Annual Review 2016

Molecular Photoscience Research Center

Kobe University

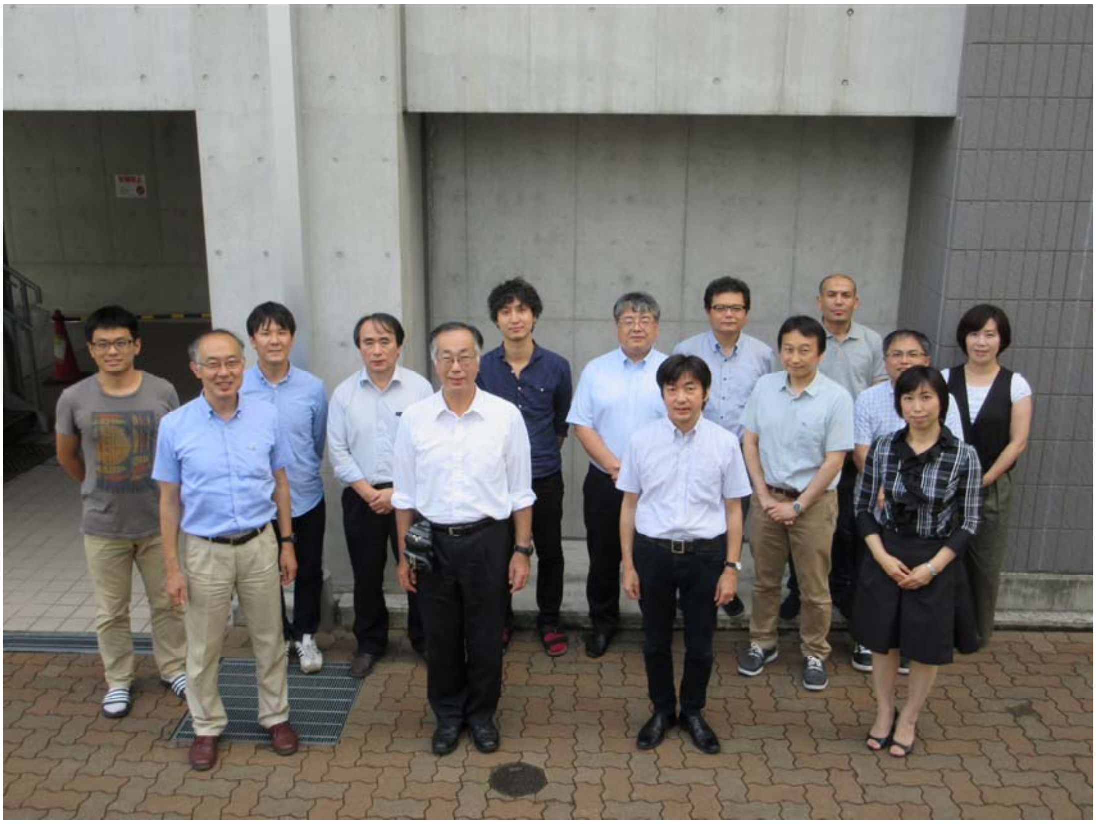
Preface

This annual review provides a summary of the research activity of Molecular Photoscience Research Center for the 2016 academic year. We are further promoting advanced research and international collaboration on molecular photoscience and related topics.

The strength and characteristic of this research center is molecular science using terahertz waves. The center has conducted studies on solid materials, liquids, and biologically important molecules using terahertz waves. Also at the Graduate School of Human Development and Environmental Studies and the Graduate School of Science of Kobe University, molecular science for the terahertz band is being conducted. Therefore, in January 2017, the research center was reorganized to further strengthen the molecular science research using the terahertz wave, with the aim of this center to become international research base of terahertz molecular science research, so that the center will be able to contribute to strengthening the function of Kobe University. We have organized the center so that researchers who are conducting molecular science for the terahertz band at Kobe University can participate in various research activities of the center. We will further develop current international research activities.

July, 2017

Keisuke Tominaga
Director of Molecular Photoscience Research Center,
Kobe University



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Members

Keisuke Tominaga	Director
Hitoshi Ohta	Vice-Director

Takako Miyazaki	Assistant
Sachiyo Tombe	Assistant

Laser Molecular Photoscience Laboratory

Akihide Wada	Professor (~ December 2016)
Shunji Kasahara	Associate Professor
Priyanka Arora	Postdoctoral Fellow (~ September 2016)
Yasuhiro Kobori	Professor (January 2017~)
Takashi Tachikawa	Associate Professor (January 2017~)

Terahertz Molecular Chemistry Laboratory

Keisuke Tominaga	Professor
Seiji Akimoto	Associate Professor (~ December 2016)
Kaoru Ohta	Research Associate Professor (~ September 2016), Researcher (October 2016 ~)
Feng Zhang	Postdoctoral Fellow (~ September 2016), Kobe University Visiting Research Fellow (October 2016 ~)
Harumi Sato	Associate Professor (Supplementary assignment from January 2017. Main assignment is Graduate School of Human Development and Environment)

Terahertz Material Physics Laboratory

Hitoshi Ohta	Professor
Susumu Okubo	Associate Professor
Khalif Benzid	Postdoctoral Fellow
Keigo Hijii	Researcher
Toshiro Kohmoto	Professor (Supplementary assignment from January 2017. Main assignment is Graduate School of Science)
Eiji Ohmichi	Associate Professor (Supplementary assignment from January 2017. Main assignment is Graduate School of Science)

Research Activity

I. Laser Molecular Photoscience Laboratory

I-A. SPIN INTERACTIONS STUDIED BY TIME RESOLVED MAGNETIC RESONANCE SPECTROSCOPY

In the natural photosynthesis, the organic solar cells and the photocatalysis, transient radical species or carriers are immediately generated by the light-induced chemical reactions for the photo-energy conversion, providing essential sources of the living energies. However, it has been unclear how those transient molecules are initially interacting each other before the carrier-conductions or charge-dissociation take place. In our group, we are developing experimental methodologies to determine molecular positions, orbital orientations and orbital overlap (electronic coupling) in the initially generated radical-pairs or electron-hole pairs in the photoactive proteins, in the solar cells, and in the photocatalysis on the basis of the transient electron paramagnetic resonance (EPR) and NMR spectroscopies. Using these methods, we have clarified several fundamental mechanisms of the energy-conversions in the photosynthesis and in the polymer-fullerene systems.

Regulated Electron Tunneling of Photoinduced Primary Charge-Separated State in the Photosystem II Reaction Center

Masashi Hasegawa, Hiroki Nagashima[1], Reina Minobe, Takashi Tachikawa, Hiroyuki Mino[1] and Yasuhiro Kobori

[1]Nagoya University

(*J. Phys. Chem. Lett.* 2017)

In initial events of the photosynthesis by higher plants, the photosystem II (PSII) generates photoinduced primary charge–separated (CS) state composed of reduced pheophytin ($\mathrm{Pheo_{D1}}^{-\bullet}$) and oxidized special pair ($\mathrm{P}^{+\bullet}$) in chlorophylls a (Chla) $\mathrm{P_{D1}}/\mathrm{P_{D2}}$ in the D1/D2 heterodimer, ultimately leading to the water oxidation at the oxygen–evolving Mn_4CaO_5 cluster by $\mathrm{P}^{+\bullet}$. To understand mechanism of the efficient generation of initially localized CS state ($\mathrm{P_{D1}}^{+\bullet}\,\mathrm{Pheo_{D1}}^{-\bullet}$), we have characterized cofactor geometries and electronic coupling of the photoinduced primary CS state in quinone pre–reduced membrane of PSII from spinach using the time-resolved EPR (TREPR) method. It has been revealed that that the electronic coupling between the charges is significantly weak in the CS state separated by 1.5 nm, showing an importance of regulated cofactor-cofactor electronic interaction between a vinyl substituent in $\mathrm{Pheo_{D1}}$ and an accessory chlorophyll to inhibit the energy-wasting charge-recombination after the primary electron-transfer processes.

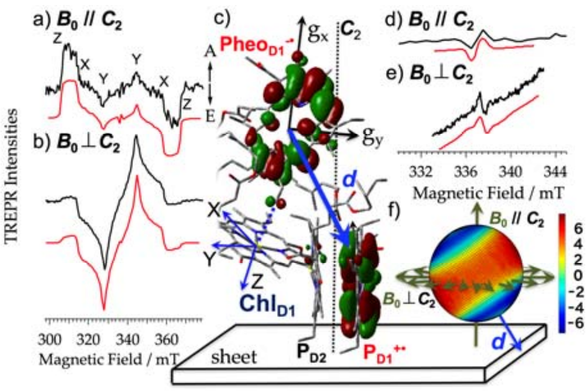

Figure 1. TREPR data of the quinone pre–reduced PSII membranes oriented as the multilayers on a plastic sheet. a) and b) were obtained for the sample orientations that the $\boldsymbol{C}_2$ axis is parallel and perpendicular to $\boldsymbol{B}_0$, respectively, at a delay time of 0.8 μs. c) Cofactor orientations are shown with respect to the $\boldsymbol{C}_2$ axis as taken from the X-ray structure. d–e) The TREPR spectra at the center field regions of 337 mT for the d) parallel and e) perpendicular orientations at 0.5 μs. Computed spectra are shown by the red lines in a), b), d) and e) for the corresponding sample orientations and the delay times. f) 3D spin polarization imaging mapped to all possible $\boldsymbol{B}_0$ directions at 338.3 mT as computed from the powder-pattern TREPR spectrum of Figure 2e. The red area denote that the A/E polarization is strong, while the blue region corresponds to the strong E/A polarization.

We have characterized the geometry, the orientation, and the electronic character of the primary CS state in PSII using the TREPR method. The localized hole distribution at $P_{D1}^{+\bullet}$ which is essential in oxidizing Mn_4CaO_5 from the secondary CS state of $P_{D1}^{+\bullet}\cdots Q_A^{-\bullet}$ has been demonstrated in the primary CS state with r_{CC} = 1.5 nm. The weak *J*-coupling between $P_{D1}^{+\bullet}$ and $Pheo_{D1}^{-\bullet}$ is explained by the limited spin density at the terminal vinyl group in $Pheo_{D1}^{-\bullet}$, regulating the orbital overlap between Chl_{D1} and $Pheo_{D1}^{-\bullet}$ to inhibit the energy-wasting recombination for the close separation distance between the cofactors. These fundamental characteristics of the regulated cofactor-cofactor interactions of the primary CS state are essential keys to the artificial light-energy conversion systems and are informative for understanding the evolutions of the molecular engineering in the higher plants.

Switching of the π-Electronic Conjugations in the Reductions of a Dithienylethene-Fused p-Benzoquinone

Eiji Saito, Takumi Ako, Yasuhiro Kobori and Akihiko Tsuda

(*RSC Adv.* 2017)

The electron accepting character of a dithienylethene-fused p-benzoquinone derivative is significantly reduced upon ring-closing isomerization. Visible light unlocks the π-electronic conjugation of the quinone utilizing it for a light-driven oxidation reaction.

In this study, we found that a dithienylethene-fused p-benzoquinone derivative DTQ changes its electronic properties dramatically through ring-opening and -closing isomerizations. Both isomers underwent one-electron reduction to give the corresponding anion radicals. The spectral studies together with DFT calculations indicate that $\mathbf{DTQ_{open}}^{\bullet-}$ adopts semiquinone form, while $\mathbf{DTQ_{closed}}^{\bullet-}$ allows spin delocalization between quinone and thiophene groups. The electron accepting character as well as oxidizability of $\mathbf{DTQ_{closed}}$ is reduced significantly in comparison with that of $\mathbf{DTQ_{open}}$. Visible light unlocks the π-electronic conjugation of the quinone in DTQ utilizing it for a light-driven oxidation reaction.

Geometries, Electronic Couplings and Hole Dissociation Dynamics of Photoinduced Electron-Hole Pairs in Polyhexylthiophene-Fullerene Dyads Rigidly Linked by Oligophenylenes

Taku Miura, Ran Tao[1], Sho Shibata[1], Tomokazu Umeyama[1], Takashi Tachikawa, Hiroshi Imahori[1] and Yasuhiro Kobori
[1]Kyoto University

(*J. Am. Chem. Soc. 2016*)

To shed a light on fundamental molecular functions of photoinduced charge conductions by organic photovoltaic materials, it is important to directly observe molecular geometries of the intermediate charges just after the photoinduced electron-transfer reactions. However, highly inhomogeneous molecular environments at the bulk heteojunction interfaces in the photoactive layers have prevented us from understanding the mechanism of the charge conductions. We have herein investigated orbital geometries, electronic couplings and hole-dissociation dynamics of photoinduced charge-separated (CS) states in a series of poly(3-hexylthiophene)-fullerene linked dyads bridged by rigid oligo-*p*-phenylene spacers (Figure 2) by using time resolved EPR spectroscopy. It has been revealed that one-dimensional intramolecular hole-dissociations exothermically take place from localized holes in initial CS states, following bridge-mediated, photoinduced charge-separations via triplet exciton diffusions in the conjugated polymer-backbones. This molecular wire property of the photoinduced charges in solution at room temperature demonstrates the potential utility of the covalently bridged polymer molecules applied for the molecular devices.

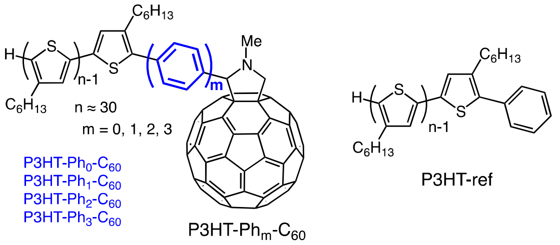

Figure 1. Structure formula of P3HT-Ph$_m$-C$_{60}$ and P3HT-ref. Averaged number of n is ≈ 30 in the P3HT units.

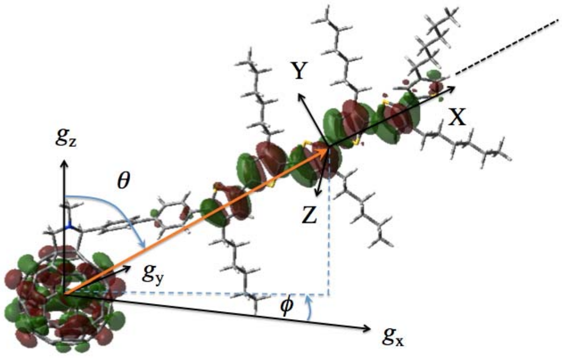

Figure 2. Geometry model of the primary CS state in P3HT-Ph$_2$-C$_{60}$. The principal axes of the g-tensor (g_x, g_y, g_z) and the ZFS tensor (X, Y, Z) are shown. The g tensor orientation (g_X, g_Y, g_Z) in P3HT$^{+\bullet}$ was set to be co-linear with the principal axes of the ZFS tensor in ^{3}P3HT*. The location of the hole (P3HT$^{+\bullet}$) in the CS state is set to be the same as that of the precursor triplet exciton (^{3}P3HT*). Non-zero electronic density is identified at -Ph- in vicinity to P3HT$^{+\bullet}$, representing the hybridization of SOMO in the P3HT moiety with HOMO in the oligo-*p*-phenylene spacer.

To clarify how the molecular environments play roles for the efficient initial charge-dissociations by the OPV related materials, we have investigated the orbital geometries, the electronic couplings and the one-dimensional hole dissociation dynamics of the photoinduced intramolecular CS states in the P3HT-Ph_m-C_{60} dyads using the TREPR. It has been clearly demonstrated that the hole dissociation takes place without going through the hot CT state; the localized hole is initially generated in the conjugated polymer region nearby the phenylene-bridge unit by the bridge-mediated electron tunneling via the triplet excitons. The entropy enhancement by the disordered side chains may play a major role to induce the one-dimensional hole-dissociation via the hybridized SOMOs in Figure 2. The present thermodynamic dissociation mechanism (as opposed to the hot CT mechanism) would be characteristic to the triplet-precursor reaction systems, since the long-lived triplet excitons are generated after the vibrational relaxations. Although the charge dissociation is slower than in the BHJ photoactive layers due to the lack of the π-π stacking interactions, the present molecular-wire property may pave a new avenue to rational designs of the efficient molecular electronics using the bridged polymer molecules.

Time Resolved EPR Study on Photoinduced Long-Range Charge-Separated State in Protein: Electron Tunneling Mediated by Arginine Residue in Human Serum Albumin

Masaaki Fuki[1], Hisao Murai[1], Takashi Tachikawa, Yasuhiro Kobori

[1]Shizuoka University

(*J. Phys. Chem. B 2016*)

To elucidate how local molecular conformations play a role on electronic couplings for the long-range photoinduced charge-separated (CS) states in protein systems, we have analyzed time-resolved electron paramagnetic resonance (TREPR) spectra by polarized laser irradiations of 9,10-anthraquinone-1-sulfonate ($AQ1S^{-}$) bound to human serum albumin (HSA). Analyses of the magnetophotoselection effects on the EPR spectra and a docking simulation clarified the molecular geometry and the electronic coupling of the long-range CS states of $AQ1S^{\bullet 2-}$–tryptophan214 radical cation ($W214^{\bullet +}$) separated by 1.2 nm. The ligand of $AQ1S^{-}$ has been demonstrated to be bound to the drug site I in HSA. Molecular conformations of the binding region were estimated by the docking simulations, indicating that an arginine218 ($R218^{+}$) residue bound to $AQ1S^{\bullet 2-}$ mediates the long-range electron-transfer. The energetics of triad states of $AQ1S^{\bullet 2-}$–$R218^{+}$–$W214^{\bullet +}$ and $AQ1S^{-}$–$R218^{\bullet}$–$W214^{\bullet +}$ have been computed on the basis of the density functional molecular orbital calculations, providing the clear evidence for the long-range electronic couplings of the CS states in terms of the superexchange tunneling model through the arginine residue.

