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Surface-Enhanced Raman Spectroscopy and Surface Plasmons

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The Raman spectra of 4-pyridine-carboxaldehyde–doped Al-Al_2O_3-Ag tunnel junctions evaporated onto CaF_2 films and optical diffraction gratings show that the molecular Raman scattering is strongly enhanced under conditions which permit the direct excitation of the surface plasmon modes of Ag. This suggests that the surface plasmon is an intermediate state in surface-enhanced Raman scattering.

The ability of conventional Raman spectroscopy to observe the vibrational modes of a molecular monolayer adsorbed on a metal surface has recently been established.[1-3] This result implies an enormous enhancement (~10^6) of the Raman cross section for the adsorbed molecules over that for the same molecules in solution, and has attracted considerable experimental and theoretical interest.[4-6] However, the mechanism for these enormous enhancements remains unknown.[6]

We have previously shown that surface-enhanced Raman (SER) scattering can be observed for 4-pyridine-carboxaldehyde (4-py-COH) adsorbed onto the oxide surface of an Al-Al_2O_3-(4-py-COH)-Ag tunneling junction structure.[3] Combined measurements of the SER scattering and the inelastic electron tunneling spectra of these samples allowed us to confirm the existence of SER scattering in this non-electrolytic-cell system and show that SER scattering is both molecule and metal selective. In this paper, we report on a detailed study of the coupling of light to the vibrational excitations of 4-py-COH in this system. We present quantitative results on the dependence of the intensity of the SER scattering on surface roughness, laser excitation energy and the angle of incidence, and polarization of the exciting light for samples evaporated on rough CaF_2 films and a diffraction grating. Our results strongly suggest that the SER scattering process on Ag can proceed through the surface plasmon of Ag as an intermediate state.

All of our measurements were made on molecular monolayers chemisorbed on the oxide grown on evaporated Al films and then covered with 20 nm of silver. The samples were evaporated either on different thicknesses of CaF_2 or on a 1200-line/mm diffraction grating. The measurements were performed at 300 K and low levels of laser power to eliminate the possibility of laser-induced damage to the sample. Lines from both Kr^+ and Ar^+ lasers were used and the Raman spectra were collected over a solid angle of ~90° and analyzed by a double monochromator.

In Fig. 1 we show the Raman spectra of three Al-Al_2O_3-(4-py-COH)-Ag structures evaporated on different thicknesses of CaF_2. Metallic films evaporated on 10- to 100-nm-thick layers of CaF_2 have been shown to be rougher than films evaporated directly onto microscope slides.[7] The rms magnitude of the surface roughness increases film thickness, reaching a value of 3 to 4 nm for a 100-nm thick CaF_2 film.[7] In Fig. 1, we show that the intensity of the SER scattering from the 4-py-COH increases monotonically with increasing CaF_2 thickness. Radioactive-tracer studies using similarly prepared structures doped with benzoic acid show that the introduction of a roughened surface produces a change in the density of adsorbed molecules of less than a factor of 3, i.e., only a small part of the observed intensity change. In Fig. 2, we show the dependence on CaF_2 thickness of the intensity of the Raman mode at 1610 cm^{-1}. In Fig. 2, we also show the results of

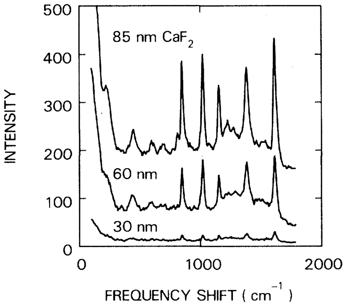

FIG. 1. Raman spectra of 4-py-COH monolayers in $Al-Al_2O_3-Ag$ junctions laid down in (a) 30 nm, (b) 60 nm, and (c) 85 nm of CaF_2. Spectra excited by 6471-Å light at 30 mW.

McCarthy and Lambe[8] on the CaF_2-thickness dependence of the intensity of the light emission due to the decay of surface plasmons excited by the inelastic tunneling (LEIT) of electrons across an insulating barrier. The surface plasmons excited by the tunneling electrons couple to light through the surface roughness. We see in Fig. 2 that the intensities of both SER scattering and LEIT increase monotonically with increasing surface roughness in the same manner. The magnitude of the increase in both cases is comparable. This suggests that surface roughness enters both the LEIT and SER scattering processes in the same way.

In Fig. 3, we show the excitation energy dependence of the Raman spectrum of our doped junctions for excitation energies between 1.8 and 3.5 eV. These measurements were made on structures evaporated on 80 nm of CaF_2. Our results are normalized against the intensity of the 470-cm^{-1} line of the Raman spectrum of quartz for these wavelengths, thereby removing, in the customary fashion, both the frequency dependence of the instrumental response and also the ω^4 dependence of the Raman cross section. The spectra in Fig. 3 show both scattering from the molecular modes of a monolayer of 4-py-COH and also the broad structures near 1550 and 1350 cm^{-1} attributed by Otto[3] to scattering from a surface carbonate of Ag. None of our sharp lines show any significant excitation-energy dependence for energies below 2.5 eV. All the lines show a rapid decrease with increasing energy for excitation energies >2.8 eV. The surface-plasmon energy, ω_{sp}, of Ag is 3.6 eV for the air-metal interface and shifts down to 3.4 eV for the metal-oxide interface.[9] McCarthy and Lambe[8] have found that the frequency dependence of the intensity of the LEIT is also relatively flat below ω_{sp} and decreases rapidly for energies approaching ω_{sp}. The roughness-induced coupling of the light and surface plasmons is strongest when the wave-vector difference between the light and the surface plasmon is comparable to the wave vectors of the dominant Fourier components of the roughness and is small at energies near ω_{sp}, where the required wave vectors are much greater than those characteristic of the surface roughness.

