

Gas-Liquid Interface of Aqueous Solutions of Surface Active Aromatic Molecules Studied Using Extreme Ultraviolet Laser Photoelectron Spectroscopy and Molecular Dynamics Simulation

Yo-ichi Yamamoto,¹ Tomonori Hirano,² Tatsuya Ishiyama,³ Akihiro Morita² and Toshinori Suzuki^{1,*}

¹Department of Chemistry, Graduate School of Science, Kyoto University, Kitashirakawa-Oiwakecho, Sakyo-Ku, Kyoto 606-8502, Japan

²Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan

³Department of Applied Chemistry, Graduate School of Science and Engineering, University of Toyama, Toyama 930-8555, Japan

ABSTRACT: We investigated the gas-liquid interface of aqueous solutions containing phenol and related aromatic compounds using extreme ultraviolet laser photoelectron spectroscopy and molecular dynamics simulations. The interfacial densities of protonated and deprotonated forms of phenol, aniline, and 4-nitrophenol were found to be primarily determined by their surface affinities and exhibit similar concentration dependences to their respective bulk densities. Despite the distinct interfacial orientations of their permanent dipole moments, these compounds monotonically decreased the surface potential at higher concentrations. The exception was sodium phenolate, whose surface potential first increased and then decreased with increasing concentration. This behavior is attributed to the opposing effects of the electric double layer formed by Na^+ and phenolate ions at the gas-liquid interface and the induced electronic polarization of phenolate.

INTRODUCTION

The structure and dynamics of molecules at the gas-liquid interface are of fundamental and practical importance in interfacial, environmental, and atmospheric chemistry.¹⁻⁴ These problems have been extensively studied using nonlinear optical spectroscopy methods such as second-harmonic generation (SHG) and sum-frequency generation (SFG).⁵⁻⁷ These methods have exclusive selectivity for the gas-liquid interface, because nonlinear optical responses do not arise from the bulk but only from the interface where the spatial symmetry is broken. Although photoelectron spectroscopy (PES) does not exhibit strict surface selectivity, photogenerated electrons have an extremely small escape depth (on the order of 1 nm or less) from the liquid surface within the electron kinetic energy range concerned in this paper (30–50 eV);⁸⁻¹¹ this provides extremely high sensitivity toward the gas-liquid interface. Furthermore, when this interface is highly enriched with solute molecules, the photoelectron (PE) signal from the bulk can be neglected, making PES an ideal tool for investigating liquid surfaces. Recent developments in high-order harmonic generation (HHG) have allowed the production of intense extreme ultraviolet (EUV) radiation using tabletop systems, paving the way for EUV-PES to become a powerful analytical tool for gas-liquid interfaces.

To demonstrate the potential of EUV-PES, the present study applied EUV-PES and molecular dynamics (MD) simulations to aqueous solutions of phenol and related organic compounds. The molecular structures and permanent dipole moments of these molecules are illustrated in Figure 1. First, we focus on the electrostatic surface potential (ϕ), more specifically the shift ($\Delta\phi$) relative to the ϕ of pure water, and the molecular aggregation structure. Thus far, ϕ and $\Delta\phi$ have been measured using

various electrochemical methods such as liquid flow,¹² Kelvin probe (vibrating plate capacitor),¹³ and ionizing electrode methods.¹⁴ Despite these experimental efforts and theoretical calculations, the absolute value of ϕ for pure water remains under debate.^{12, 14-21} Hence, the present study focuses on $\Delta\phi$ instead. Secondly, we demonstrate how EUV-PES enables highly efficient measurements of chemical equilibria at the gas-liquid interface. As an example, we consider the long-standing problem of acid/base (protonation-deprotonation) equilibrium at such an interface.²²⁻²⁴ Eisenthal and coworkers performed a pioneering vibrational SFG study on the equilibrium between phenol ($\text{C}_6\text{H}_5\text{OH}$) and phenolate ($\text{C}_6\text{H}_5\text{O}^-$).²⁵ Here, we used EUV-PES to investigate the protonation-deprotonation equilibrium for phenol,²⁶ aniline, and 4-nitrophenol (4-NP).

The fundamental principles of measuring $\Delta\phi$ through photoemission are briefly explained as follows. When liquid water is exposed to EUV radiation, an electron in the highest occupied molecular orbital (HOMO) of liquid water is excited to the conduction band, leading to its emission through the gas-liquid interface. Just outside the liquid in the vacuum, the emitted electron has a well-defined kinetic energy E_0 . As the electron travels through the vacuum chamber to reach an electron detector, it may experience some non-uniform electrostatic potential and/or work function that shifts its kinetic energy. However, such secondary effects can be calibrated using the cutoff method to accurately estimate E_0 .²⁷⁻²⁹ This measurement provides us with the energy required to promote a valence electron to zero kinetic energy just outside the liquid, which is termed the “vertical electron binding energy” (or vertical ionization energy for neutral species). The adsorption of a solute to the gas-liquid interface creates a local electric field and the associated potential. When the local field does not significantly alter the

electronic structure of the solute and solvent, their electron binding energies are equally shifted with the associated potential ($\Delta\phi$). Thus, for an aqueous solution, a different electron kinetic energy (eKE), E , will be found just outside the liquid. When E is higher than E_0 , it indicates that an electron in the aqueous solution has a higher potential energy compared to that in pure water, *i.e.* a lower electrostatic potential ϕ (since the electron has a negative charge). Thus, the relation $E = E_0 - e\Delta\phi$ holds. The potential significantly influences the kinetic energies of all electrons emitted from the liquid, irrespective of the electron orbitals they are from. Thus, our EUV-PES experiments explore the energy shifts of bound states with respect to the vacuum level and $\Delta\phi$.

In addition to the photoemission signal of solvent water, $\Delta\phi$ can also be estimated from the photoemission signal of a solute that has segregated at the liquid surface. When the HOMO of a solute has a lower electron binding energy than the HOMO of liquid water, the former can be spectrally separated from the latter for clear observation and analysis. Measuring $\Delta\phi$ using the solutes is useful for examining whether the energy shift occurs equally for all solutes and solvents. At a high concentration, the solutes disrupt the hydrogen-bonding network of liquid water, altering its electronic structure.³⁰⁻³² In such cases, it becomes more complex or impossible to isolate the influence of $\Delta\phi$ on the PE spectrum of liquid water.³³ An independent measurement of $\Delta\phi$ using the solute becomes particularly important in these cases.

For emission from the gas-liquid interface, an electron must travel from inside the liquid to the interface, during which electron-molecule scattering can occur.⁸ This scattering process encompasses electronic, vibrational, and rotational inelastic scattering, depending on the degree of freedom that plays a role in the molecular scatterers (primarily water molecules).³⁴⁻³⁸ The scattering cross-sections have a common trend of decreasing at higher electron kinetic energies, as reviewed by Itikawa and Mason for electron-water collisions in the gas phase.³⁹ When the electron kinetic energy is below 10 eV, rovibrational inelastic scattering plays a dominant role, resulting in continuous electron energy loss and significantly distorting the PE kinetic energy spectrum. Elastic scattering also has a large cross-section at a low kinetic energy, increasing the effective path length of an electron and enhancing its energy loss.⁹ In contrast, in the energy range much higher than 10 eV, as in the present study, electronic inelastic scattering becomes predominant, resulting in a larger average energy loss. Consequently, the distributions of electrons that have and have not undergone electronic inelastic scattering become distinctly separated in energy. For electrons with high kinetic energies, the influence of inelastic scattering becomes practically negligible. That is why the PE band of HOMO is generally the least influenced by the scattering effects. The photoemission of liquid water has been studied in detail, and it was demonstrated that a constant electron binding energy can be extracted across a wide range of photon energies using the cutoff method.^{29, 37}

One complication of the EUV-PES method is that it requires the vacuum condition and a continuous flow of liquid.⁴⁰⁻⁴¹ The latter is necessary to avoid evaporative freezing of the liquid and to replenish the sample under EUV irradiation. However, discharging a liquid from a nozzle causes streaming electrification, which sometimes destabilizes the electrostatic potential of the

liquid.^{40, 42-43} To mitigate this problem, a sufficient level of electric conductivity is maintained by adding a low concentration of inorganic electrolyte.⁴²⁻⁴³ Consequently, the “pure water” in PES studies using a flowing liquid actually contains dissolved inorganic salt. Nevertheless, the influence of such trace amounts (~ 30 mM) of inorganic salt on the PE spectrum of liquid water has been confirmed negligible. A previous SHG study showed that the change in ϕ is less than 10 mV in a concentration range of tens of mM.⁴⁴ In contrast, the $\Delta\phi$ values for aqueous solutions of organic molecules discussed in the present study are much larger.

Theoretical simulation is essential for understanding the relation between $\Delta\phi$ and the gas-liquid interfacial structure. In aqueous solutions of electrolytes, $\Delta\phi$ is strongly influenced by the formation of an electric double layer (EDL) at the gas-liquid interface. For example, aqueous solutions of NaI and tetrabutyl ammonium iodide (TBAI) exhibit opposite signs of $\Delta\phi$, because the local electric field of the EDL is reversed between them.^{32, 45-47} On the other hand, the detailed mechanism of creating $\Delta\phi$ is much more subtle for aqueous solutions of neutral organic molecules such as phenol, aniline, and 4-NP. These compounds contain various hydrophilic functional groups and the π -hydrogen bond,⁴⁸ and they assume different orientations at the gas-liquid interface. It is of interest to see how $\Delta\phi$ is correlated (or uncorrelated) with the dipole orientations of these molecules. Sodium phenolate is an interesting hybrid between an organic molecule and an inorganic electrolyte, because it is ionized in water to create an EDL while the anion is an organic molecule. As we will see later, sodium phenolate exhibits an interesting behavior in terms of $\Delta\phi$. To describe these systems, we found it necessary to perform polarizable MD simulations. Nevertheless, because of the prohibitive computational time (more than a month for a given bulk concentration), only a few representative data points are presented in this paper.

In the following, we first describe the experimental and theoretical methods and then discuss the general features of the PE spectra of aqueous phenol, aniline, and 4-NP solutions at neutral pH and the corresponding $\Delta\phi$ values. Next, we discuss $\Delta\phi$ for the sodium phenolate solution. Finally, the acid-base equilibrium at the gas-liquid interface is discussed for phenol, aniline, and 4-NP.

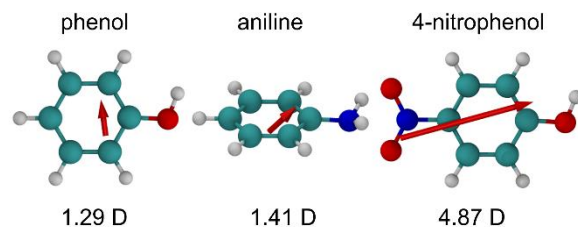


Figure 1. Molecular structure and permanent dipole moment of phenol, aniline, and 4-NP. Red arrows show the dipole moment vectors calculated using CCSD/aug-cc-pVTZ after geometry optimization using MP2/aug-cc-pVTZ.

METHODS

Experimental Methods

A one-box Ti:sapphire regenerative amplifier (5 kHz, 35 fs, 800 nm, 10 W) was used as a driving laser for HHG.³² The fundamental or the second harmonic (400 nm) was focused into an Ar gas cell using a quartz lens ($f = 300$ mm). A single harmonic was isolated using a time-preserving monochromator (500 grooves/mm).⁴⁹ A microfluidic chip made of borosilicate glass discharged two liquid jets at a total flow rate of 1.2 mL/min (0.6 mL/min each), and the collision of the two jets generated a flat liquid surface (Supporting Information (SI), Section A).⁵⁰ A sample solution of variable solute composition and concentration was supplied to the microfluidic chip using a gradient-flow HPLC pump. The length and width of the leaf-like flat jet were 2.2 and 0.7 mm for liquid water at a flow rate of 1.5 mL/min, respectively. However, these dimensions varied with the viscosity and flow rate of the liquid. The typical thickness of the flat jet was 0.7 μm , while the rim was ~ 20 μm in diameter.⁵⁰ Because the electron escape depth is ~ 1 nm, the photoemission signal intensity is independent of the thickness of the liquid. In addition to possessing a large cross-section of the liquid target, the flat liquid surface also allowed us to manipulate the incidence angle of EUV radiation on the liquid surface and investigate the photoemission induced by evanescent EUV radiation (SI, Section B). The EUV laser propagation axis and the electron detection axis were perpendicular to each other. Photoelectrons emitted from the flat jet were measured using a magnetic bottle time-of-flight electron energy analyzer described elsewhere.⁵¹ The emitted photoelectrons were guided by a magnetic field to the electron energy analyzer, so that they could be detected regardless of their emission angle θ . The electron binding energy (eBE) was determined from the difference between the photon energy ($h\nu$) and the measured eKE. The procedures to determine $h\nu$ and eKE are described in SI Sections C and D, respectively.

As a flat jet travels through vacuum, its temperature decreases due to evaporative cooling.⁵²⁻⁵³ We adopted a model discussed by Chang *et al.*⁵³ to estimate the temperature of our liquid sample at the EUV irradiation point to be 276.9 K. Details of this temperature estimation are provided in SI Section F. To study the acid-base (protonation-deprotonation) equilibria at the gas-liquid interface, we adjusted the pH of aqueous phenol and 4-NP solutions by adding NaOH and that of aqueous aniline solution by adding HCl. The pH and thermodynamic constants such as pK_a and pK_w were estimated for the temperature of a flat jet, as described in SI Section G.

Theoretical Methods

We performed preliminary MD simulations with a non-polarizable model but obtained rather scattered predictions, indicating that it is difficult to make reliable and consistent predictions. These results are summarized in SI Section L. Therefore, despite a considerably higher computational load, we performed MD simulations with a polarizable force field, namely the charge response kernel (CRK) model,⁵⁴ which accounts for electronic polarization as a fluctuation of partial charges. However, the high computational load limited these calculations to a restricted number of conditions. The CRK model

characterizes partial charge variations in response to an external electric field, and the instantaneous charges are obtained by solving the equation for intermolecular electrostatic interactions in a self-consistent manner during the simulations. The CRK model has been used in classical MD simulations⁵⁴ to describe the density, enthalpy of evaporation, diffusion coefficient, and IR/Raman and SFG spectra. CRKs for water, Na^+ , and phenol have already been developed.^{54,55-56} The CRK model is appropriate for describing surface structures where electronic polarization is induced by an asymmetric solvation environment. Furthermore, the partial charges and CRK parameters were determined to reproduce the dipole moment and polarizability obtained from quantum chemical calculation, which are important for the quantitative evaluation of the surface potential.

The partial charges and CRK parameters for aniline, 4-NP, and $\text{C}_6\text{H}_5\text{O}^-$ were newly determined at the B3LYP/aug-cc-pVTZ level of theory, and the Lennard-Jones parameters were obtained from the general AMBER force field (GAFF).⁵⁷ The Lennard-Jones interactions were treated using the Lorentz-Berthelot combining rule. The Coulombic interactions were calculated using the smooth-particle-mesh Ewald method.⁵⁸ The simulation box had dimensions of $25 \text{ \AA} \times 25 \text{ \AA} \times 150 \text{ \AA}$ and contained either 1200 water molecules for the sodium phenolate solution or 600 water molecules for phenol, aniline, and 4-NP solutions and 25 solute molecules or ion pairs. More details are provided in SI Section M.

The electric potential $\phi(Z_0)$ was then calculated using the following formulas:

$$\phi(Z_0) = - \int_{\infty}^{Z_0} dZ' E_Z(Z') \quad (1)$$

$$E_Z(Z_0) = \frac{1}{\epsilon_0} \int_{\infty}^{Z_0} dZ' \rho_q(Z') \quad (2)$$

where $E_Z(Z)$ and $\rho_q(Z)$ are the surface-normal component of the electric field and the charge density at location Z , respectively, and ϵ_0 is the dielectric permittivity of vacuum. $Z = 0$ corresponds to the Gibbs dividing surface, and $Z = \infty$ refers to a location in vacuum at an infinite distance from the surface under the field-free condition. The reference surface potential is taken as $\phi(\infty) = 0$.

The surface potential in the bulk region of the liquid, $Z = Z_0$, is expressed by the following equation,⁵⁹

$$\phi(Z_0) = \frac{1}{\epsilon_0} \left\{ \int_{\infty}^{Z_0} dZ' P_Z(Z') - Q_{ZZ}(Z_0) \right\} \quad (3)$$

where P_Z and Q_{ZZ} indicate the electrostatic dipole and quadrupole densities, respectively. The dipolar term is determined by the integral over the surface region, while the quadrupolar term is a bulk quantity. The quadrupole contribution is closely related to the electric potential inside a molecule, and it is excluded when calculating the “electrochemical” surface potential.¹⁷ In the present study, the gas-liquid interface is highly enriched with solute molecules, and the difference $\Delta\phi$ in the bulk potential is well expressed by only the difference (ΔP_Z) in the dipolar term between a solution and pure water:

$$\Delta\phi \approx -\frac{1}{\epsilon_0} \int_{-\infty}^{z_0} dz' \Delta P_z(z') \quad (4)$$

ΔP_z is composed of the dipole density of the solute and the dipole distribution change of water induced by the solute. In our previous study, we found that the sign of $\Delta\phi$ for the TBAI solution surface is determined by the solute contribution.³² In the present study, based on our MD simulation results, we argue that the direction of shift is not predicted only by the solute contributions in general.

RESULTS AND DISCUSSION

Aqueous Solutions of Phenol, Aniline, and 4-NP

Experimental results

Figures 2(a), (d) and (g) show representative EUV-PE spectra of aqueous solutions of phenol, aniline, and 4-NP, respectively. These spectra are aligned at the 1b₁ (HOMO) band for water to illustrate the variation in the band intensities as a function of the concentration. The solute bands are seen in the eBE region below 1b₁ (11.3 eV).^{29, 42} The PE intensity for phenol steadily increases with increasing concentration up to 0.2 M⁶⁰ and saturates at higher concentrations. The water band intensity decreases with increasing phenol concentration. (A reduction in the PE intensity of water due to surface adsorption of the solute is also seen for the O(1s) signal of water; see Figure S9 in SI Section J.) The intensity variation can be expressed using the Langmuir isotherm equation,⁶¹ providing the free energy change of adsorption ($-\Delta_{ads}G^\circ$) of 15.7 ± 0.8 kJ mol⁻¹ that is in fair agreement with the values of 14.7 ± 0.4 kJ mol⁻¹ in Ref. [62] and 15.8 ± 0.4 – 16.7 ± 0.3 in Ref. [26].

When solute molecules are segregated at the surface, the solute signal arises exclusively from the top layer and becomes proportional to $\rho_{solute}^{top}(C)d$, where $\rho_{solute}^{top}(C)$ is the density of solute molecules in the top layer for a bulk concentration C , and d is the thickness of the layer. The PE signal from the solvent, $I_{solvent}(C)$, arises from solvent molecules in the top layer with a density $\rho_{solvent}^{top}(C)$ and the PE flux due to the solvent molecules in deeper regions. If a bulk solvent molecule density $\rho_{solvent}$ is assumed, then $I_{solvent}(C)$ can be expressed as

$$I_{solvent}(C) \propto \rho_{solvent}^{top}(C)d + F(C) \int_d^\infty \rho_{solvent} \exp\left[-\frac{D}{\lambda(0)}\right] dD \quad (5)$$

$$\approx \rho_{solvent}^{top}(C)d + F(C)\rho_{solvent}\lambda(0)$$

where $F(C)$ is an attenuation factor associated with electron scattering by organic molecules in the top layer. $\lambda(0)$ is the electron attenuation length for pure water, and was estimated to be ~ 1 nm for eKE ~ 30 eV.^{9–11} $\lambda(0)$ is much smaller than the penetration depth (~ 25 nm) for 40.0 eV EUV radiation in liquid water and also the penetration depth (< 15 nm) for evanescent waves under total internal reflection conditions (see SI Section B). Thus, $\lambda(0)$ determines the probing depth of EUV-PES.

$F(C)$ is considered to be proportional to $\rho_{solute}^{top}(C)$. If the top layer is completely occupied by phenol molecules at a high concentration, the photoelectrons giving rise to the water 1b₁ band originate from the lower layer and are scattered by this phenol monolayer. Then, the experimental results imply that $F(C) \approx 0.5$, and $\lambda(C)$ is approximately the thickness of a phenol monolayer ($\lesssim 1$ nm). This crude estimate is close to the estimated value (~ 1 nm) for $\lambda(0)$, suggesting that electron scattering by organic molecules is not significantly different from that by water molecules.

The maximum coverage of the liquid surface (f_{max}) with a solute is estimated as follows. The surface density Γ of the solute is estimated from the PE intensity and surface tension data^{26, 60, 62} (see SI Section I). The f value is calculated as the ratio of Γ with respect to the surface density Γ_{pure} of a pure solute.²⁶

Namely, $\Gamma_{pure} = \left(\frac{\rho N_A}{M}\right)^{\frac{2}{3}}$, with ρ representing the bulk density of the solute compound and M representing its molar mass. The calculated f_{max} values are summarized in Table 1. The value of f_{max} is close to unity for phenol and aniline, indicating that the interface is almost fully covered by these solutes. (Note: the surface concentration of organic molecules typically increases with the addition of electrolytes, provided that the surface concentration is below saturation. This phenomenon is commonly known as the specific ion effect² (see SI Section K).

Table 1 Estimation of Absolute Surface Coverage

	ρ (g cm ⁻³)	Γ_{pure} (10 ¹⁴ cm ⁻²)	Γ_{max} (10 ¹⁴ cm ⁻²)	f_{max}
Phenol	1.05 ^a	3.6	2.8	0.78
Aniline	1.02 ^a	3.5	3.6	1.0
4-NP	1.48 ^a	3.4	1.6	0.47

a: From Ref. [63]

Figure 2(b) shows the same spectra as in (a) but normalized using the intensity of the 1b₁ band for water (11.3 eV)^{29, 42} without energy alignment. The accurate binding energies are summarized in Table 2. The literature values of the vertical binding energy (VBE) for aqueous phenol and aniline were corrected by referencing an inaccurate VBE value of water 1b₁ (11.16 eV^{64, 65} versus the more accurate value of 11.3 eV^{29, 42}), so that they were systematically shifted by 0.1–0.2 eV. The PE spectra shift to lower eBE with increasing phenol concentration, as shown in Figure 2(c), and the H₂O 1b₁ and solute bands shift similarly (Figure 8). The decrease in eBE corresponds to a negative sign of $\Delta\phi$.

