8th SFG Symposium

26 - 27 October, 2018

---

supported by

Saitama University

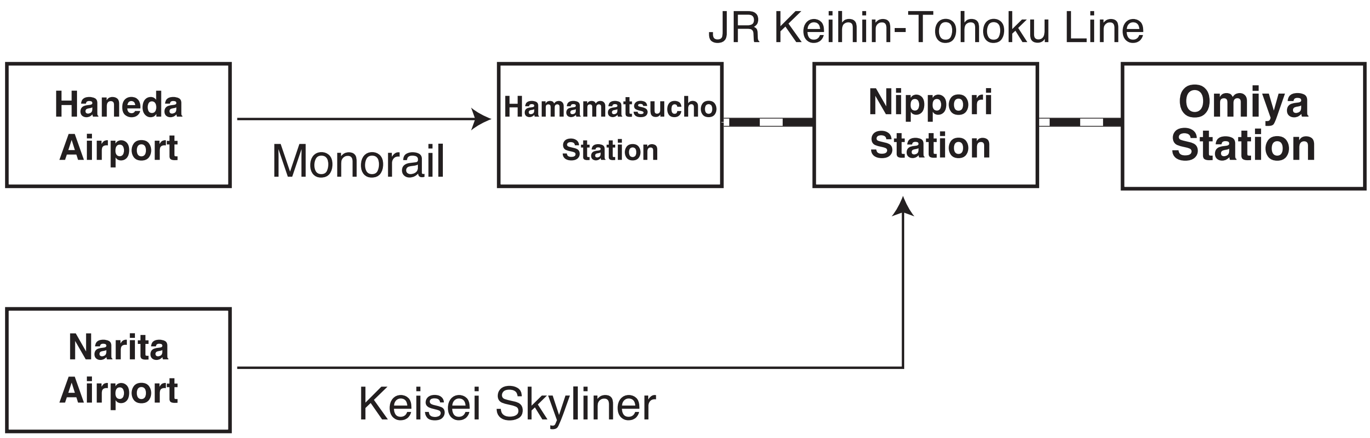
and

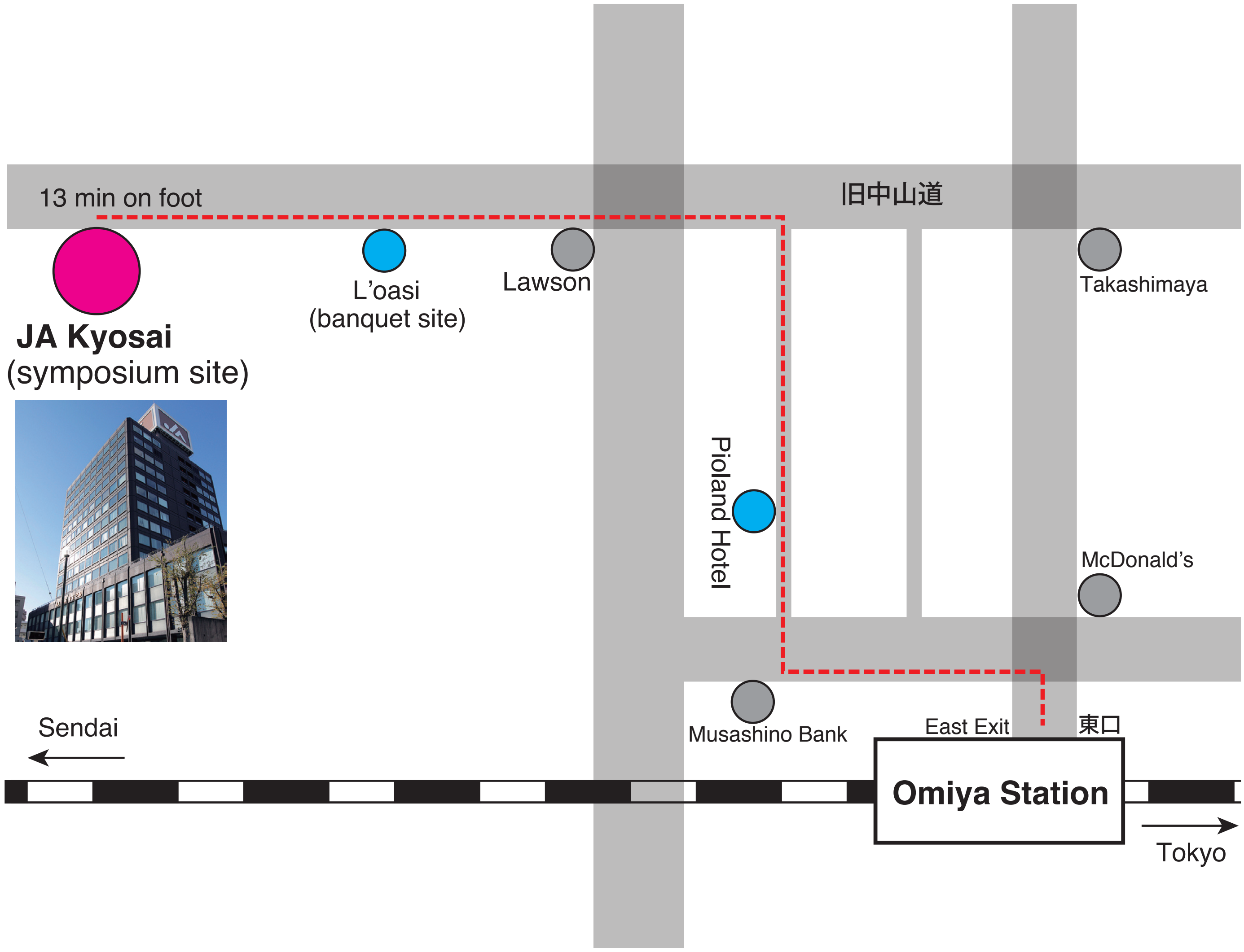
Kajima Foundation

JA Kyosai Saitama Building, Omiya, Japan

Welcome to Omiya

- 1.5 hours from Haneda or Narita to Omiya by train.
- The symposium is at Room 3 (第3会議室), 3rd floor (3階), JA Kyosai Saitama Building (JA共済埼玉ビル).





Preface

I feel very honorable to organize the 8th SFG (Sum Frequency Generation) symposium in Saitama on October 26th and 27th, 2018. The SFG symposium was originally started by Prof. Yukio Ouchi as early as 2003 in Nagoya, inviting almost all Japanese researchers who were involved in SFG spectroscopy at that time. Then the 2nd SFG symposium was held in Nagoya 2005, 3rd in Okazaki 2006, 4th in Wako 2009, 5th in Sendai 2012, 6th in Tsukuba 2014, and 7th in Tokyo 2016. The SFG community in Japan has grown greatly, thanks to the SFG symposium. I still clearly remember when I first participated in the symposium in 2006 and listened to Prof. Y. R. Shen's lecture for two hours, which strongly inspired me and my colleagues to develop heterodyne SFG.

The 8th SFG symposium is the most international to date, where I invited Prof. Y. R. Shen, Prof. A. Dhinojwala, and Prof. H. Allen from the US, Prof. E. Tyrode from Sweden, Dr. Y. Nagata and Prof. E. Backus from Germany, and Prof. M. Gaigeot from France. Following the tradition of the SFG symposium, I also invited Prof. G. Sazaki and Prof. M. Matsumoto from outside the SFG community. I hope that all participants can enjoy science and have fruitful discussion in this symposium to start another interesting and pioneering researches into surfaces and interfaces.

Please note that the 8th SFG symposium is financially supported by Saitama University and Kajima Foundation, which allows me to invite so many leading scientists from all over the world. I am very grateful to these generous supports for fundamental science.

