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Comments

Comments are short papers which comment on papers of other authors previously published in the **Physical Review**. *Each Comment should state clearly to which paper it refers and must be accompanied by a brief abstract. The same publication schedule as for regular articles is followed, and page proofs are sent to authors.*

Comment on "Role of atomic-scale roughness in surface-enhanced Raman scattering"

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The experiment recently reported by Wood is not in contradiction with considering atomic-scale roughness as playing an important role in the surface-enhanced Raman scattering process.

In Ref. 1 Wood concluded "that the role of atomic-scale roughness (ASR) in surface-enhanced Raman scattering[2] (SERS) is a sharply limited one." I reject Wood's conclusion. I will first discuss the notion of "atomic-scale roughness" versus "supra-atomic roughness," and second, the models favored by Wood (exclusive electromagnetic field enhancement) and by myself [additional "charge-transfer (CT) effect at sites of atomic-scale roughness"], and subsequently I will discuss the relevance of Wood's results. (More results in favor of an important role of ASR have become known subsequent to the first of altogether four submissions of this paper for publication; these results are included in the present Comment.)

ATOMIC-SCALE ROUGHNESS AND ITS HYPOTHETICAL ROLE IN SERS

ASR sites may be defined as sites of those surface atoms for which the primitive translations within a (111), (100), or (110) lattice plane do not lead to the full number of possible nearest neighbors within this lattice plane. Any surface atom of a fcc metal with a coordination number n smaller or equal to 6 falls under this definition (note that the coordination number involves also nearest neighbors which are not all in the same lattice plane). Whereas surface atoms in (111), (100), or (110) surface terraces have $n=9$, 8, or 7, adatoms on (111), (100), or (110) surface terraces have $n=3$, 4, or 5; adatoms at the different monatomic steps have n ranging from 4 to 6. Of course, there are also sites of atomic-scale roughness with $n>6$; for instance, surface atoms at monatomic steps have $6\leq n\leq 8$. Surface vacancies of (111), (100), and (110) terraces involve atoms with $n=8$, 7, or 6. Also, grain boundaries and dislocations ending at the surface fall under the definition given above.

Supra-atomic roughness is defined by structure in the surface roughness correlation function $S(\vec{x})$ for $|\vec{x}|$ greater or equal to twice the lattice constant ($\vec{x}$ is a distance vector parallel to the average surface). There is no supra-atomic roughness without ASR. The surface concentration of sites of ASR grows with the average of $\operatorname{grad} S(\vec{x})$. For $S(\vec{x})\approx S(|\vec{x}|)$, this average of $\operatorname{grad} S(\vec{x})$ is roughly inverse to the surface roughness correlation length. Consequently, for a given rms supra-atomic roughness, the concentration of sites of ASR is roughly inverse to the roughness correlation length. For the case of constant correlation length, the concentration of sites of ASR will grow with the rms roughness. A "silver surface with roughness features of an order of 50 Å in size"[1] will have a higher concentration of sites of ASR than a surface consisting "of 500-Å radius Ag particles (approximately spherical in shape) separated by 1500–3000 Å."[3] The skeptical reader should have a look at the atomic hard-sphere model of a field emission tip,[4] which was constructed to approximate, as closely as possible, a hemisphere. As a model of a single-crystalline "hemispherical bump" on a silver surface, it corresponds to a bump of about 85 Å diameter. Approximately one-fifth of the surface atoms are on sites of ASR. Of course, this ratio will vary with the shape of the "bump" or "protrusion." The smallest but nonvanishing concentration of sites of ASR connected with supra-atomic roughness will exist for pyramidal protrusions with low index facets. On the other hand, ASR may exist, at least in principle, without supra-atomic roughness, for instance, for a random distribution of adatoms on a smooth low index plane or for a random distribution of adatoms at a given step.

