SPECTROSCOPY EXAM 2015/16

Write your name and student number on every page containing answers. It is not allowed to use your notes, books, mobile phone, etc.

This exam consists out of 4 problems and 4 pages. The problems are subdivided in several questions respectively. Read the questions carefully before you answer them. Answer the question precisely and clearly indicate how you got to the answer. An explanation how you got to your answer counts as least as many points as the answer itself. The number of points is indicative and may be re-evaluated.

1) This question is concerns a d^8 metal.
   a. Considering the free atom, which energy term belongs to the ground state? *– 2 points*
   b. Considering the free atom, what is the energy term with the highest orbital angular momentum? *– 2 points*
   c. In addition to the answers you gave at 1a) and 1b), the other terms belonging to the d^8 configuration of a free metal atom are ^3P, ^1D and ^1S. In how many levels are these energy terms split? And the energy terms you found at 1a) and 1b)? What are the degeneracies of all these levels? *– 8 points*

   Now consider a d^8 metal which is coordinated to six ligands in an octahedral geometry.

   d. Give all the energy terms belonging to the d^8 configuration in an octahedral field. Also give the degeneracy for each term symbol *– 6 points*
   e. Which of the terms you found represents the ground state of a octahedral complex? *– 4 points*
   f. Which d-d transitions do you expect to be important in the UV-vis absorption spectrum of a d^8 cobalt complex? *– 4 points*

2) Consider the dioxygen molecule.
   a. Which term symbols belong to the configuration $\sigma^2\sigma^{*2}2\pi^4\sigma^2 2\pi^{*2}\sigma^{*0}$. *Remember that a (-) sign is only obtained for triplet Σ terms with partially filled π orbitals.* *– 8 points*
   b. In addition to the energy terms you found at 2a) the excited state terms $^3\Sigma_u^+$ and $^3\Sigma_u^-$ are important in the spectroscopy of O_2. Indicate which transitions you expect to observe in the absorption UV-vis spectrum of O_2 in the gas phase at ambient temperatures? *– 3 points*
   c. (One of) the excitation(s) to you found results in cleavage of the O-O bond, and leads to formation of two free oxygen atoms of which one atom is in a ^3P state and the other atom in a ^1D state. These are not the only energy terms that can exist for an oxygen atom with a p^4 configuration. Deduce all possible energy terms for an O atom with a p^4 configuration. *– 8 points*

3) Consider the D_{3h} point group and the molecule cyclopropane
   a. Draw all symmetry elements of the D_{3h} point group – *2 points*
   b. For a normal mode to be IR active it must have a change in dipole moment. Deduce to which irreducible representations of the incomplete character table of the D_{3h} point group a normal mode must belong in order for it to be IR active. – *6 points*
   c. To which irreducible representations do the C-H stretches of cyclopropane belong? Give and explain the degeneracies of the representations that you found. – *6 points*
   d. Indicate how the atoms of the cyclopropane molecule move during the IR active vibrations (only consider the C-H stretches). – *6 points*

4) Consider the molecule 1,4-dichlorobenzene which has a D_{2h} point group.
   a. How many normal modes does 1,4-dichlorobenzene have? – *2 points*
   b. Indicate to which irreducible representations the C-H stretches belong – *4 points*
   c. Indicate to which irreducible representations the C-Cl stretches belong – *4 points*
   d. Indicate to which irreducible representations the C-C stretches belong – *4 points*
   e. Indicate to which irreducible representations all bending modes of the molecule belong – *6 points*
   f. Given IR frequency diagram below (page 4) and your answers above; How many signals do you expect to observe in the IR spectrum? Indicate to the best of your ability at which approximate wavelengths you expect to find these signals. – *5 points*

Appendices:

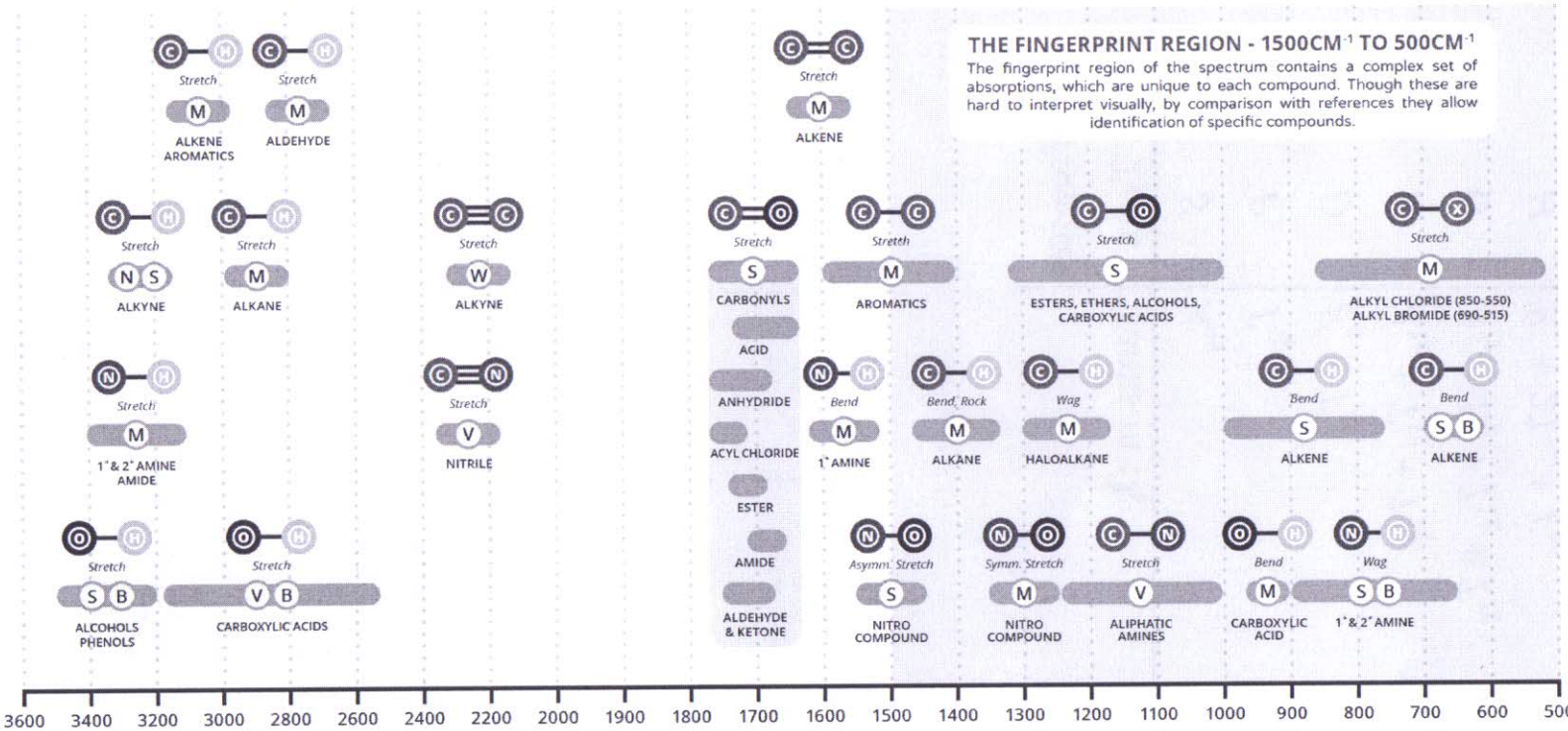
D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
A_1'	1	1	1	1	1	1		x^2+y^2, z^2
A_2'	1	1	−1	1	1	−1		
E'	2	−1	0	2	−1	0		(x^2-y^2, xy)
A_1''	1	1	1	−1	−1	−1		
A_2''	1	1	−1	−1	−1	1		
E''	2	−1	0	−2	1	0		(xz, yz)

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$		
A_g	1	1	1	1	1	1	1	1		x^2, y^2, z^2
B_{1g}	1	1	−1	−1	1	1	−1	−1	R_z	xy
B_{2g}	1	−1	1	−1	1	−1	1	−1	R_y	xz
B_{3g}	1	−1	−1	1	1	−1	−1	1	R_x	yz
A_u	1	1	1	1	−1	−1	−1	−1		
B_{1u}	1	1	−1	−1	−1	−1	1	1	z	
B_{2u}	1	−1	1	−1	−1	1	−1	1	y	
B_{3u}	1	−1	−1	1	−1	1	1	−1	x	

Free-ion Term	Terms in O_h
S	A_{1g}
P	T_{1g}
D	$E_g + T_{2g}$
F	$A_{2g} + T_{1g} + T_{2g}$
G	$A_{1g} + E_g + T_{1g} + T_{2g}$
H	$E_g + 2T_{1g} + T_{2g}$
I	$A_{1g} + A_{2g} + E_g + T_{1g} + 2T_{2g}$

ANALYTICAL CHEMISTRY - INFRARED SPECTROSCOPY

Commonly referred to as IR spectroscopy, this technique allows chemists to identify characteristic groups of atoms (functional groups) present in molecules.



Infrared frequencies make up a portion of the electromagnetic spectrum. If a range of infrared frequencies are shone through an organic compound, some of the frequencies are absorbed by the chemical bonds within the compound. Different chemical bonds absorb different frequencies of infrared radiation. There are a number of characteristic absorptions which allow functional groups (the parts of a compound which give it its particular reactivity) to be identified. This graphic shows a number of these absorptions.