

# Molecular Science of Ice



Saturday, May 13th, 2017  
Saitama University

シンポジウム  
氷の分子科学

企画・主催

新学術領域「柔らかな分子系」

埼玉大学

後援

分子科学会

日本化学会

2017年5月13日(土)

埼玉大学 総合研究棟

# ようこそ埼玉大へ

- ・ アクセスは **3** 通り、 全てバス利用.
- ・ (バスは全て後ろから乗って Suica タッチ, 前から降りるときにまたタッチ.)
- ・ JR 京浜東北線・**北浦和**駅から：  
駅西口, モスバーガー前のバス停始発の「埼玉大学行き」利用で約 15 分. 12 分に 1 本.
- ・ JR 埼京線・**南与野**駅から：  
駅西口真ん前のバス停始発のバス (全て可) 利用で約 10 分. 20 分に 1 本.  
または, 線路高架下, 北 200 メートルの南与野駅北入口バス停の「埼玉大学行き」利用で約 10 分. 12 分に 1 本.
- ・ 東武東上線・**志木**駅から：  
駅東口マルイファミリー前のターミナル 4 番バス停始発の「南与野駅西口行き」利用で約 25 分. 30 分に 1 本.

## キャンパスマップ

正門のバス停から総合研究棟まで徒歩 2 分



## はしがき

このたび「氷の分子科学」と題するシンポジウムを、新学術領域「柔らかな分子系」の第22回ワークショップとして、埼玉大学で開催することになりました。氷は最も学際的な研究対象の1つであり、これまでに優れた研究が数多く残されてきました。例えば、マイケル・ファラデーの氷表面の擬似液体層の提案、中谷宇吉郎の人工雪の製作、ライナス・ポーリングの氷結晶の残余エントロピーの見積もりなどは、歴史的にも現代的にも重要な科学の金字塔です。今回ご講演いただく先生方の専門分野は結晶成長学、地球化学、分析化学、理論化学、分子分光学、物性物理学と多岐にわたっていますが、それでもなお氷の分子科学の広大な領域を全てカバーすることはできません。このシンポジウムが、氷というキーワードを共有し各分野で精力的に研究を展開している科学者の真直な議論を行う場となり、さらに未踏領域を開拓する面白い研究を始めるきっかけとなることを願っています。

2017年5月

山口祥一  
森田明弘

## Preface

We are glad to have a symposium entitled "Molecular Science of Ice" at Saitama Univ on Saturday, May 13th, 2017. This is financially supported by Grant-in-Aid for Scientific Research (KAKENHI) on Innovative Area "Soft Molecular Systems" headed by Prof. Tahei Tahara. Ice is an exciting interdisciplinary subject on which a number of great scientific milestones were built – for instance, a quasi-liquid layer on ice surfaces proposed by Michael Faraday, artificial snowflakes first made by Ukichiro Nakaya, residual entropy of ice estimated by Linus Pauling, and so on. Invited speakers in this symposium are from various fields such as crystallography, geochemistry, analytical chemistry, theoretical chemistry, molecular spectroscopy, and condensed matter physics, but the molecular science of ice is still too vast to be fully covered by them. We hope that scientists who energetically study ice in different fields can have fruitful discussion in this symposium to start another interesting and pioneering researches into unknown properties of ice.

Shoichi Yamaguchi  
Akihiro Morita

## シンポジウム「氷の分子科学」 時間割

2017年5月13日(土)

- 12:30 - 12:40 開会の挨拶 山口祥一 (埼玉大)
- 12:40 - 13:20 鍵裕之 (東大) p. 3  
Polymorphs of ice: implications to earth and planetary science
- 13:20 - 14:00 平田聡 (イリノイ大) p. 4  
Ab initio ice, dry ice, and liquid water
- 14:00 - 14:40 藤井朱鳥 (東北大) p. 5  
Infrared spectroscopy of large-sized water clusters
- 14:40 - 15:00 休憩
- 15:00 - 15:40 古川義純 (北大) p. 6  
Adsorption of antifreeze glycoprotein on ice-water interface and its effect for crystal growth kinetics
- 15:40 - 16:20 石山達也 (富山大) p. 7  
Molecular dynamics simulation study of structure and vibrational spectroscopy at ice surface
- 16:20 - 17:00 岡田哲男 (東工大) p. 8  
Designing of analytical methods utilizing functionality of ice and frozen aqueous systems
- 17:00 - 17:40 杉本敏樹 (京大) p. 9  
Emergent high- $T_c$  ferroelectric ordering of strongly correlated and frustrated protons in crystalline-ice film
- 17:40 - 17:50 閉会の挨拶 森田明弘 (東北大)
- 17:50 - 19:30 意見交換会

