

Vorlesung PC III (LA)  
Chemische Bindung und molekulare Spektroskopie

---

Do 10-12 ct H1 Vorlesung

Übungsgruppe : Di 10-11 N140/207

60% Übungspunkte gibt 10% Bonus in Klausur

Skript auf Webseite [www.prismr.de](http://www.prismr.de)

Klausur : 19.7. 9-12 st B1

Nachklausur: 9.10. 9-12 st B1

1 DinA4 Blatt handbeschrieben, Taschenrechner

Literatur :

- Atkins Phys. Chemie VCH
- Kohn & Försterling Princ. of Phys. Chem. Wiley
- Engel & Reid Phys. Chemie Pearson
- Haken & Wolf Molekülphysik & Quantenchemie Springer
- Beuwell/McCash Molekülspektroskopie Oldenbourg
- Atkins/Friedmann Moleculer QM Oxford
- Ratner/Schatz QM in Chemistry Prentice Hall
- Mc Quarrie Quantum Chemistry University Science Books

# Inhaltsangabe

## ① Einleitung / Übersicht Methoden

- Spektralbereiche
- E-Skalen

## ② Grundlagen der QM

- Wellenfunk., Energie
- Schrödinger-Gleichung
- Potentialkurven

## ③ Molekulare Spektroskopie

- Vibrations-Spektroskopie (IR)
- Rotations-Spektroskopie (MW)
- Elektr. Anregungen (UV-Vis)
- Magnetische Resonanz (EPR/NMR)

## ④ Absorption und Emission (QM)

- Auswahlregeln
- Einstein-Koeffizienten
- Fermi's Golden Rule

## ⑤ Anwendungen

- Photoreaktionen
- ET-Reaktionen
- Einzelmolekülspektroskopie

# Einführung in die molekulare Spektroskopie



Joseph Fraunhofer (1787-1826)  
Optisches Institut in Benediktbeuern



Discrete Absorptionslinien, "Barcode"

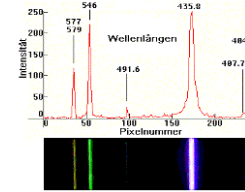


Robert Bunsen (1811-1899)  
Göttingen, Kassel, Marburg,  
Breslau, Heidelberg

Entdeckung der Alkalimetalle  
Cäsium und Rubidium im  
Dürkheimer Mineralwasser

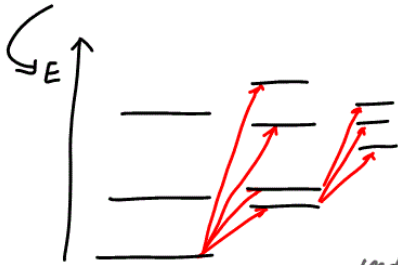


Gustav Kirchhoff (1824-1887)  
Königsberg, Breslau,  
Heidelberg, Berlin



Quecksilber Emissions-Spektrum

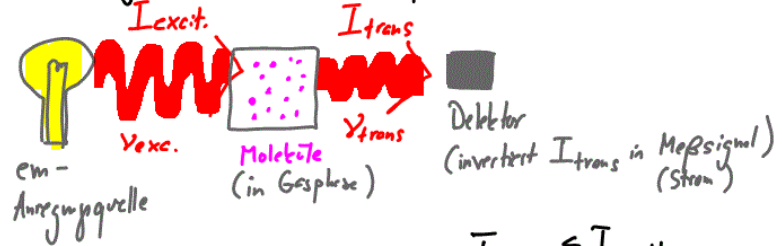
- Molekulare Spektroskopie als 'Fingerprint' zur analytischen Charakterisierung von Molekülen
- Molekulare Spektroskopie zur Überprüfung der Näherungen und zur Verfeinerung von quantenchemischen Methoden



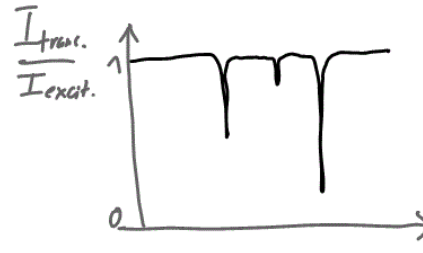
$$\Delta E = h \cdot \nu_{excit.}$$

Zusammenhang zur Spektroskopie über Eigenzustände  $E_i$  ( $\nu_{exc}$ ) und Auswahlregeln für Absorption ( $\nu_i$ )

## Grundlagen der molekularen Spektroskopie



Üblicherweise:  $\nu_{exc.} = \nu_{trans.}$ ,  $I_{trans.} \leq I_{excit.}$



Absorption erfolgt bei **diskreten** Frequenzen  $\nu_{exc.}$ . Charakteristisch für das Molekül. Erlaubt es, chem. Eigenschaften, wie Bindungsstärke, -länge, Dissoziations-E... zu bestimmen.

# Klassifizierung der Frequenzbereiche

$\log \nu$	$\lambda$	Bereich	Prozess	Methode
8	3m	RF	Kern-Zeemann	NMR
10	3cm	MW	e-Zeemann Rotation	EPR MW
13	30 $\mu$ m	IR	Vibration	IR Fluoreszenz
15	300nm	UV-VIS	e-Anregung	UV-VIS UPS
18	0.3nm	X	innere e <sup>-</sup>	Röntgen Auger
20	3pm	$\gamma$	Kernzustände	Mössbauer $\gamma$ -Spekt.

W ↓



Albert Michelson (1852-1931)  
Universität Chicago



Michelson Interferometer

Michelson, Light Waves and their uses (1903)  
Die wichtigsten Grundgesetze und Grundtatsachen der Physik sind alle schon entdeckt; unsere zukünftigen Entdeckungen müssen wir in der 6. Dezimalstelle suchen.

## Umrechnungen von Energie-Einheiten:

$$1 \text{ eV} = 1.6 \cdot 10^{-19} \text{ J} = 96 \text{ kJ/mol}$$

therm. Energie (300K)  $E_+ = k_B \cdot T = 26 \text{ meV}$

## Umrechnung von Energie in spektroskop. Einheiten ( $\nu, \lambda, \tilde{\nu}$ )

$$E = h \cdot \nu$$

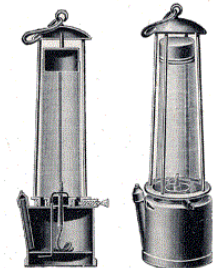
$$E \sim \nu \sim \frac{1}{\lambda} \sim \tilde{\nu}$$

Planck'sches Wirkungsquantum  $h = 6.6 \cdot 10^{-34} \text{ Js}$   
( $\hbar = h/2\pi$ )

$$1 \text{ cm}^{-1} (\tilde{\nu}) \hat{=} 30 \text{ GHz} (\nu) = 12 \text{ meV} (E)$$



Sir Humphrey Davy (1778-1829)  
Royal Institution London



Bis. 192. Davy'sche Sicherheitslampe

Sir Humphrey Davy, Elements of Chemical Philosophy (1820)  
Nichts trägt mehr zum Fortschritt der Wissenschaft bei als die Anwenden jener neuen Technik

# 19.4.12 lecture PCIII

## Chemische Bindung und Molekulare Spektroskopie (Lehramt)

### Subjects:

- black body radiation
- quantization of energy
- photoelectric effect
- hydrogen atom energy states
- wave-particle duality
- uncertainty principle

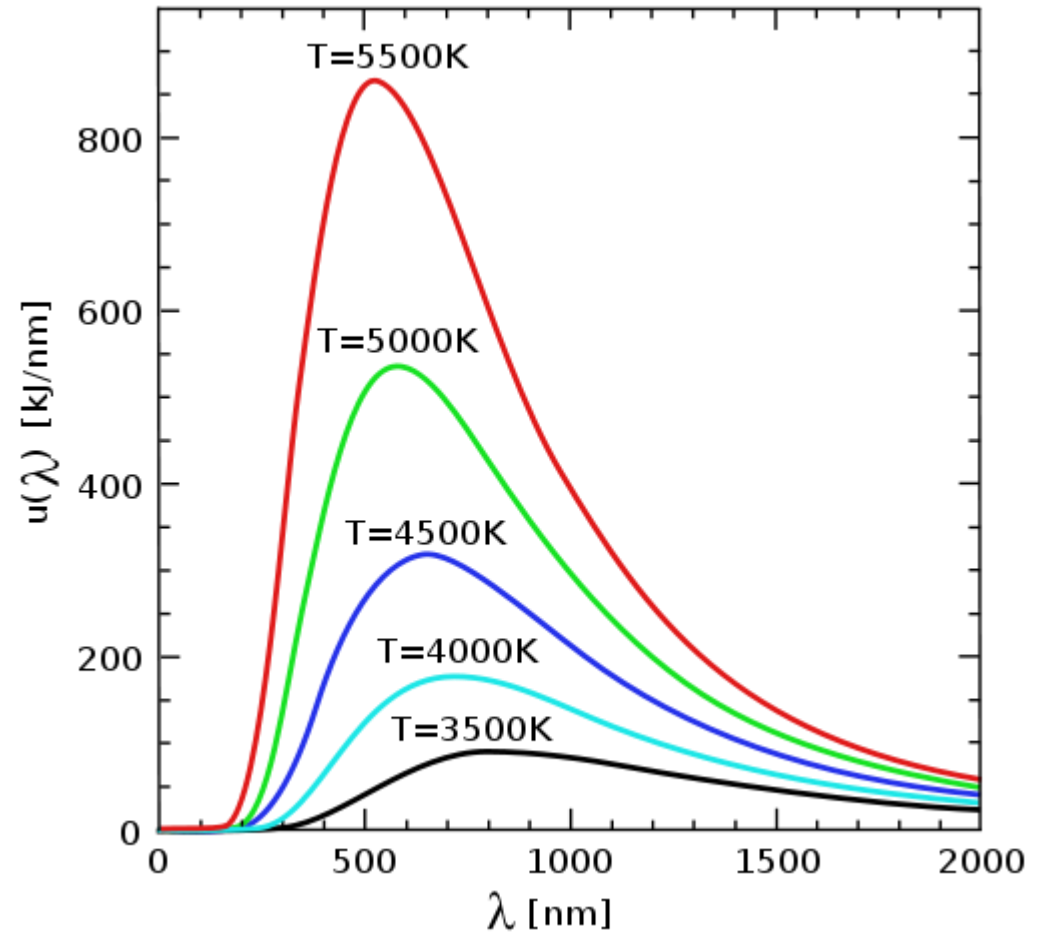


# Radiation of heated bodies (Black body radiation )



A huge plume of molten rock that is linked to volcanic eruptions has been detected below southern Africa.

*B.Israel, OurAmazingPlanet Staff Writer / June 21, 2010*



The more heated material, the more intense radiation

# Black body radiation- quantization of energy

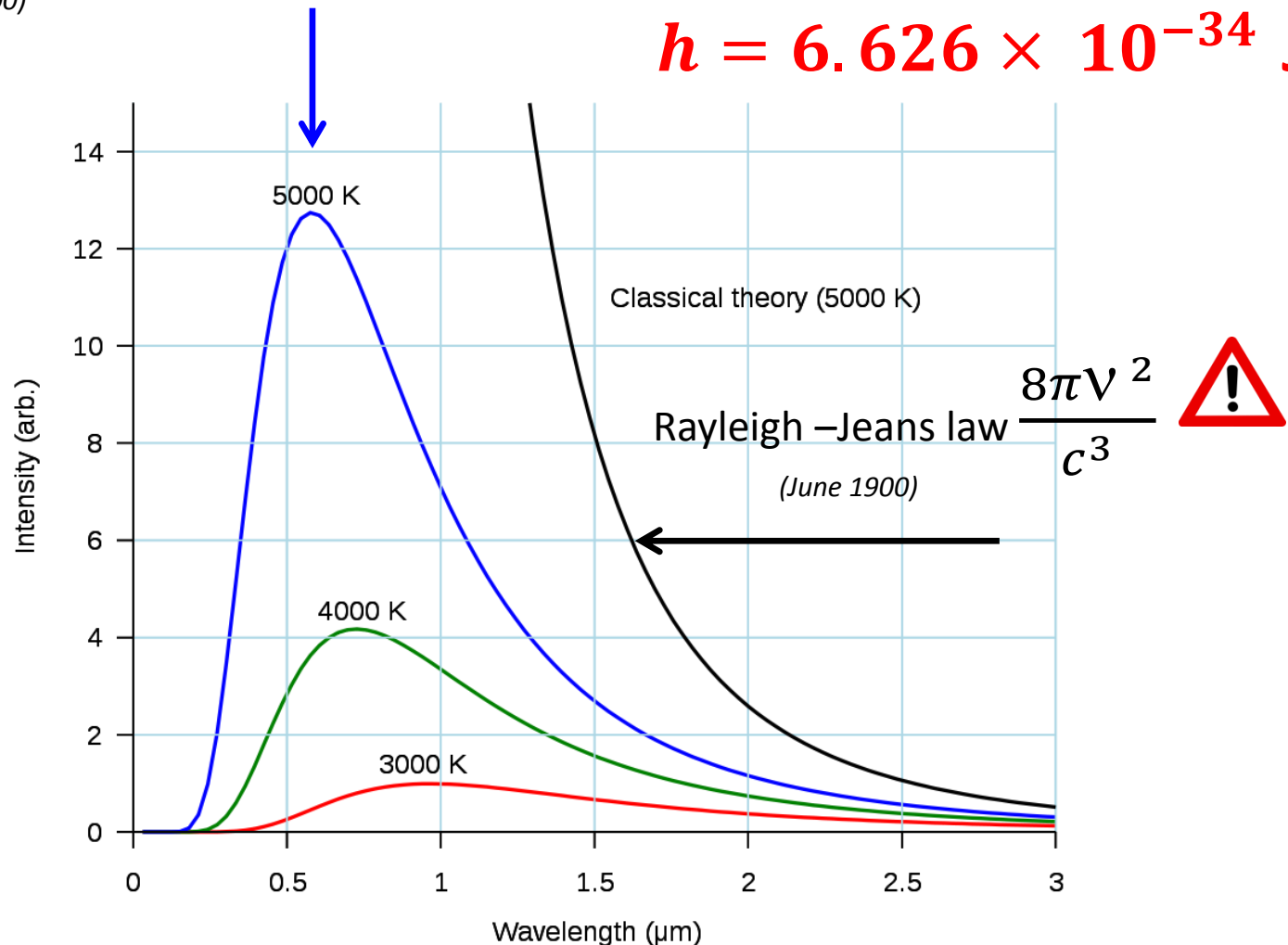
Planck law  $\frac{8\pi V^2}{c^3} \frac{h\nu}{(e^{h\nu/kBT}) - 1}$

(October-december 1900)

*Planck equation*

$E \propto n\nu, E = nh\nu$

$h = 6.626 \times 10^{-34} \text{ J.s}$



# Energy is quantized

- Quantization of energy and light :Photoelectric effect  
(A. Einstein 1905)
- *Interpretation of energy levels in Hydrogen atom*  
(N. Bohr 1913)

## microscopic vs.macroscopic world and the necessity to a new formalism

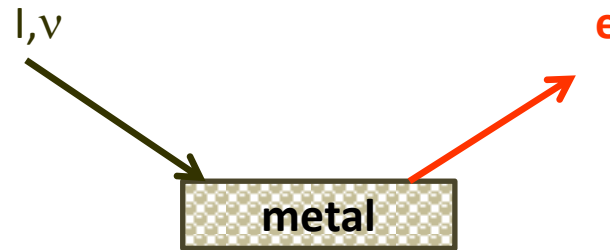
- *Wave-Particle duality (L. de Broglie 1923)*
- *Uncertainty rule (W.Heisenberg 1927)*

## Qantum mechanic formalism is born!

E.Schrödinger , W.Heisenberg, M.Born, P.Jordan (1925-1927)



# photoelectric effect : light in packets of $h\nu$



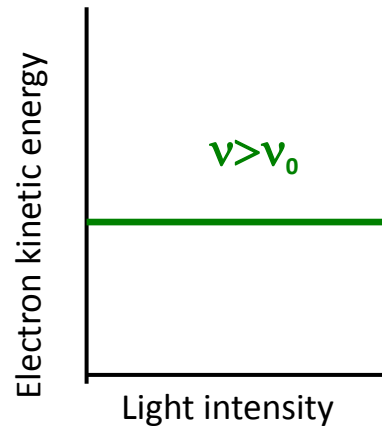
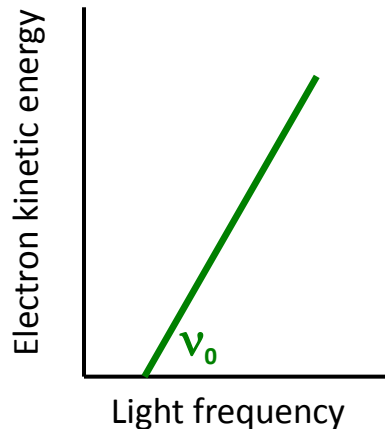
$$h\nu = E_{kin} + \Phi$$

$\Phi$ : work function

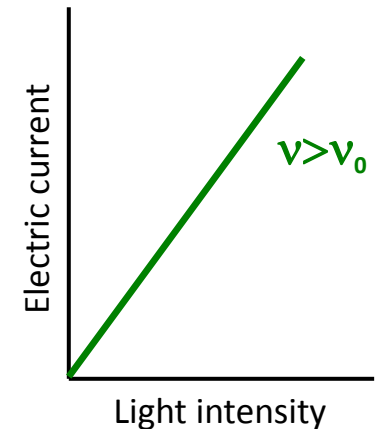
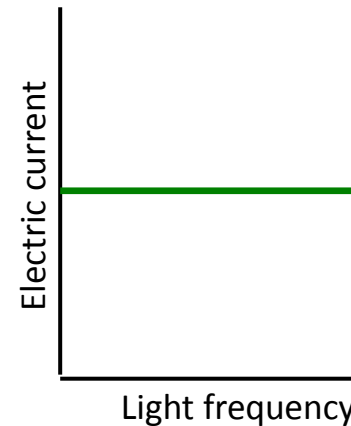
$$E_{photon} = h\nu$$

$$E_{kin} = \frac{1}{2} m v^2$$

(a)



(b)



(a) Above a certain threshold ( $\Phi = h\nu_0$ ) electron is emitted. The kinetic energy of electron increases linearly with frequency and it is independent of the light intensity.

(b) The number of electrons emitted per second (i.e. the electric current) is independent of frequency and increases linearly with the light intensity.

# Bohr and Hydrogen atom

Emission lines as finger prints or elemental barcodes: light is emitted at discrete frequencies

*Picture is adapted from [www.nasa.gov](http://www.nasa.gov)*

Hydrogen



Helium



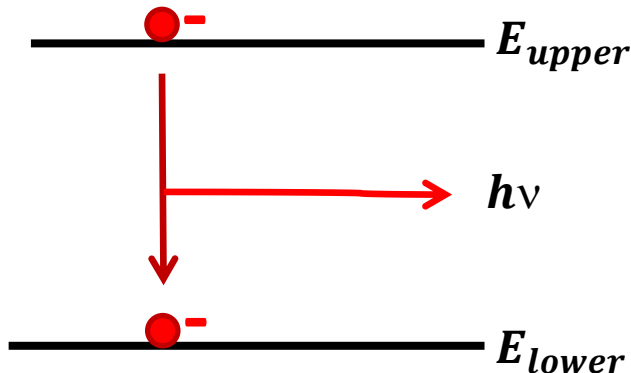
Carbon



empirically derived formula by J.Rydberg -1880

$$\frac{1}{\lambda} = R_H \left( \frac{1}{f^2} - \frac{1}{i^2} \right), i, f > 0$$
$$R_H = 109677.581 \text{ cm}^{-1}$$

Bohr approach : quantized energy levels- 1913



$$E_{upper} - E_{lower} = \Delta E = h\nu$$

$\nu$  : emission /absorbption frequency



# Wave-Particle duality of matter

Einstein :

$$\begin{array}{l} E_{\text{photon}} = h\nu \\ E_{\text{photon}} = mc^2 \end{array} \Rightarrow h\nu = mc^2, \nu = \frac{c}{\lambda} \Rightarrow \lambda_{\text{photon}} = \frac{h}{mc}$$

\* Rest mass of a photon =0 but relativistic mass of a photon  $\neq 0$

In a similar way, de Broglie suggested for a particle of mass  $m$  :

$$\lambda = \frac{h}{mv}, p = mv = \text{linear momentum}$$

Example :

-an electron travelling at  $1.0 \times 10^6 \text{ m/s} = 7.0 \times 10^{-10} \text{ \AA} = 7 \text{ \AA}$

- a particle with a mass 1.0 g travelling at  $1.0 \text{ cm/s} = 7.0 \times 10^{-27} \text{ cm}$

**Linear momentum is quantized, as well.**

**Quantum effects can not be considered for macroscopic objects and vice versa.**

# uncertainty principle



*Zeitschrift für Physik* September (1925) pp.879-893  
Über quantentheoretische Umdeutung  
kinematischer und mechanischer Beziehungen.

