

The Absorption Behavior of Water and Some Organic Liquids in the Near Infrared Studied by Photoacoustic Spectroscopy

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The optical absorption of water and some organic liquids [CH_3OH , CH_3OD , CD_3OD , $\text{C}_2\text{H}_5\text{OH}$, $\text{C}_4\text{H}_9\text{OH}$, $(\text{CH}_3)_2\text{CO}$, $(\text{C}_2\text{H}_5)_2\text{O}$ and C_6H_6] has been investigated in the near infrared by photoacoustic spectroscopy. Characteristical absorption bands of combinations and overtones of strong infrared fundamental vibrations are observed and can be used for qualitative analysis of these liquids. The amplitude of the photoacoustic signal shows an f^{-1} -dependence of the modulation frequency f of the incident light for all absorption signals, except for the hydroxyl absorption bands of water and the alcohols. The deviation of the expected frequency dependence points to a modification of the liquid structure toward the surface of the liquid-gas boundary.

Introduction

Since its rediscovery, photoacoustic spectroscopy (PAS) has attracted considerable interest as an analytical technique for the investigation of liquids [1–6]. The applications are, e.g., measurements of optical absorption coefficients from weakly absorbing solutions and liquids in the visible region of the light [2, 3] or, by extending PAS to the near infrared (NIR), the determination of moisture in solid materials [7, 8], as well as the possibility to observe fingerprint spectra [1, 5] and thus to examine surface properties of solid matter [6].

The absorption bands observed in the NIR ($\lambda \approx 750 \text{ nm}$ to 2500 nm) correspond to overtones and combinations of strong infrared fundamental vibrations of the molecules, and of their functional groups. The overtone and combination bands of the stretching and deformation vibrations, most commonly examined in the NIR, are those of carbon-hydrogen groups (C–H), oxygen-hydrogen groups (O–H) and of the carbonyl group (C=O).

In this paper, firstly we report on the optical absorption behavior of some alcohols, acetone, diethylether and benzene in the NIR with PAS. These results are similar to those obtained with other spectroscopic methods. Secondly, we present studies on water and the alcohols by observing the frequency dependence of the PA-amplitude of different absorption bands. This depth-profiling reveals a

structural modification in a region near the surface of the liquid-gas boundary for those liquids that form associates through hydrogen bonds between their hydroxyl groups.

Experimental

Apparatus: The photoacoustic (PA)-spectra were recorded using an EG & G-PAR Model 6001 photoacoustic spectrometer. The light source employed was a 1 kW high pressure Xe arc lamp, which allows to record spectra from 200 nm to 2600 nm. Light modulation over the frequency range of 10 Hz to 2 kHz was accomplished by electronic modulation of the lamp-current. The sample cell was made of stainless steel with a rectangular (4 mm \times 8 mm \times 2 mm) sample cup. An f^{-1} -dependence (f : modulation frequency) was found using carbon black as sample. The PA-signal was detected by a sensitive microphone (Brüel & Kjær type 4166) and “source-compensated” by a real-time signal, derived from a pyroelectric detector which was exposed via a fused silica beamsplitter to a fraction of the incident light beam.

Procedure: All samples were examined at room temperature (295 K) in the spectral range from 800 nm to 2600 nm. The transmitting gas in the non-resonant cell was air at atmospheric pressure. The sample-gas system was in thermodynamic equilibrium. To test reproducibility, up to ten single measurements with new fillings of the substance were carried out. If necessary several scans were

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averaged to improve the signal to noise ratio. The liquids used were generally of best grade obtainable (pro analysis, or rather spectrograde in sealed ampules, E. Merck GmbH, Darmstadt, Germany), and used without further purification.

Results and Discussion

To investigate the frequency dependence of the PA-amplitude we first determined the position of characteristic absorption bands of the liquids by examining the absorption behavior of the liquids in the NIR.

