Theory of Thin Layer Photoacoustic Cells for Determination of Volume Changes in Solution

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Received: December 19, 1997; In Final Form: April 21, 1998

The wave equation for the photoacoustic effect generated by heat deposition and molecular volume change is solved for a one-dimensional geometry for the case of excitation of a single molecular electronic state that decays to the ground state exponentially in time. The solution for a uniformly illuminated, infinite layer of fluid in contact with two infinite fluid or solid half-spaces, corresponding to a recently developed experimental geometry for generation of the photoacoustic effect is given. The solutions show the effects of finite decay of the excited state and of reflections at the interfaces.

Introduction

Although the photoacoustic effect[1−8] is generally thought of as arising from local pressure changes initiated by heat deposition, any photochemical process where the reactants and products have different specific volumes can also generate an equivalent pressure change that causes the generation of sound waves. Photochemically induced volume changes in gases[9−11] are large and give pronounced, but generally predictable effects on the acoustic wave; volume changes in liquids, on the other hand, are small but provide useful and difficult to obtain information on structural changes in reactions. Since it was first recognized that the photoacoustic effect could be used to determine molecular volume changes,[13] numerous measurements of volume changes in liquid-phase chemical reactions have been reported, as has been noted in the review by Braslavsky and Heibel.[12]

Recently, a theory for generation of the photoacoustic effect by molecular volume based on the linearized hydrodynamic equations for fluids has been given.[14] The results of the derivation give the photoacoustic pressure and temperature as dependent variables in a pair of coupled differential equations,[15] which have source terms for the consumption or liberation of energy and for volume change. In this paper the problem of an irradiated fluid layer in contact with a second fluid occupying infinite half-spaces to either side of the layer and having a different density and sound speed from the fluid in the layer is considered. On irradiation of the fluid with a δ function laser pulse in time, an electronic excited state of a solute molecule is taken to be populated with the laser simultaneously depositing heat in the fluid; the excited molecular state is then assumed to decay back to the ground state exponentially in time. The photoacoustic pressure is found from the wave equation for the velocity potential, which includes the effects of energy consumption and volume change that take place in the excitation and decay of the solute. A Fourier transform integral is derived, which is evaluated to give a closed form solution for the photoacoustic pressure. The results are applicable to a recently developed technique referred to as "front face irradiation" for measuring photoacoustic volume changes in a thin layer of fluid confined between two glass plates.[16−20]

Solution to the Wave Equation

Consider irradiation of an optically thin fluid by a laser pulse taken to be a delta function in time where the total energy per unit volume deposited by the laser in the fluid is $\bar{\alpha}E_0$, and the energy per unit volume stored by excitation of the solute is $\rho h^* n_0$, where $\bar{\alpha}$ is the optical absorption coefficient of the solution, E_0 is the energy per area in the laser beam, ρ is the density of the fluid, h^* is the enthalpy per mass of the solution per mole of the solute excited, and n_0 is the number of moles in the excited state immediately after excitation.[14] If the dimensions of the irradiated region are large compared with the heat conduction and viscous length parameters,[15] then conduction of heat can be ignored[21] and the coupled equations for pressure and temperature reduce to a wave equation for the pressure with the temperature given by a constant.[14] The wave equation for pressure can be written in terms of the velocity potential[22] ϕ as

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

where t is the time, c is the sound speed, β is the coefficient of thermal expansion, C_P is the specific heat capacity, H is the energy per volume and time deposited by the laser, n is the time-dependent concentration of excited species created by absorption of the laser radiation, and β_c is the chemical expansion coefficient,[14] which describes the change in density of the fluid with a change in excited-state concentration at constant pressure and temperature. For the problem of two chemical entities, such as a ground and an excited state of a solute molecule, or a reactant and a product, each with different molar volumes, β_c is given by $\beta_c = -\rho^{-1}(\partial\rho/\partial n)_{P,T}$, where n refers to the amount of product formed. The acoustic pressure p and velocity $\mathbf{v}$ are found from the velocity potential as

$$p = -\rho\frac{\partial\phi}{\partial t} \quad \text{and} \quad \mathbf{v} = \nabla\phi \qquad (2)$$

