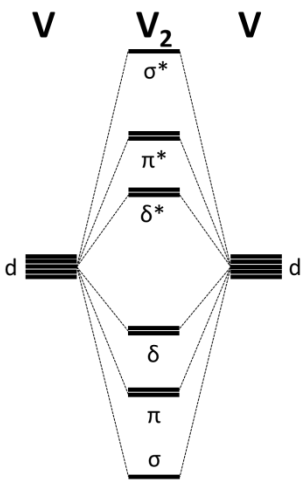
SPECTROSCOPY (ii) 2014-2015

This exam consists out of 4 problems and 4 pages. The problems are subdivided in several questions respectively. Write your name and student number on every page containing answers.

It is not allowed to use your notes, books, mobile phone, etc. Read the questions carefully before you answer them. Answer the question precisely and clearly indicate how you got to the answer. When a justification is asked, it counts as least as many points as the answer itself. The number of points is indicative and may be re-evaluated.

1. Determine how many C-Cl stretches the following molecules show in their IR spectra:
   a. CH_3Cl (C_{3v}) – *5 points*
   b. CH_2Cl_2 (C_{2v}) – *5 points*
   c. $CHCl_3$ (C_{3v}) – *5 points*
   d. CCl_4 (T_d) – *5 points*

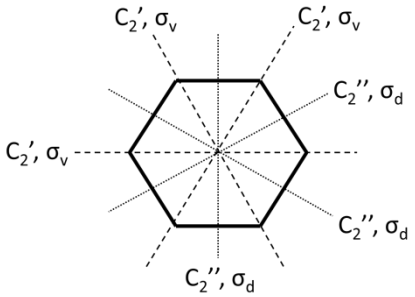
2. Consider the diatomic molecule bisvanadium (V_2) for which the axis along the V-V bond is assigned as the z-axis. To describe the spectroscopy of this molecule we only need to consider the molecular orbitals that are derived from the d-orbitals. A σ bond is formed by overlap between the d_{z^2} orbitals of both vanadium atoms. One π-orbital is formed due to overlap between the d_{xz} orbitals of both vanadium atoms and another π-orbital by overlap between the d_{xy} orbitals of both vanadium atoms. Two δ-orbitals are formed by overlap of the $d_{x^2-y^2}$ and the d_{xz} orbitals respectively.



   a. Determine whether the molecular σ, π, δ, δ*,π* and σ* orbitals are *gerade* (g) or *ungerade* (u) with respect to the center of the vanadium – vanadium bond. – *10 points*
   b. Which term symbols belong to the configuration $\sigma^2\pi^4\delta^2$? In this exercise you may ignore the (+) or (-) signs. *Hint: the order of symbols is Σ, Π, Δ, Φ, Γ.* – *10 points*
   c. Which of these terms is the ground state? – *5 points*
   d. The excited state configuration $\sigma^2\pi^3\delta^3$ gives rise to $^3\Pi_u$, $^1\Pi_u$, $^3\Phi_u$ and $^1\Phi_u$ terms. Consider transitions from the ground state (which you found at c) and the excited states, including the ones you found in exercise b). Which transitions are allowed and which ones are forbidden? Explain your answer. – *5 points*
   e. The UV-vis spectrum of V_2 contains much more lines than the number of transitions you found under e). Explain what causes these additional lines and discuss how the Franck-Condon effect is involved. – *5 points*

3. Chromium(IV) has a d^2 configuration.
    a. Which term belongs to the ground state of a d^2 atom? *– 5 points*
    b. What is the term with the highest possible orbital angular momentum? *– 5 points*
    c. The other terms belonging to a d^2 configuration are ^3P, ^1S and ^1D. Determine in how many levels al five terms are split and give their degeneracies. *– 5 points*
    d. Now consider an octahedral molecule with a chromium(IV) atom in the middle and six equivalent ligands coordinated to the chromium atom. What are the terms that belong to a d^2 configuration for this molecule? *– 5 points*
    e. What are the degeneracies of these new terms? *– 5 points*
    f. How many lines do you expect to find in the UV spectrum of a chromium(IV) complex with O_h symmetry? Explain your answer. *– 5 points*

4. Consider the benzene molecule with a D_{6h} point group. Use the character table in the appendix and the Figure below to solve the problems 4a-f.



    a. How many normal modes does benzene have? *– 5 points*
    b. To which irreducible representations do these normal modes belong? *– 5 points*
    c. Which of these irreducible representations belong to C-H stretches? *– 5 points*
    d. Which of these irreducible representations belong to C-C stretches? *Hint: in this case it is better to use arrows with arrowheads on both sides*. *– 5 points*
    e. Which of these irreducible representations belong to bending modes? *– 5 points*
    f. Aromatic C-H bonds are typically found around 3300 cm^{-1} and C-C bonds around 1500 cm^{-1}. Bending modes are found below 1200 cm^{-1}. Sketch the Stokes part of the Raman spectra that you expect to find for benzene on basis of your answers at c), d) and e), while ignoring any rotational contribution to your spectrum. Assign the peaks in your sketch both in terms of type of normal mode and the irreducible representation. Explain your answer and make sure that your drawing is readable. *– 15 points*

Character table for D_{6h} point group

	E	$2C_6$	$2C_3$	C_2	$3C'_2$	$3C''_2$	i	$2S_3$	$2S_6$	σ_h	$3\sigma_d$	$3\sigma_v$	Linear, rotations	Quadratic
A_{1g}	1	1	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	-1	-1	R_z	
B_{1g}	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1		
B_{2g}	1	-1	1	-1	-1	1	1	-1	1	-1	-1	1		
E_{1g}	2	1	-1	-2	0	0	2	1	-1	-2	0	0	(R_x, R_y)	(xz, yz)
E_{2g}	2	-1	-1	2	0	0	2	-1	-1	2	0	0		(x^2-y^2, xy)
A_{1u}	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1		
A_{2u}	1	1	1	1	-1	-1	-1	-1	-1	-1	1	1	z	
B_{1u}	1	-1	1	-1	1	-1	-1	1	-1	1	-1	1		
B_{2u}	1	-1	1	-1	-1	1	-1	1	-1	1	1	-1		
E_{1u}	2	1	-1	-2	0	0	-2	-1	1	2	0	0	(x, y)	
E_{2u}	2	-1	-1	2	0	0	-2	1	1	-2	0	0		

Character table for C_{2v} point group

	E	C_2 (z)	σ_v(xz)	σ_v(yz)	linear, rotations	quadratic
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

Character table for C_{3v} point group

	E	$2C_3$ (z)	$3\sigma_v$	linear, rotations	quadratic
A_1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	-1	R_z	
E	2	-1	0	(x, y) (R_x, R_y)	(x^2-y^2, xy) (xz, yz)

Character table for T_d point group

	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	linear, rotations	quadratic
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		$(2z^2-x^2-y^2, x^2-y^2)$
T_1	3	0	-1	1	-1	(R_x, R_y, R_z)	
T_2	3	0	-1	-1	1	(x, y, z)	(xy, xz, yz)

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	$A_{1g} + A_{2g} + E_g + T_{1g} + 2T_{2g}$