October, 2018
Shoichi Yamaguchi

Time Table

October 26, 2018

12:25 - 12:30	Opening Remark by Shoichi Yamaguchi	
Friday Session 1	chair: Yukio Ouchi	
12:30 - 13:10	**Yuen Ron Shen** (UC Berkeley) Sum-Frequency Spectroscopy on Crystalline Solid Surfaces	p. 4
13:10 - 13:40	**Tahei Tahara** (RIKEN) Catching Ultrafast Reactions at the Water Surface by Femtosecond Time-Resolved HD-VSFG Spectroscopy	p. 5
13:40 - 14:10	**Yuki Nagata** (Max Planck Inst) Orientation of the Free O-H Group Revealed by Combined SFG Simulation and Experiment	p. 6
14:10 - 14:30	Coffee Break	
Friday Session 2	chair: Taka-aki Ishibashi	
14:30 - 15:10	**Ali Dhinojwala** (Univ of Akron) Measuring Acid-Base Interactions using Surface Sensitive Spectroscopy and Its Relationship with Adhesion	p. 7
15:10 - 15:40	**Kazuya Watanabe** (Kyoto Univ) Growth of Ice Film on Rh(111) Studied by Sum-Frequency Generation	p. 8
15:40 - 16:10	**Shoichi Yamaguchi** (Saitama Univ) Surface Structure of Ice I_h Revealed by HD-SFG Spectroscopy	p. 9
16:10 - 16:30	Coffee Break	
Friday Session 3	chair: Akihiro Morita	
16:30 - 17:10	**Masakazu Matsumoto** (Okayama Univ) An Interesting Twist in Liquid Water	p. 10
17:10 - 17:40	**Ellen Backus** (Max Planck Inst) Vibrational Dynamics at the Solid-Liquid Interface	p. 11
17:40 - 18:10	**Shen Ye** (Tohoku Univ) Electrode/Electrolyte Interface Studied by *in situ* SFG Spectroscopy	p. 12
19:00 - 21:00	Banquet	

October 27, 2018		
Saturday Session 1	chair: Tahei Tahara	
9:00 - 9:40	**Heather Allen** (Ohio State Univ) Aqueous Surfaces of Selected Salts	p. 13
9:40 - 10:10	**Akihiro Morita** (Tohoku Univ) Theory of $\chi^{(3)}$ Effect in Sum Frequency Generation Spectroscopy	p. 14
10:10 - 10:30	Coffee Break	
Saturday Session 2	chair: Shoichi Yamaguchi	
10:30 - 11:00	**Eric Tyrode** (KTH Royal Inst Tech) Do Monovalent Anions Preferentially Adsorb to Extended Hydrophobic Surfaces Exposing Methyl Groups?	p. 15
11:00 - 11:30	**Taka-aki Ishibashi** (Univ of Tsukuba) Chiral VSFG Spectroscopy of Polylactic Acid Films	p. 16
11:30 - 12:00	**Toshiki Sugimoto** (Inst Mol Sci) Stimulating Exotic High-T_c Ferroelectric Proton Order in Heteroepitaxially Grown Ice Films	p. 17
12:00 - 13:00	Lunch Break	
Saturday Session 3	chair: Kazuya Watanabe	
13:00 - 13:40	**Gen Sazaki** (Hokkaido Univ) In-situ Observation of Quasi-Liquid Layers on Ice Crystal Surfaces by Advanced Optical Microscopy	p. 18
13:40 - 14:10	**Tatsuya Ishiyama** (Toyama Univ) Structure and Vibrational Spectra at Complex Aqueous Interfaces Revealed by Molecular Dynamics Simulation	p. 19
14:10 - 14:40	**Takayuki Miyamae** (AIST) Direct Probing Carrier Behavior in Highly-Efficient OLEDs by Electric-Field-Induced Doubly-Resonant SFG Spectroscopy	p. 20
14:40 - 15:00	Coffee Break	
Saturday Session 4	chair: Shen Ye	
15:00 - 15:30	**Yukio Ouchi** (Tokyo Inst Tech) IV-SFG Studies on the Effect of Li$^+$ in Extending the Electrochemical Window at Pt/RTIL Interface	p. 21
15:30 - 16:00	**Marie-Pierre Gaigeot** (UEVE Paris) Aqueous Interfaces Simulated by Ab Initio Molecular Dynamics, Making the Link between Structure and SFG Spectroscopy	p. 22
16:00 - 16:30	**Satoshi Nihonyanagi** (RIKEN) HD-VSFG Spectroscopic Study of Buried Solid Liquid Interfaces	p. 23
16:30 - 16:35	Closing Remark by Yukio Ouchi	

Sum-Frequency Spectroscopy on Crystalline Solid Surfaces

Y. Ron SHEN
Physics Department, University of California, Berkeley, CA
and Physics Department, Fudan Univeristy, Shanghai
email: yrshen@berkeley.edu

Surface-specific sum-frequency vibrational spectroscopy (SFVS) has been proven a most viable tool for probing surfaces and interfaces. Specifically, it is unique in applications to surface/interface of neat bulk materials. Many successful examples on liquids and polymeric materials can be found in the literature, but surface studies of crystalline solids have been relatively rare. This talk provides a brief review on the latter topic, with comments on both successes and failures, as well as difficulties that are yet to be overcome.

SFVS allows detection of surface phonons of a crystal that often have a spectrum different from the bulk phonons. This has been experimentally demonstrated for diamond[1] and a number of oxides.[2,3] From the surface phonon spectrum, the surface structure of the crystal could be deduced. For ice[4] and organic solids, unfortunately, the surface phonon and bulk phonon spectra generally do overlap, and extra effort is needed to try to separate the two. At present, SFVS studies on crystalline surfaces are limited to solids composed of light elements, such as oxides. Extension to solids composed of heavy elements, such as semiconductors, is compelling, especially for buried interfaces. Surface phonon dynamics and interfacial reaction studies will also be interesting. Future prospects in the field will be discussed.

References

1. R. P. Chin et al, *Phys. Rev. B* **52**, 5985 (1995).
2. W.T. Liu and Y. R. Shen, *Phys. Rev. Lett.* **101**, 0116101 (2008).
3. Y. Cao et al, *Sci. Advances* **2**, e1601162 (2016).
4. X. Wei et al, *Phys. Rev. Lett.* **86**, 1554 (2001); *Phys. Rev. B* **66**, 085401 (2002).

Catching Ultrafast Reactions at the Water Surface by Femtosecond Time-Resolved HD-VSFG Spectroscopy

Tahei TAHARA
Molecular Spectroscopy Laboratory, RIKEN, Japan
Ultrafast Spectroscopy Research Team, RIKEN Center for Advanced Photonics (RAP), Japan
E-mail: tahei@riken.jp

Liquid interfaces are unique environments where a variety of important molecular processes take place. However, our understanding of the properties of interfacial molecules is still limited. In particular, ultrafast dynamics at the liquid interface is largely veiled although several pioneering time-resolved VSFG studies have been reported. The problem of the time-resolved homodyne VSFG is that it can only provide the pump-induced change of $|\chi^{(2)}|^2$ ($\Delta|\chi^{(2)}|^2$):

$$\Delta|\chi^{(2)}|^2 = |\chi^{(2)}{}_{\mathrm{steady}} + \Delta\chi^{(2)}(t)|^2 - |\chi^{(2)}{}_{\mathrm{steady}}|^2 = 2\,\mathrm{Re}\{\chi^{(2)}{}_{\mathrm{steady}}\cdot\Delta\chi^{(2)}(t)^*\} + |\Delta\chi^{(2)}(t)|^2.$$

This quantity is so complicated that it is very difficult to interpret the time-resolved VSFG spectra measured with homodyne detection.

The drawbacks of traditional homodyne VSFG are solved by heterodyne detection that can determine the phase and amplitude of the sum-frequency signals, and heterodyne-detected VSFG (HD-VSFG) provides $\mathrm{Im}\chi^{(2)}$ spectra that can be directly compared to the absorption spectra (i.e., $\mathrm{Im}\chi^{(1)}$) in solution. Similarly, time-resolved HD-VSFG provides $\Delta\mathrm{Im}\chi^{(2)}$ spectra which correspond to time-resolved infrared absorption spectra ($\Delta\mathrm{Im}\chi^{(2)}$) in solution. Actually, we have realized infrared-pumped femtosecond time-resolved HD-VSFG and 2D HD-VSFG and clarified ultrafast vibrational dynamics of interfacial water [1].

Recently, we developed UV-excited time-resolved HD-VSFG spectroscopy that enables us to investigate reaction dynamics at the liquid interface. In this presentation, I will talk about our studies on hydrated electrons [2] and photochemical reaction of phenol [3] at the air/water interface using this novel interface-selective ultrafast spectroscopy.

