

A prelude to the multibeam photoacoustics

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Abstract

The report focuses on the introduction and validation of photoacoustics measurements in the presence of two simultaneous probing beams. The experiments, performed for three model systems: a perfect absorber - carbon black membrane, a multilayer system – acrylic paint-covered copper plate, and luminescent sample – ruby, were aimed for comparative analyses of frequency domain photoacoustic responses to a single probing beam (classical approach) and two probing beams (of different wavelength). A modulation frequency shift criterion, allowing for the simultaneous acquisition of two independent signals, was recognized. Any synergistic or cross effects of sample dual beam excitation on the photoacoustic signal generation (impacts of the beams intensities or modulation frequency effects) were not observed. The multibeam photoacoustics data appears to be (at least) equivalent to classically acquired results for stationary systems. It is considered, that the multibeam approach will broaden the applicability of the photothermal methods to the time-dependent systems, where the evolutions of distinct absorption bands is of special interest.

Keywords: photoacoustics; photothermal techniques; thermal characterization; mass transport; spectroscopy; multibeam excitation.

1. Introduction

Due to a specific relation between material thermal and optical properties and the measurable sample response to a modulated probing light, photoacoustics (along with other photothermal techniques, like PTR or PTS) found numerous applications in applied, biomedical and environmental sciences [1]. Typically, photoacoustic (PA) measurements are performed in the wavelength domain (varying wavelength λ , constant modulation frequency f ; hereafter: PhotoAcoustic Spectroscopy - PAS), or in the modulation frequency domain (constant λ , varying f ; hereafter PhotoAcoustic Depth-Profiling: PADP); depending on a sample, the two modalities can provide (under a certain theoretical frameworks) a direct access to a wide range of characteristics. These include: spectral properties (generally, the PA response proportional

to the product of sample non-radiative deactivation efficiency and light absorption coefficient), radiative quantum efficiency, thermal diffusivity/conductivity (or estimation of layer thicknesses in layered sample of known diffusivity), non-radiative relaxation/carrier recombination times, (time-dependent) pigment distribution within a sample, efficiency of photosynthesis and many more [2–4]. In some cases, PA studies involve two irradiation sources; for example: 1) the determination of photosynthesis efficiency is based upon two separate measurements, that is PADP in the presence and in the absence of non-modulated, photosynthesis-saturating white light [5]; 2) the determination of quantum efficiency of luminescent samples based on PA phase analyses, with two separate PADP experiments with distinct *pumping* beams, allowing to eliminate the effects of saturation and heat flow, as shown by Quimby and Yen [6]; 3) measurement of the energy-resolved distribution of electron traps involves absorption studies by monochromatic single modulated beam in the presence of wavelength-scanned continuous, non-modulated light (method referred to as Reversed Dual-Beam PAS) [7].

The above mentioned examples of two-beams (or dual-beam) PA involve situations, where, in fact, only one beam (at a time) can be considered as the probing beam; even in case of two simultaneous light sources, a continuous source provide a certain, global change to a system (i.e. saturates specific processes), while the modulated source probes the changed system. According to the author's survey, there are no reports on PADP modality with two (or more) simultaneous probing beams.

The report focuses on introductory and quantitative experimental tests of the f -domain photoacoustics in the presence of two probing beams. Attention is paid to the reproducibility and correspondences between two signals (responses to excitations at distinct wavelengths) recorded separately (one beam at a time), and recorded simultaneously (two beams together). To avoid any ambiguities with literature examples, the method explored here will be referred to as the MultiBeam PhotoAcoustics – MBPA.

The introduction of the MBPA is motivated by the author's recent results in the field of membrane transport studies, where photoacoustics with its depth-profiling feature (precise and non-destructive sample sectioning), appeared to serve as a unique experimental tool, providing insights into membrane transport processes unavailable to conventional modalities in this field of science [8]. The perspectives for MBPA are discussed later on.

2. Materials and methods

The multibeam approach was validated upon three model samples: (*I*) an absorbing system – here, a perfect absorber, carbon black membrane (as delivered by MTEC Photoacoustics), (*II*) a multilayer system – a copper base plate (of thickness of $38 \pm 1 \mu\text{m}$) covered with a red acrylic paint ($30 \pm 1 \mu\text{m}$), and (*III*) a luminescent sample - ruby ($\text{Al}_2\text{O}_3:\text{Cr}^{3+}$). Prior to the PADP/MBPA measurements, the samples were characterized by PAS at modulation frequency of 120 Hz. The results for samples *II* and *III* (both normalized with respect to the carbon black sample) are shown in Fig.1.

The experimental rig for the PAS measurements consisted of a 900 W xenon light source (Newport 66921), grating monochromator with adjacent mechanical chopper (Newport 74125), PAC300 photoacoustic chamber (MTEC Photoacoustics) and SR7265 lock-in amplifier. The MBPA setup consisted of two LED modules developed at CMSD UG and controlled by Siglent 2042X function generator. The modules were equipped with 420 nm and 535 nm Lumileds Luxeons. The scanning beams were routed via Y-type multicore fiber to PAC300 chamber, and the output signal was split into two independent channels with SR7265 unit in each line.

