

Calculating the Number of Modes of Vibrations in non-linear NH_3 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:

NH_3 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 NH_3 can be described using the principles of molecular spectroscopy. In NH_3 , 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



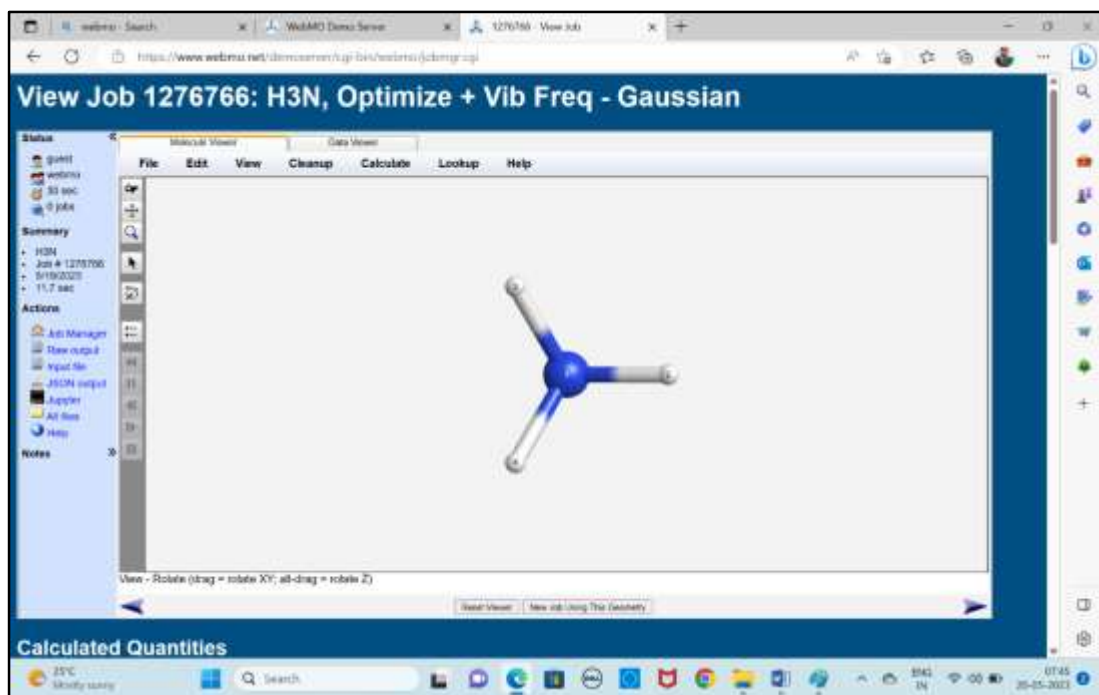
6. Generating the simulated FTIR spectra through Gaussian

- 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)

- # Configure Gaussian Job Options
-
- The screenshot shows the Gaussian 09 Job Options dialog box. The 'Job Options' tab is selected. The 'Job Name' is 'H3N'. The 'Calculation' is 'Optimize + Vib Freq'. The 'Theory' is 'B3LYP'. The 'Basis Set' is 'cc-pVDZ'. The 'Charge' is '0'. The 'Multiplicity' is 'Singlet'. The 'Unrestricted' option is 'Default'. The 'Status' bar shows 'guest', 'wellmo', '30 sec', and '0 jobs'. The 'Progress' section lists 'Job manager', 'Build molecule', 'Choose engine', and 'Job options'. The 'Help' button is at the bottom left.