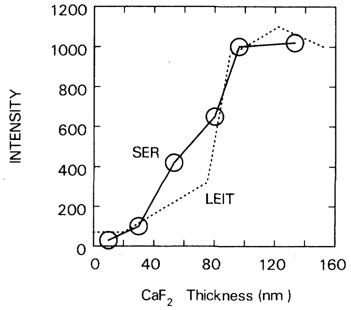

FIG. 2. Dependence of the intensity of surface Raman scattering (SER) and surface plasmon light emission (LEIT) from a tunneling junction (Ref. 8) on CaF_2 film thickness.

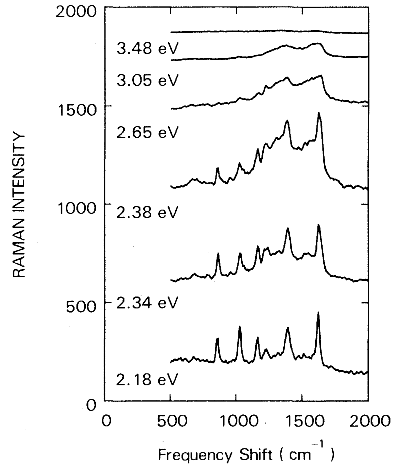

FIG. 3. Raman spectra of 4-py-COH for six different excitation energies in $Al-Al_2O_3-Ag$ junctions laid down on 80 nm of CaF_2.

We have also measured the SER spectrum of a junction doped with 4-py-COH and laid down on a 1200-line/mm diffraction grating where the light and surface plasmons can couple through the discrete Fourier components of the grating. In Fig. 4, we show the intensity of the specularly reflected beam at 530.8 nm as a function of the angle 2γ between the direction of the incident and reflected beam for this junction on a grating. These

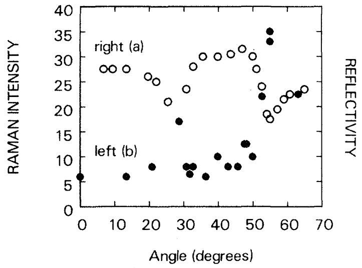

FIG. 4. (a) Dependence on the angle 2γ between the incident and reflected beams of the reflectivity of a silver diffraction grating for p-polarized light with the grating wave vector in the plane of incidence. (b) Dependence on 2γ of the intensity of the SER scattering for the same scattering geometry as (a).

data were obtained for p-polarized light when the wave vector of the grating, G, is in the plane of incidence. The intensity of the reflected beam shows dips for 2γ near 20° and 50° which are due to the grating-assisted absorption of light by the surface plasmons of our thin Ag films.[10] In Fig. 4, we also show the intensity of the 1610-cm^{-1} line in the Raman spectrum of 4-py-COH as a function of the angle 2γ for the same optical geometry as above. The intensity of the SER scattering is enhanced by almost an order of magnitude as 2γ goes through the strong dip in the grating reflectivity. If the polarization of the incident beam is changed from p to s, but G remains in the plane of incidence, the intensity of the SER scattering is almost independent of 2γ and comparable with the intensity shown in Fig. 4 for 2γ away from the reflectivity anomalies. If the incident beam is p polarized and the grating rotated so that G is normal to the plane of incidence, then the SER scattering is a factor of 20 weaker than the peak intensity shown in Fig. 4. We have also measured the intensity of the SER scattering from a junction laid down on 80 nm of CaF_2 which was first evaporated on the grating. The surface-roughness–enhanced Raman scattering is stronger than the scattering from the structure evaporated directly on the grating.

Our results show that the excitation of the surface plasmons of silver can produce a factor-of-20 enhancement in the intensity of Raman scattering from an adsorbed molecular monolayer. This is considerably less than the 10^6 enhancement required to explain the SER scattering. We have shown in Figs. 2 and 4, that the intensity of SER scattering is strongly dependent on both the magnitude of the surface roughness and the scattering geometry. Electron microscopy of our junctions on a grating shows both the periodic structure of the grating and surface roughness small on the scale of the grating but comparable with that observed for films evaporated on thin layers of CaF_2. We believe that the SER scattering shown in Fig. 4 and described above for scattering geometries away from the surface-plasmon–light resonances is a result of a combination of residual surface-roughness effects and small orientational errors in the scattering geometry. For example, the residual scattering which we observe in Fig. 4 is comparable with the scattering obtained from a junction evaporated on 20 nm of CaF_2. The residual SER scattering for p-polarized light depends only weakly on the angle of incidence and is therefore consistent with the SER scattering from the CaF_2 roughened films which also shows no strong dependence on 2γ. These considerations suggest that under ideal conditions of a microscopically smooth grating and perfect alignment, the dependence of the intensity of the SER scattering on the angle of incidence or the incident polarization would be considerably greater than the order of magnitude observed here.

