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Performance Evaluation of Infrared Microspectroscopy Station Using Human Hair

Y. Ikemoto[1] and T. Moriwaki[1]

[1]*Spectroscopy Divison, Japan Synchrotron Radiation Research Institute, Sayo, Hyogo 679-5198, Japan*

At infrared beamline BL43IR in SPring-8, microspectroscopy experiments under various sample environments have been conducted and many results have been published. Currently, SPring-8 upgrade plan is ongoing. After the upgrade, it will be difficult to obtain infrared beam due to a ring design. Therefore, it has been decided that BL43IR will be shut down in FY2025.

On the other hand, there is a high demand for research using infrared synchrotron radiation. On September 20, 2023, we held the UVSOR/SPring-8 Infrared Beamline Joint Users' Meeting, where we introduced the UVSOR infrared beamline BL6B to users of BL43IR/SPring-8. BL6B has maintained high performance of light source through facility upgrades. It was decided to start preparations for the transfer of SPring-8/BL43IR activities to BL6B at UVSOR. For the transfer, we must identify the necessary equipment to conduct experiments equivalent to those being conducted at BL43IR. In this proposal, human hair samples were measured, which have been measured at BL43IR as test samples to evaluate the spatial resolution and signal-to-noise ratio.

The sliced hair sample was put on a BaF_2 substrate (10 mm diameter, 1mm thickness) and placed on a sample stage of an infrared microscope (JASCO FT/IR-6100, IRT-7000) installed at BL6B. The absorption spectrum and its imaging were measured in the transmission configuration. The hair should be thin enough to prevent saturation of the absorption peak, which is known to be around 10 μm based on our experience, and we bring samples prepared to the appropriate thickness. The magnification of the objective mirror was x32. All measurements were performed at room temperature. Wavenumber resolution was 4 cm^{-1} and the wavenumber range is 8000-700 cm^{-1}, and a Ge/KBr beam splitter is used.

The following parameters will be varied to obtain a comparison data.

- Light source: standard light source inside the instrument, synchrotron radiation (SR)
- Measurement mode: imaging measurement using linear array detector, multi-point measurement using single element detector

In addition, a sliced hair sample were measured at the micorospectoroscopy station (BRUKER VERTEX70 and HYPERION2000) in BL43IR/SPring-8 for comparison. Wavenumber resolution, wavenumber range and beam splitter were the same as those in BL6B. Result are shown in Fig. 1. All data are mapping image, in which integrated C-H stretching band (2805 – 3141 cm^{-1}) intensity is plotted. The white bars in the figure correspond 20 μm. The samples are not exactly same but prepared at same condition and the thickness is almost same. Figure 1 (a) was measured at BL6B with standard light and 125 μm x 15 μm aperture. The detector was a linear array MCT detector. Figure 1 (b) was a result of BL6B with SR and 4 μm x 4 μm aperture. The detector was a single MCT element detector. Figure 1 (c) was measured at BL6B with SR and 125 μm x 15 μm aperture. The detector was a linear array MCT detector. Figure 1 (d) was measured at BL43IR/SPring-8 using SR with an aperture 5 μm x 5 μm. The detector was a single MCT element detector. Measurement times were 140 min, 220 min, 13min and 13 min for Fig. 1. (a) to (d), respectively. All image has lipid area called cortices are observed in the center. The size of the cortex is about 5 μm, and spatial resolutions are found to be smaller than that. In Fig. 1. (c), un-uniformity is observed, which is caused by non-uniform exposure of light to the array elements. It means that the SR spot is too small to the array detector. Measurement time is very short when array detectors are used. We propose a method at BL6B to measure a large number of samples with an array detector + standard light source, and to measure important samples over time with a single detector + SR. We will examine devices to control the sample environment such as humidification and temperature, and make preparations so that many users can continue their research at BL6B.

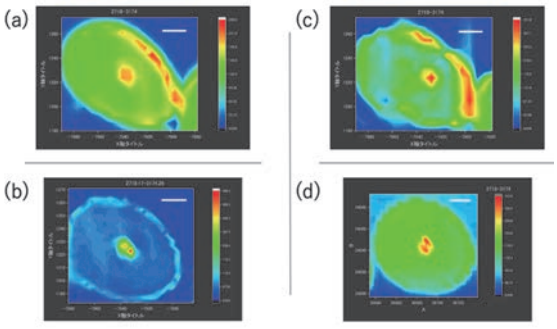

Fig. 1. CH absorption band intensity map of slice hair sample.

