Frequency modulated (FM) time delay photoacoustic and photothermal wave spectroscopies. Technique, instrumentation, and detection. Part I: Theoretical

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A conceptual basis for the technique of time delay photothermal wave spectroscopy is presented. The signal generation and appropriate system functions in the time delay and frequency domains are introduced and discussed from the point of view of correlation and spectral analysis and processing.

INTRODUCTION

The ever-growing field of photoacoustic and other photothermal wave techniques with important applications to materials' studies has recently witnessed the introduction of pseudorandom excitation methods[1-4] other than the conventional frequency-domain[5] and pulsed laser[6,7] (time-domain) schemes. The primary motivation behind the pseudorandom-binary-sequence (PRBS) method[1,2] was its ability to give time delayed information from different depths in a material after a single measurement, during which the cross-correlation function between the input and output signals was calculated. The same method was used very recently[3] to measure the optical absorption coefficient β of condensed phase samples through the dependence of the cross-correlation peak time delay on β. An additional attractive feature of cross-correlation photoacoustic spectroscopy (CPAS) is its alleged promise to yield signal-to-noise ratios (SNR) superior to pulsed time-domain PAS.[8]

Coufal[3] used FFT techniques for the analysis of photoacoustic signals obtained via excitation with pseudowhite noise generated by the linear congruential method.[9] The main advantage of this technique appears to be its ability to generate the frequency spectrum of the sample after a single measurement, thus speeding up the depth-profiling process to just seconds, instead of many minutes required by conventional lock-in detection. Although no formal comparison has been made until now between the time delay capability of CPAS and the frequency response measurements of Coufal, both methods are, in principle, capable of generating data in either the time domain or the frequency domain due to the Fourier transform relationship existing between these two domains.

In this work, the concept of a technique intermediate between time and frequency domains is introduced as an excitation method for photothermal wave systems. This technique is similar to the frequency modulation (FM) of communications systems. It was introduced by Heyser[10] in 1967 in the field of acoustical measurements of loudspeakers and was named time delay spectrometry (TDS) by the same author. Through its implementation and long-term use in acoustic engineering, TDS has been shown to out perform any other time selective technique with respect to noise rejection and nonlinearity suppression from measurements of systems with linear behavior. The time delay technique, based on a linear frequency sweep of the excitation function, has been specifically compared to the impulse response transformation method and the wide-band random noise method[12] and has been proven to have superior measurement dynamic range properties. The slightly longer measurement time required as compared to the impulse response method can be easily compensated through the use of FFT analyzers (see Part II). On the other hand, random noise methods exhibit slow response, limited dynamic range properties, and require sophisticated measurement equipment.[12] Our application of the time delay technique to a photothermal beam deflection system (Part II) and subsequent comparison with PRBS (Part III) bore results consistent with the conclusions presented in Ref. 12, thus establishing time delay photothermal wave methods as superior to more conventional types of excitation and signal analysis.

I. THEORETICAL BACKGROUND FOR TIME DELAY CORRELATION AND SPECTRAL ANALYSIS OF PHOTOTHERMAL WAVE SYSTEMS

A. Nature of the excitation function

Unlike the conventional frequency and time-domain techniques, where the variables frequency f and time t are taken to represent physical phenomena in two mathematical domains which are Fourier transforms of each other such that

$$F(t)=\int_{-\infty}^{\infty} G(f)e^{2\pi i f t}df \qquad (1a)$$

and

$$G(f)=\int_{-\infty}^{\infty} F(t)e^{-2\pi i f t}dt, \qquad (1b)$$

the time delay method is based on a linear frequency sweep with constant or slowly varying amplitude. The sweep signal can be any function of time $X(t)$, modulated between two extreme deviation frequencies, such that the instantaneous frequency $f_i(t)$ is given by[10]

$$f_i(t)=(\Delta f/T)t+[(f_2+f_1)/2]\equiv(\Delta f/T)t+f_c. \qquad (2)$$

In Eq. (2), $\Delta f=f_2-f_1$ is the carrier signal modulation

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bandwidth, $f_c = (f_2 + f_1)/2$ is the average carrier frequency, and T is the total sweep period. The form of Eq. (2) suggests that the instantaneous frequency f_i is a function of time and, therefore, cannot be formally associated with the concept of frequency in the Fourier sense; in the latter, f and t are defined as independent variables in the context of Eqs. (1). The sweep rate S is defined as the time derivative of the frequency-like quantity $f_i(t)$:

