

Original article

Salt effect on molecular orientation at air/liquid methanol interface

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ABSTRACT

The salt effects on molecular orientation at air/liquid methanol interface were investigated by the polarization-dependent sum frequency generation vibrational spectroscopy (SFG-VS). We clarified that the average tilting angle of the methyl group to be $\theta = 30^\circ \pm 5^\circ$ at the air/pure methanol surface assuming a δ -function orientational distribution. Upon the addition of 3 mol/L NaI, the methyl group tilts further away from the surface normal with a new $\theta = 41^\circ \pm 3^\circ$. This orientational change does not explain the enhancement of the SFG-VS intensities when adding NaI, implying the number density of the methanol molecules with a net polar ordering in the surface region also changed with the NaI concentrations. These spectroscopic findings shed new light on the salt effects on the surface structures of the polar organic solutions. It was also shown that the accurate determination of the bulk refractive indices and Raman depolarization ratios for different salt concentrations is crucial to quantitatively interpret the SFG-VS data.

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1. Introduction

The salt effects on the interfacial properties of the polar liquids are of vital importance for many biological, environmental and industrial processes [1–3]. In the past decade, tremendous experimental and theoretical efforts have suggested the possible enrichment of the larger and more polarizable anions at aqueous surfaces, therefore challenging the traditional belief of inorganic ions being depleted from the air/water interface [2–6]. More recently, there has been a growing interest to extend these efforts to investigate the role of the simple inorganic ions at the air/liquid interfaces of polar nonaqueous solvents [3,7–12]. Methanol is one of the simplest and widely used polar organic solvents. It contains both a hydrophobic methyl group and a hydrophilic hydroxyl group, exhibiting the surfactant-like characteristics and weaker hydrogen bonding strength compared with water. Naturally it is interesting to examine whether the salt ions influence the molecular structures at the air/methanol interface in a different way compared with the air/water interface. In this context, several

molecular dynamics (MD) simulations have been carried out and predicted that the segregation of the large polarizable iodide anions at the air/liquid methanol interface is much less than that at the air/aqueous interface [7,10,11]. In a relevant experimental work, the amorphous solid methanol surface exposed to the CsI vapor was studied by the metastable impact electron spectroscopy [8]. But other than that, the experimental investigations of the ion effects on air/liquid methanol interface are still scarce.

Interfacial molecular orientations reflect the anisotropic nature of the intermolecular interactions in the surface region. It is closely related to other important interfacial properties such as the surface tension, viscosity and surface reactivity [13,14]. Here, we investigated the influence of the sodium iodide on the molecular orientations at the air/liquid methanol interface via sum frequency generation vibrational spectroscopy (SFG-VS). As a surface-selective optical probe [15], SFG-VS has already been shown to be able to measure the molecular orientations at various liquid surfaces, including the air/pure methanol interface [13,16–23]. In the current work, we aim to use SFG-VS to obtain the direct experimental evidences for the salt effects on the surface structures of the liquid methanol by observing the change of the orientations of the interfacial methanol molecules upon the addition of salt ions. It is also shown in this work that although only slightly different from

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those of the pure liquid methanol, accurately measuring the refractive indices and Raman depolarization ratios of the salty methanol solution is the key for the precise determination of the interfacial tilting angles in the SFG-VS studies. This latter observation provides important protocols for future studies of surface orientations of other aqueous or nonaqueous electrolyte solutions.

2. Experimental

A picosecond SFG-VS spectrometer (EKSPLA) was used in the current study. The detailed description of this setup can be found elsewhere [20,21,23]. Briefly, the spectrometer is based on a mode-locked Nd:YAG laser operated at a 10-Hz repetition rate with a pulse width of 23 ps. A tunable mid-infrared beam (with the photon energy of ω_{IR}) and a visible beam with its wavelength fixed at 532 nm (ω_{VIS}) were arranged in a co-propagating configuration. The incident angles for the visible and IR beams were 45° and 58° against the surface normal, respectively. The SFG signals ($\omega_{\text{SFG}} = \omega_{\text{IR}} + \omega_{\text{VIS}}$) were collected in a reflective geometry. Each spectrum was normalized by the SFG signals from a Z-cut α -quartz. All the measurements were carried out at the controlled room temperature.

The refractive indices of the neat methanol and the 3 mol/L NaI-methanol solution were measured using an OPTILAB Rex refractometer (Wyatt Technology). The uncertainty in the refractive index measurements was within ± 0.0001 units.

To measure the Raman depolarization ratios, a confocal microscope (Witec) was employed. A cw laser (532 nm, 50 mW) was employed to irradiate the liquids. The emitted light was diffracted by an optical grating (600 g/mm) and recorded by an EMCCD. Using the polarized optics, we obtained the polarized and depolarized Raman spectra, in which the polarization of the Raman signal is parallel (I_p) or perpendicular (I_v) to that of laser. The intensity ratio I_v/I_p equals the depolarization ratio (ρ).

The methanol (+99.8%) was purchased from Alfa Aesar and used as received. The sodium iodide (NaI, 99.9%) was purchased from Alfa Aesar and baked at 210 °C for at least 10 h in a muffle furnace. The purpose of baking NaI was to remove the trace amount of the organic contaminations in the salts.

