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Unenhanced Surface Raman Spectroscopy of Nitrogen Physisorbed on Ag(111)

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ABSTRACT

The Raman spectrum of N\textsubscript{2} physisorbed on Ag(111) at 15 K is reported. The Raman intensity is unenhanced and is linear with nitrogen coverage between 1 and 353 Langmuirs (L) and with laser power from 100 mWatt to 1000 mWatt. The observed intensity of 7.6 cts s\textsuperscript{-1} W\textsuperscript{-1} L\textsuperscript{-1} is in good agreement with an intensity calculated using the gas-phase Raman cross-section. The observed line positions of multilayer physisorbed nitrogen are consistent with Raman spectra previously reported in the literature for the \textalpha -phase of bulk solid nitrogen. Background scattering associated with carbon contamination, and with silver islands produced during surface cleaning by alternative ion bombardment and annealing, affects the minimum detectable level of physisorbed species on silver. On a smooth, clean silver surface with a minimum of backgound scattering a detection limit of less than 0.1 monolayers is calculated.
INTRODUCTION

Raman spectroscopy of adsorbates on surfaces offers the possibility of studying a wide range of molecular species, including homonuclear diatomics which are difficult to study by other optical techniques, on a variety of surfaces. Surface Raman spectroscopy can provide vibrational information at wavenumber resolution over an extensive energy range (100-8000 cm\(^{-1}\)). To date, because of the low intensities associated with the Raman effect, the number of studies using unenhanced surface Raman spectrosopy (SRS) has been far exceeded by those utilizing surface enhanced Raman spectroscopy (SERS)\(^1\), although unenhanced SRS recently has been demonstrated\(^2\) to be sensitive to submonolayer coverages.

To obtain an unenhanced SRS spectrum of submonolayer coverage one must avoid surface enhancement and increase the instrumental sensitivity to compensate for the small Raman signals. By studying a physisorbed system the chemical enhancement mechanism, often associated with SERS, is eliminated\(^3\); unenhanced SRS studies by Campion et al. (University of Texas, Austin) indicate that smooth, clean surfaces of Ag(111) are free of electromagnetic enhancement.\(^1\)\(^4\) Recent technological advances in detectors and interference filters make it possible to assemble Raman instruments having enhanced sensitivity and applicable to SRS.\(^5\)

The intensity of Raman scattering from a thin, physisorbed film is given by:

\[
I_{\text{scat}} = (2I_0)N(\partial \sigma/\partial \Omega)
\]

where \(I_{\text{scat}}\) is the scattered intensity into one steradian, \(I_0\) is the laser power in photons s\(^{-1}\), \(N\) is the surface coverage in molecules cm\(^{-2}\), and \((\partial \sigma/\partial \Omega)\) is the differential Raman cross-section in cm\(^2\) sr\(^{-1}\) molecule\(^{-1}\). The factor of two arises because the laser passes through the adsorbed layer twice in the case of a highly reflecting substrate such as silver. For 1 Watt of cw laser power at 488 nm \(I_0 = 2.45 \times 10^{18}\) photons s\(^{-1}\). The saturated monolayer surface coverage of physisorbed \(N_2\) is approximately \(1 \times 10^{15}\) molecules cm\(^{-2}\) and the gas-phase Q-branch vibrational Raman cross-section of \(N_2\) is \(5.5 \times 10^{-31}\) cm\(^2\) sr\(^{-1}\) molecule\(^{-1}\).\(^6\)
The detected Raman intensity is given by:

\[ I_{det} = I_{scat}(2\Omega)R = 2700(2\Omega)R \]  

(2)

where \( \Omega \) is the collection solid angle, the factor of 2 arises from scattered light reflected from the surface and collected, and \( R \) is the instrument response. The instrument response is the fraction of light within the wavelength region of interest entering the spectrometer which is detected (assuming that the entrance slit is uniformly illuminated and that all the light imaged by the collection optics enters the spectrometer). Losses which contribute to \( R \) include absorption by the spectrometer mirrors, the efficiency of the grating(s) at the wavelength of interest, the quantum efficiency of the detector, and the fraction of the time the detector spends on each wavelength segment comprising the spectrum.

