

# Calculating the Number of Modes of Vibrations in CO<sub>2</sub> 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 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<sub>2</sub> or N<sub>2</sub>. 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 CO<sub>2</sub> molecule using the formula
- To draw the 3D structure of CO<sub>2</sub> molecule in Jmol interface
- Save the 3D structure of CO<sub>2</sub> 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 CO<sub>2</sub> molecule

- CO<sub>2</sub> molecule is a linear molecule
- The molecule has 3 atoms
- Formula used
  - $3N-5$
  - $(3 \times 3) - 5 = 4$
  - The number of modes of vibrations in CO<sub>2</sub> molecule is 4

#### 4. Drawing the 3D structure of CO<sub>2</sub> 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 from carbon to add two oxygen atoms

##### 4.1 Energy optimization of CO<sub>2</sub> molecule in Jmol interface

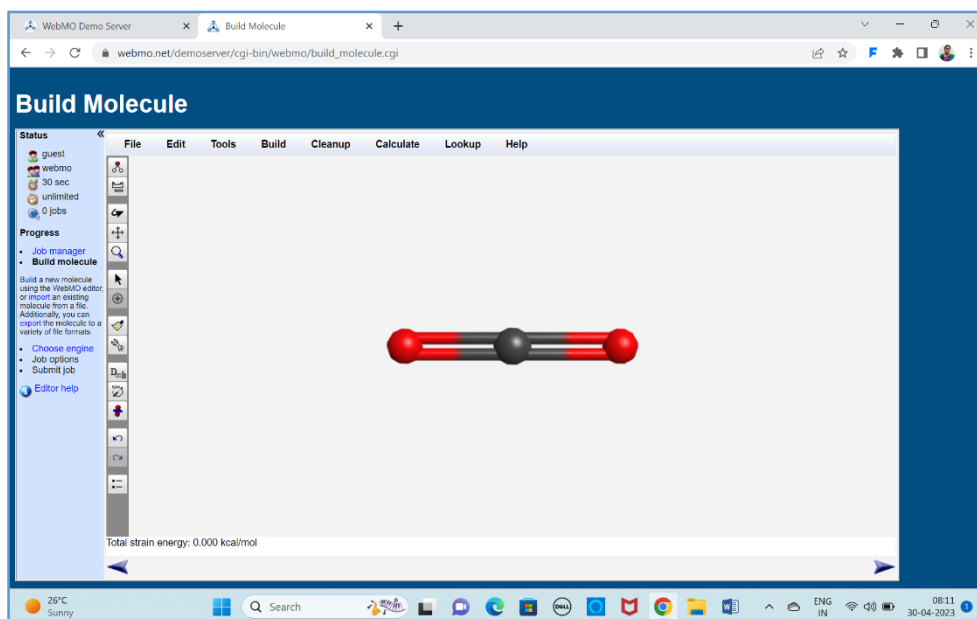
- Exit from the model kit menu
- Now right click on the molecule
- Select the option computation
- Then click optimize structure

##### 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 CO2)
  - Calculation – select as optimize+Vib Freq
  - Theory – B3LYP
  - Basis 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

The screenshot shows the WebMO Job Manager interface. The top navigation bar includes links for New Job, Refresh, Download, Move To, Delete, Utilities, and Logout. A sidebar on the left contains user information (guest, webmo, 30 sec, unlimited, 0 jobs), Folders (Inbox, Trash), Search (Search..., Displayed jobs, Search), and Help. The main area displays a table of jobs with columns for Number, Name, Description, Date, Status, Time, and Actions.