Table 2 Two Lowest VBE Values for Aqueous Solute Molecules (eV)

	phenol		C ₆ H ₅ O ⁻		aniline		4-NP		4-NP ⁻	
	Band 1	Band 2	Band 1	Band 2	Band 1	Band 2	Band 1	Band 2	Band1	Band2
This work 40.0-56.5 eV	7.90(4)	8.72(3)	7.3(1)	8.7(1)	7.74(4)	8.83(3)	7.8(1)	8.9(1)	6.9(1)	8.7(1)
XPS 200 eV	7.8 ^a	8.6 ^a	7.1 ^a	8.5 ^a	7.49 ^b	8.62 ^b				
EUV-PES 29.5 eV					7.4 ^c	8.5 ^c				

a: Ref. [⁶⁴] measured for 0.75 M solution.

b: Ref. [⁶⁵] measured for 0.127 mol/kg solution.

c: Ref. [⁶⁰] measured for 0.09 M solution.

Figure 2(d) shows the concentration dependence of the PE spectra of aqueous aniline solutions. Similar to the case for phenol, the aniline band intensity increases with concentration while the water 1b₁ band intensity decreases. The PE spectra also gradually shift to lower eBE with increasing aniline concentration; this concentration dependence is stronger than that for phenol, as shown in Figures 2(e) and 2(f). 4-NP is structurally similar to phenol, and the results of previous SHG spectroscopy studies suggested that 4-NP takes an OH-down orientation at the interface.^{62, 66} Here, “down” indicates pointing to the bulk liquid; however, this suggested OH-down orientation is actually incorrect, as will be discussed later. Figure 2(g) shows the concentration dependence of the PE spectra of aqueous 4-NP solutions,

and Figures 2(h) and 2(i) show the corresponding spectral shifts. 4-NP induces a PE energy shift in the same direction as that for phenol and aniline, although the shift is considerably smaller despite the larger permanent dipole moment of 4-NP (Figure 1).

Figures 2(b), 2(e), and 2(h) reveal a rather strong concentration dependence of the spectral features in the eBE region of 11–20 eV. This is attributed to an overlap between the PE signals from the solute and the water bands. In the present paper, we do not discuss the solute and solvent bands in this region owing to the considerable spectral overlap.

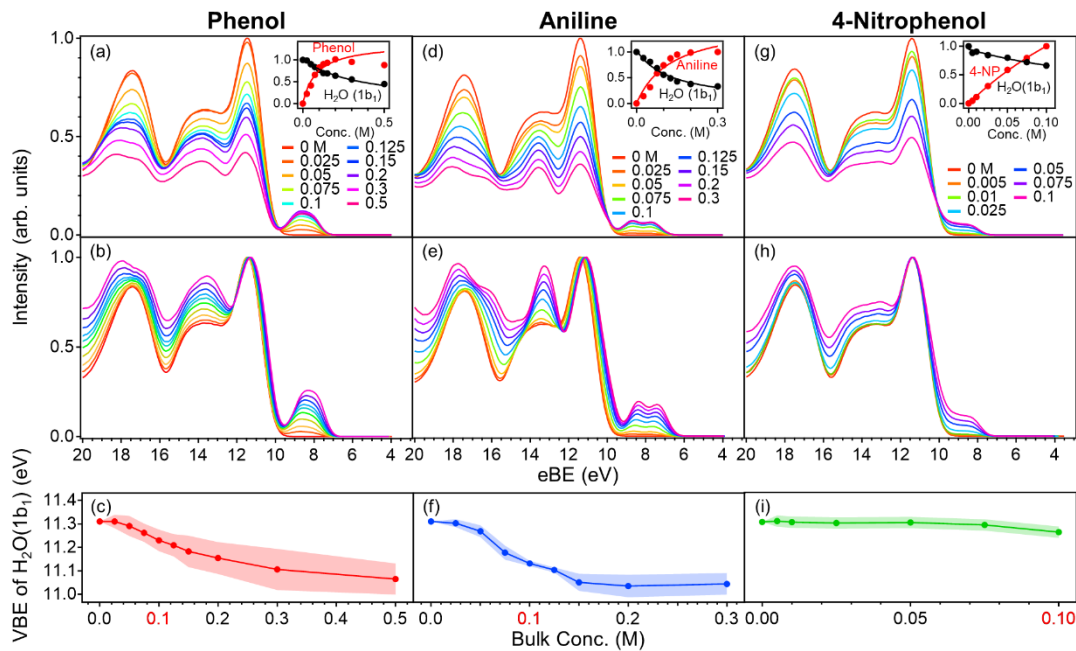


Figure 2. (a, d, g) PE spectra measured with 40.0 eV pulses for different concentrations of phenol, aniline, and 4-NP, respectively. The spectra are aligned at the H₂O 1b₁ band position. Inset: PE intensity for the H₂O 1b₁ (black) and solute (red) bands. The intensities of both H₂O and solute bands are normalized to their respective maximum intensities. The solid lines represent the best fits obtained using the Langmuir isotherm.⁶¹ (b, e, h) Same PE spectra as in (a, d, g), respectively, but with their intensity normalized by the 1b₁ peak for H₂O. (c, f, i) Dependence of the VBE for H₂O 1b₁ on the solution concentration. The shaded area represents the standard deviation ($\pm 1\sigma$) calculated from three independent measurements. To highlight the different concentration ranges, the tick labels for 0.1 M are colored in red.

MD Simulation

We performed polarizable MD simulations using CRK models. Figure 3 summarizes the calculated $\Delta\phi$ in the bulk for different solutions (see SI Section N for details). The calculated signs of $\Delta\phi$ are negative for the phenol, aniline, and 4-NP solutions, which are consistent with the experimental results. As will be shown later (Figure 6), ϕ becomes constant in the region deeper than 0.5 nm; consequently, the measured $\Delta\phi$ will not strongly depend on the probing depth of liquid PES.

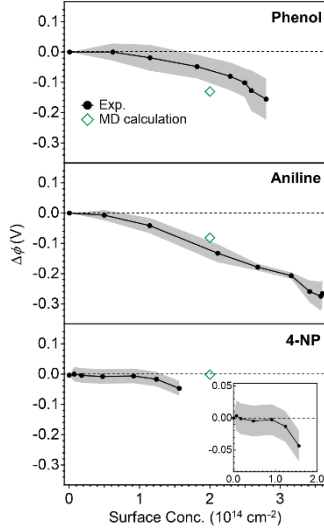


Figure 3. Comparison of $\Delta\phi$ estimated from the PE band of water $1b_1$ and from the MD calculations. The black circles and green symbols indicate data measured experimentally and calculated using the CRK model, respectively. The horizontal axis is the surface concentration of solute molecules, which was estimated from the PE band intensity for the solutes and surface tension data^{60, 62} at a certain bulk concentration (see SI Section I). The inset shows an enlarged view of $\Delta\phi$ for 4-NP.

To understand the origin of $\Delta\phi$, we need to examine key physical quantities at the interface. Figure 4(a) shows the calculated density distributions of the solute species near the interface. These calculations confirm the enhanced concentrations of solute molecules at the gas-liquid interface. These results imply surface-active characters of these aromatic species, even though they are soluble in liquid water. Figure 4(b) shows the density-weighted orientation profiles of solute species at the surface, which are represented as the product of the number density ρ and the mean orientation $\langle \cos \theta \rangle$. The calculated results of $\rho \langle \cos \theta \rangle$ indicate a noticeably large negative region at the surface $z \approx 0$ for aniline compared to other solute molecules, indicating that the dipole moment of aniline clearly points to the liquid phase. Since the dipole of aniline is oriented from the aromatic ring to the amino group in the molecule-fixed coordinates, the negative $\rho \langle \cos \theta \rangle$ in Figure 4(b) indicates that the hydrophilic amino group of aniline tends to point to the liquid phase at the interface. One might predict that such a dipole orientation of aniline would lead to a positive potential shift $\Delta\phi$ according to Eq. (4). However, this simple prediction is inconsistent with the experimental and calculated results of negative $\Delta\phi$ in Figure 3. It is noted that the sign of $\Delta\phi$ is determined by

not only the direction of the dipole moment of the adsorbed solute but also other factors, such as the orientation of water molecules and the electronic polarization of the solute and solvent. We further analyze the mechanism of the potential shift in SI Section N.

Figure 4(b) also shows a slightly positive $\rho \langle \cos \theta \rangle$ for 4-NP at the surface, indicating that the NO_2 group of 4-NP points slightly to the liquid phase. As mentioned earlier, the orientation of 4-NP at the water surface is not amenable to intuitive prediction, and it has been studied by SHG measurement.⁶⁷ However, the SHG results do not agree with the NO_2 -down orientation of 4-NP proposed here. The reason of this discrepancy is discussed in detail in SI Section O; it is suggested that there was an error in the previous analysis of the SHG signal.

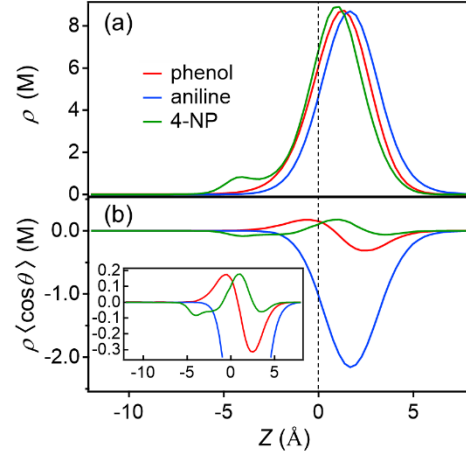


Figure 4. (a) Calculated density profiles of three solutes: phenol (red), aniline (blue), and 4-NP (green). $Z = 0$ is the Gibbs dividing surface. (b) Density-weighted orientation profiles for each species. θ is defined as the angle between the permanent dipole of the solute molecule and the surface normal. The inset shows a magnified view.

Reversal of $\Delta\phi$ in Aqueous Sodium Phenolate Solution

Experimental results

Figure 5(a) shows the concentration dependence of the PE spectra of aqueous sodium phenolate solutions measured at a photon energy of 56.5 eV. In Figure 5(b), the $\text{Na}^+(2p)$ signal increases with increasing $\text{C}_6\text{H}_5\text{O}^-$ signal intensity. Strikingly, the direction of the $1b_1$ band shift reverses with increasing phenolate concentration: according to Figure 5(c) it initially shifts to a higher VBE ($\Delta\phi > 0$), and then in the opposite direction at above 0.5 M. An aqueous NaI solution creates an EDL with I^- closer to the surface and Na^+ on the bulk side, which causes a monotonic increase in the VBE^{30, 32} (or increase in ϕ) with increasing concentration. In contrast, an aqueous TBAI solution creates an EDL with positive TBA^+ ions on the top layer and I^- on the bulk side, and hence, the VBE^{30, 32-33} (or ϕ) decreases with increasing concentration instead. For NaI or TBAI, no reversal in the sign of $\Delta\phi$ was ever observed.

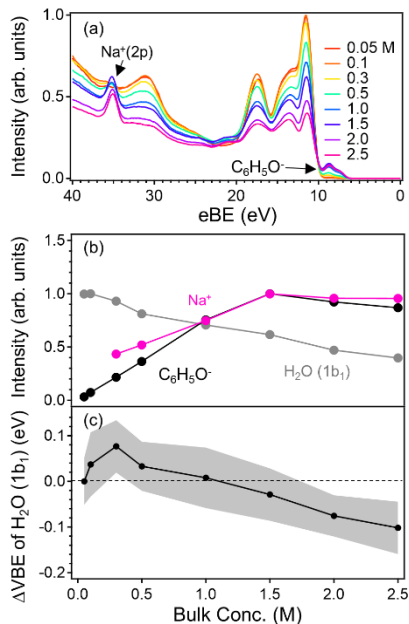


Figure 5. (a) Concentration dependence of PE spectra of sodium phenolate solutions measured with 56.5 eV pulses. (b) Comparison of the PE intensity for liquid water (gray), C₆H₅O⁻ (black), and Na⁺(2p) (pink). The intensities for water and C₆H₅O⁻ are arbitrarily scaled for comparison. (c) Dependence of the VBE shift of H₂O 1b₁ on the solution concentration. The shaded area indicates the standard deviation ($\pm 1\sigma$) calculated from the results of three independent measurements.

MD simulation

We performed MD simulations to understand the mechanism for the reversal of $\Delta\phi$ in aqueous sodium phenolate solutions. Non-polarizable MD simulations cannot reproduce the sign reversal of $\Delta\phi$ observed at high sodium phenolate concentrations (see SI Figure S13). Therefore, we analyzed $\Delta\phi$ using the CRK model. Figure 6(a) is a snapshot of the sodium phenolate solution at a bulk concentration of ~ 0.4 M. The formation of an EDL is evident. Figure 6(b) compares the density profiles of C₆H₅O⁻ calculated using polarizable and non-polarizable models, both assuming polarizable water. The polarizable model (solid curves) predicts a gas-liquid interface that is more enriched with ions than the non-polarizable model (dashed curves). As already seen in the snapshot in Figure 6(a), the C4 and O atoms of C₆H₅O⁻ reside closer to the gas-liquid interface than Na⁺. The peak C4 density (carbon in the *para* position from C-O) is located on the vacuum side, indicating that C₆H₅O⁻ takes an O-down orientation. Figure 6(c) displays the potential profiles $\phi(Z)$ obtained using the polarizable (blue curve) and non-polarizable (light blue curve) models, which are compared with that for pure water (black curve). The polarizable model shows a small negative shift of ϕ , while the non-polarizable model shows a positive value. The former is consistent with the experimental result. In Figure 6(d), we decompose $\phi(Z)$ calculated using the polarizable model into contributions from the solutes (Na⁺ and phenolate ion) and solvent. The contribution from the solutes is further divided into two components: the contribution (pink) from the original charge distribution (calculated in the

gas phase) and the correction (green) induced by electronic polarization in the solution. The positive contribution from the solute can be understood based on the orientation of the EDL (Figure 6(b)), where the anions are closer to the surface than the cations. The potential shift due to solute polarization is dominated by the polarization of C₆H₅O⁻, since the polarizability of Na⁺ is much smaller than that of C₆H₅O⁻. The strong polarization of C₆H₅O⁻ is a result of the electric field generated by the asymmetric hydration of C₆H₅O⁻ at the surface. The polarization is not strongly affected by the counter ions (Na⁺) because the electric field produced by Na⁺ is largely shielded by hydration. Consequently, the induced intramolecular polarization of C₆H₅O⁻ also helps screen the electric field associated with the EDL. The slightly negative potential shift $\Delta\phi$ is a consequence of strong screening of the field generated by the ion distribution, the water and solute orientation, and the electronic polarization.

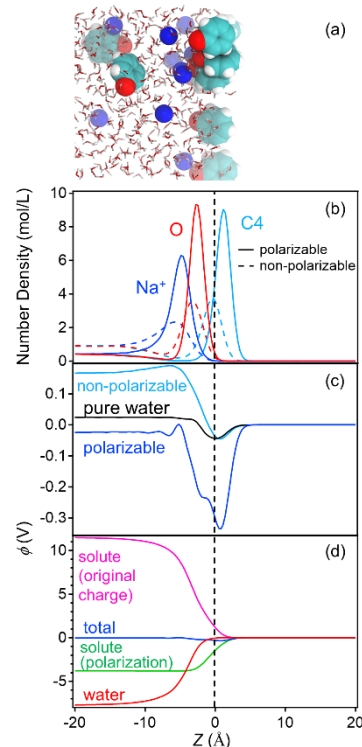


Figure 6. Calculated structure and potential for the surface of sodium phenolate solution. (a) Snapshot of the gas-liquid interface during MD simulation. The H, O, C, and Na atoms are indicated in white, red, cyan, and blue, respectively. (b) Density profiles for O (red) and C4 (light blue) atoms in C₆H₅O⁻ and for Na⁺ (blue). The solid and dashed lines show the cases with and without polarization, respectively. (c) Surface potentials calculated with (blue) and without (light blue) molecular polarization, and that for pure water (black). (d) Potentials decomposed into the contribution from water (red), contribution from the original charge distribution (pink), and the correction induced by electronic polarization in the solution (green). Note that the total potential (blue) is the same as that in the case with polarization (blue) in (c).

Here, we construct a theoretical model that qualitatively explains the reversal of $\Delta\phi$. Our MD analysis revealed that the EDL, dielectric screening of ions, and solute polarization are important for determining $\Delta\phi$. For the EDL, we assume that the

surface density of $\text{C}_6\text{H}_5\text{O}^-$ molecules, n_{surf} , is expressed by the Langmuir isotherm,⁶¹

$$n_{\text{surf}} = \frac{ac_0}{b + c_0} \quad (6)$$

where c_0 is the bulk density of $\text{C}_6\text{H}_5\text{O}^-$, and the parameters $a = 0.012 \text{ \AA}^{-2}$ and $b = 1.2 \text{ M}$ are determined by least squares fitting of the experimental results (see Figure S8 in SI Section I). The counter ions are drawn to the surface to form the EDL, and the potential shift in the bulk is assumed to follow the Gouy-Chapman model:⁶⁸

$$\begin{aligned} \Delta\phi^{\text{GC}} &= -\frac{2k_{\text{B}}T}{e} \sinh^{-1} \left(\frac{-en_{\text{surf}}}{\sqrt{8\epsilon c_0 k_{\text{B}}T}} \right) \\ &= -\frac{2k_{\text{B}}T}{e} \sinh^{-1} \left(\frac{-e}{\sqrt{8\epsilon k_{\text{B}}T}} \sqrt{\frac{(a - n_{\text{surf}})n_{\text{surf}}}{b}} \right) \end{aligned} \quad (7)$$

where k_{B} , T , e , and ϵ represent the Boltzmann constant, temperature, elementary charge, and permittivity of the solvent, respectively. In the second line of Eq. (7), c_0 is replaced with n_{surf} using Eq. (6). The dielectric screening of solvent molecules is included in Eq. (7). The polarization of $\text{C}_6\text{H}_5\text{O}^-$ provides the potential shift in the bulk as

$$\Delta\phi^{\text{dipolar}} = -\frac{n_{\text{surf}}\langle\mu_z\rangle}{\epsilon} \quad (8)$$

where $\langle\mu_z\rangle$ is the Z component of the mean dipole for a single $\text{C}_6\text{H}_5\text{O}^-$ ion at the interface. The polarization of water is described by the bulk permittivity ϵ . The induced dipole of $\text{C}_6\text{H}_5\text{O}^-$ is determined by asymmetric hydration at the interface, and $\langle\mu_z\rangle$ takes a constant value of 4.1 a.u. obtained from the MD simulation by placing the origin of the coordinates at the center of mass of the molecule. Then, $\Delta\phi^{\text{dipolar}}$ becomes proportional to n_{surf} . Figure 7 shows the potential shift as a function of n_{surf} estimated using Eqs. (7) and (8), which qualitatively reproduces the reversal of potential shift, even though the maximum value of $\Delta\phi$ is smaller than the experimental value. The plot indicates that the reversal is caused by competition between the EDL and the solute dipole.

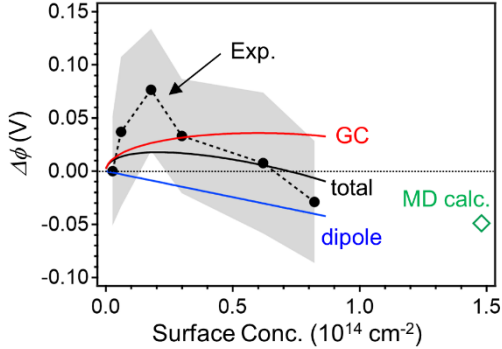


Figure 7. Surface potential shift due to the EDL (red curve) estimated using the Gouy-Chapman model, field-induced dipole moment of interfacial $\text{C}_6\text{H}_5\text{O}^-$ (blue curve), and their sum (black curve). The experimental results (black circles, same data as in Figure 5) are also plotted. The gray area indicates the estimated errors. The green open diamond indicates $\Delta\phi$ calculated by the MD simulation with the CRK model. The horizontal axis is the surface concentration of solute molecules estimated from the PE band intensity for

the solutes and surface tension data²⁶ at a certain bulk concentration (see SI Section I).

Comparison with Other Studies

Attempts have been made to measure ϕ or $\Delta\phi$ using different experimental methods^{12-14, 19, 44, 69} including nonlinear optical spectroscopy.^{44, 69} As mentioned earlier, SHG or SFG arises exclusively from the interfacial region where the isotropic spatial symmetry is broken. However, this is the case when they occur only with the second-order nonlinear susceptibility $\chi^{(2)}$ of a material. In the presence of a local static electric field, optical wave mixing can also occur through the third-order susceptibility $\chi^{(3)}$, generating SHG or SFG signals from a wider depth region that are sensitive to the local field.⁷⁰ The contribution of $\chi^{(3)}$ has been confirmed in the nonlinear optical spectra of aqueous solutions containing salts, surfactants, or lipids.^{44, 69, 71-73} For example, Wen and colleagues utilized vibrational SFG to estimate ϕ in salt solutions, discussing minute ϕ values on the order of meV at a low concentration.⁴⁴ A clear advantage of such nonlinear methods over PES is that they are applicable to hidden interfaces such as that between two liquids. On the other hand, nonlinear optical signals depend on the nature of hyperpolarizability of the molecules and the interference effects, which possibly complicate the analysis. Drier *et al.* have studied the lipid-water interface using the Kelvin probe (vibrating plate capacitor method) and nonlinear optical spectroscopy.⁷⁴ They showed that the former is sensitive to the EDL and orientation of the carbonyl group in a lipid, while the SHG intensity exhibits a nonlinear dependence on the interfacial charge. These results indicate that the experimental measurement of $\Delta\phi$ remains highly challenging. EUV-PES is a complementary approach to this difficult problem, although one of its limitations is that it can only detect relatively large $\Delta\phi$.

The measurement of $\Delta\phi$ of aqueous solutions using PES is a relatively new research topic, and there has been discussion using different terminologies such as the work function.^{29-30, 33} When a local electric field is generated by adsorbed molecules at the gas-liquid interface, the electric potential of the liquid shifts with respect to the vacuum level. This shift affects all energy levels, including the valence and conduction bands of liquid water and the energy levels of an impurity (solute) in the liquid. In solid state physics, the energy shift near the interface of a material is known as band bending. When discussing band bending, the (hypothetical) highest occupied electronic level of a material is invoked as the Fermi level, and the energy difference between the Fermi and vacuum levels is called the work function. The Fermi level is also defined for a liquid. At electrochemical equilibrium, the Fermi level is a constant in the liquid and the containing wall. When a surface potential is generated at the gas-liquid interface, the energy levels shift near the interface, also changing the local work function. Thus, the change in the surface potential is generally equivalent to the change in the work function. The present study aims to compare the observed PE band shift in EUV-PES with the charge distribution or surface potential predicted using MD simulations. Therefore, we employed the more familiar term "surface potential" instead.