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- WebMO Job Manager**
- Home | Failed | Incomplete | Search
- Home | Failed | Incomplete | Search
- | Name | Name | Description | Date | Status | Time | Actions |
|--------|----------------|---|---------------|----------|----------|---------|
| 137000 | H4H42562 | QSS-QS1-High-Accuracy Energy - Gaussian | 18/02/2017 06 | Failed | 38.0 sec | [Icons] |
| 137001 | H4H4 | Optimize - V6-Freq - Gaussian | 18/02/2017 07 | Complete | 21.7 sec | [Icons] |
| 137003 | H4H42562 | QSS-QS1-High-Accuracy Energy - Gaussian | 18/02/2017 06 | Failed | 46.0 sec | [Icons] |
| 137005 | H4H42562 | QSS-QS1-High-Accuracy Energy - Gaussian | 18/02/2017 14 | Failed | 31.0 sec | [Icons] |
| 137006 | H4H4 | Optimize - Gaussian | 18/02/2017 14 | Failed | 8.0 sec | [Icons] |
| 137007 | H4H4 | Optimize Energy - Gaussian | 18/02/2017 14 | Failed | 2.2 sec | [Icons] |
| 137008 | H4H42562 | QSS-QS1-High-Accuracy Energy - Gaussian | 18/02/2017 02 | Failed | 46.0 sec | [Icons] |
| 137009 | H4H42562 | QSS-QS1-High-Accuracy Energy - Gaussian | 18/02/2017 02 | Failed | 46.0 sec | [Icons] |
| 137010 | H4H42562 | QSS-QS1-High-Accuracy Energy - Gaussian | 18/02/2017 02 | Failed | 31.0 sec | [Icons] |
| 137011 | H4H42562 | QSS-QS1-High-Accuracy Energy - Gaussian | 18/02/2017 23 | Failed | 46.0 sec | [Icons] |
| 137012 | H4H42562 | QSS-QS1-High-Accuracy Energy - Gaussian | 18/02/2017 10 | Failed | 31.0 sec | [Icons] |
| 137013 | Partial Charge | Optimize - Gaussian | 18/02/2017 11 | Complete | 3.00 | [Icons] |
| 137014 | C2H4H4361 | Geometry Optimization - Gaussian | 18/02/2017 09 | Failed | 31.0 sec | [Icons] |
| 137015 | C2H4H4361 | Geometry Optimization - Gaussian | 18/02/2017 07 | Failed | 46.0 sec | [Icons] |
| 137016 | C2H4H4361 | Geometry Optimization - Gaussian | 18/02/2017 04 | Failed | 31.0 sec | [Icons] |
| 137017 | C2H4H4361 | QSS-QS1-High-Accuracy Energy - Gaussian | 18/02/2017 06 | Failed | 46.0 sec | [Icons] |
| 137018 | C2H4H4361 | QSS-QS1-High-Accuracy Energy - Gaussian | 18/02/2017 01 | Failed | 31.0 sec | [Icons] |
| 137019 | C2H4H4361 | Geometry Optimization - Gaussian | 18/02/2017 00 | Complete | 3.8 sec | [Icons] |
| 137020 | C2H4H4361 | Optimize - Gaussian | 18/02/2017 01 | Complete | 1.1 sec | [Icons] |

- 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

Vibrational Modes

Mode	Symmetry	Frequency (cm ⁻¹)	IR Intensity	Actions
1	A1	1124.7095	105.0062	
2	E	1675.2647	8.3010	
3	E	1675.2648	8.3263	
4	A1	3417.3114	2.0423	
5	E	3501.8279	0.0611	
6	E	3501.8279	0.0611	

Frequency Scale Factor:

Normal Mode Amplitude:

Animation Speed:

IR Spectrum:

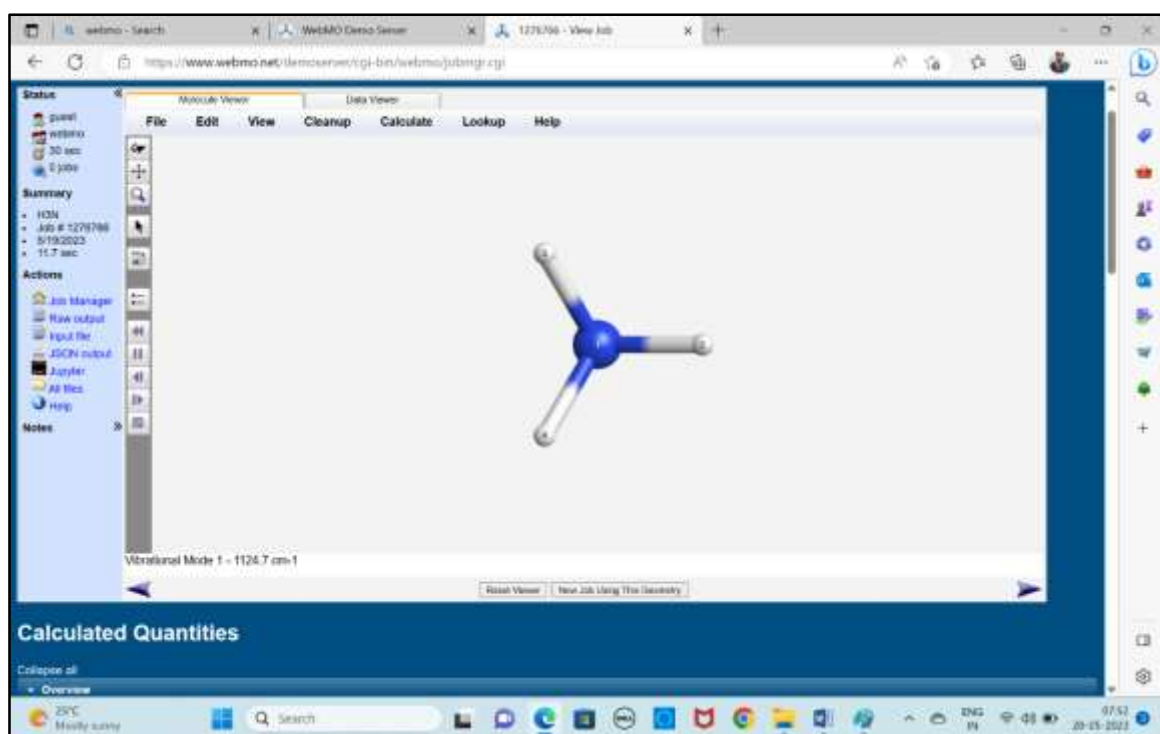
Peak Width (cm⁻¹):

