Calculating the Number of Modes of Vibrations in H_2O Molecule using Jmol and Simulated FTIR Spectra

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1. Introduction

According to Heisenberg uncertainty principle, all atoms in a molecule are always in motion. Three types of motions are expected in the molecules, they are vibrational, rotational and translational. A diatomic molecule contains only a single vibrational motion., while polyatomic molecules exhibit more complex vibrations.

1.1 Molecular Vibrations

A molecule has translational and rotational motion as a whole while each atom has its own motion. The vibrational modes can be IR or Raman active. For a mode to be observed in the IR spectrum, changes must occur in the permanent dipole (i.e. not diatomic molecules). Diatomic molecules are observed in the Raman spectra but not in the IR spectra. This is due to the fact that diatomic molecules have one band and no permanent dipole, and therefore one single vibration. An example of this would be O_2 or N_2. However, unsymmetric diatomic molecules (i.e. CN) do absorb in the IR spectra. Polyatomic molecules undergo more complex vibrations that can be summed or resolved into normal modes of vibration.

The normal modes of vibration are: asymmetric, symmetric, wagging, twisting, scissoring, and rocking for polyatomic molecules.

1.2 Calculating the number of modes of vibrations

Degree of freedom is the number of variables required to describe the motion of a particle. For an atom moving in 3-dimensional space, three coordinates are adequate so its degree of freedom is three. Its motion is purely translational. If the molecule is made up of N number of atoms, the degree of freedom becomes 3N, because each atom has 3 degrees of freedom. As the, atoms are bonded together, all motions are not translational; some become rotational, some others are vibrational. For non-linear molecules, all rotational motions can be described in terms of rotations around 3 axes, the rotational degree of freedom is 3 and the remaining 3N-6 degrees of freedom constitute vibrational motion. For a linear molecule, rotation around its

own axis is no rotation because it leaves the molecule unchanged. So there are only 2 rotational degrees of freedom for any linear molecule leaving 3N-5 degrees of freedom for vibration.

Formula for calculating number of modes of vibrations:

- Linear Molecule - **3N−5**
- Non Linear Molecule - **3N−6**

  (N = the number of atoms within the molecule)

The following steps need to be followed to calculate the number of vibrational modes:

1. Determine if the molecule is linear or nonlinear
2. Calculate how many atoms are in your molecule.
3. Substitute the number in "N" value and solve.

2. Objectives

- To calculate the number of modes of vibrations in H_2O molecule using the formula
- To draw the 3D structure of H_2O molecule in Jmol interface
- Save the 3D structure of H_2O molecule as .mol file
- Importing the .mol file to the Gaussian engine in WebMO
- Generating the simulated FTIR spectra through Gaussian
- Assigning the peaks in the simulated FTIR spectra, for the types of Vibrations
- Comparing the number of modes of vibrations obtained using the formula to the peaks obtained in the simulated FTIR spectra

3. Calculating the number of modes of vibrations in H_2O molecule

- H_2O molecule is a non-linear molecule
- The molecule has 3 atoms
- Formula used
  - **3N−6**
  - (3x3) -6 = 3
  - **The number of modes of vibrations in H_2O molecule is 3**

4. Drawing the 3D structure of H_2O molecule in Jmol interface

- Open Jmol interface select the model kit menu
- Select carbon atom, it appears as methane molecule
- Using delete atom option delete four H atoms
- Select O atom and drag to add two H atoms

