

Calculating the Number of Modes of Vibrations in non-linear NH₃ 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:

NH₃ is a triatomic molecule composed of one nitrogen atom and three hydrogen atoms. It is a polar molecule that exhibits molecular vibrations when subjected to energy input. The molecular vibrations of NH₃ can be described using the principles of molecular spectroscopy. In NH₃, there are three vibrational modes: symmetric stretch, asymmetric stretch, and bending. These vibrational modes correspond to the different ways in which the atoms in the molecule can move relative to each other.

- The symmetric stretch mode involves the stretching of all three N-H bonds simultaneously.
- The asymmetric stretch mode involves the stretching of two N-H bonds while the third is compressed.
- The bending mode involves the deformation of the H-N-H angle.

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 NH_3 molecule using the formula
- To draw the 3D structure of NH_3 molecule in Jmol interface
- Save the 3D structure of NH_3 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 NH_3 molecule

- NH_3 molecule is a linear molecule
- The molecule has 3 atoms
- Formula used
 - $3N-6$
 - $(3 \times 4) - 6 = 6$
 - **The number of modes of vibrations in NH_3 molecule is 6**

4. Drawing the 3D structure of NH_3 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 one among the four H atoms
- Select N atom from model kit menu

4.1 Energy optimization of NH₃ 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

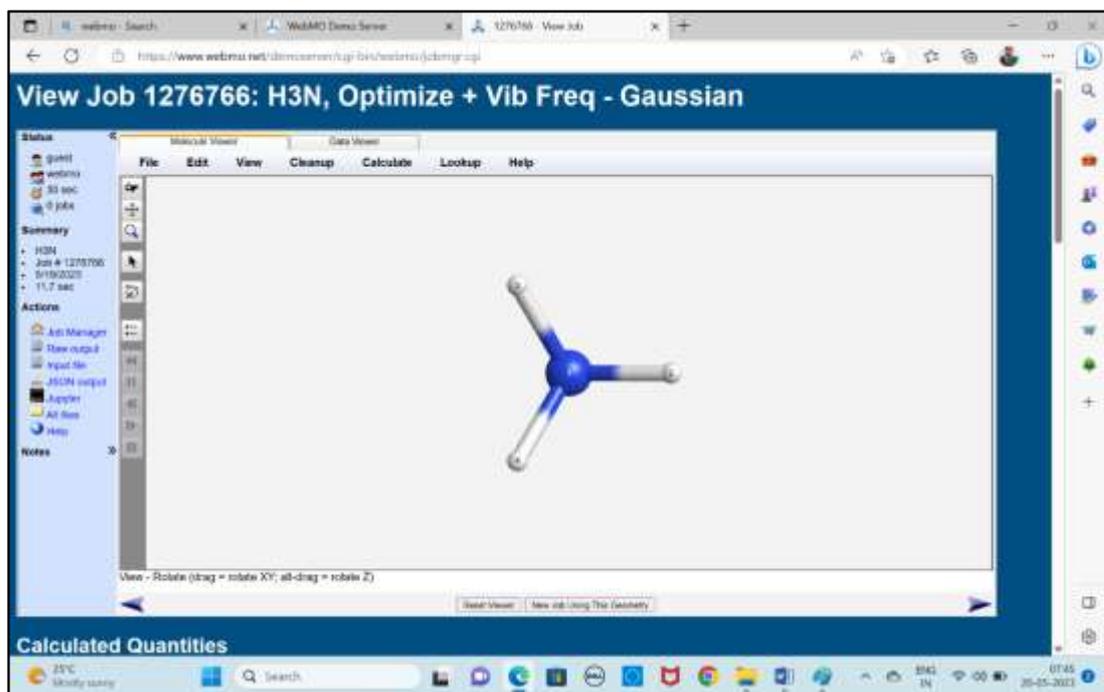
5. Importing the .mol file to the Gaussian engine in WebMO

- 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 H3N)



