lence experiments.[12,13]

In conclusion it seems that frequency generation in the noise above the critical electric field can be explained by the CDW motion in an anharmonic potential. We have shown that such a motion can be synchronized with an external rf field. Experimentally we find that the frequencies are proportional to the current carried by the CDW and that the fraction of condensed electrons is in quite good agreement with other experiments.

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Enhanced Inelastic Light Scattering from Metal Electrodes Caused by Adatoms

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The intensity of the continuous inelastic light scattering from a silver electrode in a ClO_4 electrolyte depends on the potential and the amount of redeposited silver. These experimental observations are consistently explained by the concentration of silver adatoms at the electrode surface.

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Since 1977 there has been an increasing interest in the phenomenon of surface-enhanced Raman scattering (SERS) from adsorbates on metals.[1] Billmann and Otto[2] present new experimental evidence for a local enhancement mechanism, in contrast to recent theoretical and experimental claims[3] for a nonlocal enhancement mechanism by electromagnetic resonances caused by roughness on a scale of 500 Å.

A local enhancement mechanism is the adatom hypothesis.[4,5] It predicts resonant Raman scattering from adsorbate vibrations for adsorbates chemisorbed to adatoms and a structureless background due to resonant electronic Raman scattering.[4,6] The resonance is caused by itinerant electron-hole pairs in the metal which are the intermediate state in the scattering process.[7-9] The adatom mediates strong coupling of the photon to metal electrons.

In this Letter we report new experimental evidence strongly supporting the adatom hypothesis. Then we describe the parameters which will influence the adatom concentration on an electrode (e.g., Ag adatoms on a silver electrode) and later show that the measured background intensity follows the expected concentration of adatoms.

In metallic crystal growth the important sites of atoms at the surface are the monoatomic step, the kink site within a step, and the adatom, which is an isolated atom on an atomically smooth surface.

The binding energy of a kink-site atom equals the cohesive energy of the metal (per bulk atom), whereas the binding energy of an adatom is twice the surface energy of the metal (per surface atom).[10] For all alkali, transition, and noble metals the surface energy is about $\frac{1}{6}$ of the cohesive energy.[10] Hence, for these crystals the adatom binding energy is $\frac{1}{3}$ of the kink-site binding energy. Therefore one could expect that an energy of about $\frac{2}{3}$ of the kink-site binding energy will loosen kink-site atoms and transform them diffusing on the surface terraces. These effects do indeed occur as indicated by the experimental observation that very thin vapor-deposited films of silver are initially in the liquid state for temperatures above $\frac{2}{3}$ of the bulk silver melting temperature.[11]

Silver films vapor-deposited at room temperature will have a very low concentration of silver adatoms. Adatoms originally created by the deposition diffuse quickly to steps where they are incorporated into the crystal. Only at temperatures of the order of liquid nitrogen temperature is the mobility of adatoms so low that vapor-deposited atoms exist as rather stable adatoms. This has been demonstrated by conductivity measurements for small quantities of gold evaporated onto well-annealed and smoothed gold films.[12]

On a silver electrode, silver adatoms have a much smaller mobility than at the silver-vacuum interface. This follows from silver crystal growth from an electrode by reduction of Ag^+ ions.[13] The low mobility of adatoms at an electrode surface is probably due to the first layer of ordered and bound (except at the point of zero charge) water molecules.

The concentration of adatoms on an originally smooth electrode (on an atomic scale) may be increased in two ways:

(i) Ag^+ ions present in the liquid electrolyte or in a bulk surface film (e.g., AgCl) are reduced. In an electrochemical anodic cycle, bulk silver is first oxidized to Ag^+ and subsequently Ag^+ is reduced. In this second step the concentration of adatoms is greatly increased. At the end of the reduction, when the concentration of Ag^+ is low, there is little chance for an Ag^+ ion to be incorporated at a kink or step site; it will stay at the electrode as an adatom. This explains that an anodic cycle activates the enhanced Raman scattering.[4] As the adatoms created by the reduction of Ag^+ diffuse slowly at the surface, they are eventually trapped at steps or form new clusters and steps and thus are lost for the enhanced Raman scattering.

