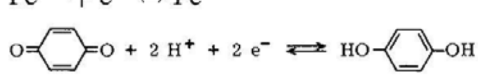
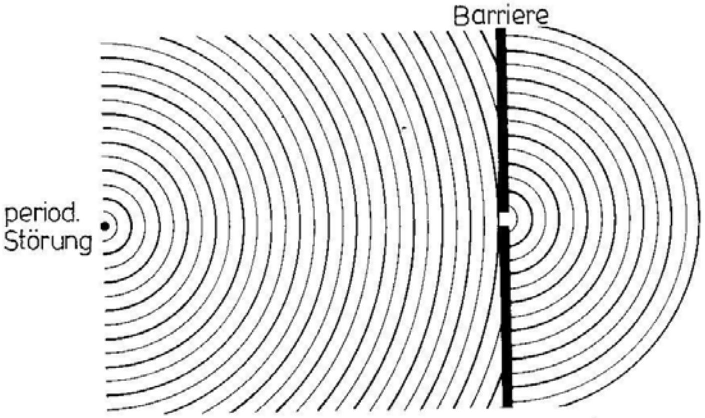
Elektrochemische Spannungsreihe

Tab. 2.8-2. Standard-Elektrodenpotentiale nach R. C. Weast (Hrsg.) Handbook of Chemistry and Physics, 60th Ed., 3. Nachdruck 1981, The Chemical Rubber Co, Boca Raton, Florida.

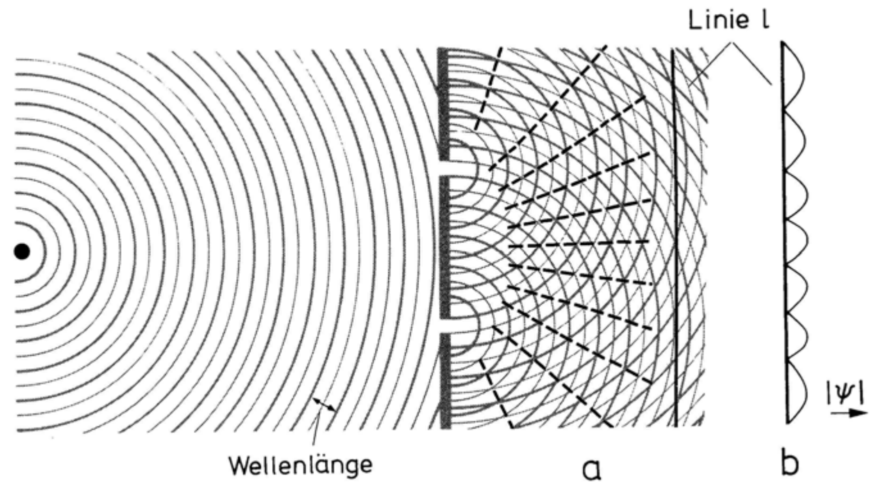
Halbzelle	Elektrodenreaktion	$\frac{E_h^0}{V}$
	Metallionenelektroden	
$Li^+ \mid Li$	$Li^+ + e^- \leftrightarrow Li$	− 3.045
$Rb^+ \mid Rb$	$Rb^+ + e^- \leftrightarrow Rb$	− 2.925
$K^+ \mid K$	$K^+ + e^- \leftrightarrow K$	− 2.924
$Cs^+ \mid Cs$	$Cs^+ + e^- \leftrightarrow Cs$	− 2.923
$Ca^{2+} \mid Ca$	$Ca^{2+} + 2e^- \leftrightarrow Ca$	− 2.76
$Na^+ \mid Na$	$Na^+ + e^- \leftrightarrow Na$	− 2.7109
$Mg^{2+} \mid Mg$	$Mg^{2+} + 2e^- \leftrightarrow Mg$	− 2.375
$Al^{3+} \mid Al$	$Al^{3+} + 3e^- \leftrightarrow Al$	− 1.66
$Zn^{2+} \mid Zn$	$Zn^{2+} + 2e^- \leftrightarrow Zn$	− 0.7628
$Fe^{2+} \mid Fe$	$Fe^{2+} + 2e^- \leftrightarrow Fe$	− 0.409
$Cd^{2+} \mid Cd$	$Cd^{2+} + 2e^- \leftrightarrow Cd$	− 0.4026
$Ni^{2+} \mid Ni$	$Ni^{2+} + 2e^- \leftrightarrow Ni$	− 0.23
$Pb^{2+} \mid Pb$	$Pb^{2+} + 2e^- \leftrightarrow Pb$	− 0.1263
$Cu^{2+} \mid Cu$	$Cu^{2+} + 2e^- \leftrightarrow Cu$	+ 0.3402
$Ag^+ \mid Ag$	$Ag^+ + e^- \leftrightarrow Ag$	+ 0.7996
$Au^+ \mid Au$	$Au^+ + e^- \leftrightarrow Au$	+ 1.68
	Gaselektroden	
$H^+ \mid H_2, Pt$	$2H^+ + 2e^- \leftrightarrow H_2$	0.00
$OH^- \mid O_2, Pt$	$O_2 + 2H_2O + 4e^- \leftrightarrow 4OH^-$	+ 0.401
$I^- \mid I_2, Pt$	$I_2 + 2e^- \leftrightarrow 2I^-$	+ 0.535
$Cl^- \mid Cl_2, Pt$	$Cl_2 + 2e^- \leftrightarrow 2Cl^-$	+ 1.3583
$F^- \mid F_2, Pt$	$F_2 + 2e^- \leftrightarrow 2F^-$	+ 2.87
	Elektroden 2. Art	
$SO_4^{2-} \mid PbSO_4 \mid Pb$	$PbSO_4 + 2e^- \leftrightarrow Pb + SO_4^{2-}$	− 0.356
$I^- \mid AgI \mid Ag$	$AgI + e^- \leftrightarrow Ag + I^-$	− 0.1519
$Cl^- \mid AgCl \mid Ag$	$AgCl + e^- \leftrightarrow Ag + Cl^-$	+ 0.2223
$Cl^- \mid Hg_2Cl_2 \mid Hg$	$Hg_2Cl_2 + 2e^- \leftrightarrow 2Hg + 2Cl^-$	+ 0.2682
	Redoxelektroden	
$Cr^{3+}, Cr^{2+} \mid Pt$	$Cr^{3+} + e^- \leftrightarrow Cr^{2+}$	− 0.41
$Fe^{3+}, Fe^{2+} \mid Pt$	$Fe^{3+} + e^- \leftrightarrow Fe^{2+}$	+ 0.770
Chinhydron|Pt		+ 0.6992
$Ce^{4+}, Ce^{3+} \mid Pt$	$Ce^{4+} + e^- \leftrightarrow Ce^{3+}$	+ 1.4430

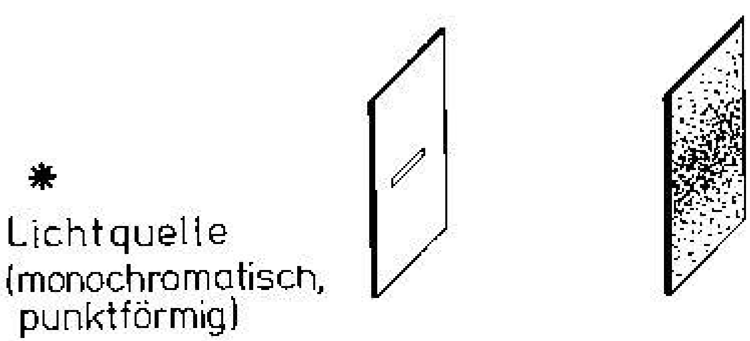
Wellennatur des Lichts – Analogie zu Wasserwellen

