PROGRESS REPORT

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Photochemical Generation of the Optoacoustic Effect

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MASTER

PROGRESS REPORT

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ABSTRACT

Research in this period has focussed on the description of the photoacoustic effect generated by small bodies, (or particles) irradiated by short pulse laser radiation. In particular, the effects of the discontinuity in acoustic properties at the interface of the body and its surrounding medium are considered. Calculations were carried out to determine the temporal profile of the photoacoustic waves generated by fluid spheres, cylinders, and layers. Similar calculations were done for a one dimensional Beer's law absorption of radiation. We find that time domain expressions for the photoacoustic waveforms can be expressed in terms of Fourier transform integrals. The temporal profiles of the waveforms depend on the geometry and dimensions of the particle and the sound speed and density ratios between the irradiated particle and its surrounding fluid. Experiments where a Nd:YAG laser irradiates a particle and the ultrasonic wave is detected by a fast polyvinylidene fluoride transducer show that the theoretical model is essentially correct in predicting the important features of the waveforms. Additional experiments are reported where an interference effect is observed, and the influence of optical pumping on the electron beam ionization of Na is determined.

A) The Photoacoustic Effect in Strongly Absorbing Fluids

1) Theory

The generation of ultrasonic waves by absorption of optical radiation, known as the photoacoustic effect, takes place in a straightforward manner: the heating of a body caused by the absorption of radiation, gives rise to an expansion of the body thereby launching a sound wave. Owing to its high sensitivity and its dependence on the pathway for thermalization of the absorbed optical radiation, the photoacoustic effect has seen side application¹⁻¹¹ in a number of diverse fields. If a single medium is involved in production of the photoacoustic effect and heat conduction can be neglected on the time scale of the sound generation process, then the properties of the acoustic waveform can be obtained by solution of the wave equation for pressure.^{12,13} In many cases, the acoustic waveform can be found by a straightforward spatial integration of the heating function over the illuminated region with the heating function evaluated at the retarded time.¹²⁻²¹

Figure 1

Here, we consider a fluid with density ρ_a and sound speed c_a that extends in the positive z direction from the xy plane and which is in contact with a second fluid as shown in Fig. 1. Fluid (b) is transparent while fluid (a) is assumed to absorb optical radiation exponentially in space according to Beer's law. The radiation is directed

along the positive z axis and is assumed to be of infinite extent in the xy plane. The problem addressed here is determination of the temporal dependence of the acoustic waveform for an incident radiation beam with a delta function temporal profile.

When heat conduction can be neglected on the time scale of the acoustic wave then the pressure obeys the wave equation,^{12,13}

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

where p is the acoustic pressure, c is the sound speed, β is the isobaric volume expansion coefficient, C_P is the isobaric heat capacity per mass, t is the time, and H is the heating function, defined as the energy absorbed per time per unit volume. First, we consider a frequency domain solution p obtained by taking the heating function to be of the form

$$H = \alpha I_0 e^{i\omega t - \alpha z} \quad z > 0, \quad (2)$$

where α is the optical absorption coefficient, and ω is the modulation frequency of the radiation intensity I_0 . The time domain acoustic response for a heating function described by a delta function in time is then obtained by Fourier transformation of the frequency domain solution.

For a pressure wave of the general form $p_M = \tilde{p}(z) \exp(-i\omega t)$ and a heating function given by Eq. 2, the wave equation reduced to a 1-dimensional differential equation for $\tilde{p}(z)$ as

$$\left(\frac{\partial^2}{\partial z^2} + \frac{\omega^2}{c_a^2}\right) \tilde{p}(z) = \frac{i \alpha \beta \omega I_0}{C_P} \exp(-\alpha z). \quad (3)$$

The solution for $\tilde{p}(z)$ in medium (a) is easily found so that p_M becomes

$$p_M = \left(\frac{i c_a \beta I_0}{C_P}\right) \frac{(k_a/\alpha) e^{i\omega t - \alpha z}}{1 + (k_a/\alpha)^2}, \quad (4)$$

which is written in terms of a dimensionless parameter k_a/α where $k_a = \omega/c_a$ is the wavevector in medium(a).

Since there is a discontinuity in acoustic properties at the interface between the two fluids, the acoustic pressure for $z > 0$ must be a sum of the driving pressure p_M and a solution to the homogeneous wave equation. Because the two fluids are infinite in the $\pm z$ directions,

traveling waves propagating away from the interface are taken as the solutions. The acoustic pressures in media (a) and (b), denoted as p_a and p_b , respectively, must then be of the form,

$$\begin{aligned} p_a &= p_M + P_a e^{i(k_a z - \omega t)} & z > 0 \\ p_b &= P_b e^{-i(k_b z + \omega t)} & z < 0, \end{aligned} \quad (5)$$

where P_a and P_b are complex constants, and k_b is the wavevector in medium (b). At the interface between the fluids, the displacement caused by the sound wave must be continuous as it is approached from either medium. Any time derivative of the displacement must be continuous as well. If the second derivative of the displacement is considered, it follows that the negative gradient of the pressure divided by the density, which is equal to the acceleration, must be continuous. Secondly, the pressure itself evaluated from either side of the interface must be continuous across the interface.¹³ These two conservation laws, in the case of the solutions given in Eq. 5, yield two equations,

$$\frac{(c_a \beta I_0 / C_P)}{1 + (k_a / \alpha)^2} - P_a + \hat{\rho} \hat{c} P_b \quad (6)$$

$$\frac{(i c_a \beta I_0 / C_P)(k_a / \alpha)}{1 + (k_a / \alpha)^2} + P_a = P_b, \quad (7)$$

where a dimensionless density $\hat{\rho}$ and sound speed $\hat{c}$ have been defined as $\hat{\rho} = \rho_a / \rho_b$ and $\hat{c} = c_a / c_b$ respectively. Solution of Eqs. 6 and 7 for P_a and P_b is straightforward; the acoustic pressures can be written as

$$\begin{aligned} p_a(q) &= \left(\frac{i \beta c_a I_0}{C_P} \right) \left[\frac{q e^{-iq\hat{z} - \hat{z}}}{1 + q^2} - \frac{(q\hat{\rho}\hat{c} + i)e^{-iq\hat{\tau}}}{(1 + q^2)(1 + \hat{\rho} - \hat{c})} \right] \\ p_b(q) &= \left(\frac{i \beta c_a I_0}{C_P} \right) \left[\frac{(q - i) e^{-iq\hat{\tau}^\dagger}}{(1 + \hat{\rho}\hat{c})(1 + q^2)} \right], \end{aligned} \quad (8)$$

where the dimensionless frequency parameter q , the dimensionless distance $\hat{z}$, the dimensionless time $\hat{t}$, and the dimensionless retarded times $\hat{\tau}$ and $\hat{\tau}^\dagger$ have been defined as

$$q = k_a / \alpha, \quad \hat{z} = z \alpha, \quad \hat{\tau} = c_a \alpha t$$

$$\hat{\tau} = c_a \alpha(t - \frac{z}{c_a}), \quad \hat{\tau}^\dagger = c_a \alpha(t + \frac{z}{c_b}).$$

It can be seen that the acoustic pressure in medium (a) contains two terms, the first of which describes a near field pressure whose amplitude decreases as $\exp(-\hat{z})$. The second term describes a wave that persists in the far field which is a function of the retarded time from the interface. The corresponding pressure in medium (b) contains only terms that depend on the retarded time.

