Relaxation time measurements in frequency and time-domain photoacoustic spectroscopy of condensed phases

A. Mandelis and B. S. H. Royce
Materials Laboratory, Princeton University, Princeton, New Jersey 08544

(Received 8 August 1979)

The use of the photoacoustic spectroscopy (PAS) technique to measure nonradiative lifetimes in either the frequency or time-domain mode is discussed. Expressions are presented for the dependence of the cell pressure upon the lifetime, and the modifications introduced by the microphone transfer function are discussed. It is shown that in both measurement modes thermally and optically thick specimens are preferred. Other sample types have contributions to the measured phase or time delay arising from the optical absorption depth and sample cell parameters. The model presented suggests that the PAS technique is suitable for the measurement of lifetimes in the range between 10^{-5} and 10^{-1} s, with the limits arising from the microphone transfer function, the finite sound velocity, and thermal transport velocity in the transducer gas.

INTRODUCTION

Photoacoustic spectroscopy (PAS) provides a method for monitoring nonradiative decay processes that can occur in solids following their excitation by the absorption of photons. If a relatively long lifetime is associated with the final state from which the nonradiative decay occurs, it can be measured using the photoacoustic response. This signal may be generated either by exciting the material with a periodically modulated light source or with a sequence of pulses of duration short compared to their repetition rate. The frequency-domain technique has been most frequently used in the PAS study of solids and liquids, and in this mode it is the phase lag of the system response with respect to the optical stimulus that provides the lifetime information. Since the excited-state lifetime is not the only source of such a phase lag, care must be taken in interpreting the data and, as will be shown below, it is usually only under certain special sets of conditions that the phase is simply related to the lifetime of interest.

When the sample is excited by a single pulse or a time sequence of well-separated pulses, the time development of the cell pressure can provide the desired lifetime information. In this time-domain mode the delay of the signal with respect to the pulse contains a contribution from the excited-state lifetime. The symmetry between the time and the frequency domain indicates that other factors such as optical absorption depth will also contribute to the measured time delay and it is to be expected that only under special conditions will it be possible to extract the lifetime from these measurements in a straightforward way.

In general, theories of the photoacoustic effect in solids have been concerned only with the expressions for the pressure of the transducer gas in the photoacoustic cell. When phase lags or time delays are important quantities in the measurements, it is necessary to take into account the transfer function of the pressure measuring device that provides the electrical output signal. Since most commercial devices will exhibit nonlinear behavior in their amplitude and phase response at both high

0030-3941/80/050474-07$00.50

and low frequencies, it is to be expected that they may modify the frequency-domain response in these regions and also affect the time-domain response at short and long times.

The relaxation times associated with radiationless decay processes have been studied using frequency-domain PAS techniques by Powell and co-authors.[1,2,3] In interpreting their data they employed the relationship between the nonradiative relaxation time and the phase of the photoacoustic response that was used for gaseous samples by Harshbarger and Robin.[4] Because of the more complex heat-transfer processes involved when a solid or liquid sample is under study, this expression holds only under very limited experimental conditions. Mandelis *et al.*[5] have derived the corresponding expressions connecting the phase of the PAS response and the nonradiative lifetime for condensed samples and the essential features of this development are discussed further below.

The authors are unaware of any time-domain PAS experiments in which lifetimes have been measured; however, Aamodt and Murphy[6] have reported a one-dimensional theoretical model for the time evolution of a PAS signal and included the effects of an excited-state lifetime in the model. The application of this model to data analysis is difficult because no analytic closed-form expressions are available for the inversion of the complex Laplace transforms involved. By simplifying the gas thermal transport equation, however, closed-form solutions can be obtained; this approach was adopted by Mandelis and Royce[7] and applied to systems with an instantaneous radiationless relaxation path. This model has now been extended to include finite-relaxation-time effects and is discussed further below.

In the present paper the essential features of the photoacoustic response of a one-dimensional system including a finite excited-state relaxation time will be discussed for both the frequency and the time domain. Expressions will be given for the cell pressure and the effect of the transfer function of a typical commercial microphone transducer will then be taken into account. The experimental conditions suitable for lifetime measurements will be examined and the limitations imposed by cell size, the velocity of sound, and the transducer response will be discussed.

