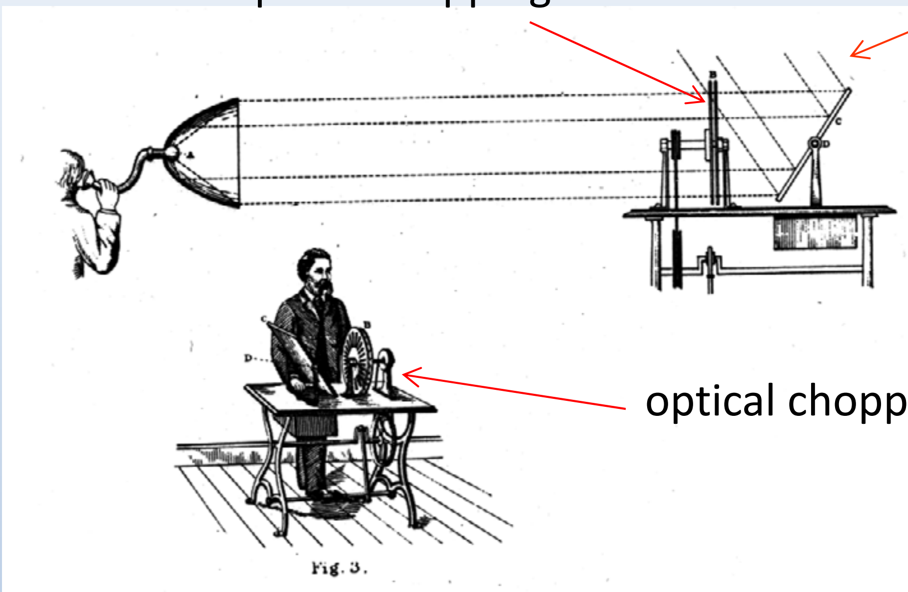
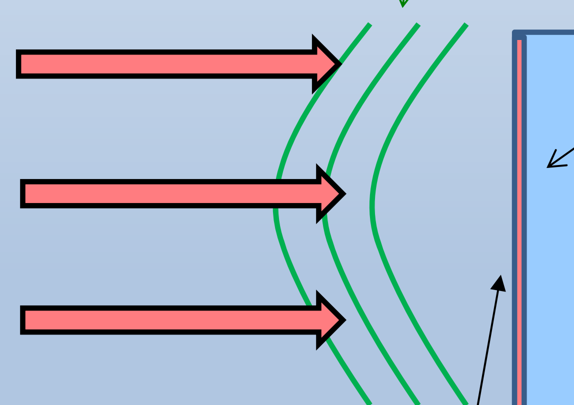
Tutorial on Photoacoustics: from the Wave Equation for Pressure to Sound Generation from Photothermal Interference

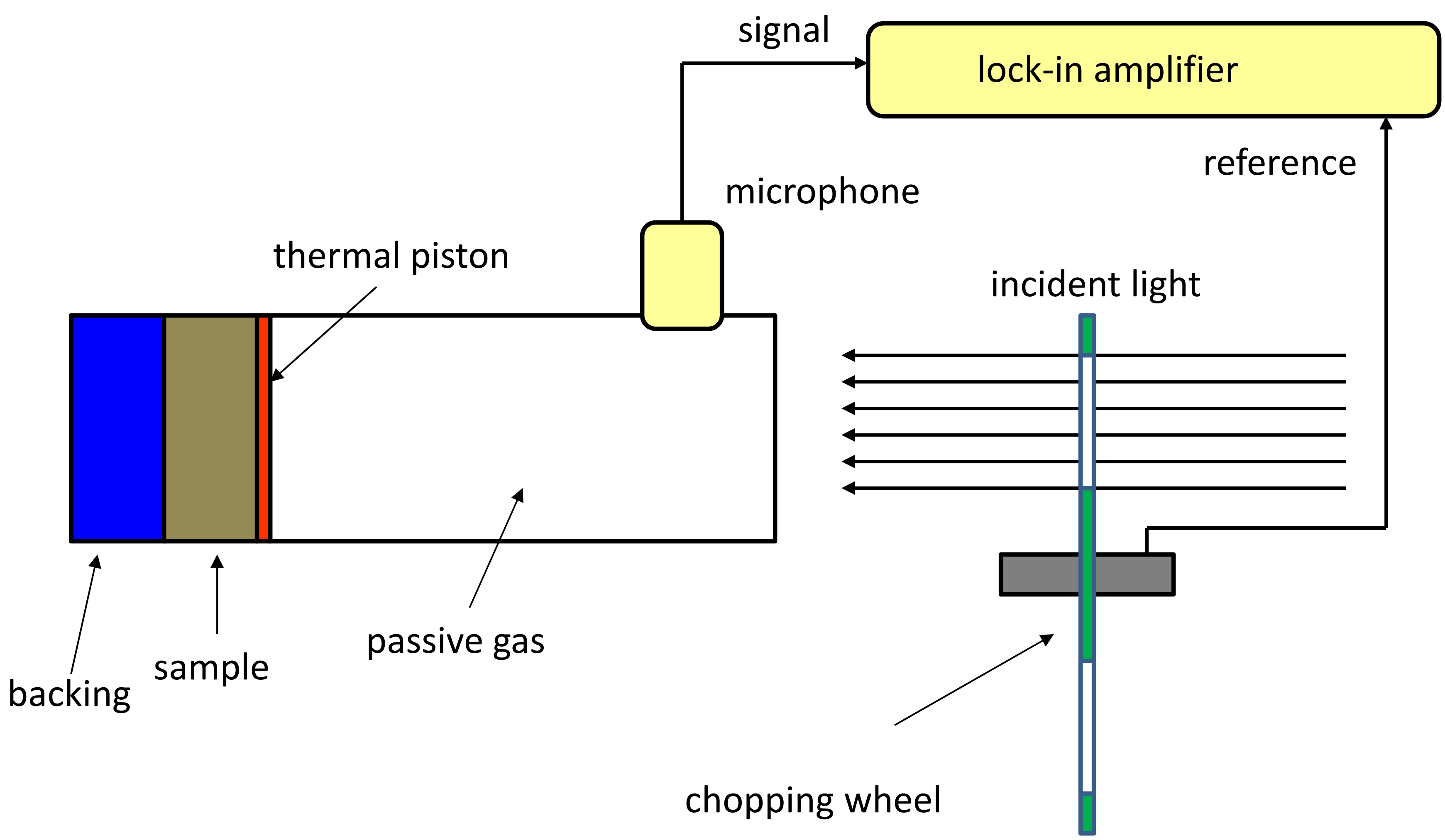
Gerald J. Diebold
Department of Chemistry
Brown University
Providence, Rhode Island
USA

Photoacoustic Effect Generated at Surfaces





Photoacoustic Cell



A. Rosencwaig , *Photoacoustics and Photoacoustic Spectroscopy*

Theory of Sound Production

Heat Diffusion Equation

$$\frac{\partial \theta}{\partial t} = \alpha \frac{\partial^2 \theta}{\partial x^2} + \frac{H}{\rho C_P}$$

$$H = \tfrac{1}{2} \beta I_0 e^{\beta x} (1 + \cos \omega t)$$

Signal amplitude Q

$$Q = \frac{(r-1)(b+1)e^{\sigma l} - (r+1)(b-1)e^{-\sigma l} + 2(b-r)e^{-\beta l}}{(g+1)(b+1)e^{\sigma l} - (g-1)(b-1)e^{-\sigma l}}$$

$$b = \frac{\kappa'' a''}{\kappa a} \quad \frac{\text{backing}}{\text{sample}} \qquad g = \frac{\kappa' a}{\kappa a} \quad \frac{\text{gas}}{\text{sample}} \qquad \sigma = (1+i)\sqrt{\frac{\omega}{2\alpha}}$$

$$r = \frac{(1-i)}{2} \beta \mu$$

α thermal diffusivity

β optical absorption coefficient

κ thermal conductivity

μ thermal diffusion length

Probing beneath the Surface of an Apple with a Wax Coating

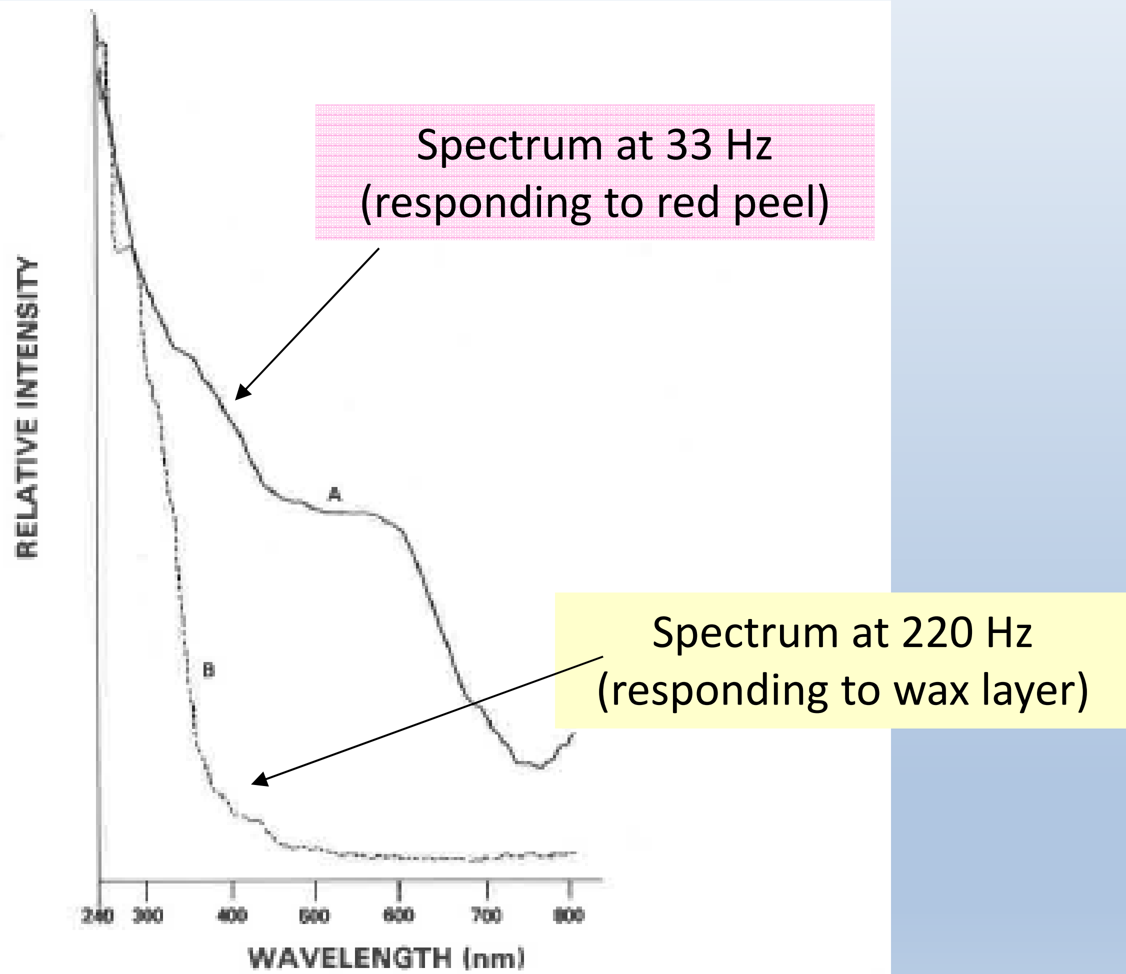
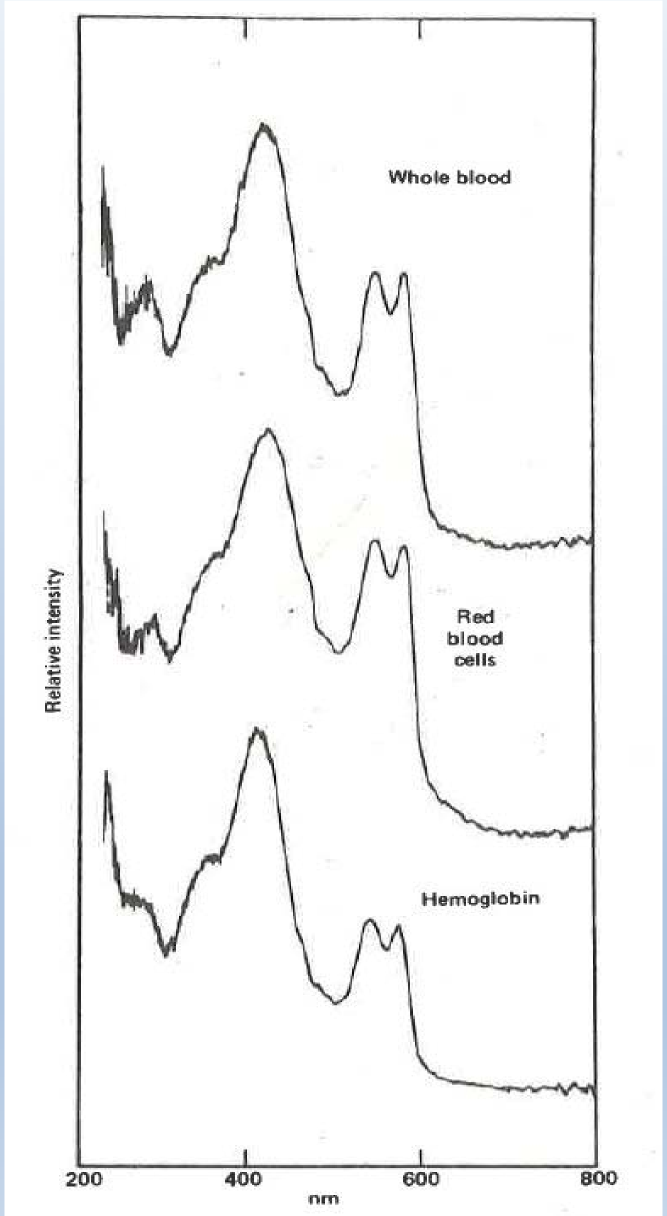


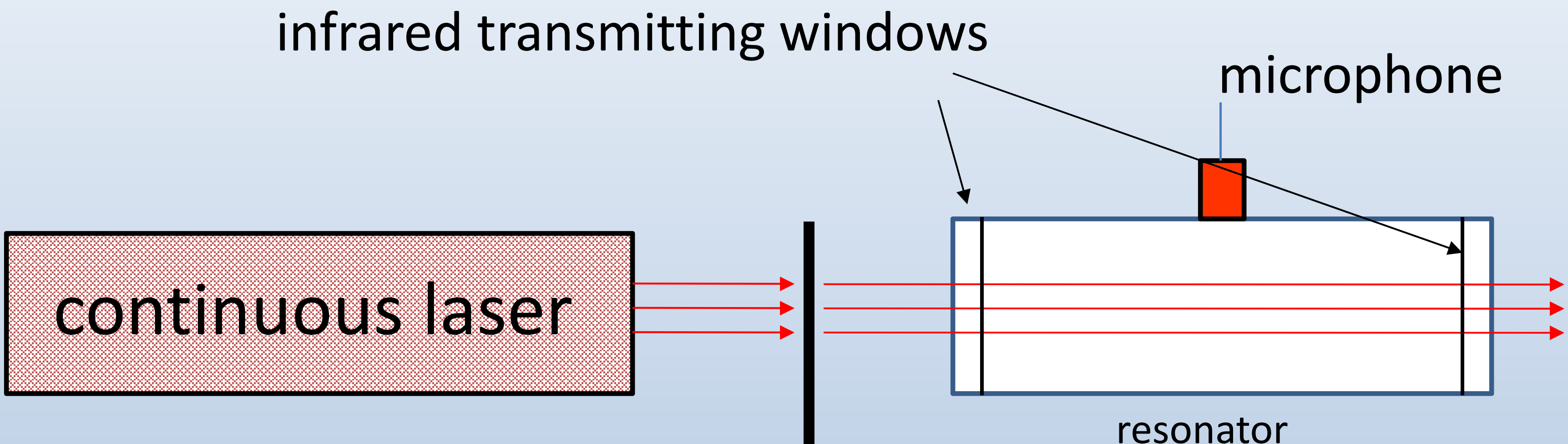
Figure 17.7 Photoacoustic spectra on intact apple peel. The dashed line spectrum was taken at 220 Hz and shows absorption only within the upper waxy layer. The solid line spectrum was taken at 33 Hz and shows absorption within the red peel below the waxy layer as well. (Reproduced by permission from Rosencwaig, 1978.)

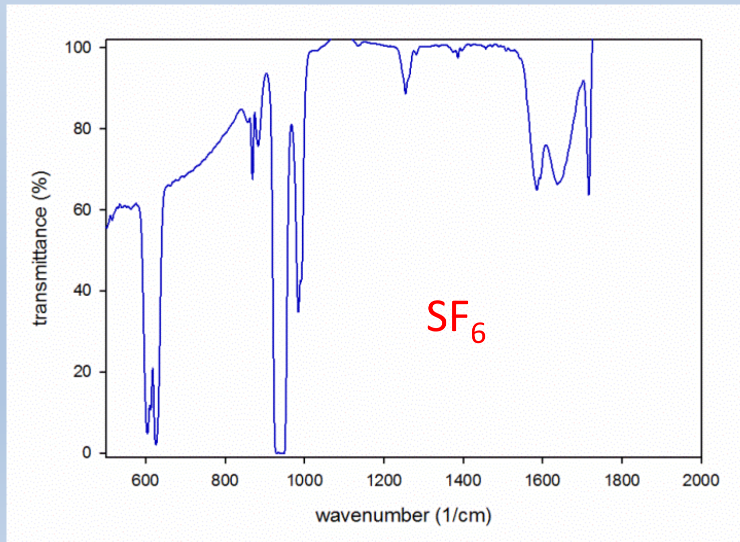
Surface Spectroscopy: Blood Samples



A. Rosencwaig , *Photoacoustics* and Photoacoustic Spectroscopy

Photoacoustic Effect in Gases and Liquids





$$PV = nRT$$

$$\left(\nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\right)p = -\frac{\beta}{C_P}\frac{\partial H(x,t)}{\partial t}$$

Trace Gas Detection

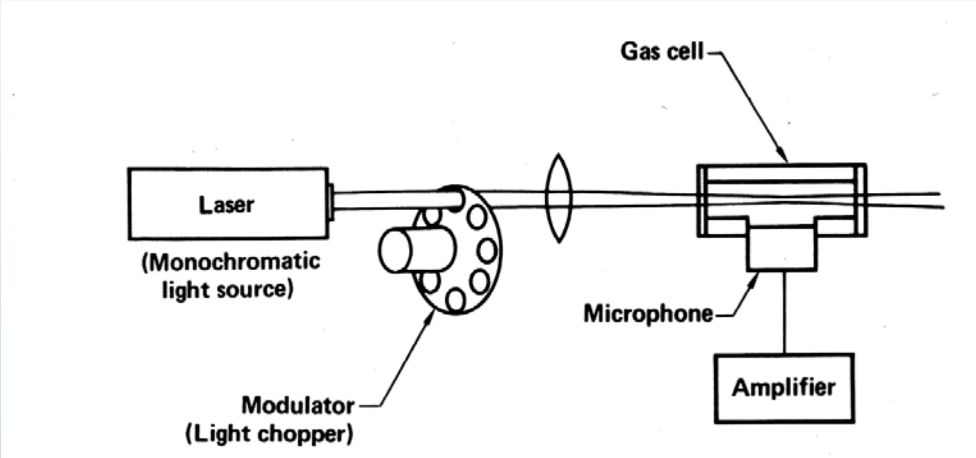


Table 1. Noise-limited sensitivities for detecting pollutant gases.

Gas	Sensitivity (ppb)	Laser	Infrared source transition	Wavelength (μm)
Ammonia	0.4	CO	P_{19-18} (15)	6.1493
Benzene	3	CO_2	00°1–02°0 P(30)	9.6392
1,3-Butadiene	1	CO	P_{20-19} (13)	6.2153
1,3-Butadiene	2	CO_2	00°1–10°0 P(30)	10.6964
1-Butene	2	CO	P_{19-18} (9)	6.0685
1-Butene	2	CO_2	00°1–10°0 P(38)	10.7874
Ethylene	0.2	CO_2	00°1–10°0 P(14)	10.5321
Methanol	0.3	CO_2	00°1–02°0 P(34)	9.6760
Nitric oxide	0.4	CO	P_{8-7} (11)	5.2148
Nitrogen dioxide	0.1	CO	P_{20-19} (14)	6.2293
Propylene	3	CO	P_{19-18} (9)	6.0685
Trichloroethylene	0.7	CO_2	00°1–10°0 P(24)	10.6321
Water	14	CO	P_{17-16} (13)	5.9417

L. B. Kreuzer, N. D. Kenyon, C. K. N. Patel, *Science* **177**, 347 (1972)

Spectroscopy with a Tunable Laser

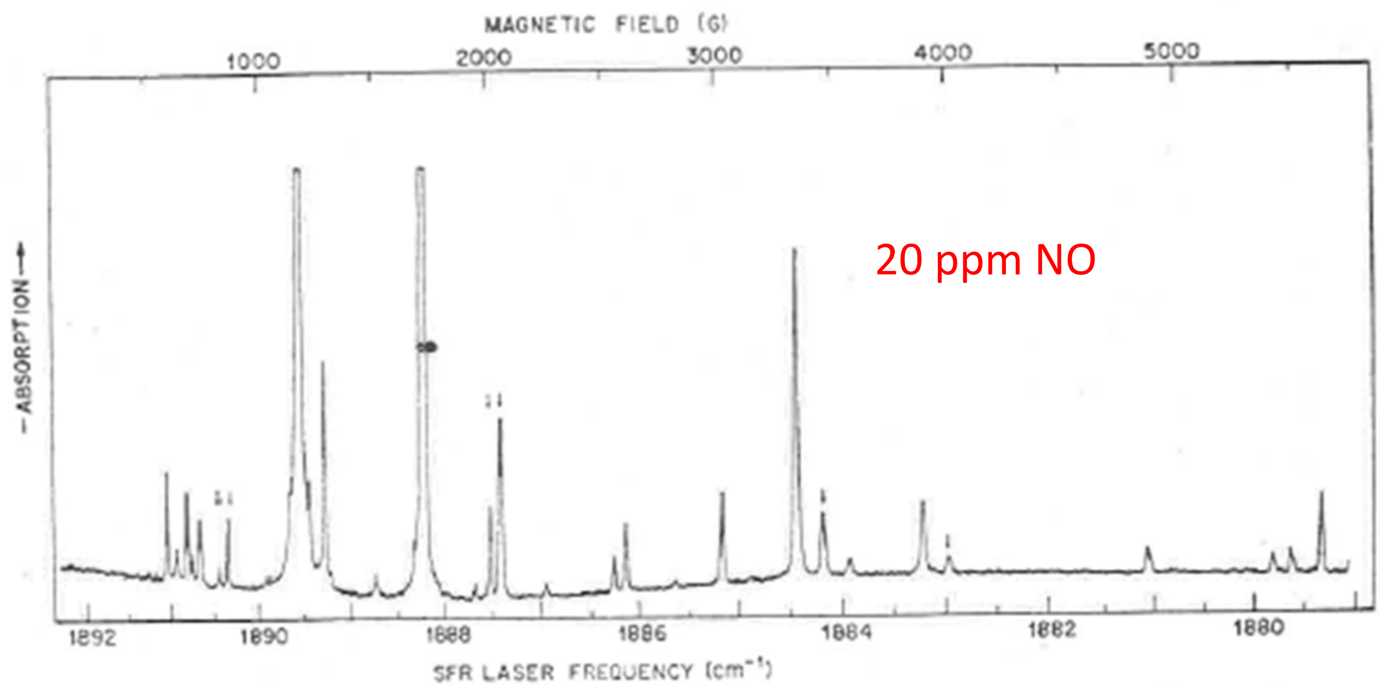


Fig. 12. Optoacoustic absorption spectrum of 20 ppm NO, 76 torr N_2, obtained with a magnetically tuned spin-flip Raman laser; pump laser at 1892.25 cm^{-1}. (From Patel, 1973.)

Sensitivity of the Human Ear

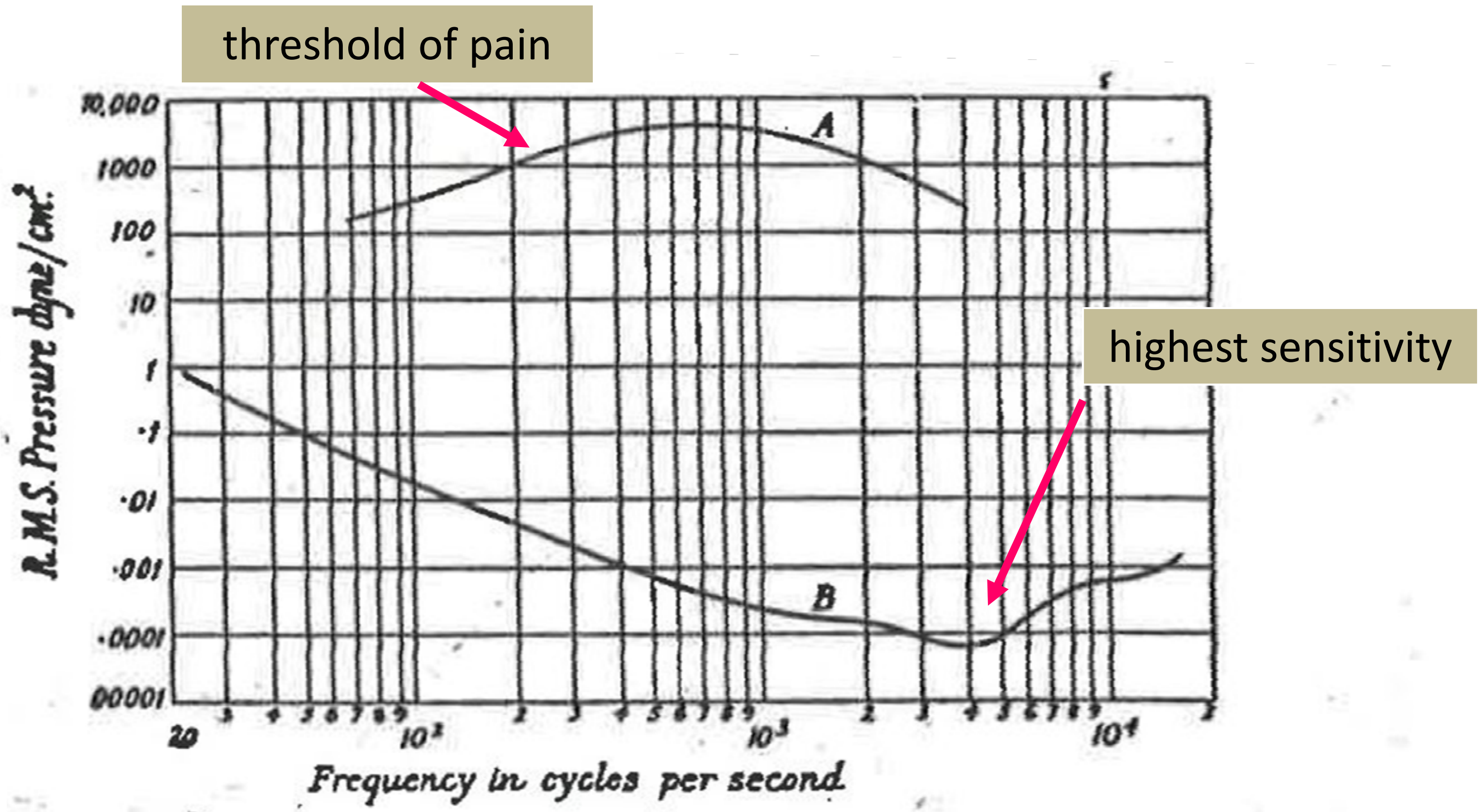


Fig. 17.4.—Limits of audibility for normal ears
A, Threshold of feeling (after Wegel)
B, Threshold of audibility (after Fletcher and Munson)

Acoustics, Alexander Wood, Interscience, 1941

Sensitivity Parameters

It is interesting to calculate the various quantities for the minimum audible sound wave at the frequency to which the ear is most sensitive. We may take the frequency as 3500 and the R.M.S. pressure amplitude as 8×10^{-5} dyne/cm.^{2}

$$\text{Intensity } I = \frac{P^2}{R} = \frac{(8 \times 10^{-5})^2}{41{\cdot}2} = 1{\cdot}55 \times 10^{-10} \text{ ergs per cm.}^2\text{/sec.}$$

$$= 1{\cdot}55 \times 10^{-11} \text{ microwatt/cm.}^2$$

$$\text{Velocity amplitude } \hat{v} = \sqrt{\frac{2I}{R}} = 2{\cdot}74 \times 10^{-6} \text{ cm./sec.}$$

$$\text{Maximum condensation } \hat{S} = \frac{\hat{v}}{c} = 8{\cdot}07 \times 10^{-11}.$$

$$\text{Displacement amplitude } a = \frac{\hat{v}}{2\pi f} = 1{\cdot}25 \times 10^{-10} \text{ cm.}$$