$$S = df_i(t)/dt = \Delta f/T. \qquad (3a)$$

S is independent of time, a general feature of linear sweep modulation systems resulting directly from the linear dependence on time of Eq. (2). Assuming the excitation function to be a cosinusoidal carrier wave,[10–12] the time delay photothermal system input will be given by

$$X(t) = A(t) \cos [\phi_i(t)], \qquad (3b)$$

where $A(t)$ is the amplitude modulation (AM) function, usually chosen to be constant, and $\phi_i(t)$ is the instantaneous phase of the input

$$\begin{aligned}\phi_i(t) &= \int_0^t 2\pi f_i(q)dq + \phi_0 \\ &= 2\pi(\Delta f/2T)t^2 + 2\pi f_c t + \phi_0 \\ &= (\pi S)t^2 + \omega_c t + \phi_0, \qquad (4)\end{aligned}$$

where $\phi_0 \equiv \phi_i(0)$ is the input phase at $t = 0$. The experimental conditions chosen for photothermal measurements in Part II of this work are $\phi_0 = 0$, $f_1 = 0$, and $\phi_i(T + \delta t) = \phi_i(\delta t)$ for $\delta t \to 0$, and A = constant. These correspond to a linear sawtooth frequency sweep between dc and $f_2 = f_{max}$ with multiple repetitions of the sweep process every period T. Under these conditions, Eq. (3) can be conveniently written in the form[10]

$$X(t) = X_+(t) + X_-(t); \quad 0 < t < T, \qquad (5)$$

where

$$X_+(t) = (A/2) \exp [i(\pi S t^2 + \omega_c t)] \qquad (6a)$$

and

$$X_-(t) = (A/2) \exp [-i(\pi S t^2 + \omega_c t)]. \qquad (6b)$$

It can be shown[10] that the frequency swept signal component functions $\exp[\pm i(\pi S t^2)]$ in Eqs. (6) can be expanded in conventional Fourier series

$$\exp [\pm i(\pi S t^2)] = \sum_{N=-\infty}^{\infty} C_N^{\pm} \exp (iN\omega_0 t) \qquad (7)$$

with

$$\begin{aligned}C_N^{\pm} &= (1/T)(1/2S)^{1/2} \exp [\mp i(N\omega_0)^2/4\pi S] \\ &\quad \times [C(\omega_{max}) \pm iS(\omega_{max})], \qquad (8)\end{aligned}$$

where $C(x)$, $S(x)$ are the Fresnel cosine and sine integrals, respectively,[13] and $\omega_0 \equiv 2\pi/T$. The importance of the Fourier expansions, Eqs. (7) and (8), lies in the ability to determine analytically the frequency content of the swept wave along with the weighting factors $C_N^{\pm}$, which ultimately give the frequency bandwidth of the Fourier transform of the input signal.

The signal generated using the linearly swept wave $X(t)$ of Eq. (5) is a special case of a more general class of phase-angle modulated systems.[14] In this context the time delay photothermal excitation can be regarded as similar to a frequency modulated (FM) wave with the time integral of the applied swept wave

$$m(t) = 2\pi \int_0^t \left(\frac{\Delta f}{T}\right) q \, dq$$

in Eq. (4) acting as the FM wave modulating the baseband signal f_c. In either case, the instantaneous frequency $f_i(t)$ is the sum of the time-varying component $m(t)$ and the unmodulated carrier wave f_c.

B. Time delay domain dynamic system response

The photothermal wave/photoacoustic information, which is contained in the output signal response of the system, can be recovered using correlation and spectral analysis techniques.[15] The frequency swept input signal can be expressed analytically as a complex function of time, Eqs. (5) and (6). The time-dependent signals obtained via correlation and convolution analysis carry information related to the delay of the output signal with respect to the input. It is, therefore, customary[10,14] to use the variable τ instead of t for time and refer to the signal temporal evolution process in the time delay domain. In the time domain the complex output of the photothermal system $Y(t)$ is given as the convolution integral between the complex FM input signal and the unit impulse response function $h(t)$ of the system, provided the latter is assumed to be time invariant

$$Y(t) = \int_0^{\infty} h(\tau) X(t - \tau) d\tau \quad [V] \qquad (9a)$$

$$\equiv h(t)^* X(t). \qquad (9b)$$

Equation (9a) assumes a causal relationship between input and system response, so that the lower limit of the integration is set to zero, rather than $-\infty$. The three time delay domain functions of importance to time delay photothermal wave spectroscopy are (i) the *autocorrelation function* of the input

$$R_{xx}(\tau) = \lim_{T \to \infty} \frac{1}{T} \int_0^T X^*(t) X(t + \tau) dt \quad [V^2]. \qquad (10)$$

