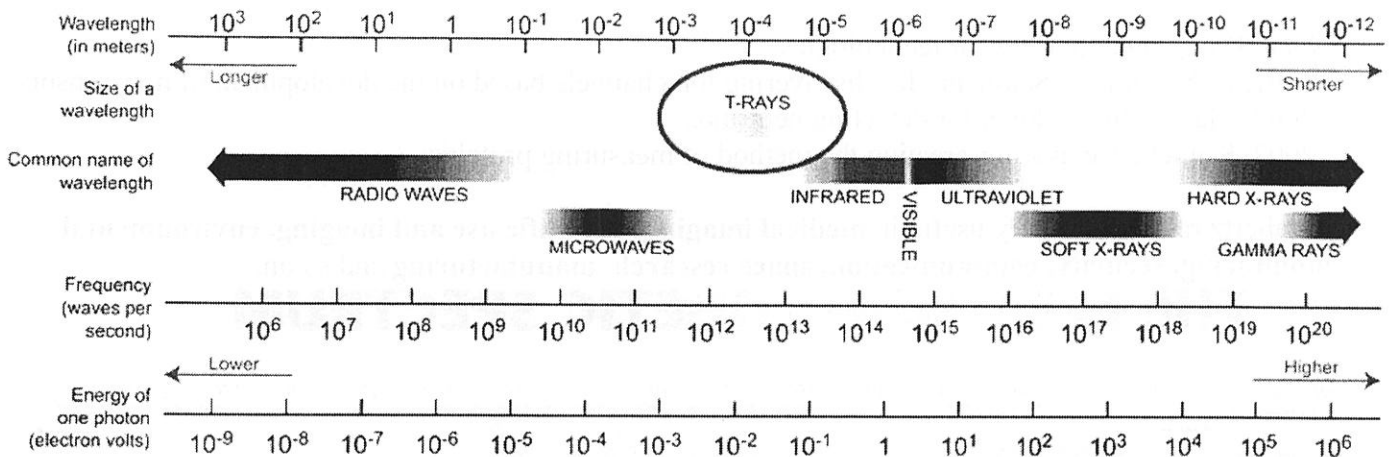


Terahertz



Contents

1. Introduction
2. How to Generate Terahertz
3. Applications of Terahertz
4. Future

1. Introduction

<What is terahertz?>

Electromagnetic waves sent at terahertz frequencies, known as terahertz radiation, submillimeter radiation, terahertz waves, terahertz light, T-rays, T-light, T-lux and THz, are in the region of the electromagnetic spectrum between 1 terahertz(1×10^{12} Hz) and 1000 terahertz (1×10^{15} Hz).

~characteristic~

Electromagnetic waves

~range~

$10^{12} \sim 10^{15}$ Hz (1~1000 THz)

or $10^{12} \sim 10^{13}$ Hz (1~10 THz,

microwave ~ far-infrared light)

~other names~

terahertz radiation, submillimeter radiation, terahertz waves, terahertz light, T-rays, T-light, T-lux

~history~

1864, electromagnetic theory was found by J. C. Maxwell.

1888, electric waves were discovered by H. R. Hertz.

⋮

1960s, application of terahertz started.

1990s, the name of terahertz was first used.

2008, a room temperature semiconductor source of coherent terahertz radiation was built.

<Knowledge helping understand terahertz>

kilohertz: kHz= 10^3 Hz

megahertz: MHz= 10^6 Hz

gigahertz: GHz= 10^9 Hz

terahertz: THz= 10^{12} Hz

petahertz: PHz= 10^{15} Hz

visible light: 400~800 THz, 380 nm~780 nm

1~1000 THz - **0.3 um~0.3 mm**

1 picosecond(ps)= 10^{-12} second

1 femtosecond(fs)= 10^{-15} second

1 ps - half-life of a bottom quark

3.3 ps (approximately) - time taken for light to move 1 millimeter

1.3 fs - cycle time for 390 nanometer light, transition from visible light to ultraviolet

2.57 fs - cycle time for 770 nanometer light, transition from visible light to near-infrared

200 fs - the swiftest chemical reactions, such as the reaction of pigments in an eye to light

<Why terahertz?>

Sensor technology, including **terahertz sensor technology**, is one of the most important technologies in the 21st century.

Nobel Prizes related to sensor technologies:

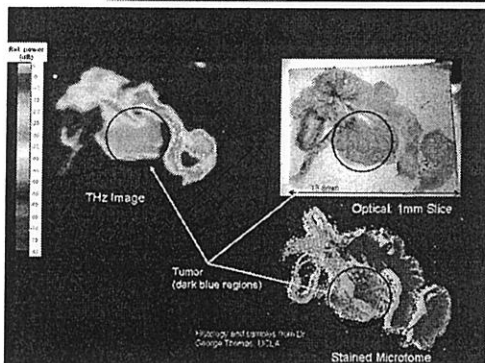
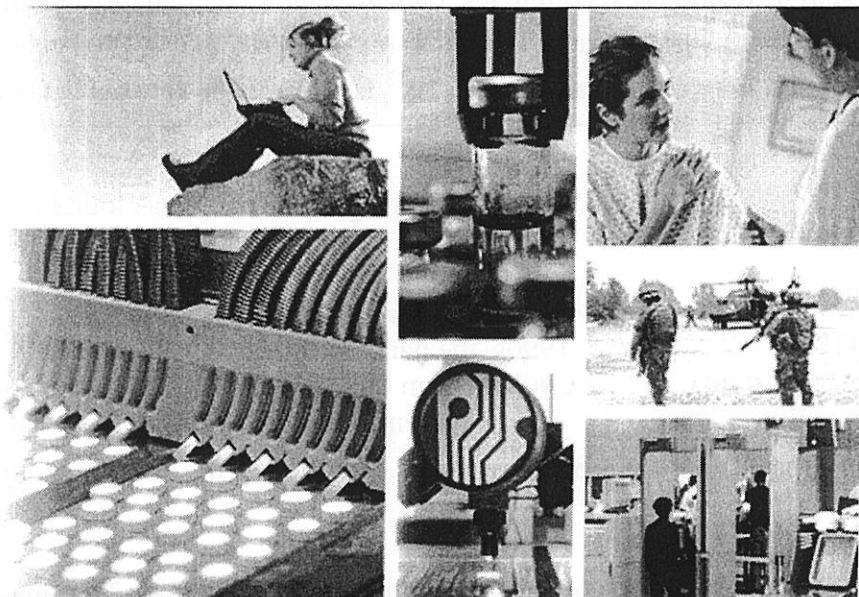
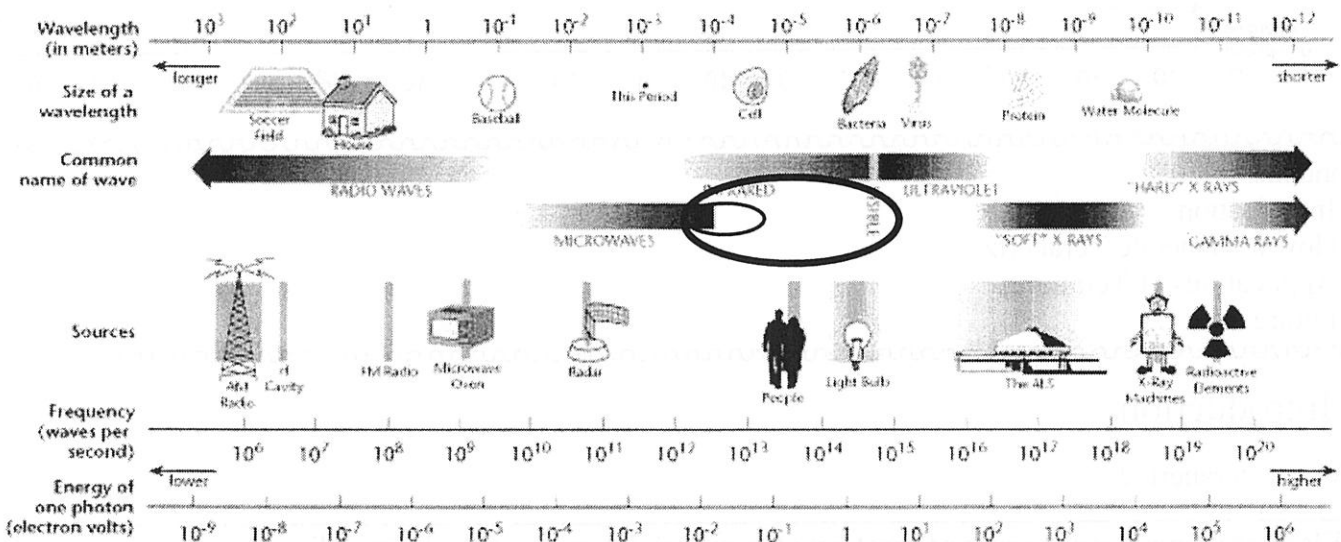
1991, E. Neher & B. Sakmann, for discovering ion channels based on the development of new sensors.

