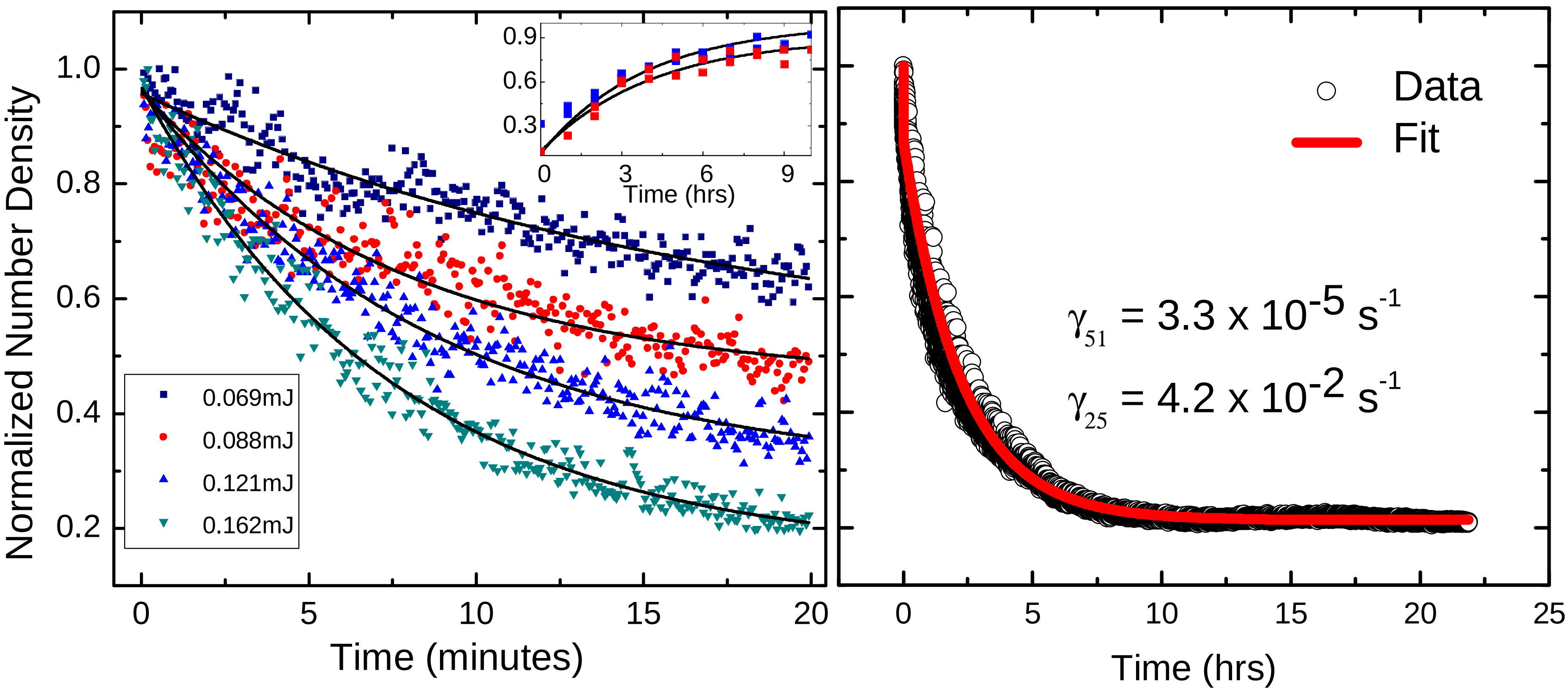


Results are consistent with dimer formation

No dichroism so molecular reorientation is not responsible

N. B. Embaye, S. K. Ramini, and M. G. Kuzyk, J. Chem. Phys. **129**, 054504 (2008).

Reversible Photodegradation in DO11/PMMA



$$dN = -N\alpha I dt + \beta (N_0 - N) dt$$

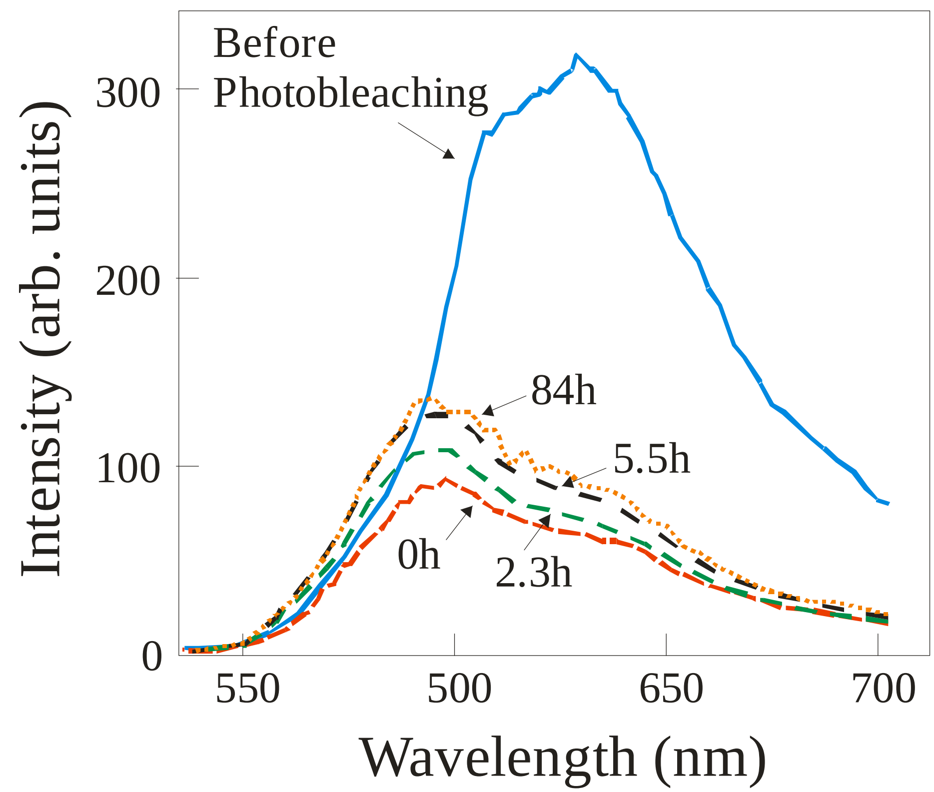
Intensity-dependent decay

$$n = \frac{\beta}{\beta + \alpha I} + \frac{\alpha I}{\beta + \alpha I} \cdot e^{-(\beta + \alpha I)t}$$

Recovery rate

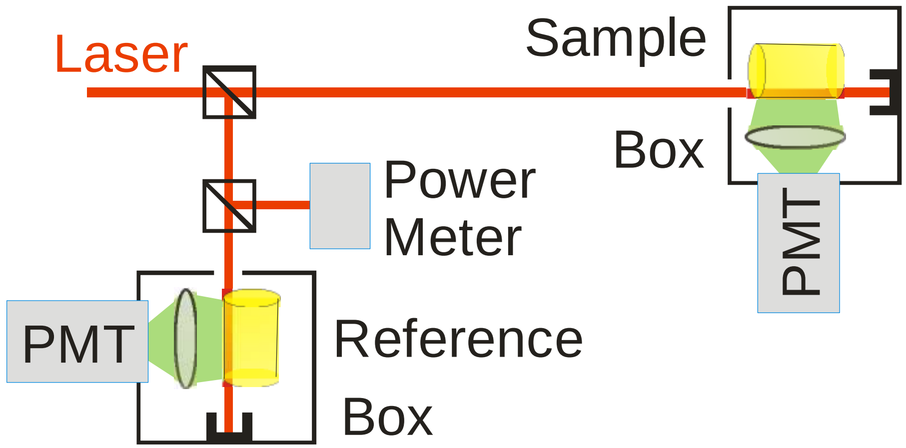
$$n = 1 - (1 - n(t_0))\, e^{-\beta t}$$

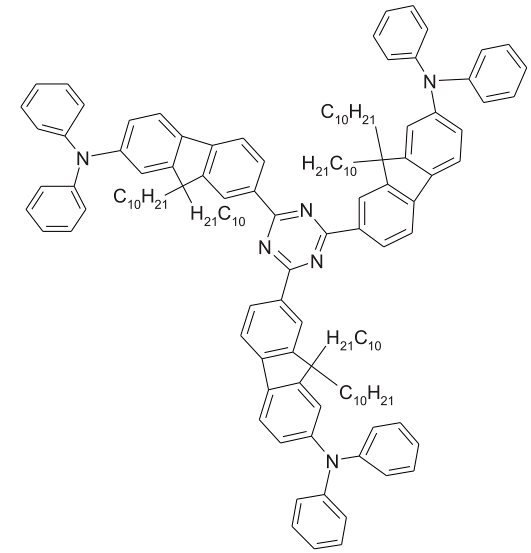
Fluorescence in Rhodamine 6B Dye-Doped Fiber

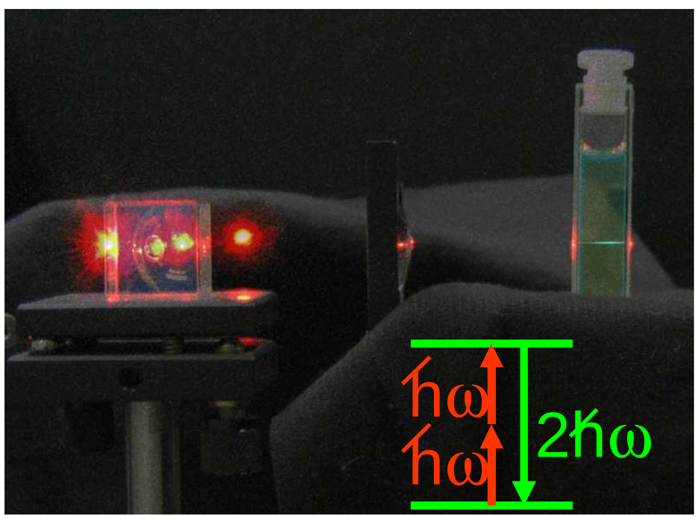


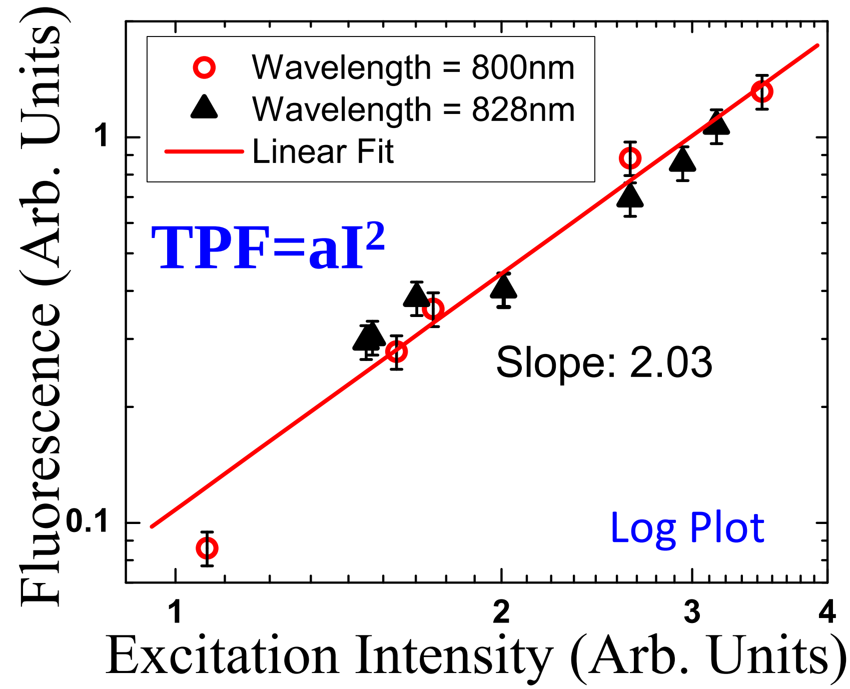
G. D. Peng, Z. Xiong, and P. L. Chu, J. Lightwave Technol. 16, 2365 (1998).

