Photothermal Determination of Absorption Coefficients in Optically Dense Fluids: Application to Oleic Acid and Water at CO Laser Wavelengths

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Values of optical absorption coefficient β in the infrared spectral region covered by the CO laser emission were measured for homogeneous, nonscattering, and optically very dense (4×10^4 m^{-1} $< \beta < 4 \times 10^5$ m^{-1}) fluids (oleic acid and water) with the use of optothermal window (OW) spectroscopy. This new approach, which combines a photothermal technique with piezoelectric detection, offers several practical advantages over conventional techniques (easy loading and cleaning, no dead volume, simple recovery of sample, etc.). A linear correlation between the optothermal signal and β exists when thermal diffusion length μ in a sample is shorter than optical penetration depth $1/\beta$. The apparatus was calibrated with distilled water ($\beta = 3.38 \times 10^4$ m^{-1} at 1781 cm^{-1} wavenumbers). Experimentally found β values for oleic acid and water are consistent with those measured by the spectrophotometric method. Satisfactory measurements could be performed for ($0.1 < \beta\mu < 3$); the optothermal signals were large enough and far from saturation.

Index Headings: Optothermal sensor; Absorption coefficient; Sapphire; Infrared spectrum; CO laser; Water; Oleic acid; Photothermal spectroscopy.

INTRODUCTION

Intense absorption bands of fatty acids and water between 4000 cm^{-1} and 200 cm^{-1} require short (<10 μm), difficult-to-reproduce pathlengths and therefore preclude quantitative studies based on conventional infrared absorption spectroscopy. The dominant O–H deformation band of water is centered[1] near 1645 cm^{-1} while C=O stretch absorption bands of dimerized fatty acids are found[2] between 1720 and 1706 cm^{-1}. The conventional cell for studies of optically dense fluids usually consists of two transparent windows separated by a spacer of fixed thickness. Occasionally, strongly absorbing undiluted fluids are examined without the spacer (neat liquids); compressing the two windows produces a thin film of sample while the windows are held together by the capillarity.[3] In several previous investigations, attempts were made to determine the (near) infrared absorption coefficients of fatty acids and water by the methods of conventional transmission,[4–6] total internal reflection, reflection-mode photopyroelectric spectroscopy, and the Kramer–Kronig approach.[4–8] In this paper the optothermal window (OW) method[9] with a sapphire window (as a sensing element) and the piezoelectric transducer was used. This approach was found to be capable of determining absorption coef-

ficient β for oleic acid and water (at 293 K) at CO laser wavelengths in a simple, reproducible, and practical way.

THEORETICAL BACKGROUND

In OW spectroscopy,[10] which belongs to the class of photothermal techniques, the signal generated at a given excitation wavelenth and modulation frequency f (s^{-1}) depends in a rather cumbersome way on a variety of the sample's thermophysical parameters and its absorption coefficient β (m^{-1}). As will be seen later, under certain experimental conditions (optically opaque and thermally thick sample), the signal is proportional to β. The optothermal spectrum is indeed expected to correlate[11] with the absorption spectrum since the absorbance A, defined as $A = -\log_{10}T$ [with transmittance $T = \exp(-\beta d)$], can be expressed as

$$A = 0.434\beta d = \epsilon C d \qquad (1)$$

where ϵ (L/mol m), C (mol/L), and d (m) represent molar decadic extinction coefficient, molar concentration, and geometrical thickness (or optical pathlength) of the sample, respectively.

The normalized amplitude of the optothermal signal depends on the temperature fluctuations taking place within approximately one thermal diffusion length from the sample/window interface. In general, thermal diffusion length μ (m) and the modulation frequency f are related through

$$\mu = (k/\pi\rho cf)^{1/2} \qquad (2)$$

where k (W/m K), ρ (kg/m^3), and c (J/kg K) are thermal conductivity, density, and volume specific heat, respectively.

