

# Workshop on liquid surfaces

Dec. 3rd – 4th, Lotte City Hotel, Seoul, Korea

## **Dec. 3rd (Thur.)**

*(Chair: Doseok Kim)*

9:00 – 9:10: Welcoming remark, Doseok Kim, Sogang University

9:10 – 9:50

Vibrational Spectroscopy of Water Interfaces

Y. R. Shen, UC Berkeley

9:50 - 10:30

Some fundamental physical and chemical properties of amorphous ice surfaces

Heon Kang, Seoul National University

10:30 - 10:50: coffee break

10:50 – 11:30

Theoretical Formulation of Vibrational Sum Frequency Generation Intensity for first principle calculation

M. Hayashi, Center for Condensed Matter Sciences, National Taiwan University

11:30 – 12:10

Theoretical Phase Analysis of Nonlinear Susceptibility for Water Surface

Tatsuya Ishiyama and Akihiro Morita, Tohoku University

12:30 – 13:40: Lunch

*(Chair: Kwanwoo Shin)*

13:40 - 14:20

Interface Structure of Neat Ionic Liquids on Electrode Studied by in situ IR-Vis SFG Vibrational Spectroscopy

Yukio Ouchi, Nagoya University

14:20 – 15:00

Solvent Adsorption on the  $\text{LiCoO}_2$  Surface Investigated by Sum-Frequency Generation (SFG) Spectroscopy

Shen Ye, Hokkaido University

15:00 - 15:20: coffee break

15:20 – 16:00

Dynamics at water/Pt interface studied by Vibrational Spectroscopy

Jun Kubota, University of Tokyo

16:00 – 16:40

Dynamics of water at interfaces and around protons

Avishek Ghosh, FOM-Institute for Atomic and Molecular Physics AMOLF

**Dec. 4th (Fri.)**

*(Chair: Yukio Ouchi)*

9:10 – 9:50

Molecular Interactions with Copolymer Films at the Air-Water Interface Using Neutron Reflectometry

Michael James, Australian Nuclear Science and Technology Organisation

9:50 - 10:30

In situ characterization of bio-mimetic thin films using by X-ray and Neutron reflectivity

Kwanwoo Shin, Sogang University

10:30 – 11:10

Recent Progress in Molecular Layering of Nonmetallic Liquids at Interfaces: X-ray Reflectivity Study

Chung-Jong Yu, Pohang Accelerator Laboratory

10:50 – 11:10: coffee break

11:10 – 11:50

Interface-Selective Heterodyne-Detected Second-Order Nonlinear Spectroscopy

Shoichi Yamaguchi, RIKEN

11:50 – 12:30

Charge inversion due to adsorption of multivalent cations on headgroups of Langmuir monolayer

Doseok Kim, Sogang University

12:40 – 14:00: Lunch

*(Chair: Shen Ye)*

14:00 – 14:20

Interference Effect on Sum Frequency Generation (SFG) Vibrational Spectroscopy from Thin Films

Yujin Tong, Hokkaido University

14:20 – 14:40

Alkyl Chain Length Dependence of Cation and Anion Configurations at the Air/Liquid Interface of Room-temperature Ionic Liquid: 1-Alkyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)amide

Takashi Iwahashi, Nagoya University

14:40 – 15:00

Potential dependent ions adsorption on Pt / neat ionic liquids interface studied by in situ IR-visible sum frequency generation spectroscopy

Wei Zhou, Nagoya University

15:00 -15:20

Interfacial Restructuring of Ionic Liquids Determined by Sum-Frequency Generation Spectroscopy and X-Ray Reflectivity

Yoonnam Jeon, Sogang University

(Dec 3rd, Thur.)

## **Vibrational Spectroscopy of Water interfaces**

Y. R. Shen

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Berkeley, California, USA*

Recent development of phase-sensitive sum-frequency vibrational spectroscopy permits complete spectroscopic measurement of the complex surface susceptibility of water interfaces,  $\chi_S^{(2)}(\omega_{IR}) = \text{Re } \chi_S^{(2)}(\omega_{IR}) + i \text{Im } \chi_S^{(2)}(\omega_{IR})$ , for  $\omega_{IR}$  in the OH stretch vibration region. The  $\text{Im } \chi_S^{(2)}(\omega_{IR})$  spectrum is particularly interesting because in analogy to  $\text{Im } \varepsilon(\omega)$  that describes a linear absorption or emission spectrum, it directly characterizes the surface vibrational resonances. It allows us to construct more detailed physical pictures of a water interface with vapor as well as with hydrophilic and hydrophobic solids. We find that all water interfaces appear as a randomly distorted ice surface, with rapidly decreasing order moving into the bulk, but the net polar orientations of different water species at the interfaces can be very different. We also learn from our study which interfacial water species contribute to which spectral regions, how the structure of the water/vapor interface can be perturbed by excess ions emerging from an acid, base, or salt solution, whether hydronium and hydroxyl ions would appear at the water/vapor interface, and what are the characteristics of a hydrophobic water interface.

