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海外特別研究員最終報告書

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(氏名は必ず自署すること)

海外特別研究員としての派遣期間を終了しましたので、下記のとおり報告いたします。

なお、下記及び別紙記載の内容については相違ありません。

記

1. 用務地（派遣先国名）用務地： ボルダー （国名：アメリカ合衆国、コロラド州）

2. 研究課題名（和文）※研究課題名は申請時のものと変わらないように記載すること。

高時空間分解能を持つ超高速走査型近接場赤外顕微鏡の開発

3. 派遣期間：平成 30 年 04 月 01 日 ～ 令和 02 年 03 月 31 日

4. 受入機関名及び部局名

Department of Physics, University of Colorado Boulder

5. 所期の目的の遂行状況及び成果…書式任意 **書式任意 (A4 判相当 3 ページ以上、英語で記入も可)**

(研究・調査実施状況及びその成果の発表・関係学会への参加状況等)

(注)「6. 研究発表」以降については様式 10－別紙 1～4 に記入の上、併せて提出すること。

JSPS Overseas Research Fellowship

Final Progress Report

Ultrafast Infrared Scanning Near-field Optical Microscopy with Extreme Spatial and Temporal Resolution

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1. Overview of the project

From energy materials to quantum materials, low-energy interactions and their ultrafast temporal evolution play major roles in defining their functionalities and properties. These materials also often exhibit spatial heterogeneity in their functional response at the unique length scale of nm – sub- μm . However, a link has been missing between such spatial heterogeneity and the fundamental low-energy processes, due to the difficulty to address the complex interplay among space, time, and the low-energy landscape in the materials.

As a JSPS Overseas Research Fellow from 2018-2020 and a postdoctoral fellow in Raschke group at University of Colorado Boulder, I tackled this outstanding problem from three different perspectives. First, using infrared vibrational nano-imaging that was already established in Raschke group, I revealed heterogeneous cation-lattice coupling in a photovoltaic film of a triple cation perovskite (Fig. 1A) [1: Nishida et al. ACS Energy Lett.]. Then I further developed heterodyne-detected ultrafast infrared nano-imaging system with spatio-temporal-spectral resolution (Fig. 1B) [2: Nishida et al. in preparation]. I applied this novel method to a triple cation perovskite film to directly probe the heterogeneity in the photoinduced processes, particularly with the focus on observing polaron absorption resonance and associated cation-polaron coupling (Fig. 1C) [3: Nishida et al. in preparation].

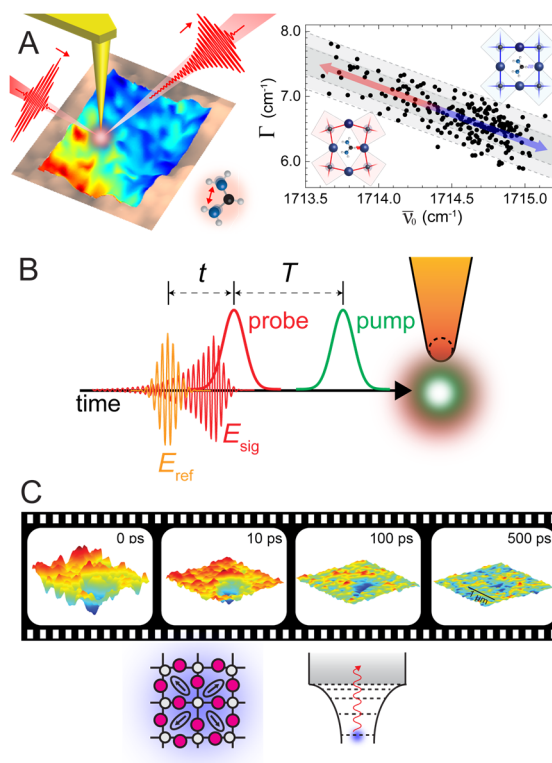


Fig. 1. A. Infrared vibrational nano-imaging on a triple cation perovskite. B. Ultrafast heterodyne-detected infrared nano-spectroscopy. C. Ultrafast imaging of polaron dynamics in a triple cation perovskite.

With these progresses combined, I established infrared vibrational nano-imaging and ultrafast infrared nano-spectroscopy as tools to unravel the elementary microscopic heterogeneity behind functional nonuniformity, such as optoelectronic response in photovoltaics. We will not only extend the applications of the techniques to study the low-energy response in a rich variety of energy and quantum materials and associated phenomena, but also will further push the limit of infrared nano-spectroscopy to single molecule detection regime by optimizing and refining the engineering of the sample platform and optical detection scheme.

