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Anomalously large electro-optic Pockels effect at the air-water interface with an electric field applied parallel to the interface

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The optical Pockels effect was observed at the air-water interface by electromodulation spectroscopy. When an AC electric field of frequency *f* was applied parallel to a water surface between Pt electrodes, the field induced a change in the transmitted light intensity synchronized at 1*f* proportional to the field strength. The 1*f* signals dominated over 2*f* signals by one order of magnitude and the signal disappeared when the electrodes were completely immersed under the water surface, strongly suggesting that the observed phenomena were due to the Pockels effect at the air-water interface. The Pockels coefficient was estimated to be $|r| = 1.4 \times 10^5$ pm/V, which is much larger than that at the solid-water interface. However, this is unusual because the parallel electric field does not induce the break in inversion symmetry required for the appearance of the Pockels effect. The electrowetting effect was experimentally ruled out as a mechanism for the Pockels effect, and this made the existence of a field perpendicular to the surface, although extremely weak, the most likely explanation. *Published by AIP Publishing.* [http://dx.doi.org/10.1063/1.4949273]

Air-water interfaces (water surfaces) are ubiquitous in nature[1] and play essential roles in such phenomena as water condensation, water evaporation, cloud formation, surface tension, water-repellent surfaces (Lotus effect), and bubble formation. However, a complete description of the physical and chemical properties of the air-water interface remains challenging. Sophisticated experimental and theoretical techniques have been employed to elucidate the properties specific to air-water interfaces including nonlinear vibrational spectroscopy,[2–6] X-ray and neutron scattering,[7–9] atomic force microscopy,[10] and molecular dynamics (MD) calculations.[11–13] Infrared-visible sum-frequency generation (SFG) has revealed the existence of non-hydrogen-bonded O–H groups at water surfaces.[2] Recently, the heterodyne-detection technique was combined with SFG to prove the existence of three distinct O–H oscillators at the surface.[5,6] These are powerful methods for studying molecular density, molecular orientation, molecular structural change, and the mutual arrangement of molecules. However, it is difficult to directly obtain the electronic structure, which is reflected in the dielectric response function, despite the fact that the refractive index of the interfacial layer has been experimentally estimated using SFG and second-harmonic generation studies[3] and the distribution of dielectric constant within a few nanometers distance from the surface has been theoretically predicted by MD simulations.[12]

Nonlinear vibrational spectroscopy such as SFG is sensitive to water surfaces because the second-order nonlinear optical effect is used. This requires broken inversion symmetry at the water surface, and as a result, the air-water interface is expected to manifest another second-order nonlinear optical effect, the optical Pockels effect. If the effect is observed, it is a powerful probe to characterize the electronic properties, including the anisotropy of the dielectric response of the surface, because the effect is controlled by the dielectric function of the surface water and thereby anisotropic orientations of water molecules at the surface.

The optical Pockels effect of water at solid interfaces has been reported to show large Pockels coefficients when compared with commercial solid Pockels crystals.[14–16] Based on these results, the air-water interface is also expected to display a large Pockels effect. In this Letter, the optical Pockels effect of water at the air-water interface was studied by electromodulation spectroscopy, and this revealed that the Pockels effect at the air-water interface is much larger than at the solid-water interface.

Figure 1 shows the experimental setup. A white light probe beam collimated from a laser-driven Xe light source (EQ90; Energetic Technology) was directed onto an air-water interface. The collimated beam was transmitted through an aperture to generate a beam of 5 mm diameter in the sampling position. Deionized water samples were contained in rectangular open cells. Two Pt electrode banks ($36 \times 36 \times 0.3\,\text{mm}^3$, each made up of three $12 \times 36 \times 0.3\,\text{mm}^3$ electrodes) were positioned 26 mm apart and facing each other so that the electric field applied was parallel to the water surface. The direct current resistance was about 1 MΩ between the electrodes. Electromodulation spectra were recorded as the normalized transmittance change ($\Delta T/T$) synchronized with an AC electric field of frequency *f* applied to the interface using a multichannel lock-in amplifier, where T is the transmitted probe light intensity and ΔT is the field-induced change in T. The