THEORETICAL MODEL AND RESULTS

The one-dimensional geometry of the photoacoustic system under consideration is shown in Fig. 1 and is essentially the same as that employed by others.[6,8] The absorbing solid s is in thermal contact with a transparent backing b and transducer gas g. The cell is closed by a transparent window w. Both the backing and the window are chosen to be arbitrarily thick and it is assumed that their outside walls remain at the ambient temperature T_0 at all times. The solid is assumed to contain a simple two-level electronic state that has an excited-state lifetime τ and which may return to its ground state with a nonradiative efficiency η. The electronic state has an associated optical absorption coefficient $\beta(\lambda)$. Monochromatic light impinges on the solid at the gas/solid interface and is either modulated periodically so that the irradiance is $(I_0/2)(1+\cos\omega_0 t)$ or has the form of a Heavyside function of duration τ_p and irradiance I_0.

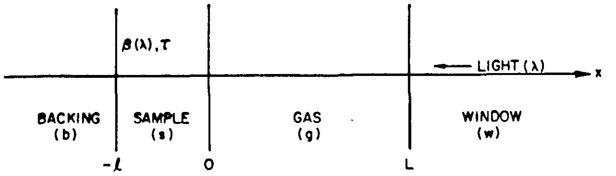

FIG. 1. One-dimensional PAS cell geometry.

For the periodically modulated light the irradiance at a distance x from the front surface of the solid is given by

$$I(x,t) = [I_0\beta\exp(-\beta|x|)/2](1+\cos\omega_0 t) \equiv A(x)\mathrm{Re}[1+\exp(i\omega_0 t)].$$

This radiation is absorbed by the electronic state, and the energy in the excited state is then

$$\frac{dE(x,t)}{dt} = I(x,t) - \frac{E(x,t)}{\tau}.$$

In the steady state $E(x,t)$ is periodic and the nonradiative decay of this excited-state population to the ground state provides a spatial- and time-dependent heat source in the solid that has the form

$$\dot{H}(x,t) = (\eta/\tau)E(x,t) = \frac{\eta I_0\beta\exp(-\beta|x|)}{2}\,\mathrm{Re}\left(\frac{\exp(i\omega_0 t)}{1+i\omega_0\tau}\right). \tag{1}$$

In the time domain the corresponding expression for $\dot{H}(x,t)$ resulting from the pulse excitation has the form

$$\dot{H}(x,t) = \beta I_0\eta\exp(-\beta|x|) \times \begin{cases} 1-\exp(-t/\tau) & 0\le t\le\tau_p \\ [\exp(\tau_p/\tau)-1]\exp(-t/\tau) & t\ge\tau_p. \end{cases} \tag{2}$$

It is these heat-source terms that cause the temperature of the sample to change and give rise to the PAS signal via heat conduction to the gas. Four coupled heat diffusion equations are involved, one for each region of the PAS system.

The present model uses the simplified equation for the gas phase that was also used by Rosencwaig and Gersho[8] and which assumes that the pressure is at all times uniform within the gas. This simplification makes it possible to obtain analytic expressions for the pressure in the PAS system. The thermal diffusion equations are

$$\frac{\partial^2 T_s(x,t)}{\partial x^2} - \frac{1}{\alpha_s}\frac{\partial}{\partial t}T_s(x,t) = -\frac{\dot{H}(x,t)}{k_s} \tag{3}$$

for the solid in which the optical absorption occurs and

$$\frac{\partial^2 T_i(x,t)}{\partial x^2} - \frac{1}{\alpha_i}\frac{\partial}{\partial t}T_i(x,t) = 0 \tag{4}$$

for the other transparent regions of the cell. The quantities α_i are the thermal diffusivities of the various regions i and k_i is the corresponding thermal conductivity.

In solving these equations in both the frequency and time domain, it has been assumed that there is temperature- and heat-flux continuity at each material interface. Recently Cesar *et al.*[9] have suggested that the temperature-continuity condition is inappropriate at both the sample-backing and sample-gas interfaces and have introduced a heat-transfer coefficient at each interface. Whereas such a procedure may be valid at the interface of the sample and the backing, it seems inappropriate for the sample-gas interface. An alternative treatment of the interface with the backing would model it as an intermediate layer, as was done by Mandelis *et al.*,[5] but would still retain the temperature-continuity constraint. In this approach the heat-transfer coefficient is replaced by the thermal properties of the interfacial region.

Solutions to the thermal diffusion equations above have been obtained in both the frequency[5] and time domain[7,10] using either Fourier or Laplace transform techniques. The spatial- and time-dependent temperature distribution in the gas is first evaluated and the time-dependent but uniform cell pressure is obtained by an integration over the cell volume.