Self-Assembled Molecular Gear: a 4:1 Complex of Rh(III)Cl Tetraarylporphyrin and Tetra(*p*-pyridyl)cavitand

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[1]Shizuoka University
[2]Bruker axs

(*J. Am. Chem. Soc. 2016*)

The components of a 4:1 mixture of Rh(III)Cl tetrakis(4-methylphenyl)porphyrin **1** and a bowl-shaped tetra(4-pyridyl)cavitand **4** self-assemble into a 4:1 complex $\mathbf{1}_4$•**4** via Rh–pyridyl axial coordination bonds. The single-crystal X-ray diffraction analysis and variable temperature (VT) ^{1}H NMR study of $\mathbf{1}_4$•**4** indicated that $\mathbf{1}_4$•**4** behaves as a quadruple interlocking gear with an inner space, wherein (i) four subunits-**1** are gear wheels and four *p*-pyridyl groups in subunit-**4** are axes of gear wheels, (ii) one subunit-**1** and two adjacent subunits-**1** interlock with one another cooperatively, and (iii) four subunits-**1** in $\mathbf{1}_4$•**4** rotate quickly at 298 K on the NMR time scale. Extremely strong porphyrin-Rh–pyridyl axial coordination bond, the rigidity of the methylene-bridge cavitand as a scaffold of the pyridyl axes, and the *cruciform arrangement* of the interdigitating *p*-tolyl groups as the teeth-moiety of the gear wheels in the assembling $\mathbf{1}_4$-unit make $\mathbf{1}_4$•**4** function as a quadruple interlocking gear in solution. The gear function of $\mathbf{1}_4$•**4** was also supported by the rotation behaviors of other 4:1 complexes: $\mathbf{2}_4$•**4** and $\mathbf{3}_4$•**4** obtained from Rh(III)Cl tetrakis[4-(4-methylphenyl)phenyl]porphyrin **2** or Rh(III)Cl tetrakis(3,5-dialkoxyphenyl)porphyrin **3** and **4** also served as quadruple interlocking gears, whereas $\mathbf{1}_4$•**5** obtained from **1** and tetrakis[4-(4-pyridyl)phenyl]cavitand **5** did not behave as a gear. The results of activation parameters ($\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta G^{\ddagger}$) obtained from Eyring plots based on line-shape analysis of the VT ^{1}H NMR spectra of $\mathbf{1}_4$•**4**, $\mathbf{2}_4$•**4**, and $\mathbf{3}_4$•**4** also support the interlocking rotation (geared coupled rotation) mechanism.

Remarkable Dependence of the Final Charge Separation Efficiency on the Donor–Acceptor Interaction in Photoinduced Electron Transfer

Tomohiro Higashino[1], Tomoki Yamada[1], Masanori Yamamoto[1], Akihiro Furube[2], Nikolai V. Tkachenko[3], Taku Miura, Yasuhiro Kobori, Ryota Jono[4], Koichi Yamashita[4] and Hiroshi Imahori[1]*
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[3]Tampere University of Technology, Finland
[4]The University of Tokyo
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(*Angew. Chem. Int. Ed. 2016*)

Photoinduced electron transfer (ET) is one of the most fundamental processes in physics, chemistry, and biology. In the reaction center of natural photosynthesis, photoinduced ET generates a long-lived charge separation (CS) state with ~100% efficiency, leading to light-to-chemical energy conversion1. In contrast, photoinduced CS at the interfaces of organic photovoltaic cells generates electron-hole pair, eventually achieving light-to-electricity conversion. However, the interfaces of semiconductor/dye and donor/acceptor (D/A) in artificial photosynthesis and organic photovoltaic cells often suffer from the partial or even large loss of the CS state at the early stage, which has not been unveiled. Here we show unprecedented dependence of the final CS efficiency (Φ_{CS}) on D-A interaction that can be changed systematically in the models. At the short D-A separation distance (R_{ee}) initially formed singlet CS state decays to the ground state and/or is competitively converted into a newly found intermediate state, which is further transformed into the triplet CS state. Optimization of the D-A interaction remarkably inhibits the undesirable rapid decay to the ground state, yielding the final long-lived triplet CS state with ~100% efficiency. Our findings open a new paradigm for rational design of artificial photosynthesis and photovoltaic cells toward efficient solar energy conversion.

Dynamics of Photoinduced Electron-Hole Pairs in Polyhexylthiophene-Fullerene Dyads Rigidly Linked by Oligophenylenes

Yasuhiro Kobori

(*2016 The 4th Awaji International Workshop on Electron Spin Science & Technology, Invited*)

For developments of the organic light-energy conversion systems, it is essential to achieve efficient long-range charge-separations (CS). Light-induced electrons and holes generated by the electron-transfer (ET) reactions are thus required to escape from the electrostatic binding at the initial stage. Concerning the mechanism of the efficient photo-career generations in the OPV systems, role of the hot charge-transfer (CT) excitons is currently under intense debate. To elucidate why and how the photo-carriers escape from the Coulomb binding, it is important to directly observe locations and orientations of the intermediate charges just after the charge-separations. Time-resolved electron paramagnetic resonance (TREPR) and pulsed EPR methods have been powerful to obtain the electron spin-spin dipolar interaction (D') and the spin-spin exchange coupling (J) in the photoinduced charge-separated (CS) states and thus have been utilized to characterize the inter-spin distances and the electronic couplings (V) of the transient CS states. [1, 2] The TREPR analyses have been useful to obtain the CS state geometries for several systems, since the electron spin polarization (ESP) as the microwave absorption (A) and the emission (E) is sensitive to the molecular conformations and to J. Recent spin polarization analyses have revealed representative geometries of the transient electron-hole pairs in the OPV blend films.[2] However, the highly inhomogeneous molecular environments at the bulk heteojunction (BHJ) interfaces induces the large special distribution in the solid-state OPV materials and would prevent us from understanding the mechanism of the charge conductions. [3] It is highly desired to investigate the structure and dynamics of the initial photo-carriers generated in a conjugated polymer-backbone in which the intramolecular orientation and the electronic interaction are well-defined at the initial CS stage.

We have herein investigated orbital geometries, electronic couplings and hole-dissociation dynamics of photoinduced charge-separated (CS) states in a series of poly(3-hexylthiophene)-fullerene linked dyad bridged by rigid oligo-*p*-phenylene spacers by using time resolved EPR spectroscopy. It has been revealed that one-dimensional intramolecular hole-dissociations exothermically take place from localized holes in initial CS states, following bridge-mediated, photoinduced charge-separations via triplet exciton diffusions in the conjugated polymer-backbones. This molecular wire property of the photoinduced charges in solution at room temperature demonstrates the potential utility of the covalently bridged polymer molecules applied for the molecular devices. [4]

[1] Bittl, R., Weber, S. *Biochim. Biophys. Acta-Bioenerg.* 2005, *1707*, 117-126.
[2] Kobori, Y., Noji, R.; Tsuganezawa, S. *J. Phys. Chem. C* 2013, *117*, 1589-1599.
[3] Lukina, E. A., Kulik, L. V. et al., *J. Phys. Chem. B* 2015, *119*, 13543-13548.
[4] Miura, T., Tao, R., Shibata, S., Umeyama, T., Tachikawa, R., Imahori, H., Kobori, Y. *J. Am. Chem. Soc.*, 2016, *138*, 5879–5885.

Primary Charge-Separation Mechanism in the Photosynthetic Reaction Center Studied by Time-Resolved EPR Spectroscopy

Yasuhiro Kobori

(*2016 Gordon Research Conference: Electron Donor-Acceptor Interaction, Invited*)

The photosynthetic reaction centers (PRC) is an integral membrane protein that undergoes light-induced electron transfers (ET) from the special pair (P) of bacteriochlorophyll molecules to a series of acceptors. The PRC from the *Rhodobacter sphearoides* R26 consists of a dimeric core, where the cofactors of P, bacteriochlorophylls (B), bacteriopheophytins (H) and quinones (Q) are bound by the polypeptides. Two nearly symmetrical cofactor chains (A and B branches) extend across the membrane. In PRC, light-driven ETs take place exclusively through the A blanch, efficiently generating so-called primary CS state ($P^{+\cdot}H_A^{-\cdot}$ in Figure 1). This $P^{+\cdot}H_A^{-\cdot}$ generation has been explained by the stepwise ETs in which $P^{+\cdot}B_A^{-\cdot}$ is first created as an intermediate from ${}^1P^*B_A$ and then the electron is immediately transferred from $B_A^{-\cdot}$ to H_A. These processes have been characterized by transfer integrals (V_{PB} and V_{BH}) between ${}^1P^*$ and B_A and between B_A and H_A, respectively on the basis of x-ray structures. In V_{BH}, it has been suggested that an overlap between a π*-orbital in B_A and a σ*-orbital in a methyl group of H_A plays a significant role as an electron-tunneling route. Characterizations of the charge-recombination (CR) in $P^{+\cdot}H_A^{-\cdot}$ are crucial as well to unveil the energy-conversion mechanism. Although the electronic coupling (V_{CR}) for the CR to the triplet P has been known to be significantly weak, origins of the electronic inhibition are not fully understood. Reorientations of quinones ($Q^{-\cdot}$) upon subsequent ET processes have been studied in photosynthetic proteins [1]. If such motions occur in $P^{+\cdot}H_A^{-\cdot}$, the tunneling routes should be affected between B_A and $H_A^{-\cdot}$ and between $H_A^{-\cdot}$ and Q_A, leading to the prevention of the CR. On the primary CS state, however, no studies have experimentally elucidated how cofactor geometries influence the V_{CR} in the PRC.

In this study, we have experimentally determined both the cofactor geometries and the electronic coupling ($V_{\mathrm{CR,S}}$) for the primary CR leading to the delayed fluorescence of $^1P^*$ in $P^{+\cdot}H_A^{-\cdot}$ by analyzing X band time-resolved electron paramagnetic resonance (TREPR) signals of the primary CS state and of $^3P^*$ using coupled stochastic-Liouville equations (SLE) for a quinone pre-reduced PRC of the *Rhodobacter sphearoides* R26 in which the subsequent ET to Q_A is blocked. We show that the initial generation of $P^{+\cdot}H_A^{-\cdot}$ does not largely modulate the cofactor conformations and that the $V_{\mathrm{CR,S}}$ is larger than that for the CR to the triplet state of $^3P^*$.

[1] T. Berthold, E. D. Gromoff, S. Santabarbara, P. Stehle, G. Link, O. G. Poluektov, P. Heathcote, C. F. Beck, M. C. Thurnauer and G. Kothe, *J. Am. Chem. Soc.* **2012**, 134, 5563-5576.

Geometry and Electron Tunneling Route of Photoinduced Primary Charge-Separated State in the Photosynthetic Reaction Center

Yasuhiro Kobori

(*2016 Molecular Photoscience Research Center International Workshop, Invited*)

In initial events of the photosynthesis by higher plants, the photosystem II (PSII) generates photoinduced primary charge–separated (CS) state composed of reduced pheophytin ($\mathrm{Pheo_{D1}}^{-\bullet}$) and oxidized special pair ($P^{+\bullet}$) in chlorophylls a (Chla) P_{D1}/P_{D2} in the D1/D2 heterodimer, ultimately leading to the water oxidation at the oxygen–evolving Mn_4CaO_5 cluster by $P^{+\bullet}$ (Fig. 1). Several studies have been performed to understand mechanisms of an extremely high redox potential of $P^{+\bullet}$ in PSII while the photosynthetic reaction centers (PRC)[1] do not have such potentials in purple bacteria.[2,3] It has been suggested that the cationic charge localization of the D1 part (P_{D1}) at 70-80 % over P_{D1}/P_{D2} may lower the singly occupied molecular orbital (SOMO) level and play a role on the exothermic Mn_4CaO_5 oxidization.[2,3] However no experimental studies have been performed to identify charge locations, molecular conformations, and electronic interaction in the primary CS state in which the anionic charge of $\mathrm{Pheo_{D1}}^{-\bullet}$ may significantly influence the electronic state in the PSII RC. In particular, $\mathrm{Pheo_{D1}}$ employs a vinyl group as a terminal substituent which is located in close proximity to $\mathrm{Chl_{D1}}$ as shown in Fig. 1, whereas the bacterial pheophytin (H_A) utilizes an acetyl group as one of the electron-tunneling routes between the accessory chlorophyll (B_A) and H_A.[4] It has been

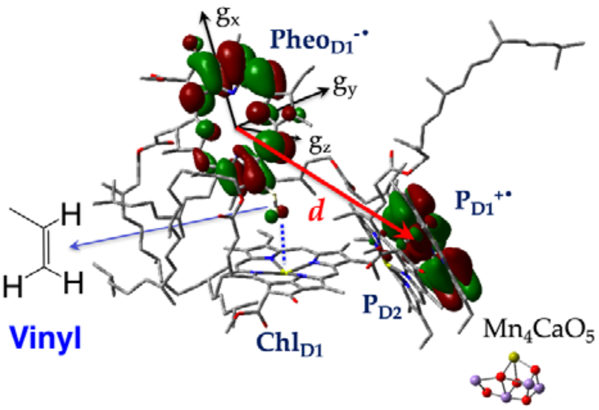

Figure 1: Geometry of the photoinduced primary CS state in the PSII reaction center

unclear how the vinyl substituent plays a role on the electronic couplings for the initial light-energy conversion.

To understand molecular mechanism of the efficient generation of the initial oxidative state, we have characterized geometries and orientations of the photoinduced CS states in the PRC from *Rhodobacter sphaeroides*[1] and in the PSII from spinach using the X-band time-resolved EPR (TREPR)[1,5-7] method. In the spinach, we have obtained the TREPR spectra of the primary CS states in quinone pre-reduced membranes of PSII in frozen solution and in oriented multilayers at 77 K. It has been revealed that the cationic charge is localized in P_{D1} of the special pair at a close distance of 1.5 nm from $Pheo_{D1}^{-\bullet}$ but that the electronic coupling between the charges is significantly weak owing to the vinyl substituent, resulting in the long-lived CS state generation in the PSII.

(1) Kobori, Y.; Ponomarenko, N.; Norris, J. R. *J. Phys. Chem. C* **2015**, *119*, 8078-8088.

(2) Okubo, T.; Tomo, T.; Sugiura, M.; Noguchi, T. *Biochemistry* **2007**, *46*, 4390-4397.

(3) Saito, K.; Ishida, T.; Sugiura, M.; Kawakami, K.; Umena, Y.; Kamiya, N.; Shen, J.-R.; Ishikita, H. *J. Am. Chem. Soc.* **2011**, *133*, 14379-14388.

(4) O'Malley, P. J. *J. Phys. Chem. B* **2000**, *104*, 2176-2182.

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(6) Kobori, Y.; Miura, T. *J. Phys. Chem. Lett.* **2015**, *6*, 113-123.

(7) Kobori, Y.; Noji, R.; Tsuganezawa, S. *J. Phys. Chem. C* **2013**, *117*, 1589-1599.

Electron Spin Polarization Imaging of Photoinduced Charge-Separated States in Photosynthetic Proteins

Yasuhiro Kobori

(*2017 Molecular Photoscience Research Center International Symposium*, *Invited*)

In the primary event of the photosynthesis by green plants and cyanobacteria, the light energy is transferred through antenna complexes to the reaction center (RC) of the photosystem II (PSII) in the thylakoid membrane. The RC is composed of the D1/D2 heterodimer, possessing the chlorophyll a (Chla) pair (P_{D1}/P_{D2}), the accessory Chla (Chl_{D1}/Chl_{D2}), the pheophytins ($Pheo_{D1}/Pheo_{D2}$), two quinones, and two additional Chla molecules as the redox active cofactors. It has been suggested that the electron is transferred to $Pheo_{D1}$ from $^{1}Chl_{D1}^{*}$ electronically excited via the antenna, following hole-transfer to the “special pair (P)” of P_{D1}/P_{D2} generating the primary charge-separated (CS) state of $P^{+\bullet}Pheo_{D1}^{-\bullet}$. Several studies have been performed to understand mechanisms of an extremely high redox potential of $P^{+\bullet}$ in PSII while the photosynthetic reaction centers (PRC) do not have such potentials in purple bacteria. For chemically oxidized PSII RC samples, the cationic charge is known to be localized on the D1 part (P_{D1}) at 70-80 % over P_{D1}/P_{D2}, lowering the singly occupied molecular orbital (SOMO) level to oxidize the Mn_4CaO_5 cluster. On the primary CS state, Matysik et al.[1] demonstrated that the cationic charge is localized at a single Chla site by using the photo-CIDNP method. Ultrafast spectroscopic studies have also denoted the predominance of the cationic charges on the D1 part in the primary CS states of $P_{D1}^{+\bullet}$ $Pheo_{D1}^{-\bullet}$ as the short-lived intermediate.

In the primary CS states, the above oxidative and localized cationic charge would cause a strong electronic interaction in $P_{D1}^{+\bullet}$ $Pheo_{D1}^{-\bullet}$ and thus suffer from an energy-wasting CR process, since the distance (1.5 nm) between $P_{D1}^{+\bullet}$ and $Pheo_{D1}^{-\bullet}$ is expected to be shorter than the CS distance of 1.8 nm in *Rhodobacter sphaeroides*[2] in which the hole distribution is highly delocalized on the special pair. However, a lifetime (τ) of 200 ns was obtained for the primary CS state in the quinone doubly-reduced membrane of PSII, while $\tau = 25$ ns is significantly shorter in *Rhodobacter sphaeroides*. On this, no experimental studies have been performed to understand how cofactor geometries play roles on the electronic interaction of the primary CS state in which the anionic charge may significantly influence the electronic state. In particular, $Pheo_{D1}$ employs a vinyl group as a terminal substituent which is located in close proximity to Chl_{D1}, whereas the bacteriopheophytin (H_A) utilizes an acetyl group as one of the electron-tunneling routes between the accessory bacteriochlorophyll (B_A) and H_A. It has been unclear how the vinyl substituent plays a role on the electronic couplings for the initial light-energy conversion in the plants. We have observed the primary CS states in quinone pre-reduced membranes of PSII from spinach in frozen solution and in oriented multilayers at 77 K using an X-band time-resolved EPR (TREPR) method. Herein, we propose a novel method of "3D spin polarization imaging" mapped to all possible magnetic field directions as computed from the powder-pattern TREPR spectrum to obtain image views of the geometries of the primary CS state.[3] We show that the electronic coupling between the charges is significantly weak although the tunneling route is geometrically active after the primary charge-separations.

