Air Pollution Control and Air Chemistry:

Fundamentals of atmospheric chemistry

(3rd lecture)

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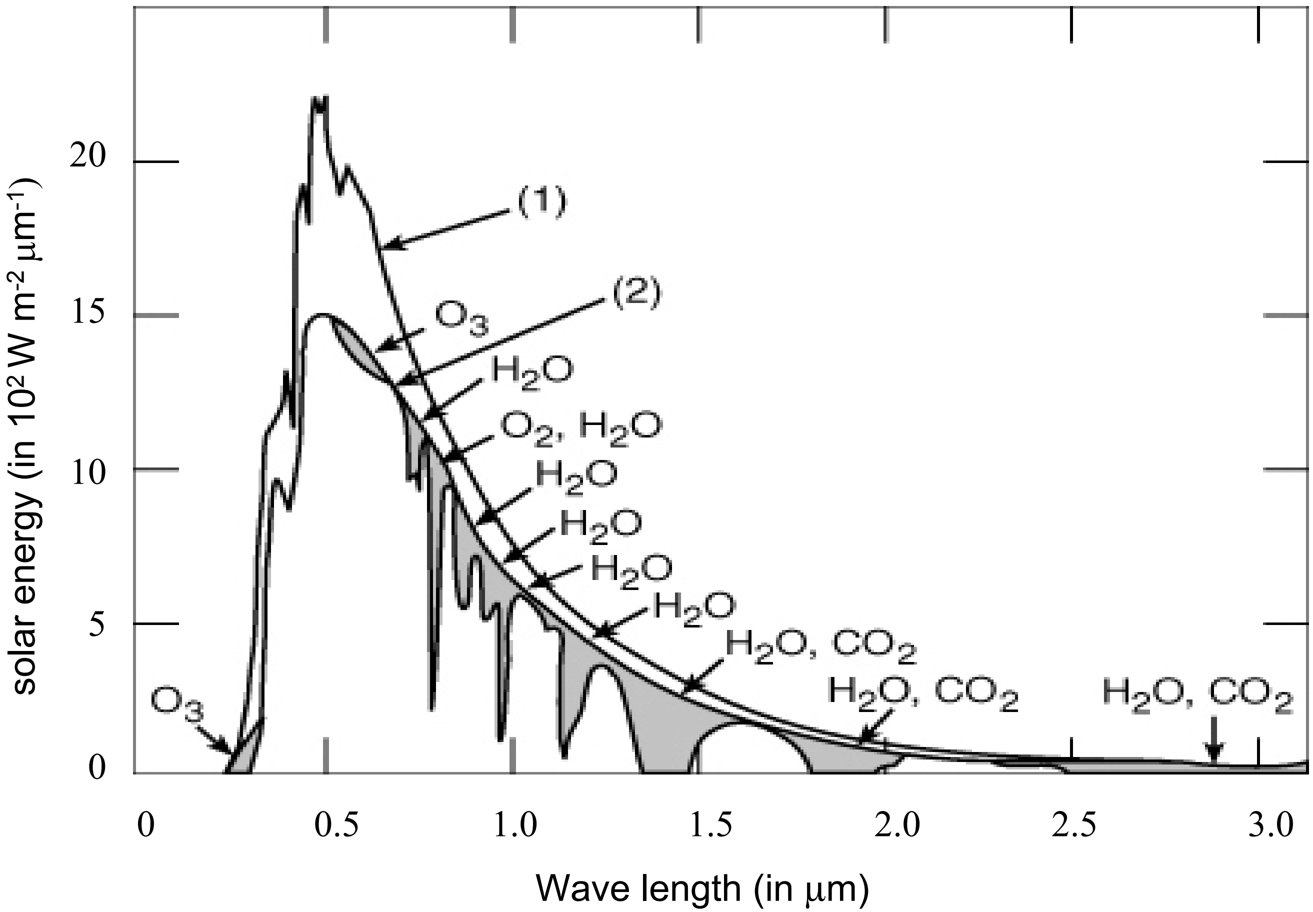
Objectives:

To describe the solar radiation and ist interactions with trace substances for understanding photochemical processes, climate change and the energy budget in the atmosphere as well human energy resources

- solar spectrum
- radiation (solar and terrestrial)
- photolysis of molecules
- earth energy budget
- solar era