2. Progress in each sub-project

I proposed four different sub-projects that I would work on as a JSPS Overseas Research Fellowship, based on infrared scattering scanning near-field optical microscopy (IR *s*-SNOM). In the following, I report progresses for each of the sub-projects.

A. Heterogeneity in lead halide perovskites

Extraordinary photovoltaic performance of lead halide perovskites is believed to arise from the low-energy liquid-like interactions among lattice ions and charge carriers. While spatial variations have been identified in the optoelectronic response of perovskites, the heterogeneity in the underlying fundamental low-energy processes has remained elusive. Using infrared vibrational nano-imaging, we identified the heterogeneity in cation-lattice coupling and its associated vibrational dynamics in a formamidinium-methylammonium-cesium triple cation perovskite film (Fig. 2A). The samples were offered in collaboration with Shaheen group at University of Colorado Boulder.

We sensitively detected and precisely characterized a molecular vibrational resonance arising from the CN anti-symmetric mode of the formamidinium cation (Fig. 2B). The spatial

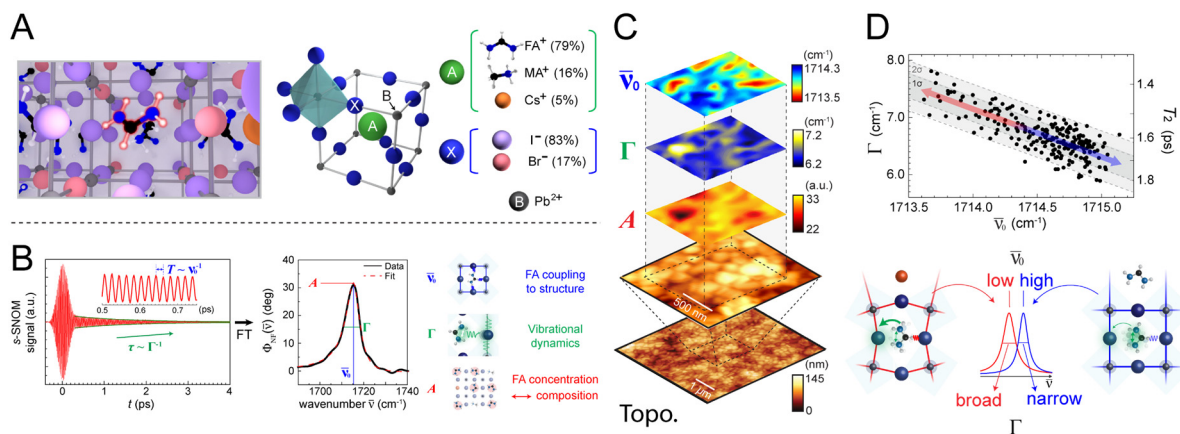


Fig. 2. Infrared vibrational nano-imaging on a triple cation perovskite. A. Triple cation perovskite. B. Nano-localized vibrational signal in time and frequency. C. Multivariate vibrational nano-imaging of the perovskite film. D. Peak position – line width anti-correlation, signifying correlated reaction field strength and vibrational damping rate that arises from heterogeneous lattice contraction.

variations in the peak area, peak position and line width were used as a local sensitive probe of molecular composition, cation-lattice coupling, and its associated vibrational dynamics (Fig. 2C). The anti-correlation between the peak position and line width signifies that the variation in the vibrational resonance stems from heterogeneous lattice contraction within the film, which can be caused by nonuniformity in cesium doping as suggested in recent theoretical studies (Fig. 2D).

The heterogeneity in the lattice contraction would imply, upon the injection of photoinduced carriers, lattices in different domains would contribute differently to polaron formation, where the lattice surrounding a charge dynamically reconfigures its structure to stabilize the carriers. Such disorder in polaron formation and dynamics would serve as a microscopic mechanism behind optoelectronic heterogeneity in perovskites. Ultrafast infrared nano-imaging, discussed below (sub-project B), aims to directly probe such polaronic heterogeneity at the transient state with the ultrafast time resolution.

B. Ultrafast heterodyne-detected infrared s-SNOM

The development of ultrafast infrared nano-imaging was the core project as seen from the title of the research proposal. Raschke group has previously demonstrated near-infrared pump/infrared-probe nano-imaging, where the scattered signal was directly detected at the intensity level, lacking phase and spectral resolution.

