

## Anomalous Low-Frequency Raman Scattering from Rough Metal Surfaces and the Origin of Surface-Enhanced Raman Scattering

D. A. Weitz, T. J. Gramila, and A. Z. Genack  
*Exxon Research and Engineering Company, Linden, New Jersey 07036*

and

J. I. Gersten

*Department of Physics, City College of the City University of New York, New York, New York 10031*  
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Anomalous, low-frequency Raman scattering from localized acoustic vibrations of roughness features on a metal surface are observed. The observed mode frequency shifts with excitation frequency and with the index of refraction of the surrounding medium. The shifts arise from resonant laser excitation of localized dipolar plasmons. This resonant optical coupling is a key to the phenomenon of enhanced Raman scattering from molecules adsorbed on rough metal surfaces.

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It has recently been established that an essential condition for the observation<sup>1</sup> of an enormous enhancement of the Raman-scattering (RS) cross section of surface-adsorbed molecules is the presence of surface roughness.<sup>2-4</sup> In this Letter, we study enhanced RS from an extremely low-frequency vibrational mode that is much lower in frequency than any molecular mode. It is characteristic of the rough metal surface itself and is attributed to a localized acoustic vibration of the roughness features themselves. Thus we are able to examine critically the necessity for and the scale of the required surface roughness. The low-frequency RS has two unusual properties. We observe a dramatic variation in the frequency shift,  $f_p$ , of the peak RS intensity, when the laser excitation frequency,  $\omega_{ex}$ , is changed and also when the index of refraction of the surrounding medium,  $n_s$ , is changed. To our knowledge, this is the first observation of such frequency shifts in RS where there is no wave-vector dependence. We ascribe these effects to the resonant optical excitation of a dipolar plasmon which selectively enhances RS from acoustic vibrations localized on some roughness features on the metal surface. We obtain good agreement with a simple, physical model, yielding information on the scale of the surface roughness. Our results also help explain the key role of roughness in surface-enhanced RS (SERS).

Most of our experiments are performed in an electrochemical cell,<sup>4</sup> using reagent grade chemicals and triply distilled and deionized water. The electrode surface was prepared using a mild anodization procedure.<sup>1</sup> We used a back-scattering optical geometry in most cases and dispersed

the scattered light with a Spex 1401 double monochromator followed by a third monochromator that was scanned in tandem. All the gratings were holographic, and the slit widths were adjusted for a band pass of  $\sim 0.2 \text{ cm}^{-1}$ , giving excellent resolution and good rejection of elastic scattering and allowing the observation of RS down to  $\sim 2 \text{ cm}^{-1}$  from the laser frequency.

Figure 1(a) shows a typical scan of both the anti-Stokes (negative frequency shift) and Stokes side of the low-frequency spectrum for a silver electrode in an electrolyte of 0.1M KI and 0.05M pyridine in water, with  $\lambda_{ex} = 514.5 \text{ nm}$ . This peak is the most intense feature of the SERS spectrum, and is  $\sim 20$  times as intense as the pyridine peak at  $1008 \text{ cm}^{-1}$ . A study of the temperature dependence down to 2°K indicates that the ratio of Stokes to anti-Stokes intensities is consistent with the low-frequency peak being vibrational in character, with a temperature-independent linewidth.<sup>5</sup> We also observe a similar low-frequency peak in RS from a copper electrode, metal sols,<sup>6</sup>

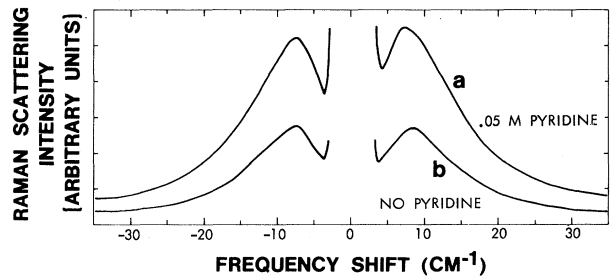


FIG. 1. Low-frequency RS spectra of an electrochemically roughened silver electrode, (a) with pyridine, (b) without pyridine.

and 50-Å silver island films.<sup>2</sup> In each case measured, the dependence of the intensity of the low-frequency RS on excitation energy and, for electrodes, on the applied voltage was the same as that of the molecular modes. Thus the peak in the low-frequency RS is a characteristic of SERS spectra.