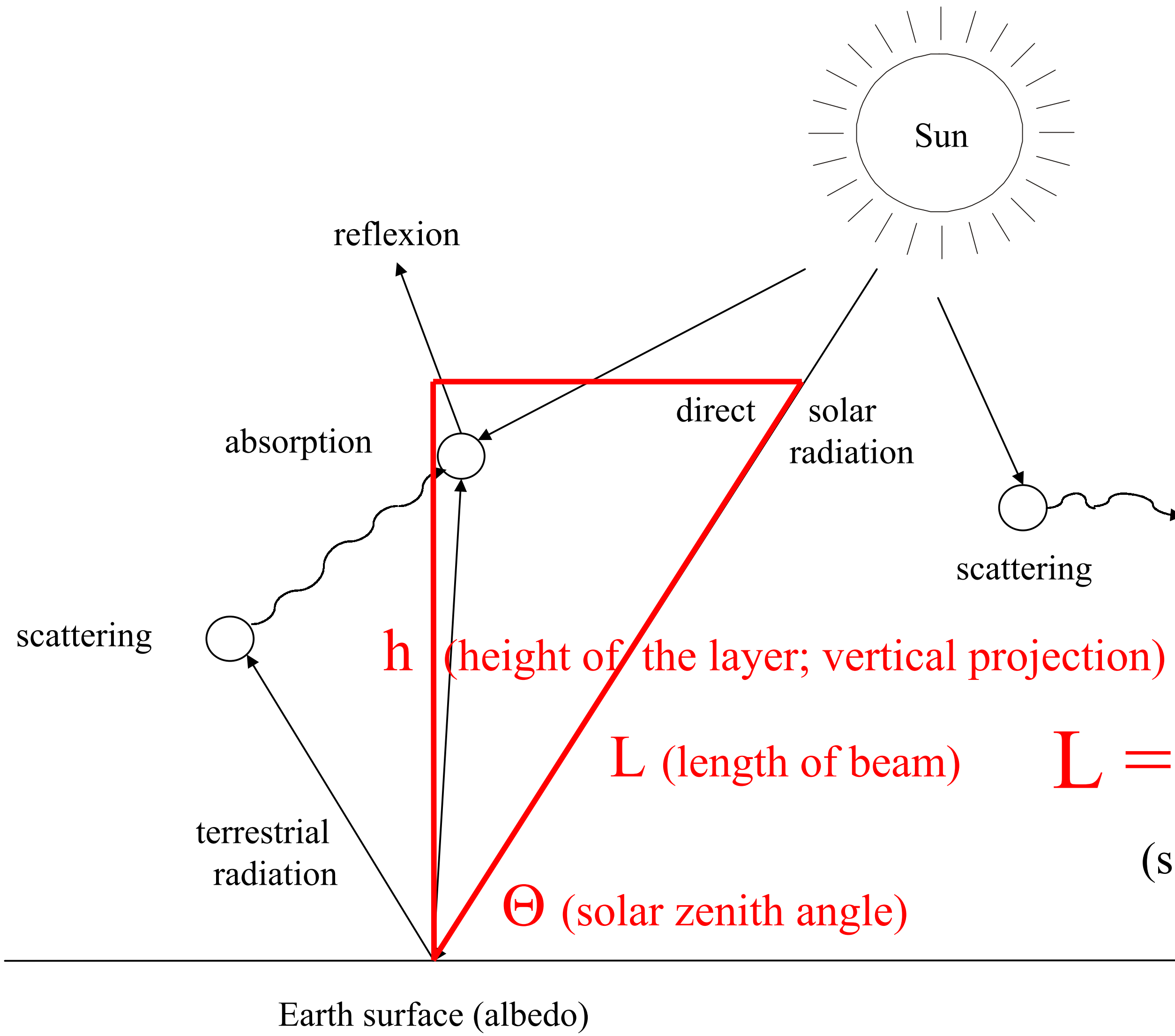


Solar spectrum at upper border of the atmosphere (1) and at earth surface (2) with showing the absorbing gases

Spectral distribution of extraterrestrial solar radiation, after WMO (1986)

