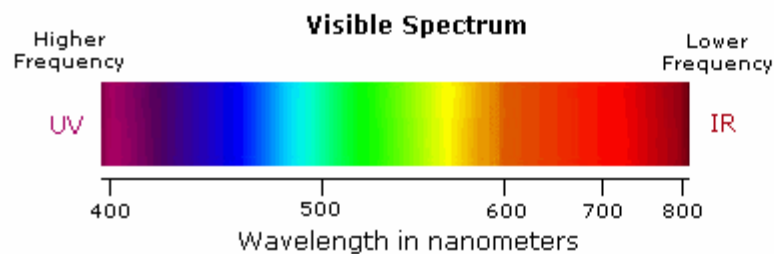
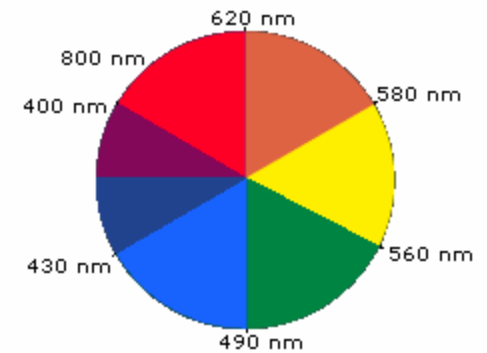
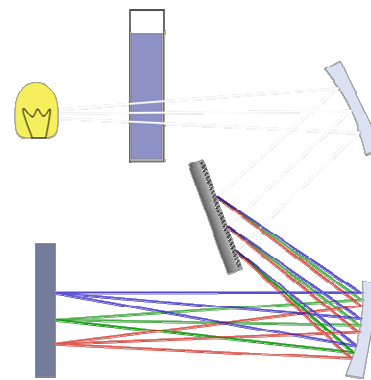
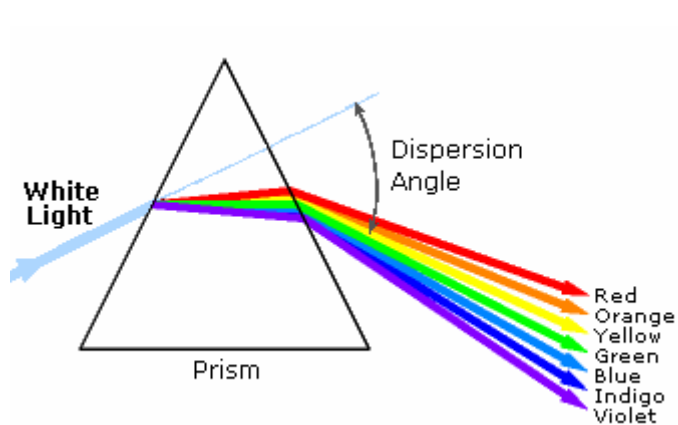


UV-Vis spectroscopy

Electronic absorption spectroscopy



- **Violet:** 400 - 420 nm
- **Indigo:** 420 - 440 nm
- **Blue:** 440 - 490 nm
- **Green:** 490 - 570 nm
- **Yellow:** 570 - 585 nm
- **Orange:** 585 - 620 nm
- **Red:** 620 - 780 nm

Absorption spectroscopy

- Provide information about presence and absence of unsaturated functional groups
- Useful adjunct to IR
- Determination of concentration, especially in chromatography
- For structure proof, usually not critical data, but essential for further studies
- NMR, MS not good for purity

