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ON THE THEORY OF SURFACE ENHANCED RAMAN SCATTERING

A theory of surface-enhanced Raman scattering is proposed. Proceeding from an assumption that plasmons serve as intermediate states, a careful account is taken of the molecule-plasmon interaction, which is supposed to be of a resonant character. The light-plasmon interaction, possible only via roughness, is employed according to the perturbation theory. The theory indicates the necessary order of the enhancement coefficient and its concentrational saturation. The expressions for the frequency and angular dependences of the effect have been obtained.

1. The surface enhanced Raman scattering (SERS), discovered in 1977, is now very intensively studied experimentally as well as theoretically. The effect lies in a 10^4 — 10^6 times enhancement of the scattering cross-section of the molecules adsorbing on some metals (Ag, Au, Cu) [1-3]. Such great interest is due to undoubtedly ample application possibilities of SERS both for scientific purposes (single-molecule spectroscopy and manifestations of various surface effects) and for practical analysis of microdoses of substance.

Although no comprehensive understanding of SERS nature has been achieved yet, the basic role of roughness on metal surface and the participation of plasmons in the process of the Raman scattering have been steadily fixed.

Based on this, a theory is proposed, which considers the interaction of light, surface plasmons and molecular excitations. Within the limits of the theory all the SERS peculiarities detected experimentally are explained: susceptibility of metals, necessity of roughness, strong depolarizability of the scattered emission, the presence of an intensive continuum, a frequency dependence uncommon for the Raman scattering [1-3], concentrational saturation [4, 5].

2. Let us model a metal as a continuous medium with a transverse permeability

$$\varepsilon(\omega) = 1 - \omega_p^2 / \omega^2, \quad (1)$$

where ω_p is the frequency of a volume plasmon.

The adsorption may manifest itself in a renormalization of the electronic levels of the molecule, in the formation of either a cluster «roughness-molecule» or of a chemical centre of some certain origin ([6] and references therein). For the present work only the manifestation of a discrete energetic level in case of adsorption is of importance, which below will be called a molecule.

Further we hold that the adsorbed molecules form a layer characterized by translational invariability along the surface. This assumption is evidently fulfilled at the concentrations close to single-layer occupation. In [7] such situation is shown to be realized at low concentrations of adsorbed molecules.

The Hamiltonian of interacting molecules, plasmons and light is the following:

$$H = H_v + H_m + H_{sp} + H_k + H_{m-k} + H_{m-sp} + H_{m-v} + H_{sp-v}, \quad (2)$$

where

$$H_v = \sum_{\vec{k}, \vec{q}, \lambda} \hbar \omega_0 c_{\vec{k} \vec{q} \lambda}^+ c_{\vec{k} \vec{q} \lambda} \quad (3)$$

is the Hamiltonian of the photon field; $\omega_0 = c(k^2 + q^2)^{1/2}$; c is the velocity of light; \vec{k} , \vec{q} — the photon wave vector components respectively parallel and perpendicular to the surface, and λ is the polarization index.

$$H_m + H_k + H_{m-k} = \sum_{\rho} [\hbar \omega_m a_{\rho}^+ a_{\rho} + \hbar \omega_k e_{\rho}^+ e_{\rho} + M a_{\rho}^+ a_{\rho} (e_{\rho}^+ + e_{\rho})] \quad (4)$$

is the Hamiltonian of vibrating molecules; summing is performed over lattice sites on the metal surface; ω_m is the frequency of the electronic transition of the molecule, ω_k denotes the phonon frequency, a_{ρ} and e_{ρ} are respectively the operators of electronic and phonon excitations on the site ρ .

$$H_{sp} = \sum_{\vec{k}} \hbar \omega_{sp, k} b_{\vec{k}}^+ b_{\vec{k}} \quad (5)$$

is the Hamiltonian of surface plasmons;

$$\omega_{sp, k}^2 = \omega_s^2 + c^2 k^2 - (\omega_s^4 + c^4 k^4)^{1/2} \quad (6)$$

is their dispersion law, $\omega_s^2 = \omega_p^2/2$.