It has been proposed in Refs. 5–7 that sites of ASR are adsorption sites, where the enhancement is stronger than at other bonding sites. The interaction of photons and metal electrons is increased at these sites compared to the coupling at an atomically smooth surface or within the ideally crystallized bulk,[5–7] because the local translational symmetry parallel to the surface is broken at sites of ASR. The vibrations of the adsorbed molecules are excited by CT. (This means photon-driven transitions of an electron from the metal side to an unoccupied molecular orbital,[7,8] or from an occupied molecular orbital to unoccupied states at the metal side.) The differences in the Raman scattering mechanism envisioned, for instance, by T. H. Wood and by myself, may best be explained by the comparison of three scattering diagrams in Fig. 1. Diagram (a) in Fig. 1 symbolizes the "classical enhancement" by electromagnetic resonances. The coupling between the free-incident and emitted photons and the electromagnetic resonance is mediated by supra-atomic roughness. The adsorbate vibration is excited by direct interaction of the electromagnetic field with the molecule, like in free space. Therefore this scattering process is usually calculated by classical electrodynamics (see Ref. 9 and discussions therein). Diagram (b) in Fig. 1 is the "nonclassical" enhancement effect discussed above, in the absence of supra-atomic roughness and hence in the absence of classical electromagnetic resonances. (However, local-field effects on atomic scale may be possible.[10]) One should note that the scattering probability increases with the fourth power of the photon-electron coupling constant. Diagram (c) in Fig. 1 is the strongest contribution to the nonclassical enhancement effect, involving both the classical field enhancement by electromagnetic resonances in supra-atomic roughness and process (b), in which the electromagnetic (EM) field of the homogeneous free photon waves (incident and reflected wave) is replaced by the resonant field in the supra-atomic roughness. Process (a) is the one favored by Wood, and process (c) is the one favored by myself. My reasons are as follows:

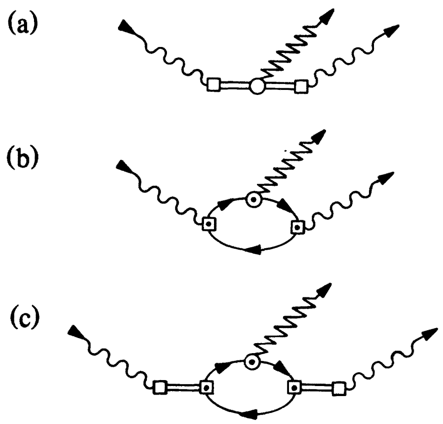

FIG. 1. Raman scattering diagrams, symbolizing the enhancement by an electromagnetic resonance (a), by the hypothetical coupling process at sites of ASR (b), and the combined scattering effect (c). Incoming (outgoing) wavy line symbolizes incident and reflected (emitted) light; quadratic vertices without point symbolize the coupling between the light waves and electromagnetic resonances by supra-atomic roughness. The electromagnetic resonances are denoted by double lines. Quadratic vertices with points symbolize the coupling of the EM fields (light waves or resonances) to the electron-hole excitations in the metal at sites of ASR. The round vertex without point symbolizes direct interaction of the EM fields with the adsorbate at all surface sites. The round vertices with points denote the coupling of the metal electrons with the adsorbate vibrations by CT at sites of ASR. Outgoing zig-zag line symbolizes an excited vibration of the adsorbate.

(1) Of course, EM resonances in supra-atomic roughness [Fig. 1(a) diagram] do enhance the Raman scattering from adsorbates; therefore process (c) will be stronger than process (b).

(2) A reasonable model for the charge-transfer mechanism of Raman scattering has been investigated by Persson.[8] With reasonable parameters he obtained an enhancement of about 30 for the Raman scattering cross section of the adsorbed molecule compared to Raman scattering from the molecule in free space.

(3) Persson's model does not involve ASR [diagram (b) in Fig. 1]. However, electron energy-loss experiments by Schmeisser *et al.*[11] and Demuth and Sanda[12] show that CT excitations at sites of ASR have a higher cross section and are more discrete in energy than CT excitations at atomically smooth parts of the surface. This fact has been tentatively explained in Ref. 13 (based on photoemission experiments[14,15]) by the relatively narrow energy distribution of the electron states of silver at sites of ASR compared to the corresponding states at the smooth surface and in bulk silver. Consequently, Raman enhancement by CT at sites of ASR would be one to two orders of magnitude stronger than at smooth crystalline terraces.

The contribution of a CT mechanism to SERS is directly indicated by recent SERS experiments[16,17] for pyridine on silver electrodes. This is discussed in detail in Ref. 9. If one assumes the same "classical enhancement" for all adsorbed molecules and neglects local-field effects on atomic scale,[10] one may draw the following conclusion: Provided that the ratio of molecules at smooth parts of the surface to molecules adsorbed at sites of ASR is smaller than the ratio of CT enhancement at sites of ASR and at smooth parts of the surface, the surface-enhanced Raman spectrum will be dominated by the signal from adsorbates at sites of ASR.