879

Von W. Heisenberg in Göttingen.  
(Eingegangen am 29. Juli 1925.)

In der Arbeit soll versucht werden, Grundlagen zu gewinnen für eine quantentheoretische Mechanik, die ausschließlich auf Beziehungen zwischen prinzipiell beobachtbaren Größen basiert ist.

Bekanntlich läßt sich gegen die formalen Regeln, die allgemein in der Quantentheorie zur Berechnung beobachtbarer Größen (z. B. der Energie im Wasserstoffatom) benutzt werden, der schwerwiegende Einwand erheben, daß jene Rechenregeln als wesentlicher Bestandteil Beziehungen enthalten können (wie z. B. Ort, Umlaufzeit des Elektrons), die also jenen Regeln offenbar jedes anschauliche physikalische Fundament mangelt, wenn man nicht immer noch an der Hoffnung festhalten will, daß jene bis jetzt unbeobachtbaren Größen später vielleicht experimentell zugänglich gemacht werden könnten. Diese Hoffnung könnte als berechtigt angesehen werden, wenn die genannten Regeln in sich konsequent und auf einen bestimmten Bereich der Hoffnungen festhalten Probleme der Quantentheorie und der Starkereffekt dieses Atoms auf sich das Wasserstoffatom und der Starkereffekt dieses Atoms auf sich nur Regeln der Quantentheorie fügen. Die Erfahrung zeigt aber, daß sich nur "gekrenzte Felder" (Wasserstoffatom in elektrischem und magnetischem Feld verschiedener Richtung) beschreiben lassen, und daß die Reaktionen der Atome auf periodisch wechselnde Felder sicher nicht durch die genannten Regeln beschrieben werden kann, und daß schließlich eine Ausdehnung der Quantenregeln auf die Behandlung der Atome mit mehreren Elektronen sich als unmöglich erwiesen hat. Es ist üblich geworden, dieses Versagen der quantentheoretischen Regeln, die in wesentlich durch die Anwendung der klassischen Mechanik

"The whole problem with the world is that fools and fanatics are always so certain of themselves, and wiser people so full of doubts." - Bertrand Russell ( 1872 - 1970 )

Measuring the exact location of a particle in a small area of space is together with an uncertainty in its momentum and conversely. It means that one can't measure  $(x,p)$  simultaneously in a precise way. In other words *one measuring effects the other!*

$$\Delta x \cdot \Delta p_x \geq \frac{h}{4\pi} \quad \text{or} \quad \Delta x \cdot m\Delta v_x \geq \frac{h}{4\pi}$$

$$\hbar = h / 2\pi$$

Example :

The minimum uncertainty on the position of (a) an electron in H atom and (b) a virus which move at speed of  $1.0 \mu\text{m}/\text{s}$  is calculated as follows:

Take  $m_e = 9.11 \times 10^{-31} \text{ kg}$  ,  $m_{\text{virus}} = 1.00 \times 10^{-15} \text{ kg}$

$$\Delta x \geq \frac{h}{4\pi m \Delta v}$$

$$(a) \Delta x_e = \frac{6.62 \times 10^{-34} \text{ j.s}}{4\pi \times 9.11 \times 10^{-31} \text{ kg} \times 1 \times 10^{-6} \text{ m/s}} = 58 \text{ m} \quad \text{far larger than the size of atom } (\approx 100 \text{ pm})$$

$$(b) \Delta x_{\text{virus}} = \frac{6.62 \times 10^{-34} \text{ j.s}}{4\pi \times 1.00 \times 10^{-15} \text{ kg} \times 1 \times 10^{-6} \text{ m/s}} = 5.3 \times 10^{-14} \text{ m}$$



Max Planck (1858-1947)

Schwarzkörper - Strahlung  
↳ Planck-Konstante  $h = 6.6 \cdot 10^{-34} \text{ J s}$   
 $\hbar = h/2\pi$



Albert Einstein (1879-1955)

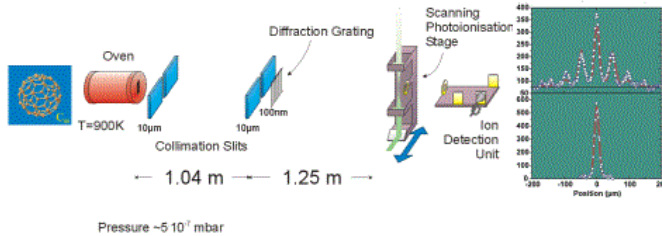
Untersuchung des Photoeffekts:  
Lichtteilchen Photon  $E_p = h \cdot \nu$   
 $p_p = h \cdot \vec{\nu} = \frac{h}{\lambda}$



Louis de Broglie (1892-1987)

Teilchen als Welle

$$m \cdot v = p = h \cdot \vec{\nu}$$
$$\frac{1}{2} m v^2 = E = h \cdot \nu$$



Arndt et al. Nature 401, 680 (1999)

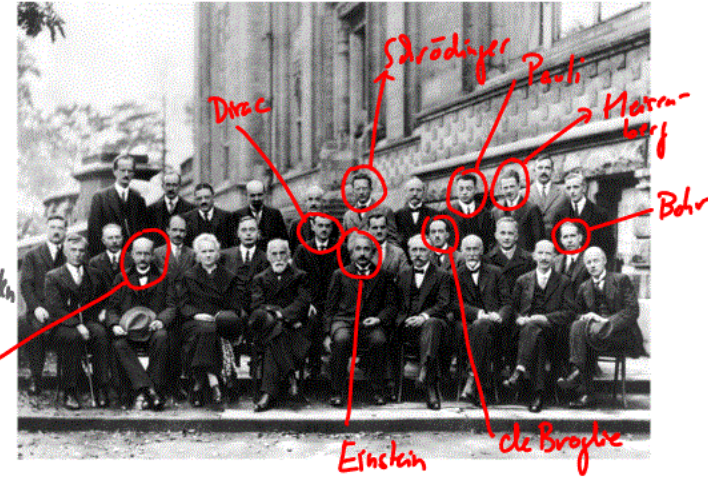


Werner Heisenberg (1901-1976)

Geburt einer neuen Theorie zur Beschreibung von nano-Objekten

Heisenbergsche Unschärferelation:  
 $\Delta x \cdot \Delta p \geq \frac{\hbar}{2}$

5. Solvay Kongress 1927



Erwin Schrödinger (1887-1961)

Schrödinger Gleichung:

$$\hat{\mathcal{E}} \psi = E \cdot \psi$$

$\psi$ : Eigenfunktionen zum  $\mathcal{E}$ -Operator

$E$ : Eigenenergien des Systems

$$\hat{\mathcal{E}} = -\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r})$$

$$\left( \Delta = \nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right)$$



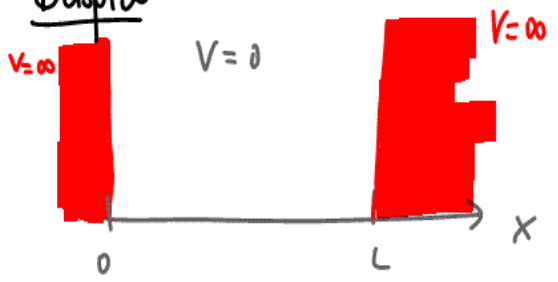
Zeitabhängige Schrödinger-Gleichung



Die Wellenfunktion  $\psi(\vec{r}, t)$  hat folgende Eigenschaften

- $\psi$  ist stetig und stetig differenzierbar
- $\psi$  ist integrierbar
- $\psi^*(\vec{r}, t) \psi(\vec{r}, t)$  ist die Wahrscheinlichkeit das qm-Objekt zur Zeit  $t$  am Orte  $\vec{r} = (x, y, z)$  zu finden  
Born'sche Wahrscheinlichkeitsinterpretation

Beispiel: Teilchen im 1D-Kasten



Außerhalb Kasten  
 $x \leq 0$  oder  $x \geq L$   
 $\psi(x) = 0$

Ansatz für  $\psi(x)$ :  $\psi(x) = A \cdot \sin kx + B \cdot \cos kx$

Stetigkeit bei  $x=0$  und  $x=L \rightarrow$

$\psi(0) = 0 \rightarrow B = 0$

$\psi(L) = 0 \rightarrow kL = n \cdot \pi \quad (n = 1, 2, \dots, \infty)$

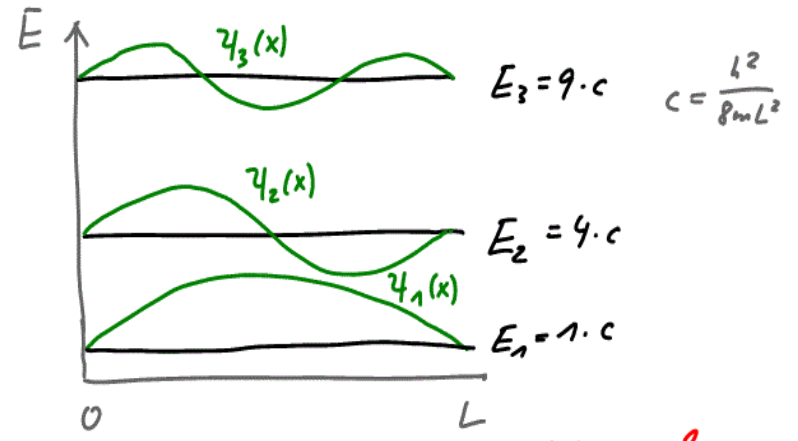
$\int_0^L A^2 \sin^2(kx) dx = 1 \rightarrow A = \sqrt{\frac{2}{L}}$

$\psi_n(x) = \sqrt{\frac{2}{L}} \cdot \sin\left(\frac{n \cdot \pi}{L} \cdot x\right)$  Eigenfunktionen

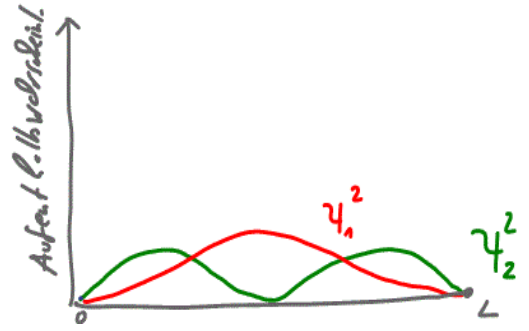
Einsetzen in SG:

$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \left( \sqrt{\frac{2}{L}} \sin\left(\frac{n \cdot \pi}{L} \cdot x\right) \right) = E_n \cdot \sqrt{\frac{2}{L}} \sin\left(\frac{n \cdot \pi}{L} \cdot x\right)$

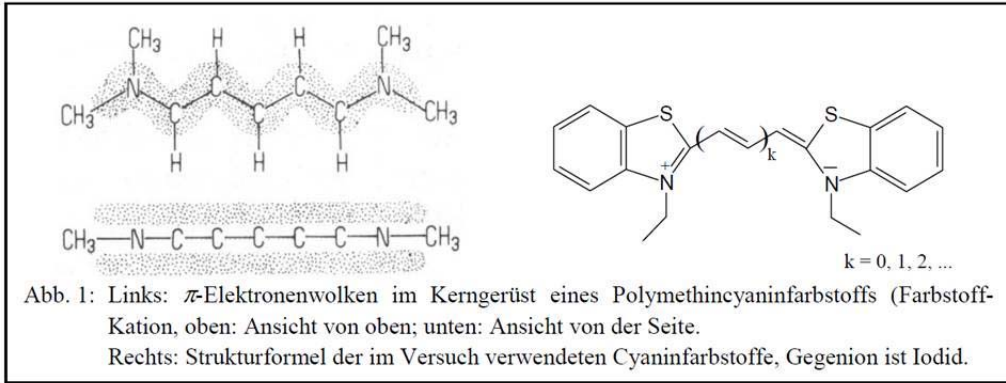
$E_n = \hbar^2 \frac{\frac{1}{2} \frac{\pi^2}{L^2}}{2m} = \hbar^2 \frac{\pi^2}{8mL^2}$  Eigenenergien des qm Objekts in Potentialkasten



qm-Teilchen kann nur diese  $E$ -Werte annehmen

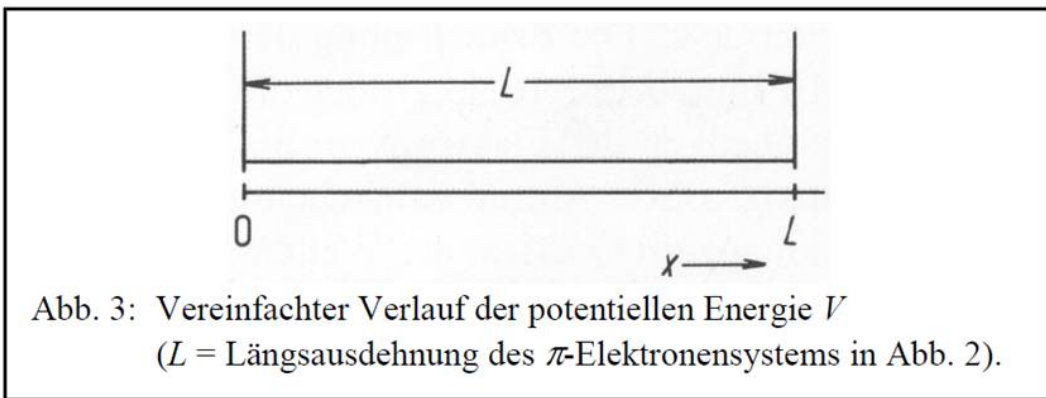
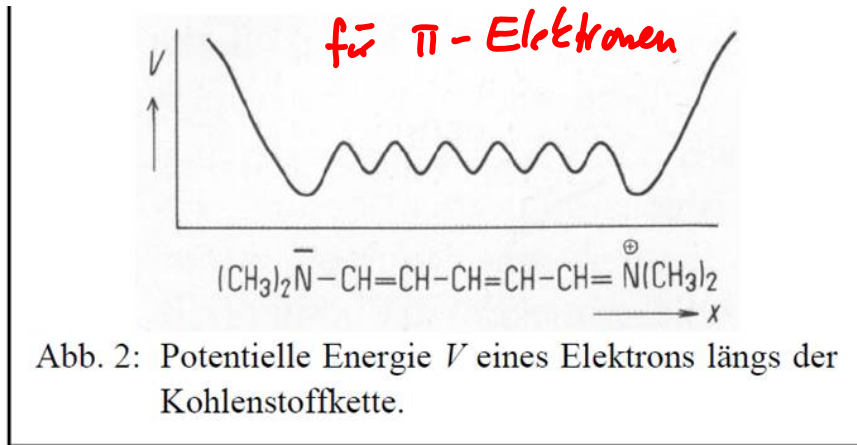


# Anregung im 1D-Potentialkasten



Delokalisierte  $\pi$ -Elektronen bewegen sich frei entlang der C-C Kette

## Realistisches Potential für $\pi$ -Elektronen

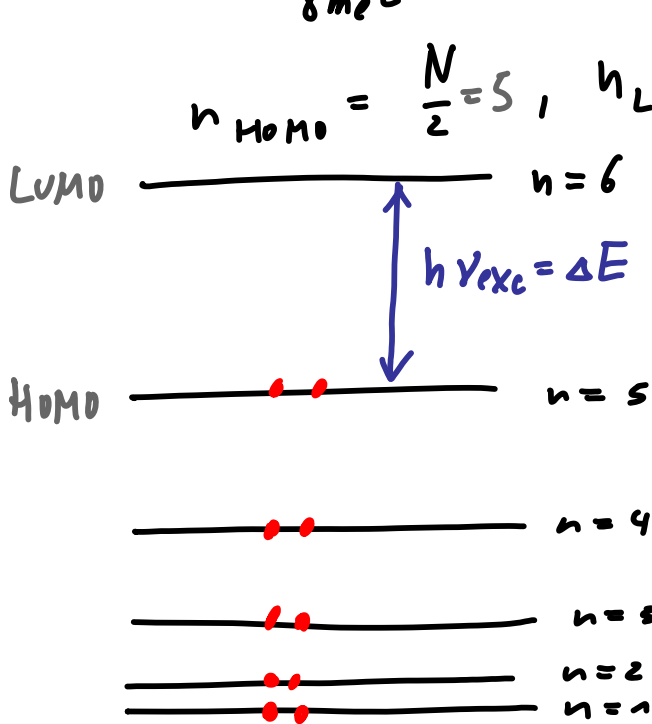


## Approximiertes Potential für $\pi$ -Elektronen



4 konjugierte Doppelbindungen :  $8 e^-$   
 2  $\pi$ -Elektronen an  $\ddot{N}$  :  $2 e^-$  } 10 freie  $\pi$ -Elektronen

$$\bar{E}_n = \frac{h^2 n^2}{8m_e L^2} \quad n \in \{1, 2, \dots\}$$



$$\Delta E = \frac{h^2}{8m_e L^2} \left\{ \left( \frac{N}{2} + 1 \right)^2 - \left( \frac{N}{2} \right)^2 \right\}$$

$$= \frac{h^2}{8m_e L^2} (N+1)$$

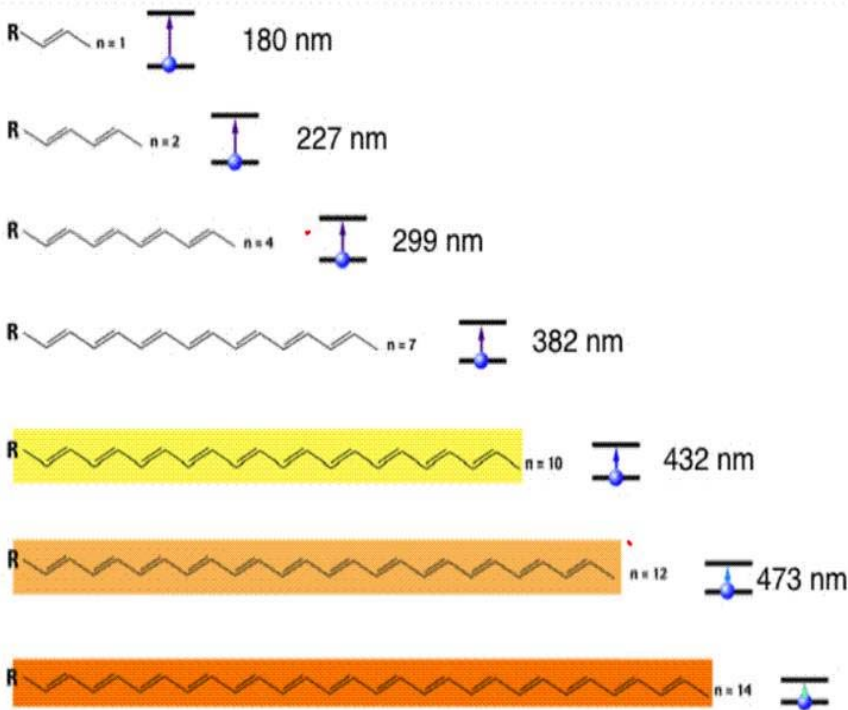
$$L = N \cdot d_0 \quad (d_0 = 140 \text{ pm})$$

$$\Delta E = \frac{h^2 (N+1)}{8m_e d_0^2 N^2}$$

$$\lambda_{exc} = \frac{c}{\nu_{exc}} = \frac{ch}{\Delta E} = \frac{8m_e d_0^2 N^2}{h (N+1)}$$

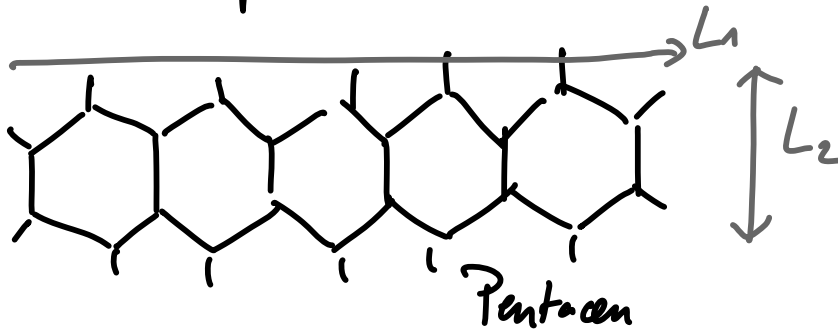
falls  $N \gg 1$  :  $\lambda_{exc} \sim N$

$N$	$\lambda_{calc} [nm]$	$\lambda_{exp} [nm]$	Farbe
6	332	373	uv
8	459	416	v
10	587	516	g
12	716	625	o
14	844	735	r
16	973	848	ir

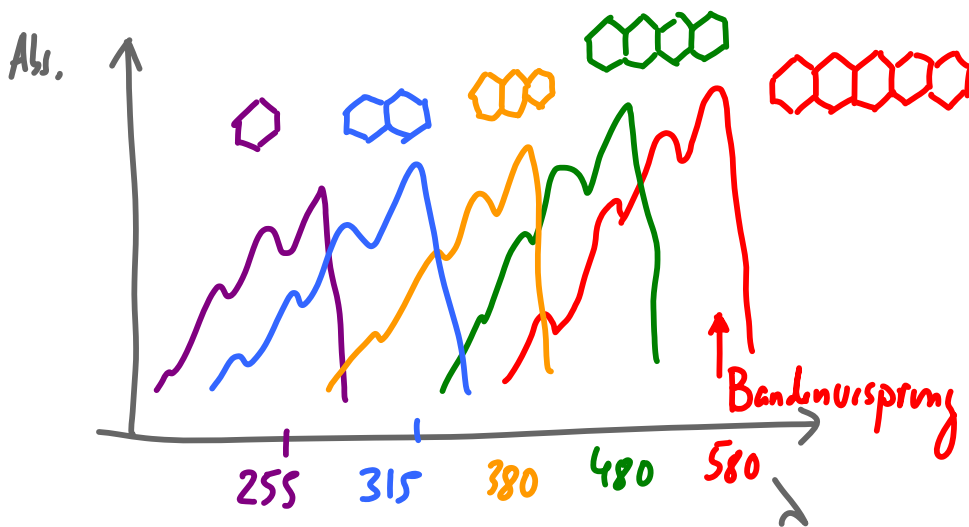


Sehr gute Übereinstimmung mit experimentellen Werten (in Anbetracht der erheblichen Vereinfachung!)  
 Farbe der Moleküle wird präzise vorher gesagt!

