



Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

Materials & Molecular Research Division

MASTER

Presented at the Vth International Conference on
Laser Spectroscopy, Alberta, Canada,
June 29-July 3, 1981

SURFACE-ENHANCED NONLINEAR OPTICAL EFFECTS AND
DETECTION OF ADSORBED MOLECULAR MONOLAYERS

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

June 1981



SURFACE-ENHANCED NONLINEAR OPTICAL EFFECTS AND DETECTION
OF ADSORBED MOLECULAR MONOLAYERS

Y. R. Shen, C. K. Chen, T. F. Heinz, and J. Ricard
Department of Physics
University of California
Berkeley, CA 94720, USA

and

Materials and Molecular Research Division
Lawrence Berkeley Laboratory
Berkeley, CA 94720, USA

In recent years, we have been interested in the study of nonlinear optical effects at interfaces. Our motivation is twofold. First, while nonlinear optics in a bulk medium is now well developed, that at an interface has not received much attention since the early investigations of BEHRENDSEN and co-workers on second-harmonic reflection from a surface [1]. Second, with the understanding of surface nonlinear optics, we hope to gain insight for the study of surface properties, in particular, for the study of molecular adsorption and overlayers on surfaces. There already exist various techniques for studies of this nature, such as photoemission, LEIS, Auger, infrared, and Raman spectroscopy [2], but laser optical techniques are intrinsically better in spectral resolution.

A few recent developments in surface nonlinear optics in relation to surface study are of interest. We have found that surface coherent anti-Stokes Raman scattering with picosecond pulses can have the sensitivity of detecting submonolayers of molecules on surfaces [3]. Then, HERITAGE [4] and LEVINE et al. [5] have demonstrated the possibility of obtaining Raman spectra of very thin films and molecular monolayers with picosecond Raman gain spectroscopy. In another area, it has been found that Raman scattering of adsorbed molecules on a rough surface of some metals can be enhanced by five or six orders of magnitude [6], enabling the study of adsorbed molecular submonolayers on those surfaces. We have realized that such surface enhancement should also occur in other nonlinear optical processes [7]. In this paper, we discuss the observation of a number of surface-enhanced nonlinear optical effects. We also show the possibility of using the nonlinear generation to detect the adsorption of molecular monolayers on a metal surface in an electrolytic solution [8].

For surface-enhanced Raman scattering (SERS), it is now believed by many researchers that the enhancement arises mainly from the large local fields present near rough metal structures [9], although it is generally also partially due to the interaction of molecules with the metal. The strong local-field effect has its origin in the resonant excitation of local surface plasmons on the rough metal structures. We can, in general, write the local field $E_{\text{loc}}(\omega) = L(\omega)E(\omega)$, with E being the incident optical field and L the local-field correction factor. On the surface of a metal spheroid, if the diameter of the spheroid is much less than the wavelength $\lambda = 2\pi c/\omega$, it is easily shown that [9]

$$L(\omega) \propto [\epsilon_m(\omega) - \epsilon(\omega)] / [\epsilon_m(\omega) + 2\epsilon(\omega)], \quad (1)$$

where $\epsilon_m(\omega)$ and $\epsilon(\omega)$ are the dielectric constants of the metal and the sur-

rounding dielectric medium, respectively. At the surface plasmon resonance, $\text{Re}[\epsilon_m(\omega) + 2\epsilon(\omega)] = 0$, and $L_{\text{max}}(\omega) \propto \text{Im}[\epsilon_m(\omega) + 2\epsilon(\omega)]^{-1}$ is resonantly enhanced. This is possible for metals because $\text{Re}[\epsilon_m]$ is negative below the bulk plasmon resonance. More generally, the local field on a particular surface area of a small metal aggregate of a certain shape can be written as $L(\omega) \propto 1/f(\epsilon)$, and the surface plasmon resonance is excited when $\text{Re}[f(\epsilon)] = 0$.