This work was supported by NSF-STC WaterCAMPWS.

# **Some fundamental physical and chemical properties of ice surfaces**

Heon Kang

*Department of Chemistry, Seoul National University,  
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This presentation describes our recent investigations of physics and chemistry of ice surfaces, with the emphases on the properties of hydronium and hydroxide ions at the ice surfaces. The ionization and dissolution processes of sodium halide salts at the ice surfaces are also presented. Cs<sup>+</sup> reactive ion scattering (RIS) and low energy sputtering (LES) techniques are used to identify neutral and ionic species, respectively, at the ice surfaces and to follow their motions and reactions. These studies demonstrate unique properties of ice surfaces as reaction media, which, at the same time, may have good correlation with interfacial water properties.

# **Theoretical Formulation of Vibrational Sum Frequency Generation Intensity for first principle calculation**

M. Hayashi

*Center for Condensed Matter Sciences, National Taiwan University, 1 Roosevelt Rd. Sec. 4,  
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Interfacial structures of liquid surfaces are fascinating properties that are not only rich of physics and chemistry but also highly relevant to critical phenomena in biology and environmental science. Sum Frequency Generation is the only technique that can provide molecular level information on liquid surfaces. Shen's group has reported new information on water interfacial structure using phase-sensitive, vibrational SFG. To deduce molecular level properties of water interfacial structure, we have recently developed a rigorous molecular theory for vibrational SFG (VSFG) intensity. Identifying explicitly the interaction Hamiltonian between molecules and radiational fields, we have formulated VSFG using density matrix technique. In this talk, the results of theoretical formulation will be presented and discussed.

# Theoretical Phase Analysis of Nonlinear Susceptibility for Water Surface

Tatsuya Ishiyama and Akihiro Morita

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Recently the phase-sensitive measurement of SFG spectroscopy expanded the applicability of the surface-specific nonlinear spectroscopy. It is revealed experimentally from the phase-sensitive SFG of OH stretching vibration of water surface that the imaginary part of  $\chi^{(2)}$  in *ssp* polarization consists of three regions, (i) positive region at about 3700  $\text{cm}^{-1}$ , (ii) negative region at about 3400  $\text{cm}^{-1}$ , and (iii) positive region at about 3000  $\text{cm}^{-1}$  [1]. While the components (i) and (ii) have been predicted by our previous MD simulation and interpreted with OH bonds pointing to the vapor and to the liquid, respectively, the third component (iii) posed a challenge to theoretical interpretation. It is found from MD simulation that this positive component is induced by the intermolecular orientational correlation of water molecules, which results in strong anisotropic local field at the surface [2].

[1] N. Ji, V. Ostroverkhov, C. S. Tian, Y. R. Shen, *Phys. Rev. Lett.* **100**, 096102 (2008).

[2] T. Ishiyama and A. Morita, *J. Phys. Chem. C* **113**, 16299 (2009).

# **Interface Structure of Neat Ionic Liquids on Electrode Studied by in situ IR-Vis SFG Vibrational Spectroscopy**

Yukio Ouchi

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A novel class of liquid salts – room temperature ionic liquids (RTILs), has initiated explosive studies during the past decade. Increasing interest extends from the rich tuneable structures of RTILs to their special physical and chemical properties such as the intrinsic ion conductivity, wide electrochemical window, high thermal stability, etc. Compared with the large growth of various applications of RTILs, the molecular level information of interface structure of RTILs on electrode surface is still insufficient, although such information is critical to improve the related performance. So far, main techniques effective for interface structure studies of RTILs on metal electrode are capacitance measurements, IR or Raman spectroscopy and theoretical simulations.

