

Lawrence Berkeley National Laboratory

Recent Work

Title

EQUILIBRIUM AND TRANSIENT STUDY OF ADSORPTION OF PYRIDINE ON SILVER IN AN ELECTROLYTIC SOLUTION

Permalink

<https://escholarship.org/uc/item/1f6488vv>

Author

Chen, C.K.

Publication Date

1981-05-01



Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

Materials & Molecular Research Division

Submitted to Chemical Physics Letters

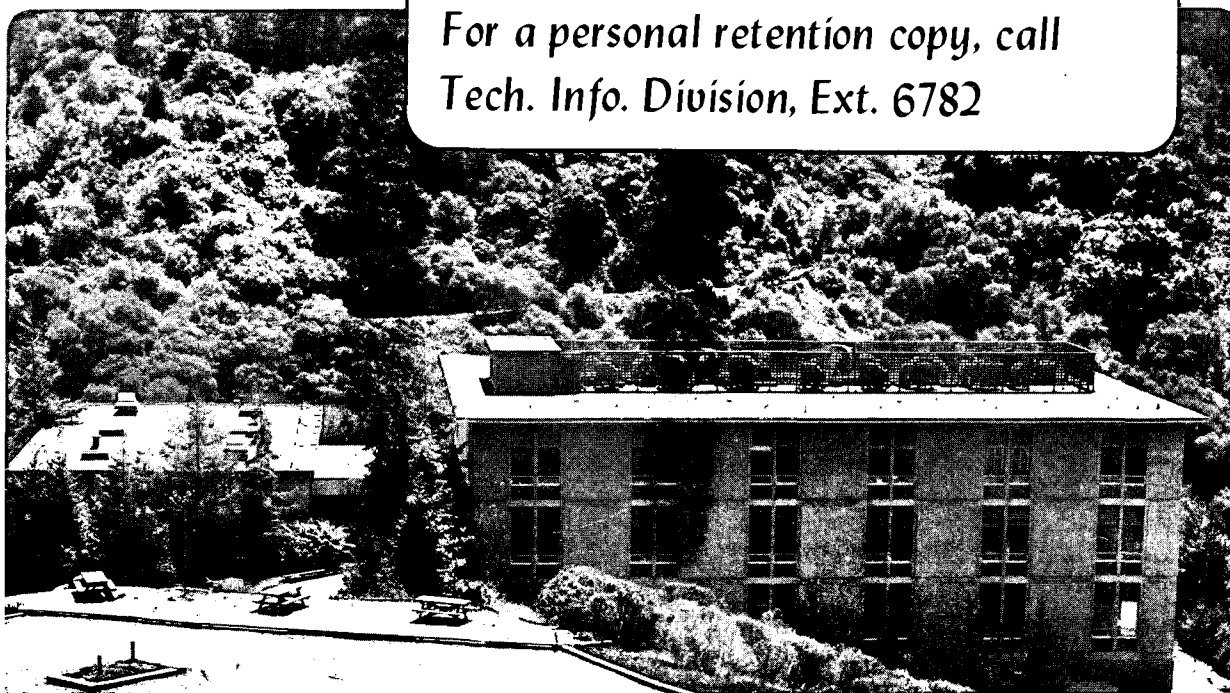
EQUILIBRIUM AND TRANSIENT STUDY OF ADSORPTION OF
PYRIDINE ON SILVER IN AN ELECTROLYTIC SOLUTION

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

May 1981

TWO-WEEK LOAN COPY

*This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 6782*



RECEIVED
MAY 26 1981
LABORATORY

LIBRARY AND
SERIALS SECTION

2
LBL-12808

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

EQUILIBRIUM AND TRANSIENT STUDY OF ADSORPTION OF PYRIDINE
ON SILVER IN AN ELECTROLYTIC SOLUTION

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

Physics Department, University of California
Berkeley, California 94720

and

Materials and Molecular Research Division
Lawrence Berkeley Laboratory, Berkeley, California 94720

May 1981

ABSTRACT

Surface-enhanced second-harmonic generation and surface-enhanced Raman scattering are used to study the adsorption of pyridine on silver in an electrolytic solution. The observed adsorption isotherms can be approximated by Langmuir curves, but the transient behaviors are difficult to understand.

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract Number W-7405-ENG-48.