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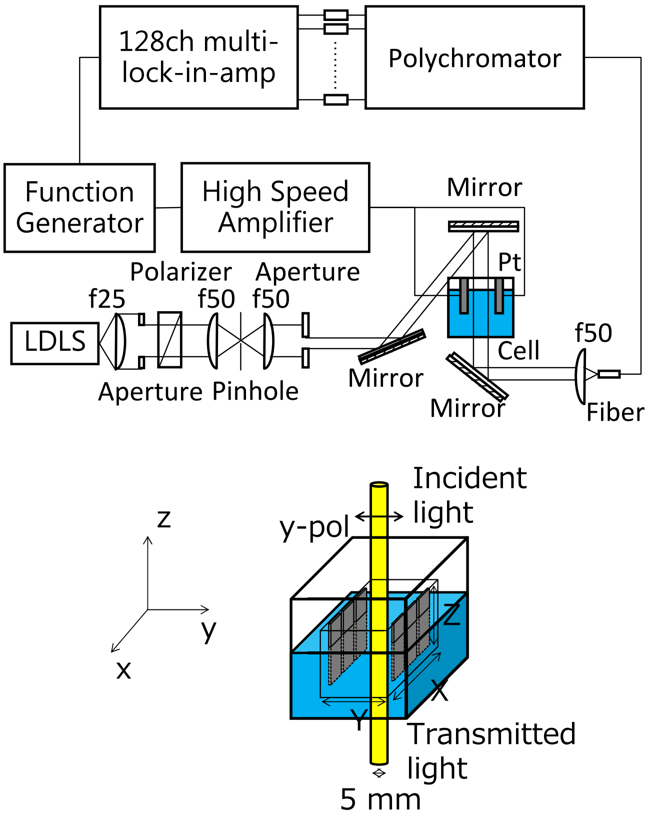


FIG. 1. Experimental setup for the $\Delta T/T$ measurements at the air-water interface.

lock-in detection was performed at both 1*f* and 2*f*, corresponding to the Pockels and Kerr effects, respectively. The applied voltage was obtained with a high-speed power amplifier (4020, NF). All measurements were performed at room temperature, 20 °C. The details of the multi-lock-in detection method have been reported previously.[14,15] A high-speed microscope (VW-9000 with VW-600 M camera; Keyence) was used to observe the dynamic behavior of the water surface under the applied AC voltage.

Figures 2(a)–2(d) show typical electric-field induced transmission changes ($\Delta T/T$) when the probe light was normally incident on the water surface, in the central point between both electrodes (electrode immersion depth around 27 mm), and polarized parallel to the applied electric field direction. Figure 2(e) shows the applied voltage dependence of $\Delta T/T$ at 631 nm. It is noteworthy that $\Delta T/T$ at 1*f* was proportional to the applied field and larger by about one order of magnitude than that at 2*f*. This suggested that the electro-optic Pockels effect was taking place at the air-water interface. A dependence on the incident light polarization was not observed within the experimental signal-to-noise ratio.

The dependence of $\Delta T/T$ on the position of the excitation beam was measured as shown in Fig. 3. The results demonstrated that $\Delta T/T$ increased in magnitude when the incident light was closer to the electrodes. However, there was no positional dependence in the direction parallel to the electrode surface. The dependence of the signal intensity on the electrode immersion depth was also examined by shifting the electrodes vertically and no remarkable changes were observed. However, when the electrodes were completely immersed in or extracted from the water (the electrodes were not touching the water surface), the Pockels effect almost disappeared ($\Delta T/T \approx 10^{-6}$ at both 1*f* and 2*f*).

To confirm that the observed Pockels effect was intrinsic to the air-water interface, the experiment was performed under the same conditions as in Fig. 2 and the water surface was covered by a 1.5-mm-thick glass microscope slide to make it a solid-water interface.[17–20] As a result, the signals indicating the Pockels effect were nearly quenched ($\Delta T/T \approx 10^{-5}$ at both 1*f* and 2*f*).

