12. UV Radiation Sources

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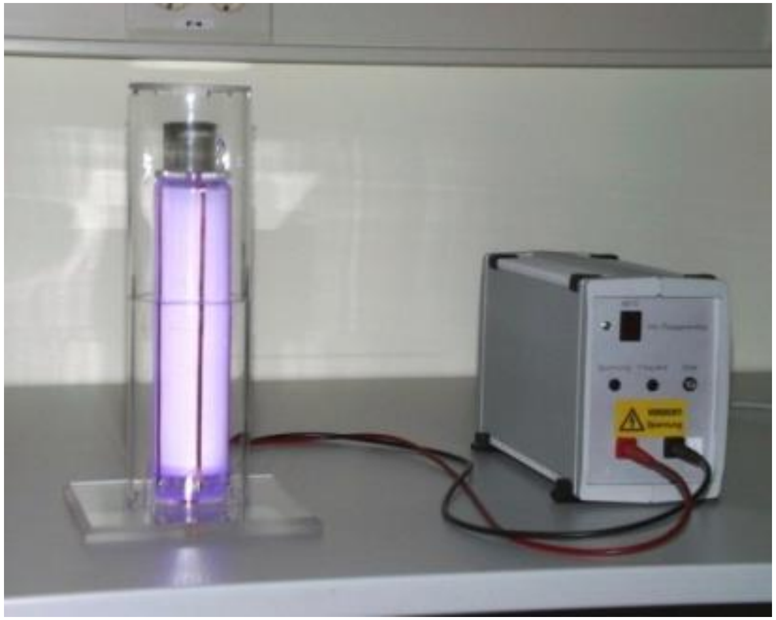
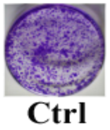
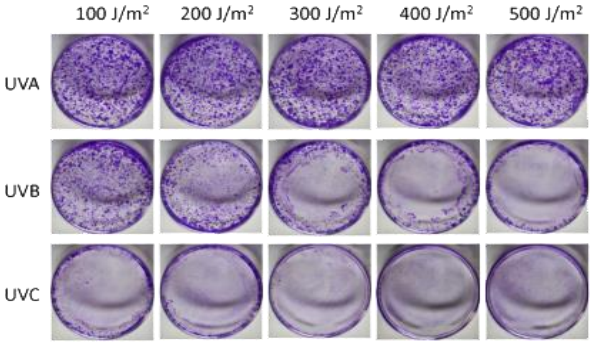






12.1 Classification of UV Radiation

100 nm 200 nm 280 nm 320 nm 400 nm

VUV	UV-C	UV-B	UV-A
12.4 - 6.2 eV	6.2 – 4.5 eV	4.5 - 3.9 eV	3.9 – 3.1 eV
Decomposition of H_2O and O_2 to radicals Ozone formation Cleavage of C-C, C-H, C-O bonds	Excitation of C=C bonds Excitation of the nucleobases Decomposition of O_3, ClO_2 and H_2O_2	Vitamin D formation Transcription of repair enzymes Formation of melanosomes in the skin	Photocatalytic reactions Oxidation of melanin in the skin Decomposition of organic pigments Activation of photocatalytic pigments
Wafer cleaning Photochemistry	Disinfection of air, H_2O and surface Photochemistry	Treatment of skin diseases (psoriasis) Tanning Photochemistry	Water and air purification using TiO_2 photocatalyst Tanning Photochemistry

12.2 Penetration Depth of UV Radiation

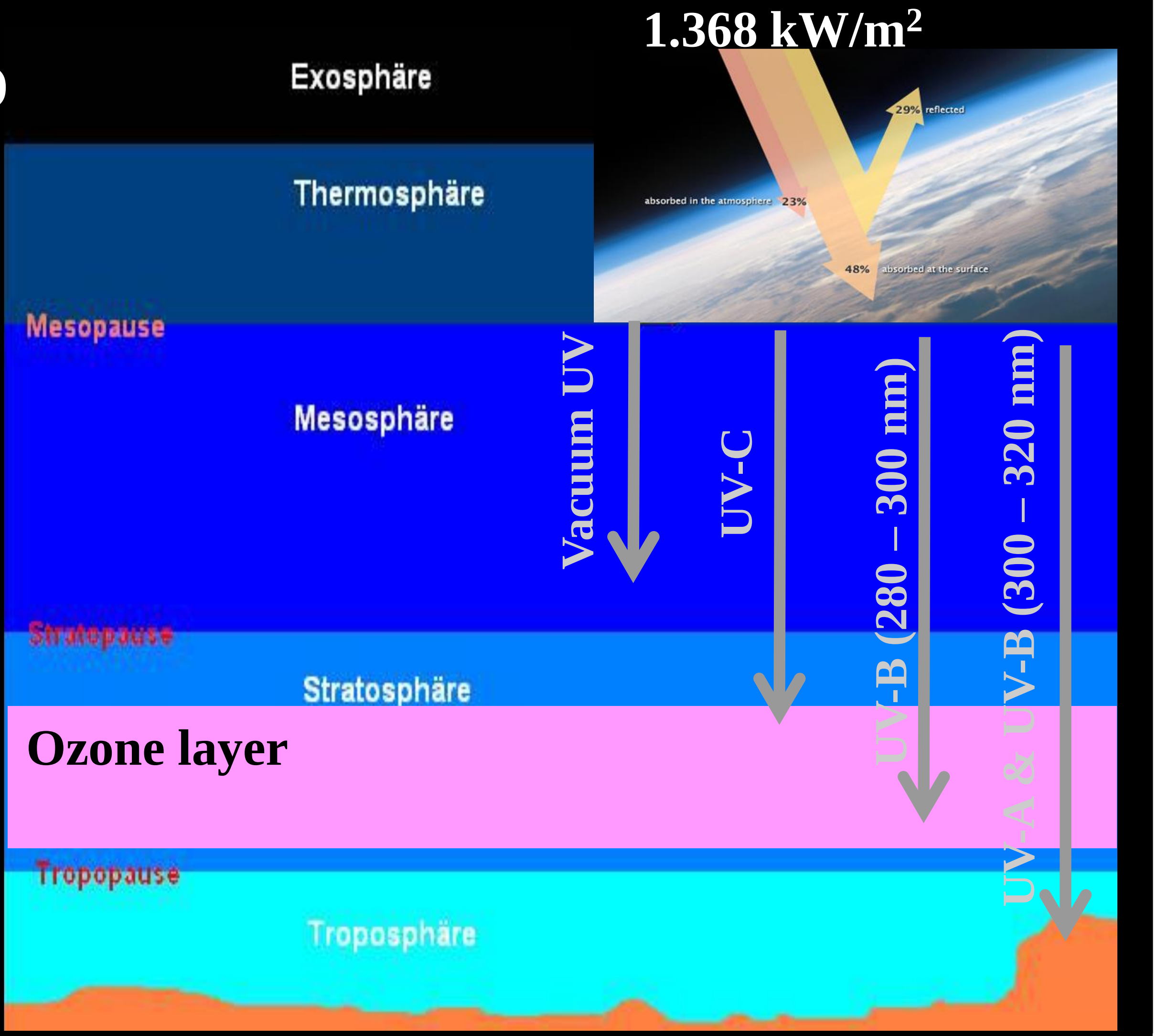
Into Earth Atmosphere

EUV radiation & x-rays (< 100 nm)
- Cleavage of N_2 and CH_4
- Nitrile formation

Vacuum UV (100 - 200 nm)
- Photolysis of water
- Cleavage of N_2 and O_2
- Ozone formation

UV-C (200 - 280 nm) &
UV-B (280 - 300 nm)
- Ozone cleavage

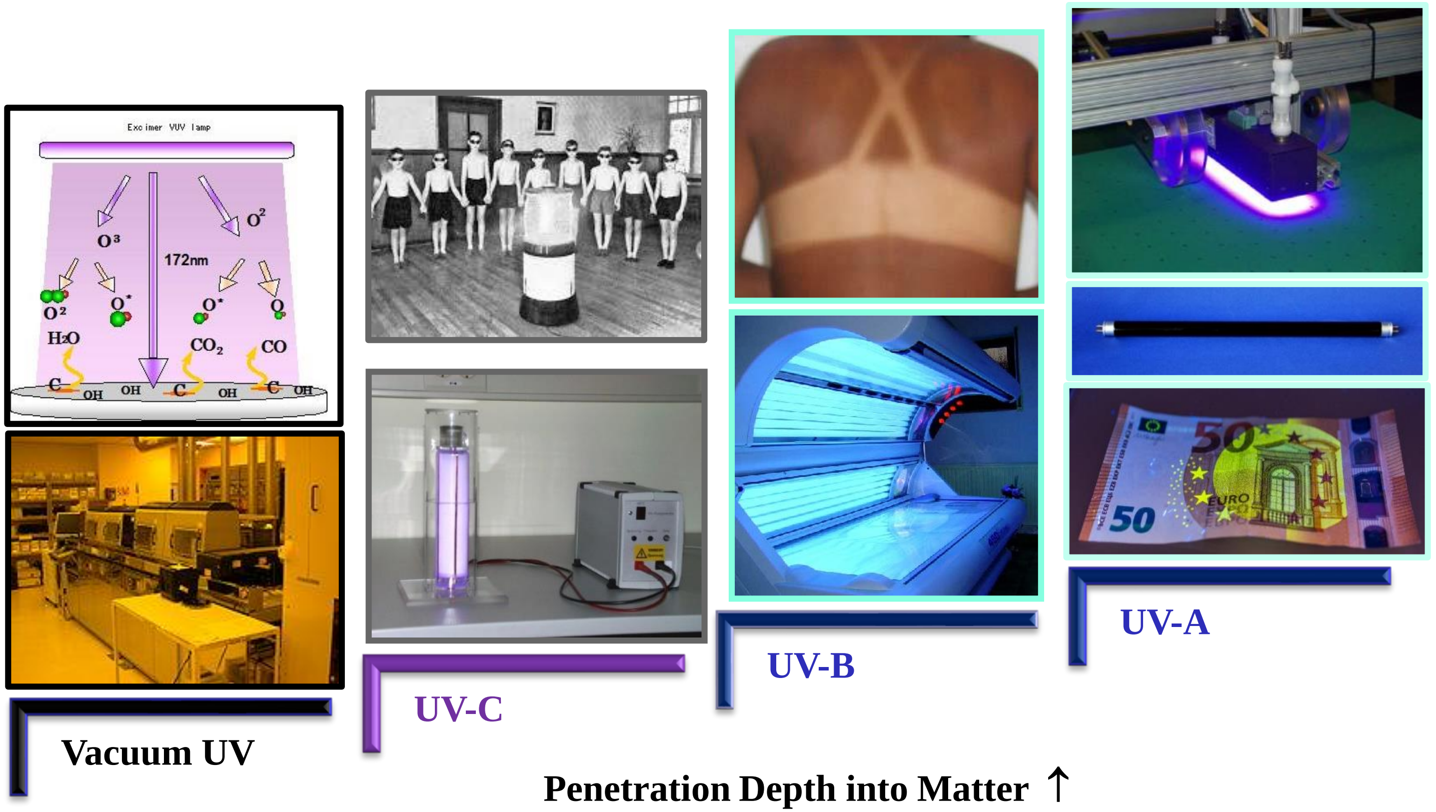
UV-B (300 - 320 nm) &
UV-A (320 - 380 nm)
- Photochemical degradation of air pollutants
- Disinfection by photocatalysis



12.2 Penetration Depth of UV Radiation

Into Matter

Rather low penetration depth: UV radiation works solely at the surface!



Vacuum UV

UV-C

UV-B

UV-A

Penetration Depth into Matter ↑

100 nm | 200 nm | 280 nm | 320 nm | 400 nm

Phototechnology | **Disinfection / Imaging** | **Skin treatment / Curing / Sensing**

↓

Mutations

→ Inactivation of harmful cells

→ Disinfection & tumour inhibition

12.3 Photochemical Applications

Chemical Bonds and Photon Energy

Energy of chemical bonds

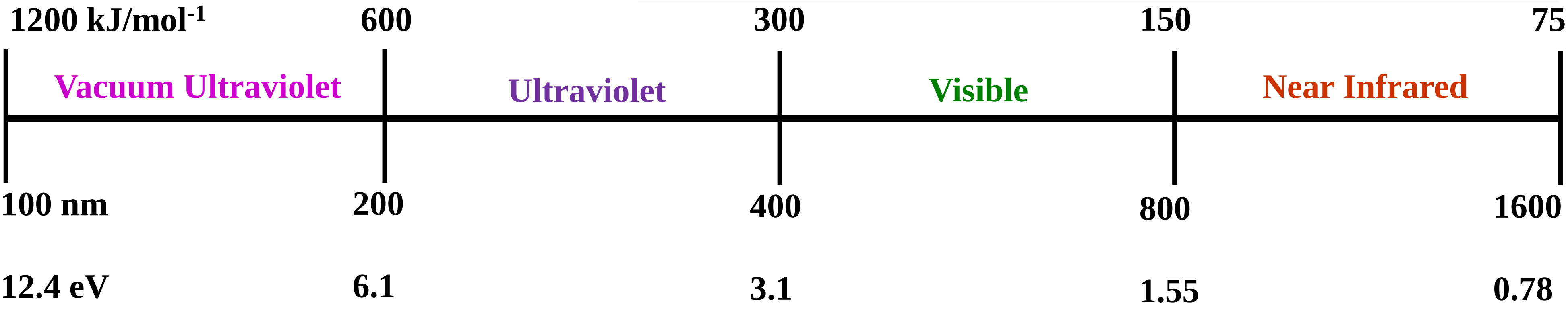
~ 10 – 1000 kJ/mol

(1 eV = 8065 cm^{-1} = 96.2 $kJmol^{-1}$)

Energy of optical radiation

$E = N_A hc/\lambda = 119226/\lambda$ [$kJmol^{-1}$]

E-E	100 – 500 kJ/mol	F-F	159 kJ/mol
		C-C	348 kJ/mol
E=E	400 – 700 kJ/mol	O=O	498 kJ/mol
		C=C	648 kJ/mol
E≡E	800 – 1100 kJ/mol	N≡N	946 kJ/mol
		C≡C	839 kJ/mol
H-bridges	10 - 160 kJ/mol	H···F > H···O > H···N	
Van-der-Waals	0.5 - 5 kJ/mol		



1200 kJ/mol^{-1} | 600 | 300 | 150 | 75

Vacuum Ultraviolet | Ultraviolet | Visible | Near Infrared

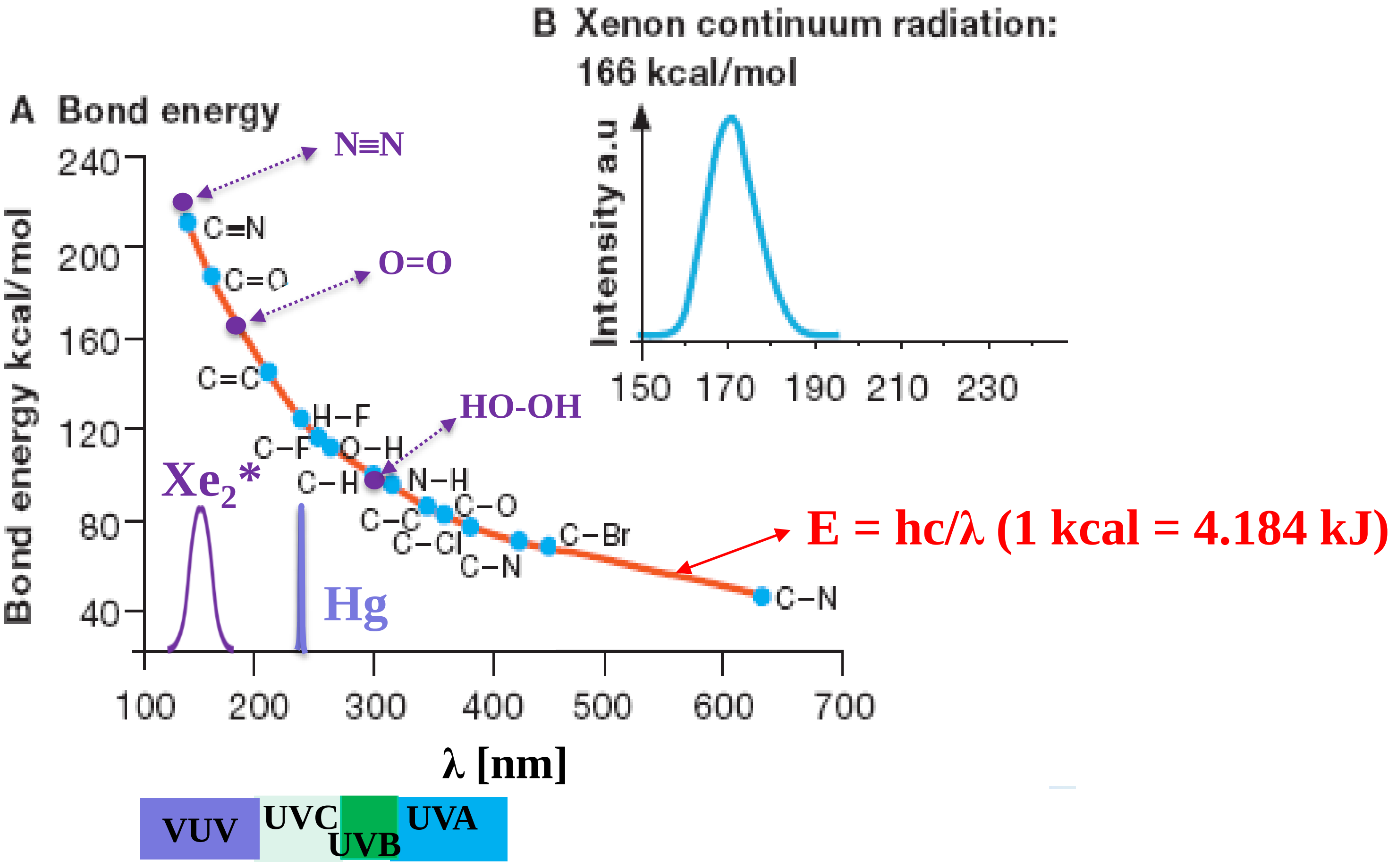
100 nm | 200 | 400 | 800 | 1600

12.4 eV | 6.1 | 3.1 | 1.55 | 0.78

Thus (V)UV to VIS radiation is able to cleave covalent chemical bonds

12.3 Photochemical Applications

Cleavage of Chemical Bonds



E = hc/λ (1 kcal = 4.184 kJ)

Ionisation potential: $A \rightarrow A^* \rightarrow A^+ + e^-$

12.3 Photochemical Applications

Photolysis reaction (selection)

- **Decomposition of azides**
  M-N=N=N + hν(< 300 nm) → M=N + N_2 with M = Cr, Mn, Fe, Ru → nitride and NH_3 chemistry!

- **Homolytic decomposition of iodine**
  I_2 + hν(520 nm) → 2 I·
- **Decomposition of HgO**
  2 HgO + hν(< 600 nm) → 2 Hg + O_2
- **Decomposition of diazo-compounds**
  R-CO-CH=N=N + hν(< 350 nm) → R-CH=C=O + N_2
- **Isomerization reactions**
  praecalciferol + hν(282 nm) → calciferol (vitamin D_3)
- **Decomposition of formic acid HCOOH**
  HCOOH + hν(< 260 nm) → CO + H_2O

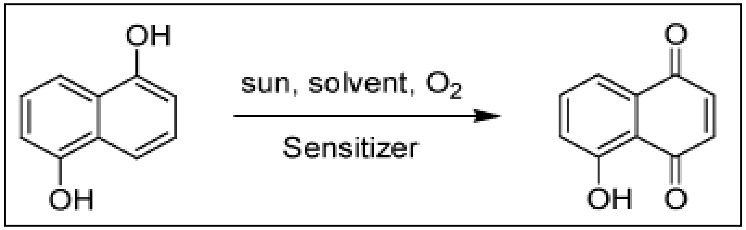
12.3 Photochemical Applications

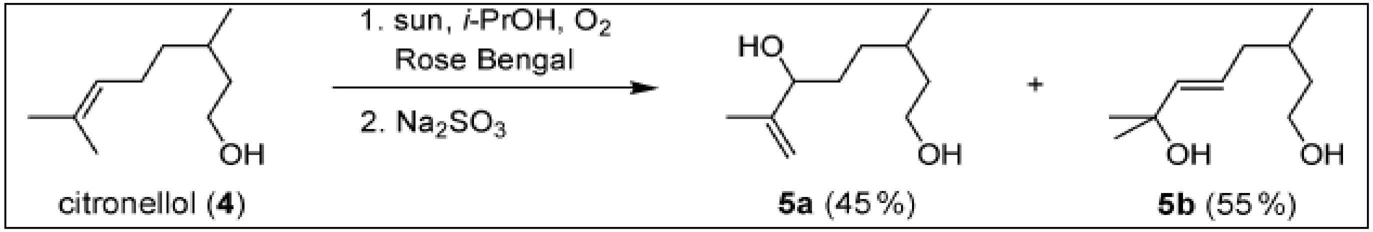
Synthesis of organic compounds

- **Photoinitiated polymerisation**
  $K[Cr(NH_3)_2(NCS)_4] + 2\ H_2O + h\nu \rightarrow K[Cr(NH_3)_2(NCS)_3(OH)] + H_3O^+ + NCS^-$
  $\rightarrow$ Anionic polymerisation of ethyl-α-cyanoacrylate by addition of NCS^- as a chain starter

- **Photooxidative initiated polymerisation**
  Flow coat process as a step of the CRT production process
  (polyvinyl alcohole + ammonium dichromate)
  $R\text{-}CH_2\text{-}OH + CrO_4^{2-} + h\nu(\text{vis.}) \rightarrow R\text{-}CH{=}O \rightarrow$ Polymerisation

- **Photooxidative synthesis of organic molecules**





12.3 Photochemical Applications

Water and surface cleaning with VUV radiation

1. Decomposition of water to radicals

$H_2O + h\nu(< 200\ \text{nm}) \rightarrow OH^{\cdot} + H^{\cdot}$

$2\ OH^{\cdot} \rightarrow H_2O_2$

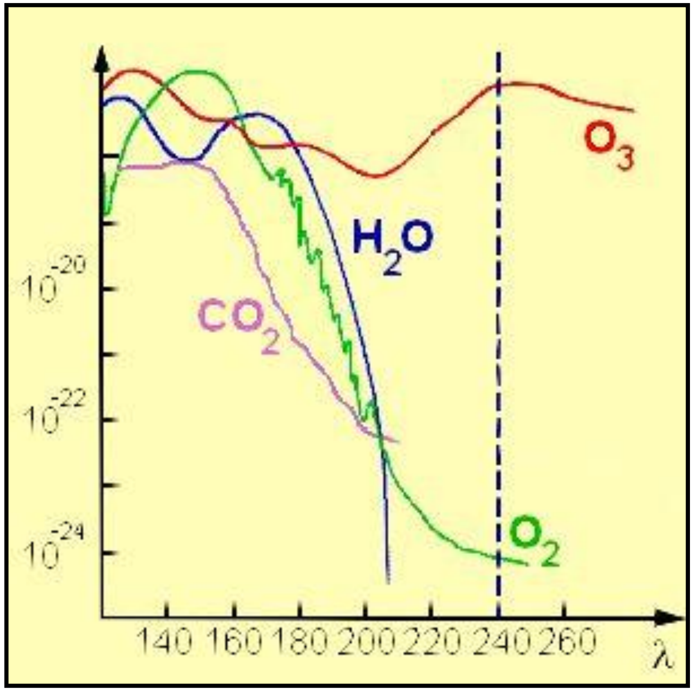
$2\ H_2O_2 \rightarrow 2\ H_2O + {}^{1}O_2$