Absorption and Emission

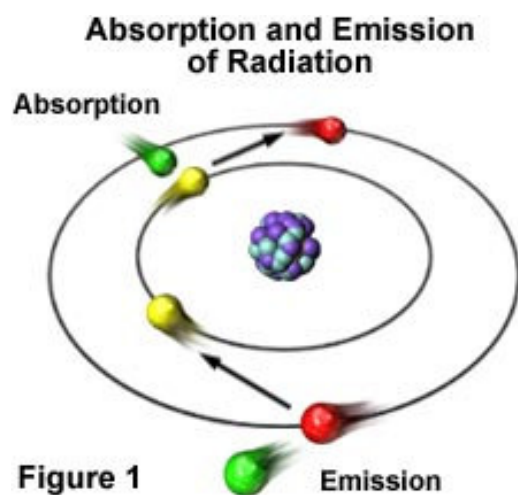
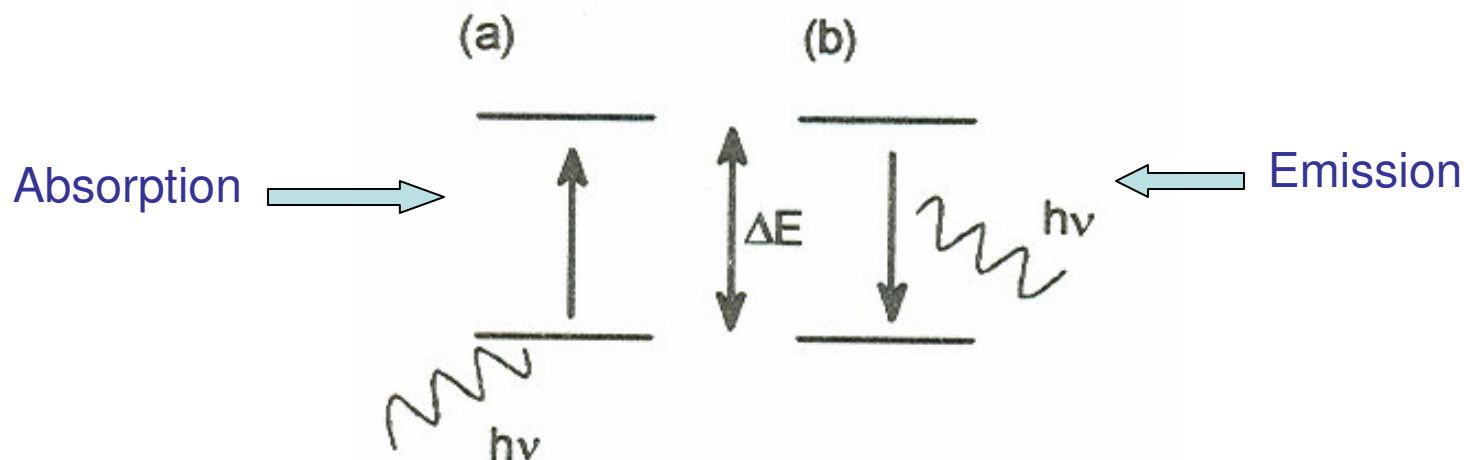
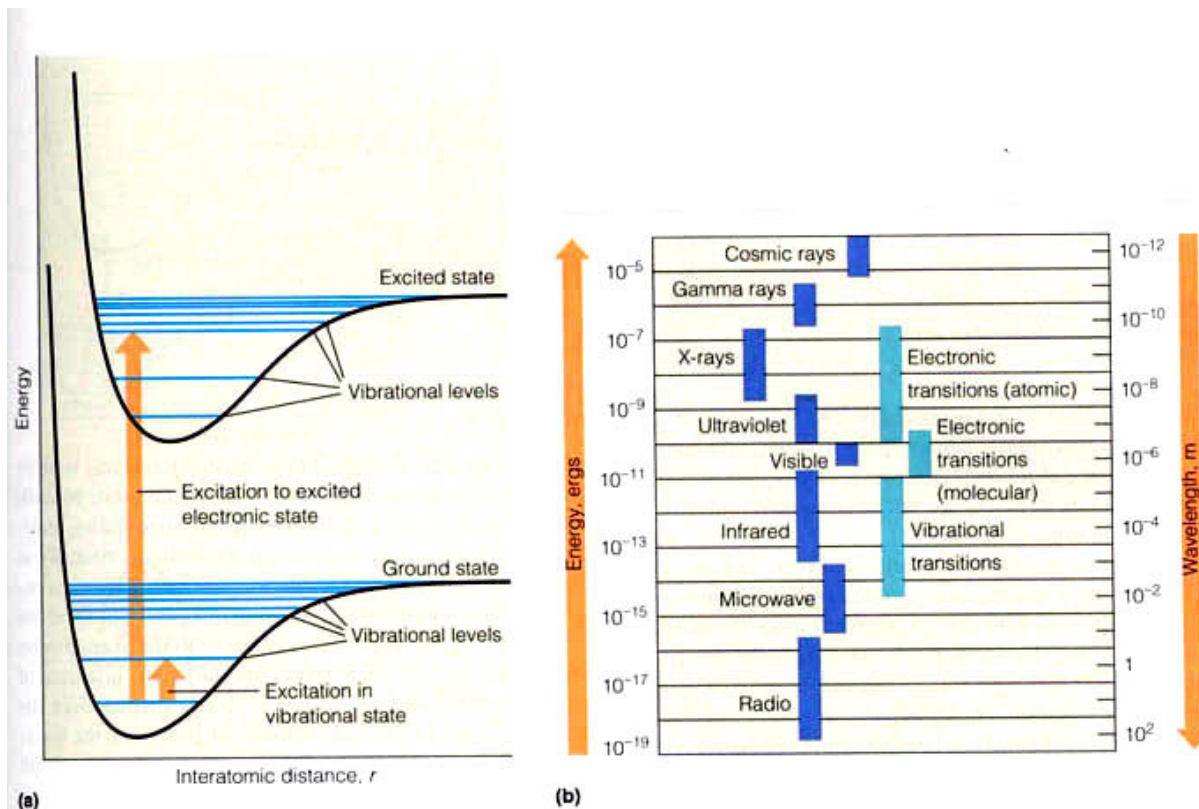