*On leave from Laboratoire d'Optique Quantique, Ecole Polytechnique, 91128 Palaiseau, France.

The detection and study of adsorbed molecules at solid-gas and solid-liquid interfaces is an area of active and intensive research.¹ While many sensitive probes have been developed for studies of surfaces in vacuo,¹ there is a lack of an in situ high-sensitivity, high-resolution probe to study adsorbed molecules at a solid-liquid interface.² The recent discovery of surface-enhanced Raman spectroscopy (SERS) may be an important breakthrough in that respect.^{3,4} More recently, we have demonstrated that molecular monolayers adsorbed at a rough silver-electrolyte interface can also be readily detected by optical second-harmonic generation (SHG).⁵ In fact, from a simple estimate, one expects that SHG should be observable without the surface enhancement due to rough surface structures.⁵ Here we apply both the SHG and SERS techniques to an in situ study of the equilibrium behavior of pyridine adsorption at a roughened silver-electrolyte interface⁶ and show that the adsorption isotherm (fractional coverage versus bulk pyridine concentration) can be approximated by a Langmuir curve.⁷ In addition, we determine that the transient response of the SHG depends strongly on the applied voltage, but only weakly on the pyridine concentration.

Our experiment was carried out on an electrolytically cycled silver electrode. We prepared the silver sample by mechanical polishing, ending with $.05 \mu\text{m Al}_2\text{O}_3$ powder. We then submerged it together with a Pt working electrode and a reference saturated calomel electrode (SCE) in a glass cell containing 0.1 M KCl in doubly distilled water, which was continuously purged by N_2 gas. The sample was initialized by running three oxidation-reduction cycles, each with a charge transfer of $\sim 90 \text{ mCoul/cm}^2$. Pyridine was subsequently added to the electrolytic solution at a

silver-SCE potential of $V_{\text{Ag-SCE}} = -0.2$ V, and SHG and SERS were measured as a function of bulk pyridine concentration at a prescribed $V_{\text{Ag-SCE}}$.

For SHG, the input beam at $1.06 \mu\text{m}$ was provided by a Q-switched Nd:YAG laser operating at 10 pulses per second. The 10 nsec laser pulses were p-polarized and incident on the silver-electrolyte interface at 45° with an energy of 0.2 mJ per pulse and a cross-section of 0.2 cm^2 . The diffuse second-harmonic (SH) signal at $.53 \mu\text{m}$ was collected using f/1 optics aligned along the specularly reflected direction, with the pump radiation rejected by color filters and an interference filter or monochromator. The signal was then detected by an RCA 7265 photomultiplier and recorded using a gated electrometer with a one second time constant and strip chart recorder. We note that additional electrolytic cycles before the introduction of pyridine had little effect on the observed signal. Electrolytic cyclings subsequent to the addition of pyridine were avoided, since they might have led to an alteration of the condition of the silver surface. Measurements were taken under successive increases in the pyridine concentration; however, in order to verify that an equilibrium had been attained and that no irreversible changes were occurring, we determined that the SH signal for a weak solution of pyridine could be recovered by the dilution of a concentrated one. We also checked that there were no laser-induced desorption effects under the given operating conditions.

The observed SH signal came from both the silver substrate and the adsorbed molecules. Neglecting local-field corrections arising from interactions between adsorbed molecules, the nonlinear polarization asso-

ciated with the adsorbed molecules should be linear in their surface density, N_a . In the presence of the metal surface, the nonlinear polarizations associated with both the silver and the adsorbed molecules are expected to be everywhere nearly perpendicular to the metal surface, and hence, parallel to each other. Therefore, assuming the two contributions to the total polarization to be in phase, we can express the SH power in the form

$$P(2\omega) = (A + B N_a)^2, \quad (1)$$

where A and B are real constants.⁸ The constant A was obtained by measuring $P(2\omega)$ in the absence of adsorbed molecules. The adsorption isotherm, N_a versus the bulk pyridine concentration ρ , could then be obtained by plotting $(\sqrt{P(2\omega)} - A)$ versus ρ . This is shown in Fig. 1 for $V_{\text{Ag-SCE}} = -1.0$ V.

