

Exercises in Computational Chemistry

Spanget-Larsen, Jens

DOI:

[10.13140/RG.2.1.1681.4160](https://doi.org/10.13140/RG.2.1.1681.4160)

Publication date:

2016

Document Version

Publisher's PDF, also known as Version of record

Citation for published version (APA):

Spanget-Larsen, J. (2016, Jan 6). Exercises in Computational Chemistry.

<https://doi.org/10.13140/RG.2.1.1681.4160>

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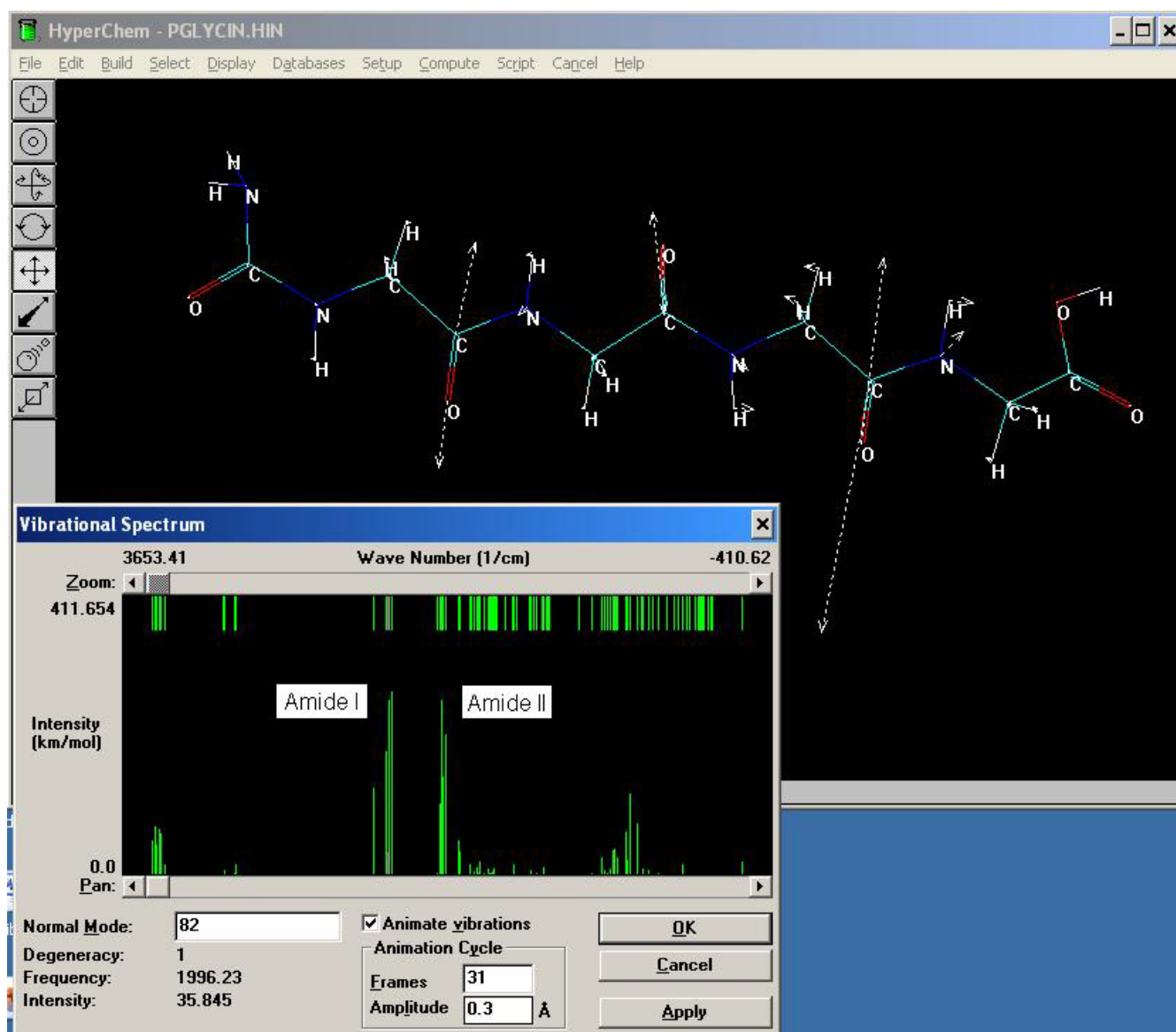
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Exercises in Computational Chemistry

Jens Spanget-Larsen
RUC 2012-16



COMPUTATIONAL CHEMISTRY

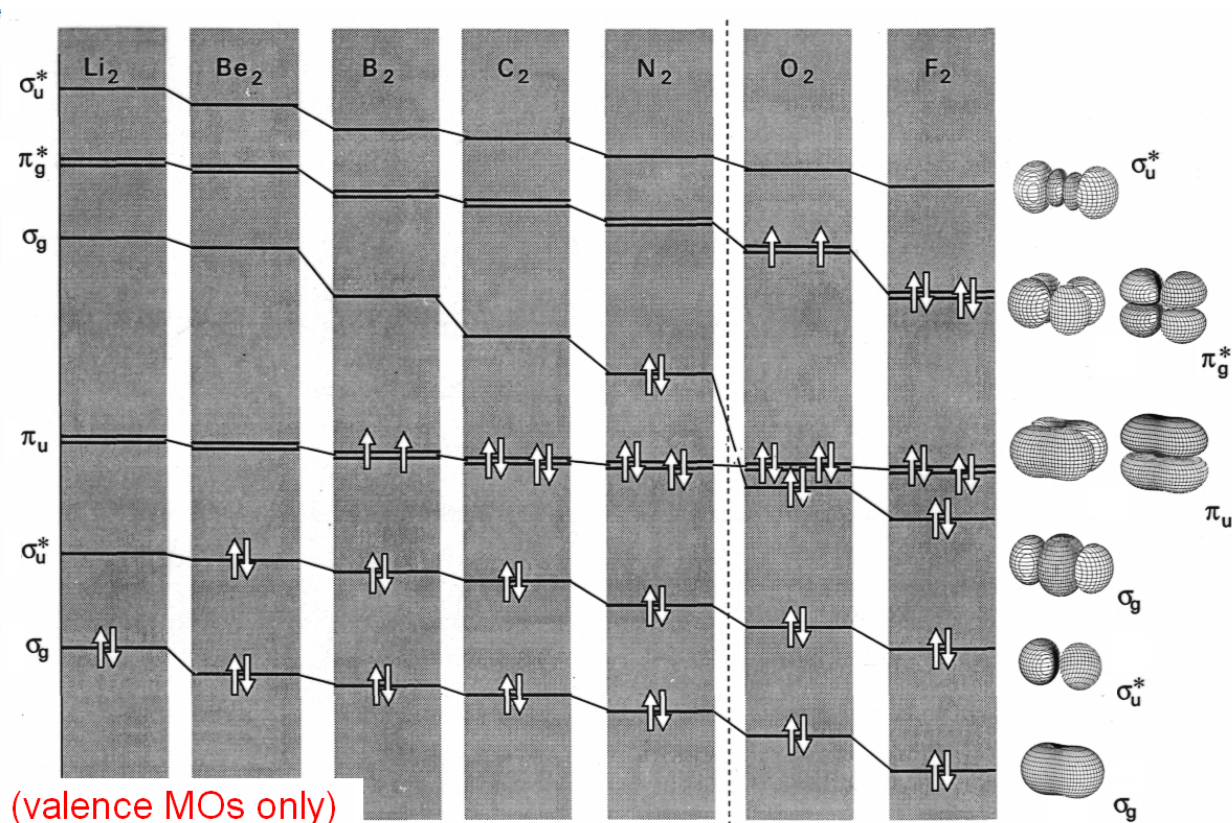
PC Exercise 1

a) Homonuclear diatomic molecules

Compute equilibrium bond lengths and electron configurations for diatomic molecules by HF/6-31G* calculations. Determine the bond lengths R by geometry optimization. For comparison, experimental bond lengths are given in the Table. – Visualize the computed MOs on the screen (option 'Orbitals'), check total number of electrons, number of core and valence electrons, and list the electron configurations according to the prescription: $(\sigma)^2(\sigma^*)^2(\pi)^2$, etc. (an example is given for O_2). Write the results in the Table. – Are the predicted configurations consistent with those given in the text-book diagram reproduced below the table?

Mol. ^{a)}	R (Å)		Electron configuration	
	Expt.	Computed	core (1s)	valence (2s, 2p)
1Li_2	2.673			
1N_2	1.098			
3O_2	1.208	1.168	$(\sigma)^2(\sigma^*)^2$	$(\sigma)^2(\sigma^*)^2(\sigma)^2(\pi)^2(\pi)^2(\pi^*)^1(\pi^*)^1$
1F_2	1.412			

a) The molecules have groundstate electron configurations with singlet spin ("Spin multiplicity = 1"), except for O_2 which has triplet spin ("Spin multiplicity = 3"). This must be specified in the "set up" menu before the calculation. For all molecules, select "RHF" (Restricted Hartree Fock = same set of MOs for electrons with α and β spin).