Our experimental results show that the interaction of light with the surface plasmons of Ag plays an important role in determining the strength of SER scattering. The qualitative and quantitative similarities between (1) the roughness dependences of the intensities of SER scattering process and LEIT through surface plasmons, (2) the excitation-energy dependence of SER scattering and the spectral distribution of LEIT, and (3) the polarization and angular dependences of SER scattering from a grating and the reflectivity minima of the grating, all show that the excitation of surface plasmons by light produces a substantial enhancement in SER scattering. Such a process can be described by the expression

$$R \sim \left| \sum\nolimits_{\text{sp}} \frac{\langle \text{g} | H_{\text{vib}} | \text{sp} \rangle \langle \text{sp} | H_{\text{rough}} | \text{g} \rangle}{h\omega_{\text{sp}}(k) - h\omega_i} \right|^2,$$

where R is the Raman tensor, $|\text{g}\rangle$ and $|\text{sp}\rangle$ are the electronic ground and surface-plasmon states, H_{rough} is the coupling between a photon and the surface plasmon through static fluctuations on the surface, H_{vib} is the operator for the scattering of a surface plasmon into a photon by the creation or destruction of a molecular phonon and the terms in the denominator are the surface-plasmon energy and the energy of the incident photon. It has been shown that the coupling of photons to surface plasmons by H_{rough} can be highly efficient.[11] Little, however, is known about H_{vib}, especially when the molecule is chemisorbed on the surface as may be the case with pyridine on Ag. If SER scattering proceeds through the resonant excitation of surface plasmons so that we can drop the sum over all intermediate states and consider only the resonant state, then the probability for the inelastic scattering of a photon by a molecular vibration is the product of the probability of the absorption of a photon by a surface plasmon and the probability of the scattering of that surface plasmon into a photon by the vibration. We find that in order to obtain the the appropriately enhanced Raman cross section of about 10^{-25} cm^2/sr per molecule, the probability of the scattering of a given surface plasmon into a photon by a vibration of a chemisorbed pyridine molecule on Ag can be as large as 10^{-9}.

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Dynamic Response of Inhomogeneous Fermi Systems

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This paper presents a theory of the linear density response to an external time-dependent scalar potential for a Fermi system whose unperturbed density varies slowly. Simple local-density–functional response theory is valid except in a region of small q and ω (wave number and frequency of the perturbation). For this region we have worked out a generalization, to the case of inhomogeneous systems of Landau Fermi-liquid theory.

This paper deals with Fermi system at zero temperature whose unperturbed density $n_0(\vec{r})$ varies slowly on a scale $l \gg p_F^{-1}$, where p_F is a typical local Fermi momentum. We wish to calculate the linear density response of such a system to an external scalar potential, $v_1^{\text{ext}}(\vec{r},t)$, which we write as

$$v_1^{\text{ext}}(\vec{r},t)=\frac{1}{(2\pi)^4}\int v_1^{\text{ext}}(\vec{q},\omega)e^{i(\vec{q}\cdot\vec{r}-\omega t)}d^3r\,d\omega . \quad (1)$$

For the time being, we consider only neutral systems with short-range forces; extension to charged systems poses no significant problems.

For several (overlapping) regimes of q and ω, the necessary theory is already available. In view of the slow spatial variation of $n_0(\vec{r})$, a plausible *Ansatz* for the density response is the local-density approximation,

$$n_1(\vec{r},\omega)=\int\chi(\vec{r}-\vec{r}\,',\omega;n_0(\vec{r}))v_1^{\text{ext}}(\vec{r}\,',\omega)\,d^3r', \quad (2)$$

where $\chi(\vec{r}-\vec{r}\,',\omega;n_0)$ is the dynamic response function of a system of uniform density n_0. This *Ansatz* is, in fact, valid under the following circumstances:

(I) $\omega \ll v_F q$ (v_F is the Fermi velocity). In this case, χ is to a good approximation the static χ, which is known to have a short range of the order of p_F^{-1} or of the range of the forces [region (I) in Fig. 1].

(II) $\omega \gg v_F/l$. Again χ has a short range of the order of v_F/ω or p_F^{-1} [region (II) in Fig. 1].

(III) $q \gg l^{-1}$. Here q denotes a characteristic wave number of v_1^{ext}. The effective range of χ is no larger than q^{-1} [region (III) in Fig. 1].[1]

It can be seen from Fig. 1 that there is a region R, shown enclosed by heavy lines, which is not covered by the above three regions. Here we develop a theory which is valid in the following regime:

(IV) $q \ll p_F$, $\omega \ll p_F^2$ [region (IV) in Fig. 1, shown enclosed by dashed lines]. This is the region of validity of the classical Landau theory of