Annual Review
2021

Molecular Photoscience Research Center

Kobe University

Preface

This annual review summarizes the research activity of Molecular Photoscience Research Center conducted in the 2021 academic year. We are further promoting advanced research and international collaboration on molecular photoscience and related topics. Any constructive comments and questions, and any suggestion for collaboration research are welcome.

Since 2017 we have been running joint usage/research project on molecular science in the terahertz frequency region, which is open to domestic universities and research institutes. In this year 33 joint research projects were accepted, and the research area spans from solid state physics, biophysics, solution chemistry, polymer science, photochemistry, theoretical physics and chemistry, so on. Although there were many difficulties and restrictions to conduct joint research due to the COVID-19, we have made good achievements in many research themes. The research center will continue to make efforts to push forward international and domestic collaborative research.

April, 2022
Keisuke Tominaga
Director of Molecular Photoscience Research Center,
Kobe University

Contents

Members

Keisuke Tominaga	Director
Hitoshi Ohta	Vice-Director
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Ryoko Ikeuchi	Assistant

Laser Molecular Photoscience Laboratory

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Shunji Kasahara	Associate Professor
Takashi Tachikawa	Associate Professor
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Tsubasa Okamoto	Project Research Assistant (September 2021 ~)
Yoshitaka Kumabe	Academic Researcher (April 2021 ~)
Appu Vengattoor Raghu	Academic Researcher (April 2021 ~ November 2021)
Masaaki Baba	Visiting Professor

Terahertz Molecular Chemistry Laboratory

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Kaoru Ohta	Research Colaborator (April ~ September 2021), Academic Researcher (October 2021~)
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Harumi Sato	Professor (Supplementary assignment. Main assignment is Graduate School of Human Development and Environment)
Yukihiro Ozaki	Visiting Professor

Terahertz Material Physics Laboratory

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Susumu Okubo	Associate Professor
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Hikaru Kawamura	Visiting Professor

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, multiexcitons, and 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) method. We have clarified several fundamental mechanisms of the energy-conversions in semiconductor nanoparticles, singlet-fission materials and in the polymer systems.

Manipulation of Charge-Transfer States by Molecular Design: Perspective from "Dynamic Exciton"

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(*Acc. Mater. Res., 2021*)

"Dynamic exciton", an umbrella term concept in photochemistry, plays an important role in nature, science, and technology, especially in photoinduced and electrically induced electron transfer (ET) between a donor (D) and an acceptor (A). Typically, an exciton in molecular D–A systems is considered a locally excited (LE) state of a donor (D*) or an acceptor (A*) molecule, but let us extend the terminology of "exciton" to an integrated class of LE, charge-transfer (CT), and charge-separated (CS) states. The degree of CT (0–100%), spin multiplicity, and D–A interaction (i.e., electronic coupling) are pivotal factors in the "exciton". Another important aspect of the "exciton" is strongly related to the "dynamic" aspect of the "exciton" by movement of atomic nuclei (i.e., vibration, rotation, and fluctuation) and their collective motions controlling behaviors of electrons and spins by the passage of time. The concept of "dynamic exciton" should cover a wide variety of the photochemical phenomena that are all essential for the energy conversion devices and processes including various kinds of living systems. In these, a huge amount of the nuclear motional modes may cooperatively be entangled to electronic orbitals. Thus, the idea behind "dynamic exciton" includes usage of the cooperation between nuclear motions and the spin–orbital, as electron–phonon coupling for innovative designs of the energy conversion materials and assemblies. For this, it is particularly important to examine how this wide variety of the motions plays roles on electronic couplings, intermediate geometries and mobilities, exciton energies, CT characters, and so on. We draw researchers' attention to this aspect of the vibronic effect, like the entropy role by collective movement of side chains of the conjugated polymer to modulate the electronic coupling time-dependently at the charge delocalization and dissociation, which is reinforced three-dimensionally at the D/A domain interface of organic photovoltaics (OPVs). In addition, to realize the ultimate high-performance OPVs, the voltage loss must be diminished; i.e., the energy difference between the band gap and the open circuit voltage is caused in part by interfacial charge recombination via vibrational relaxation. Attaining efficient excited-state migration with prevention of the vibrational relaxation at the D/A interface would possibly overcome the voltage loss issues at the primary CT event, when we understand the roles of low-frequency disorder movements by the phonon on the vibrational relaxation in the solid state. Importantly, conversion of the excited state-to-CS state in organic OPVs is an opposite process to that of the CS state-to-excited state in organic light-emitting diodes (OLEDs). Specifically, intramolecular D–A linked systems and intermolecular D–A systems hold a prominent position in both OPVs and OLEDs, and an intrinsic similarity is seen in the mutual interplay among LE, CT, and CS states of such systems facilitated by the dynamic effects. These facts encourage us to work on the manipulation of CT states by logical molecular design, achieving efficient energy conversion in OPVs and OLEDs. Along with some examples of OPVs and OLEDs, here we introduce the “dynamic exciton” as a comprehensive, CT photochemistry in molecular D–A systems, eventually making innovations in electronics, energy, medicine/health care, and functional materials.

Enthalpy–Entropy Compensation Effect for Triplet Pair Dissociation of Intramolecular Singlet Fission in Phenylene Spacer-Bridged Hexacene Dimers

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[1]Keio University
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(*J. Phys. Chem. Lett., 2021*)

Hexacene (Hc) is highly promising for singlet fission (SF). However, the number of SFs in Hc is extremely limited. As far as Hc dimers in solution are concerned, there is no report on the observation of the dissociation process from a correlated triplet pair (TT) to an individual one. The emphasis in this study is on the first observation of the quantitative TT generation together with the orientation-dependent photophysical discussions for TT dissociation using *para*- and *meta*-phenyl-bridged Hc dimers. Moreover, the activation enthalpies of Hc dimers in TT dissociation are smaller than those of pentacene (Pc) dimers, whereas the relative entropic contributions for Gibbs free energy of activation are much larger than the enthalpic ones in both Hc and Pc dimers. This implies that the vibrational motions are responsible for the intramolecular conformation changes associated with the TT dissociation. Consequently, “enthalpy–entropy compensation” has a large impact on the rate constants and quantum yields.

Synergetic Role of Conformational Flexibility and Electronic Coupling for Quantitative Intramolecular Singlet Fission

S. Nakamura[1], H. Sakai[1], H. Nagashima, M. Fuki, K. Onishi, R. Khan[2], Y. Kobori, N. V. Tkachenko[2], T. Hasobe[1]

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(*J. Phys. Chem. C., 2021*)

We present a novel design concept of molecular dimers for quantitative individual triplet yield (Φ_T) through intramolecular singlet fission. We synthesized a series of tetracene (Tc) dimers bridged by different phenylene-based linkers, focusing on the conformational flexibility in addition to the electronic coupling. In transient absorption measurements, a 4,4′-biphenyl-bridged Tc dimer with weaker electronic coupling and larger conformational flexibility exhibited the quantitative Φ_T: 196 ± 12% at high excitation energy. Moreover, decoupled spins associated with conformational change were directly characterized by time-resolved electron paramagnetic resonance. Strong interplay of the geometry change and electronic localization was revealed on the triplet pair dissociation through magnitudes of spin–spin exchange couplings. Thus, a synergetic role of conformational flexibility and electronic coupling in quantitative Φ_T was clarified.

Orientations and water dynamics of photoinduced secondary charge-separated states for magnetoreception by cryptochrome

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(*Commun. Chem., 2021*)

In the biological magnetic compass, blue-light photoreceptor protein of cryptochrome is thought to conduct the sensing of the Earth’s magnetic field by photoinduced sequential long-range charge-separation (CS) through a cascade of tryptophan residues, WA(H), WB(H) and WC(H). Mechanism of generating the weak-field sensitive radical pair (RP) is poorly understood because geometries, electronic couplings and their modulations by molecular motion have not been investigated in the secondary CS states generated prior to the terminal RP states. In this study, water dynamics control of the electronic coupling is revealed to be a key concept for sensing the direction of weak magnetic field. Geometry and exchange coupling (singlet–triplet energy gap: $2J$) of photoinduced secondary CS states composed of flavin adenine dinucleotide radical anion (FAD−•) and radical cation WB(H)+• in the cryptochrome DASH from Xenopus laevis were clarified by time-resolved electron paramagnetic resonance. We found a time-dependent energetic disorder in 2J and was interpreted by a trap CS state capturing one reorientated water molecule at 120 K. Enhanced electron-tunneling by water-libration was revealed for the terminal charge-separation event at elevated temperature. This highlights importance of optimizing the electronic coupling for regulation of the anisotropic RP yield on the possible magnetic compass senses.

Molecular Design Strategy for High-Yield and Long-Lived Individual Doubled Triplet Excitons through Intramolecular Singlet Fission

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[1]Keio University

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(*ACS Energy Lett., 2022*)

Multi-exciton generation of organic chromophores, i.e., singlet fission (SF), is highly promising for photoenergy conversion such as photocatalysis and photovoltaics. Among the reported high-yield SF systems, many systems possess only short-lived triplet excited states derived from correlated triplet pair intermediates, but not individual doubled triplet excitons. However, high-yield and long-lived individual triplet exciton generation is favorable for achieving efficient photoenergy conversion. In this Focus Review, we discuss the molecular design strategy for high-yield and long-lived individual triplet exciton generation through intramolecular SF utilizing a series of acene derivatives such as hexacene, pentacene, and tetracene. In addition to clarifying the structural and vibronic characters required for high-yield individual triplet exciton generation, specific examples of the photoenergy conversion far exceeding 100% quantum yields of subsequent electron-transfer products and singlet oxygen generation are presented.

Identification of Self-Photosensitizing Hydrogen Atom Transfer Organocatalyst System

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(*J. Am. Chem. Soc., 2022*)

We developed organocatalyst systems to promote the cleavage of stable C−H bonds, such as formyl, α-hydroxy, and benzylic C−H bonds, through a hydrogen atom transfer (HAT) process without the use of exogenous photo- sensitizers. An electronically tuned thiophosphoric acid, 7,7'-OMe-TPA, was assembled with substrate or co-catalyst N-heteroaromatics through hydrogen bonding and π−π interactions to form electron donor−acceptor (EDA) complexes. Photoirradiation of the EDA complex induced stepwise, sequential single-electron transfer (SET) processes to generate a HAT-active thiyl radical. The first SET was from the electron-rich naphthyl group of 7,7'-OMe-TPA to the protonated N-heteroaromatics and the second proton-coupled SET (PCET) from the thiophosphoric acid moiety of 7,7'-OMe-TPA to the resulting naphthyl radical cation. Spectroscopic studies and theoretical calculations characterized the stepwise SET process mediated by short-lived intermediates. This organocatalytic HAT system was applied to four different carbon−hydrogen (C−H) functionalization reactions, hydroxyalkylation and alkylation of N-heteroaromatics, acceptorless dehydrogenation of alcohols, and benzylation of imines, with high functional group tolerance.

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. We also developed in situ analysis techniques for visualizing and linking macro- and nanoscopic features of external stimulus-responsive luminescent materials.

Dynamic Symmetry Conversion in Mixed-Halide Hybrid Perovskite upon Illumination

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[3]Japan Synchrotron Radiation Research Institute

(*ACS Energy Lett., 2021*)

Organic–inorganic hybrid halide perovskites have excellent optoelectronic properties and are highly efficient photovoltaic materials, but their chemical instability impedes their development for use in next-generation solar cells, wherein they serve as the light harvesting material. Here, we report a mechanism of photoluminescence red-shift, a performance-loss phenomenon known as light-induced halide segregation, in mixed-halide perovskites ($CH_3NH_3PbBr_{1.5}I_{1.5}$) upon illumination using in situ single-particle spectroscopy and synchrotron-based X-ray techniques. Under 405 nm excitation, the photoluminescence (PL) intensity gradually increased over time, and the peak position shifted from 640 to 720 nm. To explore the mechanism of PL red-shift, we measured the PL emission from individual spots over time in two wavelength regions: 574–626 nm, originating from the as-prepared particles; and 672–696 nm, which slowly increases with a weak excitation intensity. The red PL signals from individual nanoparticles exhibited a blinking behavior (intermittent on and off PL) during the initial stage, which is a characteristic signature of a single particle. The independent blinking of the red PL signals suggests the formation and dissociation of emissive sites for lower-energy PL. The probability distribution of the red PL duration time followed a single-exponential curve with a characteristic lifetime of 6.8 s, which is close to the reciprocal of the backward rate of change. Therefore, the increasing PL under intense excitation conditions is ascribed to the accumulation of emissive local domains with a specific lifetime. Combined with the results of synchrotron-based X-ray analysis, we suggest a defect-assisted photoinduced transition from ordinary nonpolar phases to polar phases at the local scale within seconds is coupled with organic cation reorientation, which in turn narrows the bandgap (Figure 1). First-principles calculations quantitatively supported this result. Our findings provide deeper insights into the nature of local polar domains in hybrid perovskite materials and help improve device stability and efficiency.

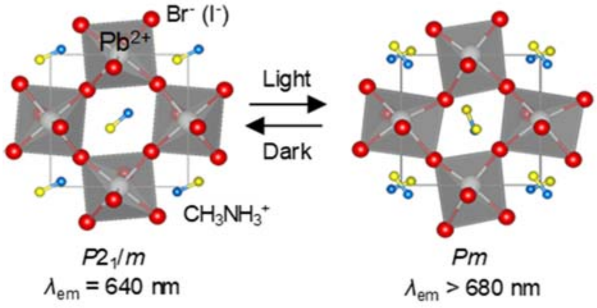

Figure 1. Photoinduced change of local structure and emission color on $CH_3NH_3PbBr_{1.5}I_{1.5}$ under 405 nm laser irradiation.

In Situ Exploration of Stimulus-Induced Emission Changes in Mechanochromic Dyes

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(*J. Phys. Chem. Lett., 2021*)

The development of in situ analysis techniques for visualizing and linking macro- and nanoscopic features of external stimulus-responsive materials is crucial for their rational design and applications. Herein, we investigate the mechanical stress induced emission changes in electron donor–acceptor type organic dye molecules in solid states through in situ single-particle fluorescence spectroscopy combined with macroscopic and nanoscopic stimulation systems. Mechanochromic luminescence (MCL) behavior is the reversible color change in the emission from solid-state dyes upon mechanical stimuli such as grinding and stretching. Phenanthroimidazolylbenzothiadiazole (PB) dyes have exhibited versatile MCL properties, e.g., the change in emission color from green to yellow by gentle grinding. The piezo-controlled mortar and pestle system developed herein reproduces the usual grinding operation and fills the gap between the macro and nanoscales. The observed mechano-induced transition from the green-emissive crystalline state to the yellow-emissive state was attributed to the partial disordering of (near) surface structures, breaking the intermolecular interactions between stacked molecules at a certain depth, thus leading to more planar conformations with increased rotational degrees of freedom. Such structural changes are more effectively produced by scrubbing or grinding the particles, rather than by simple cutting. Moreover, the correlative fluorescence and atomic force microscopy (AFM) imaging provided quantitative information about mechanically induced dissociation of stacked molecules in the crystal. Our method has the potential to become a general technique for in situ analysis of MCL processes, including structural fluctuation between different states, and other stimulus-responsive materials such as triboluminescent materials.

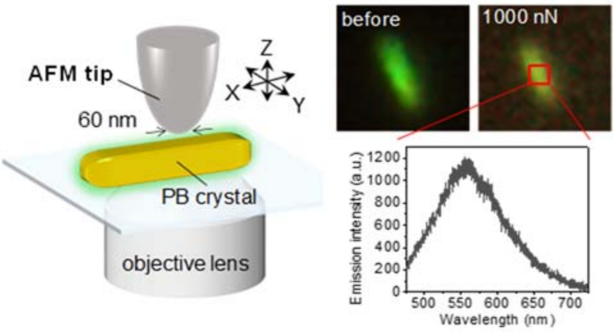

Figure 1. Illustration of the fluorescence microscope with AFM system (left). Emission images and spectrum acquired for a PB crystal before and after the stimulation with the AFM tip (right).