The Pockels coefficient was evaluated from the results described. As the microscopic mechanism is unknown and the active domain where the refractive index change occurred is unclear, the following calculations provide an order of magnitude estimate. If an isotropic refractive index change is assumed, the Pockels coefficient is given by $r = -2\Delta n_2/(n_2{}^3 E)$,[21] where n_2 is the refractive index of water and Δn_2 is the change in n_2 induced by the applied field E. From the typical experimental values $|\Delta T/T| = 1 \times 10^{-4}$ at 300 Vpp (where Vpp is the difference between the positive and negative peak voltage values) and 221 Hz with $T = 2n_1 n_2/(n_1 + n_2)^2$ and $\Delta T = 2n_1(n_2 + \Delta n_2)/(n_1 + n_2 + \Delta n_2)^2 - T$, there are two solutions for $|\Delta n_2|$, 0.58 and 9.4×10^{-4}, with $n_1 = 1.00$ (the refractive index of air) and $n_2 = 1.33$. Because the solution of 0.58 is too large to be physically acceptable, 9.4×10^{-4} is taken as a plausible solution. Assuming a uniform electric field between the electrodes with $V = Ed = 150$ V and $d = 26 \times 10^{-3}$ m, we obtain $|r| = 1.4 \times 10^5$ pm/V. This value is 10^5 times larger than that in $LiNbO_3$ used in commercial electro-optic modulators[21] and 10^3 times larger than those reported for the electric double layer between aqueous electrolyte solutions and transparent electrodes.[14,15] The characteristics of the 1*f* signals strongly support that an intrinsic Pockels effect is present at the air-water interface in these experiments for the following reasons:

(A) The magnitude of $\Delta T/T$ at 1*f* was proportional to the applied field and was larger by about one order of magnitude than that at 2*f*.
(B) The lack of electrode immersion depth dependence and the disappearance of the 1*f* signal when the electrodes were removed from the air-water interface.
(C) The quenching of the 1*f* signal when the water surface was covered by a microscope slide.

However, it is not obvious why the Pockels effect takes place when the electric field is applied in the direction parallel to the interface. For the field to break the inversion symmetry, it should be applied perpendicular to the interface. Directing the field either from air to water or from water to air gives rise to intrinsic differences at the interface, with the result that the sign of the refractive index change is reversed. The corresponding experiment with a perpendicular field was performed such that the electrodes were positioned above and below the air-water interface and Pockels signals were observed. However, the signal intensity ranged from 0.1 to 10 times that for the parallel field configuration. The reason for such a large variation (two orders of magnitude) is uncertain, and presumably, there are some uncontrolled parameters.

