



Absorption spectroscopy of atmospheric species

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pep

postgraduate programme
environmental physics

atmosphere, ocean, land, climate

Content

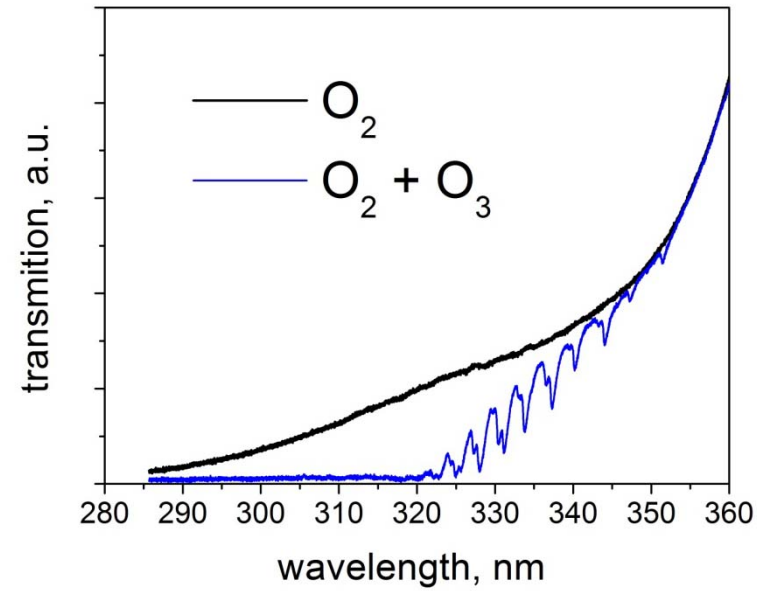
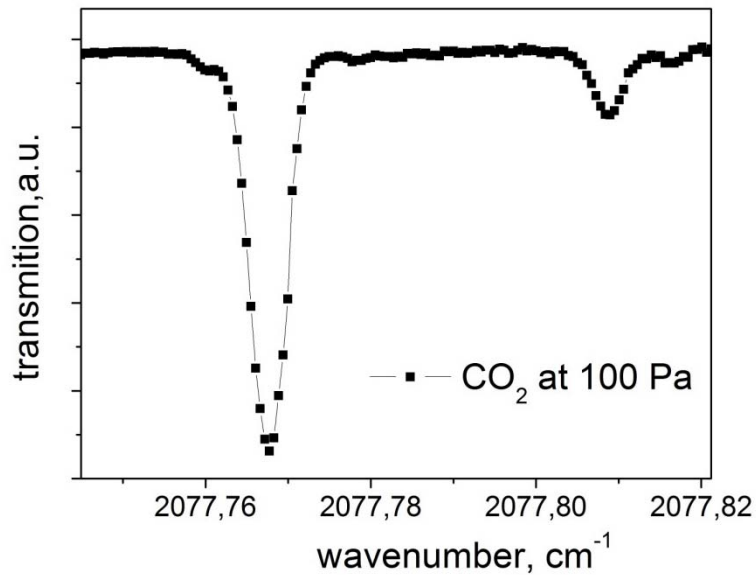
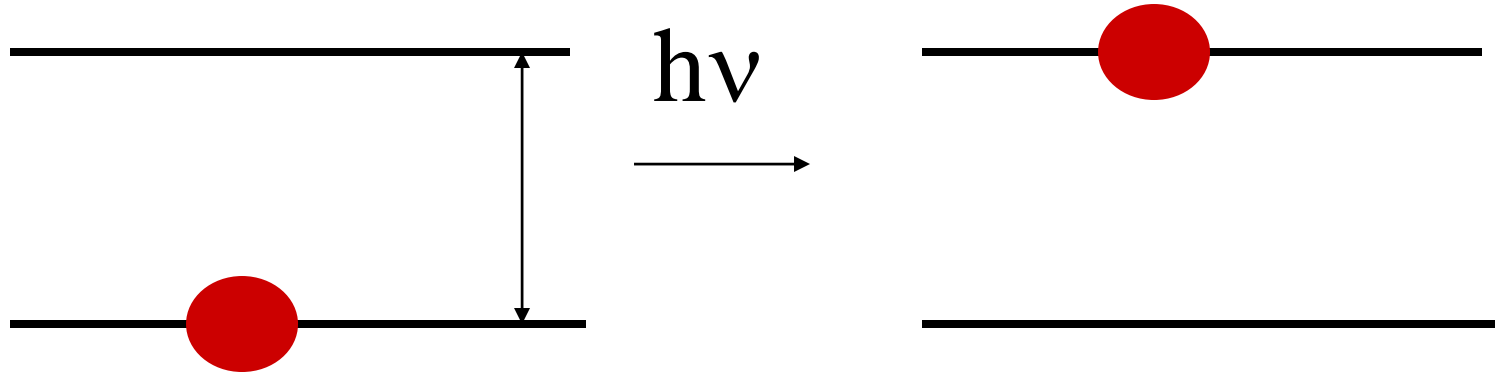
- ❖ Introduction
- ❖ Spectra origination
- ❖ Absorption experiment
- ❖ Beer-Lambert law
- ❖ Optical schemes and instruments

Instead of Introduction

- You have 2 (two) eyes only!!!!
- You need both of them!!!

SPECTRA ORIGINATION

Absorption: spectra origination



Useful conversion tool: toptica calculator

<http://www.toptica.com/page/topticalc.php>

The screenshot shows a web application window titled "spectral unit conversion". It features a "hide info" button and two main columns: "spectral position" and "linewidth/spectral shift".

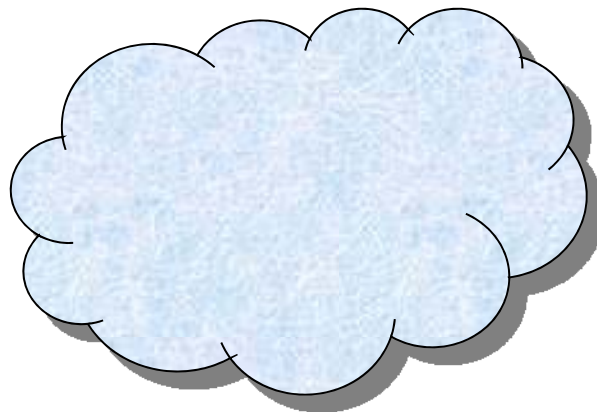
spectral position		linewidth/spectral shift	
wavelength	λ 500 nm	$\Delta\lambda$	0.025 nm
frequency	ν 599.58492 THz	$\Delta\nu$	-29.979246 GHz
		$\tau=1/\Delta\nu$	-33.35641 ps
		$\tau=1/2\pi\Delta\nu$	-5.3088375 ps
wavenumber	κ 20000 1/cm	$\Delta\kappa$	-1 1/cm
		$l=1/\Delta\kappa$	-10 mm
photon energy	E 2.4796837 eV	ΔE	-0.12398419 meV

Below the table is a color bar showing a spectrum from violet to red. Underneath, there is a "color information" section with a green square and the label "green". To the right, a "Did you know ..." section contains promotional text for TOPTICA diode lasers and a link to their websites.

index of refraction n=1 (vacuum), c=299792458 m/s

ABSORPTION EXPERIMENT

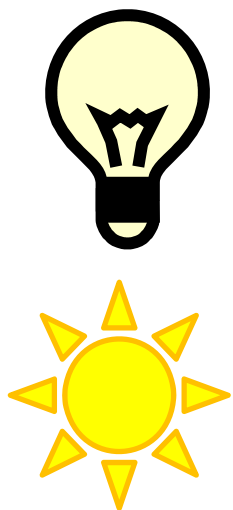
Absorption experiment: main parts?



