

# Chirality and Polarization Effects in Nonlinear Optics

Robert W. Boyd

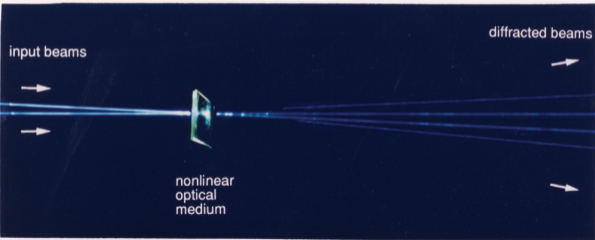
*Institute of Optics and Department of Physics and Astronomy  
University of Rochester, Rochester, New York 14627 USA*

With the help of Girish Agarwal, Martti Kauranen, John Sipe, Colin O'Sullivan-Hale, Peter Milonni, Albert Le Floch, Kazik Rzażewski, Marc Vallet, and many others.

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# The Essence of Nonlinear Optics

## Light-By-Light Scattering



## *Premise of Talk*

Polarization plays an even more important role in nonlinear optics than it does in linear optics.

Recall that the material response is related to the applied field strength by a tensor relation.

$$P_i^{(1)} = \chi_{ij}^{(1)} E_j \quad P_i^{(2)} = \chi_{ijk}^{(2)} E_j E_k \quad P_i^{(3)} = \chi_{ijkl}^{(3)} E_j E_k E_l$$

The increasing complexity of the tensor relation with increasing order of nonlinearity leads to rich polarization dependence of NLO phenomena.

### *Example*

In an isotropic, non-gyrotropic medium (that is, a medium that is isotropic under both proper and improper rotations), the dielectric response can be expressed by the completely scalar relation

$$P^{(1)} = \chi^{(1)} E.$$

But the third-order nonlinear response is expressed as (Maker and Terhune, 1965)

$$\mathbf{P} = A(\mathbf{E} \cdot \mathbf{E}^*)\mathbf{E} + \frac{1}{2}B(\mathbf{E} \cdot \mathbf{E})\mathbf{E}^*$$

where

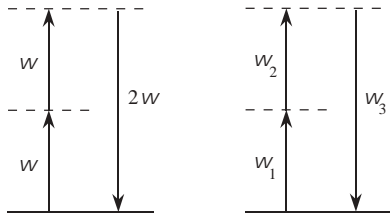
$$A = 6\chi_{1122} = 3\chi_{1122} + 3\chi_{1212} \quad B = 6\chi_{1221}$$

which is inherently polarization dependent. The first term is known as the “grating” contribution to the nonlinear response, and the second term is known as the “phase conjugating” contribution to the nonlinear response.

## Second-Harmonic Generation and Sum-Frequency Generation

The process of second-harmonic generation  $\omega + \omega \rightarrow 2\omega$  is described by the second-order nonlinear optical susceptibility  $\chi^{(2)}(2\omega, \omega, \omega)$ .

The more general process of sum-frequency generation  $\omega_1 + \omega_2 \rightarrow \omega_3$  is described by the second-order nonlinear optical susceptibility  $\chi^{(2)}(\omega_3, \omega_1, \omega_2)$ .



Fundamental symmetry considerations show that  $\chi^{(2)}$  must vanish in a material that possesses inversion symmetry. For this reason, second-order NLO interactions are usually studied in crystals.

But liquids consisting of **chiral molecules** also lack inversion symmetry!

*Notation:*  $\chi\iota\epsilon\rho$  is Greek for hand. A chiral molecule is thus one that possesses handedness. More precisely, if the mirror image of a molecule cannot be superposed onto the original, the molecule is said to be chiral.

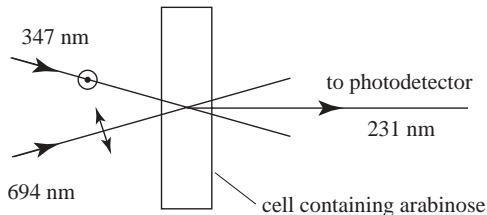
Recall that chiral materials possess the special linear optical property known as optical activity, that is, the rotation of the direction of linear polarization upon propagation through such a medium.

## *What are the nonlinear optical properties of chiral media?*

Chiral media possess unique (almost weird) nonlinear optical properties. The second-order nonlinear optical response (to two applied fields of amplitudes  $E_1$  and  $E_2$ ) can be expressed as

$$\mathbf{P}_{\text{NL}} = A_{123} \mathbf{E}_1 \times \mathbf{E}_2 \quad \text{where} \quad A_{ijk} = \frac{1}{2}(\chi_{ijk}^{(2)} - \chi_{ikj}^{(2)})$$

Thus  $A_{ijk}$  is the antisymmetric (in the last two indices) part of the nonlinear susceptibility. Note that  $\mathbf{P}_{\text{NL}}$  vanishes for second-harmonic generation. Sum-frequency generation can occur only if the two input fields are orthogonally polarized and non-collinear.



*Is there a linear electrooptic (Pockels) effect in isotropic chiral media?*

It would be very important technologically if a linear EO effect could occur in isotropic media. Such an effect would be described by  $\chi^{(2)}(\omega, \omega, 0)$ .

There is no group-theoretical reason why such an effect cannot exist. However, for a lossless material, it can be shown that  $A$  must vanish, as can be demonstrated from the condition of full-permutation symmetry (which follows from the fact that the internal energy must be a function of state in a lossless material) or from explicit quantum mechanical calculation.

For a lossy medium, there is no fundamental reason why such a linear EO effect cannot exist. However, lossy materials are described quantum mechanically in terms of decay constants that are often introduced phenomenologically. Whether or not a linear EO effect is predicted to exist thus depends on the details of how decay is added to the model.