b) Relative energies for 10 isomeric C₃H₆O compounds

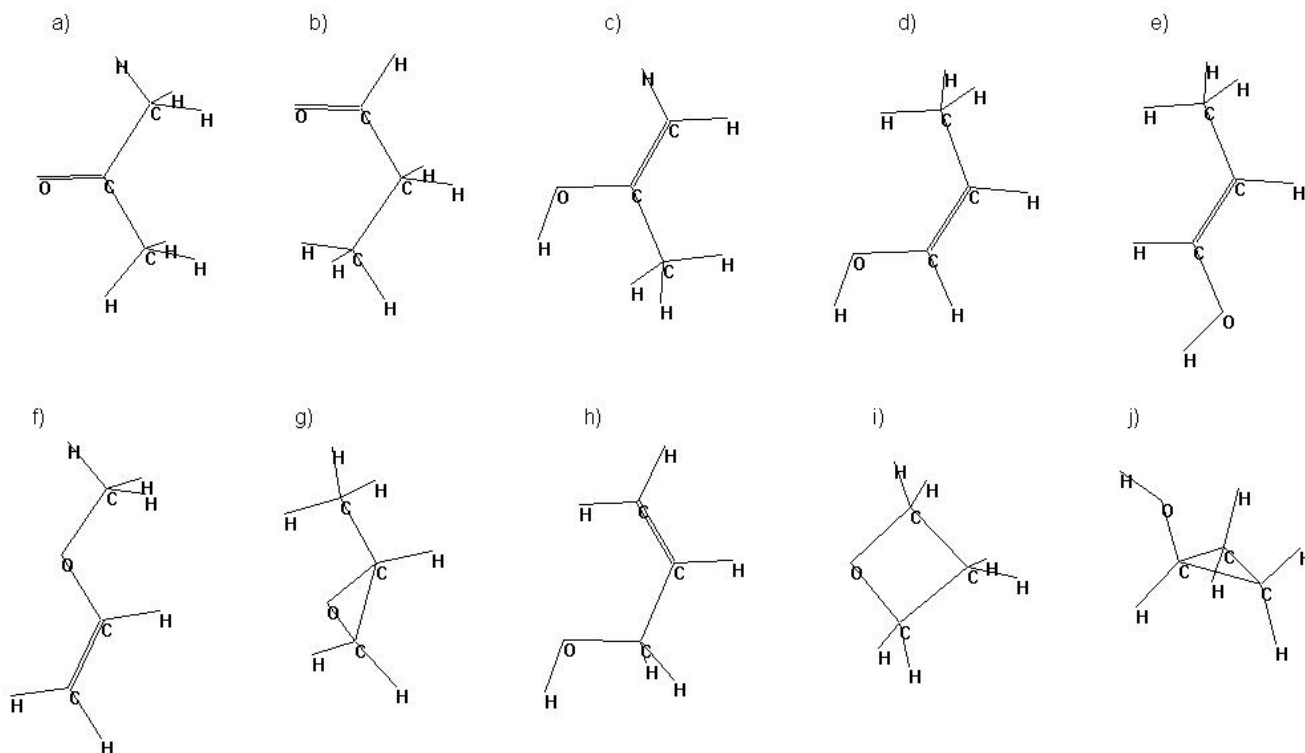
- a) Acetone
- b) Propanal
- c) Propene-2-ol
- d) [*Z*]-Propene-1-ol
- e) [*E*]-Propene-1-ol
- f) Methyl-vinyl-ether
- g) Methyl-oxiran
- h) Allylalkohol
- i) Oxetan
- j) Cyclopropanol

Apply the semi-empirical valence-electron model PM3 and the HF/3-21G procedure to predict geometries and relative energies for the 10 C₃H₆O compounds. Define the constitution of the molecules on the screen and use HyperChem's built-in model builder to generate starting structures for the geometry optimizations. Be careful to **check the generated structures!** Some of them need modification; they should correspond to those indicated below. - For each species, it is most convenient to start with the PM3 calculation, and then perform the HF/3-21G calculation with the PM3 structure as starting geometry.

When an optimization is finished, the computed energy E (kcal/mol) is displayed in the lower left corner of the screen (in case of PM3, the energy displayed is E_b , the total bonding energy; E_b is the difference between the total energy of the molecule and that of the isolated atoms). Write the results in the ensuing Table.

The Table contains relative energies computed with the DFT procedure B3LYP/6-31G*. Discuss the consistency of the predictions by the three calculational procedures!

NB! The B3LYP calculations are based on the molecular conformations indicated below. Comparison of results is most realistic if all calculations are based on these conformations:

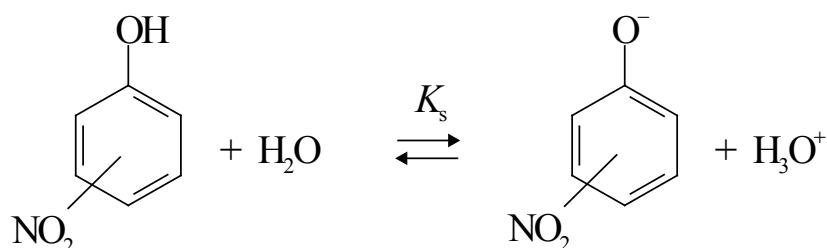


Computed energies in kcal/mol (two decimals)

	E_b (PM3)	ΔE (PM3)	E (HF)	ΔE (HF)	ΔE (DFT)
a) Acetone	-938.29	(0)		(0)	(0)
b) Propanal	-933.55	4.73			6.50
c) Propene-2-ol	-923.75	14.54			19.30
d) [Z]-Propene-1-ol					21.97
e) [E]-Propene-1-ol					22.36
f) Methyl-vinyl-ether					28.41
g) Methyl-oxiran					29.60
h) Allylalkohol					29.66
i) Oxetan					31.80
j) Cyclopropanol					33.64

c) Acid strengths for nitrophenols

Phenol is a weak acid ($K_a = 1.02 \cdot 10^{-10}$, $pK_a = 9.99$). The acidity is increased (i.e., the pK_a value is decreased) by the introduction of electronegative substituents, for example nitro groups. The inductive and mesomeric effects of the substituents lead to a reduction of the negative charge density on the hydroxyl group, thereby facilitating separation of the hydroxyl proton. At the same time, the corresponding base, i.e., the phenolate anion, is stabilized.



In this exercise it is investigated whether the computed net charges ('Charges') on the hydroxyl hydrogen can explain the observed variation of pK_a values for phenol and a series of nitro-substituted phenols (see Table). Optimize the geometries of the compounds with PM3. The computed net atomic charges are displayed on the screen by activating the option 'Charges' from the 'Labels' menu under 'Display'. Supplement the PM3 results by a single point HF/32-1G calculation on the PM3 geometry ("single point" means without optimizing the geometry). Write the computed hydroxyl hydrogen charges Q_H in the Table.

Do the results explain the observed variation of pK_a values?

Discuss the consistency of the two sets of results!

Try to predict the pK_a value for 3,4,5-Trinitrophenol!

	pK_a (obsd.)	Q_H (PM3)	Q_H (HF)
Phenol	9.99		
3-Nitrophenol	8.36		
4-nitrophenol	7.16		
3,4-Dinitrophenol*)	5.42		
3,5-Dinitrophenol	6.68		
3,4,5-Trinitrophenol*)			

*) Because of steric hindrance, the molecules with nitro groups in neighboring positions have non-planar equilibrium geometries. Start the optimization of these molecular geometries with non-planar structures!

NB: Remember to write *your name* on your report when you hand it in for approval!

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PC Exercise 2

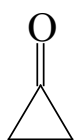
In these exercises, we consider the prediction of optical spectra (IR, UV-VIS).

a) Carbonyl stretching wavenumbers for ketones

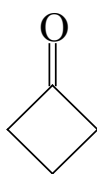
The C=O stretching vibration in ketones and other carbonyl compounds gives rise to a characteristic strong IR absorption band with wavenumber $\tilde{\nu}_{\text{C=O}}$ around 1700 cm^{-1} . This wavenumber is the most useful “group frequency” for these compounds. The observed wavenumbers depend on the chemical surroundings of the carbonyl group. For example, larger $\tilde{\nu}_{\text{C=O}}$ values are observed for cycloalkanones with strained rings, while conjugation with double bonds in the α,β -position leads to reduced values, see the table.

Test the ability of the PM3 model to predict these shifts: Compute the C=O stretching wavenumbers $\tilde{\nu}_{\text{C=O}}$ (cm^{-1}) for the ketones *a* – *g* and write the results in the table. Corresponding results obtained with DFT calculations (B3LYP/6-31G*, unscaled) are listed for comparison. Evaluate the performance of the two models! Try to establish the appropriate scaling factors α required to transform the theoretical wavenumbers into empirical scale (see lecture notes)!

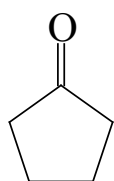
Keton	$\tilde{\nu}_{\text{C=O}}$ (obs.)	$\tilde{\nu}_{\text{C=O}}$ (PM3)	$\tilde{\nu}_{\text{C=O}}$ (DFT)
<i>a</i>) Cyclopropanone	1822		1956
<i>b</i>) Cyclobutanone	1780		1893
<i>c</i>) Cyclopentanone	1746		1846
<i>d</i>) Cyclohexanone	1713		1818
<i>e</i>) Propanone (acetone)	1710		1814
<i>f</i>) 2-Cyclohexen-1-one	1675		1782
<i>g</i>) 2,5-Cyclohexadien-1-on	1665		1763



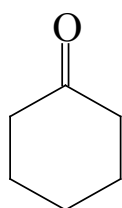
a



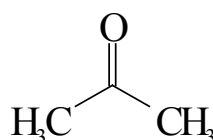
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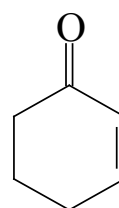
c



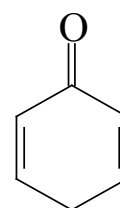
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e