Intensity: 1.5×10^{-13} W/m^2

Sound Generation through Electrostriction

$$\left(\nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\right)p = -\frac{\beta}{C_P}\frac{\partial H}{\partial t} + \frac{\zeta n c_l c^2}{2}\frac{\partial^2 I}{\partial t^2}$$

$$\zeta = (n^2 - 1) + \frac{1}{3}(n^2 - 1)^2$$

n index of refraction

c_l speed of light

c sound speed

H. M. Lai and K. Young J. Acoust. Soc. A. 72 2000 (1982)

Thermal Expansion: Equations for Pressure and Temperature in a Fluid

$$\frac{\partial}{\partial t}\left(T - \frac{\gamma - 1}{\gamma \tilde{\alpha}} p\right) = \frac{K}{\rho C_P} \nabla^2 T + \frac{H(\mathbf{r}, t)}{\rho C_P}$$

$$\left(\nabla^2 - \frac{\gamma}{c^2} \frac{\partial^2}{\partial t^2}\right) p = -\frac{\gamma \tilde{\alpha}}{c^2} \frac{\partial^2 T}{\partial t^2}$$

$$\tilde{\alpha} = \left(\frac{\partial P}{\partial T}\right)_V$$

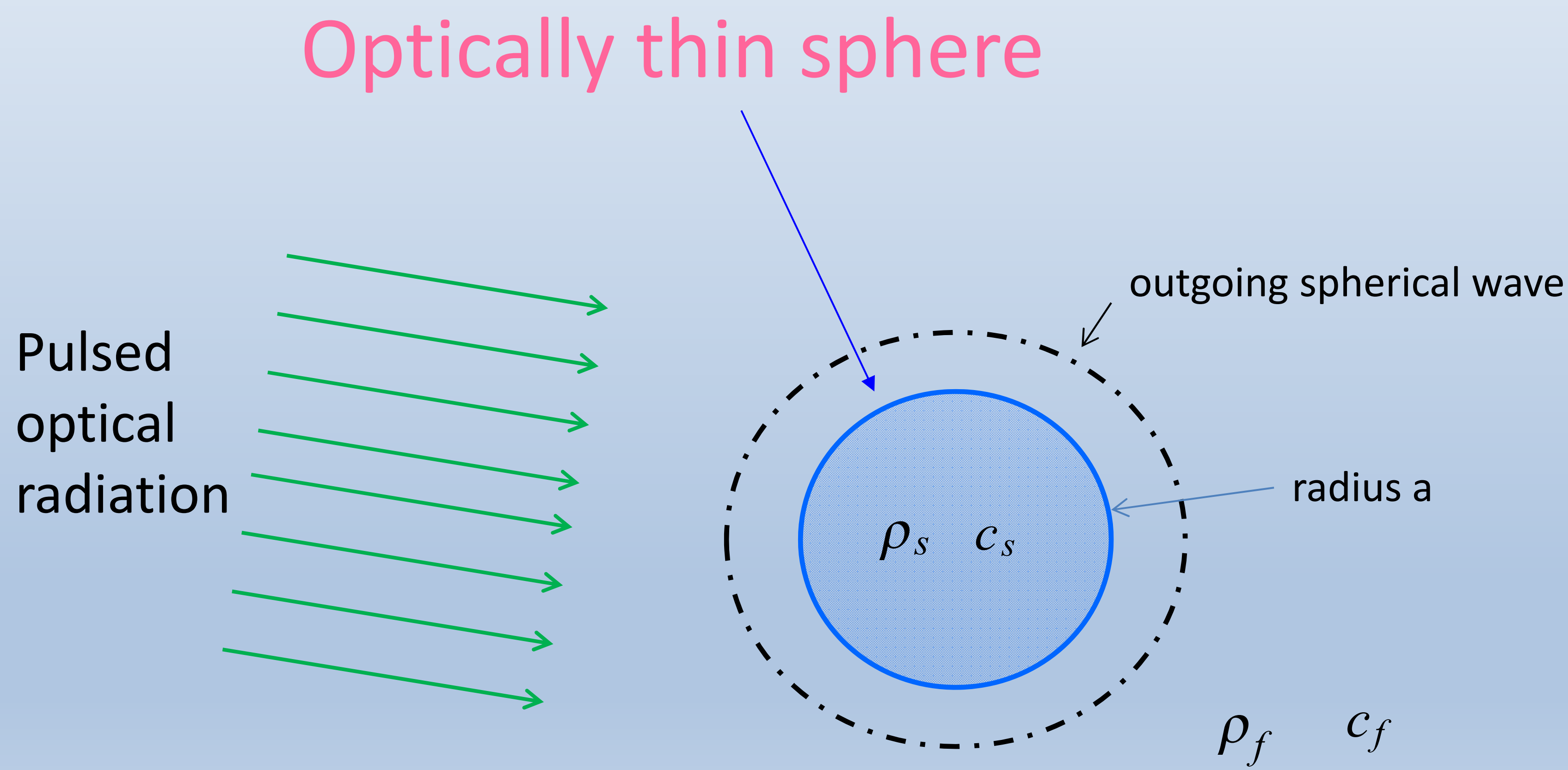
When thermal conductivity K=0

$$\left(\nabla^2 - \frac{1}{c^2} \frac{\partial^2}{\partial t^2}\right) p = -\frac{\beta}{C_P} \frac{\partial H(x, t)}{\partial t}$$

p	pressure
c	sound speed
β	thermal expansion coefficient
C_P	specific heat capacity
H	power density delivered by light source

P. Morse and K. Ingard, *Theoretical Acoustics* 1968

Simple Geometrical Bodies: Sphere Layer and Cylinder



Transform Wave Equation to Frequency Domain

Wave equation

$$(\nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2})p = -\frac{\beta}{C_P}\frac{\partial H}{\partial t}$$

$$H(r,t) = \alpha I_0 e^{-i\omega t}$$

Helmholtz equation

$$(\nabla^2 + k^2)p = \begin{cases} \frac{i\alpha\omega\beta I_0}{C_P} & \text{inside} \\ 0 & \text{outside} \end{cases}$$

$$k = \omega/c$$

$$p_s = [1 + \hat{P}_s \frac{\sin k_s r}{k_s r}]e^{-i\omega t}$$

$$p_f = (\hat{P}_f/k_f r)e^{i(k_f r - \omega t)}$$

Boundary conditions:

$$p_s = p_f$$

$$\frac{\nabla p_s}{\rho_s} = \frac{\nabla p_f}{\rho_f}$$

G. J. Diebold, and P. J. Westervelt, *J Acoust. Soc. Am.* **84**, 2245 (1988)

Pressure from Sphere

Frequency domain solution:

$$p_f(\hat{q}) = \frac{i\alpha\beta I_0 c_s a}{C_P(r/a)} \frac{[(\sin\hat{q} - \hat{q}\cos\hat{q})/\hat{q}^2]e^{-i\hat{q}\hat{\tau}}}{[(1-\hat{\rho})(\sin\hat{q}/\hat{q}) - \cos\hat{q} + i\hat{\rho}\hat{c}\sin\hat{q}]}$$

$$\hat{q} = \omega a/c_s$$

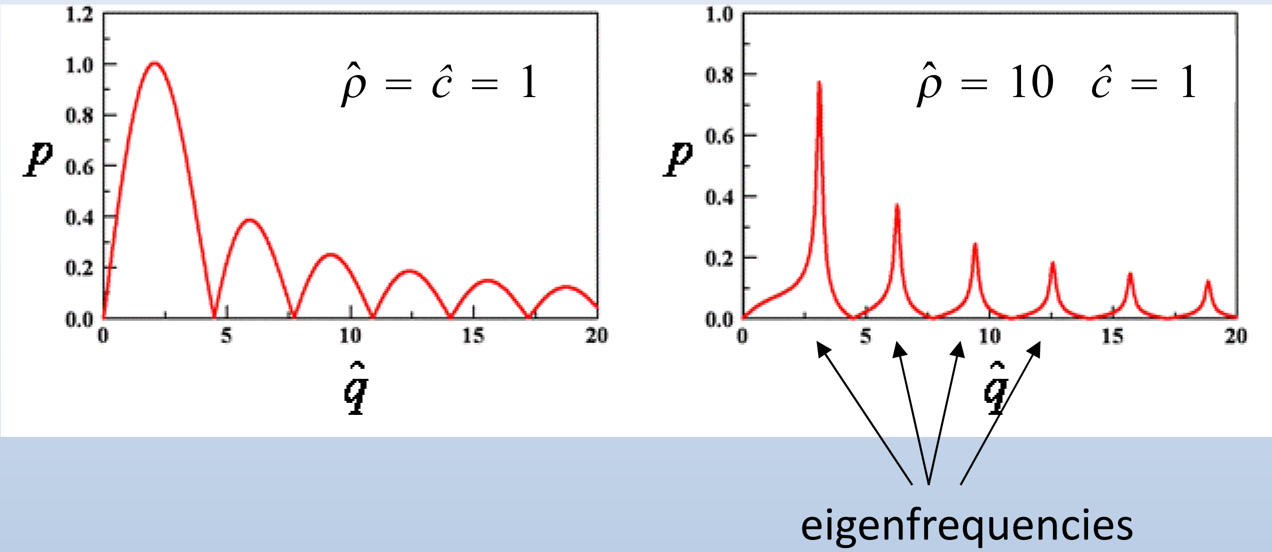
Time domain solution:

$$p_f(\hat{\tau}) = \frac{i\alpha\beta F c_s^2}{2\pi C_P(r/a)} \int_{-\infty}^{\infty} \frac{[(\sin\hat{q} - \hat{q}\cos\hat{q})/\hat{q}^2]e^{-i\hat{q}\hat{\tau}}}{[(1-\hat{\rho})(\sin\hat{q}/\hat{q}) - \cos\hat{q} + i\hat{\rho}\hat{c}\sin\hat{q}]} d\hat{q}$$

$\hat{\rho} = \rho_s/\rho_f \quad \hat{c} = c_s/c_f \qquad \hat{\tau} = (c_s/a)[t - (r-a)/c_f]$

Frequency Domain Solutions

Pressure vs. frequency

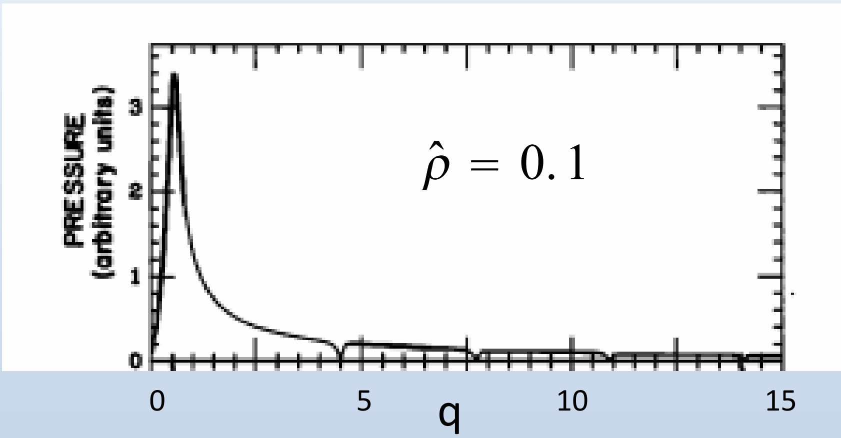


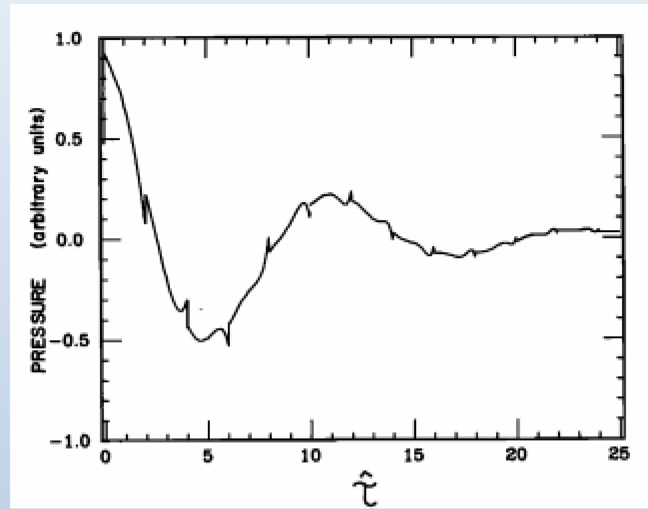
$$p_f(\hat{q}) = \frac{i\alpha\beta I_0 c_s a}{C_P(r/a)} \frac{[(\sin\hat{q} - \hat{q}\cos\hat{q})/\hat{q}^2]e^{-i\hat{q}\hat{\tau}}}{[(1-\hat{\rho})(\sin\hat{q}/\hat{q}) - \cos\hat{q} + i\hat{\rho}\hat{c}\sin\hat{q}]}$$

$$\hat{q} = \omega a / c_s$$

$$\hat{\rho} = \rho_s/\rho_f \quad \hat{c} = c_s/c_f$$

Low Density Limit: Bubble Oscillations

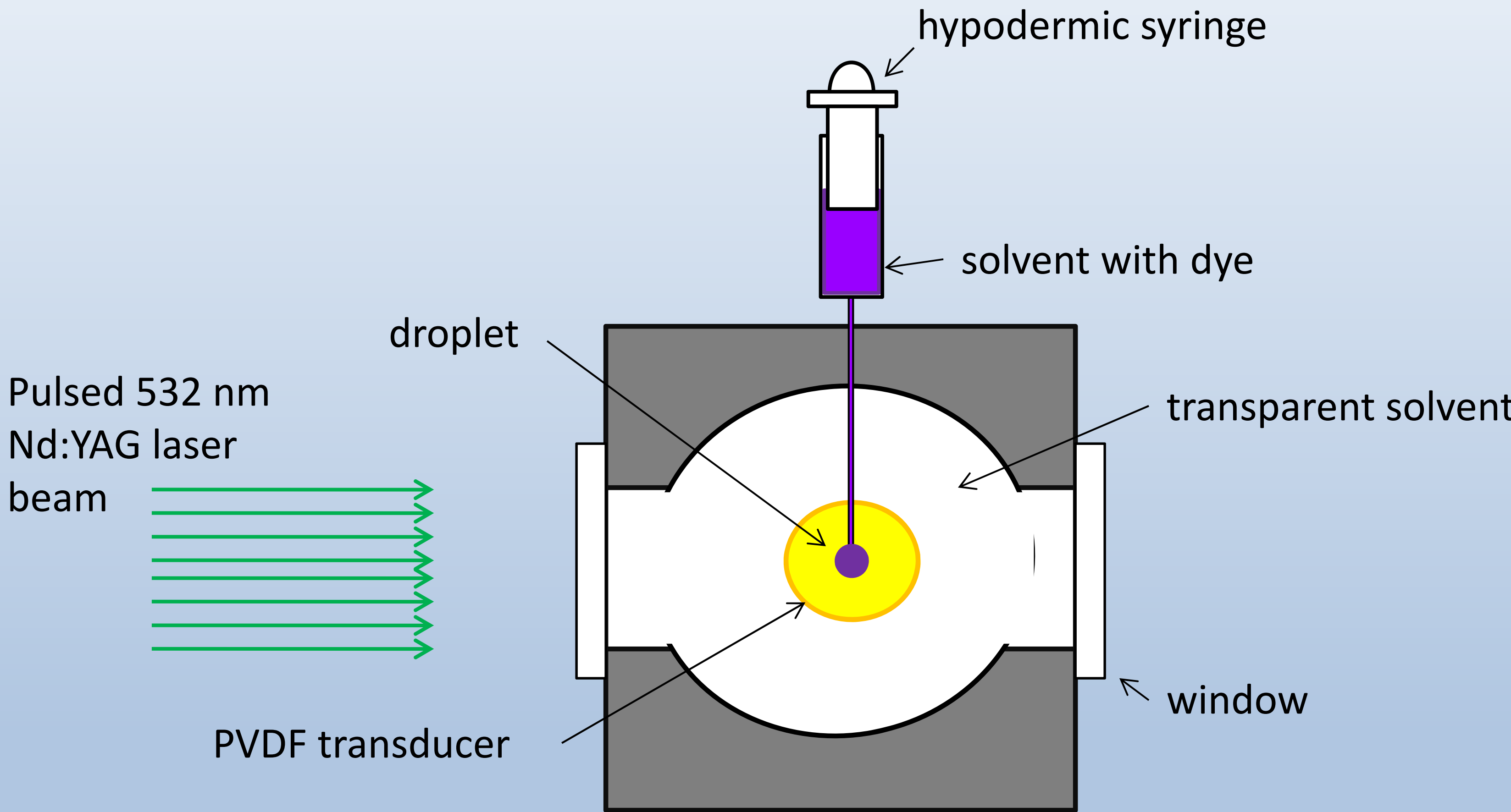


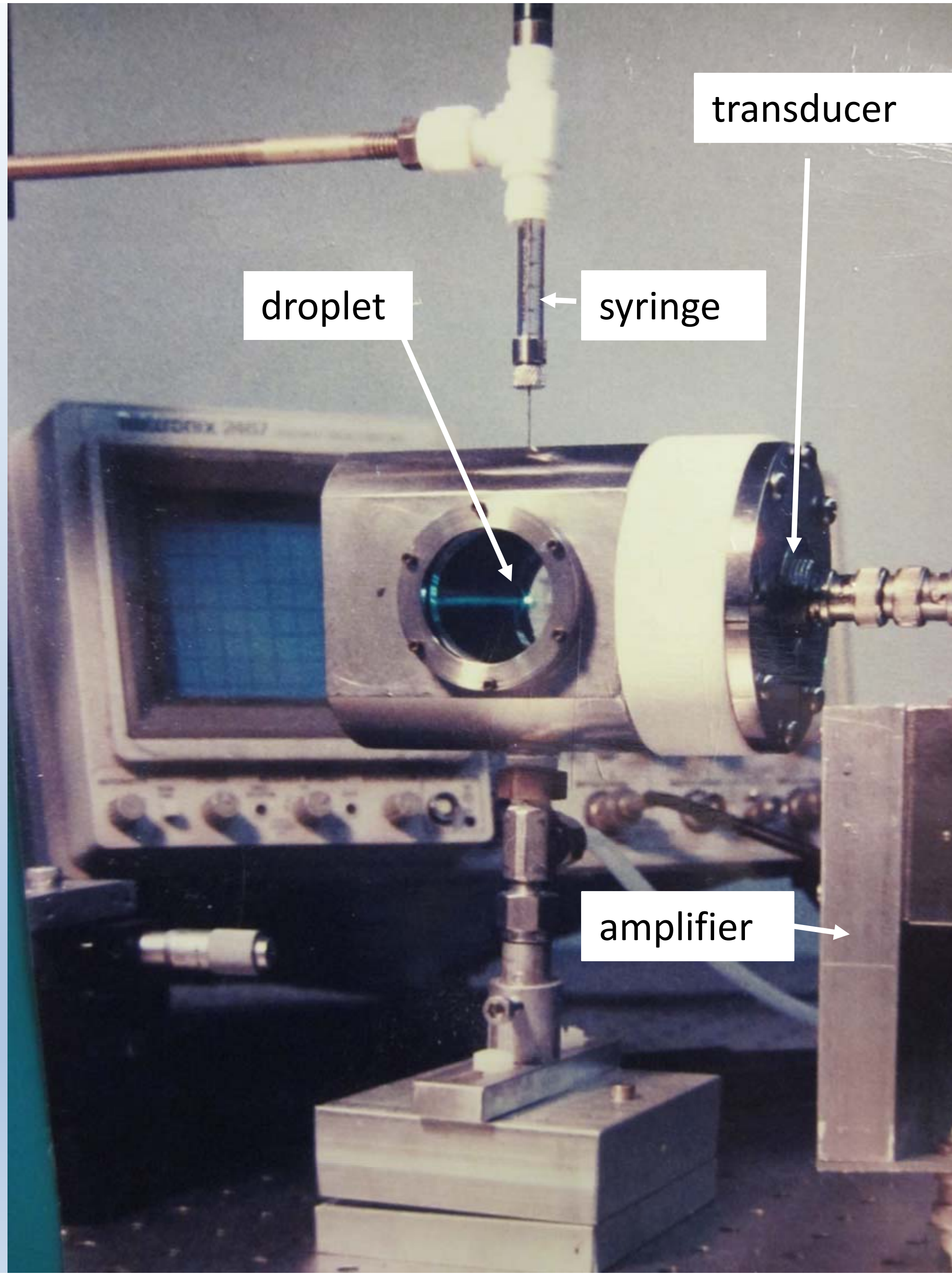


$$\omega_{Bubble} = \frac{c_s}{a}\sqrt{3\hat{\rho}}$$

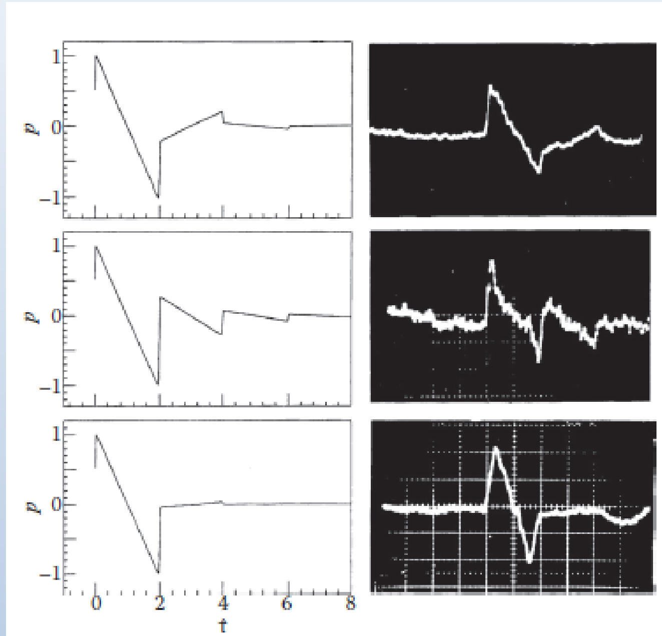
$$\gamma_{\text{Damping}} T_{\text{Oscillation}} = 3\pi\hat{c}\sqrt{\hat{\rho}/3}$$

Time Domain Experiments with Droplets




transducer
droplet
syringe
amplifier

Time Domain Experimental Results



Hexane + CCl_4 droplet in water

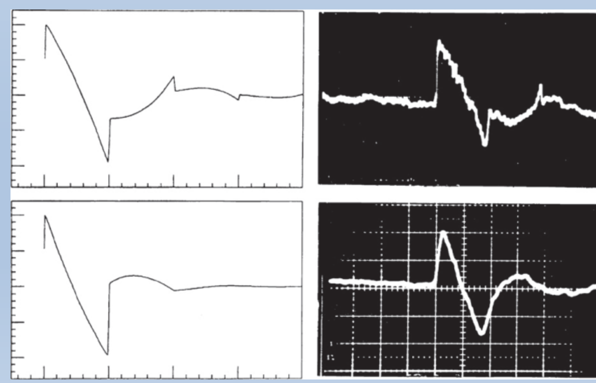
$\hat{\rho} = 1.01 \quad \hat{c} = 0.645$

Formamide droplet in hexane + CCl_4

$\hat{\rho} = 1.00 \quad \hat{c} = 1.65$

Tetralin droplet in water

$\hat{\rho} = 0.97 \quad \hat{c} = 0.962$



Hexane droplet in water

$\hat{\rho} = 0.660 \quad \hat{c} = 0.708$

CCl_4 droplet in water

$\hat{\rho} = 1.60 \quad \hat{c} = 0.618$

Photoacoustic "Signatures" of Particulate Matter: Optical Production of Acoustic Monopole Radiation

G. J. Diebold, M. I. Khan, S. M. Park*

Absorption of pulsed laser radiation by a single particle generates a photoacoustic wave whose time profile can be measured with a wideband pressure transducer. Solution of the wave equation for pressure in one, two, and three dimensions shows that the photoacoustic wave is determined by the geometry and dimensions of the particle, and by its sound speed and density relative to the fluid that surrounds it. Photoacoustic waves, referred to here as signatures, are reported in experiments in which fluid droplets, cylinders, and layers are irradiated with 10-nanosecond laser pulses.

The absorption of optical radiation by matter causes heating and, in general, subsequent expansion of the irradiated body, thereby launching an acoustic wave. Owing to its high sensitivity and its response to evolved heat, this process, known as the photoacoustic effect, has found application in a number of fields including spectroscopy, nondestructive testing, photochemistry, microscopy, semiconductor physics, and trace detection (*1*). We report here a study of a facet of the photoacoustic effect that has heretofore received only scant attention: the temporal profile of acoustic waves generated by particulate mat-

Department of Chemistry, Brown University, Providence, RI 02912.

*Present address: Department of Chemistry, University of Illinois at Chicago, Chicago, IL 60680.

Fluid spheres

Fig. 1. Calculated pressure p (in arbitrary units) versus dimensionless time $\hat{\tau}$ from Eq. 2 for fluid droplets with $\hat{\rho} = 1$. (**A**) Hexane–carbon tetrachloride (CCl_4) droplet suspended in water ($\hat{\rho} = 1.01$, $\hat{c} = 0.645$, $a = 0.5$ mm). (**B**) Formamide droplet suspended in a hexane-CCl_4 mixture ($\hat{\rho} = 1.00$, $\hat{c} = 1.65$ $a = 1.5$ mm). (**C**) 1,2,3,4-Tetrahydronaphthalene (tetralin) droplet in water ($\hat{\rho} = 0.97$, $\hat{c} = 0.962$, $a = 1.4$ mm). The experimental time scales are 500 ns per division in the top oscillogram and 1 μs per division in the other two. The slight departure of the formamide wave form from the predicted shape is caused by the addition of extra dye, which was necessitated by the small expansion coefficient of formamide and the consequent low signal-to-noise ratio in the recorded wave.

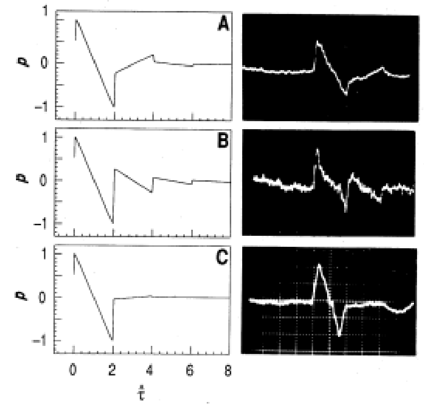
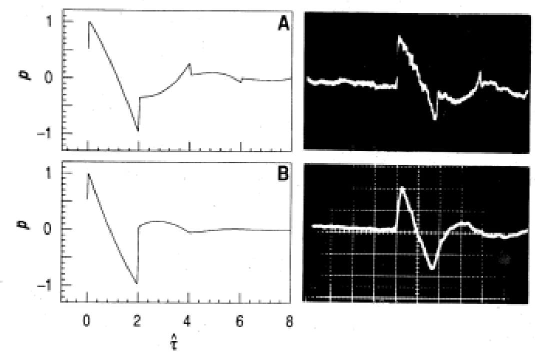


Fig. 2. Photoacoustic wave forms for droplets where $\hat{\rho} \neq 1$. (**A**) Hexane droplet in water ($\hat{\rho} = 0.66$, $\hat{c} = 0.708$, $a = 1$ mm). (**B**) CCl_4 droplet in water ($\hat{\rho} = 1.6$, $\hat{c} = 0.618$, $a = 1$ mm). The time scale in both oscillograms is 1 μs per division.



Fluid layers

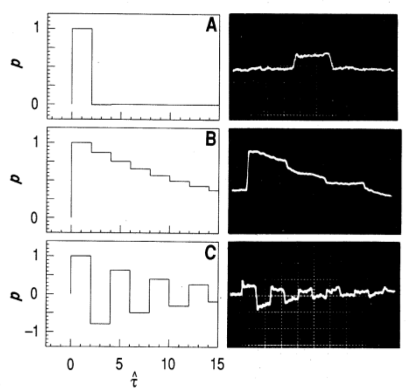


Fig. 4. Calculated (Eq. 5) and experimental photoacoustic wave forms for fluid layers (*11*). (**A**) A 2-mm-thick water layer floating between CCl_4 and castor oil ($\hat{\rho}\hat{c} = 1.03$). (**B**) A 1.5-mm acetone layer surrounded by Pyrex glass ($\hat{\rho}\hat{c} = 0.074$). (**C**) A 2.5-mm-thick colored glass slab in water ($\hat{\rho}\hat{c} = 9.4$). The time scales are 500 ns per division in each trace.

Fluid cylinders

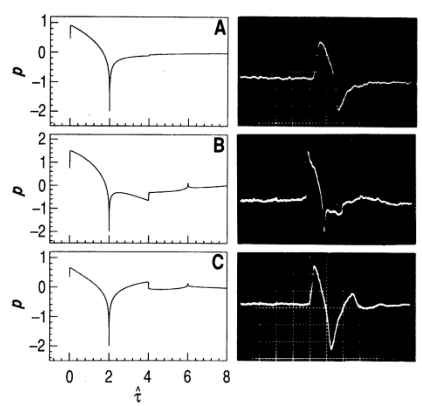


Fig. 3. Calculated (Eq. 4) and experimental photoacoustic wave forms for cylinders in water. (**A**) Tetralin cylinder in water ($\hat{\rho} = 0.97$, $\hat{c} = 0.960$, $a = 0.2$ mm). (**B**) Hexane cylinder in water ($\hat{\rho} = 0.66$, $\hat{c} = 0.708$, $a = 0.25$ mm. (**C**) Bromoform cylinder in water ($\hat{\rho} = 2.9$, $\hat{c} = 0.61$, $a = 0.3$ mm). The time scales in the oscillograms are 200 ns per division in the top trace and 500 ns per division in the other two.

