

Grain size effect on the spectral characteristics of CV using photoacoustic spectroscopy

T A EL-BROLOS^{a*}, S NEGM^b and H TALAAT^a

^aPhysics Department, Faculty of Science, Ain Shams University, Abbassia, Cairo, Egypt

^bPhysics and Mathematics Department, Faculty of Engineering, Zagazig University, Shoubra, Egypt

Abstract. Photoacoustic spectroscopy (PAS) offers a unique method to measure optical absorption of materials in the powder form. In this work we employ PAS to study the change in the peak absorption of the dye crystal violet (CV) in the powder form, as a function of the grain size which was carefully controlled. It is observed that as the grain size is comparable to the incident radiation wavelength, there is an increase in the blue shift with decreasing the grain size.

Keywords. Photoacoustic spectroscopy; dye crystal violet; peak absorption; grain size.

1. Introduction

Departures from bulk behaviour occur when the size of the sample becomes comparable to the wavelength of the important excitations in the solid, a phenomenon sometimes described as quantum size effect. The nature of the excitations then changes, and as a result, so does any property determined by those excitations. It is well known that there is a shift in the peak of the absorption band that accompanies the solvent from that in the solid form of the dyes. PAS is a powerful technique that permits study of absorption through detection of heat produced in samples by non-radiative relaxation processes¹. The basic idea of PAS is to place the sample to be investigated in a closed cell containing a gas or air and a sensitive microphone. The sample is illuminated by light that is modulated or chopped at audio frequencies. As a result of optical absorption the sample is heated through nonradiative transition and the heat is transferred to the gas in the cell. Since the sample heating is modulated the gas heating produces a pressure fluctuation within the cell which can be detected by the microphone as an acoustic signal. The resulting photoacoustic (PA) signal depends not only on the amount of heat generated by the sample, but also on the way heat diffuses through the sample. PAS offers the most suitable method to measure the absorption of solids in the form of powder^{2,3}. The data obtained in this way are expected to complement the information obtained from fluorescent spectroscopy. In this work we have employed the PAS technique to investigate the grain size effects on the spectral characteristics of CV in the powder form and then compared it with the spectrum of CV in the ethanol solution.

*For correspondence

2. Experimental

Two methods were used to prepare different grain size of the powdered dye CV. In the first, CV of the same molar concentration in ethanol was passed through sintered glass crucibles of different pore size. Since the pore diameter of the crucibles has a minimum limit ($1\text{--}2\ \mu\text{m}$), another method was used to produce smaller sizes of CV grains. In this method, CV of different molar concentrations were passed through filter papers (of the same porosity). In both cases the solution is left to dry on the other side of the crucibles or filter paper and then electron microscopy was employed to measure the grain size or resulting dried CV powder.

Our measurements were taken with conventional PAS setup as shown in figure 1. The light from a 1000 watt tungsten lamp is focused by a glass lens L_1 into the entrance slit of a grating monochromator to provide a tunable light source. A mechanical light chopper, (Boston Electronic) is located in front of the entrance slit of the monochromator to interrupt the incident beam and to provide the reference signal for detection. The monochromator is computerized to allow accurate scan of wavelength. The output light is focused on the sample inside the PA cell by (Princeton Applied Research Model 6003) using a camera lens L_2 . The signal from the PA cell is received by a lock-in amplifier (Stanford Research Model SR530) that is connected to PC for data collection. All spectra were taken at chopper frequency $f = 25\ \text{Hz}$ and normalized to carbon black.

3. Results and discussion

The normalized PA spectra for CV in ethanol ($10^{-3}\ \text{M/L}$) is shown in figure 2 together with the spectra for CV in powder form prepared by the first method. The average grain sizes produced on the dried side of the crucible and measured by electron microscope are 25 , 45 and $500\ \mu\text{m}$. The red shift of the peak absorption band (approx. $632\ \text{nm}$) of the dye in the powder form, from that in solution (approx. $592\ \text{nm}$) is clearly shown. There is no change in the peak position for these three sizes. It is also observed in this case that the PA signal amplitude increases as the grain size decreases. When the thermal penetration depth ($\mu_s = (\alpha/\pi f)^{1/2}$ where α is the thermal diffusivity) is small compared to the particle size, we may characterize the sample by the bulk thermal conductivity.