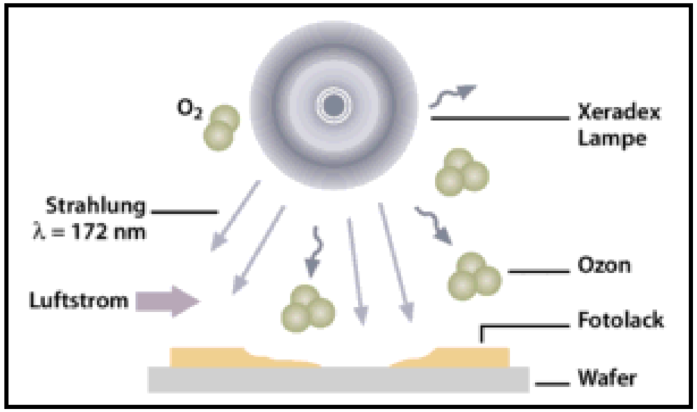
2. Ozone formation

$O_2 + h\nu(< 200\ \text{nm}) \rightarrow 2\ O^{\cdot}$

$2\ O_2 + 2\ O^{\cdot} \rightarrow 2\ O_3$

H_2O_2, ${}^{1}O_2$, and O_3 decompose organic compounds or impurities by oxidation





12.4 Biochemical Applications

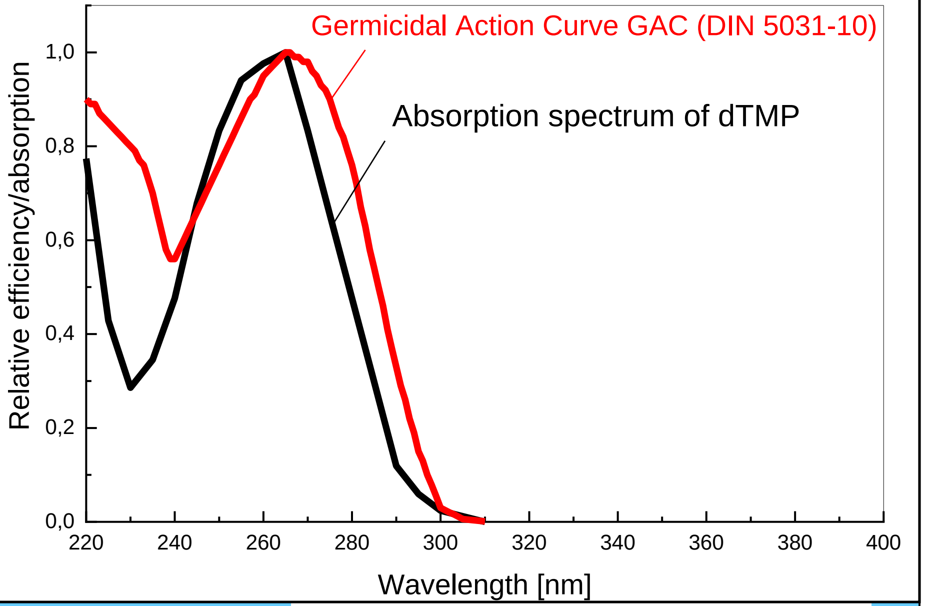
Disinfection

Water, air and surface contain microorganisms
→ fungi, bacteria, protozoa, viruses, biofilms

Killing of microorganisms by

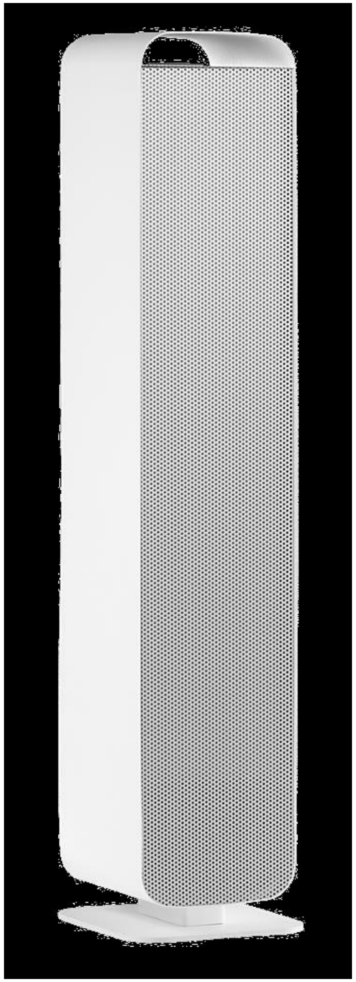
- **Heat (80 – 120 °C)**
- **Chemicals (I_2, Cl_2, ClO_2, NaOCl, NH_2Cl, O_3)**
- **Pharmaceuticals (antibiotics)**
- **UV radiation (< 300 nm), which is filtered by the ozone layer…..**

The effect of UV radiation is mainly due to the inhibition of the growth of microorganisms



12.4 Biochemical Applications

Disinfection of indoor ambient air



Example: STAMBOLI air purifier

- **Air flow: 160 m^3 h^{-1}**
- **Light sources: Hg LP UV-C lamp (253.7 nm), ozone free**
- **Voltage: 220 - 240 V**
- **Input power: 72 W (output ~ 30 W UV-C)**
- **Lifetime of UV-C lamps: 9000 hours**

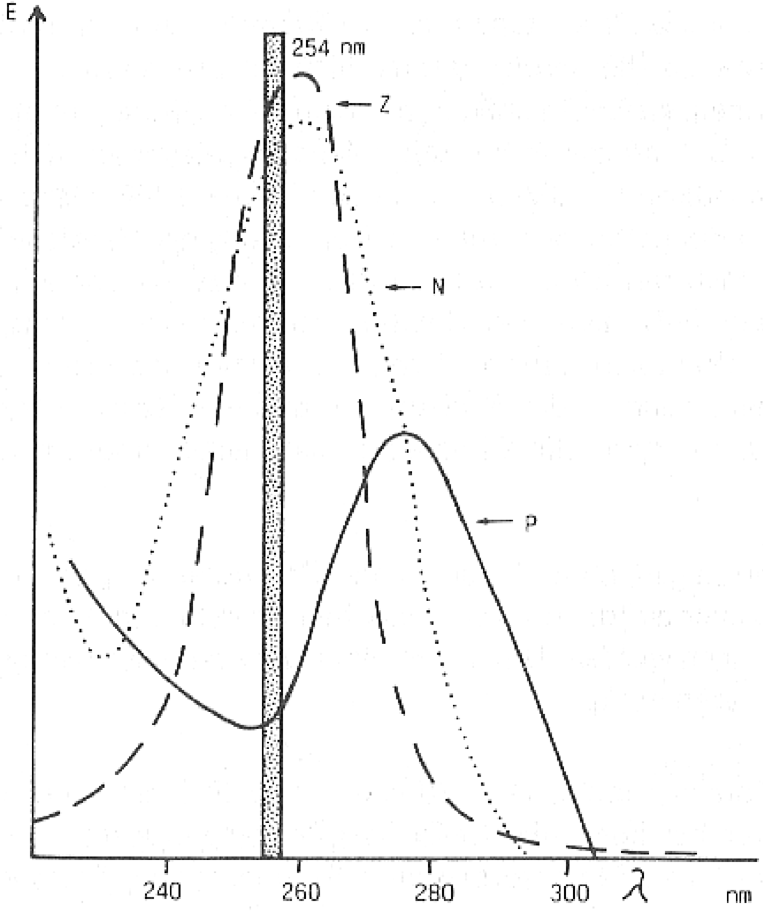
Alternative approaches

- **Photo-Fenton-reaction: $Fe^{2+} + H_2O_2 + h\nu \rightarrow Fe^{3+} + OH^- + OH^\cdot$**
- **UV-A/B LED + TiO_2 photocatalyst: $O_2^{-\cdot} + OH^\cdot$**
- **O_3 at alkaline surfaces: $Mg(OH)_2 + O_3 \rightarrow MgO + O_2 + H_2O_2$**
- **O_3 and humidity + UV-C lamp: $O_3 + H_2O + h\nu \rightarrow O_2 + H_2O_2$**
- **Atmospheric plasms: O_3**
- **Xe excimer lamp (172 nm): $3\ O_2$ cleavage $\rightarrow 2\ O_3$**
  H_2O cleavage $\rightarrow OH^\cdot + H^\cdot$

12.4 Biochemical Applications

Disinfection

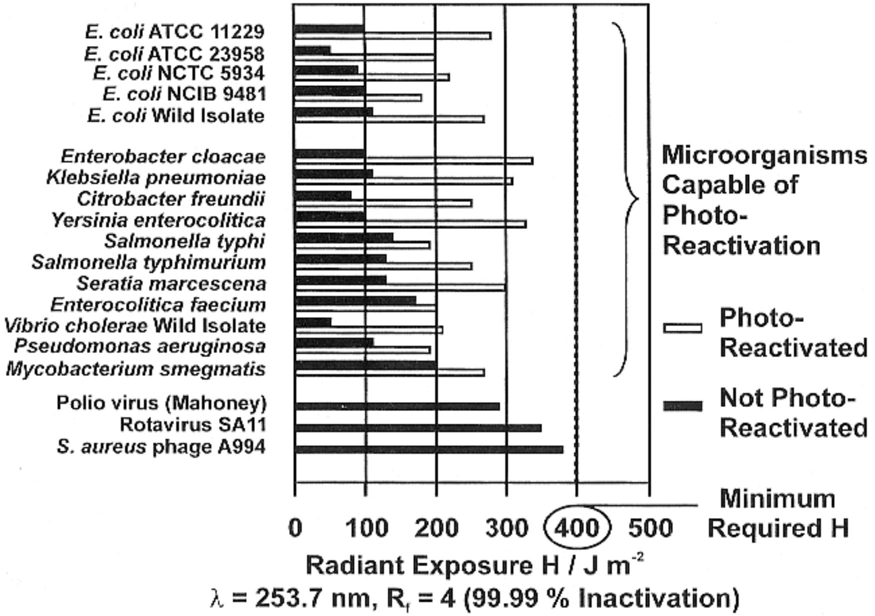
Germicidal action curve (GAC)



UV-C inactivation of germs

$$N_{active}(t) = N_0 \cdot e^{\boxed{-k \cdot E_{eff} \cdot t}}$$

$$R_f = \log \frac{N_0}{N_{active}(t)} \overset{!}{>} 4$$



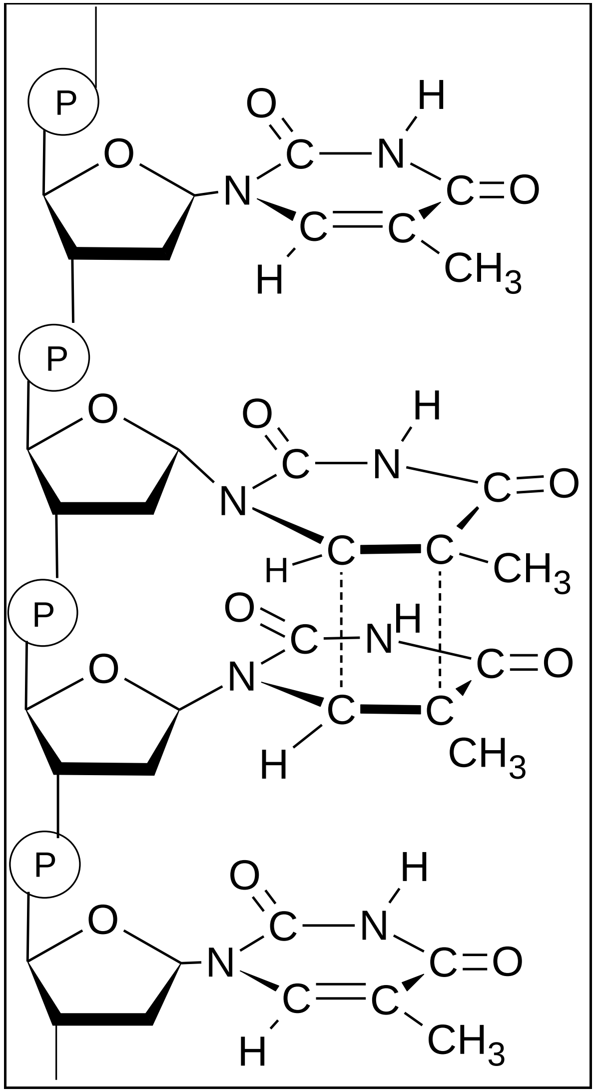
12.4 Biochemical Applications

Disinfection - Photobiology

Structure of DNA

- helical double strand of nucleotides dNMP
- dNMP = base + phosphate + deoxyribose

-A-T-A-T-G-C-T-A-G-G-C-C-
-T-A-T-A-C-G-A-T-C-C-G-G-



Mechanism of disinfection

UV-C is absorbed by purine and pyrimidine bases

⇒ Reaction between adjacent thymine bases (2 + 2 cycloaddition, a pericyclic reaction → Woodward Hoffmann rules)

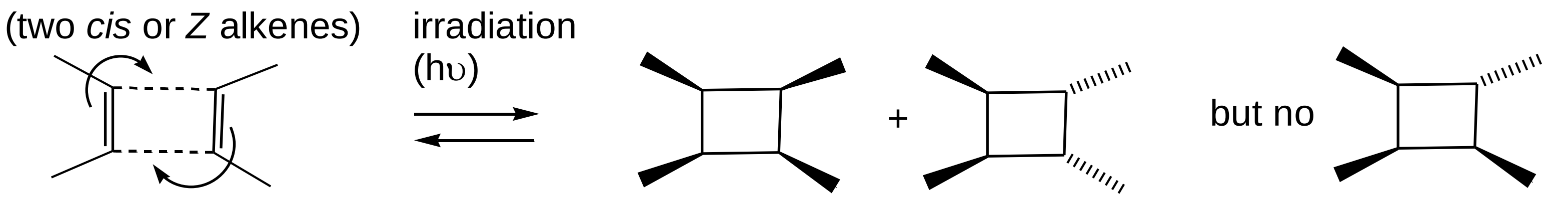
⇒ Failed to copy DNA

Nucleotide	Extinction coefficient ε at 260 nm
dAMP	15200
dTMP	8400
dGMP	12000
dCMP	7100

12.4 Biochemical Applications

Excursion: Woodward-Hoffmann rules for pericyclic reactions ("any concerted reaction in which bonds are formed or broken in a cyclic transitions state", electrons move around in a circle)

Example: Cycloaddition reactions



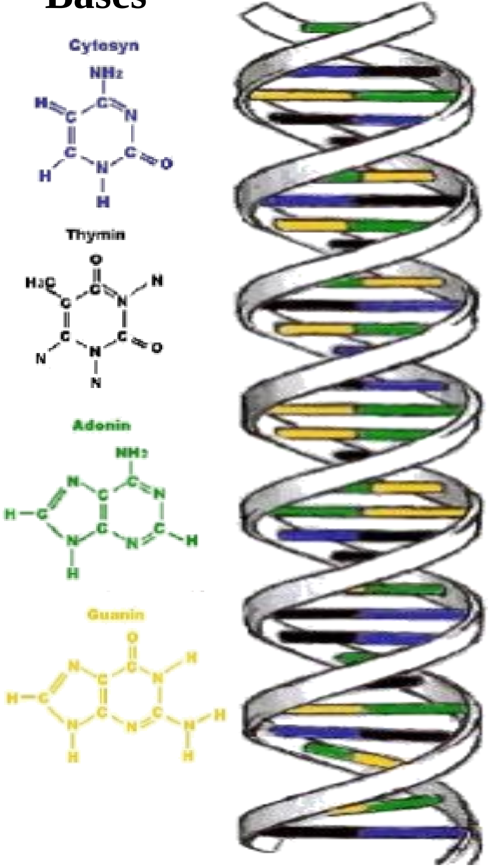
What is happening in the cyclisation is that p-orbitals (which form the π-bonds) are combining in order for a new s bond to be formed between the 'ends' of the conjugated system. However, in order for this process to happen efficiently, it is necessary for the orbitals with the same wave-function sign (phase) to 'join up'. In order to work out where these are, a quick analysis of the four molecular orbitals (formed from the 4 atomic p–orbitals) is required.

12.4 Biochemical Applications

Disinfection - Photobiology

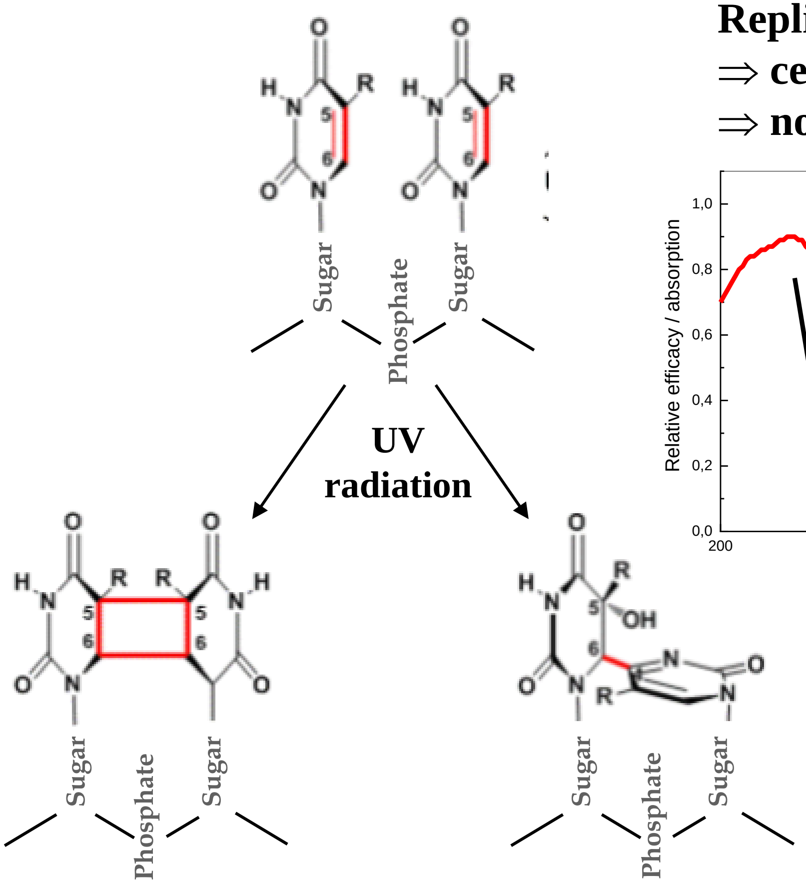
Bases

DNA double helix



and sugar and phosphate units

adjacent Thymin bases



UV radiation

Cyclobutan-Pyrimidindimer (CPD) 70-80%

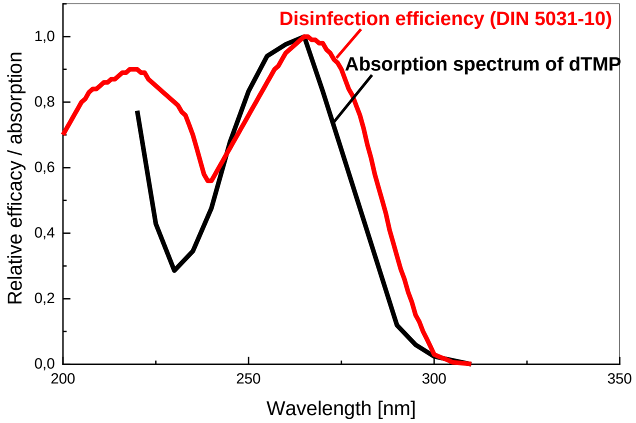
Pyrimidin-Pyrimidon-Photoproduct (64PP) 20-30%

Result of these point mutations

Replication of DNA blocked

⇒ cell mitosis inhibited

⇒ no infectious potential

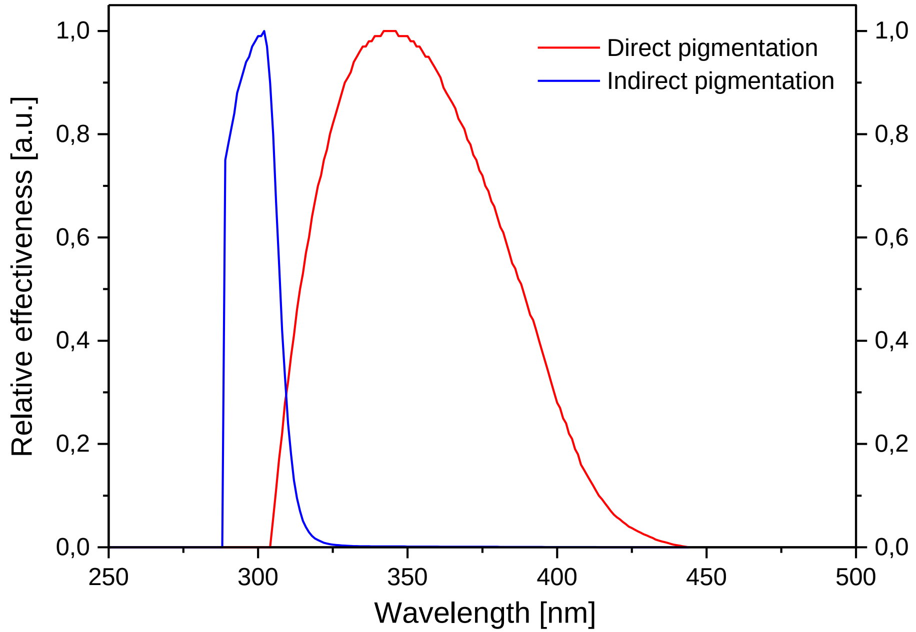


12.4 Biochemical Applications

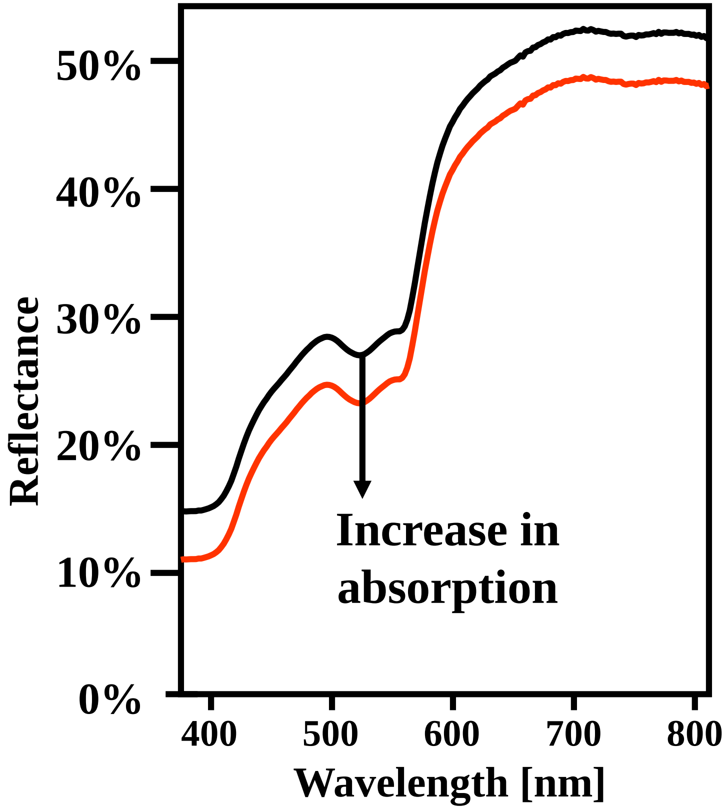
Tanning

UV-A: Direct pigmentation

UV-B: Indirect pigmentation



Tanning of human skin

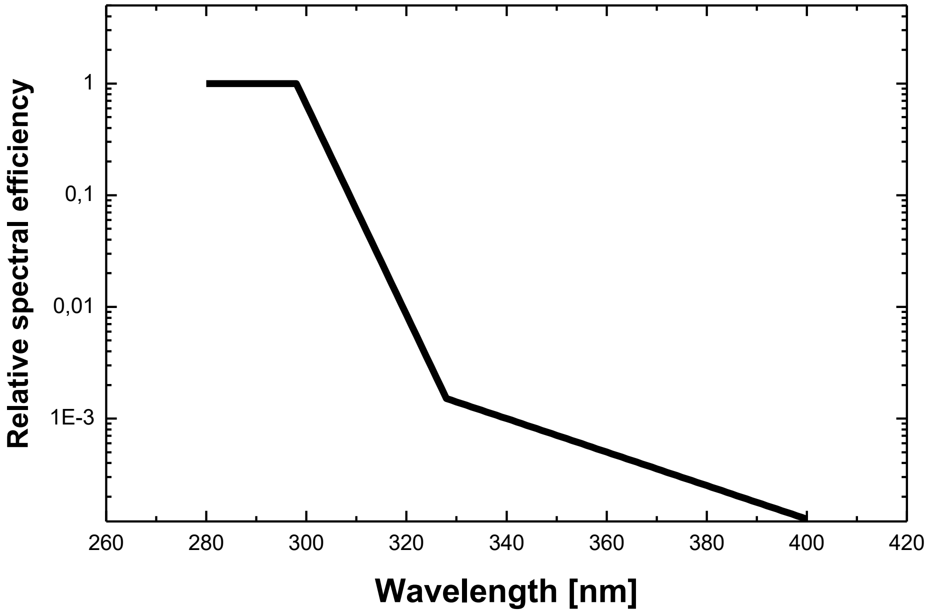


Direct pigmentation: Oxidation of melanin to melanin oxide (short term effect)