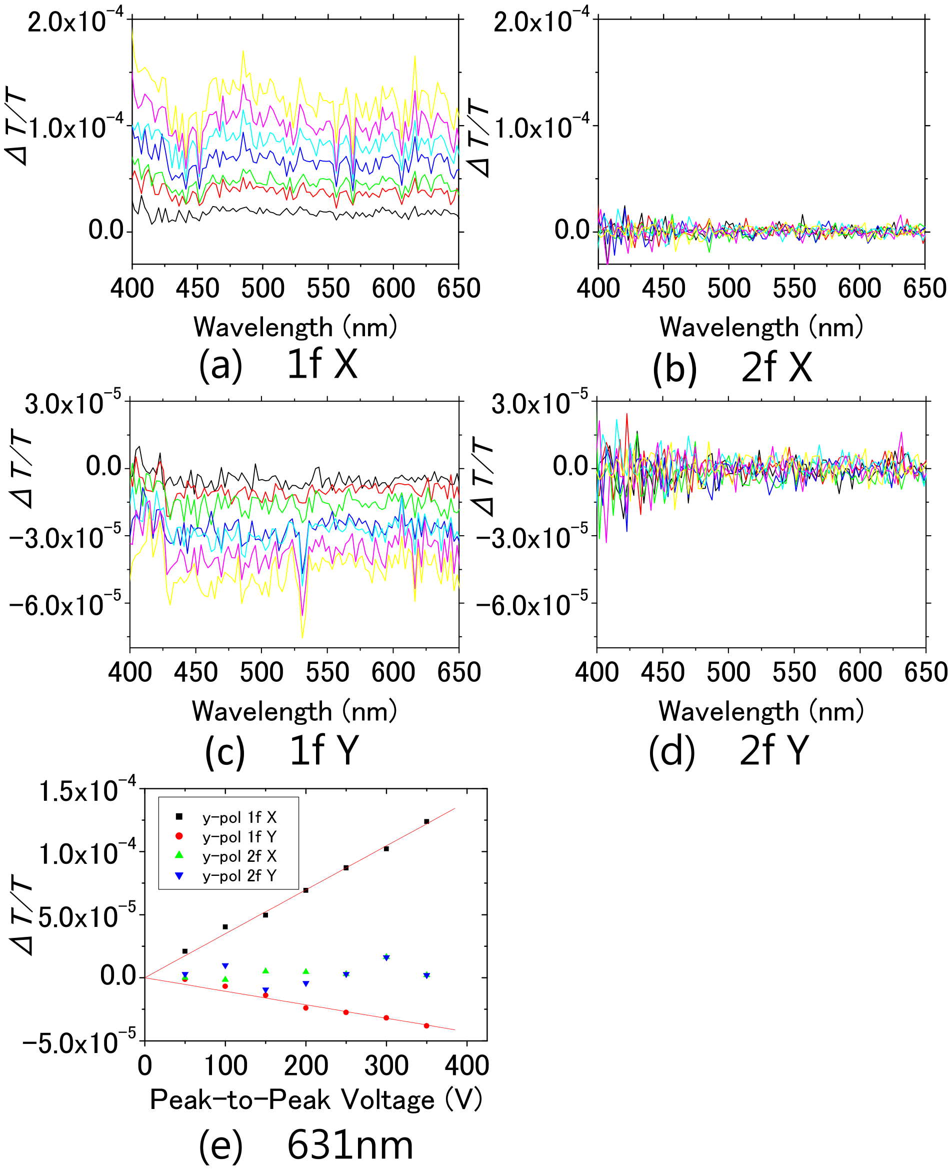


FIG. 2. Electric-field induced changes in the transmission spectra of the probe light normally incident on air-water interfaces. The light was incident on the central point between the electrodes and polarized parallel to the applied electric field. $\Delta T/T$ spectra at $1f\,X$ (a), $2f\,X$ (b), $1f\,Y$ (c), and $2f\,Y$ (d) with the AC voltage applied from 50 to 350 Vpp at 221 Hz. X is the lock-in signal synchronized with the applied AC field with the phase difference 0° (in phase), and Y is the signal with the phase difference 90° (out of phase or quadrature phase). Vpp is the difference between the positive and negative peak voltage values. (e) Applied voltage dependence of $\Delta T/T$ at 631 nm in (a)–(d).

Therefore, we have reservations with regard to reporting these results.

From the theoretical viewpoint, the Pockels effect should not be observed under the present experimental conditions with a field parallel to the interface. However, the claim that the Pockels effect takes place even with the parallel field is validated by the following experimental observation, because even the slightest asymmetry may break the inversion symmetry:

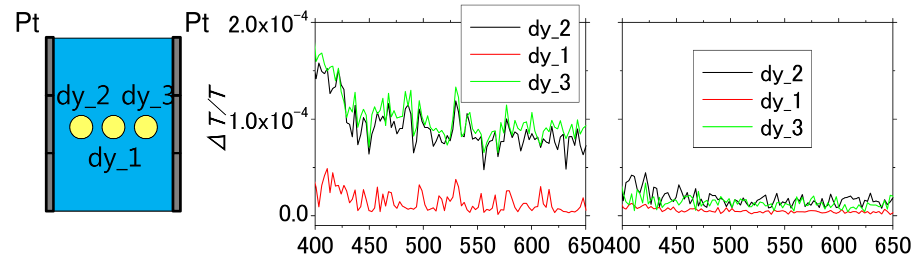
(D) There was a strong dependence on the position of the incident light. When the light was in an incident position close to an electrode, the magnitude of the $1f$ signal increased by an order of magnitude.