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I-B. SINGLE-MOLECULE STUDIES ON PHOTO-ENERGY CONVERSION PROCESSES

To design a more efficient solar energy conversion system (light energy to electrical or chemical energy), it is important to reveal and understand the mechanisms of various chemical reactions at heterogeneous interfaces. We have investigated the photochemical and photophysical processes occurring on a variety of light energy conversion systems such as photocatalysis and solar cells using advanced single-molecule, single-particle spectroscopy techniques and gain new insights related to spatial and temporal heterogeneities in reactions and structures, which are always masked by ensemble averaging.

Crystal-Face-Dependent Charge Dynamics on a $BiVO_4$ Photocatalyst Revealed by Single-Particle Spectroelectrochemistry

Takashi Tachikawa, Tomoya Ochi, and Yasuhiro Kobori

(*ACS Catal., 2016*)

The performance of semiconductor materials in solar water splitting and other applications is strongly influenced by the structure-related dynamics of charge carriers in these materials. In this study, we assessed the trapping, recombination, and surface reactions of photogenerated and electrically injected charges on specific facets of the promising visible active photocatalyst $BiVO_4$ by using single-particle photoluminescence (PL) spectroscopy. Evaluation of the electric-potential-induced PL properties and the PL response to charge scavengers revealed that the visible PL bands observed during visible laser irradiation originate from radiative recombination between holes trapped at the intraband states above the valence band and mobile (free or shallowly trapped) electrons. Figure 1 shows the potential dependence of the PL intensity captured at the crystal edge and center positions of a crystal, which correspond to lateral {110} and basal {010} facets, respectively. The PL enhancement is more pronounced on the lateral {110} facets of the crystal at an applied voltage of +1.2 V vs Ag/AgCl. On the other hand, almost uniform PL quenching over the entire crystal was induced by negative potentials. These results indicate that the trapped holes are preferentially located on the lateral {110} facets of the $BiVO_4$ crystal, while the electrons are uniformly distributed over the crystal. The methodology described in this study thus provides us with a unique opportunity to explore whether or not the crystal faces affect the charge carrier dynamics in the photocatalysis and the photoelectrocatalysis.

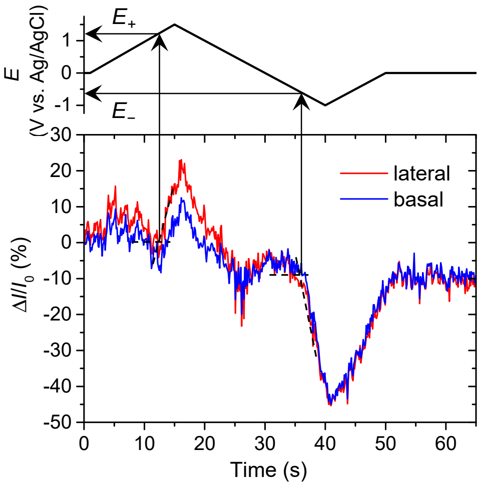

Figure 1. Applied potential dependence of the PL intensity changes obtained for the different locations of a $BiVO_4$ crystal. *I* is the integrated intensity over all wavelengths. The black lines and arrows indicate the potential at which PL ($E_\pm$) is enhanced or quenched.

In Situ Fluorine Doping of TiO_2 Superstructures for Efficient Visible-Light Driven Hydrogen Generation

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(*2016 IUPAC Photochemistry*)

Mesocrystals are superstructures with a crystallographically ordered alignment of nanoparticles. Owing to their organized structures, mesocrystals have unique characteristics such as a high surface area, pore accessibility, and good electronic conductivity. This paper presents recent developments in the applications of metal oxide mesocrystals in the fields of photocatalysis. Anatase TiO_2 mesocrystals were chosen as the typical investigation objects, which were newly synthesized by a topotactic structural transformation. The photoconductive atomic force microscopy, time-resolved diffuse reflectance spectroscopy, and single-molecule, single-particle fluorescence spectroscopy were utilized to determine the charge transport properties of TiO_2 mesocrystals. For example, novel visible-light-responsive photocatalysts were synthesized by the modification of TiO_2 mesocrystals with plasmonic Au nanoparticles by a simple impregnation method. It was found that a substantial part of electrons, injected from modified Au nanoparticles to the TiO_2 mesocrystals by the surface plasmon excitation, directionally migrate from the basal surfaces to the edges of the plate-like mesocrystals through the TiO_2 nanocrystal networks and are used for further surface reactions. As compared to the conventional nanoparticle systems, the superstructure-based systems could largely enhance charge separation and had remarkably long-lived charges, thereby exhibiting greatly increased photoconductivity and photocatalytic activity.

I-C. HIGH-RESOLUTION SPECTOSCOPY OF POLIATOMIC MOLECULES

Doppler-free high-resolution spectroscopic techniques are powerful tools for studying the structure and dynamics of excited polyatomic molecules in detail and unambiguously. Single-mode auto-scan laser systems in UV-Visible region, the absolute wavenumber measurement system, and several Doppler-free high-resolution spectroscopic measurement systems have been constructed to investigate the excited molecules. High-resolution and high-accuracy measurement of the spectral lines enable to observe rotationally-resolved electronic transition and to find out the excited state dynamics such as internal conversion (IC), intersystem crossing (ISC), and intramolecular vibrational redistribution (IVR) through the fairly deviation of the spectral line position, intensity anomaly and the change of the spectral linewidth. Recently, we observed the high-resolution spectrum and Zeeman effect of the π-π^* transition of several aromatic molecules such as benzene, naphthalene, anthracene, etc. and these molecular constants were determined in high-accuracy. We have observed the high-resolution spectrum of 2-Cl naphthalene and 1-Cl naphthalene, which are expected to find the spin-orbit interaction (ISC) from the heavy-atom effect. We also observed the high-resolution spectrum of fluorine $S_1 \leftarrow S_0$ transition, and determined these molecular constants.

High-resolution Laser Spectroscopy and Zeeman effect of $S_1 \leftarrow S_0$ Transition of naphthalene and Cl-naphthalenes

Shunji Kasahara, Ryo Yamamoto, Kenichirou Kanzawa, and Takumi Nakano

(*International Symposium: Recent Progress in Molecular Spectroscopy and Dynamics, 2016*)

High-resolution laser spectroscopy is a powerful tool for studying the structure and dynamics of excited polyatomic molecules in detail and unambiguously. High-resolution and high-accuracy of the spectral lines enable to observe rotationally-resolved electronic transition and to find out the excited state dynamics through the fairly deviation of the spectral line position, intensity anomaly and the change of the spectral linewidth [1]. In this study, we have observed the rotationally-resolved high-resolution fluorescence excitation spectra of the $S_1 \leftarrow S_0$ transition for naphthalene, 1-Cl naphthalene and 2-Cl naphthalene. The Zeeman broadening was also observed up to 1.2 T to consider the excited state dynamics.

A molecular beam was obtained by expanding of Cl naphthalene vapor with Ar gas through a pulsed nozzle into the vacuum chamber and collimated by using a skimmer and slit. Sub-Doppler fluorescence excitation spectra were measured by crossing a single-mode UV laser beam perpendicular to a collimated molecular beam. Absolute wavenumber was calibrated with accuracy 0.0002 cm^{-1} by measuring the Doppler-free saturation spectrum of iodine and a fringe pattern of the stabilized etalon.

For the naphthalene and 2-Cl naphthalene, rotationally-resolved spectra were observed for the 0-0 band, and assigned without any energy shift. The molecular constants of 2-Cl naphthalene were determined in high accuracy, which are in good agreement with the ones reported by Plusquellic et. al.[2] The Zeeman effects were also observed for these molecules. On the other hand, for the 1-Cl naphthalene, the rotational lines were not fully resolved because the fluorescence lifetime is shorter than that of 2-Cl naphthalene [3]. We determined the molecular constants of 1-Cl naphthalene from the comparison of the observed spectrum with calculated one. Remarkable Zeeman broadening was not found up to 1.2 T for the 1-Cl naphthalene.

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Rotationally-resolved high resolution laser spectroscopy of the $S_1 \leftarrow S_0$ transition of fluorene

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(*32nd Symposium on Chemical Kinetics and Dynamics*)

High-resolution laser spectroscopy is very powerful to study the molecular structure and excited state dynamics. We established the single-mode UV laser system, and measured the $S_1 \leftarrow S_0$ transition of several polyatomic molecules in UV region. Recently, the excited state dynamics has been discussed on naphthalene in the S_1 state [1]. In this study, rotationally-resolved high resolution fluorescence excitation spectra of the $S_1\ {}^1B_2 \leftarrow S_0\ {}^1A_1$ transition have been observed for fluorine.

A molecular beam was obtained by expanding of fluorene vapor with Ar gas through a pulsed nozzle into the vacuum chamber and collimated by using a skimmer and a slit. Sub-Doppler fluorescence excitation spectra were measured by crossing a single-mode UV laser beam perpendicular to a collimated molecular beam. Absolute wavenumber was calibrated with accuracy 0.0002 cm^{-1} by measuring the Doppler-free saturation spectrum of iodine and a fringe pattern of the stabilized etalon.

The high-resolution fluorescence excitation spectrum of the $S_1 \leftarrow S_0$ transition of the 0-0 band is shown in Figure 1. The observed rotational linewidth was approximately 25MHz. From the pattern of the spectrum, we found that the 0-0band is the a-type transition (selection rule: ΔK=0, ΔJ=0, ±1), whose transition moment is parallel to the long axis of the molecule. More than1300 rotational lines were assigned, and the molecular constants were determined with high accuracy. The determined molecular constants are good agreement with the reported ones [2]. We have measured the high-resolution spectrum under the external magnet field up to 1 T. However, the Zeeman effect was not found.

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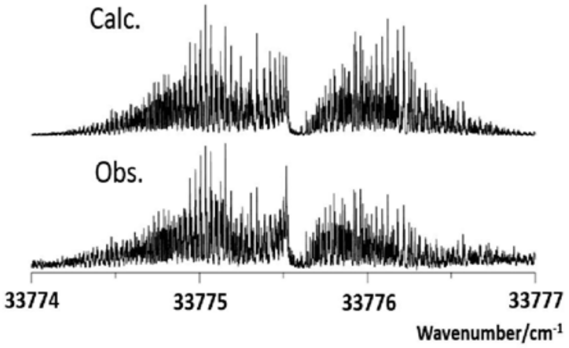

Figure 1. High-resolution fluorescence excitation spectrum of the 0-0 band of fluorene $S_1 \leftarrow S_0$ transition (lower) and the calculated spectrum (upper).

I-D. HIGH-RESOLUTION SPECTROSCOPY OF NO_3 RADICAL

Doppler-free high-resolution spectroscopy was applied to investigate the electronic states of radicals. The radicals are very sensitive to the magnetic field because the spin quantum number is a half integer, it is expected to observe large Zeeman splitting even in the small magnetic field. The Zeeman splitting is very useful to assign the observed rotational lines even in the strong perturbing region. The nitrate radical NO_3 has been known as an important intermediate in chemical reaction in the night-time atmosphere. NO_3 radical belongs with D_{3h} point group at the ground state $X\,^2A_2$’. The three lowest electronic states $X\,^2A_2$’, $A\,^2E$”, and $B\,^2E$’ are coupled by vibronic interaction, and therefore NO_3 radical becomes one of the model molecule for understanding the Jahn-Teller (JT) and pseudo Jahn-Teller (PJT) effects. The optically allowed *B-X* transition has been observed as a strong absorption and LIF excitation spectrum by several groups. The strongest absorption line at 662 nm is called as 0-0 band of *B-X* transition which is used to detect the NO_3 radical in the atmosphere, however, the rotational assignment still remained because it is too complicated. Recently, we reported the rotationally-resolved high-resolution spectrum and the Zeeman splittings of the *B-X* 0-0 band by using Doppler-free high-resolution spectroscopic technique. We expanded the measurement of the transition to vibrationally excited state observed around 628 nm.

Rotationally-resolved high resolution laser spectroscopy of NO_3 radical: 628 nm vibronic band of *B*-*X* transition

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(*32nd Symposium on Chemical Kinetics and Dynamics*)

NO_3 radical has two low-lying excited electronic states: $A\ ^2E''$ and $B\ ^2E'$. The ground electronic state ($X\ ^2A_2'$) and these excited electronic states can interact each other. Therefore, NO_3 has attracted attention as important model for understanding the vibronic interactions such as Jahn-Teller effect. We have investigated the $B\ ^2E' \leftarrow X\ ^2A_2'$ transition observed as strong absorption in visible region. Recently, we have measured the 0－0 band of the *B*-*X* transition around 662 nm and assigned a part of the rotational lines [1, 2]. In this study, we focused on the vibronic interaction of the vibrationally excited state of *B* state and observed the rotationally-resolved high resolution fluorescence excitation spectra of the 4^2_0 band around 628 nm.

NO_3 was produced by a pyrolysis reaction of N_2O_5 at 300℃ ($N_2O_5 \rightarrow NO_3 + NO_2$) with a heater attached to a pulsed nozzle. After the pyrolysis, NO_3 was collimated to a molecular beam with a skimmer and a slit. We crossed a single-mode laser beam and a molecular beam to reduce the Doppler width, then observed rotationally-resolved high resolution fluorescence excitation spectra. The absolute wavenumbers of the rotational lines were calibrated in the accuracy of 0.0001 cm^{-1} by the simultaneous measurements of the fringe patterns of a stabilized etalon and the Doppler-free saturation spectra of I_2.

More than 2000 rotational lines, which seemed to have less regularity, were detected in the observed region: 15890-15920 cm^{-1}. Then, we assigned a part of the rotational lines based on the observed Zeeman splitting patterns and the combination difference calculated from the reported molecular constants of the ground electronic state [3]. As a result, we found that several transition lines were assigned to the same transition. Therefore, several vibronic bands exist in the observed region. This results indicate that the vibrationally excited *B* state interacts with highly vabrationally excited states of the *A* state or the *X* state, and splits into several vibronic bands.

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II. Terahertz Molecular Chemistry Laboratory

II-A. LIQUID DYNAMICS STUDIED BY NONLINEAR INFRARED SPECTROSCOPY

Molecular dynamics in liquids are strongly affected by the nature of intermolecular interactions. It is greatly important to obtain the molecular description on relation between the dynamics and interactions in liquids in order to elucidate the solvent dynamical effect on chemical reactions. Fluctuations of the vibrational transition energies, which are characterized by time correlation functions of the frequency fluctuations, are very sensitive to the dynamics of surrounding environments. Vibrational energy relaxation is also affected by short-range solvent-oscillator interaction. Furthermore, orientational relaxation reflects microscopic viscosity around the oscillator. In recent years, a great deal of effort has been devoted to investigate solute-solvent interactions with infrared (IR) nonlinear spectroscopy. The vibrational frequency fluctuations can be investigated by three-pulse photon echo and two-dimensional IR spectroscopy. By polarization-sensitive pump-probe spectroscopy in the IR region we can study vibrational energy relaxation and orientational relaxation.

Rotational dynamics of solutes with multi-rotational axes in 1-alchohol solutions studied by infrared pump-probe spectroscopy

Masaki Okuda, Kaoru Ohta, and Keisuke Tominaga

(*8th International Conference on Coherent Multidimensional Spectroscopy 2016*)

So far, we have investigated the rotational dynamics of artificial amino acid molecules, which have the N_3 groups as a vibrational probe, in water with infrared (IR) pump-probe spectroscopy [1]. Reflecting the structural difference around the N_3 group, the observed anisotropy of the solutes showed different decaying behaviors; as the structural freedom around the vibrational probe increases, the decay becomes faster. According to the results, we have suggested that the rotational motion of the N_3 group has some correlations with that of the alkyl chain neighboring to the vibrational probe in the aqueous solution. The knowledge of the rotational dynamics of the solute with multi-rotational axes must be essential to understand the structural dynamics of macromolecules, such as proteins. In this study, we chose three different azide-derivatized amino acids (N_3-Ala, N_3-Pro and N_3-Nle) as solutes, and primary 1-alcohols ($CH_3(CH_2)_nOH$, n = 0 - 3) as solvents. We performed IR pump-probe measurements for these molecules in each alcohol, and in 1-BtOH at different temperatures from 283 K to 333 K. Because each of them has the different structural flexibility around the N_3 group, from the viscosity and temperature dependence of their rotational dynamics, we will be able to obtain the detailed information on the relationship between rotational motion of the N_3 group and the other rotational modes. The anisotropy decays can be characterized by a double-exponential function with sub-picosecond and picosecond time constants, which considered to reflect the thermal fluctuations and rotational dynamics of the N_3 group in 1-BtOH, respectively. Including the results for N_3-Ala and N_3-Nle in 1-BtOH, we obtained fast and slow rotational relaxation times. Although the fast time constants depend only on temperature, the slow ones depend not only on temperature but also on the solute. Based on the Stokes-Einstein-Debye theory, the temperature dependence of the slow time constant indicates that, the effective hydrodynamic volume of the N_3 group in 1-BtOH becomes smaller due to the correlated rotational motion of the N_3 group and the neighboring alkyl chains, as the structural freedom around the N_3 group increases.

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Frequency fluctuations of non-ionic vibrational probe in water studied by 2DIR spectroscopy and molecular simulation

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(*CMDS 2016*)

In aqueous solution, three-dimensional hydrogen bond network are formed among water molecules. The network evolves continuously in time due to the rearrangement of hydrogen bonds. Therefore, thorough solute-solvent interactions, such a collective dynamics strongly perturbs solutes, resulting in fluctuations of the electronic and vibrational states. So far, we examined the vibrational frequency fluctuations of ions, such as N_3^-, in water in order to discuss solute-solvent interactions and solvation dynamics [1]. In this study, we investigate the frequency fluctuations of the CN stretching mode of 2-nitro-5-thiocyanato-benzoic acid (NTBA) with two-dimensional infrared (2D-IR) spectroscopy. Because the SCN group in NTBA covalently binds to the aromatic ring, we can study the hydrophobic effects on the frequency fluctuations by comparing the results for ions. From the decay curve of the center line slope of 2D-IR spectra of NTBA in H_2O [2], it is found that the frequency-frequency correlation function (FFCF) of NTBA decays with the time constants of about 1 ps, and, according to the previous results of ions in water, this decay is related to the collective motion of waters around NTBA [1]. Moreover, no static component is contained in FFTCF of NTBA. Consequently, it could be considered that the water dynamics around NTBA is similar to those around ions. To obtain molecular pictures for the frequency fluctuations of NTBA in water, we also performed the molecular dynamics (MD) simulation. Based on the theoretical method to analyze the frequency shifts of the CN stretching mode in water [3], it is revealed that interactions between NTBA and water molecules not only in but also out of the first hydration shell are important for the frequency fluctuations of NTBA.