Figure 1

Absorption: A transition from a lower level to a higher level with transfer of energy from the radiation field to an absorber, atom, molecule, or solid.

Emission: A transition from a higher level to a lower level with transfer of energy from the emitter to the radiation field. If no radiation is emitted, the transition from higher to lower energy levels is called nonradiative decay.

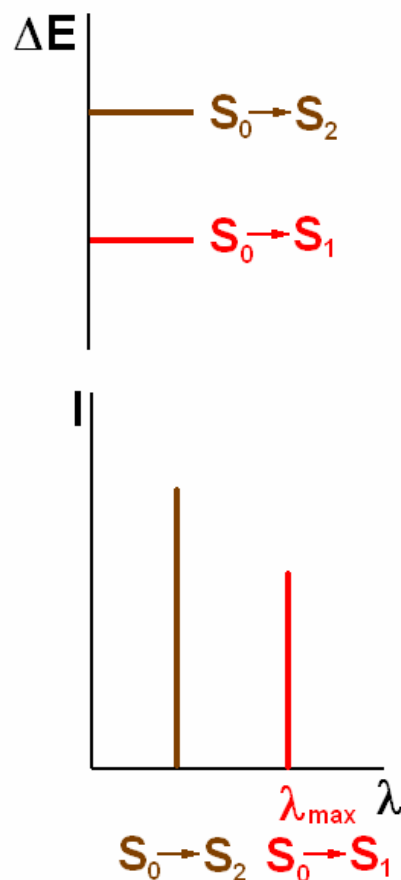
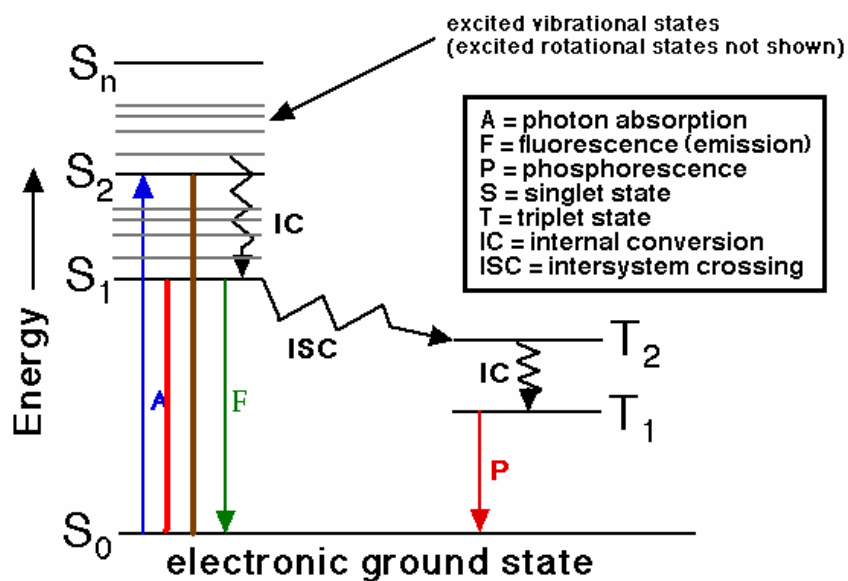
<http://www.chemistry.vt.edu/chem-ed/spec/spectros.html>



Frank-Condon Principle

- The nuclear motion (10^{-13} s) is negligible during the time required for an electronic excitation (10^{-16} s).
- Since the nuclei do not move during the excitation, the internuclear distances remain constant and “the most probable component of an electronic transition involves only the vertical transitions”.