In this study, the electrochemical interfaces of a series of RTILs including 1-butyl-3-methylimidazolium trifluoromethane sulfonate ([bmim]OTf), 1-butyl-3-methyl imidazolium bis(trifluoromethanesulfonyl)amide ([bmim]TFSA) and 1-butyl-3-methyl imidazolium bis(fluorosulfonyl)amide ([bmim]FSA) have been investigated by in situ SFG technique. We have observed potential dependent adsorption/ desorption of both the anion and the cation on electrode surface. Adsorption/desorption hysteresis effect of ca. 1V has been found for the first time. The SFG results indicate that the electrochemical interface of electrode/RTILs is characterized by double layer structure.

## Solvent Adsorption on the LiCoO<sub>2</sub> Surface Investigated by Sum Frequency Generation (SFG) Spectroscopy

Huijin Liu,<sup>†</sup> Yujin Tong,<sup>†</sup> Naoaki Kuwata<sup>‡</sup>, Masatoshi Osawa,<sup>†</sup> Junichi Kawamura<sup>‡</sup> and Shen Ye<sup>†,§</sup>

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Lithium-ion (Li<sup>+</sup>-ion) battery has been regarded as one of the most important inventions in modern energy-storage technology [1]. It has the highest energy density among all rechargeable batteries and is widely applied as a power source for many applications such as personal computer, hybrid electric vehicle (HEV) and electric vehicle (EV). To improve the performance and safety of Li<sup>+</sup>-ion battery, it is important to understand the molecular structures on the electrode/electrolyte interface under its working conditions. Many techniques such as XRD, BET isotherm, XPS, SEM, EIS, Raman, and FTIR have been employed for such purpose [1-2]. However, most of these methods are not intrinsically surface-specific, and sometimes not sensitive enough to study structures on the electrode surface at a molecular level. As a second-order nonlinear optical technique, sum frequency generation (SFG) vibrational spectroscopy shows extremely high selectivity and sensitivity on interface and allows us to obtain structures at various surfaces or interfaces [3-5]. In the present study, the molecular structural changes on the LiCoO<sub>2</sub> electrode surface, which is one of important cathode material used in Li<sup>+</sup>-ion battery, have been investigated by SFG spectroscopy in contact with non-aqueous electrolyte solution.

A LiCoO<sub>2</sub> thin-film of ca. 50 nm was deposited on the CaF<sub>2</sub> substrate surface by pulsed laser deposition (PLD) technique using a 4<sup>th</sup>-harmonic output from a Q-switched Nd:YAG laser with fluencies of 3.5mJ/cm<sup>2</sup>. SFG measurements were carried out on LiCoO<sub>2</sub> surface in contact to different kinds of non-aqueous electrolyte solution. A broad-band SFG system with a tunable femtosecond (*fs*) infrared pulse and a picosecond (*ps*) visible pulse was used in the present work [5-7]. All chemicals are Lithium Battery Grade (LBG) from Kishida Chemicals Co. Ltd (Osaka, Japan).

Figure 1 shows *ssp*- and *sps*-SFG spectra on the LiCoO<sub>2</sub> surface in contact with pure propylene carbonate (PC) solvent [8]. The *sps*-spectrum shows a strong bipolar band while the *ssp*-spectrum exhibits a weaker bipolar band reverse to that of the *sps*-spectrum. As shown in the Fig. 1, the best-fittings for the SFG observations were obtained by assuming two vibrational modes at 1830 and 1780 cm<sup>-1</sup>. The two peaks are assigned to C=O stretching mode of PC solvent adsorbed on the LiCoO<sub>2</sub> surface. Since SFG does not occur in homogenous media with inversion symmetry, the present result suggests that PC molecules align on the LiCoO<sub>2</sub> surface with a certain ordered structure.



The SFG spectra in the PC solvent on the LiCoO<sub>2</sub> surface (Fig. 1) are stable with time. However, as a small amount of water was introduced into the cell, the SFG signals quickly decrease. It is expected the adsorption of water molecules may take place on the LiCoO<sub>2</sub> to replace the PC adlayer there. On the other hand, the decomposition of the PC solvent molecules on the LiCoO<sub>2</sub> surface may also occur under the presence of water molecules.

Furthermore, the adsorption structure of PC molecule is strongly affected by the concentration of Li<sup>+</sup> ion in PC solution. It is known that Li<sup>+</sup> ion is solvated to species such as [Li(PC)<sub>3</sub>]<sup>+</sup> and [Li(PC)<sub>2</sub>]<sup>+</sup>. These solvated species with positive charge can interact strongly with and specifically adsorb on the LiCoO<sub>2</sub> surface to replace the ordered PC adlayer from the pure solvent. It is expected that the structures of these charged solvated species on the LiCoO<sub>2</sub> surface are disordered and thus give weaker SFG signals in Li<sup>+</sup> ion contained PC solution [8]. Details and discussion will be given in the presentation.