Simple Fourier transformation of Eqs. 8 and 9 gives the acoustic response to a delta function heating pulse. Thus, the time domain solution to the wave equation for instantaneous heating is given by

$$\begin{aligned} p_a(t) &= \frac{i\tilde{\kappa}}{2\pi} \int_{-\infty}^{\infty} \left[\frac{q e^{iq\hat{t}-\hat{z}}}{1+q^2} - \frac{(q\hat{\rho}\hat{c}+i)e^{-iq\hat{\tau}}}{(1+\hat{\rho}\hat{c})(1+q^2)} \right] dq \\ p_b(t) &= \frac{i\tilde{\kappa}}{2\pi(1+\hat{\rho}\hat{c})} \int_{-\infty}^{\infty} \left(\frac{q-i}{1+q^2} \right) e^{iq\hat{\tau}^\dagger} dq, \end{aligned} \quad (9)$$

where $\tilde{\kappa}$ is defined in terms of the radiation fluence E_0 as $\tilde{\kappa} = \alpha\beta E_0 c_a^2 / C_P$. These integrals can be evaluated in the complex plane using simple semicircular integration paths in the upper and lower half planes, as the poles of the integrand are located at $\pm i$. The results of the complex integration give the acoustic pressures as

$$\begin{aligned} p_a(t) &= (\tilde{\kappa}/2) \left[\text{sgn}(\hat{t}) e^{-|\hat{t}|- \hat{z}} + e^{\hat{\tau}} \right] & \hat{\tau} < 0 \\ p_b(t) &= 0 & \hat{\tau}^\dagger < 0 \end{aligned} \quad (10)$$

$$\begin{aligned} p_a(t) &= (\tilde{\kappa}/2) \left[e^{-\hat{t}-\hat{z}} + \frac{(1-\hat{\rho}\hat{c})}{1+\hat{\rho}\hat{c}} e^{-\hat{\tau}} \right] & \hat{\tau} > 0 \\ p_b(t) &= (\tilde{\kappa}/2) \left(\frac{2}{1+\hat{\rho}\hat{c}} \right) e^{-\hat{\tau}^\dagger} & \hat{\tau}^\dagger > 0, \end{aligned} \quad (11)$$

where the sgn function is defined as $+1$ or -1 depending on the sign of its argument.

The interpretation of each of the terms in Eqs. 10 and 11 is straightforward. Consider the solutions immediately after firing of the laser; the dimensionless time $\hat{t}$ is then greater than zero. For large values of $\hat{z}$ in medium (a) and for $\hat{\tau}$ less than zero, the second term

in Eq. 10a describes a pressure wave with increasing amplitude at any point in space since there is absorption of radiation for all $\hat{z} > 0$. The wave is compressive and of increasing amplitude until $\hat{\tau}$ changes sign. At this point, there is a wave of decreasing amplitude which is compressive or expansive depending on the sign of the factor $(1 - \hat{\rho}\hat{c})/(1 + \hat{\rho}\hat{c})$. This quantity is the amplitude reflection coefficient for a plane wave at a plane interface. The second term in Eq. 11a thus represents the reflection of the first wave (i.e. the wave corresponding to the second term in Eq. 10a) from the fluid interface. Of course, no reflected wave appears if $\hat{\rho}\hat{c} = 1$. In medium (b), no signal can reach a detector for negative values of the retarded time $\hat{\tau}^\dagger$; however, for $\hat{\tau}^\dagger > 0$, an exponential, compressive wave appears with an amplitude proportional to $2/(1 + \hat{\rho}\hat{c})$, the amplitude transmission coefficient for a plane wave at a plane interface.

Figure 2

The terms explicitly containing $\hat{z}$ provide for causality in the solutions. For p_a , when $\hat{t} < 0$ and $\hat{\tau} < 0$ it can be seen that the two terms in Eq. 10a cancel (since $\hat{\tau} = \hat{t} - \hat{z}$) so that there is no pressure wave before the laser fires. The pressure in medium (a) when $\hat{t} > 0$ and $\hat{\tau} < 0$ is a sum of two waves, one of increasing amplitude and another (depending explicitly on $\hat{z}$) of decreasing amplitude.

As shown in Fig. 2, the initial exponential deposition of heat gives rise to two waves which propagate in opposite directions. As time progresses so that $\hat{\tau} > 0$, the pressure wave

(corresponding to the first term in Eq. 11a) still decreases; however, now a contribution from the reflected wave is possible. It is evident from this solution that no net momentum is produced from the absorption of radiation, as compressive waves are launched in both directions. This feature is characteristic of a sound generation mechanism that is purely thermoelastic.

2) Experiment

Photoacoustic waves were generated by directing the 532 nm harmonic of an approximately 10 ns long pulse from a Q-switched Nd:YAG laser into a vessel containing solutions of methyl blue. A polyvinylidene difluoride (PVDF) transducer was fitted into the bottom of the vessel. The PVDF foil was made from a 53 μm thick piezoelectric film (Penwalt, Inc) metallized on both sides and cut into a circle with an active area of 0.2 cm^2 . The foil was glued onto the end of a rod of PVDF (1.8 cm diameter by 3 cm long) which was fitted in the center with a fine wire for the signal lead. The wire was electrically connected to the foil with a conducting epoxy. The PVDF cylinder was mounted in a stainless steel housing located at the bottom (5 mm from the liquid surface) of the vessel that contained the absorbing fluid. The output of the transducer was fed to a 1 $\text{M}\Omega$ input impedance preamplifier (Comlinear, Inc. E103-IM) that had a gain of 40 and a bandwidth of 150 MHz. The ultrasonic signals were viewed directly on a 350 MHz bandwidth oscilloscope that was operated with a 20 MHz low pass filter to reduce noise.

Figure 3

As is shown in Fig. 3, the laser beam was expanded by a diverging lens and the center portion of the beam was selected with a 4 cm diameter iris. This was done to improve the spatial uniformity of the light beam directed at the surface of the liquid. At high dye concentrations the light beam is so strongly attenuated, that the signal arising from the light beam impinging directly on the transducer is not

detectable in the noise; the laser beam can therefore be directed at perpendicular incidence to the liquid surface. Both the spatial uniformity of the light beam and its positioning relative to the transducer were found to be critical in producing the exponential waveforms.

Figure 4

The oscilloscope traces in Fig. 4 were recorded with three different boundaries: top trace, Pyrex-water; center trace, air-water; bottom trace, mineral oil-water. Dye solutions of methyl blue in distilled water were used. (In the experiment that gave the bottom trace in Fig. 4, a layer of transparent mineral oil floated on the dye solution.) The factor $(1 - \hat{\rho}\hat{c})/(1 + \hat{\rho}\hat{c})$ for the interfaces that gave the three traces in Fig. 4, from top to bottom, are 0.80, -1.0 and 0.02.

The first two of these approximate fixed and free boundaries respectively; the third corresponds to roughly equal acoustic impedances, or, equivalently, no boundary between the two media. The time scales in the three oscilloscope traces are 500 ns/division.

Additional experiments were done to make a comparison of the photoacoustically determined absorption coefficient with that determined spectrophotometrically. Aqueous solutions of methyl blue were made up in various concentrations and the optical absorption coefficient α_{SP} measured in a conventional spectrophotometer with a 0.1 mm path length cuvette. Photoacoustic data were obtained by photographically recording oscilloscope traces and plotting the signal amplitude versus time to determine a photoacoustic value of the absorption coefficient α_{PA} . A measured value for the sound speed of water, 1496 ms^{-1} was used to convert the exponential decay constants to absorption coefficients. The photoacoustically determined values of the absorption coefficient were found to be in reasonable agreement with those obtained optically over the range from 1.5 to 130 cm^{-1} .

3) Conclusion

The expressions derived here for the photoacoustic amplitude are easily shown to reduce to those given in Refs. 22 and 23 where perfectly rigid or free boundaries were considered. Since the response of the system to a delta function heating pulse is given here, it is straightforward to derive expressions for the acoustic pressure for an arbitrary heating function. The frequency domain expression, Eq. 8 can be multiplied by the Fourier transform of the heating function and the product Fourier transformed back into the time domain; alternately, a convolution integral of the heating function with the time domain function, Eqs. 10 and 11, can be computed.

B) The Photoacoustic Effect in Small Bodies

1) The Fluid Sphere

Here we consider a spherical droplet with density ρ_s and sound speed c_s in a fluid with density ρ_f and sound speed c_f . If the sphere is heated with amplitude modulated radiation where the alternating component of the heating function is given as

$$H = \alpha I_0 e^{i\omega t}, \quad (12)$$

where α is the optical absorption coefficient of the particle, I_0 is the intensity of the light, ω is the modulation frequency and t is time, then the pressure p generated by the radiation inside the sphere obeys the inhomogeneous wave equation

$$\nabla^2 p - \frac{1}{c_s^2} \frac{\partial^2 p}{\partial t^2} = \frac{-\beta}{C_p} \frac{\partial H}{\partial t}, \quad (13)$$

Since the particle is heated uniformly, H is spatially independent within the sphere so that the inhomogeneous solution for p is given by

$$p = p_s c_s^2 \left(\frac{i\alpha\beta I_0}{\rho_s \omega C_p} \right) e^{-i\omega t}. \quad (14)$$

To this must be added a solution of the homogeneous equation that is finite at the origin. The acoustic signal in the region external to the particle p_f must also be a solution to a homogeneous wave equation so that the pressures in the two media can be written (for unit driving pressure) as

$$\begin{aligned} p_s &= \left[1 + \hat{P}_s \left(\frac{\sin k_s r}{k_s r} \right) \right] e^{-i\omega t} \\ p_f &= \frac{\hat{P}_f}{k_f r} e^{i(k_f r - \omega t)} \end{aligned} \quad (15)$$

where k_s and k_f are the wave vectors in the sphere and fluid, respectively, and $\hat{P}_s$ and $\hat{P}_f$ are complex amplitude factors, and r is the distance from the center of the sphere.

