High Efficiency THz Generation in Novel Organic Nonlinear Optical Crystals

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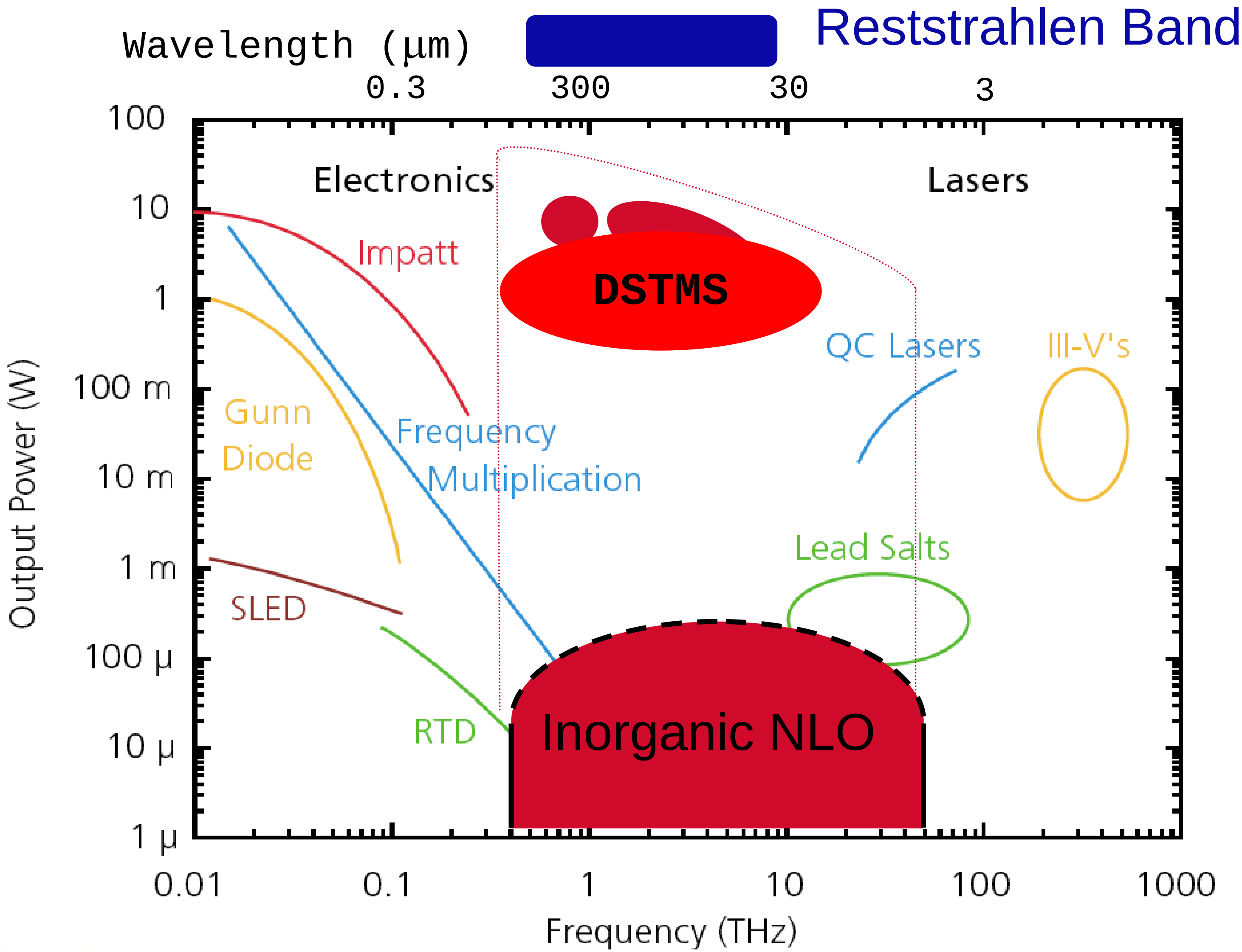
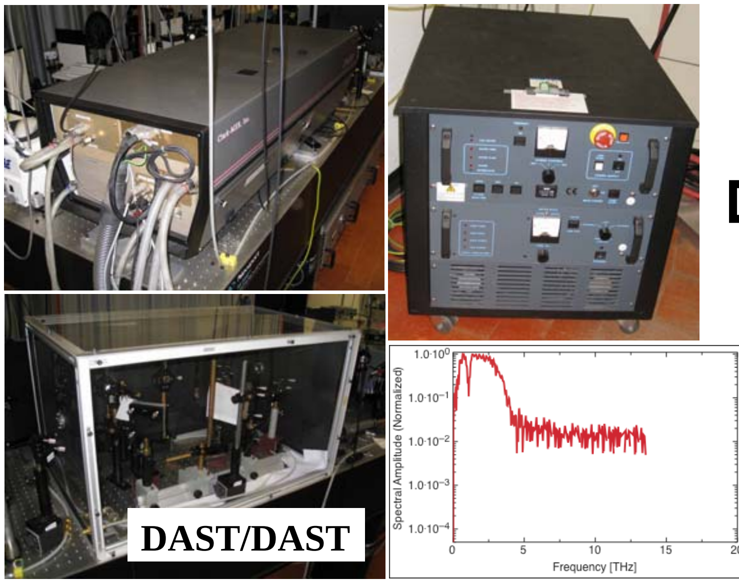
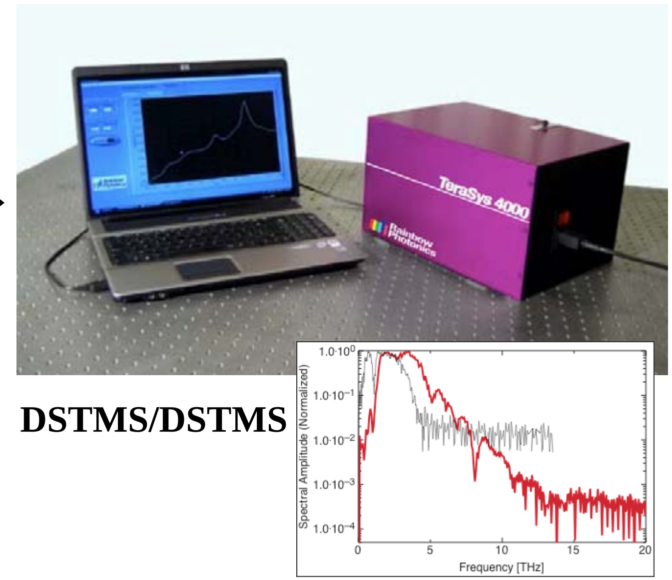
- Generation of THz Radiation in Organic Materials
- DAST and DSTMS Crystals
- THz Generation in DSTMS
- Applications in Spectroscopy and Imaging
- Conclusions

Electronics, THz Waves and Lasers



Motivation





Terahertz photonics:

Established technology but expensive and bulky and often restricted to < 3 THz

Nonlinear Optics

- Deals with the interactions between optical waves and electric fields in nonlinear optical materials

- Can be used for controlling optical beams with other optical waves or electrical signals

- Largest Effects in Highly Polarizable Polar Materials

Organic nonlinear optical materials

Molecules:

ext. electric field induces a polarization in every molecule

$$p_i = \varepsilon_o(\alpha_{ij}E_j + \beta_{ijk}E_jE_k + \gamma_{ijkl}E_jE_kE_l + \ldots)$$

β_{ijk} : first-order *hyperpolarizability* tensor

γ_{ijkl} : second-order *hyperpolarizability* tensor

Molecular crystals:

ext. electric field induces a macroscopic polarization P

$$P_i = \varepsilon_o(\chi_{ij}^{(1)}E_j + \chi_{ijk}^{(2)}E_jE_k + \chi_{ijkl}^{(3)}E_jE_kE_l + \ldots)$$

$\chi^{(n)}$: n-th order *susceptibility*

$$\chi^{(2)} = \boldsymbol{d}$$

Difference-frequency generation

difference-frequency generation

$$\omega_3 - \omega_1 \rightarrow \omega_2$$

special case: optical rectification

$$\omega - \omega \rightarrow \Omega \approx 0$$

$$\omega_1 = \omega + \Omega/2$$
$$\omega_2 = \omega - \Omega/2$$

❷ ⇦ $\omega_1 - \omega_2 = \Omega$

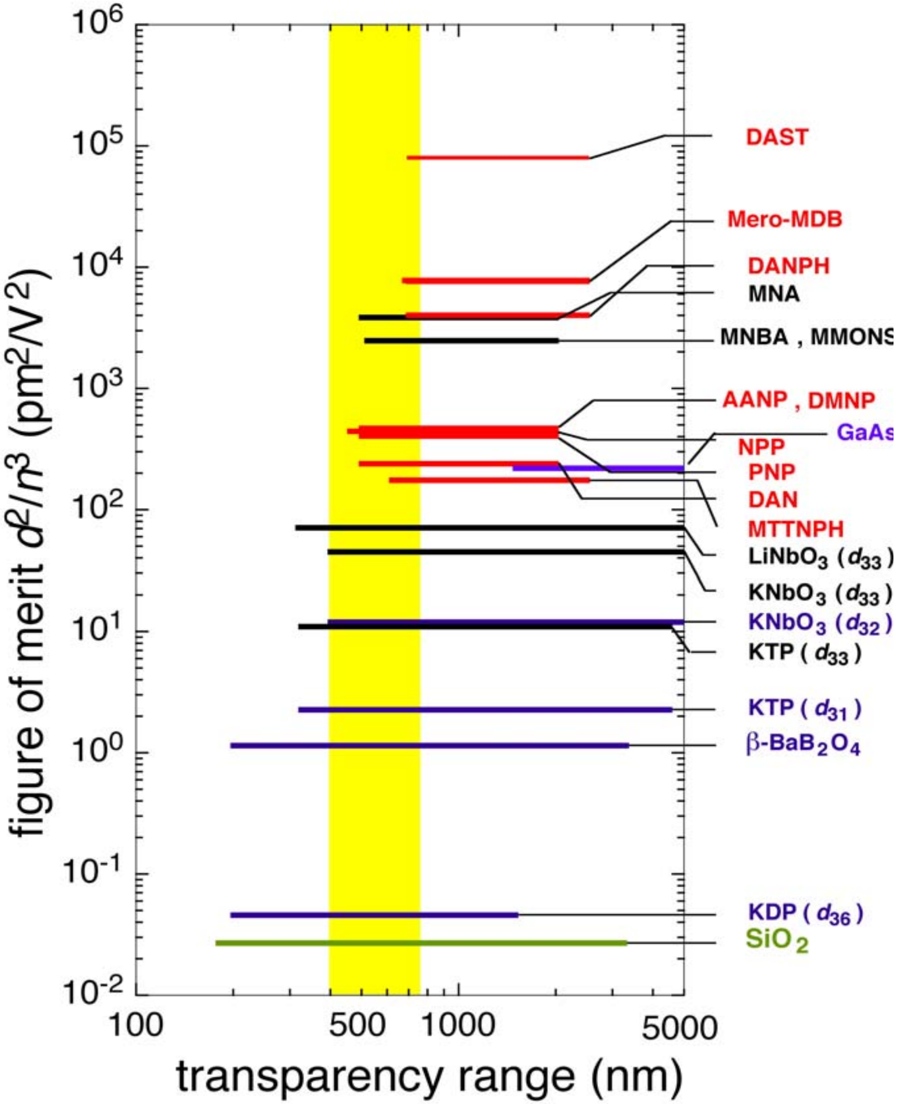
$(\ \omega \gg \Omega\ )$

Requirements for Efficient Generation

- Large nonlinear susceptibility $\chi^{(2)}$
- Low absorption
- Velocity-matching between the optical and the THz pulse

Organic crystals satisfy all these conditions particularly well!

Figure of Merit NLO

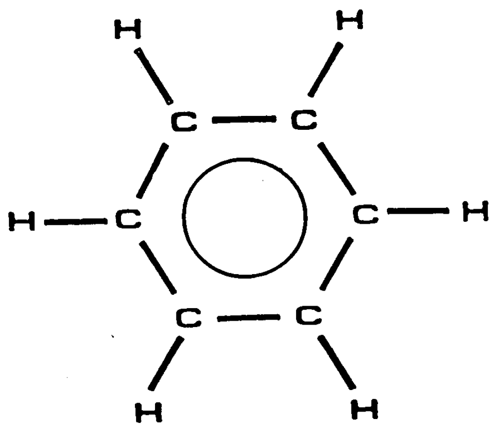


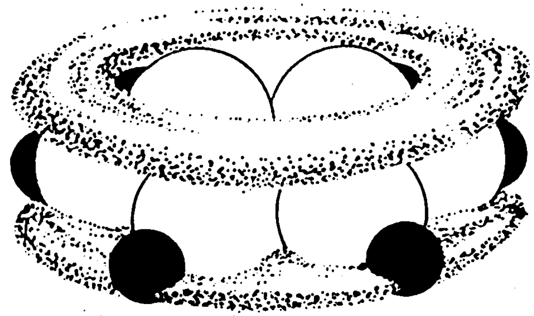
Electro-optic materials

		r (pm/V)	n	n^3r (pm/V)	ε	n^3r/ε (pm/V)	λ (nm)
Semicond.	**GaAs**	1.2	3.5	50	13	4	1020
	ZnTe	4	2.9	98			800
Ferroel.	**$LiNbO_3$**	30	2.2	320	30	10	633
	$Sn_2P_2S_6$	180	2.8	4000	230	17	1318
Organic.	**EO polymer**	100	1.6	400	3	140	1318
	DSTMS	180	2.5	2800	5.2	540	720
		53	2.2	560	5.2	110	1318

Molecular Orbitals

Benzene

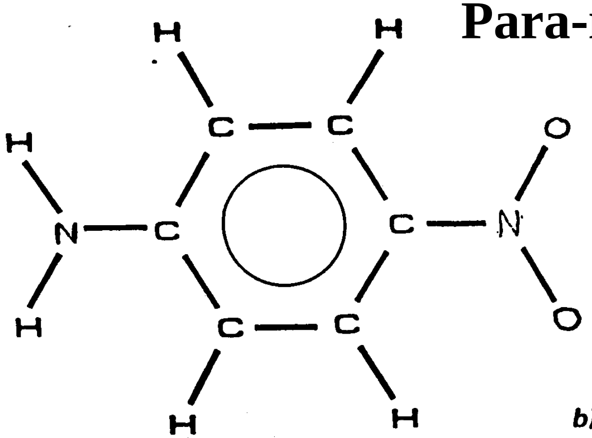


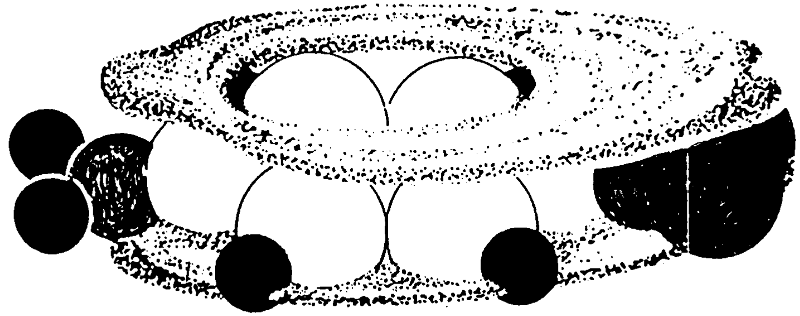


a) benzene

$\beta = 0$

Para-nitro-aniline





b) para-nitro-aniline

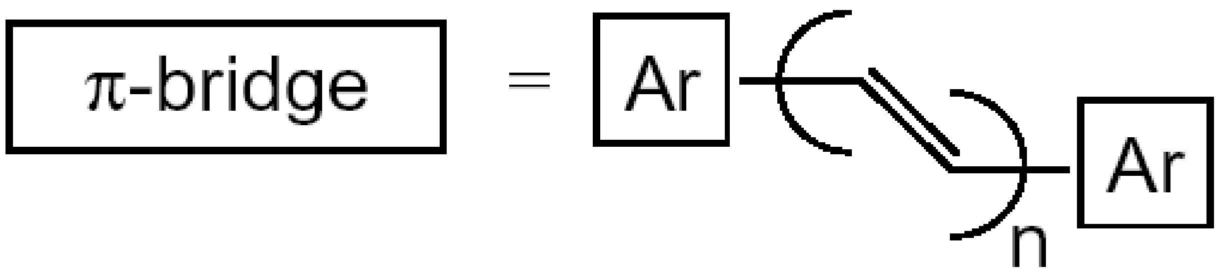
DONOR

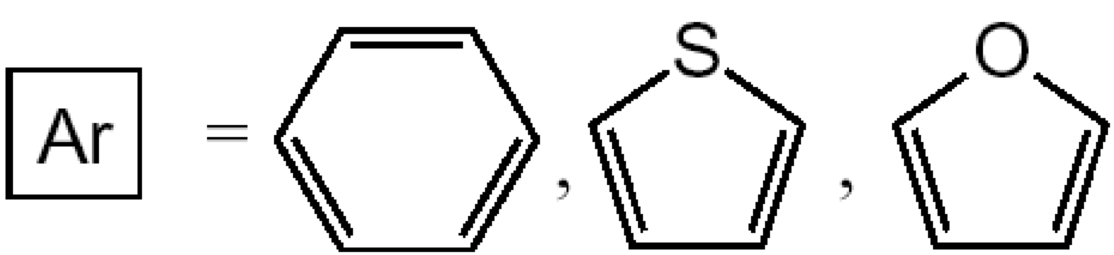
$\beta \neq 0$

ACCEPTOR

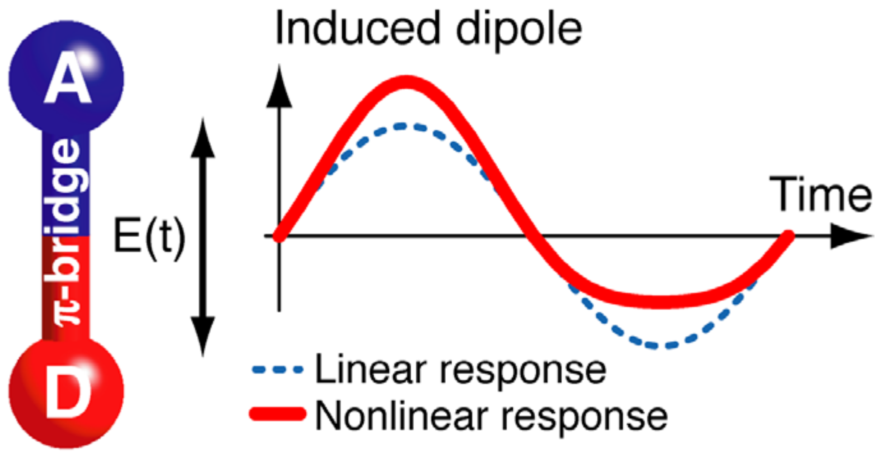
Organic Nonlinear Optical Thin Films

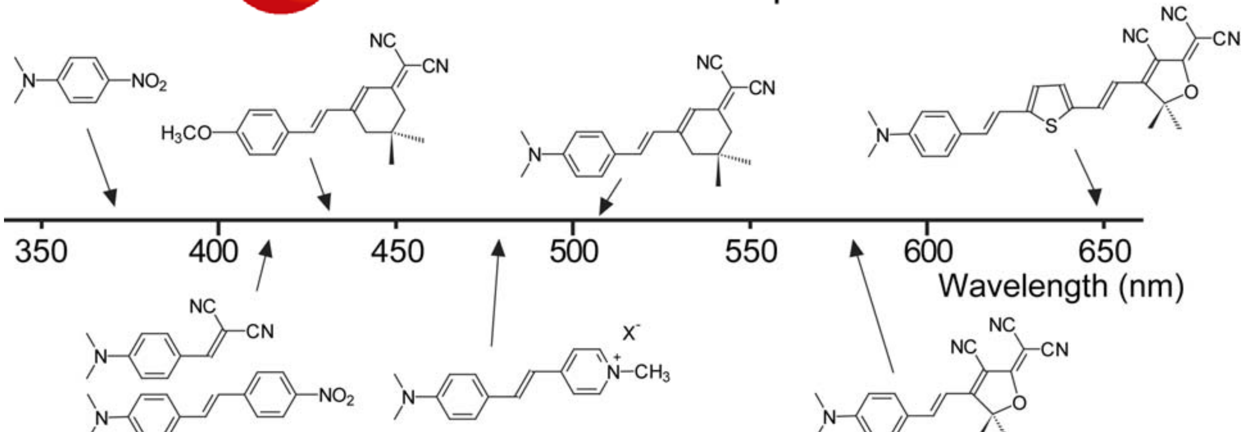
D: electron donor A: electron acceptor





Organic molecules for $\chi^{(2)}$ applications





Oriented gas-model

$$\chi^2(-\omega_3, \omega_1, \omega_2) \propto N \cdot f^3 \cdot g(\theta) \cdot \beta(-\omega_3, \omega_1, \omega_2)$$

nonlinear optics

QuickTime™ and a TIFF (Uncompressed) decompressor are needed to see this picture.

$$d_{ijj} \propto \cos(\theta) \times \sin^2(\theta)$$

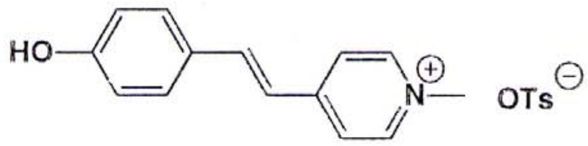
electro-optics

QuickTime™ and a TIFF (Uncompressed) decompressor are needed to see this picture.

