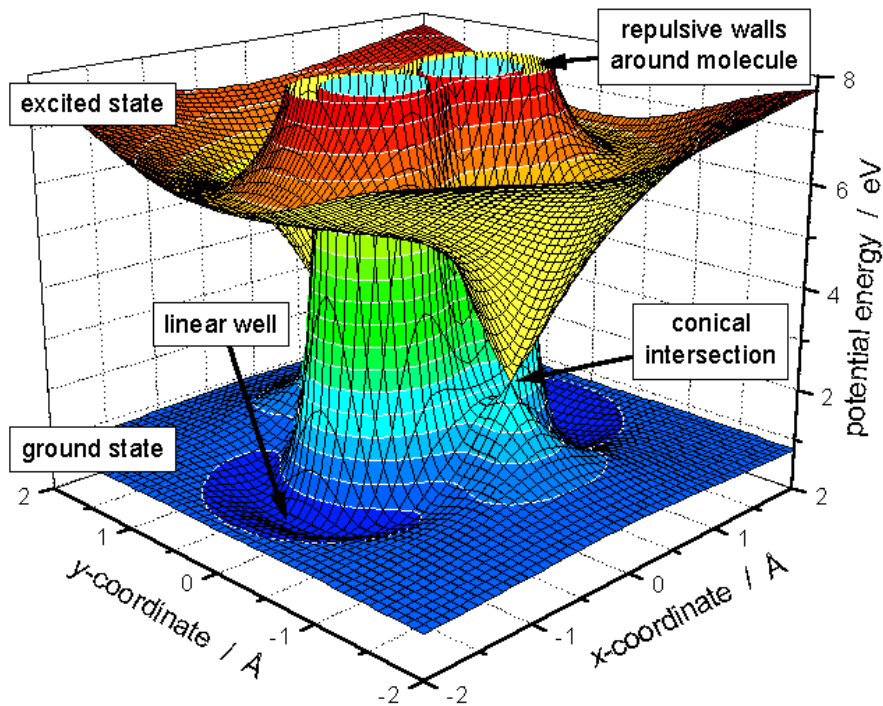# Excitované stavy
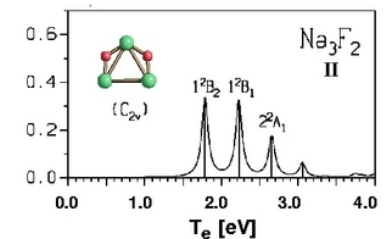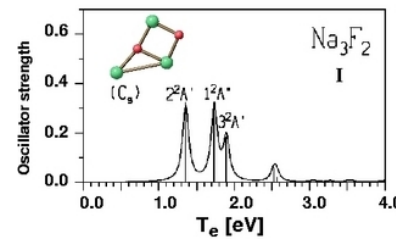
PES

◆ Potential energy (hyper)surface

■ Foto-chemická reakce
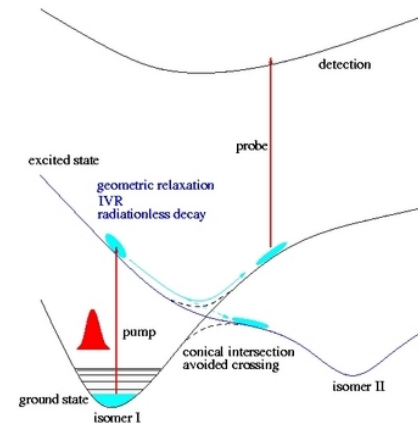
Obrázek 6.4: Princip fotochemických reakcí spočívá v převedení reaktantů ze základního stavu do stavu excitovaného, který může přes kónické křížení relaxovat do údolí produktů.

Fotochemie
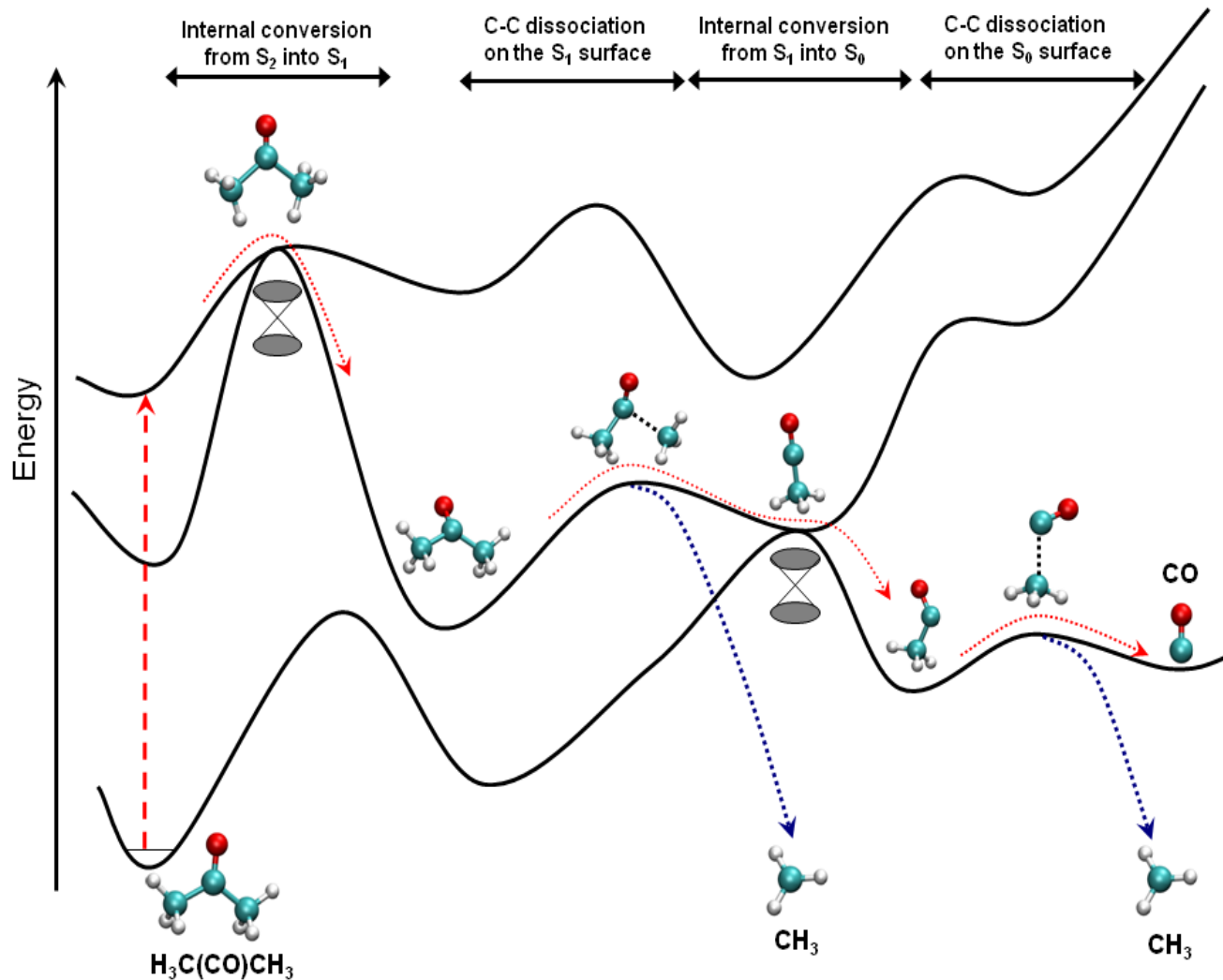
Elektronová spektra

◆ Přechody mezi el. základním a exitovanými stavy lze vyvolat absorpcí fotonu o energii cca 1-10 eV (UV-VIS oblast)
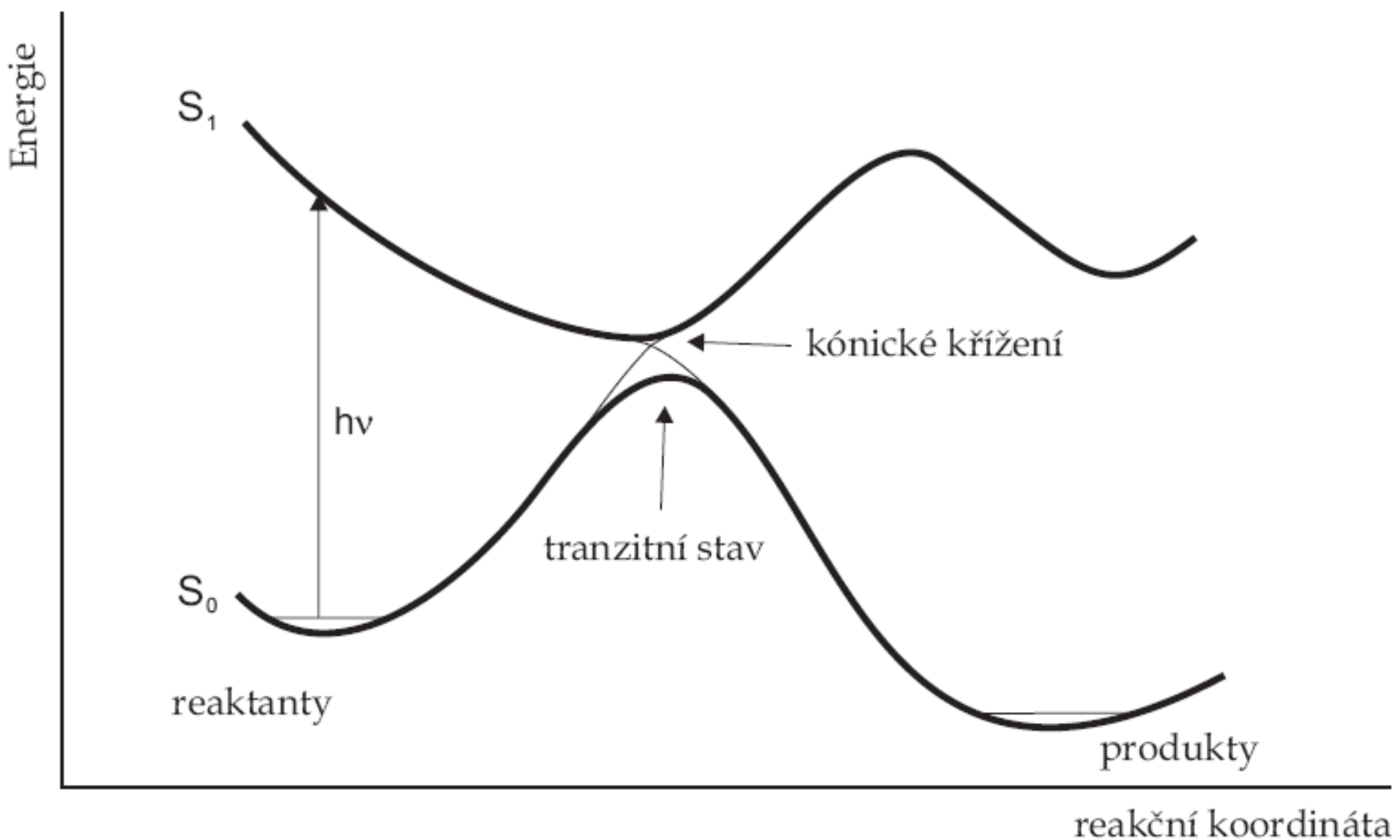
◆ Přechody lze studovat UV/VIS spektroskopií