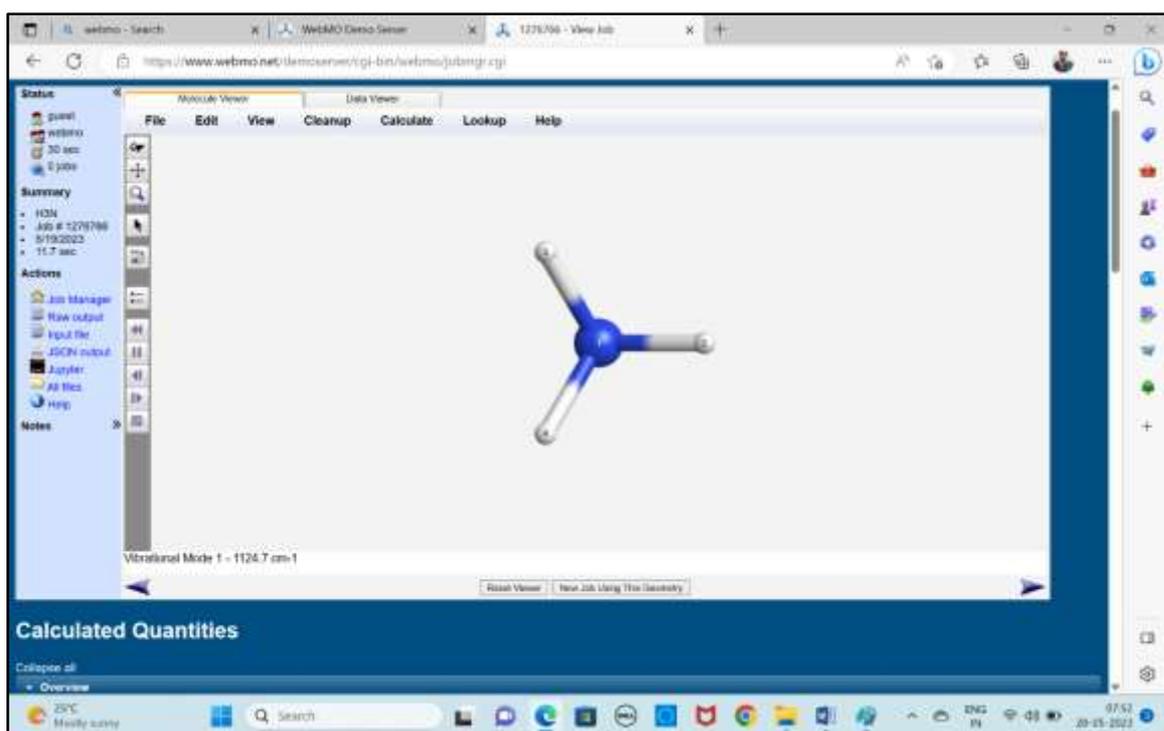
- Scroll down the page, we can look into the details of optimization and vibrational modes and so on
- At the bottom of the page the details of vibrations and IR spectrum were there

Mode	Symmetry	Frequency (cm ⁻¹)	IR Intensity	Actions
1	A1	1124.7095	105.0002	
2	E	1675.2647	8.3010	
3	E	1675.2648	8.3283	
4	A1	3417.3114	3.0423	
5	E	3501.8278	0.9611	
6	E	3501.8279	0.9611	

