

SMR: 1133/25

**WINTER COLLEGE ON  
SPECTROSCOPY AND APPLICATIONS**

( 8 - 26 February 1999)

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**"THz-Spectroscopy"**

***2. From Fundamental to Industrial Applications***

presented by:

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These are preliminary lecture notes, intended only for distribution to participants.

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## 2. From fundamental to industrial applications

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2.1 Introduction

2.2 Pulse propagation

2.3 Frequency information      Spectroscopy

Gas monitoring

2.4 Intensity information      Imaging

2.5 Time information      Tomography

Radar

2.6 Future applications



## Areas of applications for fs-THz-radiation

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- o Investigation of semiconductor elements
  - o Spectroscopy of solid state materials
  - o Spectroscopy of gases (and liquids)
  - o THz-radar
  - o Imaging applications for quality control
  - o Medicine (e. g. dermatology)
- ⇒ **Large potential due to**
- compact, efficient and cost effective fs laser systems,  
available and universal applicable software components

## Fs-THz-source

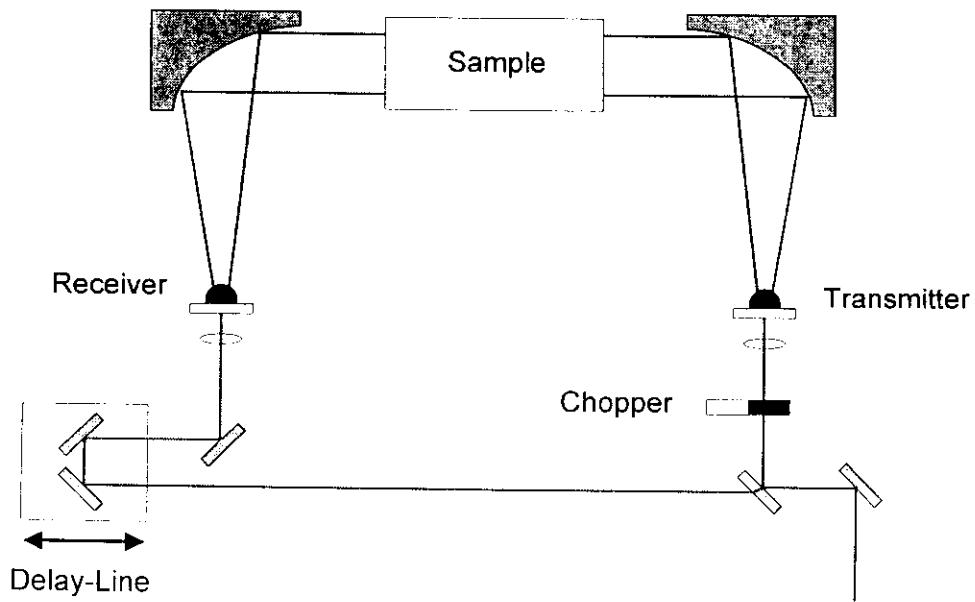
### Properties of the fs-THz-source

- o **Pulsed THz-source ( $\Delta\tau \approx 1$  ps) with high repetition rate (50 ... 100 MHz)**
- o **Broadband THz-radiation**

$$30 \text{ GHz} < \nu < 30 \text{ THz}$$

- o High S/N ratio
- o Noise suppression by means of **coherent detection** and "optical gating" ("duty cycle"  $\approx 5 \cdot 10^{-4}$ )
- o **Directed THz-radiation (point source)**
- o **THz-source based on diode lasers**

## THz set-up



Cr:LiSAF  
100fs, max. 100mW



## Information from THz pulse propagation

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What kind of information can I retrieve ??

1. Time domain: - Attenuation of THz signal

↓ - Time separation of echoes

FFT

2. Frequency domain: - Frequency dependent absorption

- Line widths, line positions

- Dispersive properties

- Index of refraction

⇒ Time and frequency resolution, sensitivity, ...



## “T-Ray“-Applications

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Intensity

Time structure

Amplitude and phase

↓

↓

↓

Imaging

Topography

Spectroscopy

„TDS“

## „Spectroscopy“

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### Spectroscopy in the THz-regime:

- o Rotational transitions in almost all polar molecules between  
10 GHz and 10 THz
  - o Wavelength range               $100 \text{ } \mu\text{m} < \lambda < 10 \text{ mm}$   
 $(3 \text{ THz} < \nu < 30 \text{ GHz})$
  - o Large absorption cross sections
  - o No absorption of atoms
- ⇒ **However:** Detectors in the THz-regime have only limited sensitivity at room temperature caused by thermal noise ( $\text{NEP} \approx 10^{-12} \text{ W/Hz}^{1/2}$  at RT)

## Pulse propagation of THz-pulses

- o „weak” THz-pulses  $\Rightarrow$  linear polarization of the medium

$\Rightarrow$  Application of linear dispersion theory

- o Frequency domain:

complex wave vector  $k(\omega) = k_0 + \Delta k(\omega) + i \frac{\alpha(\omega)}{2}$

propagation along distance  $z$  in the medium

$$E(z, \omega) = E(0, \omega) e^{ik_0 z} e^{i\Delta k(\omega) z} e^{\frac{\alpha(\omega)}{2} z}$$

- o Fourier transformation

$$E(z, t) = \int_{-\infty}^{\infty} E(z, \omega) e^{-i\omega t} d\omega$$

## Molecular Parameters

Absorption:  $\alpha_{JK}(\omega) = C_{JK} \cdot \omega \cdot g_a(\omega, \omega_K)$

$\Downarrow$                $\Downarrow$   
constant      line shape (Lorentz, van Vleck-Weißkopf)

Transition frequency:  $\omega_{JK} / 2\pi = 2(J+1)(B_v - D_{JK} K^2) - 4D_J (J+1)^3$

Dispersion:  $\Delta k_{JK} = 2C_{JK} \frac{\omega \omega_{JK}}{\omega_{JK}^2 - \omega^2} g_K(\omega, \omega_{JK})$

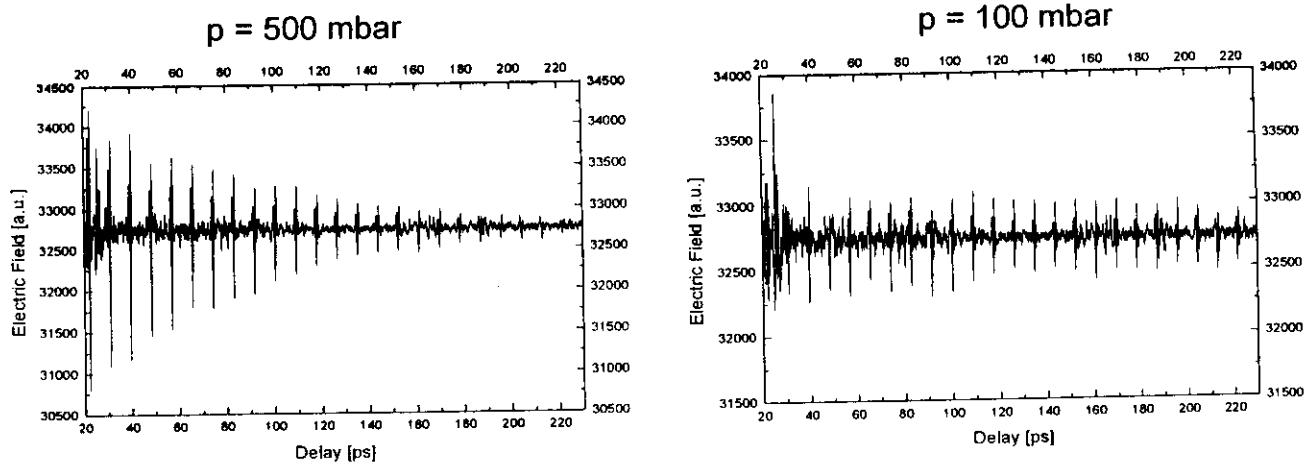
$$\alpha(\omega) = \sum_{J=0}^{\infty} \sum_{K=0}^J \alpha_{JK}(\omega) \quad \Delta k(\omega) = \sum_{J=0}^{\infty} \sum_{K=0}^J \Delta k_{JK}(\omega)$$

## THz spectroscopy of CO

- Time separation of echoes:

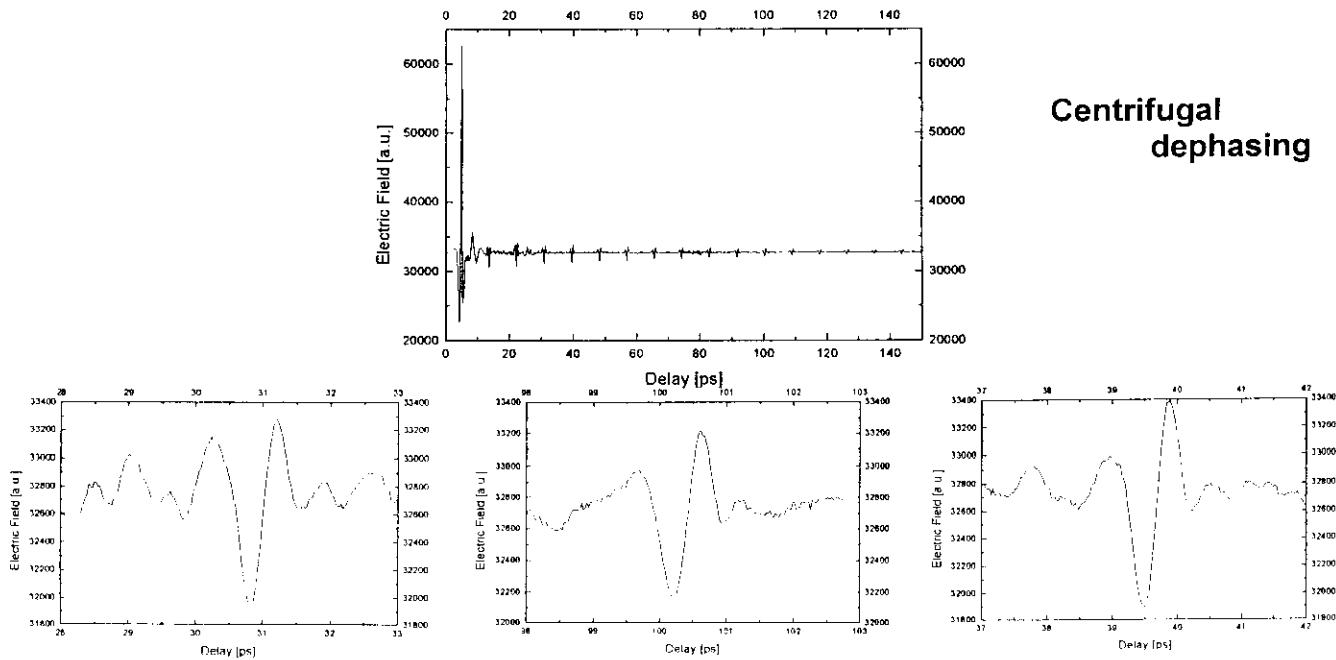
$$\text{Rotational constant } B = 57.64 \text{ GHz} \quad \Rightarrow \quad \Delta\tau = \frac{1}{2B} = 8.67 \text{ ps}$$

- Transverse relaxation time  $T_2$  depends on pressure  $p$ .

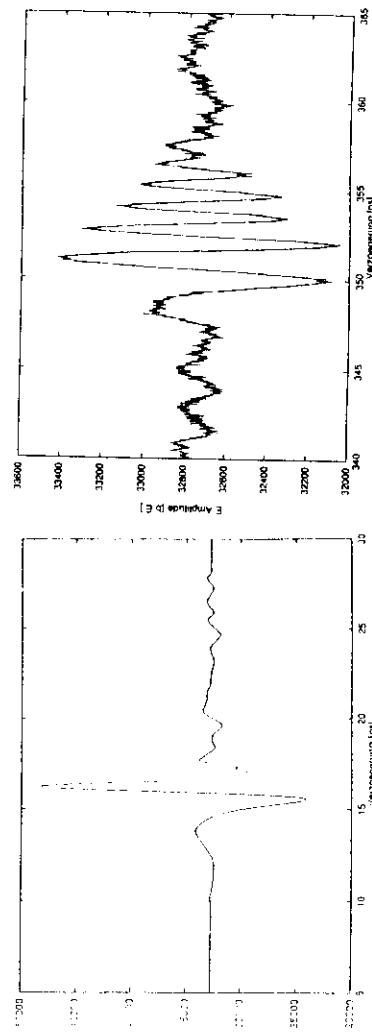
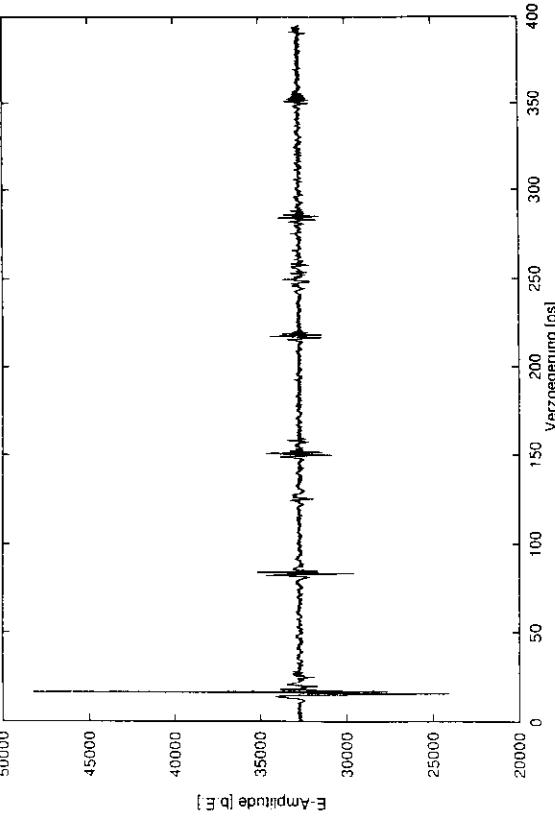


## THz spectroscopy of CO

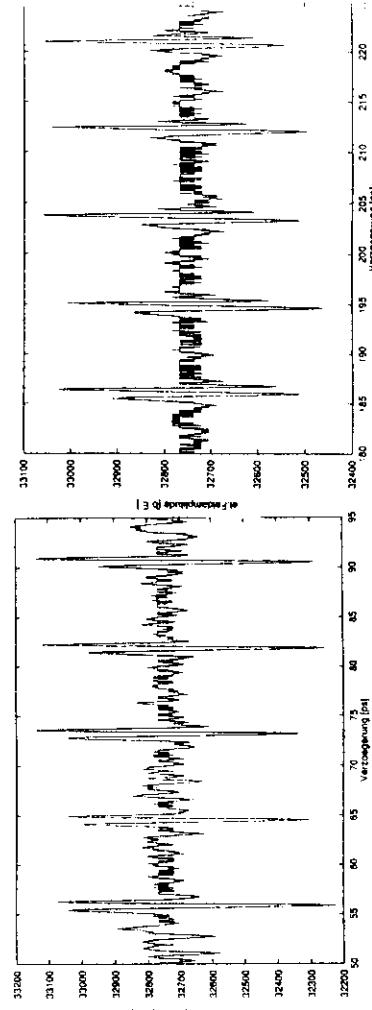
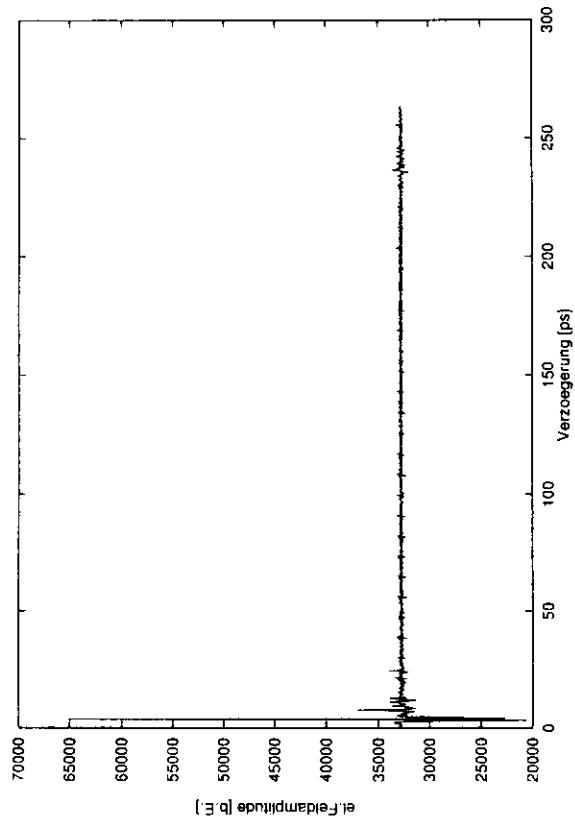
- Phase shift of pulse echoes:



## Phase shift of echoes: CH<sub>3</sub>I

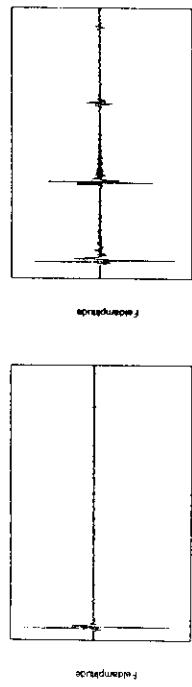


## Phase shift of echoes: CO

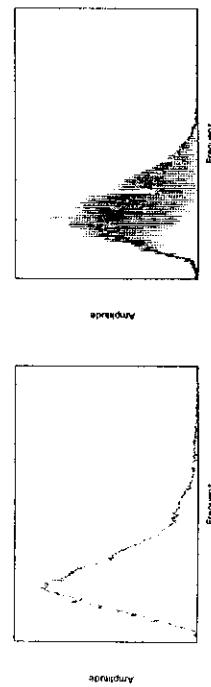


# THz spectroscopy

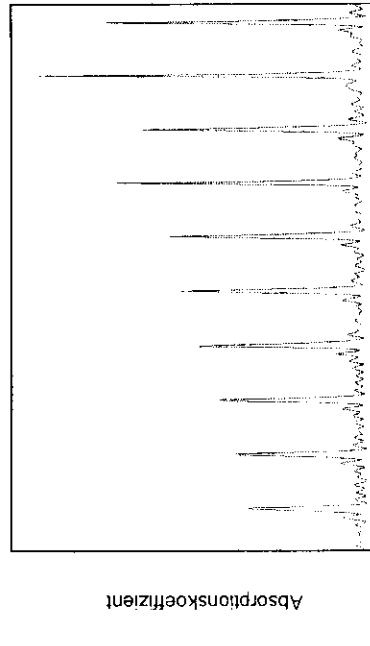
without gas



Fourier transform (FFT)