2002, Masatoshi Koshiba, for detecting neutrinos

2002, Kouichi Tanaka, for creating the method of measuring proteins

Terahertz radiation is very useful in **medical imaging, scientific use and imaging, environmental monitoring, security, communication, space research, manufacturing** and so on.

THE ELECTROMAGNETIC SPECTRUM



2. How to generate terahertz

Problem: no good sources or detectors →

Recently, laser technology developed fast.

In 1984, research by D. H. Auston made proper sources and detectors.

Since 1984, generation and application of terahertz have made remarkable development.

However, the method of generating terahertz that can be used for all the usages doesn't exist now.

2.1 By Photoconductive Emitters - Auston Switch

D.H. Auston. et al. *Appl. Phys. Lett.* **1984**, 45, 284.

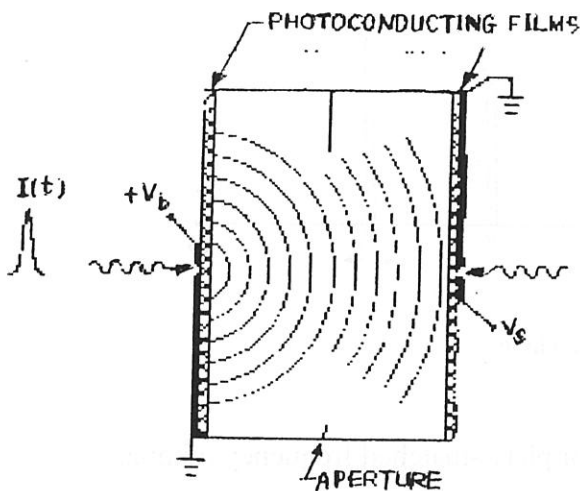


FIG. 1. Experimental configuration used to generate and detect fast electromagnetic pulses. As in Hertz's experiment, both the generator and detector are time-varying dipoles. To obtain very high speeds of response, fast photoconductive materials, illuminated by subpicosecond optical pulses are used for both dipoles. Although the distance between dipoles is small (1.1 mm), the electromagnetic pulse is sufficiently short that it is already in the far field as it reaches the receiving dipole. The transmitting dipole (left) has a dc bias and the receiving dipole which is connected directly to a low-frequency amplifier, receives its bias from the electromagnetic pulse.

~photoconducting films~

prepared by irradiating a 1-um epitaxial **silicon film on sapphire** with $3 \times 10^{15} \text{ Ar}^+$ ion/cm² at an energy of 2 MeV.

~electrodes~

a thin (1.15 mm) slab of insulating material **alumina with a 10-um gap**.

~optical pulses~

subpicosecond pulses (10^8 Hz, infrared light) produced by laser to illuminate the transmitting and receiving photoconductors. There is a **time delay**.

~bias~

a bias of 45V is applied to the electrodes of the transmitting photoconductor.

~amplifier~

a low-frequency amplifier directly connected to the receiving photoconductor to receive its bias from the electromagnetic pulse.

~features~

0.1 THz~several THz.

very high speed, a measured time response of **1.6 ps**. without requiring the intermediate excitation of waveguides, transmission lines, or radiating antennas.

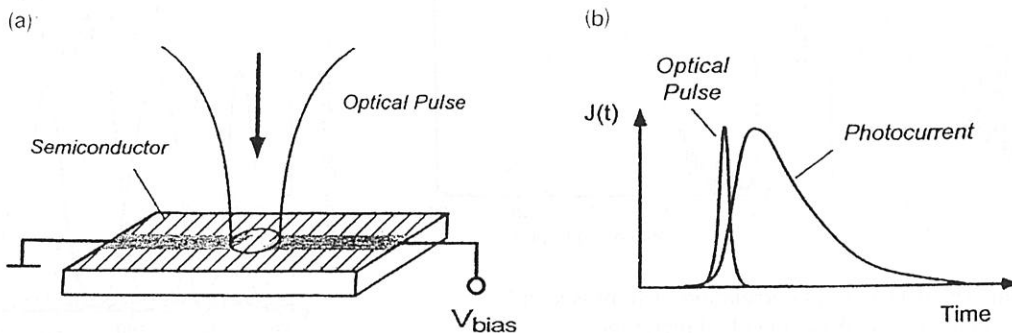


FIG. 2. Outline of photoconductive emitters

The optical laser pulse creates carriers (electron-hole pairs) in a **semiconductor material**. Effectively, the semiconductor changes abruptly from being an insulator into being a conductor. This conduction leads to a sudden electrical current across a biased antenna patterned on the semiconductor. This changing current emits terahertz radiation, similar to what happens in the antenna of a radio transmitter.

2.2 Difference Frequency Generation(DFG)

Photons are generated at a difference frequency ω_3 by **mixing** photons at frequencies ω_1 and ω_2 on a **crystal** with an appreciable second-order susceptibility.

R.A. Kaindl, et al. *OPTICS LETTERS*. 1998, 23, 861.

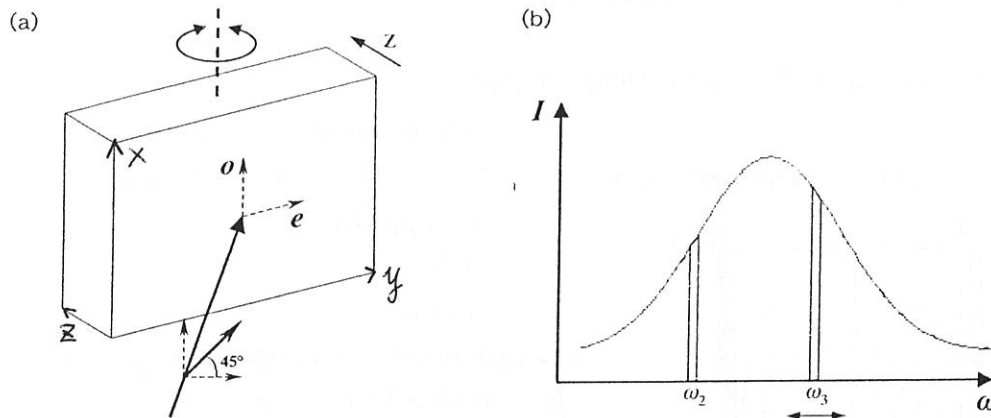


Fig. 3. Terahertz generation from GaSe

~crystal~

GaSe, 1 mm thin with fused-silica lens($f=100$ mm) on it for phase-matched frequency mixing.

