# Spectroscopy exam

Friday November 2nd 2018

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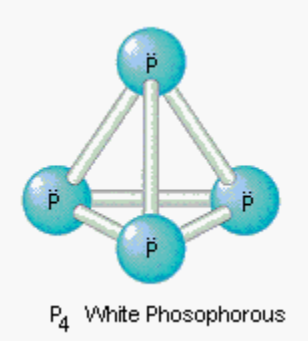
Write your name and student number on every page containing answers. It is not allowed to use your notes, books, mobile phone, etc.

This exam consists out of 3 problems and 3 pages. 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.

1. Consider the molecule $O_2$.
    a. What term symbols belong to the ground state configuration of $O_2$ wherein there are two electrons positioned in the π* orbitals. ***5 points***
    b. $A^3\Sigma_u^+$ and $B^3\Sigma_u^-$ are two exited states of the $O_2$ molecule. Take into account the terms $A^3\Sigma_u^+$ and $B^3\Sigma_u^-$ and the term symbols that you found at 1a). Which absorptions do you expect to observe at room temperature? ***5 points***
    c. The dioxygen molecule in the $A^3\Sigma_u^+$ state easily falls apart into two oxygen atoms with a $^3P$ term. What other terms can you find for an oxygen atom with a $p^4$ configuration? ***10 points***
    d. One of the transitions that is important for the atomic spectroscopy of oxygen is the absorption from $^3P$ to an exited state $^3S$. This absorption is split into several lines. How many are these? And how many lines do you expect to find for the transition from $^3P$ to $^3S$ terms when the experiment is carried out in a strong magnetic field? ***15 points***
    e. Which of the term symbols that you found at 1a) do you expect to be affected by a magnetic field? Explain your answer. ***5 points***

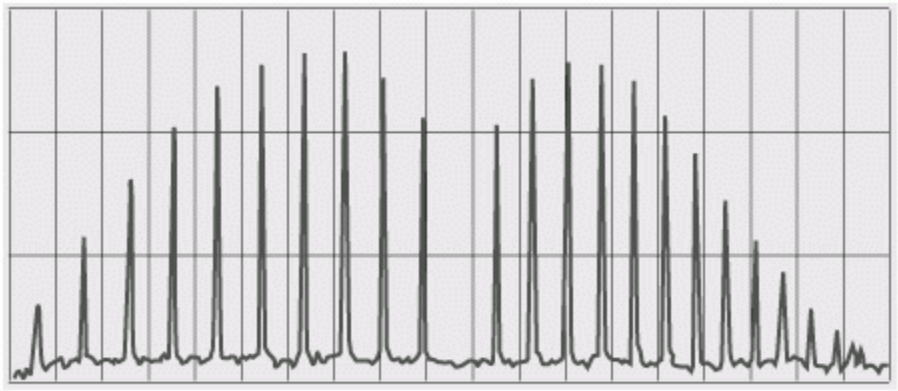
2. Consider the molecule $PCl_5$ with $D_{3h}$ symmetry. Give the normalized linear equations belonging to the P-Cl stretches. Show that the equations you found are orthogonal. ***20 points***

3. Consider the white phosphorus molecule $P_4$ with $T_d$ symmetry. *Note that the character table is not complete.*



$P_4$ White Phosophorous

a. Give all irreproducible representations belonging to the P-P stretches. ***8 points***
b. Give all irreproducible representations belonging to the $P_4$ bending modes. ***10 points***
c. How many signals do you expect to find in the IR spectrum of a solution of $P_4$? ***5 points***
d. When IR spectroscopy is measured in the gas phase, the spectra typically form much more complex patterns. Relatively broad signals, such as the ones you found at 3c) in solution, in the gas phase split into the very sharp line patterns shown below. Explain all features in the Figure below using an energy diagram. Show which type of absorptions are relevant. And which ones are not. ***7 points***



| $D_{3h}$ | $E$ | $2C_3$ | $3C_2$ | $\sigma_h$ | $2S_3$ | $3\sigma_v$ | | |
|---|---|---|---|---|---|---|---|---|
| $A_1'$ | 1 | 1 | 1 | 1 | 1 | 1 | | $x^2 + y^2, z^2$ |
| $A_2'$ | 1 | 1 | −1 | 1 | 1 | −1 | $R_z$ | |
| $E'$ | 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 | $(R_x, R_y)$ | $(xz, yz)$ |

**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 | | |
| $T_2$ | 3 | 0 | -1 | -1 | 1 | | (xy, xz, yz) |