Translated from *Uspekhi Khimii*, 54, 3-32 (1985) U.D.C. 541.13 : 543.42

# Electrochemical Optical Spectroscopy of Metals

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Modern methods of interpreting experimental results obtained by electrochemical optical spectroscopy (EOS) of metal surfaces are discussed. An attempt is made to unify the results so far obtained by this method by searching for correlations between experimental data and the special features of the electronic structure of the metal-electrolyte interface. The comparison is made in the framework of the semi-phenomenological theory.
The bibliography contains 183 references.

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## I. INTRODUCTION

In a new method of studying the physicochemical properties of the interface between an electrode and an electrolyte, the metal surface is monitored *in situ* by analysing the reflectance spectra in the frequency range from the infrared to the near ultraviolet. We shall call this field of work, which is the object of the present review, electrochemical optical spectroscopy (EOS). The method exploits the advantages of combining electrochemical and optical procedures: these include the possibility of continuously monitoring the surface and of controlling its state (including adsorption) under equilibrium conditions. Another important consideration is the high precision of the measurements by the potential modulation technique.[1]

The successful application of EOS in these systems has stimulated the transfer to other systems (with suitable modifications) of optical methods developed for the study of electrode—electrolyte interfaces. These methods offer attractive prospects for *in situ* study and control of heterogeneous catalytic processes in non-polar as well as in polar media.

Historically, one of the earliest optical methods which we could classify as EOS is the study of photo-electrochemical processes: it has already been reviewed extensively,[2-4] and will not be considered further here. Our principal aim will be to analyse methods of interpreting the results obtained in recent developments of the EOS method: ellipsometry, *electro-reflectance*, *phase modulation of the reflected light*, surface-enhanced Raman scattering spectroscopy, and surface plasmon spectroscopy. We have tried to give a unified presentation of all the results so far reported and to bring existing reviews up to date.[5-14] The conclusions which can legitimately be inferred from EOS data are examined in terms of specific experimental information.

## II. EXPERIMENTALLY MEASURABLE QUANTITIES AND BASIC FORMULAE

Most of the experimental optical methods of studying metal electrode surfaces rely on measurements of the characteristics of the reflected light. In the case of elastic reflection of light from a planar, uniform interface these characteristics are expressed through the two complex quantities $r_s$ and $r_p$ (the amplitudes of the reflection coefficients of the $s$- and $p$-polarised light respectively). The following parameters are often measured directly: the light reflection coefficient $R_{s(p)} = |r_{s(p)}|^2$, the phase $\delta_{s(p)} = (1/2i)\ln(r_{s(p)}/r^*_{s(p)})$, and the ellipsometric parameters $\psi$ and $\Delta$, defined by the expressions $\tan\psi = |r_p/r_s|$ and $\Delta = \delta_p - \delta_s$. Here $i = (-1)^{1/2}$, and the symbol * denotes the complex conjugate. The quantities $r_s$ and $r_p$ depend on the frequency of the light $\omega$, on the angle of incidence and on the orientation of the surface relative to the symmetry elements of the lattice of the monocrystalline electrode, and (most important in electrochemical applications) on the potential step $E$ and other parameters which characterise the state of the surface.

Studies of the metal—electrolyte interface can give information on the changes in $r_{s(p)}$ caused by changes in the properties of the surface. The most accurate results are obtained by using an electrochemical modulation procedure in which the potential applied to the interface has a periodic component:

$$E = E_0 + \delta E \sin \Omega t; \qquad (1)$$

and by applying noise separation techniques to the full reflected signal a harmonic of frequency $\Omega$ can be extracted. For small amplitudes of the modulation $\delta E$ the $r_{s(p)}$ values (like other characteristics of the system) can be expressed as

$$r_{s(p)} = R^{1/2}_{0s(p)}\, e^{i\delta_{0s(p)}} + \frac{d r_{s(p)}}{d E}\bigg|_{E=E_0} \delta E \sin(\Omega t + \delta'). \qquad (2)$$

where $\delta_{0s(p)}$ and $R_{0s(p)}$ are the phase and the reflection coefficient for a fixed value of the potential step $E = E_0$. Eqn.(2) is correct if the function $dr_{s(p)}/dE$ does not have a singularity at $E = E_0$. This stipulation may not apply in some special cases,[15] which therefore require a special treatment (see Section III). The phase shift $\delta'$ in Eqn.(2) is finite if the potential-induced changes in the processes which affect the optical properties of the system are slow enough (i.e. if their characteristic time is $\sim\Omega^{-1}$) (see below, p.5).

Modulation methods include electro-reflectance (ER),[1] in which the quantity $(1/R_{s(p)})dR_{s(p)}/dE$ is measured, modulation ellipsometry,[16] in which $d\Delta/dE$ and $d\psi/dE$ are measured, and the electro-modulation of the reflected phase (ERP) method,[17-19] in which $d\delta_{s,p}/dE$ is measured. The ERP method was first applied successfully very recently.[19]

We can distinguish two stages in the interpretation of light reflection data from an electrode surface and in extracting information on the structure of the electrode/electrolyte interface. The first stage consists in establishing a correlation between the optical characteristics of the surface and experimentally observable quantities. In electrochemical systems the contribution of the surface to the optical response is determined by the properties of different parts of the interface region. The most informative (as regards determining the electronic properties of the metal/electrolyte interface) is the contribution from a region of microscopic thickness (~1 Å) near the electrode surface, in which the electron density varies from values characteristic of the metal to values characteristic of the electrolyte. Another contribution to the optical response comes from the dependence of the dielectric constant of the electrolyte on the potential step in the macroscopic diffusion region near the electrode.

It has been shown[20-28] that the following three complex functions of frequency and potential are the main optical characteristics of the microscopic region:

$$\Delta\varepsilon_{2(3)}(\omega, E) = \int dx_1\, dx_1' \delta\varepsilon_{2(3)}(x_1, x_1'; \omega, E)$$

$$\Delta\varepsilon^{-1}_{(1)}(\omega, E) = \int dx_1\, dx_1' [\varepsilon^{-1}_{(1)}(x_1, x_1'; \omega, E) - \varepsilon_0^{-1}(x_1, \omega)\delta(x_1 - x_1')] \quad (3)$$

where

$$\varepsilon_0(x_1, \omega) = \varepsilon_m(\omega)\theta(-x_1) + \varepsilon_{el}\theta(x_1);$$
$$\delta\varepsilon_{2(3)} = \varepsilon_{2(3)}(x_1, x_1', \omega, E) - \varepsilon_0(x_1, \omega)\delta(x_1 - x_1').$$

Here the $X_1$ axis is normal to the electrode surface, which coincides with the $x_1 = 0$ plane; $\varepsilon_i(x_1, x_1'; \omega, E)$ are the diagonal components of the dielectric permeability tensor averaged over the surface† ($i$ = 1. 2. 3 for the $X_1$, $X_2$, $X_3$ axes respectively), which describes the linear response of the system to an external electromagnetic field; $\varepsilon_m(\omega) = \varepsilon'_m(\omega) + i\varepsilon''_m(\omega)$ is the bulk dielectric constant of the metal; $\varepsilon_{el}$ is the bulk dielectric constant of the electrolyte, which is a real quantity at optical frequencies; $\Theta(x)$ is a function of the step [$\Theta(x) = 1$ for $x > 0$ and $\Theta(x) = 0$ for $x < 0$]. The quantity $\varepsilon^{-1}_{(1)}(x_1, x_1'; \omega, E)$ which appears in Eqn.(3) is defined by the expression

$$\int dx_1'' \varepsilon_1(x_1 x_1''; \omega, E)\, \varepsilon^{-1}_{(1)}(x_1'', x_1'; \omega, E) = \delta(x_1 - x_1'). \quad (4)$$

The metal is assumed to be in the half-space $x_1 < 0$, and the electrolyte in the half-space $x_1 > 0$ (Fig.1). The integration with respect to $x_1$ is carried out over the whole space. The changes in amplitude of the light reflection coefficients $\Delta r_{s,p} = r_{s,p} - r^F_{s,p}$ are expressed in terms of the quantities (3) as follows:#

$$\frac{\Delta r_s(k_\parallel, \omega)}{r^F_s} = i\frac{2[(\omega^2/c^2)\varepsilon_{el} - k_\parallel^2]^{1/2}}{\varepsilon_{el} - \varepsilon_m}\Delta e_3$$

$$\frac{\Delta r_p(k_\parallel, \omega)}{r^F_p} = -i\frac{2\varepsilon_{el}[(\omega^2/c^2)\varepsilon_{el} - k_\parallel^2]^{1/2}\{[(\omega^2/c^2)\varepsilon_m - k_\parallel^2]\Delta\varepsilon_2 + \varepsilon_m^2 k_\parallel^2 \Delta\varepsilon^{-1}_{(1)}\}}{(\varepsilon_{el} - \varepsilon_m)[(\varepsilon_{el} + \varepsilon_m)k_\parallel^2 - (\omega^2/c^2)\varepsilon_m\varepsilon_{el}]}. \quad (5)$$

Here $r^F_{s,p}$ are the unperturbed reflection amplitudes, determined by the classical Fresnel formulae, and $k_\parallel$ is the projection of the wave vector on the plane of the electrode surface§; the ($X_1$, $X_2$) plane is assumed to coincide with the plane of incidence of the light.

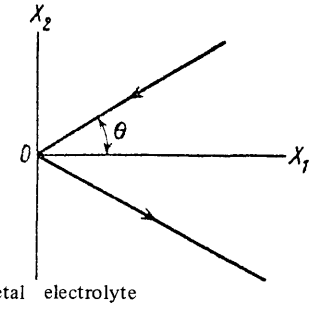



**Figure 1.** Reflection of light from the metal/electrolyte interface: ($X_1$, $X_2$) is the incidence plane of the light, the axis $X_3$ is normal to the plane of the paper, $\theta$ is the angle of incidence.

By using Eqn.(5) for the amplitude $\Delta r_{s,p}$ all the experimentally measured quantities listed above can easily be calculated:

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† Throughout this paper the term averaging over the surface will be applied to the process of averaging over a plane parallel to the surface of the electrode and at a distance $x_1$ from it.

# The spatial dispersion of the dielectric constant in the bulk of the metal, which is important only in the silver/electrolyte system at the frequencies used in electrochemistry, is ignored in formulae (5). Formulae which allow for spatial dispersion are given in Refs.20, 21, and 29.

§ Formulae (5) as written are correct if the electrode material has a cubic symmetry (say), and the orientation of the crystal relative to the incidence plane of the light is such that the directions $X_1$ and $X_2$ coincide with the crystallographic axes of the crystal. Under these conditions the dielectric permeability tensor $\delta\varepsilon_{ij}(x_1, x_1')$ is diagonalised, $\delta\varepsilon_{ij}(x_1, x_1') = \delta_{ij}\delta\varepsilon_i(x_1, x_1')$. If the surface is isotropic we also have $\delta\varepsilon_2 = \delta\varepsilon_3$. The tensor $\delta\varepsilon_{ij}$ has a diagonal form, and $\delta\varepsilon_2 = \delta\varepsilon_3$, in the frequently encountered case of a polycrystalline electrode. Formulae which apply to this case are given in Refs.20, 21, 28.

