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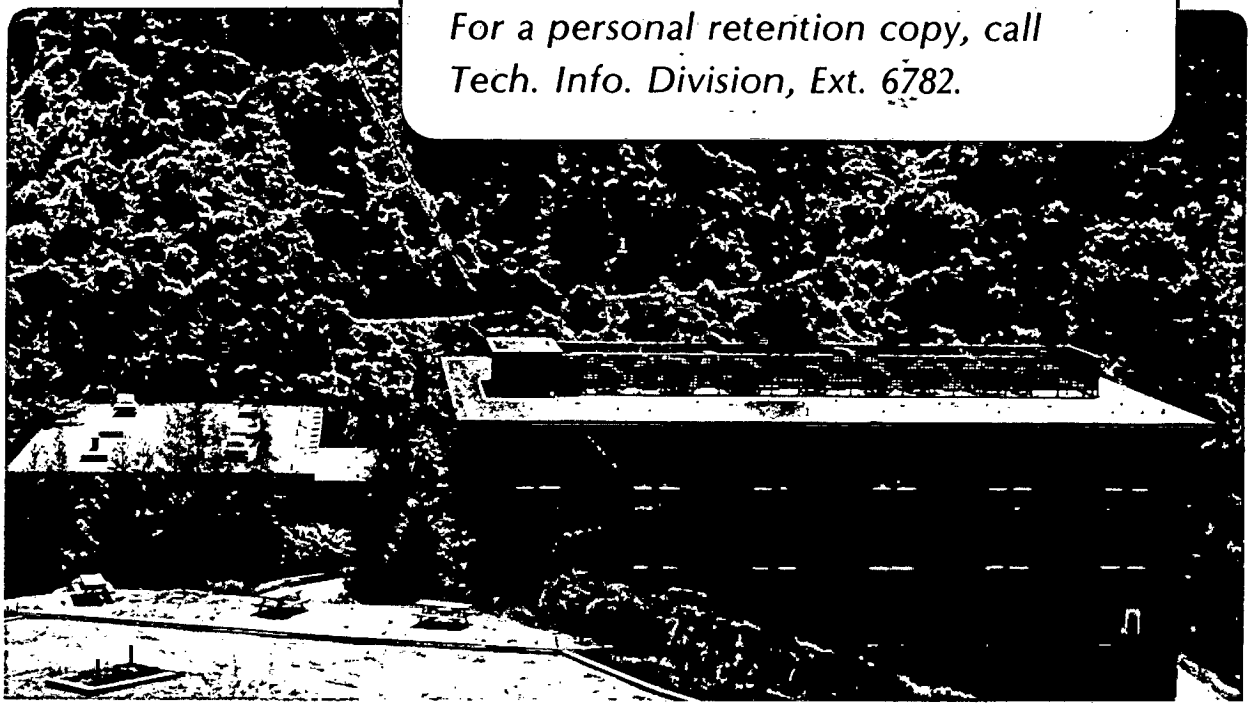

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DETERMINATION OF MOLECULAR ORIENTATION OF MONOLAYER ADSORBATES BY OPTICAL SECOND-HARMONIC GENERATION*

T. F. Heinz, H. W. K. Tom, 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

Optical second-harmonic generation has been used to deduce the average arrangement and orientation of *p*-nitrobenzoic acid molecules adsorbed at air/silica and ethanol/silica interfaces. An adsorption isotherm for the liquid/solid interface has also been obtained.

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Optical second-harmonic generation (SHG) is symmetry-forbidden in media having a center of inversion. At interfaces, however, the inversion symmetry must be broken. As a consequence, the interfacial region between two centrosymmetric media is expected to influence strongly the SH output from the system. This makes optical SHG a potentially useful probe of interfaces. Experiments have shown that the adsorption of monolayers of atoms and molecules can induce a dramatic change in the observed SH radiation from an interface.[1-3] This behavior has been exploited in the study of molecular adsorption on an electrode in an electrochemical cell.[2] More recently, spectra of electronic transitions of adsorbed monolayers have been obtained by means of resonant SHG.[3] It has also been recognized that the polarization dependence of the surface SHG can yield information about the average orientation of the molecular adsorbates.[3] In this letter, we present a scheme for deducing quite accurately the average orientation of adsorbates that can be characterized by a single axis. We have applied the technique to the problem of *p*-nitrobenzoic acid (PNBA) adsorbed on a fused silica substrate at ethanol/silica and air/silica interfaces. While the molecular group binding to the surface has already been identified,[4] no quantitative estimate of the adsorbate orientation has previously been obtained.

