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OMICS Group International is a pioneer and leading science event organizer, which publishes around 400 open access journals and conducts over 300 Medical, Clinical, Engineering, Life Sciences, Pharma scientific conferences all over the globe annually with the support of more than 1000 scientific associations and 30,000 editorial board members and 3.5 million followers to its credit.

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# Higher order structure of macromolecules studied by Terahertz spectroscopy

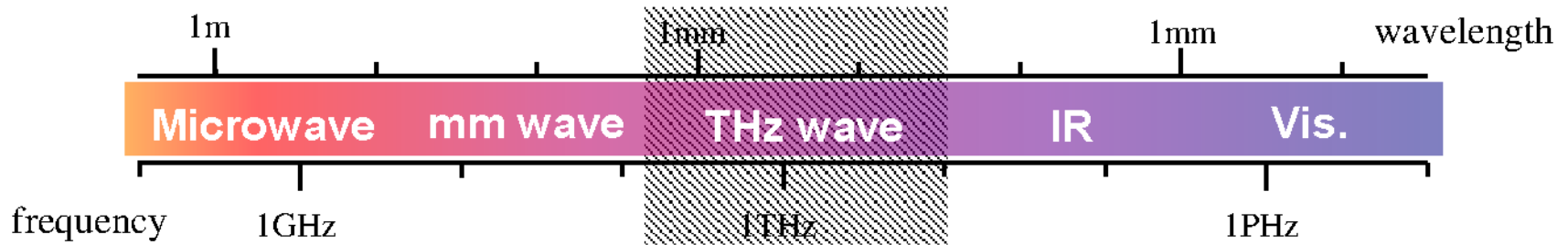
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Hirromichi Hoshina

RIKEN



# Spectroscopy in Terahertz (THz) Frequencies



$$1\text{THz} \sim 1\text{ps} \sim 300\mu\text{m} \sim 33.3\text{cm}^{-1} \sim 48\text{K} \sim 4.1\text{meV}$$

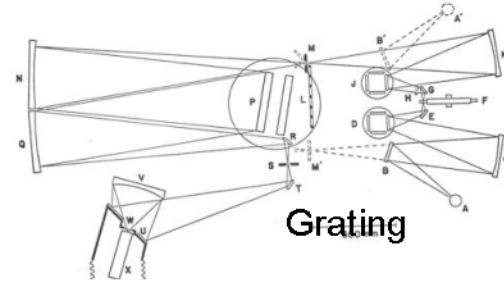
	gas	liquid	solid
Origin of absorption spectrum	<u>Molecular rotation</u> $E = BJ(J+1)$	<u>Rotational relaxation</u> $\epsilon(\omega) = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{1 + i\omega\tau_D}$ (Debye Model)	<u>Intermolecular vibration</u> <u>Phonon</u> $E = \left(v + \frac{1}{2}\right)\hbar\omega_0$
		<u>Intermolecular vibration</u> <u>Libration</u> $E = \left(v + \frac{1}{2}\right)\hbar\omega_0$	<u>Carrier mobility</u> $\epsilon(\omega) = \epsilon_0 + \frac{i\sigma_0}{\omega(1 - i\omega\tau)}$ (Drude model)
Research Targets	Interstellar molecules Atmospheric molecules Sensing of toxic gases	Water Organic solvents Amorphous polymers	Organic crystals Biomolecules Semiconductors

