

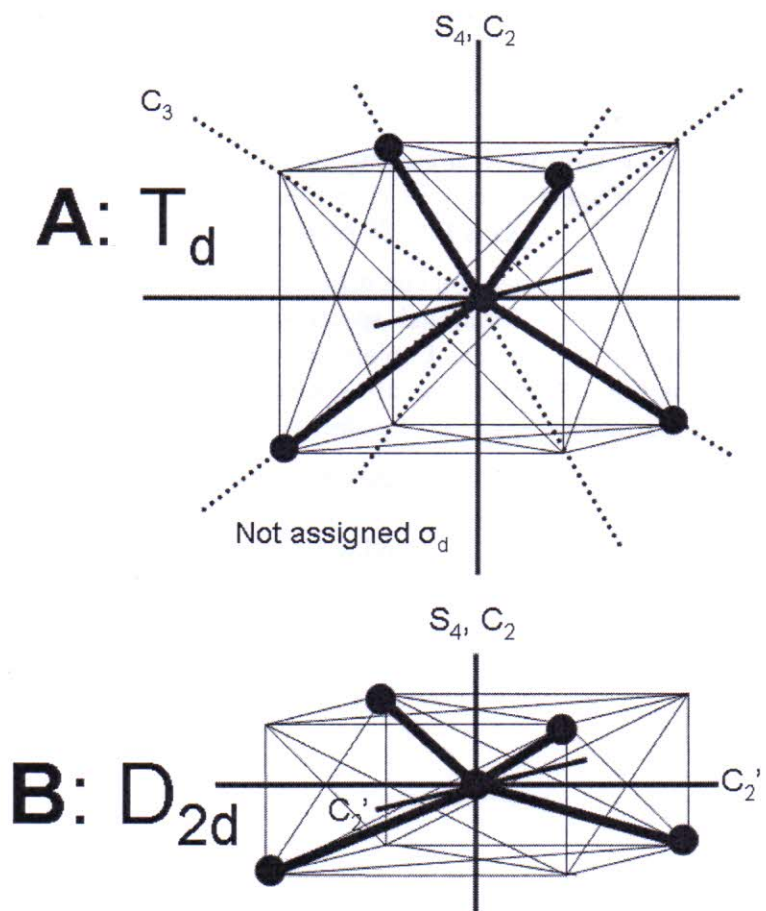
SPECTROSCOPY 2014-2015

This exam consists out of 2 problems and 4 pages. The problems are subdivided in 8 and 7 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. (MOSTLY) VIBRATIONAL SPECTROSCOPY

Consider the unknown molecule MX_4 . Koen claims that the structure of MX_4 is the tetrahedral complex **A**, which has T_d symmetry. Konstantin claims that the structure of MX_4 could also be the distorted tetrahedral complex **B**, which has D_{2d} symmetry.



The structures **A** and **B** including (some of the) symmetry operators belonging to the point groups T_d and D_{2d} . You are advised to make your own picture including all symmetry operators.

- a. How many vibrational modes do **A** and **B** have? - 5 points -
- b. To which irreducible representations of the T_d and D_{2d} point groups do the vibrational modes of **A** and **B** belong? Use the character tables in the appendix. - 30 points -
- c. Is it possible to distinguish **A** and **B** from each other by vibrational spectroscopy? Motivate your answer. - 5 points

The bending modes of a molecule typically end up in a very crowded area of the infrared spectrum, which is called the finger-print area. In this section of the spectrum it is difficult to account for all signals, especially if some of the signals are very weak and therefore difficult to observe by vibrational spectroscopy. One can restrict oneself to one particular type of stretching mode that is clearly visible in the IR and Raman spectra to assign the structure of a given complex. You will do this for MX_4 . First, it is important to prove that signals which are in the correct frequency range for an M-X stretch, indeed do belong to such M-X stretches and are not due to e.g. overtones of other signals.

- d. What are overtones? - 5 points -
- e. How can you experimentally verify that a signal in the IR or Raman spectrum indeed belongs to an M-X stretch? - 5 points -
- f. How many M-X stretching frequencies would you observe by IR and Raman spectroscopy in case the structure of MX_4 is **A**? And when the structure of MX_4 is **B**? - 20 points -
- g. Discuss whether you can differentiate between the T_d and D_{2d} symmetries on basis of vibrational spectroscopy while considering only the M-X stretch frequencies. Explain how one can do this, or why this is not possible. Assume that all allowed transitions indeed are visible in the experimental spectra. - 5 points -
- h. All X-atoms are chemically equivalent in both **A** and **B**. How many X-atoms are magnetically equivalent in each structure? Assume that the nuclear spin of X is $\frac{1}{2}$ and the nuclear spin of M is 0. Would you be able to discriminate between **A** and **B** on basis of NMR spectroscopy? - 5 points -

2. ELECTRONIC SPECTROSCOPY

Consider a free silicon atom at room temperature.

- a. Silicon has a $[\text{Ne}]3s^23p^2$ configuration. How many possibilities are there to fill three p-orbitals with 2 electrons? - 5 points -
- b. Derive which terms (^{2S+1}L) belong to the $[\text{Ne}]3s^23p^2$ configuration. - 15 points -
- c. Which terms (^{2S+1}L) belong to the excited state configurations $[\text{Ne}]3s^23p^14s^1$, $[\text{Ne}]3s^23p^13d^1$ and $[\text{Ne}]3s^23p^14p^1$? *Hint: Use the Clebsch-Gordon series to find your answer.* - 20 points -
- d. Construct a Grotrian diagram which contains all terms from question 2b) and 2c). Organize the diagram by multiplicity and by orbital angular momentum on the x-axis and by relative energy on the y-axis. *Use enough space to produce a readable drawing.* - 10 points -
- e. Indicate in the Grotrian diagram that you have just drawn, which transitions play a role in the atomic absorption spectroscopy of silicon at room temperature. - 5 points -
- f. Given a transition from a 3P term to 3D term. Into how many levels are the 3P and 3D terms split? What are the degeneracies of these levels? How many lines can be observed in the absorption spectrum for the transition of a 3P term to a 3D term? - 10 points -
- g. Explain why selection rules are rigorously obeyed in atomic spectroscopy and not in case of large molecules. - 5 points -

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)

Character table for D_{2d} point group

	E	$2S_4$	$C_2(z)$	$2C'_2$	$2\sigma_d$	linear, rotations	quadratic
A_1	1	1	1	1	1		x^2+y^2, z^2
A_2	1	1	1	-1	-1	R_z	
B_1	1	-1	1	1	-1		x^2-y^2
B_2	1	-1	1	-1	1	z	xy
E	2	0	-2	0	0	$(x, y) (R_x, R_y)$	(xz, yz)