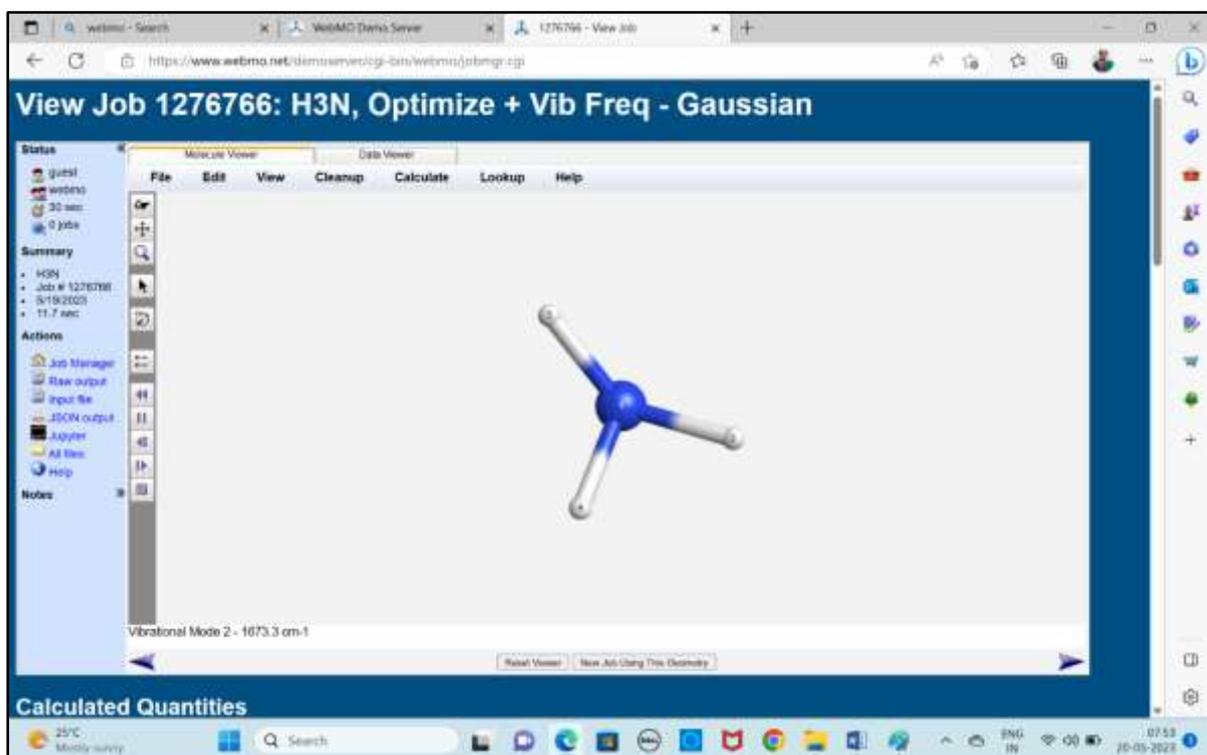
Frequency Scale Factor:
 Normal Mode Amplitude:
 Animation Speed:
 IR Spectrum Peak Width (cm⁻¹):

- As per theoretical calculation the NH₃ molecule has 6-modes of vibrations, here also we can see 6 modes of vibrations
- For each mode of vibration, the frequency and corresponding IR intensity is also obtained
- By clicking on the animate option under Action you can view the animated vibrations

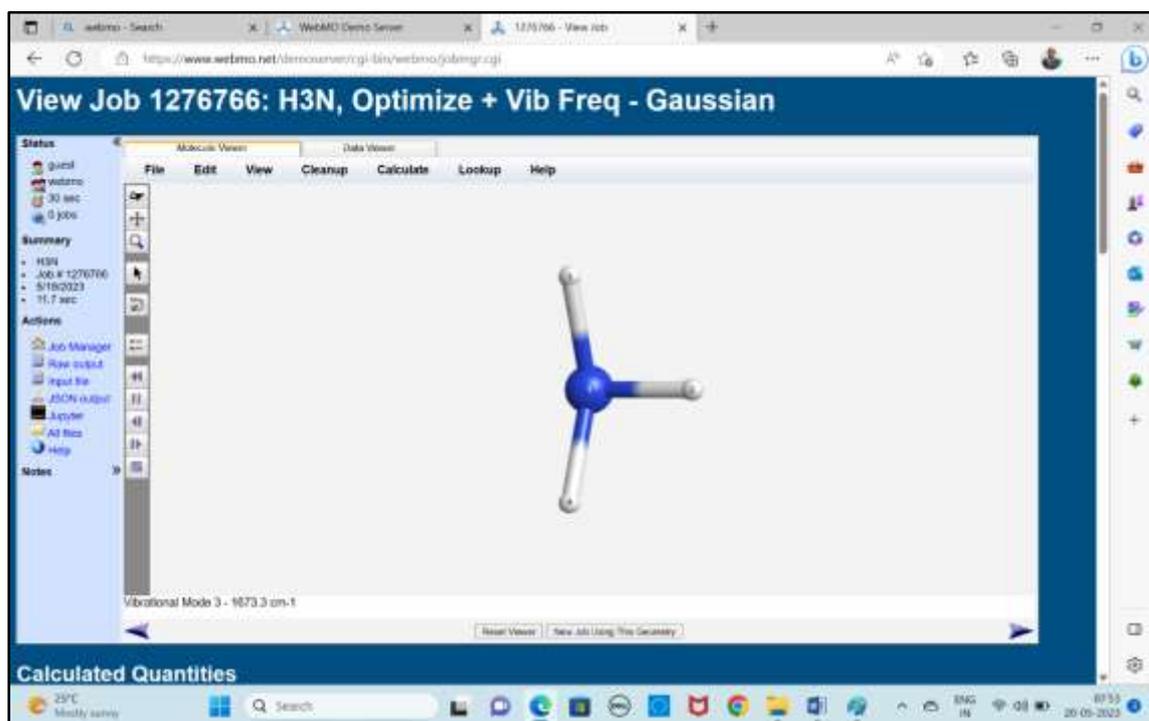
- The vibrational frequency at 1124.7 cm^{-1} corresponds to stretching of N-H bonds



