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NONLINEAR OPTICAL STUDY OF INTERFACES

C.K. Chen, T.F. Heinz, D. Ricard, and
Y.R. Shen

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NONLINEAR OPTICAL STUDY OF INTERFACES

C. K. Chen, T. F. Heinz,* D. Ricard, and Y. R. Shen**
Department of Physics
University of California
Berkeley, California 94720
and
Materials and Molecular Research Division
Lawrence Berkeley Laboratory
Berkeley, California 94720

Abstract

Surface nonlinear optics can be used for study of interfaces. It is found that nonlinear optical effects can be greatly enhanced on a rough noble metal surface because of the large local-field enhancement due to local plasmon resonances and the lightning rod effect. Second harmonic generation is sensitive enough to detect adsorbed molecular monolayers on surfaces, and can be used to study the molecular adsorption and desorption process at a solid-liquid interface. Monolayer spectroscopy by nonlinear optical techniques is also possible. The polarization dependence of the nonlinear output can yield valuable information about the molecular orientation on a surface.

In recent years, our interest in nonlinear optics has been extended from the bulk to the surface. While surface nonlinear optics is interesting in its own right,[1] it is the great potential applications of surface nonlinear optics to surface study that makes this subfield very exciting. With the anticipation that it may soon become an attractive new area of research, we present here a few examples to illustrate how surface nonlinear optics can be used to study interfaces. We consider first the surface-enhancement problem. We show that because of the local-field enhancement, nonlinear optical effects on a rough noble metal surface can be enhanced by several orders of magnitude over those on a smooth surface.[2] We then discuss the problem of monolayer detection at a silver electrode in an electrolytic solution by second harmonic generation. In the presence of surface enhancement, this turns out to be a rather trivial task.[3] Finally, we consider the problem of nonlinear spectrosocopic study of adsorbed monolayers on smooth surfaces. We demonstrate the possibility by the detection of second harmonic generation from dye adsorbates on a fused quartz plate.[4]

Surface-enhanced optical effects have recently become a hot topic in condensed matter physics. The problem was initiated when it was discovered that the Raman scattering intensity from the adsorbed molecules on a rough silver surface is $\sim 10^6$ times larger than that from the same molecules in liquid.[5] Two types of mechanisms have been proposed to explain the observed enhancement. One is the local-field enhancement. The small bumps or aggregates of the size of $\sim$ 500 Å on the rough metal surface can have local plasmon resonances in the optical range. These resonances strongly enhance the optical fields on these local structures. In addition, the local fields can be further enhanced on the pointing structures by the lightning rod effect. On rough silver surfaces, a local-field enhancement[6] of $\gtrsim 20$ is not unreasonable. The other mechanism for surface enhancement comes from the molecule-metal interaction. Experiments have shown that the vibrational frequencies of the adsorbates are not very different from those of the molecules in liquid. We therefore believe that the second mechanism is not as important as the first.

To prove that the local-field enhancement is indeed the dominant mechanism for surface enhancement, our idea is quite simple. We realize that Raman scattering is a two-photon process, and therefore is a nonlinear optical process. If the local-field enhancement exists, the Raman intensity should be strongly enhanced because of its nonlinear dependence on the fields. Then, for the same reason, other nonlinear optical effects should also be greatly enhanced. We can use the following equations for a more explicit discussion.

Let the local field at $\vec{r}$ on the surface be $E_{loc}(\omega,\vec{r}) = L(\omega,\vec{r})E(\omega)$. For simplicity, we shall not treat the field as a vectorial quantity here. It is well known in nonlinear optics that with the local-field correction, the effective n-th order nonlinear optical susceptibility should become[7]

$$\chi^{(n)}_{eff}(\omega) = L(\omega)\chi^{(n)}(\omega = \omega_1 + \text{---} + \omega_n)L(\omega_1)\ \text{---}\ L(\omega_n). \tag{1}$$

The Raman cross-section σ is known to be proportional to Im $\chi^{(3)}(\omega_s = \omega_\ell - \omega_\ell + \omega_s)$. Therefore, the local-field enhancement should be $L^2(\omega_\ell)L^2(\omega_s)$. The observed enhancement should be an average over the illuminated surface, and is given by

$$\eta_R = \frac{1}{A}\int L^2(\omega_\ell,\vec{r})L^2(\omega_s,\vec{r})dA. \tag{2}$$

The nonlinear dependence on L in the above equation suggests that the integral is dominated