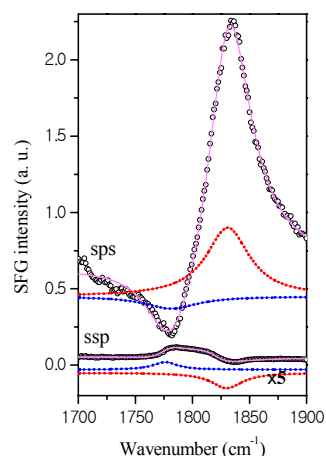


Figure 1. SFG spectra of LiCoO<sub>2</sub> surface in PC with *ssp* and *sps* polarization combinations. Circles represent observed results. Solid traces represent fitting results. Dotted traces represent simulation for two modes. The simulated components for *ssp*-polarization are multiplied by factor of 5 for clarity.

**Acknowledgment:** The work is partially supported by NEDO.

- [1] P. Balbuena and Y. Wang, *Lithium-ion Batteries*, Imperial College Press, London, **2007**.
- [2] K. Xu. *Chem. Rev.* **2004**, *104*, 4303.
- [3] Y. R. Shen, *The Principles of Nonlinear Optics*, John Wiley & Sons, Inc.: New York, **1984**.
- [4] P. Miranda, Y. R. Shen, *J. Phys. Chem. B* **1999**, *103*, 3292
- [5] S. Ye and K. Uosaki, in *Encyclopedia of Electrochemistry*, Vol.10, ed. Bard, A. J., Wiley-VCH: Weinheim, **2007**, pp513
- [6] J. Holman, P. B. Davies, T. Nishida, S. Ye, D. J. Neivandt, *J. Phys. Chem. B* (Feature Article) **2005**, *109*, 18723
- [7] S. Ye, H. Noda, S. Morita, K. Uosaki, M. Osawa, *Langmuir*, **2003**, *19*, 2238.
- [8] H. Liu, Y. Tong, N. Kuwata, M. Osawa, J. Kawamjura, S. Ye, *J. Phys. Chem. C Letter*, in press.

# Dynamics at water/Pt interface studied by Vibrational Spectroscopy

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Time-resolved vibrational spectroscopy at interfaces is a subject of intensive ongoing investigation. The dynamics of surface molecules with ps time resolution gives detailed information for elemental steps of chemical reactions at surfaces. This presentation focuses on two topics: dynamics of energy transfer at the H<sub>2</sub>O (D<sub>2</sub>O)-ice/CO/Pt(111) interface and direct observation of potential of Pt particles on photocatalysts for water splitting. Dynamics of ice/CO/Pt(111) interfaces under the irradiation with non-resonant near infrared (NIR) pulses studied by SFG spectroscopy in the ps time region has importance for understanding of the essentials of catalysis and electrochemistry. The energy transfer from the Pt substrate to the ice crystal was reported to require a few hundreds ps and this time response is much slower than that estimated by macroscopic heat diffusion simulation [1,2]. Additionally, the ultra-short temperature jump by the NIR irradiation resulted in melting and recrystallization of ice at the interface without sublimation. Photocatalytic water splitting is one of the powerful tools to convert solar energy to hydrogen. The SFG spectroscopy has also revealed dynamics of catalytic reaction on TiO<sub>2</sub> surfaces [3]. In this presentation, we shortly present that the electronic potential change at Pt particles on GaN model photocatalysts under in-situ condition was revealed by infrared spectroscopy at electrolyte/Pt interfaces [4].

- [1] J.Kubota, et al., *Chem. Phys. Lett.*, **362**, 476 (2002).
- [2] J.Kubota, et al., *Chem. Phys. Lett.*, **377**, 217 (2003).
- [3] J.Chen, et al., *J. Am. Chem. Soc.*, **131**, 4580 (2009)
- [4] M.Yoshida, et al., *J. Am. Chem. Soc.*, **131**, 13218 (2009)

# Dynamics of water at interfaces and around protons

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We report the study of the dynamics of water around protons and water at the water-air and water-lipid interfaces. Interfacial water is studied using time-resolved, surface-specific Vibrational Sum-Frequency Generation (VSFG) Spectroscopy. This allows us to investigate the vibrational dynamics of the O-H stretch vibration of the outermost monolayer of interfacial water molecules using surface-specific 4th-order VSFG spectroscopy. The O-H stretch vibration of interfacial water is resonantly excited with an intense, 100 fs infrared pulse; the vibrational relaxation dynamics are followed with femtosecond, time-resolved VSFG spectroscopy. Our results reveal that ultrafast exchange of vibrational energy can occur between water surface and bulk water, but the occurrence of ultrafast resonant vibrational energy transfer depends critically on the details of the water interface.

