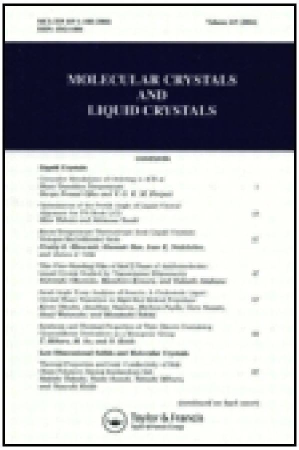

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# RESONANCE RAMAN SCATTERING IN LANGMUIR-BLODGETT FILMS OF A NEW PHTHALOCYANINE

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**Abstract** In this paper we present the results of Raman and optical spectroscopy measurements on Langmuir-Blodgett layers of a new phthalocyanine derivative. In particular we studied the eventual differences between Raman spectra obtained using the SERS advantage and those obtained without it. Furthermore the effects of resonance with the electronics states of the Q-band were studied. Finally, we made a preliminary investigation of the sensitivity of the samples to laser light.

## INTRODUCTION

Phthalocyanines (Pc) have been the object of intense study because of their potential in molecular electronics applications. Molecules in this class may lead to semiconducting, photoconducting and conducting materials[1]. Furthermore they have electrochromic and gas sensing properties, and are thermally and chemically stable[2].

Since Baker et al[3] demonstrated that Pc can be deposited as L.B. layers, much work has been devoted to producing highly ordered films of these macrocyclic molecules. Such interest is due not only to the molecular characteristics just mentioned, but also to the remarkable thermal and chemical stability of the L.B. layers made with them. This is of course very important for applications, for instance to gas sensors[4] or electronic devices[5].

Phthalocyanine is a dye, and thus optical spectroscopy has been used extensively to study it and its films. In particular work has been done on Raman spectroscopy of solutions[6] , ultrathin films[7] and also L.B. films of phthalocyanines[8].

From Raman spectra, informations can be obtained on orientation, stacking reproducibility and, in resonant conditions, not only on vibrational dynamics, but also on the layer quality, and molecular coupling of specific vibrations to the electronic states responsible for the optical absorption.

In order to increase an otherwise very low signal, most of the Raman work has been performed using the SERS (Surface Enhanced Raman Scattering) effect and/or under resonance with the optical Q-band transitions in the red. Under such conditions the signal is sufficiently strong that good reliable spectra can be taken even of a monolayer, using relatively low excitation power and integration times.

However from the point of view of sample characterization the use of resonance enhancements brings out the problem of sample-metal substrate interactions in the case of SERS or of selective resonance enhancement of specific vibrational lines. In this paper we present Raman and optical spectra of L.B. layers of a new Pc derivative, namely tetra tertiary butyl phthalocyanine monosulphonic acid (tBPcSA). In order to assess the weight of the problems we just mentioned on the characterization of the samples, we studied our L.B. mono- and multilayers in three configurations: out-of-resonance SERS, in-resonance SERS and in-resonance without SERS. Another problem specific to dyes is their optical sensitivity. Thus we have also checked quantitatively the effect of laser excitation power on the quality of our samples by studying its effects on the Raman spectra.

## EXPERIMENTAL PROCEDURES AND RESULTS

### Sample preparation

The new phthalocyanine tBPcSA (mw = 914) is dissolved in spectral grade chloroform to a concentration of 0.6 mg/ml. About 50 to 150 μl of this solution are spread onto a subphase of Milli-Q water in a Lauda film balance located in a class 100 clean room. Hydrophobic substrata were obtained by treating the pre-cleaned glasses with a dymethylchlorosylane solution for 15 minutes. The SERS substrata were obtained by evaporating on hydrophilic glasses, at room temperature, 50 Å thick silver island films, at a base pressure of $2.10^{-7}$ Torr.