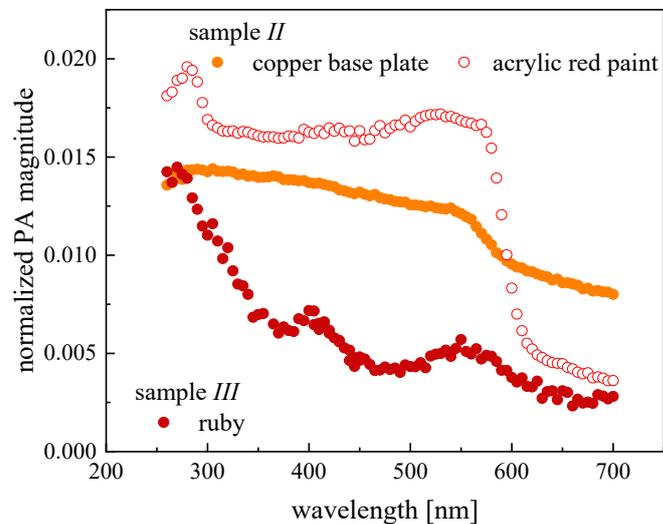


Fig.1 PA spectra of samples *II* and *III*, collected at the modulation frequency of 120 Hz.

3. Results and discussion

The studies aimed to verify the reliability of the f -domain MBPA experiments, in the special case of two simultaneous probing beams of different wavelength. Special attention was paid to answering two crucial questions. I) What are the conditions for the modulation frequencies of

two probing beams, that allow for the simultaneous acquisition of two independent PA signals?
II) For a model systems under consideration, is the sample PA response to double-beam excitation given by a direct sum of two independent (acquired separately) signals, or are there any additional and synergistic/cross effects that affect the response?

The first issue was verified in an experiment involving carbon black (CB) sample (a perfect absorber). It was found, that two PA responses to simultaneous double beam excitations (here 420 and 535 nm) characterized by a distinct modulation frequencies f_1 and f_2 are independent as long, as the modulation frequency shift between the beams, $\Delta f = f_1 - f_2$, exceeds instrumental noise and small frequency oscillations registered by lock-in amplifiers. For the experimental rig used, the magnitude of such oscillations was not larger than ~ 0.2 Hz in the whole frequency range considered (15 Hz to 1 kHz), and for $\Delta f < 0.4$ Hz the acquired PA signals appeared to be unstable. Although the PA responses recorder for Δf beyond the joint (for both channels) frequency hum were generally stable, the frequency shift adopted for the following experiments was set to 2 Hz.

To confront the f -domain MBPA and independent PADPs against each other, a comparative studies for a model CB sample in the f_1 frequency range of 16-325 Hz were performed, with the MBPA frequency shift of $\Delta f = 2$ Hz (in case of PADPs, $\Delta f = 0$). Additionally, the probing beams intensities were adjusted so the PA signals ratio registered was $\sim 10:1$. The results of the experiment are shown in Fig.2a. It can be noticed, that MBPA responses to 420 and 535 nm excitation follow a similar pattern as PADP data. Also, a supplementary MBPA experiment was conducted, where the cumulative PA response to two probing beams (with $\Delta f = 0$) was registered. A comparison between sums of MBPA signals and PADP signals is shown in Fig.2a inset; again, one recognizes similarity between the profiles. Concluding, by the incorporation of a proper frequency shift between two probing beams, it is possible to acquire two independent PA responses to distinct excitation wavelengths at the same time (an equivalence between MBPA and single PADP signals); one does not observe any influence of the beams intensity (at least up to the ratio of 10:1) or modulation frequency shifts ($\Delta f/f_1$, at least up to the ratio of $\sim 1:400$) on MBPA signals. Moreover, under the experimental conditions as described, a PA response to the double beam excitation appears to be given by a direct sum of single contributions (no non-linear or cross-effects during the PA signal generation/detection observed).

