Simple technique for obtaining photoacoustic spectra corrected for the spectral variation of the source in single scan

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A simple technique is presented to obtain normalized photoacoustic (PA) spectra corrected for the spectral variation of the source in a single scan. The input light beam is passed through the center of a dual slot chopper, which splits it into two chopped output beams at two different frequencies at a fixed ratio. The beams fall on the sample and the reference kept side-by-side in the same sample chamber. The PA signals are detected by a microphone and processed by two lock-in amplifiers tuned at two different frequencies. The technique is tested by recording the PA spectra of standard samples. © *2007 American Institute of Physics.* [DOI: 10.1063/1.2721409]

I. INTRODUCTION

Though optical spectroscopy has proved to be invaluable in obtaining information about electronic processes in reasonably transparent media such as solutions, crystals, and specularly reflective surfaces, severe limitations are experienced on working with highly light scattering and opaque substances. Techniques of diffuse reflectance, attenuated total reflection, internal reflection spectroscopy, and Raman scattering have been successfully used to study such media though with some limitations. On the other hand, photoacoustic spectroscopy (PAS) has been demonstrated to have an edge over the conventional techniques in the study of highly reflecting and optically opaque samples.

The photoacoustic (PA) effect was first reported by Bell in 1880 though the wide use of this technique for spectroscopic purposes started only almost after a century. From then, there has been a steady progress in the development of PA spectrometers in view of their potential application particularly in biological and environmental studies.[1,2] A major improvement in the sensitivity of the photoacoustic method has been brought about by the availability of laser sources, highly sensitive microphones, and other efficient acoustic detection systems.[1–4] Nagele *et al.* developed a novel type of highly sensitive multipass resonant PA cell for trace-gas detection making use of new compact low-power laser sources such as quantum-cascade lasers.[3] Muller *et al.* presented a transportable, highly sensitive photoacoustic spectrometer based on a continuous-wave dual-cavity optical parametric oscillator.[4] Innovations in the design of inexpensive and high performance photoacoustic spectrometers continue to attract recent attention, rendering this form of spectroscopy increasingly versatile.[1,2,5–7]

The PA technique is an absolute method which provides a direct measurement of the energy absorbed by a sample. The basic principles of the PA effect in condensed matter have been well established by Rosencwaig, Patel, and Tam.[8–12] The PA effect is based on the generation of acoustic signal when a sample enclosed in an airtight chamber is heated periodically on irradiation with an intensity modulated beam. The corresponding pressure fluctuation produced by the sample in the ambient gas is easily detected by a sensitive microphone.

One of the problems with PAS is the correction of the spectra for the spectral responses of the source, for which the three methods commonly used: (a) a double beam technique with two photoacoustic cells, (b) a double beam system with a pyroelectric detector in the reference channel, and (c) a signal beam with facilities for digital storage and correction of spectra.[13–17] In a double beam spectrometer, the intensity modulated and monochromatized probe beam is split into two. One of the beams falls on a thermopile or another PAS cell containing carbon black while the second beam falls on the sample. The ratio of the output from the sample cell to the output of the reference cell by a ratiometer and the normalized spectrum is recorded directly on a recorder. This, however, makes the spectrometer design rather complicated and more expensive. In addition, several other difficulties arise in the dual beam method such as the issue for identical design of dual cells and the corrections required for the wavelength dependence of the beam splitters. In the single beam technique, the spectrum of the sample is measured first and normalized with an earlier recorded carbon black spectrum. This process is time consuming and prone to errors in normalization due to unexpected disturbance such as power fluctuations during the experiment which may affect the spectrum.

Here we present a new single beam technique which actually performs a dual measurement, one on the sample and the other on the reference simultaneously which helps to obtain a corrected PA spectrum by a single spectral scan. This is achieved using a dual slot chopper to split the single rectangular beam coming from the monochromator into two separate beams chopped at two different frequencies, which are made to be incident on the sample and the reference, respectively, kept side-by-side in a specially designed sample chamber.