This function provides a measure of the similarity between the input signal $X(t)$ and its own time-delayed version $X(t + \tau)$; (ii) the *cross-correlation* function between input and output

$$R_{xy}(\tau) = \lim_{T \to \infty} \frac{1}{T} \int_0^T X^*(t) Y(t + \tau) dt \quad [V^2]. \qquad (11)$$

This function provides a measure of the similarity between the input signal $X(t)$ and a time-delayed version of the output signal $Y(t + \tau)$; and (iii) the *unit impulse response function* of the system $h(\tau)$. This function will be most conveniently defined later on in terms of frequency domain parameters of the system. In Eqs. (10) and (11) starred quantities indicate complex conjugation. Combination of Eqs. (9a), (10), and (11) yields the following important theorem:

THEOREM: The cross-correlation function of an FM system with complex stationary input and output signals is equal to the convolution of the impulse response function with the input autocorrelation function.

PROOF: From Eqs. (9a) and (11) we have

$$R_{xy}(\tau) = \lim_{T\to\infty} \frac{1}{T}\int_0^T X^*(t)\int_0^\infty h(s)X(t+\tau-s)ds\,dt$$
$$= \int_0^\infty h(s) \lim_{T\to\infty} \frac{1}{T}\int_0^T X^*(t)X(t+\tau-s)dt\,ds$$

and, from Eq. (10)

$$R_{xy}(\tau) = \int_0^\infty h(s)R_{xx}(\tau-s)ds$$
$$= h(\tau)*R_{xx}(\tau). \quad (12)$$

Once the autocorrelation function of the input is determined, the cross-correlation function can be calculated immediately from the known impulse response of the photothermal wave system. For the specific excitation function of Eq. (5) the definition (10) yields the linear superposition

$$R_{xx}(\tau) = R_{x_+x_+}(\tau) + R_{x_-x_-}(\tau) + R_{x_+x_-}(\tau) + R_{x_-x_+}(\tau). \quad (13)$$

The sum of the cross terms can be calculated from Eqs. (6a), (6b), and (10). Biering and Pedersen[16] have shown that for sweeps which include the dc level

$$R_{x_+x_-}(\tau) + R_{x_-x_+}(\tau) \cong \left|\frac{1}{8\sqrt{(\Delta f)T}}\right| \quad (14)$$

and, therefore, the cross-term contribution to Eq. (13) can be reduced to any desired level by increasing the sweep period T. When the sweep does not involve the dc level and very low frequencies, the sum of the cross term is strongly reduced, so that in all cases of experimental interest we can write instead of Eq. (12)

$$R_{xy}(\tau) \cong h(\tau)*[R_{x_+x_+}(\tau) + R_{x_-x_-}(\tau)], \quad (15)$$

with[16]

$$R_{x_+x_+}(\tau) = \frac{1}{4}\left(\frac{T-|\tau|}{T}\right)\left(\frac{e^{2\pi i S\tau(T-|\tau|)}-1}{2i\pi S\tau(T-|\tau|)}\right) \times \exp\left[i\pi\tau\left(2f_c + S|\tau|\right)\right] \quad (16a)$$

and

$$R_{x_-x_-}(\tau) = \frac{1}{4}\left(\frac{T-|\tau|}{T}\right)\left(\frac{e^{-2\pi i S\tau(T-|\tau|)}-1}{-2\pi i S\tau(T-|\tau|)}\right) \times \exp\left[-i\pi\tau\left(2f_c + S|\tau|\right)\right]. \quad (16b)$$

C. Frequency domain spectral functions

In the frequency domain the important primary functions which characterize the photothermal wave system excited by the linear frequency sweep $X(t)$ are the two-sided spectral density functions,[15] i.e., (i) the *autospectrum* of $X(t)$

$$S_{xx}(f) = \int_{-\infty}^{\infty} R_{xx}(\tau)e^{-2\pi i f\tau}d\tau \quad [V^2/\text{Hz}]. \quad (17)$$

This integral is also called the *power spectral density function*; together with its Fourier transform, the pair constitutes the Wiener–Khitchine relations.[17] The autospectrum represents physically the frequency density of the average power in the sweep FM signal $X(t)$, evaluated at the average carrier frequency f_c, assuming the photothermal wave system behaves as a narrow-band or a low-pass filter; and (ii) the *cross-spectrum* between $X(t)$ and $Y(t)$:

$$S_{xy}(f) = \int_{-\infty}^{\infty} R_{xy}(\tau)e^{-2\pi i f\tau}d\tau \quad [V^2/\text{Hz}]. \quad (18)$$

