

## Supporting information

### Specific Counter-cation Effect on the Molecular Orientation of Thiocyanate Anions at the Aqueous Solution Interfaces

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#### 1. SFG data and orientation analysis

The theoretical data analysis of SFG spectra generated from the air/liquid interface has been described elsewhere.<sup>1</sup> The SFG intensity  $I(\omega)$  can be expressed as a function of the second order susceptibility<sup>2-4</sup>

$$I(\omega) = \frac{8\pi^3 \omega^2 \sec^2 \beta}{c_0^3 n_1(\omega) n_1(\omega_1) n_1(\omega_2)} |\chi_{eff}^{(2)}|^2 I(\omega_1) I(\omega_2) \quad (1)$$

Where  $\omega$ ,  $\omega_1$ , and  $\omega_2$  are the frequencies of the SF signal, visible, and IR laser beam, respectively.  $n_1(\omega_i)$  is the refractive index of bulk medium  $i$  at the frequency of  $\omega_i$ ,  $I(\omega_i)$  is the intensity of the SFG signal or the input laser beams,  $c_0$  is the speed of light in vacuum,  $\beta_i$  is the incident or reflection angle of the  $i$ th light beams from the surface normal, which is defined as the  $z$  axis in the laboratory coordinates system ( $x, y, z$ ), and  $\chi_{eff}^{(2)}$  is the effective macroscopic second-order susceptibility.  $\chi_{eff}^{(2)}$  depends on the experimental geometry and polarizations. In the polarization dependent SFG

experiments, there are three typical polarization combinations commonly used in the SFG studies, namely, *ssp*, *sps* and *ppp*.  $\chi_{eff}^{(2)}$  under these three polarization combinations can be expressed as <sup>2, 4</sup>

$$\begin{aligned}
\chi_{eff,ssp}^{(2)} &= L_{yy}(\omega)L_{yy}(\omega_1)L_{zz}(\omega_2)\sin\beta_2\chi_{yyz} \\
\chi_{eff,sps}^{(2)} &= L_{yy}(\omega)L_{zz}(\omega_1)L_{yy}(\omega_2)\sin\beta_1\chi_{yzy} \\
\chi_{eff,ppp}^{(2)} &= +L_{zz}(\omega)L_{xx}(\omega_1)L_{xx}(\omega_2)\sin\beta\cos\beta_1\cos\beta_2\chi_{zxx} \\
&\quad - L_{xx}(\omega)L_{xx}(\omega_1)L_{zz}(\omega_2)\cos\beta\cos\beta_1\sin\beta_2\chi_{xxz} \\
&\quad - L_{xx}(\omega)L_{zz}(\omega_1)L_{xx}(\omega_2)\cos\beta\sin\beta_1\cos\beta_2\chi_{zxx} \\
&\quad + L_{zz}(\omega)L_{zz}(\omega_1)L_{zz}(\omega_2)\sin\beta\sin\beta_1\sin\beta_2\chi_{zzz}
\end{aligned} \tag{2}$$

where  $L_{ii}(\omega)$  is the tensorial Fresnel factor as shown below:

$$\begin{aligned}
L_{xx}(\omega) &= \frac{2n_1(\omega)\cos\gamma}{n_1(\omega)\cos\gamma + n_2(\omega)\cos\beta} \\
L_{yy}(\omega) &= \frac{2n_1(\omega)\cos\beta}{n_1(\omega)\cos\beta + n_2(\omega)\cos\gamma} \\
L_{zz}(\omega) &= \frac{2n_2(\omega)\cos\beta}{n_1(\omega)\cos\gamma + n_2(\omega)\cos\beta} \left( \frac{n_1(\omega)}{n'(\omega)} \right)^2
\end{aligned} \tag{3}$$

in which  $\gamma$  is the refracted angle and  $n'(\omega)$  is the effective refractive index of the interfacial layer. The macroscopic susceptibility tensors  $\chi_{ijk}^{(2)}$  are related to the microscopic hyperpolarizability tensor elements  $\beta_{ijk}^{(2)}$  in the molecular coordinates system through the ensemble average.

$$\chi_{ijk}^{(2)} = N_s \sum_{i'j'k'} \langle R_{ii'} R_{jj'} R_{kk'} \rangle \beta_{i'j'k'}^{(2)} \tag{4}$$

