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Relative Raman scattering cross sections for chemisorbed and physisorbed pyridine molecules adsorbed on surface-enhanced Raman-scattering-active Ag films in ultrahigh vacuum: Local-field effects in the low-coverage regime

J. Giergiel and S. Ushioda*
Department of Physics, University of California, Irvine, California 92717

J. C. Hemminger
Department of Chemistry, University of California, Irvine, California 92717

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We have studied the Raman scattering from pyridine adsorbed on silver films evaporated on cleaved mica (100 K) in ultrahigh vacuum. These silver films have only a small number of chemisorption sites ($\sim 2\%$). The chemisorption sites are filled preferentially during initial stages of adsorption, followed by filling of the physisorption sites. Both physisorbed and chemisorbed pyridine exhibit strongly enhanced Raman scattering. At one monolayer coverage the average scattering enhancement is a factor of 55 larger for the chemisorbed molecules. When pyridine-d_5 molecules are used to saturate the chemisorption sites, subsequent adsorption of pyridine-h_5 results in partial displacement of the pyridine-d_5 to physisorbed sites. This displacement phenomenon allows us to measure the ratio of the Raman cross sections for chemisorbed and physisorbed pyridine in the neighborhood of chemisorption sites. This ratio is less than 4. Combining this measurement with the factor-of-55-larger overall average enhancement for chemisorbed molecules compared to physisorbed molecules, we conclude that molecules (including those just physisorbed) in the neighborhood of the chemisorption site exhibit an extra enhancement. We have also analyzed the coverage dependence of the Raman intensity and found it to be well described by a simple depolarization model. The average optical polarizability in this model is ~ 10 Å^3. This value is essentially the same as the value reported for pyridine adsorbed on annealed surface-enhanced Raman-scattering-inactive silver films.

I. INTRODUCTION

A rather large enhancement ($\sim 10^6$) of Raman scattering is observed for certain molecules adsorbed on specially prepared surfaces of silver, gold, and copper. This phenomenon, which has become known as surface-enhanced Raman scattering (SERS), was first discovered on a silver surface which underwent an oxidation-reduction cycle.[1] Since then, an enhancement of similar magnitude was observed for molecules adsorbed on metal films which were evaporated and kept at low (120 K) temperatures.[2] These films are referred to in the literature as "cold films." Significantly smaller enhancement ($\sim 10^3$) is reported[3] for a third class of enhancing surfaces: island films. There are also several other systems for which enhancement has been tentatively reported,[4] although in most cases without independent confirmation.

Theoretical models proposed to explain the SERS phenomenon have been reviewed several times.[5] These models generally fall into two broad categories, "classical" and "chemical." Models which fall in the first category deal mostly with classical electromagnetic resonances of rough metal surfaces and image-charge effects. In the second category of SERS models a chemical interaction of the adsorbed molecule with the metal is thought to provide additional enhancement. An example of such interactions would be charge-transfer chemisorption. The charge-transfer model assumes the formation of low-energy, charge-transfer excitations associated with the chemisorption bond. This could lead to an enhanced Raman polarizability in the visible region of the spectrum (the resonance Raman effect). It has been suggested that this bonding-induced enhancement may play a role in the SERS of the pyridine-silver system. The SERS spectra of this system are almost always dominated by scattering from chemisorbed molecules. In addition, an electronic excitation of the chemisorbed pyridine-silver system has been observed by reflectance measurements[6] as well as by inelastic electron scattering.[7]

The SERS model which invokes electromagnetic resonances of rough surfaces is given credence by the results of Campion *et al.*,[8] who showed that molecules adsorbed on well-characterized single-crystal surfaces exhibit no enhancement. Previous to these experiments Udagawa *et al.*[9] had reported small enhancements (~ 440) for pyridine on Ag(100). This may have been due to residual roughness on the Ag(100) surface and or due to chemisorption effects. The dependence of SERS on surface morphology is most strikingly demonstrated by experiments involving cold films. These films lose their enhancing properties irreversibly as soon as they are warmed up to room temperature. The fact that annealing changes the morphology of these films has been repeatedly demonstrated by various methods.[10] However, the starting morphology, i.e., the morphology of the enhancing film, is not very well known. Some progress toward a better understanding of the structure of these films has been made recently by Albano *et al.*[11] It appears as though the cold films are porous and that the porosity may be associated with SERS activity of these films. The morphology dependence of the enhancement has also led to a suggestion of specific sites for SERS.[12]