The tBPcSA films were transferred at a constant pressure of 30 mN/m; at such pressure the Langmuir film displays good stability, and the area per molecule measurements are consistent with the molecules lying with the plane of the ring nearly perpendicular to the water surface. It should be noted that to achieve a transfer ratio of 100% within the range of experimental uncertainty, it is necessary to orient the plane of the substrate perpendicularly to the direction of film compression. We attribute this to the relative rigidity of the tBPcSA films and the geometry of the Lauda system used; the substrate can block material reaching the pressure sensor and an overcompression of the film can be generated during transfer which can lead to local film collapse. The transfer rate was 0.02mm/sec.

Following these procedures, the resulting L.B. layers were X type. We prepared a

14 layers sample for the non-SERS configuration, and 1, 3, 5, 7, 10 layer samples for the SERS configuration.

## Optical measurements

The samples were first characterized by determining their optical absorption spectra. For this we used a standard double beam spectrophotometer in the transmission mode. Although the optical density of the Q-band was found to increase roughly linearly with the number of L.B. layers, a quantitative check of linearity could not be performed due to changes, from sample to sample, in the background absorption of the silver island films. This implies a sizable film-metal interaction, since the extrapolated metal absorption spectrum was also different from that of the silver island films alone. The overall shape of the Pc-related spectra did not seem to change much with the number of layers.

However some change was apparent in the spectra of the one and three layer samples, as might be expected. In fig. 1 we show the absorption spectrum of the 14 layers, non-SERS sample, compared with the spectrum of a $3\cdot10^{-4}$ molar solution of tBPcSA in chloroform.

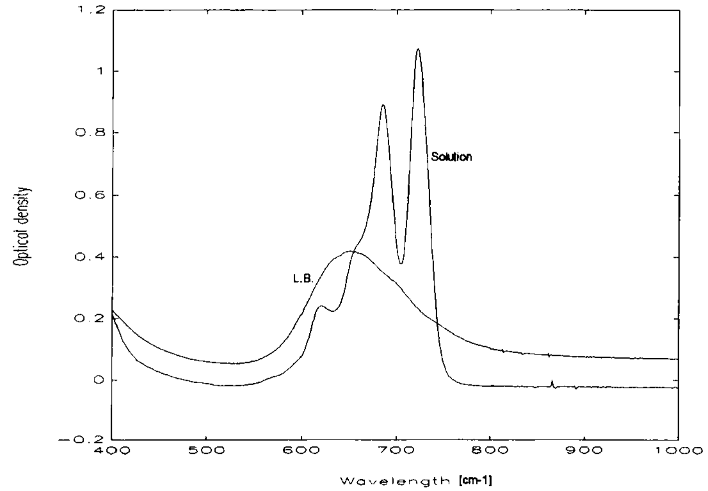

FIGURE 1. Optical absorption spectra of tBPcSA in $3\cdot10^{-4}$ M chloroform solution and of 14 layers, non-SERS sample.

Note the sharp doublet in the Q-band structure, and the spectral position of the more intense peak, which is farther in the red than is usual for phthalocyanines. The blue shift and broadening of the Q-band in the L.B. sample are well known and are attributed to the close packing of molecules and other solid state effects[9]. Such behavior indicates extreme sensitivity of the electronic states of Pc to local structure and environment. We plan to study such effects in our tBPcSA system in more detail.

## Raman Spectroscopy

Raman spectra were taken with a standard, computer-controlled spectrometer. We used a backscattering geometry with cylindrical focusing and a rotating sample configuration in order to minimize power at the sample. The angle on incidence of excitation light was approximately 20 degrees, whereas the scattered light was viewed at an angle of about 45 degrees relatively to the sample surface. Since our excitation power was always less than 40 mW, we estimate the effective power density at the eccentric, rotating sample site to be less than 0.2 W/cm$^2$.

We have found that film sensitivity to incident light depended to some extent on the quality and the age of the sample. However, for what turned out to be our best samples, at the power levels just discussed, we found no change in the Raman spectra over a period of several months. At higher power levels all samples were found to be affected, at least to some extent.

In order to study such effects more quantitatively we used a pump-probe geometry. The probe was the low power, eccentric beam; the pump was originated from the same Argon ion laser, had a power that could be varied up to 1000mW, and was incident on the center of the rotating sample, with spherical focusing. Thus its power density could be as high as $10^4$ W/cm$^2$. The distance between pump and probe could be continuously varied, from zero up to 10 mm. Successive spectra were then taken for a given pump-probe distance as a function of time exposure to a given power level.

