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Effect of the orientational disorder on the hyperpolarizability measurement of amphiphilic push-pull chromophores in Langmuir–Blodgett monolayers

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Abstract

First-order hyperpolarizabilties of two new amphiphilic push-pull chromophore derivatives of hemicyanine dyes prepared in Langmuir–Blodgett films and designed for membrane potential imaging of living cells are measured by surface second-harmonic generation (SHG). Assuming uniaxial symmetry, an effective hyperpolarizability coefficient β_e is defined, and a procedure to measure this coefficient is described. Relationships between β_e and the true hyperpolarizability coefficient β are derived on the basis of a stochastic model taking account of the tilt angle disorder of the chromophores. Maximum discrepancies between the true and the effective hyperpolarizabilities are calculated as a function of the orientation parameter D, and it is shown that the relative difference may not exceed 40% for usual distribution functions of the tilt angle. As a result, the dominant hyperpolarizability coefficient $\beta^{(2)}_{z,z,z}$ of the chromophores in LB films is found to be in the range $0.3–0.7 \times 10^{-27}$ esu at 1064 nm fundamental wavelength.

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1. Introduction

Voltage-sensitive molecular probes play an important role in biological imaging since they act as optical reporters for electrical activity of

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cell membranes [1]. Among these functionalized dyes, nonlinear push-pull chromophores with enhanced quadratic molecular response represented by the hyperpolarizability coefficient β have been recently shown to allow non-invasive recording of fast spatiotemporal modulations of action potentials in living cells via second-harmonic generation (SHG) microscopy [2]. This nonlinear approach based on coherent generation of light from amphiphilic chromophores present in the outer leaflet of cell membranes has proved to be both more sensitive [3,4] and spatially more selective [5] than the corresponding linear one-photon incoherent method based on electrochromism of fluorophores [6–9]. Electric fields associated with transmembrane potentials are indeed strong enough to induce both significant changes of hyperpolarizabilty and realignment of the chromophores [10]. Achievement of the highest molecular hyperpolarizability and electro-optic response is then at the heart of molecular design strategies [11,12], as only low concentrations of markers allow to preserve cell viability over time scales of biological processes and experiments. However, reliable hyperpolarizability measurements of such push-pull molecules are a ticklish problem. Indeed, in situ measurements are rather hazardous due to the lack of control of the marker concentration and organization when incorporated in living cells or in model bilayer lipid membranes. On the other hand, chromophore solutions used for electric-field induced second-harmonic generation (EFISHG) and hyper-Rayleigh scattering (HRS) techniques do not simulate physiological conditions, as it is well known that the solvent environment can greatly modify the optical properties of chromophores [13–15]. In particular, experimental and theoretical studies have shown that both the linear (absorption and emission) and nonlinear optical properties of charged push-pull molecules significantly depend on solvent polarity [16]. Moreover, EFISHG conducted in solution provides only the projection of the dipolar part of the β tensor on the dipole moment μ of the molecules, requiring further measurements of μ as well as local field corrections [13,14] In addition, the third- order polarizability coefficient γ is usually neglected. HRS appears more appropriate since measurement of β is possible without the need of orientating fields [15]. However, in the case of fluorescent chromophores, sophisticated time-resolved setups [17–19] and/or spectral discrimination are needed in order to isolate the weak HRS signal.

Among all possible approaches for measuring hyperpolarizability of functionalized chromophores, surface SHG from molecular monolayers in Langmuir–Blodgett (LB) films present an interesting trade-off between control of parameters (organization, concentration of chromophores, etc.), simulation of membrane environment and experimental suitability. However, although this technique was frequently used to measure the effective orientation of chromophores as well as macroscopic nonlinear susceptibility coefficients of the films [20–25], derivation of the microscopic hyperpolarizability coefficients accounting for the orientational disorder of the molecules has remained an eluded question up to now. The aim of this paper is to address this problem in the frame of surface SHG measurements of two functionalized push-pull chromophores deposited in LB monolayers and designed for membrane potential imaging [2,10,26].

2. Theory and methodology

The hyperpolarizability tensor of push-pull chromophores is usually dominated by a single axial coefficient $\beta^{(2)}_{z,z,z} \equiv \beta$ associated with the push-pull molecular axis z. To quantify β from SHG measurements on LB monolayers, the hyperpolarizabilty tensor of the individual molecule has to be related to the macroscopic susceptibility tensor of the film through summation over all possible orientations of the molecules in the monolayer. In case where isotropic orientation distribution about the normal axis Z of the film is assumed (condition easily verified from cancellation of SHG at normal incidence on the film), that is a random azimuth of the molecules within the monolayer plane (see Fig. 1), the two non-vanishing independent elements of the surface macroscopic susceptibility tensor $\chi^{(2)}$ are given by [21]