f



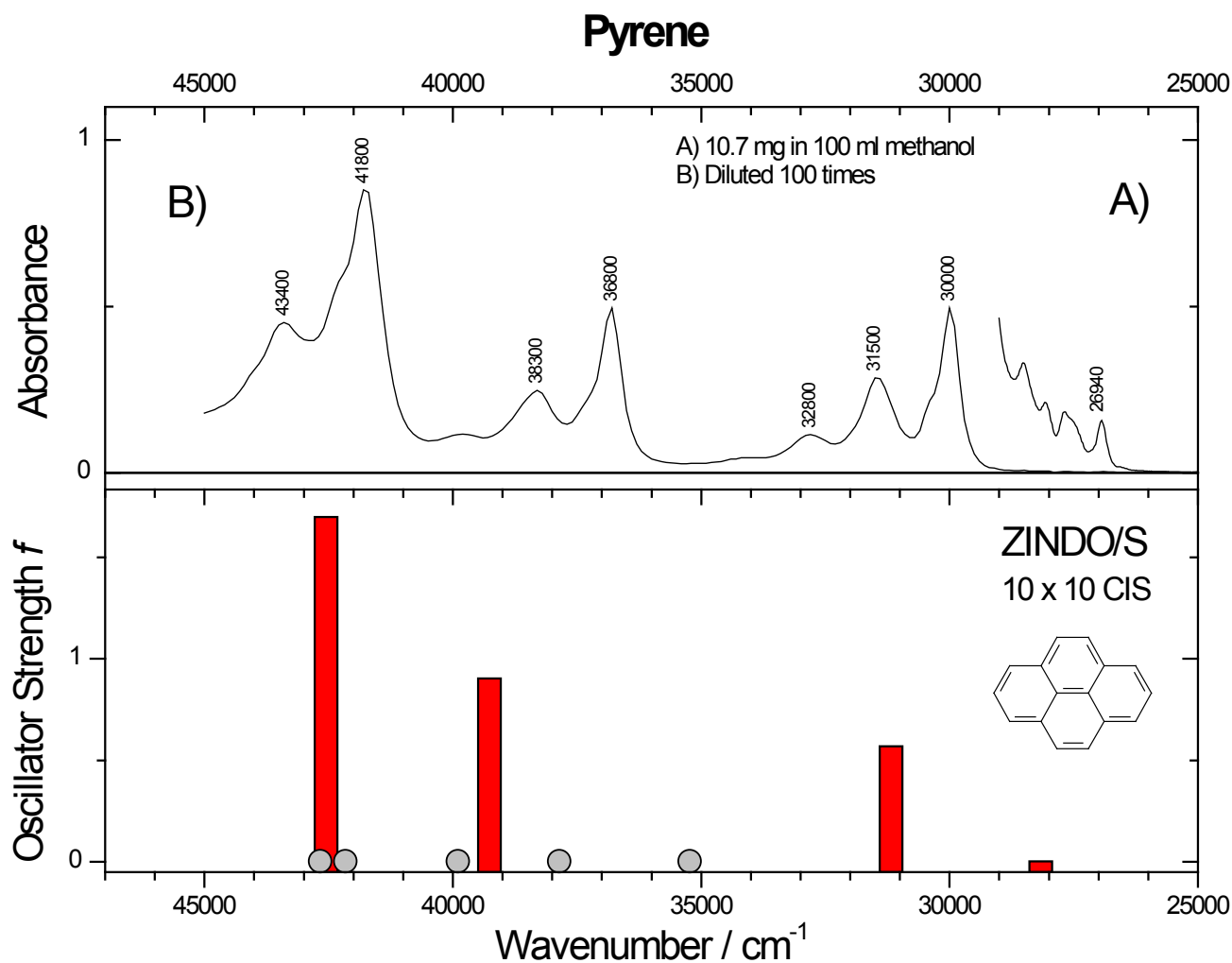
g

b) Electronic transitions

In this exercise we apply HyperChem™ to predict electronic transitions for two molecules, namely *pyrene* and *ozone*. Computation of excited electronic states is one of the most difficult tasks in quantum chemistry. HyperChem contains a semi-empirical all-valence-electrons MO-procedure, ZINDO/S, which is particularly developed for prediction of electronic transitions in the near-UV and VIS regions for organic compounds with conjugated double bonds or aromatic π systems (for those systems, the π - π overlap weighting factor in the Set Up-menu should be adjusted to the value 0.585). ZINDO/S is thus suitable for the description of transitions in the π electronic system of pyrene, but it is not always adequate for small systems like the ozone molecule. For those, other models, like f. inst. AM1, are often more useful.

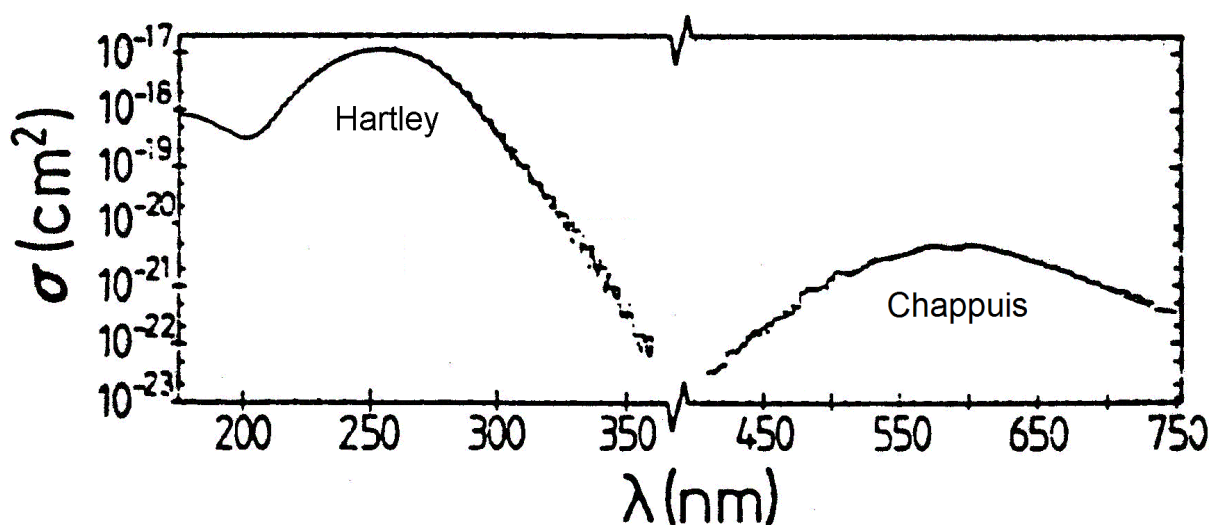
Computation of π - π^* electronic transitions in the aromatic hydrocarbon pyrene

This exercise is carried out as a class-room demonstration (ZINDO/S).



Prediction of the electronic transitions in ozone, O₃.

Ozone is a gas with a strong absorption band in the near-UV region with maximum close to 255 nm (the Hartley band). This is the band that causes the ozone layer in the outer atmosphere to absorb harmful UV radiation. Ozone has an additional, much weaker electronic transition in the visible region with maximum around 600 nm (the Chappuis band), and ozone is thus a blue gas. The ordinate in the spectrum below is the absorption cross section in cm²/molecule (note the logarithmic scale).



In this exercise the AM1 method is applied to predict the transitions of ozone. In the computation we use the CIS procedure, involving configuration interaction (CI) between singly excited electronic configurations, and the results are stored in a log-file.

- 1) Build an ozone molecule and optimize the ground state geometry with AM1 (no CI!).
- 2) Start the log-file Chem.log by activation of the option 'Start Log' in the 'File'-menu (select 'Quantum-Print-Level 9'). Then prepare AM1 in the 'Set Up'-menu for the CI procedure. Select 6 × 3 singly excited CI, which means that excited configurations are generated by excitation of electrons from the 6 highest occupied to the 3 lowest unoccupied MOs (ozone has only 3 unoccupied MOs in the AM1 model). Start the computation ('Single Point'). Close the log-file when the computation is finished.
- 3) A graphical version of the computed transitions is shown on the screen by selecting the option 'Electronic Spectrum' in the 'Compute' menu. Note that the upper window shows triplet as well as singlet transitions, corresponding to S₀ → S_n and S₀ → T_n, where S₀ indicates the singlet ground state and S_n and T_n indicate excited singlet and triplet states, respectively. S₀ → T_n transitions are spin-forbidden and they do not appear in the lower window where the transitions are displayed with their computed intensities (relative oscillator strengths). – Find the three S₀ → S_n transitions with lowest energy (AM1 computes them with wavelengths near 558, 436 and 259 nm).
- 4) Many more details are provided by the log-file. Close the log-file ('Close Log'), minimize the HyperChem window (temporarily), and read the log-file with 'Notepad' or 'Wordpad'. Find those results that correspond to the abovementioned three singlet states ("Spin S 0.00"). Write down

the computed oscillator strengths with 4 decimals, and the numbers of the MOs that are involved in the computed transitions (“Occ. MO --> Unocc. MO”). For example, the transition at 558 nm is dominated by the promotion “9 --> 10”, corresponding to the HOMO-LUMO configuration.

5) Inspect the shape of these MOs in the HyperChem window (option 'Orbitals' in the 'Compute' menu) and decide whether they are σ , σ^* , π , or π^* MOs. Then characterize the type of the three computed transitions as $\pi\text{--}\pi^*$, $\sigma\text{--}\pi^*$, $\pi\text{--}\sigma^*$ or $\sigma\text{--}\sigma^*$. Finally, assign the observed transitions (i.e., the Hartley and Chappuis bands) to the computed transitions.

Ozone	$\lambda(\text{nm})$	$\tilde{\nu}(\text{cm}^{-1})$	$f^{\text{a)}}$	Excited configuration ^{b)}	Type ^{c)}
$S_0 \rightarrow S_1$				$\rightarrow$	
$S_0 \rightarrow S_2$				$\rightarrow$	
$S_0 \rightarrow S_3$				$\rightarrow$ $\rightarrow$	

a) Oscillator strength (4 decimals!).

b) Leading electronic configuration in the excited state, e.g., $9 \rightarrow 10$.

c) $\pi\text{--}\pi^*$, $\sigma\text{--}\pi^*$, etc.

Does AM1 provide an adequate description of the electronic absorption spectrum of ozone?

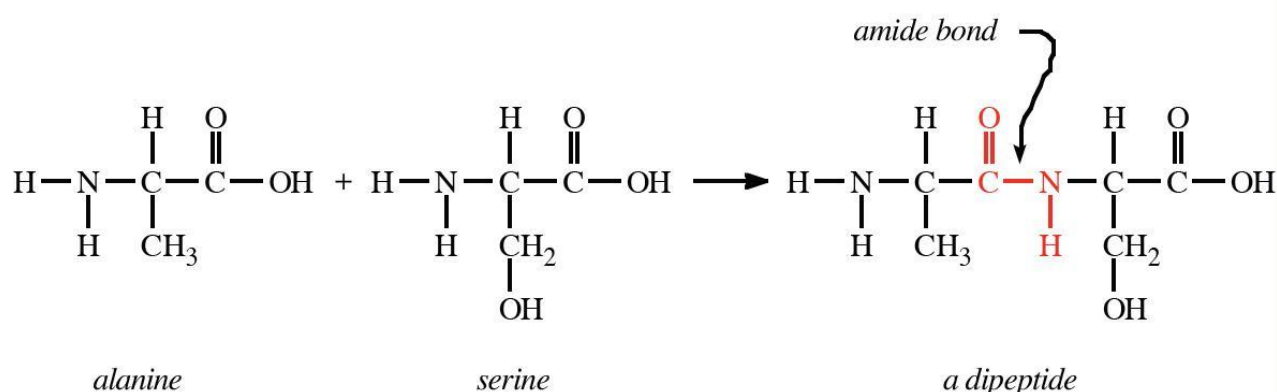
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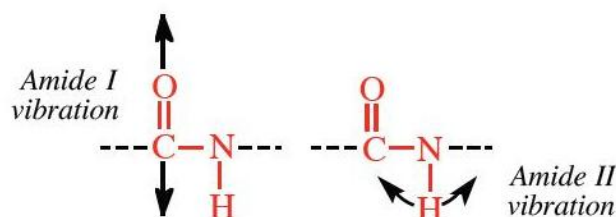
PC Exercise 3

a) Peptide *Amide I* and *Amide II* vibrational transitions

Polypeptides are built of amino acids that are linked together by amide bonds:

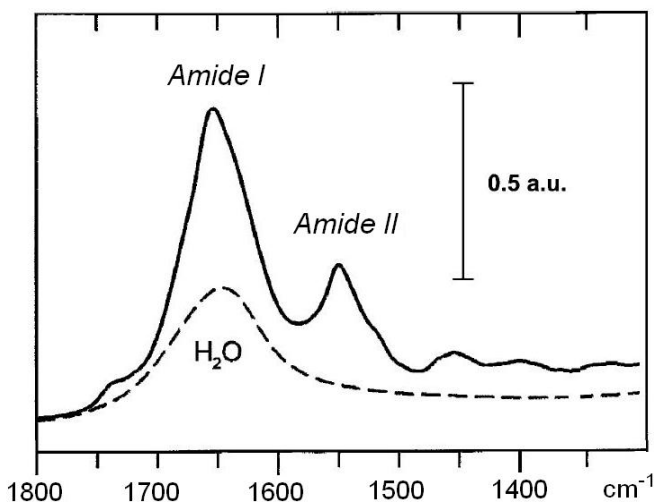


These secondary amide functions give rise to a number of characteristic, strong bands in the IR spectrum, such as *Amide I* and *Amide II* (and others):



The *Amide I* vibration is dominated by the C=O stretching motion ($\nu_{\text{C=O}}$), while *Amide II* involves primarily C–N–H bending (δ_{NH}) coupled with C–N stretching ($\nu_{\text{C-N}}$). Group frequency tables list the following typical wavenumber ranges for peptides (solution spectra):

<i>Amide I</i>	1740 – 1630 cm^{-1}
<i>Amide II</i>	1560 – 1510 cm^{-1}

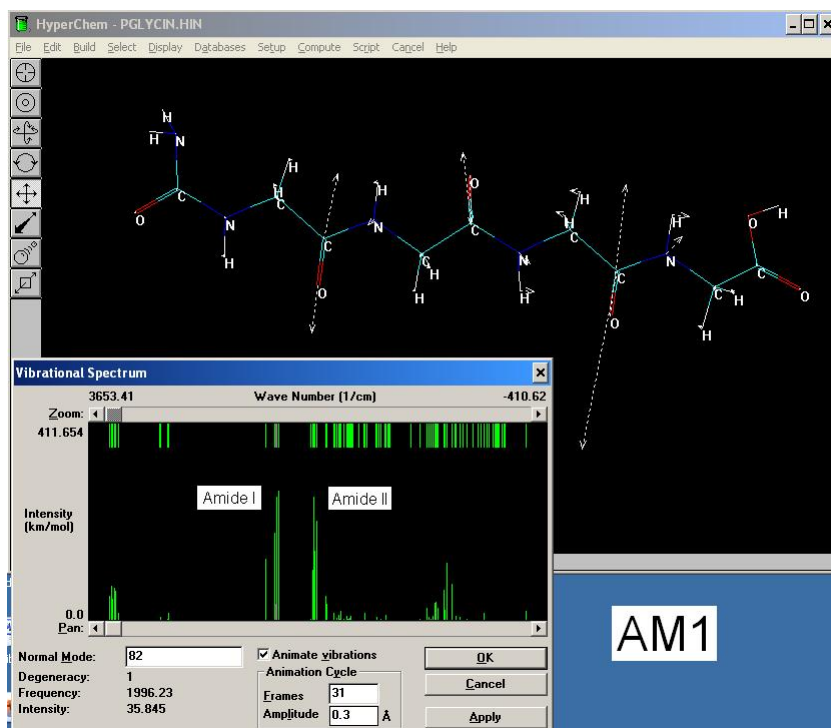


In poly-peptides like proteins, the individual *Amide I* and *Amide II* transitions depend on the tertiary structure (α -helix, β -sheet, etc). Contributions from a large number of amide groups overlap and give rise to complex overlapping bands.

The example given to the left is from an aqueous solution of thylakoid membrane enriched in Photosystem II (adapted from Hienerwadel et al., *Biochemistry* **35**, 15447 (1996)).

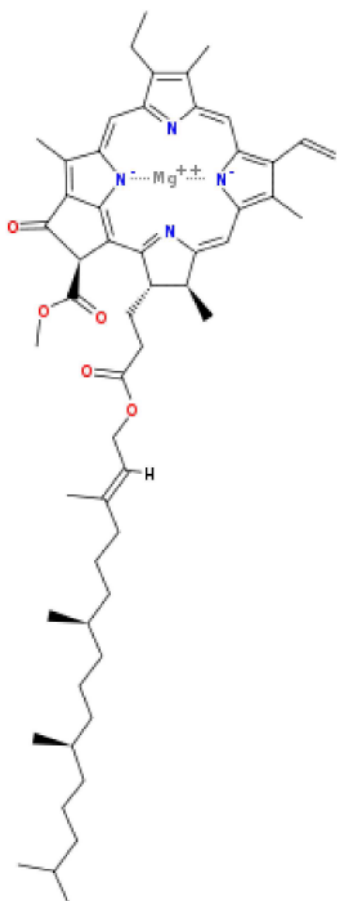
Tasks:

- 1) Build a model of *N*-Methylacetamide (*trans*-amide configuration). Optimize the geometry with a semiempirical model, f.ex. AM1, and calculate the vibrational spectrum. Animate the vibrational motions on the screen and find the *Amide I* and *Amide II* vibrations. Are the calculated transitions consistent with the description above? Write down the calculated wavenumbers and intensities of the two bands.
- 2) Perform a Hartree-Fock calculation on the model you just built. Use the STO-3G (or 3-21G, if you have time!) basis set, optimize the geometry and calculate the vibrational spectrum. How do the results compare with those obtained with the semiempirical model?
- 3) Build a dipeptide, and repeat the calculation indicated in 1). What happens to the *Amide I* and *Amide II* bands?
- 4) Build a “poly”-peptide, f.ex. a tetra- or penta-peptide. If you use HyperChem’s peptide builder to construct the peptide, remember to add the necessary atoms to finish the terminal amino and carboxyl groups. Repeat the calculation indicated in 1). Investigate the appearance of the *Amide I* and *Amide II* bands. Describe the situation!

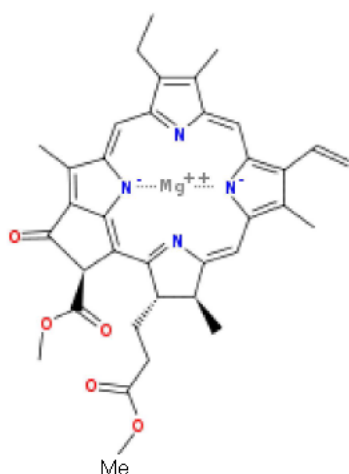


b) Electronic transitions of Chlorophyll

In this exercise we attempt to predict the visible absorption bands of *chlorophyll* (Chl), the green pigment in plants which harvest the radiation energy from sun. We shall consider Chl-a with the structure indicated below (left). This compound is rather large, so for simplicity we adopt a truncated model where the long hydrocarbon chain has been shortened to a methyl group (right):

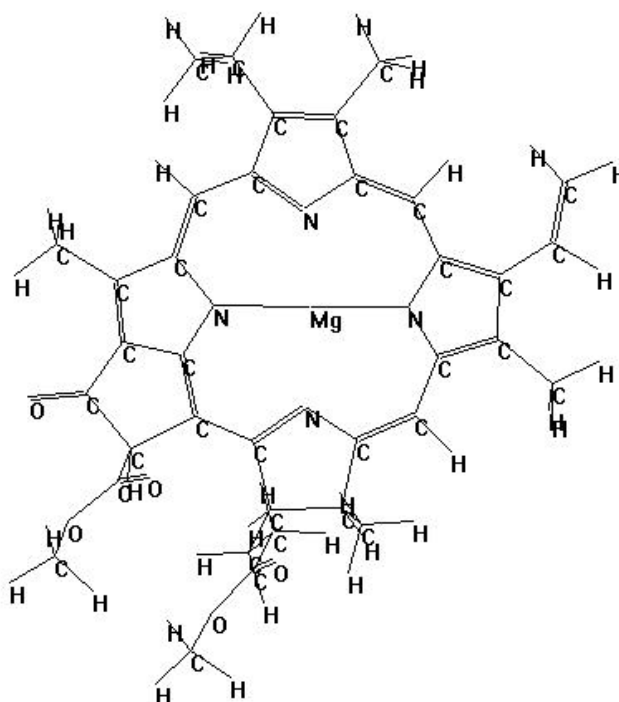


Structure of chlorophyll *a*

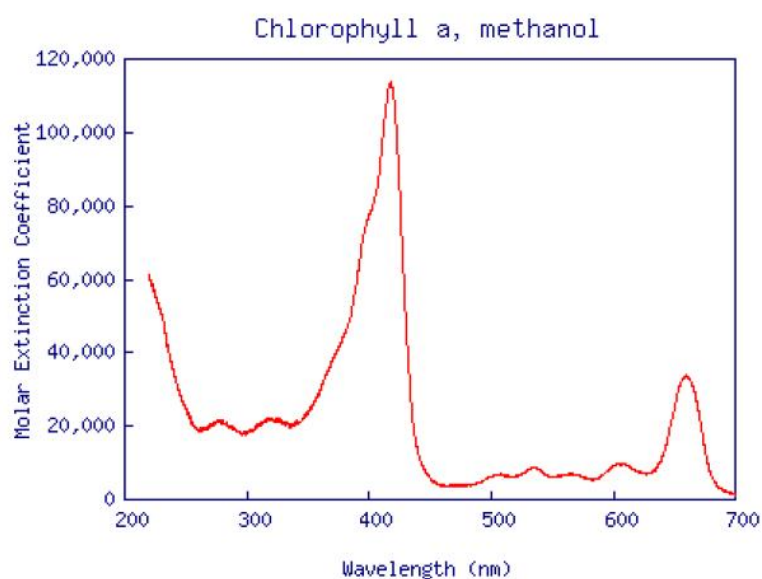
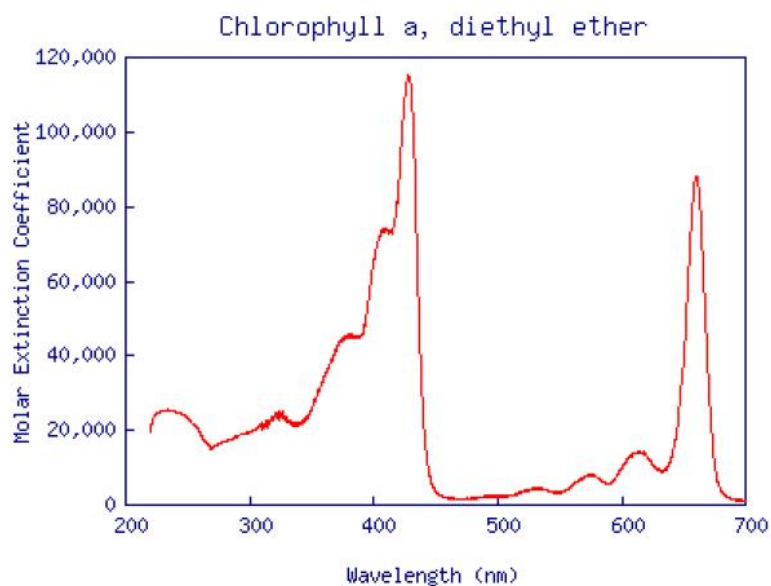