Organic photostimulated luminescence associated with persistent spin-correlated radical pairs

Manabu Sakurai, Ryota Kabe,[1] Masaaki Fuki, Zesen Lin,[1] Kazuya Jinnai,[2] Yasuhiro Kobori, Chihaya Adachi,[2] Takashi Tachikawa
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(*Commun. Mater., 2021*)

Photostimulated luminescence (PSL) allows energy or data to be stored and released using electromagnetic waves as both the input and output, and has attracted considerable interest in the fields of biomedical and information technologies. However, this phenomenon is mostly limited to solid inorganic materials. In this paper, we demonstrate purely organic PSL over a wide range of colors utilizing ultraviolet (UV) and near-infrared (NIR) light for multiple write-in and read-out cycles, respectively, by adding a molecule with dual roles as an electron trap and light emitter to the organic long persistent luminescence (LPL) systems. As a model system, we show a ternary blend film of electron donor (m-MTDATA) (1mol%), electron acceptor (PPT), and electron trap/emitter (Rb) (1mol%). Excitation of the film with UV light induces the formation of charge-separated states (CSSs) between m-MTDATA and PPT, resulting in a green emitting charge transfer (CT) excited state or exciplex. A portion of the electrons are captured by neutral Rb molecules to form the long-lived radical anions of Rb ($Rb^{\bullet -}$). Since $Rb^{\bullet -}$ possesses strong absorption bands in the NIR region, NIR excitation can induce electron transfer from doublet excited $Rb^{\bullet -}$ to neighboring PPT molecules, thereby producing mobile electrons in the PPT film for the generation of singlet excited state of Rb ($^1Rb^*$). Furthermore, the spin state of trapped charges could be controlled by magnetic fields. We investigated magnetic field effects (MFEs) on LPL/PSL by applying external magnetic fields with an electromagnet to the sample under the inverted fluorescence microscope. Interestingly, significant decreases of emission intensity (i.e., negative MFEs) were observed for LPL/PSL, while no MFE was seen for the film without Rb, implying a crucial role of trap/emitter molecules. Combined with write-in and read-out characteristics of PSL, manipulation of long-lived spin states in organic materials by weak magnetic fields will energize researchers in various fields such as molecular spintronics, which is a promising next generation technology.

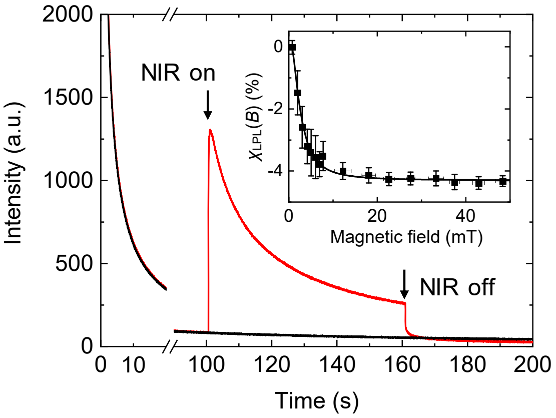

Figure 1. Emission decay profiles obtained for the m-MTDATA/PPT/Rb film with and without 800-nm light irradiation. The inset shows the MFEs on LPL.

I-C. HIGH-RESOLUTION SPECTOSCOPY OF POLIATOMIC MOLECULES

Doppler-free high-resolution spectroscopy is a powerful tool for studying the structure and dynamics of excited polyatomic molecules in detail and unambiguously. Single-mode auto-scan laser systems for the UV-Visible-NIR region, absolute wavenumber measurement systems, and Doppler-free high-resolution spectroscopic measurement systems have been constructed to investigate the excited molecules. High-resolution and high-precision measurement of spectral lines enables to observe rotationally-resolved electronic transition, then it is expected to find the excited state dynamics such as internal conversion (IC), intersystem crossing (ISC), and intramolecular vibrational redistribution (IVR) through the deviations in spectral line positions, intensity anomalies, and the changes of spectral linewidth. We have observed the high-resolution spectrum and the 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. Recently, we extended our observation to the molecules with large amplitude motion such as acetaldehyde and *trans*-stilbene.

Ultrahigh-resolution Laser Spectroscopy of acetaldehyde: Torsion-inversion-rotation interaction in the excited state

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(*2021 International Symposium on Molecular Spectroscopy*)

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Li-Hong Xu, Jon Hougen, Isabelle Kleiner, Jens-Uwe Grabow et al. beautifully analyzed ro-vibrational levels in the ground state of acetaldehyde taking CH_3-torsion rotation interaction into consideration[1,2]. For the lowest electronic excited state S_1 ($n\pi^*$) state, the ro-vibrational level structure is much more complicated because of the out-of-plane distortion in the CHO moiety (tunnel splitting due to double minimum potential) in addition to the profound level structure of CH_3 torsion[3,4]. We observed and analyzed rotationally resolved ultrahigh-resolution spectra for the $S_1 \leftarrow S_0$ transition of jet-cooled acetaldehyde, of which the resolution was much higher than those reported previously[5,6]. The effective rotational constant Aeff was found to be drastically different between the levels of below and above the barrier to CH_3 rotation. We well explained this fact by considering the mechanism of Coriolis interaction and estimating the interaction strength by a model calculation.

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1) L.-H. Xu, J. T. Hougen et al., *J. Mol. Spectrosc.* 214, 175 (2002).

2) I. Kleiner, J. T. Hougen, J.-W. Grabow et al., *J. Mol. Spectrosc.* 179, 41 (1996).

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6) I.-C. Chen et al., *J. Chem. Phys.* 115, 5089 (2001).

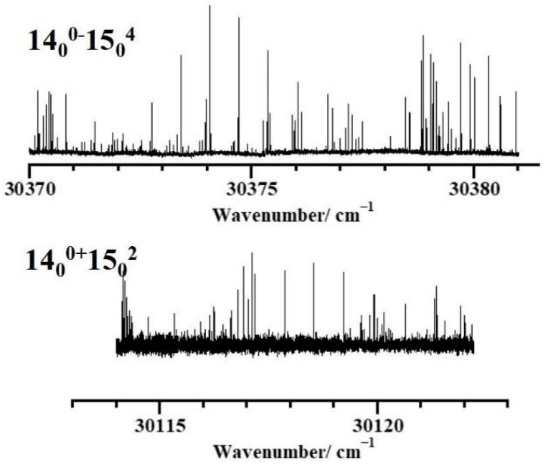

Figure 1. Observed rotationally-resolved high - resolution spectra of acetaldehyde $S_1 \leftarrow S_0$ transition around 30375 and 30118 cm^{-1}.

Ultrahigh-resolution spectroscopy of *trans*-stilbene: nonplanar structure in the ground state

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(*2021 International Symposium on Molecular*

Spectroscopy)

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Trans-stilbene is of great interest in the excited-state dynamics such as *cis*-*trans* isomerization in the electronic excited state. Zewail *et al*. reported the results of time-resolved spectroscopy and suggested its nonplanar structure in the ground S_0 state[1)]. In contrast, Pratt et al. concluded that the molecule is essentially planar both in the S_0 and S_1 states by analyzing the rotationally resolved high-resolution spectrum of the $S_1 \leftarrow S_0$ 0-0 band [2)]. We observed the spectrum with much higher accuracy and quality, and re-determined the rotational constants. Although it is impossible to accurate determine the absolute value of *A* for the *a*-type transition, we could conclude that trans-stilbene is nonplanar in the S_0 state. Theoretical calculation using WB97XD functional provided the nonplanar structure in which the phenyl rings are rotated around the C-C bond axis and take the C_2 symmetry. It suggests that steric repulsion between H atoms of ortho-position in a phenyl ring and in an ethylene part surpasses stabilization by π conjugation.

References:

1) J. A. Syage, P. M. Felker, and A. H. Zewail, *J. Chem. Phys*. 81, 4706 (1984).

2) B. B. Champagne, J. F. Pfanstiel, D. F. Plusquellic, D. W. Pratt, W. M. van Herpen, and W. L. Meerts, *J. Phys. Chem.* 94, 6 (1990).

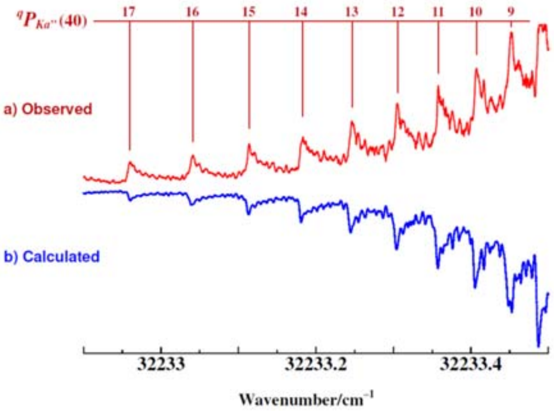

Figure 1. A part of the observed spectra of the 0-0 band of trans-stilbene $S_1 \leftarrow S_0$ transition for *P* branch region.

I-D. HIGH-RESOLUTION SPECTROSCOPY OF NO_2 AND NO_3 RADICAL

Nitrogen dioxide NO_2 and nitrate radical NO_3 have been known as an important intermediate in chemical reaction in the atmosphere. These radicals are the prototype molecules to understand vibronic interaction as followings; the Renner-Teller effect for NO_2, and the Jahn-Teller (JT) and pseudo Jahn-Teller (PJT) effects for NO_3. Optically allowed transitions have been observed as strong absorption and LIF excitation spectra by several research groups. For NO_2 radical, hyperfine splitting were observed in the high-resolution spectrum, and the magnitude of the hyperfine interaction constants suggest the state mixing between the electronic excited state and the ground state through the vibronic interaction. Recently, we reported the hyperfine-resolved high-resolution spectrum NO_2 A-X system for the 14500-16800 cm^{-1} region, and found the anomalies of the hyperfine splitting around 16200 cm^{-1}, which suggested to the interaction with other electronic state(s) in this energy region.

High-resolution Laser spectroscopy of $^{14}NO_2$ and $^{15}NO_2$ radicals

Shunji Kasahara, Kazuho Norii, Ikki Hosomi, Honoka Minamide, and Kohei Tada

(*Annual Meeting of Japan Society for Molecular Science 2021*)

Hyperfine-resolved high-resolution fluorescence excitation spectra of the $A\ ^2B_2 \leftarrow X\ ^2A_1$ electronic transition of $^{14}NO_2$ and $^{15}NO_2$ radical have been observed by crossing a single-mode laser beam perpendicular to a collimated molecular beam. Recently, we reported the hyperfine structure of the ${}^qR_0(0)$ lines ($k = 0$, $N = 1 \leftarrow 0$ transition) in 14500-16800 cm^{-1} energy region of $^{14}NO_2$. The determined Fermi contact interaction constants shows a sharp decreasing in 16200-16600 cm^{-1} region, and it may be caused by the interaction with the other electronic state. In this work, we have observed the rotational structure for 15885 and 16218 cm^{-1} bands to find the perturbations. Furthermore, the hyperfine structure of $^{15}NO_2$ 16324 cm^{-1} band was also observed.

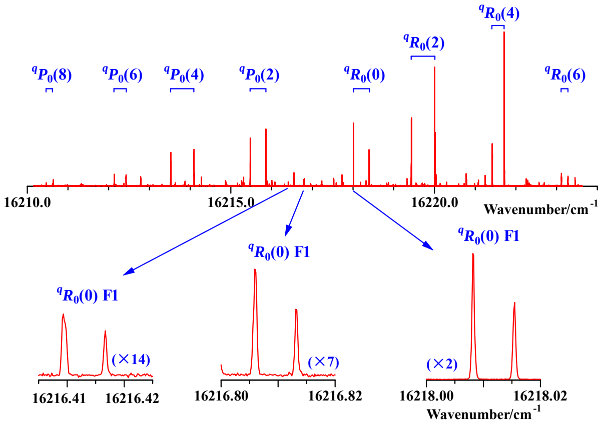

Figure 1. Observed high-resolution spectrum of 16218 cm^{-1} band. Upper trace: rotational structure. Lower trace: hyperfine splitting for ${}^qR_0(0)$ lines.

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. In solutions, a vibrational frequency of solute molecule is sensitive to changes of the solvent environment. Especially, in aqueous solution, hydrogen-bond making and breaking processes play an important role in the dynamics of water molecules surrounding the solute. 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 such as two-dimensional IR (2D-IR) spectroscopy and pump-probe spectroscopy. 2D-IR spectroscopy is a powerful tool to obtain microscopic information in solution such as ultrafast solvent dynamics and local structure of solvent by probing the vibrational frequency fluctuations. By polarization-sensitive pump-probe spectroscopy in the IR region we can study vibrational energy relaxation and orientational relaxation.

Temperature Dependence of Vibrational Frequency Fluctuation of Solutes in Water Studied by Two-Dimensional Infrared Spectroscopy

Yuki Fujii, Masaki Okuda, Kaoru Ohta, Keisuke Tominaga

(*11th Asian Photochemistry Conference, 2021*)

The vibrational frequency is sensitive to sub-ps time evolving structural fluctuation of solvent molecules and hence the frequency fluctuations provide microscopic information such as local hydration structure or solute-solvent interaction. Our group has investigated the vibrational frequency fluctuations of various ionic solutes in aqueous solutions by nonlinear infrared spectroscopy at room temperature. On the other hand, temperature dependence of the frequency fluctuation has not been studied in detail so much. Moreover, there are few detailed reports for solutes with hydrophobic groups. In this work, we studied temperature dependence of the frequency fluctuation of the CO stretching modes of solute molecules with aromatic rings of different sizes in D_2O by using two-dimensional (2D) IR spectroscopy. Furthermore, molecular dynamics (MD) simulation was performed to obtain a molecular picture of the frequency fluctuation.

In 2D-IR spectroscopy, three mid-infrared pulses were used to obtain correlation of the vibrational transition dipoles between at pump and at probe pulses irradiated. It is known that the shape of 2D-IR spectrum changes from ellipse to circle in population time reflecting the frequency fluctuation. Therefore, we applied center line slope (CLS) analysis to 2D-IR spectra to obtain decay time of correlation function of the frequency fluctuation. The CLS curves were fitted with a single exponential function. We found that the decay time becomes longer with increasing the size of aromatic ring. The decay time is originated from the structural fluctuation of hydrogen-bond network structure nearby the solute. As for temperature-dependent 2D-IR measurements, we considered Arrhenius equation for the decay times and obtained activation energy of FL (17.2 kJ/mol), ID (14.3 kJ/mol), OCP (14.8 kJ/mol) and AC (10.2 kJ/mol). It is found that similar aromatic ring size dependences were observed in both the decay times of the frequency fluctuation and its activation energy. MD simulation results showed that the hydration structures in the vicinity of the solute molecules are significantly different from those in bulk region. Therefore, it is suggested that the number of water molecules affected by the aromatic rings is important to understand the frequency fluctuations.

Vibrational Frequency Fluctuation of Carbonyl Compounds in Water Studied by Two-Dimensional Infrared Spectroscopy

Yuki Fujii, Masaki Okuda, Kaoru Ohta and Keisuke Tominaga

(*International Conference on Time-Resolved Vibrational Spectroscopy, 2021*)

A vibrational frequency of solute molecule in an aqueous solution fluctuates due to time-evolving local hydration structure around the vibrational probe, which is called as frequency fluctuation. Two-dimensional infrared (2D-IR) spectroscopic measurements have been performed to investigate the frequency fluctuation from the point of view of microscopic solute-solvent interaction.

In this study, we studied the frequency fluctuation of carbonyl (CO) stretching mode of 9-fluorenone derivative (9-FL) and 4-formylbenzoate (4-FB) in D_2O. The information on frequency fluctuation is extracted from center line slope (CLS) analysis. The CLS curves of 9-FL and 4-FB are characterized by single-exponential decay time of 2.7 and 0.8 ps, respectively. This difference may be attributed to collective orientation of water molecules with respect to transition dipole moment of the vibrational probe. For 9-FL, motion of water molecules on aromatic ring are highly perturbed, which results in elongation of effective solute-solvent interaction length, that is, low dielectric environment around the CO group. While, since the water molecules around the CO group of 4-FB are easily oriented to the solute, the solute-solvent interaction at far away from the solute can be negligible. This microscopic view suggests that 4-FB mainly experiences the fluctuation of low-collective water molecules in the vicinity of the solute, which yields the fast decay of correlation of frequency fluctuation.