II. DISCUSSION OF WOOD'S EXPERIMENT

Wood[1] starts from the observation that silver films, evaporated on substrates of 100 to 180 K, and kept at this temperature, display SERS,[18] whereas warming these films up to room temperature irreversibly destroys the "SERS activity."[18,19] This annealing probably reflects the annealing of surface roughness but, as Wood says, "determining the scale of roughness" (atomic or "roughness features on the order of 50 Å in size"[1]) "from this observation alone is very difficult." Therefore Wood starts with a thick silver film, deposited *in situ*, which had been annealed at room temperature "to remove surface roughness." [However, these films are not smooth: During annealing to room temperature the Rayleigh scattered intensity increases by about a factor of 4,[19] and thick "mirror-like" silver films, evaporated on quartz at room temperature, still show considerable roughness (see Fig. 9 in Ref. 20).] Wood's sample is then cooled to 180 K. Subsequently, more silver is evaporated onto this film with an average deposition rate of 4.2 Å/min. In different runs deposition is stopped at various average thickness of the coldly evaporated silver (10 to 150 Å), the sample is exposed to 2 L ($1\ \mathrm{L}=10^{-6}$ Torr sec) of pyridine (corresponding to about 30% of a monolayer coverage[3]), and a Raman spectrum is acquired to measure the SERS properties of the surface. After this, the sample was briefly annealed to room temperature before a new film of different thickness was coldly evaporated. Raman signals did not appear until 150 Å of silver had been deposited in this way. Then pyridine Raman bands were observed at about 1003 and 1030 cm^{-1}.

Wood expects that "adatoms can be generated by very thin (1 monolayer =3.6 Å) evaporations onto cooled substrates," quoting measurements of Chauvineau and Pariset.[21] He writes: "Equally as many adatoms and atomic-scale roughness features should be present on the surface with a 10-Å low-temperature film as with a 150-Å low-temperature film. If atomic-scale roughness were the cause of SERS, the enhanced Raman signals from the 10-Å silver film would be as strong as those from the 150-Å film." Consequently, he concludes that "the role of atomic-scale roughness in SERS is a sharply limited one." First of all, these conclusions are based on a misunderstanding of Ref. 21. Chauvineau and Pariset[21,22] performed dc conductivity measurements of gold films. Chauvineau[22] evaporated $\frac{1}{20}$ of a monolayer of gold at 10 K on a well-annealed gold film, which increased the dc resistivity of the film considerably. The additional resistance was annealed mainly in three steps at 50, 100, and 230 K. The annealing step at 50 K is attributed by Chauvineau to the migration of single gold adatoms on (111) terraces to steps, where they are trapped. The annealing pattern between 70 and 350 K is attributed to the formation of atom complexes at steps, the migration of atoms along steps, and their final incorporation into the lattice at kink sites. Pockrand and Otto[19] write: "Without knowing the details we may call the underlying process 'annealing of a fuzzy step.'" Preliminary measurements of Chauvineau on silver[23] show annealing roughly in the same temperature range as for gold. However, single silver adatoms on silver seem to start migration already at 20 K. Therefore it is inconceivable that, by an evaporation of silver on silver at 120 K (Ref. 19) or 180 K[1] one may create stable silver adatoms. In Wood's experiments, the silver atoms deposited at a relatively low rate on the surface of 180 K will migrate until they are trapped at a step or at defect sites.

It should be pointed out that the situation concerning silver adatoms on silver electrode surfaces is different. Adatoms have a much smaller mobility on silver electrodes than on silver vacuum surfaces. The low mobility of adatoms at an electrode surface is probably due to the first layer of ordered and bound water molecules[5,24] and to specifically adsorbed ions, for instance, Cl^-.[25,26] Therefore, adatoms on silver electrodes are relatively stable defects at room temperature. According to Refs. 5 and 24–29, they are responsible for strong SERS from electrode surfaces.