While it is clear that surface roughness plays a major role in SERS, the importance of chemical effects has been harder to address definitively. In this paper we report on the coverage dependence of the Raman scattering intensity of pyridine adsorbed on cold films evaporated on cleaved mica. By following the exchange between physisorbed pyridine-h_5 and chemisorbed pyridine-d_5 we are able for the first time to *measure* the relative Raman cross sections for physisorbed and chemisorbed pyridine. Both physisorbed and chemisorbed pyridine molecules show strongly enhanced Raman scattering, although on the average the enhancement is less for physisorbed molecules. Our isotopic substitution experiments suggest that the enhancement magnitude is not uniform on the surface of the cold silver film. There is an indication that the chemisorption site is a site of SERS activity extending to the nearest physisorbed molecules.

In addition, we find that the coverage dependence of the Raman line intensity of chemisorbed pyridine follows a simple depolarization model up to 75% of monolayer coverage. Our estimate for the average optical polarizability of pyridine physisorbed on a SERS-active surface gives a value which is comparable to that which we reported recently for pyridine adsorbed on a SERS-inactive film.[13]

II. EXPERIMENTAL DETAILS

The experiments were performed in a standard ion-pumped ultrahigh-vacuum (UHV) chamber with the base pressure in the low-10^{-10}-Torr range. Silver was evaporated *in situ* from a tantalum boat. During the evaporation the chamber pressure would typically rise to about 10^{-8} Torr. Auger-electron spectroscopy utilizing a cylindrical mirror analyzer (CMA) with a coaxial electron gun was used to monitor the surface cleanliness. Auger spectra of freshly evaporated films showed small amounts of oxygen. No carbon was detected within the Auger detectability limit ($\sim$2% of a monolayer).

In all experiments reported here the substrate was freshly cleaved mica, mounted on a liquid-nitrogen-cooled copper block. The typical evaporation parameters were a film thickness of 2000 Å and an evaporation rate of 5 Å/sec. The substrate temperature was in the 100-K range as measured with a thermocouple attached to the copper block. The films appeared mirrorlike to the eye. Dosing was accomplished by back-filling the vacuum chamber with pyridine. Standard spectroscopic grade (SpectrAR, Mallincrodt) pyridine C_5H_5N was used. Perdueterated pyridine C_5D_5N (99.5 at. % D) was purchased from Stohler Isotope Chemicals. Both compounds were used as delivered. Standard dosing-line procedures were followed. A mass spectrometer (UTI 100C) and an ion gauge were used to monitor exposure.

A *p*-polarized 5145-Å laser beam from an argon-ion laser was spot-focused onto the silver film at a 45° angle of incidence. Scattered light was collected normal to the surface by *f*/5 optics, analyzed by a double spectrometer set to $\sim$6 cm^{-1} resolution, and recorded by pulse-counting instrumentation.[14] Positions of the Raman peaks were determined by a least-squares fit to the Lorentzian line shape with a typical accuracy of $\pm$0.5 cm^{-1}. The same procedure yielded integrated intensities.