Infrared Absorption Measurements on Single Crystals and Amorphous Thin-Films of Rubrene

Y. Nakayama[1,2], R. Sakata[1] and Y. Baba[1]
[1]*Department of Pure and Applied Chemistry, Tokyo University of Science, Noda 278-8510, Japan*
[2]*Institute for Molecular Science, Okazaki 444-8585, Japan*

Rubrene (Fig. 1 inset) is a representative p-type organic semiconductor molecule exhibiting considerable charge carrier mobility over 10 cm^2/Vs [1] and widely dispersing intermolecular electronic bands [2] in its single-crystal (SC) phase. One peculiar character of this material is that charge carrier mobilities, crystallographic structures, and ionization energies of its vacuum-deposited thin-films (TFs) differ greatly from those of its SCs [3]. Such changes in structural and electronic properties may lead to changes in vibronic characteristics in its solid-state phases via inequivalent intermolecular interactions. In this work, infrared absorption measurements were performed on SCs and amorphous TFs of rubrene trying to compare intra-molecular vibrations depending on inter-molecular aggregation manners.

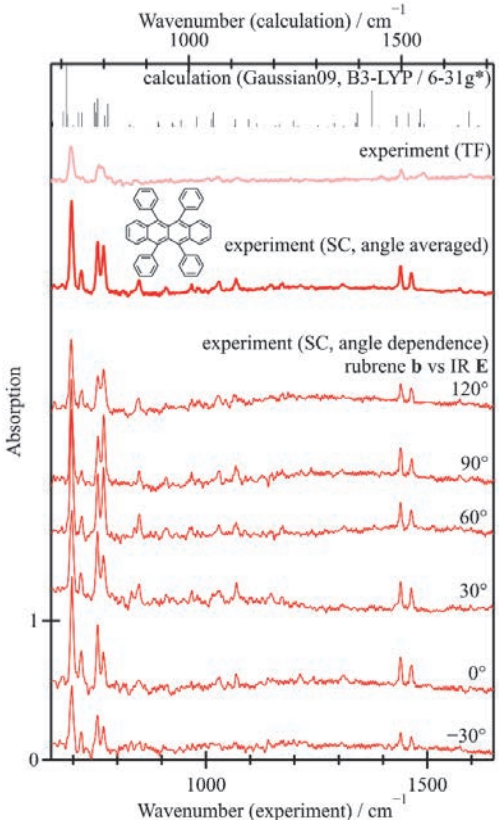

Fig. 1. Quantum chemical calculation results (black) and IR absorption spectra of an amorphous TF (pink) and SC (red) of rubrene. The bottom six curves are spectra of SC depending on orientations of the crystal principal axis **b** of rubrene to the IR **E**. The calculated wavenumber is scaled by a factor 0.9613 [5].

Rubrene SCs were produced by a horizontal physical vapor transport technique and were electrostatically fixed on polycrystalline diamond substrates. TFs of rubrene were prepared by vacuum deposition of thicknesses up to 5 μm on the polycrystalline diamond plates and were afterward taken out of the vacuum. FT-IR measurements were performed at BL6B, UVSOR. Experimental details were described previously [4].

Figure 1 shows IR absorption spectra of a TF and SC of rubrene with quantum chemical calculation results on a single rubrene molecule. While the former was much weaker than the latter due to insufficient film thickness, the peak positions were overall consistent with each other. The peak intensities of SC, especially in a low wavenumber range, clearly exhibited dependence on the in-plane orientation of the sample presumably by variations in relations between transition dipoles **μ** and the IR electric field **E** [4]. Closed-up spectra (Fig. 2) revealed that the IR absorption wavenumbers are mostly unchanged independent of the solid-state phases. Peak broadening for TFs may be caused by diverse inter-molecular conditions, whereas the emergence of peaks derived by $\boldsymbol{\mu}\cdot\mathbf{E} \approx 0$ modes for SC (#66 and #73) cannot be ruled out as possible causes of the broadening at this stage.

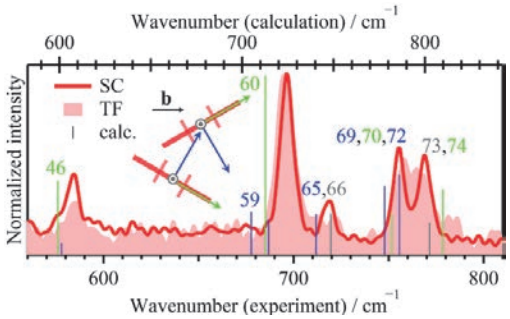

Fig. 2. Experimental and calculation results shown in extended wavenumber scales. The latter are displayed with different colors by its **μ** directions (see inset).

[1] J. Takeya, *et al.*, Appl. Phys. Lett. **90** (2007) 102120.
[2] S. Machida *et al.*, Phys. Rev. Lett. **104** (2010) 156401.
[3] Y. Nakayama, *et al.*, Appl. Phys. Lett. **93** (2008) 173305.
[4] Y. Nakayama, *et al.*, Vib. Spectrosc. **132** (2024) 103681; *idem*, Jpn. J. Appl. Phys. **63** (2024) 09SP07.
[5] J. P. Merrick, *et al.*, J. Phys. Chem. A **111** (2007) 116803.

