

# Phase-Sensitive Second-Harmonic Generation of Electrochemical Interfaces

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## Second-harmonic generation at the Pt-HClO<sub>4</sub> interface

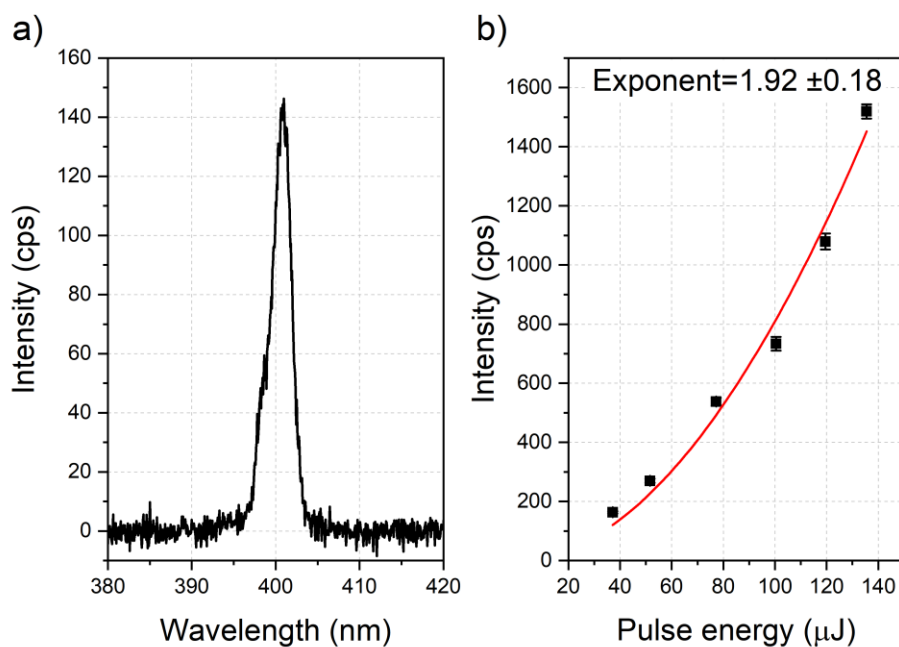


Figure S1. (a) A typical SHG spectrum of the Pt-HClO<sub>4</sub> interface measured with a pulse energy of 77  $\mu$ J. (b) The integrated SHG intensity from the Pt-HClO<sub>4</sub> interface as a function of pulse energy. Fitting the data with a power function ( $y = Ax^n$ ) yields an exponent close to 2. The Pt electrode was held at the open-circuit potential.

## Frequency-domain interference

We follow the algorithm developed by the Tahara group.<sup>1,2</sup> The total electric field of the SHG signal in time domain,  $E_{\text{total}}(t)$ , can be expressed as:

$$E_{\text{total}}(t) = E_{\text{Pt}}(t - T) + E_{\text{LO}}(t) \quad (\text{S1})$$

where  $E_{\text{Pt}}(t)$  and  $E_{\text{LO}}(t)$  are the electric field of the SHG in time domain from the Pt electrode and LO, respectively.  $T$  denotes the time delay between the two signals.

The above equation, when Fourier-transformed into the frequency domain (Figure 2b), is as follows:

$$\tilde{E}_{\text{total}} = \tilde{E}_{\text{Pt}} \exp(i\omega T) + \tilde{E}_{\text{LO}} \quad (\text{S2})$$

The corresponding electric field in the frequency domain is indicated with a tilde.  $\omega$  is the optical frequency of SHG. The total intensity ( $I$ ) therefore takes the following form:

$$I = |\tilde{E}_{\text{total}}|^2 = |\tilde{E}_{\text{Pt}}|^2 + |\tilde{E}_{\text{LO}}|^2 + \tilde{E}_{\text{Pt}} \tilde{E}_{\text{LO}}^* \exp(i\omega T) + \tilde{E}_{\text{Pt}}^* \tilde{E}_{\text{LO}} \exp(-i\omega T) \quad (\text{S3})$$

## Characterization of the potential of zero charge ( $U_{pzc}$ ) by electrochemical impedance spectroscopy (EIS)

The EIS measurements were performed in 0.1 M HClO<sub>4</sub> solution (Ar purged) using Bio-Logic SP-300 potentiostat, with a frequency range of 0.5-10<sup>4</sup> Hz and an amplitude of 5 mV. Representative experimental data is plotted in Figure S2. With an equivalent circuit (Figure S2c) considering the series resistance (R), Warburg diffusion (W), and double-layer capacitance (C), we can get reasonable fitting of the experimental values as shown by the red line in Figure S2. The fitted parameters are listed in Table S1.

