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INFRARED PHOTOACOUSTIC SPECTROMETER AND DATA ANALYSIS FOR HETEROGENEOUS OR LIQUID SAMPLES

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Résumé-Le spectromètre photoacoustique présenté permet l'obtention de spectres dans l'infrarouge de matériaux pulvéruents ou liquides. Une manipulation des données enregistrées conduit à une meilleure sensibilité aux variations du coefficient d'absorption. L'analyse du spectre reste cependant qualitative.

Abstract—By using the photoacoustic spectrometer described, infrared spectra of powdry or liquid samples are obtained. A calculation from the recorded data leads to a better sensitivity to the variations of the absorption coefficient. However, the spectrum analysis remains qualitative.

I - INTRODUCTION

The photoacoustic spectroscopy of solid or liquid samples has been rapidly developing since a few years and many results have demonstrated its interest/1-3/. It is a practical method whose main advantages are the following: a high sensitivity which is essential in the infrared range because of the low power of the available light sources, and a non destructive approach which permits analysis of the samples without altering their nature.

The method deals with the measurement of the amplitude and/or the phase of the pressure variations induced in the gas by the rise of the sample temperature which is caused by absorption of the incident modulated light /3/. The variations of these photoacoustic signals according to the wavelength lead to the determination of the absorption spectrum of the analysed sample /3/.

The purpose of the present paper is to describe a photoacoustic spectrometer used for powdry and liquid samples and to present the results obtained. A data acquisition and processing method is described which leads to a good approximation of the absorption spectrum for particular experimental conditions.

II - THEORETICAL CONSIDERATIONS

This study is concerned with samples which may have the following properties: weak optical absorption, optical scattering, thermal dilatation and heterogeneity.

The photoacoustic signal is generally expressed as the sum of two contributions/4-6/:

- one term which expresses the heat diffusion from the sample to the gas and another which represents the sample thermal dilatation. The first term is essentially due to the energy deposited in a sample layer having a thickness of the same order of magnitude as the sample heat diffusion length, while the second is proportional to all the absorbed light energy. This last term, compared to the first, can become important in some cases: weak absorption, short sample thermal diffusion lengths, large dilatation coefficient. In the case of a strong absorption, the first term is predominant and a saturation of the amplitude of the photoacoustic signal can result /3/. The absorption spectrum can also be obtained by measuring the phase of the signal /6-9/. It is this last kind of analysis that is developed here.

For thermally thick samples (thickness >> thermal diffusion length), the generalised

*Now employed by CANMET, Energie Mines Resources Canada.
The expression of the photoacoustic pressure $P$ detected in the cell (in the case of a thermally thick gas) is /4-6,10/:

$$
P = \frac{\gamma P_0}{\omega V_e} - \frac{W_0}{\rho_e c_e} \left[ I + \frac{\mu_e^{\alpha}}{\mu_G^{\alpha}} \right] \left( I + \frac{K_g \mu_e}{K_e \mu_e} + \frac{\mu_e^{\alpha}}{\mu_G^{\alpha}} \right) + \beta_e (I-R-T)$$

where $P_0$, $T_0$ are the ambient pressure and temperature of the gas, respectively, $\gamma$ the ratio of the gas heat capacities at constant pressure and at constant volume, and $W_0$ the light power entering into the medium. $K$ and $\mu$ are, respectively, the thermal conductivity and the thermal diffusion length of the gas (subscript $g$) and of the sample (subscript $e$). $\beta_e$, $\rho_e$, and $C_e$ are, respectively, the thermal dilatation coefficient, the density, and the heat capacity at constant pressure of the sample. These last five parameters are equivalent parameters in the case of an heterogeneous sample (powders for instance) /6/. This approximation is valid only if the thermal response time of the particles surrounded by a thermally thin layer of fluid is smaller than the modulation period /10/; i.e. the particle size must be smaller than the equivalent heat diffusion length $\mu$. $V_e$ is the gas volume in the cell. In the case of powders, $V_e$ is an equivalent finite volume if the pressure is uniform throughout the sample medium /6,10/, i.e. if the sample thickness is much smaller than its acoustic attenuation length.

Finally, $a$ characterizes the sample optic absorption, $a'$ the attenuation of light by scattering and absorption, $R$ the diffuse reflectance and $T$ the transmittance. In a limited range of wavelengths, the elemental (or true) scattering coefficient per unit length $s$ remains constant, while the elemental (or true) absorption coefficient per unit length $k$ can fluctuate strongly. If $k \gg s$, $a'$ has the form $k + s /10/$. If $s \gg k$ and $a'' \gg I$, $a'$ has the form $ks /10/$. In the case of strongly scattering samples, the first term in the expression (I) of $P$ is predominant compared to the second, even for weak absorptions. For weakly scattering samples, in the case of weak absorptions, the term in the expression (1) (the sample thermal dilatation) is not negligible /5,6,10/.

The variations of the absorption coefficient $k$ according to the wavelength can be obtained from the expression of $a''_e$. The calculation of $a''_e$ is done from the tangent of the phase of the first term of the pressure $P$ in equation (I) /8-10/. First, the second term must be known. It can be estimated by its mean value noted $S$, calculated on the wavelength ranges outside the spectrum bands ($a''_e \ll I$). In this range (see Eq.I), $S$ is the difference between the parts of $P$ in quadrature and in phase with the light excitation, expressed respectively as $P_{qu}$ and $P_{ph}$. We have:

$$S = \frac{P_{qu} - P_{ph}}{P_{qu}}$$

The sample spectrum is then deduced from the following manipulation:

$$a''_e = \frac{(P_{qu} - P_{ph} - S)}{P_{ph}}$$

Relation (3) generally overvalues the weak value of the absorption coefficient $k$. However, this relation leads to a better determination of the variations of $k$ in a given wavelength range than the sole study of the signal phase or the signal amplitude.