Indirect pigmentation: Incorporation of new melanosomes (long-term effect)

12.4 Biochemical Applications

Effects of exposure to UV radiation: Erythema = skin redness or sunburn



Human skin sensitivity according to

DIN 5031-10

250 - 298 nm: E = 1

298 - 328 nm: E = 1*10^(0.094*(298-λ))

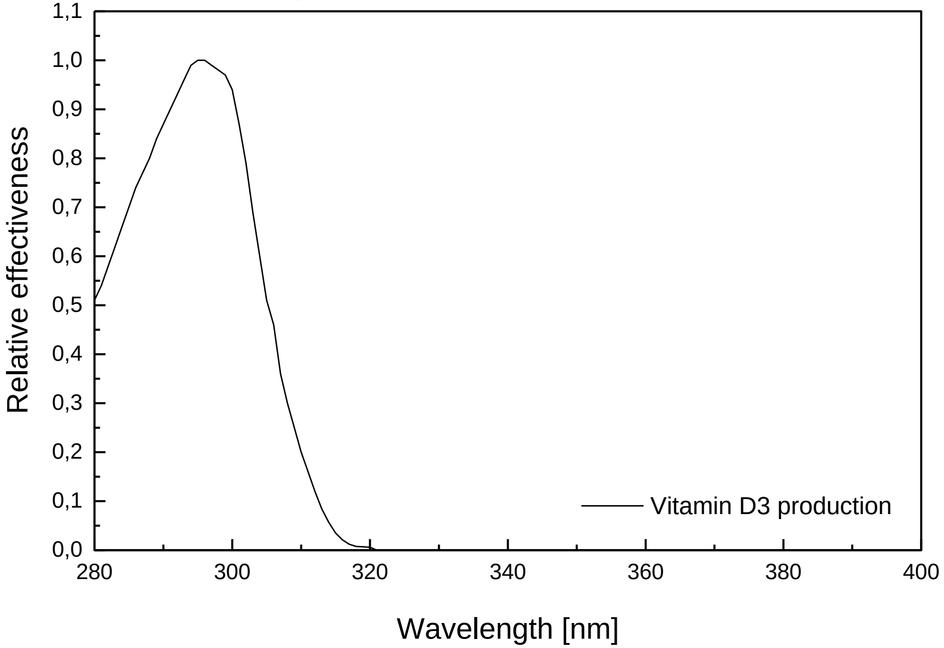
328 - 400 nm: E = 1*10^(0.015*(140-λ))

- **By UV radiation, the skin is irritated and as a result of increased blood flow reddened**
- **Prolonged UV exposure leads to phototoxic reaction (sunburn)**
- **The minimal erythemal dose (MED) is 250 – 400 J/m^2 for a skin type II middle European**

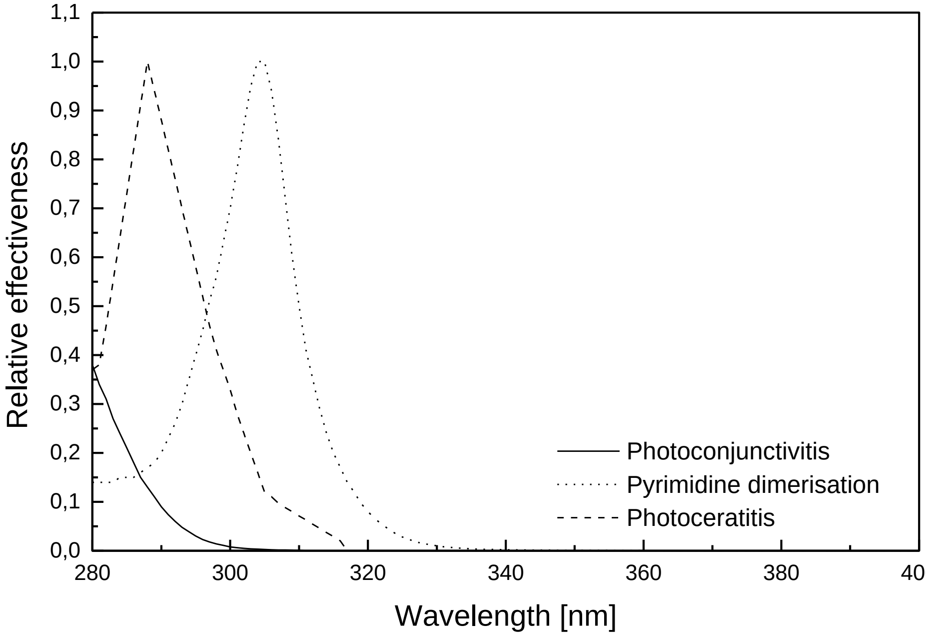
12.4 Biochemical Applications

Effects of exposure to UV radiation: Other side effects

Vitamin D_3 Production in human skin



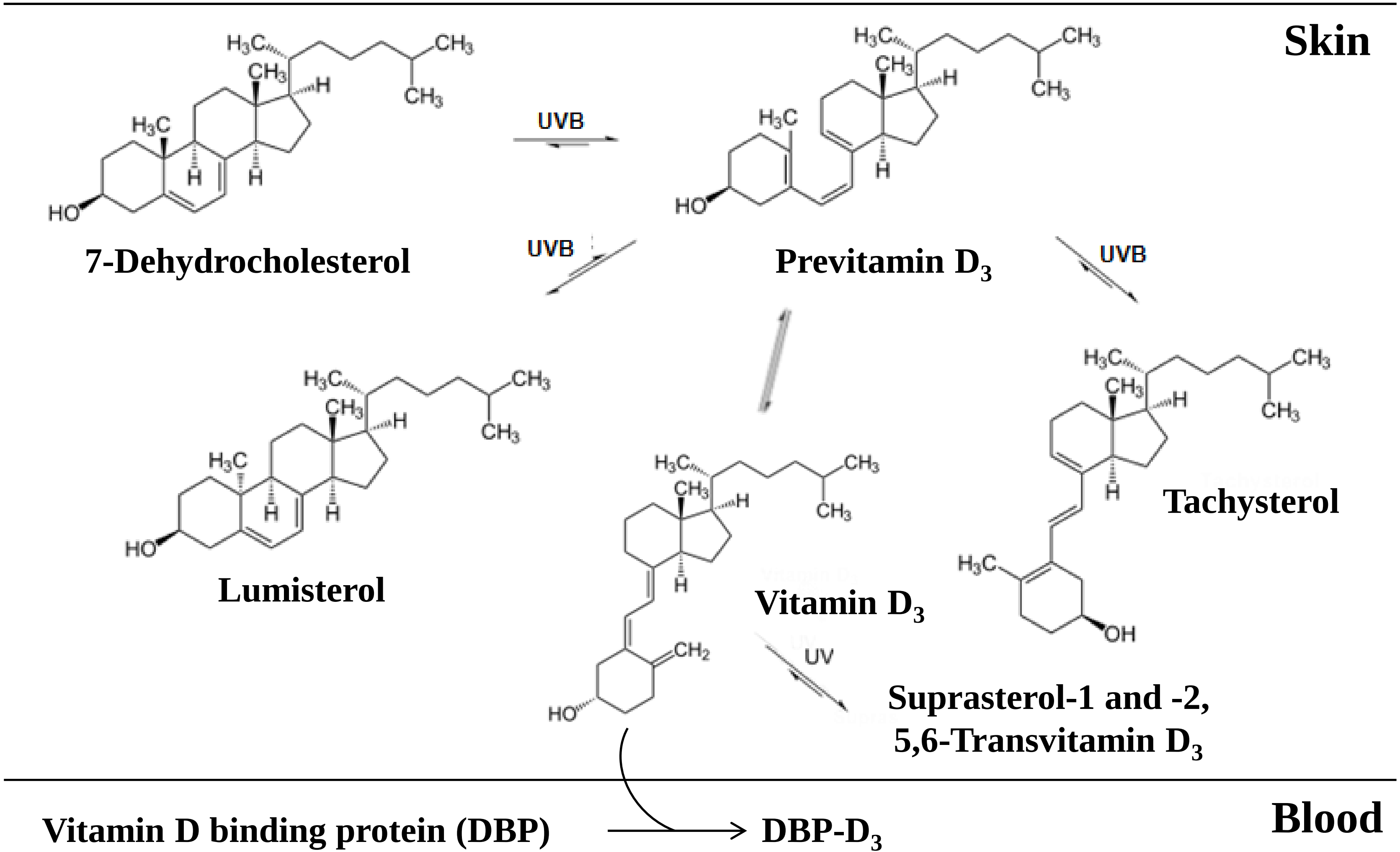
Phototoxic effects



- UV-B radiation is mainly responsible for the positive and negative effects UV exposure
- The wavelength dependency of such biological effects is rather pronounced in UV-B range

12.4 Biochemical Applications

Vitamin D_3 formation in human skin



Skin

7-Dehydrocholesterol

Previtamin D_3

Lumisterol

Tachysterol

Vitamin D_3

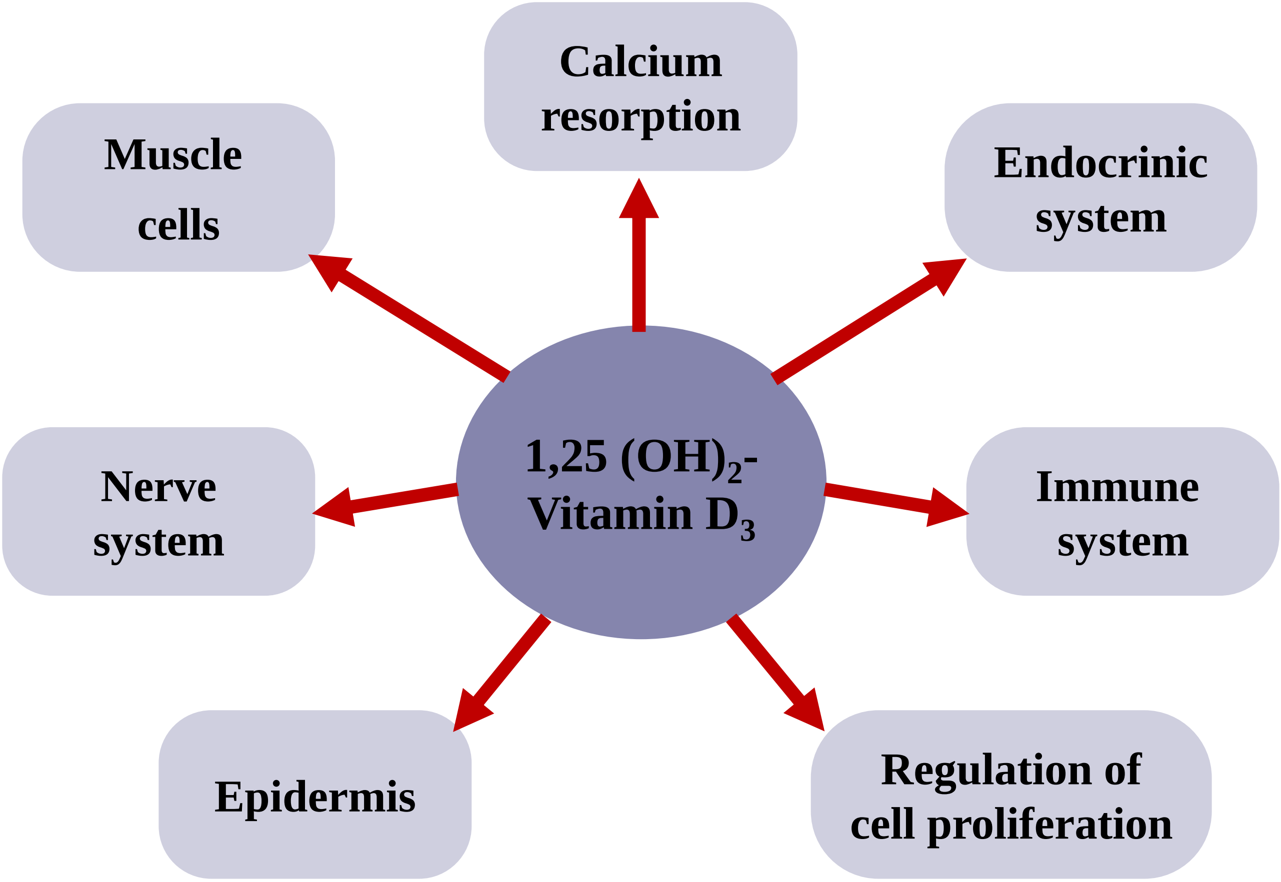
Suprasterol-1 and -2,
5,6-Transvitamin D_3

Blood

Vitamin D binding protein (DBP) → **DBP-D_3**

12.4 Biochemical Applications

Impact of Vitamin D_3 on human health



$1,25\ (OH)_2$-
Vitamin D_3

Calcium resorption

Muscle cells

Endocrinic system

Nerve system

Immune system

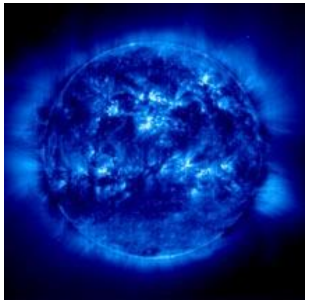
Epidermis

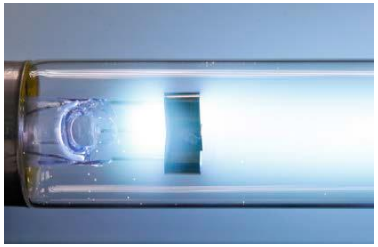
Regulation of cell proliferation

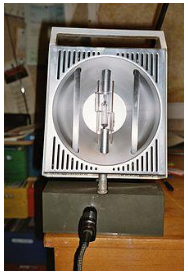
12.5 UV Radiation Sources

Overview

Solar radiation	**> 300 nm**
Hg discharge lamps	
low-pressure	**185, 254 nm**
amalgam	**185, 254 nm**
medium-pressure	**200 – 400 nm**
Xe discharge lamps	**230 – 800 nm**
D_2 discharge lamps	**110 – 400 nm**
Excimer laser (ArF*)	**193 nm**
Solid state laser (Nd^{3+} 4th harmonic)	**266 nm**
Excimer discharge lamps	**100 – 400 nm**
(Al,Ga)N LEDs	**210 – 365 nm**
(In,Ga)N LEDs	**365 – 400 nm**
x-ray/cathode ray tube & phosphor	**200 – 400 nm**

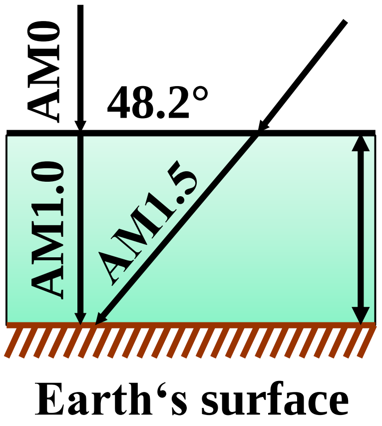


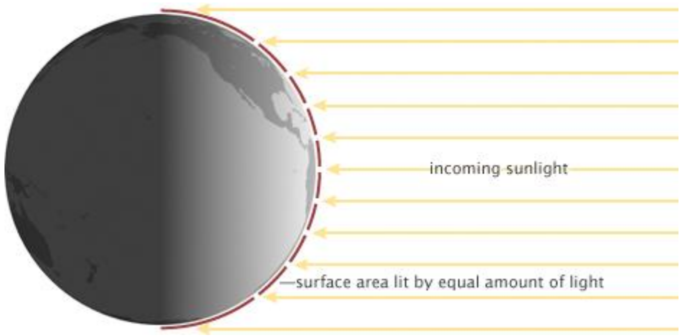




12.5 UV Radiation Sources

Solar Radiation

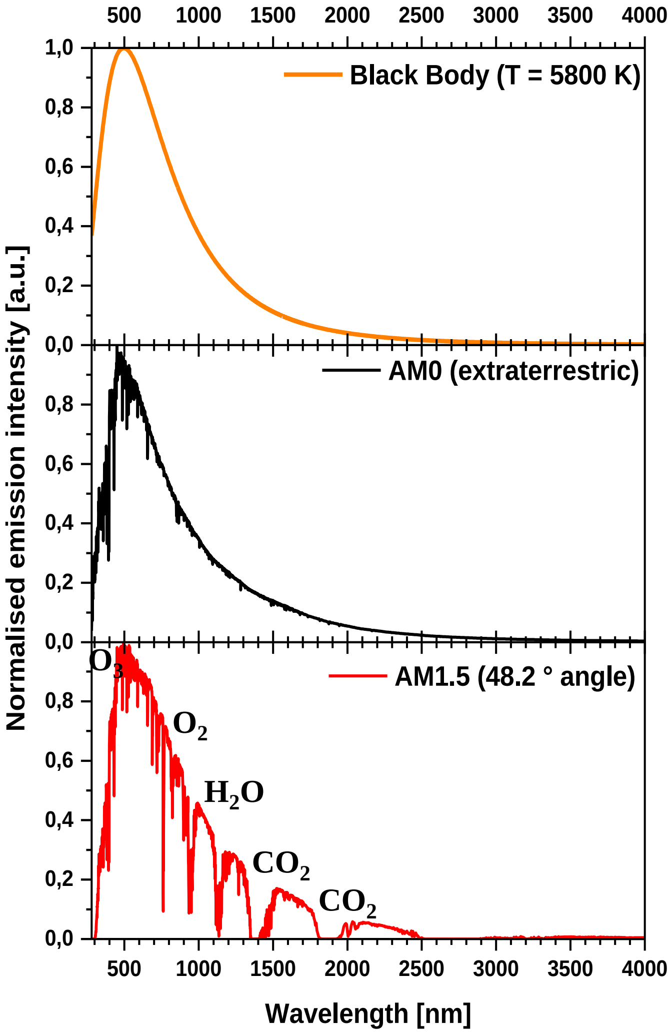




< 400	400 - 500	500 - 600	600 - 700	> 700
37.8 W/m^2 5.3%	130.4 W/m^2 18.2%	144.6 W/m^2 20.2%	134.0 W/m^2 18.7%	269.2 W/m^2 37.6%

~ 5% UV ~ 60% VIS ~ 35% IR

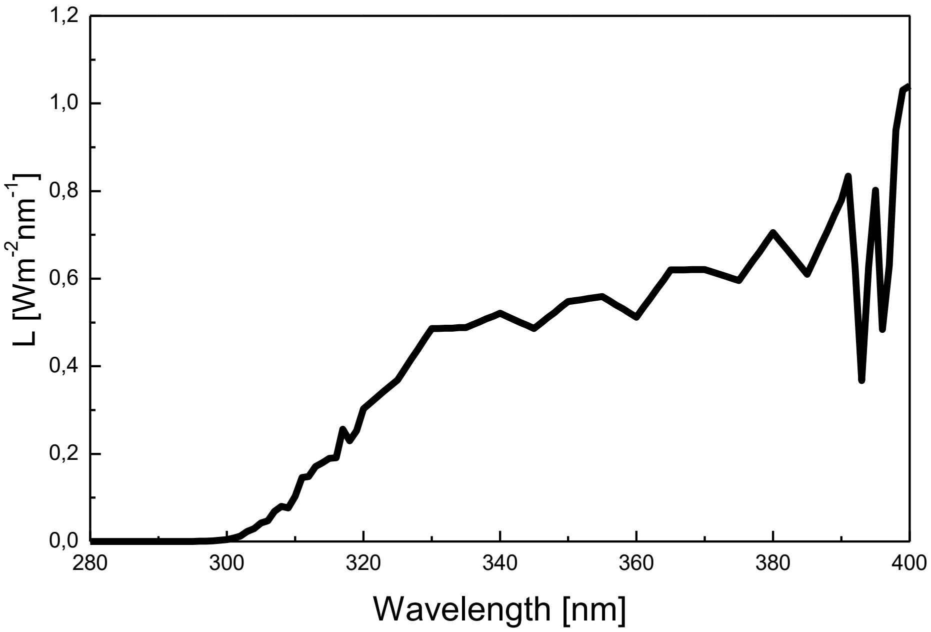
The solar spectrum depends on daytime & season, air pressure, clouds, particles (dust), elevation, and so on



