BESSY

Berliner Elektronenspeicherring-Gesellschaft
für Synchrotronstrahlung m.b.H.

Fourier-Transform Infrared Spectroscopic Ellipsometry for Material Identification

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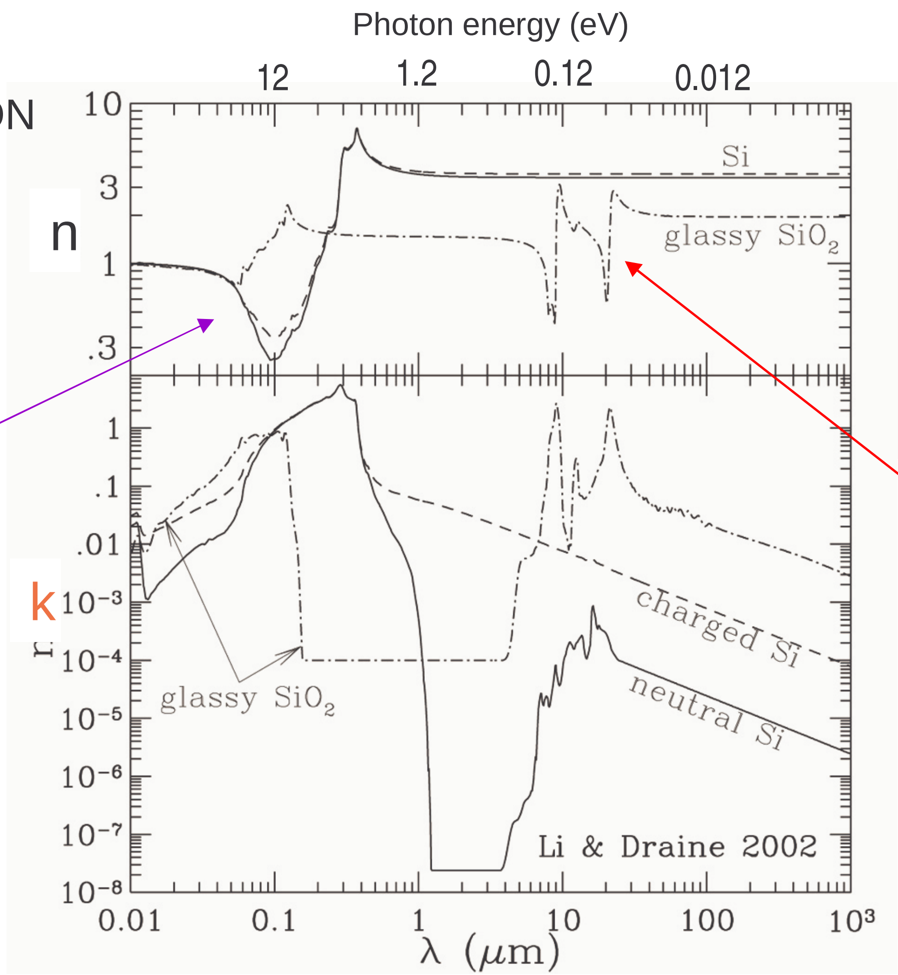
Outline of the talk

- Optical constants of solids
- Ellipsometry basics
- Fourier-transform infrared spectroscopy (FTS or FT-IR)
- Far-infrared/Terahertz setup: detectors, sources
- The case of remote identification of explosives:
  - transmission
  - reflection
  - ellipsometry

Optical constants of solids

INDEX OF REFRACTION
(COMPLEX)



Electronic
excitations
(electron-hole pairs)
(Interband transitions)

Equivalent formulations:
- Dielectric constant ε
- Optical conductivity σ

$$\epsilon_1 = n^2 - k^2$$
$$\epsilon_2 = 2nk$$
$$\sigma_1 = \frac{\omega}{4\pi}\epsilon_2$$
$$\sigma_2 = \frac{\omega}{4\pi}(\epsilon_\infty - \epsilon_1)$$

Dipolar
Lattice
Vibrations
(optical phonons)
(normal modes)