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Comparison of vibrational dynamics between non-ionic and ionic vibrational probes in water: Experimental study with two-dimensional infrared and infrared pump-probe spectroscopies

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(*J. Chem. Phys.*, *2016*)

Dynamics of the hydration structure around small vibrational probes have been extensively studied over the past few decades. However, we need to gain insight into how vibrational dynamics is affected by the molecular nature of the probe molecules in water. In this study, 2-nitro-5-thiocyanate benzoic acid (NTBA), which has an SCN group attached to an aromatic ring, and thiocyanate ion (SCN^-) were used to investigate the vibrational dynamics of two vibrational probes, including vibrational frequency fluctuations and rotational relaxation. By performing two-dimensional infrared (2D-IR) spectroscopic measurements, the vibrational frequency fluctuations of the SCN anti-stretching modes of these solutes were compared. The frequency-frequency time correlation function (FFTCF) of these solutes can be modeled by a delta function plus an exponential function and a constant. The FFTCF of NTBA was characterized by a time constant of 1.1 ps, which is similar to that of SCN^-. Moreover, no component was longer than this constant. Consequently, the loss of the correlation in frequency fluctuations of the SCN anti-stretching mode of NTBA may be controlled by a mechanism similar to that of the ionic probe, which involves the hydrogen bonding dynamics of water. Polarization-controlled IR pump-probe measurements were performed for these vibrational probes in water to study the vibrational energy relaxation (VER) and reorientational relaxation processes. The VER rate of NTBA is much smaller than that of SCN^-, which indicates that the intramolecular relaxation process is significant for VER of NTBA. Based on the rotational relaxation time of NTBA being shorter than that of SCN^-, the internal rotational motion of the SCN group around the C_{phenyl}-S bond axis, where C_{phenyl} denotes a carbon atom of the aromatic ring to which the SCN group is attached, may play an important role in the anisotropic decay of NTBA in H_2O.

Vibrational frequency fluctuations of ionic vibrational probe in water: theoretical study with molecular dynamics simulation

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(*Chem. Phys. Lett., in press*)

In the present study, we have conducted the theoretical analysis by using the classical molecular dynamics simulations to reveal relationship between the experimentally observed SCN vibrational frequency fluctuations of SCN^- in H_2O and its surrounding local environment. Based on the vibrational solvatochromism theory, we calculate the frequency-frequency time correlation function of the SCN anti-symmetric stretching mode, which is characterized by time constants of 0.13 and 1.41 ps. In order to understand the reason why the SCN frequency fluctuation of SCN^- in H_2O is characterized by the solute-independent time constant of the approximately 1 ps at a molecular level, we have investigated the HB dynamics in the hydration shell of the solute by calculating the HBCF for the hydrated water molecules. We find that the frequency fluctuation is almost determined by the electrostatic interaction from the water molecules in the first-hydration shell. It was revealed that the HBCF for the water molecules nearby SCN⁻ shows almost the same decay as that for bulk ones; the collective dynamics of the water molecules in the first-hydration shell is found to be similar to that of bulk water. However, it is interesting to note that the hydrogen bond between the ion and water molecule is very strong. Consequently, since the water molecules in the first- and second-hydration shells of SCN⁻ exhibit nearly bulk-like HB dynamics, the water molecules adjacent to SCN⁻ behave like a reporter of the structural fluctuations of the HB network in water.

II-B. DYNAMICS OF ELECTRONICALLY EXCITED STATE IN CONDENSED PHASES

Understanding of dynamics in the electronically excited state is a key issue to elucidate mechanisms in various photochemical reactions in condensed phases. It is also important for designing and developing new materials which have characteristic functions. We employ various kinds of ultrafast technique to monitor photochemical and photophysical invents in sub-pico- to picoseconds time scales. By femtosecond fluorescence up-conversion technique, dynamics in the electronically excited state can be observed with a time resolution up to 100 fs. Vibrational dynamics in the electronically excited can be investigate by UV/VIS-pump IR probe technique. Moreover, low-frequency responses by photoexcitation are investigated by UV/VIS-pump THz probe experiment. Such responses include change of low-frequency vibrational modes induced by photoexcitation and photo-induced changes of charge carrier dynamics.

Probing Charge Transfer Dynamics in Porphyrin-Based Organic Semiconductors by Time-Resolved THz Spectroscopy

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(*41st International Conference on Infrared, Millimeter, and Terahertz Waves 2016*)

Organic semiconductors have attracted much attention because of promising applications for bulk heterojunction (BHJ) solar cells. One of the reasons for widespread interest is that solution-process can be used for fabrication of such devices. This is great advantage over silicon-based devices because of potential for producing low-cost and flexible solar cells. Among these organic semiconductors, porphyrins have excellent optical and electronic properties. Compared to polymer-based systems, porphyrins have unique features such as well-defined molecular structures and weights.

In this study, we performed optical pump-terahertz (THz) probe measurements to investigate the charge carrier dynamics of tetrabenzoporphyrin (BP) and BP-based BHJ films. Generation and detection of the THz pulses are based on laser-induced air plasma and air-biased coherent detection, which allow us to measure the transient THz spectra in a broader frequency region. We measured the photo-induced change of THz electric field amplitude as a function of pump-probe delay with excitation at 400 nm. The transient signal has an instantaneous rise due to the formation of mobile charges. The signal decays within a few picosecond and a small long-lived component remains. This result suggests that most of mobile charges recombine on this time scale. From analysis of the transient complex conductivity spectra, we found that the conductivity spectra can be well reproduced by Drude-Smith model. This means that generated charge carriers are rapidly localized by preferential backscattering.

We also studied the charge carrier dynamics of diketopyrrolopyrrole-linked tetrabenzoporphyrin (DPP-BP) thin films. In contrast to BP, DPP-BP exhibits broad and intense absorption, ranging from the visible and near infrared region. Therefore, we expect to improve the power conversion efficiency for DPP-BP based solar cells. In this contribution, we will discuss the mechanism of formation and relaxation of mobile charge carriers for BP-based thin films.

II-C. MOLECULAR DYNAMICS IN THE TERAHERTZ FREQUENCY REGION IN CONDENSED PHASES

Vibrational spectroscopy has been widely used to investigate structures, interactions and dynamics of molecules and molecular complexes. The low-frequency region below several terahertz (THz; 1 THz = 33.3 cm^{-1}) corresponds to intermolecular modes of complexes and intramolecular modes with a weaker potential force and/or larger reduced mass. Intermolecular interactions such as hydrogen bonding, van der Waals forces and charge-transfer interactions play important roles in various chemical and biological processes. Moreover, the low-frequency spectra also reflect molecular dynamics on a time scale from picoseconds to femtoseconds. There has been dramatic progress in the generation and detection techniques of freely propagating THz radiation in the past two decades. The examples of the generation technique include photoconductive switching, optical rectification, and the surface photocurrent of semiconductors. Because the pulse duration of the THz radiation is in a sub-picosecond time region, it is possible to measure the electric field of the radiation by coherent detection methods, which consequently allows us to conduct THz time-domain spectroscopy (TDS). By THz-TDS we can obtain the refractive index and extinction coefficient of a medium by measuring the phase and amplitude of the radiation. THz-TDS is an attractive method for studying dynamics in condensed phases with time scales of sub-picoseconds and picoseconds. We have applied THz-TDS to investigate various kinds of condensed materials, including neat liquids and mixtures of liquids, biological polymers, and charge carrier dynamics in semiconductors and conducting polymers.

Broadband Dielectric Spectroscopy on Lysozyme in the sub-Gigahertz to Terahertz Frequency Regions: Effects of Hydration and Thermal Excitation

Naoki Yamamoto, Kaoru Ohta, Atsuo Tamura, and Keisuke Tominaga

(*J. Phys. Chem., 2016*)

We have performed dielectric spectral measurements of lysozyme in a solid state to understand the effects of hydration and thermal excitation on the low-frequency dynamics of protein. Dielectric measurements were performed under changing hydration conditions at room temperature in the frequency region of 0.5 GHz to 1.8 THz. We also studied the temperature dependence (83 K to 293 K) of the complex dielectric spectra in the THz frequency region (0.3 THz to 1.8 THz). Spectral analyses were performed using model functions for the complex dielectric constant. To reproduce the spectra, we found that two relaxational modes and two underdamped modes are necessary together with an ionic conductivity term in the model function. At room temperature, the two relaxational modes have relaxation times of ~20 ps and ~100 ps. The faster component has a major spectral intensity and is suggested to be due to coupled water-protein motion. The two underdamped modes are necessary to reproduce the temperature dependence of the spectra in the THz region satisfactorily. The protein dynamical transition is a well-known behavior in the neutron scattering experiment for proteins, where the atomic mean-square displacement shows a sudden change in the temperature dependence at approximately 200 K, when the samples are hydrated. A similar behavior has also been observed in the temperature dependence of the absorption spectra of protein in the THz frequency region. From our broadband dielectric spectroscopic measurements, we conclude that the increase in the spectral intensities in the THz region at approximately 200 K is due to a spectral blue-shift of the fast relaxational mode.

Elucidation of Chiral-symmetry Breaking in a Racemic Polymer System with Terahertz Vibrational Spectroscopy and Crystal Orbital Density Functional Theory

Feng Zhang, Houng-Wei Wang[1], Keisuke Tominaga, Michitoshi Hayashi[1], Sunglin Lee[2], and Takashi Nishino[2]

[1]National Taiwan University

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(*J. Phys. Chem. Lett.*, *2016*)

The conservation of chiral symmetry has been used as a fundamental rule to determine polymer packing-conformations in racemic systems. We have illustrated, through the interplay of polarization THz spectroscopy and solid-state density functional theory, that the chiral symmetry is not conserved in a poly(lactic acid) stereocomplex (scPLA) system. poly(L-lactic acid) (PLLA) displays a weaker violation of the 3_1 screw symmetry than poly(D-lactic acid) (PDLA), and possesses a stronger intramolecular vibrational energy, on average, in the low-frequency gamma-point phonon modes than does PDLA. Polarization THz spectroscopy adds a new dimension to polymer crystallography through which new phenomena are expected to be revealed.

Temperature-Dependent Conductivity of Graphene Oxide and Graphene Oxide-Polyaniline Nanocomposites Studied by Terahertz Time- Domain Spectroscopy

Partha Dutta,[1] Jessica Afalla, Arnab Halder,[2] Sudeshna Datta,[3] and Keisuke Tominaga

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(*J. Phys. Chem. C*, *2017*)

In this work, we have studied the temperature-dependent conductivity of graphene oxide (GO) and graphene oxide-polyaniline (GO-PANI) nano- composites by terahertz time-domain spectroscopy (THz-TDS) from 78 K to 293 K. The refractive index and absorption coefficient are related to the conductivity, and it has been found that in the THz region, the real part of the complex conductivity of GO is less than that of GO-PANI over the entire range of experimental temperatures. Both the systems exhibit an increase in these physical parameters with increasing temperature. The complex conductivity spectra of these systems in the THz region are well fitted by an analytical model that has contributions from the scattering of free electrons (Drude-Smith term) and from bound-electron oscillation (Lorentz term). The fitting analysis suggests a more ordered structure and anharmonicity for both the systems with increasing temperature and reports that GO-PANI has a greater free electron density and damping frequency of oscillation and more ordered structures than GO at all temperatures.

Application of THz vibrational spectroscopy to molecular characterization and the theoretical fundamentals: an illustration using saccharide molecules

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(*Chemistry - An Asian Journal*, *2017*)

This work illustrates the theoretical fundamentals for the application of THz vibrational spectroscopy for molecular characterization in the solid state, by using two different types of saccharide systems as an example. Four subjects have been specifically addressed: (1) qualitative difference of the molecular vibrational signatures monitored by THz and mid-IR vibrational spectroscopy ; (2) selection rule of THz vibrational spectroscopy as applied to the crystalline and amorphous systems; (3) normal mode simulation, by using the α-L-xylose as a particular example; and (4) rigorous mode analysis to quantify the percentage contributions of intermolecular and intramolecular vibrations to the normal mode of interest.

Conducting Properties of Polyaniline in the THz Region: Investigations of Various Processing Conditions

Alvin Karlo G. Tapia and Keisuke Tominaga

(*J. Infrared Milli. Terahz. Waves*, *2017*).

The terahertz (THz) conductivities of polyaniline emeraldine salts (PAni-ES) with different processing conditions were studied by using THz time-domain spectroscopy. The measurements were conducted for samples with different doping time, annealing time, compression pressure, and percentage mixtures. The measurements agreed with the Mott-Davis hopping model with the parameter *S* varying inversely with the protonation of the sample. The addition and removal of dopants led to the distinction of conduction mechanisms from vibrational processes in the THz region. The inter-chain and intra-chain conduction improved with increasing density of the pellets due to compression. Also, the conduction was affected by the network of conducting regions in the PAni-PE pellets. The usefulness of the Mott-Davis model on the THz spectra to describe the relationship between property and conduction was demonstrated. Lastly, results suggest that it is possible to standardize the measurements and use THz spectroscopy for analytical purposes and sensing applications by conductivity response due to a stimulus.

Broadband Dielectric Spectroscopy on H_2O, D_2O, and $H_2{}^{18}O$, and Theoretical Calculations on the THz Spectral Component

Mariko Nakatsuka, Takafumi Nara, Masaki Okuda, Naoki Yamamoto, Feng Zhang, Kaoru Ohta, Hideaki Shirota,[1] Shinji Saito,[2] and Keisuke Tominaga

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(*9th International Conference on Broadband Dielectric Spectroscopy and its Applications, 2016*)

It is well known that liquid water interacts with electromagnetic waves over a broad frequency range. For example, the collective rotational relaxation has its dielectric spectra from MHz to GHz frequency region, and the spectral component in the THz region is suggested to be due to fluctuation of the hydrogen bonding network. These spectral components in the different frequency regions overlap with each other. Therefore, it is necessary to perform dielectric spectroscopic measurements in a broad frequency region. In this study, we chose H_2O, $H_2{}^{18}O$, and D_2O as samples. We also measure the dielectric spectra by changing temperature from 273 K to 353 K. In the microwave region (200 MHz~20 GHz), the complex dielectric constants were measured by a vector network analyzer. In the sub-THz region (40 GHz~300 GHz) and THz region (300 GHz~2.5 THz), a pair of spiral and dipole type photoconductive antenna were used for generation and detection of the electromagnetic waves, respectively [1]. In the higher frequency side of the THz region (2.5 THz~7 THz), the THz pulse was generated by focusing the output and its second harmonics from a regenerative amplifier into air. For the far-IR and mid-IR regions, the absorption spectra were measured by using FTIR spectrometers. The complex dielectric spectra of water from 200 MHz to 30 are analyzed using a model function with Debey relaxtion and damped oscillator functions. The Raman spectra provide complementary information about the molecular dyanmics in liquids. We also discuss the low-frequency Raman spectra of water obtained by optical Kerr effect measurements with femtosecond laser pulse. We also perfomed molecular dynamics simulation and instateneous normal mode analysis for liquid water to understand the spectral component in the THz frequency region.

1. N. Yamamoto, et al., *J. Phys. Chem B.* **120** (21), 4743-4755 (2016).

II-D. INTERMOLECULAR INTERACTIONS OF POLYMER STUDIED BY TERAHERTZ SPECTROSCOPY

Terahertz (THz) spectroscopy has recently much attention from biomolecules, medicine, and polymer materials, since it very sensitive to the hydrogen bonding. Especially, the low-frequency vibrational modes reflect the higher order conformations of large molecules, it is a very powerful tool for the investigation of various material properties such as hydrogen bonding of the polymers. We have investigated the isothermal crystallization of several kinds of polymer by means of THz and infrared (IR) spectroscopy, and small angle X-ray scattering (SAXS) and wide angle X-ray diffraction (WAXD) simultaneous measurements. THz spectroscopy, we can obtain detailed information about how hydrogen bonding results in the higher-order conformation of polymers.

THz and low-frequency Raman Spectroscopy of polymers

Harumi Sato

(20th European Symposium on Polymer Spectroscopy)

Recently, Terahertz (THz) spectroscopy has received an increasing interest from biomolecules, medicine, and polymer materials. Since the low-frequency vibrational modes reflect the higher order conformations of large molecules, it is a very powerful tool for the investigation of various material properties such as hydrogen bonding of the polymers. One of the most prominent characteristics of THz and low frequency Raman spectroscopy is these spectroscopy is that it is possible to detect the inter- and intramolecular vibrations and orientation of the polymer chains sensitively.

In the present study, we have investigated the characterization of the various biodegradable polyesters by using THz and low frequency Raman spectroscopy. Especially we focused on the changing of the THz spectra for crystallization process, thermal behavior, hydrogen bonding of the polymers. Moreover, we also have been investigated the correlation between low frequency spectra and the changes of physical behavior in polymer by comparing with ordinal spectroscopic methods, IR and Raman. The isothermal crystallization of polyglycolic acid (PGA) was studied by monitoring the temporal evolution of THz absorption spectra with 2DCOS analysis. These results indicated that the hydrogen bonding of PGA are initially formed before well-defined crystal structure are established.

Higher-Order Structure of the Biodegradable Polymer Studied by Terahertz Spectroscopy

Harumi Sato

(Japan-Taiwan Medical Spectroscopy International Symposium 2016)

Terahertz (THz) spectroscopy is a very powerful tool for the investigation of various material properties such as hydrogen bonding of the polymers.[1-3] THz and low frequency Raman spectroscopy is able to detect the inter- and intramolecular vibrations and orientation of the polymer chains sensitively.

