Direct Observation of Adsorption Morphologies of Cationic Surfactants at the Gold Metal-Liquid Interface

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1.	Synthesis and purification of alkylbenzyldimethylammonium bromide (Quats)	S1
2.	Sample preparation	S1
3.	SFG theory	S2
4.	Data acquisition	S3
5.	Fitting equation	
6.	Fitting parameters for C4 Quat in D ₂ O at liquid-solid interface	S5
7.	Fitting parameters for C12 Quat in D ₂ O at liquid-solid interface	S6
8.	Supporting SFG spectra	S7
9.	Peak assignment of C4 and C12 Quats	S8
10.	Simulation details	S9
11.	References	S14

1. Synthesis and purification of alkylbenzyldimethylammonium bromide (Quats)

Alkylbenzyldimethylammonium bromides containing two different alkyl tail lengths butyl (C4), and dodecyl (C12) were synthesized using established methods.¹⁻² Equimolar N, Ndimethylbenzylamine, respective bromoalkane, and acetonitrile solvent were added into the threenecked round-bottom flask. After that, the solution was heated to a reflux temperature of 82°C for 24 hours. The synthesized products were purified by recrystallization process with deionized water. The structure and the purity of Quats were confirmed by ¹H-NMR spectra with their corresponding purity values available in earlier publications.²⁻³

2. Sample Preparation

A 1 cm x 1 cm gold thin film on a silicon substrate (99.999% Au, 1000 Å thick from Sigma Aldrich, St. Louis MO) was cleaned with ethanol and dried with nitrogen gas. The cleaning procedure was followed by plasma cleaning to remove any impurities and surface contaminants. The freshly prepared Quat solution (\sim 5 ml) in D₂O was injected into the Teflon sample cell (**Figure S1**) containing the gold thin film substrate. Both visible and IR beams were temporally and spatially overlapped at the liquid-gold metal interface to generate the SFG signal.



Figure S1. Cross-sectional cartoon of the liquid-solid sample cell. The cell contains an inlet, an outlet, a fused silica window that helps seal the cell, a Teflon spacer (~254 μ m), and a sample holder with an adjustable height to maintain an exact volume of the deuterated aqueous solution between the window and the metal surface.

3. SFG Theory

The SFG signal (ω_{SF}) generates with the temporal and spatial overlaps of broadband IR beam (ω_{IR}) and a narrowband visible beam (ω_{VIS}) at the interface.²⁻³

$$\omega_{SF} = \omega_{VIS} + \omega_{IR} \tag{1}$$

The efficiency of the SFG process is directly related to the second-order nonlinear effective susceptibility $\chi_{eff}^{(2)}$, the combination of both resonant susceptibility, $\chi_{R}^{(2)}$, and the nonresonant susceptibility, $\chi_{NR}^{(2)}$.

$$\chi_{eff}^{(2)} = \chi_R^{(2)} + \chi_{NR}^{(2)} \tag{2}$$

The nonresonant term, $\chi_{NR}^{(2)}$, depends on the substrate surface of solid and is almost negligible for liquid and dielectric surfaces.³ When the frequency of the incident IR beam is in resonance with the vibrational modes of adsorbed molecules at the interface, the resonant term, $\chi_{R}^{(2)}$, becomes large and contributes in intensity of the SFG signal.⁴⁻⁵

All the SFG spectra were collected either ssp or ppp polarization combinations. Herein, (s) and (p) refer to incident beam perpendicular and parallel to the plane of incidence, respectively.³ The ssp

indicates the SFG beam is (s) polarized, visible beam is (s) polarized, and the IR beam is (p) polarized as the order of decreasing energy and ppp indicates all three beams are (p) polarized.²

4. Data Acquisition

SFG spectra were acquired at the CH region centered at 2900 cm⁻¹ with ssp and ppp polarization combinations. Each spectrum was collected for 9 minutes and corrected for background, smoothed, and fitted with Lorentzian line shape equation shown below.²⁻³ The fitting results are available in Table S1 and Table S2. The average tilt angle values of methyl (CH₃) terminal group were estimated from the fitted data.²

5. Fitting equation

The analysis of each polarization combination and the line broadening were considered by the following Lorentzian line shape equation.²⁻³

$$I_{SFG} \propto \left|\chi^{(2)}\right|^2 \propto \left|\sum_q \frac{N\langle\beta^{(2)}\rangle}{(\omega_{IR} - \omega_q + i\Gamma_q)} + \left|\chi^{(2)}_{NR}\right|e^{i\rho}\right|^2$$
(3)

Where ρ is the phase of the nonresonant response. The nonresonant contribution from the gold substrate and the Gaussian equation are both included in the fitting equation to account for the mid-infrared beam's broadband pulse width. The simplified version of the fitting equation that accounts for the CH vibrational modes are presented below.

$$I_{SFG}\left(\omega+\omega_{vis}\right) \propto exp\left[-\frac{(\omega-\omega_{IR}^{L})^{2}}{2(\delta\omega_{L})^{2}}\right] \times \left|\sum_{q}\frac{A_{q}}{\omega_{IR}-\omega_{q}+i\Gamma_{q}}+A_{NR}e^{i\rho}\right|^{2}$$
(4)

