Physics of Condensed Matter I

1100-4INZ`PC

Molecules 4

Faculty of Physics UW

Jacek.Szczytko@fuw.edu.pl

Chemical bonding and molecules

Born Oppenheimer approximation

Max Born

(1882-1970)

Jacob R. Oppenheimer

(1904-1967)

Molecules

Hybridization

A summary of hybrid orbitals, valence bond theory, VSEPR, resonance structures, and octet rule.

| Linear	Trigonal planar	Tetrahedral	Trigonal bipyramidal	Octahedral
sp	sp^2	sp^3	dsp^3	d^2sp^3
BeH_2	BH_3	CH_4	PF_5	SF_6
BeF_2	BF_3	CF_4	PCl_5	IOF_5
CO_2	CH_2O	CCl_4	$PFCl_4$	PF_6^-
HCN	$(>C=O)$	CH_3Cl	$:SF_4$	SiF_6^{2-}
HC^oCH	$>C=C<$	NH_4^+	$:TeF_4$	$:BrF_5$
	CO_3^{2-}	$:NH_3$	$::ClF_3$	$:IF_5$
	benzene	$:PF_3$	$::BrF_3$	$::XeF_4$
	graphite	$:SOF_2$	$:::XeF_2$	
	fullerenes	$::OH_2$	$:::I_3^-$	
	$\cdot NO_2$	$::SF_2$	$(:::I\,I_2^-)$	
	N_3^-		$:::ICl_2^-$	
	$:OO_2\,(O_3)$	SiO_4^{4-}		
	$:SO_2$	PO_4^{3-}		
	SO_3	SO_4^{2-}		
		ClO_4^-		

• a lone odd electron   : a lone electron pair

Atomic orbitals combined	Hybrid orbitals formed	Bonding electron pairs and lone pairs around central atom	VSEPR geometry
1 s orbital & 1 p orbital	sp hybrid (2 orbitals)	2	linear
1 s orbital & 2 p orbitals	sp2 hybrid (3 orbitals)	3	trigonal planar
1 s orbital & 3 p orbitals	sp3 hybrid (4 orbitals)	4	tetrahedral
1 s orbital & 3 p orbitals & 1 d orbital	dsp3 hybrid (5 orbitals)	5	trigonal bipyramidal
1 s orbital & 3 p orbitals & 2 d orbitals	d2sp3 hybrid (6 orbitals)	6	octahedral

Chemical bonding and molecules
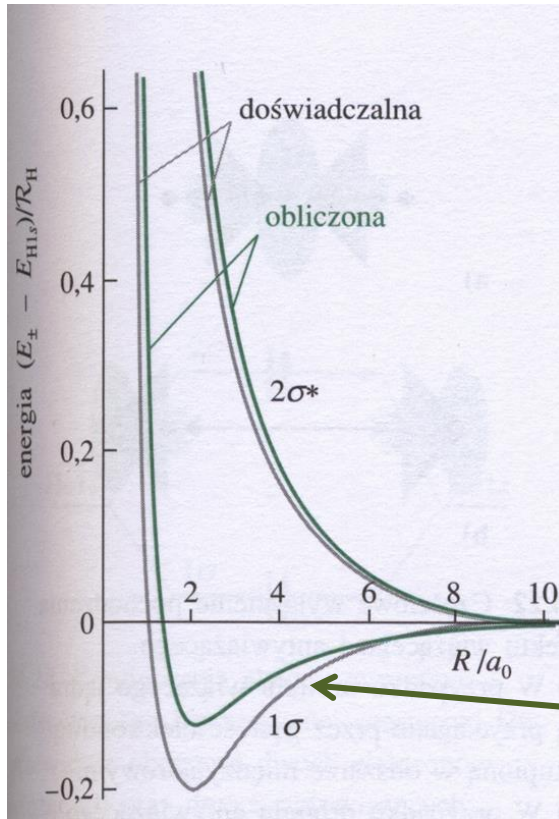
$\chi^n(\vec{R})$ is the wave function describing the motion of nuclei (ions) in their mutual interaction potential $G(\vec{R})$ adiabatic electron contribution to the energy of the motion of nuclei (ions) $E_{el}^k(\vec{R})$

Born-Oppenheimer approximation **is not fulfilled** when the potential energy surfaces of two electronic states are too close.

the potential energy surface

Schrodinger equation of the motion of nuclei with repulsive potential $G(\vec{R})$:

$$[\hat{T}_N + E_{el}(\vec{r}, \vec{R}) + G(\vec{R})]\chi^n(\vec{R}) = E^n\chi^n(\vec{R})$$

effective potential

Chemical bonding and molecules

Approximations

$$\left[\hat{T}_N + E_{el}(\vec{r}, \vec{R}) + G(\vec{R})\right]\chi^n(\vec{R}) = E^n \chi^n(\vec{R})$$

The kinetic energy separates on vibration (oscillation) and rotation energy – we assume "small" oscillations and slow speed of rotataion.
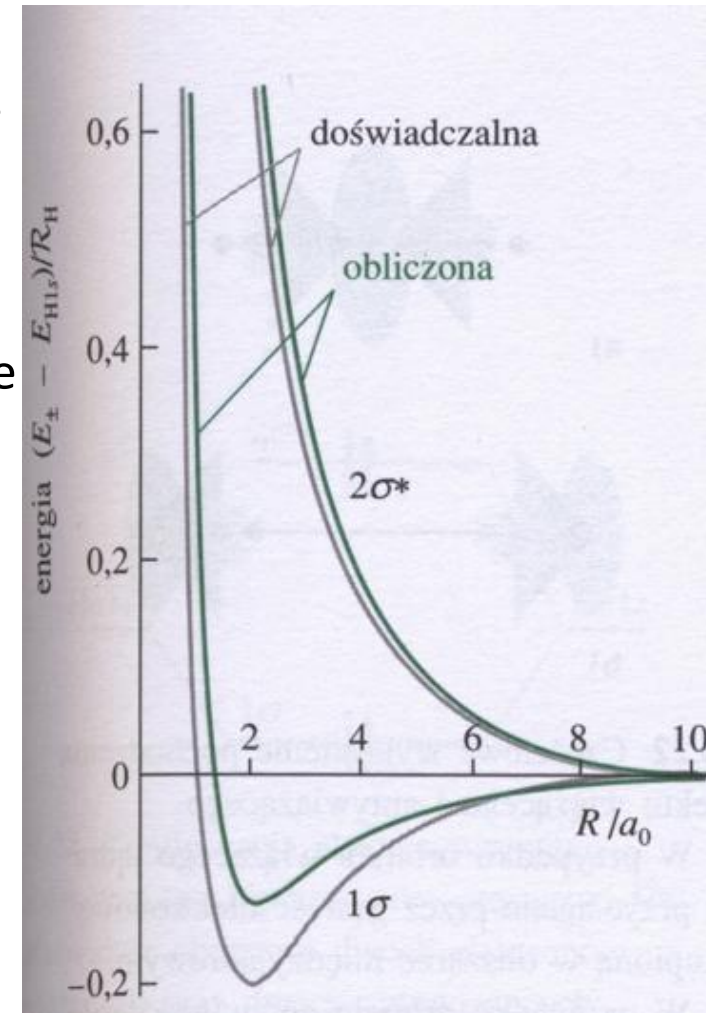
$$\left[\hat{T}_{osc} + \hat{T}_{rot} + E_{el}(\vec{r}, \vec{R}) + G(\vec{R})\right]\chi^n(\vec{R}) = E^n \chi^n(\vec{R})$$

Operators act on different coordinates: we can we separate the variables:

$$\chi^n(\vec{R}) = \chi^n_{osc}(R)\chi^n_{rot}(\theta, \varphi)$$
$$E^n = E^n_{osc} + E^n_{rot}$$

Altogether:

$$\Psi(\vec{r}, \vec{R}) = \chi^n(\vec{R})\Psi^n_{el}(\vec{r}, \vec{R}) = \chi^n_{osc}(R)\chi^n_{rot}(\theta, \varphi)\Psi^n_{el}(\vec{r}, \vec{R})$$
$$E^n = E^n_{osc} + E^n_{rot} + E_{el}$$

Chemical bonding and molecules

Approximations

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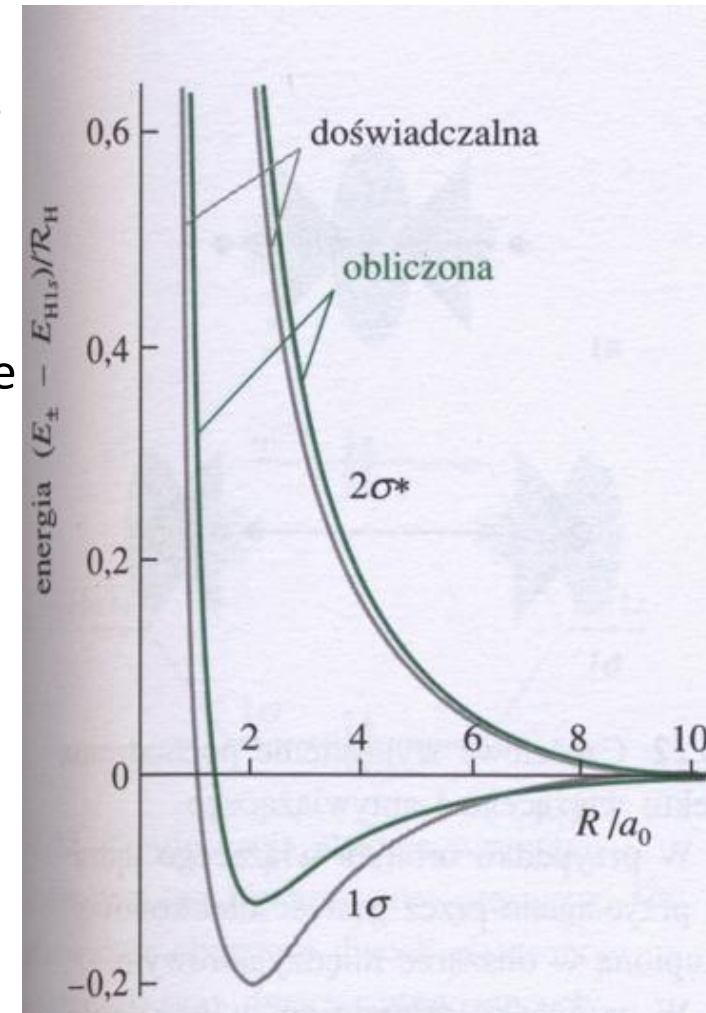
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$$E^n = E^n_{osc} + E^n_{rot} + E_{el}$$

Diatomic molecules

Approximations

Diatomic molecule in the center-of-mass coordinates

$$\left[-\frac{\hbar^2}{2\mu}\nabla_R^2 + E_{el}^n(\vec{R})\right]\chi^n(\vec{R}) = E^n\chi^n(\vec{R})$$

$$\left[-\frac{\hbar^2}{2\mu R^2}\frac{\partial}{\partial R}\left(R^2\frac{\partial}{\partial R}\right) + \frac{\hat{L}^2}{2\mu R^2} + E_{el}^n(\vec{R})\right]\chi^n(\vec{R}) = E^n\chi^n(\vec{R})$$

Operators act on different coordinates, we can separate the variables in spherical coordinate system.

$$\chi^n(\vec{R}) = \frac{1}{R}\chi_{osc}^n(R)\chi_{rot}^n(\theta,\varphi)$$

radial coordinates
$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dR^2} + \left(\frac{\lambda}{2\mu R^2} + E_{el}^n(\vec{R})\right)\right]\chi_{osc}^n(R) = E\chi_{osc}^n(R)$$

angular coordinates
$$\hat{L}^2\chi_{rot}^n(\theta,\varphi) = \lambda\chi_{rot}^n(\theta,\varphi)$$

Rotation spectra

Rotation

Diatomic molecule in the center-of-mass coordinates

$$\hat{L}^2 \chi_{rot}^n(\theta, \varphi) = \lambda \chi_{rot}^n(\theta, \varphi)$$

$$\chi_{rot}^n(\theta, \varphi) = Y_J^M(\theta, \varphi) \qquad J = 0, 1, 2 \; \dots \quad M = -J, -J+1, \dots, J-1, J$$

$$\lambda = \hbar^2 J(J+1)$$

$$E_{rot}^J = \frac{\hbar^2 J(J+1)}{2\mu R^2} = \frac{\hbar^2 J(J+1)}{2I}$$

I – **Moment of inertia** (or **angular mass** or **rotational inertia**)
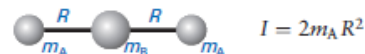
$$I = \int_{m \, (mass)} r^2 \, dm$$

$$\frac{1}{\mu} = \frac{1}{M_1} + \frac{1}{M_2}$$

Moment of inertia nuclei with respect to the axis passing through the center of the mass perpendicular to the molecule axis

Rotation spectra

Rotation

Generaly:

$$\hat{H} = \frac{\hat{J}_x^2}{2I_{xx}} + \frac{\hat{J}_y^2}{2I_{yy}} + \frac{\hat{J}_z^2}{2I_{zz}}$$

$$E(J, K, M_J) = \frac{\hbar^2 J(J+1)}{2I_\perp} + \hbar^2 \left(\frac{1}{2I_\parallel} - \frac{1}{2I_\perp}\right)K^2$$