Wood[1] concludes that "the relevant roughness features are significantly larger than atomic scale, although a precise size cannot be assigned to them from this experiment[1] alone." As Wood excludes mechanism other than classical enhancement he has logically no other choice then to assign the observed trend to increasing supra-atomic roughness with an increasing amount of coldly deposited silver. He quotes indications that the relevant roughness features are on the order of 50 Å in size. It is probably correct that there are supra-atomic roughness features on the scale of about 50–200 Å when a silver film of a thickness of at least 150 Å is evaporated at temperatures below 180 K. The big optical absorption for cold evaporated silver films of about 2000-Å thickness[7,30] is probably caused by electromagnetic resonances in supra-atomic roughness with a correlation length between 50 to 200 Å, though additional optical absorption caused by point-like bulk defects cannot be excluded. This is discussed in detail in Ref. 9. [In Ref. 7, I have overemphasized the second aspect; I take the opportunity to withdraw my speculation in Ref. 7, Chap. IIb, related to Figs. 4(b) and 4(c).] As discussed in Sec. I, the concentration of sites of ASR may grow when supra-atomic roughness grows. In the following I describe a possible mechanism. I expect that adatoms at steps or clusters of adatoms at steps (and steps of course) are relatively stable up to 180 K. In other words, I expect silver surface atoms at sites with coordination $4 \leqslant n \leqslant 6$ to be relatively stable at 180 K. Before any "cold deposition," the annealed, relatively smooth silver surface will have a relatively low surface concentration of steps—the great majority of the surface atoms are incorporated in smooth terraces. When about one monolayer of silver is deposited on this film, most of the additional silver atoms are incorporated onto sites with $n \geq 7$ by the following mechanism: The impinging atoms will migrate to steps, where they are trapped. Atoms which arrive later at the steps will increase the coordination number of the atoms arrived before until they are incorporated in the terrace. In this way, the film grows by a displacement of the steps. The steps will become "more fuzzy," but as the original surface concentration of steps was relatively low, the surface concentration of sites with $4 \leq n \leq 6$ is still relatively low. However, with increasing cold deposition of silver, three-dimensional clusters start to grow and eventually form the "bumpy surface." As discussed above, for a given correlation length of the bumpy surface, the concentration of sites of atomic-scale roughness grows with the rms roughness. In this way, the atomic-scale roughness features may grow with the quantity of coldly deposited silver. However, as our knowledge of the growth of coldly deposited silver films is still poor, one cannot prove this directly.

III. SOME EXPERIMENTAL INDICATIONS FOR THE IMPORTANCE OF ASR IN SERS

The analogous experiment to the one described by Wood[1] has been performed at silver electrode surfaces by Pettinger and co-workers,[31,32] already five years ago. Pettinger *et al.* started with "smooth" epitaxial silver layer electrodes and monitored the relative SERS intensity of the 1009-cm^{-1} pyridine vibration as a function of the amount of dissolved and redeposited silver (see Fig. 2). There is an appreciable intensity already after redeposition of one monolayer silver, quite in contrast to Wood's experiment at the silver vacuum interface. It is highly unlikely that one forms "roughness features on the order of 50 Å in size"[1] after dissolving and redepositing one monolayer of silver. It is much more likely that one creates "adatom roughness" in this way. Note that this would not be possible on silver vacuum interface for temperatures above 20 K.[23] The further increase of the SERS signal by about a factor of 100 up to the maximum signal at about 7 recycled monolayers[31] may be ascribed partly to the classical electromagnetic field enhancement by supra-atomic roughness. The concentrations of sites of ASR may also be deduced from photoelectron spectroscopy. Koch *et al.*[14] observed an extra photoemission at the top of the Ag *d* band about 4.2 eV below the Fermi energy after cold deposition of 3 Å of silver on a silver film, which had been deposited at room temperature (sample A). This extra structure was assigned to localized *d*-electron states at sites of ASR. This extra intensity was considerably higher when a thick silver film was coldly deposited (sample B).[15] From the ratio of the intensity of the extra structure to the overall *d*-band emission follows the surface concentration of defects responsible for this structure. It was about 12% for sample B but only 2% for sample A. Apparently, the concentration of sites of ASR increases with the amount of coldly deposited silver. The extra structure disappeared for samples A and B after warming up to room temperature.[14,15] This corresponds to the irreversible loss of the enhancing capacity of sample B after warming to room temperature,[18,19] which was explained by annealing of ASR.[19]