1. Vibration Spectra of Functional Groups

Alcohols: From the spectroscopic point of view, organic hydroxy compounds can be regarded as derivatives of water, formed by substitution of a hydrogen atom with an organic radical. Therefore they show, in analogy to water, the frequencies of the functional O–H group perturbed by the vicinity of the organic radical. Consequently, the characteristic features in their NIR spectra are overtones and combinations of the stretching and deformation modes of the O–H and the C–H groups. For alcohols, the first and second overtone of the O–H stretching vibration should occur at about 1.4 μm and 0.9 μm , respectively, whereas the combination band appears at about 2.1 μm [9–13]. The fundamental C–H stretching vibration gives rise to an absorption band at about 3.3 μm to 3.5 μm , and the first and second overtone at about 1.7 μm and 1.2 μm , respectively [9–13]. Another band with relatively high intensity exists near 2.3 μm , which belongs to the second overtone of the carbon-hydrogen “bending” vibration at about 6.9 μm [10, 12, 13].

The PA-spectra of methanol and ethanol are shown in Figure 1. The first overtone of the free hydroxyl stretching vibration is observed at 1394 nm (1399 nm) for methanol (ethanol), and the second overtone at 961 nm (964 nm). This is confirmed for methanol, e.g., by comparison of the spectrum to that of methanol- d_1 (the hydrogen of the O–H group is substituted by a deuterium atom) (Figure 2). The first overtone of the O–D stretching vibration occurs at 1870 nm, i.e., the peak is shifted by a factor 1.34 towards longer wavelengths

relative to that of the O–H stretching overtone. This result is in agreement with the value 1.339, obtained by spectrophotometrical investigations of the vibrational isotope effect in the NIR [13]. For methanol (ethanol) the first and second overtone of the C–H stretching vibration are observed at 1704 nm (1715 nm) and 1199 nm (1202 nm), respectively. The results of the studies on the vibrational isotope effect on the C–H group of methanol (Fig. 3) help to confirm the assignments of the C–H stretching vibrations. The absorption band of the first C–H stretching overtone of methanol (1704 nm) is shifted to 2258 nm for methanol- d_4 (CD_3OD). The absorption bands of methanol and ethanol in the wavelength region of ca. 2300 nm to 2600 nm (Fig. 1) are due to C–H combination vibrations [12, 13]. The matching combinations of C–D vibrations, however, would be outside the region of observation (above 2600 nm). The absorption bands in the range from about 1900 nm to 2200 nm correspond to O–H, C–H and C–O combination vibrations [10, 13]. Table 1 summarizes the

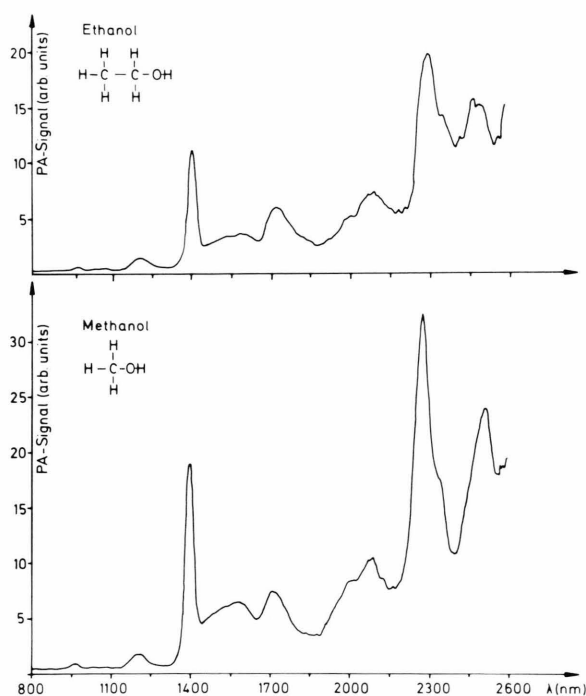


Fig. 1. PA-Spectra of methanol and ethanol (60 μl liquid, resp.); modulation frequency 37 Hz. For positions and assignments of the absorption bands see Table 1.