Truncated Chl-a structure

- 1) Build a model of truncated Chl-a (you do not need to indicate the formal charges). Be careful with the stereochemistry! - the MM+ molecular mechanics yields a reasonable structure. Optimization with the semiempirical ZINDO/1 method also tends to produce a useful model, but this calculation is much more time consuming. – The resulting model on the PC screen may look somewhat like the picture below:



- 2) Use ZINDO/S to predict the electronic transitions in the visible region. An 8×8 or 10×10 CIS calculation should be appropriate. Remember to change the ZINDO/S π - π parameter to the value 0.585. – Compare the results with the experimental spectra given below. Discuss whether the model calculation provides a satisfactory description of this chromophore!



NB: Remember to write *your name* on your report when you hand it in for approval!

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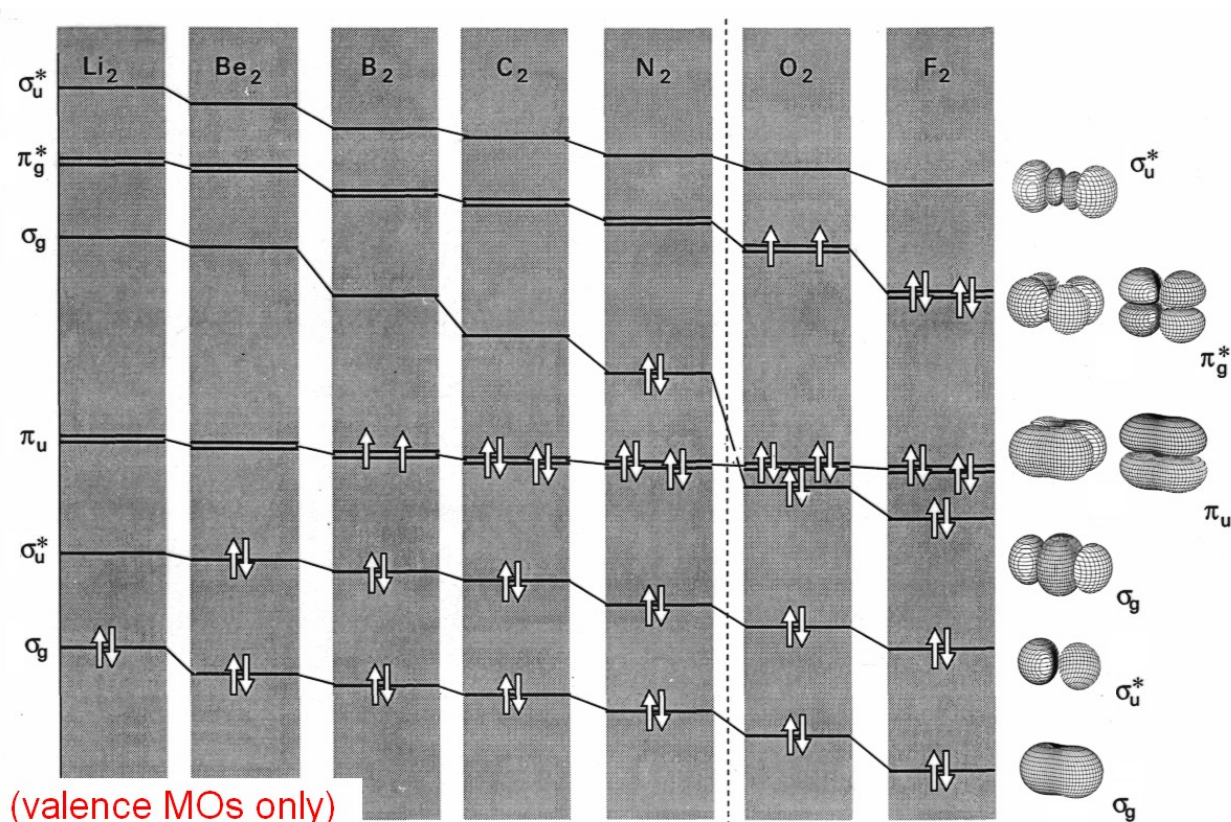
PC Exercise 1 - RESULTS

a) Homonuclear diatomic molecules

Compute equilibrium bond lengths and electron configurations for diatomic molecules by HF/6-31G* calculations. Determine the bond lengths R by geometry optimization. For comparison, experimental bond lengths are given in the Table. – Visualize the computed MOs on the screen (option 'Orbitals'), check total number of electrons, number of core and valence electrons, and list the electron configurations according to the prescription: $(\sigma)^2(\sigma^*)^2(\pi)^2$, etc. (an example is given for O_2). Write the results in the Table. – Are the predicted configurations consistent with those given in the text-book diagram reproduced below the table?

Mol. ^{a)}	R (Å)		Electron configuration	
	Expt.	Computed	core (1s)	valence (2s,2p)
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1N_2	1.098	1.078	$(\sigma)^2(\sigma^*)^2$	$(\sigma)^2(\sigma^*)^2(\sigma)^2(\pi)^2(\pi)^2$
3O_2	1.208	1.168	$(\sigma)^2(\sigma^*)^2$	$(\sigma)^2(\sigma^*)^2(\sigma)^2(\pi)^2(\pi)^2(\pi^*)^1(\pi^*)^1$
1F_2	1.412	1.345	$(\sigma)^2(\sigma^*)^2$	$(\sigma)^2(\sigma^*)^2(\pi)^2(\pi)^2(\sigma)^2(\pi^*)^2(\pi^*)^2$

a) The molecules have groundstate electron configurations with singlet spin ("Spin multiplicity = 1"), except for O_2 which has triplet spin ("Spin multiplicity = 3"). This must be specified in the "set up" menu before the calculation. For all molecules, select "RHF" (Restricted Hartree Fock = same set of MOs for electrons with α and β spin).



b) Relative energies for 10 isomeric C₃H₆O compounds

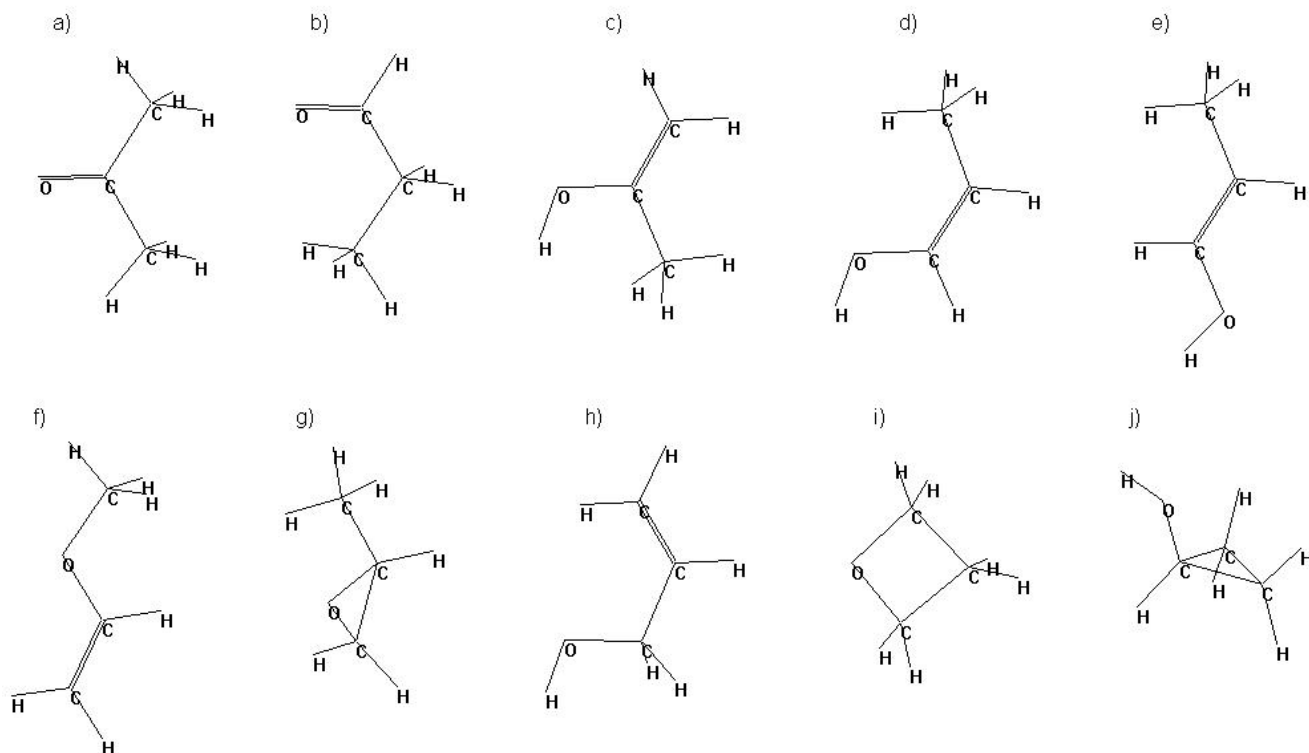
- a) Acetone
- b) Propanal
- c) Propene-2-ol
- d) [*Z*]-Propene-1-ol
- e) [*E*]-Propene-1-ol
- f) Methyl-vinyl-ether
- g) Methyl-oxiran
- h) Allylalkohol
- i) Oxetan
- j) Cyclopropanol

Apply the semi-empirical valence-electron model PM3 and the HF/6-31G* procedure to predict geometries and relative energies for the 10 C₃H₆O compounds. Define the constitution of the molecules on the screen and use HyperChem's built-in model builder to generate starting structures for the geometry optimizations. Be careful to **check the generated structures!** They may need modification.; they should correspond to those indicated below. - For each species, it is most convenient to start with the PM3 calculation, and then perform the HF/6-31G* calculation with the PM3 structure as starting geometry.