4.1 Energy optimization of H_2O molecule in Jmol interface

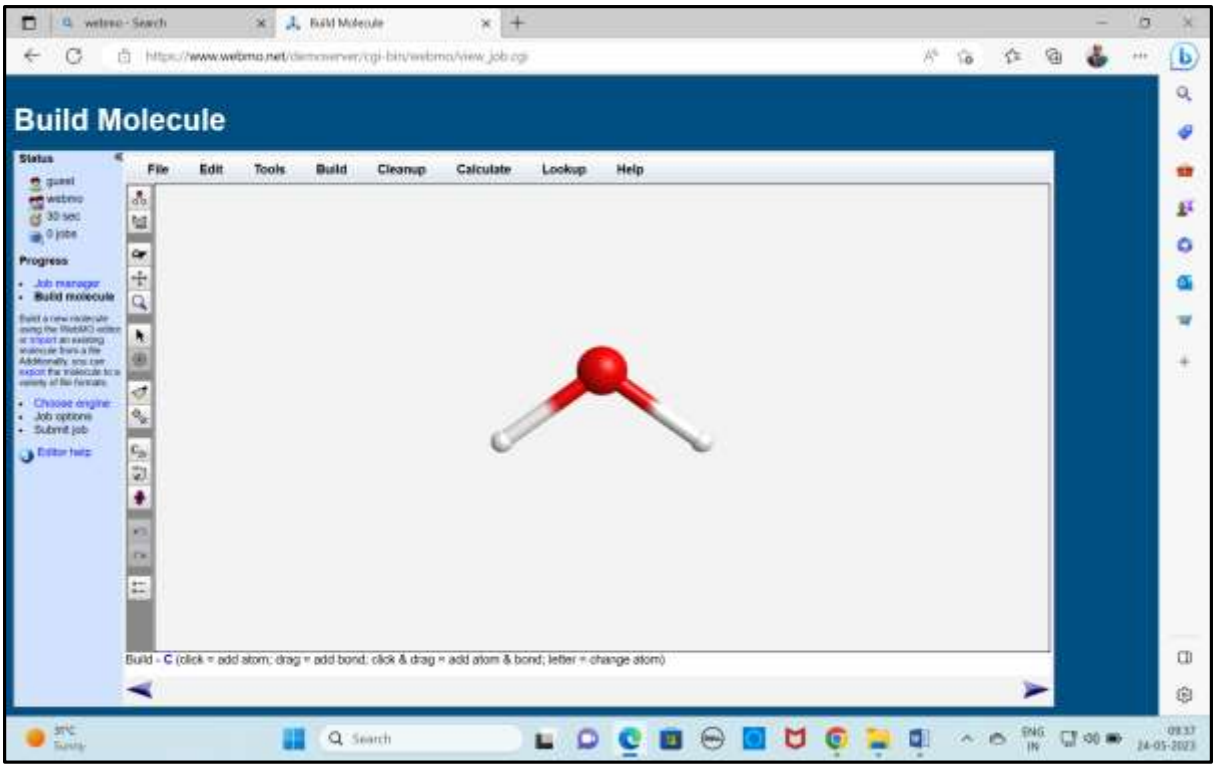
- Exit from the model kit menu
- Now right click on the molecule
- Select the option computation
- Then click optimize structure

4.2 Save the 3D structure as .mol file

- Click the model kit menu
- In the drop down list select the last option
- Click on the save file option
- Now the structure is saved in the .mol format

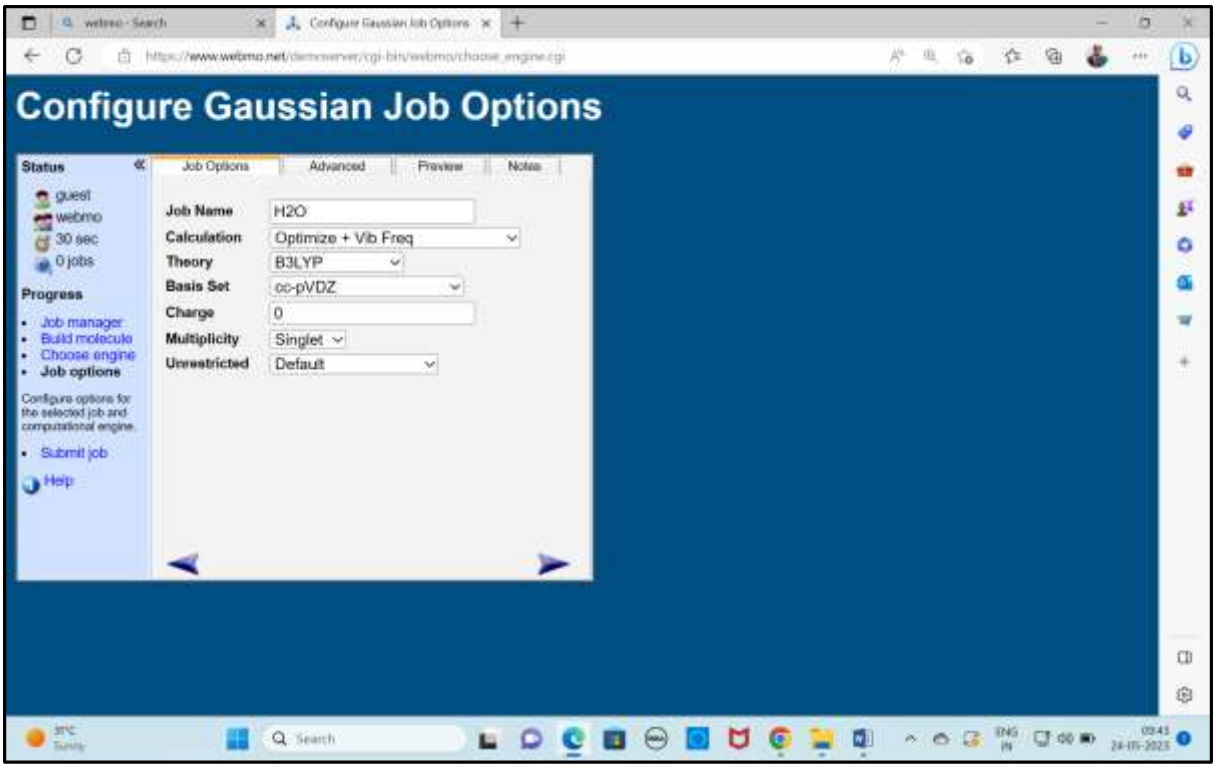
5. Importing the .mol file to the Gaussian engine in WebMO