~pulses~

a mode-locked Ti:sapphire laser, with a duration of 20 fs

~phase-matched difference-frequency mixing~

$n^e w^2 - n^0 w^1 = n^0 w^3$ (n^0, n^e : refractive index; w^1, w^2 : frequency; w^3 : **difference frequency**.)

~detector~

a nitrogen-cooled HgCdTe detector with a sensitivity range extending to 20 μm .

~features~

When the crystal rotates, n^e changes. Femtosecond pulses **tunable from 9 μm to 18 μm (17~33 THz)** at an 88-MHz repetition rate with a measured time response of **160 fs** are generated.

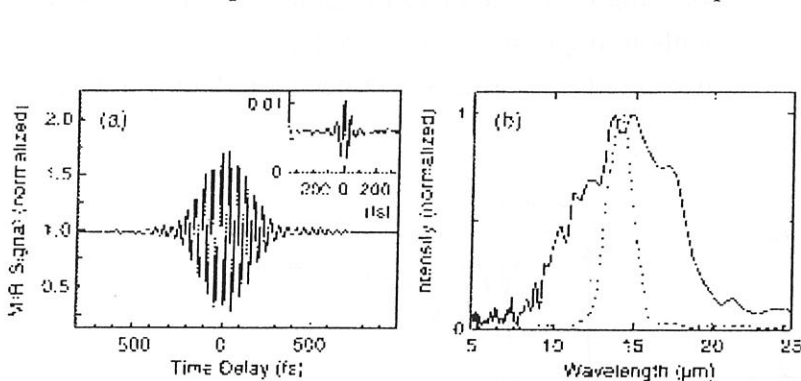


Fig. 4. (a) Interferometric electric field correlation of femtosecond mid-infrared pulses generated by phase-matched difference-frequency mixing in GaSe. The signal is plotted as a function of delay time between the pulse and its replica. Inset, electric field autocorrelation of a pulse generated by non-phase-matched optical rectification at the surface of a GaSe crystal. (b) Normalized spectra of the pulses in (a). Solid curve, optical rectification; dashed curve, difference-frequency mixing.

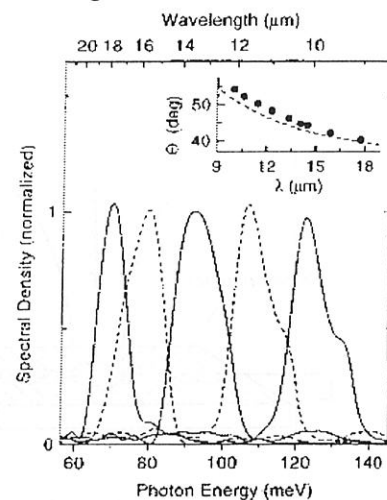


Fig. 5. Normalized spectra of femtosecond mid-infrared pulses continuously tunable from 9 to 18 μm . The spectra are derived from electric field correlations. Inset, tuning curve of GaSe. The (external) phase-matching angle is plotted versus the center wavelength of the pulses (filled circles). Dashed curve, calculated phase-matching curve. 4/12

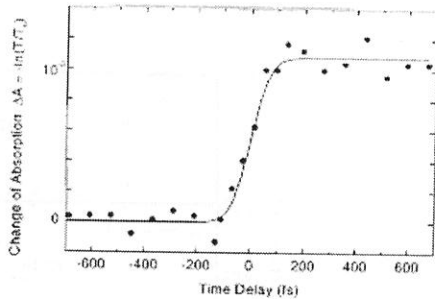


Fig. 6. Transient absorption of germanium at a probe wavelength of 11.5 μm after excitation by a 20-fs pulse at 830 nm.

2.3 From the Surface of Semiconductors

Femtosecond ultrashort laser pulses are used to directly illuminate semiconductors, which generate terahertz radiation from the **surface** of the semiconductors. This is a very useful and common way to generate terahertz.

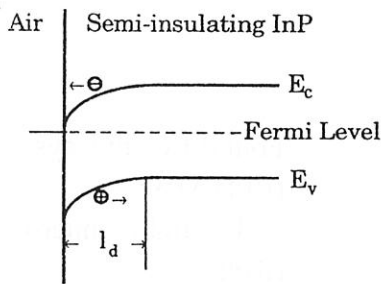


Fig. 7. Energy bands of InP

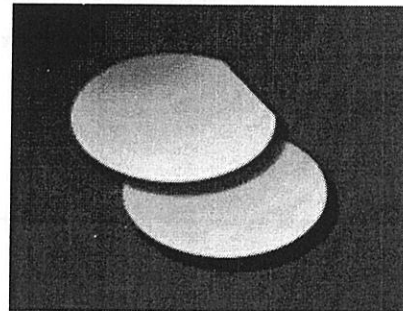


Fig. 8. GaAs

~materials~

GaAs, InP, InAs, InSb...

~mechanism~

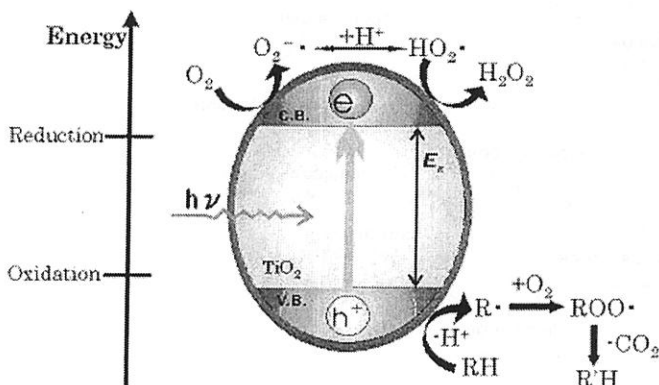
difference frequency mixing or photoexcitation

3. Applications of Terahertz

3.1 Photocatalysis and Terahertz

In chemistry, photocatalysis is the acceleration of a photoreaction in the presence of a catalyst.

Its comprehension has been made possible ever since the discovery of water electrolysis by means of the TiO_2 in 1972. (A. Fujishima, K. Honda, *Nature* **1972**, 238, 37.)



Photocatalysis over a semiconductor oxide such as TiO_2 is initiated by the absorption of a photon with energy equal to or greater than the band gap of the semiconductor (3.2 eV for TiO_2), producing electron-hole (e^-/h^+) pairs.