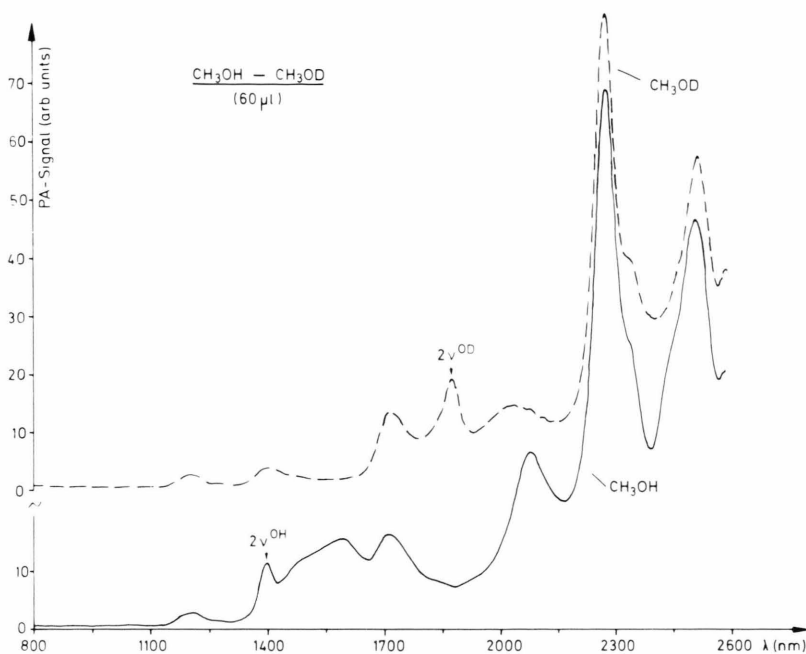


Fig. 2. PA-Spectra of methanol and methanol- d_1 in the NIR; modulation frequency 13 Hz. (The differences in the signal amplitude of methanol at about 1400 nm in Fig. 1 and Fig. 2 is due to the different modulation frequencies used and will be discussed in the text.)

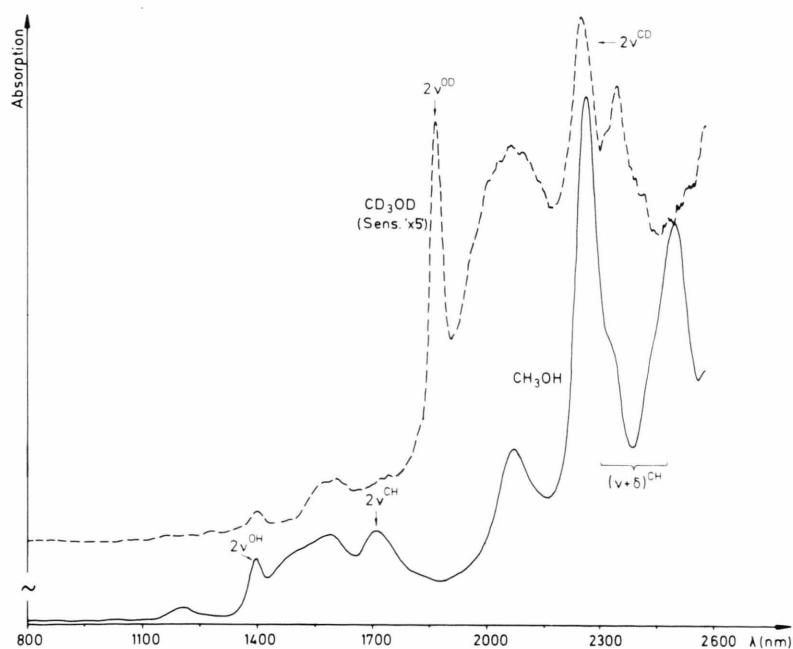


Fig. 3. NIR spectrum of methanol and methanol- d_4 by PAS (60 μl liquid); modulation frequency 13 Hz.

positions of the absorption bands observed and their assignment to overtone and combination vibrations of corresponding characteristic groups of the investigated alcohols. The similarity in the spectra of the different alcohols in the absorption

range 800 nm to 2200 nm is evident, while differences can be observed in the absorption region of C-H combination vibrations (ca. 2300 nm to 2600 nm) because of the increasing number of methylene and methine groups.