The Hamiltonian of the interaction of molecules with surface plasmons is of the form:

$$H_{m-sp} = \sum_{\vec{\rho}} (-e/mc) \vec{A}_{sp}(\vec{\rho}) \vec{p}(\vec{\rho}), \quad (7)$$

where \vec{p} is the operator of the optical electron momentum of the molecule:

$$\vec{p} = i \omega_m m \vec{d} (a_{\rho}^+ - a_{\rho}); \quad (8)$$

\vec{d} is the dipole moment of the transition, e and m are respectively the electron charge and mass, and $\vec{A}_{sp}(\vec{\rho})$ is the vector potential of the field created by plasmons outside the metal [8];

$$\begin{aligned} \vec{A}_{sp}(\vec{\rho}) = \sum_{\vec{k}} (4\pi \hbar c / L^2 p_k)^{1/2} (i \vec{\kappa} + \vec{\xi} k / v_{0k}) \exp(v_{0k} z) \times \\ \times \exp(i \vec{k} \vec{\rho}) (b_{\vec{k}} + b_{-\vec{k}}^+); \end{aligned} \quad (9)$$

z is the distance between the metal surface and molecule; the positive direction of the Z axis is into the metal; L^2 — the metal surface area; $v_{0k}^2 = k^2 - \omega_{sp, k}^2 / c^2$; $\varepsilon_k \equiv \varepsilon(\omega_{sp, k})$; $p_k \equiv (\varepsilon_k^4 - 1) / [\varepsilon_k^2 (-\varepsilon - 1)^{1/2}]$; $\vec{\kappa}$ and $\vec{\xi}$ are the unitary vectors in the directions of the wave vector of the plasmon and of the Z axis, respectively. Introducing new exciton-type excitations

$$a_{\vec{k}} = N^{-1/2} \sum_{\vec{\rho}} \exp(-i \vec{k} \vec{\rho}) a_{\rho}, \quad (10)$$

where N is the number of adsorbed molecules, we have

$$H_{m-sp} = \sum_{\vec{k}} \hbar \omega_m D_k (a_{\vec{k}}^+ - a_{-\vec{k}}) (b_{\vec{k}} + b_{-\vec{k}}^+), \quad (11)$$

where $D_k = -ie(4\pi\hbar N/L^2\rho_k c)^{1/2} [\vec{d}(\vec{\kappa} + \vec{\xi}k/v_{0k})] \exp(v_{0k}z)$.

On a plain surface the photon-plasmon transformation is not possible — the conservation laws of the energy and momentum are not fulfilled simultaneously. The photon-plasmon interaction is possible only via the surface roughness. The Hamiltonian of the process is the following [9]:

$$H_{sp-v} = e/c \times \int d\vec{r} [n(\vec{r}) - n_0 \Theta(z)] \vec{A}(\vec{q}) \vec{v}_s(\vec{q}), \quad (12)$$

where $\Theta(z)$ is the step function; $n(\vec{r})$ is the concentration of electrons in the point \vec{r} ; n_0 — an average concentration of electrons in the metal;

$$\vec{v}_s(\vec{q}) = \sum_{\vec{k}} (\hbar \omega_{sp,k} / L^2 m n_0)^{1/2} \exp(-v_k z) \exp(i\vec{k} \cdot \vec{q}) \times \\ \times [\vec{v}_k^3 k^2 / (v_k^4 + k^4)]^{1/2} (\vec{\kappa} + i\vec{\xi}k/v_k) (b_{\vec{k}} + b_{-\vec{k}}) \quad (13)$$

is the velocity operator of the plasmon [9],

$$v_k^2 = k^2 + (\omega_p^2 - \omega_{sp,k}^2)/c^2; \quad (14)$$

$\vec{A}(\vec{q})$ is the vector potential of the incident electromagnetic field inside the metal.

