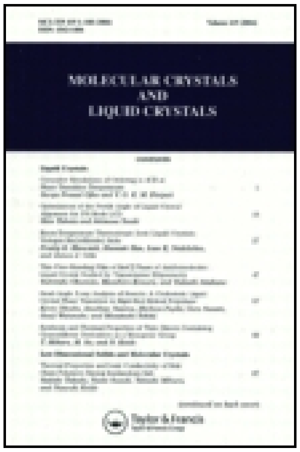

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Photothermal Deflection Spectroscopy: A Sensitive Absorption Technique for Organic Thin Films

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PHOTOTHERMAL DEFLECTION SPECTROSCOPY: A SENSITIVE ABSORPTION TECHNIQUE FOR ORGANIC THIN FILMS

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Abstract An important property of an organic film is its absorption spectrum. However, because of the short optical path length in a thin film, only very strong electronic transitions can be measured by standard spectrometric techniques. With the sensitive photothermal deflection approach it is possible to measure the absorption from transitions which can be as much as four orders of magnitude weaker than the main electronic transitions.

We have applied photothermal deflection spectroscopy to a variety of organic thin films with the thickness ranging from sub-micron to hundreds of microns. Several small molecule and polymer binding matrix systems have been studied. Some results are presented and compared with standard UV-Vis spectra.

INTRODUCTION

One of the important signatures of organic thin films is the absorption spectrum. Typically, for these films of order 1 micron thick, a UV-Vis spectrometer is used to measure the strong short wavelength electronic transitions. Additionally, FTIR spectrometers are used for the strong vibrational (IR active) transitions in the mid-to far-IR region. However, both these approaches can have their limitations in sensitivity and range. The sensitivity limit is in part due to the method of detection, namely the transmitted optical beam is subtracted from the incident beam. Thus for very weak absorption, or for very thin films, the difference is too small to resolve. In this case, a different approach must be employed. Ideally suited for this low absorption regime is the technique of photothermal deflection spectroscopy (PDS)[1] which has previously been successfully applied to inorganic thin films of amorphous silicon.[2]

EXPERIMENTAL CONSIDERATIONS

The details of PDS are described in reference 1 and the essential features are shown in Fig. 1. The basic concept is to use the sample as its own detector by measuring the optically generated heat pulse that results from the incident light. The pump beam is absorbed (weakly), non-radiative transitions heat the film and the surrounding liquid. A probe beam which skims along the surface experiences a change in the index of refraction at the film's surface and is bent away. This bending is monitored and the absorbance can be extracted. With synchronous detection, both magnitude and phase information can be obtained. One of the most important features of this approach is that it is not sensitive to scattering and so gives a measure of the true absorption. Note that if strong luminescence is present, there will be a reduction in the PDS strength, but in the materials studied this effect was negligible. It can be taken into account if necessary.

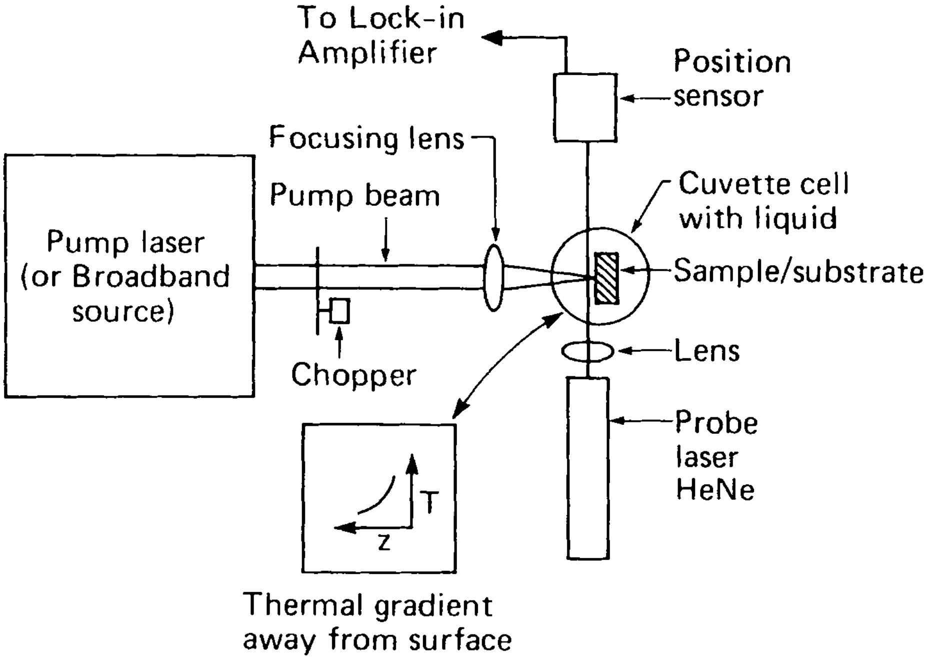

Figure 1

We have studied a wide series of organic thin films but have emphasized those used in a photoconductive context where the optical properties are of critical importance. The films consisted of a small transport molecule and a polymer binder, in combination with various proportions. The materials were dissolved in THF solvent and both spin coated and dip coated on quartz slides. The thickness varied from less than 1 micron to over 100 microns.