See: Atkins, Fridman *Molecular QM*

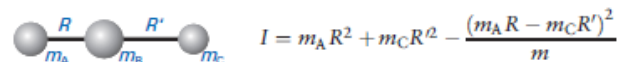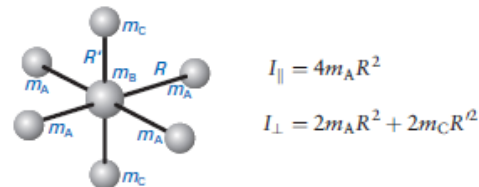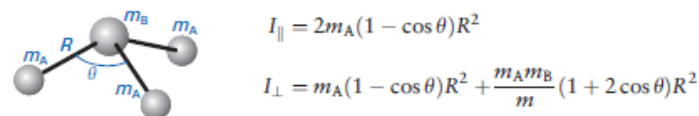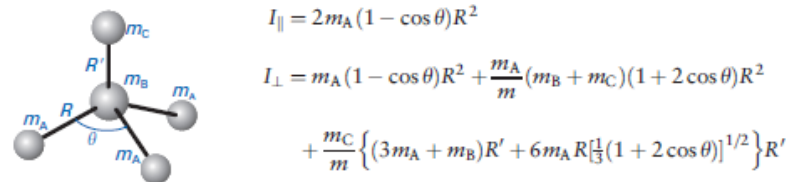$$\frac{1}{\mu} = \frac{1}{M_1} + \frac{1}{M_2}$$

Table 10.1 Moments of inertia*

1. Diatomic molecules

$$I = \mu R^2 \quad \mu = \frac{m_A m_B}{m}$$

2. Triatomic linear rotors

$$I = m_A R^2 + m_C R'^2 - \frac{(m_A R - m_C R')^2}{m}$$

$$I = 2m_A R^2$$

3. Symmetric rotors

$$I_\parallel = 2m_A(1 - \cos\theta)R^2$$

$$I_\perp = m_A(1 - \cos\theta)R^2 + \frac{m_A}{m}(m_B + m_C)(1 + 2\cos\theta)R^2$$

$$+ \frac{m_C}{m}\left\{(3m_A + m_B)R' + 6m_A R[\tfrac{1}{3}(1 + 2\cos\theta)]^{1/2}\right\}R'$$

$$I_\parallel = 2m_A(1 - \cos\theta)R^2$$

$$I_\perp = m_A(1 - \cos\theta)R^2 + \frac{m_A m_B}{m}(1 + 2\cos\theta)R^2$$

$$I_\parallel = 4m_A R^2$$

$$I_\perp = 2m_A R^2 + 2m_C R'^2$$

4. Spherical rotors

$$I = \tfrac{8}{3}m_A R^2$$

$$I = 4m_A R^2$$
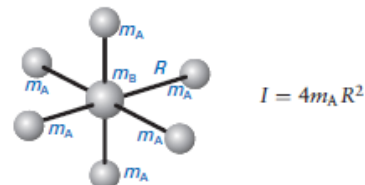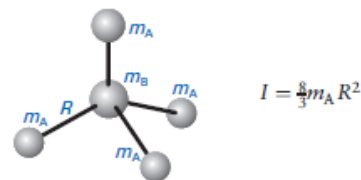
Rotation spectra

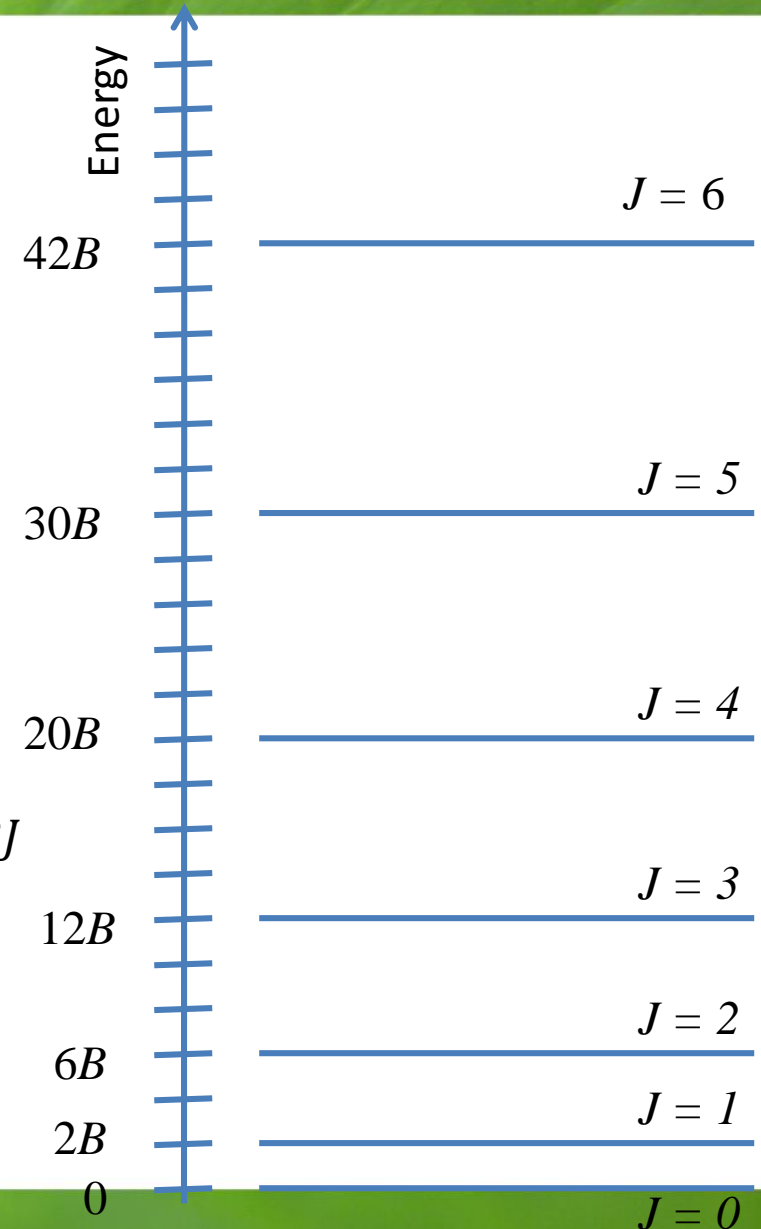## Rigid rotor approximation

The rotational constant B

$$B = \frac{\hbar^2}{2\mu R^2}$$

$$E_{rot}^J = \frac{\hbar^2 J(J+1)}{2\mu R^2} = BJ(J+1)$$

Subsequent energy levels

$$\Delta E_{rot}^J = E_{rot}^J - E_{rot}^{J-1} = B[J(J+1) - (J-1)J] = 2BJ$$

0,1-10 cm^{-1}

Energy

$42B$	$J = 6$
$30B$	$J = 5$
$20B$	$J = 4$
$12B$	$J = 3$
$6B$	$J = 2$
$2B$	$J = 1$
0	$J = 0$

Rotation spectra
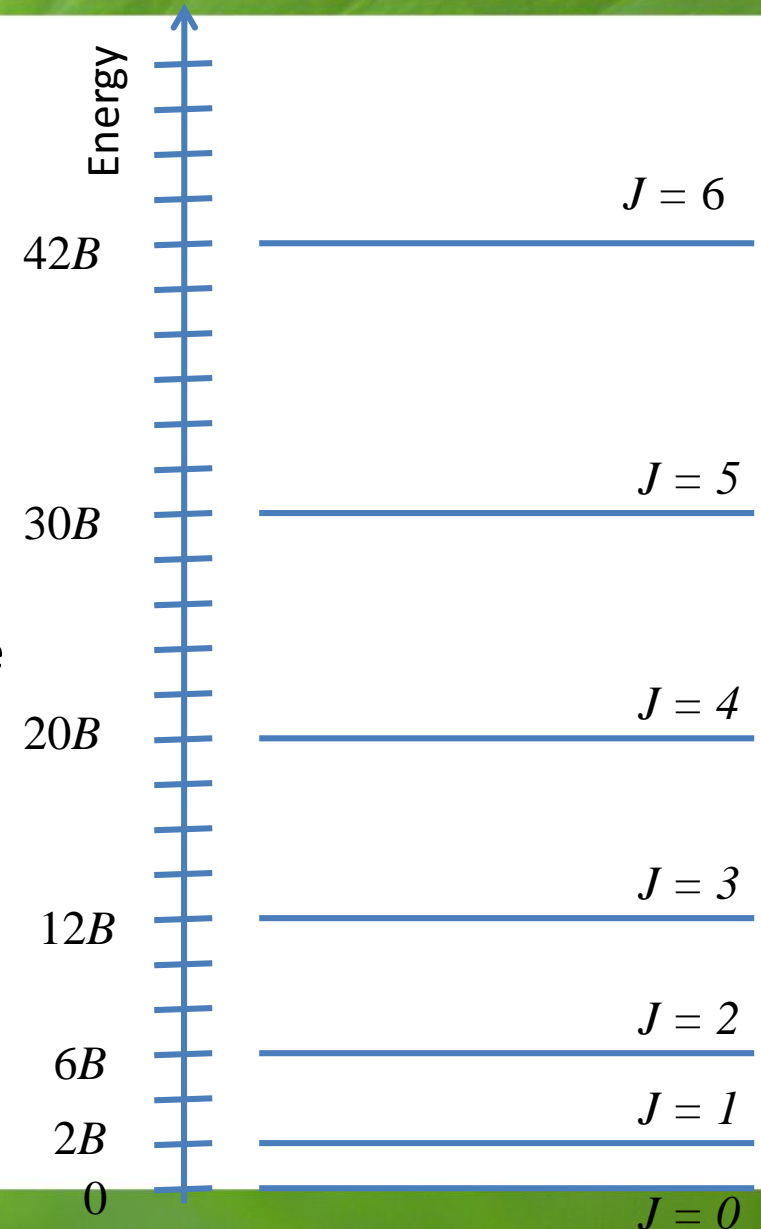
Rigid rotor approximation

Optical transitions:

$$\Delta E_{rot}^{J} = E_{rot}^{J} - E_{rot}^{J-1} = 2BJ \qquad \text{(0,1-10 cm}^{-1}\text{)}$$

The molecule must be polar i.e. it must have **permanent dipole moment**.

Homonuclear diatomic molecules and symmetric linear molecules, for example CO_2 are **inactive**.

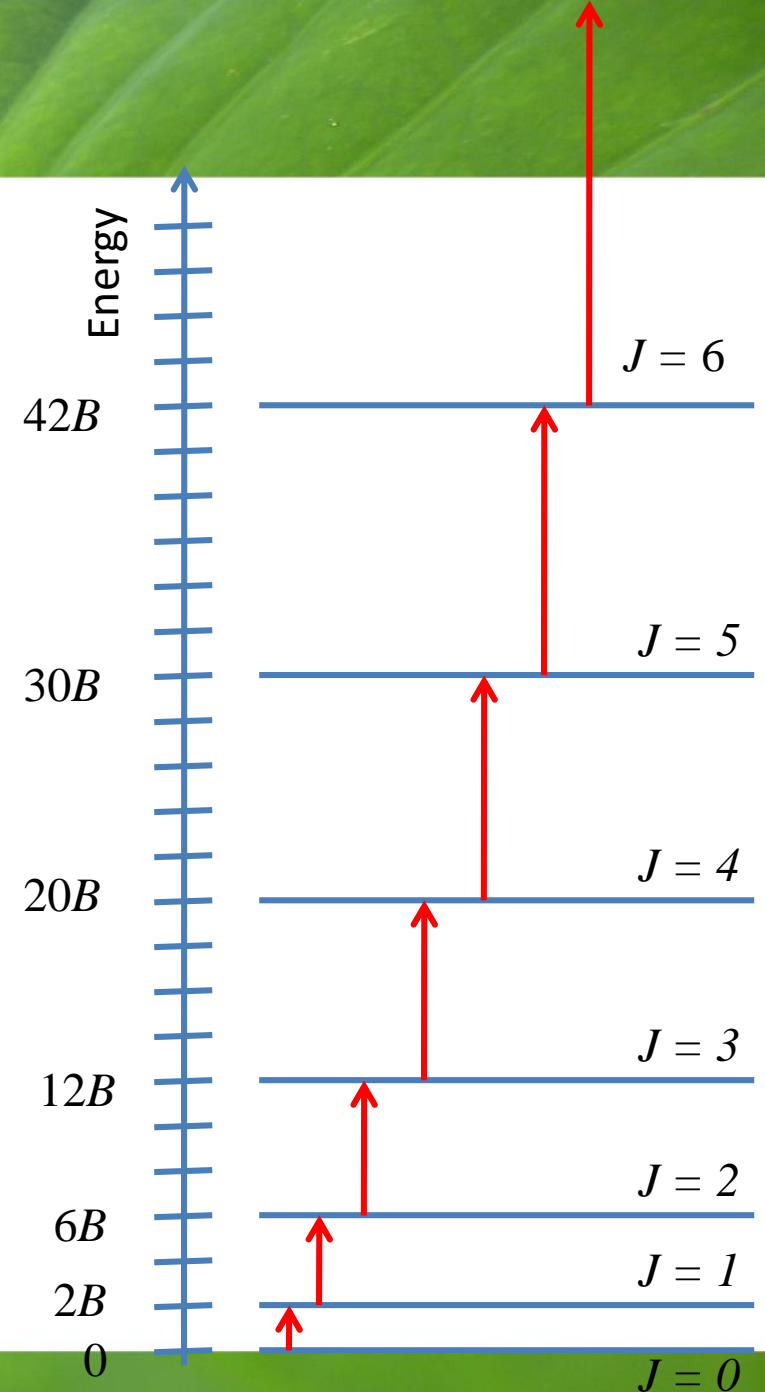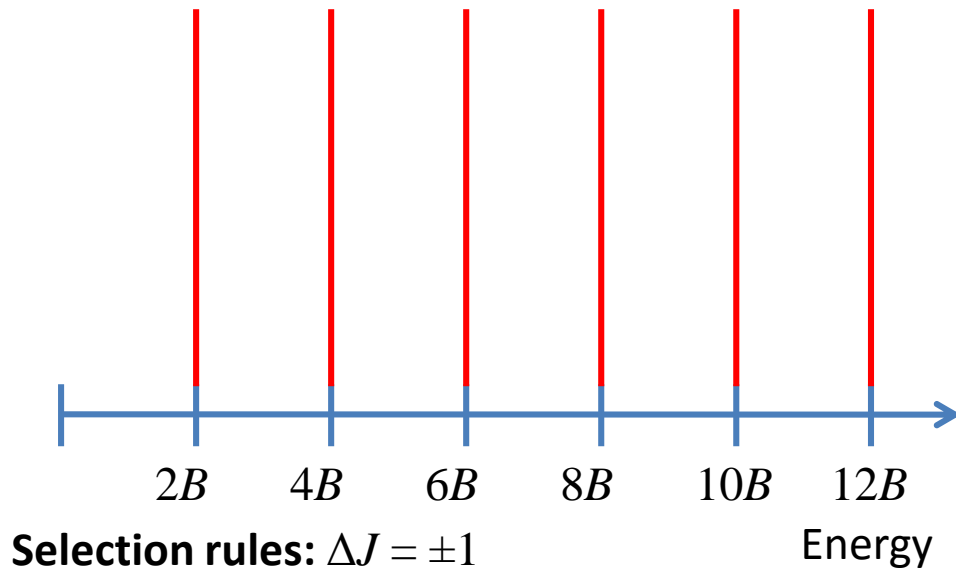Heteronuclear molecules are active (plus e.g. np. H_2O, OCS)