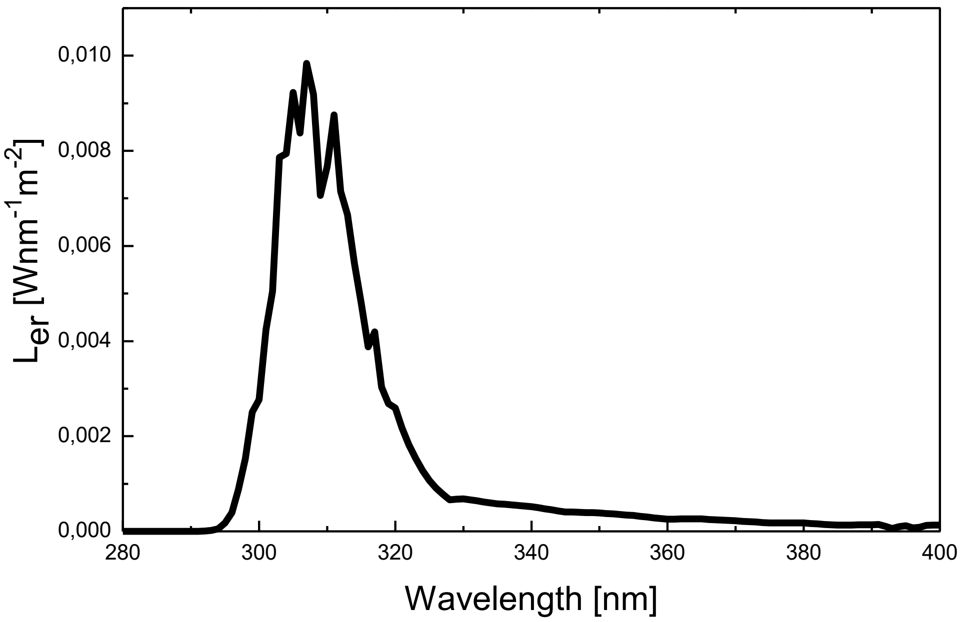
12.5 UV Radiation Sources

Solar UV Radiation

UV spectrum at 60° solar elevation angle



Analogous erythema spectrum

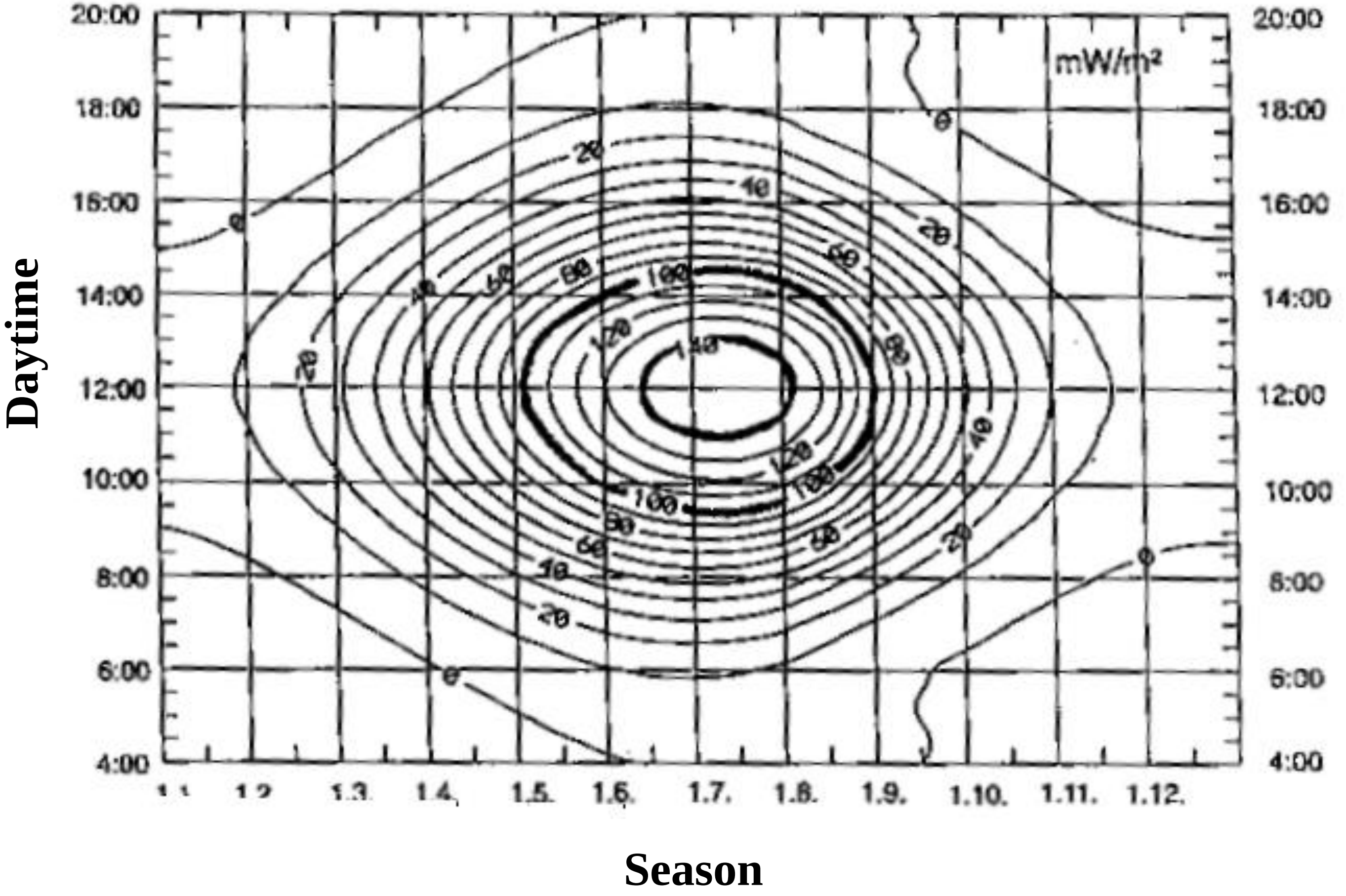


$$\boxed{L_{er,tot} = \int_{280}^{400} L(\lambda)E(\lambda)d\lambda}$$

⇒ **Skin redness or sunburn are mainly caused by UV-B radiation**

12.5 UV Radiation Sources

Time dependent distribution of solar UV radiation (Norderney: 53.2° north latitude)



12.5 UV Radiation Sources

Local distribution of UV radiation (on 21st June at high noon)

Solar height	Latitude [°] N	Nearest location at 10° E	UV-B [W/m^2]	UV-A [W/m^2]	UV-B [%]	$E_{<320}$ [W/m^2]	$E_{>320}$ [W/m^2]	$E_{<320}/E_{>320}$
83.5	30	Ghadames, Libya	1.66	61.0	2.65	0.1654	0.0380	4.35
78.5	35	Sfax, Tunisia	1.61	59.9	2.61	0.1587	0.0373	4.25
73.5	40	Sardinia	1.52	58.0	2.55	0.1487	0.0360	4.13
68.5	45	La Spezia, Italy	1.41	55.7	2.47	0.1359	0.0345	3.94
63.5	50	Schweinfurt, Germany	1.28	52.7	2.37	0.1208	0.0325	3.72
60	**53.5**	**Hamburg, Germany**	**1.18**	**50.2**	**2.30**	**0.1094**	**0.0309**	**3.54**
58.5	55	Århus, Denmark	1.13	49.1	2.25	0.1043	0.0302	3.45
53.5	60	Oslo, Norway	0.97	45.0	2.11	0.0870	0.0275	3.16
48.5	65	Trondheim, Norway	0.80	40.5	1.94	0.0697	0.0246	2.83

At high latitudes is very little UV-B radiation in solar light

Hamburg (~53.5° north latitude) on 21st June, at midday (solar elevation angle ~ 60°)

- **UV-B/UV-A [%] 2.30**
- **E(<320)/E(>320) 3.54**

Remark: June 21st Day of sun protection

12.6 Artificial UV Radiation Sources

Lamp types

Hg discharge lamps

• Low-pressure	185, 254 nm
• Medium pressure + filter	200 - 400 nm
• Low-pressure + phosphor	200 - 400 nm

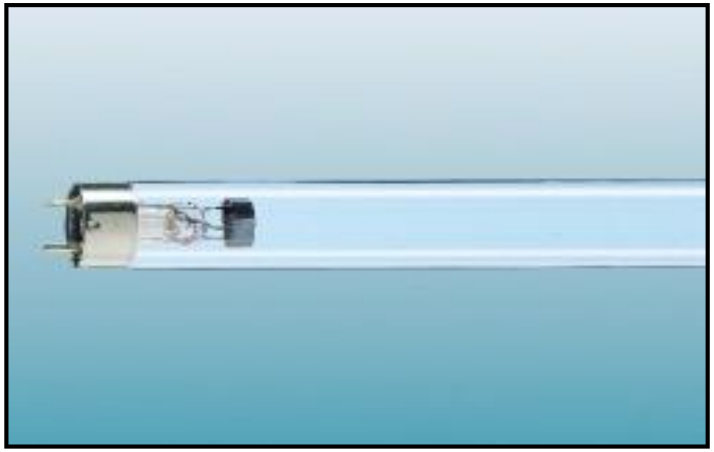
Excimer lamps

• Xe_2*	172 nm
• KrCl*	222 nm
• XeBr*	282 nm
• XeCl*	308 nm
• Xe_2* + phosphor	180 - 400 nm

LEDs and laser diodes

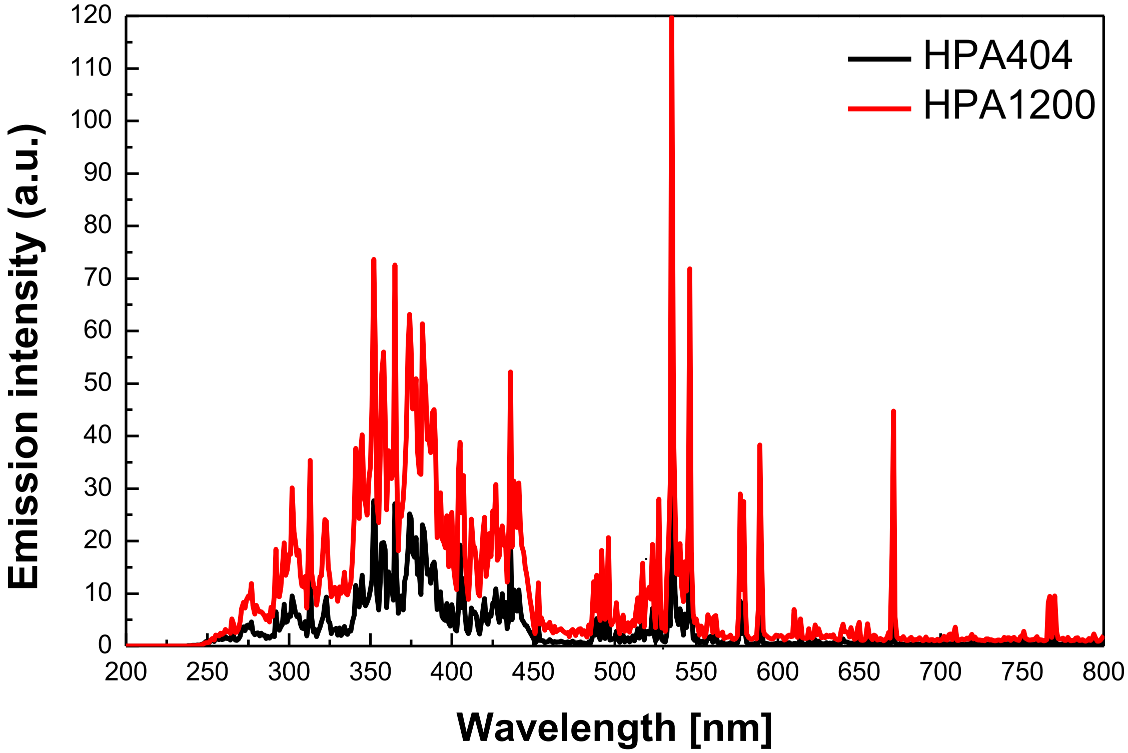
• (Al,Ga)N LEDs	210 – 365 nm
• (In,Ga)N LEDs	365 – 400 nm

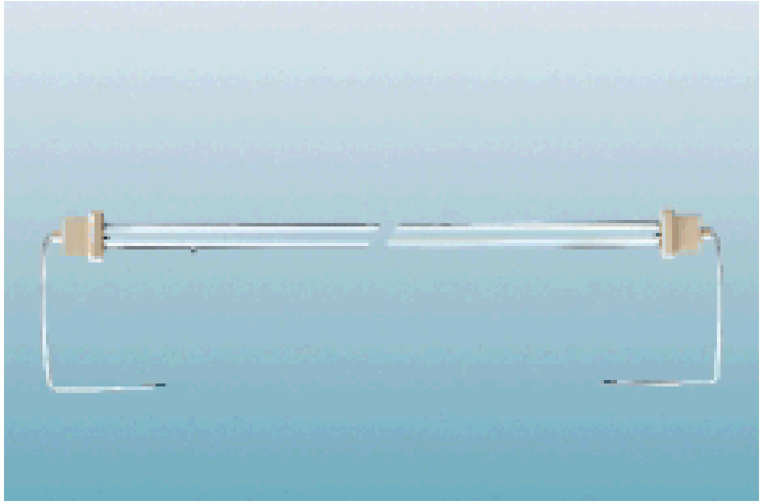
UV-C emitting Hg discharge lamp



12.6 Artificial UV Radiation Sources

Medium pressure mercury lamps



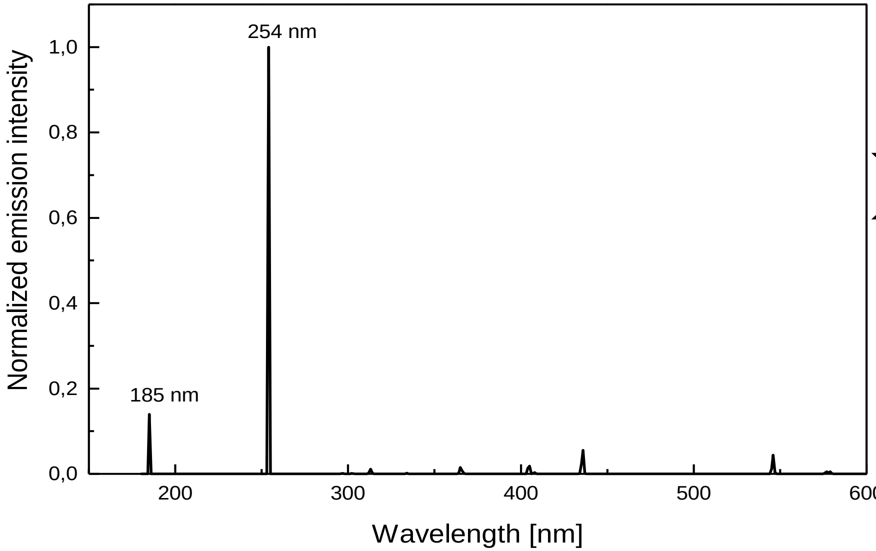


- **Lamp glass and filter: No emission below 250 nm!**
- **High UV-B percentage ~ 10% ⇒ Face tanner**

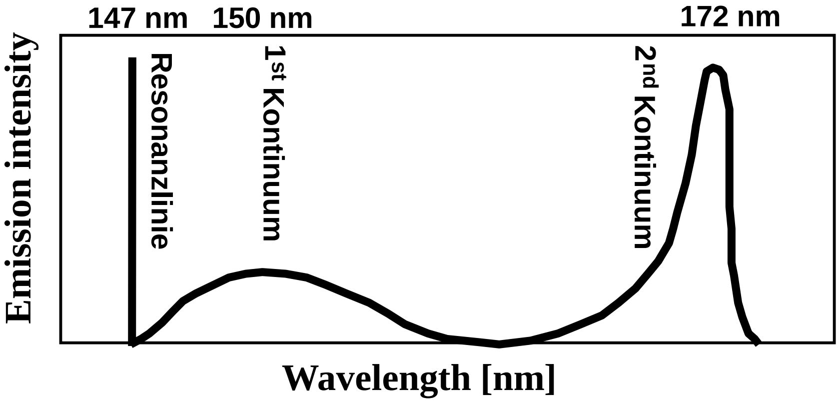
12.6 Artificial UV Radiation Sources

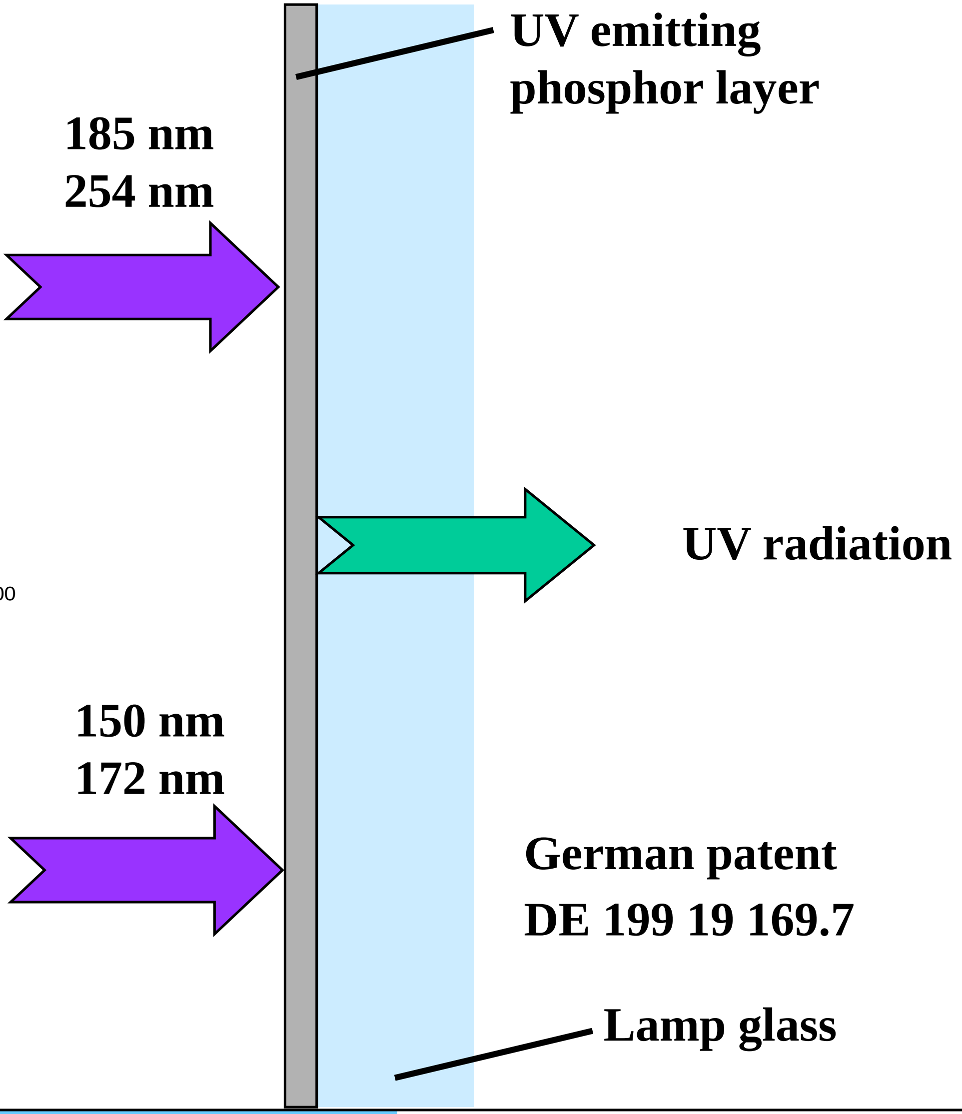
Fluorescent lamps

Low-pressure mercury discharge



Xe_2*-excimer discharge



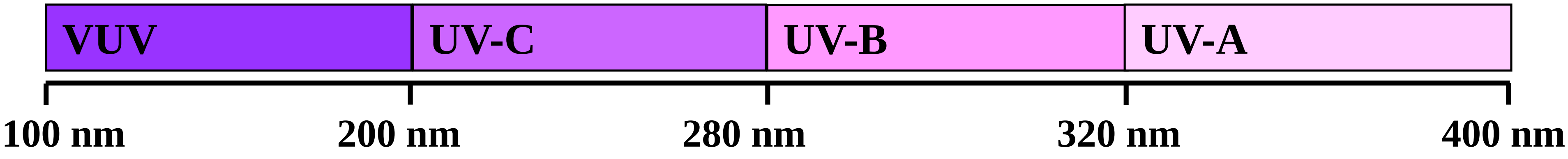


German patent

DE 199 19 169.7

12.7 UV-Phosphors

Overview: Inorganic hosts and activator ions



VUV | UV-C | UV-B | UV-A

100 nm | 200 nm | 280 nm | 320 nm | 400 nm

Hosts

Fluoride   Phosphate   Borate   Silicate   Aluminate

Activator ions

Nd^{3+}

Tl^{+}, Pb^{2+}, Pr^{3+}, Bi^{3+}

Gd^{3+}, Bi^{3+}, Pr^{3+}, Ce^{3+}

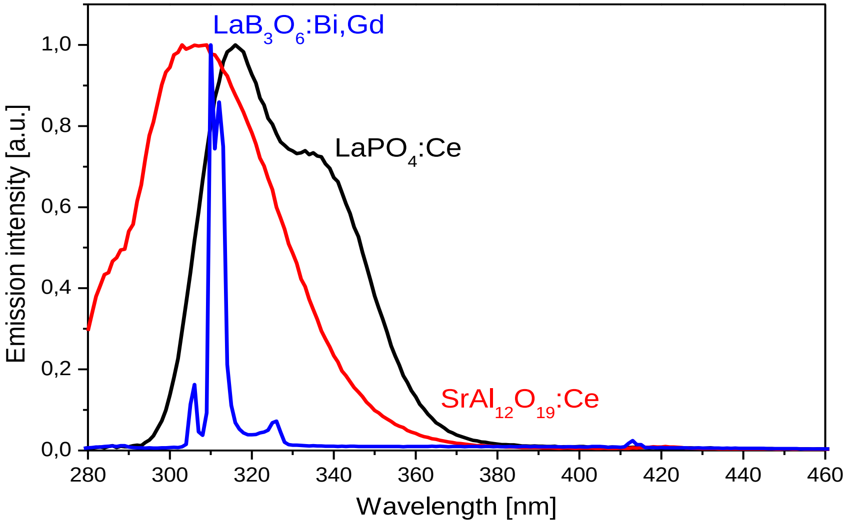
Tm^{3+}, Pb^{2+}, Ce^{3+}, Eu^{2+}

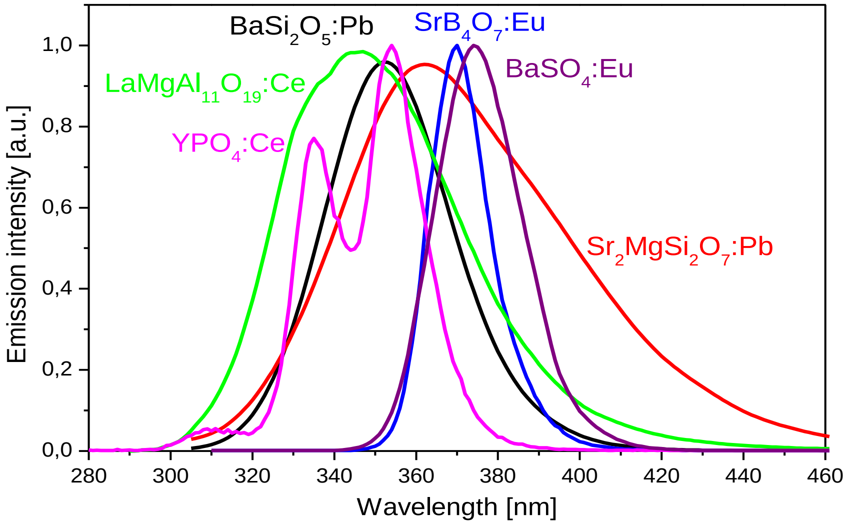
12.7 UV-Phosphors

Commercial phosphors for UV light sources on the basis of a low-pressure mercury discharge