(ii*a*) Ag adatoms are also formed when kink-site atoms are loosened. At a metal-vacuum interface this process requires about $\frac{2}{3}$ of the melting temperature as shown above. The kink-site atoms at an electrode surface do not leave it as neutral atoms by thermal evaporation but as positive ions. They gain energy in the potential step ΔP at the electrode-electrolyte interface. Nevertheless we think that the two mechanisms have some analogies. We expect that at some ΔP between zero (the point of zero charge) and ΔP for anodic dissolution (1.5 V) the kink-site atoms start to diffuse out to the terraces. They may do so because as adatoms they gain a fractional positive charge and subsequently gain some energy from ΔP and from partial solvation. The fractional positive charge of isoatomic adatoms is plausible because the fractional positive charge of step atoms is well documented. At the metal-vacuum interface steps lead to a decrease of the work function,[14] and at a metal-electrolyte interface to a decrease of the potential of zero charge.[15]

(ii*b*) When a newly formed electrode surface is brought to the potential of kink-site atom-adatom transformation, the concentration of adatoms before reaching equilibrium will depend on the concentration of kink sites. An electrode with a high density of microcrystallites at the surface, created by fast redeposition of electrode material in an anodic cycle, will have a higher concentration of kink sites than an electropolished electrode surface.

We have studied the potential dependence of the inelastic background light scattering from a silver electrode in a saturated $KClO_4$ electrolyte. The experimental setup has been described in Ref. 4. Before monitoring the spectrum displayed in Fig. 1, the potential was stepped from -1.0 V versus

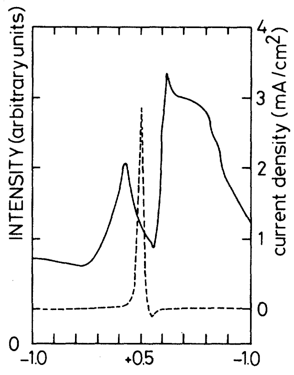

FIG. 1. Intensity of the background signal at $\nu = 4200$ cm^{-1} (solid line) and current (dashed line) vs potential, taken with a scan rate of 10 mV/s in a saturated $KClO_4$ solution, after redeposition of a silver layer of about 200 Å.

standard calomel electrode (SCE) to 0.5 V and back so that a surface of the average thickness of about 200 Å is dissolved and redeposited. This will lead to a surface of microcrystalline roughness[16] and in addition to some adatom concentration (i). The initial background is seen at – 1.0 V in Fig. 1. After this pretreatment, the potential of the silver slug is linearly swept from – 1.0 to 0.5 V and back to – 1.0 V at 10 mV/s. Up to about 0.4 V only a very small current is observed because of the charging of the double layer capacity and reduction of residual oxygen dissolved in the electrolyte. Above 0.4 V the dissolution $\mathrm{Ag}_{\mathrm{metal}} \rightarrow \mathrm{Ag}^{+}_{\mathrm{aqueous}}$ starts, indicated by the increase in current. Some of the Ag^{+} is redeposited as can be seen by the negative current in the back sweep.

The intensity of the backgroud signal (in Fig. 1 at 4200 cm^{-1}) starts to increase in the anodic sweep about halfway between – 1.0 V (approximately the point of zero charge) and the potential of dissolution at 0.5 V according to mechanism (ii*a*). The sharp decrease in intensity at about 0.4 V exactly coincides with the start of dissolution. Here the adatom will go into solution, preferentially before kink-site, step-site, and fully incorporated atoms. In the cathodic sweep silver is redeposited and the background intensity increases by mechanism (i). It decays with time[9] and with decreasing potential (about 60 min at – 0.8 V vs SCE and about 1 min at – 0.6 V vs SCE) because of diffusion of the adatoms to steps where they are trapped at lower potential. The decrease of intensity at the most positive potential in the triangular sweep is absent when the potential of beginning dissolution is not reached.

Intensity variations analogous to those depicted in Fig. 1 have been observed also in SO_4^{--} and OH^- electrolytes. To exclude the possibility that the background intensity is caused in some way by an unknown impurity of the electrolyte, or some unknown Helmholtz-layer reorientation, we have performed the experiment displayed in Fig. 2. We started with a polycrystalline silver slug after etching it in an $\mathrm{H_2O_2/NH_3}$ solution[17] and inserted it into the electrolyte at – 1.0 V. These electrode surfaces show the enhanced Raman effect only after anodic activation.[4,17] At – 1.0 V the background signal increases with *d*, the average thickness of the redeposited layer of silver, up to $d \approx 250$ Å. This is analogous to the increase of the signal from pyridine vibration with the amount of redeposited silver[18] and our observation in an OH^- electrolyte.[9] Mechanism (ii*b*) explains that the increase in intensity between – 1.0 V and 0.2 V grows with *d* because the microcrystallite density at the surface will increase with *d*. If this increase were caused by a potential dependent adsorption of a neutral species, it should not strongly depend on *d*.

