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FOURIER TRANSFORM INFRARED PHOTOACOUSTIC SPECTROSCOPY OF CONDENSED PHASES

B. S. H. ROYCE and Y. C. TENG
APPLIED PHYSICS and MATERIALS LABORATORY, PRINCETON UNIVERSITY,
PRINCETON, NEW JERSEY 08544 USA.

Photoacoustic spectroscopy provides a method of obtaining optical information about samples that are hard to prepare as transparent films, which have high internal light scattering or which are coated onto opaque or strongly light scattering substrates. The method is normally detector noise limited and so benefits from the use of higher powered light sources. In the infrared spectral region high powered sources tunable over a wide spectral range are not generally available and techniques must be found which obtain the maximum benefit from thermal sources such as globars. The Fourier Transform spectrometer provides a suitable approach to extending PAS measurements into the infrared spectral region between about 4000 and 400 cm^{-1} and this method has recently been employed by a number of groups to study gas phase [1] or solid and liquid [2-4] samples. This paper is concerned with a discussion of procedures required to make FTIR-PAS spectroscopy quantitative and examples of PAS spectra obtained from surface groups on 120Å SiO_2 powders and highly light scattering RTV polymers.

In an FTIR-PAS experiment the photoacoustic cell, which contains the material to be studied, is placed in the sample compartment of the spectrometer and replaces the instrument's detector. The sample is exposed to the full radiation output from the interferometer and consequently sees a range of modulation frequencies which depend upon both wavenumber and the mirror velocity. This means that the effective photoacoustic sampling depth, the thermal diffusion length in the sample, is wavenumber dependent and the PAS signal contains this thermal information as well as the information about the sample's optical properties. For a mirror velocity on the order of 0.06 cm sec^{-1} the effective optical modulation frequency range extends between 50 and 500 Hz and the sampling depth will therefore vary between about 40μ and 10μ. It has been found advantageous to electronically filter the cell output sharply (18 dB per octave) outside this frequency range to reduce the effect of environmental noise on the interferogram and to use a non-resonant photoacoustic cell.

The interferogram has the form normally associated with an emission spectrum because the sample in the PAS cell is a selective absorber and the "central burst" feature of the interferogram is also smaller than that obtained with a black absorber due to the lower total energy absorption. When the interferogram is Fourier transformed an uncorrected absorption spectrum of the sample is obtained. This has peaks located at the correct wavenumber but their relative amplitudes are not the same as those that would be obtained in a transmission spectrum since they are dependent upon the spectral output of the light source and upon the thermal diffusion length which changes across the spectral region studied. The spectral output of the light source is best accounted for by replacing the sample with a black absorber and recording the amplitude response of the PAS signal. Since the black absorber is operating in the saturation region of the PAS signal the response is just proportional to the energy absorbed at each wavenumber. Dividing the sample spectrum by the black body response partially corrects the spectrum but the thermal absorption depth change must still be accounted for. Teng and Royce [5] have pointed out that since a systematic frequency change can be made over the complete wavenumber range by changing the velocity of the Michelson interferometer mirrors, a comparison of the normalized spectra obtained at two different mirror velocities enables a correction to be made for the thermal diffusion depth. Peak height ratios that are in good agreement with transmission data can therefore be obtained. Fig. 1 shows the results of this procedure applied to the PAS spectrum of poly-(methylmethacrylate).

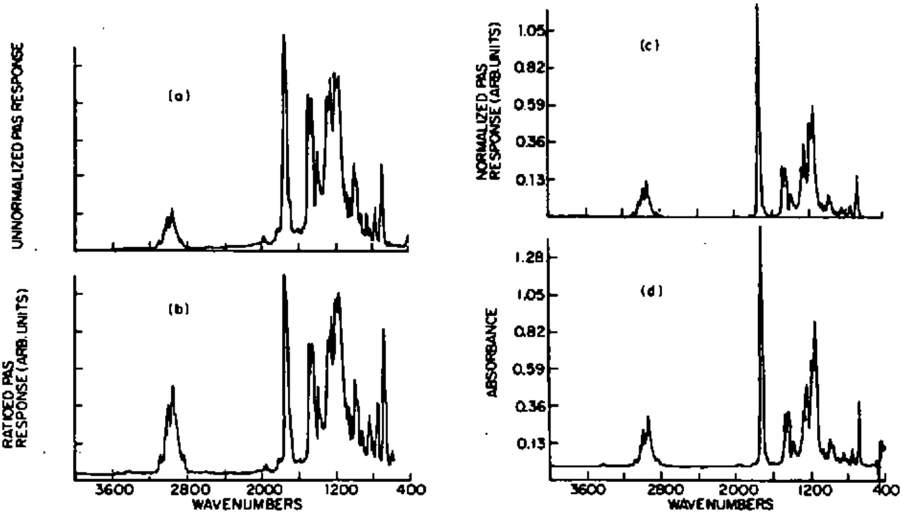

Fig. 1 Normalization procedures: a) Unnormalized, b) Ratioed to black body, c) Two velocity normalization, d) Transmission spectra.