◆ Pozn. povaha el. přechodů atomů a molekul se diametrálně liší

  ▪ Atomy – čárová spektra (využití AAS, rychlost pohybu hězd …)

  ▪ Molekuly – pásová spektra (přibývají roto-vibrační stavy + vliv. kond. fáze)

UV/VIS spektra

molekula I_2 (*g*)

atom H

H_α H_β H_γ H_δ H_∞

656,28 nm   486,13 nm   434,05 nm   410,17 nm
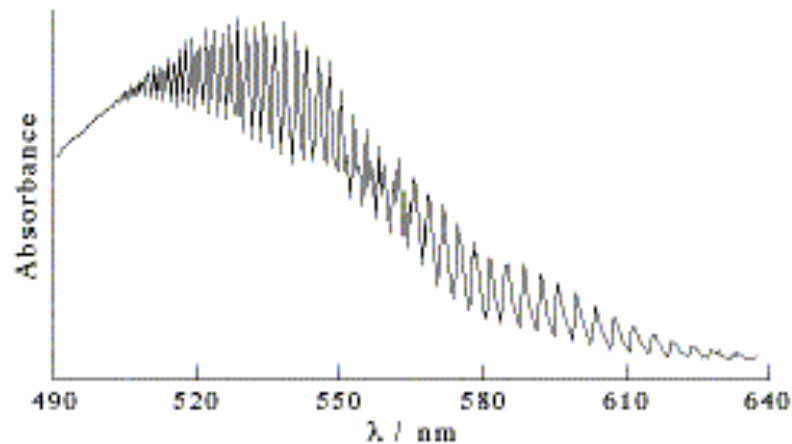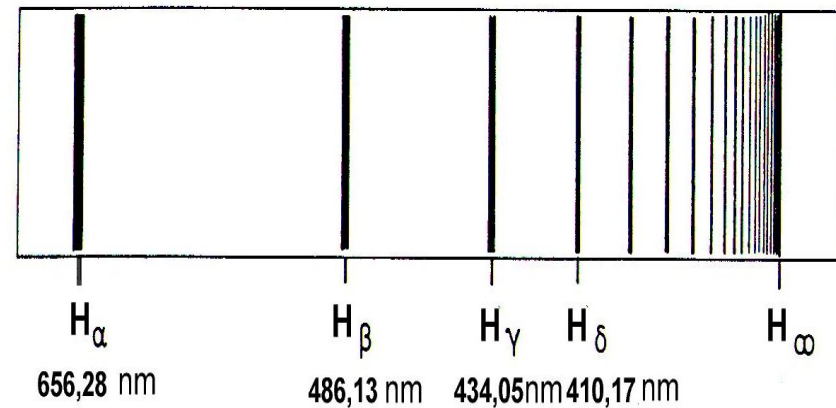
spektra molekul - pásová   **spektra atomů - čárová**

Absorpce fotonu

Energie

excitovaný stav
vzbuzený stav

S_1

excitovaný singletový stav
elektrony obsazují vyšší en.
hladiny, porušuje se párování
elektronů na hladinách

velmi rychlý proces ($\sim 10^{-15}$ s)
spin elektronů se při excitaci nemění
nemění se geometrie – Frank-Condonův princip

S_0

světlo (energie)

základní stav   singletový stav
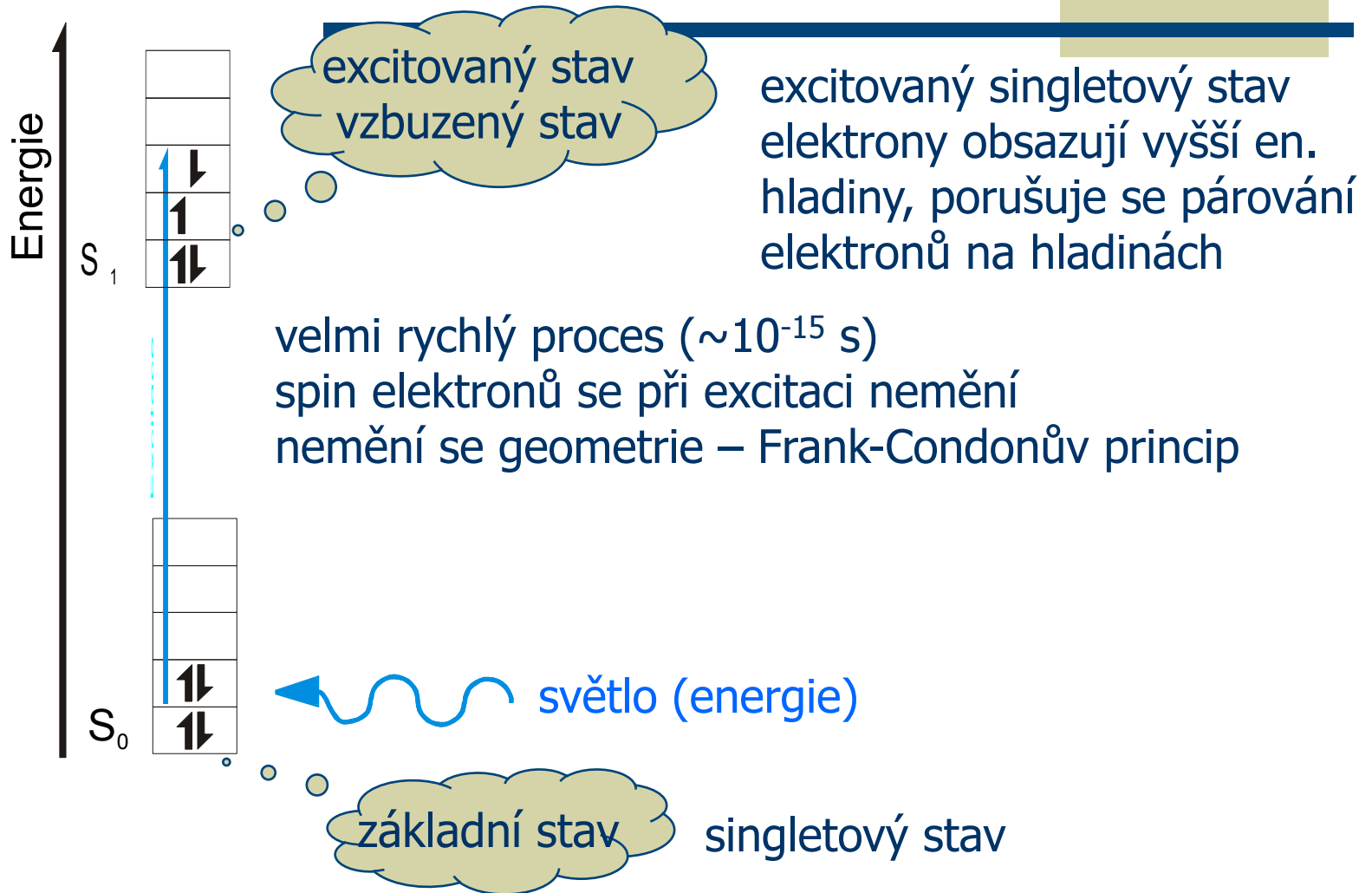
Excitace

◆ Musí být splněna rezonanční podmínka

$$E_i - E_j \ = \ h\nu$$

◆ Fotofyzikální jevy – relaxace molekuly bez chemické změny

◆ Fotochemické změny – dojde k chemické přeměně

Time Scales: From Milli to Femtosecond Physical, Chemical, and Biological Changes

