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[a] Present address: Lawrence Livermore Laboratory, Livermore, California 94550.

[1] W. H. Bostick, Phys. Rev. 106, 404 (1957).

[2] W. H. Bostick, Phys. Rev. 104, 292 (1956).

[3] A. L. Peratt, M. Gersten, R. Richardson, and W. Clark, Bull. Am. Phys. Soc. 24, 1079 (1979).

[4] S. Chandrasekhar and E. Fermi, Astrophys. J. 118, 116 (1953).

[5] V. P. Shafranov, in *Reviews of Plasma Physics*, edited by M. A. Leontovich (Consultants Bureau, New York, 1966), Vol. 2.

[6] H. Lamb, *Hydrodynamics* (Dover Publications, New York, 1932), 6th ed., p. 233.

[7] W. H. Bennett, Phys. Rev. 45, 890 (1934).

[8] G. S. Murty, Ark. Fys. 19, 483 (1961).

[9] J. Davidson and D. R. Wells, Phys. Fluids 22, 379 (1979).

[10] S. Chandrasekhar, Proc. Natl. Acad. Sci. U. S. A. 42, 1 (1956).

[11] D. E. Nielsen, Jr., Stanford University Institute for Plasma Research Report No. SU-IPR 776, 1979 (unpublished).

[12] D. Nielsen, J. Green, and O. Buneman, Phys. Rev. Lett. 42, 1974 (1979).

Ultrahigh-Vacuum Studies of Enhanced Raman Scattering from Pyridine on Ag Surfaces

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Studies of surface-enhanced Raman scattering from pyridine adsorbed on Ag surfaces in ultrahigh vacuum show a strong dependence on both surface roughness and pyridine coverage. The observation of enhancement (10^4) for physisorbed pyridine multilayers in addition to the first molecular layer implies that the enhanced effect is electromagnetic rather than chemical in origin.

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Recent observations of Raman scattering from adsorbed molecules near Ag surfaces have been interpreted in terms of a giant enhancement ($\sim 10^4 - 10^6$) of the Raman cross section of molecules in the first monolayer in contact with the Ag surface. These experiments have been performed with solid-solid interfaces[1] (i.e., tunnel-junction geometries), solid-liquid interfaces[2] (i.e., electrochemical cells), and more recently solid-vacuum studies in ultrahigh vacuum (UHV).[3] The last geometry has some specific advantages because of the possibilities of *in situ* surface characterization and continuous variation of surface coverage. Both of these features are important to test several of the proposed theoretical mechanisms of the surface-enhanced Raman effect. We have studied surface-enhanced Raman scattering (SERS) by performing UHV measurements on a variety of Ag surfaces characterized by Auger-electron spectroscopy (AES) and low-energy electron diffraction (LEED). Both surface-roughness and adsorbate-coverage dependences have been measured which suggest that the dominant contribution to SERS is electromagnetic rather than chemical in origin.

The apparatus used for Raman measurements was a multiple-technique UHV chamber which has been previously described.[4] The Raman scattering was performed primarily with the 4880-Å line from an Ar-ion laser although some measurements were also performed at 5145 and 4965 Å to verify the inelastic scattering nature of the main features observed. The laser light was directed at the Ag sample at $\theta_1 = 65°$ angle of incidence; it was p polarized and the scattered light was collected in a $\sim 40°$ cone near the surface normal. This geometry is similar to that previously used in most electrochemical cell experiments. The scattered light was analyzed by a double-grating spectrometer and photon counting detection operated with a resolution typically ~ 8 cm^{-1}.

Pyridine was deposited with sample temperature $T \approx 135$ K by filling the experimental chamber with pyridine vapor to a pressure 10^{-7}–10^{-6} Torr and the coverage was determined from condensation kinetics measured by AES measurements at a pressure of 10^{-9} Torr.[5] Figure 1

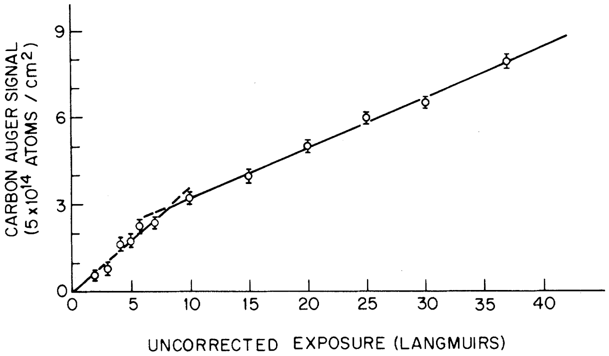

FIG. 1. Carbon Auger signal vs uncorrected ion-gauge exposure (1L= 10^{-6} Torr sec). The initial clean Ag surface has less than 10^{14} atoms/cm^2 carbon impurities.