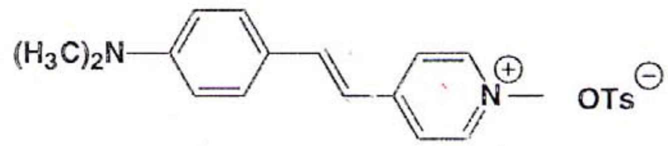
$$r_{iii} \propto \cos^3(\theta)$$

Engineering strategies

(3) Use of ionic salt approach

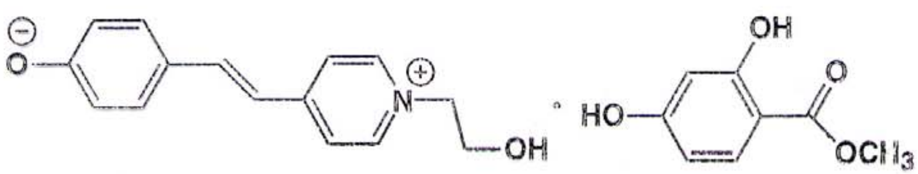


MC-PTS



DAST

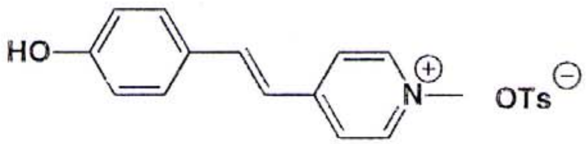
(4) Use of co-crystal approach



Mero-MDB

Engineering strategies II

(3) Use of ionic salt approach



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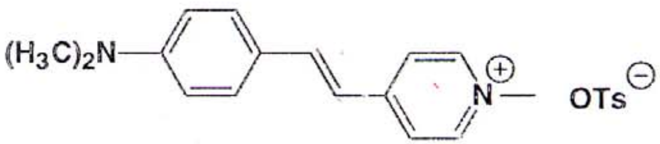

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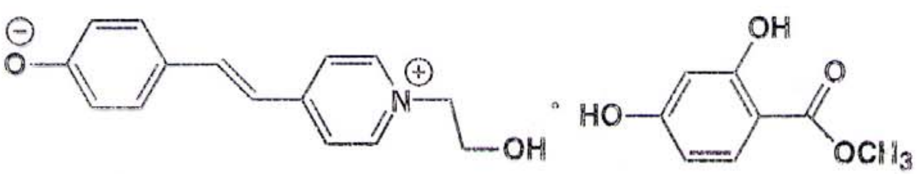
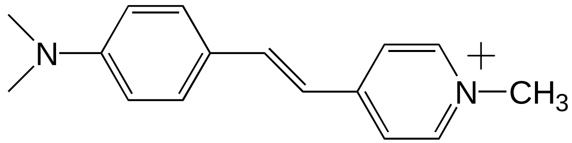
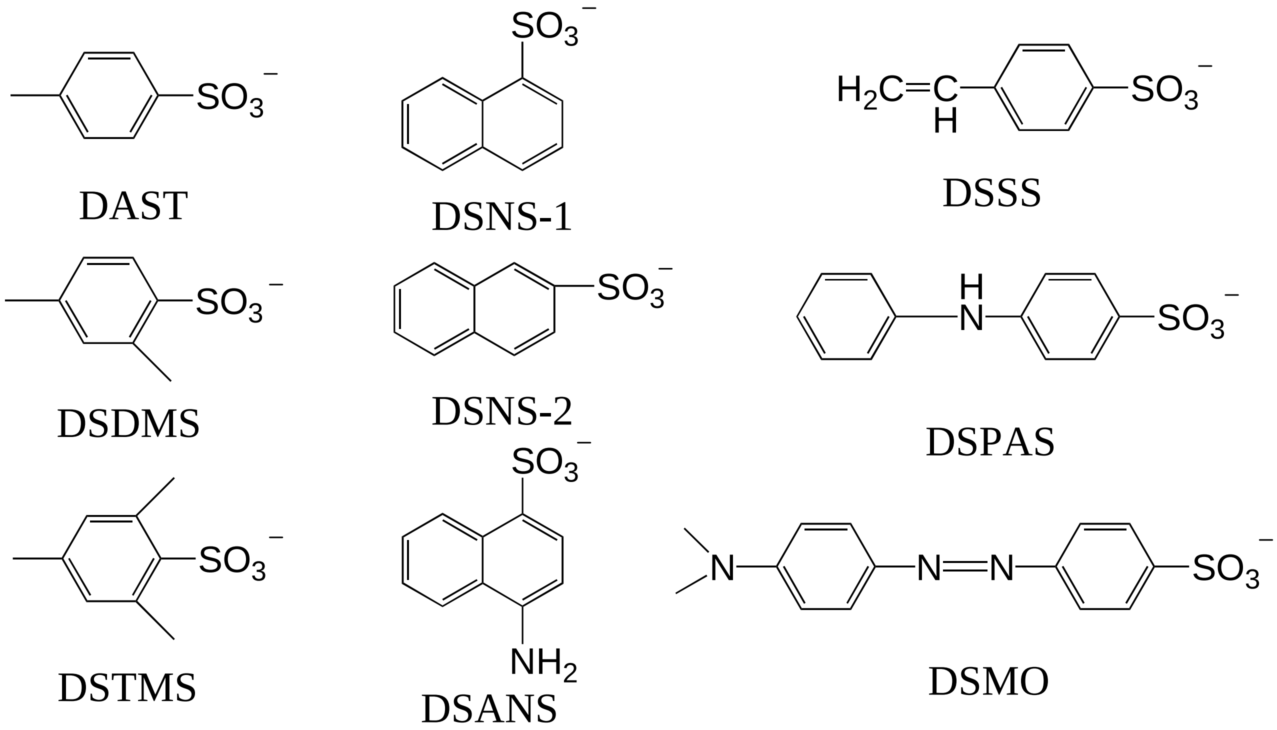


Mero-MDB

NLO Stilbazolium Salts



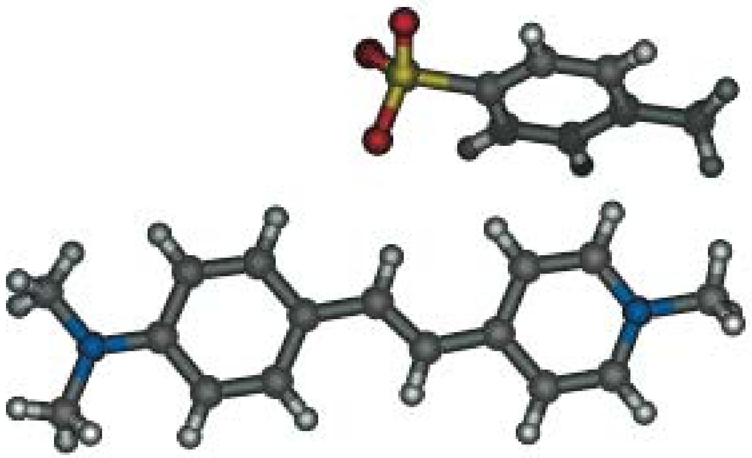
Counter anions and SHG intensities:



Z. Yang et.al.,Cryst. Growth and Design **7**, 83 (2007)

The Organic EO Crystal DAST

(4-N,N-dimethylamino-4'-N'-methyl stilbazolium tosylate)



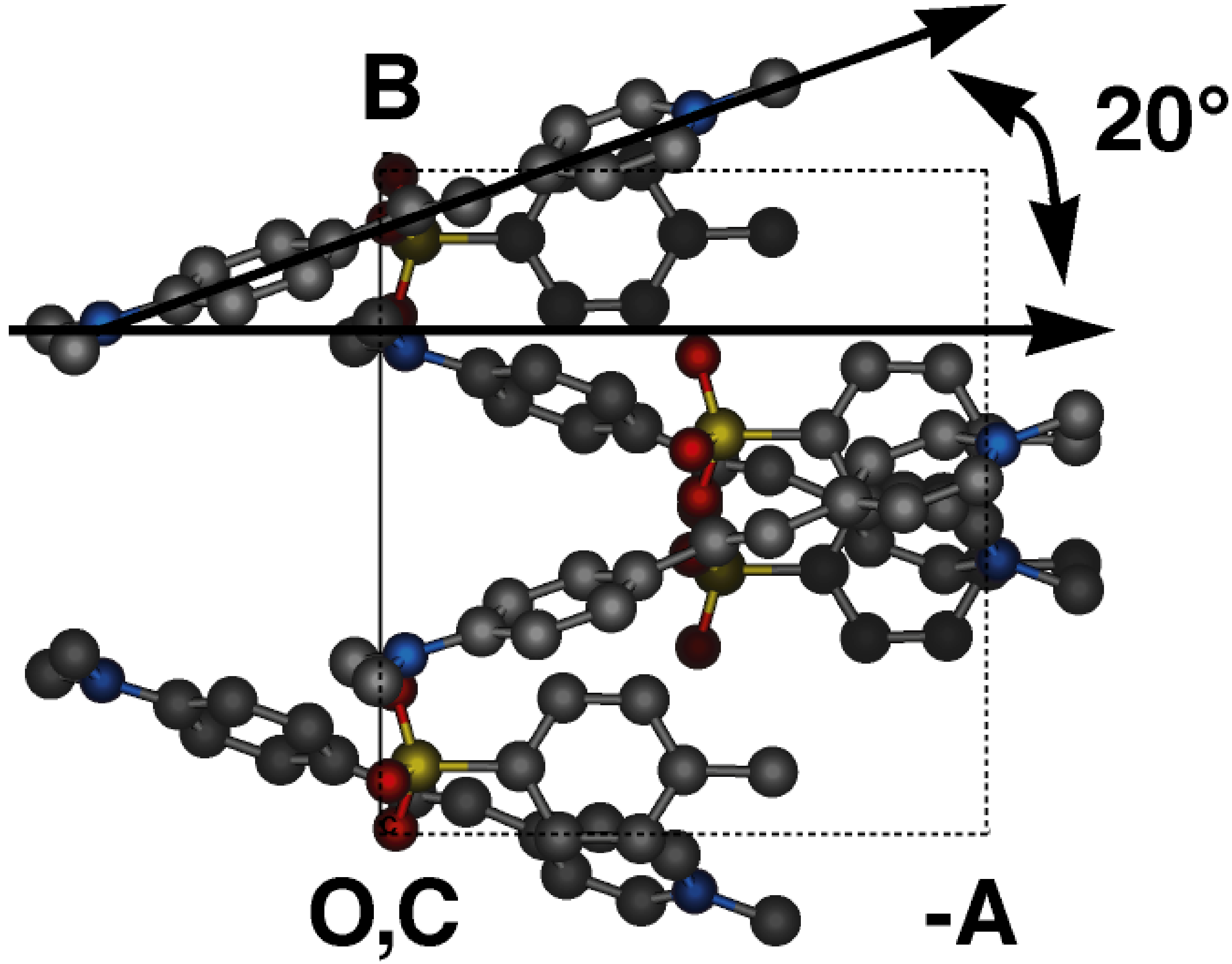
Highly birefringent (n_1-n_2 = 0.7 @ 800 nm)

Electro-optic coefficient r_{11} = 77 pm/V

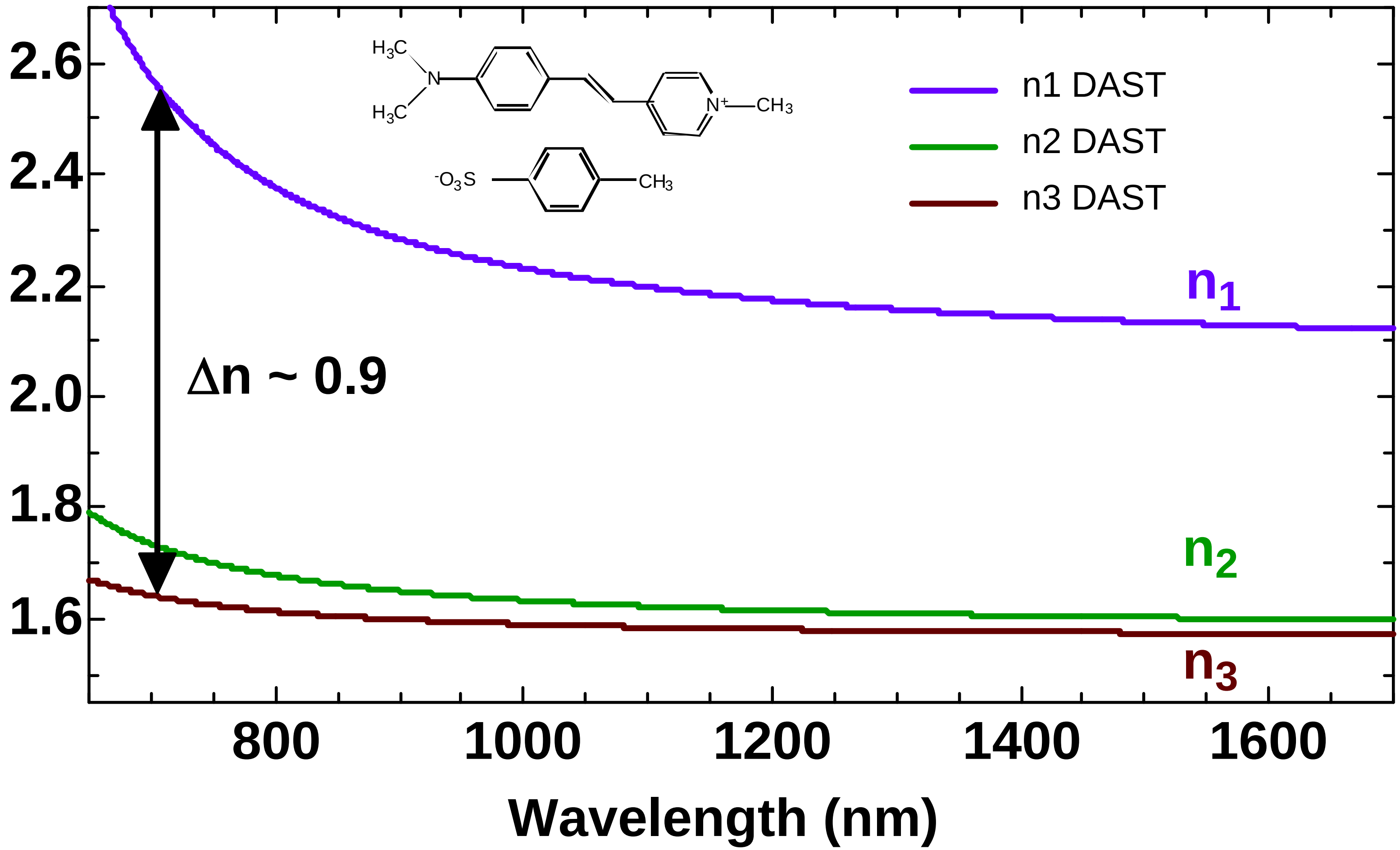
(ZnTe: 4 pm/V, GaAs: 1.5 pm/V)

Producer: Rainbow Photonics AG

DAST Crystal Structure (PGS: 2)



Refractive indices of DAST



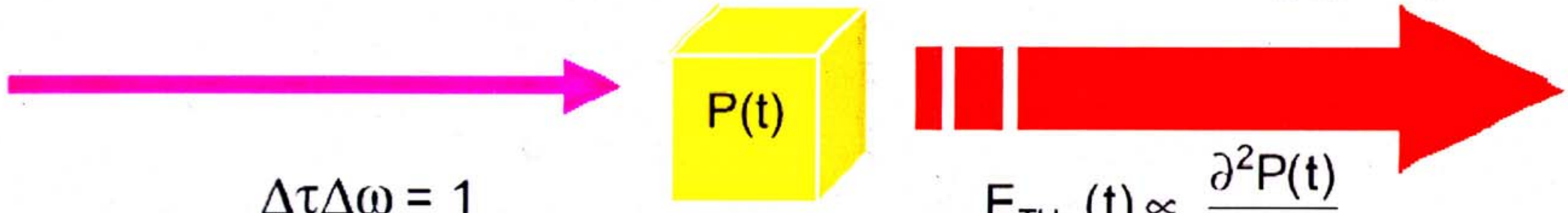
Organic EO/THz Materials

Small Lattice Polarizability leads to:

- Similar Refractive Indices at Optical, Electrical and THz Frequencies
- Mainly Electronic EO Effect
- Fast EO Response
- Small Mismatch of Electrical and Optical Waves in Travelling Wave EO Modulators
- Phase Matched THz Generation

THz Optical Rectification

Input laser pulse $I(t, \omega, \Delta\omega)$ EO crystal THz pulse $E_{THz}(t, \Omega)$



$\Delta\tau\Delta\omega = 1$

$$E_{THz}(t) \propto \frac{\partial^2 P(t)}{\partial^2 t}$$

Beating frequency $\Omega < \Delta\omega$ (laser bandwidth)

Dielectric polarization: $P(\Omega) = \chi^{(2)}(\Omega, \omega+\Omega, -\omega)\, E(\omega+\Omega)E^*(\omega)$

$$E_{THz}(t) \propto \frac{\partial J(t)}{\partial t} = \frac{\partial^2 P(t)}{\partial^2 t} = \chi^{(2)} \frac{\partial^2 I(t)}{\partial^2 t}$$

NLO fs pulses

THz Spectrum (Theory)

$$S(\omega) = S_0\, \chi^{(2)}\, \omega^2\, e^{-\tau^2\omega^2/2}$$

$$\times \frac{1 - \exp\left(-\alpha(\omega)\, L_{crys}/2 - i\, \Delta k(\omega)\, L_{crys}\right)}{\alpha(\omega)/2 + i\Delta k(\omega)}$$

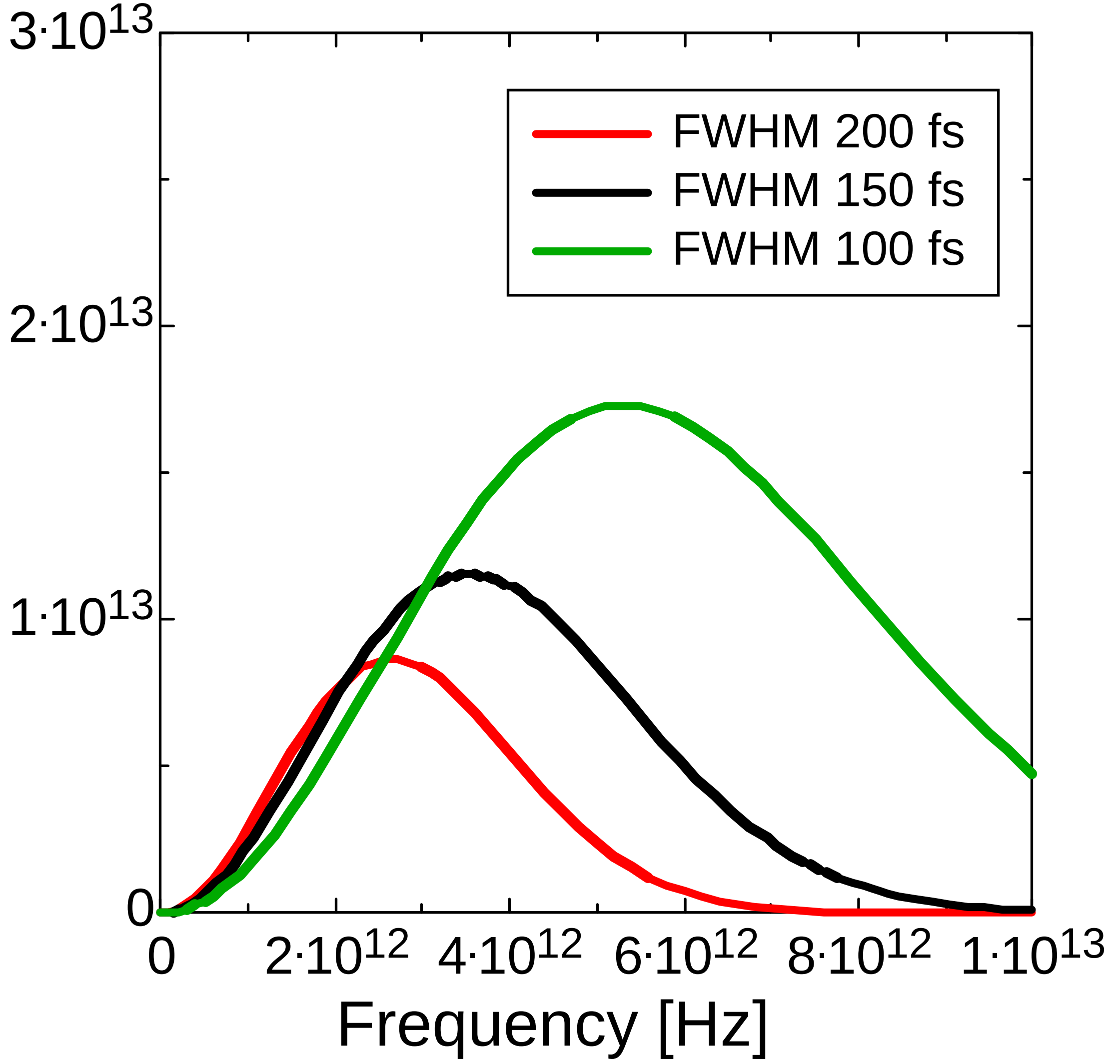
with $$\Delta k(\omega) = \frac{\omega\, \left(n(\omega) - n_{g,opt}\right)}{c}$$