http://nobelprize.org/nobel_prizes/chemistry/laureates/1999/zewail-lecture.pdf

Franck-Condon (FC) Principle
Franckův-Condonův princip

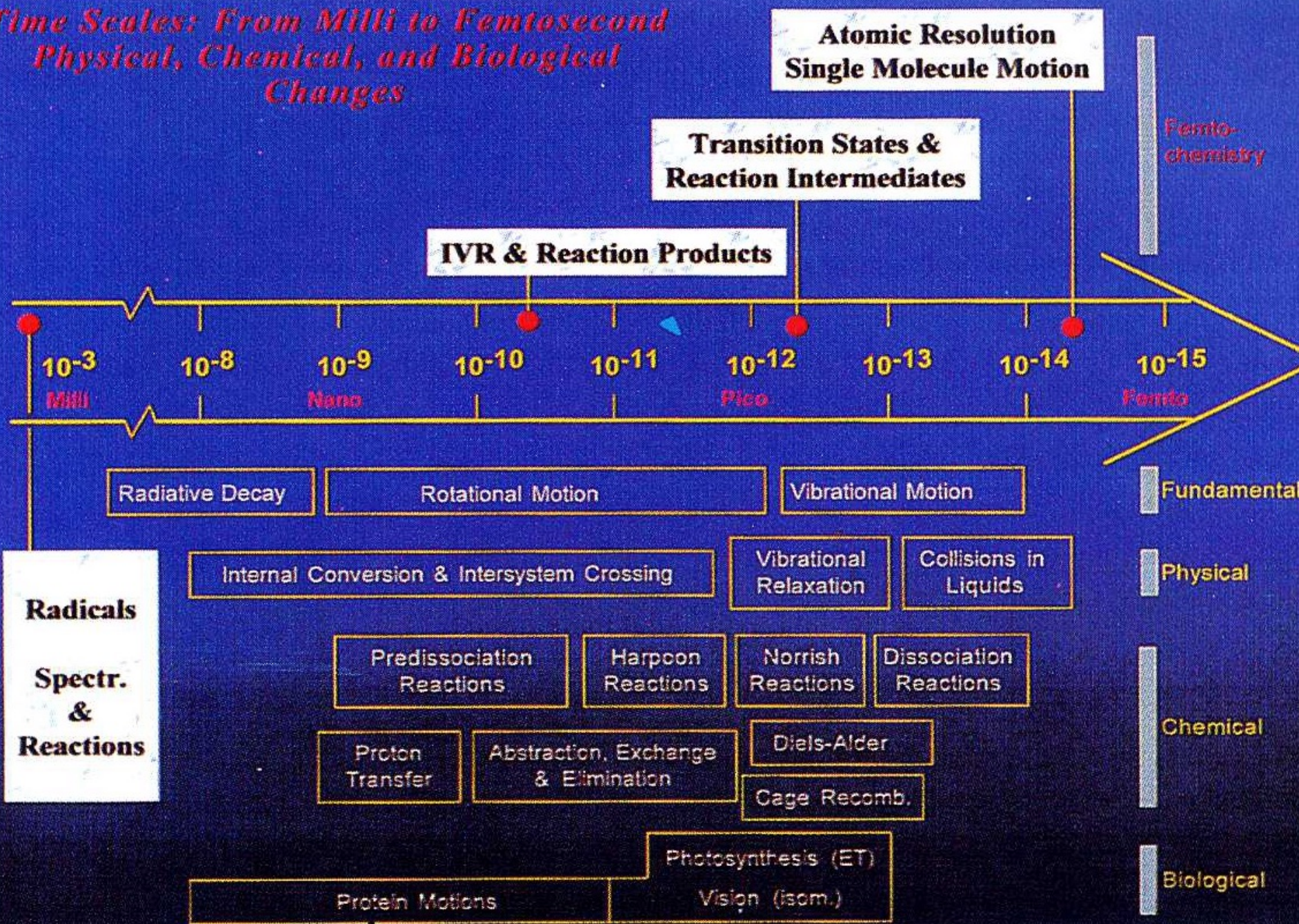◆ The FC principle states that during an electronic transition, a change from one vibrational energy level to another will be more likely to happen if the two vibrational wave functions overlap more significantly.

◆ Classically, the FC principle is the approximation that an electronic transition is most likely to occur **without changes in the positions of the nuclei** in the molecular entity and its environment. The resulting state is called a FC state, and the transition involved, a **vertical transition**. The quantum mechanical formulation of this principle is that the intensity of a vibronic transition is proportional to the square of the overlap integral between the vibrational wavefunctions of the two states that are involved in the transition.

▪ — IUPAC Compendium of Chemical Terminology, 2nd Edition (1997)

FC princip

◆ **Figure 1.** Franck-Condon principle energy diagram. Since electronic transitions are very fast compared with nuclear motions, vibrational levels are favored when they correspond to a minimal change in the nuclear coordinates. The potential wells are shown favoring transitions between $v = 0$ and $v = 2$.
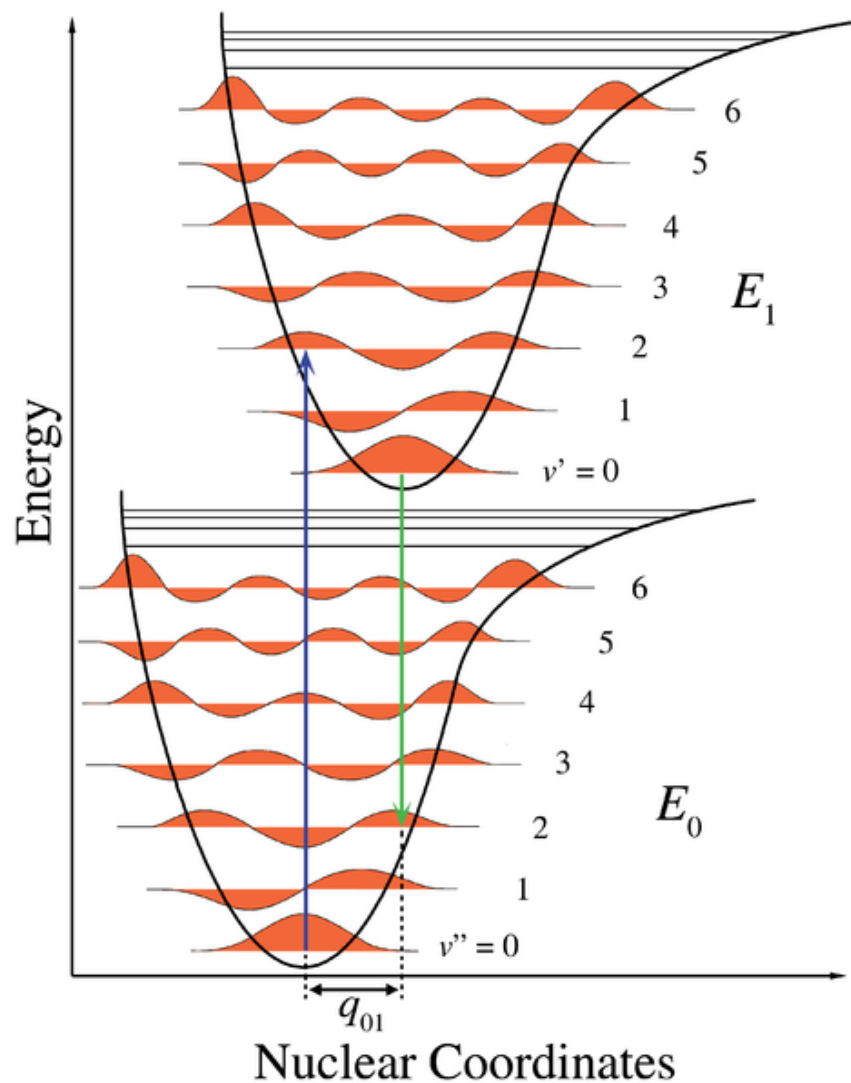
FC - QM

- Pravděpodobnost přechodu, mezi dvěma stavy, **μ** operátor dipól. momentu

$$P = \langle \psi' | \, \boldsymbol{\mu} \, | \psi \rangle = \int \psi'^* \boldsymbol{\mu} \psi d\tau$$

- Vlnová fce má tvar součinu vlnových fcí elektronické, jaderné (vibrační) a spinové (tzn. platí B-O aproximace!)

$$\psi = \psi_e \psi_v \psi_s$$

$$P = \langle \psi'_e \psi'_v \psi'_s | \, \boldsymbol{\mu} \, | \psi_e \psi_v \psi_s \rangle = \int \psi'^*_e \psi'^*_v \psi'^*_s (\boldsymbol{\mu}_e + \boldsymbol{\mu}_N) \psi_e \psi_v \psi_s \, d\tau$$

$$= \int \psi'^*_e \psi'^*_v \psi'^*_s \boldsymbol{\mu}_e \psi_e \psi_v \psi_s d\tau + \int \psi'^*_e \psi'^*_v \psi'^*_s \boldsymbol{\mu}_N \psi_e \psi_v \psi_s d\tau$$

$$= \underbrace{\int \psi'^*_v \psi_v d\tau_n}_{\substack{Franck-Condon \\ factor}} \underbrace{\int \psi'^*_e \boldsymbol{\mu}_e \psi_e d\tau_e}_{\substack{Orbital \\ selection\ rules}} \underbrace{\int \psi'^*_s \psi_s d\tau_s}_{\substack{Spin \\ selection\ rules}} + \underbrace{\int \psi'^*_e \psi_e d\tau_e \int \psi'^*_v \boldsymbol{\mu}_N \psi_v d\tau_v \int \psi'^*_s \psi_s d\tau_s}_{\substack{\| \\ 0}}$$

FC – QM, důsledky

- P ~ intenzitě přechodu (např. intenzitě pásu v UV/VIS spektru)
- FC faktor moduluje slabě intenzitu přechodu
- Orbitální výb. pravidlo je slabší než spinové výb. pravidlo

Intenzity přechodů

	Range of extinction coefficient (ε) values (moles^{-1} cm^{-1})
Spin and orbitally allowed	10^3 to 10^5
Spin allowed but orbitally forbidden	10^0 to 10^3
Spin forbidden but orbitally allowed	10^{-5} to 10^0

Kashovo pravidlo

- In the electronic excited state molecules quickly relax to the lowest vibrational level (Kasha's rule), and from there can decay to the lowest electronic state via photon emission. The Franck–Condon principle is applied equally to absorption and to fluorescence.

- The Kasha's rule states that photon emission (fluorescence or phosphorescence) occurs only from **the lowest-energy excited electronic state of a molecule**. It is named for American spectroscopist Michael Kasha, who proposed it in 1950.

