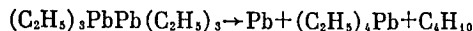


In order to evaluate the preparative possibilities of this method under the most favorable conditions (Table 5, test No. 3) we conducted two parallel tests. After these two operations, the organic layers were subjected to vacuum distillation in order to isolate tetraethyllead. Hexaethyldilead is known to be unstable under fractionating conditions and decomposes according to the equation



into tetraethyllead, butane, and metallic lead. Hence the tetraethyllead yield in the isolated product is higher than that formed in electrolysis. The results obtained for the balance of lead are presented in Table 6.

Thus, 94% of the lead dissolved from the cathode is found as metal-organic compounds in the organic layer. Upon distillation of the organic layer, tetraethyllead is isolated with a yield of 81.7% in terms of lead dissolved, 9.5% of the lead is found as sludge in the distillation flask, and 2% is found as sludge in the catholyte. The data obtained show that under the conditions found, cathodic alkylation is fully suitable for tetraethyllead synthesis for preparative purposes.

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MECHANISM OF ANOMALOUSLY INTENSE RAMAN SCATTERING DURING ADSORPTION ON ELECTRODES

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UDC 541.13:535.375

The intensity rise of resonance Raman scattering (RRS) of pyridine and tetraalkylammonium ions adsorbed on silver, copper, and gold which is found after reduction of a layer of halide salt on silver or during the electrodeposition of silver, copper, or gold is caused by increasing metal adatom concentration. The electronic transition responsible for RRS occurs between a local level of the adatom-adsorbate complex and the metal's Fermi level. In the case of pyridine adsorption, an additional nonresonance signal amplification arises with increasing pyridine concentration in the solution; this is due to partly coherent scattering arising from a correlation of the adsorbate molecule vibrations at coverages close to a monolayer.

The Raman scattering (RS) of pyridine adsorbed on silver which had first been observed in [1] was later found [2-4] to have an anomalously high intensity. Possible reasons offered to explain this effect were: an effect of the double-layer field on RS intensity [2], interaction of the pyridine molecules with surface plasmons [5], modulation of the optical constants of the metal surface layer by the vibrations of the adsorbed molecules [6], capillary condensation of pyridine in a porous layer on the silver [7], and the development of resonance RS

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(RRS) during pyridine adsorption [3, 4, 8]. The most convincing arguments have been obtained in favor of RRS [8, 9], but the origin of the absorption band giving rise to RRS of the adsorbate has remained obscure. Nor could the reason be found for the increase of the RS signal by three orders of magnitude which was observed in [2, 4, 10] when approximately ten monolayers of AgCl were formed and reduced on smooth silver in a single operation not producing any substantial surface development. With the pyridine concentrations used in [2, 4, 10], surface coverage was close to limiting [11], and hence could not increase so strongly during said surface treatment. Therefore, the increase in the RRS signal of pyridine must be attributed to a strong increase occurring during said treatment in the number of adsorption sites responsible for RRS. In the present work we make an attempt to elucidate the nature of these sites and to establish the origin of the electron transition which is relevant for adsorbate RRS. In addition to pyridine we also studied tetraalkylammonium ions and varied the nature of the metal, since anomalously intense RS is observed for a number of other systems as well [2, 6, 12-14].