Material independent: ***Optical Rectification***

Material: ***Nonlinearity***

Material: ***Propagation effects (Velocity-matching, absorption)***

Source Term



3·10^13
2·10^13
1·10^13
0
FWHM 200 fs
FWHM 150 fs
FWHM 100 fs
0
2·10^12
4·10^12
6·10^12
8·10^12
1·10^13
Frequency [Hz]

THz Spectrum (Theory)

$$S(\omega) = S_0 \, \chi^{(2)} \, \omega^2 \, e^{-\tau^2\omega^2/2}$$

$$\times \frac{1 - \exp\left(-\alpha(\omega) L_{crys}/2 - i\,\Delta k(\omega) L_{crys}\right)}{\alpha(\omega)/2 + i\Delta k(\omega)}$$

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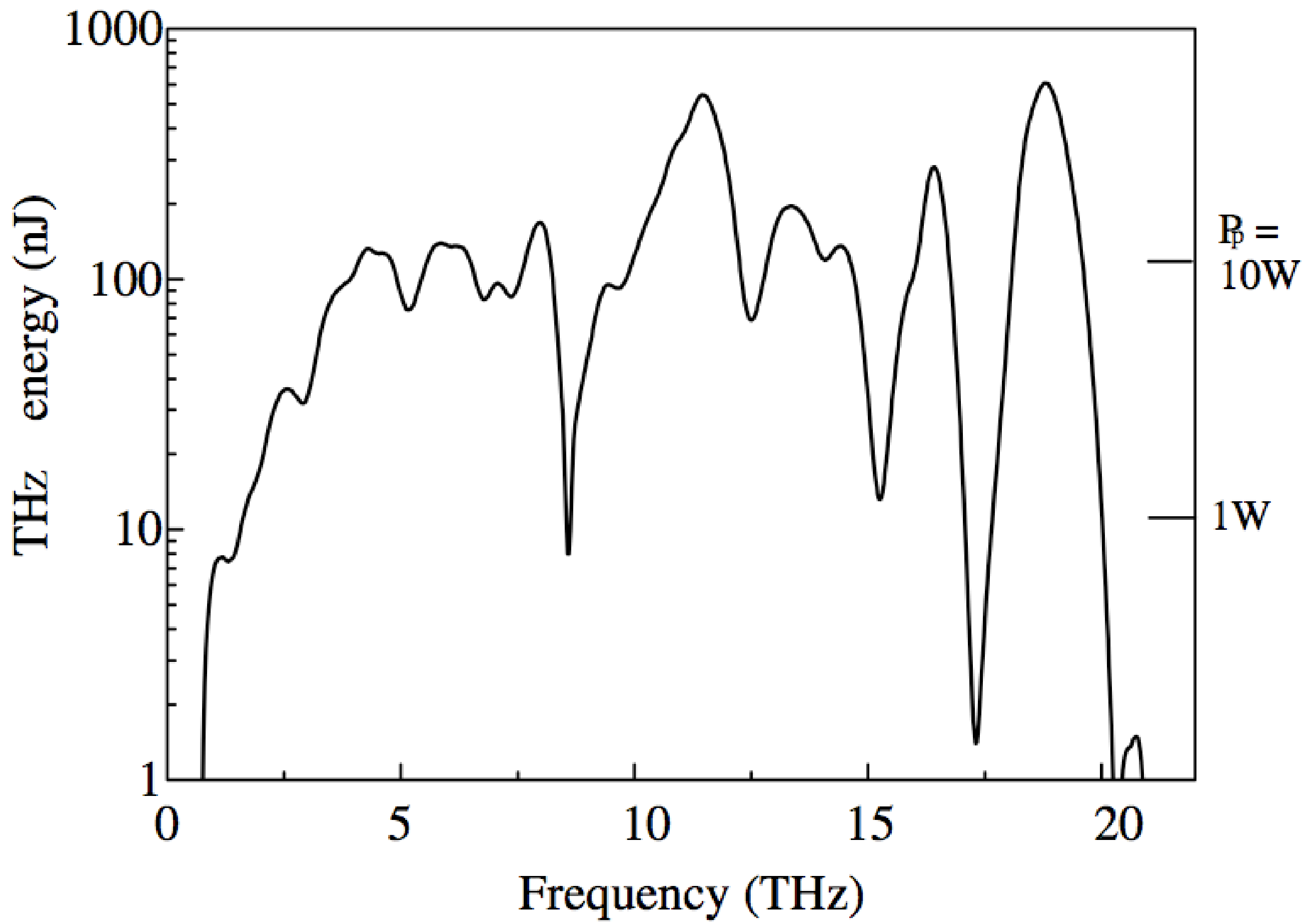
Energy of THz-Waves Generated in DAST



Reference: T. Taniuchi et al., *Nonlinear Optics, Quantum Optics*, **34**, 57 (2005)

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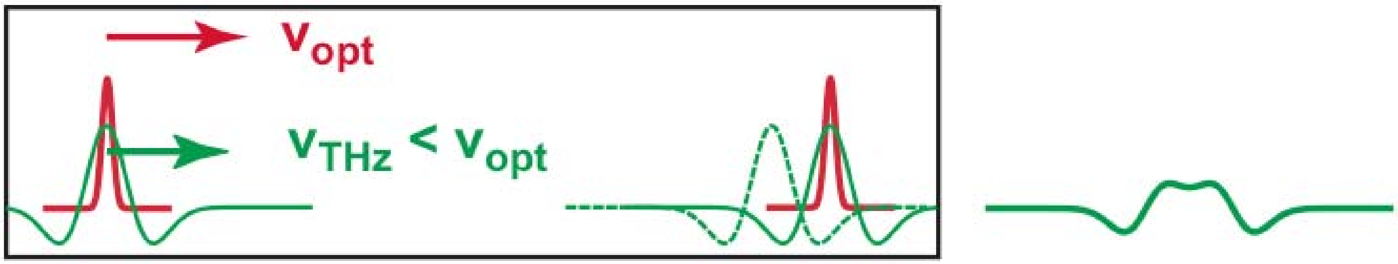
Material independent: ***Optical Rectification***

Material: ***Nonlinearity***

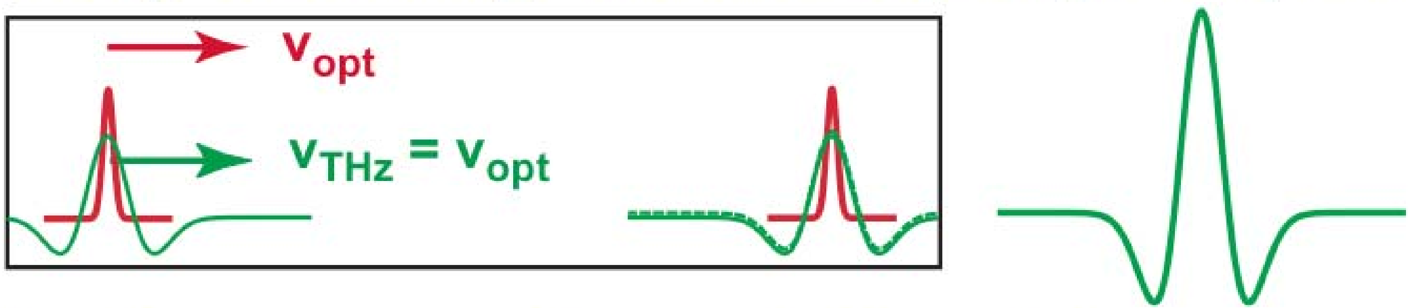
Material: ***Propagation effects***
(Velocity-matching, absorption)

Velocity-matching

Velocity-mismatch: Distortion, low output

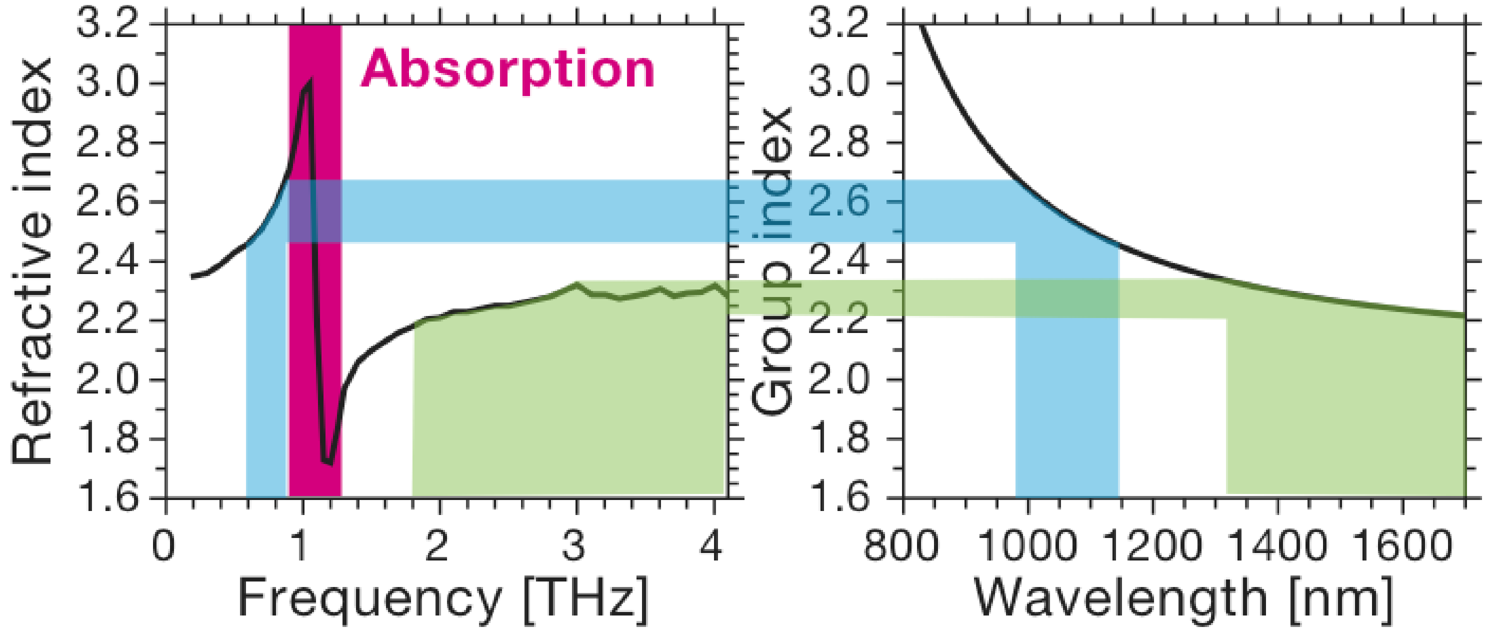


Velocity-matching: Undistorted high output



Effect increases with crystal length!