shows the carbon atom thickness as a function of pyridine exposure. The AES calibration used escape depths of 8 Å and measurements on clean elemental Ag and C samples to determine the sensitivity factors for our spectrometer in units of atoms/cm^2. For our low-resolution AES ($\Delta E > 3$ eV) we assume no difference in the sensitivity factor for pyridine-carbon AES intensity and elemental carbon. For an estimated ion gauge factor of 3 for pyridine vapor, the sticking or condensation coefficient at sample temperatures $T \leq 150\,^\circ$K ranged from $\alpha = 0.6-0.7$ at low coverage [less than $\theta = (3 \pm 1) \times 10^{14}$ molecules/cm^2] to $\alpha = 0.3-0.4$ at higher coverage. We find that the condensation coefficient remains at $\alpha = 0.3-0.4$ from $\theta = 3 \times 10^{14}$ to $\theta \geq 8 \times 10^{14}$ molecules/cm^2 (i.e., from 1 to 3 monolayers) and assume that this value represents growth of the bulk pyridine solid. The average area of adsorbed pyridine relative to the observed Ag atom density is ~33 Å^2 per molecule and the observed break in condensation corresponds to completion of one molecular layer. Direct Auger determination of the coverage was limited to less than $(8.5 \pm 1.0) \times 10^{14}$ molecules/cm^2, i.e., 3 layers, because of irreversible electron-beam-induced damage. Higher coverages were extrapolated from the sticking coefficient determined by Auger spectroscopy for the second and third layer since bulk condensation has already occurred.

The main results on surface roughness and sample dependence that were observed for SERS of adsorbed pyridine are given in Table I. We observe no Raman signal for a monolayer of pyridine for low-index Ag(111) and Ag(100) surfaces, for stepped Ag(100) surfaces, or selectively etched Ag(100) with ~2-5-μm facets. The Raman enhancement must be less than 10^2, the sensitivity threshold of our Raman spectrometer for 3×10^{14} pyridine molecules/cm^2. We could observe measurable signals from thick condensed layers with a typical thickness of $\gtrsim 5 \times 10^{15}$ molecules/cm^2. The Ag particle dimensions of the lower four samples listed in Table I were determined by scanning electron microscopy (SEM) in a separate apparatus after the UHV Raman experiments were completed. The low-index and stepped Ag surfaces show only shallow ripples of vertical height ~150 Å under SEM.

The samples which we find show a large SERS (factors of ~5×10^4 for low coverage) have a sur-

TABLE I. Summary of UHV raman experiments for samples vs roughness.

Sample	Raman enhancement	Roughness (average radius or step height)
Ag(111)	$1 \rightarrow 10^{2\,a}$	Smooth—shallow ripples < 200 Å
Ag(100)	$1 \rightarrow 10^{2\,a}$	Smooth—shallow ripples < 200 Å
Ag(100) 6°	$1 \rightarrow 10^{2\,a}$	Atomic steps (~2 Å × 20 Å)[b]
Ag(100) + CN$^-$ solution	~10^4	~500-Å particles
Ag(100) + I film		
A	~5×10^4	~500-Å particles
B	~5×10^3	~2000-Å particles
Ag(100) + H_2O_2 etch	$1 \rightarrow 10^2$	~2-5-μm facets

[a] Raman signals were observed only for pyridine films of 20-50 monolayers which we interpret as evidence for a maximum enhancement factor ~10^2.

[b] These samples were cut 6° away from the (100) surface in a [110] azimuth which displayed LEED spot splitting due to atomic steps.

face roughness consisting of ~500-Å-radius Ag particles (approximately spherical in shape) separated by ~1500–3000 Å. Sample *A* (viz., data shown in Fig. 1 and Table I) was prepared by exposing a UHV-cleaned Ag (100) surface to I_2 vapor and 4880 Å laser light, producing ~500 Å-radius Ag particles photochemically. Rutherford backscattering results in a channeling alignment of the Ag crystal revealed the presence of "disordered" Ag consistent with the size and density of the ~500-Å-radius Ag particles. Very similar size Ag particles were produced on samples processed in an electrochemical cell with a single oxidation-reduction cycle as described by Bergman *et al.*[6] and by Furtak.[7] The large SERS due to adsorbed pyridine was also found on electrochemically roughened Ag samples after they were Ar-sputter etched in UHV to remove all impurities detectable by AES prior to pyridine adsorption. Thus the presence of the AgI film (~10–15 Å) on some Ag surfaces does not appear to have influenced our SERS results. For Sample *B* (see Table I) with ~2000-Å-radius particles of Ag which touch and overlap we find Raman signals about 10 times smaller at the monolayer coverage (~3×10^{14} molecules/cm^2). The fact that only ~500 Å-scale roughness gave rise to large SERS effects suggests that adatom models,[8] image-charge models,[2,9,10] electronic resonance models,[9,11,12] and conventional surface-plasmon models[1,13] of SERS must be modified to include the electromagnetic antennalike enhancement of the small Ag particles.[14]