  - Exceptions to Kasha's rule arise when there are large energy gaps between excited states. An example is azulene, the classical explanation for this is that the S_1 and S_2 states lie sufficiently far apart that fluorescence is observed from both of them.
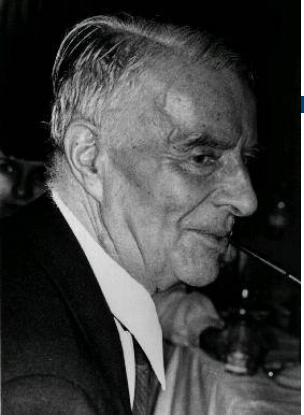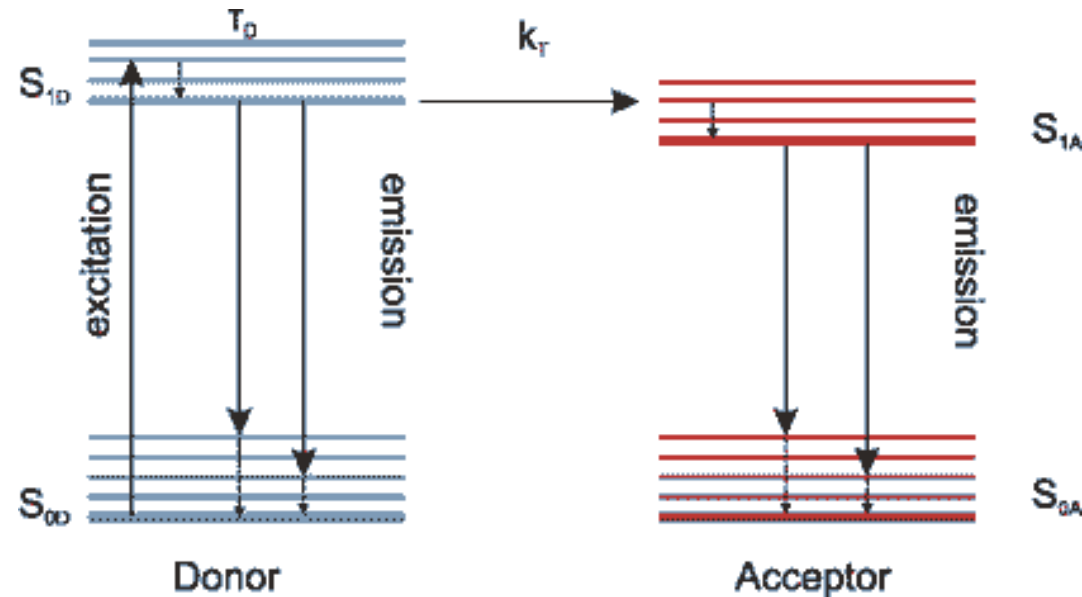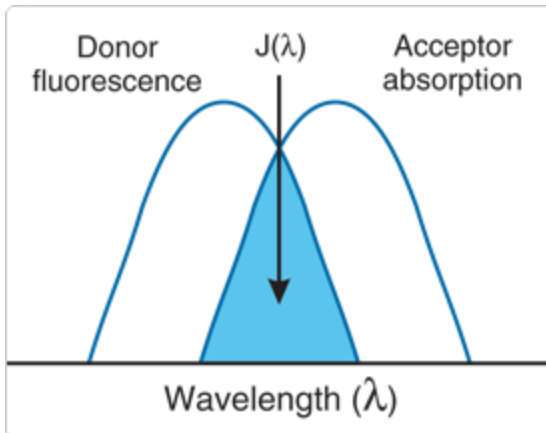
Jabłoński diagram
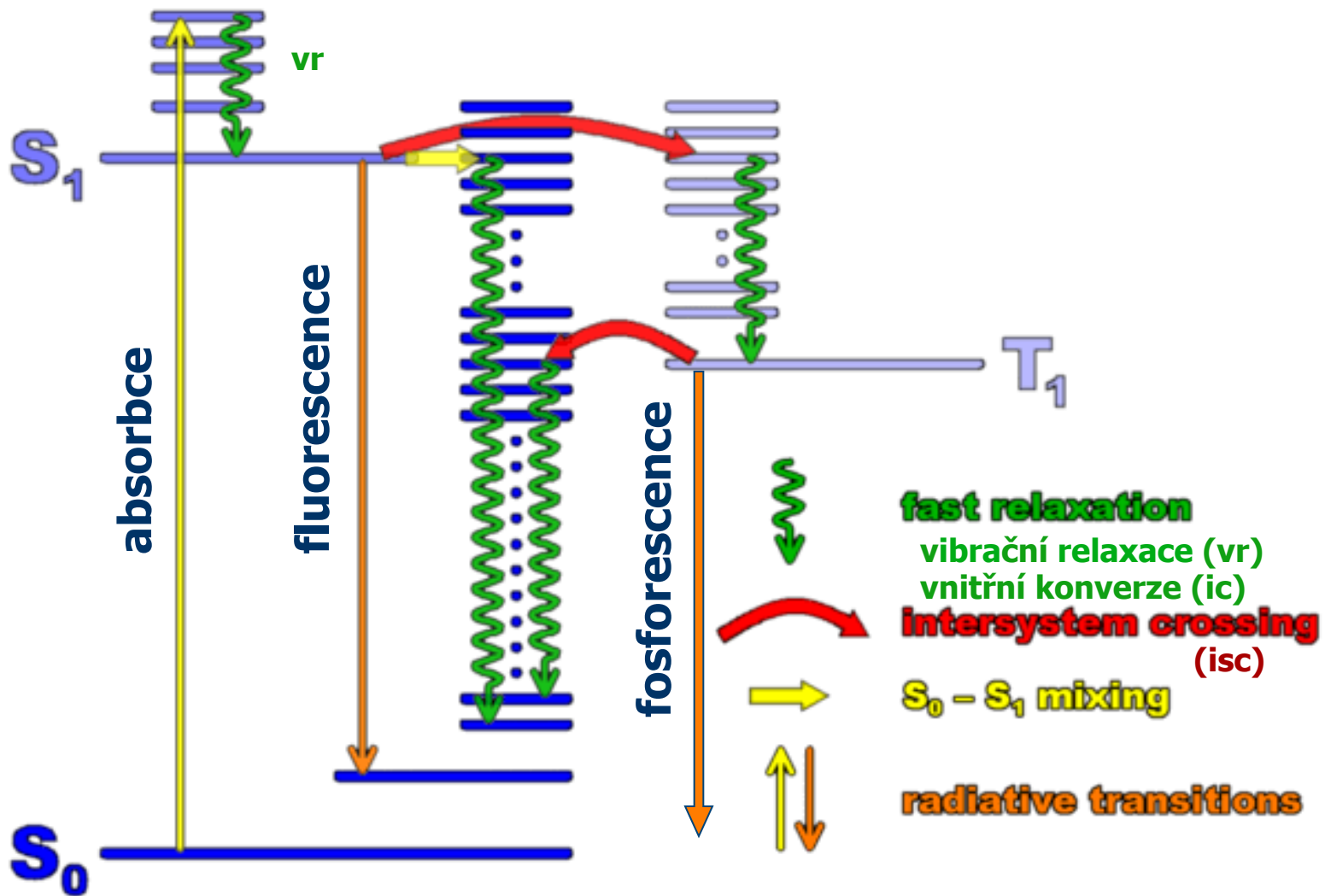
Conical Intersection
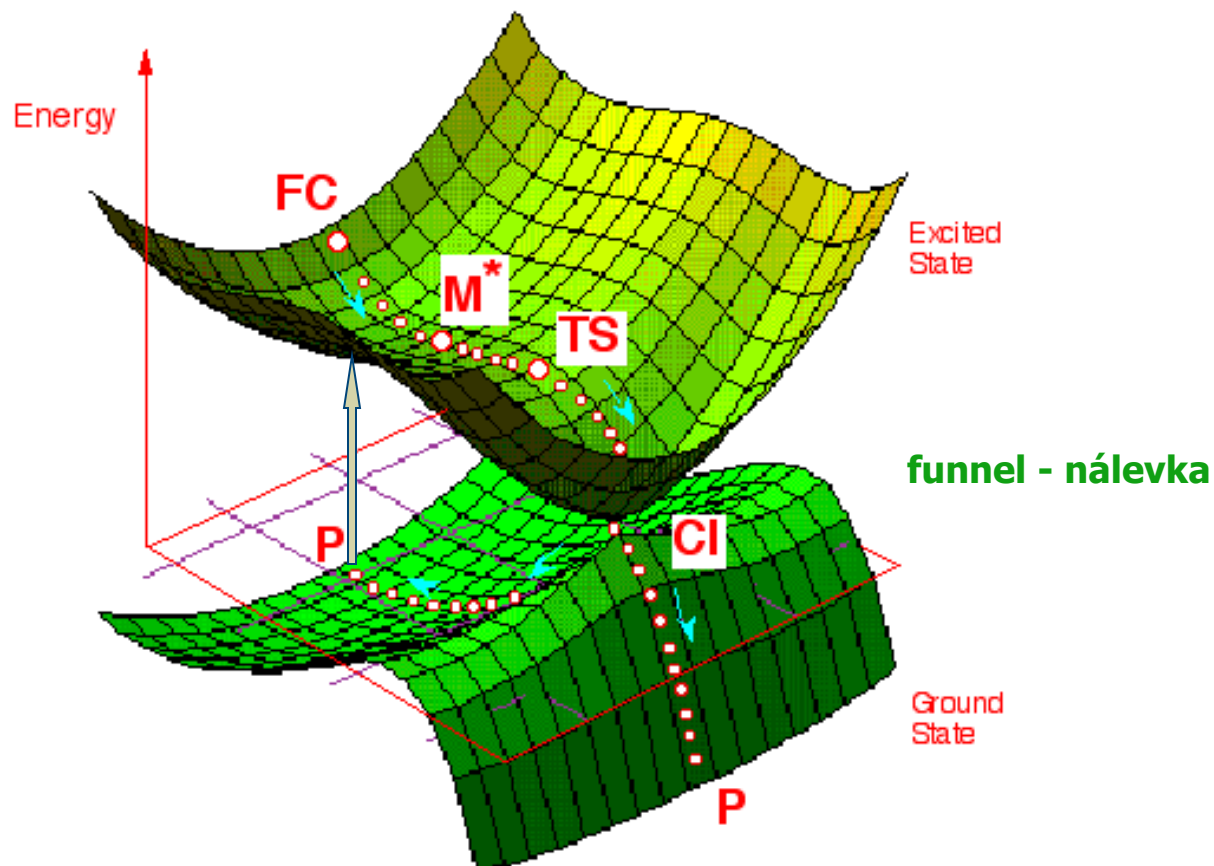
FRET

◆ Förster resonance energy transfer (fluorescence res. en. transfer)