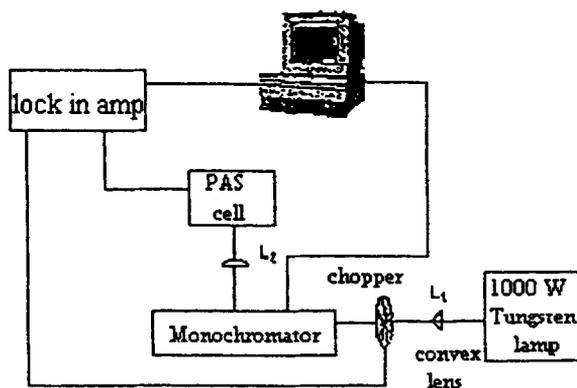


Figure 1. Experimental setup of PAS

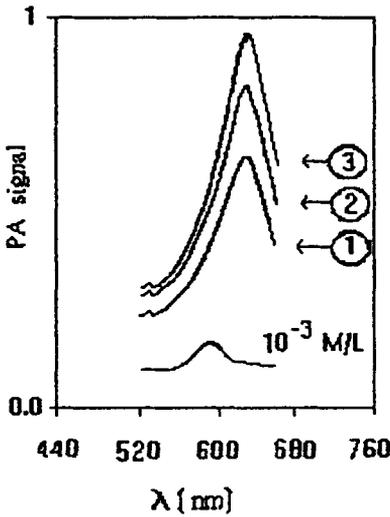


Figure 2. Normalized PA spectra of CV solution 10^{-3} M/L together with that of CV powder of grain sizes (1) $500\ \mu\text{m}$ (2) $45\ \mu\text{m}$ (3) $25\ \mu\text{m}$.

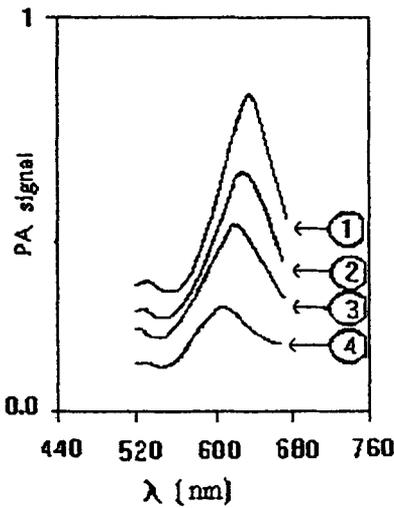


Figure 3. Normalized PA spectra of CV powder of grain sizes (1) $2\ \mu\text{m}$ (2) $0.52\ \mu\text{m}$ (3) $0.32\ \mu\text{m}$ (4) $0.18\ \mu\text{m}$.

As the particle size becomes comparable to the thermal diffusion length, this results in an enhancement in the sample gas coupling that leads to the observed increase in the PA signal. This effect continues to enhance the PA signal as the particle size becomes smaller and smaller than μ_s , and it will saturate when the particle size becomes very small compared to μ_s . In this case all the heat produced in the sample is transferred to the gas with maximum efficiency.

PA spectra for the dye grains of smaller sizes, 2, 0.5, 0.32 and 0.18 μm prepared by the second method are shown in figure 3. The decrease in the signal amplitude is due to the

decrease in the solution concentrations used in this method to obtain the (relatively small) grain size of the dye. There is also a reduction in the FWHM with decreasing the grain size. This may be understood in terms of the decreased probability in the nonradiative decay through internal conversion. The observed blue shift in the absorption peak from the large grain size starts to be observed at about $0.5 \mu\text{m}$ and gradually increases with decreasing the grain size.

Unlike molecules that have single bonds where the first excited energy can only be brought about by absorption of ultraviolet radiation, CV molecules have alternate single and double bonds. In such molecules there are p -orbitals on several neighbouring atoms that are capable of forming an extended system of π orbital (conjugated π systems). These π electrons are delocalized over the whole system and are not confined to a given atom or even to a given bond position. Consequently, the position of absorption peak for these conjugated molecules moves progressively to a longer wavelength as the size of the system increases.

In the present case, the blue shift in the absorption peak of CV particles is due to some decrease in the degree of electron delocalization that results from decreasing the particle size to be comparable to the excitation wavelength. The over simplified particle in a box view of matter leads to the same conclusion; as the size of the box decreases so does the distance between successive energy levels increase.

The importance of these results lie in the fact that one may be able to control the position of the absorption peak for the powdered dye by controlling the grain size. On the other hand, the reverse process can also be used whereby from the determination of the absorption peak of the powder dye, one can infer the size of the powder grain.

References

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