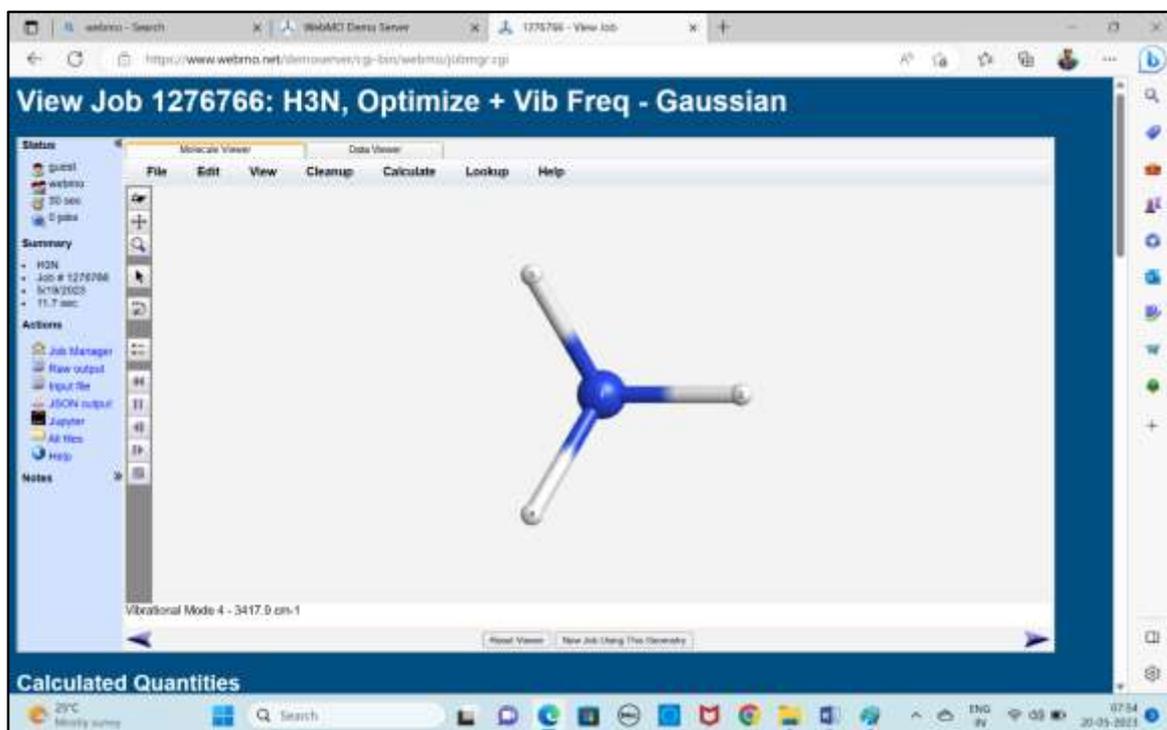
- The vibrational frequency at 1673.3 cm^{-1} corresponds to bending of N-H bonds