To foreshadow the following development, we present here a summary of the current state of the understanding of this effect.

Buckingham and Fischer (2000); Stedman et al. (2001) conclude that a linear EO effect **does not exist** in chiral EO materials. (But it is not clear if their conclusions hold in general.)

Koroteev (1997) and Kauranen and Persoons (1999) conclude that a linear EO effect **does exist** for lossy optical materials if decay is treated properly.

Agarwal and Boyd (2003) conclude that the linear EO effect vanishes for radiative damping and is very small for other damping mechanisms.

*Is there a linear electrooptic (Pockels) effect in isotropic chiral media?*

In detail, Kauranen and Persoons find that each term in the expression for  $\chi^{(2)}$  is proportional to  $i\gamma_{nm}$ , where  $\gamma_{nm}$  is the damping rate of the transition between levels  $n$  and  $m$ .

Thus, the linear EO effect is inherently dependent on the existence of decay phenomena. Consequently, the predictions of the calculation are critically dependent on the assumptions made in introducing decay into the calculation.

For this reason, Agarwal and Boyd decided to treat the case of radiative broadening. Even though most material systems of interest are unlikely to be radiatively broadened, the case of radiative broadening is one in which the calculation can be performed explicitly starting from first principles.

In brief summary, Agarwal and Boyd agree with the formula of Kauranen and Persoons, but find that the damping rate  $\gamma_{nm}$  is really a function of frequency, and that the relevant damping rate for the electrooptic effect is  $\gamma_{nm}(\omega = 0)$  which vanishes. This result makes sense in that for radiative damping  $\gamma_{nm}$  is equal to the Einstein  $A$  coefficient, which scales with frequency as  $\omega^3$ .

# Density-matrix theory with damping

$$\begin{aligned}
 \mathbf{c} \sim & - \sum_{m,n} \frac{i2\mathbf{g}_{ng}}{\omega_{ng} - i\mathbf{g}_{ng}} \frac{\mathbf{m}_{gn} \cdot \mathbf{m}_{nm} \times \mathbf{m}_{mg}}{(\omega_{mg} - \omega - i\mathbf{g}_{mg})(\omega_{ng} + i\mathbf{g}_{ng})} \\
 & - \sum_{m,n} \frac{i2\mathbf{g}_{mg}}{\omega_{mg} + i\mathbf{g}_{mg}} \frac{\mathbf{m}_{gn} \cdot \mathbf{m}_{nm} \times \mathbf{m}_{mg}}{(\omega_{ng} + \omega + i\mathbf{g}_{ng})(\omega_{mg} - i\mathbf{g}_{ng})} \\
 & + \sum_{m,n} \frac{i(\mathbf{g}_{mn} - \mathbf{g}_{mg} - \mathbf{g}_{ng})}{\omega_{mn} - \omega - i\mathbf{g}_{mn}} \frac{\mathbf{m}_{gn} \cdot \mathbf{m}_{nm} \times \mathbf{m}_{mg}}{(\omega_{mg} - \omega - i\mathbf{g}_{mg})(\omega_{ng} + i\mathbf{g}_{ng})} \\
 & - \sum_{m,n} \frac{i(\mathbf{g}_{mn} - \mathbf{g}_{mg} - \mathbf{g}_{ng})}{\omega_{mn} - \omega - i\mathbf{g}_{mn}} \frac{\mathbf{m}_{gn} \cdot \mathbf{m}_{nm} \times \mathbf{m}_{mg}}{(\omega_{ng} + \omega + i\mathbf{g}_{ng})(\omega_{mg} - i\mathbf{g}_{ng})}
 \end{aligned}$$

## *A Controversy*

Considerable controversy has developed because one of the early theoretical treatments of the linear EO effect in chiral media (Andrews et al. 1998) concludes that the resonance nature of the optical response (stated for simplicity for the linear response) is expressed by

$$\frac{1}{\omega_0 - \omega - i\Gamma} + \frac{1}{\omega_0 + \omega - i\Gamma} \quad (\text{same-sign convention})$$

rather than the more generally accepted result

$$\frac{1}{\omega_0 - \omega - i\Gamma} + \frac{1}{\omega_0 + \omega + i\Gamma} \quad (\text{opposite-sign convention}).$$

In support of their conclusion, Andrews et al. state that

- Cohen-Tannoudji et al., QM text, agrees with their result
- Weisskopf (1931) agrees with their result

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But inspection of Cohen-Tannoudji's book shows that only the resonant term is displayed, and thus the issue of the correct form of the antiresonant term is not addressed.

Also, inspection of the Weisskopf paper shows that a simple sign error (perhaps just a misprint) was introduced into the calculation. Unfortunately, this form of the expression with the wrong sign of the damping term in the antiresonant contribution has been reproduced (with proper citation!) in many subsequent treatments.

Buckingham and Fischer (2000) have more recently argued that the analysis of Andrews et al. is necessarily incorrect in that it leads to non-physical behavior, namely:

- The same-sign convention violates the reality condition  $\chi(\omega) = \chi(-\omega)^*$ . Thus the *physical* polarization created by a physical (real) electric field is complex.

- The same-sign convention violates causality in that it possesses poles in both the upper and lower half planes.

In response to this criticism, Stedman, Andrews et al. respond that one obtains the opposite-sign convention when treating the problem semiclassically, but obtains the same-sign convention when treating the problem as a scattering problem using a fully quantum (and presumably correct) approach. I reserve judgment on this point. But these authors are entirely correct that response functions, such as susceptibilities, are semiclassical concepts.