Absorption and emission pathways



Origin of electronic spectra

Absorptions of UV-vis photons by molecule results in electronic excitation of molecule with chromophore.

chromophore Any group of atoms that absorbs light whether or not a color is thereby produced.

The electronic transition involves promotion of electron from a electronic ground state to higher energy state, usually from a molecular orbital called HOMO to LUMO.

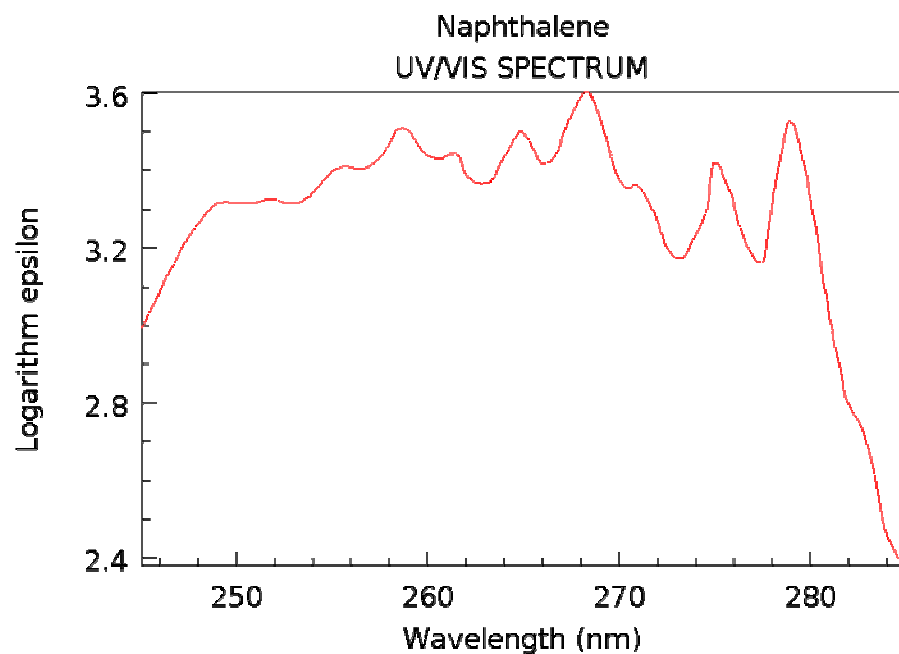
Biological chromophores

1. The peptide bonds and amino acids in proteins

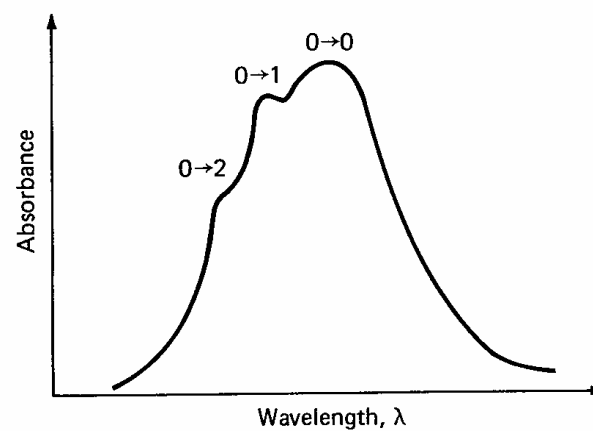
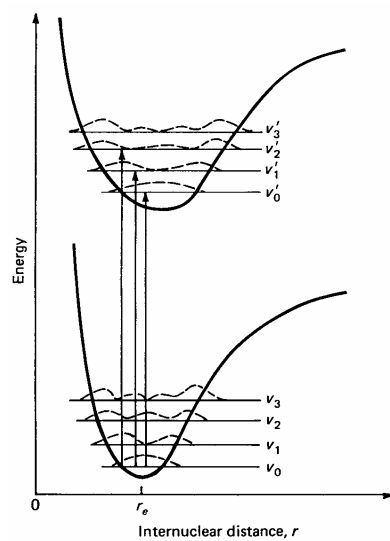
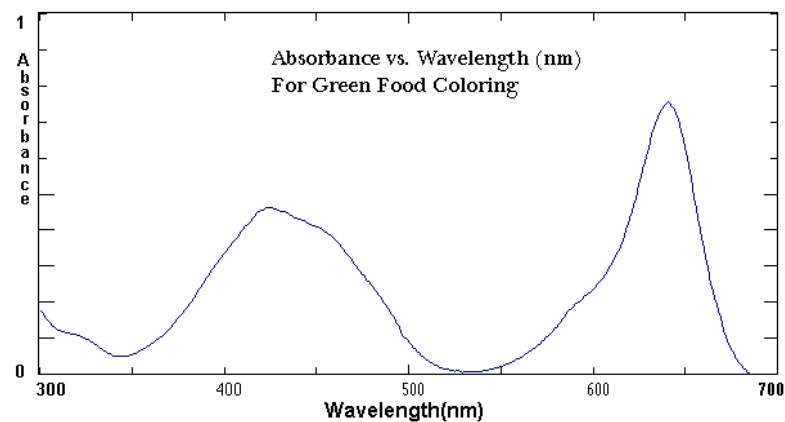
- The p electrons of the peptide group are delocalized over the carbon, nitrogen, and oxygen atoms. The $n\text{-}\pi^*$ transition is typically observed at 210-220 nm, while the main $\pi\text{-}\pi^*$ transition occurs at ~ 190 nm.
- Aromatic side chains contribute to absorption at $\lambda > 230$ nm