Selection rules: $\Delta J = \pm 1$

Energy

$J = 6$

$42B$

$J = 5$

$30B$

$J = 4$

$20B$

$J = 3$

$12B$

$J = 2$

$6B$

$J = 1$

$2B$

0

$J = 0$

Rotation spectra

Rigid rotor approximation

Optical transitions:

$$\Delta E_{rot}^{J} = E_{rot}^{J} - E_{rot}^{J-1} = 2BJ$$

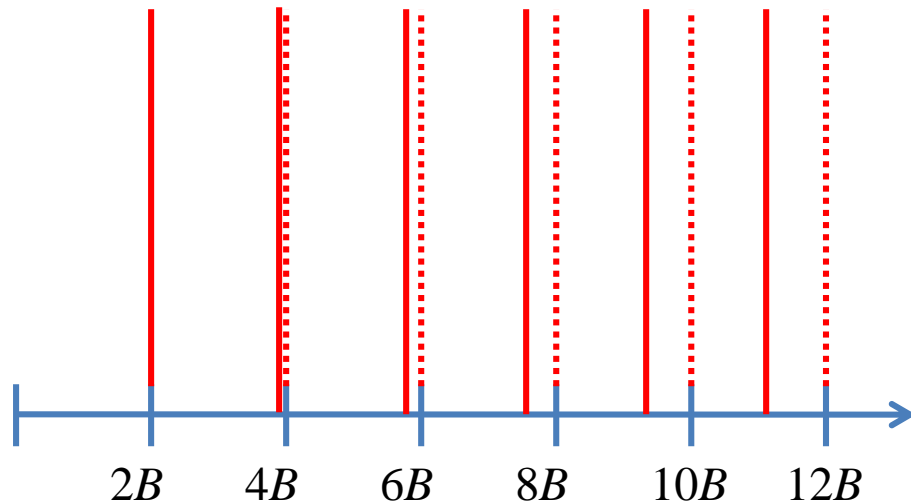Selection rules: $\Delta J = \pm 1$

$2B \qquad 4B \qquad 6B \qquad 8B \qquad 10B \qquad 12B$

Energy

Energy

$42B$

$30B$

$20B$

$12B$

$6B$

$2B$

0

$J = 6$

$J = 5$

$J = 4$

$J = 3$

$J = 2$

$J = 1$

$J = 0$

Rotation spectra

Rigid rotor approximation

Optical transitions: $\Delta E_{rot}^J = E_{rot}^J - E_{rot}^{J-1} = 2BJ$
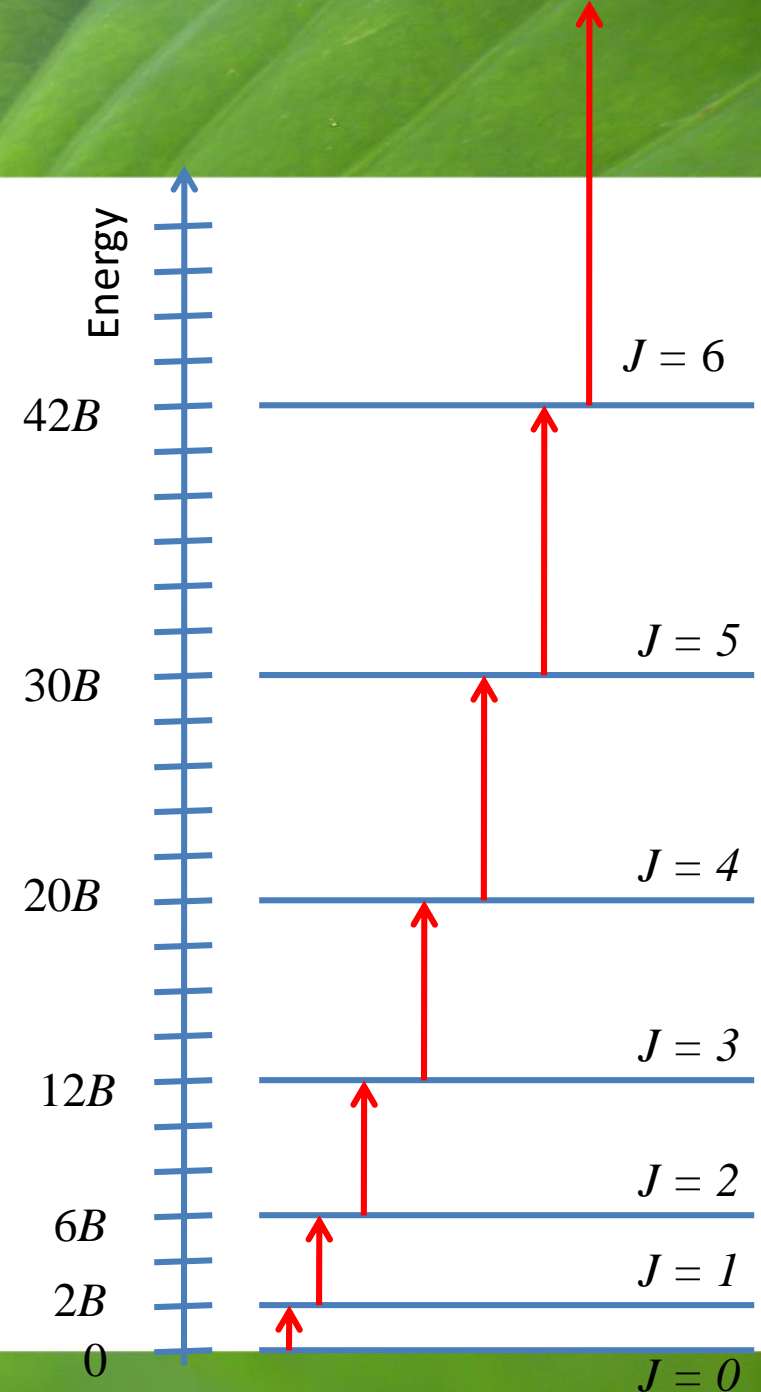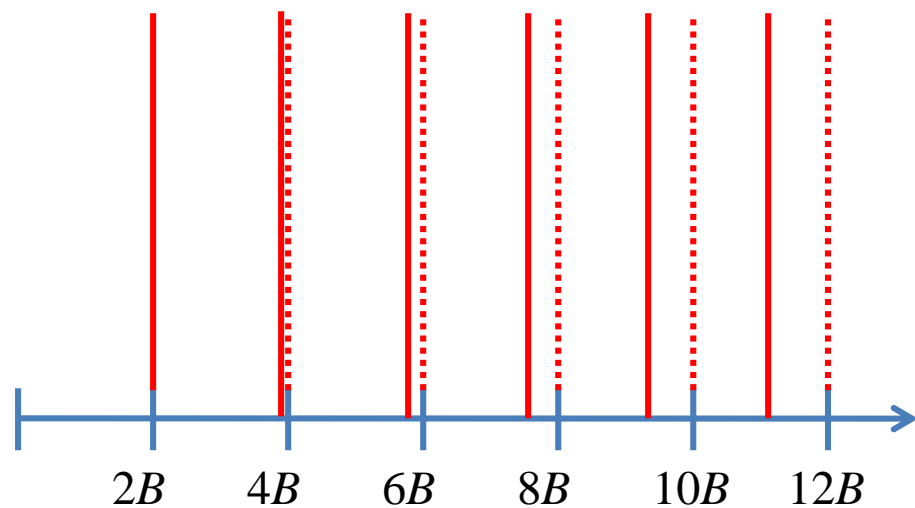
taking into account the centrifugal force

Selection rules: $\Delta J = \pm 1$

$2B \quad 4B \quad 6B \quad 8B \quad 10B \quad 12B \qquad$ Energy

$B_\nu = B - \alpha\left(\nu + \dfrac{1}{2}\right)$ Stała odkształcenia odśrodkowego   Centrifugal distortion constant

$\Delta E_{rot}^J = B_\nu J(J+1) - D_\nu [J(J+1)]^2$

Energy

$42B$ — $J = 6$

$30B$ — $J = 5$

$20B$ — $J = 4$

$12B$ — $J = 3$

$6B$ — $J = 2$

$2B$ — $J = 1$

0 — $J = 0$

Rotation spectra

Rigid rotor approximation

Optical transitions: $\Delta E^J_{rot} = E^J_{rot} - E^{J-1}_{rot} = 2BJ$

taking into account the centrifugal force

Selection rules: $\Delta J = \pm 1$

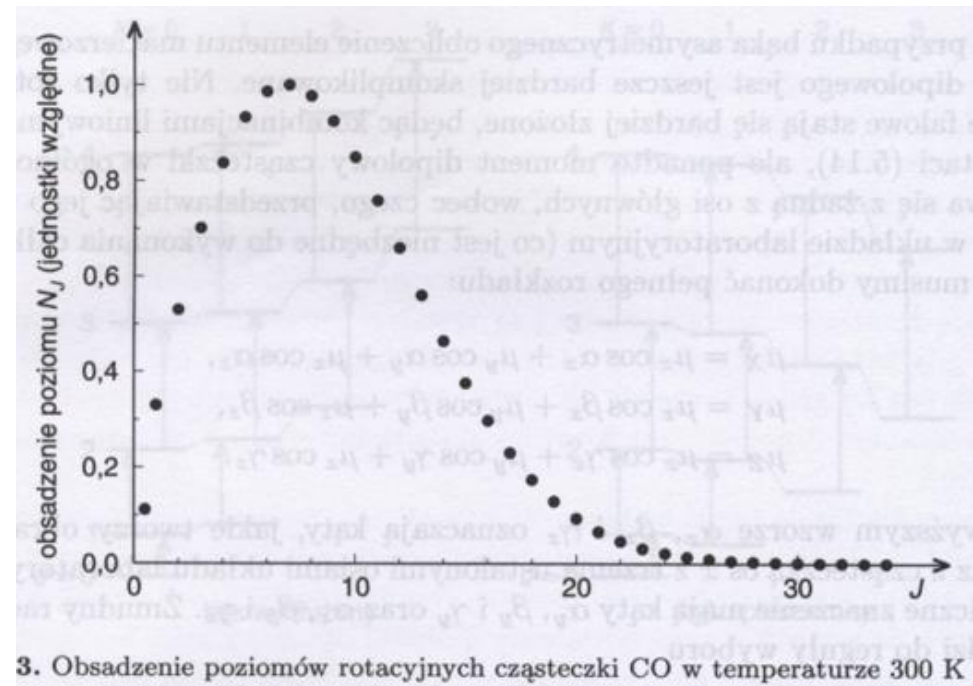$B_v = B - \alpha\left(v + \dfrac{1}{2}\right)$ Stała odkształcenia odśrodkowego   Centrifugal distortion constant

$\Delta E^J_{rot} = B_v J(J+1) - D_v [J(J+1)]^2$

Cząsteczka	B (meV)	R_0 Å
OH	2,341	0,97
HCl	1,32	1,27
NO	0,211	1,15
CO	0,239	1,13
KBr	0,01	2,94

