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Pockels effect of water in the electric double layer at the interface between water and transparent electrode

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Abstract

We have obtained the first experimental evidence for the Pockels effect of water, which is induced by a high electric field in the electric double layer (EDL) on the water–transparent electrode interface. The electric-field induced energy shift of the visible interference fringes of a 300 nm indium–tin–oxide (ITO) electrode layer is observed, indicating a negative refractive index change at the interface. Numerical calculation reproduces well the experimental observation, showing that the signal mainly originates from water in the EDL. The Pockels constants of water are estimated to be $r_{33} = 5.1 \times 100$ pm/V and $r_{13} = 1.7 \times 100$ pm/V. The large anisotropy of the Pockels effect of water is deduced from the incidence angle dependence of the *p*-polarization signal. At the same time, the ITO shows a blue shift of the band gap in the UV due to the band population effect in the space charge layer. The plasma frequency in the near IR is also expected to increase due to the band population effect, since the ITO has a high doped carrier population close to metal. A negative refractive index change in the ITO space charge layer is induced from both effects, but its effect on the signal is estimated to be much smaller than that of the negative refractive index change of water in the EDL.

Keywords: Water; Pockels effect; Optical nonlinearity; Electric double layer; Indium oxides; Solid–liquid interfaces; Semiconducting surfaces; Metallic surfaces; ITO; Indium tin oxides; Refractive index; Electrolyte; Lock-in detection; Space charge layer; Transmission spectrum; Field effect; Visible/ultraviolet absorption spectroscopy; Non-linear optical methods; Interference

1. Introduction

Interaction between water molecules and biomolecules or solid surfaces turns water into new phases, different from bulk water. One of the most important is the electric double layer (EDL), which provides a field of various electrochemical reactions at the solid–aqueous solution interface. The thickness of the EDL is restricted to a nanometer scale, and it has been reported that water molecules have an orientational order in the EDL. As a result, the static dielectric constant decreases to less than 10 from its bulk value of 80 [1–3]. This means that the orientational contribution to the polarizability is quenched while the vibrational and electronic contribution remains.

The orientational order of water molecules in the solid–liquid interface has been extensively studied both theoretically and experimentally [4,5]. The information on the molecular structure and molecular arrangement of interfacial water on various solid surfaces has been studied theoretically with various models [4] and experimentally by surface selective IR spectroscopy [5–9] as well as by surface X-ray scattering [10]. On the other hand, the optical properties, which reflect the electronic states, of water molecules on spatially restricted conditions are less understood than

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the structural properties of them because of the lack of experimental study.

The purely electronic response of such a highly ordered layer of water can be measured by the refractive index in the visible region. This is the Pockels effect of water, represented by the coefficient n_1 in the electric-field dependent refractive index $n = n_0 + n_1E + n_2E^2 + \cdots$ or by the second-order susceptibility of $\chi^{(2)}_{ijk}(\omega;\omega,0)$. A large number of study was devoted to the optical Kerr effect of water [11,12], expressed by the coefficient n_2, or the third-order susceptibility of $\chi^{(3)}_{ijkl}(\omega;\omega,-\omega,\omega)$, because an intense electric field is readily applicable by using high-peak-power femtosecond optical pulses. In contrast, the Pockels effect of water has never been reported to the best of our knowledge. This is because the application of a high DC electric field is difficult due to the conductivity of water, and because bulk water has macroscopic centrosymmetry insensitive to the second-order nonlinear optical effects.

The electrolyte method for electroreflection spectroscopy [13,14] is a powerful tool for sensitively detecting the energy structure of doped semiconductors above the band gap and of metals. Even with an applied voltage as low as 1 V, a nanometer-scale electric double layer is formed at the water–semiconductor interface, where the voltage is concentrated. The space charge layer is then formed in the semiconductor surface due to the high electric field in the EDL. As a result, the carrier spatial and energy distribution function changes, which is accompanied by the reflectivity change. This is a kind of electrooptic effect, i.e., the Pockels effect, where the nonlinear refractive index change is proportional to the applied electric field. Although materials of a large electrooptic constant have been eagerly searched for from the requirement of optical information processing, the electrooptic constant involved in the electrolyte method has scarcely been evaluated. For most of the studies, furthermore, much attention has been paid to the refractive index change in the solid surface layer, but not in the EDL, with only a few exceptions [15,16]. Difficulty in evaluating the Pockels effect of water resides in the fact that the contribution of water to the refractive index change can hardly be separated from that of solid.