Typical Raman spectra for sample *A* listed in Table I are shown in Fig. 2 for coverages ranging from a background spectrum with no intentional exposure to pyridine vapor up to a pyridine coverage of 11×10^{14} molecules/cm^2. The different coverage behavior of the Raman peaks with $\Delta\nu = 991$ cm^{-1} and $\Delta\nu = 1003$ cm^{-1} is interpreted as due to the ν_1 modes[15] of two different adsorbed states corresponding to the first layer and succeeding layers, respectively, with overlapping ν_{12} modes[15] at 1032 cm^{-1}. The Raman shift between the two species is comparable to the shift between neat liquid pyridine and pyridine hydrogen-bonded to a polar molecule,[16] although in UHV surface experiments both species are weakly bound to the Ag surface and desorb below room temperature.

The coverage dependence of the SERS intensity is shown in Fig. 3 where the error bars repre-

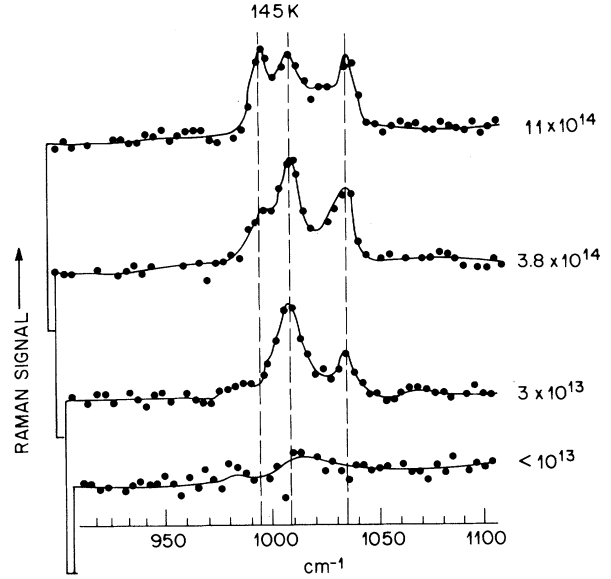

FIG. 2. Raman spectra for pyridine adsorbed on Ag(100) which was roughened with the iodine film treatment (see text). The coverage of pyridine molecules per cm^2 is given on the right of each curve. The zero-intensity position is given at the left of each curve.

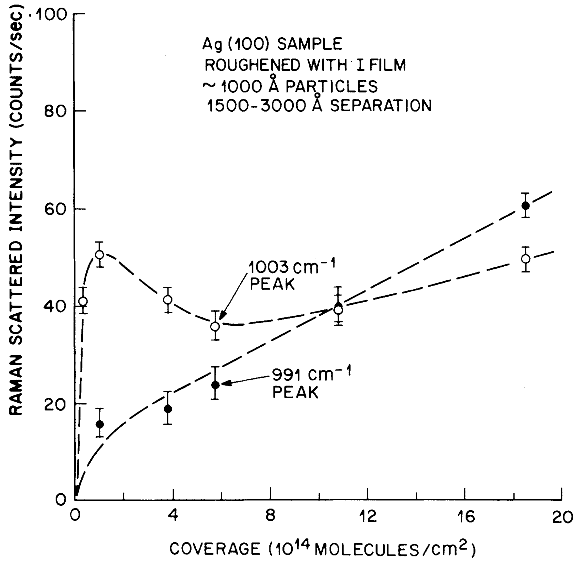

FIG. 3. Raman scattering intensity as a function of coverage of pyridine molecules per cm^2. The intensity of the 1003- and 991-cm^{-1} peaks was measured above the smooth background. The 1032-cm^{-1} peak has a coverage dependence which is intermediate between that of the 1003- and 991-cm^{-1} peaks. The error bars include only counting statistics and do not allow for systematic uncertainties due to overlapping peaks.

