

Raman scattering cross section of adsorbed pyridine molecules on a smooth silver surface

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(Received 1 December 1980; revised manuscript received 10 March 1981)

We have determined the Raman scattering cross section of pyridine molecules adsorbed on a "smooth" surface of silver prepared and characterized in an ultrahigh-vacuum chamber. The Raman intensity of the 1004-cm^{-1} line of adsorbed pyridine was calibrated against the scattering intensity of the same mode from gaseous pyridine and liquid pyridine. The cross section for pyridine molecules adsorbed on a "smooth" silver (100) surface is 4.4×10^2 times greater than that of gaseous and liquid pyridine molecules. This measured cross section is an upper limit for that on a theoretically perfect, flat plane of silver atoms.

In the past few years there has been an extraordinary amount of interest and excitement over the so-called "giant" or "surface-enhanced" Raman scattering by adsorbed organic molecules on metal surfaces.¹ In spite of the large number of experimental and theoretical reports that have appeared on this subject, no definitive explanation for the reported large enhancement factor (10^4 – 10^6) has emerged. However, it appears clear by now that surface roughness of the metal substrate plays an important role in various combined ways.² In their recent paper Rowe, Shank, Zwermer, and Murray³ reported that they could not observe Raman signals from a monolayer of pyridine molecules adsorbed on a "smooth" silver (100) surface. They could observe molecular vibrations of pyridine in the vicinity of 1000 cm^{-1} only after they roughened the silver surface. They concluded that the enhancement factor for their "smooth" surface is less than 10^2 from the fact that they could not observe the Raman peaks.

In this Communication we describe the first successful observation of the Raman peaks from a monolayer of pyridine molecules on a "smooth" silver surface in ultrahigh vacuum (UHV), and further present the results of relative cross-section measurements for adsorbed pyridine.

For a silver substrate, an oriented single crystal of pure silver was cut and polished to have a large (100) surface of $\sim 1\text{ cm}^2$. The polishing was done in stages using successively smaller powder sizes of alumina down to $0.05\text{ }\mu\text{m}$. The resultant surface was mirror-like in smoothness and scratch-free over most of the sample face. After polishing in air the sample was sealed in a UHV chamber with a base pressure of $\sim 1 \times 10^{-10}$ torr. The surface was cleaned by argon sputtering and annealing in UHV at $\sim 400^\circ\text{C}$. The argon ion sputtering was carried out at 500 V to minimize surface damage. The impurity peaks in the Auger spectrum of the clean surface were less

than 0.5% of the main silver peak at 351 V. The surface preparation procedure described above defines the "clean" and "smooth" surface which was used in the Raman scattering experiments. We should emphasize here that our surface preparation procedures are the standard ones used to prepare surfaces sufficiently smooth and damage-free to produce clearly defined low-energy electron diffraction (LEED) patterns.

Adsorption of pyridine on the sample surface was tried in several ways, and Auger peaks of carbon and silver were monitored at each stage. The Raman scattering data presented here were obtained after 1, 10, and 100 L (10^{-6} torr sec) of exposure at pyridine partial pressures of 10^{-8} to 10^{-7} torr with varied exposure time. All pressure measurements were made with an ion gauge calibrated for N_2 , and no correction was made for the sensitivity of pyridine relative to N_2 . The silver substrate was kept at $\sim 150\text{ K}$ during the gas exposure and the Raman measurements. The coverage versus exposure curve for our system is shown in Fig. 1. It is a plot of the ratio of the carbon signal I_{272}^C at 272 V (corrected for the contribution from silver at this voltage) to the silver signal I_{301}^A at 301 V. The break in the straight line at $\sim 5\text{-L}$ exposure (uncorrected for ion gauge sensitivity) is indicative of monolayer formation.⁴ This result agrees well with the exposures necessary for monolayer formation reported by Rowe *et al.*³ and Easley.⁵

Raman measurements were made through an 8-in. window on the UHV chamber. The incident light was the $5145\text{-}\text{\AA}$ line of an argon ion laser linearly polarized perpendicular to the plane of incidence. The angle of incidence on the silver surface was approximately 23° from the surface normal, and the scattered light emerging within a solid angle of 1.59×10^{-1} sr (26° cone) about the surface normal was collected. The scattered light was not analyzed with respect to polarization. The spectrum of the

