Spectroscopy Exam (ii) 2015

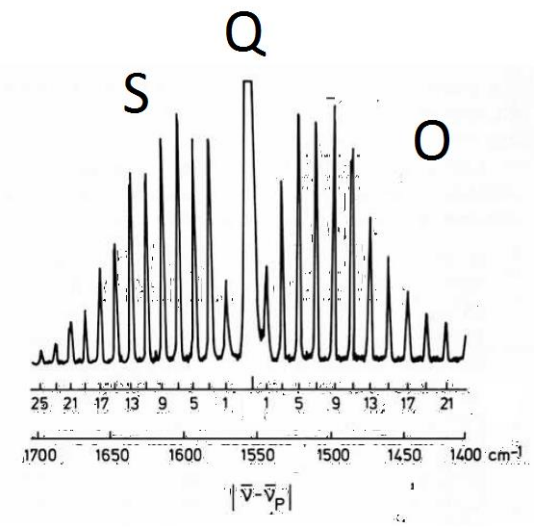
Write your name and student number on every page containing answers. It is not allowed to use your notes, books, laptop, mobile phone, etc.

This exam consists out of 4 problems and 3 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.

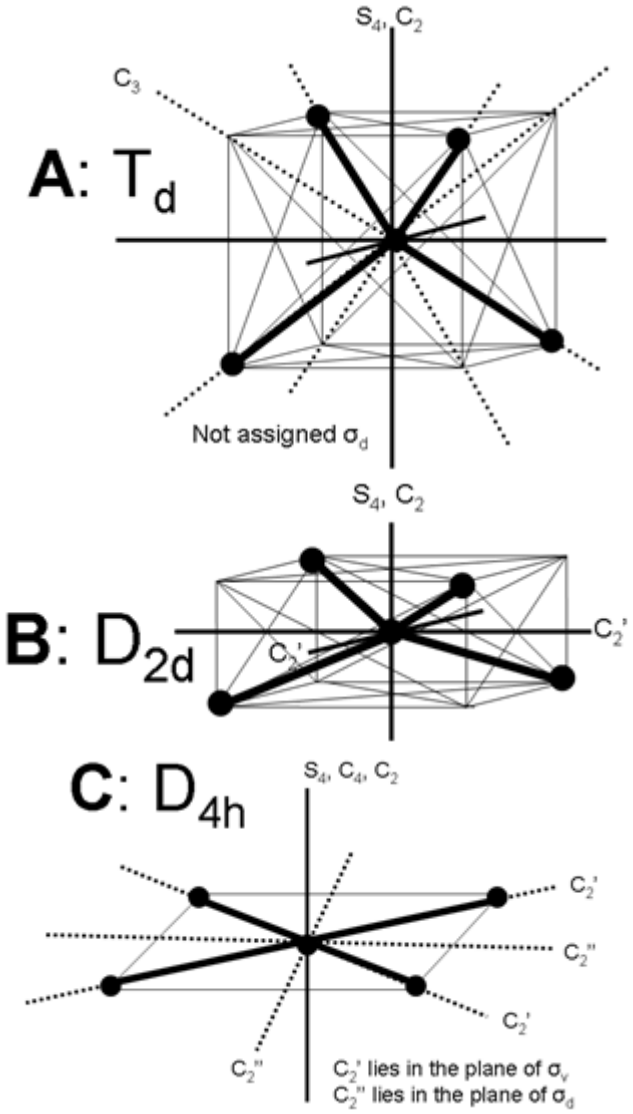
1. This question concerns a free carbon atom
    a. Deduce the term symbols belonging to the $[He]2s^2 2p^2$ configuration and indicate which of these terms is the ground state. ***–8 points***
    b. Use a Clebsch-Gordon series to find the term symbols belonging to the configurations $[He]2s^2 2p^1 3s^1$, $[He]2s^2 2p^1 3p^2$ and $[He]2s^2 2p^1 3d^1$. ***–7 points***
    c. Produce a Grotrian diagram where all terms you found in question 1a) and 1b) are categorized by multiplicity and angular momentum on the x-axis and their energy is depicted on the y-axis. Indicate for every entry in you diagram from which configuration it originated. ***–7 points***
    d. Indicate in your diagram which transitions are important in the emission spectroscopy of carbon at extremely high temperatures. ***–7 points***