Rotation spectra

Occupation of states
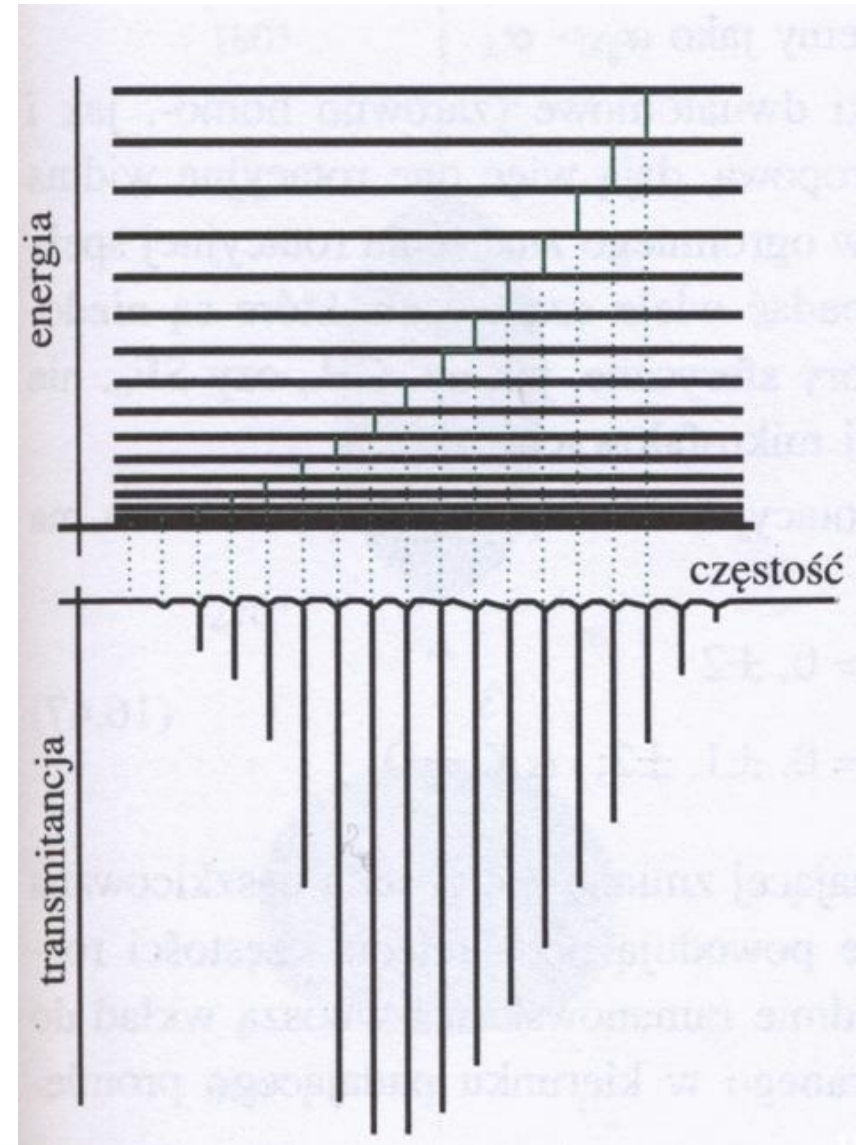
3. Obsadzenie poziomów rotacyjnych cząsteczki CO w temperaturze 300 K

P. Kowalczyk

P. Atkins

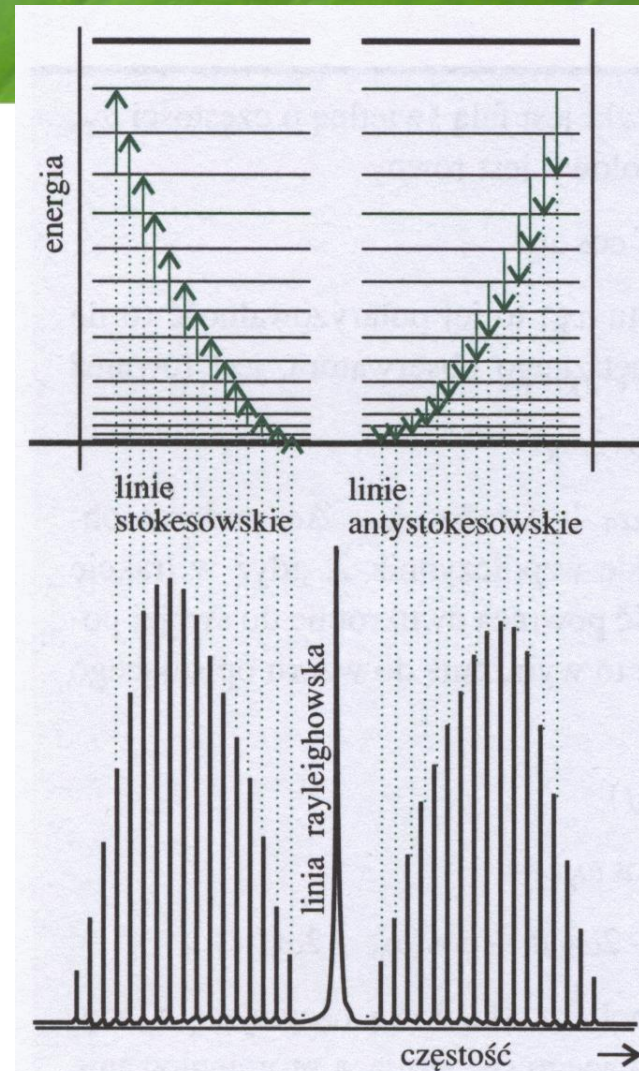# Rotation spectra

Rotational Raman Transitions

Rotational Raman selection rules

The general rule:
Polarizability of the molecule must be anisotropic.
For the linear rotor it means: $\Delta J = 0, \pm 2$

P. Atkins

16.27 Poziomy energii rotacyjnej rotatora liniowego oraz przejścia dozwolone przez ramanowską regułę wyboru $\Delta J = \pm 2$. Pokazano także typową postać rotacyjnego widma ramanowskiego

Rotation spectra

Rotational Raman Transitions

Rotational Raman selection rules

The general rule:

Polarizability of the molecule must be anisotropic.

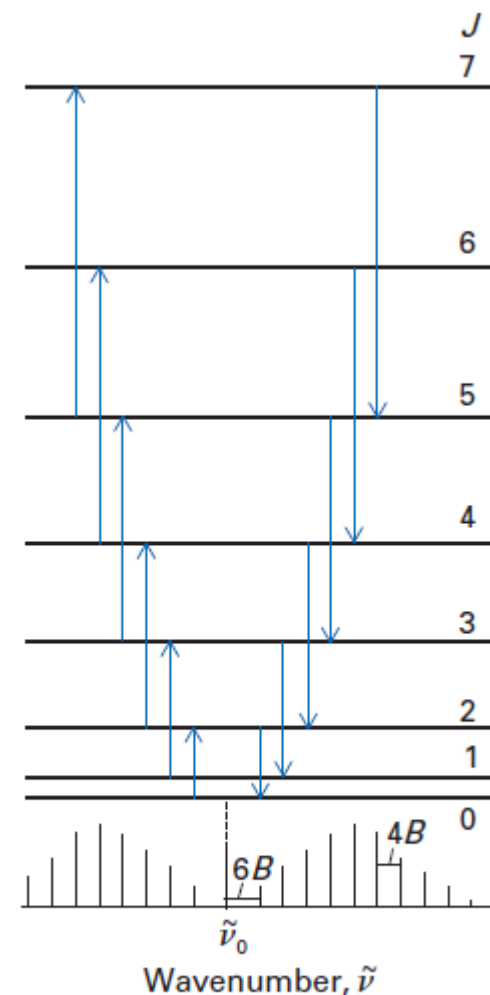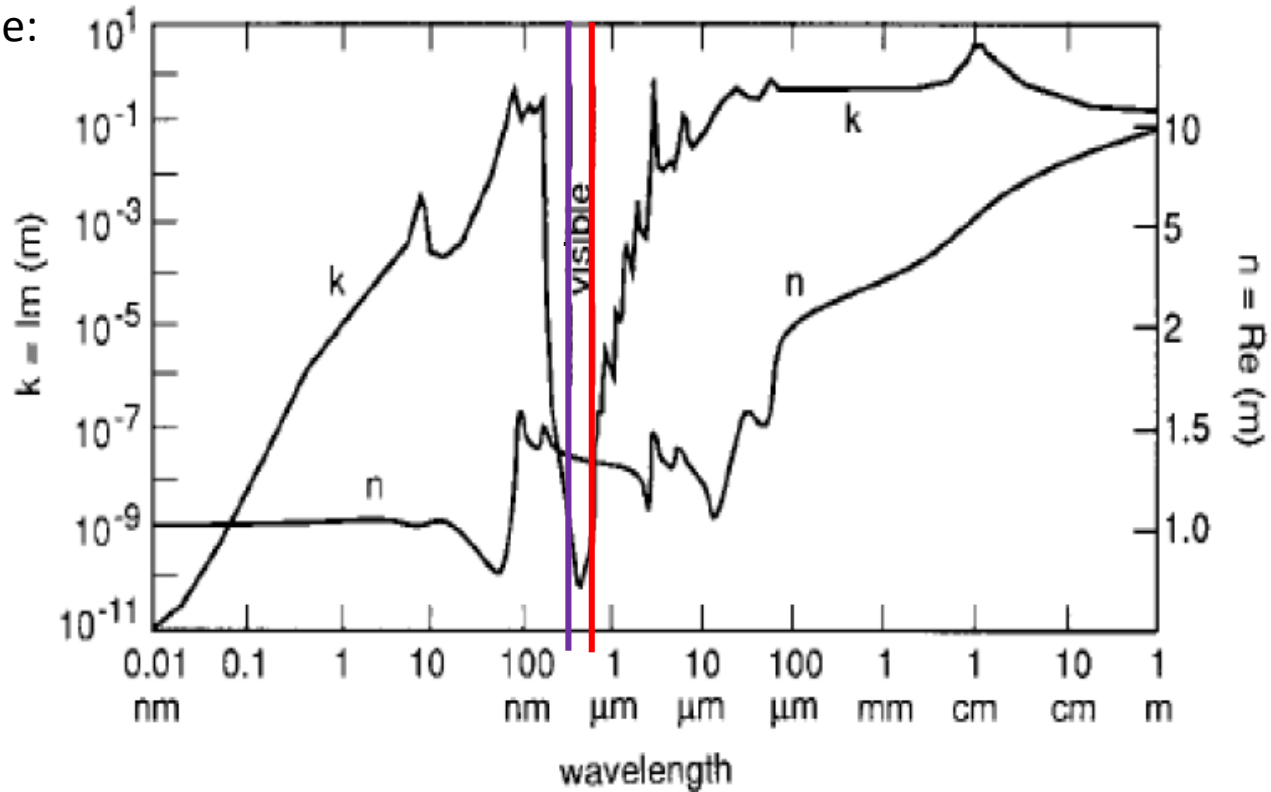For the linear rotor it means: $\Delta J = 0, \pm 2$

P. Atkins

Fig. 10.12 The rotational Raman transitions of a linear molecule.

The Lorentz Oscillator model

Water example:

V. M. Zoloratev and A. V. Demin, "Optical Constants of Water over a Broad Range of Wavelengths, 0.1 Å–1 m," *Opt. Spectrosc.* (U.S.S.R.) **43**(2):157 (Aug. 1977).
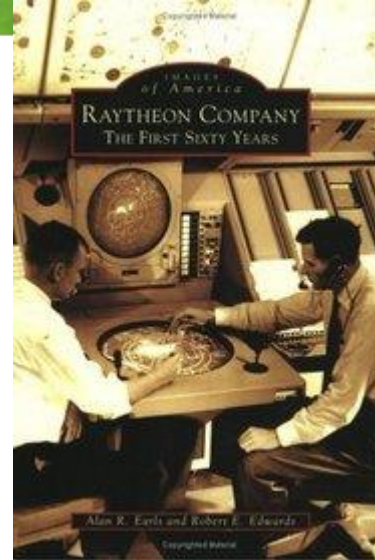
In 1946 first microwave oven called „Radarange" was sold. It was almost 1.8 metres tall, weighed 340 kilograms and cost about US$5,000 ($52,809 in today's dollars) .

https://en.wikipedia.org/wiki/Microwave_oven

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Electronic states

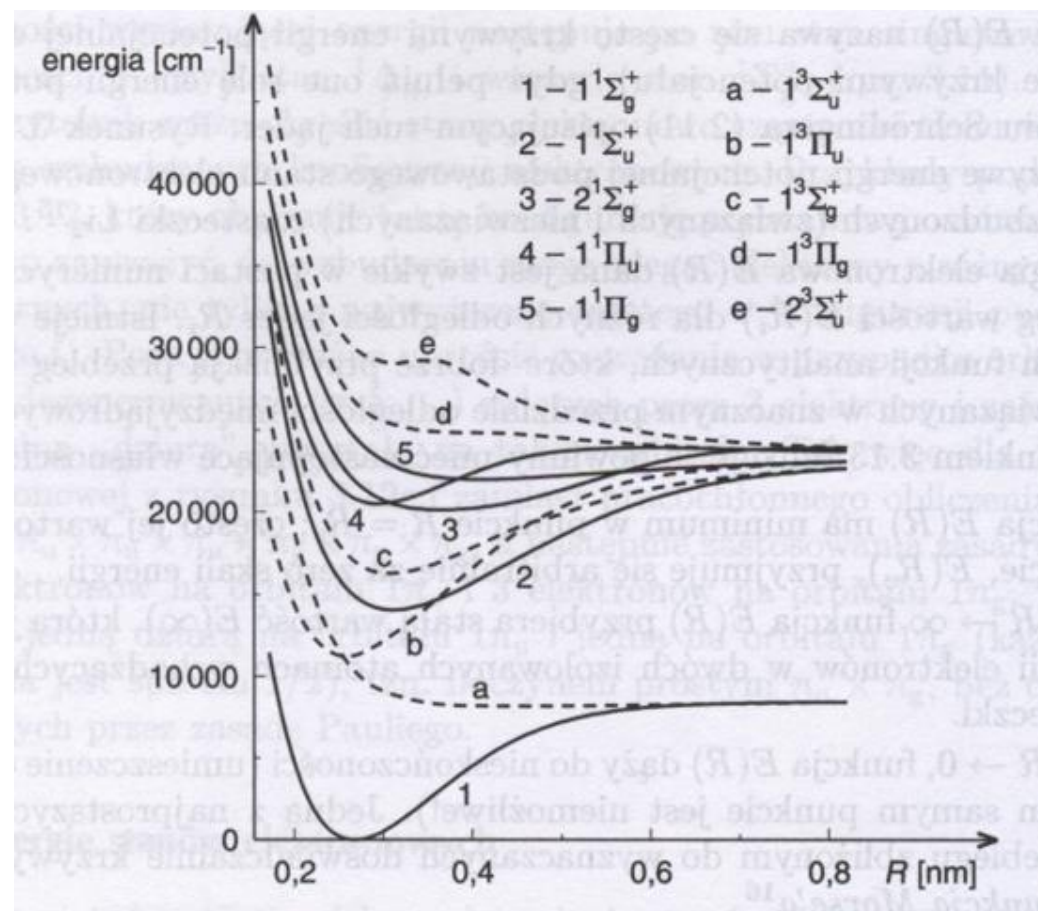Electrons energy strongly depends on the distance between nuclei.