Table I compares the expected Raman signal from a monolayer of \( \text{N}_2 \) physisorbed on a silver surface calculated for various instrumental configurations. For all systems the quantum efficiency of the detector and the efficiency of the first grating are the same. The major additional loss for the double monochromator/PMT instrument is due to single channel detection which results in a small fraction of the total time being spent on each wavelength segment, with additional small losses due to the second grating and necessary mirrors. The major additional loss for the triple spectrometer/intensified photodiode array instrument is due to the small height of the active area of the detector which is sensitive to only 12.5% of the slit height, with smaller losses due to the extra gratings and accompanying mirrors. The calculations indicate that the instrumentation used in this study\(^8\)–based on an imaging photomultiplier tube (PMT)–should be able to obtain unenhanced SRS from a physisorbed layer in a reasonable time.

In this paper we report on the Raman spectra of \( \text{N}_2 \) physisorbed on clean, smooth Ag(111) at 15 K. Dosages are given in Langmuirs (1x10\(^{-6}\) Torr sec). The results include values of the intensity and line positions as functions of laser power and dose. We also report on background noise limitations associated with impurities and surface roughening. From the results the capability of unenhanced SRS to
study monolayer and submonolayer coverages of adsorbates on well-characterized, single-crystal surfaces is evaluated.

Experimental

The experimental apparatus consisting of a Raman spectrometer\(^5\) and an ultra-high vacuum (UHV) chamber with surface characterization and sample cryogenic cooling\(^7\) has been described. Briefly, the Raman spectroscopy instrument consists of an Ar\(^+\) laser, beam shaping and collection optics, single spectrometer, imaging PMT detector, and computer data acquisition electronics. The laser plasma lines are removed by a notch filter centered at 488 nm with a 10 nm bandpass; an interference longpass filter with cutoff at 506 nm is used to reduce the Rayleigh line by a factor greater than \(10^6\) before the spectrometer entrance slit. The UHV chamber is equipped with low energy electron diffraction (LEED)/retarding field Auger electron spectroscopy (AES) and quadrupole mass spectrometer for surface characterization, ion bombardment gun and electron bombardment heating for cleaning and annealing the surface, and a cryogenic sample manipulator with off-axis rotation capable of holding a sample at temperatures down to 14 K.\(^8\) In addition, the UHV chamber has optical ports for laser entry and exit and a single light collection port containing a f/0.95 lens.

The optimum geometry for SRS from a metal surface with known optical properties has been calculated with classical electrodynamics by Greenler and Slager.\(^9\) Fig. 1 shows the optical configuration used in the present study. The laser entry and exit ports are at \(90^\circ - \theta = 70^\circ\) with respect to the surface normal and the collection optics are at \(\phi = 45^\circ\) with respect to the laser plane of incidence. The laser beam is polarized with the electric vector parallel to the plane of incidence (p-polarization).\(^4,9\) The scattered light is collected using a 5.0 cm focal length f/0.95 television camera lens and focused onto the entrance slit of the spectrometer using a 30.0 cm focal length f/6.0 achromat. The illuminated area on the sample is imaged
with x6.3 magnification onto the entrance slit by the collection optics.

The laser is focused onto the sample using a 5.0 cm focal length lens located 40.0 cm from the laser head followed by a 16.0 cm focal length lens located at an additional distance of 46.0 cm. The sample is 25.0 cm beyond the final lens. The position of the laser spot on the sample is adjusted by moving the sample using the precision sample manipulator and directing the laser with a turning mirror located just outside the UHV laser entry port. Careful alignment of the sample and the position of the laser beam on the sample ensures that the scattered light is collimated by the fixed collection lens and centered at the spectrometer entrance slit. The final focusing lens is inserted and aligned so that the scattered light is focused onto the entrance slit of the spectrometer. The best focus is determined by moving the focusing lens so as to maximise the intensity on the detector of the background light scattered from the surface.