The reorientational dynamics of water around protons in acid solutions is obtained from time-domain TeraHertz spectroscopy. Our results reveal that some ~20 water molecules are involved in proton transport. These results are consistent with the notion that reorientational motion of water in the hydrogen bonded network close to the proton is the rate limiting step in proton transfer. Accordingly, the suppression of water reorientation by the addition of hydrophobic molecules to water causes the proton mobility to decrease dramatically.

(Dec 4th, Fri.)

## **Molecular Interactions with Copolymer Films at the Air-Water Interface Using Neutron Reflectometry**

Michael James,<sup>1</sup> Andrew Nelson,<sup>1</sup> Tsang-Lang Lin,<sup>2</sup> Karen Edler,<sup>3</sup> and Matthew Wasbrough<sup>3</sup>

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2009 has seen the newly commissioned *Platypus* time-of-flight neutron reflectometer come on-line at the 20 MW OPAL research reactor in Sydney, enabling molecular processes and interactions to be probed at solid and liquid interfaces. *Platypus* is one of 6 instrument that are currently available as part of an international user facility, with a further 7 instruments either under construction or being commissioned. This presentation will detail the capacity of *Platypus* to study nanoscale chemical and biological interactions at surfaces and interfaces. A key capacity of the *Platypus* reflectometer is the ability to tailor the instrumental resolution to suit the problem being investigated; with the high-resolution mode allowing study of films greater than 300 nm and the low-resolution mode providing 7× the neutron flux to efficiently probe molecular layers as thin as 1 nm. While the penetrating power of the neutron allows for investigation of solid-liquids interfaces, and spin polarization enables investigation of magnetic thin-films, this presentation will concentrate on studies of molecular interactions with diblock copolymers at the air-water interface.

# ***In situ* characterization of bio-mimetic thin films using by X-ray and Neutron Reflectivity**

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In recent years, soft matter science, including biological systems and organic thin films, has received more and more attention for its extensive applications in medical and biotechnological fields, since many important biological processes are regulated at a membrane surface and interface. As the vital component of all living cells, a biological cell membrane acts as a reaction front for an immune response, cell metabolism and adherence, protein transfusion and other crucial life activities. Therefore, the large amount of recent research in surface science has mainly been focused, on developing new ways to prepare, characterize, and understand the surface/interface properties of biological thin films. Neutron and X-ray reflections, in particular, have been great important in the last decades for the study of organic interfaces. They can offer several advantages for the study of structural details of biomembrane in aqueous environment because of non-destructive and higher depth resolution than other techniques. Recently, neutron and X-ray reflectometers have been utilized to investigate many applications in biological membrane system. In this talk, current activities using the neutron reflectometer at the HANARO, which is the first neutron reflectometer dedicated to the liquid surfaces in Korea, and recent experimental results using by X-ray will be given to confirm its structural and surface dynamics for studying polymer, lipid mono- & bilayer and multilayer systems at the air-liquid interfaces or the liquid-solid interfaces, interacting with cell penetrating peptides & proteins.

## **Recent Progress in Molecular Layering of Nonmetallic Liquids at Interfaces: X-ray Reflectivity Study**

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Nonmetallic liquids have shown molecular layering at the solid-liquid interface due to the confinement effect. At the air-liquid interface, it had been believed that the confinement effect is much reduced and molecular layering is thus hardly observable. In recent years, however, there has been experimental evidence of molecular layering at the air-liquid interface in “cold” phase, which is agreed with a molecular dynamics result. We will present recent progress in this subject including structural studies of nanoconfined liquids and structural signal of glass transition.