The pressure and velocity must be continuous across the interface between the two media. Continuity of the velocity requires that the acceleration also be continuous, and since the acceleration equals the negative of the pressure gradient divided by the density, the following two equations must be satisfied.

$$1 + \hat{P}_s \left(\frac{\sin k_s a}{k_s a} \right) = \hat{P}_f \left(\frac{e^{ik_f a}}{k_f a} \right)$$

$$\frac{\hat{P}_s}{\rho_s} \left(\cos k_s a - \frac{\sin k_s a}{k_s a} \right) = \frac{\hat{P}_f}{\rho_f} \left(i e^{ik_f a} - \frac{e^{ik_f a}}{k_f a} \right), \quad (16)$$

where a is the radius of the sphere

Solution of these equations for the acoustic amplitudes gives the pressures inside and outside the sphere as

$$p_s(q) = \left(\frac{i\alpha\beta I_0 c_s a}{C_p q} \right) \left\{ 1 + \frac{(\hat{\rho} - i\hat{\rho}\hat{c}q) \left(\frac{\sin q \hat{r}}{q \hat{r}} \right)}{[(1 - \hat{\rho}) \frac{\sin q}{q} - \cos q + i\hat{\rho}\hat{c} \sin q]} \right\} e^{iq\hat{t}} \quad (17)$$

$$p_f(q) = \left(\frac{i\alpha\beta I_0 c_s a}{C_p \hat{r}} \right) \frac{\left(\frac{\sin q - q \cos q}{q^2} \right) e^{-iq\hat{t}}}{[(1 - \hat{\rho}) \frac{\sin q}{q} - \cos q + i\hat{\rho}\hat{c} \sin q]}, \quad (18)$$

which are expressed in terms of the parameters

$$\hat{r} = \frac{c_s}{a} \left(t - \frac{r - a}{c_f} \right) \quad \hat{\rho} = \rho_s / \rho_f$$

$$q = \omega a / c_s \quad \hat{c} = c_s / c_f$$

$$\hat{r} = r / a \quad \hat{t} = \frac{c_s}{a} t.$$

For equal densities ($\hat{\rho} = 1$) and sound speeds ($\hat{c} = 1$) in the two media, the pressure p_f reduces to

$$p_f(q) = \frac{-i\alpha\beta I_0 c a}{C_p \hat{r}} \left(\frac{\sin q - q \cos q}{q^2} \right) e^{iq(\hat{r}-1)} \quad (19)$$

which can be obtained from integration of the heating function over a sphere at the retarded time.

Figure 5

Figure 6

Figs. 5 through 6 show the amplitude and phase (relative to the retarded time) of the emitted signal as a function of modulation frequency for different values of the density ratio in the two media, as given by Eq. 18. The signal amplitude shows destructive and constructive interference resulting from phase cancellation or addition of contributions from different volume elements within the sphere. The zeroes occur at frequencies that satisfy the equation $\tan q = q$.

As Fig. 5 shows, when $\hat{\rho}$ is greater than one, the pressure response approaches a series of resonances. As the density ratio becomes greater, the widths of the resonances become progressively narrower. For large values of q , the maxima become equally spaced and are found where q is a multiple of π . The phase is seen to undergo rapid variation at the resonances with small changes in the intervening regions. At the opposite extreme, when $\hat{\rho}$ is small compared with one, a single peak at low values of q appears (See Fig. 6).

The time domain signal can be obtained by simple Fourier transformation of the frequency domain expression for the pressure. However, owing to the complicated dependence of the pressure on frequency, evaluation of the Fourier transform integral can be carried out to give a closed form expression in only a few limiting cases. For a delta function heating pulse

normalized to have a total energy fluence E_0 , the time domain signal can be written as $\hat{r}$ in denominator

$$p_f(t) = \frac{i\bar{\kappa}}{2\pi\hat{r}} \int_{-\infty}^{\infty} \frac{(\sin q - q \cos q) e^{iq\hat{r}}}{q^2[(1-\hat{\rho})\frac{\sin q}{q} - \cos q + i\hat{\rho}\hat{c} \sin q]} dq \quad (20)$$

or, equivalently, as a double integral,

$$p_f(t) = \frac{\bar{\kappa}}{4\pi\hat{r}} \int_{-1}^1 r' d r' \int_{-\infty}^{\infty} \frac{e^{iq(\hat{r}-r')}}{[(1-\hat{\rho})\frac{\sin q}{q} - \cos q + i\hat{\rho}\hat{c} \sin q]} dq, \quad (21)$$

where $\bar{\kappa}$ is defined (as in the previous section) as

$$\bar{\kappa} = \frac{\alpha\beta E_0 c_s^2}{C_p}.$$

Expressions for the time behavior of the acoustic signal $P_f(t)$ generated by an arbitrary radiation intensity $I(t)$ can be obtained by convolution of the intensity function with the unit amplitude delta function pressure response as

$$P_f(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} p_f(y) I(t-y) dy. \quad (22)$$

It is easy to see that the integrand in Eq. 21 becomes a periodic function of q when $\hat{\rho} = 1$. If the denominator in Eq. 21 is written in terms of exponential functions, it can be factored as $(1 + \hat{c})e^{iq}(1 + \xi e^{2iq})$ and expanded in a series, which then gives a power series expansion for $p_f(t)$ of the form

$$p_f(t) = \frac{-\bar{\kappa}}{2\pi\hat{r}(1+\hat{c})} \int_{-1}^1 r' d r' \int_{-\infty}^{\infty} e^{iq(\hat{r}-r'-1)} [1 - \xi e^{2iq} + \xi^2 e^{4iq} - \xi^3 e^{6iq} + \dots] dq \quad (23)$$

where

$$\xi = \frac{1-\hat{c}}{1+\hat{c}}$$

The integration over q gives a series of delta functions so that $p_f(t)$ becomes

$$p_f(t) = \frac{-\bar{\kappa}}{\hat{r}(1+\hat{c})} \int_{-1}^1 r' d r' [\delta(\hat{r}-r'-1) - \xi \delta(\hat{r}-r'-3) + \xi^2 \delta(\hat{r}-r'-5) - \dots]. \quad (24)$$

The r' integration over each delta function in Eq. 19 gives $p_f(t)$ as a linear function of $\hat{\tau}$; however, since each delta function is of the form of $\delta(\hat{\tau}_0 - r')$ where $\tau_0 = \hat{\tau} - n(n = 1, 3, 5 \dots)$ and since the r' integration is restricted to the range -1 and 1 , each term contributes to $p_f(t)$ over a fixed time interval starting at successively longer times as n increases. The acoustic signal thus can be written

$$p_f(t) = \frac{-\bar{\kappa}}{\hat{\tau}(1 + \hat{c})} [(\hat{\tau} - 1)\bar{\Theta}_{0,2}(\hat{\tau}) - \xi(\hat{\tau} - 3)\bar{\Theta}_{2,4}(\hat{\tau}) + \xi^2(\hat{\tau} - 5)\bar{\Theta}_{4,6}(\hat{\tau}) - \dots] \quad (25)$$

where $\bar{\Theta}_{j,k}(\tau)$ is a square wave function defined by $\bar{\Theta}_{j,k}(\hat{\tau}) = 1$ for $j < \tau < k$ and is zero otherwise.

Figure 7

The acoustic signal is thus a sawtooth wave, with each 'tooth' having an amplitude diminished by a factor of ξ relative to the preceding tooth. If the expansion parameter ξ is negative (corresponding to $\hat{c} > 1$), then each term in Eq. 25 is positive so that each of the teeth in wave train has the same phase. If the parameter ξ is positive ($\hat{c} < 1$), then the slope alternates from one tooth to the next.