In the frequency domain,

$$\langle p_g(t;\omega_0)\rangle = \frac{p_0}{T_0 L}\int_0^L T_g(x,t;\omega_0)\,dx$$

which yields a PAS signal of the form

$$\langle p_g(t;\omega_0)\rangle = \left(\frac{p_0 I_0 \eta\beta}{2k_s T_0 L}\right) \mathrm{Re}\left[\left(\frac{\exp[i(\omega_0 t-\pi/4)]}{\sqrt{2}a_g(1+i\omega_0\tau)(\beta^2-\sigma_s^2)}\right) \times\left(\frac{(r-1)(b+1)\exp(\sigma_s l)-(r+1)(b-1)\exp(-\sigma_s l)+2(b-r)\exp(-\beta l)}{(b+1)\exp(\sigma_s l)+(b-1)\exp(-\sigma_s l)}\right)\right], \quad (5)$$

where the symbols have their conventional meanings and are defined in Ref. 5. From the point of view of relaxation-time measurements, it is the phase lag of this signal with respect to the light source modulation that is important. This is obtained from the real and imaginary parts of the above expression for the pressure. Following Rosencwaig and Gersho[8] and defining

$$\langle p_g(t;\omega_0)\rangle \equiv \mathrm{Re}\{Q\exp[i(\omega_0 t-\pi/4)]\}$$
$$\equiv \mathrm{Re}\{q\exp[(i\omega_0 t-\pi/4)-\psi]\}$$

such that

$$Q = Q_1 + iQ_2 = q\exp(-i\psi),$$

the phase lag of the signal with respect to the light source modulation is given by

$$\Phi = \pi/4 + \psi,$$

with

$$\psi = \tan^{-1}[-(Q_2/Q_1)].$$

From (5) it can be seen that the variable contribution to the phase ψ depends upon the optical absorption coefficient of the solid, its physical dimensions, the ratio of the thermal properties of the solid and the backing material, the relaxation time of the nonradiative deexcitation processes, the modulation frequency of the light, and the thermal properties of the solid and the gas in the cell. Only in certain limiting cases is ψ directly related to τ.

From an experimental viewpoint the most useful such case is that of an optically and thermally thick sample. Under these conditions the variable component of the phase is given by

$$\psi(\beta,\tau,\omega_0) = \tan^{-1}(-\omega_0\tau_\beta) + \tan^{-1}(\omega_0\tau) - \tan^{-1}\left(\frac{-1}{1-\sqrt{2\omega_0\tau_\beta}}\right), \quad (6)$$

where $\tau_\beta \equiv (1/\beta^2\alpha_s)$ and is a characteristic relaxation time for the system. At chopping frequencies for which $\mu_s > \mu_\beta$ and $\omega_0\tau_\beta \simeq 0$

$$\psi(\tau,\omega_0) \simeq \pi/4 + \tan^{-1}(\omega_0\tau), \quad (7)$$

and the phase information provides a direct measure of the relaxation time τ of the nonradiative processes.

Figure 2 shows ψ evaluated for several choices of the nonradiative relaxation time for the above case. For this figure $b = 1$ and the optical absorption coefficient $\beta = 2\times10^5\ \mathrm{cm}^{-1}$. No contribution to the phase shift arises from the optical absorption depth since over the full frequency range $\mu_s > \mu_\beta$, however, as has been pointed out by Roark *et al.*,[11] there is always an unknown instrumental contribution to the measured phase. In order to obtain a meaningful lifetime measurement it is therefore necessary to measure the phase over a range of frequencies and to use a PAS cell with no resonances in the frequency range covered.

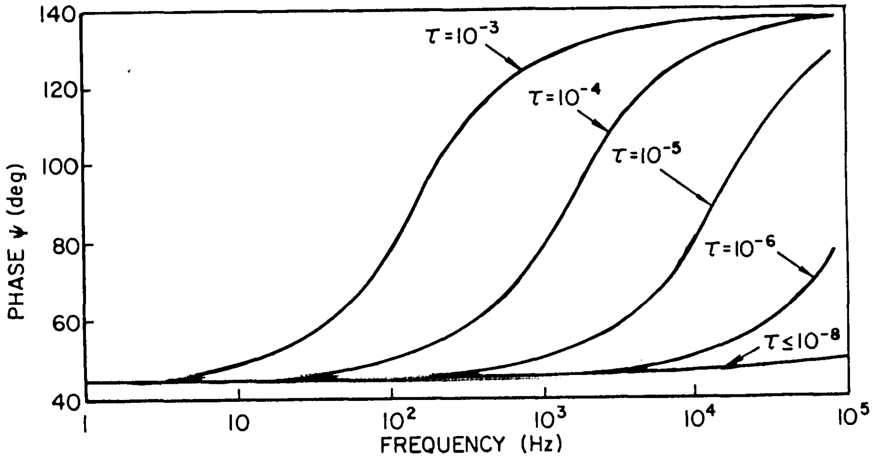

FIG. 2. Relaxation-time effects on PAS phase.