G. J. Diebold , M. I. Khan, S. M. Park *Science* **250**, 101 (1990)

Mappings from Space to Time for Delta Function Heat Deposition

$$H(\hat{\xi},t) = \alpha E_0 h(\hat{\xi})\delta(t) \qquad \hat{\xi} = \xi/\xi_0$$

heat deposition in space

One dimension

$$p(\hat{\tau}) = \frac{\alpha\beta E_0 c^2}{2C_P} h(\hat{\tau}) \qquad \hat{\tau} = \frac{c}{\xi_0}\left(t - \frac{\xi}{c}\right)$$

Two dimensions

$$p(\hat{\rho},\hat{t}) = \frac{\alpha\beta E_0 c^2}{C_P} \int_{-\infty}^{\hat{t}-\hat{\rho}} \frac{f'(\hat{\zeta})+f'(-\hat{\zeta})}{[(\hat{t}-\hat{\zeta})^2-\hat{\rho}^2]^{1/2}} d\hat{\zeta}$$

where

$$f(\hat{\eta}) = -\frac{1}{\pi} \int_{\hat{\eta}}^{\infty} \frac{\hat{\rho} h(\hat{\rho})}{(\hat{\rho}^2-\hat{\eta}^2)^{1/2}} d\hat{\rho}$$

Three dimensions

$$p(\hat{\tau}) = \frac{\alpha\beta E_0 c^2}{2C_P(r/a)} \hat{\tau}[h(-\hat{\tau}) + h(\hat{\tau})]$$

G. J. Diebold, T. Sun and M. I. Khan, *Phys. Rev. Lett.* **67**, 3384 (1991)

Layer, Infinite Cylinder, Sphere

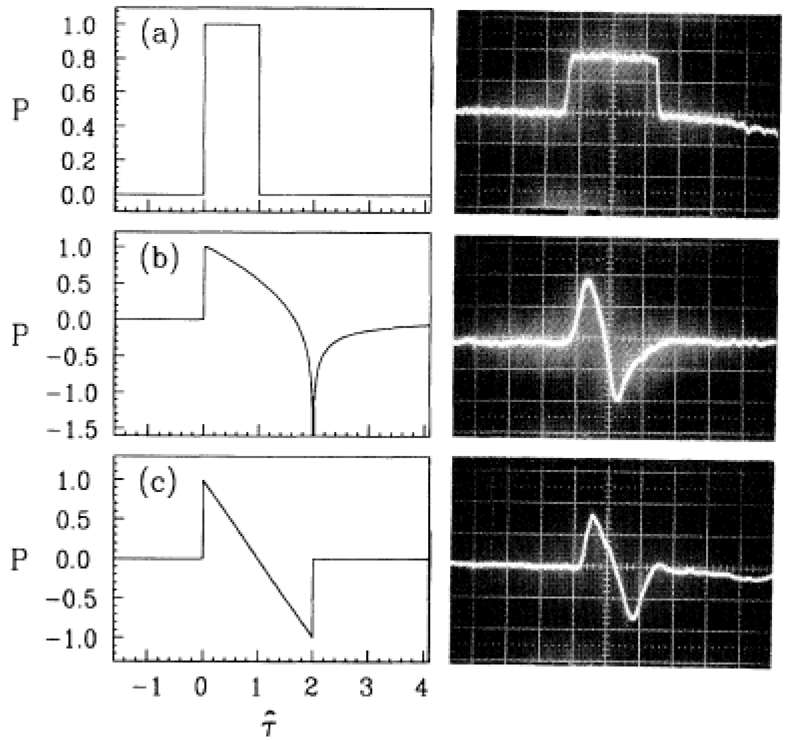


FIG. 1. Photoacoustic wave forms from short laser pulses. Left column: photoacoustic pressure P in arbitrary units vs dimensionless time $\hat{\tau}$ for (a) a fluid layer, (b) a cylinder, and (c) a sphere. The equations in the text were evaluated with $\kappa/2=1$, $\kappa/2\hat{\rho}^{1/2}=1$, and $\kappa/2\hat{r}=1$ in (a), (b), and (c), respectively. Right column: experimental wave forms obtained by irradiating (a) a 3-mm-thick layer, (b) a 150-μm-radius cylinder, and (c) a 500-μm-radius droplet. The time and voltage scales on the oscilloscope are (a) 1 μsec/div and 20 mV/div, (b) 200 nsec/div and 20 mV/div, (c) 500 nsec/div and 50 mV/div. The laser

Long Optical Pulses:
One to Three Dimensions

$$P_l(\tilde{\tau}_l) = \frac{\alpha\beta F c}{2C_P\hat{\Theta}} S(\tilde{\tau}_l)$$

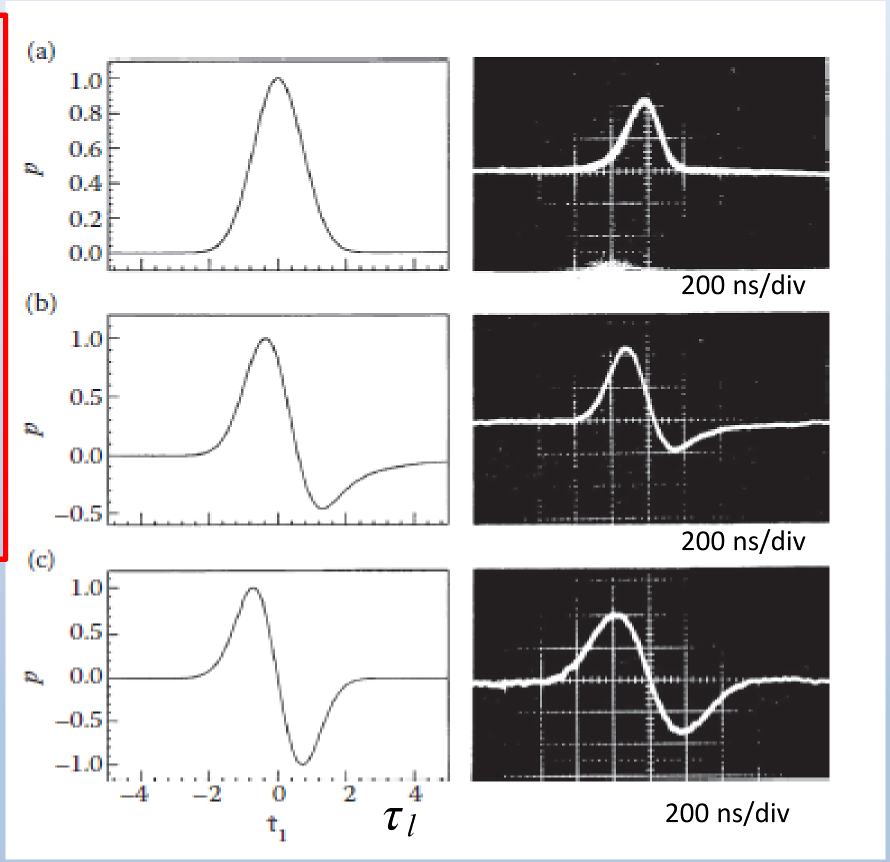
$$P(\tilde{\tau}_l) = \frac{\alpha\beta F c}{\sqrt{2\bar{\rho}}\, C_P \hat{\Theta}^{3/2}} \int_{-\infty}^{\hat{\tau}_l} \frac{dS(T)/dT}{\sqrt{\tilde{\tau}_l - T}} dT$$

$$P_l(\tilde{\tau}_l) = \frac{\alpha\beta F c}{C_P (r/\xi_l)\hat{\Theta}^2} \frac{d}{d\tilde{\tau}_l} S(\tilde{\tau}_l)$$

$$I(t) = \frac{F}{\Theta} S(t/\Theta)$$

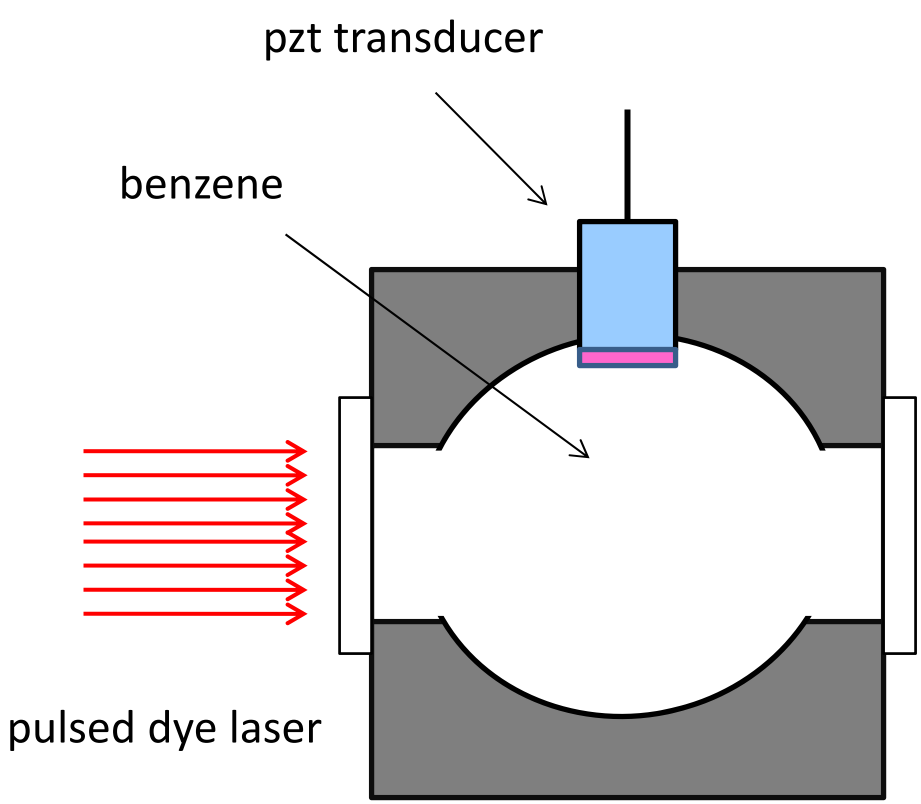
Gaussian

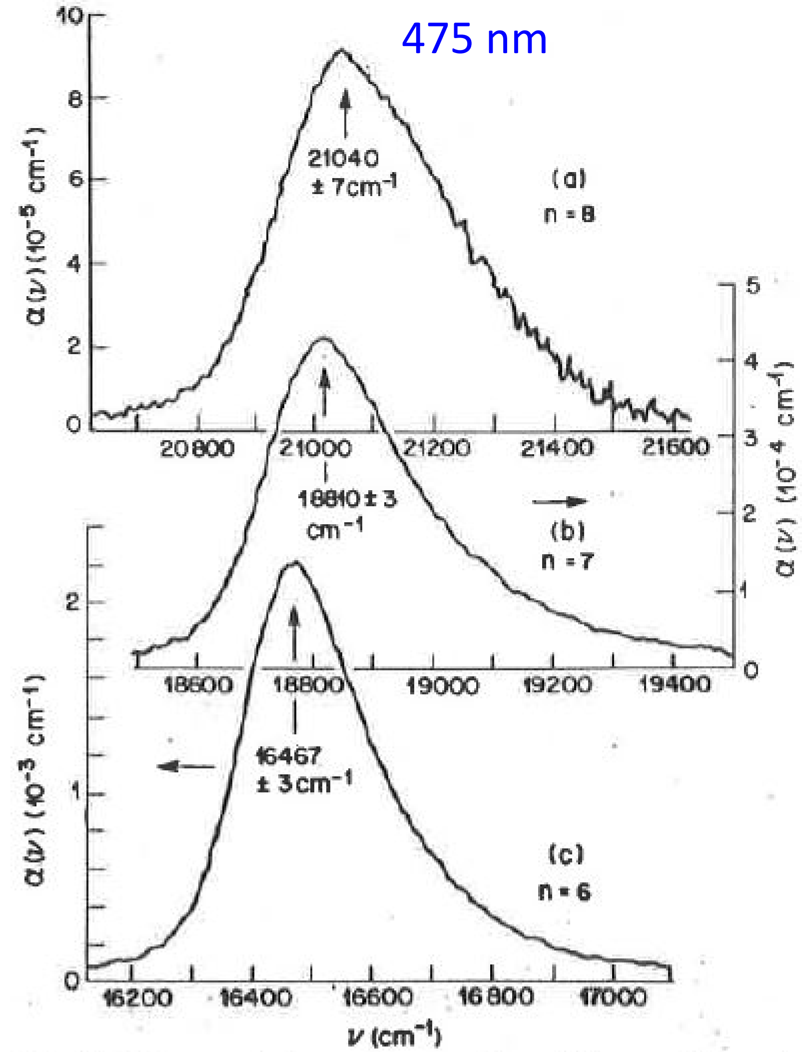
$$\tilde{\tau}_l = \frac{c}{\xi_l}\left(t - \frac{\xi}{c}\right)$$



Benzaldehyde in water layer
100 µm radius cylinder
200 µm radius sphere

Overtone Spectroscopy in Liquids



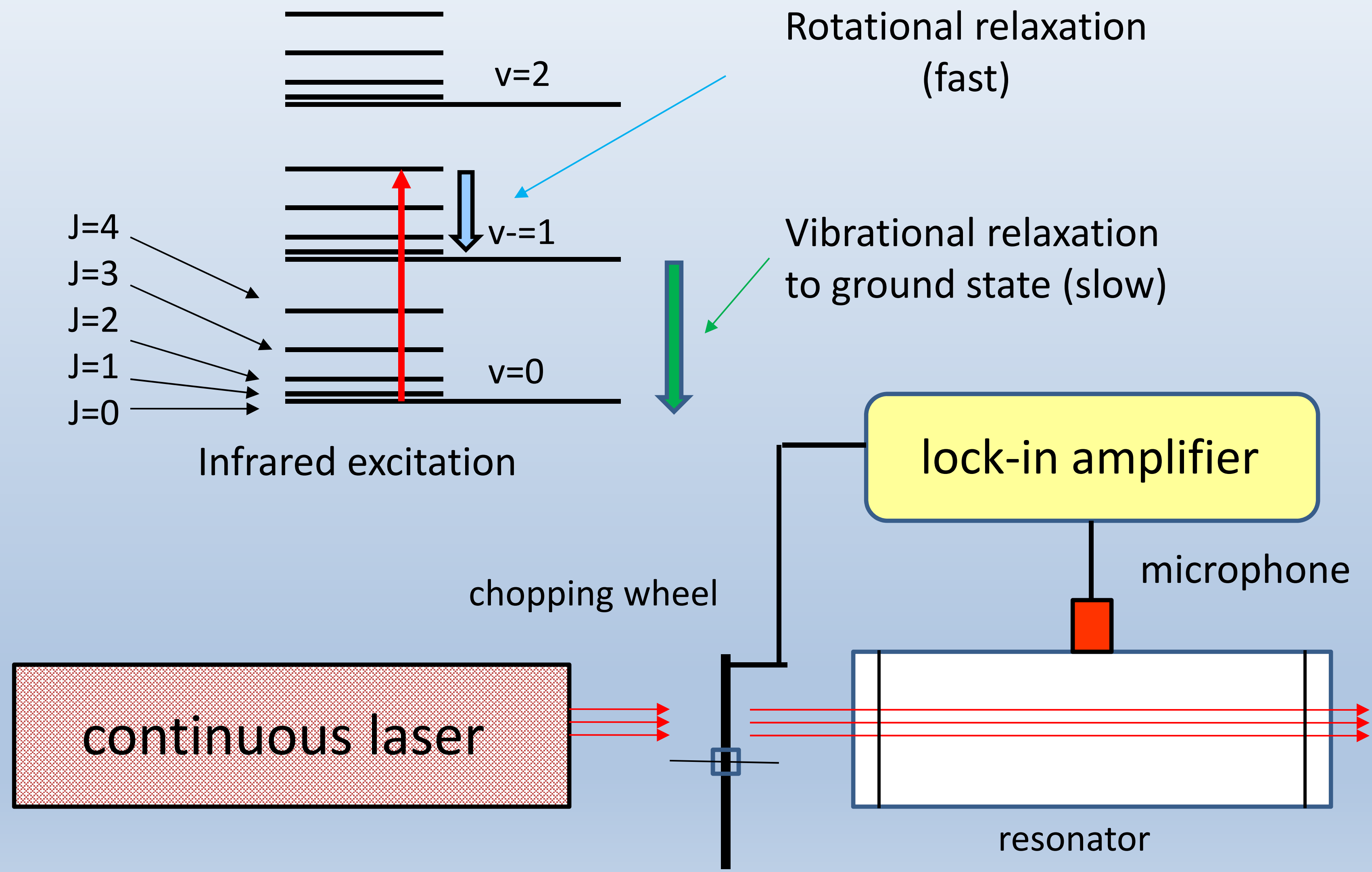


C. K. N. Patel and A. C. Tam, *Rev Mod. Phys.* **53**, 517 (1981)

FIG. 17. Measured absorption profiles of the $n = 8$ to $n = 6$ harmonics of the C–H stretch in liquid benzene by laser OA spectroscopy.

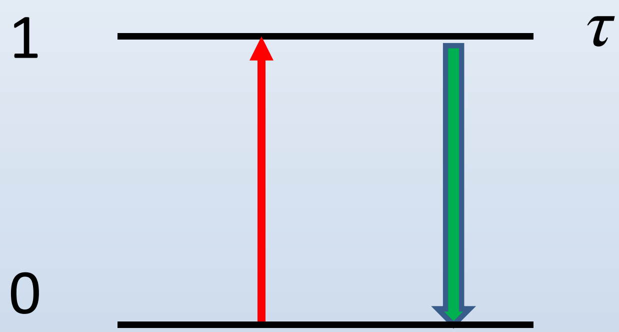
Vibrational Relaxation

Diatomic molecule



M. Jacox and S. Bauer, J. Phys. Chem. **61** 833 (1957)

Phase Shift for Vibrational Relaxation



Two level atom

$$\frac{dn_1}{dt} = -\frac{n_1}{\tau} + \rho_R B(1 + \sin \omega t)$$

$$n_1 = \frac{\rho_R B \tau}{\sqrt{1+\lambda^2}} \cos(\omega t - \phi)$$

$$\tan \phi = \lambda = \omega \tau$$

$$p \sim \frac{\rho_R B}{\omega \sqrt{1+\lambda^2}} \cos(\omega t - \phi)$$

Photochemical Generation of Sound

Thermal Expansion with Chemical Reaction

new

$$\frac{\partial}{\partial t}\left(T - \frac{\gamma-1}{\gamma\tilde{\alpha}}p\right) = \frac{K}{\rho C_P}\nabla^2 T + \frac{H(\mathbf{r},t)}{\rho C_P} - \frac{\tilde{h}}{C_P}\frac{\partial n}{\partial t}$$

$$\left(\nabla^2 - \frac{\gamma}{c^2}\frac{\partial^2}{\partial t^2}\right)p = -\rho\beta\frac{\partial^2 T}{\partial t^2} - \rho\beta_c\frac{\partial^2 n}{\partial t^2}$$

new

$$\beta_c = -\frac{1}{\rho}\left(\frac{\partial\rho}{\partial N}\right)_{P,T}$$ chemical expansion coefficient

$$\tilde{h} = \left(\frac{\partial h}{\partial N}\right)_{P,T}$$ chemical potential

Wave Equation with Chemical Effects

Thermal Expansion plus Chemical Reaction

$$\left(\nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\right)p = -\frac{\beta}{C_P}\frac{\partial}{\partial t}\left(H - \rho\tilde{h}\frac{\partial n}{\partial t}\right) - \rho\beta_c\frac{\partial n}{\partial t}$$

enthalpy change

chemical expansion

$$\beta_c = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial N}\right)_{P,T}$$

$$\tilde{h} = \left(\frac{\partial h}{\partial N}\right)_{P,T}$$

Photochemical Generation of Sound

Short wavelength photon hv at
476.5 nm from Ar ion laser

$$Cl_2 + h\nu \rightarrow 2\ Cl$$

Optical energy added

$$2Cl + M \rightarrow Cl_2 + M$$

Energy returned
Sound generated!

Sound Generation:

Recoil energy of photofragments

Mole number increase

Energy release from three body recombination

Nonlinear Chemical Kinetics

$$\frac{dx}{dt} + ax^2 = 2\rho_R B(1 + d\sin\omega t)$$

$2Cl + M \rightarrow Cl_2 + M$

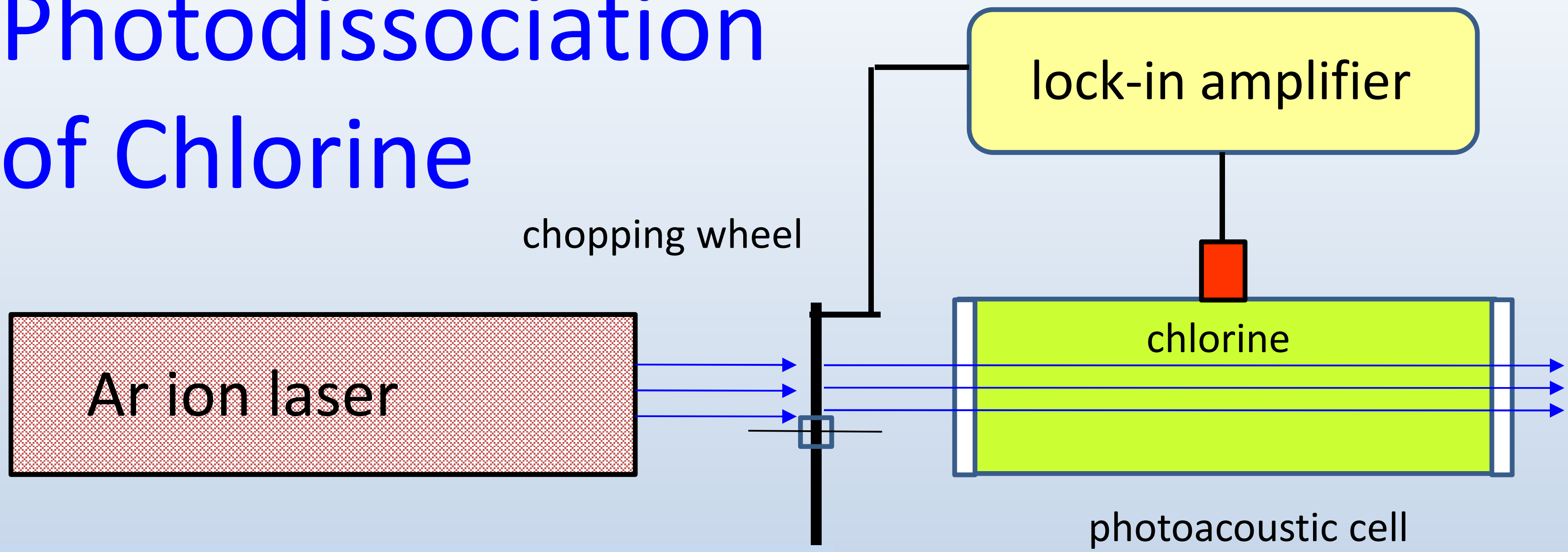
$$x = \frac{[X]}{[X_2]} \qquad a = 2k_r[X_2][M]$$

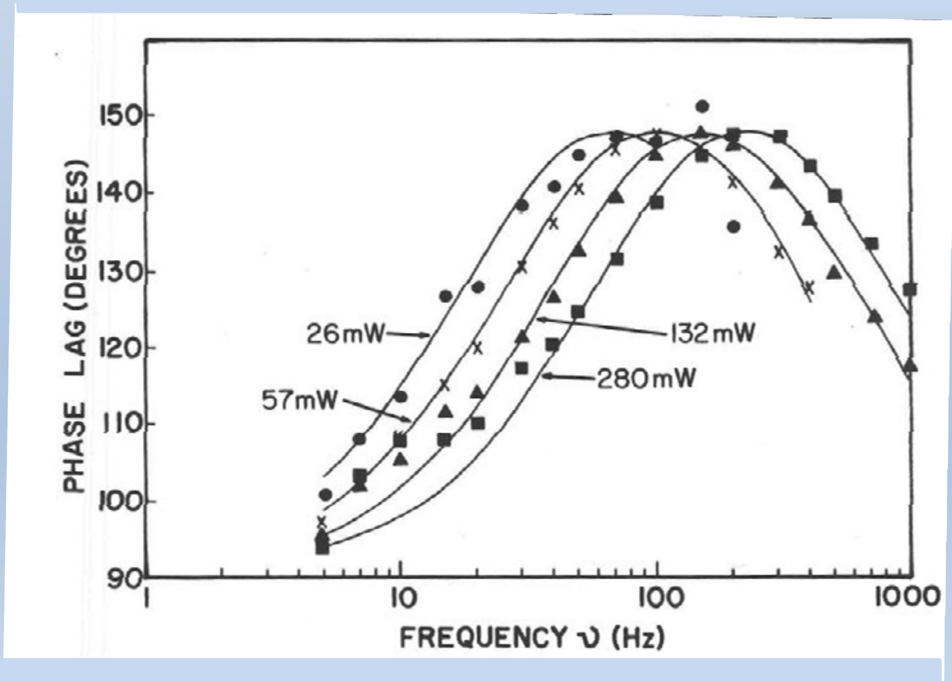
$$p = -\frac{2}{5} d \frac{\rho_R B D_0 [X_2]}{\omega(1+\lambda^2)^{1/2}} \cos(\omega t - \phi)$$

$$\tan\phi = \lambda = \frac{\omega}{2\sqrt{\rho_R B k_r [X_2][M]}}$$

$$\tan\phi \sim \frac{\omega}{\sqrt{\text{light intensity}}} \quad ?$$

Photodissociation of Chlorine





$$\tan\phi \sim \frac{\omega}{\sqrt{\text{light intensity}}}$$

Generation of Sound with Chain Reactions

$Cl_2 + h\nu \rightarrow 2\ Cl$ Optical energy added

HUGE Energy Release

$Cl + H_2 \rightarrow HCl + H$

Chain reactions

$H + Cl_2 \rightarrow HCl + Cl$

$2Cl + M \rightarrow Cl_2 + M$ Chain termination

Chemical Amplification of the Photoacoustic Effect

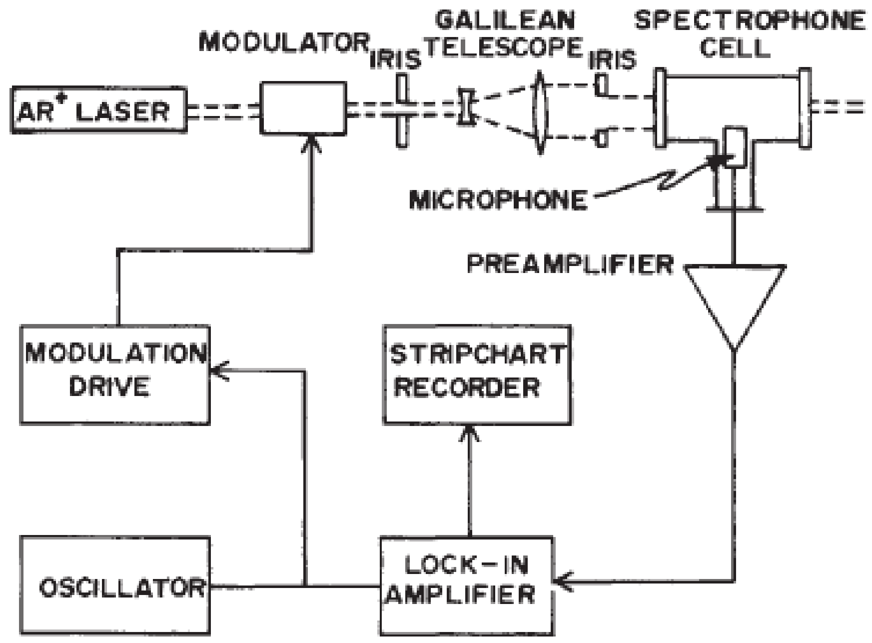
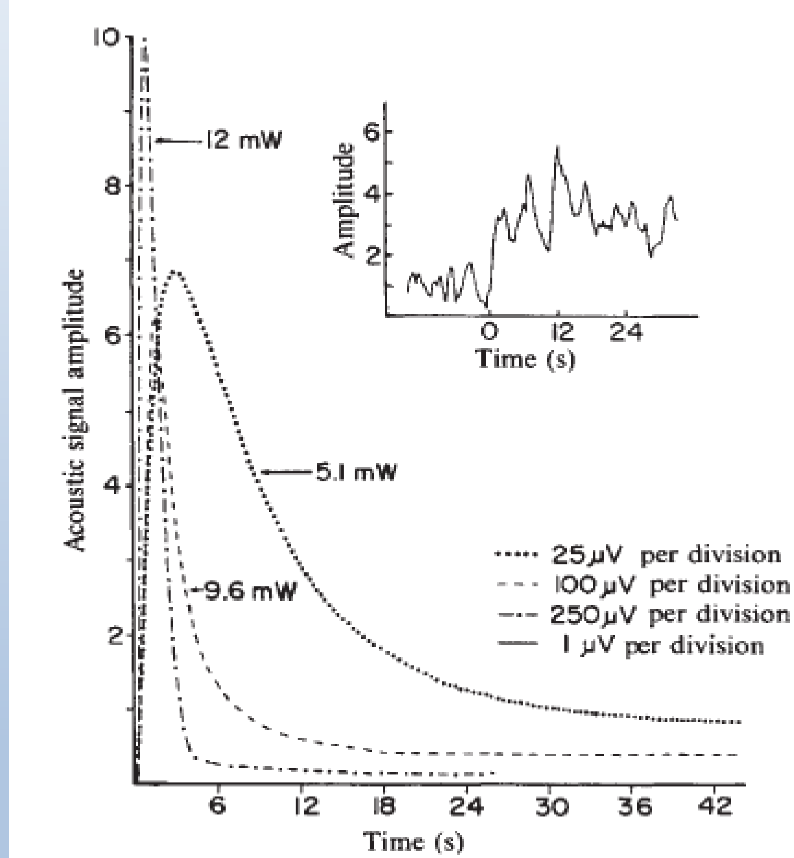
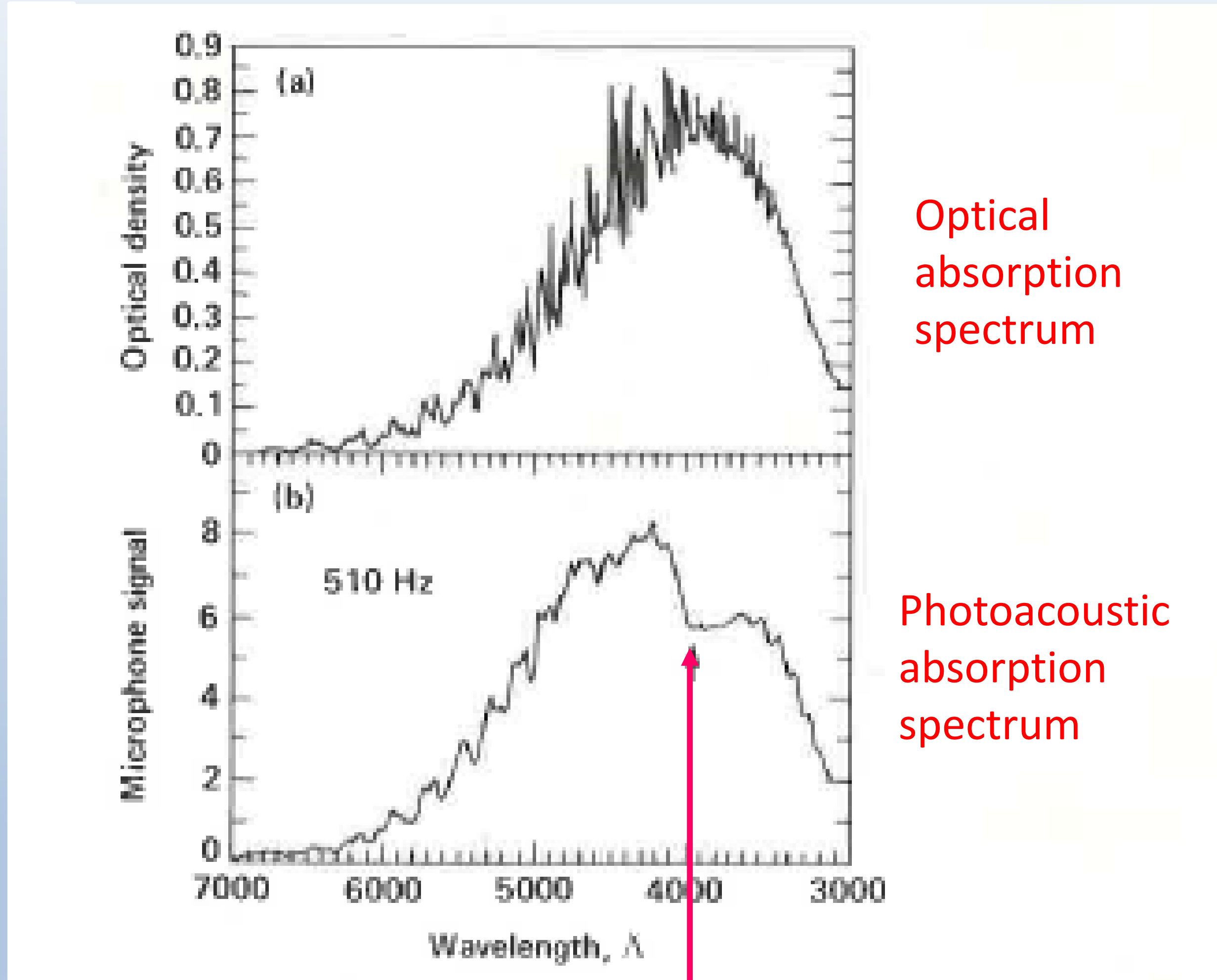


Fig. 1 Schematic diagram of the experimental apparatus used to record optoacoustic signals in a static mixture of H_2 and Cl_2 in a buffer of N_2.