The RS spectra of the adsorbed molecules were obtained with the instrument described in [3], at a wavelength of the exciting light, λ_x , of 632.8 nm. The solutions were prepared from recrystallized salts and twice distilled water. The iodides of tetramethylammonium (TMA^+) and tetraethylammonium (TEA^+) were recrystallized twice. The nitrates of TMA^+ and TEA^+ were obtained by treating TMAI and TEAI with silver nitrate and then electrodepositing excess silver. The tetrabutylammonium (TBA^+) salts were prepared from TBAOH and the corresponding acids. Where required they also were treated with AgNO_3 in order to remove traces of halide ions. Pyridine, of "pure" grade, was purified by distillation. The silver nitrate, copper sulfate, and gold chloride used for electrodeposition were of "analytically pure" grade, and were not additionally purified. The electrodes were mechanically polished, degreased by boiling in 2 N NaOH, and washed with hot twice-distilled water, whereupon they were cathodically polarized in 0.1 N H_2SO_4 for an hour with a current of 50 mA/cm². The potentials, ϕ , are stated relative to the saturated silver-silver chloride electrode. The potentiodynamic curves were recorded with a sweep rate, $d\phi/dt$, of 25 mV/sec in all experiments except those particularly mentioned. The spectral width of the slit was 10 cm⁻¹ and was increased to 20 cm⁻¹ when necessary, which was more than the small frequency shift of the lines examined which occurred as a function of ϕ .

Consider the ϕ -dependence of RS intensity seen for pyridine (Fig. 1) and tetraalkylammonium ions (Fig. 2) on silver under cyclic potentiodynamic conditions securing the formation and reduction of 10 to 20 monolayers of silver halide in each cycle (for the sake of brevity, this operation will be referred to as anodization). Anodization raises the maximum RS signal of adsorbed pyridine by two to three orders of magnitude (see curves 1 and 2 in Fig. 1, a, b, and c). For the tetraalkylammonium ions, the signals on smooth silver are so low that they cannot be recorded. However, considering that the RS signal of the adsorbed cations observed after anodization (Fig. 2) exceeds the noise level by about two orders of magnitude, one can assume that in this case, too, the RS signal of the adsorbate is increasing by at least two orders of magnitude during anodization. The RS signal of pyridine (curves 2 in Fig. 1) and that of the tetraalkylammonium ions (curves 1 and 2 in Fig. 2a and curve 1 in Fig. 2b) obtained on the anodized electrodes decrease irreversibly when the electrodes are kept at sufficiently negative ϕ and are not recovered during the anodic ϕ -sweep. Repeated anodization is required to restore the RS signal to its old size. This indicates that most of the adsorption sites which are produced by anodization and give rise to RRS are unstable at sufficiently negative ϕ . This instability is particularly pronounced at ϕ -values more negative than the maximum in curves 2 of Fig. 1, where the RS signal decreases with time by almost two orders of magnitude even at constant ϕ . But at ϕ -values more positive than the maximum the signal is highly stable. One could think that the sites being discussed are specifically adsorbed anions, since the ϕ -value of the maximum in the cathodic branches of curves 2 in Fig. 1, a, b, and c is shifting in the negative direction as one goes from Cl^- to I^- . However, halide-ion adsorption which undoubtedly occurs during the anodic ϕ -sweep on anodized surfaces does not produce higher RRS (i.e., more adsorption sites). Thus, although halide-ion adsorption appears to be important for stabilization of the adsorption sites produced upon anodization, the anions themselves are not the sites responsible for RRS. The adsorption of Br^- and I^- on non-anodized electrodes in fact produces a marked decrease in the RS signal of pyridine on silver at ϕ more positive than the pzc (curves 1 in Fig. 1, b, and c). This appears to be due to competition between pyridine and the halide ions. Residual silver halide also cannot constitute the sites responsible for RRS, since the RS signals at ϕ corresponding to the existence of silver halide are very low (Fig. 1). One must suggest, therefore, that the reinforcement of RRS is due to unstable metal surface defects produced during anodization in particularly large amounts.

