ENGLISH

NORGES TEKNISK-NATURVITENSKAPELIGE UNIVERSITET
INSTITUTT FOR KJEMI
KJ1041 KJEMISK BINDING, SPEKTROSKOPI OG KINETIKK

HØSTEN 2011

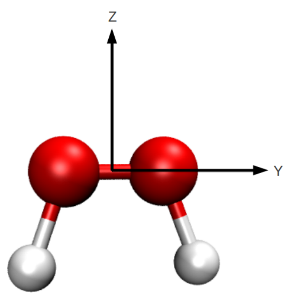
Onsdag 14. Desember 2011 Tid: 09.00 – 13.00
Faglig kontakt under eksamen: Professor Henrik Koch, tlf. 92838083

Hjelpemidler: Alle trykte og håndskrevne hjelpemidler er tillatt. Alle kalkulatorer er tillatt, med de vanlige begrensninger, som gjelder for hjelpemiddelkode A.

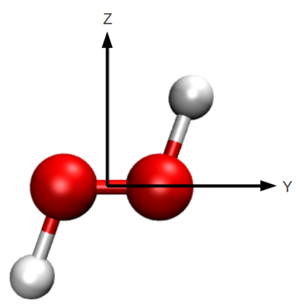
Alle de 12 underspørsmålene har lik vekt.

Exercise 1.

Consider the two planar conformations of the hydrogen peroxide (H_2O_2) molecule labeled (i) and (ii)



(i)

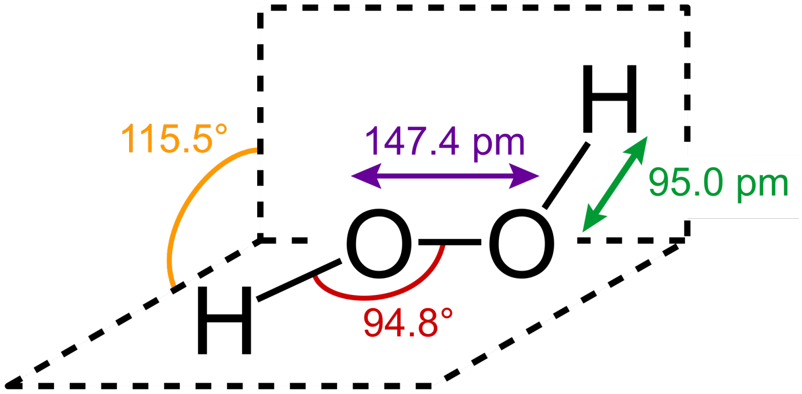


(ii)

A. Determine the point group symmetry of the conformations (i) and (ii) and show the symmetry operations on a figure.

B. Conformation (ii) can be obtained from (i) by rotating one OH group 180 degrees around the y-axis (keeping the angle between the OH bond and the y-axis constant). Find the point group that is conserved during this rotation.

Experimentally the equilibrium geometry of hydrogen is found to be non-planar as shown in (iii)



(iii)

where the dihedral angel of 115.5 degrees is the angle between the two planes defined by the HOO atoms and the OOH atoms. Determine the point group symmetry of conformation (iii).

C. For each of the conformations (i) - (iii) determine the components of the dipole moment that are zero and those that are expected to be different from zero (use group theoretical arguments).

D. The optical activity of a molecule is determined by the matrix elements

$$R^{i}_{on} = <\psi_0 | \mu_i | \psi_n >< \psi_n | m_i | \psi_0 > \quad , \quad i = x, y, z$$

where ψ_0 is the ground state wave function (assumed totally symmetric) and ψ_n is an excited state (can have any irreducible symmetry). The dipole operator $\vec{\mu}$ has the same symmetry as (x,y,z) coordinates and the magnetic dipole operator $\vec{m}$ has the same symmetry as the rotations (R_x, R_y, R_z).

Determine those R^{i}_{on} (i = x,y,z) that can be different from zero when the point group is C_2 ,C_{2v} and C_{2h}(use group theoretical argument).

E. From the result of D we would expect H_2O_2 to be optically active. However, a solution of H_2O_2 in water does not show this property. This can be explained by H_2O_2 having two energetically equivalent equilibrium structures that rotate the light equally in opposite directions. Describe these two equivalent equilibrium structures.

Exercise 2.

We consider the hydrogen peroxide molecule in conformation (i) from the previous exercise. The electronic structure is described by one 1s atomic orbital on each of the hydrogen atoms and 1s, 2s and 2p atomic orbitals on each of the oxygen atoms. Use the point group C_{2v}, with the same coordinate system as in (i).

A. Divide the atomic orbitals into equivalent sets and determine the symmetry of each of these sets.

The results of a Hartree-Fock calculation (for the (i) configuration) using the DALTON program are given at the end of exercise 4.

B. Determine the electron configuration for the ground state and the first two excited states. Specify the term symbol for all the states.

C. Estimate the ionization energy of H_2O_2 in the (i) conformation and determine the term symbol of the ionized state.

Exercise 3.

A. In the Born-Oppenheimer approximation we approximate the total wave function as a product:

$$\psi(\vec{r},\vec{R}) = \psi^{e}(\vec{r};\vec{R})\chi(\vec{R})$$

Explain (briefly) the reasoning behind this form and the equations used to determine the two functions in the product.

B. We consider the hydrogen peroxide molecule in the (ii) conformation, and use the same coordinate system as in Exercise 1. Determine the symmetries of the vibrational modes.

C. How many of the vibrational modes are active (use group theoretical argument).

Exercise 4.

We consider the Rield-Pfleiderer process for the production of hydrogen peroxide. The overall reaction equation is:

$$H_2 + O_2 \rightarrow H_2O_2$$

We assume this is a second order process.

A. Find an expression for the concentration of hydrogen, when the initial concentration of hydrogen and oxygen are equal and is given by C_0 and the reaction constant is k.

Determine an expression for the halftime of hydrogen.