# Interface-Selective Heterodyne-Detected Second-Order Nonlinear Spectroscopy

Shoichi Yamaguchi and Tahei Tahara

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“Interface” is now one of the most important keywords in materials and life science. Among a lot of experimental techniques to investigate interfaces, the second-order nonlinear spectroscopy holds a special and unique position that cannot be replaced by the others. One can obtain electronic and vibrational spectra of interfaces noninvasively in the ambient atmosphere by using second harmonic generation (SHG) and vibrational sum frequency generation (VSFG), respectively, which provide essential information for identifying interfacial species, determining structure and orientation, and considering microscopic functions of the interfaces. We recently developed electronic sum frequency generation (ESFG) that can provide electronic  $|\chi^{(2)}|^2$  spectra with a much higher signal to noise ratio and far denser spectral data points than SHG [1, 2]. SHG, VSFG, and ESFG measurements provide data representing  $|\chi^{(2)}|^2$ , not  $\chi^{(2)}$  itself, because of the homodyne nature of signal detection. This feature sometimes makes interpretation of data difficult, and even worse, it hides essential information inherent in  $\chi^{(2)}$ . The most crucial information lost in the homodyne detection is the sign of  $\chi^{(2)}$  that is directly related to the “up” versus “down” alignment of interfacial molecules. Very recently, we have realized the heterodyne detection of ESFG and VSFG [3, 4]. These new methods, HD-ESFG and HD-VSFG, can provide electronic and vibrational complex  $\chi^{(2)}$  spectra of interfacial molecules, respectively. We are now studying interesting topics such as absolute orientation of interfacial molecules, pH difference between the aqueous bulk and interface, and higher order structure of proteins adsorbed on interfaces, by using HD-ESFG and HD-VSFG.

[1] S. Yamaguchi and T. Tahara, *Laser Photonics Rev.* **2** (2008) 74.

[2] S. Sen, S. Yamaguchi, and T. Tahara, *Angew. Chem. Int. Ed.* **48** (2009) 6439.

[3] S. Yamaguchi and T. Tahara, *J. Chem. Phys.* **129** (2008) 101102.

[4] S. Nihonyanagi, S. Yamaguchi, and T. Tahara, *J. Chem. Phys.* **130** (2009) 204704.

# **Charge inversion due to adsorption of multivalent cations on headgroups of Langmuir monolayer**

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Sum-frequency generation vibrational spectroscopy was used to investigate Langmuir monolayers having oppositely charged headgroups and the nearby water molecules at the interface. The spectra in the  $\text{CH}_x$  vibration region changed sensitively between the lipids having positively- and negatively charged headgroups. This observation was explained in terms of the interference of the sum-frequency signal from lipid  $\text{CH}_x$  groups with that from the OH group of the interfacial water molecules, which changed sign as net polar orientation is inverted following the charge of the lipid headgroups. This sign change was confirmed by directly measuring the phase of the sum-frequency signal in the OH spectral region using phase-sensitive sum-frequency measurement.

These systems were then investigated for the adsorption of counterions from the subphase to the headgroups of the lipid molecules at the interface. Langmuir monolayer of lipid molecules having negatively charged headgroups were investigated by sum-frequency vibrational spectroscopy as  $\text{LaCl}_3$  concentration in the subphase was changed. Adsorption of  $\text{La}^{3+}$  cation on lipid headgroups increased with higher  $\text{LaCl}_3$  concentration, finally overcompensating negative charges of the lipid headgroups.



# Interference Effect on Sum Frequency Generation (SFG) Vibrational Spectroscopy from Thin Films

Yujin Tong,<sup>†</sup> Yanbao Zhao,<sup>†</sup> Na Li,<sup>†</sup> Masatoshi Osawa,<sup>†</sup> Paul B. Davies,<sup>‡</sup> Shen Ye<sup>\*,†,§</sup>

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Recently, IR-visible sum frequency generation (SFG) vibrational spectroscopy has been widely employed to investigate molecular structure at various surfaces and interfaces [1]. Since SFG is a coherent optical process, interference effects such as interference between resonant and non-resonant signals [2], interference between different polarization combination [3] or different vibrational modes [4] are always involved in the SFG observation, which have been successfully employed to determine the absolute molecular orientation and chirality. However, as the thickness of the thin film sample is comparable to the wavelength of the pumped and/or emitted lights, the interference effect from the thin film will play important roles in the observed SFG spectra [5]. It is therefore quite essential to quantitatively analyze this interference effect. There have been several studies on solving thickness interference problems in surface optics such as SFG and second harmonic generation (SHG) [6]. However, few of them have interpreted how the thickness affects the spectra line-shapes. Lambert *et al* proposed a theoretical model to simulate the interference effect for the thin film on metal surface [5a]. However, their model is dependent upon their counter-propagating incident beam geometry SFG setup which is rarely used nowadays. On the other hand, the multiple reflections within the thin film are not well illustrated. In the present study, we experimentally constructed an ideal thin film model system using Langmuir-Blodgett (LB) multilayer films of regular or deuterated fatty acids on the gold surface and then recorded SFG spectra of different film thickness with different polarization combinations [7]. It was found that, both intensities and phases of the vibrational modes in the SFG spectra change significantly with the film thickness for the three polarization combinations. It is interesting to note that the intensity of the ssp- polarized SFG spectra changes ca. two orders within 220 nm. In order to interpret these observations in SFG spectra, a theoretical model is proposed to simulate the interference with the film thickness. The good agreement between the simulated results and the experimental observations has been obtained, suggests the validity of the simulation. We also further extended the present simulation to other thin films involving polymer thin film on metal or dielectric substrate, electrochemical thin layer system. The effect of incident beam geometries and substrate are also discussed.