The wave equation can be solved by Fourier transformation according to the convention

$$\tilde{f}(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} f(t)\, e^{i\omega t}\, dt \quad \text{and} \quad f(t) = \int_{-\infty}^{\infty} \tilde{f}(\omega)\, e^{-i\omega t}\, d\omega \qquad (3)$$

For a δ function laser pulse in time and exponential decay of the excited state with a time constant θ, the frequency domain expressions for H and n become

$$\tilde{H} = \frac{\bar{\alpha}E_0}{2\pi} \quad \text{and} \quad \tilde{n} = \frac{n_0}{2\pi}\left(\frac{\theta}{1 - i\omega\theta}\right)$$

S1089-5647(98)00583-5 CCC: $15.00
Published on Web 06/17/1998

Fourier transformation of eq 1 gives the Helmholtz equation

$$(\nabla^2 + k^2)\tilde{\phi} = \frac{\beta}{2\pi\rho C_P}\left[\bar{\alpha}E_0 + \rho h^* n_0\left(\frac{i\omega\theta}{1 - i\omega\theta}\right)\right] - \frac{n_0\beta_c}{2\pi}\left(\frac{i\omega\theta}{1 - i\omega\theta}\right) \quad (4)$$

where k is given by $k = \omega/c$.

For the problem of a uniformly irradiated, infinite layer of thickness l, whose midpoint is placed at the origin of the z-axis, the solution to eq 4 is a space-independent constant $\tilde{\phi}_0$ that is a solution to the inhomogeneous wave equation plus left- and right-going waves that are solutions to the homogeneous wave equation. The amplitudes of the latter, are, by symmetry, identical. Outside the irradiated layer, the solutions in the surrounding fluid are outgoing plane waves. The solution to the wave equation can thus be written

$$\tilde{\phi} = \tilde{\phi}_0(1 + \hat{A}\, e^{ik_l z} + \hat{A}\, e^{-ik_l z}) \quad (5)$$

$$\tilde{\phi}_R = \tilde{\phi}_0 \hat{A}_R\, e^{ik_f(z - l/2)} \quad (6)$$

$$\tilde{\phi}_L = \tilde{\phi}_0\, \hat{A}_L\, e^{-ik_f(z + l/2)} \quad (7)$$

where the subscripts l, R, and L refer to the irradiated layer, the right-going wave that propagates along the positive z-axis, and the left-going wave that propagates along the negative z-axis, respectively, the quantities $\hat{A}$ are complex constants, and $\tilde{\phi}_0$ is given by

$$\tilde{\phi}_0 = \frac{\beta c_l^2}{2\pi\omega^2\rho C_P}\left[\bar{\alpha}E_0 + \rho h^* n_0\left(\frac{i\omega\theta}{1 - i\omega\theta}\right)\right] - \frac{n_0\beta_c c_l^2}{\omega^2}\left(\frac{i\omega\theta}{1 - i\omega\theta}\right) \quad (8)$$

The complex constants can be found by requiring the pressure and velocity to be continuous across the interfaces between the two fluids[23] at $\pm l/2$. Fourier transformation of eqs 2 gives the frequency domain pressure and z-component of the velocity as $p = -i\omega\rho\tilde{\phi}$ and $\tilde{v}_z = \partial\tilde{\phi}/\partial z$. The requirements of continuity of pressure and velocity at $z = l/2$ can be shown to give

$$\hat{\rho}(1 + 2A\cos\hat{q}) = \hat{A}_R$$

$$2\hat{A}\sin\hat{q} = -i\hat{c}\,\hat{A}_R \quad (9)$$

where dimensionless density $\hat{\rho}$, sound speed $\hat{c}$, and frequency parameters have been defined as

$$\hat{\rho} = \rho_l/\rho_f, \quad \hat{c} = c_l/c_f, \quad \text{and} \quad \hat{q} = k_l l/2 = \omega l/2c_l$$