*National Science Foundation Graduate Fellow.
**Miller Research Professor, Miller Institute, University of California, 1981-82.

by regions where the integrand is near the maximum. Let f be the fractional area where $L^2(\omega_\ell)L^2(\omega_s)$ is close to the maximum. Then, we have

$$\eta_R \approx [L^2(\omega_\ell)L^2(\omega_s)]_{max} f. \tag{3}$$

A similar local-field enhancement is expected for other nonlinear optical processes. Thus, for second harmonic generation, the output $I(2\omega)$ is proportional to $|\chi^{(2)}(2\omega = \omega + \omega)|^2$, and therefore, the enhancement should be

$$\eta_{SH} = \frac{1}{A}\int L^4(\omega,\vec{r})L^2(2\omega,\vec{r})dA$$
$$\approx [L^4(\omega)L^2(2\omega)]_{max} f. \tag{4}$$

Since ω and 2ω are very different, we expect that if $L(\omega)$ is maximum, then $L(2\omega)$ is probably close to 1. We therefore write

$$\eta_{SH} \approx [L^4(\omega)]_{max} f. \tag{6}$$

Similarly, the enhancement factors for sum-frequency generation, third harmonic generation, multiphoton-excited luminescence, etc. can also be derived. Assuming $L(\omega) \approx L(\omega_\ell) \approx L(\omega_s) \approx 20$ and $f \approx 0.05$ on rough silver, we find $\eta_R \sim 10^4$ and $\eta_{SH} \sim 10^4$. Such an enhancement should of course, be easily observable. We note that in the presence of the molecule-metal interaction, the total enhancement factor can be appreciably larger. In surface Raman scattering, for example, an additional enhancement factor of ~ 100 can result from the molecule-metal interaction.

We have actually observed strong surface enhancement for a number of nonlinear processes. Here, we use only second harmonic generation (SHG) for illustration.[2] It should be noted that experiments of SHG are usually rather simple. In our case, the Nd:YAG laser beam was directed onto an electrochemically roughened silver surface, and then the diffused SH signal from the surface was collected and recorded by the detection system. To ensure that the signal was indeed second-harmonic, the spectrum of the output was analyzed, and the quadratic dependence of the output on the input laser power was confirmed, as shown in Fig. 1. The signal was then compared with that from a smooth silver surface. As seen from Fig. 1, the observed enhancement was 1×10^4, which implies a local-field enhancement factor $L(\omega) \sim 20$ if $f \sim 0.05$. The interesting point of this experiment is that no adsorbed molecules are required for SHG, because the bare silver surface already provides a detectable SH signal. Thus, the molecule-metal interaction does not come into the picture, and the observed surface enhancement is purely due to the local-field enhancement.

Study of molecular adsorbates at an interface is, nevertheless, important in surface studies. We then ask if nonlinear optical techniques can be used to detect a surface monolayer. In the past, we have demonstrated that surface coherent antiStokes Raman scattering has the sensitivity to detect a submonolayer of molecules.[8] Heritage et al.[9] have succeeded in detecting a molecular monolayer by the stimulated Raman gain technique. Both techniques are, however, quite complicated in the experimental setups. It would be most attractive if a second-order process can be used to detect monolayers because of the relative experimental simplicity. It turns out that not only a second-order nonlinear optical effect from a monolayer should be observable, but it also has the additional advantage of being surface-specific. Because the surface monolayer lacks inversion symmetry, its contribution to SHG is electric-dipole allowed. On the other hand, SHG in a bulk medium with inversion symmetry is possible only through electric-quadrupole and magnetic-dipole contributions. Therefore, the surface monolayer contributes to SHG as much as several hundred layers of atoms or molecules in the bulk within the coherent length. This makes SHG particularly sensitive to changes at the interface. That SHG from a monolayer should be observable can be seen explicitly from the following numerical estimate.