Note that when solutes dissolve in water at a high concentration, the electronic structure of water itself may change.³⁰⁻³² As a result, the energy shifts of the valence and conduction bands of

water may occur in a complex manner and differ from the electrostatic potential change at the surface, making the shift in the PE band distinct from the potential change. Pugini *et al.* concluded that 75% of the observed energy shift in the PE spectrum of TBAI aqueous solution is due to a change in the work function, and 25% of it is due to a change in the electronic state of water.³³ The change in the electronic structure is primarily attributed to the disruption of the hydrogen-bonding network of water and strong interactions with ions. It is generally difficult to quantitatively estimate the influence from the electronic structure of water, especially for the molecular solutes discussed here, because the PE spectrum of the solute is congested and overlaps with that of water. However, the experimentally observed shifts in the PE bands for the solute and solvent molecules generally agree with each other (Figure 8) within the relatively large error range of PES. These findings led us to conclude that the shifts in the PE bands are primarily due to changes in the surface potential at the interface. This conclusion is consistent with the claim by Pugini *et al.* for an aqueous TBAI solution.³³

While a fully quantum mechanical calculation of the electronic structure at the gas-liquid interface would be ideal, the computational cost is prohibitively high. Even with the CRK method employed in this study, which incorporate molecular polarization, calculations for a single system can exceed one month, limiting our simulation. Nevertheless, our simulation semi-quantitatively explained the shifts observed in PES experiments. Although the change in the electronic structure of liquid water cannot be ruled out and likely occurs at high solute concentrations, the energy shift of the PE spectrum is primarily attributed to $\Delta\phi$.

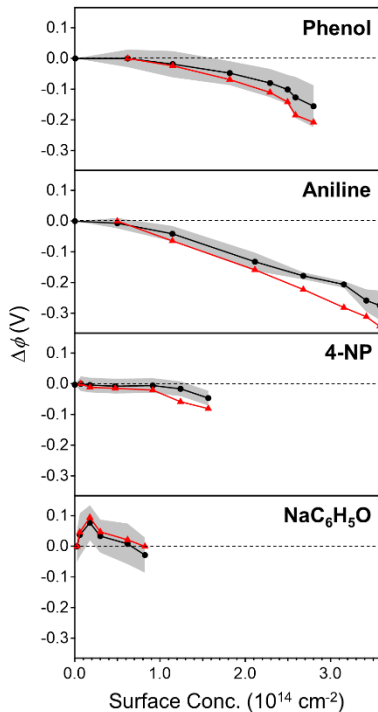


Figure 8. Comparison of $\Delta\phi$ estimated from the $1b_1$ band shift for H_2O (black circles, same as Figures 3 and 7) and HOMO of solute

bands (red triangles) for phenol, aniline, 4-NP, and sodium phenolate solutions. The error bars for the solutes are similar to those for H_2O $1b_1$.

Acid-base Equilibria

To investigate the protonation-deprotonation equilibrium for phenol/ $C_6H_5O^-$, we measured the PE spectra at different pH levels while maintaining the total bulk concentration $[phenol] + [C_6H_5O^-]$ at 0.025 M. Figure 9(a) shows the PE spectra aligned at the $1b_1$ band for liquid water. The intensity of the solute bands monotonically decreases with increasing pH, because phenol molecules are converted into $C_6H_5O^-$ species that tends to reside in the bulk. To analyze the PE spectra at intermediate pH levels, we obtained PE spectra of phenol at pH 7.4 and $C_6H_5O^-$ at pH 12.6, as shown in Figure 9(b). Using the PE spectra of phenol and $C_6H_5O^-$, we decomposed the spectra measured at intermediate pH levels to estimate the interfacial concentrations of phenol and $C_6H_5O^-$ (Figure 9(c)). Their concentrations become equal at pH 10.7, which is higher than the bulk pK_a (10.3 at 277 K). However, the individual curves for phenol and $C_6H_5O^-$ exhibit midpoint PE intensities at pH levels of 10.2 and 10.0, respectively, both of which are close to the bulk pK_a .

The acidity constant K_a is defined as follows,

$$K_a = \frac{a_{H_3O^+} \cdot a_{A^-}}{a_{HA}} \approx \frac{[H_3O^+][A^-]}{[HA]} \quad (9)$$

where a_X denotes the activity of species X, $[X]$ is the concentration of X, and HA denotes the acid that dissociates into the conjugate base A^- and a hydrogen ion H^+ . At $pH = pK_a$, the relation $a_{A^-} = a_{HA}$ holds. If the activity coefficients are considered to be unity at low concentrations, this relation implies that $[A^-] = [HA]$. Assuming $[A^-] + [HA] = C_{total}$, $[HA]$ becomes almost equal to C_{total} at a low pH, approximately $(1/2)C_{total}$ at $pH = pK_a$, and almost zero at high pH. The opposite behavior is expected for $[A^-]$. A notable feature of these pH dependences is that half of the asymptotic concentration is achieved at $pH = pK_a$. Note also that $[HA]$ and/or $[A^-]$ in the interfacial region can deviate considerably from C_{total} owing to the surface affinity of these species. Specifically, if HA has a high surface affinity, it will become concentrated at the interface, while A^- may be depleted, and *vice versa*. This behavior is dictated by the adsorption isotherm for individual species. Consequently, the relation $[A^-] = [HA]$ is unlikely to hold in the interfacial region at $pH = pK_a$. However, the midpoint of the pH-dependent concentration in the interfacial region should occur at the bulk pK_a value, because the chemical equilibrium between HA and A^- is dictated by the bulk. Thus, the interfacial concentrations of phenol and $C_6H_5O^-$ are primarily determined by the acid-base equilibrium in the bulk and the affinity (adsorption isotherm) of the solute molecules for the liquid surface.

Our quantum chemical calculations for protonated aniline in the gas phase predict VBE > 13 eV, which is in a spectral region containing intense water bands, making other protonated form undetectable. The pH dependence of the spectra of aniline solutions is shown in Figure 9(d). Figure 9(e) compares the spectrum obtained at pH 7.8 in the present study to that reported by Tentscher *et al.*⁶⁵ The integrated band intensities obtained here are shown in Figure 9(f), revealing that the midpoint intensity occurs at pH 5.41, which is comparable to the pK_a value (pH 5.3 at 277 K) in the bulk. The two lowest VBE values for 0.025

M aqueous aniline are determined to be 7.74 ± 0.04 and 8.83 ± 0.03 eV (Table 2).

Figure 9(g) shows the pH dependence of the PE spectra for a 0.025 M aqueous solution of 4-NP. Figure 9(h) presents the PE spectra of 4-NP and 4-NP⁻ measured at pH 5.5 and 8.1,

respectively, which enabled the estimation of the relative intensities for 4-NP and 4-NP⁻ (Figure 9(i)). The midpoint intensity for 4-NP is at pH 7.41, which is close to the bulk pK_a value of 7.4 at 277 K. The midpoint intensity for 4-NP⁻ is at pH 6.91. Thus, the interfacial concentrations of 4-NP and 4-NP⁻ are balanced at pH 8.00. The VBE values are summarized in Table 2.

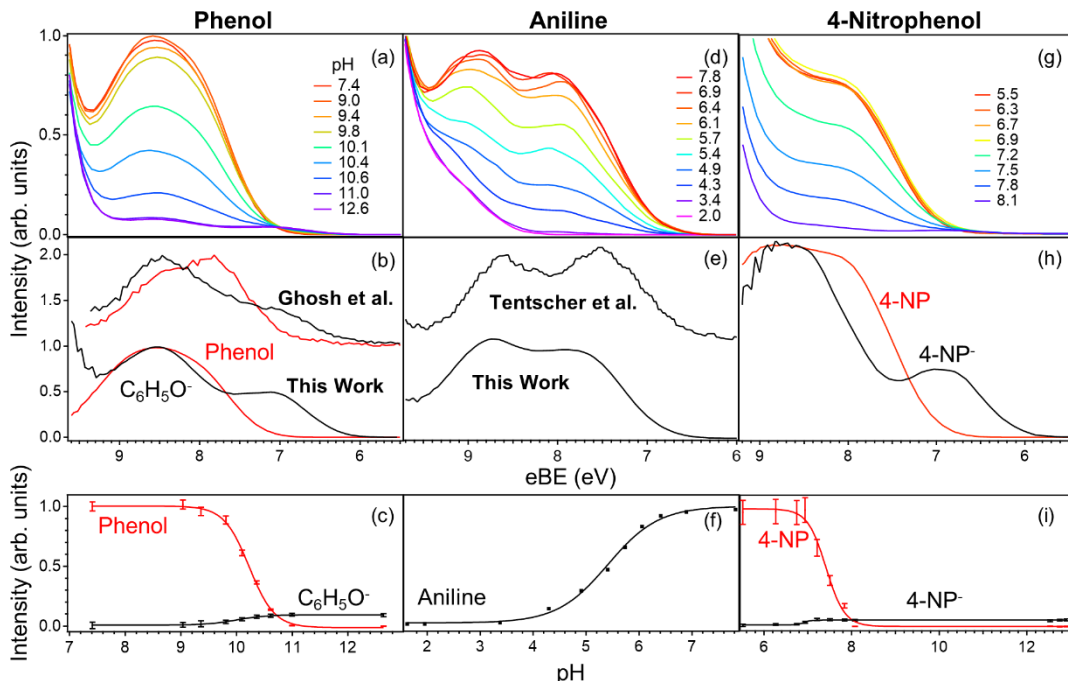


Figure 9. PE spectra of aqueous 0.025 M (a) phenol, (d) aniline, and (g) 4-NP solutions at different pH levels. The spectra are aligned at the $1b_1$ band for liquid water. (b) PE spectra of phenol and $C_6H_5O^-$ measured at pH 7.4 and 12.6, along with those reported by Ghosh *et al.*⁶⁴ (e) PE spectrum of aniline at pH 7.8 along with that reported by Tentscher *et al.*⁶⁵ (h) PE spectra of 4-NP and 4-NP⁻ at pH 5.5 and 8.1. The contribution from the water signal at >9 eV was subtracted in (b), (e), and (h). pH dependence of the PE intensities extracted for (c) phenol and $C_6H_5O^-$, (f) aniline, and (i) 4-NP and 4-NP⁻. The solid lines are best fits obtained using sigmoidal functions. The error bars in (c) and (i) are the estimated standard deviations of the fitting coefficients (see SI Section H). The relatively large error estimated for 4-NP is attributed to a large spectral overlap of the solute band and H_2O $1b_1$ band. The pH is corrected for the temperature dependence of pK_a and pK_w (SI Section G).

CONCLUSION

We studied the gas-liquid interface of aqueous solutions of selected aromatic molecules using EUV-PES and MD simulations. Because the electron escape depth in EUV-PES is on the order of 1 nm and the solute molecules are highly concentrated at the gas-liquid interface, EUV-PES acts as a selective probe for interfacial molecules. The PE bands of solute and solvent (water) exhibited similar energy shifts, and the magnitudes of these shifts paralleled the predictions from MD simulations. For all neutral molecules studied here, the surface potential (ϕ) decreased with increasing concentration, even though the permanent dipole moment of the solute molecules had different orientations at the interface. Specifically, the dipole moment of aniline pointed toward the bulk, while that of 4-NP pointed toward the vacuum. The complex relationship between the dipole and $\Delta\phi$ illustrates the difficulty in intuitively predicting $\Delta\phi$ based solely on the orientation of the solute dipole. For aqueous sodium phenolate solutions, a reversal of $\Delta\phi$ was observed at high concentrations, which is attributed to opposite contributions from the EDL and the solute polarization. The result clearly

indicates the importance of polarization of solutes in determination of the surface potential. The acid-base titration curves for individual species exhibited midpoints at pH levels within 0.5 units from the respective bulk pK_a , indicating that the chemical equilibrium is dictated by the bulk, and that the interfacial concentrations of neutral and ionic species are strongly affected by their surface affinities.

The present study demonstrates the effectiveness of EUV-PES for probing the electronic structure and potential at gas-liquid interfaces. Comparative analyses between PES on liquid jets and nonlinear spectroscopy on stationary liquids hold promise for future investigations. A particularly interesting topic is exploring the consistency between different methods for the same solutions. Another important extension of this study is time-resolved measurements of photo-induced surface reactions, and efforts in this direction are currently underway in our laboratory. The computational modeling of liquids is essential for extracting atomistic information on solute-solvent interactions and specific structural and dynamics properties of gas-liquid interfaces of aqueous solutions. Simulations based on machine

learning will reduce the computational load and are expected to be useful in future studies.

ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.4c12310>. Liquid target and electron detection, angular dependence of photoemission and short electron attenuation length, photon energy, energy calibration and cutoff method, analysis of VBE values of H₂O 1b₁ and solute bands, temperature of flat liquid jet, pK_a and pH at the temperature of a flat jet, decomposition of spectra measured at intermediate pH, surface concentration, electron scattering in XPS, specific ion effect, classical (non-polarizable) MD simulations, details of CRK modeling and MD settings, results of CRK calculations, orientation and hyperpolarizability of 4-NP, and rapid change in electrostatic potential at the interface (PDF).

AUTHOR INFORMATION

Corresponding Author

* Toshinori Suzuki, Department of Chemistry, Graduate School of Science, Kyoto University, Kitashirakawa-Oiwakecho, Sakyo-Ku, Kyoto 606-8502, Japan.
E-mail: suzuki@kuchem.kyoto-u.ac.jp

ACKNOWLEDGMENT

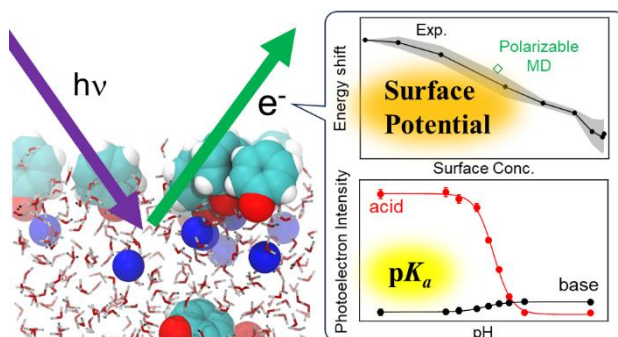
This work was supported by JSPS KAKENHI Grants (Nos. 21H04970, 20H00368, 21H01878, 24K08340) and the Mitsubishi Foundation. Part of the MD calculations was performed using the supercomputers at the Research Center for Computational Science, Okazaki, Japan. The data presented here are available on request to suzuki@kuchem.kyoto-u.ac.jp.

REFERENCES

- (1) Tobias, D. J.; Stern, A. C.; Baer, M. D.; Levin, Y.; Mundy, C. J. Simulation and Theory of Ions at Atmospherically Relevant Aqueous Liquid-Air Interfaces. *Annu. Rev. Phys. Chem.* **2013**, *64*, 339–359.
- (2) Jungwirth, P.; Tobias, D. J. Specific Ion Effects at the Air/Water Interface. *Chem. Rev.* **2006**, *106* (4), 1259–1281.
- (3) Knipping, E. M.; Lakin, M. J.; Foster, K. L.; Jungwirth, P.; Tobias, D. J.; Gerber, R. B.; Dabdub, D.; Finlayson-Pitts, B. J. Experiments and Simulations of Ion-Enhanced Interfacial Chemistry on Aqueous NaCl Aerosols. *Science* **2000**, *288* (5464), 301–306.
- (4) Nathanson, G. M.; Davidovits, P.; Worsnop, D. R.; Kolb, C. E. Dynamics and Kinetics at the Gas-Liquid Interface. *J. Phys. Chem.* **1996**, *100* (31), 13007–13020.
- (5) Shen, Y. R. *Fundamentals of Sum-Frequency Spectroscopy*. Cambridge University Press: Cambridge, 2016.
- (6) Richmond, G. L. Molecular Bonding and Interactions at Aqueous Surfaces as Probed by Vibrational Sum Frequency Spectroscopy. *Chem. Rev.* **2002**, *102* (8), 2693–2724.
- (7) Nihonyanagi, S.; Mondal, J. A.; Yamaguchi, S.; Tahara, T. Structure and Dynamics of Interfacial Water Studied by Heterodyne-Detected Vibrational Sum-Frequency Generation. *Annu. Rev. Phys. Chem.* **2013**, *64*, 579–603.
- (8) Suzuki, T. Ultrafast Photoelectron Spectroscopy of Aqueous Solutions. *J. Chem. Phys.* **2019**, *151* (9), 090901.
- (9) Suzuki, Y. I.; Nishizawa, K.; Kurahashi, N.; Suzuki, T. Effective Attenuation Length of an Electron in Liquid Water between 10 and 600 eV. *Phys. Rev. E* **2014**, *90* (1), 010302(R).
- (10) Thürmer, S.; Seidel, R.; Faubel, M.; Eberhardt, W.; Hemminger, J. C.; Bradforth, S. E.; Winter, B. Photoelectron Angular Distributions from Liquid Water: Effects of Electron Scattering. *Phys. Rev. Lett.* **2013**, *111* (17), 173005.
- (11) Jablonski, A.; Powell, C. J. Effective Attenuation Lengths for Different Quantitative Applications of X-ray Photoelectron Spectroscopy. *J. Phys. Chem. Ref. Data* **2020**, *49* (3), 033102.
- (12) Parfenyuk, V. I. Surface Potential at the Gas–Aqueous Solution Interface. *Colloid J.* **2002**, *64* (5), 588–595.
- (13) Casper, C. B.; Verreault, D.; Adams, E. M.; Hua, W.; Allen, H. C. Surface Potential of DPPC Monolayers on Concentrated Aqueous Salt Solutions. *J. Phys. Chem. B* **2016**, *120* (8), 2043–2052.
- (14) Adel, T.; Velez-Alvarez, J.; Co, A. C.; Allen, H. C. Circuit Analysis of Ionizing Surface Potential Measurements of Electrolyte Solutions. *J. Electrochem. Soc.* **2021**, *168* (1), 016507.
- (15) Kathmann, S. M.; Kuo, I. F. W.; Mundy, C. J. Electronic Effects on the Surface Potential at the Vapor-Liquid Interface of Water. *J. Am. Chem. Soc.* **2008**, *130* (49), 16556–16561.
- (16) Kathmann, S. M.; Kuo, I. F. W.; Mundy, C. J. Electronic Effects on the Surface Potential at the Vapor–Liquid Interface of Water. *J. Am. Chem. Soc.* **2009**, *131* (47), 17522.
- (17) Kathmann, S. M.; Kuo, I. F. W.; Mundy, C. J.; Schenter, G. K. Understanding the Surface Potential of Water. *J. Phys. Chem. B* **2011**, *115* (15), 4369–4377.
- (18) Kathmann, S. M. Electric Fields and Potentials in Condensed Phases. *Phys. Chem. Chem. Phys.* **2021**, *23* (41), 23836–23849.
- (19) Paluch, M. Electrical Properties of Free Surface of Water and Aqueous Solutions. *Adv. Colloid Interf. Sci.* **2000**, *84* (1), 27–45.
- (20) Becker, M. R.; Loche, P.; Netz, R. R. Electrokinetic, Electrochemical, and Electrostatic Surface Potentials of the Pristine Water Liquid–Vapor Interface. *J. Chem. Phys.* **2022**, *157* (24), 240902.
- (21) Yesibolati, M. N.; Laganà, S.; Sun, H.; Beleggia, M.; Kathmann, S. M.; Kasama, T.; Mølhave, K. Mean Inner Potential of Liquid Water. *Phys. Rev. Lett.* **2020**, *124* (6), 065502.
- (22) Zhao, X. L.; Ong, S. W.; Wang, H. F.; Eienthal, K. B. New Method for Determination of Surface pK_a Using Second Harmonic Generation. *Chem. Phys. Lett.* **1993**, *214* (2), 203–207.
- (23) Werner, J.; Jülin, J.; Dalirian, M.; Prisle, N. L.; Ohrwall, G.; Persson, I.; Björneholm, O.; Riipinen, I. Succinic Acid in Aqueous Solution: Connecting Microscopic Surface Composition and Macroscopic Surface Tension. *Phys. Chem. Chem. Phys.* **2014**, *16* (39), 21486–21495.
- (24) Werner, J.; Persson, I.; Björneholm, O.; Kaweck, D.; Saak, C. M.; Walz, M. M.; Ekholm, V.; Unger, I.; Valt, C.; Caleman, C.; Ohrwall, G.; Prisle, N. L. Shifted Equilibria of Organic Acids and Bases in the Aqueous Surface Region. *Phys. Chem. Chem. Phys.* **2018**, *20* (36), 23281–23293.
- (25) Rao, Y.; Subir, M.; McArthur, E. A.; Turro, N. J.; Eienthal, K. B. Organic Ions at the Air/Water Interface. *Chem. Phys. Lett.* **2009**, *477* (4–6), 241–244.
- (26) Richter, C.; Dupuy, R.; Trinter, F.; Buttersack, T.; Cablit, L.; Gholami, S.; Sterner, D.; Nicolas, C.; Seidel, R.; Winter, B.; Bluhm, H. Surface Accumulation and Acid–Base Equilibrium of Phenol at the Liquid–Vapor Interface. *Phys. Chem. Chem. Phys.* **2024**, *26*, 27292–27300.
- (27) Cahen, D.; Kahn, A. Electron Energetics at Surfaces and Interfaces: Concepts and Experiments. *Adv. Mater.* **2003**, *15* (4), 271–277.
- (28) Helander, M. G.; Greiner, M. T.; Wang, Z. B.; Lu, Z. H. Pitfalls in Measuring Work Function Using Photoelectron Spectroscopy. *Appl. Surf. Sci.* **2010**, *256* (8), 2602–2605.
- (29) Thürmer, S.; Malerz, S.; Trinter, F.; Hergenhausen, U.; Lee, C.; Neumark, D. M.; Meijer, G.; Winter, B.; Wilkinson, I. Accurate Vertical Ionization Energy and Work Function Determinations of Liquid Water and Aqueous Solutions. *Chem. Sci.* **2021**, *12* (31), 10558–10582.
- (30) Credidio, B.; Pugini, M.; Malerz, S.; Trinter, F.; Hergenhausen, U.; Wilkinson, I.; Thürmer, S.; Winter, B. Quantitative Electronic Structure and Work-Function Changes of Liquid Water Induced by Solute. *Phys. Chem. Chem. Phys.* **2022**, *24* (3), 1310–1325.
- (31) Nishizawa, K.; Kurahashi, N.; Sekiguchi, K.; Mizuno, T.; Ogi, Y.; Horio, T.; Oura, M.; Kosugi, N.; Suzuki, T. High-Resolution Soft X-Ray Photoelectron Spectroscopy of Liquid Water. *Phys. Chem. Chem. Phys.* **2011**, *13* (2), 413–417.
- (32) Yamamoto, Y.; Ishiyama, T.; Morita, A.; Suzuki, T. Exploration of Gas-Liquid Interfaces for Liquid Water and Methanol Using Extreme Ultraviolet Laser Photoemission Spectroscopy. *J. Phys. Chem. B* **2021**, *125* (37), 10514–10526.
- (33) Pugini, M.; Credidio, B.; Walter, I.; Malerz, S.; Trinter, F.; Sterner, D.; Hergenhausen, U.; Meijer, G.; Wilkinson, I.; Winter, B.; Thürmer, S. How to Measure Work Functions from Aqueous Solutions. *Chem. Sci.* **2023**, *14* (35), 9574–9588.