M. T. O'Connor and G. J. Diebold, *Nature* **301** 321 (1983)

Chemical Effects in NO_2



Optical absorption spectrum

Photoacoustic absorption spectrum

$$NO_2 + h\nu \rightarrow NO(^2\Pi) + O(^3P)$$

W. R. Harshbarger and M. B. Robin, Acc. Chem. Res. **6**, 329 (1973)

Moving Photoacoustic Sources

$$(\nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2})p = -\frac{\beta}{C_P}\frac{\partial}{\partial t}H(\mathbf{x},t)$$

$$(\nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2})\phi = \frac{\beta}{\rho C_P}H(\mathbf{x},t)$$

velocity potential

$$p = -\rho\frac{\partial\phi}{\partial t}$$

Gaussian Source Moving in One Dimension

Heating function

$$H(z,t) = \bar{\alpha} I_0 e^{-(t-z/v)^2/\theta^2} \mathrm{u}(t)$$

D'Alembert solution

$$\phi = -\frac{\bar{\alpha}\beta I_0 c}{2\rho C_P} \int_0^t dt' \underbrace{\int_{z-c(t-t')}^{z+c(t-t')} e^{-(t'-z'/v)^2/\theta^2} dz'}$$

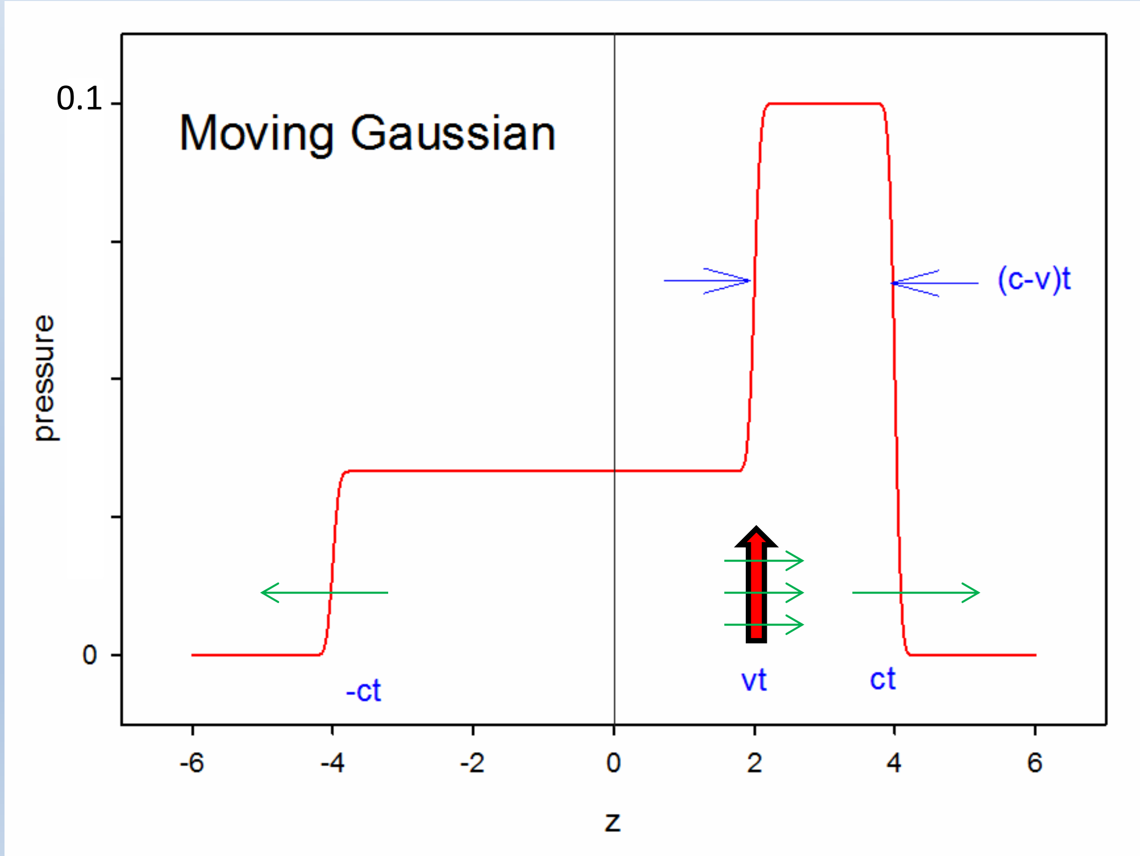
$$\phi = -\frac{\bar{\alpha}\beta I_0 c}{2\rho C_P} \int_0^t dt' \frac{\sqrt{\pi}\, v\theta}{2} \left\{ \mathrm{erf}\left[\frac{ct-z+(v-c)t'}{v\theta}\right] + \mathrm{erf}\left[\frac{ct+z-(v+c)t'}{v\theta}\right] \right\}$$

$$p = -\rho \frac{\partial \phi}{\partial t}$$

1-D Gaussian Moving Source

$$p(z,t) = \frac{\sqrt{\pi}\,\overline{\alpha}\beta I_0 c^2 v\theta}{4C_p}\left[\frac{-\mathrm{erf}(\frac{z-ct}{c\theta})+\mathrm{erf}(\frac{z-vt}{c\theta})}{c-v} + \frac{\mathrm{erf}(\frac{z+ct}{c\theta})-\mathrm{erf}(\frac{z-vt}{c\theta})}{c+v}\right]$$

t=4 c=1 v=1/2 and θ=0.1



Gusev and Karabutov
“Laser Optoacoustics”

Gaussian Source with v = c

Heating function

$$H(z,t) = \bar{\alpha} I_0 e^{-(t-z/c)^2/\theta^2} \mathbf{u}(t)$$

D'Alembert solution

$$\phi = -\frac{\bar{\alpha}\beta I_0 c}{2\rho C_P} \int_0^t dt' \underbrace{\int_{z-c(t-t')}^{z+c(t-t')} e^{-(t'-z'/c)^2/\theta^2} dz'}$$

$$\phi = -\frac{\bar{\alpha}\beta I_0 c}{2\rho C_P} \int_0^t dt' \frac{\sqrt{\pi}\, c\theta}{2} \left\{ \mathrm{erf}\left[\frac{ct-z}{v\theta}\right] + \mathrm{erf}\left[\frac{ct+z-2ct'}{v\theta}\right] \right\}$$

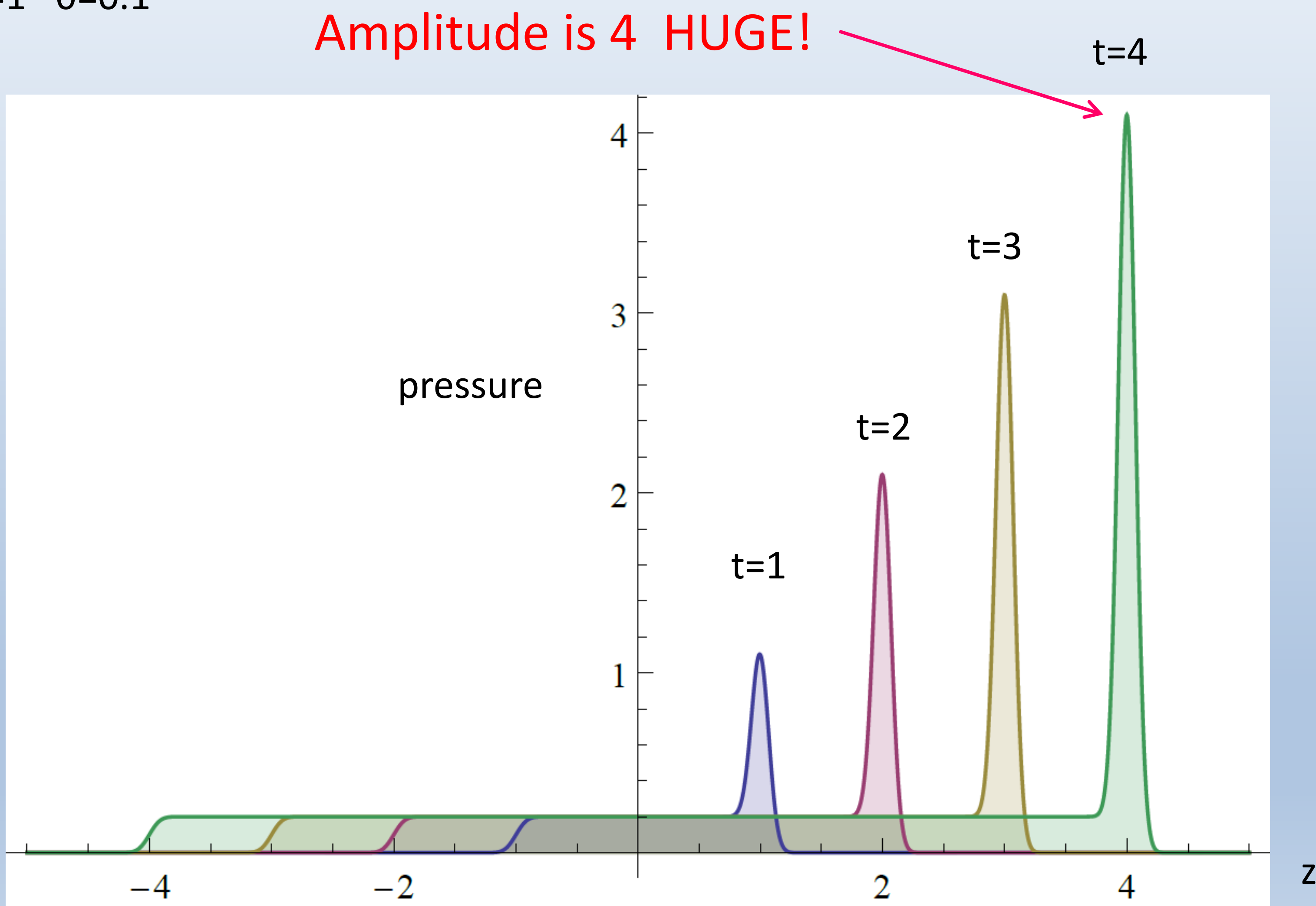
$$p(z,t) = \frac{\bar{\alpha}\beta I_0 c^2\theta}{2C_p} \left\{ \frac{t}{\theta} e^{\left(\frac{t-z/c}{\theta}\right)^2} + \frac{\sqrt{\pi}}{4} \left[\mathrm{erf}\left(\frac{t-z/c}{\theta}\right) - \mathrm{erf}\left(\frac{t+z/c}{\theta}\right) \right] \right\}$$

Gusev and Karabutov
"Laser Optoacoustics"

Amazing!

Gaussian Source with v = c

c=1 θ=0.1

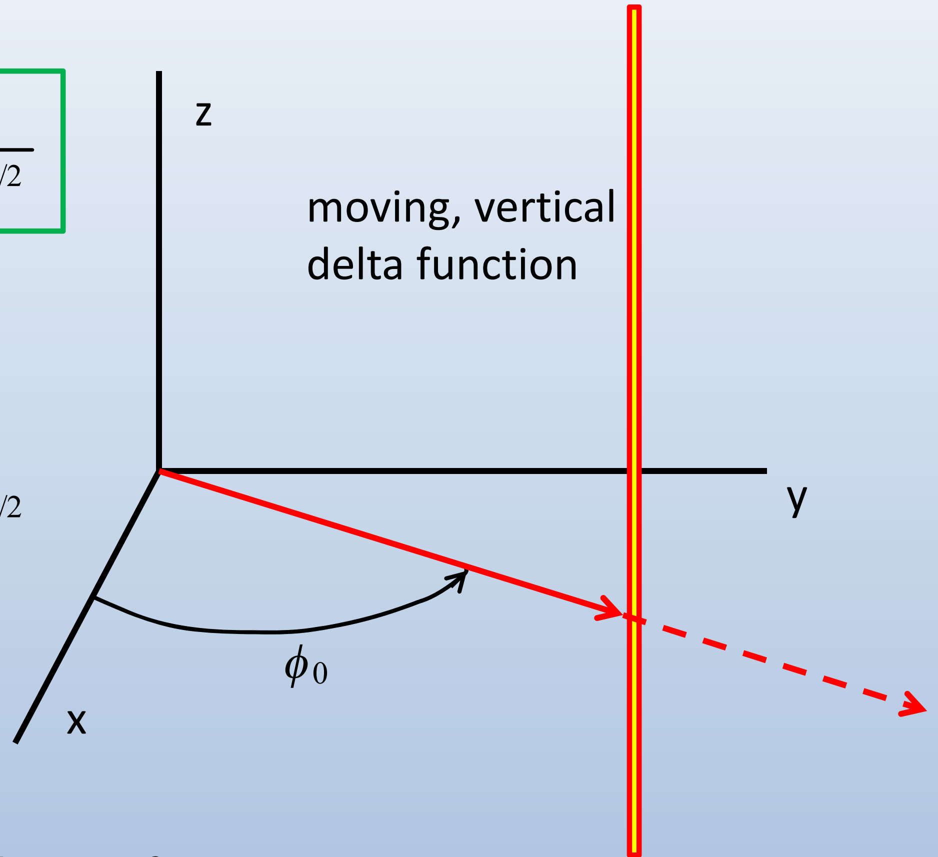


Moving Delta Function in Two Dimensions

$$g(\boldsymbol{\rho}, \boldsymbol{\rho}'; t, t') = 2c \frac{\mathrm{u}(c[t-t'] - |\boldsymbol{\rho}-\boldsymbol{\rho}'|)}{[c^2(t-t')^2 - |\boldsymbol{\rho}-\boldsymbol{\rho}'|]^{1/2}}$$

$$H(\rho, \phi, t) = P_L \frac{\delta(\rho - vt)}{\rho} \frac{\delta(\phi - \phi_0)}{2\pi}$$

$$|\vec{\rho} - \overrightarrow{\rho'}| = [\rho^2 + \rho'^2 - 2\rho\rho' \cos(\varphi - \varphi')]^{1/2}$$



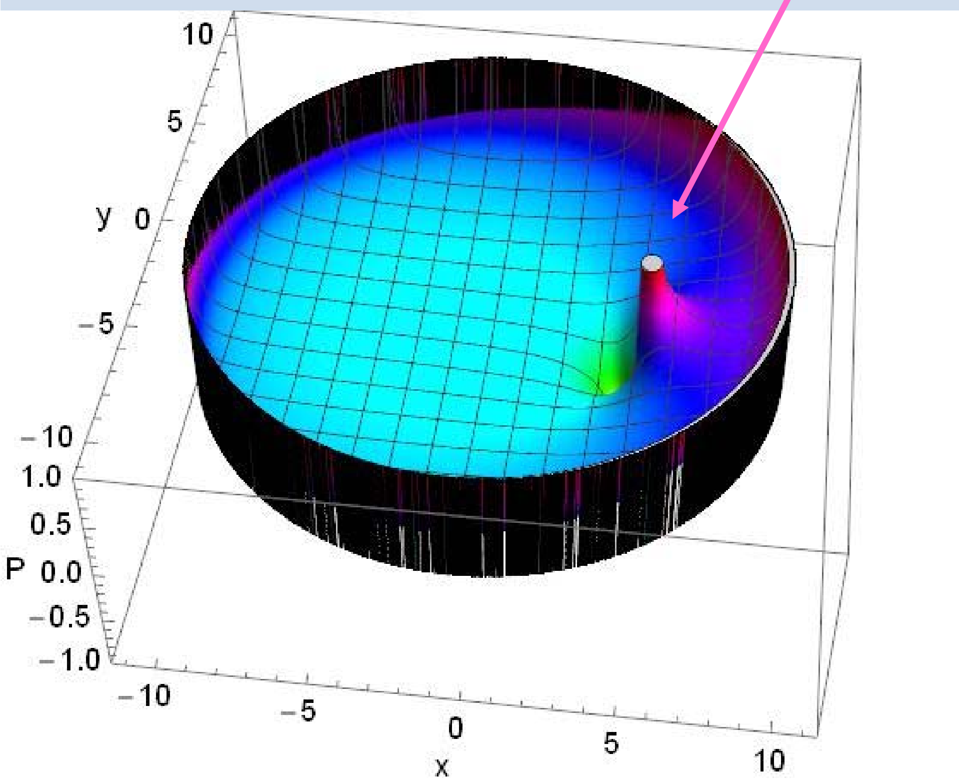
$$\phi^{2-D} = -\frac{P_L \beta c}{4\pi^2 \rho C_P} \int_0^t dt' \int_0^{2\pi} d\varphi' \int_0^{\rho} d\rho' \delta(\varphi' - \varphi_0) \delta(\rho' - vt')$$

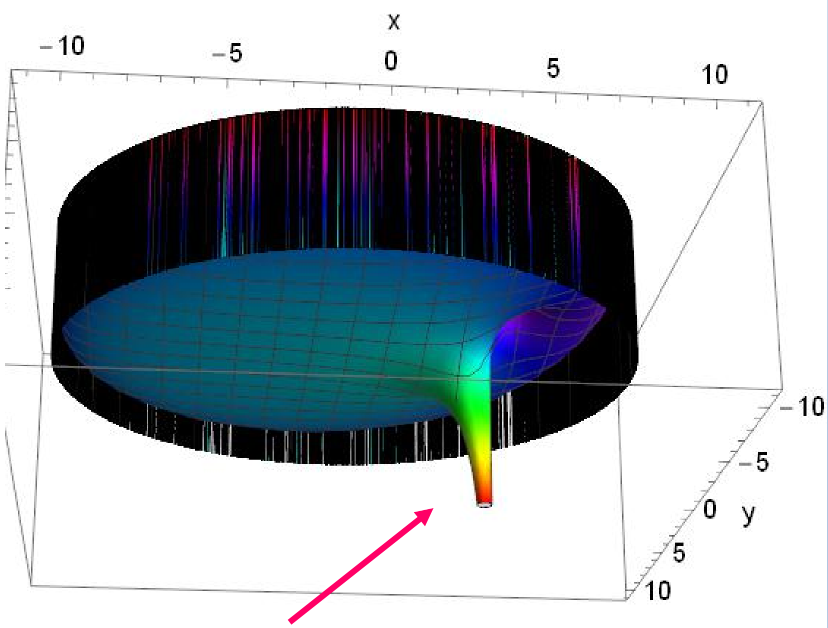
$$\times \frac{\mathrm{u}[c(t-t') - \sqrt{\rho^2 + (vt)^2 - 2\rho vt \cos(\varphi - \varphi_0)}\,]}{\{c^2(t-t')^2 - [\rho^2 + \rho'^2 - 2\rho\rho' \cos(\varphi - \varphi')]\}^{1/2}}$$

Moving Vertical Delta Function in Two Dimensions

compression

c=1 v=1/2 t=10





rarefaction

Moving Delta Function in Three Dimensions

Trajectory $\mathbf{x} = \boldsymbol{\xi}(t)$

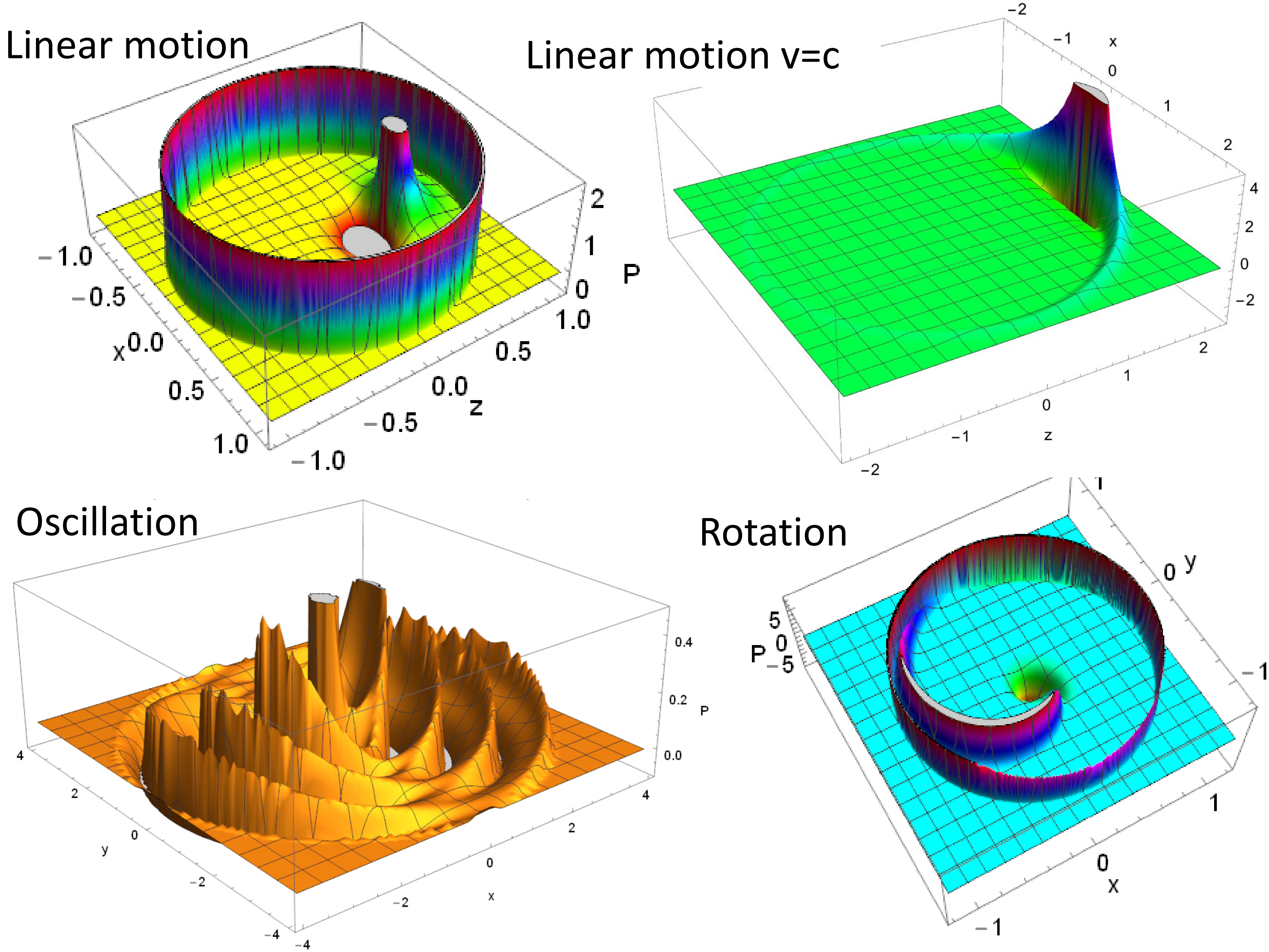
$$\varphi = -\frac{\beta P_0}{4\pi\rho C_P}\int_0^t \frac{\delta[t' - (t - \frac{|\mathbf{x} - \boldsymbol{\xi}(t')|}{c})]}{|\mathbf{x} - \boldsymbol{\xi}(t')|} dt'$$

Lienard-Wiéchert Potential

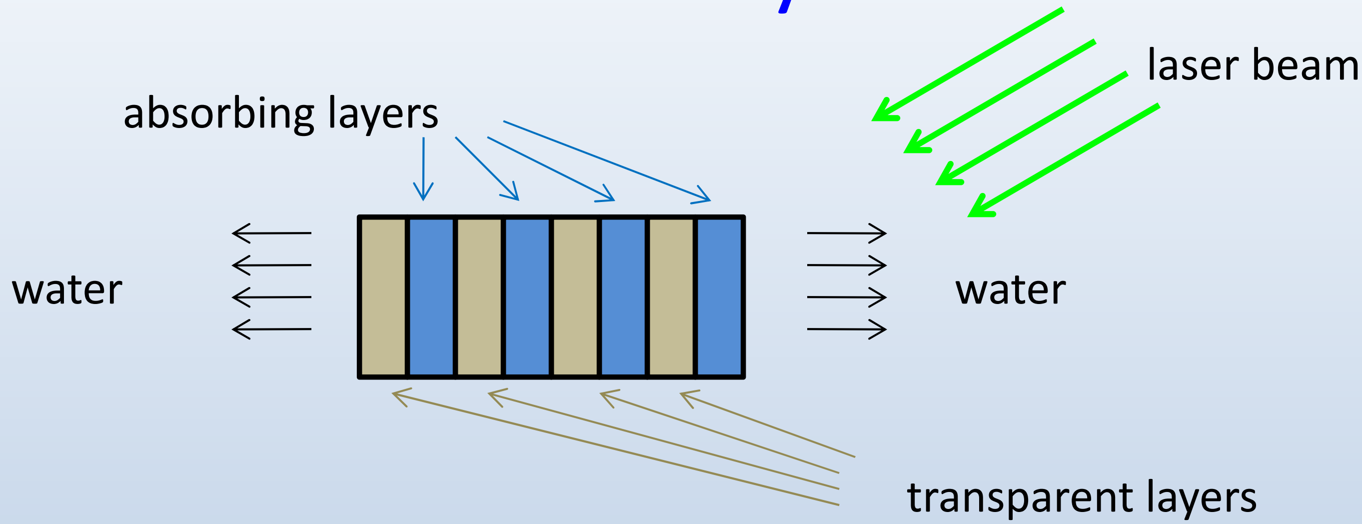
$$\varphi = -\frac{\beta P_0}{4\pi\rho C_P}\frac{u(t_r)u(t - t_r)}{|\mathbf{x} - \boldsymbol{\xi}(t_r)| - \dot{\boldsymbol{\xi}}(t_r)\cdot[\mathbf{x} - \boldsymbol{\xi}(t_r)]/c}$$

$$t_r = t - |\mathbf{x} - \boldsymbol{\xi}(t_r)|/c$$

$$p = -\rho\frac{\partial\varphi}{\partial t}$$


Linear motion
Linear motion v=c
Oscillation
Rotation
P
x
z
y

Coherent Generation: Layered structures



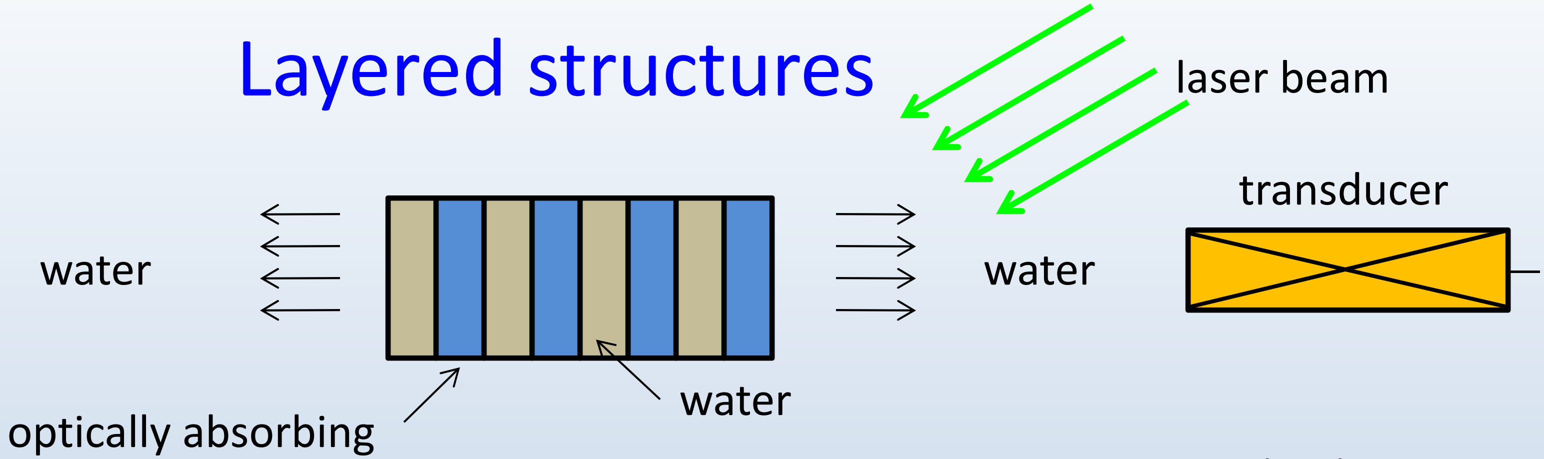
$$[\alpha\beta]^{N-n}[\alpha_0]\begin{bmatrix} 0 \\ B_{2N}^{(j)} e^{ik_t x_{2N-1}} \end{bmatrix} - \begin{bmatrix} \kappa_f/\hat{q} \\ \kappa_f/\hat{q} \end{bmatrix} = [\xi][\alpha^*\beta^*]^{n-1}[\alpha_0^*]\begin{bmatrix} A_0^{(j)} e^{-ik_t x_a} \\ 0 \end{bmatrix} - [\xi]\begin{bmatrix} \kappa_f/\hat{q} \\ \kappa_f/\hat{q} \end{bmatrix}$$

$$\alpha = \tfrac{1}{2}\begin{bmatrix} e^{ik_t s}(1+\hat{\rho}\hat{c}) & e^{-ik_t s}(1-\hat{\rho}\hat{c}) \\ e^{ik_t s}(1-\hat{\rho}\hat{c}) & e^{-ik_t s}(1-\hat{\rho}\hat{c}) \end{bmatrix}$$