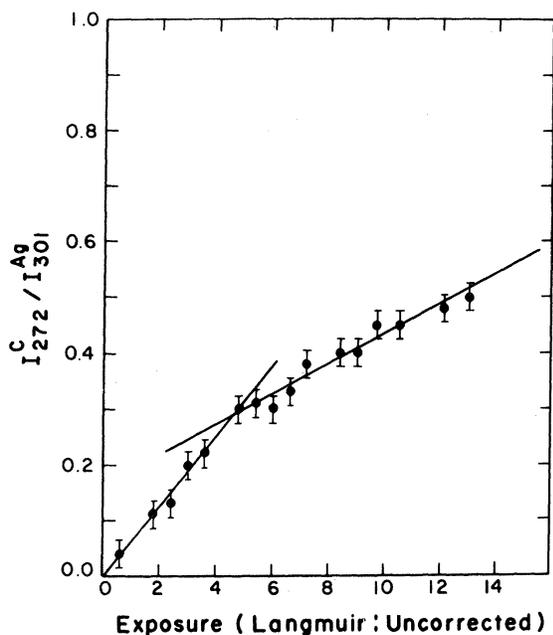


FIG. 1. Pyridine exposure vs coverage. (See text for the definition of I_{272}^C and I_{301}^{Ag} .)

scattered light was analyzed by a 0.75-m double-grating spectrometer interfaced to a minicomputer, and the number of scattered photons was accumulated for as long as 100 sec. The Raman spectra obtained in this manner are shown in the top three traces in Fig. 2 for different exposures. The incident laser power was 100 mW cw for these three spectra. We see in Fig. 2 that approximately 1.5 monolayers (10-L exposure) of pyridine on a smooth silver (100) surface can indeed be observed by Raman scattering. The peaks appearing at 1004 and 1032 cm^{-1} have similar positions and widths to the ones observed by Rowe *et al.*³ on a roughened surface. When the exposure is increased to ~ 100 L a new peak appears at 991 cm^{-1} , corresponding to the peak seen in the gas and liquid phases (two bottom traces). This change in the Raman spectrum was also observed on a roughened surface by Rowe *et al.*³ We were able to measure the weak scattering peaks on a "smooth" surface by integrating the signal for a long time (100 sec) at each frequency step. We note the presence of a background of the order of 20 photons/sec for all three exposures. The background level for rougher surfaces is considerably higher than is observed here. The low background in our experiments is significant for two reasons. First, the small signals we have observed could not have been observed in the presence of high background. Second, the correlation between high background and surface roughness has been observed in many laboratories.^{1,2,6} This then is

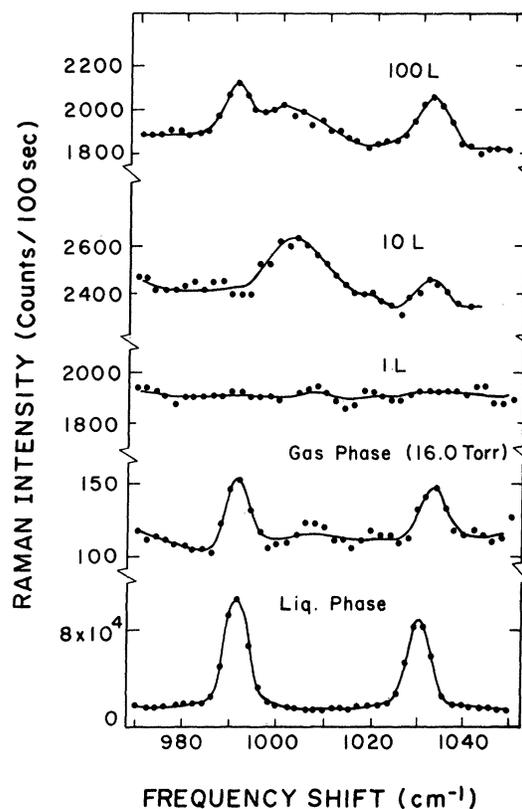


FIG. 2. Raman spectra of pyridine molecules on a smooth Ag(100) surface for three exposures, and in the gaseous and liquid phases. The incident laser power is 100 mW at 5145 Å, and the spectrometer slit width is 5.5 cm^{-1} (FWHM). The dots are the data points obtained after a three-point digital-averaging process, and the solid curves are guides to the eye. Note the intensity scale is counts per 100 sec.

another measure of the smoothness of the surface used in these experiments. The peak intensity at 1004 cm^{-1} is about 2 photons/sec above background. The area on the silver surface sampled in taking these spectra was $8.1 \times 10^{-3} \text{ cm}^2$.⁷ Each spectrometer step was 2 cm^{-1} , and the slit width was 5.5 cm^{-1} [full width at half maximum (FWHM)].