The low-frequency peak was never observed in RS from a smooth, unanodized surface, indicating that the surface roughness that is necessary for the large enhancement of the molecular RS<sup>2-4</sup> is also necessary for the observation of this peak. We have observed the peak when the silver surface adsorbate is pyridine, deuterated pyridine, 4-cyanopyridine, cyanide, and nitrobenzoic acid. However, despite the fact that the RS spectra due to the molecular modes are quite different for each surface adsorbate,  $f_p$  is identical, within experimental error, in each case. Furthermore, the presence of a surface-adsorbed organic molecule is not essential for its observation as shown in Fig. 1(b) for a silver surface prepared in an electrolyte containing only KI. The low-frequency peak is again observed at the same value of  $f_p$  as with pyridine, although at about half the intensity. A scan of the full spectrum indicates no molecular peaks due to surface-adsorbed molecules, except a weak peak at  $\Delta\omega \approx 115 \text{ cm}^{-1}$ , attributed to an Ag-I stretch. We conclude that the peak is RS from a vibration characteristic of the rough metal surface itself.

A most striking and unusual aspect of the low-

frequency RS is observed when the excitation energy is changed. We find that  $f_p$  changes as  $\omega_{ex}$  is changed. This is illustrated in Fig. 2, which shows low-frequency RS spectra for pyridine adsorbed on silver for three different excitation energies. As shown in Fig. 3,  $f_p$  increases monotonically with increasing  $\omega_{ex}$ . A similar behavior is observed from both silver and copper surfaces, both with and without adsorbed organic molecules. However,  $f_p$  does not vary if  $\omega_{ex}$  is held constant and the angle of incidence or collection is changed. Thus the variation of  $f_p$  is not a wave-vector-dependent effect.

A second unusual aspect of the low-frequency RS was observed when the index of refraction of the surrounding medium was changed. A silver surface was prepared in an electrolyte containing 0.1M K<sub>2</sub>SO<sub>4</sub> and 0.01M KCN. A spectrum was taken; then the electrolyte was forced out of the cell with nitrogen gas, and the spectrum of the dried surface in nitrogen was recorded, without changing  $\omega_{ex}$ . We found that  $f_p$  changed substantially, shifting down from  $\sim 8.0 \text{ cm}^{-1}$  in water to  $\sim 6.0 \text{ cm}^{-1}$  in N<sub>2</sub> for  $\omega_{ex} = 19436 \text{ cm}^{-1}$ . Similar results were obtained for a surface prepared in an electrolyte containing only KI. Furthermore, the frequency of the mode for an island film in air was similarly reduced.

In order to explain our results, we must account for low-frequency RS from a vibration of the metal that has no wave-vector dependence and, therefore, lacks long-range ( $\sim \lambda_{ex}$ ) order.

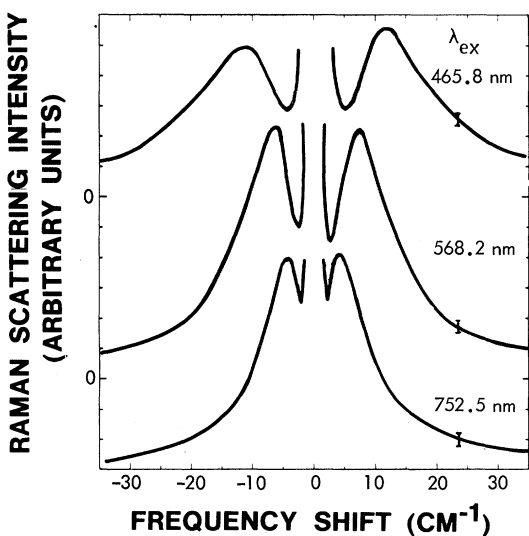


FIG. 2. Low-frequency SERS spectra of pyridine on silver with three excitation wavelengths.