- (34) Scholz, M. S.; Fortune, W. G.; Tau, O.; Fielding, H. H. Accurate Vertical Ionization Energy of Water and Retrieval of True Ultraviolet Photoelectron Spectra of Aqueous Solutions. *J. Phys. Chem. Lett.* **2022**, *13* (30), 6889–6895.
- (35) Luckhaus, D.; Yamamoto, Y.; Suzuki, T.; Signorelli, R. Genuine Binding Energy of the Hydrated Electron. *Sci. Adv.* **2017**, *3* (4), e1603224.
- (36) Schild, A.; Peper, M.; Perry, C.; Rattenbacher, D.; Wörner, H. J. Alternative Approach for the Determination of Mean Free Paths of Electron Scattering in Liquid Water Based on Experimental Data. *J. Phys. Chem. Lett.* **2020**, *11* (3), 1128–1134.
- (37) Malerz, S.; Trinter, F.; Hergenbahn, U.; Ghrist, A.; Ali, H.; Nicolas, C.; Saak, C.-M.; Richter, C.; Hartweg, S.; Nahon, L.; Lee, C.; Goy, C.; Neumark, D. M.; Meijer, G.; Wilkinson, I.; Winter, B.; Thürmer, S. Low-Energy Constraints on Photoelectron Spectra Measured from Liquid Water and Aqueous Solutions. *Phys. Chem. Chem. Phys.* **2021**, *23* (14), 8246–8260.
- (38) Perry, C. F.; Jordan, I.; Zhang, P.; von Conta, A.; Nunes, F. B.; Wörner, H. J. Photoelectron Spectroscopy of Liquid Water with Tunable Extreme-Ultraviolet Radiation: Effects of Electron Scattering. *J. Phys. Chem. Lett.* **2021**, *12* (11), 2990–2996.
- (39) Itikawa, Y.; Mason, N. Cross Sections for Electron Collisions with Water Molecules. *J. Phys. Chem. Ref. Data* **2005**, *34* (1), 1–22.
- (40) Faubel, M.; Steiner, B.; Toennies, J. P. Photoelectron Spectroscopy of Liquid Water, Some Alcohols, and Pure Nonane in Free Micro Jets. *J. Chem. Phys.* **1997**, *106* (22), 9013–9031.
- (41) Wilson, K. R.; Rude, B. S.; Smith, J.; Cappa, C.; Co, D. T.; Schaller, R. D.; Larsson, M.; Catalano, T.; Saykally, R. J. Investigation of Volatile Liquid Surfaces by Synchrotron X-Ray Spectroscopy of Liquid Microjets. *Rev. Sci. Instrum.* **2004**, *75* (3), 725–736.
- (42) Kurahashi, N.; Karashima, S.; Tang, Y.; Horio, T.; Abulimiti, B.; Suzuki, Y. I.; Ogi, Y.; Oura, M.; Suzuki, T. Photoelectron Spectroscopy of Aqueous Solutions: Streaming Potentials of NaX (X = Cl, Br, and I) Solutions and Electron Binding Energies of Liquid Water and X. *J. Chem. Phys.* **2014**, *140* (17), 174506.
- (43) Preissler, N.; Buchner, F.; Schultz, T.; Lübcke, A. Electrokinetic Charging and Evidence for Charge Evaporation in Liquid Microjets of Aqueous Salt Solution. *J. Phys. Chem. B* **2013**, *117* (8), 2422–2428.
- (44) Dalstein, L.; Chiang, K.-Y.; Wen, Y.-C. Surface Potential at Electrolyte/Air Interfaces: A Quantitative Analysis via Sum-Frequency Vibrational Spectroscopy. *J. Phys. Chem. B* **2023**, *127* (21), 4915–4921.
- (45) Ishiyama, T.; Morita, A. Molecular Dynamics Study of Gas-Liquid Aqueous Sodium Halide Interfaces. I. Flexible and Polarizable Molecular Modeling and Interfacial Properties. *J. Phys. Chem. C* **2007**, *111* (2), 721–737.
- (46) Wick, C.; Dang, L.; Jungwirth, P. Simulated Surface Potentials at the Vapor-Water Interface for the KCl Aqueous Electrolyte Solution. *J. Chem. Phys.* **2006**, *125*, 024706.
- (47) Wick, C.; Kuo, I.; Mundy, C.; Dang, L. The Effect of Polarizability for Understanding the Molecular Structure of Aqueous Interfaces. *J. Chem. Theory Comput.* **2007**, *3*, 2002–2010.
- (48) Mons, M.; Dimicoli, I.; Piuze, F. Gas Phase Hydrogen-Bonded Complexes of Aromatic Molecules: Photoionization and Energetics. *Int. Rev. Phys. Chem.* **2002**, *21* (1), 101–135.
- (49) Frassetto, F.; Cacho, C.; Froud, C. A.; Turcu, I. C. E.; Villaresi, P.; Bryan, W. A.; Springate, E.; Poletto, L. Single-Grating Monochromator for Extreme-Ultraviolet Ultrashort Pulses. *Opt. Express* **2011**, *19* (20), 19169–19181.
- (50) Yamamoto, Y.; Yano, H.; Karashima, S.; Uenishi, R.; Orimo, N.; Nishitani, J.; Suzuki, T. Extreme Ultraviolet Laser Photoelectron Spectroscopy of Flat Liquid Jet Generated Using Microfluidic Device. *Bull. Chem. Soc. Jpn* **2023**, *96*, 938–942.
- (51) Kurahashi, N.; Thürmer, S.; Liu, S. Y.; Yamamoto, Y.; Karashima, S.; Bhattacharya, A.; Ogi, Y.; Horio, T.; Suzuki, T. Design and Characterization of a Magnetic Bottle Electron Spectrometer for Time-Resolved Extreme UV and X-Ray Photoemission Spectroscopy of Liquid Microjets. *Struct. Dyn.* **2021**, *8* (3), 034303.
- (52) Buttersack, T.; Haak, H.; Bluhm, H.; Hergenbahn, U.; Meijer, G.; Winter, B. Imaging Temperature and Thickness of Thin Planar Liquid Water Jets in Vacuum. *Struct. Dyn.* **2023**, *10* (3), 034901.
- (53) Chang, Y.-P.; Yin, Z.; Balciunas, T.; Wörner, H. J.; Wolf, J.-P. Temperature Measurements of Liquid Flat Jets in Vacuum. *Struct. Dyn.* **2022**, *9* (1), 014901.
- (54) Ishiyama, T.; Morita, A. Analysis of Anisotropic Local Field in Sum Frequency Generation Spectroscopy with the Charge Response Kernel Water Model. *J. Chem. Phys.* **2009**, *131* (24), 244714.
- (55) Imamura, T.; Mizukoshi, Y.; Ishiyama, T.; Morita, A. Surface Structures of NaF and Na₂SO₄ Aqueous Solutions: Specific Effects of Hard Ions on Surface Vibrational Spectra. *J. Phys. Chem. C* **2012**, *116* (20), 11082–11090.
- (56) Kusaka, R.; Ishiyama, T.; Nihonyanagi, S.; Morita, A.; Tahara, T. Structure at the Air/Water Interface in the Presence of Phenol: A Study Using Heterodyne-detected Vibrational Sum Frequency Generation and Molecular Dynamics Simulation. *Phys. Chem. Chem. Phys.* **2018**, *20* (5), 3002–3009.
- (57) Wang, J.; Wolf, R. M.; Caldwell, J. W.; Kollman, P. A.; Case, D. A. Development and Testing of a General Amber Force Field. *J. Comput. Chem.* **2004**, *25*, 1157–1174.
- (58) Darden, T.; York, D.; Pedersen, L. Particle Mesh Ewald: An N · log(N) method for Ewald Sums in Large Systems. *J. Chem. Phys.* **1993**, *98* (12), 10089–10092.
- (59) Wilson, M. A.; Pohorille, A.; Pratt, L. R. Comment on "Study on the Liquid Vapor Interface of Water. I. Simulation Results of Thermodynamic Properties and Orientational Structure". *J. Chem. Phys.* **1989**, *90* (9), 5211–5213.
- (60) West, C. W.; Nishitani, J.; Higashimura, C.; Suzuki, T. Extreme Ultraviolet Time-Resolved Photoelectron Spectroscopy of Aqueous Aniline Solution: Enhanced Surface Concentration and Pump-Induced Space Charge Effect. *Mol. Phys.* **2021**, *119* (1–2), e1748240.
- (61) Atkins, P. W.; Paula, J. D. *Physical Chemistry*. 8th Ed.; W. H. Freeman: 2006; Vol. 2.
- (62) Tamburello-Luca, A. A.; Hebert, P.; Brevet, P. F.; Girault, H. H. Resonant-Surface Second-Harmonic Generation Studies of Phenol Derivatives at Air/Water and Hexane/Water Interfaces. *J. Chem. Soc. Faraday Trans.* **1996**, *92* (17), 3079–3085.
- (63) Haynes, W. M.; Lide, D. R.; Bruno, T. J. *CRC Handbook of Chemistry and Physics*. 91st Ed.; CRC Press: Boca Raton, Florida, 2010.
- (64) Ghosh, D.; Roy, A.; Seidel, R.; Winter, B.; Bradforth, S.; Krylov, A. I. First-Principle Protocol for Calculating Ionization Energies and Redox Potentials of Solvated Molecules and Ions: Theory and Application to Aqueous Phenol and Phenolate. *J. Phys. Chem. B* **2012**, *116* (24), 7269–7280.
- (65) Tentscher, P. R.; Seidel, R.; Winter, B.; Guerard, J. J.; Arey, J. S. Exploring the Aqueous Vertical Ionization of Organic Molecules by Molecular Simulation and Liquid Microjet Photoelectron Spectroscopy. *J. Phys. Chem. B* **2015**, *119* (1), 238–256.
- (66) Headley, D.; Young, R. S.; Reece, M.; Subir, M. Variation in Average Molecular Orientation of an Organic Anion at the Air-Aqueous Interface: Influence of Halide Ions. *J. Phys. Chem. C* **2018**, *122* (9), 4945–4954.
- (67) Higgins, D. A.; Abrams, M. B.; Byerly, S. K.; Corn, R. M. Resonant Second Harmonic Generation Studies of p-Nitrophenol Adsorption at Condensed-Phase Interfaces. *Langmuir* **1992**, *8* (8), 1994–2000.
- (68) Adamson, A. W.; Gast, A. P. *Physical Chemistry of Surfaces*. 6th Ed.; Wiley: New York, 1997.
- (69) Dalstein, L.; Chiang, K.-Y.; Wen, Y.-C. Direct Quantification of Water Surface Charge by Phase-Sensitive Second Harmonic Spectroscopy. *J. Phys. Chem. Lett.* **2019**, *10* (17), 5200–5205.
- (70) Shen, Y. R. *The Principles of Nonlinear Optics*. 1st Ed.; Wiley-Interscience: 1984.
- (71) 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.
- (72) Ohno, P. E.; Wang, H.-f.; Geiger, F. M. Second-Order Spectral Lineshapes from Charged Interfaces. *Nat. Commun.* **2017**, *8* (1), 1032.
- (73) Wen, Y.-C.; Zha, S.; Liu, X.; Yang, S.; Guo, P.; Shi, G.; Fang, H.; Shen, Y. R.; Tian, C. Unveiling Microscopic Structures of Charged Water Interfaces by Surface-Specific Vibrational Spectroscopy. *Phys. Rev. Lett.* **2016**, *116* (1), 016101.
- (74) Dreier, L. B.; Bernhard, C.; Gonella, G.; Backus, E. H. G.; Bonn, M. Surface Potential of a Planar Charged Lipid–Water Interface. What Do Vibrating Plate Methods, Second Harmonic and Sum Frequency Measure? *J. Phys. Chem. Lett.* **2018**, *9* (19), 5685–5691.

Table of Contents



Supporting Information

Gas-Liquid Interface of Aqueous Solutions of Surface Active Aromatic Molecules Studied Using Extreme Ultraviolet Laser Photoelectron Spectroscopy and Molecular Dynamics Simulation

Yo-ichi Yamamoto,¹ Tomonori Hirano,² Tatsuya Ishiyama,³ Akihiro Morita² and Toshinori Suzuki^{1,*}

¹*Department of Chemistry, Graduate School of Science, Kyoto University, Kitashirakawa-Oiwakecho, Sakyo-Ku, Kyoto 606-8502, Japan*

²*Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan*

³*Department of Applied Chemistry, Graduate School of Science and Engineering, University of Toyama, Toyama 930-8555, Japan*

* Corresponding author: suzuki@kuchem.kyoto-u.ac.jp

A. Liquid target and electron detection

We describe the detailed design of the microfluidic device to create the flat liquid jet¹ and the electron detection method. The flow channels were designed based on an earlier study on liquid-liquid collision.² A crossing angle of 70° was chosen between the two jets, and the liquid-liquid collision point was located at 0.1 mm downstream from the end of the microchip. The two flow channels were mirror images of each other to ensure well-balanced liquid flow rates between the two microjets. A rectangular-shaped flow channel was fabricated with two exits each having the dimensions of $20\ \mu\text{m} \times 20\ \mu\text{m}$. The liquid film was created as a chain of “leaves” that were mutually orthogonal, and the first (and largest) leaf was used for photoelectron spectroscopy (PES) measurements. The size of the first leaf grew upon increasing the liquid flow rate, from $0.3\ \text{mm} \times 1.0\ \text{mm}$ at 1.0 mL/min to $0.7\ \text{mm} \times 2.2\ \text{mm}$ at 1.5 mL/min. These sizes are much larger than the laser focal spot size. When the flow rate was 1.5 mL/min, the liquid film in the middle of the first leaf had a thickness of $0.7\ \mu\text{m}$, whereas the rim of the leaf was much thicker. The traveling speed of the flat liquid jet was estimated to be over 20 m/s at the total flow rate of 1.5 mL/min.

The flat liquid jet was discharged in a vacuum, as shown in Figure S1(a). The dimensions of this jet varied with the viscosity and flow rate of the liquid. The chip body was coated with graphite and electrically connected to a power supply to provide a bias voltage. The bias voltage ($-70.0\ \text{V}$) increased the kinetic energy of photoelectrons emitted from the liquid and separated their energy distribution from that of the photoelectrons from the evaporated gas from the sample. The chamber pressure during operation was 10^{-3} – 10^{-4} Torr. Figure S1(b) shows a top view of the experimental geometry, with the extreme ultraviolet (EUV) laser propagation axis and electron detection axis perpendicular to each other. Photoelectrons emitted from the liquid film were measured using a magnetic bottle time-of-flight (MBTOF) electron energy analyzer described elsewhere.³ A magnetic field was employed to guide the emitted photoelectrons to the electron energy analyzer, so that they can be detected regardless of their emission angle θ . Consequently, the obtained photoelectron (PE) spectra represent an average across all electron takeoff angles. The flight tube of the MBTOF analyzer was separated from the photoionization region by a skimmer cone with a hole (diameter: 0.5 mm), and the pressure was maintained below 3×10^{-6} Torr. All electrons were decelerated in the flight tube by applying a retarding potential of $-60.0\ \text{V}$ to reduce the pass energy and improve the energy resolution. The overall resolution including the EUV radiation bandwidth was estimated to be 0.3 eV. For the 56.5 eV experiment, we increased the bias and retarding voltages to -30.0 and $-20.0\ \text{V}$, respectively, to prevent sinusoidal intensity fluctuation of the PE spectra. This fluctuation is caused by the kinetic energy-dependent transmission efficiency of the MBTOF analyzer.⁴ High-energy electrons with large cyclotron radii can be intercepted by the skimmer cone, leading to variations in the detected electron signal.

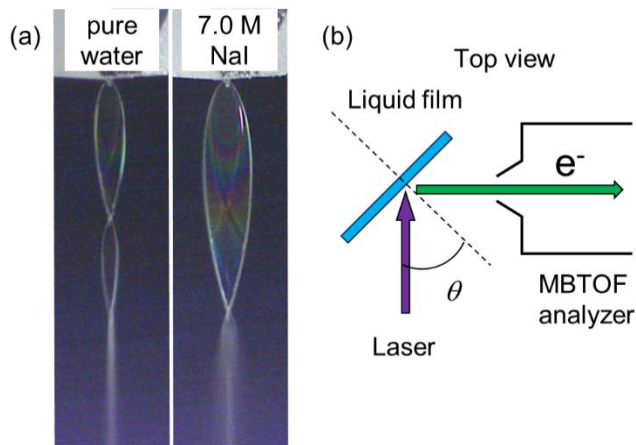


Figure S1. (a) Photographs of flat jets of pure water and 7.0 M NaI aqueous solution at a flow rate of 1.2 mL/min. The size and shape of the liquid film vary with the solution composition. (b) Experimental geometry for PES measurements.

B. Angular dependence of photoemission and short electron attenuation length

The short electron attenuation length makes EUV-PES highly surface-selective. As an example, Figure S2(a) shows the PE spectra measured for an aqueous phenol solution under 40.0 eV radiation at various incidence angles relative to the liquid film surface. The integrated intensity is plotted in Figure S2(b). Based on inelastic X-ray scattering data obtained by Hayashi *et al.*,⁵⁻⁶ the refractive index of water at 40 eV was estimated to be 0.92.

When the refractive index is less than unity, the radiation is totally reflected at incidence angles larger than a critical value, which in this case is 66.9° . Beyond this angle, radiation can penetrate the liquid water as an evanescent wave. Figure S2 clearly shows that photoemission can occur with such an evanescent wave. The penetration distance for an evanescent wave was estimated using the following equation:

$$d = \frac{\lambda}{2\pi\sqrt{n_1^2 \sin^2 \theta_1 - n_2^2}} \quad (\text{S1})$$

where λ is the radiation wavelength, n_1 is the refractive index in region 1 (vacuum in this case), θ_1 is the radiation incidence angle on the liquid surface, and n_2 is the refractive index of the aqueous phase (liquid water in this case). For $\theta_1 > 66.9^\circ$, d becomes less than 15 nm. Considering the extinction of EUV light by liquid water, the penetration distance becomes shorter than 10 nm for $\theta_1 > 66.9^\circ$. There is no abrupt change in the observed photoemission intensity at 66.9° because the estimated electron escape depth is only ~ 1 nm. The incidence angle dependence of the photoemission intensity was found to be the same for irradiation at 27.6 and 40.0 eV.

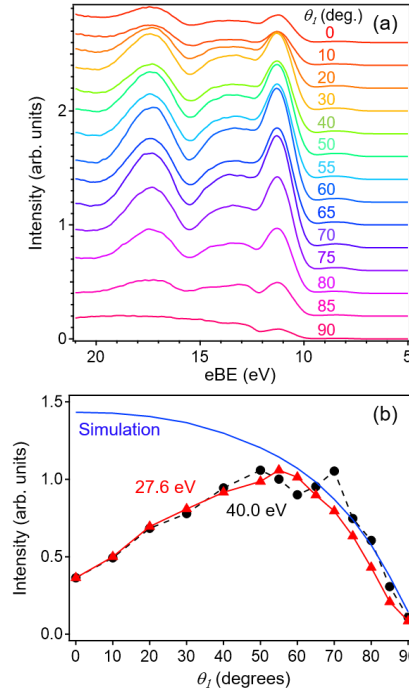


Figure S2. (a) PE spectra measured for aqueous 0.025 M phenol solution using 40.0 eV radiation at various incidence angles (θ_1) relative to the liquid film surface. The spectra are vertically offset for comparison. (b) Relative intensity of the $1b_1$ band for liquid water as a function of θ_1 . Black solid circles and red triangles denote the results measured using 40.0 and 27.6 eV radiation, respectively. The blue curve represents the simulated θ_1 dependence, which was calculated by considering only the region of overlap between the laser spot and liquid film.

C. Photon energy

The EUV photon energy was determined by analyzing the PE spectra of Ar and Kr measured using multiple orders of high harmonics with the following formula:

$$VBE^i = nh\nu - \left(At_n^{i-2} + E_0\right) \quad (\text{S2})$$

where n is the order of the harmonic, VBE^i is the known vertical binding energy (VBE) of sample gas i , t_n^i is the corresponding peak position in the time-of-flight spectrum observed using the n^{th} -order harmonic, A is a calibration parameter related to the effective flight length for electrons, and E_0 is the energy offset due to a stray electric field or other apparatus-specific sources. $h\nu$ is the photon energy (3.1 eV) of the driving laser. We employed Kr (VBE = 14.00 and 14.66 eV)⁷ and Ar (VBE = 15.76 eV)⁸ with the harmonic orders of 7, 9, 11, and 13, and performed least-squares fitting to determine $h\nu$, A , and E_0 . From the fitting results, we determined the driving laser photon

energy to be $h\nu = 3.08 \pm 0.06$ eV and the photon energy of the 13th harmonic to be 40.0 ± 0.8 eV. The estimated error (0.8 eV) for the latter is rather large; however, it does not significantly impact the precision of our $\Delta\phi$ measurement. For the sodium phenolate solution, we employed two different photon energies of 40.0 and 56.5 eV and obtained consistent results. The main source of experimental errors in eBE is the day-to-day fluctuation of the PE spectra, which amounts to tens of meV.

D. Energy calibration and cutoff method

The cutoff energy is widely used as the absolute energy reference in the PES analysis of condensed matter.⁹⁻¹¹ The details of the cutoff method can be found, for example, in Ref. [11], and we only briefly describe it here. The PE spectra of liquids exhibit an intense low-electron kinetic energy (eKE) tail, known as LET, which is primarily caused by low-energy electrons generated in inelastic scattering events (some are from the secondary electron impact ionization etc.). The intensity of the LET must be zero at $\text{eKE} = 0$, which is referred to as the cutoff energy. Because electrons with zero kinetic energy never reach the detector, a negative bias voltage must be applied to the liquid to accelerate the electrons.¹¹ Moreover, note that the detection efficiency of a magnetic bottle photoelectron spectrometer drops for $\text{eKE} < 0.5$ eV.¹² Therefore, we applied a bias voltage of -10 V to the liquid to ensure that all electrons have an eKE higher than 10 eV. In the numerical analysis used to determine the cutoff energy, the tangent method is commonly employed.^{11, 13} This method identifies the cutoff energy as the crossing point between the tangent drawn from the inflection point of the LET and the baseline of the PE spectra.