In the present study, we have investigated the characterization of the various biodegradable polyesters by using THz and low frequency Raman spectroscopy, and X-ray diffraction. We focused on the changing of the THz spectra during the crystallization process, thermal behavior, and polymer degradation process of the polymers.

The terahertz spectra were measured by using a Fourier-transform spectrometer (JASCO FARIS) with a resolution of 2 cm^{-1} and an accumulation of 100 times and a TAS7400 terahertz spectroscopy system from Advantest Corp with an accumulation of 1024 times in the 10-150 cm^{-1} wavenumber region.

We can obtain information about changes in intermolecular interactions of PGA in a film during isothermal from THz spectroscopy, which is a powerful tool for monitoring higher order conformations of polymer. The isothermal crystallization of polyglycolic acid (PGA) was studied by monitoring the temporal evolution of THz absorption spectra with two-dimensional correlation analysis (2DCOS) analysis.

The 2DCOS analysis was applied to a series of time-dependent THz spectra and it revealed the formation of the lamellar structure with C-H···O (ether) intermolecular interaction of PGA. These results also indicated that the hydrogen bonding of PGA are initially formed before the well-defined crystal structure are established. Therefore, it can be said that the hydrogen bond is controlling the crystallization of PGA.

[1] H. Hoshina *et al*., *Phys. Chem. Chem. Phys.,* **13**, 9173 (2011).

[2] H. Hoshina *et al*., *Appl. Phys. Lett*. **96**, 101904 (2010).

[3] H. Hoshina *et al*., *Appl. Phys. Lett.* **100**, 011907-1-3 (2012).

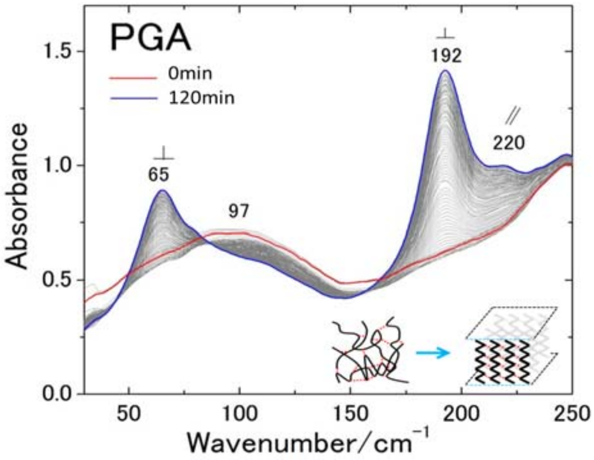

Figure 1. Time-dependent terahertz absorption spectra collected during the melt crystallization process of PGA at 185 °C.

Low-Frequency Vibrational Modes of Poly(glycolic acid) and Thermal Expansion of Crystal Lattice Assigned On the Basis of DFT-Spectral Simulation Aided with a Fragment Method

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[3]Kwansei Gakuin University

(*J. Phys. Chem. B 2017*)

Low-frequency vibrational modes of lamellar crystalline poly(glycolic acid) (PGA) were measured on Raman and far-infrared (FIR) spectra. Among the observed bands, an FIR band at ~70 cm^{-1} and a Raman band at 125 cm^{-1} showed a gradual lower-frequency shift with increasing temperature from 20 °C to the melting point at ~ 230 °C. Their polarization direction was perpendicular to the chain axis of PGA. Both spectra were quantum-mechanically simulated with the aid of a fragment method, the Cartesian-coordinate tensor transfer, which enabled an explicit consideration of molecular interactions between two adjacent polymer chains. Good agreement was achieved between the experiment and theory in both spectra. The temperature-sensitive bands at ~70 cm^{-1} in FIR and at 125 cm^{-1} in Raman comprise the out-of-plane C=O bending motion. The temperature-dependent shifts of the low-frequency bands were successfully simulated by the DFT-spectral calculation, exploring that the main origin of the shifts is the thermal expansion of the crystal lattice. This result indicates that the thermally shifted bands may be used as an indicator of the lattice expansion of PGA. Possible changes in intermolecular interactions of PGA under temperature rising were ascribed on the basis of natural bond orbital theory. The steric repulsion between the carbonyl O atom in one chain and the H−C bond in the adjacent chain will be a dominant interaction in the lattice expanding process, which would cause the observed thermal shifts of the bending modes. Comparisons of the spectral assignment for PGA obtained in this study and that for poly-(R)-3-hydroxybutyrate (PHB) reported by us suggest that crystalline polyesters give vibrational modes composed of out-of-plane bending motion of C=O groups between ~70 and ~125 cm^{-1}, the modes of which are sensitive to the thermal expansion of crystal lattice and its concomitant changes in their intermolecular interactions.

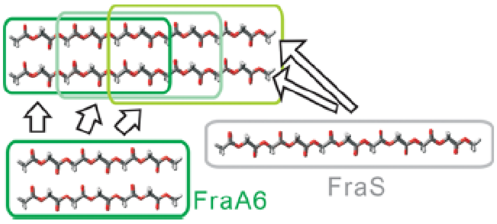

Figure 1. Schematic presentation of a typical tensor transfer as applied to two PGA chains with the length of 10 monomer units.

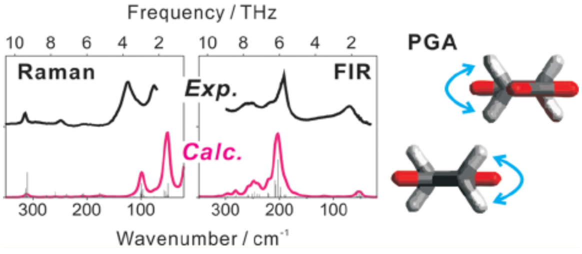

Figure 2. Comparison of the experimental (top) and calculated (bottom) Raman and FIR spectra of crystalline PGA.

II-E. TERAHERTZ IMAGING OF POLYMERS

Terahertz (THz) imaging has been a subject of considerable interest since this technique can be used to visualize the distribution of the different components in a nonhomogeneous material such as pharmaceutical tablets, semiconductor wafers, and biomedical subjects. One of the main advantages is that, compared to IR and Raman imaging, in THz imaging areas in a fairly wide size range can be imaged. Other advantages are that THz spectroscopy enables the nondestructive development of a THz image even for thick samples, and in addition, images mapping the distribution of the higher order structure in large molecules can be obtained. We have applied THz imaging spectroscopy to investigate the crystalline orientation, distribution of crystallinity, and the changes in the higher order structure of polymer film.

Terahertz Imaging of the Distribution of Crystallinity and Crystalline Orientation in a Poly(e-caprolactone) Film

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[2] Kwansei Gakuin University

(*Appl. Spectrosc., 2017*)

The distribution of crystallinity and the crystalline orientation of a poly(ε-caprolactone) (PCL) film have been studied using terahertz (THz) imaging. Terahertz images were developed by using the intensity ratio of the two spectral peaks at 1.42 and 2.03 THz that are assigned to the crystalline modes parallel and perpendicular to the c-axis (Io/Ijj) of the PCL film. The obtained THz images show that the distribution of crystallinity and crystalline orientation vary considerably between the different regions in the PCL film, even though this inhomogeneity is not visible in the corresponding optical image. Our results clearly illustrate that THz imaging is a promising technique to characterize the physical properties of semicrystalline polymers.

In this study, for the first time, the crystalline orientation, distribution of crystallinity, and the changes in the higher order structure in a PCL film were investigated by THz imaging spectroscopy. The peaks at 1.42 and 2.03 THz assigned to the crystalline mode of the PCL film were used to construct the crystallinity image and the distribution of crystallinity. In addition, the changes in the higher order structure in PCL were also imaged. Our results show that THz imaging holds considerable promise to monitor the crystallinity and crystalline orientation of semi-crystalline polymer films; this technique also has application in polymer industry. Because THz spectroscopy is sensitive to changes in the conformation of polymers and is capable of probing large areas, THz imaging may be applied to the monitoring of various physical properties of polymer films during processing.

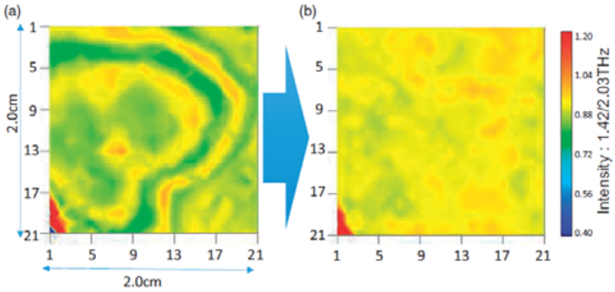

Figure 1. The THz images of a PCL film (a) just after hot pressed and (b) after melting.

III Terahertz Material Physics Laboratory

III-A. HIGH FIELD ELECTRON SPIN RESONANCE (ESR) STUDIES OF QUANTUM SPIN SYSTEMS

Quantum spin system shows distinct quantum effects due to its strong quantum fluctuation. Recently, quasi-one or two dimensional quantum spin systems have attracted much interest, and their short-range order and their ground state at low temperature should be clarified. High frequency high field ESR turns out to be a powerful means to observe the short-range order and the ground state of the system. Moreover, frustrated magnetic systems have also attracted much interest recently. The frustration in the magnetic system suppresses the conventional magnetic order and a unique ground state appears at low temperature. Especially the competition is expected between the frustration and low dimensionality. Following the trends from a Grant-in-Aid for Scientific Research on Priority Areas “Novel states of matter induced by frustration” (No.473, 2007-2011, Headed by Prof. H. Kawamura (Osaka University) and H. Ohta was a member), we are studying these low dimensional antiferromagnets with frustration and related multiferroic materials intensively. High field ESR measurements of S=3/2 perfect kagome lattice antiferromagnet, $KCr_3(OH)_6(SO_4)_2$ (Cr-jarosite), has been studied. Magnetic anisotropy of Cr-jarosite is investigated using single crystals. Components of d vector of Dzyaloshinsky-Moriya (DM) interaction is estimated by analysis of antiferromagnetic resonances with easy plane anisotropy and DM interaction.

H. Ohta gave invited presentations at “Energy Materials Nanotechnology Meeting on Terahertz (EMN meeting)” (May 14-18, San Sebastian, Spain), “The 4rd Awaji International Workshop on Electron Spin Science & Technology (AWEST 2016)” (June 19-21, 2016, Awaji, Japan), “The 4th Forum EMR-PL” (June 27-29, Poznan, Poland), “The Annual Meeting of The Society of Electron Spin Science and Technology (SEST 2016)” (Nov. 10-12, 2016, Osaka, Japan), and “Modern Development of Magnetic Resonance (MDMR)” (Oct. 31- Nov. 4, 2016, Kazan, Russia), and introduced the recent results of high field ESR in Kobe.

In meantime H. Ohta was appointed as the President of International EPR (ESR) Society (IES) since January, 2015 and attended four EPR/ESR related international conferences to increase the visibility of IES by organizing AGM and presenting IES awards. H. Ohta is also acting as the Vice-President of APES (Asia-Pacific EPR/ESR Society), the Vice-President of the Japan Society of Infrared Science and Technology, and the Council Member of SEST.

Moreover, in order to strengthen the pulsed magnetic field researches in western Japan region, we have set up The KOFUC (Kobe-Osaka-Fukui Universities Centers) Network since 2014. The introductory seminar 2016 and the annual meeting 2016 were organized at Kobe University and University of Fukui, respectively.

Dzyaloshinsky-Moriya interaction and the ground state in S=3/2 perfect kagome lattice antiferromagnet $KCr_3(OH)_6(SO_4)_2$(Cr-jarosite) studied by X-band and high-frequency ESR

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(*J. Phys. Soc. Jpn. 86, 024703* (*2017*))

A single-crystal $S = 3/2$ perfect kagome lattice antiferromagnet, $KCr_3(OH)_6(SO_4)_2$ (Cr-jarosite), has been studied by X-band and high-frequency electron spin resonance (ESR). The g-values perpendicular to the kagome plane (c-axis) and in the plane were determined to be $g_c = 1.9704 \pm 0.0002$ and $g_\xi = 1.9720 \pm 0.0003$, respectively, by high-frequency ESR observed at 265 K. Antiferromagnetic resonances (AFMRs) with an antiferromagnetic gap of 120 GHz were observed at 1.9 K, which is below $T_N = 4.5$ K. The analysis of AFMR modes using the conventional molecular field theory gave $d_p = 0.27$ K and $d_z = 0.07$ K, where d_p and d_z are in-plane and out-of-plane components of d vector of the Dzyaloshinsky–Moriya (DM) interaction, respectively. On the basis of these results and the exchange interaction of $J = 6.15$ K estimated by Okuta et al., the ground state of Cr-jarosite was discussed in connection with the Monte Carlo simulation results with classical Heisenberg spins on the kagome lattice by Elhajal et al. Finally, the angular dependence of the linewidth and lineshape observed at 296 K by X-band ESR showed the typical behavior of a two-dimensional Heisenberg antiferromagnet, suggesting the good two-dimensionality of Cr-jarosite.

III-B. ESR AND MAGNETIC PROPERTY MEASUREMENTS OF 4f-ELECTRON MATERIAL

The 4f-electron systems, which consist of rare-earth elements, have attracted much attention to a heavy-fermion metal, exotic supercoductivity and peculiar conductivity. These materials often show unique magnetic properties. Investigation of magnetic properties from microscopic measurements have been performed mainly using the nuclear magnetic resonance, muon spin relaxation, and the neutron measurements. Peculiar magnetic field dependence of the exciton peak in the nonsuperconducting CeB_6 has been investigated by inelastic neutron scattering and high frequency ESR measurements. The high frequency ESR measurements make it clear due to its higher resolution. This work has been performed under international cooperation.

Magnetic field dependence of the neutron spin resonance in CeB_6

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[7]Jülich Center for Neutron Science (JCNS)Jülich Center for Neutron Science (JCNS)

[8]Institut Laue-Langevin, 6 rue Jules Horowitz

[9]Quantum Condensed Matter Division, Oak Ridge National Laboratory (ORNL)

(*Phys. Rev. B 94, 035114/1-6* (*2016*))

In zero magnetic field, the famous neutron spin resonance in the *f*-electron superconductor $CeCoIn_5$ is similar to the recently discovered exciton peak in the non-superconducting CeB_6. Magnetic field splits the resonance in $CeCoIn_5$ into two components, indicating that it is a doublet. Here we employ inelastic neutron scattering (INS) to scrutinize the field dependence of spin fluctuations in CeB_6. The exciton shows a markedly different behavior without any field splitting. Instead, we observe a second field-induced magnon whose energy increases with field. At the ferromagnetic zone center, however, we find only a single mode with a non-monotonic field dependence. At low fields, it is initially suppressed to zero together with the antiferromagnetic order parameter, but then reappears at higher fields inside the hidden-order phase, following the energy of an electron spin resonance (ESR). This is a unique example of a ferromagnetic resonance in a heavy-fermion metal seen by both ESR and INS consistently over a broad range of magnetic fields.

III-C. DEVELOPMENTS OF MULTI-EXTREME ESR SYSTEM, SQUID ESR AND MICRO-CANTILEVER ESR

High frequency high field ESR measurement has many advantages compared with the conventional X-band ESR, for instance, the high spectral resolution, measurements beyond a magnetic phase transition, and the detection of spin systems that have a large zero-field splitting, which is not possible by X-band ESR. However, THz ESR has the limitation of sensitivity at the moment. Therefore, a new, highly sensitive detection technique for THz ESR compatible with a high magnetic field is required for its wide application, and we are developing the highly sensitive THz ESR system using the micro-cantilever. E. Ohmichi is working on the microfabrication of MEMS cantilever for micro-cantilever ESR. E. Ohmichi and H. Takahashi developed a high-sensitivity cantilever ESR system using a fiber-optic interferometer and a Faraday method. H. Takahashi received the Best Presentation Award at SEST 2016. The doctor course student T. Okamoto received the Best Presentation Award at the Japan Society of Infrared Science and

Technology.

Moreover, the pressure region is expanded to 2.7 GPa using the hybrid-type piston-cylinder pressure cell, and the transmission-type high-field ESR system is developed with the combination of this pressure cell and the cryogen-free 10 T superconducting magnet in 2014 by the collaboration with Prof. Uwatoko (ISSP, University of Tokyo). This new high-pressure ESR system is applied to the Shastry-Sutherland Model Compound $SrCu_2(BO_3)_2$, and the pressure induced phase transition is discovered around 1.8 GPa. The paper is in preparation. T. Sakurai, S. Okubo, and H. Ohta received the Excellent Paper Award at the Japan Society of Infrared Science and Technology. H. Ohta gave an invited presentations about the multi-extreme ESR system including the high-pressure ESR, the SQUID ESR and the micro-cantilever ESR at "Energy Materials Nanotechnology Meeting on Terahertz (EMN meeting)" (May 14-18, San Sebastian, Spain), "The 4rd Awaji International Workshop on Electron Spin Science & Technology (AWEST 2016)" (June 19-21, 2016, Awaji, Japan), "6th Euro-Asian Symposium 'Trends in MAGnetism' (EASTMAG-2016)" (Aug 15-19, Krasnoyarsk, Russia), "The Annual Meeting of The Society of Electron Spin Science and Technology (SEST 2016)" (Nov. 10-12, 2016, Osaka, Japan), and "Modern Development of Magnetic Resonance (MDMR)" (Oct. 31- Nov. 4, 2016, Kazan, Russia),.

Cantilever detected ferromagnetic resonance in thin $Fe_{50}Ni_{50}$, $Co_2FeAl_{0.5}Si_{0.5}$ and Sr_2FeMoO_6 films using a double modulation technique

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[2]Graduate School of Science, Kobe University

[3]Leibniz Institute for Solid State and Materials Research Dresden

[4]Department of Physics, The Ohio State University

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[6]Technishe Universität Dresden

(*J. Mag. Res. 270, 183–186* (*2016*))

In this work we introduce a new method, which employs commercial piezo-cantilevers, for a ferromagnetic resonance (FMR) detection from thin, nm-size, films. Our setup has an option to rotate the sample in the magnetic field and it operates up to the high microwave frequencies of 160 GHz. Using our cantilever based FMR spectrometer we have investigated a set of samples, namely quasi-bulk and 84nm film $Co_2FeAl_{0.5}Si_{0.5}$ samples, 16nm $Fe_{50}Ni_{50}$ film and 150 nm Sr_2FeMoO_6 film. Low frequency and room temperature test of our setup using 84 nm $Co_2FeAl_{0.5}Si_{0.5}$ film yielded a result identical to a standard X-Band spectrometer, namely a single line with quite small linewidth. Our measurements at low temperatures and high frequencies revealed a quite strong FMR response detected in all samples. The FMR spectra share common features, such as the emergence of the second line with an opposite angular dependence, and a drastic increase of the linewidths with increasing microwave frequency. We believe that these findings are results of the complicated dynamics of the magnetization at low temperatures and high frequencies, which we were able to probe using our cantilever based FMR setup.