Investigated media:

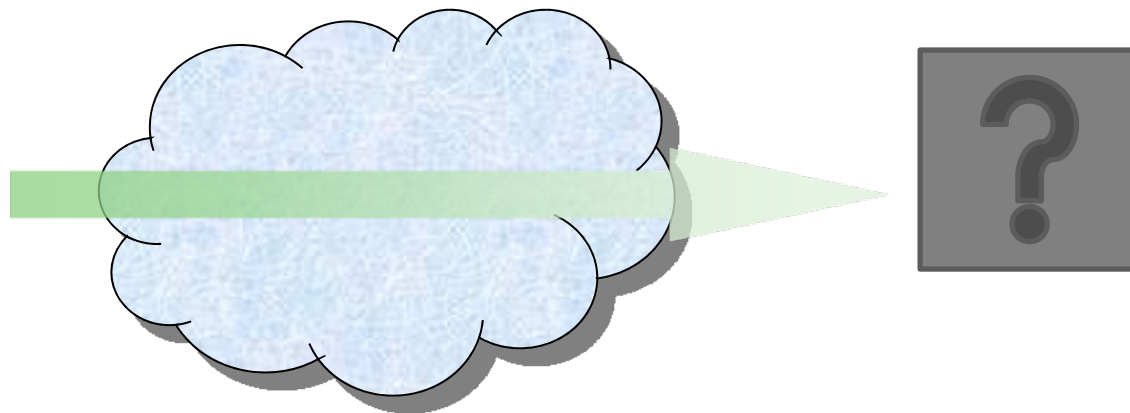
Atmosphere
Sample

Absorption experiment: main parts?



Light source:

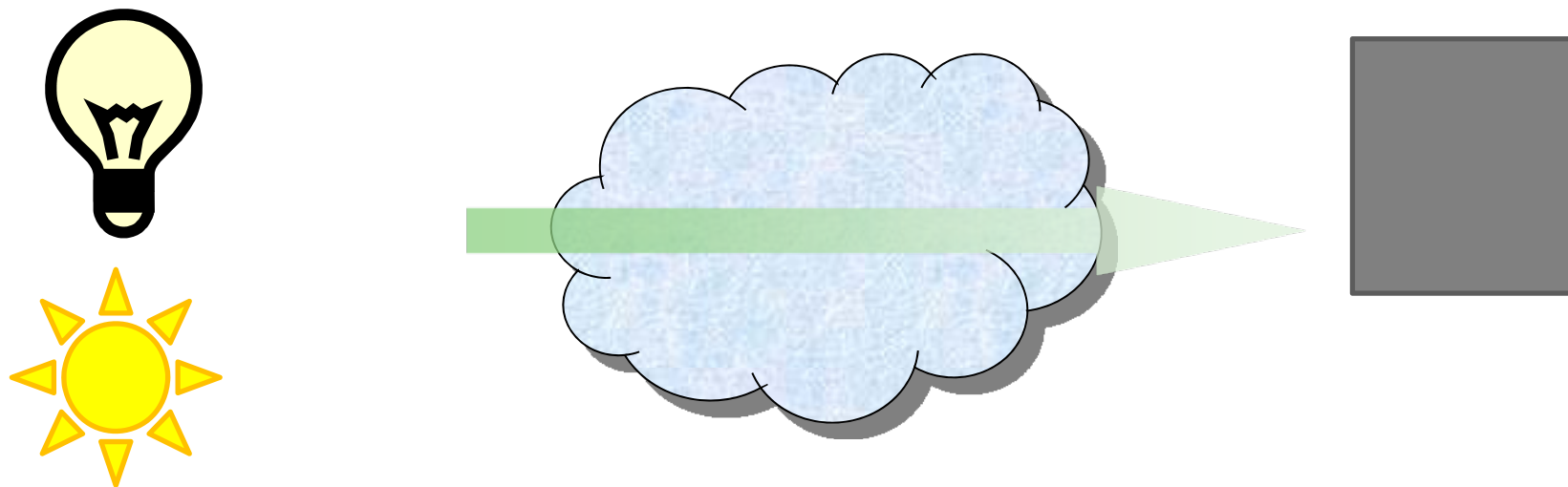
lamp;
sun;
laser



Investigated media:

Atmosphere
Sample

Absorption experiment: main parts?



Light source:

lamp;
sun;
laser

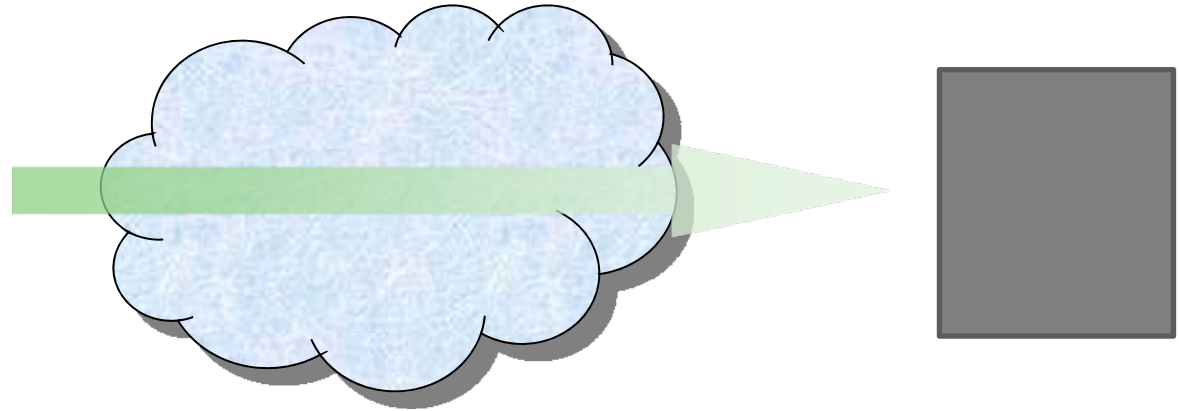
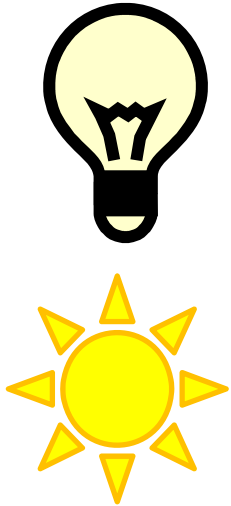
Investigated media:

Atmosphere
Sample

Detector:

Photoplate;
Semiconductor:
- Single;
- Array;
- Matrix.

Absorption experiment: main parts



Light source:

Lamp;
Sun;
Laser

Investigated media:

Atmosphere:

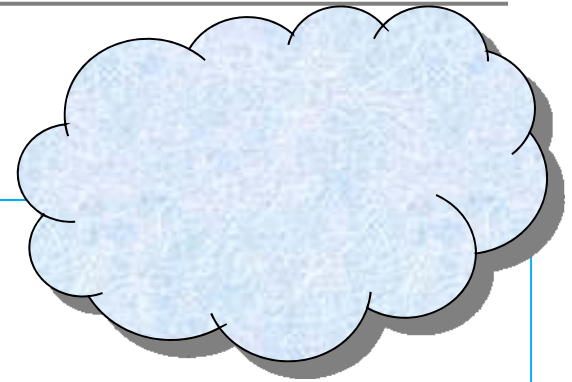
a lot of species (N_2 , O_2 , H_2O , CO_2 etc) at different partial pressures and temperatures scattering and absorbing at different wavelengths.