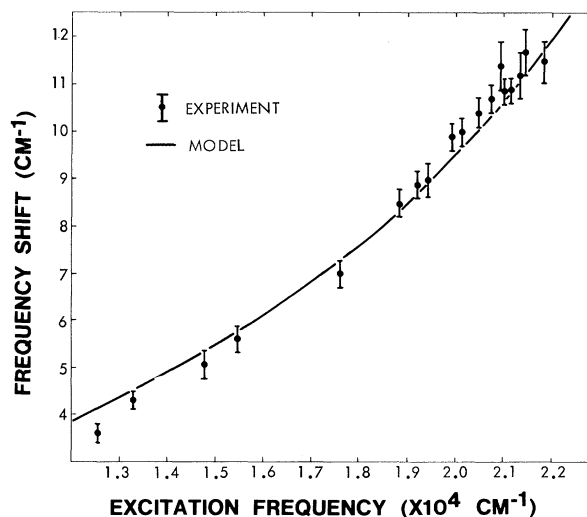


FIG. 3. Dependence of frequency of peaks of intensity of low-frequency RS on the laser excitation frequency.

Since the electrode surfaces exhibiting SERS are known to be extremely rough,<sup>3</sup> we attribute the low-frequency mode to an acoustic vibration localized to a single protrusion or roughness feature on the surface. The fundamental frequency of this vibration is approximately  $f \sim v/d$ , where  $v$  is the speed of sound in the metal and  $d$  is the characteristic dimension of the protrusion. The shift in  $f_p$  with  $\omega_{ex}$  then implies a resonant enhancement of the scattering from roughness features of some characteristic size or shape at each  $\omega_{ex}$ . Thus a resonant intermediate state must be involved in the RS both from the acoustic vibration and from the surface adsorbates. The unusual behavior of the low-frequency RS allows us to examine critically the nature of this state. The dependence of  $f_p$  on  $n_s$  suggests the excited state is not completely spatially localized in the vicinity of a surface-adsorbed molecule. However, the magnitude of  $f_p$  implies  $d \sim 100 \text{ \AA}$  for  $v = 3 \times 10^3 \text{ m/sec}$ , suggesting that the spatial extent of the intermediate state is, in fact, less than  $\lambda_{ex}$ . One form of excitation that may have a spatial extent of this scale is a localized surface plasmon.<sup>7</sup> The role of surface plasmons in SERS has been investigated by other groups,<sup>8,9</sup> and Gersten and Nitzan<sup>10</sup> have recently proposed a theory for SERS in which a plasmon, localized on a surface roughness feature, is a resonant intermediate state contributing to the enhancement. Depolarization effects make the plasmon frequency sensitive to the shape of the roughness feature and can shift the resonant frequency down into the visible. Thus, we attribute the low-frequency mode to an acoustic vibration of surface features selected by the resonant excitation of a localized plasmon.

To obtain a more detailed description of the behavior of the data shown in Fig. 3, we need a model for the rough metal surface and for the electronic and vibrational excitations. The extreme roughness characteristic of these surfaces<sup>3</sup> is difficult to model in detail. However, we can use the data to compare with the predictions of a model and perhaps extract details of the surface. The localized nature of the excited states implied by the data suggests considering the excitations of individual roughness features. The data then imply that the characteristic dimensions of the roughness features increase as their resonant plasmon frequencies decrease.

We have considered<sup>11</sup> in detail a rough surface modeled as consisting of an inhomogeneous array of hemispheroidal protrusions of varying sizes

and shapes. While this is certainly an overly simplified model for the surface, solutions can be obtained for both the dipolar plasmon and an acoustic vibration of the spheroid. We use the solution for the plasmon obtained recently<sup>10</sup> and consider a spheroidal vibration where the two axes of the spheroid oscillate  $180^\circ$  out of phase. By using this model with possible distributions of the spheroid sizes that make up the rough surface, we can make a comparison to the data. We get the good agreement shown in Fig. 3 for a distribution of spheroid minor diameters peaked at  $\sim 100 \text{ \AA}$  and with a typical size of  $\sim 200 \text{ \AA}$ . This is in agreement with the size of silver islands that are observed to give the greatest SERS.<sup>12</sup> The observed increase in the RS intensity when highly polarizable molecules are adsorbed on the surface is also predicted by the theory and is attributed to enhanced Rayleigh scattering of the adsorbate, modulated by the acoustic vibration.