The general principle behind the determination of the average molecular orientation by SHG can be understood easily. Let us consider a thin layer of partially aligned molecules with a finite second-order nonlinear polarizability $\overleftrightarrow{\alpha}^{(2)}(2\omega = \omega + \omega)$. Without local-field corrections, the surface nonlinear susceptibility $\overleftrightarrow{\chi}_s^{(2)}$, can be written as $\chi_s^{(2)} = N_s\langle\overleftrightarrow{\alpha}^{(2)}\rangle$, where N_s is the surface density of molecules and the pointed brackets

signify an average over molecular orientations. With a knowledge of $\overleftrightarrow{\chi}_s^{(2)}$ and $\overleftrightarrow{\alpha}^{(2)}$, we can infer values for the components of the third-rank tensor relating the molecular axes to the fixed laboratory axes and, hence, find moments of the molecular orientation distribution.

In this paper, we restrict ourselves to the case of molecules for which $\overleftrightarrow{\alpha}^{(2)}$ is dominated by a single axial component $\alpha^{(2)}_{\zeta\zeta\zeta}$. This behavior would be exhibited by long, rod-like molecules. If the molecules in the layer have no preferred direction in the plane, then the only independent nonvanishing components of $\overleftrightarrow{\chi}_s^{(2)}$ are

$$\left(\chi_s^{(2)}\right)_{\perp\parallel\parallel} = \left(\chi_s^{(2)}\right)_{\parallel\perp\parallel} = \tfrac{1}{2}N_s\langle\cos\theta\ \sin^2\theta\rangle\alpha^{(2)}_{\zeta\zeta\zeta}$$

$$\left(\chi_s^{(2)}\right)_{\perp\perp\perp} = N_s\langle\cos^3\theta\rangle\alpha^{(2)}_{\zeta\zeta\zeta}, \tag{1}$$

where θ is the angle between the molecular ζ-axis and the surface normal. To determine the average molecular orientation, we need only consider the ratio of the two independent components of $\overleftrightarrow{\chi}_s^{(2)}$. Such a ratio is independent of N_s and $\alpha^{(2)}_{\zeta\zeta\zeta}$. It is convenient to define

$$A = 2\left(\chi_s^{(2)}\right)_{\parallel\perp\parallel}\Big/\left[\left(\chi_s^{(2)}\right)_{\perp\perp\perp} + 2\left(\chi_s^{(2)}\right)_{\perp\parallel\parallel}\right], \tag{2}$$

which, according to Eq. (1), is related to the molecular orientation by

$$A = \langle\sin^2\theta\ \cos\theta\rangle/\langle\cos\theta\rangle. \tag{3}$$

If the distribution of molecular orientations is sharply peaked, then A

gives the angle of the molecular axes directly as $\theta = \sin^{-1}\sqrt{A}$.

For a pump beam intensity $I(\omega)$, the molecular layer gives rise to SH radiation in the reflected direction with an intensity[5]

$$I(2\omega) = \frac{32\pi^3\omega^2\sec^2\Theta}{c^3\varepsilon(\omega)\varepsilon^{\frac{1}{2}}(2\omega)} \left|\vec{e}(2\omega) \cdot \chi_s^{(2)} : \vec{e}(\omega)\vec{e}(\omega)\right|^2 I^2(\omega). \tag{4}$$

Here, Θ is the angle of reflection of the SH output, ε is the linear dielectric constant of the medium through which the incident and reflected beams propagate, and $\vec{e}(\omega)$ and $\vec{e}(2\omega)$ are the products of the polarization vectors and the Fresnel factors for the pump and SH fields in the layer. Note that the ratio A, specified by $(\chi^{(2)})_{\|\perp\|}$ and $(\chi^{(2)})_{\perp\perp\perp}$, can be determined experimentally from measurements of $I(2\omega)/I^2(\omega)$ for various input and output polarizations. From a practical point of view, it is often difficult to obtain accurate results from independent intensity measurements because of laser fluctuations and problems of signal calibration. For our purposes, however, we can measure the ratio A using a simple nulling scheme. By setting the output polarizer to block the SH output, we have $\vec{e}(2\omega) \cdot \overleftrightarrow{\chi}_s^{(2)} : \vec{e}(\omega)\vec{e}(\omega) = 0$ from Eq. (4). In the case of a nonlinear layer having azimuthal symmetry, this relation can be reformulated as

$$\frac{2\left(\chi_s^{(2)}\right)_{\|\perp\|}}{\left(\chi_s^{(2)}\right)_{\perp\perp\perp} + [e_\|(\omega)/e_\perp(\omega)]^2\left(\chi_s^{(2)}\right)_{\perp\|\|}} = \frac{-e_\perp(\omega)e_\perp(2\omega)}{\vec{e}_\|(\omega) \cdot \vec{e}_\|(2\omega)} . \tag{5}$$