◆ Příklad bimolekulárního relaxačního procesu

$$D^* + A \rightarrow D + A^*$$

FRET Efficiency (E)

$$E = \frac{1}{1 + (r/R_0)^6}$$

$$R_O = [8.8 \times 10^{23} \cdot \kappa^2 \cdot n^{-4} \cdot QY_D \cdot J(\lambda)]^{1/6} \text{ Å}$$

where κ^2 = dipole orientation factor (range 0 to 4; κ^2 = 2/3 for randomly oriented donors and acceptors)

QY_D = fluorescence quantum yield of the donor in the absence of the acceptor

n = refractive index

$J(\lambda)$ = spectral overlap integral (see figure)

$= \int \epsilon_A(\lambda) \cdot F_D(\lambda) \cdot \lambda^4 d\lambda \text{ cm}^3 M^{-1}$

where ϵ_A = extinction coefficient of acceptor

F_D = fluorescence emission intensity of donor as a fraction of the total integrated intensity

Donor fluorescence $J(\lambda)$ Acceptor absorption

Wavelength (λ)

$$J = \int f_D(\lambda)\, \epsilon_A(\lambda)\, \lambda^4\, d\lambda$$

$$R_0{}^6 = \frac{9000\, Q_0\, (\ln 10)\kappa^2\, J}{128\, \pi^5\, n^4\, N_A}$$

FRET

- Fluorescence Resonance Energy Transfer (FRET) is a technique to measure distances of a few nanometers between two fluorescent dyes. A donor fluorophore that is excited by a laser transfers a part of its energy non-radiatively to an acceptor fluorophore. The transfer efficiency is dependent on the interfluorophore distance. Detecting the emission of the donor and acceptor fluorophore seperatly allows us to calculate the transfer efficiency and therefore the distance between the fluorophores.
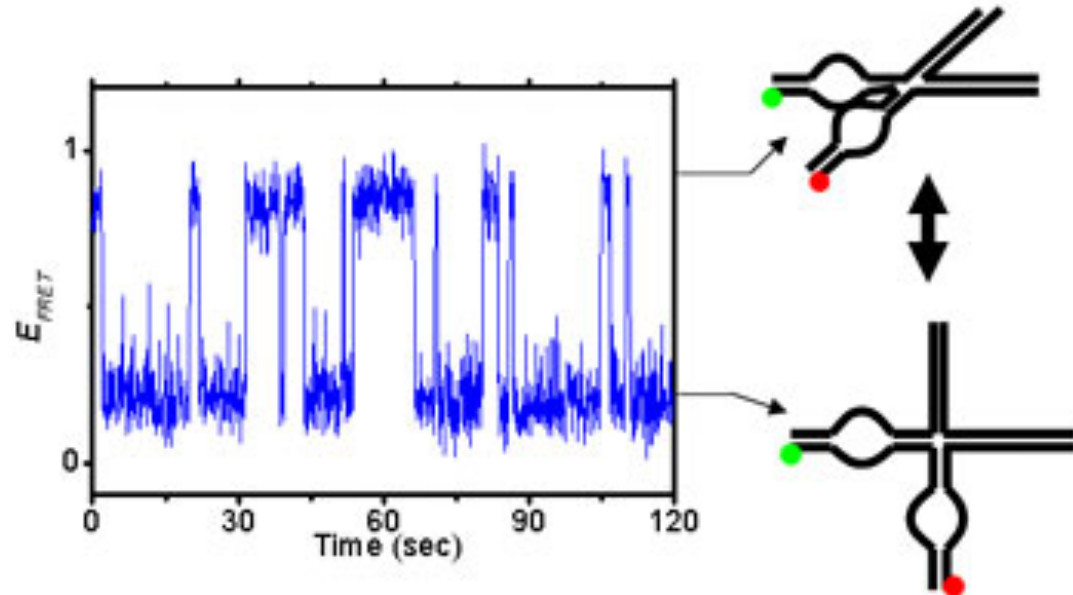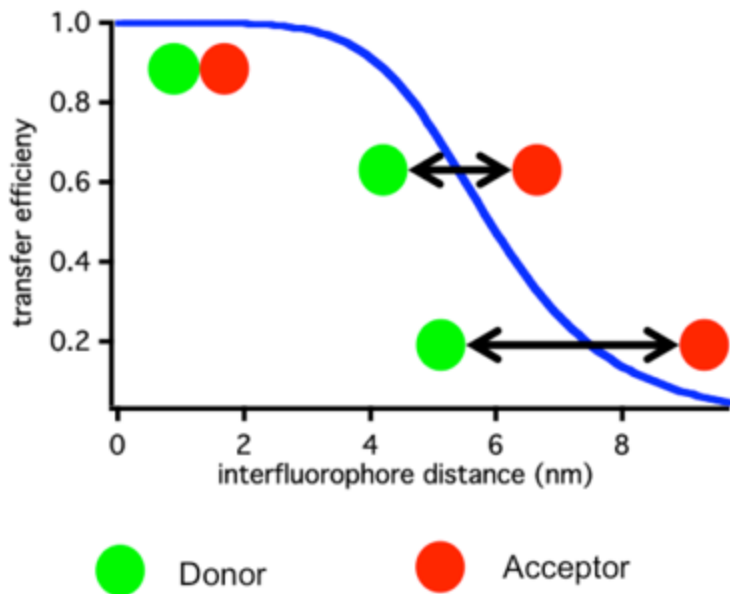
QCH popis exitovaných stavů

◆ V základním stavu často stačí jeden Slat. det.

◆ V excitovaném je často třeba vzít v úvahu dynamickou a statickou el. korelaci

- Jednoreferenční Slat. det
  - CIS, deriváty CCSD(T) např. SAC-CI
- Multireferenční metody

◆ Flexibilnější báze

Multireferenční metody

$|\Psi_{MCSCF}> = \Sigma_I c_I |\Psi_I>$, Ψ_I je Slaterův determinant $det(\varphi_i)$, c_I and $c_{i,\mu}$ MO LCAO jsou optimalizovány

• MCSCF – nezahrnuje dynamickou el. korelaci

Single, Double, Triple, ….. CI excitace (MRCI(SDT), …..)

  • není size-konsistentní, alternativní téměř size-konzistentní - MR-ACPF, MR-AQCC
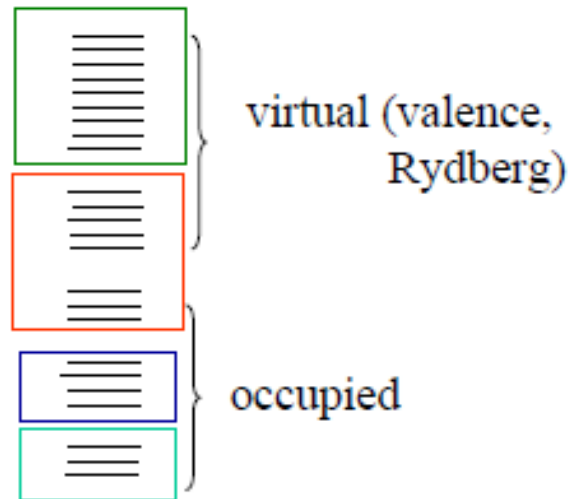 • aplikovatelné na velmi malé systémy

Coupled cluster excitations (MR-CCSD)

  • aplikovatelná na velmi malé systémy

Möller-Plesset Perturbation - CASPT2

  • aplikovatelná na středně velké systémy
  • problémy s určením aktivního prostoru

Aktivní prostor

virtual (valence, Rydberg)

occupied

Secondary kept virtual

Active all possible occupation respecting the symmetry and spin

Valence space - **always correct**

Inactive doubly occupied

Core taken from previous SCF calculations, not optimized

THE CONSTRUCTION AND INTERPRETATION OF MCSCF WAVEFUNCTIONS

MCSCF

Michael W. Schmidt and Mark S. Gordon
Department of Chemistry, Iowa State University, Ames, Iowa 50011;
e-mail: mark@si.fi.ameslab.gov

DYNAMIC CORRELATION METHODS

Although the MCSCF wavefunction has sufficient flexibility to model the large changes in electronic structure that can occur during chemical reactions, its energy unfortunately does not possess sufficient accuracy. It is common for barrier heights or overall reaction thermodynamics to be in error by 10–15 kcal/mol or even more. The origin of the error is clear: Many of the valence electrons have been treated as filled closed-shell orbitals with no recovery of correlation energy, whereas the active electrons have only a partial recovery of correlation.

MR-CI

The most obvious approach to dynamic correlation, and therefore the first that received significant attention for molecular calculations, is MR-CI, using the MCSCF as the reference wavefunction. The immediate problem is that there are very many configurations in such a CI. The smallest conceivable systematic

Table 2 Total energies and singlet-triplet splitting of CH_2 for various second-order multireference perturbation theories