III - EXPERIMENTAL SETUP

Figure I illustrates the experimental setup. The infrared source is a Nernst glower focalised on the input slit of the monochromator by a concave mirror (focal length 108 mm): the input aperture of the monochromator is f/4. The monochromator is a grating model with a low resolution (Spex Minimate 1670, focal length 220 mm). Two different gratings can be used: grating 1, blazed at 3 \mu m with 300 grooves/mm which, with input and output slits of 1.25 mm width, gives a resolution of about 19 cm^-1;
The studied wavelength ranges are from 2 \( \mu m \) to 4 \( \mu m \) with a high pass filter at 2 \( \mu m \) for grating 1, and from 8 \( \mu m \) to 16 \( \mu m \) with a high pass filter at 8 \( \mu m \) for grating 2. The scanning speeds are, respectively, 0.031 \( \mu m/nm \) and 0.125 \( \mu m/mm \).

The light beam modulation is produced in front of the monochromator input slit by a galvanometer modulator at a frequency around 50 Hz which may be adjusted depending on the samples, to satisfy the conditions previously described in paragraph II.

Behind the monochromator output, a concave mirror (focal length 135 mm) focuses the light beam toward a cylindrical mirror (focal length 9.5 mm) which allows part of the beam to propagate toward the pyroelectric detector (Moletron PI-45) while it focuses the other part on the photoacoustic cell input. The position of the cell is adjusted to obtain the optimum signal. The light paths between the output slit and the pyroelectric detector, and the photoacoustic cell are equal to eliminate the influence of the atmospheric absorption.

A first lock-in amplifier gives the amplitude I of the signal given by the pyroelectric detector, thus leading to the source spectrum. This amplitude is then used to normalize the signals, in phase and in quadrature with the light excitation \((P', P'')\), given by a second lock-in amplifier from the signal detected by the microphone of the cell. The data \((P_{ph}, P_{qu})\), recorded by a micro-computer (HP 85) in a experiment file, are so independent of the excitation power. The micro computer manages all the experiment: it commands the experimental process, records the data, and finally calculates the samples spectra.

The photoacoustic cell was built to obtain a very small gas volume \(<16 \text{ mm}^3\). The cell is shown in figure 2. The overall dimensions are: height 27 mm, diameter 50.5 mm. All the parts of the cell are made of brass, except the sample holder which is in stainless steel; the inner walls of the cell are finely polished. The sample holder is mounted on a removable piston sliding in the cell body and can be changed according to the studied samples in order to have different sample cavity dimensions. The cell window is in ZnSe, transparent up to 16 \( \mu m \), A conduit can be used to create a vacuum in the cell and to fill it at the desired pressure with a selected gas. Finally, the microphone used is a miniature model from Knowles-Electronics (BL 1785) with a sensitivity of the order of 3 mV/Pa.
IV - EXPERIMENTAL RESULTS

The phase reference must first be defined. For this purpose, a black carbon powder was used. Theoretically, for such a sample the phase is constant and equal to $-\pi/2$ rad. Figure 3 shows experimental data recorded between 2 and 4 μm. The phase is almost constant and the mean value obtained is $-1.3$ rad. This value depends only slightly on the experimental filling of the photoacoustic cell by the sample because of the small volume of the cell. The same experimental filling condition must be verified for each sample.

Figure 4 shows the flow chart of the program needed for data acquisition and manipulation. In this program, the operator has to give the bands limiting wavelengths from the recorded data (in phase and in quadrature signals) in order to determine the value of $\theta$ and then the sample spectrum.

The spectra of mineral oil are given in figure 5. Figure 5a shows the in quadrature and the in phase spectra, whereas the corresponding calculated spectrum is given in figure 5b. Figure 6 shows the same results obtained for an epoxy powder.

Outside the absorption bands, the difference between the in quadrature and the in phase spectra is proportional to the thermal dilatation of the sample. Moreover, in the case of a non-scattering sample, the in phase signal is null outside the bands as we can see in figure 5a for the mineral oil. For a scattering sample like the epoxy powder, this signal and the in quadrature signal can be important even for very small values of the absorption coefficient (see Fig. 6a).

In the absorption bands, for an increasing absorption coefficient $k$ which is not too large ($k\mu < 1$) /10/, the in phase signal begins to increase (see arrows 1 in Fig. 5a and 6a); then, as $k$ increases more this signal decreases, whereas the in quadrature signal is saturated (see arrows 2 in Fig. 5a and 6a). The in phase signal tends to zero as $k$ tends to infinity (Eq. 1).

The recommended data manipulation allows the elimination of the saturation effects, leading to a more precise determination of the absorption bands (arrows 3 in Fig. 5 and 6). Moreover this manipulation eliminates the background signals due to the combination of two important effects in the photoacoustic spectroscopy:
thermal dilatation of the sample and the light scattering by the sample.

V - CONCLUSION

The experimental setup described in this paper can be used to obtain infrared spectra of different heterogeneous or liquid samples. The effects due to the light scattering, the sample thermal dilatation, and the photoacoustic saturation, often present in photoacoustic spectroscopy of such samples, are overcome by a data manipulation. However the obtained spectra remain qualitative. A more precise data analysis needs a more complex theoretical background which is presented elsewhere/10/.
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