Fig. 1a shows the unnormalized spectrum given by Fourier transforming the interferogram. Ratioing this spectrum with the corresponding response of a black absorber gives the spectrum shown in 1b. Peaks in the spectral region of 3000 cm^{-1} have been increased in size due to the low light output in this region while those in the region of peak spectral output (circa 1500 cm^{-1}) are reduced in size. A comparison of this ratioed spectrum with the transmission spectrum of 1d shows that this procedure is inadequate for quantitative PAS measurements as peak heights differ between the two spectra by as much as a factor of two. Using the two velocity procedure of [5] the spectrum shown in 1c is obtained. This is in much better agreement with the transmission spectrum with peak heights agreeing to better than 20%.

The samples used for the above measurements were in the form of thin solid films and consequently closely approximate the one dimensional system modelled in [5]. However, one of the interesting features of PAS is its ability to obtain spectra from powdered samples. The method of reference [5] has been applied to samples of this type but has been found to yield poor results. It is believed that this is due to the high light scattering of these powders which alters the energy distribution profile predicted by the one dimensional theory and also to the complex thermal conduction properties of the powder compared to the homogeneous absorber of the model. Quantitative FTIR-PAS of powders therefore seems to offer a challenge to both theoretical and experimental workers.

To illustrate the use of FTIR-PAS to study highly light scattering systems a problem concerning a polymeric matrix loaded with a powdered silica filler material will be discussed. Materials of this type are of importance as inert encapsulating compounds for microelectric components and both the initial surface condition of the filler material and the bonds in the cured loaded polymer are of interest. Both of these problems can be tackled using the photoacoustic method although, as discussed above, the results are currently only qualitative.

In preparing an SiO_2 material for use as a filler in a polymeric matrix a material such as $SiCl_4$ may be reacted with hydrogen and oxygen to yield particles of SiO_2 and HCl gas. The SiO_2 so produced has some OH groups attached to its surface and groups of this type may act as chain terminators in the polymerization reaction of a matrix material such as RTV. The surface of the SiO_2 may be made less active by reacting with hexamethyldioxane after which the hydroxyl groups are replaced by methyl groups on the surface as $Si(CH_3)_3$. Such a surface no longer interacts with the polymerizing molecules to terminate the chains. Fig. 2 shows an FTIR-PAS spectrum of both activated and deactivated SiO_2 powder prepared in the manner outlined above. The powder size is on the order of 120Å diameter. This material gives a very strong PAS signal and comparison between the two spectra clearly indicate a reduction in the surface OH content and bands due to CH_3 groups at circa 3000 and 1400 cm^{-1} in the deactivated material. Fig. 3 shows an FTIR-PAS spectrum of an RTV silicone rubber loaded with SiO_2 powder of the type just discussed together with TiO_2 which acts as an opaque white pigment. Conventional reflectance and transmission measurement are unable to provide an IR spectrum of the rubber whereas it is seen that the PAS method yields clearly resolved spectral features all of which correspond exactly to bands measured in transmission for an unloaded RTV sample.

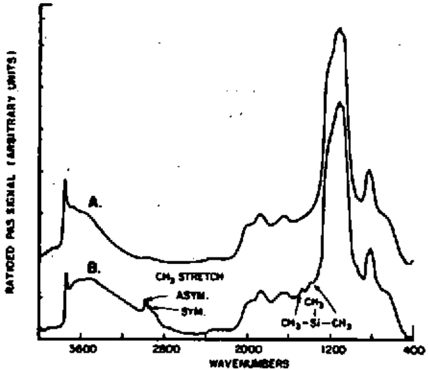

Fig. 2 FTIR-PAS Spectra of a) Activated and b) Deactivated SiO_2.

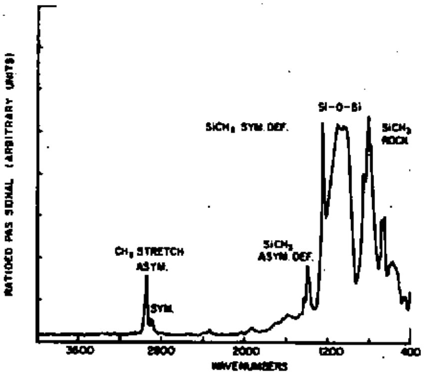

Fig. 3 FTIR-PAS spectrum of RTV rubber containing SiO_2 and TiO_2.

The spectrum of Fig. 3 does not show features due to the SiO_2 or the TiO_2 since these particles are encapsulated in a relatively thick RTV layer and their PAS response is therefore attenuated. These spectra provide the basis for a systematic study of the interaction between the SiO_2 and the RTV under various conditions of surface pretreatment and care.

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