THE BACKGROUND SIGNALS IN RAMAN SPECTRA OF SILVER-ELECTRODE SURFACES

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The anomalously intense background in the Raman spectra of silver-electrode surfaces is due to silver adatoms. The potential dependence of background intensity coincides with that of the lines of adsorbate Raman spectra (of pyridine or the Cl^- ions). At frequencies of $|\Delta\nu| > 200$ cm^{-1}, the background is due to electronic Raman effect, but at frequencies of $|\Delta\nu| < 200$ cm^{-1} it is due to Rayleigh scattering of the light by adatom–adsorbate complexes. In both cases the background is amplified owing to resonance between the exciting light and an adatom–metal electronic transition.

The anomalously intense Raman spectra of molecules adsorbed on silver are attended by a strong background not arising from parasitic light scattering [1-3]. It has been noticed [1] that the background intensity is similar to the intensity of anomalously intense adsorbate Raman spectra. The background spectrum does not display any substantial dependence on scattered-light frequency and extends into the Stokes region far beyond 3000 cm^{-1} from the exciting line [2]. Appreciable background is seen both at copper and at gold, where adsorbate molecules – as in the case of silver – produce anomalously intense Raman effects [3]. On the other hand, at surfaces of iron, platinum, and nickel where we were unable to detect an anomalously intense Raman effect in pyridine adsorption, the background is very insignificant and hard to distinguish from the background due to parasitic light scattering. One can assume, therefore, that the presence of strong background is one of the aspects of an anomalously intense Raman effect. The latter chiefly arises as resonance Raman effect (RRE) of adsorbate molecules forming complexes with metal adatoms; here the actual electronic transition occurs in the adatom–metal system [3-6]. It is of interest for an understanding of the mechanism of anomalously intense Raman effects to compare the intensities of the background and adsorbate Raman spectrum during a cyclic scan of electrode potential, E, as used in [3]. This has been done in the present work with a view to detecting a possible link between background intensity and the presence of metal adatoms [2].

The Raman spectra were observed with the apparatus described in [7], where a DFS-12 monochromator was used instead of the two MDR-2 monochromators. Solution and electrode preparation has been described in [3]. The values of E are stated relative to a saturated silver–silver chloride electrode. The wavelength, λ_e, of the exciting light was 632.8 nm in all experiments.

We studied the intensities of background and exciting light scattered by the electrode as functions of E in order to distinguish the background due to frequency-shifted scattering from that of parasitic scattering. In the latter case the monochromator was adjusted to λ_e, and a light filter was placed in front of the entrance slit of the monochromator in order not to put the photomultiplier out of commission by overly intense light. The measurements were made during cyclic potential variation in such a way that after a scan, approximately ten monolayers of AgCl had been formed and reduced close to the equilibrium potential, $E^0_{Ag/AgCl}$, of Ag/AgCl (in the following we shall call this operation anodization, as in [3]). One can see from Figs. 1a and 2a that the intensity of exciting light scattered by the electrode is lowered when the AgCl film appears. One can assume, therefore, that the curves of Figs. 1b and 2b which are completely different in shape from those of Figs. 1a and 2a describe the behavior of the Raman signal background. We note that the potential dependence of background intensity at all other wavelengths of the scattered light is fully identical with that shown in Figs. 1 and 2.

Let us now separately examine the results of Figs. 1 and 2. In the presence of pyridine, the background intensity depends on E during electrode anodization exactly like the adsorbate's Raman intensity. The behav-

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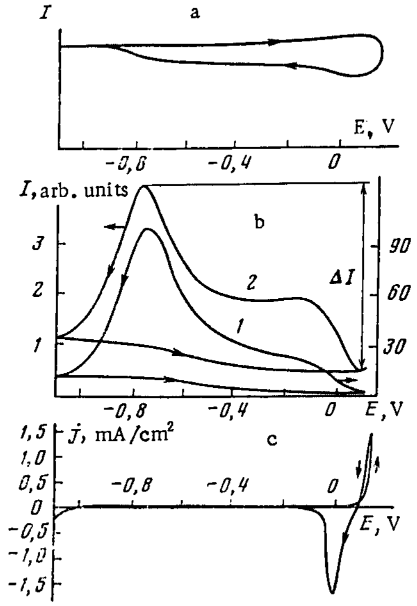