3.1.1 Research on Photocatalysis by Terahertz

S. Hirokoshi, et al. *Environ. Sci. Technol.* 2004, 38, 2198.

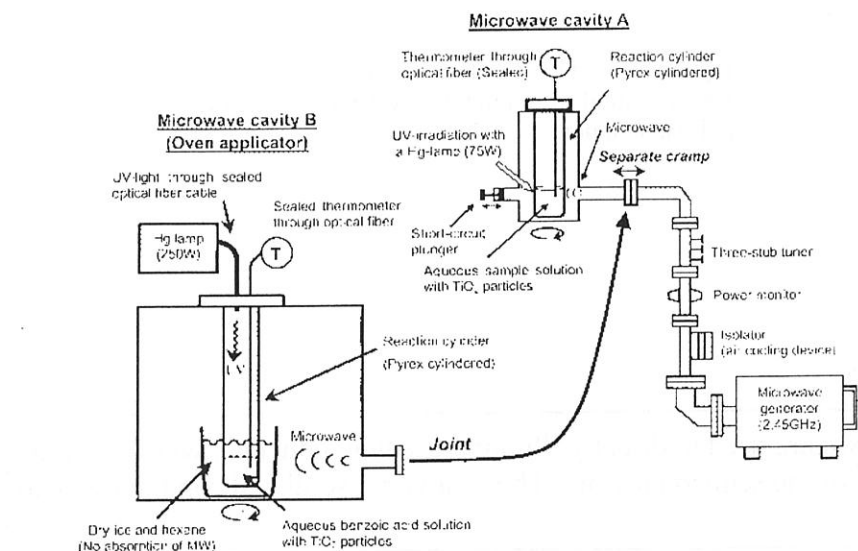
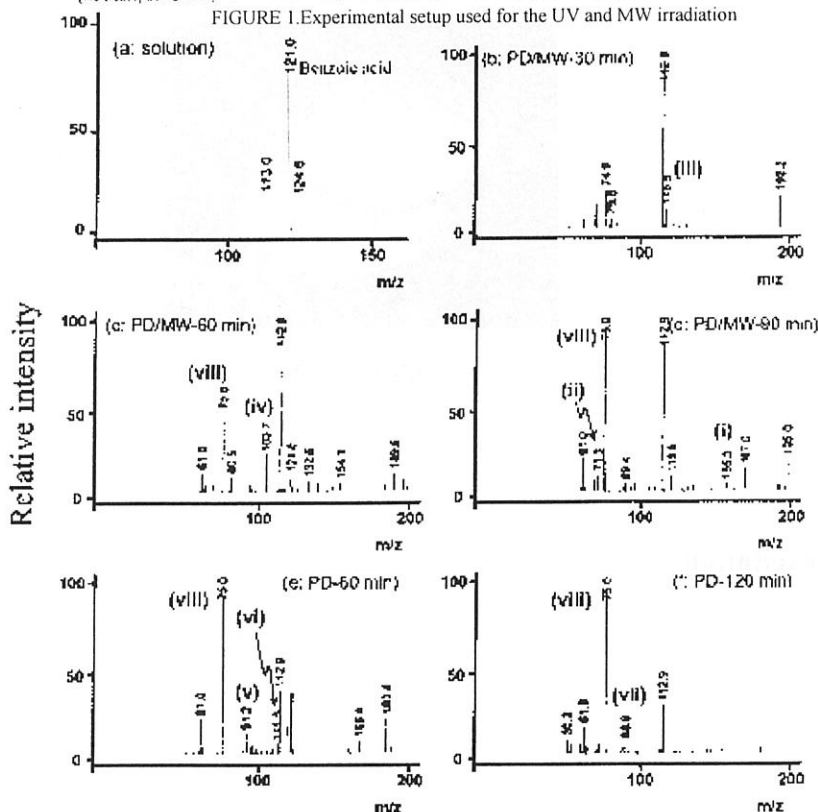


FIGURE 1. Experimental setup used for the UV and MW irradiation



SCHEME 1. Proposed Mechanism for the Degradation of Benzoic Acid by the PD and PD/MW Routes

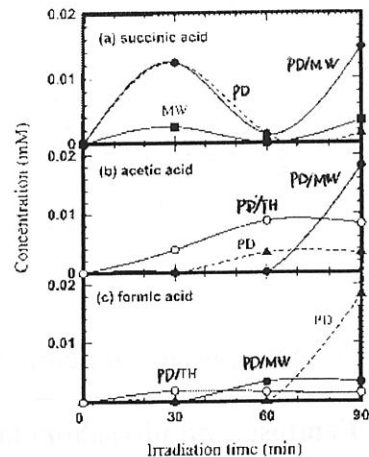
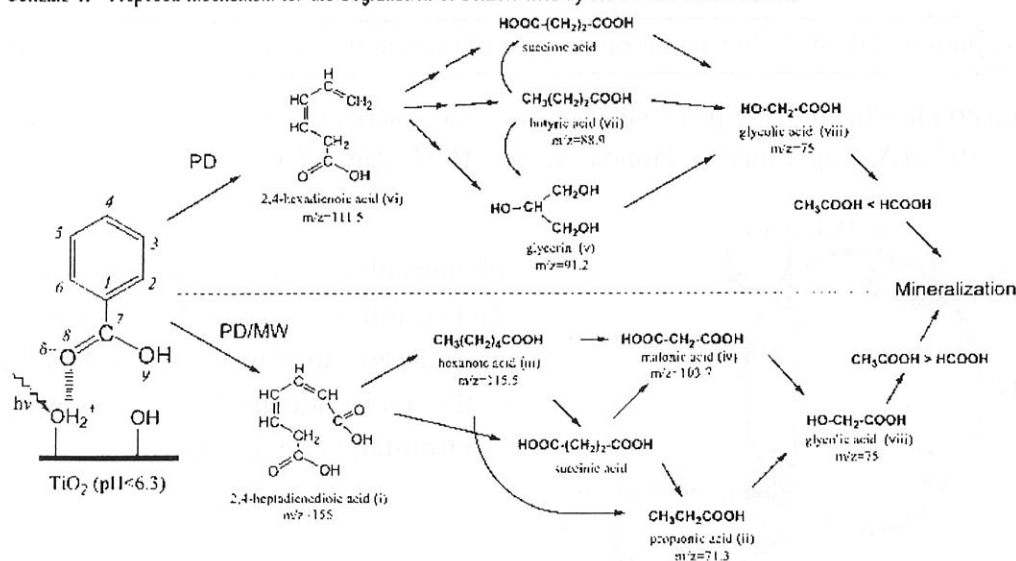


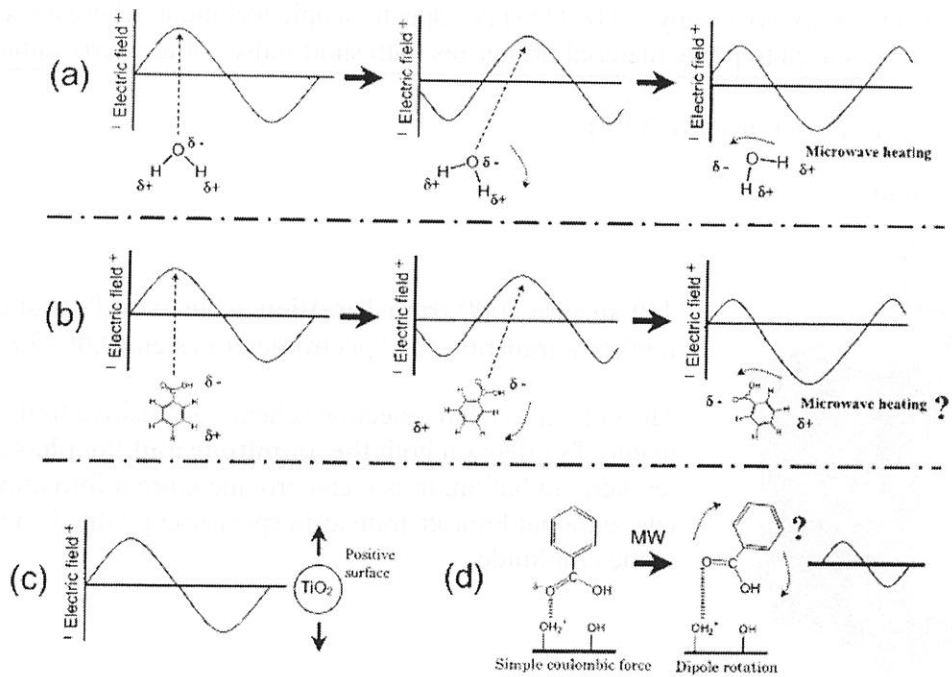
FIGURE 3. Temporal evolution of carboxylic acid intermediates: (a) succinic acid, (b) acetic acid, and (c) formic acid during the degradation of benzoic acid (0.1 mM).