$E(R)$ - usually in numerical form.

Approximations: Morse potential
eg. Lithium

$$V(r) = D_e \left[1 - e^{-\alpha(r - r_0)} \right] + V(r_0)$$

Approximations: Lenard-Jones potential

$$V(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right] + V(r_0)$$

P. Kowalczyk

Electronic states

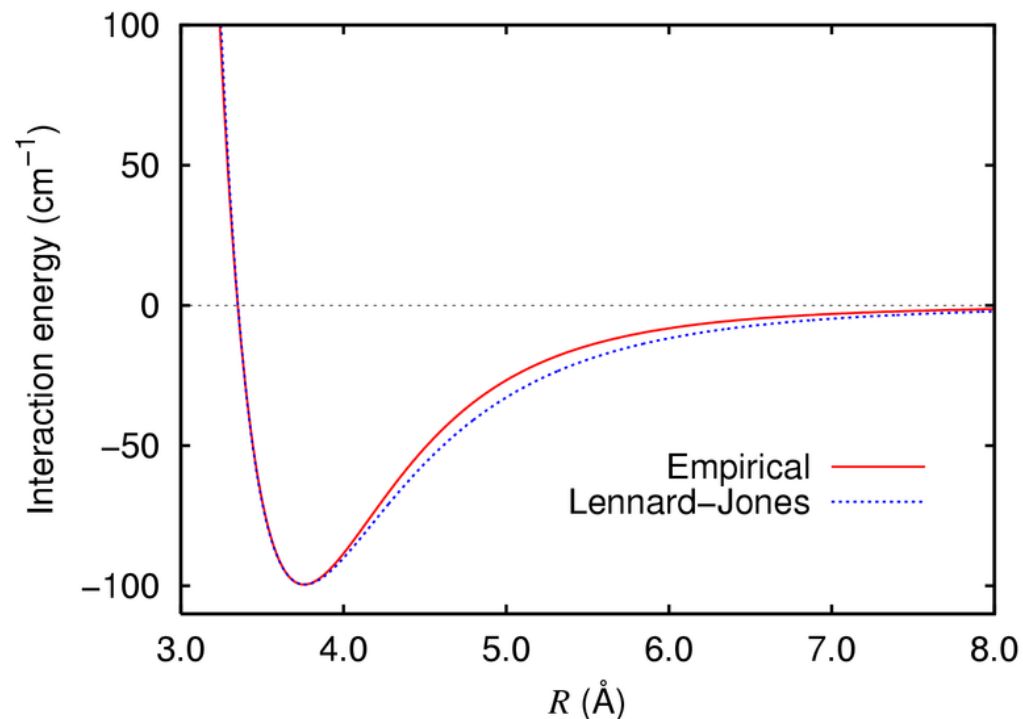Electrons energy strongly depends on the distance between nuclei.

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Wikipedia

Electronic states

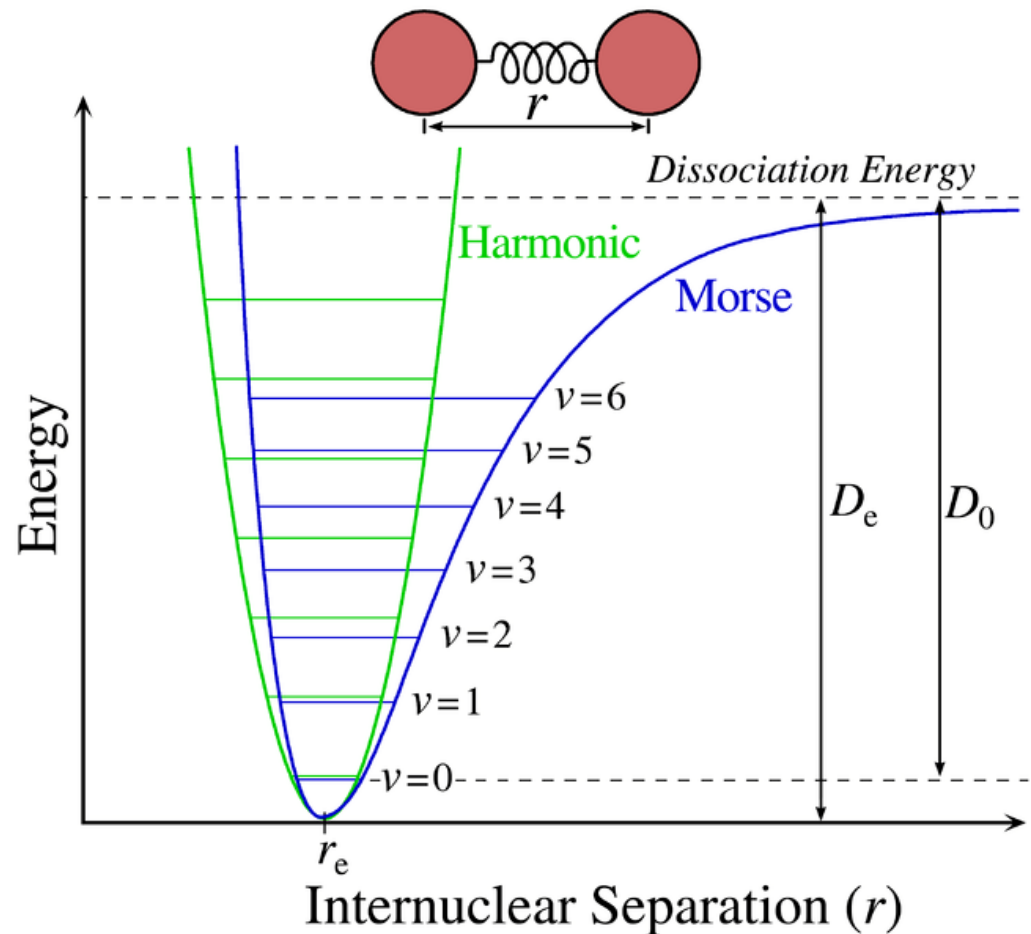Electrons energy strongly depends on the distance between nuclei.

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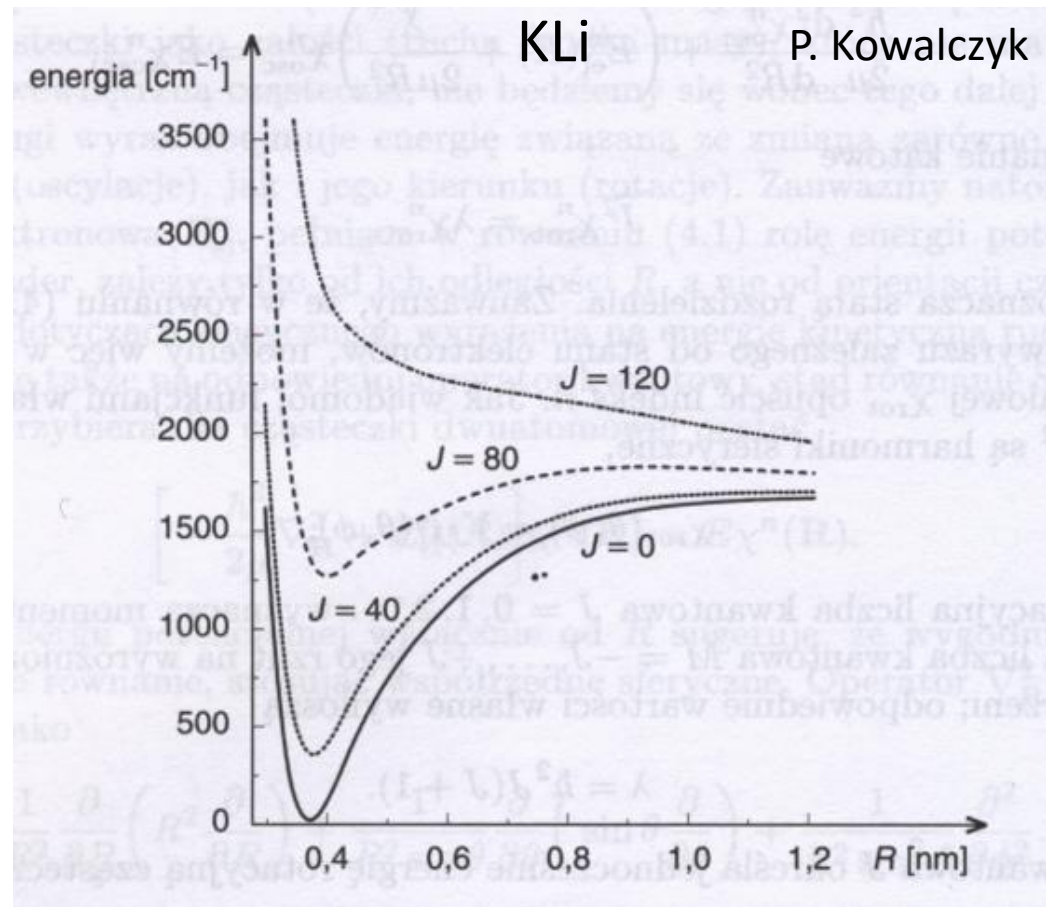
Vibration–rotation spectra

The vibrations of diatomic molecules

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dR^2} + \left(\frac{\hbar J(J+1)}{2\mu R^2} + E_{el}^n(\vec{R})\right)\right]\chi_{osc}^{nvJ}(R) = E\chi_{osc}^{nvJ}(R)$$

$$\frac{\hbar J(J+1)}{2\mu R^2} + E_{el}^n(\vec{R}) = V_{eff}(\vec{R})$$

The energy of electrons does not only depend on the distance between nuclei, but also on how quickly molecule rotates.

$$\Psi(\vec{r}, \vec{R}) = \chi_{osc}^n(R)\chi_{rot}^n(\theta, \varphi)\Psi_{el}^n(\vec{r}, \vec{R})$$
$$E^n = E_{osc}^n + E_{rot}^n + E_{el}$$

KLi

P. Kowalczyk

Vibration–rotation spectra

Harmonic approximation

We are expanding potential around the equilibrium point

$$V(r) = D_e\left[1 - e^{-\alpha(r-r_0)}\right] + V(r_0)$$

$$E_{el}^n(R) \approx \frac{1}{2}k_n(R - R_e)^2$$

Harmonic oscillator

$$\chi_{osc}^v = N_v e^{-\frac{x^2}{2}} H_v(x)$$

$$E_v = \hbar\omega_e\left(v + \frac{1}{2}\right) \qquad 10^2\text{-}10^3\text{cm}^{-1}$$

Dissociation Energy

Harmonic

Morse

$v=6$
$v=5$
$v=4$
$v=3$
$v=2$
$v=1$
$v=0$

D_e D_0

Energy

R_e
Internuclear separation (R)

Wikipedia

Vibration–rotation spectra

Harmonic approximation

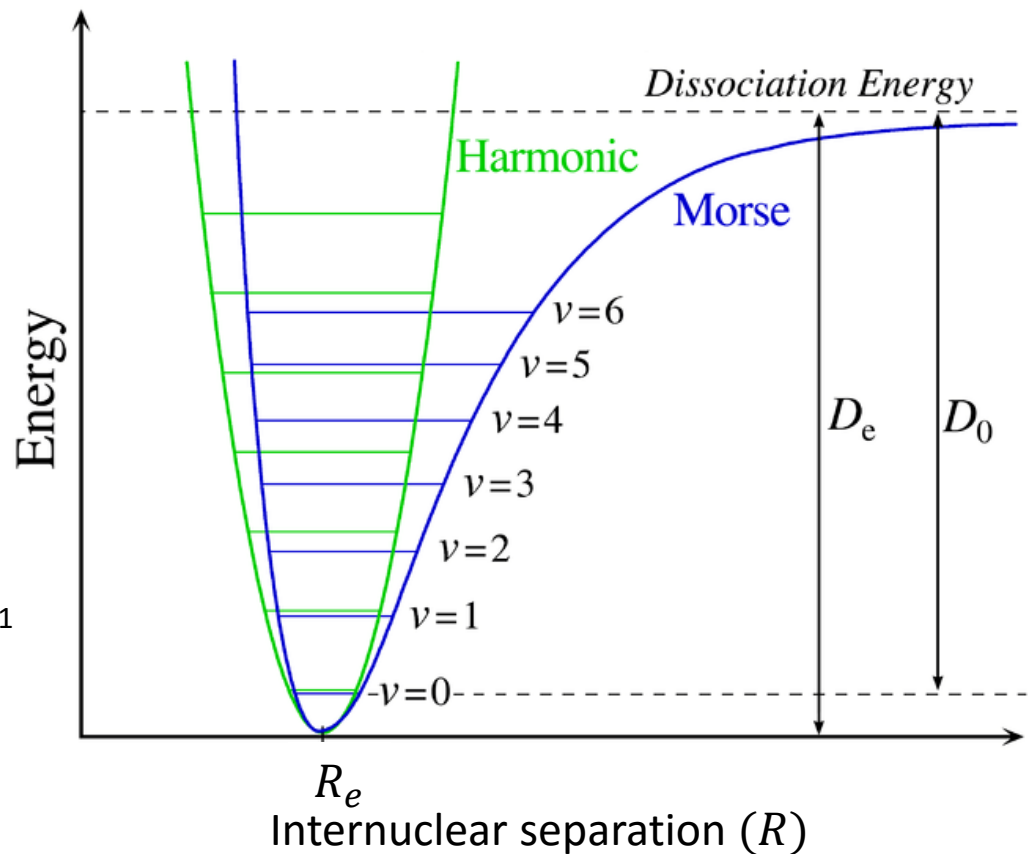We are expanding potential around the equilibrium point