Without taking into account any local-filed correction, the second harmonic signal from a monolayer is given by[10]

$$S = \frac{128\pi^3\omega}{\hbar c^3}|N_A\alpha^{(2)}|^2 I_1^2 AT \quad \text{photons/pulse} \tag{6}$$

where N_A is the surface density of molecules, $\alpha^{(2)}$ is the second-order polarizability, I_1 is the laser beam intensity, A is the surface area of illumination, and T is the laser pulsewidth, all in esu. Substitution of $N_A \sim 4 \times 10^{14}/cm^2$, $\alpha^{(2)} \sim 10^{-29}$ esu, $I_1 \sim 1$ MW/cm^2 at 1.06 μm, $A \sim 0.2$ cm^2, and $T \sim 10$ nsec (corresponding to a pump uplse of 2 mJ/pulse) into the above equation, yields a signal $S \sim 1.5 \times 10^3$ photons/pulse. This is certainly large enough to be detected. With local-field enhancement at the surface, the signal can be even much larger. Surface alignment of the molecules also helps in increasing the effective value of $\alpha^{(2)}$, and hence the signal.

Because of the large surface enhancement and hence the relative ease of detecting the adsorbed monolayers by SHG, we decided to try out the monolayer detection experiment on a roughened silver electrode in an electrolytic cell undergoing an electrolytic cycling. With 0.1 M KCℓ in water as the electrolytic solution, Ag is oxidized into AgCℓ during the oxidation half cycle, and AgCℓ is reduced to Ag and Cℓ during the reduction half cycle. By monitoring the SH signal from the Ag electrode, we hoped to observe the formation and removal

of the first few monolayers of AgCl on Ag. Indeed, as shown in Fig. 2, the SH signal increased sharply at the beginning of the oxidation cycle. From the amount of charge transfer we estimated that the sharp rise of the signal corresponded to the formation of an average of 3 or 4 monolayers of AgCl on Ag. The SH signal also decreased sharply at the end of the reduction cycle, corresponding to the removal of the last 3 or 4 monolayers of AgCl on Ag. Thus, the result in Fig. 2 clearly demonstrates the sensitivity of SHG for detecting adsorbed monolayers on the Ag electrode.

The monolayer detection capability of SHG is more clearly demonstrated in the following experiment. If at the end of an electroltyic cycle, 0.05 M pyridine is added into the electrolytic solution, and the bias potential on the Ag electrode with respect to a standard calomel electrode $V_{Ag\text{-}SCE}$ is decreased to a sufficiently negative value, it is known that a monolayer of pyridine should then appear on the Ag electrode. In our experiment, corresponding to the appearance of the pyridine monolayer, the SH signal increased by ~ 50 times from the background. For a Q-switched Nd:YAG laser input of 0.2 mJ/pulse over a surface area of 0.2 cm^2, the observed SH signal from the adsorbed pyridine monolayer was 8×10^5 photons/pulse. This indicates that SHG should have the sensitivity of detecting even a submonolayer of adsorbed pyridine. Assuming a surface local-field enhancement of 10^4, we can deduce an effective value of $\alpha^{(2)}$ for the adsorbed pyridine molecules from Eq. (6). We find $\alpha^{(2)} \approx 2 \times 10^{-29}$ esu. This value may be larger by an order of magnitude than what one would expect.[11] Such an enhancement in $\alpha^{(2)}$ could result from the molecule-metal interaction. The dependence of the SH signal from the pyridine adsorbates on the bias voltage $V_{Ag\text{-}SCE}$ is shown in Fig. 3. It shows that pyridine adsorption on Ag occurs only if $V_{Ag\text{-}SCE} \lesssim -0.6$v. The data in Fig. 3 also indicate that the SH signal does not come from the dc-field-induced SHG in the bulk around the interface.

Although SHG is sensitive enough to detect adsorbed monolayers, it clearly lacks the spectral selectivity. Then, will it still be useful for the study of molecular adsorption and desorption at an interface? The answer is yes, and we will illustrate it here with two examples. First, because of its capability to detect a submonolayer of pyridine, SHG can be used to measure the adsorption isotherm of pyridine at the Ag-electrode interface.[12] This is shown in Fig. 4, where the surface density of pyridine N_a is plotted as a function of the pyridine concentration ρ in the electrolytic solution. Note that N_a should be proportional to $\sqrt{P(2\omega)} - A$, where $P(2\omega)$ is the total SH output, and A is the background signal from Ag without pyridine. The data in Fig. 4 can be fit by a simple Langmuir adsorption isotherm equation