In order to compare the Raman cross section of the adsorbed pyridine molecules with that of the free-gas molecules, we used the following procedure. After all the measurements on the silver surface were completed, the entire vacuum system plus the sample were allowed to come up to room temperature (295 K). Then an ampoule containing liquid pyridine was opened to the system, filling the UHV chamber with the saturated vapor (16.0 torr) of pyridine in equilibrium with liquid at room temperature. All optical elements were kept rigidly in place during this process, so that no change in optical alignment occurred.

Then the silver sample was rotated out of the incident laser beam, and the Raman spectrum of gaseous pyridine at 16.0 torr was measured (see the gas-phase spectrum in Fig. 2). In this experiment the scattering volume in the gas was estimated to be $4.5 \times 10^{-4} \text{ cm}^3$ from the focal depth of the collection optics and the geometry of measurement.⁸

Now we compare the cross section per molecule of pyridine for adsorbed species on silver (100) and free gaseous species. Here we must assume that the 1004-cm^{-1} line of the adsorbed species corresponds to the same vibrational mode that appears at 991 cm^{-1} for the gaseous and liquid species of pyridine. From Fig. 1 we see that the 10-L exposure corresponds to a 1.53 monolayer coverage. If we follow Rowe *et al.*³ and adopt the density of 3×10^{14} molecules/ cm^2 for monolayer coverage, the surface density for a 10-L exposure is 4.6×10^{14} molecules/ cm^2 . Since the scattering area on the sample is $8.1 \times 10^{-3} \text{ cm}^2$, the total number of molecules participating in the observed scattering process is 3.7×10^{12} molecules. The integrated number of scattered photons under the 1004-cm^{-1} peak is 1098 photons/(100 sec)(100 mW) after subtracting the background. Thus the number of observed scattered photons per molecule is 3.0×10^{-10} photons/(100 sec)(100 mW)(molecule). For the gaseous phase the corresponding number is 6.8×10^{-13} photons/(100 sec)(100 mW)(molecule) based on the estimated scattering volume of $4.7 \times 10^{-4} \text{ cm}^3$ and assuming the ideal gas law for pyridine. Thus we conclude that the enhancement factor for the adsorbed species is 4.4×10^2 over the gaseous species. On the basis of this enhancement factor, the "apparent absolute cross section" of the pyridine molecules adsorbed on a smooth silver (100) surface is approximately $2.8 \times 10^{-27} \text{ cm}^2/\text{sr cm}^{-1}$ molecule.

In order to check our cross-section calibration using the scattering intensity from the saturated vapor, we also compared the scattering intensity ratio between the gaseous and liquid pyridine at room temperature. The intensity ratio between these two states agrees with the density ratio within $\pm 20\%$, using a similar comparison method that was used before. Therefore, we conclude that our calibration of relative intensity is good to about $\pm 20\%$.

The greatest source of possible error in this measurement is the surface density of adsorbed molecules. Following Rowe *et al.*,³ we assumed the molecular density for monolayer coverage to be 3.0×10^{14} molecules/ cm^2 . This number depends on the calibration of Auger intensity for carbon, and may require a substantial correction.⁹ The enhancement factor we measured is inversely proportional to the surface density of molecules; so the correction can readily be made, when the precise value of surface density of molecules is found.

While care was taken in preparing the Ag(100) sur-

face used in these experiments, defects certainly exist on any real surface. Thus, we must rule out the situation in which all of the observed intensity arises from molecules bound to defect sites which may (owing to the rough surface in the neighborhood of the defect) exhibit enhancement factors of 10^4 or 10^6 . This situation could lead to an average enhancement of 440 while we are only sampling a very small fraction of the pyridine molecules. This effect can be ruled out by looking at the coverage dependence of the scattering intensity. The fact that a 1-L exposure ($\sim 20\%$ of a monolayer coverage) does not lead to an observable spectrum (Fig. 2) eliminates this possibility. The pyridine molecules should be more strongly bound to defect sites on the crystal surface. Thus, these sites will be filled preferentially, at low exposure. If molecules at defects were contributing a significant amount of the spectrum, we would expect the 1-L spectrum to have an intensity similar to the 10-L spectrum. This is obviously not the case.

