Vibrational properties of formaldehyde

Introduction

During the lab, you will familiarize yourselves with Gaussian, the software for quantum chemical calculations of molecular systems, and Gaussview which is used to visualize the obtained results. We will calculate the vibrational spectrum of formaldehyde and compare the results with the experiment.

Preparation for the lab:

1. Find out how we calculate the energy of harmonic classical oscillator and harmonic quantum oscillator.
2. Analyze how to create Z-matrix for H_2O_2 for calculations in Gaussian (see example below)

Z-matrix in Gaussian

Z-matrix is a specially formatted command that describes the structure of the molecule(s). It is the input for Gaussian for geometry optimization and other calculations

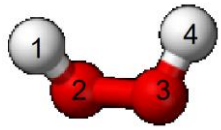
How to prepare Z-matrix?

To create Z-matrix we use the internal coordinates: the position of an atom is given relative to another atom by specifying interatomic distance, bond angle, and torsion angle. We will then describe the relationships between this atom (bond length angles) and other atoms in the molecule.

Each line of the Z-matrix describes the position of one atom. The line number is the same as the atom number (the first line describes the atom we have chosen as atom number 1, and so on). The line has the following construction:

[label of atom n], atom 2, [distance between atom n and atom 1], atom 2, [angle formed by the following atoms: (atom 2, atom 1, atom n)], atom 3, [torsional angle between atoms: (atom 3, atom 2, atom 1, atom n)]

Let us see the exemplary Z-Matrix for H_2O_2:



H
O 1 0.9
O 2 1.4 1 105.0
H 3 0.9 2 105.0 1 120.0

- In the first line we define the atom with number 1 (H)
- In the second line we define the atom with number 2 (O) and the distance between atom 1 and 2 (O-H) which is equal to 0.9 Å
- In third line we define the atom with number 3 (O - the second oxygen in H_2O_2 molecule), the distance between atoms 3 and 2 (O-O, 1.4 Å), and the angle between atoms 3, 2, and 1 (∠OOH, 105.0°)
- In the last line we define atom with number 4, the distance between atoms 4 and 3 (O-H, 0.9 Å), the angle between atoms 4,3, and 2 (∠OOH, 105.0°), and torsional angle formed by all atoms (HOOH, 120.0°)

I. Geometry optimization of formaldehyde

a) Open Gausssian and select File->New. In the **panel Molecule Specification**

Write Z-macierz of the formaldehyde using the atom numbering from Figure below:

Use the following geometrical parameters:
C=O bond length: 1.1480 Å
C-H bond length: 1.0914 Å
∠HCO: 122,14˚
Torsional angle: 180˚

b) In % Section create Checkpoint file (a file where temporal results will be store) using the commend **"%Chk=<any name>"**

c) In Route Section write the set of commands that start geometry optimization of the formaldehyde and calculate its vibrational spectrum. The set of commands for this task is:

 # b3lyp/6-31g* opt freq

d) In **Title Section** write the tittle of the calculations

e) In the section **Charge & Multipl.** write the value of the charge of the molecule and its multiplicity. It should be: **0 1**

f) Press **Run** and wait for the end of the calculations

II. Analysis of calculation results

a) Open the output file with **Gaussview** software (the output file has the file extension ".out")
b) Go to **vibrations → vibrational spectrum** and see the vibrational spectrum
c) Write the frequencies of the calculated vibrations in Table 1.
d) See the animation of each vibration and interpret it. You can tick "**show displacement vectors**" option to see atom displacements during a vibration more clearly. Write your interpretation in Table 1.
e) Draw the sketches presenting each vibration schematically. In each sketch draw displacement vectors of atoms taking part in the vibrations.

Table 1

Mode number	Assignment	Theoretical frequency (cm^{-1})	Experimental frequency (cm^{-1})
ν_1			
ν_2			
ν_3			
ν_4			
ν_5			
ν_6			

III. Thermochemistry

a) Gaussian also calculates thermodynamic quantities such as heat capacity and entropy. Find these values write down their values. with the experimental values.

b) Find the vibrational energy at 0K (Zero-Point Energy) in Gaussian output and also write down its value.

IV. Record experimental IR spectrum of aquoeous solution of formaldehyde using FTIR spectrometer.

The report should contain the following parts:

1. A brief description of the calculations performed during the lab.
2. Table 1 filled with experimental and theoretical vibrational properties for formaldehyde and interpretations of each vibrations.
3. Sketches presenting each vibrational mode with displacement vectors. Each sketch should refer to proper vibration frequency in Table 1.
4. Table with thermochemical parameters obtained from Gaussian (heat capacity, entropy, Zero-Point Energy)
5. Conclusions:

    a) Compare theoretical and experimental (taken from gas phase spectrum of formaldehyde) values of vibrational frequencies. Discuss the differences between them.
    b) Compare thermochemical properties obtained with Gaussian (heat capacity and entropy) with experimental values you find in chemical tables. Discuss the differences between them.
    c) Answer the question: why the molecule vibrates at the temperature where according to classical physics all motion should cease.

The report should be returned in two weeks from the laboratory. Please deliver the report to secretary of MITR (room 101 at the ground floor of the building). The 0.5 will be deducted from the final grade after each week of the delay in delivery of the report.

Literature:

1. Z.Kęcki, Podstawy spektroskopii molekularnej, PWN, Warszawa 1992
2. Peter Atkins, Atkins' Physical Chemistry
3. H. Barańska, A. Łabudzińska, J. Terpiński, Laserowa spektrometria ramanowska. Zastosowania analityczne, PWN, Warszawa 1981
4. H. Abramczyk, Wstep do spektroskopii laserowej, PWN, 2000