- Open the WebMO web page https://www.webmo.net/
- Click on the DEMO icon
- Login into demo server https://www.webmo.net/demoserver/cgi-bin/webmo/login.cgi
- Click on the new job option- select – create new job
- Now Build molecule page opens
- Click on File menu-import molecule-select file type as mol
- Choose the .mol file saved already in the laptop/desktop
- Now the .mol file will be imported

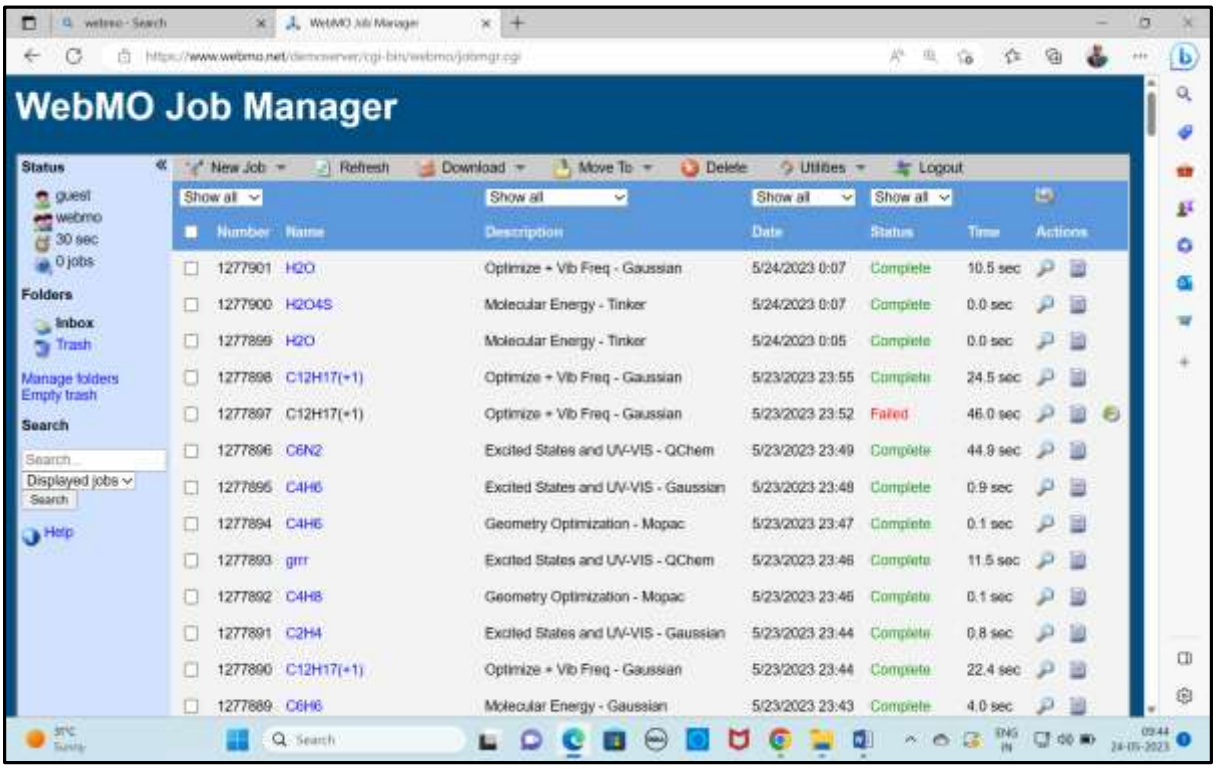


6. Generating the simulated FTIR spectra through Gaussian