Helander has shown[12] that, for a thermally thick and optically opaque sample [μ_s, $1/\beta_s$, $< d_s$ (subscript s refers to sample)] and a thermally thick window [$\mu_w < d_w$ (subscript w refers to window)], the amplitude ψ and phase ϕ of the optothermal signal are given by

$$\psi = \beta_s\mu_s[(1 + \beta_s\mu_s)^2 + 1]^{-1/2}(1 + e_s/e_w)^{-1} \qquad (3)$$

and

$$\phi = -\arctan(1 + \beta_s\mu_s)^{-1}. \qquad (4)$$

The e (W s$^{1/2}$/m^2 K) in Eq. 3 is thermal effusivity defined in general as

$$e = (k\rho c)^{1/2}. \qquad (5)$$

TABLE I. Thermophysical data for water, oleic acid, and sapphire at modulation frequencies of 250 Hz and 600 Hz.[13,14] Density, ρ; specific heat, c; thermal conductivity, k; thermal effusivity, e; and thermal diffusion length, μ.

Parameter	Water	Oleic acid	Sapphire
ρ (kg/m^3)	1000	$\approx$880	3980
c (J/kg K)	4180	2300	752
k (W/m K)	0.595	0.230	32.8
e (Ws$^{1/2}$/m^2 K)	1577	682	9900
μ (μm) at 250 Hz	13.6	12.0	118
μ (μm) at 600 Hz	8.78	7.76	76.2

One introduces the reduced, dimensionless, optothermal signal amplitude S as

$$S = \beta_s\mu_s[(1 + \beta_s\mu_s)^2 + 1]^{-1/2}$$
$$= \psi(1 + e_s/e_w)$$
$$= NV(1 + e_s/e_w) \tag{6}$$

which depends solely on the effective optical pathlength $\beta_s\mu_s$ in the sample. Likewise, N and V represent the sensitivity constant and the measured signal amplitude, respectively. The reduced amplitude S and the phase ϕ are normalized in the sense that, for $\beta_s\mu_s \gg 1$, Eqs. 6 and 4 give $S = 1$ and $\phi = 0$, that is to say, an optical saturation. In the opposite case when $\beta_s\mu_s \ll 1$, one has $S = \beta_s\mu_s/\sqrt{2}$ and $\phi = -45°$. By combining this result with Eq. 1, one obtains $S = 1.63A$, which implies that the signal is directly proportional to the absorbance A of a sample, when its thickness equals the thermal diffusion length ($d = \mu_s$) at the actual modulation frequency. For strongly absorbing samples (high β), short μ_s values are required to satisfy the condition $\beta_s\mu_s \ll 1$. This requirement implies the need for high modulation frequencies; however the penalty one has when working in this regime is a low level of generated signals.

No phase information was used in this work because, in contrast to the signal amplitude, the phase is saturated (for high, as well as for low, absorptions), and only within a limited interval ($0.3 < \beta_s\mu_s < 5$) sensitive to the sample's optical properties.

The relevant thermophysical properties of water, oleic acid, and sapphire window are summarized in Table I. Substituting the appropriate values, the correction factor ($1 + e_s/e_w$) from Eq. 6 is 1.069 (for oleic acid) and 1.159 (for water). For a series of measurements on samples having comparable effusivities, this correction factor is the same, and there is no need to determine it explicitly. However, when samples of different effusivities are being compared, a correction (ratio of respective factors) must be made. In our case, the OW cell was calibrated at a specified wavelength with the use of the absorption coefficient of water taken from the literature. In order to extend calibration to the oleic acid, the magnitute V of the signal obtained with water must be multiplied by the factor $1.159/1.069 = 1.084$ (an increase of 8.4%). It should be noted that the correction is relatively small when compared to the actual effusivity ratio [1577/682 = 2.31; a difference of 100(2.31 − 1) = 131%] of water and oleic acid. This observation supports the idea that the OW cell is, in the first place, sensitive to the optical absorption properties of the samples.

The three theoretical calibration curves (Fig. 1) calculated by means of Eq. 6 show dependence of reduced
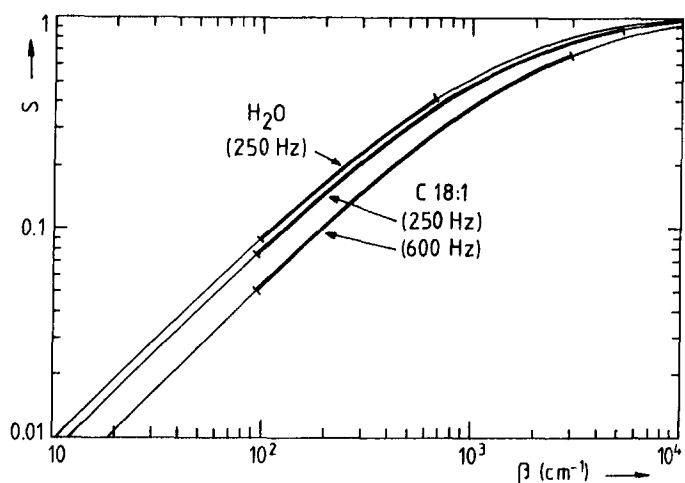