This equation provides a measure of the frequency interrelationship between the sweep FM input signal $X(t)$ and the output signal $Y(t)$. From the defining Eqs. (17) and (18) a number of experimentally useful functions can be defined, such as the *one-sided autospectral density*

$$G_{xx}(f) = \begin{cases} 2S_{xx}(f); & f \geqslant 0 \\ 0; & f < 0 \end{cases} \quad (19a)$$
$$= 4\int_0^\infty R_{xx}(\tau)\cos(2\pi f\tau)d\tau \quad [V^2/\text{Hz}] \quad (19b)$$

and the *one-sided cross-spectral density*

$$G_{xy}(f) = \begin{cases} 2S_{xy}(f); & f \geqslant 0 \\ 0; & f < 0 \end{cases} \quad (20a)$$
$$= 4\int_0^\infty R_{xy}(\tau)\cos(2\pi f\tau)d\tau \quad [V^2/\text{Hz}]. \quad (20b)$$

Equations (19) and (20) can be further used to define the *cross spectrum* $G_{xy}(f)$ in terms of its real and imaginary parts

$$G_{xy}(f) = 2\int_{-\infty}^{\infty} R_{xy}(\tau)e^{-2\pi i f\tau}d\tau$$
$$\equiv C_{xy}(f) - iQ_{xy}(f). \quad (21)$$

The real part

$$C_{xy}(f) = 2\int_{-\infty}^{\infty} R_{xy}(\tau)\cos(2\pi f\tau)d\tau \quad (22)$$

is called the *cospectrum*, while the imaginary part

$$Q_{xy}(f) = 2\int_{-\infty}^{\infty} R_{xy}(\tau)\sin(2\pi f\tau)d\tau \quad (23)$$

is called the *quadspectrum*. In polar coordinate notation the magnitude and phase of the cross spectrum are given by

$$G_{xy}(f) = [C^2_{xy}(f) + Q^2_{xy}(f)]^{1/2} \quad [V^2/\text{Hz}] \quad (24)$$

and

$$\theta_{xy}(f) = \tan^{-1}[Q_{xy}(f)/C_{xy}(f)] \quad [\text{rad}]. \quad (25)$$

Physically, the cross-spectral magnitude is a measure of the frequency content of the causal response of a system induced by an input $X(t)$, while the phase carries information about the propagation time between input and output, which manifests itself as a linear phase shift. The *coherence function* is defined as

$$\gamma^2_{xy}(f) = \frac{|G_{xy}(f)|^2}{G_{xx}(f)G_{yy}(f)}; \quad 0 \leqslant \gamma^2_{xy}(f) \leqslant 1 \quad (26)$$

and constitutes a powerful indicator of the strength of the relation between the input signal and output response of the system. In Eq. (26), $G_{yy}(f)$ can be determined from the output autocorrelation function $R_{yy}(\tau)$ in a manner analogous to the one used for the determination of $G_{xx}(f)$. A very useful related function is the *coherent output power spectrum*

$$\gamma_{xy}^2(f)G_{yy}(f) = |G_{xy}(f)|^2/G_{xx}(f). \tag{27}$$

This function is a measure of the output power spectrum caused by the input excitation in the presence of noncoherent noise. The ability of the system to respond to the input signal frequency spectrum is determined by the complex *transfer function* or frequency response function $H(f)$ defined by

$$H(f) = G_{xy}(f)/G_{xx}(f) = S_{xy}(f)/S_{xx}(f). \tag{28}$$

Writing $H(f)$ in polar coordinate form

$$H(f) = |H(f)|e^{-i\phi(f)}, \tag{29}$$

it can be shown from Eqs. (24), (25), and (29) that

$$|H(f)| = |G_{xy}(f)|/G_{xx}(f) \tag{30}$$

and

$$\phi(f) = \theta_{xy}(f). \tag{31}$$

The transfer function $H(f)$ and the unit impulse response function $h(\tau)$ are Fourier transforms of each other[15]

$$H(f) = \int_{-\infty}^{\infty} h(\tau)e^{-2\pi i f\tau}d\tau \tag{32}$$

and

$$h(\tau) = \int_{-\infty}^{\infty} h(f)e^{2\pi i f\tau}df. \tag{33}$$

II. DISCUSSION

Substituting Eq. (28) into (33) gives

$$h(\tau) = \int_{-\infty}^{\infty} \left(\frac{S_{xy}(f)}{S_{xx}(f)}\right) e^{2\pi i f\tau}df. \tag{34}$$