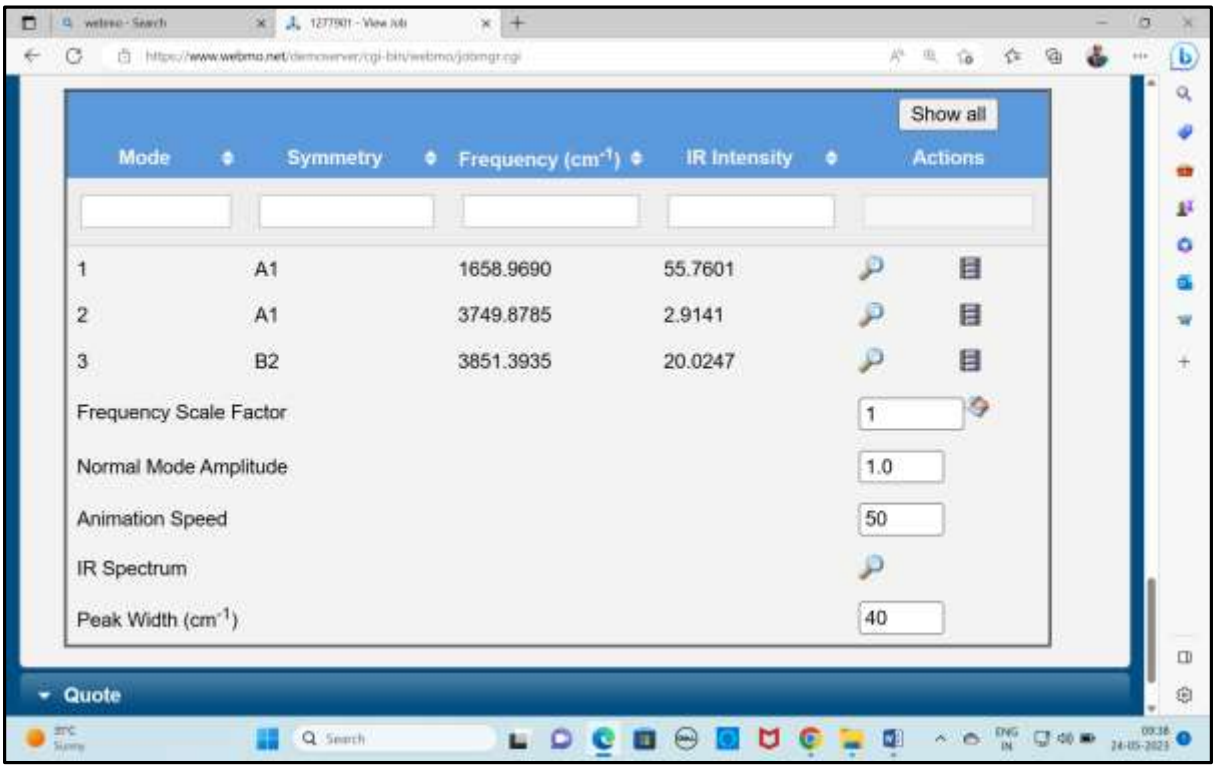
- Click the next arrow in the bottom right corner of the Build molecule page
- Choose computational engine page opens
- Select Gaussian and click next arrow at the right corner
- Configure Gaussian Job option page opens
    - Give the Job name (here we have given as H2O)
    - Calculation – select as optimize+Vib Freq
    - Theory – B3YLP
    - Basic set – cc-pVDZ
    - Charge – 0
    - Multiplicity – Singlet