A nonlinear optical process is usually governed by the nonlinear polarization [10]

$$P^{(n)}(\omega) = \chi^{(n)}(\omega = \omega_1 + \dots + \omega_n) E_1 \dots E_n \quad (2)$$

with $\chi^{(n)} = L(\omega)L(\omega_1) \dots L(\omega_n) N \alpha^{(n)}$, where $\alpha^{(n)}$ and $\chi^{(n)}$ are the n th-order polarizability and susceptibility, respectively, and N is the density of atoms or molecules. We note that if $L(\omega)$, $L(\omega_1)$, ..., $L(\omega_n)$ are all resonantly enhanced, then $\chi^{(n)}$ and the corresponding nonlinear optical effect would be greatly magnified. In the case of Raman scattering, the effective Raman cross-section σ_{eff} is proportional to $\chi^{(3)}(\omega_s = \omega_2 - \omega_1 + \omega_3)$. Therefore, we have

$$\sigma_{\text{eff}} = L^2(\omega_2) L^2(\omega_s) \sigma \quad (3)$$

If $L(\omega_2) = L(\omega_s) = 20$, which is a conservative estimate on silver, one finds $\sigma_{\text{eff}} = 1.6 \times 10^5 \sigma$. On top of this local-field enhancement, the Raman cross-section can, of course, be further enhanced through the interaction of the molecules with the metal.

Eq.(2) suggests that other nonlinear optical processes should also experience such a local-field enhancement. In particular, second-harmonic generation is proportional to $|\chi^{(2)}(2\omega)|^2$ and there one has a local-field enhancement factor $n_{\text{loc}}(2\omega) = L^4(\omega)L^2(2\omega)$. Similarly, third-harmonic generation has $n_{\text{loc}}(3\omega) = L^6(\omega)L^2(3\omega)$, and coherent anti-Stokes Raman scattering has $n_{\text{loc}}(\omega_a) = L^4(\omega_i)L^2(\omega_s)L^2(\omega_a)$. If we assume, appropriate for rough silver, $L(\omega) = L(\omega_i) = L(\omega_s) = L(\omega_a) = 20$ and $L(2\omega) = L(3\omega) = 1$, we find $n_{\text{loc}}(2\omega) = 1.6 \times 10^5$, $n_{\text{loc}}(3\omega) = 6.4 \times 10^7$, and $n_{\text{loc}}(\omega_a) = 2.6 \times 10^{10}$. These are huge enhancement factors, suggesting that even if only a monolayer of atoms or molecules contributes to the nonlinear optical effects, they could be observable.

We have indeed observed surface-enhanced second-harmonic generation (SHG) from a roughened silver surface [7]. In this case, SHG from a metal surface is believed to come from the first one or two surface layers of metal atoms. The enhancement can be directly measured by comparing the signal with the second-harmonic reflection from a smooth silver film. A Q-switched Nd:YAG laser at $1.06 \mu\text{m}$ was used in the experiment to provide the pump beam. The sample was roughened by an electrolytic oxidation-reduction process and then rinsed in distilled water and dried by nitrogen. The second-harmonic (SH) reflection from the rough surface was highly diffuse. Its integrated power over the nearly isotropic angular distribution was found to be $\sim 1 \cdot 10^7$ times larger than the collimated second-harmonic signal from the smooth surface. The results are shown in Fig.1. That the signals were indeed from SHG is confirmed by the quadratic dependence of the signals on the input laser power, together with a measurement of the spectrum. To find the actual local-field enhancement, we realize that essentially all the enhanced SHG came from the silver aggregates on the roughened surface. Electron micro-

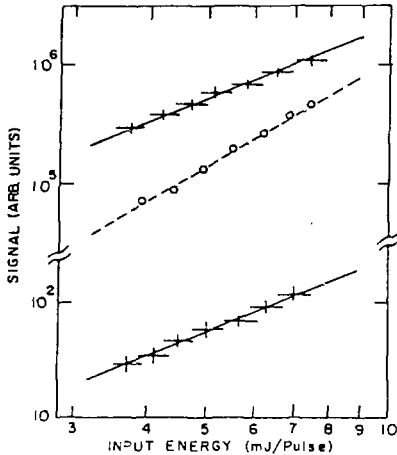


Fig.1 Power-law dependences of the nonlinear signal on silver. The upper and lower solid curves show the quadratic dependence of the diffuse SH signal from the rough bulk sample and of the collimated SH signal from the smooth film, respectively; the dashed curve shows the cubic dependence of the diffuse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