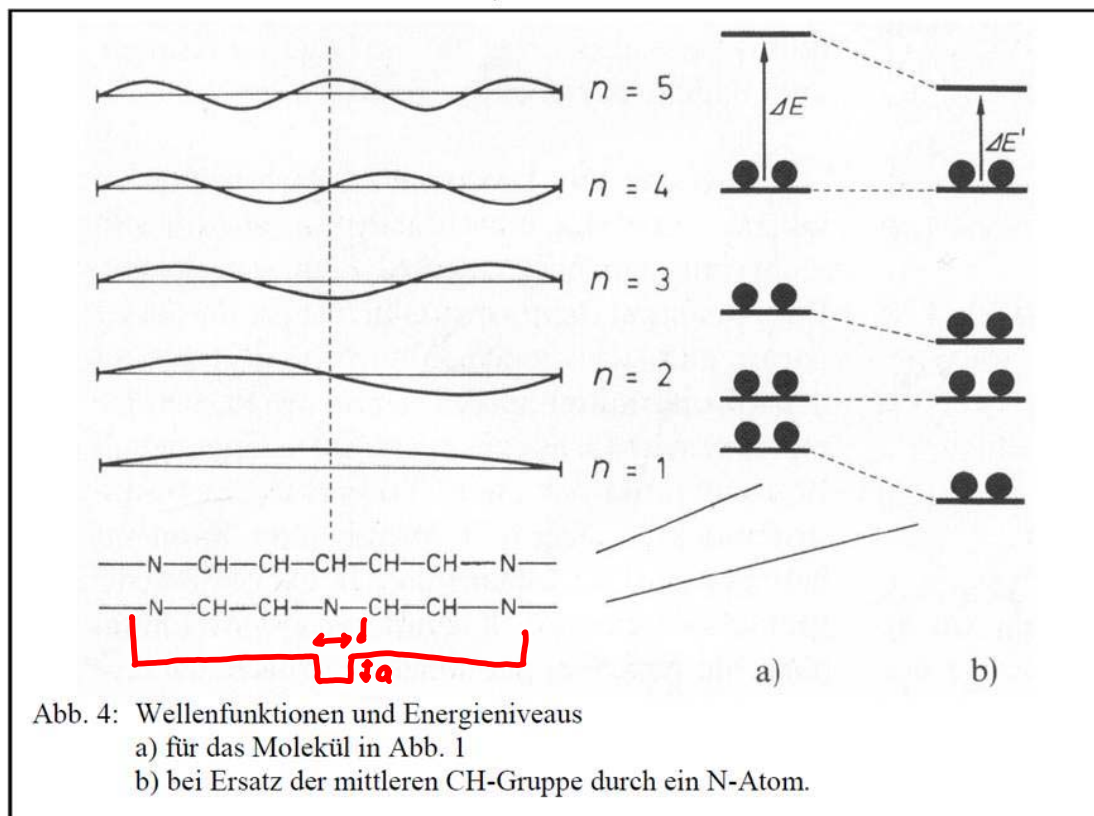
Dasselbe Prinzip kann auch auf Aromaten angewendet werden:



2-dimensionaler Potentialkasten



Durch Einbau von N (anstatt C) kann die Absorptionsfrequenz vergrößert ( $N/2$  ungerade) oder verkleinert ( $N/2$  gerade) werden



Grund dafür ist eine Absenkung des Potentials an der N-Stelle

Die Wellenfunktionen für  $n$  gerade haben an dieser Stelle eine Nullstelle  $\rightarrow$  kein Einfluss auf  $E_n$

Die Wellenfunktionen mit ungeradem  $n$  haben an dieser Stelle ein Maximum  $\rightarrow$  Absenkung der Energie  $E_n$



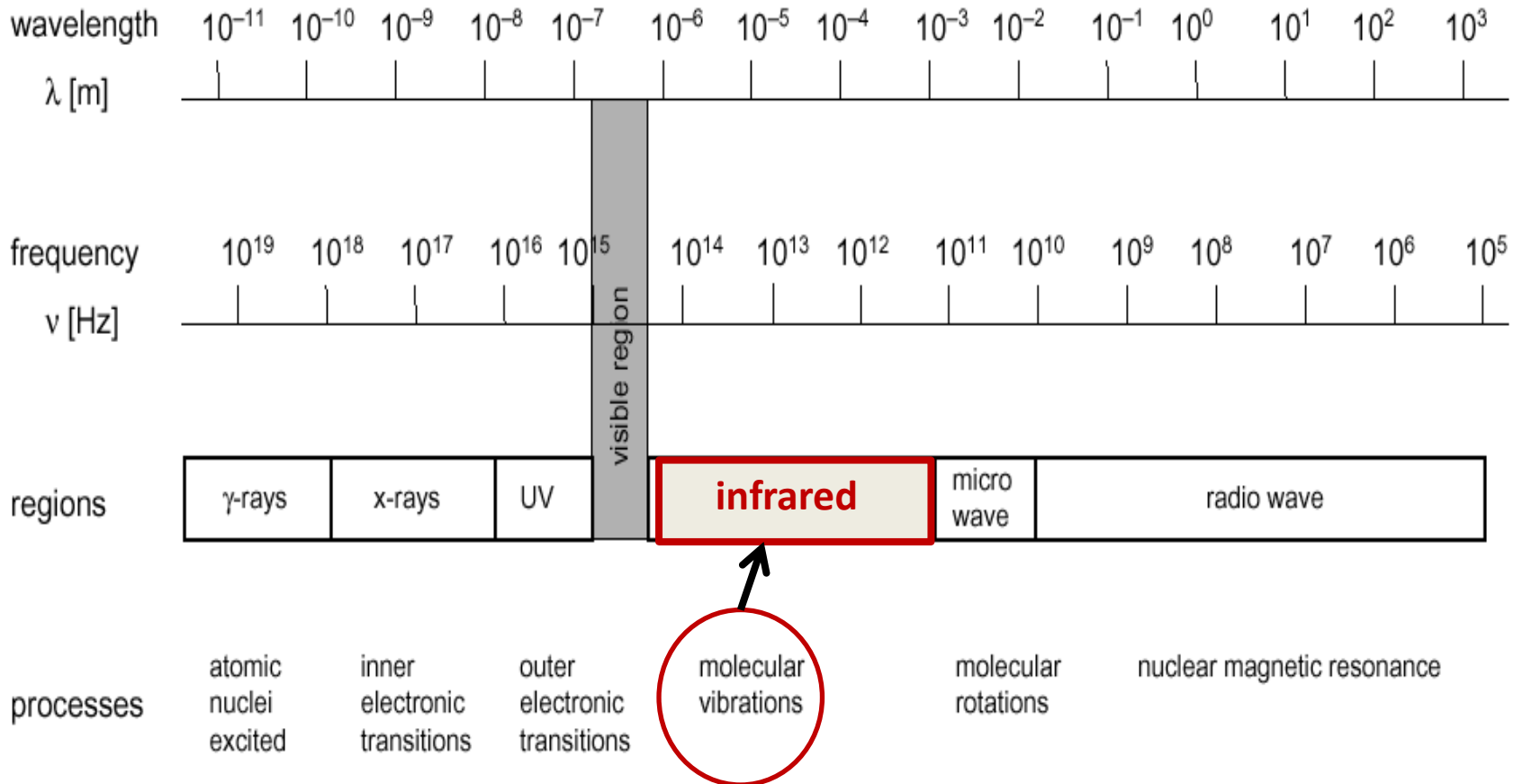


## **10.5.12 lecture PCIII**

# **Chemische Bindung und Molekulare Spektroskopie (Lehramt)**

## **Schwingungsspektroskopie**

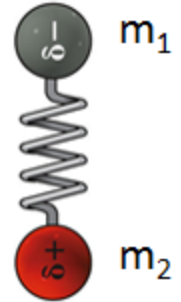
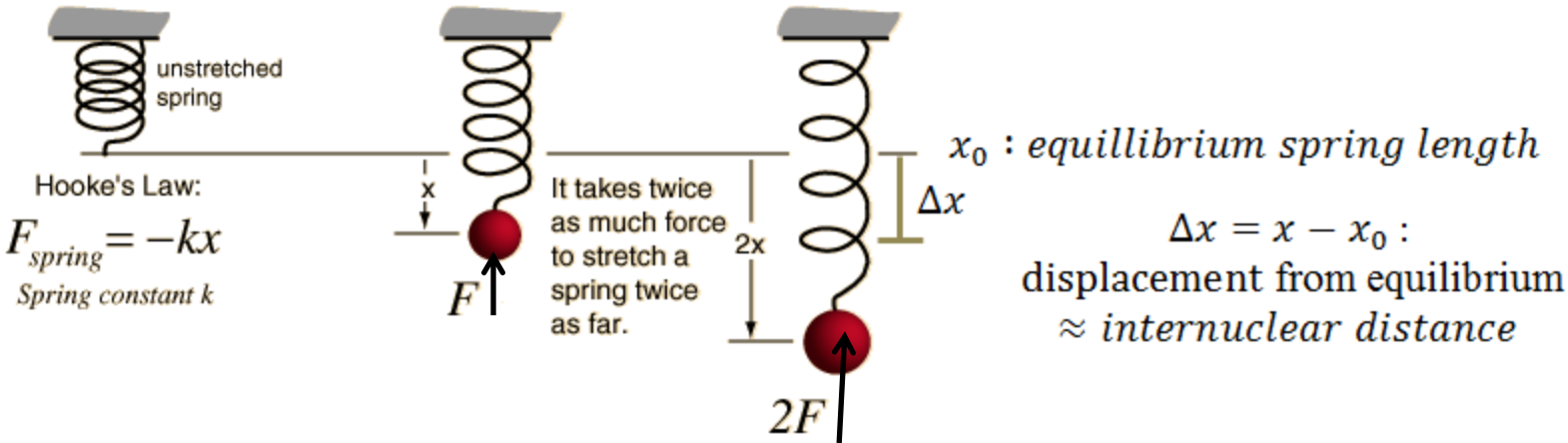
# Whereabouts



# describing molecular vibrations

- Classical model : simple Harmonic Oscillator (SHO)
- Quantum SHO (QSHO)
- first example with potential energy in Hamiltonian operator
- Difference between classic/QM models : Zero Point Energy (ZPE)

# Classical model (Harmonischer Oszillator)



1D-problem

2D-problem

Hook's law      Newton's second law

$$F = -kx, F = ma = m \frac{d^2}{dx^2}$$

$$\frac{d^2}{dx^2} + \left(\frac{k}{m}\right) x = 0$$

$\omega^2$ : oscillation frequency

$$x(t) = A(\sin \omega t + b)$$

$$\omega_{osc} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \text{ (Hz)}, \mu = \frac{m_1 m_2}{m_1 + m_2}$$

$\mu$  = reduced mass (Reduzierte Masse)

# Quantum SHO (QSHO)

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x)$$

- free particle :  $V(x) = 0$

Quantized systems

- particle in box:  $V(x) = 0$

- vibration :  $V(x) = \frac{1}{2} k x^2$

What makes difference between systems is the potential term definition

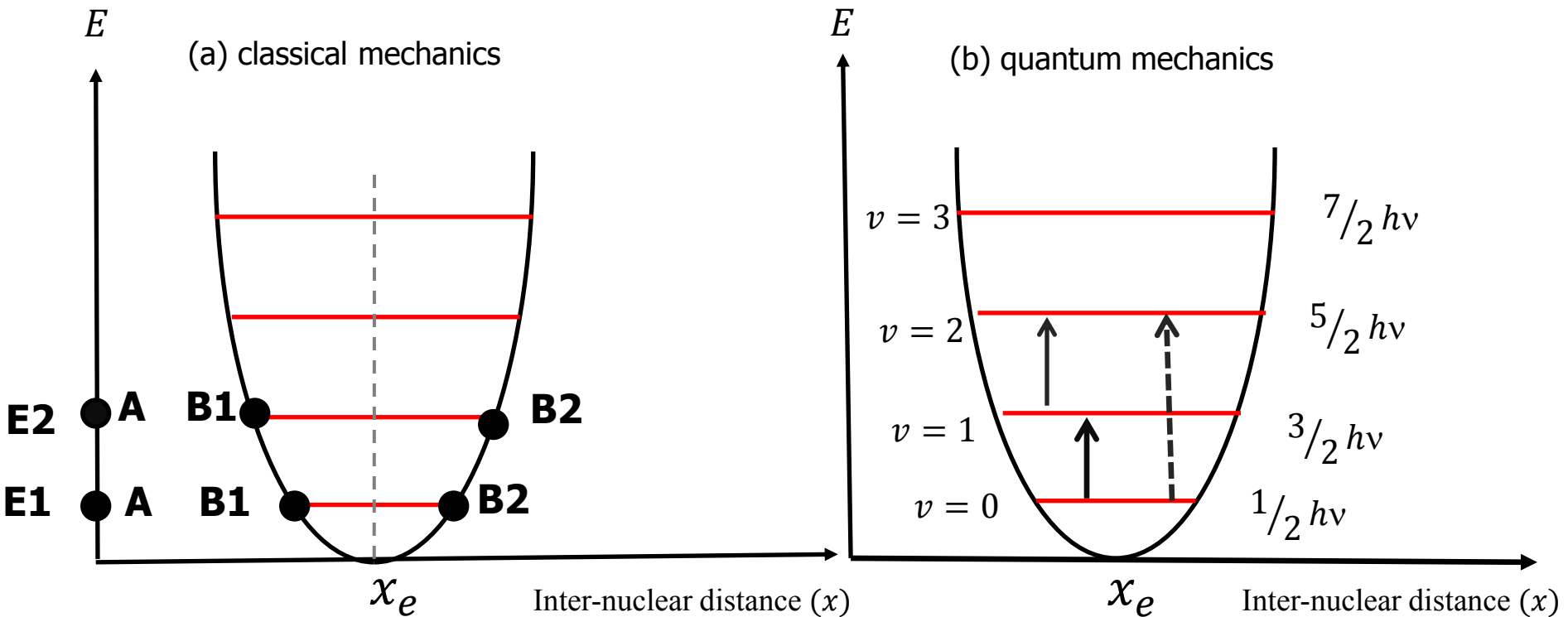
Solutions to the problem :

$$\psi_{vib} = f(x) \cdot \exp\left(-\frac{\alpha x^2}{2}\right) \text{ (vibrational wave function)}$$

$$E_{vib} = \sum_{i=1}^{3N-6} \left(v_i + \frac{1}{2}\right) h\nu, v_i = 0,1,2,3 \text{ (vibrational quantum number)}$$

selection rule :  $\Delta v = \mp 1$

# classical vs. quantum mechanics, energy curves



$$E = \frac{1}{2} k(x - x_e)^2$$

$$x = x_e \rightarrow E = 0$$

$$E_{vib} = (v_i + \frac{1}{2})h\nu$$

- ZPE : Zero point energy =  $\frac{1}{2} h\nu$
- allowed and forbidden transitions (selection rules)
- transition energies =  $h\nu$



# QHSO- wave functions

$$\psi_0 = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2}$$

$$\psi_1 = \sqrt{2} \left(\frac{\alpha}{\pi}\right)^{1/4} \alpha^{1/2} x e^{-\alpha x^2/2}$$

$$\psi_2 = \frac{1}{\sqrt{2}} \left(\frac{\alpha}{\pi}\right)^{1/4} (2\alpha x^2 - 1) e^{-\alpha x^2/2}$$

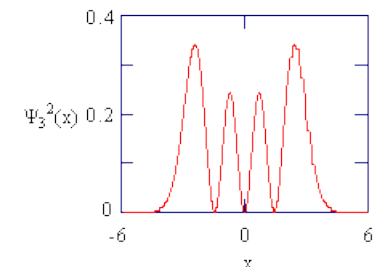
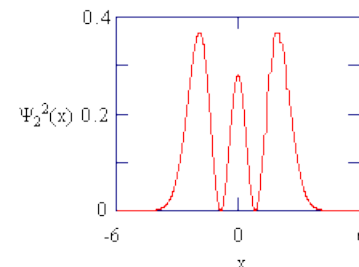
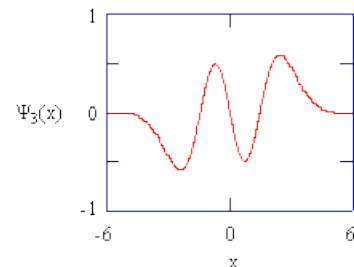
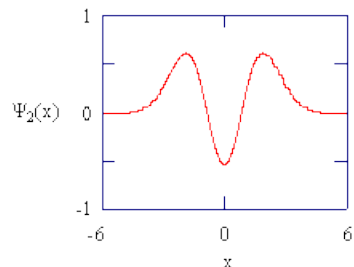
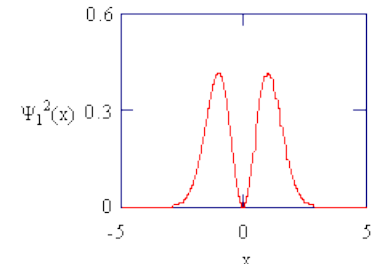
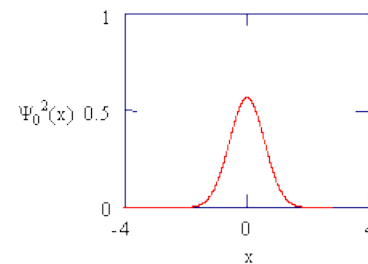
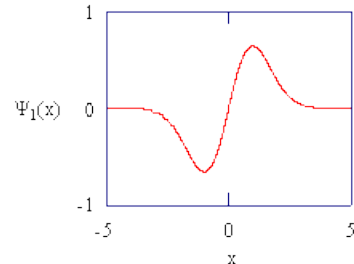
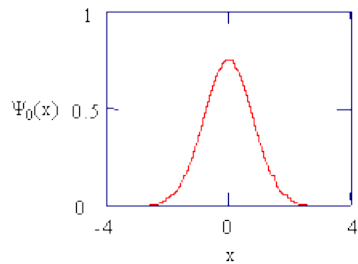
$$\psi_3 = \sqrt{3} \left(\frac{\alpha}{\pi}\right)^{1/4} (2\alpha^{3/2} x^3/3 - \alpha^{1/2} x) e^{-\alpha x^2/2}$$

$$\psi_4 = \frac{1}{\sqrt{6}} \left(\frac{\alpha}{\pi}\right)^{1/4} (2\alpha^2 x^4 - 6\alpha x^2 + 3/2) e^{-\alpha x^2/2}$$

$$\psi_5 = \frac{1}{\sqrt{15}} \left(\frac{\alpha}{\pi}\right)^{1/4} (2\alpha^{5/2} x^5 - 10\alpha^{3/2} x^3 + 15\alpha^{1/2} x/2) e^{-\alpha x^2/2}$$

$$\psi_\nu = \left(\frac{1}{2^\nu \nu!}\right)^{1/2} \left(\frac{\alpha}{\pi}\right)^{1/4} H_\nu(\alpha^{1/2} x) e^{-\alpha x^2/2}, \quad \alpha = \mu\omega/\hbar$$