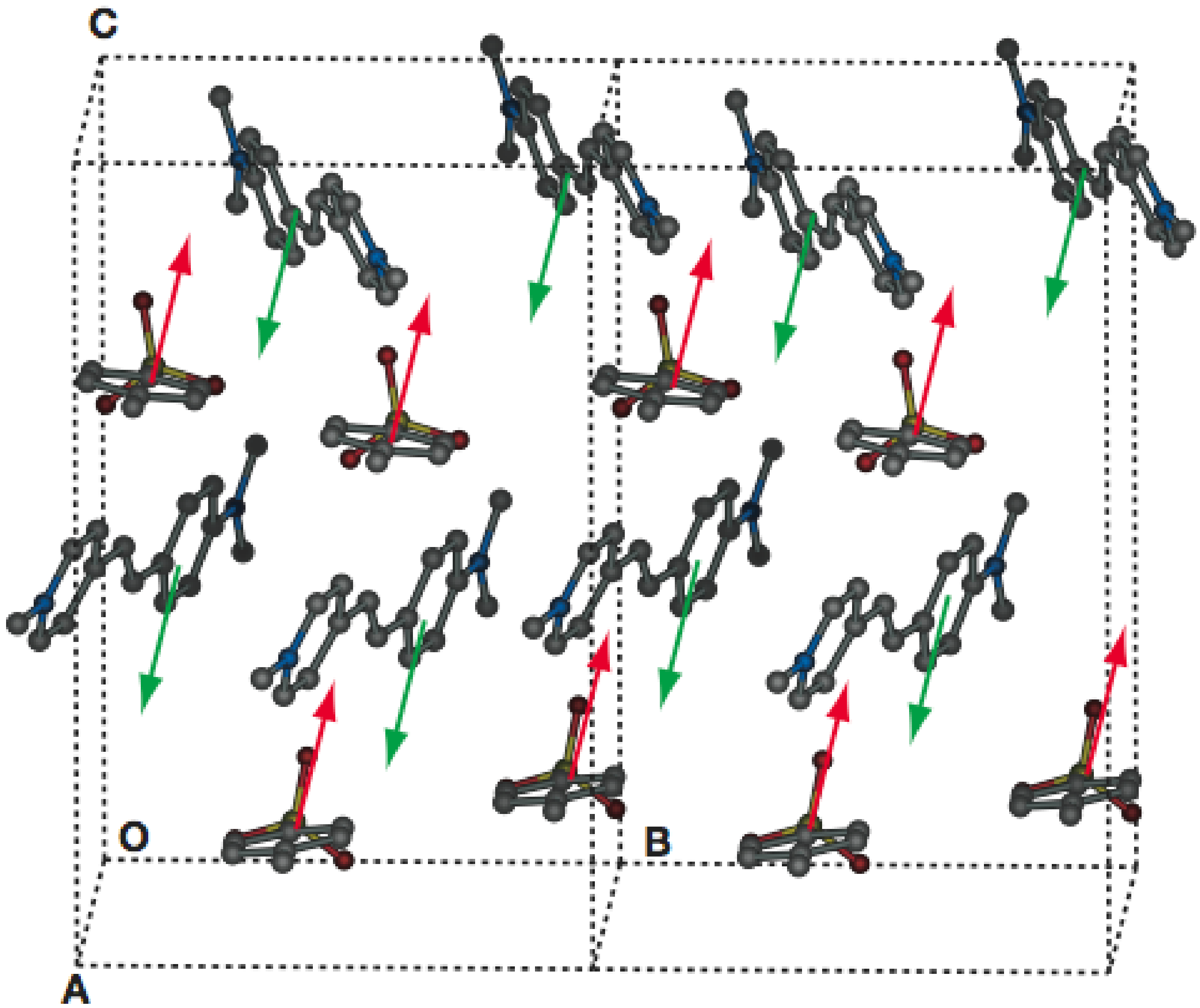
DAST: Dispersion of Refractive Indices



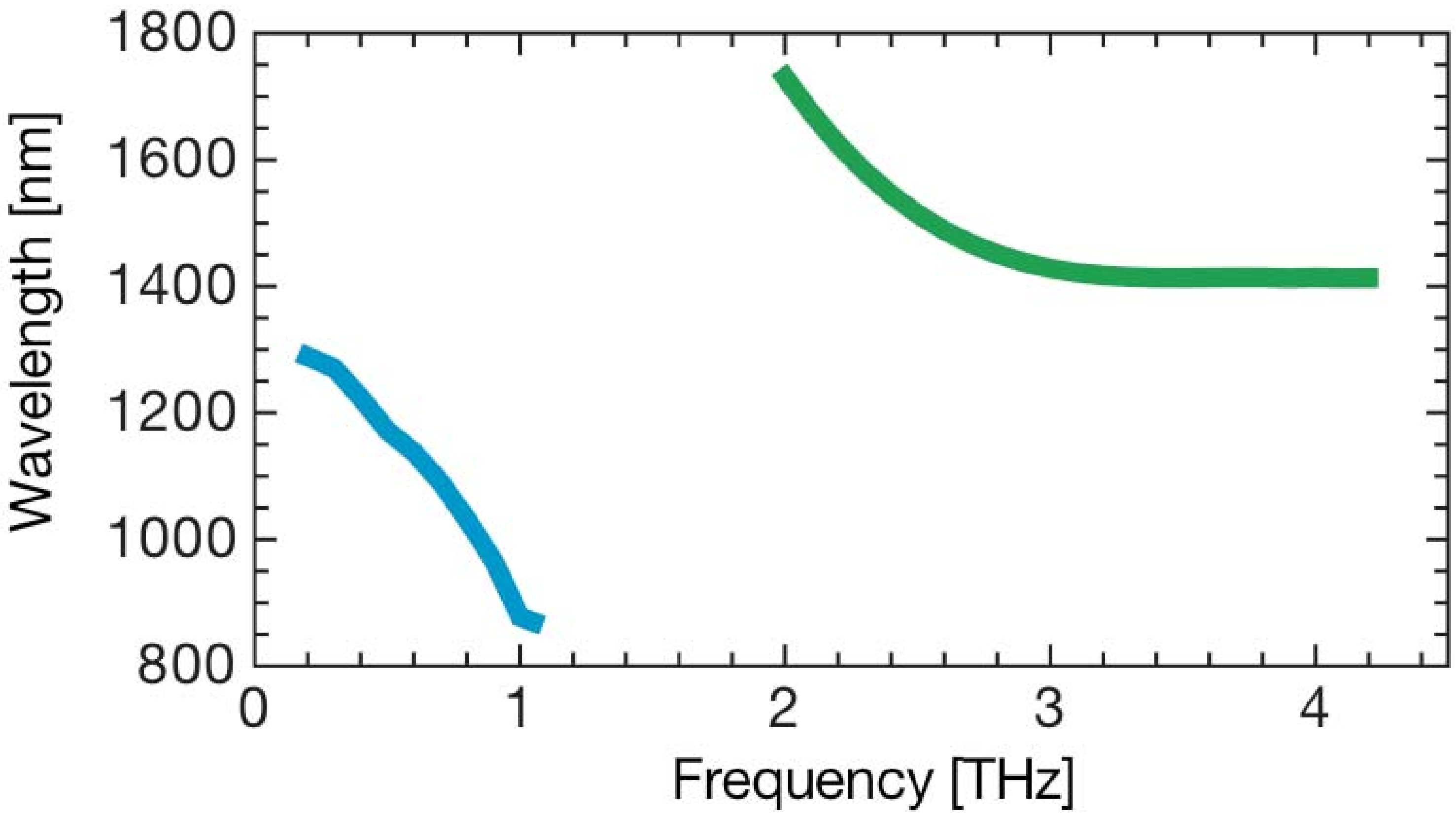
0.5 ... 0.8 THz matches 950 ... 1150 nm

1.8 ... >4 THz matches 1300 ... 1700 nm

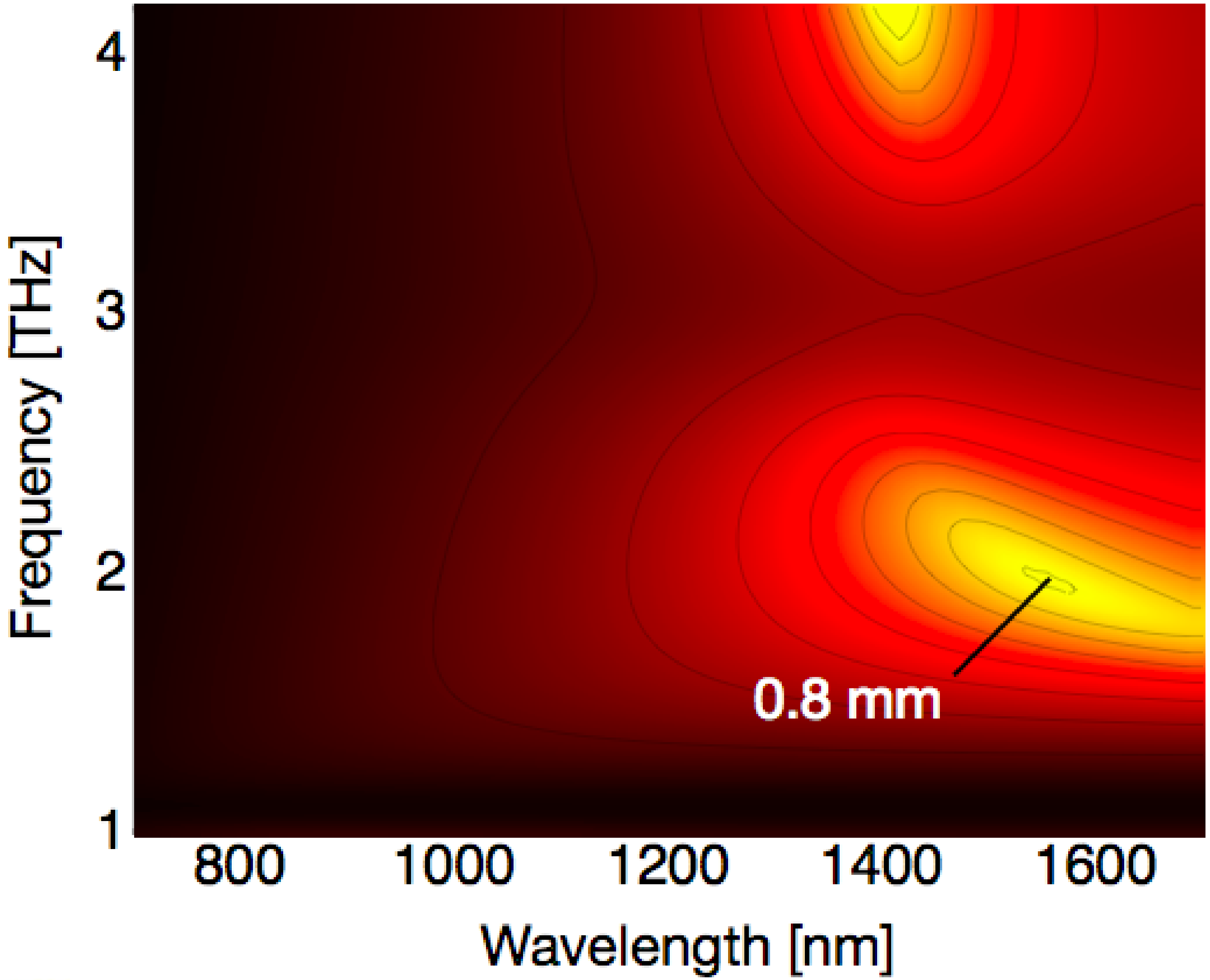
TO Phonon in DAST (1.1 THz)



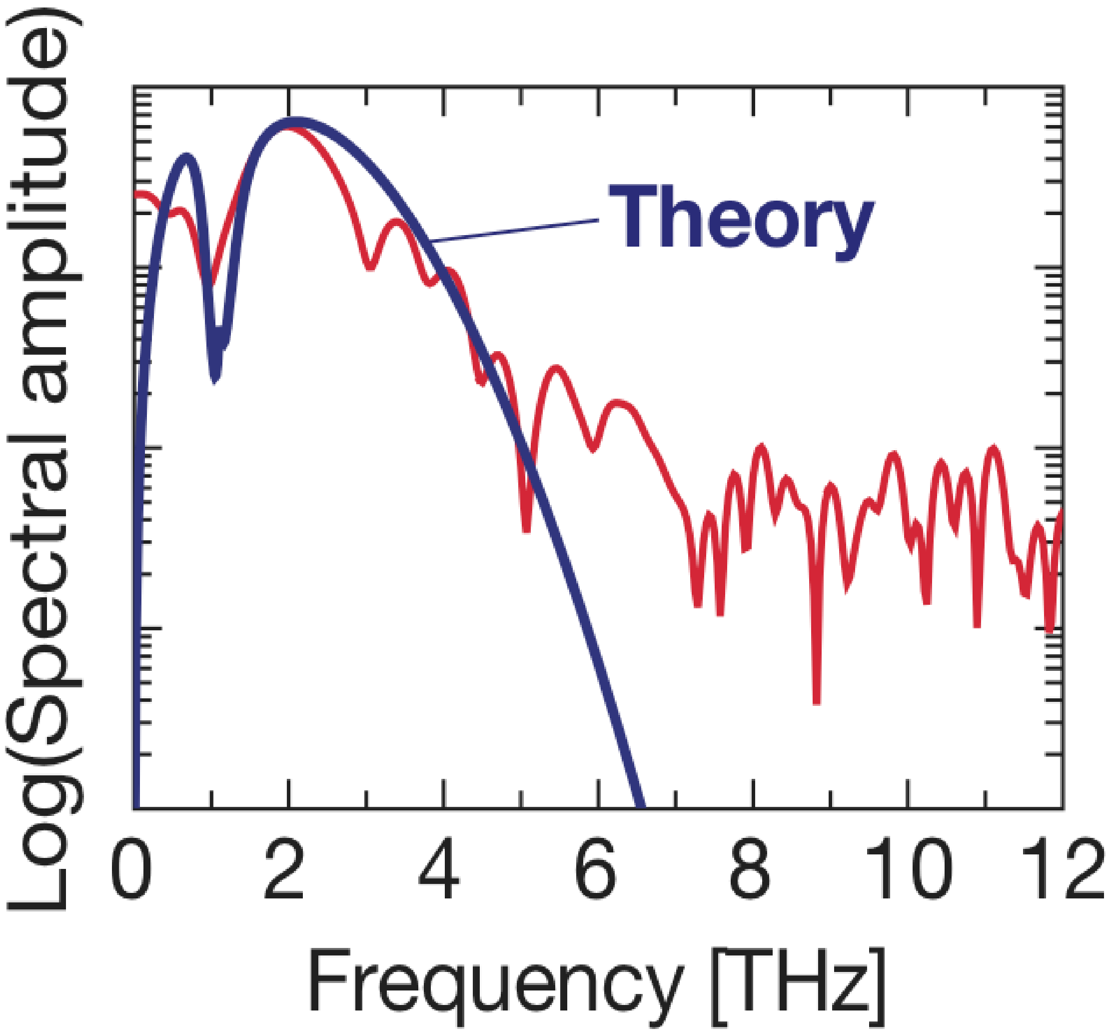
Velocity-matching in DAST



Effective generation length in DAST



THz Pulse Amplitude (λ = 1350 nm)



2005

DAST Derivatives

How to bridge the gap?

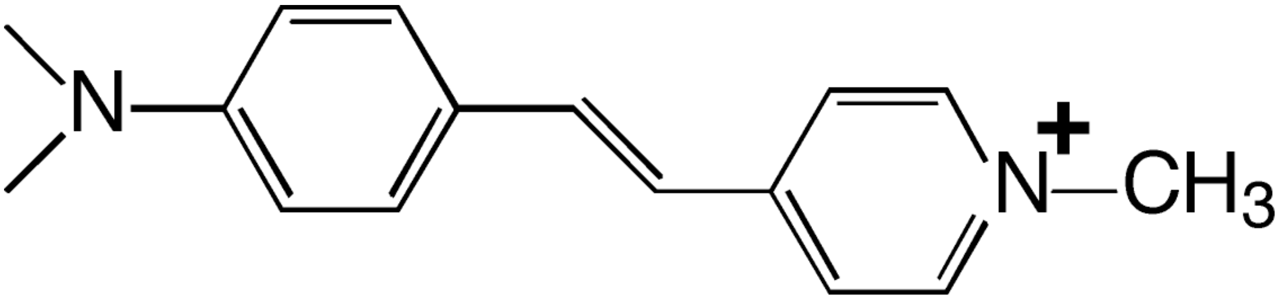
⇨ Modify the chemical structure of DAST without compromising its high nonlinearity

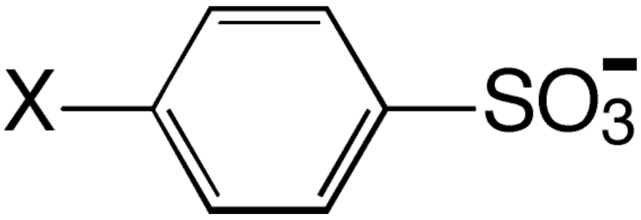
Behavior of the TO phonon at 1.1 THz?

- Reduction of the absorption coefficient

Derivatives:	- DSMOS	- DSXYS
	- DASC	- DSTMS
	- DANS	- …

Stilbazolium Salts I

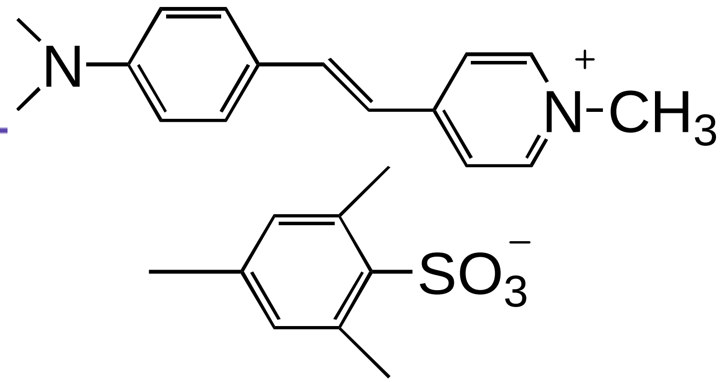




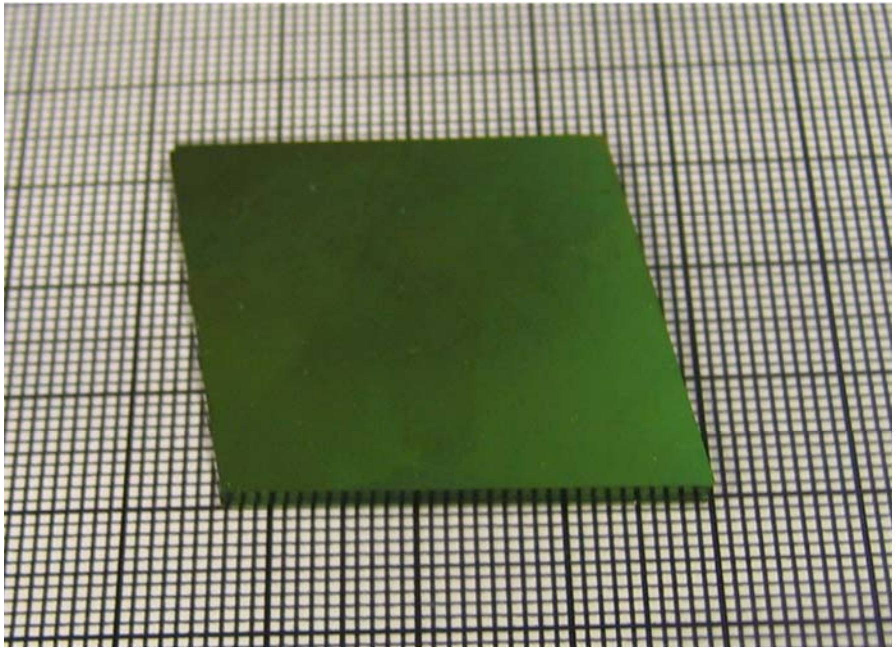
X	Abbreviation
OH	DSHS
OCH_3	DSTMS *
NH_2	DSAS
$N(CH_3)_2$	DSMAS
CH_3	DAST

*: 4-N,N-**D**imethylamino-4'-N'-methyl-**ST**ilbazolium 2,4,6-tri**M**ethylbenzene**S**ulfonate

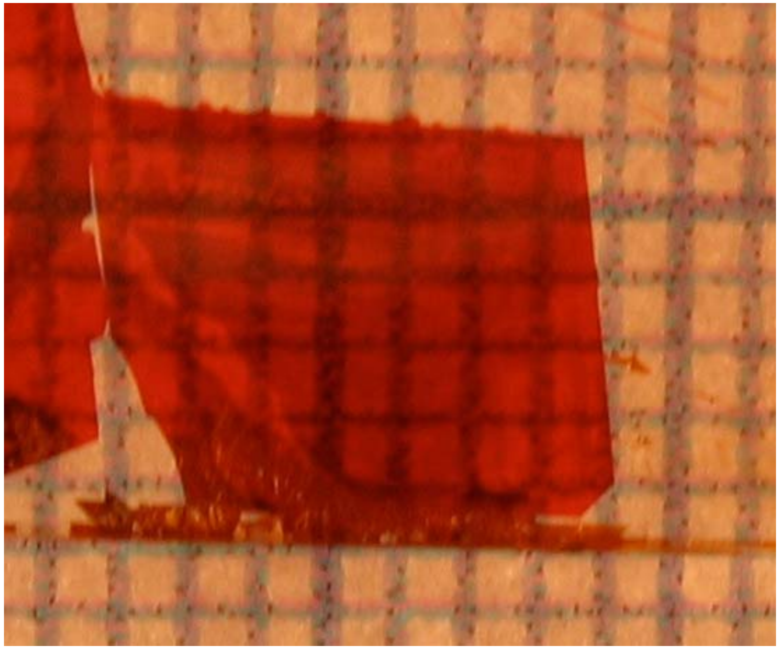
DSTMS



BULK 33 x 33 x 2 mm^3



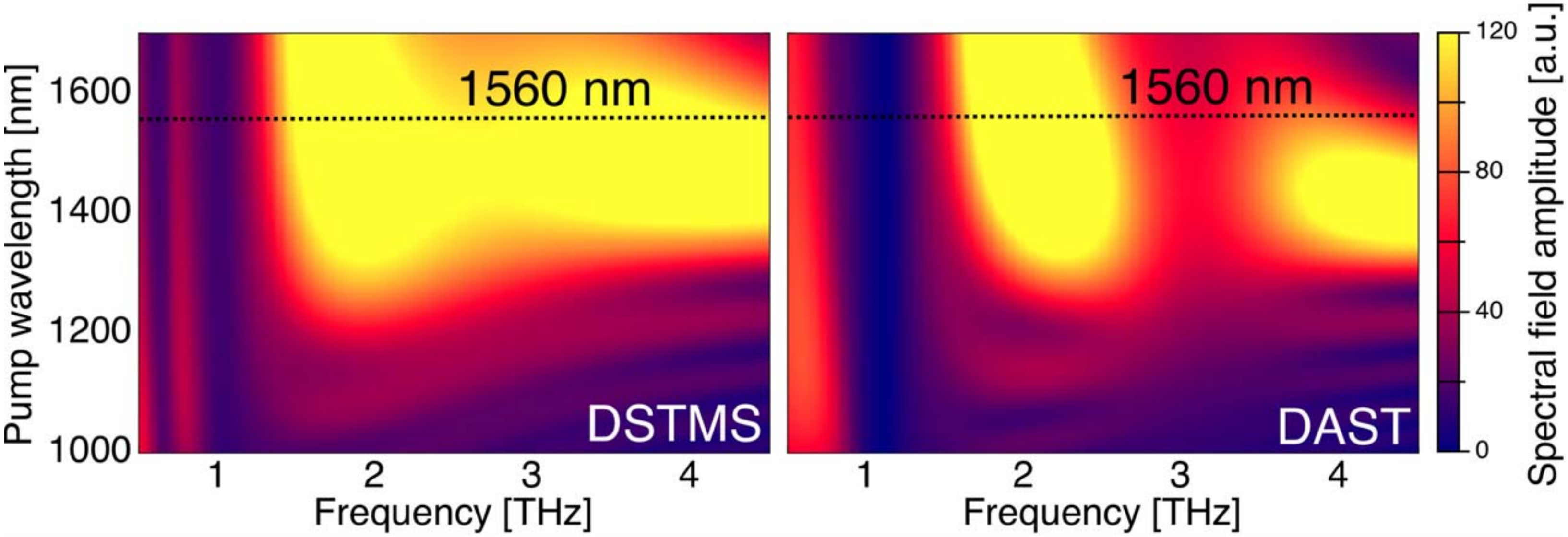
THIN 6 x 5 x 0.03 mm^3



Z. Yang et al, Adv. Funct. Mater. 17 (2007)

Emitted THz Field

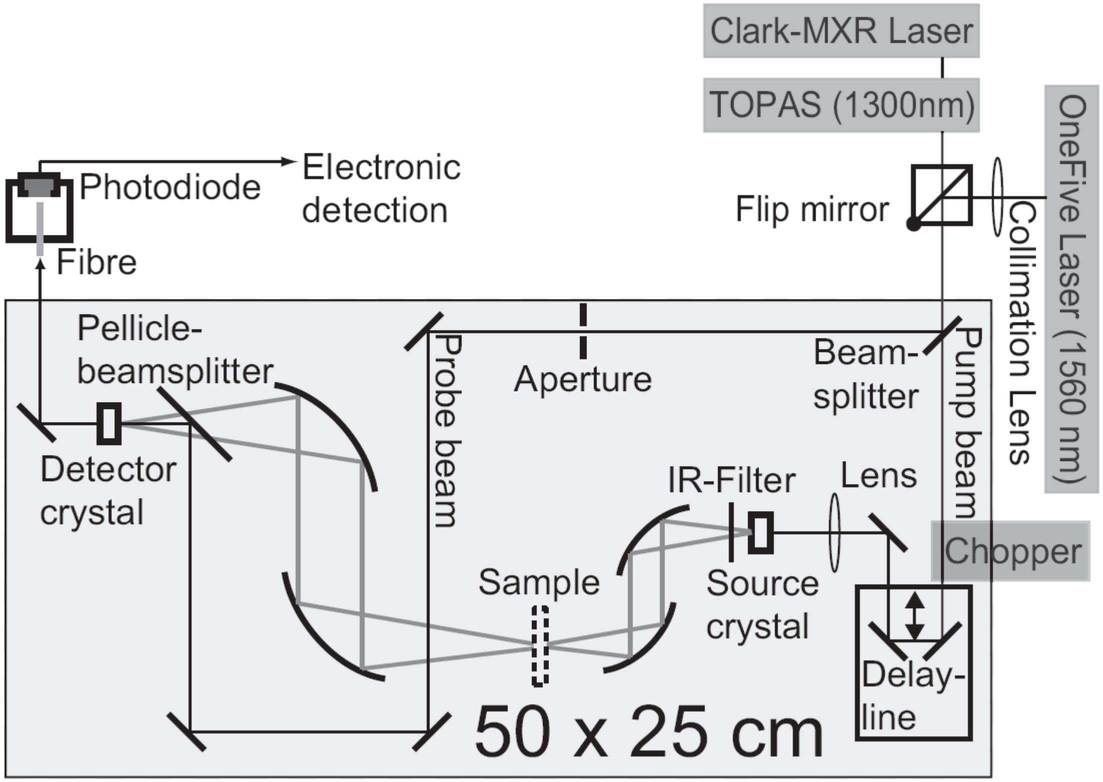
Source: 0.45 mm, FWHM = 100 fs



- Increased amplitude near the resonances around 1 THz and 3 THz

  ⇨ flatter THz spectrum than for DAST

Set up THz Generation and Detection



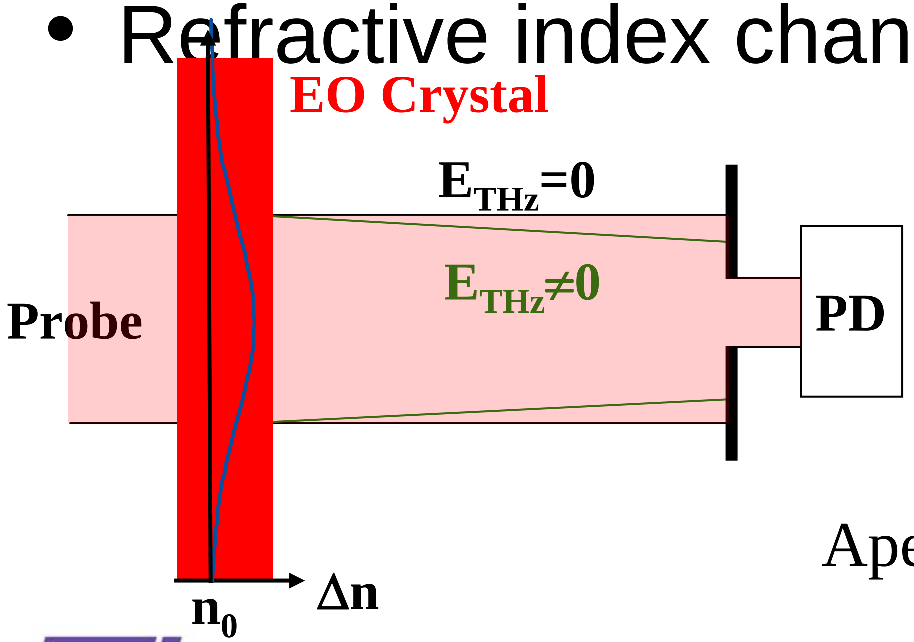
THz Pulse Generation by Optical Rectification, Detection : THz-induced Lensing .

