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Role of refractive index in sum frequency generation intensity of salt solution interfaces

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ABSTRACT

Sum frequency generation spectroscopy (SFG) has been widely used to study the interfacial chemistry of aqueous salt solutions of biological or environmental importance. Most of the SFG data analysis used the same bulk refractive index for different salt concentrations despite of the variations of the refractive indices. Here we systematically investigate the influence of the refractive index on the SFG intensities at various experimental conditions. It is discovered that the SFG intensities are the most sensitive to the refractive index at solid/liquid interfaces nearby the total internal reflection geometries. At air/liquid interfaces, the effect of the refractive indices is also nonegligible. Consequently some important SFG results, such as the response of water structures to the ionic strength at the SiO_2/aqueous interfaces, are necessary to be reevaluated. These conclusions on the effect of the small variations of the refractive index are generally useful for the common practice of SFG data analysis.

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1. Introduction

The interfacial chemistry of salt solutions plays important roles in numerous atmospheric, geochemical and biological processes. Simple inorganic ions can enhance the reactions of the gaseous molecules at the outmost layer of the aqueous salt particles [1], alter the electrostatic fields at the mineral surfaces [2,3], and regulate the secondary structures of the proteins [4]. Among the variety of surface analysis tools, sum frequency generation vibrational spectroscopy (SFG-VS) has drawn particular attentions owing to its intrinsic surface selectivity [3,5–11]. By comparing the SFG-VS spectra obtained before and after adding the salts, one can deduce the structures of the interfacial hydrogen bond network, the surface propensities of ions [7–10,12,13], and the nature of the electrical double layers near the charged surfaces [2,3,14,15].

With the growing number of SFG-VS studies on the salt solution interfaces, the quantitative interpretation of the spectra has become increasingly important. In the SFG-VS data analysis, the refractive indices are crucial parameters determining the magnitude of the local electric fields at the interfaces in relation to the incident laser fields [5,16]. Most previous SFG data treatments used a constant refractive index for different salt concentrations

because the refractive indices only vary by a few percentages when salt concentration increases [13]. However, in a recent report comparing the water structures at different solid/aqueous interfaces, it was demonstrated that the local electric field correction can sometimes differ significantly even with a small change of bulk refractive indices [15].

It is therefore necessary to examine the potential influence of refractive indices on the SFG intensity measurements in order to reevaluate the accuracy of the quantitative results. By simulating the local field corrections, we aim to generalize the circumstances under which the small variations of the refractive index can cause the significant impact on SFG-VS intensities. Different experimental scenarios, including the types of bulk media, the laser incident angles and polarizations, were considered. The effect of the IR dispersions has been thoroughly discussed in literature and will not be covered in this work [5,13,15,17]. The influence of refractive indices on the SFG-VS intensities as discussed here can be used as a rule of thumb for any other liquid mixtures of which the refractive index varies with the bulk concentrations.

2. Theoretical background

In a SFG-VS process, an infrared (IR) photon with the frequency of ω_{IR} is upconverted by a visible photon with the frequency of ω_{vis}, resulting in the emission of a new photon with the sum frequency $\omega_{SF} = \omega_{IR} + \omega_{vis}$. The SFG intensity is proportional to the square of

the effective second order susceptibility $\chi_{eff}^{(2)}$ $\left(I_{SF} \propto |\chi_{eff}^{(2)}|^2\right)$ [5,11,16], while $\chi_{eff}^{(2)}$ for an achiral and rotationally isotropic interface can be expressed by the macroscopic susceptibilities $\chi_{ijk}^{(2)}$ ($i = x, y, z$) through [5,16]:

$$\chi_{eff,ssp}^{(2)} = L_{yy}(\omega_{SF})L_{yy}(\omega_{vis})L_{zz}(\omega_{IR})sin\beta_{IR}\chi_{yyz}^{(2)} = F_{ssp}^{yyz}\chi_{yyz}^{(2)}$$