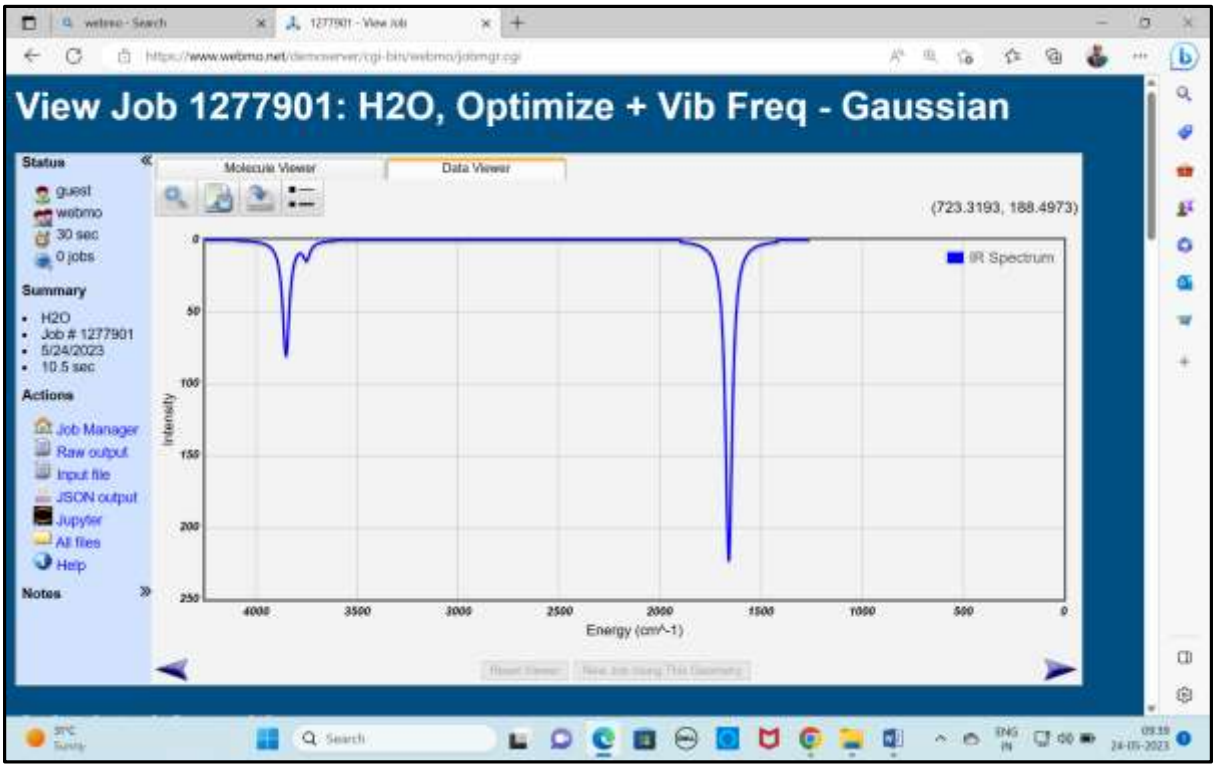


- After providing all the above options click the next arrow
- We will get into WebMO Job Manager page
- We can view the execution of the job in progress
- Once the status of the Job is complete click to view the job



- Now the page with Job No. , Job Name and Job details appears
- Scroll down the page, we can look into the details of optimization and vibrational modes and so on
- At the bottom of the page the details of vibrations and IR spectrum were there
- Click the view symbol next to the IR Spectrum option – IR can be viewed