The adsorption isotherm can in general be quite complicated, depending on the mechanism of molecular adsorption. In many cases, however, it can be approximated by the Langmuir curve⁷

$$N_a = \frac{\rho}{K + \rho} N_{as}, \quad (2)$$

where K is a constant at fixed temperature T and N_{as} is the saturated value of N_a for a monolayer surface coverage. In terms of the adsorption free energy ΔG in aqueous solution, we have⁷

$$K = 55 \exp(-\Delta G/RT) \quad (3)$$

in mole/l (M), where $R = 1.99$ cal/mole - K is the gas constant. We found that in the present case, Eq. (2) with $K = 1.11 \times 10^{-2}$ M actually gives a good fit to the experimental data, as shown in Fig. 1. The corresponding adsorption free energy ΔG is therefore 5.1 Kcal/mole for pyridine on silver.

In addition to SHG, we also measured the pyridine SERS-signal versus bulk pyridine concentration to provide an alternative method of finding the adsorption isotherm. An argon ion laser at 5145 Å was used for excitation. It generated a p-polarized 30 mW beam, which was focused to ~ 2 mm \times .25 mm on the silver-electrolyte interface at $\sim 20^\circ$ from the surface normal. The SERS signal resulting from adsorbed pyridine molecules was collected along the surface normal. As in the SH case, the pyridine concentration was changed at $V_{\text{Ag-SCE}} = -0.2$ V. The equilibrium SERS signal was measured at $V_{\text{Ag-SCE}} = -0.6$ V. As Fig. 2 illustrates, the SERS signal for the 1005 cm^{-1} Raman mode of pyridine versus pyridine concentration with its characteristic saturation behavior resembles that of Fig. 1.⁹ The solid curve in the figure is, as before, a theoretical fit using the Langmuir model of Eq. (2) with $K = 4 \times 10^{-3}$ M. The corresponding adsorption free energy is $\Delta G_{\text{SERS}} = 5.7$ Kcal/mole.

In comparing the results for SHG and SERS, we note that although the adsorption isotherms in Figs. 1 and 2 are somewhat different, the adsorption free energies are essentially the same. The differences can be explained by the facts that (1) the signals were measured at different values of $V_{\text{Ag-SCE}}$ and (2) different input frequencies were used. Since both the SHG and the SERS were surface enhanced through excitation of localized surface plasmons on the rough structures,¹⁰ the two tech-

niques with inputs of different frequencies would tend to probe pyridine adsorbed at different sites, which could have slightly different adsorption free energies and adsorption isotherms.

A simple Langmuir model has the following dynamic equation governing the adsorption of molecules at a surface:

$$\frac{dN_a}{dt} = -\alpha N_a + \beta \rho (N_{as} - N_a), \quad (4)$$

where α and β are constants related to desorption and adsorption, respectively, with $\alpha/\beta = K$. The equilibrium solution of Eq. (4) takes the form of Eq. (2), which appears to fit the experimental results fairly well, as shown in Figs. 1 and 2. The transient solution of Eq. (4) has the form

$$N_a(t) = \frac{\rho N_{as}}{K + \rho} + \left(N_a(0) - \frac{\rho N_{as}}{K + \rho} \right) \exp(-t/\tau), \quad (5)$$

where $\tau = (\alpha + \beta\rho)^{-1}$. We wondered whether Eq. (5) would also predict the transient behavior of N_a . We therefore measured the SHG and SERS signals as a function of time immediately after the final V_{Ag-SCE} value was applied following the completion of an electrolytic cycle. A large transient effect was observed. In the case of SERS, with 50 mM pyridine and $V_{Ag-SCE} = -0.8$ V, for example, the signal, as shown in Fig. 3, first increased rapidly to a certain large magnitude and then decayed exponentially to the equilibrium value with a time constant $\tau \sim 36$ sec. This presumably indicates that during the establishment of the double layer at the silver electrode, more pyridine molecules appeared in re-

gions with large surface enhancement before relaxing to their equilibrium configuration.