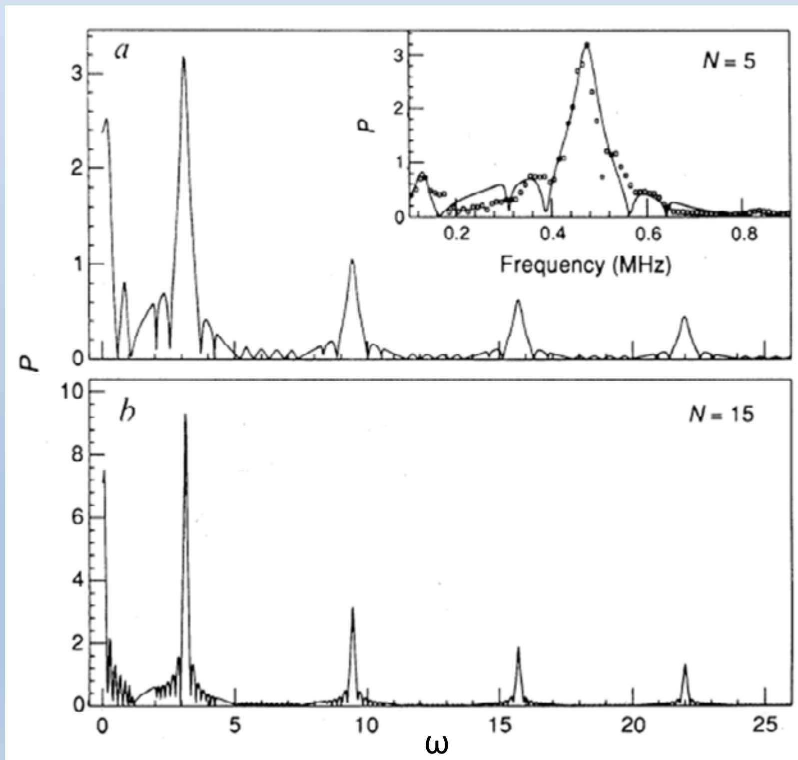
$$\beta = \tfrac{1}{2}\begin{bmatrix} e^{ik_t s}(1+1/\hat{\rho}\hat{c}) & e^{-ik_t s}(1-1/\hat{\rho}\hat{c}) \\ e^{ik_t s}(1-1/\hat{\rho}\hat{c}) & e^{-ik_t s}(1-1/Z) \end{bmatrix}$$

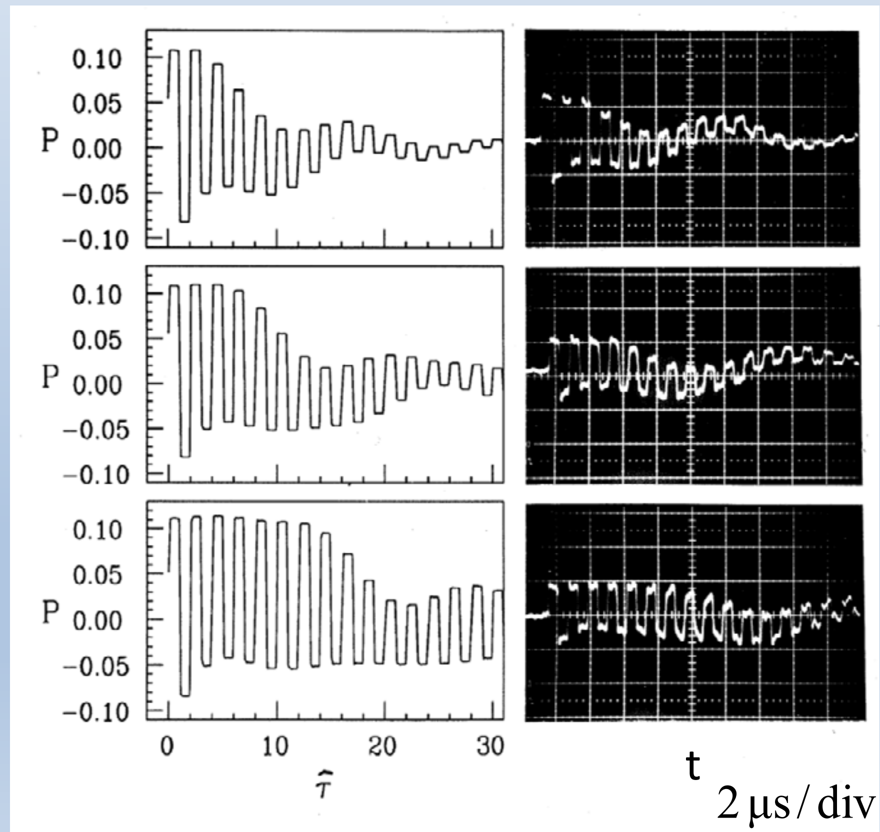
$$\kappa_f = i\alpha\beta I_0 cl/2C_P$$

Layered structures

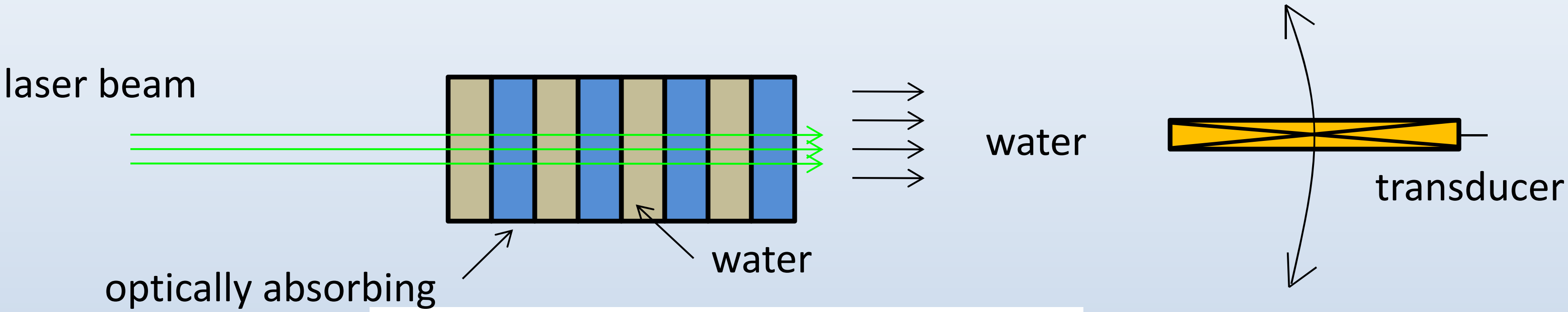


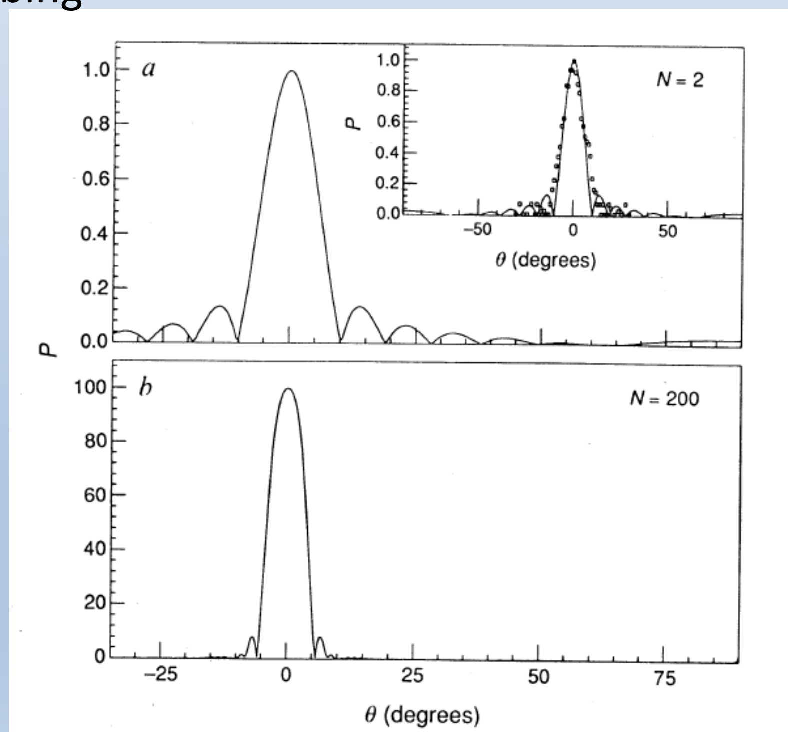
3.26 mm glass layers





Angular distribution of acoustic radiation

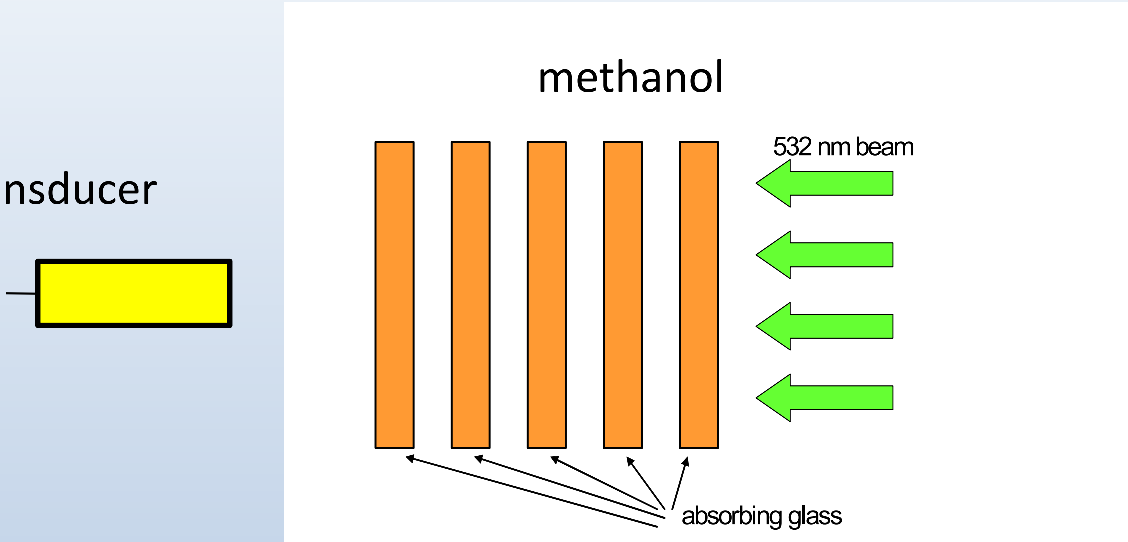


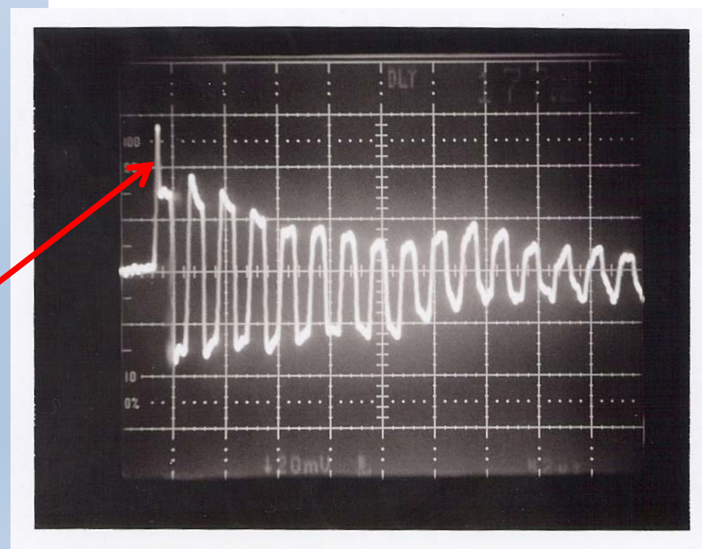


Tom Sun and Gerald Diebold, *Nature* **355**, 806 (1992)

Experiments with Multiple Layers

PVDF transducer

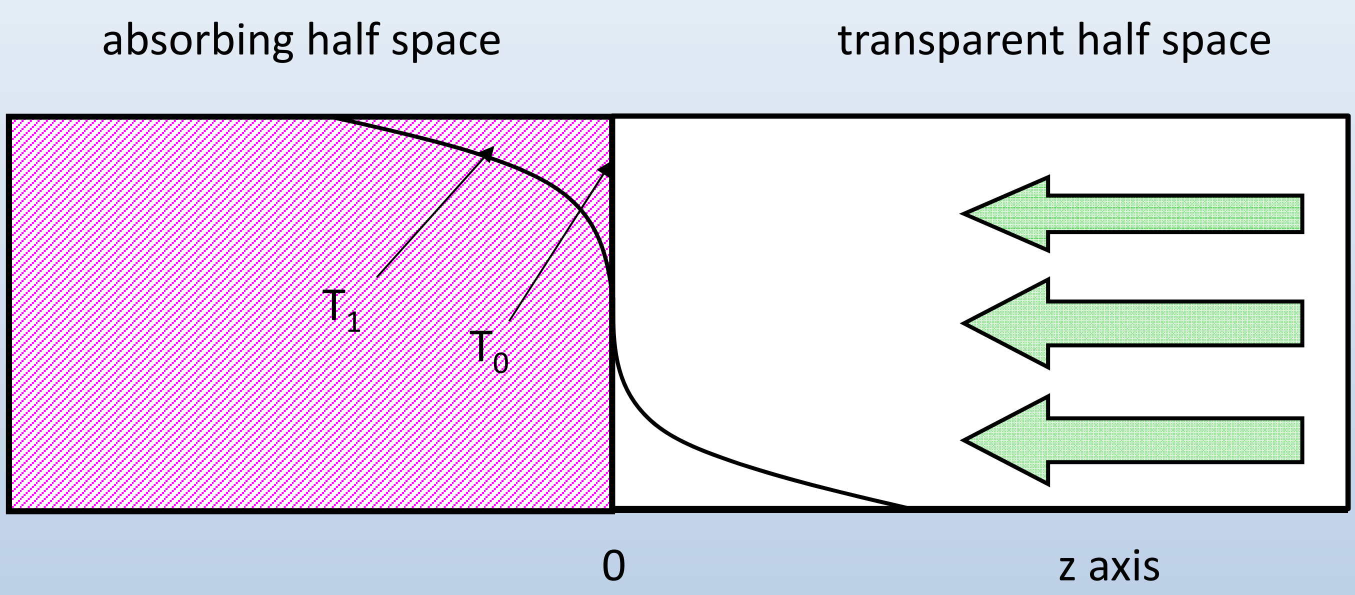




?

2 µs/division

Temperature Gradients



Laser	Energy	Temperature gradient
10 ns	1.0 J	3.5×10^5 K/m
40 ps	100 mJ	6.1×10^6 K/m
35 fs	5 mJ	1.0×10^7 K/m

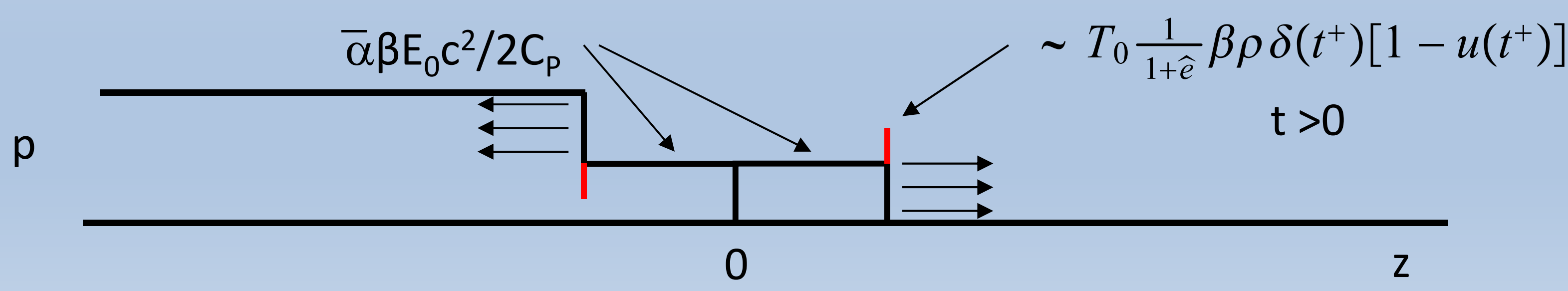
Heat Conduction: Coupled Equations for T and p

$$\frac{\partial}{\partial t}\left(T - \frac{\gamma-1}{\gamma\tilde{\alpha}}p\right) = \frac{K}{\rho C_P}\nabla^2 T + \frac{H(\mathbf{r},t)}{\rho C_P}$$

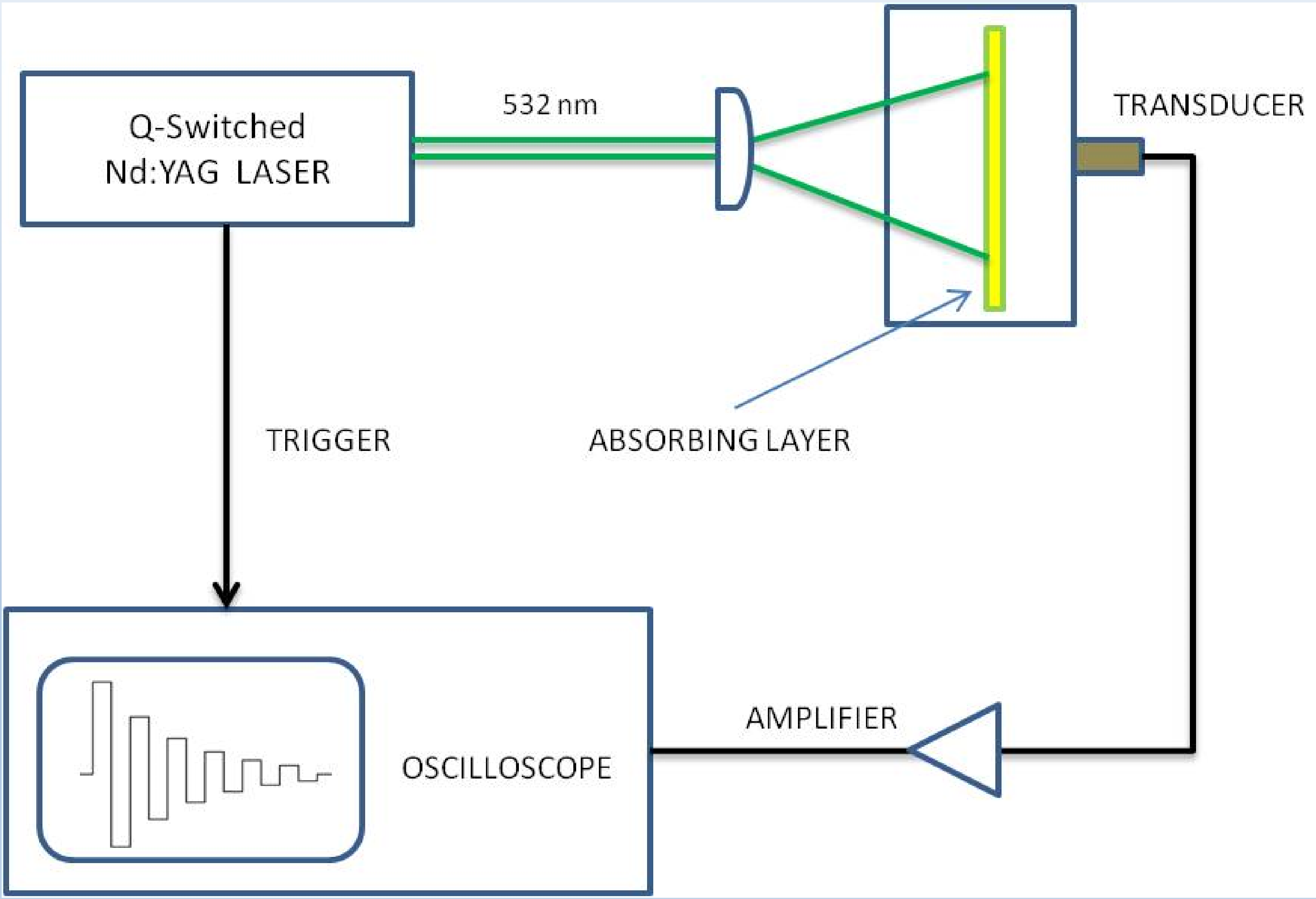
$$\left(\nabla^2 - \frac{\gamma}{c^2}\right)p = -\frac{\tilde{\alpha}\gamma}{c^2}\frac{\partial^2}{\partial t^2}T$$

Let γ≃1

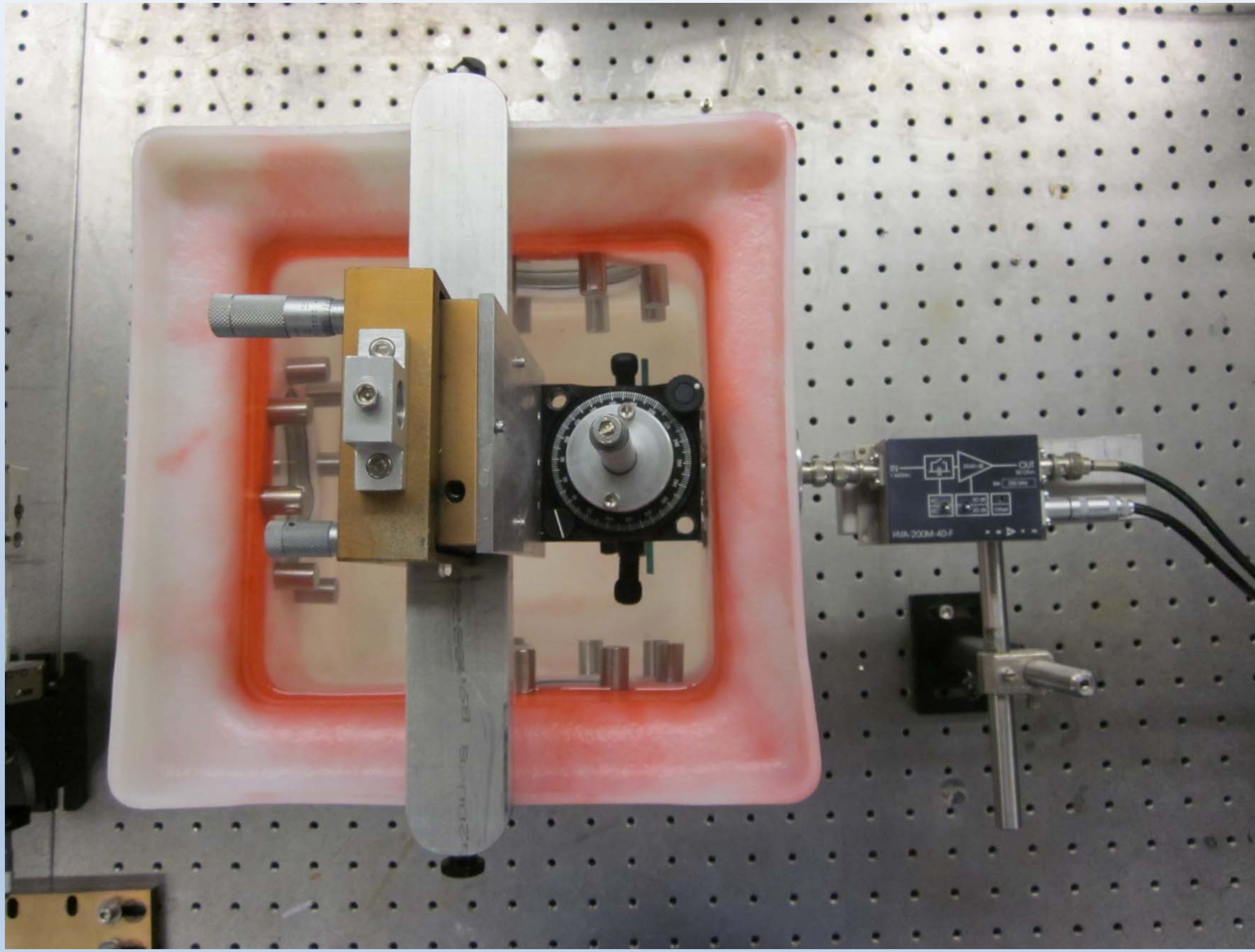
$$\left(\nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\right)p = -\frac{\beta}{C_P}\frac{\partial H}{\partial t} - \rho\beta\chi\frac{\partial}{\partial t}\nabla^2 T$$



Experimental apparatus



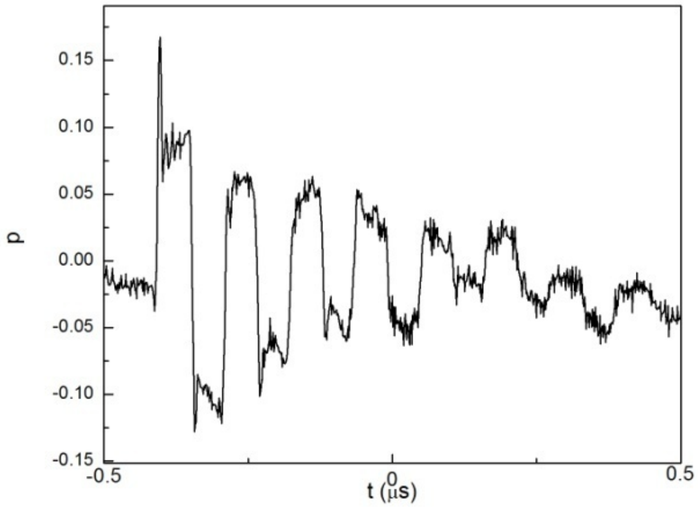
Apparatus



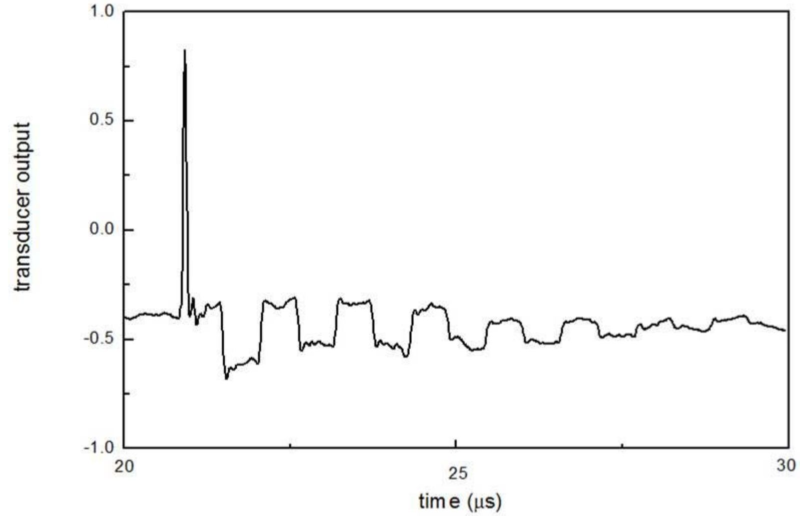
Experimental Results

fluence : 13 J/m^2

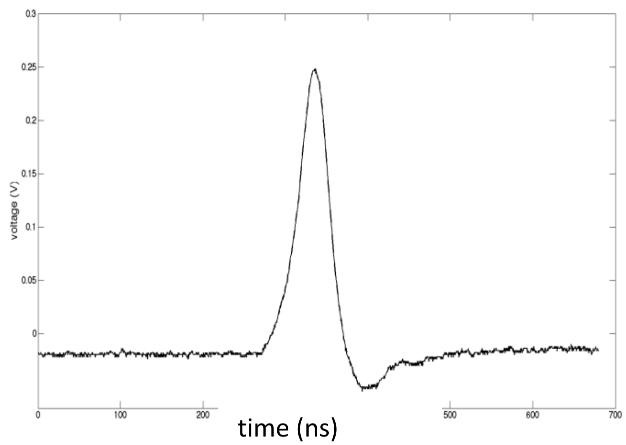
glass layer in water



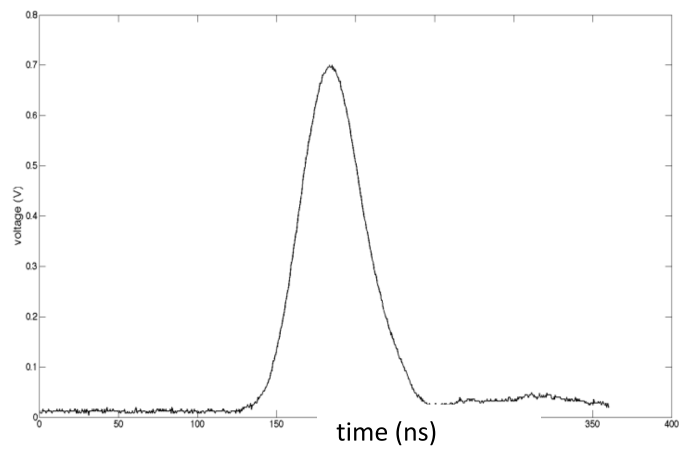
glass layer in methanol



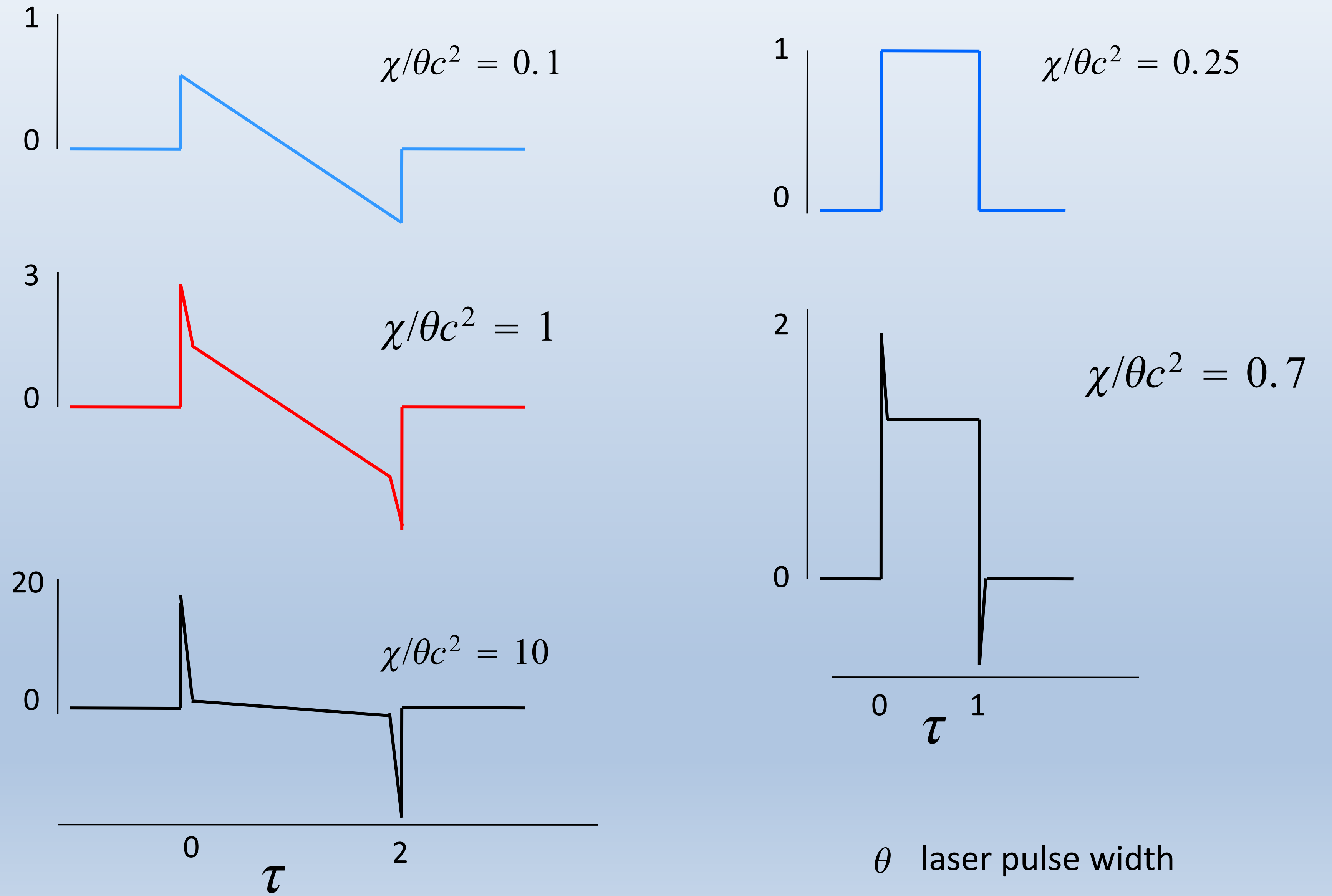
0.5 μ gold target in water



25 μ silver target in water

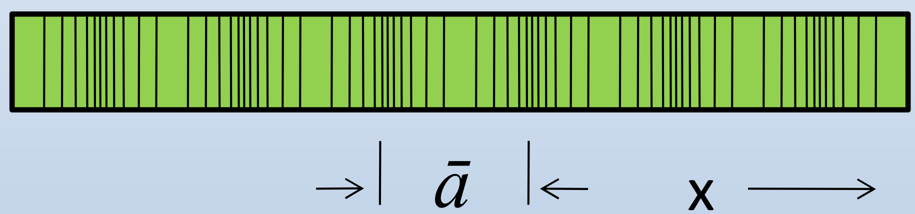


Sphere and Layer



θ laser pulse width

Photoacoustic Effects
in
Periodically Modulated Structures



$$\frac{1}{c^2} = \frac{1}{c_0^2}\left[1 - 2\gamma\cos\left(\frac{2\pi x}{\bar{a}}\right)\right]$$