Order-of-magnitude changes in the concentration of surface defects in the region of ϕ more negative than the maximum of curves 2 in Fig. 1 where phase changes do not occur on the silver surface are possible only when these defects are point defects, i.e., vacancies, kinks, and adatoms [15]. Reactions are possible between

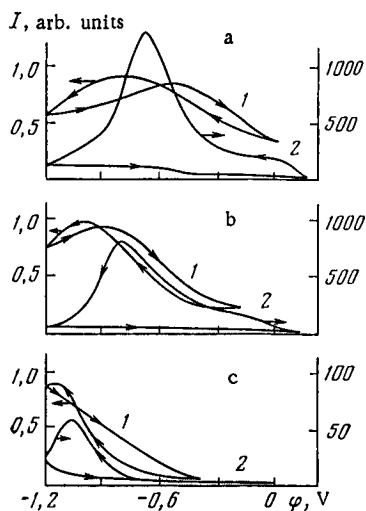


Fig. 1

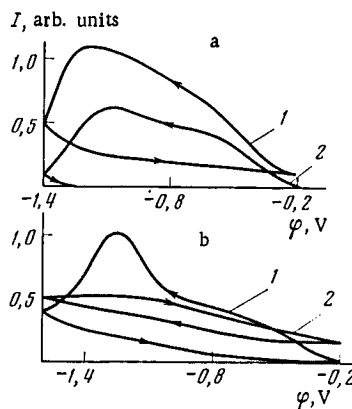


Fig. 2

Fig. 1. The ϕ -dependence of intensity of the line at 1005 cm^{-1} of pyridine adsorbed on silver in $0.1\text{ N NaClO}_4 + 0.05\text{ M C}_5\text{H}_5\text{N}$ containing 0.01 N NaCl (a), KBr (b), or NaI (c): 1) without anodization, and 2) with anodization. The intensities on the ordinate axes to the left and right are stated in identical units in each of the plots of Figs. 1 and 3.

Fig. 2. The ϕ -dependence of RS intensity of tetraalkylammonium ions adsorbed on silver: a1) TEA^+ (the line of 2912 cm^{-1}) in 0.1 N TEAI ; a2) TMA^+ (the line of 2920 cm^{-1}) in 0.1 N TMAI ; b) TBA^+ (the line of 2875 cm^{-1}) in $0.1\text{ N Na}_2\text{SO}_4 + 3 \cdot 10^{-3}\text{ N TBANO}_3$ with the addition of 10^{-3} N NaI (1) or AgNO_3 (2).

these defects which are responsible for the instability of adatoms and vacancies: $\text{kink} + \text{adatom} \rightleftharpoons \text{kink}$ or $\text{vacancy} + \text{adatom} \rightleftharpoons \text{plane}$. The condition under which these reactions will occur is surface diffusion of adatoms, which can be strongly hindered by the adsorption of foreign matter [15]. In our case the adsorption of halide ions can function in this way; it interferes with adatom diffusion and in this way stabilizes all point defects of the surface. In fact, a shift of ϕ in the negative direction occurring in the region of ϕ of about -0.7 to -0.8 V , for example, will lead to lower Cl^- ion adsorption [16], and in the same region of ϕ one finds the maximum of curve 2 in Fig. 1a. The same coincidence is found in the cases of Br^- and I^- . This means that partial halide ion desorption leads to a higher rate of surface diffusion of the adatoms, and thus to a lower number of surface defects responsible for RRS. These defects cannot be the kinks, since they are rather stable. One can conclude, therefore, that adatoms or vacancies give rise to RRS of the adsorbate. On the mere basis of defect instability one cannot, it seems, choose between adatoms and vacancies, since they are equally unstable. It will be shown below that spectroscopic data can be used to decide in favor of the adatoms.

The simplest way of adatom formation is by metal electrodeposition. We tried to influence the RS of pyridine and tetraalkylammonium ions by the electrodeposition of silver, copper, and gold onto smooth surfaces of these metals. Electrodeposition increases the RS signal of adsorbed pyridine by almost two orders of magnitude relative to the corresponding smooth metal (Fig. 3). The RS intensity of TBA^+ obtained during silver electrodeposition (curve 2 of Fig. 2b) has approximately the same value as that obtained on anodized silver; this implies that electrodeposition, too, raises the RS of TBA^+ by two orders of magnitude relative to the RS on smooth metal. It is important to note that during electrodeposition one does not find the irreversible RS decrease of the adsorbate at sufficiently negative ϕ which is seen after anodization. It is obvious that some constant concentration of adatoms is preserved at all ϕ during electrodeposition under conditions of the limiting current for the cations in solution, and the shape of curves 2 in Fig. 3 is chiefly determined by the effect of ϕ on the concentration of adsorbed pyridine (a direct effect of ϕ on the RS intensity of adsorbed molecules is also possible when their orientation relative to the surface changes [9]). The disappearance of the RS signal of pyridine on gold which occurs quite reversibly at negative ϕ (Fig. 3c) most likely is to be explained exactly by pyridine desorption occurring at these ϕ . In fact, the potential at which the RS signal of pyridine on gold is