EUV-PES has a low energy resolution due to the use of a broad-band femtosecond laser and time-of-flight energy analysis. Therefore, we tested how the energy resolution influences the cutoff method. Figure S3 shows the PE spectrum of liquid water measured with He(II) radiation and a hemispherical energy analyzer¹⁴ (HEA, with the best instrumental resolution being 0.06 eV), as well as the convolution of this spectrum with a Gaussian having a full-width-at-half-maximum (FWHM) of 0.1–0.5 eV. The spectral slope in the cutoff region becomes more gradual at a lower energy resolution. We applied a standard procedure of the cutoff method, by calculating the inflection point in the slope and then drawing a tangent to find the crossing point with the baseline. Using this procedure, we found that a low spectral resolution shifts the cutoff energy lower than the true value, leading to a higher eKE or lower electron binding energy (eBE). The shift is almost linear with regard to the FWHM of the instrumental resolution, as shown in the inset of Figure S3. Based on this relation, we calibrated the cutoff energy. More specifically, the spectral shape of our LET is well described using an energy resolution of 0.3 eV, so that the cutoff energy was obtained by adding +0.085 eV to the value determined using the tangential method. The instrumental resolution primarily arises from the bandwidth of our EUV pulses and does not change throughout the experiments.

The cutoff method is currently the most reliable method for energy correction. However, the physics behind PE emission in the low-energy region is not fully understood. For example, the shape of the LET is known to be influenced by the presence of solutes. Figure S4 shows the concentration dependence of the LET shape for NaI solutions and tetrabutyl ammonium iodide (TBAI) solutions. The peak position of the LET shifts in the opposite direction as the concentration changes. This reversal in direction coincides with the polarity reversal of the electric double layer (EDL) at the interface. Therefore, the shape of the LET reflects the change in the surface potential. Despite the variation of LET profile, Credidio *et al.* showed that the shape near the low kinetic energy region below the LET peak remains unchanged regardless of the concentration,¹⁵ ensuring the validity of the cutoff method for aqueous solutions of different concentrations. Currently, the cutoff method is a pragmatic solution in energy calibration. Understanding the relationship between the surface potential and the LET shape remains a subject for future investigation.

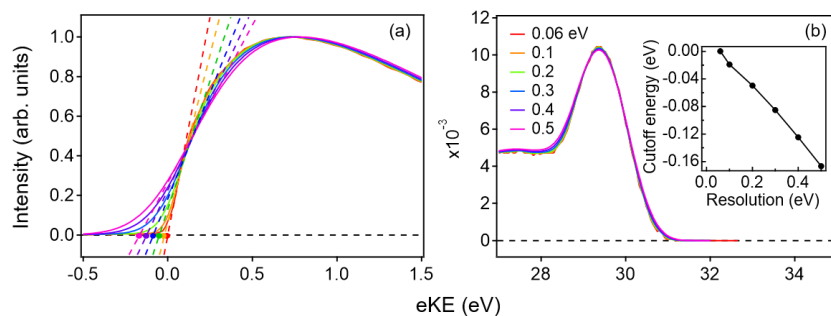


Figure S3. PE spectra of liquid water. The spectrum indicated as “0.06 eV” (red) is the He(II) PE spectrum of liquid water, and the others are simulated spectra obtained by convoluting it with Gaussian having an FWHM of 0.1–0.5 eV. The horizontal axis is aligned at the peak position of the H₂O 1b₁ band. (a) LET region. The intensity is normalized at the peak intensity of the LET. Dashed colored lines are tangents of the LET waveforms at their inflection points. The crossing points of the tangent and baseline (black dashed line), indicated by filled circles, are the cutoff energies. (b) Water valence band region. The inset shows the eKE corresponding to the cutoff energy at several energy resolutions.

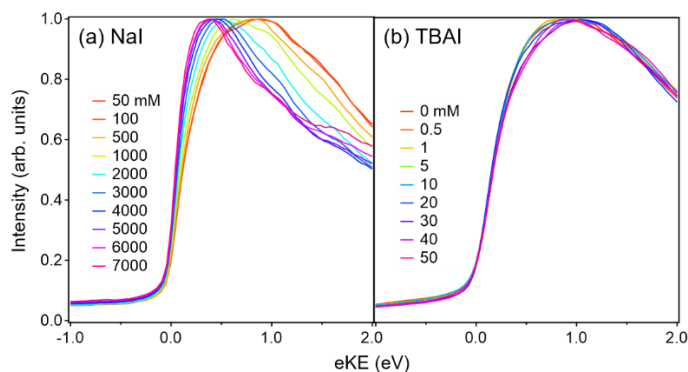


Figure S4. PE spectra of the LET region measured for (a) NaI and (b) TBAI aqueous solutions at several concentrations. The photon energy was 27.5 eV. The intensity is normalized at the peak position.

During the energy calibration of the PE spectra, we determined A and E_0 in the relation $eKE = At^{-2} + E_0$ using the PE spectrum of a 50 mM NaCl aqueous solution. Independently from measurements of the gaseous species, A and E_0 were determined through least-squares fitting of t_i and eKE_i , where t_i is the measured flight time and eKE_i is the expected eKE for t_i . We employed the following equations: $eKE_1 = h\nu_{13} - VBE(\text{H}_2\text{O } 1b_1)$, $eKE_2 = h\nu_{13} - VBE(\text{H}_2\text{O } 1b_2)$, $eKE_3 = E_{cut}$, where $h\nu_{13}$ represents photon energy of the 13th harmonic (40.0 eV), and E_{cut} is the cutoff energy (−0.085 eV in our case). Once A and E_0 were determined, A was kept constant for the other solutions, while E_0 was adjusted for each solution to align the cutoff position with that of the 50 mM NaCl solution. A depends on the bias voltage applied to the liquid and the retarding potential of the flight tube. The eBE value was determined from the difference between the photon energy ($h\nu_{13}$) and measured eKE.

E. Analysis of VBE values of H₂O 1b₁ and solute bands

Figure 2 and Table 2 show the VBE values of H₂O 1b₁ and the two highest orbitals of solutes estimated using least-squares fitting with multiple Gaussian functions. We performed the fitting in the eBE region < 13.5 eV employing a total of four Gaussians: two for H₂O 1b₁ and 3a₁L bands,¹⁶ and another two for the solute bands. The

ratio of the bandwidths of the H₂O 1b₁ and 3a₁L bands was fixed at the literature value¹⁶ (The 3a₁ band is the HOMO-1 band of water, which splits into two bands due to interactions through hydrogen bonding, and L in 3a₁L denotes the band with a lower binding energy.¹⁷) We employed the ratio of the width, rather than the width itself, because the width observed in our PE spectra is slightly larger than that in X-ray photoelectron spectroscopy (XPS) due to the lower energy resolution of our instrument. The error bars on the peak positions in Figure 2 and Table 2 represent the standard deviation calculated from three independent measurements, and this standard deviation is larger than the error of individual fitting.

F. Temperature of flat liquid jet

When a flat liquid jet is injected into vacuum, its temperature decreases due to evaporative cooling.¹⁸⁻¹⁹ Here, we estimate its temperature following the method of Chang *et al.*¹⁹ The temperature change per unit length of distance traveled (z) is described by¹⁹

$$\frac{dT}{dz} = -\frac{2H_v}{N_A C_m M l(z)} \frac{J_\gamma}{v_z} F(z) \quad (S3)$$

where H_v is the evaporation enthalpy, N_A is the Avogadro constant, C_m is the molar specific heat, M is the molar density, J_γ is the simplified mass flux evaporating from the liquid surface described by the Hertz-Knudsen equation,²⁰⁻²¹ and v_z is the velocity of the liquid jet along the z axis. $F(z) = \frac{\epsilon}{z}$ is a correction function for the geometric properties of the flat jet, where ϵ is a correction constant.

$l(z)$ is the thickness of the flat jet estimated by the Hasson-Peck model as²²

$$l(z) = \frac{l_0}{z} + l_c \quad (S4)$$

which is slightly modified from that of Chang *et al.*, since the actual sheet thickness of the flat jet converges to a finite value l_c instead of zero.¹⁸ The T -dependence of flux J_γ is described as¹⁹

$$\begin{aligned} J_\gamma &= \frac{\gamma P_v}{\sqrt{2\pi m k_B T}} \\ &= \frac{\gamma P_{ref}}{\sqrt{2\pi m k_B T}} \exp \left[-\frac{H_v}{k_B T_{ref}} \left(\frac{T_{ref} - T}{T} \right) \right] \end{aligned} \quad (S5)$$

where γ is a unitless proportion constant, k_B is the Boltzmann constant, T_{ref} is a reference temperature, m is the molecular mass, and P_{ref} is the vapor pressure at T_{ref} . In the second line of the equation, the temperature dependence of the equilibrium vapor pressure P_v is replaced by the Clausius-Clapeyron equation.²³ From these equations, Eq. (S3) is written as

$$\begin{aligned} \frac{dT}{dz} &= -\frac{2H_v}{N_A C_m M l(z)} \frac{J_\gamma}{v_z} F(z) \\ &= -2\epsilon\gamma \frac{H_v}{N_A C_m M v_z (l_0 + l_c z)} \frac{P_{ref}}{\sqrt{2\pi m k_B T}} \exp \left[-\frac{H_v}{k_B T_{ref}} \left(\frac{T_{ref} - T}{T} \right) \right] \end{aligned} \quad (S6)$$

In the original paper,¹⁹ $2\epsilon\gamma$ was defined as α and determined to be 4.00×10^{-4} m by fitting the experimental data for the flat jet generated using liquid microjets discharged from the orifices (diameter: 18 μ m). Because our liquid jet aperture has similar dimensions (20 μ m $\times$ 20 μ m), we used this value in our calculations.

By numerically integrating Eq. (S6), we estimated the temperature of the flat jet as a function of the z position, as shown in Figure S5 with $T_{ref} = 298.15$ K. The temperature at the irradiation point ($z = 0.5$ mm) is 3.7°C (276.85 K). The parameters used in the calculation are listed in Table S1.

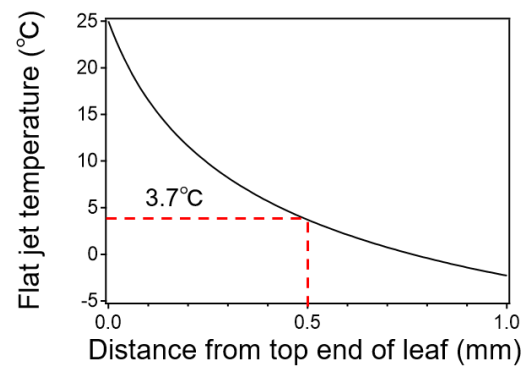


Figure S5. Temperature of the flat jet as a function of the position

Table S1. Parameters used for calculating the flat jet temperature.

H_v (kJ/mol)	C_m (J/mol*K)	M (mol/L)	v_z (m/s)	l_0 (10^{-10} m ²)	l_c (10^{-7} m)	P_{ref} (kPa)	m (10^{-23} g)	$2\epsilon\gamma$ (10^{-4} m)
44.0 ^a	75.3 ^b	55.3 ^b	25.0 ^c	2.82 ^d	4.00 ^d	3.17 ^b	2.99 ^c	4.00 ^f

a: From Ref. 24

b: From Ref. 25

c: Calculated from a flow rate of 1.2 mL/min (0.6 mL/min for each aperture). Aperture dimensions: 20 μm $\times$ 20 μm .

d: Best fitting result of Figure 1(d) in Ref. 1 using Eq. (S4).

e: Calculated from the molar mass of water (18.0 g/mol).²⁴

f: From Ref. 19

G. pK_a and pH at the temperature of a flat jet

Thermodynamic constants such as pK_a and the dissociation constant of water pK_w depend on the temperature. Therefore, the pH of a solution also depends on the temperature. In our PES experiments, the liquid temperature was lower than room temperature due to evaporative cooling. In this section, we calculate the thermodynamic constants and pH at the flat jet temperature.

First, we calculate the pK_a values at the estimated flat jet temperature (277 K) using the reported pK_a value at 298 K and enthalpy of deprotonation (ΔH_r). The temperature dependence of K_a is described by the van't Hoff equation:²³

$$\frac{d\ln K_a}{d(1/T)} = -\frac{\Delta H_r}{R} \quad (\text{S7})$$

where R is the gas constant. By integrating Eq. (S7) from temperature T_1 to T_2 while assuming temperature independence of ΔH_r , we obtain the following equations:

$$\begin{aligned} \ln K_a(T_2) - \ln K_a(T_1) &= -\frac{\Delta H_r}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \\ K_a(T_2) &= K_a(T_1) \exp \left[-\frac{\Delta H_r}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \right] \end{aligned} \quad (\text{S8})$$

The parameters from the literature and calculated here are listed in Table S2. In all cases, pK_a becomes higher at a lower temperature.

The pH also depends on the temperature, as mentioned above. We measured the solution pH using a pH meter (HORIBA, LAQUAtwin) in the air and at room temperature. Next, we need to consider the difference between room temperature (298 K) and the flat jet temperature (277 K). The pH of a solution can be calculated by solving the following coupled equations:

$$\begin{cases} \frac{[A^-][H_3O^+]}{[AH]} = K_a \\ [H_3O^+][OH^-] = K_w \\ [A^-] + [AH] = C_{tot} \\ [A^-] + [OH^-] = [H_3O^+] + C_{NaOH} \end{cases} \quad (\text{S9})$$

where $[X]$ is the concentration of chemical species X, C_{tot} is the total concentration of the solute (25 mM in our case), and C_{NaOH} is the concentration of added NaOH to adjust the solution pH. The third and fourth equations of

(S9) describe the mass and charge balance, respectively. The pK_w at 276.8 K was estimated by interpolating the reported values at 273.15 K (14.947) and 278.15 K (14.734).⁸

Figure S6 compares the measured (black dots) and calculated (black line) pH levels for aqueous phenol solutions at room temperature. They agree well with each other. We also calculated the pH at 277 K using pK_a and pK_w (red line). The pH increased from that at 298 K by approximately 5% on average. The legend and horizontal axis in Figure 9 in the main text are the pH levels after applying this correction.

Table S2. pK_a calculated at the flat jet temperature.

	$pK_a(277\text{ K})$	$pK_a(298\text{ K})$	$\Delta H_f(\text{kJ/mol})$
Phenol	10.30	9.99 ^a	22.9 ^b
Aniline	5.29	4.87 ^a	30.8 ^c
4-NP	7.42	7.15 ^a	19.7 ^d

a: From Ref. 8

b: From Ref. 26

c: From Ref. 27

d: From Ref. 28

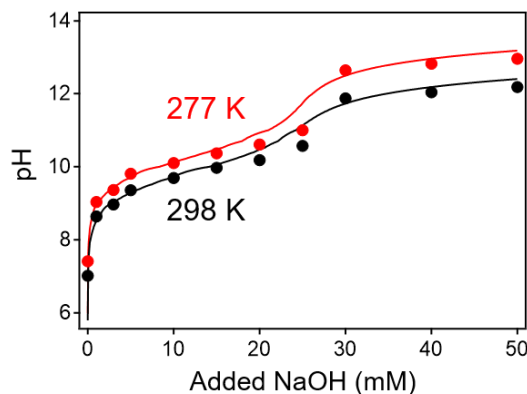


Figure S6. Correction of pH for the temperature difference. Black dots and lines are the pH levels experimentally determined and calculated using Eq. (S9), respectively. The red curve is the pH calculated at the flat jet temperature from Eq. (S9). Red dots are the measured pH levels corrected for the temperature difference.

H. Decomposition of spectra measured at intermediate pH

To decompose the spectra measured at various pH levels into contributions from phenol (4-NP) and the phenolate anion (4-NP⁻), we employed a least-squares fitting procedure. This fitting was restricted to the lower eBE region (below 10 eV) and involved the following function:

$$S(eBE) = a_{phenol}S_{phenol}(eBE) + a_{phenolate}S_{phenolate}(eBE) + a_{water}S_{water}(eBE) \quad (S10)$$

where S_x represents the spectrum of species x normalized by its spectral area, and a_x is the corresponding amplitude. S_{water} accounts for the background signal from the H₂O 1b₁ band centered at 11.3 eV.^{11, 16} By assuming identical photoionization cross-sections for phenol and phenolate, a_x is directly proportional to the surface concentration of the respective species. Both S_{phenol} and $S_{phenolate}$ were modeled using a sum of two Gaussian functions:

$$S_x(eBE) = \sum_{i=1}^2 b_i \exp \left(-4 \ln 2 * \left(\frac{eBE - VBE_i}{FWHM_i} \right)^2 \right) \quad (S11)$$

where b_i , VBE_i , and $FWHM_i$ represent the amplitude, VBE, and FWHM of each Gaussian component, respectively. Figure S7(a) and Table S3 present the fitting results and parameters for the phenol solutions measured at pH 7.4 and 12.6. These parameters were fixed when fitting the spectra at intermediate pH levels. Figure S7(b) illustrates the fitting result for pH 10.6 using Eq. (S10), demonstrating good agreement with the experimental data. The error bars in Figure 9 in the main text are estimated from the standard deviations of the fitting coefficients a_{phenol} and $a_{phenolate}$, as well as the areas of S_{phenol} and $S_{phenolate}$.

Table S3. Parameters of solute bands obtained by least-squares fitting using Eq. (S11).

	b_1/b_2	VBE_1 (eV)	VBE_2 (eV)	$FWHM_1$ (eV)	$FWHM_2$ (eV)
Phenol	0.51(4)	7.90(4)	8.72(3)	0.92(1)	1.24(3)
Phenolate	0.44(1)	7.3(1)	8.7(1)	0.96(1)	1.45(2)
4-NP	0.7(1)	7.8(1)	8.9(1)	1.01(2)	1.3(1)
4-NP ⁻	0.32(2)	6.9(1)	8.7(1)	0.94(8)	1.6(2)

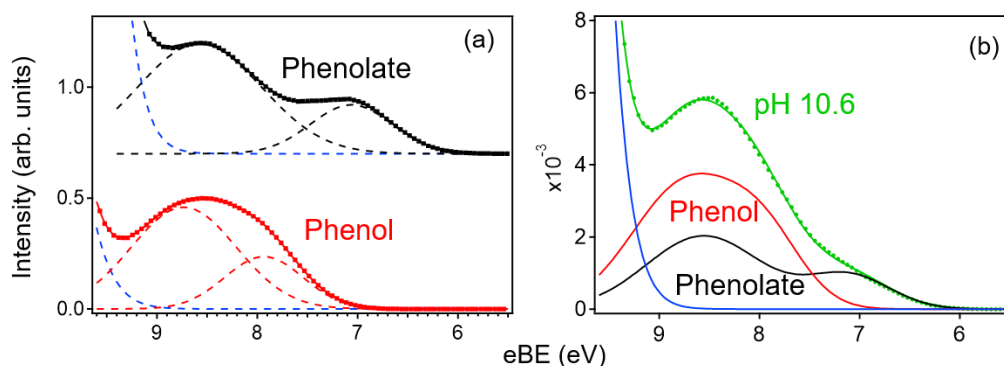


Figure S7. (a) Fitting results of phenol (red, pH 7.4) and phenolate (black, pH 12.6) spectra. Experimental data are shown as dots. Solid lines are the best fit, while broken lines indicate individual Gaussian components, with blue lines representing the H₂O 1b₁ contribution. The intensities are adjusted and offset for visibility. (b) Fitting result of the spectrum at intermediate pH 10.6. The green line shows the best fit, with the red, black, and blue curves representing the contributions from phenol, phenolate, and water, respectively. The intensity is normalized to the peak height of the H₂O 1b₁ band (not shown).

I. Surface concentration

The surface concentration of the solute molecules was calculated based on the bulk concentration dependence of the PE band intensity for the solute and surface tension data for a certain bulk concentration. The relative surface concentration can be estimated from the PE intensity, as discussed in the main text and in a previous publication,²⁹ whereas the absolute surface concentration is difficult to determine from the PE signal intensity. Hence, the absolute surface concentration (Γ) was calculated from the bulk concentration dependence of the surface tension using the Gibbs adsorption equation:³⁰

$$\Gamma = -\frac{1}{nRT} \frac{d\gamma}{d \ln C} \quad (S12)$$

where γ , C , R , and T are the surface tension, bulk concentration, gas constant, and temperature, respectively. n is a parameter that depends on the type of surfactant: $n = 1$ for a solution of neutral surfactant and $n = 2$ for that of a monovalent ion pair. The absolute surface concentration and corresponding bulk concentration used for the estimation are listed in Table S4. Figure S8 shows the relationship between the bulk and surface concentrations, which agrees very well with that estimated from the surface tension data.

Table S4. Surface concentration (Γ) for phenol, aniline, and 4-nitrophenol solutions.

	$\Gamma(10^{14} \text{ cm}^{-2})$	
Phenol	2.8 @200 mM	Ref. 29
Phenolate	0.82 @1500 mM	Ref. 31
Aniline	3.6 @200 mM	Ref. 29
4-Nitrophenol (4-NP)	1.24 @75 mM	Calculated from the surface tension in Ref. 32

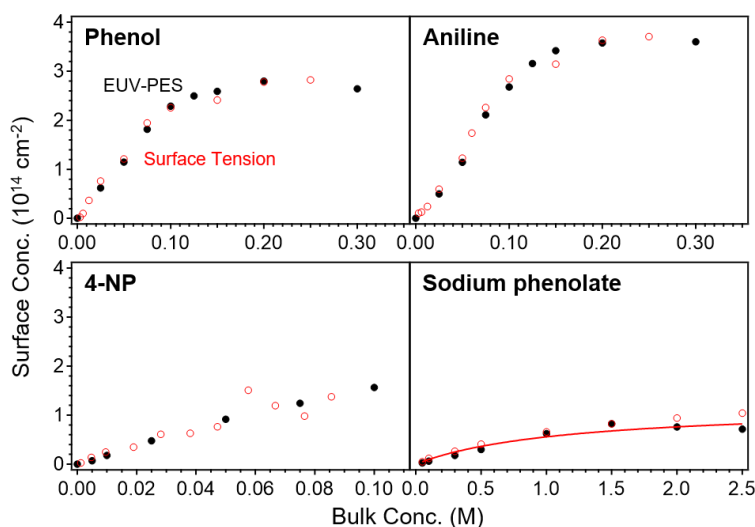


Figure S8. Relationship between bulk and surface concentrations estimated by EUV-PES (black circles). Red circles indicate the values calculated from surface tension data. The solid red line for the sodium phenolate data was obtained by fitting using Eq. 6 in the main text.

J. Electron scattering in XPS

Figure S9 shows the evolution of the XPS O(1s) profiles for liquid water under 600 eV radiation as the sample solution is switched from 0.02 M TBAI to 0.03 M NaI. The experiment was conducted at Spring 8, BL17, using the HEA. A detailed description of the experimental setup can be found in Ref. [16]. The sample solution was injected into the vacuum chamber as a liquid jet at a flow rate of 0.5 mL/min using a gradient flow HPLC pump (JASCO, PU-2089) in order to continuously alter the solution composition. It took several minutes for the solution to fully change from one composition to another. Each spectrum, or sweep, was measured in approximately 6 s. Therefore, the spectra shown in Figure S9 represent the real-time evolution over a 10-min period. When

hydrophobic TBA^+ covers the liquid surface, the $\text{O}(1s)$ signal is relatively weak, but it strengthens when the solute is changed to NaI . Because the TBA^+ molecular layer prevents water from evaporating from the surface, the $\text{O}(1s)$ signal for gaseous water is also smaller for the TBAI solution.