At this point the laser beam focus is optimised on the sample. The vertical extent of the background scattered light detected by the imaging PMT is used to determine the length of the laser spot image on the entrance slit. When the laser is at a sharp focus at the surface, the length of the laser spot image on the entrance slit is at a minimum. At the best focus, in the present experiments, the laser spot image is an ellipse 2.5 mm x 0.85 mm, on a slit 20.0 mm x 0.048 mm. The effect of this is considered in the discussion.

A single-crystal silver rod (Aremco Products Inc.) was oriented to within 1° of the (111) face by means of reflection X-ray diffraction (Laue photography). Individual samples (9mmx1.5mm) were cut and the experimental face was polished to produce a smooth surface with very few pits as observed under x400 magnification.7

Before characterization of the sample crystal, the entire vacuum chamber is baked out at 200° C for several days attaining a UHV base pressure of less than 2x10^{-10} Torr. The sample crystal initially is bombarded with Ar⁺ at 400 K for a total period of 1 h (5 x 10^{-5} Torr Ar at 500 eV kinetic energy) and then annealed (800 K) to optimal sharpness of the LEED pattern. Sample cleanliness is monitored by AES after each cleaning cycle. Brief ion- bombardment is adequate for subse-
quent experiments. Once cleaned, the sample is cooled to cryogenic temperatures and recharacterized. LEED patterns of the ordered surface are observed after each Auger spectrum. The sample is dosed at 15 K by isolating the cryopump and filling the chamber to $1 \times 10^{-7}$ Torr of nitrogen as measured on the ion gauge for a specified time, i.e. for a dose of 1 L ten seconds is used. Pumpdown from $1 \times 10^{-7}$ Torr to $1 \times 10^{-9}$ Torr, using the cryopump, is achieved in a few seconds. After a number of cleaning cycles it was found that sputtering from the silver plate used to secure the sample formed a thin film of silver islands on the Ag(111) surface. The silver islands were especially prevalent when 2 KeV ions were used.\textsuperscript{10}

The effect of the incident laser on the sample temperature was tested by attaching a temperature sensor directly to a surrogate sample and focusing the laser onto the sensor. Since the sensor surface is more absorbing than the surface of the polished Ag crystal the observed increase in temperature should equal or exceed the increase in temperature of the silver sample. Fig. 2 shows the temperature of the sensor as a function of time with increasing laser power. The temperature stabilized within a few seconds and increased by $1.0^\circ$ per Watt of incident laser power. The temperature of a silver surface is expected to be the same as the temperature of the bulk for cw illumination.\textsuperscript{11}

Unless otherwise indicated, Raman spectra are taken using 100 mW of laser power measured at the laser head (75\% of the laser power reaches the sample) and an integration time of 450 seconds.

\section*{Results}

The Raman spectrum of physisorbed nitrogen on clean, smooth Ag(111) at 15 K was studied as a function of nitrogen exposure, laser power, and polarization of the scattered light. In addition, we observed and attempted to characterize a dramatic increase in background scattering when the Ag surface had a low coverage of carbon, as shown by AES, or became textured. Fig. 3 shows a Raman spectrum
for a dose of 4 Langmuirs nitrogen. This spectrum, and all others obtained at low multilayer exposures, is characterized by a single peak at 2328 cm\(^{-1}\). The peak does not shift as the dosage is increased. At high exposures additional weak peaks appear which are not observed at lower exposures due to their low intensity.

A) \(N_2\) Exposure

Experiments at high exposures showed the \(N_2\) Raman intensity to be stable for many hours at 15 K. Sequential dosing of the Ag surface at 15 K at a pressure of 1x10\(^{-7}\) Torr of nitrogen was therefore used to obtain increasing coverages without loss of previously adsorbed nitrogen. Each dose was followed immediately by Raman data collection. Comparison of the intensity of m/e 28 from the mass spectrometer, taken immediately after a dose with and without the sample being illuminated by the laser, showed no increase in the nitrogen pressure, confirming the stability of the condensed layer when exposed to the focused laser beam. Raman data for exposures of 1, 4, 13, 23, 113, 143, 173, and 353 L were collected over a period of 1.5 hours. Above 13 L a dosing pressure of 1x10\(^{-6}\) Torr of nitrogen was used. The Raman intensity was determined by integrating the observed peak and subtracting a background determined immediately adjacent to the peak.