Chemical element identification

ULTRAVIOLET

INFRARED

Chemical species identification

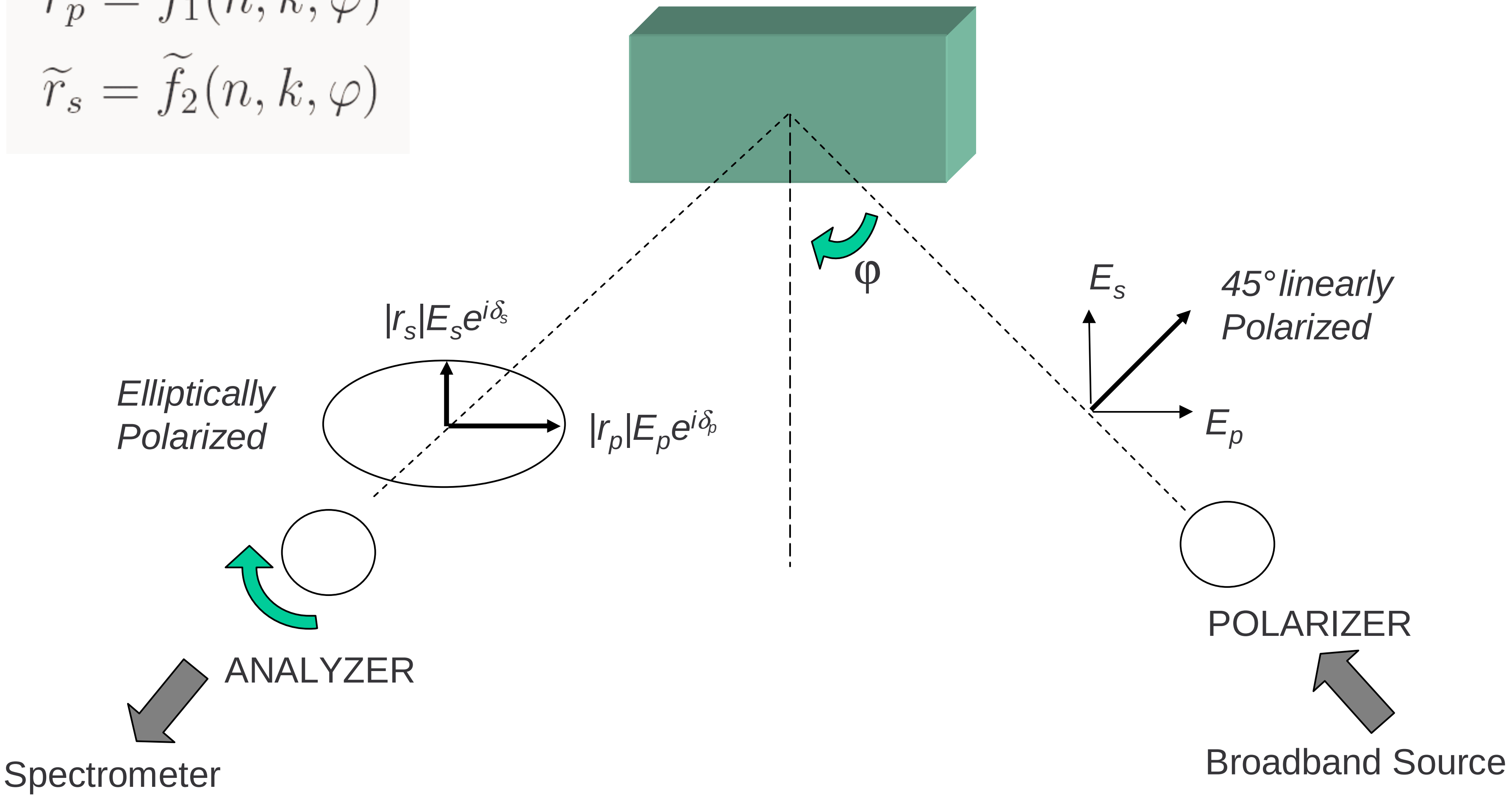
Ellipsometry

Fresnel formulae

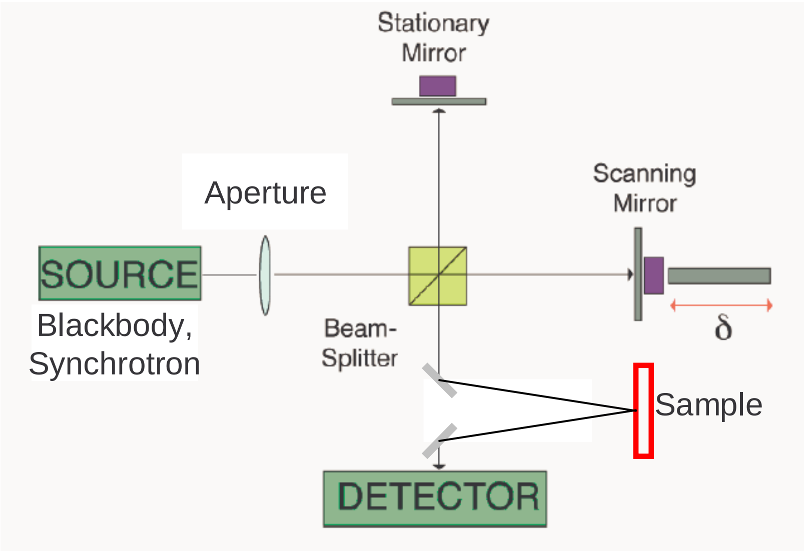
$$\widetilde{r}_p = \widetilde{f}_1(n, k, \varphi)$$
$$\widetilde{r}_s = \widetilde{f}_2(n, k, \varphi)$$

Material under analysis

$$n + \imath k$$



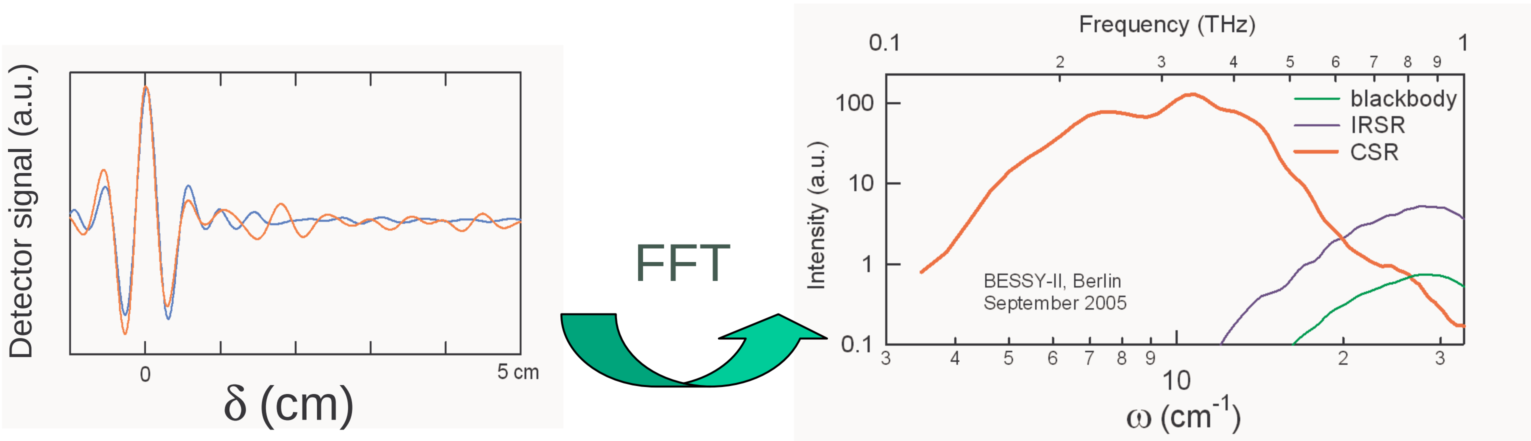
Fourier-Transform Infrared Spectroscopy



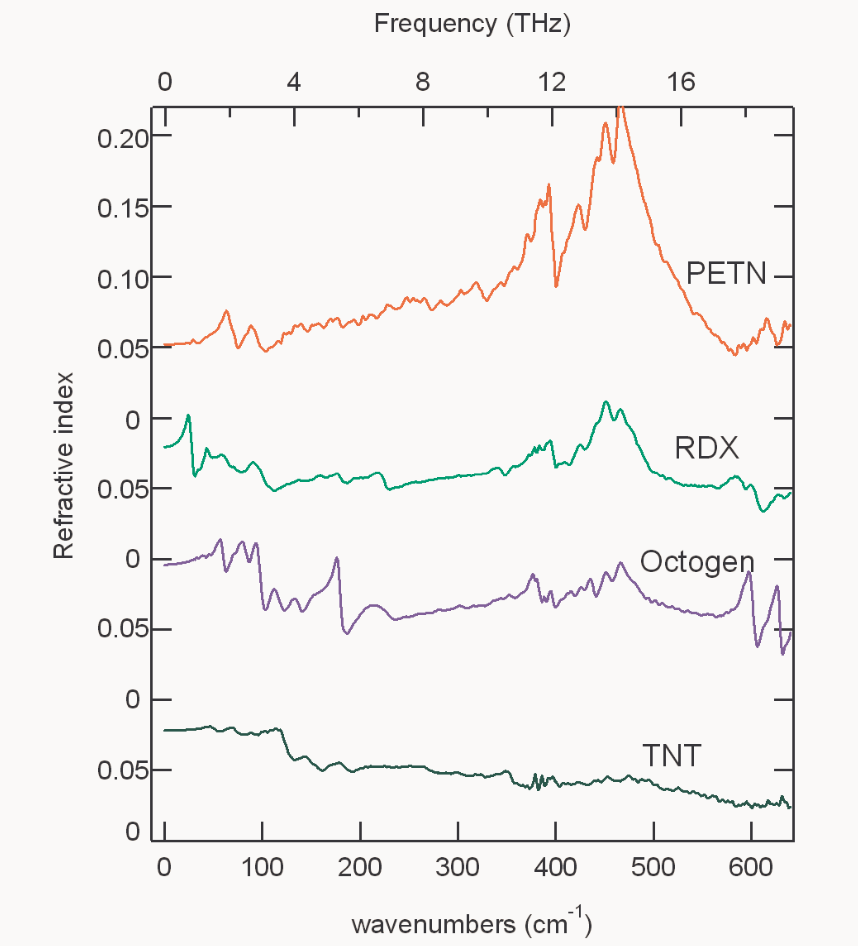
Infrared spectrometer: Michelson Interferometer

- Reflected and/or Transmitted Power spectra are measured as a function of the frequency ω
- Optical constants are derived by Kramers-Kronig analysis or by Ellipsometry

Frequency range: 0.1 THz – 2 PHz
Energy resolution: up to 0.01 THz



Material identification by Terahertz Spectroscopy



- **Far-Infrared spectra**
  "Fingerprint" region: each solid substance has a specific spectrum, or frequency-dependent optical constants
  (like a spectrometer)

- **Terahertz frequencies**
  Clothes, tissues, plastic, paper and atmosphere are partly transparent: remote identification is possible
  (like a radar)

Applications:

⇒ Remote security controls

⇒ Explosive detection

Infrared Spectroscopic Ellipsometry

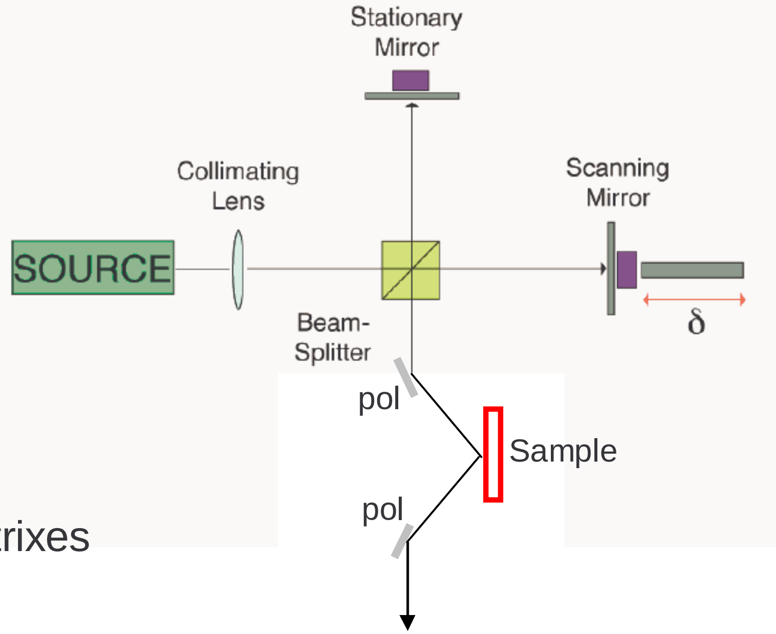
Fresnel relations: trascendental

$$\left.\begin{aligned}\widetilde{r}_p &= \frac{(n+\imath k)\cos(\varphi)-\cos(\varphi\prime)}{(n+\imath k)\cos(\varphi)+\cos(\varphi\prime)} = |\widetilde{r}_p|e^{\imath\delta_p}\\ \widetilde{r}_s &= \frac{\cos(\varphi)-(n+\imath k)\cos(\varphi\prime)}{\cos(\varphi)+(n+\imath k)\cos(\varphi\prime)} = |\widetilde{r}_s|e^{\imath\delta_s}\\ \sin(\varphi) &= (n+ik)\sin(\varphi\prime)\end{aligned}\right\} \Rightarrow \mathrm{n} + \imath k$$

Michelson: intrinsic beam polarization!

$$\widetilde{\rho} = \frac{\widetilde{r}_p}{\widetilde{r}_s} = \frac{(n+\imath k)\cos(\varphi)-\cos(\varphi\prime)}{\cos(\varphi)-(n+\imath k)\cos(\varphi\prime)} = \tan\Psi e^{\imath\Delta}$$

$$\tan\Psi = \frac{|\widetilde{r}_p|}{|\widetilde{r}_s|} \qquad \Delta = \delta_p - \delta_s$$

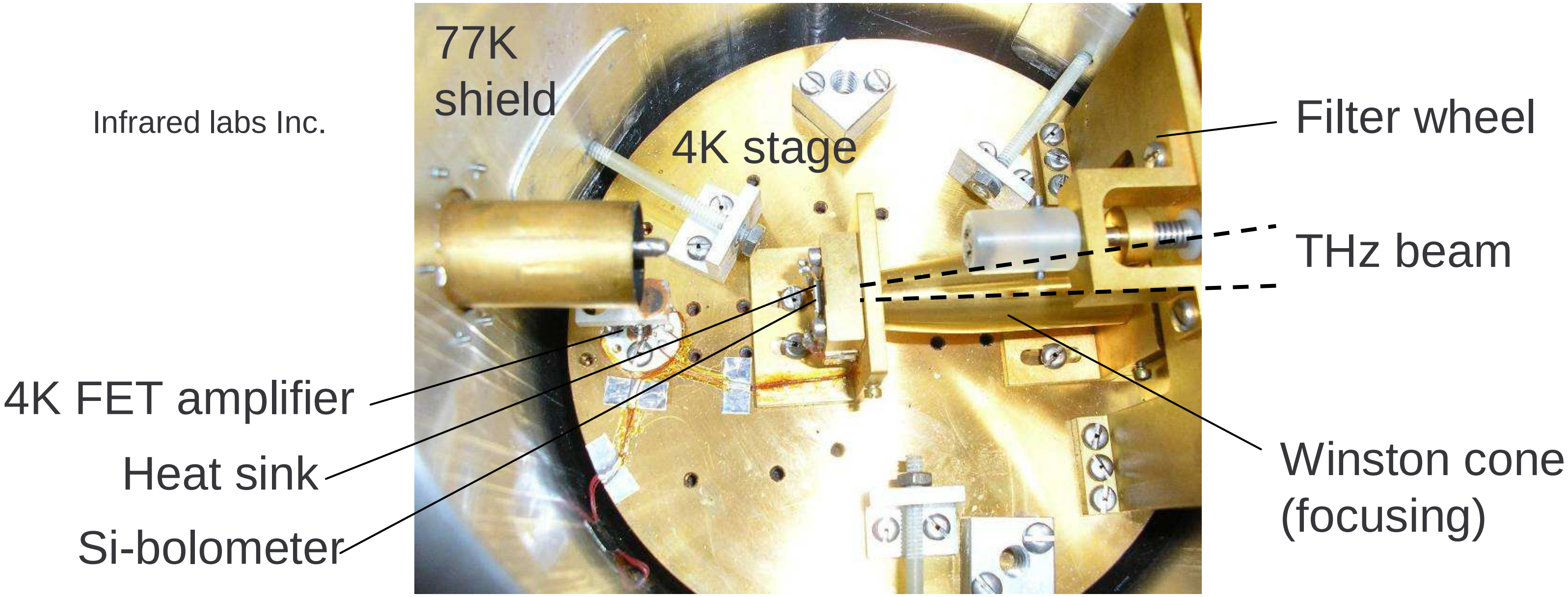


Infrared ellipsometry requires calibration !
Normalized Stokes parameters calc with Mueller matrixes

$$\begin{aligned}&\cos 2\Psi\\ &\sin 2\Psi\cos\Delta\\ &\sin 2\Psi\sin\Delta\end{aligned} \Rightarrow \mathrm{n} + \imath k$$

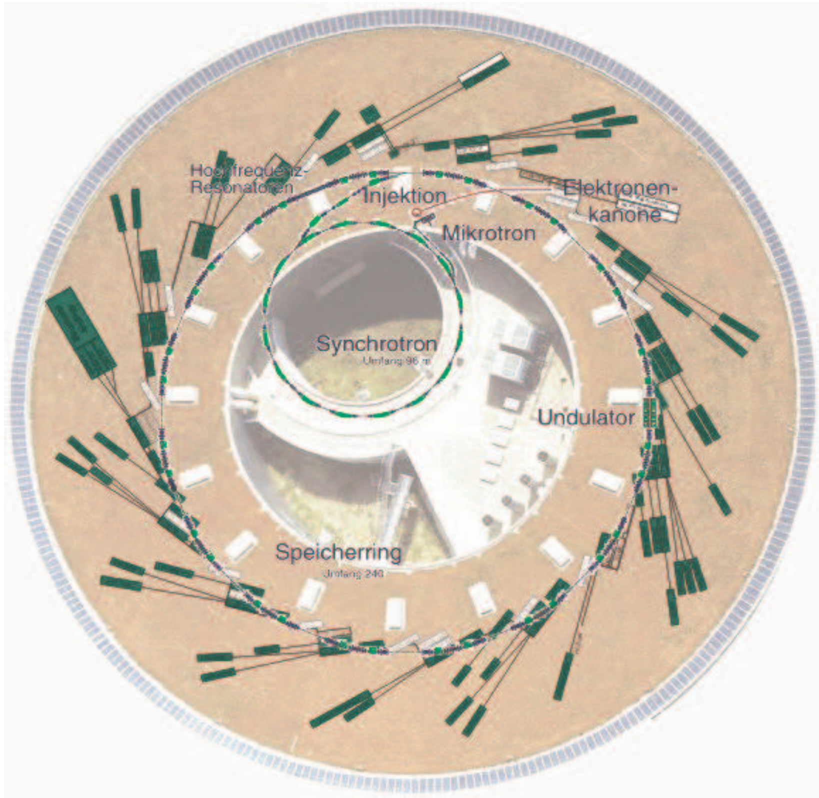
in the whole infrared range!

Detector: Liquid Helium-cooled Bolometer



- Room-temperature detectors (Pyroelectrics, Golay cells) are also available, but noise figures are 10^3 times higher
- Development of sensitive detectors working at higher temperatures is ongoing (e.g. closed-cycle cooled, liquid nitrogen).
- CNR-IFN in Rome is developing superconducting bolometers.

