

Photoacoustic spectrum of samarium phthalocyanine powder

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Abstract

Photoacoustic spectrum of samarium phthalocyanine powder is recorded and compared with previously reported UV–vis absorption spectra of the same dissolved in different liquid and solid host media. The Davydov splitting of Q band is observed in the PA spectrum but the two bands are overlapped considerably and the shorter wavelength band is more intense and dominating one in the powder spectrum.

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1. Introduction

During the past decade phthalocyanines have gained considerable attraction of scientists and technologists owing to their unique optical and electrical properties [1–3]. Not only the easily modifiable structure but also the electronic and morphologic characteristics that are highly favorable for semiconductive or conductive properties have let phthalocyanines in finding a comfortable place among the organic semiconductors. Moreover, superior to many other conducting and semiconducting organic compounds such as charge-transfer complexes, doped poly-acetylene, poly-pyrrole, poly-thiophene and poly-aniline, metal substituted phthalocyanines possess substantially strong chemical and thermal stability. Optical data storage, gas sensing and electrochromic displays are some among the numerous potential applications of this wonderful compound [4–6]. Phthalocyanines of rare-earth metals primarily occur in the form

of diphthalocyanines with a sandwich type structure and the cation is eightfold coordinated to the two macrocycles [7]. One of these phthalocyanine rings is virtually planar while the other is significantly distorted. Among the large number of studies on phthalocyanine compounds reported in the literature, samarium phthalocyanine (SmPc) is one of the least investigated and exploited member of this family. A recent degenerate four wave mixing study by Unnikrishnan et al. shows that SmPc dissolved in DMF possess a very high third-order susceptibility which makes it a potential candidate in nonlinear optics [8].

In this paper we report the photoacoustic (PA) spectroscopic studies carried out on SmPc powder. Discovered by A.G. Bell more than a century ago, the PA technique is one of the oldest and extensively used multipurpose spectroscopic technique adopted in a vast variety of scientific fields [9,10]. Essentially the PA technique is a closed cavity detection of energy liberated by atoms or molecules through the nonradiative channel, subsequent to the light absorption by a sample. Consequently the PA technique has certain unique advantages over conventional spectroscopic methods and is also free

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from many of the predicaments faced during the latter approach. The most important aspect of PA technique is that only the absorbed light, and not the reflected or scattered light, contributes to the PA signal. Moreover, irrespective of the state of the sample (solid, gaseous, liquid or liquid crystalline), PA technique is extremely useful for the investigation of optically transparent to perfectly opaque samples [11,12]. In fact, PA spectroscopy is the most appropriate technique for the study of powdered samples and the conventional UV–vis absorption/transmission spectroscopy cannot be used in such cases.

2. Experimental

Domestically synthesized high purity SmPc is used for the investigation. Chemical structure of SmPc is available elsewhere [8]. Powdered SmPc is initially vacuum sublimated on to a glass plate and the fine powder of the sample is then collected from that. The sample is then gently smeared over a very thin layer of silicon grease on a microscopic glass slide and excess SmPc powder is then carefully blown up. The sample is then placed on top of an open photoacoustic cell (OPC) with the SmPc layer facing the air chamber of the OPC.

A specially designed minimum-volume OPC with a very high signal to noise ratio is used for the PA spectral recording. The design and fabrication details of the OPC are given elsewhere [13]. Out of the two different possible experimental configurations using an OPC, we used the reflection configuration. The reflection configuration simply means that the optical excitation and the acoustic detection are made at the same side of the sample. Schematic view of the single beam PA spectrometer used in our investigation is shown in Fig. 1. A 1000 W Xenon arc lamp (Oriel 6269) is used as the optical source. In order to protect the monochromator from overheating, the infrared portion of the lamp emission is filtered out using a 5 cm long water column (in a glass cube) placed in front of the lamp. White light from the lamp is then

wavelength scanned using a 0.1 m grating monochromator (Oriel 7250) and is then focused on to the sample using a series of double convex lenses. Light intensity at the focal point is measured using a power meter and is about 1.5 mW at 550 nm corresponding to a 5 nm spectral bandwidth. A further decrease in spectral bandwidth causes a substantial decrease in PA signal and hence cannot be used for a good quality spectral recording with our experimental set up. A mechanical chopper introduced at the exit of the monochromator is used for the intensity modulation of light which is necessary to observe the PA effect. The PA spectrometer is operated at 30 Hz and the PA spectrum is recorded using a lock-in-amplifier. Since the PA signal is not only proportional to the optical absorption coefficient of the sample but also to the intensity of incident light, the recorded PA spectrum is corrected for the Xenon arc emission profile which is previously recorded using a carbon black sample. Unfortunately, the grating monochromator used in our set up has a very low throughput in the UV region and hence we could not record the PA spectrum in the entire UV region where phthalocyanines show very strong absorption, called the Soret band or the B band.