Here  $N_s$  is the number density of interfacial molecules. When the IR frequency is resonance to the molecular vibrational transitions, the second order molecular polarizability is described as the following

$$\beta^{(2)} = \beta_{NR}^{(2)} + \sum_q \frac{\beta_q^{(2)}}{\omega_{IR} - \omega_q + i\Gamma_q} \tag{5}$$

where  $\beta_{NR}^{(2)}$  is the non-resonant contribution,  $\beta_q^{(2)}$ ,  $\omega_q$ ,  $\Gamma_q$  are the strength factor tensor, resonant frequency and damping constant of the  $q$ th vibrational mode,

respectively. For  $\text{SCN}^-$  anion which can be treated as  $C_{\infty v}$  symmetry, the nonzero second-order hyperpolarizabilities are  $\beta_{aac} = \beta_{bbc}, \beta_{ccc}$ . Thus the macroscopic susceptibility tensors under three different polarizations can be given in the following

$$\begin{aligned}\chi_{xxz} = \chi_{yyz} &= \frac{1}{2} N_s \beta_{ccc} \left[ (1+r) \langle \cos \theta \rangle - (1-r) \langle \cos^3 \theta \rangle \right] \\ \chi_{xzx} = \chi_{zxx} = \chi_{yzy} = \chi_{zyy} &= \frac{1}{2} N_s \beta_{ccc} \left[ (1-r) \langle \cos \theta \rangle - \langle \cos^3 \theta \rangle \right] \\ \chi_{zzz} &= N_s \beta_{ccc} \left[ r \langle \cos \theta \rangle + (1-r) \langle \cos^3 \theta \rangle \right]\end{aligned}\quad (6)$$

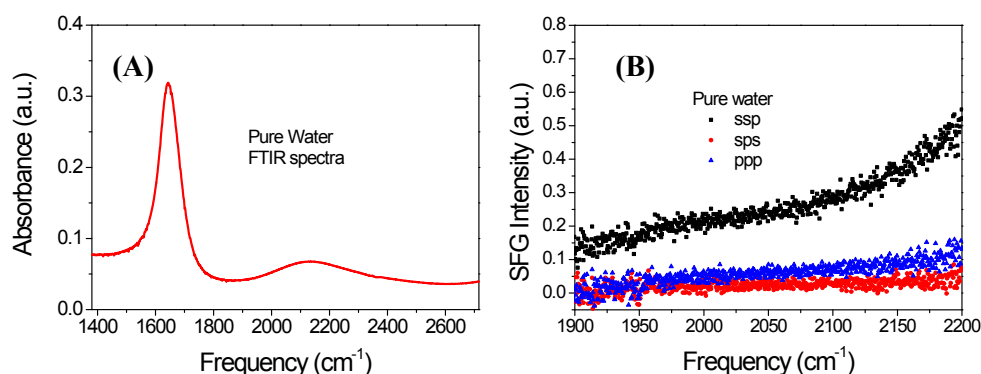
where  $r$  is the ratio of  $\beta_{aac} / \beta_{ccc}$ , which can be determined through the polarized Raman measurements.  $\theta$  is the tilt angle of  $\text{SCN}^-$  transition dipole (CN stretching) from the surface normal.

By using the SFG intensity ratio method, the orientational parameter  $D = \langle \cos \theta \rangle / \langle \cos^3 \theta \rangle$  can be determined. With orientational parameter  $D$  known, the relative number of  $\text{SCN}^-$  anions adsorbed at the air/water interface can be calculated from the following expression

$$I(\omega) \propto |\chi_{eff}|^2 \propto N_s^2 |r(\theta)|^2 \quad (7)$$

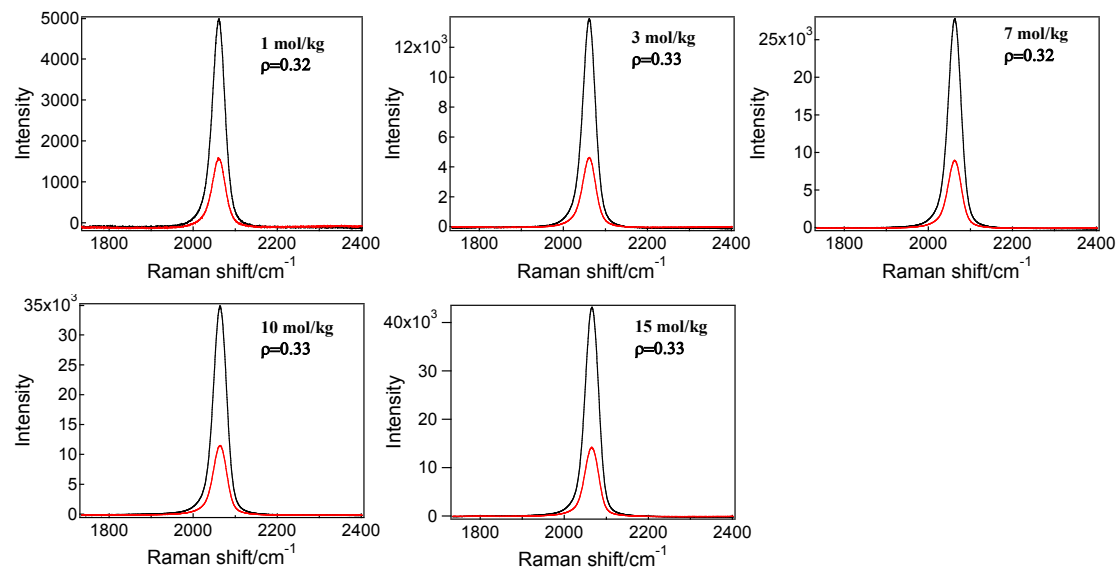
$r(\theta)$  is the orientational function related to the orientational parameter  $D$ .<sup>5, 6</sup> The SFG intensity is proportional to the product of the square of the surface density and the orientational function, and their contributions can be easily separated through the polarization SFG analysis.