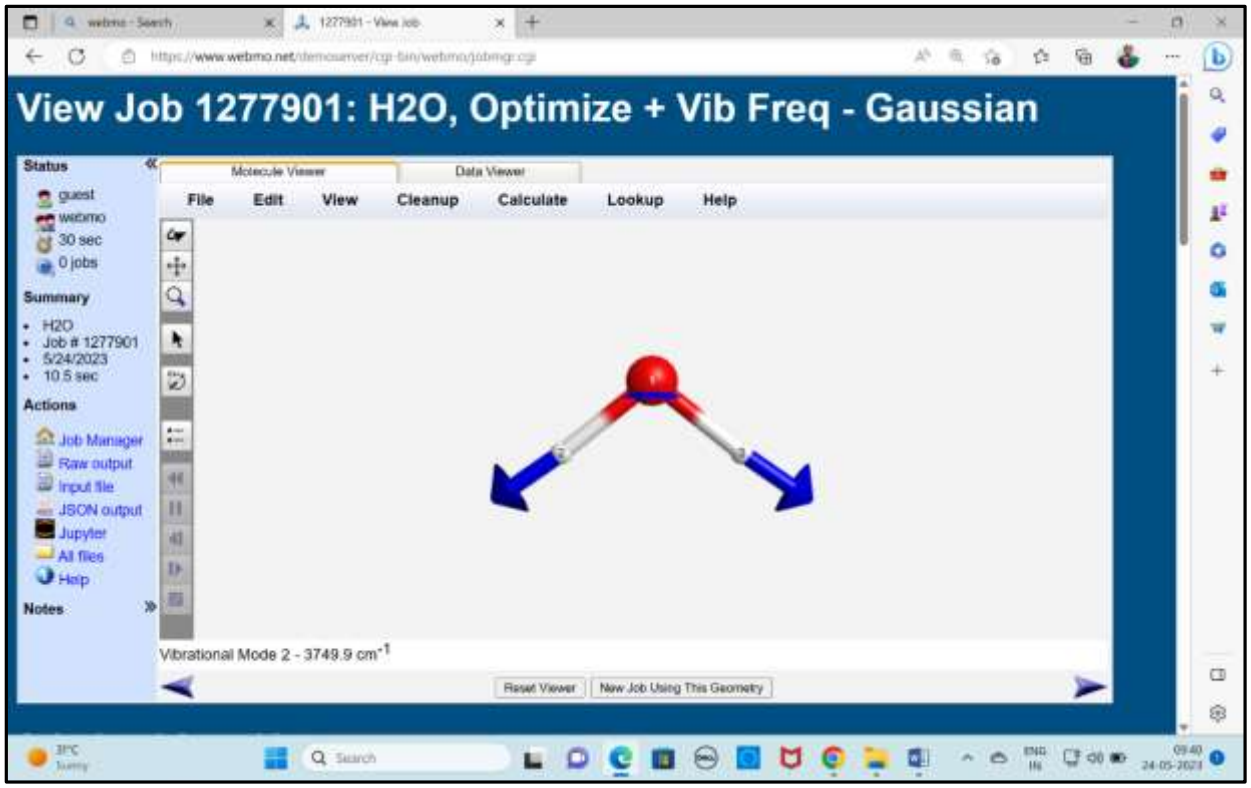




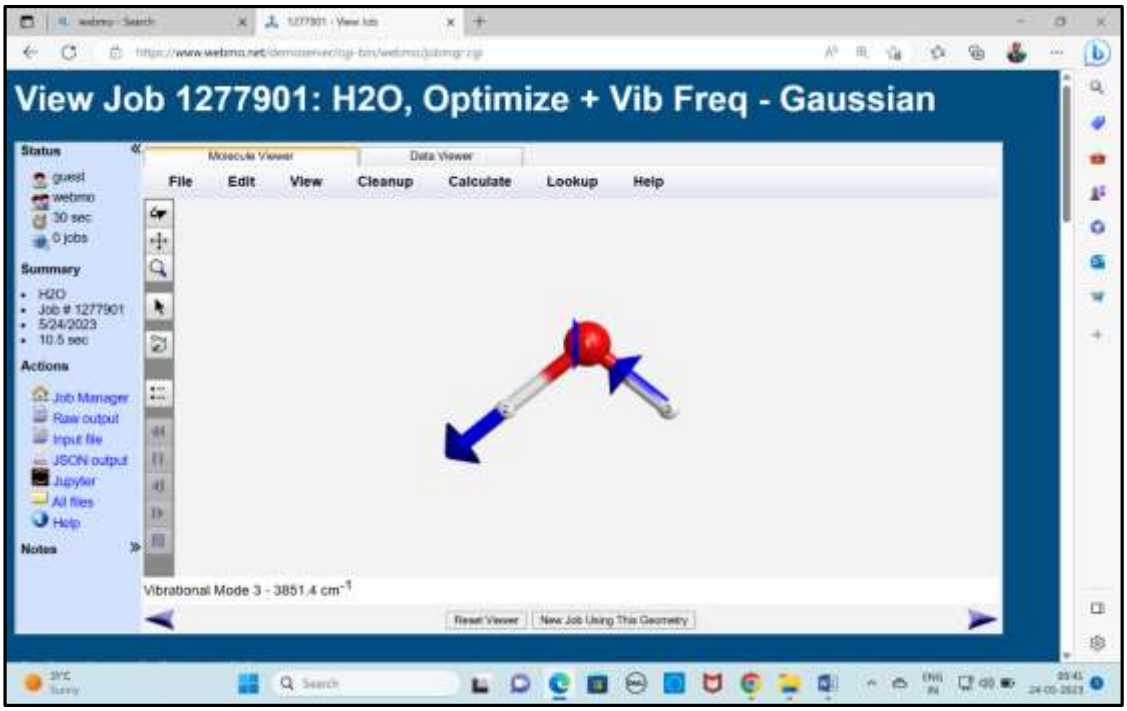
7. Assigning the peaks in the simulated FTIR spectra, for the types of Vibrations