References

1. S. Nihonyanagi, S. Yamaguchi and T. Tahara, *Chem. Rev.* **117**, 10665-10693 (2017).
2. K. Matsuzaki, R. Kusaka, S. Nihonyanagi, S. Yamaguchi and T. Tahara, *J. Am. Chem. Soc.* **138**, 7551-7557 (2016).
3. R. Kusaka, S. Nihonyanagi and T. Tahara, *in preparation*.

Tahei TAHARA

1989	D. Sc., Department of Chemistry, University of Tokyo
1989	Research Associate, Department of Chemistry, University of Tokyo
1990	Research Associate, Kanagawa Academy of Science and Technology
1995	Associate Professor, Institute for Molecular Science
2001	Chief Scientist, RIKEN

Orientation of the free O-H Group Revealed by Combined SFG Simulation and Experiment

Yuki NAGATA

Max Planck Institute for Polymer Research, Mainz, Germany

E-mail: nagata@mpip-mainz.mpg.de

At the interface of water with hydrophobic media, the hydrogen-bond (H-bond) network of water is interrupted, making the O-H groups of the topmost interfacial water molecules dangling (free) from the H-bond network. The free O-H SFG response measured with *ssp* and *ppp* polarization combinations provides information about their orientation, by assuming the Gaussian-shaped or stepwise function-shaped distribution of the free O-H orientation. The estimated average angle of the free O-H group and surface normal was 30-40^0 [1,2]. Independently, we computed the orientation of the free O-H group from molecular dynamics simulations using the optimized geometrical definition for the free O-H group [3]. Surprisingly, these simulations predict an average angle formed by the free O-H group and the surface normal to be ~63^0, much larger than the previously estimated values of 30-40^0. This discrepancy casts doubts on either the quality of the water force field model or the assumption of the Gaussian/stepwise shaped orientational distribution of the free O-H groups. Here, by combining simulation and experiment, we unveil the orientational distribution of the free O-H group at the water-air interface. Our data suggests that the distribution is broad and exponentially shaped, rather than narrow Gaussian/stepwise shaped [4]. We discuss the sensitivity of the free O-H SFG feature to the average angle and present a physical argument for the existence of a broad orientational distribution, in particular, the free O-H groups pointing *down* to the bulk.

References

[1] X. Wei and Y. R. Shen, Phys. Rev. Lett. **86**, 4799 (2001).
[2] W. Gan, D. Wu, Z. Zhang, R. R. Feng, and H. F. Wang, J. Chem. Phys. **124**, 114705 (2006).
[3] F. Tang, T. Ohto, T. Hasegawa, W. J. Xie, L. Xu, M. Bonn, and Y. Nagata, J. Chem. Theory Comput. **14**, 357 (2018).
[4] S. Sun, F. Tang, S. Imoto, D. R. Moberg, T. Ohto, F. Paesani, M. Bonn, E. H. G. Backus, and Y. Nagata, submitted.

Yuki NAGATA

2002	BS, Department of Chemical System Engineering, University of Tokyo
2004	MS, Department of Chemical System Engineering, University of Tokyo
2007	PhD, Department of Chemistry, Kyoto University
2007-2009	BASF SE (Ludwigshafen, Germany)
2009-2011	Postdoc, University of California, Irvine (Prof. Shaul Mukamel)
2011-	Group Leader at Max Planck Institute for Polymer Research
2016-2018	Visiting Associate Professor at Institute for Molecular Science

Measuring Acid-Base Interactions using Surface Sensitive Spectroscopy and Its Relationship with Adhesion

Ali DHINOJWALA

Department of Polymer Science, The University of Akron

E-mail: ali4@uakron.edu

The work of adhesion has important implications in interfacial science. I will discuss how we can use the shift of the surface hydroxyl peak to determine the enthalpy of interaction and consequently the work of adhesion. Will discuss experimental measurements for several liquids (strong base and acids) and polymers in contact with high energy sapphire substrate. The relationship between the shift and strength of acid-base interactions will be presented in context with Drago-Wayland and Fowkes approach. These results provide important insights into understanding adhesion, friction, wetting, and self assembly.

Growth of ice film on Rh(111) studied by sum-frequency generation

Kazuya WATANABE
Department of Chemistry, Graduate School of Science, Kyoto University
E-mail: kw@kuchem.kyoto-u.ac.jp

Water adsorption on well-defined metal surface has attracted considerable attention for many years. Close packed metal surfaces have been used as templates to grow ice films, paving the way for the study of ice surface structure and reactivity.[1] Despite numerous efforts by using sophisticated surface science techniques under ultra-high vacuum (UHV) conditions, our knowledges on the structure of thin ice films on metal substrates is still scant. The complexity arises from the fact that typical water-metal adsorption energy is close to those of intermolecular hydrogen bonding, leading to a delicate balance among different growth modes of ice films, which depends on chemical identity and structure of metal surface.

In this talk, our recent study on ice film growth on Rh(111) by using a phase-sensitive sum-frequency generation technique under an UHV[2,3] will be described. The Rh(111) surface has a hexagonal atomic arrangement with lattice spacing close to (3% greater than) the lateral spacing of bulk ice Ih, providing an interesting platform for studying the effect of substrate on epitaxial ice growth. While the first layer wets the surface with hexagonal commensurate arrangement, further growth of crystalline ice occurs with Stranski-Krastanov (SK) mode at 135 K.[4] Although the surface of thus grown multilayer ice has been believed to be close to that of bilayer terminated basal plane of ice Ih, details on structural evolution during the SK growth remains to be elucidated. We have reported on a bipolar shape O-H stretching band of HOD multilayer ice on Rh(111), which has been attributed to a manifestation of a subsurface relaxation at the ice/vacuum interface.[5] Here we focus on a growth mechanism of the multilayer crystalline ice on Rh(111) based on a systematic measurement of coverage dependence of the OH band from the first bilayer to multilayer crystalline ice.

References

1. A. Hodgson and S. Haq, *Surf. Sci. Rep.* **64**, 381-451 (2009).
2. K. Watanabe, K.-i. Inoue, I. F. Nakai, and Y. Matsumoto, *Phys. Rev. B.* **81**, 241408 (2010).
3. K.-i. Inoue, K. Watanabe, T. Sugimoto, Y. Matsumoto, and T. Yasuike, *Phys. Rev. Lett.,* **117**, 186101 (2016).
4. A. Beniya, Y. Sakaguchi, T. Narushima, K. Mukai, Y. Yamashita, S, Yoshimoto, and J. Yoshinobu, *J. Chem. Phys.* **130**, 034706 (2009).
5. Y. Otsuki, T. Sugimoto, T. Ishiyama, A. Morita, K. Watanabe, and Y. Matsumoto, *Phys. Rev. B* **96**, 115405, (2017).

Kazuya WATANABE

1997	PhD, Department of Applied Physics, Osaka University
1997	Research Associate, Institute for Molecular Science
1999	Research Associate, Graduate School for Advanced Studies
2004	Research Associate, Institute for Molecular Science
2007	Associate Professor, Department of Chemistry, Kyoto University

Surface Structure of Ice I_h Revealed by HD-SFG Spectroscopy

Shoichi YAMAGUCHI

Department of Applied Chemistry, Graduate School of Science and Engineering, Saitama University

E-mail: shoichi@apc.saitama-u.ac.jp

On ice surfaces, there still remain a lot of intriguing physicochemical problems such as proton ordering, quasi-liquid layer, hydrogen-bond dynamics, etc. However, ice is a very challenging material due to its high vapor pressure that hinders the use of some ultrahigh vacuum techniques conventionally used in surface science. Sum frequency generation (SFG) spectroscopy is known as a powerful tool to interrogate surfaces and interfaces in ambient conditions. Shen and co-workers first applied SFG to the basal face of ice I_h and studied surface melting. They measured the temperature dependence of the vibrational $|\chi^{(2)}|^2$ spectra of free OH ($\chi^{(2)}$: second-order nonlinear optical susceptibility) and found that surface disordering sets in around 200 K.[1] Shultz and co-workers obtained the $|\chi^{(2)}|^2$ spectra of the prism as well as basal faces of ice I_h and discussed the vibrational assignments of hydrogen-bonded OH bands.[2] Sugimoto *et al.* investigated proton ordering in an ice film heteroepitaxially grown on a metal surface using heterodyne-detected (HD-) SFG that allows for measuring the imaginary part of $\chi^{(2)}$ (Im $\chi^{(2)}$).[3] Bonn *et al.* reported a stepwise weakening of the hydrogen bond at ice surfaces as a function of temperature using SFG and molecular dynamics (MD) simulations.[4] For neat ice surfaces grown from liquid water, HD-SFG experiments were first reported in 2017 by the Bakker group[5] and my group,[6] which showed 90° phase difference in complex $\chi^{(2)}$ spectra against each other. In the symposium, I will discuss surface structure of ice I_h on the basis of new experimental data (Figure 1) and theoretical modeling.