$$\frac{1}{R_s}\cdot\frac{dR_s}{dE}=-\frac{4\omega(\varepsilon_{el})^{1/2}\cos\theta}{c}\,\mathrm{Im}\left[\frac{d\Delta\varepsilon_3/dE}{\varepsilon_{el}-\varepsilon_m}\right] \quad (6a)$$

$$\frac{1}{R_p}\frac{dR_p}{dE}=-\frac{4\omega(\varepsilon_{el})^{1/2}\cos\theta}{c}\times$$
$$\times\,\mathrm{Im}\left[\frac{(\varepsilon_m-\varepsilon_{el}\sin^2\theta)\,d\Delta\varepsilon_3/dE+\varepsilon_{el}\varepsilon_m^2\sin^2\theta\,d\Delta\varepsilon_{(1)}^{-1}/dE]}{(\varepsilon_m-\varepsilon_{el})(\varepsilon_{el}\sin^2\theta-\varepsilon_m\cos^2\theta)}\right] \quad (6b)$$

$$\frac{d\delta_s}{dE}=\frac{2\omega(\varepsilon_{el})^{1/2}\cos\theta}{c}\,\mathrm{Re}\left[\frac{d\Delta\varepsilon_3/dE}{\varepsilon_{el}-\varepsilon_m}\right] \quad (6c)$$

$$\frac{d\delta_p}{dE}=\frac{2\omega(\varepsilon_{el})^{1/2}\cos\theta}{c}\,\mathrm{Re}\left[\frac{(\varepsilon_m-\varepsilon_{el}\sin^2\theta)\,d\Delta\varepsilon_3/dE+\varepsilon_{el}\varepsilon_m^2\sin^2\theta d\Delta\varepsilon_{(1)}^{-1}/dE}{(\varepsilon_m-\varepsilon_{el})(\varepsilon_{el}\sin^2\theta-\varepsilon_m\cos^2\theta)}\right] \quad (6d)$$

$$\frac{d\psi}{dE}=-\frac{\tan\psi^F}{1+\tan^2\psi^F}\cdot\frac{4\omega(\varepsilon_{el})^{1/2}\cos\theta}{c}\times$$
$$\times\,\mathrm{Im}\,\frac{\varepsilon_{el}\varepsilon_m^2\sin^2\theta d\Delta\varepsilon_{(1)}^{-1}/dE+\varepsilon_{el}\sin^2\theta\dfrac{d}{dE}(\Delta\varepsilon_3-\Delta\varepsilon_3)+\varepsilon_m\dfrac{d}{dE}(\Delta\varepsilon_3-\Delta\varepsilon_3\cos^2\theta)}{(\varepsilon_m-\varepsilon_{el})(\varepsilon_{el}\sin^2\theta-\varepsilon_m\cos^2\theta)} \quad (6e)$$

$$\frac{d\Delta}{dE}=-\frac{2\omega(\varepsilon_{el})^{1/2}\cos\theta}{c}\times$$
$$\times\,\mathrm{Re}\,\frac{\varepsilon_{el}\varepsilon_m^2\sin^2\theta\,d\Delta\varepsilon_{(1)}^{-1}/dE+\varepsilon_{el}\sin^2\theta\dfrac{d}{dE}(\Delta\varepsilon_3-\Delta\varepsilon_3)+\varepsilon_m\dfrac{d}{dE}(\Delta\varepsilon_3-\Delta\varepsilon_3\cos^2\theta)}{(\varepsilon_m-\varepsilon_{el})(\varepsilon_{el}\sin^2\theta-\varepsilon_m\cos^2\theta)}. \quad (6f)$$

Here $\tan\psi^F=|r_p^F/r_s^F|$. We note that the form of Eqn.(6) is independent of the specific model chosen to describe the optical properties of the surface.

Formulae (6a) and (6b) differ from the expressions obtained from the standard three-layer model,[5] in which two parameters are used to describe the optical properties of a reflecting surface: the thickness $d$ and the dielectric constant $\varepsilon_l$ of the transition layer. In the calculation by this model Eqns.(6a) and (6b) are replaced by

$$\frac{1}{R_s}\frac{dR_s}{dE}=-\frac{4d\omega(\varepsilon_{el})^{1/2}\cos\theta}{c}\cdot\frac{d}{dE}\,\mathrm{Im}\,\frac{\varepsilon_l-\varepsilon_m}{\varepsilon_{el}-\varepsilon_m} \quad (7a)$$

$$\frac{1}{R_p}\frac{dR_p}{dE}=\frac{4d\omega(\varepsilon_{el})^{1/2}\cos\theta}{c}\cdot\frac{d}{dE}\cdot\mathrm{Im}\left[\frac{\varepsilon_l-\varepsilon_m}{\varepsilon_m-\varepsilon_{el}}\,\frac{1-\dfrac{\varepsilon_{el}}{\varepsilon_l\varepsilon_m}(\varepsilon_m+\varepsilon_l)\sin^2\theta}{1-\dfrac{1}{\varepsilon_m}(\varepsilon_m+\varepsilon_{el})\sin^2\theta}\right] \quad (7b)$$

Whereas the expressions (6a) and (7a) for the reflection of s-polarised light are structurally similar, the expression (6b) for $p$-polarised light is very different from the corresponding expression (7b) given by the three-layer model. This difference arises partly because in real systems the quantity $\Delta\varepsilon_{(1)}^{-1}$ which appears in (6b) cannot be expressed through the average value of the dielectric constant for the layer ($\varepsilon_l$). However, the most important consideration is that the formal use of the three-layer model (with an anisotropic active layer) complicates the interpretation of experimental data at the microscopic level (see Section III).

Changes in the potential step at the electrode/solution boundary affect not only the electronic properties of the surface but also the distribution of the components in the diffusion layer of the solution, thus affecting the dielectric constant in this region. Hence the measured quantities are determined both by the optical characteristics of the microscopic surface layer and by the characteristics of the macroscopic diffusion layer. In the linear approximation to the interaction of light with the surface region¶ the full ER and ERP signals are described by a sum of terms for the separation effects of these layers. It has been shown[30-32] that under certain conditions the ER and ERP signals are determined by the interaction of the incident light with the macroscopic diffusion layer of the electrolyte. The corresponding expressions for the active components† of the ER and ERP signals are:[32]

$$\left(\frac{1}{R_s}\frac{dR_s}{dE}\right)_a=\sum_i\frac{\partial\varepsilon_{el}}{\partial c_{i,0}}\frac{dc_i(d)}{dE}\cdot\frac{1}{Z_1}\cdot\frac{2l}{(l^4+1)\cos\theta}\times$$
$$\times\{\cos\delta_i[l(1-l^2)-b_1\cos\theta\cdot l^2]+\sin\delta_i\cdot[b_1\cos\theta+l(l^2+1)]\} \quad (8a)$$

$$\left(\frac{d\delta_s}{dE}\right)_a=\frac{1}{2}\sum_i\frac{\partial\varepsilon_{el}}{dc_{i\,0}}\frac{dc_i(d)}{dE}\cdot\frac{l}{(l^4+1)\cos\theta}\times$$
$$\times\left\{\frac{1}{n_{el}^2\cos\theta}[l^2\cos\delta_i-(2+l^4)\sin\delta_i]-\frac{2}{Z_2}[\cos\delta_i(l^2b_2\cos\theta+\right.$$
$$\left.+(1-l^2)l)-\sin\delta_i(b_2\cos\theta-(1+l^2)l)]\right\} \quad (8b)$$

$$\left(\frac{1}{R_p}\frac{dR_p}{dE}\right)_a=\sum_i\frac{\partial\varepsilon_{el}}{\partial c_{i.0}}\frac{dc_i(d)}{dE}\cdot\frac{[4l\cos2\theta]}{l^4+1}\cdot\frac{n_m'n_m''}{f_1(\theta)}\times$$
$$\times\frac{\cos\delta_i[l(1-l^2)-l^2f_1(0)]+\sin\delta_i[l(1+l^2)+f_1(\theta)]}{\{[(n_m')^2-(n_m'')^2]\cos^2\theta-n_{el}^2\}^2+4(n_m'n_m'')^2\cos^4\theta} \quad (8c)$$

$$\left(\frac{d\delta_p}{dE}\right)_a=\frac{1}{2}\sum_i\frac{\partial\varepsilon_{el}}{\partial\varepsilon_{i,0}}\cdot\frac{dc_i(d)}{dE}\cdot\frac{l\cos2\theta}{(l^4+1)\,n_{el}\cos\theta}\left\{\frac{l^2\cos\delta_i-\left(1+\dfrac{1+l^4}{\cos2\theta}\right)\sin\delta_i}{n_{el}\cos\theta}-\right.$$
$$\left.-\frac{\sqrt{2}\,n_m''\{[(n_m')^2+(n_m'')^2]\cos^2\theta+n_{el}^2\}\{\cos\delta_i[l(1-l^2)+f_2(\theta)l^2]-\sin\delta_i[f_2(\theta)-l(1+l^2)]\}}{[(n_m')^2-(n_m'')^2]^2\cos^2\theta-n_{el}^2]^2+4(n_m'n_m'')^2\cos^4\theta}\right\} \quad (8d)$$

$$l=2\frac{\omega}{c}\xi_0n_{el}\cos\theta;\quad n_{el}=(\varepsilon_{el})^{1/2};$$

$$n_m'+in_m''=(\varepsilon_m)^{1/2};$$

$$b_1=\frac{2\sqrt{2}\,n_m''n_{el}}{(n_m')^2+(n_m'')^2-n_{el}^2};\quad b_2=\frac{\sqrt{2}\,n_{el}[(n_m')^2-(n_m'')^2-n_{el}^2]}{n_m''[(n_m')^2+(n_m'')^2+n_{el}^2]};$$

$$Z_1=\frac{\sqrt{2}\,n_{el}\{[(n_m')^2-(n_m'')^2-n_{el}^2]^2+4(n_m'n_m'')^2\}}{n_m'[(n_m')^2+(n_m'')^2-n_{el}^2]};$$

$$Z_2=\frac{\sqrt{2}\,n_{el}[(n_m')^2-(n_m'')^2-n_{el}^2]^2}{n_m''[(n_m')^2+(n_m'')^2+n_{el}^2]};\quad f_1(\theta)=\frac{2\sqrt{2}\,n_m''n_{el}\cos\theta}{[(n_m')^2+(n_m'')^2]\cos^2\theta-n_{el}^2}$$

$$f_2(\theta)=\frac{\sqrt{2}\,n_{el}\{[(n_m')^2-(n_m'')^2]\cos^2\theta-n_{el}^2\}}{n_m''\{[n_m')^2+(n_m'')^2]\cos^2\theta+n_{el}^2\}}.$$

Here $\xi_0=(2D_i/\Omega)^{1/2}$; $D_i$ and $c_i(d)$ are the diffusion coefficient and the concentration of particles of kind $i$ at the outer boundary of the diffusion layer of thickness $d$; $\delta_i$ is the phase shift between the molecular flow and the potential. In the derivation of these formulae the distribution of concentrations of the various species was expressed by the standard equation[33]

$$c_i(x_1,t)=c_{i,0}+c_i(d)\,e^{-x_1/\xi_0}\sin(\Omega t+\delta_i-x_1/\xi_0-\pi/4), \quad (9)$$

¶ The precision of experimental data does not justify the use of approximations higher than the linear.

† The reactive components $[(1/R_{s(p)}\cdot dR_{s(p)}/dE]_r$ and $(d\delta_{s(p)}/dE)_r$ are obtained from the formulae (8) by replacing the phases $\delta_i$ by $\delta_i+(\pi/2)$.

where $c_{i,0}$ is the concentration of particles of kind $i$ in the bulk of the solution. In contrast to Eqn.(6), the quantities in Eqn.(8) show a phase shift with respect to the potential (1). It follows from the formulae (6) and (8) that the angular dependences of $(1/R).(dR/dE)$ and $(d\delta/dE)$, corresponding to the changes in optical properties of the layer of atomic dimensions near the boundary and to the concentration changes in the diffusion layer respectively, are substantially different and can therefore be separated. At low enough frequencies ($\Omega$), when $\xi_0^{-1} > 2\pi c/\omega$, the signal measured at low angles of incidence is determined mainly by the first contribution, and at higher angles of incidence mainly by the second.

## III. MICROSCOPIC ELECTRO-MODULATION MECHANISMS

The second main stage in the analysis of light reflectance data is to define the relationship between the parameters $\Delta\varepsilon_{2,3}$ and $\Delta\varepsilon_{(1)}^{-1}$ and the microscopic characteristics of the metal/electrolyte interface, and also to examine the various mechanisms used to modulate the optical properties of the surface. Without these clarifications the information of relevance to chemical studies of the surface phenomena cannot be extracted from the optical data. One possible approach is to use the relationship between the dielectric permeability tensor $\varepsilon_{ij}(\bar{x}, \bar{x}'; \omega)$ and the multi-particle Green function of the system. A simple expression for the non-local dielectric permeability tensor, given by the random phase approximation (RPA),[34,35] is often used at present. This approximation gives a reasonably accurate quantitative relationship between the spectral parameters of the system of electrons in the inhomogeneous medium under study and the behaviour of the reflectance coefficient of the light in the visible and near-u.v. frequency range, without excessively cumbersome formulae.