Four different ways:

- (i) PD/MW: UV light + microwave
- (ii) PD: UV light
- (iii) MW: microwave (without TiO₂)
- (iv) PD/TH: UV light + heating

FIGURE 2. Negative ion ESI mass spectra recorded at various times during the degradation of benzoic acid by the PD/MW route (b-d) and by the PD route (e, f). (a) Initial mass spectrum of a benzoic acid solution.

SCHEME 3. Orientation Polarization^a



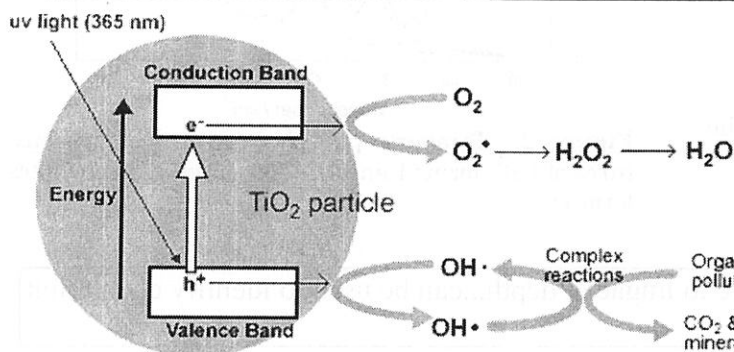
Conclusion(Microwave heating effect):

Together with UV light it can increase the activity of TiO₂.

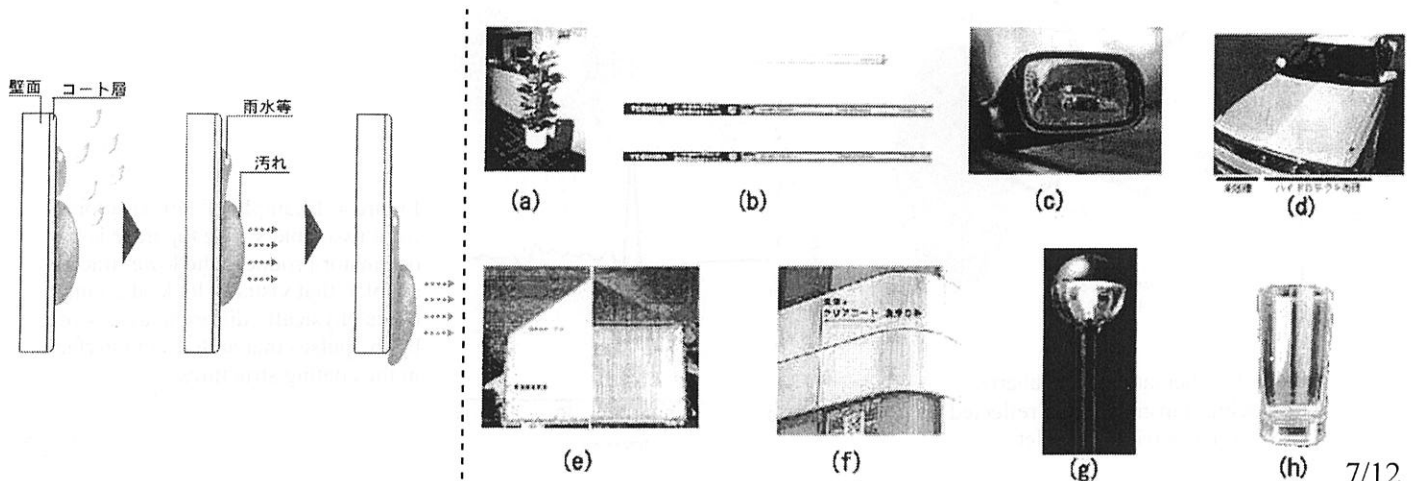
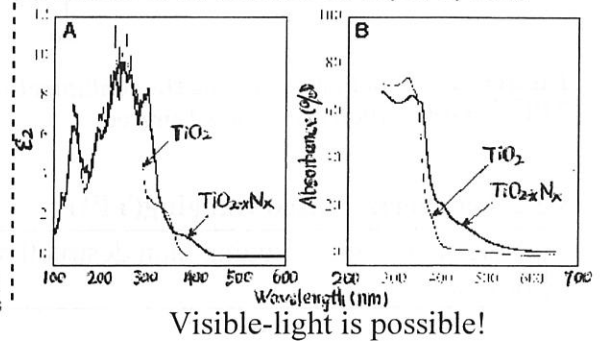
Further more it can change the reaction rate by inducing the rotation of the substrate.

3.1.2 Application of Photocatalyst in Daily Life

TiO₂ is the most focused photocatalyst because of its high reactivity and chemical stability under UV. Others: ZnO, WO₃, FeTiO₃, and SrTiO₃...



R. Asahi, et al. *Science* **2001**, 293, 269.



3.2 Application of Terahertz in Pharmaceutical Technology

Terahertz time-domain spectroscopy (THz-TDS) is a spectroscopic technique where a special generation and detection scheme is used to probe material properties with short pulses of terahertz radiation.

3.2.1 Terahertz Pulsed Spectroscopy(TPS)

TPI spectra 1000



TPI spectra 1000 from TeraView is the world's first commercial terahertz transmission spectrometer system(0.06~3.6 THz).

The generation and detection scheme is sensitive to the sample material's effect on both **the amplitude and the phase** of the terahertz radiation, thus it can provide more information than conventional Fourier-transform spectroscopy that is only sensitive to the amplitude.

Terahertz pulsed spectroscopy can be used to quantify pharmaceutical polymorphism and crystallinity, basing on intermolecular hydrogen bonding vibrations and crystalline-structure lattice vibrations.