Wave Equation for pressure

$$(\nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2})\text{p} = -\frac{\beta}{C_P}\frac{\partial H}{\partial t}$$

Frequency domain

$$\frac{d^2}{dz^2}p + [a - 2q\cos(2z)]p = \frac{i\hat{\omega}\bar{\alpha}\beta\bar{a}c_0}{\pi C_P}I(z)$$

where

$$q = \gamma a$$

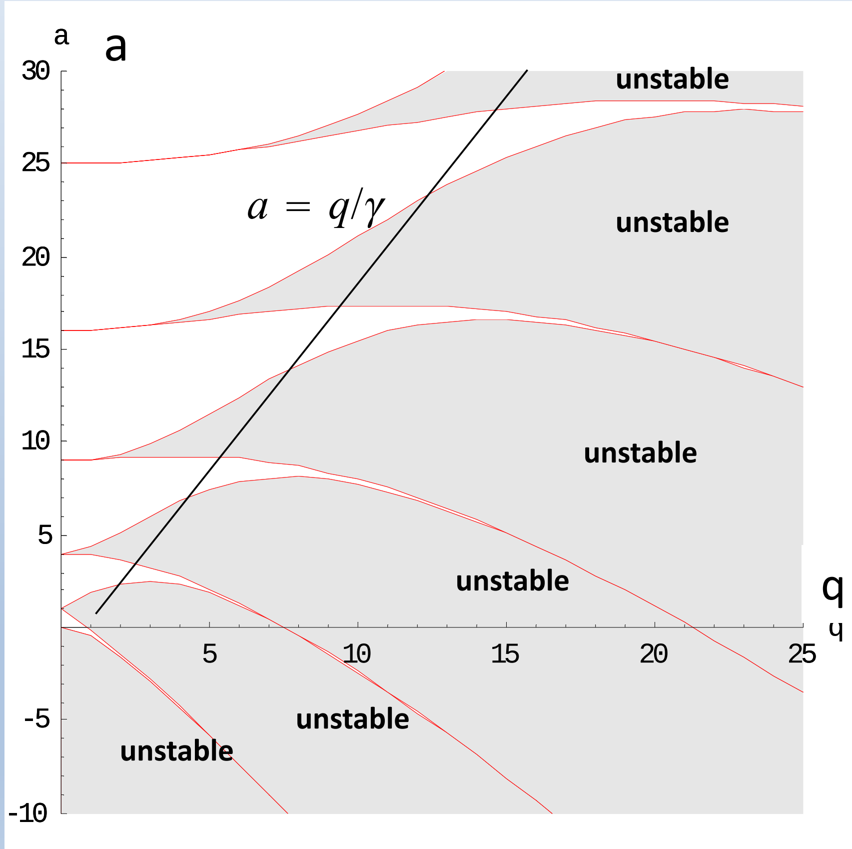
$$a = (\frac{\omega\bar{a}}{\pi c_0})^2$$

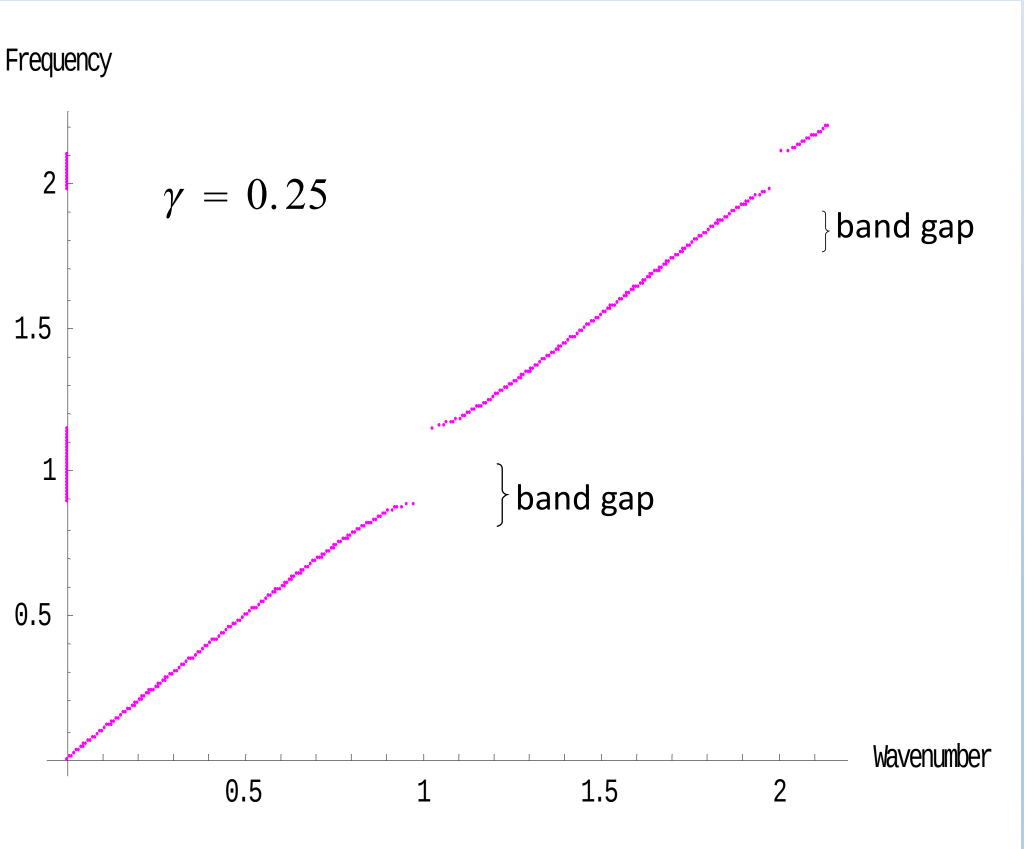
$$z = \frac{\pi}{\bar{a}}x$$

$$\hat{\omega} = \frac{\bar{a}}{\pi c_0}\omega$$

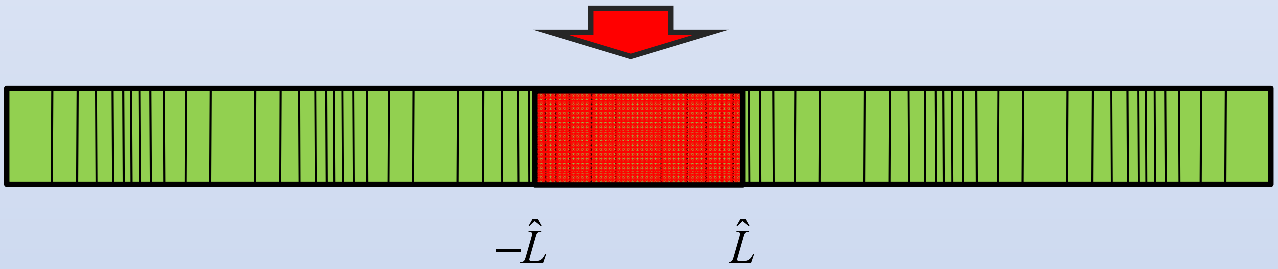
Stability diagram for Mathieu functions

Floquet solution: $p(z) = Ae^{\mu z}\phi(z) + Be^{-\mu z}\phi(-z)$





Infinite structure: central heating



Boundary conditions : finite at $\pm\infty$

Define:
Elliptic "Hankel" functions

$$\begin{aligned} he^{(1)}(a,q,z) &= ce(a,q,z) + i\,se(a,q,z) \\ he^{(2)}(a,q,z) &= ce(a,q,z) - i\,se(a,q,z) \end{aligned}$$

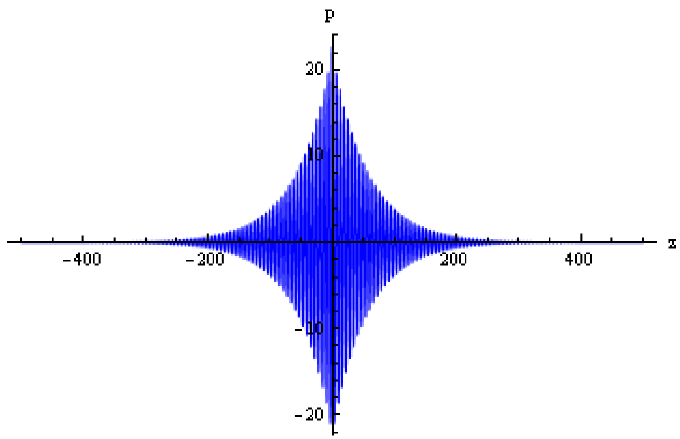
Variation of parameters solution:

$$p_R(z) = -he^{(1)}(z)\int_{-\hat{L}}^{z} \frac{he^{(2)}(z')}{\bar{W}} f(z')dz' - he^{(2)}(z)\int_{z}^{\hat{L}} \frac{he^{(1)}(z')}{\bar{W}} f(z')dz'$$

Excitation Inside the Band Bap

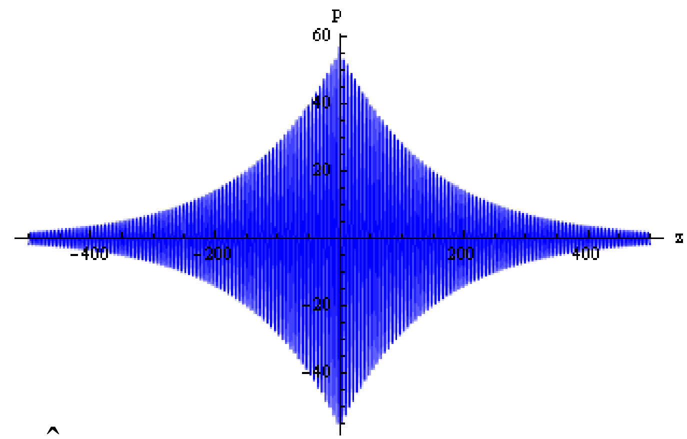
$\hat{\omega} = 1.21700$

Characteristic exponent = 0.017



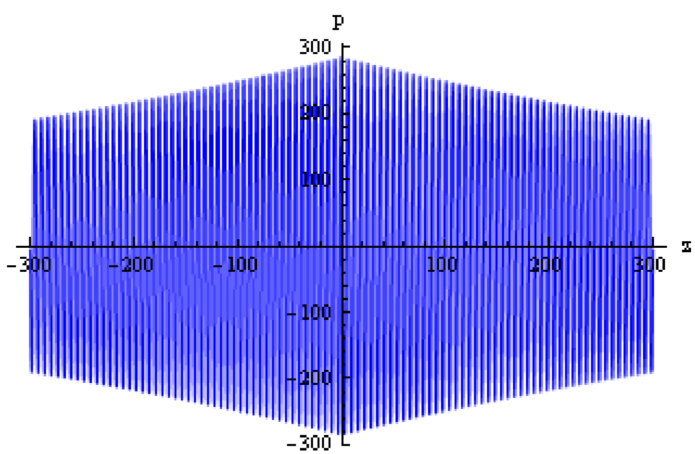
$\hat{\omega} = 1.21774$

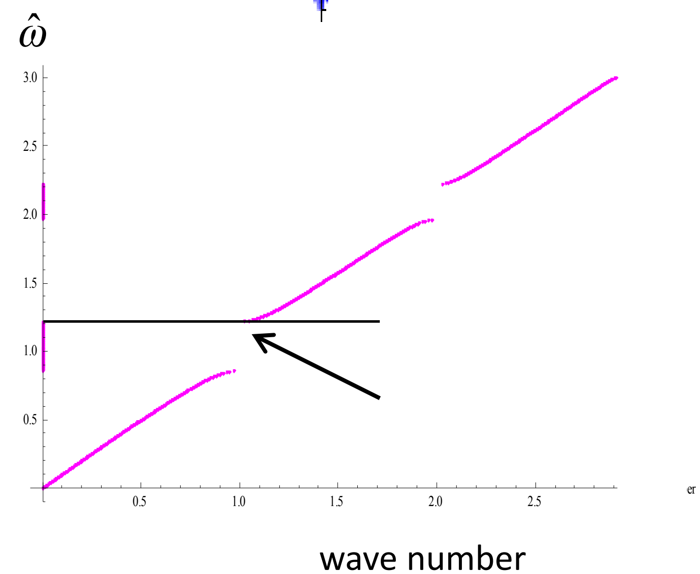
Characteristic exponent = 0.016



$\hat{\omega} = 1.21787$

Characteristic exponent = 0.0013

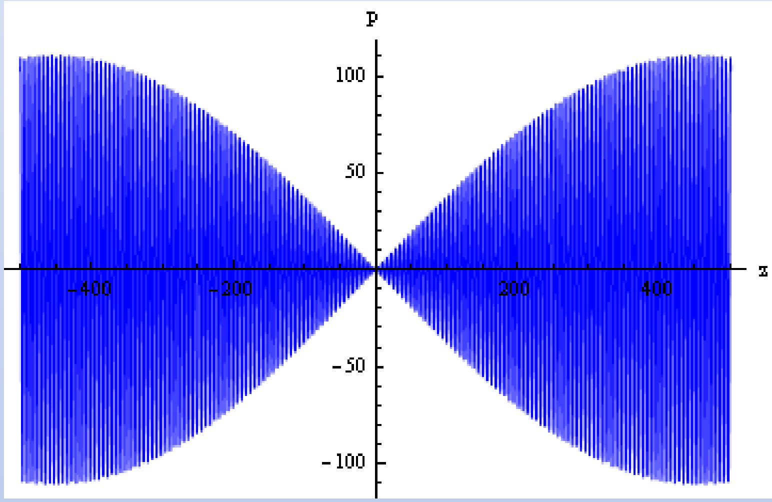




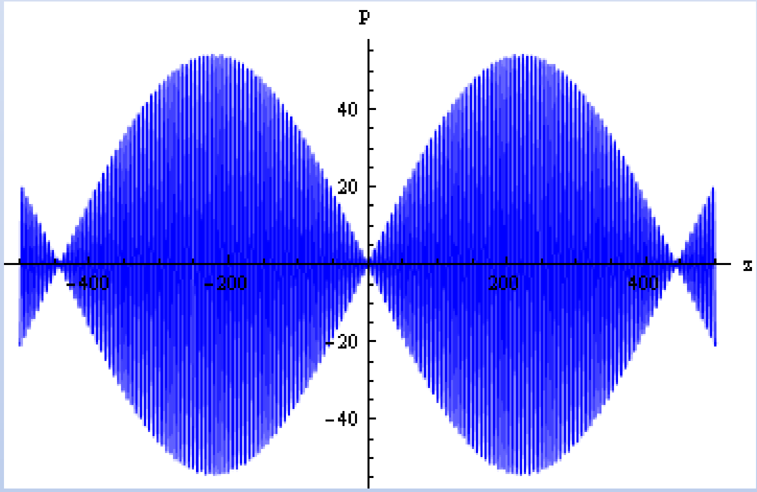
$\gamma = 0.35$

Outside the Band Gap (high frequency edge)

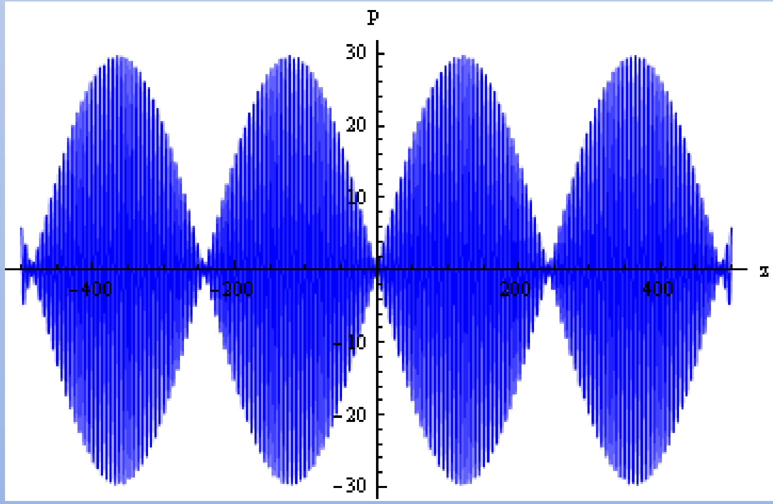
$\hat{\omega} = 1.21791$

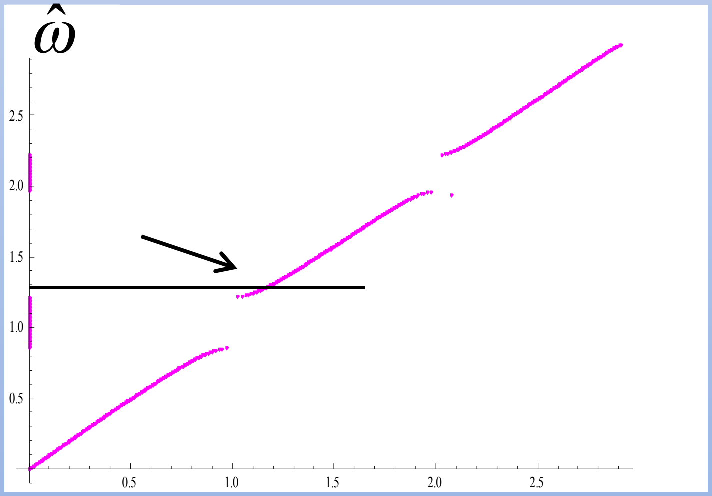


$\hat{\omega} = 1.21802$



$\hat{\omega} = 1.21836$

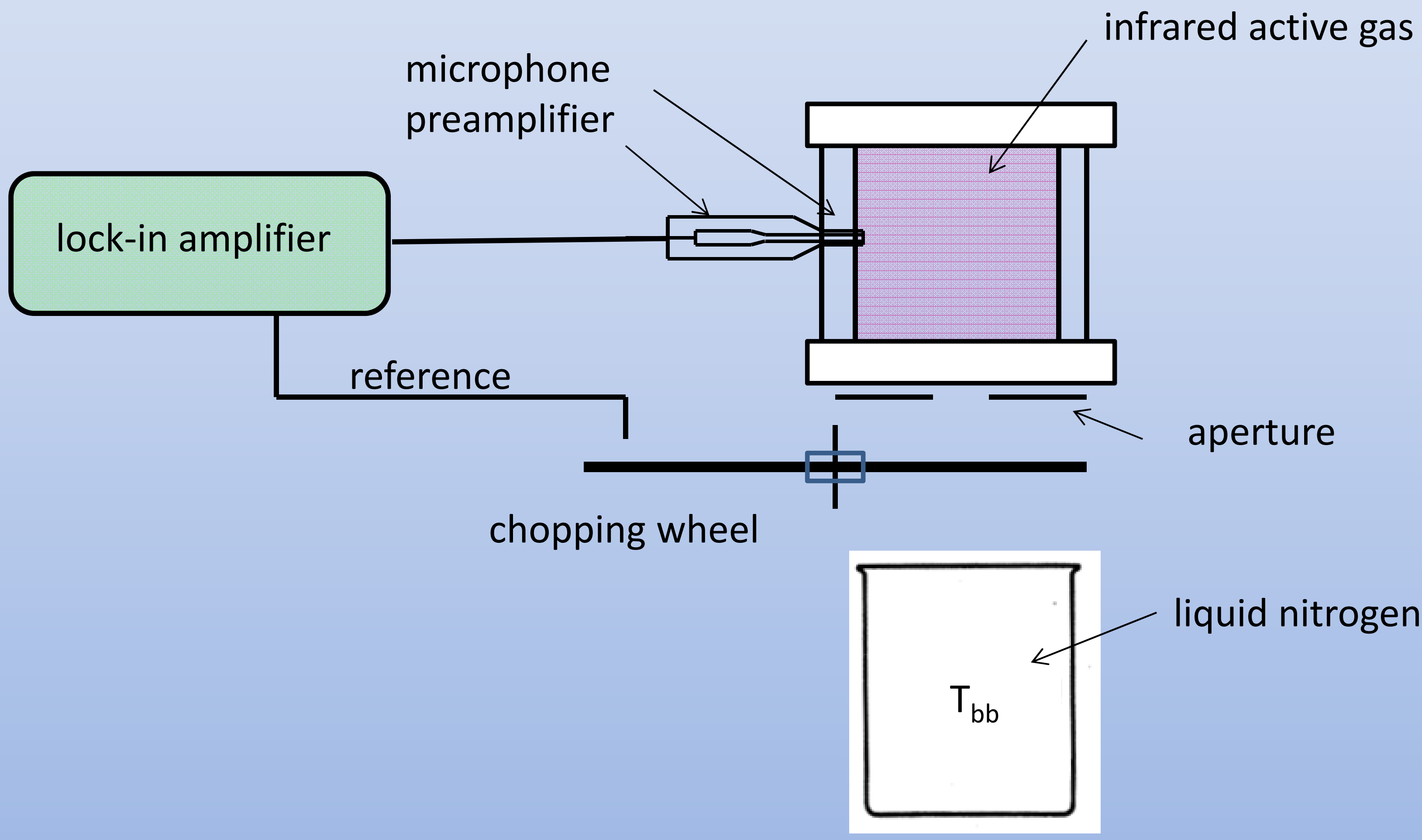




wave number

$\gamma = 0.35$

“Inverse” Photoacoustic Effect



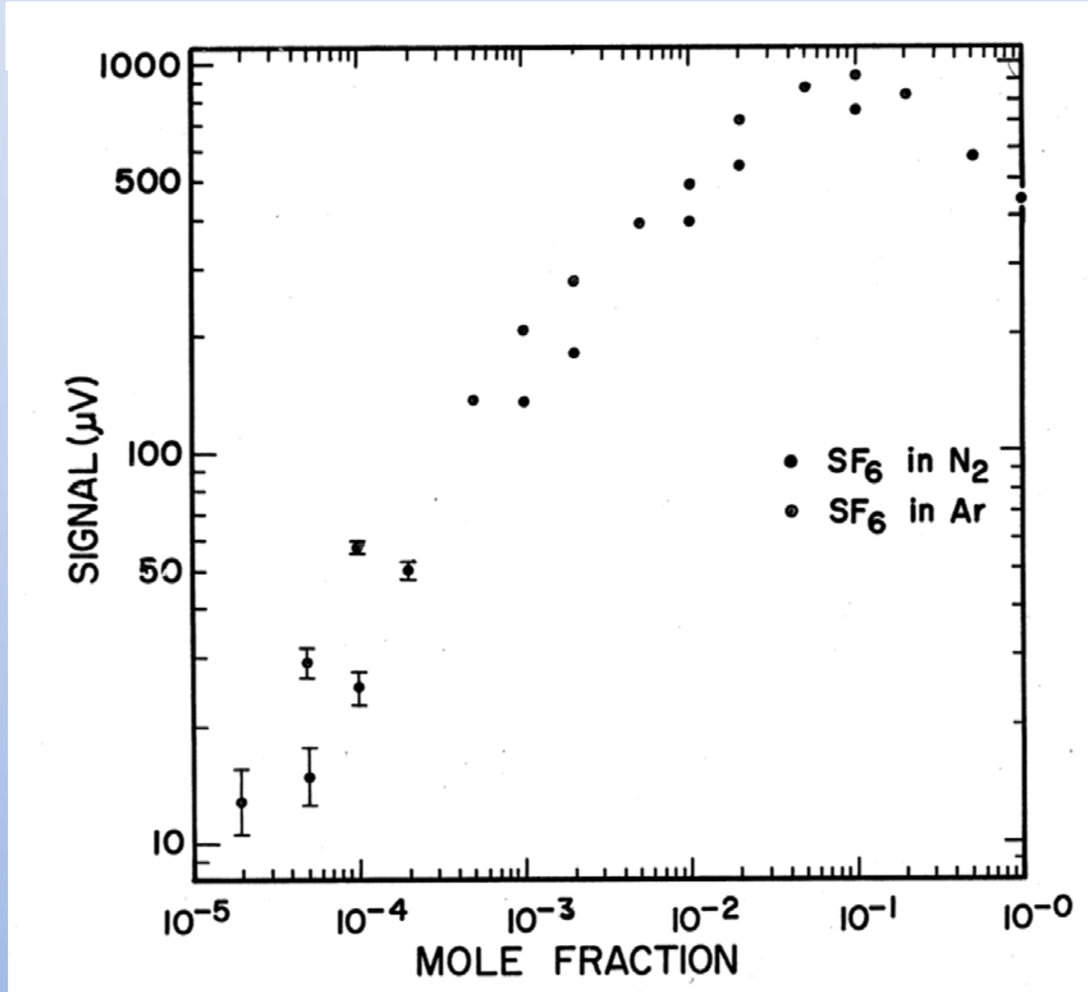
M. Veingerov, Y. Gerlovin, and N. Pankratov, *Opt. Spektrosk* **1**, 1025 (1956)

Signal amplitude

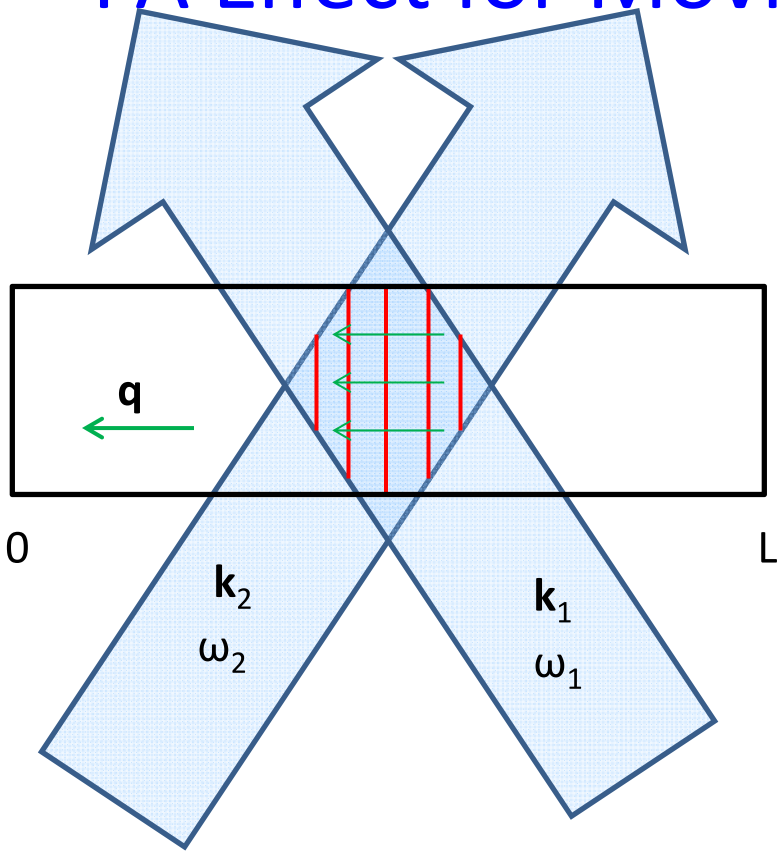
Species	Signal (μV)
C_2H_4	300
C_3H_6	200
CO_2	105
SF_6	62
CH_4	38
CO	6.5

Liquid nitrogen in Dewar flask
Chopping frequency 44 Hz

Signal Amplitude vs. Mole Fraction SF_6



PA Effect for Moving Grating in a Cavity



$$I(t) = I_0[1 + \cos(\mathbf{q} \cdot \mathbf{r} - \Omega t)]$$

$$\mathbf{q} = \mathbf{k}_1 - \mathbf{k}_2$$

$$\Lambda = \frac{\lambda}{2\sin(\theta/2)} \qquad \Omega = \omega_1 - \omega_2$$