The integrated intensity of the vibrational band of physisorbed \(N_2\) on Ag(111) as a function of exposure is given in Table II. The intensity is given as both total counts (450 s integration, laser power at the sample is 75 mW) and cts s\(^{-1}\) W\(^{-1}\) L\(^{-1}\). The average intensity normalized to exposure is 7.6 ± 1.4 cts s\(^{-1}\) W\(^{-1}\) L\(^{-1}\). The integrated intensity increases linearly with exposure. No substantial change in the sticking coefficient with increasing exposure is observed. The comparison of the observed intensity (Table II) and calculated intensity (Table I) is considered further in the discussion section.

At the highest coverage of 353 L additional weak peaks were observed near the main peak, Fig. 4. The peak positions and relative intensities are given in Table III. The peak at 2292 cm\(^{-1}\) is assigned to the vibrational stretch of \(^{14}N^{15}N\). The
relative height is 0.006 of the $^{14}$N$_2$ peak, in good agreement with the $^{15}$N natural relative abundance of 0.004. The peaks at 2364 and 2374 cm$^{-1}$ have been observed by others$^{13}$ in the Raman spectra of the $\alpha$-phase of bulk solid nitrogen and are assigned to combination bands of the vibrational stretch with librations. The relative intensities of the 2364 cm$^{-1}$ and 2374 cm$^{-1}$ peaks, compared to the 2292 cm$^{-1}$ peak, are in good agreement with the corresponding relative intensities observed for the $\alpha$-phase of bulk solid nitrogen. The peak position of the main feature at 2328 cm$^{-1}$ also coincides with the 2327 cm$^{-1}$ peak position observed in the $\alpha$-phase of bulk solid nitrogen. The temperature below which the $\alpha$-phase of bulk solid nitrogen first forms is 35.5 K.$^{14}$ These observations indicate that the $\alpha$-phase of solid nitrogen is the structure of the nitrogen thin film formed at an exposure of 353 L on Ag(111) at 15 K.

B) Laser power

The nitrogen Raman spectra was observed as a function of increasing laser power. A nitrogen exposure of 100 L and an integration time of 45 s was used. The integrated intensity and the scattered light background as a function of laser power are given in Table IV. Both the integrated intensity and background increase linearly with increasing laser power. By increasing the laser power by a factor of 10 the S/N is observed to increase by a factor of 4, within experimental error of the expected increase in the S/N of $\sqrt{10}$ based on statistical noise.

The observed linear increase in the integrated signal with increasing laser power is evidence that the nitrogen number density remains constant within the focused laser spot on the surface. At the highest laser power used the photon flux had no effect on the relatively fragile physisorbed nitrogen film. The spot size is estimated to be $4 \times 10^{-4}$ cm$^2$ yielding a power density of 2000 W cm$^{-2}$.

The integrated intensity, 0.4 cts s$^{-1}$ W$^{-1}$ L$^{-1}$, observed in this experiment was smaller by a factor of almost 20 than the integrated intensity observed with the same sample in the N$_2$ exposure study. This reduction in intensity for the same
coverage is related to changes in the surface morphology as the sample undergoes repeated cleaning cycles. This observation is discussed in more detail in the surface morphology section.

C) Surface morphology and cleanliness

A thin film of sputtered silver was deposited inadvertently onto the clean, smooth Ag(111) surface during repeated ion bombardment and annealing cycles. Ex-situ examination of the surface by optical microscopy revealed island structures with a smoothly decreasing distribution in island size across the sample.

Fig. 5 shows optical micrographs of three distinct regions of the silver surface at x400 magnification and the corresponding Raman spectra. The three regions represent the transition from large silver islands to a region where no islands are visible. The observed island growth and island shapes are similar to those observed when Ag is deposited on Mo(100)\textsuperscript{16}, W(110)\textsuperscript{17}, Si(100)\textsuperscript{18,19}, and Si(111)\textsuperscript{20}. Fig. 5A shows the smooth surface covered with large islands 5 \(\mu\)m in width. The island facets follow the crystallographic axes of the Ag(111) plane. The islands in Fig. 5B have more irregular shapes with a width of about 2-3 \(\mu\)m. By contrast, a smooth, featureless surface is observed in Fig. 5C.