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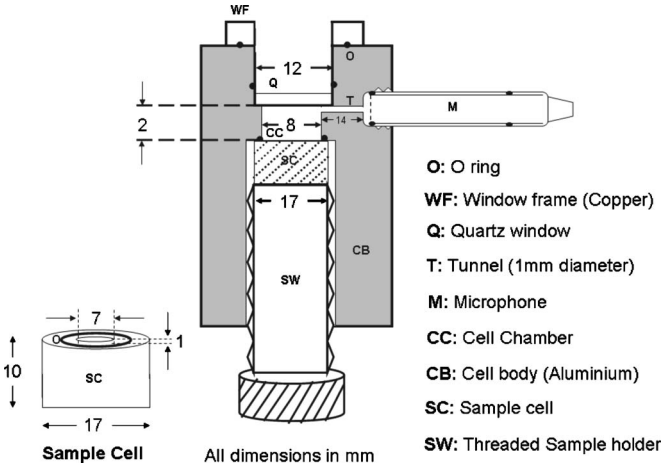

FIG. 1. Schematic diagram of the photoacoustic cell.

II. EXPERIMENTAL DETAILS

The PA cell (Fig. 1) is made of aluminum with a cylindrical cell chamber of radius 8 mm and depth 2 mm. The top of the chamber is closed with a quartz window (Q) of thickness 5 mm through which the probing optical beam enters the chamber. This optical window has a high percentage of transmission in the wavelength range of interest. A microphone is fixed at the side of this cell chamber and connected to the chamber by a narrow tunnel of 1 mm of diameter and 14 mm length, which is bored just below the optical window. The purpose of this tunnel is to enable the microphone to detect the acoustic waves in the chamber while keeping itself away from the optical beam. The microphone used is 1/2 in. (12.7 mm) prepolarized, free-field microphone Type 40AE from G.R.A.S of sensitivity 50 mV/Pa with flat frequency response in the range 5–10 kHz. The sample cell is made of a brass rod of 10 mm thickness and 17 mm diameter with a depression of depth 1 mm and diameter 7 mm on the flat surface. The experimental sample is placed in this depression of the sample cell which is then kept on a threaded sample holder. The sample holder is inserted in to the PA cell through the passage at its bottom and is screwed into the cell body shown in the figure in such a way that the O ring at the top of the sample cell is pressed firmly against the base of the chamber. Now the light entering the cell chamber through the top quartz plate is incident directly on the sample, which is in an airtight environment.

A schematic diagram of the photoacoustic setup is given in Fig. 2. A 500 W xenon arc lamp is used as the light source. The light beam from the source is focused on the input slit of the "microtrouble free" 100 mm monochromator from Jobin Yvon which has a type IV aberration-corrected concave holographic grating with fixed slits 1 mm. The beam coming out of the monochromator is rectangular in cross section of dimension 6 mm$\times$2 mm immediately after the exit slit. A mechanical chopper is used to modulate the intensity of the beam. The modulation is achieved by making the monochromatized beam to fall on a 1/5 dual slot mechanical chopper in such a way that light spreads on both the outer and the inner rows of the slots of the chopper, as indicated in Fig. 2. The upper part of the beam is chopped by the outer row of slots on the wheel and the other is chopped by the inner row of slots. Thus the output from a single source is chopped at two different frequencies, leading to two output beams chopped at different frequencies, one being five times the other in the present case. The diameter of the chopper blade is 102 mm. The outer and inner slot widths are 21, and 16 mm, respectively. The openings of upper and lower slots are positioned in such a way that light does not pass through both these slots at the same time. Thus the light beams from these two slots excite the sample and reference at different times.