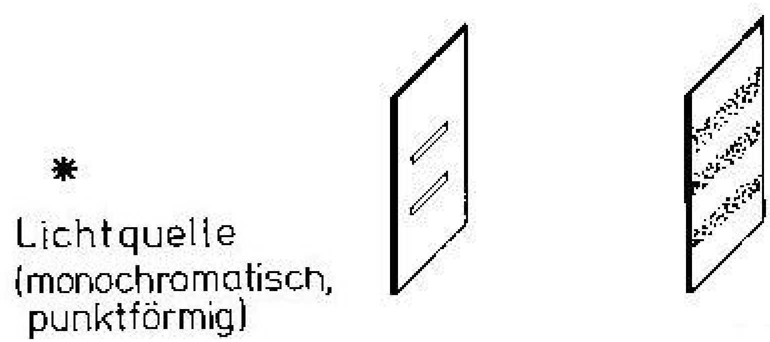
Beugung am Spalt



Interferenz am Doppelspalt

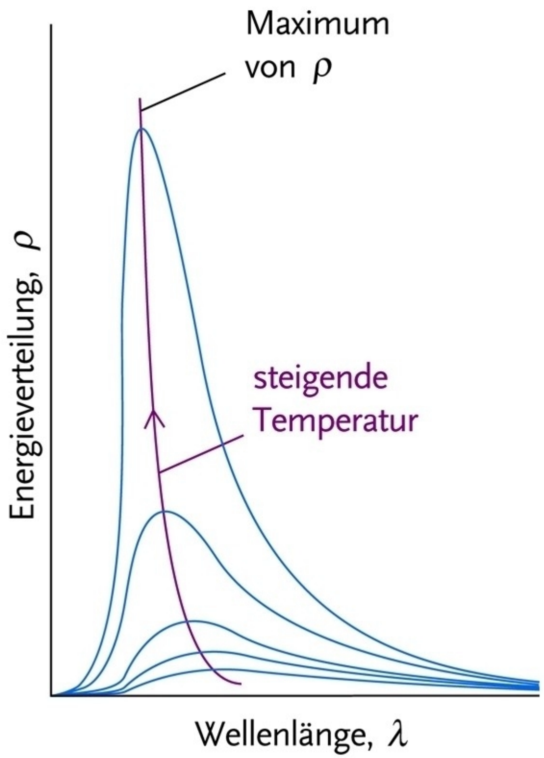




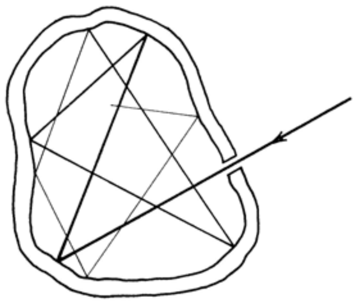


Energieverteilung eines schwarzen Strahlers

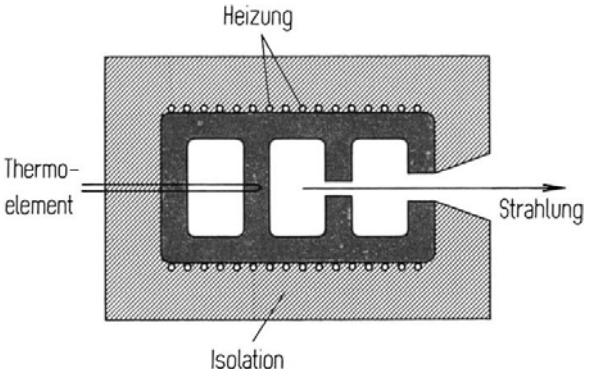
Typisches Spektrum



Experimentelle Realisierung eines Hohlraumstrahlers = Schwarzer Strahler

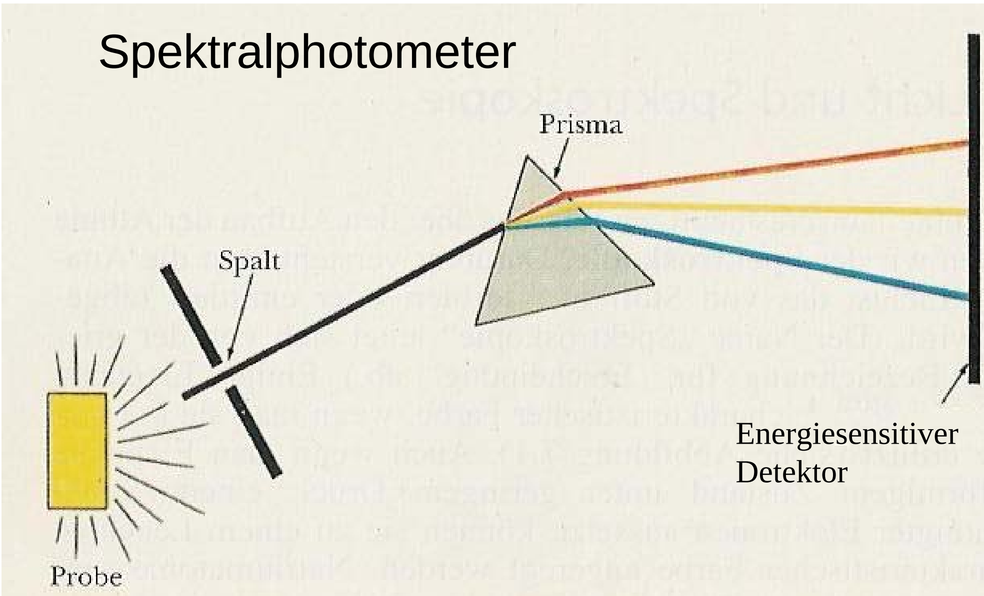


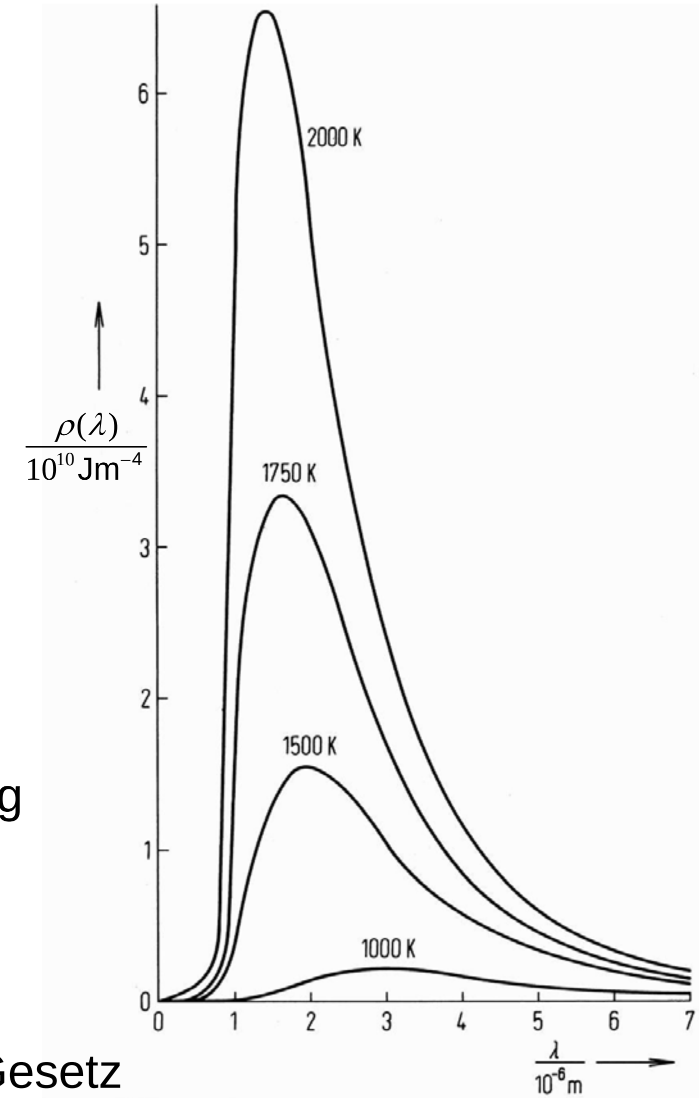
Prinzip



Experimenteller Aufbau

Messung der Schwarzkörper-Strahlung





Zusammenhang zur Messgröße:

$$M = \frac{dQ}{dAdt} = \frac{1}{4}\rho c$$ Spezifische Ausstrahlung

$$M = \sigma \cdot T^4$$ Stefansches Gesetz

$$\lambda_{\max} \cdot T = const$$ Wiensches Verschiebungs-Gesetz

Boltzmannverteilung – Kontinuierlich

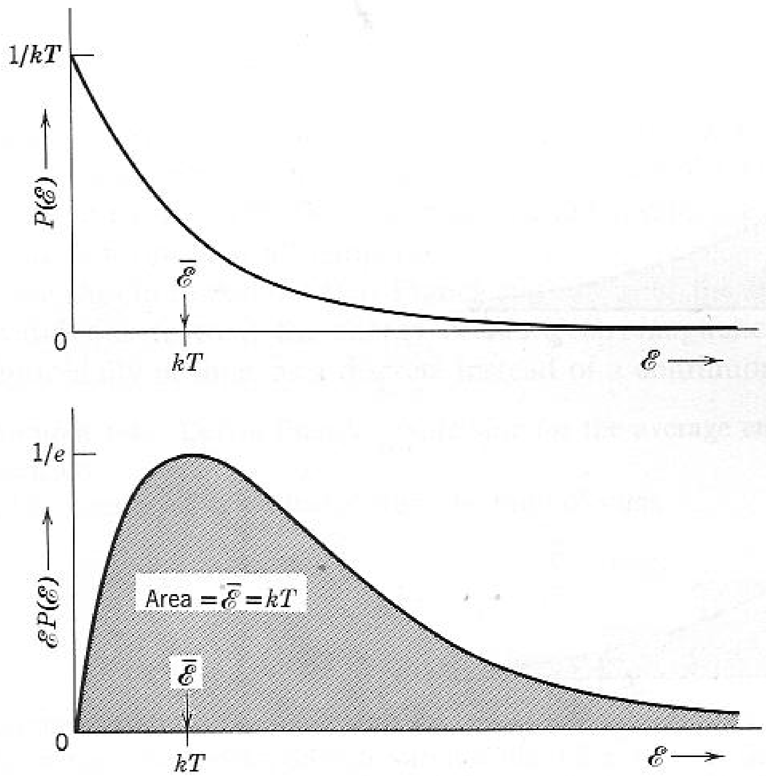
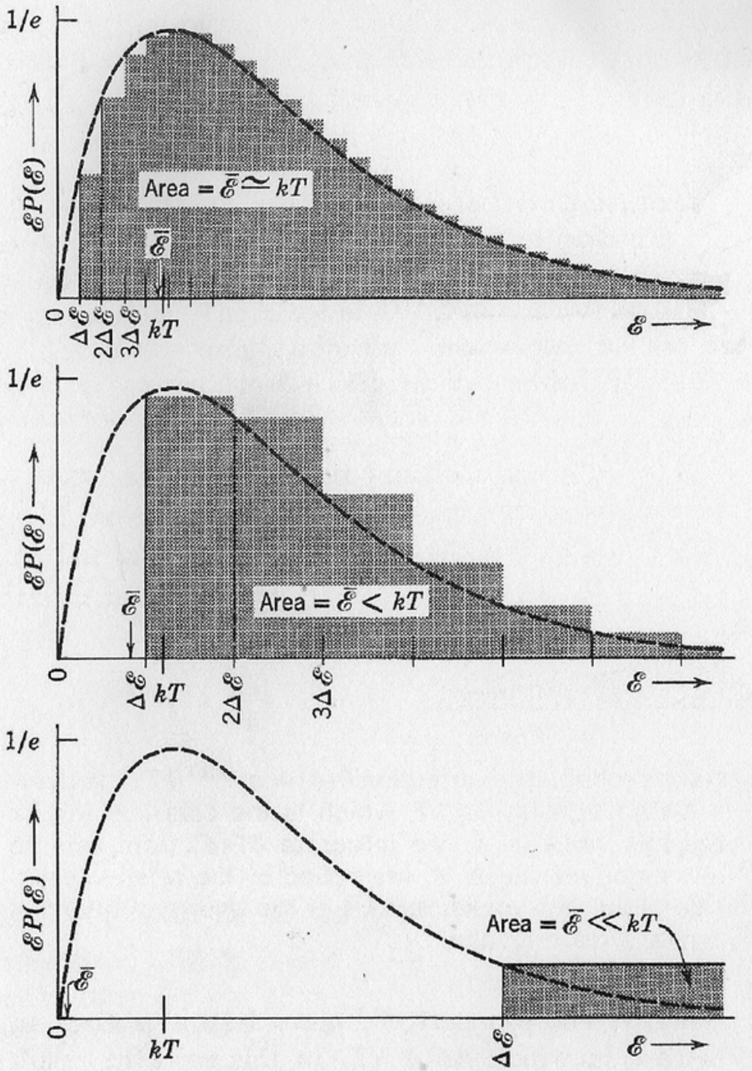


Figure 1-9 *Top:* A plot of the Boltzmann probability distribution $P(\mathcal{E}) = e^{-\mathcal{E}/kT}/kT$. The average value of the energy $\mathcal{E}$ for this distribution is $\overline{\mathcal{E}} = kT$, which is the classical law of equipartition of energy. To calculate this value of $\overline{\mathcal{E}}$, we integrate $\mathcal{E}P(\mathcal{E})$ from zero to infinity. This is just the quantity that is being averaged, $\mathcal{E}$, multiplied by the relative probability $P(\mathcal{E})$ that the value of $\mathcal{E}$ will be found in a measurement of the energy. *Bottom:* A plot of $\mathcal{E}P(\mathcal{E})$. The area under this curve gives the value of $\overline{\mathcal{E}}$.

$$P(E) = \frac{1}{k_B T} e^{-E/k_B T}$$

$$\overline{E} = \frac{\int_0^\infty E \cdot P(E) dE}{\int_0^\infty P(E) dE} = k_B T$$