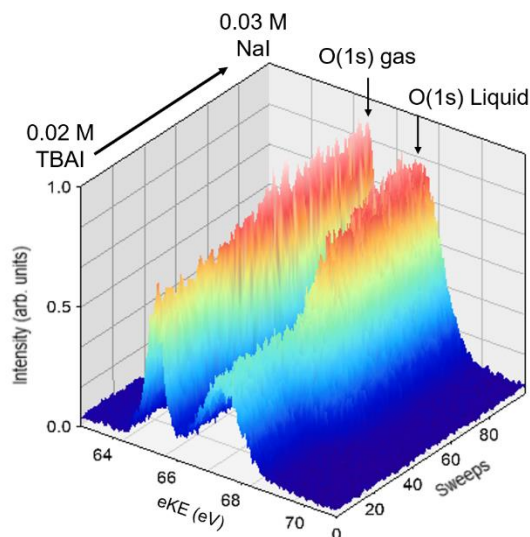


Figure S9. $\text{O}(1s)$ XPS profiles of water measured at a photon energy of 600 eV when the sample solution is changed from 0.02 M TBAI to 0.03 M NaI . In the former solution, both TBA^+ and I^- ions are concentrated at the gas-liquid interface. The bands at lower and higher eKE are due to gaseous and liquid water, respectively.

K. Specific ion effect

The solubility of organic molecules (especially their ions) in bulk solutions generally decreases upon adding electrolytes, causing the enrichment of organic molecules at the surface. This is often referred as the specific ion effect,³³ analogous to the precipitation of proteins from aqueous solutions by the addition of ions in the Hofmeister series. Figure S10(a) shows the dependence of the PE spectra of an aqueous 0.025 M phenol solution on the concentration of added NaCl . The inset shows that the relative intensity of the phenol band increases slightly with increasing NaCl concentration. The enrichment is negligible at 0.5 M (the NaCl concentration of sea water). Figure S10(b) shows the results for similar measurements for a 0.2 M aqueous sodium phenolate solution (pH 11.6). The $\text{C}_6\text{H}_5\text{O}^-$ signal increases more steeply with increasing NaCl concentration than in the case of phenol.

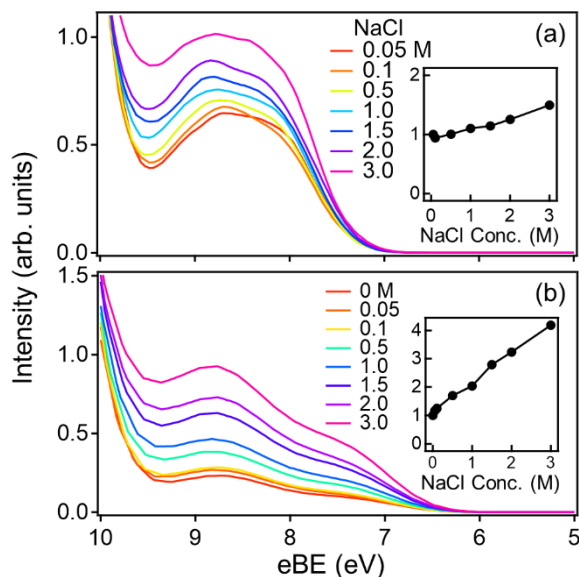


Figure S10. NaCl concentration dependence of PE spectra measured for (a) 0.025 M phenol solution with 40.0 eV pulses and (b) 0.2 M sodium phenolate solution with 56.5 eV pulses. The insets show the relative intensity of the solute signal as a function of the NaCl concentration.

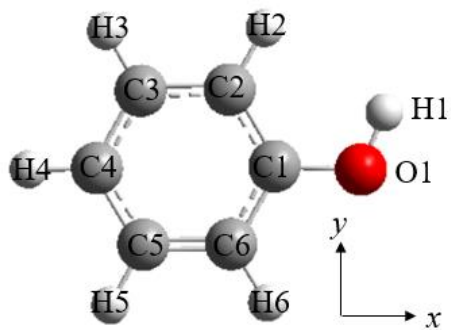
L. Classical (non-polarizable) MD simulations

In the main text, we described the results of polarizable MD simulations using the CRK. We also performed non-polarizable MD simulations for phenol, aniline, 4-NP, and sodium phenolate solutions for comparison with the experimental data, but the results lacked sufficient accuracy. Here, we describe the detailed settings used for the non-polarizable MD simulations and summarize the calculation results. Non-polarizable MD simulations were performed using the SPC/E³⁴ or TIP4P/2005 model for water,³⁵ and the general AMBER force field (GAFF)³⁶ for phenol, aniline, 4-NP, and phenolate species. The partial charges shown in Table S5 were determined by fitting the electrostatic potential calculated at the B3LYP/6-31G(d,p) or Hartree-Fock (HF)/6-31G(d) level of theory using the restrained electrostatic potential (RESP).³⁷ The force field for Na⁺ was taken from the literature.³⁸ We used a rectangular simulation box (25 Å × 25 Å × 150 Å) containing water and solute molecules in a slab geometry with the interface parallel to the *X-Y* plane. Initially, the water and solute molecules were placed at random positions in the central region of the cell and orientated using the PACKMOL package.³⁹ The steepest descent method was applied to remove the initial overlap between molecules. Newton's equation of motion was solved using the leap-frog algorithm⁴⁰ with a time step of $\Delta t = 2.0$ fs under three-dimensional periodic boundary conditions. Bonds involving hydrogen atoms were constrained using the LINCS algorithm.⁴¹ In the equilibration step, the NVT ensemble with a constant volume and temperature ($T = 298.15$ K) was considered with a Nose-Hoover thermostat.^{42,43} Long-range Coulombic interactions were treated using the particle-mesh Ewald method,^{44,45} with a separation parameter of $0.26 \text{ \AA}^{-1}$ and a grid spacing of $0.016 \text{ \AA}$. The cutoff length for the Lennard-Jones (LJ) interactions and the real-space part of the Ewald sum was set to $12 \text{ \AA}$. The equilibration run was performed for 50 ns to ensure that the system reached a steady state, which was confirmed by monitoring the time evolution of the averaged physical quantities. Subsequently, a 10 ns production run was conducted with 30 parallel computations starting from different initial configurations, resulting in a total ensemble average of 300 ns. Trajectory calculations were carried out using the Gromacs package (version 5.1.2).⁴⁶ The potential profile, denoted as $\phi(Z)$, was computed using Eqs. (1) and (2) in the main text. These calculations correspond to bulk concentrations of 15–32 mM for phenol, 30–84 mM for aniline, and 6–39 mM for 4-NP.

Table S5. Partial charges in the present model determined at the Hartree-Fock [HF/6-31G(d)] and DFT [B3LYP/6-31G(d)] levels of theory. Values of the dipole moments are summarized in Table S6.

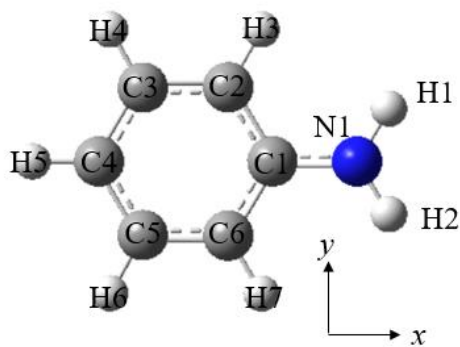
Phenol

	HF	DFT
H1	0.3755	0.3540
O1	-0.5619	-0.4955
C1	0.4612	0.3618
C2	-0.3515	-0.2685
C3	-0.0652	-0.0945
C4	-0.2207	-0.1544
C5	-0.0652	-0.0945
C6	-0.3515	-0.2685
H2	0.1809	0.1503
H3	0.1376	0.1212
H4	0.1422	0.1169
H5	0.1376	0.1212
H6	0.1809	0.1503



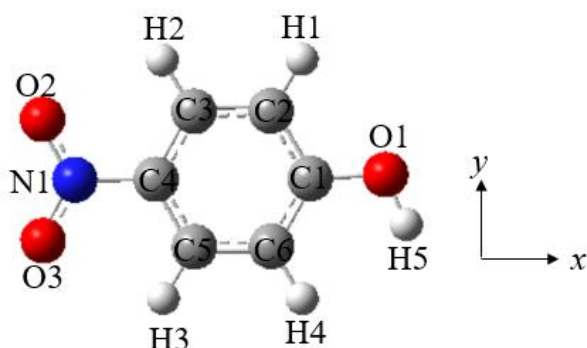
Aniline

	HF	DFT
N1	-1.0950	-0.9503
H1	0.4386	0.4041
H2	0.4386	0.4041
C1	0.6683	0.4967
C2	-0.4083	-0.2864
H3	0.1575	0.1224
C3	-0.0241	-0.0830
H4	0.1343	0.1195
C4	-0.3227	-0.2243
H5	0.1533	0.1246
C5	-0.0241	-0.0830
H6	0.1343	0.1195
C6	-0.4083	-0.2864
H7	0.1575	0.1224



4-Nitrophenol

	HF	DFT
C3	-0.2882	-0.3062
H2	0.1750	0.1511
C2	-0.2743	-0.1788
H1	0.2035	0.1706
C1	0.3892	0.2804
O1	-0.5463	-0.4794
H5	0.3973	0.3752
C6	-0.2743	-0.1788
H4	0.2035	0.1706
C5	-0.2882	-0.3062
H3	0.1750	0.1511
C4	0.6052	0.5634
N1	0.0970	0.1102
O3	-0.2872	-0.2615
O2	-0.2872	-0.2615



Phenolate

	HF	DFT
O1	-0.8185	-0.7200
C1	0.6601	0.5065
C2	-0.4487	-0.3334
C3	-0.0398	-0.1044
C4	-0.4039	-0.2999
C5	-0.0398	-0.1044
C6	-0.4487	-0.3334
H2	0.1249	0.0861
H3	0.0882	0.0680
H4	0.1132	0.0806
H5	0.0882	0.0680
H6	0.1249	0.0861

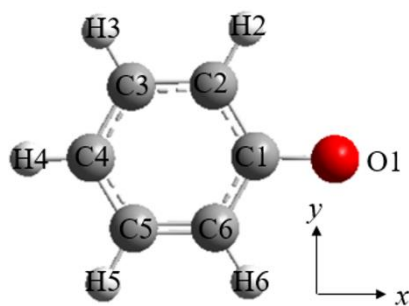


Table S6. Dipole moment (Debye) for each monomer in the coordinate system (see the figures in Table S5) determined at the HF/6-31G(d) level of theory.

	Phenol	Aniline	4-Nitrophenol
<i>x</i>	-0.2459	1.5914	5.2444
<i>y</i>	-1.4316	0.0000	-1.4343
<i>z</i>	0.0000	0.0000	0.0000

Figure S11 summarizes the calculated depth profiles for representative atoms in the solute molecules, orientation distributions of the solvent and solute molecules, and electrostatic potentials created by the solvent and solute. The density distributions show that the solute molecules are well adsorbed to the surface. The depth profiles for phenol in Figures S11(b) and S11(c) show that the C4 atom (for atomic labeling, see Table S5) is closer to the surface than the O atom, implying that the dipole moment for a phenol molecule at the interface is directed toward the bulk. Similarly, the dipole moment for an aniline molecule is directed toward the bulk, since its C4 atom is closer to the surface than the N atom. For 4-NP, the direction of the dipole moment is not clear, but Figure S11(q) indicates that the nitro group is located deeper than the hydroxyl group. The depth profiles and orientation distributions for solute molecules are similar among the different methods. However, TIP4P/2005 predicts a higher degree of orientation for water molecules at the interface than SPC/E. Figure S12 displays the calculated depth profiles for solute molecules and the electrostatic potentials for 1.0 and 3.3 M sodium phenolate solutions. In both cases, phenolate resides closer to the surface than Na^+ .

Table S7 lists the bulk surface potential difference ($\Delta\phi$) for aqueous solutions and pure water, calculated using different combinations of water models (SPC/E or TIP4P/2005) and quantum chemical calculation methods (DFT or HF) for the partial charges of solute molecules. The comparison with the experimental results is shown in Figure S13. The SPC/E+DFT calculations fail to accurately predict the sign of $\Delta\phi$ (the direction of the energy shift). On the other hand, the TIP4P/2005+HF calculations predict a negative value of $\Delta\phi$, in agreement with the experimental results. However, they do not correctly predict the much stronger influence of aniline and the particularly weak influence of 4-NP compared to other solutes.

TIP4P/2005 is a well-established rigid non-polarizable model for water, and its combination with HF provides the correct sign of $\Delta\phi$ for non-ionic species. However, the $\Delta\phi$ values predicted by the non-polarizable models contain a large degree of scatter. Furthermore, the experimentally observed negative $\Delta\phi$ of the concentrated sodium phenolate solution is not reproduced even by the combined TIP4P/2005 and HF models, indicating a clear limitation of the non-polarizable MD simulations.

The calculated potentials exhibit rapid changes within a spatial range comparable to the size of the solute molecules. This is because the potential is obtained by integrating the Poisson equation over all partial charges for the solute and solvent molecules. This rapid change is not directly related to any experimental observable, and the values computed for the region below the top molecular layer are considered to be the surface potential ϕ in our discussion. On the other hand, because the solute and solvent molecules have different depth profiles, the influence of the potential on their PE bands is possibly different (see Section P).

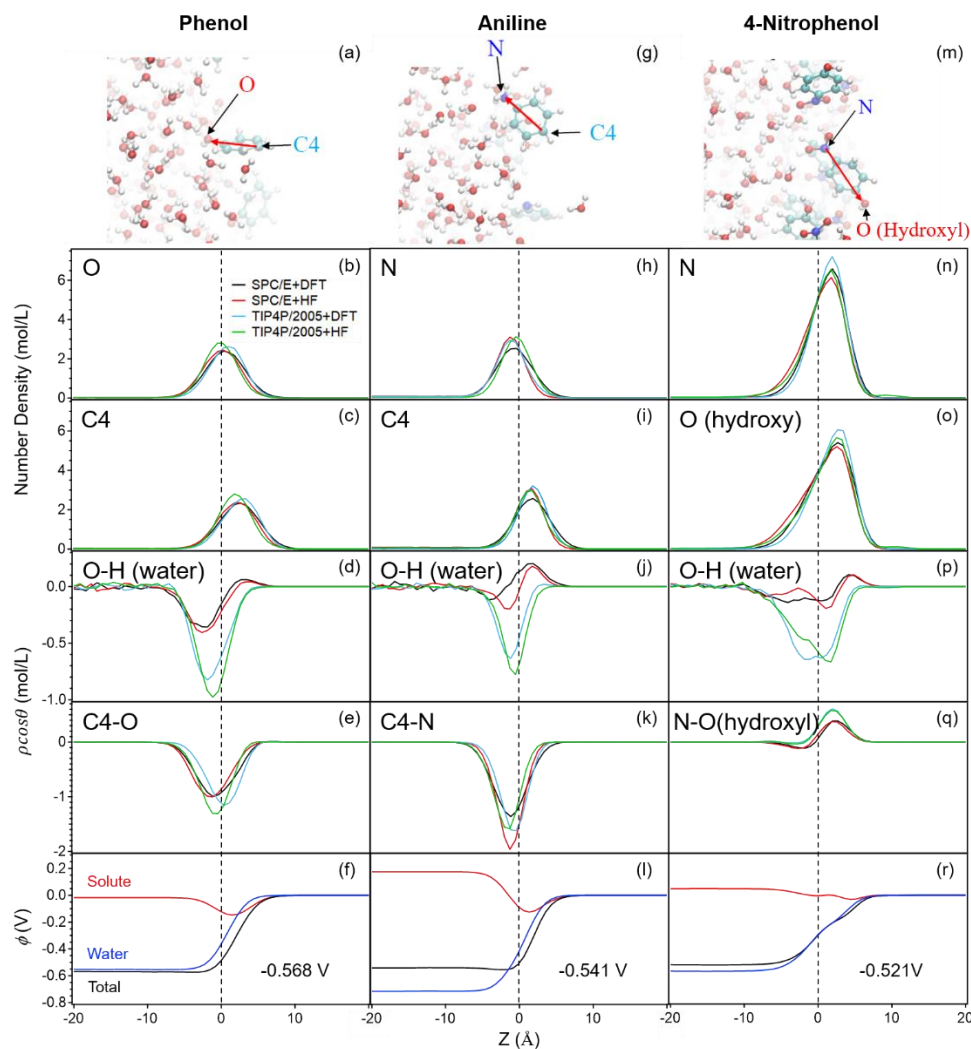


Figure S11. MD simulation results for aqueous phenol, aniline, and 4-NP solutions using different theoretical models. (a, g, m) Snapshots at the gas-liquid interface. The H, O, C, and N atoms are colored in light grey, red, cyan, and blue, respectively. The arrows indicate the orientation of the solute molecule. Depth profiles for specific solute atoms (b, c, h, i, n, o) and orientation distribution $\rho\langle\cos\theta\rangle$ for O-H in water (d, j, p) and solute molecules (e, k, q) calculated by SPC/E+DFT (black), SPC/E+HF (red), TIP4P/2005+DFT (light blue), and TIP4P/2005+HF (green). A positive value of $\rho\langle\cos\theta\rangle$ indicates that the vector is directed toward the vacuum side. (f, l, r) Electric potential calculated by the TIP4P/2005+HF model. The total potential (black) is decomposed into contributions from solute (red) and water (blue) molecules. The numerical values represent the surface potential for the solution. The zero on the horizontal axis indicates the Gibbs dividing surface, and negative and positive values correspond to inside and outside the solution, respectively.

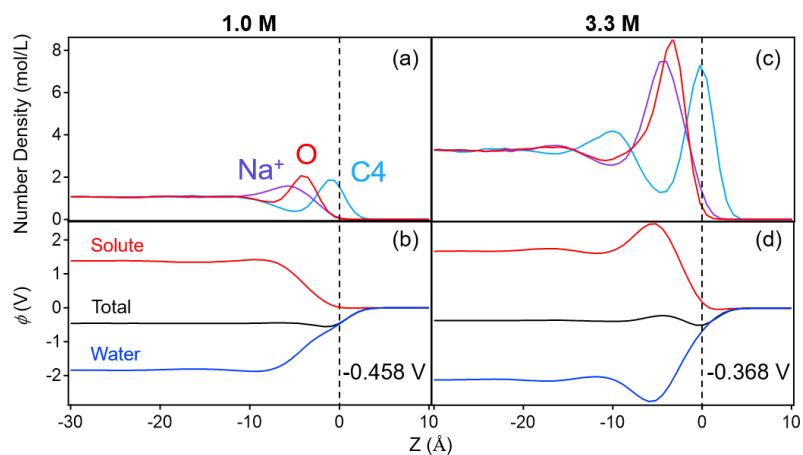


Figure S12. Results of MD simulations for 1.0 and 3.3 M sodium phenolate solutions calculated using the TIP4P/2005+HF model. (a, c) Depth profiles for specific atoms in the solute molecule. (b, d) Electric potential. The total potential (black) is decomposed into contributions from solute (red) and water (blue) molecules. The numerical values represent the surface potential for the solution. The zero on the horizontal axis indicates the Gibbs dividing surface, and negative and positive values correspond to inside and outside the solution, respectively.

Table S7. Bulk surface potential calculated using different theoretical models. (Units: V)

	SPC/E, DFT		SPC/E, HF		TIP4P/2005, DFT		TIP4P/2005, HF	
	ϕ	$\Delta\phi^a$	ϕ	$\Delta\phi^a$	ϕ	$\Delta\phi^a$	ϕ	$\Delta\phi^a$
water	-0.601(3)	-	-0.601(3)	-	-0.502(4)	-	-0.502(4)	-
Phenol	-0.598(3)	0.003	-0.647(3)	-0.046	-0.529(4)	-0.027	-0.568(4)	-0.066
Aniline	-0.563(2)	0.038	-0.617(3)	-0.016	-0.488(4)	0.014	-0.541(4)	-0.039
4-NP	-0.488(3)	0.113	-0.536(3)	0.065	-0.477(4)	0.025	-0.520(4)	-0.018
NaC ₆ H ₅ O (1.0 M)							-0.458(5)	0.044
NaC ₆ H ₅ O (3.3 M)							-0.368(8)	0.134

a: The difference in ϕ from the value for pure water.

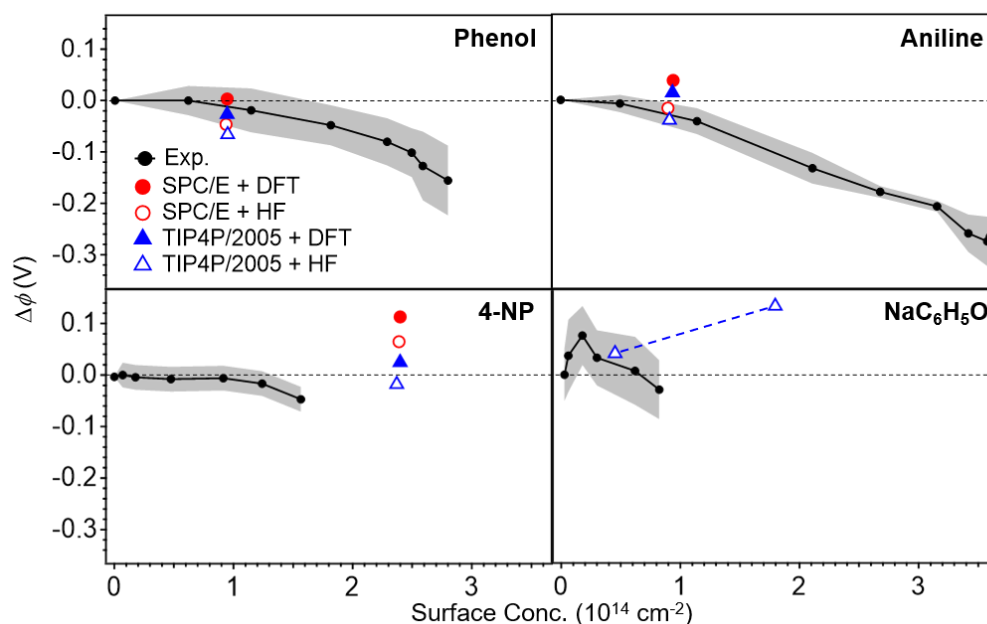


Figure S13. Comparison of $\Delta\phi$ obtained by EUV-PES measurements and non-polarizable MD calculations. The black circles indicate the experimental values and the colored symbols indicate the values calculated using different theoretical models.