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.

Nature of Local Charge Carrier Motions in Porphyrin-Based Bulk Heterojunction Films Revealed by Time-Resolved Optical Pump-Terahertz Probe Spectroscopy

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(*Chem. Lett., 2021*)

Local charge carrier dynamics in diketopyrrolopyrrole (DPP)-tetrabenzoporphyrin (BP)-based bulk heterojunction (BHJ) films are investigated by optical pump-terahertz probe spectroscopy. Here we focus on the effect of the alkyl chain lengths of DPP on the carrier dynamics. By changing a series of linear alkyl-chains to DPP chromophores in BP compounds, one can manipulate the morphology and miscibility in BHJ structure. In contrast to intuitive expectation based on the structural difference, we found that carrier mobility weighted by the yield of the photo-generated charge carriers is similar to each other. In contrast to the large difference in the power conversion efficiency, similar dynamics are observed between C10-DPP-BP and C4-DPP-BP BHJ films. We consider that this similarity comes from the molecular-scale mobility of the photo-generated polarons probed by time-resolved OPTP spectroscopy.

Ultrafast Charge Carrier Dynamics in Tetrabenzoporphyrin Derivatives Studied by Time-Resolved Terahertz Spectroscopy

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(*11th Asian Photochemistry Conference, 2021*)

Organic semiconductors made of, for example, conjugated polymers or small-molecules are important materials for efficient solar cells. They have a couple of advantages over inorganic-based ones because cost-effective and flexible devices can be produced by using solution processing. Tetrabenzoporphrin (BP) is a well-known *p*-type organic semiconductor that possesses excellent photophysical properties such as a large absorption cross section in the visible region and high hole mobility. We have been studying the charge carrier dynamics of BP derivatives and BP-based bulk heterojunction (BHJ) thin films using time-resolved THz spectroscopy.

Time-resolved THz spectroscopy, i.e., optical pump-THz probe spectroscopy, is known to be a unique technique to obtain the complex-valued conductivity of photogenerated charge carriers in various systems. In contrast to time-of-flight methods, time-resolved THz spectroscopy is a contact-free method that is intrinsically sensitive to the local charge carrier dynamics with subpicosecond time resolution. Since the scattering frequency of the charge carriers in semiconductors is typically in the THz region, THz spectroscopy provides detailed information on both carrier density and mobility for the systems. Though time-resolved THz spectroscopy has been used to study the charge carrier dynamics of small-molecule-based organic semiconductors, porphyrin-based organic semiconductors has not been examined by this method.

For BP thin films, the majority of the signal decays to zero with time constants of 0.5 ps and 6 ps. In the BP-based BHJ thin films, approximately 10% of the transient signal does not decay within 35 ps, indicating the survival of free charge carriers. For a BP:PC61BM BHJ film, it is reported that the power conversion efficiency (PCE) is only 0.02%. We considered that a slower recombination may be involve in the relaxation process of the charge carriers. Furthermore, we extend our studies to the charge carrier dynamics of diketopyrrolopyrrole-linked tetrabenzoporphyrin thin films where the diketopyrrolopyrrole (DPP) unit has two *n*-butyl groups. In contrast to BP, C4-DPP-BP exhibits broad and intense absorption, ranging from the visible and near infrared region. A recent study showed that PCE of the C4-DPP-BP-based BHJ solar cell is high (5.2%) compared with those of BP-based. Therefore, it is very interesting to see whether the charge carrier dynamics in C4-DPP-BP:PC61BM BHJ film is different from BP or not. Furthermore attaching *n*-decyl (C10) group to DPP unit induces the perpendicular orientation to the substrate (edge-on geometry), which is different from that of C4-DPP-BP of face-on geometry with respect to the substrate. Consequently, PCE of the C10-based OPV cell drops down to 0.19%. In contrast to the large difference in PCE, similar dynamics are observed between C10-DPP-BP and C4-DPP-BP BHJ films in the transient THz signals. We discuss the origin of similarity in terms of nature of the high frequency response of photo-generated charge carriers.

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 the refractive index and extinction coefficient of a medium are obtained 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 the low-frequency dynamics of various kinds of condensed materials, including neat liquids and mixtures of liquids, biological polymers, and conducting polymers.

A quantitative interpretation for the difference of terahertz spectra of DL- and L-alanine - origins of IR intensities in THz spectroscopy

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(*J. Phys. Chem. B, 2021*)

Motivated by explaining the THz spectra of DL- and L-alanine crystals recorded by Yamaguchi et al. (*Appl. Phys. Lett.* **2005,** *86* (5), 053903) we calculated the THz spectra of DL- and L-alanine by solid-state density functional theory to perform a rigorous discussion of IR intensities in THz spectroscopy. The two crystals give rise to similar normal modes in the 5-80 cm^{-1} frequency range, and all the modes feature predominantly intermolecular translations. We have found two critical aspects regarding the intensities of the THz bands. We note that one is the cancelation of the transition dipole moments in the unit cell: even an individual molecule in a unit cell has a non-zero transition dipole moment, a total transition dipole moment of the unit cell is zero due to the cancellation of the contributions from the molecules. The second one is that these THz normal modes of DL- and L-alanine are dominated by the intermolecular translations, which are intrinsically infrared inactive if the molecules are not polarized. Our analysis shows that the IR intensities of these "almost pure" intermolecular translations are due to a subtle balance between IR activities induced by the polarization effect of translations and IR activities of the librations and intramolecular vibrations, which have marginal presences in these normal modes.

Terahertz Spectroscopic Measurements and Solid-state Density Functional Calculations on $CH_3NH_3PbBr_3$ Perovskites -Short-Range Order of Methylammonium

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(*J. Phys. Chem. C, 2021*)

Temperature dependence of the vibrational absorption spectra of $MAPbBr_3$ (MA = methylammonium) perovskites was studied in the frequency range from 20 cm^{-1} to 200 cm^{-1} from 10 K to 293 K. The spectrum at 10 K shows several sharp bands from 20 cm^{-1} to 120 cm^{-1}, and there is a broad band centered at 155 cm^{-1}. From 40 cm^{-1} to 120 cm^{-1} the spectrum looks like a sum of the sharp bands and a broad background. These broad spectral features are not usually observed at very low temperatures for molecular crystals. The THz spectrum at 10 K was calculated using solid-state DFT, and it turns out that the calculation failed to reproduce the observed spectra. Here we propose a structural model in which the MA cations can take two possible orientations at equal probability, which situation leads to the coexistence of 16 unit-cell configurations in terms of MA cations' orientations. By calculating the THz modes associated with the 16 unit-cell configurations under the periodic boundary conditions, we have qualitatively captured the characteristics of the observed THz spectra. Regarding the spatial distributions of the 16 unit-cell configurations, our study suggests that short-range ordered domains should exist and the polarized domains can be in the majority.

Low-frequency Vibrational Modes of DMPG Lipid Bilayer Studied by Terahertz Spectroscopy and Solid-state Density Functional Theory

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[2]National Taiwan University

(*IRMMW-THz, 2021*)

The structure-encoded low-frequency normal modes (LFNM) of biomolecules have long been a curiosity of biophysicists. Functionally important motions are expected to be achieved through the nonlinear coupling of LFNM. The LFNMs of biomolecules have been studied extensively using molecular dynamic simulations. However, a consistent agreement between experimentation and theory in terms of the LFNMs of biomolecules has been rarely achieved. This work examines the LFNM of the lipid bilayer of DMPG through an interplay between THz spectroscopy and solid-state density functional theory.

For the calculations of such a large molecular crystal, a vital challenge is to make the geometry optimization reach a stable state, either a stable local minimum or the global minimum of the potential surface; so that no negative frequencies appear. Starting with a 1D model under the periodic boundary condition and successively approaching an actual 3D crystal structure, we have removed all the negative frequencies in the finally optimized crystal structure. All the observed THz bands can be assigned. The prominent peak, locating at 71 cm^{-1}, has been reproduced, and a few secondary peaks can find consistent correspondence with the calculated ones. Note that discrepancies between the experimental observation and theoretical calculation still exist in terms of both the frequency and IR intensity. DMPG represents, so far, the largest molecule crystal whose THz spectrum has been satisfactorily reproduced. We did a preliminary analysis of the vibrational density of states. The result shows that DMPG favors the energy regime of 0-200 cm^{-1}, accommodating about 60% of all the normal modes distributing in the 0-600 cm^{-1} frequency range. This observation implies the tendency of the atomic motions in DMPG to establish a correlated relationship and form collective motions.

Hydration Dynamics of Thermo-responsive Polymers Investigated by Broadband Spectroscopy

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(*11th Asian Photochemistry Conference, 2021*)

Poly(*N*-isopropylacrylamide) (PNiPA) and poly(*N,N*-diethylacrylamide) (PdEA) in aqueous solutions change their conformations from a hydrophilic coil-state to a hydrophobic globule-state with increasing temperature. The hydration state of the hydrophobic alkyl and hydrophilic amide groups influence the coil-to-globule transition, but the detail of the molecular mechanism of the transition remains to be elucidated. In this work, we performed the broadband dielectric spectroscopic measurements from the sub-GHz to THz frequency region and FT-IR measurements on the OH stretching band of the solutions to obtain information about dynamics and structures of the hydration water around the solute molecules.

The broadband dielectric spectra of aqueous solutions of PNiPA, PdEA and their monomers were measured by a vector network analyzer and THz time-domain spectrometer. The temperature dependence of the complex permittivity spectra was obtained from 5°C to the transition temperature. The complex permittivity spectra were assumed to consist of three Debye relaxation components and one underdamped oscillation. The three Debye components corresponds to the hydration water, bulk-like water, and the fast relaxation of these water. The dielectric strength of the hydration water decreases with increasing temperature, which is consistent with a picture that the polymer dehydrates when the temperature approaches to the transition temperature.

II-D. DEVELOPMENT OF WAVEFRONT SHAPING TECHNIQUE FOR ULTRAFAST OPTICAL PULSES

Ultrafast nonlinear optical spectroscopy has become an indispensable tool to investigate various dynamical processes in the condensed phase. Even though such spectroscopy is of great interest due to unique features of the structural and dynamical resolution, it is very difficult to perform the measurements in the scattering media. Generally, when coherent light propagates in scattering media, the scattered light forms a destructive interference pattern, so-called, “speckle”. Wavefront shaping by spatial light modulator was shown to control light propagation through scattering media. One can use this method to control input wavefront to design the output field, for example, to focus the light at a desired position. However, it still remains a challenge to control both spatial and temporal properties of ultrashort pulses simultaneously in scattering media. We are developing the wavefront and pulse-shaping techniques to control both the amplitude and phase of ultrashort pulses in scattering media.

Time-Reversal Focusing of Ultrashort Pulses through Thin Scattering Media

Kaoru Ohta

(*Optics Express, 2022*)

When ultrashort pulses propagate through a disordered medium, scattering occurs and the intensity of the ballistic component decreases drastically. This limits the applicability of time-resolved nonlinear optical spectroscopy and microscopy. The wavefront shaping technique makes it possible to focus light through the scattering medium; however, complete time-reversal of the ultrashort pulses (as short as 10 fs) is still a very challenging problem. This is due to the in-depth characterization and precise control needed for such pulses in the time domain in order to compress down the Fourier-transform limit. In this work, we develop new spatiotemporal wavefront shaping techniques to focus ultrashort pulses at the target position through a thin scattering medium. Compared to other studies, one significant advantage of this method is that most of the characterization of the spectrally-resolved transmission matrix and temporal profile of the ultrashort pulses can be done using single-beam geometry. An interferometer with external reference is necessary to measure the difference of the phase profile between the focused and reference pulses. Furthermore, the number of controllable phase components in the spectral domain is not limited by the spectral correlations of the speckle patterns because we used a pulse shaper in the time domain to optimize the temporal properties of the ultrashort focused pulse. Our new method provides increased flexibility and precise control for manipulating extremely ultrashort pulses through thin scattering media in order to achieve time-reversal focusing at the target position.

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

Low-frequency vibrational bands observed in the low-frequency Raman and terahertz (THz) spectra originate from the higher-order structure, crystalline structure, and intermolecular interactions of polymer materials. Therefore, THz and low-frequency Raman spectroscopy are unique techniques for analyzing higher-order conformations and intermolecular hydrogen bonding in semi-crystalline polymers. However, the band assignment of THz spectra of polymers has not been studied well. Therefore, it is necessary to develop band assignment methods in order to establish THz spectroscopy as a powerful and unique method for exploring the structure and physical properties of polymers.

Visualization of Inter- and Intramolecular Interactions in Poly(3-hydroxybutyrate)/Poly(L-lactic acid) (PHB/PLLA) Blends During Isothermal Melt Crystallization Using Attenuated Total Reflection Fourier Transform infrared (ATR FT-IR) Spectroscopic Imaging

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(*Applied Spectroscopy, 2021*)

Inter- and intramolecular interactions in multicomponent polymer systems influence their physical and chemical properties significantly and thus have implications on their synthesis and processing. In the present study, chemical images were obtained by plotting the peak position of a spectral band from the data sets generated using in situ attenuated total reflection Fourier transform infrared (ATR FT-IR) spectroscopic imaging. This approach was successfully used to visualize changes in intra- and intermolecular interactions in poly(3-hydroxybutyrate)/poly(L-lactic acid) (PHB/PLLA) blends during the isothermal melt crystallization. The peak position of ν(C=O) band, which reflects the nature of the intermolecular interaction, shows that the intermolecular interactions between PHB and PLLA in the miscible state (1733 cm^{-1}) changes to the inter- and intramolecular interaction ($CH_3\cdots O=C$, 1720 cm^{-1}) within PHB crystal during the isothermal melt crystallization. Compared with spectroscopic images obtained by plotting the distribution of absorbance of spectral bands, which reveals the spatial distribution of blend components, the approach of plotting the peak position of a spectral band reflects the spatial distribution of different intra- and intermolecular interactions. With the process of isothermal meltcrystallization, the disappearance of the intermolecular interaction between PHB and PLLA and the appearance of the inter- and intramolecular interactions within the PHB crystal were both visualized through the images based on the observation of the band position. This work shows the potential of using in-situ ATR FT-IR spectroscopic imaging to visualize different types of inter- or intramolecular interactions between polymer molecules or between polymer and other additives in various types of multicomponent polymer systems.

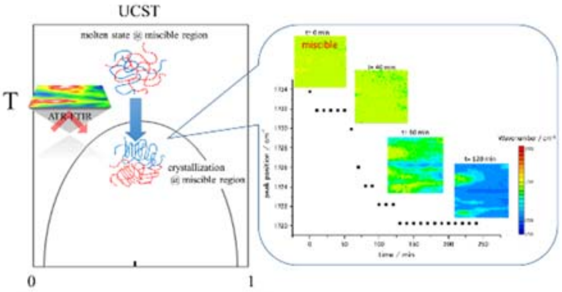

Figure 1. Phase diagram and spectroscopic imagings.

Water-induced conformational changes in the powder and film of ε-poly(L)lysine studied by infrared and Raman spectroscopy

M. Nochi, Y. Ozaki, H. Sato

(*Spectrochimica Acta Part A, 2021*)

In this study, we have investigated the water absorption-induced structural changes and thermal behavior of ε-poly(L)lysine-hydrochloride (EPLHCl) in the powder and film samples using infrared (IR) and Raman spectroscopy. An X-ray diffraction measurement reveals that the crystal structure of ε-poly(L)lysine (EPL) is similar to that of the γ-crystal of nylon-6. The powder form of EPLHCl absorbs water from the air and solidifies into a film (18% water content). The film does not transform into the powder form with increasing temperature; it remains as a film, suggesting that the transformation from powder to film is irreversible. The IR spectra in the amide I region of the powder and film are distinctly different, indicating that the secondary structure of EPLHCl changes upon water absorption. The position of the amide I band suggests that the powder form of EPLHCl has a β-sheet structure, while the film has two types of β-sheet structures. Raman spectra of EPLHCl in the region 1490–1440 cm^{-1} indicate that the EPLHCl film has a trans amide structure, unlike its powder form. Hence, it is highly probable that the differences in the secondary structures of the EPLHCl powder and film originate due to the twisting of the amide group induced by water absorption.