In the limit of $\xi \ll 1$ the pressure behaves as a decaying sawtooth wave; for $\xi \gg 1$ the pressure approximates a triangular waveform. Fig. 7 shows the pressure signal for $\hat{c} = 10$. Note that when $\hat{c} = 1$ ($\xi = 0$) a single N shape pulse is predicted by Eq. 25 in agreement with a numerical Fourier transform evaluation of Eq. 20.

For a Gaussian light pulse with a halfwidth of Θ the acoustic signal can be obtained as

$$p_f(t) = \frac{-\bar{\kappa}}{\hat{\tau}(1 + \hat{\rho}\hat{c})\bar{\Theta}} \sum_{n=0}^{\infty} (-\xi)^n \int_{2n}^{2n+2} [y - (2n + 1)] e^{-(y - \hat{\tau})^2} / \bar{\Theta}^2 dy \quad (26)$$

where

$$\hat{\Theta} = c_s \Theta / a$$

which can be expressed in terms of exponential and error functions.

The denominator in Eq. 21 in the general case of unequal densities and sound speeds can be written to be proportional to the quantity $e^{iq}(1 + e^{2iq}r)$, so that the integrand can be expanded in a power series as

$$p_f(t) = \frac{-\tilde{\kappa}}{2\pi\hat{r}} \int_{-1}^1 r' d r' \int_{-\infty}^{\infty} dq \frac{(iq) e^{iq(\hat{r}-r'-1)}}{[(1-\hat{\rho}) + iq(1+\hat{\rho}\hat{c})]} \{1 - e^{2iq}R + e^{4iq}R^2 - \dots\}, \quad (27)$$

Consider the first term in this expansion when $\hat{\rho} > 1$. Evaluation of the first term in this integral gives

$$p_f^{(1)}(t) = \frac{-\tilde{\kappa}}{\hat{r}(1+\hat{\rho}\hat{c})} \left\{ (\hat{r}-1)\tilde{\Theta}_{0,2}(\hat{r}) - \frac{\tilde{\Theta}_{0,2}(\hat{r})}{\lambda} [\lambda(\hat{r}-1) - 1 + e^{-\lambda\hat{r}}(\lambda+1)] \right. \\ \left. - 2\lambda e^{-\lambda(\hat{r}-1)}\tilde{\Theta}_{2,\infty}(\hat{r}) \left[\frac{\cos \lambda}{\lambda} - \frac{\sinh \lambda}{\lambda^2} \right] \right\} \quad (28)$$

where $\lambda = \frac{\hat{\rho}-1}{1+\hat{\rho}\hat{c}}$. Thus the expansion in Eq. 22 gives contributions to the signal for $\hat{r}$ between 0 and 2 and for $\hat{r}$ between 2 and ∞ . In the region between 0 and 2, Eq. 28 describes a sawtooth wave modified by a term that has both exponential and linear dependences on $\hat{r}$. For $\lambda \ll 1$, the second term can be approximated at $-\tilde{\kappa}\lambda\hat{r}\tilde{\Theta}_{0,2}(\hat{r})/(1+\hat{\rho}\hat{c})\hat{r}$; also, the second term has a positive second derivative, and hence a positive curvature for any allowed value of λ . Alternately, the terms with a factor $\tilde{\Theta}_{0,2}(\hat{r})$ can be grouped to give $[e^{-\lambda\hat{r}}(\lambda+1) - 1]$ which shows the exponential character of the signal amplitude in time.

In the limit where the density of the sphere is much lower than that of the surrounding fluid, a plot of the integrand in Eq. 20 shows that the main contribution to this integral is at low frequencies. The integral in Eq. 20 can thus be expanded in powers of q to give

$$p_f(t) = \frac{i\tilde{\kappa}}{2\pi\hat{r}} \int_{-\infty}^{\infty} \frac{q e^{iq\hat{r}}}{q^2 + 2i\hat{\gamma}q - \hat{\omega}_0^2} dq, \quad (29)$$

where a dimensionless oscillation frequency $\hat{\omega}_0$ and damping constant $\hat{\gamma}$ are defined as

$$\hat{\omega}_0 = (3\hat{\rho})^{\frac{1}{2}}$$

and

$$\hat{\gamma} = 3\hat{\rho}\hat{c}/2$$

The complex integration is easily carried out giving

$$p_f(t) = \frac{\tilde{\kappa}}{\hat{r}} \frac{d}{d\hat{\tau}} \left[\theta(\hat{\tau}) e^{-\hat{\gamma}\hat{\tau}} \frac{\sin(\hat{\omega}_0^2 - \hat{\gamma}^2)^{\frac{1}{2}} \hat{\tau}}{(\hat{\omega}_0^2 - \hat{\gamma}^2)^{\frac{1}{2}}} \right], \quad (30)$$

For a lightly damped oscillator (i.e. where $\hat{\gamma}/\hat{\omega}_0 \ll 1$) this expression reduces to

$$p_f(t) = \frac{\tilde{\kappa}}{\hat{r}} (\hat{\tau}) e^{-\hat{\gamma}\hat{\tau}} \cos(\hat{\omega}_0^2 - \hat{\gamma}^2)^{\frac{1}{2}} \hat{\tau} \quad (31)$$

which, of course, describes the motion of a damped oscillator. The response of the system for $\hat{\rho} = 0.1$ is shown in Fig. 8. As the density ratio $\hat{\rho}$ is made smaller, the frequency of oscillation decreases and the damping rate become smaller.

Figure 8

The results given here are derived as a solution to a boundary value problem with a spatially constant driving force inside the sphere. The effects of surface tension are left for future investigation. In addition, implicit in the results given here is the restriction that heat conduction to the fluid surrounding the particle should be negligible during the period that sound is emitted.

The time response of the acoustic signal can be understood by consideration of the reflection and transmission coefficients for a spherical waves at a spherical interface. Consider a unit incident wave P_I and a reflected wave P_R inside the sphere, and a transmitted wave P_T in the fluid outside the sphere of the form

$$P_I = \left(\frac{1}{r} \right) e^{-i\omega(t - \frac{r-a}{c_s})}$$

$$\begin{aligned}
P_R &= \left(\frac{R}{r}\right) e^{-i\omega(t + \frac{r-a}{c_s})} \\
P_T &= \left(\frac{T}{r}\right) e^{-i\omega(t - \frac{r-a}{c_s})}
\end{aligned} \tag{32}$$

where R and T are reflection and transmission coefficients respectively. (In the time domain each of these waves represents delta functions originating at the spherical interface at $t = 0$). If the boundary conditions described in Section II are applied to these waves, then the reflection and transmission coefficients are found to be

$$\begin{aligned}
R &= \frac{-(1 - \hat{\rho}) + iq(1 - \hat{\rho}\hat{c})}{(1 - \hat{\rho}) + iq(1 + \hat{\rho}\hat{c})} \\
T &= \frac{2iq}{(1 + \hat{\rho}) + iq(1 + \hat{\rho}\hat{c})}
\end{aligned} \tag{33}$$

which are, in general, frequency dependent. The pressure signal generated by a delta function heating of the sphere can thus be written as

$$p_f(t) = \frac{-i\tilde{\kappa}}{2\pi\hat{r}} \sum_{n=0}^{\infty} \int_{-\infty}^{\infty} dq \left(\frac{\sin q - q \cos q}{q^2} \right) T(-e^{2iq}R)^n e^{iq(\hat{r}-1)} \tag{34}$$

which shows that the pressure signal is the response of a sphere in a uniform medium modified by the effects of frequency dependent transmission and reflection coefficients at the boundary of the sphere.

When the densities of the two media are identical, then R equals ξ and T reduced to $2/(1 + \hat{c})$. According to the solution of the "bursting balloon" problem, which has been solved for identical media,^{24,25} when the balloon bursts an outward going compressive N shaped wave is created along with an inward propagating expansive N wave. Here, however, since the media are different, only an amount T of the outgoing wave is transmitted. As the inward propagating wave approaches the origin, the pressure and velocity must remain finite, hence a counterpropagating wave must arise from the origin³¹ which, in turn, propagates to the interface and is transmitted (beginning at $\hat{r} = 2$). This process is repeated with each successive wave diminished in amplitude by the factor ξ , (which can be positive or negative

depending on the relative sound speed in the media) and with each successive N wave appearing delayed in the time by a/c_s .

When the densities of the two media are not the same, the identical reflection phenomena takes place, but R and T become frequency dependent. However, the series expansions have the same interpretation in terms of reflections at the spherical interface. Since the integrand in Eq. 34 is no longer simple periodic function of q , the evaluation of the various terms in the series becomes much more difficult.