If the pump is arranged to satisfy $[e_\|(\omega)/e_\perp(\omega)]^2 = 2$, we can readily obtain the value of $A = \langle\sin^2\theta\cos\theta\rangle/\langle\cos\theta\rangle$ from Eq. (5).

In our discussion up to this point, we have not included the (dipole-forbidden) linear response of the bulk centrosymmetric media or of the

interfacial region in the absence of adsorbed molecules. If the SHG from these sources is appreciable, we must measure the SH electric field arising from the interface without the adsorbed layer and subtract it away from the SH field from the interface with the adsorbed layer before using the analysis given above.

We now turn to the application of the surface SHG technique to the determination of the orientation of PNBA adsorbed at ethanol/silica and air/silica interfaces. The structures of free and adsorbed molecules of PNBA are shown in Fig. 1. The nature of the adsorbed species has been inferred from the vibrational spectra of various carboxylic acids adsorbed on alumina and glass.[4] As far as the second-order polarizability of PNBA is concerned, the axial component $\alpha^{(2)}_{\zeta\zeta\zeta}$ should dominate $\overleftrightarrow{\alpha}^{(2)}$ for *p*-disubstituted benzene derivatives, as the inversion symmetry of the π-electron system is broken in the ζ-direction. Recent numerical calculations by Lalama and Garito[6] show that $\alpha^{(2)}_{\zeta\zeta\zeta}$ typically exceeds the other symmetry-allowed in-plane components of $\alpha^{(2)}$ by an order of magnitude and the remaining symmetry-allowed elements by a further order of magnitude. The inclusion of the in-plane components with values $\leqslant .1\alpha^{(2)}_{\zeta\zeta\zeta}$ in Eq. (1) leads to a correction in the value of $\langle\sin^2\theta\cos\theta\rangle/\langle\cos\theta\rangle$ in Eq. (3) that is within our experimental uncertainty. Therefore, in the following, we shall neglect all components of $\overleftrightarrow{\alpha}^{(2)}$ other than $\alpha^{(2)}_{\zeta\zeta\zeta}$.

Half-monolayer samples of adsorbed PNBA ($\sim 2 \times 10^{14}$ cm^{-2}) were prepared on an optically flat suprasil window. For the air/silica interface, a small amount of a dilute PNBA/ethanol solution was allowed to evaporate from the surface of the subtrate. This procedure left behind a fairly uniform layer of the adsorbate at a known coverage. For the ethanol/silica

interface, the cleaned window was installed in a small cell, which was then filled with a solution of PNBA dissolved in ethanol. The appropriate concentration of PNBA in solution was determined from the adsorption isotherm shown in Fig. 2. The surface coverage was obtained by measuring the intensity of the SHG from the molecule-covered interface and compensating for the contribution to the SHG from the clean interface. Note the distinct saturation behavior in the surface coverage corresponding to the chemisorption of a full monolayer. From the slope of the isotherm at low coverage, one deduces an adsorption free energy at infinite dilution, $\Delta G°$, of ~ 8 kcal/mole.[7]

The interfaces were illuminated by pump radiation at 532 nm of 100 mJ energy and 10 ns pulse duration provided by the frequency-doubled output of a Nd^{3+}:YAG laser. With the laser beam focused to ~ 0.2 cm^2, on the order of 100 SH photons per pulse were generated by the adsorbed layer. The SH output was found to be independent of rotation of the sample about its surface normal. This indicated that the azimuthal distribution of the adsorbed PNBA molecules was indeed isotropic. For the orientation measurement, the criterion $[e_{\parallel}(\omega)/e_{\perp}(\omega)]^2 = 2$ was met by adjusting the pump beam to have an angle of incidence $\theta_i = 50°$ and a polarization $\phi_i = 54.6°$ from the plane of incidence for the front-face excitation of the air/silica interface. For the excitation of the ethanol/silica interface through the fused silica window, $\theta_i = 65°$ and $\phi_i = 29.7°$. We used refractive indices of 1.46 and 1.36 for fused silica and ethanol, respectively. The index of the adsorbed PNBA layer was taken to be that of the ambient medium, i.e., either of air or of ethanol.