The Gaussian curve equation is defined with the spectral width $\delta \omega_L$ centered at ω_{IR}^L . The spectral width $\delta \omega_L$ centered at ω_{IR}^L is included in the Gaussian function. The amplitude factors, A_q and A_{NR} , are proportional to the molecular hyperpolarizabilities as shown above in equation 4.²⁻³

Parameters	meters SSP		Parameters	PPP	
	Estimated	Standard		Estimated	Standard
	Value	Error		Value	Error
A1	50	36.2	A1	78.8	6.7
A2	50	32.5	A2	195	9.7
A3	174.5	9.9	A3	5.2 x 10 ⁻⁸	44.87
A4	20	5.3	A4	60	5.7
F1	13.3	9.5	F1	7.6	0.8
F2	10	3.8	F2	8	0.3
F3	7.5	0.2	F3	59.4	1.1 x 10 ⁹
F4	7.9	1.7	F4	5	0.6
ω1	2865	6.2	ω1	2873.1	0.5
ω2	2885	2.1	ω2	2916.2	0.2
ω3	2907.4	0.1	ω3	2950.5	0.006
ω4	2951	0.9	ω4	2972	3.8 x 10 ⁹
n	6.2	0.4	n	8.2	0.8
Р	-0.05	0.1	Р	4.4	0.04
n1	176.1`	3.2	n1	272.1	9.0
R ²	0.96		R ²	0.96	

Table S1: Fitting parameters for C4 Quat in D₂O at liquid-solid interface.^{2-3, 6}

Parameters	ameters SSP		Parameters	PPP	
	Estimated	Standard		Estimated	Standard
	Value	Error		Value	Error
A1	1.5 x 10 ⁻⁶	1.6	A1	229.2	0.1
A2	210.9	0.2	A2	0	0.2
A3	1.4 x 10 ⁻⁶	1.9	A3	19.5	0.07
A4	131.4	0.1	A4	144.3	0.1
F1	61.9	3.6 x 10 ⁶	F1	6.8	0.002
F2	8.9	0.007	F2	9.9	1.6 x 10 ⁻¹⁶
F3	74.1	2.5 x 10 ⁶	F3	1.9	0.009
F4	7.7	0.007	F4	5.5	0.003
ω1	2859.9	2.9 x 10 ⁷	ω1	2882	0.002
ω2	2882.4	0.005	ω2	2920	2.7 x 10 ⁻¹⁷
ω3	2909.9	3.1 x 10 ⁷	ω3	2943.9	0.006
ω4	2945.5	0.006	ω4	2968.5	0.003
n	10.20	0.01	n	4.6	0.01
Р	-0.9	0.001	Р	-1.1	0.001
n1	188.1`	0.15	n1	282.6	0.0997
R ²	0.96		R ²	0.94	

Table S2: Fitting parameters for C12 Quat in D₂O at liquid-solid interface.^{2-3, 6}



Figure S2. ssp and ppp SFG spectra of a C12 quat acquired at different delays.

Table S3. Peak assignments from the fitted SFG spectra of C4 Quat at ssp and ppp polarization

 combinations.

Peak assignments	ssp wavenumber cm ⁻¹	ppp wavenumber cm ⁻¹
Methylene symmetric stretch (CH ₂ SS) $^{2-3, 7-8}$	~2860	-
Methyl symmetric stretch (CH ₃ SS) ^{2-3, 7-8}	~2885	~2880
Methylene asymmetric stretch (CH ₂ AS) ⁹⁻¹⁰	~2907	~2917
Methyl symmetric stretch split by the Fermi resonance interaction with the methyl bending mode (CH ₃ FR) ^{8, 11}	~2951	-
Methyl asymmetric stretch (CH ₃ AS) ¹²	-	~2972

Table S4. Peak assignments from the fitted SFG spectra of C12 Quat at ssp and ppp polarization combinations.

Peak assignments	ssp wavenumber cm ⁻¹	ppp wavenumber cm ⁻¹
Methylene symmetric stretch $(CH_2 SS)^{2-3, 7-8}$	~2859	-
Methyl symmetric stretch (CH ₃ SS) ^{2-3, 7-8}	~2884	~2882
Methyl symmetric stretch split by the Fermi resonance	~2945	~2944
interaction with the methyl bending mode (CH ₃ FR) ^{8, 11}		
Methyl asymmetric stretch (CH ₃ AS) ¹²	-	~2968

Table S6. Orientation parameters were obtained from the simulation curves for the polarization intensity and amplitude ratios of CH₃ SS/CH₃ AS vibrational modes to estimate average tilt angles and distribution angles. The errors presented are calculated at the 95% CI.