Equation (34) can be used as the operational definition of the time delay domain unit impulse response. Comparison of Eq. (34) to the cross-correlation function given by the Fourier transform of $S_{xy}(f)$ in Eq. (18)

$$R_{xy}(\tau) = \int_{-\infty}^{\infty} S_{xy}(f)e^{2\pi i f\tau}df \tag{35}$$

shows clearly that, unlike a system randomly excited by white noise[1,3] the cross-correlation function in a FM photothermal system is equal to the unit impulse response of the system *only* in the special event of a uniform autospectrum of the input $X(t)$, i.e., only if $S_{xx}(f) = 1$. In the case of a linear frequency sweep it can be shown[16] that the necessary and sufficient condition for the uniformity of the input autospectrum is

$$|(\Delta f)T| \gg 1. \tag{36}$$

In practice, the physical requirement imposed on the photothermal system is

$$|\tau| \ll T \text{ for any } |\tau| < |1/\Delta f|, \tag{37}$$

i.e., the total sweep time must be long compared to the time delay response of the system. The powerful implication of Eqs. (34)–(37) is that, under the (experimentally easily realizable) conditions (36) or (37), a measurement of the cross correlation $R_{xy}(\tau)$ will be equal to a high degree of approximation to the unit impulse response $h(\tau)$ of the system. In Part III of this work it will be shown that time delay photothermal wave spectroscopy exhibits substantially superior input autospectral flatness to the PRBS method. This important fact renders our FM time delay technique an optimal candidate for photoacoustic and photothermal impulse response measurements.

The complex domain nature of the theoretical input and output signals in FM time delay photoacoustic and photothermal wave spectroscopy leads naturally to magnitude and phase channels of the pertinent frequency domain functions, such as the cross spectrum, Eqs. (24) and (25), and the transfer function, Eqs. (30) and (31). The intermediate nature of the technique between time and frequency-dependent descriptions implies, however, that the time delay domain functions will also be expressed as complex quantities, Eqs. (10), (11), (16a), and (16b). The actual physical system output is, of course, going to be real and based on the impulse response. It can be shown[18] that the time delay domain representation of the correlation functions of a transmission system is the real part of a complex vector quantity, whose imaginary part is the Hilbert transform of the real part. A function $G(t)$ and its Hilbert transform $\hat{g}(t)$ constitute the Hilbert transform pair

$$G(t) = -\frac{1}{\pi} P \int_{-\infty}^{\infty} \frac{\hat{g}(t_0)}{t - t_0} dt_0 \tag{38a}$$

and

$$\hat{g}(t) = \frac{1}{\pi} P \int_{-\infty}^{\infty} \frac{G(t_0)}{t - t_0} dt_0, \tag{38b}$$

where the symbol P indicates the Cauchy principal value of the improper integral whose integrand has a singularity at $t = t_0$. The real part of the complex vector is associated with the system response to an excitation by a Dirac delta function type of input defined as the limit

$$\delta(t) = \lim_{A\to\infty} (\sin At/\pi t). \tag{39}$$

The imaginary part, on the other hand, is the system response to a special excitation signal defined as the limit

$$D(t) = \lim_{A\to\infty} [(\cos At - 1)/\pi t] \tag{40}$$

and called a doublet operator by Heyser,[19] drawing from its analogy to a physical doublet, as defined in Classical Electrodynamics.[20] The doublet response is the Hilbert transform of the unit impulse response $h(\tau)$ of the system. Its Fourier transform is identical to that of the unit impulse response $H(f)$ phase shifted by $\pi/2$. The above theoretical considerations guarantee that the FM time delay photothermal wave signal generated using a cw light source and swept wave modulation is equivalent to a system response to a pulsed light source with a short pulse duration resembling a Dirac delta function excitation on the time scale of the experiment. The major attractions of this signal equivalence are (i) the truly nondestructive nature of the swept wave excitation, compared to the unavoidable sample perturbation common with pulsed laser systems; and (ii) the simplicity of signal interpretation available through, and only limited by, the Green's function formulation and knowledge of any given photothermal wave system (Part II).

III. CONCLUSIONS

Time delay photothermal wave spectroscopy has been shown to rely on the determination of the pertinent correlation and spectral functions of the photothermal system. Expressions for the FM linear frequency sweep as the input signal have been presented and incorporated into all the identified essential system functions. The photothermal system has been modeled as a single input/single output transmission system or, more appropriately, a bandpass filter. The advantage of this technique over other excitations is the accurate determination of the impulse response function, owing to the superior dynamic range properties inherent in this mode of measurement.

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