$$N_a = \frac{\rho}{K + \rho} (N_a)_{max}. \qquad (7)$$

The coefficient K is related to the adsorption free energy ΔG by $K = 55 \exp(-\Delta G/RT)$. The theoretical fit to the data yields a value of $\Delta G = 5.1$ KCal/mole. Another example shows the sensitivity of SHG to molecule-metal interaction for a certain type of adsorbed molecule.[13] Pyridine with a molecule structure  and pyrazine with  are quite similar, but one has no inversion symmetry and the other has. Consequently, $\alpha^{(2)} \neq 0$ for free pyridine and $\alpha^{(2)} \approx 0$ for free pyrazine. However, if the pyrazine molecules are adsorbed on a surface, then the inversion symmetry of pyrazine is broken by the molecule-substrate interaction, and $\alpha^{(2)}$ becomes finite, the value of which increases with the molecule-substrate interaction. By adding pyrazine instead of pyridine into the electrolytic solution at the end of an electrolytic cycle, we actually observed a SH signal from the adsorbed pyrazine on Ag when the bias voltage $V_{Ag\text{-}SCE}$ was sufficiently negative, as shown in Fig. 5. The maximum signal, which presumably corresponds to a monolayer of adsorbed pyrazine, is only ~ 4 times smaller than that from adsorbed pyridine. This means that $\alpha^{(2)}$ for adsorbed pyrazine on Ag is only 2 times less than $\alpha^{(2)}$ for adsorbed pyridine. The larger value of $\alpha^{(2)}$ for the adsorbed molecules must result from the molecule-silver interaction.

Study of molecular adsorption on an electrode in an electrolytic cell is interesting and important in electrochemistry. Unfortunately, difficulty in characterizing a rough metal surface makes the problem very difficult to analyze. The problem that is most interesting in surface science nowadays is on spectroscopy of adsorbates on smooth surfaces. Various methods have been invented for this purpose.[14] One can use, for example, electron loss spectroscopy to study adsorbed molecules. It has tremendous sensitivity, but the resolution is limited to ~ 10^{-2} eV. If optical spectroscopic methods can be used, one could have a resolution better than 10^{-6} eV. We therefore ask whether it is possible to do nonlinear optical spectroscopy on molecules adsorbed on a smooth surface. Since there is no surface local-field enhancement on a smooth surface, the nonlinear optical signal is weak. Yet, according to our earlier estimate following Eq. (6), SHG from a smooth monolayer should still be observable, and therfore, we believe that monolayer spectroscopy by a second-order nonlinear process is possible. (Monolayer spectroscopy by the stimulated Raman gain technique has already been demonstrated by Heritage et al.[9])

We have recently tried out SH spectroscopy on dye adsorbates on a smooth fused quartz plate.* Dye molecules were deposited on the substrate with a surface density of ~ 5×10^{13} molecules/cm^2. A dye laser pumped by a doubled Nd:YAG laser was directed onto the surface with a 45° angle of incidence. Its frequency was tuned so that the SH frequency would scan over the $S_0 \rightarrow S_2$ electronic transition of the molecules (see Fig. 6). The resonant spectrum of SHG was then recorded. Two different dye molecules, Rhodamine 6G and Rhodamine 110, were

used in the experiment. The results are shown in Fig. 7. The resonant peak corresponding to the $S_0 \rightarrow S_2$ transition is very pronounced. The peak shift resulting from the difference in the structures of the two dye molecules is clearly resolved. This preliminary success on the dye molecules points to the possibility of extending the SH spectroscopy to the sum-frequency spectroscopy. With ω_1 tunable in the infrared and ω_2 fixed in the visible, it is then possible to carry out vibrational spectroscopy on adsorbed molecules. If successful, the high-resolution and time-resolved capability of the nonlinear optical technique could have revolutionary effects on the future of surface science research.

Aside from the spectroscopic information, SHG from the adsorbates can also yield information about the molecular orientation on the surface through its polarization dependence. In the present case of dye molecules, we found that the SH output was p-polarized for a laser input either s- or p-polarized. This implies that the molecular arrangement should have reflection symmetry about the $\hat{x}$-$\hat{z}$ and $\hat{y}$-$\hat{z}$ planes, where we denote the surface plane to be the $\hat{x}$-$\hat{y}$ plane. Then, the only nonvanishing elements of the surface susceptibility tensor $s\chi^{(2)}_{ijk}$ are $s\chi^{(2)}_{zii}$, $s\chi^{(2)}_{izi}$, and $s\chi^{(2)}_{iiz}$. We also found that the output remained unchanged when the sample was rotated about the z-axis. This immediately suggests that the molecular arrangement is isotropic in the surface plane.