Two-Photon Fluorescence in AF455 Chromophore



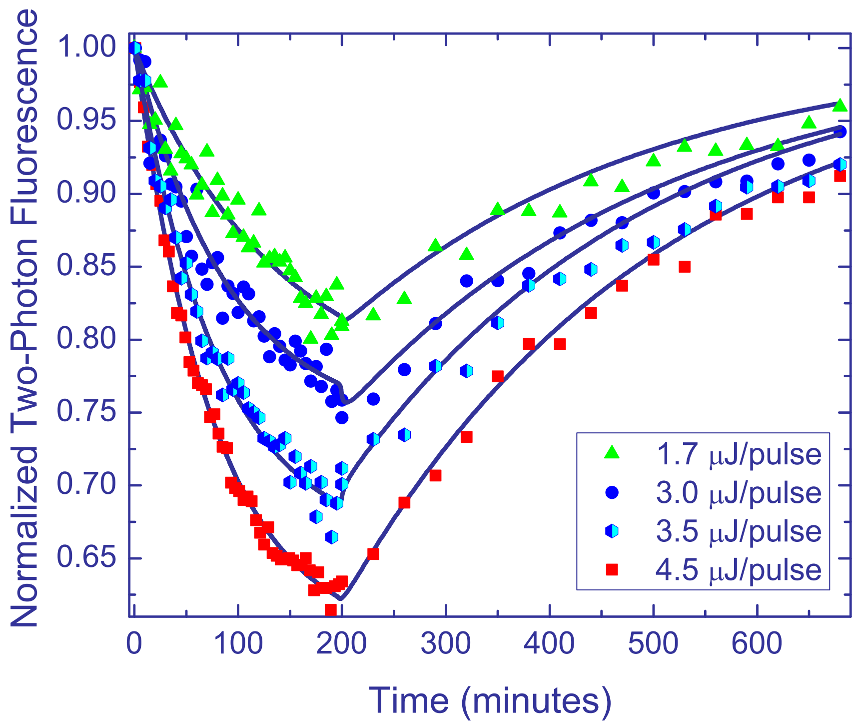


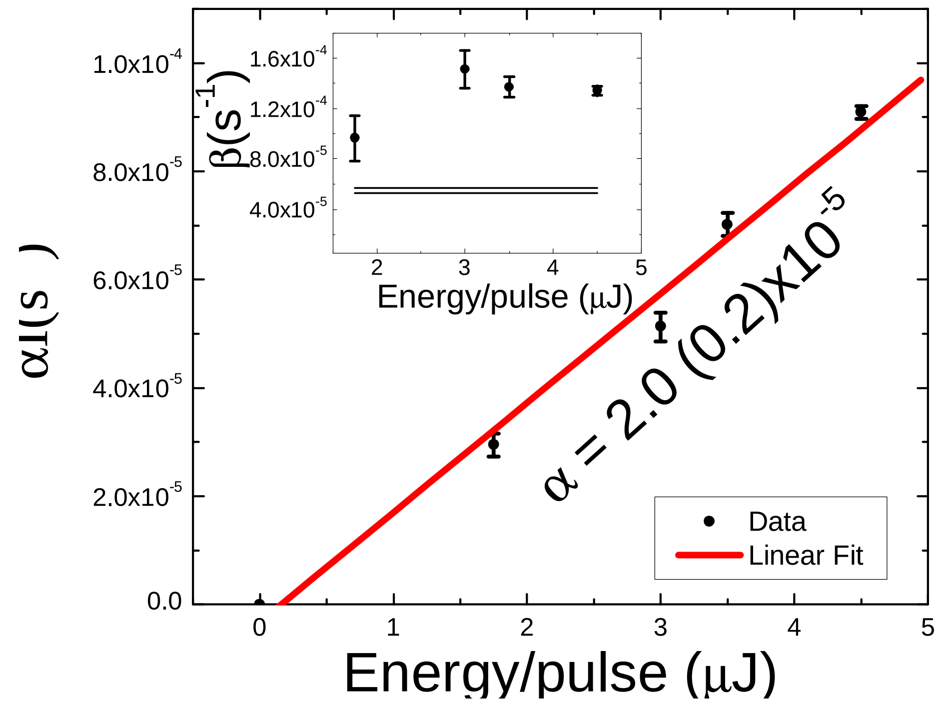




Ye Zhu, Juefei Zhou, and Mark G. Kuzyk, Opt. Lett. **32**, 958-960 (2007).

Reversible Photodegradation in AF455/PMMA





$$dN = -N\alpha I dt + \beta\left(N_0 - N\right)dt$$

Intensity-dependent decay

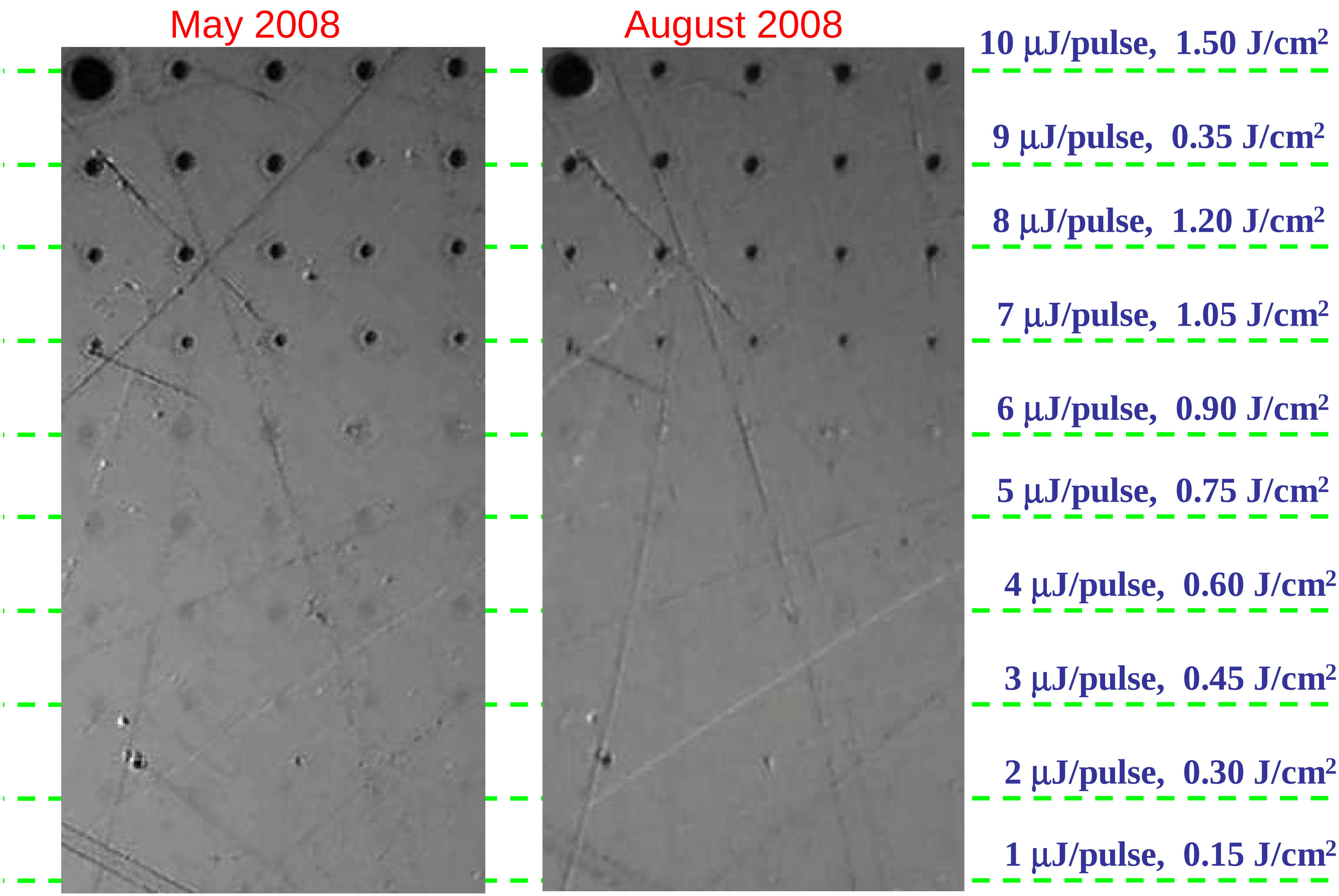
$$n = \frac{\beta}{\beta+\alpha I} + \frac{\alpha I}{\beta+\alpha I}\cdot e^{-(\beta+\alpha I)t}$$

Recovery rate

$$n = 1 - \left(1 - n(t_0)\right)e^{-\beta t}$$

Ye Zhu, Juefei Zhou, and Mark G. Kuzyk, “Two-photon fluorescence measurements of reversible photodegradation in a dye-doped polymer,” Opt. Lett. **32**, 958-960 (2007).

Damage Induced by High-Intensity Femtosecond Pulses in AF455/PMMA



Logan DesAutels, Mark G. Kuzyk, and Chris Brewer, "Opt. Express **17**, 18808-18819 (2009).

Observations

- Many very different molecules self heal in a polymer
- Polymer self heals in the presence of dye molecules

Questions

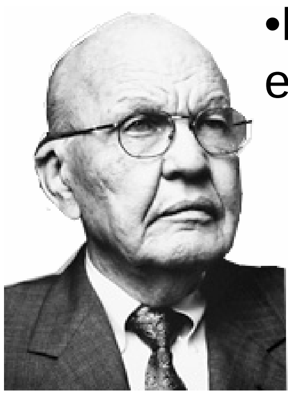
- What are the mechanisms of self healing?
  - N. B. Embaye, S. K. Ramini, and M. G. Kuzyk, J. Chem. Phys. **129**, 054504 (2008).
  - Ye Zhu, Juefei Zhou, and Mark G. Kuzyk, Opt. Lett. **32**, 958-960 (2007).
  - **www.NLOsource.com**
- Universality?
  - Is self healing a common phenomena?
- Underlying Physics
  - **Emergent** properties of polymer plays a role in enforcing reversibility
- Dye-doped polymer provides model system
  - Distinction between irreversibility and reversibility
  - Obvious usefulness in many applications

Can we design new systems and materials from the ground up?

Outline – History of Electrical and Optical Materials

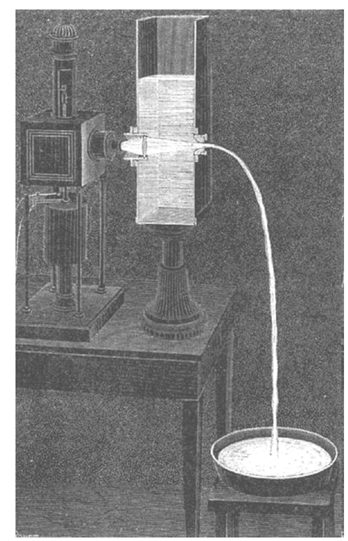
- **Semiconductor Point-Contact Rectifier Effect (1875)**
  - Ferdinand Braun shared the 1909 Nobel Prize in Physics

- **The Invention of the transistor (Late 1947)**
  - Bardeen, Brittain and Shockley win 1956 Nobel Prize in Physics
  - Made possible control of electrical currents with electrical currents



- **The Invention of the integrated circuit (Sept. 12, 1958)**
  - Jack S. Kilby wins ½ of Nobel Prize in Physics in 2000
  - Made possible the integration of many transistors

- **Optical waveguide demonstrated by Colladon and Babinet (1840s)**
  - Charles K. Kao wins ½ of Nobel Physics in 2009, “for groundbreaking achievements concerning the transmission of light in fibers for optical communication”



Overview

1. Design OPTICAL materials from the ground up

2. Make waveguide devices (In analogy to transistor)

3. Investigate methods for integrating devices (in analogy to integrated circuits)

4. Investigate unique combinations of functionality **that are not available to electronics**

5. Design highly interconnected devices for ultra-smart functionality

6. Look for emergence

Device Classes – Optics vs. Electronics

	Optics	**Electronics**
Transmission	Optical Fiber Optical Interconnects	Wires Printed Wire Boards
Sensing	Fiber Interferometer Fluorescent Dyes	Thermistor Transducer
Switching/Logic	Electrooptic Materials Intensity Dependent n	Transistor
Actuation	Photostriction and Photomechanical Effects	Motor Piezoelectrics
Power	Laser	Battery/Power Supply

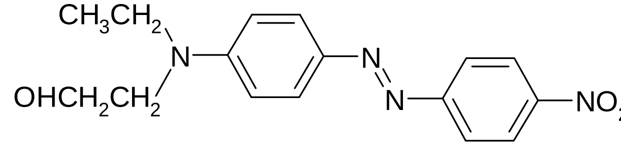
Optics is better than electronics

Materials for Nonlinear Optics and Photomechanics

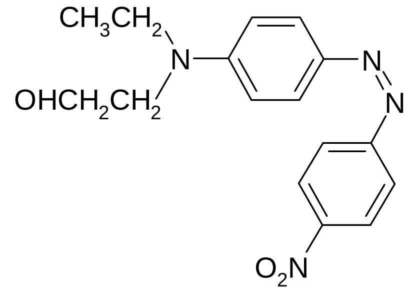
1) Polymer
    a) High transparency
    b) Good optical quality
    c) Easy to Process
        I) Thin films
        II) Fibers
        III) Tailored orientation
        IV) Stacked structures
    d) Not very nonlinear
    e) Low dielectric constant
2) Organic crystal
    1) High nonlinearity
    2) Highly stable
    3) Optical quality not always good
    4) Crystal structure can't be changed
3) Dye-Doped Polymer
    a) High transparency
    b) Good optical quality
    c) Easy to process
        I) Thin films
        II) Fibers
        III) Ordered materials
        IV) Tailored orientation
        V) Stacked structures
    d) Moderate nonlinearity
    e) Low dielectric constant
    f) Underlying structure can be controlled
    g) Photomechanical effects
    h) Sensing
    i) Interesting Physics – Microscopic response
    j) Stability issues

Interaction of Light with Matter: Photomechanical Effects

$$\Delta L / L = bI$$



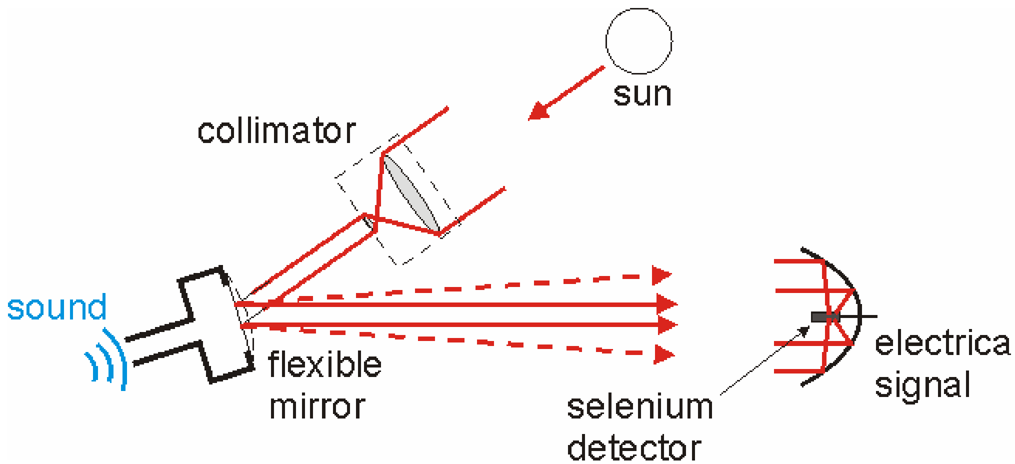
Trans Isomer

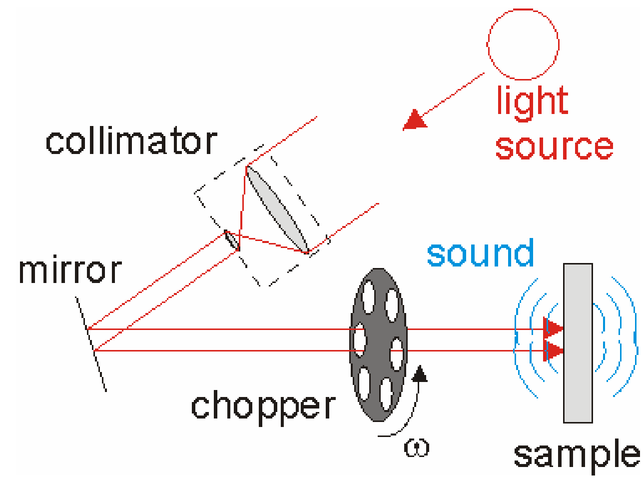


Cis Isomer

- What mechanisms are responsible for the length change?
- What can we do with photomechanical effects?