The transient behavior of SHG is even more complicated. For $V_{\text{Ag-SCE}} < -0.7$ V, the signal also overshoot its steady-state value and then decayed (Fig. 3). The time dependent decay of $(\sqrt{P(2\omega)} - A) = B N_a$ can be approximated fairly well by the sum of two exponentials with time constants τ_1 and τ_2 . For -0.9 V $> V_{\text{Ag-SCE}} > -1.0$ V and 2.5 mM $< \rho < 70$ mM, τ_1 ranged from 5 to 12 seconds and τ_2 ranged from 24 to 84 seconds. The time constants for SHG and SERS did not depend strongly on ρ and appeared to increase rather than decrease as ρ was augmented. This suggests that the Langmuir model of Eq. (4) is probably too simple to explain the dynamics of adsorption and desorption in the present case. At 50 mM concentration, as $V_{\text{Ag-SCE}}$ was increased from -1.1 to -0.9 V, the decay showed only slight changes, but when $V_{\text{Ag-SCE}}$ was further increased to the $-(0.75 - 0.85)$ range, τ_2 grew dramatically to 360 sec. Then for $V_{\text{Ag-SCE}} \gtrsim -0.7$ V, the signal no longer overshoot its steady-state value, but instead approached the steady state from below. A similar voltage dependence was also observed at $\rho = 5$ mM. This more complicated transient behavior of SHG as compared to SERS suggests that reorientation and rearrangement of adsorbed molecules may be important, since they should affect SHG more strongly. However, we were unable to formulate a simple model explaining the observed transient behaviors of both SERS and SHG.

In conclusion, we have demonstrated that surface-enhanced SHG, similar to SERS, can be used as a sensitive in situ probe to study adsorption of molecules at a solid-liquid interface. The observed SHG and SERS

signals from adsorbed pyridine on silver as functions of pyridine concentration in solution can be explained by the Langmuir model, but their transient behaviors are difficult to understand.

One of us (TFH) gratefully acknowledges partial support from an NSF graduate fellowship. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract Number W-7405-ENG-48.