In the limit where $\hat{\rho} \gg 1$ the parameter λ approaches one and R becomes equal to approximately minus one. Thus, reflection at the spherical interface takes place with almost perfect efficiency, giving a long train of emitted waves.

At low values of $\hat{\rho}$ the restoring force is provided by the sphere giving an effective spring constant of $12\pi a/\kappa_s$, where κ_s is the adiabatic compressibility of the sphere. The effective mass²⁶ of the fluid surrounding the sphere at low frequency is $4\pi a^3 \rho_s$. The oscillation frequency ω_0 is then given by

$$\omega_0 = \frac{c_s}{a} \left(\frac{3\rho_s}{\rho_f} \right)^{\frac{1}{2}} \quad (35)$$

The damping constant can be found by integration of the internal pressure over the surface of the sphere; this gives a damping constant γ as $\gamma = c_f k_f^2 a$. The damping in one cycle of oscillation γT_{osc} , where $T_{osc} = 2\pi/\omega_0$, is thus

$$\gamma T_{osc} = 3\pi \frac{c_s}{c_f} \sqrt{\frac{\rho_s}{2\rho_f}} \quad (36)$$

These results are identical with those given by Eq. 29 given for both the damping and the period of the oscillation. Of course, only the effects of radiation damping have been included in the formulation of the problem here; other damping mechanisms such as thermal and viscous damping can clearly play a role in determining the overall damping rate.²⁷⁻²⁹

Several experimental and theoretical waveforms for droplets are given in Fig. 9. They are as follows:

Calculated pressure p (in arbitrary units) versus dimensionless time $\hat{\tau}$ from Eq. 2 for fluid droplets with $\hat{\rho} = 1$. Top: Hexane-carbon tetrachloride droplet suspended in water ($\hat{\rho} = 1.01$, $\hat{c} = 0.645$, $a = 0.5 \text{ mm}$). Center: Formamide droplet suspended in a hexane-carbon tetrachloride mixture ($\hat{\rho} = 1.00$, $\hat{c} = 1.65$, $a = 1.5 \text{ mm}$). Bottom: Tetralin droplet in water ($\hat{\rho} = 0.97$, $\hat{c} = 0.962$, $a = 1.4 \text{ mm}$). The experimental time scales are 500 ns/div in the top oscillogram and 1 μs /div in the other two.

In Fig. 10 photoacoustic waveforms for droplets where $\hat{\rho} \neq 1$ were studied. Top: Hexane droplet in water ($\hat{\rho} = 0.66$, $\hat{c} = 0.708$, $a = 1 \text{ mm}$). Bottom: Carbon tetrachloride droplet in water ($\hat{\rho} = 1.6$, $\hat{c} = 0.618$, $a = 1 \text{ mm}$). The time scale in both oscillograms is 1 μs /div.

2) The Fluid Cylinder

The problem of the photoacoustic effect generated by an infinite fluid cylinder can be treated as in the case of a sphere by solving the wave equation for pressure, but this time with two dimensional solutions of the wave equation representing the outgoing wave and the internal wave. We thus take the pressure inside the cylinder p_c and in the fluid surrounding p_f the cylinder, as proportional to Bessel functions and Hankel functions, respectively, as

$$P_c = 1 + \hat{P}_c J_0(k_c r) \quad (37)$$

$$P_f = \hat{P}_f H_0(k_f) \quad (38)$$

where $\hat{P}$ is a complex constant and where quantities with a subscript c refer to those inside the cylinder and those with a subscript f refer to those in the surrounding fluid. If the acoustic conservation equations are employed, as in the case of the sphere, then the constants $\hat{P}_c$ and $\hat{P}_f$ are found as solutions of the equations

Figure 9

Figure 10

$$1 + \hat{P}_c J_0(k_c a) = \hat{P}_f H_0(k_f a) \quad (39)$$

$$\hat{P}_c J'_0(k_c a) = \left(\frac{\rho_c k_f}{\rho_f k_c} \right) H'_0(k_f a) \quad (40)$$

After some algebraic manipulation, the pressure in the cylinder and the fluid are found to be

$$p_c(q) = \frac{i\tilde{\kappa}}{q} \left\{ 1 + \frac{\hat{\rho}\hat{c} H_1(\hat{c}q) J_0(q\hat{r})}{[J_1(q) H_0(\hat{c}q) - \hat{\rho}\hat{c} J_0(q) H_1(\hat{c}q)]} \right\} e^{-iqt} \quad (41)$$

$$p_f(q) = \frac{i\tilde{\kappa}}{q} \left\{ \frac{J_1(q) H_0(\hat{c}q\hat{r})}{[J_1(q) H_0(\hat{c}q) - \hat{\rho}\hat{c} J_0(q) H_1(\hat{c}q)]} \right\} e^{-iqt} \quad (42)$$

These frequency domain expressions describe the response of the cylinder to amplitude modulated continuous radiation. It can be seen in Fig 11 that the acoustic pressure measured in the fluid is similar to that seen for the sphere under the conditions that $\hat{\rho} = 1$ and $\hat{c} = 1$.

Figure 11

Note that both functional dependences are quite different in these two cases as the zeroes are different and the shapes of the peaks are only similar to the eye. It is clear though that the effects of constructive and destructive interference are present in the addition of the amplitudes at a given field point. As the sound speed in the cylinder is increased relative to the surrounding fluid, the peaks become sharper and eventually approach a spiked appearance. Here, the effect of

the surrounding fluid becomes small because the cylinder has a much higher stiffness than the surrounding fluid, and is thus only mildly influenced by its presence. A similar response is found when the density of the cylinder is made large compared with the surrounding fluid.

Here, the effect is a result of the increased inertia of the cylinder rather than the stiffness. For a very low sound speed in the cylinder, the appearance of the frequency domain plot is that of a single dominant peak at low frequency. This, as in the case of the sphere at low density is a result of a gas bubble-like behavior with the primary response centered around the resonance frequency corresponding to adiabatic expansion and contraction of the cylinder.

The time domain response of the cylinder is found as above by Fourier transformation of the frequency domain expressions. The delta function response of the cylinder is thus given by

$$P_f = \frac{i\tilde{\kappa}}{2\pi} \int_{-\infty}^{\infty} \left\{ \frac{J_1(q) H_0(\hat{c} q \hat{r})}{q[J_1(q) H_0(\hat{c} q) - \hat{\rho} \hat{c} J_0(q) H_1(\hat{c} q)]} \right\} e^{-iqt} dq \quad (43)$$

Note that this integral is different than the corresponding result for a sphere, not only in the functional dependence of the integrand, which is given in terms of Bessel and Hankel functions instead of sinusoidal functions, but also in the parameters which determine the shape of the waveform. The retarded time from the edge of cylinder does not appear, and a new parameter $\hat{r}$ is introduced into the integral. In fact, both of these differences disappear in the far field limit where the Hankel function can be expanded as

$$H_0(z) = \sqrt{\frac{2}{\pi z}} e^{iz - i\pi/4} \quad (44)$$

This gives the far field acoustic pressure as

$$P_f = \frac{i\tilde{\kappa}}{1\pi} \left(\frac{2}{\pi \hat{c} \hat{r}} \right)^{\frac{1}{2}} \int_{-\infty}^{\infty} \frac{J_1(q) e^{iq\hat{r} - i\pi/4}}{q^{\frac{3}{2}} [J_1(q) H_0(\hat{c} q) - \hat{\rho} \hat{c} J_0(q) H_1(\hat{c} q)]} dq \quad (45)$$

Another important limit is attainable when $\hat{\rho} = \hat{c} = 1$. In this instance, the identity

$$J_1(z) H_0(z) - J_0(z) H_1(z) = 2i/\pi z \quad (46)$$

can be used to give the time domain signal as

$$P_f = \tilde{\kappa} \left(\frac{2}{\pi \hat{c} \hat{r}} \right) \int_{-\infty}^{\infty} \frac{J_1(q)}{q^{\frac{1}{2}}} e^{iq\hat{r} - i\pi/4} dq \quad (47)$$

Numerical evaluation of Eq. 43 using the fast Fourier transform algorithm gives the waveforms shown in Fig. 12. The photoacoustic wave with $\hat{\rho}\hat{c} = 1$ is completely different than the corresponding wave generated by a sphere. Of note is the slow decay of the wave back toward the baseline, characteristic of waves in two dimensions. When the sound speed ratio is made greater than one, the reflected part of the wave between $\hat{\tau} = 2$ and $\hat{\tau} = 4$ appears with a maximum amplitude that is greater than the baseline value: when $\hat{c}$ is less than one, the same part of the wave gives only a rarefaction. A similar effect can be seen for changes in the density ratio for values of $\hat{\rho}$ near 1. The bubble-like response can be seen when the density ratio becomes small, as in the case with a sphere.