Under the 532 nm excitation, the SHG by the adsorbed PNBA was enhanced

by the resonance of the SH frequency with that of the first strong molecular electronic ($A_1 \rightarrow A_1$) transition. The resonant character of the SHG in the adsorbed layer was verified by the phase shifts observed between $\overleftrightarrow{\chi}_s^{(2)}$ for the adsorbed layer and for the nonresonant interface without adsorbed PNBA. By interfering the surface SH signals with those originating in a reference quartz plate excited by the same pump beam,[8] we deduced values of 90° ± 5° and 75° ± 5° for these phase shifts at the air/silica and ethanol/silica interfaces, respectively.

The SH intensity of the interface with the partial monolayer coverage of adsorbed PNBA was 5-10 times greater than that of the bare interface. After compensating for the weaker SHG by the substrate (using the phase shifts given above), we obtained A(ethanol/silica) = 0.36 ± 0.04 and A(air/silica) = 0.88 ± 0.03.[9] For a narrow distribution of molecular orientations, these values for $\langle \sin^2\theta \cos\theta \rangle / \langle \cos\theta \rangle$ would correspond to θ = 38° ± 3° for the ethanol interface and θ = 70° ± 3° for the air interface. These results are consistent with the suggestion of Hall and Hansma[4] that adsorbed benzoic carboxylic acids do not assume an orientation strictly perpendicular to the surface. The smaller value of θ for the PNBA adsorbed out of ethanol can be interpreted as arising from the dielectric screening of the interaction between their static dipole moments and/or the solvation energy of PNBA in ethanol. The large average value of θ in the case of the adsorbate at the air interface indicates that the nitro group may interact strongly with the surface.[10] By calibrating our SHG signal against a quartz plate ($d_{11} = .85 \times 10^{-9}$ esu), we measured $\left(\chi_s^{(2)}\right)_{\|\perp\|} = 9.0 \times 10^{-17}$ esu and 1.6×10^{-17} esu and deduced, assuming a narrow distributuion of molecular orientation, $\alpha^{(2)}_{\zeta\zeta\zeta} = 4.0 \times 10^{-30}$ and 7.2×10^{-31} esu for 532 nm and

1.06 μm excitations, respectively.[11]

In our analysis, we have not considered the influence of local-field effects arising from interactions between the adsorbed molecules and between the molecules and the substrate. Including these corrections, we must write $\overleftrightarrow{\chi}_s^{(2)} = N_s \langle \overleftrightarrow{\alpha}^{(2)} : \overleftrightarrow{L}(2\omega)\overleftrightarrow{L}(\omega)\overleftrightarrow{L}(\omega) \rangle$. Clearly, our analysis is valid only if the local-field corrections are small. Using the approach of Bagchi et al.[12] for a model system of rod-like molecules with a linear polarizability of $\alpha^{(1)} = 10$ Å^3 at a surface density of $N_s = 2 \times 10^{14}$ cm^2, we found diagonal local-field correction factors with $L_{\parallel} \sim 1$ and $L_{\perp} \sim (1 + \frac{1}{4}\cos^2\theta)^{-1}$. This shows that local-field effects should be relatively minor.[13] In order to verify this contention experimentally, we repeated our measurements for the ethanol/silica interface with pump excitation at 683 nm and 1.06 μm. The measured values for A and the corresponding molecular orientations θ are displayed in Table 1. The local-field corrections for resonant (532 nm), near-resonant (683 nm) and off-resonant (1.06 μm) excitation will certainly be different, so the agreement of the measured orientations within experimental error for the three cases implies that these corrections are not significant. The SH intensity associated with the adsorbed PNBA increased ~ 30-fold in changing from 1.06 μm to 532 nm pump excitation.

In conclusion, we have presented a technique for determining the average orientation of molecular adsorbates from the surface-sensitive signals of optical SHG. Molecules of PNBA were found to adsorb to fused silica with their principal axes lying fairly close to the surface normal

at an interface with ethanol, but to assume a more inclined position at an interface with air. By compensating for the residual SHG from the interface and by taking advantage of resonant enhancements in the SHG by the adsorbed species, as was done in this experiment, one should be able to apply the method to a variety of problems.

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7. For low solute concentrations ρ, the fractional adsorbate surface coverage is given by $(\rho/55.5M)\exp(\Delta G^{\circ}/RT)$, where R is the gas constant. See M. J. Rosen, Surfactants and Interfacial Phenomena (Wiley, New York, 1978), Ch.2.