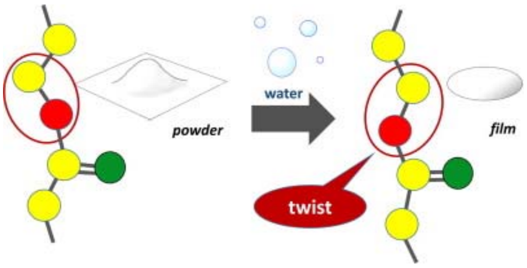

Figure 1. A schematic illustration of water-induced conformational changes in the powder and film of ε-poly(L)lysine.

Study of Co-crystallization and Intermolecular Hydrogen Bondings of Poly(glycolide-co-L-lactide) Copolymers by Terahertz and Low-Frequency Raman Spectroscopy

A. Nishimae, H. Sato

(*Macromolecules*, *2021*)

The co-crystallization and intermolecular hydrogen bonding of poly(glycolide-*co*-l-lactide) [P(GA-*co*-LLA)] copolymers have been studied using differential scanning calorimetry (DSC), wide-angle

X-ray diffraction (WAXD), small-angle X-ray scattering, and infrared (IR), terahertz, and low-frequency Raman spectroscopy. The DSC and WAXD results confirm that the melting point of the P(GA-*co*-LLA) copolymers decreases linearly and the spacing of the (110) and (020) planes expands as the concentration of polyglycolic acid (PGA) in the copolymers decreases. Furthermore, the lamellar thickness of the P(GA-*co*-LLA) copolymers increases with an increase in the concentration of polylactic acid (PLA), which is the same as that of poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate), a co-crystallized copolymer. These results indicate that P(GA-*co*-LLA) copolymers are co-crystallized. The copolymers show a terahertz band at approximately 75 cm^{-1} and Raman bands at approximately 130 and 80 cm^{-1}. The corresponding terahertz band at 75 cm^{-1} and Raman bands at 130 and 80 cm^{-1} of the PGA homopolymer show a shift to a relatively low frequency during the heating process because of thermal expansion. However, the terahertz band of the P(GA-*co*-LLA) copolymers at approximately 75 cm^{-1} shifts to a relatively high wavenumber, and their Raman bands at approximately 130 and 80 cm^{-1} do not show any shift despite the expansion of the crystal lattice of the P(GA-*co*-LLA) copolymers with the increasing concentration of PLA. The different behaviors of the shifts between the PGA homopolymer and P(GA-*co*-LLA) copolymers are due to the presence of PLA, and the co-crystallization can induce the formation of new intermolecular interactions between PGA and PLA. The temperature dependence of the IR bands of the P(GA-*co*-LLA) copolymers in the C═O, CH_2, and C–O–C stretching regions suggests that the new intermolecular interaction of C═O···H_3C is formed because of the co-crystallization of the P(GA-*co*-LLA) copolymers and the C–H···O(ether) hydrogen bonding in the PGA homopolymer is maintained in the P(GA-*co*-LLA) copolymers. Therefore, P(GA-*co*-LLA) copolymers that form co-crystallization have two types of hydrogen bondings: C═O···H_3C and C–H···O(ether) hydrogen bondings.

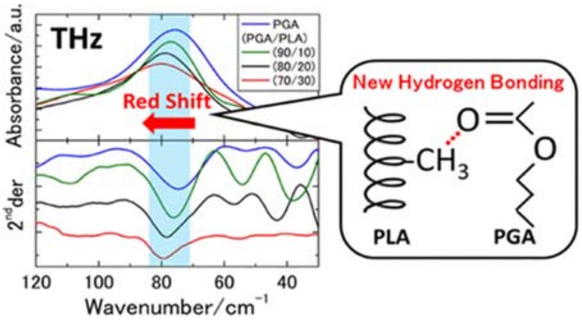

Figure 1. THz spectra of PGA and P(GA-*co*-LLA) copolymers.

Solvent Effect on Competition Between Weak and Strong Interactions in Phenol Solutions Studied by Near-infrared Spectroscopy and DFT Calculations

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(*Phys. Chem. Chem. Phys., 2021*)

Near-infrared (NIR) spectra of phenol in a series of non-aromatic and aromatic solvents were recorded to study the competition between various types of solute–solute and solute–solvent interactions. Depending on the phenol concentration, the free OH and OH involved in the OH···OH interactions in the dimers and higher associates are present in cyclohexane solutions. On the other hand, free OH does not appear in Cl-containing solvents since at a low phenol content the OH groups participate in the OH···Cl interactions. In CCl_4 and tetrachloroethylene this interaction is weak, while in chlorobenzene the strength of this interaction is higher. In the aromatic solvents the solute–solute OH···OH interactions compete with the solute–solvent OH···π and aromatic CH···OH ones. Consequently, the degree of self-association of phenol in aromatic solvents is smaller than that in non-aromatic ones. The strength of the OH···π interactions increases with growing electron-donating ability of the substituents in the benzene derivatives. This observation obtained from the NIR spectra is in line with the results of the theoretical calculations (DFT). A clear correlation appears between the number of methyl groups in aromatic solvents and the population of the free OH groups. The methyl groups are steric hindrances and impede the formation of the OH···OH and OH···π interactions. Our results suggest the presence of aromatic CH···OH solute–solvent interactions, not observed in previous studies. NIR spectroscopy appears to be a powerful tool for exploration of free and weakly-bonded OH groups.

Correlation of physical aging and glass transition temperatures in ultrathin polystyrene films supported on SiO_2

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(*Polymer, 2021*)

This study examined the effects of the aging temperature (T_{age}) on structural relaxation in ultrathin-supported polystyrene (PS) films with thickness ~0.2Rg. X-ray reflectivity and differential scanning calorimetry were used to evaluate the glass transition temperature (T_g) of ultrathin PS and bulk PS, respectively. The ultrathin films in their confined state showed anomalous thickness relaxation behaviors that could be classified into three types: (1) $T_{\mathrm{age}} \leq 60^{\circ}C$, a slow increase in thickness with time and a decrease in relaxation magnitude with temperature; (2) $70^{\circ}C \leq T_{\mathrm{age}} \leq 110^{\circ}C$, a slow decrease in thickness with time and an increase in relaxation magnitude with temperature; (3) $T_{\mathrm{age}} > 110\,^{\circ}C$, an increase in thickness with time due to dewetting of PS films deposited on SiO_2. Such an interesting relaxation behavior can arise from the enhanced dynamics at the surface and reduced mobility at the interface inherent in ultrathin-supported films. Two distinct T_gs peculiar to ultrathin films were confirmed. The lower T_g has not been reported for supported PS films. The relaxation summarized above revealed a strong correlation with the T_g values The de Gennes modified sliding motion model was applied to explain the correlation with relaxation dynamics.

III Terahertz Material Physics Laboratory

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

The quantum effects and the spin frustration effects prevent long-range order due to strong quantum fluctuation and frustration. Their ground states at low temperature are attractive issues in field of solid state physics. High-frequency high-field ESR is a powerful spectroscopic method to investigate the ground state and lower excited state of the system, because the ESR observes directly the magnetic excitation. These study of quantum spin and spin frustration systems has been extended recently. In the quantum spin systems, new phases have been discovered in S=1/2 1D Heisenberg antiferromagnetic chains with staggered fields associated with the Oshikawa-Affleck theory and in S=1/2 1D Heisenberg antiferromagnetic chains with a triangular lattice structure perpendicular to the chain associated with both of the magnetic anisotropy and effective spin size. In addition, new concepts related to the spin texture, such as Z_2 vortices and skyrmion lattices, have been discovered in spin frustrated systems. We are continuing detailed research on quantum spin systems. The appearance of breather, soliton and antisoliton modes are expected in wide frequency-field ESR measurements of S=1/2 Heisenberg antiferromagnetic chain with staggered g-tensor and D vector system. Such peculiar behavior has been found in pure system $KCuMoO_4(OH)$ by our group and doped system $CuGeO_3$ by S. Demishev, which have been performed under the joint research program of Molecular Photoscience Research Center, Kobe University. We also continue to study three-dimensionally correlated frustrated magnets $GeCo_2O_4$ and 4f-electron magnets CeB_6. Research on CeB_6 magnetic has been performed under a joint research project. We have made many achievements in the study of triangular lattice antiferromagnets through our high pressure ESR measurements and cooperation with theorists. High pressure ESR measurements are one of the features of our center. The appearance of Higgs amplitude modes in the S=1/2 dimer system $KCuCl_3$ under high magnetic field and high pressure has been found theoretically using extended spin-wave theory by M. Matsumoto. In the S=1/2 triangular lattice antiferromagnet $CsCuCl_3$, we have experimentally found that the exchange interaction and magnetic anisotropy change drastically under applied pressure. Collaborator D. Yamamoto have succeeded in explaining this behavior theoretically by an effective change in the spin size in the spin chain. In a joint Japanese-German project, ESR measurements of the two dimer system $CuVOF_4(H_2O)_6{\cdot}H_2O$, which consists with S=1/2 spins of Cu^{2+} and V^{4+} ions, has been performed. ESR revealed the gap of two dimer system. M. Akaki in our group is strongly performing high-field ESR measurements of multiferroics materials, dichroic $Pb(TiO)Cu_4(PO_4)_4$, and a quasi-one-dimensional spin system $BaCo_2V_2O_6$, and clarified their spin states. H. Kawamura, a visiting professor who came to our group in 2020, is theoretically conducting research on spin textures related to spin frustration. Kawamura's collaborator, K. Aoyama, theoretically applied the spin texture of the classical Heisenberg antiferromagnetic Hedgehog lattice to a breathing pyrochlore lattice. K. Uematsu shows that spin frustration induces quantum spin liquid behavior in the S=1/2 random-bond Heisenberg antiferromagnet on the zigzag chain. And also Kawamura's collaborators Dr. Tomiyasu and Dr. Mizuta have observed the Z_2 vortex and found its cause through experimental and theoretical studies of inelastic neutron scattering in the triangular-lattice

Heisenberg antiferromagnet $NaCrO_2$. K. Mitsumoto in our group showed the Scarmion crystal in two-dimensional triangular lattices and clarified the replica symmetry of the Scarmion crystal.

For other joint researches, high-field ESR and the magnetic susceptibility measurements of many materials have been performed to obtain magnetic information. And we also have joint research with theoretical groups for obtaining experimental parameters from quantum calculations. In total, our joint researches have been performed with 18 groups, and we have organized one scientific meeting with joint research groups.

Our group has received research and paper awards again. H. Ohta has received research achievement award from the Japan Society of Infrared Science and Technology. Y. Kitahara, S. Hara, T. Sakurai, S. Okubo, H. Ohta have received paper award from the Japan Society of Infrared Science and Technology. M. Akaki has received Young Scientist Award of the Physical Society of Japan. N. Nagawasa has received Research Presentation Excellence Award from the Japan Society of Infrared Science and Technology.

H. Ohta is becoming the President of the Japan Society of Infrared Science and Technology (2021-2023). H. Ohta is also acting as the Advisory Council of APES (Asia-Pacific EPR/ESR Society), and the Council Member of the Society of Electron Spin Science and Technology (SEST), the International EPR Society (IES) Associate Editor Asia-Pacific, a board member of Yukawa Memorial Foundation and the chairman of the Mochizuki Foundation in Yukawa Memorial Foundation. H. Ohta is the Local Organizing Committee Chair and S. Okubo is the member of the fund-raising committee of the ISMAR-APNMR 2021 which will be held in Aug., 2021 as the online conference.

Moreover, in order to strengthen the pulsed magnetic field researches in the western Japan region, we have been continuing the activities of The KOFUC (Kobe-Osaka-Osaka Prefecture-Fukui Universities Centers) Network since 2014.

Staggered Field in Quantum Antiferromagnetic $S = 1/2$ Spin Chain Probed by High - Frequency EPR (the Case of Doped $CuGeO_3$)

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(*Appl. Mag. Res., 2021*)

The flashback of the investigation of $CuGeO_3$ doped with magnetic impurities carried out by high-frequency EPR brings to light physics still actual for one-dimensional $S = 1/2$ quantum spin chains and covering a vast area from disorder-driven quantum critical phenomena to a new type of magnetic oscillations. It is shown that a key opening the door for a better understanding of this field of research is the Oshikawa and Affleck (OA) theory and, especially, following from it the universal link between the line width and g factor. The most puzzling problem appears around the staggered field, which contributes to different physical properties and serves as a driving force in the onset of anomalous growth of the line width and g factor at low temperatures. Accent is made on unsolved problems still providing a challenge for the theoretical explanation, including the genesis of the staggered field in doped systems, the contribution of the staggered magnetization to the integrated intensity, and spin susceptibility of a Griffiths phase and its magnetic properties on the nanoscale. A new type of magnetic oscillations, having explanation neither in OA theory nor within the framework of the semi-classical magnetization motion, is described in detail. This experimental finding poses the most difficult case and a touchstone for theory, as long as the corresponding modes of magnetic oscillations may be likely treated as violating Landau–Lifshits equation of motion.

THz ESR Study of Peculiar Co Pyrochlore System $GeCo_2O_4$ Using Pulsed High Magnetic Field

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(*Appl. Mag. Res., 2021*)

THz electron spin resonance (ESR) measurements of the spinel compound $GeCo_2O_4$, which consists of the Co^{2+} pyrochlore structure, were performed. The temperature dependence measurements revealed new antiferromagnetic phases, AF_1 and AF_2, below T_N. Moreover, a wide magnetic field range of ESR study using a single crystal at 1.8 K also revealed various field-induced phases due to the competition between the spin–lattice coupling and the spin frustration. Critical field resonances were observed at 5.0 T, 8.6 T, and 11.0 T for B // [111] and 5.1 T, 7.7 T, 11.2 T, and 13.0 T for B // 110] at 1.8 K. Although it became difficult to observe ESR above 86 K, the g-values of Co^{2+} ions were estimated to be $g_{[111]} = 3.34$ and $g_{[110]} = 3.27$ for [111] and [110], respectively, from the observed ESR mode above the saturation field at 1.8 K. Detailed frequency-field diagrams of the ESR modes at 1.8 K suggested the existence of spin–lattice coupling energy of 250 GHz (= 1.03 meV = 12 K) at the critical field resonances. The spin gap mode in the frequency-field diagram at 1.8 K showed excitation energies of $E_{[111]}$ = 1004 GHz (= 4.15 meV = 48 K) and $E_{[110]}$ = 1044 GHz (= 4.32 meV = 50 K) for [111] and [110], respectively. These results will be discussed in connection with the di-tetramer model suggested previously.

Heavy Fermion Metal CeB_6 in SubTHz and THz Range: The Electron Spin Resonance and Neutron Scattering Studies

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(*Appl. Mag. Res., 2021*)

Cerium hexaboride attracts attention of solid-state community for almost 50 years. Nowadays, this material is considered as a unique example of a system with orbital ordering resulting in formation of low-temperature magnetic phase with quadrupolar order, the so-called antiferroquadrupole phase. In crystal electric field $4f^1$ state of Ce^{3+} splits into Γ_7 doublet and Γ_8 quartet, the latter is believed to be the ground state, as long as just Γ_8 allows quadrupolar effects. An additional tool for studying rich physics of CeB_6 appeared since the discovery in this material the ESR, which is specific to antiferroquadrupole (AFQ) phase and is missing in the paramagnetic phase. In the present review, we have brought together electron spin resonance and inelastic neutron scattering data, which allowed obtaining most detailed structure of the magnetic resonance modes in the AFQ phase in a wide-frequency range up to 0.6 THz. It is shown that apart paramagnetic resonance main mode with homogeneous precession of the magnetization, there are antiferromagnetic resonance modes as well, some of them existing in the AFQ phase. Analysis of the *g* factors demonstrates that available theories based on Γ_8 ground state are facing difficulties with accounting experimental data, thus providing a challenge for developing of a theory correctly describing dynamic magnetic properties of this interesting material.