3. Results and discussion

Up to date, there have been no previous SFG-VS reports on the air/salty methanol interface. In the current work, the molecular orientations at the air/salty methanol interface were obtained by comparing the SFG-VS intensities recorded at different polarization combinations. Fig. 1 shows the SFG-VS spectra at the air/liquid methanol interface taken with the SSP and PPP polarizations before and after adding the NaI salts. Here the indices of SSP and PPP are defined by the polarizations in the order of the SFG, visible and IR beams. The SSP and PPP spectra for the same interface were globally fitted by the Lorentzian lineshapes [13,15,22]:

$$I_{\text{SF}} \propto \left| \chi_{\text{NR}}^{(2)} + \sum_q \frac{\chi_{\text{eff},q}^{(2)}}{\omega_{\text{IR}} - \omega_q + i\Gamma_q} \right|^2 \quad (1)$$

where $\chi_{\text{NR}}^{(2)}$ denotes the non-resonant term; $\chi_{\text{eff},q}^{(2)}$, ω_q and Γ_q represent the effective second order susceptibility, resonant frequency and damping constant of the q th vibrational mode, respectively. According to the previous SFG-VS studies on the air/pure methanol interface [16,17,20,24], three characteristic peaks centered at $\sim 2840 \text{ cm}^{-1}$, $\sim 2920 \text{ cm}^{-1}$ and $\sim 2940 \text{ cm}^{-1}$ can be assigned to the symmetric stretching (s.s.) mode and two Fermi resonance bands of CH_3 , respectively. To fit the tail at the blue side

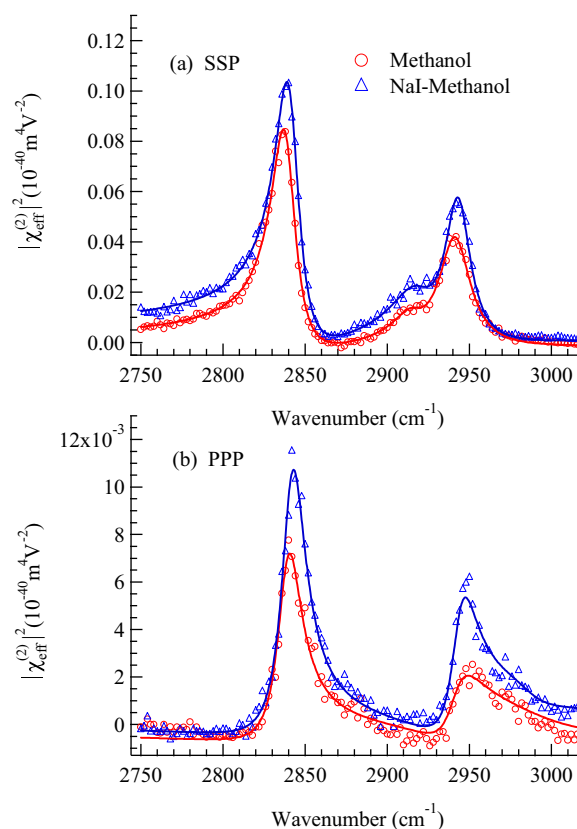


Fig. 1. (a) SSP and (b) PPP spectra of the air/methanol interface before and after adding 3 mol/L NaI salts. Solid lines represent the global fitting results with Lorentzian lineshapes.

in the PPP spectra for both the salted and unsalted methanol interface, a peak around 2990 cm^{-1} has to be included, which might be related to the long-time seeking methyl antisymmetric stretching mode for methanol in the SFG-VS studies. However, the fitting of this peak led to an unusually broad width and large error bars (Table S2 in Supporting information). Therefore the details of this blue-side tail in the PPP spectra are still due to further investigations in the future. In the rest of this report, the discussions will be merely limited to the CH_3 s.s. peak around 2840 cm^{-1} that can be more accurately fitted.

The SFG-VS peaks after the addition of 3 mol/L NaI showed a $\sim 2 \text{ cm}^{-1}$ blue shift compared with those from the pure methanol. But the most obvious change after adding NaI was the increase of the spectral intensity as shown in Fig. 1. Several important factors may potentially contribute to the increase of the SFG-VS intensity [13,15,22], including the alternation of the tilting angles and the orientational distributions, the variation of the surface number density per unit area (N_s), and the change of the microscopic Infrared and Raman polarizabilities of the interfacial molecules. In this short letter, we will mainly analyze the salt effects on the methanol orientation at the air/liquid interface. The latter factors such as the surface density and microscopic molecular polarizability are more complicated and will be discussed in detail in a follow-up full article.

Before the investigation of the effects of NaI salts on the interfacial methanol orientations, we first reexamined the molecular tilting angles at the pure methanol interface without the addition of NaI salts. The interfacial molecular orientations are possible to be determined in an SFG-VS experiment because the measured $\chi_{\text{eff}}^{(2)}$ are related to $\langle R_{ii'} R_{jj'} R_{kk'} \rangle$, the ensemble average over all of the possible molecular orientations in the Euler

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