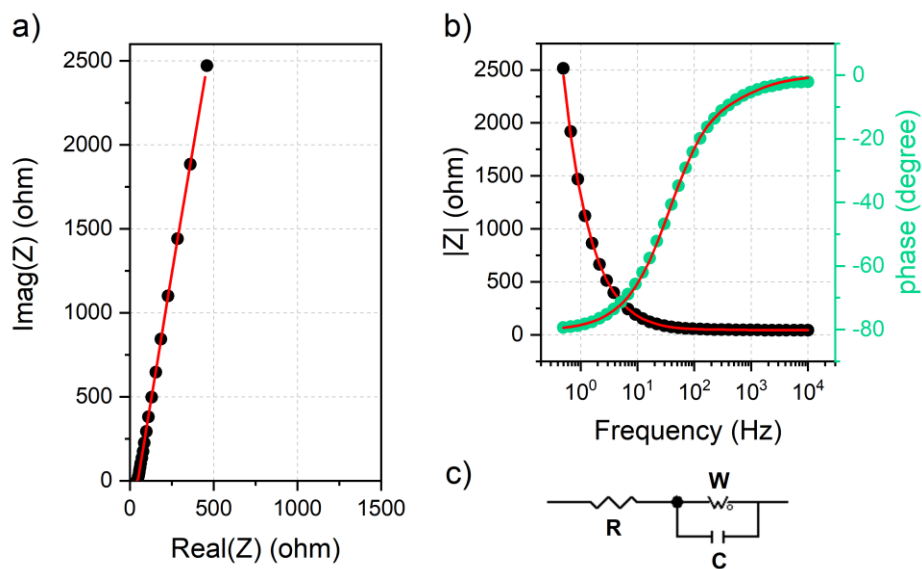


Figure S2. The Nyquist plot (a) and Bode plot (b) of an EIS measurement at 0.359 V vs RHE. Dotted points are experimental values; red lines are the fitted data; the equivalent circuit is shown in (c). The electric elements are series resistance (R), Warburg diffusion (W), and double-layer capacitance (C). Fitted parameters are presented in Table S1.

Table S1. The fitted parameters for the EIS data in Figure S2.

Electric element (unit)		Value	Fitting error
	R (ohm)	43.36	0.15
	C ( $\mu\text{F}/\text{cm}^2$ )	62.13	4.88
W*	W <sub>R</sub> (ohm)	30.54	2.24
	W <sub>P</sub> (1)	0.44	0.01
	W <sub>T</sub> (msec)	1.72	0.11

\*The formula for the impedance of W is  $Z = W_R \coth(iW_T\omega)^{W_P} / (iW_T\omega)^{W_P}$

By conducting EIS measurement at a series of potentials, we obtained the potential-dependent double-layer capacitance as shown in Figure S3. According to the Gouy-Chapman-Stern (GCS) theory,<sup>3</sup> the double-layer capacitance ( $C_{\text{EDL}}$ ) can be approximated as two components in series from the Helmholtz layer ( $C_{\text{H}}$ ) and the diffuse layer ( $C_{\text{D}}$ ) with the following formula:

$$\frac{1}{C_{\text{EDL}}} = \frac{1}{C_{\text{H}}} + \frac{1}{C_{\text{D}}} \quad (\text{S4})$$

While  $C_{\text{H}}$  is a constant independent of the surface potential ( $U_0$ ),  $C_{\text{D}}$  takes the form of

$$C_{\text{D}} = \left( \frac{2m^2 e^2 \epsilon \epsilon_0 c}{k_B T} \right)^{1/2} \cosh \left( \frac{meU_0}{2k_B T} \right) \quad (\text{S5})$$

where  $V_0$  is defined as the difference between the applied potential and  $V_{\text{pzc}}$ , and other parameters are listed in Table S2:

Table S2. Parameters used for the GCS model

Symbol	Name	Value	Unit
$e$	Electric charge	$1.602 \times 10^{-19}$	C
$k_B$	Boltzmann constant	$8.617 \times 10^{-5}$	eV/K
$T$	Temperature	298.5	K
$c$	Electrolyte concentration	0.1	mol/L
$m$	Ion charge	1	1
$\epsilon_0$	Permittivity of free space	$8.854 \times 10^{-12}$	F/m
$\epsilon$	Dielectric constant of water	78.49	1

Using Equation (S4) and (S5), we can fit the experimental data in Figure S3, which produces

$$U_{\text{pzc}} = 0.652 \pm 0.005 \text{ V and } C_{\text{H}} = 65.5 \pm 1.0 \text{ } \mu\text{F}/\text{cm}^2.$$

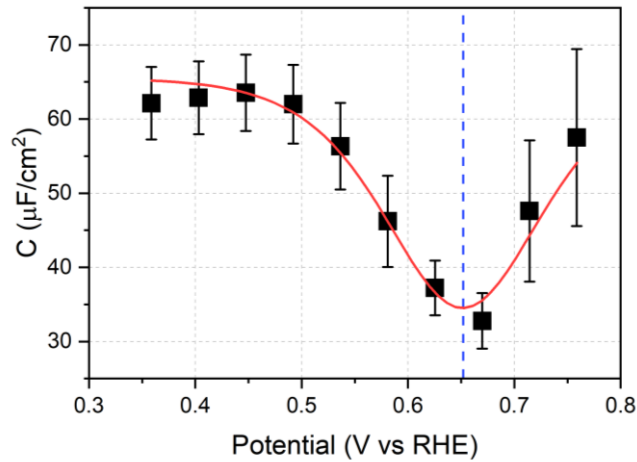


Figure S3. Black square: the double-layer capacitance as a function of the applied potential. Red line: the least-square fitting with Equation (S4). Blue dash indicates the fitted  $U_{\text{pzc}}$  (0.652 V).

## SHG intensity and phase stability over time

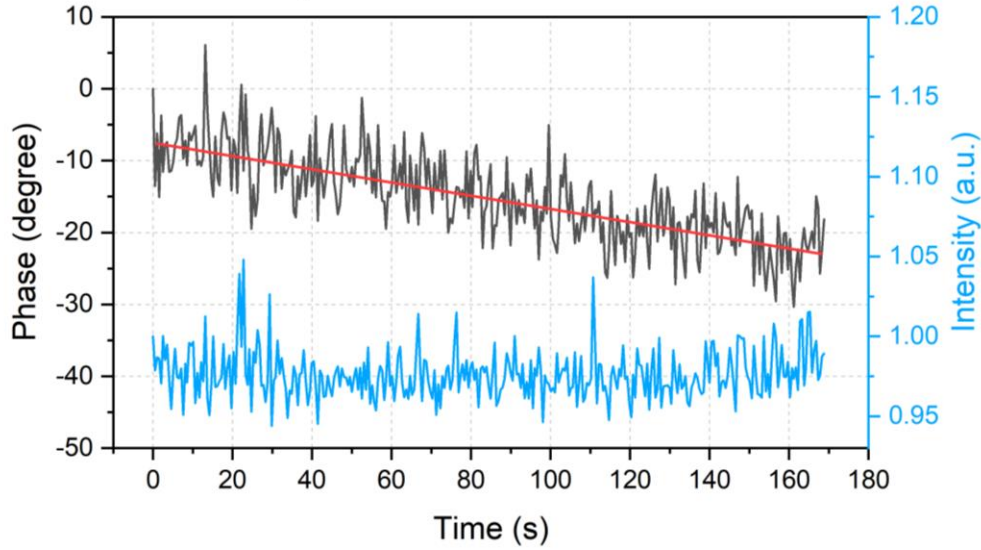


Figure S4. The stability of the SHG phase (black) and the integrated intensity (blue) over time determined by PS-SHG. A linear fit (red) of the phase change with time yields a slope of -0.095 degree/second. The Pt electrode was held at open-circuit potential during the measurement. Data at 0 s was used for normalization.

