

Experimental evidence of second harmonic photoacoustic signal generation in metals

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The capability of photoacoustic (PA) spectroscopy for the detection of the second harmonic thermal waves on metal surfaces is investigated. Expressions for the first and second harmonic amplitude and phase PA spectra are derived from the one-dimensional nonlinear heat conduction equation using stepwise successive approximation method. First and second harmonic amplitude and phase PA spectra of nickel sample are measured in a heat reflection PA configuration. PA amplitude intensity dependence on excitation intensity exhibit characteristic behavior, it has linear dependence in the case of first harmonic and square dependence in the case of second. Experimental data were in excellent agreement with theoretical calculations. Modulation frequency dependence of amplitude and phase provided sufficient data for the thermal properties evaluation from PA measurements.

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1. Introduction

Optical interactions with solids resulting in generation of heat comes under the general heading of photothermal phenomena, and the experimental methods utilizing such interactions are known as photoacoustic and photothermal techniques. In recent years these techniques have proved to be valuable tools for characterization of thermal properties of solids. The photoacoustic (PA) spectroscopy has been demonstrated by several groups to be simple and reliable technique for measuring the thermal diffusivity, conductivity and effusivity of materials as diverse as glass, semiconductors, polymers, intact plant leaves and food [1-11]. These measurements can be made at fixed incident light wavelength by monitoring either the magnitude or phase of the PA signal as a function of modulation frequency. Recently, theoretical and experimental studies of photoacoustic and photothermal effects in anisotropic and inhomogeneous materials have been also successfully performed [12-15].

In its simplest form photoacoustic data can be obtained by illuminating a sample with the periodic light at appropriate wavelength and monitoring pressure changes as the generated heat diffuses to the surface and surrounding gas in the measurement cell. The sample to be studied is placed inside a specially designed acoustically sealed cell containing air (or other gas transparent to the incoming radiation) and a sensitive microphone. The sample is then illuminated with light, usually monochromatic, which enters the photoacoustic cell through an appropriate window. If the sample within the cell absorbs any of the incoming radiation, then some energy levels within the sample have been excited. These de-excite (almost instantaneously at room temperature)

generally by a nonradiative or heat-producing mechanism. The periodic excitation of the sample by the intensity-modulated light results in a periodic heat flow from the sample to the surrounding gas, which in turn produces small but detectable changes in the gas pressure in the cell, changes that are sensed by the microphone.

Nonlinear photothermal effects become apparent when photo-induced thermal waves propagate through media where thermophysical parameters depend on the temperature. These effects are manifested as 2nd harmonic photothermal signals and could be important for the future improvement of photothermal diagnostic capabilities, especially in the photothermal microscopy where the spatial resolution can be enhanced utilizing higher harmonics of thermal waves. The aim of this paper is to investigate potential of photoacoustic technique for the detection of second harmonics of thermal waves and thermal properties investigations.

2. Theory

Let us consider an isotropic homogenous semi-infinite solid which has arbitrary values of temperature-dependent thermal conductivity $k(T)$ and heat capacity $C(T) = \rho c_p$, where ρ denote density of solid and c_p is the heat capacity per unit mass at constant pressure. Let us also assume that the surface of solid is heated by a periodically modulated light beam, uniformly, so that one dimensional mathematical treatment is adequate. The geometry of the discussed problem is schematically presented in Fig. 1.

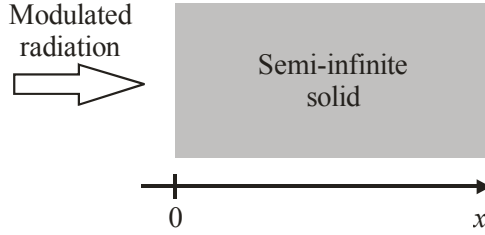


Fig. 1. A semi-infinite solid illuminated uniformly with a modulated flux of radiation.