# Development of THz Spectroscopy

1950

Far Infrared Spectrometer

1960



1970

hours

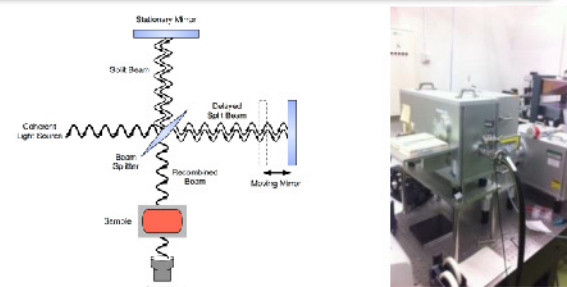
Simple Spectroscopy

1980

FT-IR



1990



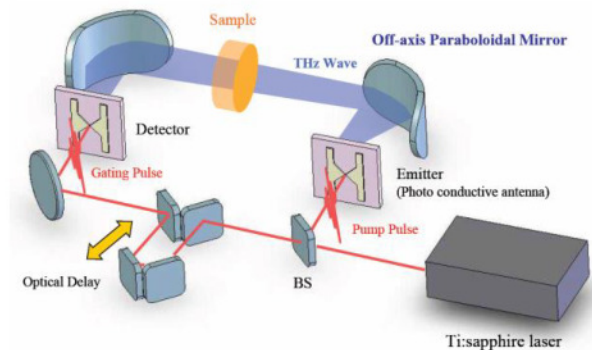
minutes

2000

THz-TDS



2010

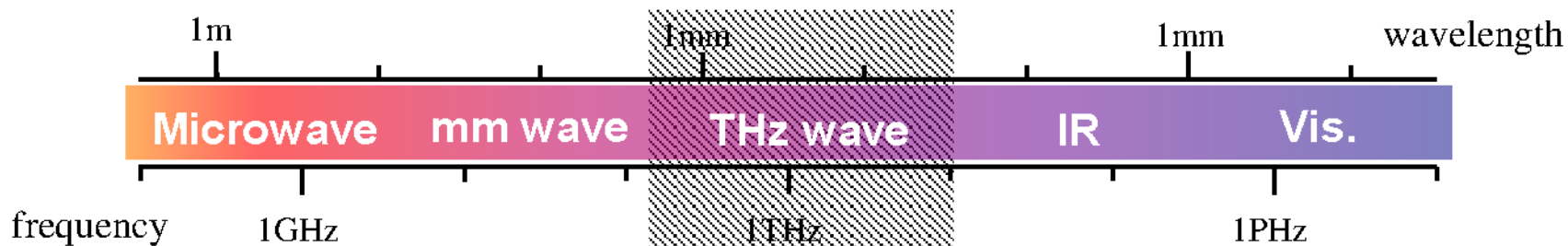


seconds

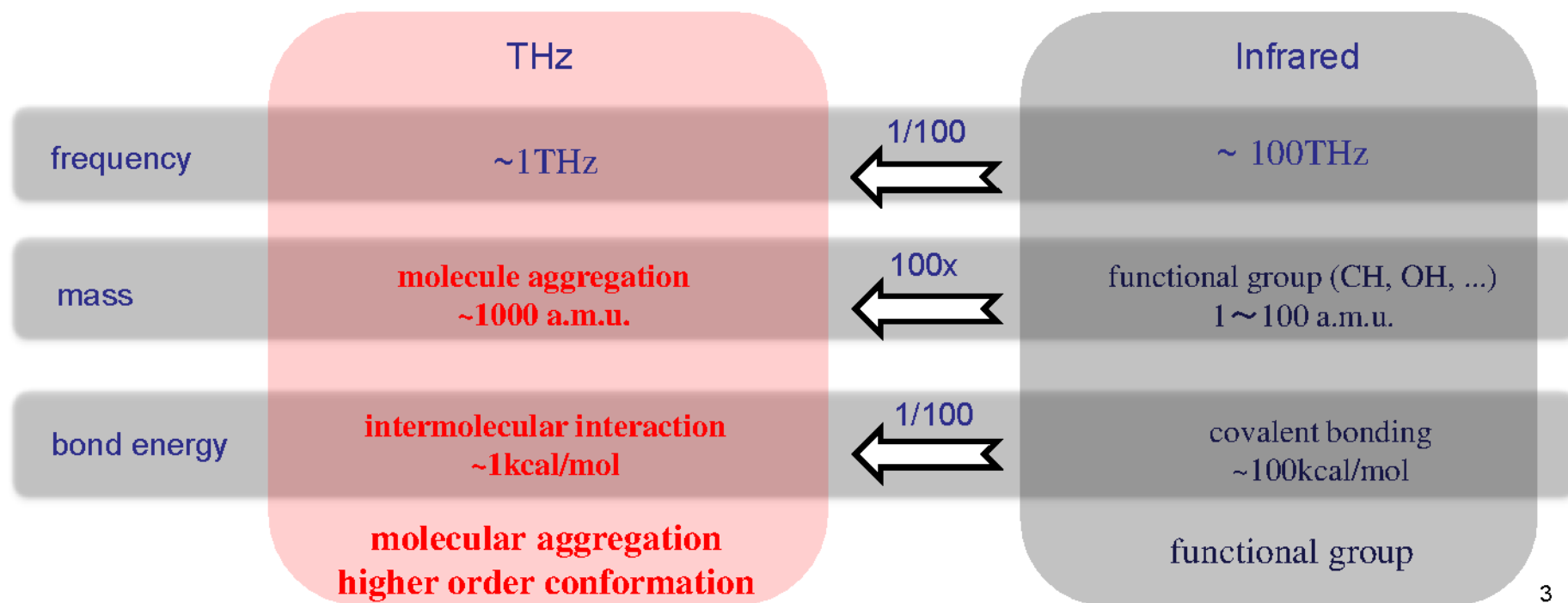
2020

Temperature Dependence  
Temporal Change  
Pump-Probe Spectroscopy  
Spectroscopic Imaging  
etc...