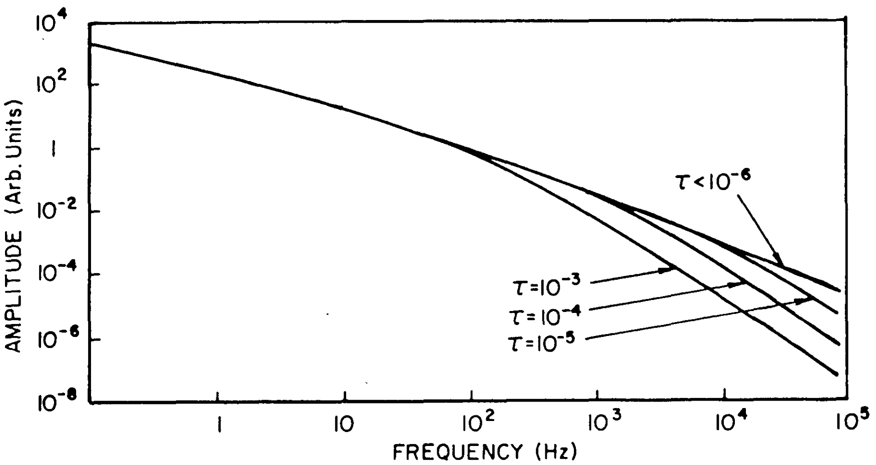

FIG. 3. Relaxation-time effects on frequency-domain PAS amplitude.

The amplitude of the frequency-domain PAS response is also dependent upon the relaxation time of the excited state as shown in Fig. 3. The dependence of the thermal diffusion length μ_s upon the modulation frequency of the light means that for a sample with instantaneous nonradiative deexcitation processes the amplitude of the PAS signal has an ω^{-1} dependence at low modulation frequencies and an $\omega^{-3/2}$ dependence at high frequencies. For a sample in which the nonradiative processes have a finite relaxation time, the high-frequency slope is changed as is shown in Fig. 3. The curves for the finite relaxation times break away from the instantaneous curve at a point for which $\omega_0\tau \simeq 1.0$ and for all values of τ approach a limiting logarithmic slope higher by one than that of the instantaneous curve. In general, it is expected that this change in slope will be more difficult to measure than the corresponding phase change.

In the time domain, relaxation-time measurements are also most suitably made on samples that are thermally thick and have a high optical absorption coefficient. It is convenient to regard the thermal diffusion length in the solid as being a time-dependent quantity $\mu_s(t)$ and to describe a material as thermally thick if $\mu_s(t) < l$ for all times of interest. The material will also be optically opaque if $\mu_s(t) > \mu_\beta$ for all times larger than the first time at which measurements of pressure can be made following the excitation pulse. For a system with instantaneous relaxation processes from the excited state the cell pressure is given by (7):

$$\begin{aligned}\langle p_g(t;0)\rangle = {} & \frac{\alpha_s\eta\beta I_0 p_0\sqrt{\alpha_g}\,\tau_\beta}{T_0 L k_s} \\ & \times\left\{\left(\frac{t}{\sqrt{\tau_\beta}}\right) - 2\left(\frac{t}{\pi}\right)^{1/2} + \sqrt{\tau_\beta}\left[1-\exp\left(\frac{t}{\tau_\beta}\right)\operatorname{erfc}\sqrt{\frac{t}{\tau_\beta}}\right.\right. \\ & + 2\sum_{n=1}^{\infty}(-1)^n\left\{\operatorname{erfc}\left(\frac{nL}{\sqrt{4\alpha_g t}}\right) - 2\left(\frac{t}{\tau_\beta}\right)^{1/2} i\operatorname{erfc}\left(\frac{nL}{\sqrt{4\alpha_g t}}\right)\right. \\ & -\exp\left[\left(\frac{t}{\tau_\beta}\right)+\frac{nL}{\sqrt{\alpha_g\tau_\beta}}\right]\operatorname{erfc}\left[\left(\frac{t}{\tau_\beta}\right)^{1/2}+\frac{nL}{\sqrt{4\alpha_g t}}\right] \\ & \left.\left.\left. + 4\left(\frac{t}{\tau_\beta}\right) i^2\operatorname{erfc}\left(\frac{nL}{\sqrt{4\alpha_g t}}\right)\right\}\right]\right\};\ t<\tau_p \qquad (8)\end{aligned}$$