3. Results and discussion

Normalized PA spectrum of SmPc powder shown in Fig. 2 clearly shows the salient features of phthalocyanines. The portion of B band visible in Fig. 2 is already more intense than the Q band in the visible region which is the characteristic behavior of phthalocyanines. Davydov splitting of the Q band into Q_x (longer wavelength band) and Q_y (shorter wavelength band) is typical of these materials and is clearly noticeable in the recorded PA spectrum of powdered SmPC also. A comparison of the PA spectrum with the conventional absorption spectrum of SmPc dissolved in different media like DMF, DMSO and sol–gel glass shows a good agreement in the position and separation of Q bands [8,14]. From

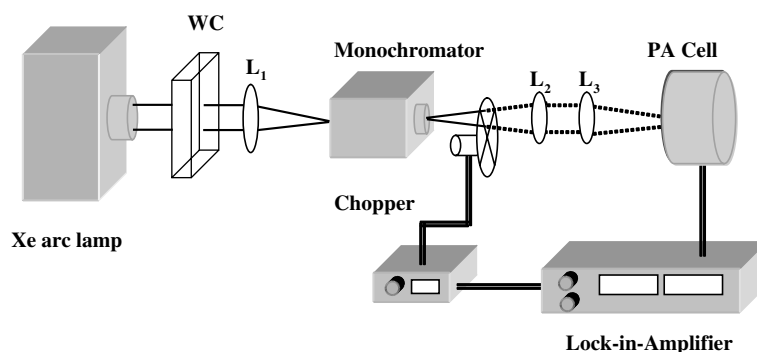


Fig. 1. Schematic view of the single beam PA spectrometer. Here WC is the water column and L_1 , L_2 and L_3 are the focusing lenses.

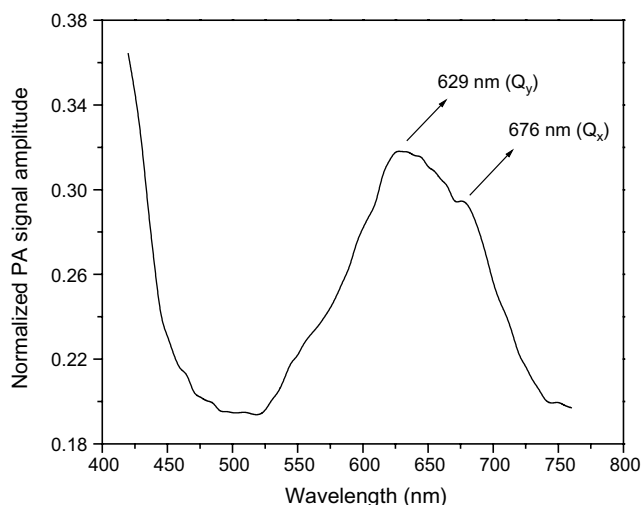


Fig. 2. Photoacoustic spectrum of samarium phthalocyanine powder.

the PA spectrum we identified the position of Q_y and Q_x bands are at around 629 nm and 676 nm, respectively. It is worthwhile to note that in the present case the two bands are overlapped considerably but the relative positions are not changed. According to the UV–vis absorption studies by Maruszewski et al. the intensity of shorter wavelength band increases with respect to the longer wavelength band with an increase in concentration of SmPc dissolved in a liquid medium [14]. But they noticed a complete overlapping of the two bands when SmPc is incorporated in a sol-gel glass media and in that case the longer wavelength band found to dominates. Our investigations on SmPc powder show a substantial suppression of the Q_x band and the shorter wavelength band is the predominant one, but the Q_x band is still distinguishable in the PA spectrum. Even though there exists different explanations for the domination of either Q_x or Q_y band under different experimental conditions, all of them suggest the single point that a leading shorter wavelength band in the absorption spectrum corresponds to the material in its neutral diphthalocyanine state, whereas an enhanced longer wavelength band could be due to an oxidized cation radical form or a monophthalocyanine (SmPc^+) compound [15–17]. In fact the powdered SmPc sample used in our investigation is in its pure form and is expected to be a diphthalocyanine

and the recorded PA spectrum is also in accordance with previous theoretical explanations supporting this fact.

Our investigations show that PA technique is a powerful spectroscopic method for the optical absorption studies on powdered samples. Although the spectral bandwidth is a limiting factor when an arc lamp is used in the PA spectrometer, a very high spectral resolution can be achieved with the aid of a tunable laser as the optical source.

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