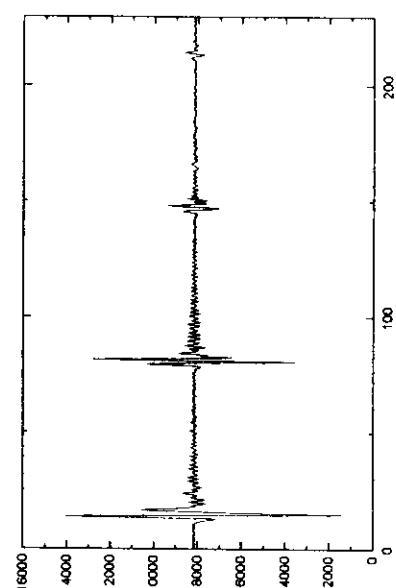


Division



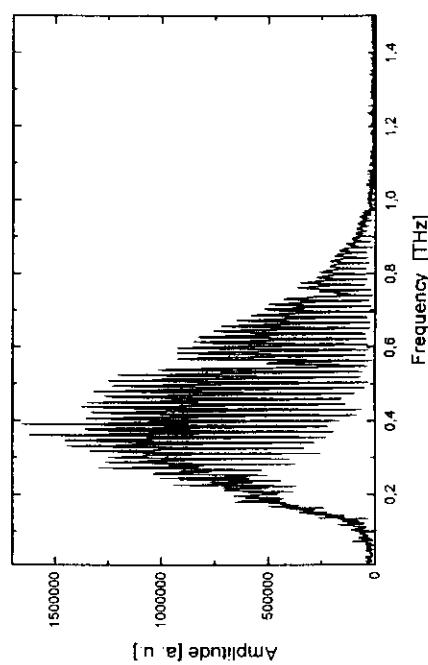
# Spectroscopy of $\text{CH}_3\text{I}$

Time domain:



Fourier Transform

Frequency domain:



# THz-Spectroscopy of $\text{CH}_3\text{-X}$ ( $\text{X} = \text{F}, \text{Cl}, \text{Br}$ )

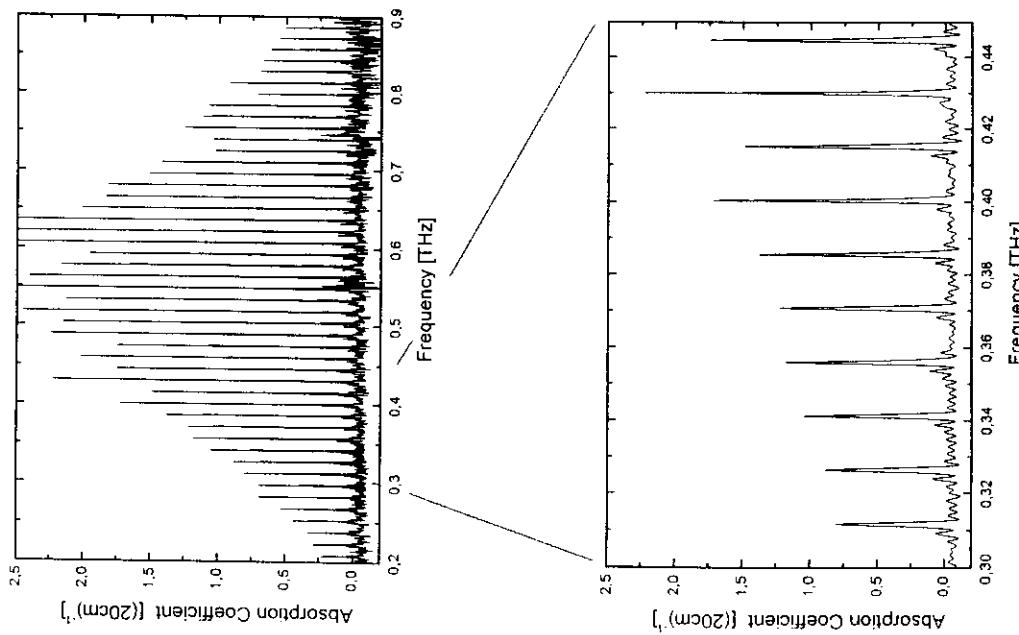
D. Grischkowsky, H. Harde et al.

3652 *J. Phys. Chem. A*, Vol. 101, No. 20, 1997

TABLE I: Molecular Parameters Used in the Theoretical Comparisons to the Measurements<sup>a</sup>

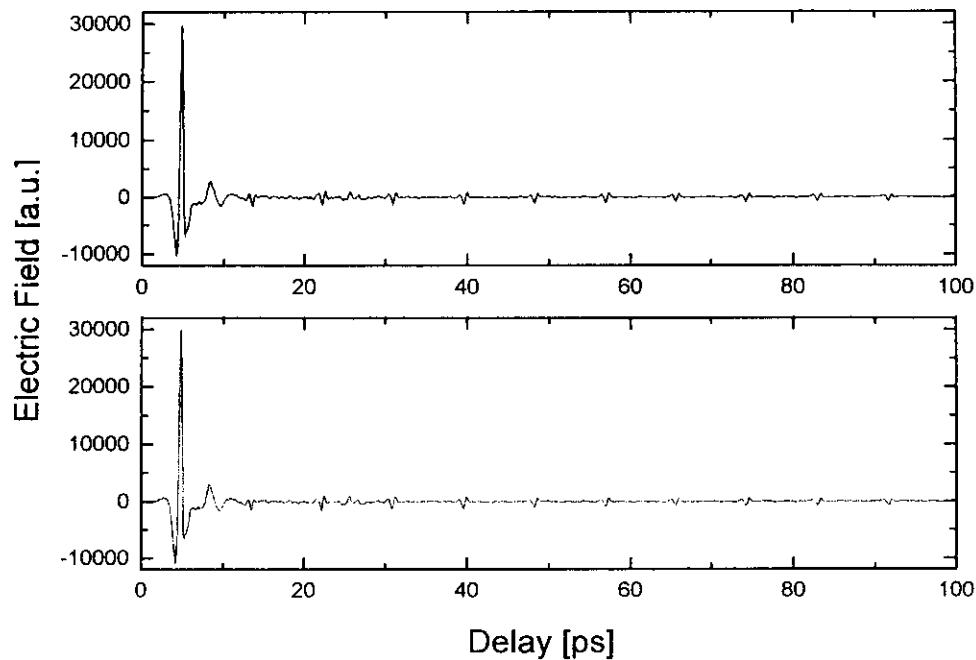
gas	$\text{CH}_3^{37}\text{Br}$	$\text{CH}_3^{37}\text{Br}$	$\text{CH}_3^{35}\text{Cl}$	$\text{CH}_3^{37}\text{Cl}$	$\text{CH}_3^{19}\text{F}$
isotope (%)	(50.6)	(49.4)	(75.4)	(24.6)	(100)
$\mu$ (D)	(1.797)	(1.797)	(1.869)	(1.869)	(1.790)
$A_v$ (GHz)	(150)	(150)	(156.05)	(156.445)	(154)
$B_v$ (GHz)	9.565 (9.56819)	9.528 (9.53184)	13.289 (13.292876)	13.083 (13.088129)	25.524 (25.53612)
$D_J$ (kHz)	9 (10.0)	9 (10.0)	17.9 (18.089)	17.2 (17.72)	59.0 (59.0)
$D_{JK}$ (kHz)	128 (128)	128 (128)	150 (198.764)	90 (193.67)	445.0 (445.0)
$\tau_c$ (fs)			220	220	190

## Spectroscopy of $\text{CH}_3\text{I}$



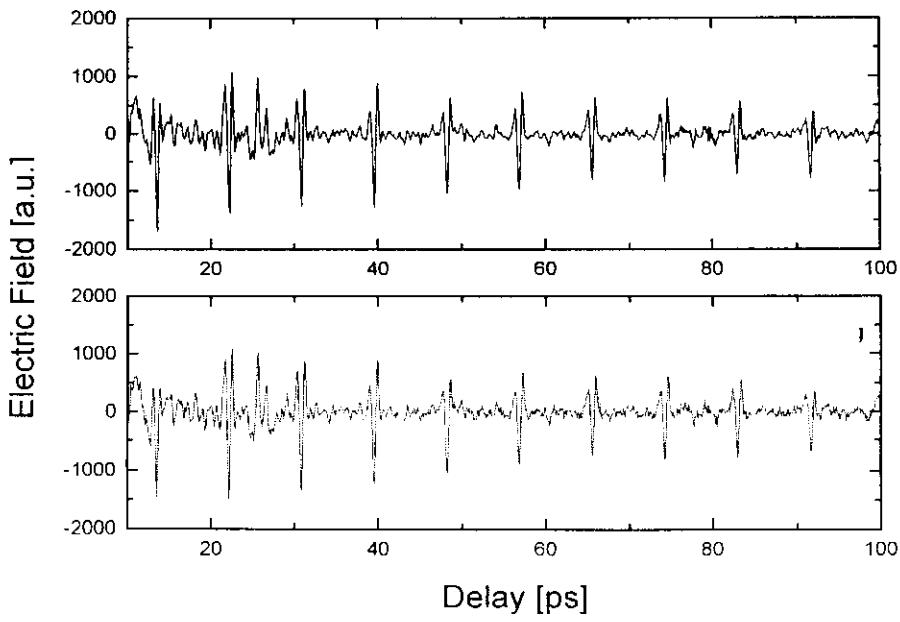
# THz-Spectroscopy of CO

Time domain:



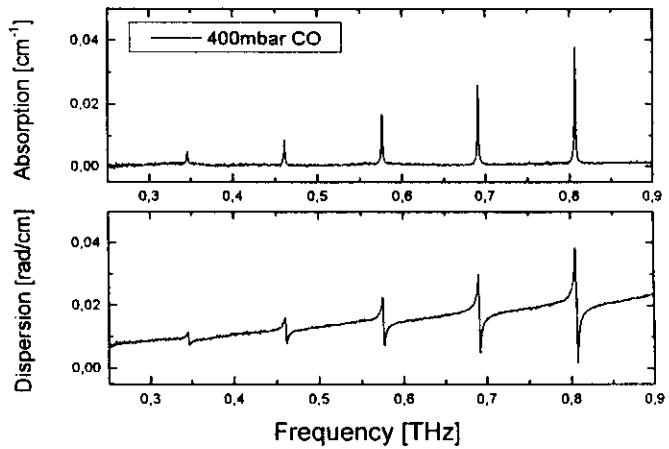
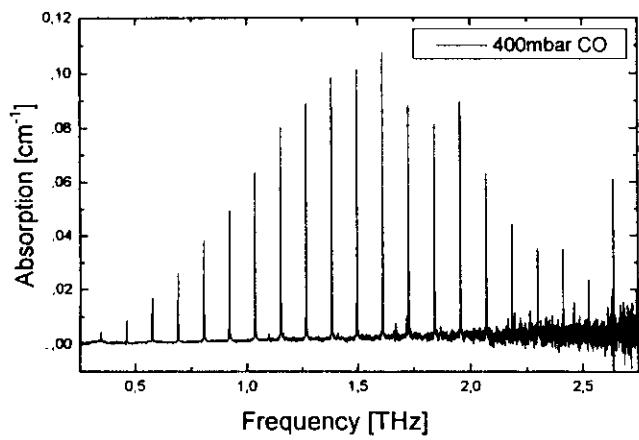
# THz-Spectroscopy of CO

Time domain:



# THz-Spectroscopy of CO

Frequency domain:





## THz spectroscopy: Fouriertransformation

- o Fast Fouriertransformation (FFT)

$$E(m \cdot \Delta\omega) = \sum_{n=0}^{N-1} E(n \cdot \Delta t) \cdot e^{-j \frac{n \cdot m}{N}} \quad N = 2^k \quad k = 0, 1, 2, \dots$$

Step width:  
- frequency domain  $\Delta\omega$   
- time domain  $\Delta t$

- o Spectral resolution  $\Delta\omega = \frac{1}{N \cdot \Delta t}$

- o "Zero filling"  $E((2^k + 1) \cdot \Delta t), \dots, E((2^{k+1}) \cdot \Delta t) = 0,$

$$E((2^{k+1} + 1) \cdot \Delta t), \dots, E((2^{k+2}) \cdot \Delta t) = 0$$

⇒ interpolation between neighboring data points

## THz spectroscopy: Fourier transform

- o Reduction of data points

⇒ increase in line width

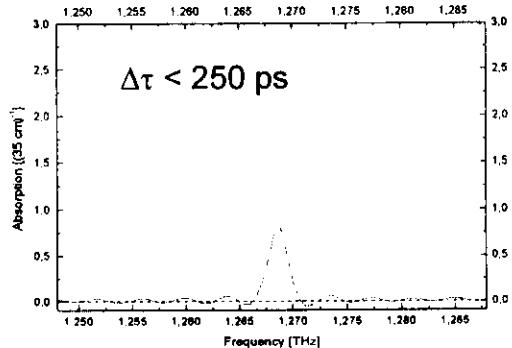
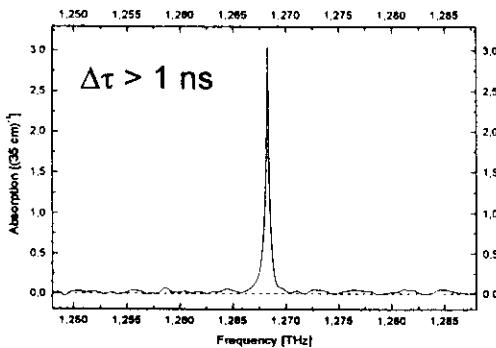
$$\Delta\nu_R = \frac{1}{T_{\max}}$$

⇒ if  $\Delta\nu_R > \Delta\nu_J$ ,

then decrease of maximum absorption

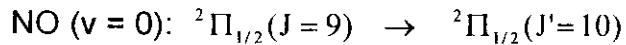
$$\alpha_{\max} \propto \frac{1}{\Delta\nu}$$

⇒ decrease in sensitivity



## THz spectroscopy: Fouriertransformation

- o "Zero filling":

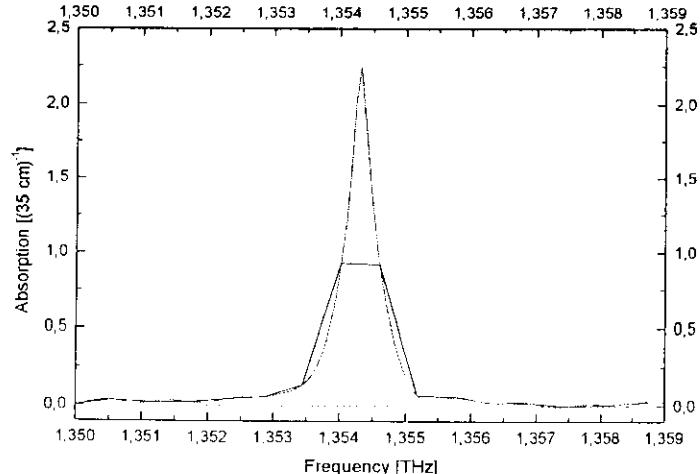


- Original data:

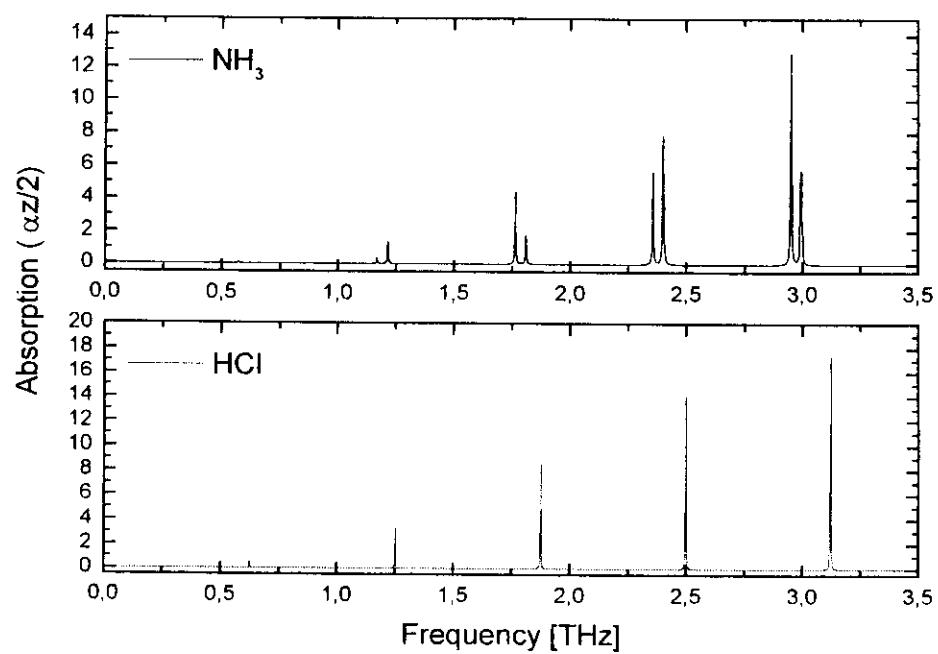
$$E(t=0) \dots E(t=N \cdot \Delta t), \quad N = 2^k$$

- Zero filling:

$$E((2^k + l) \cdot \Delta t) \dots E((2^{k+4}) \cdot \Delta t) = 0$$

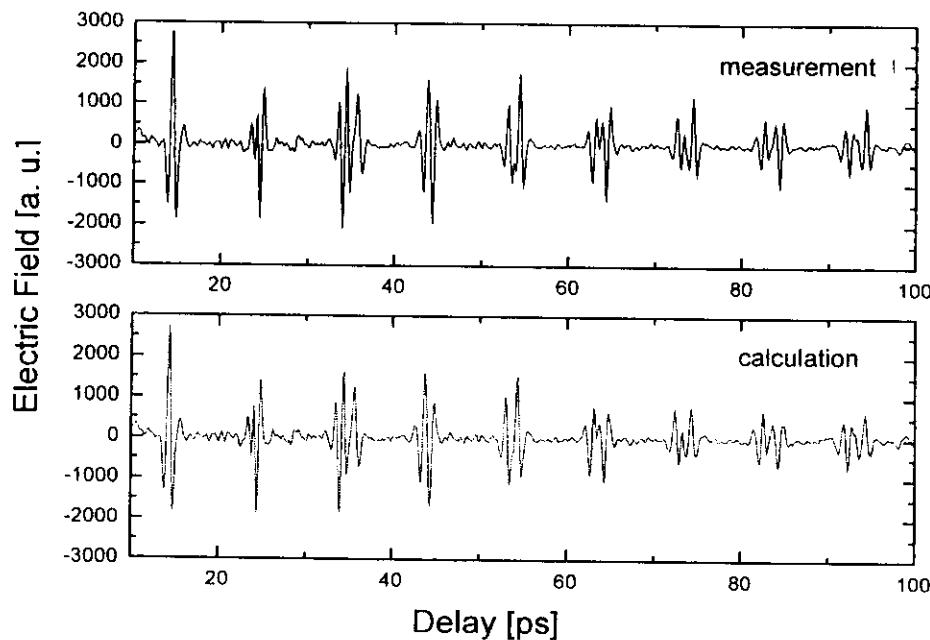


## Rotational spectra: NH<sub>3</sub> and HCl



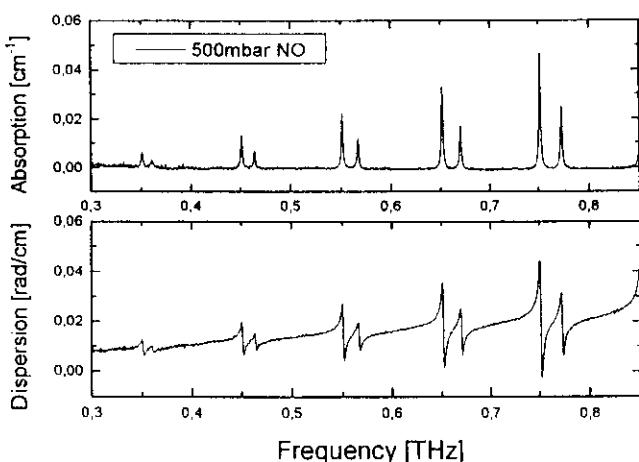
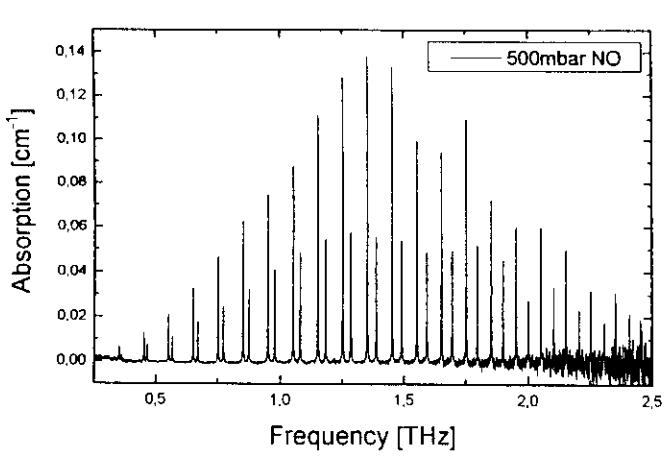
# THz-Spectroscopy of NO

Time domain:



# THz-Spectroscopy of NO

Frequency domain:



## Fs-THz-system for environmental measurements

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Compact and efficient diode laser based THz-system with time resolved THz detection for simultaneous gas analysis of different molecules at low concentration

### Special features:

- o Simultaneous detection of different molecules
- o Diode laser based system
- o High S/N-ratio
- o "on-line"-monitoring possible
- o Applicable for almost all relevant molecules (NO, CO, CO<sub>2</sub>, NH<sub>3</sub>,...)

## THz gas monitoring

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### o Sensitivity:

- Signal to noise ratio                      S/N = 10<sup>4</sup> ... 10<sup>6</sup>
- Absorption coefficient                      molecule dependent
  - consideration of
    - Doppler broadening                      negligible ( $\Delta\nu_D \approx 1 \dots 2$  MHz)
    - pressure broadening                      self broadening
    - foreign gas broadening
- Spectral resolution
  - Fourier transformation                      number of data points  
"zero filling"

⇒ spectral resolution and maximum absorption are not independent    ⇐

## THz spectroscopy: spectral resolution

- o Halfwidths of rotational lines  $\Delta\nu = \sigma_J \cdot p$  (pressure broadening)

- o Spectral resolution limited by Fouriertransformation

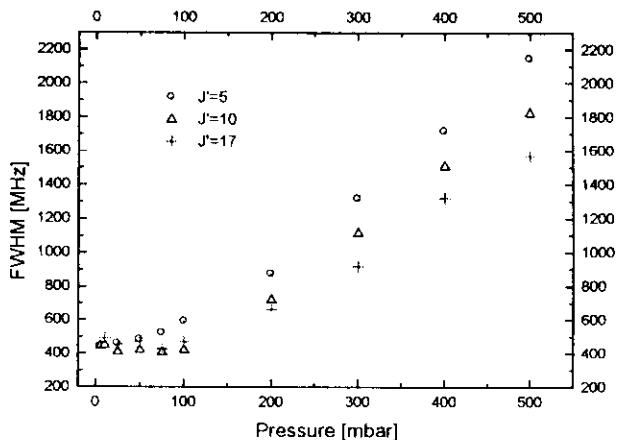
$$T_{\max} = 1 \text{ ns} \Rightarrow \Delta\nu_D = 1 \text{ GHz} \Rightarrow \text{"zero filling"} \Rightarrow \Delta\nu_R = 450 \text{ MHz}$$

↓

limited spectral resolution

will determine

sensitivity of the system



## THz spectroscopy: sensitivity

- o Pressure broadening: Maximum absorption is independent of pressure

$$\alpha_{\max} \propto \frac{N \cdot v_0}{\Delta\nu_J}, \quad N \propto p, \quad \Delta\nu_J \propto p \Rightarrow \alpha_{\max} \neq f(p)$$

However:

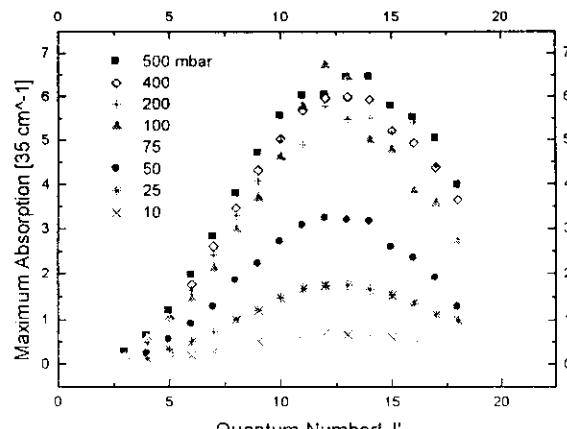
If  $\Delta\nu_R \geq \Delta\nu_J$

then  $\alpha_{\max} = f(p)$

↓

$$\alpha_{\max} (\Delta\nu_R \geq \Delta\nu_J) \ll \alpha_{\max} (\Delta\nu_R \leq \Delta\nu_J)$$

⇒ reduction in sensitivity



# THz spectroscopy: sensitivity

- o Reduction of data points

⇒ increase in line width

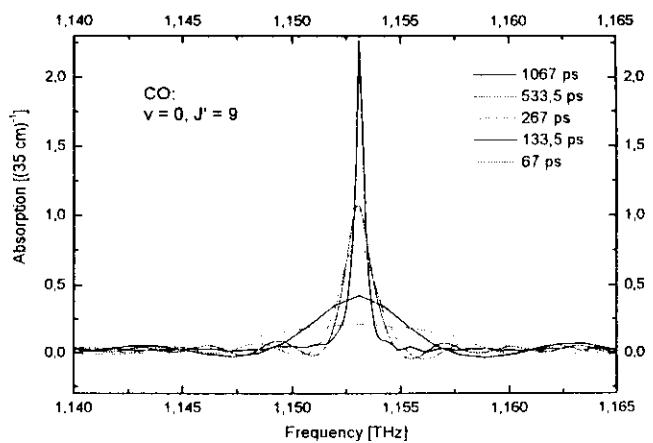
$$\Delta\nu_R = \frac{1}{T_{\max}}$$

⇒ if  $\Delta\nu_R > \Delta\nu_J$ ,

then decrease of maximum absorption

$$\alpha_{\max} \propto \frac{1}{\Delta\nu}$$

⇒ decrease in sensitivity



## THz spectroscopy: sensitivity

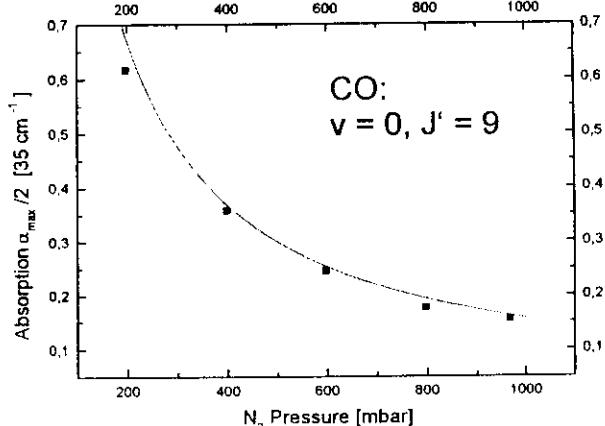
- o Measurements in a real environment: Foreign gas broadening
  - ⇒ increase in line width with constant number of absorbing molecules
  - ⇒ reduction of maximum absorption

$$\alpha_{\max} \propto \frac{1}{\sigma_J + \sigma_{fg} \cdot \frac{p_{fg}}{p}}$$