graphs showed that the surface consists of ~ 500 Å Ag aggregates separated by 1500 – 3000 Å. We therefore estimate that the aggregates occupied a fraction of roughly 5% of the total surface. Then, if we assume that the coherent dimension of surface second-harmonic generation is approximately equal to the size of the aggregates, the actual local field enhancement of SHG from the aggregates is $n_{\text{loc}}(2\omega) \cdot 10^4/0.05 = 2 \times 10^5$. This may still be an underestimate, since not all aggregates give the maximum local-field enhancement. Since ω is very different from 2ω , $L(\omega)$ and $L(2\omega)$ cannot both be at surface plasmon resonances. For the maximum enhancement, we expect $L(\omega)$ to be appreciable, but $L(2\omega) \sim 1$. Then, from $n_{\text{loc}}(2\omega) = L^4(\omega)L^2(2\omega)$, we infer $L(\omega) \sim 20$, which seems reasonable.

We have used, in a separate experiment [11], a pump beam at 0.53 and 0.68 μm and found that the surface enhancement of SHG was only $\sim 10^2$. This is expected because $L(\omega)$ is roughly proportional to $\text{Im}\{\epsilon_m(\omega)\}/\text{Im}\{\epsilon_m(\omega)\}$ and therefore decreases as ω approaches the bulk plasmon resonance of the metal. We have also found that the surface enhancement of sum-frequency generation with ω_1 at 1.06 μm and ω_2 at 0.53 μm is about three orders of magnitude smaller than that of SHG with ω at 1.06 μm , which can be understood from the relation $n_{\text{loc}}(\omega_1 + \omega_2)/n_{\text{loc}}(2\omega) = L^2(\omega_1 + \omega_2)L^2(\omega)$. Surface-enhanced SHG from copper and gold has also been seen. The enhancement is at least one order of magnitude weaker than that for silver and can be explained by the smaller L resulting from the heightened values of $\text{Im}\epsilon$ for copper and gold [7].

Among the surface-enhanced nonlinear optical effects, BOYD and YU [11] in our laboratory have observed third-harmonic generation from a roughened gold surface with a pump beam at 1.06 μm . For a 10 nsec pulse, with peak intensity of 5 MW/cm² in an area of .2 cm², a rough estimate suggests that the third-harmonic signal from a smooth gold surface is about 3 orders of magnitude weaker than the second-harmonic signal in the absence of any surface enhancement. With surface enhancement, it should be about 1 order of magnitude weaker, in general agreement with our measurements. We have also observed surface-enhanced luminescence from roughened surfaces of silver, cop-

per, and gold with one- and two-photon excitation. Luminescence with one-photon excitation from a smooth silver surface was rather weak, and that with two-photon excitation is not observable. We can consider luminescence with n -photon excitation as an $(n + 1)$ -photon process, but the surface enhancement factor in this case is more difficult to estimate because the radiation efficiencies from smooth and rough surfaces may be very different. Hyper-Raman scattering is another three-photon process. It is rather weak and not easily observable even in bulk media. With surface enhancement, however, it even becomes possible to observe hyper-Raman scattering from molecules adsorbed on surfaces, as has recently been reported by CHANG for SO_2 on silver powder [12]. The local-field enhancement factor in this case is $[\eta_{\text{loc}}]_{\text{HR}} = L^4(\omega_2)L^2(\omega_S) = 1.6 \times 10^5$, if $L(\omega_2) = 20$ and $L(\omega_S) = 1$. Surface-enhanced coherent anti-Stokes Raman scattering (CARS) is especially interesting, since, as we mentioned earlier, the local-field enhancement factor is as high as 2.6×10^{10} for $L(\omega) = 20$. In addition, interactions between the molecules and metal can further enhance the process. One would then expect that it would be possible to observe surface-enhanced CARS from molecules adsorbed on silver. Unfortunately, discrimination of the anti-Stokes signal against elastic scattering of the pump beams from the rough surface is difficult. Work to detect surface-enhanced CARS is presently still in progress.