Boltzmannverteilung – Diskret



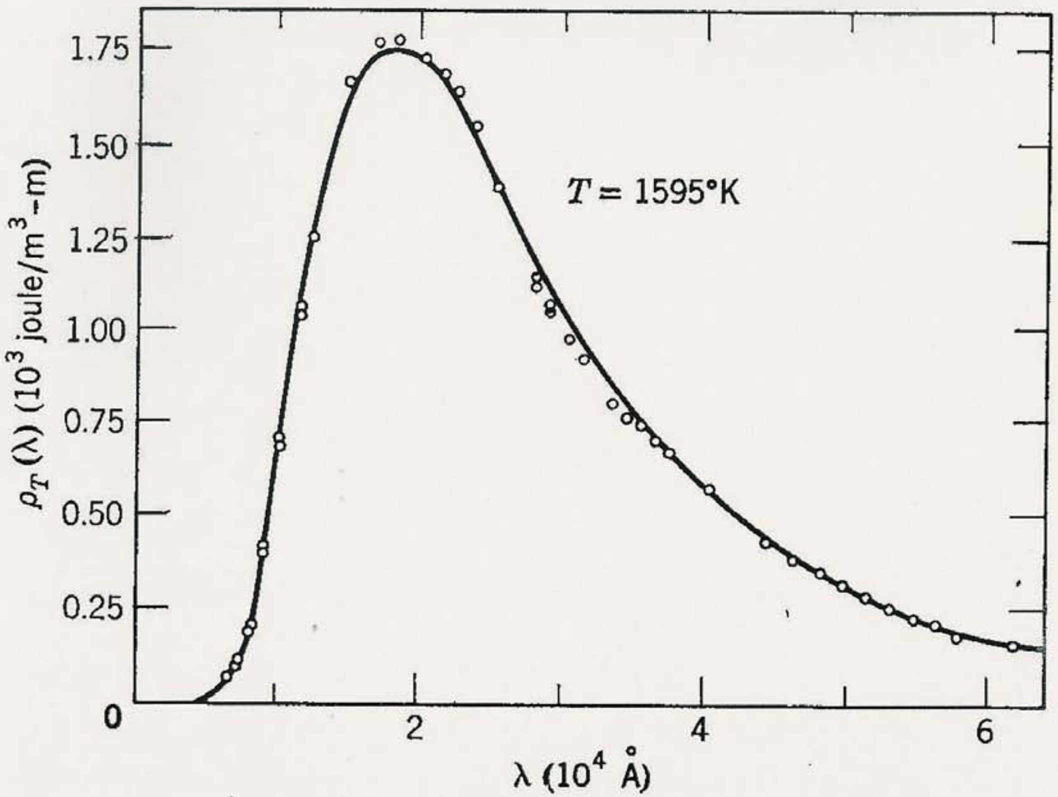
$$P(E_n) = \frac{1}{k_B T} e^{-E_n / k_B T} \qquad n = 0,1,2,3,\cdots$$

$$E_n = n \cdot \Delta E$$

$$\overline{E} = \frac{\sum_{n=0}^{\infty} E_n \cdot P(E_n)}{\sum_{n=0}^{\infty} P(E_n)}$$

Figure 1-10 *Top:* If the energy $\mathcal{E}$ is not a continuous variable but is instead restricted to discrete values 0, $\Delta\mathcal{E}$, $2\Delta\mathcal{E}$, $3\Delta\mathcal{E}$, . . . , as indicated by the ticks on the $\mathcal{E}$ axis of the figure, the integral used to calculate the average value $\bar{\mathcal{E}}$ must be replaced by a summation. The average value is thus a sum of areas of rectangles, each of width $\Delta\mathcal{E}$, and with heights given by the allowed values of $\mathcal{E}$ times $P(\mathcal{E})$ at the beginning of each interval. In this figure $\Delta\mathcal{E} \ll kT$, and the allowed energies being closely spaced the area of all the rectangles differs but little from the area under the smooth curve. Thus the average value $\bar{\mathcal{E}}$ is nearly equal to kT, the value found in Figure 1-9. *Middle:* $\Delta\mathcal{E} \simeq kT$, and $\bar{\mathcal{E}}$ has a smaller value than it has in the case of the top figure. *Bottom:* $\Delta\mathcal{E} \gg kT$, and $\bar{\mathcal{E}}$ is further reduced. In all three figures the rectangles show the contribution to the total area of $\mathcal{E}P(\mathcal{E})$ for each allowed energy. The rectangle for $\mathcal{E} = 0$ of course is always of zero height. This will make a large effect on the total area if the widths of the rectangles are large.

Plancksches Spektrum eines Schwarzen Körpers

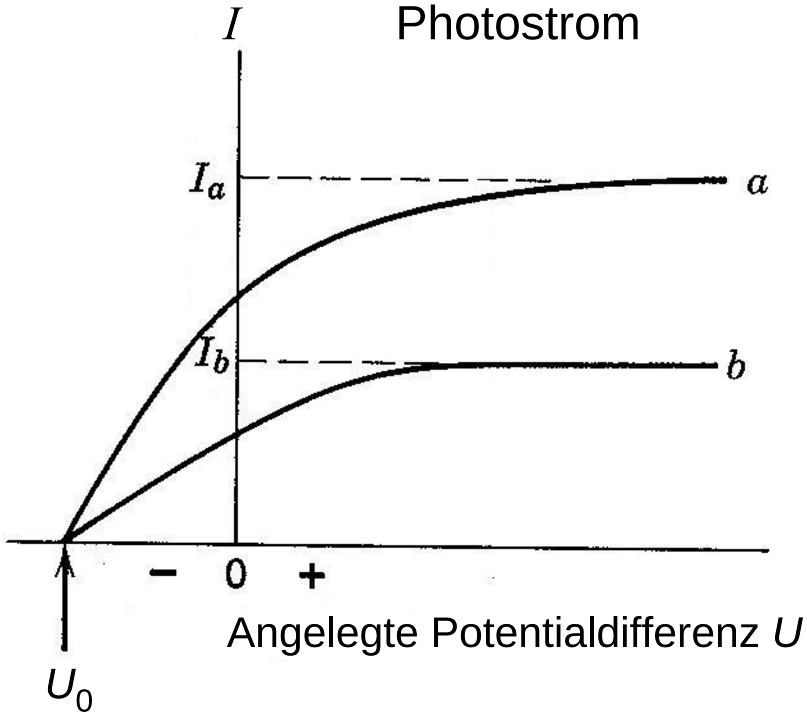


$$\rho_T(\lambda) = \frac{8\pi hc}{\lambda^5}\frac{1}{e^{hc/\lambda k_B T}-1}$$

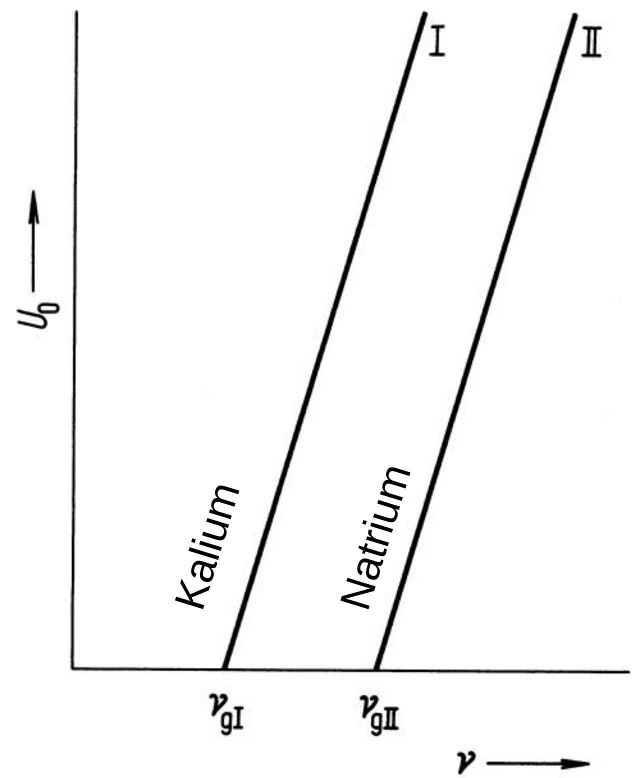
Figure 1-11 Planck's energy density prediction (solid line) compared to the experimental results (circles) for the energy density of a blackbody. The data were reported by Coblentz in 1916 and apply to a temperature of 1595°K. The author remarked in his paper that after drawing the spectral energy curves resulting from his measurements, "owing to eye fatigue it was impossible for months thereafter to give attention to the reduction of the data." The data, when finally reduced, led to a value for Planck's constant of 6.57×10^{-34} joule-sec.