Multi-frequency force-detected electron spin resonance in the millimeter-wave region up to 150 GHz

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(*Rev. Sci. Inst. 87, 073904/1-8* (*2016*))

In this article, a novel technique is developed for multi-frequency force-detected electron spin resonance (ESR) in the millimeter-wave region. We constructed a compact ESR probehead, in which the cantilever bending is sensitively detected by a fiber-optic Fabry-Perot interferometer. With this setup, ESR absorption of diphenyl-picrylhydrazyl radical (< 1 μg) was clearly observed at multiple frequencies of up to 150 GHz. We also observed the hyperfine splitting of low-concentration Mn^{2+} impurities(~0.2%) in MgO.

Wide-Dynamic-Range Cantilever Magnetometry Using a Fiber-Optic Interferometer and its Application to High-frequency Electron Spin Resonance Spectroscopy

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We present a method of broadening the dynamic range of optical interferometric detection of cantilever displacement. The key idea of this method is the use of a wavelength-tunable laser source. The wavelength is subject to proportional-integral control, which is used to keep the cavity detuning constant. Under this control, the change in wavelength is proportional to the cantilever displacement. Using this technique, we can measure large displacements (>1 μm) without degrading the sensitivity. We apply this technique to high-frequency electron spin resonance spectroscopy and succeed in removing an irregular background signal that arises from the constantly varying sensitivity of the interferometer.

Development of Ultrasensitive Terahertz ESR Spectroscopy for Metalloprotein Using a Microcantilever

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(*J. Infrared Milli THz Waves 37, 1173-1184* (*2016*))

In this article, we report a novel method for ultrasensitive high-frequency electron spin resonance (HFESR) using a microcantilever. With this method, a field-gradient force exerting on a sample-holding cantilever is detected as cantilever displacement. A unique feature of this method is that a very tiny sample (~1 μg) is sufficient for HFESR measurement in the terahertz region. Thus, the application of this method to metalloprotein is expected to be of particular interest in the future. In this study, we developed two types of HFESR techniques: one for fiber-optic detection and the other for piezoresistive detection. We applied these techniques to multi-frequency HFESR measurements of metal-containing porphyrin compounds as a model metalloprotein substance and evaluated the sensitivity and feasibility of each technique.

High-Frequency Electron Paramagnetic Resonance of Metal-Containing Porphyrin Compounds Using a Microcantilever

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(*J. Inorganic Biochemistry 162, 190-193* (*2016*))

In this article, we report a novel technique of high-frequency electron paramagnetic resonance (HFEPR) using a microcantilever. In this method, a sample is mounted on a cantilever, and the field-gradient force associated with EPR absorption is detected as a cantilever bending. By using a micrometer-sized cantilever, this technique can be applied to a very tiny sample on the order of μg. In addition, the use of a piezoresistive cantilever makes the experimental setup easy and compact. In this study, we applied this technique to multi-frequency HFEPR measurements of metal-containing porphyrin compounds, which are an important composing element of metal-containing proteins and coenzymes such as hemoglobin and cyanocobalamin.

III-D. MAGNETIZATION MEASUREMENTS USING SQUID MAGNETOMETER

The installation of SQUID magnetometer in 2010 by a Grant-in-Aid Creative Scientific Research “Development of properties and functionalities by precise control of rare-earth doping” (2007-2011, Prof. Y. Fujiwara (Osaka University)) opened up wide varieties of collaborative researches. In 2015 users of SQUID magnetometer are Mochida and Takahashi groups, Uchino group (Department of Chemistry, Kobe University), Sugawara and Matsuoka group (Department of Physics, Kobe University), T. Sakurai and S. Hara (Center for Supports to Research and Education Activities, Kobe University). It is also used for the development of SQUID ESR.

A New Family of Anionic FeIII Spin Crossover Complexes Featuring a Weak-Field N_2O_4 Coordination Octahedron

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(*Chem. Eur. J. 22, 1253-1257* (*2016*))

Unprecedented anionic Fe^{III} spin crossover (SCO) complexes involving a weak-field O,N,O-tridentate ligand were discovered. The SCO transition was evidenced by the temperature variations in magnetic susceptibility, Mössbauer spectrum, and coordination structure. The DFT calculations suggested that larger coefficients on the azo group in the HOMO—1 of a ligand might contribute to the enhancement of a ligand-field splitting energy. The present anionic SCO complex also exhibited the light- induced excited-spin-state trapping effect.

The Role of Coulomb Interactions for Spin Crossover Behaviors and Crystal Structural Transformation in Novel Anionic Fe(III) Complexes from a π-Extended ONO Ligand

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(*Crystals 6 (2016) 49/1-16* (*2016*))

To investigate the π-extension effect on an unusual negative-charged spin crossover (SCO) Fe^{III} complex with a weak N_2O_4 first coordination sphere, we designed and synthesized a series of anionic Fe^{III} complexes from a π-extended naphthalene derivative ligand. Acetonitrile-solvate tetramethylammonium (TMA) salt 1 exhibited an SCO conversion, while acetone-solvate TMA salt 2 was in a high-spin state. The crystal structural analysis for 2 revealed that two-leg ladder-like cation-anion arrays derived from π-stacking interactions between π-ligands of the Fe^{III} complex anion and Coulomb interactions were found and the solvated acetone molecules were in one-dimensional channels between the cation-anion arrays. A desolvation-induced single-crystal-to-single-crystal transformation to desolvate compound 2’ may be driven by Coulomb energy gain. Furthermore, the structural comparison between quasi-polymorphic compounds 1 and 2 revealed that the synergy between Coulomb and π-stacking interactions induces a significant distortion of coordination structure of 2.

III-E. SPIN AND LATTICE DYNAMICS STUDIED BY OPTICAL PUMP-PROBE SPECTROSCOPY

The ultrafast spin dynamics and optical spin control in magnetic materials are attractive topics because of the potential applications in the developments of ultrafast spin control, spintronics, quantum computing, and optical control of correlated spin systems. For the ultrafast spin control and device applications, solid-state materials are more desirable. We studied the spin and lattice dynamics in solid-state materials using optical pump-probe spectroscopy. The generation and detection of magnetization and birefringence using optical and electric pulses are very useful to observe the ultrafast spin and lattice dynamics in antiferromagnetic, multiferroic, and magnetoelectric materials. The time-domain spectroscopy has a large potential for the ultrafast, broadband, and accurate observation of elementary excitation dynamics in the terahertz region.

The Observation of Ultrafast Magnon Dynamics in Antiferromagnets NiO and MnO by Pump-Probe and Terahertz Time-Domain Spectroscopies

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(*Nova Science, 2017*)

We have studied the ultrafast magnon dynamics in antiferromagnetic 3d-transition-metal monoxides NiO and MnO using optical pump-probe spectroscopy and terahertz time-domain spectroscopy (THz-TDS). Terahertz damped oscillations of magnons were observed in the Faraday rotation signal by pump-probe spectroscopy and in the transmitted THz electric field by THz-TDS. In MnO, the magnon signal was not observed in the experiment of pump-probe spectroscopy but was observed in the experiment of THz-TDS. This suggests that the magnon in MnO is not Raman active. On the other hand, in NiO, the magnon signals were observed in both experiments of pump-probe spectroscopy and THz-TDS. This shows that both Raman- and infrared-active modes are included in the magnon modes in NiO. The relaxation rate of magnons observed by THz-TDS was found to be nearly constant up to the Néel temperature and to increase abruptly near the Néel temperature in both NiO and MnO. In our experiment, the softening of the magnon frequency near the Néel temperature was observed more clearly than that in the other experiments such as infrared and Raman spectroscopies. This result shows that pump-probe technique and THz-TDS have high frequency resolution and high S/N ratio in the terahertz region than the other experiments. To explain the temperature dependence of the magnon frequency, we tried to fit the observed frequency by using three types of molecular field theories: the classical molecular field, the square root of classical molecular field, and the molecular field including biquadratic exchange. From an analysis of the observed results, we found that the molecular field including biquadratic exchange can explain well the observed behavior of magnons in both NiO and MnO.

Critical Behavior of Relaxational Lattice Modes in Multiferroic Cupric Oxide

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(*UP 2016*)

Cupric oxide CuO has been found to be a unique magnetic ferroelectric material with a transition temperature T_{N2} = 230 K, which is much higher than the critical temperatures of other magnetic ferroelectric materials. CuO undergoes two successive magnetic phase transitions at T_{N1} = 213 K and T_{N2} = 230 K. In the low-temperature phase ($T < T_{N1}$), the magnetic moments are aligned collinearly and order antiferromagnetically. A multiferroic phase appears in the temperature range between T_{N1} and T_{N2}. In this phase ($T_{N1} < T < T_{N2}$), the magnetic order is qualitatively different; a noncollinear and incommensurate antiferromagnetic order with a ferroelectric polarization. The spiral spin structure of this phase is the result of frustration between ferromagnetic and antiferromagnetic exchange interactions and results in a ferroelectric polarization along the *b* axis. Both magnetic and ferroelectric orders vanish above T_{N2}. In this report, the optically induced ultrafast lattice dynamics in CuO was studied by a transient birefringence measurement with the pump-probe technique. We observed the critical behaviors of the relaxational lattice modes and discuss the character of the ferroelectric phase transitions.

Dynamics of the Electric-Field Induced Magnetization in Antiferromagnetic Chromium Oxide Measured by Faraday Rotation

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(*LEES 2016*)

In recent years, various type of multiferroic materials, in which ferroelectric and magnetic orders coexist, have been found. Many of them are antiferromagnets which have spin structures of spiral type. Chromium (III) oxide (Cr_2O_3) is not multiferroic, but has been interested in for a long time by its magnetoelectric effect. In the present study, we pay attention to the magnetization induced by the electric field in the magnetoelectric effect. We observed the dynamics of the electric-field induced magnetization by a Faraday rotation measurement using a pulsed electric field and a delayed probe light pulse (800 nm, 0.2 ps). The critical behaviors of the amplitude and the time response around the Néel temperature T_N (= 307 K) are investigated. In our experiment, very small Faraday rotation angle less than 10^{-6} rad can be detected. The rise time of the Faraday rotation signal above T_N becomes longer than that below T_N. The observed Faraday rotation angle decreases toward the Néel temperature. This fact means the observed Faraday rotation signal arises from the electric-field induced magnetization.

III-F. SPIN AND CARRIER DYNAMICS STUDIED BY TERAHERTZ SPECTROSCOPY

The terahertz region in the electromagnetic spectrum has attracted research attention, because elementary excitations in solid-state materials such as phonons and magnons play important roles, and many of those dynamics appear in this energy region. We studied the magnetic properties of antiferromagnets and the photo-excited carrier dynamics of semiconductors using terahertz time-domain spectroscopy (THz-TDS). The principle of THz-TDS is similar to that of conventional magnetic resonance or infrared absorption in the thermal distribution. However, in THz-TDS in which monocycle terahertz pulses are used instead of microwaves or infrared light, the time resolution and the frequency bandwidth are improved remarkably. Ultrahigh-frequency modes and their ultrafast dynamics, which could not be observed by conventional spectroscopy, can be observed, and broadband absorption spectra can be obtained from the Fourier transform of the transmitted THz electric field.

Internal Energy in Cobalt Oxide Observed by THz-TDS

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(*PASPS9*, *2016*)

In the previous study, on an antiferromagnet manganese oxide (MnO), we showed that the lattice and magnetostrictive contributions to the internal energy can be observed by terahertz time domain spectroscopy (THz-TDS). In the present study, the refractive index in the terahertz region of an antiferromagnet cobalt oxide (CoO), whose Néel temperature T_N is reported to be about 290 K, is obtained from the peak shift of the transmitted THz electric field. We discuss that the lattice and the magnetostrictive contributions to the internal energy appear on the temperature dependence of the refractive index. As the temperature increases, the shift of the peak time of the transmitted THz electric field increases. It is considered that the refractive index in CoO increases and the speed of the THz wave decreases. We can derive the change Δn in averaged refractive index from the peak time shift. The change Δn in averaged refractive index reflects the internal energy in the system. Above T_N, it is considered that the lattice contribution is dominant to the internal energy. On the other hand, below T_N, the magnetstriction is considered to be also dominant in addition to the lattice contribution.

Observation of Negative Pulse Delay in Photo-Excited Silicon by THz-TDS

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(*LEES 2016*)

By using terahertz time domain spectroscopy (THz-TDS), transient spectra can be observed with femtosecond time resolution. Recently, in the photo-excited Si, the formation dynamics of excitons and electron-hole droplets (EHDs), the exciton Mott transition, and the carrier dynamics have been investigated using the optical-pump/terahertz-probe spectroscopy. In the present study, we investigate the carrier dynamics of photo-excited Si at room temperature by using THz-TDS. Negative delay of the transmitted terahertz pulse was observed under the photo-excitation. The optical pulses for the THz generation, the THz detection, and the photo-excitation are provided by a Ti:sapphire regenerative amplifier. Their wavelength, pulse width, pulse energy, and repetition rate are 810 nm, 0.15 ps, 700 μJ, and 1 kHz, respectively. The THz pulse is emitted from ambient air irradiated by a symmetry-broken laser field composed of the fundamental and its second harmonic laser pulses, and detected by the EO sampling using a 1-mm thick ZnTe <110> crystal. The sample of Si is photo-excited ~10 ps before the THz pulse. The transmitted terahertz pulse has a negative delay under the photo-excitation. The THz peak shift has negative value; namely the THz pulse propagates faster in the photo-excited Si than in no excited Si. The absolute value of the THz pulse peak shift increases as the fluence increases in the low fluence region (< ~170 μJ/cm^2), and then it decreases in the higher fluence region above ~170 μJ/cm^2.

Original Papers 発表論文

authors	title	journal	Vol.	page	year
高木鉄也、山崎緑平、和田昭英	複数の励起レーザーを用いた過渡吸収交差項の選択的検出システムの作製	分光研究	**65**	164-166	2016
Masashi Hasegawa, Hiroki Nagashima, Reina Minobe, Takashi Tachikawa, Hiroyuki Mino, and Yasuhiro Kobori	Regulated Electron Tunneling of Photoinduced Primary Charge-Separated State in the Photosystem II Reaction Center	*J. Phys. Chem. Lett.*	**8**	1179-1184	2017
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Masaki Okuda, Kaoru Ohta, and Keisuke Tominaga	Comparison of vibrational dynamics between non-ionic and ionic vibrational probes in water: Experimental study with two-dimensional infrared and infrared pump-probe spectroscopies	*J. Chem. Phys.*	**145**(11)	114503	2016
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Partha Dutta, Jessica Afalla, Arnab Halder, Sudeshna Datta, and Keisuke Tominaga	Temperature-Dependent Conductivity of Graphene Oxide and Graphene Oxide-Polyaniline Nanocomposites Studied by Terahertz Time-Domain Spectroscopy	*J. Phys. Chem. C*	**121** (3)	1442–1448	2017
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E. Ohmichi, T. Okamoto, M. Mitani, H. Takahashi, H. Ohta	High-Frequency Electron Paramagnetic Resonance of Metal-Containing Porphyrin Compounds Using a Microcantilever	*Journal of Inorganic Biochemistry*	**162**	190-193	2016

Invited Talks (domestic and international) 招待講演(国内および国際研究集会)