C. J. Strachan. et al. *J. Pharmaceutical Sci.* **2005**, *94*, 837.

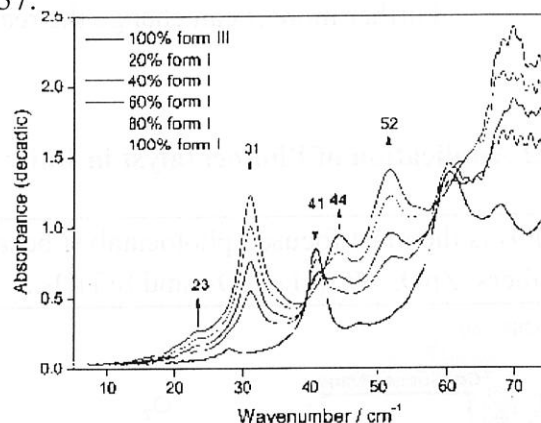
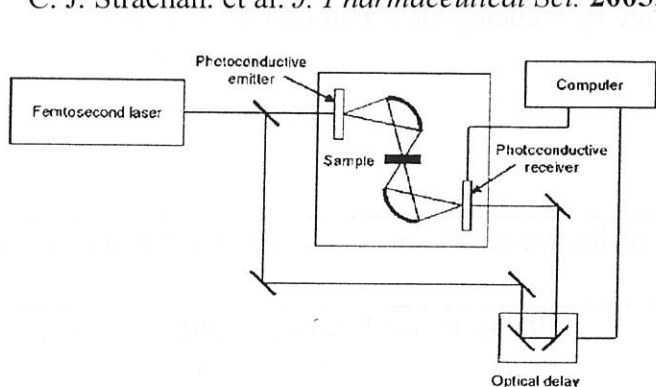


Figure 1. Schematic showing the configuration of the TPI™ spectra 1000 (TeraView Limited).

Figure 2. Terahertz pulsed spectra of binary mixtures of CBZ forms I and III (20% intervals, 0 to 100% form I).

3.2.2 Terahertz Pulsed Imaging(TPI)

Advantages: non ionizing, non destructive, able to imgae at depth...can be used to identify counterfeit products

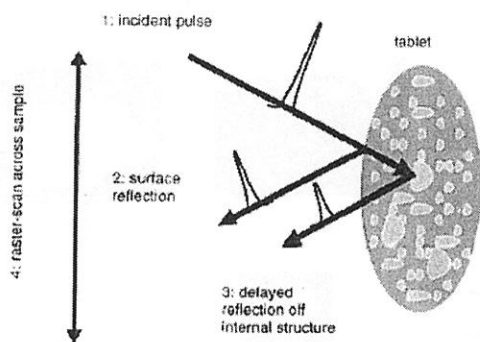


Figure 3. Schematic of a terahertz pulse being transmitted and reflected from interfaces within a tablet.

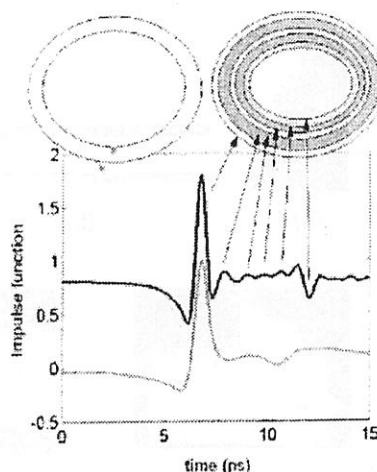


Figure 4. Example of TPI waveforms from two tablets. The top trace is the originator product. The lower trace is a tablet that visually looks the same but is physically different, as shown by the pulses that arise from interfaces in the coating structures.

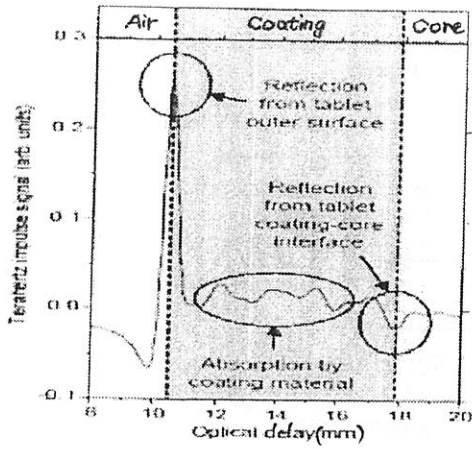


Figure 5. The peaks in the waveform can be clearly attributed to the coating and core parts of a tablet.

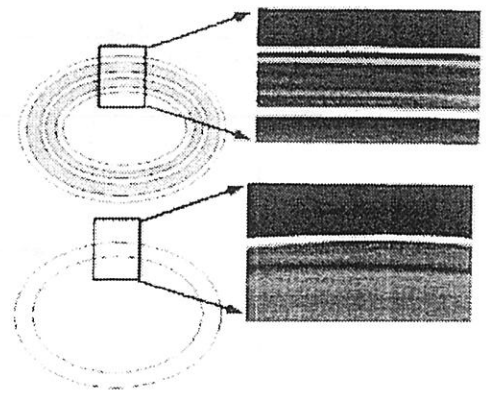
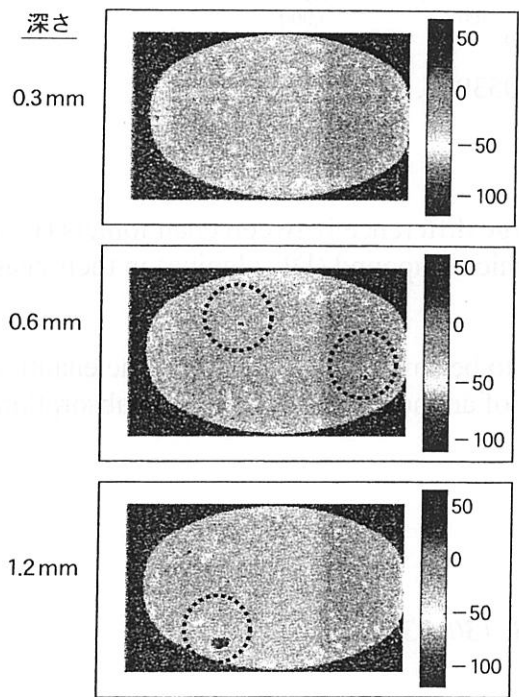
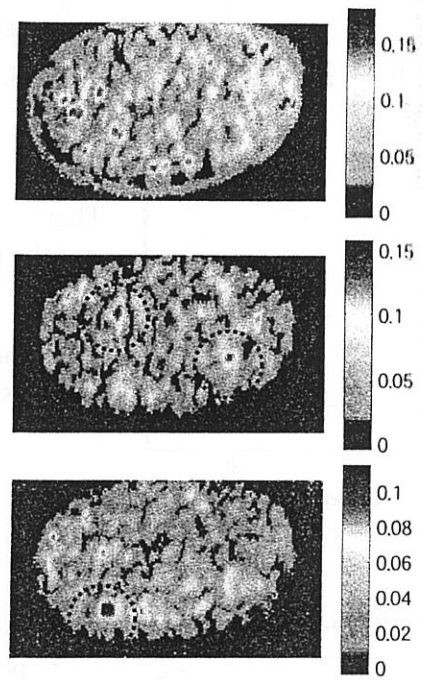


Figure 6. Depth profile of the tablets clearly show the interfaces and demonstrate the complexity of the originators product.



