

Surface-Enhanced Raman Scattering from Surface and Subsurface Oxygen Species at Microscopically Well-Defined Ag Surfaces

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Ag(111) and Ag(110) surfaces exposed to oxygen at elevated temperatures (~ 800 K) exhibit strongly enhanced Raman bands at 803 and 627 cm^{-1} which are attributed to O atoms strongly chemisorbed on the surface (O_γ) or held in subsurface sites (O_β), respectively. In contrast to usual experience, surface-enhanced Raman scattering is occurring here under well-defined conditions up to temperatures of 900 K which is attributed to the joint operation of delocalized electromagnetic enhancement (caused by surface roughness provided by oxygen-induced faceting) and local resonance due to the particular electronic properties of the surface sites.

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Surface-enhanced Raman scattering (SERS) offers the possibility of an enormous increase in sensitivity for studying processes at surfaces. Unfortunately this effect is restricted to a few metals and usually requires special preparation of their surfaces into structurally metastable and ill-defined states, so that application under realistic catalytic conditions, e.g., at high temperatures, has been prevented [1-4]. (So far only a few observations of weak SERS effects with flat single crystal surfaces have been reported [5,6], while very smooth Ag surfaces exhibit no noticeable surface enhancement and hence hardly detectable signals [7].) We report here on a system for which, by contrast, SERS is observed with well-defined species at microscopically flat surfaces up to 900 K. In particular it will be demonstrated that even particles located *beneath* the surface may be subject to this effect, which, on the other hand, is strongly influenced by the actual chemical state *on* the surface.

The experiments were performed with Ag(110) and Ag(111) single crystal surfaces interacting with O_2 around 800 K near atmospheric pressures, conditions close to those applied industrially in the partial oxidation of methanol to formaldehyde over silver catalysts [8]. The experimental arrangement for *in situ* Raman spectroscopy including reaction cell, an elliptical mirror for efficient collection of the scattered light, etc., has been de-

scribed elsewhere [9,10]. For a faceted Ag(110) surface, SERS has been observed at all orientations of the $(1\bar{1}0)$ direction relative to the plane of incidence.

Prior to the measurements, the samples were exposed to 0.2 bar O_2 at 930 K for several hours. Such a treatment causes restructuring of the Ag(111) surface into a $(\frac{26}{1}\frac{1}{26})$ phase associated with a fairly high density of steps and with formation of strongly chemisorbed O atoms (γ state) and migration of oxygen to subsurface and bulk locations (in the following we do not distinguish between the latter two and denote them as the β state) [11,12]. The Ag(110) surface undergoes pronounced faceting. As can be seen from Fig. 1 this is fairly regular, mainly in the $[110]$ direction, with the dimensions of the facets being typically in the range of ~ 1 μm . The associated reflection high-energy electron diffraction (RHEED) pattern [Fig. 1(b)] exhibits diagonal stripes, signaling a (111) orientation. Hence it has to be concluded that both single crystal samples undergo restructuring into (111) planes with a well-defined microstructure and with mesoscopic (i.e., on the scale of ≈ 1 μm) roughness.

Because of this identical local nature of the surface sites achieved in the course of the O_2 pretreatment, the Raman spectra from both samples look quite similar.

Figure 2 shows a series of spectra obtained with a new

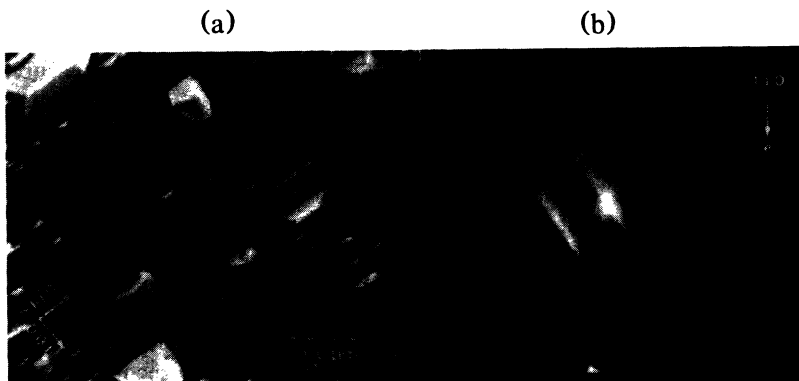


FIG. 1. (a) SEM picture of a faceted Ag(110) surface after pretreatment at 930 K for 6 h using a gas mixture of 0.8 bar $\text{N}_2 + 0.2$ bar O_2 . (b) RHEED picture of a faceted Ag(110) surface, pretreatment as in (a).