Source: Synchrotron BESSY in Berlin

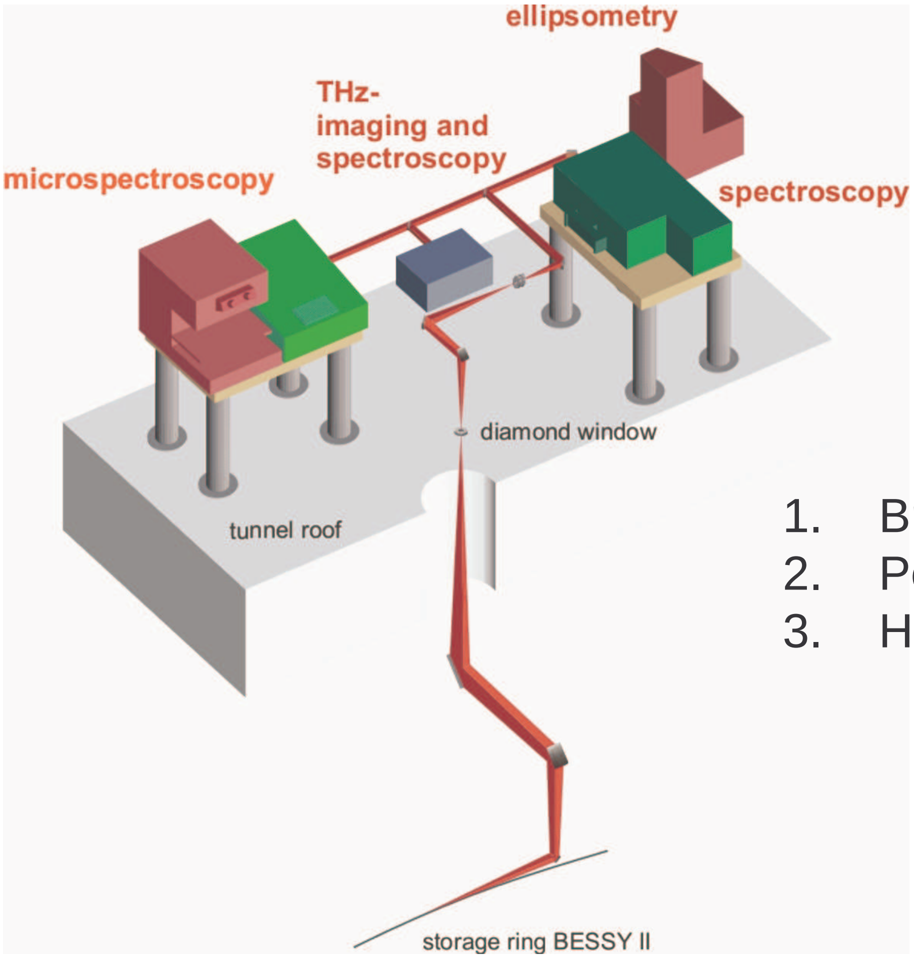


Start user operation:	1999
Circumference of the synchrotron:	96 m
Circumference of the storage ring:	240 m
Number of bending dipoles:	2 x 16
Number of possible insertion devices:	15
Number of beamlines commissioned:	~ 50

Commissioning of the IR-beamline IRIS: 2002

It is the only storage ring producing steady-state Coherent Synchrotron Radiation
=> high power, pulsed source in the 0.1-1 THz range based on electron bunch acceleration