Fig. 1. The normalized optothermal signal S plotted against the absorption coefficent β (in cm^{-1}) as calculated according to Eq. 6 with numerical values from Table I (solid lines). The range of β values determined in this experiment is also specified (bold segments).

signal S on the absorption coefficient β. Thermal diffusion length μ depends (Table I) on the sample under investigation and on the modulation frequency, causing the curves in Fig. 1 to shift from one another in the horizontal direction. One observes that the signal being proportional to the absorption coefficient for low β becomes saturated in the case of strong absorption.

EXPERIMENTAL

The experimental arrangement used in this study is shown schematically in Fig. 2. A parallel beam **L** of mechanically modulated (chopper **C**, Model 219 manufactured by EG&G Instruments) radiation emitted from a home-made, tunable, and cryogenic (cooling jacket at 230 K) CO laser passes through a 2-mm diaphragm **P**. In order to measure the amount of incident laser power (typically several tens of milliwatts on some forty lines), a home-made pyroelectric detector **D** consisting of a 25-μm-thick PVDF foil can be inserted (by means of mirror **M$_1$**) into the radiation path of the CO laser whenever needed. The strength of the pyroelectric signal at the modulation frequency was measured with an Ithaco NF 3921 lock-in amplifier. The laser beam then reaches an aluminium plane mirror **M$_2$** (at 45°), passes through the annular piezoelectric transducer **PZT** [made of Pb, Zr, and Ti oxide (PZT) ceramic] and the transparent sapphire window **W**, before finally being absorbed in a droplet of liquid sample **Sa**. The saphhire window (having high transmission from 0.25 to 6 μm and a large thermal expansion coefficient) is a disk 14 mm in diameter and d_w = 0.3 mm thick. The diameter of the sensitive area (4 mm) equals the inner diameter of the PZT ceramic ring. Both the OW cell (manufactured by AB Varilab, Huddinge, Sweden) and mirror **M$_2$** are mounted in an aluminium holder (provided with an opening 1 cm in diameter), bolted to an x-y-z translation stage for precise optical adjustment with respect to the CO laser beam. The diameter of the laser beam (approximately 2 mm) is small enough for unobstructed passage through the cell. The optothermal signal at specified modulation frequencies was measured by an EG&G/PAR
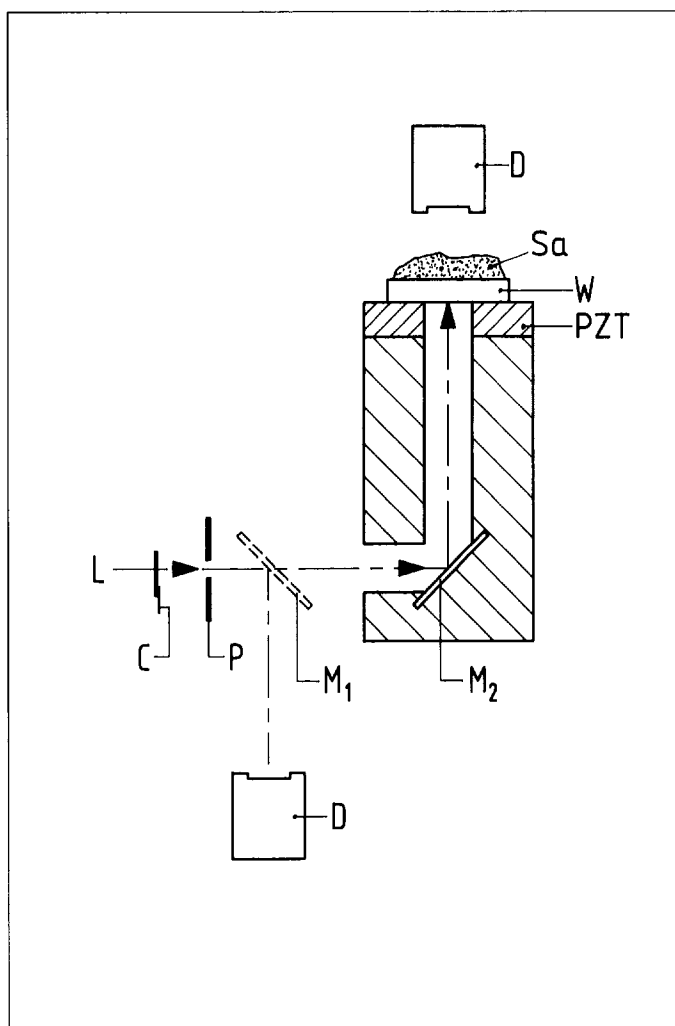
Fig. 2. The experimental setup used for laser optothermal spectroscopy of liquids and the cross-sectional view of optothermal window (OW) cell: CO laser beam (L), chopper (C), diaphragm (P), mirrors (M_1, M_2), annular piezoelectric transducer (PZT), sapphire window (W), liquid sample (Sa), and pyroelectric detector (D).