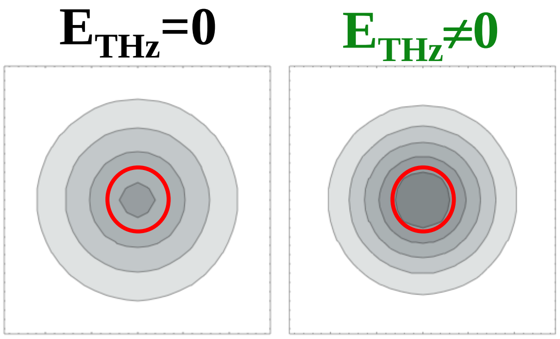
Terahertz-Induced Lensing

- THz signal on the detector crystal induces a refractive index change that follows the field distribution:

$$\Delta n(x,y) = -\frac{n^3}{2} r E_{THz}(x,y)$$

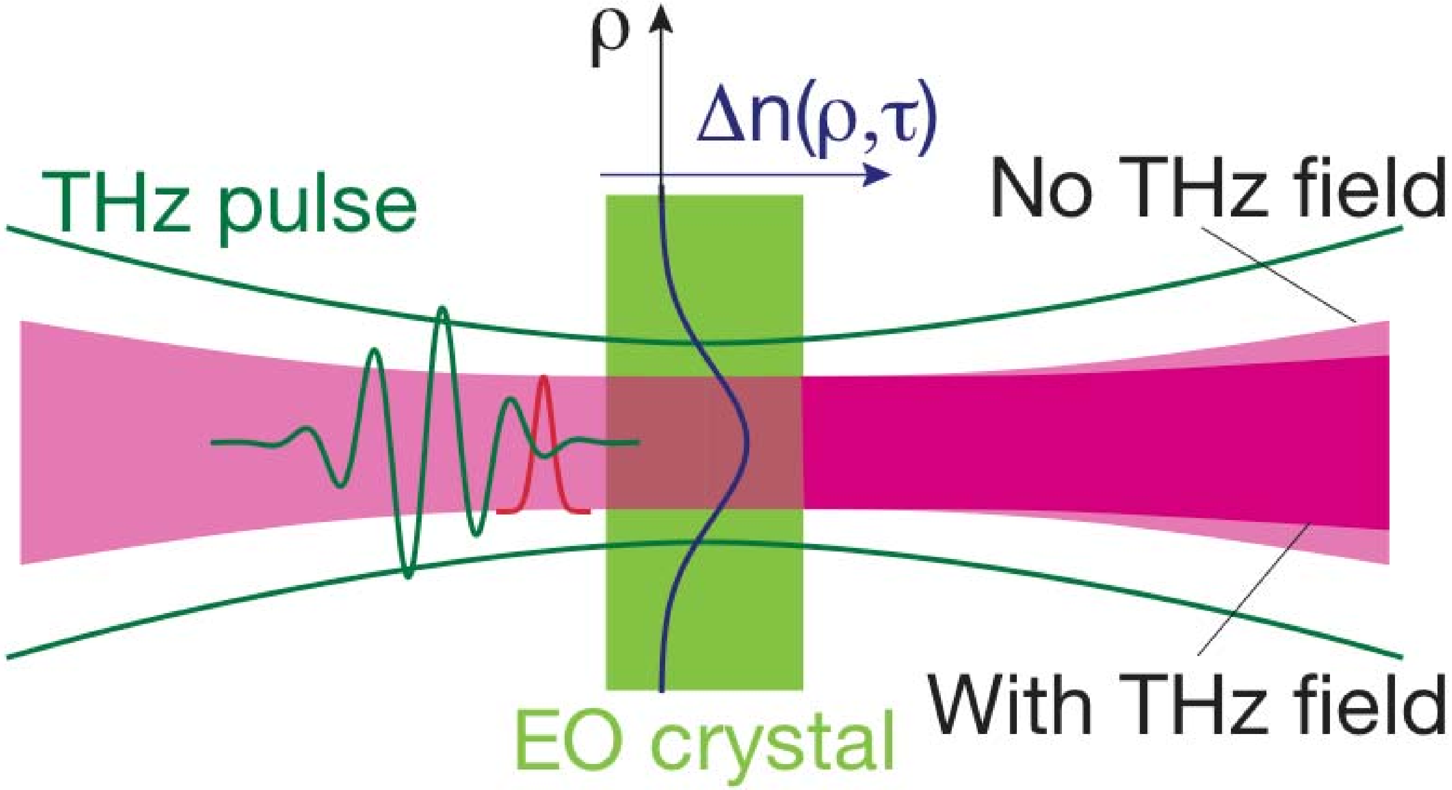
- Refractive index change acts as a lens



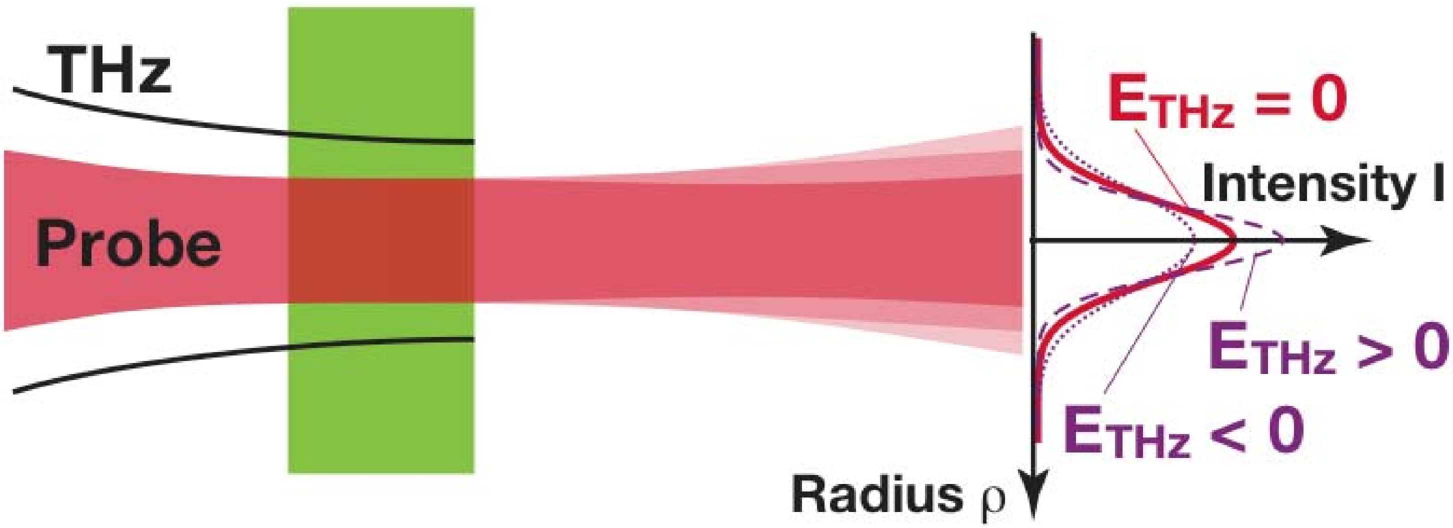


Aperture: detect central intensity

THz-induced lensing (TIL)



Read-out of THz-induced lensing



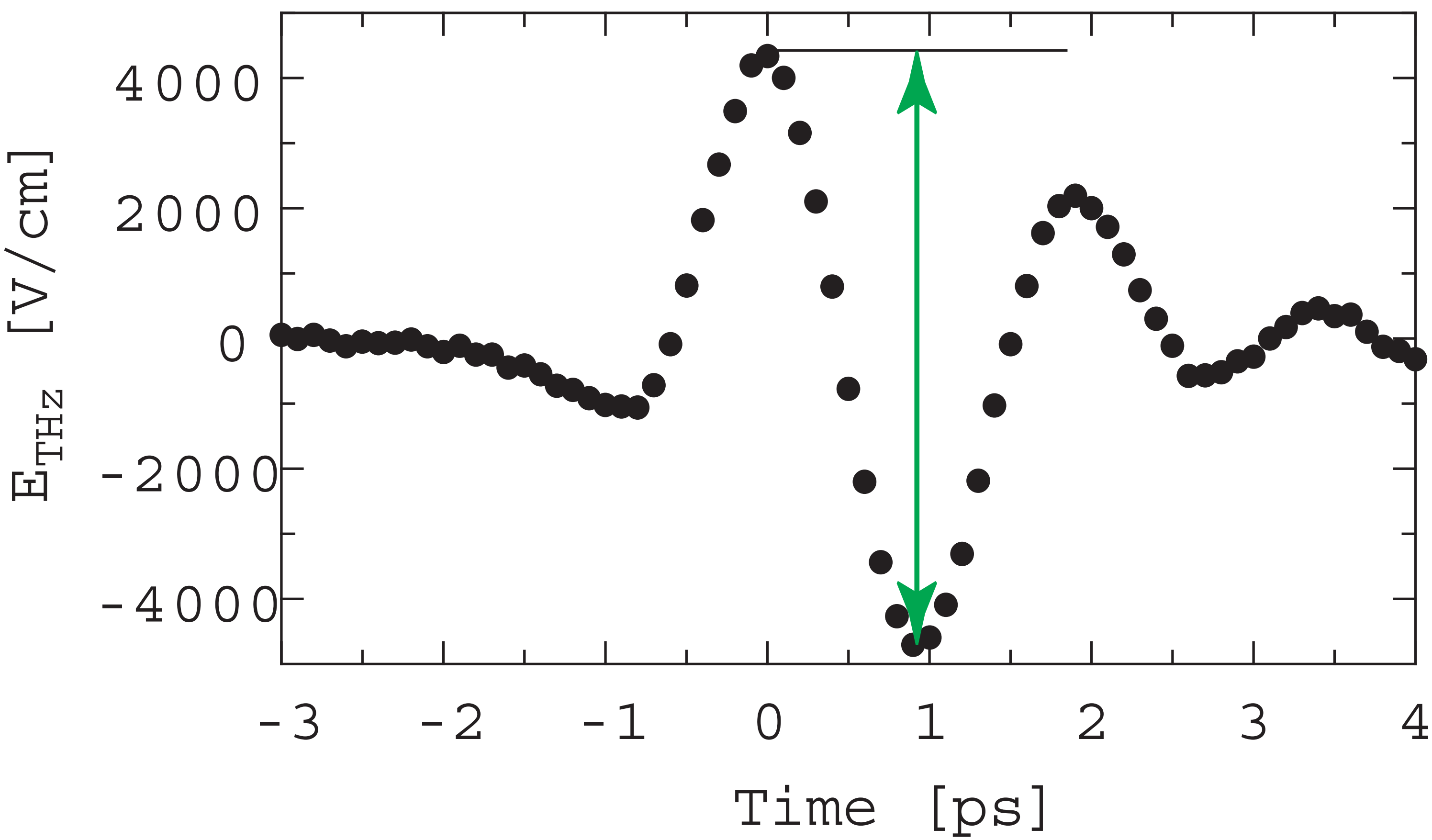
First order approximation: $\Delta I(\rho=0) \sim E_{THz}$

Delay probe pulse relative to THz pulse
-> Sample $E_{THz}(\tau)$

Ref: A. Schneider et al., APL **84**, 2229 (2004)

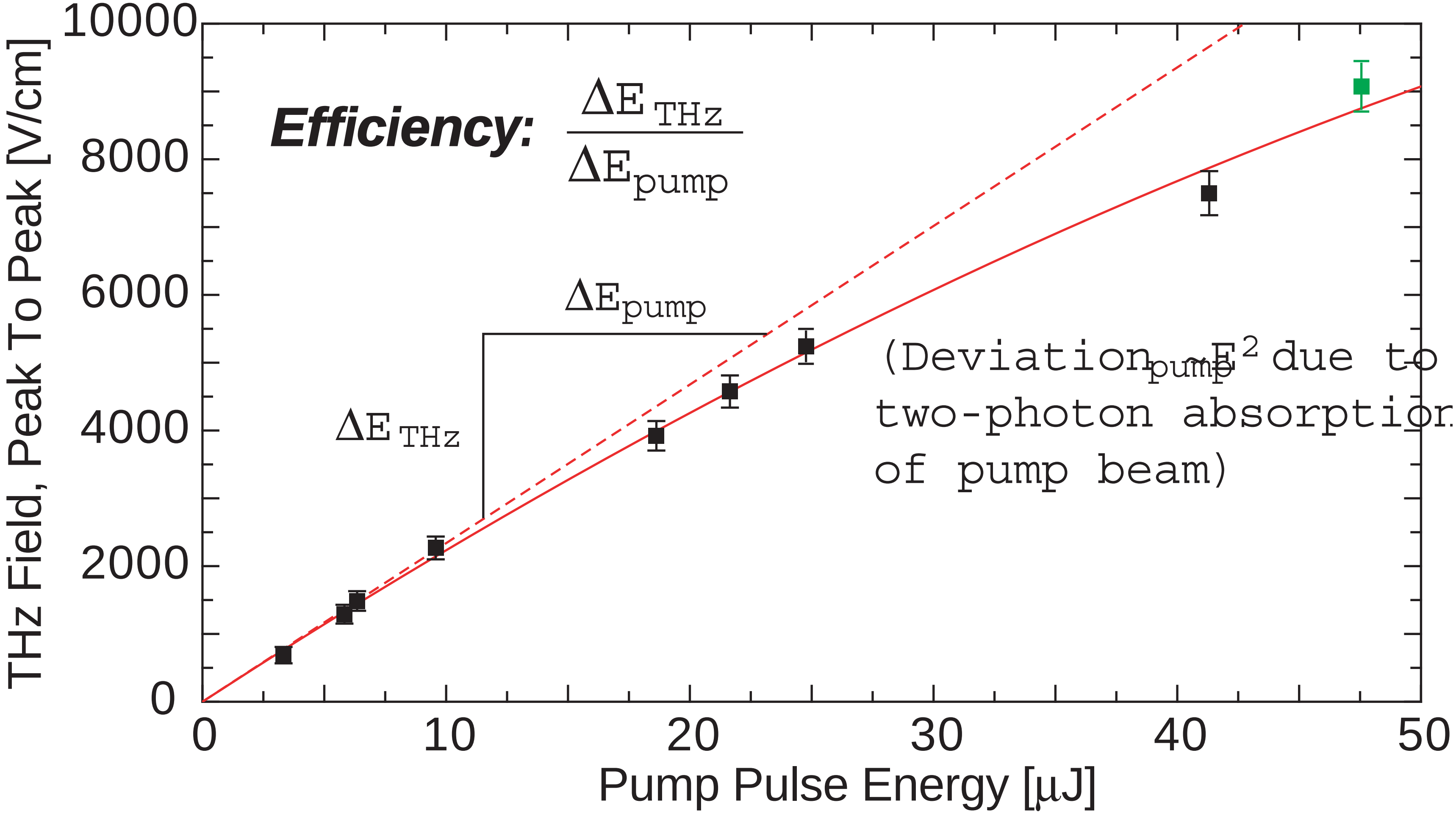
THz Temporal Waveform

- λ = 1125 nm, pump pulse energy E = 48 μJ

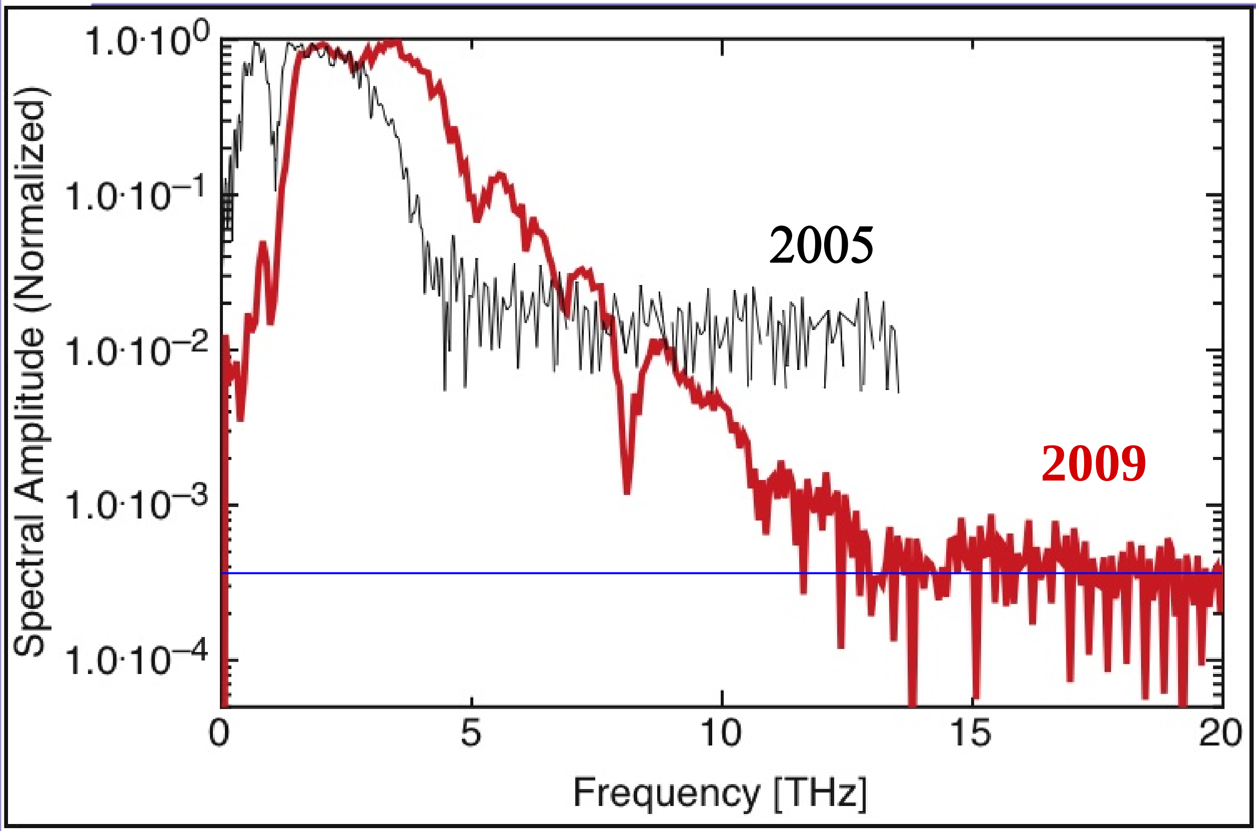


Pump Energy Dependence of E_{THz}

- λ = 1125 nm



THz Generation in DSTMS



<u>1.5 μm Laser:</u>
- 70 fs
- 100 MHz
- P_{avg}=150 mW

- 0.3 to 12 THz
  (Small Resonances at 0.65/1.02/2.7/5.1/8.05 THz)
- Dynamic Range: 3 10^3 (65 dB Spectral Power)
- Scan Time: 20 s

Summary: DSTMS Crystals

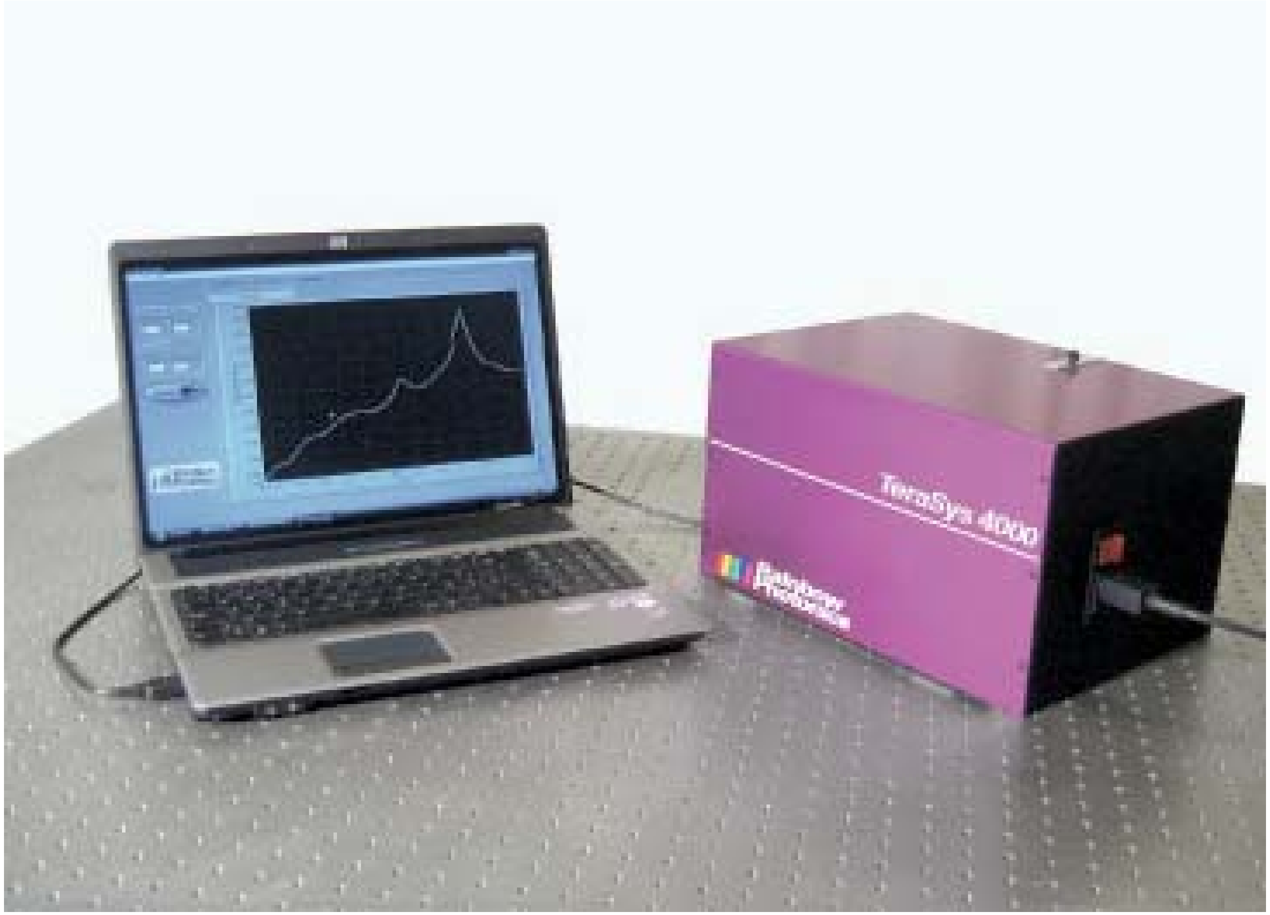
	DSTMS (organic)	**ZnTe*** (inorganic)
Velocity-matching Wavelength λ_m:	1400-1700 nm	750-850 nm
$\chi^{(2)}$ (Generation)	490 pm/V	137 pm/V
r (Detection)	47 pm/V	4.2 pm/V

Telecom Lasers!