2. Purine and pyrimidine bases in nucleic acids and their derivatives

3. Highly conjugated double bond systems



NIST Chemistry WebBook (<http://webbook.nist.gov/chemistry>)



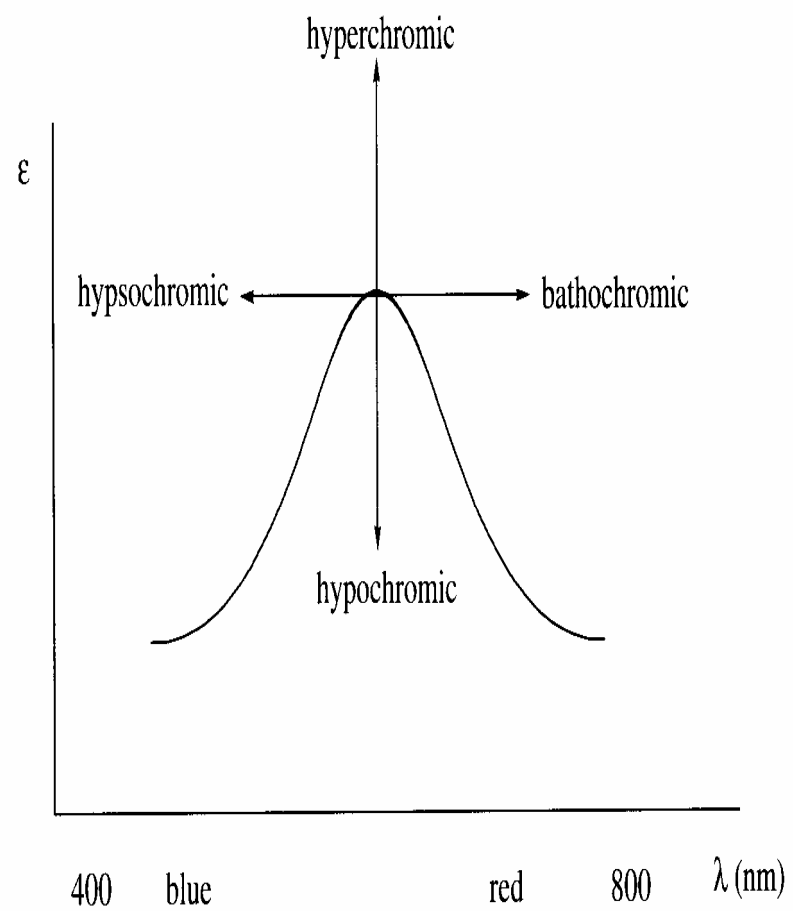


FIGURE 9.1 UV spectra nomenclature.