Since one can observe SHG from one or two layers of metal atoms on a metal surface, one would expect that it is also possible to observe SHG from a monolayer of adsorbed molecules. This is confirmed by a theoretical estimate using the equation [8]

$$S = \frac{256\pi^3\omega}{hc^3} |N_a \alpha^{(2)}|^2 I_1^2 A T \text{ photons/pulse,} \quad (3)$$

where S is the SHG signal, N_a is the surface density of molecules, $\alpha^{(2)}$ is the second-order polarizability, I_1 is the intensity of a p-polarized pump beam incident at 45° , A is the beam cross-section, and T is the pulsewidth, all in cgs units. If $\alpha^{(2)} \sim 1 \times 10^{-23}$ esu, $N_a \sim 4 \times 10^{14}$ cm^{-2} , $I_1 \sim 1$ MN/cm^2 at 1.06 μm , $A = 0.2$ cm^2 , and $T = 10$ nsec, we find that $S \sim 1.5 \times 10^3$ photons/pulse. Thus, even without surface enhancement, SHG from a monolayer of adsorbed molecules with $|N_a \alpha^{(2)}| \geq 10^{-15}$ esu should be detectable if the pump beam does not induce surface damage.

By preparing a monolayer of p-nitrobenzoic acid adsorbed on an aluminum oxide surface, we have obtained direct evidence for the detectability of a molecular monolayer by SHG in the absence of any surface enhancement effects. In this case, the adsorbed monolayer produced ~ 5 times as much second-harmonic signal as the substrate alone. In another case of interest, we have studied SHG from a smooth Ag electrode in an electrolytic cell, which consisted of a glass cell containing 0.1M KCl in doubly distilled water. In addition to the Ag electrode, a Pt working electrode and a saturated calomel electrode were submerged in the electrolytic cell, with a bias voltage applied between the Pt and Ag electrodes. The effect of the double charge layer in the solution at the Ag surface on SHG can be readily seen. The observed reflected second-harmonic signal as a function of the voltage drop between Ag and the reference saturated calomel electrode (SCE), $V_{\text{Ag-SCE}}$, appears in Fig.2. This curve can be understood as the result of interference between the SHG from Ag and the field-induced SHG from the double charge layer. In fact, the data can be fit very well by an effective nonlinear susceptibility

$$\chi_{\text{eff}}^{(2)} = \chi_{\text{Ag}}^{(2)} + \chi_{\text{DC}}^{(2)} \quad (4)$$

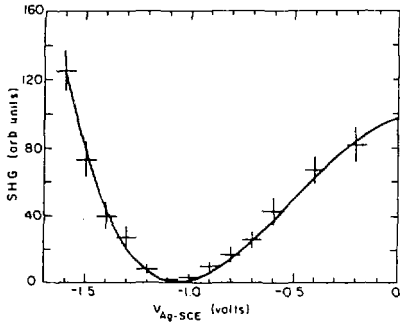


Fig.2 SH from a smooth silver film in 0.1M KCl versus V_{Ag-SCE}

with $\chi_{DC}^{(2)} = aE_0 + bE_0^2$, where E_0 is the DC electric field in the double charge layer and is assumed to be linear in V_{Ag-SCE} [13]. We assume that $\chi_{Ag}^{(2)}$ is independent of V_{Ag-SCE} .

With surface enhancement, SHG from adsorbed molecules is even more easily observable [8]. This can be shown by monitoring the diffuse SH from the Ag electrode submerged in the electrolytic cell during an oxidation-reduction cycle. The first one or two electrolytic cycles roughen the Ag surface and presumably activate the adsorption sites. The SHG signal from the roughened Ag electrode is then monitored during a subsequent cycle. A typical result is shown in Fig.3. At the beginning of the oxidation cycle, the signal rises

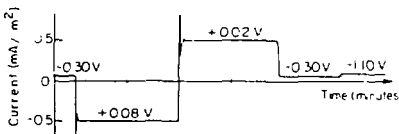
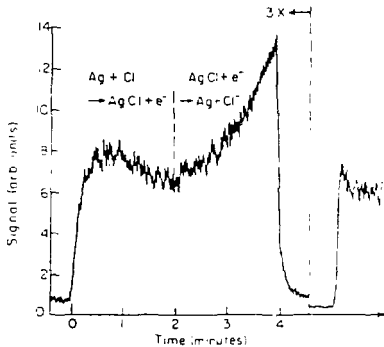


Fig.3 Current and diffuse SH as a function of time during and after an electrolytic cycle. The voltages listed in the lower curve are V_{Ag-SCE} . Pyridine (.05M) was added to the 0.1M KCl solution following the completion of the electrolytic cycle

sharply, indicating the formation of AgCl on the surface. The signal levels off after an average of 3 or 4 monolayers of AgCl are formed, as judged from the amount of charge transfer that occurred. This confirms the picture that only the surface layers of molecules contribute to SHG. In the present case, the field-induced SHG in the solution is presumably averaged out at the rough surface, and the signal from AgCl in Fig.3 is rather insensitive to V_{Ag-SCE} . At the end of the reduction cycle, the signal drops suddenly as the last 3 or 4 layers of AgCl are reduced. The rise in the signal near the end of the cycle can probably be explained by the increase of surface roughness through redeposition of silver.