Solution to eqs 9 gives the frequency domain velocity potentials as

$$\tilde{\phi} = \tilde{\phi}_0\left[1 - \frac{i\hat{\rho}\hat{c}\cos(\hat{q}\hat{z})}{\sin\hat{q} + i\hat{\rho}\hat{c}\cos\hat{q}}\right]$$

$$\tilde{\phi}_R = \tilde{\phi}_0\left[\frac{\hat{\rho}\sin\hat{q}}{\sin\hat{q} + i\hat{\rho}\hat{c}\cos\hat{q}}\right] e^{i[k_f(z - (l/2))]} \quad (10)$$

The photoacoustic pressure in the frequency domain can then be found from eqs 2 and the resulting expression transformed back to the time domain giving the acoustic pressure in the layer $p(t)$ and in the half-space along the positive x-coordinate $p_R(t)$ as

$$p(\hat{t}) = \frac{i\bar{\alpha}\beta E_0 c_l^2}{2\pi C_P}\int_{-\infty}^{\infty}\left(1 + \zeta\frac{i\hat{q}\hat{\theta}}{1 - i\hat{q}\hat{\theta}}\right)\times \left[1 - \frac{i\hat{\rho}\hat{c}\sin(\hat{q}\hat{z})}{\sin\hat{q} + i\hat{\rho}\hat{c}\cos\hat{q}}\right]\frac{e^{-i\hat{q}\hat{t}}}{\hat{q}}\,d\hat{q} + \frac{\rho_l\beta_c n_0 c_l^2}{2\pi}\int_{-\infty}^{\infty}\left(\frac{\hat{q}\hat{\theta}}{1 - i\hat{q}\hat{\theta}}\right)\times \left[1 - \frac{i\hat{\rho}\hat{c}\cos(\hat{q}\hat{z})}{\sin\hat{q} + i\hat{\rho}\hat{c}\cos\hat{q}}\right]\frac{e^{-i\hat{q}\hat{t}}}{\hat{q}}\,d\hat{q} \quad (11)$$

$$p_R(\hat{t}) = \frac{i\bar{\alpha}\beta E_0 c_l^2}{2\pi C_P}\int_{-\infty}^{\infty}\left(1 + \zeta\frac{i\hat{q}\hat{\theta}}{1 - i\hat{q}\hat{\theta}}\right)\left[\frac{\operatorname{sinc}\hat{q}}{\sin\hat{q} + i\hat{\rho}\hat{c}\cos\hat{q}}\right] e^{-i\hat{q}\hat{\tau}_R}\,d\hat{q} + \frac{\rho_l\beta_c n_0 c_l^2}{2\pi}\int_{-\infty}^{\infty}\left(\frac{\hat{q}\hat{\theta}}{1 - i\hat{q}\hat{\theta}}\right)\left[\frac{\operatorname{sinc}\hat{q}}{\sin\hat{q} + i\hat{\rho}\hat{c}\cos\hat{q}}\right] e^{-i\hat{q}\hat{\tau}_R}\,d\hat{q} \quad (12)$$

where a dimensionless time $\hat{t}$, a dimensionless retarded time $\hat{\tau}_R$ from the point $z = l/2$, a dimensionless coordinate $\hat{z}$, a dimensionless decay constant $\hat{\theta}$, and a ratio of the stored energy to the incident energy ζ have been defined as

$$\hat{t} = \frac{2c_l}{l}, \quad \hat{z} = \frac{2z}{l}, \quad \zeta = \frac{n_0\rho h^*}{\bar{\alpha}E_0}, \quad \hat{\theta} = \frac{2c_l}{l}\theta, \quad \text{and}$$

$$\hat{\tau}_R = \frac{2c_l}{l}\left(t - \frac{z - l/2}{c_f}\right)$$

and where the function sinc $\hat{q}$ is defined as $\operatorname{sinc}\hat{q} = \sin(\hat{q})/\hat{q}$. It can be seen that the integrand in eq 12 of the first Fourier integral describing thermal expansion is the sum of two terms, the first corresponding to that of a uniformly irradiated layer with no energy storage[24] and the second, a term representing the frequency domain response of a uniformly irradiated layer modified by the effects of exponential energy release. The chemical expansion term, the second integral in eq 12, has essentially the same time dependence as the term describing exponential deposition of heat.