In the RPA the tensor $\varepsilon_{ij}(\bar{x}, \bar{x}'; \omega)$ is written as

$$\varepsilon_{ij}(\bar{x}, \bar{x}'; \omega) = \varepsilon_p(\bar{x}, \omega)\delta_{ij}\delta(\bar{x} - \bar{x}') + \varepsilon_{ij}^{tr}(\bar{x}, \bar{x}'; \omega) . \quad (10)$$

The first term in (10) is the plasma component of the dielectric permeability, and the second describes various optical transitions. At the absolute zero of temperature the terms which appear in (10) can be expressed as follows through the Green function:

$$\varepsilon_p(\bar{x}, \omega) = 1 - \frac{4e^2}{m\omega^2}\int d\hat{E} 2\Theta(-\hat{E})\,\mathrm{Im}\,G(\bar{x}, \bar{x}'; \hat{E})$$

$$\varepsilon_{ij}^{tr}(\bar{x}, \bar{x}'; \omega) = -\frac{e^2\hbar^2}{m^2\omega^2}\int d\hat{E} 2\Theta(-\hat{E})\cdot\left\{\mathrm{Im}\,G(\bar{x}, \bar{x}'; \hat{E})\overleftrightarrow{\frac{\partial}{\partial x_i}}\cdot\right.$$

$$\left.\cdot\overleftrightarrow{\frac{\partial}{\partial x_j'}}G(\bar{x}, \bar{x}'; \hat{E}+\hbar\omega) - \mathrm{Im}\,G(\bar{x}, \bar{x}'; \hat{E})\overleftrightarrow{\frac{\partial}{\partial x_i'}}\overleftrightarrow{\frac{\partial}{\partial x_j}}G^*(\bar{x}, \bar{x}'; \hat{E}-\hbar\omega)\right\}, \quad (11)$$

where the meaning of the operation $\overleftrightarrow{\partial}/\partial x$ follows from the equality

$$f(\bar{x})\overleftrightarrow{\frac{\partial}{\partial x_i}}g(\bar{x}) = f(\bar{x})\frac{\partial g(\bar{x})}{\partial x_i} - g(\bar{x})\frac{\partial f(\bar{x})}{\partial x_i}$$

Here the symbol $G(\bar{x}, \bar{x}'; \hat{E})$ refers to the one-electron Green function with energy $\hat{E}$, and $m$ and $e$ are the effective mass and the charge of the electron in the metal. Energies are measured from the Fermi level of the metal, and therefore the distribution function at $T = 0$ is of the $2\Theta(-\hat{E})$ type. The integral of the energy which appears in the expression for $\varepsilon_p(\bar{x}, \omega)$ is the distribution of electron density in the system, $\rho(\bar{x})$.

Complete calculations by formulae (11) require extensive information on the electronic structure of the metal/electrolyte system; the procedure is complex and can only be applied in a few special cases, even by using a computer. An alternative approach, less artificial and now widely used, relies on a semi-phenomenological comparison of various properties of the electron spectrum with the behaviour of $\Delta\varepsilon_{2,3}$ and $\Delta\varepsilon_{(1)}^{-1}$ in selected frequency ranges. Approximate expressions for the Green function, which allow a simple physical interpretation, can be used. In the following subsections we shall examine these approximations for different types of spectrum and therefore also for different microscopic mechanisms of the interaction between the light and the surface.

### 1. Plasma ER

The plasma ER model[36] assumes that the ER effect is due to modulation of the plasma component of the $\varepsilon_{ij}$ tensor [first term in (10)] by the change in electron density near the interface caused by the application of the modulation potential, and that the second term in (10) is unaffected by these changes. The latter assumption can be justified only in the range of $\omega$ and $E$ values most remote from the photo-emission threshold, and for frequencies far from the optical transition frequencies of the surface layer. The plasma component of the dielectric permeability $\varepsilon_p(x_1, \omega)$, averaged over the surface and allowing also for the collisions between electrons in the bulk of the metal, is often expressed as[10,11]

$$\varepsilon_p(x_1, \omega) = \varepsilon_{el} + (\varepsilon_f(\omega) - \varepsilon_{el})\rho(x_1)/N \quad (12)$$

$$\varepsilon_f(\omega) = 1 - \frac{\omega_p^2}{\omega(\omega + i/\tau)}; \quad \omega_p^2 = 4\pi Ne^2/m; \quad \omega\tau \gg 1 ,$$

where $\tau$ is the relaxation time, $\rho(x_1)$ is the electron density (averaged over the surface), and $N$ is the concentration of electrons in the bulk of the metal. For normal incidence of the light on the electrode the model gives the following expression for the relative change in light reflection coefficient and for the phase change:

$$\frac{\Delta R_s}{R_s} = -\frac{4\omega(\varepsilon_{el})^{1/2}}{c}\frac{\Delta Q}{eN}\,\mathrm{Im}\,\frac{\varepsilon_{el} - \varepsilon_f}{\varepsilon_{el} - \varepsilon_m} = -\frac{4\omega(\varepsilon_{el})^{1/2}}{c}\frac{C_{dl}\Delta E}{eN}\,\mathrm{Im}\,\frac{\varepsilon_{el} - \varepsilon_f}{\varepsilon_{el} - \varepsilon_m} \quad (13a)$$

$$\Delta\delta_s = \frac{2\omega(\varepsilon_{el})^{1/2}\Delta Q}{ceN}\,\mathrm{Re}\,\frac{\varepsilon_{el} - \varepsilon_f}{\varepsilon_{el} - \varepsilon_m} = \frac{2\omega(\varepsilon_{el})^{1/2}C_{dl}\Delta E}{ceN}\,\mathrm{Re}\,\frac{\varepsilon_{el} - \varepsilon_f}{\varepsilon_{el} - \varepsilon_m} \quad (13b)$$

where

$$\Delta Q = -e\Delta\rho = -e\int dx_1\Delta\rho(x_1); \quad C_{dl} = dQ/dE , \quad (14)$$

$\Delta Q$ is the change in surface charge caused by a change $\Delta E$ in the surface potential step, and $C_{dl}$ is the differential double layer capacitance.

According to (13) the intensity of the integral ER signal varies linearly with the density of surface charge, and the differential ER signal is proportional to the differential capacity. These predictions have been confirmed qualitatively for several systems.[37-39] In particular, it was found[38,39] that for $\hbar\omega = 1.3$ eV a lead electrode in 0.1 and 0.25 M solutions of NaF at negative potentials (i.e. in the absence of specific adsorption) gives a linear dependence of $\Delta R/R$ on the charge $\Delta Q$. It follows from (13) that for strongly reflecting metals such as Ag, Au, and Cu, for which $\mathrm{Im}\,\varepsilon_m \ll |\mathrm{Re}\,\varepsilon_m|$, the contribution of the plasma mechanism to $d\delta_s/dE$ is much greater than the contribution to $(1/R_s)dR_s/dE$.

Let us consider the plasma ER in *p*-polarised light. The quantity $\Delta\varepsilon_{(1)}^{-1}$ in the expression for the ER signal in *p*-polarised light [unlike $\Delta\varepsilon_{2(3)}$] is strongly dependent not only on the surface charge $Q$ but also on the distribution of electron density $\rho(x_1)$ near the surface. Consider first a simple model for $\rho(x_1)$ [40,41] in which

$$\rho(x_1) = \begin{cases} N - \frac{1}{2}(\beta Q/e + N)\,e^{\beta x_1}, & x_1 < 0 \\ \frac{1}{2}(N - \beta Q/e)\,e^{-\beta x_1}, & x_1 > 0 \end{cases} \qquad (15)$$

Here $\beta$ is an adjustable parameter, defined by the condition of minimum energy of the ground state of the electron gas in an external field.[41] For metals such as Ag, In, etc. (whose bulk properties are accurately described by the plasma part of the expression for the dielectric constant $\varepsilon_f$) we have, for the condition $|\beta Q| < eN$,

$$\frac{d\,\Delta\varepsilon_{(1)}^{-1}}{dE} \approx \frac{\varepsilon_m - \varepsilon_{el}}{\varepsilon_m\,\varepsilon_{el}}\frac{C_{dl}}{eN} + \frac{1}{\beta^2}\frac{d\beta}{dE}\left[\frac{\varepsilon_m + \varepsilon_{el}}{\varepsilon_m\varepsilon_{el}}\ln\left(-\frac{\varepsilon_m + \varepsilon_{el}}{2}\right) - \right.$$
$$\left. - \frac{1}{\varepsilon_m}\ln(-\varepsilon_m) - \frac{1}{\varepsilon_{el}}\ln\varepsilon_{el} + \frac{i\pi}{\varepsilon_{el}}\right] \qquad (16)$$

This expression shows that the main contribution to $\mathrm{Im}\,(d\,\Delta\varepsilon_{(1)}^{-1}/dE)$ in the case of weak bulk attenuation comes from the region near the point $x_1 = x_1^0$, defined as the solution of the equation $\mathrm{Re}\,\varepsilon_p(x_1) = 0$. This point exists near the surface if the frequency is consistent with $\mathrm{Re}\,\varepsilon_m < 0$, since $\varepsilon_{el}$ is always positive. In the frequency range considered the condition $\mathrm{Re}\,\varepsilon_m < 0$ is obeyed by the great majority of metals. When $\mathrm{Re}\,\varepsilon_p(x_1^0)$ vanishes, a positive term proportional to $d\beta/dE$ appears in $(1/R_p)(dR_p/dE)$: this term does not disappear even for the real $\varepsilon_m$ values. This effect has been attributed[20,42] to the steep rise of the normal component of the electromagnetic field $\mathscr{E}_1$ at the point $x_1 = x_1^0$, and cannot in principle be described by the three-layer model.

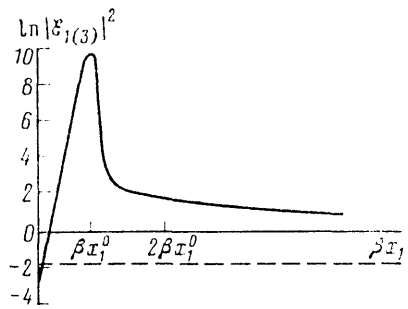



**Figure 2.** Plots of $\lg|\mathscr{E}_3|^2$ (broken line) and $\ln|\mathscr{E}_1|^2$ (full line) against $x_1$ for a fixed value of $x_2 = 0$; silver electrode, $\hbar\omega = 2$ eV. The point $x_1^0$ is found from the condition $\mathrm{Re}\,\varepsilon(x_1^0) = 0$, the parameter $\beta$ defines the slope of the electron density outside the metal.

The ER spectra in *p*-polarised light for In and Pb have been calculated[43] by using an expression for $\rho(x_1)$ similar to (15). For $d\beta/dE = 0$ the parameter $(1/R_p)(dR_p/dE)$ for In was found to be negative, becoming positive (in keeping with experimental results[44,45]) for $d\beta^{-1}/dE < -0.02$ Å $V^{-1}$. For frequencies below the photo-emission threshold (since near the threshold the ER signal is determined by a different effect, see below) the values of $(1/R_p)(dR_p/dE)$ calculated[43] for $d\beta^{-1}/dE = -0.06$ Å $V^{-1}$ agree with the experimental values (see Figs. 3 and 4). It is clear from the experimental results that $d\beta^{-1}/dE$ is very sensitive to the nature of the metal. Thus the study of the plasma ER in *p*-polarised light can identify the dependence on surface potential of the steepness of the electron density curve outside the metal.

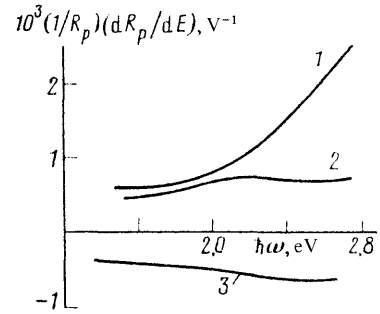



**Figure 3.** Comparison of the experimental ER spectrum of indium (*1*) in a 0.1 *N* solution of $Na_2SO_4$ with theoretical spectra, calculated by the plasma model of ER for $d(1/\beta)/dE$ values of $-0.06$ Å $V^{-1}$ (curve *2*) and zero (curve *3*), and $E = -1.2$ V (saturated silver chloride electrode);[43] *p*-polarised light, $\theta = 70°$.