$SrAl_{12}O_{19}:Ce^{3+}$	305 nm
$LaB_3O_6:Bi^{3+},Gd^{3+}$	311 nm
$LaPO_4:Ce^{3+}$	320 nm
$LaMgAl_{11}O_{19}:Ce^{3+}$	340 nm
$(Y,Gd)PO_4:Ce^{3+}$	335, 355 nm
$BaSi_2O_5:Pb^{2+}$	350 nm
$Sr_2MgSi_2O_7:Pb^{2+}$	365 nm
$SrB_4O_7:Eu^{2+}$	370 nm
$BaSO_4:Eu^{2+}$	375 nm

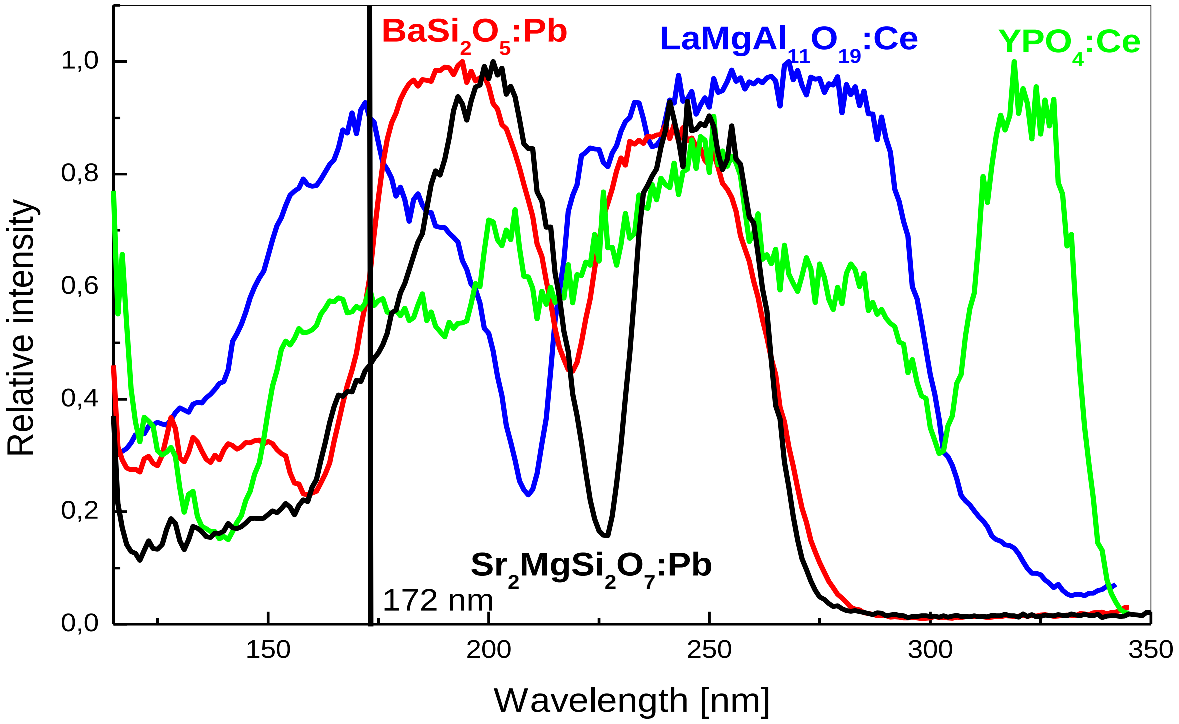
Activators: Ce^{3+}, Gd^{3+}, Pb^{2+}, Eu^{2+}





12.7 UV-Phosphors

UV and VUV efficiency of UV-A phosphors (Ce^{3+} and Pb^{2+} activated)



254 nm efficiency : $LaMgAl_{11}O_{19}$:Ce ~ YPO_4:Ce ~ $BaSi_2O_5$:Pb ~ $Sr_2MgSi_2O_7$:Pb

172 nm efficiency : $LaMgAl_{11}O_{19}$:Ce > YPO_4:Ce ~ $BaSi_2O_5$:Pb > $Sr_2MgSi_2O_7$:Pb

12.8 Tanning Lamps

Historical development

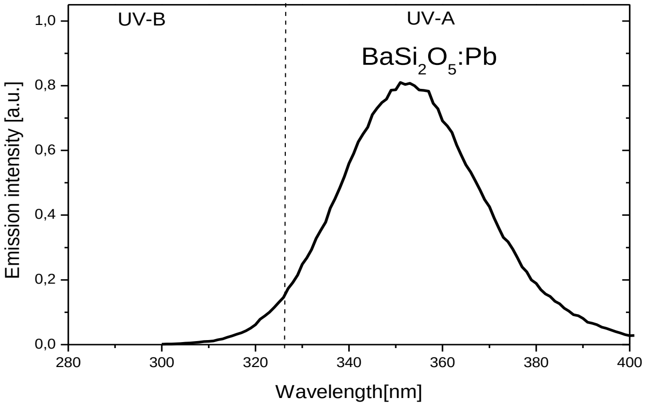
60s and early 70ties	Hard UV radiation sources (UV-C!) "sunlamps"
the mid 70ties	Hard UV radiation damages the DNA TL lamps with UV-A fluorescent
late 70ties	TL lamps with enhanced UV-A fluorescent
80ties	Tanning with UV-A radiation is safe TL lamps with UV-fluorescent compounds High-pressure mercury lamp with filter
early 90ties	UV-B/UV-A balanced ratio is favorable Lamps with glass with high UV transparency (and UV-B fluorescent)
late 90ties	Optimal are radiation sources with daylight UV-spectrum UV-B/UV-A phosphor mixtures
Since ~ 2000	Mainly UV-A phosphors

12.8 Tanning Lamps

Fluorescent lamps - Historical development

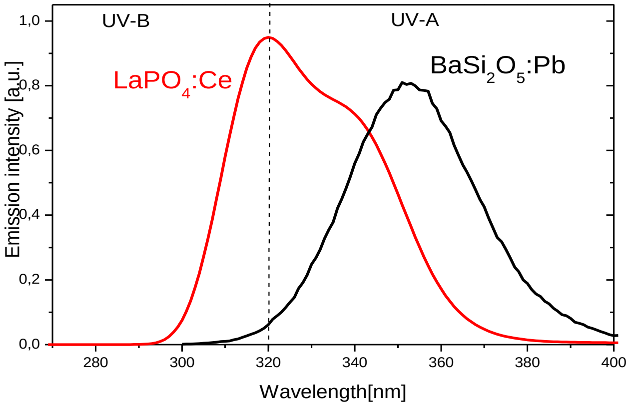
1st Generation

$BaSi_2O_5$:Pb
or $Sr_2MgSi_2O_7$:Pb



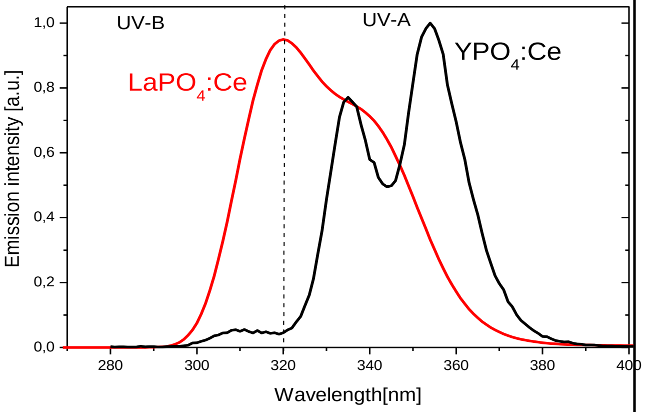
2nd Generation

$BaSi_2O_5$:Pb
+ $LaPO_4$:Ce



3rd Generation

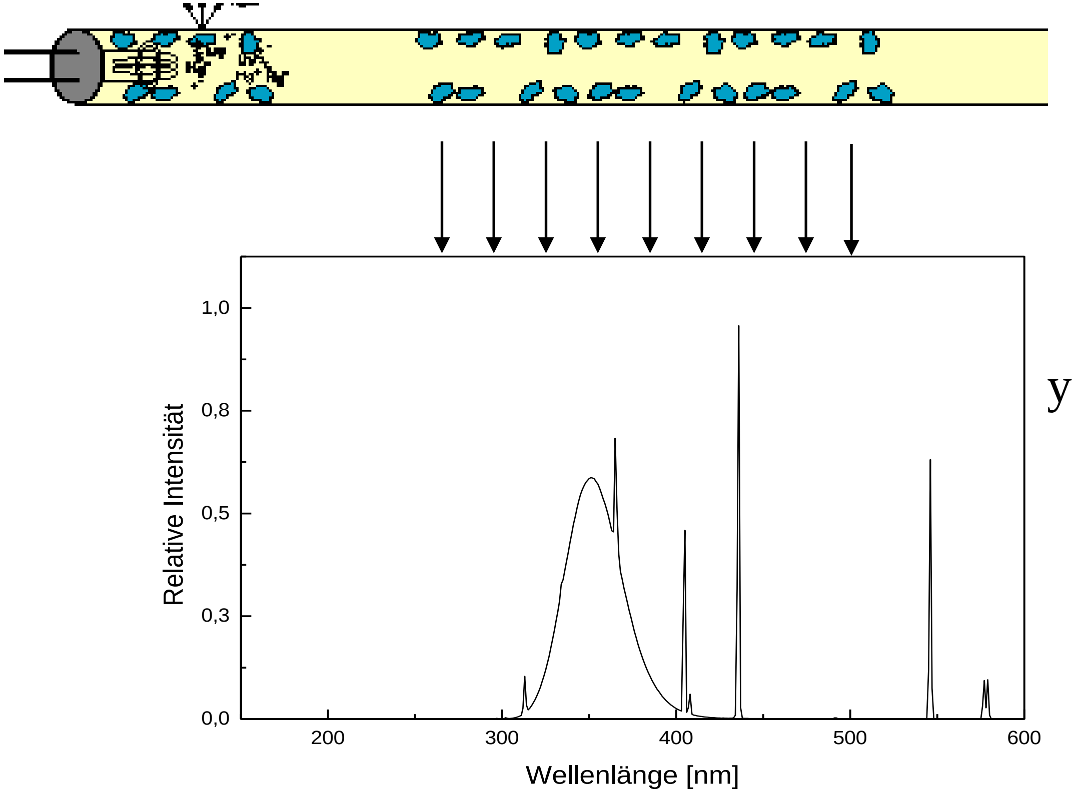
YPO_4:Ce
+ $LaPO_4$:Ce

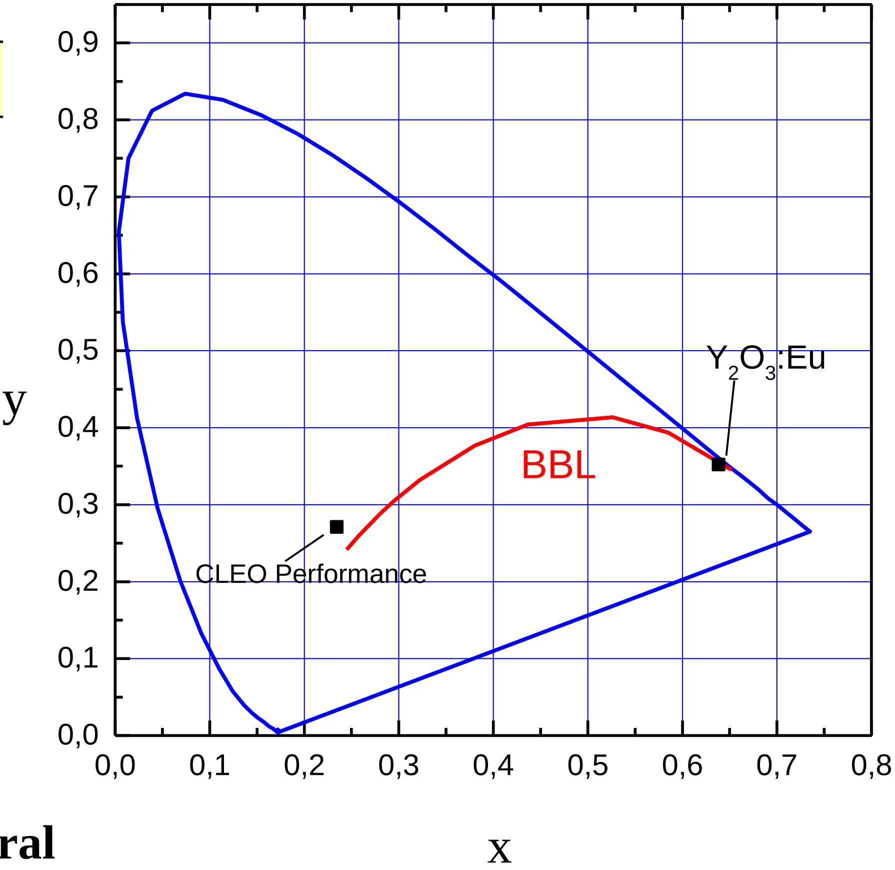


The stability of Pb^{2+} phosphors limits the lifetime of tanning lamps to about 1000 h, thus they were widely replaced by Ce^{3+} phosphors (also RoHS driven)

12.8 Tanning Lamps

Fluorescent lamps – Spectra & color point





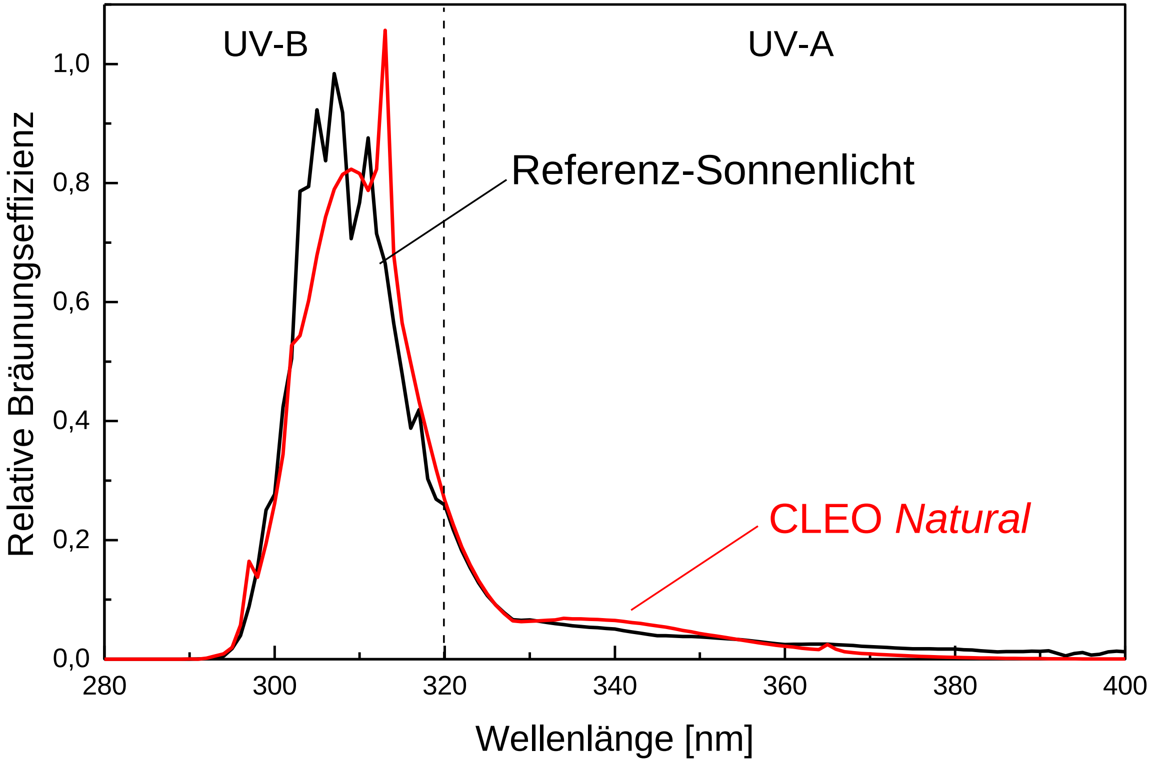
Due to the presence of Hg lines in the visible spectral range tanning lamps emit blue light

⇒ Conversion into a white light spectrum by adding a red-emitting phosphor, such as Y_2O_3:Eu

12.8 Tanning Lamps

Fluorescent light sources with daylight erythema spectrum

⇒ **UV-A + UV-B phosphor, e.g. $LaPO_4$:Ce + $BaSi_2O_5$:Pb**



12.9 Psoriasis Lamps

Treatment of skin diseases

Psoriasis, vitiligo, atopic dermatitis and other skin diseases can be treated with UV-B radiation

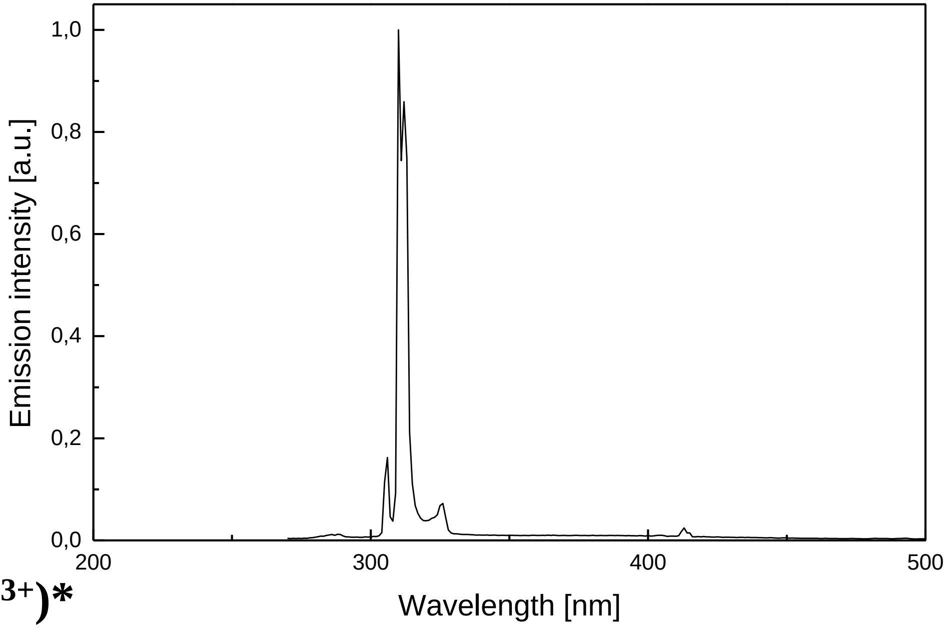
Psoriasis lamps

Low-pressure mercury lamps
+ UV-B phosphor

Standard phosphor

$LaB_3O_6:Bi^{3+},Gd^{3+}$
UV-B line emitter!

Emission spectrum of LaB_3O_6:Bi,Gd (254 nm excitation)

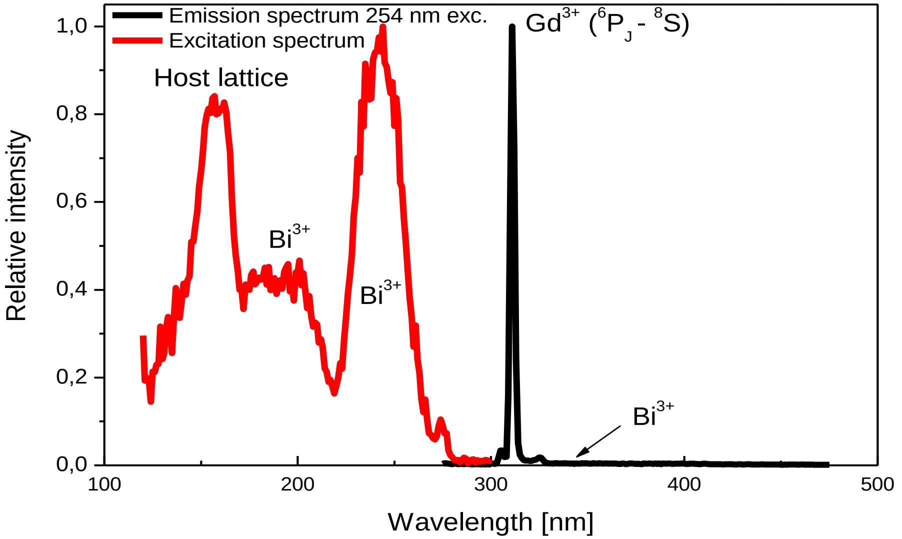


Excitation	$Bi^{3+} \rightarrow (Bi^{3+})^*$
Energy transfer	$(Bi^{3+})^* + Gd^{3+} \rightarrow Bi^{3+} + (Gd^{3+})^*$
Emission	$(Gd^{3+})^* \rightarrow Gd^{3+}$ + 311 nm ($^6P_{7/2} \rightarrow {}^8S$)

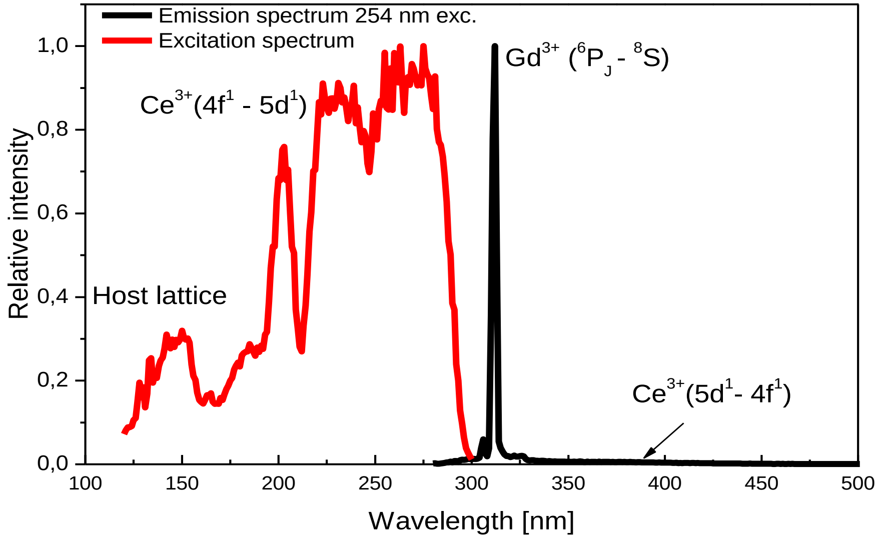
12.9 Psoriasis Lamps

Phosphors for UV-B fluorescent lamps

Standard $LaB_3O_6:Bi^{3+},Gd^{3+}$ as UV-B emitter



Alternative material $LaMgAl_{11}O_{19}:Gd^{3+}$ Sensitization is required ⇒ Ce^{3+} or Pr^{3+}