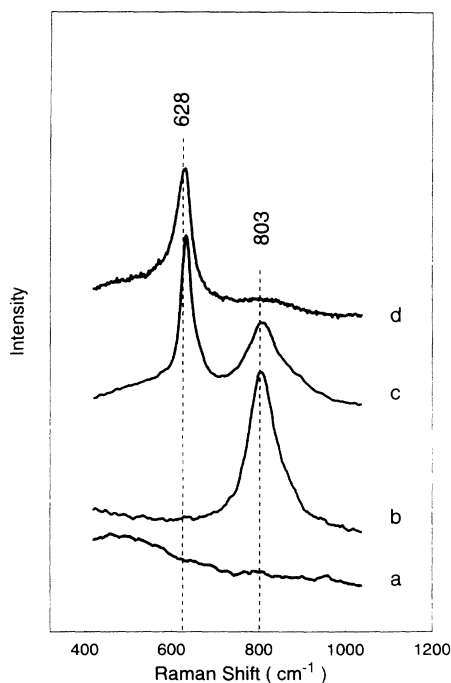


FIG. 2. Raman spectra at Ag(111) surface exposed to 0.8 bar N_2 +0.2 bar O_2 at temperatures (a) 620 K, (b) 780 K, (c) 830 K, and (d) 920 K.

Ag(111) sample in the course of the above mentioned pretreatment. Exposure to 0.2 bar O_2 at 780 K caused a strong band at 803 cm^{-1} (O_γ) to appear. Increasing the temperature to 830 K caused a decrease in intensity for this band and the emergence of another one centered at 628 cm^{-1} (O_β). At 920 K the band at 803 cm^{-1} had nearly vanished and also the 628 cm^{-1} band had lost intensity. The two bands are attributed to species strongly chemisorbed on the surface (O_γ) and held in subsurface sites (O_β), respectively, as verified in more detail elsewhere [11] and below. The high intensity of the Raman bands indicates pronounced enhancement of the scattering; whereas for normal Raman scattering of an adsorbate layer we would expect an intensity around 1 cps or lower, we observe a SERS intensity of 10^3 cps or higher. Hence, we estimate roughly an enhancement factor of the order of 10^3 .

A series of spectra recorded with the Ag(110) sample at constant temperature (680 K) but under varying gas atmosphere is reproduced in Fig. 3. Prolonged exposures to O_2 caused saturation of the O_γ adlayer which accordingly appeared with maximum intensity at 803 cm^{-1} , i.e., at the same frequency as with the Ag(111) sample demonstrating the identical nature of the local adsorption site. At this stage no band at $\sim 630\text{ cm}^{-1}$ was discernible, but nevertheless the β species in subsurface sites was present. This was confirmed by the x-ray photoelectron spectroscopy (XPS) data reproduced in Fig. 4. The O_{1s} spectrum corresponding to the situation of Fig. 3(a) is

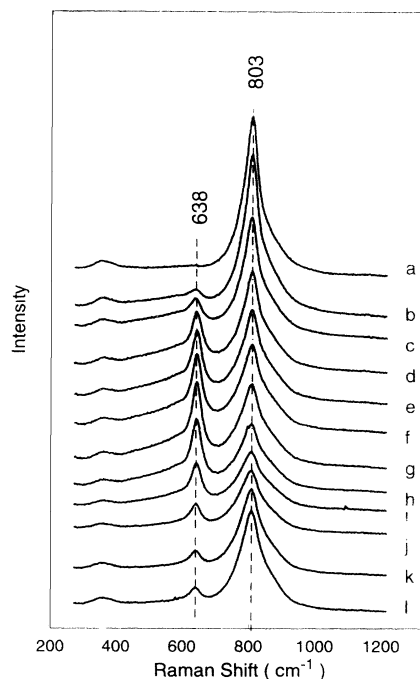


FIG. 3. Raman spectra from a Ag(110) surface prepared as in Fig. 1 and recorded at 680 K. (a) In 0.8 bar N_2 +0.2 bar O_2 after 30 min; (b)-(h) in 1 bar N_2 after 2, 5, 8, 12, 15, 20, and 30 min; (i)-(l) again in 0.8 bar N_2 +0.2 bar O_2 after 1, 2, 5, and 10 min.

composed of two contributions centered at 529.0 and 530.3 eV, corresponding to O_γ and O_β species, respectively [11]. These energies indicate atomic oxygen rather than molecular oxygen present at the surface; hence, our findings contradict a recently reported [13] assignment of the 803 cm^{-1} line to molecular oxygen.