First ESR Detection of Higgs Amplitude Mode and Analysis with Extended Spin-Wave Theory in Dimer System $KCuCl_3$

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(*Appl. Mag. Res., 2021*)

$KCuCl_3$ is known to show a quantum phase transition from the disordered to antiferromagnetically ordered phases by applying pressure. There is a longitudinal excitation mode (Higgs amplitude mode) in the vicinity of the quantum critical point in the ordered phase. To detect the Higgs amplitude mode, high-pressure ESR measurements are performed in $KCuCl_3$. The experimental data are analyzed by the extended spin-wave theory on the basis of the vector spin chirality. We report the first ESR detection of the Higgs amplitude mode and the important role of the electric dipole described by the vector spin chirality.

Continuous control of classical-quantum crossover by external high pressure in the coupled chain compound $CsCuCl_3$

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(*Nature Communications, 2021*)

In solid materials, the parameters relevant to quantum effects, such as the spin quantum number, are basically determined and fixed at the chemical synthesis, which makes it challenging to control the amount of quantum correlations. We propose and demonstrate a method for active control of the classical-quantum crossover in magnetic insulators by applying external pressure. As a concrete example, we perform high-field, high-pressure measurements on $CsCuCl_3$, which has the structure of weakly-coupled spin chains. The magnetization process experiences a continuous evolution from the semi-classical realm to the highly-quantum regime with increasing pressure. Based on the idea of "squashing" the spin chains onto a plane, we characterize the change in the quantum correlations by the change in the value of the local spin quantum number of an effective two-dimensional model. This opens a way to access the tunable classical-quantum crossover of two-dimensional spin systems by using alternative systems of coupled-chain compounds.

Nonreciprocal linear dichroism observed in electron spin resonance spectra of the magnetoelectric multiferroic $Pb(TiO)Cu_4(PO_4)_4$

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(*Phys. Rev. Research 3, 2021*)

It is known that magnetic excitations in magnetoelectric multiferroics can be induced by the oscillation of electric polarization, called electromagnons, which often cause nonreciprocal optical phenomena. Energy diagrams of the excitations in the magnetoelectric multiferroic $Pb(TiO)Cu_4(PO_4)_4$ were obtained in wide ranges of magnetic fields up to 50 T and frequencies below 2 THz. Some of the observed resonance modes were reproduced qualitatively by a numerical analysis based on the generalized spin-wave theory. Moreover, we found that electron spin resonance (ESR) signals on some of the modes can be modulated by applying an electric field. This result implies the presence of nonreciprocal linear dichroism on the ESR signals in $Pb(TiO)Cu_4(PO_4)_4$.

Optical selection rules of the magnetic excitation in the S=1/2 one-dimensional Ising-like antiferromagnet $BaCo_2V_2O_8$

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(*Phys. Rev. B., 2022*)

In this study, we clarify the selection rules of optical transitions from the ground state to the magnetic excited states in the quasi-one-dimensional quantum Ising-like antiferromagnet $BaCo_2V_2O_8$ with spin S=1/2 using the high-field electron spin resonance measurement with illuminating polarized electromagnetic waves. We demonstrate that the unconventional magnetic excitation via the pair creation of quasipaticles at wave numbers $q_z = \pi/2$ and π in the field-induced quantum critical state can couple with both oscillating magnetic and electric fields. Our density matrix renormalization group calculations indicate that the observed selection rules can be explained by two- and four-fold periodical spin interactions, originating from the screw chain structure in $BaCo_2V_2O_8$, in addition to the magnetoelectric coupling between spins and electric dipoles.

Anomalous magnetic exchange in a dimerized quantum magnet composed of unlike spin species

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(*Phys. Rev. B., 2021*)

We present here a study of the magnetic properties of the antiferromagnetic dimer material $CuVOF_4(H_2O)_6\cdot H_2O$, in which the dimer unit is composed of two different $S = 1/2$ species, Cu(II) and V(IV). An applied magnetic field of $\mu_0 H_{c1} = 13.1(1)$ T is found to close the singlet-triplet energy gap, the magnitude of which is governed by the antiferromagnetic intradimer $J_0 \approx 21$ K, and interdimer $J' \approx 1$ K, exchange energies, determined from magnetometry and electron-spin resonance measurements. The results of density functional theory (DFT) calculations are consistent with the experimental results. The DFT calculations predict antiferromagnetic coupling along all nearest-neighbor bonds, with the magnetic ground state comprising spins of different species aligning antiparallel to one another, while spins of the same species are aligned parallel. The magnetism in this system cannot be accurately described by the overlap between localized V orbitals and magnetic Cu orbitals lying in the Jahn-Teller (JT) plane, with a tight-binding model based on such a set of orbitals incorrectly predicting that interdimer exchange should be dominant. DFT calculations indicate significant spin density on the bridging oxide, suggesting instead an unusual mechanism in which intradimer exchange is mediated through the O atom on the Cu(II) JT axis.

Effects of spin-lattice coupling and a magnetic field in classical Heisenberg antiferromagnets on the breathing pyrochlore lattice

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(*Phys. Rev. B., 2021*)

We theoretically investigate spin-lattice coupling (SLC) effects on the in-field ordering properties of classical Heisenberg antiferromagnets on the breathing pyrochlore lattice. Here, we use the two possible simplified models describing the effect of local lattice distortions on the spin ordering via the SLC, the bond-phonon and site-phonon models. It is found by means of Monte Carlo simulations that in both models, the 1/2 plateau shows up in the magnetization curve being relatively robust against the breathing bond alternation, although magnetic long-range orders (LRO's) are realized only in the site-phonon model. In the bond-phonon model, additional further neighbor interactions are necessary to induce a magnetic LRO. In the site-phonon model, it is also found that in addition to the low-field, middle-field 1/2 plateau, and high-field phases appearing on both the uniform and breathing pyrochlore lattices, various types of unconventional phases which can be viewed as LRO's in units of tetrahedron are induced by the breathing bond alternation just below the 1/2 plateau and the saturation field. The occurrence of these tetrahedron-based orders could be attributed to the nature characteristic of the breathing pyrochlore lattice, i.e., the existence of the nonequivalent small and large tetrahedra. Experimental implications of our result are also discussed.

Replica symmetry breaking in the RKKY skyrmion-crystal system

K. Mitsumoto and H. Kawamura

(*Phys. Rev. B., 2021*)

We study the RKKY Heisenberg model on a three-dimensional stacked-triangular lattice under magnetic fields by extensive Monte Carlo simulations to get insight into the chiral-degenerate symmetric skyrmion crystal (SkX) in centrosymmetric metallic magnets. The triple-*q* SkX and the double-*q* states are realized, together with the single-*q* state. We find an unexpected phenomenon of the replica-symmetry breaking (RSB) well known in glassy systems, although the Hamiltonian and the ordered state are entirely regular. In the RSB SkX phase, the triple-*q* SkX state macroscopically coexists with the single-*q* state, even though these ordered states cannot be transformed via any Hamiltonian-symmetry operation. In the thermodynamic limit, the free energies of these states are degenerate whereas the free-energy barrier between the states diverges, breaking the ergodicity. A similar RSB is also observed in the RSB double-*q* phase where the double-*q* state macroscopically coexists with the single-*q* state. Experimental implications are discussed.

Frustration-induced quantum spin liquid behavior in the $s = 1/2$ random-bond Heisenberg antiferromagnet on the zigzag chain

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(*J. Phys. Soc. Jpn., 2021*)

Recent studies have revealed that the randomness-induced quantum spin liquid (QSL)-like state is stabilized in certain frustrated quantum magnets in two and three dimensions. In order to clarify the nature of this gapless QSL-like state, we investigate both zero- and finite-temperature properties of the random-bond one-dimensional (1D) $s = 1/2$ Heisenberg model with the competing nearest-neighbor and next-nearest-neighbor antiferromagnetic interactions, J_1 and J_2, by means of the exact diagonalization, density-matrix renormalization-group and Hams–de Raedt methods. We find that, on increasing the frustration J_2, the gapless nonmagnetic state stabilized in the unfrustrated model with $J_2 = 0$, the *unfrustrated* random-singlet (RS) state, exhibits a phase transition into different gapless nonmagnetic state, the *frustrated* RS state. This frustrated RS state in 1D has properties quite similar to the randomness-induced QSL-like state recently identified in 2D and 3D frustrated magnets exhibiting the T-linear low-temperature (T) specific heat, while the unfrustrated RS state is more or less specific to the unfrustrated 1D system exhibiting the $\sim 1 = |\log T|^3$ low-T specific heat. Universal features and the robustness against perturbations of the frustrated RS state are emphasized.

Spin Dynamics Simulation of the Z_2-vortex Fluctuations

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(*J. Phys. Soc. Jpn., 2022*)

Motivated by the recent quasi-elastic neutron scattering experiment, we extend the spin-dynamics simulation on the triangular-lattice Heisenberg antiferromagnet, to observe a sharp central peak of its energy width ~0.001J (J the exchange coupling) of the Z_2-vortex origin, consistently with the experiment.

Skyrmion crystal in the RKKY system on the two-dimensional triangular lattice

K. Mitsumoto and H. Kawamura

(*Phys. Rev. B., 2022*)

We study the ordering properties of the isotropic RKKY Heisenberg model on the two-dimensional (2D) triangular lattice by extensive Monte Carlo simulations to get insights into the chiral-degenerate skyrmion crystal (SkX) of metallic magnets. Our Hamiltonian contains only the spin-quadratic RKKY interaction derived from the spherical Fermi surface, containing neither the nesting nor the many-body interaction. The SkX phase is stabilized under applied fields where the frustration associated with the oscillating nature of the RKKY interaction and the emergent many-body interactions generated by thermal fluctuations play important roles. Replica symmetry breaking, reported in our recent paper on the 3D RKKY model [K. Mitsumoto and H. Kawamura, *Phys. Rev. B* 104, 184432 (2021)], turns out to be absent in the present 2D model. Implications to the SkX formation mechanism are discussed.

Observation of topological Z_2 vortex fluctuations in the frustrated Heisenberg magnet $NaCrO_2$

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Spin fluctuations in the triangular-lattice Heisenberg antiferromagnet $NaCrO_2$ are investigated by means of quasi-elastic neutron scattering with high energy resolution and wide energy band. Three components of spin fluctuations, which are different in temperature dependence and time scale, are captured. The slowest component is described by a very sharp quasi-elastic scattering with energy width of approximately 0.01 meV (~ 0.001J, where J the exchange coupling), which is significant in the middle-temperature range of 30-40 K and goes away both in the lower and higher temperature ranges. The experimental features are checked against the Z_2 vortex theory to arrive at a natural explanation, indicating that the elusive Z_2 vortex fluctuations are finally detected directly.

III-B. DEVELOPMENT OF NOVEL ESR TECHNIQUES IN THE THz REGION USING THERMAL AND PHOTOMIXING DETECTION METHODS

Thermal detection of ESR signal is a powerful technique for sensitive detection of small-volume samples. In this technique, heat relaxation of a sample accompanied by ESR absorption is converted to temperature increase of a thermometer attached to the sample. We developed a novel thermal detection technique in the terahertz region for protein solution sample. This technique was first applied to hemin, which is known as a model substance of hemoproteins, in order to evaluate its performance. We successfully observed ESR signals characteristic for ferric ions with a substantial signal-to-noise ratio. As a next step, a solution sample of hemoprotein will be tested in the future.

We also developed a force-detected ESR technique using a high-power terahertz source, gyrotoron, installed at Fukui University. This technique is suitable for low-concentration spin systems such as metalloproteins. The measurements system was optimized at Fukui University with helps of Dr. Ishikawa and Prof. Mitsudo. This technique is promising for future applications to a solution sample of metalloproteins at room temperature.

We also developed a frequency-domain ESR spectroscopy technique using photomixing devices. By combining an active phase modulation technique, high spectral resolution as high as 1 MHz was attained. With this technique, we successfully observed narrow ESR signals of a mixed powder of DPPH and TEMPOL radicals. This technique was also applied to a single crystal of NiO, and antigerromagnetic resonance (AFMR) signals were clearly observed. We also investigated the magnetic field dependence of the AFMR mode in three different field orientations for the first time. In particular, it was found that the AFMR mode split into two branches in the <111> axis. These results will be analyzed taking the magnetic domain structure into account.

Collaborative researches with Dr. Horitani at Saga University and with Dr Inanami at Hokkaido University were carried out. H. Takahashi continuously conducted the research project from JST-PRESTO's program "Thermal Science and Control of Spectral Energy Transport", in which the heat transport of magnetic materials was studied by high-frequency ESR spectroscopy.

Mr. Shoji gave an oral talk entitled “High-resolution frequency-domain terahertz spectroscopy and its application to electron paramagnetic resonance” at International Conference on Infrared, Millimeter, and Terahertz Waves (IRMMW-THz 2021).

Mechanically Detected Terahertz Electron Spin Resonance

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(*Appl. Mag. Res., 2021*)

In this review, mechanically detected electron spin resonance (MDESR) in the terahertz (THz) region is described to demonstrate its usability as a novel methodology for obtaining microscopic insights into local electronic structures. Using micro-mechanical devices, the sensitivity to a small-volume sample is greatly enhanced even for a cavityless setup. Moreover, there are plenty of options in the setup of MDESR, including detection modes, mechanical devices, and detection techniques. ESR spectroscopy of single-crystalline, powder, and frozen solution samples in the THz region are demonstrated.

Field-angle-dependent multi-frequency electron spin resonance spectroscopy in submillimeter wave range based on thermal detection

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(*Rev. Sci. Instrum., 2021*)

We report the thermally detected electron spin resonance (ESR) spectroscopy in the frequency range of millimeter and submillimeter waves. Under high vacuum conditions, a cantilever-shaped device detects ESR absorption of a mounted sample as a temperature difference in its beam direction. Despite the simple experimental setup, the spin sensitivity of the order of 10^{12} spins/G was achieved at 10 K. The developed sample stage is small enough to be used in a 10 T split-pair superconducting magnet with a bore of 25 mm, enabling precise field-angle-dependent ESR measurements at multi-frequencies above 500 GHz. We demonstrate its usefulness by studying the field-angle dependence of the excitation energy of the dimer triplet state in the Shastry–Sutherland magnet $SrCu_2(BO_3)_2$.

Frequency-domain electron spin resonance spectroscopy using continuously frequency-tunable terahertz photomixers

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(*Appl. Phys. Lett., 2021*)

Frequency-domain electron spin resonance (FDESR) spectroscopy in the terahertz (THz) region using continuously tunable photomixers was demonstrated. Spectral resolution was greatly improved with the use of a pair of fiber stretchers. In this setup, the amplitude of the THz electric field was determined at each frequency by externally sweeping the optical path difference, resulting in a spectral resolution of about 1-MHz. With this technique, we observed narrow ESR spectra with a 20-MHz linewidth, enabling high-resolution FDESR spectroscopy in a broad frequency range.

This work was supported by Competitive Funding Programs "Collaborative Research Based on Industrial Demand" from Japan Science and Technology Agency (JPMJSK1615) and by the Amada Foundation.

Angle-dependent force-detected terahertz ESR measurement of non-centrosymmetric magnet CuB_2O_4

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It is known that the non-centrosymmetric copper metaborate CuB_2O_4 exhibits nonreciprocal directional dichroism where the optical absorption changes with the reversal of the direction of light propagation. Such non-reciprocity has also been observed in the microwave region. Although their origins are supposed to originate from its complex magnetic structure, the details still remail unclear. In this study, we performed angle-dependent force-detected electron spin resonance measurements in the terahertz region to clarify the magnetic properties of CuB_2O_4 from the microscopic viewpoint.