To describe generation of photoacoustic signals in the gas chamber adjacent to solid surface it is necessary to first calculate temperature variations at the surface induced by optical heating. We start calculation from the one-dimensional form of the heat conduction equation in a medium with non-constant thermophysical parameters [16]:

$$C(T) \frac{\partial T(x, t)}{\partial t} - \frac{\partial}{\partial x} \left[k(T) \frac{\partial T(x, t)}{\partial x} \right] = 0, \quad (1)$$

with boundary conditions describing the continuity of heat flux and temperature at surface ($x=0$):

$$\begin{aligned} -k(T) \frac{\partial T(x, t)}{\partial x} \Big|_{x=0}^{+0} &= \text{Re}[I_0 \exp(i\omega t)], \\ T(x, t) \Big|_{x=0}^{+0} &= 0, \end{aligned} \quad (2)$$

where $i = (-1)^{1/2}$.

External heating initiates an increase in temperature T_1 relative to its initial value T_0 , $T = T_1 + T_0$. For small temperature variations, regularly encountered in photothermal experiments, we may suppose that the thermal parameters of the sample are linear temperature dependent:

$$\begin{aligned} C(T) &\sim C(T_0) + \left[\frac{\partial C}{\partial T}(T_0) \right] \cdot T_1 = C_0(1 + \delta_1 T_1), \text{ where } \delta_1 = \frac{1}{C_0} \frac{\partial C}{\partial T}(T_0) \text{ and} \\ k(T) &\sim k(T_0) + \left[\frac{\partial k}{\partial T}(T_0) \right] \cdot T_1 = k_0(1 + \delta_1 T_1), \text{ where } \delta_1 = \frac{1}{k_0} \frac{\partial k}{\partial T}(T_0) \end{aligned} \quad (3)$$

The solution of the problem of physical interest for applications in photoacoustic and photothermal techniques is the one related to the time-dependant component, so the above defined problem can be solved in terms of two temperature fields, $T_\omega(x, t)$ and $T_{2\omega}(x, t)$, one oscillating at the same frequency as incidence radiation (first harmonic thermal waves) and the second oscillating at doubled frequency (second harmonic thermal waves):

$$\begin{aligned} T_\omega(x, t) &= \text{Re}[\Theta_\omega(x) \exp(i\omega t)], \\ T_{2\omega}(x, t) &= \text{Re}[\Theta_{2\omega}(x) \exp(2i\omega t)]. \end{aligned} \quad (4)$$

By applying the stepwise successive approximation method, described in detail for this type of problem in Ref. 17, we obtain two sets of ordinary differential equations with supplementary boundary conditions to describe behavior of thermal waves. First harmonic thermal waves are calculated from:

$$\begin{aligned} \left[\frac{d^2}{dx^2} - \sigma^2 \right] \Theta_\omega(x) &= 0, \\ -k_0 \frac{d\Theta_\omega(x)}{dx} \Big|_{x=0} &= I_0, \quad \lim_{x \rightarrow \infty} \Theta_\omega(x) = 0, \end{aligned} \quad (5)$$

where $\sigma = (i\omega C_0/k_0)^{1/2}$ is the complex wavenumber of the thermal wave. Then in succession the second harmonic thermal waves can be calculated from:

$$\begin{aligned} \left(\frac{d^2}{dx^2} - 2\sigma^2 \right) \Theta_{2\omega}(x) &= -\frac{1}{4} \left(\delta_2 \frac{d^2}{dx^2} - 2\delta_1 \sigma^2 \right) \Theta_\omega^2(x), \\ k_0 \frac{d}{dx} \left(\Theta_{2\omega}(x) + \frac{1}{4} \delta_2 \Theta_\omega^2(x) \right) \Big|_{x=0} &= 0, \\ \lim_{x \rightarrow \infty} \Theta_{2\omega}(x) &= 0. \end{aligned}$$

Evaluation of previous equations leads to the following solution:

$$\begin{aligned} \Theta_\omega(x) &= \frac{I_0}{k_0} \frac{\exp(-\sigma x)}{\sigma}, \\ \Theta_{2\omega}(x) &= \left(\frac{I_0}{k_0} \right)^2 \frac{1}{2\sqrt{2}\sigma^2} \left[(\delta_2 - \delta_1) \exp(-\sqrt{2}\sigma x) + \frac{1}{\sqrt{2}} (\delta_2 - 2\delta_1) \exp(-2\sigma x) \right]. \end{aligned} \quad (6)$$