## 2. Experimental results



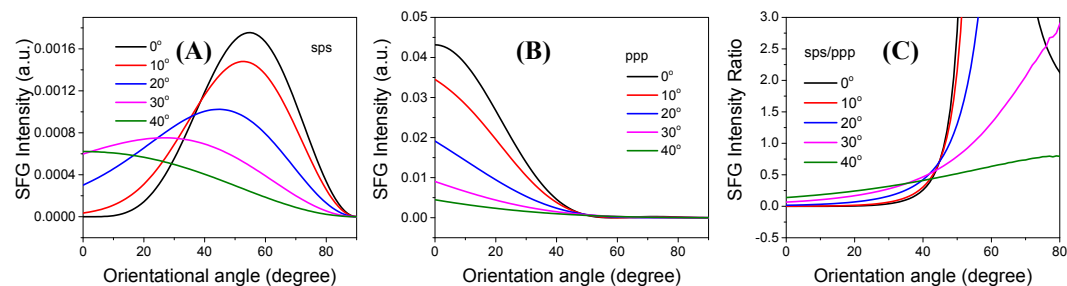
**Figure S1.** (A) FTIR spectra of pure water solution. The peak positioned at  $1650 \text{ cm}^{-1}$

is assigned to the OH bending stretch of water molecule. While the broad peak with the central frequency at  $2150\text{ cm}^{-1}$  is originated from the combination band of water molecule. (B) SFG spectra generated from air/ neat water interface under three different polarization combinations.

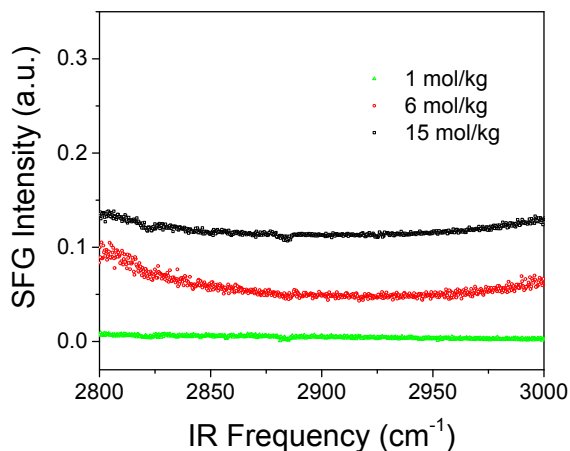


**Figure S2.** Polarized Raman spectra of NaSCN aqueous solution at different bulk concentrations. The value of depolarization ratio  $\rho$  of  $\text{SCN}^-$  anion is determined to be  $0.325 \pm 0.002$ . Therefore,  $r$  ( $\beta_{aac} / \beta_{ccc}$ ) can be calculated based on the equation of

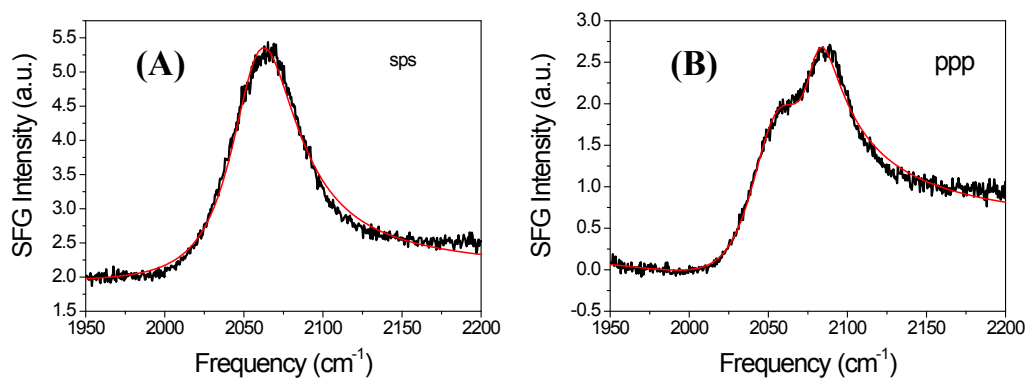
$$\rho = \frac{3}{4 + 5[(1 + 2r) / (1 - r)]^2},^7$$
 which is determined to be  $0.007 \pm 0.002$  by solving the equation.