When an optimization is finished, the computed energy E (kcal/mol) is displayed in the lower left corner of the screen (in case of PM3, the energy displayed is E_b , the total bonding energy; E_b is the difference between the total energy of the molecule and that of the isolated atoms). Write the results in the ensuing Table.

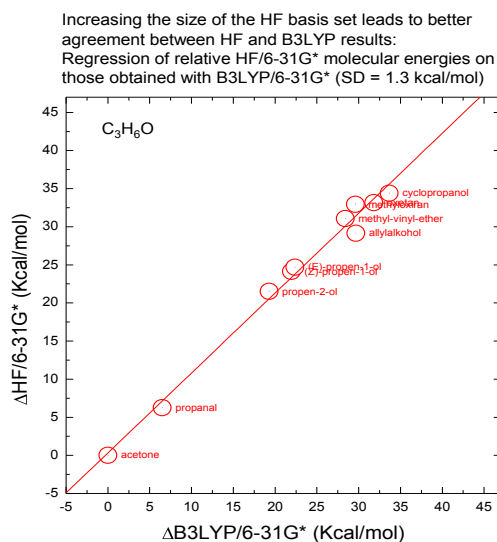
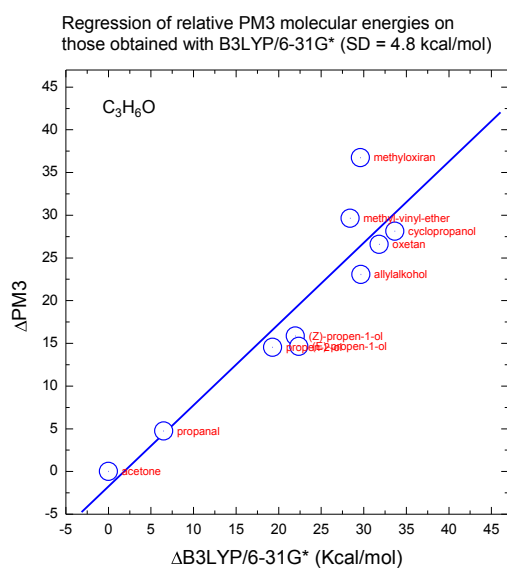
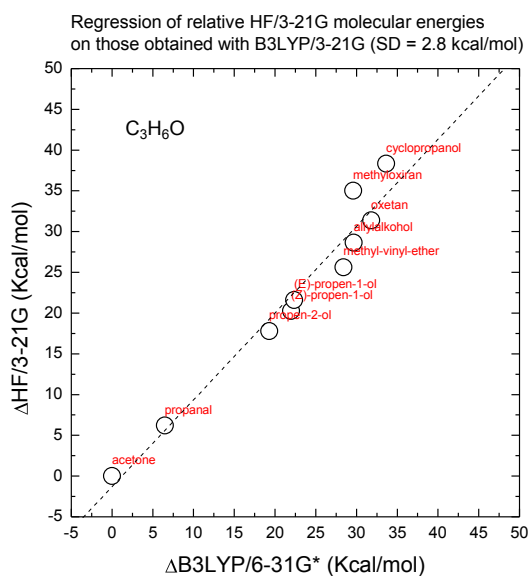
The Table contains relative energies computed with the DFT procedure B3LYP/6-31G*. Discuss the consistency of the predictions by the three calculational procedures!

NB! The B3LYP calculations are based on the molecular conformations indicated below. Comparison of results is most realistic if all calculations are based on these conformations:



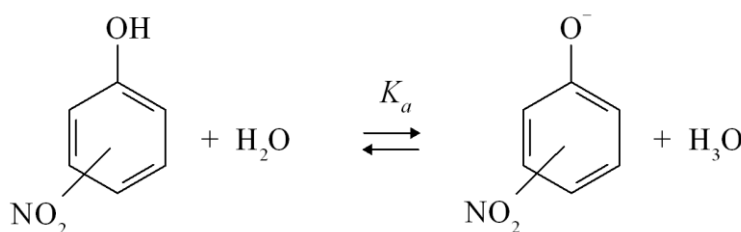
Computed energies in kcal/mol (two decimals)

	E_b (PM3)	ΔE (PM3)	E (HF)	ΔE (HF)	ΔE (DFT)
a) Acetone	-938.29	(0)	-120540.11	(0)	(0)
b) Propanal	-933.55	4.73	-120533.89	6.22	6.50
c) Propene-2-ol	-923.75	14.54	-120522.31	17.79	19.30
d) [Z]-Propene-1-ol	-922.42	15.87	-120519.85	20.25	21.97
e) [E]-Propene-1-ol	-923.63	14.65	-120518.50	21.60	22.36
f) Methyl-vinyl-ether	-908.65	29.63	-120514.51	25.60	28.41
g) Methyl-oxiran	-901.56	36.73	-120505.09	35.01	29.60
h) Allylalkohol	-915.22	23.07	-120511.47	28.64	29.66
i) Oxetan	-911.69	26.60	-120508.74	31.37	31.80
j) Cyclopropanol	-910.15	28.14	-120501.77	38.34	33.64



c) Acid strengths for nitrophenols

Phenol is a weak acid ($K_a = 1.02 \cdot 10^{-10}$, $pK_a = 9.99$). The acidity is increased (i.e., the pK_a value is decreased) by the introduction of electronegative substituents, for example nitro groups. The inductive and mesomeric effects of the substituents leads to a reduction of the negative charge density on the hydroxyl group, thereby facilitating separation of the hydroxyl proton. At the same time, the corresponding base, i.e., the phenolate anion, is stabilized.



In this exercise it is investigated whether the computed net charges ('Charges') on the hydroxyl hydrogen can explain the observed variation of pK_a values for phenol and a series of nitro-substituted phenols (see Tabel). Apply the semi-empirical valence-electron model PM3 and the HF/3-21G procedure. The geometries of the compounds are optimized and the computed net atomic charges are displayed on the screen ved activating the option 'Charges' from the 'Labels' menu under 'Display'. Write the computed hydroxyl hydrogen charges Q_H skives in the Tabel.

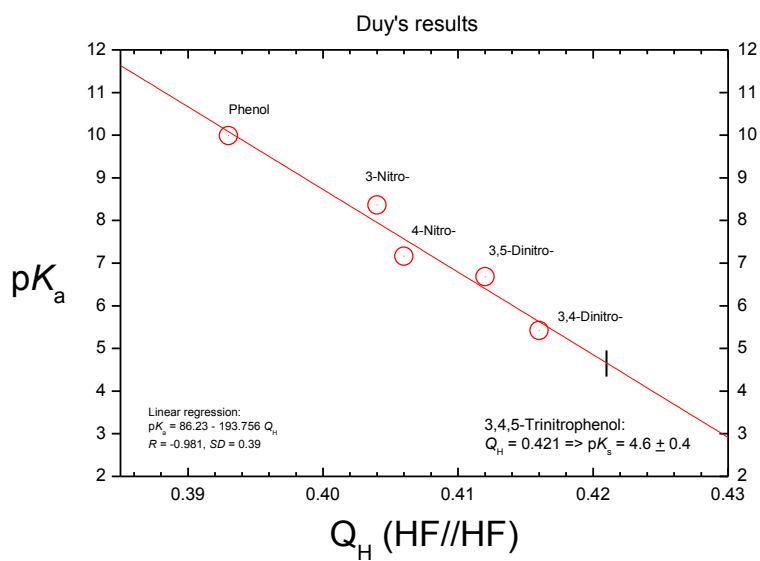
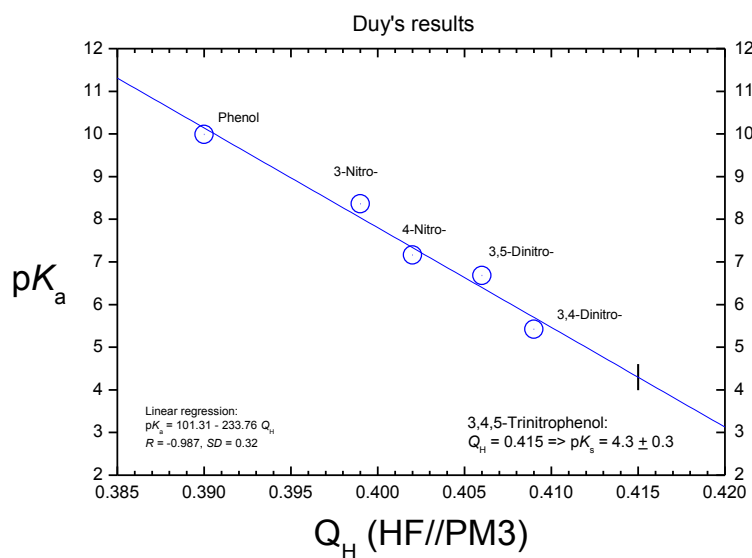
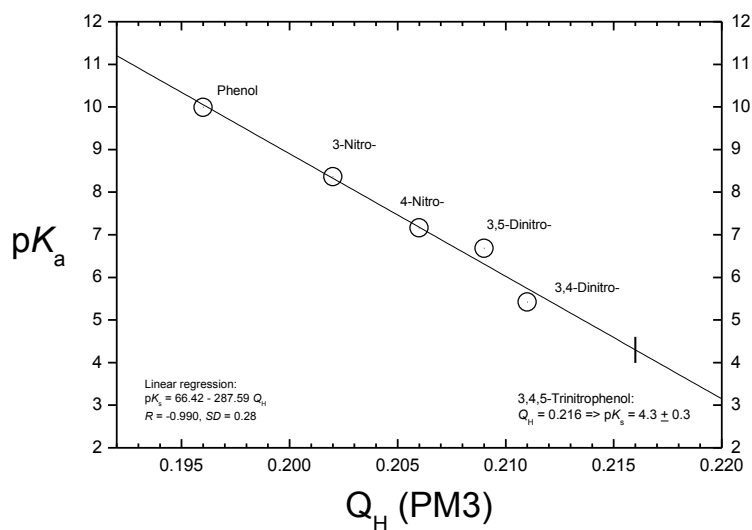
Do the results explain the observed variation of pK_a values?