Mild sputtering of the surface removed the adlayer, and as a consequence only the contribution from the subsurface species was left [Fig. 4(b)]. Likewise O_γ species may leave the surface by thermal desorption if the sample is kept at 780 K in an oxygen-free atmosphere, and the XPS data show a similar behavior to that in Fig. 4(b). Progressive thermal desorption is reflected in the Raman spectra of Figs. 3(b)-(h): The intensity of the 803 cm^{-1} band is continuously decreasing, while simultaneously the 630 cm^{-1} band grows up, although the concentration of subsurface O_β (as verified by separate XPS measurements using analogous pretreatments and temperature cycles) remains essentially unchanged. Admission of 0.2 bar O_2 caused a continuous reversal of the spectral features [(i)-(l)].

Electron-energy-loss spectroscopy investigations on oxygen adsorbed on Ag(110) show that molecular oxygen is adsorbed at $T < 150\text{ K}$ exhibiting a vibration around 630 cm^{-1} ; heating up to $T > 150\text{ K}$ molecular oxygen is decomposed to atomic oxygen, giving rise to a vibration around 320 cm^{-1} [14]. These species recombine and

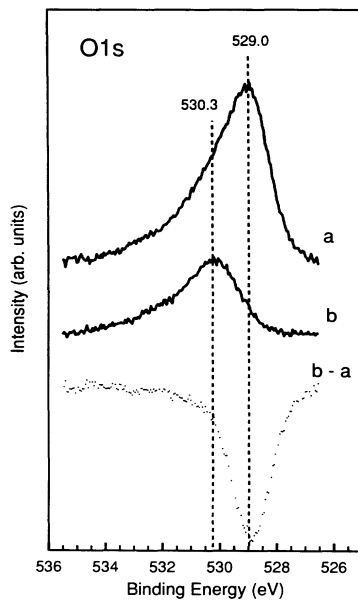


FIG. 4. XPS spectra for Ag(111) showing the O_{1s} peaks. (a) Recorded at 780 K after pretreatment in 0.8 bar $N_2+0.2$ bar O_2 at 780 K and transfer to UHV chamber; (b) XPS recorded at 780 K after mild sputtering with defocused He^+ ion beam. (b) - (a) difference spectrum of the spectra (a) and (b).

desorb at around 600 K. Silver oxide with vibrations around 432 cm^{-1} decomposes around 600 K. Contrary to this we observe, after the pretreatment, which reconstructs the sample, the above denoted O_γ and O_β species in a wide temperature range from 300 K up to 900 K, with the desorption temperature for O_γ around 900 K. Raman and XPS experiments reveal the same dependence on pretreatment, temperature, and sputtering and the same chemical reactivity for the oxygen species observed, despite the different conditions, confirming that identical species are being observed in both techniques.

These data demonstrate clearly that (i) SERS is not restricted to particles chemisorbed on a surface, but may be operating also with species located below the topmost layer of metal atoms, and (ii) the magnitude of the enhancement in the latter case is sensitive to the actual state of the surface. Obviously the presence of O_γ "shields" the O_β particles beneath.

The frequencies of the two bands decrease with increasing temperature as reproduced in Fig. 5. However, the slopes are different: $\partial\nu_\beta/\partial T = -0.0293\text{ cm}^{-1}\text{ K}^{-1}$ for O_β , and $\partial\nu_\gamma/\partial T = -0.0132\text{ cm}^{-1}\text{ K}^{-1}$ for O_γ . This effect is attributed to a mode anharmonicity, e.g., to a variation of the shapes of the potentials for the vibrating O atoms associated with thermal expansion [such temperature dependences of essentially the same order of magnitude are frequently reported for minerals or metal oxides (see Refs. in [15])]. Obviously this effect is more pro-

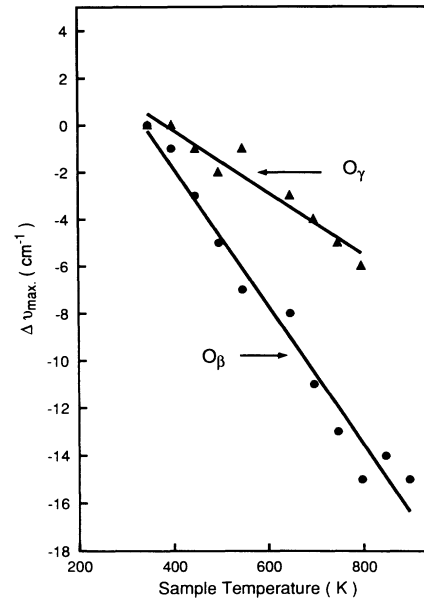


FIG. 5. Raman frequency of $Ag-O_\gamma$ and $Ag-O_\beta$ vs sample temperature, after preparation as in Fig. 1.