### *Interesting Aside*

It should also be noted that D. A. Long, *The Raman Effect*, Wiley, 2001 presents an appendix that reviews the history of the sign of the damping terms in the Raman susceptibility. He notes that Placzek had the signs correct (that is, used the opposite sign convention) in his original treatment of the problem, but that the sign of the damping factor in the antiresonant term inexplicably was inverted in many subsequent papers that supposedly relied on the same calculation. Long now (2001) favors the opposite sign convention.

### *Editorial Comment*

This field seems to have become a comedy of errors.

## *So What Really is the Correct Form for the Linear Susceptibility?*

First, a reality check:

Consider first the simple harmonic oscillator with phenomenological damping.

$$\ddot{x} + 2\gamma\dot{x} + \omega_0^2 x = (-e/m)Ee^{-i\omega t}$$

Let  $p(t) = -ex(t) = \alpha(\omega)Ee^{-i\omega t}$  where  $\alpha$  is the polarizability. Then

$$\alpha(\omega) = \frac{(e^2/m)}{\omega_0^2 - \omega^2 - 2i\omega\gamma} = \frac{e^2}{2m\omega_0} \left( \frac{1}{\omega_0 - \omega - i\gamma} + \frac{1}{\omega_0 + \omega + i\gamma} \right)$$

The second form is approximate (assumes  $\gamma \ll \omega_0$ ), but can be made exact through a redefinition of  $\omega_0$ .

This equation constitutes the standard result (the “opposite sign convention”).



## *But Radiative Damping Need Not be Treated Phenomenologically*

Let us treat radiative damping in terms of radiation reaction. Let  $E_T$  denote the total field that the atom experiences, that is, the sum of the applied field and the radiation reaction field. The equation of motion is taken to be undamped of the form

$$\ddot{x} + \omega_0^2 x = (-e/m)E_T e^{-i\omega t}$$

The solution can be expressed as

$$p(\omega) = -ex(\omega) = \alpha_0(\omega)E_T \quad \text{where} \quad \alpha_0(\omega) = \frac{(e^2/m)}{\omega_0^2 - \omega^2}.$$

By the standard treatment of radiation reaction, we know that  $E_T = E_0 + \frac{2}{3}i\tilde{\omega}^3 p$ , where  $\tilde{\omega} = \omega/c$ , and by definition we know that  $p(\omega) = \alpha(\omega)E_0$ . By combining these equations we find that

$$\alpha(\omega) = \frac{(e^2/m)}{\omega_0^2 - \omega^2 - \frac{2}{3}i(e^2/mc^3)\omega^3}.$$

This is the exact (within the context of the present model) result. Note that the damping is explicitly frequency dependent. It also is non causal.

## *Radiative Damping Modeled through Radiation Reaction*

We can rewrite our result as follows:

$$\begin{aligned}\alpha(\omega) &= \frac{(e^2/m)}{\omega_0^2 - \omega^2 - \frac{2}{3}i(e^2/mc^3)\omega^3} \\ &= \frac{e^2}{2m\omega'_0} \left[ \frac{1}{\omega'_0 - \omega - i\gamma(\omega)} + \frac{1}{\omega'_0 + \omega + i\gamma(\omega)} \right].\end{aligned}$$

where  $\gamma(\omega) = \frac{1}{3}(e^2/mc^3)\omega^3$  and  $\omega'_0 = \sqrt{\omega_0^2 - \gamma^2}$ .

This result has the form of the opposite-sign convention, but with frequency-dependent damping.

## *Conclusions*

In general, the damping factor  $\gamma$  is frequency dependent. Only close to resonance can one take  $\gamma$  to be a constant. It is in this case that phenomenological damping models are expected to be reliable.

In any case, a linear EO effect has not yet been observed in isotropic chiral materials. The analysis of Kauranen and Persoons suggest that the best opportunity to observe such an effect is afforded by lossy materials.

## *Magneto-chiral Birefringence*

Although the linear EO effect has not yet been observed, magneto-chiral birefringence is a nonlinear effect that relies on the properties of chiral material and has been observed (Vallet et al., PRL 87, 183003, 2001).

It has been shown by Baranova and Zeldovich (1979) that the dielectric constant of a collection of chiral molecules for right hand (−) and left hand (+) polarized light can be represented as

$$\epsilon_{\pm}(\omega, \mathbf{k}, \mathbf{B}) = \epsilon(\omega) \pm a_{\text{F}}(\omega)B \pm a_{\text{OA}}(\omega)k + a_{\text{MC}}(\omega)(\mathbf{B} \cdot \mathbf{k})$$