Sample: prepared mixture at known(?) pressure and temperature

Detector:

Photoplate;
Semiconductor:
- Single;
- Array;
- Matrix.

Investigated media



Atmosphere:

a lot of species (N_2 , O_2 , H_2O , CO_2 etc) at different partial pressures and temperatures scattering and absorbing at different wavelengths.

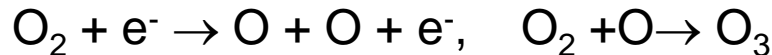
Samples:

- In the air-born or field measurements: probe of air (contains CO , CO_2 etc) collected through the special inlets
- In the laboratory: prepared mixture at known(?) pressure and temperature
 - CH_4 , CO_2 – no problem
 - CO – dangerous, safety rules
 - O_3 – dangerous , unstable

Investigated media: ozone

Ozone production in the laboratory:
co-axial cylindrical capacitor, 'silent' discharge

Ozone generator on:



Ozone generator off:



M – surrounding molecules

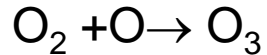
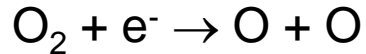
$$\frac{dn_{\text{O}_3}}{dt} = -k \cdot n_{\text{M}} \cdot n_{\text{O}_3}$$

k – decay rate [$\text{cm}^3/\text{molecule/s}$],
depends on temperature T and
surrounding molecules

Why?

Investigated media: ozone

Ozone generator on



Ozone generator off:

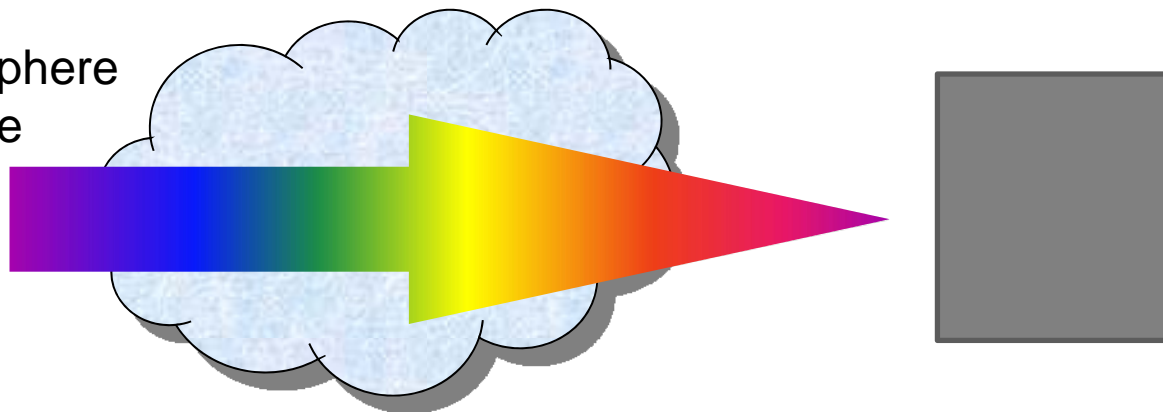
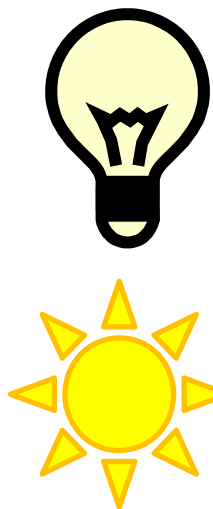


$$\frac{dn_{\text{O}_3}}{dt} = -k \cdot n_{\text{M}} \cdot n_{\text{O}_3} \quad n_{\text{O}_3}(t) = n_0 \cdot \exp\{-k_{\text{decay}}(T) \cdot n_{\text{M}} \cdot t\}$$

Absorption experiment: main parts

Investigated media:

Atmosphere
Sample



Light source:

Lamp;
Sun;
Laser.

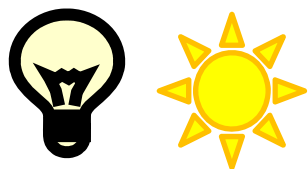
Wavelength selection:

Time: FTS, tunable laser
Space: prism, grating

Detector:

Photoplate;
Semiconductor:
- Single;
- Array;
- Matrix.

Absorption experiment: main parts



Light source:

lamp;
sun;
laser

Important properties:

Spectrum;
Tunability;
Broad- or narrow-band.

Wavelength selection:

Time: FTS, tunable laser
Space: prism, grating

Important properties:

Resolution;
Dispersion;
Transitivity/ reflectivity

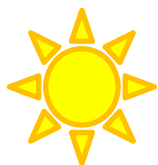
Detector:

Photoplate;
Semiconductor:
single, array, matrix

Important properties:

Sensitivity;
Response curve;
Time constant;
Dynamic range

Ideal absorption experiment



Light source:

Broad or tunable
Flat spectrum
Stable intensity

Wavelength selection:

High resolution;
High transmittivity/reflectivity.

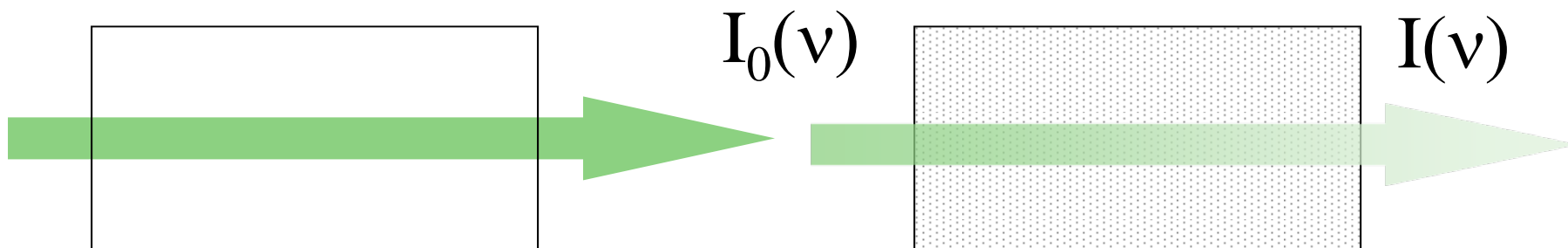
Detector:

Sensitive in broad spectral
range with wide dynamic
range;
Fast;
Flat response curve;
Low noise