# Polymorphs of ice: implications to earth and planetary science

Hiroyuki KAGI

*Geochemical Research Center, Graduate School of Science, University of Tokyo*

E-mail: kagi@eqchem.s.u-tokyo.ac.jp

Hydrogen is the most abundant element and water is the third abundant molecular species in the solar system. Evidence for existence of crystalline water ice in the outer solar system has been clarified through infrared observations. On the surface of the earth, more than 95% of water exists as liquid in oceans and about 1.5 % of water exists as ice in glaciers.

If we draw attentions to the interior of earth and planets having wide pressure-temperature ranges, the variety of crystalline ice extends tremendously<sup>1</sup>. So far seventeen polymorphs of ice have been reported from experimental studies<sup>2</sup>. Stability field of ice extends to high-temperature region at high pressure; it was suggested that ice VII may exist in cold subducting slabs<sup>3</sup>. Near infrared spectroscopic analysis suggested ice VI as inclusions in natural diamonds<sup>4</sup>.

Satzmann et al. raised five unsolved questions on the polymorphs of ice<sup>1</sup>, such as disorder-order pairs, salt incorporations into ice structure, and so on. To solve these questions, it is necessary to determine precisely hydrogen positions in crystalline ice at extreme conditions. We have constructed a beamline for neutron diffraction measurements at high-pressure conditions at MLF, J-PARC<sup>5</sup>. Using the facility, we found that partially ordered states are established as a mixture of ordered domains in disordered ice VI<sup>6</sup>. It means that the order–disorder pairs in ice polymorphs are not one-to-one correspondent pairs but rather have one-to-*n* correspondence. Moreover, a salt incorporation process to ice VII has been proposed<sup>7</sup>.

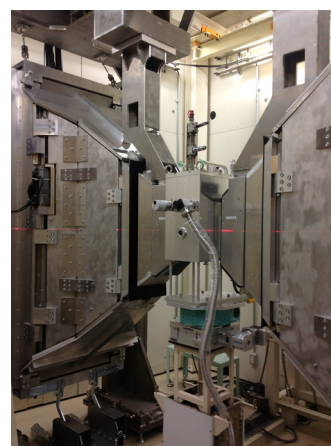


Fig.1 Neutron diffraction measurement system for high pressure and low temperature conditions at MLF, J-PARC

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## Hiroyuki KAGI

1988 BS, Department of Chemistry, University of Tokyo  
1990 MS, Department of Chemistry, University of Tokyo  
1991 Research Associate, Institute of Material Science, University of Tsukuba  
1994 PhD, Department of Chemistry, University of Tokyo  
1996 Visiting Scientist, State University of New York at Stony Brook  
1998 Lecturer, Graduate School of Science, University of Tokyo  
2000 Associate Professor, Graduate School of Science, University of Tokyo  
2010 Professor, Graduate School of Science, University of Tokyo

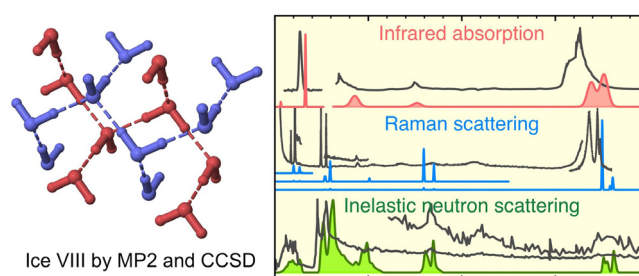
# Ab Initio Ice, Dry Ice, and Liquid Water