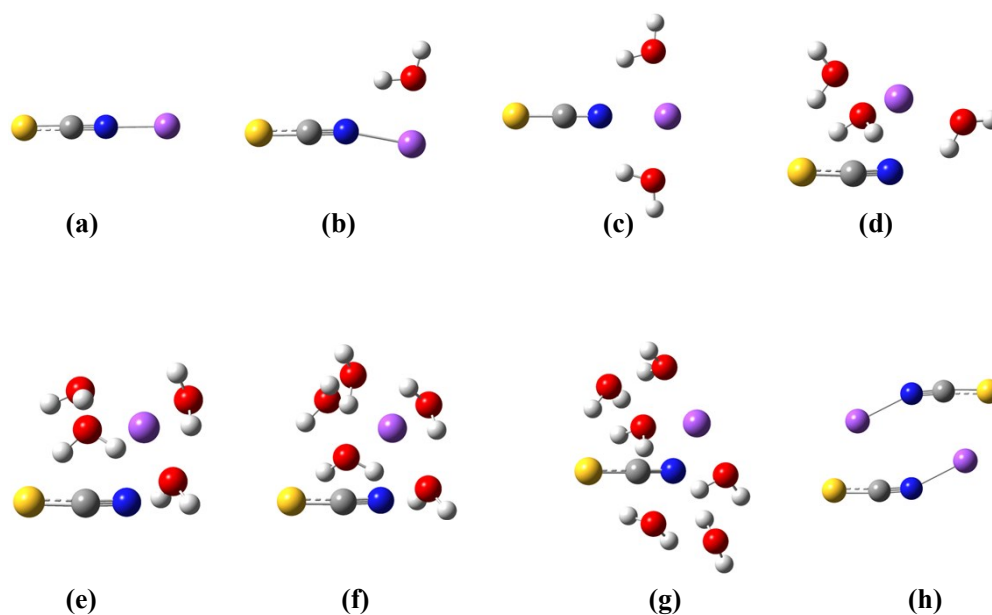
**Figure S3.** Simulated SFG intensities for (A) sps (B) ppp polarizations and (C) their ratio ( $I_{\text{sps}}/I_{\text{ppp}}$ ) for the air/1.0 mol/kg NaSCN aqueous solution interface with respect to the molecular orientation of  $\text{SCN}^-$  anion. The distribution width is considered with a Gaussian function.



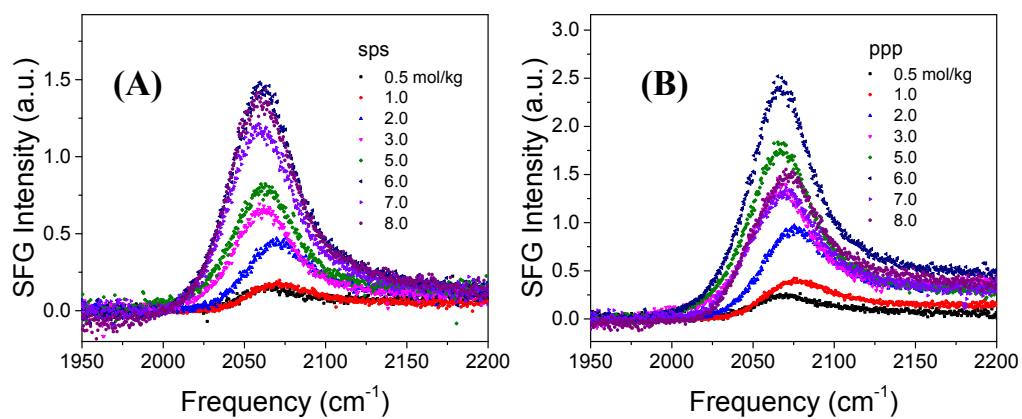
**Figure S4.** The ssp SFG spectra of the surface of the NaSCN aqueous solutions at three different concentrations in the 2800 to 3000  $\text{cm}^{-1}$  region. The SFG spectra for 6 mol/kg and 15 mol/kg NaSCN aqueous solutions have been offset for clarification.