From the microscopic point of view, the dye molecule has a reflection symmetry about a vertical plane symmetrically dividing the molecule. It is known that the $\langle S_0|$ and $\langle S_2|$ states are even with respect to reflection about this symmetry plane, while $\langle S_1|$ is odd.[15] Therefore, with $\hat{x}'$, $\hat{y}'$, and $\hat{z}'$ defined in Fig. 6, we see that the nonvanishing matrix elements are $\langle S_0|x'|S_1\rangle$, $\langle S_1|x'|S_2\rangle$, and $\langle S_0|z'|S_2\rangle$. If $\langle S_1|$ is the dominant intermediate state in the two-photon transition from $\langle S_0|$ to $\langle S_2|$, then the only nonvanishing component of the second-order polarizability is $\alpha^{(2)}_{z'x'x'} \propto \langle S_0|z'|S_2\rangle\langle S_2|x'|S_1\rangle\langle S_1|x'|S_0\rangle$. From $\alpha^{(2)}_{z'x'x'}$, if the molecular orientation on the surface is known, we can calculate $s\chi^{(2)}_{ijk}$. Experimentally, the ratio of the SH signals with p-polarized excitation and with s-polarized excitation can be measured. This ratio is given by

$$r = \frac{|s\chi^{(2)}_{zzz} + s\chi^{(2)}_{zxx}|^2}{2|\chi^{(2)}_{zyy}|^2}. \tag{8}$$

The measured ratio was ~ 2, which cannot be explained by either the $\hat{x}'$ or the $\hat{z}'$ axis of the molecules lying in the surface plane, but is consistent with $\hat{y}'$ lying in the surface plane. This result leads to the conclusion that the dye molecules do not lie flat on the surface, but are standing up with the molecular plane perpendicular to the surface plane.

In summary, we have shown that nonlinear optical effects can be greatly enhanced on a rough noble metal surface because of the large local-field enhancement. The surface enhancement makes the detection of adsorbed molecular monolayers by SHG very simple. In general, SHG can be used to study molecular adsorption and desorption at a solid-liquid interface, in particular, at the electrode-electrolyte interface in an electrolytic cell. Monolayer spectroscopy using nonlinear optical techniques is also found to be possible, and may become an important tool for surface science study.

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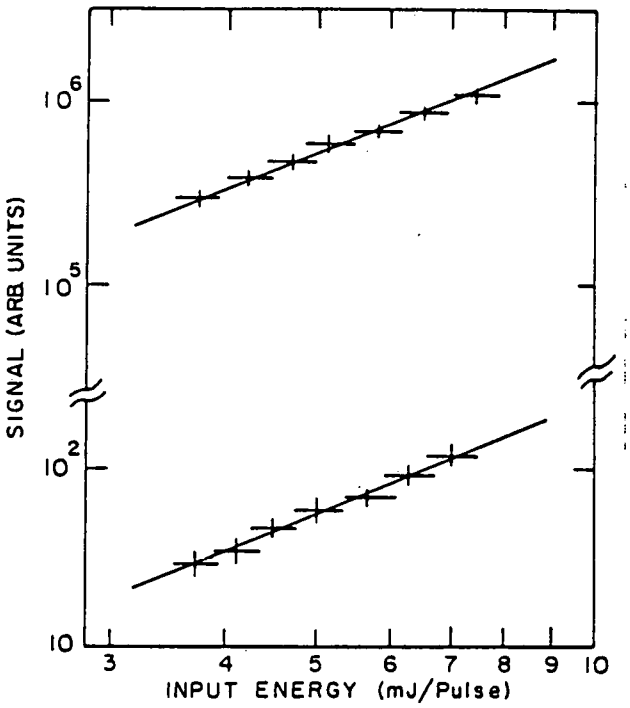

Fig. 1 Power-law dependences of the nonlinear signal on silver. The upper and lower solid curves show the quadratic dependence of the diffuse SH signal from the rough bulk sample and of the collimated SH signal from the smooth film, respectively.