The dipolar plasmon excitation responsible for the behavior of the low-frequency mode reported in this Letter will also form a resonant intermediate state for RS from surface adsorbate molecules, and leads to considerable enhancement of the RS. These results account for the necessity of roughness in order to obtain the large enhancement, and suggest the characteristic dimension of the roughness that is important for SERS. This dimension is also consistent with a predicted peak in the RS intensity when  $2a \sim 500 \text{ \AA}$ , based on a consideration of the damping of the dipolar plasmon,<sup>11</sup> which is minimized when the size of the roughness feature becomes comparable to the electron mean free path. For larger sizes, retardation effects would diminish the coupling to the dipolar plasmon. An increase in the imaginary part of dielectric constant of the bulk metal will also be reflected as increased damping of the plasmon and accounts, in part, for the observed frequency dependence of SERS on different metals.<sup>11</sup> The spatially delocalized nature of the dipolar plasmon intermediate state accounts for the lack of harmonics characteristic of SERS, since the molecular potential is not altered appreciably in the excited state. Finally, the extent of the electromagnetic field of the dipolar plasmon outside the protrusion is in accord with the recent observation of SERS from molecules some distance ( $\sim 50 \text{ \AA}$ ) from the surface.<sup>4</sup>

In conclusion, we expect that the enhancement of RS from molecules near the resonantly selected roughness features is considerably higher than

that reported for the average over the entire sample. This may be observable as a sharp increase in the intensity of RS over a narrowed excitation-frequency range from a surface containing more nearly uniform metal features.

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## Hydrogen-Associated Disorder Modes in Amorphous Si:H Films

W. E. Carlos and P. C. Taylor

*Naval Research Laboratory, Washington, D. C. 20375*

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NMR spin-lattice relaxation rates  $T_1^{-1}$  of  $^1\text{H}$  in  $a\text{-Si:H}$  films exhibit a maximum near 40 K. Both the magnitude, the temperature, and frequency dependences of  $T_1$  are well described by a model which assumes a coupling to disorder modes which are associated with some hydrogen atoms. Results suggest that some hydrogen sites may contribute to the electronic states within the gap.

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The existence in many amorphous solids of atoms or groups of atoms which at low temperatures can exist in two positions of local equilibrium is well documented.<sup>1</sup> Such disorder modes are a common feature of oxide and chalcogenide glasses, but they have yet to be observed<sup>2</sup> in amorphous Ge, Si, or Si:H.

In this Letter we report pulsed  $^1\text{H}$  NMR experiments which indicate the presence of disorder modes associated with hydrogen in  $a\text{-Si:H}$ . We propose a model which explains both the magnitude and the temperature and frequency dependences of the spin-lattice relaxation time  $T_1$  for the hydrogen atoms. Because the disorder modes may also influence the electronic properties of an amorphous solid,<sup>3</sup> the present results suggest some interesting new considerations for both the defects and electronic densities of states in  $a\text{-Si:H}$ .

Samples were obtained from several different sources and contained between 7 and 15 at.% H.

All samples were deposited on heated substrates (250–330 °C) at relatively slow rates ( $\sim 300 \text{ \AA}/\text{min}$ ) by use of pure silane gas. Sample thicknesses ranged from 1 to 10  $\mu\text{m}$ . All samples were found by ESR measurements to be free of detectable paramagnetic impurities except for the usual "intrinsic" signal whose magnitude varied between  $\sim 10^{14}$  and  $10^{16}$  spins per cubic centimeter. Other common impurities, oxygen and nitrogen, varied between about 2 and 0.2 at.% and between 0.1 and 0.01 at.%, respectively. Voids were seen in some samples by use of small-angle x-ray scattering<sup>4</sup> but no microstructure was seen by electron microscopy.<sup>1</sup>

The  $^1\text{H}$  pulsed NMR data were taken with a standard setup. Frequencies were varied from  $\sim 10$  to  $\sim 42$  MHz and temperatures from  $\sim 4$  to  $\sim 475$  K. Spin-lattice relaxation time ( $T_1$ ) measurements were taken on the free-induction-decay (FID) signal with a repetition-rate technique.<sup>5</sup> All decay curves were exponential within experimental er-