Photoelektrischer Effekt – Experimente

Photostrom



Cut-off Spannung



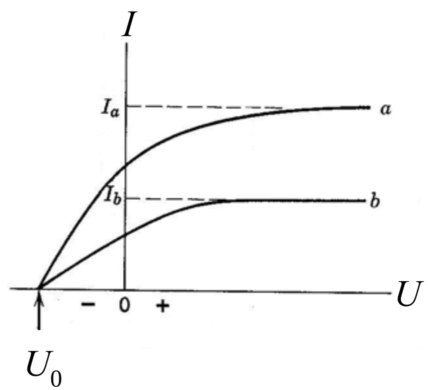
Photoelektr.Effekt – Widersprüche zw. Expt. und klassischer Wellen-Theorie des Lichts

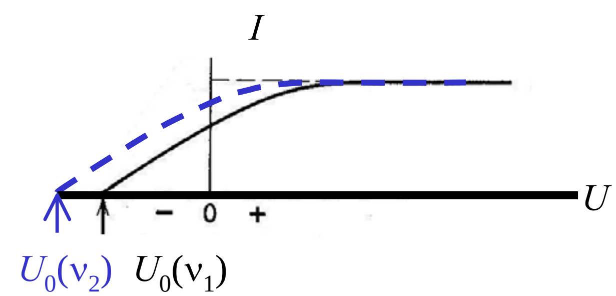
1. $E_{kin} = eU_o$ sollte mit der Lichtintensität I_{licht} zunehmen:

$$I_{Licht} \propto \left|\vec{E}\right|^2$$

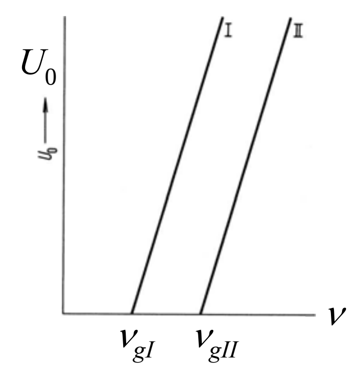
$$\Rightarrow \vec{F}_E = e\vec{E} \propto I_{Licht}$$

$$\Rightarrow E_{kin} \propto I_{Licht}$$



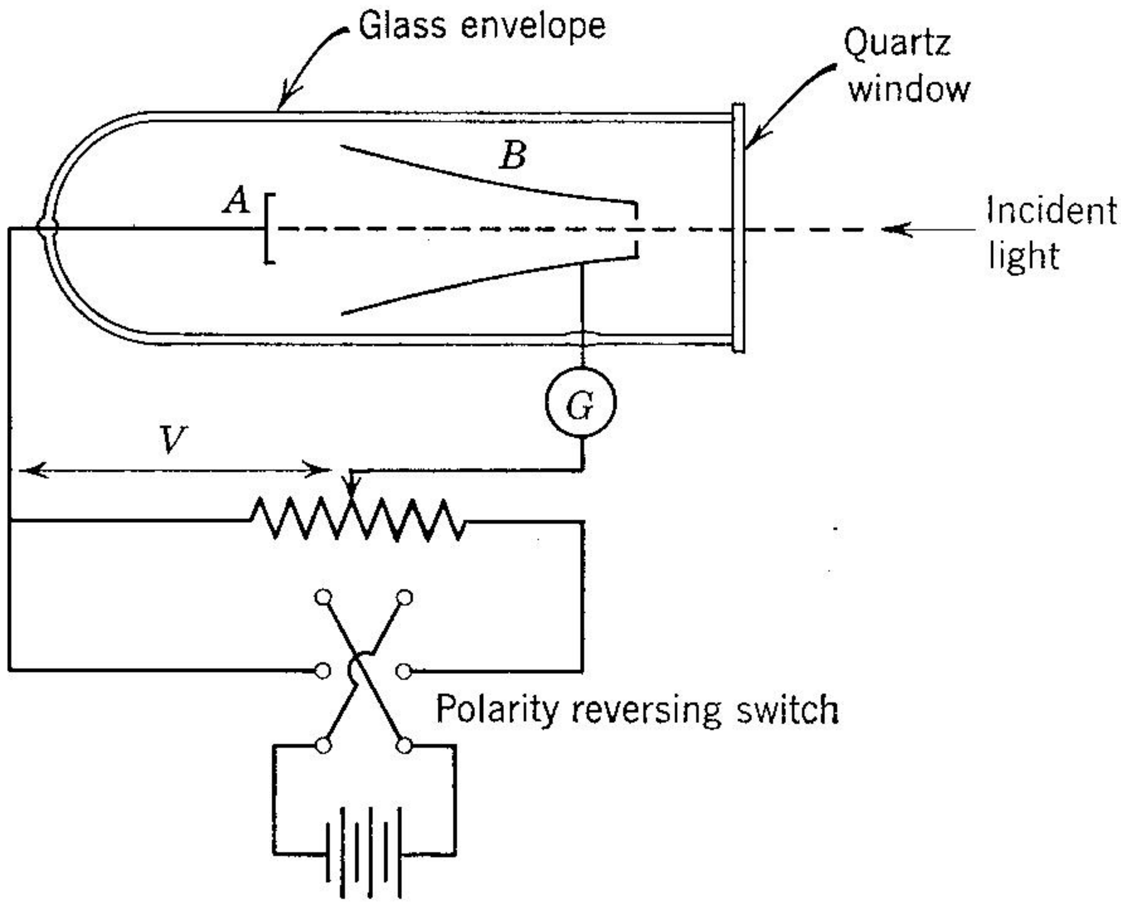


2. Photoelektr. Effekt sollte bei allen Frequenzen auftreten, sofern die Lichtintensität nur hinreichend hoch ist ⇒ keine „Cutoff"-Frequenz