## Nonlinear response from the electrochemical double layer

In GCS theory,<sup>3</sup> the electrode potential ( $U$ ) profile in the electrochemical double layer can be modeled with the following set of equations:

$$\frac{\tanh(meU/4k_B T)}{\tanh(meU_2/4k_B T)} = e^{-\kappa(z-z_2)}, z \geq z_2 \quad (\text{S6})$$

$$U = U_2 - (z_2 - z) \left( \frac{dU}{dz} \right)_{z=z_2}, 0 \leq z < z_2 \quad (\text{S7})$$

$$\kappa = \left( \frac{2cm^2 e^2}{\epsilon \epsilon_0 k_B T} \right)^{1/2} \quad (\text{S8})$$

The electric field distribution is:

$$E_{DC}(z) = -\frac{dU}{dz} \quad (\text{S9})$$

Here  $z$  represents the distance normal to the electrode surface and  $z_2$  is the Helmholtz plane at which the potential is  $U_2$ . Using the  $C_H$  value fitted from EIS measurements, we can calculate  $z_2 = \epsilon\epsilon_0/C_H = 1.061 \text{ nm}$ . All other parameters can be found in Table S2. For reference, the simulated potential profiles at surface potentials of 0.1, 0.3, and 0.5 V ( $U_{z=0}$ , relative to the potential of zero charge) are plotted in Figure S5.

The nonlinear response from the electrochemical double layer can be calculated from:<sup>4</sup>

$$\chi_{\text{eff}}^{(2)} = \chi^{(2)} + \chi^{(3)} \int_0^{+\infty} E_{\text{DC}}(z) e^{i\Delta k_z z} dz \quad (\text{S10})$$

where  $\chi^{(2)}$  represents the second-order optical susceptibility from the surface-bonded species;  $\chi^{(3)}$  is the third-order optical susceptibility of the water molecules;  $\Delta k_z$  is the wavevector mismatch (calculation is provided in the next section). For silica-water interfaces,  $\chi^{(2)}$  and  $\chi^{(3)}$  have values of the same magnitude.<sup>5</sup>

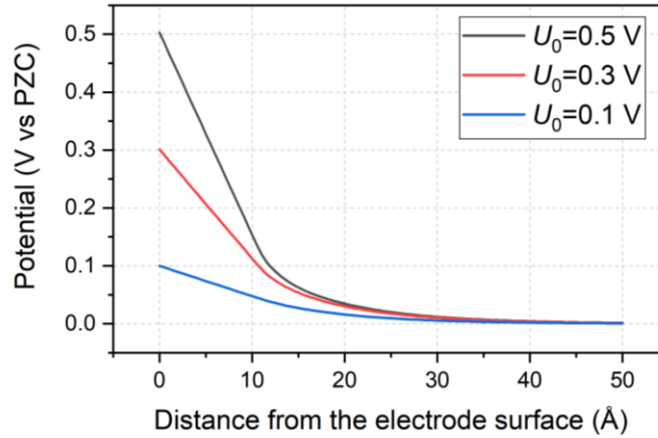


Figure S5. The potential profiles in the electrochemical double layer at different surface potentials, simulated by Equation (S6) – (S9).

## Wavevector mismatch calculation

As show in Figure S6, the fundamental beam impinges the Pt-water interface at an incident angle of  $\theta_1$ , with SHG reflected at an angle of  $\theta_0$ . In our experimental,  $\theta_1 = 45^\circ$ , then we can calculate  $\theta_0$  from the Snell's law:

$$n_1 \sin \theta_1 = n_0 \sin \theta_0 \quad (\text{S11})$$

The wavevector mismatch is given by:

$$\Delta k_z = |k_{1z} + k_{2z} - k_{0z}| = 2k_{1z} + k_{0z} \quad (\text{S12})$$

$$k_{jz} = \frac{2\pi n_j}{\lambda_j} \cos \theta_j, j = 1 \text{ or } 0 \quad (\text{S13})$$

All the above symbols are listed in Table S3. We calculated  $\Delta k_z = 0.030 \text{ nm}^{-1}$ .