DSTMS Detector

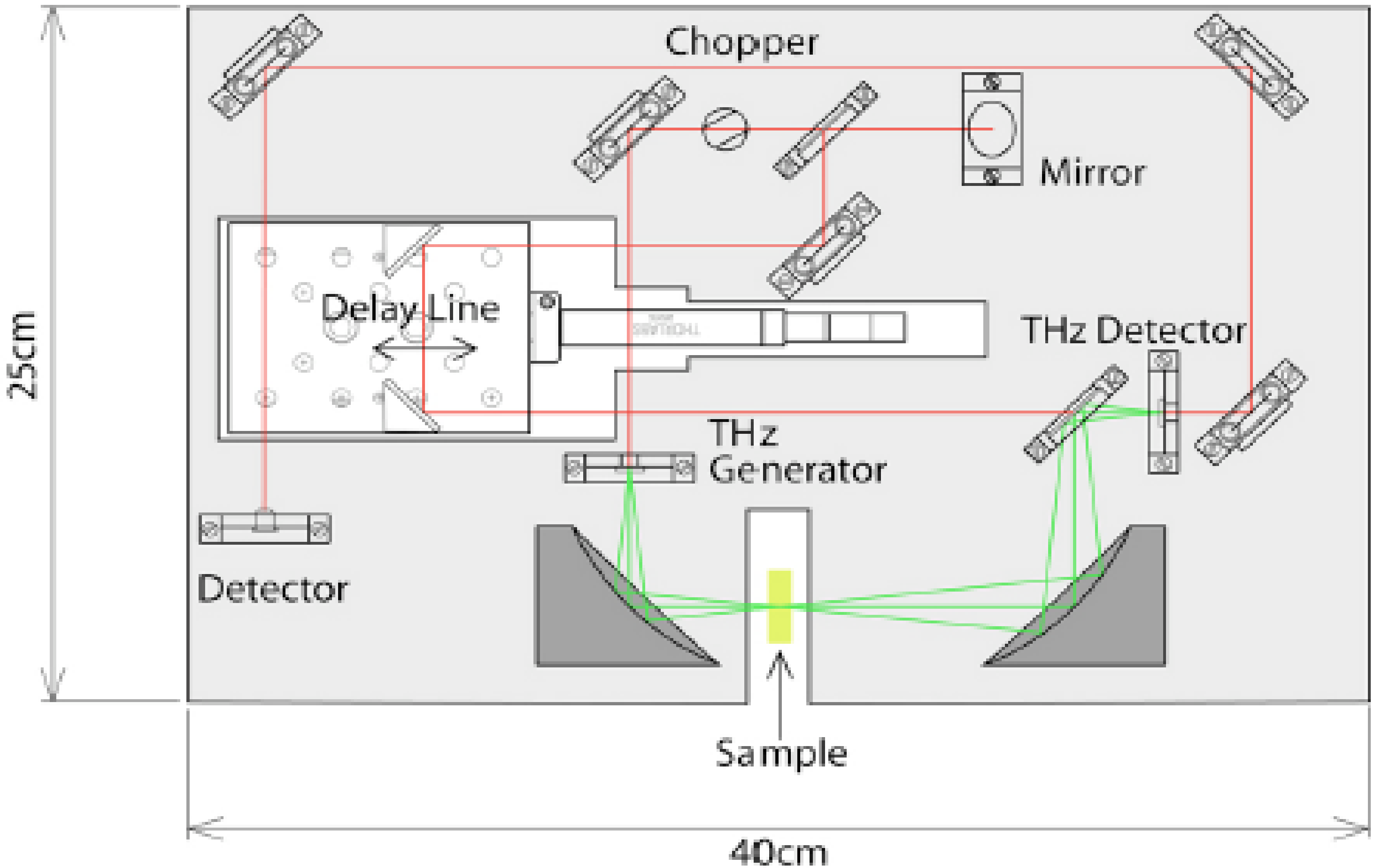
A. Schneider, M. Stillhart, P. Günter,
Opt. Express **14**, 5376-5384 (2006)

TeraSys 4000 (0.3 - 4 THz)

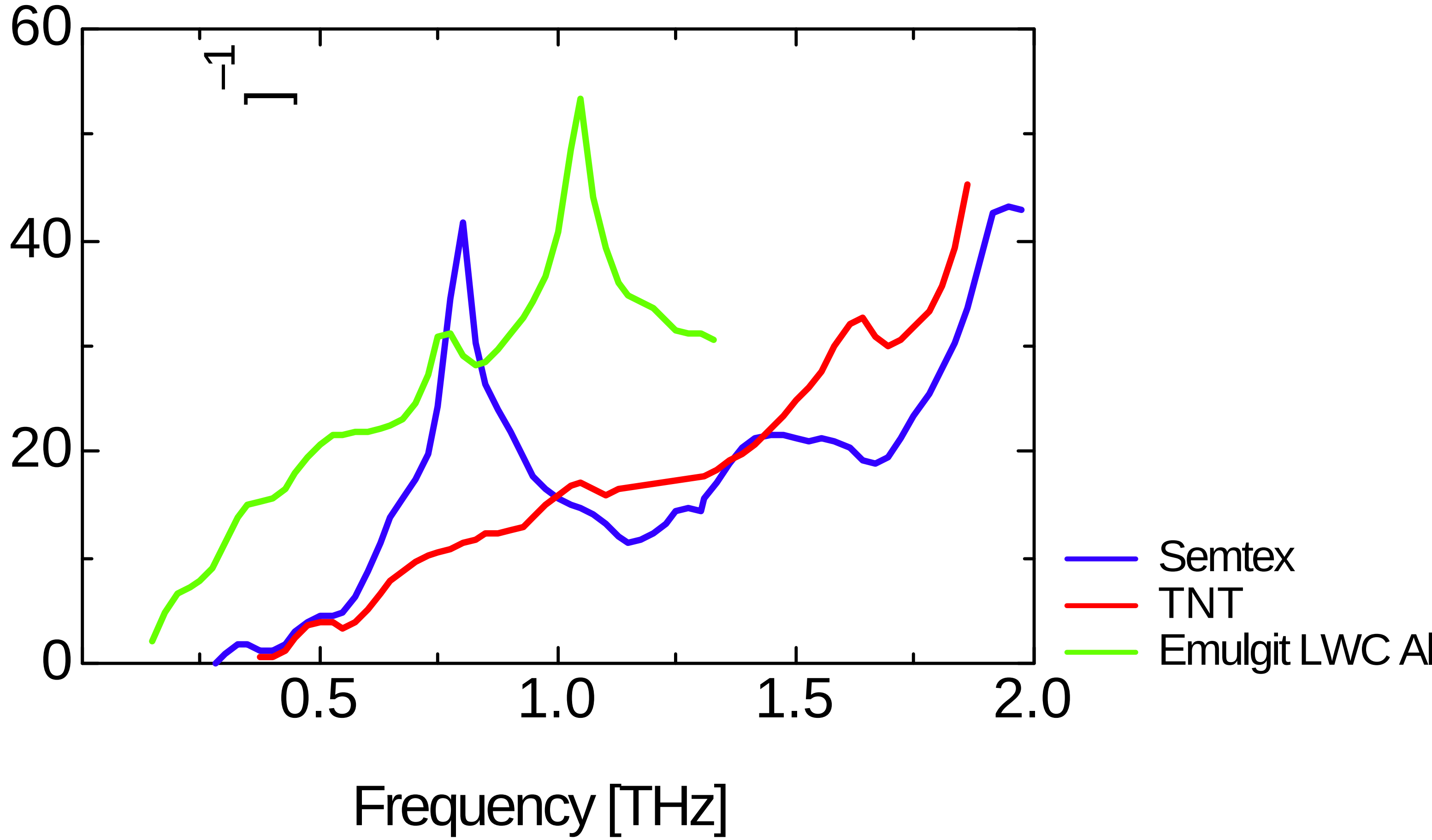


Rainbow Photonics Ltd

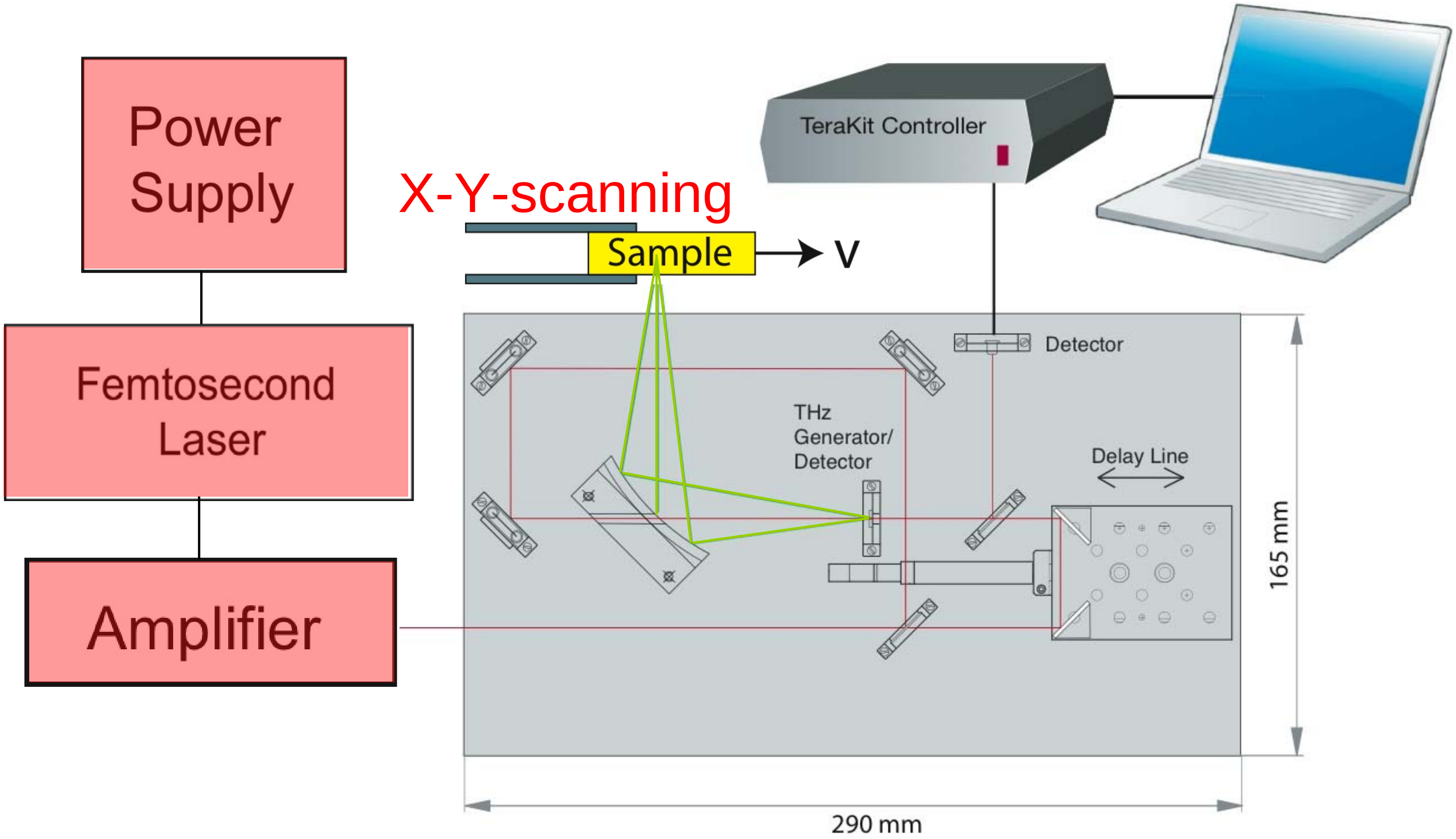
Rainbow Photonics TeraSys 4000



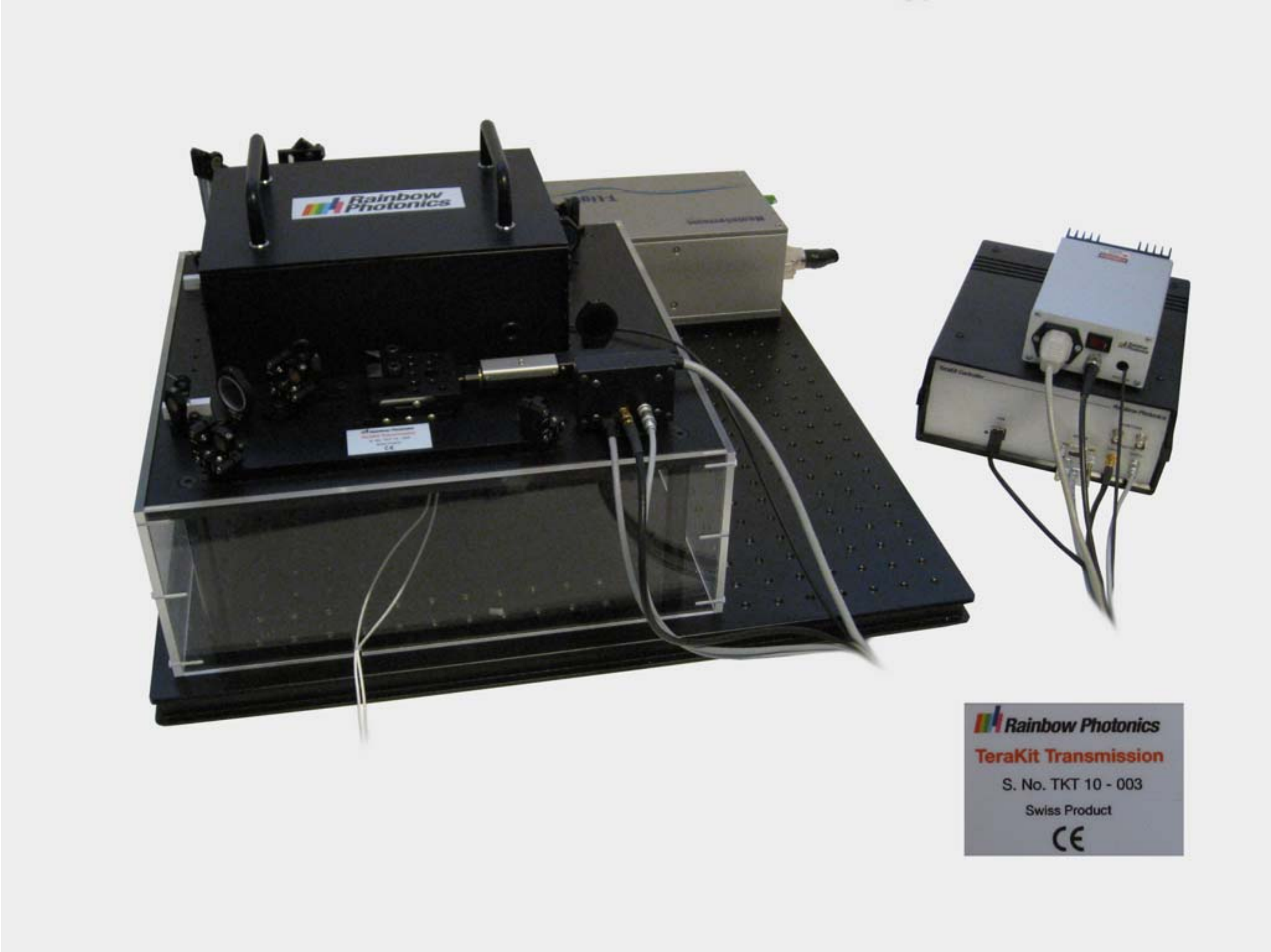
THz Absorption of 3 Explosives



Reflection Mode

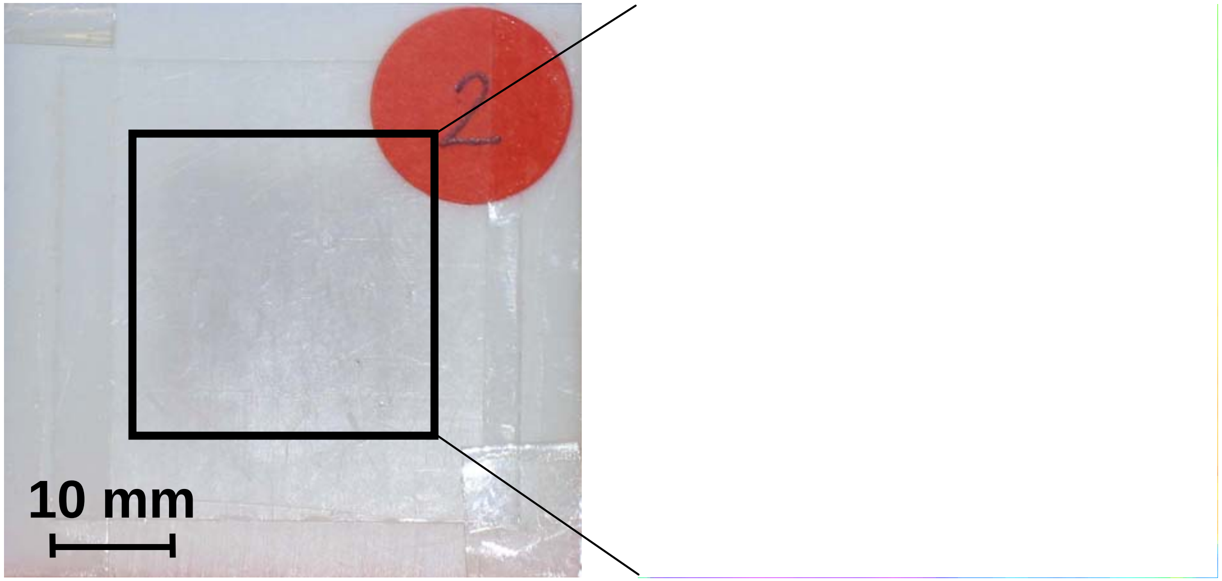


TeraKit with Imaging Option



THz-Image of Semtex

(a) (b)