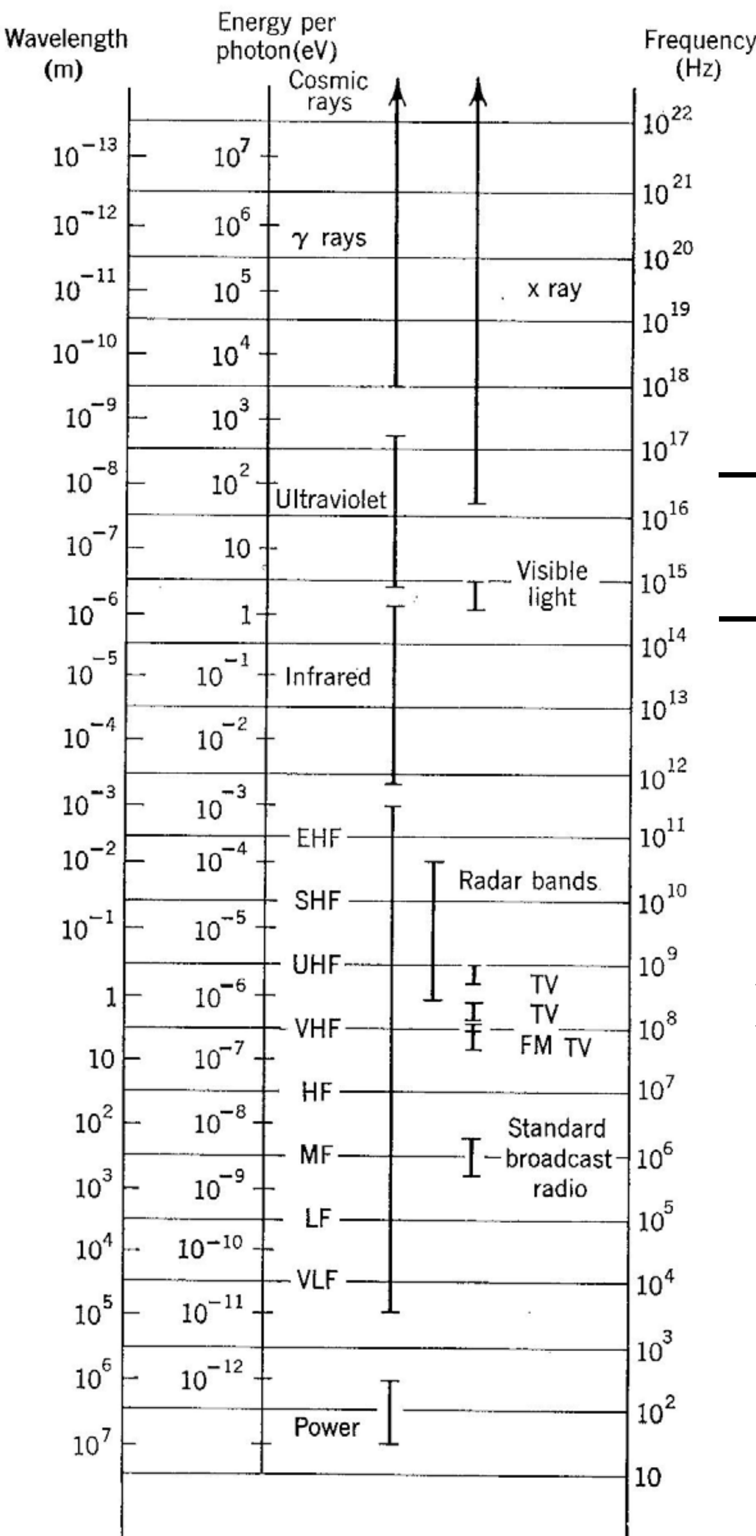


3. Zeitverzögerung zwischen Absorption und Photoelektronenemission – im Expt. nie beobachtet

Photoelektrischer Effekt – Messapparatur



Photoelektrischer Effekt und elektro-magnetisches Spektrum



$E_{photon} >> w_A$

⇒Herauslösen innerer, Stark gebundener e^-

$E_{photon} \cong w_A$

⇒Herauslösen von e^- aus dem Leitungsband

$E_{photon} << w_A$

⇒Kein photoelektrischer Effekt

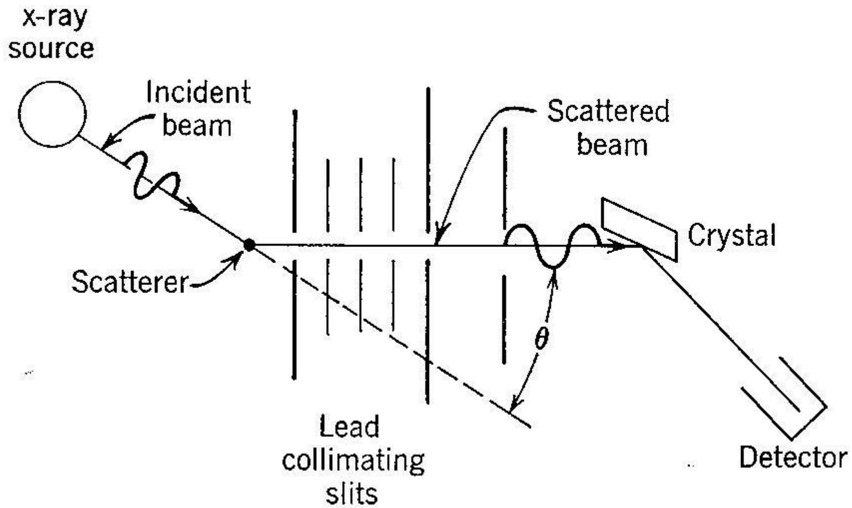
Photoelektrischer Effekt – Historie

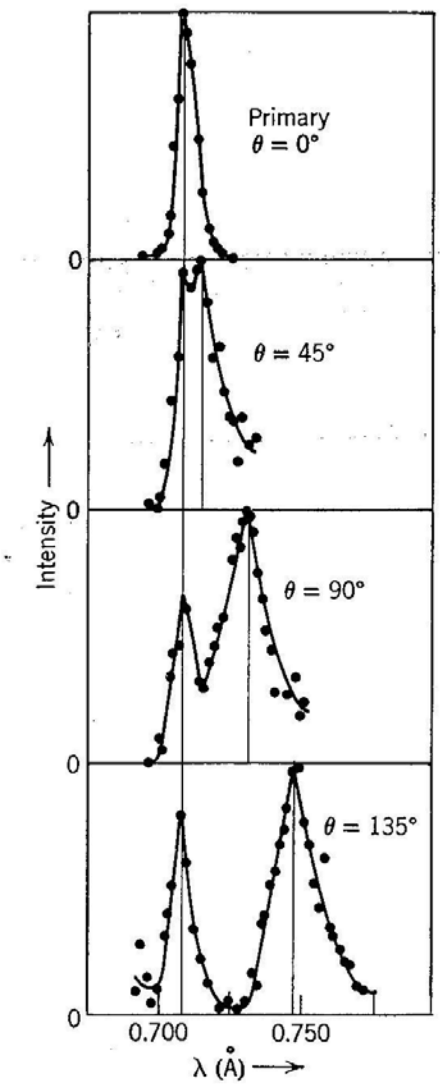
$$h = 6.6262 \times 10^{-34} \text{ joule-sec}$$

To quote Millikan: "The photoelectric effect . . . furnishes a proof which is quite independent of the facts of blackbody radiation of the correctness of the fundamental assumption of the quantum theory, namely, the assumption of a discontinuous or explosive emission of the energy absorbed by the electronic constituents of atoms from . . . waves. It materializes, so to speak, the quantity *h* discovered by Planck through the study of blackbody radiation and gives us a confidence inspired by no other type of phenomenon that the primary physical conception underlying Planck's work corresponds to reality."

In 1921 Einstein received the Nobel Prize for predicting theoretically the law of the photoelectric effect. Before Millikan's complete experimental validation of this law in 1914, Einstein was recommended to membership in the Prussian Academy of Sciences by Planck and others. Their early negative attitude toward the photon hypothesis is revealed in their signed affidavit, praising Einstein, in which they wrote: "Summing up, we may say that there is hardly one among the great problems, in which modern physics is so rich, to which Einstein has not made an important contribution. That he may have sometimes missed the target in his speculations, as, for example, in his hypothesis of light quanta (photons), cannot really be held too much against him, for it is not possible to introduce fundamentally new ideas, even in the most exact sciences, without occasionally taking a risk."