Figure 12

Some experimental data is given in Fig. 13 for various fluid cylinders which were generated by pumping a dyed fluid through narrow bore tubing into a photoacoustic cell containing a second fluid immiscible with the first. The waveforms in Fig. 13 are as follows.

Calculated and experimental photoacoustic waveforms for cylinders in water. Top: Tetralin cylinder in water ($\hat{\rho} = 0.97$, $\hat{c} = 0.960$, $a = 0.2 \text{ mm}$).

Center: Hexane cylinder in water ($\hat{\rho} = 0.66$, $\hat{c} = 0.708$, $a = 0.25 \text{ mm}$). Bottom: Bromoform cylinder in water ($\hat{\rho} = 2.9$, $\hat{c} = 0.61$, $a = 0.3 \text{ mm}$). The time scales of the oscillograms are 200 ns/div in the top trace and 500 ns/div in the other two.

The analysis of the cylindrical waveforms has not been carried out with the same degree of rigor as that for spheres. Part of the proposed research plan is to investigate the solution given by Eq. 43 in more detail.

Figure 13

Figure 14

3) The Infinite Fluid Layer

The solution to the wave equation for a fluid layer requires standing plane waves inside the layer, and travelling plane waves in the surrounding medium if the area of irradiation is so large as to preclude excitation of Lamb waves. The slab is taken to have a thickness a , and to be centered at the origin. Accordingly, the acoustic pressures in the layer p_l , to the right of the layer p_R (i.e., along the positive x axis) and to the left of the layer p_L are taken for unit driving intensity as

$$p_l = 1 + \hat{P}_1 e^{i k_l x} + \hat{P}_2 e^{-i k_l x} \quad (48)$$

$$p_R = \hat{P}_R e^{i k_f (x-a/2)} \quad (49)$$

$$p_L = P_L e^{-i k_f (x+a/2)} \quad (50)$$

where the capitalized letters are complex constants, and the subscript l refers to quantities inside the layer. Again the acoustic conservation equations can be employed, which, along with symmetry considerations, give the acoustic pressure as

$$P_R = \left(\frac{i \alpha \beta I_0 c_l a}{2 C_P q} \right) \frac{\sin q e^{-i q \tau}}{\sin q + i \hat{\rho} \hat{c} \cos q} \quad (51)$$

The corresponding time domain expression which represents the response of the slab to delta function heating is thus given by

$$P_R = \frac{i \bar{\kappa}}{2\pi} \int_{-\infty}^{\infty} \frac{\sin q e^{i q \tau}}{q(\sin q + i \hat{\rho} \hat{c} \cos q)} dq \quad (52)$$

As before, the fast Fourier transform algorithm can be used to evaluate the integral. However, in this case the integral can be evaluated exactly by writing the sinusoidal functions in the denominator as

$$\sin q + i \hat{\rho} \hat{c} \cos q = (1 + \hat{\rho} \hat{c}) (1 - e^{2i q \xi}) \quad (53)$$

where ξ is given by

$$\xi = \frac{1 - \hat{\rho} \hat{c}}{1 + \hat{\rho} \hat{c}}$$

The expansion of the denominator in a power series permits the integration to be carried out exactly giving the photoacoustic signal as

$$p_R = \frac{\bar{\kappa}}{(1 + \hat{\rho}\hat{c})} \left[\bar{\Theta}_{0,2}(\hat{\tau}) + \xi \bar{\Theta}_{2,4}(\hat{\tau}) + \xi^2 \bar{\Theta}_{4,6}(\hat{\tau}) + \dots \right] \quad (54)$$

Unlike the equivalent results for the sphere and the cylinder, the fluid layer generates a waveform whose temporal properties are dependent on the product of $\hat{\rho}$ and $\hat{c}$.

For uniform media, both $\hat{\rho} = 1$ and $\hat{c} = 1$ so that ξ is zero. According to Eq. 54, there is only a single compressive pulse that is generated along the positive x axis. Note that an identical compressive pulse travels along the negative x axis so that there is no net momentum generated by the photoacoustic effect. This is in accord with a general property of the photoacoustic effect that *no net momentum is carried in the emitted waves*. In the case of two and three dimensions the integral of the pressure over time (or, equivalently, over all space) must be zero.

When the product $\hat{\rho}\hat{c}$ is much less than unity, the sinusoidal function in the denominator of Eq 52 can be written in terms of exponential functions and expanded to first order in q .

$$p_R = \frac{i\bar{\kappa}}{2\pi} \int_{-\infty}^{\infty} \frac{e^{-iq\hat{\tau}}}{q + i\hat{\rho}\hat{c}} dq \quad (55)$$

The resulting integral can be evaluated using the residue theorem to give

$$p_R = \bar{\kappa} \Theta(\hat{t}) e^{-\hat{\rho}\hat{c}\hat{\tau}} \quad (56)$$

which gives the photoacoustic wave as an exponential function of the density and sound speed parameters.

The interpretation of the signal as given by the series expansion in Eq. 54 can be seen by calculation of the amplitude reflection and transmission coefficients R and T , respectively for a plane wave at a plane interface. A straightforward solution to this problem gives these quantities as

$$R = \frac{1 - \hat{\rho}\hat{c}}{1 + \hat{\rho}\hat{c}} \quad T = \frac{2}{1 + \hat{\rho}\hat{c}} \quad (57)$$

The integral in Eq. 52 can thus be written as

$$P_R = \frac{1}{2} \left(\frac{i\kappa}{2\pi} \right) \sum_{n=0}^{\infty} \int_{-\infty}^{\infty} \left[\frac{\sin q}{q} e^{-i q \tau} \right] T \sum_{n=0}^{\infty} (e^{2i q R})^n \quad (58)$$

which shows the signal to be the uniform medium signal modified by the effects of a single transmission and multiple reflections at the surface with an appropriate time delay.

Some experimental results are given in Fig 14 showing the three general kinds of response that obtain for the parameter equal to zero, greater than zero and less than zero. Top: A 2 mm thick water layer floating between carbon tetrachloride and castor oil ($\hat{\rho}\hat{c} = 1.03$). Center 1.5 mm acetone layer surrounded by pyrex glass ($\hat{\rho}\hat{c} = 0.074$). Bottom: A 2.5 mm thick colored glass slab in water ($\hat{\rho}\hat{c} = 9.4$). The time scales are 500 ns/div in each trace.

C) Anisotropic Pressure Wave Generation

Photodissociation of diatomic molecules by linearly polarized light is known to produce spatial distributions of recoiling photofragments that are inherently anisotropic. In the limit where the recoil energy of the fragments is far greater than the rotational energy of the parent molecules, the angular distribution of the fragments $P(\Omega)$ can be described by

$$P(\Omega) = \frac{1}{4\pi} [1 + \beta P_2(\cos \theta)] , \quad (59)$$

where Ω represents polar and azimuthal angles relative to the electric vector of the exciting radiation, P_2 is the second Legendre polynomial, and β is the asymmetry parameter. In this limit, known as the axial recoil limit, a $\Pi \leftarrow \Sigma$ transition gives $\beta = 2$ and $P(\Omega)$ proportional to $\cos^2 \theta$. More complicated cases of photodissociation that involve corrections to Eq. 59 have been treated theoretically as well. The experimental study of such angular distributions can be used to determine the symmetry of the repulsive molecular state and is sometimes referred to as the spectroscopy of the dissociative state.

The process of sound generation in a gas through molecular photodissociation can be thought of in the following way. First, the individual recoiling atoms possess linear momen-

tum, which is transferred through collision partners. The original linear momentum of a given fragment is always conserved, even in inelastic collisions. Second, the transfer of the original kinetic energy of the fragments into random motion of the collision partners constitutes a thermalization process, which launches a sound wave as a consequence of the pressure rise in the irradiated volume associated with a temperature increase. Finally, a net increase in mole number within the irradiated volume is produced by photodissociation; this causes a pressure increase in the irradiated volume, which is also responsible for generation of a sound wave. Insofar as the production of pressure waves is concerned, the last two of these processes are inherently isotropic, whereas, the first, which is generated by a quadrupolar distribution of atomic momentum, can be visualized as generating an anisotropic pressure wave, at least in the limit of low gas pressure where collisions are infrequent.