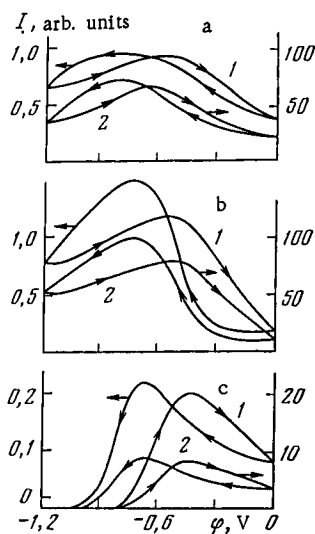


Fig. 3

Fig. 3. Effect of metal electrodeposition on the intensity of the line around 1005 cm^{-1} for pyridine adsorbed on Ag (a), Cu (b), and Au (c): 1) $0.1\text{ N Na}_2\text{SO}_4 + 0.05\text{ M C}_5\text{H}_5\text{N}$; 2) the same, with the addition of 10^{-3} N AgNO_3 (a), 10^{-3} M CuSO_4 (b), or $10^{-3}\text{ N HAU-Cl}_4$ (c).

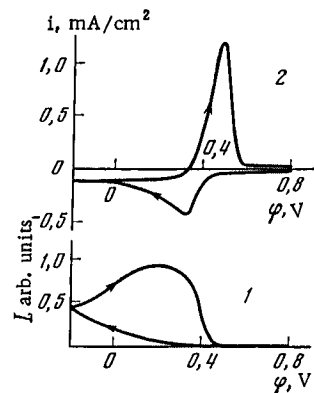


Fig. 4

Fig. 4. The effect of silver electrodeposition on gold on the intensity of the line of 2875 cm^{-1} for TBA^+ in $0.5\text{ N H}_2\text{SO}_4 + 3 \cdot 10^{-3}\text{ N TBAOH} + 10^{-3}\text{ N AgNO}_3$ (1) and the voltammogram (2); $d\phi/dt = 10\text{ mV/sec}$.

falling off is close to the potential of the cathodic desorption peak on the differential capacity curves of gold recorded in the presence of pyridine [17].

The existence of RRS for adsorbates on smooth electrodes (curves 1 in Figs. 1 and 3) presupposes sufficient stability of at least a small number of adatoms under these conditions. Such highly stable adatoms can exist; the activation energy of surface diffusion which can lead to their disappearance is between 0.07 and 0.82 eV for platinum adatoms on different faces of platinum, for example [18]. The concentration of these stable adatoms ought to depend little on ϕ . In fact, the RS of pyridine on smooth electrodes depends on ϕ in the same way as it does during electrodeposition (curves 1 and 2 of Fig. 3).

The shape of the potentiodynamic curves obtained under the conditions of anodization (Figs. 1 and 2) is mainly determined, in addition to above factors, by the dependence of the adatom concentration on ϕ . These curves can be interpreted approximately as follows. Reduction of the silver-halide layer during the cathodic sweep leaves an amount of silver atoms (adatoms) on the surface which is an order of magnitude larger than that on a smooth electrode; these adatoms are not incorporated into the lattice but are stabilized by adsorbed halide. Gradual weakening of the bond between the halide ions and the metal during the cathodic ϕ -sweep at first gives rise to conditions favorable for an interaction of pyridine with the adatoms, and the RS signal increases (curves 2 of Fig. 1). Surface diffusion of the adatoms is facilitated when the anions begin to desorb, which leads to a lower adatom concentration, and the RS signal decreases. It is very likely, too, that pyridine itself can stabilize the adatoms by preventing their diffusion to growth sites. Adatoms vanish at the end of the cathodic sweep and in the early part of the anodic sweep, and RS then remains very weak until anodization is repeated.