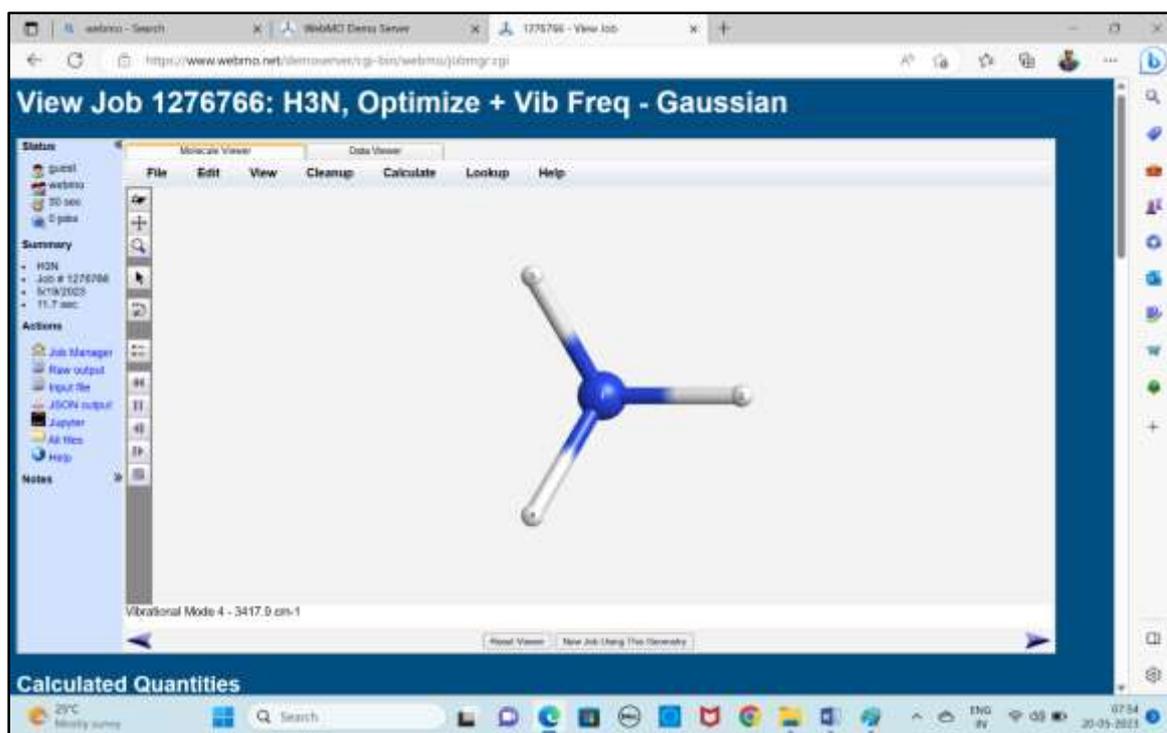
- The vibrational frequency at 1673.3 cm^{-1} corresponds to bending of N-H bonds, two types of bending vibrations occurs in the same frequency



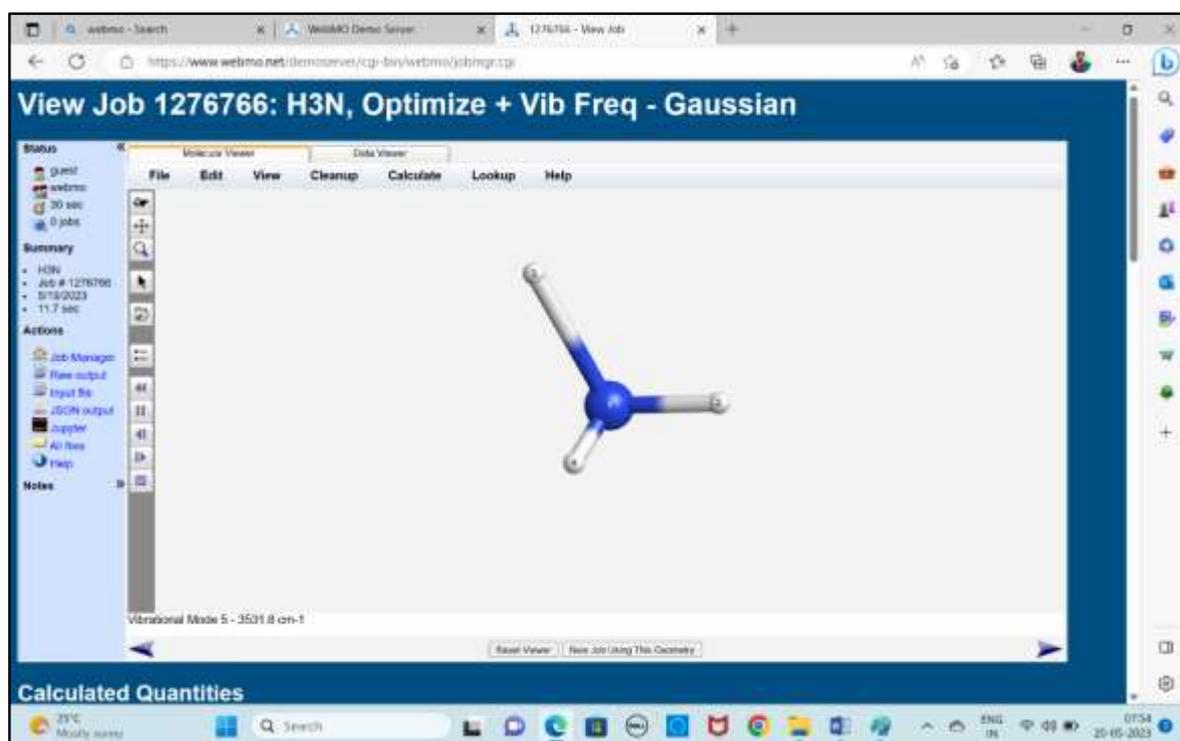
- The vibrational frequency at 3417.9 cm^{-1} corresponds to stretching of N-H bonds