Compton-Effekt



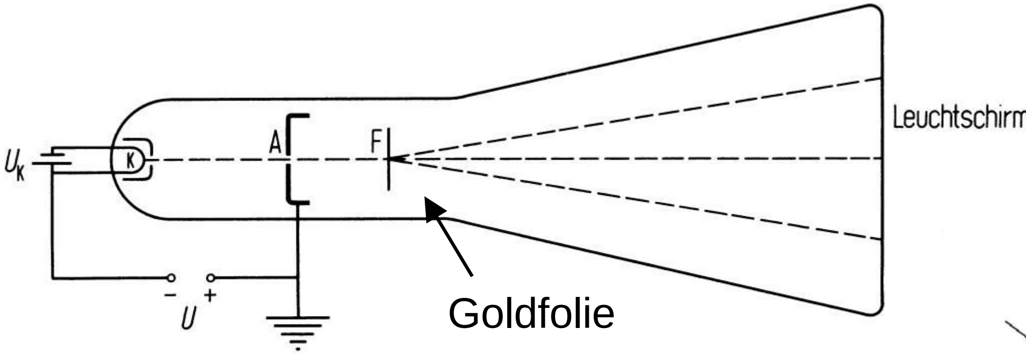


$$\lambda' = \lambda + \lambda_C (1 - \cos\theta)$$

$$\lambda_C = \frac{h}{m_e c} = 1.2 \cdot 10^{-12} m$$ Compton-Wellenlänge

Wellennatur des Elektrons - Elektronenbeugung

G.P. Thomson 1927: Messaparatur



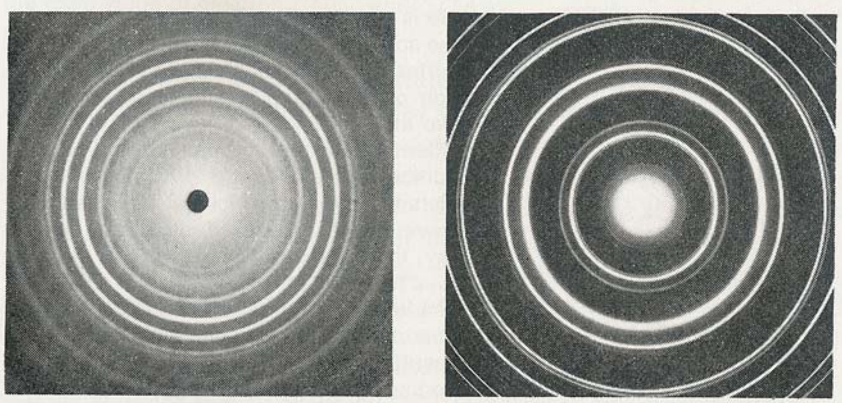
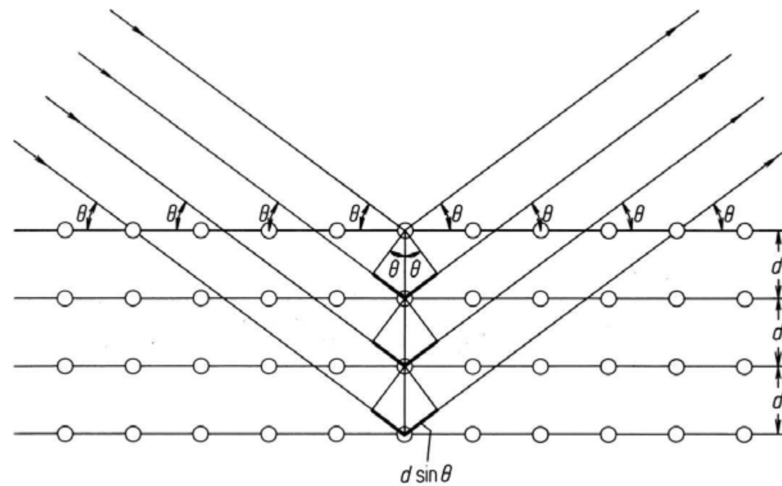


Figure 3-4 *Top:* The experimental arrangement for Debye-Scherrer diffraction of x rays or electrons by a polycrystalline material. *Bottom left:* Debye-Scherrer pattern of x-ray diffraction by zirconium oxide crystals. *Bottom right:* Debye-Scherrer pattern of electron diffraction by gold crystals.