The first integral in eq 12 can be evaluated by writing the sinusoidal functions in the denominator of the integrand in exponential form and then expanding the denominator in a power series in the reflection and transmission coefficients of a plane wave at a plane interface.[24] Through use of the well-know property of Fourier transforms of products[25]

$$\frac{1}{2\pi}\int_{-\infty}^{\infty} V_1(\omega)\, V_2(\omega)\, e^{-i\omega t} = \int_{-\infty}^{\infty} \upsilon_1(t - y)\, \upsilon_2(y)\, dy \quad (13)$$

where V and υ are Fourier transform pairs, it can be shown that the following identity holds for the integral containing $\hat{\theta}$ appearing in both eqs 11 and 12

$$\frac{1}{2\pi}\int_{-\infty}^{\infty}\left(\frac{-i\hat{q}\hat{\theta}}{1 - i\hat{q}\hat{\theta}}\right)\left(\frac{i\operatorname{sinc}\hat{q}}{\sin\hat{q} - i\hat{\rho}\hat{c}\cos\hat{q}}\right) e^{-i\hat{q}\hat{\tau}_R}\,d\hat{q} = \frac{1}{(1 + \hat{\rho}\hat{c})}\sum_{n=2,4,6}^{\infty}\int_{-\infty}^{\infty}[\delta(\hat{\tau}_R - \hat{y}) - \hat{\theta}^{-1}\, u(\hat{\tau}_R - \hat{y})\, e^{-(\hat{\tau}_R - \hat{y})/\hat{\theta}}]\,\xi^n\,\Theta_{n,n+2}(\hat{y})\,d\hat{y}$$

where $\delta(\hat{\tau}_R)$ is the Dirac delta function, $u(\hat{\tau}_R)$ is the Heaviside function, and ξ is the reflection coefficient of a plane wave at a plane interface

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

The photoacoustic pressure, as given in eq 12, can thus be found as

$$p_R(\hat{\tau}_R) = \frac{\bar{\alpha}\beta E_0 c_l^2}{(1+\hat{\rho}\hat{c})C_P}[Q(\hat{\tau}_R) - \zeta E(\hat{\tau}_R)] + \frac{\rho_l \beta_c n_0 c_l^2}{(1+\hat{\rho}\hat{c})}E(\hat{\tau}_R) \tag{14}$$

where the functions $Q(\hat{\tau}_R)$ and $E(\hat{\tau}_R)$ have been defined as

$$Q(\hat{\tau}_R) = \sum_{n=0}^{\infty} \xi^n \Theta_{2n,2n+2}(\hat{\tau}_R)$$

$$E(\hat{\tau}_R) = \sum_{n=0}^{\infty} \xi^n \Theta_{2n,2n+2}(\hat{\tau}_R) e^{-(\hat{\tau}_R - 2n)/\hat{\theta}} + \sum_{n=0}^{\infty} u(\hat{\tau}_R - 2n - 2)\xi^n [e^{-(\hat{\tau}_R - 2n)/\hat{\theta}} - e^{-(\hat{\tau}_R - 2n - 2)/\hat{\theta}}]$$

and where $\Theta_{m,n}(\hat{y})$ is a square wave function that is unity for $\hat{y}$ greater than m and less than n and zero otherwise. For identical media, ξ must equal zero. There are no reflections at the interfaces so the expressions for $Q(\hat{\tau}_R)$ and $E(\hat{\tau}_R)$ in eq 14 should have only the $n = 0$ term, which can be formally taken into account by defining ξ^0 as unity for $\xi = 0$.