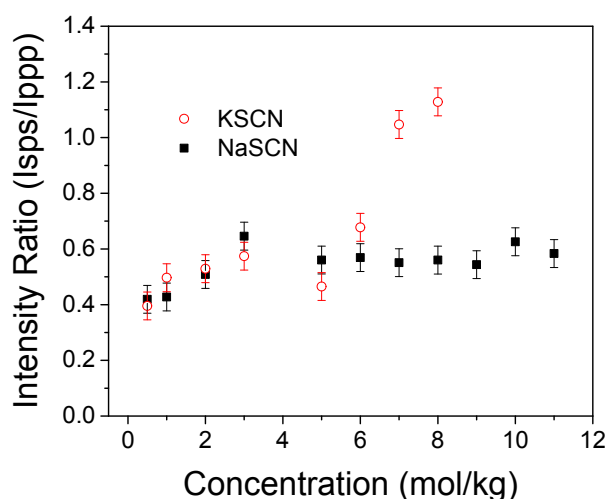
**Figure S5.** SFG spectra of the anti-symmetric stretch of the  $\text{SCN}^-$  anions adsorbed at the air/NaSCN aqueous solution interface under (A) sps and (B) ppp polarizations at the concentration of 15.0 mol/kg. The solid lines with red color are the fitting results. Fitting parameters are listed in Table S1.



**Figure S6.** Calculated structure of NaSCN and complex structure between NaSCN and water molecules in gas phase using DFT method.



**Figure S7.** Concentration-dependent SFG spectra of the anti-symmetric stretch of the  $\text{SCN}^-$  anions adsorbed at the air/KSCN aqueous solution surfaces with the polarization combinations controlled at (A) sps and (B) ppp.



**Figure S8.** The SFG intensity ratio  $I_{sps}/I_{ppp}$  for the NaSCN (solid square) and KSCN (open circle) solution interfaces with different bulk concentrations.

**Table S1.** Fitting results using Equation (5) for the SFG spectra of the CN stretching of the  $SCN^-$  at air/NaSCN aqueous solution interface under sps and ppp polarization combinations.

Concentration (mol/kg)	sps			ppp		
	$\beta_q$	$\omega_q$ (cm <sup>-1</sup> )	$\Gamma_q$ (cm <sup>-1</sup> )	$\beta_q$	$\omega_q$ (cm <sup>-1</sup> )	$\Gamma_q$ (cm <sup>-1</sup> )
0.5	4.480	2061.2	17.55	7.601	2064.7	21.08
1	7.673	2060.7	19.32	12.982	2067.9	23.06
2	12.843	2061.7	21.00	20.886	2065.9	24.36
3	18.261	2056.3	20.21	25.443	2060.8	22.73
5	28.251	2056.7	23.27	38.567	2061.0	24.51
6	31.164	2056.0	23.76	41.409	2061.2	24.03
7	32.186	2055.6	24.67	43.553	2060.8	25.05
8	32.476	2055.5	24.32	44.145	2060.7	24.96
9	25.820	2057.2	24.40	49.559	2061.4	25.54
10	38.410	2053.2	25.63	49.640	2058.3	26.38

11	40.648	2055.1	25.52	50.790	2059.1	24.83
13	39.067	2053.2	25.64	57.429	2059.4	25.86
15	45.944	2058.5	25.57	29.505	2050.2	25.65
					(peak1)	
				6.367	2079.3	12.60
					(peak2)	

**Table S2.** Calculated frequency of CN stretching mode in NaSCN and the complex structure between NaSCN and water molecules (shown in Figure S6) using different level of calculations. The calculation based on M06-2X level is more consistent with the experimental results.

Configuration	M06-2X (scaling factor=0.94)		B3lyp (scaling factor=0.96)	
	Calculated frequency (cm <sup>-1</sup> )	Corrected Frequency(cm <sup>-1</sup> )	Calculated frequency(cm <sup>-1</sup> )	Corrected Frequency(cm <sup>-1</sup> )
a	2171.9	2041.6	2160.0	2073.6
b	2157.3	2027.8	2146.3	2060.4
c	2152.5	2023.4	2136.4	2050.9
d	2223.4	2089.9	2201.2	2113.1
e	2158.3	2028.8	2140.5	2054.8
f	2175.0	2044.5	2153.7	2067.5
g	2203.3	2071.1	2184.3	2096.9
h	2228.5	2094.8	2210.0	2121.6

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