Raman spectra of the three regions were taken in the 1150-1850 cm\(^{-1}\) range. A low background intensity (2 cts s\(^{-1}\)) is observed in region C, the smooth Ag(111) surface. Region B yielded a two-fold increase in background intensity and the appearance of a broad amorphous carbon peak with maximum intensity at 1580 cm\(^{-1}\). The Raman spectrum of region A showed an additional increase in background with only a minimal change over region B in the carbon intensity. The LEED patterns of this sample and of samples with more uniform distributions of silver island sizes were sharp. The presence of the silver islands is not detectable by LEED. Elemental analysis by scanning Auger microscopy (SAM) of region A with a spatial resolution of 40.0 nm showed both the substrate and islands to be silver and indicated no carbon contamination, Fig. 6. An increase in background scattered light is associ-
ated with the presence of silver islands. The accompanying carbon contamination, as observed in the Raman spectrum, also contributes to the background scattered light as described below.

An additional effect of the silver islands is a reduction in the intensity of the Raman spectrum of physisorbed nitrogen. When the entire surface is covered with islands similar to those shown in region A the surface appears cloudy rather than shiny. The intensities of the Raman spectra of physisorbed nitrogen on such surfaces, which still yield clean Auger spectra and a sharp LEED pattern, are lower by a factor of 10 or more and no nitrogen peaks are observed at doses below 17 L. The nitrogen may have occupied regions which are shadowed from either the laser or collection optics. The island structures are much larger than the wavelength of light and the observed reduction in the Raman signal shows that formation of these islands does not lead to surface enhancement of the Raman signal.

Auger spectra and Raman spectra (950-2000 cm\(^{-1}\)) from two smooth Ag(111) surfaces (no observable silver islands) are shown in Fig. 7. The Auger spectrum of one surface, Fig. 7A, shows no detectable carbon at the surface of the crystal as indicated by the ratio Ag(260,266)/Ag(303).\(^{21}\) The corresponding Raman spectrum, however, reveals a small amorphous carbon peak and low background intensity. The other surface, shown in Fig. 7B, has greater carbon contamination, observable by both Auger and Raman spectroscopy. In this case, the contamination causes a dramatic increase in the Raman background. Carbon contamination of the surface is more readily detected by SRS than by AES. When the carbon contamination is sufficient to be observed by AES, the SRS background associated with carbon masks the small Raman signals from low coverages of physisorbed nitrogen.

**Discussion**

In order to compare the calculated intensity of the vibrational band of physisorbed \(\text{N}_2\) given in Table I (140) to the observed intensity in Table II (7.6),
the sticking coefficient and the fraction of scattered light entering the spectrometer must be known. The sticking coefficient for nitrogen at 15 K is assumed to be unity (although it may be somewhat lower). The vapor pressure of N\(_2\) at 15 K is less than 1\(\times\)10\(^{-11}\) Torr; therefore a thin film of N\(_2\) will form when the silver sample is exposed to the dosing pressure of 1\(\times\)10\(^{-7}\) Torr of nitrogen. The linear increase in intensity with increasing dose and the stability of the intensity for many hours indicates that this is the case.

Vignetting at the spectrometer slits (losses due to overfilling the slit aperture) is a common problem in spectroscopy and in many cases can be ignored. However, when signals are extremely low and accurate estimates of the intensity are needed vignetting must be considered. Estimating the amount of light lost is simplified with a single spectrometer and multichannel detection because only the entrance slit needs to be considered. The fraction of the collected light entering the spectrometer is determined by the size of the image of the laser spot on the entrance slit of the spectrometer and the dimensions of the slit. The size of the image of the laser spot on the entrance slit of the spectrometer can be estimated from the height of the signal on the imaging PMT; the entrance slit is imaged 1:1 on the detector. The signal fills approximately 0.1 of the height of the detector which has a diameter of 25 mm. The laser spot on the sample, which is imaged onto the entrance slit, forms an ellipse with the ratio of the large and small diameters given by the cosine of the angle of incidence. Using the height of the scattered light on the detector and an angle of 70° the width of the laser spot image on the entrance slit is calculated to be 850 \(\mu\)m. With the 48 \(\mu\)m entrance slit, 6% of the collected scattered light enters the spectrometer. An independent assessment of the fraction of light entering the spectrometer was determined by measuring the integrated intensity of the Raman peak as the entrance slit width was increased, while other experimental parameters were held constant. This measurement confirmed that about 5% of the collected light enters the spectrometer with a 48 \(\mu\)m slit width.