Quote

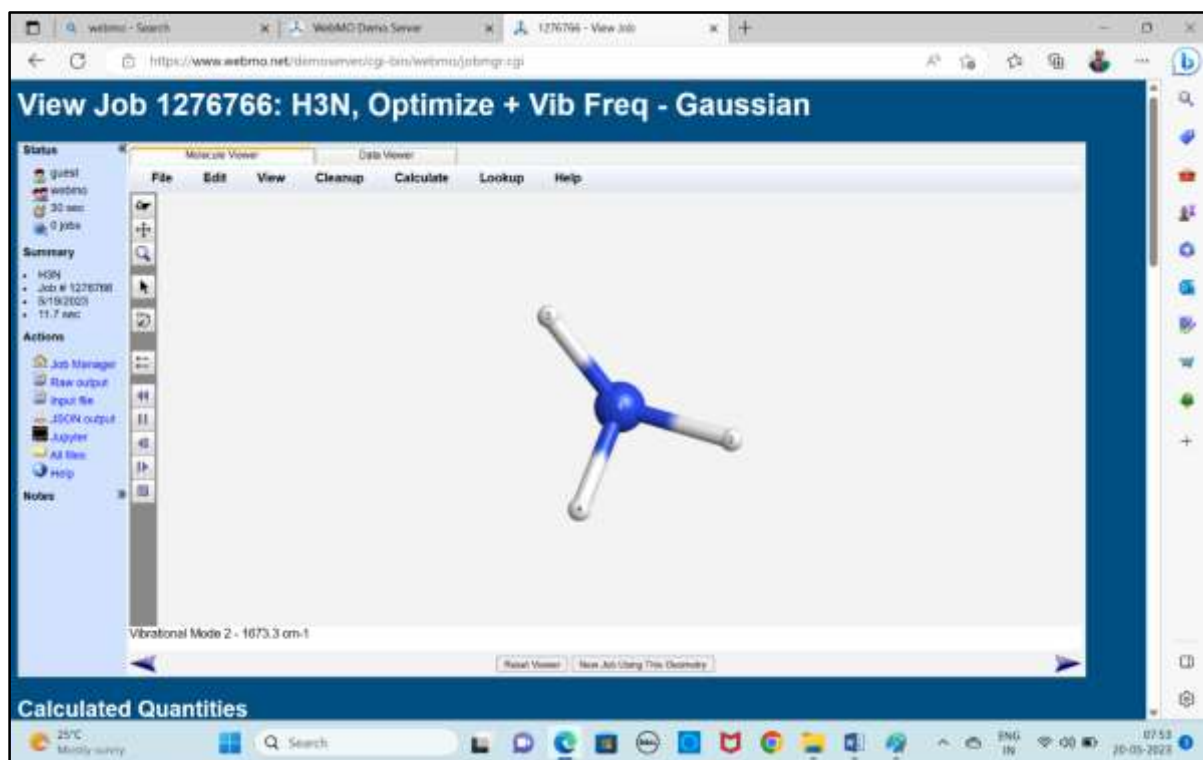
BLACK HOLES SUCK.