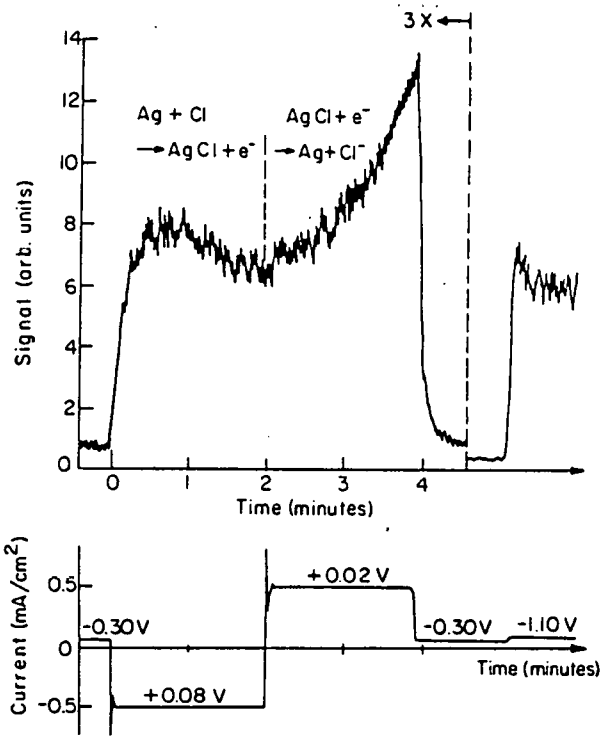

Fig. 2 Current and diffuse SH as a function of time during and after an electrolytic cycle. The voltages listed in the lower curve are V_{Ag-SCE}. Pyridine (.05M) was added to the 0.1 M KCℓ solution following the completion of the electrolytic cylce.

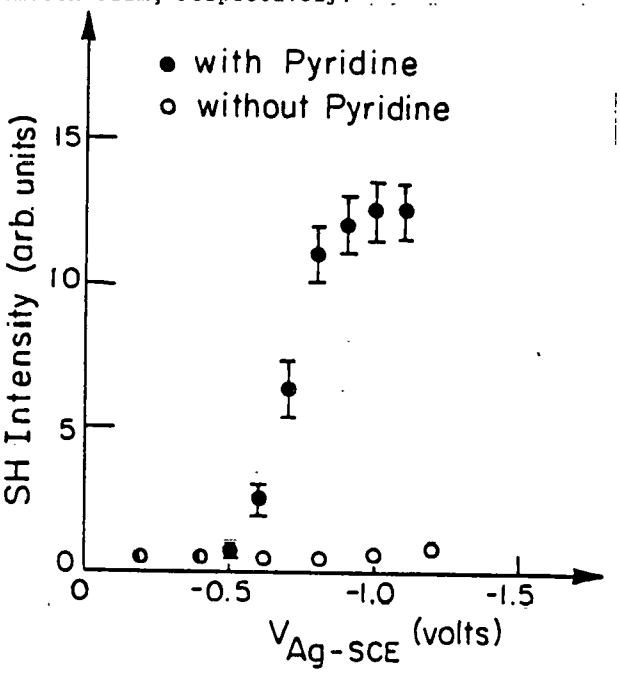

Fig. 3 Diffuse second harmonic signal versus V_{Ag-SCE} following an electrolytic cycle, with .05 M pyridine and 0.1 M KCℓ dissolved in water.

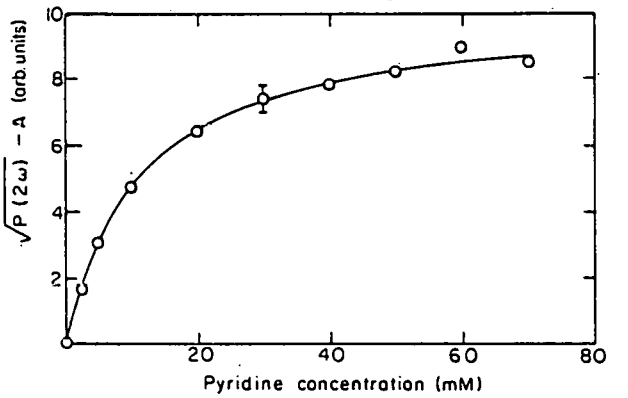

Fig. 4 Equilibrium ($\sqrt{P(2\omega)}$ - A) versus bulk pyridine concentration. The solid curve is a theoretical fit to the experimental data using the Langmuir model.