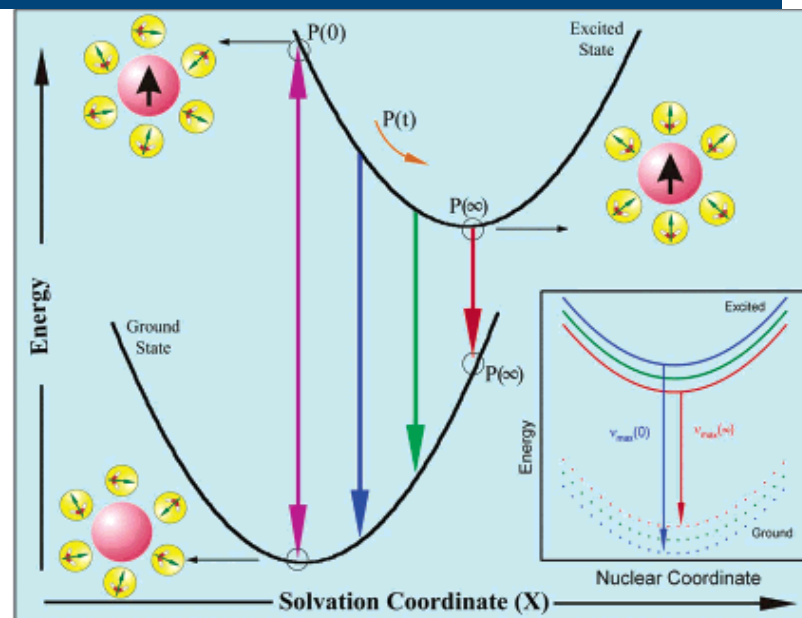| Method	Reference	$^1A_1$	$^3B_1$	Splitting (Kcal/mol)
HF	Authors	−38.886297	−38.927947	26.14
MP2	Authors	−38.996127	−39.024889[a]	18.05
MCSCF	Authors	−38.945529	−38.965954	12.82
FOCI	Authors	−38.980168	−39.003242	14.48
SOCI	Authors	−39.025804	−39.044928	12.00
Full CI	182	−39.027183	−39.046260	11.97
CASPT2D	150	−39.011773	−39.036804	15.71
CASPT2N	150	−39.013078	−39.037664	15.43
CASPT2 (g3)	151	−39.013049	−39.033686	12.95
CASPT3	152	−39.023397	−39.044195	12.30[b]
GMP2	153	−39.01331	−39.03794	15.45
GMP3	153	−39.02322	−39.04338	12.65[b]
MRMP2, F_{av}	159	−39.011715	−39.036886	15.79
MRMP2, F_{hs}	159	−39.011715	−39.033025	13.37
GVVPT2	163	−39.014948	−39.033647	11.73
GVVPT3	163	−39.023090	−39.042709	12.31[b]
MCQDPT	165	−39.011978	−39.037028	15.72[c]
MROPT1	167	−39.012836	−39.037929	15.75
MROPT2	167	−39.013328	−39.032886	12.27
MROPT3	167	−39.011706	−39.032335	12.94
MROPT4	167	−39.011404	−39.032242	13.07
CAS/A	174	−39.000997	−39.024564	14.79
ZTE-EN2	176	−39.027388	−39.048230	13.08

Nasazení multireferenčních metod

◆ Disociace vazeb

◆ Virtuální orbitaly mají nízkou energii

◆ Tranzitní stavy

◆ Tranzitní kovy

◆ Excitované stavy

Chování v solventu

- V základním stavu mají zejména molekuly nesoucí dip. moment velmi strukturovaný solvatační obal (polárních solventů, např. vody)

- Např. relaxace hydratačních obalů trvá desítky ps

- Po excitaci dochází ke „stresu" solvatačního obalu

  - Polární prostředí posouvá excitační pásy k vyšším energiím (resp. S klesající polaritou prostředí je pozorován červený posun, např. vliv tenzidů)

  - Dochází k relaxaci solv. obalu

Chem. Rev. **2004,** *104,* 2099-2123

Vliv solventu

(b) Wavelength λ (nm)

Molar absorption coefficient, ε

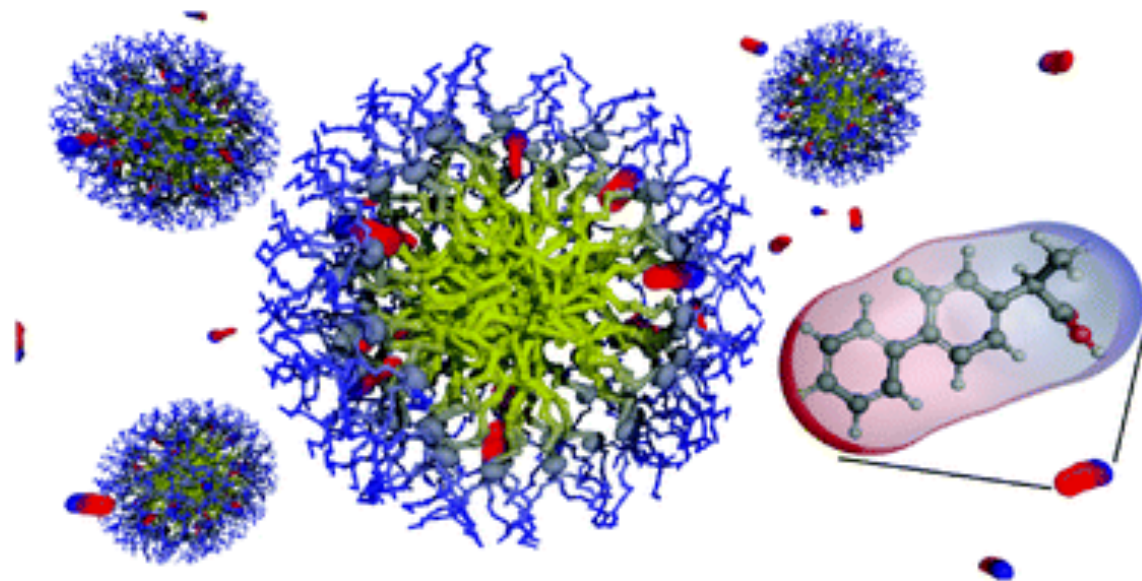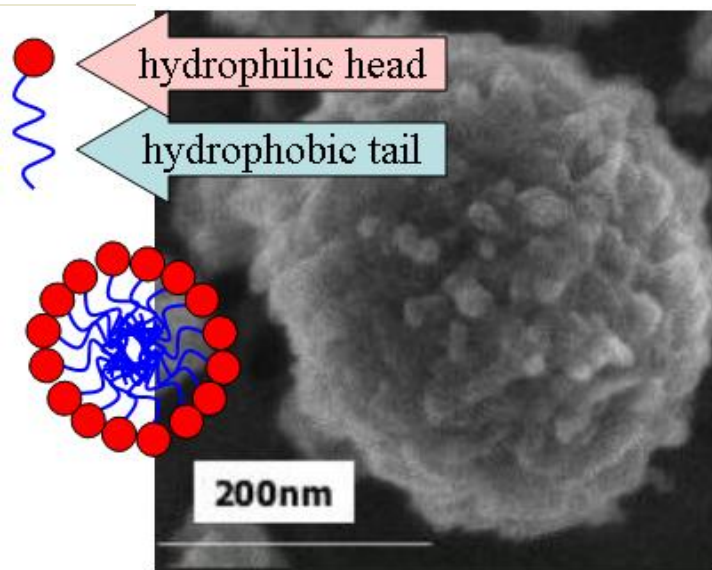250 260 270 280 290 300
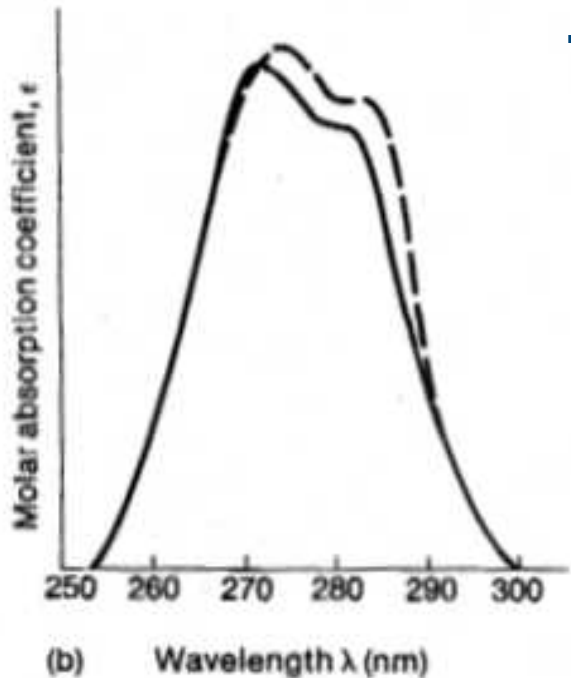
spektrum tyrosinu

—————— Solvent = H_2O
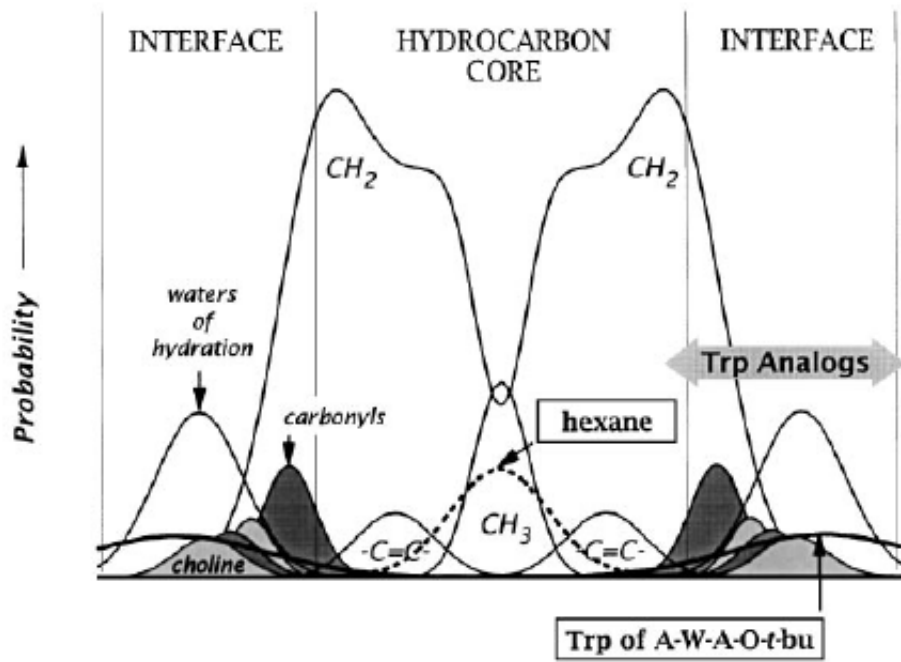
— — — Solvent = 20% Ethylene Glycol / 80% H_2O

v méně polárním prostředí se λ_{max} posouvá k delším vlnovým délkám - **batochromní posun (červený posun)**