5101 lock-in amplifier. The output signal contains both amplitude (which varies as f^{-1}) and phase information. The output impedance of the detector (3Ω at 100 Hz) also depends on the modulation frequency as f^{-1}. The optimum position of the cell corresponded to that of the minimal optothermal signal (recorded without the sample) with simultaneous maximal radiation throughput. It was determined by placing the detector D just above the unloaded cell while adjusting the x-y position of the translation stage.

With a fluid sample placed atop the window W, the modulated laser radiation is absorbed by the sample, which generates heat that diffuses into the sapphire, causing its periodic expansion. This expansion in turn exerts a pressure on the piezoelectric ring mounted under the sapphire window, producing an ac voltage signal. Only the heat that during a single chopping period can diffuse from the sample to the window contributes significantly to the signal; this condition is the qualitative explanation for a sample depth being on the order of one thermal diffusion length. The thickness d_s of the sample does not affect the signal as long as $\mu_s < d_s$. One droplet of oleic acid or

water (thickness typically $d_s = 2$ mm) deposited on the center portion of the sapphire disk and confined within the circular edge made of silicone rubber was usually sufficient to satisfy requirements for the sample's thermal thickness and optical opacity. With samples of that thickness, no laser power could be detected with pyroelectric sensor D mounted just above the sample.

The unloaded cell produces a background signal due to (1) the surface and bulk absorption in the window material and (2) the scattered light that reaches the PZT transducer directly. This residual radiation also generates a synchronous signal by the pyroelectric effect associated with the piezoelectric one. The total background, which was stable and reproducible, represents up to 10% of the signal obtained with the sample. The raw signals were corrected (by vectorial subtraction) for the background component and then ratioed to laser intensity measured (with detector D placed in front of the cell) at each laser line. The resulting amplitudes V (expressed in units of V/W) representing the averages of three consecutive measurements were then used to further process collected data.

RESULTS AND DISCUSSION

In the theoretical section above it was shown that the measured optothermal signal must be normalized to that obtained with the calibrating substance which yields a saturated signal at the same modulation frequency as used in the actual experiment. In addition, the calibrating substance and the specimen under investigation should have comparable thermal effusivities. At visible wavelengths, it is easy to prepare strongly absorbing aqueous solutions (e.g., China drawing ink). In the infrared, however, the absorption of samples is intrinsically very high, making the choice of a calibrating substance with an even stronger absorption a difficult task.

