Lesson 10

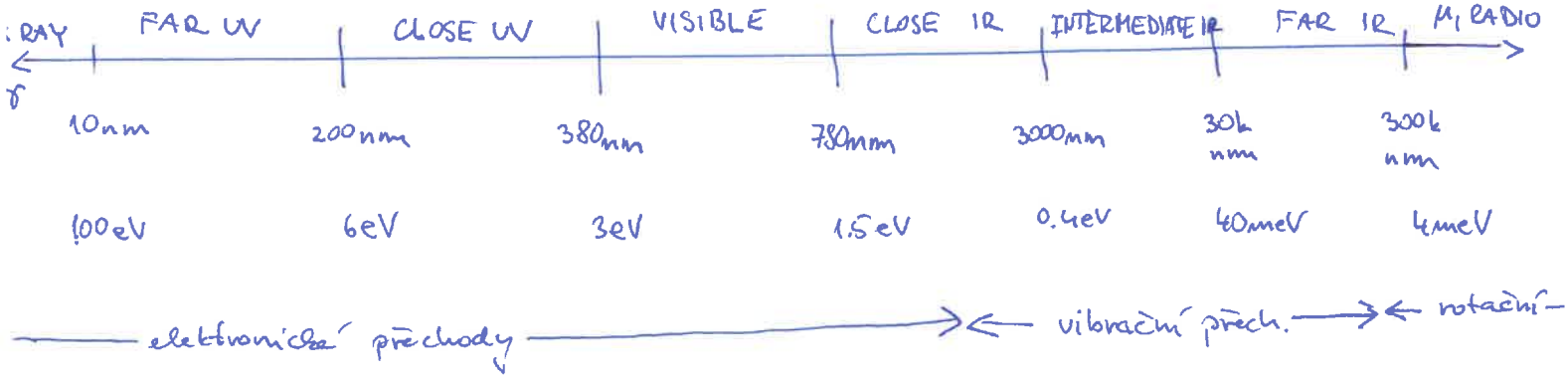
Introduction to the molecular spectroscopy

following Peter Bernath, Spectra of Atoms and Molecules

by R. Čurík

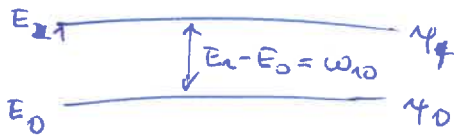
- Photon spectroscopy studies the interaction between the light and the matter
- The light creates an electrical field in the molecular world:

$$\vec{E}(\vec{r},t) = \vec{E}_0 \cos(\vec{k}\cdot\vec{r} - \omega t) \qquad \omega = 2\pi\nu = \frac{2\pi}{T} \; ; \; k = \frac{2\pi}{\lambda} \; ; \; \lambda\nu = c$$



Two-state model system described by the Hamiltonian H

$$H\psi_i = E_i\psi_i \; ; \; i = 0, 1$$



Task: Solution of the system within the external field

$$\vec{E}(\vec{r},t) = \vec{E}_0 \cos(\vec{k}\cdot\vec{r} - \omega t)$$

Two possible approaches:

1.) **Vector potential** $\vec{A}$: $\vec{E} = -\frac{\partial \vec{A}}{\partial t} - \nabla\varphi$; $\vec{B} = \nabla \times \vec{A}$

Ambiguity in the ~~calibrations~~ gauge: $\vec{A} = \vec{A}' + \nabla\chi$; $\varphi = \varphi' - \frac{\partial\chi}{\partial t}$ $\Rightarrow$ Choice of the Coulomb gauge

→ canonical momentum: $\hat{\vec{p}} \to \hat{\vec{p}} - q\hat{\vec{A}}$; kinetic energy: $\frac{(\vec{p} - q\vec{A})^2}{2m}$

2.) **Semiclassical approach** $H' = -\vec{\mu}\cdot\vec{E}(t) = -\vec{\mu}\cdot\vec{E}_0\cos(\vec{k}\vec{r} - \omega t)$

often $H' = -\mu_z E_z \cos(\vec{k}\vec{r} - \omega t)$

↑ size of the molecule/atom, check the wavelength

Lesson 10

- Operator of the dipole moment: for the molecules/atoms

operator ↓ , vector ↓

$$\hat{\vec{\mu}} = \sum_{i=1}^{N} \hat{\vec{r}}_i - \sum_{A=1}^{M} Z_A \vec{R}_A$$

- Time-dependent Schrödinger equation

$$\frac{i\,\partial\Psi}{\partial t} = \left[\hat{H} + \hat{H}'(t)\right]\Psi \qquad \text{(TDSE)}$$

- For $H' = 0$ there are 2 solutions:

$$\Psi_0(t) = \psi_0(\vec{r})\, e^{-iE_0 t} = \psi_0 e^{-i\omega_0 t}$$
$$\psi_1(t) = \psi_1(\vec{r})\, e^{-iE_1 t} = \psi_1 e^{-i\omega_1 t}$$