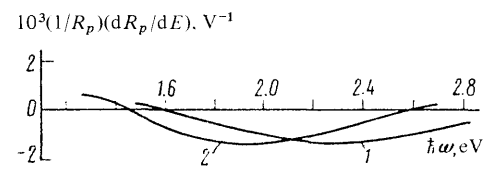



**Figure 4.** Comparison of the experimental ER spectrum of lead (*1*) in a 0.1 *N* solution of $Na_2SO_4$ with the theoretical spectrum (*2*) calculated by the plasma model of ER for $d(1/\beta)/dE = -0.14$ Å $V^{-1}$ and $E = -1.0$ V (saturated silver chloride electrode),[43] *p*-polarised light, $\theta = 70°$.

Changes in the potential step at the surface can reorient the dipolar solvent molecules near the electrode surface. This effect also leads to a change in the distribution of electron density, and should therefore be observable in electron-reflection in *p*-polarised light. We have discussed this mechanism[46] using the simplest model of the fixed part of the double layer,[47] i.e. assuming that the solvent dipoles can exist in two states and replacing the discrete distribution of charges from the dipoles by a continuous distribution. The dipole layer is treated as a capacitor in which the density of charge on the plates $q(E)$ is determined by the orientation of the dipoles: $q(E) = ze(N_2 - N_1)/S$, where

$N_1$ and $N_2$ are the numbers of dipoles with their positive and their negative pole oriented towards the metal, $S$ is the surface area of the electrode, and $ze$ is the charge on the positive pole of the dipole.[48] The distribution of electron density outside the metal is described by the expression

$$\rho(x_1, E) = \rho_0(E) \exp\left[-2\int_0^{x_1} dx\,((2m/\hbar^2)(W_0 + eU(x, E)))^{1/2}\right], \quad (17)$$

where $W_0$ is the electronic work function at the zero charge potential (z.c.p.), $U(x, E)$ is the potential distribution in the double layer, and $\rho_0(E)$ is the density of electrons on the electrode surface. By making these assumptions the following expression was obtained[46] for strongly reflecting metals in concentrated electrolytes at potentials close to the z.c.p.:

$$\mathrm{Im}\,\frac{d}{dE}\Delta\varepsilon^{-1}_{(1)} = \frac{\pi^2 e}{\varepsilon_0\varepsilon_{el}(2m/\hbar^2)^{1/2}W_0^{3/2}}\left[C_{dl} + \frac{dq}{dE}\right]x_1^0(0), \quad (18)$$

where

$$x_1^0(0) = \frac{1}{2(2mW_0/\hbar^2)^{1/2}}\ln\frac{(\varepsilon_{el} - \varepsilon_i')\rho_0(0)}{Ne_{el}}, \quad \varepsilon_i' = \mathrm{Re}\,\varepsilon_i.$$

In Eqn.(18) the symbol $\varepsilon_0$ denotes the static dielectric constant of the double layer.

It is clear from (18) that the quantity $dq/dE$, which defines the rate of reorientation of the dipoles, can be determined in principle by simultaneous treatment of experimental ER and capacitance data. We can show (for example, by model[47] calculations of $C_{dl}$ and $q$) that in the region of the z.c.p. the reorientation of the dipoles produces a change in sign of the quantity $\mathrm{Im}\,(d\Delta\varepsilon^{-1}_{(1)}/dE)$, and therefore also of $(1/R_p)\cdot(dR_p/dE)$, as compared to a system where reorientation of the adsorbed molecules does not take place. The reason for this effect is that near the double layer, where changes in electric potential have a large effect on the distribution of electron density, the field created by the reorientation of the dipole and the field created by the ions and by the surface charge on the electrode have opposite orientations.

However, not all the effects observed experimentally in the reflection of light by metals can be attributed to modulation of the surface charge. Measurements[49,50] of the electroreflectance and electro-transmittance spectra of $s$-polarised light for a silver electrode in 1 $N$ $Na_2SO_4$ solution gave $\mathrm{Re}\Delta\varepsilon$ and $\mathrm{Im}\Delta\varepsilon$ values of similar absolute value but different sign over a wide range of frequency. This result is inconsistent with the prediction from the plasma model that these quantities should have the same sign. The discrepancy was explained[50] by postulating changes in the relaxation time as well as in the concentration of the near-surface electrons in response to changes in the potential step at the surface#. Alternative explanations of the form of the ER signal in $s$-polarised light at frequencies where the contribution from optical transitions is negligible (and the plasma model should "work") rely on the dependence of the effective mass of the electrons on $x_1$ near the metal surface. We also note that when conduction is mainly by holes the sign of the ER signal must be the opposite of that given by formula (13a). This may be the reason for the positive sign of the ER signal reported in Ref. 45. Mutually consistent explanations of all these effects would be valuable.

In all the models which allow for the modulation of the surface charge and of the relaxation time the optical characteristics of the surface layer are smooth functions of frequency. Therefore the models cannot explain the experimentally observed maxima and minima in the dependence of $\Delta\varepsilon_{2(3)}$ and $\Delta\varepsilon^{-1}_{(1)}$ on $\omega$. To account for these effects we must allow for the influence of the potential step $E$ on the part of the expression for the dielectric permeability which refers to optical transitions (band-to-band, or within-band, transitions, or transitions involving surface states). The main problem is to identify the physical mechanism of the dependence of $\Delta\varepsilon_{2(3)}$ and $\Delta\varepsilon^{-1}_{(1)}$ on the surface potential step.

### 2. Effect of Band-to-band and Within-band Optical Transitions

Almost without exception the modulation of band-to-band transitions is described in terms of concepts previously developed to interpret ER in semiconductors. For example, shifts in the Fermi level,[51] bending of the bands,[52] and changes in the relaxation time of band-to-band transitions[53] have been assumed to be produced by the application of an electric field to the sample. That work has already been reviewed in detail.[5,7,9] However, those mechanisms cannot play a major role in metals, because in order to perturb the electronic band structure in the bulk of the metal the external electric field would need to penetrate into the electrode to a depth much greater than atomic dimensions.

A more realistic mechanism of the electro-modulation of band-to-band transitions in metals was suggested in Ref. 54. It applies to the reflection of $s$-polarised light by polyvalent metals at frequencies close to those of allowed optical transitions between almost parallel bands. It was assumed that at frequencies and potentials far from the photo-emission threshold the dependence of the $\Delta\varepsilon$ tensor on surface potential is determined by the amplitudes of the reflection coefficients of the electron waves incident on the surface from the bulk of the metal. Allowance was made for the dependence on $E$ of the amplitudes of the reflection coefficients of electron waves in the ground and in the excited state. Calculations[54] showed that extrema should appear in the ER spectra at frequencies close to those of allowed band-to-band transitions, due partly to the presence of an interface, which overcomes the requirement of conservation of the normal component of the quasi-momentum in the optical transition, and partly to the possibility of a bulk optical transition in which all the components of the quasi-momentum are conserved. The width of the peak is determined by the mean free path of the electrons in the excited state. A weak dependence of the position of extrema of this type on the surface potential step is typical of bulk optical transitions.

This theory[54] has been used to explain the characteristic features of the ER spectrum of lead in $s$-polarised light. The band structure of lead[55] contains, near the point $W$ of the Brillouin zone close to the Fermi surface, three almost parallel bands, two of which are partially filled while the third (and uppermost) is empty. Experimental and theoretical frequency dependences of $\hbar\omega\,\mathrm{Im}\,\Delta\varepsilon$ are compared in Fig. 5. The extremum close to $\hbar\omega = 1.2$ eV corresponds to transitions between the highest filled band and the empty band, while the other extremum close to $\hbar\omega = 2.3$ eV corresponds to transitions from the second filled band to the

# The possible influence of the modulation of the relaxation time on the ER was first pointed out in Ref. 51. However, allowing for the relaxation time in the dielectric permeability of a thin surface layer poses serious fundamental difficulties.[177]

empty band. Differences between the extrema are ascribed to the special properties of the wave functions of electrons in different bands.

Like the transitions between the electronic bands in the bulk of the metal, transitions involving the surface bands of the metal can affect the dielectric constant of the surface layer. Changes in the surface potential at the metal/electrolyte interface alter the position of the surface band relative to the Fermi level of the metal, thus affecting the contribution from this band to $\Delta\varepsilon_{2(3)}$ and $\Delta\varepsilon^{-1}_{(1)}$. It has been suggested[178] that the maximum at $\hbar\omega = 2.6$ eV observed in the ER spectrum of gold in 1 *N* $HClO_4$ is due to a transition from the surface *d* band to the Fermi level. Increasing the potential shifts the maximum towards lower frequencies, as expected theoretically.[179]

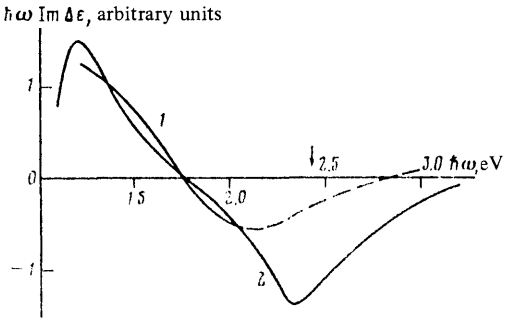



**Figure 5.** Plots of $\hbar\omega \mathrm{Im}\Delta\varepsilon(\omega)$ against frequency obtained by processing the experimental ER spectrum (*1*) and by calculation (*2*).[54] Lead in a 0.1 M solution of NaF, *s*-polarised light. The broken line is the portion of curve *1* which does not coincide with the calculated relationship because of the photo-emission mechanism of ER; the arrow shows the photo-emission threshold.

The presence of an interface infringes the translational invariance of the system and therefore invalidates the law of conservation of the normal component of the quasi-momentum: optical transitions between states in the same band of the metal therefore become allowed. The contribution of these transitions to the ER should be very sensitive to the structure of the surface: their importance was first pointed out in Ref. 44 and 56. The effect of within-band transitions on the ER signals was later examined in detail,[45, 57–59] using a modulation mechanism based on the effect of the surface potential on the amplitudes of the reflection coefficients of photo-excited electrons at the metal surface. The calculations included the elastic reflection of the electrons from the surface and the possible emission of electrons into the electrolyte.[2] The photo-emission threshold $\hbar\omega_0(E) = \hbar\omega_0 + eE$ (where $\hbar\omega_0$ is the emission threshold at $E = 0$) is a singularity in the electronic spectrum of the metal/electrolyte system. It has been shown[45,57] that this spectral feature is present in the electro-reflectance of the system, and a relationship between the photo-emission current and the ER signal has been obtained.

The existence of a relationship between the photo-emission and the ER offers the possibility of a more rational choice of mechanism for both these phenomena and of extracting more convincing information on the structure of the surface. By combining experimental data on photo-emission and on electro-reflectance we can determine the phases of the matrix elements for the photo-initiated transitions, $\gamma_s$ and $\gamma_p$, which contain information on the surface properties. The phase of $\gamma_p$ is determined by the properties of the wave functions of the metal electrons in their initial and their final state and by the selection rules of the photo-transition, and depends on the size of the region of the crystal in which the photo-electrons are generated; $\gamma_p$ is related to the phase of the reflection of the electrons on the Fermi surface from the metal surface.[60] If the photo-excitation is assumed to take place on the surface barrier (surface photo-emission mechanism) the parameter $\tan\gamma_p$ is close to zero.[60] A fairly large value of $\tan\gamma_p$ suggests that the main role in the photo-excitation is played by transitions on the ion cores of the metal near the surface.[61]

For comparison with experiment the most convenient quantities are the second differentials $(1/R)(d^2R/dE^2)$ which, like the first differentials $(1/R)(dR/dE)$, can be measured directly.[45] The expressions for the second differentials contain fewer parameters, and they identify more precisely the singularity at the threshold. Expressions of the following type have been used[57,60] for $(1/R)(d^2R/dE^2)$ in the region of the outer photo-emission threshold:

$$\frac{1}{R}\frac{d^2R}{dE^2} = A + B(\hbar\omega - \hbar\omega_0 - eE)^{1/2}\Theta(\hbar\omega - \hbar\omega_0 - eE) + C(\hbar\omega_0 + eE - \hbar\omega)^{1/2}\Theta(\hbar\omega_0 + eE - \hbar\omega). \quad (19)$$

Formula (19) is valid in the vicinity of the photo-emission theshold to with $[(\hbar\omega - \hbar\omega_0 - eE)/\hbar\omega_0]^2$. The parameters *A*, *B*, and *C* in (19) are functions of the frequency and of the angle of incidence: they are independent of *E* and can be expressed in terms of the bulk dielectric constants of the metal and of the electrolyte. The functions are given in an explicit form in Ref. 57.