A striking demonstration of the capability of SHG for detecting a monolayer of adsorbed molecules is provided by the case of pyridine adsorbed on the silver electrode in an electrolytic solution. As shown in Fig.3, after the reduction cycle is completed, if pyridine (0.05M) is added to the solution and a bias corresponding to $V_{Ag-SCE} = -1.1$ v is applied, the second-harmonic signal increased by 25 - 50 times. This signal arises from the adsorption of a monolayer of pyridine on the Ag surface, which is known to depend on V_{Ag-SCE} [6]. The SHG data in Fig.4 show that pyridine begins to be adsorbed at $V_{Ag-SCE} \sim -0.6$ v and reaches a monolayer at ~ -0.9 v.

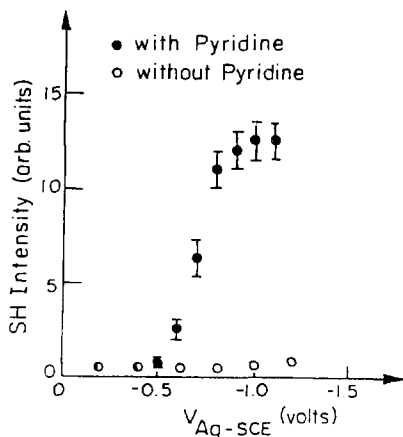


Fig.4 Diffuse SH signal versus V_{Ag-SCE} following an electrolytic cycle, with .05M pyridine and 0.1M KCl dissolved in water

We can use SHG from adsorbed pyridine to obtain the adsorption isotherm, *i.e.*, the surface density of adsorbed pyridine molecules versus pyridine concentration in the electrolytic solution. We assume that the second harmonic signal can be expressed by $P(2\omega) = (A + BN_a)^2$, where the BN_a term is from adsorbed pyridine, with N_a being the surface density of pyridine molecules, and the A term coming from the Ag background. Fig.5 gives the measured $(\sqrt{P(2\omega)} - A) \propto N_a$ versus the pyridine concentration, in the electrolytic solution for $V_{Ag-SCE} = -1.0$ v. It happens that the result can be fit nicely with the simple Langmuir equation [14]

$$N_a = \frac{c}{K + c} N_{as}$$

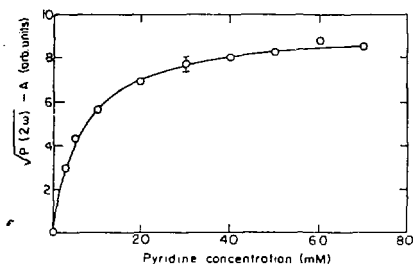


Fig.5 Equilibrium ($\sqrt{P(2\omega)} - A$) versus bulk pyridine concentration. The solid curve is a theoretical fit to the experimental data using the Langmuir model

where N_{AS} is the saturated value of N_a and K (in mole/l) is related to the adsorption free energy ΔG by

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

From the theoretical fit, we find $\Delta G = 5.1$ kcal/mole for pyridine on silver in 0.1M KCl aqueous solution. From surface-enhanced Raman scattering, we have deduced a very similar adsorption isotherm, differing only in that the initial slope of the curve is somewhat higher, with a corresponding $\Delta G = 5.7$ kcal/mole.