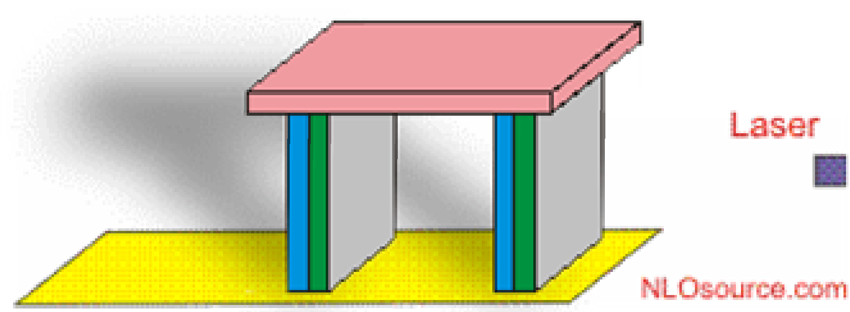
Alexander Graham Bell Experiments





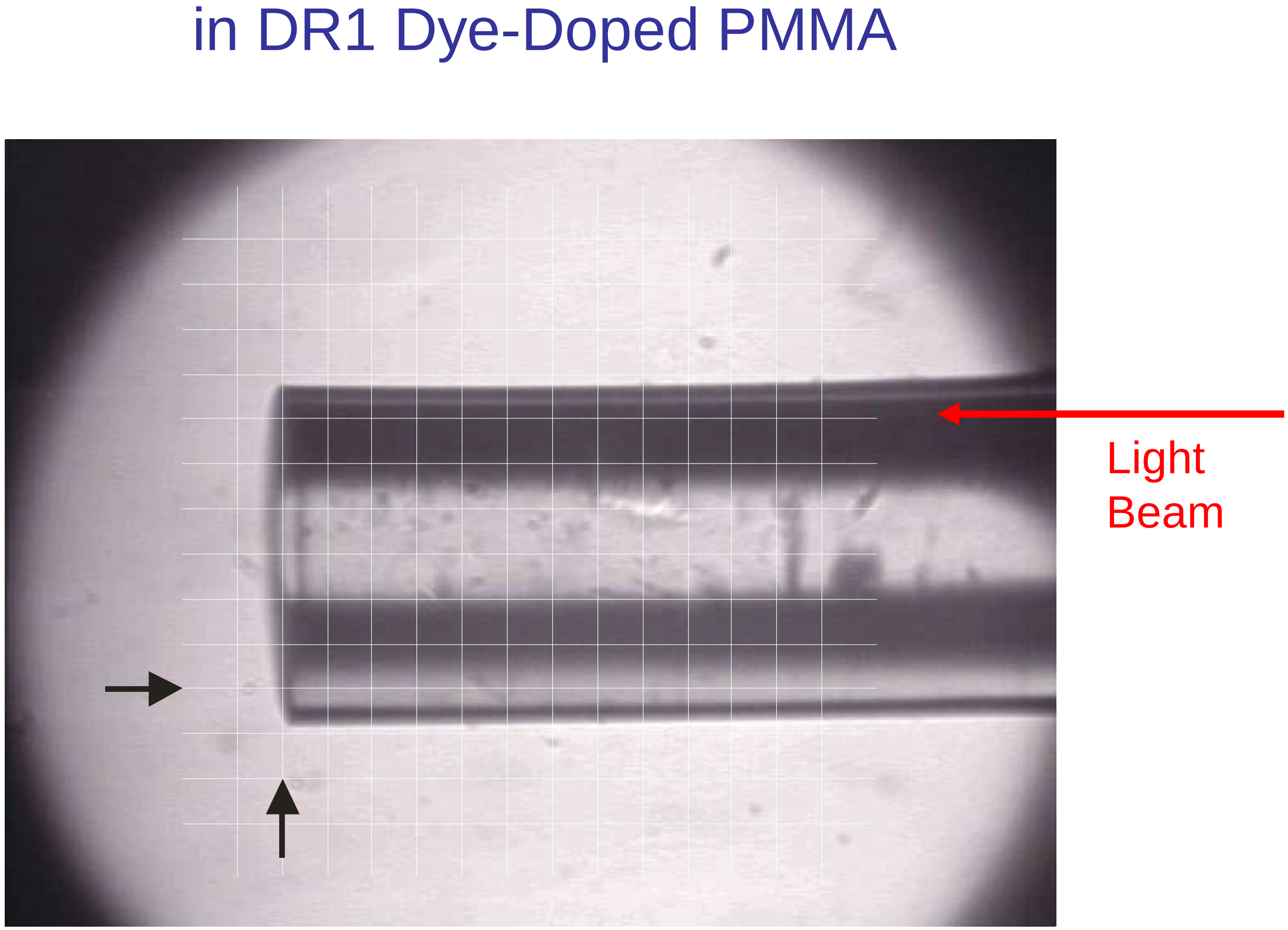
A. G. Bell, *Proceedings of the American Association for the Advancement of Science* **29,** 115 (1881)

Uchino Walker



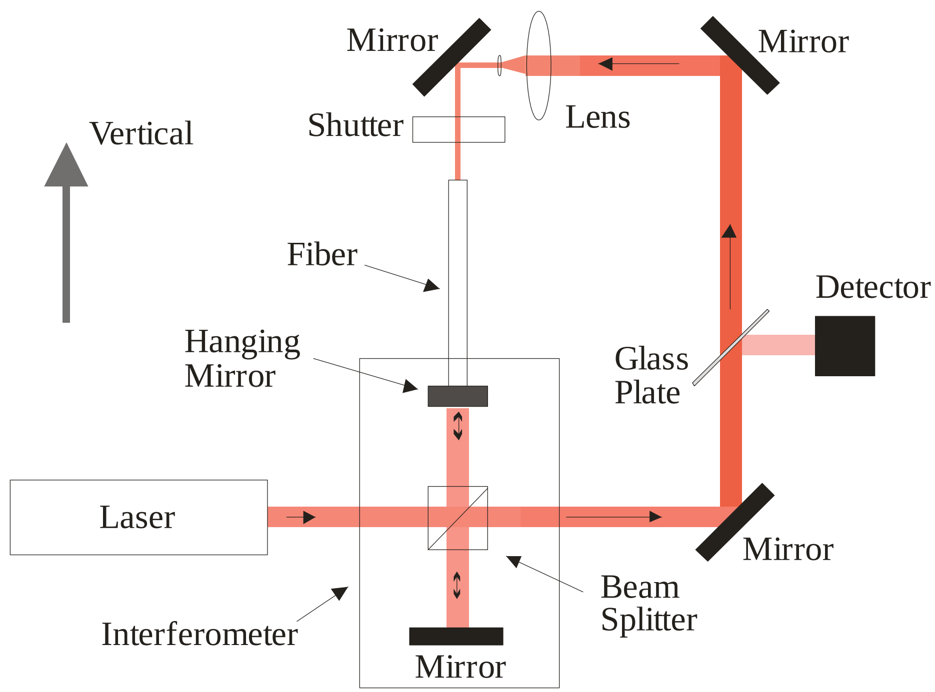
K. Uchino and E. L. Cross, *Japanese Journal of Applied Physics* **19,** 171 (1980); K. Uchino, Ultrasonics Symposium , 721 (1990).

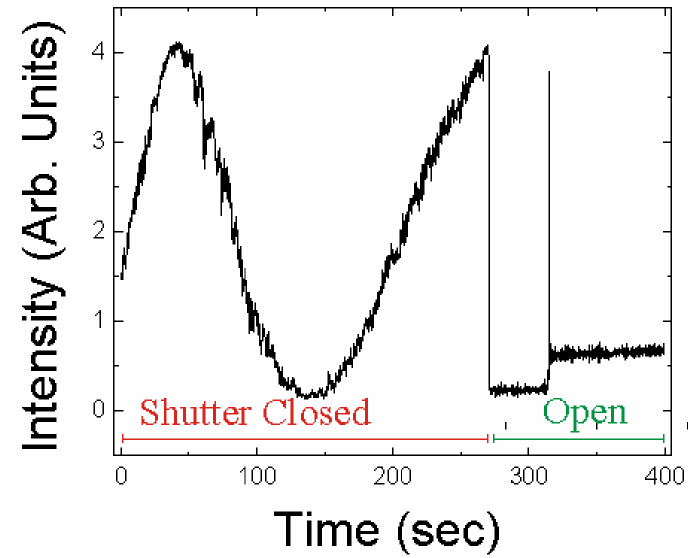
Photomechanical Bending – Fiber Cantilever in DR1 Dye-Doped PMMA

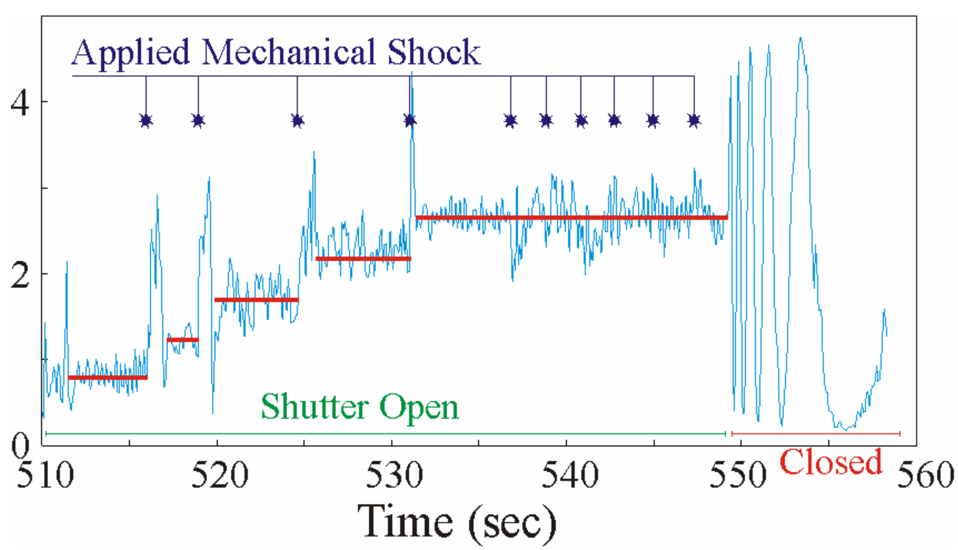


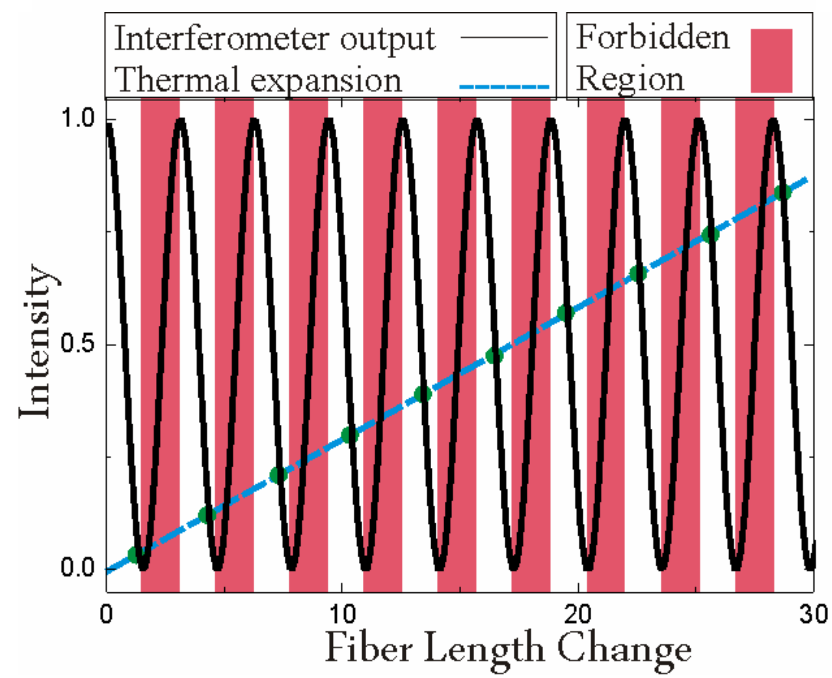
Shaoping Bian, Dirk Robinson, and Mark G. Kuzyk, J. Opt. Soc. Am. B. **23**, 697-708 (2006).

