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FOURIER TRANSFORM INFRARED PHOTOACOUSTIC SPECTROSCOPY OF SOLID SAMPLES

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The Helmholtz resonance effect of the photoacoustic cell and the effect of the thermal properties of samples in the Fourier transform infrared photoacoustic spectroscopy have been discussed. Infrared photoacoustic spectra of several kinds of polymers have been measured without troublesome sample preparations.

Although the usefulness of the Fourier transform infrared photoacoustic spectroscopy(FTIR-PAS) for opaque solid samples has been demonstrated recently,[1,2] few discussions on the characteristics of the FTIR-PAS have been made. In the present investigation, the FTIR-PAS system has been constructed and some discussions on the FTIR-photoacoustic(PA) spectral features have been made.

The PAS system was mainly based on a Digilab FTS-15 FTIR spectrometer. Infrared radiation from a nichrome wire was modulated with a Michelson interferometer(240-2400 Hz for 400-4000 cm^{-1}). The PAS system developed in our previous report[2] was modified as follows. The modulated radiation was reflected by a plane mirror to a 90° off-axis toroidal mirror which focussed the beam on to the sample in the PAS cell. The PAS cell was placed inside an acoustically insulated chamber which was set up outside a FTS-15 spectrometer. The PAS cell was machined from brass and was sealed with o-rings. Its internal volume was approximately 0.95 cm^3(11mm ∅ - 10mm depth). A KBr plate(3mm thick) was used as a cell window and a 1/2 inch B&K 4165 condenser microphone was used as a transducer. The PA signal from the microphone was amplified with a Brookdeal 9454 ac amplifier and was fed to the HgCdTe detector amplifier section of the FTIR spectrometer. All of the spectra were measured at 4 cm^{-1} resolution using 900 scans.

The carbon black(CB) PA spectrum and the source spectrum measured by a pyroelectric detector(TGS = triglycine sulfate) are shown in Fig. 1. Both of these spectra are known to be virtually identical each other in the dispersive PAS system with fixed frequency light modulation.[3] As shown in Fig. 1, the above identity is not observed in the case of FTIR-PAS where the modulation frequencies vary with the spectral frequencies(wavenumbers). This observation can be mainly attributed to the Helmholtz resonance effect of the PAS cell, since the CB PA spectral features are found to vary depending on the volumes in front of the microphone diaphragm, V_2. A good linear correlation is obtained between the resonance spectral frequencies ν_0 and $[(1/V_1)+(1/V_2)]^{1/2}$, as shown in Fig. 2, where V_1 represents the volume of the sample cavity. The observed resonance frequency(2.0 kHz) obtained by dividing the CB PA spectrum with the source spectrum presented in Fig. 1 is almost coincident with the calculted one(1.9 k

Hz) using a Helmholtz resonance formula.4) The above effect, however, can be compensated when the normalization for the sample PA spectra is carried out using a CB PA spectrum measured by a same PAS cell as a reference.

Infrared PA spectra of several kinds of polymers such as cloths, cured resins etc. have been measured. FTIR-PA spectra of cotton cloth and glass epoxy plate are shown in Fig. 3. The features of these spectra are fairly similar to those of published spectra measured by a KBr method.5) Infrared PA spectral intensities, however, have been found to be greater in the lower wavenumber regions. This result can be attributed to the thermal properties of the samples. The samples investigated in this study can be considered to be thermally thick solids for which PA signals depend on $\omega^{-3/2}$, where ω represents the modulation frequency.6) In this case further normalization must be carried out for FTIR-PA spectra by multiplying a factor of $(2V\nu)^{1/2}$ after the normalization with a CB PA spectrum, since a CB PA spectrum depends on ω^{-1} and the modulation frequencies in the FTIR-PAS vary with the spectral frequencies according to the formula, $\omega=2V\nu$, where V and ν represent the velocity of the moving mirror in a Michelson interfeometer and the spectral frequencies, respectively.7)

Although there are several factors which affect the FTIR-PA spectra, FTIR-PAS can be said to be a very attractive method for the structure elucidation of opaque organic substances as shown in Fig. 3.

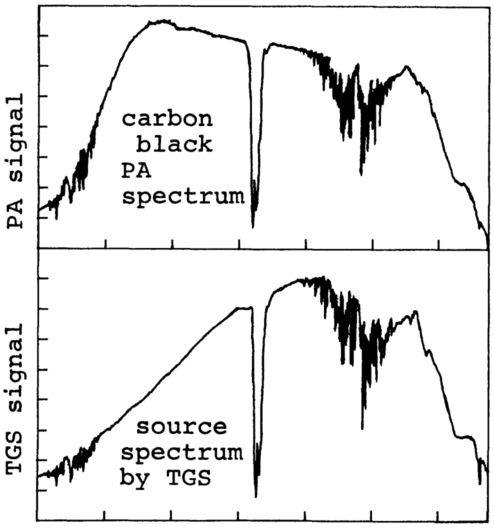

Fig.1 PA and source spectra

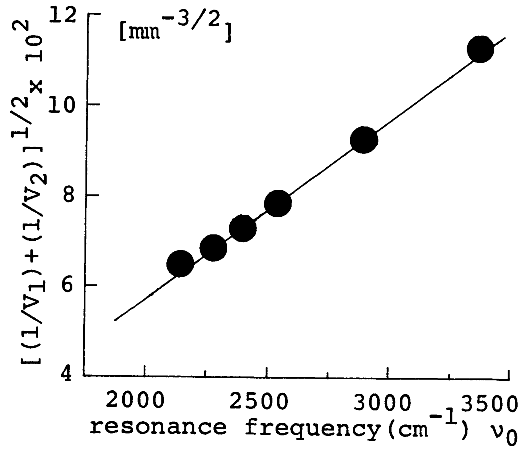

Fig.2 Correlation between ν_0 and $[(1/V_1)+(1/V_2)]^{1/2}$

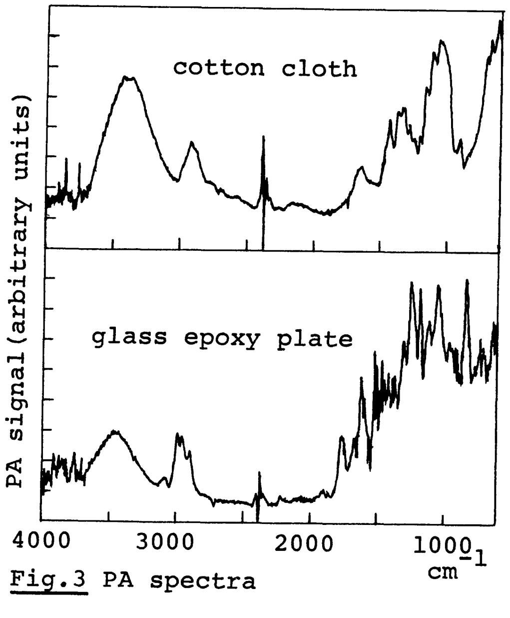

Fig.3 PA spectra

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