We should stress that the appearance of the threshold singularity in the expression for $(1/R)(d^2R/dE^2)$ is qualitative and unrelated to the details of the calculation. Experimental detection of this singularity is convincing proof of the validity of the chosen physical mechanism of ER.

Formula (19) was obtained by assuming an infinitesimally small amplitude of the modulation $\delta E$. However, in experiments the quantity $\delta E$ is finite, and cannot be too small. Therefore, in view of the singularity in the function $(1/R)\cdot(d^2R/dE^2)$, we need to allow more carefully for the non-zero value of $\delta E$. An analysis of this problem[15] has shown that a finite value of $\delta E$ broadens the threshold peaks. In addition to this broadening, however, the fluctuations in the polarisation of the medium near the surface can also affect the dependence of $(1/R)(d^2R/dE^2)$ on *E* in the region of the photo-emission threshold. The prospect of characterising these fluctuations is very important in the study of electrode reactions. In order to separate the effect of the polarisation fluctuations we must either design experiments with a smaller modulation amplitude or study systems in which these fluctuations are large.

An analysis of published results[44] shows that the ER of indium, cadmium, lead, and tin includes a substantial contribution from the modulation mechanism considered here. In Fig. 6 the theoretical $(1/R_p)(d^2R_p/dE^2)$ curves are compared with experimental curves for indium in a 0.01 *N* solution of $Na_2SO_4$. In the calculation of the theoretical curves the moduli of the matrix elements were taken from independent photo-emission experiments.[62,63] The phase $\gamma_p$ of the matrix element of the optical transition excited by a field normal to the surface was treated as an adjustable parameter.

It was found that $\tan \gamma_p = -0.7$, i.e. that the surface mechanism of photo-emission does not play an appreciable part in the case of indium.

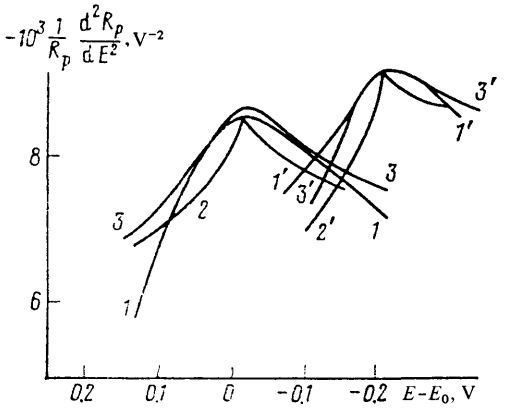



**Figure 7.** Effect of the modulation amplitude on the potential dependence of $(1/R_p)(d^2R_p/dE^2)$ for indium in a 0.01 *N* solution of $Na_2SO_4$ with $\theta = 70°$. The experimental curves *1* and *1'* were obtained at frequencies of 2.2 and 2.0 eV respectively, with $\delta E = 0.06$ V.[45] The theoretical curves are for the same frequencies without a correction for broadening (curves *2* and *2'*)[57] and with a correction for broadening (curves *3* and *3'*);[15] $\delta E = 0.06$ V.

Fig. 7, reproduced from Ref. 15, shows the effect of a finite modulation amplitude $\delta E$ on the threshold behaviour of the ER signal. We note that allowing for instrumental broadening in the theoretical curves brings them into satisfactory agreement with experiment.

## IV. ADSORPTION STUDIES

Adsorption on electrodes is one of the basic problems in electrochemistry, and its study is essential to a correct understanding of the mechanism of various electrode reactions. However, the traditional electrochemical methods of determining and studying adsorption, relying exclusively on the measurement of quantities of electricity (i.e. of capacitance), give only limited information. In particular, they cannot distinguish different paths for the transfer of charge between phases. In other words, the quantity of electricity used in the adsorption of the substance is difficult (and sometimes impossible) to separate from the quantity of electricity used in charging the double layer or in the associated Faraday process. The optical methods of studying adsorption discussed in this review usefully complement the traditional methods and offer direct information on the adsorbed species.

### 1. Determination of Adsorption on an Electrode Surface

Under reversible conditions the adsorption of particles on an electrode surface can be determined strictly by EOS methods.[30-32] Changes in the number of adsorbed particles

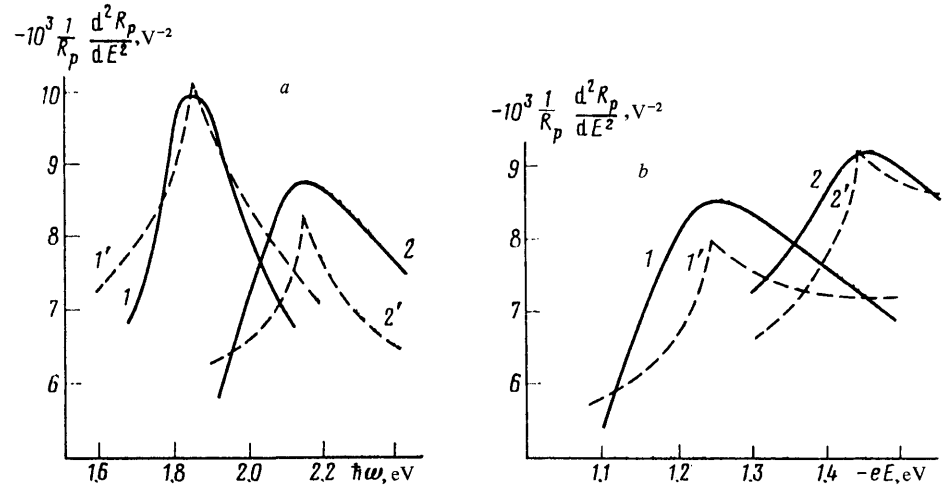



**Figure 6.** Comparison of experimental and theoretical plots of $(1/R_p)(d^2R_p/dE^2)$ against frequency (*a*) and potential (*b*). The full lines are experimental ER data for indium in a 0.01 *N* solution of $Na_2SO_4$ for $\theta = 70°$;[45] the broken lines are theoretical;[57] (*a*) curves *1* and *1'* correspond to a potential of −1.6 V, curves *2* and *2'* to −1.3 V (saturated silver chloride electrode); (*b*) curves *1* and *1'* correspond to a frequency of 2.2 eV, curves *2* and *2'* to 2.0 eV.

on the electrode produce changes in the number of particles in the diffusion layer, leading to the experimentally observed effect described by formulae (8). We shall illustrate these effects by considering a 1–1 electrolyte in which neutral molecules of an organic compound are dissolved. Changes in surface potential produce changes in the concentration of particles, both as a result of changes in adsorption and of electro-migration, and the electron-neutrality condition must be obeyed in the region of the diffusion layer. It is easy to show[30,31] that the quantities $dc_i(d)/dE$ and

$$\int_d^\infty dx_1[c_i(x_1)-c_{i0}]$$

which appear in Eqn.(8) can be expressed in terms of the adsorption of particles as follows

$$\frac{d}{dE}c_{org}(d)=\frac{1}{\xi_0}\frac{d\Gamma_{org}}{dE};\quad \frac{dc_A(d)}{dE}=\frac{1}{\xi_0}\left(\frac{\partial\Gamma_A}{dE}+\frac{t^+}{i\Omega F\hat{Z}}\right)$$

$$\frac{dc_B(d)}{dE}=\frac{1}{\xi_0}\left(\frac{d\Gamma_B}{dE}-\frac{t^-}{i\Omega F\hat{Z}}\right)$$

$$\frac{d}{dE}\int_d^\infty dx_1[c_{org}(x_1)-c_{org,0}]=\frac{d\Gamma_{org}}{dE}, \qquad (20)$$

where $t^+$ and $t^-$ are the transport numbers of the cations (A) and of the anions (B) in the electrolyte; $\hat{Z}$ is the total impedance of the electrode; $\Gamma_{org}$, $\Gamma_A$, and $\Gamma_B$ are the surface excesses of the organic compound, the cations, and the anions respectively, equal to the corresponding Gibbs adsorptions under equilibrium conditions; $F$ is the Faraday.

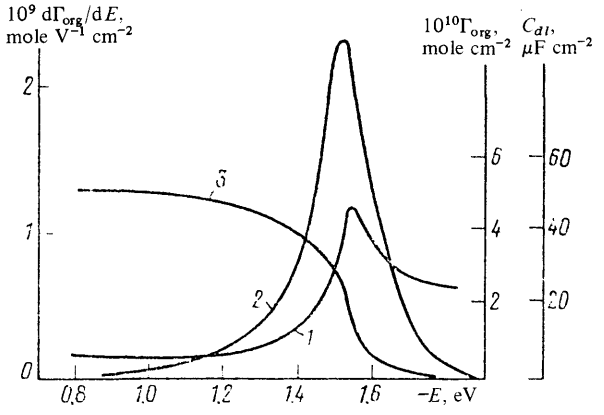



**Figure 8.** Dependence of the differential capacity (*1*), $d\Gamma_{org}/dE$ (*2*), and $\Gamma_{org}$ (*3*) on the potential of a lead electrode in a solution of 0.5 *N* $Na_2SO_4$ + 0.1 M n-$C_4H_9OH$; modulation frequency $\Omega$ = 375 Hz.[30]

By combining formulae (20) and (8b) it has been shown[30] that if the solution is free from organic impurities the differentials $d\Gamma_A/dE$ and $d\Gamma_B/dE$ can be determined as a function of the potential step from the experimental dependence of the impedance $\hat{Z}$ and of $d\delta/dE$ on $E$. The dependences of $d\Gamma_{A,B}/dE$ on $E$ thus obtained[30] for a lead electrode in a 0.5 *N* solution of $Na_2SO_4$ are consistent with the result of the Gouy–Chapman theory. If the solution contains an organic substance the above experiments are insufficient to determine $d\Gamma_{org}/dE$, and furthermore the dependence of $d\Gamma_{A,B}/dE$ on $E$ must be calculated theoretically.

The same paper[30] discusses the system consisting of a lead electrode in a 0.5 *N* $Na_2SO_4$ + 0.1 M n-$C_4H_9OH$ solution. The $d\Gamma_{org}/dE$ curve (curve *2* of Fig.8) was plotted from experimental results by using the dependence of $d\Gamma_{Na^+}/dE$ on $E$ calculated by the Gouy–Chapman theory.

Curve *3* in Fig.8, obtained by integrating curve *2*, is a plot of $\Gamma_{org}$ against $E$. The maximum value of $\Gamma_{org}$ is $5\times10^{-10}$ mole cm$^{-2}$, which agrees well with the limiting adsorption on mercury.

The contribution of the diffusion layer to ER was first detected[31] in the system indium electrode in a 0.5 *N* $Na_2SO_4$ + 0.1 M n-$C_4H_9OH$ solution. The most characteristic feature of this ER mechanism is the dependence of the signal on the modulation frequency of the surface potential [see formula (8)].

We should stress that the method gives direct information on adsorption by solid electrodes without an assumed model. Recent work[30–32] should provide a foundation for the development of adequate experimental techniques for determining adsorption by this method.

The method can be used also to study the kinetics of processes taking place near a surface. In particular, by combining it with the photo-emission method of modulating surface concentrations of particles[64] we can, in principle, study fast processes (up to the picosecond range).

## 2. Determination of the Microscopic Characteristics of Adsorbed Particles

The most important property of optical modulation methods is their ability to provide direct information on the electronic structure of adsorbed particles, on their vibrations, intermolecular interactions, charge transfer, and other microscopic characteristics. This is exactly the information which was lacking in studies of the electrode/solution interface.

Adsorption produces a large change in the electron spectrum of the metal/electrolyte system. As a result of their interaction with the metal the electronic levels of the adsorbed species (atoms and molecules) are both shifted (by an amount $\Lambda$) and broadened (by an amount $\Delta$). The parameters $\Lambda$ and $\Delta$ are the basic microscopic characteristics of the adsorbed particles. They depend on the electronic structure of the isolated particles, on the band structure of the metal, and on the potential step at the interface. A knowledge of $\Lambda$ and $\Delta$ is essential for the solution of many problems in the thermodynamics and kinetics of surface phenomena. In particular, the charge $q_a$ on the adsorbed particle[65] can be expressed through $\Lambda$ and $\Delta$:

$$q_a=Z_a+\frac{2}{\pi}\left[\arctan\frac{\hat{E}_0+\Lambda}{\Delta}-\frac{\pi}{2}\right], \qquad (21)$$

where $Z_a$ is the charge on the ion core of the adsorbed particle, and $\hat{E}_0$ is the position of the energy level of the isolated particle relative to the Fermi level of the metal.