I implemented optical heterodyne detection to the ultrafast IR *s*-SNOM nano-imaging system (Fig. 3A), thereby achieving spatio-temporal-spectral resolution. By modulating the pump intensity and operating the AFM in the tapping mode, we detect the signal component that is both dependent on the pump modulation and AFM tapping frequency, allowing us to sensitively detect

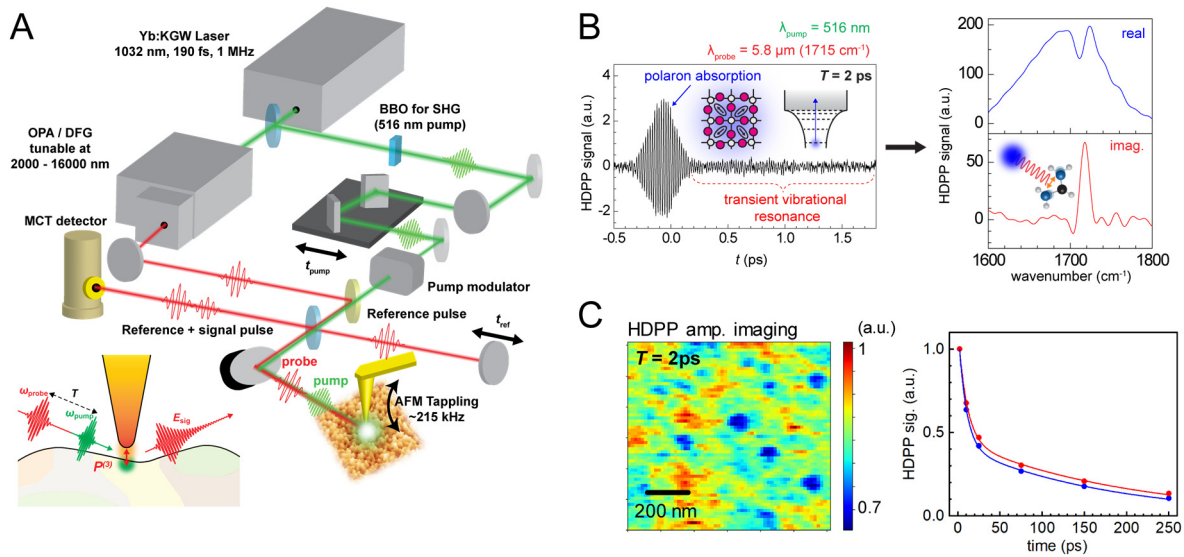


Fig. 3. A. Experimental setup for heterodyne-detected pump-probe IR *s*-SNOM. B. Pump-probe interferogram in time-domain and resulting Fourier transform in frequency-domain. C. Ultrafast mapping with heterodyne-detected pump-probe signal. Different locations exhibit different relaxation time.

the pump-probe signal of the near-field origin in a background-free manner. By further scanning the timing of the reference pulse relative to the signal field, we acquire pump-probe interferogram, the Fourier transform of which gives rise to frequency and phase resolved nano-localized pump-probe signal.

Fig. 3B shows such a nano-localized pump-probe interferogram acquired for a triple cation perovskite, and its Fourier transform. In the transient pump-probe response, we observed transient molecular vibrational resonance with <100 nm resolution as a lasting coherence. Acquiring such transient vibrational signal with high spatial resolution has been an outstanding challenge in the field of ultrafast vibrational spectroscopy. We currently evaluate how the transient vibrational signal could be potentially affected by the scattering process from the gold tip apex, as well as trying to evaluate the heterogeneity in such transient vibrational resonance in relation to cation-polaron coupling.

We found a large heterodyne-detected pump-probe signal when the mid-infrared spectrum is tuned to $\sim 1200\text{ cm}^{-1}$, where polaron absorption has been recently reported by others (K. Munson et al. *Chem* 2018, 4 2826). The large signal allows us to acquire the time-dependent image of the heterodyne-detected pump-probe signal (Fig. 3C), suggesting the heterogeneity both in polaron formation and dynamics. The nonuniformity in such dynamic property of polaron likely accounts for the heterogeneity in optoelectronic response of perovskites, which have been intensely studied in recent years.

C. Pushing the limit of IR *s*-SNOM: single molecule vibrational spectroscopy

The detection of a molecular vibrational signal from a single molecule could lead to a variety of applications in chemistry and biochemistry, such as real-time *in situ* observations of chemical reactions and protein folding.