Problem: Photostability of Bi^{3+}

Solution: Use Ce^{3+} (or Pr^{3+}) as a photosensitizer

⇒ Small splitting of the 5d-orbitals of Ce^{3+} is required (e.g. in phosphates)

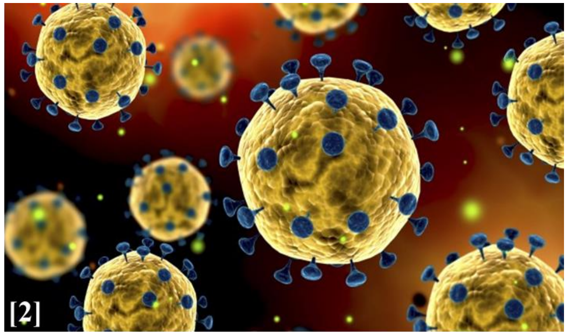
⇒ Host lattices with high coordination number of trivalent lanthanide ions

12.10 Radiation Sources for Disinfection Purposes

Motivation: Dawn of the post-antibiotic age

Period	Virus/ -type	Spread	Remarks
1917 - 1920	Spanish flu	Worldwide	Death toll > $1 \cdot 10^8$
2002 - 2003	SARS-CoV-1	Worldwide	
since 2004	Marburg	Angola and Uganda	Aerosols play a minor role, but are not insignificant
2004 - 2016	A/H5N1	Worldwide	Aerosols hardly play a role, but transmission by aerosol droplets is possible
2009 - 2010	H1N1	Worldwide	
2019 - 2023	SARS-CoV-2	Worldwide	Death toll by 02/23~ $6.8 \cdot 10^6$ [3]
Yearly	Influenza	Worldwide	Estimated 290,000 to 645,000 people die each year [1]

Viruses = Volatile particles often spread by aerosols


[2]

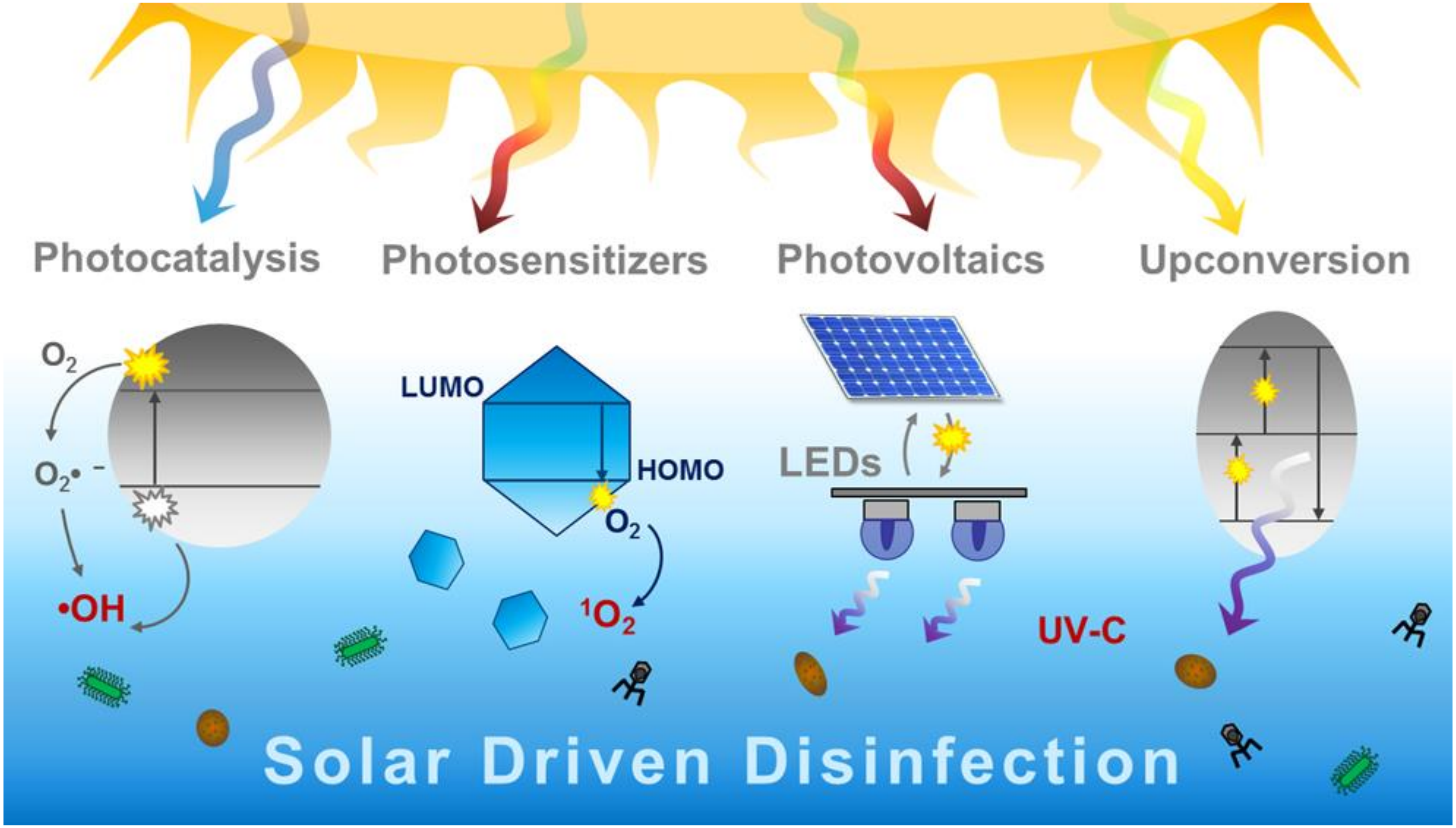
Lit.:

[1] A. Danielle Iuliano et al., Estimates of global seasonal influenza-associated respiratory mortality: A modelling study, The Lancet, Volume 391, Issue 10127, P1285-1300, March 31, 2018 https://doi.org/10.1016/S0140-6736(17)33293- [2] Corona-Update: Wie weit ist die Forschung? DAZ.online, 12.03.2020

[3] Worldometer: https://www.worldometers.info/coronavirus/

12.10 Radiation Sources for Disinfection Purposes

Solar radiation to disinfect water, air, and surfaces



TiO_2 / Titanates **W/Mo Cluster*** **(Al,Ga)N LEDs** **Pr^{3+} up-converter**

***Lit.: PD properties of tungsten iodide clusters, T. Jüstel, H.-J. Meyer et. al, RSC Advances 10 (2020) 22257**

12.10 Radiation Sources for Disinfection Purposes

Artificial UV sources to disinfect water, air, and surfaces

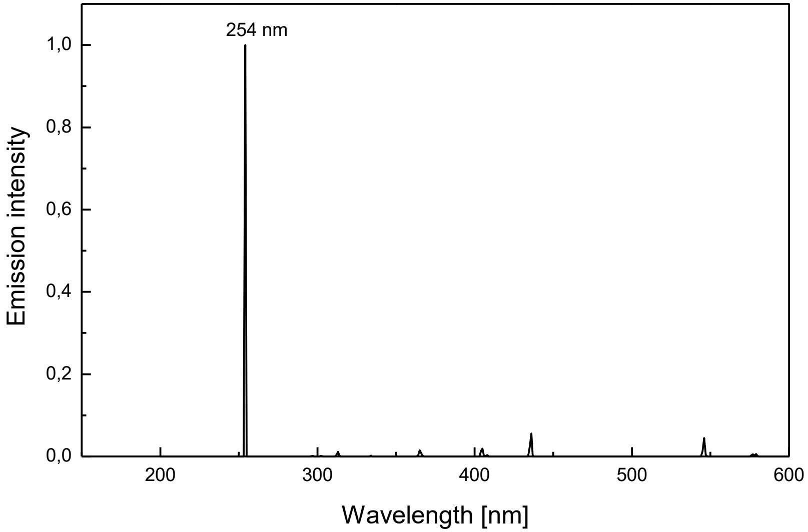
Requirements

- **Emission between 230 and 280 nm**
- **No radiation < 230 nm, otherwise photoreduction of NO_3^- to NO_2^- (in water)**
- **No radiation < 200 nm, otherwise photoreduction of H_2O into $H^\cdot + OH^\cdot$**

Suitable lamp types

- **Hg-low pressure discharge lamps**
  Line emission at 254 nm (185 nm filtered off)
- **Hg-medium pressure discharge lamps**
  Emission in the entire UV range
- **Hg-high pressure discharge lamps**
  Emission in the entire UV range

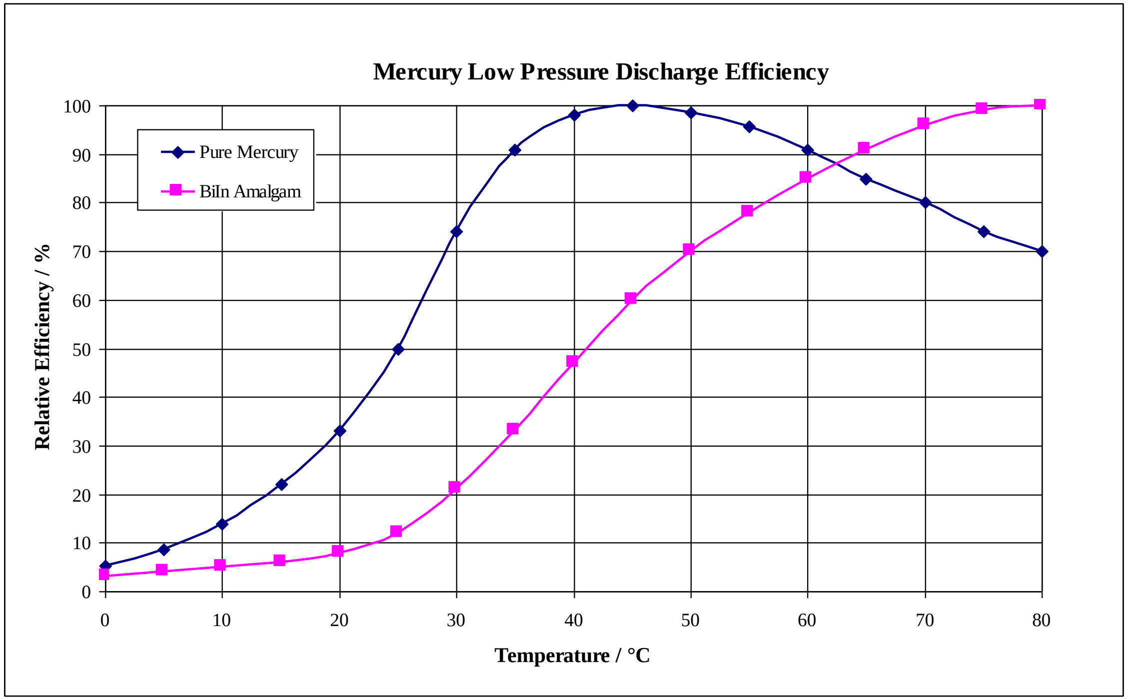
Spectrum of a Hg-low pressure discharge lamps



12.10 Radiation Sources for Disinfection Purposes

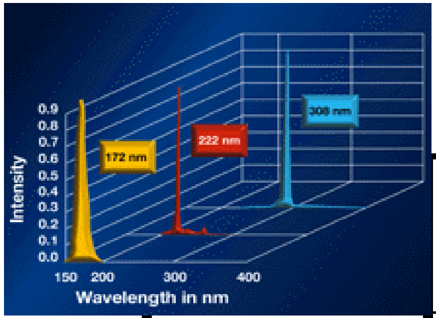
Hg discharge lamps: Drawbacks

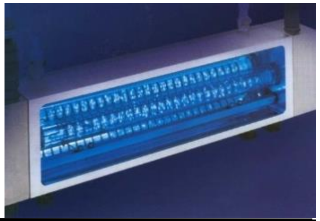
- **Environmental compatibility (Hg content) → RoHS**
- **Sensitivity to fast switching cycles**
- **Temperature dependence of the discharge efficiency and UV light output (water temperature ~ 10 – 15 °C)**
- **Cylindrical geometry**



12.10 Radiation Sources for Disinfection Purposes

Dielectric barrier excimer discharge lamps

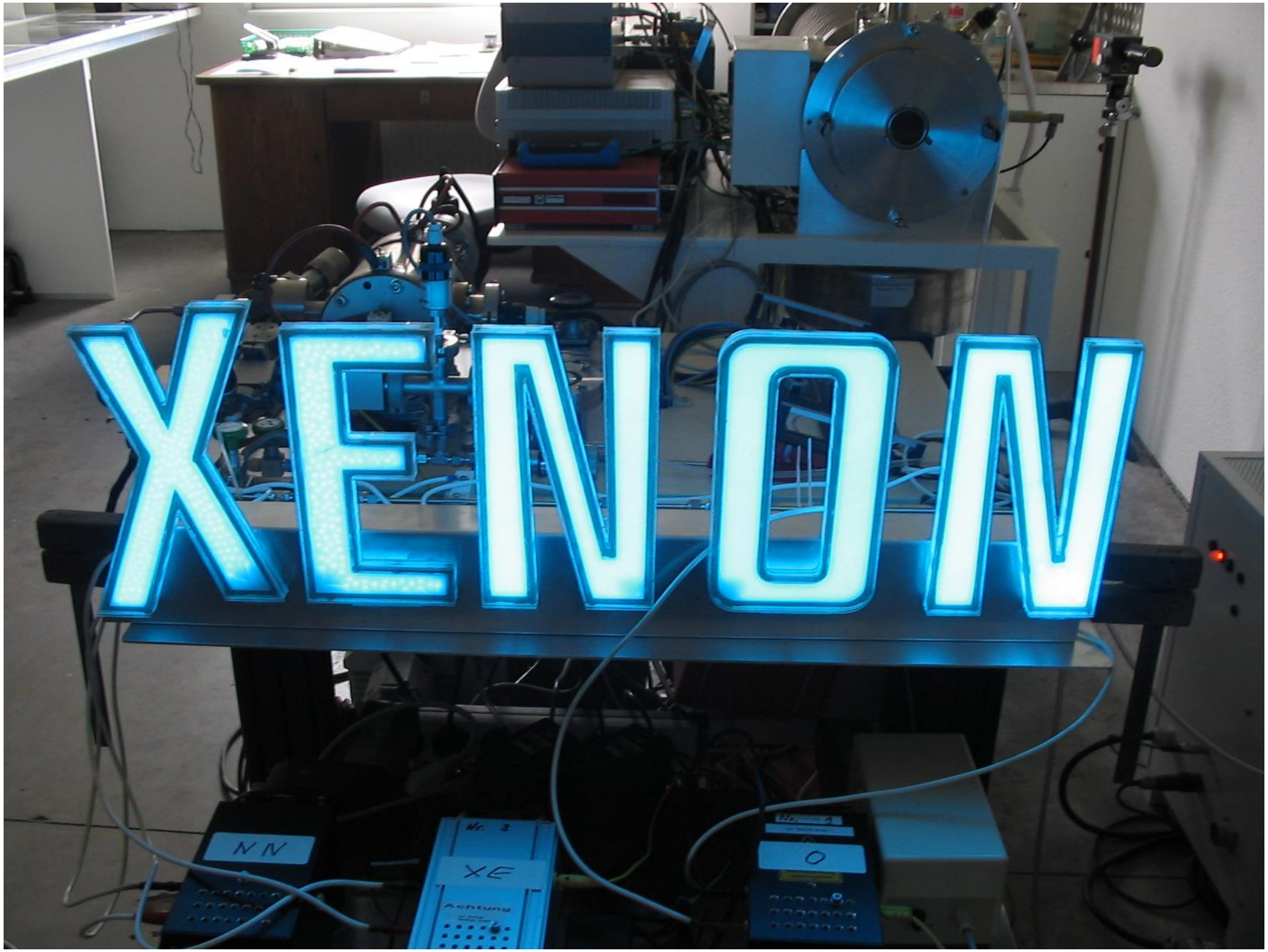




	F	Cl	Br	I	Pure noble gases
Pure halides	158 nm	258 nm	293 nm	342 nm	-
Ar	> 10% 193 nm	ca. 5% 175 nm	< 0.1% 161 nm	-	Ar^*_2 ~10% 126 nm
Kr	> 10% 248 nm	18% 222 nm	ca. 5% 207 nm	< 0.1% 185 nm	Kr^*_2 ~15% 146 nm
Xe	> 10% 351 nm	14% 308 nm	15% 282 nm	ca. 5% 253 nm	Xe^*_2 30% 172 nm

12.10 Radiation Sources for Disinfection Purposes

Dielectric barrier excimer discharge lamps (e.g. Xe_2^*)



Xe_2^* excimer lamp coated with $BaMgAl_{10}O_{17}:Eu^{2+}$ (λ_{max} = 453 nm) at Berger GmbH, Kamp-Lintfort, Germany

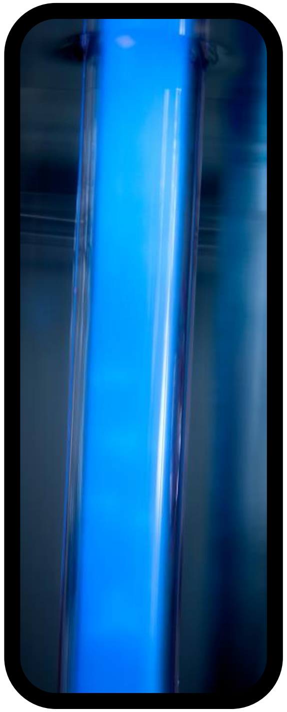
Lamp is under operation since Y2004

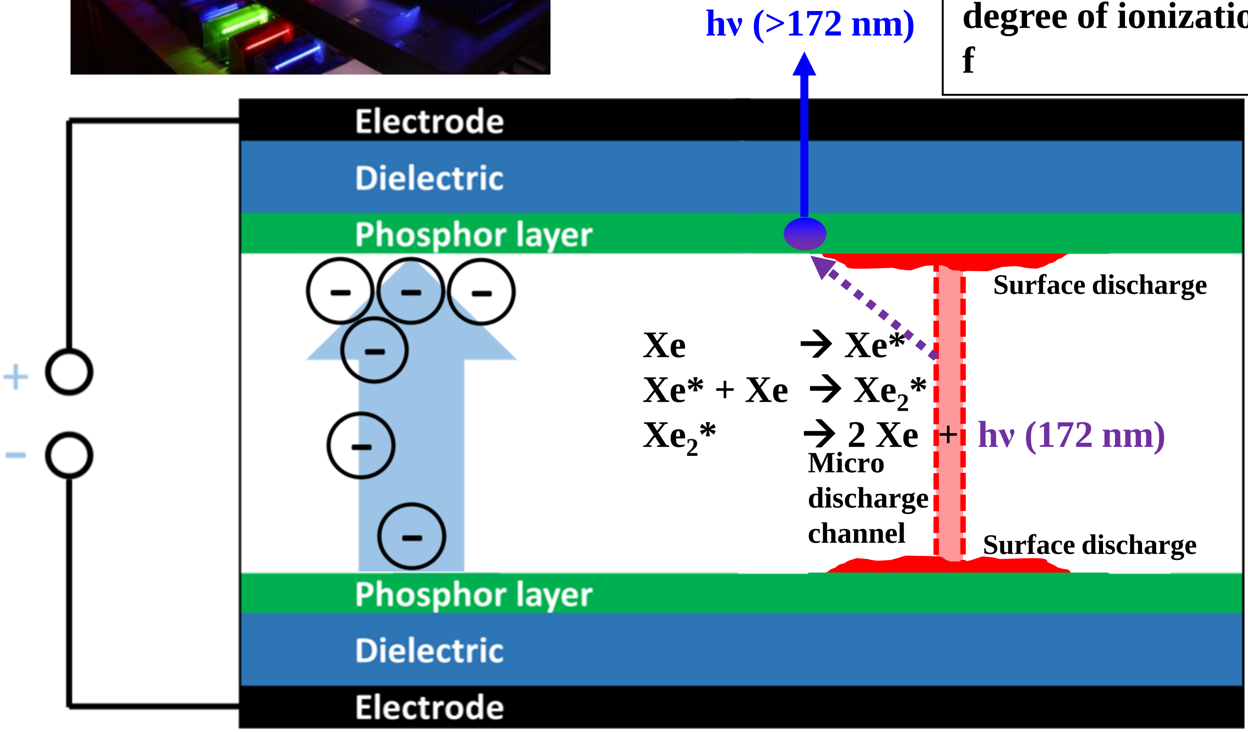
12.10 Radiation Sources for Disinfection Purposes

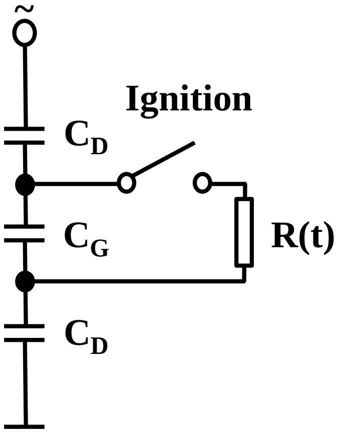
Dielectric barrier discharge lamps (Xe excimer lamps)

Characteristic parameters

t_{MD}	≈ 10 ns
pressure	0.2 - 1 bar
gap	1 mm - 1 cm
E_{gap}	0.1 – 100 kV/cm
$T_{electron}$	1 – 10 eV
$N_{electron}$	10^{14} cm^{-3}
degree of ionization	10^{-4}
f	10 - 50 kHz

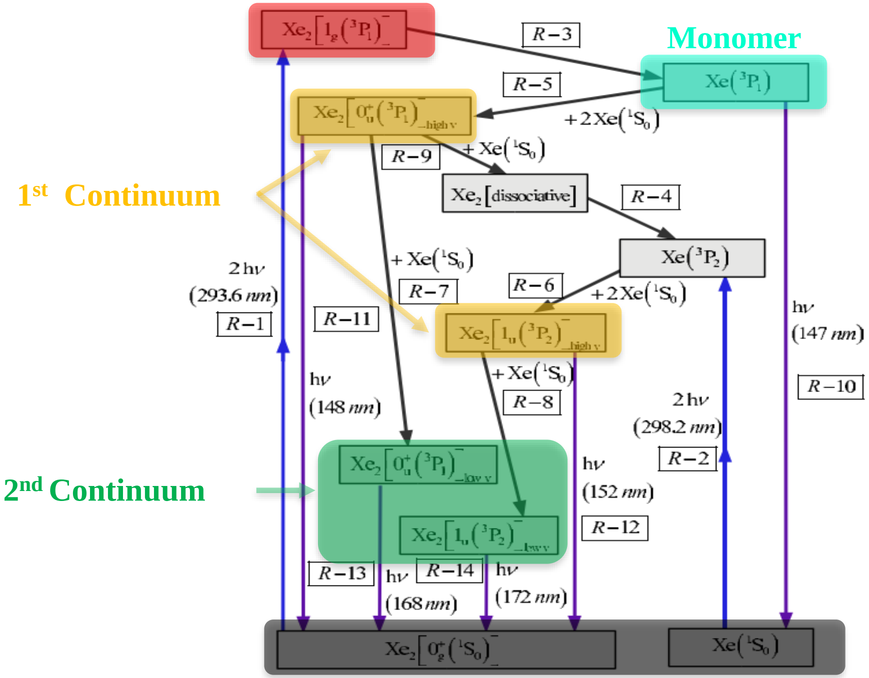






12.10 Radiation Sources for Disinfection Purposes

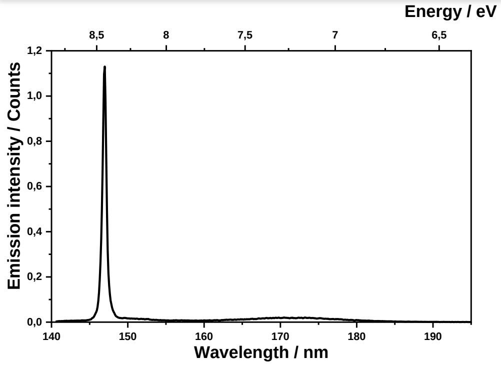
Dielectric barrier discharge lamps (Xe excimer lamps): Emission spectrum