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Vibration–rotation spectra

Harmonic approximation
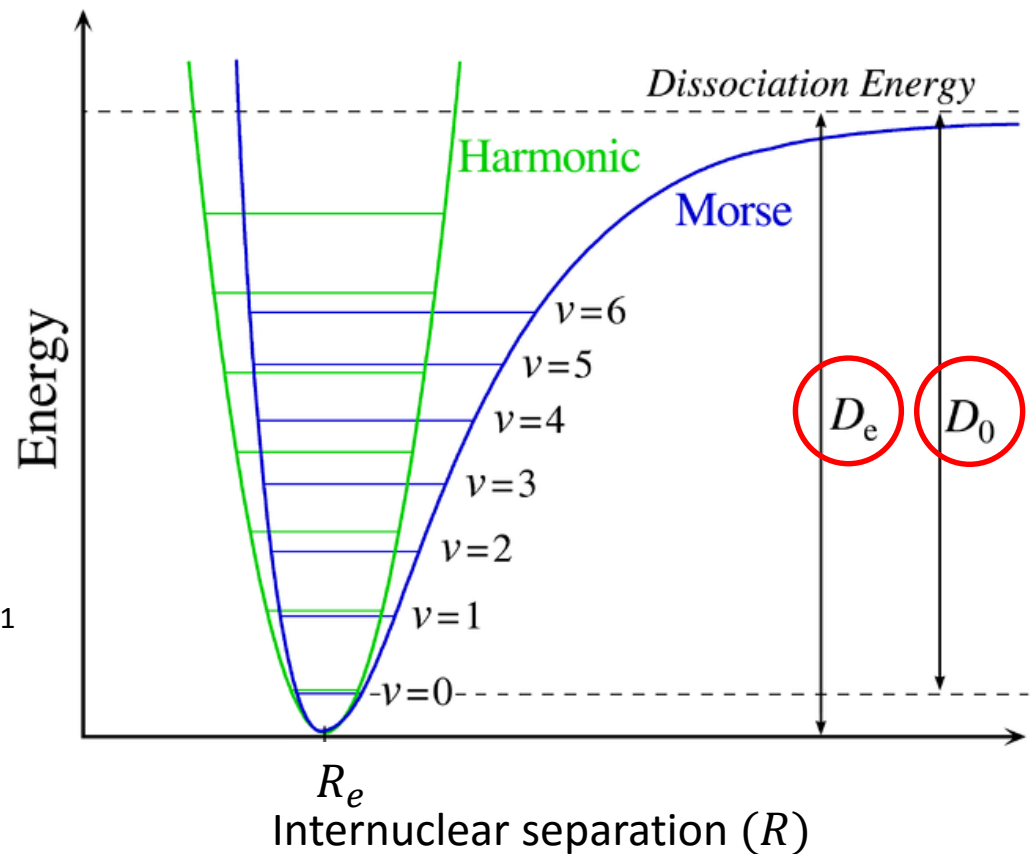
We are expanding potential around the equilibrium point

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Harmonic oscillator

$$\chi_{osc}^v = N_v e^{-\frac{x^2}{2}}H_v(x)$$

$$E_v = \hbar\omega_e\left(v + \frac{1}{2}\right) \qquad 10^2\text{-}10^3\text{cm}^{-1}$$

Molecule	Energy $h\nu$ (eV)
C_2	0,204
N_2	0,293
O_2	0,196
HCl	0,357
HBr	0,316
HJ	0,491

Anharmonicity: $\quad E_v = \hbar\omega_e\left(v + \frac{1}{2}\right) - \hbar\omega_e\chi_e\left(v + \frac{1}{2}\right)^2$

Vibration–rotation spectra

Harmonic approximation

Vibration-rotation energy levels

$$\Psi(\vec{r}, \vec{R}) = \chi_{osc}^n(R)\chi_{rot}^n(\theta, \varphi)\Psi_{el}^n(\vec{r}, \vec{R})$$

$$E^n = E_{el} + E_{rot}^n + E_{osc}^n$$

$$E = E_{el}^n + BJ(J+1) + \hbar\omega_e\left(v + \frac{1}{2}\right)$$

Energy

$J = 6$

$J = 5$

$J = 4$

$J = 3$

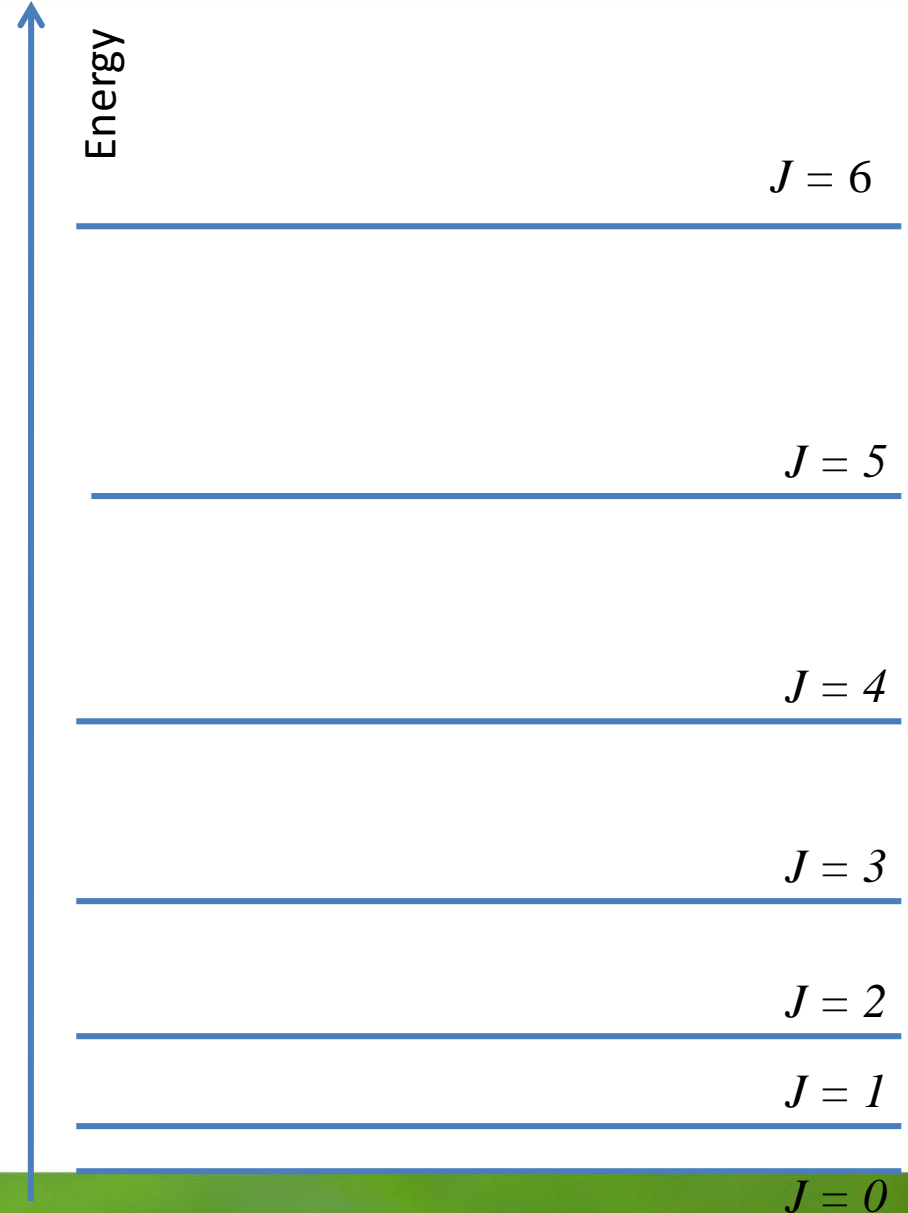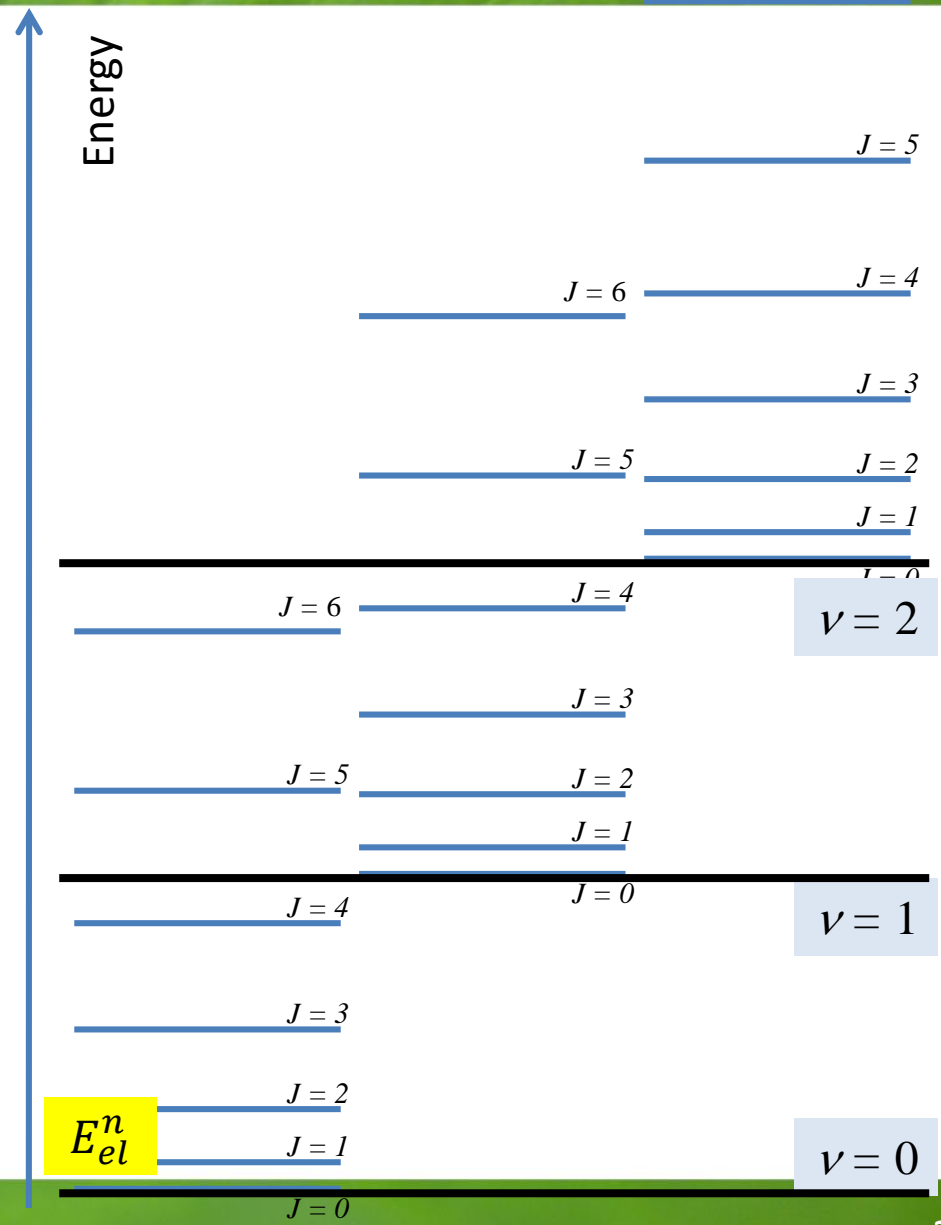$J = 2$

$J = 1$

$J = 0$

Vibration–rotation spectra

Harmonic approximation

Vibration-rotation energy levels

$$\Psi(\vec{r}, \vec{R}) = \chi_{osc}^n(R)\chi_{rot}^n(\theta, \varphi)\Psi_{el}^n(\vec{r}, \vec{R})$$

$$E^n = E_{el} + E_{rot}^n + E_{osc}^n$$

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Energy

$J = 6$

$J = 5$

$J = 6$ $J = 4$

$J = 3$

$J = 5$ $J = 2$

$J = 1$

$J = 0$

$\nu = 2$

$J = 6$ $J = 4$

$J = 3$

$J = 5$ $J = 2$

$J = 1$

$J = 0$

$\nu = 1$

$J = 4$

$J = 3$

$J = 2$

E_{el}^n $J = 1$

$\nu = 0$

$J = 0$

Vibration–rotation spectra

Harmonic approximation

Vibration-rotation energy levels

Selection rule: Δv = ±1

Typically for vibration-rotation transitions: $B_{v'} \approx B_{v''}$

R branch

$$\Delta J = J' - J'' = +1$$

$$\Delta E = \hbar\omega_e + 2B_{v'} + (3B_{v'} - B_{v''})J'' + (B_{v'} - B_{v''})J''^2$$
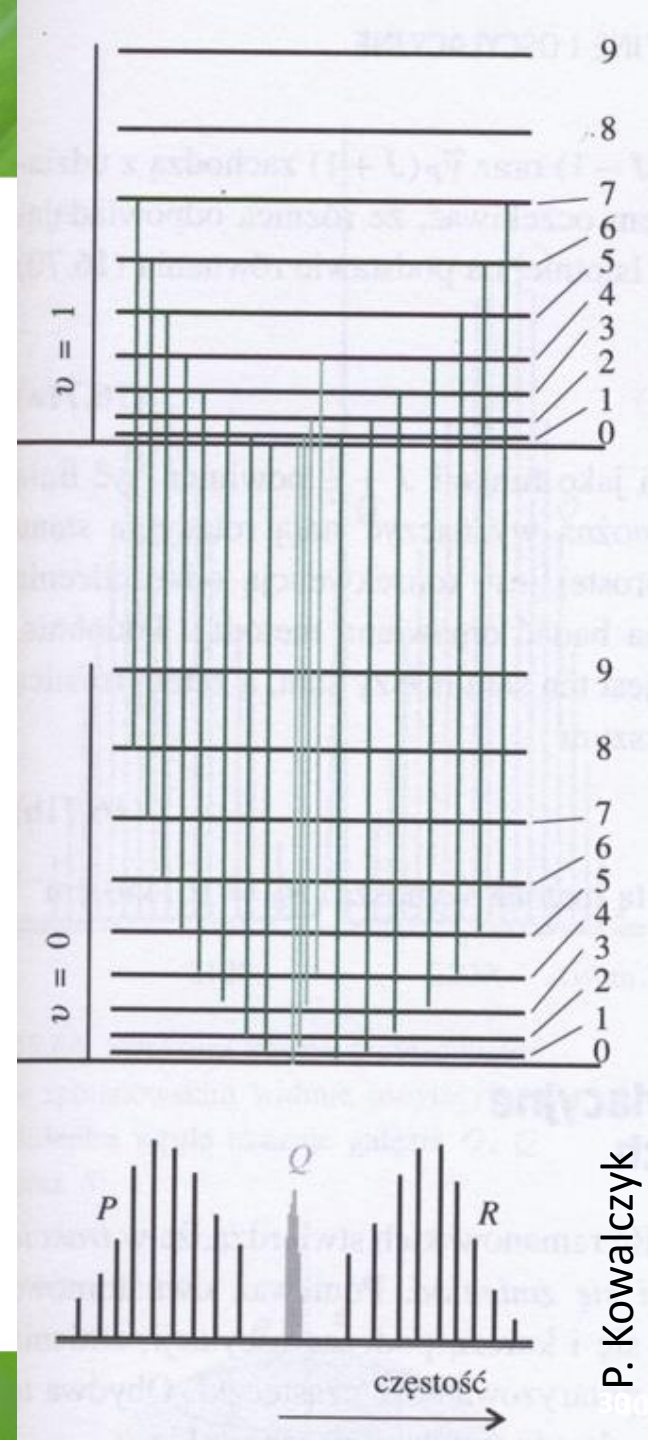
Q branch