The spectroscopy by IR *s*-SNOM offers both enhancement and high degree of localization of the infrared field, potentially leading to a platform to achieve single molecule vibrational spectroscopy. We applied IR *s*-SNOM to a monolayer functionalized with a metal carbonyl head group, which has a large transition dipole moment at the mid-infrared. Fig. 4A shows the IR *s*-SNOM signal measured for such a monolayer. Based on the tip radius (~ 20 nm), we estimate the signal arises from ~ 400 of vibrational oscillators. However, the signal-to-noise level is clearly not sufficient to detect a single vibrational signal.

Our group has recently demonstrated that the detection of a vibrational signal from a thin layer of a polymer is facilitated when the polymer coated on a mid-infrared nano-antenna. This is enabled by Purcell enhancement, particularly in combination with the further field enhancement offered by the metallic tip [4]. Extending this approach, we coated the metal carbonyl monolayer, in collaboration with Altug group at EPFL, on a nano-fabricated mid-infrared gold antenna to offer another degree of field enhancement, and then bring the tip to the antenna terminal where the field enhancement is the largest (Fig. 4B). Owing to the coupling between the molecular vibration and the antenna mode, the vibrational signal amplitude is significantly enhanced (Fig. 4C). With this

signal-to-noise ratio, we estimate that we can reduce the density of head groups to ~ 10 s of molecules per tip volume and still observe sufficient signal above noise level. However, a careful attention needs to be paid on the origin of the vibrational signal for such a geometry – does the signal only arise from the tip apex, or as the molecular vibration hybridizes with the antenna mode, do the molecules all around the antenna contribute to the observed signal? These are indeed intriguing problems, and we will address this in our future experimental and theoretical studies.

While it remains difficult to detect a single vibrational oscillator, acquiring a signal from a single protein appears more promising. A single protein typically consists of hundreds of amino acids, each of which contains one C=O carbonyl group as a strong infrared oscillator. In collaboration with Perkins group at University of Colorado Boulder, we prepared a monolayer of proteins and acquired a good signal arising from amide-I mode of the protein (Fig. 4D). We are now optimizing the sample preparation so that one protein would appear in the tip excitation volume. The detection of vibrational signal from a single protein based on ultrafast infrared pulse, if achieved, will lead to a completely new avenue of protein physics and chemistry, as well as nonlinear infrared spectroscopy at the single molecule regime.

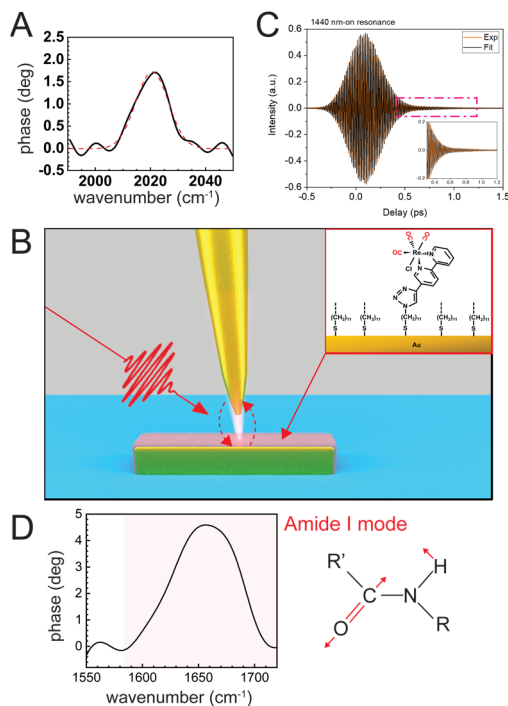


Fig. 4. A. The vibrational infrared *s*-SNOM signal, arising from ~ 400 of vibrational oscillators. B. Antenna-coupled monolayer system. C. Vibrational FID acquired at the terminal at the vibration-antenna coupled system. Following nonresonant center burst, a long lasting coherence from the molecular vibration is evident. D. The amide-I vibrational mode acquired on a protein monolayer. Figure courtesy of B. Dr. Daehan Yoo, C. Liang-Chun Lin.

D. Two-dimensional infrared nano-spectroscopy

Two-dimensional spectroscopy has been successful in tracking the ultrafast motion of molecules in a variety of condensed phase systems, as well as unraveling couplings among different degrees of freedom. While I set an ambitious goal of implementing two-dimensional infrared nano-spectroscopy, it so far has appeared difficult to realize this in any realistic, meaningful and useful manner. The demonstration of the ultrafast heterodyne-detected infrared *s*-SNOM (sub-project B) does suggest that such a spectroscopy is in principle possible. However, extending this to two-dimensional spectroscopy will require scanning another timing axis, which would cost enormous data acquisition time. Fortunately, a recent technological development in dual-comb and resonant-scanner-based spectroscopy could be combined with the IR *s*-SNOM to facilitate the data acquisition, which is discussed below.