III. RESULTS AND DISCUSSION

The Raman spectrum of pyridine adsorbed on silver films shows two peaks in the region of the symmetric ring breathing mode. The lower-frequency peak (991 cm^{-1} for C_5H_5N and 963 cm^{-1} for perdeuterated pyridine C_5D_5N) is unshifted from its liquid-phase value and originates from pyridine molecules which are physisorbed on the silver surface. The other peak at 1003 cm^{-1} (972 cm^{-1} for C_5D_5N) is characteristic of the weakly chemisorbed pyridine. The two adsorption sites differ in their binding energies. The chemisorbed pyridine does not desorb below 240 K,[15] while the physisorbed species do not stay on the surface above 160 K.[16]

Figure 1 shows intensities of these two peaks recorded as a function of time as the freshly evaporated silver film was exposed to pyridine-d_5. The silver film was evaporat-

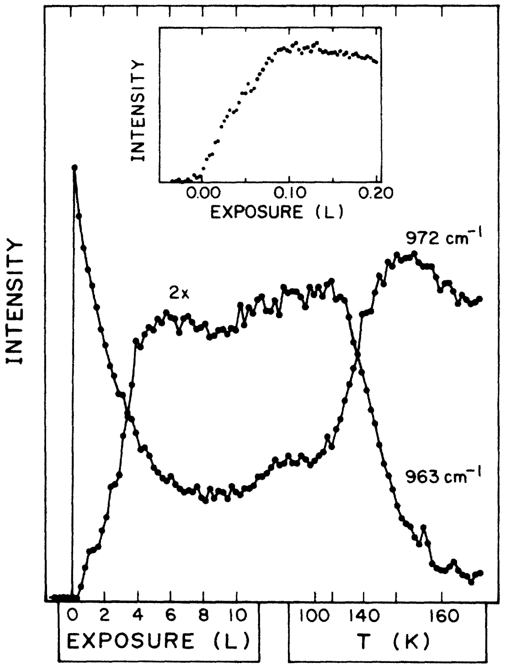

FIG. 1. Intensity of 963- and 972-cm^{-1} Raman peaks of pyridine-d_5 on a cold silver film under SERS conditions. The signal was recorded as a function of time as the film was exposed to pyridine, the exposure terminated, the chamber pumped-out, and finally the sample warmed from initial $T = 100$ K to 160 K. The laser beam was 5145 Å, 24 mW, and spot-focused. The inset shows the low-coverage behavior of the intensity of the Raman line of chemisorbed pyridine (972 cm^{-1}).

ed and dosed at 102 K. Dosing was terminated at approximately 10 L (1 langmuir$=10^{-6}$ Torr sec) exposure, and after the chamber pressure stabilized the film was warmed by turning off the liquid-nitrogen cooling. The sample temperature went from 100 to 160 K with an average rate of 2.4 K/min.

The trends shown in Fig. 1 varied little from sample to sample and were also seen when naturally abundant pyridine (C_5H_5N) was used instead of perdeuterated pyridine.

A. Number of chemisorption sites on cold Ag-mica films

An immediate conclusion from the data in Fig. 1 is that the Ag films evaporated onto the cleaved mica surface have a much smaller number of chemisorption sites than the Ag films evaporated on a polished surface of polycrystalline copper (Pockrand *et al.*[2]) or an iodine-roughened Ag surface (Rowe *et al.*[17]). The inset of Fig. 1 shows the coverage dependence of the 972-cm^{-1} Raman peak in the (0—0.2)-L range (different sample, similar experimental conditions). The signal grows linearly with exposure and reaches a maximum at 0.08 L. Since, as we argue later, the monolayer coverage is reached at ~6 L, the number of chemisorption sites on this SERS surface is on the order of 2% of the monolayer coverage if we ignore depolarization effects. Including the depolarization effects, the coverage dependence of the Raman signal can be written in the form

$$I_R \sim n\gamma_R^2(\alpha_R\gamma_D E_0)^2 , \tag{1}$$

where n is the number of molecules and α_R is the Raman polarizability. The factor γ_D is the ratio of the intensity of the local field (E_{loc}) at the average adsorption site to its value (E_0) in the absence of any adsorbed molecules. The local field changes with coverage because of depolarization effects of neighboring molecules. Following Murray *et al.*,[18] we include a similar factor (γ_R) for the Raman emission channel.