$$\chi_{eff,sps}^{(2)} = L_{yy}(\omega_{SF})L_{zz}(\omega_{vis})L_{yy}(\omega_{IR})sin\beta_{vis}\chi_{yzy}^{(2)} = F_{sps}^{yzy}\chi_{yzy}^{(2)}$$

$$\chi_{eff,pss}^{(2)} = L_{zz}(\omega_{SF})L_{yy}(\omega_{vis})L_{yy}(\omega_{IR})sin\beta_{SF}\chi_{zyy}^{(2)} = F_{pss}^{zyy}\chi_{zyy}^{(2)}$$

$$\chi_{eff,ppp}^{(2)} = -L_{xx}(\omega_{SF})L_{xx}(\omega_{vis})L_{zz}(\omega_{IR})cos\beta_{SF}cos\beta_{vis}sin\beta_{IR}\chi_{xxz}^{(2)}$$
$$-L_{xx}(\omega_{SF})L_{zz}(\omega_{vis})L_{xx}(\omega_{IR})cos\beta_{SF}sin\beta_{vis}cos\beta_{IR}\chi_{xzx}^{(2)}$$
$$+L_{zz}(\omega_{SF})L_{xx}(\omega_{vis})L_{xx}(\omega_{IR})sin\beta_{SF}cos\beta_{vis}cos\beta_{IR}\chi_{zxx}^{(2)}$$
$$+L_{zz}(\omega_{SF})L_{zz}(\omega_{vis})L_{zz}(\omega_{IR})sin\beta_{SF}sin\beta_{vis}sin\beta_{IR}\chi_{zzz}^{(2)}$$
$$= F_{ppp}^{xxz}\chi_{xxz}^{(2)} + F_{ppp}^{xzx}\chi_{xzx}^{(2)} + F_{ppp}^{zxx}\chi_{zxx}^{(2)} + F_{ppp}^{zzz}\chi_{zzz}^{(2)}$$

(1)

where the indices of ssp, sps, pss and ppp are defined by the polarizations in the order of the SFG, visible and IR beams; β_i is the incident angle against the surface normal. The L_{ii} ($i = x, y, z$) terms are the Fresnel factors for the local field corrections, which can be calculated with the knowledge of β_i and refractive indices n_1, n_2 and n'. Namely, n_1, n_2 and n' are for media 1 (the air or solids through which incident and SFG photons propagate), media 2 (the liquid phase), and the interfacial layer, respectively. The n' values were estimated by the modified Lorentz model [16]. Here we only consider the common experimental arrangements with the co-propagating laser configurations and the collection of the reflected SFG signals.

For the ease of discussions, we define a coefficient F^{ijk} to represent the product of all the Fresnel factors L_{ii} as well as the sines and cosines in front of the $\chi_{ijk}^{(2)}$ ($i, j, k = x, y, z$) term (Eq. (1)). The F^{ijk} coefficient carries all the information of the refractive indices, laser incident angles and polarizations. On the other hand, the molecular information is imbedded in the $\chi_{ijk}^{(2)}$ term, which is determined by the microscopic hyperpolarizability tensors and average tilting angles of the interfacial molecules and has nothing to do with the refractive indices [5,11,16].

3. Results and discussion

As shown in Eq. (1), the contributions from the refractive indices are all contained in the F^{ijk} coefficients and readily to be separated from the $\chi_{ijk}^{(2)}$ terms. Therefore, to find out whether it is necessary to correct the SFG intensity (I_{SF}) when the refractive indices change with the salt concentrations, one only needs to look into the dependence of F^{ijk} on n_2. In this context, we simulated F^{ijk} for both the typical air/liquid and solid/liquid interfaces. We used 5 mol/L NaCl solution as the model system of the salt solutions and compared the simulated F^{ijk} values (represented by F^{ijk} (NaCl)) with those for the pure water (represented by F^{ijk} (H$_2$O)). Since the refractive indices for the 5 mol/L NaCl solution are among the typical values for the concentrated aqueous salt solutions, the results obtained here can generally be used for other similar solutions.