# THz vibrational spectroscopy

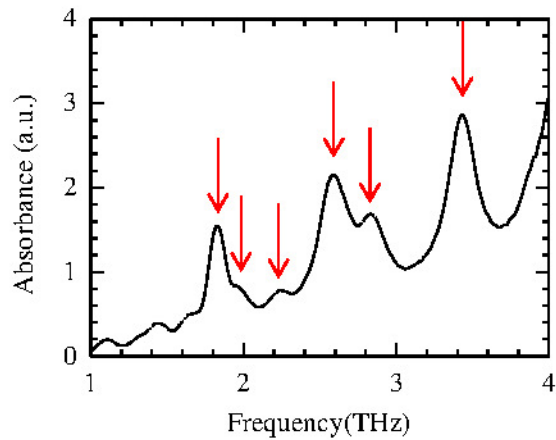


vibrational frequency  $f = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$       k: force constant  
 $\mu$ : reduced mass

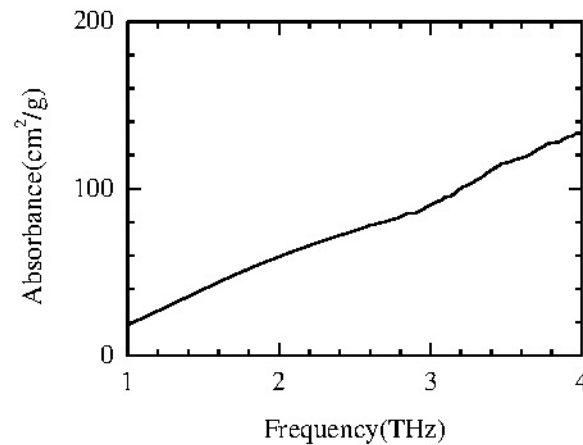


# THz absorption spectra of crystal / glass sucrose

Sugar (Sucrose)  
crystal



Cotton Candy (Sucrose)  
glass

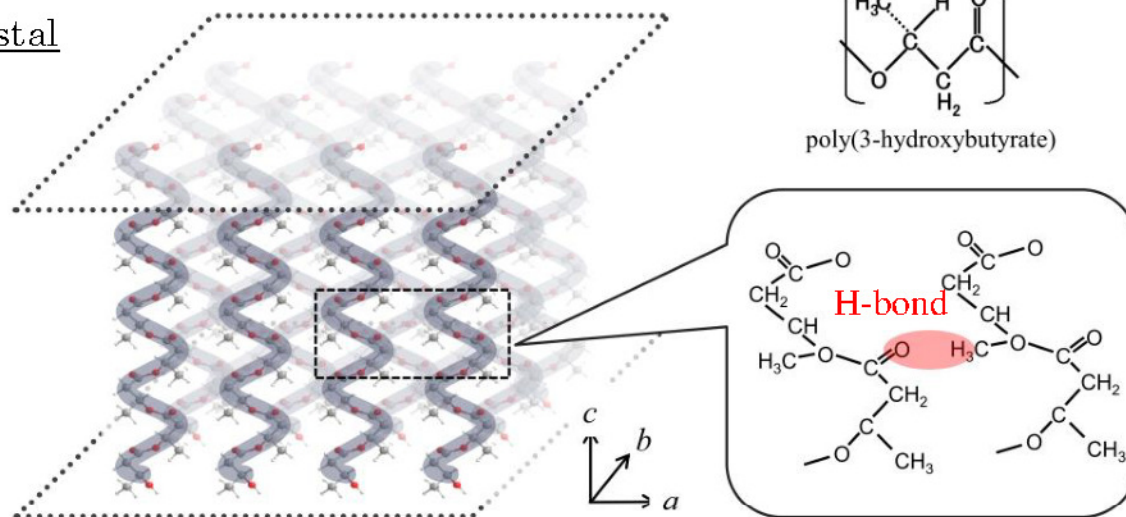


Hoshina et al. 2010

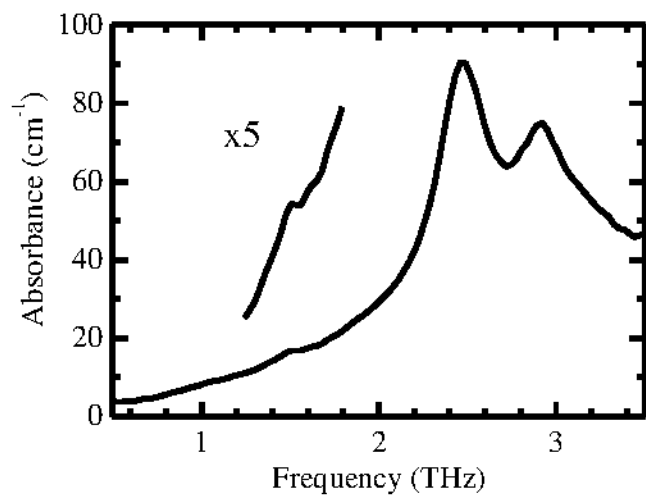