This suggests that the Pockels effect at the center was caused by slight displacements of the incident position from the exact center (within the beam diameter of 5 mm).

Note that the change in the transmitted light intensity could be caused by the refractive index changes at the interface or by a change in the gradient of the water surface, which is equivalent to a change in the light incidence angle. In this respect, the effect of electrowetting[22,23] needed to be examined. Electrowetting occurs when the applied voltage at the electrode induces a change in the contact angle between the liquid surface and the electrodes, and we show that the electrowetting effect cannot be the origin of the Pockels effect below.

(1) The angle changes quadratically with the voltage during electrowetting,[22,23] so that the electrowetting effect could be the origin of the electro-optic Kerr effect. The apparent Pockels effect can take place only when the electrowetting effect has a voltage-linear component, which is not known, and the incident light position is displaced from the center.

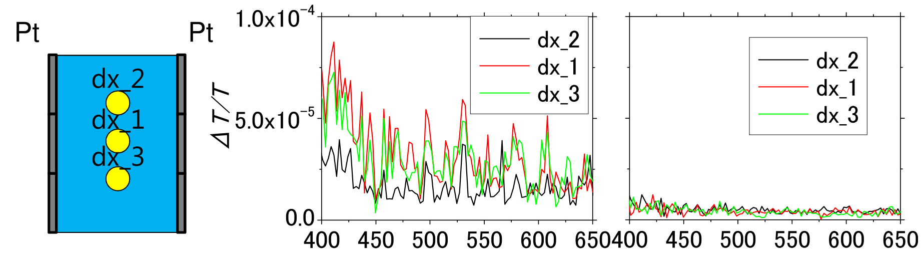
(2) If the plane-wave light is incident on the air-water interface from the air side with the refractive index n_1 to the water side with the refractive index n_2, then Fresnel's formulas for the transmittance for P and S polarized radiation are given by $T_p = 4\alpha\beta/(\alpha+\beta)^2$ and $T_s = 4\alpha\beta/(1+\alpha\beta)^2$ with $\alpha = \cos\theta_T/\cos\theta_I = \sqrt{1-\sin^2\theta_T}/\cos\theta_I = \sqrt{1-(n_1/n_2)^2\sin^2\theta_I}/\cos\theta_I \equiv \alpha(\theta_I)$ and $\beta = n_2/n_1$, where θ_I is the incidence angle and θ_T is the refracted



(a) Light incidence positions between the electrodes displaced in the y-direction

(b) 1f Magnitude

(c) 2f Magnitude



(d) Light incidence positions between the electrodes displaced in the x-direction

(e) 1f Magnitude

(f) 2f Magnitude

FIG. 3. Dependence of the signal on the incidence light positions with an applied voltage of 300 Vpp at 221 Hz. The incidence positions were displaced from the center by ±7 mm in the direction parallel to the applied field in (a)–(c) and by ±8 mm in the direction perpendicular to the field in (d)–(f). Signal magnitudes $\sqrt{X^2+Y^2}$ at 1*f* [(b) and (e)] and 2*f* [(c) and (f)].

angle. Assuming that the incidence angle θ_I is changed by an infinitesimally small angle to $\theta_I+\Delta\theta_I$, then $\Delta T/T=(T(\theta_I+\Delta\theta_I)-T(\theta_I))/T(\theta_I)\cong(T^{(1)}(\theta_I)/T(\theta_I))\Delta\theta_I+(1/2)(T^{(2)}(\theta_I)/T(\theta_I))(\Delta\theta_I)^2$. The first term on the right-hand side of this equation corresponds to the 1*f* signal and the second term to the 2*f* signal. At normal incidence ($\theta_I=0°$), the first term in the 1*f* signal is zero because $T^{(1)}(\theta_I=0)=0$, while the second term for the 2*f* signal is nonzero, contradicting the experimental observation that the 1*f* signal is larger than the 2*f* signal in magnitude.