Since Ag-mica films show maximum intensity of the 972-cm^{-1} Raman peak at a very low coverage, depolarization effects can be safely ignored in estimating the number of chemisorption sites. The maximum intensity of the Raman signal from chemisorbed molecules represents true saturation of the chemisorption sites available on the surface. In contrast, the data of Pockrand[2] and Rowe[17] show maximum intensities of the Raman peak for chemisorbed pyridine at exposures in the (0.8—3)-L range. This corresponds to 15—50% of the monolayer coverage. In this range the depolarization effects are significant and, when included, will shift the exposure at which saturation of chemisorption sites occurs to higher values.

The smaller number of chemisorption sites on our Ag-mica surfaces is not surprising in view of the well-known tendency of silver films to grow epitaxially on cleaved mica.[19] An extended epitaxy is observed only when the cleaved mica substrate is kept at elevated temperatures.[19] Films grown on substrates kept at liquid-nitrogen temperatures will most likely consist of small crystallites with low-index crystallographic planes oriented parallel to the substrate. Since pyridine does not chemisorb on low-index planes,[8] the chemisorption will occur on grain boundaries, surface defects, or inside intercrystallite crevices, as was postulated by Albano *et al.*[11] Apparently our Ag-mica films consist of crystallites larger than in silver films grown on polycrystalline copper,[2] or iodine-treated bulk silver.[17]

B. Coverage dependence of Raman line intensities

Contrary to the observation of Pockrand *et al.*[2] and Ertürk *et al.*,[20] we observe Raman scattering from physisorbed pyridine well below monolayer coverage. Monolayer coverage is taken here to correspond to 6 L exposure, since at this coverage both the 972- and 963-cm^{-1} peak intensities stabilize. Clearly, both physisorbed and chemisorbed pyridine show enhancement of the Raman signal on this surface.

The monotonic decrease which we observe for coverages above 0.08 L of the intensity of the 972-cm^{-1} Raman line (chemisorbed molecule) is clearly connected with increasing the number of physisorbed molecules on the surface. The data of Fig. 1 show that when the physisorbed pyridine starts to desorb at ~140 K the chemisorbed pyridine Raman line increases in intensity. The recovery of this signal is almost complete. The small difference between the original intensity and the maximum intensity attained upon desorption of physisorbed pyridine (160 K) could be explained by a small irreversible loss of SERS activity as the cold film is warmed. At least two effects could be responsible for the observed decrease of the intensity of the 972-cm^{-1} Raman line with increasing coverage. These are (a) coverage-induced changes in the position and the width of the symmetric ring breathing mode, and (b) the depolarization effects. Since the first effect has been reported by Pockrand *et al.*[2] for pyridine adsorbed on silver film evaporated on copper substrate, we carefully checked our films for similar behavior. We found no significant change in either the position or the width of the 972-cm^{-1} Raman line in the (0.02—6)-L coverage range.

The contribution of the depolarization effects [γ_D and γ_R factors in Eq. (1)] to the observed coverage dependence is estimated using the following model. The molecule and its screening charge is taken as a single entity represented by a point dipole with an effective polarizability α. This approximation is certainly applicable in the low-coverage regime and avoids problems associated with the evaluation of the screening response of metal. Taking the long-wavelength limit and assuming that the electric field is normal to the surface and that the polarizability tensor is diagonal in the coordinate system of the surface, the local field is given by

$$E_{\text{loc}} = E_0 - \sum_{\substack{i,j \\ i=j\neq 0}} \frac{\alpha E_{\text{loc}}}{r_{ij}^3} . \tag{2}$$

To evaluate the dipole sum in Eq. (2), we assume that the molecules are randomly distributed on the two-dimensional (2D) lattice sites with the average occupation probability equal to the fractional coverage Θ. Under these assumptions the dipole sum is equal to the product of the dipole sum for a completely filled monolayer and the fractional coverage.[21] The preceding equation then becomes

$$\gamma_D \equiv \frac{E_{\rm loc}}{E_0} = (1+CN_0^{3/2}\alpha\Theta)^{-1} , \tag{3}$$