# poly(3-hydroxybutyrate) (PHB)

Hoshina et al. Appl. Phys. Lett. **96**, 101904 (2010)  
Hoshina et al. PCCP, **13**, 9173 (2011)

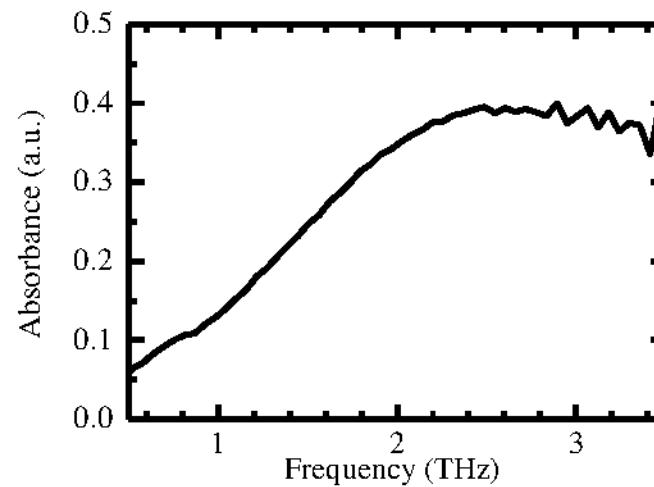
Lamellar crystal



Crystalline PHB



Amorphous PHB

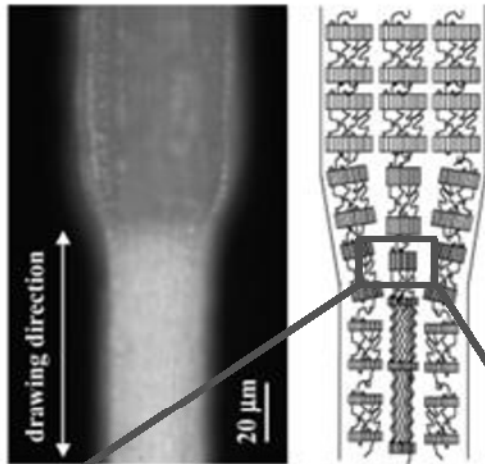




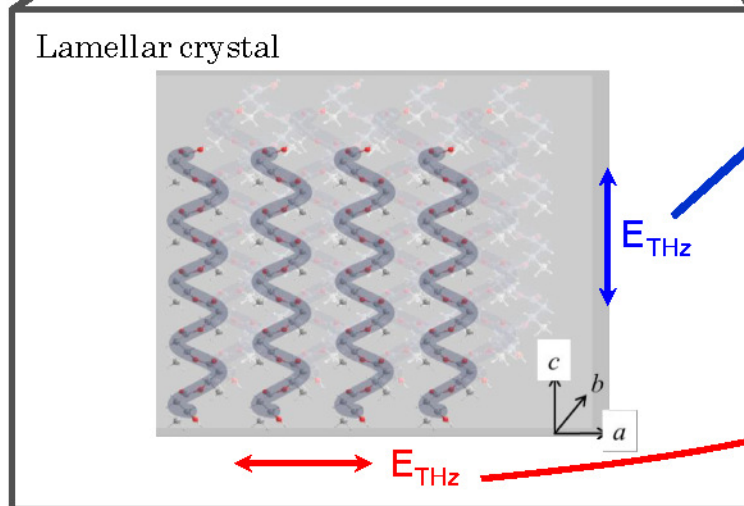
# THz polarization spectroscopy

Hoshina et al. Appl. Phys. Lett. **96**, 101904 (2010)  
Hoshina et al. PCCP, **13**, 9173 (2011)