Hermite polynomials



# Normal modes (Normalschwingungen)

linear molecule:  $3N - 5$

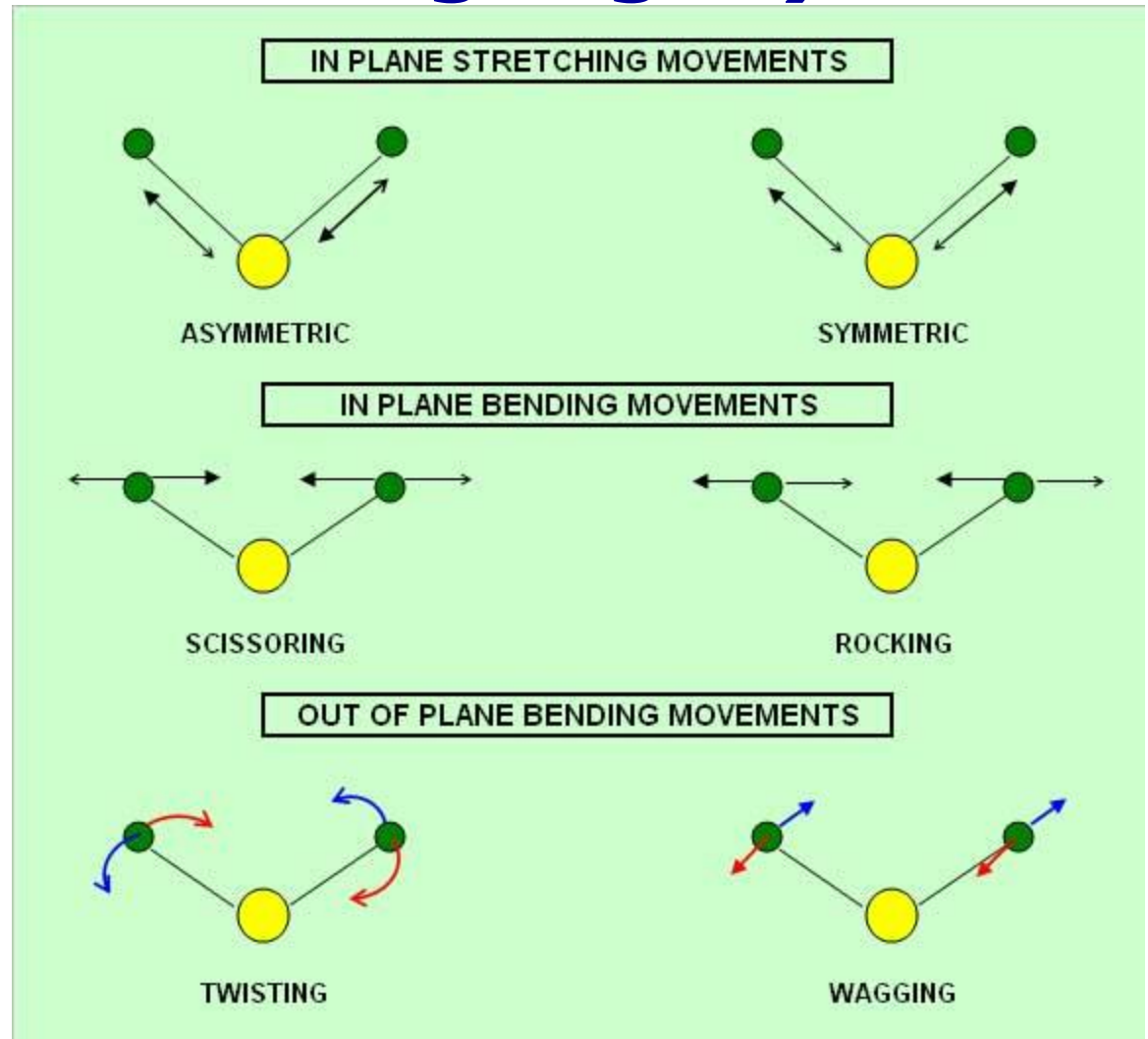
non linear molecule:  $3N - 6$

basic movements:

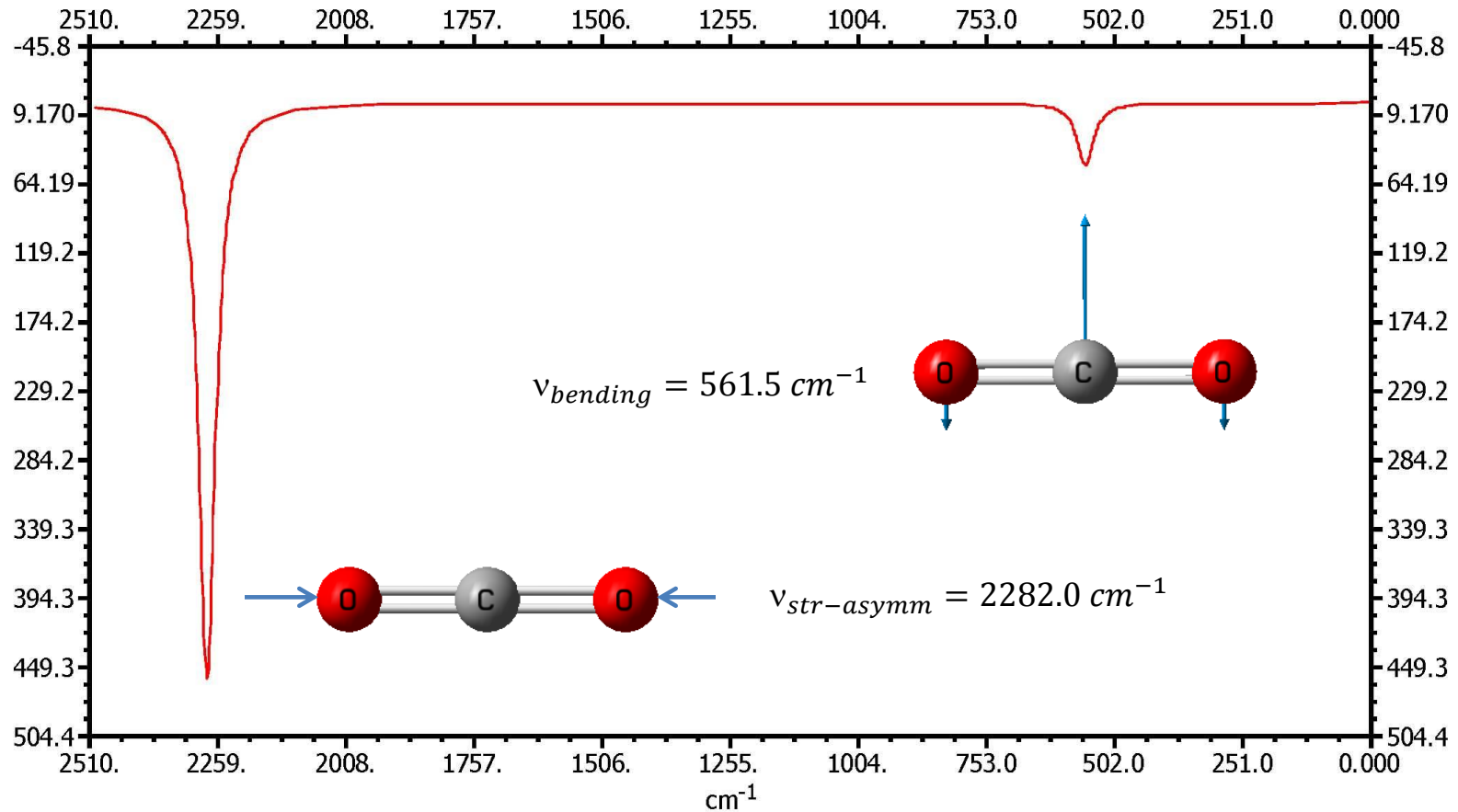
1,2) stretching (symm – asymm)  
(Symmetrische/Asymmetrische  
Streckschwingung)

3) bending  
(Deformationsschwingungen  
Oder Biege/Beugeschwingungen)

$$\nu_{str-asymm} > \nu_{str-symm} > \nu_{bend}$$



# Example 1: linear carbon dioxide

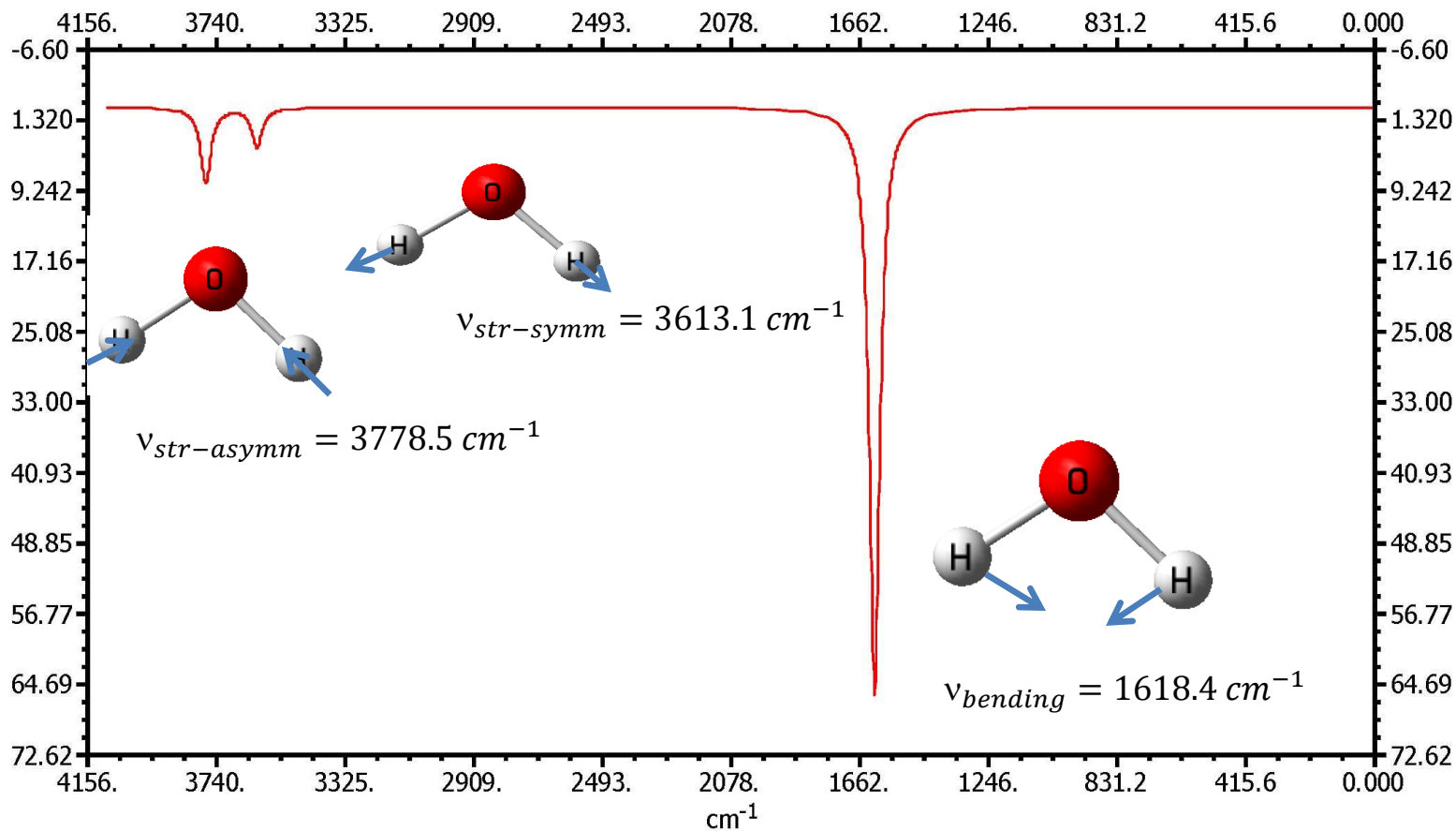


$$\neq \text{normal modes} : 3N - 5 = 4,$$

**experimental values** :  $\nu_{\text{str-asyymm}} = 2349 \text{ cm}^{-1} > \nu_{\text{str-symm}} = 1340 \text{ cm}^{-1} > \nu_{\text{bending}} = 667 \text{ cm}^{-1}$

**Points to remember: line intensity, degeneracy**

# Example2: non linear water

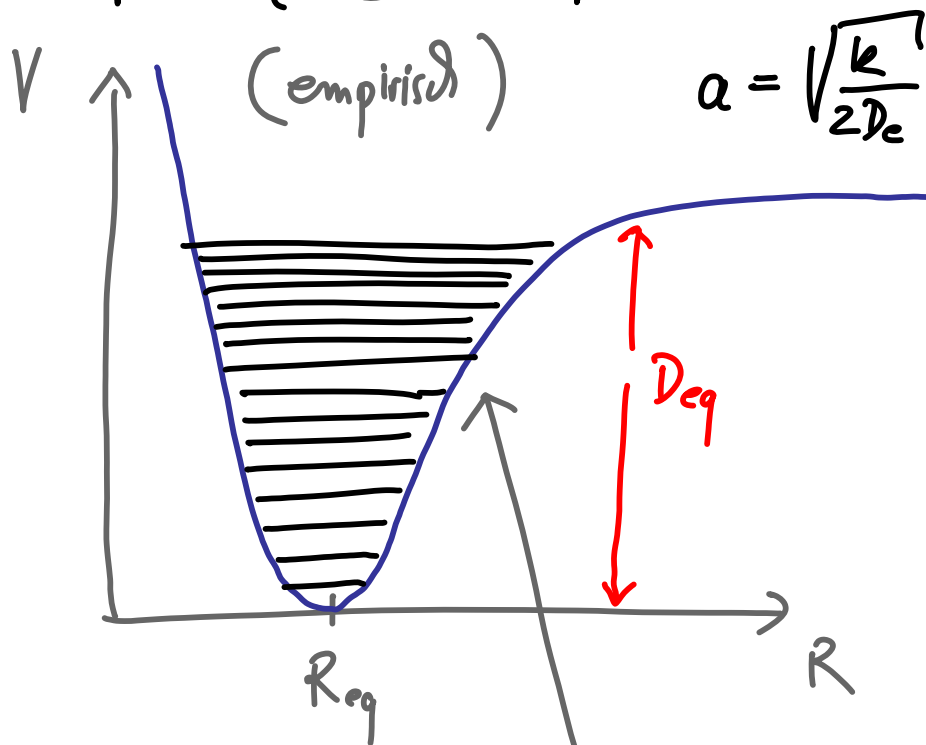


$$\neq \text{normal modes} : 3N - 6 = 3,$$

**experimental values** :  $\nu_{str-asymm} = 3755.9 \text{ cm}^{-1} > \nu_{str-symm} = 3657.1 \text{ cm}^{-1} > \nu_{bending} = 1594.7 \text{ cm}^{-1}$

## Anharmonischer Oszillator (Morse Potential)

$$V = D_e \cdot [1 - \exp(a(R_{eq} - R))]^2$$



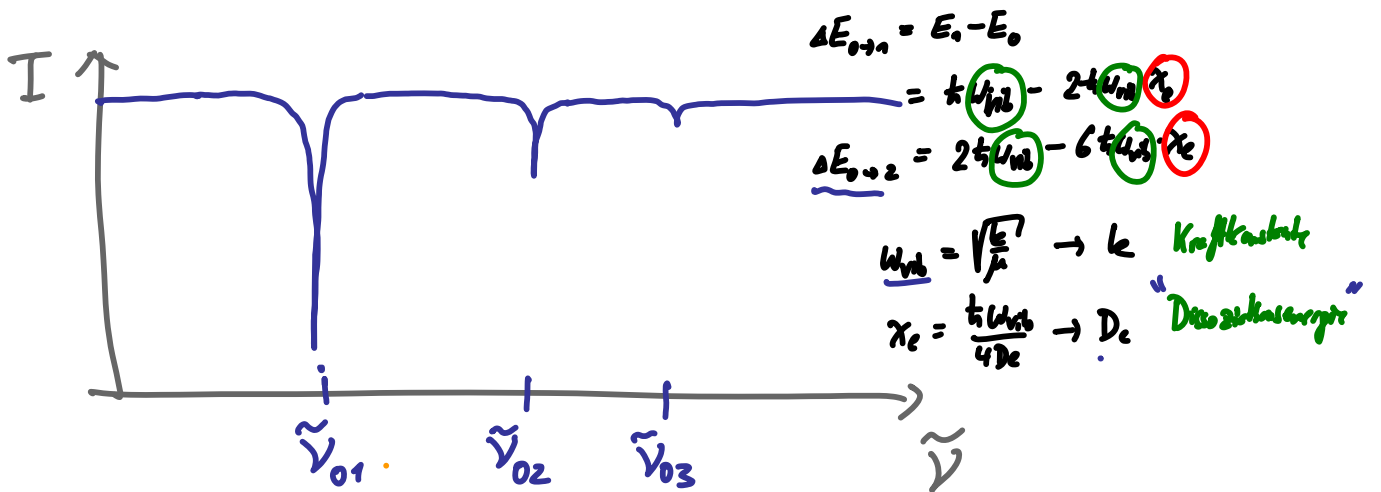
E-Niveaus nicht mehr  
äquidistant

$$E_\nu = \hbar \left( \nu + \frac{1}{2} \right) \omega_{vib} - \hbar \left( \nu + \frac{1}{2} \right)^2 \omega_{vib} \cdot x_e$$

$$x_e : \text{Anharmonizitätskonstante} = \frac{\hbar \omega_{vib}}{4D_e} \ll 1$$

$$\text{Dissoziationsenergie } E_{dis} = D_e - \frac{\hbar \omega_{vib}}{2}$$

Auswahlregeln für Absorption  $\Delta \nu = \pm 1, \pm 2, \pm 3$   
 da anharm. Oszill.  
 sind wech. Intensität



→  $k$  (Bindungskonstante)  
 →  $E_{dis}$  (Dissoziationsenergie)

### Beispiele

Molekül	$\tilde{\nu}_{vib} [cm^{-1}]$	$\chi_e$	$k [\frac{N}{m}]$	$D_e [\frac{kcal}{mol}]$
HF	4138.5	0.0218	966	135
HBr	2649.7	0.0171	412	87
HI	2309.5	0.0172	319	71
CO	2169.7	6.0061	1902	257
NO	1904.0	0.0073	1595	150
N <sub>2</sub>	2330.7		2260	227

Auswahlregeln für IR - Vibrationspektroskopie:

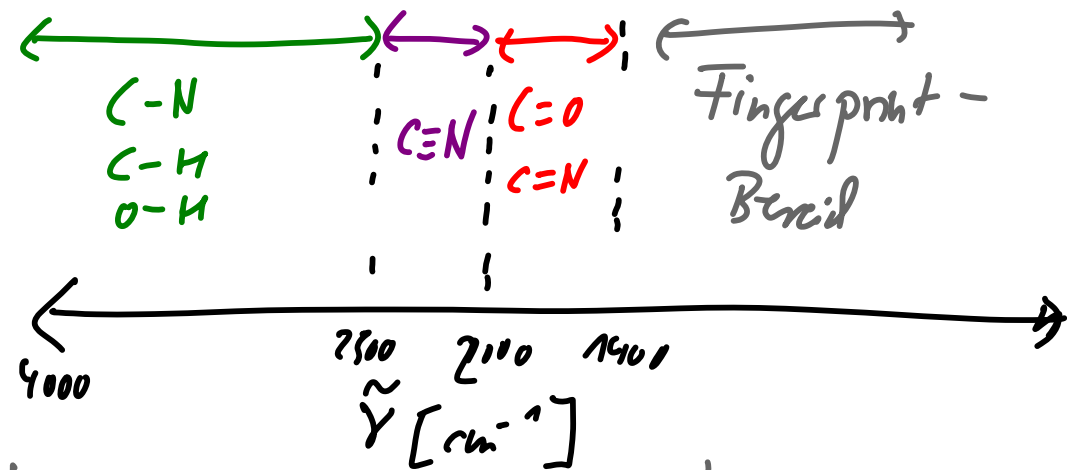
1)  $\nu_{\text{ex}} = \Delta E/h$ ,  $\Delta E = E_i - E_f$  ( $i, f \in 1, 2, \dots$ )

2)  $n_i \neq 0$ , Besetzung nach Boltzmann-Gesetz  

$$\frac{n_i}{n_0} = e^{-(E_i - E_0)/kT}$$

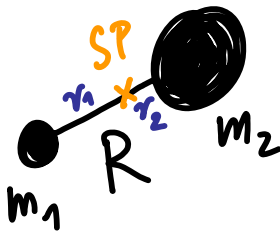
3)  $\left(\frac{\partial \mu}{\partial x}\right)_0 \neq 0$  Änderung des elektr. Dipols des Moleküls bei Schwingung.