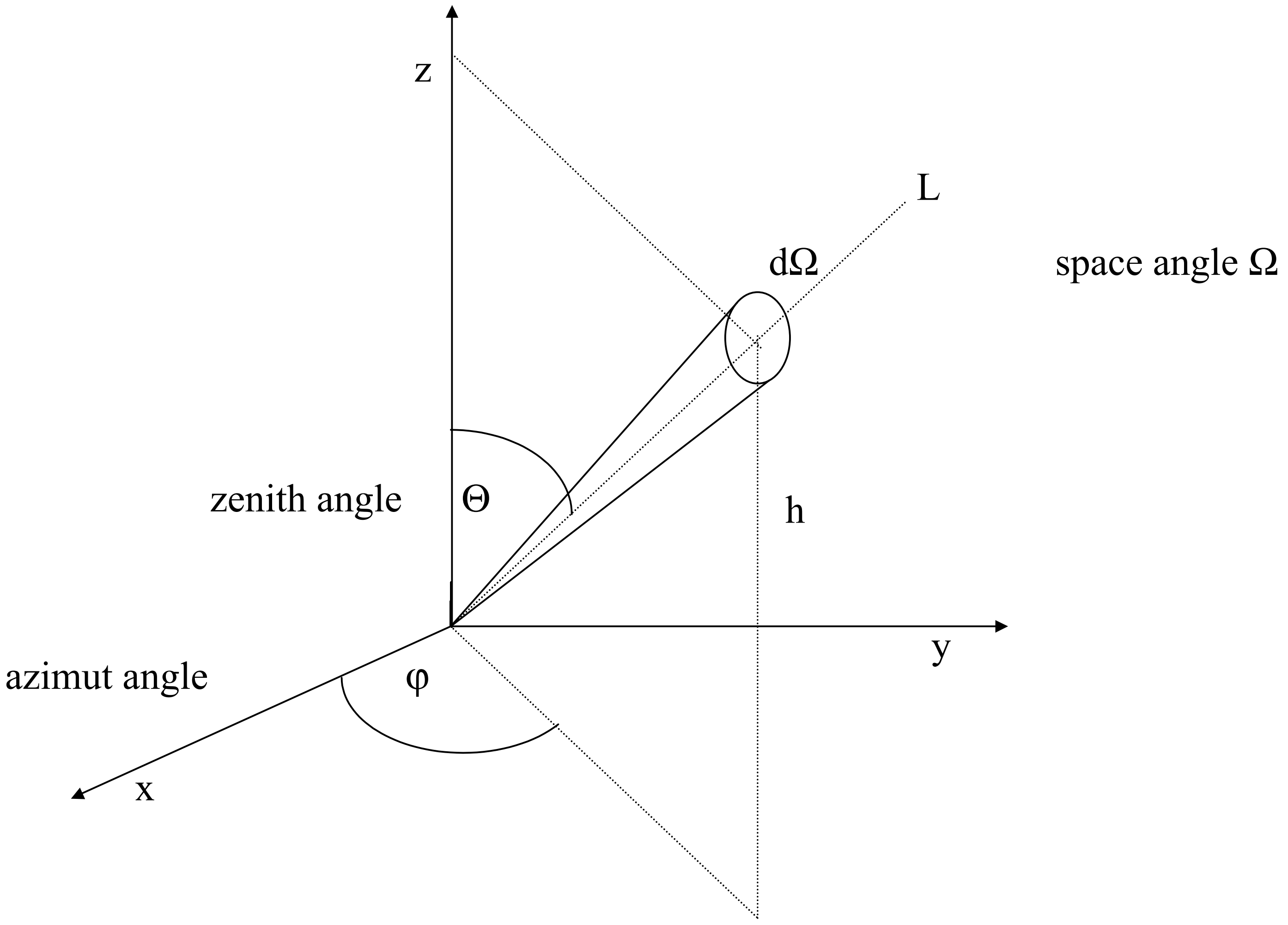
region	wave length (in nm)	radiation flux density (in W m^{-2})	percentage at total radiation (in %)
UV-C	100-280	7,0	0,5
UV-B	280-315	16,8	1,2
UV-A	315-400	84,1	6,2
UV tital	100-400	107,9	7,9
visible light	400-760	610,9	44,7
infrared light	760-10^6	648,2	47,4
total	10^2-10^6	1367	100

Different radiative interactions through the atmosphere



$$L = h \cdot \sec\Theta$$

(sec = 1/cos)



Scheme of the geometry of radiation

Absorption (Lambert-Beer Law)

The German mathematician Johann Heinrich Lambert (1728-1777) found that the weakening of a light beam is proportional to the layer thickness:

$$\Delta I \sim L \cdot I$$

Lambert Law: $$\frac{dI}{dL} = - m' \cdot I$$ *Extinction modul* m´

The German mathematician, chemist and physician August Beer (1825-1863) found that the radiation weakenig depends from the concentrations of substance within the medium:

$$m = \varepsilon_e [X]$$ where ε_e *Extinktion coefficient*

Combining both observations, we obtain the *Lambert-Beer* Law:

$$I = I_0 \exp\left(- \varepsilon_e [X] \sec\Theta\right)$$

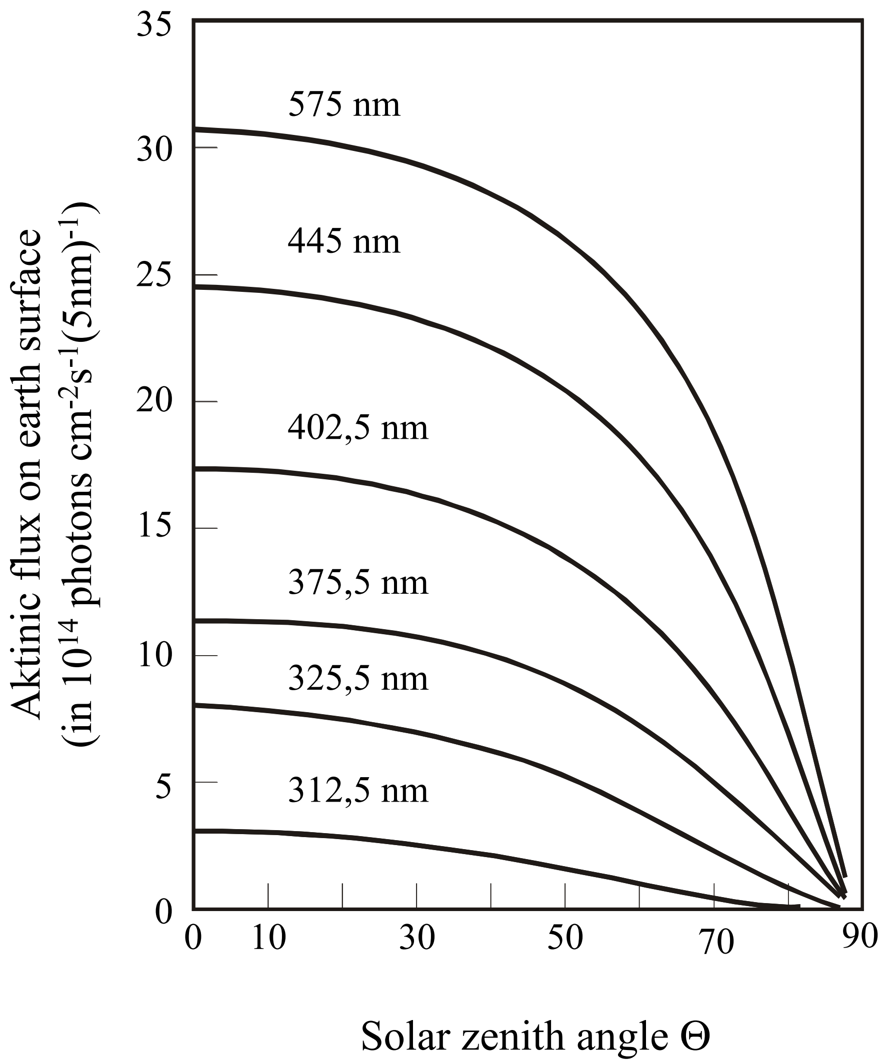
The extinction coefficient depends from *absorption* and *scattering* of all gaseous and particulate substances:

$$\varepsilon_e = \varepsilon_a^g + \varepsilon_s^g + \varepsilon_a^p + \varepsilon_s^p$$

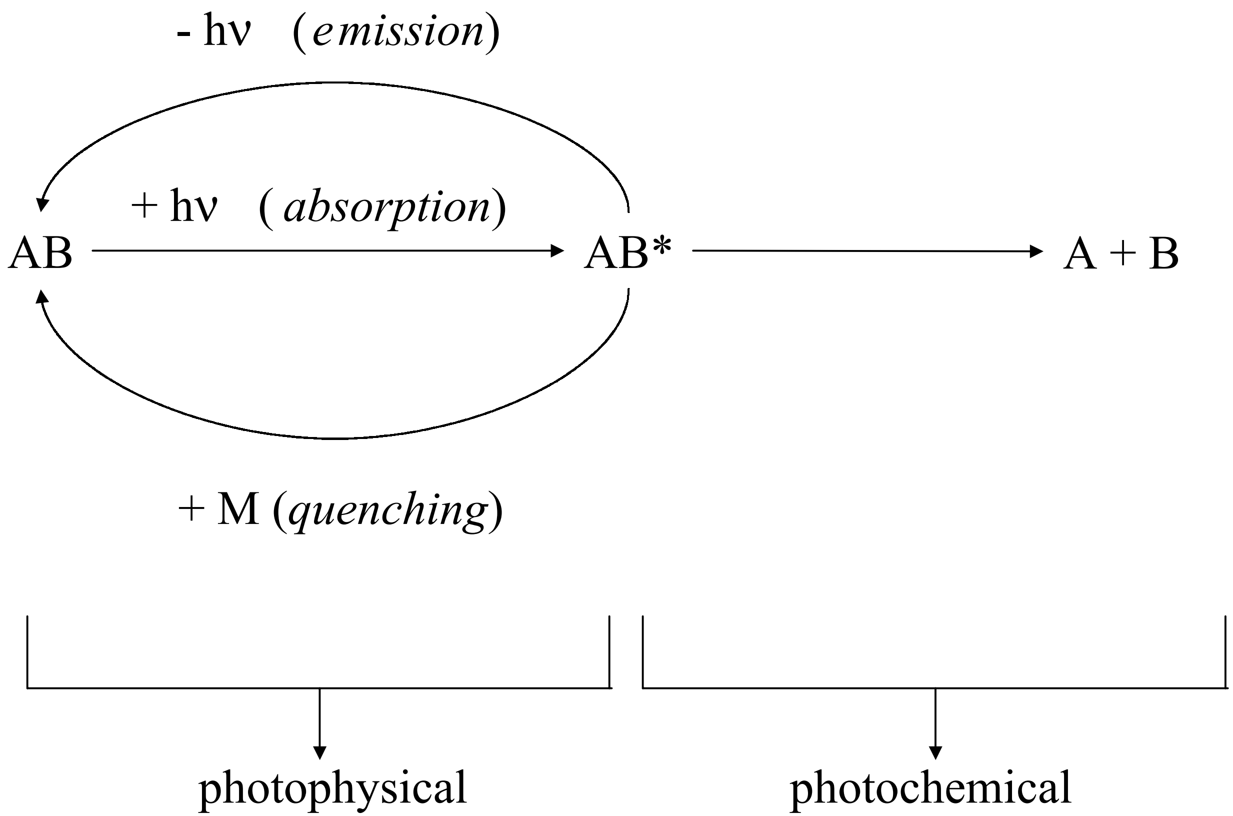
The radiation absorbed by a substance x is proportional to the radiation intensity I and the concentration [X]:

$$I_x^{abs}(\lambda) = I(\lambda)\sigma_x(\lambda)[X]$$

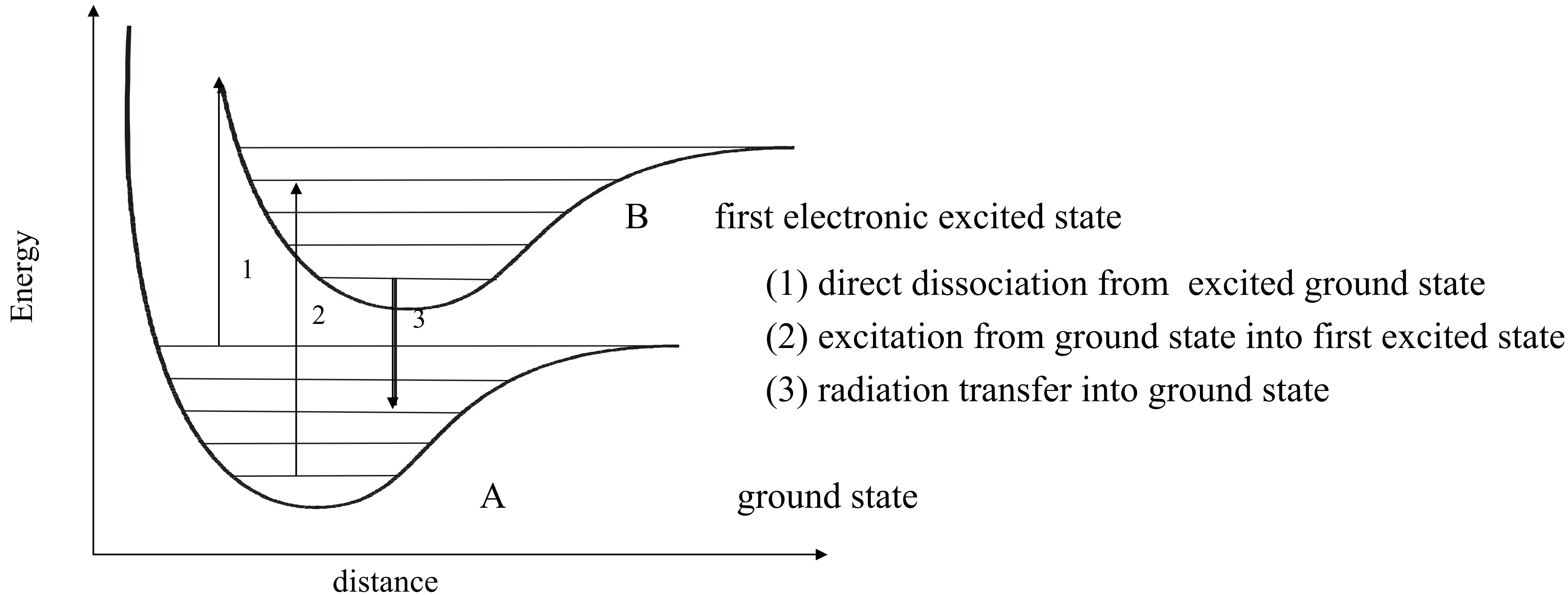
where σ *absorption cross section* (dimension: cm^2 $molecule^{-1}$).



Wave length depending solar flux for different zenith angles



Absorption by molecules, dissociation (photolysis) and deactivation



Scheme of electronical excitation of a two-atomic molecule, also called potential curve of an AB molecule (anharmonic oscillator; harmonic oszillators showing a parabel curve).

Kinetics of a photochemical process

$A + h\nu \rightarrow B + C$ (chemical reaction: mechanism)

$$\frac{d[A]}{dt} = -j_A[A]$$ (first-order rate law)

j *specific photolysis rate* or *photolysis frequency* (dimension: s^{-1})

j is a function of the spectral *actinic flux*[1] I, the spectral *absorption cross section* σ and the spectral *quantum yield* Φ over the whole wave length region in dependence from temperature (T). *Spectral* means the relation to the wavelength (λ).

$$j(\lambda, T) = \int_{\lambda_{min}}^{\lambda_{max}} I(\lambda)\sigma(\lambda, T)\Phi(\lambda, T)\,d\lambda$$

Simplified by summing over Δλ:

$$j = \sum_{\lambda=290nm}^{\lambda_i} \bar{I}(\lambda)\bar{\sigma}(\lambda)\bar{\Phi}(\lambda)$$