Table S3. Symbols used in Equation(S11)-(S13)

Symbol	Value	Unit	Name
$\lambda_1$	800	nm	Fundamental wavelength
$\lambda_0$	400	nm	SHG wavelength
$n_1$	1.329		index of refraction of water for 800nm
$n_0$	1.339		index of refraction of water for 400nm



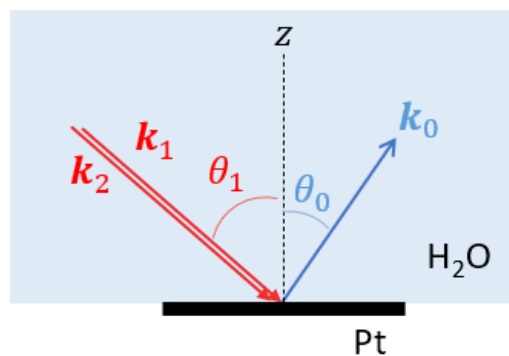


Figure S6. Optical geometry of the SHG reflection at Pt-water interface. Red arrows ( $k_1, k_2$ ) refer to the wavevectors of fundamental beams at an incident angle of  $\theta_1$  and the blue arrow ( $k_0$ ) is the wavevector of the SHG beam reflected at an angle of  $\theta_0$ . In SHG,  $k_1 = k_2$ .

### Graphic representation of Equation (4)

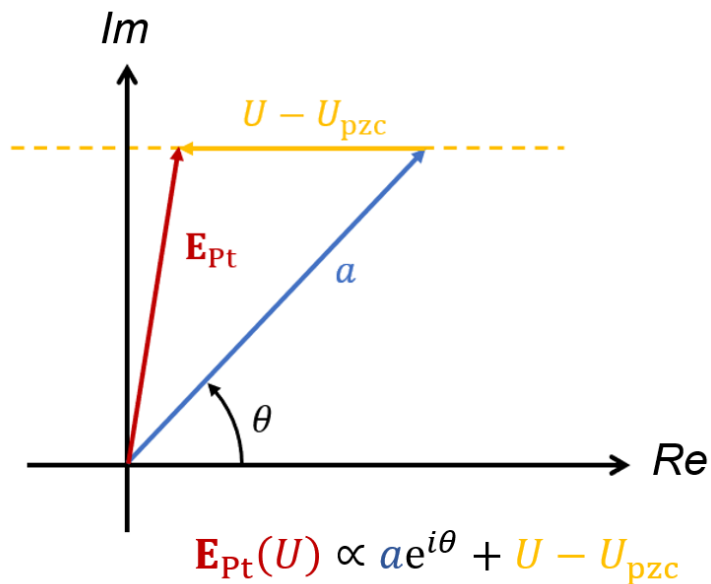


Figure S7. An Argand diagram of Equation (4), demonstrating that only when  $\theta = 90^\circ$ ,  $U = U_{\text{pzc}}$  corresponds to the minimum of  $|\mathbf{E}_{\text{Pt}}|$ . The dashed line indicates possible values of  $U - U_{\text{pzc}}$ .

## Reference

- (1) Yamaguchi, S.; Tahara, T. Heterodyne-Detected Electronic Sum Frequency Generation: “Up” versus “down” Alignment of Interfacial Molecules. *J. Chem. Phys.* **2008**, *129* (10), 101102.
- (2) Nihonyanagi, S.; Yamaguchi, S.; Tahara, T. Direct Evidence for Orientational Flip-Flop of Water Molecules at Charged Interfaces: A Heterodyne-Detected Vibrational Sum Frequency Generation Study. *J. Chem. Phys.* **2009**, *130* (20), 204704.
- (3) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods : Fundamentals and Applications*, 2nd ed.; Wiley and Sons, 2000.
- (4) Gonella, G.; Lütgebaucks, C.; de Beer, A. G. F.; Roke, S. Second Harmonic and Sum-Frequency Generation from Aqueous Interfaces Is Modulated by Interference. *J. Phys. Chem. C* **2016**, *120* (17), 9165–9173.
- (5) Chang, H.; Ohno, P. E.; Liu, Y.; Lozier, E. H.; Dalchand, N.; Geiger, F. M. Direct Measurement of Charge Reversal on Lipid Bilayers Using Heterodyne-Detected Second Harmonic Generation Spectroscopy. *J. Phys. Chem. B* **2020**, *124* (4), 641–649.