Waves in One Dimension

Before evaluating eq 14, it is useful to consider the effects of time-dependent heat deposition on the generation of photoacoustic waves. When no reflections take place as a result of boundaries, the solution of the wave equation for the velocity potential

$$\left(\nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\right)\phi = \frac{\beta}{\rho C_P}H \tag{15}$$

for field points outside of the region of heat deposition, i.e., for $z \geq z'$, can be written as a two-dimensional integral of a Green's function[28] over the heating function giving the velocity potential as

$$\phi(z,t) = \frac{-\beta c}{2\rho C_P}\int_0^t dt' \int dz' \, H(z',t') \, u\left(t - t' - \frac{z-z'}{c}\right) \tag{16}$$

where the heating function $H(z, t)$, for the present problem, is taken to be of the form

$$H(z,t) = \bar{\alpha} \, I_0 \, f(t) \, g(z) \tag{17}$$

and where the functions $f(t)$ and $g(z)$ describe the temporal and spatial deposition of heat, respectively, and I_0 is the intensity of the radiation. Differentiation of the velocity potential with respect to time according to eq 2 gives the photoacoustic pressure as

$$p(z,t) = \frac{\bar{\alpha}\beta I_0 c}{2C_P}\int dz' \, g(z') \int_0^t dt' \, f(t') \, \delta\left(t' - \left(t - \frac{z-z'}{c}\right)\right) \tag{18}$$

Evaluation of the time integral over the δ function in eq 18 gives the photoacoustic pressure as the space integral

$$p(z,t) = \frac{\bar{\alpha}\beta I_0 c}{2C_P}\int dz' \, g(z') \, f\left(t - \frac{z-z'}{c}\right) \tag{19}$$

The integral expression given by eq 19 can be used to determine the time dependence of photoacoustic wave generated by gradual deposition of heat. The result is valid for uniform fluid media for waves traveling to the right of the source region and is to be contrasted with the corresponding expression in refs 26 and 27 for delta function deposition of heat in time.

Consider now the problem of heat deposition that is uniform in a layer extending from $-l/2$ to $l/2$ along the z-axis and that is exponential in time with a time constant θ. The functions $f(t)$ and $g(t)$ in the heating function are given by

$$f(t) = u(t) \, e^{-t/\theta}$$

$$g(z) = u(z + l/2) - u(z - l/2) \tag{20}$$

which, according to eq 19, gives the photoacoustic pressure as

$$p(z,t) = \frac{\bar{\alpha}\beta I_0 c}{2C_P}\int_{-l/2}^{l/2} u\left(t - \frac{z-z'}{c}\right) \exp\left(-\left(t - \frac{z-z'}{c}\right)/\theta\right) dz' \tag{21}$$

A simple change of variable permits the integral to be rewritten as

$$p(z,t) = \frac{\bar{\alpha}\beta I_0 c^2}{2C_P}\int_{\bar{\tau}_L}^{\bar{\tau}_R} u(\lambda) \, e^{-\lambda/\theta} \, d\lambda \tag{22}$$

where the retarded time from the right $\bar{\tau}_R$ and left $\bar{\tau}_L$ sides of the layer scaled to the relaxation time are defined as

$$\bar{\tau}_R = \left(t - \frac{z - l/2}{c}\right)/\theta \quad \text{and} \quad \bar{\tau}_L = \left(t - \frac{z + l/2}{c}\right)/\theta$$

Evaluation of eq 22 gives the photoacoustic pressure to the right of the heated layer for $\bar{\tau}_R > 0$ as

$$p(z,t) = \frac{\bar{\alpha}\beta I_0 c^2 \theta}{2C_P}(1 - e^{-\bar{\tau}_R}) \quad \text{for} \quad \bar{\tau}_L < 0$$

$$p(z,t) = \frac{\bar{\alpha}\beta I_0 c^2 \theta}{2C_P}(e^{-\bar{\tau}_L} - e^{-\bar{\tau}_R}) \quad \text{for} \quad \bar{\tau}_L > 0 \tag{23}$$

Discussion

When heat is deposited in the layer with no storage of chemical energy, the waveforms as determined by eq 14 are a series of square waves with amplitudes determined by the reflection and transmission coefficients of a plane wave at an interface, as given in ref 24. Waveforms that give information about heat liberation and volume changes are found when ζ is different from zero.

From eq 23 it is clear that the form of the photoacoustic wave for exponential depositon of heat in a layer is a rising exponential followed by decay to the baseline, as shown in Figure 1 where the photoacoustic pressure is plotted as a function of the dimensionless retarded time from $l/2$, $\bar{\tau}_R$. The rise in the acoustic pressure is caused by gradual deposition of heat in the layer: near $\bar{\tau}_R = 0$, the wave passes into the transparent layer at the same time heat is being delivered to the fluid during exponential decay of the excited state, resulting in a rising pressure. According to the theorem given in refs 26 and 27, the shape of the waveform should be a convolution of the spatial deposition of heat in the layer, a constant, with an exponential in time.