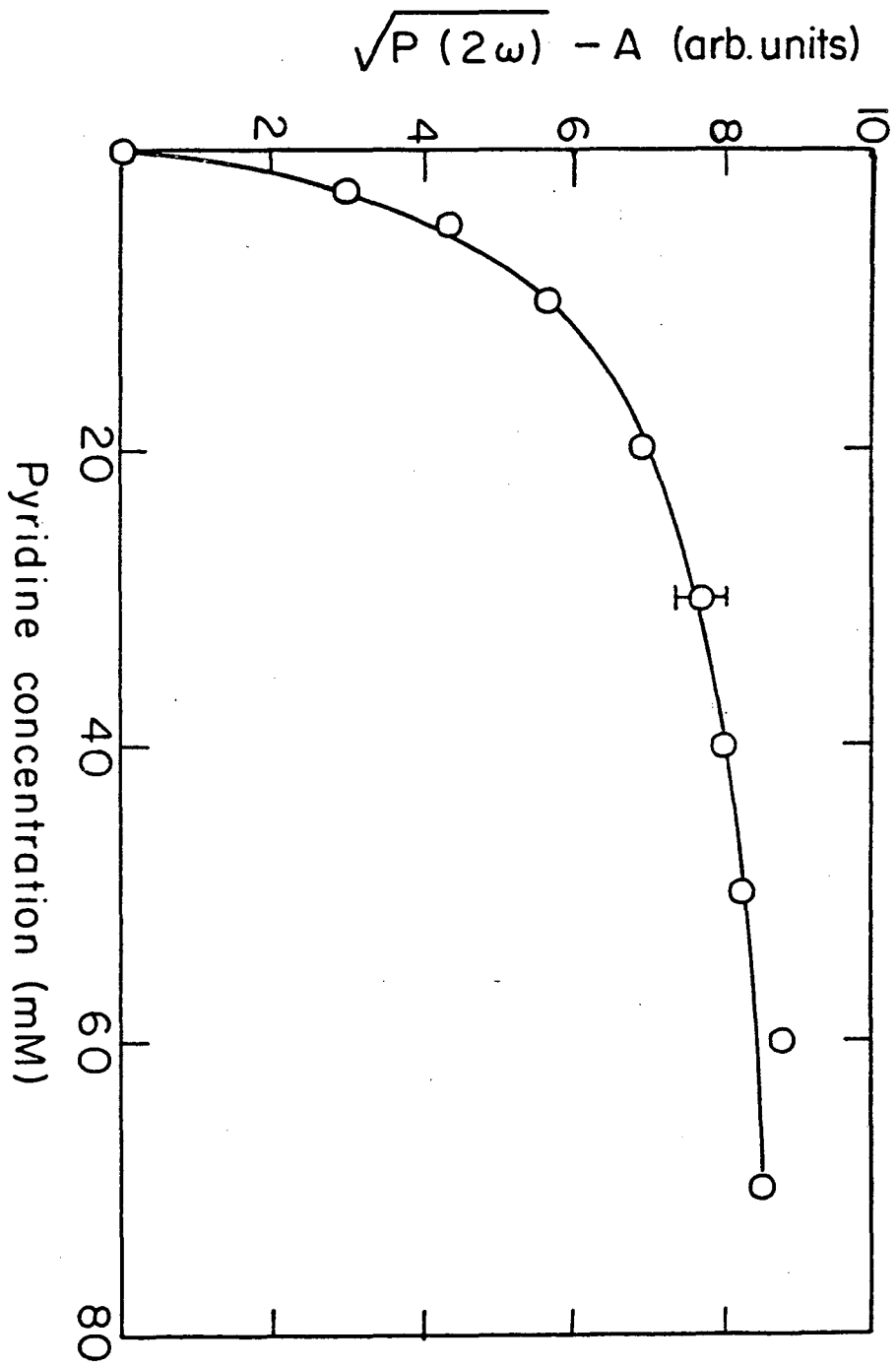
References

1. See, for example, G. A. Somorjai and M. A. Van Hove, Adsorbed Monolayers on Solid Surfaces (Springer-Verlag, New York, 1979); G. A. Somorjai, Chemistry in Two Dimensions: Surfaces (Cornell University Press, Ithaca, NY, 1981) and references therein.
2. For an overview of conventional physical chemistry techniques used, see, for example, A. W. Adamson, Physical Chemistry of Surfaces, 3rd ed. (J. Wiley and Sons, New York, 1976) and references therein.
3. D. L. Jeanmaire and R. P. Van Duyne, J. Electroanal. Chem. 84 (1977) 1; M. Fleishmann, P. J. Hendra, and A. J. McQuillan, Chem. Phys. Lett. 26 (1974) 163.
4. For a recent review of SERS, see T. E. Furtak and J. Reyes, Surf. Sci. 93 (1980) 351.
5. C. K. Chen, T. F. Heinz, D. Ricard, and Y. R. Shen, Phys. Rev. Lett. 46 (1981) 1010.
6. A study on the adsorption of pyridine to a silver surface in ultra-high vacuum has recently been completed. See J. E. Demuth, K. Christmann, and P. N. Sanda, Chem. Phys. Lett. 76 (1980) 201.
7. See, for example, M. J. Rosen, Surfactants and Interfacial Phenomena (J. Wiley and Sons, New York, 1978), Chap. 2.
8. In general, A and B can be complex, but we have observed interference effects that indicate that these constants have the same phase (unpublished results).
9. We note that our result differs from that of Jeanmaire and Van Duyne of Ref. 3. Their data show an "S" shaped adsorption isotherm, which may be the result of different sample preparation.

