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# 3D-quantification of biomolecular covers using surface plasmon-polariton resonance experiment

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ABSTRACT

The concentration of surface molecules $N_s$ and components of molecular susceptibility $\chi_{ji}(\omega)$ can both be determined from surface plasmon-polariton resonance (SPPR) experiments, instead of effective layer thickness and index of refraction, which are usually determined. The theoretical consideration of a molecular layer as monolayer of separated 3D-oscillators provides a new perspective for investigating molecules during SPPR experiment. It is shown that SPPR response and the form of the reflective curve depend on the form of a biomolecule and its orientation relative to the surface of the metal-carrier of plasmon oscillations. The experimental data for immunological reaction for the calculation of surface molecular concentration and mass of biomolecular covering are presented.



## 1. Introduction

The surface plasmon resonance (SPR) effect is widely used in modern sensors as a sensitive method for the study of physical properties of molecular layers or coverings at the surface of solids [1]. The main principle of the method is a measurement of the shifts of resonant angle if the molecular covering is present at the sensitive surface of the sensor. The angle shift is, of course, dependent on molecular concentration as well as the type of the molecules. The physical models usually used for the description of this shift are based mainly on the concept of an additional layer on the surface of SPR-converter, which is characterized by the effective thickness $h$ and refractive index $N$, analogous to the similar idea of ellipsometry of thin films [1–4]. Another approach is based on the idea of ultra-thin film representation [5]. The main point of this approach is the representation of the molecular layer as effective ultra-thin homogeneous film characterized by any susceptibility, which was calculated with self-consistent equations for local field using molecular polarization and effective film thickness. The calculations do not utilize boundary conditions and molecules are represented as point-like objects. It is clear that similar approaches do not allow one to obtain information about the concentration or individual dielectric properties of molecules at the surface. To describe the optical properties of molecular coverings at the surfaces, one needs to take the individual properties of the adsorbed molecules, their interaction with the surface and intermolecular (lateral) interactions into account. Bobbert and Vlieger have shown [6] that one solution of the problem of light reflection from a substrate covered with spherical particles can be obtained by definition of the reflected electromagnetic wave as a sum of Fresnel's plane wave and number of the spherical waves, which are raised at the scattering on the spherical particles in accordance to Mie theory. Another method of calculation of reflection coefficient for the surface covered by molecular layer is based on the Green function concept [7]. Here we develop an approach based on the linear response concept for the non-point-like protein molecules, which have the shape of oblate or prolate ellipsoids.

## 2. Theory

### 2.1. Susceptibility of molecular layer at the surface

To calculate the reflection coefficient one needs to know the effective susceptibility of the molecular layer. We consider the

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dilute thin layer of organic molecules homogeneously distributed on the surface. The molecular susceptibility $\chi_{jl}(\omega)$ is considered as known. The molecules are assumed as prolate or oblate ellipsoids. The field at an arbitrary point in the system obeys the equation [8]:

$$E_i(\vec{R},\omega) = E_i^{(0)}(\vec{R},\omega) - a\sum_{\alpha=1}^{Q}\int_{V_\alpha} d\vec{R}' G_{ij}(\vec{R},\vec{R}',\omega)\chi_{jl}(\omega)E_l(\vec{R}',\omega), \quad (1)$$

where $E_i^{(0)}(\vec{R},\omega)$ is the external long-range field, $a$ is the coefficient defined by the system of units (for SI $a = \omega^2/c^2\varepsilon_0$), $Q$ is the number of molecules on the surface, $V_\alpha$ is the molecular volume, $G_{ij}(\vec{R},\vec{R}',\omega)$ is a photon propagator that describes propagation of light of frequency $\omega$ from point $\vec{R}'$ to point $\vec{R}$ [9]. Summation is made over all positions which are occupied by the molecules. Because molecular linear dimensions are much less than light wavelength and average distances between the molecules are considered to be larger than molecular linear dimension (submonolayer cover), one can make the next approximation:

$$\sum_\alpha \int_{V_\alpha} d\vec{R}' G_{ij}(\vec{R},\vec{R}',\omega)\chi_{jl}(\omega)E_l(\vec{R}')$$

$$\approx \sum_\alpha G_{ij}(\vec{r}-\vec{r}_\alpha, z, z_\alpha, \omega)\tilde{\chi}_{jl}(\omega)E_l(\vec{r}_\alpha, z_\alpha), \quad (2)$$

where $\tilde{\chi}_{jl}(\omega) = V_\alpha\chi_{jl}(\omega)$, $V_\alpha$ is the molecular volume. Here $\tilde{\chi}_{jl}(\omega)$ is the response on the local (total) field which connects the polarization of the molecule and the local field via

$$P_j(\vec{r}_\alpha, z_\alpha, \omega) = \tilde{\chi}_{jl}(\omega)E_l(\vec{r}_\alpha, z_\alpha, \omega). \quad (3)$$