C4 Quat		C12 Quat		
Average tilt	51°±13°	Average tilt	46°± 0.1°	
angle		angle		
Distribu	tion angles	Distribution angles		
$22^{\circ}\pm 2$ (for 60° tilt angle)		27°±0.03 (for 50° tilt angle)		
27°±3 (for 70	° tilt angle)	$34^{\circ}\pm0.04$ (for 60° tilt angle)		
29°±4 (for 80	° tilt angle)	$37^{\circ}\pm0.04$ (for 70° tilt angle)		
		$38^{\circ}\pm0.04$ (for 80° tilt angle)		

Simulation Details

The molecular dynamics (MD) simulation system comprised of 42 surfactant molecules, their counter-ions, and 1502 water molecules near a metal slab. The simulation box was 34.62 Å x 34.98 Å x 80 Å in dimensions and was periodic in the X and Y directions. The Z-direction was non-periodic because of the presence of a metal slab at one side (spanning from Z = 0 Å to Z = 11.78 Å) of the simulation box. The metal slab comprised of six layers of gold atoms arranged in (111) planes of face-centered cubic (fcc) crystal structure, with a lattice constant of 4.08 Å. The aqueous medium extended up to ~60 Å in the Z direction. Simulations were performed at a temperature, T = 300 K in the isothermal-isochoric (NVT) ensemble. A vacuum space of ~20 Å was kept beyond the aqueous column so that the system pressure is maintained at the equilibrium vapor pressure at T = 300 K.¹³ The face of the simulation box opposite of the metal slab had an athermal surface to prevent molecules from leaving the box.

Partial charges on the surfactant molecules were determined by performing density functional theory (DFT) calculations on the Gaussian 16 program.¹⁴ DFT calculations were performed by employing B3LYP hybrid functional with 6-31G(d,p) basis set and water as the implicit solvent. Interactions of surfactant molecules were modeled using the general AMBER force field (GAFF), which is a widely used force field for organic molecules.¹⁵ The quat molecules are protonated and carry a charge of +1. Bromide ions were introduced as the counter-ions to keep the entire system charge neutral. Interaction parameters of bromide ions were obtained from the Joung-Cheatham's model.¹⁶ Water was modeled via the extended simple point charge (SPC/E) model.¹⁷ The parameters for gold atoms were obtained from the interface force field developed by Heinz and co-workers, a force field that is compatible with GAFF.¹⁸ The Lennard-Jones and shortrange Coulombic interactions were cut-off at a distance of 10 Å. Long-range Coulombic

interactions were computed using the particle-particle particle-mesh (PPPM) method. All MD simulations were performed using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS).¹⁹



Figure S3. Snapshots of configuration of (a) C4 molecules, and (b) C12 molecules at t = 0 ns.



Figure S4. Tilt angle distribution of terminal methyl groups with respect to the surface normal. The angle is measured between the terminal CH₂-CH₃ vector and the surface normal. The distribution is plotted for the adsorbed molecules whose tilt angle lies within 90° with the surface normal. The average value of tilt angles was found to be $59.3^{\circ} \pm 1.4^{\circ}$ for C4 Quat molecules and $52.1^{\circ} \pm 1.0^{\circ}$ for C12 Quat molecules.



Figure S5. Distribution for intra-molecular orientation of alkyl tails with respect to the normal vector of the aromatic rings of adsorbed C4 and C12 Quat molecules. A value close to 90° implies that the molecule is not bent with respect to its bulk phase conformation (kindly also refer to Figure S6). A broad distribution from 0° to 45° in this figure shows that a good fraction of the adsorbed molecules are bent such that their alkyl tails are not aligned parallel to the plane of their aromatic rings.



Figure S6. Distribution for intra-molecular orientation of alkyl tails with respect to the normal vector to the aromatic rings of (A) C4 molecules, and (B) C12 molecules in the bulk aqueous phase. A peak close to 90° shows that the molecules in the bulk aqueous phase have their alkyl tails aligned parallel to the plane of their aromatic rings. Some error bars are smaller than the size of the markers.



Figure S7. Distribution of nitrogens and terminal carbons (carbon atom of the terminal CH_3 groups) of adsorbed (A) C4 molecules, and (B) C12 molecules as a function of distance from the metal surface, ξ . The location of the peaks shows that unlike C4 molecules, C12 molecules mostly stand-up on the surface.



Figure S8. Density profile of water as a function of distance from the gold surface, ξ in presence of adsorbed (A) C4 molecules, and (B) C12 molecules. The bulk density in (A) is less than 1 g/cc

because of the presence of unadsorbed C4 molecules in the bulk aqueous phase (refer Figure 4 of main text).



Figure S9. Density profile of water as a function of distance from the gold surface, ξ in absence of surfactant molecules in the system. Adapted with permission from Singh and Sharma.²⁰ Copyright (2020) American Chemical Society.



Figure S10. Distribution of orientation of (A) alkyl tails, and (B) normal vector of the aromatic rings with respect to the surface normal of adsorbed C12 molecules, in the simulation box of size $49.05 \text{ Å} \times 49.97 \text{ Å} \times 80 \text{ Å}$ consisting of 81 C12 molecules. The profiles obtained in this simulation system are similar to the profiles observed in Figure 5 (main text) thus confirming the absence of finite size effects on our simulation results. Inset in (A) shows the configuration of the system after t=150 ns of simulation. Error bars in (B) are smaller than the size of the markers.

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