16時間かけたX線CTイメージングでも化学情報がみられない



TPIイメージングでは数分でも科学的構造的観測できる

図7 密度に差異がある同一錠剤の3段階の深さ方向におけるX線CT法(左側)とテラヘルツパルスイメージング(TPI)法(右側)のイメージの比較

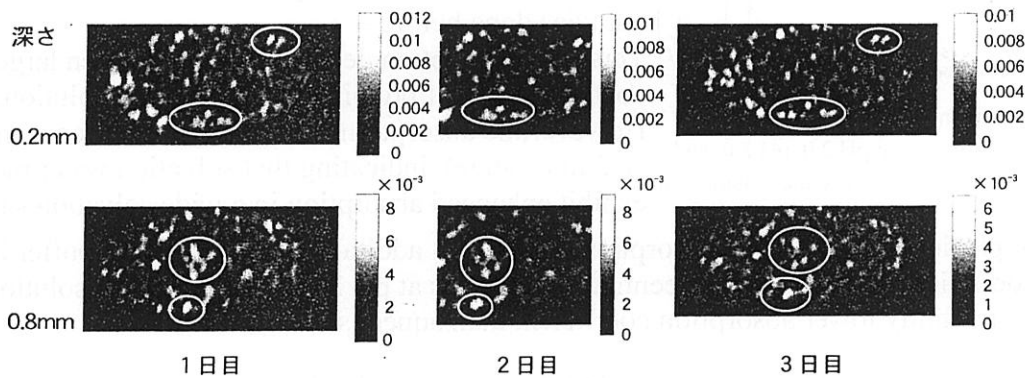
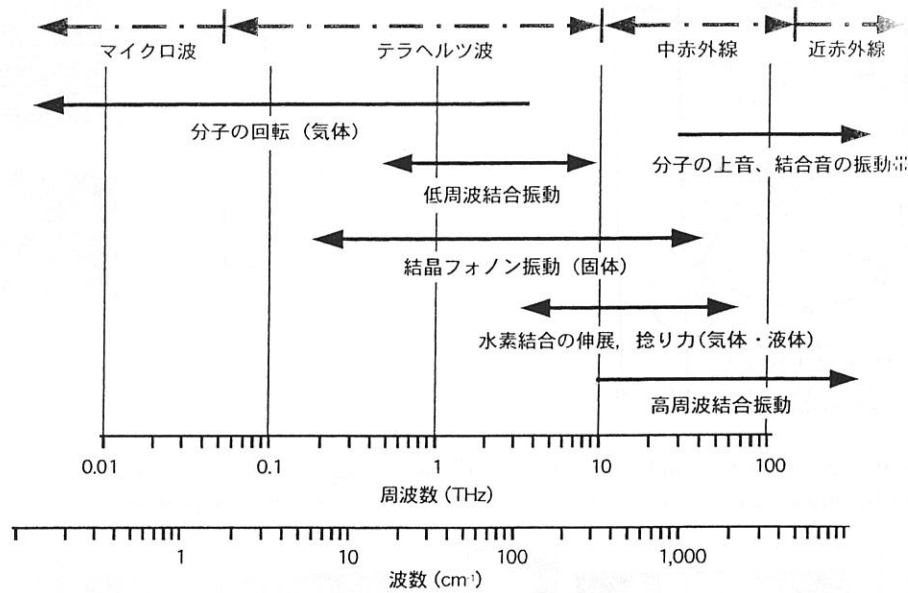
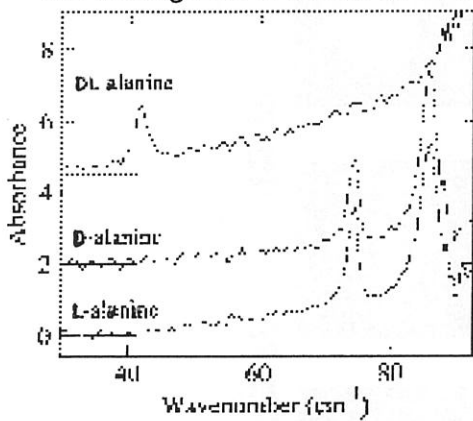


図8 3日にわたって記録された医薬品のテラヘルツマッピング
このマッピングは錠剤深さ方向2ヵ所で測定された。測定の安定性が非常によいことが分かる。

3.3 Life Science and Terahertz



M. Yamaguchi, et al. *Appl. Phys. Lett.* **2005**, *86*, 053903.



There is a large difference between enantiomers (L- and D-alanine) and the racemic compound (DL-alanine) in their peak frequencies.

It is thought to be a method to determine the enantiometric composition of amino acids from the THz absorption spectra.

Figure 1. THz absorption spectra of L-, D-, and DL-alanine.

Simon Ebbinghaus, et al. *J. Am. Chem. Soc.* **2008**, *130*, 2374.

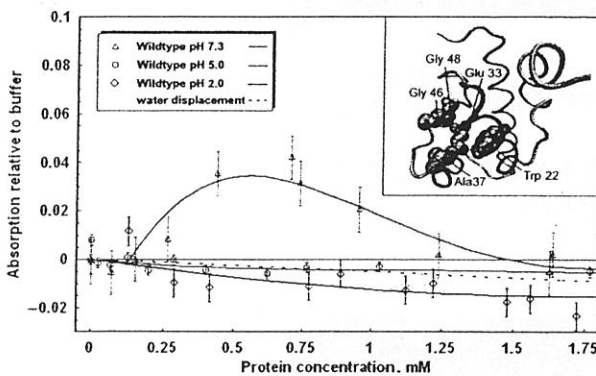


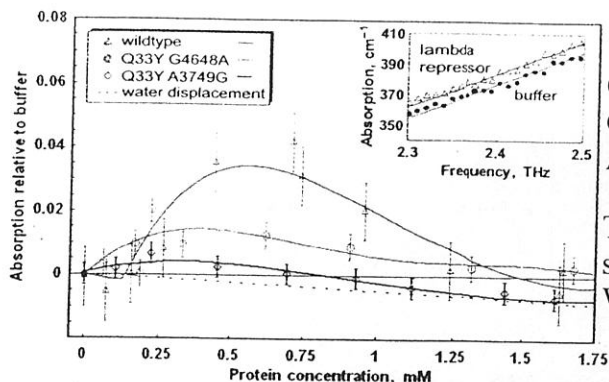
Figure 2. Difference in the integrated THz absorption coefficient (2.1-2.8 THz) of λ_{6-85} at pH 2.0, pH 5.0, and pH 7.3. The inset shows the structure and the mutation sites.

~point~
to detect changes in solvation dynamics around protein;
experimentally challenging because of the strong THz
absorption of water
~protein~
pseudo-wild-type lambda repressor protein, 80 residue 5 helix
~spectroscopy~
terahertz in 2.1-2.8 THz region
~studies done before~

Terahertz absorption decreases linearly when large concentrations of protein are added to the solution. However, the absorption is nonlinear at low concentrations (1-5 mM range), indicating that solvation water molecules exhibit enhanced absorption in a wide solvation shell.

There is a strong pH dependence of the absorption. At pH 7.3, addition of protein to the buffer increases the absorption coefficient at 0.5-1 mM concentration, whereas at pH 2 and 5, the protein solution has almost the same or slightly lower absorption coefficient than aqueous buffer.

The pH 5 data follow the dotted line accurately, but this appears to be due to a compensation between solvation water of enhanced absorptivity (native protein) and solvation water of reduced absorptivity (pH 2 unfolded state).



Q33Y: Gln→Tyr by site-directed mutagenesis
 G4648A: helix-stabilizing Gly-Ala mutations
 A3749G: helix-destabilizing Ala-Gly mutations

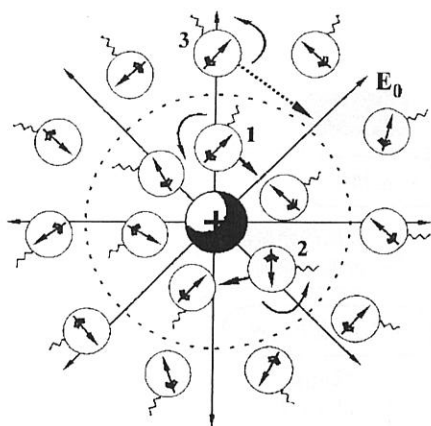
The Tyr mutant coupled with Ala-Gly mutations(Q33Y A3749G) shows a concentration dependence similar to the low pH proteins. When coupled with Gly-Ala mutations(Q33Y G4648A)...