The Infrared beamline at BESSY

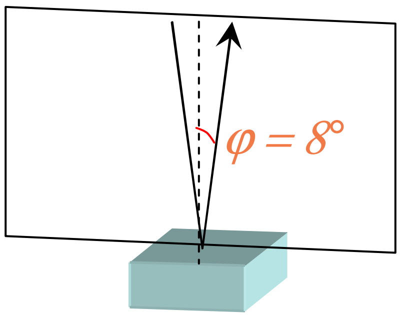


1. Broadband spectrum (MMW to UV)
2. Point-like source (tight focus)
3. High brilliance (photon density at focus)

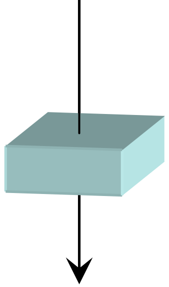
Far-infrared Ellipsometry

Optical setups for measuring the optical constants

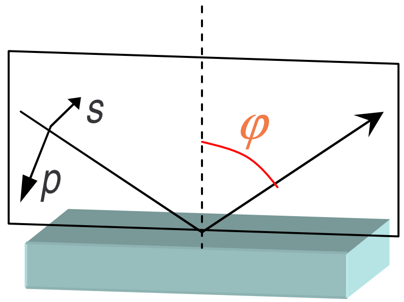
- Normal Incidence Reflectance



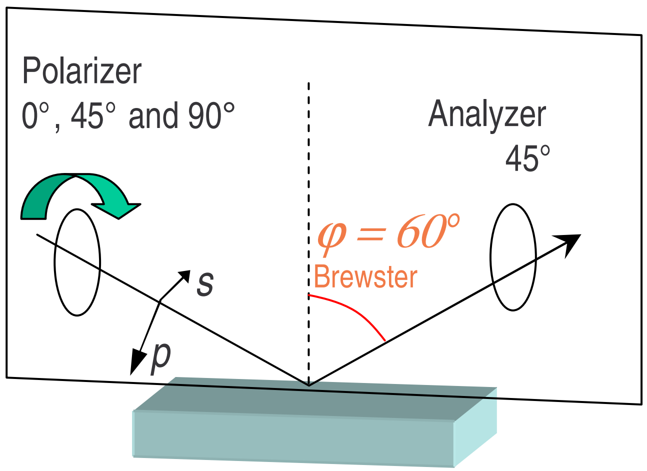
- Transmittance



- Variable Angle Reflectance

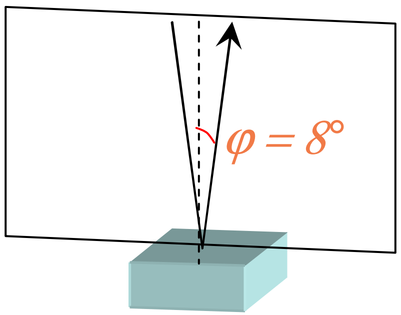


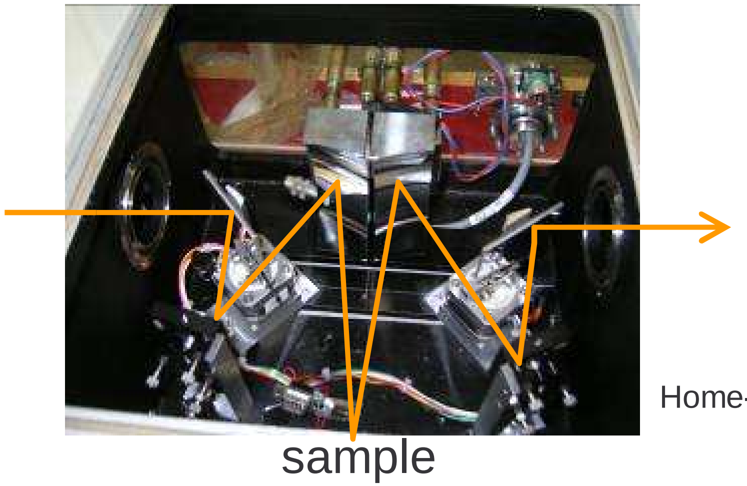
- Ellipsometry



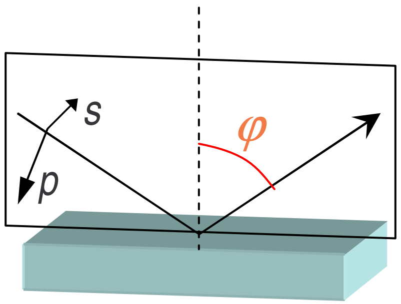
Optical setups

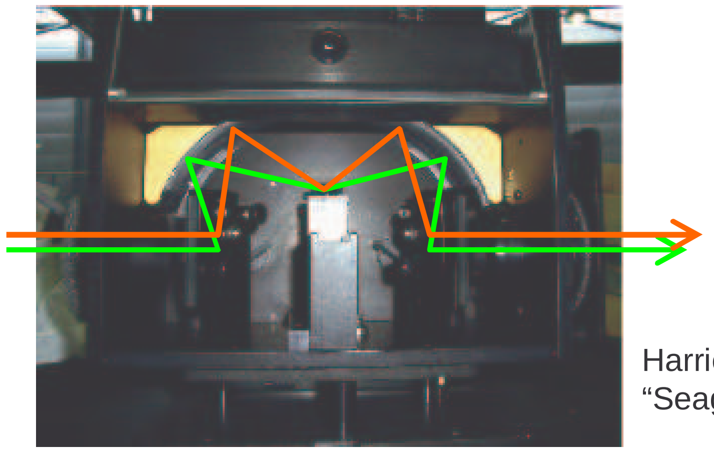
- Normal Incidence



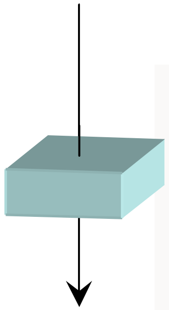


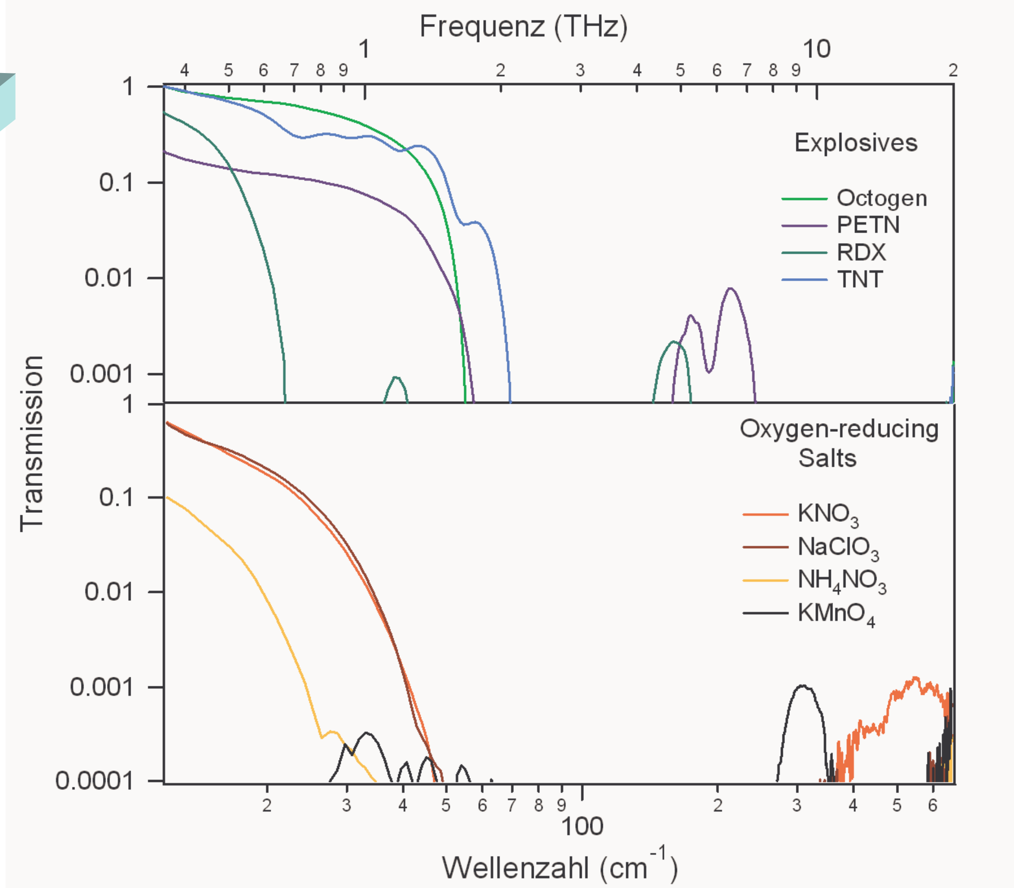
- Variable Angle





Transmission of pure pellets of explosives and Oxygen-reducing salts





Pure Material pellets
Thickness: 2.0 mm

Bulk Polyethilene sample holder, 15°wedged

High Transparency only below 1 THz

⇒ No strong material-specific features

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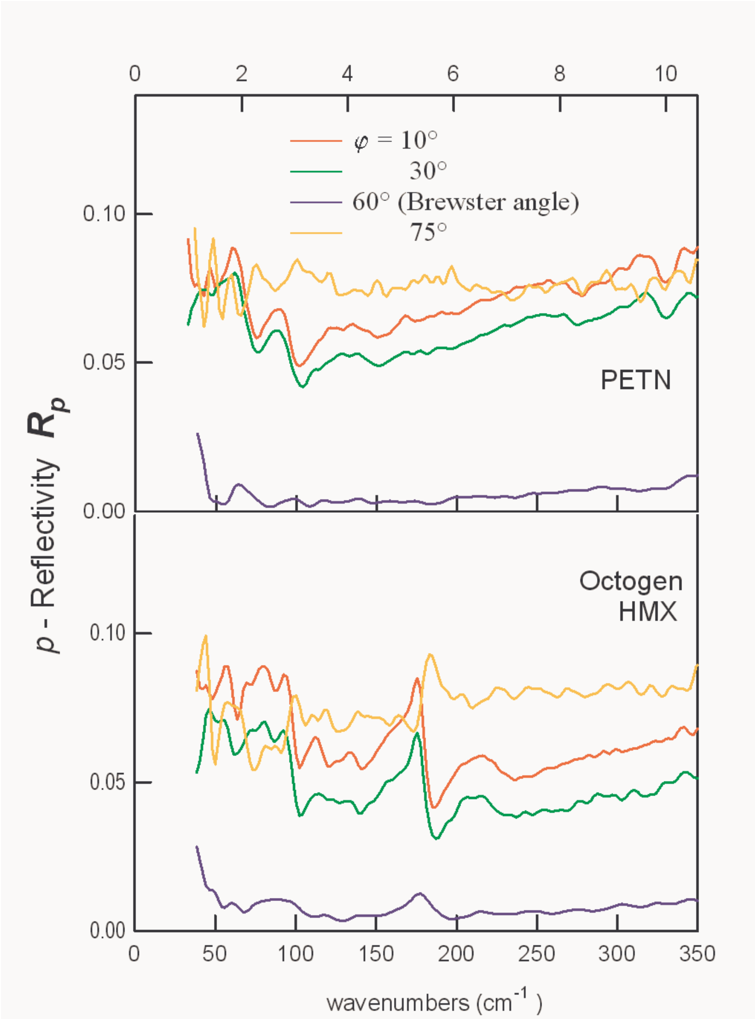
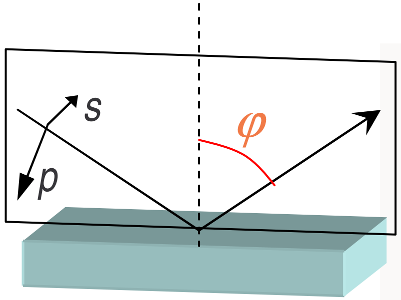
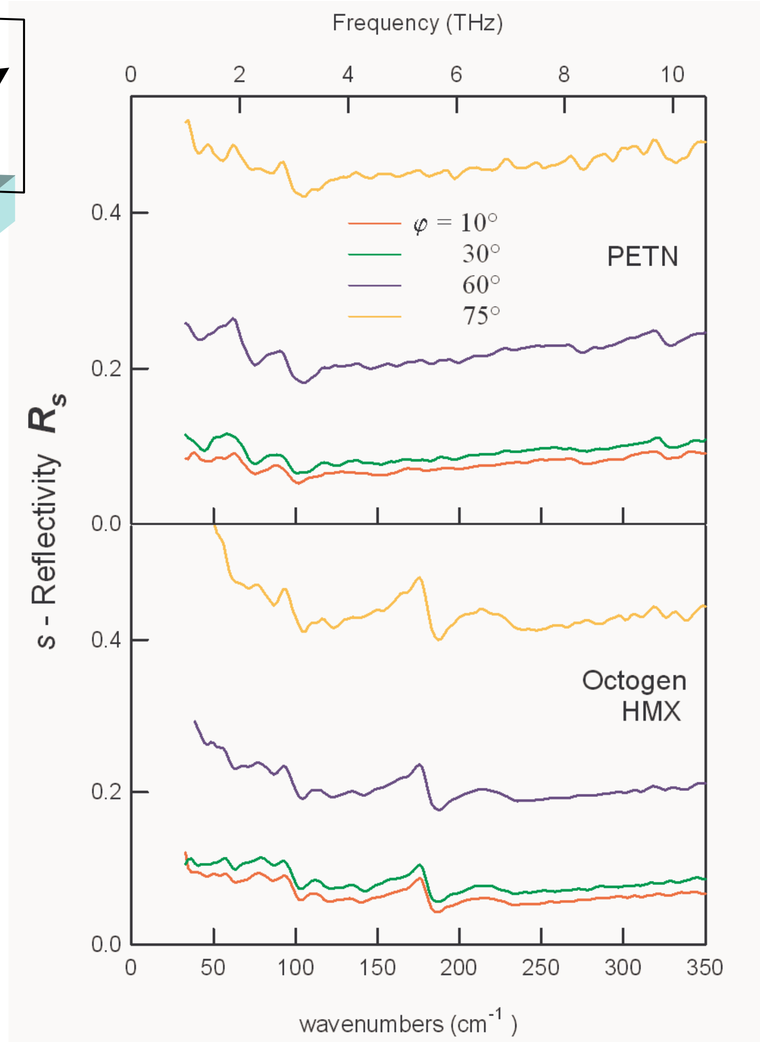
Absolute Reflectivity of pure explosive pellets for different angles of incidence