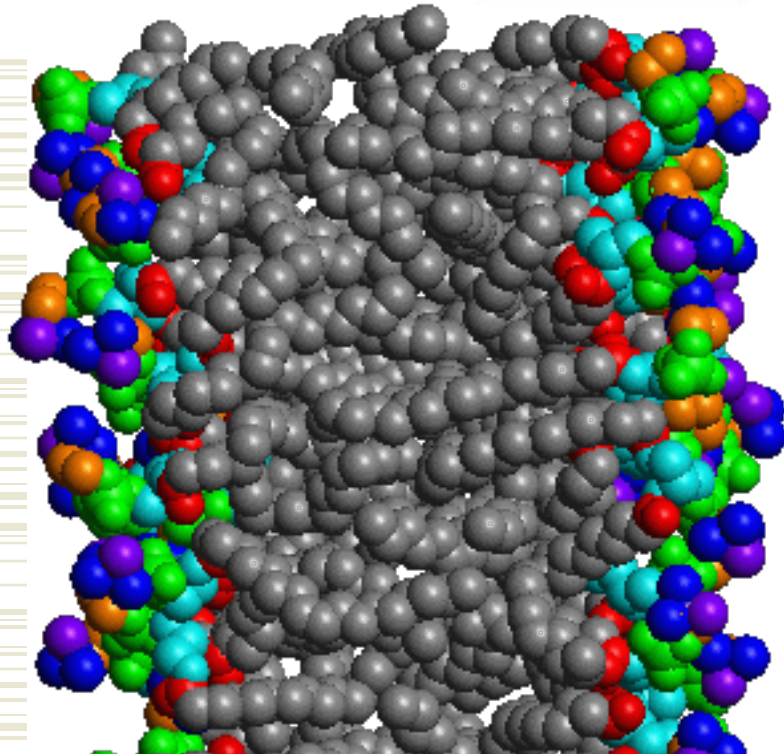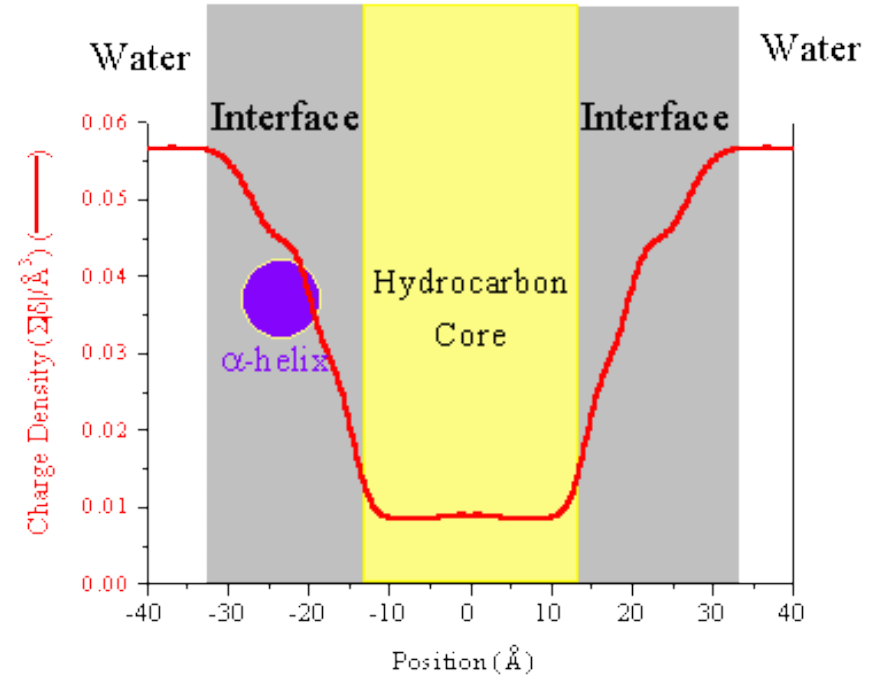absorpční spektrum může ovlivnit i přítomnost povrchově-aktivních látek!

Micellar solubilization

Position in membrane

Another representation of the polarity gradient across the lipid bilayer membrane. Notice that the two interfaces occupy approximately half the thickness of the membrane, and can easily accomodate peptides and proteins as shown by the a-helix cross section which is drawn to scale in this figure.

Pozn: Rydbergův stav

- A Rydberg state is a state of an atom or molecule in which one of the electrons has been excited to a high principal quantum number orbital. Classically, such a state corresponds to putting one electron into an orbit whose dimensions are very large compared to the size of the leftover ion core. **Among the novel properties of these states are extreme sensitivity to external influences such as fields and collisions, extreme reactivity, and huge probabilities for interacting with microwave radiation**. A wide variety of types of experiments of current interest in atomic, molecular, and optical physics involve the use of Rydberg states.

Rydberg state
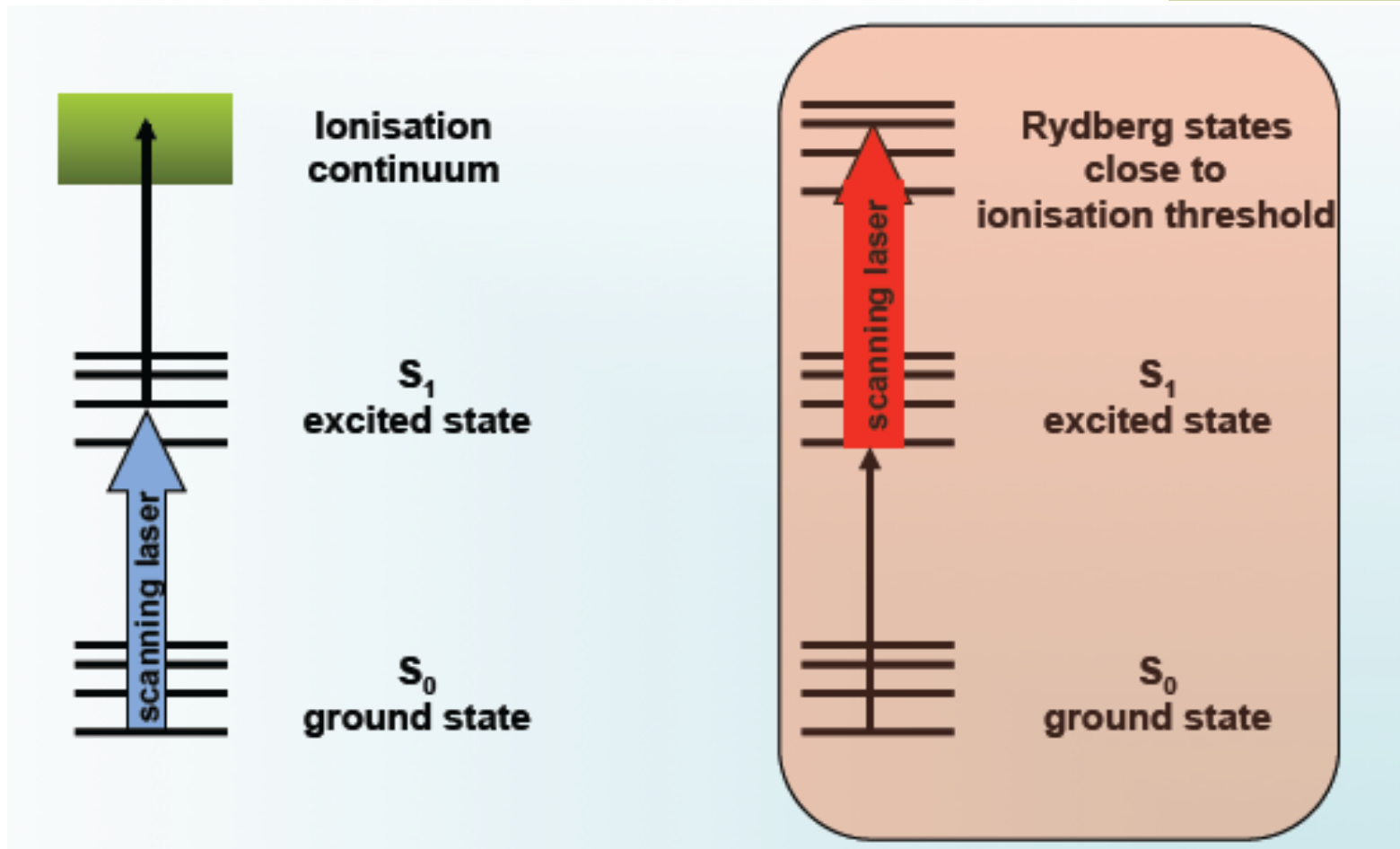
Rydberg state
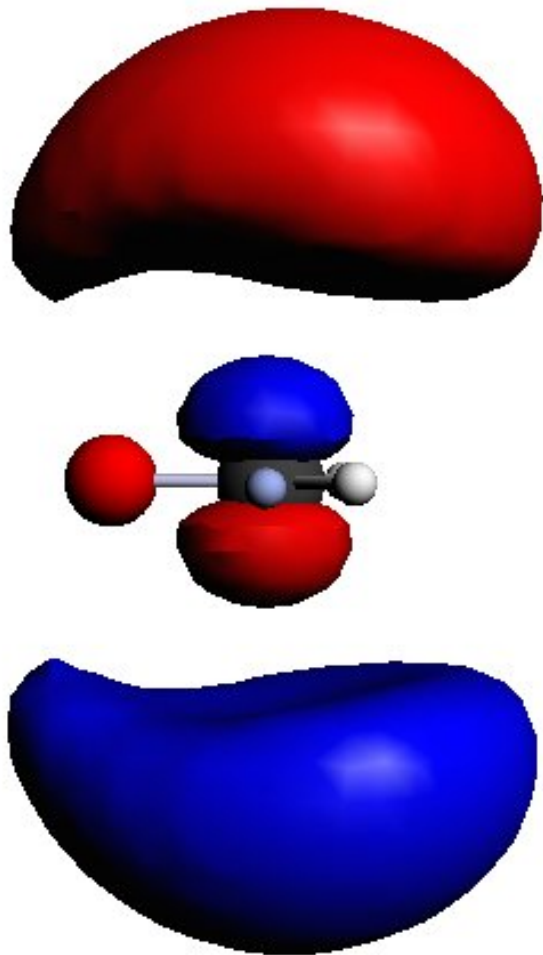
- One particular type of excited state needs special consideration in order for there to be any hope of treating them correctly: Rydberg States.
- A Rydberg state is a state where one electron is very weakly bound to the rest of the molecule. This electron spends most of its time a long way from the molecule. From a distance, a molecule with one electron removed looks a lot like a point charge. Another system we know where an electron sees a point charge is the hydrogen atom. It may not surprise you then that Rydberg states behave a lot like the excited states of the hydrogen atom. They form series that can be indexed by a principle quantum number n and converge on an ionization potential of the molecule. In terms of orbitals, calculations put the excited electron in an orbital that looks like a very big atomic orbital with s, p, d or higher symmetry. A picture of a Rydberg 3p-like orbital of formaldehyde can be seen in figure.
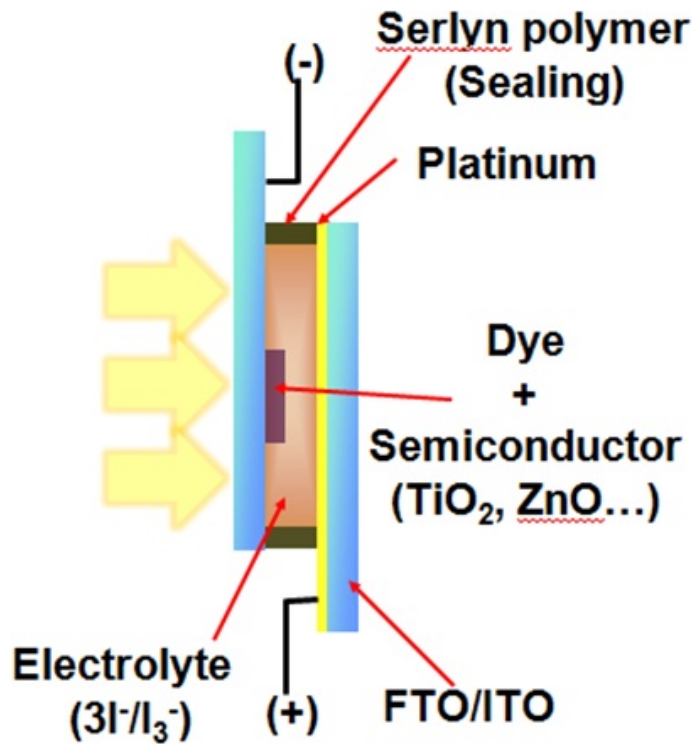
Rydberg atom