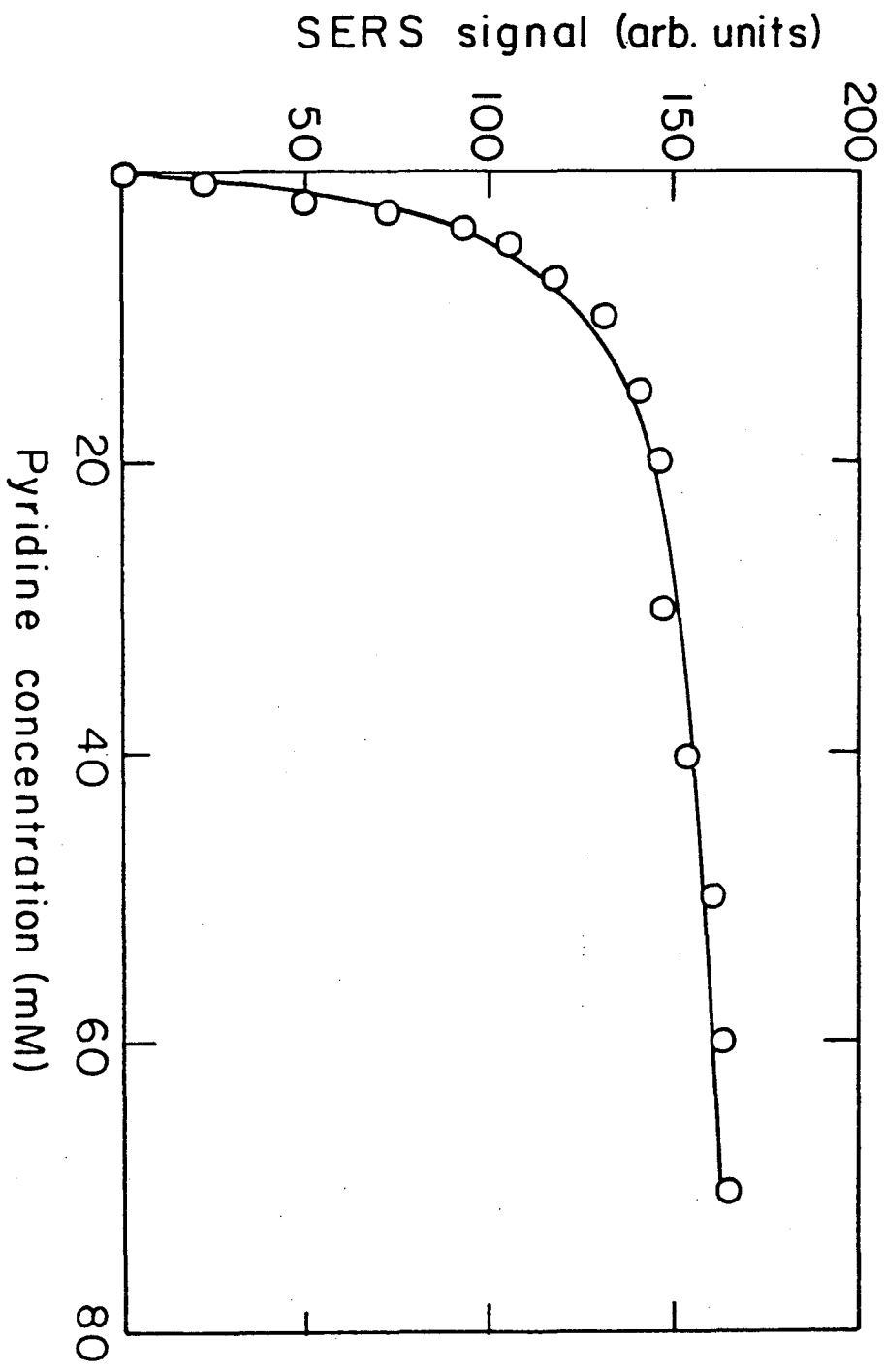
10. C. K. Chen, A. R. B. de Castro, and Y. R. Shen, Phys. Rev. Lett. 46 (1981) 145; S. L. McCall, P. M. Platzman, and P. A. Wolff, Phys. Lett. 77A (1980) 331; J. Gersten and A. Nitzan, J. Chem. Phys. 73 (1980) 3023.