BEER-LAMBERT LAW

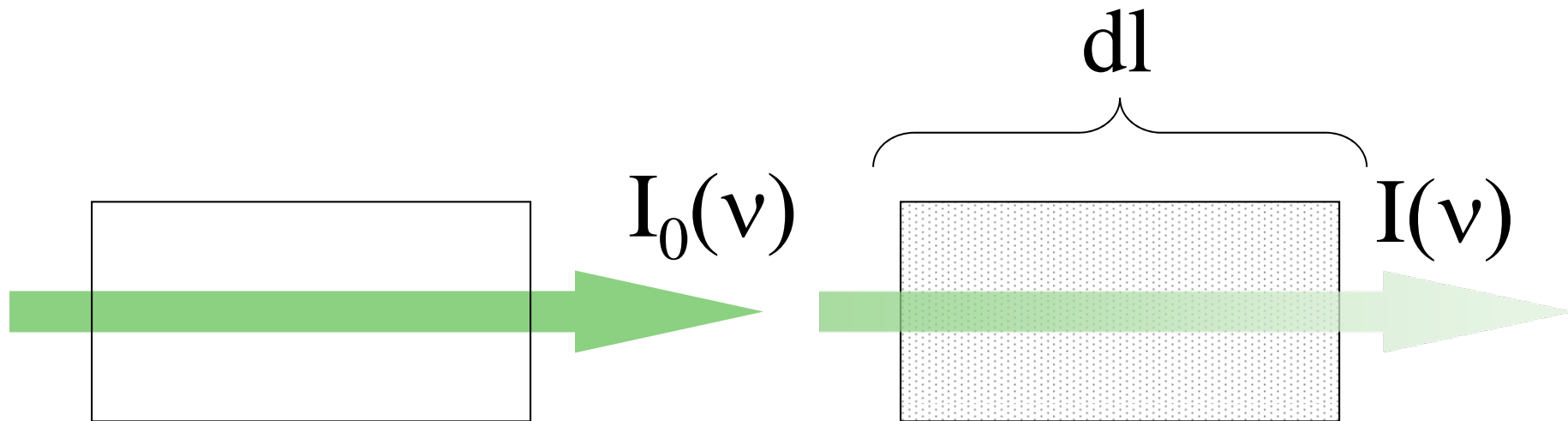
Beer-Lambert law

- **Beer's law = Lambert–Beer law = Beer–Lambert–Bouguer law**
- relates the *absorption* of light to the *properties* of the material through which the light is travelling.



What else can happen?

Absorption: Beer-Lambert law



$$dI = ?$$

$$dI = -I \cdot n \cdot \sigma \cdot dl$$

Absorption: Beer-Lambert law

$$\frac{dI}{I} = -n \cdot \sigma \cdot dl$$

$$\int_0^L \frac{dI}{I} = -\int_0^L n \cdot \sigma \cdot dl$$

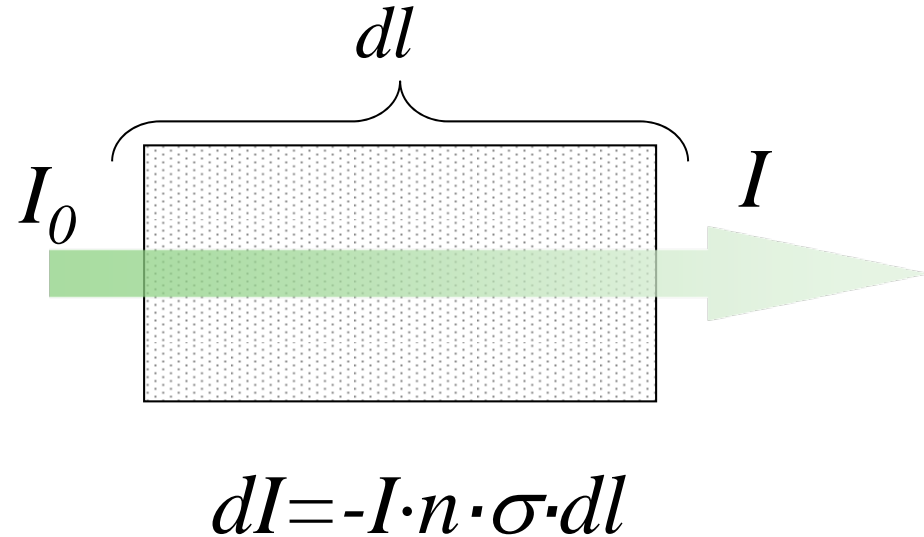
$$\ln I = -\int_0^L n \cdot \sigma \cdot dl + const$$

$$I(\nu) = I_0(\nu) \exp \left\{ -\int_0^L n(l) \cdot \sigma(\nu) \cdot dl \right\}$$

I – intensity; I_0 – initial intensity

ν – wavenumber; n – density of absorbing particles

L – absorbing media length; σ – absorption cross-section



Absorption: terms and units

Spatial isotropic case (n, T):
$$I(\nu) = I_0(\nu) \exp\{-n \cdot \sigma(\nu) \cdot L\}$$

Optical density:
$$OD = -\ln \frac{I(\nu)}{I_0(\nu)} = n \cdot \sigma(p, T, \nu) \cdot L$$

I, I_0 – transmitted intensity with or without absorber

ν, ν_0 or λ [nm or cm^{-1}] wavelength or wavenumber

n [**molecules/cm³**] **density**

L [cm] absorbing media length

σ [$\text{cm}^2/\text{molecule}$] absorption cross-section

Most important conditions:

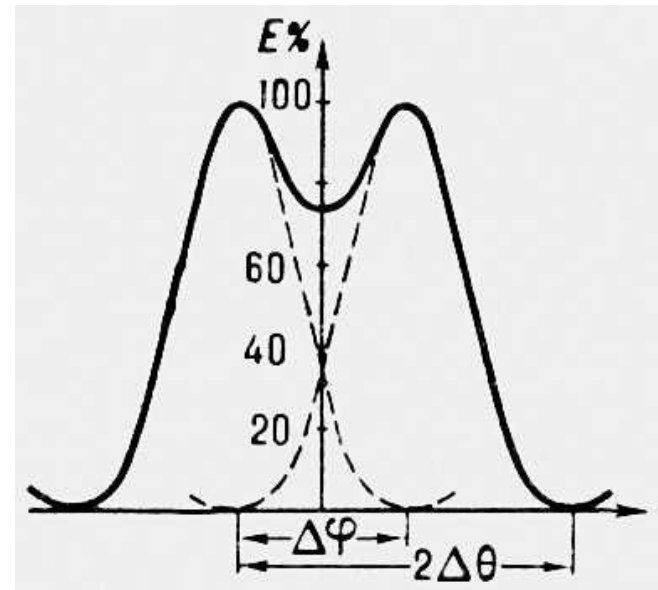
- The absorbing medium must be *homogeneously* distributed in the interaction volume and must *not scatter* the radiation;
- The incident radiation must consist of *parallel* rays, each traversing the same length in the absorbing medium;
- The incident radiation should preferably be *monochromatic*, or have at least a width that is more narrow than the absorbing transition;
- The incident flux *must not influence* the atoms or molecules:
 - the light should not cause optical saturation or optical pumping (such effects will deplete the lower level and possibly give rise to stimulated emission).