Finally, photoacoustic signal originated from illuminated surface of the sample can be derived from calculated temperature variations at $x=0$ using Eq. (6) and well known Rosencwaig-Gersho equation [18] For the first harmonic of photoacoustic signal we obtain:

$$S_\omega = K_{cell} \frac{\Theta_\omega(x=0)}{\sigma_g(\omega)} = K_{cell} \frac{I_0}{k_0 \sigma \sigma_g(\omega)}, \quad (7)$$

where $K_{cell} = \kappa P_0 / (T_0 l_g)$ denotes characteristic coefficient of the photoacoustic cell with P_0 representing pressure of the gas in the cell, T_0 – ambient temperature, l_g – length of gas chamber, κ – adiabatic constant and σ_g – complex thermal wavenumber of the gas [4,18].

In the same way, second harmonic photoacoustic signal can be described with:

$$S_{2\omega} = K_{cell} \frac{\Theta_{2\omega}(x=0)}{\sigma_g(2\omega)} = K_{cell} \frac{I_0^2}{4k_0^2 \sigma^2 \sigma_g(2\omega)} \left[\sqrt{2}(\delta_2 - \delta_1) + (\delta_2 - 2\delta_1) \right]. \quad (8)$$

From Eq. (7) we find amplitude A_ω and phase ϕ_ω of the PA signal first harmonic:

$$A_{\omega} = K_{cell} \frac{\sqrt{D_0 D_g}}{4k_0} \frac{I_0}{\omega}, \quad (9)$$

$$\phi_{\omega} = \frac{\pi}{2} [\text{rad}] = 90^\circ = \text{const.}$$

Here D_0 and D_g stand for coefficients of thermal diffusivity of sample and gas, respectively, ($D = k / C$).

From Eq. (3) one can find second harmonic PA signal amplitude and phase as:

$$A_{2\omega} = K_{cell} \frac{D_0 \sqrt{2D_g}}{64k_0^2} \left| \sqrt{2}(\delta_2 - \delta_1) - (\delta_2 - 2\delta_1) \right| \frac{I_0^2}{\sqrt{\omega^3}}, \quad (10)$$

$$\phi_{2\omega} = \begin{cases} \frac{3\pi}{4} [\text{rad}] = 135^\circ & \text{for } \sqrt{2}(\delta_2 - \delta_1) - (\delta_2 - 2\delta_1) > 0, \\ -\frac{\pi}{4} [\text{rad}] = -45^\circ & \text{for } \sqrt{2}(\delta_2 - \delta_1) - (\delta_2 - 2\delta_1) < 0. \end{cases}$$

The obtained expressions for the first and second harmonic PA signal, Eqs. (9) and (10), clearly show their dependence on optical excitation intensity and modulation frequency. Result for the case of first harmonic is known and expected [2-8]. Phase lag is constant having value of $\pi/2$ [rad]. Amplitude is linear function of optical excitation intensity I_0 and inversely proportional to angular modulation frequency ω . Second harmonic phase lag is also constant; it is $3\pi/4$ or $-\pi/4$ [rad] depending on the values of nonlinear coefficients δ_1 and δ_2 . Amplitude is squared function optical excitation intensity and has $\omega^{-3/2}$ dependence on modulation frequency.

3. Experimental

To investigate capability of photoacoustic spectroscopy for the detection of second harmonic thermal waves we have performed measurements of thin nickel samples in a heat reflection configuration. Amplitude and phase of the both first and the second harmonics of PA signals are measured in a frequency range from 65 to 250 Hz.

The experimental setup is shown on Fig. 2. For excitation source we have used continuous wave Nd:YAG laser ("Viasho") operating at 532 nm that is capable to provide optical power up to 200 mW. The output power is selected by the laser driver and monitored using power meter ("Viasho"). The laser beam is modulated by an optical chopper ("Stanford Research SR540") and directed in a custom made photoacoustic cell [4]. The PA cell is designed for the detection in so called heat reflection configuration, i.e. for the detection of pressure changes in the air compartment mounted on the excited sample surface. Electret microphone (Brüel&Kjær) is used as pressure sensor. PA signals are measured using low-noise preamplifier and lock-in amplifier ("Stanford Research SR850").