Für mehratomige Moleküle gibt es  $3N - 6$  Normalschwingungen  
 (für lineare Moleküle  $3N - 5$ )



Schwingungen von spez. Teilgruppen des Moleküls

# Rotation von Molekülen



Bestimme SP des Moleküls:

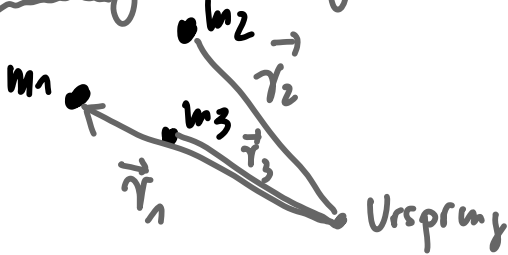
Es muß gelten

$$\left. \begin{aligned} r_1 \cdot m_1 &= r_2 \cdot m_2 \\ r_1 + r_2 &= R \end{aligned} \right\} \begin{aligned} r_1 &= \frac{m_2}{M} \cdot R \\ r_2 &= \frac{m_1}{M} \cdot R \end{aligned}$$

Ausgedrückt über red. Masse  $\mu = \frac{m_1 \cdot m_2}{m_1 + m_2}$ :  $M = m_1 + m_2$

$$\begin{aligned} r_1 &= \frac{\mu}{m_1} \cdot R \\ r_2 &= \frac{\mu}{m_2} \cdot R \end{aligned}$$

Bemerkung: Für allgemeine Moleküle (mehr als 2 Atome)



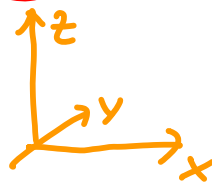
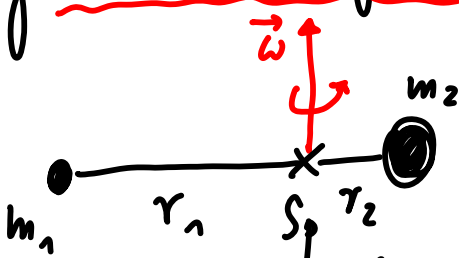
SP in diesem Koordinatensystem:

$$\vec{r}_{sp} = \sum_{i=1}^3 m_i \cdot \vec{r}_i$$

Neues Schwerpunktsystem:

$$\vec{r}_i' = \vec{r}_i - \vec{r}_{sp}$$

# Drehung von 2-atomigem Molekül (klassisch)



Koordinatensystem  $x \parallel R$

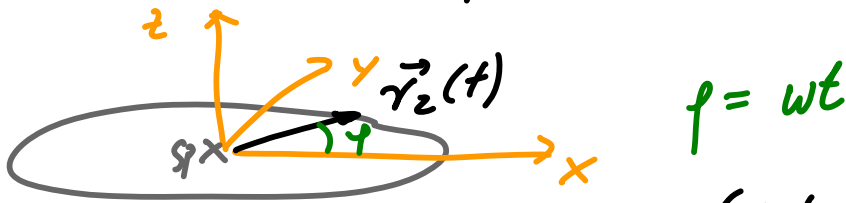
Drehung des Moleküls (bspweise um z-Achse) mit Winkelgeschwindigkeit  $\omega$

$$\vec{\omega} = \begin{pmatrix} 0 \\ 0 \\ \omega \end{pmatrix}$$



Beschreibung von den Vektoren  $\vec{r}_1$  und  $\vec{r}_2$  bei Rotation:

$$\vec{r}_2(t=0) = \begin{pmatrix} r_2 \\ 0 \\ 0 \end{pmatrix} \quad \vec{r}_2(t) = \begin{pmatrix} r_2 \cdot \cos(\omega t) \\ r_2 \cdot \sin(\omega t) \\ 0 \end{pmatrix}$$



Kinetische Energie für Rotation (klassisch)

$$E_{rot} = \frac{1}{2} I_{\omega} \cdot \omega^2$$

$I_{\omega}$ : Trägheitsmoment für Rotation um Achse  $\vec{\omega}$

Berechnung des Trägheitsmoment:  $I_{\omega} = \sum_{i=1}^n m_i \underbrace{r_{iL}^2}_{\substack{n \text{ Atome} \\ \text{Abstand von Dreh-} \\ \text{achse}}}$

2-atomiges Molekül:

$$I_z = I_y = m_1 r_1^2 + m_2 r_2^2 = \mu R^2 \rightarrow E_{rot} = \frac{1}{2} \mu R^2 \omega^2$$

$$I_x = 0 \rightarrow E_{rot} = 0$$

im Allgemeinen:

$$I_{\omega} = \frac{\vec{\omega}}{\omega} \cdot \tilde{I} \cdot \frac{\vec{\omega}}{\omega} \quad \tilde{I}: \text{Trägheitstensor (3x3 Matrix)}$$

$$= \begin{pmatrix} \frac{\omega_x}{\omega} & \frac{\omega_y}{\omega} & \frac{\omega_z}{\omega} \end{pmatrix} \begin{pmatrix} I_{xx} & I_{xy} & I_{xz} \\ I_{yx} & I_{yy} & I_{yz} \\ I_{zx} & I_{zy} & I_{zz} \end{pmatrix} \begin{pmatrix} \frac{\omega_x}{\omega} \\ \frac{\omega_y}{\omega} \\ \frac{\omega_z}{\omega} \end{pmatrix}$$

Zeilenvektor                      3x3 Matrix                      Spaltenvektor

$$I_{xx} = \sum_{i=1}^N m_i (y_i^2 + z_i^2)$$

$$\vec{r}_i = \begin{pmatrix} x_i \\ y_i \\ z_i \end{pmatrix}$$

$$I_{yy} = \sum_{i=1}^N m_i (x_i^2 + z_i^2)$$

$$I_{zz} = \sum_{i=1}^N m_i (x_i^2 + y_i^2)$$

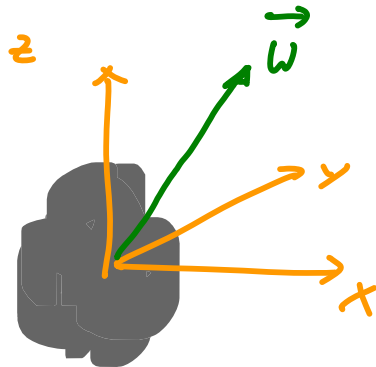
$$I_{xy} = I_{yx} = - \sum_i m_i x_i y_i$$

$$I_{xz} = I_{zx} = - \sum_i m_i x_i z_i$$

$$I_{yz} = I_{zy} = - \sum_i m_i y_i z_i$$

Symmetrische Matrix

Allgemeine Bezeichnung  
vom Trägheitsmoment  $\tilde{I}$   
im KS  $(x, y, z)$



$$E_{rot} = \frac{1}{2} \tilde{I} \omega^2 = \frac{1}{2} \frac{\vec{\omega}}{\omega} \tilde{I} \frac{\vec{\omega}}{\omega} \cdot \omega^2 = \frac{1}{2} \vec{\omega} \tilde{I} \vec{\omega}$$

beim 2-atomigen Molekül:

$$\tilde{I} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & \mu R^2 & 0 \\ 0 & 0 & \mu R^2 \end{pmatrix}$$

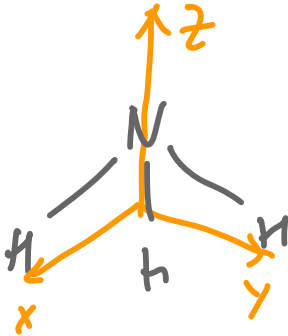
Bemerkung: Es läßt sich für jedes Molekül ein Koordinatensystem finden, in dem  $\tilde{I}$  diagonal ist

$$\tilde{I} = \begin{pmatrix} I_{xx} & 0 & 0 \\ 0 & I_{yy} & 0 \\ 0 & 0 & I_{zz} \end{pmatrix}$$

$I_{xx}, I_{yy}, I_{zz}$  : Hauptträgheitsmomente  
 $x, y, z$  Hauptträgheitsachsen

Das Achsensystem wird durch Molekülsymmetrie vorgegeben

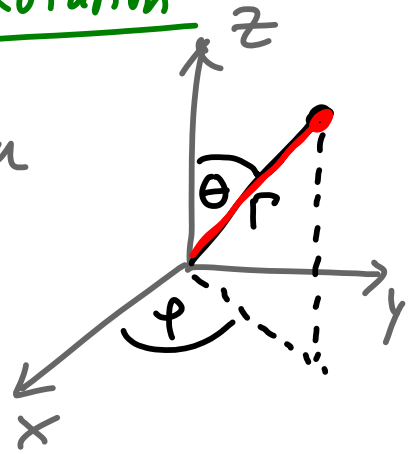
Bsp.



( $x, y$  können beliebig  $\perp$  zu  $z$  gewählt werden)

## Quantenmechanische Formelung für Rotation

1) Wähle Kugelkoordinaten



$$\hat{\mathcal{H}}_{\text{rot}} = -\frac{\hbar^2}{2\mu} \underbrace{\Delta_{r,\theta,\varphi}}_{\text{Laplace-Operator in Kugelkoordinaten}}$$

$$\Delta_{r,\theta,\varphi} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \left( \sin \theta \frac{\partial}{\partial \theta} \right)$$

Bei starrem Rotor ( $R = \text{konst}$ )

$$\rightarrow \text{erster Term } \frac{\partial}{\partial r} = 0$$

$$\hat{\mathcal{H}}_r \psi_r(\theta, \varphi) = E_r \psi_r(\theta, \varphi)$$

$$-\frac{\hbar^2}{2\mu R^2 \sin^2 \theta} \left\{ \frac{\partial^2 \psi}{\partial \varphi^2} + \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \psi}{\partial \theta} \right) \right\} = E_r \psi$$

Lösungen: 
$$E_J = J(J+1) \underbrace{\frac{\hbar^2}{2I}}_B$$

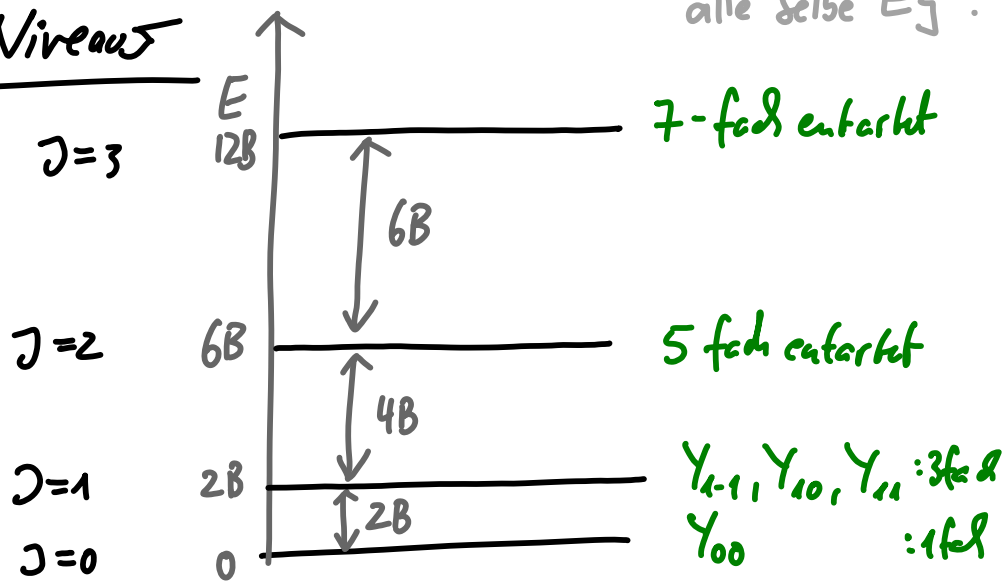
B: Rotationskonstante in J

$J = 0, 1, 2, 3, \dots$

$\psi_r(\theta, \varphi) = Y_{J,K}$  Kugelwellenfunktionen

$K = -J, \dots, +J$   
alle selbe  $E_J$ !

1) E - Niveaus



- $E_{rot}$  ist ebenfalls diskret!
- E-Abstände steigen nach oben an
- E-Niveaus haben Entartungsgrad  $(2J+1)$

## 2) Wellenfunktionen:

$$Y_{00} = \frac{1}{\sqrt{4\pi}}$$

$$Y_{10} = \sqrt{\frac{3}{4\pi}} \cos\theta$$

$$Y_{11} = \sqrt{\frac{3}{8\pi}} \sin\theta e^{i\varphi}$$

$$Y_{1-1} = \sqrt{\frac{3}{8\pi}} \sin\theta e^{-i\varphi}$$

Normierungsbedingung

$$\int_0^{2\pi} \int_0^{\pi} Y_{00}^* Y_{00} \underbrace{\sin\theta d\theta d\varphi}_{\text{in Kugelkoordin.}} = 1$$

} komplex

### Bemerkung:

Diese Gleichung entspricht vollständig dem Bahndrehimpuls des  $e^-$  im H-Atom

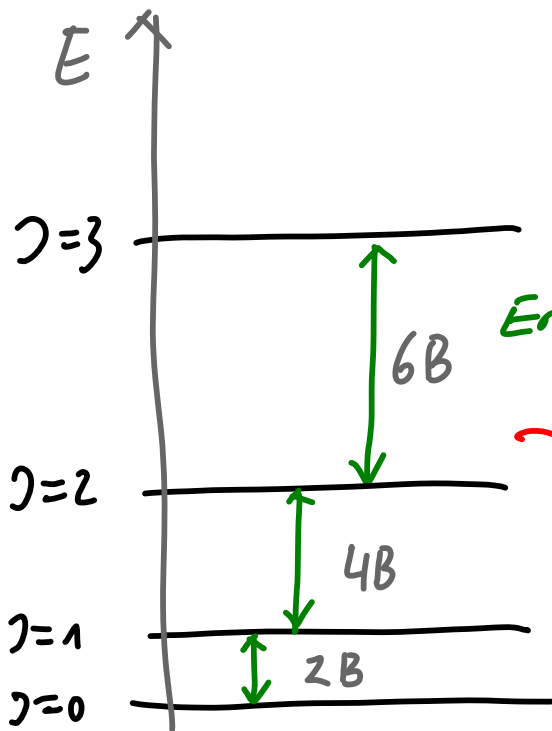
→ Gleiche mathematische Lösungen wie dort, aber jetzt Rotation von Molekül

### 3) Auswahlregeln für Rotations-Spektroskopie

- $\mu_e \neq 0$  Molekül muss elektr. Dipolmoment besitzen
- $\Delta J = \pm 1$  folgt aus den Kugelwellenfktn.
- $n_J \neq 0$  Niveaumüssen besetzt sein

also:

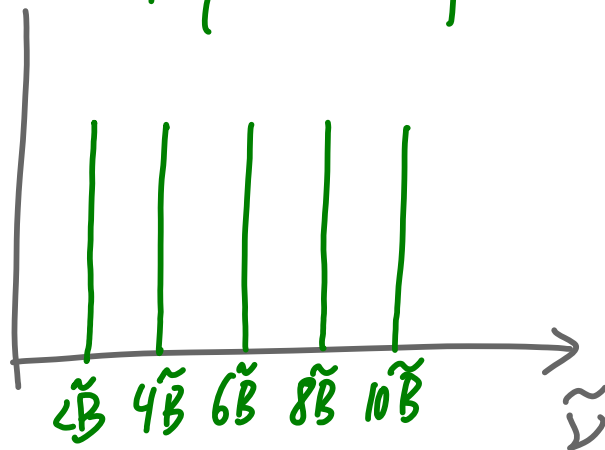
$$\tilde{B} = \frac{B}{h \cdot c} \quad , \quad B = \frac{\hbar^2}{2I}$$



Erlaubte Absorptions-Übergänge

Äquidistante Spektrallinien

Frequenzbereich ist im MW-Bereich



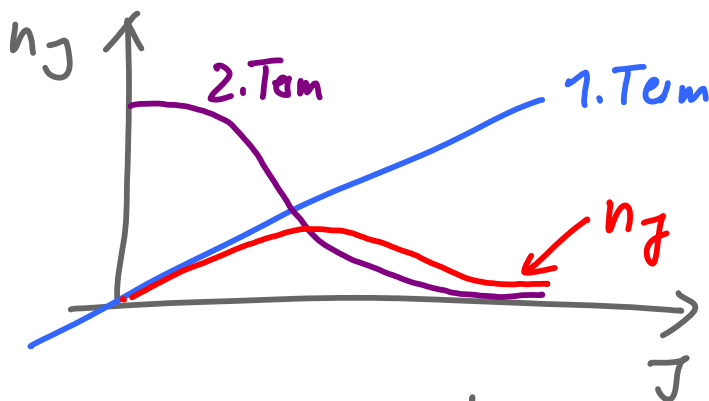
Die Intensitäten der Spektrallinien ergeben sich aus Besetzungszahl  $n_j$  der entsprechenden Niveaus

$$\frac{n_j}{n_0} = \left( \frac{g_j}{g_0} \right) \cdot e^{-\frac{(E_j - E_0)}{kT}}$$

$g_0$ : Entartungsgrad =  $2J+1$

$$E_0 = 0(J+1)B, \quad E_0 = 0$$

$$\hookrightarrow \frac{n_j}{n_0} = (2J+1) \cdot e^{-\frac{J(J+1)B}{kT}}$$



Maximum in  $n_j$ :  $0 = \frac{\partial}{\partial J} \left( \frac{n_j}{n_0} \right)$

$$J_{\max} = \sqrt{\frac{kT}{2B}} - \frac{1}{2}$$

erlaubt Bestimmung der Temperatur



**21.06.12 lecture PCIII**

**Chemische Bindung und  
Molekulare Spektroskopie  
(Lehramt)**

**Raman-Spektroskopie**

# RAMAN Spectroscopy



Sir C.V.Raman (1788-1970)

- Discovered the *inelastic scattering phenomenon* in 1928,
- Was awarded the Nobel Prize for Physics for his work on the scattering of light and for the discovery of the effect named after him in 1930.

[http://nobelprize.org/nobel\\_prizes/physics/laureates/1930/raman-lecture.pdf](http://nobelprize.org/nobel_prizes/physics/laureates/1930/raman-lecture.pdf)

*Nature* 121, 501-502 (31 March 1928)  
A New Type of Secondary Radiation  
C. V. RAMAN & K. S. KRISHNAN

*Nature* 121, 619-619 (21 April 1928)  
A Change of Wave-length in Light Scattering  
C. V. RAMAN

FURTHER observations by Mr. Krishnan and myself on the new kind of light-scattering discovered by us have been made and have led to some very surprising and interesting results.

In order to convince ourselves that the secondary radiation observed by us was a true scattering and not a fluorescence, we proceeded to examine the effect in greater detail. The principal difficulty in observing the effect with gases and vapours was its excessive feebleness. In the case of substances of sufficient light-scattering power, this difficulty was overcome by using an enclosed bulb and heating it up so as to secure an adequate density of vapour. Using a blue-violet filter in the track of the incident radiation was complementary green-yellow scattered radiation was observed with a number of organic vapours, and it was even possible to determine its state of polarisation. It was found that in certain cases, for example pentane, it was strongly polarised, while in others, for example naphthalene, it was unpolarised. Liquid carbon dioxide was studied, and a note was published in the *Proceedings of the Royal Society* in 1928.



Was ist Lichtstreuung?

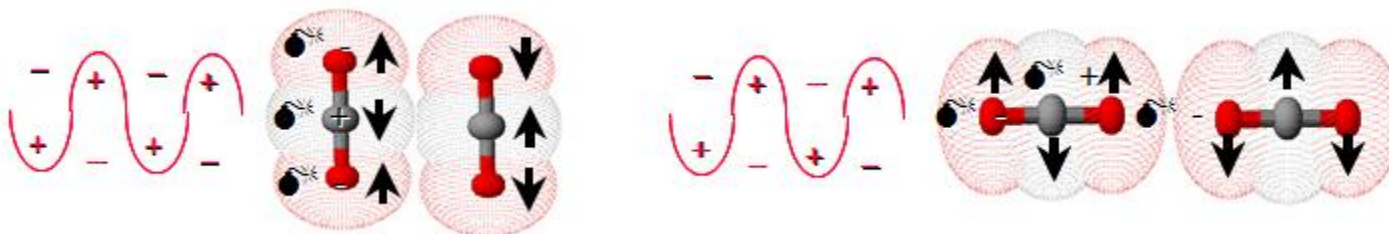
Raman-Streuung und Rayleigh-Streuung

# IR and RAMAN spectroscopies-I

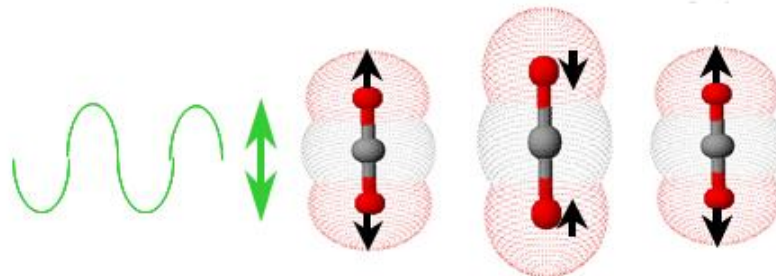
- Raman spectroscopy probes the vibration modes of materials, much like infrared (IR) spectroscopy.
- They both results from the same type of quantized vibrational changes. Thus, the difference in wavelength between the incident and scattered visible radiation corresponds to wavelengths in the mid-infrared region.
- However, whereas **IR** bands arise from a **change in the dipole moment**, **Raman** bands arise from a **change in the polarizability**.
- In many cases, transitions that are allowed in Raman are forbidden in IR, so these techniques are often complementary.

