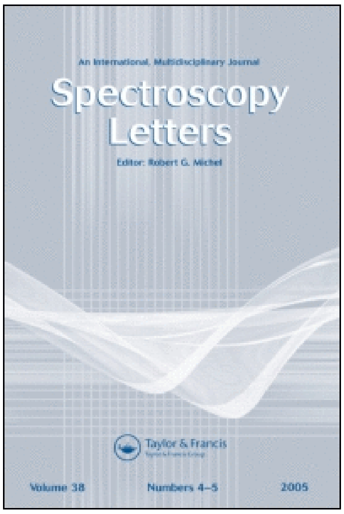

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Dispersion of Electric Dichroism for Macromolecules and Particles in Suspension

B. R. Jennings[a]; A. R. Foweraker[a]
[a] Physics Department, Brunel University, Uxbridge, U.K.

To cite this Article Jennings, B. R. and Foweraker, A. R.(1974) 'Dispersion of Electric Dichroism for Macromolecules and Particles in Suspension', Spectroscopy Letters, 7: 8, 371 — 375

To link to this Article: DOI: 10.1080/00387017408067260

URL: http://dx.doi.org/10.1080/00387017408067260

SPECTROSCOPY LETTERS, 7(8), 371-375 (1974)

DISPERSION OF ELECTRIC DICHROISM FOR MACROMOLECULES AND PARTICLES IN SUSPENSION

B.R.Jennings and A.R.Foweraker
Physics Department,
Brunel University,
Uxbridge, U.K.

The wavelength dependence of the optical absorption of solids, liquids and solutions has long been recognised as an indicator of electronic transitions and hence the associated electronic structure of these materials. With solids and highly ordered systems, a useful extension is the study of the absorption at a given wavelength (λ) as a function of the state of polarisation of incident, linearly polarised light. Such 'dichroism' data enable one to locate the principal directions of the transition moments in the crystal should a single absorbing chromophore be the sole origin of the effect. This may be done by evaluating the principal components ϵ_{ii} with i = 1, 2 or 3 of the extinction coefficient tensor which describes the system. For cylindrically symmetric particles, $\epsilon_{11} = \epsilon_{22}$. Dispersion data of dichroism is thus of double value.

Dichroic studies on solutions and suspensions are more difficult. In these systems, uncharged particles or molecules adopt a random array. Only if some degree of orientational order is imposed on the optically anisotropic particles will dichroism be observed. Of late, interest has grown in both the flow[1] and the electrically[2] induced dichroism of dilute suspensions of colloids and macromolecules. In this communication we present data from a preliminary study on an aqueous suspension of copper phthalocyanine crystallites. By determining both ϵ_{33} and ϵ_{11} ($= \epsilon_{22}$) for these particles the presence was revealed of a certain energy transition which was not apparent at comparable resolution from a conventional absorption spectrum of the particles in random array. In addition, the directions of the relevant transition moments within the crystallites were evaluated.

For a suspension of concentration (c) held in a cell of length (l) which transmits light of intensity I_t from an incident intensity I^*, the extinction coefficient (ϵ) is defined as

$$I_t = I^* \exp (-\epsilon c l)$$

Recent publications from this research group have indicated how theoretically[3] and experimentally[4,5] the coefficients ϵ_u, ϵ_{33} and ϵ_{11} may be obtained with ease for dilute suspensions of rigid rod-like particles when in suspension. The parameter ϵ_u is the extinction coefficient for unpolarised light on a suspension of randomly arrayed particles. The coefficients ϵ_{33} and ϵ_{11} are for light which is both incident and detected for a polarisation state parallel to (ϵ_{33}) and perpendicular to (ϵ_{11}) the major rod axis respectively. For a single chromophore origin, the direction and magnitude of the transition moment can be obtained by compounding ϵ_{33} and ϵ_{11}. An absence of dichroism can arise from optically isotropic particles, anisotropic particles in random orientation, or completely oriented particles which have a transition moment directed at $54^\circ\ 44'$ to their major axis[6]. Otherwise dichroism is observed and the predominance of ϵ_{33} over ϵ_{11} indicates that the major contributory transition moment at any wavelength of observation is closer to the major axis (i.e. the 3 axis) than this angle.

Copper phthalocyanine forms blue, rod-like crystallites which can be dispersed in water. The sample used here was kindly supplied by Dr. D. Horn of B.A.S.F. Ludwigshafen, Germany. Suspension of some 3×10^{-6}g.ml^{-1} was studied over the visible wavelength range of $500 < \lambda(\text{nm}) < 750$. Pulsed electric fields of up to 10kVcm^{-1} and of 1 ms duration were used. From saturation data in the high strength fields, ϵ_{33} and ϵ_{11} were obtained in the manner indicated elsewhere[3].

An absorption spectrum in the absence of any electrically induced orientation is given in terms of ϵ_u in figure 1. Although the resolution