Fig. 1

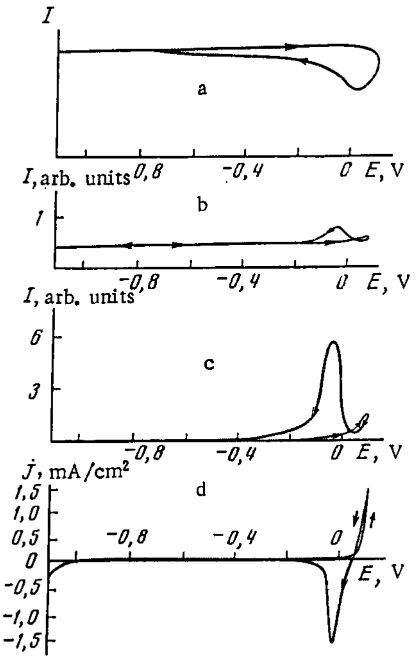

Fig. 2

Fig. 1. a) Potential dependence of the intensity of exciting light scattered by the electrode in 0.1 N KCl + 0.05 M C_5H_5N for a linear potential scan rate of dE/dt = 25 mV/sec; b) the same for the line at $\Delta\nu$ = 1005 cm^{-1} in the Raman spectrum of adsorbed pyridine (1) and for the background close to this line (2); c) a current–potential curve recorded under the conditions of Fig. 1a.

Fig. 2. a) Potential dependence of the intensity of exciting light scattered by the electrode in 0.1 N KCl solution for dE/dt = 25 mV/sec; b) the same for the background at $\Delta\nu$ = 1005 cm^{-1}; c) the same for the Raman line at $\Delta\nu$ = 236 cm^{-1}; d) a current–potential curve recorded under the conditions of Fig. 2a.

ior of the latter is due to the potential variation of the number of adatom–adsorbate complexes where the RRE of adsorbed pyridine takes place [3]. One obviously can conclude when comparing the shape of the curves of Fig. 1b that the background also is linked to the existence of adatoms.

Considering this result one evidently must examine the behavior of the background in the absence of pyridine. We notice that a line with a frequency, $\Delta\nu$, of about 236 cm^{-1} having anomalously high intensity, like the Raman lines of adsorbed pyridine, is seen, in the Raman spectrum during silver anodization in chloride solution, both in the presence of pyridine [8] and in its absence [9]. According to [8], it is related to metal–pyridine bond vibrations. But it is more correct to attribute it to vibrations of the Ag–Cl bond, as done in [9]. In accordance with [9], we observed this line only during anodization in chloride solutions, but not in bromide or iodide solutions, regardless of the presence of pyridine. Moreover, its frequency is close to that of the line at 240 cm^{-1} seen in the Raman spectrum of crystalline AgCl [10]. One can see from Fig. 2 that the potential dependence of the background in the absence of pyridine coincides with that of the Raman line at $\Delta\nu$ = 236 cm^{-1}. On the assumption that the mechanism of the anomalously intense Raman effect [3, 4] holds for this line, one can conclude at once that the background in Fig. 2b also is caused by metal adatoms. The potential dependence of the line intensity at $\Delta\nu$ = 236 cm^{-1} is an argument for said assumption. One can see from Figs. 2c and d that it goes through a minimum when the thickness of the AgCl film is at a maximum. It follows that the line at 236 cm^{-1} is unrelated to the AgCl phase film. But the intensity maximum of this line is attained approximately at the maximum of current consumed for the formation of reduction of AgCl. It follows that the line at 236 cm^{-1} is to be attributed to the vibration of some intermediate produced during the reaction $Ag + Cl^- \rightleftarrows AgCl + e$. Allowing for the anomalous Raman line intensity of this intermediate Ag–Cl

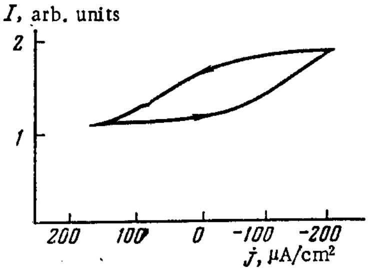

Fig. 3

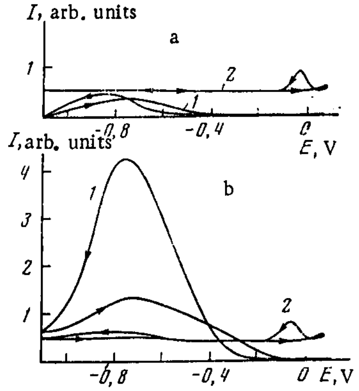

Fig. 4

Fig. 3. Background intensity at $\Delta\nu = 1005\ \text{cm}^{-1}$ as a function of current density j in 0.1 N $AgNO_3$ + 1 N $HClO_4$ solution for dj/dt = 8 μA/sec.