- Vibrational modes detail show three types of vibrations for the H_2O molecule
- The three types of vibrations are given with Frequency and IR intensity
    - Symmetric stretch -3749.9 cm^{-1}; a small peak is obtained as the symmetric stretch won't change the dipole moment drastically
    - Asymmetric stretch - 3851.4 cm^{-1}; a medium peak is obtained as the asymmetric stretch changes the dipole moment to a considerable extent
    - Bending vibrations – 1658 $cm^{-1;}$ strong peak is obtained as the bending vibration changes the Dipole moment to a larger extent
- By clicking on the animate option under Action you can view the animated bending vibrations

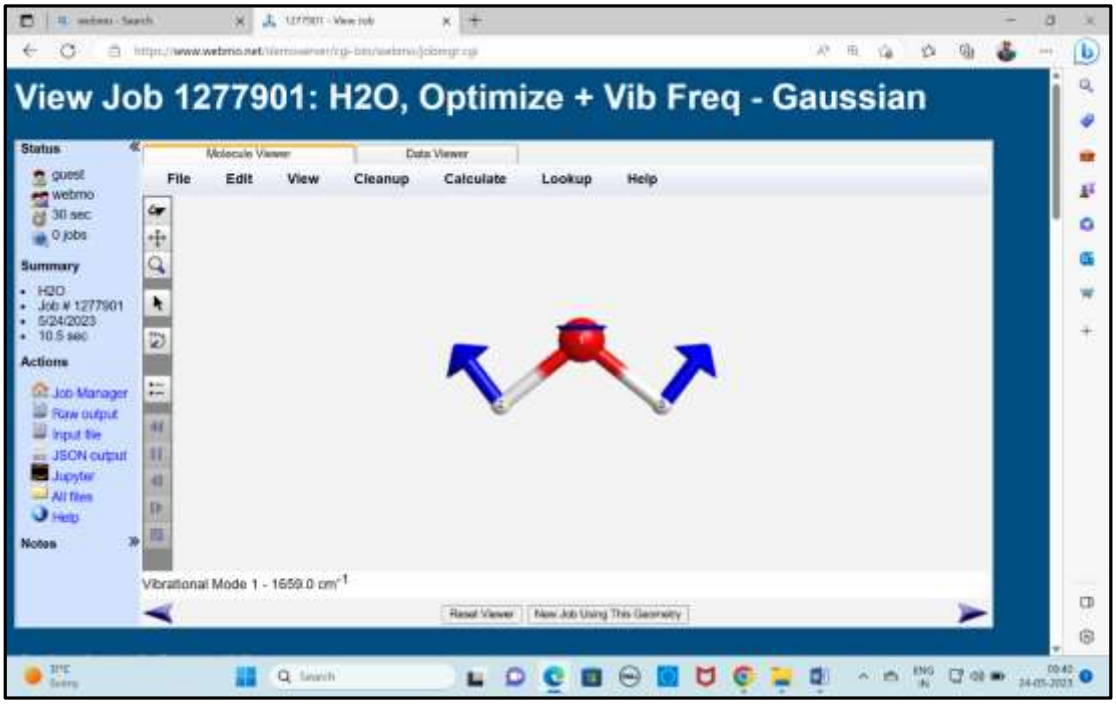
Symmetric stretch at 3749.9 cm^{-1} in in H_2O molecule



Asymmetric stretch at 3851.4 cm^{-1} in in H_2O molecule



Bending Vibrations at 1659 cm^{-1} in H_2O molecule



8. Comparing the number of modes of vibrations obtained using the formula to the peaks obtained in the simulated FTIR spectra

- The theoretical calculation of number of mode of vibrations using the formula 3N-5 for H_2O molecule results in 3 types of vibrations
- The three types of vibrations are symmetric stretch, asymmetric stretch and bending vibrations
- The simulated FTIR spectrum of water molecule obtained from Gaussian computational engine also shows three peaks which means the theoretical calculations matches with the simulated FTIR spectrum.

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