We conducted experiments to detect the anisotropy in the pressure wave arising from photodissociation of Cl_2 with an electret microphone as a detector. The apparatus for these measurements (see Fig. 15) consists of an electret microphone, which was placed in a stainless-steel vacuum chamber. The vacuum chamber is equipped with a peak valve used to introduce and maintain a constant pressure of Cl_2 . The microphone has an entrance aperture of approximately 2 mm and was placed 5 mm from the focal zone of the 355-nm beam, which was focussed into the vacuum chamber by a quartz lens with a focal length of 35 mm. The 355-nm harmonic of a Q-switched Nd:YAG laser is passed first through a calcite polarizer (to improve the degree of polarization) and then through a Pockels cell to rotate the polarization direction of the beam.

Figure 15

Figure 16

Note that a microphone operated at low pressure has a completely different response from its typically flat frequency response at 2 atm. As the pressure is reduced there is a reduction in the viscous damping of the membrane by the surrounding gas as well as a reduction in the restoring force in the membrane arising from compression of the gas layer between the membrane and its backing electrode. This results in a response at low pressure that is strongly peaked at the resonance frequency of the membrane (as determined by the tension in the membrane and by membrane's mass per unit area). A short burst of gas directed at the microphone produces an exponentially damped voltage, analogous to the impulse response of a simple harmonic oscillator, that can be directly recorded on an oscilloscope.

Since the quality factor of common microphones is typically greater than 1000, the ringing of the membrane persists on a time scale of tens of milliseconds. The signal-processing electronics used in these experiments were designed to capture as much of the transient decay of the microphone signal as possible. The signal is first passed through a tuned amplifier set at the resonance frequency of the microphone, 7.5 kHz. A burst generator triggered by the firing of the laser provides a 50-msec-long train of square pulses, the period of each pulse being matched to the oscillation period of the membrane. Both the period of the pulse train

and its initiation point in time relative to the firing of the laser are variable. An oscilloscope recording of a signal from the burst generator and a typical output voltage from the tuned amplifier are shown in Fig. 16.

When the phase and the period of the burst generator are correctly adjusted, the output of the mixer is proportional to the envelope of the decay of the microphone signal. A typical output from the mixer is shown in the bottom trace of Fig. 16. The signal is averaged in a boxcar integrator whose output is displayed on a strip-chart recorder. In these experiments the time constant of the integrator was set to 1 sec, which provided an adequate signal-to-noise ratio in the boxcar averager output at the pressures employed. Pressures were recorded by a thermocouple gauge which gave rough measurements at low pressures.

The signal amplitude was recorded as a function of voltage on the Pockels cell, as shown in Fig. 17 for several Cl_2 pressures. At 0 V on the Pockels cell, the polarization of the laser beam is in the direction of the detector; at 3 kV it is perpendicular to this direction. At 1.5 kV on the Pockels cell the laser beam is circularly polarized, while at intermediate voltages the beam is elliptically polarized.

Figure 17

The data (see Fig. 17) show a greater modulation depth as the pressure is decreased. At the lowest pressure, 0.6 Pa (5 mTorr), the mean free path of a Cl atom is 10 mm, which means that on average a photofragment reaches the detector without suffering a collision. Clearly, the highest anisotropy is attained in experiments of this kind when the mean free path of the atomic fragments far exceeds the

dimensions of the irradiated zone and the distance between the irradiated zone and the

detector. For pressures for which the mean free path of the fragments is commensurate with the laser beam diameter, collisions within the irradiated region led to averaging of the momentum of the photofragments, which, in turn, reduces the anisotropy of the force exerted on the passive volume surrounding the irradiated region. At high pressures, where fluid dynamics are operative, a quadrupolar acoustic wave can be transmitted without a loss in anisotropy; however, in this pressure regime the quadrupolar distribution of force in the irradiated region is lost. The data in Fig. 17 clearly show that the signal peaks when the polarization of the laser beam is perpendicular to the flight path of the fragments to the detector. This indicates a predominantly perpendicular transition in Cl_2 at 355 nm.

Note that even in the low-pressure limit the modulation depth depends on the ratio of the recoil velocity of the fragments to the thermal velocity of the parent molecules. That is, the distribution of recoil axes of the fragments must be convoluted with the velocity distributions of the parent molecules. In the present case of Cl_2 dissociated at 355 nm, the ratio of the translational recoil velocity of the fragments to the mean thermal speed of the Cl_2 is 8.2 (where the fine-structure splitting has been ignored). When this ratio becomes large, the distribution of recoil velocities given by Eq. 59 should be regained. In addition to these factors, which govern the modulation depth of the signal, there is also a purely instrumental effect of integrating over the acceptance angle of the detector.

In summary, we have shown the existence of what may loosely be called an anisotropic photoacoustic effect. We find the transition of Cl_2 at 355 nm to be predominantly perpendicular, in agreement with the results of Busch *et al.* at the nearby wavelength of 346 nm.

D) Interference in Two-Photon Absorption

The research conducted on selective ionization of isotopes represents ancillary work and

will be given brief discussion here. Details are given in the full paper,³⁰ which is now in print.

In a simple $J = 0 \leftarrow J = 1 \leftarrow J = 0$ energy-level scheme, the rate of nonresonant two-photon absorption (i.e., with the first photon off resonance with the $J = 1 \leftarrow J = 0$ transition) can become zero as a result of an interference effect.³¹ When the electric vectors of two linearly polarized light beams are expressed as coherent superpositions of σ^+ and σ^- beams, two pathways with probability amplitudes P_1 and P_2 for population of the upper state exist, as shown in Fig. 18. When the electric vectors of the two light beams are parallel, the signs and amplitudes of P_1 and P_2 are identical, so the interference is constructive and the population rate of the upper state is finite; when the light-beam polarizations are orthogonal, a phase shift of π is introduced into the relative probability amplitude resulting in completely destructive interference with a population transfer rate to the final state of zero. This effect was recently observed³¹ in Sr where the degree of destructive interference was measured as a function of the angle between two linearly polarized laser beams by monitoring the population of the $7s^1S$ state.

On first inspection it is natural to conclude that orthogonally polarized laser beams could be used to populate selectively the upper 1S state of atoms with nonzero nuclear spin through nonresonant excitation of a $^1S \leftarrow ^1P \leftarrow ^1S$ sequence. That is, isotopes with no nuclear spin have energy-level schemes as shown in Fig. 18 and would not be excited in a nonresonant two-photon process owing to the interference effect. Isotopes with a nuclear spin I and 1, for instance, would be excited through pathways such as those shown in Fig. 18(a), but additional pathways, such as P_3 shown in Fig. 18(b), where interference cannot take place, would always be present, so that irrespective of the light-beam polarizations, two-photon absorption would always occur.

Since absorption of a third photon from either of the two laser beams can ionize the

excited atom, a clear discrimination against zero-nuclear-spin isotopes in the ion current should be observed as the relative polarization of the two laser beams is rotated through angles from parallel to perpendicular. Surprisingly, experiments with ^{138}Ba and ^{137}Ba irradiated with 8-ns-long dye-laser pulses showed no statistically significant variation in the ratio of the ion currents from these two isotopes as the relative polarization of the radiation beams was varied — the presence of excitation paths such as P_3 did not alter the isotope ratio.

In retrospect, the explanation for this behavior is elementary. The initiation of the first laser beam produces a “virtual state” that is a coherent superposition of coupled angular momentum states. The time evolution of these states, governed by the magnitude of the hyperfine splittings, is sufficiently slow compared with the virtual-state lifetime that the flow of

Figure 18
probability amplitude into states that can be excited by the second laser beam is negligible. Thus, the hyperfine interaction in the nonzero spin isotopes appears to be nonoperative or “frozen” on the time scale of the experiment as set by the magnitude of the detuning of the first laser beam from resonance.