We performed measurements in the range of 10 to 120 mW of the laser excitations for two modulation frequencies, 70 and 220 Hz. The results for the first

harmonic are presented on Fig. 3, and for the second harmonic on Fig. 4. One can clearly see that the experimental spectra firmly follow theoretical predictions. For both modulation frequencies amplitude of the first harmonic linearly increases with laser power intensity, while the second harmonic amplitude increases with square of laser intensity.

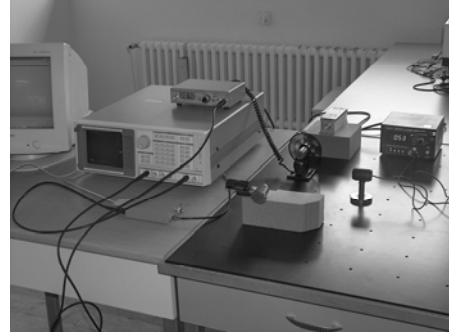


Fig. 2. Photoacoustic experimental setup.

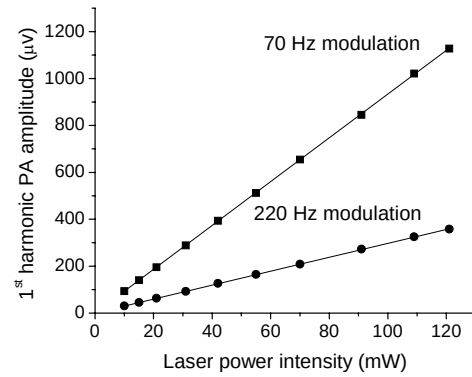


Fig. 3. First harmonic PA amplitude intensity dependence on the excitation intensity measured on modulation frequencies 70 Hz (squares) and 220 Hz (circles). The line represents linear regression.

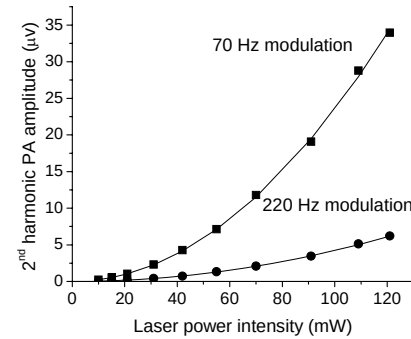


Fig. 4. Second harmonic PA amplitude intensity dependence on the excitation intensity measured on modulation frequencies 70 Hz (squares) and 220 Hz (circles). The line represents quadratic regression.

Dependence of PA signal on modulation frequency is shown on Figs. 5 to 8. PA phase spectra of the first and the second harmonic are presented on Fig. 5 and Fig. 6, respectively. Scatters stand for the experimental data and full lines for the calculated spectra. Theoretical consideration for the case of heat reflection PA configuration predicts constant phase, 90° in the case of first harmonic and -45° in the case of the second, Eqs. (4) and (5). It is evident that the experimental results are in very good agreement with the theory. PA amplitude spectra of the first and the second harmonic are presented on Fig. 7 and Fig. 8, respectively. Their dependence on modulation frequency is ω^{-1} for the first harmonic amplitude and $\omega^{-3/2}$ for the second, just as stated in Eqs. (4) and (5). The intensity of the second harmonic amplitude is considerably lower compared to one of the first harmonic. These very low values are the biggest experimental problem for the application of second harmonics PA spectroscopy. The problem is even more pronounced on a high modulation frequencies since the second harmonic PA amplitude decay faster compared to the first harmonic as can be seen on Figs. 7 and 8. This could also be a problem with measurements in a heat-transmission PA configuration where PA amplitude has lower values compared to the heat-reflection due to thermal wave attenuation over the sample depth. However, application of a good low-noise preamplifiers and pressure sensors should help to overcome the low-signal problems.

