**ENGLISH**

**NORGES TEKNISK-NATURVITENSKAPELIGE UNIVERSITET**
**INSTITUTT FOR KJEMI**
**KJ1041 KJEMISK BINDING, SPEKTROSKOPI OG KINETIKK**
**HØSTEN 2010**

Onsdag 8. Desember 2010 Tid: 15.00 – 19.00
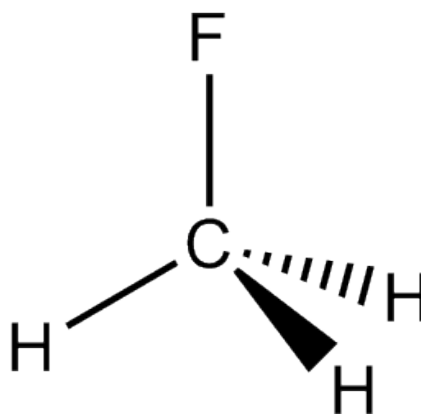Faglig kontakt under eksamen: Professor Henrik Koch, tlf. 92838083

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**

a)      Determine the molecular point groups for the 3 molecules (i) - (iii)



(i)



(ii)
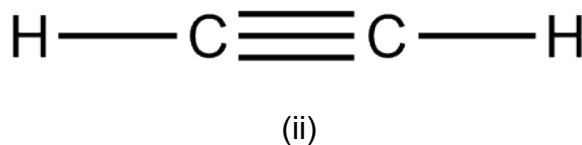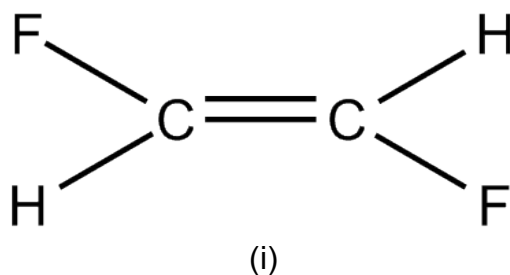
(iii)

b)      The dipole operator $\vec{\mu} = (\mu_x, \mu_y, \mu_z)$ have the same symmetry as the x,y og z coordinates. The expectation value

$$< \vec{\mu} > = < \psi \,|\, \vec{\mu}\psi > = \int \psi(\tau)^* \vec{\mu}\psi(\tau)\, d\tau$$

for a normalized wave function is equal to the molecules dipole moment.

We assume the wave function is totally symmetric in the molecular point group.

State if the molecules (i) – (iii) has a dipole moment. Use group theoretical arguments.

Will these conclusions change if the wave function is not totally symmetric ?

c)      An operator is given by the expression

$$D_x = \frac{1}{2}(xp_x + p_x x).$$

Show that the operator can be written as $D_x = xp_x - i\dfrac{\hbar}{2}$.

Is the wave function $\psi(x) = \exp(ikx)$ an eigenfunction for $D_x$ ?

Use the definition of a Hermitian operator (that is $< \psi \,|\, H\varphi > = < H\psi \,|\, \varphi >$) and show that $D_x$ is Hermitian.

d)      The electrons internal spin is described as an angular momentum with value S = ½. Determine by coupling of angular momentum the possible values of the total spin for 2 and 3 electrons. Specify for each value the number of spin functions.

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**Exercise 2**

In this exercise we consider the molecule
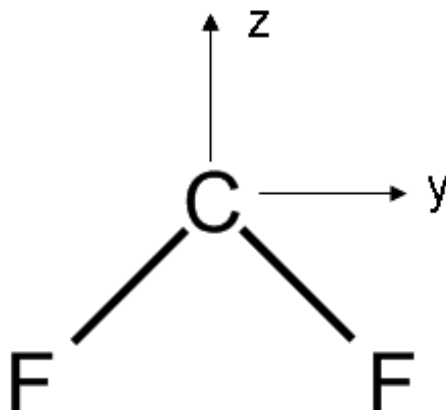


and the molecules point group is $C_{2v}$. We disregard the 1s orbitals and use the 2s and 2p atomic orbitals on carbon and fluorine atoms.

a)      Divide the atomic orbitals into equivalent sets and determine the symmetry of these sets in the molecular point group.

A Hartree-Fock calculation of the molecular orbitals gives the HOMO and LUMO orbital energies

$$\varepsilon_{HOMO} = -0.356 \quad Hartree$$
$$\varepsilon_{LUMO} = -0.164 \quad Hartree$$

and the symmetry of these orbitals are $b_1$ and $b_2$, respectively.

b)      Specify the symmetry and spin of the ground state and the first two excited states. Is the dipole transition between the ground state and the excited states allowed ?

c)      Estimate the lowest ionization energy of the $CF_2$ molecule in electronvolts and specify the symmetry and spin of the ionized state.

## Exercise 3

In this exercise we consider the two molecules $H_2$ og HD, where D is deuterium. We use the Born-Oppenheimer approximation.

a)      Draw a figure of the electronic ground state potential curve for the $H_2$ molecule. Specify on the figure the electronic equilibrium distance, $R_e$, the lowest vibrational state and the dissociation energy $D_0$ when $H_2$ is in the lowest possible state.

b)      What should hold for $R_e(H_2)$ and $R_e(HD)$ within the Born-Oppenheimer approximation ?

Experimentally one has determine $R_e(H_2) = 0.74166$ Å and $R_e(HD) = 0.74136$ Å, how can we explain this difference ?

c)      We now use the harmonic oscillator to describe the vibrations in the two molecules.

What can we expect about the size of $\omega(H_2)$ compared to $\omega(HD)$?

What can we say about $D_0(H_2)$ compared to $D_0(HD)$ ?

(present arguments for the answers)

## Exercise 4

In this exercise we consider a photochemical reaction, where a molecule A is excited from the ground state, that is a singlet ($S_0$), to the excited state $A^*$, that is also a singlet ($S_1$). In the excited state the molecule undergoes an intersystem crossing and convert to an energetically close triplet state ($T_1$). The molecule then decays to the ground state and radiates a photon.
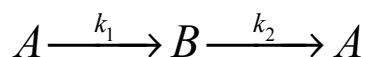
We have the following reaction :

$$A(S_0) + h\nu_1 \xrightarrow{k_1} \left[ A^*(S_1) \to A^*(T_1) \right] \xrightarrow{k_2} A(S_0) + h\nu_2$$
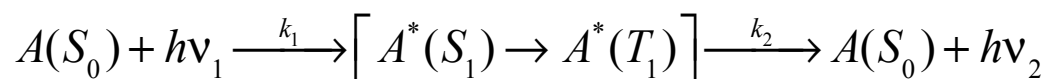
where $k_1$ og $k_2$ are rate constants.

a) Draw a figure with potential curves that illustrate the above reactions. Why is $k_1 \gg k_2$ ?  What is the relative size of the frequencies of the photons ? What is the name of the phenomena that this reaction is an example of ?

We now disregard the mechanism behind the conversion in the excited state and write an idealized reaction as

$$A \xrightarrow{\ k_1\ } B \xrightarrow{\ k_2\ } A$$

As the final product is A we may regard the reaction as an equilibrium reaction and we assume that $k_2 = k_1/100$. Both reactions are considered first order.

b) Show the following expression for the concentration of B

$$[B]_t = [A]_o \frac{100}{101}\left(1 - \exp(-k_1 \tfrac{101}{100} t)\right),$$

when we assume the concentration of B is zero in the beginning (t=0) and the start concentration of A is denoted $[A]_0$.

Determine $[B]_\infty$ og $[B]_\infty / [A]_\infty$. Give a physical argument for the result.