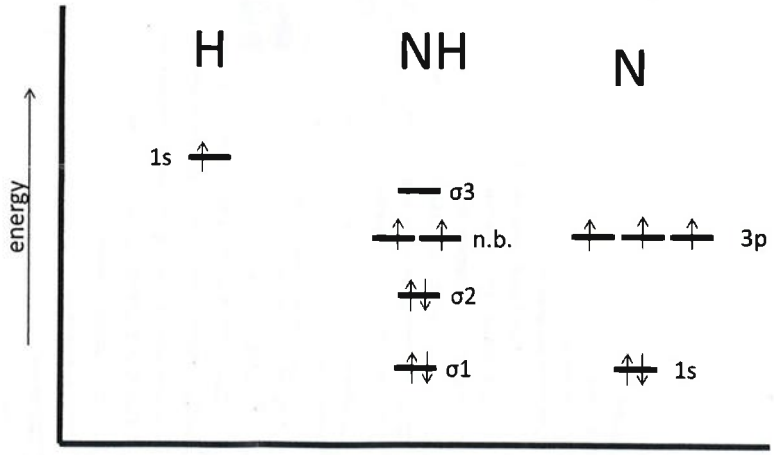
EXAM

(Spectroscopy, November 2nd 2017, 14:00 – 17:00)

This exam consists out of 5 problems and 4 pages. ***Write your name and student number on every page containing answers.*** *It is not allowed to use your notes, books, mobile phone, etc. The use of a molecular model kit is allowed. 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 at least as many points as the answer itself. The number of points (total = 90) is indicative and may be re-evaluated.*

1) Shown below is the MO diagram of the diatomic molecule NH. Note that only one possible arrangement of the electrons is given.



a. How many different possibilities are there to put two electrons in both non-bonding (n.b.) orbitals of NH? – 2 points

b. Give all term symbols belonging to the answer you gave in question a). – 10 points

Note 1: you should treat the n.b. orbitals in the same way as π orbitals

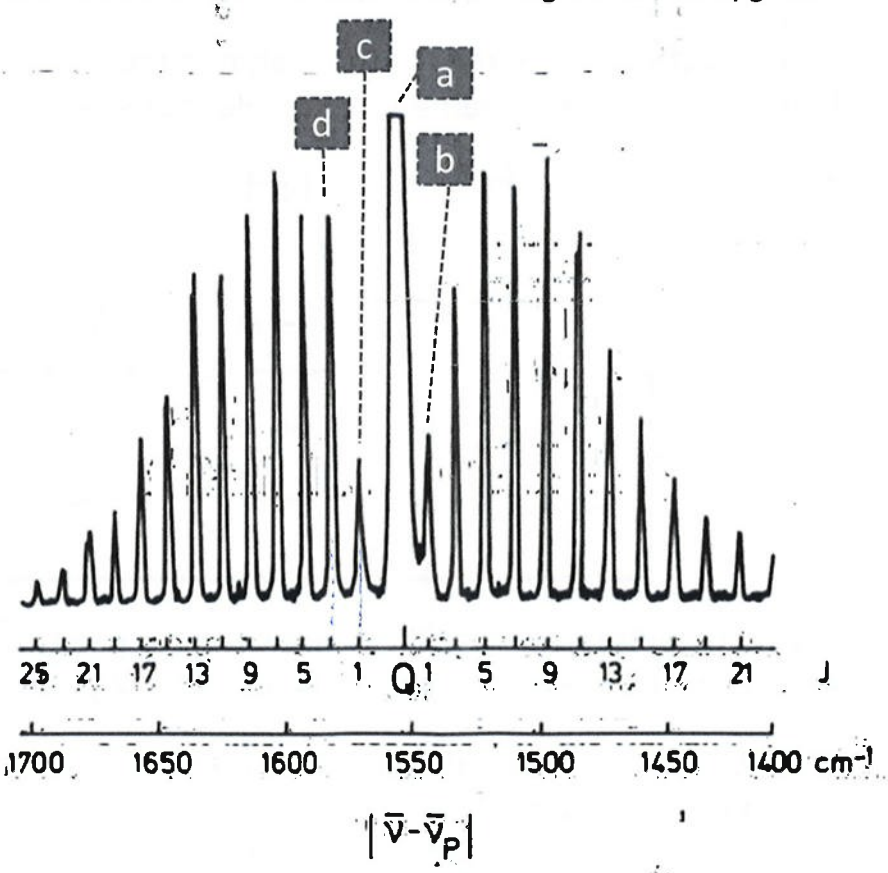
Note 2: For partially filled MOs of π symmetry, if Σ terms arise, the triplet state is associated with -, and the singlet state with +

2) In the Grotrian Diagram of nitrogen you can find a transition from the ^3P ground state to a ^3D excited state.

   a. In how many levels are the ^3P and ^3D terms split? Give the degeneracy of each term and give the degeneracy of all their levels. – 5 points

   b. How many lines do you expect to observe for the $^3P \rightarrow {}^3D$ absorption in the absence and in the presence of a strong magnetic field? Explain your answer. – 10 points

3) Shown below is the Stokes Raman signal of dioxygen.



   a. Assign peaks a, b, c and d. Make an energy diagram wherein you highlight the transitions a, b, c and d, and indicate the quantum numbers of the system before and after the Raman scattering event. – 12 points

   b. Describe what the anti-Stokes part of the spectrum would look like. –6 points

4) Show how the C-Cl stretching modes move for the following molecules. Give your answers in the form of normalized linear combinations and proof that these modes are orthogonal.

   a. 1,2,4,5-tetrachlorobenzene (D_{2h}) – 10 points

   b. $CHCl_3$ (C_{3v}) – 10 points

5) Consider the molecule PCl_5 with D_{3h} symmetry.

   a. How many normal modes does PCl_5 have? – 2 points

   b. Give the irreducible representations of all normal modes. Show how you got to your answer. – 17 points

   c. How many peaks do you expect to find in the IR spectrum? And in the Raman spectrum? – 6 points

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 D_{2h} point group

	E	C_2 (z)	C_2 (y)	C_2 (x)	i	σ (xy)	σ (xz)	σ (yz)	linear, rotations	quadratic
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	

Character table for D_{3h} point group

	E	$2C_3$	$3C'_2$	σ_h	$2S_3$	$3\sigma_v$	linear, rotations	quadratic
A'_1	1	1	1	1	1	1		x^2+y^2, z^2
A'_2	1	1	-1	1	1	-1	R_z	
E'	2	-1	0	2	-1	0	(x, y)	(x^2-y^2, xy)
A''_1	1	1	1	-1	-1	-1		
A''_2	1	1	-1	-1	-1	1	z	
E''	2	-1	0	-2	1	0	(R_x, R_y)	(xz, yz)