The resonant Raman scattering data were taken using a dye laser that was pumped by the Argon laser. The spectral quality of the dye laser beam was improved by filtering it with a double monochromator. After such filtering, no background of spurious laser emission was observable at the sensitivity level of our experiment. All resonant spectra were corrected for sample absorption and incident power. Spectral bandpass for all reported spectra was set at 3cm$^{-1}$ and the spectra were taken at intervals of 1cm$^{-1}$ with an integration time of either 1s or 3s. In figs. 2 and 3 we show the Raman spectra taken at 514.5nm and at 655.8nm using the SERS configuration. The spectra are significantly different. Apart from differences in the background, many peak intensities change considerably at resonance. Note the intensity inversions of the Davydov doublets: particularly clear is that of the Pyrrole stretch peak in the 1500-1540cm$^{-1}$ range. Note also the anti-resonant behavior of the peak at 1400cm$^{-1}$, which disappears at resonance. Also interesting is the same behavior observed for the broad low frequency scattering below 300cm$^{-1}$. In fig. 4 we show the resonant behavior of the peak at 1540cm$^{-1}$. Such behavior is qualitatively shared by the other resonant peaks, and is in good agreement with the observations of Brotman and Burstein[7] of a sharp resonance in the excitation Raman spectra of free-base phthalocyanine at 674nm.

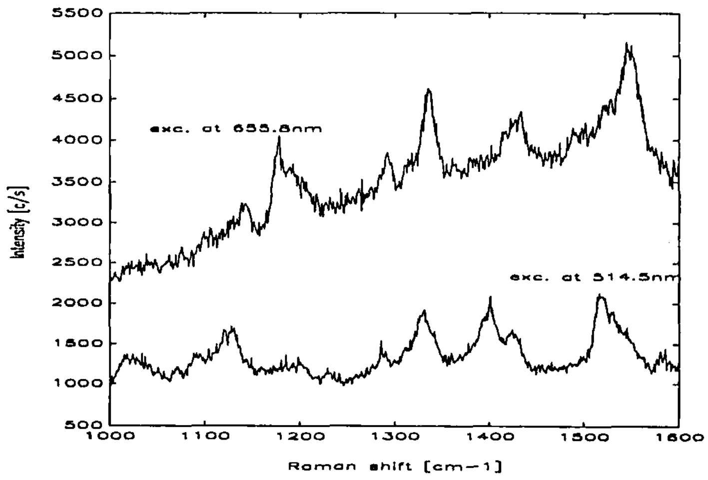

FIGURE 2. Raman spectrum of the 10 layers L.B. sample in the SERS configuration in resonance and out of resonance conditions.

The resonant Raman scattering excitation profile, which has a maximum at the maximum of the Q-band optical absorption (in our case, roughly 650nm), does not follow the broad outline of such spectrum. Rather, it singles out the structure in the electronic energy levels which are resonantly coupled to the vibrational modes which are enhanced by resonance.