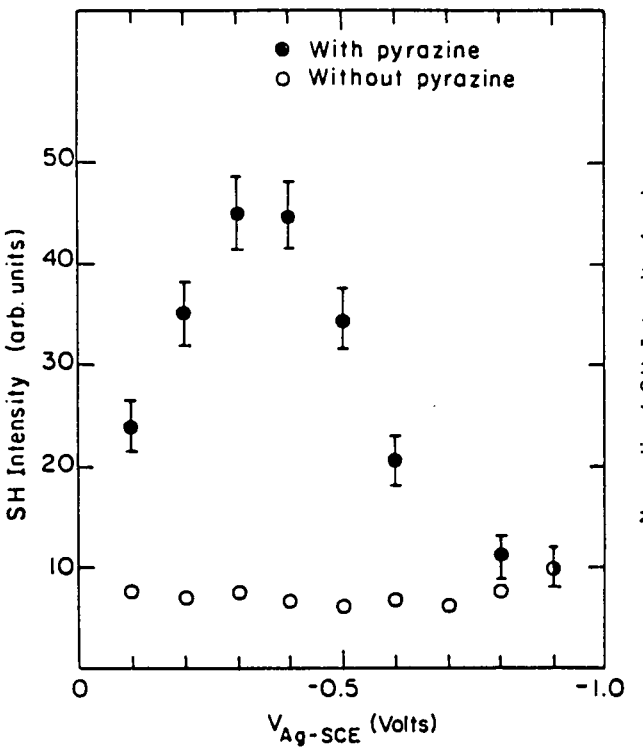

Fig. 5 Diffuse second harmonic signal versus V_{Ag-SCE} following an electrolytic cycle in 0.1 M KCl, with and without 0.5 M pyrazine present.

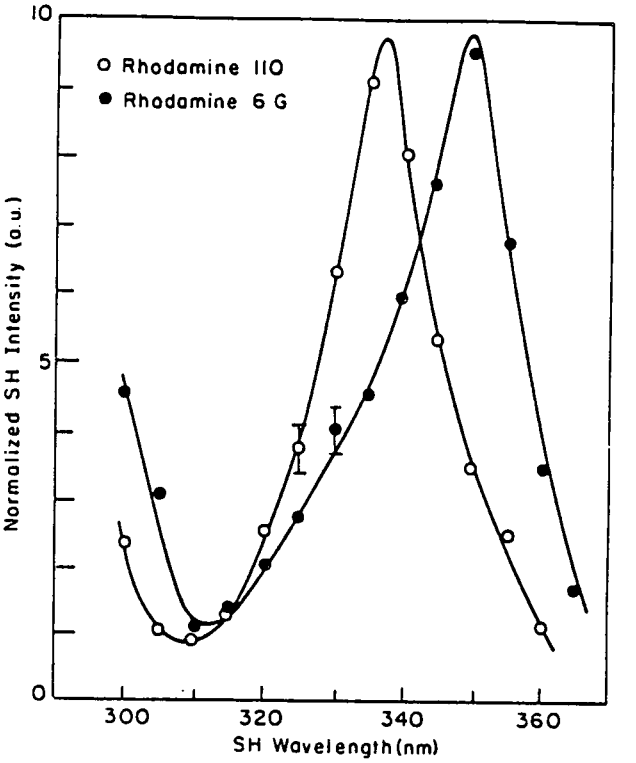

Fig. 7 Normalized SH intensity for p-polarized excitation of monolayer samples of rhodamine 110 and rhodamine 6G on fused silica as a function of the SH wavelength in the region of the $S_0 \rightarrow S_2$ transition.

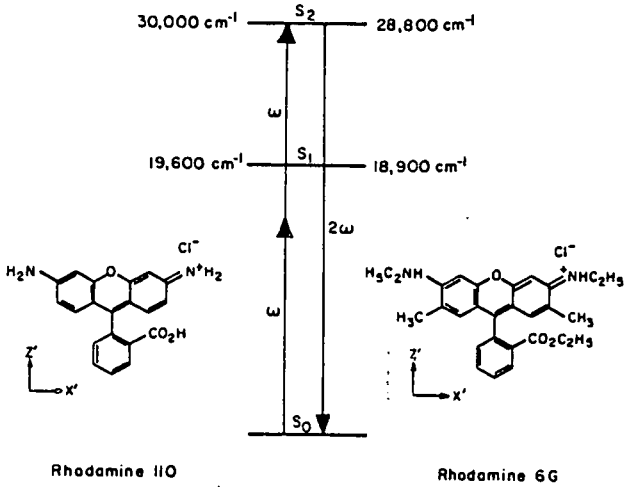

Fig. 6 Energy level diagrams for rhodamine 110 and rhodamine 6G with the linecenters for the linear absorption of the dyes dissolved in ethanol given in units of cm^{-1}. The structure of the dyes and the molecular axes referred to in the text are indicated.

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