nounced for the subsurface O_β species interacting with a larger number of neighboring metal atoms. Finally, the sign of the $\partial\nu_\gamma/\partial T$ term indicates that O_γ is an atomic species (if it were a molecular unit, higher temperatures would lead to a decrease of the strength of $Ag-O_2$ bonding thereby increasing the intramolecular bonding).

There is now general agreement that there exist two requirements for the occurrence of the SERS effect: (a) the "electromagnetic" (EM) enhancement associated with the creation for strong electromagnetic fields through excitation of surface plasmons, and (b) the so-called "chemical" or "charge transfer" (CT) enhancement involving adatoms. The Raman scattering cross section is then enhanced by a factor F_{SERS} given by the product from both contributions, $F_{SERS} = F_{EM} \times F_{CT}$ [2-4]. The present results demonstrate the operation of both effects:

(a) The *delocalized* EM enhancement requires coupling of the incident field to the field of surface plasmons via surface roughness on a length scale comparable to the wavelength of the light; in the present case this "roughness" is provided by the adsorbate-induced faceting of the Ag(110) surfaces; and in the case of Ag(111) or non-faceted Ag(110) the presence of a slight roughness in the form of terraces cannot be ruled out. Additionally, possible EM contributions to SERS will be different for species in the adsorbate (O_γ), subsurface (O_β), or deep-in-metal location (O_β), because of the varying dielectric function across the interface [$\epsilon \rightarrow \epsilon(z)$].

(b) The *localized* CT enhancement is frequently attributed to special "SERS active sites" which are identified as special adsorption sites, cavities, or other ill-defined defect sites. These are usually metastable and are annealed

at elevated temperatures, quite in contrast to the conditions in the present study. In general terms, the CT enhancement has to be considered as a resonance Raman effect associated with the *local* (i.e., atomic) electronic structure, whose origin may be charge-transfer, electronic resonance of the adsorbate alone, or the particular electronic properties of the adlayer [3]. Obviously, the presence of the O_γ species alters the SERS effect for the O_β species. That means the electronic levels of that part of the Ag- O_β structure which is close to the surface are sensitive to the presence of neighboring O_γ species. The latter tune the SERS for O_β out of resonance, and hence the intensity of the respective band is strongly suppressed even without noticeable change of the concentration. Analogous effects have been reported repeatedly for "normal" SERS occurring at metastable sites at low temperatures and are referred to as "quenching of SERS" by dosing a SERS active sample with oxygen (see Refs. in [4]).

In conclusion, the present work demonstrates that SERS may occur at crystalline surfaces with well-defined adsorption sites and at temperatures up to 900 K. The above findings indicate in addition that SERS is not restricted to particles adsorbed *on* the surface (O_γ), but is operating also with species directly *below* the topmost atomic layer of the surface (O_β). Evidence is also provided for an electronic interaction between the O_γ and O_β state.

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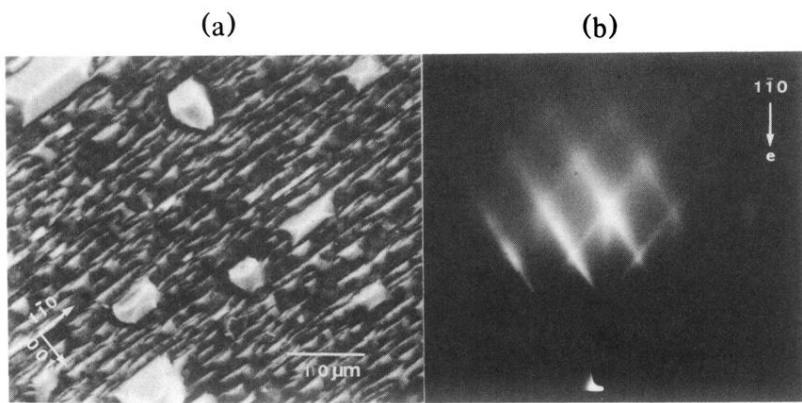


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