and

$$\begin{aligned}\Delta p(t>\tau_p) = {} & [\Delta p(t<\tau_p)]_{t=t} \\ & - [\Delta p(t<\tau_p)]_{t=(t-\tau_p)};\ t>\tau_p,\end{aligned}$$

where

$$i^2\operatorname{erfc}x = \int_x^\infty i\operatorname{erfc}y\,dy$$

and

$$i\operatorname{erfc}x = \int_x^\infty \operatorname{erfc}y\,dy.$$

When the excited state has a relaxation time τ the expression for the cell pressure becomes[10]

$$\begin{aligned}\langle p_g(t;\tau)\rangle = {} & \langle p_g(t;0)\rangle \\ & - [(\alpha_s\beta\eta I_0 p_0\sqrt{\alpha_g})/T_0 L k_s]\times\{J(0,t;\tau,\tau_\beta) \\ & + 2\sum_{n=1}^{\infty}(-1)^n J[(nL/\sqrt{\alpha_g}),t;\tau,\tau_\beta]\},\ t\le\tau_p, \qquad (9)\end{aligned}$$

$$\begin{aligned}\langle p_g[(t>\tau_p);\tau]\rangle = {} & \langle p_g[(t<\tau_p);\tau]\rangle_{t=t} \\ & - \langle p_g[(t<\tau_p);\tau]\rangle_{t=(t-\tau_p)};\ t\ge\tau_p,\end{aligned}$$

where $\langle p_g(t;0)\rangle$ is given by Eq. (8) above and J is defined in the Appendix.

The results of evaluating Eq. (9) are shown in Fig. 4 together with the corresponding time dependence of the heat release rate $\dot{H}(t;\tau)$ given by Eq. (2). For $\dot{H}(t;\tau)$ the relaxation time was taken to be 10^{-4} s, which is long compared to the pulse duration τ_p of 5.5×10^{-6} s. Under these circumstances the excited-state population continues to build up for the duration of the pulse and $\dot{H}(t;\tau)$, therefore, exhibits its maximum value at the end of the pulse. When the stimulus is removed, the excited-state population decreases with its characteristic relaxation time τ and the heat input to the solid exhibits a parallel decrease. Throughout this period the pressure in the gas is increasing owing to heat transfer to it from the solid. The pressure response has an inflection point at $t\simeq\tau$ provided τ is short compared to a thermal transit time of the cell but long compared to τ_p. These limitations restrict measurements of τ to the approximate range $10^{-5}\text{ s}\le\tau\le0.1$ s. By $t\simeq10\tau$ the excited-state population is depleted and no more heat is supplied to the solid. The surface temperature of the solid has not yet decayed to T_0 and some heat is still being supplied to the gas. At longer times heat-transfer processes to the cell window reduce the gas pressure to its preexcitation value. For very long relaxation times the in-

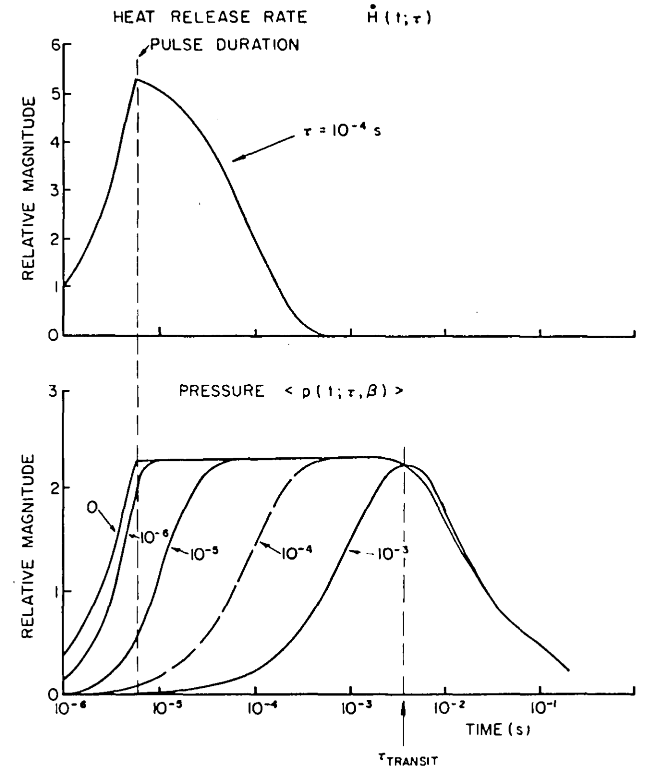

FIG. 4. Heat-release rate and relaxation-time effects in time-domain PAS.