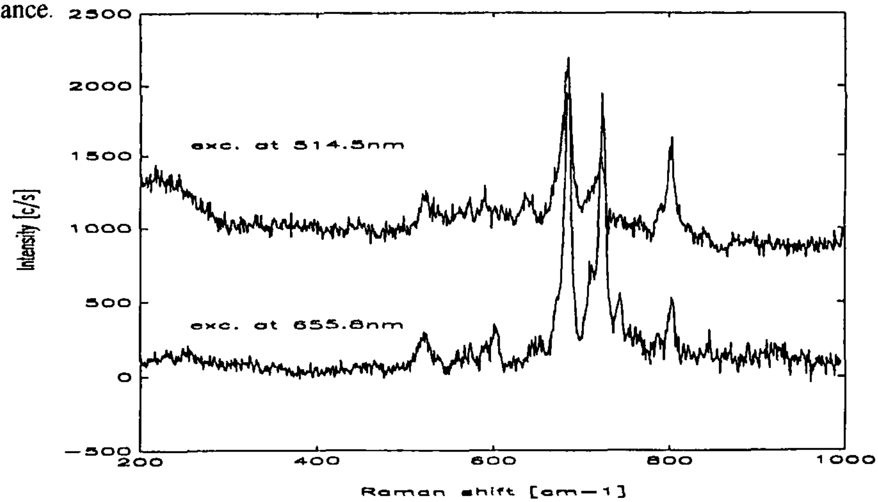

FIGURE 3. Same as fig.2, for the lower frequency spectral range. In this case the steeply rising background for excitation at 655.8nm was subtracted.

In this sense, as has already been stated, resonant Raman scattering is a form of microscopic modulation spectroscopy[10], and quite detailed information on electronic structure and how it may be affected by changes in local order, both chemical and structural, may be obtained by such technique. We plan to pursue such investigation further.

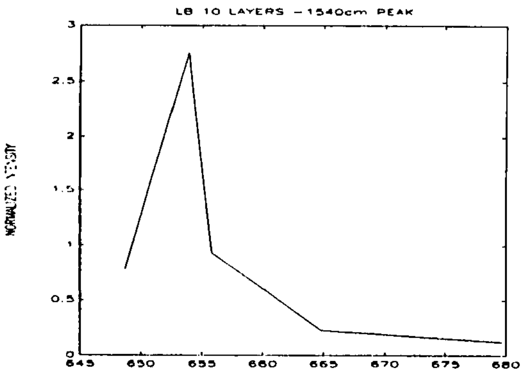

FIGURE 4. Exicitation spectrum for the 1540cm$^{-1}$ Raman line in the 10 layers L.B. sample, SERS configuration.

The spectra obtained in the non-SERS configuration are shown in fig. 5. Excitation was at 655.8nm; thus the spectra are resonant and should be compared with the resonant spectra in figs. 2 and 3. The only major difference is the presence of a peak at 1371cm$^{-1}$ in the non-SERS spectra. Such peak is either absent or very weak in the other spectra. Apart from this, and expected differences in background scattering, the SERS and non-SERS spectra are remarkably similar. Thus for many applications of Raman spectroscopy to the study of L.B. layers, the SERS effect may be used to obtain more intense spectra without having to use the more complex techniques of integrated optics and optical multichannel detection[11] .

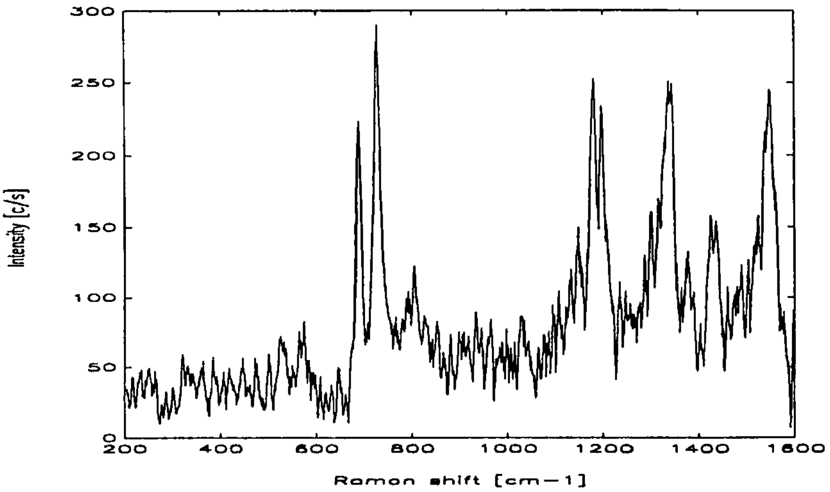

FIGURE 5. Raman spectrum of 14 layers L.B. sample, non SERS configuration, the strong background was subtracted.