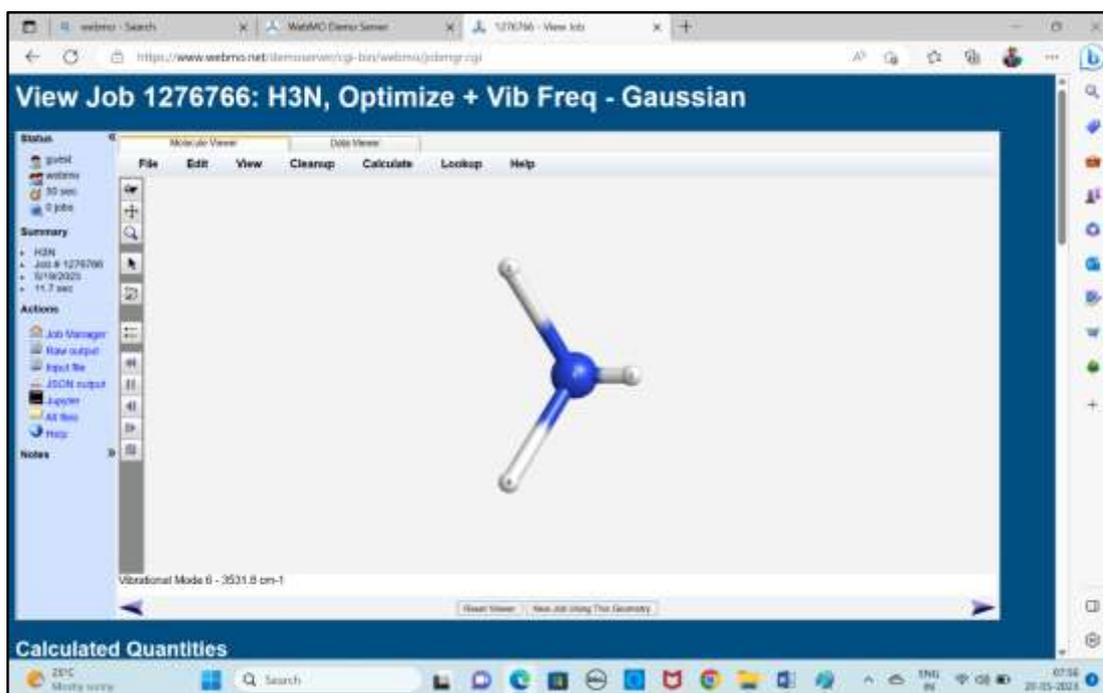
- The vibrational frequency at 3417.9 cm^{-1} corresponds to stretching of N-H bonds



- The vibrational frequency at 3531.8 cm^{-1} corresponds to asymmetric stretching of N-H bonds