Figure 3. Comparison of the integrated THz absorbance of the pseudo-wild-type lambda repressor with three mutants of the protein at pH 7.3. The inset shows the frequency dependence of the THz absorption for buffer and the solvated protein at a given concentration of 0.37 mM.

Conclusion: Global perturbations of the protein **hydration shell** by **pH** and local perturbation by surface **site-specific mutation** both produce significant changes in the terahertz absorption spectrum of aqueous protein.
 Such changes can be used in the future as sensitive probes of protein-solvent dynamics, opening up the possibility of **using THz absorption as a probe for protein** folding kinetics and functional dynamics measurements.

<What is a hydration shell?>

Samir Kumar Pal. et al. *J. Phys. Chem. B* **2002**, *106*, 12376.



The group of water molecules oriented around an ion is called a **hydration shell**.

When an ion is inserted into a water configuration, it changes the structure of the hydrogen bond network. A water molecule tends to rotate or translate(reorient, breaking the hydrogen bonds to their nearest neighbors) so that its polarized charge concentration faces the opposite charge of the ion to attain the minimum energy configuration.

Figure 4. Schematic illustration of solvation of an ion (or dipole) by water.

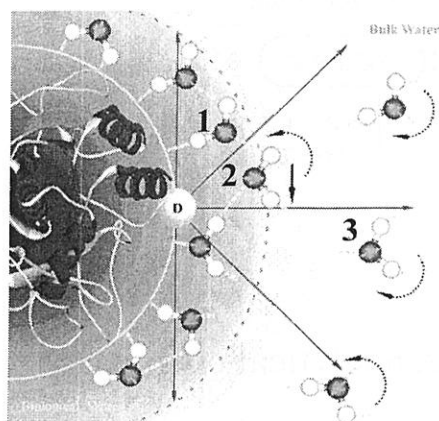
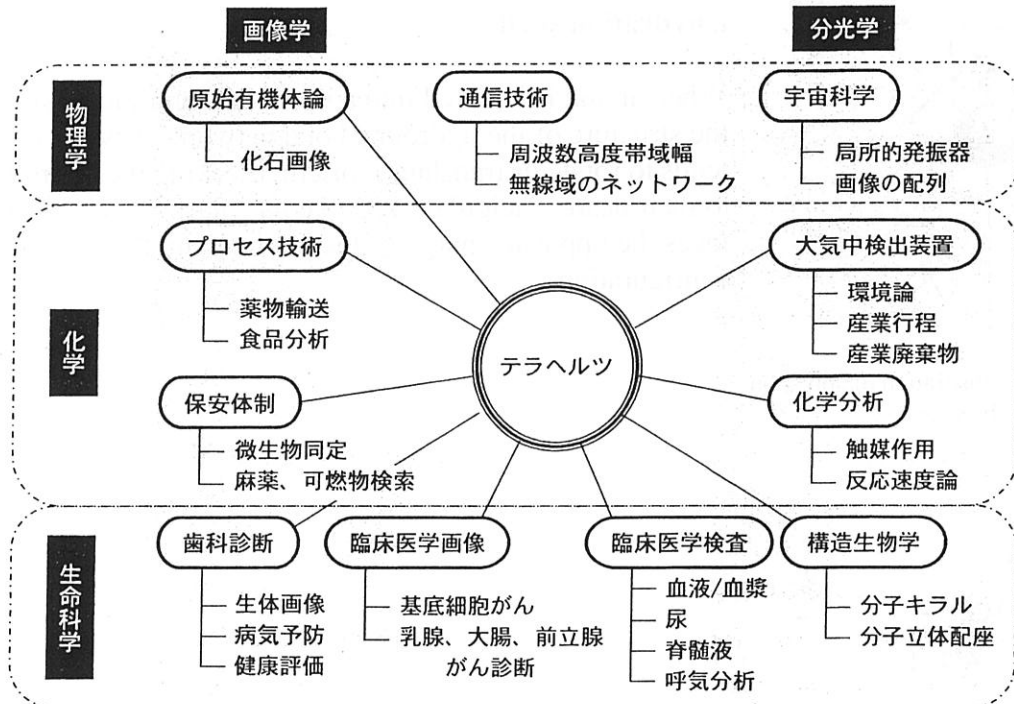
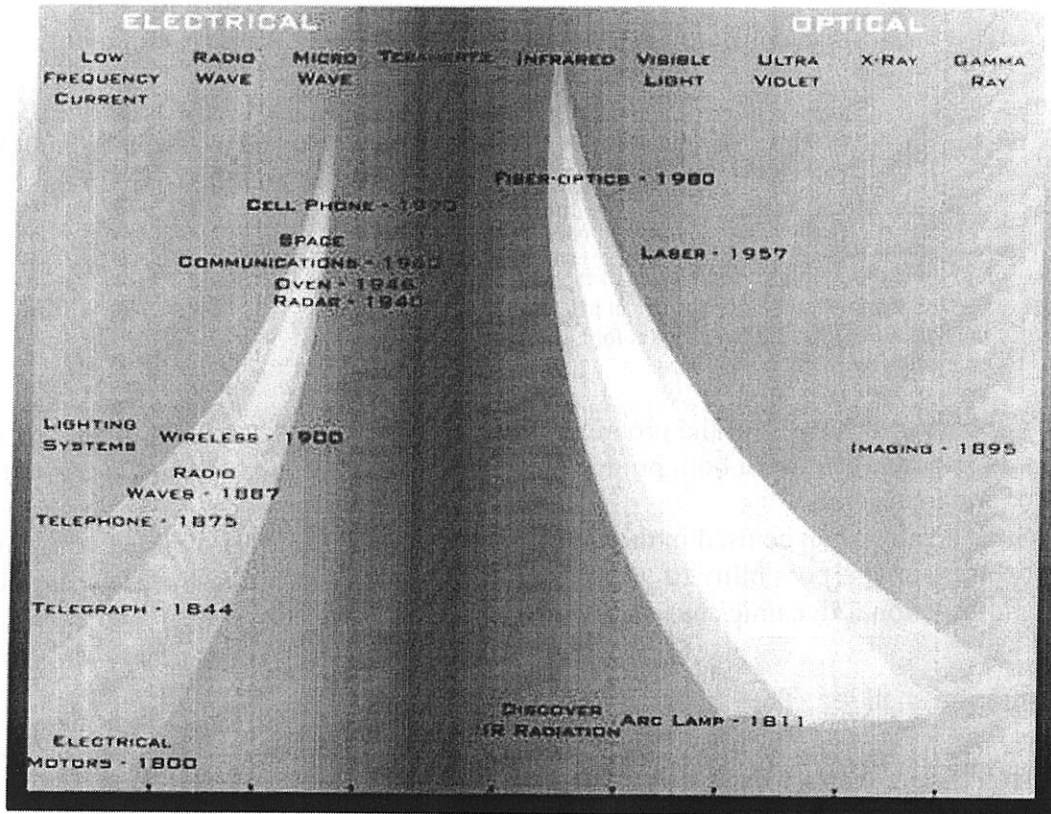


Figure 5. An illustration of the dynamic equilibrium in the hydration layer of a protein, with bound (1) quasi-free (2) and free water molecules(3).

4. Future



Applications to chemistry: catalysis, reaction kinetics, analytical chemistry, ...