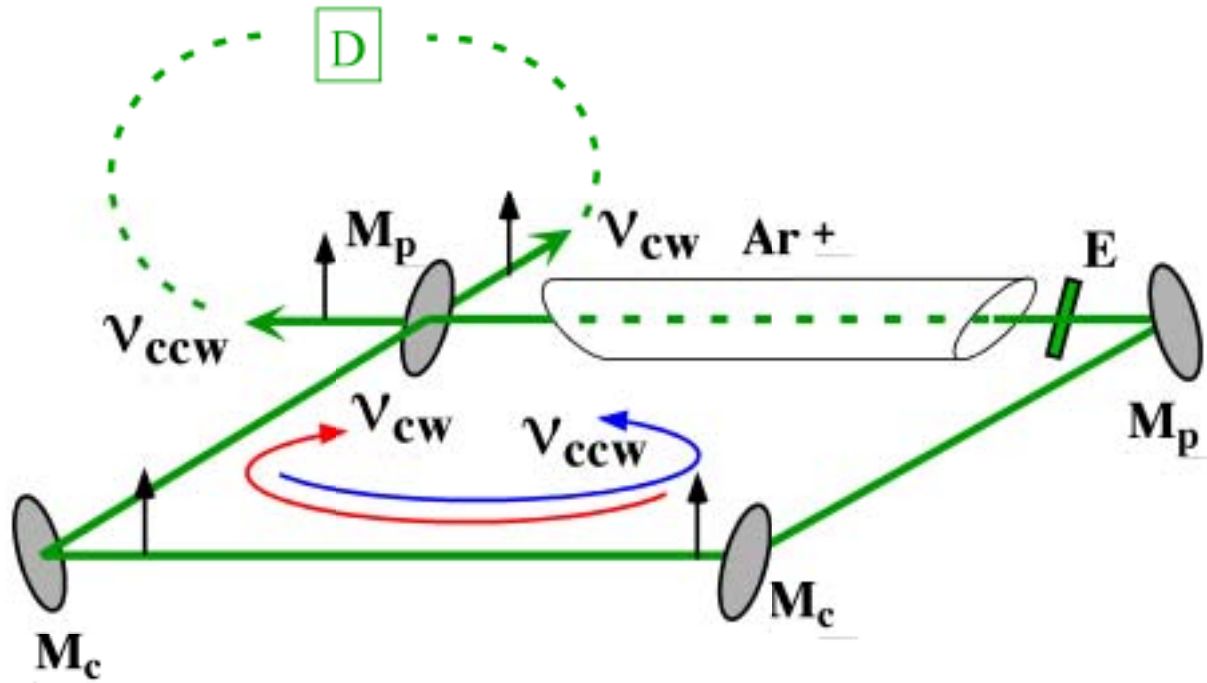
where  $a_{\text{F}}(\omega)$ ,  $a_{\text{OA}}(\omega)$ , and  $a_{\text{MC}}(\omega)$  are the coefficients of the Faraday effect, optical activity, and the magneto-chiral effect respectively. This last term changes sign as one changes between the two enantiomers of a chiral medium.

By a generalization of the Becquerel formula, one finds that

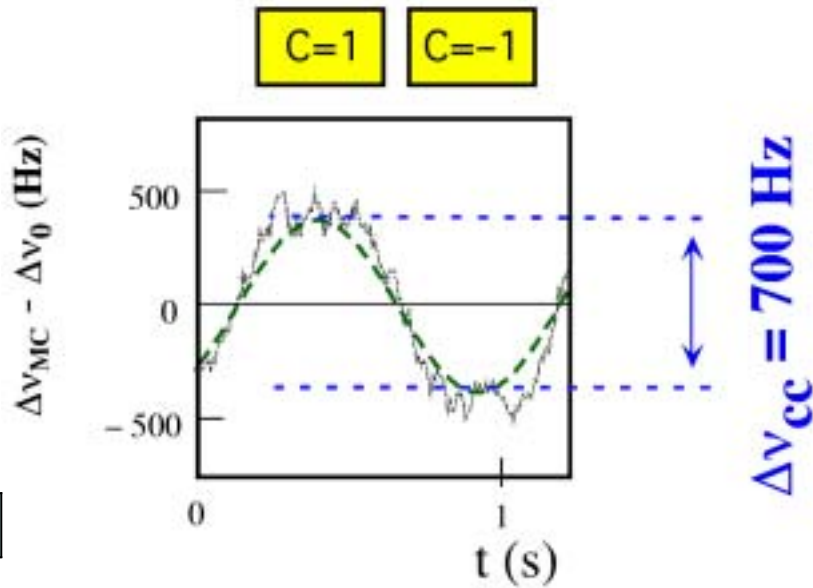
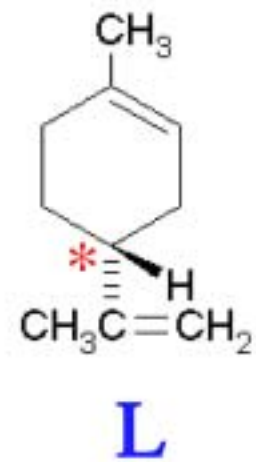
$$a_{\text{MC}}(\omega) = \frac{e}{2mc} \frac{d}{d\omega} a_{\text{OA}}(\omega)$$

Numerically, one predicts that  $\Delta n \approx 2 \times 10^{-11}$

# Active Interferometer



# Limonene



## ■ Observation of magnetochiral birefringence

- \*  $\Delta n = 10 \pm 1.6) \times 10^{-11}$  (  $B = 1300$  G )
- \* approx. agreement with Zel'dovich ( $\sim 2 \times 10^{-11}$  )
- \* proportional to O.A.
- \* independant of the direction of polarization

## Special Thanks to My Research Group



# Interest in Slow Light

Fundamentals of optical physics

Intrigue: Can (group) refractive index really be  $10^6$ ?

Optical delay lines, optical storage, optical memories

Implications for quantum information



# Challenge/Goal

Slow light in room-temperature solid-state material.

- Slow light in room temperature ruby  
(facilitated by a novel quantum coherence effect)
- Slow light in a structured waveguide

# Slow Light in Ruby

Need a large  $dn/d\omega$ . (How?)

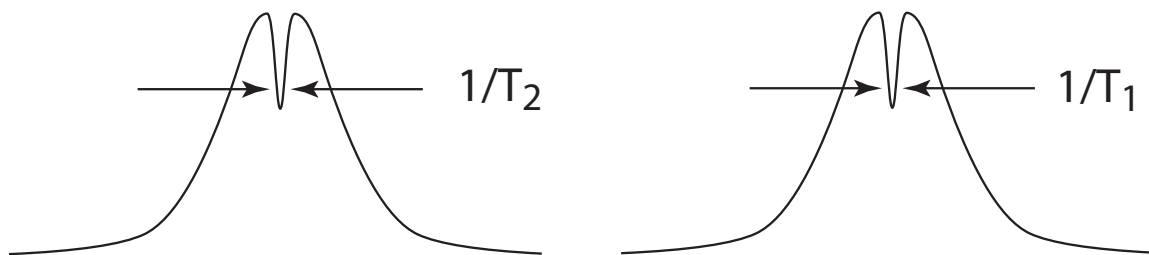
Kramers-Kronig relations:

Want a very narrow absorption line.