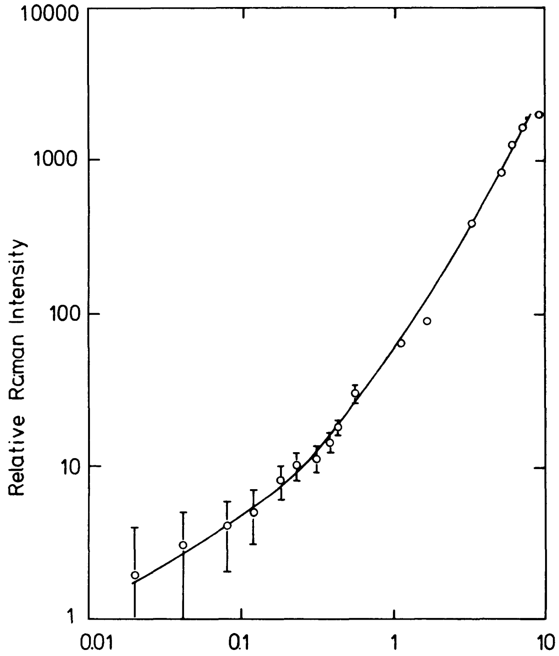

FIG. 2. Raman intensities of pyridine at 1009 cm^{-1} adsorbed on a silver (111) electrode at −0.6 V versus saturated calomel electrode as a function of anodic (dissolved), cathodic (redeposited) charge transfer in units of silver monolayers (after Ref. 31).

Much may be learned from a comparison of the frequency of the ring breathing mode of pyridine under various circumstances (for a detailed discussion see Ref. 9): in vapor, 992 cm^{-1},[33] in liquid, 991 cm^{-1},[34] matrix isolated 992 cm^{-1},[35] and in SERS, from silver electrodes at about 1006 cm^{-1} (e.g., Ref. 36), from coldly evaporated silver at about 1006 cm^{-1} (e.g., Refs. 35 and 37) to 1003 cm^{-1}.[3] The frequency of 1003 cm^{-1} reported by Wood in Ref. 1 is within 5-cm^{-1} agreement with all other SERS data. As small line shifts are observed in SERS both on electrodes and on cold films, and some allowance must be made for small errors of wave-number calibration, I conclude that in SERS from electrodes and cold films there is a common origin of the 1006 ±3-cm^{-1} line. Recent experiments by Campion and Mullins[38] and Tsang *et al.*[39] demonstrate that one observes only a signal at about 992 cm^{-1} but none at 1006 ±3 cm^{-1} for pyridine directly adsorbed to silver, when the surface concentration of ASR is low. Campion and Mullins[38] investigated Ag(111), (110), and (100) single-crystalline surfaces, and Tsang *et al.* optical gratings on which silver was deposited at room temperature. No short-range enhancement mechanism for this type of adsorbed pyridine was noticeable. After cold deposition of only 10 Å of silver on this silver grating, Tsang *et al.* observed a strong signal at about 1006 cm^{-1} after pyridine exposure. For this line a short-range enhancement mechanism of at least a factor of 20 is apparent—probably due to the CT enhancement mechanism discussed above. Therefore I assign the frequency of about 992 cm^{-1} to pyridine adsorbed on atomically smooth parts of the surface (and to "multilayer pyridine"[3]) and the frequency at 1006 ±3 cm^{-1} to pyridine at sites of ASR. According to infrared absorption experiment on matrix-isolated pyridine silver complexes,[40] it needs only one or two silver atoms to shift the breathing mode of pyridine from 992 cm^{-1} to 1000 and 1010 cm^{-1}, respectively.

Consequently, I interpret Wood's results thus: With increasing thickness of coldly evaporated silver, there increases the surface concentration of sites of ASR and the supra-atomic roughness. However, the classical enhancement is not enough to raise the Raman signal from all the adsorbed pyridine above the noise level, given the sensitivity of Wood's setup. (According to Ref. 3, enhancements of less than 100 are too small to yield a signal above the noise level.) At 150-Å cold silver thickness, the surface concentration of pyridine adsorbed at sites of ASR is high enough to raise the corresponding signal of 1003 cm^{-1} about 10 times above the noise level, with the help of the extra short-range mechanism at sites of ASR.

Note added in proof. Recent SERS investigations of pyridine on coldly deposited copper by Ertürk, Pockrand, and Otto provide evidence for an extra enhancement at sites of ASR of two orders. This is not unreasonable: one to two orders are delivered by dynamic CT,[13,16] one order by local field effects at sites of ASR.[10]

ACKNOWLEDGMENT

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[1] T. H. Wood, Phys. Rev. B 24, 2289 (1981).

[2] *Surface Enhanced Raman Scattering,* edited by R. K. Chang and T. E. Furtak (Plenum, New York, 1982).