Photomechanical Effects – Light-Induced Material Shape Change





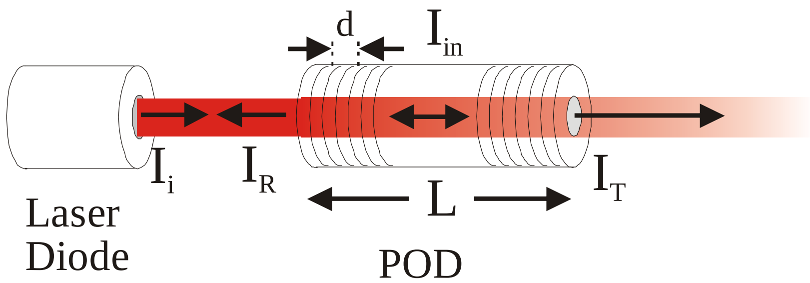


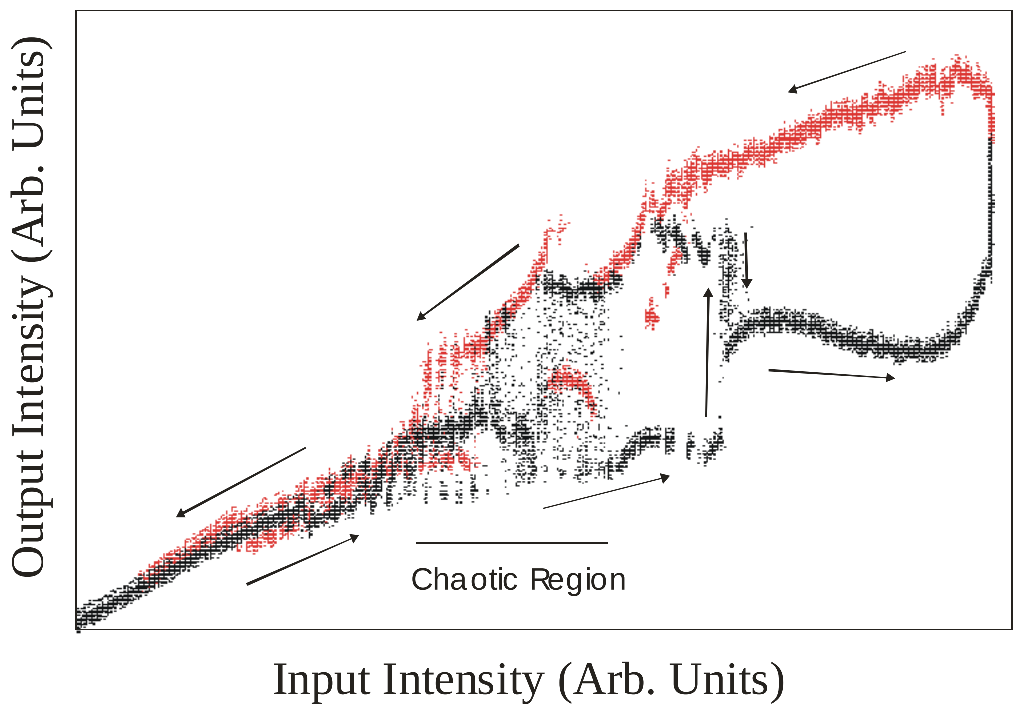


D. J. Welker and M. G. Kuzyk, Appl. Phys. Lett. **64**, 809 (1994).

$$\Delta L/L = 3\,\mathrm{nm}/30\,\mathrm{cm} = 3 \times 10^{-8}$$

Photomechanical Optical Device (POD)





Transistor

- One current controls another one

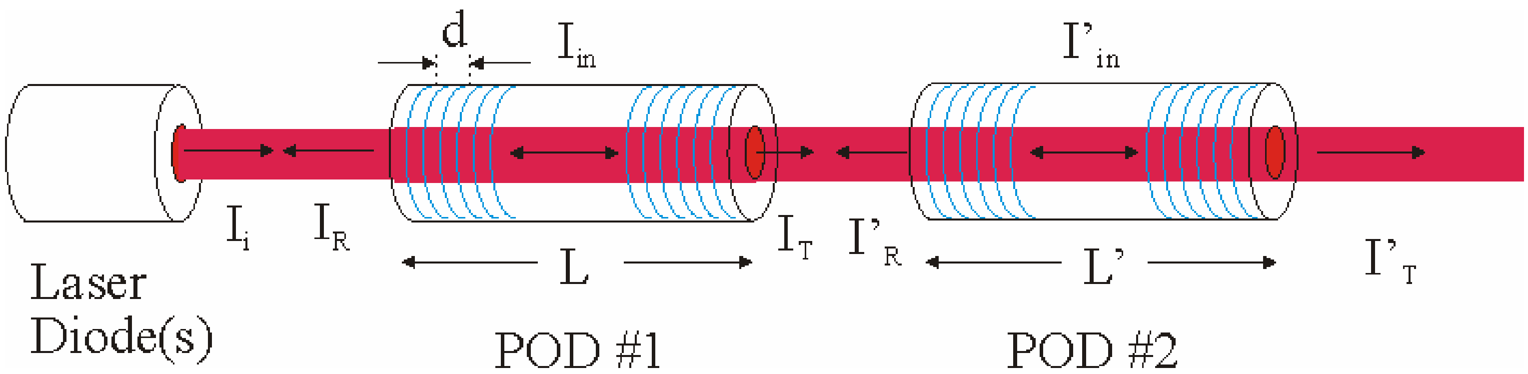
POD

- One light beam controls another one
- External stress/chemical/etc. controls the light beam (sensing)
- Multi-stability of light outputs and length states for single input intensity
- Capable of optical actuation

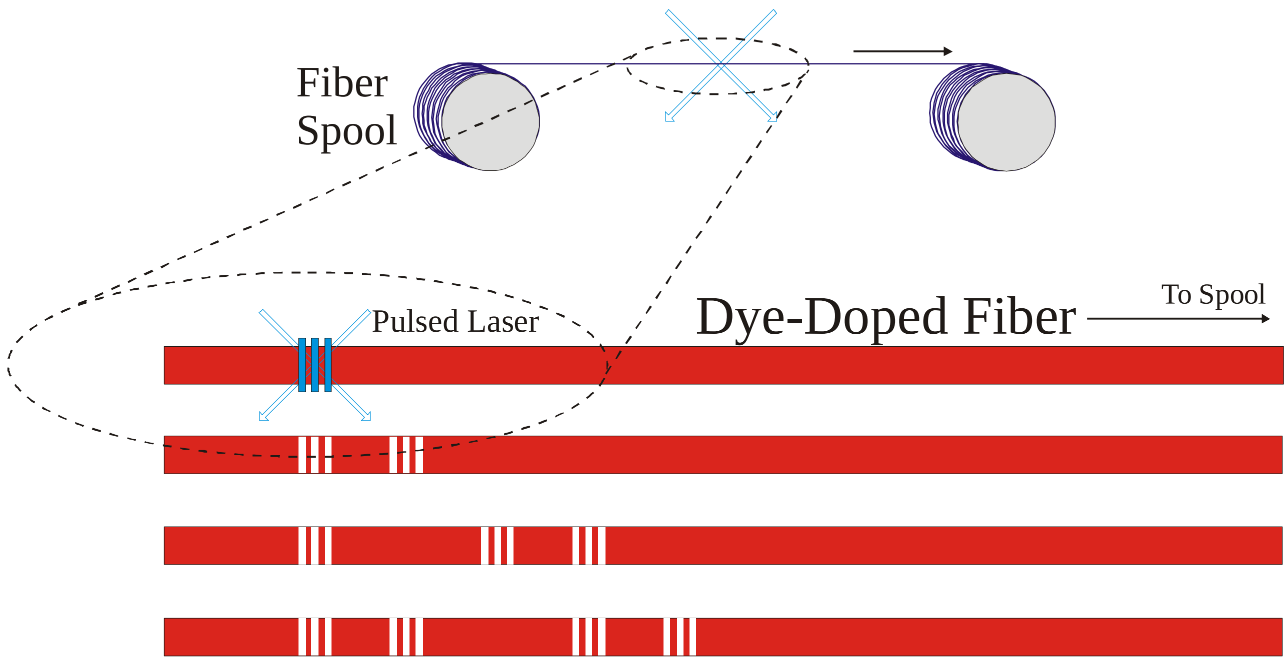
A POD integrates sensing, actuation, and logic (i.e. like many transistors) in one element

D. J. Welker and M. G. Kuzyk, Applied Phys. Lett. **66**, 2792 (1995).

Coupled PODs



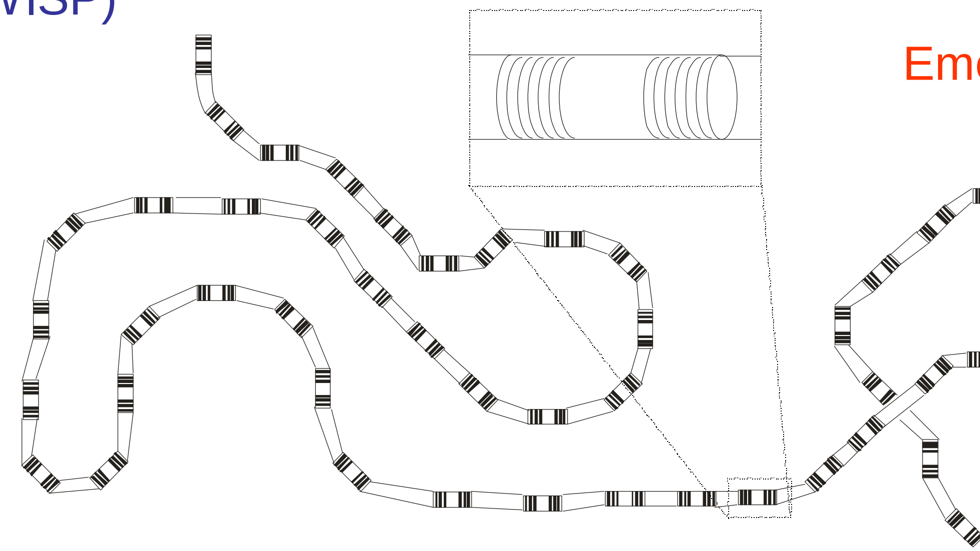
Integrated PODs



Pak L. Chu, Optics and Photonics News **16**, 52 (2005).

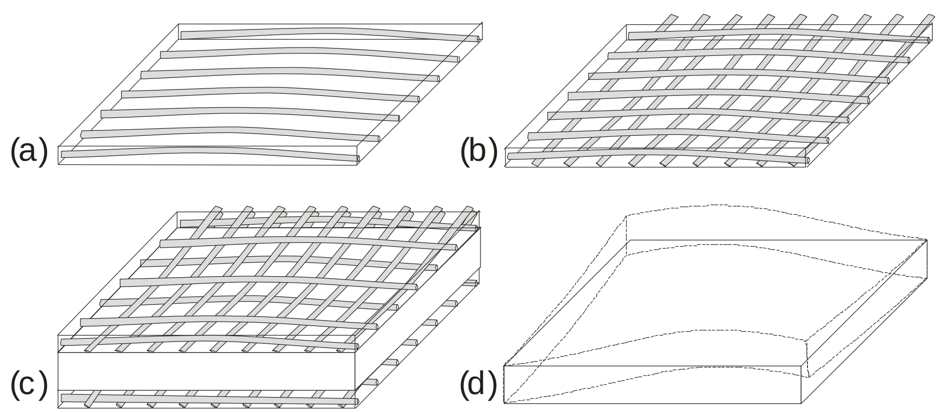
Coupled PODs

Smart Thread (**W**aveguide-**I**ntegrated
Smart **P**OD -WISP)



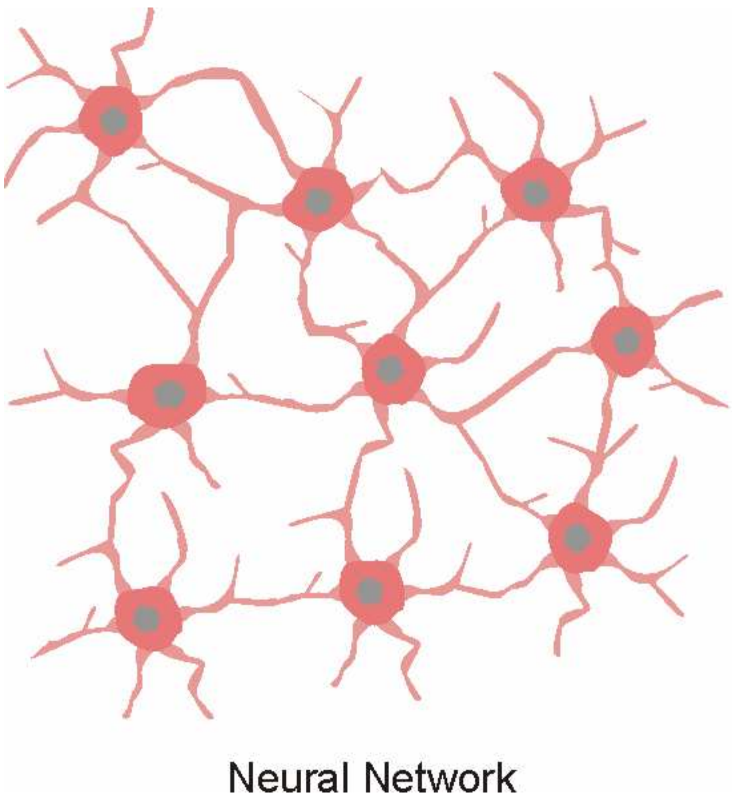
Emergence?