発表者氏名	開催時期	開催地	plenary or invite	学会名	講演題目
小堀康博 Y. Kobori	2017.3	Kobe	invite	Molecular Photoscience Research Center International Symposium "Recent Advances in Terahertz Molecular Science”	Electron Spin Polarization Imaging of Photoinduced Charge-Separated States in Photosynthetic Proteins
立川貴士 T. Tachikawa	2017.1	大阪	invite	2017 機能分子の先端ビーム化学	単一粒子・単一分子化学によるナノマテリアルの新機能創出
	2017.2	京都	invite	The 3rd SPIRIT international symposium, Light Opening up Frontier of DNA and Nanocrystal Superstructures	Correlated Dynamics of Photogenerated Charges and Ions in Organolead Halide Perovskites
富永圭介 K. Tominaga	2016.11	Kanpur, India	invite	Indo-Japan Workshop on “Frontiers in Molecular Spectroscopy: From Fundamentals to Applications on Material Science and Biology”	Frequency fluctuations of non-ionic vibrational probe in water studied by 2DIR spectroscopy and molecular simulation
	2017.2	Manila, Philippines	invite	1st Philippine-Japan Terahertz Research Workshop	Terahertz Spectroscopy on the Condensed Matter
秋本誠志 S. Akimoto	2016.6	Pushchino, Russia	oral	7th International Conference Photosynthesis Research for Sustainability-2016	Changes in light-harvesting and energy-transfer processes under different growth conditions
太田薫 K. Ohta	2016.10	神戸	invite	平成 28 年度第 1 回テラヘルツ技術セミナー「テラヘルツ分子科学の進展」	時間分解テラヘルツ分光法で観る有機薄膜の電荷キャリアダイナミクス
	2016.12	Singapore	invite	9th Asian and Oceanian Photochemistry Conference	Charge Carrier Dynamics in Porphyrin-Based Organic Semiconductors Studied by Optical Pump-Terahertz Probe Spectroscopy
山本直樹 N. Yamamoto （理学研究科）	2016.3	茨城	invite	第 4 回 Neutrons in Biology 研究会　「疾病関連蛋白質の構造・ダイナミクス解析 -疾病発症機構の分子基盤の理解を目指して-」	タンパク質ダイナミクスにおける水和および熱励起効果の観測 -広帯域誘電分光によるアプローチ
	2016.8	三田	invite	Spring-8 シンポジウム放射光赤外研究会サテライトミーティング「振動分光でわかること：赤外分光の今後と方向性」	THz 分光および広帯域誘電分光による水和タンパク質ダイナミクスの観測
	2016.10	神戸	invite	テラヘルツテクノロジーフォーラム　平成 28 年度　第 1 回技術セミナー「テラヘルツ分子科学の進展」	広帯域誘電分光で観るタンパク質ダイナミクスの水和および熱励起効果
	2016.11	Kanpur, India	invite	Indo-Japan Discussion Meeting on Frontiers in Molecular Spectroscopy: From Fundamental to Applications on material	Hydration and thermal-excitation effects of purple membrane dynamics probed by broadband dielectric spectroscopy

				science and biology	
	2016.11	神戸	invite	2nd International Aquaphotomics Symposium	Effects of hydration on protein dynamics and its thermal excitation studied by broadband dielectric spectroscopy
	2017.2	Manila, Philippines	invite	1st Philippine-Japan Terahertz Research Workshop	Protein hydration and its thermal excitation studied by broadband dielectric spectroscopy
Feng Zhang	2016.10	神戸	invite	テラヘルツテクノロジーフォーラム　平成 28 年度第 1 回技術セミナー「テラヘルツ分子科学の進展」	A THz Vibrational Signature of Symmetry-breaking Structure of a Crystalline Polymer System
奥田真紀 M. Okuda	2016.11	Kanpur, India	invite	Indo-Japan Discussion Meeting on Frontiers in Molecular Spectroscopy: From Fundamentals to Applications on Material Science and Biology	Hydrogen-bond dynamics of 9-fluorenone derivatives in water probed by two-dimensional infrared spectroscopy
佐藤春実 H. Sato （人間発達環境学研究科）	2017.3	Kobe	invite	Molecular Photoscience Research Center International Symposium "Recent Advances in Terahertz Molecular Science”	Higher-Order Structure of Biodegradable Polyesters Studied by Terahertz Spectroscopy
太田仁 H. Ohta	2016.5	San Sebastian, Spain	invite	Energy Materials Nanotechnology (EMN) Meeting on Terahertz	Development of THz High Field ESR Under High Pressure and Its Applications
	2016.5	八王子	invite	第 12 回 ESR 入門セミナー	超入門
	2016.5	八王子	invite	第 12 回 ESR 入門セミナー	スペクトル解析 II（固体）
	2016.6	淡路島	invite	4th Awaji International Workshop on Electron Spin Science & Technology (AWEST 2016)	Multi-Extreme ESR Measurements in Kobe
	2016.6	Poznan, Poland	invite	研究所セミナー	Multi-Extreme THz ESR: Its Developments and Applications to Magnetic Systems
	2016.6	Poznan, Poland	plenary	4th Forum EMR-PL	Exotic Quantum Spin Systems Studied by Multi-Extreme THz EMR
	2016.7	Warsaw, Poland	invite	研究所セミナー	Multi-Extreme THz ESR: Its Developments and Applications
	2016.8	福岡	invite	第 14 回 ESR 夏の学校	電子スピン共鳴（ESR)序論　Introductory to ESR Spectroscopy
	2016.8	Krasnoyarsk, Russia	invite	EASTMAG-2016 VI Euro-Asian Symposium "Trends in MAGnetism"	Development of Multi-Extreme THz ESR and Its Application to Shastry- Sutherland Model Substance SrCu$_2$(BO$_3$)$_2$
	2016.8	Irkutsk, Russia	plenary	Asia-Pacific EPR/ESR Symposium 2016	Multi-extreme THz ESR: New developments and applications
	2016.10	Kazan, Russia	plenary	Modern Development of Magnetic Resonance	Multi-Extreme THz ESR: Recent Developments and Future

	2016.12	福井	invite	第 11 回量子スピン系研究会	圧力下 THz ESR による量子スピンにおける圧力誘起現象の探索
	2016.12	愛知	invite	分子研研究会	神戸大学における多重極限 THz ESR の現状と将来
大道英二 E. Ohmichi (理学研究科）	2016.10	神戸	invite	テラヘルツテクノロジーフォーラム　平成 28 年度第 1 回技術セミナー「テラヘルツ分子科学の進展」	カンチレバーを用いたテラヘルツ領域における電子スピン共鳴測定
	2017.2	大阪	invite	テラヘルツ波科学技術と産業開拓 182 委員会第 30 回研究会	マイクロカンチレバーを用いたテラヘルツ電子スピン共鳴測定とその応用
	2017.3	神戸	invite	Molecular Photoscience Research Center International Symposium "Recent Advances in Terahertz Molecular Science”	Development of mechanically detected terahertz electron spin resonance technique
髙橋英幸 H. Takahashi （先端融合研究環）	2016.11	神戸	invite	MR-THz 2016	Development and application of force-detected THz-ESR measurement system
	2017.2	Manila, Philippines	invite	1st Philippine-Japan Terahertz Research Workshop	Apparatus for force-detected electron spin resonance spectroscopy in the terahertz region
Khalif Benzid	2016.9	広島	invite	New Frontier of Multi-functional Magnets (NFM2016)	ESR study of nonmagnetic impurity effect of S=1/2 two legs spin ladder antiferromagnet $[\mathrm{Ph(NH_3)}](18\text{-crown-6})[\mathrm{Ni(dmit)_2}]_{1-x}[\mathrm{Au(dmit)_2}]_x$
河本敏郎 T. Kohmoto （理学研究科）	2017.3	神戸	invite	Molecular Photoscience Research Center International Symposium "Recent Advances in Terahertz Molecular Science”	Observation of ultrafast spin dynamics in antiferromagnetic transition metal oxides by pump-probe and terahertz spectroscopies

Presentation at conferences (international and domestic) 一般講演

発表者氏名	開催時期	開催地	plenary or invite	学会名	講演題目
和田 昭英	2016.6	埼玉	poster	32nd Symposium on Chemical Kinetics and Dynamics	Selective Observation of Double Resonance Effect in Fourier Transform Two Dimensional Transient Absorption Spectrum
笠原俊二	2016.6	Illinois, USA	oral	71st International Symposium on Molecular Spectroscopy	High-Resolution Laser Spectroscopy of the B-X transition of $^{14}NO_3$ Radical: Vibrationally excited states of the B state
	2016.7	福岡	poster	International Symposium: Recent Progress in Molecular Spectroscopy and Dynamics	High-resolution laser spectroscopy and Zeeman effect of S_1←S_0 Transition of naphthalene and Cl-naphthalenes
	2016.9	神戸	poster	第 10 回分子科学討論会	NO_2ラジカル 615-670 nm 領域の高分解能レーザー分光
富永圭介	2016.6	Groningen, Netherlands	oral	8th International Conference on Coherent Multidimensional Spectroscopy	Frequency fluctuations of non-ionic vibrational probe in water studied by 2DIR spectroscopy and molecular simulation
	2016.9	Pisa, Italy	oral	9th International Conference on Broadband Dielectric Spectroscopy and its Applications	Broadband Dielectric Spectrocopy from MHz to THz on Proteins; Comaprison between Globular Proteins and Membrane Proteins
	2016.9	Pisa, Italy	poster	9th International Conference on Broadband Dielectric Spectroscopy and its Applications	Broadband Dielectric Spectroscopy on H_2O, D_2O, and $H_2{}^{18}O$, and Theoretical Calculations on the THz Spectral Component
	2017.3	Fukui	poster	6th International Workshop on Far-Infrared Technologies and 2nd International Symposium on Development of High Power Terahertz Science and Technology	Development of Sub-Terahertz Time-Domain Spectroscopy and its Application to Molecular Science
太田薫	2016.9	Copenhagen, Denmark	poster	41st International Conference on Infrared, Millimeter, and Terahertz Waves	Probing Charge Transfer Dynamics in Porphyrin-Based Organic Semiconductors by Time-Resolved THz Spectroscopy
	2016.9	神戸	oral	第 10 回分子科学討論会	時間分解テラヘルツ分光法によるジケトピロロピロール連結テトラベンゾポルフィリン薄膜の電荷キャリアダイナミクス
	2016.12	Singapore	poster	9th Asian and Oceanian Photochemistry Conference	Development of Wavefront Shaping Technique for Ultrashort Optical Pulse
山本直樹 N. Yamamoto （理学研究科）	2016.6	名古屋	oral	第 43 回生体分子科学討論会	広帯域誘電分光を用いた紫膜のダイナミクスにおける温度および水和依存性の観測
	2016.9	神戸	oral	第 10 回分子科学討論会	広帯域誘電分光を用いた紫膜ダイナミクスの観測；サブ GHz-THz 領域における水和および温度依存性の評価
	2016.11	茨城	poster	第 54 回日本生物物理学会年会	Effects of hydration and thermal excitation of globular and membrane proteins studied by broadband dielectric spectroscopy
	2016.12	Awaji, Japan	oral	Japan-Taiwan Medical Spectroscopy International Symposium	Protein hydration dynamics studied by broadband dielectric spectroscopy

太田仁	2016.7	Aarhus, Denmark	oral	EUROMAR 2016	Multi-Extreme THz ESR: Recent Developments in Kobe
	2016.7	Colorado, USA	oral	58th Annual Rocky Mountain Conference on Magnetic Resonance	Multi-Extreme THz ESR: Development of Micro-Cantilever ESR up to the THz Region
	2016.9	Torino, Italy	oral	Xth EFEPR Conference	Development of Multi-Extreme THz ESR System
	2016.9	Copenhagen, Denmark	oral	IRMMW-THz 2016 (41st International Conference on Infrared, Millimeter and Terahertz Waves)	Multi-Extreme THz ESR: Recent Achievements in Kobe
	2016.11	大阪	oral	第 55 回電子スピンサイエンス学会年会（SEST2016）	多重極限 THz ESR の開発とその応用
	2016.11	東京	oral	第 26 回（平成 28 年度）日本赤外線学会研究発表会	多重極限 THz ESR の現状
	2017.3	福井	oral	6th International Workshop on Far-Infrared Technologies and 2nd International Symposium on Development of High Power Terahertz Science and Technology	Recent Developments of Multi-Extreme THz ESR in Kobe
大道英二（理学研究科）	2016.5	神戸	oral	強磁場実験入門講習会	強磁場実験入門
	2016.9	福井	oral	第三回西日本強磁場科学研究会	カンチレバーを用いた磁気共鳴法の現状
	2017.3	大阪	oral	日本物理学会　第 72 回年次大会（2017 年）	メンブレン型ピエゾ抵抗センサーを用いた微小試料の磁気測定
大久保晋	2016.8	Irkutsk, Russia	poster	Asia-Pacific EPR/ESR Symposium 2016	Terahertz ESR Measurements
	2016.9	福井	poster	第三回西日本強磁場科学研究会	S=1/2 J_1-J_2 フラストレート磁性鎖 $NaCuMoO_4(OH)$のスピンネマチック相の探索
	2016.9	金沢	poster	日本物理学会　2016 年秋季大会	$NaCuMoO_4(OH)$配向試料の強磁場 ESR 測定 3
	2016.11	大阪	oral	第 55 回電子スピンサイエンス学会年会（SEST2016）	S=1/2 擬 1 次元 J_1-J_2 フラストレート磁性体 $NaCuMoO_4(OH)$の磁場中配向試料を用いたテラヘルツ ESR によるスピンネマチック相の探索
	2016.11	東京	oral	第 26 回（平成 28 年度）日本赤外線学会研究発表会	S=1/2 擬 1 次元 J_1-J_2 フラストレート磁性体 $NaCuMoO_4(OH)$の THz ESR 測定
	2016.12	福井	oral	第 11 回量子スピン系研究会	頂点共有・稜共有三角形をもつ MKS 格子反強磁性体 $K_2Mn_3(OH)_2(VO_4)_2$ の ESR 測定
	2016.12	愛知	oral	分子研研究会	1 次元フラストレート系 $NaCuMoO_4(OH)$の強磁場 ESR による新奇磁性相の探索

	2017.3	福井	poster	6th International Workshop on Far-Infrared Technologies and 2nd International Symposium on Development of High Power Terahertz Science and Technology	Far-Infrared ESR Measurements of S=1/2 Frustrated J_1-J_2 Chain System $NaCuMoO_4(OH)$
	2017.3	大阪	oral	日本物理学会　第72回年次大会(2017年)	2次元正方格子磁性体 $Sr_2MnO_2Cl_2$ の ESR 測定 3
高橋英幸	2016.8	Irkutsk, Russia	oral	Asia-Pacific EPR/ESR Symposium 2016	Improved setup for force-detected ESR measurement using fiber-optic interferometry
	2016.9	福井	poster	第三回西日本強磁場科学研究会	ファイバー干渉光学系を用いた力検出型高周波 ESR 測定系の改良
	2016.9	金沢	oral	日本物理学会 2016年秋季大会	ファイバー干渉光学系を用いた広ダイナミックレンジ磁化測定と高周波 ESR 測定への応用
	2016.11	大阪	oral	第55回電子スピンサイエンス学会年会(SEST2016)	ファイバー干渉光学系を用いた力検出型 THz-ESR 測定システムの開発
櫻井敬博(研究基盤センター)	2016.9	金沢	oral	日本物理学会 2016年秋季大会	三角格子反強磁性体 $CsCuCl_3$ の圧力下 THz-ESR 測定
	2016.12	愛知	oral	分子研研究会	圧力下 THz ESR 装置の開発と応用
	2017.3	福井	poster	6th International Workshop on Far-Infrared Technologies and 2nd International Symposium on Development of High Power Terahertz Science and Technology	Development of Ceramics for the Inner Parts of the Pressure Cell by Electromagnetic Wave Heating
	2017.3	大阪	oral	日本物理学会　第72回年次大会(2017年)	$KCuCl_3$ における圧力下 THz-ESR 測定による圧力誘起相転移の観測

Presentation by Graduate Students and Postdocs

院生、ポストドクの学会発表

指導教員	発表者氏名	学年	時期	学会名	講演題目
和田 昭英 A. Wada	山崎 緑平	M1	2016.9	第 10 回分子科学討論会	レーザー励起下における白色光励起二重共鳴 2 次元過渡吸収スペクトルの測定
	山崎 緑平	M1	2016.10	第 7 回サイエンスフロンティア研究発表会	レーザー励起下における白色光励起二重共鳴 2 次元過渡吸収スペクトルの測定
笠原俊二 S. Kasahara	黒田真司	M1	2016.5	第 16 回分子分光研究会	高分解能レーザー分光によるフルオレンの $S_1 \leftarrow S_0$ 遷移に関する研究
	平田通啓	M1	2016.5	第 16 回分子分光研究会	NO_3 ラジカル B-X 遷移 15900 cm^{-1} バンドの高分解能レーザー分光
	黒田真司	M1	2016.6	32nd Symposium on Chemical Kinetics and Dynamics	Rotationally-resolved high-resolution laser spectroscopy of the S_1-S_0 transition of fluorene
	平田通啓	M1	2016.6	32nd Symposium on Chemical Kinetics and Dynamics	Rotationally-resolved high-resolution laser spectroscopy of $^{14}NO_3$ radical; 628 nm vibronic band of B-X transition
	平田通啓	M1	2016.7	International Symposium: Recent Progress in Molecular Spectroscopy and Dynamics	High-resolution laser spectroscopy and Zeeman effect of NO_3 radical: The vibrationally excited state
	黒田真司	M1	2016.9	第 10 回分子科学討論会	フルオレンの S_1-S_0 遷移の高分解能レーザー分光
	平田通啓	M1	2016.9	第 10 回分子科学討論会	NO_3 ラジカルの B 状態の高分解能レーザー分光
立川貴士 T. Tachikawa	狩俣出	M2	2017.3	日本化学会第 97 春季年会(2017)	Charge Carrier Dynamics of $CH_3NH_3PbBr_{3-x}I_x$ with Hetero-Band Structures
	櫻井学	M1	2017.3	日本化学会第 97 春季年会(2017)	光誘起電子移動反応における磁場効果を利用した新規蛍光顕微鏡観察手法の開発
富永圭介 K. Tominaga	奥田真紀	D3	2016.6	8th International Conference on Coherent Multidimensional Spectroscopy	Rotational Dynamics of Solutes with Multi-Rotational Axes in 1-Alcohol Solutions Studied by Infrared Pump-Probe Spectroscopy
	Feng Zhang	PD	2016.9	第 10 回分子科学討論会	A THz Vibrational Signature of Symmetry-breaking Structure of a Crystalline Polymer System
	奥田真紀	D3	2016.9	第 10 回分子科学討論会	二次元赤外分光法および分子動力学シミュレーションによる水溶液中における溶質分子の振動数揺らぎの解明
	中塚真莉子	M2	2016.9	第 10 回分子科学討論会	$H_2{}^{18}O$ とその同位体の複素誘電率測定と水素結合ダイナミクスに関する理論計算
	飯沼美紀	M2	2016.9	第 10 回分子科学討論会	広帯域分光法による水/ジメチルスルホキシドニ成分液体中におけるタンパク質の構造安定性
	奈良隆史	M1	2016.9	第 10 回分子科学討論会	広帯域分光法によるテトラフェニルホウ酸イオンの水和水の動的挙動に関する研究
	奈良隆史	M1	2016.10	サイエンスフロンティア研究発表会	広帯域分光法によるテトラフェニルホウ酸イオンの水和水の動的挙動に関する研究