Discuss the consistency of the two sets of results!

Predict the pK_a value for 3,4,5-Trinitrophenol!

	pK_a (obsd.)	Q_H (PM3)	Q_H (HF//PM3)	Q_H (HF//HF)
Phenol	9.99	+0.196	+0.390	+0.393
3-Nitrophenol	8.36	+0.202	+0.399	+0.404
4-nitrophenol	7.16	+0.206	+0.402	+0.406
3,4-Dinitrophenol*)	5.42	+0.211	+0.409	+0.416
3,5-Dinitrophenol	6.68	+0.209	+0.406	+0.412
3,4,5-Trinitrophenol*)	4.3 ± 0.3	+0.216	+0.415	+0.421

*) Because of steric hindrance, the molecules with nitro groups in neighboring positions have non-planar equilibrium geometries. Start the optimization of these molecular geometries with non-planar structures!



COMPUTATIONAL CHEMISTRY

PC Exercise 2 RESULTS

In these exercises, we consider the prediction of optical spectra (IR, UV-VIS).

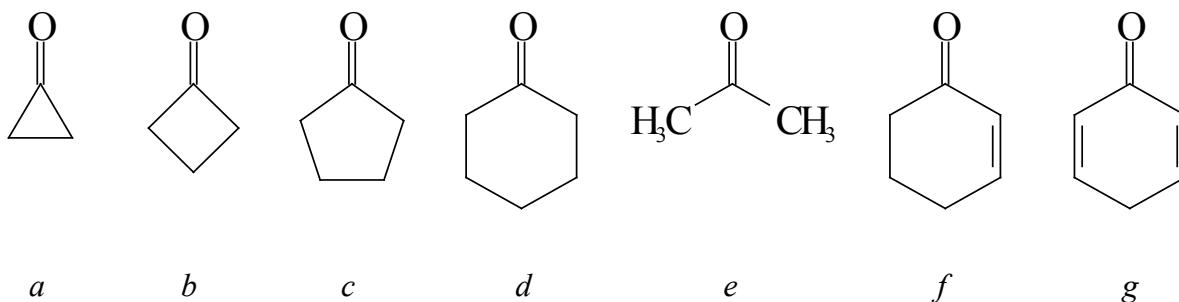
a) Carbonyl stretching wavenumbers for ketones

The C=O stretching vibration in ketones and other carbonyl compounds gives rise to a characteristic strong IR absorption band with wavenumber $\tilde{\nu}_{\text{C=O}}$ around 1700 cm^{-1} . This wavenumber is the most useful “group frequency” for these compounds. The observed wavenumbers depend on the chemical surroundings of the carbonyl group. For example, enlarged $\tilde{\nu}_{\text{C=O}}$ values are observed for cycloalkanones with strained rings, while conjugation with double bonds in the α,β -position leads to reduced values $\tilde{\nu}_{\text{C=O}}$, see the table.

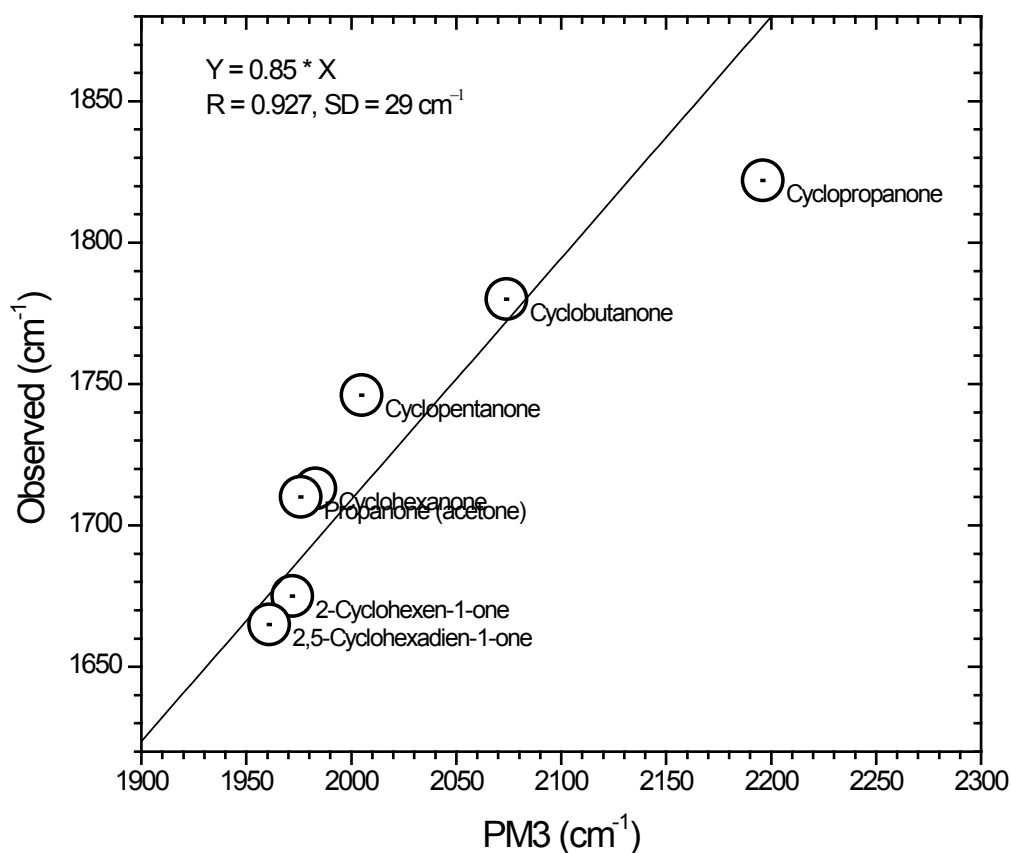
Test the ability of the PM3 model to predict these shifts: Compute the C=O stretching wavenumbers $\tilde{\nu}_{\text{C=O}}$ (cm^{-1}) for the ketones *a* – *g* and write the results in the table. Corresponding results obtained with DFT calculations (B3LYP/6-31G*, unscaled) are listed for comparison. Evaluate the performance of the two models! Try to establish the appropriate scaling factors α required to transform the theoretical wavenumbers into empirical scale (see lecture notes)!

Keton	$\tilde{\nu}_{\text{C=O}}$ (obs.)	$\tilde{\nu}_{\text{C=O}}$ (PM3)	$\tilde{\nu}_{\text{C=O}}$ (DFT)
<i>a</i>) Cyclopropanone	1822	2196	1956
<i>b</i>) Cyclobutanone	1780	2074	1893
<i>c</i>) Cyclopentanone	1746	2005	1846
<i>d</i>) Cyclohexanone	1713	1983	1818
<i>e</i>) Propanone (acetone)	1710	1976	1814
<i>f</i>) 2-Cyclohexen-1-one	1675	1972	1782
<i>g</i>) 2,5-Cyclohexadien-1-on	1665	1961	1763

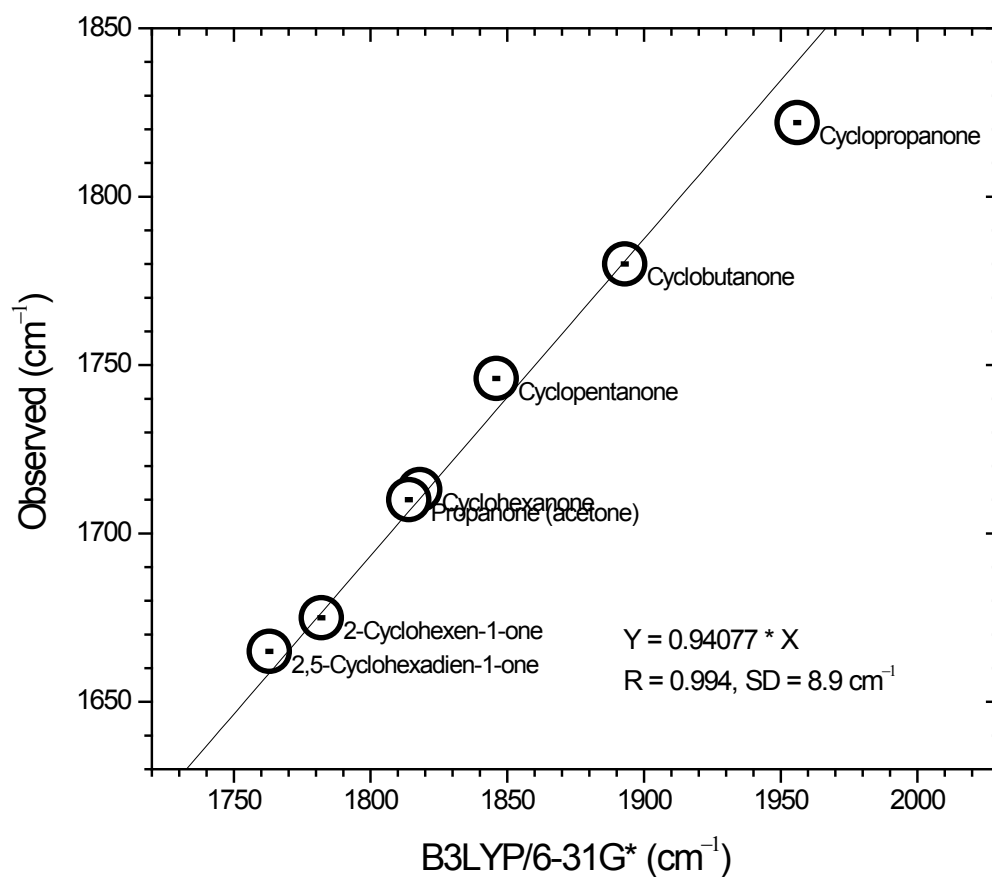
Scaling factor: $\alpha = 0.85$ $\alpha = 0.94$
(scaling regressions on next page)