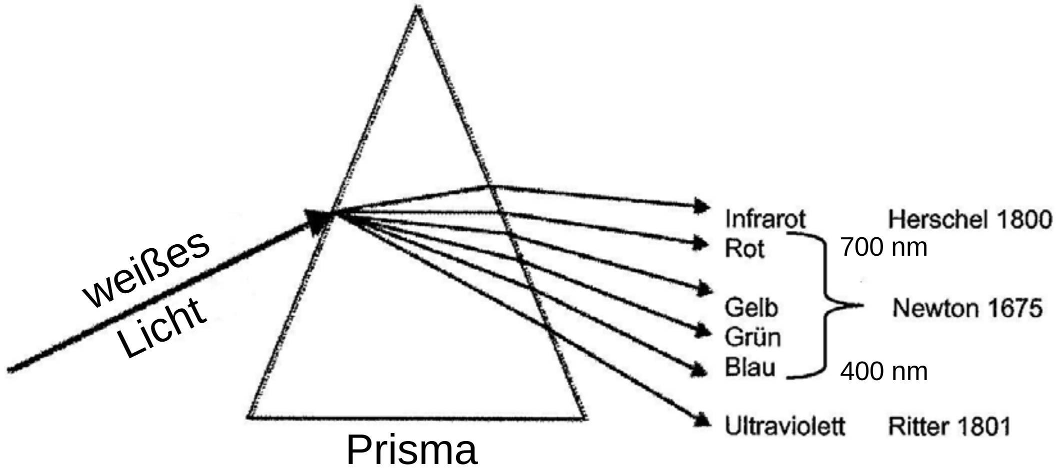
Bragg-Streuung

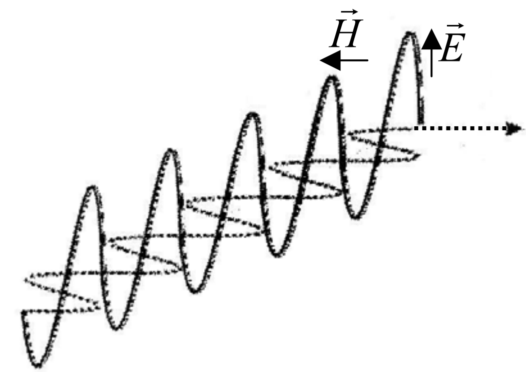


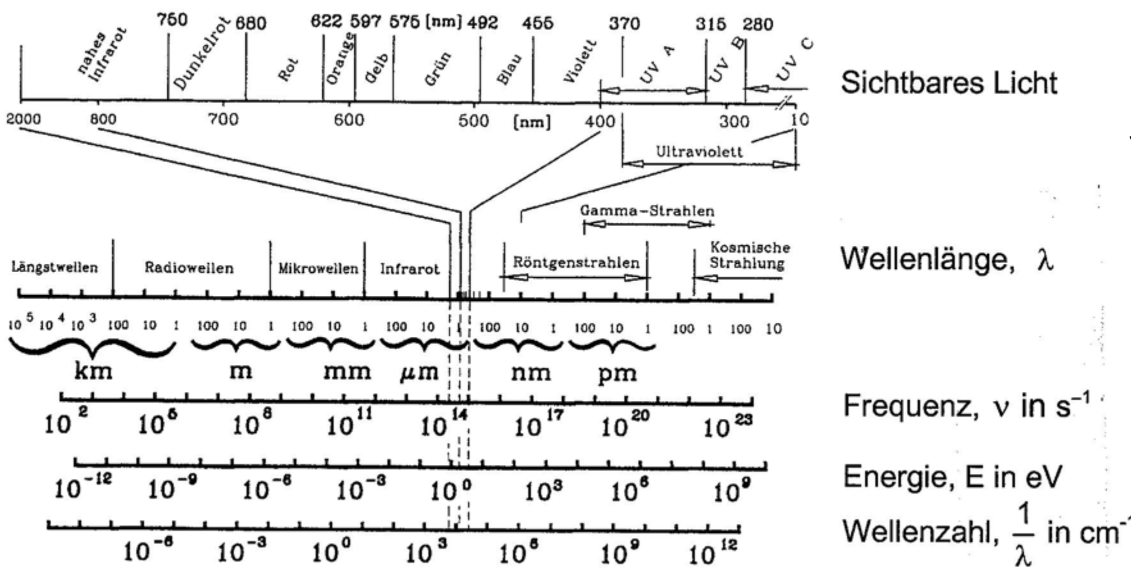
Braggsche Gleichung

$$n \cdot \lambda = 2d \sin \theta_n$$

Grundlagen der Spektroskopie

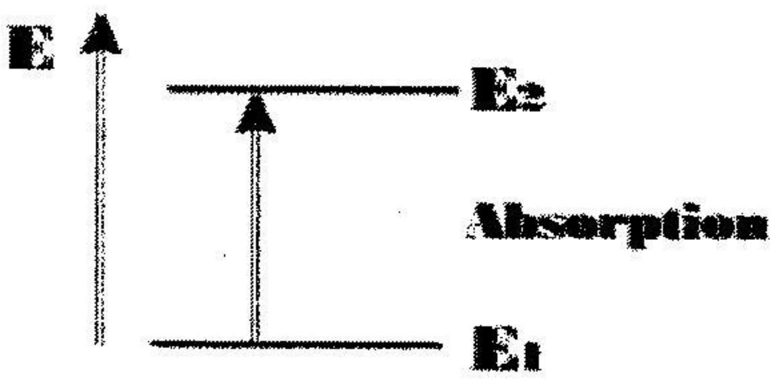


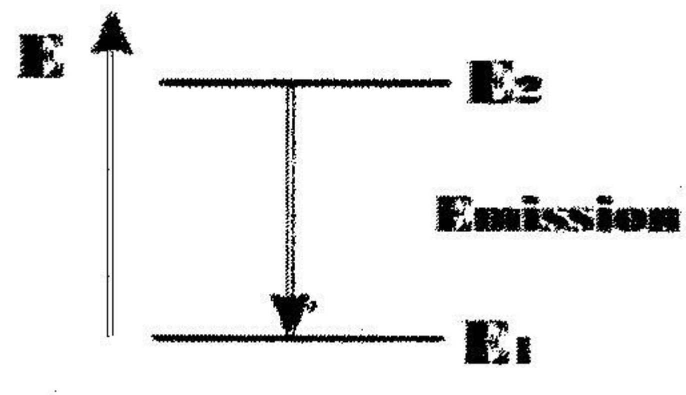


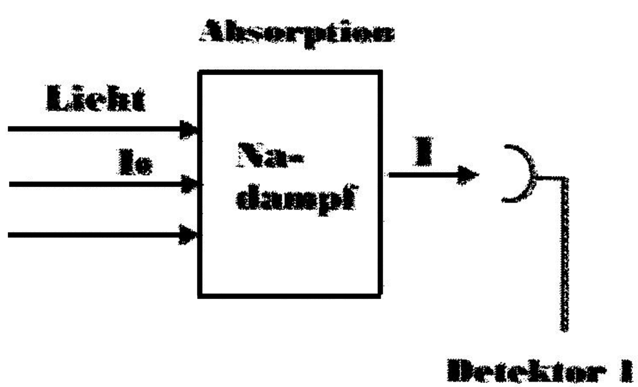


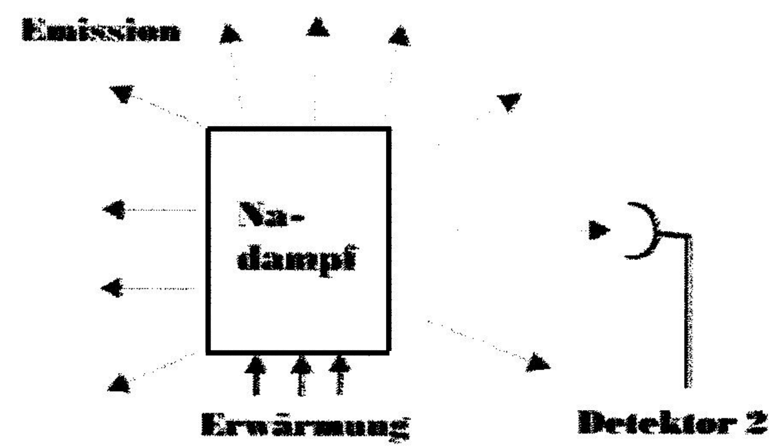
Elektromagnetisches Spektrum des Lichts

Absorption und Emission



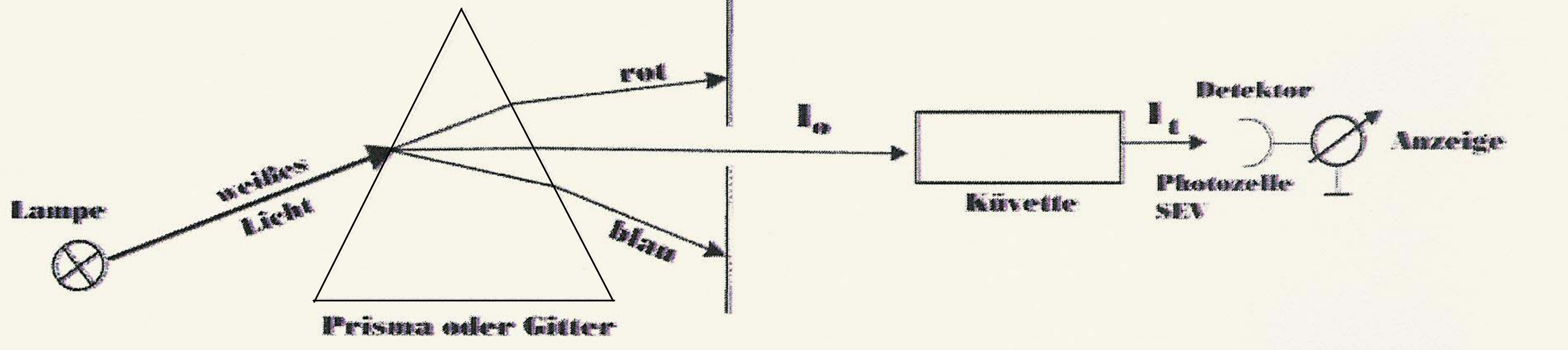




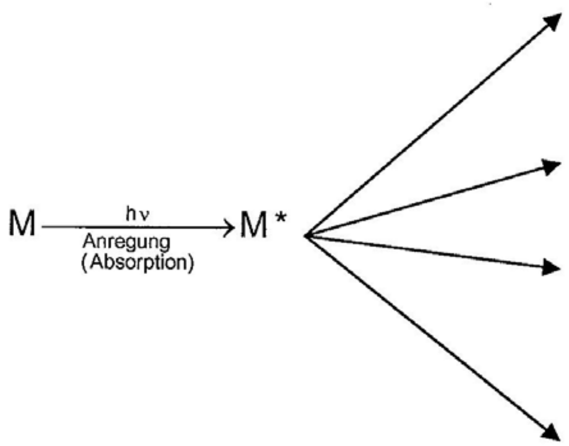


Grundlagen der Spektroskopie

Aufbau eines Photometers



Mechanismen der Deaktivierung



1. Thermische Desaktivierung (Anregungsenergie wird in Bewegungsenergie (Wärme) umgewandelt.
2. Emission von Strahlung (Fluoreszenz) (Anregungsenergie wird als Licht ausgesendet).
3. Photochemische Reaktion (Anregungsenergie wird für chemische Reaktion benutzt) z.B. Photosynthese.
4. Energietransfer (Anregungsenergie wird auf ein anderes Molekül übertragen).