# How is Raman Different from IR?

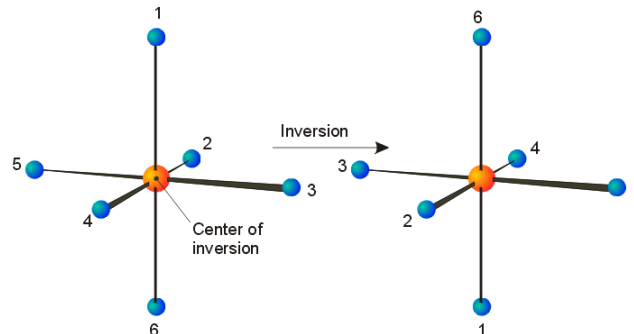
**IR-Change in Dipole Moment :  $\Delta\mu \neq 0$**



**Raman-Change in Polarizability:  $\Delta\alpha \neq 0$**

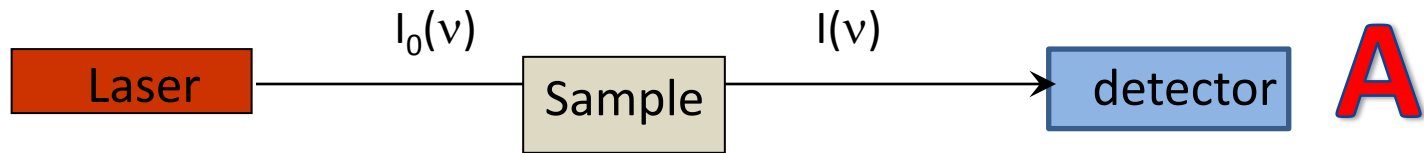


Selection rules are therefore different and can be exclusive for **centrosymmetric** molecules.

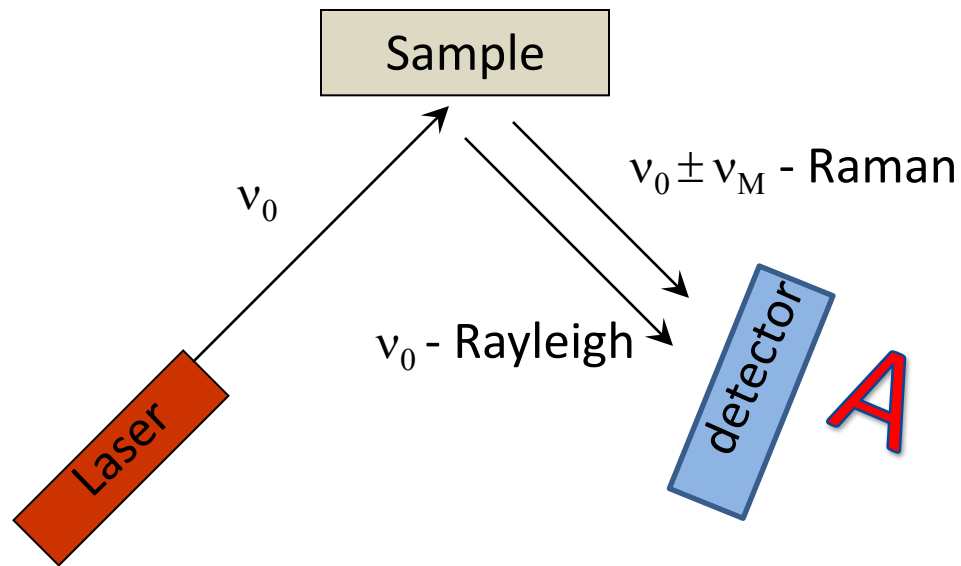


**Rule of mutual exclusion  
(Ausschlußregel)**

# IR Spectrography - Absorption



# Raman Spectrography - Scattering

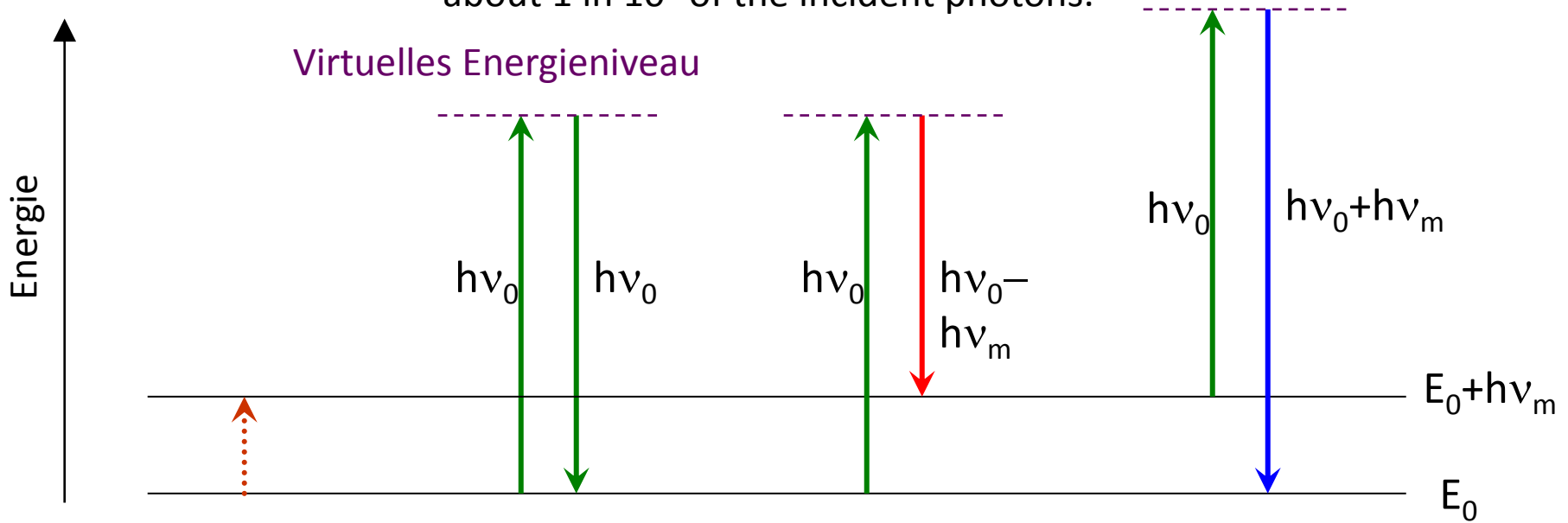


**Elastic scattering (Rayleigh): original frequency shift:  $\nu_0$**

**Inelastic scattering (Raman): with frequency shift:  $\nu_0 \pm \nu_M$**

# Photon scattering energy scheme

The Raman effect comprises a very small fraction, about 1 in  $10^7$  of the incident photons.



**IR Absorption**  
 $\Delta E_{vib} = h\nu_{vib}$

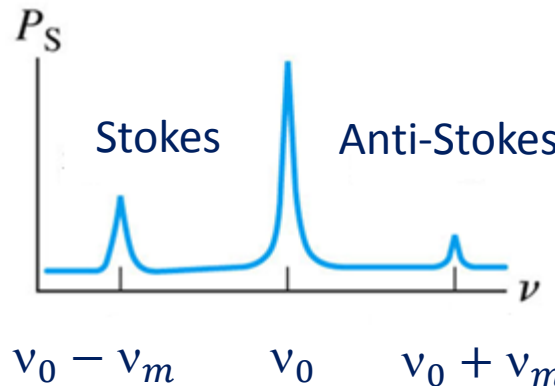
**Rayleigh Streuung (elastic)**

**Stokes Streuung**

**Anti-Stokes Streuung**

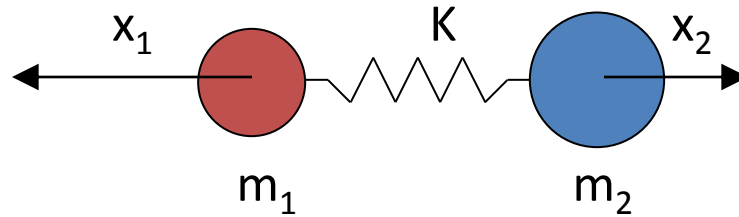
**Raman (inelastic)**

Grundzustand:  $E_0$   
 erster angeregter  
 zustand:  $E_0 + h\nu_m$



Notice: Stokes line is stronger

# Scattering of radiation by diatomic molecule



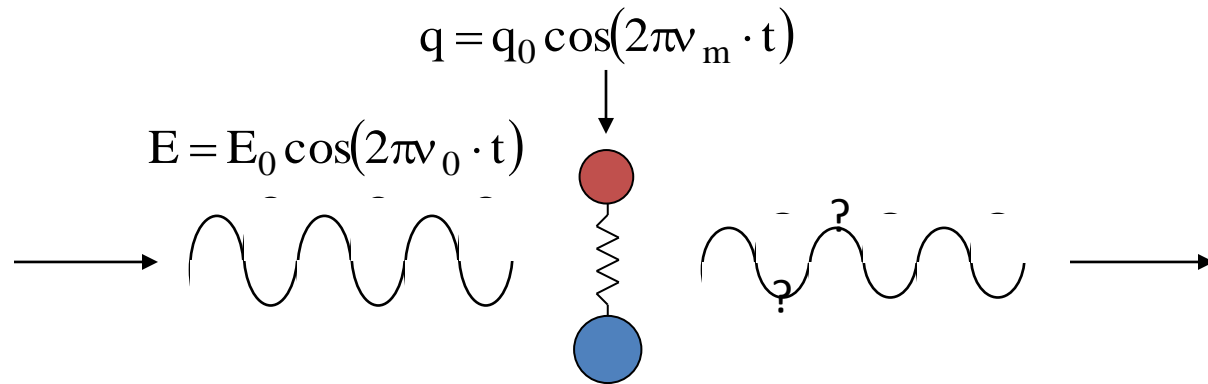
$$\frac{m_1 m_2}{m_1 + m_2} \left( \frac{d^2 x_1}{dt^2} + \frac{d^2 x_2}{dt^2} \right) = -K(x_1 + x_2)$$

Just like  
Hooke's law:  
 $F = kX$

Reduced mass  $\mu$   $\frac{d^2 q}{dt^2} = -K \cdot q$  displacement

$$\Rightarrow q = q_0 \cos(2\pi \nu_m \cdot t)$$

Where:  $\nu_m = \frac{1}{2\pi} \sqrt{\frac{K}{\mu}}$

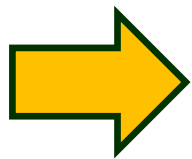


Induced dipole moment:

$$\mu = \alpha \cdot E = \alpha \cdot E_0 \cos(2\pi\nu_0 \cdot t)$$

For a small amplitude of vibration, the polarizability  $\alpha$  is a linear function of  $q$ :

$$\alpha = \alpha_0 + \left( \frac{\partial \alpha}{\partial q} \right)_{q=0} \cdot q + \dots$$



$$\mu = \alpha_0 E_0 \cos(2\pi\nu_0 \cdot t) + \left( \frac{\partial \alpha}{\partial q} \right)_{q=0} \cdot q_0 \cos(2\pi\nu_m \cdot t) \cdot E_0 \cos(2\pi\nu_0 \cdot t) =$$

$$= \alpha_0 E_0 \cos(2\pi\nu_0 \cdot t) + \frac{1}{2} \left( \frac{\partial \alpha}{\partial q} \right)_{q=0} q_0 E_0 [\cos(2\pi\{\nu_0 - \nu_m\} \cdot t) + \cos(2\pi\{\nu_0 + \nu_m\} \cdot t)]$$

Rayleigh  
scattering

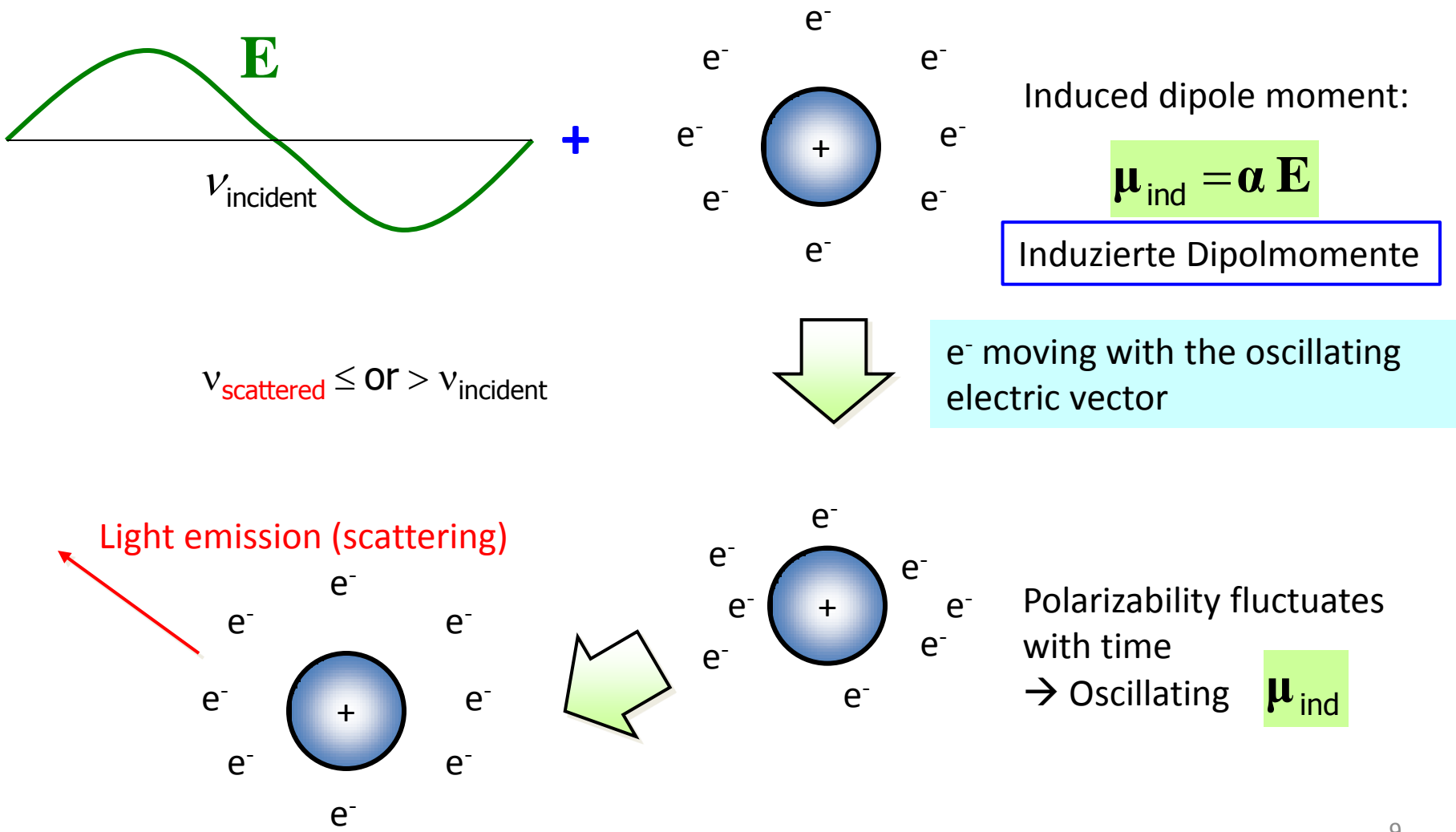
Stokes  
scattering

Anti-Stokes  
scattering

$$\cos A \cdot \cos B = 1/2 [\cos(A + B) + \cos(A - B)]$$

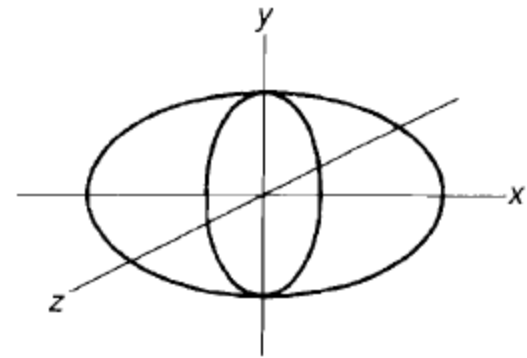


- A **Change in Polarizability** of the Molecules upon Interaction with the Incident Light



$$\begin{bmatrix} \mu_x \\ \mu_y \\ \mu_z \end{bmatrix} = \begin{bmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{bmatrix} \begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix}$$

The polarizability tensor



The polarizability ellipsoid

**Polarizability is affected by**

1- Atomic number Z:

$\mu \propto$  the amount of electrons,  
Electrons become less control by nuclear charge.

2- Bond Length:

$\mu \propto$  Bond Length

3- Atomic or Molecular Size:

$\mu \propto$  Size,

4- Molecular orientation with respect to an electric field

Parallel or perpendicular (Exp: Parallel has more effect)

5- Bond Strength (Bond order):

$\mu \propto$  1/strength of bond C=C, and C $\equiv$ C, C $\equiv$ N bonds are strong scatterers, bonds undergo polarization.

6- Electronegativity difference:

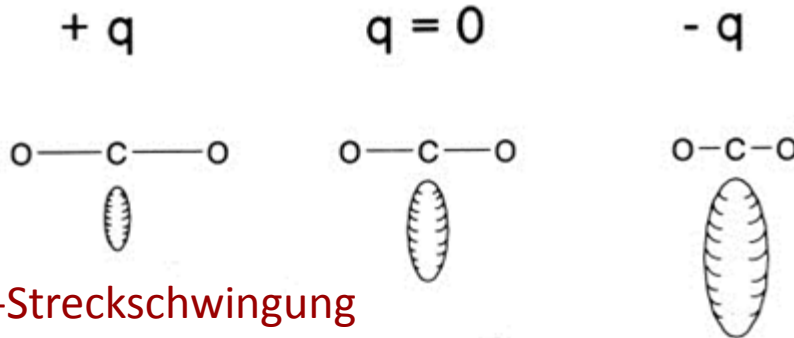
$\mu \propto$  1/ difference in electronegativity

7- Covalent bonds more polarizable than ionic bonds.

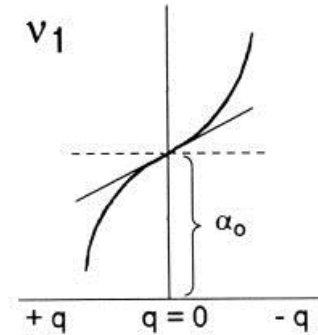
# Example 1: the vibration modes of CO<sub>2</sub>

Ausschlußregel !!!