The averaging over molecular coordinates if molecules are homogeneously distributed along the surface is performed using the equation:

$$\overline{\sum_{\alpha=1}^{Q} G_{ij}(\vec{r}-\vec{r}_\alpha, z, z_\alpha, \omega)\tilde{\chi}_{jl}(\omega)E_l(\vec{r}_\alpha, z_\alpha, \omega)}$$

$$= \frac{1}{S^{Q-1}}\int d\vec{r}_1 d\vec{r}_2 \ldots d\vec{r}_N \sum_{\alpha=1}^{Q}\int \frac{d\vec{k}}{(2\pi)^2} e^{-i\vec{k}(\vec{r}-\vec{r}_\alpha)}$$

$$G_{ij}(\vec{k}, z, z_\alpha, \omega)\tilde{\chi}_{jl}(\omega)\int \frac{d\vec{k}'}{(2\pi)^2} e^{-i\vec{k}'\vec{r}_\alpha}E_l(\vec{k}', z_\alpha, \omega)$$

$$= N_s\int \frac{d\vec{k}}{(2\pi)^2} e^{-i\vec{k}\vec{r}}G_{ij}(\vec{k}, z, z_\alpha, \omega)\tilde{\chi}_{jl}(\omega)E_l(\vec{k}, z_\alpha, \omega), \quad (4)$$

where $S$ is the area of the surface at which the $Q$ molecules are situated, $N_s = Q/S$ is molecular concentration. Then, an equation of self-consistent field in the Wail-representation can be written as

$$E_i(\vec{k}, z_\alpha, \omega) = E_i^{(0)}(\vec{k}, z_\alpha, \omega) - N_s a G_{ij}(\vec{k}, z_\alpha, z_\alpha, \omega)\tilde{\chi}_{jl}(\omega)$$

$$E_l(\vec{k}, z_\alpha, \omega). \quad (5)$$

Making Fourier transformation in the plane of the surface, one obtains from Eq. (3):

$$E_l(\vec{k}, z_\alpha, \omega) = (\tilde{\chi}_{jl}(\omega))^{-1}P_j(\vec{k}, z_\alpha, \omega). \quad (6)$$

Then, Eq. (5) can be rewritten in the form:

$$(\tilde{\chi}_{ij}(\omega))^{-1}P_j(\vec{k}, z_\alpha, \omega) = E_i^{(0)}(\vec{k}, z_\alpha, \omega) - N_s a G_{ij}(\vec{k}, z_\alpha, z_\alpha, \omega)$$

$$P_j(\vec{k}, z_\alpha, \omega). \quad (7)$$

The solution of this equation is

$$P_j(\vec{k}, z_\alpha, \omega) = [(\tilde{\chi}_{ji}(\omega))^{-1} + N_s a G_{ij}(\vec{k}, z_\alpha, z_\alpha, \omega)]^{-1}E_i^{(0)}(\vec{k}, z_\alpha, \omega). \quad (8)$$

Then, the effective susceptibility of sub-monolayer of the molecules at the surface which connects the Fourier-transformants of layer polarization and external field has a form:

$$\tilde{X}_{ij}(\vec{k}, z_\alpha, \omega) = [(\tilde{\chi}_{ij}(\omega))^{-1} + N_s a G_{ji}(\vec{k}, z_\alpha, z_\alpha, \omega)]^{-1}. \quad (9)$$

### 2.2. Reflection coefficient

For SPPR simulation one needs to know the reflection coefficient of the molecular layer (see Fig. 1a). For calculation of the reflection coefficient, let us consider the planar layered medium, the electrodynamical properties of which are characterized by photon propagator $G_{ji}(\vec{k}, z, z', \omega)$. Let the light propagation from semispace $z>0$ to the same semispace be described by photon propagator $G_{ij}^{(+,+)}(\vec{k}, z, z', \omega)$, the light propagation from semispace $z<0$ to semispace $z>0$ – by photon propagator $G_{ij}^{(+,-)}(\vec{k}, z, z', \omega)$, and the light propagation from semispace $z>0$ to semispace $z<0$ – by photon propagator $G_{ij}^{(-,+)}(\vec{k}, z, z', \omega)$. Then, an effective susceptibility of the molecular layer situated at the surface of semispace $z<0$ is defined by equation (9) with photon propagator $G_{ij}^{(-,-)}(\vec{k}, z, z', \omega)$. If the field $E_i^{(0)}(\vec{k}, z, \omega)$ acts at the molecular layer, the field reflected by the layer will be written as

$$E_i^{(R)}(\vec{k}, z, \omega) = N_s G_{ij}^{(+,-)}(\vec{k}, z, z_\alpha, \omega)X_{jl}(\vec{k}, \omega)E_l^{(0)}(\vec{k}, z_\alpha, \omega), \quad (10)$$

where $z_\alpha$ is $z$-coordinate of the centre of molecule. Then, the reflection coefficient of the molecular layer, which connects the amplitudes of reflected by the layer and incident p-polarized fields $E_p^{(R)} = R_p E_p^{(0)}$, can be written in the form:

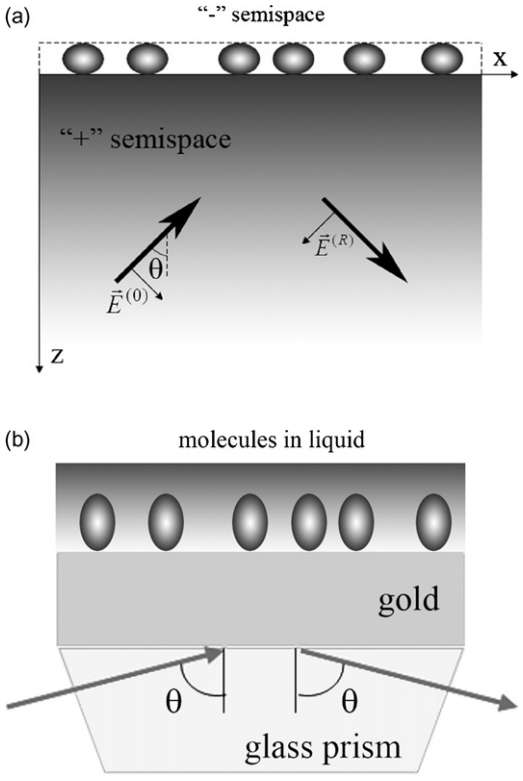


**Fig. 1.** (a) Reflection of the light by molecular layer situated at a surface. (b) Schematic presentation of the system under investigation.