Acknowledgment: The work is partially supported by PRESTO, JST.

- [1]. (a) Shen, Y. R. et al., *Chem. Rev.* **2006**, *106*, 1140; (b) Bain, C. D. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 1281;  
[2]. (a) Ostroverkhov, V.; Waychunas, G.; Shen, Y. R., *Phys. Rev. Lett.* **2005**, *94*, 046102 (b) Holman, J.; Davies, P. B.; Nishida, T.; Ye, S.; Neivandt, D. J., *J. Phys. Chem. B* **2005**, *109*, 18723-18732. (c) Nishida, T.; Johnson, C. M.; Holman, J.; Osawa, M.; Davies, P. B.; Ye, S., *Phys. Rev. Lett.* **2006**, *96*, 077402.

- [3]. (a) Belkin, M. A.; Kulakov, T. A.; Ernst, K. H.; Yan, L.; Shen, Y. R., *Phys. Rev. Lett.* **2000**, *85*, 4474-4477. (b) Wang, J.; Clarke, M. L.; Chen, Z., *Anal. Chem.* **2004**, *76*, 2159-2167.
- [4]. Brown, M. G.; Raymond, E. A.; Allen, H. C.; Scatena, L. F.; Richmond, G. L., *J. Phys. Chem. A* **2000**, *104*, 10220-10226.
- [5]. (a) Lambert, A.G. *et al.*, *J. Phys. Chem. B.* **2002**, *106*, 5461. (b). Briggman, K. A. *et al.*, *J. Phys. Chem. B*, **2001**, *105*, 2785.
- [6]. (a) Feller, M. B.; Chen, W.; Shen, Y. R., *Phys. Rev. A* **1991**, *43*, 6778-6792. (b) Bethune, D. S., *J. Opt. Soc. Am. B: Opt. Phys.* **1991**, *8*, 367-373. (c) Sipe, J. E., *J. Opt. Soc. Am. B: Opt. Phys.* **1987**, *4*, 481-489. [6]. Holman, J. *et al.*, *J. Phys. Chem. B*, **2004**, *108*, 1396.
- [7]. Tong, Y.; Zhao, Y.; Li, N.; Osawa, M.; Davies, P.B.; Ye, S. *submitted*

# Alkyl Chain Length Dependence of Cation and Anion Configurations at the Air/Liquid Interface of Room-temperature Ionic Liquid: 1- Alkyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)amide

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Room-temperature ionic liquids (RTILs), which are salts with a liquid phase at room temperature, have attracted much interest due to their unique nature. It is well known that most of the typical cations within RTILs contain alkyl chains of various lengths (Fig. 1(a); typical carbon numbers  $n$  range from 2 to 12), and the properties of RTILs strongly depend on the alkyl chain length.[1] As surfaces and interfaces of RTILs are a key issue for numerous potential applications, the microscopic structures of RTIL surfaces and interfaces should be studied thoroughly. However, there has been little structural information obtained about the anion due to experimental difficulties. In this study, we examine the alkyl chain length dependence of both the cation and anion configurations at the air/RTIL interface by using infrared-visible sum frequency generation spectroscopy (IVSFG).