So HIRATA

Department of Chemistry, University of Illinois at Urbana-Champaign

E-mail: sohirata@illinois.edu

Simulations of bulk solids and liquids at an accurate *ab initio* theoretical level treating all electrons quantum mechanically have long been unthinkable. We present just such simulations for a whole range of structural, dynamical, thermodynamic and response properties of ice (solid H<sub>2</sub>O phase Ih),<sup>1,2</sup> high-pressure ice (solid H<sub>2</sub>O phase VIII),<sup>3</sup> dry ice (solid CO<sub>2</sub> phase I),<sup>4-7</sup> high-pressure dry ice (solid CO<sub>2</sub> phase III)<sup>7</sup> and liquid water.<sup>8</sup> They have been made possible by combining an algorithmic breakthrough (the embedded-fragmentation technique) with the massively parallel supercomputing power. The calculated properties include structures, equation of state, bulk modulus, thermal expansion, volume isotope effect, heat capacities, pressure tuning of Fermi resonance, infrared, Raman, and inelastic neutron scattering spectra, solid-solid phase transition, amorphization, self-diffusion coefficients, Raman noncoincidence, hydrogen-bond lifetime and reorganization in the liquid, some of which accessible only by predictive high-performance computing.



**Figure 1.** Calculated (color) and observed (grey) IR, Raman, and INS spectra of high-pressure, proton-ordered phase VIII of ice.

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## So HIRATA

1994 B.S., Department of Chemistry, The University of Tokyo  
1996 M.S., Department of Chemistry, The University of Tokyo  
1998 Ph.D., The Graduate University for Advanced Studies & Institute for Molecular Science  
1998 Visiting Scholar, Department of Chemistry, University of California, Berkeley  
1999 Postdoctoral Research Associate, Department of Chemistry, University of Florida  
2001 Senior Research Scientist, Pacific Northwest National Laboratory  
2004 Assistant Professor, Departments of Chemistry and Physics, University of Florida  
2009 Associate Professor, Departments of Chemistry and Physics, University of Florida  
2010 Professor, Department of Chemistry, University of Illinois at Urbana-Champaign

# Infrared Spectroscopy of Large-Sized Water Clusters

Asuka FUJII

*Department of Chemistry, Graduate School of Science, Tohoku University*

E-mail: asukafujii@m.tohoku.ac.jp

The nature of water is governed by its hydrogen bonds (H-bonds), and a variety of H-bond network structures of water have been a subject of great interest. Water clusters,  $(\text{H}_2\text{O})_n$ , enable us to establish a microscopic picture of complicated H-bonded networks. Spectroscopic studies of water clusters, however, have been practically limited to the relatively small-sized region ( $n \leq 10$ ) because of the difficulties in the size selection and spectral analysis. The H-bond networks in this size region are very different from those expected in bulk water. Therefore, spectroscopic studies of the much larger size region have been requested to bridge the gap between the well-known small water clusters and bulk water.

We have applied size-selective infrared (IR) spectroscopy to large-sized water clusters ( $n=20-50$ ) and probed the structural development process of water networks.<sup>1-3</sup> For neutral water clusters, we introduced a phenol molecule as a chromophore for the resonance enhanced multiphoton ionization (REMPI) detection, and we achieved the moderate size-selectivity ( $\Delta n \leq 6$ ) by the modified ultraviolet-infrared double resonance scheme. We observed the spectral change in the H-bonded OH stretch region, and we identified the H-bonded OH stretch band of 4-coordinated water sites, which indicate the growth of the “interior” in the cluster.<sup>3</sup> We also performed IR spectroscopy of large protonated water clusters  $\text{H}^+(\text{H}_2\text{O})_n$  ( $n=20-200$ ) as “charge-labeled” water clusters.<sup>4</sup> Because of the excess proton, the precise size-selection of the large clusters can be achieved by mass spectrometric techniques. The H-bonded OH stretch band of 4-coordinated water sites showed a gradual low-frequency shift in  $n \geq 100$ . This shift is interpreted in terms of the crystallization of the interior of the cluster in this size range. Surface condition of the clusters and its similarity to the bulk water is discussed with the free OH stretch frequency.