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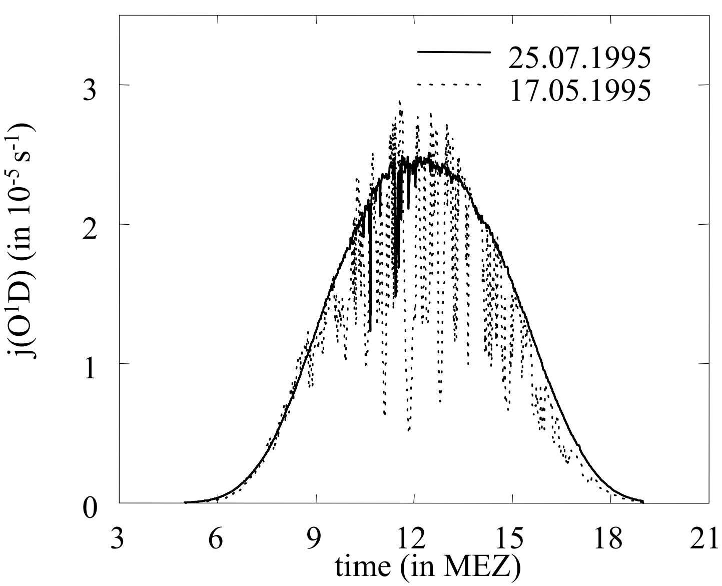
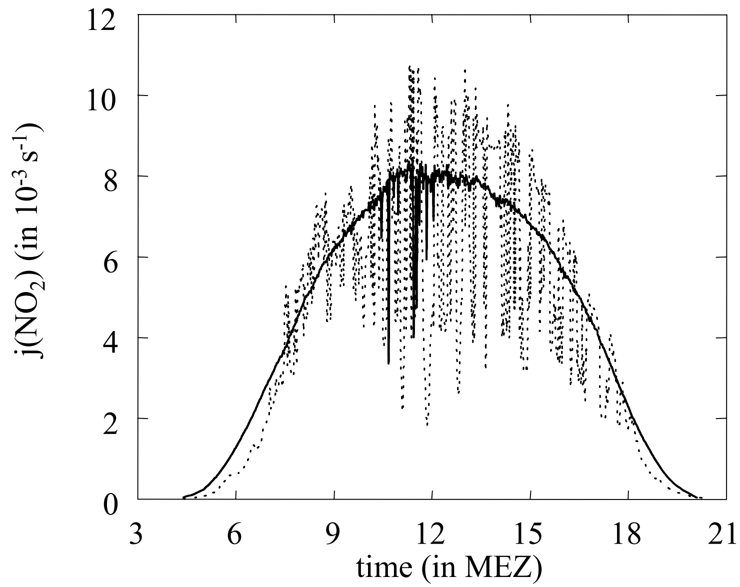
1 The actinic flux is spheric, i.e. photons come from all directions: $I(\lambda) = \int_0^{2\pi}\int_0^{\pi} R(\lambda, \Theta, j)\,d\Omega$

$O_3 + h\nu\ (\lambda < 336\ nm) \rightarrow O(^1D) + O_2$

$NO_2 + h\nu\ (\lambda < 420\ nm) \rightarrow O(^3P) + NO$





Diurnal variation of $j_{O(^1D)}$ and j_{NO2} (summer days in 1995 airport Munic, after Reder 1999)

Some definitions on energy

J = Joule
N = Newton
W = Watt

Energy is the capacity to do work (or produce heat)

There are different kinds of energy

Heat is the transfer of thermal energy from one object to another

Radiation is the transfer of energy by elctromagnetic waves from one object to another

energy ≡ heat ≡ radiation ≡ work ($1\ J = 1\ N\ m = 1\ kg\ m^2\ s^{-2}$)

Temperature is an expression of the inner of energy of a system

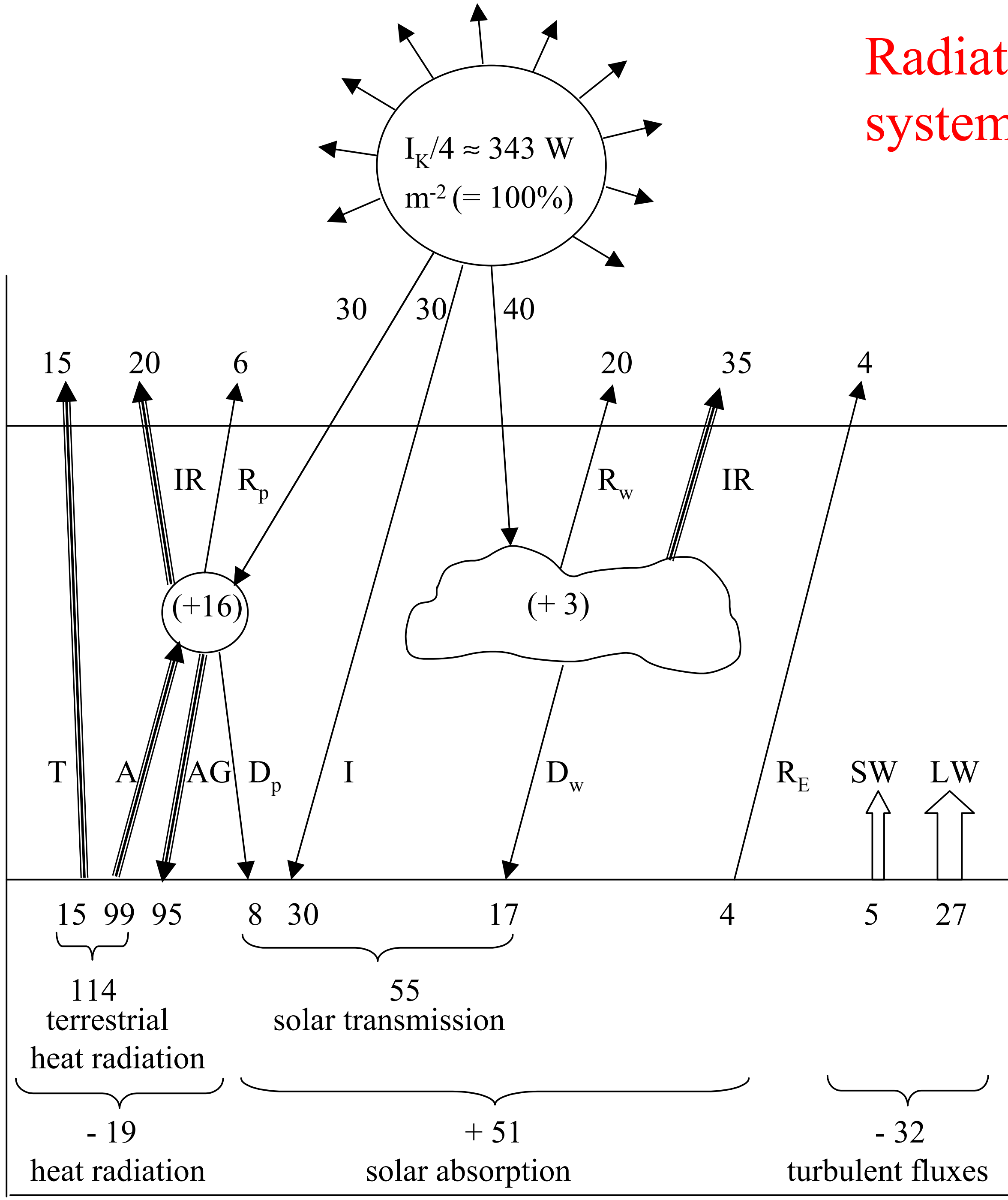
Power is the rate of energy change ($1\ J\ s^{-1} = 1\ W = 1\ kg\ m^{-2}\ s^3$)