(3) If the typical experimental value $\Delta T/T=1\times10^{-4}$ is due to electrowetting, the change in the incidence angle (surface gradient) should be $\Delta\theta_I=3.27°$, which is a solution for $|(T_{p,s}(\Delta\,\theta_I)-T(0))/T(0)|=1\times10^{(-4)}$. With a high-speed microscope camera, we recorded a movie to monitor the time evolution of the meniscus shape formed by the water surface on one of the electrodes under AC voltage application. The movie shows a much smaller water surface gradient change than $\Delta\theta_I=3.27°$ as no recognizable change was observed. For example, Fig. 4 shows two consecutive frames in an elapsed time of 3.75 ms extracted from the movie (an AC voltage was applied at 221 Hz, corresponding to a period of 4.52 ms).

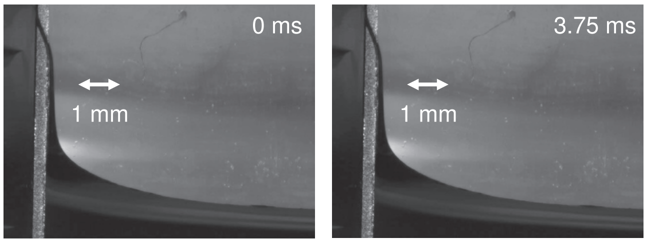


FIG. 4. Two consecutive microscope images of the water surface at an electrode in an elapsed time of 3.75 ms. Images were extracted from the movie recorded with an exposure time of 1/8000 s, a frame rate of 4000 fps, and with 640 × 480 pixels.

By these observations, the electrowetting effect was therefore ruled out as the mechanism of the Pockels effect.

Although it is difficult to identify the physical mechanism of the Pockels effect, the experimental result (D) suggests the following possible mechanism. Even a tiny asymmetry in the system would bring about the required break in inversion symmetry for the Pockels effect, and therefore if the field vector has a component perpendicular to the air-water interface, the Pockels effect could take place. To examine whether this mechanism is possible, the field distribution at the interface was calculated by the finite element method with EEM-STF software, in which a spatially discretized Poisson equation was solved by the conjugate gradient method. In the calculation, the electrodes-dielectric system was assumed to be the same as the experimental setup: air and water with a horizontal boundary were placed between vertical electrodes of the same size as used in the experiments. The dielectric constants ε of air and water were assumed to be 1.0006 and 80.4, respectively, at 20 °C. Any interfacial layers continuously varying the dielectric constant from that in bulk water to that in the air were neglected.[3,12]

The results of these calculations are shown in Fig. 5. Figures 5(a) and 5(b) depict cross-sectional views of the voltage distribution on the plane which is normal to the water surface and intersects the centers of the electrodes for symmetrical (a) and slightly asymmetrical (b) electrode configurations, respectively. In Fig. 5(b), the left electrode was displaced downwards by 0.1 mm, while the right electrode was displaced upwards by 0.1 mm when compared with Fig. 5(a). Figures 5(c) and 5(d) show the distribution of the *z* (vertical) and *y* (horizontal) components of the electric field at the air-water interface for these symmetrical (c) and slightly asymmetrical (d) configurations, respectively. The calculated results clearly demonstrate that a vertical component of the electric field exists at the interface, although it is smaller by three orders of magnitude than the field parallel to the interface. Interestingly,