The appearance of new energy levels creates new paths for the adsorption of light, based on electronic transitions from the filled levels of the adsorbed particle to the conduction band of the metal or to the external medium, from the metal to the empty levels of the adsorbed particle, and between the levels of the adsorbed particle. The corresponding changes in the optical properties of the system can in principle be determined by spectroscopic modulation methods.

In order to extract the relevant information from spectroscopic data we need to know the relation between the functions $\Delta\varepsilon_{2(3)}$ and $\Delta\varepsilon^{-1}_{(1)}$ which appear in Eqn.(6) for the experimentally measurable quantities, and also between the parameters $\Lambda$ and $\Delta$.

Let us consider first the case of small interactions between the adsorbed particles, so that $\Delta\varepsilon_{2(3)}$ can be assumed to be proportional to the number of adsorbed particles $N_a$. For an adatom with one $s$ level lying below the Fermi level of the metal the imaginary part of $\Delta\varepsilon_{2(3)}$ can be expressed as[66,67]

$$\Delta\varepsilon''_{2(3)}(\omega, E) \sim \frac{N_a}{\omega^4}\rho(0)\left[\arctan\frac{\hat{E}_0+\Lambda+\hbar\omega}{\Delta} - \arctan\frac{\hat{E}_0+\Lambda}{\Delta}\right], \quad (22)$$

where $\rho(0)$ is the density of states having unit orbital momentum on the Fermi surface. In this case the quantity $\Delta\varepsilon''_{2(3)}$ refers to an optical transition from a filled (or partially filled) level of the adatom to the conduction band of the metal. The real part $\Delta\varepsilon'_{2(3)}$ is expressed in terms of $\Delta\varepsilon''_{2(3)}$ by using the Kramers–Kronig relation.

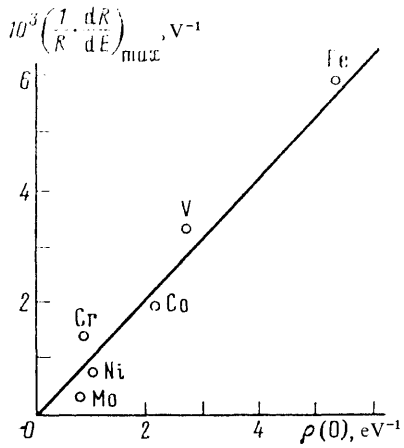



**Figure 9.** Dependence of the maximum in the ER signal $[(1/R)(dR/dE)]_{max}$ on the density of electronic states at the Fermi level of the metal $\rho(0)$ (calculated per metal atom).[68]

Similar formulae have been obtained[66,67] for transitions from filled states of the metal to empty levels of the adatoms. It follows from (22) that the function $\Delta\varepsilon''_{2(3)}$ has a maximum in the region of the frequency $\hbar\omega_{max} = |\hat{E}_0 + \Lambda|$, and is asymmetric with respect to this frequency. The physical meaning of the formula (22) is relatively simple: the imaginary part of the dielectric permeability tensor is proportional to the product of the number of filled initial states (the term in square brackets) and the number of final states $\rho_0$ into which the transition can take place. Since $\Delta\varepsilon'_{2(3)}$ is related to $\Delta\varepsilon''_{2(3)}$ by the Kramers–Kronig transformation we can easily show that at $\omega \cong \omega_{max}$ we have $|\Delta\varepsilon'_{2(3)}(\omega)| \ll |\Delta\varepsilon''_{2(3)}(\omega)|$. Therefore it follows from (6a) and (22) that $\Delta R_S/R_S$ goes through a maximum at $\omega \cong \omega_{max}$, so that in the adsorption of the same atoms on different metals $(\Delta R_S/R_S)_{max}$ is proportional to $\rho(0)$. This behaviour of $(\Delta R_S/R_S)_{max}$ has been observed experimentally[68] in a study of the adsorption of water on various transition metals (see Fig.9).

This theory has been applied[69] to the results of experiments on the adsorption of atomic oxygen on platinum immersed in a solution of 0.01 $N$ $H_2SO_4$ + 1 $N$ $Na_2SO_4$ at a potential of $E$ = 900 mV relative to the normal hydrogen electrode. The results[69] clearly show a characteristic maximum in the ER signal at frequencies in the range 1.5 eV < $\hbar\omega$ < 3 eV. By comparing these curves[69] with the formulae of Refs.66 and 67 we conclude that in the adsorption of oxygen on platinum (at 0.5 monolayer coverage) the highest initially unoccupied 2$p$ level of the oxygen atom is converted into a resonance level lying 2 eV below the Fermi level of platinum and having a width $\Delta$ = 0.3 eV.

At the light frequencies used in ER experiments ($\hbar\omega \cong$ 1.5 to 4.5 eV) electronic transitions to the outer medium are possible for adatom levels lying close to the Fermi surface. We have known[70] that $d\Delta\varepsilon''/dE$ can vary quite sharply near the frequency $\hbar\omega \cong \hbar\omega_e(E) = -\hat{E}_0 - \Lambda + \hbar\omega + eE$, which is the threshold for the transition of the electron from the adatom level of energy $\hat{E}_0 + \Lambda$ to the outer medium. The form of the ER signal is strongly dependent on the symmetry of the wave function of the highest filled state of the adatom.

The expression (6b) for $(1/R_p)(dR_p/dE)$ includes, as well as $d\Delta\varepsilon_{(2,3)}/dE$, the quantity $d\Delta\varepsilon^{-1}_{(1)}/dE$, which can be expressed as

$$\frac{d}{dE}\Delta\varepsilon^{-1}_{(1)} = -\int dx\,dx'\,dx''\,dx'''\varepsilon^{-1}_{(1)}(x, x')\left[\frac{d}{dE}\varepsilon_1(x', x'')\right]\varepsilon^{-1}_{(1)}(x'', x'''). \quad (23)$$

Calculations by this formula are cumbersome in general. However, a useful estimate of $d\Delta\varepsilon^{-1}_{(1)}/dE$ can be obtained by the formula

$$\frac{d}{dE}\Delta\varepsilon^{-1}_{(1)} \simeq -\frac{1}{\varepsilon^2_{eff}}\frac{d\,\Delta\varepsilon_1}{dE}, \quad (24)$$

where $\varepsilon_{eff}$ is a parameter independent of $E$ and physically equivalent to the dielectric constant of the medium at the adsorption site of the particle. If the adsorbed particle is sufficiently near the metal the parameter $\varepsilon_{eff}$ can be replaced by the dielectric constant of the metal.

The effects so far discussed are associated with optical transitions between the levels of an adsorbed particle and the conduction band of the metal, and are usually observed in ER experiments with $s$- and $p$-polarised light, i.e. their polarisation selectivity is not high. This property can be explained by the different symmetries of the electronic states of the metal with energies close to the Fermi level. As a result, whatever the direction of the applied electromagnetic field, we find an allowed optical transition from a level (or to a level) of the adsorbed particle having the prescribed symmetry. However, it has been shown experimentally[71,72] that adsorption can also cause changes in the ER spectra in which the selectivity is marked (the changes in the ER signal caused by adsorption being stronger in $p$-polarised light than in $s$-polarised light).

The selectivity of ER is partly due to the bulk optical properties of the metal. The electromagnetic field experienced by the particle is proportional to $1 + r^F_s$ in the case of $s$-polarised light, and in the case of $p$-polarised light the normal component of the active field is proportional to $(1 + r^F_p)\sin\theta$. In the optical frequency range for most metals $\varepsilon'_m \ll -1$, and therefore $r^F_s$ is close to $-1$ and $r^F_p$ is close to 1. Therefore if the angle of incidence is not too small the field acting on the particles is substantially greater for $p$-polarisation than for $s$-polarisation of the incident wave. The selectivity of the ER can also be attributed to the increase in the normal component $\mathscr{E}_1$ of

the electromagnetic field near the surface. We note that near the surface the field is $\mathscr{E}_1(x_1) = D_1(0)/\varepsilon(x_1, \omega)$, where $D_1(x_1)$ is the normal component of the electromagnetic induction, which varies only slowly near the surface. Therefore in the neighbourhood of the point $x_1 = x_1^0$, where $\mathrm{Re}\,\varepsilon(x_1^0, \omega) = 0$, the intensity of the field $\mathscr{E}_1(x_1)$ increases (see Fig. 2) if the absorption $\varepsilon''(x_1^0, \omega)$ is small at this point. These effects are not directly related to adsorption, and are typical of any microscopic mechanism of ER and ERP. As a result, signals measured in *p*-polarised light are usually stronger than the corresponding signals in *s*-polarised light.

Adsorption can contribute additional polarisation selectivity, due to the optical transitions between the energy levels of the adsorbed particles. In intramolecular transitions the absorption of light is characteristically related to the orientation of the field relative to the symmetry elements of the molecule. Furthermore, adsorption perturbs the symmetry of the states of the molecule, the changes being most marked in a direction normal to the metal surface. This makes available to the adsorbed particle transitions which are forbidden to the same particles in solution, but these transitions can only take place under the influence of the component of the electric field of the light wave normal to the surface (i.e. for *p*-polarisation). Hence the effect shows a strong polarisation selectivity.

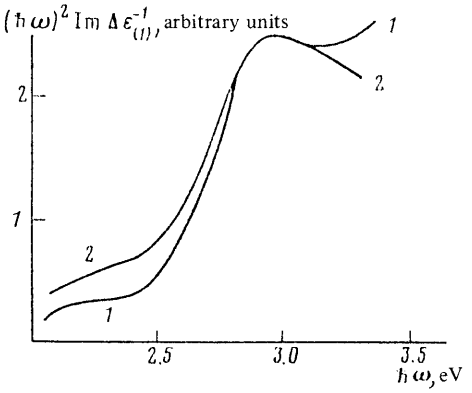



**Figure 10.** Contribution to the ER of lead from the adsorption of aniline from a solution of 0.1 *N* $Na_2SO_4$ + 0.0016 M $C_6H_5NH_2$:[73] *1*) experimental plot of the difference between the signals for the above solution and for a solution not containing aniline; *2*) calculated curve.

We have studied[73] the ER of lead in a solution of 0.1 *N* $Na_2SO_4$ + $1.6 \times 10^{-3}$ M $C_6H_5NH_2$, allowing for intramolecular optical transitions in the aniline molecules adsorbed on the lead surface. The ER spectra of the lead + aniline system differ from those of pure lead by the appearance of a new minimum in the ER signal at $\hbar\omega = 2.8$ eV in *p*-polarised light, whereas in *s*-polarised light the change in the signal is only slight.[71,72] At this aniline concentration and at a potential $E = -0.7$ V (relative to the silver chloride electrode) the adsorbed aniline molecules are arranged mainly parallel to the lead surface, and furthermore the rate of change in the number of adsorbed molecules oriented normally to the surface is almost zero. This suggests that only adsorbed molecules parallel to the metal surface can affect the ER signal.

Partial charge transfer from the metal to the molecule has been detected electrochemically for the "parallel" adsorption of aniline. Therefore in analysing the experimental results[73] the $^3B_{1u}$ level (which is unoccupied in the molecules in solution) was assumed to be partially filled in adsorption. In this case the observed minimum in the ER signal can be attributed to an optical transition from this level to the $^3B_{2u}$ state. We should stress that this transition is forbidden in the bulk and becomes allowed only under the influence of the normal component of the electric field of the *p*-polarised light, which perturbs the symmetry of the adsorbed molecule in relation to its plane. The symmetry of the initial molecule allows only transitions between these levels in the relevant frequency region.[74]

Theoretical calculations are compared with experimental data in Fig. 10. In the processing of the experiment we found the initial and the final state relative to the Fermi level to be $E_i = 0.4$ eV and $E_f = 2.8$ eV, and their widths to be $\Delta_i = 0.3$ eV and $\Delta_f = 0.4$ eV. From these values of $\hat{E}_{i(f)}$ and $\Delta_{i(f)}$ the charge transfer to the adsorbed molecule can be calculated. By using formula (21) we find $q \approx 0.2$, which is consistent with electrochemical results.