	奈良隆史	M1	2016.11	テラヘルツ科学の最先端Ⅲ	広帯域誘電分光法及び赤外分光によるテトラフェニルホウ酸イオンの水和水の動的挙動に関する研究
	奈良隆史	M1	2016.12	若手フロンティア 2016	広帯域誘電分光法及び赤外分光による有機イオンの水和水の動的挙動
	奥田真紀	D3	2017.2	スーパーコンピューターワークショップ 2016「これまでの理論・計算科学を振り返り今後を展望する」	二次元赤外分光法および分子動力学シミュレーションによる水溶液中における溶質分子の振動数揺らぎの解明
	奈良隆史	M1	2017.2	スーパーコンピューターワークショップ 2016「これまでの理論・計算科学を振り返り今後を展望する」	広帯域誘電分光法及び赤外分光による有機イオンの水和水の動的挙動
秋本誠志 S. Akimoto	植野嘉文	D1	2016.6	7th International Conference Photosynthesis Research for Sustainability-2016	Excitation energy transfer processes among photosynthetic complexes in cyanobacterial cells
	植野嘉文	D1	2016.7	第 24 回「光合成セミナー2016：反応中心と色素系の多様性」	絶対蛍光強度測定による緑藻 *Chlamydomonas reinhardtii* における光捕集機能変化の解明
	池田志保	M2	2016.7	第 24 回「光合成セミナー2016：反応中心と色素系の多様性」	高濃度 CO_2 条件下における光合成初期過程 –時間分解蛍光分光法による観測–
	藤本かおり	M1	2016.7	第 24 回「光合成セミナー2016：反応中心と色素系の多様性」	77 K における蛍光の絶対強度測定–シアノバクテリアの光応答–
	植野嘉文	D1	2016.9	第 10 回分子科学討論会	ピコ秒時間分解蛍光分光法によるフィコビリソームから光化学系への励起エネルギー移動過程に関する研究
	池田志保	M2	2016.9	第 10 回分子科学討論会	異なる CO_2 濃度下で培養されたシアノバクテリア *Synechocystis* sp. PCC 6803 の光合成初期過程の変化
	関戸彩乃	M2	2016.9	第 10 回分子科学討論会	時間分解蛍光分光法による緑藻 *Chlamydomonas reinhardtii* の光環境応答に関する研究
	藤本かおり	M1	2016.9	第 10 回分子科学討論会	高濃度二酸化炭素条件下で培養したシアノバクテリアの光応答
	藤本かおり	M1	2016.12	若手フロンティア研究会 2016	CO_2 濃度変化に伴うシアノバクテリアの励起エネルギー移動の変化
太田仁 H. Ohta	岡本翔	D1	2016.7	58th Annual Rocky Mountain Conference on Magnetic Resonance	Development of High-frequency Cantilever-detected ESR Technique and its Application to Metalloporphyrin Complex
	岡本翔	D1	2016.8	Asia-Pacific EPR/ESR Symposium 2016	Force-detected ESR measurements in a terahertz range up to 0.4 THz
	K. Benzid	PD	2016.9	New Frontier of Multi-functional Magnets (NFM2016)	ESR study of nonmagnetic impurity effect of S=1/2 two legs spin ladder antiferromagnet $[Ph(NH_3)](18\text{-crown-}6)[Ni(dmit)_2]_{1-x}[Au(dmit)_2]_x$
	森満新	M2	2016.9	第三回西日本強磁場科学研究会	マルチフェロイクス物質 $BiFe_{0.9}Co_{0.1}O_3$ のテラヘルツ ESR 測定
	藤本雅哉	M1	2016.9	第三回西日本強磁場科学研究会	マルチカゴメストライプ構造を持つ磁性体 $K_2Mn_3(OH)_2(VO_4)_2$ の ESR 測定

大木瑛登	M1	2016.9	第三回西日本強磁場科学研究会	反射型圧力下 ESR 装置の開発
岡本翔	D1	2016.9	第三回西日本強磁場科学研究会	カンチレバーを用いた金属ポルフィリン錯体の強磁場 ESR
藤本雅哉	M1	2016.9	日本物理学会　2016 年秋季大会	フラストレート磁性体 $K_2Mn_3(OH)_2(VO_4)_2$ の ESR 測定
平尾祐樹	M2	2016.9	日本物理学会　2016 年秋季大会	強磁場高圧複合極限下における ESR 装置の開発
岡本翔	D1	2016.9	日本物理学会　2016 年秋季大会	微量ミオグロビン試料の力検出高周波 ESR 測定
森満新	M2	2016.9	日本物理学会　2016 年秋季大会	マルチフェロイクス物質 $BiFe_{1-x}Co_xO_3$ の強磁場 ESR 測定 II
高橋昭彦	M2	2016.9	日本物理学会　2016 年秋季大会	２次元正方格子磁性体 $Sr_2MnO_2Cl_2$ の ESR 測定（２）
岡本翔	D1	2016.11	MR-THz 2016	Terahertz ESR Measurement of Metalloporphyrin Complexes
三木俊裕	M2	2016.11	MR-THz 2016	Fabrication of Fabry-Perot type cantilever for high-sensitivity force-detected ESR measurement
宮崎晃和	M2	2016.11	MR-THz 2016	Development of a piezoelectric translational stage for magnetic resonance force microscopy
堀江秀和	M1	2016.11	MR-THz 2016	Development of a microforce measurement apparatus using a cantilever
藤本雅哉	M1	2016.11	MR-THz 2016	ESR study of kagome like frustrated magnet $K_2Mn_3(OH)_2(VO_4)_2$
高橋昭彦	M2	2016.11	MR-THz 2016	Spin dynamics of two-dimensional square lattice magnet $Sr_2MnO_2Cl_2$
宮崎大輔	M1	2016.11	MR-THz 2016	Submillimeter wave ESR measurements of S=1/2 distorted diamond chain $Cu_3(OH)_2(CH_3CO_2)_2(H_2O)_xX_y$
森満新	M2	2016.11	MR-THz 2016	Terahertz ESR measurements of Multiferroic compound $BiFe_{0.9}Co_{0.1}O_3$
久保田創	M1	2016.11	MR-THz 2016	High Frequency ESR Measurements of S=1/2 antiferromagnetic chain $KCuMoO_4(OH)$
平尾祐樹	M2	2016.11	MR-THz 2016	High pressure THz ESR measurements of spin-gap system $KCuCl_3$
大木瑛登	M1	2016.11	MR-THz 2016	Development of high pressure and high field ESR system and its application to quantum spin systems
K. Benzid	PD	2016.11	MR-THz 2016	ESR study of nonmagnetic impurity effect of S=1/2 two legs spin ladder antiferromagnet $[Ph(NH_3)](18\text{-crown-}6)[Ni(dmit)_2]_{1-x}[Au(dmit)_2]_x$
久保田創	M1	2016.11	第 55 回電子スピンサイエンス学会年会（SEST2016)	S=1/2 半強磁性鎖 $KCuMoO_4(OH)$ のサブミリ波 ESR 測定
宮崎大輔	M1	2016.11	第 55 回電子スピンサイエンス学会年会（SEST2016)	S=1/2 歪んだダイアモンド鎖化合物 $(Cu_3(OH)_2(CH_3CO_2)_2(H_2O)_xX_y)$ の ESR 測定

高橋昭彦	M2	2016.11	第 55 回電子スピンサイエンス学会年会（SEST2016)	2 次元正方格子磁性体 $Sr_2MnO_2Cl_2$ の高周波 ESR 測定
森満新	M2	2016.11	第 55 回電子スピンサイエンス学会年会（SEST2016)	マルチフェロイック物質 $BiFe_{1-x}Co_xO_3$ のテラヘルツ ESR 測定
大木瑛登	M1	2016.11	第 55 回電子スピンサイエンス学会年会（SEST2016)	新しい高圧力下強磁場 ESR 装置の開発と量子スピン系への応用
藤本雅哉	M1	2016.11	第 55 回電子スピンサイエンス学会年会（SEST2016)	フラストレート磁性体 $K_2Mn_3(OH)_2(VO_4)_2$ の ESR による次元性の研究
平尾祐樹	M2	2016.11	第 55 回電子スピンサイエンス学会年会（SEST2016)	テラヘルツ領域における圧力下 ESR 装置の開発とスピンギャップ系への応用
岡本翔	D1	2016.11	第 55 回電子スピンサイエンス学会年会（SEST2016)	力検出 ESR 測定法の金属ポルフィリン錯体への応用
宮崎晃和	M2	2016.11	第 55 回電子スピンサイエンス学会年会（SEST2016)	磁気共鳴力顕微鏡のための 3 軸ピエゾ駆動ステージの開発
三木俊裕	M2	2016.11	第 55 回電子スピンサイエンス学会年会（SEST2016)	高感度 ESR 測定に向けた低バネ定数カンチレバーの作製
岡本翔	D1	2016.11	第 26 回（平成 28 年度）日本赤外線学会研究発表会	力検出型 THz-ESR 測定法のダイナミックレンジ拡張とヘムタンパク質モデル錯体への応用
高橋昭彦	M2	2016.11	第 26 回（平成 28 年度）日本赤外線学会研究発表会	2 次元正方格子磁性体 $Sr_2MnO_2Cl_2$ のテラヘルツ光 ESR 測定 2
大木瑛登	M1	2016.11	第 26 回（平成 28 年度）日本赤外線学会研究発表会	高圧下サブミリ波 ESR 装置の開発と量子スピン系への応用
K. Benzid	PD	2016.11	物理学専攻　談話会	The effect of magnetic anisotropy (ZFS) on the dynamical and the geometrical phases of the electron spin QUBITs of isolated transition metals; Mn^{2+}, Co^{2+}, Fe^{3+} and Fe^{3+} complexes in ZnO single crystal.
岡本翔	D1	2016.12	分子研研究会	ヘミンのテラヘルツ ESR 測定
藤本雅哉	M1	2016.12	若手フロンティア研究会	低次元フラストレート磁性体 $K_2Mn_3(OH)_2(VO_4)_2$ の ESR 測定
岡本翔	D1	2016.12	若手フロンティア研究会	ヘムタンパク質モデル錯体ヘミンのテラヘルツ ESR 測定
堀江秀和	M1	2016.12	若手フロンティア研究会	カンチレバーを用いた微小力測定装置の開発
三木俊裕	M2	2016.12	若手フロンティア研究会	高感度 ESR 測定に向けたカスタムカンチレバーの作製
宮崎晃和	M2	2016.12	若手フロンティア研究会	磁気共鳴力顕微鏡のためのピエゾ駆動ステージの開発
平尾祐樹	M2	2016.12	若手フロンティア研究会	THz 領域における圧力下 ESR 測定装置のスピンギャップ系への応用
森満新	M2	2016.12	若手フロンティア研究会	マルチフェロイック物質 $BiFe_{0.9}Co_{0.1}O_3$ のテラヘルツ ESR 測定

	久保田創	M1	2016.12	若手フロンティア研究会	S=1/2 反強磁性鎖 $KCuMoO_4(OH)$の ESR 測定
	高橋昭彦	M2	2016.12	若手フロンティア研究会	２次元正方格子磁性体 $Sr_2MnO_2Cl_2$ の高周波 ESR 測定２
	川崎航平	M2	2016.12	若手フロンティア研究会	ルビーの蛍光を用いた圧力較正法の圧力下 ESR への応用
	大木瑛登	M1	2016.12	若手フロンティア研究会	三角格子反強磁性体 $CsCuCl_3$ の圧力下 THz-ESR 測定
	宮崎大輔	M1	2016.12	若手フロンティア研究会	S=1/2 歪んだダイアモンド鎖化合物 $(Cu_3(OH)_2(CH_3CO_2)_2(H_2O)_xX_y)$の高周波 ESR 測定
	久保田創	M1	2017.3	日本物理学会　第 72 回年次大会（2017 年）	S=1/2 反強磁性鎖 $KCuMoO_4(OH)$の高周波 ESR 測定
	岡本翔	D1	2017.3	日本物理学会　第 72 回年次大会（2017 年）	ヘムタンパク質モデル錯体ヘミンの多周波 ESR 測定
	宮崎大輔	M1	2017.3	日本物理学会　第 72 回年次大会（2017 年）	S=1/2 歪んだダイアモンド鎖化合物 $(Cu_3(OH)_2(CH_3CO_2)_2(H_2O)_xX_y)$のサブミリ波 ESR
	堀江秀和	M1	2017.3	日本物理学会　第 72 回年次大会（2017 年）	マイクロカンチレバーを用いたカシミール力測定装置の開発テキスト
	藤本雅哉	M1	2017.3	日本物理学会　第 72 回年次大会（2017 年）	フラストレート磁性体 $K_2Mn_3(OH)_2(VO_4)_2$ の ESR 測定 II
	大木瑛登	M1	2017.3	日本物理学会　第 72 回年次大会（2017 年）	三角格子反強磁性体 $CsCuCl_3$ の圧力下 THz-ESR 測定 II
	K. Benzid	PD	2017.3	日本物理学会　第 72 回年次大会（2017 年）	High frequency ESR measurements of $BiFe_{0.9}Co_{0.1}O_3$ compound
河本敏郎	蓮沼 貴史	M1	2017.3	日本物理学会　第 72 回年次大会（2017 年）	YIG における電場誘起磁化
	新海貴大	M2	2017.3	日本物理学会　第 72 回年次大会（2017 年）	反強磁性体 Cr_2O_3 における電場誘起磁化のダイナミクス
	立松雅大	M2	2017.3	日本物理学会　第 72 回年次大会（2017 年）	反強磁性体 NiO におけるコヒーレントマグノンの磁場依存性

Books 著書

著者（共著者も含む）	書名	出版社名	ページ数	発行年
佐藤春実	「テラヘルツイメージング分光による高分子材料の劣化の可視化と分析」　in:「高分子の残留応力対策-発生メカニズムと低減化ノウハウ-」(技術情報協会編)	㈱技術情報協会	82-88	2017
T. Moriyasu and T. Kohmoto	"The Observation of Ultrafast Magnon Dynamics in Antiferromagnets NiO and MnO by Pump-Probe and Terahertz Time-Domain Spectroscopies," in "Advances in Materials Science Research 28," edited by M. C. Wythers	Nova Science Publishers	69-92	2017

Other Publications 参考論文･記事･報告

著者	タイトル	出版物名	巻・号・ページ	発行年
Feng Zhang, Houng-Wei Wang, Keisuke Tominaga, and Michitoshi Hayashi	Mixing of Intermolecular and Intramolecular Vibrations in Optical Phonon Modes: Terahertz Spectroscopy and Solid-State Density Functional Theory	*WIREs Computational Molecular Science*	6 (4) 386-409	2016
山本直樹，太田薫、田村厚夫、富永圭介	タンパク質の動的挙動に及ぼす水和および熱活性の影響；広帯域誘電分光法による観測	応用物理	85 巻・8 号 689-692　ページ	2016

Lecture to Public

講演、模擬授業など

氏名	講演題目	集会名	日時	場所
Keisuke Tominaga	Terahertz Spectroscopy on the Condensed Matter	Mini-Symposium on Many-Particle Dynamics and Spectroscopy of Materials	2017.2.24	Los Banos, Philippines

Awards 受賞

氏名	受賞研究題目	賞名	団体、学会名
植野嘉文	Excitation energy transfer processes among photosystethic complexes in cyanobacterial cells	Young talent 賞	7th International Conference Photosynthesis Research for Sustainability
植野嘉文	絶対蛍光強度測定による緑藻 *Chlamydomonas reinhardtii* における光捕集機能変化の解明	三室賞	第 24 回光合成セミナー
植野嘉文	ピコ秒時間分解蛍光分光法によるフィコビリソームから光化学系への励起エネルギー移動過程に関する研究	優秀ポスター賞	第 10 回分子科学討論会
櫻井敬博、藤本皓大、大久保晋、太田仁	SQUID 磁束計を用いたミリ波 ESR 測定装置の開発	論文賞	日本赤外線学会
髙橋英幸	ファイバー干渉光学系を用いた力検出型 THz-ESR 測定システムの開発	優秀発表賞	電子スピンサイエンス学会
岡本翔	力検出型 THz-ESR 測定法のダイナミックレンジ拡張とヘムタンパク質モデル錯体への応用	優秀発表賞	日本赤外線学会

Conference Organization 学術集会の開催

氏名	学術集会	共同主催者	場所	時期	参加者概数
富永圭介 (日本側代表)	Indo-Japan Joint Workshop on "Frontiers in Molecular Spectroscopy: Fundamentals and Applications on Material Science and Biology "	Prof. Chandra Amalendu (Indian Institute of Technology Kanpur, Department of Chemistry)（代表）	Indian Institute of Technology, Kanpur, India	2016.11.13-16	約 70 名
富永圭介 (日本側代表)	1st Philippine-Japan Terahertz Research Workshop	Prof. Elmer Estacio (University of the Philippines, Diliman), Prof. Masahiko Tani (University of Fukui)	De La Salle University, Philippines	2017.2.20-23	約 40 名
富永圭介 (代表)	Molecular Photoscience Research Center International Symposium "Recent Advances in Terahertz Molecular Science"	太田仁（神戸大） 大久保晋（神戸大） 谷正彦（福井大）	神戸大学瀧川記念学術会館	2017.3.10	約 40 名
大道英二、太田仁（共同で主催）	Molecular Photoscience Research Center International Workshop, "Novel Magnetic Resonance Techniques in Millimeter and Terahertz Waves and their Applications to Bioscience" (MR-THz2016)		神戸大学	2016.11.8-9	約 50 名

Recent Advances in Terahertz Molecular Science

Seminars セミナー

Date	Name	Affiliation	Title
5.10.2016	世良正文教授	広島大学	三角格子反強磁性体 $CsCuCl_3$ における圧力誘起秩序相について
5.26.2016	Dr. Jessica Afalla	National Institute of Physics, University of the Philippines Diliman, and Molecular Photoscience Research Center, Kobe University	Photoconductivity investigation of room temperature tunneling in GaAs/AlGaAs asymmetric double quantum wells through optical pump terahertz probe
6.14.2016	Dr. Susumu Takahashi	University of Southern California	Electron spin resonance spectroscopy using NV centers in diamond
7.12.2016	Dr. Oliver Portugall	Laboratoire National des Champs Magnetiques Intenses CNRS	The quest for next-generation photovoltaic (PV) materials: high-field spectroscopy on hybrid organic-inorganic perovskites (HOP) in Toulouse
8.3.2016	Prof. Alvin Karlo G. Tapia	Institute of Mathematical Sciences and Physics, University of the Philippines Los Baños	Charge Dynamics in Organic Materials in the DC and Low-Frequency Regions”
10.11.2016	Prof. Glenn Hefter	Department of Chemistry, Murdoch University, Perth, Western Australia	Electrolyte Hydration and Association using Dielectric Spectroscopy

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