The effect of reflections for a fluid confined between two infinite half spaces is given by eq 14. When the fluids in the half-spaces have a density and sound speed greater than that of the layer, i.e., when $\xi < 1$, the shape of the waveform can be understood as an initial production of an exponentially rising

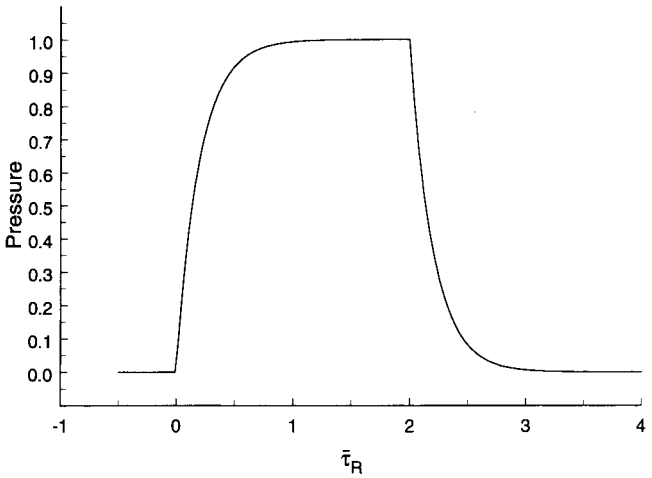

Figure 1. Photoacoustic pressure in arbitrary units versus dimensionless retarded time $\bar{\tau}_R$ from eq 23 for $\theta = 0.2$.

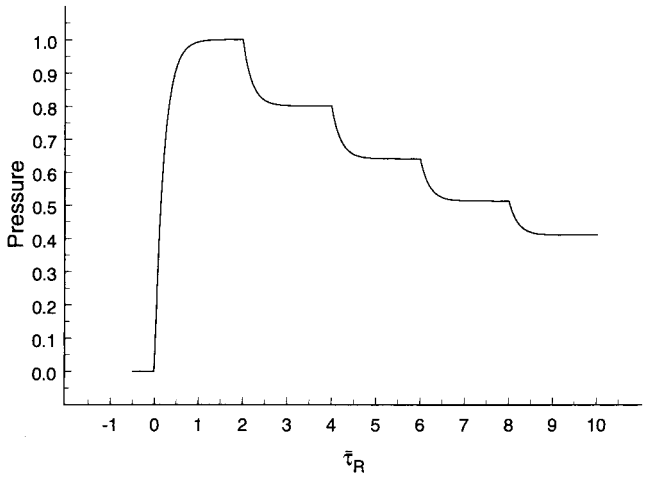

Figure 2. Photoacoustic pressure in arbitrary units versus retarded time $\bar{\tau}_R$ from eq 14 for $\zeta = 0.99$, $\hat{\theta} = 0.2$. $\xi = 0.8$ with the amplitude prefactors for thermal and chemical expansion set to unity and zero, respectively.

wave inside the fluid layer followed by a series of internal reflections at the interfaces. Consider when a wave with the parameters corresponding to those in Figure 1 is launched in a layer where reflections are characterized by a positive amplitude reflection coefficient ξ taken as 0.8. Since the effect of the first interface at $l/2$ is to transmit part of the wave, the first part of the photoacoustic wave seen is simply the original wave, diminished in amplitude by the reflection coefficient, as can be seen in Figure 2. As the first part of wave exits from the layer, a wave traveling in the opposite direction is simultaneously launched in the direction of the negative z-axis. (For a detector placed to the left of $-l/2$, the left-going wave has the same time profile as the wave traveling to the right of the layer.) As the right-going wave is transmitted through the interface at $l/2$, the left-going wave reflects off the interface at $-l/2$ losing part of its amplitude to transmission, with the remainder of the wave reflecting from the interface, traversing the layer, and appearing at the right interface where it, in turn, is partially transmitted. The amplitude of the transmitted wave for the dimensionless retarded time $\bar{\tau}_R$ between 2 and 4 is thus the sum of the first transmitted wave, which at this point in time is decaying to the baseline (it is the difference of two exponential functions), and the reflected left-going wave, which is a rising exponential function. The sum of these two functions, for the set of parameters chosen here, has an amplitude at $\bar{\tau}_R = 2$ equal to