In this paper, we report the Pockels effect of water for the first time to the best of our knowledge. As an electrode for the electrolyte method, indium–tin–oxide (ITO) which is transparent in the visible is used. The applied voltage drops at the liquid–solid interface, i.e., in both the space charge layer of ITO and the electric double layer of electrolyte solution. The shift in the interference fringes of the thin ITO layer (nominally 300 nm) is detected in the transmission spectrum of the ITO in the electrolyte solution. The nonlinear refractive index change in the visible is readily evaluated from the shift. The contribution of the ITO to the signal is estimated from the spectral change in the UV absorption, where the band population effect induces the energy shift of the absorption edge. The result of analysis shows that most of the signal is caused by water in the EDL.

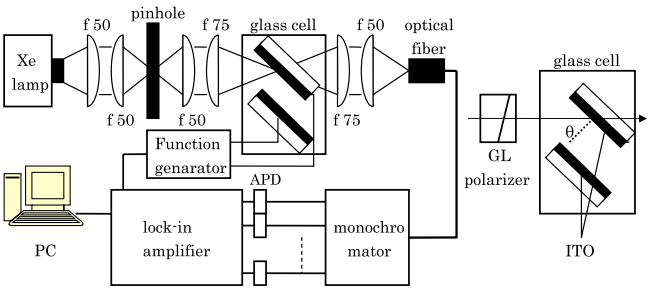

Fig. 1. Experimental setup. APD: avalanche photodiode. GL-polarizer: Glan-Laser polarizer. For lenses, the focal length of them are shown.

2. Experimental

We used electrodes made of ITO (Indium–Tin Oxide, Geomatec), where electrically conductive ITO thin films were formed by sputtering on glass substrates. The ITO is nearly transparent in the visible region. Its thickness, resistivity, and carrier density are 300 nm, $1.3 \times 10^{-4}\ \Omega$ cm, and 1.2×10^{21} cm^{-3}, respectively. A typical experimental apparatus for electro-modulation measurement is shown in Fig. 1. A strong electrolyte solution, 0.1 M NaCl aqueous solution, was prepared from distilled water. Two ITO-electrodes were immersed in the solution filled in the glass cell. One electrode was grounded and AC voltage of 2 V (peak amplitude) was applied to the other at the frequency of $f = 20$–500 Hz. A Xe lamp (Hamamatsu L2274) was used as a visible light source. The light from the lamp was incident into the glass cell and transmitted through the latter ITO electrode. The transmitted probe light was focused into a fiber-bundle input. The fiber bundle was connected to the input slit of a monochromator (Acton SP-308), and the laterally dispersed light by a grating (300 grooves/500 nm blaze) was received by 128 channel fiber bundle arrays at the exit of the monochromator. Each channel of the bundle fibers was connected to a Si avalanche photodiode (APD, Hamamatsu S5343). Photocurrents of 128 APDs were detected by a 128-channel lock-in amplifier [17,18]. The amplitude-modulated components of the APD photocurrents at the frequency of f were simultaneously measured as a function of channel number, each of which corresponds to a wavelength. This provides a difference transmission spectrum in the visible region induced by the first-order electrooptic (Pockels) effect. The probe light was made linearly-polarized by a Glan-Laser Polarizer, and the incidence angle dependence on the ITO for *s*- and *p*-polarization was investigated at the incidence angles of $\theta = 0°$, 30°, and 45°. We tried also to measure the Kerr signal at $2f$ frequency, but detected a much smaller signal. Therefore, we limit our discussion on the f signal below.

3. Results

The thick solid curve in Fig. 2(a) shows the transmission spectrum of the ITO substrate. In the spectrum there are interference fringes which are due to the ITO layer of