Fig. 4. Potential dependence of the line intensity of adsorbed pyridine at $\Delta\nu = 1005\ \text{cm}^{-1}$ (1) and of the background intensity close to this line (2) in 0.1 N KCl containing $5\cdot10^{-4}$ M (a) or $5\cdot10^{-3}$ M (b) C_5H_5N for dE/dt = 25 mV/sec.

compound one can conclude that it must be the complex of an adsorbed chloride ion with a silver adatom.

It remains an open question whether the background only arises from adatoms forming complexes with adsorbed species (pyridine or Cl^- ions), or whether the adatoms themselves can give rise to background. To elucidate this problem we studied background intensity as a function of current during silver electrodeposition in the absence of adsorbed components. One can see from Fig. 3 that the background is high even under these conditions. The increase in background under cathodic current close to the equilibrium potential of the Ag/Ag^+ electrode, E_{Ag}, and its decrease under anodic current are in harmony with the characteristic concentration changes of silver adatoms close to E_{Ag} [11]. One can conclude, therefore, that the background is due to metal adatoms and its intensity is determined only by the concentration of adatoms, regardless of their interaction with adsorbate molecules.

This result helps to explain certain special features of the curves in Figs. 1 and 2. Thus, the background in Fig. 2 after anodization of the electrode is rather significant at $E < E^0_{Ag/AgCl}$, whereas the line intensity at 236 cm^{-1} is extremely low at these potentials (the intensities of background and Raman signal are reported in arbitrary units in all figures). It is obvious that a marked amount of adatoms not forming complexes with adsorbed Cl^- exists at these potentials. The background recorded in the presence of pyridine is several times stronger than that recorded without pyridine (compare Figs. 1b and 2b), which appears to be due to the significant increase in the number of adatoms stabilized by complex formation with pyridine upon reduction of the AgCl layer. Under these conditions the curves of Fig. 1b evidently ought to be practically completely identical in shape. We also tried to find the effect of pyridine on the number of silver adatoms produced upon anodization, and to this end studied the effect of pyridine concentration in the solution on the potential dependence of background intensity and of the Raman intensity of adsorbed pyridine (Fig. 4). At low pyridine concentrations, the background depends on E as it does in the absence of pyridine (Figs. 2b and 4a). It is important to note that the background remains practically constant at $E < E^0_{Ag/AgCl}$, i.e., in the main, stable silver adatoms the concentration of which is almost independent of E and pyridine adsorption exist on the surface under these conditions (curve 2 of Fig. 4a). The background increases with increasing pyridine concentration (curves 2 in Figs. 4b and 1), which is an indication for rising adatom concentration, but the Raman signal of pyridine also increases, which is evidence for a rising number of adatom–pyridine complexes. Under these conditions the curves 1 and 2 of Fig. 4 come closer in shape and tend toward the shape of curves 1 and 2 of Fig. 1; it follows that at high pyridine concentrations, almost all silver adatoms exist in the form of complexes with pyridine.

The number of adatoms when increasing as a result of pyridine adsorption also influences their interaction with adsorbed Cl^-. One can see from Fig. 5 that the line intensity at 236 cm^{-1} which is related to the adatom–Cl^- bond becomes somewhat higher in the presence of pyridine (compare Figs. 5 and 2c). Moreover,

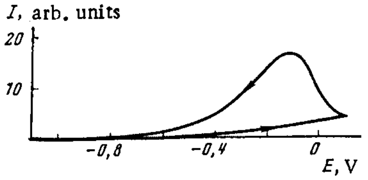

Fig. 5

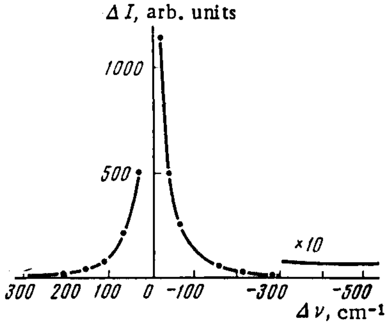

Fig. 6

Fig. 5. Potential dependence of the line intensity at $\Delta\nu = 236$ cm^{-1} in the presence of pyridine, under the conditions of Fig. 1.

Fig. 6. Spectrum of the maximum background intensity increment, ΔI (see Fig. 1).

this line has conspicuous intensity even at $E < E^0_{Ag/AgCl}$. This increase can be interpreted as resulting from stabilization of a larger number of adatoms owing to pyridine adsorption.