In the case of a light polarized perpendicularly to Z axis (with s polarization)

$$\vec{A}^{(s)}(\vec{q}) = \sum_{\vec{k}, \vec{q}} 2\pi (\vec{k} \times \vec{\xi}) (4\hbar c^2 \omega_0 \mu^2 / \omega_p^2 L^3)^{1/2} \times \\ \times \exp(-v_{1k}z) \exp(i\vec{k} \cdot \vec{q}) (c_{\vec{q}s} + c_{-\vec{q}s}^+), \quad (15)$$

where $\mu = cq/\omega_0$, $v_{1k}^2 = k^2 + (\omega_p^2 - \omega_0^2)/c^2$.

For the light polarized parallel to the plain intersecting $\vec{\xi}$ and \vec{k} (with p polarization)

$$\vec{A}^{(p)}(\vec{q}) = \sum_{\vec{k}, \vec{q}} 2\pi (i\vec{\kappa} - \vec{\xi}k/v_{1k}) (4\hbar c^2 \mu^2 / L^3 \omega_0)^{1/2} \times \\ \times \cos \eta \exp(-v_{1k}z) \exp(i\vec{k} \cdot \vec{q}) (c_{\vec{q}p} + c_{-\vec{q}p}^+), \quad (16)$$

where $\cos \eta \equiv \sigma/(\sigma^2 + \mu^2 \epsilon_k)$, $\sigma \equiv (1 - \epsilon_k - \mu^2)^{1/2}$ [8]. With allowance made for (13)–(16), the Hamiltonian of the photon-plasmon interaction acquires the form

$$H_{sp-v} = H_{sp-v}^{(s)} + H_{sp-v}^{(p)}, \quad (17)$$

where the first and second terms include s and p polarizations of light, respectively,

$$H_{sp-v}^{(s)} = \sum_{\vec{h}, \vec{h}', q} 2\pi^{1/2} (\hbar^2 \omega_{sp} c^2 q^2 / L^5 \omega_0)^{1/2} (v s^{(s)}) (v_h^3 k^2 / (v_h^4 + k^4))^{1/2} R_{hh'q} \times \\ \times (b_{\vec{h}} + b_{-\vec{h}}^+) (c_{\vec{h}'q} + c_{-\vec{h}'q}^+), \quad (18)$$

$$H_{sp-v}^{(p)} = \sum_{\vec{h}, \vec{h}', q} 2^{1/2} \pi^{1/2} (\hbar^2 \omega_{sp}^3 c^2 q^2 / L^5 \omega_0^3)^{1/2} (v s^{(p)}) \cos \eta (v_h^3 k^2 / (v_h^4 + k^4))^{1/2} \times \\ \times R_{hh'q} (b_{\vec{h}} + b_{-\vec{h}}^+) (c_{\vec{h}'q} + c_{-\vec{h}'q}^+), \quad (19)$$

where

$$\vec{v} \equiv \vec{\kappa} + i \xi \vec{k} / v_h, \quad \vec{S}^{(s)} \equiv \vec{\kappa}' \times \vec{\xi}, \quad \vec{S}^{(p)} \equiv i \vec{\kappa}' - \xi \vec{k}' / v_{hk'}.$$

By $R_{hh'q}$ the following expression is denoted:

$$\int d\vec{r} (n(\vec{r}) / n_0 - \Theta(z)) \exp(-(v+v_1)z) \exp(i(\vec{k} + \vec{k}') \vec{q}). \quad (20)$$

Let us calculate $R_{hh'q}$ for the simplest model. Take $n(\vec{r}) / n_0 - \Theta(z)$ different from zero in a thin layer $-\xi(x, y) < z < 0$; $\xi(x, y) \ll (v+v_1)^{-1}$, where $\xi(x, y)$ is the equation of a rough surface. Inside the layer this difference is constant and equal to 1. Then

$$R_{hh'q} = \int d\vec{q} \exp(i(\vec{k} + \vec{k}') \vec{q}) \int_0^{\xi(x,y)} \exp(-(v+v_1)z) dz = \\ = \int d\vec{q} \xi(\vec{q}) \exp(i(\vec{k} + \vec{k}') \vec{q}); \quad (21)$$

$$|R_{hh'q}|^2 = L^2 \int d\vec{q} \exp(i(\vec{k} + \vec{k}') \vec{q}) G(\vec{q}) \langle \xi^2 \rangle,$$