The image of the slit is condensed to 6 mm in height using a suitable condenser lens assembly and is directed to the sample surface using a beam steerer. The measurements are carried out at room temperature in steps of 2 nm between the wavelength ranges from 360 to 700 nm with the help of the motorized monochromator controlled through the LPT1 of the computer. The microphone detects the photoacoustic signal and the output is amplified by a SR560 low noise preamplifier and monitored by a two-phase lock in amplifier SR830 with frequency and phase resolutions of 0.1 mHz and 0.01°, respectively. All the instrument functions are controlled through the RS232 interface. The data are usually averaged in order to improve signal-to-noise ratio. Quimby and Yen have analyzed the three dimensional flow and found that a distance of the order of μ_g, the thermal diffusion

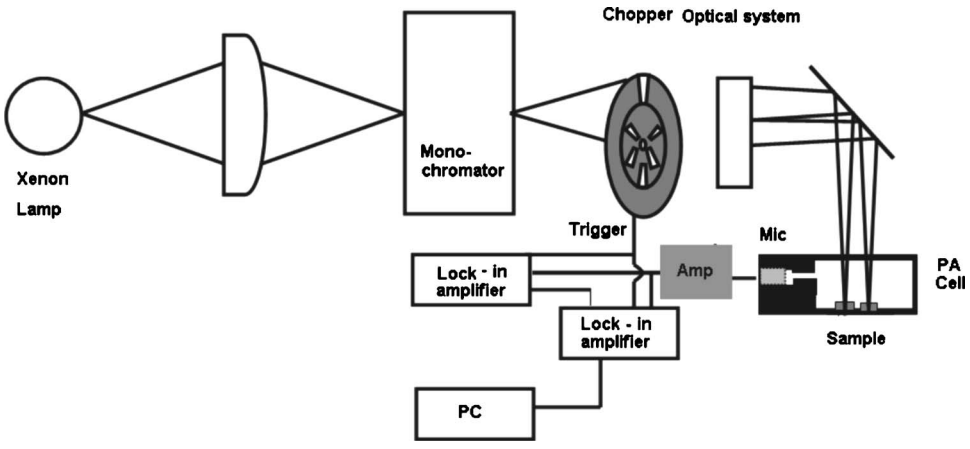

FIG. 2. Block diagram of the photoacoustic spectrometer.

length in the gas, should be maintained between the sample and the cell walls.[18] The dimension of our cell and sample holder takes this into account for the lowest chopping frequencies (2–10 Hz) and the largest slit widths. Carbon black being a very good absorber of light compared to most of the other samples, only a small part of the split beam needs to be incident on the carbon black and the larger part is to be made available to excite the sample as the amplitude of the PA signal depends linearly on power. Thus the ratio of the amounts of light falling on the sample and carbon black is designed to be in the ratio 7:3 in the present work. The power of light at 633 nm is about 160 μW as measured at the location of the sample. The amount of light falling on the sample is varied by moving up or down the position of the chopper. The sample and the reference (carbon black) are placed well separated from each other in the cell but within the dimension of focused beam to get well resolved and interference-free individual signals from the sample and the reference. The signal from the microphone is fed to the inputs of two separate lock in amplifiers simultaneously. One of these lock-in amplifiers (LA1) is tuned to detect signals at frequency f_{outer} (the chopping frequency of the light incident on the reference) and the other (LA2) is tuned to frequency f_{inner} (the chopping frequency of the light incident on the sample). Thus the two amplifiers process the signals from the sample and the reference separately. The output signal from LA2 is fed to the AUX IN (auxiliary input) terminal of LA1 which is operated in the ratio measurement mode, thus the signal from the sample is divided by the signal from carbon black to get the normalized spectrum of the sample corrected for the spectral response of the source and also for any fluctuation in source intensity is obtained in real time.

The optical absorption spectra of the experimental samples are recorded using a ultraviolet (UV)-visible spectrometer from JASCO in the wavelength range 300 to 800 nm. These spectra are used for comparison with the PA spectra.

III. RESULTS AND DISCUSSIONS

The PA cell is characterized by recording its frequency response using standard carbon black as the sample, employing the single beam technique. The experiment is done using a 13 mW He-Ne laser as source and the intensity is modulated by the variable mechanical chopper. The result is shown in Fig. 3 where the logarithm of the measured PA signal from the carbon black sample is plotted as a function of logarithm of chopping frequency. The data points fit to a straight line of slope –1, which is in accordance with Rosencwaig's theory[19] for optically opaque and thermally thin samples.