terplay between energy transfer to the gas from the photoexcited solid and energy loss to the window determines the form of the pressure response. This is illustrated in Fig. 4 by the $\tau = 10^{-3}$ s curve which does not reach the same maximum value of the pressure despite the fact that the total energy in the pulse was the same as for the other curves. This effect is even more marked for longer relaxation times or shorter thermal transit times.

The cell pressures in the frequency and time domain given by Eqs. (5) and (9) above are normally measured using a sensitive microphone and preamplifier. The electrical output is related to the pressure via the transfer function of this transducer. When an extended frequency range or time span is involved in the measurements, the detector assembly may modify the output signal of an instantaneously relaxing system in such a way as to give the appearance of a relaxation time. This fact will restrict the range of lifetimes that can be measured accurately and indicates the need to know the transfer function of the pressure transducer. Mandelis and Royce[10] have considered these effects for B & K condenser microphones used in both the frequency and time domain. Because of its flat high-frequency response, a (1/8)" B & K microphone type 4138 was used for modeling purposes. The transfer function was obtained by fitting the computed response of a mechanical model of the microphone to the manufacturer's published frequency-response data. The quality of the function so obtained was verified by comparing the computed frequency dependence of the phase with published data. Linear control theory techniques[12] were then used to evaluate the time-domain response of the same microphone using the coefficients from the frequency-domain modeling. This time-domain response was also checked by comparing a computed response to a 20-μs pulse with the manufacturer's data.

Figure 5(a) shows the effect of the microphone on the measured amplitude of a frequency-domain PAS signal. As can be seen the microphone accurately reproduces the cell pressure between approximately 10 and 5 × 10^4 Hz. At low and high frequencies, however, the nonlinearity of the microphone amplitude response gives rise to small departures from the actual signal. Figure 5(b) shows the corresponding phase behavior. At high frequencies the amplitude response of the microphone is made more linear by the manufacturer through the use of the protection grid as a Helmholtz resonator. This has the effect of causing a phase shift between the input pressure to the microphone and its electrical output, as is clearly shown above 10^4 Hz in the figure.

Figure 6 shows the corresponding time-domain effects. For the $\tau = 0$ pressure pulse it is seen that the high-frequency drop-off of the microphone response gives rise to a delay in the leading edge of the output signal that could be mistaken for an excited-state lifetime. At long times the low-frequency response characteristics give rise to an artificial drop-off in the output signal which masks the thermal-wave transit time of the cell. For excited-state lifetimes of 10^{-5} s or longer, the (1/8)″ microphone is able to follow the leading edge of the pressure pulse; however, it still obscures the transit-time data. The 4138 microphone has a rather poor sensitivity and (1/2)″ or (1)″ microphones are, therefore, more frequently used in