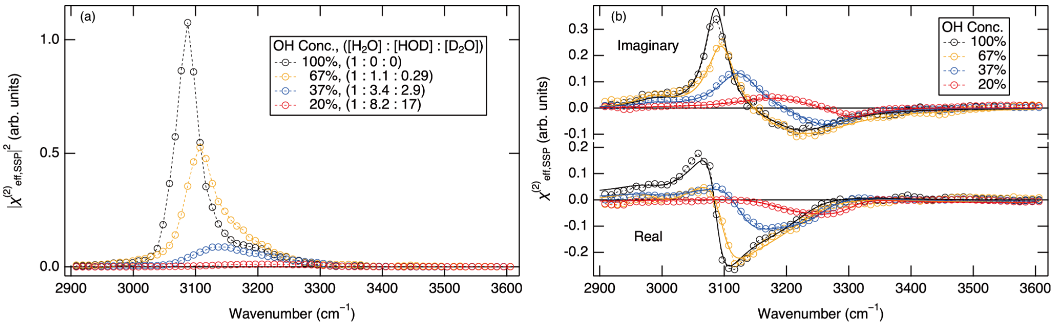


Figure 1. SFG spectra of the basal faces of isotopically-diluted ice I_h by the conventional (a) and heterodyne (b) detection.

References

1. X. Wei, P. B. Miranda, and Y. R. Shen, *Phys. Rev. Lett.* **86**, 1554-1557 (2001). 2. P. J. Bisson and M. J. Shultz, *J. Phys. Chem. A* **117**, 6116-6125 (2013). 3. T. Sugimoto *et al.*, *Nature Phys.* **12**, 1063-1068 (2016). 4. M. A. Sánchez *et al.*, *Proc. Natl. Acad. Sci. USA* **114** (2), 227-232 (2017). 5. W. J. Smit *et al.*, *J. Phys. Chem. Lett.* **8**, 3656-3660 (2017). 6. Y. Nojima, Y. Suzuki, M. Takahashi, and S. Yamaguchi, *J. Phys. Chem. Lett.* **8**, 5031-5034 (2017).

Shoichi YAMAGUCHI

1990	BS, Department of Physics, University of Tokyo
1992	MS, Department of Physics, University of Tokyo
1992	Research Associate, Kanagawa Academy of Science and Technology
1995	Research Associate, Graduate School of Arts and Science, University of Tokyo
1998	Researcher, Yokohama Research Center, Mitsubishi Chemical Co.
1998	PhD, Department of Chemistry, University of Tokyo
2002	Researcher, Molecular Spectroscopy Laboratory, RIKEN
2014	Professor, Department of Applied Chemistry, Saitama University

An Interesting Twist in Liquid Water

Masakazu MATSUMOTO

Research Institute for Interdisciplinary Science, Okayama University

E-mail: vitroid@gmail.com

When liquid water is cooled below its freezing point, it gradually changes its structure into a more ordered less dense state. The state is often expressed as "ice-like", but this change does not originate in the formation of ice but reflects the emergence of the ordered liquid, namely low-density liquid water (LDL). In order to distinguish LDL from ice, we define a simple (but practically a complex number) order parameter called *bond twist*, [1] defined for each hydrogen bond in the following formula:

$$\chi_{\mathrm{B}} = \frac{1}{MN}\sum_{i}^{M}\sum_{j}^{N} \exp 3i\theta_{ij},$$

where θ_{ij} is a dihedral angle containing the given hydrogen bond. In ice, each end of a given hydrogen bond has three other hydrogen bonds connected, i.e., $M = N = 3,$ and therefore there are nine dihedral angles at the given hydrogen bonds (Fig. 1). χ_{B} is an average of the "twists" of nine dihedral angles. Its absolute value is close to unity when both ends of the given hydrogen bond are in regular tetrahedral configuration, while it is close to zero when the structure is distorted and the dihedral angles are randomly distributed. The imaginary part of χ_{B} indicates the twist at a bond (Figure 2). The structures of normal water, supercooled water, and ices can be identified by their χ_{B} distributions. In this talk, I will demonstrate the structural difference in bulk liquid water, ices, and water in the vicinity of liquid-solid and liquid-vapor interfaces.

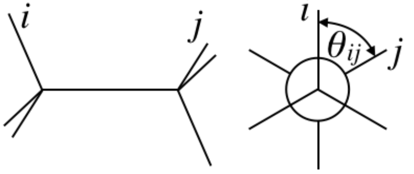


Figure 1. Dihedral angles at a hydrogen bond.

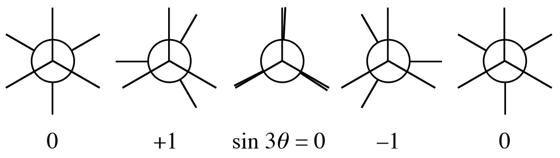
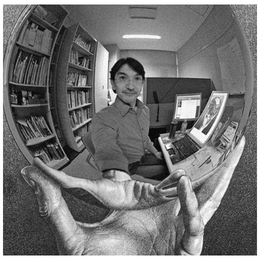


Figure 2. sin 3θ of a dihedral angle indicates the twist.

References

1. M. Matsumoto, T. Yagasaki, and H. Tanaka, Phys. Rev. Lett. **115**, 197801 (2015).



Masakazu MATSUMOTO

1990 B. Eng., Department of Industrial Chemistry, Faculty of Engineering, Kyoto University.
1992 M. Eng., Department of Molecular Engineering, Kyoto University
1996 Ph.D., Department of Structural Molecular Science, The Graduate University for Advanced Studies (SOKENDAI)
1996 Assistant Professor, Department of Chemistry, Nagoya University
2010 Associate Professor, Department of Chemistry, Okayama University
2016 Associate Professor, Research Institute for Interdisciplinary Science, Okayama University

Vibrational dynamics at the solid-liquid interface

Ellen BACKUS

Department for Molecular Spectroscopy, Max Planck Institute for Polymer Research, Mainz

Department of Physical Chemistry, University of Vienna

E-mail: backus@mpip-mainz.mpg.de

The interaction of water with minerals like calcium fluorite (CaF_2) and silica (SiO_2) is relevant for industrial, environmental and medical applications. At the interface between the solid and water, the properties of water may be drastically different from those observed in the bulk. For water at polar solids, i.e. at mineral surfaces, the charge at the surface as well as the polar groups can give rise to specific hydrogen bonds and water alignment through strong electrostatic interactions. Characterizing these mineral/water interfaces on a molecular level is crucial for understanding the adsorption and reaction of water on the mineral surface. Here, we use besides phase-resolved sum frequency generation, time-resolved spectroscopy to shed light on the interaction of water with these important surfaces. We vibrationally excite specific subgroups of water molecules at the interface and record their vibrational lifetime and/or reorientation time. The results are discussed with the help of simulations.