where N_0 is the monolayer coverage density and C is a constant which only weakly depends on the type of 2D lattice (9.0336 for a square lattice and 8.8904 for a planar triangular lattice.[21] Following Murray *et al.*,[18] we assume a similar form for the depolarization factor for the Raman emission channel [γ_R in Eq. (1)]. Equation (1) can be now written in the form

$$I_R \sim n\alpha_R^2 E_0^2 (1+CN_0^{3/2}\alpha\Theta)^{-4} . \tag{4}$$

We now apply this model to the data of Fig. 1. As discussed above, the chemisorption sites available on this surface are saturated at ~0.08 L exposure. Additional absorption of physisorbed species will lower the local field through the depolarization effects, thereby restricting the intensity of Raman scattering from the chemisorbed species (972 cm^{-1}). In other words, the few chemisorbed species act as a probe of local fields. In Fig. 2 we plot the negative fourth root of the intensity of the 972-cm^{-1} Raman line. According to Eq. (4) this quantity should vary linearly with coverage. We see that the agreement between theory and experiment is very good. At higher exposures (above 4.5 L) the data start to deviate from a straight line, as might be expected due to the simplicity of this model. To our knowledge this is the first unambiguous demonstration of depolarization effects in surface-enhanced Raman scattering on cold silver films. Depolarization effects have been previously reported for Raman scattering from molecules adsorbed on island films.[18] These films, however, exhibit significantly lower enhancement and it is not clear whether the enhancement mechanism which is operational there (localized electromagnetic resonances) is active on cold films with their giant enhancement.

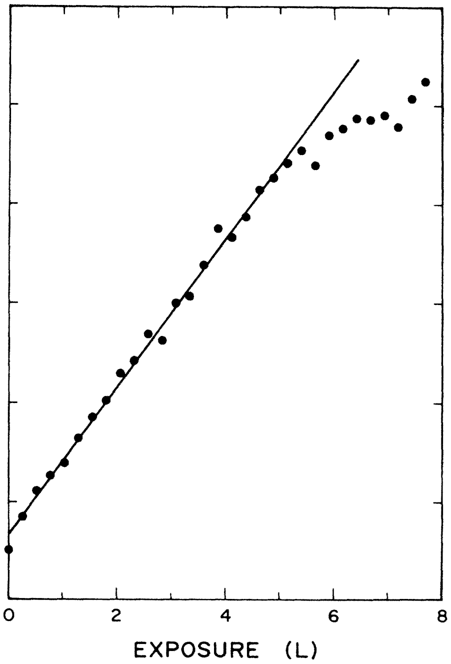

FIG. 2. Inverse fourth root of the intensity of the 972-cm^{-1} Raman line of chemisorbed pyridine [$I(972\ \text{cm}^{-1})^{-1/4}$] as a function of exposure. The solid straight line is the least-squares fit to the (0—4.5)-L range.

The depolarization effects of Raman line intensities have also been suggested by Eesley[22] in order to explain his coverage-dependence data for pyridine adsorbed on polycrystalline silver foil. The Raman spectra reported by Eesley were not enhanced and showed linear increase of Raman line intensities with coverage saturating at approximately 3 L exposure. A somewhat puzzling feature of his Raman data is the coexistence of both physisorbed and chemisorbed pyridine Raman lines at even the smallest coverages. In view of the well-documented mobility of pyridine molecules on silver surfaces (this work and Refs. 11 and 16) at 120 K, one expects chemisorption sites to be occupied before physisorption sites. This is exactly what we observe (Fig. 1) in our data.

We also note that the depolarization effects offer an attractively simple explanation for the so-called "high-temperature anneal" of the SERS signal.[23] To quote from Ref. 16, "In the high temperature anneal the SERS signal increases as the substrate is warmed, even though the surface coverage of the molecule is decreasing, and reaches a maximum at about 190 K." We observe exactly the same effect (see Fig. 1), but in view of our model the Raman signal increases precisely because the surface coverage is decreasing, which leads to larger local fields. Restructuring of the surface so as to destroy the "active sites" clearly does not take place in this temperature range.