- For $H' \neq 0$ the solution is written as a linear combination of ψ_0 an ψ_1

$$\psi(t) = a_0(t)\,\psi_0\, e^{-i\omega_0 t} + a_1(t)\,\psi_1\, e^{-\omega_1 t}$$

- Substitution to the TDSE gives

$$i\left(\dot{a}_0\psi_0 e^{-i\omega_0 t} + \dot{a}_1\psi_1 e^{-i\omega_1 t}\right) = H' a_0\psi_0 e^{-i\omega_0 t} + H' a_1\psi_1 e^{-i\omega_1 t}$$

1.) $\int \psi_0^* e^{i\omega_0 t}$

2.) $\int \psi_1^* e^{i\omega_1 t}$

$$i\dot{a}_0 = a_0\langle\psi_0|H'|\psi_0\rangle + a_1\langle\psi_0|H'|\psi_1\rangle e^{-i\omega_{10}t}$$
$$i\dot{a}_1 = a_0\langle\psi_1|H'|\psi_0\rangle e^{i\omega_{10}t} + a_1\langle\psi_1|H'|\psi_1\rangle$$

- Definition of the transition dipole moment

$$\vec{M}_{10} = \vec{M}_{01} \equiv \langle\psi_1|\hat{\vec{\mu}}|\psi_0\rangle$$

parity of $\vec{\mu}$

$$i\dot{a}_0 = -a_1 M_{01} E e^{-i\omega_{10}t}\cos\omega t$$
$$i\dot{a}_1 = -a_0 M_{01} E e^{i\omega_{10}t}\cos\omega t$$

- Rabi frequency $\omega_R = M_{01}E$

$$\dot{a}_0 = \frac{i a_1 \omega_R}{2}\left[e^{-i(\omega_{10}-\omega)t} + e^{-i(\omega_{10}+\omega)t}\right]$$
$$\dot{a}_1 = \frac{i a_0 \omega_R}{2}\left[e^{i(\omega_{10}-\omega)t} + e^{i(\omega_{10}+\omega)t}\right]$$

$(\omega_{10}-\omega) = \Delta$ / detuning

high frequency gives "0" after the averaging

- Analytic solutions for $a_0(0)=1$; $a_1(0)=0$:

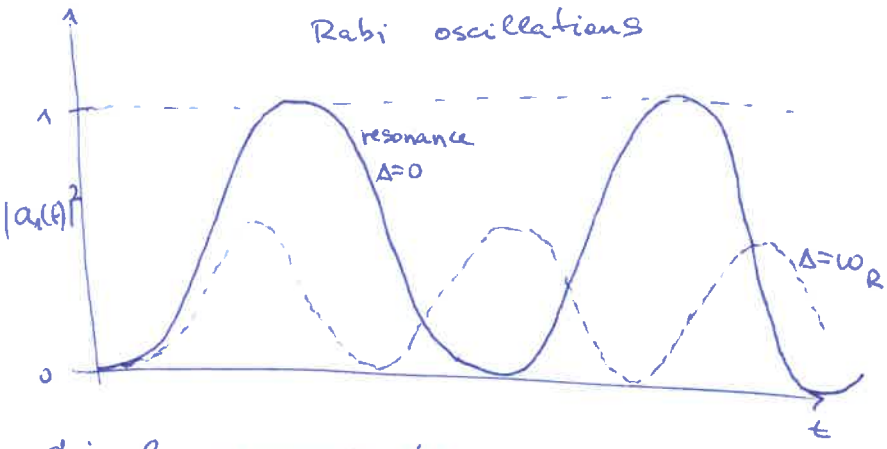
$$a_0(t) = \left[\cos\frac{\Omega t}{2} - i\left(\frac{\Delta}{\Omega}\right)\sin\frac{\Omega t}{2}\right] e^{i\Delta t/2}$$
$$a_1(t) = i\frac{\omega_R}{\Omega}\sin\frac{\Omega t}{2}\, e^{-i\Delta t/2}$$

$$\Omega^2 = \omega_R^2 + \Delta^2$$

Population of the upper state is

$$|a_1(t)|^2 = \frac{\omega_R^2}{\Omega^2} \sin^2 \frac{\Omega t}{2}$$

Rabi oscillations



For $\Delta = 0$ the Bohr resonance condition is satisfied

Selection rules within the dipole approximation

$$\psi(\vec{r},\vec{R}) \overset{BOA}{=} \psi_e(\vec{r};\vec{R})\,\psi_r(\hat{R})\,\psi_v(\vec{R})$$