- A Rydberg atom is an excited atom with one or more electrons that have a very high principal quantum number. These atoms have a number of peculiar properties including an exaggerated response to electric and magnetic fields, long decay periods.
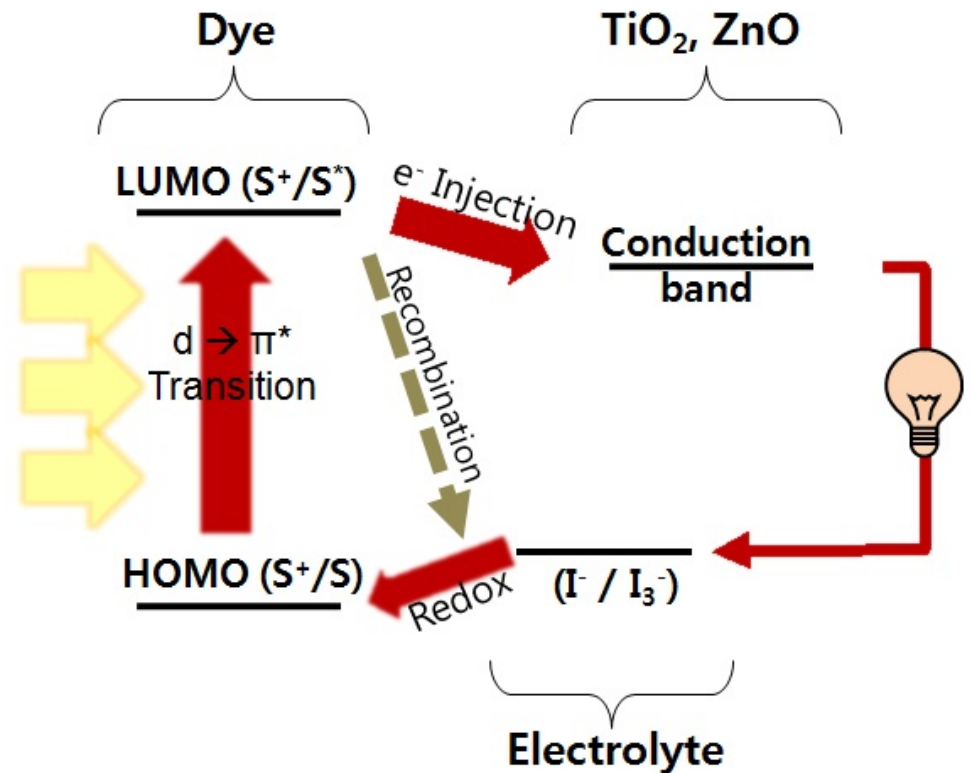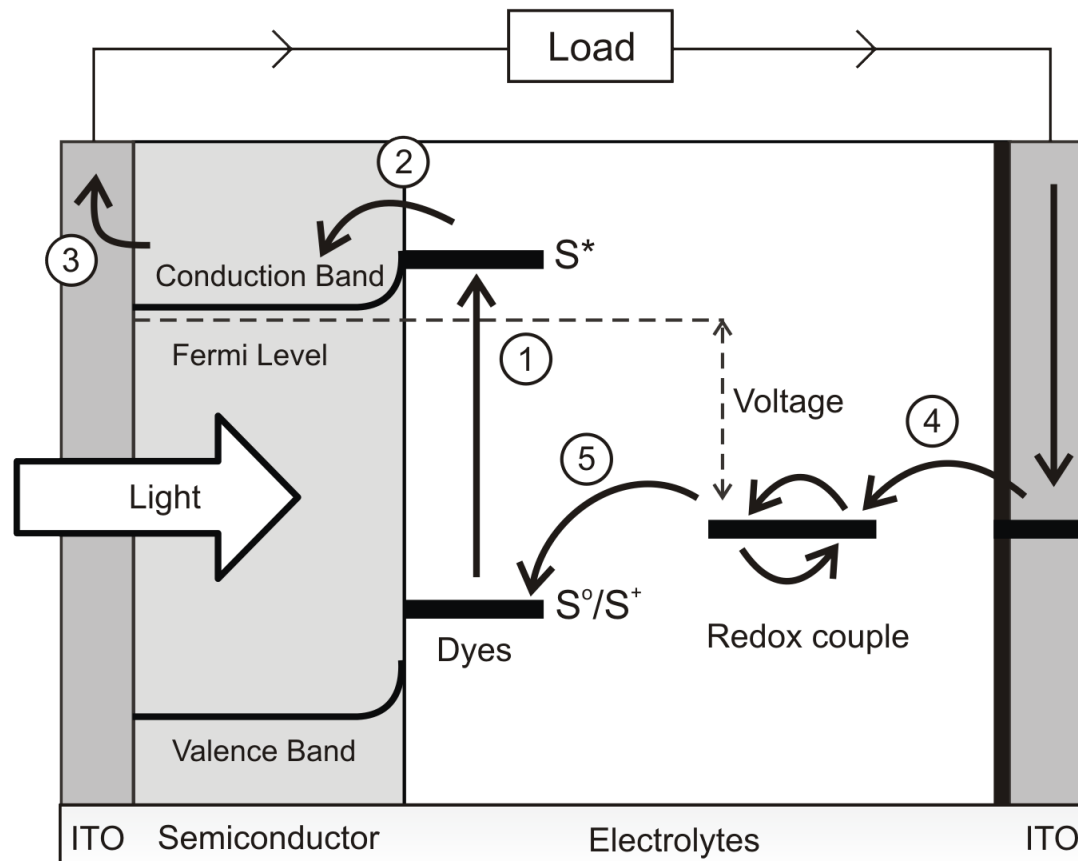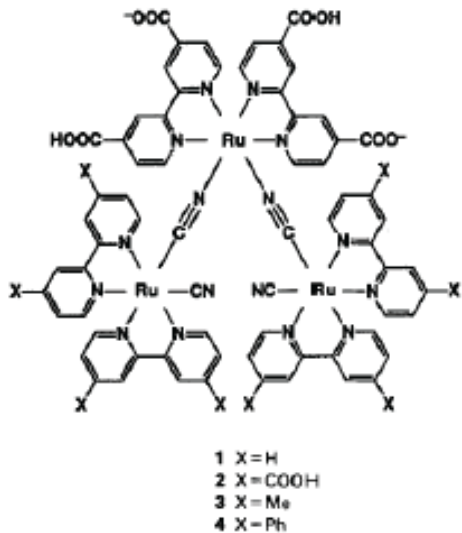
- Více na wikipedia

Grätzel Solar Cell

Dye Sensitized Solar Cell

1 X=H
2 X=COOH
3 X=Me
4 X=Ph

- Semiconductor
  - TiO_2
  - $E_g = 3.2\,eV$ (Anatase)
  - alternatives: wide range of semiconducting metal oxides
- Dye
  - Ru-2,2'-bipyridine-4,4'dicarboxylic-acid(μ-(CN)Ru(CN)-2,2'-bipyridine)
  - alternatives: other complexes of Ruthenium and Osmium, porphyrins, cyanides and phthalocyanines
- Electrolyte
  - $HClO_4$ with redox systems (e.g. I_3^-/I^- with Li^+ as counterion)
- Electrodes
  - transparent electrodes on insulating transparent materials (e.g. ITO on glass)

Grätzel solar cell
- Compounds for each task
- low- to medium-purity materials sufficient
- low-cost processes
- lower efficiency (> 10 %)

Conventional semiconductor solar cell
- One compound
- high-purity materials needed
- expensive production
- higher efficiency (> 20 %)

Singlet fission

- A molecular system that could be used to enhance the efficiency of solar cells by 35 percent has been recently discovered by NREL and University of Colorado, Boulder (UCB) researchers.

- Their discovery focuses on a phenomenon called "singlet fission", which produces two triplet states from an excited singlet state of a molecule.