We have also measured simultaneously the Rayleigh-scattered light by separating about 8% of the collected scattered light. The variations of the Rayleigh-scattered light with potential are small with little correlation to the variation of the inelastic scattered intensity [Fig. 2(b)]. This shows that there is no drastic structure change of the electrode surface at scales greater than atomic.[9]

It is interesting to note that the Rayleigh intensity is decreasing with *d*. In contrast to Bergman *et al.*,[19] who used a smooth evaporated film, we started with the etched sample which is quite rough on the lateral scale of 10–100 μm and hence shows strong Rayleigh scattering. After redeposition of a layer of thickness *d*, the bulk microcrystals are covered by much finer crystals, thus smoothing the electrode surface on a macroscopic scale. The opposite intensity variations of

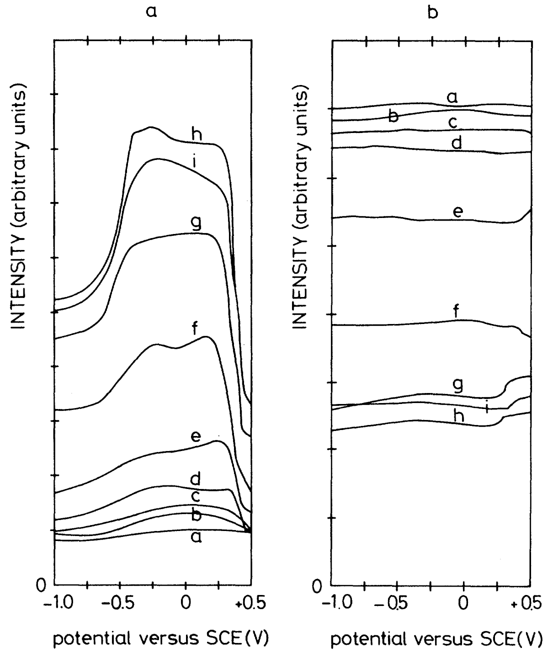

FIG. 2. Intensity (a) of the background signal at $\nu = 4285\ \mathrm{cm}^{-1}$, and (b) of the Rayleigh scattered light, vs potential, taken with a scan rate of 10 mV/s in a saturated $\mathrm{KClO_4}$ solution, after redeposition of a silver layer of the average thickness of 0 Å, curve *a*; 40 Å, curve *b*; 60 Å, curve *c*; 80 Å, curve *d*; 120 Å, curve *e*; 160 Å, curve *f*; 200 Å, curve *g*; 240 Å, curve *h*; 300 Å, curve *i*.

Raman and Rayleigh scattered light (as opposed to Ref. 19) show that microcrystalline roughness is not an important factor in the enhancement mechanism.

When we had finished this work, we found related ideas in the literature: Lazorenko-Manevich, Marinyuk, and Kolotyrkin[20] conclude that there are two groups of adsorption centers giving rise to the enhanced Raman effect. They suggest that both centers are adatoms on different crystallographic planes. It is possible that the sampels of Figs. 1 and 2 had different ratios of (111) to (100) and (110) surface planes. Hence, the ratio of different kinds of adatoms could also be different. This would explain the different onset potentials for the increase of intensity in Figs. 1 and 2.

The variation of the inelastic background light scattering with electrode potential and with the amount of redeposited electrode material can be explained in a consistent way by the adatom concentration. Together with the observation that (i) cyanide on silver shows an enhanced Raman effect only when chemisorbed to silver adatoms,[4,21,22] (ii) the Raman signal decays with time because of surface diffusion of silver adatoms to steps (in contrast to the nearly invariant Rayleigh-scattered light[9]), (iii) a deposition of 0.15 monolayers of Ag on a smooth Au film induces SERS,[23] and (iv) a silver film evaporated at 120 K displays SERS, but not after annealing to room temperature and recooling[24] (discussed in Ref. 5), we consider this a strong indication that adatoms (more general atomic-scale surface roughness) are the important "ingredient" of SERS.

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