$$\Delta J = 0$$

$$\Delta E = \hbar\omega_e + (B_{v'} - B_{v''})J'' + (B_{v'} - B_{v''})J''^2$$

P branch

$$\Delta J = J' - J'' = -1$$

$$\Delta E = \hbar\omega_e - (B_{v'} + B_{v''})J'' + (B_{v'} - B_{v''})J''^2$$

P. Kowalczyk

Vibration–rotation spectra

Harmonic approximation

Vibration-rotation energy levels

Selection rule: Δv = ±1

Typically for vibration-rotation transitions: $B_{v'} \approx B_{v''}$

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$\Delta J = J' - J'' = +1$

$\Delta E = \hbar\omega_e + 2B_{v'} + (3B_{v'} - B_{v''})J''$
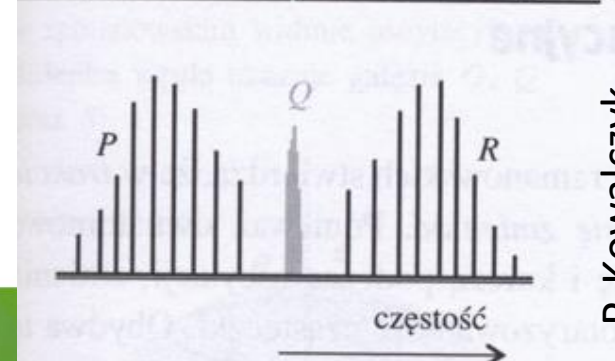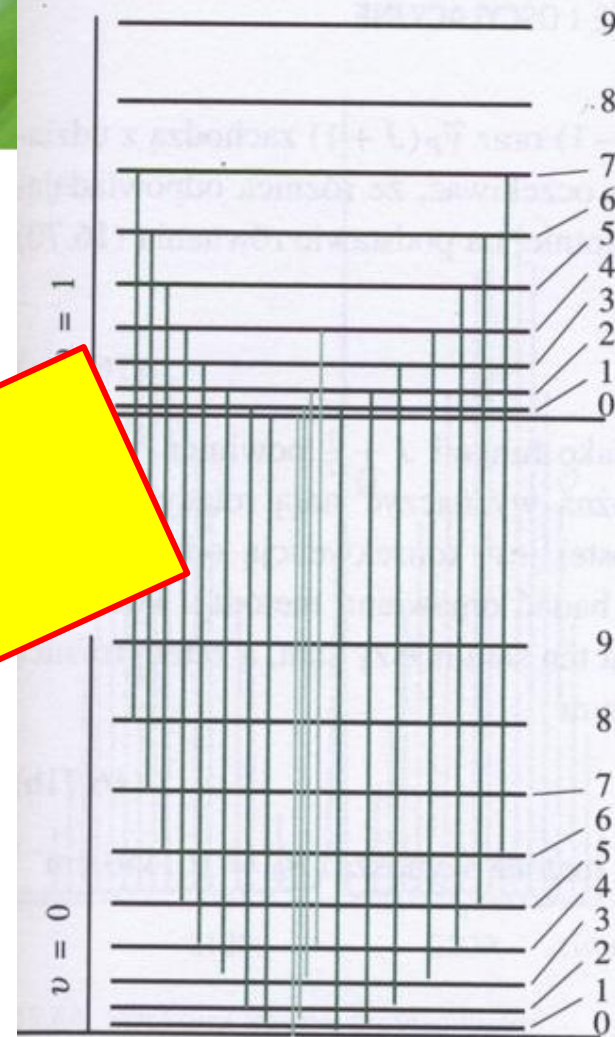
Q branch

$\Delta J = 0$

$\Delta E = \hbar\omega_e + (B_{v'} - B_{v''})J'' + (B_{v'} - B_{v''})J''^2$

P branch

$\Delta J = J' - J'' = -1$

$\Delta E = \hbar\omega_e - (B_{v'} + B_{v''})J'' + (B_{v'} - B_{v''})J''^2$

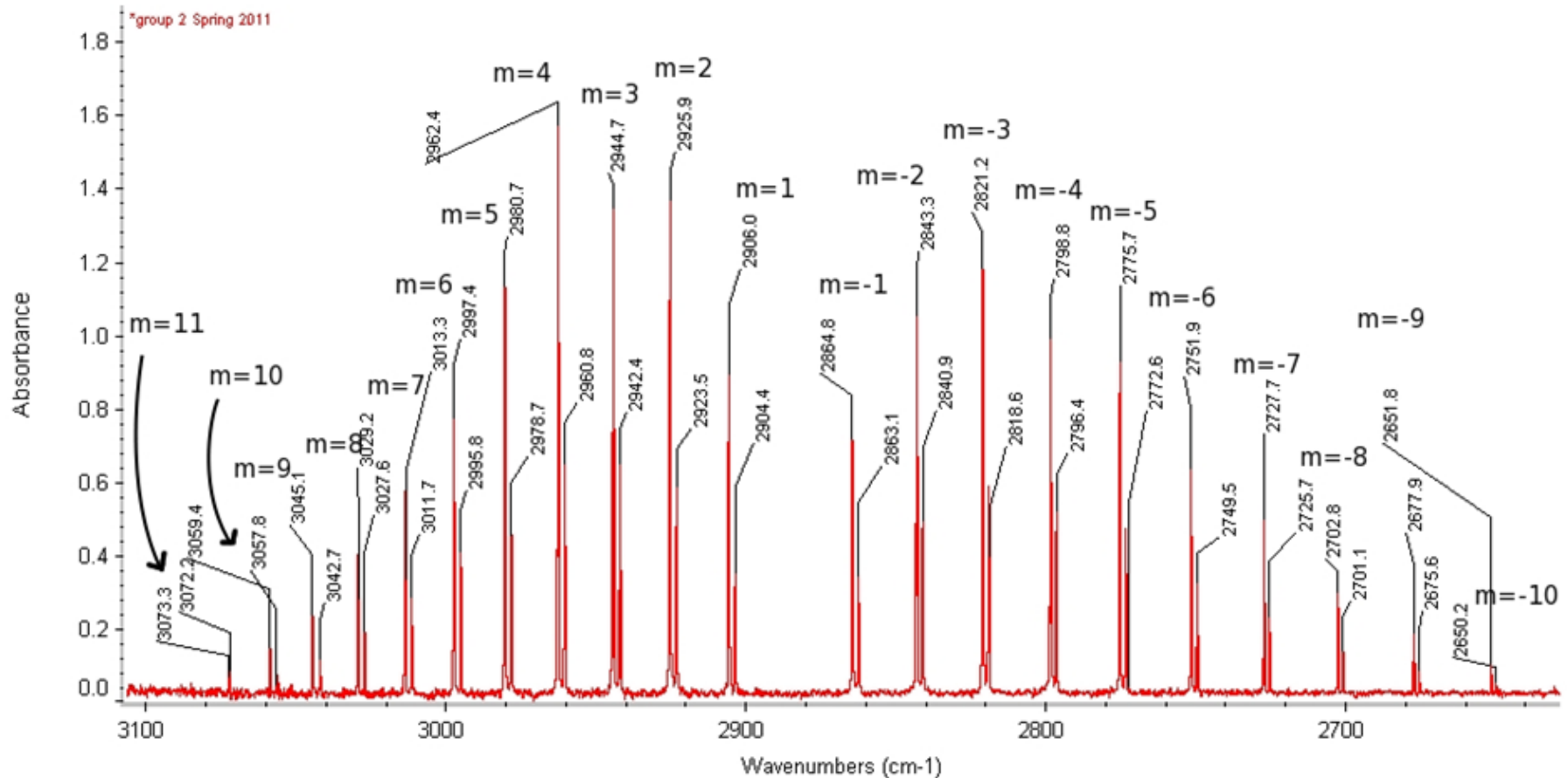On exercises!

P. Kowalczyk

Vibration–rotation spectra

Figure 1: The HCl spectrum in the mid-infrared region

http://www.odinity.com/vibration-rotation-spectroscopy-hcl/

Vibration–rotation spectra

Harmonic approximation

Vibration-rotation energy levels

$$\Psi(\vec{r}, \vec{R}) = \chi_{osc}^n(R)\chi_{rot}^n(\theta, \varphi)\Psi_{el}^n(\vec{r}, \vec{R})$$

$$E^n = E_{el} + E_{rot}^n + E_{osc}^n$$

$$E = E_{el}^n + BJ(J + 1) + \hbar\omega_e\left(\nu + \frac{1}{2}\right)$$

Franck-Condon principle

The nuclei are much heavier than electrons, therefore electron transitions occur much faster than nuclei are able to respond.

The transition between vibronic states $|\varepsilon\nu\rangle$ to $|\varepsilon'\nu'\rangle$

$$\mu_{\varepsilon'\varepsilon\,\nu'\nu} = \mu_{\varepsilon'\varepsilon} + \mu_{\nu'\nu}$$

$$\langle\varepsilon'\nu'|\mu_{\varepsilon'\varepsilon\,\nu'\nu}|\varepsilon\nu\rangle = \int \Psi'^*_{\varepsilon'\nu'}(\vec{r},\vec{R})\mu_{\varepsilon'\varepsilon\,\nu'\nu}\Psi_{\varepsilon\nu}(\vec{r},\vec{R})dR \approx$$

$$\approx \mu_{\varepsilon'\varepsilon}\int \Psi^*_{el}(\vec{r},\vec{R})\Psi'_{el}(\vec{r},\vec{R})d\boldsymbol{R} = \mu_{\varepsilon'\varepsilon}S(\nu',\nu)$$

overlap integral between the two vibrational states ν',ν

See: Atkins, Fridman *Molecular QM*

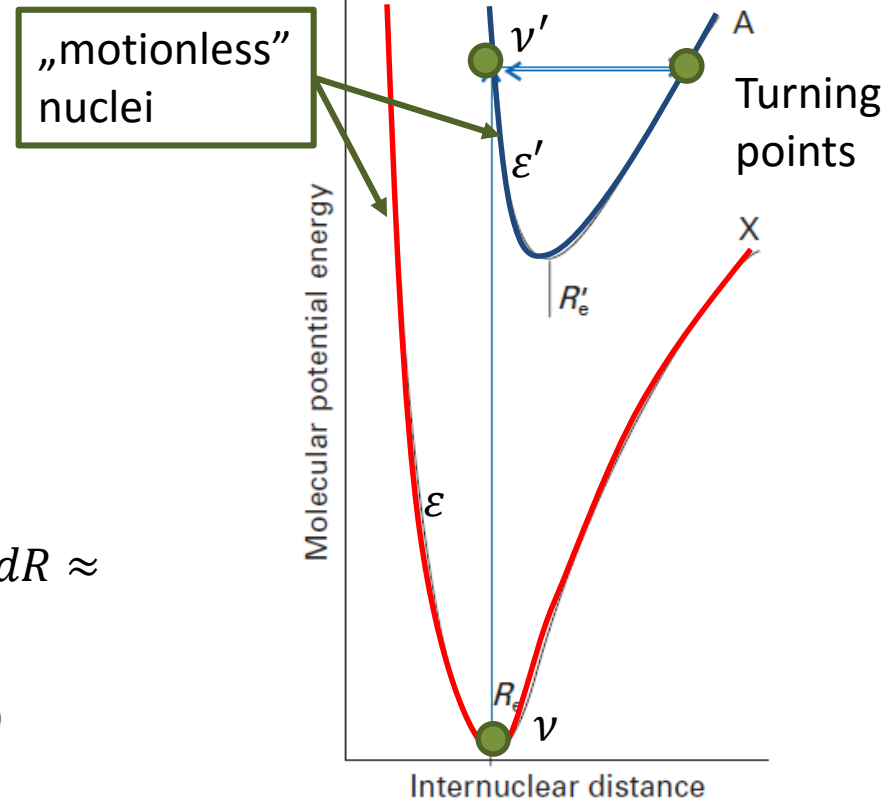

„motionless" nuclei

Turning points

Fig. 11.9 The classical basis of the Franck–Condon principle in which the molecule makes a vertical transition that terminates at the turning point of the excited state. The nuclei neither change their locations nor accelerate while the transition is in progress.