The solid straight line in Fig. 2 is the least-squares fit to the data in the (0—4.5)-L exposure range. From its slope we obtain an estimate of the polarizability of pyridine molecules physisorbed on this SERS-active silver film. Taking $C=9$ and $N_0=5\times10^{14}$ cm^{-2},[24] the effective polarizability is on the order of 10 ± 2 Å^3. This is essentially the same effective polarizability we reported recently[13] for pyridine adsorbed on silver films which were evaporated at room temperature. Since room-temperature evaporated films show no enhancement of the Raman signal we have here an important result: the optical polarizability of physisorbed pyridine molecules is not enhanced on a SERS-active silver surface. In the foregoing analysis we have assumed that the coverage is linear in exposure. This is the case for single-crystal silver surface as shown by Ugadawa *et al.*[9] and Sanda *et al.*[25] In principle, this assumption could be tested for our surface in the following way. Using Eq. (4), the ratio of $I(963\ \text{cm}^{-1})/I(972\ \text{cm}^{-1})$ for a fixed number of chemisorbed species is proportional to $n(963\ \text{cm}^{-1})\alpha_R^2(963\ \text{cm}^{-1})$ and, with a constant polarizability derivative $\alpha_R(963\ \text{cm}^{-1})$, should be proportional to exposure if the sticking coefficient is constant. Unfortunately, as we show later, $\alpha_R(963\ \text{cm}^{-1})$ is not constant and the test cannot be applied.

We now turn our attention to enhancement of Raman scattering due to the specifics of bonding as opposed to the local-field effects. From the data of Fig. 1 we obtain the ratio of the average Raman cross sections chemisorbed and physisorbed pyridine molecules. It is clear that, on the average, the magnitude of enhancement is much lower for physisorbed species. For example, at 1 L exposure the intensity of the 963-cm^{-1} line (physisorbed) is still much lower than that of the 972-cm^{-1} line (chemisorbed) despite the fact that at this coverage the number of physisorbed molecules is much higher than the number of chemisorbed molecules. Assuming that the physisorbed coverage is linear in exposure and using the fact that the chemisorbed coverage saturates at 0.08 L exposure, we can use the peak intensities at 6 L to calculate the ratio of average Raman cross sections:

$$\left[\frac{\alpha_R(972\ \mathrm{cm}^{-1})}{\alpha_R(963\ \mathrm{cm}^{-1})}\right]^2=\frac{I(972\ \mathrm{cm}^{-1})}{I(963\ \mathrm{cm}^{-1})}\,\frac{0.08\ \mathrm{L}}{5\ L}=55\ .$$

Thus the average Raman cross section for the symmetric ring breathing mode of physisorbed pyridine-d_5 appears to be significantly smaller than that for the same molecule in the chemisorbed state. This analysis assumes that chemisorbed molecules and physisorbed molecules experience the same local field.

Coadsorption experiment

In order to further characterize the effects of bonding site on the Raman scattering intensity on these Ag films, we performed the following experiment.