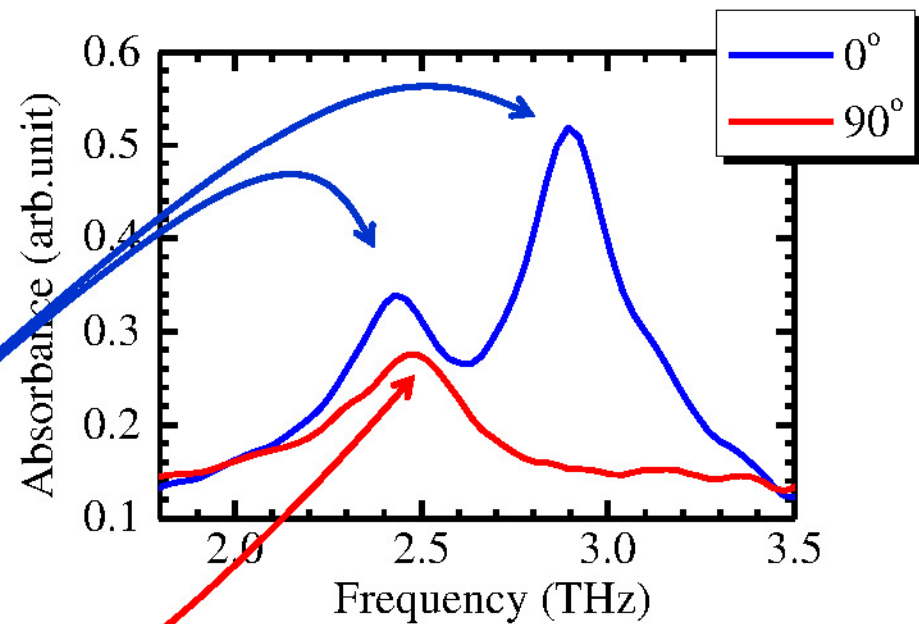
## Stretched sample



(Macromolecules **2006**, 39, 5789-5795)



Vibration along helix structure  
→ skeletal vibration (spring motion?)



Vibration between helix structure  
→ due to hydrogen bonding

# Calculation based on DFT

Yamamoto et al. J. Phys. Chem. B, 117, 2180 (2013)

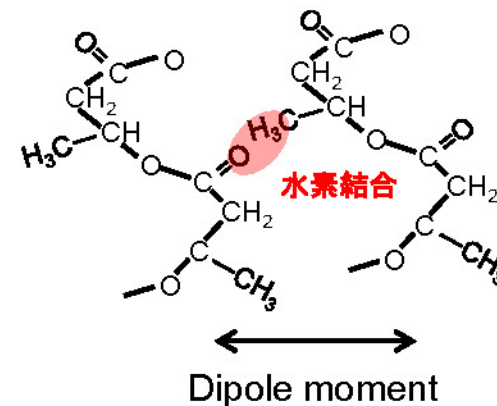
THE JOURNAL OF  
PHYSICAL CHEMISTRY B

Article  
pubs.acs.org/JPCB

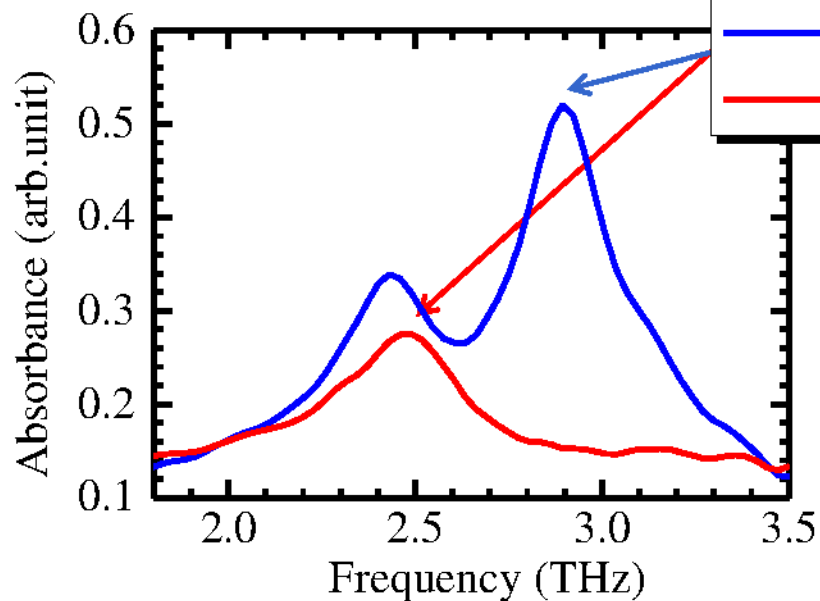
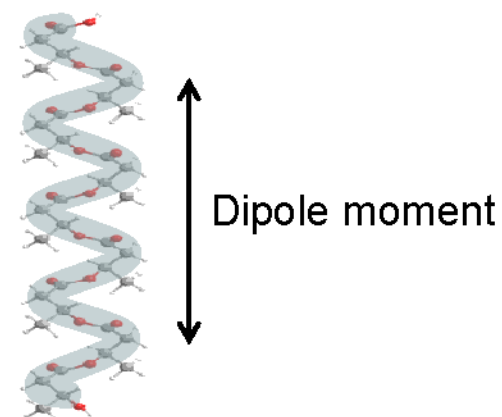
## Quantum Mechanical Interpretation of Intermolecular Vibrational Modes of Crystalline Poly-(R)-3-Hydroxybutyrate Observed in Low-Frequency Raman and Terahertz Spectra