The instrument response of the present apparatus has been checked using the gas-phase Raman spectrum of oxygen.\(^5\) The observed integrated intensity of the
gas-phase oxygen vibration was found to be within a factor of three of the intensity calculated for this band in the same manner as used for Table I. The \(x3\) lower intensity observed for the gas-phase spectrum as compared to the calculated intensity is probably due to over-filling the entrance slit, as indicated previously.\(^5\)

The expected integrated Raman intensity of physisorbed nitrogen calculated using the gas-phase Raman cross-section and the instrument response of the present apparatus is given in Table II as 140 cts s\(^{-1}\) W\(^{-1}\) monolayer. Using a sticking coefficient of 1.0 and 0.06 as the fraction of collected light entering the spectrometer an expected intensity of 8 cts s\(^{-1}\) W\(^{-1}\) L\(^{-1}\) is calculated. This value is, perhaps fortuitously, very close to the observed intensity in Table II, well within the experimental error for the estimation of various collection and sticking efficiencies. The agreement between observed and calculated intensities indicates that Raman scattering from thin films of nitrogen on Ag(111) is not significantly surface enhanced. Further evidence for no surface enhancement is that the scattering cross-section does not change with coverage, within experimental error, over the range of 1 to 353 L; for SERS the cross-section would decrease with increasing coverage.

The detection limit of SRS, using the present apparatus and the same integration time as in this work (450 s), can be calculated from the observed S/N ratio for a given dose along with the increases in both signal and background expected when higher laser powers are used and losses at the entrance slit are minimized. The intensity and background are linear with laser power as shown in Table IV so an increase by a factor of 15 in laser power to 1.5 W will increase the S/N by 3.9. Increasing the fraction of scattered light entering the spectrometer from 0.05 to 0.5 will further increase the S/N by a factor of 3.3. A conservative estimate of the observed S/N for the 4 L dose is 5, thus a S/N of 60 is expected under the improved conditions. Sensitivity to 0.1 monolayers with a S/N of 3.3 is calculated for N\(_2\) physisorbed on Ag(111). Other diatomic molecules with similar Raman cross-sections will have the same detection limit.

No shift in the line position of the nitrogen peak at 2328 cm\(^{-1}\) was observed for the coverages studied, within the experimental uncertainty. As described above, the
Raman spectrum (Fig. 4) indicates that a 353 L thin film is composed primarily of \(\alpha\)-N\(_2\). Since the observed fundamental line does not shift at the lower coverages, the structure of physisorbed nitrogen formed at low coverages may also be \(\alpha\)-N\(_2\).

IV. CONCLUSION

Unenhanced surface Raman spectra of physisorbed nitrogen on Ag(111) at 15 K are presented. It is shown that the nitrogen thin film is stable under increasing laser powers up to the maximum power used, 1.0 W. The SRS intensity increases linearly with increasing dose as a multilayer thin film forms. The observed line positions for a 353 L multilayer indicate that the structure of the thin film is the same as that of the \(\alpha\)-phase of bulk solid nitrogen. No shift in the observed fundamental line was observed at low coverages suggesting that the structure of physisorbed nitrogen may be the \(\alpha\)-phase of bulk solid nitrogen at all coverages. The observed intensities are consistent with an N\(_2\) sticking coefficient at 15 K of close to 1.0.