- 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

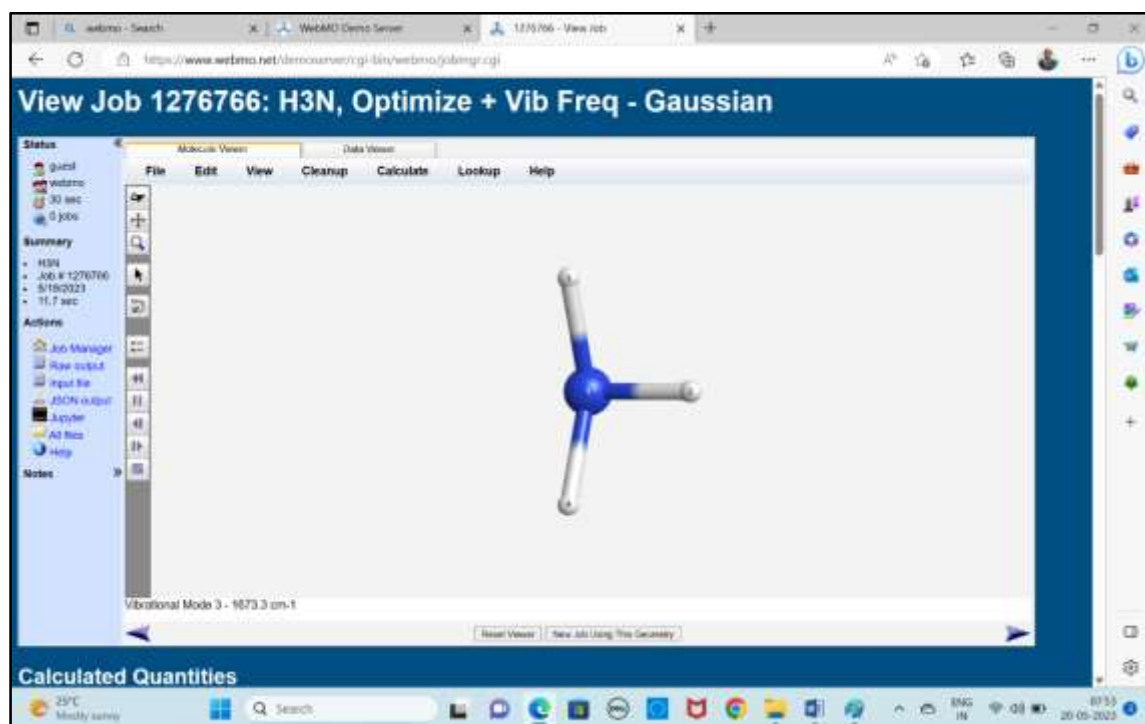
- The vibrational frequency at 1124.7 cm^{-1} corresponds to stretching of N-H bonds