Well-known (to the few people how know it well) how to do so:

Make use of “spectral holes” due to population oscillations.

Hole-burning in a homogeneously broadened line; requires  $T_2 \ll T_1$ .

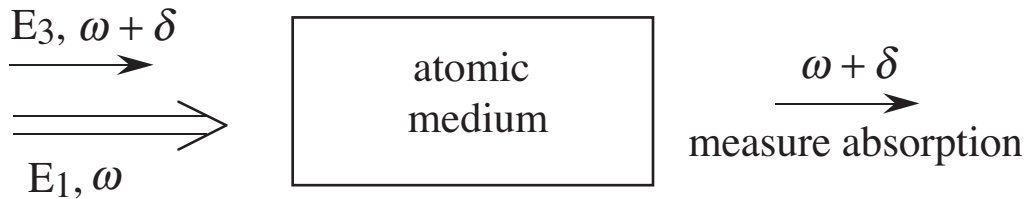
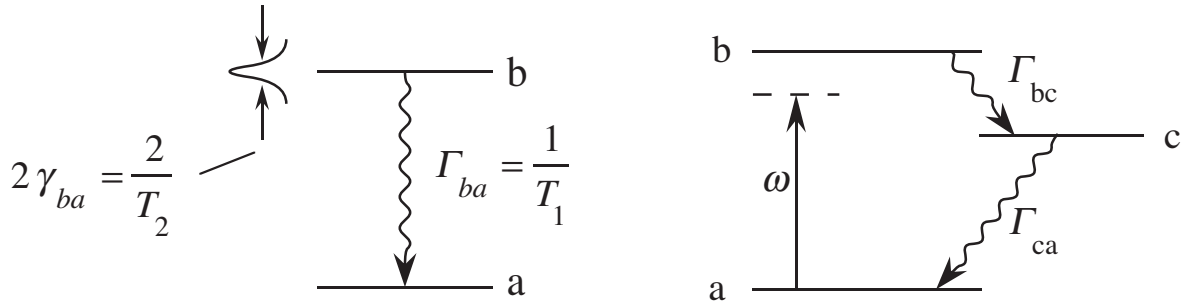


inhomogeneously  
broadened medium

homogeneously  
broadened medium  
(or inhomogeneously  
broadened)

PRL 90,113903(2003); see also news story in Nature.

# Spectral Holes Due to Population Oscillations



Population inversion:

$$(\rho_{bb} - \rho_{aa}) = w \quad w(t) \approx w^{(0)} + w^{(-\delta)} e^{i\delta t} + w^{(\delta)} e^{-i\delta t}$$

population oscillation terms important only for  $\delta \leq 1/T_1$

Probe-beam response:

$$\rho_{ba}(\omega + \delta) = \frac{\mu_{ba}}{\hbar} \frac{1}{\omega - \omega_{ba} + i/T_2} \left[ E_3 w^{(0)} + E_1 w^{(\delta)} \right]$$

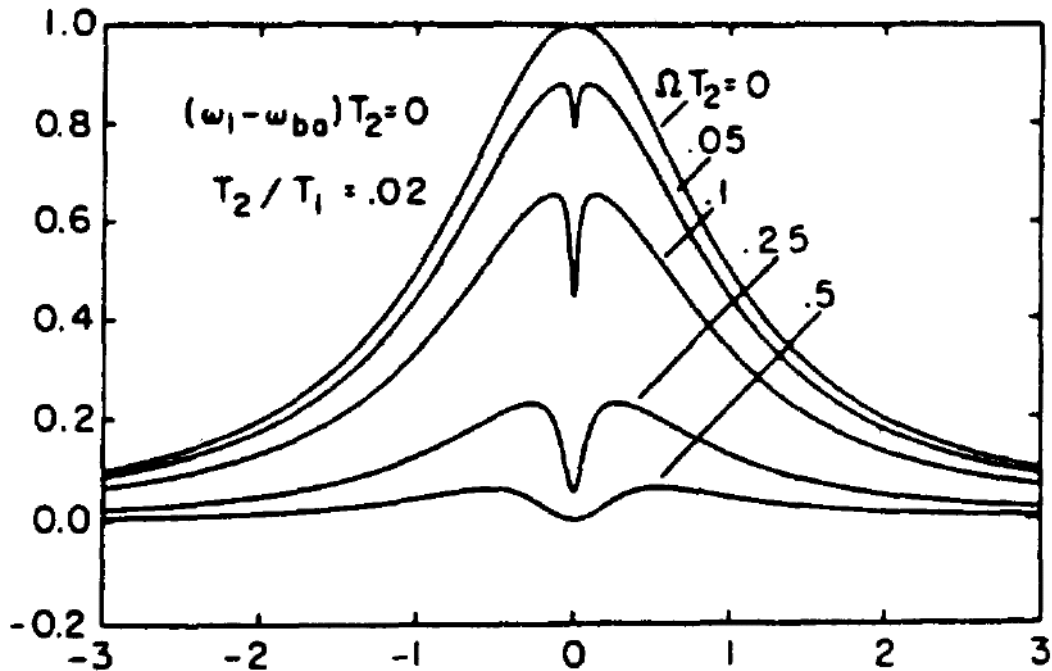
Probe-beam absorption:

$$\alpha(\omega + \delta) \propto \left[ w^{(0)} - \frac{\Omega^2 T_2}{T_1} \frac{1}{\delta^2 + \beta^2} \right]$$

linewidth  $\beta = (1/T_1)(1 + \Omega^2 T_1 T_2)$

# Spectral Holes in Homogeneously Broadened Materials

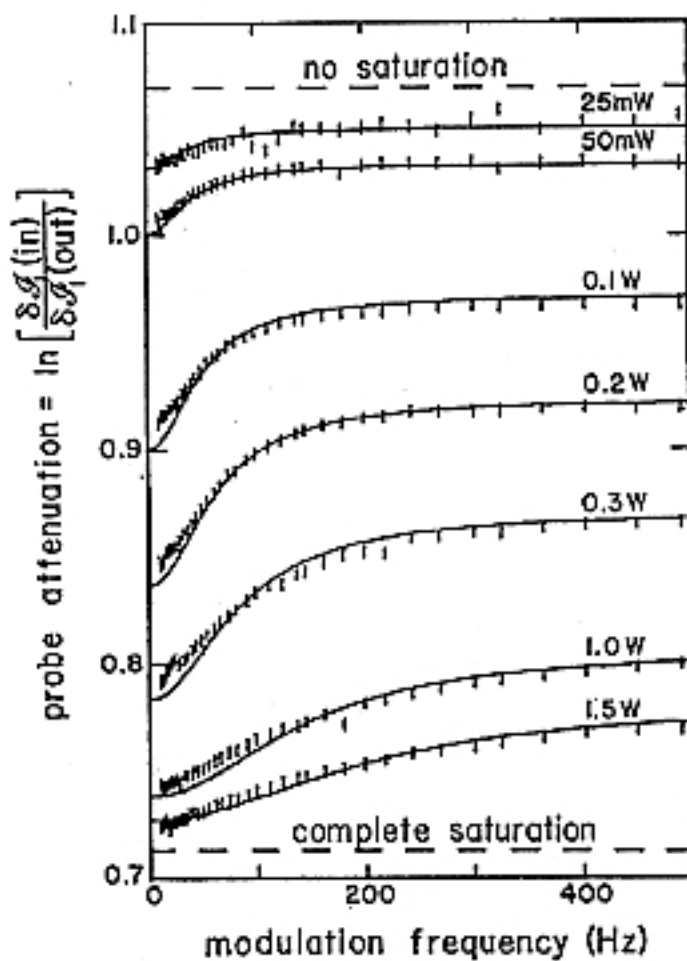
Occurs only in collisionally broadened media ( $T_2 \ll T_1$ )



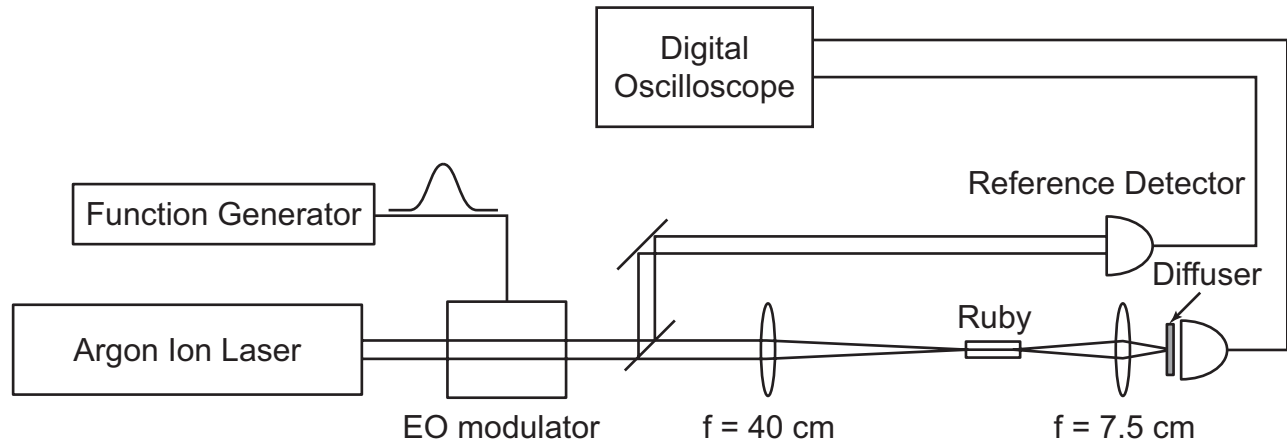
Boyd, Raymer, Narum and Harter, Phys. Rev. A24, 411, 1981.

**OBSERVATION OF A SPECTRAL HOLE DUE TO POPULATION OSCILLATIONS  
IN A HOMOGENEOUSLY BROADENED OPTICAL ABSORPTION LINE**

Lloyd W. HILLMAN, Robert W. BOYD, Jerzy KRASINSKI and C.R. STROUD, Jr.  
*The Institute of Optics, University of Rochester, Rochester, NY 14627, USA*