where $\langle \xi^2 \rangle$ is the mean square of the roughness amplitude,

$$G(\vec{q}) = L^{-2} \langle \xi^2 \rangle^{-1} \int d\vec{q}' \xi(\vec{q}') \xi(\vec{q} + \vec{q}') \quad (22)$$

is the correlation function of roughnesses. Its form is dependent on the method of surface preparation. Let us take in conformity with [10] $G(\vec{q}) = \exp(-q^2 / \sigma^2)$. Then

$$|R_{hh'q}|^2 = \langle \xi^2 \rangle \sigma^2 \pi \exp(-\sigma^2 (\vec{k} + \vec{k}')^2 / 4) L^2. \quad (23)$$

A direct interaction of molecules with light does not increase the scattering cross-section and further H_{m-v} is not taken into account. Note that in the full Hamiltonian (2) the direct interaction between molecules was not taken into account either. Besides, the interaction with phonons of the metal was neglected. Since phonon frequencies in the metal are considerably lower than those of the vibrations of small molecules, the account of this interaction leads but to a small broadening of the Raman scattering lines at the expense of the anharmonic decay of molecular vibrations into metal phonons.

3. The interaction H_{m-sp} cannot be correctly taken into account in any finite order of the perturbation theory, because of the resonant character of the transition caused by it. Let us take the following way of action: exactly diagonalize a part of a full Hamiltonian

$$H_1 = H_m + H_{sp} + H_{m-sp} = \sum_{\vec{h}} [\hbar \omega_m a_{\vec{h}}^+ a_{\vec{h}} + \hbar \omega_{sp, h} b_{\vec{h}}^+ b_{\vec{h}} +$$

$$+\hbar\omega_m D_k \left(a_{\vec{k}}^+ - a_{-\vec{k}} \right) \left(b_{\vec{k}} + b_{-\vec{k}}^+ \right)] \quad (24)$$

and then, via the operators of new exciton-plasmon-type surface excitations obtained, express a full Hamiltonian. The interaction operators of elementary excitations in it may be taken into account proceeding from the perturbation theory. At low excitation intensities all the operators in (24) satisfy the Bose commutation relations. The Hamiltonian H_1 is diagonalized with the Bogolyubov-Tyablikov canonical transformation,

$$H_1 = \sum_{\vec{k}, \mu} \hbar\omega_{\vec{k}, \mu} \alpha_{\vec{k}, \mu}^+ \alpha_{\vec{k}, \mu} + \text{const}, \quad (25)$$

where $\alpha_{\vec{k}, \mu}$ are the operators of new elementary excitations. At small \vec{k} ($|\vec{k}| \ll \omega_{sp}/c$), $\alpha_{\vec{k}, \mu}$ and $\alpha_{-\vec{k}, \mu}$ are close respectively to $a_{\vec{k}}$ and $b_{-\vec{k}}$. Such terms describe the emission of molecules and plasmons separately and, particularly, the intensive continuum SERS. But since we are not interested in these processes, the terms with the wave vectors $k \gg \omega_{sp}/c$ may remain in the Hamiltonian H_1 . In this region one may neglect the dispersion of plasmons: $\omega_{sp, k} = \omega_{sp}$. Then, taking into consideration that $\omega_m \approx \omega_{sp}$, after some standard transformation we obtain

$$\omega_{\mu, k} = \omega_m (1 \pm |D_k|), \quad (26)$$

$$a_{\vec{k}} = 2^{-1/2} (\alpha_{\vec{k}} + \alpha_{-\vec{k}}), \quad (27)$$

$$b_{\vec{k}} = 2^{-1/2} i (\alpha_{\vec{k}} - \alpha_{-\vec{k}}).$$

Now, for the interaction operators we have

$$H_{sp-v}^{(s)} = \sum_{\vec{k}, \vec{k}', q} i\pi^{1/2} (\hbar^2 \omega_{sp} c^2 q^2 / L^5 \omega_0)^{1/2} k^{1/2} R_{k k' q} (\vec{v} S^{(s)}) [(\alpha_{\vec{k}} - \alpha_{-\vec{k}}^+) \times \\ \times (c_{\vec{k}' q s} + c_{-\vec{k}' q s}^+) - (\alpha_{\vec{k}} - \alpha_{-\vec{k}}^+) (c_{\vec{k}'(\alpha) q s} + c_{-\vec{k}'(\alpha) q s}^+)], \quad (28)$$