OPTICAL SCHEMES

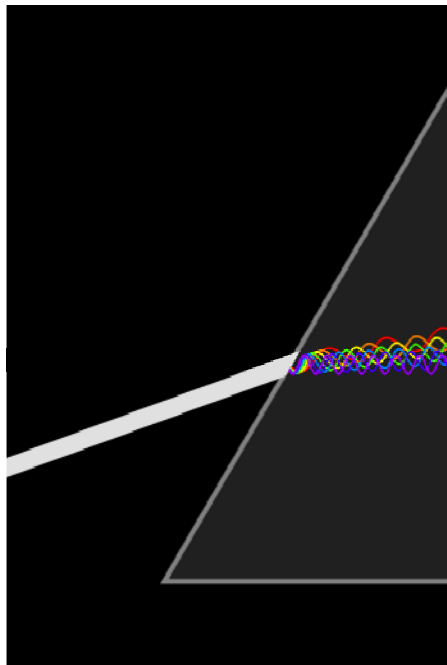
Dispersive elements

- Prism
- Diffractive grating

- Important properties:
 - Dispersion
 - Resolution
 - Response function, slit function



Dispersive elements: prism



Dispersive elements: prism

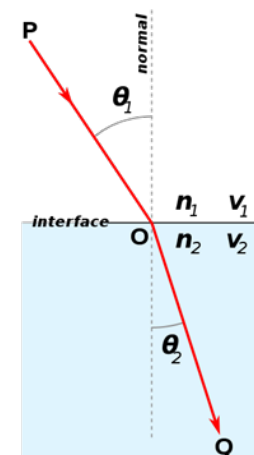
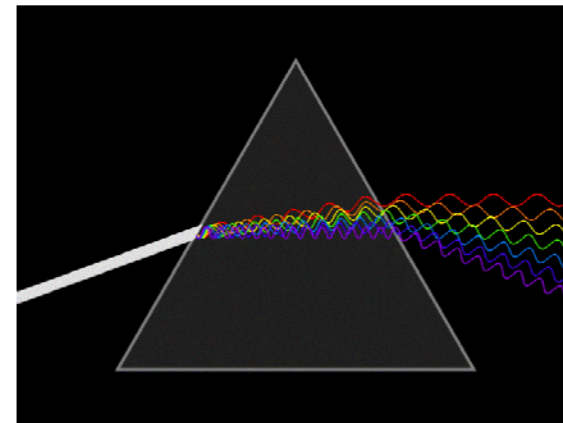
$$n = \sqrt{\epsilon\mu}$$

$$n_1 \sin \theta_1 = n_2 \sin \theta_2$$

n – refraction index;

$\epsilon(\lambda)$ - material's relative permittivity;

μ - relative permeability (~ 1 for many optical materials).

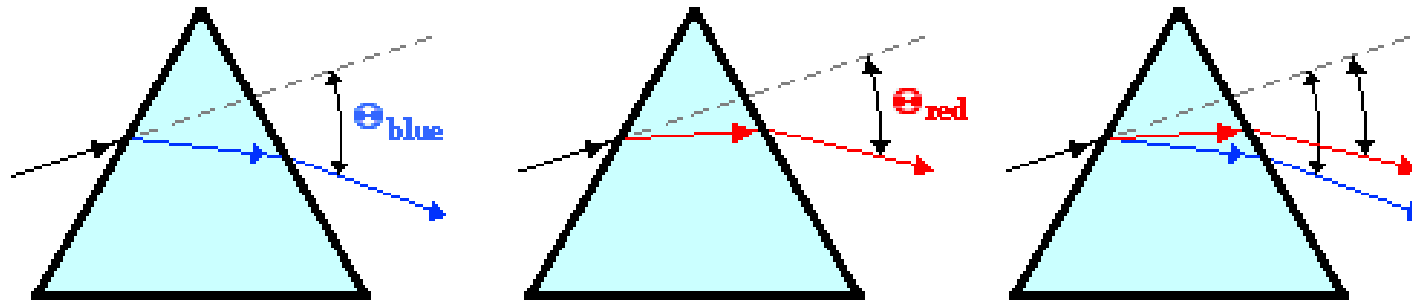


Dispersive elements: properties

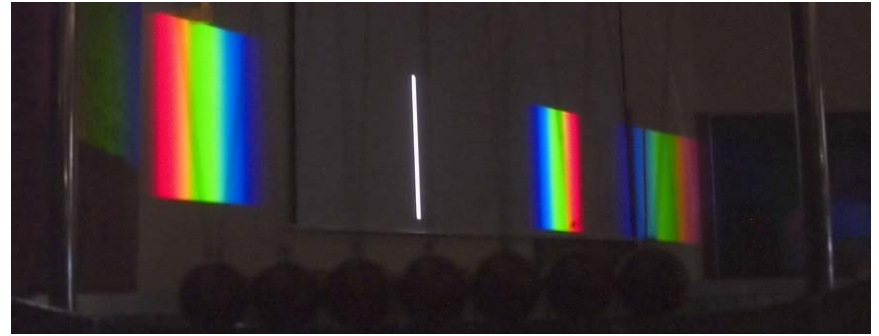
- Dispersion $d\theta/d\lambda$
 - For prism angle 60° and parallel beam

$$\frac{d\theta}{d\lambda} = \frac{2}{\sqrt{4-n^2}} \frac{dn}{d\lambda}$$

- Spectral transitivity
 - Depends on material



Diffraction grating



Periodic structure

Principle of work:

- 1) Diffraction on every slit/stripe
- 2) Interference of beams created by the neighbor slits/stripes/grooves

Diffractive grating

1) Diffraction on every slit/stripe

“Maximums” condition:

$$b(\sin \varphi + \sin \psi) = q \cdot \lambda$$

Distance between maximums λ/b

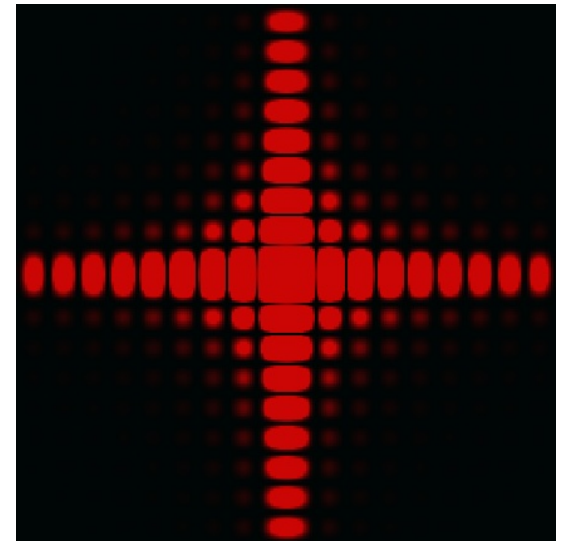
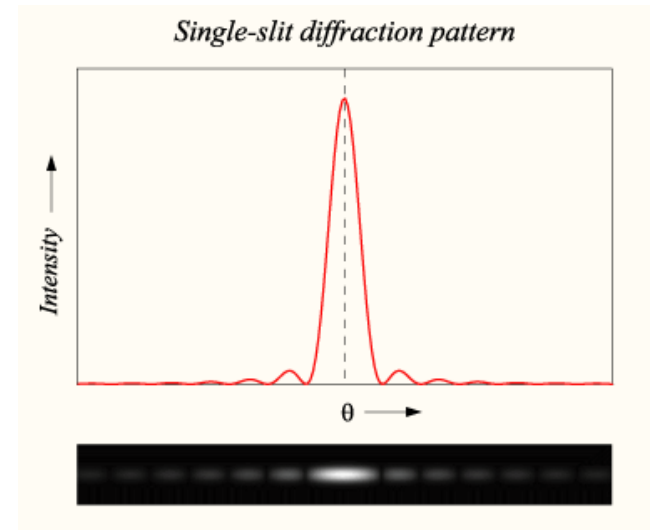
d – distance between slits/grooves