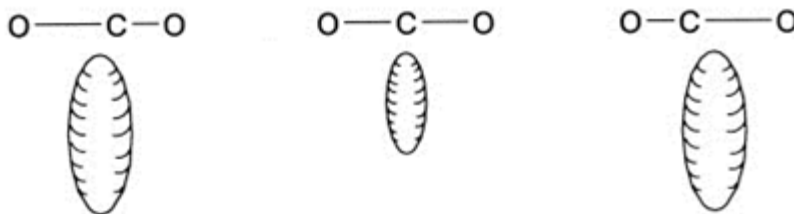
**v<sub>1</sub>**  
Symmetrische-Streckschwingung



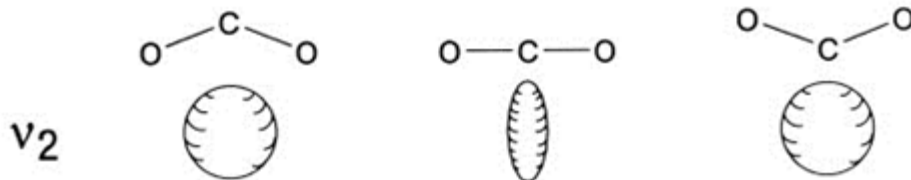
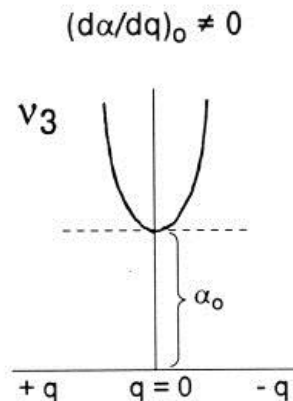
Raman Active



**v<sub>3</sub>**  
Asymmetrische-Streckschwingung



IR Active

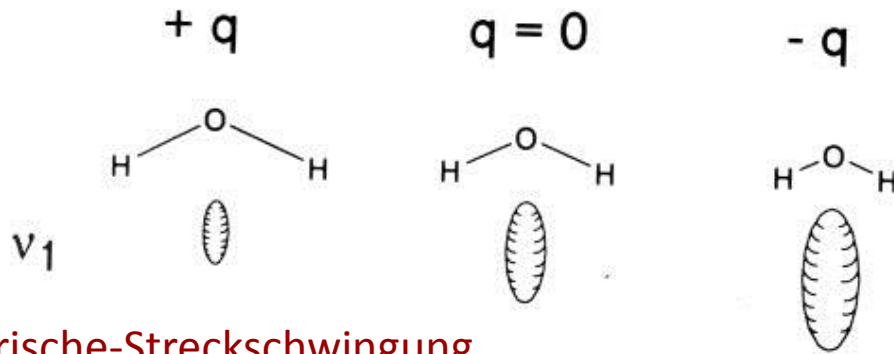


IR Active

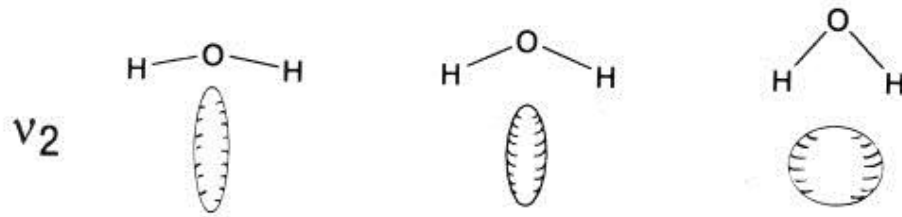
Biegeschwingung

$$P = \alpha_0 E_0 \cos(2\pi\nu_0 \cdot t) + \frac{1}{2} \left( \frac{\partial \alpha}{\partial q} \right)_{q=0} q_0 E_0 [\cos(2\pi\{\nu_0 - \nu_m\} \cdot t) + \cos(2\pi\{\nu_0 + \nu_m\} \cdot t)] \quad 11$$

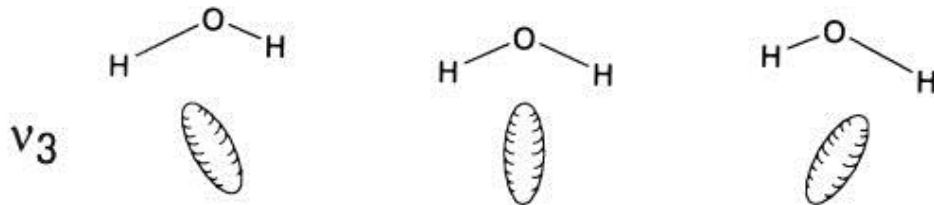
# Example 2: the vibration modes of H<sub>2</sub>O



Symmetrische-Streckschwingung



Biegeschwingung



Asymmetrische-Streckschwingung

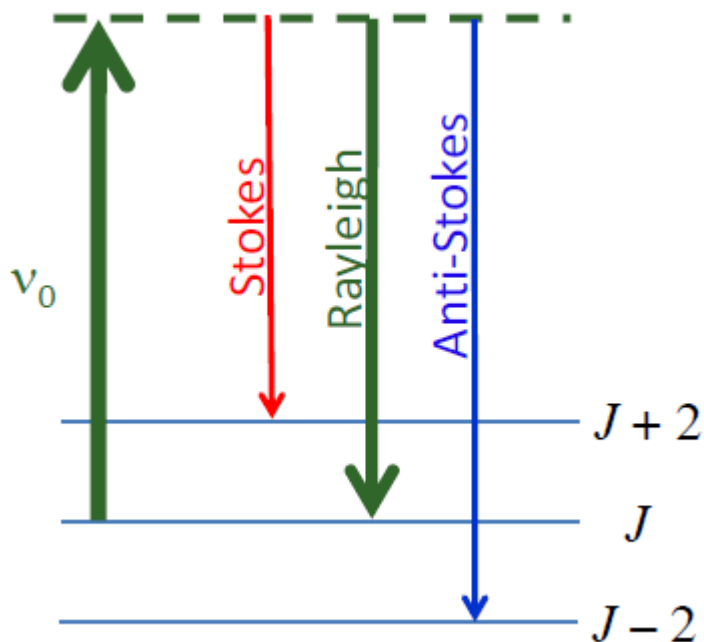
No inversion center!

All the modes are both  
Raman & IR Active

# Selection rules (Auswahlregel)

As a molecule rotates, the polarizability presented to the electric field changes:

- the induced dipole is modulated by rotation,
- results in rotational transitions.



$$\Delta J = 0, \mp 2$$

$\Delta J = 0$  : Rayleigh  
 $\Delta J = +2$  : stokes line  
 $\Delta J = -2$  : Anti-stokes line

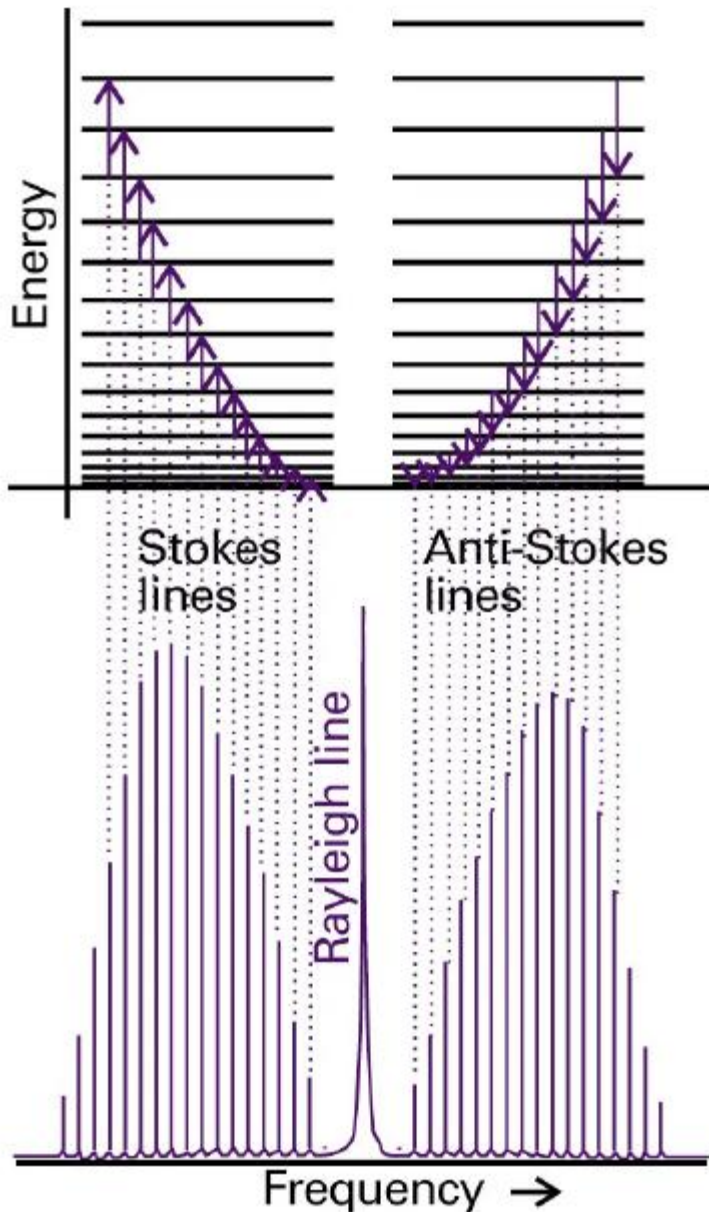
## Example: Rigid rotor

$$E_J = BJ(J + 1), \text{ cm}^{-1} \quad (J = 0, 1, 2, \dots)$$

Stokes and Anti-Stokes lines are observable at

$$\Delta E = \{(E_{J+2}) - E_J\} = B(4J + 6), \text{ cm}^{-1}$$

$$\bar{\nu} = \nu_0 \mp B(4J + 6), \text{ cm}^{-1}$$



- a gap of  $6B$  between  $\nu_0$  and 1st lines of each branch

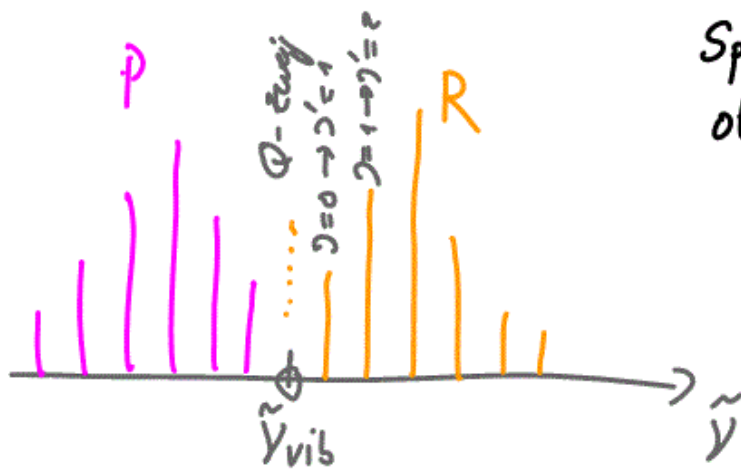
- lines in each branch of equal spacing =  $4B$

# IR and RAMAN spectroscopies-II

- Advantages
  - detects vibration motions for symmetric structures,
  - Raman is more sensitive in some cases (like rough surfaces),
  - useful for studying the catalyst itself (crystalline phases, low frequency vibrations whereas IR is more useful for molecules and adsorbates,
  - needs a small sample volume (laser spot)
  - Can be used for aqueous samples (biological applications)
  - Glass /quartz cell (no NaCl tablet!)
  - Few intense overtone/combination bands , so few spectral overlaps
  - Single shot/scan between 4000-50cm<sup>-1</sup> without setup modifications
- Problems:
  - Laser source/ heating or decomposition of sample,
  - Can cause fluorescence,
  - Expensive apparatus,
  - Obtaining high res RO/RO-Vib spectra is difficult .

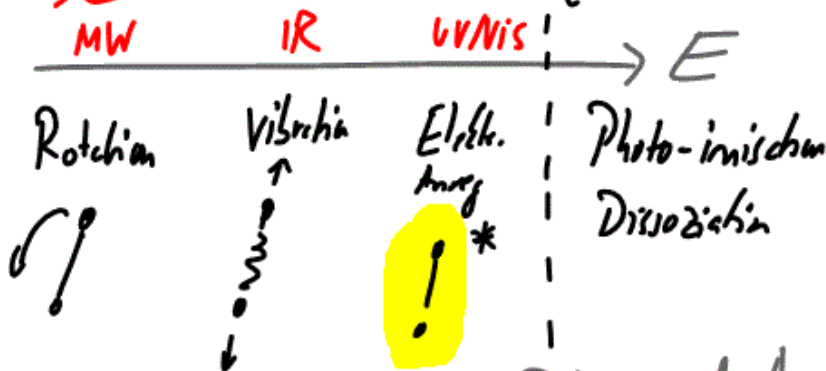






Spektrum, das dem  
 obigen E-Diagramm  
 entspricht  
 (für  $\beta' = \beta$ )

## Elektronische Anregungen von Molekülen

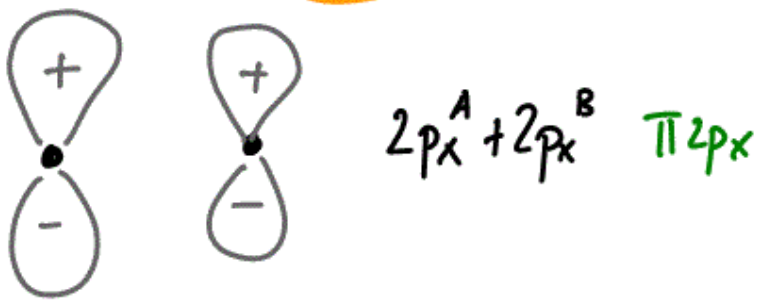
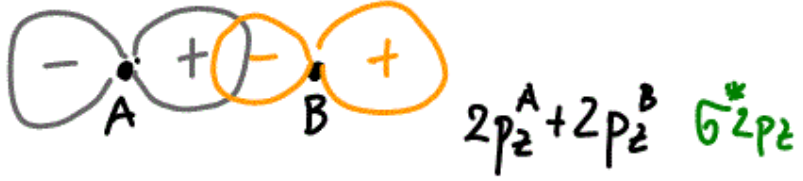
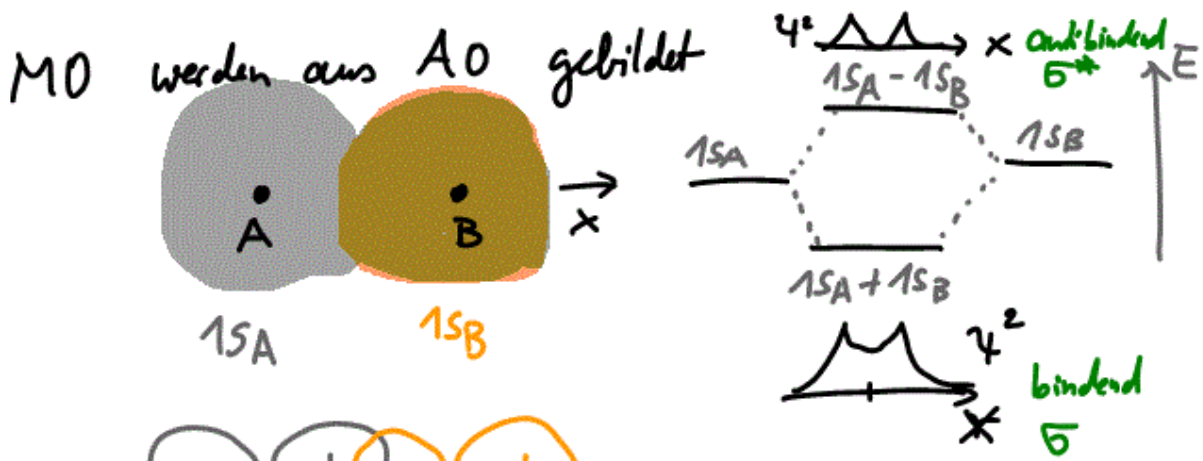


Als Beispiel hatten wir schon Polyene und Aromaten

- allgemeiner: Chromophore { lone Pair,  $e^-$  von lokalen Gruppen wie C=O, N=O, N=O<sub>2</sub> }

- Übergangsmetall-Komplexe  $\begin{array}{c} \text{---} \\ \uparrow \Delta \\ \text{---} \end{array}$  d-Orbitale

im allgemeinen Anregung von  $1e^-$  aus HOMO  $\rightarrow$  LUMO



Aus der Symmetrie der MO für HOMO und LUMO ergeben sich die Auswahlregeln für elektronische Anreg.

- $h\nu_{ex} = \Delta E = E_{LUMO} - E_{HOMO}$  (wie vorher)
- $n_{HOMO} \neq 0$  (per det.)
- $\Delta S = 0$       Gesamtspin bleibt erhalten
- $\Delta M_L = \pm 1, 0$       WW mit Photon

Dabei ergibt sich  $S$  aus den einzelnen Spins  $\vec{S}$  der  $e^-$

$$\vec{S} = \vec{S}_1 + \vec{S}_2 + \dots + \vec{S}_n \quad S \in 0, \frac{1}{2}, 1, \frac{3}{2}, 2, \dots$$

$$M_S = +S, +S-1, \dots, -S$$

$$1e^- : S = \frac{1}{2}, \quad m_S = +\frac{1}{2} \text{ oder } -\frac{1}{2}$$

$$2e^- : S = 0, \quad m_S = 0 \quad \} \text{ Singulett}$$

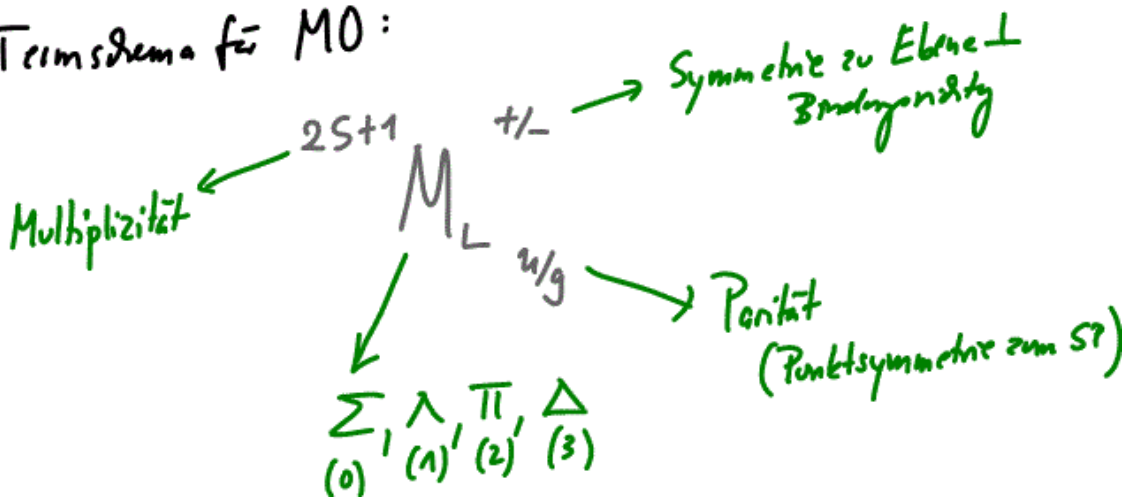
$$\text{oder} \\ S = 1, \quad m_S = +1, 0, -1 \quad \} \text{ Triplett}$$

Genauso mit Bahnmomenten  $\vec{L}$  der  $e^-$

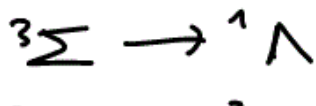
$$\vec{L} = \vec{L}_1 + \vec{L}_2 + \dots \quad L \in 0, 1, 2, 3, \dots$$

$$M_L = +L, +L-1, \dots, -L$$

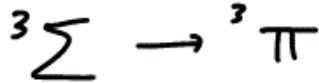
Termschema für MO:



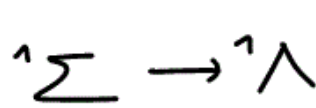
Beispiele:



nicht erlaubt, wegen  $\Delta S \neq 0$



nicht erlaubt, wegen  $\Delta M_L \neq 0$

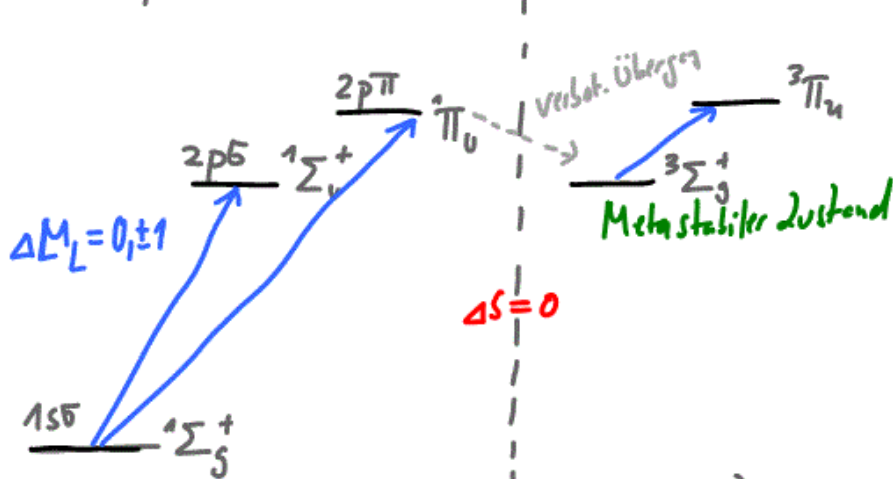


erlaubt, da  $\Delta S = 0, \Delta M_L = 1$

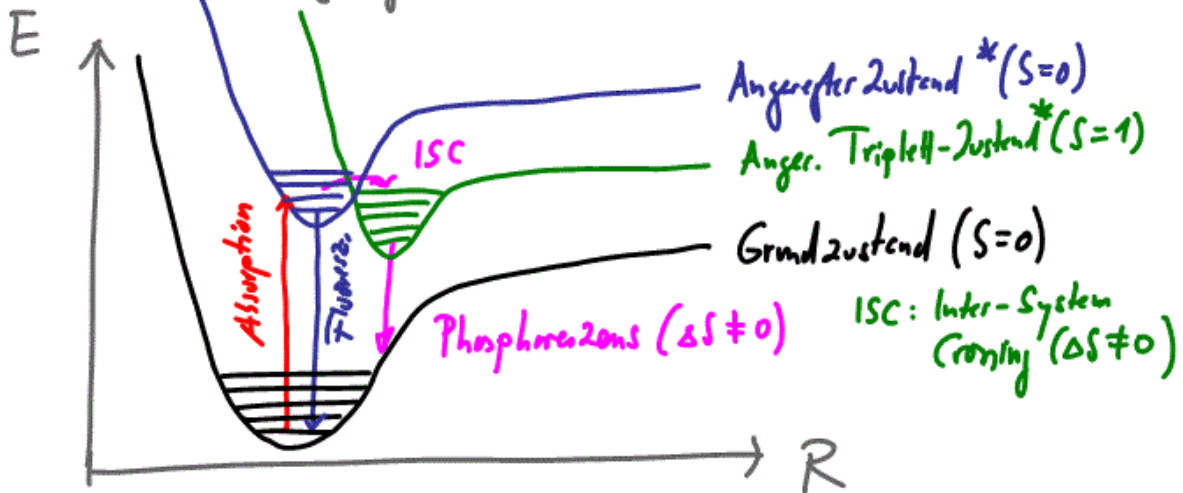
H<sub>2</sub> Molekül

para-H<sub>2</sub>

ortho-H<sub>2</sub>

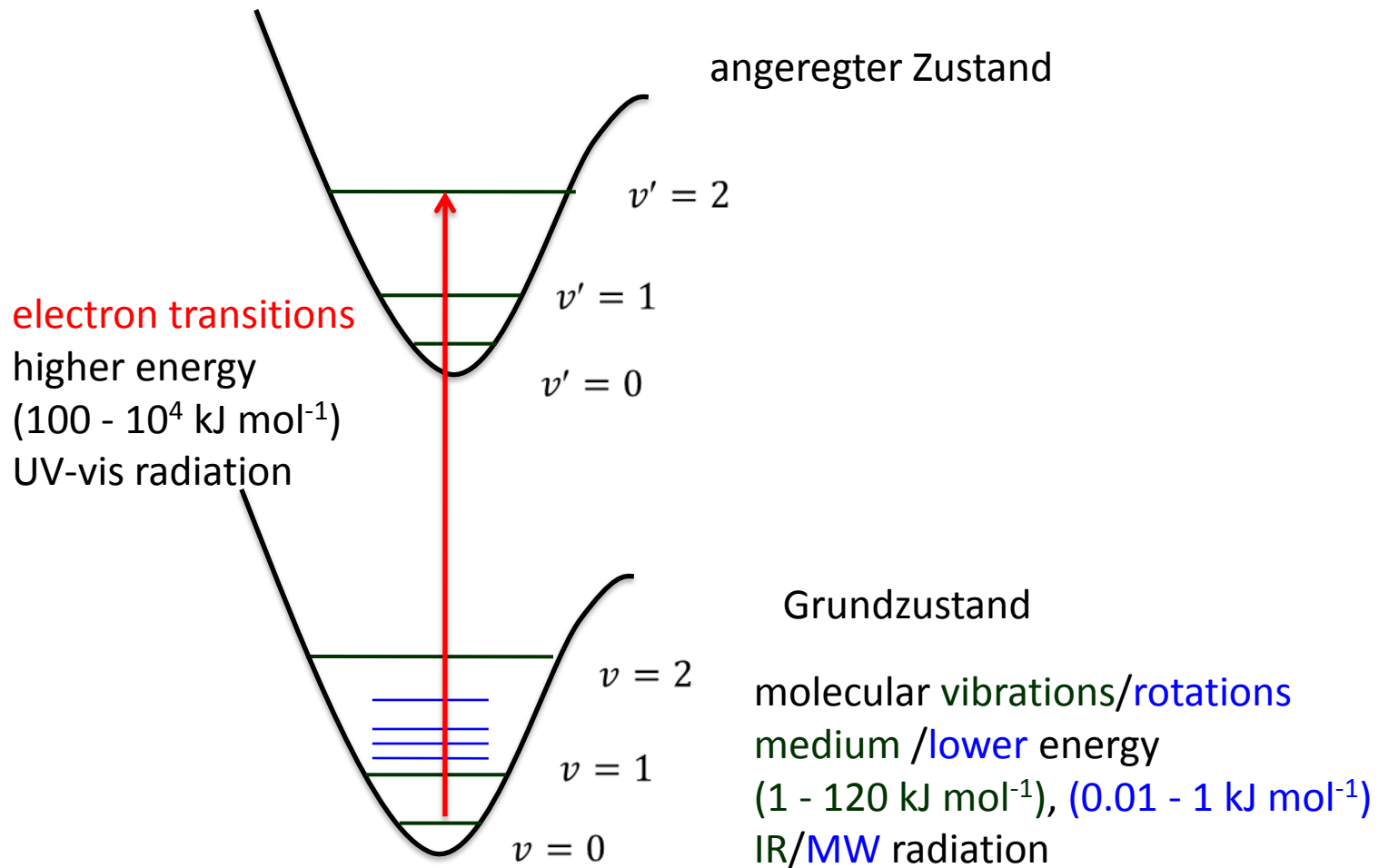


$$\left\{ \begin{array}{l} \Sigma^+ \rightarrow \Sigma^+, \quad \Sigma^- \rightarrow \Sigma^- \\ g \rightarrow u, \quad u \rightarrow g \end{array} \right\}$$





# Molecular transitions - outline



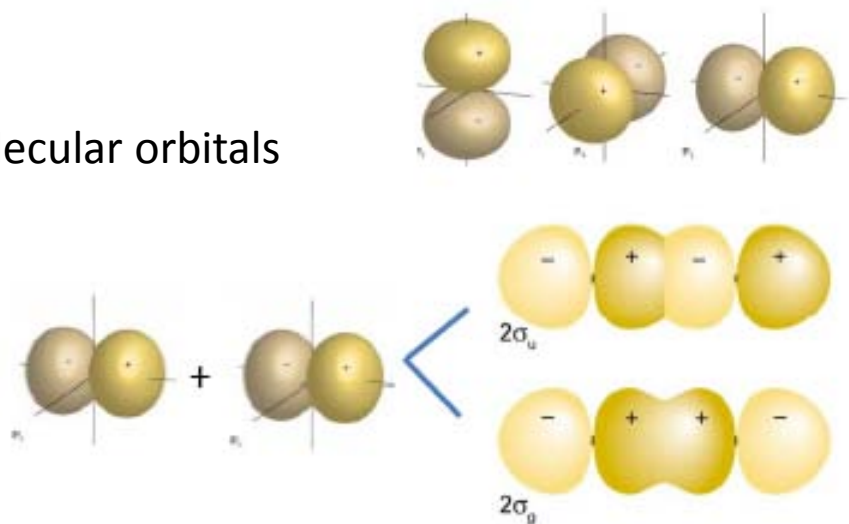
# Molecular term symbols: diatomic molecules

Classify according to angular momentum around the internuclear axis,  $\lambda$ .

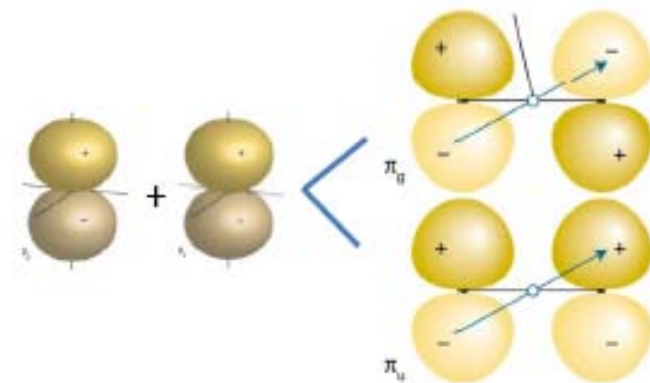
$\lambda$  is similar to  $m_l$  in atoms, so for a  $p$  orbital:  $\lambda=0, \pm 1$

Two  $p$  orbitals : sigma( $\sigma$ ) and pi( $\pi$ ) molecular orbitals

$p_z$  ( $m_l=0$ ) so ( $\lambda =0$ ):  $\sigma, \sigma^*$  MOs

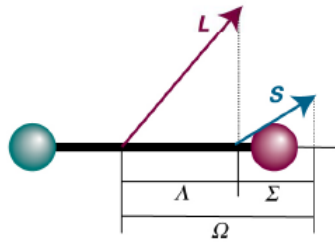


$p_{x,y}$  ( $m_l = \pm 1$ ) so ( $\lambda = \pm 1$ ):  $\pi, \pi^*$  MOs



$$\Lambda = \sum_i \lambda_i = \lambda_1 + \lambda_2 + \lambda_3 + \dots$$

Overall angular momentum on the internuclear axis



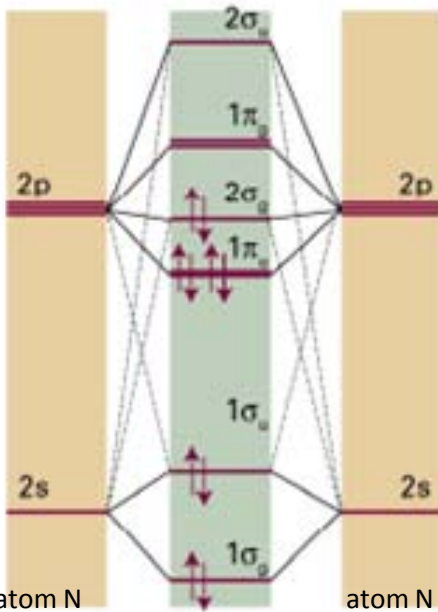
Spin-orbit levels :  $\Omega = |\Lambda + \Sigma|$ ,  
 $\Sigma$  is the projection of S on internuclear axis

spin multiplicity  $= (2s+1)$

Singlet, doublet and triplet states

$2\Pi_{3/2}$

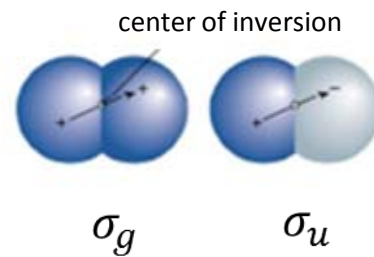
$\Lambda$  values, according to:  
 $\Sigma$  for  $\Lambda=0$ ,  $\Pi$  for  $\Lambda=\pm 1$   
 $\Delta$  for  $\Lambda=\pm 2$ ,  $\Phi$  for  $\Lambda=\pm 3, \dots$



$N_2$ -ground state

$1\Sigma_g^+$

$$(2s\sigma_g)^2(2s\sigma_u)^2(2p\pi_u)^4(2p\sigma_g)^2$$

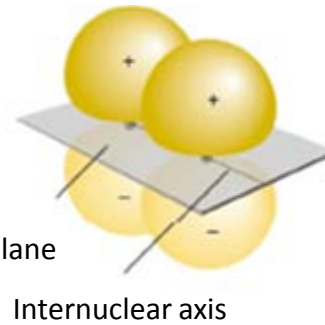


$$g \otimes g = g$$

$$u \otimes g = u$$

$$u \otimes u = g$$

$$\hat{i}\Psi_e = \mp\Psi_e$$



$$\hat{\sigma}_v \Psi_e = \mp\Psi_e$$

For *sigma terms*, the symmetry is shown as (+/-) considering the reflection in a plane contains the internuclear axis.



# Selection rules

1.  $\Delta\Lambda = 0, \pm 1,$

example: transitions  $\Sigma$ - $\Sigma$ ,  $\Pi$ - $\Sigma$ ,  $\Delta$ - $\Pi$  and so on are allowed but  $\Delta$ - $\Sigma$  or  $\Pi$ - $\Phi$  are forbidden .

2.  $\Delta S = 0,$

(true for light atoms, however does not hold for very heavy atoms, for example in  $I_2$ ).

3.  $\Delta\Omega=0,\pm 1,$

for transitions between multiple components.

4. Further subdivision for  $\Sigma$  states: only  $\Sigma^+ - \Sigma^+$  or  $\Sigma^- - \Sigma^-$  transitions are allowed.

notice:  $\Sigma^+ - \Pi$  ,  $\Sigma^- - \Pi$  are both allowed.

5.  $g \leftrightarrow u,$

g to g or u to u transitions are forbidden.

# Transition dipole moment integral

(Time dependent hamiltonian , how are the selection rules obtained)

$$\hat{H} = \hat{H}^0 + \hat{H}^1(t)$$

$$\hat{H}^1(t) = -\mu_z \cos\omega t$$

$$R_{21} = \int \psi^*_2 \hat{\mu} \psi_1 d\tau = \langle \psi_2 | \mu | \psi_1 \rangle \quad \mu_x = ex, \mu_y = ey, \mu_z = ez$$

2: final state, 1: initial state

*Übergangsdipolmomentintegral*

Born-Oppenheimer Näherung:  $\psi_{tot} = \psi_e(r) \cdot \psi_{vib}(R)$

$$R_{21} = \langle \psi'_{el} \psi'_{vib} | \hat{\mu} | \psi''_{el} \psi''_{vib} \rangle = -e \iint \psi'^*_{el}(r) \psi'^*_{vib}(R) r \psi''_{el}(r) \psi''_{vib}(R) dr dR$$

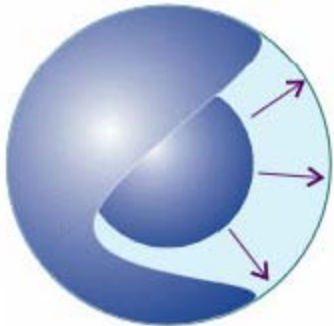
$$R_{21} = -e \underbrace{\int \psi'^*_{el}(r) r \psi''_{el}(r) dr}_{\text{Electronic transition moment}} \underbrace{\int \psi'^*_{vib}(R) \psi''_{vib}(R) dR}_{\text{Vibrational overlap } S(v,v')}$$

*Überlappungsintegral*

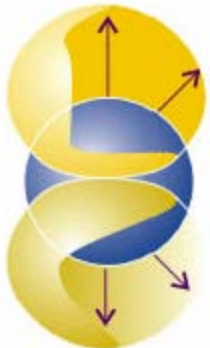
$$\text{Transition intensity} \propto R_{21}^2 \propto \left( \int \psi'^*_{el}(r) r \psi''_{el}(r) dr \right)^2 \left( \int \psi'^*_{vib}(R) \psi''_{vib}(R) dR \right)^2$$

**Franck-Condon factor**  
(square of the vibrational overlap integral)

$$\begin{aligned} \Delta L &= 0, \pm 1 \\ \Delta S &= 0 \text{ and } \Delta \Sigma = 0 \\ g &\leftrightarrow u \text{ (where } g, u \text{ exist)} \\ + &\leftrightarrow + ; - \leftrightarrow - \text{ (for } \Sigma \text{--}\Sigma \text{ transitions)} \end{aligned}$$

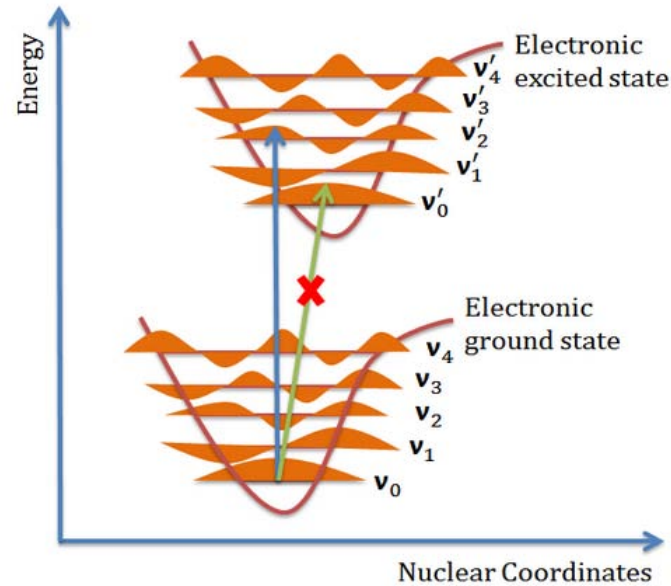
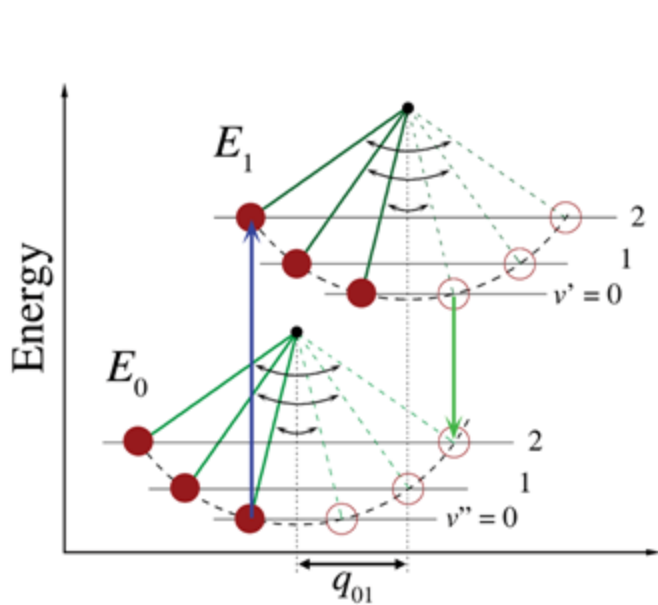


1s ---> 2s  
verboten



1s ---> 2p  
✓ Erlaubt

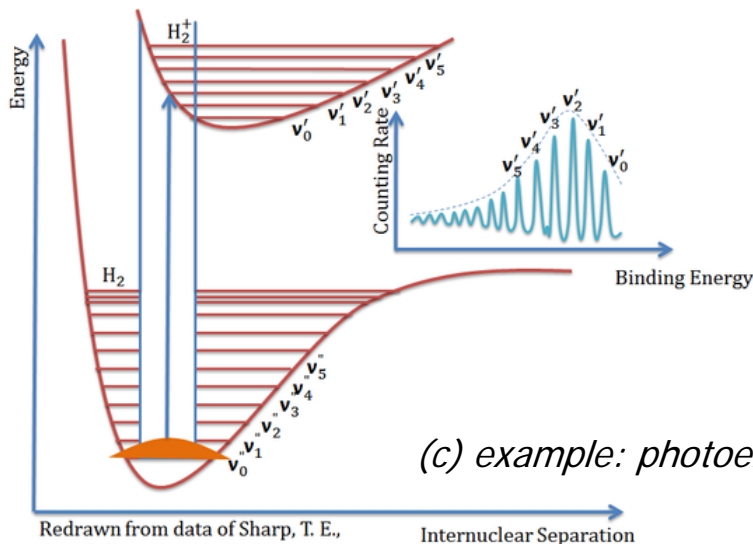
# Franck-Condon principle



(a) How does the internuclear distance change?

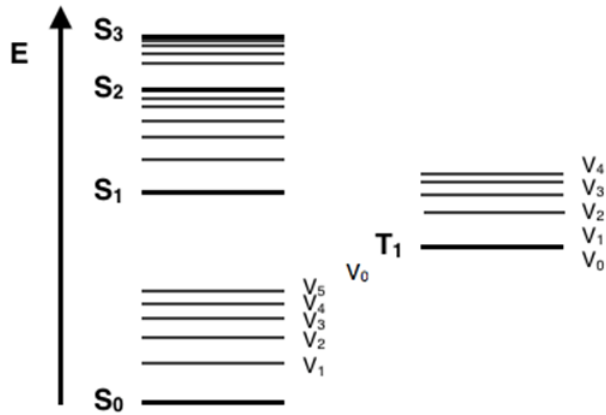
(b) Franck-Condon energy diagram

(Vertical transitions)

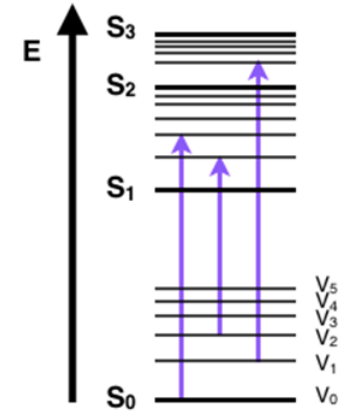


(c) example: photoelectron spectrum of the ionization  $H_2$

# Fate of molecule? Jablonski diagram

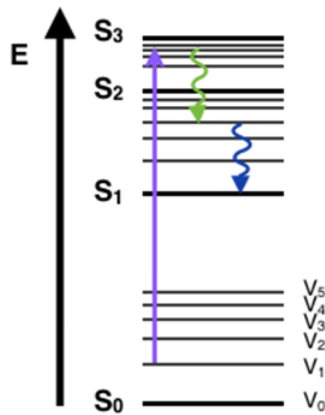


- schematic energy diagram ,
- specific multiplicities,
- electronic states (bold),
- vibronic energy states/rotations,
- continuous energy band,
- straight/curved lines.

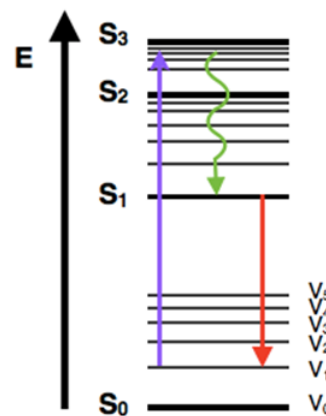


The foundation of a typical Jablonski diagram

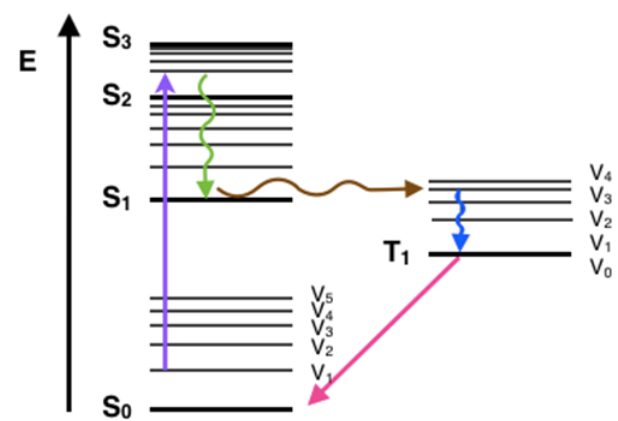
Possible absorptions ( $10^{-15}$ s)



Absorbance, internal conversion and vibrational relaxation ( $10^{-14}$ - $10^{-11}$ s)



Fluorescence ( $10^{-9}$ - $10^{-7}$ s)



Intersystem crossing ( $10^{-8}$ - $10^{-3}$ s), phosphorescence ( $10^{-4}$ - $10^{-1}$ s)