$$H_{sp-v}^{(p)} = \sum_{\vec{k}, \vec{k}', q} i\pi^{1/2} 2^{1/2} (\hbar^2 \omega_{sp}^3 c^2 q^2 / L^5 \omega_0^3)^{1/2} k^{1/2} R_{k k' q} (\vec{v} S^{(p)}) \cos \eta [(\alpha_{\vec{k}} - \alpha_{-\vec{k}}^+) \times \\ \times (c_{\vec{k}' q p} + c_{-\vec{k}' q p}^+) - (\alpha_{\vec{k}} - \alpha_{-\vec{k}}^+) (c_{\vec{k}' q p} + c_{-\vec{k}' q p}^+)], \quad (29)$$

where

$$\cos \eta = (1 - c^2 q^2 / 2 \omega_0^2)^{1/2}, \quad R_{k k' q} = \langle \xi^2 \rangle^{1/2} \sigma \pi^{1/2} \exp(-\sigma^2 k^2 / 8) L.$$

The operator of molecular vibronic interaction is expressed through operators (27) in the form

$$H_{m-k} = \sum_{\vec{k}, q, i} (MN^{-1/2} / 2) \alpha_{i\vec{k}+q}^+ \alpha_{i\vec{k}} (e_{-q}^+ + e_q) + \\ + \sum_{\vec{k}, q, i \neq j} (MN^{-1/2} / 2) \alpha_{i\vec{k}+q}^+ \alpha_{j\vec{k}} (e_{-q}^+ + e_q), \quad (30)$$

where $e_{\vec{q}} = N^{-1/2} \sum_{\vec{p}} \exp(-i\vec{q} \cdot \vec{r}) e_{\vec{p}}$ are travelling vibrational excitations. The latter term describes a transition of quasi-particles from one type into another under an interaction with phonons. Since $\omega_h \ll \omega_{sp}$, the phase-space volume of such processes is determined by the wave vectors $k_1 \sim \omega_{sp}/c$, while the phase volume of the processes described by the forms sum is determined by $k_2 \sim 2\pi N^{1/2} L^{-1}$, $k_2 \gg k_1$. Therefore, the contribution of the latter term may be neglected as compared to the forms one.

4. To characterize the optical properties of the molecules adsorbed on the metal, the constant Γ describing the decay of surface exciton-plasmon into photons must be known. The initial state is the excitation $\alpha_{\mu\hbar}^+ |0\rangle$, the final one, the photon $c_{\vec{k}'q\lambda}^+ |0\rangle$ of $\omega_0 = c(k'^2 + q^2)^{1/2}$ frequency and λ polarization. The density of final states equals

$$\rho = (2\pi)^{-3} L^3 \omega_0^2 / c^3 \hbar. \quad (31)$$

By the definition

$$\Gamma = \int_{\lambda} \sum_{\vec{k}} 2\pi \hbar^{-1} |\langle 0 | c_{\vec{k}'q\lambda} H_{sp-v} \alpha_{\mu\hbar}^+ | 0 \rangle|^2 \rho d\Omega, \quad (32)$$

where the integration is performed in the directions of photon emission and the summing, over polarizations. Substituting (28) and (29) into (32), after elementary calculations we obtain

$$\Gamma = \omega_{sp}^4 \hbar R_{\hbar\hbar'}^2 / 3c^3 L^2 = \pi \langle \xi^2 \rangle \sigma^2 k \omega_{sp}^4 \exp(-\sigma^2 k^2 / 4) / 3c^3. \quad (33)$$

The radiational decay constant does not contain the Planck constant. It is natural, because the scattering of the surface electromagnetic wave on roughness is present in a classical case as well.