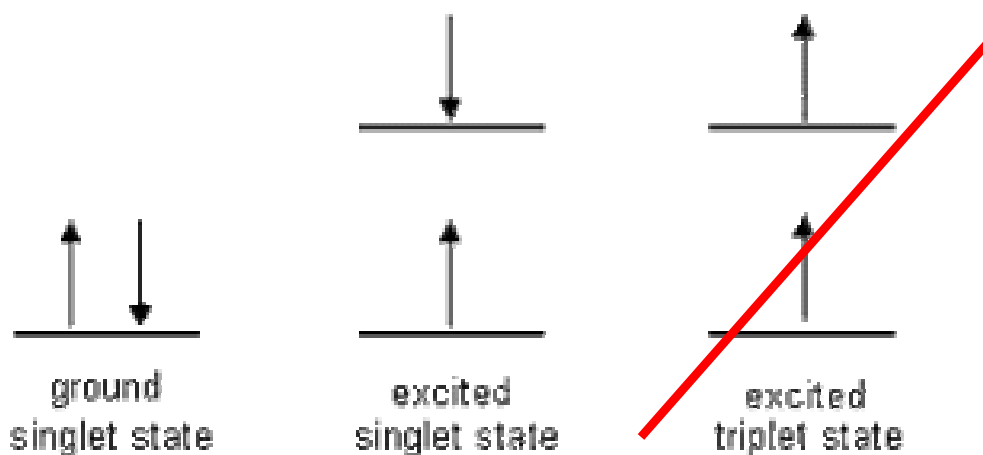
Selection Rules

1. Spin selection rule: $\Delta S = 0$

allowed transitions: singlet \rightarrow singlet or triplet \rightarrow triplet

forbidden transitions: singlet \rightarrow triplet or triplet \rightarrow singlet

Changes in spin multiplicity are forbidden



Selection rules

2. Laporte selection rule: there must be a change in the parity (symmetry) of the complex

Electric dipole transition can occur only between states of opposite parity.

Laporte-allowed transitions: $g \rightarrow u$ or $u \rightarrow g$

Laporte-forbidden transitions: $g \rightarrow g$ or $u \rightarrow u$

g stands for *gerade* – compound with a center of symmetry

u stands for *ungerade* – compound without a center of symmetry

Selection rules can be relaxed due to:

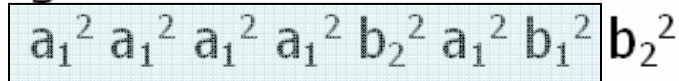
- vibronic coupling
- spin-orbit coupling
- geometry relaxation during transition

- Spin-forbidden transitions
 - Transitions involving a change in the spin state of the molecule are forbidden
 - Strongly obeyed
 - Relaxed by effects that make spin a poor quantum number (heavy atoms)
- Symmetry-forbidden transitions
 - Transitions between states of the same parity are forbidden
 - Particularly important for centro-symmetric molecules (ethene)
 - Relaxed by coupling of electronic transitions to vibrational transitions (vibronic coupling)

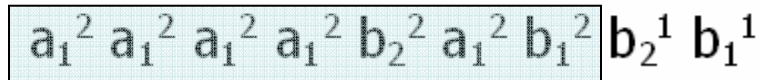
Excited state symmetry

Formaldehyde

ground state:



first excited state



C_{2v}	I	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$			
A_1	1	1	1	1	z	x^2, y^2, z^2	$z^3, z(x^2-y^2)$
A_2	1	1	-1	-1	R_z	xy	xyz
B_1	1	-1	1	-1	x, R_y	xz	$xz^2, x(x^2-3y^2)$
B_2	1	-1	-1	1	y, R_x	yz	$yz^2, y(3x^2-y^2)$
$\Gamma_{x,y,z}$	3	-1	1	1			

$$B_2 \times B_1 = 1 \ 1 \ -1 \ -1 = A_2$$

The symmetry of the first excited state of formaldehyde (as a result of HOMO-LUMO transition)