The performance of the PA setup based on the new technique is tested by recording the PA spectrum of holmium oxide powder, which is normally used as the standard in view of its rich spectral features. Figure 4 shows the PA spectrum (solid line) of holmium oxide obtained. The optical absorption (OA) spectrum of the same sample also is shown in the same figure (dashed line) for the purpose of comparison. The OA spectrum is recorded by dissolving the powder

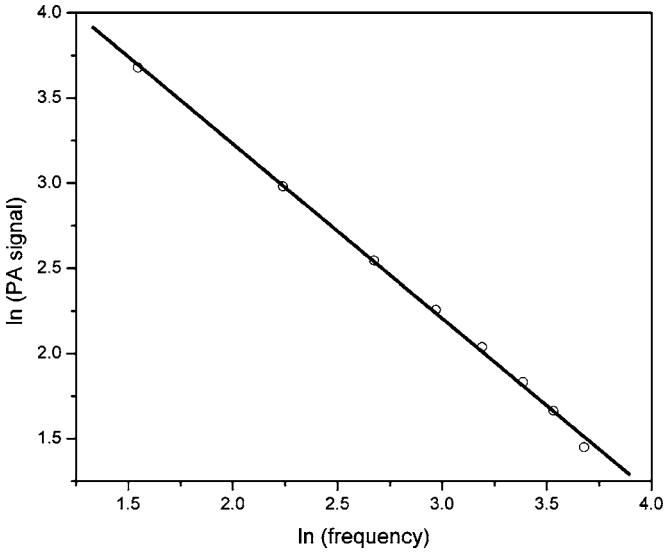

FIG. 3. Frequency response of the PA spectrometer.

sample in perchloric acid. Holmium oxide (H_2O_3) exhibits seven major absorption peaks in the visible and near-UV portions of the optical absorption spectrum, at 372, 422, 450, 486, 540, 640, and 650 nm. The origin of these peaks is optical absorption by electrons occupying the partially filled $4f$ levels of the Ho^{3+} ion. The PA spectrum reveals all the features obtained in the OA spectrum but with some redshift in the absorption peaks to the tune of a few nanometers and agrees well with the reported PA spectrum of the material.[20]

The PA setup is tested further by recording the spectrum of vanadyl-tetraphenylporphine (VoTPP) which is shown in Fig. 5. Here the solid line is the PA spectrum and the dashed line is the OA spectrum. OA spectrum of VoTPP is obtained from VoTPP solution prepared in chloroform of about 10^{-6} M. Both PA and OA spectra show well resolved Soret band (around 420 nm) and Q band (around 550 nm) which arise due to the coupling of the two transitions between the highest occupied molecular orbitals and the lowest unoccupied molecular orbitals ($\pi - \pi^*$).[21]

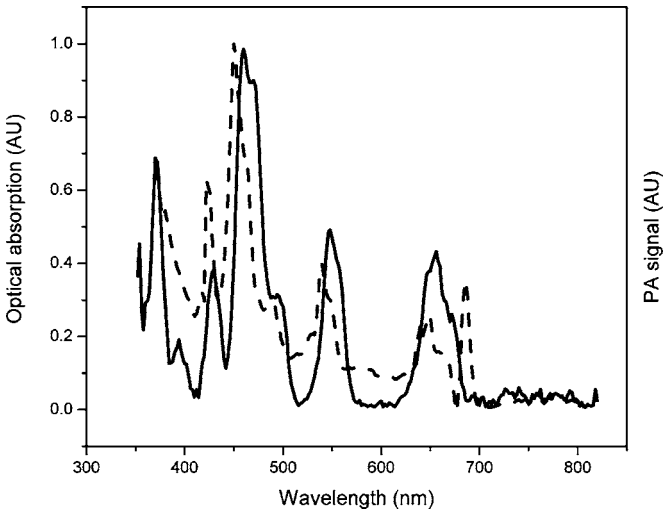

FIG. 4. Normalized photoacoustic spectrum (solid line) of holmium oxide powder and the normalized optical absorption spectrum (dashed line) of a solution of holmium oxide in perchloric acid.