b – slit/groove width

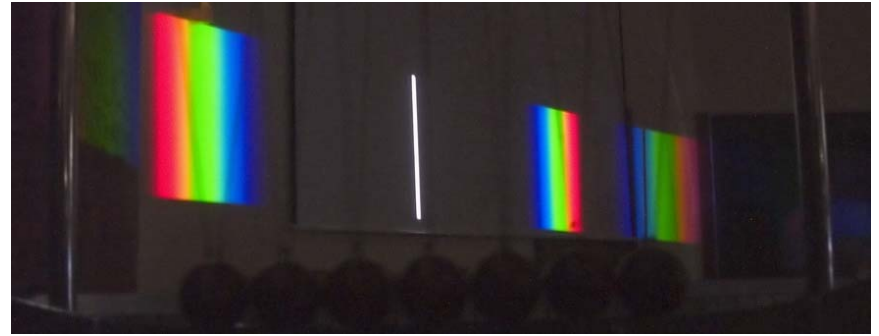
ψ – incidence angle

φ – diffraction angle

q – number



Diffraction grating



2) interference of beams reflected from the neighbor slits/stripes/grooves

“Maximums” condition:

$$d (\sin \varphi + \sin \psi) = q \cdot \lambda$$

Distance between maximums λ/d

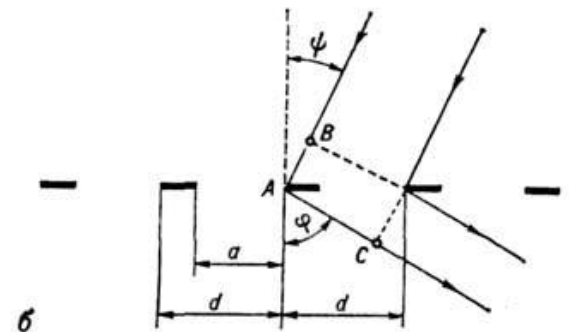
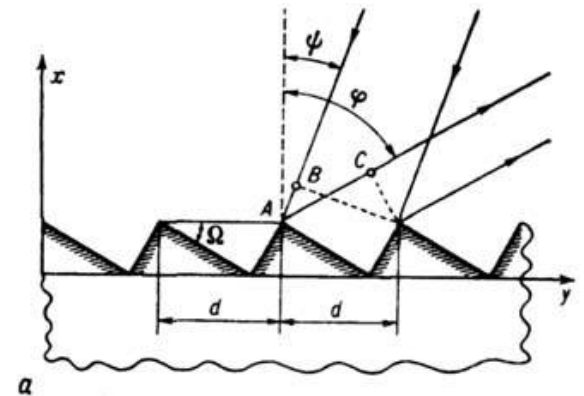
d – distance between grooves

b – slit/groove width

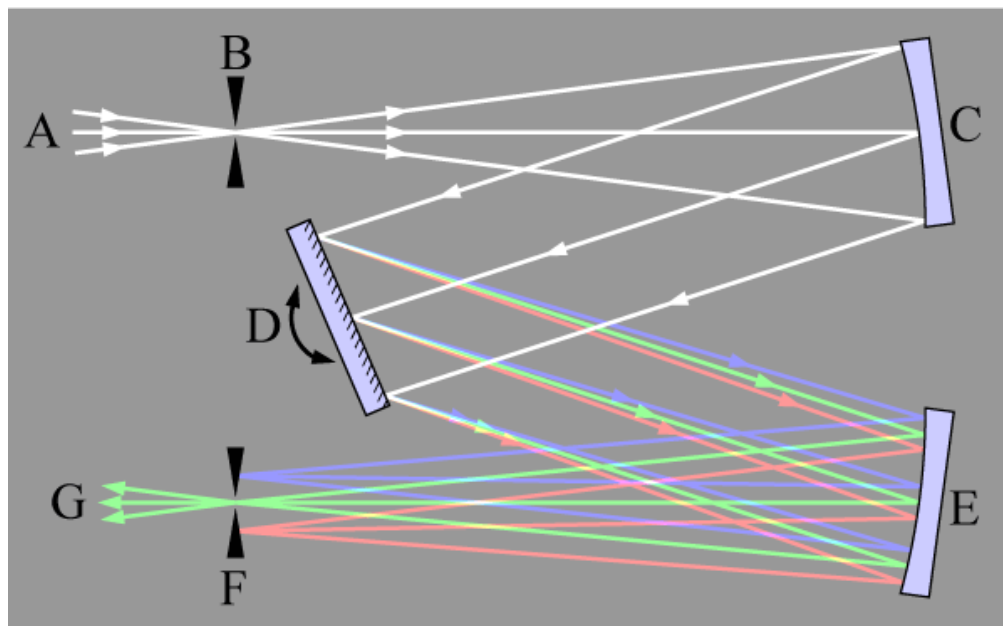
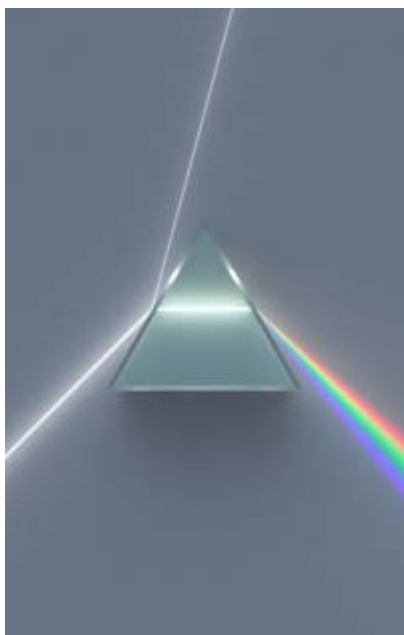
ψ – incidence angle

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q – number

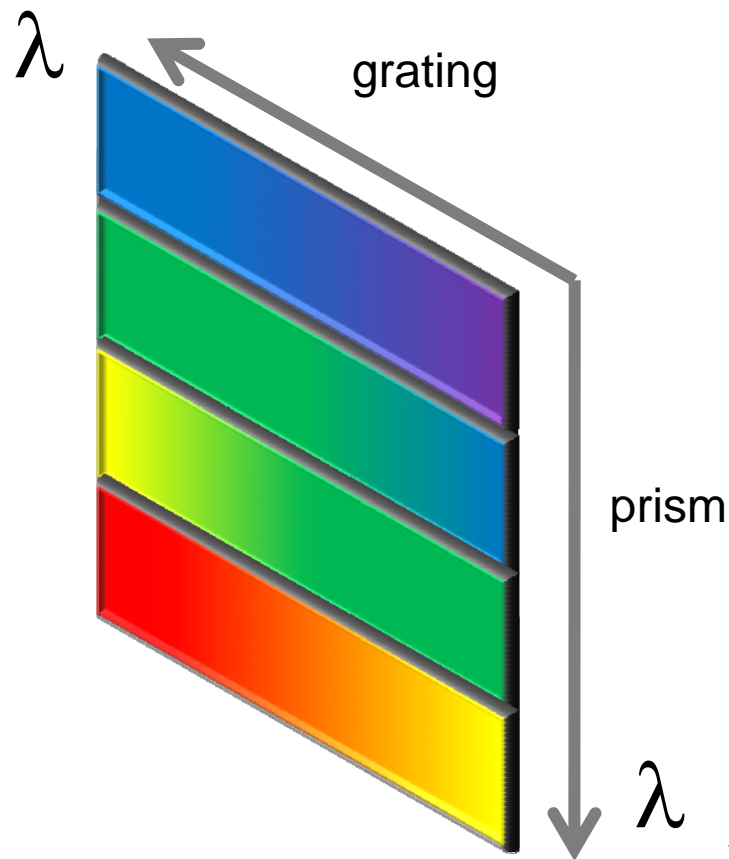
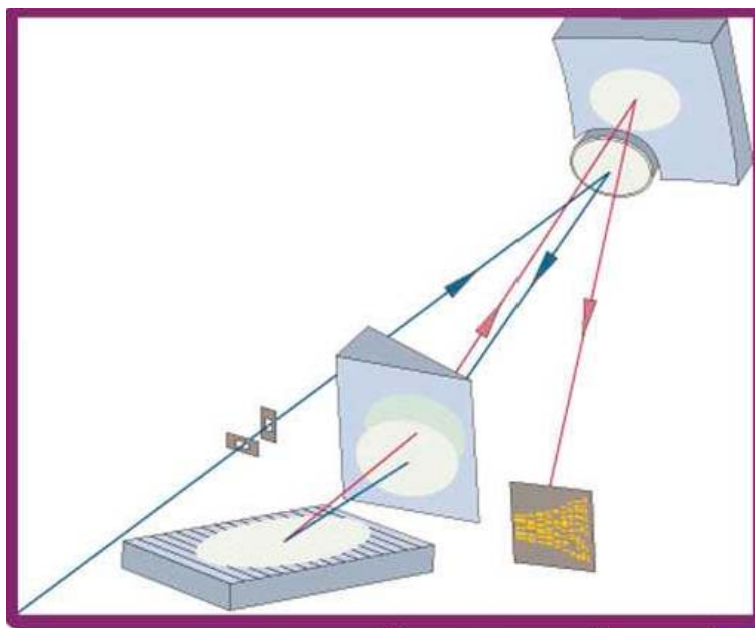