Figure Captions

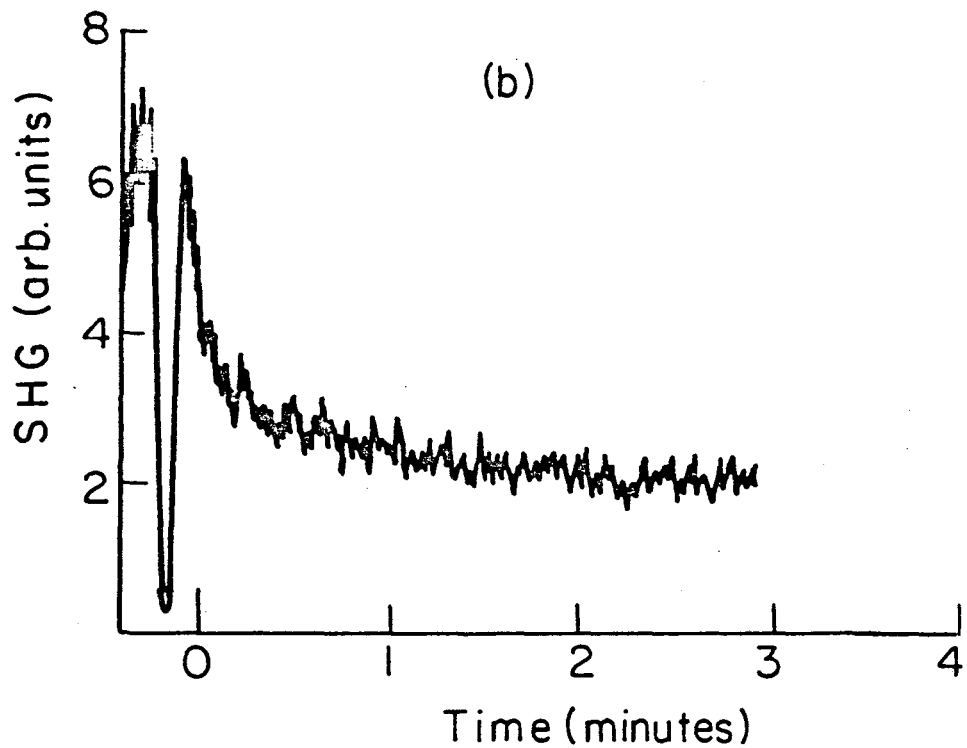
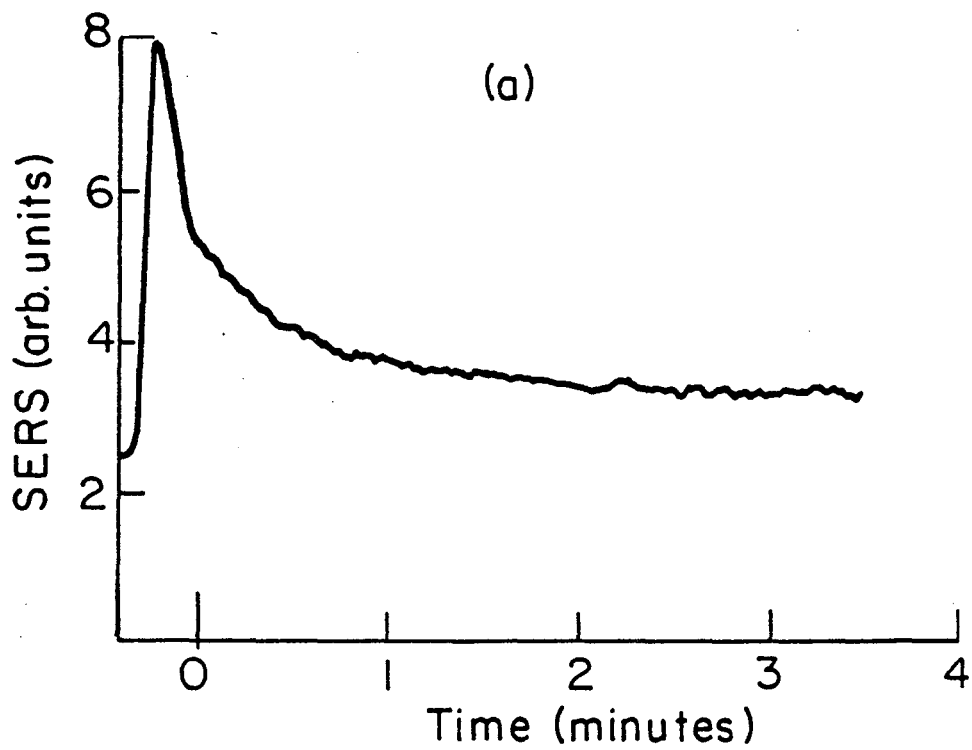
- Fig. 1 Equilibrium $(\sqrt{P(2\omega)} - A)$ versus bulk pyridine concentration. The solid curve is a theoretical fit to the experimental data using the Langmuir model.
- Fig. 2 Equilibrium SERS of the 1005 cm^{-1} mode at $V_{\text{Ag-SCE}} = -0.6 \text{ V}$ versus bulk pyridine concentration. The solid curve is a theoretical fit to the experimental data using the Langmuir model.
- Fig. 3 Transient SERS (a) and SHG (b) at $5 \times 10^{-3} \text{ M}$ pyridine concentration immediately following an oxidation-reduction cycle. $V_{\text{Ag-SCE}}$ remains constant for $t \geq 0$.



XBL 815-5824



X BL 815 - 5825



XBL 815-5826

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720