Ellen BACKUS

2000	MS, Department of Chemistry, University of Amsterdam
2005	PhD, Department of Chemistry, Leiden University
2006	PostDoc, Department of Chemistry, University Zurich
2008	PostDoc, AMOLF, Amsterdam
2012	Groupleader, Max Planck Institute for Polymer Research, Mainz
2018	Professor, Department of Physical Chemistry, University of Vienna

Electrode/Electrolyte Interface Studied by *in situ* SFG Spectroscopy

Shen YE

Department of Chemistry, Graduate School of Science, Tohoku University

E-mail: ye.shen@tohoku.ac.jp

As an important rechargeable battery, Li-ion batteries are widely used as power sources for portable electric devices due to their high capacity and output voltage.[1-3] Typically, the mixed cyclic carbonates (such as PC and EC) and linear carbonates (such as DME and DEC) with Li-salt are used as electrolyte solutions in the commercial Li-ion batteries.[1-3] It is extremely important to understand the structures at the electrode/electrolyte interface where the charging / discharging reactions occur. The structures can significantly affect the reversibility and the capacity fading cycling of the Li-ion batteries. As a 2nd-order nonlinear optical technique, sum frequency generation (SFG) vibrational spectroscopy is highly selective and sensitive to the structures on the surface and interface. By using this technique, we have systematically investigated the adsorption structure of the carbonates solvents on the surfaces of $LiCoO_2$ cathode[4-5] and carbon anode,[6] for Li-ion battery. It was found that the cyclic carbonates seem to be preferentially adsorbed on these electrode surfaces in comparison to linear carbonates. Furthermore, the adsorption of vinylene carbonates (VC) and fluoroethylene carbonates (FEC), which are commonly used as additives in the electrolyte solutions of the Li-ion battery, were also evaluated. The roles of the additives in the formation of the solid electrolyte interphase (SEI) will be discussed in comparison with that of the organic carbonate solvents.

Our recent *in situ* SFG studies on the oxygen reduction and evolution reactions (ORR/OER) on a well-defined graphene electrode surface in nonaqueous solutions, which are basis for the cathode reactions in the Li-O_2 battery, will also be reported if time permits.

References

1. K. Xu, *Chem.Rev.* **104**, 4303 (2004).
2. K. Xu, *Chem.Rev.* **114**, 11503 (2014)
3. D. Aurbach, *J. Power Sources* **89**, 206 (2000).
4. H. Liu, Y. Tong, N. Kuwata, M. Osawa, J. Kawamura, S. Ye, *J. Phys. Chem. B.* **113**, 20531(2009).
5. L. Yu, Y. Wang, N. Kuwata, M. Osawa, J. Kawamura. S. Ye, *Anew. Chem. Int. Ed.* **52**, 5753 (2013).
6. Q. Peng, H. Liu, S. Ye, *J. Electroanal. Chem.* **800**, 134 (2017).

Shen YE

1993	PhD, Department of Chemistry, Hokkaido University
1993	Staff, Department of Chemistry, Hokkaido University
1994	Assistant Professor, Department of Chemistry, Hokkaido University
2001	Associate Professor, Catalysis Research Center, Hokkaido University
2015	Adjunct Associate Professor, Elements Strategy Initiative for Catalysts and Batteries (ESICB), Kyoto University
2017	Professor, Department of Chemistry, Graduate School of Science, Tohoku University
2017	Adjunct Professor, ESICB, Kyoto University

Aqueous Surfaces of Selected Salts

Heather C. Allen*, Lu Lin, Stephen M. Baumler, Ka Chon Ng

Department of Chemistry and Biochemistry, The Ohio State University

E-mail: allen@chemistry.ohio-state.edu

Ions hydrate in water to form solvated complexes. The nature of their solvation and thus speciation is related to their surface properties and are unique to the salt where the counter ion plays an important role. Organization within the aqueous surface and subsurface regions occurs and gives rise to interfacial electric fields, the surface potential. Current understanding of doubly and triply charged ions at aqueous surfaces is sparse. Here, vibrational sum frequency generation (VSFG), surface potential, and surface tension studies provide insight into the hydrated speciation of selected salts at the air/aqueous interface.

Theory of $\chi^{(3)}$ Effect in Sum Frequency Generation Spectroscopy

Akihiro MORITA

Department of Chemistry, Graduate School of Science, Tohoku University

E-mail: morita@tohoku.ac.jp

When the SFG spectroscopy is applied to liquid interfaces in contact with charged materials, the observed spectra are influenced by so-called "$\chi^{(3)}$ effect." The charge at the interface generates electrostatic field in the liquid, and the penetrated field induces anisotropic molecular orientation in the liquid region. This orientation becomes a source of SFG response, which is called the $\chi^{(3)}$ effect and described with bulk properties of the liquid. The SFG signal of $\chi^{(3)}$ origin is attributed to the diffuse double layer in the liquid, whereas the usual SFG signal of $\chi^{(2)}$ origin arises from the interface at a molecular scale. In order to analyze the interfacial structure with the SFG spectra, understanding of $\chi^{(2)}$ and $\chi^{(3)}$ effects is indispensable.

The present work provides the calculated SFG spectra of water of the $\chi^{(2)}$ and $\chi^{(3)}$ origin separately on the same accuracy. Based on the two spectra, one can define the unambiguous analysis to separate the $\chi^{(3)}$ contribution described with the bulk properties from the observed SFG spectra. The result of the analysis yields the pure $\chi^{(2)}$ contribution, which clarifies interfacial structure at the molecular level. The present work also elucidates the $\chi^{(3)}$ contributions of various polarizations, effect of temperature and electrolyte on the $\chi^{(3)}$, and quantitative comparison of $\chi^{(2)}$ and $\chi(3)$ contributions under various conditions.

This work was performed in collaboration with Dr. Tatsuya Joutsuka at Ibaraki University, Mr. Tomonori Hirano at Tohoku University, and Prof. Michiel Sprik at Cambridge University. It was supported by the Grant-in-Aid "Soft Molecular Systems" from JSPS, Japan.

References

1. T. Joutsuka, T. Hirano, M. Sprik, and A. Morita, *Phys. Chem. Chem. Phys.* **20**, 3040-3053 (2018).
2. T. Joutsuka and A. Morita, *J. Phys. Chem. C* **122**, 11407-11413 (2018).
3. A. Morita, Theory of Sum Frequency Generation Spectroscopy, *Leture Notes in Chemistry*, **97** (2018) Springer.

Akihiro MORITA

1988	BS, Department of Chemistry, University of Tokyo
1990	MS, Department of Multidisciplinary Sciences, University of Tokyo
1992	Research Associate, Department of Chemistry, Kyoto University
1995	Ph. D, Department of Chemistry, Kyoto University
2004	Associate Professor, Institute for Molecular Science
2007	Professor, Department of Chemistry, Tohoku University

Do monovalent anions preferentially adsorb to extended hydrophobic surfaces exposing methyl groups?

Eric Tyrode

Department of Chemistry, KTH Royal Institute of Technology, SE-10044 Stockholm, Sweden

The preferential affinity of selected anions to interfaces exposing organic hydrophobic moieties plays, in connection to the incompletely understood Hofmeister effects, a vital role in a number of complex biological processes. The prototypical model surface for studying ion adsorption has been the air/water interface, where potential effects of the nature of the hydrophobic surface have been neglected. Here, we investigate the interactions of the monovalent anions Cl^-, Br^-, I^-, and SCN^- with a hydrophobic solid surface exposing methyl groups to solution. Molecular information is obtained using vibrational sum frequency spectroscopy by targeting water molecules in the first monolayer as well as the $C\equiv N$ stretch of the adsorbing SCN^- anion. Although the relative affinity for the interface follows the Hofmeister ordering with $SCN^- > I^- > Br^- > Cl^-$, chlorine and bromide are found to be expelled from the interfacial region, with thiocyanate showing a net enrichment. Molecular dynamics simulations of NaSCN solutions at the interface with air and with an alkane monolayer provide additional quantitative insight and confirm the comparatively higher affinity of SCN^- anions to methyl-terminated hydrophobic surfaces.

Chiral VSFG spectroscopy of polylactic acid films

Taka-aki Ishibashi and Masanari Okuno

Division of Chemistry, Faculty of Pure and Applied Sciences, University of Tsukuba

E-mail: takaaki.ishibashi.gn@u.tsukuba.ac.jp

Chiral vibrational sum frequency generation (VSFG) spectroscopy is a new, sensitive spectroscopic tool for detecting chirality.[1] As a second order process, SFG is forbidden in centrosymmetric media under the electric dipole approximation. SFG is often used to selectively observe an interface between two centrosymmetric bulk media since the centrosymmetry is broken at the interface. The chirality of a sample also breaks the centrosymmetry, and therefore can be probed by SFG process. We have developed the first heterodyne-detected (HD) multiplex chiral VSFG spectrometer,[2] and applied it to chiral liquids[2], chiral solution[3], proteins at air-water interfaces,[3] and chiral monolayers on water.[4] Thanks to the heterodyne detection, we can detect the phase of the VSFG signal electric field that carries the information on which chirality the sample has.