III-C. DEVELOPMENT AND APPLICATION OF HIGH-PRESSURE THz ESR SYSTEM

High pressure ESR measurement is very useful for studying the pressure effect of magnetic materials and we have developed very unique high pressure THz ESR systems so far. For the transmission type system, we established a ratio of inner and outer diameters of pressure cell cylinder which generates a pressure beyond 2 GPa repeatedly. The previous pressure cell cylinder had an inner diameter of 4 mm and the inner/outer diameter ratio of 5.9. By changing the ratio to 7 (the outer diameter to 28 mm) to suppress its deformation under load, we reduced damage to ceramic internal parts. As a result, we succeeded in observing the pressure dependence of the direct transition from the singlet ground state to the excited triplet states up to 2.3 GPa for $CuVOF_4(H_2O)_6 \cdot H_2O$, in which the antiferromagnetic dimer units composed of two different $S = 1/2$ species Cu^{2+} and V^{4+}. It was found that the direct transition ESR mode disappeared above 2 GPa. Further investigation is ongoing to clarify the origin of disappearance for the direct ESR transition mode above 2 GPa. This study is collaboration with Dr. Dmytro Kamenskyi, Augsburg University, Germany.

We also developed high pressure ESR measurement technique based on the thermal detection method, in which ESR is observed by detecting the temperature change of the sample at resonance condition. As the ESR probe becomes compact with this method, it can be combined with a various type superconducting magnets. In this study, we developed a system where we can perform the field angle dependence measurement under high pressure in combination with a split-pair type superconducting magnet. We succeeded in observing detailed pressure changes in the crystal field of the spin gap substance Cu_2(1,4-diazacycloheptane)$_2Cl_4$ by this system. A master course student N. Nagasawa received the excellent presentation award at the 30th annual meeting of the Japan Society of Infrared Science and Technology on his development of this thermal detection type high-pressure ESR system.

High‐Pressure THz ESR

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In solid-state physics, pressure is an essential parameter, which can continuously change the interaction between electrons. The combination of terahertz electron spin resonance (THz ESR) with pressure is a powerful approach to clarify the spin state under pressure from the microscopic point of view, especially for quantum mag-nets. The most important feature of our high-pressure THz ESR system is that our pressure cell ensures the high pressure and wide frequency range using ceramics in internal parts, which are well balanced in terms of toughness and transmittance of electromagnetic waves. This approach allowed to very accurately describe the spin state under pressure. In this review, high-pressure ESR systems are reviewed with a focus on those in the high-frequency region.

In addition, we show differences between other systems and our system. Moreover, we show the usefulness of our system by showing application examples of several magnetic materials of interest.

Development of Pressure Calibration Method in High‐Pressure THz ESR System

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(*Appl. Mag. Res., 2021*)

We have developed a pressure calibration method in the high-pressure THz ESR system using induction coils set outside the pressure cell. The pressure is calibrated using alternating current (AC) magnetization measurements of the superconducting transition temperature of tin set inside the pressure cell with an ESR sample. The system fits the developed pressure cell with a wide frequency range of 0.05–0.8 THz. The pressure range was extended to 2.8 GPa. The ESR system was applied to the well-known cobalt Tutton's salt $(NH_4)_2Co(SO_4)_2{\cdot}6H_2O$, and its g principal values at 0 GPa were determined as g_1=6.61 , g_2=3.05 , and g_3=2.94 for the first time. Furthermore, we succeeded in observing the large change in these *g* values with pressure.

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. From 2010 applications of SQUID magnetometer to various material researches spread out continuously. It is also supporting the user programs of Molecular Photoscience Research Center, Kobe University since 2017. Users of SQUID magnetometer are Mochida and Takahashi group, Uchino group (Department of Chemistry, Kobe University), Sugawara and Matsuoka group, and Kotegawa and Tou group (Department of Physics, Kobe University), T. Sakurai, S. Hara and Y. Saito (Center for Supports to Research and Education Activities, Kobe University). The magnetic anisotropy of the thin film neodymium magnets is revealed by the magnetization measurements by K. Koike group in joint researches programs of Molecular Photoscience Research Center, Kobe University.

Effect of Mo monoatomic interlayer on magnetic properties of in-plane anisotropic Nd-Fe-B/Mo/FeCo nanocomposite multilayered films

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(*AIP Advances, 2021*)

The Nd-Fe-B/Mo/Fe-Co multilayered films on MgO(001) were fabricated by UHV sputtering method. The as-deposited films showed soft magnetic properties with weak perpendicular magnetic anisotropy, and after annealing above 650°C, these films showed in-plane magnetic anisotropy, good squareness, and hard magnetic properties with high coercivity of about 8 kOe. The (220) peak of $Nd_2Fe_{14}B$ was identified in the XRD pattern after annealing of the film, which means that the c-axis, which is the easy axis of magnetization, points in the plane of the film, consistent with the measurement of the magnetization curve. The positive peak of ΔM plot of in-plane direction of the film annealed at 800°C was shown. This result suggests existence of exchange coupling between the Nd-Fe-B and Fe-Co layers in the in-plane anisotropic multilayered film with monoatomic Mo interlayer.

III-E. SPIN AND LATTICE DYNAMICS STUDIED BY PUMP-PROBE AND TERAHERTZ SPECTROSCOPIES

The terahertz region in the electromagnetic spectrum has attracted research attention in solid-state physics, 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. 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. We studied the spin and lattice dynamics in solid-state materials using optical pump-probe spectroscopy and terahertz time-domain spectroscopy (THz-TDS). The generation and detection of magnetization and birefringence using optical and electric pulses are very useful to observe the spin and lattice dynamics in ferromagnetic, 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.

Longitudinal electric-field induced magnetization in YIG: First- and second-order magnetoelectric effects observed by Faraday rotation

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(submitted)

We observed the electric-field induced magnetization due to the change in the magnitude of magnetization in yttrium iron garnet $Y_3Fe_5O_{12}$ (YIG) using Faraday rotation, and investigated its behavior with respect to the applied electric and magnetic fields. It was found that the magnitude of the electric-field induced magnetization in YIG is proportional to and is 10^3 times smaller than that of the magnetic-field induced magnetization in our experiment. The observed amplitude of the electric-field induced magnetization can be given by a sum of two components linear and quadratic in the electric field due to the first- and second-order magnetoelectric (ME) effects. Different ME domains are generated depending on the relative direction of the cooling electric and magnetic fields, and the electric-field dependence of the electric-field induced magnetization shows different curves. Even for fixed directions of the cooling electric and magnetic fields, ME domains with opposite signs were observed, and they are considered to distribute in the sample. Increasing the beam diameter of the Faraday-rotating probe light reduced the signal amplitude of the electric-field induced magnetization. This behavior can be qualitatively explained by a simple model of statistical physics. At low temperatures, the first-order ME effect is dominant, but above 200 K, the second-order ME effect is dominant. It may be considered that, at low temperatures, excess electrons are localized to specific Fe^{2+} ions formed near oxygen defects to show the first-order ME effect, and that, at high temperatures, they are delocalized by electron hopping to show the second-order ME effect.

Dynamics of the electric-field induced magnetization and the domain switching in an antiferromagnet Cr_2O_3

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(*32nd Symp. Assoc. Cond. Matter Photophysics*)

We studied the dynamics of the electric-field induced magnetization and the domain switching in an antiferromagnet Cr_2O_3 using the Faraday effect. The time evolution of the Faraday rotation signal in the nanosecond region was observed in a pulsed electric field. The rise time of the electric-field induced magnetization was found to be less than the response time of our measurement system, 10 ns. The Faraday rotation amplitude becomes smaller as the temperature increases toward T_N (= 307 K). It was confirmed that, when the magnetic field is inverted in an electric field and the magnitude of the magnetic field exceeds a certain threshold value, the Faraday rotation signal is inverted. This shows that the antiferromagnetic domain switching occurs. The inversion behavior does not change for different laser beam spot sizes. This suggests that the domain switching occurs globally rather than locally. From the observation of the domain switching in the millisecond region, it is found that the domain switching occurs instantaneously in the millisecond range. The domain switching in Cr_2O_3 is considered to be a dynamic cooperative phenomenon in the antiferromagnetic ordered state, and it can be controlled by the electric field using the magnetoelectric effect.

Observation of magnetic Kerr rotation in magnetite

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(*32nd Symp. Assoc. Cond. Matter Photophysics*)

The magnetization in a ferrimagnet Fe_3O_4 was observed by a magneto-optical effect called magnetic Kerr rotation, in which the polarization plane of the reflected light of a linearly polarized probe light rotates, to study the electromagnetic effect, crystal axis switching, and magnetic domain switching. We observed the magnetic-field induced axis switching in the monoclinic crystal by using the axis-dependent shape of the magnetization curve. The axis switching was observed at the temperatures 90, 100 and 110 K, but not observed at 80 K in the magnetic field up to 5 T. It is considered that there is a threshold value of the external magnetic field at each temperature, above that the axis switching occurs.

Original Papers 発表論文

authors	title	Journal	Vol.	page	year
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Shunta Nakamura, Hayato Sakai, Masaaki Fuki, Yasuhiro Kobori, Nikolai V. Tkachenko, and Taku Hasobe	Enthalpy–Entropy Compensation Effect for Triplet Pair Dissociation of Intramolecular Singlet Fission in Phenylene Spacer-Bridged Hexacene Dimers	*J. Phys. Chem. Lett.*	**12**	6457–6463	2021.7.8
Manabu Sakurai, Ryota Kabe, Masaaki Fuki, Zesen Lin, Kazuya Jinnai, Yasuhiro Kobori, Chihaya Adachi, and Takashi Tachikawa	Organic photostimulated luminescence associated with persistent spin-correlated radical pairs	*Communications Materials*	**2**	Article number:74	2021.7.13
Shunta Nakamura, Hayato Sakai, Hiroki Nagashima, Masaaki Fuki, Kakeru Onishi, Ramsha Khan, Yasuhiro Kobori, Nikolai V. Tkachenko, and Taku Hasobe	Synergetic Role of Conformational Flexibility and Electronic Coupling for Quantitative Intramolecular Singlet Fission	*J. Phys. Chem. C*	**125**	18287-18296	2021.8.13
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Hiromu Fuse, Yu Irie, Masaaki Fuki, Yasuhiro Kobori, Kosaku Kato, Akira Yamakata, Masahiro Higashi, Harunobu Mitsunuma, Motomu Kanai	Identification of Self-Photosensitizing Hydrogen Atom Transfer Organocatalyst System	*J. Am. Chem. Soc.*		In press	2022
S. Tominaka, I. Karimata, T. Matsuoka, M. Sakamoto, T. Nakajima, K. Ohara, T. Tachikawa	Dynamic Symmetry Conversion in Mixed-Halide Hybrid Perovskite upon Illumination	*ACS Energy Lett.*	**6**	3858-3863	2021
M. Yamashita, S. Nagai, S. Ito, T. Tachikawa	In Situ Exploration of Stimulus-Induced Emission Changes in Mechanochromic Dyes	*J. Phys. Chem. Lett.*	**12 (32)**	7826-7831	2021
S. Ito, S. Nagai, T. Ubukata, T. Tachikawa	Multi-color mechanochromic luminescence of three polymorphic crystals of a donor-acceptor-type benzothiadiazole derivative	*CrystEngComm.*	**23 (34)**	5899-5907	2021
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N. Haraguchi, T. Okunaga, Y. Shimoyama, N. Ogiwara, S. Kikkawa, S. Yamazoe, M. Inada, T. Tachikawa, S. Uchida	Formation of Mixed-Valence Luminescent Silver Clusters via Cation-Coupled Electron-Transfer in a Redox-Active Ionic Crystal Based on a Dawson-type Polyoxometalate with Closed Pores	*Eur. J. Inorg. Chem.*	**2021 (16)**	1531-1535	2021.3.18
K. Ogawa, R. Sakamoto, C. Zhong, H. Suzuki, K. Kato, O. Tomita, K. Nakashima, A. Yamakata, T. Tachikawa, A. Saeki, H. Kageyama, R. Abe	Manipulation of charge carrier flow in Bi_4NbO_8Cl nanoplate photocatalyst with metal loading	*Chem. Sci.,*	**13 (11)**	3118-3128	2022
Z. Zhang, T. Tsuchimochi, T. Ina, Y. Kumabe, S. Muto, K. Ohara, H. Yamada, S. L. Ten-no, T. Tachikawa	Binary dopant segregation enables hematite-based heterostructures for highly efficient solar H_2O_2 synthesis	*Nat. Commun.*	**13**	1499	2022
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Erika Mitani, Yukihiro Ozaki, and Harumi Sato	Two Types of C=O···HO Hydrogen Bonds and OH···OH (Dimer, Trimer, Oligomer) Hydrogen Bonds in PVA with 88% Saponification/PMMA and PVA with 99% Saponification/PMMA Blends and Their Thermal Behavior Studied by Infrared Spectroscopy	*Polymer*			in press

Harumi Sato, Yusuke Morisawa, Satoshi Takaya, Yukihiro Ozaki	A Study of C=O···HO and OH···OH (Dimer, Trimer, and Oligomer) Hydrogen Bondings in a Poly(4-vinylphenol)30%/Poly(methyl methacrylate)70% Blend and its Thermal Behaviour Using Near-infrared Spectroscopy and Infrared Spectroscopy and Infrared Spectroscopy	*Applied Spectroscopy*			in press
Huiqiang Lu, Harumi Sato, Sergei G. Kazarian	Visualization of Inter-and Intramolecular Interactions in Poly(3-hydroxybutyrate)/ Poly(L-lactic acid)(PHB/PLLA) Blends During Isothermal Melt Crystallization Using Attenuated Total Reflection Fourier Transform infrared (ATR FT-IR) Spectroscopic Imaging	*Applied Spectroscopy*	**75**	0003702821 10102	2021.4.22
Atsushi Nishimae, Harumi Sato	Study of Co-crystallization and Intermolecular Hydrogen Bondings of Poly(glycolide-*co*-L-lactide) Copolymers by Terahertz and Low-Frequency Raman Spectroscopy	*Macromolecules*	**54**	6440-6448	2021.6.16
Mirosław Antoni Czarnecki, Yusuke Morisawa, Yukiteru Katsumoto, Tomoyuki Takaya, Swapnil Singh, Harumi Sato and Yukihiro Ozaki	Solvent Effect on Competition Between Weak and Strong Interactions in Phenol Solutions Studied by Near-infrared Spectroscopy and DFT Calculations	*Phys. Chem. Chem. Phys.*	**23**	19188-19194	2021.8.12
Tulika Sharma, Yoshiaki Nishio, Yuichiro Tamano, Harumi Sato, Isao Takahashi	Correlation of physical aging and glass transition temperatures in ultrathin polystyrene films supported on SiO_2	*Polymer*	**230**	124103	2021.9.16
Mao Nochi, Yukihiro Ozaki, Harumi Sato	Water-induced conformational changes in the powder and film of ε-poly(L)lysine studied by infrared and Raman spectroscopy	*Spectrochimica Acta Part A*	**260**	119900	2021.11
T. Sakurai, H. Ohta, S. Hara, and Y. Saito	High-Pressure THz ESR（Invited review)	*Appl. Mag. Res*	**52**	267-281	2021.4
E. Ohmichi, T. Okamoto, H. Takahashi, H. Ohta	Mechanically Detected Terahertz Electron Spin Resonance（Invited review)	*Appl. Mag. Res.*	**52**	283-304	2021.4
S. V. Demishev, A. V. Semeno, and H. Ohta	Staggered Field in Quantum Antiferromagnetic $S = 1/2$ Spin Chain Probed by High-Frequency EPR (the Case of Doped $CuGeO_3$)（Invited review)	*Appl. Mag. Res*	**52**	379-410	2021.4
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H. Takahashi, T. Sakurai, E. Ohmichi, H. Ohta	Field-angle-dependent multi-frequency electron spin resonance spectroscopy in submillimeter wave range based on thermal detection	*Rev. Sci. Instrum*	**92**	083901/1-6	2021.8
D. Yamamoto , T. Sakurai, R. Okuto, S. Okubo, H. Ohta, H. Tanaka, and Y. Uwatoko	Continuous control of classical-quantum crossover by external high pressure in the coupled chain compound $CsCuCl_3$	*Nature Communications*	**12**	4263/1-9	2021.7
T. Sakurai, Y. Yasutani, H. Sugawara, S. Okubo, H. Ohta	Development of Pressure Calibration Method in High-Pressure THz ESR System	*Appl. Mag. Res*			2021.7
E. Ohmichi, Y. Shoji, H. Takahashi, H. Ohta	Frequency-domain electron spin resonance spectroscopy using continuously frequency- tunable terahertz photomixers	*Appl. Phys. Res*	**119**	162404/1-5	2021.10
Kunihiro Koike, Kazuki Ohashi, Takuya Suzuki, Chihiro Okita, Nobuyuki Inaba, Hiroaki Kato, Masaru Itakura, Shigeo Hara, Yu Saito, Susumu Okubo, and Hitoshi Ohta	Effect of Mo monoatomic interlayer on magnetic properties of in-plane anisotropic Nd-Fe-B/Mo/FeCo nanocomposite multilayered films	*AIP Advances*	**11**	015134/	2021.1
Mitsuru Akaki, Kenta Kimura, Yasuyuki Kato, Yuya Sawada, Yasuo Narumi, Hitoshi Ohta, Tsuyoshi Kimura, Yukitoshi Motome, and Masayuki Hagiwara	Nonreciprocal Linear dichroism observed in electron spin resonance spectra of the magnetoelectric multiferroic $Pb(TiO)Cu_4(PO_4)_4$	*Physical Review Research*	**3**	L042043	2021.1
S. Kimura, H. Onishi, A. Okutani, M. Akaki, Y. Narumi, M. Hagiwara, K. Okunishi, K. Kindo, Z. He, T. Taniyama, and M. Itoh	Optical selection rules of the magnetic excitation in the S=1/2 one-dimensional Ising-like antiferromagnet $BaCo_2V_2O_8$	*Phys. Rev. B*	**105**	014417	2022.1
S. P. M. Curley, B. M. Huddart, D. Kamenskyi, M. J. Coak, R. C. Williams, S. Ghannadzadeh, A. Schneider, S. Okubo, T. Sakurai, H. Ohta, J. P. Tidey, D. Graf, S. J. Clark, S. J. Blundell, F. L. Pratt, M. T. F. Telling, T. Lancaster, J. L. Manson, and P. A. Goddard	Anomalous magnetic exchange in a dimerized quantum magnet composed of unlike spin species	*Phys. Rev. B*	**104**	214435/1-11	2021.9