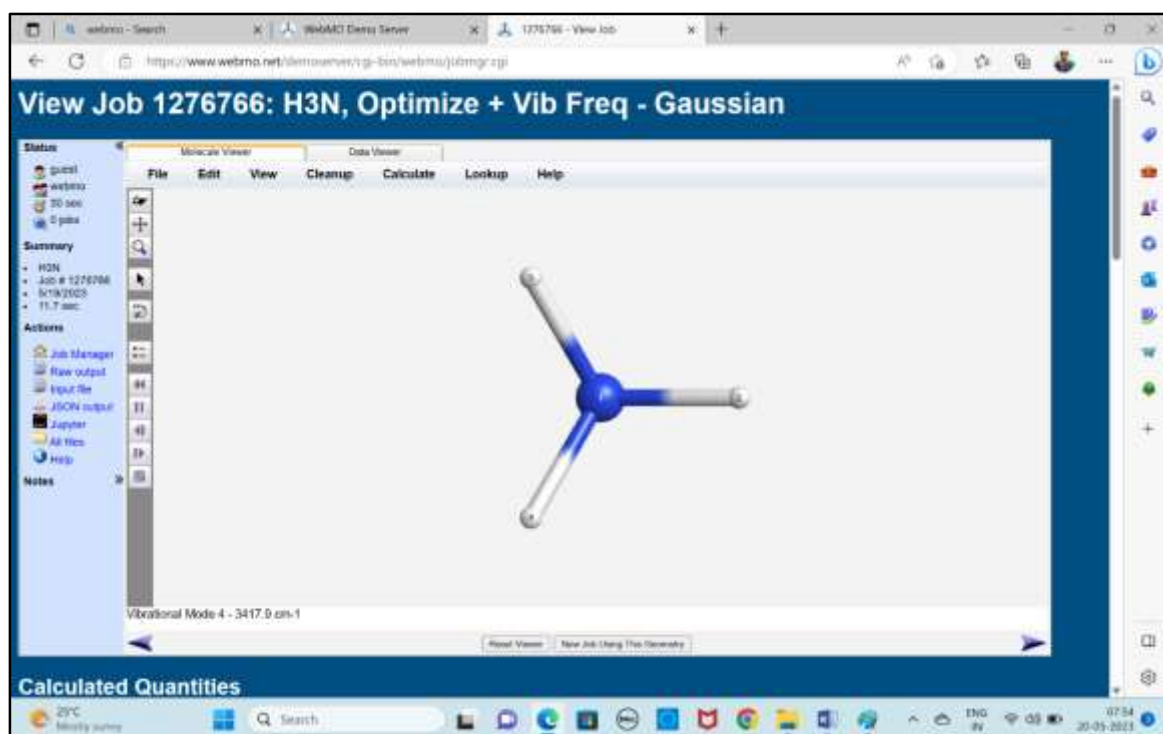
- The vibrational frequency at 1673.3 cm^{-1} corresponds to bending of N-H bonds



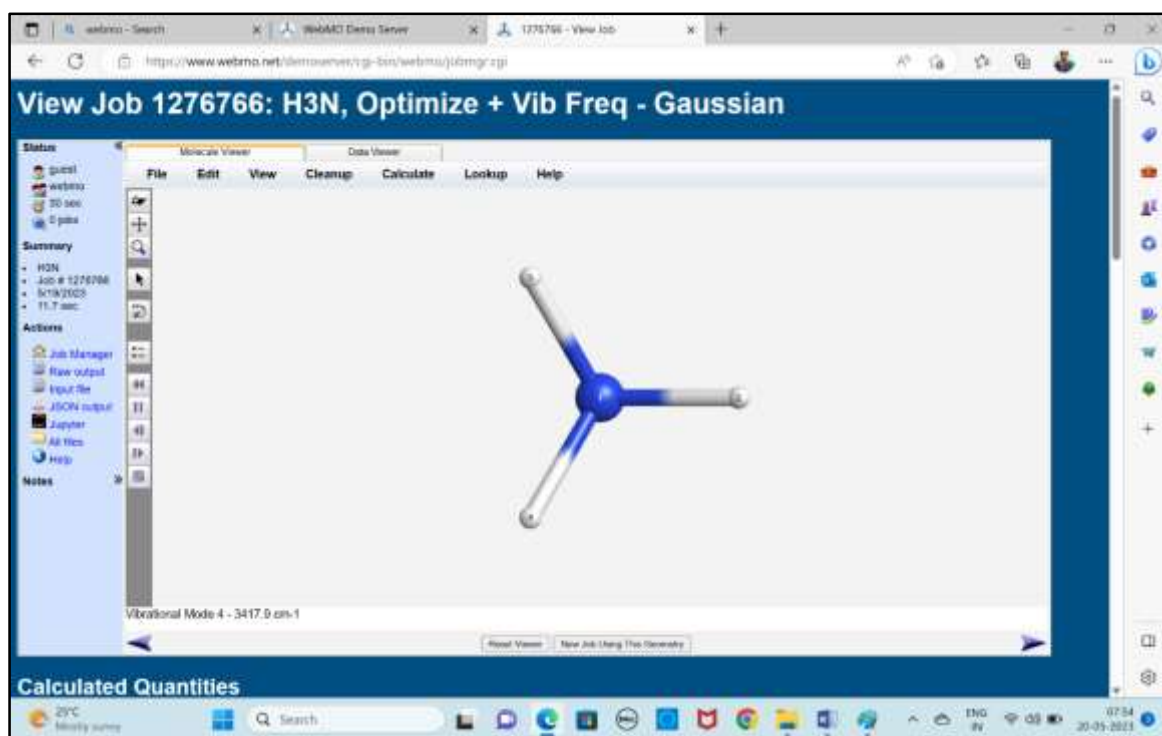
- The vibrational frequency at 1673.3 cm^{-1} corresponds to bending of N-H bonds, two types of bending vibrations occurs in the same frequency