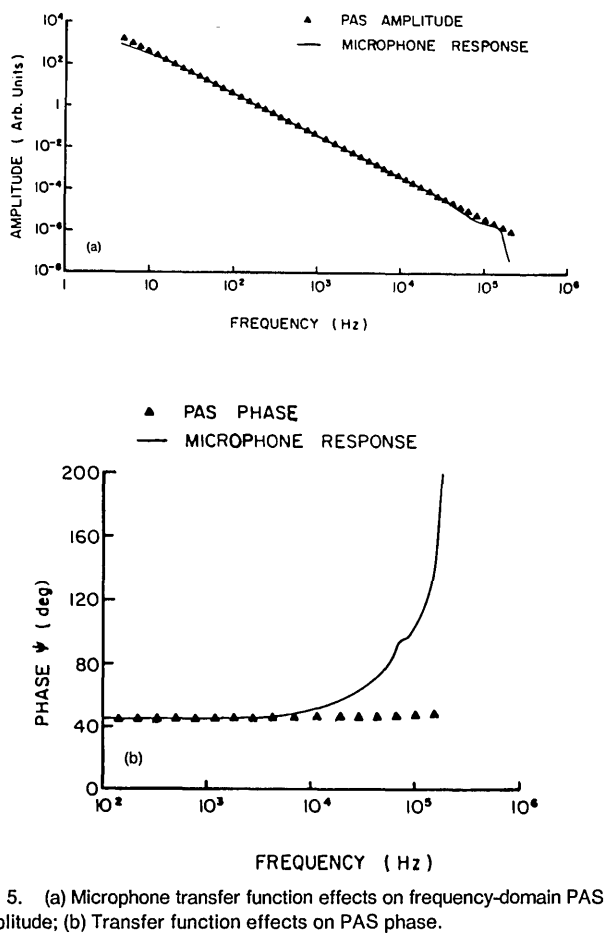

FIG. 5. (a) Microphone transfer function effects on frequency-domain PAS amplitude; (b) Transfer function effects on PAS phase.

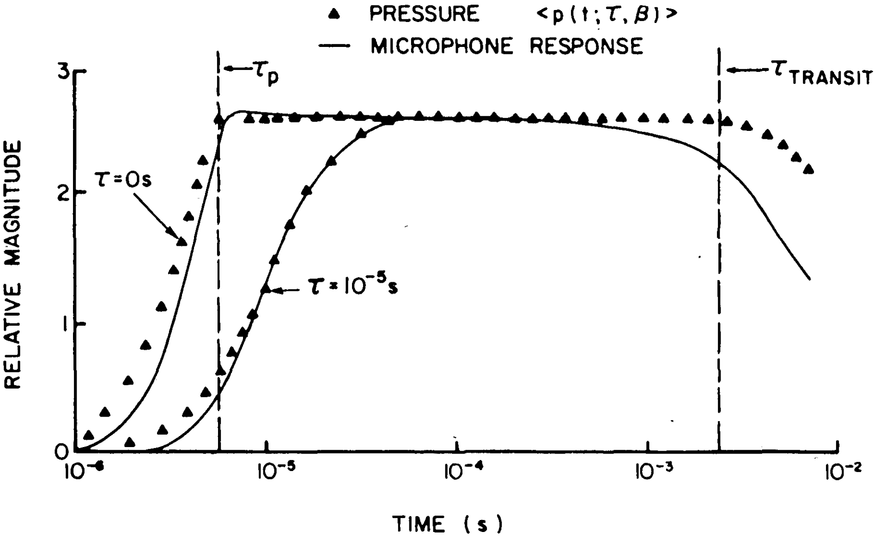

FIG. 6. Microphone transfer function effects on time-domain PAS response.

PAS data acquisition. Both of these B & K microphones have a high-frequency roll-off that starts at lower frequencies than that of the (1/8)″ microphone and consequently causes longer delays in the leading edge of the instantaneous response curve and further restricts the range of lifetimes that can be measured.

DISCUSSION

Two approaches to the measurement of nonradiative relaxation times employing the photoacoustic technique have been considered using a theoretical model in which a simplified form of the gas thermal transport equation was employed. This model does not predict the steps in cell pressure computed by Aamodt and Murphy[6] in their more exact model which takes into account the finite velocity of sound; however, the magnitude of these steps is only about 10^{-4} of the final value of the cell pressure and after about six acoustic transit times of the cell these effects are damped out. The advantage of the simplified model in both the frequency and time domain is that it permits the development of analytic expressions for the cell pressure that can be readily compared to experimental measurements.

On the basis of the models presented it is seen that an unambiguous determination of the excited-state lifetime requires a sample that is both thermally thick and optically opaque. Other sample conditions will give rise to phase changes or time delays that involve other parameters of the system such as its optical absorption depth or thermal coupling to the sample backing and cell window.

Because of the difficulty in making an absolute phase angle determination in a photoacoustic system, it is necessary to measure the phase shift associated with the relaxation time in a sample over a wide range of modulation frequencies. If the cell and detector have a flat phase response as a function of frequency, the inflection point in the phase versus frequency curve may be used to measure the lifetime. Resonances in the PAS cell should, therefore, occur at as high a frequency as possible. Since Helmholtz resonances tend to be those of the lowest frequency in a PAS cell, care should be taken to avoid a sample chamber-microphone chamber configuration that can give rise to these.

A disadvantage of the frequency-domain method is that the amplitude of the PAS signal decreases as the modulation frequency increases, causing phase instability at high modulation frequencies due to a reduced signal-to-noise ratio. In this respect the time-domain approach seems to be advantageous as the short time signal amplitude is strong and the effect of the excited-state lifetime on the maximum signal from a given energy pulse is only important when the thermal transit time in the cell becomes of the same order as this lifetime. The availability of high irradiance tunable pulsed laser sources also makes the time-domain technique attractive.