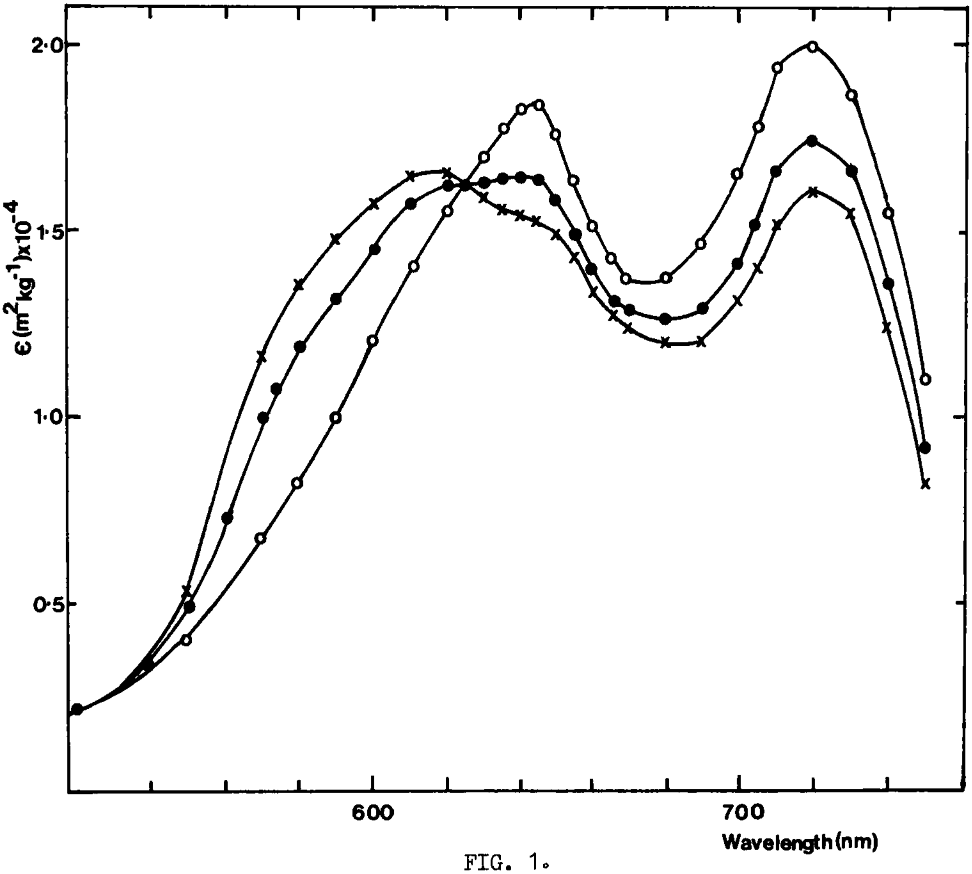

FIG. 1.

Wavelength dependence of the extinction coefficients ϵ_u, ϵ_{33} and ϵ_{11}, represented by •, o, and x respectively, for an aqueous dispersion of copper phthalocyanine.

is not high, two distinct peaks are seen at wavelengths of 720 nm and 640nm. These are well known and are attributed to $\pi \rightarrow \pi^*$ transitions due to electron displacement towards the periphery of the molecules[7]. On the same plot, the wavelength dependence of ϵ_{33} and ϵ_{11}, obtained from the electrically induced dichroism, is shown. In each case, the same two peaks are apparent. An additional factor is also evident. At a wavelength of approximately 625nm there is a crossover of the curves for ϵ_{33} and ϵ_{11}. There must therefore be an absorption peak centred on a wavelength below 625nm, for which the corresponding transition moment is more closely associated with a transverse rather than the major particle axis.

By working from the long wavelength side of the curve for ϵ_u (Fig.1) and treating each curve as being composed of three absorption peaks, each with a gaussian spread in energies, we have been able to reconstruct the experimental curves and characterize each of the three underlying peaks in amplitude, spread and position. The three absorptions appear at wavelengths of 710, 645 and 580 nm. Full details of the fitting procedure will be presented elsewhere. Using the peak amplitude values, the directions of the relevant transition moments were calculated using the equation[3] following,

$$\alpha = \tan^{-1}\left[(2\,\epsilon_{11}/\epsilon_{33})^{\frac{1}{2}}\right]$$

Here α is the angle between the apparent transition moment direction for the crystallites and their long axes, assuming this to be the direction of the electric dipole moment. Current work is being undertaken in an attempt to relate this transition moment direction to the structure of the individual molecules through a knowledge of the orientations and stacking of these molecules within the crystallites. Such information may be available through X-ray data.

We have recently shown in this laboratory that electric dichroic experiments can be made in a simply modified spectrophotometer. Furthermore, using pulsed electric fields, molecular relaxation times can be evaluated from the transient behaviour of the observed absorption changes. In the present case, a relaxation time of some 0.96ms was indicated, corresponding to a rod length[8] of about 0.13μm for the crystallites. This was the magnitude indicated by electron microscopy.

We therefore conclude that, from suitable electric dichroic rather than simple optical absorption measurements, dilute suspensions of macroparticles can be studied and the particle sizes, and the directions of their electronic transition moments can be determined. In certain cases the presence of additional peaks may be inferred from the data which were not obvious from conventional absorption spectra on the solution of the randomly oriented particles.

ACKNOWLEDGMENTS

The Science Research Council is thanked for a grant with which much of the original equipment was purchased, and by one of us (A.R.F.) for a studentship. Part of the apparatus was purchased from funds provided by Messrs. I.C.I. Ltd.

REFERENCES

1. P.R.Callis and N.Davidsonm Biopolyers, 7, 335 (1969).
2. C.Houssier and E.Fredericq, 'Electric Birefringence and Electric Dichroism', Oxford Univ. Press London (1974).
3. A.R.Foweraker and B.R.Jennings, Applied Optics, 12, 1983 (1973).
4. B.R.Jennings and E.D.Baily, Nature (Phys. Sci.), 233, 162 (1971).
5. A.R.Foweraker and B.R.Jennings, Adv. in Mol. Relaxation Processes, imminent, (1974).
6. R.D.B.Fraser, J.Chem.Phys; 21, 1511 (1953).
7. F.Jones, 'Pigments', ed. D.Patterson, p.26, Elsevier Pub.Co.Ltd; England, (1967).
8. J.M.Burgers, Verh.Kon.Ned.Akad.Wetenschap.Afdel.Natuurk, 16, 113 (1968).

Received June 10, 1974

Accepted June 17, 1974