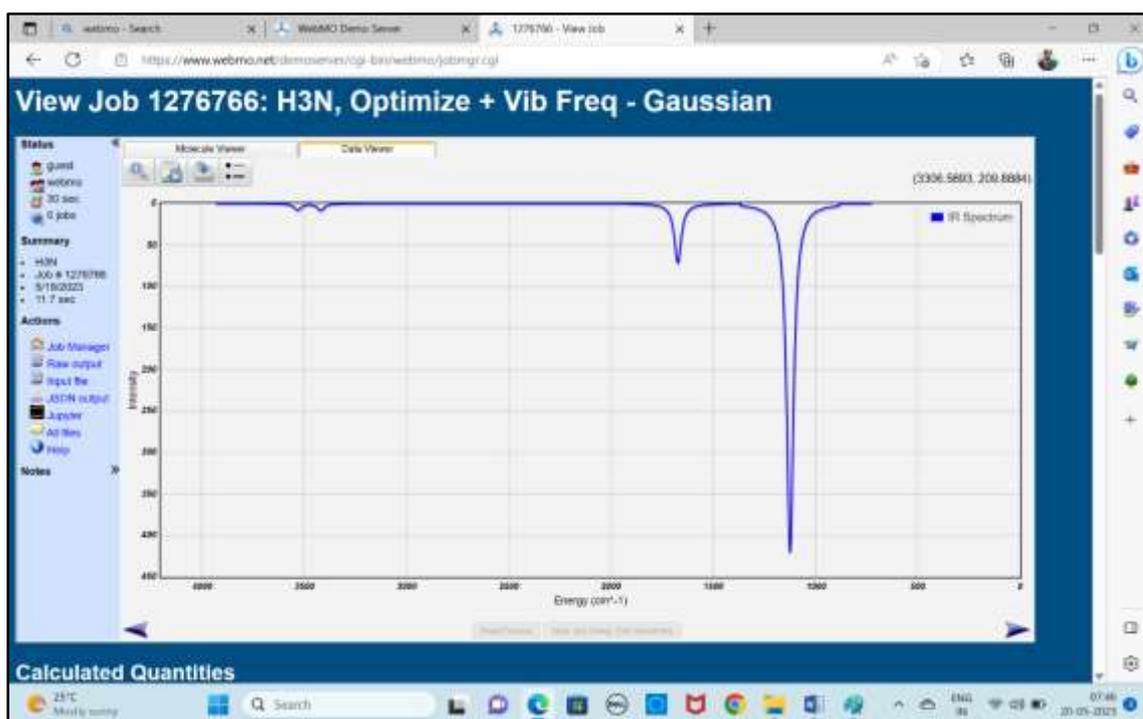


- The vibrational frequency at 3531.8 cm^{-1} corresponds to asymmetric stretching of N-H bonds



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

- Vibrational modes detail show 6 types of vibrations for the NH_3 molecule
- The 6 types of vibrations are given with Frequency and IR intensity
- By clicking on the view button near IR spectrum we can view the simulated IR spectrum of NH_3 molecule



- Though we get 6 modes of vibrations for NH₃ molecule, only four peaks are obtained in the simulated FTIR spectra
- The small peak at 3531.8 cm⁻¹ corresponds to the asymmetric stretching of N-H bonds
- The next small peak at 3417.9 cm⁻¹ corresponds to the symmetric stretching of all the three N-H bonds
- The medium peak at 1673.7 cm⁻¹ corresponds to the bending (scissoring and rocking motion) of N-H bonds
- The strong peak at 1124.7 cm⁻¹ corresponds to the bending (wagging motion) of N-H bonds

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 $3N-6$ for NH₃ molecule results in 6 types of vibrations
- The six types of vibrations are symmetric stretch, two types of asymmetric stretch and three types bending vibrations
- The two types of asymmetric stretch occur in same frequency so we get a single peak for both of the asymmetric stretch at 3531.8 cm⁻¹
- Three types of bending vibrations occur in the NH₃ molecule, scissoring and rocking at 1673.7 cm⁻¹ and wagging occurs at 1124.7 cm⁻¹
- Among the six types of vibrations the symmetric and asymmetric stretch will change the dipole moment to a minimum extent therefore IR peak corresponding to the symmetric and asymmetric stretch was very small
- The three types of bending vibrations will change the dipole moment to a large extent so we get a medium and a strong peak for three bending vibrations
- The wagging type of bending motion will change the dipole moment drastically as it occurs out of the plane therefore we get a strong peak at 1124.7 cm⁻¹ in simulated IR spectrum.

Acknowledgement

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