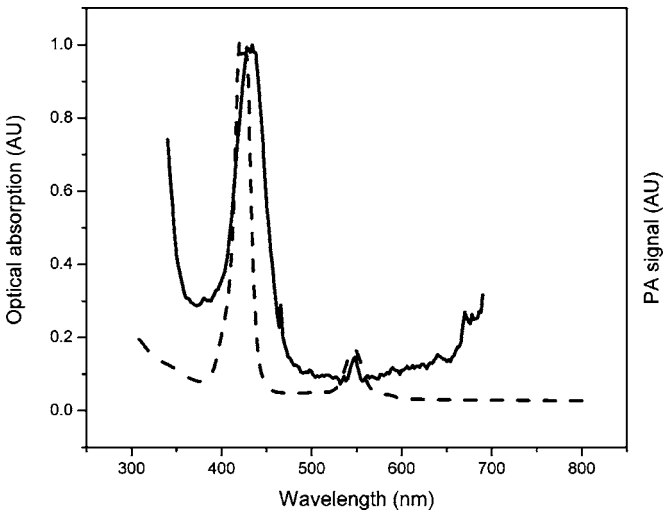

FIG. 5. Normalized photoacoustic spectrum (dashed line) of VoTPP powder and the normalized optical absorption spectrum (solid line) of a solution of 10^{-6} M VoTPP in chloroform.

The experimental parameters such as the ratios of the relative intensities and frequency of light incident on the sample and the reference have to be designed carefully. The intensity ratio of light incident on the sample and the reference are varied and an optimal result is obtained at a ratio 7:3. This is understandable as the PA response of the reference, carbon black, is much larger than that of the sample and the experimental sample under study requires sufficient intensity to generate acoustical signal to be detected by the microphone.

The modulation frequency of the incident beam affects parameters such as the signal strength, signal-to-noise ratio, and resolution. The phase dependence of PA signal arising from sample is an important factor to be considered while choosing the chopping frequency. The phase dependence arises mainly due to two important contributions, namely, the lifetime of the excited states and the time taken for the temperature distribution to thermally diffuse to the sample-gas interface. The effect due to the former can be neglected in our studies as the lifetimes of the excited states involved are expected to be of the order of a few nanoseconds. But the flow of heat from the point of generation to the surface is slow and the resultant phase shift (θ) in the PA signal is given by

$$\theta = x\sqrt{\frac{\omega}{2\alpha}},$$

where x is the distance of the surface from the point of actual heat generation, α is the absorption coefficient, and ω is the chopping frequency.

The ratio of chopping frequencies at the outer slot to the inner slot, $f_{\text{outer}}/f_{\text{inner}}$, is so chosen that interference of the acoustic signals due to variation in the phase produced by the sample before reaching the microphone is avoided. Both samples are kept side by side and positioned at right angles with respect to microphone so that the samples are at equal distances from the position of the microphone. In the present study a 1/5 dual slot chopper used for modulating incident light at two different frequencies, 2 Hz (f_{outer}) and 10 Hz (f_{inner}), did not produce any interference effect on recorded signal.

Signal saturation is a potential problem for PAS of solid samples and is normally experienced with strong absorbers such as porphyrins. Signal saturation occurs when the optical thickness (α^{-1}) becomes equivalent to the thermal thickness (μ is the thermal diffusion length) of the sample. In this case PA signal would be independent of α. In order to obtain the true photoacoustic response of the sample and to eliminate signal saturation effects, the sample thickness has to be reduced below the optical thickness α^{-1}. Hence, in the case of strongly absorbing samples such as porphyrins, only a few micrograms are required. It has been found that the new technique reproduces the PA spectra of known samples with the additional advantage of *in situ* spectral correction and normalization.

IV. CONCLUSION

In conclusion, a newly designed single beam PA setup is shown to perform a dual measurement of the PA signals from a sample as well as a reference, making it convenient to obtain a normalized spectrum of the sample corrected *in situ* for the spectral variation and thermal fluctuations of the source. The setup is tested with samples with rich spectral features such as holmium oxide and VoTPP and found to give reliable PA spectra. The proposed technique avoids the usage of two separate PA cells and other cumbersome optical geometries usually employed for conventional dual beam techniques, making the PA setup very compact and versatile.

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