Using the numerical values of the parameters of (33), obtained in [10], we get $\Gamma \sim 10^{10} - 10^{11} \text{ s}^{-1}$. Such a high value of the damping constant indicates a high value of the interaction of surface exciton-plasmons with light via roughness and it widens the prospects of single-molecule spectroscopy on the surface.

The problem for the resonance secondary emission (RSE) of the molecules adsorbed on the metal is analogous to that of RSE of excitons [11]. However, here the interaction of surface exciton-plasmon excitations with phonons does not tend to zero at small wave vectors. Therefore, the greatest contribution into the scattering cross-section is made by one-phonon and not by two-phonon processes.

Using the methods of [11] for the ratio of the SERS cross-sections and ordinary Raman scattering (RS), we obtain

$$\frac{d\sigma_{\text{SERS}}}{d\sigma_{\text{RS}}} = \frac{\left| \int_0^{\hbar_{\max}} dk k \Gamma(k) \right|^2}{\left| \int_0^{\hbar_{\max}} dk k \gamma \right|^2}. \quad (34)$$

Here γ is the radiational decay constant of molecular excitations, which in its order of magnitude coincides with that of a free molecule. Let us discuss briefly the value of the upper limit of integration in (34). In (24) the summing over the wave vectors of the exciton excitation is limited by the quantity $k_0 \sim 2\pi N^{1/2} L^{-1}$ ($LN^{-1/2}$ is the average distance between molecules). The type of the interaction operator in (24) suggests that

the plasmons with the wave vector $k > k_0$ do not interact with exciton excitations. Therefore, in formula (25), the upper limit of the variation of $|\vec{k}|$ is k_0 . Consequently, in (34) $k_{\max} \sim 2\pi N^{1/2} L^{-1}$.

Formula (34) gives a concentrated saturation of the enhancement coefficient of SERS. Indeed, in case $k_{\max} \ll \sigma^{-1}$

$$\frac{d\sigma_{\text{SERS}}}{d\sigma_{\text{RS}}} \sim k_{\max}^2 \sim n, \quad (35)$$

where n is the concentration of adsorbed molecules. If $k_{\max} \gg \sigma^{-1}$, the integral in numerator (34) does not depend on the upper limit, i.e. saturation is obtained. From the position of the inflection of the SERS intensity curve as the function of the concentration of adsorbed molecules σ — an important surface characteristics can be determined.

In case of a single-layer occupation in conformity with the experiment $d\sigma_{\text{SERS}}/d\sigma_{\text{RS}} \sim 10^4 - 10^8$.

5. The general structure of the cross-section of the processes described by the second order of the perturbation theory is the following:

$$d\sigma \sim \sum |\langle H \rangle_{in}|^2 |\langle H \rangle_{out}|^2 F \varrho, \quad (36)$$

where $\langle H \rangle_{in}$, $\langle H \rangle_{out}$ are the matrix elements of the Hamiltonian, corresponding respectively to the absorption and emission of the photon; F is the slowly varying function of ω , ϱ stands for the density of photon states; $\varrho \sim \omega_0^2$; ω_0 is the frequency of light. Considering that for the processes with the photons of s polarization $\langle H \rangle \sim \omega_0^{1/2}$ and for the processes with the photons of p polarization $\langle H \rangle \sim \omega_0^{-1/2}$, we obtain for the frequency dependences of the scattering cross-section: $d\sigma \sim \omega_0^4$ in case of $s-s$ scattering, $d\sigma \sim \omega_0^2$ in case of $s-p$ and $p-s$ scattering and $d\sigma \sim \omega_0^0$ in case of $p-p$ scattering.