In our specific case, an alternative procedure was followed. Instead of normalizing the signals wih respect to the saturation value, we calibrated the OW cell in terms of S signals (Eq. 6) at an intermediate value ($0 < S < 1$) using pure water of known absorption coefficient β_c (subscript c refers to the calibrating substance) as a reference specimen. The 1781-cm^{-1} laser line (absorption coefficient of water $\beta_c = 3.38 \times 10^4$ m^{-1}) was chosen for calibration.[6] At a modulation frequency of 250 Hz, the product $\beta_c \mu_c$ for water is 0.460, and according to Eq. 6 the expected optothermal signal S_c is equal to 0.260. Using the same Eq. 6, one can compare two different samples, so that the following expression for water (V_c, S_c) and oleic acid (V_o, S_o) holds true:

$$S_o/V_o = S_c/1.084 V_c. \tag{7}$$

A factor of 1.084 was used here to correct for a difference in effusivities between water and oleic acid, as mentioned above. From experimentally obtained values for V_o and V_c at 1781 cm^{-1} and by means of Eq. 7, one obtains $S_o = 0.180$. The inversion of Eq. 6 yields

$$\beta_o \mu_o = 2[(2S_o^{-2} - 1)^{1/2} - 1]^{-1}, \tag{8}$$

giving $\beta_o \mu_o = 0.294$, from which $\beta_o = 2.45 \times 10^4$ m^{-1}. The values for β_o' at other CO laser lines were computed from signals V_o' via
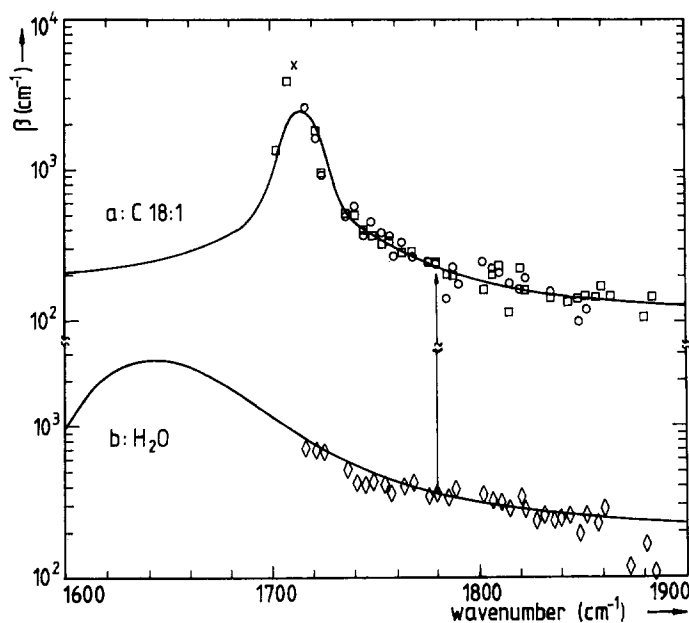
FIG. 3. Experimental results for absorption coefficient β (cm^{-1}) at CO laser lines; oleic acid (a) at 250 Hz (squares) and 600 Hz (circles), and water (b) at 250 Hz. Solid lines show the absorption spectrum of oleic acid (a) recorded by means of the classical spectrophotometer, and the β spectrum of water (b) constructed from literature data.[6] The OW cell was calibrated at 1781 cm^{-1} wavenumbers with water as a reference.

$$S_o'/V_o' = S_o/V_o \qquad (9)$$

and by using Eq. 8 again. The results for oleic acid at the modulation frequency of 250 Hz are plotted in Fig. 3a (squares), together with another series of measurements made at 600 Hz (circles). The normalization factor N (see Eq. 6) for measurements carried out at 600 Hz was determined from the condition that values of β_o at 250 Hz and 600 Hz should coincide at 1781 cm^{-1}. As expected, the laser optothermal spectrum is not influenced by the modulation frequency. The spreading of experimental results is due to the fact that the measurement of optothermal signals and of laser intensity at each line could not be performed simultaneously.

The solid line in Fig. 3a is the absorption spectrum of oleic acid recorded with a conventional Philips PU9706 infrared spectrophotometer (resolution 3 cm^{-1}) after the natural logarithm of the transmittance spectrum was taken. According to Eq. 1 the latter is proportional to the β spectrum. The cell comprised two IR windows without the spacers, so that exact optical pathlength could not be specified. The proportionality constant N in Eq. 6 is unknown, and therefore the spectrum was translated in the vertical direction to achieve the best fit, with experimental points in a wavelength range outside the peak region (between 1740 and 1880 cm^{-1}). The conventional and laser optothermal spectra indicate qualitative similarity. However, in the classical spectrum, the peak between 1690 and 1730 cm^{-1} is lower and broader than the optothermal peak, which is probably due to the high monochromaticity of laser radiation used in the latter study. The apparent shift towards lower wavenumbers of the optothermal peak might also be an artifact due to the lack of a sufficient number of laser lines in this region. To check for the reliability of these results, we also recorded the