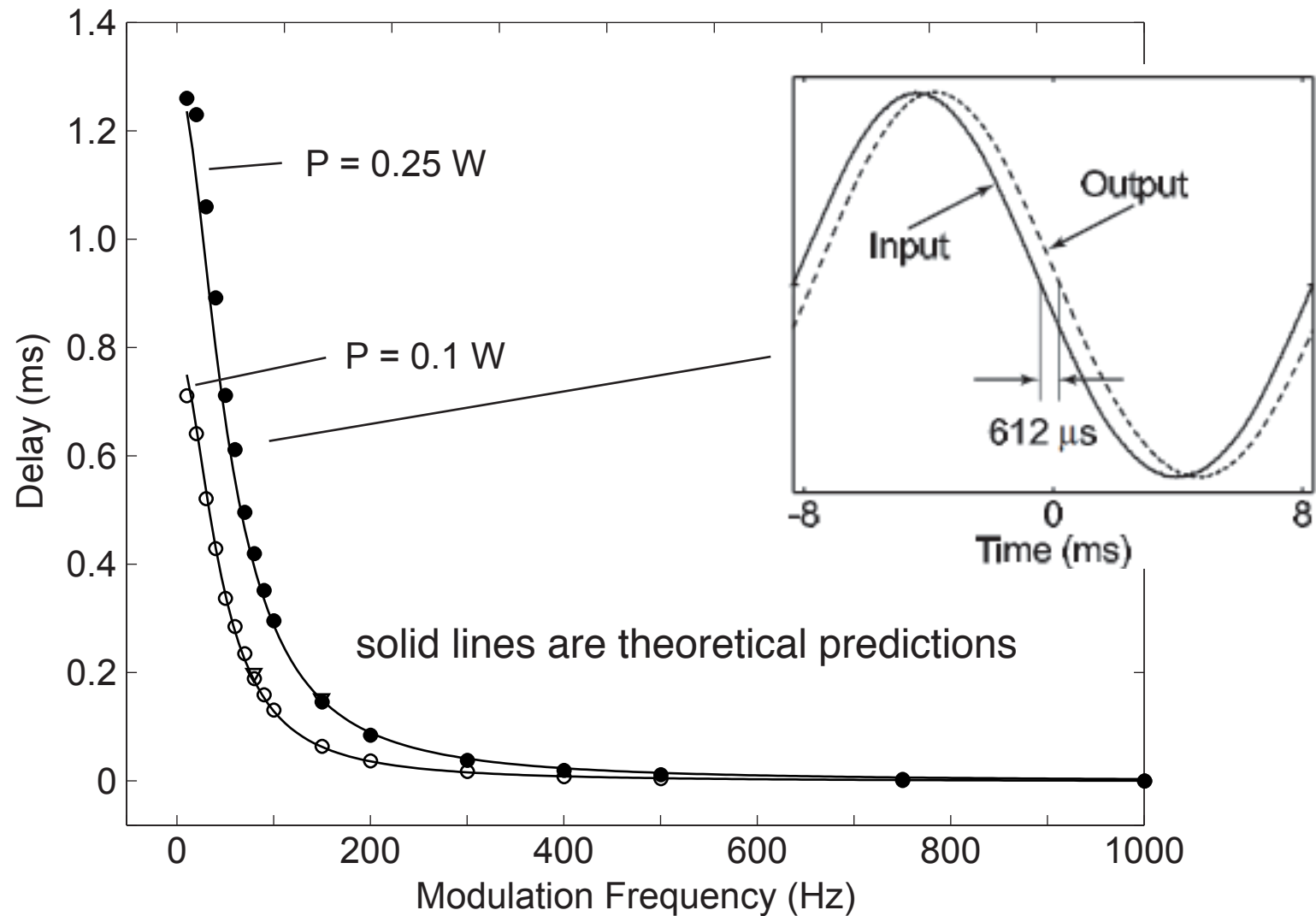


# Experimental Setup Used to Observe Slow Light in Ruby



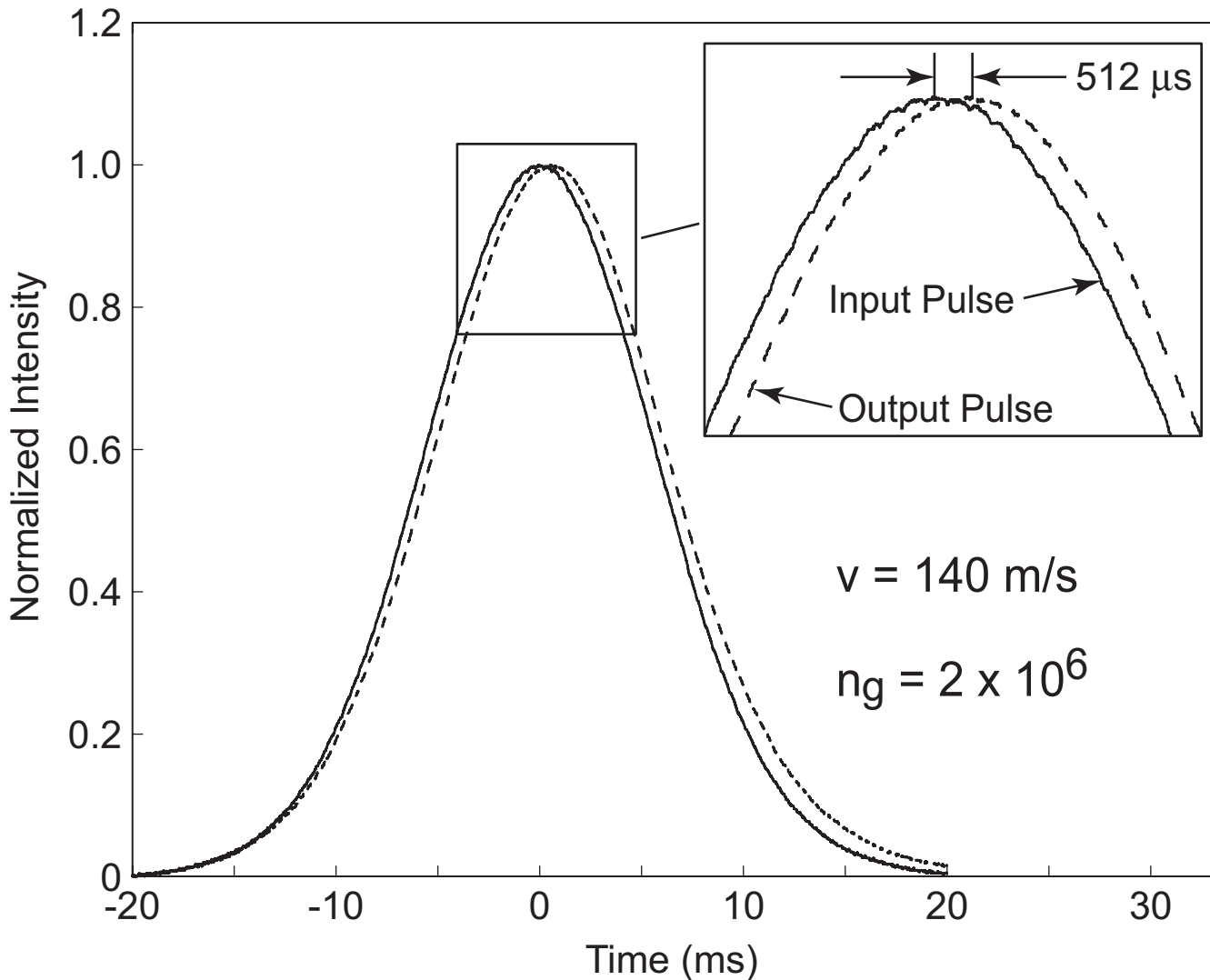
7.25 cm ruby laser rod (pink ruby)