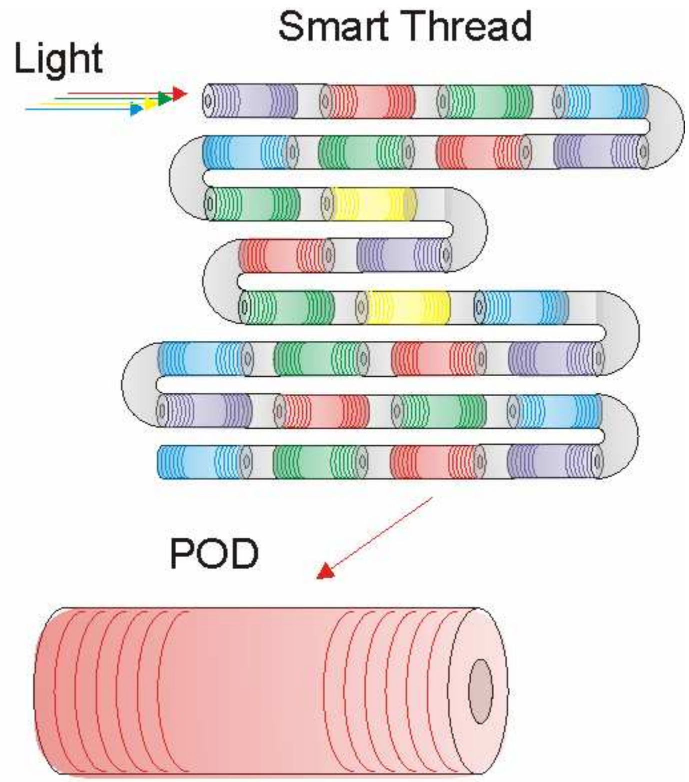
Smart Fabric



Smart Materials

The power of coupled PODs

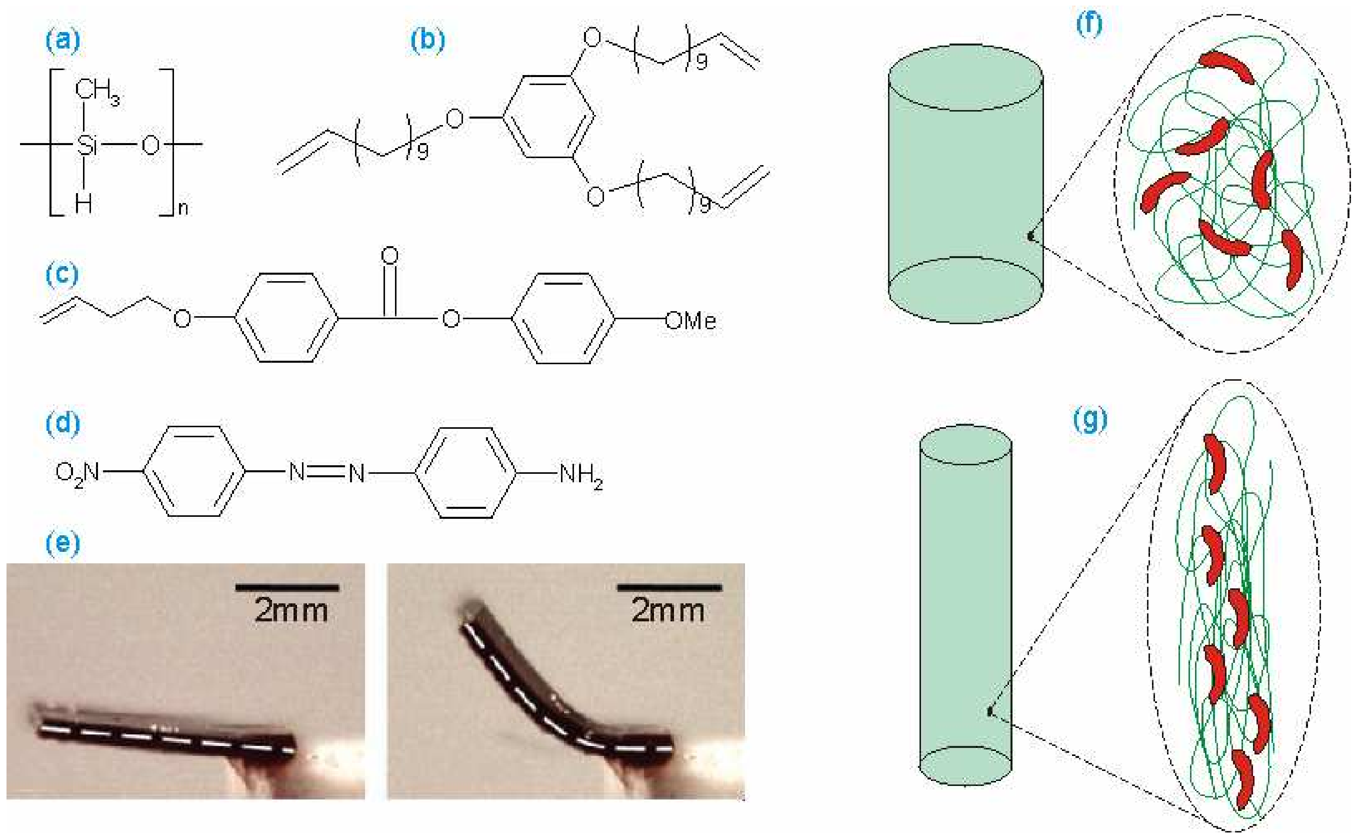




- Neurons connected to a few nearest neighbors
- Perform logic

- PODs interconnected to all others
- Interconnections determined by light color
- Perform complex logic
- Perform sensing
- Perform actuation
- Make morphing materials

Liquid Crystal Elastomers as Photomechanical Materials



- Large photomechanical effect
- Poor optical quality

M. Camacho-Lopez,H. Finkelmann, P. Palffy-Muhoray, and M. Shelley, Nature Materials **3**, 307 (2004).

Characterizing PODs

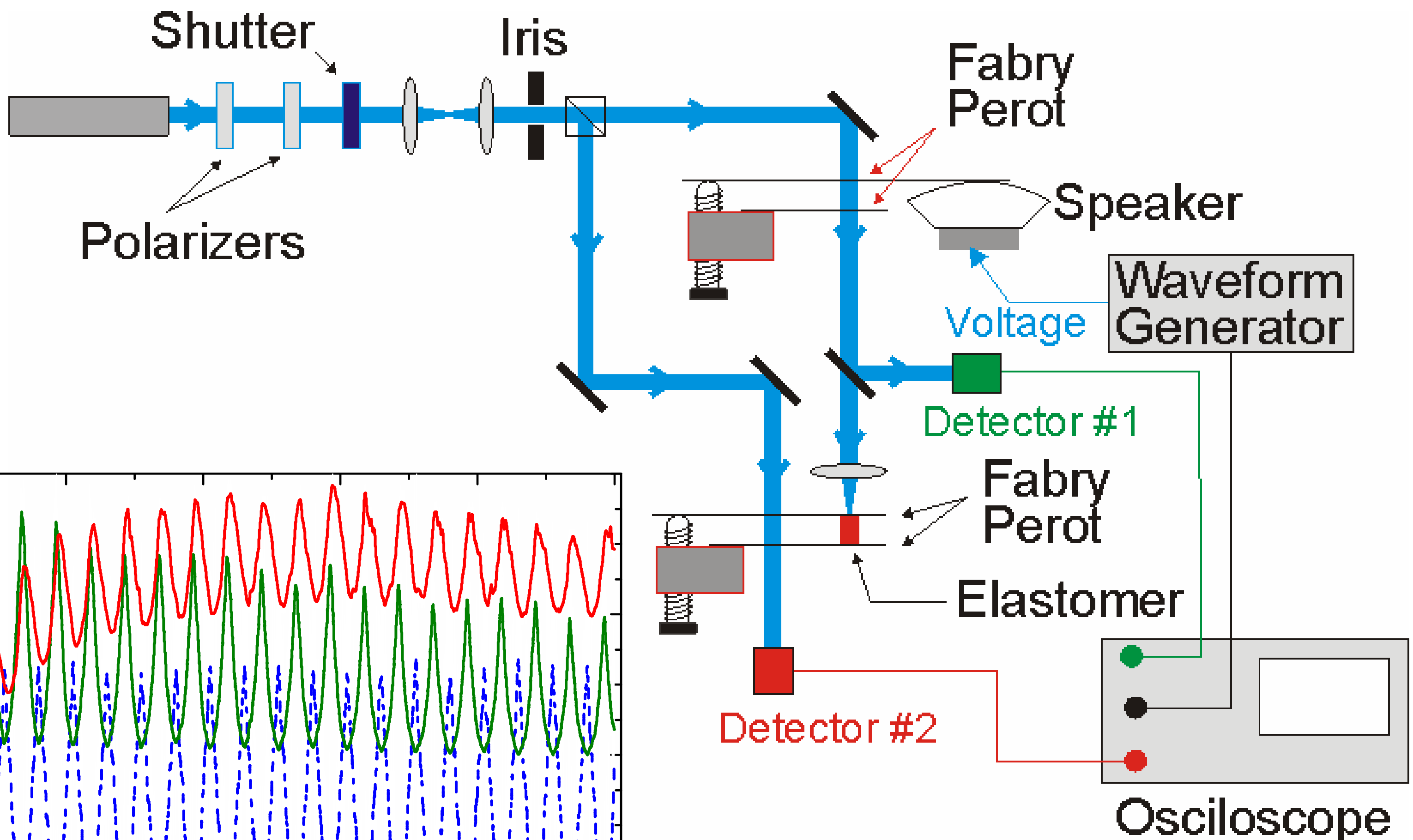
1. Characterize single POD
2. Develop theory of POD response
   a) mechanisms of material response
   b) Account for surrounding material
3. Validate theory

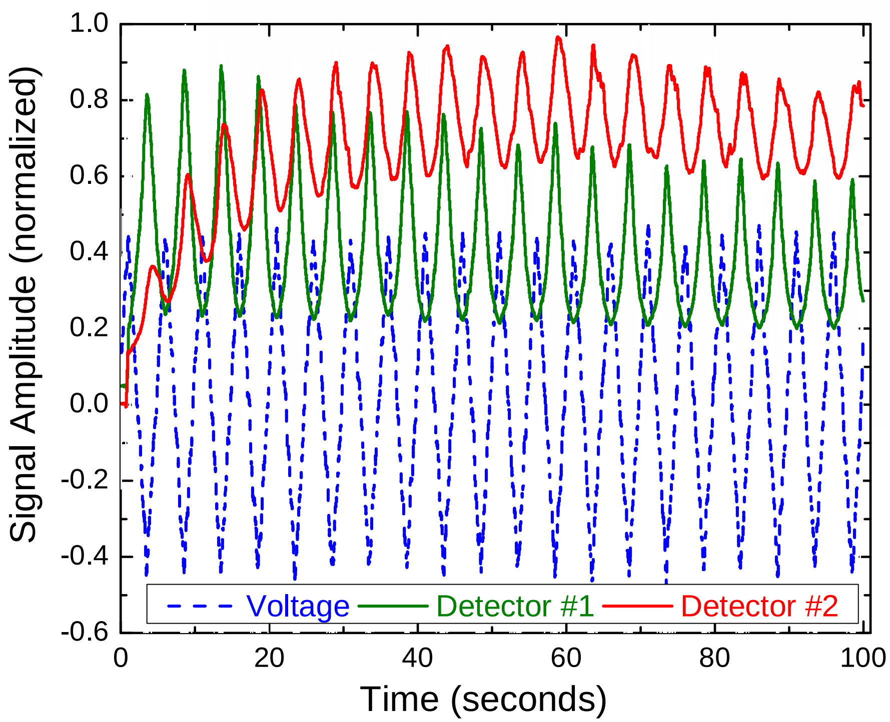
First principles calculations

4. Characterize response function of POD
5. Use response function to predict cascaded devices
6. Validate theory

Response functions

Transmitting a force on a light beam – low-frequency response to a Triangular Waveform