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## Asuka FUJII

1987 BS, Department of Chemistry, Tohoku University  
1989 MS, Department of Chemistry, Tohoku University  
1989 Research Associate, Institute for Molecular Science  
1993 Research Associate, Department of Chemistry, Tohoku University  
1993 PhD, Department of Chemistry, Tohoku University  
1996-7 Visiting Scientist, Institute of Atomic and Molecular Sciences, Taiwan  
2002 Associate Professor, Department of Chemistry, Tohoku University



# Adsorption of antifreeze glycoprotein on ice-water interface and its effect for crystal growth kinetics

Yoshinori FURUKAWA

*Institute of Low Temperature Science, Hokkaido University*

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

Fishes living underneath the sea ice never freeze even though their blood is kept in a supercooled state<sup>1</sup>. The reason comes from that the blood contains some special kinds of proteins called as antifreeze glycoproteins (AFGP) or antifreeze proteins (AFP), bio-macromolecules that function as ‘antifreeze’ in living organisms in a subzero environment. These protein molecules adsorb on ice-water interface and control the ice crystal growth. However, there still remain a lot of missing pieces of the puzzle for the growth control mechanism, because the direct observation and measurement of ice-water interfaces are difficult to carry out due to their low light reflection.

The basic observations based on the crystal growth, for example, precise measurements of growth rates<sup>2,3</sup>, in-situ observation of the adsorption states of these molecules on ice-water interface using the fluorescent-labeled method<sup>4</sup>, the MD simulation<sup>5</sup>, the FT-IR<sup>6</sup> and so on<sup>7</sup>. We obtained a direct experimental evidence by the fluorescent observation that the adsorbed AFGP molecules strongly prohibit the growth of the prismatic faces of ice crystal. On the other hand, precise measurements of growth rates during the free growth of an ice single crystal in supercooled water containing a small amount of AFGP, which were carried out in the microgravity condition in International Space Station, clarified that the AFGP molecules work to promote the growth for the basal faces of ice crystal but to inhibit the growth for prism and pyramidal faces. These results mean that adsorbed AFGP molecules may function as the promotor or inhibitor depending on the crystallographic orientation of adsorbed interfaces.

These findings will lead to a better understanding of a novel kinetic process for growth enhancement due to the adsorption of protein molecules and will shed light on the role that crystal growth kinetics has in the onset of the mysterious antifreeze effect in living organisms, namely, how this protein may prevent fish freezing.

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## Yoshinori FURUKAWA



1973 BS, Department of Geophysics, Hokkaido University  
1978 Research Associate, Institute of Low Temperature Science, Hokkaido University  
1981 Ph.D., Department of Geophysics, Hokkaido University  
1991 Associate Professor, Institute of Low Temperature Science, Hokkaido University  
2007 Professor Institute of Low Temperature Science, Hokkaido University  
2011 Director, Institute of Low Temperature Science, Hokkaido University  
2014 Specially-Appointed Professor, Hokkaido University  
2016 Professor Emeritus, Hokkaido University

# Molecular Dynamics Simulation Study of Structure and Vibrational Spectroscopy at Ice Surface

Tatsuya ISHIYAMA

*Dept. of Applied Chem., Graduate School of Science and Engineering, Univ. of Toyama*

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

In this talk, we discuss molecular structures and vibrational sum frequency generation (VSFG) spectra at ice surface by molecular dynamics (MD) simulations. Previously, we published three papers<sup>1,2,3</sup> related to molecular structures and its vibrational spectroscopic response at the basal plane surface of ice Ih. In the studies, we focused on orientational order of water molecules at the topmost surface as a function of temperature below the melting point of water, and how the so-called “surface melting of ice” can be interpreted by the observed VSFG spectra. We will review our previous theoretical studies, and discuss the ongoing study in a close collaboration with experimental studies. In the following, we briefly summarize our previous papers published until now.

It is well known that the VSFG spectrum of the basal plane ice surface shows a very intense response at about 3200 cm<sup>-1</sup> in comparison with that of liquid water<sup>4</sup>. In our first paper, we elucidated the reason why the ice surface generates such intense band by using MD simulation combined with quantum mechanics/molecular mechanics (QM/MM) calculation<sup>1</sup>. “Intermolecular charge transfer” and “vibrational delocalization” are key factors to account for the observed spectra. In the subsequent paper<sup>2</sup>, we further focused on to what extent a vibration of OH stretching mode is delocalized in space. Recently, we elucidated the melting of the second bilayer at the ice surface takes place at about 250 K<sup>3</sup>. Our MD simulation actually showed a discontinuous change of the surface structure in the second bilayer and an abrupt peak shift of the VSFG response in the hydrogen-bonding stretching region<sup>3</sup>.

Our recent study in collaboration with the experimental group<sup>5</sup> have elucidated a bipolar response, namely, a positive-negative feature for the heterodyne-detected VSFG spectrum in the hydrogen-bonding stretching region. We will discuss a mechanism of this spectroscopic response pertinent to molecular structure at the basal plane surface of ice Ih.