Semtex hidden in Teflon

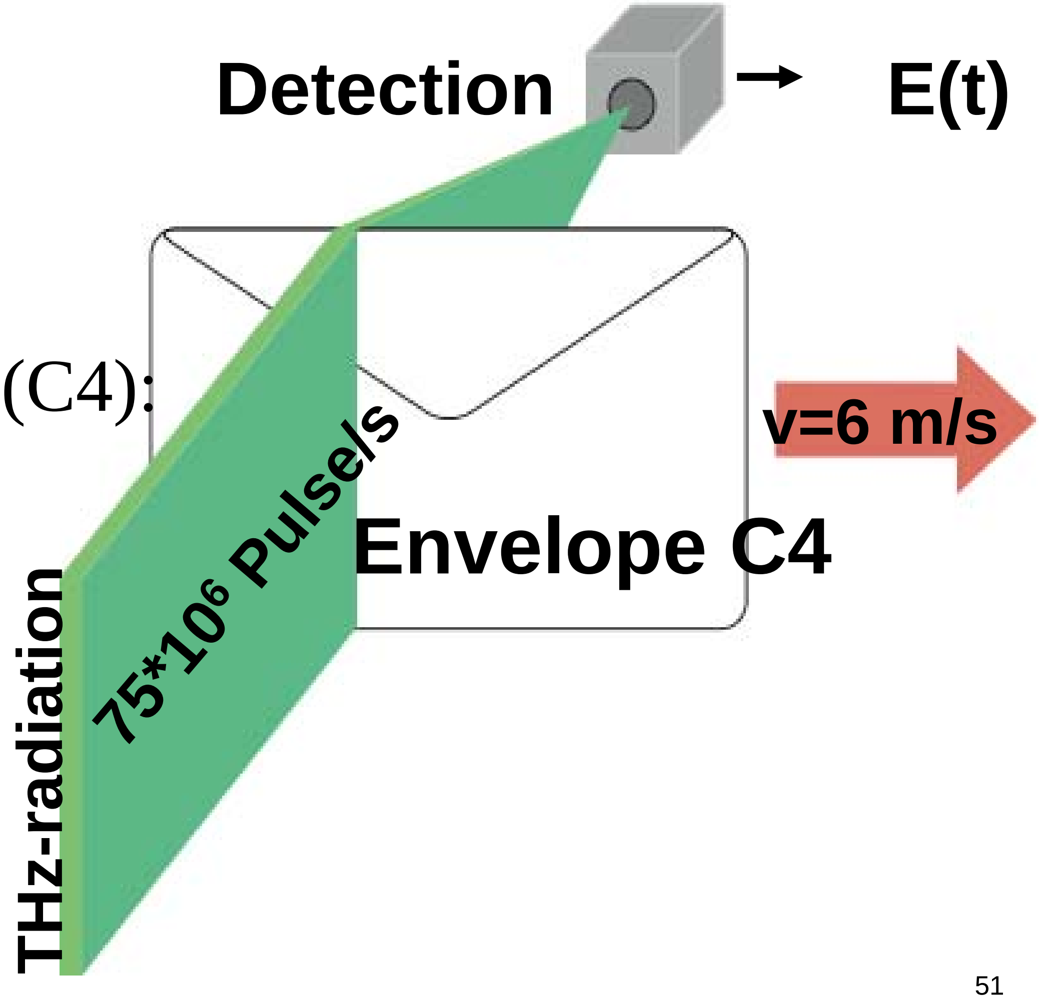
Size: 25 x 25 mm

- No explosive
- Explosive
- Red paper sticker in upper right corner.

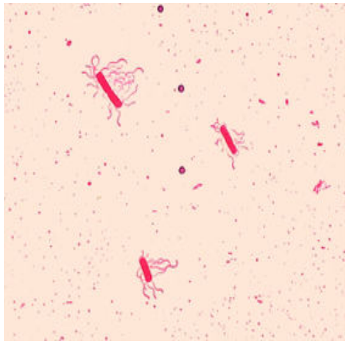
THz-Application: Mail Inspection

Velocity (C4): **50ms**

→Number of pulses (C4): **375’000**

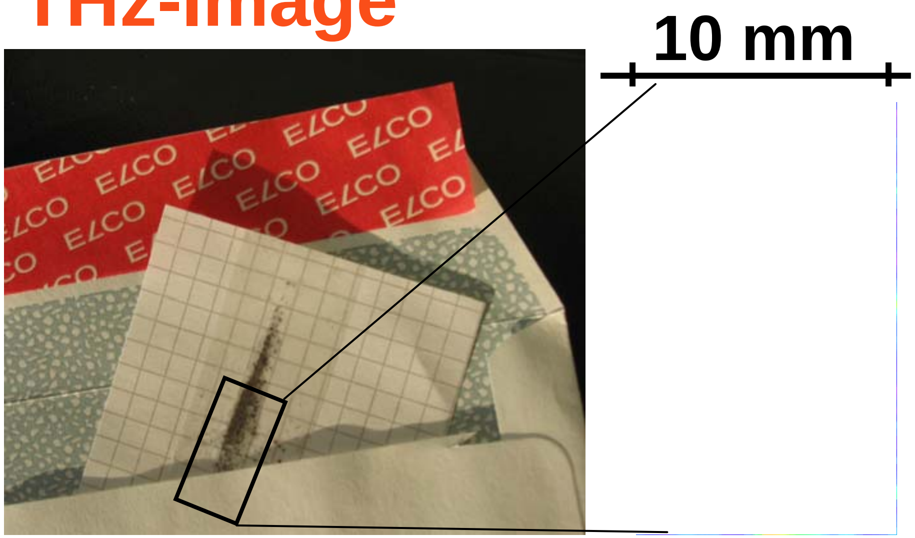


THz imaging: Bacillus cereus spores



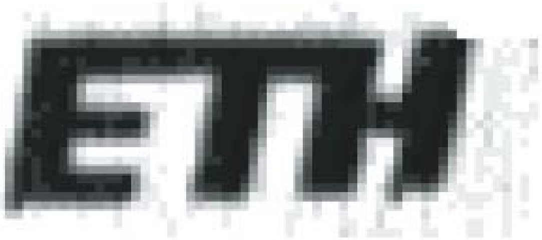
Bacillary, anaerobic and spore forming bacteria
→Food poisoning
→Closely related to B. anthracis!

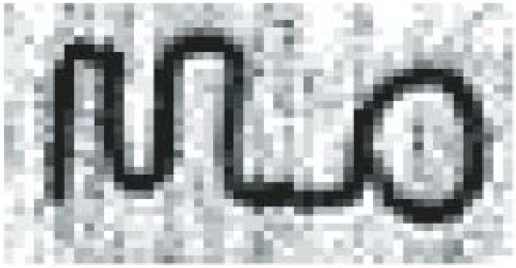
THz-Image

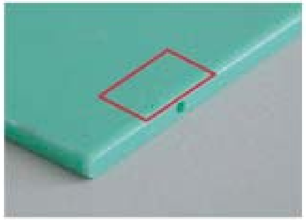


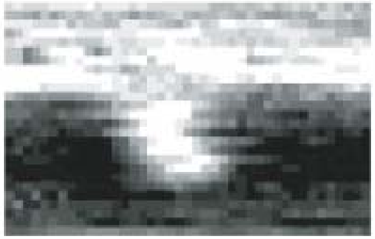
- Particle size ~1 micron
- ~ Monolayer
- Scanned area:
  7.5 x 15 mm
- 0.25 x 0.25 mm/pixel

THz Images





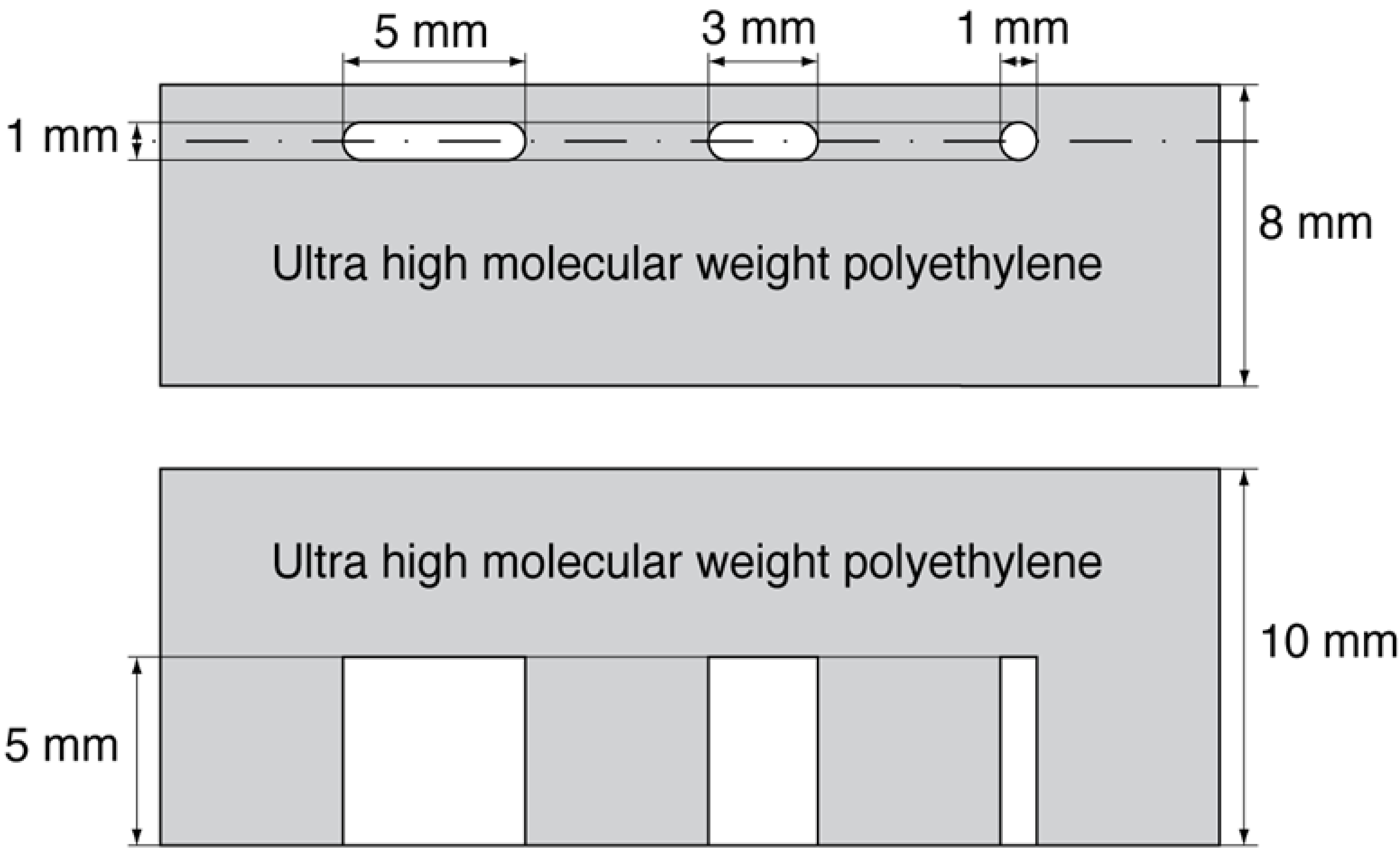




Application: THz Imaging

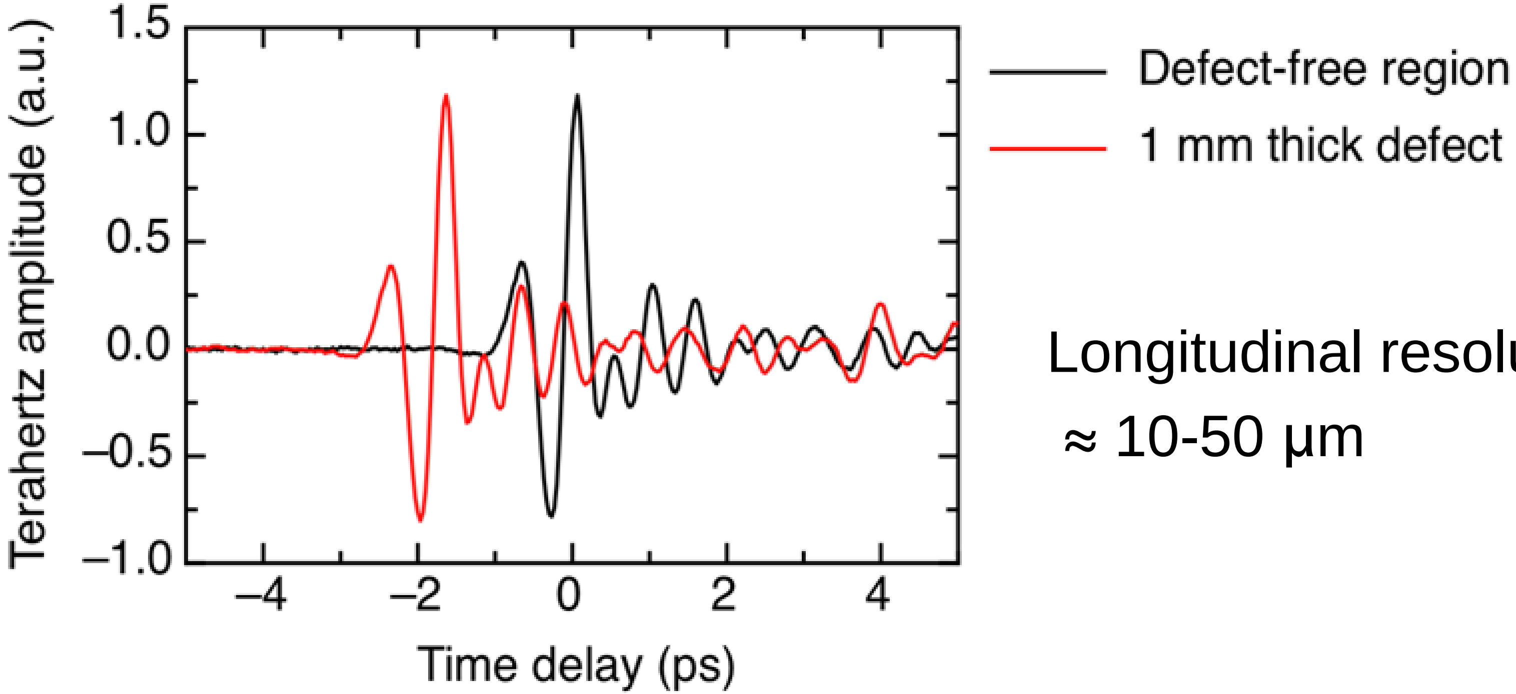
- Most dielectrics are transparent
- Conductors are opaque

UHMWPE Sample



UHMWPE plate with three different defects used for terahertz pulse imaging.

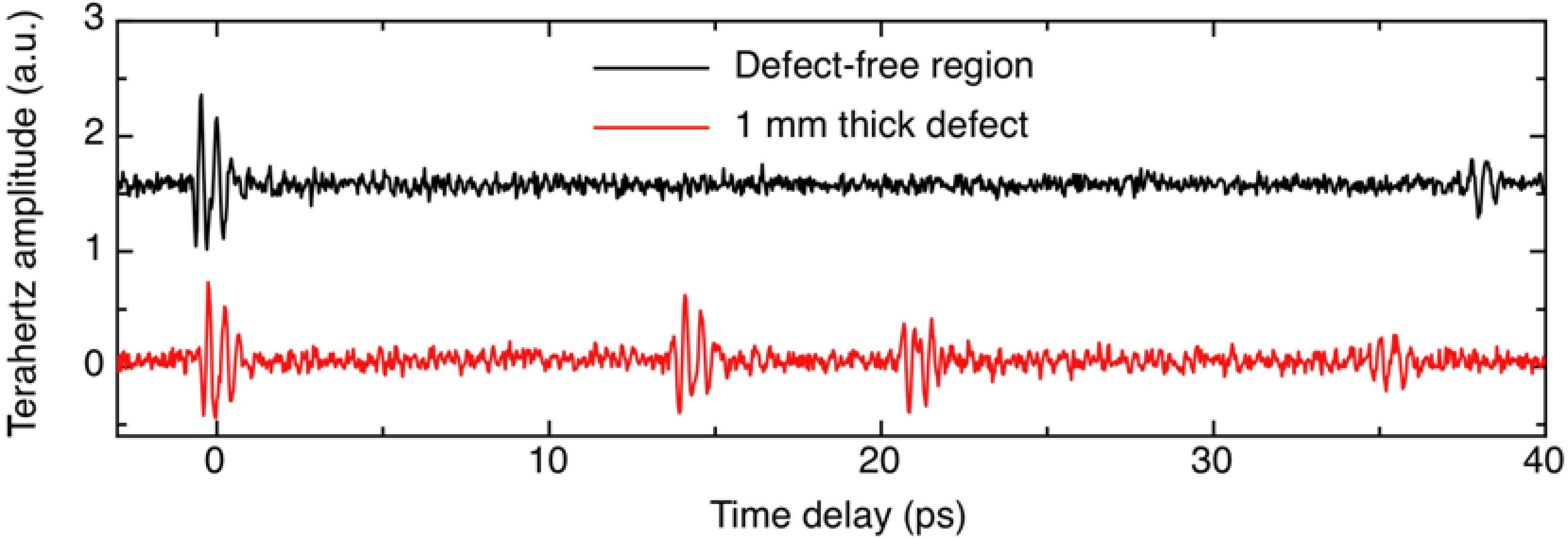
Terahertz Pulse Imaging

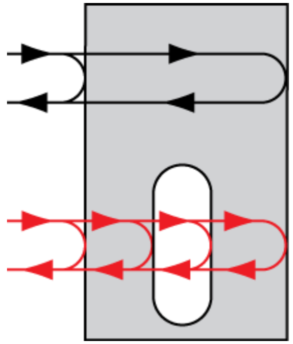


Longitudinal resolution ≈ 10-50 µm

Terahertz pulses transmitted through an 8 mm thick UHMWPE plate in a region with a 1 mm thick hole and in a defect-free region, respectively.

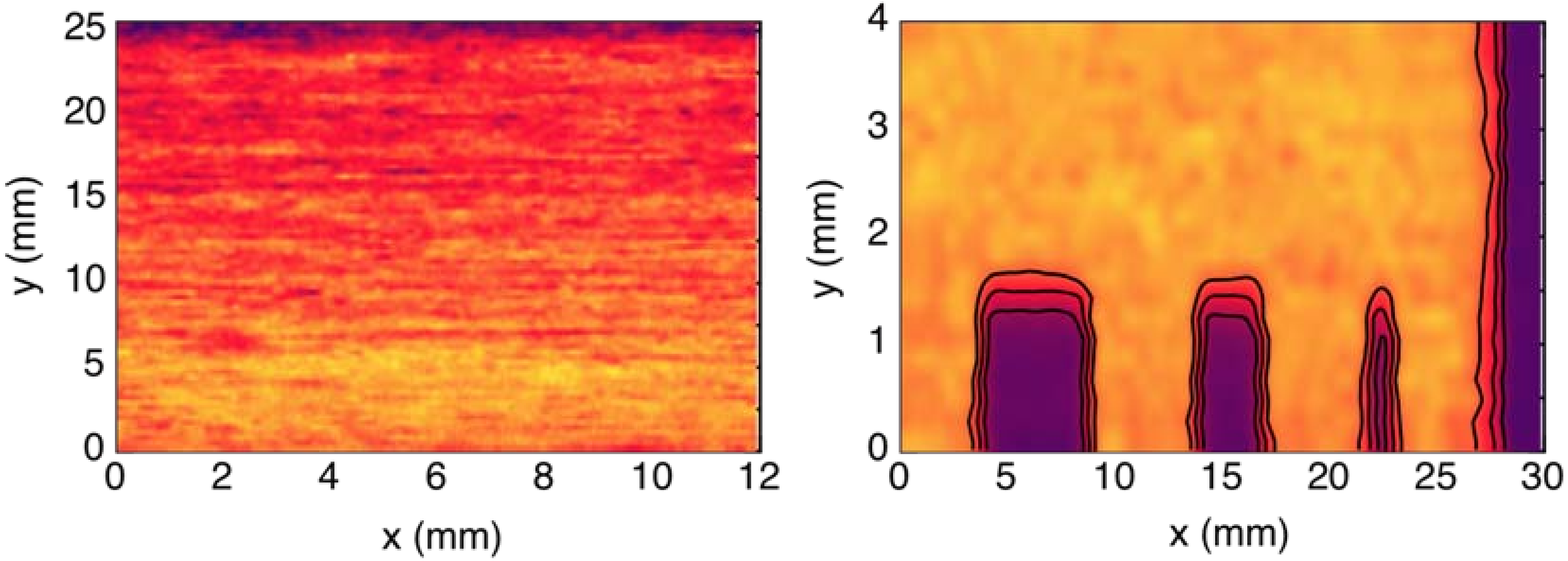
Terahertz reflection tomography





Terahertz pulses reflected from a 4 mm thick UHMWPE plate with a 1 mm thick defect.