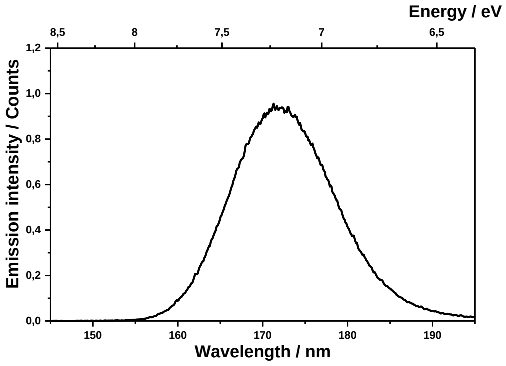


Excited monomeric Xe species:
Emits 147 nm (8.44 eV)
Xe resonance line

1st Emission continuum:
148 nm (8.38 eV)
$Xe_2[0^+_U(^3P_1)_{high\ n}] \rightarrow Xe_2[0^+_g(^1S_0)]$
152 nm (8.16 eV)
$Xe_2[1_U(^3P_2)_{high\ n}] \rightarrow Xe_2[0^+_g(^1S_0)]$

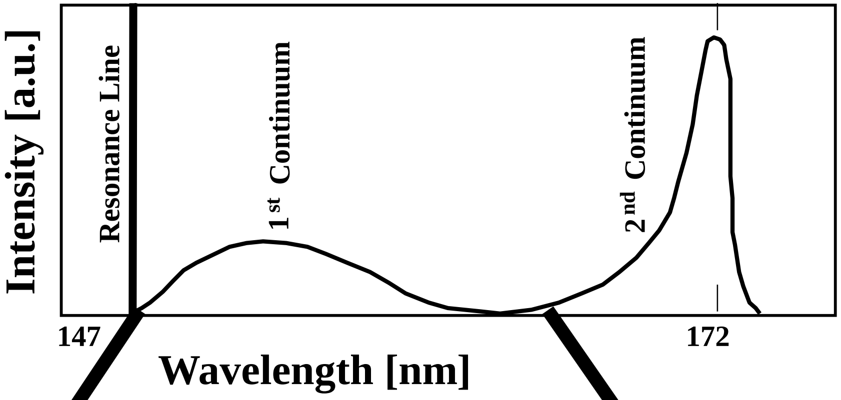
2nd Emission continuum:
186 nm (7.38 eV)
$Xe_2[0^+_U(^3P_1)_{low\ n}] \rightarrow Xe_2[0^+_g(^1S_0)]$
172 nm (7.21 eV)
$Xe_2[1_U(^3P_2)_{low\ n}] \rightarrow Xe_2[0^+_g(^1S_0)]$





12.10 Radiation Sources for Disinfection Purposes

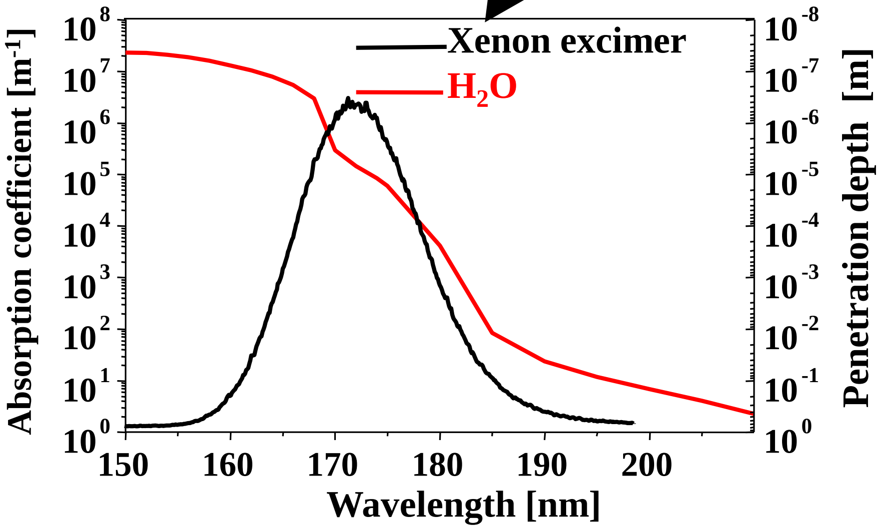
Xe excimer lamps

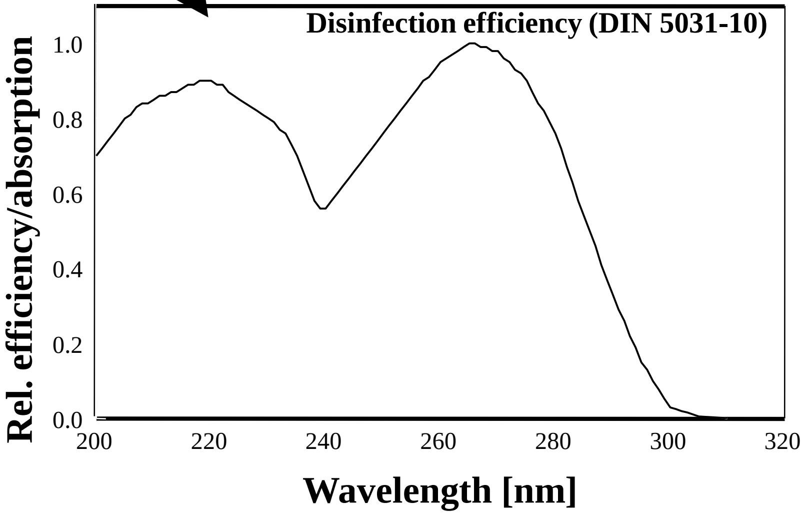


Xe_2* excimer discharge emission spectrum

convert to 190 - 200 nm

convert to 200 - 280 nm





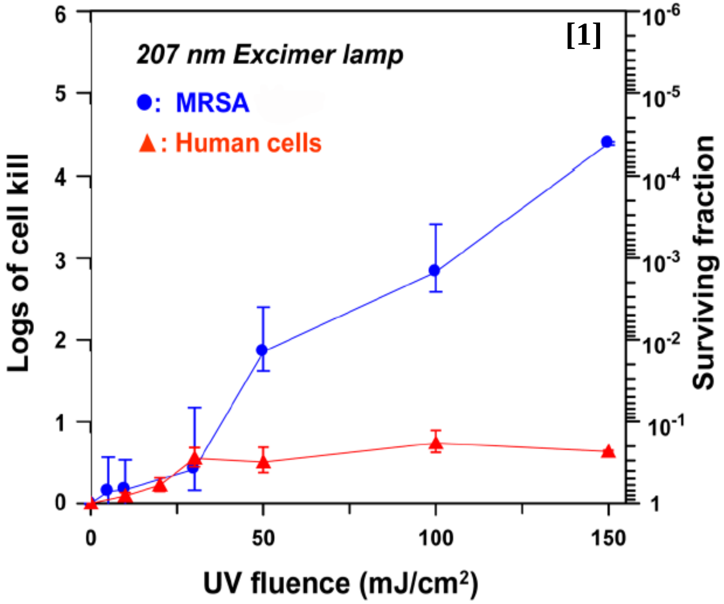
To increase the penetration depth

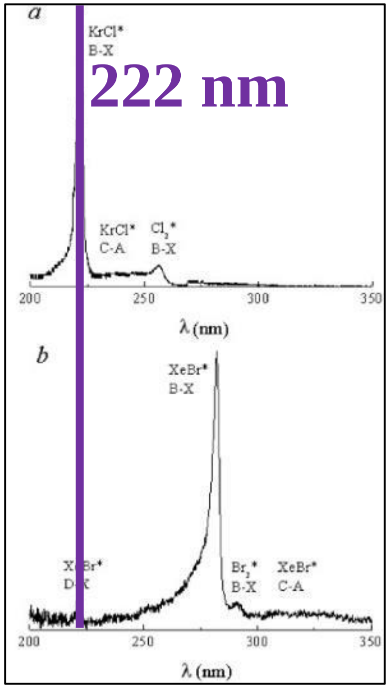
To increase the "GAC-overlap"

12.10 Radiation Sources for Disinfection Purposes

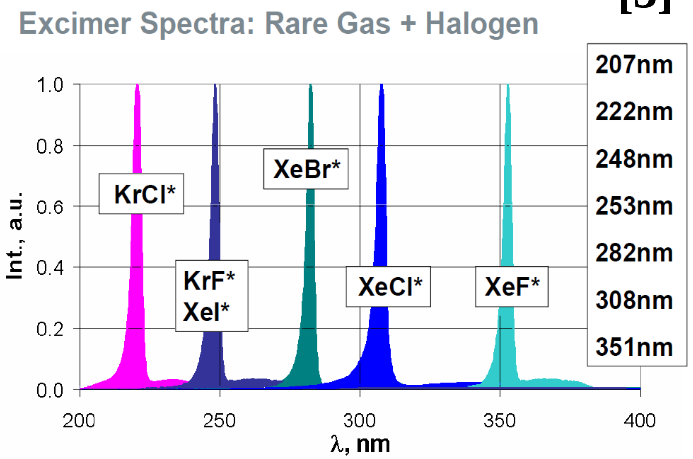
Excimer lamps for indoor air disinfection

- Recent publications on the influence of deep UV-C radiation on human skin and eye cells showed, that radiation between 207 and 222 nm efficiently kills pathogens without harm to expos. human tissues [1]
- KrBr* excimer discharge lamps (207 nm) have been successfully tested [2]
- Alternative: KrCl* excimer discharge (222 nm) shows undesired spectral features at 230 nm (Cl_2*)





[3]



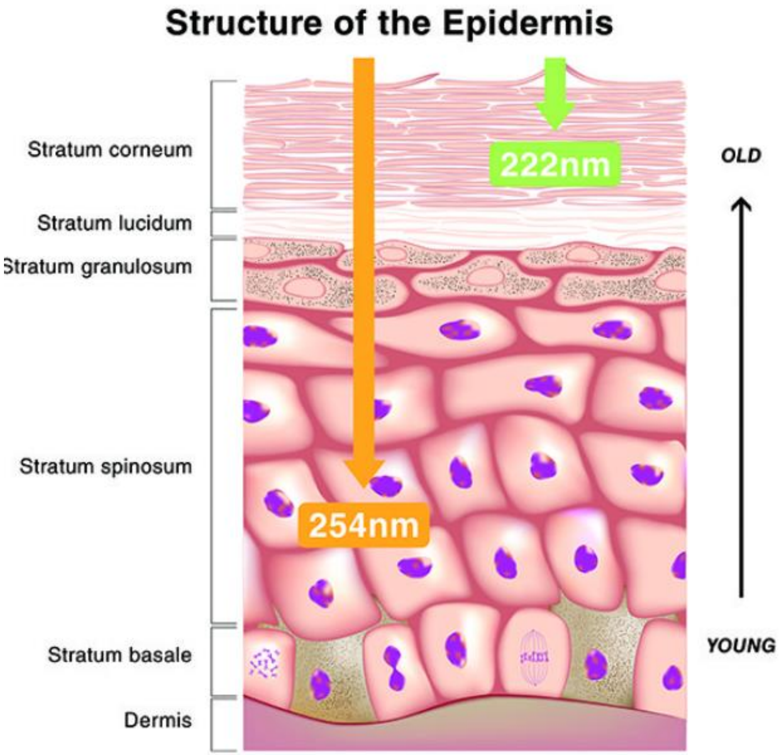
Lit.: [1] D.J. Brenner et al., Radiat. Res. 187 (2017) 483

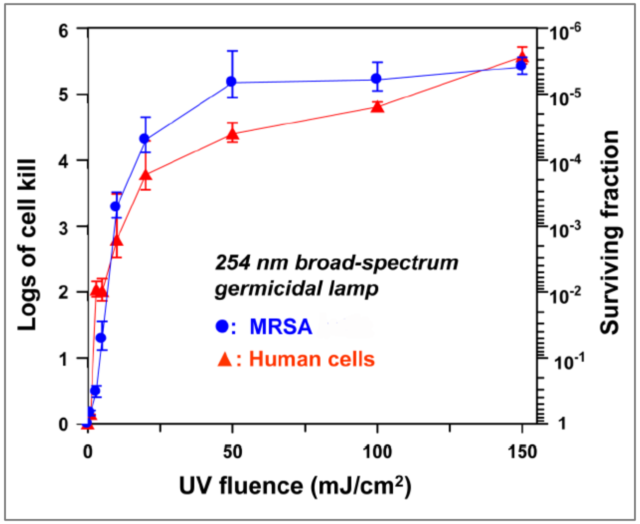
[2] M. Erofeev, V.F. Tarasenko, Quantum Electronics, 2008, 38, 401-403

[3] A. Voronov, Heraeus, Übersicht der UV-Lampen und ihre Einsatzgebiete, Darmstadt Okt. 2009

12.10 Radiation Sources for Disinfection Purposes

KrCl* Excimer lamps for indoor air disinfection





Source: Ushio Homepage

12.10 Radiation Sources for Disinfection Purposes

UV-C phosphors for Xe excimer lamps

Requirements

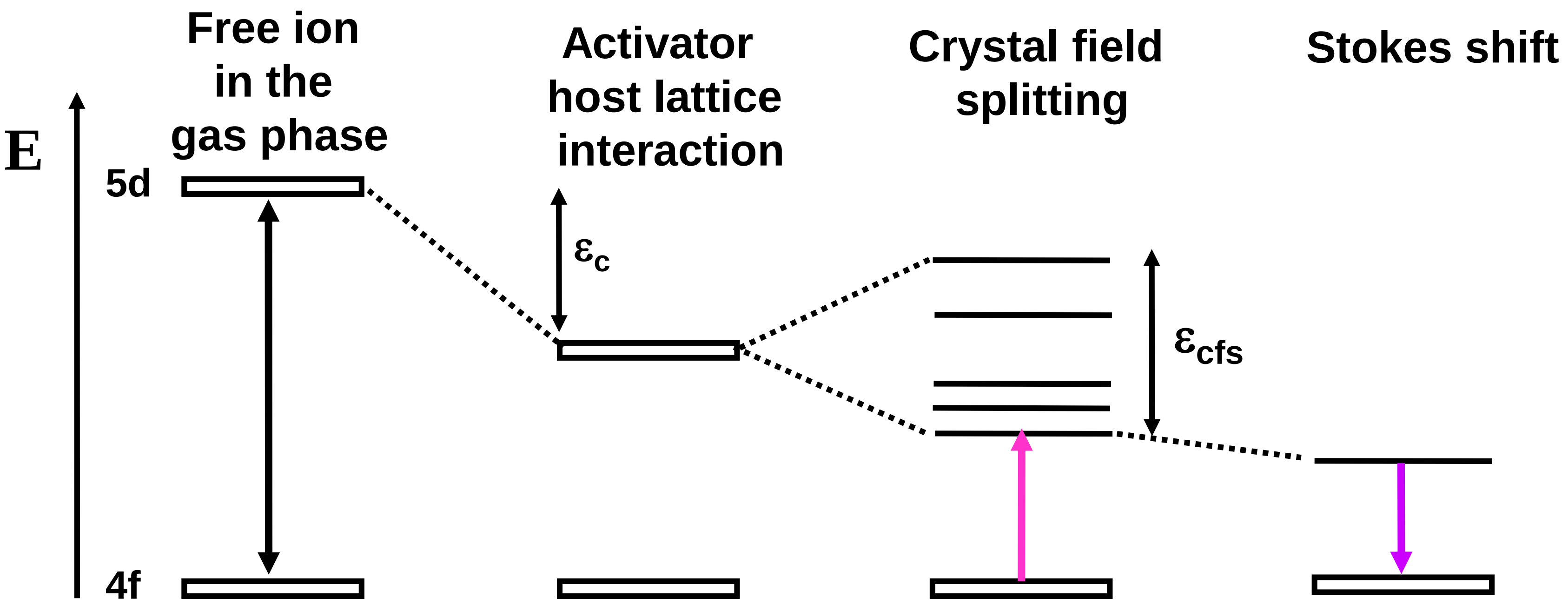
- Emission band in the region (190) 200 - 280 nm
- High light output under 172 nm excitation
- VUV high stability

⇒ Host lattice with wide band gap > 6.0 eV and redox inert activator ions

Phosphor	=	host lattice	+	activator	optical transition
		Fluoride		Tl^{+}	6s-6p
		Phosphate		Pb^{2+}	6s-6p
		Sulfate		Bi^{3+}	6s-6p
		Borat		Nd^{3+}	4f-5d
		Oxide		Pr^{3+}	4f-5d

12.10 Radiation Sources for Disinfection Purposes

UV-C phosphors - Tuning of the activator absorption and emission spectra



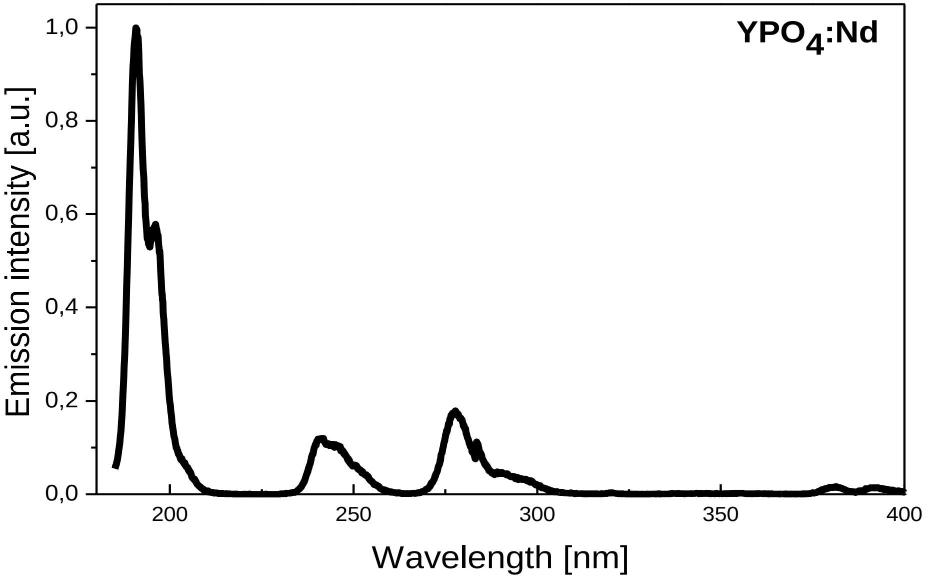
Free Ion	Eu^{2+}	Ce^{3+}	Pr^{3+}	Nd^{3+}	Gd^{3+}
$4f^{n-1}5d^1$	34000 cm^{-1}	49340 cm^{-1}	61580 cm^{-1}	72100 cm^{-1}	95200 cm^{-1}
	295 nm	203 nm	162 nm	139 nm	105 nm

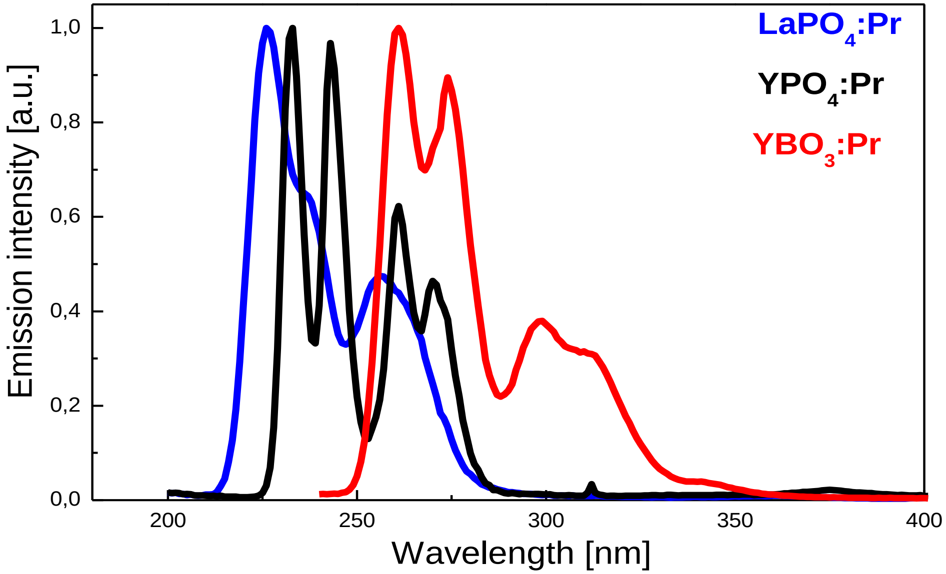
12.10 Radiation Sources for Disinfection Purposes