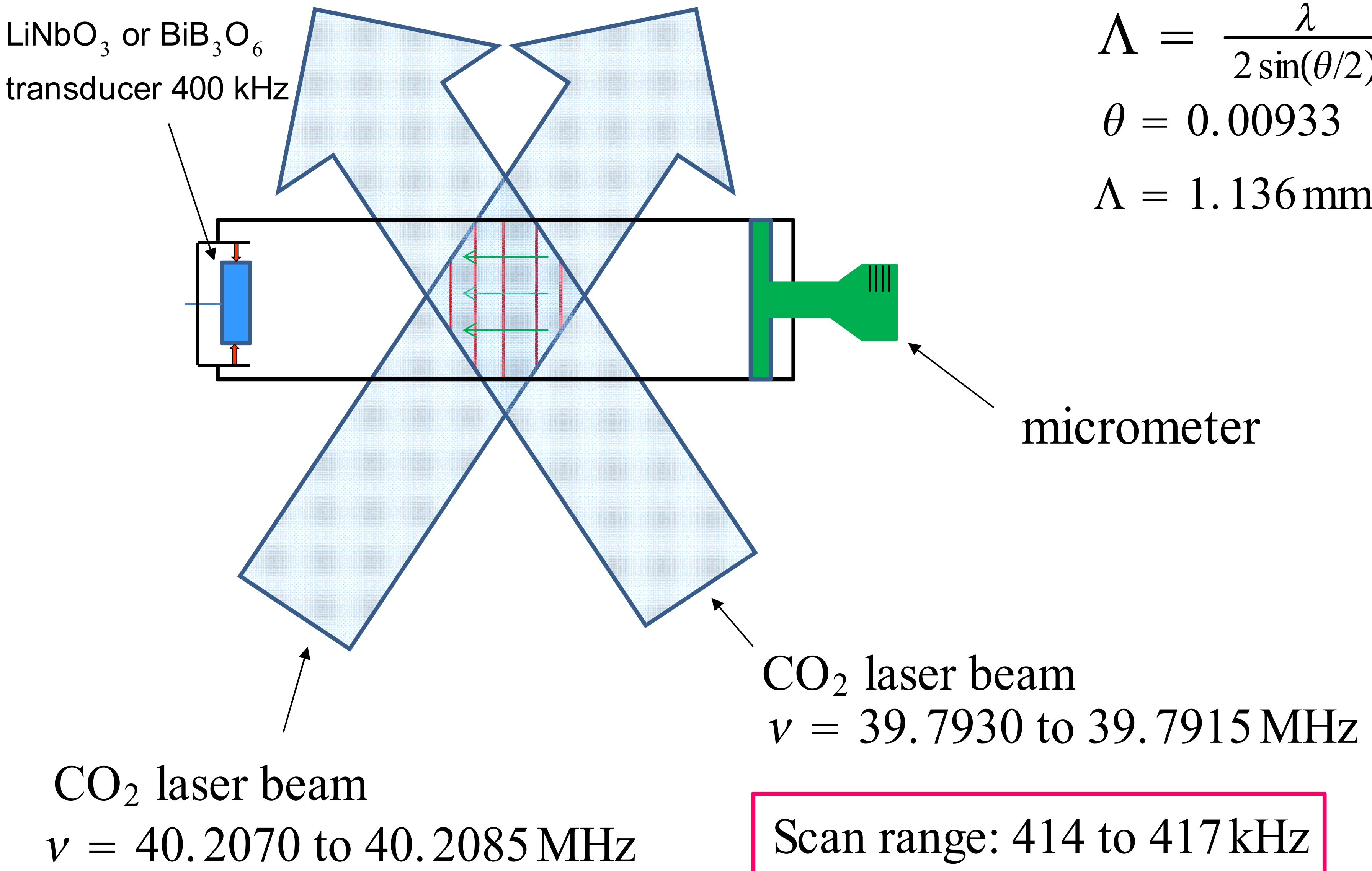
$$p(t) = -\frac{\bar{\alpha}\beta I_0 \Omega L^2}{C_P} \sum_{n=0}^{\infty} \left[\frac{\cos k_n z}{(\frac{\Omega L}{c})^2 - (n\pi)^2} \right] \left\{ \cos \Omega t \left[\frac{\cos(k_n - q)L - 1}{(k_n - q)L} - \frac{\cos(k_n + q)L - 1}{(k_n + q)L} \right] + \sin \Omega t \left[\frac{\sin(k_n - q)L}{(k_n - q)L} - \frac{\sin(k_n + q)L}{(k_n + q)L} \right] \right\}$$

Eichler, Gunter, and Pohl, Laser-induced Dynamic Gratings, Springer-Verlag (1986)

$$\Lambda = 2L/n \qquad \Omega\Lambda = 2\pi c$$

$$k_n = n\pi/L$$

Moving Grating in a Cavity: Experiment

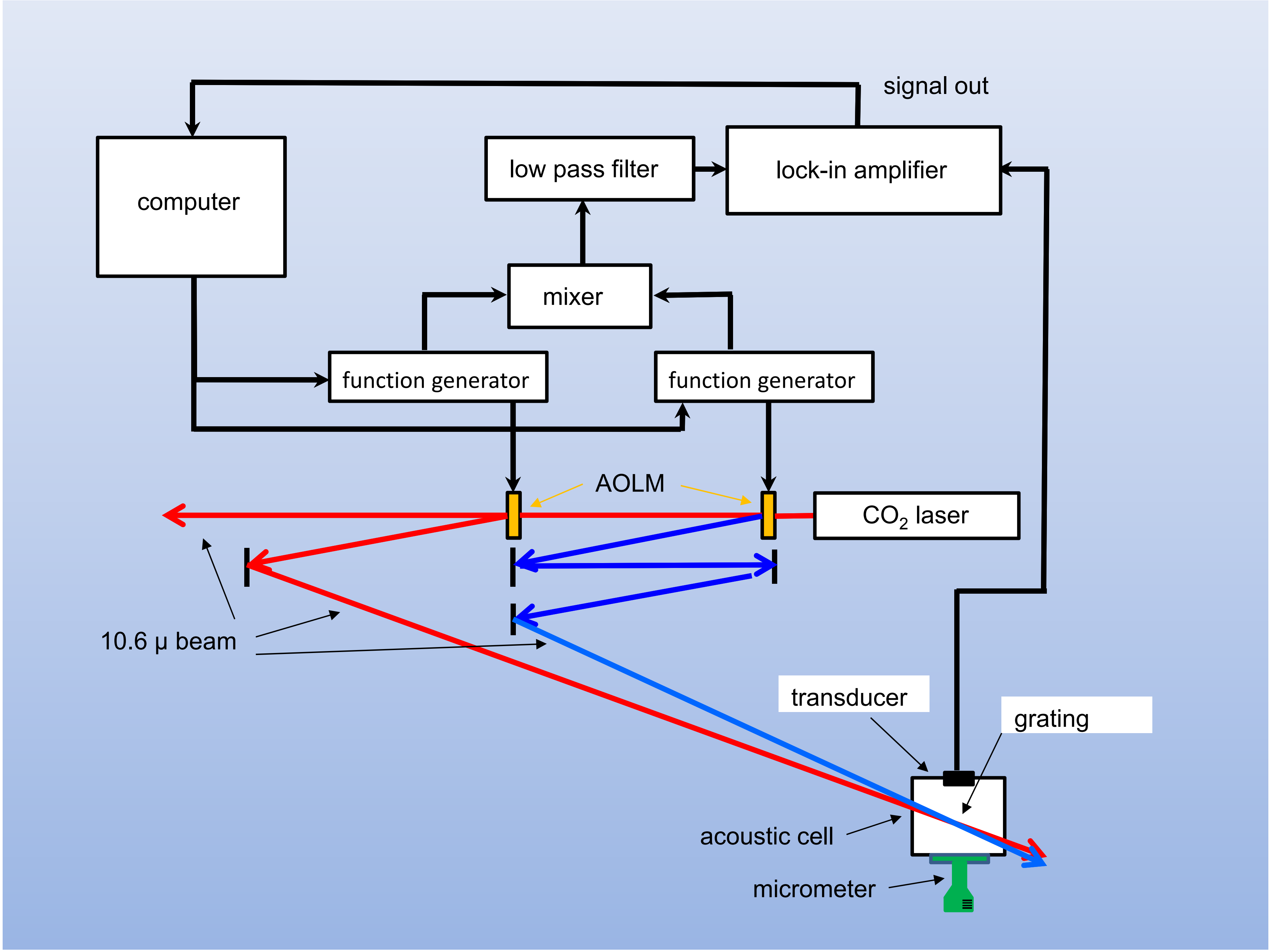


$$\Lambda = \frac{\lambda}{2\sin(\theta/2)}$$

$$\theta = 0.00933$$

$$\Lambda = 1.136\,\text{mm}$$

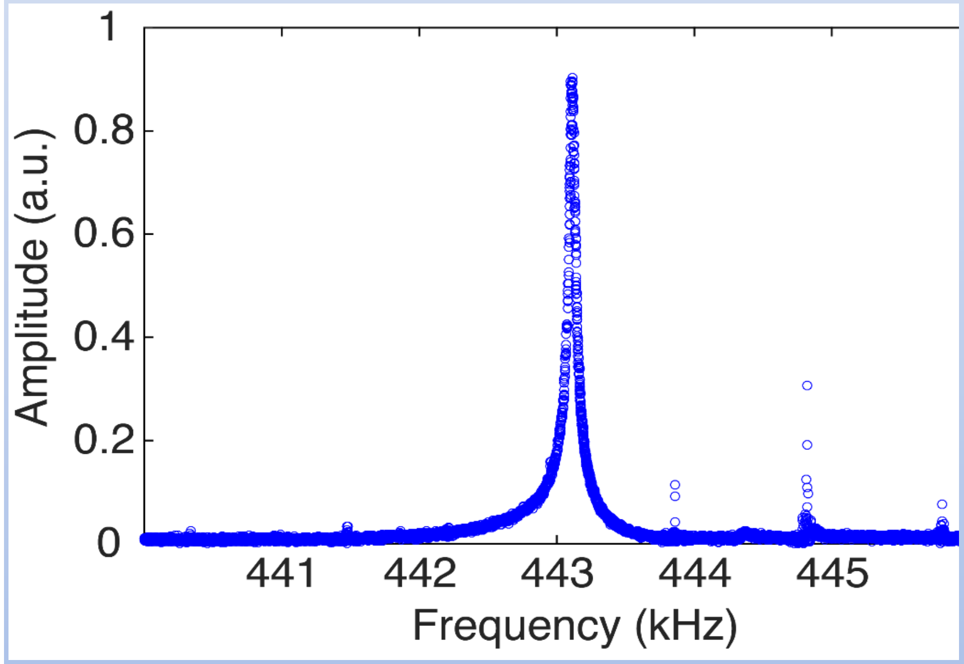
Scan range: 414 to 417 kHz

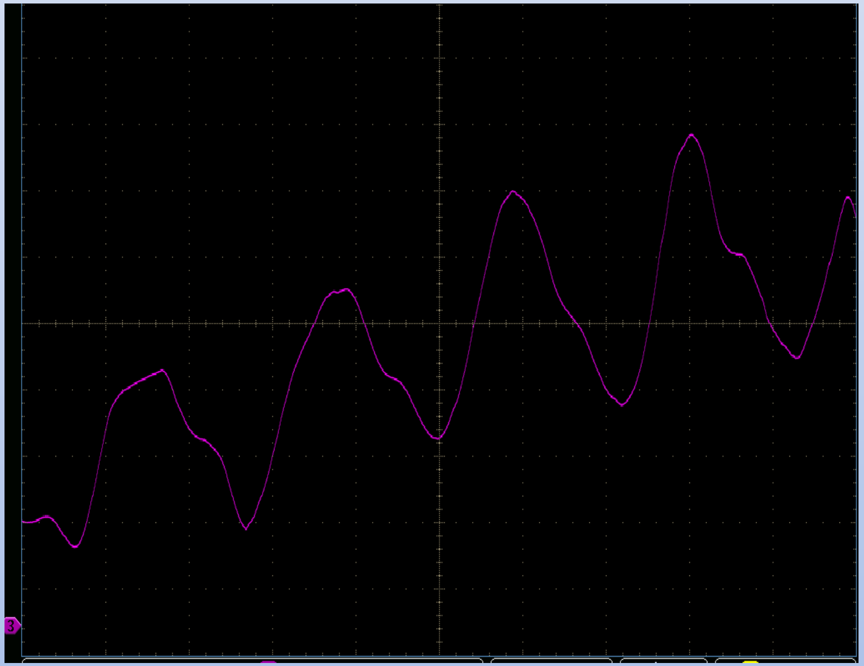

signal out
computer
low pass filter
lock-in amplifier
mixer
function generator
function generator
AOLM
CO_2 laser
10.6 μ beam
transducer
grating
acoustic cell
micrometer

Frequency and Cavity Length Variation

transducer resonance

10 ppb SF_6 in N_2



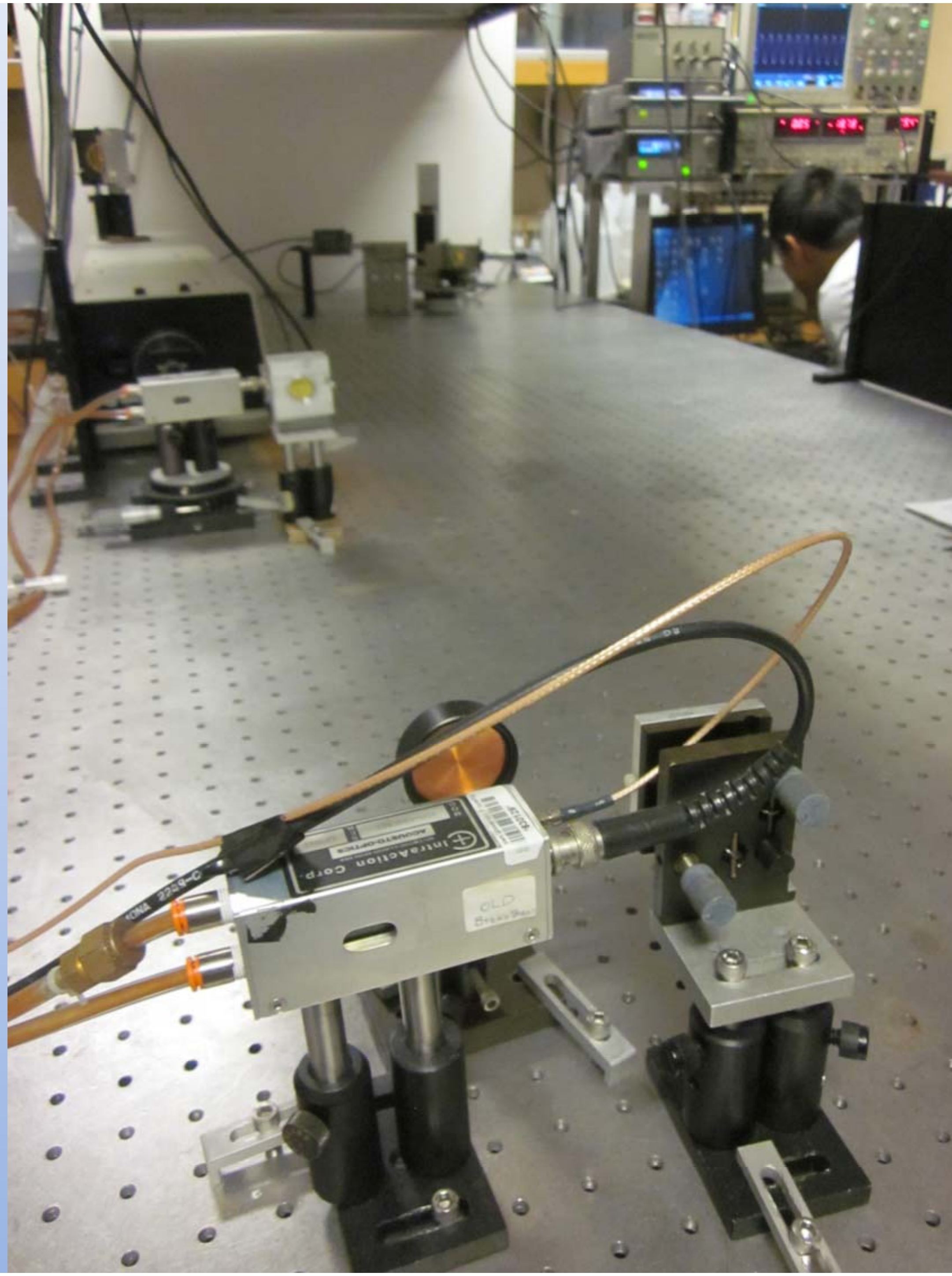


$$\Omega\Lambda = 2\pi c$$

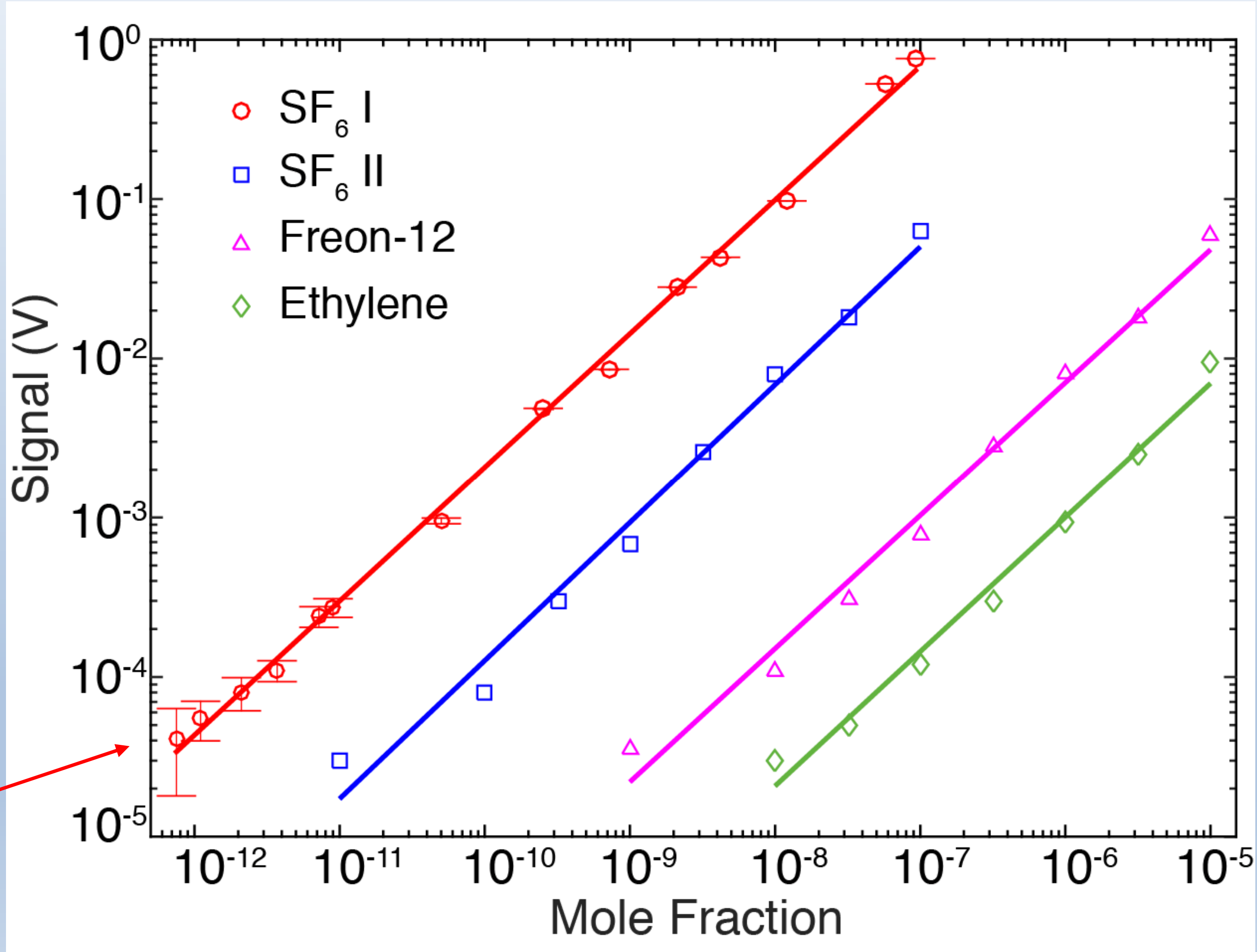
Q=10,800

Cavity Length

$$\Lambda = 2L/n$$

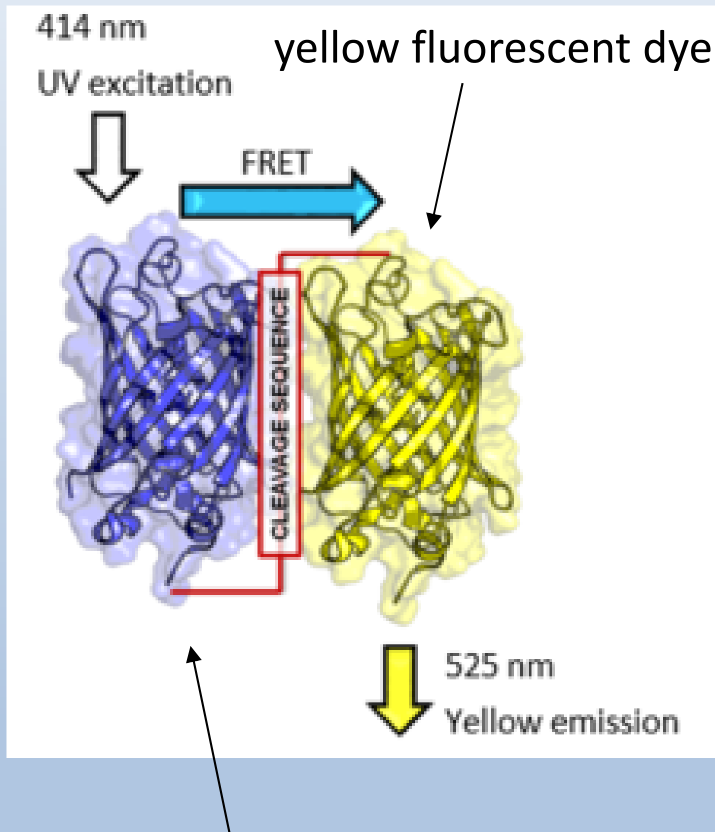

IntraAction Corp.

Signal vs. Trace Gas Concentration

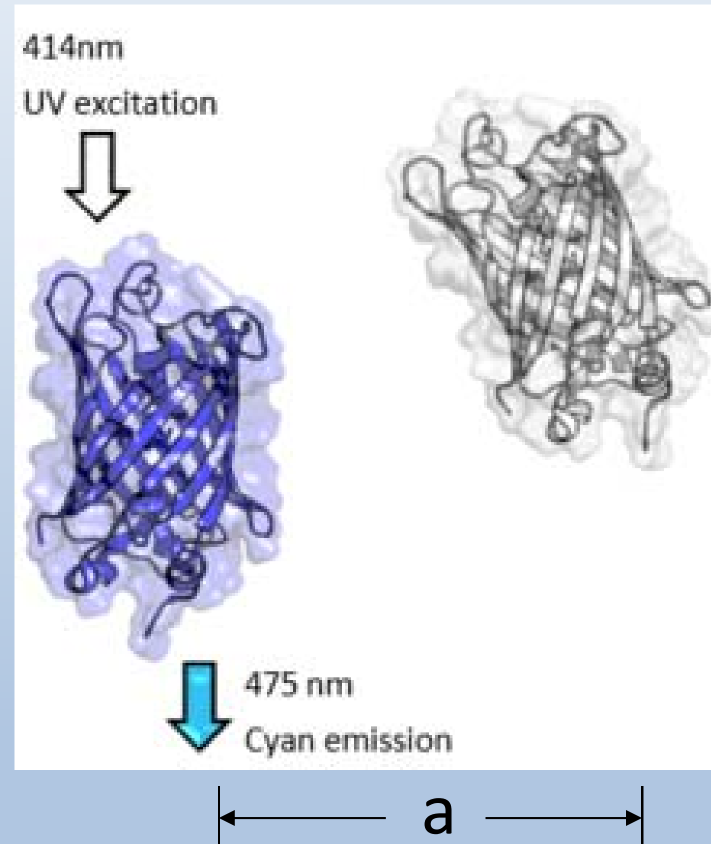


750 parts per quadrillion

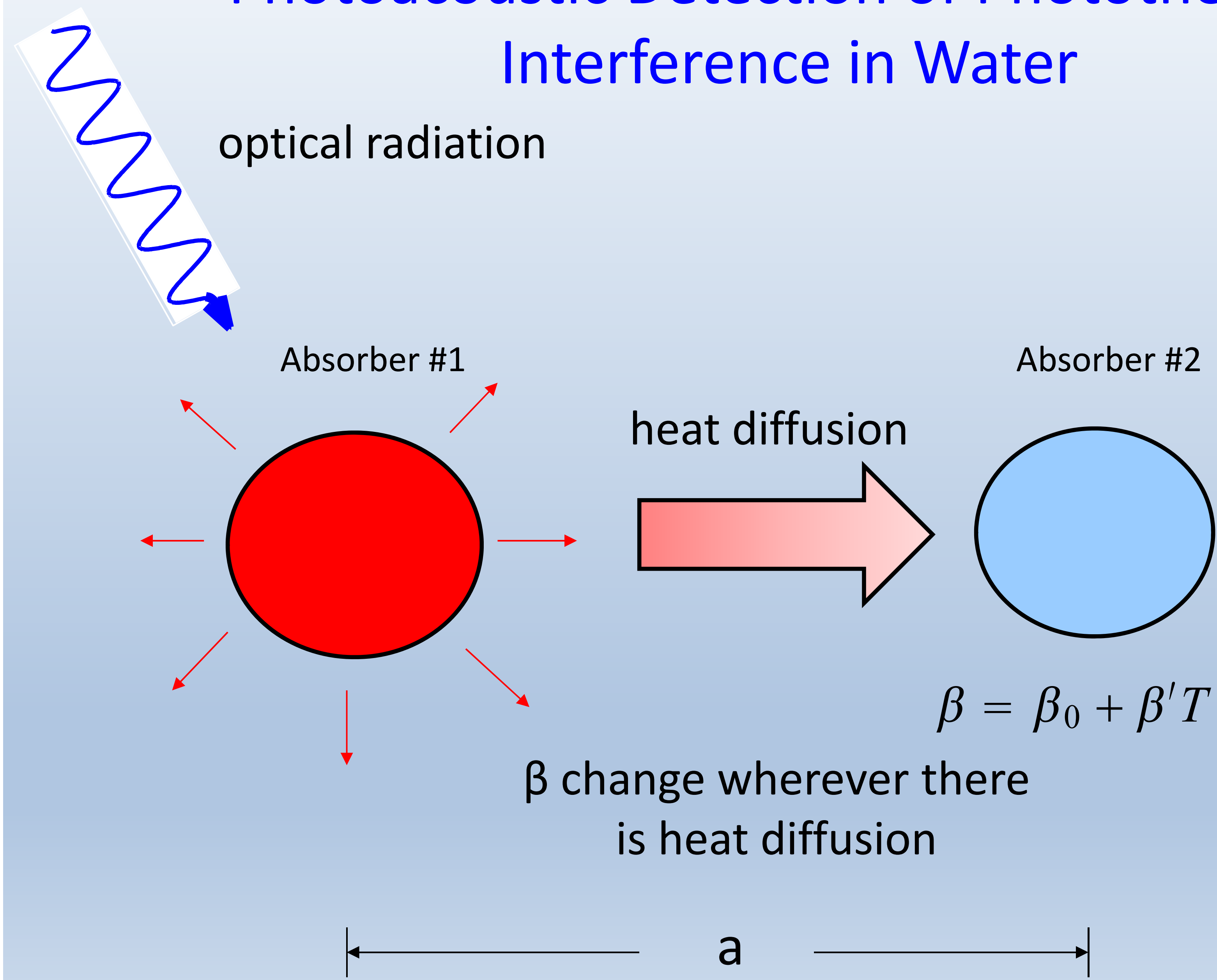
Forster Resonant Energy Transfer (FRET)



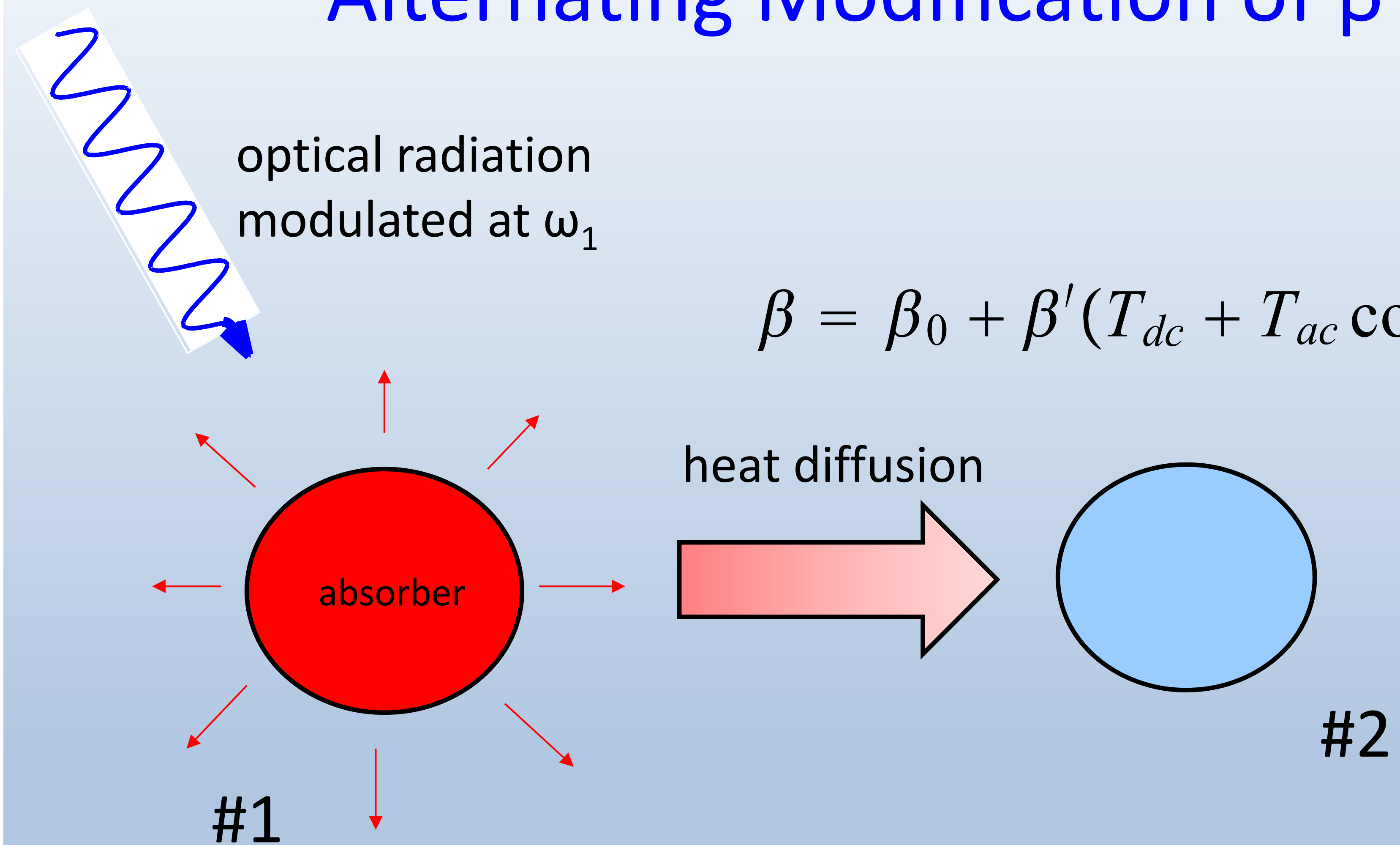
cyan fluorescent dye
475 nm fluorescence



