Concentration dependence of Surface Non-linear Susceptibility of Vanadyl-Porphyrin at silica surfaces.

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ABSTRACT

Resonant molecular optical second harmonic generation (SHG) has been obtained from [2, 3, 7, 8, 12, 13, 17, 18-Octaethyl-porphinato] vanadyl, (OEP)V=O, adsorbed on the hypotenuse face of a glass prism. Rotational intensity patterns are showed by plotting the second harmonic intensity as a function of the incident polarization angle of the fundamental wave, at a fixed angle of incidence. Evaluation of these patterns by Fourier analysis allowed the determination of the second order susceptibilities components of the adsorbed layers. Assuming a delta distribution function, the mean orientation angles from normal to the surface plane, were obtained for different solution concentrations. Our results indicate an abrupt change in the angle for two concentration ranges.

Keywords: Second Harmonic Generation, Surface Non-linear Susceptibility, Vanadyl Porphyrin.

1. INTRODUCTION

Metals are, in some extend, present in the form of Metalloporphyrins in Heavy (*H*) and extra-heavy (*XH*) type crude oils. In order to reduce the metal quantity, and to improve the quality of the oil, catalytic hidroprocessing has been proposed as a possible alternative. Understanding the way a reactant is adsorbed on a catalysts surface could help to design a more specific catalyst for a given reaction.

Second Harmonic Generation (SHG) has proved to be a powerful technique to study equilibrium and dynamic process at interfaces[1-3]. A special feature of this technique is that it is electric dipole forbidden in centrosymmetric media [4-6].

This paper describes the experiments to measure the polarization dependence of the molecular SHG for (OEP)V=O, adsorbed over fused silica substrates.

1.1. Theory

The productiogn of *SHG* signal from a film deposited on the hypotenuse of 45º glass prism has been extremely well described by Felderhof[7]. The fundamental radiation ω is incident from the glass side and is totally reflected from the hypotenuse side. The reflected electric field of the incident laser radiation is evanescent and interacts nonlinearly with the adsorbate. After transmission through the prism, radiation at frequency 2ω of generated *SH* signal is detected.

We assume that the film is isotropic in the *xy* plane of the surface, but lacks inversion symmetry with respect to this plane, the susceptibility tensor reduces to:

$$\chi = \begin{bmatrix} 0 & 0 & 0 & \chi_{xyz} & \chi_{xzx} & 0 \\ 0 & 0 & 0 & \chi_{xzx} & -\chi_{xyz} & 0 \\ \chi_{zxx} & \chi_{zxx} & \chi_{zzz} & 0 & 0 & 0 \end{bmatrix} \tag{1}$$

The components of the second harmonic field generated can be, conveniently, expressed in terms of the parallel (*p)* and perpendicular (s) components of the incident field

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$$\begin{pmatrix} E_p(2\omega) \\ E_s(2\omega) \end{pmatrix} = \begin{pmatrix} a_{ppp} & a_{pss} & a_{pps} \\ a_{spp} & 0 & a_{sps} \end{pmatrix} \begin{pmatrix} E_p^2(\omega) \\ E_s^2(\omega) \\ E_p(\omega)E_s(\omega) \end{pmatrix} \qquad (2)$$

After transmission through a polarizer with polarization angle Ψ, the outgoing *SH* field has the form

$$\mathbf{E}_\Psi(2\omega) = E_p(2\omega)\cos\Psi + E_s(2\omega)\sin\Psi \qquad (3)$$

The intensity of the *SH* field, relative to the incident intensity, is

$$\frac{I_{\Psi,OUT}(2\omega)}{I_{IN}(\omega)} = \frac{|\mathbf{E}_\Psi(2\omega)|^2}{|\mathbf{E}(\omega)|^2} \qquad (4)$$

To determine the real and imaginary parts of $\chi_S^{(2)}$, we analyse the polarization dependence of the outgoing *SH* radiation and the incident fundamental light. For this, a half-wave plate is introduced to change the polarization of the fundamental radiation by an angle φ. The detected SH intensity depends on the rotation angle φ of the half wave plate

$$I\psi(2\omega,\varphi) = \sum_n \left[S_n \sin(n2\varphi) + C_n \cos(n2\varphi) \right] \qquad (5)$$

2. EXPERIMENTAL SECTION

A schematic of the experimental setup employed for the orientation measurements is shown in Fig. 1. A nanosecond Nd YAG laser, (Continuum, model Surelite I), provides *p*-polarized fundamental light, of frequency ω (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 is controlled by passing them through a quartz, zero-order, half-wave plate. A couple of appropriate colour glass filters remove any extraneous second harmonic light.
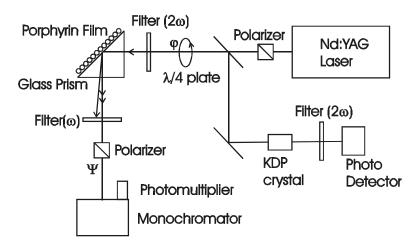

Fig. 1   Schematic diagram of the experimental setup employed for the orientation measurements.