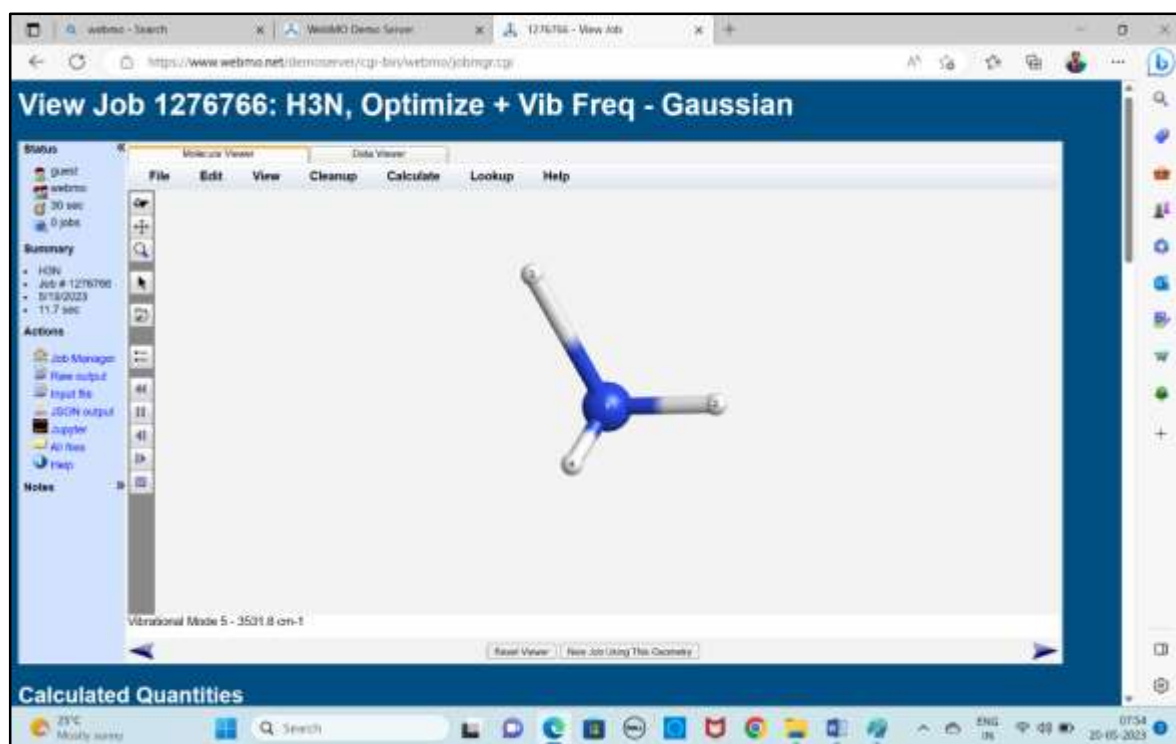
- The vibrational frequency at 3417.9 cm^{-1} corresponds to stretching of N-H bonds