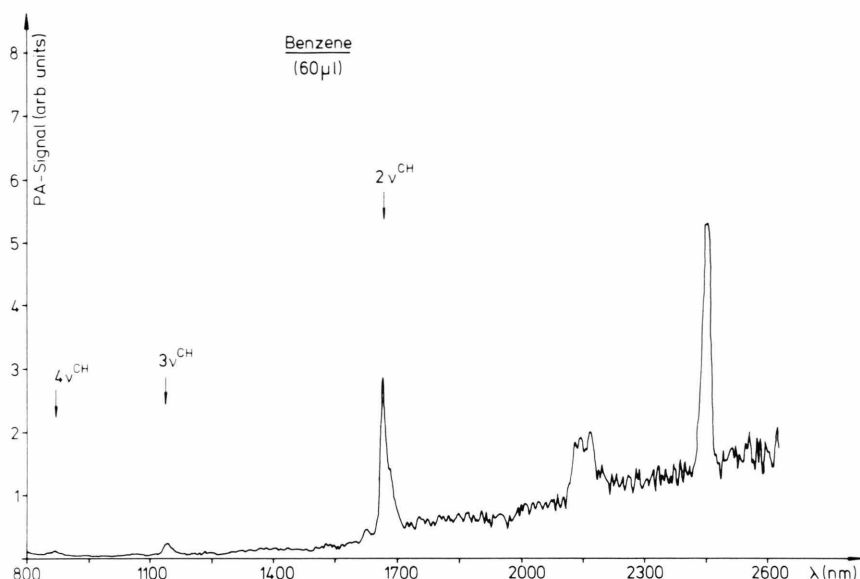


Fig. 4. The overtones $n\nu^{\text{CH}}$ and combination bands of benzene in the NIR (60 μl liquid); modulation frequency 37 Hz. Spectral bandwidth: 8 nm.

Table 1. Wavelengths of the observed positions ($\lambda_k \pm 4$) nm or regions of absorption bands for some alcohols and the assignment to corresponding overtone and combination vibrations of functional groups of the alcohols [1, 5, 9–13].

methanol	961	1199	1394	1704	from	from
ethanol	964	1202	1399	1715	about	about
1-propanol	969	1207	1401	1722	1900	2200
2-propanol	968	1193	1403	1714	to about	to about
1-butanol	968	1208	1400	1727	2200	2600
assignment	$3\nu^{\text{OH}}$	$3\nu^{\text{CH}}$	$2\nu^{\text{OH}}$	$2\nu^{\text{CH}}$	OH, CH and CO combination vibrations	CH combination vibrations

In order to obtain further information about peak positions of carbon-hydrogen vibrations in hydroxyl-free organic liquids in the NIR we also examined *diethylether* and *acetone*. The absorption band of the first overtone of the C–H stretching vibration occurs for diethylether as well as for acetone at about 1700 nm. Similar to the alcohols case, the combinations of the fundamental carbon-hydrogen vibrations are observed for both liquids in the spectral range 2300 nm to 2600 nm. The spectrum of acetone shows a further absorption band at about 1913 nm due to the second overtone of the C=O fundamental stretching vibration [11].

