Second harmonic Generation Studies of Metal and non-Metal Porphyrins at Silica Surfaces.

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ABSTRACT

Resonant molecular optical second harmonic generation (SHG) was obtained from [2, 3, 7, 8, 12, 13, 17, 18- Octaethyl-porphinato]M, with M = none, vanadyl and Ni(II), adsorbed onto fused silica substrates. The Polarization dependence of the SHG signals at 1064nm allowed the determination of average molecular orientations. For the vanadium porphyrin the average angle between the long axis molecules and the surface normal was 38°, while, for the Nickel porphyrin, and the non-metal porphyrin the angle was close to 0°. These results can be understood in terms of the different symmetries of the molecules.

Keywords: Second Harmonic Dependence, Interfaces, nonlinear optics.

1. INTRODUCTION

The nonlinear conversion of two photons of frequency ω to a single photon of frequency 2ω is known as optical second harmonic generation (SHG). Optical Second Harmonic Generation (SHG) requires a noncentrosymetric medium. This attribute give to the SHG an intrinsic surface sensitivity, for studying the interface between two centrosymmetric media [1,2]. SHG has bee employed extensively at a wide variety of interfaces (solid/air[3,4], solid/liquid[3,5], liquid/vapor[3,6] and liquid/liquid[7]).

In addition to the numerous applications of interfacial SHG to the study of molecular adsorption, SHG experiments have been frequently utilized, at both liquid and solid surfaces, to determine the average orientation within the interfacial region [5,8,10]. For systems where the SHG from the interface is dominated by molecular contributions to the surface nonlinear susceptibility, the average orientation of the molecules at the interface can be obtained from measurements of the polarization dependence and phase of the molecular SHG[6,11].

This paper describes the experiments to measure the polarization dependence of the molecular SHG for 2, 3, 7, 8, 12, 13, 17, 18- Octaethyl porphyrin, (OetP), 2, 3, 7, 8, 12, 13, 17, 18- Octaethyl vanadyl porphyrin, (OetVP), and 2, 3, 7, 8, 12, 13, 17, 18- Octaethyl porphinato of Ni(II) (OetNiP), adsorbed over fused silica substrates.

2. EXPERIMENTAL SECTION

A schematic of the experimental setup employed for the orientation measurements is shown in Figure 1. A nanosecond Nd YAG laser, (Continuum, model Surelite I), provides light at 1064 nm (10 Hz repetition, ~ 9 ns pulse width), with a typical surface energy density of 8 mJ/cm^2. The polarization of the incident pulses was controlled by passing them through a quartz, zero-order, half-wave plate. The beam is then passed through a couple of appropriate color glass filters in order to remove any extraneous second harmonic light.

An optical quality, synthetic fused silica, scalene prism was used as a substrate. Preparation of the interface was carried out by placing a few drops of 1×10^{-4}M solutions, of the respective porphyrin in dichloromethane, on the previously cleaned large face of the prism, and then allowing the solution to slowly flow from the surface upon removal. The 1064 nm light was directed at the small face of the prism, in order to achieve a total reflection condition on the large face of the prism. Near the critical angle of total reflection, harmonic intensity is larger than the intensity away from this angle [7,10,14,15]. The second harmonic light, created at the interface, was sent through a Glan-Thompson polarizer, set to pass either s-polarized or p-polarized light from the surface. Suitable UV-passing filter and a suitable monochromator were used to filter out any reflected fundamental light. The second harmonic photons were detected with a photomultiplier tube (Hammamatsu, R955) and the analog signal was amplified and then averaged with a boxcar averager (Stanford Research Instruments, SR 250).