Dispersive elements: monochromator

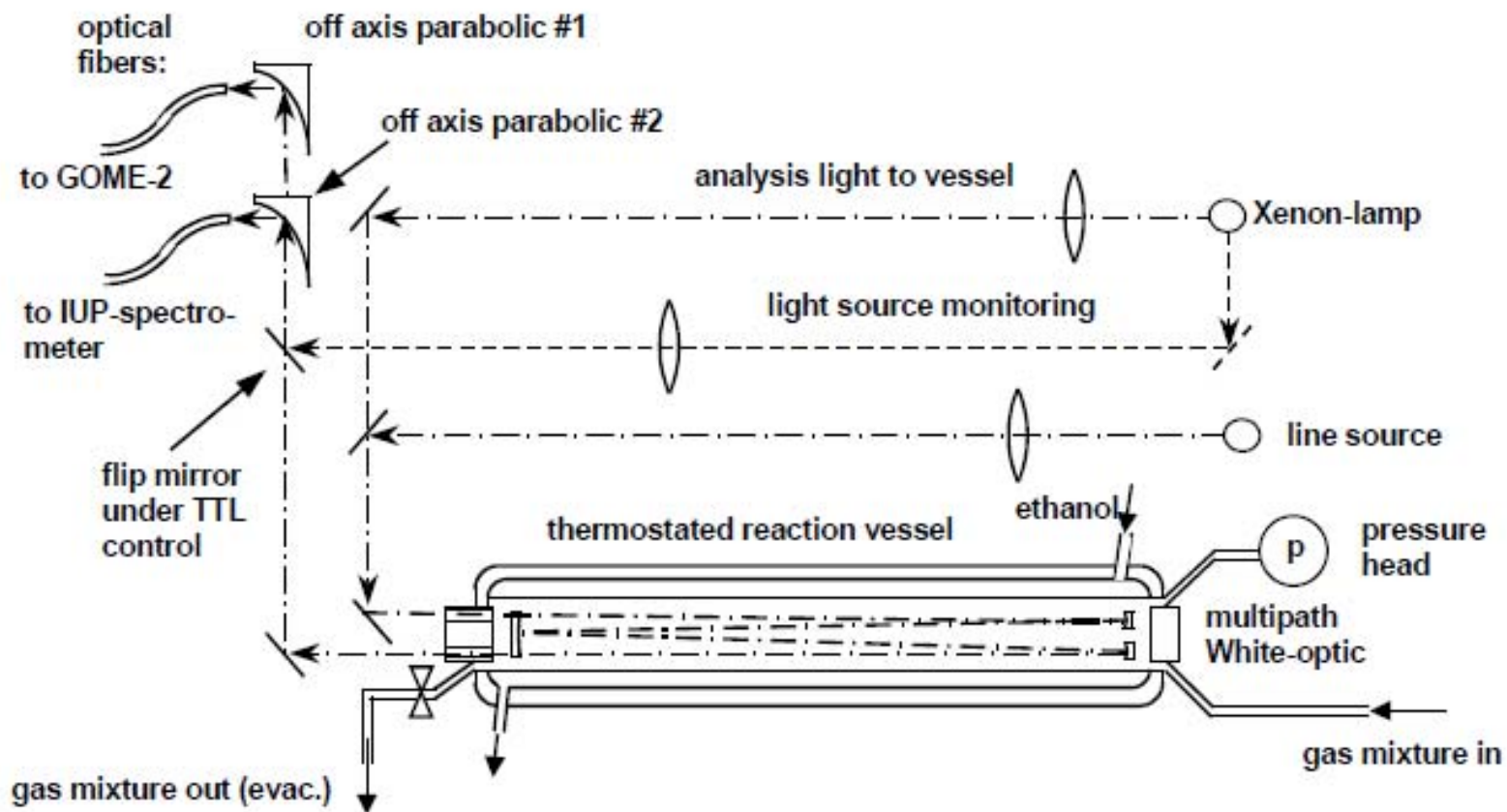


Dispersive elements: cross-dispersion

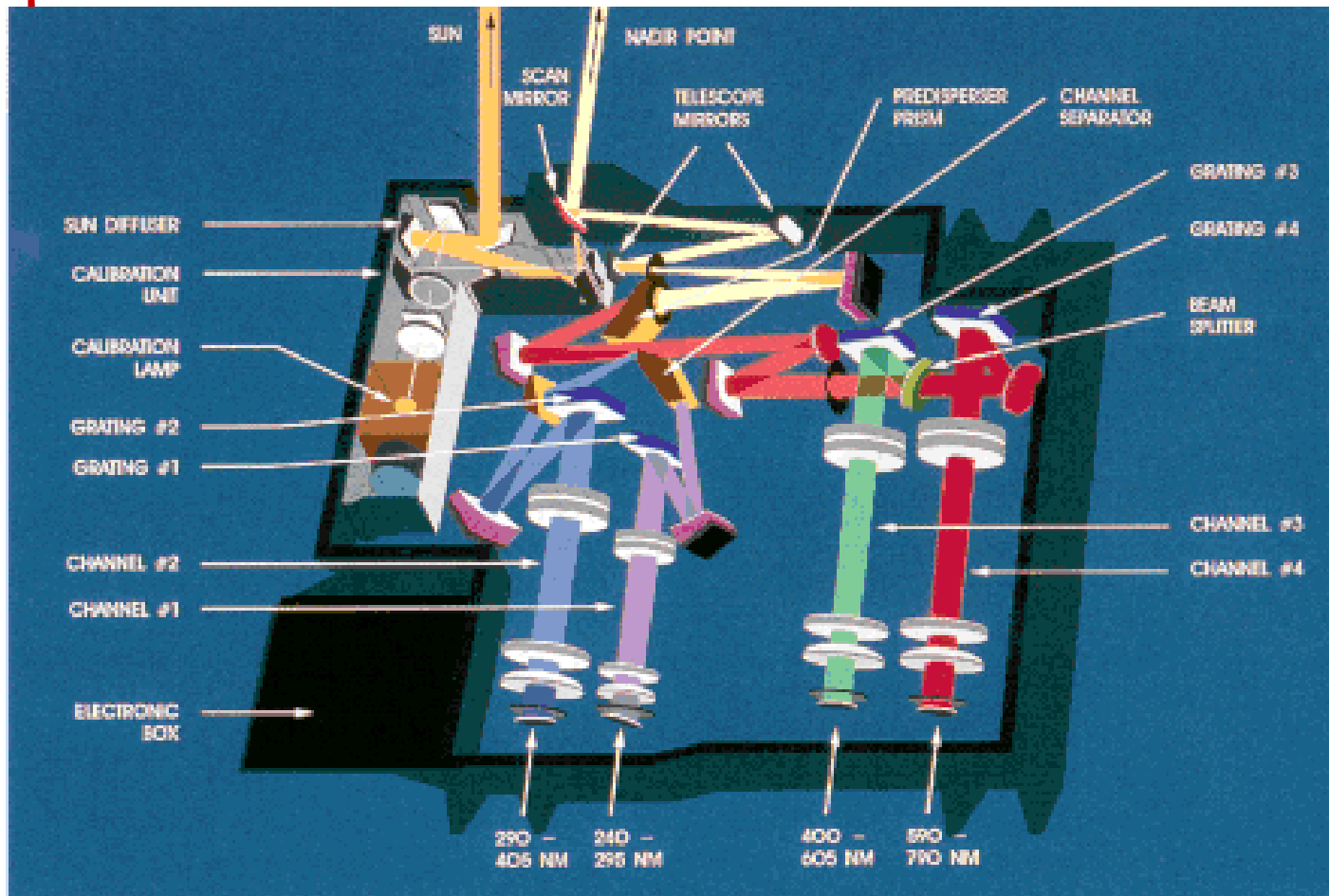
Advantages: combination of broad spectral region with high resolution