The effects of the pressure transducers on the measured response impose a limitation on the range of excited-state lifetimes that can be measured. With conventional microphones this range is between approximately 10^{-5} and 10^{-1} s. The finite sound velocity also restricts lifetime measurements to values greater than around 10^{-5}, a fact which provides further justification for the use of the simplified model presented.

ACKNOWLEDGMENT

This work was supported in part by ARO Contract No. DAAG29-76-C-0054.

APPENDIX

$$\begin{aligned} J[Y,t;\tau,\tau_\beta] &\equiv L^{-1}[\exp(-Y\sqrt{s})/s(s+\tau^{-1})(\sqrt{s} \\ &\quad + 1/\sqrt{\tau_\beta})] = \tau\sqrt{\tau_\beta}\{\operatorname{erfc}(Y/2\sqrt{t}) - (T/\tau)\exp[(t/\tau_\beta) \\ &\quad + Y\sqrt{\tau_\beta}]\operatorname{erfc}(Y/2\sqrt{t} + \sqrt{t}/\tau_\beta) \\ &\quad - (1/2)\exp(-Y^2/4t)\{(T/\tau_\beta)[\operatorname{Re}\{\exp(Z^2)\operatorname{erfc}Z\} \\ &\quad + \operatorname{Re}\{\exp[(Z^*)^2]\operatorname{erfc}(Z^*)\}] - (T/\sqrt{\tau\tau_\beta})[\operatorname{Im}\{\exp(Z^2)\operatorname{erfc}Z\} \\ &\quad - \operatorname{Im}\{\exp[(Z^*)^2]\operatorname{erfc}(Z^*)\}]\}\}, \end{aligned}$$

where

$$\begin{Bmatrix} Z \\ Z^* \end{Bmatrix} = Y/2\sqrt{t} \pm i\sqrt{t}/\tau;\; T^{-1} \equiv \tau^{-1} + \tau_\beta^{-1}.$$

[1] L. D. Merkle and R. C. Powell, "PAS Investigation of Radiationless Transitions in Eu^{2+} Ions in KCl Crystals," Chem. Phys. Lett. **46**, 303–306 (1977).

[2] L. D. Merkle, R. C. Powell, and T. M. Wilson, "Radiationless processes in KCl:Eu^{2+}," J. Phys. C **11**, 3103–3119 (1978).

[3] R. G. Peterson and R. C. Powell, "PAS Investigation of Radiationless Relaxation Processes of Cr^{3+} in Crystals," Chem. Phys. Lett. **53**, 366–368 (1978).

[4] W. R. Harshbarger and M. B. Robin, "The Opto-acoustic Effect: Revival of an Old Technique for Molecular Spectroscopy," Acc. Chem. Res. **6**, 329–334 (1973).

[5] A. Mandelis, Y. C. Teng, and B. S. H. Royce, "Phase measurements in frequency domain PAS of solids," J. Appl. Phys. **50**, 7138–7146 (1979).

[6] L. C. Aamodt and J. C. Murphy, "Size considerations in the design of cells for photoacoustic spectroscopy. II. Pulsed excitation response," J. Appl. Phys. **49**, 3036–3045 (1978).

[7] A. Mandelis and B. S. H. Royce, "Time domain PAS of solids," J. Appl. Phys. **50**, 4330–4338 (1979).

[8] A. Rosencwaig and A. Gersho, "Theory of the photoacoustic effect with solids," J. Appl. Phys. **47**, 64–69 (1976).

[9] C. L. Cesar, H. Vargas, J. A. Meyer, and L. C. M. Miranda, "Photoacoustic effect in solids," Phys. Rev. Lett. **42**, 1570–1572 (1979).

[10] A. Mandelis and B. S. H. Royce, "Nonradiative lifetime measurements in time domain PAS of condensed phases," J. Appl. Phys. **51**, 610–615 (1980).

[11] J. C. Roark, R. A. Palmer, and J. S. Hutchison, "Quantitative Absorption Spectra via Photoacoustic Phase Angle Spectroscopy," Chem. Phys. Lett. **60**, 112–116 (1978).

[12] D. G. Schultz and J. L. Melsa, *State Functions and Linear Control Systems* (McGraw-Hill, New York, 1967).

0030-3941/80/050480-06$00.50