Finally, we wish to discuss our preliminary results on the effect of laser illumination. In fig. 6 we show a specific change induced by a 300 s. exposure of the sample to 300mW of 514.5nm laser light. The strongest effect was observed on the pyrrole stretch vibration at 1330cm$^{-1}$. No other major changes were detectable. We must note however that the change was induced by pumping at a distance of 10mm from the probe beam. Such sensitivity at a distance may be at least partly due to coupling to the Ag island films. Thus our measurements should be repeated in a non-SERS configuration.

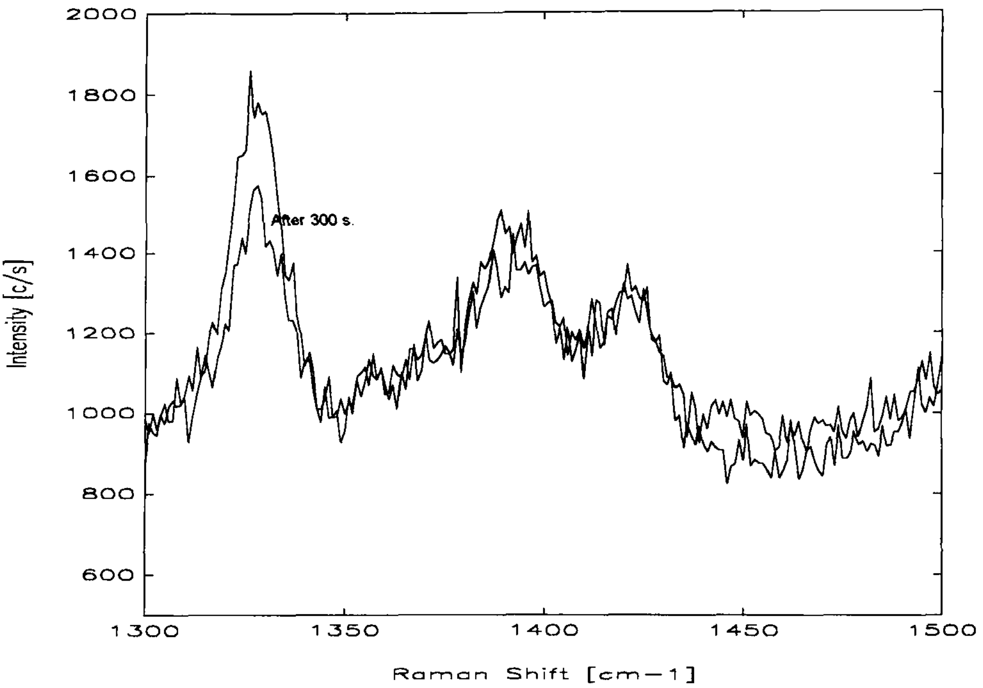

FIGURE 6. Effect of excitation power on a selected portion of Raman spectra of 10 layers L.B. sample.

In any case, qualitatively we found that the photosensitivity of the samples was connected to the overall quality of the L.B. deposition: the samples which gave the strongest, sharpest and more time-stable spectra were also the least influenced by pump light.

## CONCLUSIONS

The similarity of the spectra obtained for the SERS and non-SERS configurations, indicates that the SERS intensity advantage may be used to apply Raman spectroscopy to study the structure and dynamics of L.B. layers. In particular the similarity of the macrocycle vibrations peaks is consistent with the near perpendicular orientation of the molecules relatively to the substrate. This conclusion is also supported by the independence of the spectra on the number of layers in our samples.

There are strong resonance effects on most of the prominent peaks of the spectrum. We expect this for perpendicular alignment of the molecules, since in our geometry this would make the electric field vector of the incident light co-planar with the transition dipole moment of the $\pi$-$\pi^*$ transition responsible for the Q-band. This and the sharp resonance in the Raman excitation profile of the $1540 cm^{-1}$ peak show that these Pc molecules can be useful to use resonance effects to study in detail the electronic structure of L.B. layers made with them.

Finally, we found some preliminary evidence of sensitivity of the pyrrole stretch peak at $1330 cm^{-1}$ to pumping at a distance. Such photosensitivity effect may be used to test excitation energy transfer between different regions of the sample. It remains to be seen whether the presence of the Ag island films is necessary.

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