C=O stretching wavenumbers for ketones



C=O stretching wavenumbers for ketones

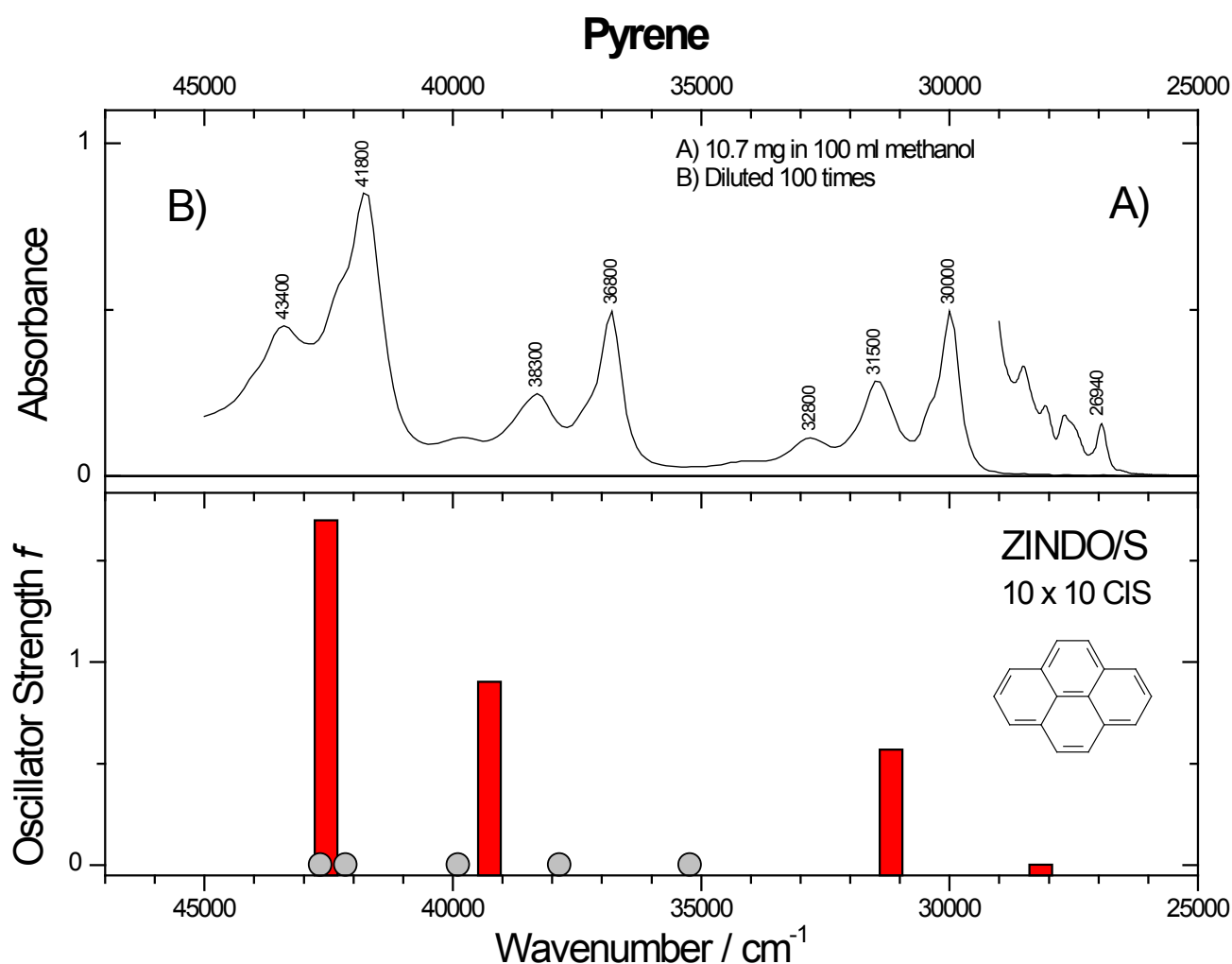


b) Electronic transitions

In this exercise we apply HyperChem™ to predict electronic transitions for two molecules, namely *pyrene* and *ozone*. Computation of excited electronic states is one of the most difficult tasks in quantum chemistry. HyperChem contains a semi-empirical all-valence-electrons MO-procedure, ZINDO/S, which is particularly developed for prediction of electronic transitions in the near-UV and VIS regions for organic compounds with conjugated double bonds or aromatic π systems (for those systems, the π - π overlap weighting factor in the Set Up-menu should be adjusted to the value 0.585). ZINDO/S is thus suitable for the description of transitions in the π electronic system of pyrene, but it is not always adequate for small systems like the ozone molecule. For those, other models, like f. inst. AM1, are often more useful.

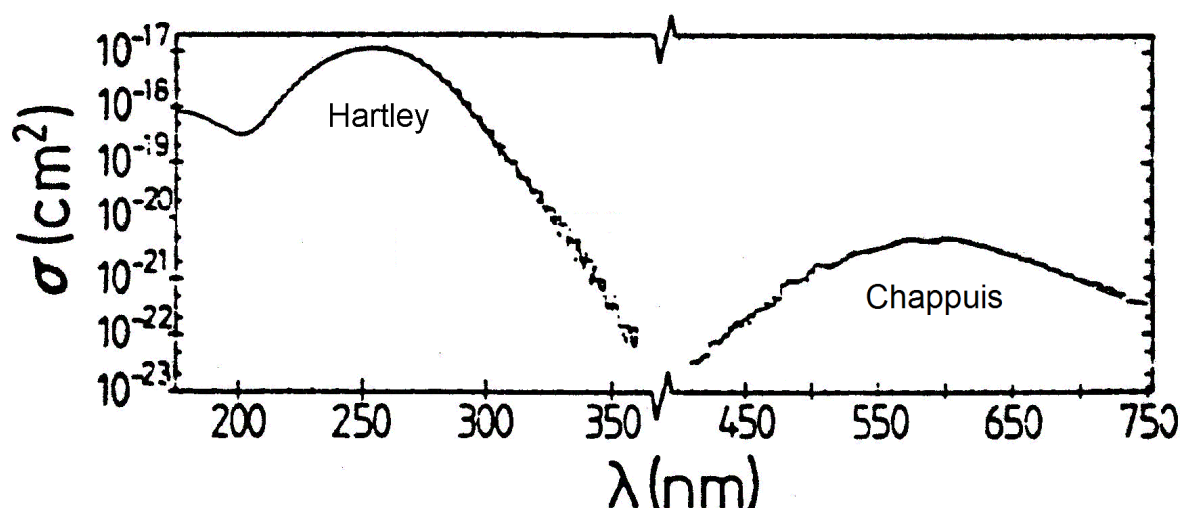
Computation of π - π^* electronic transitions in the aromatic hydrocarbon pyrene

This exercise is carried out as a class-room demonstration (ZINDO/S).



Prediction of the electronic transitions in ozone, O₃.

Ozone is a gas with a strong absorption band in the near-UV region with maximum close to 255 nm (the Hartley band). This is the band that causes the ozone layer in the outer atmosphere to absorb harmful UV radiation. Ozone has an additional, much weaker electronic transition in the visible region with maximum around 600 nm (the Chappuis band), and ozone is thus a blue gas. The ordinate in the spectrum below is the absorption cross section in cm²/molecule (note the logarithmic scale).



In this exercise the AM1 method is applied to predict the transitions of ozone. In the computation we use the CIS procedure, involving configuration interaction (CI) between singly excited electronic configurations, and the results are stored in a log-file.

- 1) Build an ozone molecule and optimize the ground state geometry with AM1 (no CI!).
- 2) Start the log-file Chem.log by activation of the option 'Start Log' in the 'File'-menu (select 'Quantum-Print-Level 9'). Then prepare AM1 in the 'Set Up'-menu for the CI procedure. Select 6×3 singly excited CI, which means that excited configurations are generated by excitation of electrons from the 6 highest occupied to the 3 lowest unoccupied MOs (ozone has only 3 unoccupied MOs in the AM1 model). Start the computation ('Single Point'). Close the log-file when the computation is finished.
- 3) A graphical version of the computed transitions is shown on the screen by selecting the option 'Electronic Spectrum' in the 'Compute' menu. Note that the upper window shows triplet as well as singlet transitions, corresponding to $S_0 \rightarrow S_n$ and $S_0 \rightarrow T_n$, where S_0 indicates the singlet groundstate and S_n and T_n indicate excited singlet and triplet states, respectively. $S_0 \rightarrow T_n$ transitions are spin-forbidden and they do not appear in the lower window where the transitions are displayed with their computed intensities (relative oscillator strengths). – Find the three $S_0 \rightarrow S_n$ transitions with lowest energy (AM1 computes them with wavelengths near 558, 436 and 259 nm).
- 4) Many more details are provided by the log-file. Close or minimize the HyperChem window (temporarily) and open the log-file. Find those results that correspond to the abovementioned three singlet states ("Spin S 0.00"). Write down the computed oscillator strengths with 4 decimals, and the numbers of the MOs that are involved in the computed transitions ("Occ. MO --> Unocc.

MO”). For example, the transition at 558 nm is dominated by the promotion “9 → 10”, corresponding to the HOMO-LUMO configuration.

5) Inspect the shape of these MOs in the HyperChem window (option 'Orbitals' in the 'Compute' menu) and decide whether they are σ , σ^* , π , or π^* MOs. Then characterize the type of the three computed transitions as $\pi\text{--}\pi^*$, $\sigma\text{--}\pi^*$, $\pi\text{--}\sigma^*$ or $\sigma\text{--}\sigma^*$. Finally, assign the observed transitions (i.e., the Hartley and Chappuis bands) to the computed transitions. – Does AM1 provide an adequate description of the electronic absorption spectrum of ozone?

Ozone	$\lambda(\text{nm})$	$\tilde{\nu}(\text{cm}^{-1})$	$f^{\text{a)}}$	Excited configuration ^{b)}	Type ^{c)}
$S_0 \rightarrow S_1$	558	17928	0.0002	9 → 10	$\sigma\text{--}\pi^*$
$S_0 \rightarrow S_2$	436	22932	0.0000	7 → 10	$\sigma\text{--}\pi^*$
$S_0 \rightarrow S_3$	259	38578	0.1300	8 → 10 7 → 11	$\pi\text{--}\pi^*$ $\sigma\text{--}\sigma^*$

a) Oscillator strength (4 decimals!).

b) Leading electronic configuration in the excited state, e.g., 9 → 10.

c) $\pi\text{--}\pi^*$, $\sigma\text{--}\pi^*$, etc.

Summary:

	Observed			AM1-CIS		
	$\lambda(\text{nm})$	$\tilde{\nu}(\text{cm}^{-1})$	Intensity	$\lambda(\text{nm})$	$\tilde{\nu}(\text{cm}^{-1})$	f
<i>Chappuis</i>	~600	~17000	very weak	558	17900	0.0002
<i>Hartley</i>	255	39000	strong	259	38600	0.13

AM1 provides an excellent description of the main features of the UV-VIS absorption spectrum of ozone! Unfortunately, such excellent performance of AM1 cannot be expected in general.

NB: Remember to write *your name* on your report when you hand it in for approval!