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9. The major contribution to the experimental uncertainty was from the slight ($\sim$ 5%) ellipticity in the SH polarization due to weak birefringence in the fused silica substrate.

10. Tunneling spectroscopy indicates that for o-nitrobenzoic acid both the NO_2^- and COO^--groups are bound to the surface. See Korman and Coleman, ref.4.

11. These values of $\alpha^{(2)}_{\zeta\zeta\zeta}$ are comparable to those calculated for other *p*-disubstituted benzene derivatives in ref.6.

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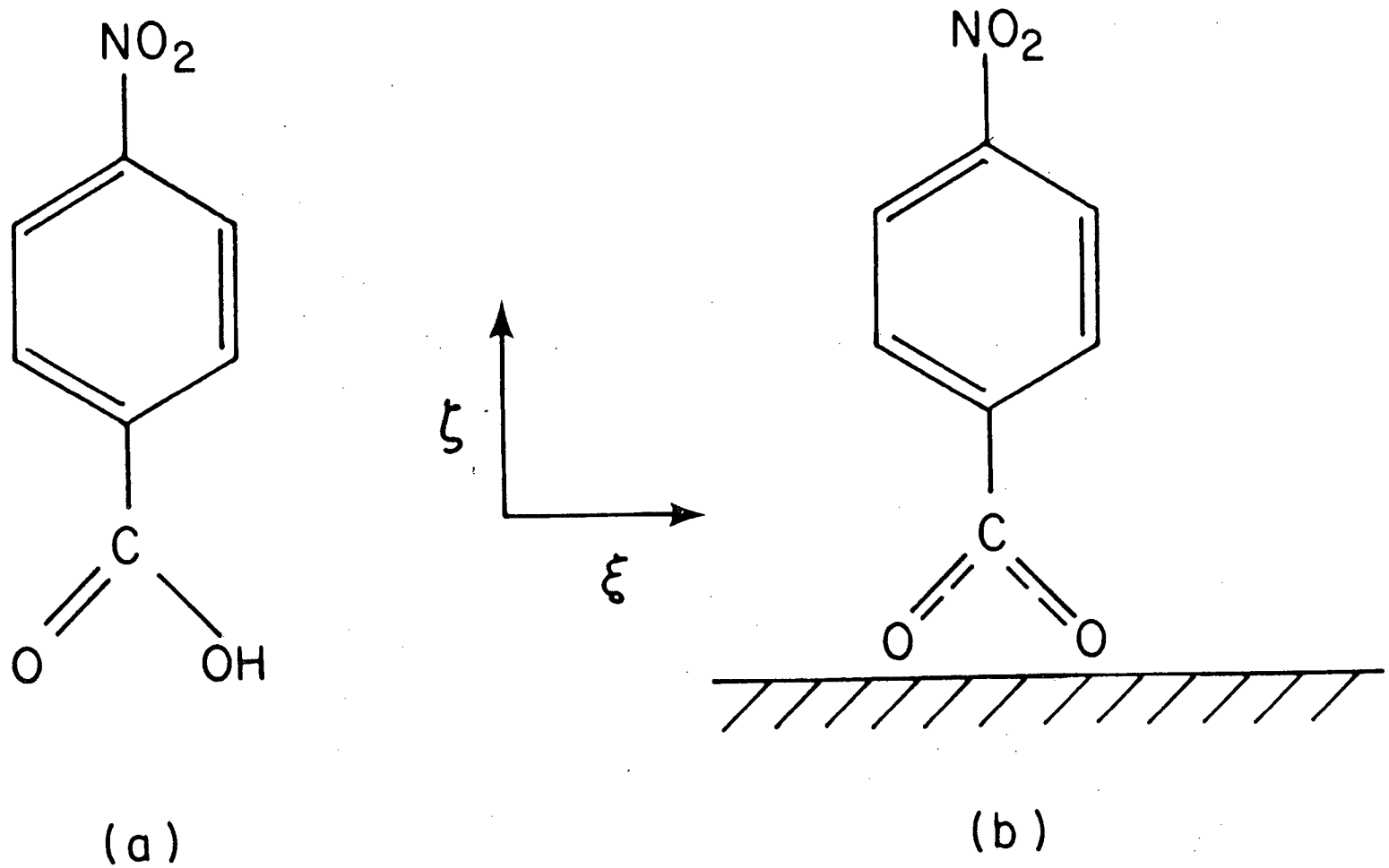
Figure Captions

Fig. 1 Structure of *p*-nitrobenzoic (a) as a free molecule and (b) as adsorbed on a fused silica surface.