2. Deduce the Term symbols belonging to the molecules and configurations below. Indicate for each entry which of the term symbols is the ground state. *Remember that a (-) sign is only obtained for triple Σ terms and in case the π orbitals are only half filled.*
    a. N_2 with a $(\sigma_{2s})^2$, $(\sigma^*_{2s})^2$, $(\pi_{2p})^4$, $(\sigma_{2p})^2$, $(\pi^*_{2p})^0$, $(\sigma^*_{2p})^0$ configuration ***– 4 points***
    b. NO with a $(\sigma_{2s})^2$, $(\sigma^*_{2s})^2$, $(\pi_{2p})^4$, $(\sigma_{2p})^2$, $(\pi^*_{2p})^1$, $(\sigma^*_{2p})^0$ configuration ***– 4 points***
    c. O_2 with a $(\sigma_{2s})^2$, $(\sigma^*_{2s})^2$, $(\sigma_{2p})^2$, $(\pi_{2p})^4$, $(\pi^*_{2p})^2$, $(\sigma^*_{2p})^0$ configuration ***– 8 points***

3. At the right is given the Stokes part of the gas phase Raman spectrum of O_2.
    a. Indicate how the quantum numbers n and J change in the S, Q and O branch. ***–5 points***
    b. Why do the S and O branch contain many lines while the Q branch only gives a single line? Use an energy diagram to explain your answer ***– 10 points***



4. The molecule MX_4 can have different geometries (**A**, **B** and **C**) that have either a T_d, a D_{2d} or a D_{4h} point group. In the figure below are given the structure of **A**, **B** and **C** and some of the symmetry elements of their point groups.



   a. Deduce to which irreducible representations of the (incomplete) character tables of the T_d, the D_{2d} and the D_{4h} point groups a normal mode vibration must belong in order for it to be IR active. *– 9 points*
   b. Determine to which irreducible representations the M-X stretching modes belong. Do this for structure **A**, **B** and **C**. *– 8 points*
   c. Indicate how the X atoms move in the M-X stretching modes of the molecules **A**, **B** and **C** that you found in question 4b). *– 8 points*
   d. Indicate which of the M-X stretches of **A**, **B** and **C** can be detected by IR spectroscopy and which ones can be detected by Raman spectroscopy. Discuss how one can distinguish the structures **A**, **B** and **C** on basis of vibrational spectroscopy. *– 5 points*

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
A_1	1	1	1	1	1		$x^2+y^2+z^2$
A_2	1	1	1	−1	−1		
E	2	−1	2	0	0		$(2z^2-x^2-y^2,\ \sqrt{3}\ (x^2-y^2)$
T_1	3	0	−1	1	−1	(R_x, R_y, R_z)	
T_2	3	0	−1	−1	1		(xy, xz, yz)

D_{2d}	E	$2S_4$	C_2	$2C_2'$	$2\sigma_d$		
A_1	1	1	1	1	1		x^2+y^2, z^2
A_2	1	1	1	−1	−1	R_z	
B_1	1	−1	1	1	−1		x^2-y^2
B_2	1	−1	1	−1	1		xy
E	2	0	−2	0	0	(R_x, R_y)	(xz, yz)

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		x^2+y^2, z^2
A_{2g}	1	1	1	−1	−1	1	1	1	−1	−1	R_z	
B_{1g}	1	−1	1	1	−1	1	−1	1	1	−1		x^2-y^2
B_{2g}	1	−1	1	−1	1	1	−1	1	−1	1		xy
E_g	2	0	−2	0	0	2	0	−2	0	0	(R_x, R_y)	(xz, yz)
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1		
A_{2u}	1	1	1	−1	−1	−1	−1	−1	1	1		
B_{1u}	1	−1	1	1	−1	−1	1	−1	−1	1		
B_{2u}	1	−1	1	−1	1	−1	1	−1	1	−1		
E_u	2	0	−2	0	0	−2	0	2	0	0		