P. Atkins

Franck-Condon principle

The nuclei are much heavier than electrons, therefore electron transitions occur much faster than nuclei are able to respond.

The transition between vibronic states $|\varepsilon\nu\rangle$ to $|\varepsilon'\nu'\rangle$

$$\mu_{\varepsilon'\varepsilon\,\nu'\nu} = \mu_{\varepsilon'\varepsilon} + \mu_{\nu'\nu}$$

$$\langle\varepsilon'\nu'|\mu_{\varepsilon'\varepsilon\,\nu'\nu}|\varepsilon\nu\rangle = \int \Psi'^{*}_{\varepsilon'\nu'}(\vec{r},\vec{R})\mu_{\varepsilon'\varepsilon\,\nu'\nu}\Psi_{\varepsilon\nu}(\vec{r},\vec{R})dR \approx$$

$$\approx \mu_{\varepsilon'\varepsilon}\int \Psi^{*}_{el}(\vec{r},\vec{R})\Psi'_{el}(\vec{r},\vec{R})d\mathbf{R} = \mu_{\varepsilon'\varepsilon}S(\nu',\nu)$$

overlap integral between the two vibrational states ν', ν

See: Atkins, Fridman *Molecular QM*
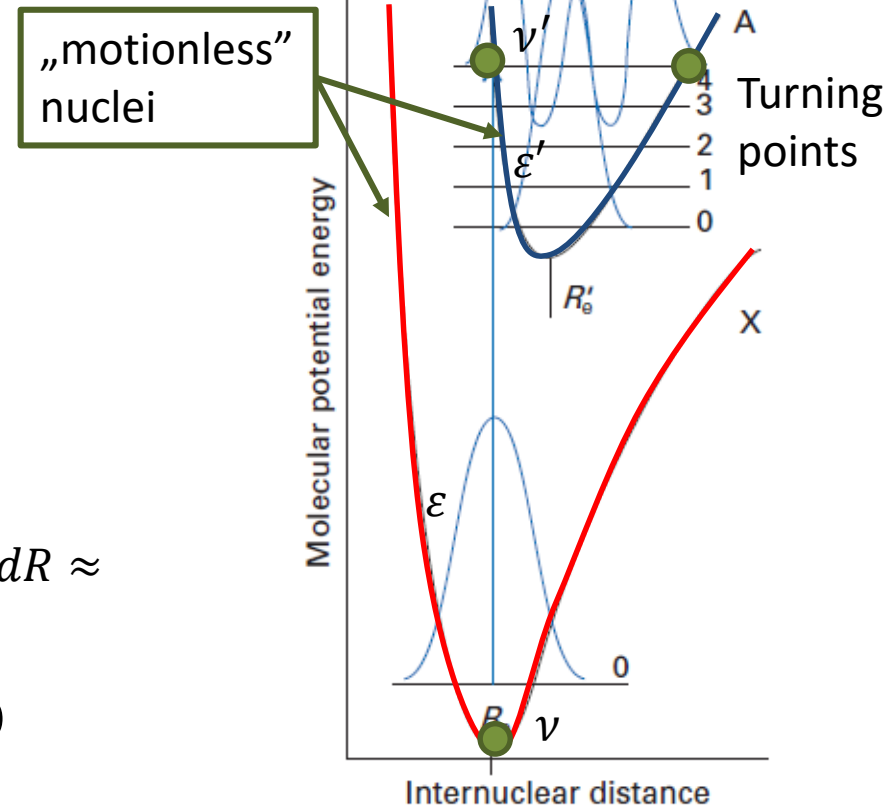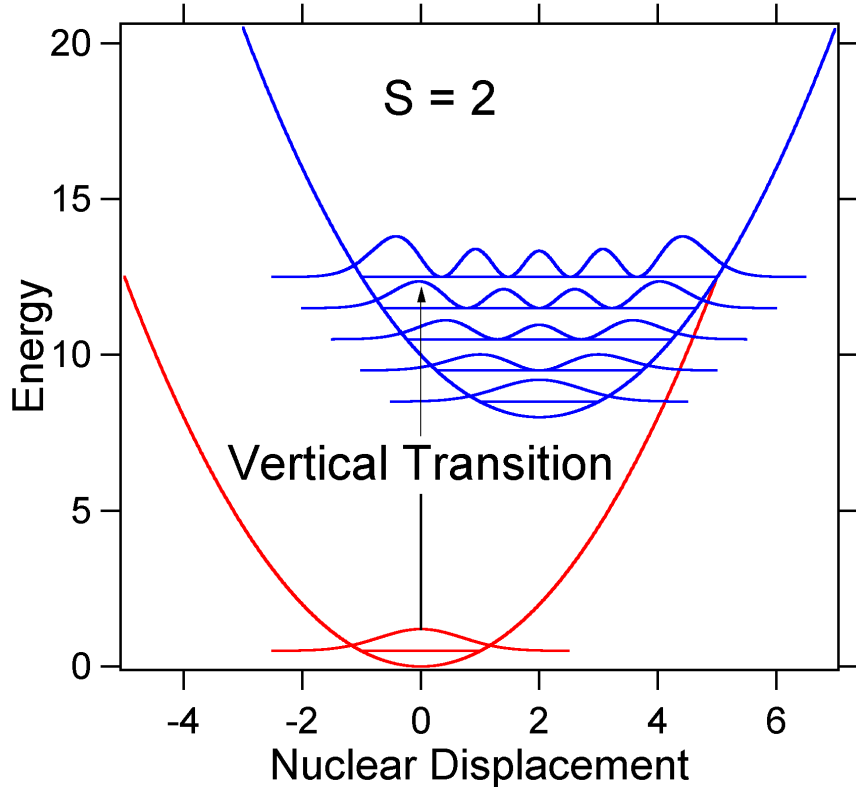

„motionless" nuclei

Turning points

Fig. 11.10 The quantum mechanical version of the Franck–Condon principle. The molecule makes a transition from the ground vibrational state to the state with a vibrational wavefunction that most strongly resembles the initial vibrational wavefunction.

P. Atkins

Franck-Condon principle

The nuclei are much heavier than electrons, therefore electron transitions occur much faster than nuclei are able to respond.
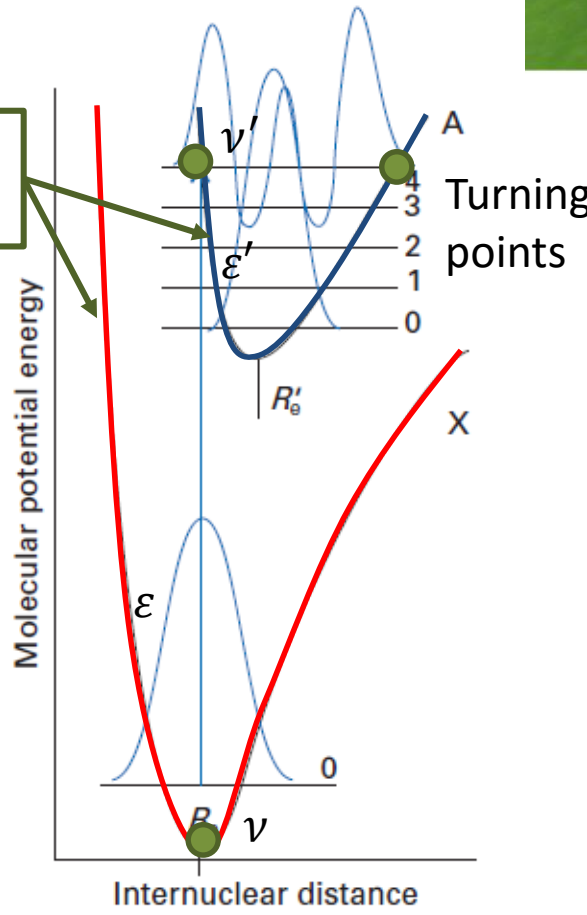
„motionless" nuclei

Turning points

S = 2

Vertical Transition

Energy

Nuclear Displacement

Molecular potential energy

Internuclear distance

Fig. 11.10 The quantum mechanical version of the Franck–Condon principle. The molecule makes a transition from the ground vibrational state to the state with a vibrational wavefunction that most strongly resembles the initial vibrational wavefunction.
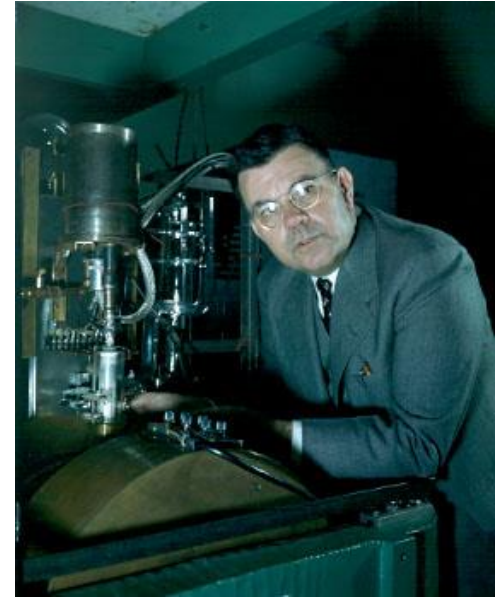
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Electronic-vibration–rotation spectra

Franck-Condon principle

James Franck
1882 – 1964

Edward U. Condon
1902 – 1974

**Rotational spectra** are associated only with the change of rotational movement – λ~ 0.1 – 10 cm (microwaves)

Vibration–rotation spectra correspond to both the change in vibration and rotation of the molecule – λ ~ 1 – 100 μm (IR)

Electronic-vibration–rotation spectra are related to the change in electron cloud state, which is accompanied by a change in oscillation and rotation– λ ~ 100 nm – 1 μm (UV-VIS)

Fluorescence and phosphorescence

Fluorescence

The Decay is immediate after switching off the excitation radiation ($10^{-8} - 10^{-4}$ s)

Nonradiative transitions
$10^{-11} - 10^{-9}$ s
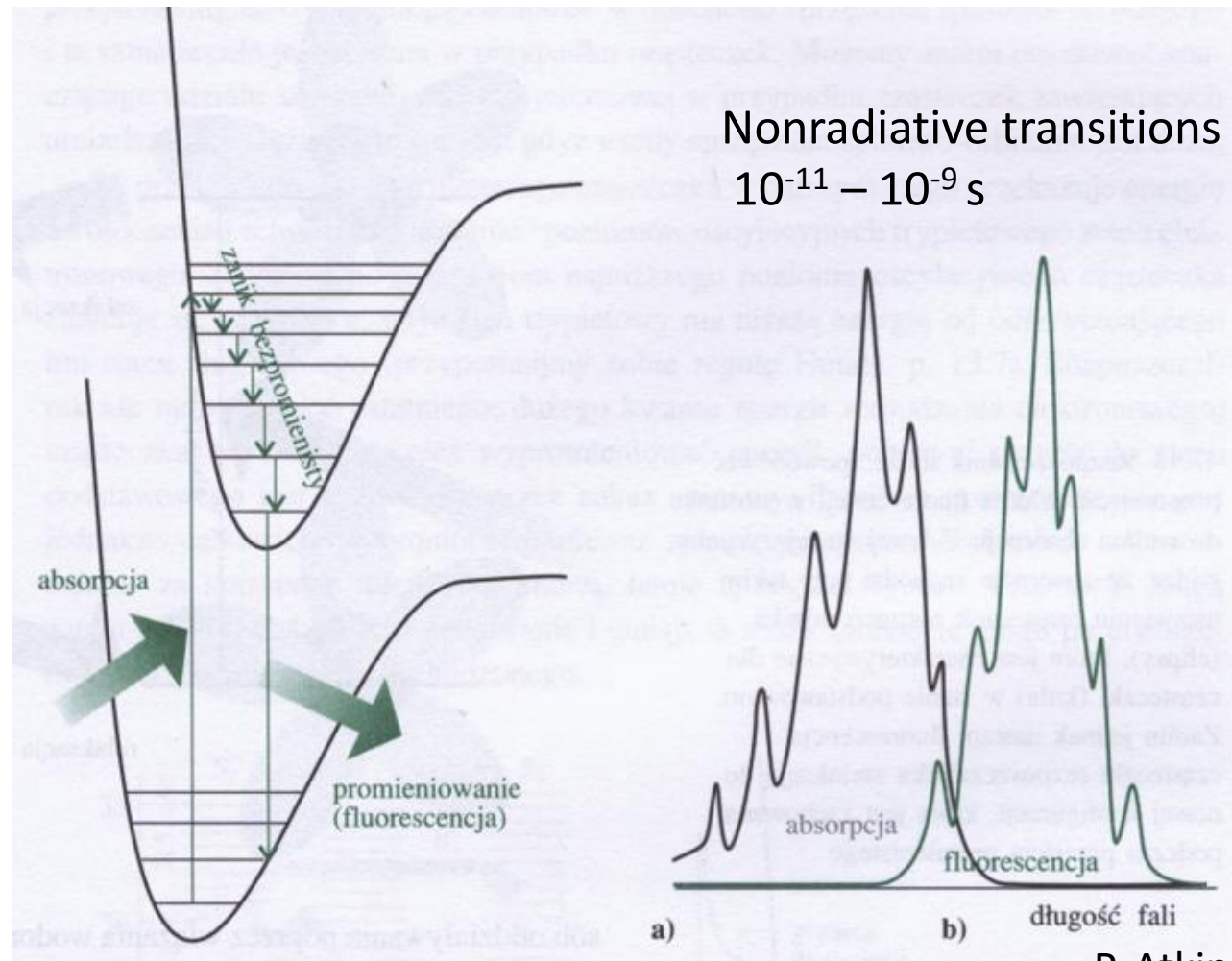
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Fluorescence and phosphorescence

Phosphorescence
The spontaneous emission may persist for a long time (from 10^{-4} seconds to hours)

Nonradiative transitions $10^{-11} – 10^{-9}$ s

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