1.) Electronic transitions

governed by the transition moment

$$\vec{M} = \langle \psi_e' | \hat{\vec{\mu}} | \psi_e'' \rangle$$

Atomic example:

$$\psi_e(\vec{r}) = R_{nl}(r)\,Y_{lm}(\hat{r})$$

$$M_z = \langle R_{n'l'} | r^3 | R_{n''l''} \rangle \langle Y_{l'm'} | \underbrace{\cos\vartheta}_{\sim Y_{10}} | Y_{l''m''} \rangle$$

$$|l'-l''| \le 1 \le |l'+l''|$$

$$\boxed{\begin{aligned} \Delta l &= \pm 1 \\ \Delta S &= 0 \end{aligned}}$$

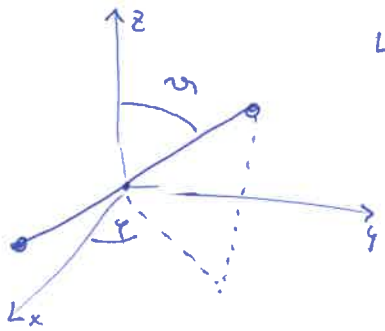
2.) Rotational transitions

If the electronic state does not change, the molecule needs to have a permanent dipole moment. Otherwise the transition is of a higher order – Raman effect.

Example: diatomic molecule

$$\psi_r(\vartheta,\varphi) \sim Y_{jm}(\vartheta,\varphi)$$

Dipole moment in the direction of the molecular axis:



$$M_z = \langle \psi_r' | \underbrace{\cos\vartheta}_{Y_{10}} | \psi_r'' \rangle \Rightarrow \boxed{\Delta j = \pm 1}$$

3.) Vibrational transitions

$$M_z = \langle \psi_e'(\vec{r};Q)\,\psi_v'(Q) \mid \hat{\mu}_z \mid \psi_e''(\vec{r};Q)\,\psi_v''(Q)\rangle =$$

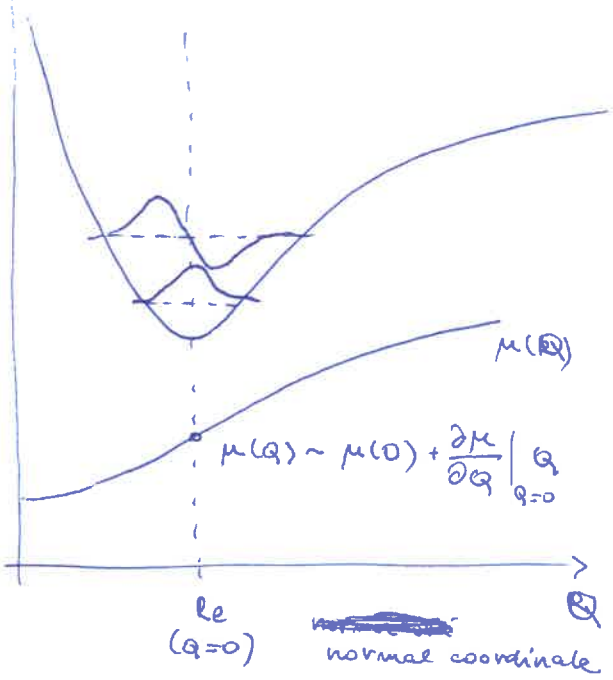
$$= \langle \psi_v'(Q) \mid \mu_z(Q) \mid \psi_v''(Q)\rangle ;$$

where

$$\mu_z(Q) = \langle \psi_e'(\vec{r};Q) \mid \hat{\mu}_z \mid \psi_e''(\vec{r};Q)\rangle_{\vec{r}}$$

$$M_z = \mu_z(0)\langle \psi_v' \mid \psi_v''\rangle + \frac{\partial \mu_z}{\partial Q}\langle \psi_v' \mid Q \mid \psi_v''\rangle$$

zero for nontrivial trans.



- Harmonic approximation — the eigenfunctions of the harmonic oscillator $H_n(Q)$

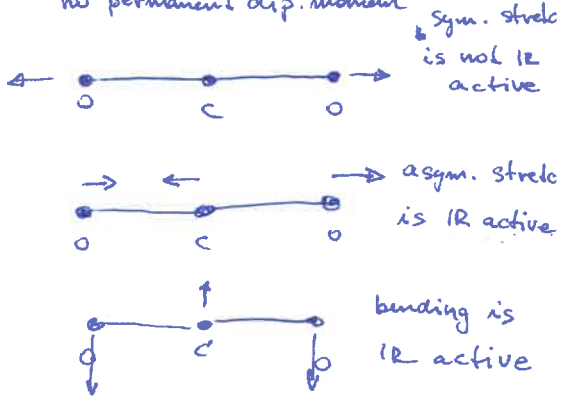
$$2Q\,H_n(Q) = H_{n+1}(Q) + 2n\,H_{n-1}(Q)$$

For $\frac{\partial \mu}{\partial Q} \neq 0$; $\Delta n = \pm 1$

↑ Infrared active mode

Permanent dipole moment is not necessary!

Example CO_2 has no permanent dip. moment



- Raman spectroscopy

- Induced dipole moment

$$\vec{\mu} = \overleftrightarrow{\alpha}\cdot\vec{E}$$

↑ polarizability tensor

a higher-order process, weaker absorption generally

$H' \sim \alpha E^2$; Raman activity $\frac{\partial \alpha}{\partial Q} \neq 0$