Shigeki Yamamoto,<sup>\*,†</sup> Yusuke Morisawa,<sup>‡</sup> Harumi Sato,<sup>†</sup> Hiromichi Hoshina,<sup>§</sup> and Yukihiro Ozaki<sup>\*,†</sup>

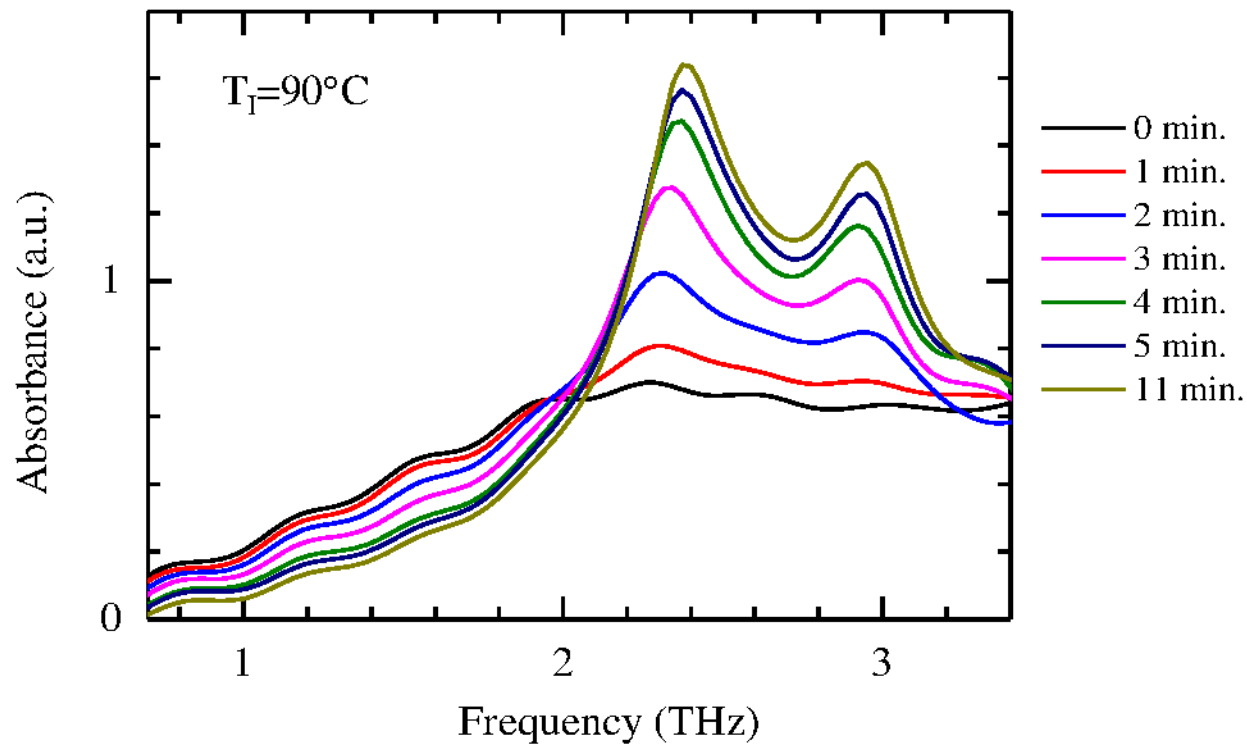
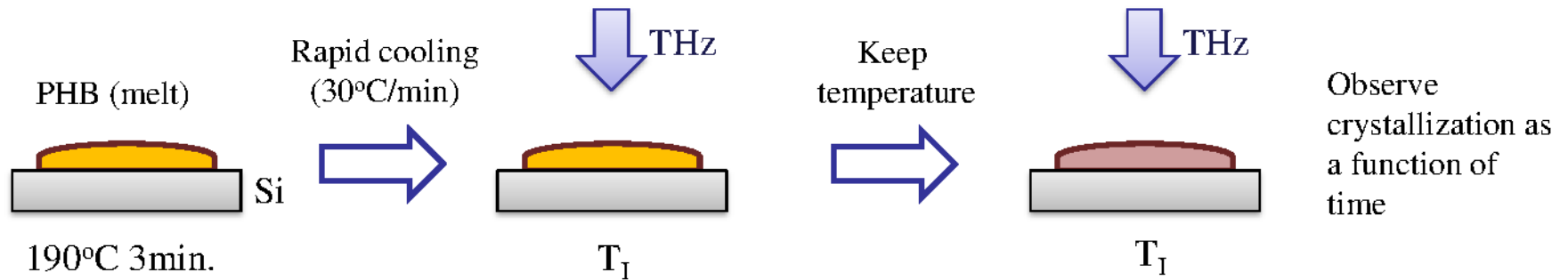
(a) C=O o.o.p. + CH<sub>3</sub> (2.2 THz)