Force is the change of energy on distance ($1\ J\ m^{-1} = 1\ N = 1\ kg\ m\ s^{-2}$)

power = force · velocity
force = mass · acceleration
work = power · distance

Climate forcing is expressed by the energy flux ($1\ W\ m^{-2} = 1\ J\ s^{-1} m^{-2}$)

Radiation and heat budget of the system atmosphere - earth



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A absorption of terrestrial radiation by gas molekules (incl. water vapour)

T transmission of terrestrial radiation to space

I direct olar radiation

D_p diffuse solar radiation by particles

D_w diffuse solar radiation by clouds

R_w reflexion of shortwave solar radiation at clouds

R_p reflexion of shortwave solar radiation particles

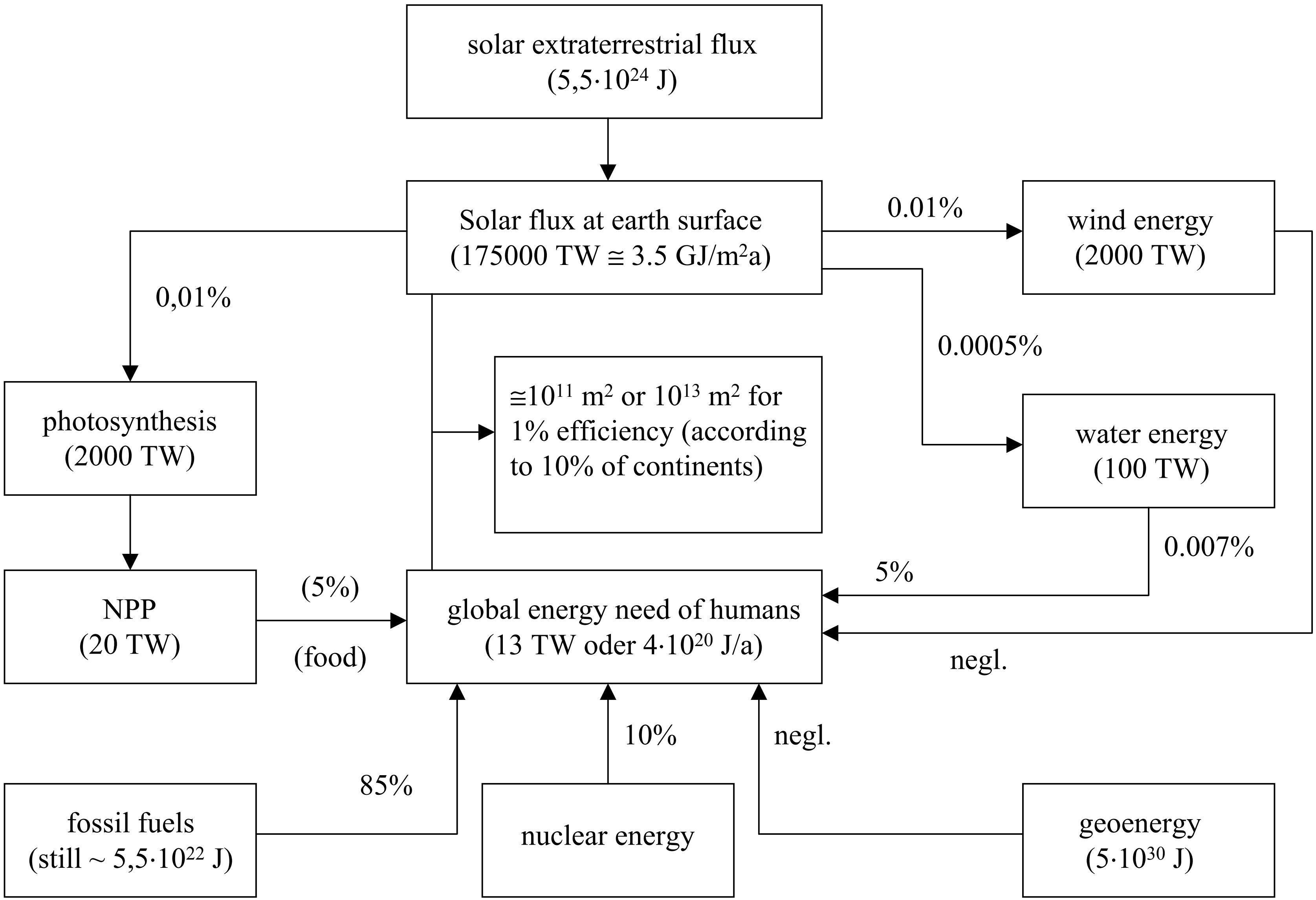
R_E reflexion of shortwave solar radiation earth surface