ground state
 A_1

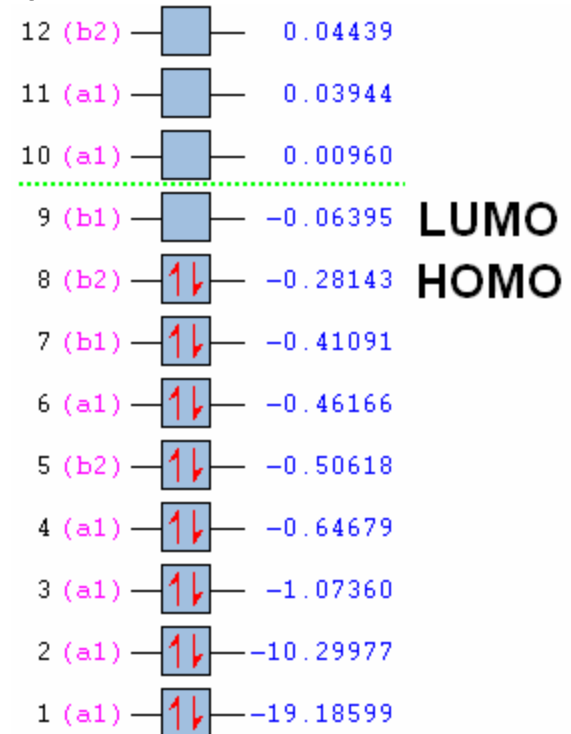
moment dipole component
 $A_1 (\mu_z)$
 $B_1 (\mu_x)$
 $B_2 (\mu_y)$

excited state
 A_2

$$P = \int \psi'^* \hat{\mu} \psi d\tau$$

$$\begin{aligned} A_1 \times A_1 \times A_2 &= A_2 \\ A_1 \times B_1 \times A_2 &= B_2 \\ A_1 \times B_2 \times A_2 &= B_1 \end{aligned}$$

Thus, HOMO-LUMO transition is not allowed!
Transitions HOMO-LUMO+1, HOMO-LUMO+2 are allowed



Calculation of electronic spectra

- TD-DFT (time-dependent DFT)
 - #P TD(nstates=5) B3LYP/6-31+G(d,p)
 - Run this job on an optimized geometry of formaldehyde

Excitation energies and oscillator strengths:

Excited State 1: Singlet-A2 3.9538 eV 313.58 nm f=0.0000
8 -> 9 0.68108

This state for optimization and/or second-order correction.

Total Energy, E(RPA) = -114.366224997

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-B2 6.8829 eV 180.13 nm f=0.0316
8 -> 10 0.70042

Excited State 3: Singlet-B2 7.6373 eV 162.34 nm f=0.0265
8 -> 11 0.70104

Excited State 4: Singlet-A1 7.8659 eV 157.62 nm f=0.0492
8 -> 12 0.70382

Excited State 5: Singlet-A2 8.3746 eV 148.05 nm f=0.0000
8 -> 13 0.70602

Leave Link 914 at Fri Mar 27 08:55:02 2009, MaxMem= 6291456 cpu: 26.0

(Enter c:\G03W\l601.exe)

Copying SCF densities to generalized density rwf, ISCF=0 IROHF=0.

1PDM for each excited state written to RWF 633
Ground to excited state Transition electric dipole moments (Au):

state	X	Y	Z	Osc.
1	0.0000	0.0000	0.0000	0.0000
2	0.0000	0.4327	0.0000	0.0316
3	0.0000	0.3762	0.0000	0.0265
4	0.0000	0.0000	-0.5050	0.0492
5	0.0000	0.0000	0.0000	0.0000

Plot the HOMO-2, HOMO-1, HOMO, LUMO, LUMO+1, LUMO+2, LUMO+3 orbitals, using the Gaussview program.

Use a chk file in your Gaussian calculation

Table 6

Excitation energies (in eV) and oscillator strengths (*f*) of LiP and MgP calculated with the time-dependent DFT^a