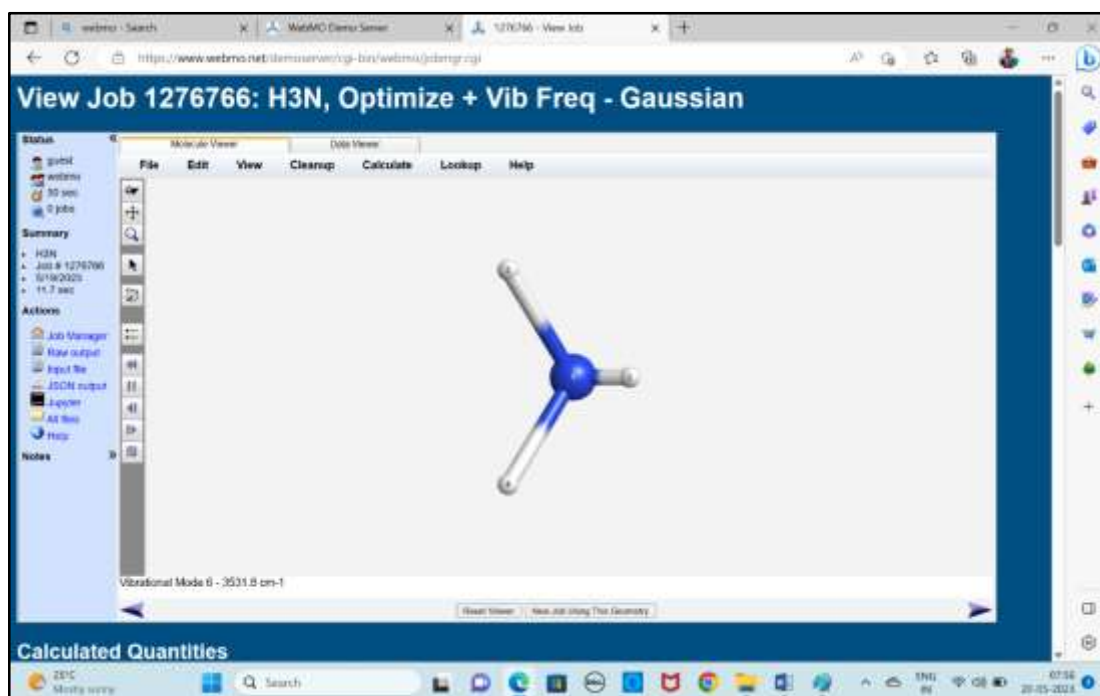
- The vibrational frequency at 3417.9 cm^{-1} corresponds to stretching of N-H bonds



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

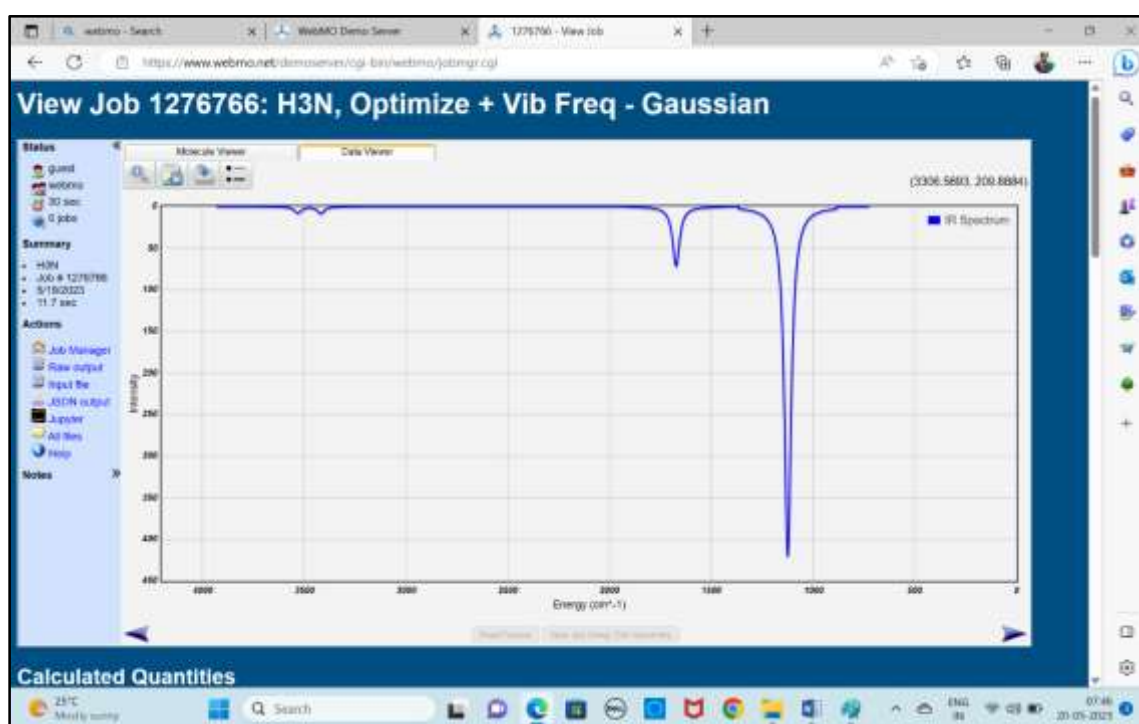


- The vibrational frequency at 3531.8 cm^{-1} corresponds to asymmetric stretching of N-H bonds



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 NH_3 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 NH_3 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 NH_3 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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