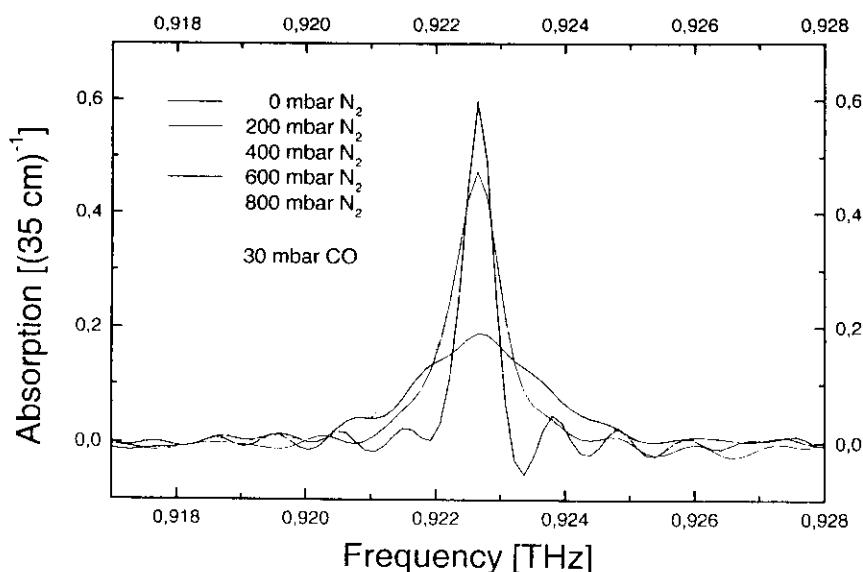
decrease in sensitivity

- o e. g.: CO broadened by N<sub>2</sub>



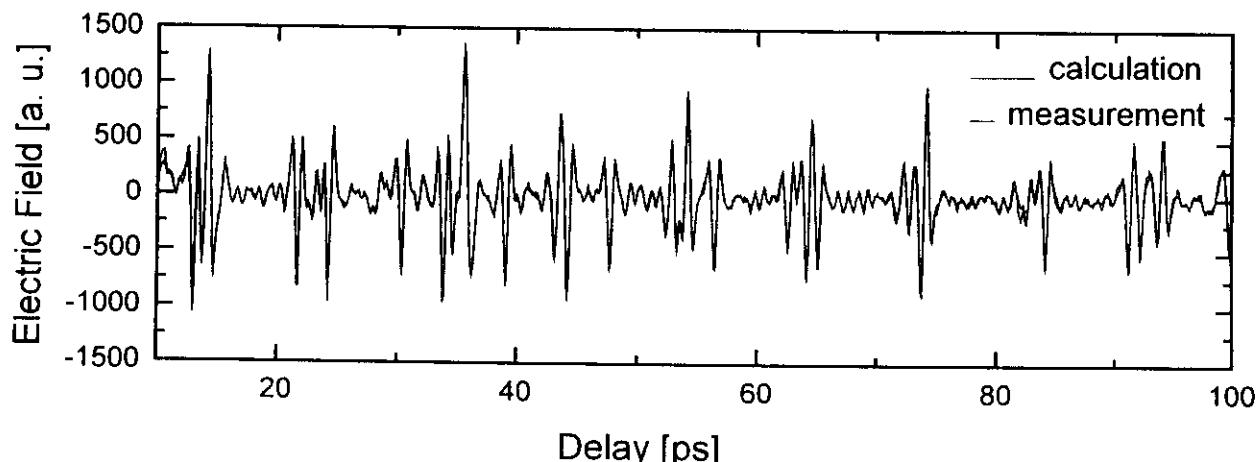
## THz spectroscopy: line broadening

- o Line broadening of CO rotational lines by N<sub>2</sub>



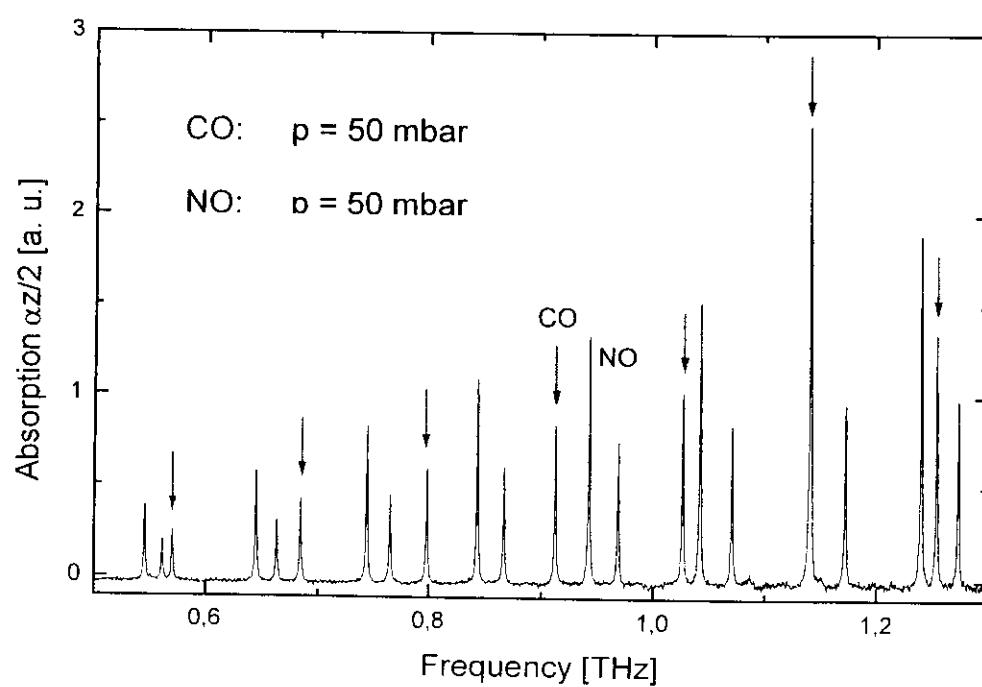
## THz-spectroscopy of NO/CO

Time domain:



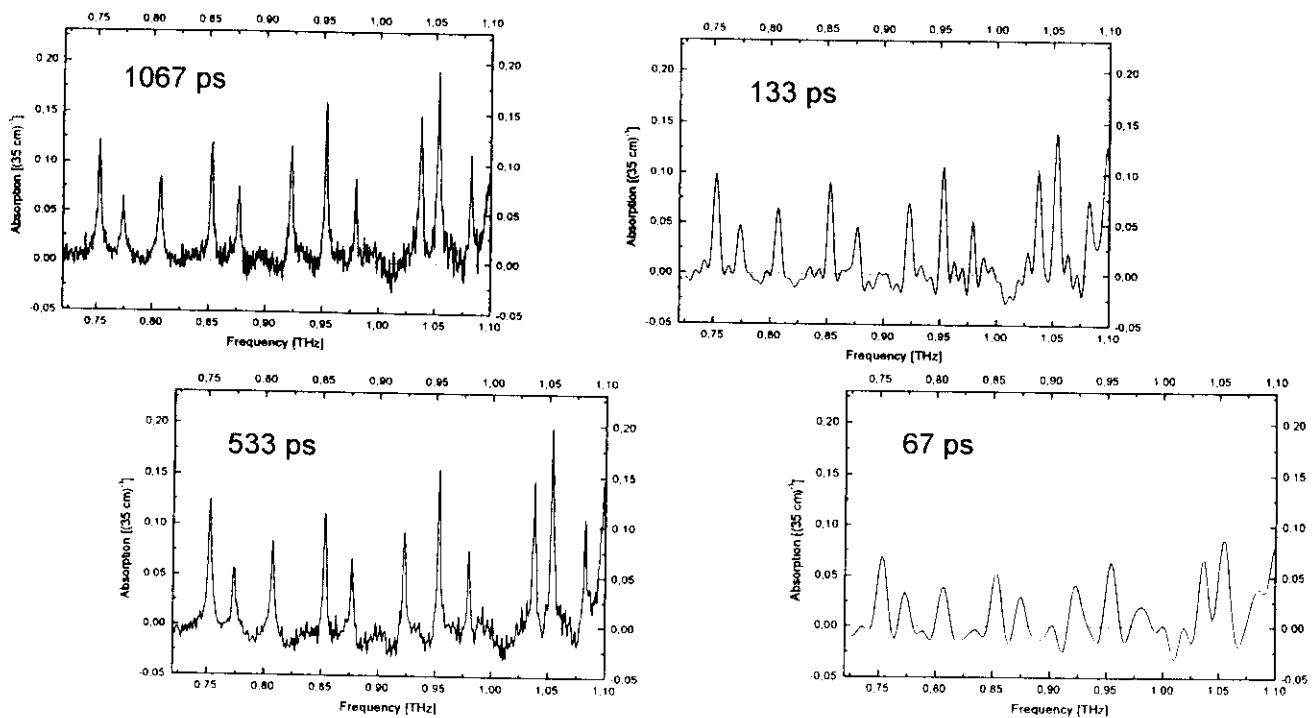
$p_{\text{CO}} = p_{\text{NO}} = 200 \text{ mbar}$

## Rotational spectra: CO/NO



# THz spectroscopy: spectral resolution

CO: 30 mbar, NO: 30 mbar, N<sub>2</sub>: 940 mbar





## THz spectroscopy

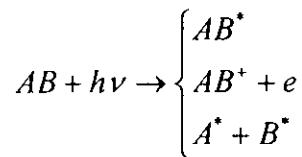
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Typical data:

Spectral range:	$100 \text{ GHz} < \lambda < 3,5 \text{ THz}$
Time resolution:	$\Delta\tau \geq 10 \text{ fs}$ (wave form) $\Delta\tau \geq 100 \text{ fs}$ (pump probe)
Spectral resolution:	$\Delta\nu \approx 500 \text{ MHz}$
Sensitivity:	molecule dependent ... ppm (ppb ?)
S/N ratio:	$10^4 < \text{S/N} < 10^6$
Repetition rate:	50 ... 250 MHz
Average power:	$10 \text{ nW} < P < 100 \mu\text{W}$