The second harmonic photons were detected with a photomultiplier tube (Hammamatsu, R955) and the analog signal was amplified and then averaged with a gated integrator and boxcar averager (Stanford Research Instruments, SR 250). UV-Visible Spectra of porphyrin films and solutions were recorded with a fiber optic spectrometer, Ocean Optics S2000, equipped with a 600 lines, blazed at 500 nm grating, and 2048 element linear CCD array detector.   As was discussed in the theory section, a BK7 optical glass, right angle prism was used as a substrate. Preparation of the interface was carried out by immersing a clean substrate in a dichloromethane solution of the porphyrin by 48 h. After slow removal, the non total internal reflection surfaces were wiped out with a dichloromethane soaked Kimwipe. The fundamental light is directed normal at the first face of the prism, therefore the angle of incidence on the hypotenuse face is 45°. Near the

critical angle of total reflection, harmonic intensity is larger than the intensity away from this angle[8;9]. The second harmonic light, created at the interface, was sent through a polarizer (dichroic sheet), 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.

3. EXPERIMENTAL RESULTS

To determine the complex-valued tensor components $a_{\alpha\beta\gamma} = \mathrm{Re}\{a_{\alpha\beta\gamma}\} + i\,\mathrm{Im}\{a_{\alpha\beta\gamma}\}]$, we performed a Fourier analysis for the sum of the two contributions R_{10} and R_{100}. :

$$R_{10°}(2\omega) = \left| a_{ppp}E_{0p}^2 + a_{pss}E_{0s}^2 + a_{pps}E_{0p}E_{0s} + \frac{1}{5}\left(a_{spp}E_{0p}^2 + a_{sps}E_{0p}E_{0s}\right)\right|^2$$

$$R_{100°}(2\omega) = \left| a_{spp}E_{0p}^2 + a_{sps}E_{0p}E_{0s} + \frac{1}{5}\left(a_{ppp}E_{0p}^2 + a_{pss}E_{0s}^2 + a_{pps}E_{0p}E_{0s}\right)\right|^2$$

(6)

The experimental data is fit to the combination of two Fourier Series based upon coefficients Fourier indicated above as

$$R_{10°} + R_{100°} = \sum_{n=0}^{4}[(C_{n,10°} + C_{n,100°})\cos n2\varphi + (S_{n,10°} + S_{n,100°})\sin n2\varphi]$$ (7)

Fig. 2 illustrates the observed polarization dependence the sum of the two contributions R_{10} and R_{100} for one surface coverage. The experimentally determined values (individual points) are plotted against the incident beam polarization angle. The solid line is a fit of this data to equation (7). The functional dependence of the SH response on the polarization angle φ shows that the assumed isotropic distributions of the molecules in the surface plane are well confirmed for the metalloporphyrin studied.
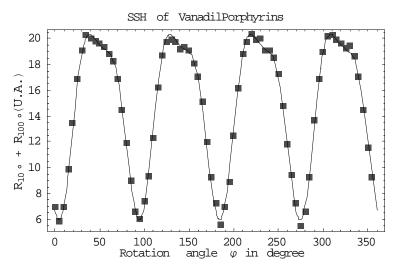

Fig. 2 Rotation patterns for the combination lineal of two data sets and the curve fit, representing the two-detection angle 10° and 100°.

In Table 1 we present the tensor components $\chi_{ijk}^{(2)}$ derived from the best fit of the data for two different solution concentrations. Note the axial component, $\chi_{zzz}^{(2)}$, dominates $\chi_{s}^{(2)}$, demonstrating that the inversion symmetry is broken in the z direction.

Table 1 : Relative second order nonlinear surface susceptibility components .

	Solution concentration (M)	
	8×10^{-6}	1×10^{-4}
$\chi_{xyz}^{(2)}$	(0.11) exp[i (119°)]	(0.13) exp[i (129°)]
$\chi_{xzx}^{(2)}$	(0.20) exp[i (121°)]	(0.21) exp[i (109°)]
$\chi_{zxx}^{(2)}$	(0.30) exp[i (-160°)]	(0.28) exp[i (-176°)]
$\chi_{zzz}^{(2)}$	1	1

From the experimental data a $\chi_{zxx}^{(2)}/\chi_{zzz}^{(2)}$ ratio was determined for each concentration, resulting in the θ tilt angles[10] illustrated in the Fig. 3.
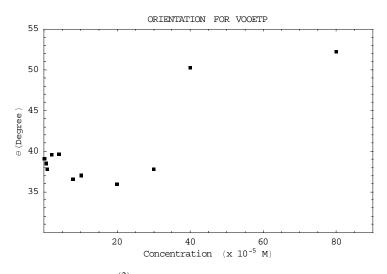

Fig. 3 Dependence of the tensor components $\chi_{ijk}^{(2)}$, with the solution concentration.

It is evident that two well defined range of concentrations, with a different behavior of the molecular orientation in each one, are present. At low surface concentrations the angle is about 40°, for higher concentrations it is increased to about 50°. This change can be attributed to a change in porphyrin interaction, becoming in a dimmer formation or another porphyrin aggregation form[11;12].

CONCLUSIONS.

We have presented a simple technique to determine the complex-valued tensor components of the second-order surface susceptibility tensor $\chi_s^{(2)}$ of (OEP)V=O adsorbed over glass. Total reflection geometry shows a sensitive dependence on the angles of polarization rising a enhanced SH intensity. The analysis of characteristic rotation patterns with respect to their Fourier components, yielded complex valued susceptibility tensor components. Polarized HG have shown that the averaged molecular orientation has a strong concentration dependence. These results provide a direct measure of the molecular interaction at the interface.

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