The behavior of the RRS of TMA^+ ions (Fig. 2) on anodized electrodes is basically the same as that of neutral pyridine molecules. This means that the variation of the amount of adatoms with ϕ is of chief importance in both cases. However, certain differences exist as well. The negative shift of the maximum in the curves of Fig. 2 which is found as one goes from TMA^+ to TBA^+ is caused, most probably, by enhanced I^- adsorption which occurs in the presence of specifically adsorbed cations, similar to the case of mercury [19]. But I^- adsorption in turn stabilizes the silver adatoms. However, this is not the only function of the anions.

Thus, during silver electrodeposition from nitrate solutions, an RS spectrum of TMA^+ could not be detected. This can only be observed after anodization in the presence of I^- , but not after anodization in the presence of Cl^- or Br^- . But the spectrum for TEA^+ was observed after anodization, both in the presence of I^- and Br^- ; it cannot be observed after anodization in the presence of Cl^- . Thus, the RRS is less sensitive to the anion the higher the cation's adsorbability. These observations can be understood when remembering the adsorption increase of organic cations in the presence of certain anions known for mercury [20]. These anions can be arranged in the sequence of $\text{ClO}_4^- > \text{I}^- > \text{Br}^- > \text{NO}_3^- > \text{Cl}^-$, according to their effect on cation adsorption; this sequence differs markedly from that of their adsorbabilities on mercury. The same series holds for the effect of the anions on the RRS of cations. Thus, the importance of anions for the RRS of organic cations is not merely that of stabilizing the adatoms after anodization, but also that of raising the adsorption of the cations. It is interesting to note that ClO_4^- has the largest effect, according to [20]. In harmony with this observation, RS of adsorbed pyridinium cations could only be detected by us in 1 N HClO_4 during silver electrodeposition. The RS of TMA^+ cannot be observed at all under these conditions, apparently because the "anion effect" is weak in this case [20] and electrodeposition produces a smaller amount of adatoms than anodization.

Direct evidence for the importance of the adatoms themselves in the development of RRS of adsorbates would be obtained when RS is found in the region of underpotential deposition of silver on another metal [21], where the adatoms are the only possible form of existence of silver. In this case an adsorbate must be used which does not display RRS on the substrate metal. The system of TBA^+ on gold was chosen in this capacity. One can see from Fig. 4 that TBA^+ do not show RS on gold in the region of underpotential deposition of silver (the possible reasons for this will be discussed below); RS only appears when about five monolayers of silver have been deposited onto the gold. An argument in favor of the decisive role of silver adatoms on the deposited silver layer is the signal drop which is seen during the anodic sweep and which occurs simultaneously with the drop in the cathodic current as one goes from the diffusion mode to the region of true kinetics (Fig. 4); at this point the adatom concentration must decrease. We note that the base signal also increases significantly during silver deposition, and this background signal is not due to parasitic scattering in the monochromator; possibly this is the basic RS signal of the adsorbate. The intensity of the RS line in Fig. 4 was obtained by subtracting the background signal close to the line from the line-plus-background signal.