Experimental setup in the MolSpecLab

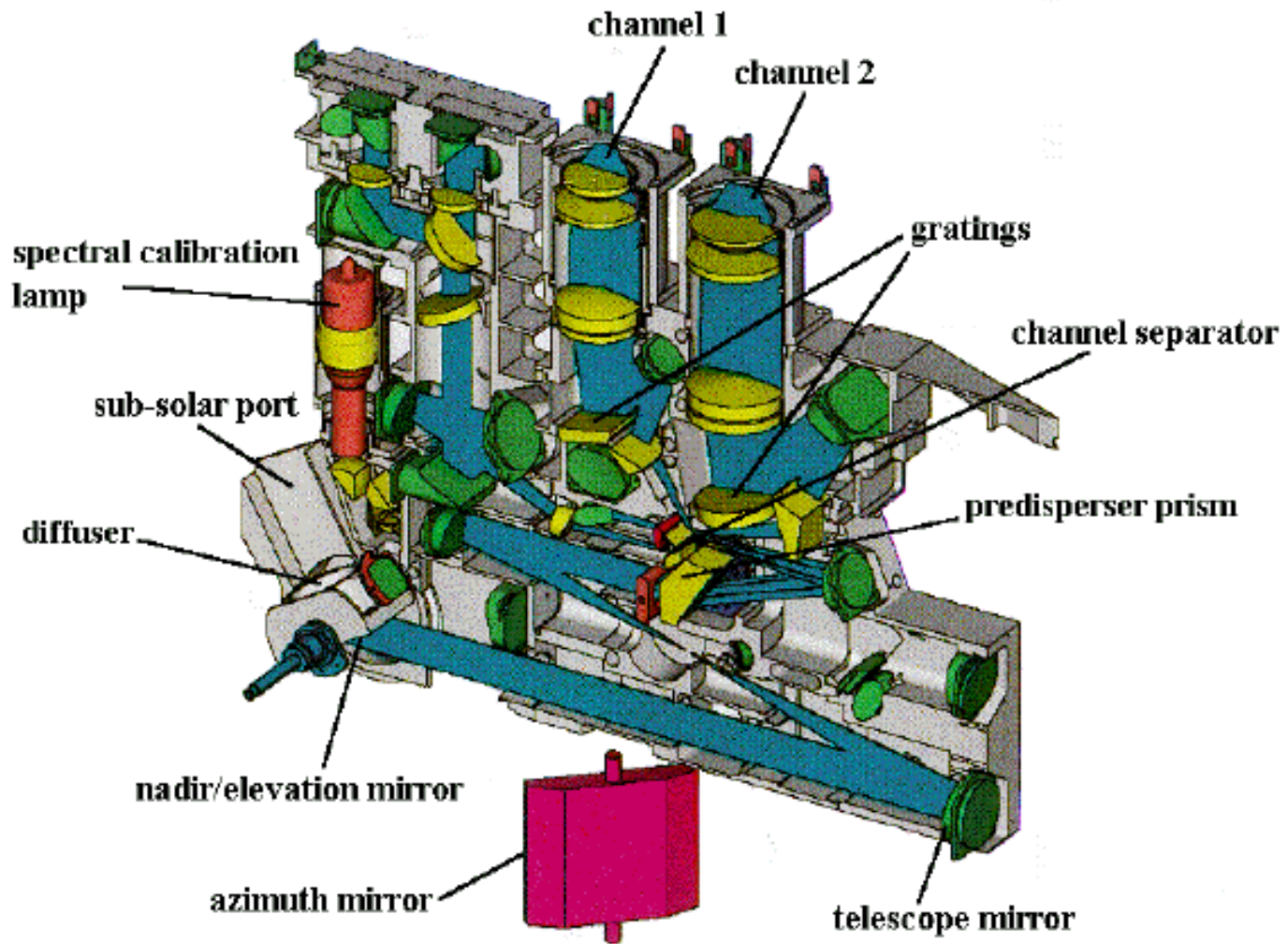


GOME: global ozone monitoring experiment



SCIAMACHY:

Scanning Imaging Absorption Spectrometer for Atmospheric CHartography



Satellite instruments

<http://earth.esa.int/object/index.cfm?fobjectid=4004>

esa earthnet online

European Space Agency

ESA Earth Home Missions Data Products Resources Applications

19-Apr-2011

EO Data Access

ESA Missions

- CryoSat
- SMOS
- GOCE
- Envisat
- ERS
- Proba
- ESA Earth Observation Campaigns Data
- ESA Future Missions
- ESA/EUMETSAT Missions

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ENVISAT

SCIAMACHY

SCIAMACHY is an imaging spectrometer whose primary mission objective is to perform global measurements of trace gases in the troposphere and in the stratosphere. The solar radiation transmitted, backscattered and reflected from the atmosphere is recorded at relatively high resolution (0.2 nm to 0.5 nm) over the range 240 nm to 1700 nm, and in selected regions between 2000 nm and 2400 nm. The high resolution and the wide wavelength range make it possible to detect many different trace gases despite low concentrations (The mixing ratios of most constituents are of the order of 10⁻⁶ or less). The large wavelength range is also ideally suited for the detection of clouds and aerosols. SCIAMACHY has three different viewing geometries: nadir, limb, and sun/moon occultations which yield total column values as well as distribution profiles in the stratosphere and (in some cases) the troposphere for trace gases and aerosols.

Envisat in depth

- News
- Overview
- Satellite Design
- Instruments
- SCIAMACHY in depth
 - » Design
 - » Applications
 - » Performance
 - » Data Products
- Resources

Key Resources

- Envisat Handbooks
- Access to Envisat Data (pdf - 4,32 MB)
- Instruments Availability Interruptions
- Satellite and Instruments status
- Status of Envisat Products

Good luck!