Fig. 2 and 3 show the SFG spectra of the air/RTIL interfaces of 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl) amide ( $[C_n\text{mim}]\text{TFSA}$ ;  $n = 4$  and 10, shown in Fig. 1) at CH stretch, and CF and SO stretch regions, respectively. The polarization combination is ssp (referring to s-polarized SF, s-polarized visible, and p-polarized IR fields, respectively). We can clearly see that the SF signal intensity in the CH stretch region shown in Fig. 2, which originates from the alkyl chain of the cation, only differs at CH<sub>2</sub> symmetric (d<sup>+</sup>) and asymmetric (d<sup>-</sup>) stretch modes at  $\sim 2860$  cm<sup>-1</sup> and  $\sim 2920$  cm<sup>-1</sup>, respectively. The increase in the d<sup>+</sup> and d<sup>-</sup> mode intensities for the RTIL with the longer alkyl chain should be due to an increase in the number of CH<sub>2</sub> functional group. On the other hand, the SF signal intensity in the CF and SO stretch region shown in Fig. 3, which derives from the TFSA anion, drastically decreases for the RTIL with the longer alkyl chain. This decrease in the TFSA anion signal, however, can hardly be explained in terms of the surface number density of the TFSA anions because the number of pairs of the cation and anion does not depend on the alkyl chain length.[2] The decrease clearly demonstrates that the TFSA anion changes its configuration from the SF-active C1 conformer to the SF-inactive C2 conformer at the surface as the chain length increases.

[1] See for example: Triolo, A.; Russina, O.; Bleif, H.-J.; Di Cola, E. *J. Phys. Chem. B* **2007**, *111*, 4641.

[2] Iimori, T.; Iwahashi, T.; Kanai, K.; Seki, K.; Sung, J.; Kim, D.; Hamaguchi, H.; Ouchi, Y. *J. Phys. Chem. B* **2007**, *111*, 4860.

# Potential dependent ions adsorption on Pt / neat ionic liquids interface studied by in situ IR-visible sum frequency generation spectroscopy

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Room temperature ionic liquids (RTILs) as novel liquid salts have been widely studied due to their special structures and properties. There has been a large growth of employments of RTILs as new electrolyte in electrochemical applications. However, the basic issue of the electrochemical interface structure of RTILs on metal electrode remains as unresolved in spite of recent increasing studies on this topic by using various surface analysis techniques as well as theoretical calculations [1, 2].

Herein, we studied Pt electrode/RTILs interface structure by using in situ IR-visible sum frequency generation (SFG) spectroscopy. SFG as a 2nd order nonlinear vibrational spectroscopy is highly effective to give molecular level information of the electrochemical interface due to its surface specificity. Compared with IR and Raman, SFG technique shows two unique features for probing the electrochemical interface. First, SFG signal is only generated in a noncentrosymmetric environment such as an electrochemical interface. Second, SFG provides absolute vibrational information without the need to perform a subtractive operation with respect to a reference spectrum generally taken at different potential, while such an operation is necessary for in situ IR measurement. These features make SFG an ideal technique for the study on the electrochemical interface structure.

In this study, the electrochemical interfaces of a series of RTILs including 1-butyl-3-methylimidazolium trifluoromethane sulfonate ([bmim]OTf), 1-butyl-3-methyl imidazolium bis(trifluoromethanesulfonyl)amide ([bmim]TFSA) and 1-butyl-3-methyl imidazolium bis(fluorosulfonyl)amide ([bmim]FSA) have been investigated by in situ SFG technique. We have observed potential dependent adsorption/ desorption of both the anion and the cation on electrode surface. Adsorption/desorption hysteresis effect of ca. 1V has been found for the first time. The SFG results indicate that the electrochemical interface of electrode/RTILs is characterized by double layer structure.

[1] S. Baldelli, *Accounts Chem. Res.*, 41 (2008) 421-431

[2] A. A. Kornyshev, *J. Phys. Chem. B*, 111 (2007) 5545-5557

# Interfacial Restructuring of Ionic Liquids Determined by Sum-Frequency Generation Spectroscopy and X-ray Reflectivity

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Surface sum-frequency generation spectroscopy and X-ray reflectivity were used to study the surface of [BMIM][X] ionic liquids (BMIM = 1-butyl-3-methylimidazolium cation, X = BF<sub>4</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup>, and I<sup>-</sup>). Sum-frequency signal strength from the terminal methyl groups of the cation at the surface indicates that the topmost surface of these ionic liquids are occupied by polar-oriented hydrophobic butyl chains having approximately 1/3 of the in-plane density of fully-packed alkyl chains as observed by the same method for hexadecanol Langmuir monolayer. X-ray reflectivity data reveal a layer with density larger than that of bulk. However, the reflectivity is not sufficiently sensitive to the exact location of this layer either at the vacuum interface or sandwiched between the bulk and the low-density alkyl chain, as observed in the sum-frequency measurements. Analysis of the reflectivity data in conjunction with the sum-frequency spectra strongly suggests the molecules forming the topmost layer are on average polar-oriented with their (loosely packed) butyl chains towards the gas/liquid interface while the (densely-packed) imidazolium cores/anions are in contact with the bulk liquid.