As we show below, selective excitation of nonzero spin isotopes is possible using pulsed lasers provided the first laser is tuned to resonance with the first excited state and the state is allowed to evolve in time before the second laser is fired. The complete theory for sequential two-photon excitation with polarized light beams is quite involved. (A full explanation of the analysis in terms of statistical tensors required 12 pages in S. M. Park’s thesis). Here, we give only the result for the density matrix³³ of the excited state, which is given^{34,30} as

function of time as .

$$\begin{aligned}
\rho^f(t) = & \sum_{p, p', p'', p''', F_e, F_e', k, k', q, q', K, Q, Q'} \frac{\sqrt{3}}{27} \frac{(-1)^{p+p''+F_e'+k-k'+Q'+I}}{2I+1} (2F_e+1)(2F_e'+1) \\
& \times (2K+1)(2k+1)\sqrt{(2k'+1)} |\langle 1||D_{eg}||0\rangle|^2 |\langle 0||D_{fe}||1\rangle|^2 e^{-\lambda_1} e^{-\lambda_1^*} e^{-\lambda_2} e^{-\lambda_2^*} e^{-\lambda_3} e^{-\lambda_3^*} \\
& \times \begin{bmatrix} 1 & 1 & k \\ -p & p' & -q \end{bmatrix} \begin{bmatrix} K & k' & k \\ Q & q' & -q \end{bmatrix} \begin{bmatrix} K & 1 & 1 \\ Q & p''' & -Q' \end{bmatrix} \begin{bmatrix} 1 & 1 & 0 \\ -p'' & Q' & 0 \end{bmatrix} \\
& \times \begin{bmatrix} 1 & 1 & k \\ F_e & F_e' & I \end{bmatrix} \begin{bmatrix} 1 & 1 & K \\ I & I & k' \\ F_e & F_e' & k \end{bmatrix} e^{(i\omega_{F_e F_e'} - \Gamma)t} T_{00}^J(00) T_{k'q'}^I(II) .
\end{aligned} \tag{60}$$

The summation is over values of the polarization indices that describe the light beams the hyperfine states F_3 , k and K which range from 0 to 2, k' which ranges from 0 and $2I$, and the magnetic quantum numbers Q , Q' , and q' which take on values determined by the total angular-momentum quantum number.

It can be seen that Eq. 60 describes a sum over tensor operators $T_{k'q'}(II)$ of the form

$$\rho^f(t) = \sum_{k'q'} \langle T_{k'q'}^\dagger(II) \rangle T_{k'q'}(II) . \tag{61}$$

The time-dependent state multipoles $\langle T_{k'q'}^\dagger(II) \rangle$ are found from Eq. 60 as coefficients of the tensor operators $T_{k'q'}(II)$. The rank of the state multipoles of the nuclear angular momentum in the final state according to Eq. 60 ranges from 0 to $2I$. From Eq. 60 the monopole moments (populations) of the final state can be calculated for ^{138}Ba and ^{137}Ba as a function of delay time between the two lasers and as a function of the angle between the laser polarization vectors. Under the assumption that the ionization signal is proportional to the final state population, a time-dependent isotope ratio can be calculated.

Figure 19

Figure 20

Such plots are given in Figs 19 and 20 for two isotopes of *Ba* and *Sr*. The insets in each figure shows the hyperfine structure of the intermediate excited state for ^{137}Ba and ^{87}Sr . The variation in intensity of isotope ratios follows as a consequence of the existence of three hyperfine states that give rise to several frequency components in the final state population that add in phase or out of phase as a function of time.

Figure 21

The production of a nuclear quadrupole moment in a final state can be seen as a function of the delay time between the two lasers in Figs. 21(a) and 21(b) where the $q' = 0$ and 2 components of the second-rank tensor $T_{2q'}(II)$ are plotted for ^{137}Ba (with $I = \frac{3}{2}$). Experimental measurements of isotope ratios in atomic beams of *Ba* and *Sr* were made by averaging the ion current from a quadrupole mass spectrometer. The laser beams were

directed (unfocussed) into the ionizer region of the mass spectrometer, the resulting ions were then focussed and accelerated into the mass filter. The dye lasers were pumped by harmonics of a Nd:YAG laser that operated at 10 Hz. As is shown in Fig 22, an optical delay was inserted into the path of the second dye laser. Experiments were done in a differentially pumped high-vacuum chamber operated at a pressure of less than 5×10^{-6} Torr

Figure 22

Figure 23

Atomic beams with divergences of 2 mrad were produced by vaoprizing *Ba* and *Sr* metal (with naturally occurring isotope ratios) in an electrically heated oven. The linewidth of the first dye laser was 0.012 nm (10-GHz full width at half maximum) as determined in a separate laser-induced fluorescence experiment. As a consequence of the small ion signals found in these experiments, the mass filter could not be operated to completely resolve the various masses. Ion current ratios were therefore computed from peak heights in the spectrum and thus do not represent exactly the isotope ratios in the elements.

An initial nonresonant experiment was done with the first dye laser tuned to 553.1 nm, which is 390 GHz off resonance with the $6s6p\ ^1P_1$ state of *Ba*. This detuning is approximately three orders of magnitude greater than the hyperfine splittings within the 1P_1 state. The

second laser was tuned to to 613.3 nm to excite the $6s8s\ ^1S_0$ state through a two-photon nonresonant process. As shown in Fig. 23, (open circles) the ratio of the ^{138}Ba to ^{137}Ba ion signal showed no significant variation as the angle between the polarization vectors of the two lasers was varied from parallel to perpendicular.

In a resonant excitation when a time delay is introduced between the two laser beams, it is possible to ionize ^{137}Ba selectively (relative to ^{138}Ba). With the first and second dye lasers tuned to 553.5 and 612.9 nm respectively to excite resonantly the sequence $6s8s\ ^1S_0 \leftarrow 6s6p\ ^1P_1 \leftarrow 6S\ ^1S_0$ and with a delay of 12 ns between the two laser beams, the Ba mass spectrum was recorded as a function of angle between the polarization vectors of the two lasers. Separate experiments done over a range of about three orders of magnitude in the intensities of both laser beams indicated that no saturation effects were present in the ion signal. The data as shown in Fig. 24 show a clearly observable change in the ^{138}Ba to ^{137}Ba ion current ratio in the mass filter as the relative polarization of the two dye laser beams is rotated from parallel to perpendicular. The distinction between the resonant and nonresonant experiments is evident: given the comparatively short pulse widths of the lasers used here, the time evolution of the excited-state probability amplitudes can be used for selective excitation only when the first laser is on resonance and the excited-state lifetime is governed by the comparatively slow process of radiative decay.

Figure 24

The splittings in ^{87}Sr are significantly smaller than those in ^{137}Ba , and permit the effect of the time delay between the laser pulses to be seen without significant reduction in the modulation depth in the isotope ratio as a result of the finite laser pulsewidth. Data were taken with the laser polarization vectors perpendicular as the delay time

was varied. The data were in substantial agreement with the theoretical dependence on time.

It is clear from the experimental results given here that it is possible to excite selectively and ionize nonzero-spin atoms relative to zero-spin atoms based on destructive interference in the excitation pathways in a $J_f = 0 \leftarrow J_e = 1 \leftarrow J_g = 0$ two-photon resonant sequence. A necessary condition for discrimination between zero and nonzero nuclear spin atoms is that a sufficient time delay be introduced before the second laser pulse interacts with the sample so that the probability amplitudes in the excited state depart from their values immediately after absorption of the first laser pulse.

In addition to the straightforward effects described here in the excitation of atoms, a general principle about the observation of small splittings in double resonance studies follows, namely, when short pulses are used to probe any atomic or molecular splitting, the presence of the splitting will be manifest in the two-photon spectrum only when the precession period of the interaction giving rise to the splitting is short compared with the laser pulsewidth, and when the second probe is initiated after an appropriate delay time to allow sufficient development of the coherent superposition of states created by the first pulse.

E) Additional Research

We have conducted experiments and carried out calculations on the laser enhanced electron impact ionization of atomic Na . Again we choose to give only a very brief report of the results since the main thrust of the research on this grant is concerned with the photoacoustic effect. In this study we have observed laser enhanced electron impact ionization of Na in an atomic beam by tuning a continuous laser to certain hyperfine transitions in Na . Fig. 25 shows the relative ion signal recorded in a quadrupole mass spectrometer as a function of the electron bombardment energy (solid circles). The influence of the optical excitation on what is essentially the cross-section for ionization is clearly evident in the shift of the

ionization peak in the experimental data. An important feature of the work done here is calculation of effects of optical pumping on the detected ion signal. Optical pumping acts to trap population into states that cannot be excited by the laser, and thus to reduce or eliminate the ion signal altogether. We have given a quantitative description of the effect of the laser pulsewidth and residence time of the atoms in the ionizer on the overall ion signal.

Figure 25

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