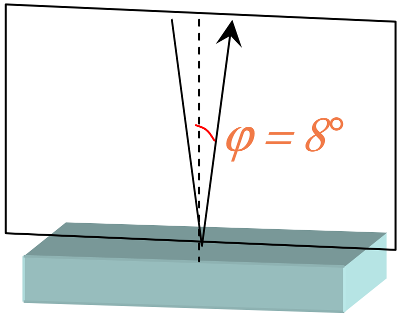




- Reference is a gold mirror
- R_s~R_p for φ ~ 0, R_s>R_p anywhere else
- R_p goes to 0 at the Brewster angle (~60°)
- The slope and the sharp features are material-specific and do not depend much on φ



Optical constants of explosives:
Absolute Reflectivity and Kramers-Kronig analysis



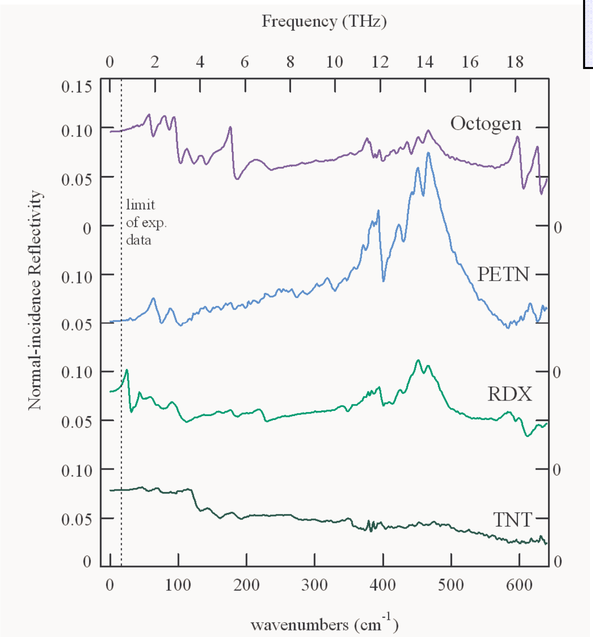
KK

$$\phi_r(\omega) = -\frac{2\omega}{\pi}\mathcal{P}\int_0^\infty \frac{\ln\sqrt{R(\omega')}}{\omega'^2-\omega^2}d\omega'$$

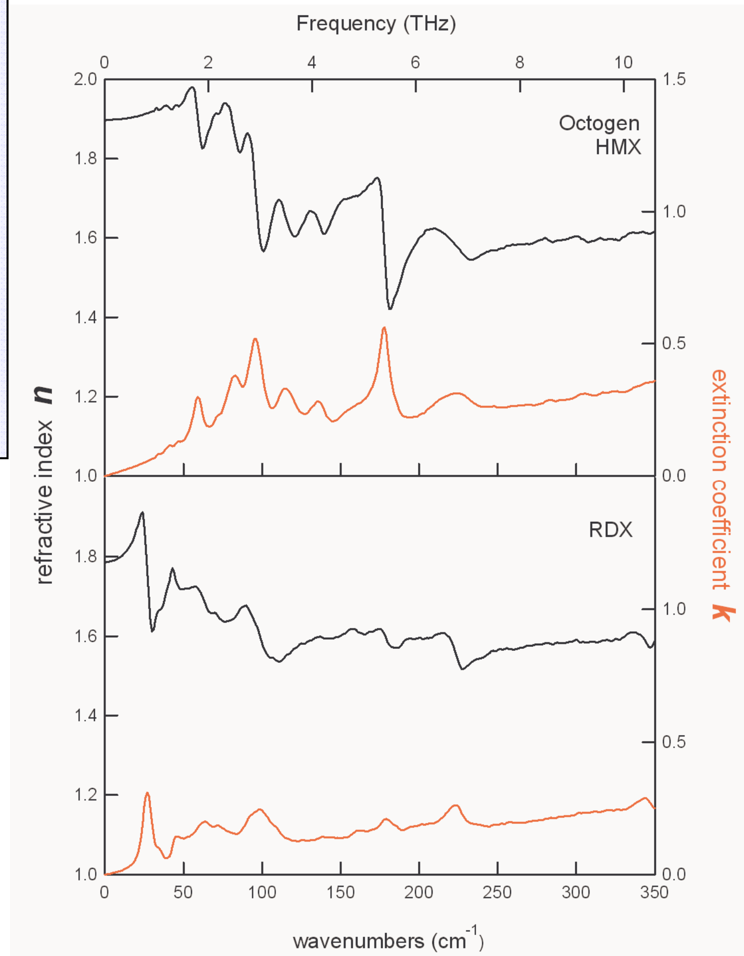
Absolute reflectivity R is measured at quasi-normal incidence from 0.7 to 20 THz to correctly evaluate the integral.

$$= Re^{i\phi}$$
$$= n + i\,k$$

$$\tilde{n} = \frac{1+\tilde{r}}{1-\tilde{r}}.$$

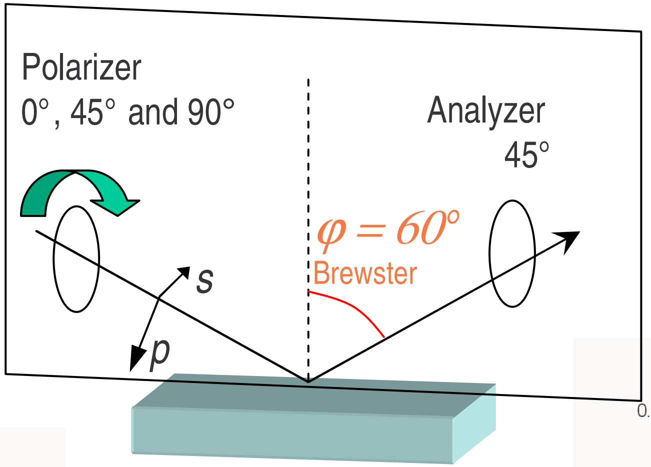


- High signal intensity
- Practical geometry
- High output quality
- Need a reference measurement on a mirror
- Very sensitive to absolute value (acceptable: ±5%)
- Need for a databank of high frequency extrapolations