While the effects of short-range roughness can be ruled out by looking at the coverage dependence of the Raman signal, similar effects due to large-scale roughness (which may not affect the sticking probability) cannot be ruled out. Thus, the enhancement factor of 440 which we have measured must be taken as an upper limit for that of a perfect atomically flat plane of silver.

In comparing the Raman spectra for 10- and 100-L exposures in Fig. 2, we note that the intensity of the 1004-cm^{-1} peak remains approximately the same for both exposures. If we assume that the sticking coefficient stays constant beyond a monolayer, $\sim 100\text{-L}$ exposure corresponds to about 10 monolayers. Thus it appears that the layers above the first and second monolayers do not contribute to the scattering at 1004 cm^{-1} . Our interpretation of this observation is that the peak at 1004 cm^{-1} arises from pyridine molecules in close contact with the silver surface (probably chemisorbed). The molecules in the layers separated from the silver surface by more than one or two monolayers vibrate at the frequency of the free molecules at 991 cm^{-1} . Thus the peak at 991 cm^{-1} grows with increased coverage, but the 1004-cm^{-1} peak remains constant.

To conclude, we have determined the enhancement factor for the Raman cross section of pyridine molecules adsorbed on a smooth silver (100) surface relative to its cross section in the free gaseous state. The extremely low inelastic background of ~ 20 counts/sec which we observe is indicative of the high quality of the surface used in these experiments. Two aspects of this work require future improvement: one is the precise determination of coverage in terms of the number of molecules per unit area, and the other is the quantitative determination of smoothness. Both of these are very difficult problems.

ACKNOWLEDGMENTS

We have benefitted from discussions with many colleagues in the course of this work; particularly, we would like to thank D. L. Mills, E. Burstein, and R. M. Macfarlane for helpful discussions. Financially, we are indebted to the Focused Research Program in the Chemistry and Physics of Crystal Surfaces of the University of California at Irvine for funding this project.

¹See, for example, M. Fleischmann, P. J. Hendra, and A. J. McQuillan, *Chem. Phys. Lett.* **26**, 123 (1974); D. L. Jeamire and R. P. Van Duyne, *J. Electroanal. Chem.* **84**, 1 (1977); C. Y. Chen, E. Burstein, and S. Lundquist, *Solid State Commun.* **32**, 63 (1979); W. H. Weber and G. W. Ford, *Phys. Rev. Lett.* **44**, 1774 (1980), and references therein.

²See, for example, J. I. Gersten, *J. Chem. Phys.* **72**, 5779 (1980); J. C. Tsang, J. R. Kirtley, and J. A. Bradley, *Phys. Rev. Lett.* **43**, 772 (1979); C. Y. Chen and E. Burstein, *ibid.* **45**, 1287 (1980), and references therein.

³J. E. Rowe, C. V. Shank, D. A. Zwermer, and C. A. Murray, *Phys. Rev. Lett.* **44**, 1770 (1980).

⁴A possible alternate interpretation of the break in Fig. 1 is the existence of a compressional phase change which has been observed for pyridine on Ag(111). This does not

change the numbers for the pyridine coverage, as this phase change is thought to occur at a coverage of $\sim 3 \times 10^{14}$ molecules/cm². J. E. Demuth, K. Christman, and P. N. Sanda, *Chem. Phys. Lett.* **76**, 201 (1980).

⁵G. L. Easley (private communication).

⁶R. L. Birke, J. R. Lombardi, and J. I. Gersten, *Phys. Rev. Lett.* **43**, 71 (1979).

⁷This is essentially the cross-sectional area of the incident laser beam, and it gets divided out when the ratio with the scattering intensity of the gas is taken. Thus the exact value of this area is immaterial for our intensity calibration.

⁸The details of the method for determining this volume are planned to be reported in a full-length paper.

⁹I. Wachs and S. Kellerman (private communication).