[3] J. E. Rowe, C. V. Shank, D. A. Zwemer, and C. A. Murray, Phys. Rev. Lett. 44, 1770 (1980).

[4] J. M. Blakeley, *Introduction to the Properties of Crystal Surfaces* (Pergamon, New York, 1973), Figs. 6 and 8(b).

[5] J. Billmann, G. Kovacs, and A. Otto, Surf. Sci. 92, 153 (1980).

[6] A. Otto, Appl. Surf. Sci. 6, 309 (1980).

[7] A. Otto, I. Pockrand, J. Billmann, and C. Pettenkofer, in Ref. 2.

[8] B. N. J. Persson, Chem. Phys. Lett. 82, 561 (1981).

[9] A. Otto, in *Light Scattering in Solids,* edited by M. Cardona and G. Güntherodt (Springer, Berlin, in press), Vol. 4.

[10] A. Otto, Verh. Dtsch. Phys. Ges. 5, 943 (1982).

[11] D. Schmeisser, J. E. Demuth, and P. Avouris, Chem. Phys. Lett. 87, 324 (1982).

[12] J. E. Demuth and P. N. Sanda, Phys. Rev. Lett. 47, 57 (1981).

[13] A. Otto, J. Electron Spectrosc. Relat. Phenom. (in press).

[14] E. E. Koch, J. Barth, J. H. Fock, A. Goldmann, and A. Otto, Solid State Commun. 42, 897 (1982).

[15] J. Eickmans, A. Goldmann, and A. Otto, Surf. Sci. (in press).

[16] J. Billmann and A. Otto, Solid State Commun. 44, 105 (1982).

[17] T. E. Furtak and S. H. Macomber (unpublished).

[18] T. H. Wood and M. V. Klein, Solid State Commun. 35, 263 (1980).

[19] I. Pockrand and A. Otto, Solid State Commun. 38, 1159 (1981).

[20] P. Rouard and A. Meesen, Prog. Opt. 15, 76 (1977).

[21] C. Pariset and J. P. Chauvineau, Surf. Sci. 78, 478 (1978).

[22] J. P. Chauvineau, Surf. Sci. 93, 471 (1980) (in French).

[23] J. P. Chauvineau and C. Pariset (private communication).

[24] A. Otto, J. Timper, J. Billmann, and I. Pockrand, Phys. Rev. Lett. 45, 46 (1980).

[25] R. M. Lazorenko-Manevich, V. C. Marinyuk, and Ya. M. Kolotyrkin, Dokl. Akad. Nauk SSSR 244, 641 (1979) (translation in Proc. Acad. Sci. USSR, Phys. Chem. Sec.).

[26] H. Wetzel, H. Gerischer, and B. Pettinger, Chem. Phys. Lett. 80, 159 (1981).

[27] K. A. Bunding, R. L. Birke, and J. R. Lombardi, Chem. Phys. 54, 115 (1980).

[28] R. K. Chang, Crit. Rev. Solid State Sci. (in press).

[29] S. H. Macomber and T. E. Furtak, Solid State Commun. 45, 267 (1983).

[30] D. P. DiLella, R. H. Lipson, P. McBreen, and M. Moskovits, J. Vac. Sci. Technol. 18, 453 (1981).

[31] B. Pettinger and U. Wenning, Chem. Phys. Lett. 56, 253 (1978).

[32] B. Pettinger, U. Wenning, and D. M. Kolb, Ber. Bunsenges. Phys. Chem. 82, 1326 (1978).

[33] M. Udagawa, Chih-Cong Chou, J. C. Hemminger, and S. Ushioda, Phys. Rev. B 23, 6843 (1981).

[34] D. C. Jeanmarie and R. P. VanDuyne, J. Electroanal. Chem. 84, 1 (1977).

[35] H. D. Ladouceur, D. E. Tevault, and R. R. Smardzewski, J. Chem. Phys. (in press).

[36] R. Dornhaus, M. B. Long, R. E. Benner, and R. K. Chang, Surf. Sci. 93, 240 (1980).

[37] I. Pockrand and A. Otto, Solid State Commun. 35, 86 (1980).

[38] A. Campion and D. R. Mullins, Chem. Phys. Lett. 94, 576 (1983).

[39] J. C. Tsang, J. R. Kirtley, and T. N. Theis, J. Chem. Phys. 77, 641 (1982).

[40] D. E. Tevault and R. R. Smardzewski, J. Chem. Phys. 11, 222 (1982).