Benzene: The fundamental stretching vibration of the carbon-hydrogen bond of an aromatic ring gives rise to a band at lower wavelengths (about 3.27 μm) than those of saturated bonds. The same behavior is shown by the overtones. Figure 4 shows, e.g., the PA-spectrum of benzene in the NIR. Besides the first, second and third overtone of the C–H stretching vibration, the spectrum contains two absorption bands at 2155 nm and 2450 nm, which can be assigned to C–H combination vibrations [1, 5, 12]. The peak positions λ_n of the n -th stretching overtone $n\nu^{\text{CH}}$ are in rather good agreement with the results of Patel et al. [14]. They determined the positions of the C–H overtone $n = 1$ to $n = 5$ of benzene by conventional spectrophotometry and obtained: for $n = 2$: (1671.4 ± 0.6) nm, for $n = 3$: (1141.6 ± 0.3) nm and for $n = 4$: (874 ± 0.2) nm. The values obtained in the present work are: for $n = 2$: (1671 ± 1) nm, for $n = 3$: (1142 ± 1) nm and for $n = 4$: (876 ± 3) nm.

II. The Frequency Dependence of the PA-amplitude for Water and Organic Liquids in the NIR

The PA-signal is determined by the optical absorption and the thermal diffusivity of the sample. Therefore, PAS can be utilized to obtain optical absorption spectra. In addition, it is possible to obtain a depth-profile analysis of the optical prop-

erties of a substance by varying the modulation frequency f of the incident light. Thereby, the thermal diffusion length $\mu_s = 1/a_s$ varies, where a_s is the thermal diffusion coefficient of the sample, given as $a_s = (\pi f/\alpha_s)^{1/2}$ with α_s the thermal diffusivity of the sample (subscript s). As pointed out by Rosencwaig et al. [15], the PA-signal amplitude varies as $f^{-3/2}$, for thermally thick and optically transparent (weakly absorbing) materials. In our case, however, an f^{-1} -dependence is observed (Fig. 5) for the two wavelengths of the C–H absorption bands in the case of methanol and benzene in the NIR. This frequency dependence can be explained with the so called “composite-piston” model, developed for the first time by McDonald et al. [16] and re-elaborated by Rosencwaig [2]. In a recently published paper Korpiun [17] also reports on an experimentally observed f^{-1} -dependence for the PA-signal amplitude. With the assumption of an opaque sample ($\beta/a_s > 1$), the author shows that this frequency dependence can be described if in addition to the periodically varying diffusion of heat a contribution of an oscillating mass transfer from the sample to the pressure variation in the gas is considered.

The f^{-1} -dependence of the PA-signal amplitude of liquids proves to be valid on alcohols for the C–H absorption bands only. The O–H absorption bands of the alcohols and of water reveal, however, a different frequency dependence (Fig. 8 and Figure 9).

Water, as well as the alcohols, forms associates through hydrogen bonds between the hydroxyl

groups. In concentrated solutions the formation of the associates results in a displacement of the fundamental stretching vibration. It is a well known fact that at low concentrations of the liquid a single sharp band is observed, which can be assigned to the free hydroxyl. As concentration increases, a diffuse polymer band appears at a slightly longer wavelength, whereas the absorption at the wavelength of the sharp band increases very slowly. Similar effects are observed in the case of overtones [12, 13, 18]. We also studied this phenomenon using PAS to determine the positions of the monomeric and polymeric hydroxyl absorption bands of water and the alcohols, by diluting the liquids with carbon tetrachloride.

We especially examined the first overtone absorption bands of the free and H-bonded hydroxyl vibrations of water and the alcohols as pure liquids, by varying f . A variation of f between 10 Hz and 2 kHz decreases the thermal diffusion length from about 50 μm (60 μm) to about 4 μm (5 μm) for methanol (water). For methanol (Fig. 6) at $f = 13$ Hz a sharp absorption band (monomers) at 1394 nm and a more diffuse band (associates) about 1550 nm are observed. The latter band decreases considerably, relative to that of the monomers, with decreasing thermal diffusion length μ_s . Equivalent results were obtained for ethanol, propanol and butanol. Water shows a relatively broad absorption band at about 1460 nm (Fig. 7) for $f = 13$ Hz. This band can be ascribed to the absorption of the hydrogen bonded water associates [13, 19] (Polymer in Figure 9). At