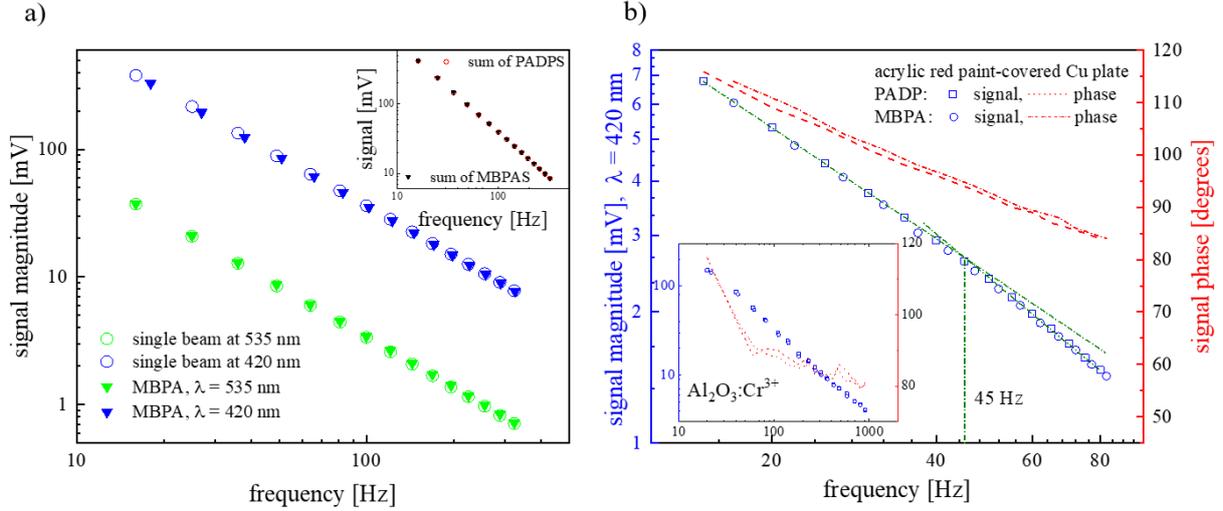


Fig.2 Comparison of PADP and MBPA results for: a) carbon black sample (inset – cumulative MBPA and PADP responses for $\Delta f = 0$), b) a multilayer sample II (main figure, along with a breakthrough frequency of 45 Hz) and a luminescent sample III (inset).

A similar conclusions regarding the PA signal magnitudes can be drawn when considering results for the other samples: a multilayer system - acrylic red paint-covered copper plate (Fig.2b, $f_1 \in (16; 80)$ Hz; for clarity, only PADP/MBPA response to 420 nm beams is shown) and a luminescent sample - $\text{Al}_2\text{O}_3:\text{Cr}^{3+}$ (Fig.2b inset, $f_1 \in (16; 900)$ Hz, signal in μV), where the beams were adjusted to provide the signal ratio of 1:2 and 1:1, respectively. In all the cases considered, the signals phase behaviours for PADP and MBPA were also similar (observable deviations are considered to be within $\pm 1^\circ$ experimental error).

Nowadays, photothermal techniques are considered as a *methods-of-choice* for the characterization of thermal properties of materials. In case of layered samples, thermal diffusivity of a layer, β , can be quantified upon the determination of a characteristic cut-off frequency f_c (Fig.2b – intersection of the linear fits to the low and high frequency data), and is related to the measurable layer thickness l (assumed to be equal to thermal diffusion length) via: $\beta = l^2 \Pi f_c$. In the case of sample II, both PADP and MBPA data revealed f_c to be ~ 46 Hz (which corresponds to the paint layer of thickness of $l = 30 \pm 1 \mu\text{m}$). As such, the acrylic paint thermal diffusivity was found to be $(1.30 \pm 0.04) \cdot 10^{-3} \text{ cm}^2 \text{ s}^{-1}$, which stands in agreement with the literature data [9], and provides an additional proof for the MBPA usability.

4. Conclusions and perspectives

The report focuses on some experimental tests validating PA measurements in the presence of two simultaneous frequency-modulated probing beams. The crucial findings indicate, that the PA responses to two modulated beams (of distinct wavelength) are independent as long, as the

modulation frequency shift between the modulation frequencies of the beams exceeds instrumental instability, and the cumulative signal is given by a simple sum of the two PA contributions (no synergistic or cross effects detected). Other possible factors influencing a single PA response in the two-beams configuration (beams intensity ratio, relative modulation frequency shift) were not recognized.

It is understood, that the perspectives for the MBPA modality are focused on dynamic systems, where simultaneous PA detection/observation of distinct species/pigment/sites is of special interest, rather than the characterization of stationary systems, where a single beam PA suffices. From the author's point of view, MBPA can find application in areas, where even now a single beam PA is considered as a unique experimental tool. This includes:

- transdermal delivery of drugs/membrane transport; as recently shown, in contrast to majority of *methods-of-choice* in the field, PAS and PADP allows to identify physical processes underlying mass permeation [8]. Up to now, only the detection of a single permeant type (characterized by a certain absorption signature) was possible. Application of MBPA may extend the PA potential, and allow for the characterization of multiple permeating species simultaneously. In particular, for the first time quantification of photophysical and photochemical processes, like drug degradation or binding [2], crucial in the field of pharmacy, will be directly accessible;
- photosynthesis (PS) is considered as one of the most important physical processes. The PA-based quantification of the process efficiency involves PADP studies in the chlorophyll red band region. The band, in fact, consists of two partially overlapping bands related to two distinct photosystems. As such, the MBPA may allow to extend the PS efficiency quantification into *real-time* measurements with additional differentiation between contributions of each of the reaction centres; alternatively, an overall PS efficiency could serve as a multiparameter air/water quality indicator, if tested against other pollutants presence. The idea for the PA-based water quality sensors, with separate modes for the microplastics detection and PS efficiency quantification, was recently developed and tested for model systems [5].

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5. References

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