Phase image (fixed time-delay)



Phase image acquired by terahertz pulse imaging.

Left panel: UHMWPE plate without any defects.

Right panel: UHMWPE plate with defects.

THz Wave Technology Offers

- Coherent Radiation with Amplitude and Phase Information
- High Spectral Resolution (up to 0.005 THz (0.17 cm^{-1}))
- Wide Spectrum for Spectral Fingerprint Selectivity (particularly with DSTMS)
- 2 (and 3)- Dimensional Images
- Spatial Resolution of Less Than 0.1 mm

Conclusions

- Efficient THz generation in DSTMS crystals (high nonlinearity, velocity-matching)
- Broadband THz waves (0.3 - 12 THz) generated/detected (up to 20 THz possible)
- Compact turn-key operated THz spectrometer / Imager realized
- Terahertz-induced lensing is an attractive technique for the detection of THz pulses

Collaborators

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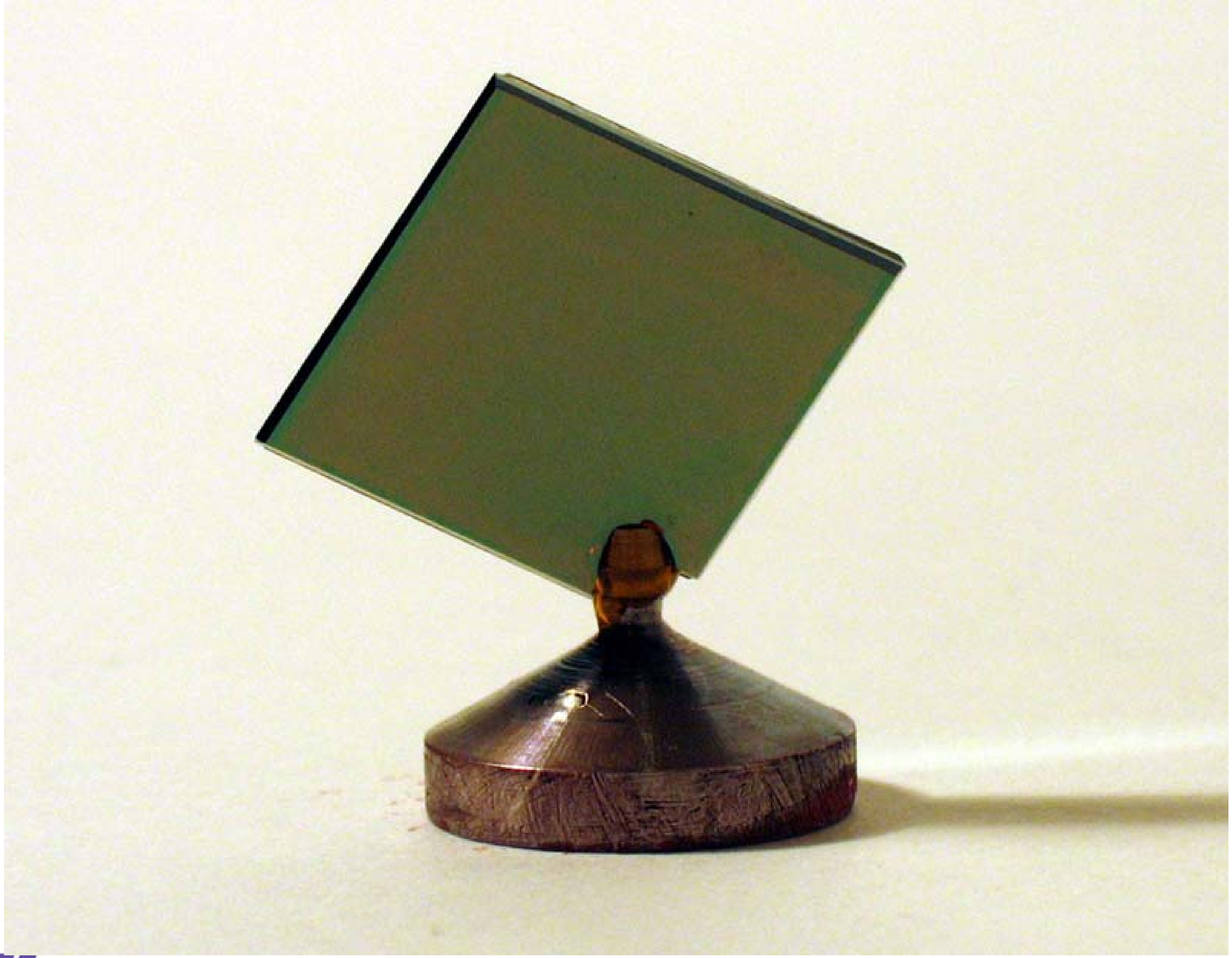
Dr. C. Medrano (RP)

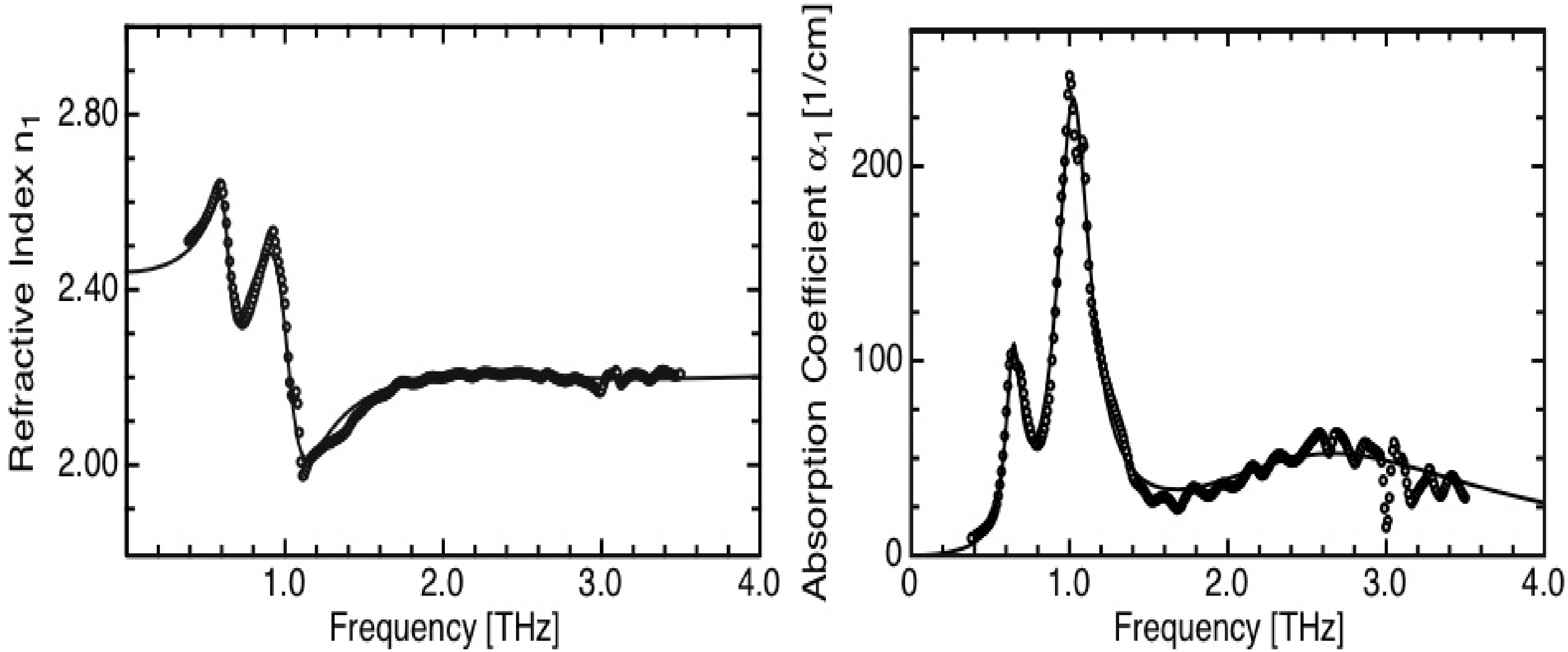
Dr. T. Bach (RP)

DAST Crystal



Optical Properties of DSTMS

Optical properties in the THz spectral range:



Theoretical: Three harmonic oscillators model

Organic $\chi^{(2)}$ crystals

A. Conventional molecular crystals (COANP, DAN, MNA…): moderate EO $n^3 r < 40$ pm/V

- **Large-scale integration possible**

B. State-of-the-art: organic salts such as DAST, DSTMS: very high EO $n_1^3 r_{11} > 400$ pm/V

- **EO waveguides possible, but very difficult on-chip integration**

- **New materials combining both high electro-optic activity and good processability needed**

DAST: EO and NLO Properties

Large EO and NLO coefficients:

r_{11} = 400±150 pm/V @ 820 nm

r_{11} = 62 ± 8 pm/V @ 1300 nm

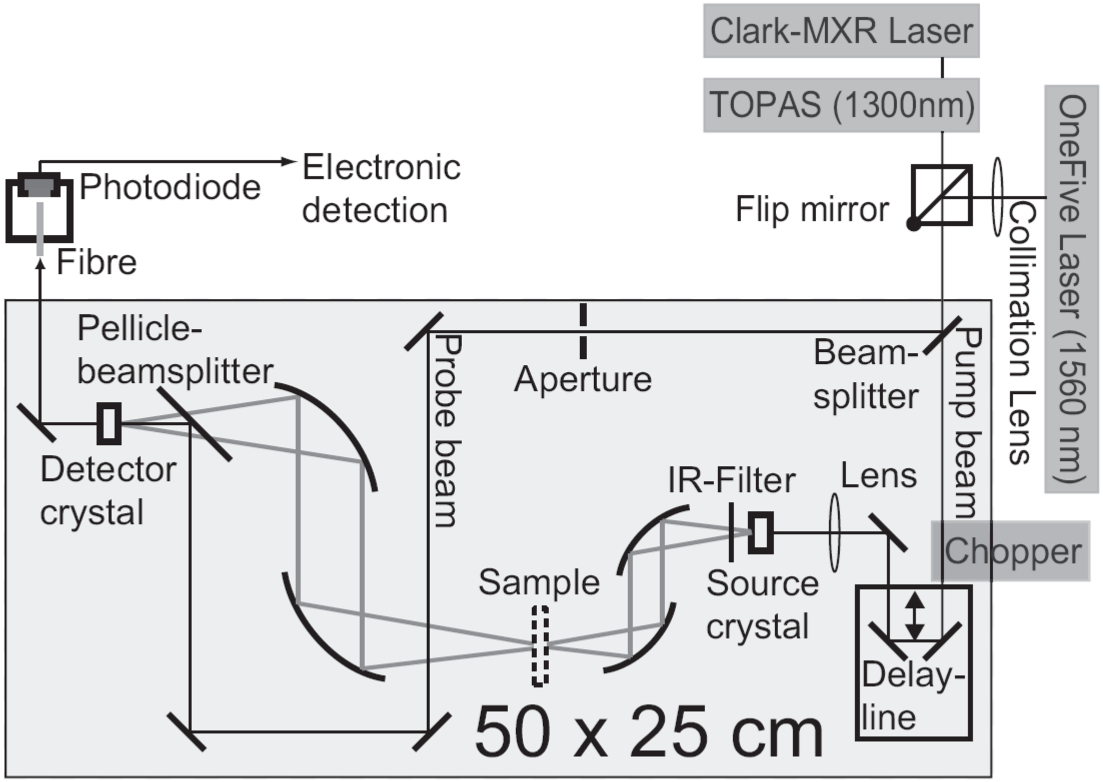
d_{11} = 1010±110 pm/V @ 1318 nm

d_{11} = 290±15 pm/V @ 1542 nm

+ Superior EO & NLO Properties and Stability

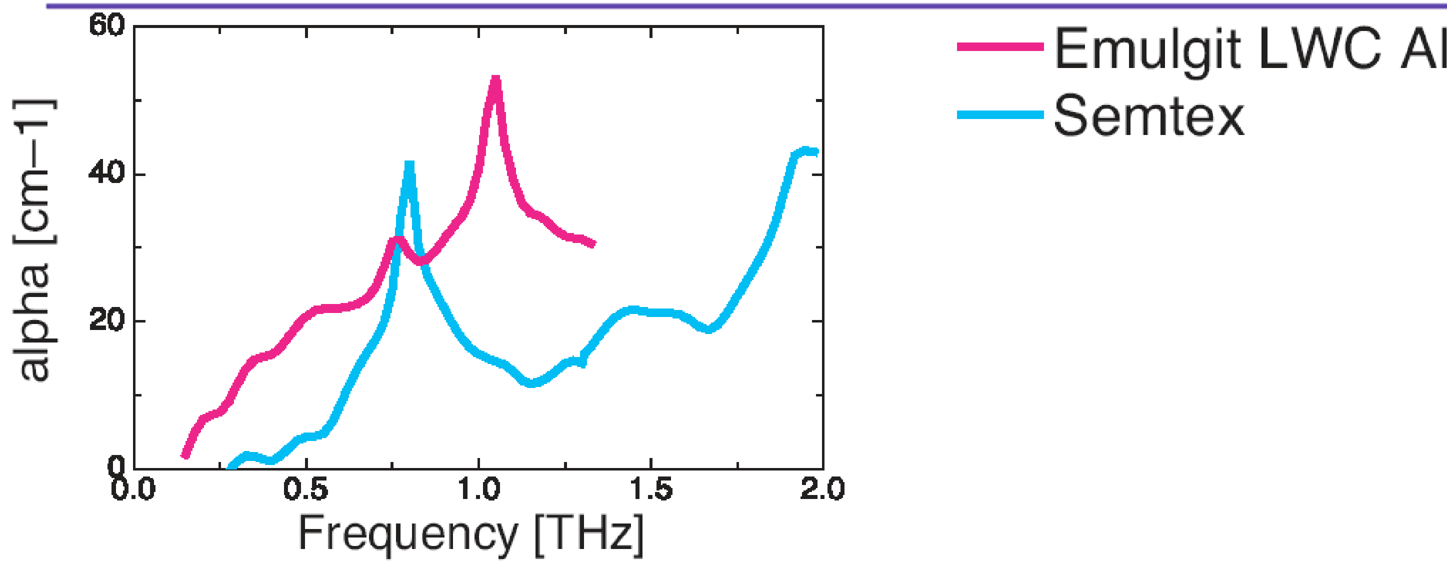
- Difficult to process using standard techniques

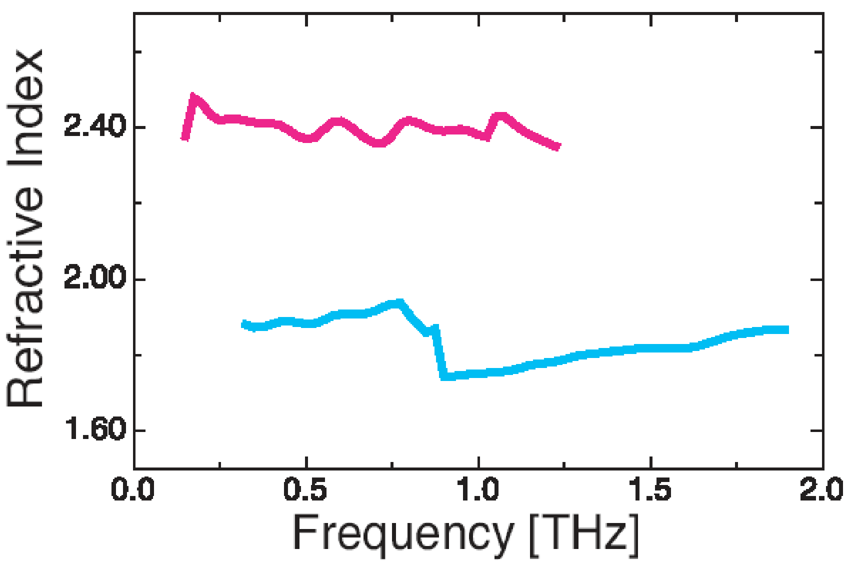
Set up THz Generation and Detection



THz Pulse Generation by Optical Rectification, Detection via THz-induced Lensing .

Distinct Absorption Lines





- Cut-off at 2.0 THz
- Dispersion for Semtex
- Signatures at 0.8 (Semtex) and 0.75/1.1 THz (Emulgit)

THz Wave Technology offers

- Coherent Radiation with Amplitude AND Phase Information
- High Spectral Resolution (up to 0.005 THz (0.17 cm^{-1})
- Wide Spectrum for Spectral Fingerprint Selectivity (particularly with DAST)
- 2 (and 3)- Dimensional Images
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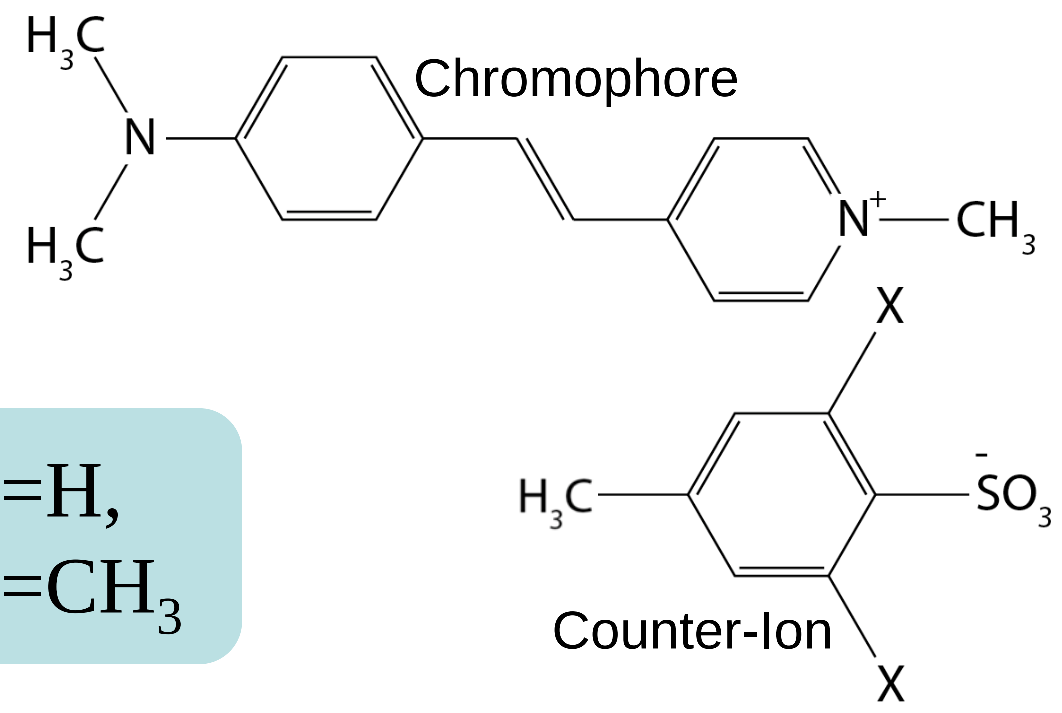
Chemical Structure of DSTMS

DSTMS: 4-N,N-dimethylamino-4'-N'-methyl-stilbazolium 2,4,6-trimethylbenzenesulfonate



DAST: X=H,

DSTMS[1]: $X=CH_3$

[1] Z. Yang, Adv. Funct. Mater. **17**, 2018 (2007)

Materials at λ = 800 nm

Material	r (pm/V)	d (pm/V)
CdTe	4.5[26]	81.8
GaAs	1.43[26]	65.6
GaP	0.97[22]	24.8
ZnTe	4.04[26]	68.5
GaSe	1.7[15]	28.0
$LiTaO_3$	30.5[26]	161
$LiNbO_3$	30.9[26]	168
DAST	77[13]	618

Rainbow Photonics Ltd

Specification [1]	TeraSys 4000
Frequency range	0.3 - 4 Thz
Output power	> 50 nW
Spectral resolution	< 0.01 THz
Polarisation, linear	> 100 : 1, vertical
Input voltage	110V / 240V, 50 or 60 Hz
Power consumption	< 60 W
Warm-up time	15 min.
Operating ambient temperature	18°C - 30°C
Dimensions	40x25x18 cm3