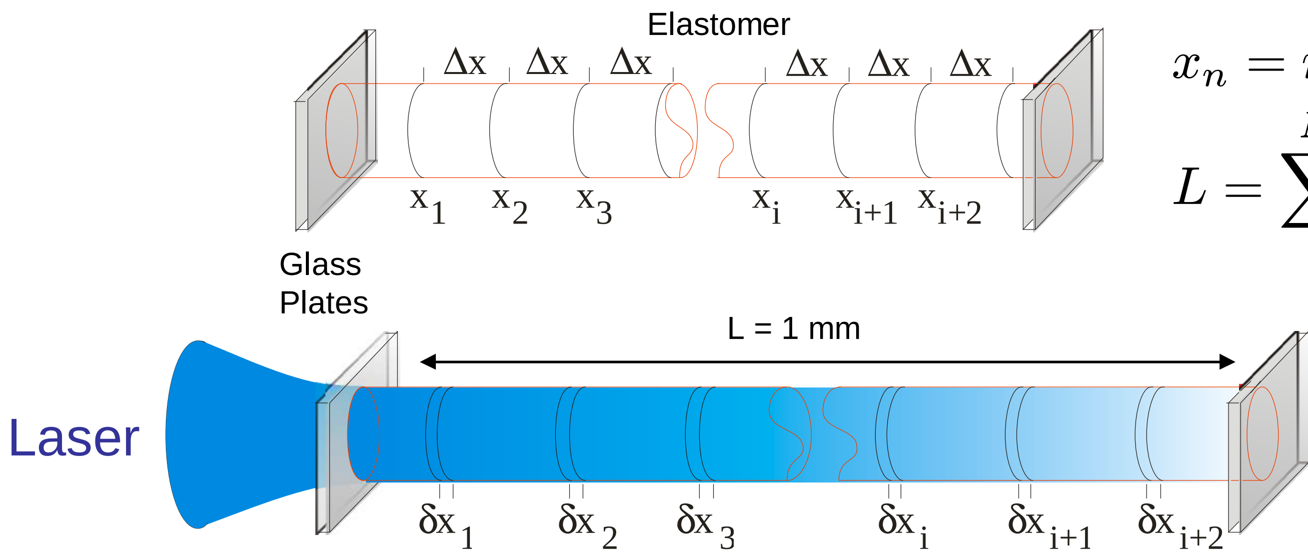




Electrical Signal ⟶ Stress

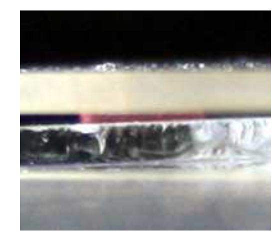
⟶ Light ⟶ Stress

Modeling the Photomechanical Response



$$x_n = n\Delta x$$

$$L = \sum_0^N \Delta x = N\Delta X$$



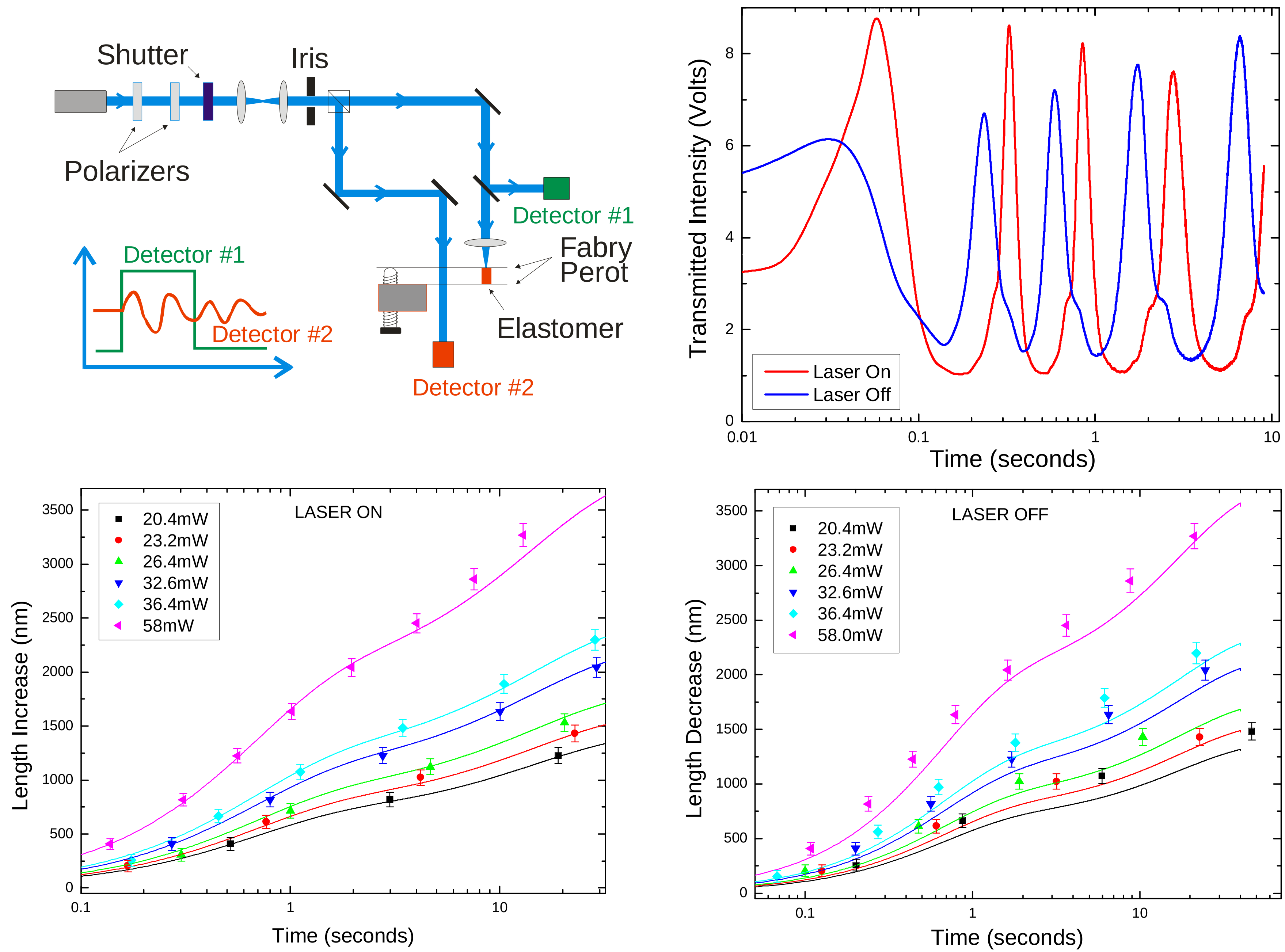
$$\Delta L = \sum_{n=0}^{N} \pm x_n = \sum_{n=0}^{N} \mu(x_n)\Delta X \rightarrow \int_0^L \mu(x,t)\, dx \qquad \Delta L \ll L$$

Strain: $\mu(x,t) = \underbrace{\alpha_T T(x,t)}_{\text{Thermal Expansion}} + \underbrace{bI(x,t)}_{\text{Molecular Reorientation}}$

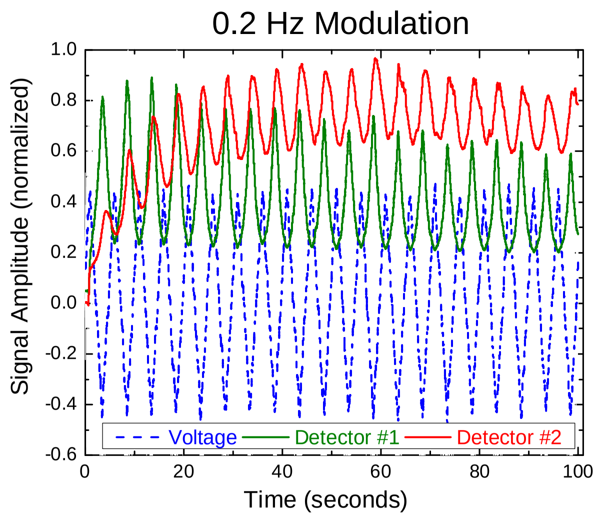
$$\frac{d}{dt}T(x,t) - K\frac{d^2}{dx^2}T(x,t) = H_{source}(x,t) = I_0 \exp\left[-\int_0^x \alpha N(x_2,t)\, dx_2\right]$$

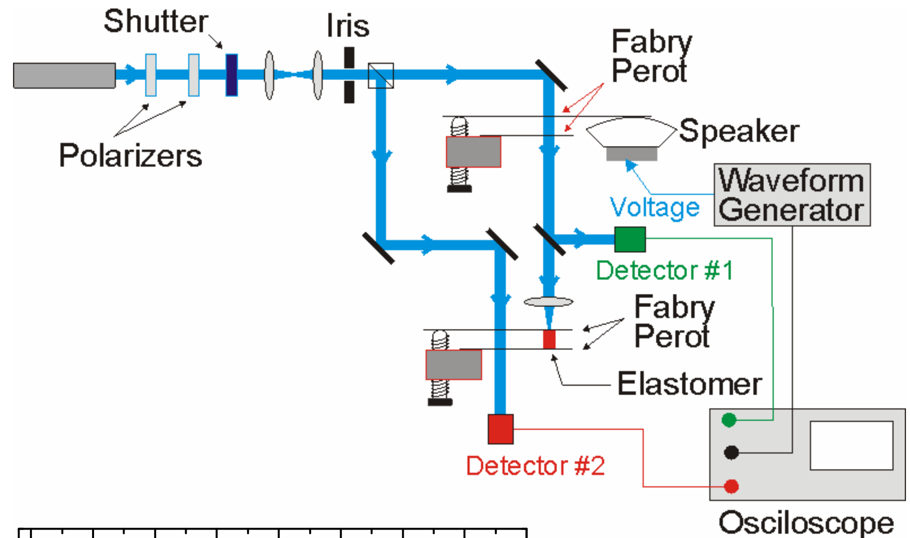
Population of dyes aligned along light polarization

Theory Validation



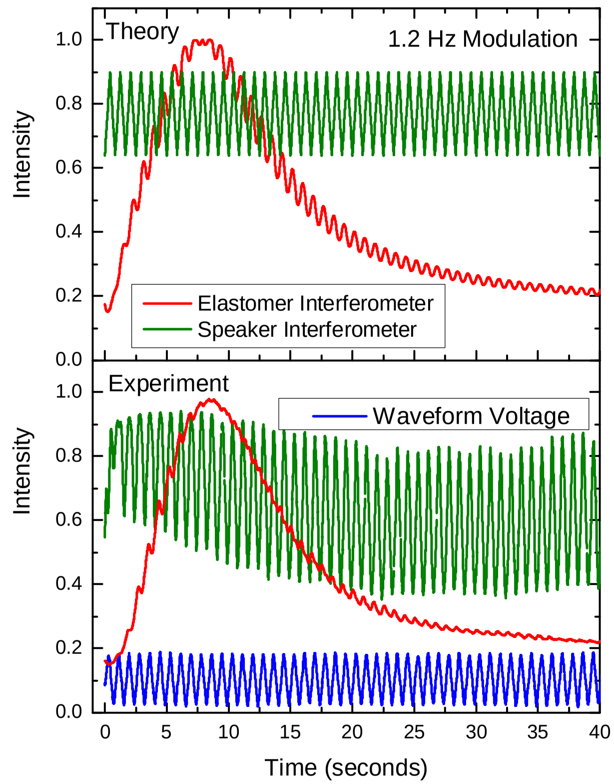
Frequency Dependence of Elastomer Response