Chiral VSFG is applicable to both bulk and isotropic interfaces. The polarization combinations for chiral-specific VSFG measurements are common to bulk and interfacial samples. Therefore, when target molecules locate both in bulk and at an interface, one needs to judge by some means whether a chiral signal is from bulk or interfacial regions. We studied thin films of poly lactic acid, a helical polymer with chirality, on silica substrates by heterodyne-detected chiral VSFG spectroscopy with visible light far from electronic resonances. The enantiomers of polylactic acid films on silica substrates were successfully distinguished, and their chiral VSFG signals were assigned not to bulk but to the interface by comparing chiral signals observed in reflection in the PSP and SPP polarization combinations. The method employed for assigning the source of chiral signals to the bulk or the interface may be useful for organic films on substrates with low refractive indices and thick samples.

References

1. Belkin, M. A.; Shen, Y. R., *Int. Rev. Phys. Chem.*, **24**, 257 (2005).
2. M. Okuno, T. Ishibashi, *J. Phys. Chem. Lett.* **5** (2014) 2874.
3. M. Okuno, T. Ishibashi, *Anal. Chem.* **87** (2015) 10103.
4. M. Okuno, T. Ishibashi, *J. Phys. Chem. C* **119** (2015) 9947.
5. M. Okuno, D. Ishikawa, W. Nakanishi, K. Ariga, T. Ishibashi, *J. Phys. Chem. C*, **121**, 11241 (2017).

Taka-aki ISHIBASHI

1986 BS, Department of Chemistry, The University of Tokyo
1988 MS, Department of Chemistry, The University of Tokyo
1990 Research Associate, Kanagawa Academy of Science and Technology (KAST)
1997 Research Associate, Graduate School of Science, The University of Tokyo
1999 Research Project sub-leader, Kanagawa Academy of Science and Technology (KAST)
2004 Associate Professor, Department of Chemistry, Hiroshima University
2012 Professor, Division of Chemistry, University of Tsukuba

Stimulating exotic high-T_c ferroelectric proton order in heteroepitaxially grown ice films

Toshiki SUGIMOTO
Department of Materials Molecular Science, Institute for Molecular Science,
E-mail: toshiki-sugimoto@ims.ac.jp

Materials with a strongly correlated and highly frustrated degree of freedom have potential for exhibiting dramatic and unusual responses to external stimuli. In the case of common water ice, protons in the hydrogen-bond network are strongly correlated and highly frustrated under the Bernal-Fowler-Pauling ice rules. The ubiquity of water ice makes it essential to clarify the fundamental physicochemical properties of the strongly correlated many-body proton system. It is, however, extremely difficult to directly access the local configuration of protons and their ordering dynamics through traditional experimental approaches. Moreover, the strongly correlated protons inevitably lose ergodicity at low temperature. These problems prevent us from fully understanding cooperative thermodynamic and electric responses of the many-body protons to external stimuli at the low temperature[1]. Unveiling and controlling the deeply hidden protonic ordered states in crystalline ice have thus been a longstanding challenge in the physical chemistry of ice [1].

To open up a new route to unveil hidden exotic properties of many-body protons in ice, we have investigated a possibility of interface-induced ferroelectric proton ordering [2-4] by focusing on heteroepitaxially grown crystalline-ice films on Pt(111) and Rh(111) substrates as model systems [5,6,7]. Using SFG technique, we have succeeded in directly demonstrating that the adsorbed first-layer water molecules prefer an net-H-down configuration on Pt(111) [2,4]. The coverage dependence of the Im$\chi^{(2)}$ SFG spectra in the hydrogen-bonded OH stretching regions clearly reveals that the H-down proton ordering in the first layer is significantly pinned by the Pt(111) substrate and is subsequently propagated to the overlayer during the multilayer film growth. Temperature dependent SFG measurement revealed that such a ferroelectric proton ordering is thermodynamically stable and has an extremely high critical temperature of ~175 K [2,4], which is more than twice as large as that of ferroelectric bulk ice XI (T_c~72 K). In addition to these results, I will discuss in details our recent challenges on the interface engineering for modulation of the ferroelectric proton ordering.

References

[1] C. G. Salzmann, et al. *Science* **311**, 1758 (2006); *Phys. Chem. Chem. Phys.* **13**, 18468 (2011).
[2] T. Sugimoto et al., *Nature Phys.* **12**, 1063 (2016). [3] Y. Otsuki, T. Sugimoto et al. *Phys. Rev. B* **96**, 115405 (2017). [4] N. Aiga, T. Sugimoto et al. *Phys .Rev. B* **97**, 075410 (2018);
[5] X. Su et al. *Phys. Rev. Lett.* **80**, 1533 (1998). [6] A. Hodgson et al. *Surf. Sci. Rep*. 64, 381 (2009).
[7] Detailed results on Rh(111) will be presented at this symposium by my coworker: Kazuya Watanabe.

Toshiki SUGIMOTO

2011	PhD, Department of Applied Physics, The University of Tokyo.
2011	Post-doc, Department of Applied Physics, The University of Tokyo.
2012	Assistant Professor, Department of Chemistry, Kyoto University.
2016	JST -PRESTO researcher.
2018	Associate Professor, Department of Materials Molecular Science, IMS.

In-situ Observation of Quasi-Liquid Layers on Ice Crystal Surfaces by Advanced Optical Microscopy

Gen SAZAKI

Institute of Low Temperature Science, Hokkaido University

E-mail: sazaki@lowtem.hokudai.ac.jp

The phase transition of ice crystals governs a wide variety of phenomena on the earth. Hence, the molecular level understanding of the phase transition of ice is crucial to unlock the secrets of various phenomena. To visualize ice crystal surfaces at the molecular level, we and Olympus Corporation developed advanced optical microscopy: laser confocal microscopy combined with differential interference contrast microscopy (LCM-DIM) [1], which can visualize individual elementary steps (0.37 nm in height) on ice crystal surface [2]. By using LCM-DIM, we observed in-situ ice crystal surfaces under various conditions. In the symposium, we will show the following two topics.

1) Thermodynamic origin of two-types of quasi-liquid layers (QLLs) with different morphologies (droplets and thin layers) [3]: with increasing water vapor pressure, the wettability between QLLs and ice crystal surfaces become significantly better, resulting in the changes in the wetting states from partial wetting (droplets) to pseudo-partial wetting (the coexistence of droplets and thin layers). The thickness of the thin layers agrees with the value predicted by the quantum theory calculation [4].

2) Novel uptake mechanism of HCl in ice crystals as HCl droplets [5]: HCl gas is adsorbed on ice crystal surfaces, and droplets of a HCl aqueous solution appear on the ice crystals surfaces. As the ice crystals grow, the HCl droplets are embedded in the ice crystals. This novel uptake mechanism allows ice crystals to store ten-times larger amount of HCl in ice crystals than the solubility of HCl in ice crystals.

References

[1] G. Sazaki, T. Matsui, K. Tsukamoto, N. Usami, T. Ujihara, K. Fujiwara, K. Nakajima, *J. Cryst. Growth*, **262**, 536-542 (2004).
[2] G. Sazaki, S. Zepeda, S. Nakatsubo, E. Yokoyama, Y. Furukawa, *Proc. Nat. Acad. Sci. USA.*, **107**, 19702-19707 (2010).
[3] K. Murata, H. Asakawa, K. Nagashima, Y. Furukawa, G. Sazaki, *Proc. Nat. Acad. Sci. USA.*, **113**, E6741-E6748 (2016).
[4] M. Elbaum, M. Schick, *Phys. Rev. Lett.*, **66**, 1713-1716 (1991).
[5] K. Nagashima, G. Sazaki, T. Hama, K. Murata, Y. Furukawa, *Cryst. Growth Des.,* **18**, 4117-4122 (2018).