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Probing Molecular Vibration Dynamics of Layered Borophene Oxide Thin Films using *In-Situ* Variable-Temperature Infrared Spectroscopy

K. Kaminaga[1], K. Sasaki[1], H. Murakami[1], F. Teshima[2], A Kikuchi[1], K. Tanaka[2], S. Maruyama[1] and Y. Matsumoto[1]

[1]*Department of Applied Chemistry, Tohoku University, Sendai 980-8579, Japan*

[2]*Institute for Molecular Science (IMS), National Institutes of Natural Sciences, 38 Nishigonaka, Myodaiji, Okazaki 444-8585, Japan*

Liquid crystals represent a distinctive mesophase exhibiting properties characteristic of both fluids and crystalline solids, and they are well-established as functional materials in electronic display technologies. While the field has historically been dominated by organic compounds due to their molecular flexibility, the synthesis of inorganic liquid crystals has proven challenging, largely attributed to the rigidity inherent in inorganic bonding. Nevertheless, the development of stable inorganic liquid crystals holds significant promise for applications in extreme environments where organic materials often prove inadequate.

A key advancement occurred in 2022 with the report of layered borophene oxide (BoL), synthesized from potassium borohydride (KBH_4) [1]. This material undergoes a structural phase transition to a liquid crystalline state at approximately 120°C, a process associated with dehydration reactions [2]. Notably, this liquid crystalline phase can be rendered metastable at ambient temperature through supercooling. Recognizing the potential for semiconductor applications, our research group has developed a vapor-phase synthesis protocol for BoL thin films using infrared laser deposition. This method involves the selective oxidation of KBH_4 precursor molecules, catalyzed by acetonitrile vapor under vacuum conditions (Fig.1 inset).

Previous infrared spectroscopic studies on bulk BoL characterized the modulation of O-H and B-O vibrational modes during the transition between crystalline and liquid crystalline phases [2]. However, despite X-ray diffraction analyses confirming the reversibility of this phase transition in thin films, the specific molecular-level structural alterations occurring within these films remain insufficiently understood.

To address this gap, the present investigation utilized temperature-variable Fourier-transform infrared (FT-IR) spectroscopy to analyze BoL thin films deposited on double side polished Si substrates. FT-IR spectroscopy was performed with a FT-IR microscope (JASCO, IRT-7000) at beamline BL6B. Infrared radiation was directed through a Michelson-type interferometer (JASCO, FT/IR-6100). The measurements were conducted in a reflectance configuration, with the incident IR beam aligned perpendicular to the surfaces of samples. To mitigate atmospheric interference, the IR absorbance spectra were derived by normalizing the reflectance spectra of the KBH_4 samples against that of a gold (Au) film. Measurements performed under atmospheric conditions successfully detected the characteristic B-O (~1500 cm^{-1}) and O-H (~3000 cm^{-1}) vibrational modes, thereby confirming the successful synthesis of the target thin films (Fig.1). On the other hand, attempts to perform measurements under vacuum were hindered by instrumental difficulties related to optical alignment.

In conclusion, future experimental work will focus on implementing refined optical axis calibration procedures to enable reliable vacuum-environment FT-IR measurements. This refinement is crucial for facilitating comprehensive in-situ observation of the temperature-dependent phase transition, free from atmospheric interference. Such optimized methodology will permit a systematic vibrational spectroscopic analysis of the structural reversibility between the crystalline and liquid crystalline phases at the molecular level.

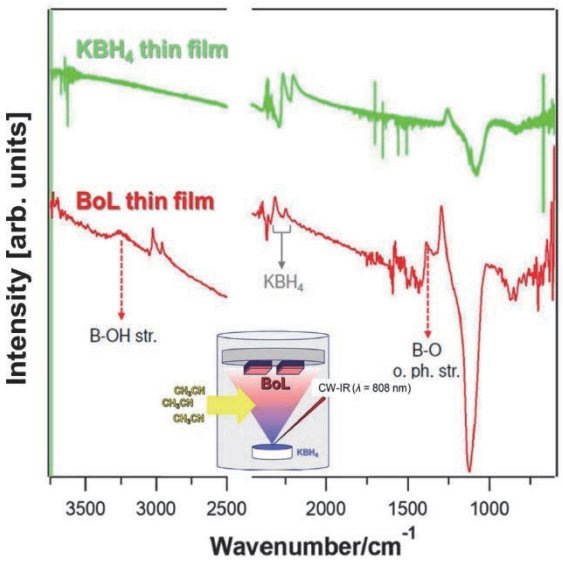

Fig. 1. IR spectra of KBH_4 thin film (green) and BoL thin film (red) under atmospheric conditions. Inset: Schematic of the experimental setup for BoL thin film growth.

[1] T. Kambe *et al*., J. Am. Chem. Soc. **141** (2019) 12984.
[2] T. Kambe *et al*., Nat Commun. **13** (2022) 1037.