System/Symmetry ^b		TDDFT		Exp.	Assign.
		ΔE	<i>f</i>	ΔE	
<i>LiP</i>				<i>LiTPP</i> ^c	
1 2E_g	$3e_g \rightarrow 3a_{2u}$ (81%), $3a_{2u} \rightarrow 4e_g$ (11%)	1.61	0.0014	1.78	β ($\pi \rightarrow \pi^*$)
2 2E_g	$1a_{1u} \rightarrow 4e_g$ (84%), $3a_{2u} \rightarrow 4e_g$ (9%)	1.90	0.0112	1.93	Q ($\pi \rightarrow \pi^*$)
3 2E_g	$3a_{2u} \rightarrow 4e_g$ (49%), $2e_g \rightarrow 3a_{2u}$ (30%) $1a_{1u} \rightarrow 4e_g$ (7%)	2.32	0.0007	2.27	α_1 ($\pi \rightarrow \pi^*$)
4 2E_g	$1a_{1u} \rightarrow 4e_g$ (47%), $2e_g \rightarrow 3a_{2u}$ (40%) $3a_{2u} \rightarrow 4e_g$ (7%)	2.83	0.0061	2.44	α_2 ($\pi \rightarrow \pi^*$)
5 2E_g	$2b_{2u} \rightarrow 4e_g$ (62%), $2a_{2u} \rightarrow 4e_g$ (7%)	3.11	0.0033		($\pi \rightarrow \pi^*$)
6 2E_g	$1a_{1u} \rightarrow 4e_g$ (30%), $3a_{2u} \rightarrow 4e_g$ (14%) $2e_g \rightarrow 3a_{2u}$ (14%), $2a_{2u} \rightarrow 4e_g$ (13%) $2b_{2u} \rightarrow 4e_g$ (11%)	3.53	0.6873	2.97	B ($\pi \rightarrow \pi^*$)
1 $^2A_{1g}$	$12a_{1g} \rightarrow 3a_{2u}$ (92%)	3.57	0.0020		(Li $\rightarrow \pi^*$)
7 2E_g	$2a_{2u} \rightarrow 4e_g$ (54%), $2b_{2u} \rightarrow 4e_g$ (31%)	3.70	0.0098		($\pi \rightarrow \pi^*$)
8 2E_g	$2b_{2u} \rightarrow 4e_g$ (78%), $2a_{2u} \rightarrow 4e_g$ (8%)	3.83	0.2079	3.48	($\pi \rightarrow \pi^*$)
9 2E_g	$2a_{2u} \rightarrow 4e_g$ (90%)	4.27	0.3255		N ($\pi \rightarrow \pi^*$)
<i>MgP</i>				<i>MgTPP</i> ^d	
1 1E_u	$4a_{2u} \rightarrow 4e_g$ (51%), $1a_{1u} \rightarrow 4e_g$ (48%)	2.39	0.0006	2.20(2.07)	Q ($\pi \rightarrow \pi^*$)
2 1E_u	$1a_{1u} \rightarrow 4e_g$ (43%), $4a_{2u} \rightarrow 4e_g$ (35%) $3a_{2u} \rightarrow 4e_g$ (8%), $2b_{2u} \rightarrow 4e_g$ (6%)	3.52	0.9008	3.05	B ($\pi \rightarrow \pi^*$)
3 1E_u	$2b_{2u} \rightarrow 4e_g$ (95%)	3.79	0.0618	3.14	($\pi \rightarrow \pi^*$)
4 1E_u	$3a_{2u} \rightarrow 4e_g$ (95%)	4.24	0.2335	3.97	N ($\pi \rightarrow \pi^*$)
1 $^1A_{2u}$	$4a_{2u} \rightarrow 14a_{1g}$ (99%)	5.34	0.0083		($\pi \rightarrow$ Mg)
2 $^1A_{2u}$	$18e_u \rightarrow 4e_g$ (98%)	5.43	0.0027		($\pi \rightarrow \pi^*$)
5 1E_u	$3e_g \rightarrow 2b_{1u}$ (98%)	5.51	0.0844	5.17	L ($\pi \rightarrow \pi^*$)
6 1E_u	$1b_{1u} \rightarrow 4e_g$ (89%), $2e_g \rightarrow 2b_{1u}$ (4%)	5.99	0.0053		($\pi \rightarrow \pi^*$)
7 1E_u	$4a_{2u} \rightarrow 5e_g$ (91%)	6.29	0.0573		M ($\pi \rightarrow \pi^*$)
8 1E_u	$2e_g \rightarrow 2b_{1u}$ (56%), $1a_{1u} \rightarrow 5e_g$ (43%)	6.45	0.0041		$\pi \rightarrow \pi^*$
9 1E_u	$1a_{1u} \rightarrow 5e_g$ (49%), $2e_g \rightarrow 2b_{1u}$ (32%)	6.56	0.0112		$\pi \rightarrow \pi^*$

^a Calculated with UB3LYP/6-31G* for LiP radical and with RB3LYP/6-31G* for MgP.^b Contributions of the main configurations are shown in parentheses.^c Solution spectral result of LiTPP from [15].^d Vapor-phase spectral result of MgTPP from [40].Available online at www.sciencedirect.com

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Density functional theory studies of lithium porphyrin radicals

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