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## 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

# Designing of Analytical Methods Utilizing Functionality of Ice and Frozen Aqueous Systems

Tetsuo OKADA

*Department of Chemistry, School of Science, Tokyo Institute of Technology*

E-mail: tokada@chem.titech.ac.jp

Ice and frozen aqueous solutions have received much attention in various communities because they are not only of scientific interest but also of practical importance. We developed ice chromatography, in which ice particles are used as the liquid chromatographic stationary phase.<sup>1</sup> This method is practically not very useful because of low separation performance, but has interesting features as a tool for probing phenomena occurring at ice interfaces. Ice chromatography has successfully revealed the molecular interactions occurring on the ice surface,<sup>2</sup> growth of a quasi-liquid layer at the ice/organic phase interface,<sup>3</sup> the distribution of solutes into a liquid phase that coexists with ice etc. In this lecture, we will show our recent achievements in the developments of analytical methods based on the functionality of ice and frozen aqueous systems, and present some anomalous phenomena found through measurements.

Aqueous solutions are separated into ice and liquid phase upon freezing in a particular temperature range. One of the efficient properties of the frozen aqueous solutions is the freeze concentration of solutes into the liquid phase. We can control the concentration ratio and the volume of the liquid phase by changing temperature and solute concentration in an original unfrozen solution. Freeze concentration leads to high sensitivity in the subsequent analyses. However, since it is usually difficult to pick out the liquid phase from the frozen solutions, freeze concentration has not been recognized as a useful analytical approach. We have shown that the combinations of freeze concentration with capillary electrophoresis and with in-situ measurements including spectrometry and voltammetry are efficient for designing analyses of high sensitivity.<sup>4</sup> Also, we have developed micro- or nano-fluidic systems for separation and reactions with frozen aqueous systems.<sup>5</sup> Of importance is that the liquid phase size is tunable by controlling e.g. temperature. Some interesting phenomena have been found in such systems, including four-order of magnitude enhancement of crown ether complexation,<sup>6</sup> weakened hydrophobic interactions,<sup>7</sup> the formation of ZnO from Zn<sup>2+</sup> solution<sup>8</sup> etc.

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## Tetsuo OKADA

1981 BS, Department of Chemistry, Kyoto University  
1986 Ph.D, Department of Chemistry, Kyoto University  
1986 Research Associate, Faculty of Liberal Arts, Shizuoka University  
1989 Associate Professor, Faculty of Liberal Arts, Shizuoka University  
1995 Associate Professor, School of Science, Tokyo Institute of Technology  
2000 Professor, School of Science, Tokyo Institute of Technology  
2015 Dean, School of Science, Tokyo Institute of Technology

# Emergent high- $T_c$ ferroelectric ordering of strongly correlated and frustrated protons in crystalline-ice film

Toshiki SUGIMOTO

*Department of Chemistry, Graduate School of Science, Kyoto University*

*Precursory Research for Embryonic Science and Technology, Japan Science and Technology Agency,*

E-mail: toshiki@kuchem.kyoto-u.ac.jp

Materials containing strong correlation and frustration have a potential to exhibit dramatic and unusual response to external perturbation. In the case of common water ice (ice Ih), protons in the hydrogen-bond (HB) network are strongly correlated and highly frustrated under the Bernal-Fowler-Pauling ice rules<sup>1</sup>. Because the strongly correlated protons have an extremely long dielectric relaxation time and lose ergodicity at low temperature, disordered proton structures are inevitably frozen as a protonic glass upon cooling, resulting in finite macroscopic residual entropy. Thus, unveiling deeply hidden protonic ordered states in crystalline ice has been a longstanding challenge in the physical chemistry of ice.

Based on the sum frequency generation (SFG) spectroscopy of crystalline-ice films heteroepitaxially grown on Pt(111), oxygen precovered Pt(111), and Rh(111) substrate, here we demonstrate emergent ferroelectric ordering and exotic thermodynamic features of protons in ice<sup>2-5</sup>. During heteroepitaxial growth of ice on Pt(111), we observed that first-layer water molecules are significantly aligned and pointing to substrate with H-down configuration, and the net-H-down ordering progressively propagates into overlayer<sup>2</sup>. In contrast, there was no substantial proton ordering in the ice films on oxygen precovered Pt(111) and Rh(111) where first-layer water molecules do not have preferential H-up and H-down orientational ordering<sup>3-5</sup>. Line shapes of  $\text{Im}\chi^{(2)}$  spectra of the ferroelectric ice films on Pt(111) were completely different from those of the paraelectric ice films on Rh(111)<sup>2-5</sup>.