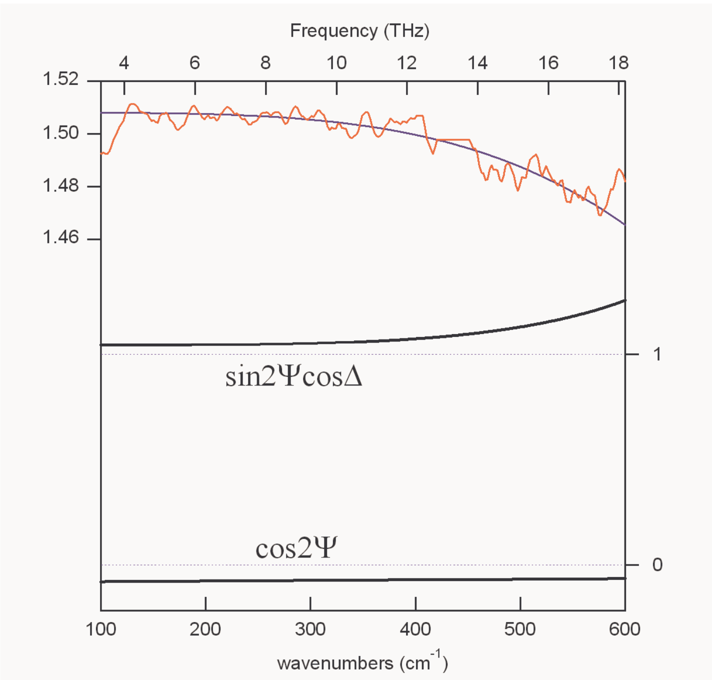


Spectroscopic Ellipsometry: optical constants with no reference measurement

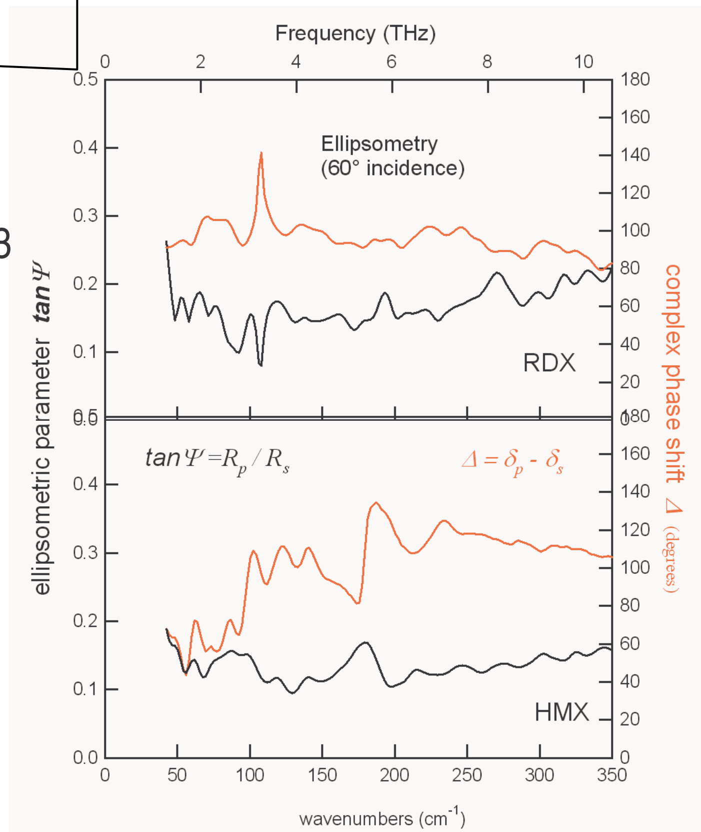
Calibration: a known, non-absorbing material at his Brewster angle, where the ellipse is most excentric



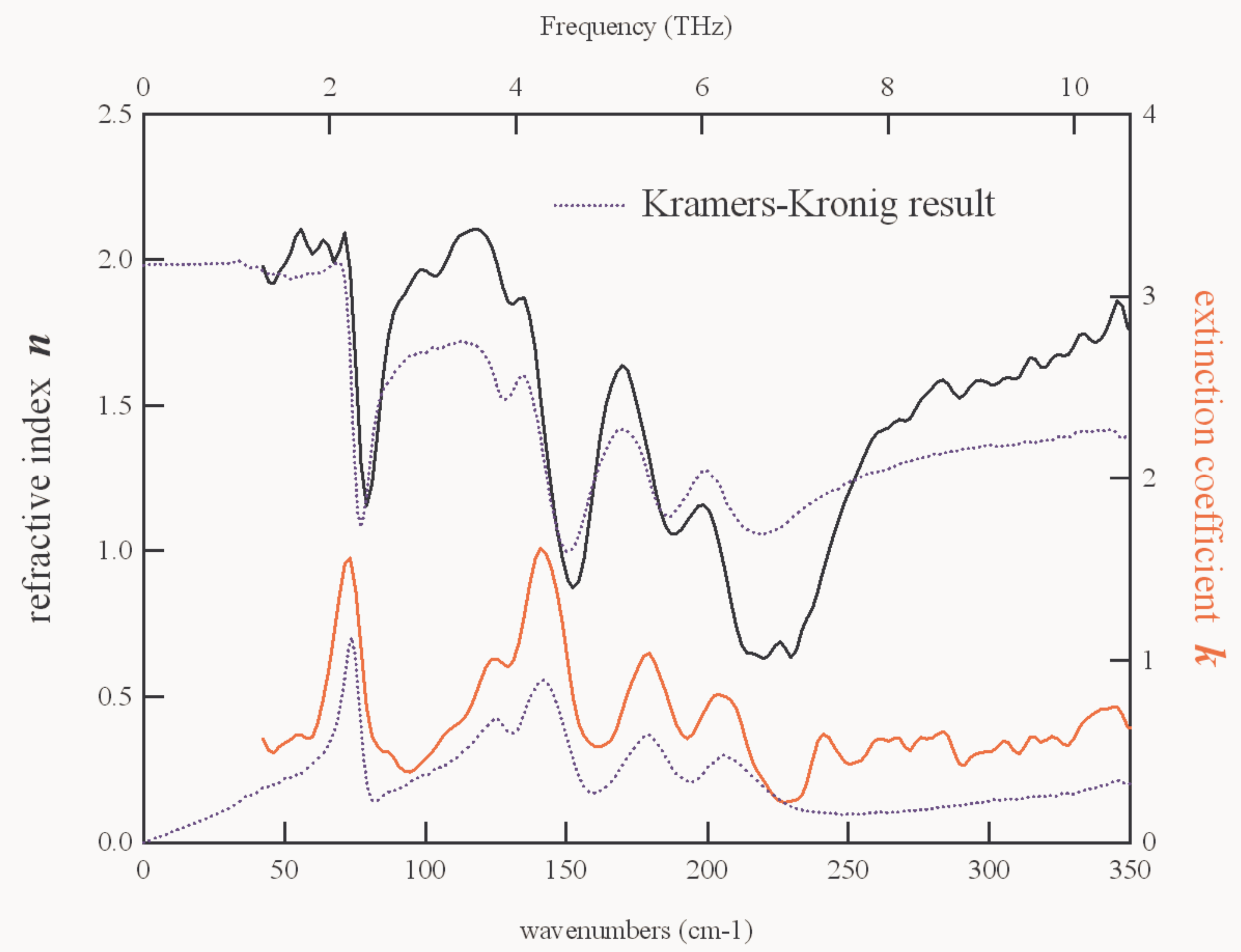
Data harvest:close to Brewster angle
Polarizer rotated instead of analyzer (equivalent)