D. Hachiya, H. Takahashi, T. Arima, S. Toyoda, M. Saito, E. Ohmichi, S. Okubo and H. Ohta	Angle-dependent force-detected terahertz ESR measurement of non-centrosymmetric magnet CuB_2O_4	*J. Jpn. Soc. Infrared Science & Technology*	**31 NO. 1**		2021
K. Aoyama and H. Kawamura	Effects of spin-lattice coupling and a magnetic field in classical Heisenberg antiferromagnets on the breathing pyrochlore lattice	*Phys. Rev. B*	**104**	184411	2021.8
K. Mitsumoto and H. Kawamura	Replica symmetry breaking in the RKKY skyrmion-crystal system	*Phys. Rev. B*	**104**	184432	2021.8
K. Uematsu, T. Hikihara, and H. Kawamura	Frustration-induced quantum spin liquid behavior in the $s = 1/2$ random-bond Heisenberg antiferromagnet on the zigzag chain	*J. Phys. Soc. Jpn.*	**90**	124703/1-10	2021.11
Y. P. Mizuta, K. Aoyama, K. Tomiyasu, M. Matsuura, and H. Kawamura	Spin Dynamics Simulation of the Z2-vortex Fluctuations	*J. Phys. Soc. Jpn.*	**91**	035001	2022.2
K. Mitsumoto and H. Kawamura	Skyrmion crystal in the RKKY system on the two-dimensional triangular lattice	*Phys. Rev. B*	**105**	094427	2022.3
K. Tomiyasu, Y. P. Mizuta, M. Matsuura, K. Aoyama, and H. Kawamura	Observation of topological Z_2 vortex fluctuations in the frustrated Heisenberg magnet $NaCrO_2$	*(ar Xiv)*			2021.10

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	2021 6. 4	online	invite	ECS Meeting	Vibronic Effect of Donor-Acceptor Interaction Determines Fate of Mutiexciton Spins Generated By Singlet Fission
	2021. 12. 18	online	invite	7th Kanto Area Spin Chemistry Meeting （KASC 7)	Water dynamics control of the magnetic compass
	2021. 9. 7	online	invite	第一回広帯域極限電磁波生命理工連携研究会	「電子スピン分極映像化による超高効率光エネルギー変換機構の解明」
	2021. 9. 9	online	invite	第 19 回 ESR 夏の学校講演会	「電子スピン分極映像化による超高効率光エネルギー変換機構の解明」
	2021. 9.16	online	invite	量子生命科学会第 3 回大会	光合成光電荷分離のスピン量子コヒーレンスとデコヒーレンス
	2021. 10.1	online	invite	ICFPE2021	Conformation change and electronic de-coupling via intramolecular singlet fissions
	2021. 11.1	online	invite	Modern Development of Magnetic Resonance	Vibronic Spins in Singlet Fissions
	2021. 11.26	online	invite	第 15 回物性科学領域横断研究会	動物の磁気コンパスにおける水和運動の役割:光受容タンパク質の長距離電荷分離機構
	2021. 12.17	online	invite	Pacifichem2021	Spin-entanglement transport via singlet-fission as studied by transient EPR
	2021. 12.19	online	invite	Pacifichem2021	Heterogeneous charge-separation geometries at bulk-heterojunction interfaces in organic solar cell studied by transient EPR
	2022. 1.28	京大桂キャンパス	invite	京都大学分子工学研究科特別講演会	電子スピン分極の空間映像化による動的エキシトン機構解析
	2022. 3.25	online	invite	日本化学会春季年会特別企画「光化学の新展開」	電荷移動によるスピンの動きを捉える
岡本翔 T. Okamoto	2022. 3.16	online	invite	第二回広帯域極限電磁波生命理工連携研究会	光線力学療法への応用に向けた新しい光アップコンバージョン材料の開発
婦木正明 M. Fuki	2021. 7.28	online	Invite	第 4 回動的エキシトン若手セミナー	分子内一重項励起子分裂における一重項－五重項変換および解離のスピンダイナミクス
立川貴士 T. Tachikawa	2021.11. 1-4	Korea (online)	invite	11th Asian Photochemistry Conference	Development of hematite mesocrystal-based photoanodes for solar fuel production
富永圭介 K. Tominaga	2021.5. 10-12	東京大学物性研究所	invite	ガラスおよび関連する複雑系の最先端研究	水和したソフトマターの広帯域誘電分光

	2021.11.1-4	Korea (online)	invite	11th Asian Photochemistry Conference	Ultrafast Charge Carrier Dynamics in Tetrabenzoporphyrin Derivatives Studied by Time-resolved Terahertz Spectroscopy
	2021.11.12-14	Mumbai, India (online)	invite	Ultrafast Science (UFS) - 2021	THz Molecular Science in Condensed Phases
太田仁 H. Ohta	2021.5.15-16	online	invite	第 16 回 ESR 入門セミナー	超入門
	2021.8.22-27	online	invite	22nd International Society of Magnetic Resonance Conference 9th Asia-Pacific NMR Symposium (APNMR9) ISMAR-THz 2021	Multi-extreme THz ESR: Recent Developments and Applications
	2021.8.29-9.3	online	invite	The International Society of Infrared, Millimeter, and Terahertz Waves (IRMMW-THz 2021)	Multi-Extreme THz ESR At The Present Stage
	2021.10.21-22	online	invite	第 30 回(2021 年度)日本赤外線学会研究発表会	多重極限 THz 電子スピン共鳴測定装置の開発
	2021.11.1-5	online	invite	Modern Development of Magnetic Resonance	Multi-extreme THz ESR: Current Status and Future
	2021.12.16-21	online	invite	2021 International Chemical Congress of Pacific Basin Societies	Developments of highly-sensitive mechanically detected THz ESR for micro-size single crystals
大久保晋 S. Okubo	2021.11.1-5	online	invite	Modern Development of Magnetic Resonance	Multi-Frequency ESR Study of S=1/2 Antiferromagnetic Chain with Staggered Field System $KCuMoO_4(OH)$ by Force Detection ESR Method Using Single Microcrystal
髙橋英幸 H. Takahashi	2021.4.8	online	invite	テラヘルツ波科学技術と産業開拓第 182 委員会	テラヘルツ領域における機械検出型磁気共鳴法
赤木暢 M. Akaki	2021.9.20-23	online	invite	日本物理学会 2021 年秋季大会	パルス強磁場電子スピン共鳴によるスピン多極子の観測
	2022.3.15-19	online	invite	日本物理学会第 77 回年次大会	パルス強磁場を用いた電気磁気効果の研究
光元亨汰 K. Mitsumoto	2021.12.22-23	ハイブリッド（神戸国際会議場）	Oral	International Conference on Frustration, Topology, and spin Textures	Chiral-degenerate skyrmion crystal in frustrated RKKY Heisenberg model
川村光 H. Kawamura	2021.12.22-23	online	invite	International Conference on Frustration, Topology, and Spin Textures	Frustration-induced spin textures
	2022.3.8	online	invite	令和 3 年度神戸大学分子フォトサイエンス研究センター共同利用共同研究成果報告会	フラストレーションが創るスピンテクスチャ

Presentation at conferences (international and domestic) 一般講演

発表者 氏名	開催 時期	開催地	Oral or Poster	学会名	講演題目
小堀康博 Y. Kobori	2021. 9. 15	オンライン		2021 年光化学討論会	結晶性薄膜の一重項励起子分裂：活性化多重励起子の構造と解離に対する動的効果
	2021. 9. 19	オンライン		第 15 回分子科学討論会	分子内励起子分裂に伴う立体構造変化と電子的デカップリング： 電子スピン分極映像化による解析
婦木正明 M. Fuki	2021.8. 22-27	オンライン		ISMAR-APNMR2021	Geometries and Oscillating Motions Driving Quintet Multiexcitons and Triplet-Triplet Dissociations via the Intramolecular Singlet Fissions
	2021.9. 14-16	オンライン		2021 年光化学討論会	テトラセン分子ワイヤーにおける一重項励起子分裂で生成した多重励起子のスピンダイナミクス
岡本翔 T. Okamoto	2021. 10.21-22	オンライン		第 30 回日本赤外線学会研究発表会	メンブレン型メカニカルセンサーを用いた微量溶液試料向け THz-ESR 装置の開発
	2022.3. 23-25	オンライン		日本化学会第 102 春季年会 (2022)	電子スピン共鳴法を用いた有機半導体光アップコンバージョン材料のドナー/アクセプター界面で生成する三重項励起子のダイナミクス
立川貴士 T. Tachikawa	2021. 9.14	オンライン	Oral	2021 年光化学討論会	有機材料を用いた輝尽発光システムの開発
	2021. 12.2	オンライン	Oral	第 40 回固体・表面光化学討論会	ハロゲン交換反応による有機無機ペロブスカイトナノ粒子の構造変換
笠原俊二 S. Kasahara	2021.9. 18-21	札幌 （オンライン）	Poster	第 15 回分子科学討論会	$^{14}\mathrm{NO}_2$ および $^{15}\mathrm{NO}_2$ ラジカルの高分解能レーザー分光
馬場正昭 M. Baba	2021.6. 21-25	オンライン	Oral	2021 International Symposium on Molecular Spectroscopy	Ro-vibrationally averaged molecular structure of benzene I. Almost the same bond lengths for the C–H and C–D bonds
	2021.6. 21-15	オンライン	Oral	2021 International Symposium on Molecular Spectroscopy	High-resolution and high-precision laser spectroscopy of α-benzanthracene
	2021.9. 18-21	札幌 （オンライン）	Oral	第 15 回分子科学討論会	ベンゼンの振動平均構造：Planar but Non-flat Structure
佐藤春実 S. Sato	2021. 5.26	オンライン	Poster	第 70 回高分子学会年次大会	低波数ラマン分光法を用いたスチレンアクリロニトリル共重合体の熱挙動に関する研究
	2021. 5.26	オンライン	Poster	第 70 回高分子学会年次大会	赤外分光法及び量子化学計算によるポリブチレンサクシネートの分子間水素結合の検討
	2021. 5.27	オンライン	Poster	第 70 回高分子学会年次大会	振動分光法を用いた PVA/PMMA ブレンドの分子間相互作用に関する研究

太田仁 H. Ohta	2021.12.1-3	オンライン	Poster	Asia-Pasific Conference on Condensed Matter Physics 2021	Development of Multi-Extreme THx ESR system and Its Applications in Kobe
大久保晋 S. Okubo	2021.5.7	オンライン	Oral	第七回強磁場実験入門セミナー	強磁場発生の歴史
	2021.8.22-27	オンライン	Poster	22nd International Society of Magnetic Resonance Conference 9th Asia-Pacific NMR Symposium (APNMR9) ISMAR-APNMR2021	Multi-frequency Force Detection ESR measurements of Single Microcrystal KCuMoO$_4$(OH) As S=1/2 Antiferromagnetic Chain with Staggered Field system
	2022.3.15-19	オンライン	Oral	日本物理学会第 77 回年次大会	S=1/2 反強磁性鎖 KCuMoO$_4$(OH)の単結晶 ESR 測定 IV
髙橋英幸 H. Takahashi	2021.8.22-27	オンライン	Poster	22nd International Society of Magnetic Resonance Conference 9th Asia-Pacific NMR Symposium (APNMR9) ISMAR-APNMR2021	Development of the field-angle-dependent high-frequency ESR spectroscopy based on thermal detection method
	2021.9.24	オンライン	Oral	第八回西日本強磁場科学研究会	熱検出型高周波 ESR 法の開発と応用
赤木暢 M. Akaki	2021.8.22-27	オンライン	Poster	22nd International Society of Magnetic Resonance Conference 9th Asia-Pacific NMR Symposium (APNMR9) ISMAR-APNMR2021	Pulsed High-field ESR Study of Electromagnons in Multiferroic Sr$_2$CoSi$_2$O$_7$
	2021.12.17-18	ハイブリッド（新温泉町立文化会館）	Oral	第 16 回量子スピン系研究会	Sr$_2$CoSi$_2$O$_7$ におけるマグノンと 3 マグノン
光元亨汰 K. Mitsumoto	2021.9.20-23	オンライン	Oral	日本物理学会 2021 年秋季大会	三角格子上の二次元 RKKY ハイゼンベルク模型のスカーミオン格子相
	2021.12.17-18	ハイブリッド（新温泉町立文化会館）	Oral	第 16 回量子スピン系研究会	RKKY 系におけるフラストレーション誘起のスカーミオン格子相
	2022.3.15-19	オンライン	Oral	日本物理学会第 77 回年次大会	RKKY ハイゼンベルク模型における Z$_2$ 渦
嵯峨慎 M. Saga	2022.3.23-26	オンライン	Oral	日本化学会第 102 春季年会 (2022)	Co(II/III)錯体の反応性の違いを利用した還元剤の分析法の開発
川村光 H. Kawamura	2021.12.17-18	ハイブリッド（新温泉町立文化会館）	Oral	第 16 回量子スピン系研究会	Randomness-induced quantum spin liquid in the nuclear magnetism of 2D 3He