The ferroelectric ice films on Pt(111) showed reversible and gradual thermal depolarization/repolarization during heating/cooling process with unexpectedly high critical temperature of  $T_c \geq 160 \text{ K}$ <sup>2,5</sup>, which is in stark contrast to the ferroelectric bulk ice XI that shows extremely hysteric and sudden depolarization to ice Ih at  $T_c \sim 72 \text{ K}$ <sup>6,7</sup>. In addition to these results, isotope effects<sup>5</sup> on the thermodynamic stability of ferroelectric state will be discussed.

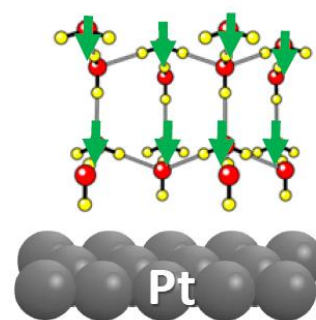


Figure 1. Schematic illustration of the growth of ferroelectric ice film on Pt(111).

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## 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-PREST researcher.

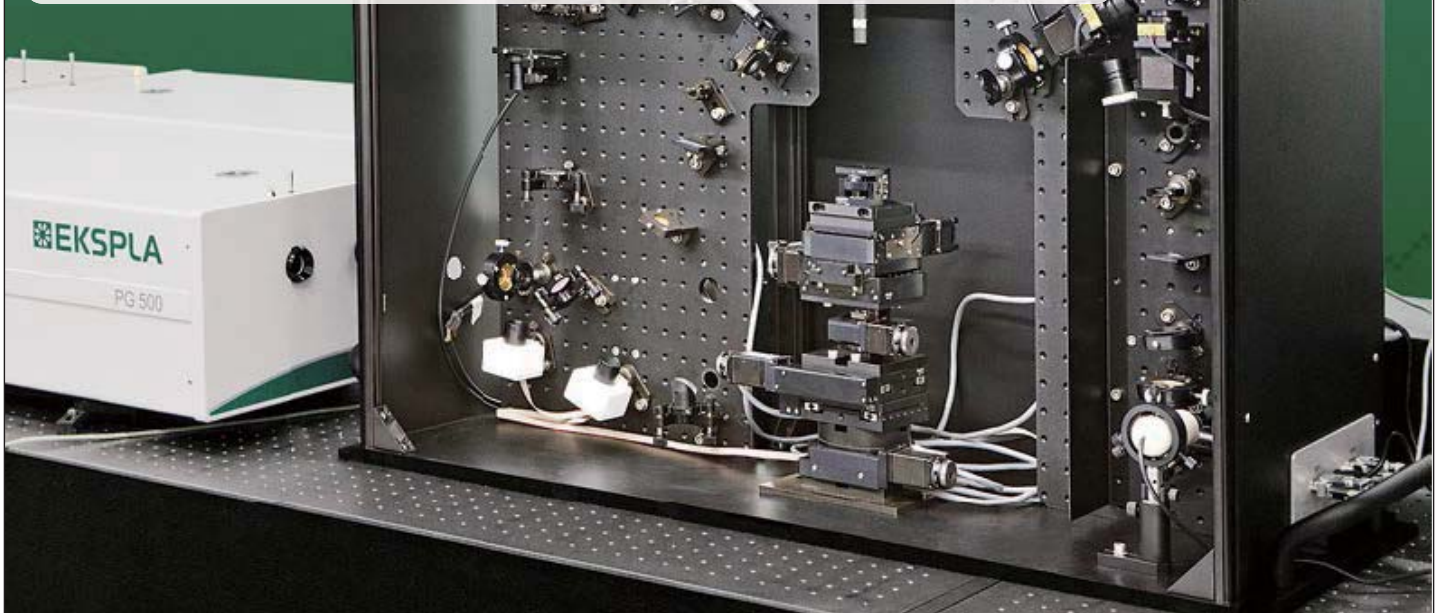
## 参加予定者（順不同）

- |                    |                    |
|--------------------|--------------------|
| 石山達也（富山大）          | 大槻友志（京大）           |
| 岡田哲男（東工大）          | 中川清子（都立産業技術研究センター） |
| 鍵裕之（東大）            | 戸澗一孔（旭リサーチセンター）    |
| 杉本敏樹（京大）           | 原田国明（京大）           |
| 平田聡（イリノイ大）         | 長谷川太祐（京大）          |
| 藤井朱鳥（東北大）          | 半田友衣子（埼玉大）         |
| 古川義純（北大）           | 吉川真帆（埼玉大）          |
| 森田明弘（東北大）          | 長谷川一途（理研）          |
| 高柳敏幸（埼玉大）          | 中野陽介（埼玉大）          |
| 前田公憲（埼玉大）          | 浦島周平（理研）           |
| 沖野隼之介（学習院大）        | 磯昂平（埼玉大）           |