### 3. Effect of Coverage on the ER Spectra

Experimental results[50,75–83] show that in many cases the ER signal is proportional to the differential with respect to potential of the number of adsorbed particles $N_a$ per unit surface area, $dN_a/dE$, even at coverages close to a monolayer. For example, in experiments on the dependence of $\Delta R/R$ on the surface coverage of Au and Ag by Pb, Tl, and Cu [82] it was found that in the frequency region where the spectral changes resulting from adsorption do not include structural effects from optical transitions the signal is linearly dependent on $N_a$ at all coverages up to monolayer coverage.

A recent reviewer[84] has explained these results through the effect of the adsorbate on the optical properties of the substrate. One possible mechanism of this effect is a change in the plasma component of the ER due to partial charge transfer between the adsorbed particle and the electrode during adsorption (chemisorption). Electrons injected into the metal influence the density of electrons in the conduction band near the interface and contribute to the plasma component of the ER. In this case the expression for $d\Delta\varepsilon_{2(3)}/dE$ becomes[73]

$$\frac{d}{dE}\Delta\varepsilon_{2(3)}(\omega, E) = (\varepsilon_{el} - \varepsilon_f)\left[C_a - \frac{d}{dE}(q^{tr}N_a)\right]/eN, \qquad (25)$$

where $C_a(E)$ is the differential capacity of the double layer in the presence of the adsorbed molecules; $q^{tr}$ is the charge of the electrons transferred to the electrode; in the case of charge transfer to the molecule the parameter $q^{tr}$ in Eqn. (25) appears with a minus sign. The ER spectrum produced by this mechanism is similar to the plasma ER spectrum of the pure metal and is determined by the frequency dependence of the dielectric constant of the metal. When $q^{tr}$ is only weakly dependent on $N_a$ the parameter $\Delta R_s/R_s$ is proportional to $N_a$. It also follows from formula (25) that (in contrast to the plasma ER from a pure surface) in this case the quantity $d\Delta\varepsilon'_{2(3)}/dE$ can be either positive or negative. A change in sign of the plasma component of the ER signal ("inversion" of the plasma ER) has been reported[85] for the adsorption of hydrogen on platinum. Clearly, this observation can be explained by the suggested mechanism.

At frequencies for which the $\Delta R/R$ spectrum is determined by the optical properties of the adsorbate we expect a non-linear dependence of the signal on the coverage of the surface. The effect has been observed in experiments on the adsorption of Cu on Pt and Pb on Pt,[80] and in many other systems.[84]

To explain the experimentally observed non-linearity of the dependence of $\Delta R/R$ on $N_a$ we must allow for the mutual effects between adsorbed particles. In optical experiments these effects may arise mainly for two reasons. On the one hand, because of the effect of adsorbate–adsorbate interactions at higher coverages on the density and other characteristics of the electronic states in the surface layer; the resonance levels of individual adsorbed particles are shifted, their width $\Gamma$ is changed, and new structures appear, such as a surface band of resonance states.[86] The result is a change in the part of the dielectric permeability tensor (10) corresponding to optical transitions. No detailed discussions of these effects have been published so far: we can only refer to a calculation[87] of $\Delta\varepsilon$ for a metal surface covered with an ordered two-dimensional array of atoms, in which no allowance was made for the interaction with the metal. Starting from the expression for the dielectric permeability tensor (10), (11) in the RPA these workers showed that van Hove singularities in the two-dimensional band structure of the surface layer of atoms can lead to qualitative differences in the reflection coefficients.

On the other hand, at high enough coverages and in the appropriate frequency range the corrections for the local field due to the presence of adsorbed particles may become important. In spite of the many publications already devoted to this topic[83,88–93] the problem is still far from clear. In most of the work so far the surface layer is modelled by a two-dimensional array of dipoles interacting with the light. The results obtained from these models have already been discussed in several reviews.[5,6,83]

A general shortcoming of all the published local field calculations is their reliance on dipole models, which cannot take account of the properties of the adsorbed particles at optical frequencies.[65,94–96] Furthermore, local field effects are important in the same frequency region as the effects caused by changes in the electronic structure of the adsorbed particles as the coverage is increased. This greatly complicates the problems of separating the contributions from different effects. No great reliance can therefore be placed on published comparisons[88–93,97,98] of the local field theory with experiment.

## V. ELECTRO-REFLECTION FROM SINGLE CRYSTALS

Until recently ER spectra had been measured mainly on polycrystalline electrodes, with a corresponding loss of information (due to the averaging of the results over all crystallographic directions) and of ease of interpreting the results. Experimental studies of the ER of monocrystals have been reported more recently.[99–109] It was shown that on metals such as Ag, Au, and Cu the ER spectra and their potential dependence depend on the crystallographic face used for the measurement. The effect is not surprising, since the differential capacity, the work function, the matrix elements of the expression for the photo-emission, and the two-dimensional sections of the Brillouin zones are all different on different faces.

Anisotropy of the ER spectra on a clean (110) face of Ag, Cu, and Au crystals was also observed,[99–109] i.e. a dependence of the ER on the orientation of the electric vector of the incident wave with respect to the crystallographic axes of the metal crystal. The anisotropy of the ER is most marked at frequencies close to those of allowed band-to-band transitions.[106] It has been suggested[106] that this effect arises from the anisotropy of bulk band-to-band transitions modulated by the low-frequency field of the double layer.

This phenomenon has been described by using the concepts developed in the theory of ER by semiconductors.[110,111] The double layer field has been assumed[106] to relieve the degeneracy of the bulk states in the region of the critical points lying far from the centre of the Brillouin zone. Under these conditions the matrix elements of the band-to-band transitions become dependent on the angle between the principal symmetry axis at the critical point and the electric vector of the electromagnetic field and of the field of the dipole layer. Furthermore, a model based on the modulation of indirect band-to-band transitions has also been used.[8,99,100] In these studies the azimuthal anisotropy of the ER and the differences in the ER spectra on the (111) and (110) faces of a silver crystal in $s$- and $p$-modulated light were qualitatively accounted for. However, there are serious objections to the application of the suggested mechanism (modulation of the bulk characteristics) to metals.

In contrast to the above approach, based on the anisotropic properties of the bulk states, there have been attempts to relate the azimuthal anisotropy effect to the properties of the surface states of the metal.[109,112] It has been shown theoretically[113] that at the contact between a (110) silver face and an electrolyte a surface band having $s$ symmetry is created from the highest level of the bulk band near the Fermi level: this relieves the degeneracy of the $p$ states in the bulk band. The bottom of the surface band lies 4 eV above the Fermi level. As a result the matrix element of the transition between states in the bulk band and in the surface $s$-band depends on the direction of the electric component of the electromagnetic field in the plane of the surface: it is zero for $\bar{\mathscr{E}} \parallel \langle 110 \rangle$ and non-zero for $\bar{\mathscr{E}} \perp \langle 110 \rangle$. The quantity dependent on the potential step at the surface is now the bottom of the surface band $\hat{E}_s(E)$. We note that comparison with experiment[109] reveals a strong dependence of $\hat{E}_s$ on $E$: $(1/e)(dE_s/dE) \cong 3-4$ for the (110) face of a silver crystal. This effect has not been explained satisfactorily so far.

Several papers[80,103,114–117] stress the important role of adsorption factors in the crystallographic and azimuthal anisotropy of ER phenomena. Azimuthal anisotropy in the observed on metal faces which showed no anisotropy in the absence of the adsorbate. A possible explanation is the formation of an anisotropic layer at submonolayer coverages. For example, the adatoms can form regular two-dimensional arrays in which the cell dimensions in two mutually perpendicular directions are very different. At near-monolayer coverages, when the adsorbed lattice is matched to the lattice of the substrate and is therefore isotropic, the ER anisotropy should disappear. This type of dependence of the ER signal on coverage has been observed experimentally.[110] Further theoretical and experimental studies of ER anisotropy are needed to clarify various problems in the structure of adsorbed layers.

## VI. I.R. SPECTROSCOPY

Important information on the properties of the metal/electrolyte interface can be obtained by using electrochemical modulation in the i.r. region of the spectrum. By analysing the resulting vibrational spectra we can identify the adsorbed species, determine their mutual arrangement and

their position relative to the atoms of the substrate, and measure their bond lengths and other parameters.[118,119]

However, *in-situ* electrochemical experimentation in the i.r. region of the spectrum is complicated by the absorption of light by the electrolyte under these conditions. As a result, very few attempts to combine i.r. spectroscopy with electrochemistry were reported in recent years, but more recently some significant progress has been made. In a series of investigations[120–123] modulation methods were successfully applied to the study of a platinum electrode in a thin-layer cell. Two different experimental methods were used. In the first the external modulation was supplied through the surface potential step, i.e. this method was essentially the ER technique applied to the i.r. region. The second method, previously used at the metal/vacuum interface, relied on modulation of the polarisation of the incident light. In this case the measured quantity is the difference between the reflection coefficients of *p*- and *s*-polarised light. Unlike the ER method, this technique can be used to determine characteristics of the surface which are not dependent on the potential.

In the i.r. spectra region the vibrational degrees of freedom provide the major contribution to the dielectric permeability tensor. The process obeys the "surface selection rule",[123–125] i.e. the reflection coefficients of the light are unaffected by the vibrations of the adsorbed molecules in directions parallel to the metal surface. The need for this selection rule has been explained as follows. Firstly, as was stated above (p.7), the component of the electric field of the light wave normal to the electrode surface, which acts on the adsorbed molecule, is much greater than the components parallel to the surface (see Fig.2). We should stress that this effect is even more marked in the i.r. than in the visible region. Secondly, it has been suggested[124] that far from the metal surface the fields generated by a dipole parallel to the surface and by its image cancel each other out. However, we note that these conclusions[124] apply only to elastic light scattering, and that very different results may be obtained by allowing for spatial dispersion (screening of the charges), which causes qualitative changes in the pattern of charge distributions.[126] Another possible reason for the enhancement of the effect in *p*-polarised light, mentioned above, has so far been ignored in the publications on i.r. spectroscopy: the increase in the amplitude of the normal component of the field acting on an adsorbed particle resulting from the disappearance of the real part of the dielectric permeability of the system in the vicinity of the surface.

The formulae (6), which are applicable to experiments in the i.r. region, are greatly simplified by the surface selection rule, the terms containing $\Delta\varepsilon_{2(3)}$ effectively vanishing. As a result only the reflection coefficient of the *p*-polarised light is affected by adsorption.

## VII. SURFACE PLASMON SPECTROSCOPY

A special type of electromagnetic surface wave (surface polaritons) can exist on solid surfaces: in metals these waves are known as surface plasmons. Surface plasmons are localised near the phase boundary and are propagated along the boundary with a wave vector $\mathbf{k}_\parallel = \mathbf{k}_S(\omega)$, related to the frequency $\omega$ by the dispersion law $\omega_S = \omega_S(k_\parallel)$. The dispersion law of surface plasmons is very sensitive to the state of the boundary surface. In electrochemical applications it is important to note that this law depends on the surface potential, on the adsorption, and on the degree of non-uniformity of the surface. The dependence of $\omega_S$ on the surface potential was first pointed out in Ref.127. A detailed experimental study of the dependence of $\omega_S(k_\parallel)$ on the potential for silver and gold electrodes in a 0.5 M solution of $NaClO_4$ was later reported.[128,129] Measurements were made both on polycrystalline and on monocrystalline electrodes at potentials believed to exclude specific adsorption. The dependence of $\omega_S$ on $E$ was found to change sharply (see Fig.11) near the point of zero charge. For silver at potentials more positive than the point of zero charge the quantity $\hbar\omega_S$ decreases at the rate of $d(\hbar\omega_S)/dE \cong -2 \times 10^{-2}$ eV $V^{-1}$, whereas at potentials more negative than the point of zero charge $\hbar\omega_S$ is practically constant. Similar experiments in electrolytes containing ions having different polarisabilities gave almost the same results. This means that the effect is produced by the changes in the electronic properties of the metal induced by the changes in the potential step. The effect has been explained[21,130] by postulating a plasma model of the dielectric permeability (12), and the electron density near the point of zero charge was expressed as

$$\rho(x_1) = \rho_0(x_1) - \frac{Q}{e} f(x_1); \int dx_1 f(x_1) = 1, \qquad (26)$$

where $\rho_0(x_1)$ is the distribution of electron density at the point of zero charge ($Q = 0$), and $f(x_1)$ is independent of $E$.

