Simulation of Vibrational Spectrum by Density Functional Theory Analysis

Experiment No:

Date:

1 Aim

To simulate the vibrational spectrum of carbon dioxide (CO_2), water (H_2O) and methane (CH_4) by density functional theory and to assign its vibrational components.

2 Motivation

Computational materials science involves computational tools for solving materials related problems. There exist different mathematical models for investigating problems at multiple length and time scales which help in understanding evolution of material structures (at different length scales) and how these structures effectively control material properties. With this understanding we can select materials for specific applications and also design advanced materials for new applications. At electronic level, Density Functional Theory (DFT) is a popular computational tool while Molecular Dynamics (MD) and Monte Carlo (MC) methods are considered as preferred tools for atomistic simulations. This experiment is intent to perform some basic steps in computational materials science such as geometry optimization and the simulation of vibratioanl spectrum.

3 Basics

3.1 Density Functional Theory

Quantum chemical wavefunctions can be used derive the complete information about a system. But it is hard to solve the quantum equations as it is. DFT is one

of the available methods, in a simplified form, to solve those equations. In DFT, molecular properties of a many electron system is determined by fucntionals, which is nothing but the spatial distribution electron density. These functionals are pre-implemented in many packages and for the present analysis, DFT implemented in Orca 2.9 is used.

3.2 Basis sets

In DFT, in order to perform the desired calculations, basis sets have to be specified. Basis sets are nothing but mathematical functions that represents electronic wave functions. Present case, 6-31G** basis set, which has the support for the atoms H through Zn is used for the analysis. 6-31G** is a valence double-zeta polarized basis set and it is one of the widely used basis set in DFT calculations.

3.3 Vibrational spectrum

Absorption of energy by specific bonds of the molecule can induce a specific pattern corresponds to particular bonds. These finger prints can be used to confirm the molecular structure.

3.4 Simulation of vibrational spectrum

Vibrations that result in change of dipole moment give rise to IR absorptions. So, the computer program simulates an oscillating electric field of the radiation that couples with the molecular vibration to cause an alternating electric field produced by the changing dipole.

3.5 Types of molecular vibrations

1. *Stretching* (ν) vibrations that alter the bond lengths

2. *Bending or deformation* vibrations that alter the bond angles, (the bond lengths remain unchanged). They can be subdivided into in-plane (δ) and out-of-plane modes (γ). These modes are often referred to as twisting, wagging, and rocking vibration of a fragment.

3. *Torsional vibrations* involve an alternation of the torsion angle. A further division into symmetric (s), antisymmetric (as), and degenerated (e) vibrations are possible.

4 Procedure

1. Login into the system with your credentials.

2. Open Avogadro package and draw the corresponding molecular structure and save it in .mol format

3. Open the saved .mol file (in Avogadro package) and optimize it with UFF algorithm.

4. After optimization, export the structure as to Gabedit.

5. Choose ORCA and generate the commands for geometry optimization and vibrational spectrum simulation.

6. Save the file as .inp and then run the it through command prompt ($ orca input.inp > output.out).

7. View the output in Gabedit and note down the frequencies, and the corresponding intensities.

5 Input files

5.1 Water

```
# ===================================================================
# Water Input File
# ===================================================================
! Opt NumFreq B3LYP
! PrintBasis 6-31G**
%output
    print[p_mos] 1
 end #output
* xyz 0 1
 O -3.585100 0.294600 -0.193800
 H -2.615100 0.294600 -0.193800
 H -3.908400 -0.261500 0.532200
*
```

5.2 Carbon dioxide

```
# ===================================================================
# Carbon-dioxide Input File
# ===================================================================
! Opt NumFreq B3LYP
! PrintBasis 6-31G**
%output
    print[p_mos] 1
 end #output
* xyz 0 1
 C -2.689300 1.268700 0.014100
 O -1.496600 1.176700 0.001600
 O -3.882100 1.360700 0.026700
*
```

5.3 Methane

```
# ==================================================================
# Methane Input File
# ==================================================================
! Opt NumFreq B3LYP
! PrintBasis 6-31G**
%output
    print[p_mos] 1
 end #output
* xyz 0 1
 C -1.415200 0.100900 0.000000
 H -0.345200 0.100900 0.000000
 H -1.771900 0.741300 -0.779500
 H -1.771900 0.455800 0.944300
 H -1.771900 -0.894300 -0.164800
*
```

6 Observations

6.1 Water

6.1.1 *Optimized geometry*

Atom	x	y	z
O			
H			
H			

6.1.2 *Vibrations*

S. No	Frequency	Intensity	Assignment
1.			
2.			
3.			

6.2 Carbon dioxide

6.2.1 *Optimized geometry*

Atom	x	y	z
C			
O			
O			

6.2.2 *Vibrations*

S. No	Frequency	Intensity	Assignment
1.			
2.			
3.			

6.3 Methane

6.3.1 *Optimized geometry*

Atom	x	y	z
C			
H			
H			
H			
H			

6.3.2 *Vibrations*

S. No	Frequency	Intensity	Assignment
1.			
2.			
3.			
4.			

7 Results

Vibrational spectra of the given molecules are simulated and their molecular vibrational components are assigned.