| 相賀則宏（京大）           | 井上賢一（理研）           |
| 加藤史明（京大）           | 福浦麻衣子（本田技研）        |
| 五月女光（阪大）           | 堤孝義（リテックス）欠席       |
| 田村健治（首都大・産技高専品川）欠席 | 大場優生（横浜市大）         |
| 越野雅至（産総研）欠席        | 熊田大晃（横浜市大）         |
| 金鋼（阪大）             | 小座間瑛記（埼玉大）         |
| 石川春樹（北里大）          | 小井土勝一（埼玉大）         |
| 宮崎淳（北陸大）           | 安達サディア（埼玉大）        |
| 関悠佑（埼玉大）           | 中富大喜（埼玉大）          |
| 鵜崎千裕（埼玉大）          | 鈴木健人（埼玉大）          |
| 高江恭平（東大）           | 松谷寛（日立化成）          |
| 笹原茂生（富士化学）         | 稲川有徳（東工大）          |
| 藤沼修平（埼玉大）          | 鳴海旭（埼玉大）           |
| 桑名竜之介（埼玉大）         | 長谷川貴一（埼玉大）         |
| 山口祥一（埼玉大）          | 高橋実里（埼玉大）          |
| 乙須拓洋（埼玉大）          | 多田一輝（埼玉大）          |
| 野嶋優妃（埼玉大）          | 土屋慎之助（埼玉大）         |
| 小林海斗（埼玉大）          | 針生弘光（埼玉大）          |
| 塩谷優紀（埼玉大）          | 山本康太（埼玉大）          |
| 島田良輔（埼玉大）          | 脇田禅（埼玉大）欠席         |
| 関大輔（埼玉大）           |                    |

# SFG(和周波発生)分光システム

## 表面・界面研究のパワフルツール

### 界面の振動スペクトル計測



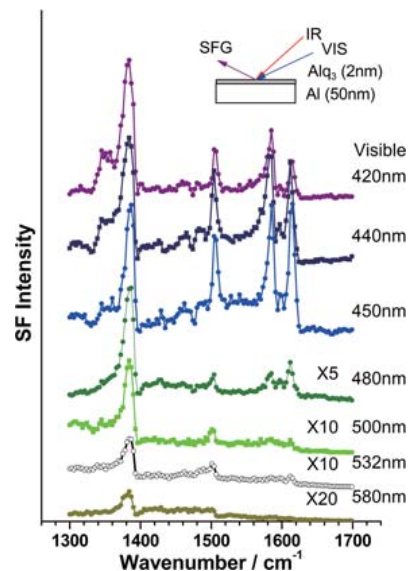
## 特長

- 高い界面選択性
- 各種界面(固体-固体、固体-液体、固体-気体、液体-液体)の測定
- 非接触・非破壊測定
- 高感度検出 単分子膜の計測が可能
- 超高速時間分解計測

## 用途

- 固体・液体・ポリマー・生体膜等の表面・界面の研究
- 表面状態・化学組成・分子配向の測定
- 固液界面のその場計測(電極反応など)
- 表面反応の超ダイナミクス観察
- エピタキシャル成長・電気化学・材料工学・環境科学の研究

## 振動スペクトル測定例 (Alq<sub>3</sub>超薄膜)



Alq<sub>3</sub>超薄膜のSFGの可視光励起波長依存性  
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国立研究開発法人 産業技術総合研究所 宮前孝行様 提供

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