For the excitation and observation in unpolarized light

$$d\sigma \sim A + B\omega^2 + C\omega^4. \quad (37)$$

Let us consider the angular dependence of SERS in the experiments on 90° scattering. For the quantities in $\langle H \rangle_{in}$: $q = \omega_0 \cos \varphi / c$, $k = \omega_0 \sin \varphi / c$, where φ is the incidence angle of the beam. In $\langle H \rangle_{out}$ we have $q = \omega_0 \sin \varphi / c$, $k = \omega_0 \cos \varphi / c$. As a result, for the processes of $s-s$ scattering the angular dependence is $\cos^2 \varphi \sin^2 \varphi$. The expression has the maximum at $\varphi_{ss} = 45^\circ$. For the processes of $s-p$ scattering the angular dependence is the following:

$$\begin{aligned} & \cos^2 \varphi (1 - \cos^2 \varphi) [\cos^2 \varphi / (\cos^2 \varphi - \varepsilon) + 1/2] (-\varepsilon - \cos^2 \varphi) \times \\ & \times (1 - \varepsilon + (\varepsilon^2 - 1) (1 - \cos^2 \varphi))^{-1}. \end{aligned} \quad (38)$$

For each $\varepsilon(\omega)$ this expression has a single maximum. For $\varepsilon = -10$; $\varphi_{sp} = 27,97^\circ$. For the processes of $p-s$ scattering an expression is obtained, which is analogous to the previous one with the substitution of $\cos \varphi$ with $\sin \varphi$. It can be seen easily that the maximum in $p-s$ scattering lies at $\varphi_{p-s} = (\pi/2) - \varphi_{sp}$. For $\varepsilon = -10$, $\varphi_{ps} = 62,03^\circ$. For $p-p$ scattering processes the angular multiplies are the following:

$$\begin{aligned} & \cos^2 \varphi \sin^2 \varphi [\cos^2 \varphi / (\cos^2 \varphi - \varepsilon) + 1/2] \times \\ & \times [\sin^2 \varphi / (\sin^2 \varphi - \varepsilon) + 1/2] (1 - \varepsilon - \sin^2 \varphi) (1 - \varepsilon - \cos^2 \varphi) \times \end{aligned}$$

$$\times [(1 - \varepsilon + (\varepsilon^2 - 1) \sin^2 \varphi) (1 - \varepsilon + (\varepsilon^2 - 1) \cos^2 \varphi)]^{-1}. \quad (39)$$

This expression has a single maximum at $\varphi_{pp} = \varphi_{ss} = 45^\circ$.

Often, in the experiment, 10^3 – 10^5 layers of adsorbed molecules are present. Although the theory developed here is not directly applicable to this case, the angular and frequency dependences must remain unchanged with the only difference that in a multilayer case the notion «interaction of the molecule with the polarized light» has no meaning any more: owing to a multifold reflection from the interfaces the metal-adsorbed layer and the adsorbed layer-vacuum, the field effectively acting upon the molecule is essentially depolarized. In this case, in the spectrum of 90° scattering three peaks should be observable: at $\varphi = \varphi_{ss}$, $\varphi = \varphi_{sp}$ and at $\varphi = \varphi_{ps}$.

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KOMBINATSIOONHAJUMISE VÖIMENDUMISE TEOORIA METALLI PINNAL ADSORBEERITUD MOLEKULI KORRAL

Teooria kirjeldab metalli pinnal adsorbeeritud molekuli kombinatsioonhajumise võimendumist. Lähtudes eeldusest, et pinnaplasmoonid on vahepealsed seisundid, on täpselt arvutatud molekuli ja plasmoonide resonantsinteraktsioon. Valguse ja plasmoonide interaktsiooni (viimane johtub pinna karedusest) arvestamisel on aluseks häiritusteooria. Teooria määrab võimenduskoeffitsiendi suurusjärgu ja kontsentratsioonilise küllastuse. On leitud võimendusefekti sagedus- ja nurksõltuvuse avaldised.

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К ТЕОРИИ УСИЛЕНИЯ КОМБИНАЦИОННОГО РАССЕЯНИЯ МОЛЕКУЛ ПОВЕРХНОСТЬЮ МЕТАЛЛА

Предлагается теория усиления комбинационного рассеяния молекул поверхностью металла. Исходя из предположения о поверхностных плазмонах как о промежуточных состояниях, точно учитывается резонансное взаимодействие молекула—плазмон. Взаимодействие свет—плазмоны, возможное только через шероховатости, учитывается по теории возмущений. Теория дает необходимый порядок коэффициента усиления и его концентрационное насыщение. Получены выражения для частотной и угловой зависимостей эффекта.