Gen SAZAKI

1994	Ph.D., Department of Applied Chemistry, Osaka City University
1994	Research Associate, Institute for Materials Research, Tohoku University
2001	Lecturer, Institute for Materials Research, Tohoku University
2007	Specially Appointed Professor, Osaka University
2007	Researcher, Instituto Andalz de Ciencias de la Tierra
2008	Associate Professor, Institute of Low Temperature Science, Hokkaido University
2012	Professor, Institute of Low Temperature Science, Hokkaido University

Structure and Vibrational Spectra at Complex Aqueous Interfaces Revealed by Molecular Dynamics Simulation

Tatsuya ISHIYAMA

Department of Applied Chemistry, Graduate School of Science and Engineering, University of Toyama

E-mail: ishiyama@eng.u-toyama.ac.jp

Molecular dynamics (MD) simulation is now very powerful tool to unveil aqueous interfacial structures. The simulation studies combined with vibrational sum frequency generation spectroscopy have opened a new avenue in the study of interfacial molecular structure. Here we focus on water structure at complex aqueous interfaces, such as lipid interfaces and polymer interfaces.

Specific cation effect at aqueous solution/phospholipid interfaces: Function of biological membrane mainly consisting of phospholipid molecules is influenced by water and solvated ions contacting with it. In particular, the specific interaction of cations near the bilayer headgroups has a strong effect on structure, dynamics, and stability of the membranes. In this talk, molecular structures at zwitterionic phospholipid/aqueous KCl, NaCl, and $CaCl_2$ solution interfaces are discussed on the basis of MD simulation that reproduces experimentally observed interface-specific vibrational spectra[1].

Water structure at acrylate polymer interfaces: Biocompatibility of polymer is one of the crucial characteristic for biomedical application. Poly(2-methoxyethylacrylate) (PMEA) is known as the biocompatible (blood compatible, hemocompatible) materials that show low adsorption of proteins with low denaturation. Water-polymer interaction has been recognized to be vital for predicting the biocompatibility, because biological activity usually appears in aqueous environments. Here we focus on interfacial structure between water phase and solid polymers such as PMEA and poly(methyl methacrylate) (PMMA) that is less biocompatible than PMEA, particularly focusing on differences of molecular structures at both interfaces in terms of the experimentally measurable interface-specific nonlinear optical spectroscopy[2].

References

1. T. Ishiyama, S. Shirai, T. Okumura, and A. Morita, J. Chem. Phys. **148**, 22801 (2018).
2. S. Kishinaka, A. Morita, and T. Ishiyama, in preparation.

Tatsuya ISHIYAMA

2004	PhD, Department of Mechanical Science, Hokkaido University
2005	Post-doc, Institute for Molecular Science
2007	Assistant Professor, Department of Chemistry, Tohoku University
2014	Lecturer, Department of Applied Chemistry, University of Toyama
2015	Associate Professor, Department of Applied Chemistry, University of Toyama

Direct Probing Carrier Behavior in Highly-Efficient OLEDs by Electric-Field-Induced Doubly-Resonant SFG Spectroscopy

Takayuki MIYAMAE
National Institute of Advanced Industrial Science and Technology (AIST)
E-mail: t-miyamae@aist.go.jp

Currently, organic light-emitting diodes (OLEDs) have attracted significant attention as next-generation full-color display devices and are beginning to be widely used in mobile phones and high-resolution OLED TV sets.1,2) OLEDs also exhibit potential for providing energy savings in a range of applications, including lighting and flexible panel displays. In their structure, OLEDs have a characteristic multilayered structure, where each organic layer has a different function.3) Especially, the interfacial structures and properties of the OLEDs are extremely important in determining their charge carrier behavior, since both the charge transport and the charge densities in organic layers are directly associated with the performance of the OLEDs. Therefore, examination of the carrier activity in OLEDs under operation is required. Recently, we have succeeded in probing buried organic layers in OLEDs during operation by electric-field-induced sum-frequency generation (EFI-SFG) under doubly-resonant condition.4) When a strong DC electric field $\boldsymbol{E}_0$ is applied to the device, it leads to a significant increase in the SFG intensity produced by the internal carriers. Furthermore, we report the direct observation of the carrier behavior in OLEDs by time-resolved EFI-SFG technique.5) The use of this new technique allows us to observe the carrier behavior at the organic interfaces varied with time in response to the applied pulse bias voltage non-destructively.

In this paper, we will report the charge accumulation and transport mechanisms of the highly-efficient phosphorescent green OLEDs and fluorescent blue OLEDs under the operation.

References

1. M. A. McCarthy, B. Liu, E. P. Donoghue, I. Kravchenko, D. Y. Kim, F. So, and A. G. Rinzler, *Science*, **332**, 570 (2011).
2 C. Adachi, *Jpn. J. Appl. Phys.* **53**, 060101 (2014).
3. T. Tsutsui, M. J. Yang, M. Yahiro, K. Nakamura, T. Watanabe, T. Tsuji, Y. Fukuda, T. Wakumoto, and S. Miyaguchi, *Jpn. J. Appl. Phys.* **38**, L1502 (1999).
4. T. Miyamae, N. Takada, and T. Tsutsui, *Appl. Phys. Lett.* **101**, 073304 (2012).
5. T. Miyamae, N. Takada, H. Ohata, and T. Tsutsui, *Appl. Phys. Express*., **10**, 102101 (2017).

Takayuki Miyamae

1990	B. Sc., Department of Chemistry, Faculty of Science, Nagoya University.
1995	Ph. D, Department of Chemistry, Graduate School of Science, Nagoya University.
1995	JSPS Research Fellow, Chiba University and Institute for Molecular Science.
1997	IMS Research Fellow, Institute for Molecular Science.
1999	Research Scientist, National Institute of Materials and Chemical Research
2001	Research Scientist, National Institute of Advanced Industrial Science and Technology.

IV-SFG Studies on the Effect of Li^+ in Extending the Electrochemical Window at Pt/RTIL Interface

Yukio OUCHI

Department of Materials Science and Engineering, Tokyo Institute of Technology,

E-mail: ouchi.y.ab@m.titech.ac.jp

The adsorption/desorption of ions at an electrolyte/electrode interface plays a vital role in the electrochemical reactions used in various applications, including supercapacitors and batteries. In the case of the lithium-ion battery, the formation of a Li dendrite at an anode surface during charging-discharging processes results in a degradation of battery performance due to narrowing of the active area and shunt. Such degradation is known to be suppressed by the formation of a solid electrolyte interphase (SEI) at the anode surface, which is composed of Li precipitated with reduced anion components. Therefore, controlling the electrolyte/electrode interface structure should be highly beneficial to the development of more efficient electrochemical systems. Furthermore, when using room temperature ionic liquids (RTILs) as an electrolyte in lithium batteries, an extension of the electrochemical window (EW) at the negative edge has also been reported[1] when Li^+ is added to the RTIL electrolyte. Several models for the EW extension, including SEI and anion/Li^+ double-layered structure, have been proposed, but the actual mechanism of the EW extension caused by the added Li^+ is still unclear due to lack of information on the microscopic structure of the electrode/ RTIL interface.

In this study, we present the applied potential response of adsorption/desorption behavior of anion at the interface of 1-ethyl-3-methylimidazolium bis(fluorosulfonyl) amide ([C_2mim][FSA] and a Pt electrode, with and without Li^+, using infrared-visible sum-frequency generation (IV-SFG) vibrational spectroscopy[2,3]. The EW extension of >1.0 V at the negative edge is obtained for the Pt | [C_2mim][FSA] system with Li^+. We have found that the $[FSA]^-$ anion at the Pt | [C_2mim][FSA] interface interacts with Li^+ at the interface with the negatively-charged Pt electrode. The $[FSA]^-$ anion layer anchored through Li^+ suppresses $[C_2mim]^+$ cation adsorption on the negatively-charged Pt electrode, resulting in a wider electrochemical window. Pt | [C_2mim][TFSA] system also behaves with a similar manner and the details will be discussed in the presentation.