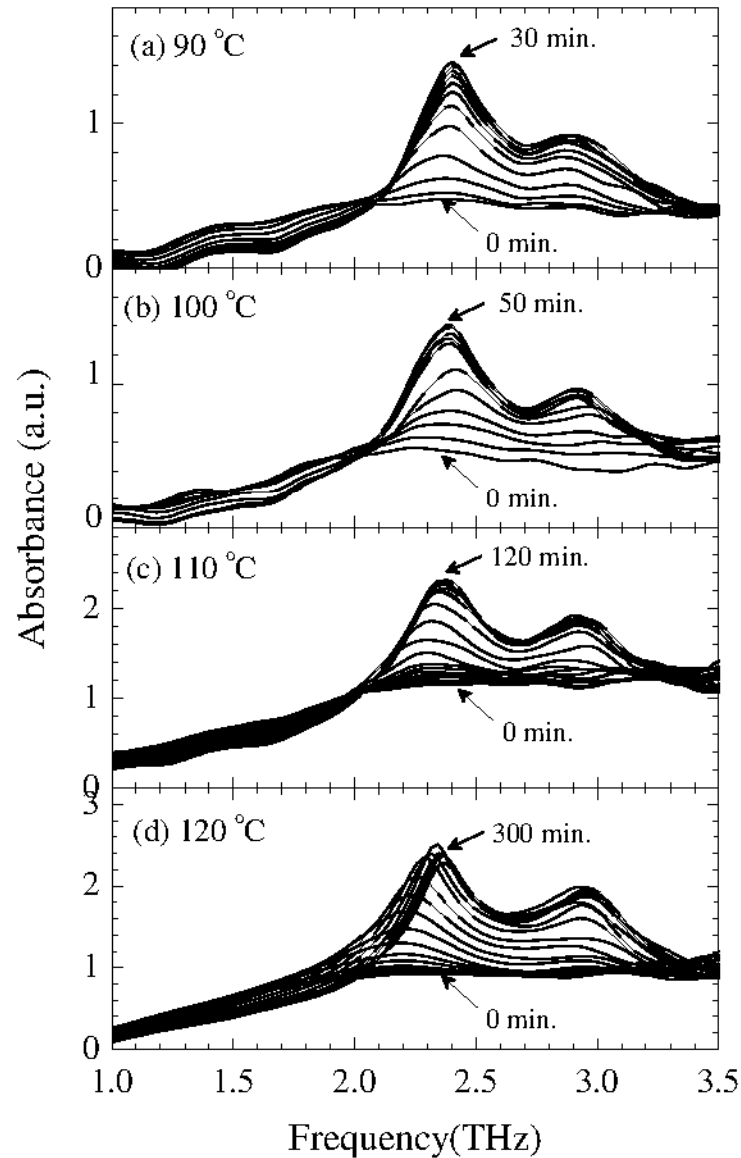
(b) CH<sub>2</sub>+CH<sub>3</sub> (2.7 THz)