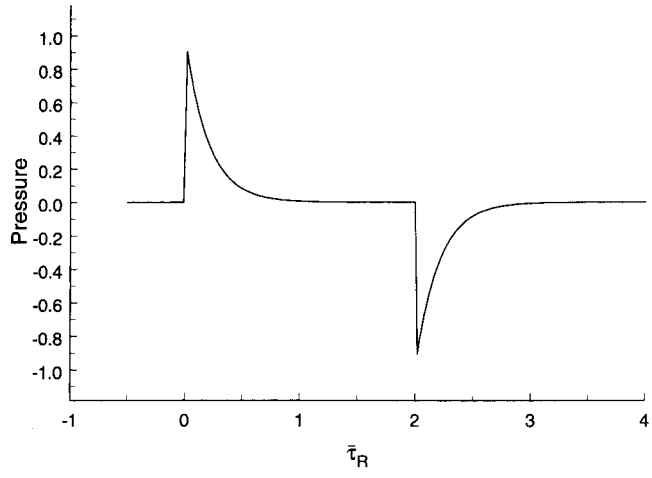

Figure 3. Photoacoustic pressure in arbitrary units versus retarded time $\bar{\tau}_R$ from eq 14 for $\zeta = 0.99$, $\hat{\theta} = 0.2$, $\xi = 0$ with the amplitude prefactors for thermal and chemical expansion set to zero and unity, respectively, showing the effect of a rapid chemical expansion and contraction in a layer bounded by two infinite half-spaces with identical acoustic properties.

that of the peak value of the first transmitted wave. The wave then decays to a final value at $\bar{\tau}_R = 4$ approximately equal to ξ times the amplitude of the peak value of the originally transmitted wave. In general, successive reflections of the wave originally launched within the layer give amplitudes at $\bar{\tau}_R$ equal to 2, 4, 6, 8, and 10, of $T\xi^0$, $T\xi^1$, $T\xi^2$, $T\xi^3$, $T\xi^4$, where T, the amplitude transmission coefficient, is related to the reflection coefficient through $1 + \xi = T$. Figure 2 shows the wave calculated from eq 14 using the parameters for Figure 1, but which includes the effects of reflection. It can be seen that the qualitative picture given in terms of reflections at the two interfaces is borne out by the time profile of the waveform.

Consider now the effect of volume expansion alone with no heat deposition, as would take place when a molecule is excited to an upper state where the result of the excitation is a net positive volume change in the fluid. The initial effect of absorption of radiation is thus to cause a rapid, positive pressure increase in the fluid layer, which launches a compressive sound wave in both the positive and negative z-directions. Consider, first, the case where the layer has the same density and sound speed as the surrounding media and θ is 0.2. As the right-going wave propagates outside the layer, the excited state decays causing a contraction of the fluid that gradually cancels out the compression. Before a time corresponding to the thickness of the layer has passed, significant decay of the excited molecular state has taken place resulting in a partial cancellation of the pressure increase for values $\bar{\tau}$ between 0 and 2, as is shown in Figure 3. As the excited state decays, the fluid returns to its original volume. The shape of the wave can perhaps best be understood by noting that the effect of an expansion followed by a contraction can be described by a compressive wave $f(t - h)$ followed by a rarefaction $-f(t + h)$. For small values of h, the resulting waveform should be $f(t - h) - f(t + h) = 2hf'(t)$: the waveform thus should resemble the time derivative of that in Figure 1. Note that although heat deposition and volume change act the same way in producing acoustic waves,[14] heat deposition is always positive, and volume changes can be both positive and negative.

The effect of reflections on a photoacoustic wave generated by an expansion followed by a contraction is shown in Figure 4. The time development of the waveform can be understood in terms of successive reflections as for the the case of the thermally generated wave discussed above.