A freshly evaporated silver film (thickness ~2000 Å, $T_s=110$ K) was exposed to 2 L of pyridine-d_5. Figure 3(a) shows the ring breathing region of the Raman spectrum taken immediately after the exposure. The spectrum shows the 972-cm^{-1} Raman line characteristic of chemisorbed pyridine-d_5 with a very weak shoulder at the frequency where the 963-cm^{-1} line of physisorbed pyridine-d_5 is expected. We also observe only a very weak asymmetric ring breathing mode of the pyridine-d_5 at 1002 cm^{-1}. After the spectrum of Fig. 3(a) was taken, the sample was exposed to naturally abundant pyridine C_5H_5N in 0.5-L steps. This exposure was monitored with a mass spectrometer to ensure that no further exposure to C_5D_5N was taking place. Raman spectra were taken after each exposure step and are shown in Figs. 3(b)—3(f). Since all available chemisorption sites are already occupied by pyridine-d_5, we expect pyridine-h_5 to go into physisorption sites. The spectrum, however, shows, in addition to the 991-cm^{-1} Raman line which is characteristic of physisorbed pyridine-h_5, the 1002-cm^{-1} Raman line which is characteristic of chemisorbed pyridine-h_5. Moreover, the spectrum shows the 963-cm^{-1} Raman line of physisorbed pyridine-d_5. Thus the data indicate that in the process of coadsorbing pyridine-h_5 the previously adsorbed pyridine-d_5 is displaced from chemisorption sites into physisorption sites. We have used the data of Fig. 3 to obtain an independent estimate for the ratio of enhancement factor for chemisorbed and physisorbed pyridine-d_5. From the spectrum in Fig. 3(a) we conclude that all chemisorption sites available on this surface are already occupied with 2 L of pyridine-d_5 exposure. Thus the number of molecules which give rise to the Raman line at 1003 cm^{-1} (chemisorbed pyridine-h_5) is equal to the number of molecules of pyridine-d_5 which were displaced from chemisorption sites. The displaced molecules of pyridine-d_5 move into physisorption sites (963-cm^{-1} Raman line). Thus the ratio of integrated intensity of the 1003-cm^{-1} Raman line to that of the 963-cm^{-1} line gives, directly, the ratio of the Raman cross sections of chemisorbed pyridine-h_5 to that of physisorbed pyridine-d_5. This ratio, obtained from a least-squares fit to the data of Figs. 3(b)—3(f), varied little between the individual spectra and is 2.4±0.4.

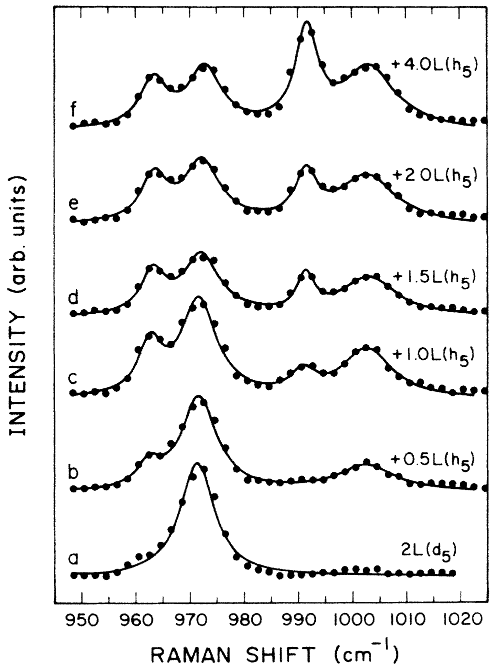

FIG. 3. Raman spectra of pyridine molecules adsorbed on a cold silver film. The film was (a) dosed with 2 L of pyridine-d_5, followed by (b)—(f) incremental exposures to pyridine-h_5. Experimental conditions were the same as in Fig. 1. The solid line is the least-squares fit using Lorentzian line shapes and constant background.

We have also performed an experiment in which the order of dosing was reversed, i.e., 2 L of pyridine-h_5 was followed by incremental exposure to pyridine-d_5. Similar behavior was observed, i.e., pyridine-d_5 displaced chemisorbed pyridine-h_5, causing the initially nonexistent 991-cm^{-1} Raman peak to appear in the spectrum. The ratio of Raman cross sections of chemisorbed pyridine-d_5 to that of physisorbed pyridine-h_5 was obtained in an analogous way and is 4±0.5.

In a separate experiment we compared the Raman cross sections of chemisorbed pyridine-h_5 and chemisorbed pyridine-d_5. The cold SERS-active silver film was dosed with 10 L of pyridine-d_5 to saturate the chemisorption sites. The incident laser power was then increased until no physisorbed molecules were seen in the spectrum. This power level did not cause irreversible annealing of the silver film or desorption of chemisorbed molecules since the intensity of the 972-cm^{-1} line (chemisorbed pyridine-d_5) stayed constant after the physisorbed molecules were desorbed. The sample was then dosed with pyridine-h_5, while the intensity of the 972- and 1003-cm^{-1} (chemisorbed pyridine-h_5) Raman lines were recorded with unchanged laser power level. The total intensity (972 plus

1003 cm^{-1}) stayed constant throughout the exposure, with the 972-cm^{-1} line gradually disappearing from the spectrum. Since in this experiment laser heating prevents physisorption, any changes in the intensities of Raman lines must come from pyridine-h_5 replacing pyridine-d_5 molecules in chemisorption sites. We conclude, therefore, that pyridine-h_5 and pyridine-d_5—in their chemisorption states—have similar Raman cross sections.