# Isothermal crystallization

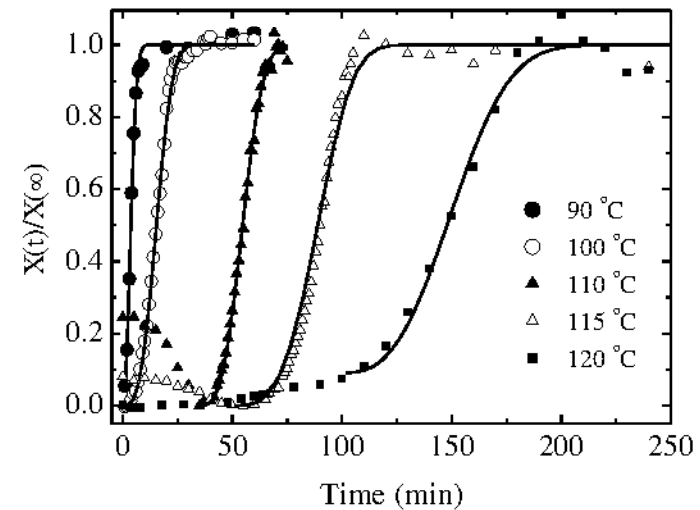


# Isothermal crystallization



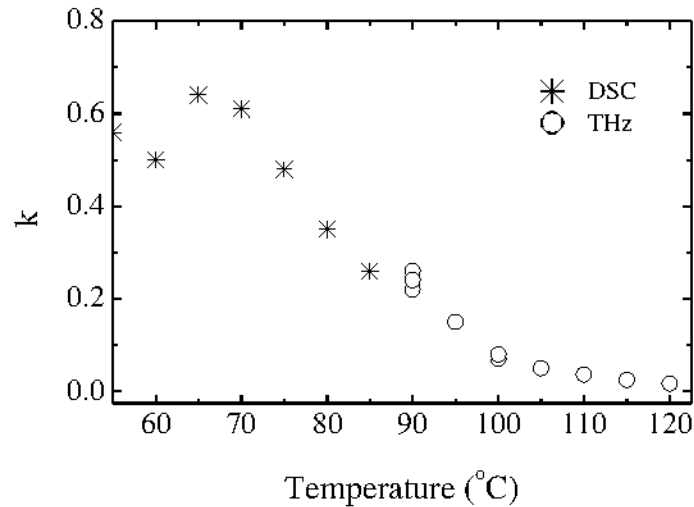
Molar ratio of crystalline PHB

$$X(t) = \frac{I(t) - I(0)}{I(\infty) - I(0)} X(\infty)$$



# Isothermal crystallization

Hoshina et al. IEEE Trans. Terahertz Sci. Tech., 3, 248 (2013)

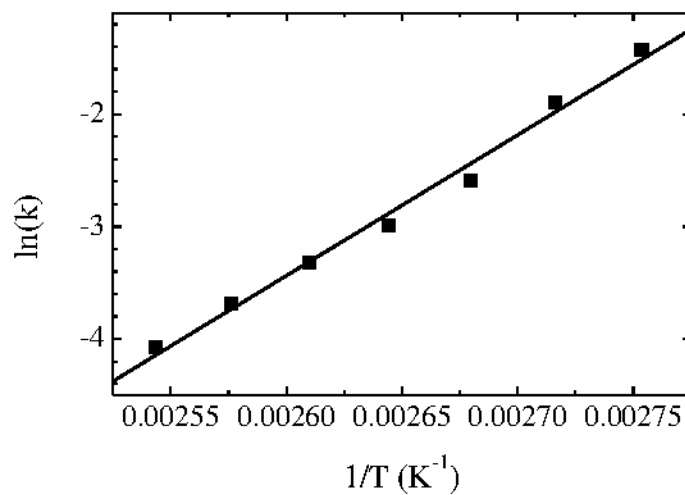


## Avrami's equation

$$X(t) / X(\infty) = 1 - \exp\left(- (k(t - t_0))^n\right)$$

$k$ : rate constant

$n$ : Avrami exponent



## Arrhenius Plot:

activation energy  $E_a = 104 \pm 5$  kJ/mol  
(cf. 83 kJ/mol obtained by DSC)

# Summary



- THz spectroscopy of PHB
  - Clearly show the difference of higher order conformations
  - Vibrational peaks are assigned by polarization spectra
  - The assignment was in good agreement with the DFT calculation
- Isothermal crystallization of PHB
  - The crystallization rate constants were obtained by Avrami's equation
  - The rate constants were in good agreements with those by DSC
  - THz-2DCOS visualize the detailed change of spectra
- THz spectroscopy of Nylon
  - Fingerprint peaks assigned
  - Phase transition was observed by THz spectroscopy

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Harumi Sato → [Kobe univ.](#)  
Shigeki Yamamoto → [Osaka univ.](#)  
Yukihiro Ozaki



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Isao Noda → [Univ. of Delaware](#)



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