3. Future perspective

Vibrational nano-imaging of perovskites will be further extended to study other outstanding and intriguing phenomena, such as photoinduced ion migration in mixed anion perovskites and disorder in two-dimensional perovskites.

To achieve the goal of the *single molecule vibrational spectroscopy*, we will further refine the protein sample preparation and characterization to set up an ideal platform to detect a single protein vibrational signal. To detect a *single vibrational oscillator*, further efforts need to be implemented in terms of the design principle of the nano-phonic structures that can further enhance the vibrational signal, as well as seeking a different optical process which could potentially enhance the detection.

Now that *ultrafast heterodyne-detected infrared s-SNOM* is successfully implemented, we will not only apply this technique to different types of perovskites, but extend this technique to a variety of material systems. While this could be equally well applied to different energy materials such as organic heterojunction photovoltaics, the method should be a powerful tool to elucidate the complex nonlinear interaction and response in quantum materials, ranging from optically-induced superconductor and exciton-phonon coupling in two-dimensional materials.

The implementation of *two-dimensional nano-spectroscopy* will require major refinement in the manner IR *s*-SNOM signal is acquired. Currently, the scattered nano-localized infrared signal is acquired by operating the AFM in a tapping mode and detecting a signal component that is modulated by the harmonics of the tapping frequency, using a lock-in amplifier. Such a data acquisition modality is not compatible with the fast scanning method such as dual-comb and resonant-scanner methods, which could facilitate the acquisition of 2D nano-spectra in time domain. Thus I believe it is important to develop a new scheme of IR *s*-SNOM data acquisition, where the IR signal is continuously recorded in real-time together with the tip motion and pulse timings, followed by the reconstruction of the *s*-SNOM interferogram.

4. Progress summary

| Project | Status | Summary and Perspective |
|--|-------------------|---|
| Heterogeneity in perovskites | Published | <ul style="list-style-type: none">- Using infrared vibrational nano-imaging, we successfully revealed heterogeneity in fundamental cation-lattice interaction and dynamics in a triple cation perovskite.- We will apply this to other perovskite systems and intriguing phenomena. |
| Ultrafast heterodyne-detected infrared nano-spectroscopy | In major progress | <ul style="list-style-type: none">- We successfully implemented and demonstrated ultrafast heterodyne-detected infrared nano-imaging with spatio-temporal-spectral resolution.- We applied this to a triple cation perovskite and demonstrated transient vibrational nano-spectroscopy.- We mapped the ultrafast time-dependent heterogeneity in the nano-localized pump-probe signal, which might be associated with polaron formation and its dynamics. |
| Single molecule | In progress | <ul style="list-style-type: none">- Signal arising from ~400 oscillators is sensitively detected.- Further refined antenna design or fundamentally new optical process is necessary to detect a vibrational signal from a single oscillator. |

| | | |
|--------------------------|------------------|--|
| vibrational spectroscopy | | - Detection of a vibrational signal from a single protein, consisting of hundreds of C=O oscillators, appears more promising. |
| 2D IR nano-spectroscopy | Limited progress | - The implementation of the ultrafast heterodyne-detected infrared nano-spectroscopy is the first step to achieve the two-dimensional nano-spectroscopy. - A major refinement is necessary in the manner with which nano-localized infrared signal is induced and detected. |

5. Publications

- [1] Nishida, J.; Alfai, A. H.; Gray, T. P.; Shaheen, S. E.; Raschke, M. B. *ACS Energy Lett.* **2020**, 5, 1636.
- [2] Nishida, J.; Dönges, S. A.; Chang, P. T. S.; Khatib, O.; Alfai, A. H.; Ye J.; Shaheen, S. E.; Raschke, M. B., *in preparation*
- [3] Nishida, J.; Chang, P. T. S.; Johnson, S. C.; Ye, J.; Shaheen, S. E.; Raschke, M. B., *in preparation*
- [4] Metzger, B.; Muller, E.; Nishida, J.; Pollard, B.; Hentschel, M.; Raschke, M. B., *Phys. Rev. Lett.*, **2019**, 123, 153001.

6. Acknowledgement

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