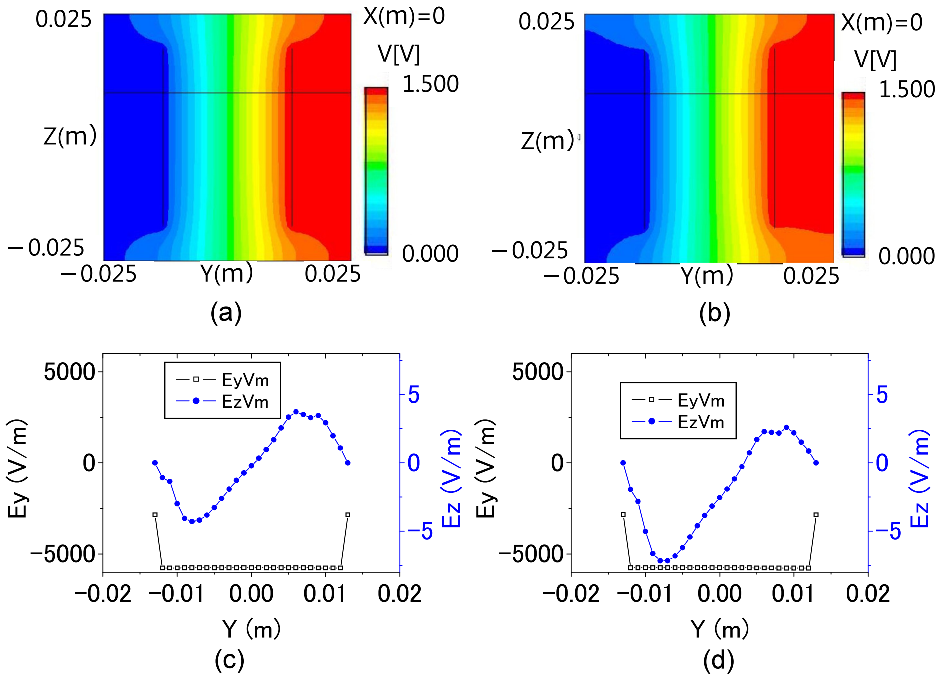


FIG. 5. Finite element method calculation results for the experimental electrodes-dielectric system comprising air ($\varepsilon = 1.0006$) and water ($\varepsilon = 80.4$) with a horizontal interface between vertical electrodes. Simulations used an experimental AC voltage of 300 Vpp and 150 V was applied to the right electrode with the left electrode grounded (0 V). (a) and (b) Cross-sectional views of the voltage distribution on the plane which is normal to the water surface and intersects the electrode centers for symmetrical (a) and slightly asymmetrical (b) electrode configurations. In (b), the left electrode is displaced downwards by 0.1 mm, while the right electrode is displaced upwards by 0.1 mm. (c) and (d) Distribution of the z (vertical) and y (horizontal) components of the electric field at the air-water interface. The x-component (parallel to both the interface and the electrode surface, direction normal to the page) is zero because the cross sections are taken at the center of the electrodes.

even with the completely symmetric configuration used in Figs. 5(a) and 5(c) (where the vertical field is zero at the exact center between the electrodes), an asymmetric vertical field distribution arises, which is associated with the asymmetry (polarity) of the applied voltage. This field distribution is consistent with the position-dependent results in Fig. 3 and experimental observation (D). When the electrodes were asymmetrically positioned [Figs. 5(b) and 5(d)], a vertical field as large as −2.55 V/m was present at the center. It was thus confirmed that the Pockels effect was caused by the incident light being slightly displaced from the center or by asymmetrically positioned electrodes. Surprisingly, this means that the Pockels coefficients are 1000 times larger than the original estimate of $|r| = 1.4 \times 10^5$ pm/V because only the weak vertical field is responsible for the Pockels effect.

Such an unusually large Pockels effect is considered to be owing to liberated water at the surface where water molecules are not bound by hydrogen bonding in the upward direction. As a result, they are more susceptible to the vertical electric field, causing a larger Pockels effect than at the solid-water interface.[14,15,17–20] This is consistent with experimental observation (C). Although the mechanism due to the vertical field is qualitatively sound, the enhancement by many orders of magnitude in the Pockels coefficient is yet to be quantitatively resolved. If this effect were to be confirmed, it is a promising candidate for electro-optic modulators as well as a sensitive tool to detect weak electric field distributions.

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