IR infrared radiation to space

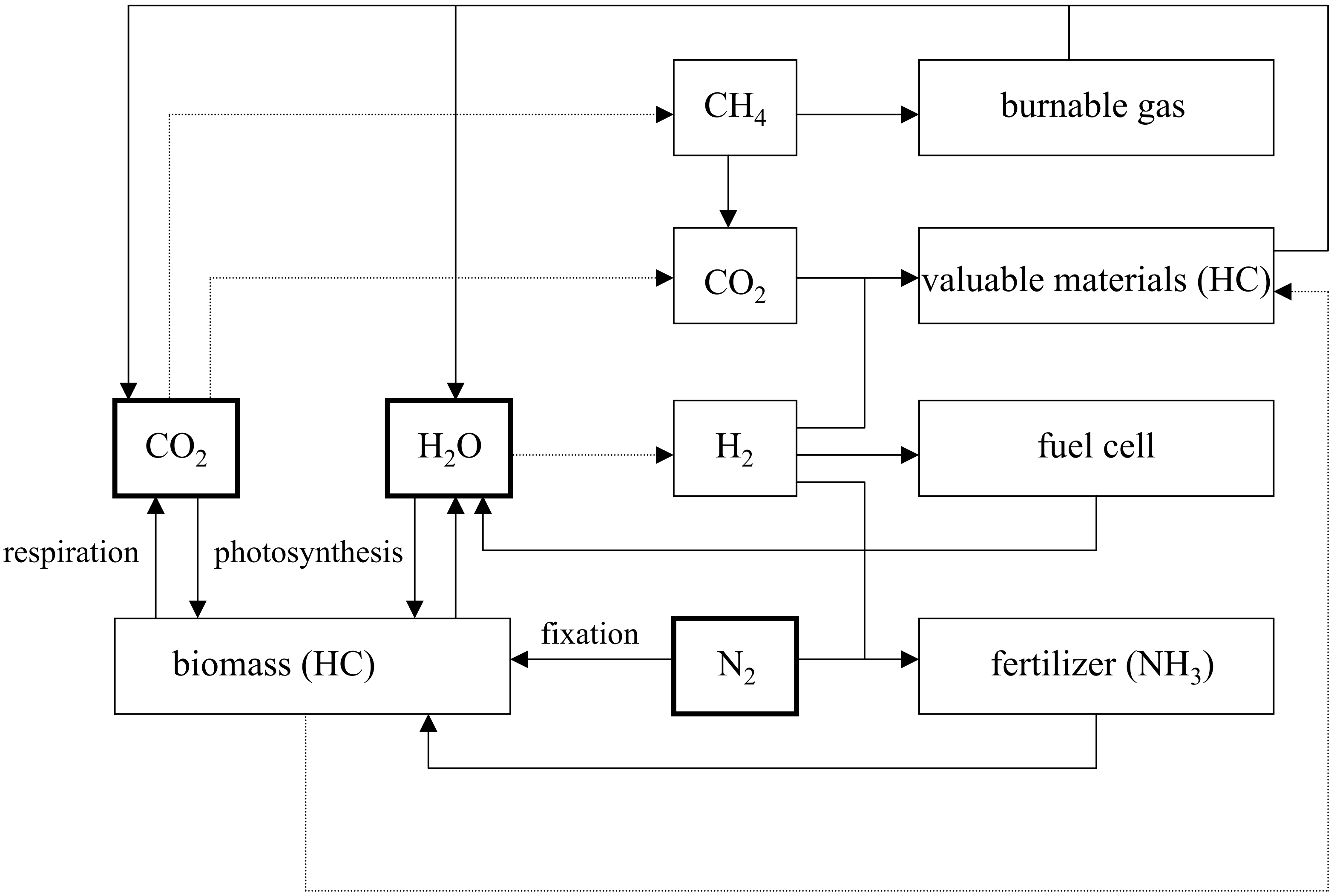
AG atmospheric counter radiation

SW sensible heat flux

LW latent heat flux



Human energy sources



The atmosphere as resource reservoir („solar era“)