M. Details of CRK modeling and MD settings

We describe the parametrization procedure for the CRK model and details of the polarizable simulations. The atomic sites in a phenolate molecule are labeled as shown in Table S5. The partial charges and CRK parameters for aniline, phenolate, and 4-NP were obtained by DFT calculations using the B3LYP functional⁴⁷⁻⁴⁸ and the aug-cc-pVTZ⁴⁹ basis set. The obtained parameters are listed in Tables S8 to S13. The LJ parameters for aniline, phenolate, and 4-NP molecules were obtained from the GAFF, and the LJ interactions were treated using the Lorentz-Berthelot combining rule.

For each system, 48 independent initial configurations were prepared, equilibrated for >20 ns, and sampled for 10 ns, giving a total sampling time of 480 ns. Three-dimensional periodic boundary conditions were used. The cutoff length for the LJ interactions and the real term in the Ewald method was set to 12 Å. The equation of motion was numerically integrated using RESPA⁵⁰ with time steps for inter- and intra-molecular interactions of 2 and 0.4 fs, respectively. The mass of the hydrogen atoms in the water molecules was set to three times the real value to allow a large time step in the calculations. The temperature was maintained at 298.15 K by a Nosé-Hoover thermostat.^{43, 51} The splitting parameter in the Ewald method was set to 0.26 Å⁻¹. The grid interval for calculating the reciprocal terms in the Ewald sum was ~1.6 Å. The short-range damping parameter for avoiding a polarization catastrophe⁵² was set to $\xi = 0.7$ Å for aniline and phenolate, and $\xi = 0.593$ Å for 4-NP, based on the CRKs for fluoride⁵³ and water,⁵² respectively. The internal configuration of the solute molecules was assumed to be rigid using the RATTLE method,⁵⁴ except for internal rotations of hydroxyl, amino, and nitro groups. The water molecules were treated as fully flexible. The torsional potentials of hydroxyl, amino, and nitro groups were obtained from the GAFF. Here, space-fixed coordinates are expressed using uppercase letters (X, Y, Z), while molecule-fixed coordinates are expressed using lowercase letters (x, y, z). Unless stated otherwise, the Z axis is along the surface-normal direction, and the z -axis is along the C-O or C-N bond direction. The electrostatic potentials were calculated using Eqs. (1) and (2) in the main text with polarized partial charges.

Table S8. Partial charges for the isolated aniline molecule. (Units: e)

N1	H1/H2	C1	C2/C6	C3/C5	C4	H3/H7	H4/H6	H5
-0.4840	0.2452	0.0427	-0.0456	-0.1213	-0.0846	0.0751	0.0735	0.0719

Table S9. CRK parameters K_{ij} for the aniline molecule. (Units: atomic units)

	$j = \text{N1}$	H1	H2	C1	C2	C3	C4	C5	C6	H3	H4	H5	H6	H7
$i = \text{N1}$	-38.181	13.086	13.086	14.400	2.239	-3.134	-1.093	-3.134	2.239	-1.685	1.262	1.340	1.262	-1.685
H1	13.086	-6.229	-3.766	-4.183	-0.733	0.870	0.482	0.870	-0.733	0.719	-0.367	-0.366	-0.367	0.719
H2	13.086	-3.766	-6.229	-4.183	-0.733	0.870	0.482	0.870	-0.733	0.719	-0.367	-0.366	-0.367	0.719
C1	14.400	-4.183	-4.183	-10.888	0.078	3.085	-0.846	3.085	0.078	0.948	-0.981	-0.557	-0.981	0.948
C2	2.239	-0.733	-0.733	0.078	-5.576	0.193	2.111	-0.803	1.794	1.922	0.626	-0.550	-0.200	-0.368
C3	-3.134	0.870	0.870	3.085	0.193	-5.604	0.260	1.730	-0.803	0.616	1.846	0.689	-0.393	-0.223
C4	-1.093	0.482	0.482	-0.846	2.111	0.260	-5.534	0.260	2.111	-0.638	0.615	1.814	0.615	-0.638
C5	-3.134	0.870	0.870	3.085	-0.803	1.730	0.260	-5.604	0.193	-0.223	-0.393	0.689	1.846	0.616
C6	2.239	-0.733	-0.733	0.078	1.794	-0.803	2.111	0.193	-5.576	-0.368	-0.200	-0.550	0.626	1.922
H3	-1.685	0.719	0.719	0.948	1.922	0.616	-0.638	-0.223	-0.368	-2.450	-0.080	0.191	0.287	0.043
H4	1.262	-0.367	-0.367	-0.981	0.626	1.846	0.615	-0.393	-0.200	-0.080	-2.212	-0.147	0.111	0.287
H5	1.340	-0.366	-0.366	-0.557	-0.550	0.689	1.814	0.689	-0.550	0.191	-0.147	-2.232	-0.147	0.191
H6	1.262	-0.367	-0.367	-0.981	-0.200	-0.393	0.615	1.846	0.626	0.287	0.111	-0.147	-2.212	-0.080
H7	-1.685	0.719	0.719	0.948	-0.368	-0.223	-0.638	0.616	1.922	0.043	0.287	0.191	-0.080	-2.450

Table S10. Partial charges for the isolated 4-NP molecule. (Units: e)

C1	C2/C6	C3/C5	C4	H1/H4	H2/H3	O1	H5	N1	O2/O3
0.1884	-0.0814	-0.1521	0.1588	0.1086	0.1206	-0.4742	0.3783	0.4734	-0.3581

Table S11. CRK parameters K_{ij} for the 4-NP molecule. (Units: atomic units)

	$j=C1$	C2	C3	C4	C5	C6	H1	H2	H3	H4	O1	H5	N1	O2	O3
$i=C1$	-6.107	0.538	2.257	-1.481	2.257	0.538	0.426	-0.724	-0.724	0.426	2.647	-0.365	-0.221	0.266	0.266
C2	0.538	-4.850	-0.233	1.830	-0.883	1.648	1.626	0.861	0.028	-0.475	0.572	-0.164	-0.039	-0.229	-0.229
C3	2.257	-0.233	-5.235	0.771	1.532	-0.883	0.712	1.889	-0.254	-0.085	-0.683	0.080	0.898	-0.383	-0.383
C4	-1.481	1.830	0.771	-4.790	0.771	1.830	-0.340	-0.032	-0.032	-0.340	-0.022	0.047	0.441	0.673	0.673
C5	2.257	-0.883	1.532	0.771	-5.235	-0.233	-0.085	-0.254	1.889	0.712	-0.683	0.080	0.898	-0.383	-0.383
C6	0.538	1.648	-0.883	1.830	-0.233	-4.850	-0.475	0.028	0.861	1.626	0.572	-0.164	-0.039	-0.229	-0.229
H1	0.426	1.626	0.712	-0.340	-0.085	-0.475	-2.119	-0.194	0.187	0.150	-0.102	0.177	-0.237	0.137	0.137
H2	-0.724	0.861	1.889	-0.032	-0.254	0.028	-0.194	-2.455	-0.044	0.187	0.171	-0.010	-0.166	0.372	0.372
H3	-0.724	0.028	-0.254	-0.032	1.889	0.861	0.187	-0.044	-2.455	-0.194	0.171	-0.010	-0.166	0.372	0.372
H4	0.426	-0.475	-0.085	-0.340	0.712	1.626	0.150	0.187	-0.194	-2.119	-0.102	0.177	-0.237	0.137	0.137
O1	2.647	0.572	-0.683	-0.022	-0.683	0.572	-0.102	0.171	-0.102	-5.553	2.678	0.181	0.078	0.078	0.078
H5	-0.365	-0.164	0.080	0.047	0.080	-0.164	0.177	-0.010	-0.010	0.177	2.678	-2.556	0.010	0.010	0.010
N1	-0.221	-0.039	0.898	0.441	0.898	-0.039	-0.237	-0.166	-0.166	-0.237	0.181	0.010	-6.628	2.653	2.653
O2	0.266	-0.229	-0.383	0.673	-0.383	-0.229	0.137	0.372	0.372	0.137	0.078	0.010	2.653	-3.636	0.163
O3	0.266	-0.229	-0.383	0.673	-0.383	-0.229	0.137	0.372	0.372	0.137	0.078	0.010	2.653	0.163	-3.636

Table S12. Partial charges for the isolated phenolate molecule. (Units: e)

O1	C1	C2/C6	C3/C5	C4	H2/H6	H3/H5	H4
-0.7641	0.3594	-0.0592	-0.2184	-0.1204	-0.0095	0.0453	0.0088

Table S13. CRK parameters K_{ij} for the phenolate molecule. (Units: atomic units)

	$j=O1$	C1	C2	C3	C4	C5	C6	H2	H3	H4	H5	H6
$i=O1$	-4.117	3.458	0.518	-0.921	0.109	-0.921	0.518	0.058	0.367	0.507	0.367	0.058
C1	3.458	-7.369	0.560	2.385	-1.437	2.385	0.560	0.559	-0.724	-0.211	-0.724	0.559
C2	0.518	0.560	-6.158	0.152	2.333	-1.001	2.087	2.221	0.776	-0.639	-0.222	-0.627
C3	-0.921	2.385	0.152	-6.113	0.331	2.362	-1.001	0.885	2.122	0.702	-0.600	-0.302
C4	0.109	-1.437	2.333	0.331	-6.132	0.331	2.333	-0.649	0.644	2.141	0.644	-0.649
C5	-0.921	2.385	-1.001	2.362	0.331	-6.113	0.152	-0.302	-0.600	0.702	2.122	0.885
C6	0.518	0.560	2.087	-1.001	2.333	0.152	-6.158	-0.627	-0.222	-0.639	0.776	2.221
H2	0.058	0.559	2.221	0.885	-0.649	-0.302	-0.627	-2.942	-0.161	0.215	0.354	0.390
H3	0.367	-0.724	0.776	2.122	0.644	-0.600	-0.222	-0.161	-2.639	-0.141	0.224	0.354
H4	0.507	-0.211	-0.639	0.702	2.141	0.702	-0.639	0.215	-0.141	-2.714	-0.141	0.215
H5	0.367	-0.724	-0.222	-0.600	0.644	2.122	0.776	0.354	0.224	-0.141	-2.639	-0.161
H6	0.058	0.559	-0.627	-0.302	-0.649	0.885	2.221	0.390	0.354	0.215	-0.161	-2.942

N. Results of CRK calculations

This section describes supplementary calculation results for the phenol, aniline, and 4-NP solutions using the CRK models.

For aqueous solutions of aniline and phenol, non-polarizable MD simulations using the TIP4P/2005 and HF methods provided a sign of $\Delta\phi$, consistent with the experimental results. Does this mean that polarization is unimportant for an aqueous phenol solution? To address this, the influence of the polarization in an aqueous phenol solution was evaluated using the CRK model. Figure S14(a) shows the calculated $\phi(Z)$ profiles for an aqueous phenol solution (surface concentration $\sim 2 \times 10^{14} \text{ cm}^{-2}$) (blue) and pure water (black). The calculated $\Delta\phi$ value is -0.13 V , in fair agreement with the experimental value of -0.06 V . The solid light blue line shows the case in which the polarization of phenol is not considered; the $\Delta\phi$ value is similar to that for polarizable phenol. This is because the local electric field is too weak to induce an appreciable polarization of phenol.

Figure S14(b) shows the decomposition of $\phi(Z)$ into contributions from water (red) and phenol (green). In the present results, the contribution from water (difference between the black and red lines) is larger than that of phenol, and it produces a negative shift in total. The calculated orientation profile of the C4-O vector of phenol is shown as $\rho \cos \theta_{\text{C-O}}(Z)$ in Figure S14(c). The negative $\rho \cos \theta_{\text{C-O}}(Z)$ band near the interface at $Z \approx 0$ indicates that the aromatic ring tends to point toward the gas phase. Since the permanent dipole vector of phenol is nearly perpendicular to the C4-O vector as shown in Figure 1 of the main text, the dipole vector of phenol does not provide a large polarization along the Z axis. The integral of $\rho \cos \theta$ is slightly negative, and therefore, the solute contribution to $\Delta\phi$ is positive.

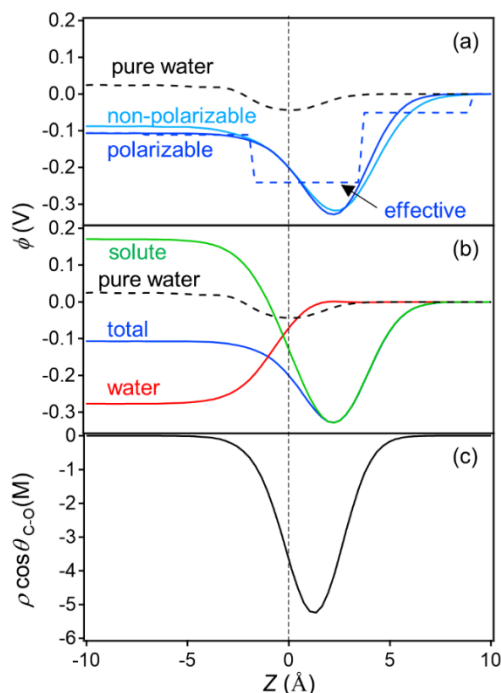


Figure S14. (a) Potential profile $\phi(Z)$ for the phenol solution (blue and light blue) and pure water (black). The dashed blue line shows the profile averaged over the size of a single molecule. The light blue curve is the profile obtained by neglecting polarization in the MD simulations. (b) Decomposition of $\phi(Z)$ into contributions from water (red) and phenol (green). The blue and black curves are the same as those in (a). (c) Product of the number density ρ and $\cos \theta_{\text{C-O}}$ for phenol as a function of Z , where $\theta_{\text{C-O}}$ is the tilt angle between the vector from C4 (carbon in the *para* position of OH) to the O of phenol and the surface normal.

Aniline solution

The electric potential profile calculated using the CRK model for aniline at a surface concentration of $\sim 2 \times 10^{14} \text{ cm}^{-2}$ is shown in Figure S15(a). There is a negative shift in the electric potential ($\Delta\phi \sim -0.08 \text{ V}$), which is

consistent with the experimental value $\Delta\phi \sim -0.1\text{V}$ (see Figure 3 of the main text). The decomposition to the species displayed in Figure S15(b) shows a similar behavior to that of the phenol solution. It indicates that the solute makes a positive contribution to $\Delta\phi$, while the solvent contribution overcompensates the solute contribution to produce the negative shift in total.

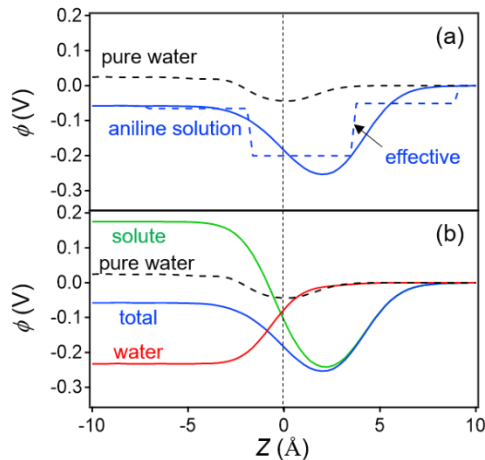


Figure S15. (a) Potential profile $\phi(Z)$ for the aniline solution (blue) and pure water (black). The dashed line is the profile averaged over the size of a single molecule. (b) Decomposition of $\phi(Z)$ into contributions from water (red) and aniline (green). The blue and black curves are the same as those in (a).

4-NP solution

A noteworthy feature of 4-NP is a much smaller magnitude of $\Delta\phi$ than those of phenol and aniline, even though 4-NP has a larger permanent dipole moment (Figure 1 in the main text). Figure S16(a) presents $\phi(Z)$ for an aqueous 4-NP solution (surface concentration $\sim 2 \times 10^{14} \text{ cm}^{-2}$) calculated using Eqs. (1) and (2) in the main text. $\Delta\phi$ is much less than 0.1 V, in agreement with the experiment. The dashed line shows the effective $\phi(Z)$ estimated by coarse-graining for each molecular thickness, considering the insensitivity of EUV-PES to changes in $\Delta\phi$ within a single molecule. The potential is ~ 0.1 eV for the top layer but nearly zero below it. We decomposed the calculated $\phi(Z)$ into contributions from the solute and solvent water (Figure S16(b)) using the charge density $\rho_q(Z)$. Both, the solute and solvent, provide positive $\Delta\phi$ at the top layer, but the influence of the solute almost vanishes below it, leaving a very similar ϕ to that of pure water. Figure S16(c) shows the product of the number density ρ and the orientation $\cos \theta$ as a function of Z . The value of $\rho \cos \theta(Z)$ is a good index of the degree of anisotropic molecular orientation.⁵⁵⁻⁵⁶ As shown in Figure 4 in the main text, the polarization density of 4-NP is much lower than that of aniline and oscillates at the surface. Consequently, the integrated value of the polarization density is much lower than that of aniline, and the solute contribution to $\Delta\phi$ is small. In a previous SHG study, the orientation of 4-NP was determined to be nitro-up, *i.e.*, the nitro group points to the gas phase.⁵⁷ To compare with the previous result, we calculated the orientation distribution of 4-NP at the surface, and the result is shown in Figure S16(c). Here, θ is defined as the angle between the C4-O vector and the surface normal axis. In the figure, $\rho \cos \theta > 0$ indicates a NO_2 -down orientation, which is apparently inconsistent with Ref. [57]. Therefore, we performed further calculations of the nonlinear susceptibility and have described the details in the next section.

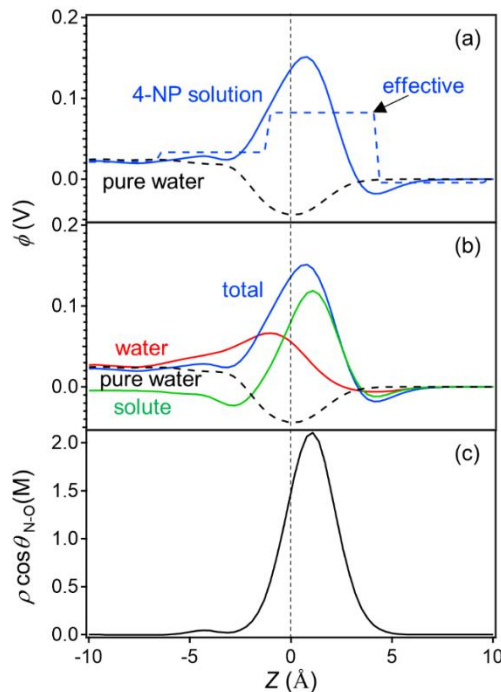


Figure S16. (a) Potential profile $\phi(Z)$ for 4-NP solution (blue) and pure water (black) as a function of the normal coordinate Z . The dashed line shows the profile averaged over the size of a single molecule. The origin of the potential $\phi(Z) = 0$ is in the asymptotic vapor as $Z \rightarrow \infty$. (b) Decomposition of the $\phi(Z)$ profile for the 4-NP solution (blue) into contributions from water (red) and solute (green). (c) Product of the number density ρ and $\cos \theta_{N-O}$ for 4-NP as a function of Z , where θ_{N-O} is the tilt angle between the vector from the nitrogen atom to the oxygen atom in the hydroxyl group of 4-NP and the surface normal.

O. Orientation and hyperpolarizability of 4-NP

Orientation distribution

Figure S17(a) illustrates the molecule-fixed coordinate system (x, y, z) used in the simulations, where the 4-NP molecule is on the x - z plane and the z axis is along the vector from the nitrogen atom to the oxygen atom in the hydroxy group. Figure S17(b) shows the Euler angles (α, θ, ψ) describing the orientation of a 4-NP molecule with respect to the liquid surface; here, Z is defined relative to the surface normal. $Z = 0$ indicates the Gibbs dividing surface, and $Z > 0$ ($Z < 0$) refers to the vapor (liquid) phase. Figure S17(c) displays the orientation distribution for 4-NP molecules at the water surface calculated using CRK. Because the distribution is symmetric around the angle α , it can be represented using the two-dimensional probability density function, $P(\cos \theta, \psi)$, which is normalized according to $\int_{-1}^1 d \cos \theta \int_0^\pi d \psi P(\cos \theta, \psi) = 1$. The results indicate that the regions of maximum probability are located at $\cos \theta \simeq 0$ and $\psi = 0$ and π . Therefore, the N-O axis is nearly parallel to the liquid surface and the phenyl ring is perpendicular to the surface. It should also be noted that the regions of maximum probability are slightly shifted to positive values of $\cos \theta$, indicating a slight NO₂-down orientation with a mean tilt angle $\langle \theta \rangle \simeq 78^\circ$. This result is qualitatively consistent with the non-polarizable calculations shown in Figure S11(q).

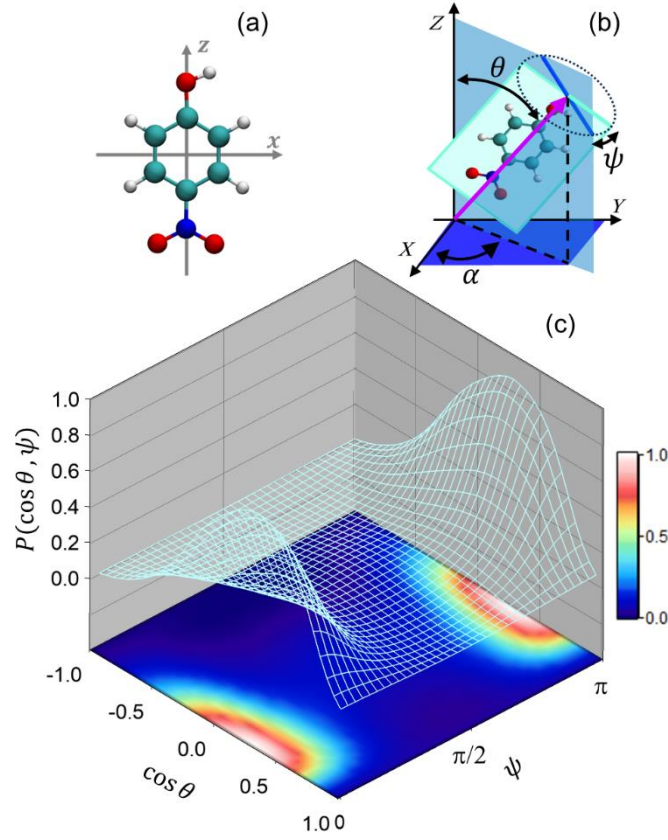


Figure S17. Orientation of 4-NP molecules at the aqueous solution surface. Panels (a) and (b) show molecule-fixed coordinates and Euler angles (α, θ, ψ) in space-fixed coordinates, respectively. α is the azimuthal angle about Z , θ is the angle between the surface-normal axis Z and the molecular axis z , and ψ is the dihedral angle between the molecular plane and the plane containing the surface normal and the molecular z axis. (c) Probability distribution for molecular orientation, $P(\cos\theta, \psi)$, for 4-NP molecules at the aqueous solution surface.