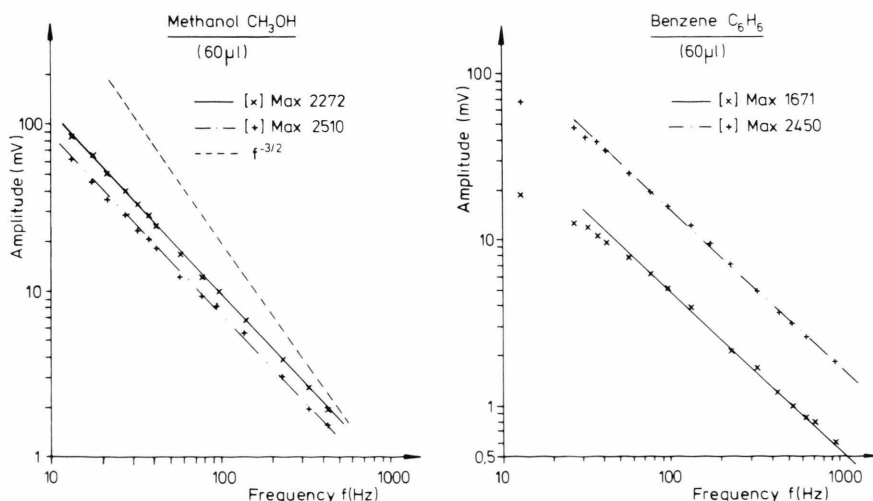


Fig. 5. The amplitude of the C–H absorption bands of methanol and benzene in the NIR as a function of the modulation frequency f ; Max 2272 and Max 2510 correspond to the positions of the absorption band of the C–H combinations of methanol; Max 1671 marks the position of the first overtone and Max 2450 of the combinations of the C–H fundamental vibrations of benzene; the dashed line indicates an $f^{-3/2}$ -dependence.