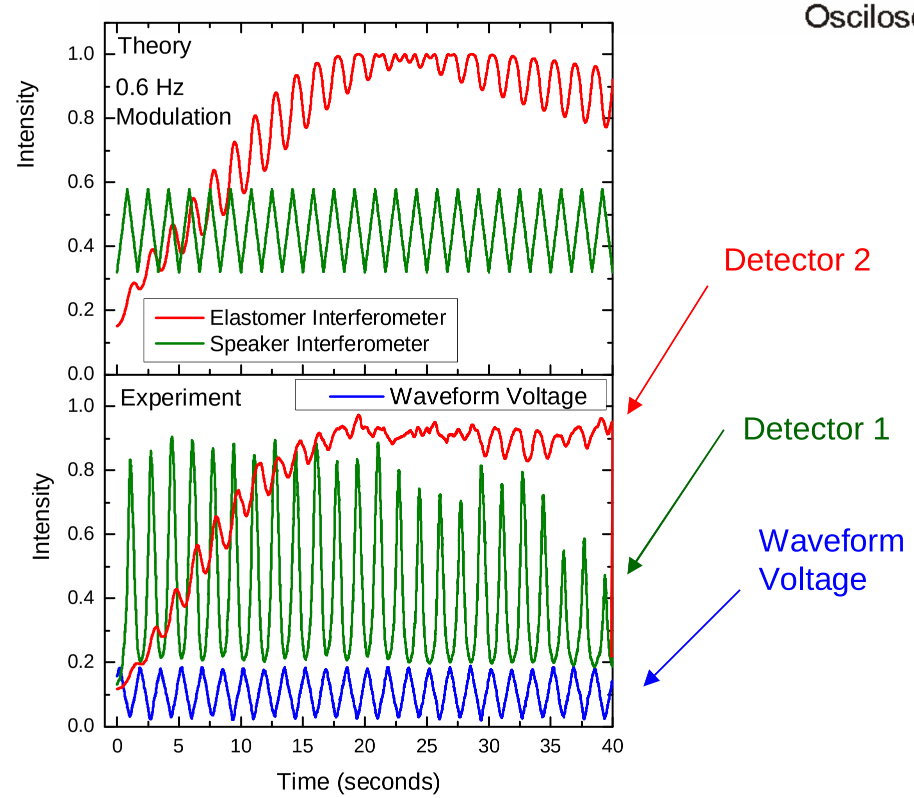




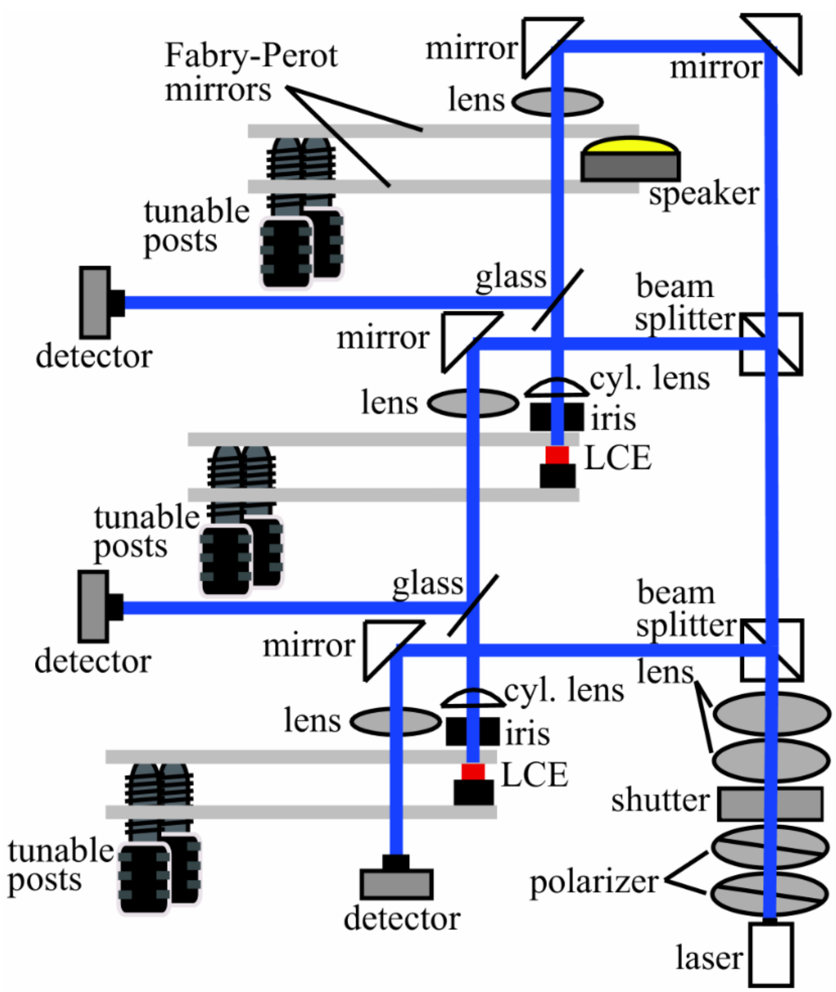
Theory

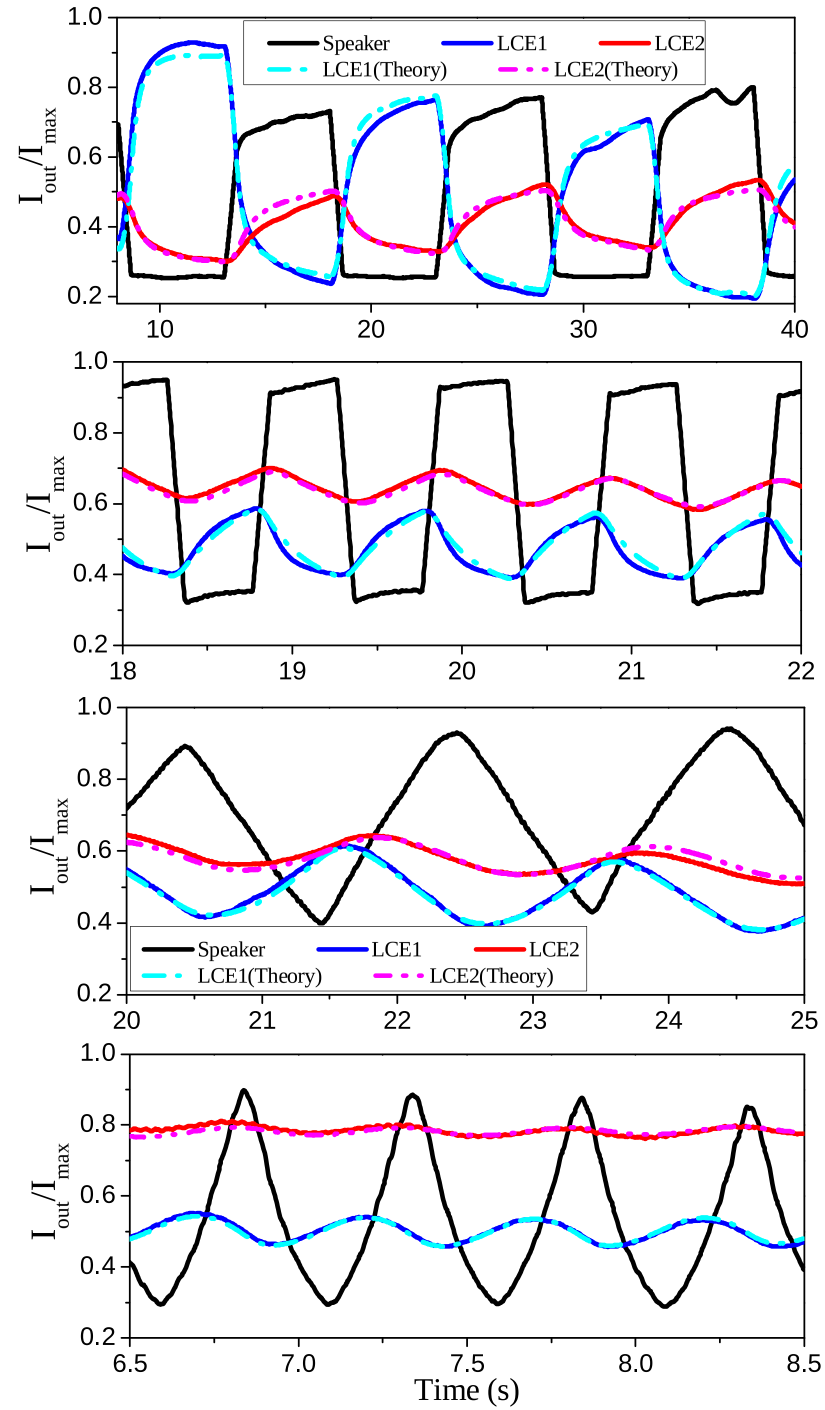
Experiment





Cascading PODs



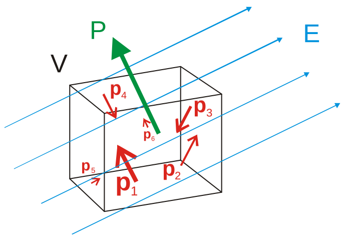


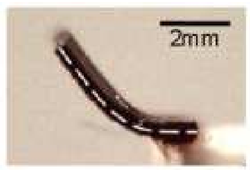
1. Characterize response function of one POD
2. Use this to predict response of cascaded PODs excited with arbitrary waveform
3. Compare theory with experiment