The similarities found for the behavior of the RS of pyridine and organic cations adsorbed on silver during anodization and electrodeposition as well as during changes in λ_x [13] give rise to the suggestion that RRS in both cases is produced by the same electron transition. The RS intensity of pyridine on copper and gold is increasing with λ_x just as it does on silver [9]. It follows that on all three metals the energy of this transition is given by $\hbar\nu_e < 1.96 \text{ eV}$ ($\lambda_e > 632.8 \text{ nm}$). It is important to note in this connection that thin, nonannealed films of these metals have absorption bands around 1.5 eV [22-24] which arise upon excitation of an electron from the local level of a point defect to the metal's Fermi level [25]. It is precisely the adatoms on the surface which have local levels of this sort which are sufficiently close to the Fermi level [26]: the highest occupied level of the adatom is between the metal's Fermi level and the highest occupied level of the free atom, which in the case of silver is between 4.5-4.7 eV (the work function) and 7.57 eV (the ionization potential of the free silver atom). Thus, the local level of the adatom should be 1.5 to 2.0 eV below the metal's Fermi level. Transition of electrons from this adatom level to the Fermi level actually seems to be responsible for the RRS of adsorbates in the red region. During RRS the vibrations of the molecules must strongly modulate the energy and probability of this electron transition, and this is possible when the adsorbed species forms a complex with the metal adatom.

The lack of RRS in the region of underpotential deposition (at $\varphi > 0.5 \text{ V}$) of silver on gold (Fig. 4) that had been mentioned above can be explained, under this aspect, by observing that the work function of gold, which is high relative to that of silver, is reducing the transition energy from the silver adatoms to gold, so that the RRS intensity at $\lambda_x = 632.8 \text{ nm}$ is falling off strongly.

It is interesting to note that in the electroreflectance (ER) spectra of silver one also sees a rather weak absorption band at energies of about 1.6 eV which has a half-width, Γ , of 0.1 to 0.2 eV (Fig. 5). It is observed under normal incidence, provided the modulation amplitude is high so that AgCl is formed during the anodic half period, and Cl^- ions are desorbed during the cathodic half period. The reproducibility of the observations is about 50% here. It is characteristic that this band only appears in the spectrum of the ER component that is 90° phase-shifted relative to the oscillations of φ . This is an argument, (i) for its surface rather than bulk origin, and (ii) for marked inertia of the processes yielding and eliminating silver adatoms. A similar band had also been observed in [8], but under somewhat different conditions. It had not been demonstrated up to now that it is precisely this band, and only it, which is related to RRS of the adsorbate. However, its connection with surface imperfection cannot be doubted.

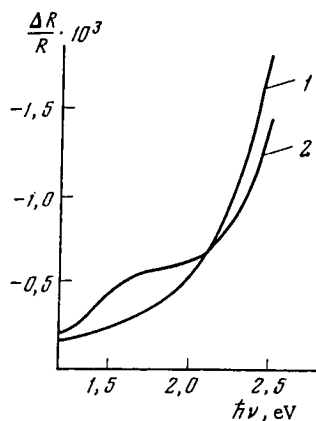


Fig. 5

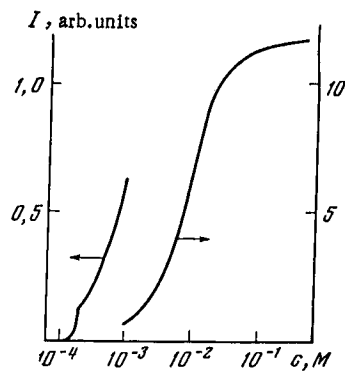


Fig. 6

Fig. 5. The ER spectrum of silver in 0.1 N KCl at $\varphi = -0.3$ V, 1) in phase with the oscillations of φ , and 2) shifted by 90° . The modulation frequency: 21 Hz, the amplitude: 0.4 V (eff.).

Fig. 6. The maximum RS intensity of pyridine on silver during anodization under the conditions of Fig. 1a, plotted against pyridine concentration in the solution.