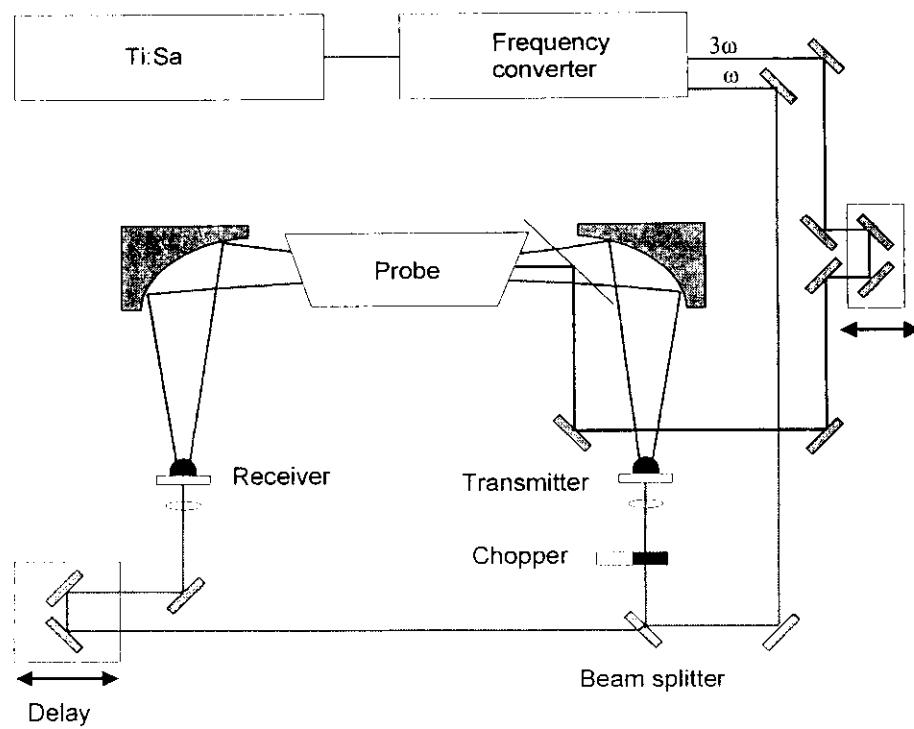
## Relaxation Processes

- o Energy relaxation in molecules
  - excitation (rot., vib.)
  - ionisation
  - fragmentation

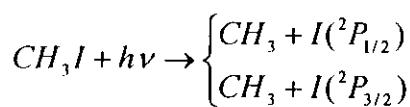


- o Photodissociation
  - ⇒ change of the moments of inertia
  - ⇒ change of the rotational spectrum
- o Measurement of the rotational spectrum during the dissociation process
  - ⇒ microwave spectroscopy (THz-range)

## Experimental set-up



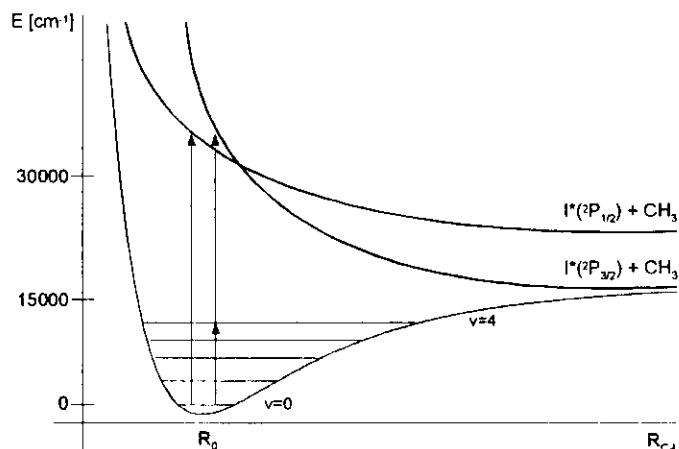
# Photodissociation of CH<sub>3</sub>I



220 nm < λ < 320 nm

Small rotational excitation  
of CH<sub>3</sub> during dissociation  
(CH<sub>3</sub>I is a „linear” molecule)

Fast recombination of the radicales  
(k ≈ 10<sup>-11</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>)



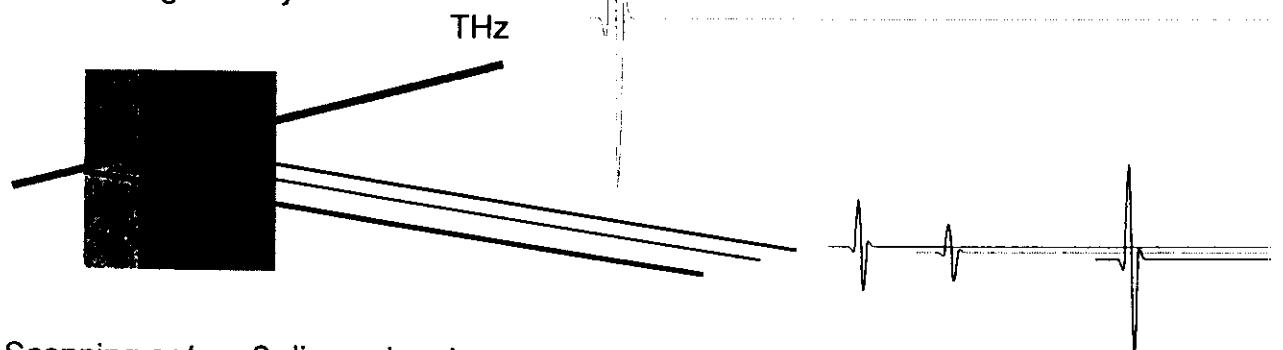
model system for photodissociation processes

single and multi step photodissociation possible

dramatic change of the moment of inertia    ⇒    B(CH<sub>3</sub>I) = 0.25 cm<sup>-1</sup>  
B(CH<sub>3</sub>) = 9.57 cm<sup>-1</sup>

## THz tomography

- o Signal acquisition in the time domain
- o Reflection geometry

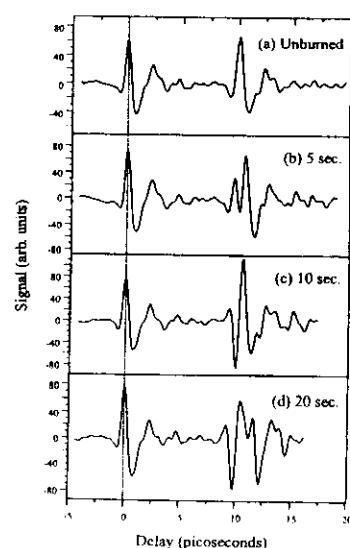
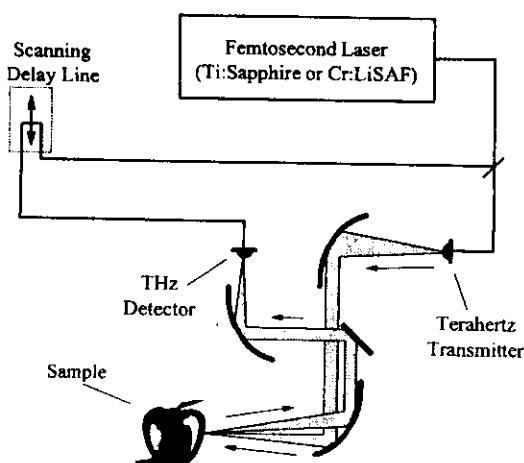


- o Scanning or true 2-dimensional measurements
- o Measurement of the reflected THz signals caused by Fresnel reflection
- o Spectral information of material transmitted by THz radiation

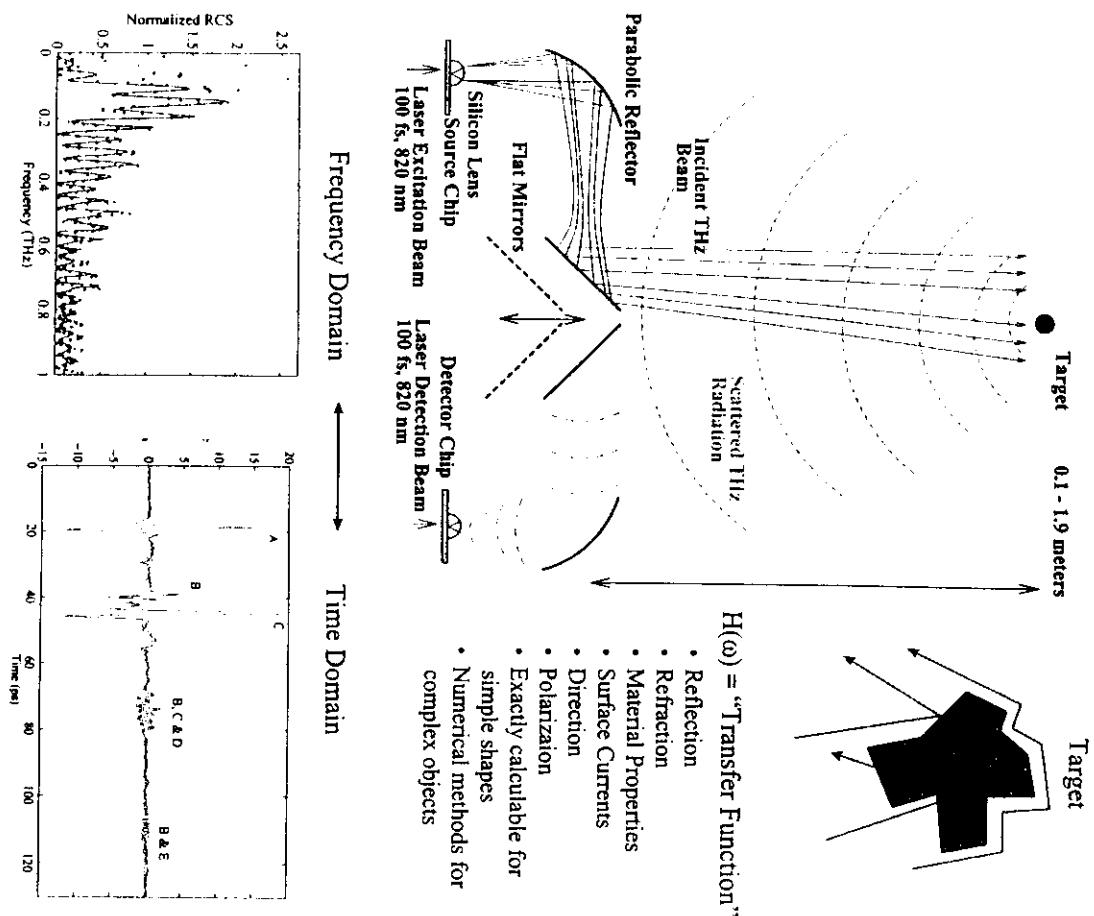
## THz-Tomography

Principle:

Medical application:



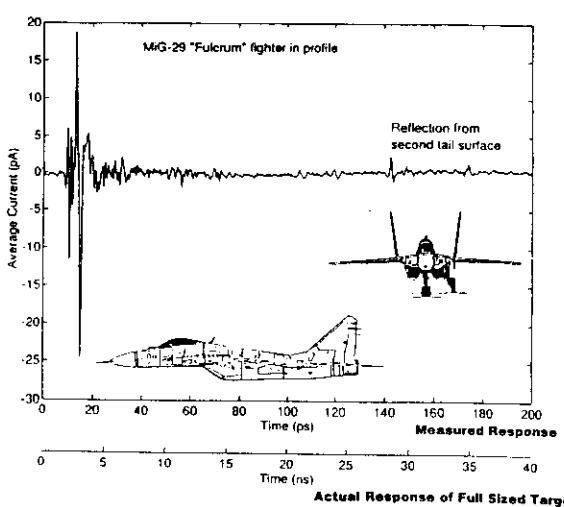
## THz-Ranging



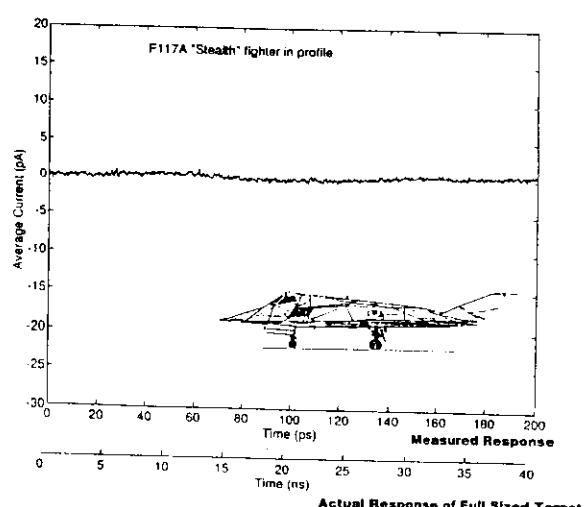
## THz Radar

o reduced target size according to wavelength ratio  $\Rightarrow 100 \text{ GHz} \rightarrow 2 \text{ THz}$

$\sim 1:200$  Scale MiG-29 "Fulcrum" at 1.07 m  
(100 GHz - 2 THz)



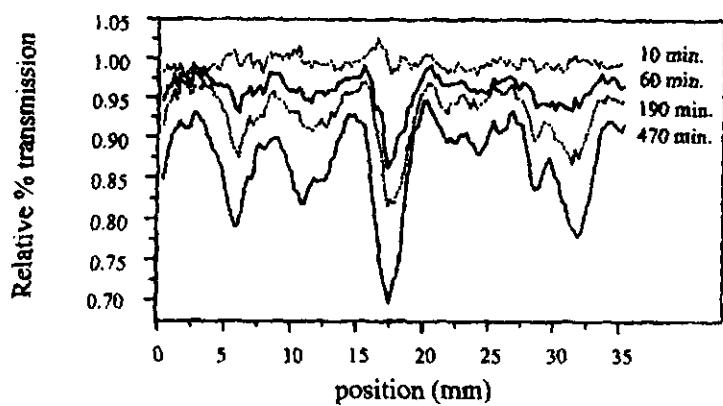
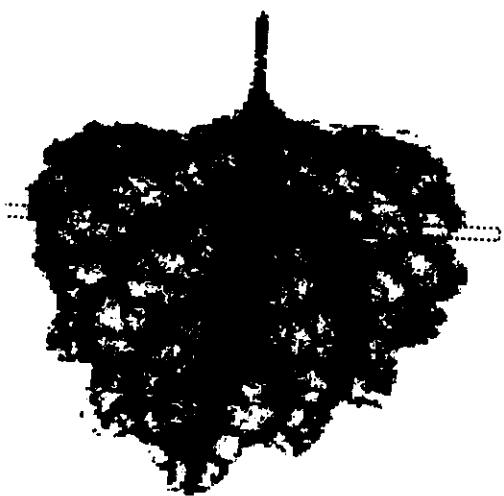
$\sim 1:200$  Scale F117A "Stealth" at 1.07 m  
(100 GHz - 2 THz)



Full Size MiG-29 at 230 meters (500 MHz to 10 GHz)

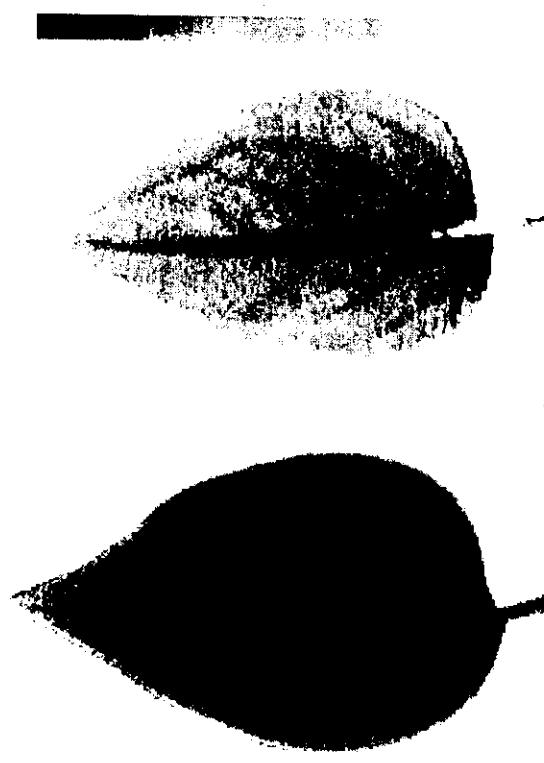
Full Size F117A at 230 meters (500 MHz to 10 GHz)

# THz-Imaging

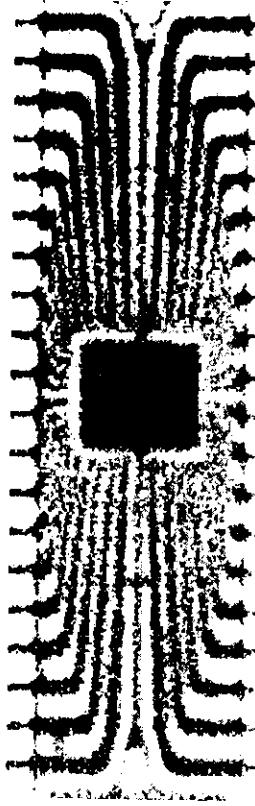


## Sample T-Ray Images

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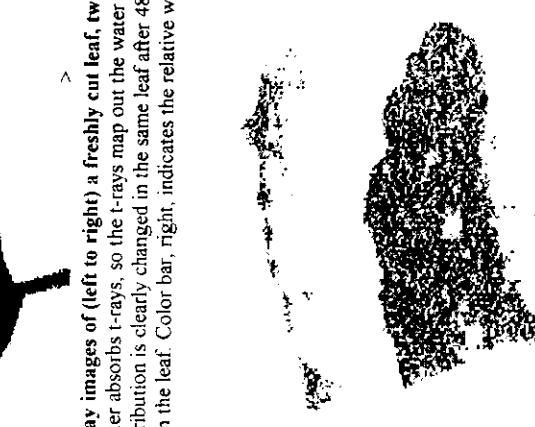
T-ray image of a piece of bacon.  
White colors in this image correspond to no absorption, and red correspond to strong absorption of t-rays. The fatty portions of meat are almost transparent to t-rays, while the lean portions absorb roughly 25 times as much t-rays.



T-ray image of a packaged semiconductor chip.  
Most plastics are transparent to t-rays, so that the silicon circuit as well as the metal leads can be made out inside the package.



T-ray image of an AT&T SmartCard.  
The inductive loops for powering as well as some of microchips inside can be seen through the plastic package.



T-ray images of (left to right) a freshly cut leaf, two-day old leaf, color bar.  
Water absorbs t-rays, so the t-rays map out the water distribution inside the fresh leaf, left. The water distribution is clearly changed in the same leaf after 48 hours, center. Water has selectively evaporated from the leaf. Color bar, right, indicates the relative water concentration inside the leaves.

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## Conclusion

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- o Generation of THz radiation using fast photconductive switches
- o Coherent detection ⇒ high S/N-ratio
  - ⇒ THz-Spectroscopy of hot gases
- o Simple (?) and reliable systems
- o Application of fs-THz-radiation in:
  - Spectroscopy of solid state materials and gases (fs-THz-TDS)
  - Environmental analysis / "on-line"-process monitoring
  - Imaging
  - Medicine