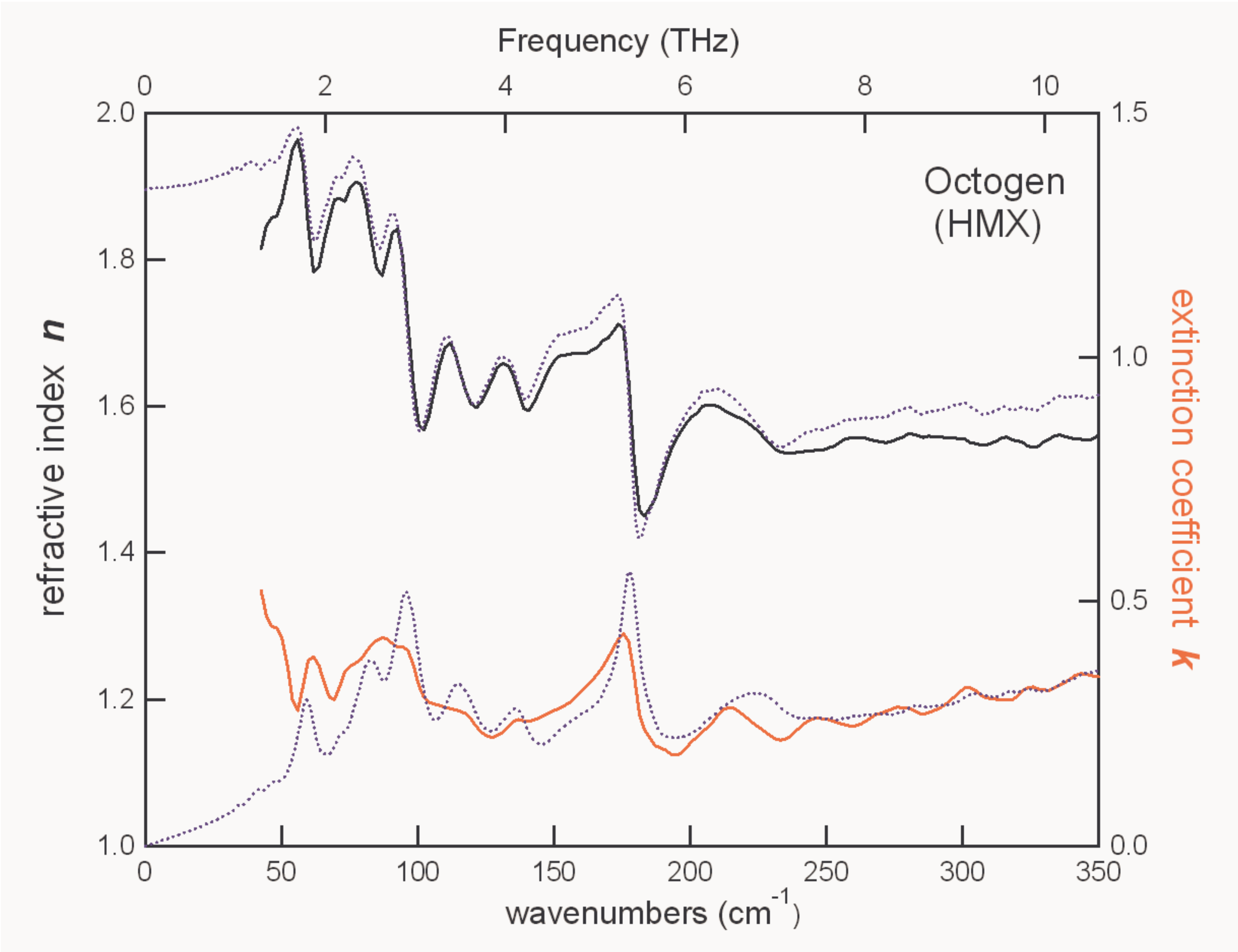
- n, k or Ψ, Δ determined from 3 sample spectra only (no mirror)
- the incidence angle has to be large (>50°) and known (±0.5°)
- High sensitivity to noise (trigonometric functions)
- Low signal at low frequency (2 polarizers + 60° incidence)



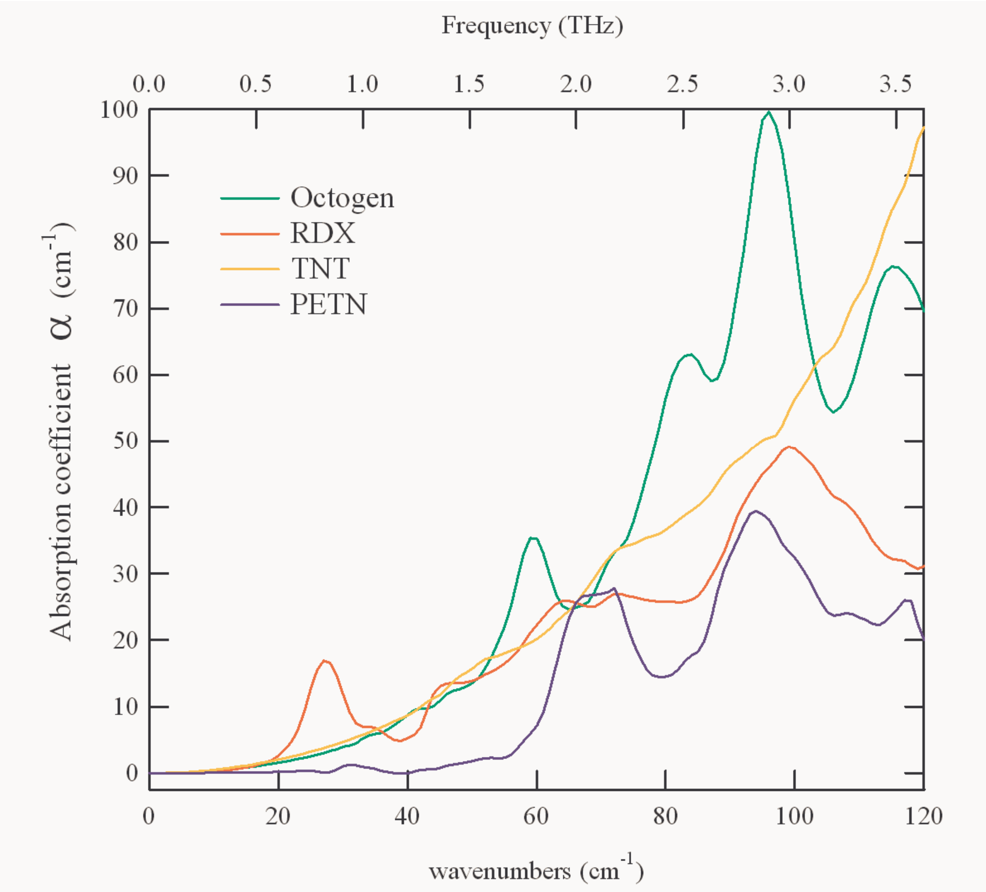
Result 1: $NaClO_3$ (a salt)

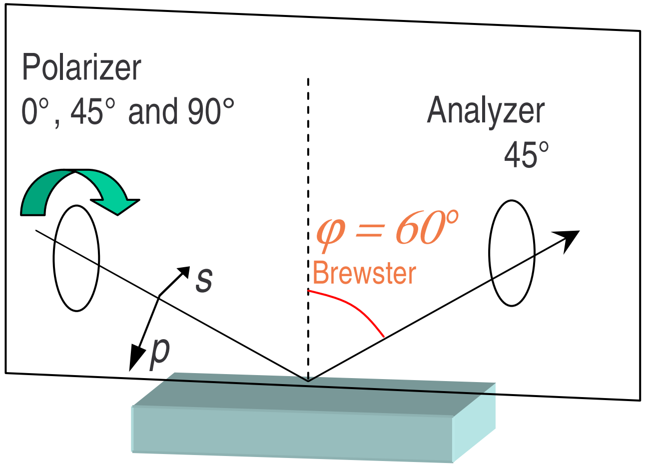


Result 2: Octogen (an explosive)



Absorption coefficient of explosives in the THz range





Optical constants determined by
<u>Far-infrared ellipsometry</u>

⇒ No need for reference measurements to correct for the frequency-dependent incident power

⇒ Up to 4 THz, no role of surface roughness (common-use objects are "shiny")