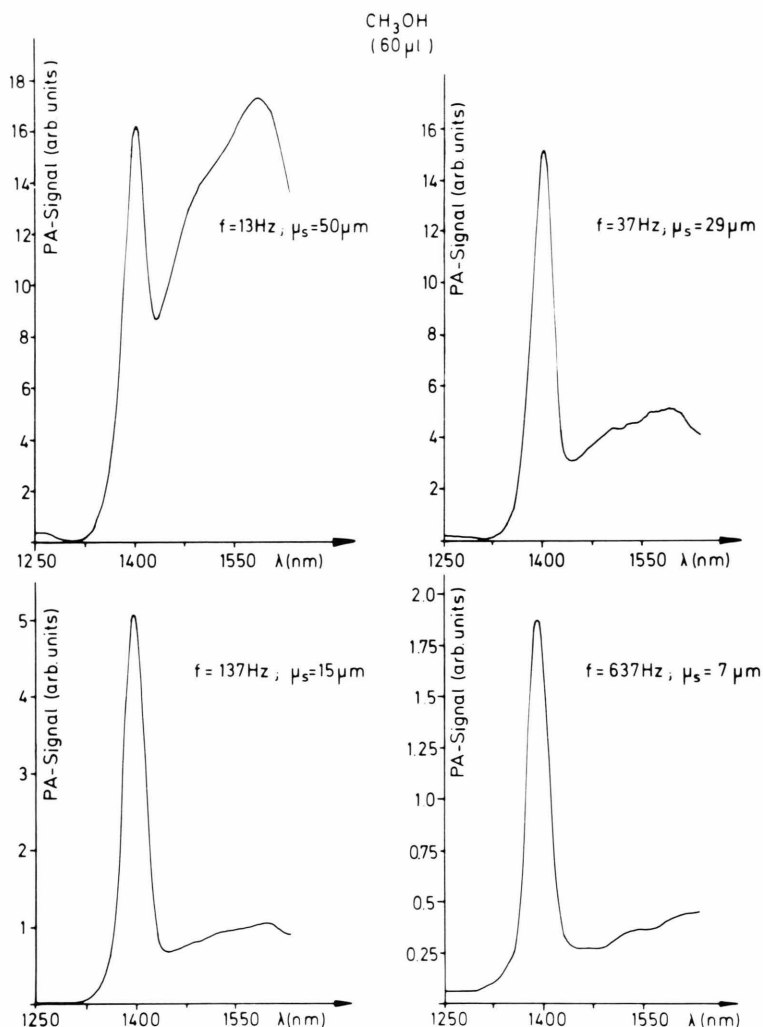


Fig. 6. The PA-signal of the first overtone of the hydroxyl vibration of methanol at different modulation frequencies f of the incident light, as written on each diagram. μ_s is the thermal diffusion length in the liquid.

higher f a shoulder at the short-wave side of the hydroxyl absorption band appears (Fig. 7), which grows with increasing f , i.e., decreasing μ_s . For $f = 937$ Hz ($\mu_s \approx 7$ μ m) the band at 1460 nm appears as a small shoulder on the long-wave side of a relatively small absorption band at about 1386 nm. The latter band can be assigned [9, 10, 13] to the absorption of the monomer species of water (Monomer in Figure 9).

For thermally thick and optically transparent samples the PA-signal reflects the absorption behavior of the material in a region that is determined by the thermal diffusion length μ_s . Increasing modulation frequency means decreasing μ_s , and for the PA-signal amplitude an f^{-1} -dependence should

be valid. The absorption of the “free” and H-bonded hydroxyls of water and the alcohols, however, exhibits a deviation of this frequency dependence (Fig. 8 and Figure 9). Therefore, we conclude from our investigations that water and the alcohols (liquids which show association to polymer-like structures through hydrogen bonds) reveal a structural modification from the inside of the liquid toward its surface.

A possible contribution from an absorption of the liquid vapor in the gas volume within the optical pathway above the liquid can be neglected. This was tested by creating a vapor pressure of the respective liquids, with the liquid itself in a non-illuminated zone of the sample cell. For methanol,

