Vibrational properties of H_2O and H_3O^+

Introduction

The main goal of the exercise is to compare the vibrational spectrum of water recorded by the Raman spectrometer with the theoretical one obtained from quantum chemical calculations in HyperChem software. The comparison of experimental and theoretical vibrational frequencies, supported by the visualization of vibrational modes, will allow us to interpret all normal modes in the vibrational spectrum of water. From these calculations we will also obtain the optimal geometry of water (geometry corresponding to minimum energy) and the value of energy for this geometry. In the next step, we will repeat quantum chemical calculations for hydronium anion (H_3O^+). Finally, from obtained energies of optimized structures of H_2O and H_3O^+ we will calculate the theoretical value of protonation energy for a water molecule.

Preparation for the lab:

1. Revise the basics of infrared (IR) absorption spectroscopy and Raman spectroscopy. Revise the differences in selection rules for these two spectroscopies.
2. Can explain the following terms: normal vibrational mode, resonance frequency in IR spectroscopy, degenerate vibrational modes, overtones in IR spectroscopy, a virtual state in Raman spectroscopy, torsional angle.

I. Drawing the H_2O molecule

To enable drawing, select the drawing cursor from the toolbar (⊕)

a) From the menu **Build** select **Default Element**.
b) From the menu Display select **Labels→Atoms→Symbol**. The atomic symbols will be shown in the drawing.
c) Select the oxygen atom from the periodic table.
d) Tick two options at the bottom of the window: **Explicit Hydrogens** (it prevents HyperChem from adding hydrogens to complete octets) and select **Allow Arbitrary Value** (it allows to draw ions - will be necessary for the next step - hydronium ion calculations)
b) Draw the water molecule.

II. Choosing a Basis Set

a) From the menu **Setup** select **Ab Initio**
b) In the **Ab Initio Method** window select the basis set, start from **STO-3G**

III. Transformation to 3D structure

To convert the planar structure of water into a 3D structure, select **Build→ Model Build.** You can translate and rotate the molecule if you change the drawing tool (⊕) to translate or rotate tools in the top panel.

IV. Geometry optimization - calculation of the H_2O geometry for which the energy has a minimum value (Minimum Energy Structure)

a) From the menu **Setup** select **Ab Initio →Options**
c) Make sure the parameters for geometry optimization are the following:
Total charge = 0
Spin Multiplicity = 1
Spin Pairing = RHF
Convergence Limit = 0,01 kcal/mol
Iteration Limit = 50
Accelerate convergence = YES
d) From the menu **Compute** select **Geometry Optimization**
The parameters for geometry optimization should be the following :
Polak-Ribiere Method
RMS Gradient = 0,01

When the calculations are finished select the pointing cursor (choose ◎ from the toolbar) and check the OH bond length and the value of ∡HOH. Write down these values in Table 1.

V. Calculation of the total energy of the H_2O molecule

In the menu **Compute** choose **Single Point.** Write down the calculated total energy (it is shown at the bottom of the window) for the STO3G basis set in Table 1.

VI. Vibrational properties of H_2O

a) From the menu **Compute** select **Vibration, Rotation Analysis.** This will start the calculations of the vibrational spectrum of H_2O.
b) When the calculations are finished in the menu **Compute** the option **Vibrational Spectrum** becomes active. You can see there the vibrational spectrum of H_2O.

c) In the next step, you should assign the calculated vibrational modes to particular types of vibrational normal modes. These assignments can be performed based on visualizations of already calculated vibrations. To open the visualization panel choose **Compute→Vibrational Spectrum→Animate Vibrations** and click **Apply**. Adjust parameters **Frames** and **Amplitude** to see the vibration well.

d) To see displacements of atoms during a vibration more clearly activate vectors attached to each atom. From the menu **Display** select **Rendering →Vector and Line Options→IR Vectors**)

e) Select the vibrational mode having the lowest frequency. Look at the animation of the selected vibrational mode and interpret it. Write down the value of the frequency and your assignment in Table 2. Next, see and interpret other modes and also write down the results in Table 2.

f) Repeat the calculations of geometry optimization and vibrational properties (points II-IV) for other basis sets for H_2O: 3-21G and 6-31G*. To change a basis set **Setup→Ab Initio→3-21G**. After performing calculations of geometry optimization and vibrational spectrum write down the values of geometrical and vibrational parameters in Tables 1 and 2.

VI. Geometry optimization and vibrational properties of hydronium ion (H_3O^+)

a) Repeat steps I-V for H_3O^+. Start from the drawing H_3O^+ molecule for the H_3O^+ molecule as a new file. Pay attention that the charge of the H_3O^+ molecule should be set to 1. You can set it after drawing the H_3O^+ molecule. Select **Ab Intio→Options** and set **Total charge = 1**

b) In each case write down geometrical parameters (OH bond length and the value of ∡HOH) and vibrational properties (frequencies and their assignments) in Tables 1 and 2.

VII. Registration of the experimental Raman spectrum of water

a) Insert small portion of water to a glass vial.

b) Record the Raman spectrum of water using the software for the spectrometer.

Table 1

	STO-3G		**3–21G**		**6–31G***	
	Optimized structure		**Optimized structure**		**Optimized structure**	
	Geometry	**Energy**	**Geometry**	**Energy**	**Geometry**	**Energy**
H_2O	**OH bond length:** **∢HOH:**	**E=**	**OH bond length:** **∢HOH:**	**E=**	**OH bond length:** **∢HOH:**	**E=**
H_3O^+	**OH bond length:** **∢HOH:** **Torsional angle :**	**E=**	**OH bond length:** **∢HOH:** **Torsional angle :**	**E=**	**OH bond length:** **HOH:** **Torsional angle :**	**E=**
Theoretical protonation energy $\Delta E^{theor.} = E(H_3O^+) - E(H_2O)=$						
(*)Experimental protonation energy $\Delta E^{exp}=$						

Table 2

Basis set		assignment	Experimental frequency $H_2O^{exp.}$ (cm^{-1})	Theoretical frequency $H_2O^{theor.}$ (cm^{-1})	Theoretical frequency $H_3O^{+\ theor.}$ (cm^{-1})
STO-3G	ν_1				
	ν_2				
	ν_3				
	ν_4				
3-21G	ν_1				
	ν_2				
	ν_3				
	ν_4				
6-31G*	ν_1				
	ν_2				
	ν_3				
	ν_4				

The report should contain the following parts:

1. A concise theoretical background describing experimental tools used to study molecular vibrations experimentally: IR and Raman spectroscopies. Describe the major differences between these two spectroscopies taking into account character of physical phenomena in each case and differences in selection rules.
2. A brief description of the calculations performed during the lab.
3. Tables with calculated geometrical and vibrational properties for water and hydronium ion, and protonation energies for each Basis Set.
4. Conclusions:
   a) compare calculated in HyperChem theoretical values of bond lengths and angles for water with the experimental ones which can be found in chemical tables (or other resources)
   b) For which Basis Set the calculated structure of water (bond lengths and angles) most closely resemble “real” water (water studied experimentally)?
   c) Does the best performer (the best Basis Set) for prediction of water geometry is also the most reliable in case of prediction of molecular vibrations frequencies?
   d) Why are there differences between theoretical and experimental values? Which interactions have not been taken into account in calculations in HyperChem?

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