Photoacoustic Detection of Photothermal Interference in Water



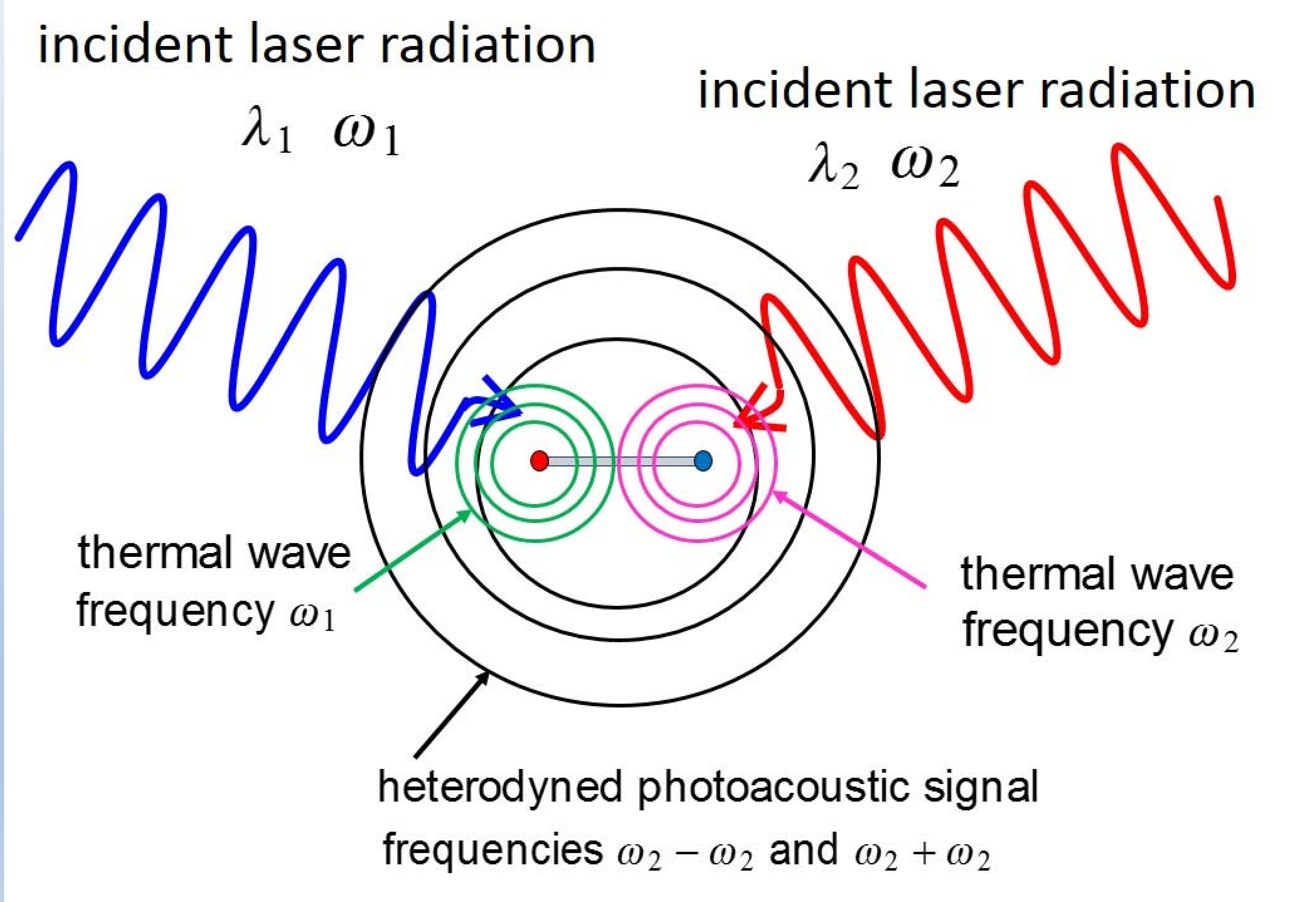
Alternating Modification of β



$$\beta = \beta_0 + \beta'(T_{dc} + T_{ac}\cos\omega_1 t)$$

Alternating change in β change
wherever there is heat diffusion

Photothermal Modification of β



Sound Generation through Heterodyning

$$(\nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2})p = -\rho\frac{\partial^2}{\partial t^2}(\beta\tau)$$

$$\Box^2 p = -\rho\frac{\partial^2}{\partial t^2}\{\underbrace{[\beta_0 + \beta'(\tau_1 + \tau_2)]}_{\beta}\underbrace{(\tau_1 + \tau_2)}_{\tau}\}$$

$$\boxed{\Box^2\varphi = 2\beta'(\mathring{\tau}_1\tau_2 + \tau_1\mathring{\tau}_2)}$$

heterodyned source terms

$\omega_1 + \omega_2$ and $\omega_1 - \omega_2$

$(\nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}) = \Box^2$ d'Alembert operator

Heterodyned Photoacoustic Signal: One Dimension

$$p^{(+)} = \Delta\Phi_C \frac{\Omega^{(+)}}{\sqrt{\omega_1\omega_2}} \sin[\Omega^{(+)}\tau_R^{(1)} + \theta^{(+)}]$$

$$p^{(-)} = \Delta\Phi_B \frac{\Omega^{(-)}}{\sqrt{\omega_1\omega_2}} \sin[\Omega^{(-)}\tau_R^{(1)} - \theta^{(-)}]$$

$$\Omega^{(\pm)} = \omega_1 \pm \omega_2$$

$$\Delta = \frac{\beta' I_1 I_2 c a}{2\rho C_P^2 \chi}$$

$$\Phi_C = \sqrt{(\mathrm{Re}\, C_a)^2 + (\mathrm{Im}\, C_a)^2}$$

$$\Phi_B = \sqrt{(\mathrm{Re}\, B_a)^2 + (\mathrm{Im}\, B_a)^2}$$

$$\theta^{(+)} = \arctan \frac{\mathrm{Re}\, C_a}{\mathrm{Im}\, C_a}$$

$$\theta^{(-)} = \arctan \frac{\mathrm{Im}\, B_a}{\mathrm{Re}\, B_a}$$

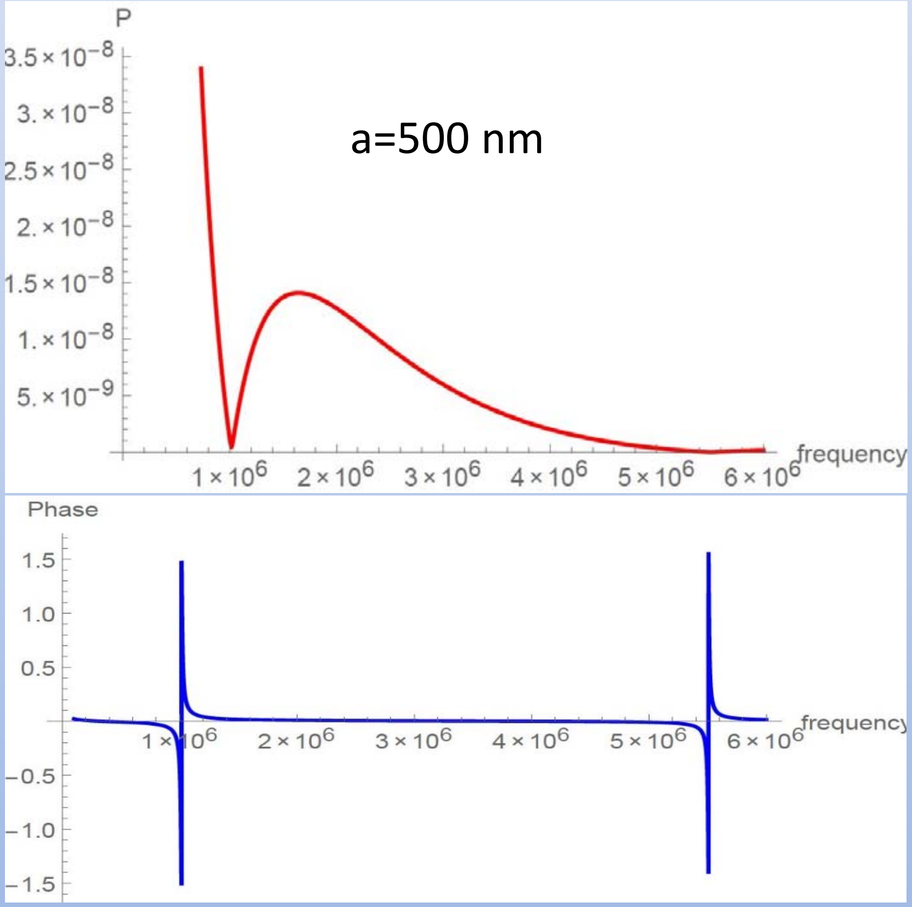
$$C_a = \frac{1}{a}\int_{-\infty}^{\infty} e^{(i-1)k_1|z'-a/2|+(i-1)k_2|z'+a/2|} dz'$$

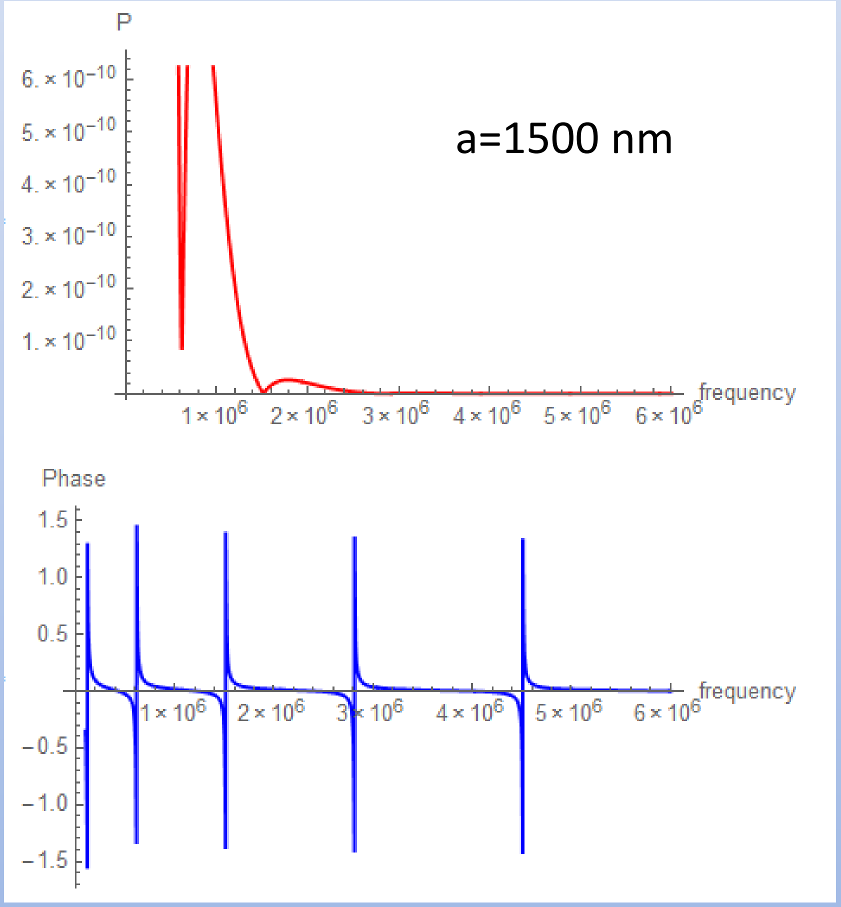
$$B_a = \frac{1}{a}\int_{-\infty}^{\infty} e^{(i-1)k_1|z'-a/2|-(i+1)k_2|z'+a/2|} dz'$$

Photoacoustic Amplitude and Phase

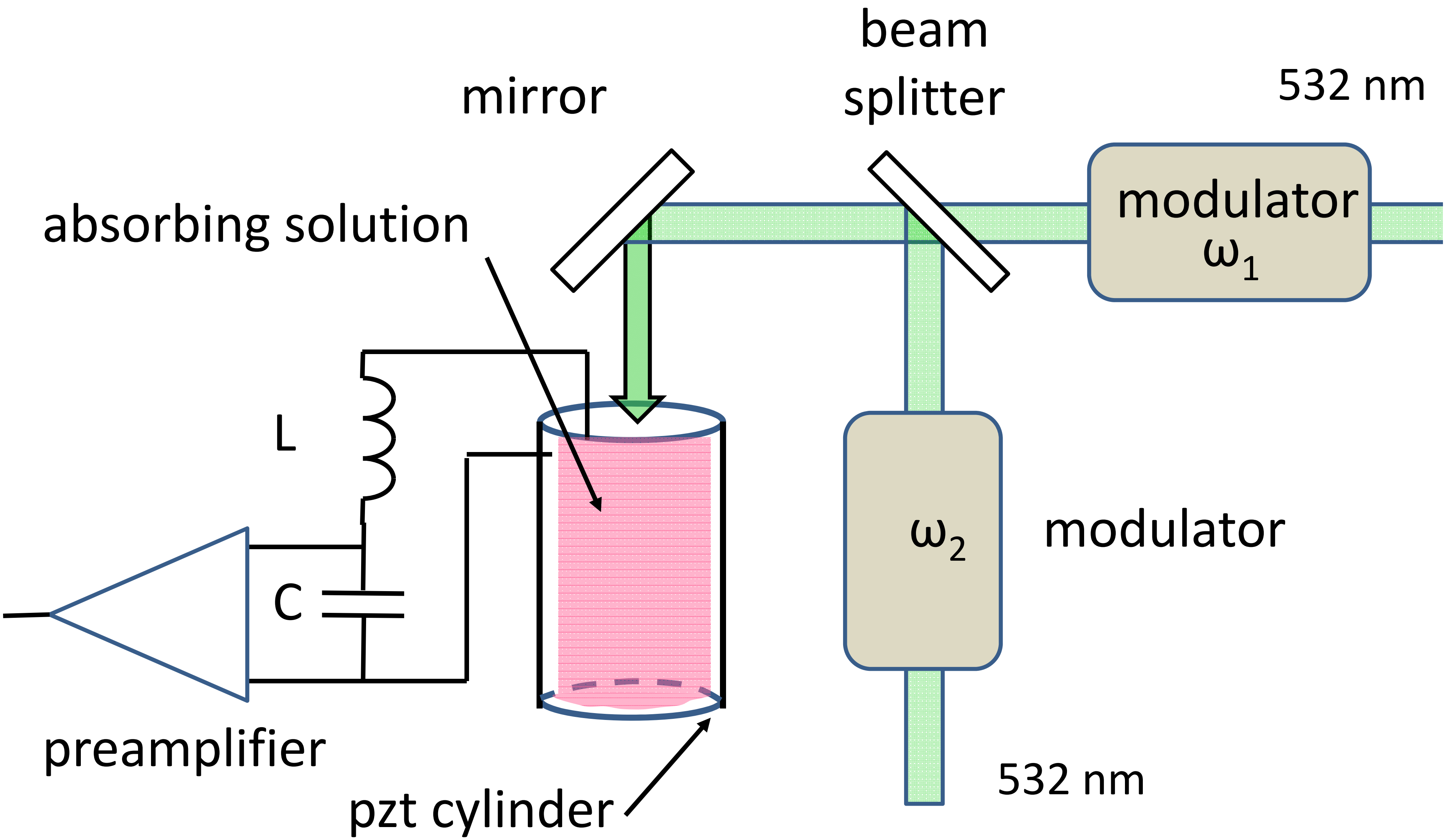
ω_1 varied with $\Omega^{(-)} = 2\pi \times 10^4$

$$\Omega^{(-)} = \omega_1 - \omega_2$$



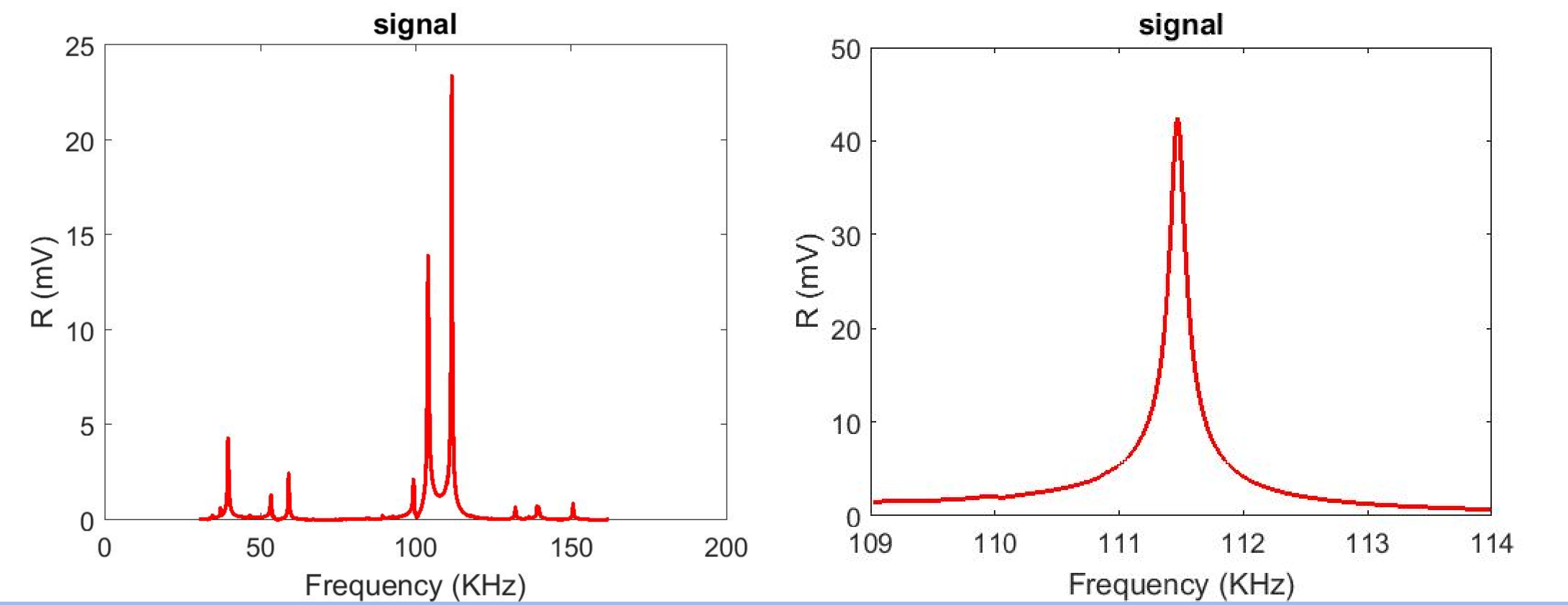


Resonant Cylindrical Resonator



Frequency Response of Cylindrical Resonator

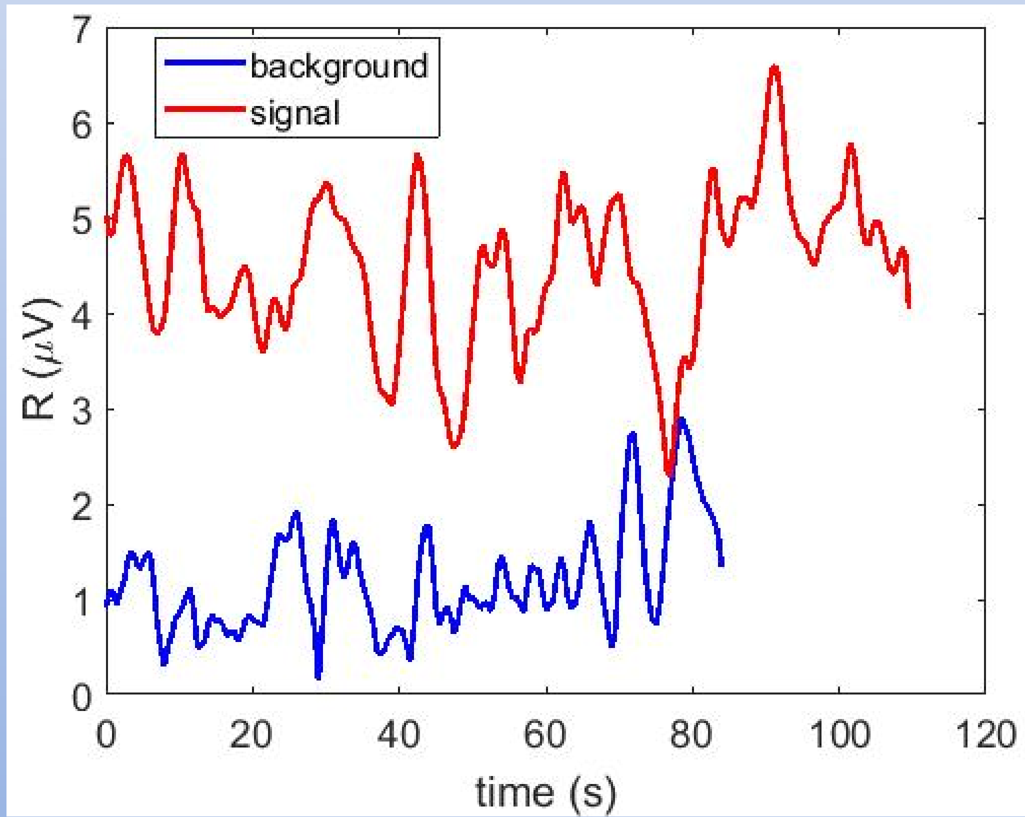
Absorber: 50 nm diameter colloidal Au
Laser power: 80mw
Transducer: Cylindrical PZT tube
22mm inner diameter and 25mm height



Single particle Two 532 nm Beams

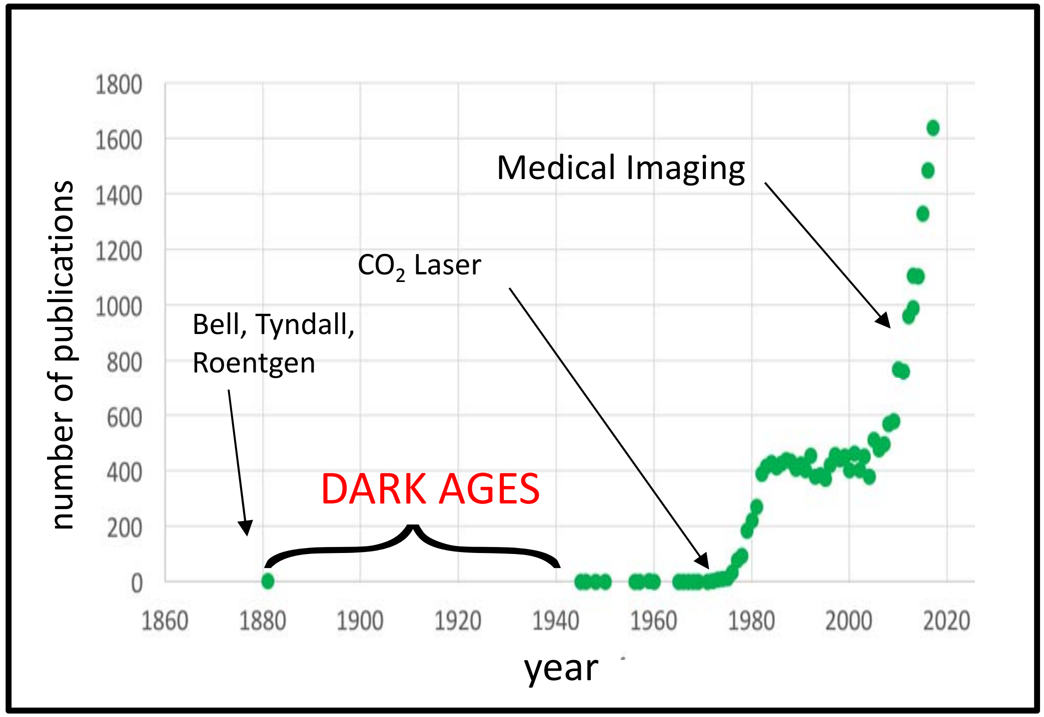
Beam #1: 391.46 kHz (88mw)
Beam #1: 280.00 kHz (20mw)
Difference frequency: 111.46 kHz (cell resonance frequency)

Absorber: 50 nm Au colloid
Lock-in amplifier time constant: 1s.



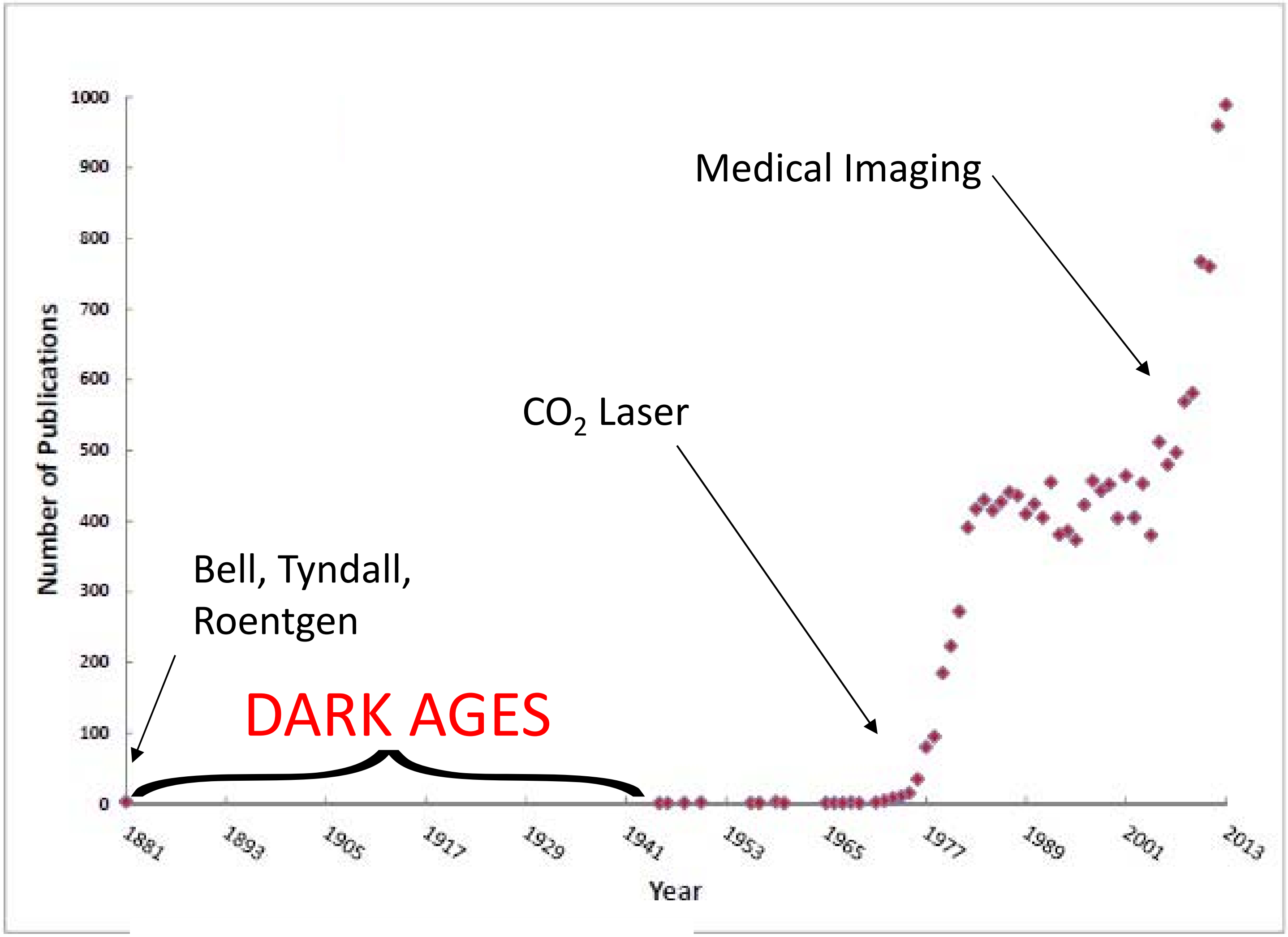
Coworkers:

Clifford Frez
Tom Sun
Iltaf Khan
Mike O'Connor
Binbin Wu
Xiangling Meng
Wenyu Bai
Yaqi Zhang

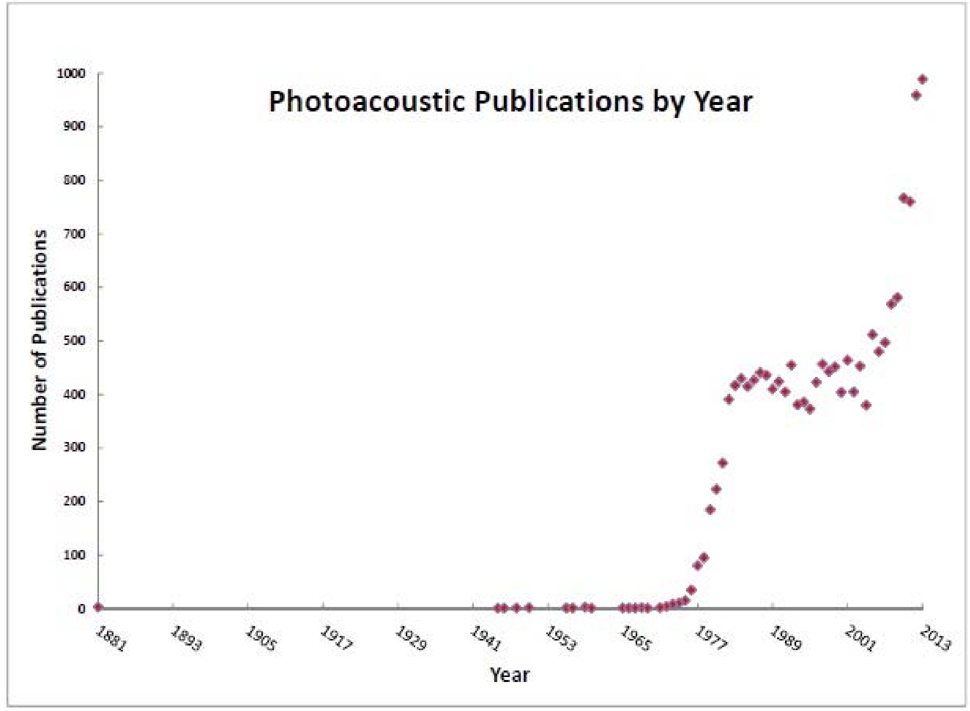


Support:

US Department of Energy



Medical Imaging
CO_2 Laser
Bell, Tyndall, Roentgen
DARK AGES
Number of Publications
1000
900
800
700
600
500
400
300
200
100
0
1881
1893
1905
1917
1929
1941
1953
1965
1977
1989
2001
2013
Year


Photoacoustic Publications by Year
Number of Publications
1000
900
800
700
600
500
400
300
200
100
0
1881
1893
1905
1917
1929
1941
1953
1965
1977
1989
2001
2013
Year