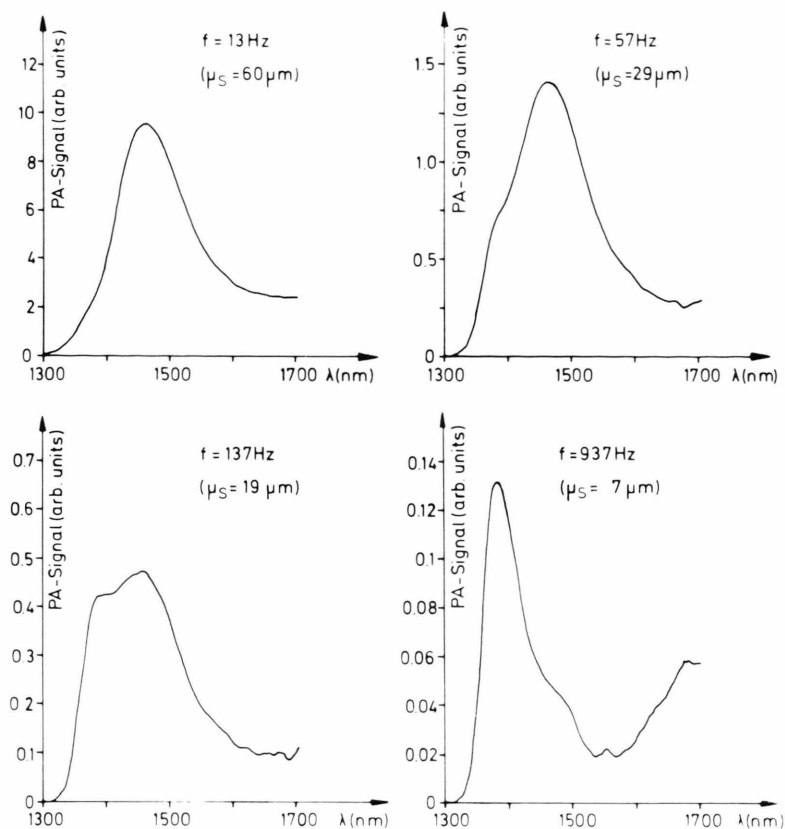
first overtone $2\nu^{\text{OH}}$ 

Fig. 7. The PA-signal of the first overtone absorption band of the hydroxyl vibration of water at different modulation frequencies f , as written on each diagram.

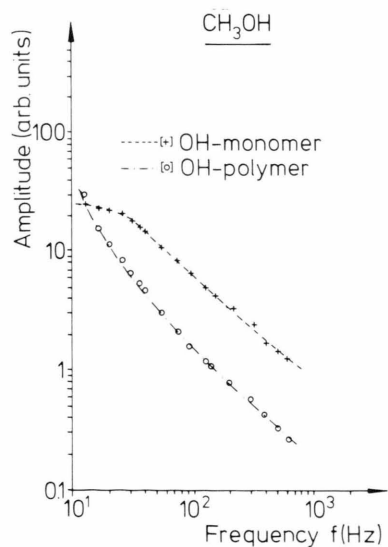


Fig. 8. PA-amplitude of the hydroxyl overtone absorption of methanol in the NIR as a function of modulation frequency f ; OH-monomer and polymer correspond to the absorption band of the first overtone of the hydroxyl vibration of "free" and through hydrogen bonds associated hydroxyls, resp.

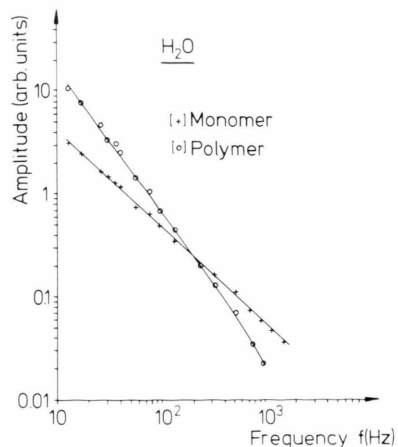


Fig. 9. Dependence of the PA-amplitude of the hydroxyl overtone of water on the modulation frequency f ; Monomer ($\lambda \approx 1386$ nm) and polymer ($\lambda \approx 1460$ nm) assigns the absorption band of the "free" and hydrogen bonded water molecule, resp.

the liquid with the highest vapor pressure at room temperature of those used, a remarkable contribution from an absorption in the vapor could only be observed by, at least, a 100-fold increase of the sensitivity necessary for the measurements on liquid methanol. For butanol and water, the liquids with the lowest vapor pressure of those used at the prevailing temperature, no contribution from an absorption in the vapor could be detected. With substances like Cetyl-, Miristyl- and Lauryl alcohol spread on the surface of water, which decreases the vapor pressure on the top of the interface, the same absorption behavior of the hydroxyl group was observed.

Conclusions

PAS can be used in the NIR for the identification of different organic liquids. Accurate assignment of overtone and combination absorption bands from characteristic groups, such as O-H, C-H, C=O,

permit the use of PAS as a qualitative analytical tool. A quantitative determination of physical data of the liquids investigated, e.g. of absorption coefficients or thermal properties, requires additional knowledge about the PA-effect itself and of standard samples.

Furthermore, the investigations in the NIR have shown that the PA-amplitude of liquids reveals an f^{-1} -dependence of the modulation frequency f of the incident light, except in the case of the hydroxyl absorption bands of water and the alcohols. The deviations in these cases point to an increase of the monomers and a decrease of the polymer-like structure of these liquids toward the liquid-gas boundary. Further investigations on this subject are in progress.

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