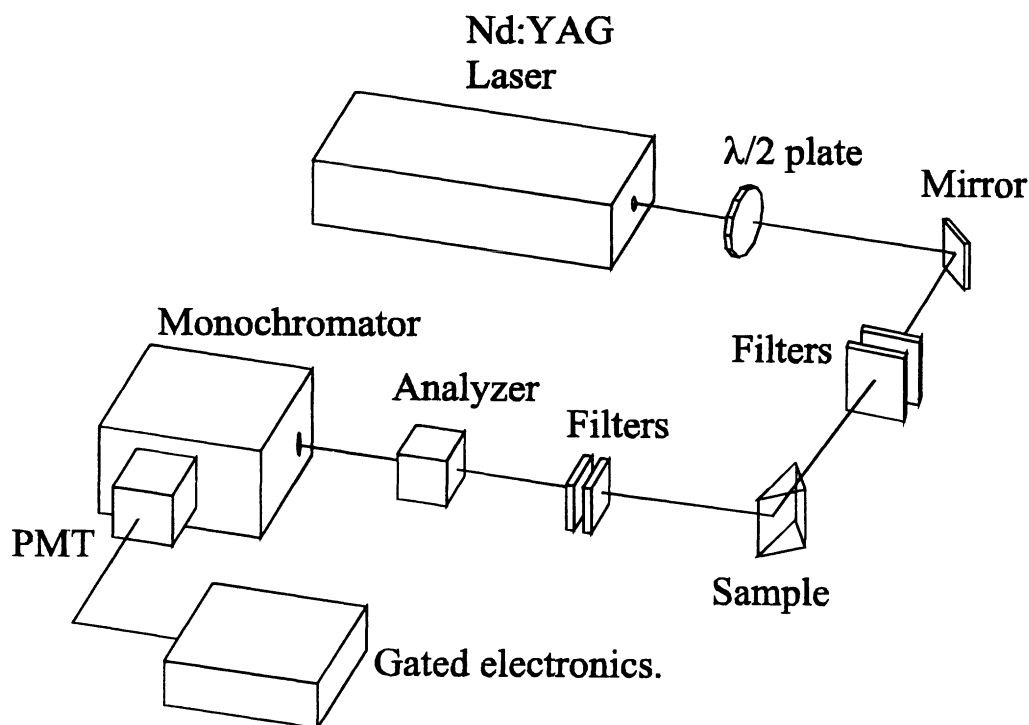* to whom the correspondence should be addressed. E-mail mcaetano@ciens.ucv.ve

Figure 1.- A schematic of the experimental setup employed for the orientation measurements.

3. RESULTS AND DISCUSSION.

1. SHG Polarization dependence.

The average molecular orientation within an adsorbed monolayer can be expressed by[13]:

$$I(2\omega) = \frac{32\pi^3 \omega^2 \sec^2 \theta_{2\omega}}{c^3} \left| e(2\omega) \cdot \chi^{(2)} \cdot e(\omega)e(\omega) \right|^2 I^2(\omega) \qquad (1)$$

In this equation the linear susceptibility of the material has been neglected, and $I(\omega)$ is the intensity of the input laser light, $\theta_{2\omega}$ is the angle from the surface normal at which the SHG signal occurs, the vectors $e(\omega)$ and $e(2\omega)$ describe the polarization and fresnel factors for the fundamental and second harmonics light fields at the surface. A is the illuminated surface area.