RESULTS

The absorption spectra were measured for films of the small molecule DEH (diethylaminobenzaldehyde dilphenylhydrazone) in a binder of polycarbonate and a binder of polyarylate. In the 300 nm to 500 nm regime the spectra are completely dominated by the transitions of the small molecule. Figure 2 shows the results and a comparison between PDS and a UV-Vis spectrometer. For the latter, a typical spectrum yields the log of the intensity decrement or in other words the optical density, OD, where $I_T = I_0 10^{-OD}$. The value of OD generally

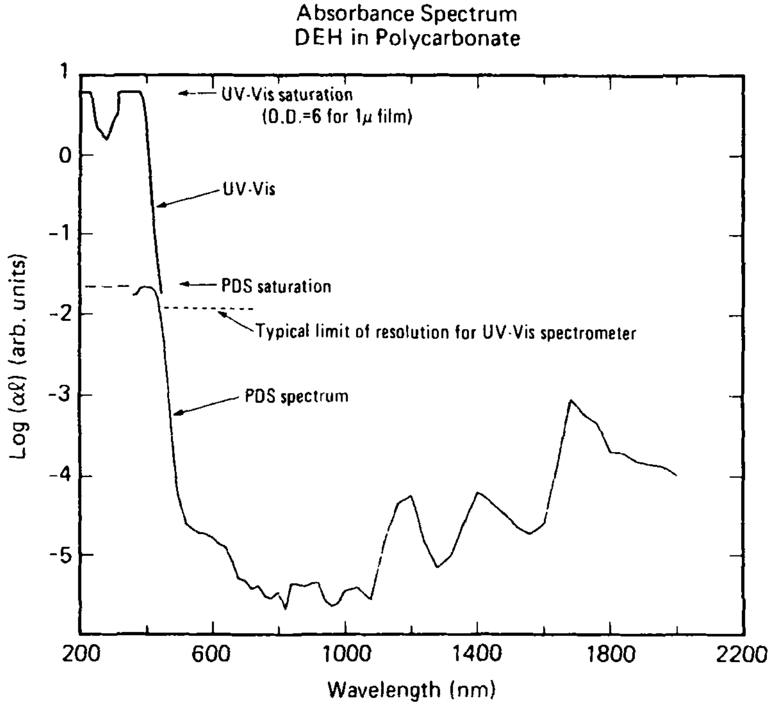
Absorbance Spectrum
DEH in Polycarbonate

Figure 2

ranges from 0 to 6, but small OD's of less than 0.1 are usually not resolved since it is the difference $I_{UV-Vis} = I_0 - I_T$ that is measured. Often at these low OD's the decrease in transmission is due to scattering and not true absorption. In general $I_T = I_0 - A - R - S$ so that $I_{UV-Vis} = I_0 - I_T = A + R + S$ and when A is small, the reflected (R) and scattered (S) components cannot be ignored. Since PDS measures **only** A, it has a strong advantage – i.e., it is insensitive to scattering. Here, $I_{PDS} = I_0 - R - S - I_T = A$ so that $I_{PDS} = I_{in} - I_T$ where now $I_T = I_{in}e^{-\alpha l} = I_{in}10^{\frac{-\alpha l}{2.303}}$, In this equation α is the absorption coefficient and l is the path length or thickness. In the case of negligible R and S, then $OD = \frac{\alpha l}{2.303}$.

Note that figure 2 shows a plot of the **logarithm** of the absorbance (or equivalently the **log** of the optical density) and combines the results of the UV-Vis and the PDS spectra. For a 1 micron film the former saturates at an OD of 6 as shown, where as the PDS spectrum saturates at an "OD" of about 0.02 which is about at the limit of the former. As can be seen from the figure, the PDS spectrum allows 3-4 orders of magnitude greater sensitivity. In addition it covers the energy region from the UV into the mid-IR.