Fig. 2 Isotherm for the adsorption of *p*-nitrobenzoic acid to fused silica from ethanolic solution.

Table 1. Orientational parameters for *p*-nitrobenzoic acid at the ethanol/silica interface under excitation of different wavelengths.

λ	$A = \langle \sin^2\theta \cos\theta \rangle / \langle \cos\theta \rangle$	θ
1.06 μm	0.38 ± 0.04	38° ± 3°
683 nm	0.46 ± 0.04	43° ± 3°
532 nm	0.36 ± 0.04	37° ± 3°



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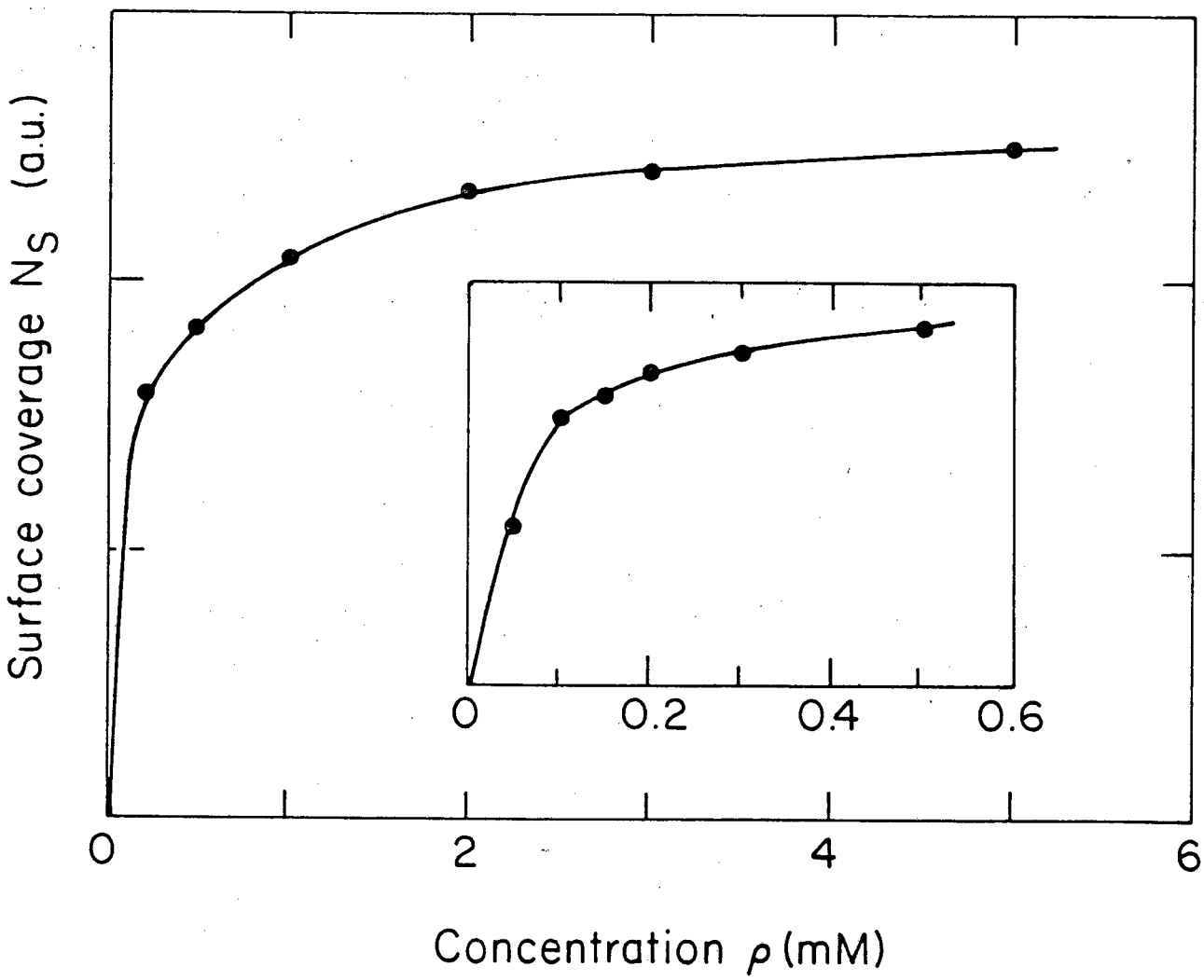

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