Smart Materials

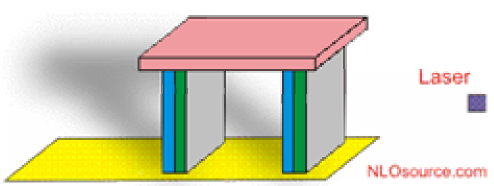
Developing Materials

Building materials from the ground up

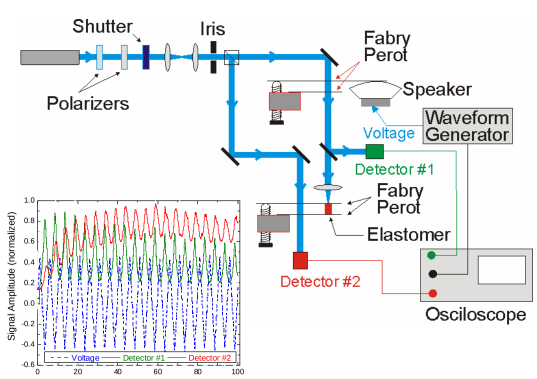




Design materials with new functionality

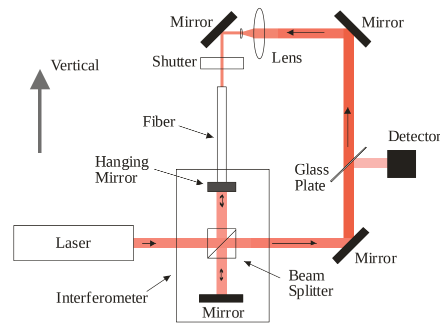


Materials Characterization

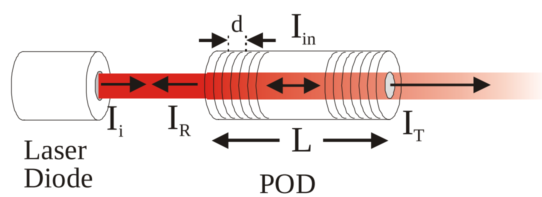


Developing Devices Concepts

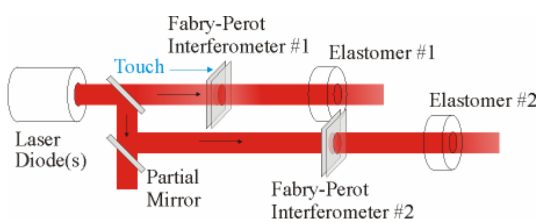
Bulk Devices

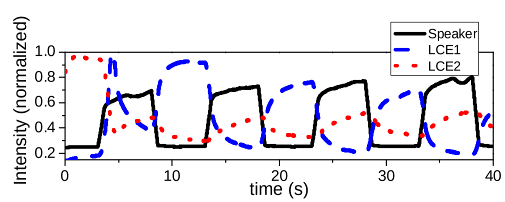


Waveguide Devices



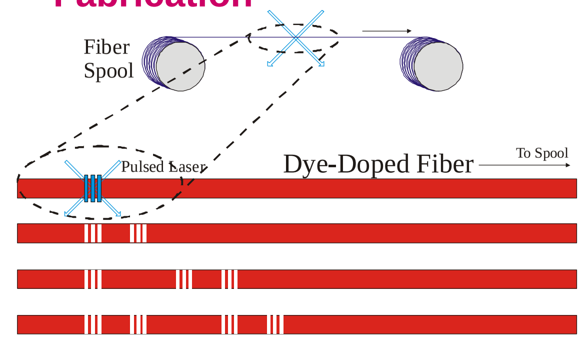
Cascaded Devices



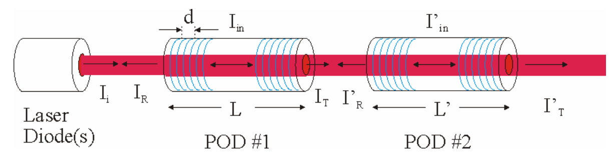


Device Integration

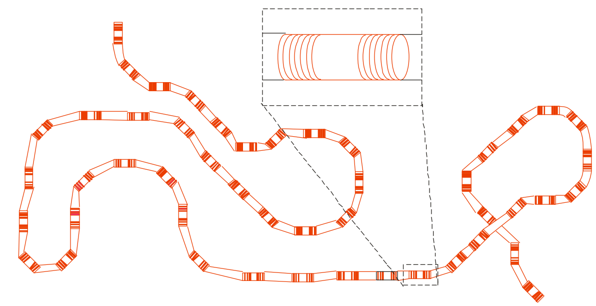
Fabrication

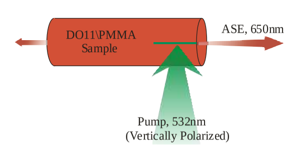


Integration/Characterization



Emergence





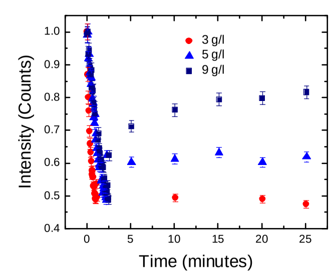
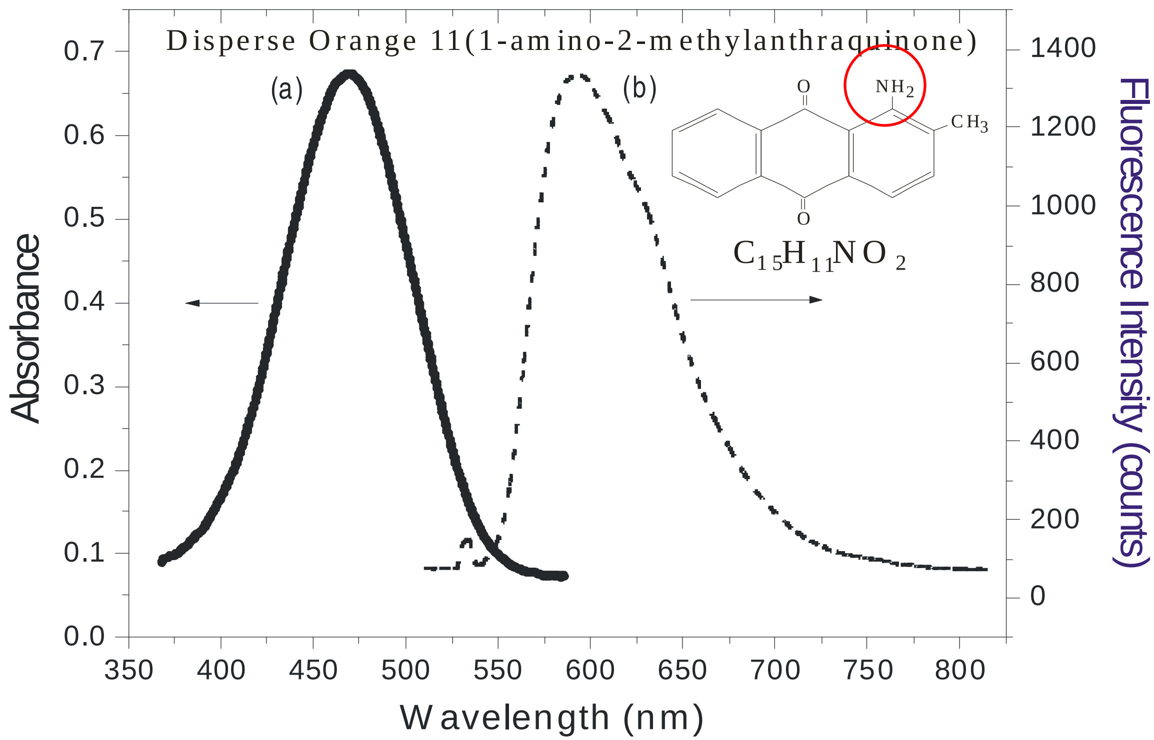
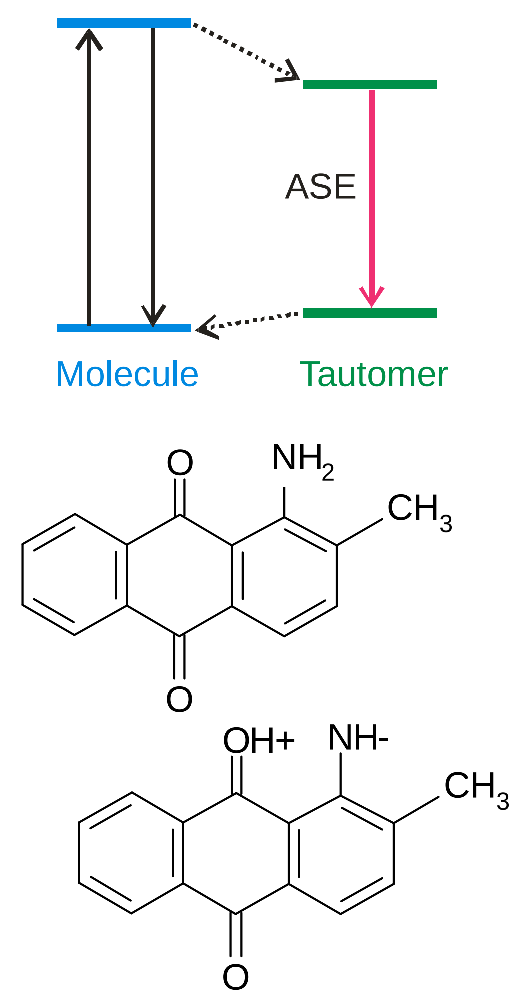


Photo-Tautomerization in DO11 Dye



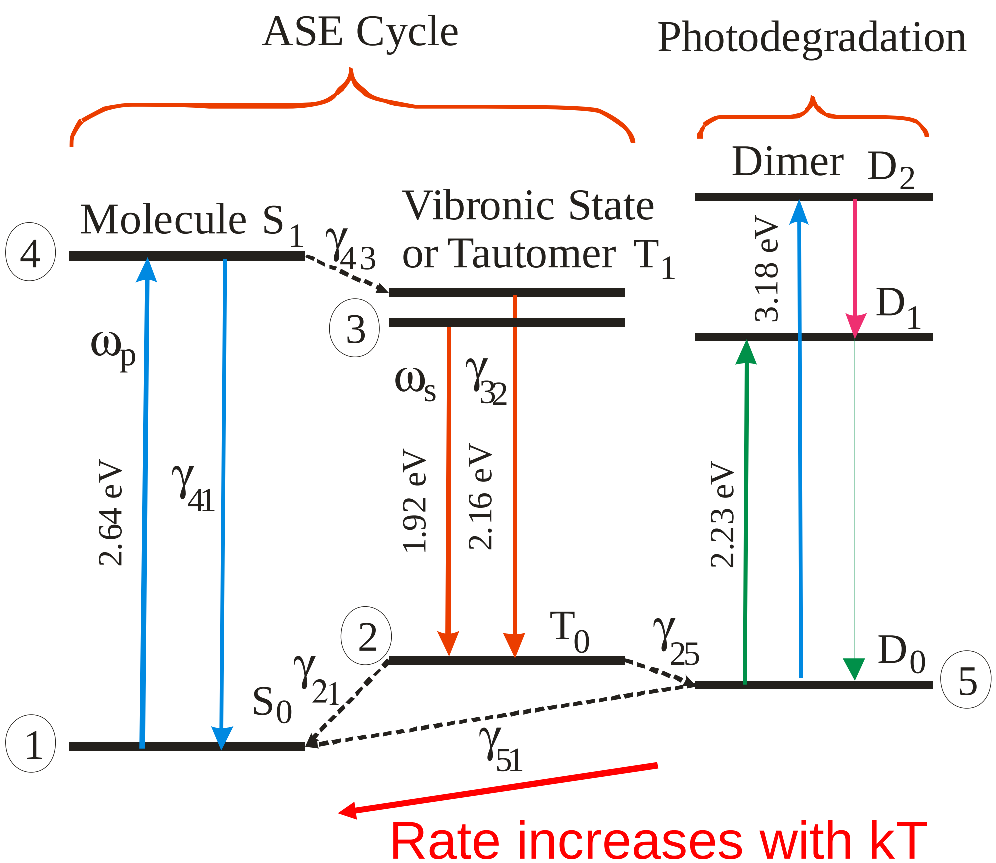
Tautomerization

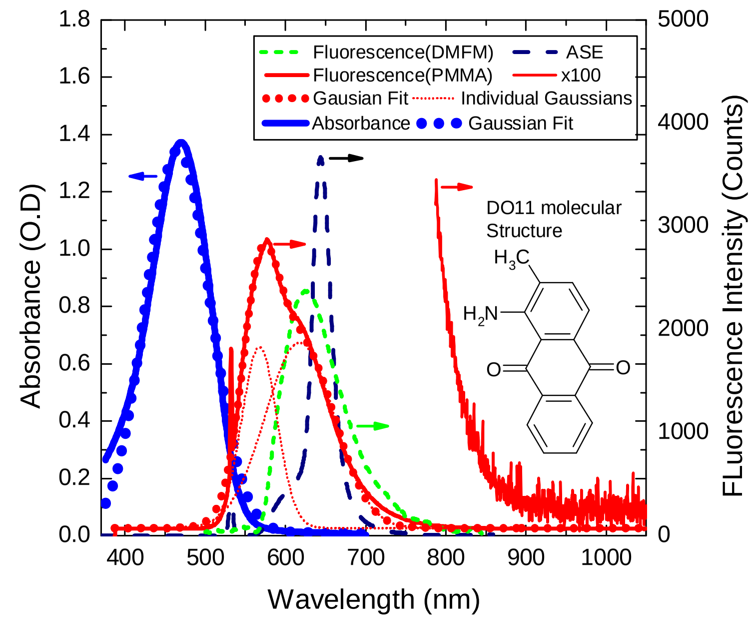


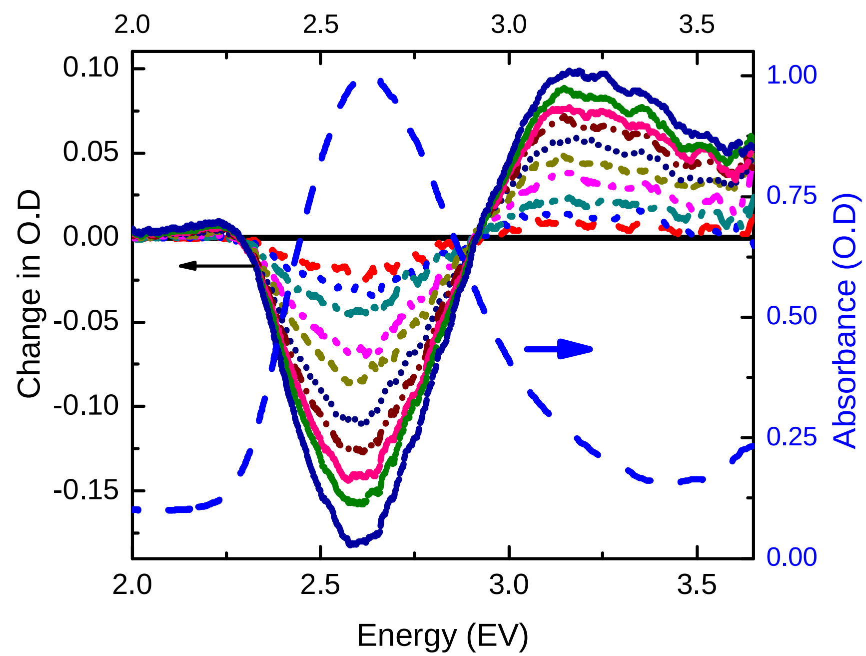
- Absorption and emission peaks are well separated
- Tautomer has much larger dipole moment than molecule

B. Howell and M. G. Kuzyk, Journal of the Optical Society of America B **19** (8), 1790 (2002).

Energy-Level Diagram



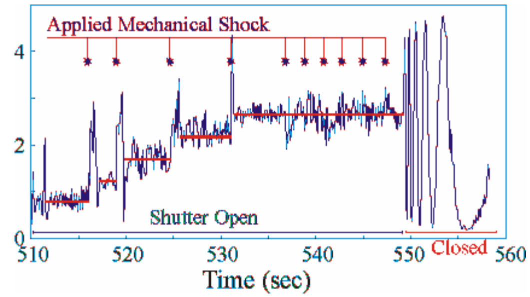


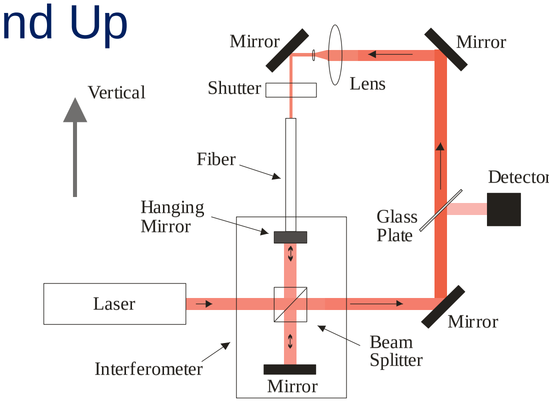


N. B. Embaye, S. K. Ramini, and M. G. Kuzyk, J. Chem. Phys. **129**, 054504 (2008).

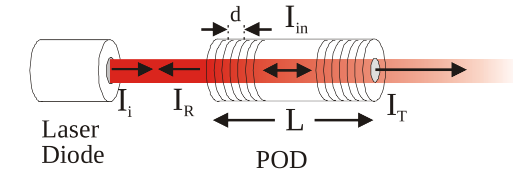
Building Ultra-Smart Materials from the Ground Up

1. Device with all-optical sensing/logic/actuation has been demonstrated

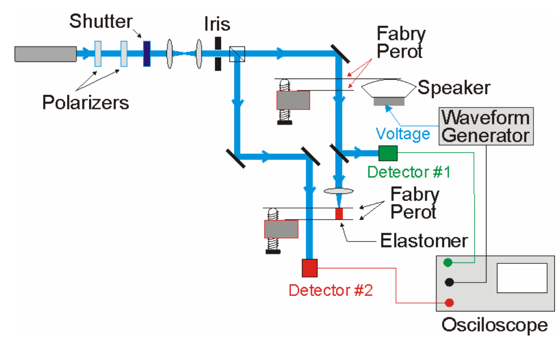


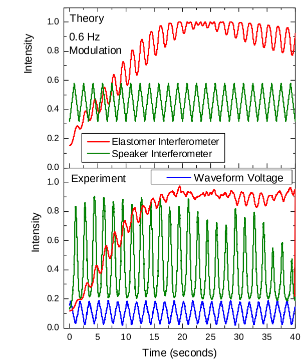


2. Above device has been miniaturized into a POD and multi-stability observed

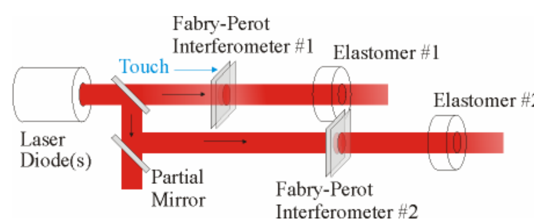


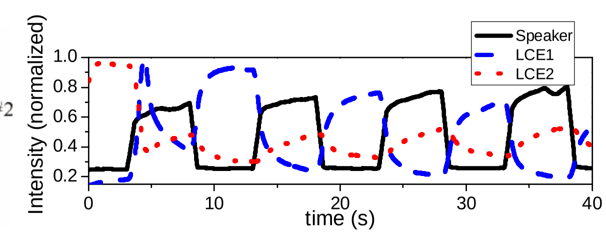
3. The photomechanical effect in an elastomer has been modeled and characterized





4. Elastomer devices have been combined in series to demonstrate integration





5. Future – Integrate waveguide-based PODs