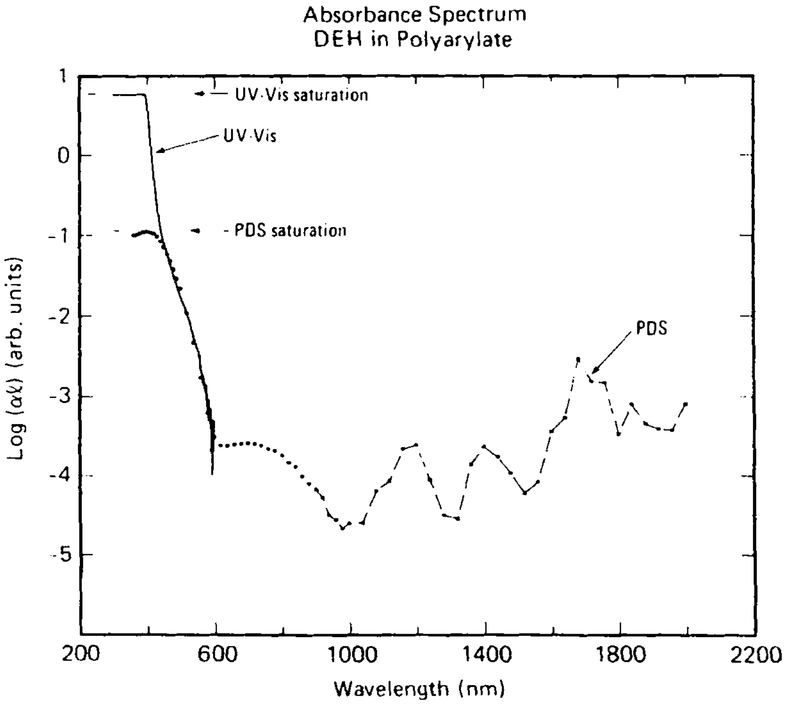

Figure 3

Figure 3 show a similar comparison for a different material combination where the film was cast to minimize scattering in order to obtain the "best" UV-Vis spectrum. The two spectra line up nicely in the region where the UV-Vis begins to lose resolution.

The spectrum of DEH in polycarbonate is shown in more detail in figure 4 obtained from PDS. Three important spectral regions can be distinguished. The higher energies show the singlet-singlet transitions and their "tail" into the visible due to the random orientations and environments in the solid state. The region from roughly 500 nm to 800 nm appears to be electronic transitions due to very weak material interactions and to surface related transitions. The former could be weak charge transfer complex formation[3] or longer range molecular interactions which would yield lower energy electronic states due to delocalization. Surface transitions may be due to the symmetry breaking of normally forbidden transitions. The region beyond 800 nm contains overtones of vibrational transitions in the bulk[4] and compliments FTIR spectroscopy.

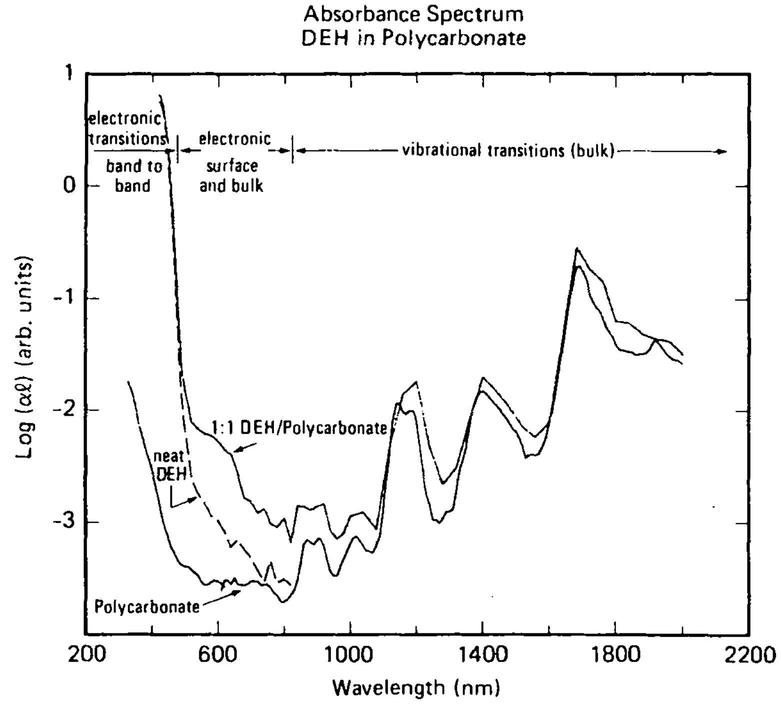

Figure 4

CONCLUSION

The use of photothermal deflection spectroscopy offers clear advantages when measuring the weak absorption of organic thin films. It can provide greater sensitivity than standard UV-Vis and also FTIR spectroscopy, while covering a wide energy range. New features are discernible in the absorption spectra which can be directly attributed to the films absorption since scattering and reflection do not influence the measurement. It should be possible to observe singlet-triplet transitions, and measurements are in progress.

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