Other molecules adsorbed on Ag, including CN, cyanopyridines, pyrimidine, and pyrazine, have also been studied. In all these cases, adsorption and desorption of a molecular monolayer by control of the bias voltage can be observed. The case of pyrazine is of special interest. While the pyridine molecule C1=CC=NC=C1 is not centrosymmetric, the pyrazine molecule C1=CC=NN=C1 does have inversion symmetry. Therefore, the former has a nonvanishing $\alpha^{(2)}$, but the latter has a vanishing $\alpha^{(2)}$. If, however, the molecules are chemically adsorbed on silver, then both will have nonvanishing $\alpha^{(2)}$ because the interaction between molecules and metal breaks the symmetry. The SHG signal from the adsorbed pyrazine versus V_{Ag-SCE} is presented in Fig.6. In comparison with Fig.4, it is seen that the maximum signal from pyrazine is only 4 - 5 times smaller than that from pyridine. This means that $\alpha^{(2)}$ for pyrazine is only ~2 times smaller than $\alpha^{(2)}$ for pyridine. This result confirms the fact that pyrazine is chemically adsorbed on Ag with a strong metal-adsorbate interaction, as previously suggested by the Raman measurements [15].

Detection of molecular monolayers by SHG unfortunately lacks spectral selectivity. The technique can, however, be extended with sum- and difference-frequency generation. As one or both frequencies approach resonances, the signal is expected to be greatly enhanced. The resonant enhancement feature should then allow us to carry out spectroscopic studies of adsorbed molecules. With pulsed lasers, transient spectroscopy of adsorbed molecules may also become possible.

Acknowledgement T.F.H. acknowledges partial support as an NSF graduate fellow. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Science Division of the U.S. Department of Energy under Contract Number W-7405-ENG-48.

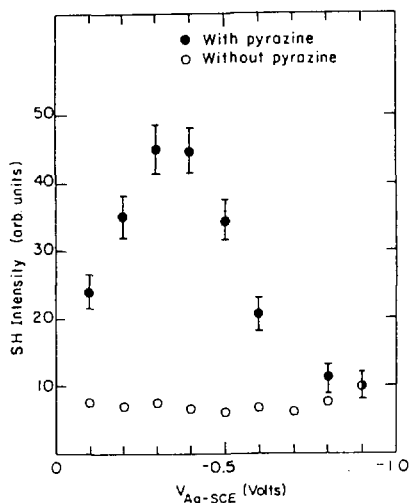


Fig.6 Diffuse SH signal versus V_{Ag-SCE} following an electrolytic cycle in 1M KCl, with and without .05M pyrazine present

References

1. N. Bloembergen and P. S. Pershan, *Phys. Rev.* **128**, 606 (1962); N. Bloembergen, R. K. Chang, S. S. Jha, and C. H. Lee, *Phys. Rev.* **174**, 813 (1968)
2. See, for example, G. A. Somorjai and M. A. Van Hove, *Adsorbed Monolayers on Solid Surfaces* (Springer-Verlag, Berlin, 1979)
3. C. K. Chen, A. R. B. de Castro, Y. R. Shen, and F. DeMartini, *Phys. Rev.* **43**, 946 (1979)
4. J. P. Heritage and D. L. Allara, *Chem. Phys. Lett.* **74**, 507 (1980)
5. B. F. Levine, C. G. Bethea, A. R. Tretola, and M. Korngor, *Appl. Phys. Lett.* **37**, 595 (1980)
6. M. Fleischmann, P. J. Hendra, and A. J. McQuillan, *Chem. Phys. Lett.* **26**, 163 (1974); D. L. Jeanmaire and R. P. Van Duyne, *J. Electroanal. Chem.* **34**, 1 (1977)
7. C. K. Chen, A. R. B. de Castro, and Y. R. Shen, *Phys. Rev. Lett.* **46**, 145 (1981)
8. C. K. Chen, T. F. Heinz, D. Ricard, and Y. R. Shen, *Phys. Rev. Lett.* **46**, 1010 (1981)
9. See J. Gersten and A. Nitzan, *J. Chem. Phys.* **73**, 3023 (1980) and references therein
10. See, for example, N. Bloembergen, *Nonlinear Optics* (Benjamin, New York, 1964)
11. G. T. Boyd and Z. H. Yu (unpublished)
12. R. K. Chang (to be published)
13. For weak static fields, see B. F. Levine and C. G. Bethea, *J. Chem. Phys.* **63**, 2666 (1975)
14. See, for example, M. J. Rosen, *Surfactants and Interfacial Phenomena* (J. Wiley and Sons, New York, 1978), Chap.2
15. R. Dornhaus, B. M. Long, R. E. Benner, and R. K. Chang, *Surf. Sci.* **93**, 240 (1980)