sent counting statistical uncertainty and the dashed lines are a guide to the general trend. Our coverage does not agree with the results of Ref. 3 since we fill the UHV chamber to an equilibrium pressure and keep the sample below the condensation temperature. Reducing the pressure by a factor of ~ 500 does not cause evaporation of condensed pyridine. Thus we can determine the coverage directly from the incident molecular flux if a condensation coefficient near unity is assumed. Apparently the authors of Ref. 3 by using a nozzle dosing technique underestimate their pyridine flux by a factor of $\sim 60-100$. The 1003-cm^{-1} species Raman signal reaches a maximum at 10^{14} pyridine molecules/cm^2, corresponding to a Raman enhancement of $(5\pm2)\times10^4$. Above 1 monolayer the 991-cm^{-1} Raman signal increases linearly with increasing coverage up to $\sim 2\times10^{15}$ molecules/cm^2 or nearly 7 monolayers, with an average enhancement of 1×10^4. Contrary to many of the proposed theoretical models of SERS,[2,8-13] the Raman enhancement induced by the Ag surface extends well beyond the first monolayer of adsorbed molecules.

In summary, we have presented the first detailed coverage dependence of SERS from pyridine adsorbed in UHV on several Ag surfaces. A roughness with dimensions near 500 Å appears to be necessary on our surfaces for SERS since macroscopic and atomic scale roughness did not give large enhancements. The observation of a large enhancement ($\sim 10^4$) for physisorbed multilayers requires a mechanism which can contribute an enhancement for molecules with distances ranging up to 50 Å or more from the surface.

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[1] J. C. Tsang, J. R. Kirtley, and J. A. Bradley, Phys. Rev. Lett. 43, 771 (1979).

[2] F. W. King, R. P. Van Duyne, and G. Schatz, J. Chem. Phys. 69, 4472 (1978), and references therein.

[3] T. A. Wood and M. V. Klein, J. Vac. Sci. Technol. 16, 459 (1979); R. R. Smardzewski, R. J. Colton, and J. S. Murday, Chem. Phys. Lett. 68, 53 (1979).

[4] J. E. Rowe, H. Ibach, and H. Froitzheim, Surf. Sci. 48, 44 (1975).

[5] Escape depths and elemental sensitivities for Ag and C are taken from P. W. Palmberg and T. N. Rhodin, J. Appl. Phys. 39, 2425 (1968), and from K. Jacobi and J. Holzl, Surf. Sci. 26, 54 (1971), respectively. For our spectrometer, relative sensitivity is consistent with L. E. Davis *et al.*, *Handbook of Auger Electron Spectroscopy* (Physical Electronics Industries, Eden Prairie, 1976). Using an incident electron energy of 3 keV and current of ~ 1 μA, we have determined carbon and nitrogen-atom coverage relative to the clean Ag-surface-atom coverage at the beginning of the experiment, with relative sensitivity factors from the Auger handbook corrected for the density difference of Ag and graphite. We have also assumed mean escape lengths for AES transitions of both pure Ag and graphite corresponding to 8 Å.

[6] J. G. Bergman, J. P. Heritage, A. Pinczuk, J. M. Worlock, and J. H. McFee, Chem. Phys. Lett. 68, 412 (1979).

[7] T. E. Furtak, Solid State Commun. 28, 903 (1978).

[8] A. Otto, in Proceedings of the Conference on Vibrations in Adsorbed Layers, Jülich, Germany, 1978 (unpublished).

[9] S. Efrima and H. Metiu, Chem. Phys. Lett. 60, 59 (1978), and J. Chem. Phys. 70, 1602, 1939, 2297 (1979).

[10] G. L. Eesley and J. R. Smith, Solid State Commun. 31, 815 (1979).

[11] J. I. Gersten, B. Birke, and J. Lombardi, Phys. Rev. Lett. 43, 147 (1979).

[12] E. Burstein, Y. J. Chen, C. Y. Chen, S. Lundquist, and E. Tosatti, Solid State Commun. 29, 567 (1979).

[13] J. R. Kirtley, S. S. Jha, and J. C. Tsang, to be published.

[14] The importance of collective electron resonances of small particles has been previously considered by M. Moscovits, J. Chem. Phys. 69, 4159 (1978), and E. Burstein, C. Y. Chen, and S. Lundquist, in *Proceedings of the Second Joint U.S.-U.S.S.R. Symposium on Light Scattering, New York*, edited by J. Birman, H. Cummins, and K. Rebane (Plenum, New York, 1979), p. 479; S. M. McCall, P. M. Paltzman, and P. A. Wolff (to be published) point out that large enhancements can occur if these resonances serve both to enhance the local field at the molecule and also to couple out the Raman radiation.

[15] L. Corrsin, B. J. Fax, and R. C. Lord, J. Chem. Phys. 21, 1170 (1953).

[16] W. Schindler and H. Posch, Chem. Phys. 43, 9 (1979).