Concerning the nature of the background discussed here, it has been suggested in [2] that it arises by light scattering at the metal's conduction electrons. It was found in [12] when using picosecond laser pulses, on the other hand, that at least part of the background is emitted with a delay of up to 10^{-11} sec, i.e., this part evidently is due to fluorescence. To elucidate the origin of the background observed here we studied its spectra in the Stokes and anti-Stokes region (Fig. 6). The curves reported in this figure represent spectra of the maximum increments, ΔI, of background intensity upon anodization recorded at the corresponding values of E (Fig. 1b). Under these conditions one can distinguish the background due to frequency-shifted scattering, even against the very appreciable background due to the scattering of exciting light; it had been pointed out above that the latter has a substantially different potential dependence of intensity (Fig. 1a). One can see that in the Stokes region at $|\Delta\nu| > 200$ cm^{-1}, the background does not display any important dependence on $|\Delta\nu| > 200$ cm^{-1}, which corresponds to the data obtained in [2]. In the anti-Stokes region at $\Delta\nu$, the background is much lower and can only be observed in the presence of pyridine, when it is particularly high in the Stokes region. It was found that the intensity ratio of the background at $|\Delta\nu| > 200$ cm^{-1} in the Stokes and anti-Stokes region coincides with that of the Stokes and anti-Stokes Raman line of adsorbed pyridine in the same range of $\Delta\nu$, which according to [5, 6] is characteristic for RRE. It follows that the background in Figs. 1b and 2b also is due to RRE. It follows from this coincidence, moreover, that the electronic transition responsible for RRE is the same in both cases. This evidently is a transition in the adatom–metal system [3-6]. It also follows from the results reported that the background caused by fluorescence [12] under our conditions apparently is much lower than that seen in Figs. 1b and 2b.

The ideas of [2] concerning an involvement of adatoms in the generation of the electronic Raman effect giving rise to the background have been developed further in [13]. It is suggested that during the interaction of conduction electrons with adatoms, optical intraband transitions become allowed, since the requirement of momentum conservation during such transitions is removed. This can result in resonance between the incident light and one of the intraband transitions and should lead to high intensity of the electronic Raman spectrum. In [13] this mechanism is used as well to explain the RRE of adsorbate molecules interacting with adatoms. According to this mechanism, strict resonance should occur at any frequency of the exciting light. However, the entire set of data [5, 6, 14] shows that actually, resonance occurs on silver only with one electronic transition which, according to [5, 6], has an energy of about 1.9 eV and a half-width of 0.2 eV. These data can be explained much more readily when an electronic transition from the adatoms to the metal is suggested to exist [3-6]. On the other hand, conduction electrons having energies close to the energy of the upper filled adatom level ought to have the strongest interaction with the adatoms. One can suggest that precisely such electrons provide the chief contribution to the intraband transitions discussed in [2, 13]. From the viewpoint of the mechanism of [2, 13], then, resonance ought to be strongest at energies close to that of the adatom–metal transition.

At $|\Delta\nu| < 200$ cm^{-1} one sees a strong background rise as one approaches the exciting line (Fig. 6), and the background is approximately symmetric relative to this line. It is logical to attribute this background to tails of the Rayleigh scattering line which can extend to $|\Delta\nu| \approx 150$ cm^{-1} and beyond [15]. In resonance, the intensity of Rayleigh scattering increases to approximately the same extent as the Raman intensity [16] (by six orders of magnitude in the present case); we therefore have been able to observe this scattering against the background of parasitically scattered light up to $|\Delta\nu| = 20$ cm^{-1}. One can suggest that the background at $|\Delta\nu| < 200$ cm^{-1} is due to Rayleigh scattering, both at the adsorbate molecules forming complexes with adatoms, and apparently at the adatoms themselves.

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THE ADMITTANCE OF HETEROGENEOUS METAL–ELECTROLYTE SYSTEMS

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Numerical calculations were performed for the components of admittance (capacitance and conductance) of a distributed structure representing the disordered mixture of particles of an electronic conductor and of a solid electrolyte. The calculations were based on the effective-medium model while allowing for the character of impedance of the metal/solid electrolyte interface and assuming close packing of the particles with a coordination number of $z = 12$. A conduction threshold and corresponding capacitance maximum were shown to exist. High- and low-frequency limits of conductance and a low-frequency limit of capacitance were shown to exist for heterogeneous metal–solid electrolyte systems.

With the advent of solid electrolytes it has become possible to examine heterogeneous systems produced by mixing powders of ionic and electronic conductivity. In particular, different versions of electrochemical cells of the type of

$$\mathrm{Ag,\ Ag_4RbI_5/Ag_4RbI_5/Ag_4RbI_5,\ C}$$

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