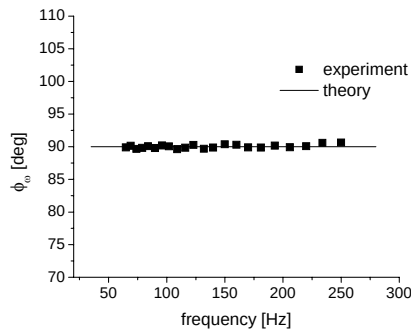


Fig. 5. PA first harmonic phase dependence on modulation frequency (scatters represent measured spectra and full line calculated).

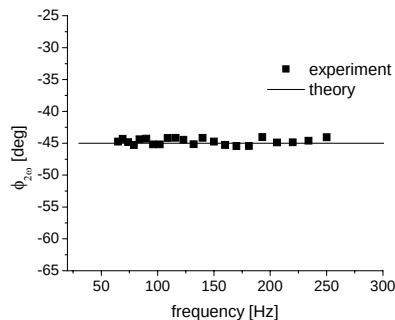


Fig. 6. PA second harmonic phase dependence on modulation frequency (scatters represent measured spectra and full line calculated).

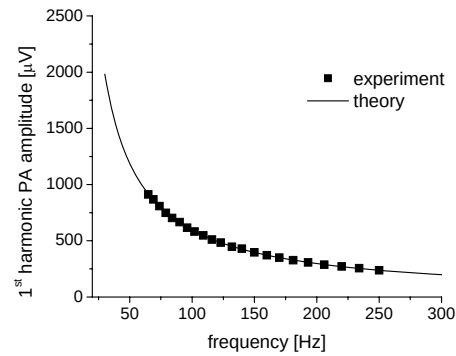


Fig. 7. PA first harmonic amplitude dependence on modulation frequency (scatters represent measured spectra and full line calculated).

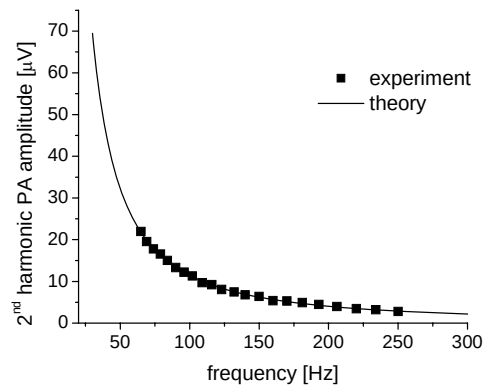


Fig. 8. PA second harmonic amplitude dependence on modulation frequency (scatters represent measured spectra and full line calculated).

To test the applicability of the second harmonics PA spectroscopy we have used measured experimental amplitude spectra to calculate coefficients of thermal conductivity and heat capacity of the investigated nickel sample. By simultaneously fitting of both the first and the second harmonic amplitude to the theoretical expressions Eqs. (4) and (5) we have obtained values of thermal coefficients that are in a very good agreement with the previously published data [20]. The obtained results are given in Table 1.

Table 1. Values of coefficients of thermal conductivity and heat capacity determined from PA first and second harmonics amplitude spectra compared to the values published in literature.

Ni	k [W m ⁻¹ K ⁻¹]	ρc [$\times 10^{-6}$ J m ⁻³ K ⁻¹]
From experiment	92.3	3.92
Literature [20]	91.0	3.95

4. Conclusions

Photoacoustic spectroscopy measurements in a heat-reflection configuration have the capability to detect second harmonic thermal waves generated on a metal surface by a modulated laser action. Experimental results validate theoretical calculations based on the application of stepwise successive approximation method for derivation of nonlinear thermal conduction equation. Quality of measurements provides for the opportunity to use this technique for characterization of thermal properties of solids as a stand alone application or as a complementary tool to existing PA techniques.

Assessment of obtained results and discussions given previously in the literature [17,19] brought us to the following conclusions: (i) 2nd harmonic PA signals should be detectable in a nonlinear materials when sufficient optical power is introduced and/or when highly sensitive detection system is used for measurements; (ii) 2nd harmonic PA signals are considerably lesser compared to the first; (iii) 2nd harmonic PA amplitude is squared function optical excitation intensity and has $\omega^{-3/2}$ dependence on modulation frequency and (iv) stepwise successive approximation method for solution of nonlinear heat diffusion problems provides good theoretical description when applied for photoacoustic and photothermal investigations.

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