absorption spectrum of oleic acid using a Bio-Rad 7 FT-IR spectrophotometer (resolution 4 cm^{-1}). Counting of interferometric fringes observed with an empty cell (consisting of two KBr windows) gives a 12-μm cell pathlength. An absorbance $A = 2.75$ at 1711 cm^{-1} was measured (when the same cell was loaded with oleic acid), yielding $\beta_o = 5.28 \times 10^5$ m^{-1} (the point marked by × in Fig. 3). However the FT-IR data for absorbances exceeding the value of 2 are thought to be subjected to extensive errors. The maximum value for oleic acid determined by the optothermal method is $\beta_o = 3.84 \times 10^5$ m^{-1} at a slightly different wavenumber (1708 cm^{-1}). Again, the insufficient number of laser lines does not allow for definite conclusions.

Figure 3 compares measured data for pure water obtained at the CO laser lines with an OW cell to an absorption spectrum (solid line) of water from a reliable literature source.[6] The agreement is satisfactory between 1717 and 1860 cm^{-1}, but the three points in the vicinity of 1880 cm^{-1} are obviously wrong (the cause for this result is probably the low laser power available on these lines). The vertical arrow at 1781 cm^{-1} indicates (as explained before) the experimental value chosen for calibration in measurements with the oleic acid. Because of the unavailability of the laser emission below 1700 cm^{-1} (this range becomes accessible only when the temperature of the laser cooling jacket is lower than 173 K), it was not possible to determine the value of β associated with the O–H deformation band of water at 1645 cm^{-1}.

The range of experimentally obtained β values is marked on the theoretical calibration curves in Fig. 1. Inspection of this figure suggests that experimental parameters (modulation frequency in the first place) were properly selected; that is to say, the best compromise was attained between the linearity, high sensitivity, and avoidance of signal saturation.

CONCLUSION

This paper deals with an application of the optothermal window (OW) method, a variant of photoacoustic spectroscopy. Its main objective was to provide a measurement of absolute absorption coefficient β for optically dense fluids. A tunable CO laser source was used in this study. For realization of the full benefit of this new method, investigated samples (oleic acid and water) should be homogeneous, nonscattering, optically opaque, and thermally thick, and must in addition make a good thermal contact with a sapphire window. A linear correlation between optothermal signal and β exists when the thermal diffusion length μ in the sample (at the given modulation frequency) is shorter than the inverse of the absorption coefficient $1/\beta_s$. Unlike the case of traditional infrared transmission spectroscopy, where the thickness is a restrictive factor in dealing with strongly absorbing samples, the effective optical pathlength $\beta\mu$ in the optothermal approach is determined also by the modulation frequency $[\mu = (k/\pi\rho cf)^{1/2}]$, thus allowing for reasonably more flexibility.

Experimentally found values of absorption coefficients for oleic acid C18:1 ($\beta_{max} = 3.84 \times 10^5$ m^{-1}) and water ($\beta_{max} = 7.00 \times 10^4$ m^{-1}) in the region of the CO laser are in agreement with results obtained by other methods. The

accuracy of the results depends in the first place on the β value for water used for calibration purposes. It should be noted that optimization for the $\beta\mu$ product through the control of the modulation frequency is of essential importance for quantitative interpretation of the results. Satisfactory measurements could be performed for $0.1 < \beta\mu < 3$; the amplitude of the optothermal signal was high enough but far from being saturated. Contrary to traditionally used closed and thin cells, the optothermal window cell is open, simple to clean, has no dead volumes, and enables easy recovery of sample. The method can easily be extended to other substances and wavelengths provided that the excitation of sample can be achieved and the transparency of the window in the spectral region of interest is guaranteed. Work is now in progress to develop a new, low-cost, dedicated optothermal device with a ZnSe (instead of sapphire) window, which would allow measurements at CO_2 laser wavelengths and possibly could be used as a potential candidate instrument to determine the amount of *trans* fatty acids in margarine and to control the degree of adulteration in edible oils.

ACKNOWLEDGMENTS

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