Interpretation of previous SHG results

Why did the previous SHG study and our simulations infer opposite orientations for 4-NP? In the SHG measurements, the angular frequency ω of the incident light was doubled as a result of the nonlinear susceptibility $\chi^{(2)}$, which is non-zero at an interface with broken inversion symmetry. The molecular orientation determined by SHG measurements is related to the sign of the imaginary component of $\chi^{(2)}$. Higgins *et al.* reported that the sign of the imaginary $\chi_{XXZ}^{(2)}$ component is positive in a pre-resonance condition for 4-NP at $\omega \simeq 2$ eV.⁵⁷ We evaluated $\chi^{(2)}$ from the orientation distribution shown in Figure S17(c). $\chi_{PQR}^{(2)}$ is given by

$$\chi_{PQR}^{(2)} = n_s \langle \beta_{PQR} \rangle = n_s \sum_{p,q,r}^{x-z} \langle D_{Pp} D_{Qq} D_{Rr} \rangle \beta_{pqr} \quad (\text{S13})$$

where the suffixes P , Q , and R respectively denote X , Y , and Z in the space-fixed coordinates while p , q , and r denote the corresponding molecule-fixed coordinates. n_s is the number density of molecules at the interface, and D indicates the rotation matrix from the molecule-fixed coordinates to the space-fixed coordinates. β_{pqr} is the molecular hyperpolarizability given by the following sum-over-state expression,⁵⁸

$$\begin{aligned}
\beta_{pqr} = \frac{1}{\hbar^2} \sum_{n,m} & \left[\frac{\langle g|\mu_p|n\rangle\{\langle n|\mu_q|m\rangle\langle m|\mu_r|g\rangle + \langle n|\mu_r|m\rangle\langle m|\mu_q|g\rangle\}}{(2\omega - \omega_{ng} + i\Gamma_{ng})(\omega - \omega_{mg} + i\Gamma_{mg})} \right. \\
& + \frac{\{\langle g|\mu_r|m\rangle\langle m|\mu_q|n\rangle + \langle g|\mu_q|m\rangle\langle m|\mu_r|n\rangle\}\langle n|\mu_p|g\rangle}{(2\omega + \omega_{ng} + i\Gamma_{ng})(\omega + \omega_{mg} + i\Gamma_{mg})} \\
& + \frac{\{\langle g|\mu_r|m\rangle\langle n|\mu_q|g\rangle + \langle g|\mu_q|m\rangle\langle n|\mu_r|g\rangle\}\langle m|\mu_p|n\rangle}{2\omega - \omega_{nm} + i\Gamma_{nm}} \\
& \left. \times \left(\frac{1}{\omega + \omega_{mg} + i\Gamma_{mg}} + \frac{1}{\omega - \omega_{ng} + i\Gamma_{ng}} \right) \right] \quad (S14)
\end{aligned}$$

where $\hbar$ is the Dirac constant, $\langle a|\mu_p|b\rangle$ and ω_{ab} are respectively the transition dipole moment and the angular frequency for the transition from $|b\rangle$ to $|a\rangle$, and Γ_{ab} is the decay constant. $|g\rangle$ denotes the electronic ground state, while $|m\rangle$ and $|n\rangle$ are intermediate states in the perturbation expansion. We note that the hyperpolarizability given in Eq. (1) of Higgins *et al.*⁵⁷ is the complex conjugate of the present definition.

To evaluate β_{pqr} in Eq. (S14), we calculated the transition dipole moments and the excitation energies by time-dependent DFT⁵⁹ using the B3LYP functional⁴⁷⁻⁴⁸ with the aug-cc-pVTZ basis set⁴⁹ for C, O, and N, and cc-pVTZ⁴⁹ for H. All matrix elements of the decay constants were set to $\Gamma_{ab} = 2000 \text{ cm}^{-1}$ based on the experimentally measured electronic spectrum.⁵⁷ We performed the summation over 100 electronically excited states to confirm convergence. The calculated β_{pqr} and the statistical samples of orientation D in Figure S17(c) were used to derive $\chi^{(2)}$ in Eq. (S13).

Figure S18 summarizes the hyperpolarizability calculated in the present study together with the previously reported results. Figures S18(a) and S18(b) show the two dominant elements of the molecular hyperpolarizability tensor, β_{zzz} and β_{xxx} , in the molecule-fixed coordinates, respectively. Between the present results (solid curves) and those obtained by Higgins *et al.* (dashed curves), the signs of the real parts agree while those of the imaginary parts are opposite to each other. This discrepancy originates from the different definitions of complex hyperpolarizability. Based on the hyperpolarizability tensor and the orientation, $\chi_{XXZ}^{(2)}$ was calculated using Eq. (S13) as shown in Figure S18(c). Our MD simulations based on the NO₂-down configuration predicted a positive imaginary $\chi^{(2)}$, which agrees with the experimental result obtained by Higgins *et al.* Thus, the orientation distribution of 4-NP determined in the present study explains the SHG result well. It is highly likely that the different conclusions by Higgins *et al.* originate from their confusion in the analysis of hyperpolarizability.

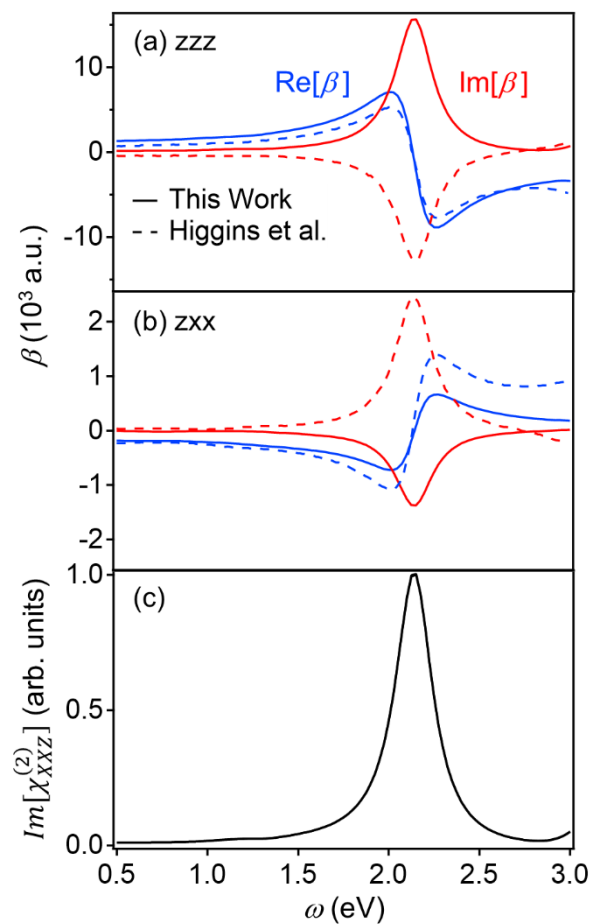


Figure S18. Hyperpolarizabilities (a) β_{zzz} and (b) β_{zxx} for 4-NP as functions of the input frequency ω . Solid lines are calculated using Eq. (S14) in the present work, and dashed lines are by Higgins *et al.*⁵⁷ (c) Imaginary spectrum $\text{Im}[\chi_{xxz}^{(2)}]$ calculated using Eq. (S13).

P. Rapid change in electrostatic potential at the interface

The theoretical ϕ values presented above exhibit unrealistic rapid oscillations even on a length scale smaller than a single molecule. This is because ϕ is obtained by integrating the Poisson equation over the assumed partial charges of solute and solvent molecules. However, EUV-PES is insensitive to such short-range changes in ϕ . Therefore, we present the effective ϕ values in Figures S14, S15, and S16 by averaging over the molecular scale. We observe that ϕ is possibly different for organic molecules segregated at the interface and the water molecules below them. This implies that different $\Delta\phi$ values may be obtained from the energy shifts of the PE bands for the solute and solvent molecules ($1b_1$ for water). Because the solute molecules are concentrated in the top molecular layer, their effect cannot be completely counteracted by the solvent molecules. However, the response of water molecules is highly effective in deeper regions. As seen in Figure 8 in the main text, for neutral organic solutes, the sign of $\Delta\phi$ is always the same for the solute and water molecules, although the magnitude is larger for the former.

References

- (1) Yamamoto, Y.; Yano, H.; Karashima, S.; Uenishi, R.; Orimo, N.; Nishitani, J.; Suzuki, T. Extreme Ultraviolet Laser Photoelectron Spectroscopy of Flat Liquid Jet Generated Using Microfluidic Device. *Bull. Chem. Soc. Jpn* **2023**, *96*, 938–942.
- (2) Li, R.; Ashgriz, N. Characteristics of Liquid Sheets Formed by Two Impinging Jets. *Phys. Fluids* **2006**, *18* (8), 087104.
- (3) Kurahashi, N.; Thürmer, S.; Liu, S. Y.; Yamamoto, Y.; Karashima, S.; Bhattacharya, A.; Ogi, Y.; Horio, T.; Suzuki, T. Design and Characterization of a Magnetic Bottle Electron Spectrometer for Time-Resolved Extreme UV and X-Ray Photoemission Spectroscopy of Liquid Microjets. *Struct. Dyn.* **2021**, *8* (3), 034303.
- (4) O'Neal, J. T. Tracking Charge Migration with Attosecond X-Ray Pulses from a Free-Electron Laser. Dissertation, Stanford University, United States California, 2022.
- (5) Hayashi, H.; Hiraoka, N. Accurate Measurements of Dielectric and Optical Functions of Liquid Water and Liquid Benzene in the VUV Region (1–100 eV) Using Small-Angle Inelastic X-ray Scattering. *J. Phys. Chem. B* **2015**, *119* (17), 5609–5623.
- (6) Hayashi, H.; Watanabe, N.; Udagawa, Y.; Kao, C. C. The Complete Optical Spectrum of Liquid Water Measured by Inelastic X-Ray Scattering. *Proc. Natl. Acad. Sci. USA* **2000**, *97* (12), 6264–6266.
- (7) Yoshino, K.; Tanaka, Y. Absorption Spectrum of Krypton in the Vacuum UV Region. *J. Opt. Soc. Am.* **1979**, *69* (1), 159–165.
- (8) Haynes, W. M.; Lide, D. R.; Bruno, T. J. *CRC Handbook of Chemistry and Physics*. 91st Ed.; CRC Press: Boca Raton, Florida, 2010.
- (9) Cahen, D.; Kahn, A. Electron Energetics at Surfaces and Interfaces: Concepts and Experiments. *Adv. Mater.* **2003**, *15* (4), 271–277.
- (10) Helander, M. G.; Greiner, M. T.; Wang, Z. B.; Lu, Z. H. Pitfalls in Measuring Work Function Using Photoelectron Spectroscopy. *Appl. Surf. Sci.* **2010**, *256* (8), 2602–2605.
- (11) Thürmer, S.; Malerz, S.; Trinter, F.; Hergenhausen, U.; Lee, C.; Neumark, D. M.; Meijer, G.; Winter, B.; Wilkinson, I. Accurate Vertical Ionization Energy and Work Function Determinations of Liquid Water and Aqueous Solutions. *Chem. Sci.* **2021**, *12* (31), 10558–10582.
- (12) Yamamoto, Y.; Suzuki, T. Distortion Correction of Low-Energy Photoelectron Spectra of Liquids Using Spectroscopic Data for Solvated Electrons. *J. Phys. Chem. A* **2023**, *127* (11), 2440–2452.
- (13) Abdulrazzaq, O.; Bourdo, S. E.; Saini, V.; Watanabe, F.; Barnes, B.; Ghosh, A.; Biris, A. S. Tuning the Work Function of Polyaniline via Camphor-sulfonic Acid: an X-Ray Photoelectron Spectroscopy Investigation. *RSC Adv.* **2015**, *5* (1), 33–40.
- (14) Thürmer, S.; Shinno, T.; Suzuki, T. Valence Photoelectron Spectra of Liquid Methanol and Ethanol Measured Using He II Radiation. *J. Phys. Chem. A* **2021**, *125* (12), 2492–2503.
- (15) Credidio, B.; Pugini, M.; Malerz, S.; Trinter, F.; Hergenhausen, U.; Wilkinson, I.; Thürmer, S.; Winter, B. Quantitative Electronic Structure and Work-Function Changes of Liquid Water Induced by Solute. *Phys. Chem. Chem. Phys.* **2022**, *24* (3), 1310–1325.
- (16) Kurahashi, N.; Karashima, S.; Tang, Y.; Horio, T.; Abulimiti, B.; Suzuki, Y. I.; Ogi, Y.; Oura, M.; Suzuki, T. Photoelectron Spectroscopy of Aqueous Solutions: Streaming Potentials of NaX (X = Cl, Br, and I) Solutions and Electron Binding Energies of Liquid Water and X⁻. *J. Chem. Phys.* **2014**, *140* (17), 174506.
- (17) Nishizawa, K.; Kurahashi, N.; Sekiguchi, K.; Mizuno, T.; Ogi, Y.; Horio, T.; Oura, M.; Kosugi, N.; Suzuki, T. High-Resolution Soft X-Ray Photoelectron Spectroscopy of Liquid Water. *Phys. Chem. Chem. Phys.* **2011**, *13* (2), 413–417.
- (18) Buttersack, T.; Haak, H.; Bluhm, H.; Hergenhausen, U.; Meijer, G.; Winter, B. Imaging Temperature and Thickness of Thin Planar Liquid Water Jets in Vacuum. *Struct. Dyn.* **2023**, *10* (3), 034901.
- (19) Chang, Y.-P.; Yin, Z.; Balciunas, T.; Wörner, H. J.; Wolf, J.-P. Temperature Measurements of Liquid Flat Jets in Vacuum. *Struct. Dyn.* **2022**, *9* (1), 014901.
- (20) Knudsen, M.; Partington, J. R. The Kinetic Theory of Gases. Some Modern Aspects. *J. Phys. Chem.* **1935**, *39* (2), 307–307.
- (21) Persad, A. H.; Ward, C. A. Expressions for the Evaporation and Condensation Coefficients in the Hertz-Knudsen Relation. *Chem. Rev.* **2016**, *116* (14), 7727–7767.
- (22) Hasson, D.; Peck, R. E. Thickness Distribution in a Sheet Formed by Impinging Jets. *AIChE J.* **1964**, *10* (5), 752–754.
- (23) Atkins, P. W.; Paula, J. D. *Physical Chemistry*. 8th Ed.; W. H. Freeman: 2006; Vol. 1.
- (24) Chase, M. W., Jr. NIST-JANAF Thermochemical Tables, Fourth Edition. *J. Phys. Chem. Ref. Data* **1998**, *Monograph 9*, 1–1951.
- (25) Lemmon, E. W.; Bell, I. H.; Huber, M. L.; McLinden, M. O., Thermophysical Properties of Fluid Systems. In *NIST Chemistry WebBook*, National Institute of Standards and Technology: Gaithersburg MD, 20899, Vol. NIST Standard Reference Database Number 69.
- (26) Bolton, P. D.; Hall, F. M.; Reece, I. H. Thermodynamic Ionization Constants of p-Halogenophenols from Spectrophotometric Measurements. *Spectrochim. Acta* **1966**, *22* (6), 1149–1155.
- (27) Bolton, P.; Hall, F. Thermodynamic Functions of Ionization of the Anilinium and Toluidinium Ions. *Aust. J. Chem.* **1967**, *20* (9), 1797–1804.
- (28) Allen, G. F.; Robinson, R. A.; Bower, V. E. The Ionization Constant of p-Nitrophenol from 0 to 60°. *J. Phys. Chem.* **1962**, *66* (1), 171–172.
- (29) West, C. W.; Nishitani, J.; Higashimura, C.; Suzuki, T. Extreme Ultraviolet Time-Resolved Photoelectron Spectroscopy of Aqueous Aniline Solution: Enhanced Surface Concentration and Pump-Induced Space Charge Effect. *Mol. Phys.* **2021**, *119* (1–2), e1748240.
- (30) Chatteraj, D. K.; Birdi, K. S. *Adsorption and the Gibbs Surface Excess*. 1st Ed.; Springer: New York, NY, 1984.
- (31) Richter, C.; Dupuy, R.; Trinter, F.; Buttersack, T.; Cablit, L.; Gholami, S.; Stemer, D.; Nicolas, C.; Seidel, R.; Winter, B.; Bluhm, H. Surface Accumulation and Acid–Base Equilibrium of Phenol at the Liquid–Vapor Interface. *Phys. Chem. Chem. Phys.* **2024**, *26*, 27292–27300.
- (32) Tamburello-Luca, A. A.; Hebert, P.; Brevet, P. F.; Girault, H. H. Resonant-Surface Second-Harmonic Generation Studies of Phenol Derivatives at Air/Water and Hexane/Water Interfaces. *J. Chem. Soc. Faraday Trans.* **1996**, *92* (17), 3079–3085.
- (33) Jungwirth, P.; Tobias, D. J. Specific Ion Effects at the Air/Water Interface. *Chem. Rev.* **2006**, *106* (4), 1259–1281.
- (34) Berendsen, H. J. C.; Grigera, J. R.; Straatsma, T. P. The Missing Term in Effective Pair Potentials. *J. Phys. Chem.* **1987**, *91*, 6269–6271.
- (35) Abascal, J. L.; Vega, C. A General Purpose Model for the Condensed Phases of Water: TIP4P/2005. *J. Chem. Phys.* **2005**, *123* (23), 234505.
- (36) Wang, J.; Wolf, R. M.; Caldwell, J. W.; Kollman, P. A.; Case, D. A. Development and Testing of a General Amber Force Field. *J. Comput. Chem.* **2004**, *25*, 1157–1174.
- (37) Bayly, C. I.; Cieplak, P.; Cornell, W. D.; Kollman, P. A. A Well-Behaved Electrostatic Potential Based Method Using Charge Restraints for Deriving Atomic Charges: The RESP Model. *J. Phys. Chem.* **1993**, *97*, 10269–10280.
- (38) Joung, I. S.; Thomas E. Cheatham, I. Determination of Alkali and Halide Monovalent Ion Parameters for Use in Explicitly Solvated Biomolecular Simulations. *J. Phys. Chem. B* **2008**, *112*, 9020–9041.
- (39) Martinez, L.; Andrade, R.; Birgin, E. G.; Martinez, J. M. PACKMOL: A Package for Building Initial Configurations for Molecular Dynamics Simulations. *J. Comput. Chem.* **2009**, *30* (13), 2157–2164.
- (40) Allen, M. P.; Tildesley, D. J. *Computer Simulation of Liquids*. Clarendon Press: Oxford, 1987.
- (41) Hess, B.; Bekker, H.; Berendsen, H. J. C.; Fraaije, J. G. E. M. LINCS: A Linear Constraint Solver for Molecular Simulations. *J. Comput. Chem.* **1997**, *18*, 1463–1472.
- (42) Nosé, S. A Unified Formulation of the Constant Temperature Molecular Dynamics Methods. *J. Chem. Phys.* **1984**, *81*, 511–519.
- (43) Hoover, W. G. Canonical Dynamics: Equilibrium Phase-Space Distributions. *Phys. Rev. A* **1985**, *31* (3), 1695–1697.

- (44) Darden, T.; York, D.; Pedersen, L. Particle Mesh Ewald: An $N \cdot \log(N)$ method for Ewald Sums in Large Systems. *J. Chem. Phys.* **1993**, *98* (12), 10089–10092.
 - (45) Perera, L.; Essmann, U.; Berkowitz, M. L. Effect of the Treatment of Long-Range Forces on the Dynamics of Ions in Aqueous Solutions. *J. Chem. Phys.* **1995**, *102*, 450–456.
 - (46) Van Der Spoel, D.; Lindahl, E.; Hess, B.; Groenhof, G.; Mark, A. E.; Berendsen, H. J. GROMACS: Fast, Flexible, and Free. *J. Comput. Chem.* **2005**, *26* (16), 1701–1718.
 - (47) Becke, A. D. Density-Functional Thermochemistry. III. The Role of Exact Exchange. *J. Chem. Phys.* **1993**, *98* (7), 5648–5652.
 - (48) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti Correlation-Energy Formula into a Functional of the Electron Density. *Phys. Rev. B* **1988**, *37* (2), 785–789.
 - (49) Dunning, T. H. Gaussian-Basis Sets for Use in Correlated Molecular Calculations. I. The Atoms Boron through Neon and Hydrogen. *J. Chem. Phys.* **1989**, *90* (2), 1007–1023.
 - (50) Tuckerman, M.; Berne, B. J.; Martyna, G. J. Reversible Multiple Time Scale Molecular Dynamics. *J. Chem. Phys.* **1992**, *97* (3), 1990–2001.
 - (51) Nosé, S. A Molecular Dynamics Method for Simulations in the Canonical Ensemble. *Mol. Phys.* **1984**, *52* (2), 255–268.
 - (52) Ishiyama, T.; Morita, A. Analysis of Anisotropic Local Field in Sum Frequency Generation Spectroscopy with the Charge Response Kernel Water Model. *J. Chem. Phys.* **2009**, *131* (24), 244714.
 - (53) Imamura, T.; Mizukoshi, Y.; Ishiyama, T.; Morita, A. Surface Structures of NaF and Na₂SO₄ Aqueous Solutions: Specific Effects of Hard Ions on Surface Vibrational Spectra. *J. Phys. Chem. C* **2012**, *116* (20), 11082–11090.
 - (54) Andersen, H. C. Rattle: A "Velocity" Version of the Shake Algorithm for Molecular Dynamics Calculations. *J. Comput. Phys.* **1983**, *52* (1), 24–34.
 - (55) Ishihara, T.; Ishiyama, T.; Morita, A. Surface Structure of Methanol/Water Solutions via Sum Frequency Orientational Analysis and Molecular Dynamics Simulation. *J. Phys. Chem. C* **2015**, *119* (18), 9879–9889.
 - (56) Saito, K.; Peng, Q.; Qiao, L.; Wang, L.; Joutsuka, T.; Ishiyama, T.; Ye, S.; Morita, A. Theoretical and Experimental Examination of SFG Polarization Analysis at Acetonitrile-Water Solution Surfaces. *Phys. Chem. Chem. Phys.* **2017**, *19*, 8941–8961.
 - (57) Higgins, D. A.; Abrams, M. B.; Byerly, S. K.; Corn, R. M. Resonant Second Harmonic Generation Studies of p-Nitrophenol Adsorption at Condensed-Phase Interfaces. *Langmuir* **1992**, *8* (8), 1994–2000.
 - (58) Morita, A. *Theory of Sum Frequency Generation Spectroscopy*. 1st Ed.; Springer Singapore: 2018.
 - (59) Casida, M. E.; Jamorski, C.; Casida, K. C.; Salahub, D. R. Molecular Excitation Energies to High-Lying Bound States from Time-Dependent Density-Functional Response Theory: Characterization and Correction of the Time-Dependent Local Density Approximation Ionization Threshold. *J. Chem. Phys.* **1998**, *108* (11), 4439–4449.
-