For smooth, clean Ag(111) the observed intensity is 7.6 cts s\(^{-1}\) W\(^{-1}\) L\(^{-1}\) and in agreement with the intensity calculated from the gas-phase vibrational Raman cross-section for the present experimental conditions. In this work we readily observed a Raman spectrum from a 4 L N\(_2\) film and retrieved a weak signal form a 1 L film. The experimental conditions used in this study can be improved to increase the sensitivity by using higher laser powers and focusing the laser to a smaller spot. With these improvements, a sensitivity to 0.1 monolayers of physisorbed nitrogen on Ag with a S/N of 3.3 is calculated. For physisorbed molecules on silver the gas-phase vibrational Raman cross-section can be used to estimate the expected SRS intensity. Diatomic molecules with vibrational Raman cross-sections similar to nitrogen will have the same 0.1 monolayer detection limit. Organic molecules generally have larger Raman cross-sections but also have lower monolayer saturated coverages, as pointed out previously.\(^1\) If the Raman cross-section is essentially the same as that of those molecules in the gas phase, the detection limits for most molec-
ular species will be 0.1 monolayer. There is no evidence for surface enhancement of the SRS intensity in the N$_2$/Ag system.

Under the best of conditions the SRS intensity from submonolayer coverages is small and can be masked by the presence of background signals. An increased background in the Raman spectrum is observed when the surface is either contaminated with small amounts of carbon or covered with silver islands. In both cases, the LEED pattern is sharp and unchanged from the initial smooth, clean surface. It is found that background signals capable of masking SRS signals are associated with surface carbon contamination at levels not detectable by AES. When carbon contamination is sufficient to be observed by AES, a strong carbon signal is seen in the Raman spectrum accompanied by a strong background. In addition, in the present work cleaning cycles using ion bombardment and annealing introduced texture onto the surface; such a surface has a Raman background sufficient to mask SRS signals. Thus, surface characterization of silver by LEED/AES is not sufficient to determine if the sample can be used for SRS studies. For silver the SRS background intensity is more sensitive to changes in the condition of the surface than is LEED or AES. These interferences may be exclusive to silver, but if they are universal, extreme care in cleanliness and surface preparation will be necessary to obtain unenhanced surface Raman scattering signals.
ACKNOWLEDGMENTS

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REFERENCES


Table I. Comparison between Raman instruments of the calculated Raman intensity from a monolayer of N$_2$ physisorbed on Ag(111). Laser power of 1 W at 488.0 nm, saturation surface coverage of $10^{15}$ molecules cm$^{-2}$, and a collection solid angle of 0.87 sr is assumed. The gas-phase Raman cross-section for N$_2$ is $5.5 \times 10^{-31}$ cm$^2$ sr$^{-1}$.

<table>
<thead>
<tr>
<th>INSTRUMENT</th>
<th>R</th>
<th>$I_{\text{det}}$ (Photons s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOUBLE MONOCHROMATOR WITH PMT</td>
<td>$1.0 \times 10^{-4}$</td>
<td>0.5</td>
</tr>
<tr>
<td>TRIPLE SPECTROMETER WITH INTENSIFIED PHOTODIODE ARRAY</td>
<td>$1.3 \times 10^{-3}$</td>
<td>6.1</td>
</tr>
<tr>
<td>SINGLE SPECTROMETER WITH IMAGING PMT</td>
<td>$3.0 \times 10^{-2}$</td>
<td>140</td>
</tr>
</tbody>
</table>
Table II. Integrated intensity of the vibrational Raman peak of nitrogen as a function of exposure. The incident laser power is 75 mW.

<table>
<thead>
<tr>
<th>Exposure (Langmuirs)</th>
<th>Intensity (counts)</th>
<th>Intensity (cts s$^{-1}$ W$^{-1}$ L$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>262</td>
<td>7.8</td>
</tr>
<tr>
<td>4</td>
<td>1033</td>
<td>7.7</td>
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<td>13</td>
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<td>9.7</td>
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<tr>
<td>23</td>
<td>5791</td>
<td>6.8</td>
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<tr>
<td>113</td>
<td>19964</td>
<td>5.2</td>
</tr>
<tr>
<td>143</td>
<td>33434</td>
<td>6.9</td>
</tr>
<tr>
<td>173</td>
<td>45580</td>
<td>7.8</td>
</tr>
<tr>
<td>353</td>
<td>106116</td>
<td>8.9</td>
</tr>
</tbody>
</table>

Average intensity = 7.6 ± 1.4 counts s$^{-1}$ W$^{-1}$ L$^{-1}$
Table III. Peak positions observed at 353 L exposure compared to reported values for the α-phase of solid nitrogen. The intensity is estimated from the observed peak height. Literature assignment of the peaks are noted.