The fact that the RRS signal of pyridine on silver which is obtained under transient conditions is almost completely determined by unstable adatoms calls for a refinement of earlier estimates of the ratio of scattering cross sections of adsorbed (σ_S) and liquid (σ_V) pyridine [3]. The figure of $\sigma_S/\sigma_V \cong 3000$ was obtained in [3] on the assumption of monolayer pyridine coverage and with a roughness factor of about 10 for the silver surface. It had been shown above, however, that on the smooth electrode used in [3], only the RRS of pyridine associated with a small number of stable adatoms is observed. On the assumption that RRS of the entire pyridine monolayer is only seen in the maximum of curve 2 in Fig. 1a, where it is at least three orders of magnitude more intense, then in reality as a minimum one has $\sigma_S/\sigma_V = 3 \cdot 10^6$. An intensity increase of RS in resonance by six to seven orders of magnitude is only known for the polyene compounds; these have very powerful absorption bands with a half width smaller than the energy of the vibrational transition [27].

The question arises whether the adatom's rather more strongly broadened absorption band can sustain such a high RRS intensity. To answer this question, let us estimate the oscillator strength, f_e , of this band. Our measurements have shown that for the line of liquid pyridine at 991 cm^{-1} , σ_V is roughly half that for the line of liquid benzene at 992 cm^{-1} . The latter is $5.6 \cdot 10^{-29} \text{ cm}^2$ at $\lambda_X = 632.8 \text{ nm}$ [28]. Hence, $\sigma_S \cong 8.4 \cdot 10^{-23} \text{ cm}^2$. For the calculation we shall use the following relation from [29] (with a notation slightly modified relative to [29]):

$$\sigma = \frac{8\pi(\nu_X - \omega)^4}{9c^4} \sum_{i,k} \beta_{ik} \beta_{ik}^*, \quad (1)$$

where ν_X is the frequency of the exciting photon, ω is the vibrational frequency of the molecule, c is the velocity of light, and the β_{ik} are the Cartesian components of the scattering tensor ($d\alpha/dQ \Delta Q$ ($d\alpha/dQ$ is the derivative of the molecule's electronic polarizability, α , with respect to the vibrational coordinate Q , and ΔQ is the vibration amplitude). Considering that the three-dimensional tensor β_{ik} has nine components we obtain the following estimate from (1): the RS tensor has components such that $(d\alpha/dQ) \Delta Q \gg 10^{-20} \text{ cm}^3$. In resonance, and counting that there is one electron transition per Cartesian component, one can use the relation [30]

$$\frac{d\alpha}{dQ} = \frac{e^2}{2\pi m} \left[\frac{f_e'}{\nu_e^2 - \nu_X^2 + i\nu_X\Gamma} - \frac{2f_e\nu_e\nu_e'}{(\nu_e^2 - \nu_X + i\nu_X\Gamma)^2} \right], \quad (2)$$

for a calculation of f_e ; here, e and m are the electronic charge and mass, f_e' and ν_e' are the derivatives of f_e and ν_e with respect to Q . On the assumptions that $\nu_e = \nu_X$, $\hbar\nu_e = 1.6 \text{ eV}$, $\Gamma \geq 0.1 \text{ eV}$, and at least $f_e \geq f_e' \Delta Q$ and $\nu_e \geq \nu_e' \Delta Q$, we find that $f_e \geq 3$. This of course is a very low estimate, since actually $f_e \gg f_e' \Delta Q$ and $\nu_e \gg \nu_e' \Delta Q$. Moreover, by using the condition of $\nu_X = \nu_e$ in (2) (even though $\nu_X = 1.96 \text{ eV}$ in our case) we knowingly underestimate f_e . It is important to note, however, that even with such assumptions one obtains an improbably high

oscillator strength. It becomes clear, therefore, that a single absorption of the pyridine-silver adatom complex cannot completely sustain the observed RRS intensity. Thus, in addition to resonance excitation of the RS of pyridine one must assume another mechanism to be present which does not involve resonance with ν_x but contributes to the RS intensity rise occurring during adsorption.