Figure 2 depicted the relation between the molecular axis x', y', and z' and the surface axis X,Y and Z for an adsorbed porphyrin and defines the angles necessary to simplify and evaluate the product of direction cosines that define the molecular orientation on the surface. The Surface normal is defined as the laboratory Z axis. The molecular orientation distribution in α and ϕ is assumed to be random with a further assumption of the δ-function for the θ angle. This assumption for ϕ was verified experimentally by demonstrating that the surface SHG signal is invariant with respect to rotation of the surface about the Z axis. As a consequence of this isotropic behavior $\chi^{(2)}$ has only three unique elements: χ_{XZZ}, χ_{ZXX} and χ_{ZZZ}. The intensity s-
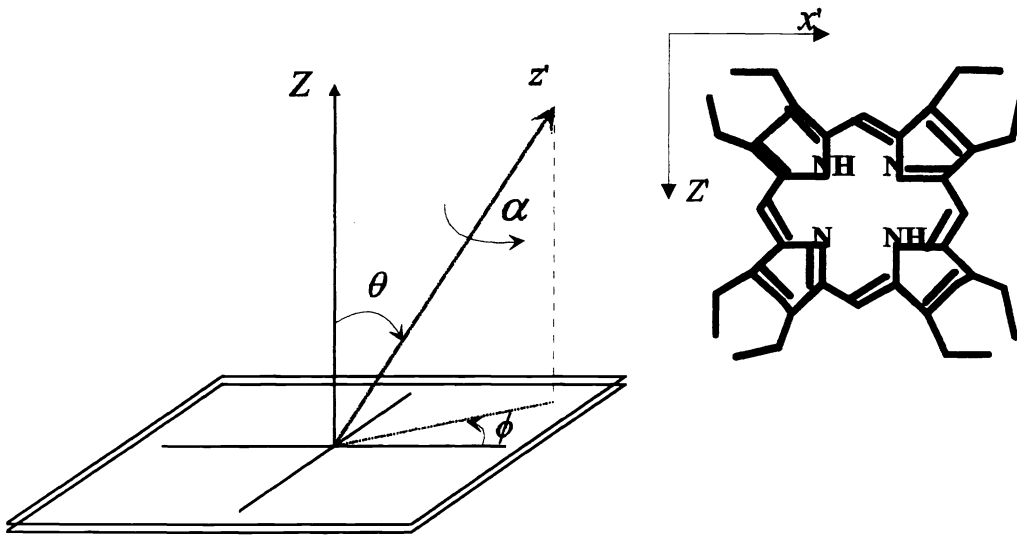
polarized SHG component, $I_s(2\omega)$ α

Figure 2.- relation between the molecular axis x', y', and z' and the surface axis X, Y and Z for an adsorbed porphyrin
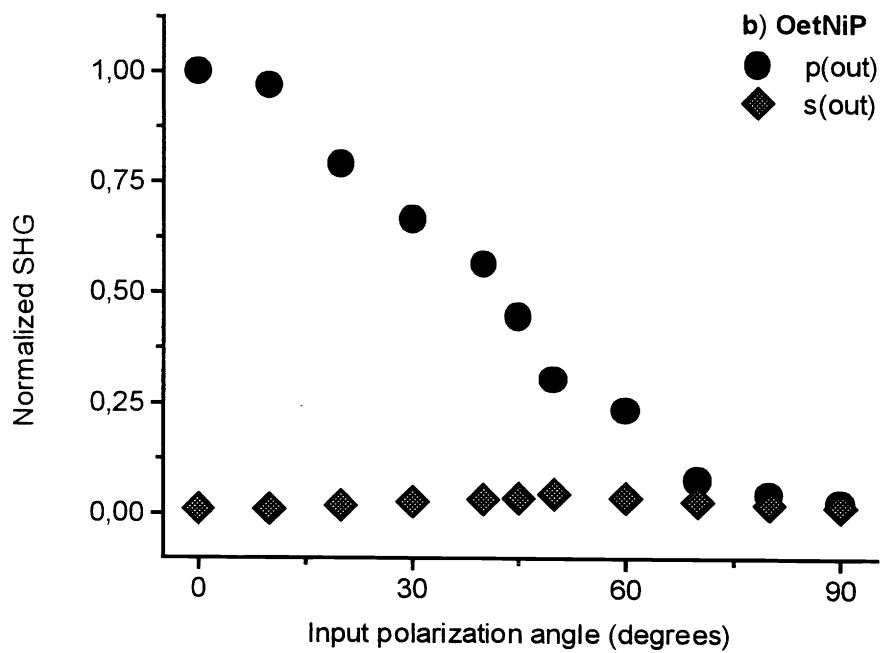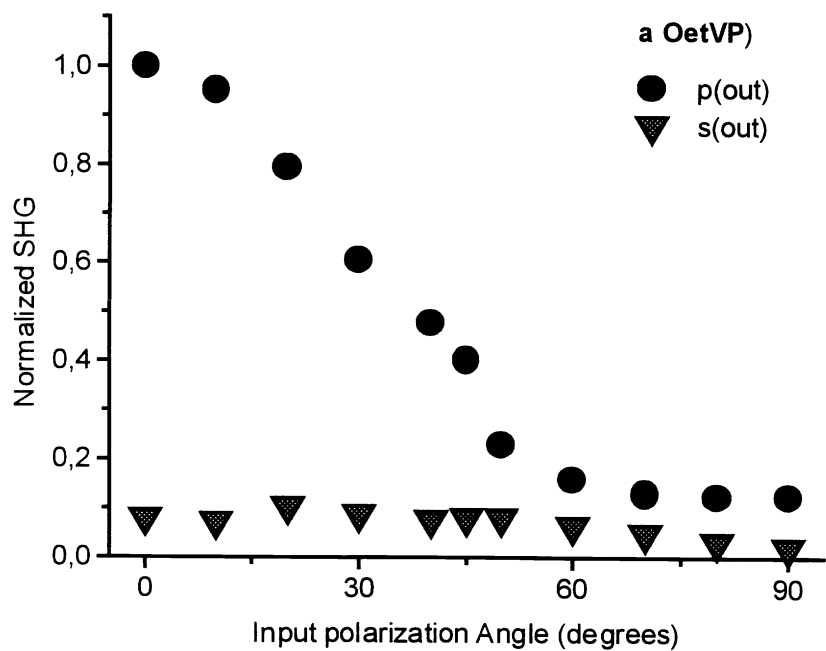
(perpendicular to the plane of incidence) and the p-polarized, $I_p(2\omega)$ (parallel to the plane of incidence) can be related to these element through the relations:

$$I_S(2\omega) \propto \left| a_1 \chi_{xxz} \sin^2 \gamma \right|^2 I(\omega)^2 ,$$ (2)

$$I_P(2\omega) \propto \left| (a_2 \chi_{xxz} + a_3 \chi_{zxx} + a_4 \chi_{zzz}) \cos^2 \gamma + a_5 \chi_{zxx} \sin^2 \gamma \right|^2 I(\omega)^2$$ (3)

where γ is the polarization angle of the incident light ($\gamma = 0°$ for p-polarized light, and $\gamma = 90$ for s-polarized light). The a_i terms in the equations 2 and 3 above describe the magnitudes of the electric fields $e(\omega)$ and $e(2\omega)$ in the surface monolayer and are proportional to the Fresnel factors describing transmission and reflection at each interface encountered, and the dielectric constants $\varepsilon'(\omega)$ and $\varepsilon'(2\omega)$ for the materials employed.

The p-polarized and s-polarized SHG signals from OetVP, OetNiP and OetP monolayers, as a function of the input polarization are shown in the part a, b, and c of figure 3, respectively. The SHG signal is normalized to the maximum second harmonic response observed. Figure 3 shows considerable difference in the relative intensities of the p- to s- polarized responses.
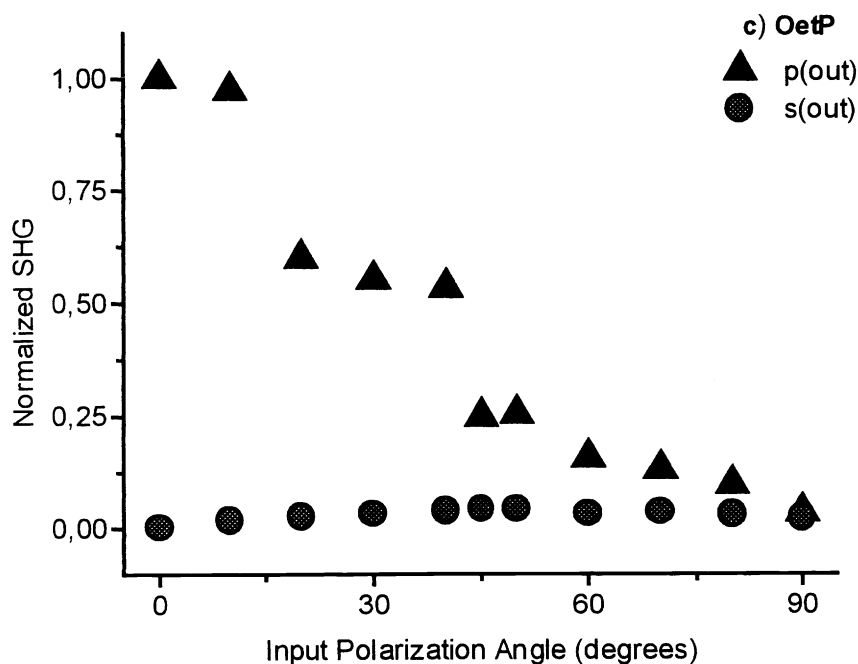
364

a OetVP)
- ● p(out)
- ▼ s(out)

Normalized SHG

Input polarization Angle (degrees)

b) OetNiP
- ● p(out)
- ◆ s(out)

Normalized SHG

Input polarization angle (degrees)

Figure 3.- The p-polarized and s-polarized SHG signals from OetVP a), OetNiP b) and OetP c) monolayers, as a function of the input polarization.

The p-polarized and s-polarized SHG signals from OetVP, OetNiP and OetP monolayers, as a function of the input polarization are shown in the part a, b, and c of figure 3, respectively

In this paper, we restrict ourselves to the case of molecules for which β is dominated by a single axial component $\beta_{zzz}^{(2)}$. For a monolayer of these molecules with only one dominant tensor element, an orientation parameter R can be obtained[8]:

$$R = \frac{\langle \cos^3 \theta \rangle}{\langle \cos \theta \rangle} = \frac{\chi_{zzz}^{(2)}}{\chi_{zzz}^{(2)} + \chi_{xxz}^{(2)}}$$ (1)

This equation has been used frequently to obtain molecular orientation information for adsorbed molecules at condensed phase interfaces[11] (where the interactions between molecules in the monolayer can be neglected).

2. Results

In table 1 the average z'- axis orientation angles, θ for the different porphyrins are showed. These angles were determined by using the values of the tensor elements from the polarization dependence curves (fig 2).

Table 1: Average z'- axis orientation angles, θ for the different porphyrins.

Porphyrin	$\cos\theta$	θ
OetP	1,00	0
OetNiP	1,00	0
OetVP	0,79	38

By examining the experimentally determined orientation angles some inferences about the possible adsorbate-susbtrate interaction can be made. OetP and OetNiP molecules have the same symmetry, (C4h), and considering the angle value, $\theta = 0$, clearly indicates that that both molecules are lying on the substrate. The main interaction seems to be between the nitrogen atoms in the macrocycle and the surface. In contrast, the OetVP molecules (C4v) interact with the surface through the two unpaired electrons over the oxygen atom, and adopt an orientation in which the z' molecular axis lies at an angle of 38° with respect to the surface normal.

4. CONCLUSIONS.

In conclusion, the average molecular orientation of [2, 3, 7, 8, 12, 13, 17, 18- Octaethyl-porphinato]M, with M = none, vanadyl and Ni(II), adsorbed onto a fused silica substrate have been calculated, from the polarized SHG. Adsorbate-Substrate interaction leads to well defined geometries such that the z' molecular axis of OetP and OetNiP lies at an angle of 0° with respect to the surface normal, while OetVP have an angle estimated of 38° with respect to the surface normal.

5. ACKNOWLEDGMENTS

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