Nd^{3+} and Pr^{3+} phosphors

$[Xe]4f^25d^1 \rightarrow [Xe]4f^3\ (^4I_J)$

$[Xe]4f^15d^1 \rightarrow [Xe]4f^2\ (^4H_J,\ ^3F_2)$



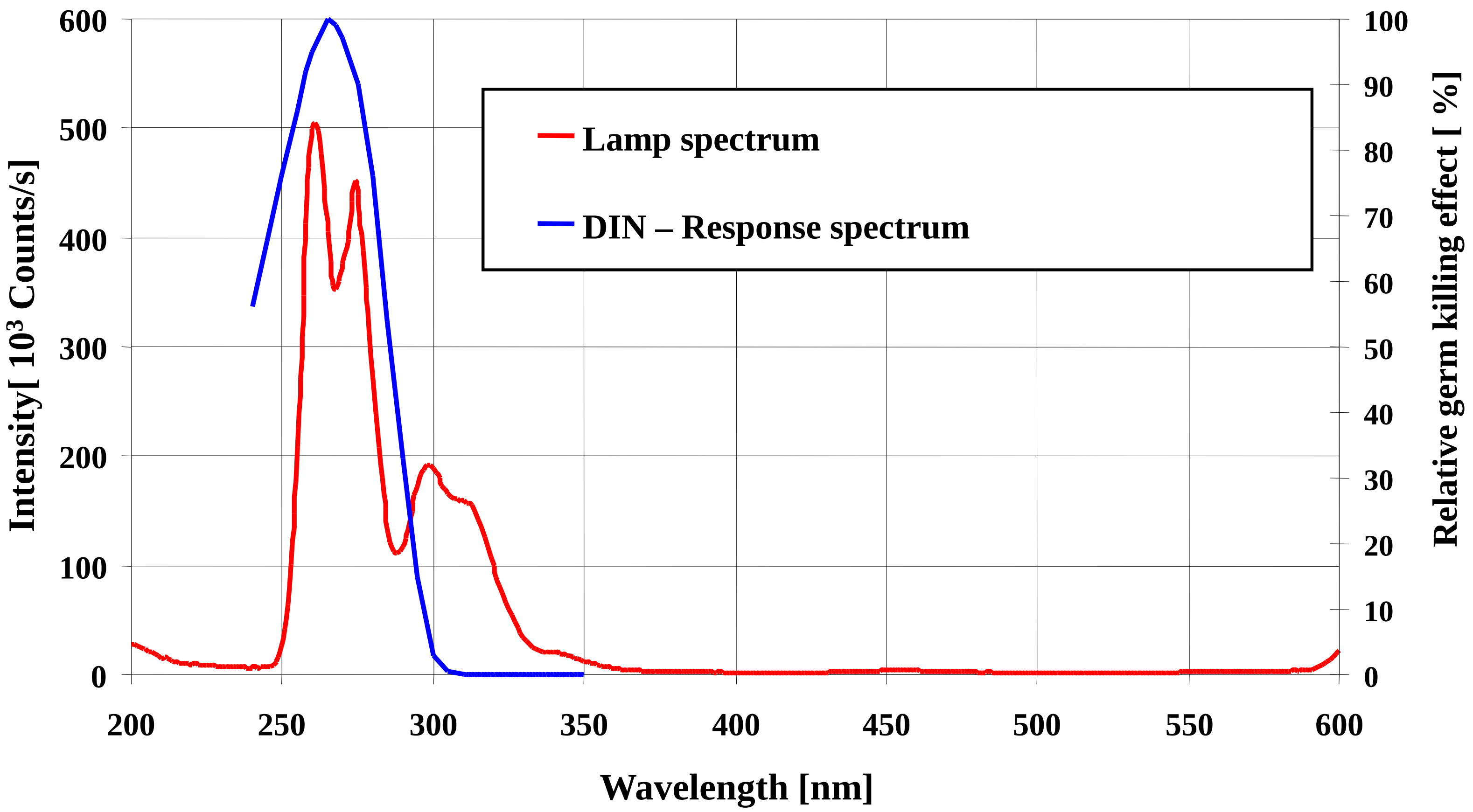


Nd^{3+} phosphors ⇒ VUV radiation sources 180 – 200 nm

Pr^{3+} phosphors ⇒ UV-C radiation sources 200 – 400 nm

12.10 Radiation Sources for Disinfection Purposes

Spectrum of a Xe excimer lamp with YBO_3:Pr as VUV to UV-C converter



12.11 UV Emitting LEDs

Chips based on (Al,Ga)N semiconductors

Semiconductor	Band gap [eV]	[nm]
GaN	3.5	365
AlN	6.2	205

Status November 2012

265 nm 70% IQE @ 25 mW

Focus on application in

• Curing	365 nm
• Tanning	350 nm
• Disinfection	265 nm
• Skin safe disinfection	222 nm

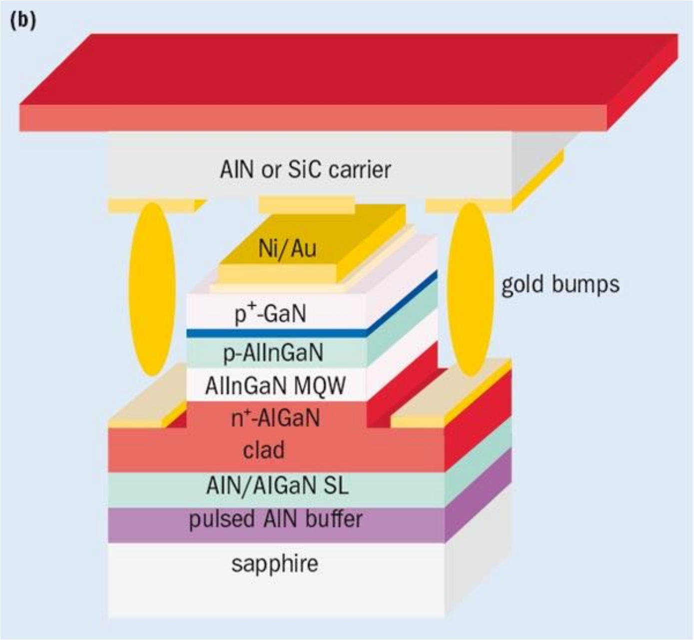
Overview on (Al,Ga)N LED applications

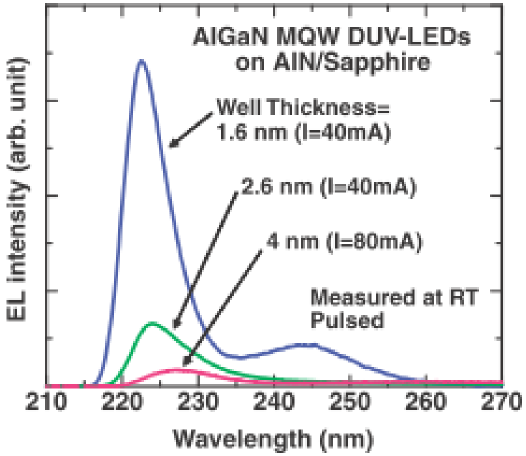
12.11 UV Emitting LEDs

UV emitting LEDs

Development / Outlook

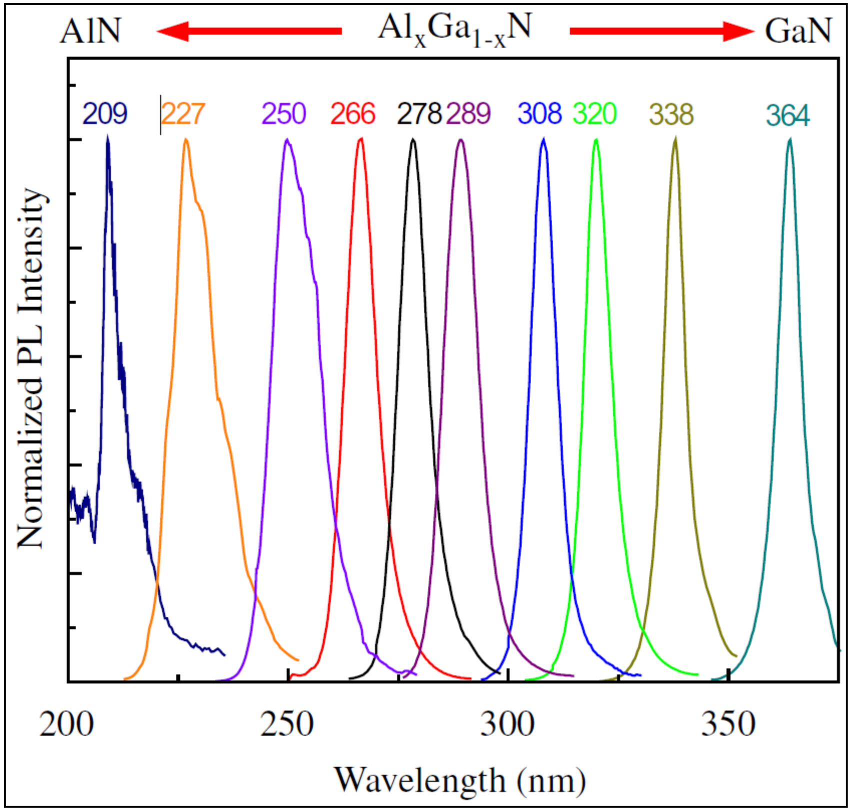
- **Heat dissipation: Output and lifetime limit**
- **DUV-LED → DUV Laser Diode: Challenging!**
- **Wavelength: Theoretical limit is 205 nm, Present experimental limit is 220 nm**
- **Fabrication issues to be solved yet: Quality + mass production**
- **Increase efficiency: Layer processing, reduce resistive losses**
- **Multiple chip packaging: 11 mW @ 280 nm**





12.11 UV Emitting LEDs

(Al,Ga)N LEDs - Band gap engineering



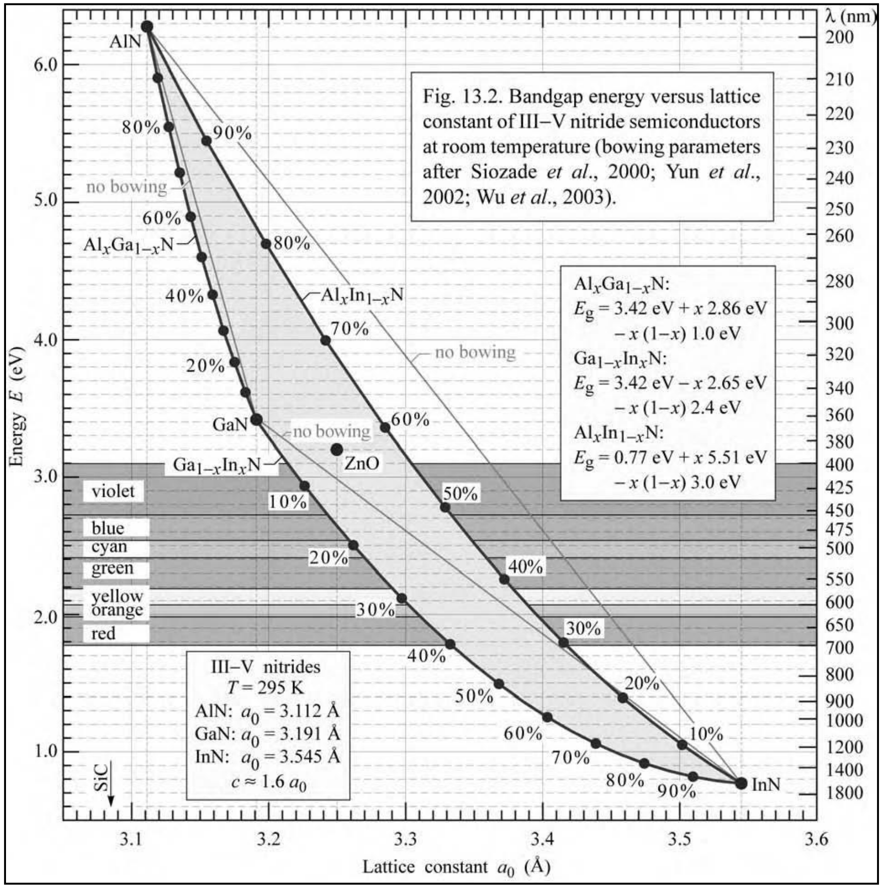


Fig. 13.2. Bandgap energy versus lattice constant of III–V nitride semiconductors at room temperature (bowing parameters after Siozade *et al.*, 2000; Yun *et al.*, 2002; Wu *et al.*, 2003).

$Al_xGa_{1-x}N$:
$E_g = 3.42\ \text{eV} + x\ 2.86\ \text{eV} - x\,(1-x)\ 1.0\ \text{eV}$
$Ga_{1-x}In_xN$:
$E_g = 3.42\ \text{eV} - x\ 2.65\ \text{eV} - x\,(1-x)\ 2.4\ \text{eV}$
$Al_xIn_{1-x}N$:
$E_g = 0.77\ \text{eV} + x\ 5.51\ \text{eV} - x\,(1-x)\ 3.0\ \text{eV}$

III–V nitrides
$T = 295$ K
AlN: $a_0 = 3.112$ Å
GaN: $a_0 = 3.191$ Å
InN: $a_0 = 3.545$ Å
$c \approx 1.6\ a_0$

PL spectra of (Al,Ga)N samples

Band gap energy – lattice constant relation

12.11 UV Emitting LEDs

(Al,Ga)N LEDs – Status Quo 2020: WPE ~ 10%, 265 nm

External Quantum Efficiency (EQE)

$$\eta_{\mathrm{EQE}} = \eta_{\mathrm{inj}} * \eta_{\mathrm{rad}} * \eta_{\mathrm{exit}} = \eta_{\mathrm{IQE}} * \eta_{\mathrm{exit}}$$

Wall Plug Efficiency (WPE)

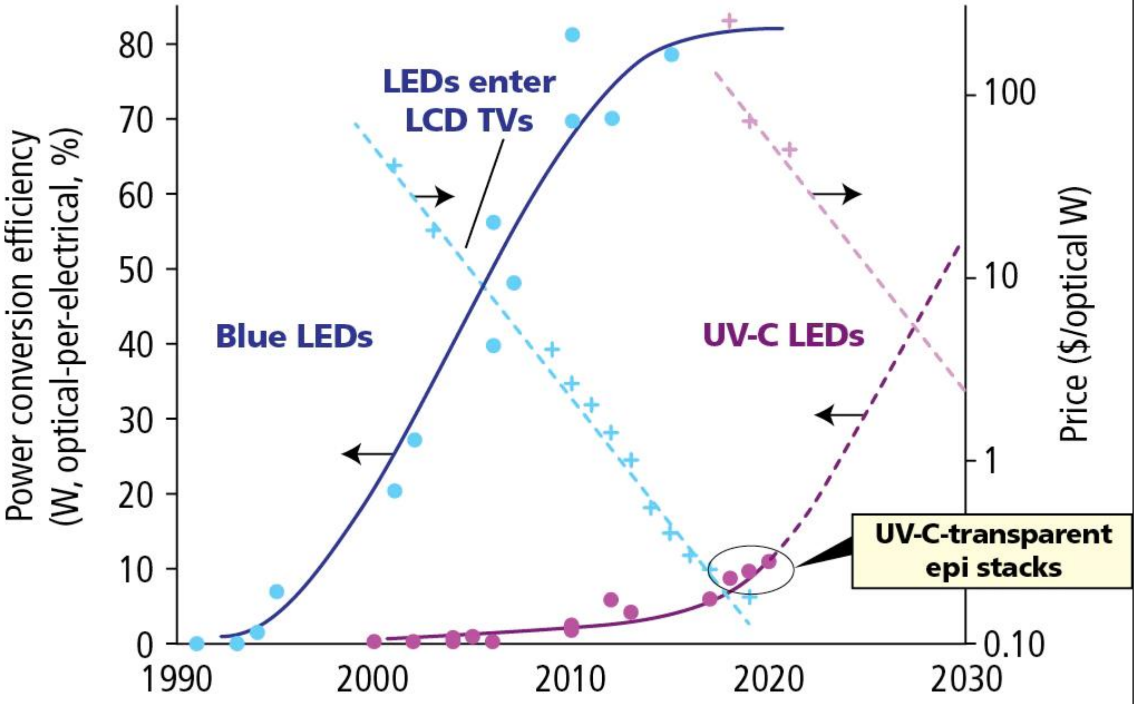
$$WPE = \frac{P_{out}}{I_{op}{*}V} = \eta_{EQE}\frac{\hbar\omega}{e{*}V} = \eta_{EQE}{}^{*}\,\eta_{electric}$$

Optical power (P_{Out})

$$P_{\mathrm{out}} = \eta_{\mathrm{EQE}}\frac{\hbar\omega}{e}I_{\mathrm{op}} = I_{\mathrm{op}} * V * \mathrm{WPE}$$

Maximum electrical power ($P_{\mathrm{el.,max}}$)

$$P_{\mathrm{el.,max}} = I_{\mathrm{op}} * V = \frac{T_{\mathrm{jmax}} - T_{\mathrm{h\alpha}}}{R_{\mathrm{th}} * (1 - WPE)}$$



Running development goals

- Internal quantum efficiency ↑
- Light outcoupling ↑
- Power density ↑
- Life time ↑

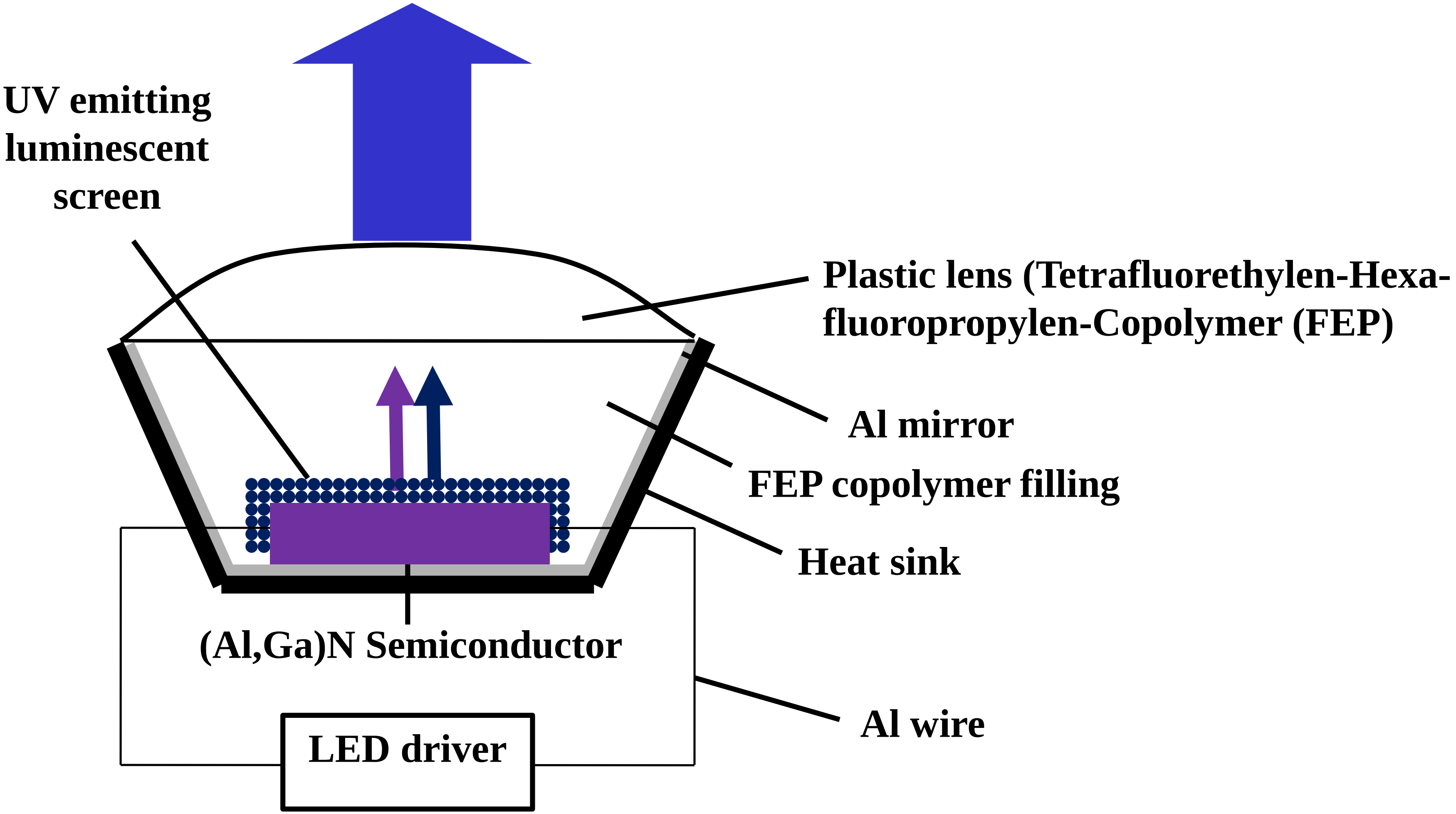
Lit.:

a) M. Kneissl et al., Nature Photonics 13 (2019) 233

b) LED Magazine, July 24th, 2020

12.11 UV Emitting LEDs

(Al,Ga)N LEDs – Phosphor Conversion



UV emitting luminescent screen

Plastic lens (Tetrafluorethylen-Hexa-fluoropropylen-Copolymer (FEP)

Al mirror

FEP copolymer filling

Heat sink

(Al,Ga)N Semiconductor

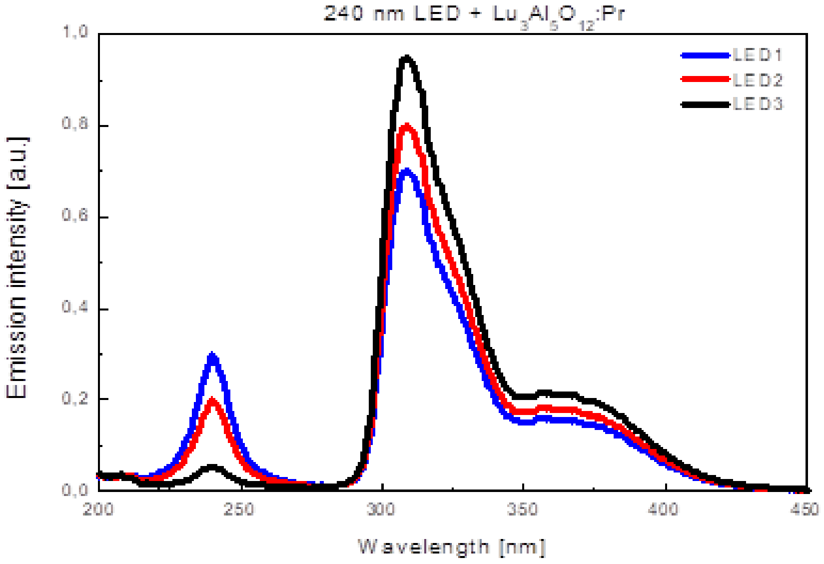
Al wire

LED driver

12.11 UV Emitting LEDs

(Al,Ga)N LEDs – Phosphor conversion to obtain broad band UV spectra

Phosphor	Peak emission wavelength of 5d-4f transition (nm)
$CaSO_4:Pr^{3+}$	218
$LaPO_4:Pr^{3+}$	225
$LuPO_4:Pr^{3+}$	233
$YPO_4:Pr^{3+}$	235
$YAlO_3:Pr^{3+}$	245
$La_2Si_2O_7:Pr^{3+}$	247
$CaLi_2SiO_4:Pr^{3+}$	253
$YBO_3:Pr^{3+}$	263
$Lu_2Si_2O_7:Pr^{3+}$	266
$Y_2Si_2O_7:Pr^{3+}$	267
$Y_2SiO_5:Pr^{3+}$	270
$Lu_2SiO_5:Pr^{3+}$	272
$Lu_3Ga_2Al_3O_{12}:Pr^{3+}$	300
$Lu_3Al_5O_{12}:Pr^{3+}$	310
$Y_3Al_5O_{12}:Pr^{3+}$	320



12.12 Summary

Standard UV radiation sources: Hg discharge lamps (LP, amalgam LP, MP, and HP)

- Very efficient and effective
- But many disadvantages in application, e.g. Hg content, bad run-up and switching behaviour, lifetime, and temperature dependence, Hg ban?

Excimer discharge lamps

- Many emission spectra available, but efficiency is low, e.g. KrCl* at 222 nm
- Xe_2^* excimer discharge is the most efficient one (172 nm)
- phosphor converted lamps offer arbitrary UV spectra between 180 and 400 nm adjustable to application demands

UV emitting LEDs

- AlN and GaN form a solid solution, which offer band gap engineering and emission peak adjustment between about 210 and 365 nm
- Main problems: n-type and p-type doping
- UV radiation flux and efficiency is still low, package degrades quickly
- LEDs are small and flexible low-voltage devices

Other technologies: Up-conversion, NLO materials, x-ray or cathode ray lamps