Another indication for the existence of such a mechanism is the two-order of magnitude intensity increase of the RRS of pyridine on silver occurring when the pyridine concentration, c , is raised from 10^{-4} to 10^{-1} M [3], when surface coverage is close to a monolayer [11]. In the potentiodynamic mode of Fig. 1 it is also only at $c = 10^{-4}$ M that an RS signal suddenly appears (Fig. 6). This means that said mechanism only begins to operate at close-to-monolayer surface coverage.

During crystallization, e.g., of benzene and stilbene, RS intensity is known to increase by a factor of 20 [31]. This is due to spontaneous coherent emission in the solid phase, when correlation between the vibrations of neighboring molecules arise on account of intermolecular interactions that are stronger than those in the liquid [32]. A similar situation can arise in adsorbate layers at high coverages. When there is correlation in the vibrations of the molecules, the signal is proportional to the square of the number of molecules having correlated vibrations [32]; hence, to satisfy the observed RRS increase of pyridine (Fig. 6) one must postulate that on the surface at coverages close to a monolayer, groups of tens of molecules exist for which the RS process is coherent. On the basis of above estimates one can assume that RRS of the adatom-pyridine complex furnishes three to four orders of magnitude of the signal increase relative to the RS of liquid pyridine, while an additional two to three orders of magnitude of the increase arise from correlation of the vibrations of adsorbate molecules at high coverages and, possibly, at a certain degree of ordering of the adsorption layer.

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EFFECT OF THE SPECIFIC ADSORPTION OF IONS
IN ELECTRODE KINETICS

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The paper discusses the statistical averaging of the likelihood of elementary acts of irreversible electrochemical electron transfer reactions occurring at the metal/solution interface in the presence of specifically adsorbed, electrochemically inert ions. Analytic expressions are obtained for the polarization characteristics of the interface in cases where the planes containing the centers of the reactant ions in the reaction state are located in the compact or diffuse part of the electric double layer. Experimental data for hydrogen ion discharge on mercury in the presence of halide ions which are available in the literature are analyzed in terms of the theory developed.

The mechanism of the effect of specific adsorption of ions on electrode kinetics is a question of fundamental importance, since it is directly related to the problem of an adequate theoretical description of the importance of the electric double layer in electrochemical kinetics. This question has received considerable attention in the literature [1-10]. The progress achieved in recent years in the interpretation of data for kinetics complicated by the specific adsorption of ionic and dipole components of the solution is chiefly due to a substantiation of the importance of discreteness effects [11-16]. The local electric field acting near the interface upon the discrete species carrying an electric charge or dipole moment is differing, because of polarization of the interface by these species, from the average field described by the macroscopic equations of electrodynamics involving a continuous distribution of charges and dipole moments.

The characteristic relaxation times of the "electrostatic self-image" forces, i.e., the redistribution times of free and bound charges at the interface that are related to polarization of this interface by the discrete species present in the solution are of an order of magnitude of 10^{-15} to 10^{-14} sec. But the times required to accomplish many types of electrochemical reaction are comparable to the time of fluctuational reorientation of the solvent dipole molecules in the solvation sheaths of the reactants ($\sim 10^{-11}$ sec), i.e., three to four orders of magnitude longer than the relaxation times of the "electrostatic self-image" forces. For this reason the discrete nature of the charges and dipole moments should have an effect on the likelihood of elementary acts of electrochemical processes. Moreover, the local electric field associated with the discreteness effect can influence the rate of electrochemical processes via changes in the concentration of reactants and reaction products next to the electrode. The magnitude of the electric field set up by the "electrostatic image" forces substantially depends on the polarization state of the solvent close to the electrode; therefore, an adequate description of spatial nonuniformity of the dielectric properties of the solvent in the layer next to the electrode should be of extreme importance in quantitative discussions of the effects of the electric double layer and of discreteness on the rate of electrode processes. Equations for electrochemical reaction rate which allow for the local electric field and have been derived with correct regard to quantum mechanics and statistical physics are another and no less important aspect of the problem encountered when the fine structure of the double layer is taken into account in electrochemical kinetics.

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