Most of the SFG-VS studies explored the O–H stretching vibrations between 3000 and 3800 cm^{-1} [2,3,6–10,12–15,18]. Thus during the simulations we first chose the IR wavelength to be 3400 cm^{-1}, which is at the center of this vibrational region and nearby a typical SFG peak often assigned to the "liquid-like" water molecules [2,7]. The visible wavelength was chosen to be 532 nm, a commonly employed visible wavelength in the SFG experiments.

Since the IR refractive indices contain imaginary parts, F^{ijk} is a complex number. For the ssp, sps and pss polarizations, only one $\chi_{ijk}^{(2)}$ term is involved (Eq. (1)) [5,16]. Consequently the absolute values $|F^{yyz}|$ are sufficient enough to evaluate the changes of $|\chi_{eff}^{(2)}|$ as a function of n_2 in the ssp, sps and pss spectra. For the ppp polarization, the spectral shape is determined by the interference of four $\chi_{ijk}^{(2)}$ terms (Eq. (1)) [5]. Therefore the phase term in each of the four F^{ijk} factors plays a role in the ppp intensity and it is difficult to draw a general conclusion. But as discussed below, we still can obtain some qualitative predictions by simulating the individual $|F^{ijk}|$ for each of the four $\chi_{ijk}^{(2)}$ terms in the ppp polarizations.

We first considered the air/liquid interfaces. Fig. 1a and b illustrate the simulated $|F^{ijk}(H_2O)|$ and $|F^{ijk}(NaCl)|$ for the air/liquid interface as a function of the visible incident angle β_{vis}. During the simulation, the IR incident angle β_{IR} was fixed to 58°, which is in the range of the commonly used β_{IR} values. The F^{yyz} and F^{yzy} in Fig. 1a correspond to the ssp and sps polarizations, respectively, while the F^{xxz}, F^{xzx}, F^{zxx} and F^{zzz} in Fig. 1b are for the four independent $\chi_{ijk}^{(2)}$ terms in the ppp polarization. The pss polarization yields similar spectra as sps, therefore will not be discussed.

The change of n_2 caused by the increasing salt concentrations indeed plays an important role in the observed I_{SF}. Fig. 1a and b shows that $|F^{ijk}(H_2O)|$ is always larger than $|F^{ijk}(NaCl)|$ at the
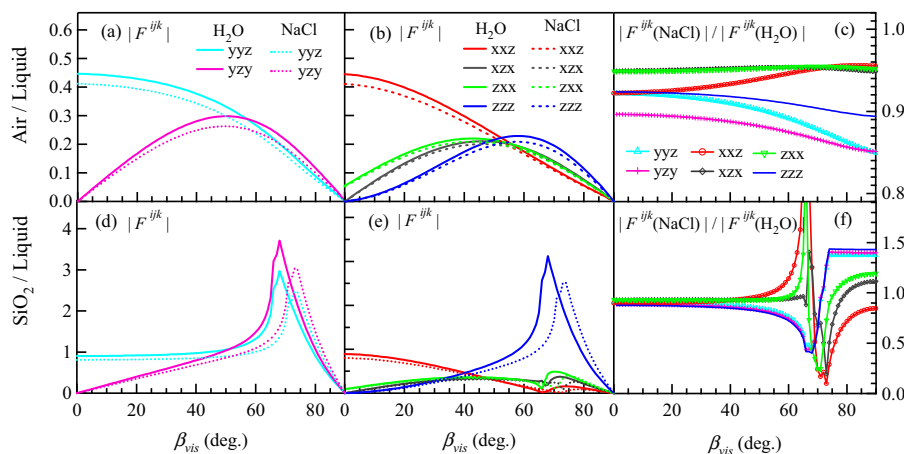

Fig. 1. The left and middle columns: $|F^{ijk}|$ as a function of β_{vis} at (a) and (b) the air/liquid interface; (d) and (e) the fused silica/liquid interface. The solid lines are for the pure water and the dotted lines are for the 5 mol/L NaCl solutions. The right columns: $|F^{ijk}(NaCl)|/|F^{ijk}(H_2O)|$ ratios vs. β_{vis} at (c) the air/liquid and (f) fused silica/liquid interfaces.