PHOTOACOUSTIC SPECTROSCOPY ON SOME PORPHYRINS

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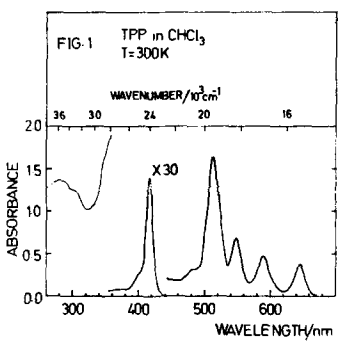
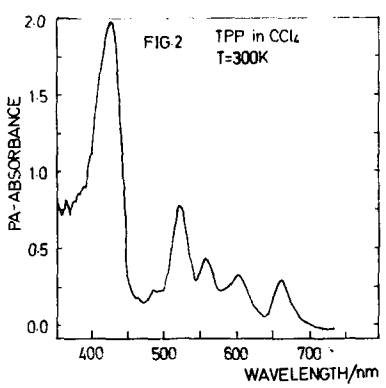
A combination of photoacoustic (PA) and conventional optical spectroscopy provides a possibility to differentiate between various energy transfer processes in light absorbing systems such as porphyrin and its metallo complexes.
The PA signal amplitude is proportional to the absorbed light energy which is converted into heat.If a desactivation of the excited electron states by radiative transitions occurs, the PA signal amplitude is given as,





$$S \sim P(\lambda) \cdot \beta(\lambda) \cdot \mu_s \cdot \mu_g / \varkappa_s \qquad (1)$$

Eq.1 holds for an optically thin and thermally thick sample,i.e.,the response to the light absorbed within the thermal diffusion length μs. $P(\lambda)$ describes the desactivation by radiative transitions and may be given as,

$$P(\lambda) = 1 - f(\phi_F, \lambda, \lambda_F) \qquad (2)$$

with λ_F, the wavelength of fluorescence and ϕ_F, the corresponding quantum yield.While the absorbance in a transmission experiment (cf.Fig.1)is defined by $A_{OP} = \log(I_o/I)$ with I_o and I, the incident and transmitted light intensities, the PA-absorbance is given as

$$A_{PA} = S/S_o$$

S is defined by eq.1 and S_o gives the amplitude of a reference sample such as carbon black.From the ratio of the absorbances

$$A_{PA}/A_{OP} = R \cdot P(\lambda)$$

the interesting quantity $P(\lambda)$ can be extracted;where R is independent of λ and depends on the thermal and geometrical properties of the sample and the reference material.

Experimental results from tetraphenylporphyrin (TPP) at room temperature are shown in Fig.1 and 2. The overall changes of the PA amplitude between $400nm \lesssim \lambda \lesssim 700nm$ is much less pronounced than it is for the optical transmission spectrum shown in Fig.1. Although the Soret absorption at $\lambda \approx 400nm$ is still saturated in Fig.2, the coefficient of energy conversion $P(\lambda)$ displays a reduction with decreasing wavelengths. Qualitatively these observations are in accordance with recent studies of the fluorescence on porphyrins at 77K.