<table>
<thead>
<tr>
<th>Position (cm⁻¹)</th>
<th>Intensity (relative)</th>
<th>Literaturea (cm⁻¹)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>2292</td>
<td>0.6</td>
<td>2289(2292b)</td>
<td>$^{15}$N$^{14}$N</td>
</tr>
<tr>
<td>2328</td>
<td>100.0</td>
<td>2327</td>
<td>nitrogen fundamental</td>
</tr>
<tr>
<td>2352</td>
<td>0.6</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>2364</td>
<td>0.4</td>
<td>2365</td>
<td>vibration-libration</td>
</tr>
<tr>
<td>2374</td>
<td>0.1</td>
<td>2374</td>
<td>vibration-libration</td>
</tr>
</tbody>
</table>

a Reference 13
b Reference 12
Table IV. Integrated intensity of the vibrational Raman band of nitrogen and background as a function of incident laser power. The laser power is measured at the laser head; 75% of the light is incident on the sample.

<table>
<thead>
<tr>
<th>Laser Power (mWatt)</th>
<th>Intensity (counts)</th>
<th>Background (counts)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>218</td>
<td>68</td>
</tr>
<tr>
<td>200</td>
<td>602</td>
<td>110</td>
</tr>
<tr>
<td>400</td>
<td>830</td>
<td>183</td>
</tr>
<tr>
<td>600</td>
<td>1630</td>
<td>391</td>
</tr>
<tr>
<td>800</td>
<td>2450</td>
<td>710</td>
</tr>
<tr>
<td>1000</td>
<td>2540</td>
<td>646</td>
</tr>
</tbody>
</table>
FIGURE CAPTIONS

FIGURE 1: Schematic of the optical interface between the UHV system and the Raman spectroscopy system. A telescope is used to expand the laser beam which is then focused onto the sample. A f/0.95 collection lens is used to collimate the scattered light followed by a f/6.0 imaging lens located outside the UHV chamber. The laser is incident at 70° from the surface normal and is polarized in the plane of incidence; the scattered light is collected at 45° to the plane of incidence.

FIGURE 2: Laser heating of a diode sensor attached directly to a surrogate sample with increasing laser power. The focused laser impinges directly upon the sensor. The laser is unblocked at time t=10 s and blocked at time t=60 s. The sensor is sensitive to changes in temperature of 0.01° K at these temperatures.

FIGURE 3: Raman spectrum of the Q-branch of physisorbed N₂ on a clean, smooth Ag(111) surface at 15 K. Exposure was 4 Langmuirs, laser power was 100 mW, and integration time was 450 s.

FIGURE 4: Raman spectrum of the vibrational fundamental of physisorbed nitrogen on Ag(111) at 15 K with 353 Langmuir exposure. The inset is a x20 intensity blow-up of the region surrounding the nitrogen peak. Four peaks are observed in the inset region at 2292, 2352, 2364, and 2374 cm⁻¹.

FIGURE 5: Raman spectra and optical micrographs of a sputtered Ag(111) surface: (A) region with large silver islands, with facets following the (111) plane; (B) region of smooth surface with smaller islands randomly distributed and ; (C) a smooth featureless surface.

FIGURE 6: (a)Optical micrograph of a sputtered surface displaying island facets in the (111) plane. (b) Scanning Auger spectrum of the surface and islands
confirming deposition of Ag/Ag(111).

**FIGURE 7:** Auger and Raman spectra of two smooth Ag(111) surfaces: (A) clean and (B) carbon contaminated.
Atmosphere

Ultra-high vacuum

\[ \theta_s = 20^\circ \]
\[ \phi = 45^\circ \]

Figure 1
Figure 2
Figure 3
Figure 4
Figure 5
Kinetic energy, eV

Figure 6
Figure 7