# Measurement of Delay Time for Harmonic Modulation



For 1.2 ms delay,  $v = 60 \text{ m/s}$  and  $n_g = 5 \times 10^6$

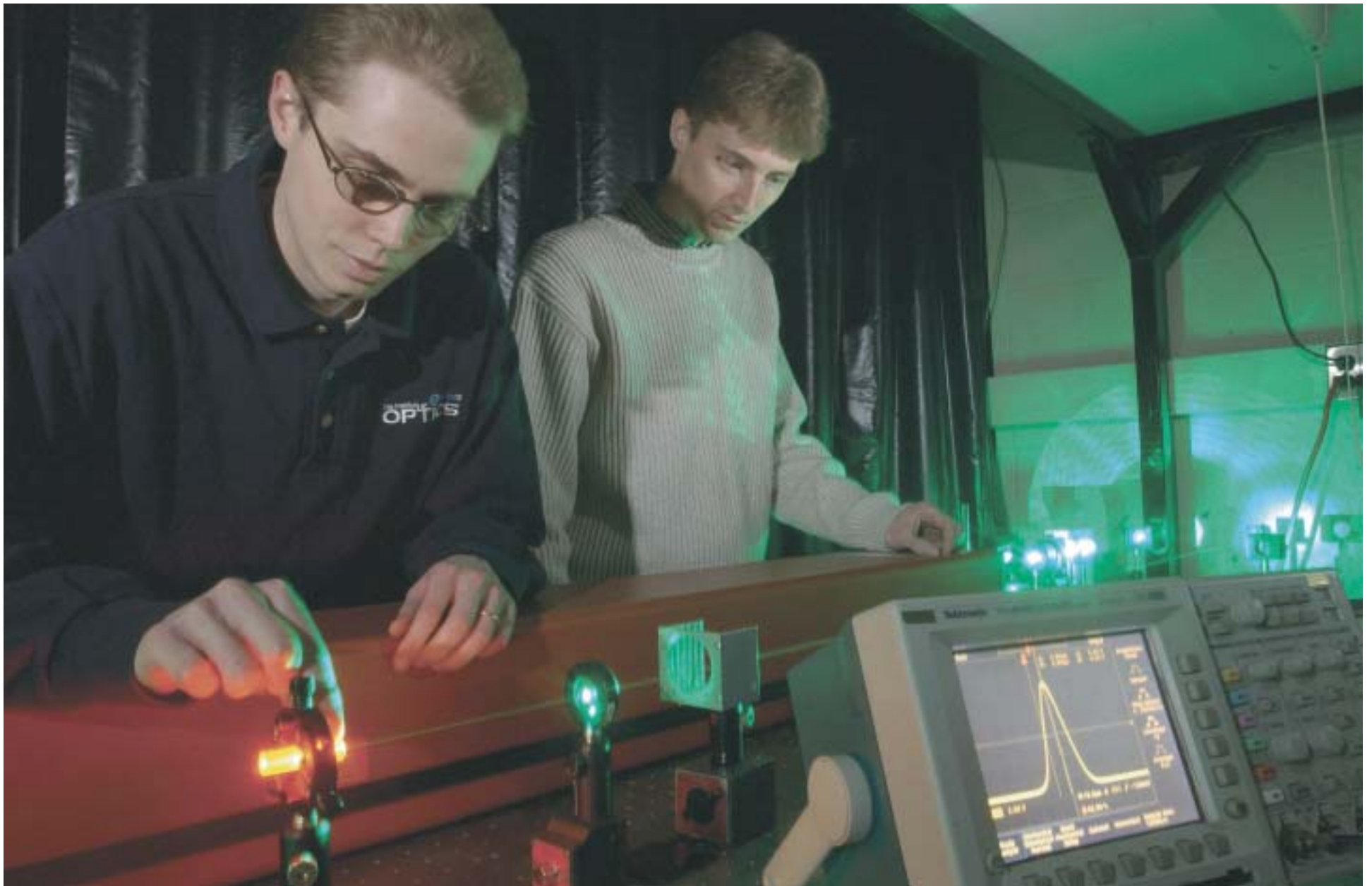
# Gaussian Pulse Propagation Through Ruby



No pulse distortion!



# Matt Bigelow and Nick Lepeshkin in the Lab



**Thank you for your attention.**