References

1) M. Yamagata et al, *Electrochim. Acta*, **110**, 181-190 (2013). 2) W. Zhou et al, *Electrochem. Commun.* **12**, 672–675(2010). 3) T. Iwahashi et al, *Electrochem. Commun.* **72**, 54–58(2016).

Yukio OUCHI

1987	Dr. Eng., Department of Organic and Polymeric Materials, Tokyo Institute of Technology
1987	Research Associate, Tokyo Institute of Technology
1990	Visiting Researcher, Department of Physics, UC Berkeley
1992	Associate Professor, Department of Chemistry, Nagoya University
2013	Professor, Department of Materials Science and Engineering, Tokyo Institute of Technology

Aqueous interfaces simulated by Ab Initio Molecular Dynamics, making the link between structure and SFG spectroscopy

Marie-Pierre GAIGEOT

LAMBE UMR 8587, Laboratoire Analyse et Modélisation pour la Biologie et l'Environnement,

Université d'Evry val d'Essonne, Université Paris Saclay, France

E-mail: mgaigeot@univ-evry.fr

In this presentation, we review our recent theoretical works on the characterization of mineral/liquid water & air/liquid water interfaces, making the link between structure and non-linear SFG (Sum Frequency Generation) experiments. Non-linear SFG spectroscopy in the 3000-4000 cm^{-1} spectral domain is one method of choice to probe complex inhomogeneous solid/liquid and liquid/air interfaces. Although an extremely powerful technique, the detailed interpretation of the experimental signatures requires associated calculations. This is the challenge we have been tackling with Ab Initio DFT-based molecular dynamics simulations (DFT-MD).

We will illustrate here some of our recent works showing how to separate vibrational signatures arising from the different layers of water at the interface, how to define the only three spatial regions of interest at any charged interfaces (BIL, Binding Interfacial Layer; DL, Diffuse Layer; Bulk) contributing to SFG, how to provide a direct interpretation of the H-Bond networks at play at interfaces (water-water *vs* solid-water networks), including our recent works unraveling 2-dimensional interfacial water networks. We will also show how our deconvolution schemes for SFG spectral interpretation provide direct knowledge of the isoelectric point at any aqueous surface and direct knowledge of the formation of an Electric Double Layer (EDL) when aqueous ionic solutions are considered at the interface. We will unravel trends in going from hydrophobic to hydrophilic surfaces at the interface with liquid water.

Acknowledgments. Collaborative works with Prof. Y. Ron Shen at the University of California at Berkeley, USA, Prof E. Borguet at Temple University, USA, Dr E. Backus, Max Planck Institute in Mainz, Germany. Works achieved with PhD/Post-Doc students S. Pezzotti, D. Galimberti, M. Pfeiffer-Laplaud, L. Potier, F. Siro Brigiano, A. Cimas. **Works funded by** ANR-DFG DYNAWIN, ANR SLIMCAT 'Stimuler le Renouveau Industriel', Excellence Lab LABEX CHARM$_3$AT.

References

1. S. Pezzotti, D. R. Galimberti, Y. R. Shen, M.-P. Gaigeot, *Minerals*, **8**, 305-321 (2018)
2. S. Pezzotti, A. Serva, M.-P. Gaigeot, *J. Chem. Phys.*, **148**, 174701-10 (2018)
3. S. Pezzotti, D. Galimberti, , Y.R. Shen, M.-P. Gaigeot, *Phys. Chem. Chem. Phys.*, **20**,5190-5199 (2018)
4. S. Pezzotti, D.R. Galimberti, M.-P. Gaigeot, *J. Phys. Chem. Letters*, **8**, 3133 (2017)
5. M. Pfeiffer-Laplaud, M.P. Gaigeot, *J. Phys. Chem. C.*, **120**, 14034 (2016)

Marie-Pierre GAIGEOT

1993	Education in Physics, Master in Physics, University of Toulouse, France
1997	PhD, Theoretical Chemistry Laboratory, CEA Atomic Energy Center, Paris, France
1998	Researcher at the Atomic Energy Center CEA, Paris, France
1999	Assistant Professor, Department of Physics, University Pierre & Marie Curie, Paris VI, Paris, France
2007	Professor, Department of Physics, University Evry val d'Essonne, & Department of Chemistry, University Paris-Saclay, Paris, France

HD-VSFG Spectroscopic Study of Buried Solid Liquid Interfaces

Satoshi NIHONYANAGI

Molecular Spectroscopy Lab, RIKEN

E-mail: nsatoshi@riken.jp

Interfaces between two immiscible phases are closely related with various interfacial phenomena which are crucially important for both fundamental and applied sciences. Vibrational sum frequency generation (VSFG) spectroscopy has been utilized for investigating molecular structure at almost any interfaces including gas/liquid, gas/solid, liquid/liquid, solid/liquid, and solid/solid interfaces. In particular, heterodyne-detection (or phase-sensitive) technique developed in the last decade enables us to measure complex second-order nonlinear susceptibility ($\chi^{(2)}$) spectra, which drastically improve interpretation of VSFG spectra and hence understanding of molecular pictures of interfaces.[1] Heterodyne-detected VSFG (HD-VSFG) spectroscopy developed in our lab employs femtosecond IR source and multiplex detection of broad bandwidth VSFG.[2] This method is very powerful for exposed interfaces such as air/water interface and it can be extended to femtosecond time-resolved measurements. Recently, HD-VSFG has been extended to buried solid/liquid interfaces.[3] This makes it possible to measure $\chi^{(2)}$ spectra of various functional-material interfaces constructed on solid supports such as photo-catalysts, functional polymers, lipid bilayer, etc. Using this, now we are trying to elucidate fundamental molecular mechanisms of various interfacial phenomena which are important in applied sciences.

In the present talk, first I will explain technical background of HD-VSFG measurements for buried interfaces showing the results on the water structure at silica/water interface as an example. Second, I will discuss a structure-function relation of a bio-compatible polymer / water interface. Finally, I will show the possibility of HD-VSFG measurements of electrode/electrolyte solution interfaces.

References

1. Y. R. Shen, *Ann. Rev. Phys. Chem.* **64**, 129-150 (2013).
2. S. Nihonyanagi, J. A. Mondal, S. Yamaguchi, T. Tahara, *Ann. Rev. Phys. Chem.* **64**, 579-603 (2013).
3. A. Myalitsin, S. Urashima, S. Nihonyanagi, S. Yamaguchi, T. Tahara, *J. Phys. Chem. C* **120**, 9357-9363 (2016).

Satoshi Nihonyanagi

1999	BS, Department of Chemistry, Hokkaido University
2001	MS, Department of Chemistry, Hokkaido University
2004	PhD, Department of Chemistry, Hokkaido University
2004	Postdoctoral Researcher, Department of Chemistry, Temple University
2007	Special Postdoctoral Researcher, Molecular Spectroscopy Lab, RIKEN
2011	Research Scientist (termed), Molecular Spectroscopy Lab, RIKEN
2014	Research Scientist, Molecular Spectroscopy Lab, RIKEN
2016	Senior Research Scientist, Molecular Spectroscopy Lab, RIKEN

Physical Chemistry Laboratory, Department of Applied Chemistry, Saitama University

International Workshop on Quantum Reactive Scattering (QRS2019 Workshop)

July 1-5, 2019 | Theater Room of Saitama University

TOPICS

Gas-phase reactions / Development of quantum methods / Semiclassical approaches / Stereodynamics / Theory of non-adiabatic processes / Potential energy surfaces / Reactions at low and ultra-low temperatures / Gas-surface reactions / Astrochemistry

ORGANIZING COMMITTE

Toshiyuki Takayanagi, Saitama University, Japan (Chairperson)
Tetsuya Taketsugu, Hokkaido University (Vice chairperson)
Shinkoh Nanbu, Sophia University, Japan
Motoyuki Shiga, Japan Atomic Energy Agency, Japan
Kiyoshi Yagi, RIKEN, Japan
Motomichi Tashiro, Toyo University, Japan

Please visit http://gts18.qcweb.jp/qrs.html
Contact: *tako@mail.saitama-u.ac.jp* (T. Takayanagi)

Saitama University

70th
つなげよう未来へ

公益財団法人
鹿島学術振興財団
THE KAJIMA FOUNDATION