The main result of these experiments is that the Raman cross sections for physisorbed pyridine can be quite close to that of chemisorbed pyridine (α_R(chemisorbed)/$[\alpha_R$(physisorbed)$]^2<4$). We recall that the ratio of scattering cross sections obtained in the preceding subsection for monolayer coverage is much higher (α_R(chemisorbed)/$[\alpha_R$(physisorbed)$]^2\sim 55$). A possible explanation of these observations may involve the concept of a SERS-active site and the so-called "proximity effect." According to this concept only those molecules which are on or in the vicinity of an "active site" exhibit strong enhancement of Raman scattering.[12] Our data are compatible with this hypothesis if we assume that the chemisorption site is the SERS-active site and that the displaced molecules in the just-discussed coadsorption experiments remain in close proximity to the active site. Such molecules would then share in the enhancement provided by the active sites through the proximity effect. On the other hand, the majority of physisorbed molecules would be outside the range of the proximity effect, so that the average enhancement for physisorbed species at monolayer coverage is much smaller than that for molecules which were displaced from and remained close to the "active site."

IV. CONCLUSIONS

We now present a summary of our experimental results. We have studied SERS from pyridine adsorbed on cold silver films evaporated onto cleaved mica in ultrahigh vacuum. Our principal findings are as follows.

(a) Pyridine molecules are found in two adsorption states (physisorbed and chemisorbed) on this surface. The majority of molecules are physisorbed, with only ~2% of the molecules at chemisorption sites.

(b) Raman scattering by chemisorbed pyridine is enhanced. The intensity of Raman scattering by these molecules strongly depends on the total coverage. This coverage dependence is shown to be electromagnetic in origin; a simple model involving depolarization effects accounts for our experimental data up to 75% of monolayer coverage.

(c) The average optical polarizability of physisorbed pyridine is not enhanced. Our estimate gives the same value as that reported for pyridine adsorbed on the SERS-inactive silver surface.[13]

(d) Raman scattering by physisorbed pyridine is enhanced. The strength of enhancement is nonuniform on the surface. At monolayer coverage the Raman signal per average physisorbed molecule is $\frac{1}{55}$ of that for chemisorbed pyridine. On the other hand, the Raman cross section for physisorbed pyridine after it was displaced from chemisorption site is comparable ($>\frac{1}{4}$) to that of chemisorbed pyridine.

Our results again stress the importance of the depolarization effects in Raman scattering from adsorbed overlayers, as was first pointed out by Murray *et al.*[18] Such effects are especially important when the relative Raman cross sections from molecules adsorbed in different configurations are to be compared. Clearly, direct comparison of Raman line intensities evaluated at different coverages is not justified. Even when the local-field effects are properly included, the analysis of the data is hindered by the fact that in most cases the exact coverage is not known. We have been able to obtain the relative cross sections for pyridine molecules chemisorbed and physisorbed on our SERS-active surface by following intensities of Raman lines in the isotope coadsorption experiment where the relative population of the two bonding sites was determined solely by displacement. Our results are consistent with a hypothesis of SERS-active sites and the "proximity effect." The SERS-active site seems to be associated with the chemisorption site. However, the extra enhancement in the vicinity of these sites is not associated with the phenomena of chemisorption. Thus we feel that charge-transfer excitations localized on chemisorbed molecules cannot be used to explain this extra enhancement. Our data do not directly address the question of the SERS mechanism. This, in our opinion, still awaits further investigation.

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[*] Present address: Research Institute of Electrical Communication, Tohoku University, Sendai 980, Japan.

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