大道英二 （理学研究科） E. Ohmichi	2021.8.22-27	オンライン	Poster	22nd International Society of Magnetic Resonance Conference 9th Asia-Pacific NMR Symposium (APNMR9) ISMAR-APNMR2021	Terahertz Electron Paramagnetic Resonance Spectroscopy Using Compact Frequency-Tunable Photomixing Devices
櫻井敬博 (研究基盤センター) T. Sakurai	2021.8.22-27	オンライン	Poster	22nd International Society of Magnetic Resonance Conference 9th Asia-Pacific NMR Symposium (APNMR9) ISMAR-APNMR2021	Development of Multi-extreme THz ESR System and Its Application to Cobalt Tutton's Salt
	2021.9.20-23	オンライン	Poster	日本物理学会 2021 年秋季大会	圧力下 THz ESR 装置における圧力較正手法の開発と応用 II
	2022.3.10	オンライン	Oral	2021 年度福井大学遠赤外領域開発研究センター共同研究成果報告会	ESR 測定に適した圧力セル内部部品のジャイロトロンセラミックス焼結装置による作製
	2022.3.15-19	オンライン	Poster	日本物理学会第 77 回年次大会	スピンギャップ系物質 $Cu_2(C_5H_{12}N_2)_2Cl_4$ の圧力効果
原茂生 (研究基盤センター) S. Hara	2022.3.15-19	オンライン	Poster	日本物理学会第 77 回年次大会	$BaCo_2(SeO_3)_3$・$3(H_2O)$単結晶育成と磁気異方性測定

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	開催時期	学会名	講演題目
小堀康博 Y. Kobori	長友敬晃	M2	2021.8. 22-27	ISMAR-APNMR2021	Generation domain of quintet multiexcitons via singlet fission in organic thin films as studied by time-resolved EPR
	長友敬晃	M2	2021.9. 14-16	2021 年光化学討論会	ベンゾポルフィリン－ジケトピロロピロールをドナーとするバルクヘテロ接合界面の電荷移動と電荷解離：時間分解 EPR による解析
	大西翔	M1	2021.9. 14-16	2021 年光化学討論会	時間分解 EPR によるビフェニル連結テトラセンダイマーの分子内励起子分裂機構の解明
	勝平譲治	M1	2021.9. 14-16	2021 年光化学討論会	時間分解 EPR 法による熱活性化遅延蛍光分子の励起状態の解析
	勝平譲治	M1	2022.3. 23-25	日本化学会第 102 春季年会(2022)	時間分解 EPR 法による熱活性化遅延蛍光分子の励起状態の解析
	楠本遼太	B4	2022.3. 23-25	日本化学会第 102 春季年会(2022)	分子内一重項励起子分裂で生成する多重励起子の構造変化：時間分解 EPR 法による解析
	村山加純	B4	2022.3. 23-25	日本化学会第 102 春季年会(2022)	時間分解電子スピン共鳴法による非フラーレン型太陽電池材料の界面電荷分離構造解析
笠原俊二 S. Kasahara	清水暘	M2	2021.6. 21-25	2021 International Symposium on Molecular Spectroscopy	High-resolution Laser spectroscopy of trans-stilbene : Nonplanar structure in the ground state
	中島康輔	M2	2021.6. 21-25	2021 International Symposium on Molecular Spectroscopy	Ultrahigh-resolution Laser spectroscopy of acetaldehyde: Torsion-inversion-rotation interaction in the excited state
	清水暘	M2	2021.9. 18-21	第 15 回分子科学討論会	*trans*-スチルベンの $S_1 \leftarrow S_0$ 遷移の超高分解能レーザー分光
	中島康輔	M2	2021.9. 18.21	第 15 回分子科学討論会	高分解能レーザー分光によるアセトアルデヒドの大振幅振動にかんする研究
富永圭介 T. Tominaga	藤井悠生	D1	2021.6. 13-18	Time Resolved Vibrational Spectroscopy 2021	Vibrational Frequency Fluctuation of Carbonyl Compounds in Water Studied by Two-Dimensional Infrared Spectroscopy
	高本和也	M2	2021.9. 14-16	光化学討論会	時間分解分光法による 9-アリールカルバゾールの電荷移動状態に及ぼす溶媒効果
	藤井悠生	D1	2021.9. 18-21	分子科学討論会	二次元赤外分光法による水溶液中における振動数揺らぎに芳香環が及ぼす影響の解明
	藤井悠生	D1	2021.10. 21-22	日本赤外線学会研究発表会	二次元赤外分光法による水溶液中における振動数揺らぎに対する炭化水素基の影響

	藤井悠生	D1	2021.10.28-29	第43回溶液化学シンポジウム	二次元赤外分光法による水溶液中における振動数揺らぎの温度依存性
	高本和也	M2	2021.10.28-29	第43回溶液化学シンポジウム	フェムト秒過渡吸収分光法による9-アリールカルバゾールの分子内電荷移動ダイナミクス
	井岡光	M1	2021.10.28-29	第43回溶液化学シンポジウム	広帯域分光測定による温度応答性高分子の水和ダイナミクス
	藤井悠生	D1	2021.10.31-11.4	11th Asian Photochemistry Conference	Temperature Dependence of Vibrational Frequency Fluctuation of Solutes in Water Studied by Two-Dimensional Infrared Spectroscopy
	井岡光	M1	2021.10.31-11.4	11th Asian Photochemistry Conference	Hydration Dynamics of Thermo-responsive Polymers Investigated by Broadband Spectroscopy
	高本和也	M2	2021.12.22-23	溶液化学研究会若手の会第1回冬季発表会	時間分解分光法及び量子化学計算による9-アリールカルバゾールの分子内電荷移動状態に対する溶媒効果
	藤井悠生	D1	2021.12.24	神戸大学研究基盤センター若手フロンティア研究会2021	二次元赤外分光法による水溶液中における振動数揺らぎの温度依存性
	高本和也	M2	2021.12.24	神戸大学研究基盤センター若手フロンティア研究会2021	時間分解分光法及び量子化学計算による9-アリールカルバゾールの分子内電荷移動反応
	井岡光	M1	2021.12.24	神戸大学研究基盤センター若手フロンティア研究会2021	温度応答性高分子の水和ダイナミクス
太田仁 T. Ohta	小路悠斗	M2	2021.8.22-27	22nd International Society of Magnetic Resonance Conference 9th Asia-Pacific NMR Symposium (APNMR9)	High-Resolution Frequency-Domain Electron Paramagnetic Resonance Spectroscopy in the Terahertz Region
	長澤直生	M1	2021.8.22-27	22nd International Society of Magnetic Resonance Conference 9th Asia-Pacific NMR Symposium (APNMR9)	Application of Thermal Detection Method to High Pressure THz ESR Measurement
	竹原良祐	M2	2021.8.22-27	22nd International Society of Magnetic Resonance Conference 9th Asia-Pacific NMR Symposium (APNMR9)	High-pressure ESR Study on Pressure-induced Nonmagnetic-magnetic Transition in Spin Gap System $Cu_2(C_5H_{12}N_2)_2Cl_4$
	増田祥大	M1	2021.8.22-27	22nd International Society of Magnetic Resonance Conference 9th Asia-Pacific NMR Symposium (APNMR9)	High-Frequency Electron Paramagnetic Resonance Technique for Spectroscopic Studies of Metalloproteins under Pressure
	小路悠斗	M2	2021.8.29-9.3	The International Society of Infrared, Millimeter, and Terahertz Waves (IRMMW-THz 2021)	High-Resolution Frequency-Domain Terahertz Spectroscopy And Its Application To Electron Paramagnetic Resonance

	竹原良祐	M2	2021.9.20-23	日本物理学会2021年秋季	スピンギャップ系物質$Cu_2(C_5H_{12}N_2)_2Cl_4$における圧力誘起非磁性-磁性転移
	小路悠斗	M2	2021.9.20-23	日本物理学会2021年秋季	連続波長可変テラヘルツ光源を用いた周波数掃引型反強磁性共鳴分光法の開発
	長澤直生	M1	2021.9.20-23	日本物理学会2021年秋季	熱的検出による高圧力下ESR測定手法の開発と応用
	小路悠斗	M2	2021.9.24	第八回西日本強磁場科学研究会	連続波長可変テラヘルツ光源を用いた周波数掃引型反強磁性共鳴分光法の開発
	竹原良祐	M2	2021.9.24	第八回西日本強磁場科学研究会	スピンギャップ系物質$Cu_2(C_5H_{12}N_2)_2Cl_4$における圧力誘起非磁性-磁性転移
	小路悠斗	M2	2021.10.21-22	第30回(2021年度)日本赤外線学会研究発表会	連続波長可変テラヘルツ光源による高分解能周波数領域電子スピン共鳴法の開発
	増田祥大	M1	2021.10.21-22	第30回(2021年度)日本赤外線学会研究発表会	圧力下におけるタンパク質の高周波電子スピン共鳴分光
	仲恭平	M2	2021.10.21-22	第30回(2021年度)日本赤外線学会研究発表会	55Tパルス磁石を用いたテラヘルツ光ESR装置の開発
	長澤直生	M1	2021.10.21-22	第30回(2021年度)日本赤外線学会研究発表会	熱的検出による高圧力下ESR測定手法の開発と応用
	伊神早紀	M2	2021.10.21-22	第30回(2021年度)日本赤外線学会研究発表会	ディスク型WGM共振器の製作と評価
	深川韻	M1	2021.10.21-22	第30回(2021年度)日本赤外線学会研究発表会	低温におけるESR測定の感度向上を目的としたマイクロデバイス作製
	竹原良祐	M2	2021.10.21-22	第30回(2021年度)日本赤外線学会研究発表会	スピンギャップ系物質$Cu_2(C_5H_{12}N_2)_2Cl_4$の圧力下THz ESR測定
	小路悠斗	M2	2021.12.24	若手フロンティア研究会2021	連続波長可変テラヘルツ光源を用いた高分解能周波数領域電子スピン共鳴法の開発
	長澤直生	M1	2021.12.24	若手フロンティア研究会2021	熱検出型高圧下ESR測定手法の開発
	長澤直生	M1	2022.3.15-19	日本物理学会第77回年次大会	熱的検出による高圧下角度回転ESR測定手法の開発
	小路悠斗	M2	2022.3.22-26	第69回応用物理学会春季学術講演会	連続波長可変テラヘルツ光源を用いた周波数掃引型電子スピン共鳴法の開発と応用
河本敏郎 T. Kohmoto	川端将馬	M2	2021.10.13-15	日本分光学会年次講演会	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
	喜多将之	M2	2021.10.13-15	日本分光学会年次講演会	マグネタイトにおける磁気カー回転の観測
	虫明侑一郎	M2	2021.10.13-15	日本分光学会年次講演会	YIGにおける光励起キャリアの拡散ダイナミクス
	喜多将之	M2	2021.12.10-11	第32回光物性研究会	マグネタイトにおける磁気カー回転の観測

	虫明侑一郎	M2	2021.12.10-11	第 32 回光物性研究会	YIG における光励起キャリアの拡散ダイナミクス
	川端将馬	M2	2021.12.10-11	第 32 回光物性研究会	反強磁性体 Cr_2O_3 における電場誘起磁化とドメインスイッチのダイナミクス
	喜多将之	M2	2021.12.24	若手フロンティア研究会	マグネタイトにおける磁気カー回転の測定
	虫明侑一郎	M2	2021.12.24	若手フロンティア研究会	YIG における光励起キャリアの拡散ダイナミクス
	川端将馬	M2	2021.12.24	若手フロンティア研究会	反強磁性体 Cr_2O_3 における電場誘起磁化とドメインスイッチのダイナミクス
	虫明侑一郎	M2	2022.3.15-19	日本物理学会第 77 回年次大会	YIG における光励起キャリアの拡散ダイナミクス
	川端将馬	M2	2022.3.15-19	日本物理学会第 77 回年次大会	反強磁性体 Cr_2O_3 における電場誘起磁化とドメインスイッチのダイナミクス

Books 著書

著者（共著者も含む）	書名	出版社名	ページ数	発行年

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
喜多将之、岩佐祐里奈、河本敏郎	マグネタイトにおける磁気カー回転の観測	光物性研究会論文集	32 巻・43-46	2021
虫明侑一郎、永富寛弥、川井恵介、河本敏郎	YIG における光励起キャリアの拡散ダイナミクス	光物性研究会論文集	32 巻・115-118	2021
川端将馬、岡本淳、前田悠貴、河本敏郎	反強磁性体 Cr_2O_3 における電場誘起磁化とドメインスイッチのダイナミクス	光物性研究会論文集	32 巻・191-194	2021

Lecture to Public　　講演、模擬授業など

氏名	講演題目	集会名	日時	場所
小堀康博	光電荷分離の動的効果:電子スピン分極による解明	第19回ESR夏の学校	2021.9.8-10	オンライン
	時間分解電子スピン共鳴法を用いた光化学過程の動的機構解明	京都大学分子工学研究科分子工学特論第三(後半)集中講義	2022.1.27-28	京都大学桂キャンパス
笠原俊二	温室ガス効果ってなーに？	第16回女子中高生のための関西科学塾	2021.11.7	オンライン
富永圭介	Vibrational Spectroscopy and Global Warming	学部生向け授業	2022.3.23	タイ・タンマサート大学シリントーン国際工学部

Awards 受賞

氏名	受賞研究題目	賞名	団体、学会名
立川貴士		令和 3 年度学長表彰	国立大学法人神戸大学
太田仁	多重極限 THz 電子スピン共鳴測定装置の開発	第 6 回業績賞	日本赤外線学会
高本和也	時間分解分光法及び量子化学計算による 9-アリールカルバゾールの分子内電荷移動状態に対する溶媒効果	優秀発表賞	溶液化学研究会若手の会第 1 回冬季発表会
北原遥子、原茂生、櫻井敬博、大久保晋、太田仁、木村史子、木村恒久、那波和宏、岡本佳比古、廣井善二	$NaCuMoO_4(OH)$の磁場中配向試料によるテラヘルツ ESR 測定	第 7 回論文賞	日本赤外線学会
小路悠斗	連続波長可変テラヘルツ光源を用いた周波数掃引型反強磁性共鳴分光法の開発	ポスター賞	第八回西日本強磁場科学研究会
赤木暢	パルス強磁場を用いた電気磁気効果の研究	第 16 回(2022 年)日本物理学会若手奨励賞	日本物理学会
長澤直生	熱的検出による高圧下 ESR 測定手法の開発と応用	優秀発表賞	第三十回日本赤外線学会研究発表会
小路悠斗	連続波長可変テラヘルツ光源を用いた高分解能周波数領域電子スピン共鳴法の開発	極低温部門賞	若手フロンティア研究会 2021
小路悠斗	周波数掃引型テラヘルツ領域電子スピン共鳴分光法の開発	優秀発表賞	修士論文審査会
伊神早紀	Whispering gallery mode センシングデバイス開発に向けたディスク型共振器の作製	優秀発表賞	修士論文審査会

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
立川貴士	先端融合研究環 開拓プロジェクト「階層縦断的アプローチによる革新的光エネルギー変換系の開拓」最終シンポジウム		オンライン	2022.3.4	約 40 名
笠原俊二	日本分光学会関西支部講演会		オンライン	2022.3.2	30 名
富永圭介	第 2 回広帯域極限電磁波生命理工連携研究会「光線力学療法・光免疫療法の進展と光分子科学研究の展開」		オンライン	2022.3.16	55 名
太田仁 大久保晋 大道英二	ISMAR-APNMR2021	ISMAR-APNMR-NMRSJ-SEST2021 合同会議組織委員会 国際磁気共鳴学会 アジア太平洋核磁気共鳴学会 日本核磁気共鳴学会 電子スピンサイエンス学会	オンライン（大阪）	2021.8.22-27	920 人
太田仁 大久保晋	第 16 回量子スピン系研究会	分子フォトサイエンス研究センター	ハイブリッド（新温泉町立文化会館）	2021.12.17-18	95 人
川村光 太田仁 大久保晋	International Conference on Frustration, Topology, and Spin Textures	科学研究費補助金　基盤 S「フラストレーションを創るスピンテクスチャ」 代表者　川村光	ハイブリット（神戸国際会議場）	2021.12.22-23	180 人

Seminars セミナー

Date	Name	Affiliation	Title
2021.12.11	光元亨汰	分子フォトサイエンス研究センター	外的な乱れのない系におけるレプリカ対称性の破れ
2021.12.11	嵯峨慎	分子フォトサイエンス研究センター	金属錯体よもやま話

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