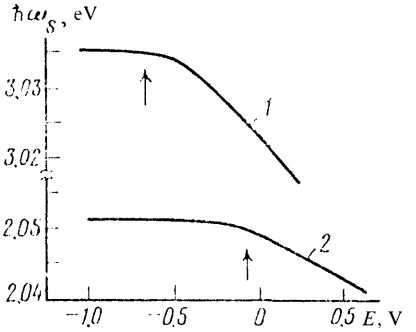



**Figure 11.** Dependence of the surface plasmon energy on the potential $E$ for polycrystalline Ag (*1*) and Au (*2*) in a 0.5 M solution of $NaClO_4$.[128] $E$ is measured from the potential of the saturated calomel electrode; the arrows denote the points of zero charge.

Explicit forms of the functions $\rho_0(x_1)$ and $f(x_1)$ are given in Ref.131. For the quoted assumptions, the following expression for $d(\hbar\omega_S)/dE$ was obtained:

$$\frac{d(\hbar\omega_s)}{dE} = (\varepsilon_m - \varepsilon_{el}) \frac{C_{dl}(E)}{eN} k_\parallel \hbar B(\omega_s^0) \times \times \left\{1 - \varepsilon_{el}\varepsilon_m \int dx_1 \frac{f(x_1)}{[(\varepsilon_m - \varepsilon_{el})\rho_0(x_1)/N + \varepsilon_{el}]^2}\right\}, \qquad (27)$$

where

$$B(\omega_s^0) = \frac{2(\varepsilon_{el})^{1/2}(-\varepsilon_m)^{3/2}}{(\varepsilon_m - \varepsilon_{el})[\varepsilon_{el}\, d\ln\varepsilon_m/d\omega + 2(\varepsilon_{el} + \varepsilon_m)/\omega]}.$$

Allowing for the steep increase in the differential capacity $C_{dl}(E)$ of this system near the point of zero charge§, Eqn. (27) is qualitatively consistent with experimental results.[128,129]

However, retaining only the first-order terms in $Q$ in the expression for the electron density $\rho(x_1)$ [Eqn.(26)] is justified only at low surface charges (for $Q < 10$ μC cm$^{-2}$). Therefore Eqn.(27) is valid only in the immediate vicinity of the point of zero charge. To determine the spectrum of surface plasmons over the whole range of potential used in the experiments[128,129] we must allow for the function $f(x_1)$ in (26), and in particular for the dependence of the electron density ($\beta$) on $E$. As was stated above, effects associated with the reorientation of solvent molecules in the double layer may be important in this context. Furthermore, at potentials lying to the right of the point of zero charge oxidation of the electrode is in general possible, and this can substantially affect the $\hbar\omega_s(E)$ dependence. Thus further theoretical and experimental studies are needed to establish unambiguously the electronic structure of the interface between a silver electrode and a solution of an indifferent electrolyte.

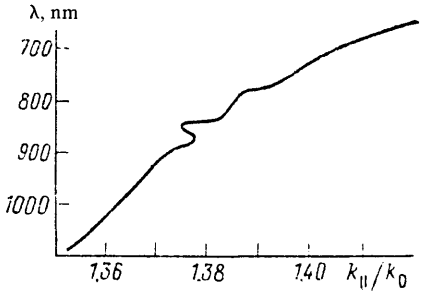



**Figure 12.** Dispersion curve for the (111) surface of a silver electrode in a 0.1 M solution of NaCl after six activation cycles in the presence of pyridine; $k_0 = \omega/c$.[141]

More than 10 papers have already appeared on the application of surface plasmon spectroscopy to the study of adsorption at metal/air[133–136] and metal/electrolyte interfaces[137–141] (see also the review in Ref.12). The most revealing experiments are the measurements of the frequency dependence of $k_s$ (or of the angle dependence of $\omega_s$) at different potentials. Those measurements were made[141] on a (111) silver face in a solution of 0.1 M NaCl + $10^{-2}$ M pyridine: they showed that silver–pyridine complexes are formed on the surface, and that they absorb in the region of $\hbar\omega \cong 1.9$ eV. The formation of an absorption region in the surface layer is responsible for some unusual effects in the dispersion curve for the surface plasmons (Fig.12). The double singularity arises from the splitting of the surface plasmon spectrum, which occurs when the resonant frequency for $\Delta\varepsilon_{2(3)}$ or $\Delta\varepsilon^{-1}_{(1)}$ falls into the surface plasmon region. These features in the dispersion curve have been predicted theoretically[142] by using a three-layer model with an absorption region in the surface layer.

Another application of surface plasmon spectroscopy in electrochemical studies should be mentioned. We know from low-energy electron diffraction experiments at the metal/vacuum interface that adsorbates can form superlattices on the surface at sub-monolayer coverages. A similar effect has been observed[143,144] in adsorption at the metal/electrolyte boundary. For example, identical geometrical structures are observed by comparing the adsorptions of Pb on a (111) silver surface in a vacuum and in an electrochemical cell.[145] at low coverages $\theta_a$ ($0 < \theta_a < 0.2$) the lead atoms are randomly adsorbed on the surface, but for $0.2 < \theta_a < 0.5$ they form a superstructure of the ($\sqrt{3} \times \sqrt{3}$) type, which disappears at still higher coverages.

The reflection of light from a surface bearing an ordered structure should create surface plasmons with a predetermined value of the wave vector. The effect has been observed[146] in measurements of the differential reflectance ($\Delta R/R$) spectra of a lead-covered (111) silver face. It was shown[146] that at the coverages corresponding to the formation of a superlattice a sharp minimum (denoting the formation of surface plasmons) appears in the $\Delta R/R$ spectrum. The minimum is not observed at low coverages, or at full monolayer coverage. This very important result demonstrates the possibility of obtaining direct information by optical methods on the geometric structure of an adsorbed layer at the metal/electrolyte interface. However, as the authors themselves point out,[146] more experimental results and theoretical studies are needed, and far-reaching conclusions would be premature at present.

## VIII. SURFACE-ENHANCED RAMAN SCATTERING

Studies of surface-enhanced Raman scattering occupy a central place in electrochemical optical spectroscopy. The phenomenon, discovered in electrochemical experiments, has stimulated a great deal of interest, both because of its unusual features and through the prospect of new and meaningful ways of studying surfaces. Hundreds of papers, and several reviews, have been written on this topic in the last five years.[162–166,176] The interest shown in this phenomenon is reflected by the original English name ("giant Raman effect") and by the name applied to it in the Soviet literature (anomalously strong Raman scattering, ASRS).

The first report of a Raman scattering (RS) spectrum from pyridine adsorbed on silver was by Fleischmann and coworkers.[147] However, no attempt was made to compare the intensities of the surface and the bulk effect, and the special aspects of the phenomenon were not revealed. Subsequent (though almost simultaneous) publications[148–153] clearly showed that this spectrum is much stronger than the bulk RS spectrum of pyridine. Enhanced Raman effects were soon observed in a large number of systems: aromatic and heterocyclic molecules adsorbed on silver,[148,154] ions adsorbed on silver,[155] and molecules adsorbed on gold and copper electrodes.[156,157] Some very recent papers[158–160] discuss the ASRS from water molecules adsorbed on silver.

The highest enhancement, observed for pyridine adsorbed on a silver electrode, was estimated to be six orders of magnitude. It had been previously assumed that all the adsorbed molecules contribute to the Raman scattering. However, recent work has shown[161] that only a fraction of a monolayer of pyridine is involved in the scattering process. Therefore the enhancement factor could even be 1 or 2 orders

§ A change in $Q$ from −20 to 4 μC cm$^{-2}$ increases the differential capacity from 15 to 130 μF cm$^{-2}$.[132]

greater. This enhancement effect allows us to study the vibrational characteristics of molecules close to the surface even in the presence of many of the same molecules in the bulk of the electrolyte.

Two explanations have been proposed for the anomalously high intensity of the surface RS. The first relies on the increase in the electromagnetic field near the surface. On an electrode surface, which is rough on a microscopic scale, such an increase can take place through the excitation of surface plasmons.[167,168] This mechanism is controlled mainly by the properties of the metal and of its surface: it is relatively insensitive to the specific characteristics of the adsorbed molecule, and it can therefore be expected to enhance the RS of any molecule which is close enough to the surface. We calculate[169] that the enhancement by this mechanism cannot be greater than two orders of magnitude. A mechanism[171,175] which strengthens the normal component of the electromagnetic field is based on the fact that the real part of the dielectric permittivity of the system vanishes at the point $x_1^0$ [$\mathrm{Re}\varepsilon(x_1^0, \omega) = 0$]. This mechanism will be effective in RS if the adsorbed molecule is at a distance of approximately $x_1^0$ from the surface.

The second explanation of the enhanced RS effect depends on the possibility of optical transitions of the electrons from localised surface states (which interact with the vibrations of the adsorbed molecules) into unoccupied states of the conduction band of the metal. It is usually assumed that the localised states are hybridised states of adatoms on the metal electrode and adsorbed molecules.[160,170] Under these conditions resonance Raman scattering (RRS) can take place. However, we should stress that in the case of surface RS the enhancement is due not so much to the fact that the energy of the exciting light is close to the resonance energy (since the state of the adatom–molecule complex is relatively wide) as to the high density of the intermediate states lying near the middle of conduction band of the metal.[171]

Some experimental results can only be explained by the resonance RS hypothesis. For example, on the faces of Ag single crystals no enhancement is observed, and a special pre-treatment of the electrode surface is needed to produce the effect.[170] The treatment consists in alternate formation of a layer of AgCl and reduction to Ag. This produces a large number of Ag adatoms. It has been shown[170,172,173] that the parameters of the absorption band of the adatoms are the same whether they are calculated from the dependence of the ratio of the Stokes and anti-Stokes line intensities on the wavelength of the exciting light or from the ER spectra. This justifies attributing the enhanced RS signal to the presence of adatoms. An irreversible quenching of the enhancement in the Ag + pyridine system has been reported.[174] The effect was produced by applying a cathodic pulse to the surface, causing desorption of the pyridine. At the end of the pulse the RS signal was only 5% of the initial signal, in spite of the readsorption of the pyridine. This observation can be explained by irreversible breakdown of the adatom–adsorbate complexes. Additional evidence in support of the adatom hypothesis is given in Ref.163.

The importance of a knowledge of the angle and polarisation dependence of the Raman scattering cross-section in studies of the mechanism of enhancement has been stressed.[125,171]

Enhanced Raman scattering has already been successfully applied in many laboratories to the study of adsorption. The effect of the surface potential on the orientation of molecules with respect to the electrode surface has been demonstrated by ASRS studies.[152,154] A strong dependence of the shape of the RS line of water on the type of cation and on the pH of the electrolyte has been noted,[160] and it has been suggested[160] that the adsorbed water molecules which contribute to the Raman scattering are not reoriented under the influence of the potential step.

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The results considered in this review convincingly show that EOS methods can provide important information on the microscopic structure of the metal/electrolyte interface and on processes taking place near this interface. EOS methods and their interpretation are now being rapidly developed, and it may be useful to list some of the directions of current work. In methods whose microscopic mechanism is relatively well understood (for example, electro-reflectance) we need many more experimental results, and their interpretation, especially for systems including monocrystalline electrodes. EOS studies of phase transitions in near-surface regions are also of great interest.

The possibilities offered by the spectroscopy of surface plasmons and of other surface excited states (polaritons) have been inadequately exploited so far. It would be interesting, for example, to establish the influence of surface plasmons and polaritons on electrochemical reactions.

The search for a comprehensive explanation of the surface enhancement of Raman scattering by adsorbed molecules is currently of interest. We believe that non-linear processes may play an important role in these phenomena. More data not only on the frequency dependence but also on the polarisation and angular dependence of the intensity of the surface Raman scattering of light are needed to solve these problems.

Second harmonic generation at the boundary between two media and its amplification on rough surfaces are currently of interest.[180–183] This phenomenon is closely related to surface Raman scattering, and is potentially very attractive for studying the microscopic structure of surfaces.

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