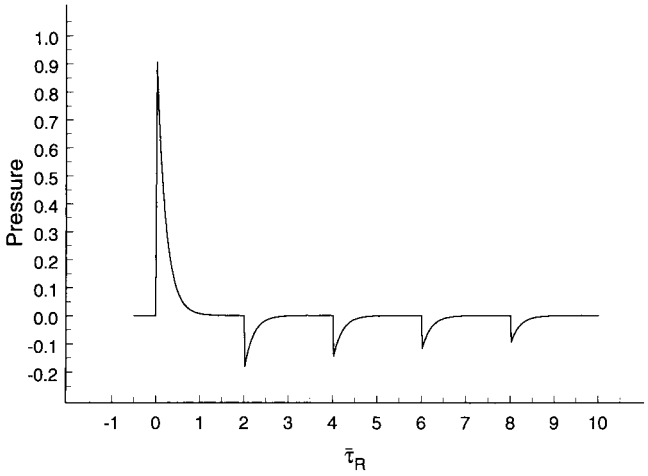

Figure 4. Photoacoustic pressure in arbitrary units versus retarded time $\bar{\tau}_R$ from eq 14 for $\zeta = 0.99$, $\theta = 0.2$, $\xi = 0.8$ with the amplitude prefactors for thermal and chemical expansion set to zero and unity, respectively, showing the effect of reflections on the waveform in Figure 3.

Although the problem discussed here has been formulated for a fluid layer in contact with two infinite fluid half-spaces, the results are valid for a fluid layer confined by isotropic solids, provided there is symmetry in one dimension.[24] Of course, in experiments, it is only necessary to make the diameter of the region of irradiation large in comparison with the thickness of the layer to realize conditions that ensure the validity of the results given here.

Typical front face illumination experiments employ transducers that have resonant behavior so that the response of the overall apparatus to, for instance, rapid deposition of heat is a somewhat complicated waveform. The approach to a quantitative description of this less than ideal behavior has been to record a waveform known as the "T-wave" from a solution that gives what is considered to be an instantaneous release of heat in a reference fluid and then to record the photoacoustic waveform of the solution of interest,[29] which is referred to as the "E-wave". The E-wave is then described by a convolution integral of the T-wave with the function describing the heat released per volume and time in the fluid. Depending on the kinetics of the chemical system studied, various functional forms for the heat release have been employed; a sum of exponentials is frequently used.[16,17,19] Reference 20 treats heat release in a general way using frequency domain functions and includes the full effects of reflections, the response of the transducer, and acoustic absorption. As the method relies on multiplication of the various frequency domain response functions, the effects of arbitrary heat release mechanisms can be found. When used in conjunction with the results of a previous calculation by the same group,[30] the formalism given is completely general since it can determine the photoacoustic wave for any arbitrary scheme for heat release and molecular volume change.

The present calculation was carried out to show the time domain response of heat release and volume change in a front face illumination cell for a simple, but commonly encountered,[31−34] kinetic decay scheme, namely, rapid heat deposition for a fraction of the absorbed optical energy followed by a single-exponential release of the remaining fraction of the absorbed energy. The advantage of determining time domain waveforms is that the closed form solutions show clearly the time dependence of the photoacoustic waveforms without numerical Fourier transformation. In addition, provided the kinetic decay scheme is appropriate for the system under study, the extraction of fitted parameters can be carried using least-squares fitting methods directly without the employment of Fourier transformation or convolution integrals.

As has been noted,[16−20] the salient feature of the experimental method based on irradiation of a layer is its time resolution. Since the method relies on measurement of an acoustic rise time, when the response of the acoustic transducer is ignored, the ultimate time resolution of the method is governed by the flatness of the interface, the pulse width of the exciting laser pulse, and, at high frequencies, by the viscoelastic properties of the irradiated fluid itself.

Acknowledgment. The authors are grateful for the support of this research by the U.S. Department of Energy, Office of Basic Energy Studies, under Grant ER13235. The support of the Alcoa Research Foundation for a contribution to the author's laboratory is also acknowledged.

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