Number	Name	Description	Date	Status	Time	Actions
<input type="checkbox"/> 1265175	CO2	Optimize + Vib Freq - Gaussian	4/29/2023 22:59	Complete	7.3 sec	
<input type="checkbox"/> 1265174	CO2	Optimize + Vib Freq - Gaussian	4/29/2023 22:49	Complete	10.7 sec	
<input type="checkbox"/> 1265173	CO2	Optimize + Vib Freq - Gaussian	4/29/2023 22:47	Complete	8.9 sec	
<input type="checkbox"/> 1265164	S2- SP	SP - Gaussian	4/29/2023 22:07	Complete	1.2 sec	
<input type="checkbox"/> 1265163	S SP	SP - Gaussian	4/29/2023 22:07	Complete	1.2 sec	
<input type="checkbox"/> 1265162	DHB	Import - ORCA	4/29/2023 22:00	Complete	38:01	
<input type="checkbox"/> 1265157	S	Molecular Energy - Gaussian	4/29/2023 20:45	Complete	1.2 sec	
<input type="checkbox"/> 1265155	C	Molecular Orbitals - Gaussian	4/29/2023 18:57	Complete	1.1 sec	
<input type="checkbox"/> 1265154	CH4	Molecular Orbitals - Gaussian	4/29/2023 18:52	Complete	1.2 sec	
<input type="checkbox"/> 1265151	MP2(3-21G) N+ fin	SP - Gaussian	4/29/2023 18:29	Complete	1.1 sec	
<input type="checkbox"/> 1265150	P+	SP - Gaussian	4/29/2023 18:23	Complete	1.1 sec	
<input type="checkbox"/> 1265149	P	r - Gaussian	4/29/2023 18:22	Complete	1.1 sec	
<input type="checkbox"/> 1265148	P	SP - Gaussian	4/29/2023 18:15	Complete	1.1 sec	
<input type="checkbox"/> 1265147	N+	SP - Gaussian	4/29/2023 18:14	Failed	0.3 sec	
<input type="checkbox"/> 1265146	MP2(3-21G) N+ try	SP - Gaussian	4/29/2023 18:12	Failed	0.3 sec	
<input type="checkbox"/> 1265145	MP2(3-21G) N+	SP - Gaussian	4/29/2023 18:10	Failed	0.3 sec	
<input type="checkbox"/> 1265144	MP2(3-21G) N	r - Gaussian	4/29/2023 18:02	Complete	1.1 sec	

- Now the page with Job No. , Job Name and Job details appears

The screenshot shows the WebMO View Job 1265175: CO2, Optimize + Vib Freq - Gaussian interface. The top navigation bar includes links for File, Edit, View, Cleanup, Calculate, Lookup, and Help. A sidebar on the left contains user information (guest, webmo, 30 sec, unlimited, 0 jobs), Summary (CO2, Job # 1265175, 4/29/2023, 7.3 sec), Actions (Job Manager, Raw output, JSON output, Jupyter, All files, Help), and Notes. The main area displays a 3D molecular model of CO2. Below the model, there are buttons for Reset Viewer and New Job Using This Geometry. The bottom section shows Calculated Quantities.

View - Rotate (drag = rotate XY; alt-drag = rotate Z)

Reset Viewer New Job Using This Geometry

Calculated Quantities

- 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

WebMO Demo Server | 1265175 - View Job | Microsoft Word - ws4.docx

webmo.net/demoserver/cgi-bin/webmo/jobmgr.cgi

### Partial Charges

Atom	Symbol	Charge
1	C	0.288548
2	O	-0.144274
3	O	-0.144274

### Vibrational Modes

Mode	Symmetry	Frequency (cm <sup>-1</sup> )	IR Intensity	Actions
1	PIU	655.0514	28.6543	
2	PIU	655.0514	28.6543	
3	SGG	1362.3580	0.0000	
4	SGU	2421.4072	577.5542	

Frequency Scale Factor:

Normal Mode Amplitude:

Animation Speed:

IR Spectrum:

Peak Width (cm<sup>-1</sup>):

Quote: MARY HAD A LITTLE LAMB HIS FEET WERE BLACK AS SOOT, AND EVERYWHERE THAT MARY WENT HIS SOOTY FOOT HE PUT. – NONAME

25°C Mostly sunny | Search | 08:36 30-04-2023

WebMO Demo Server | 1265175 - View Job | Microsoft Word - ws4.docx

webmo.net/demoserver/cgi-bin/webmo/jobmgr.cgi

## View Job 1265175: CO<sub>2</sub>, Optimize + Vib Freq - Gaussian

**Status**

guest  
webmo  
30 sec  
unlimited  
0 jobs

**Summary**

- CO<sub>2</sub>
- Job # 1265175
- 4/29/2023
- 7.3 sec

**Actions**

- Job Manager
- Raw output
- JSON output
- Jupyter
- All files
- Help

**Notes**

Molecule Viewer | Data Viewer

(1857.3705, 1427.9514)

Intensity

Energy (cm<sup>-1</sup>)

Reset Viewer | New Job Using This Geometry

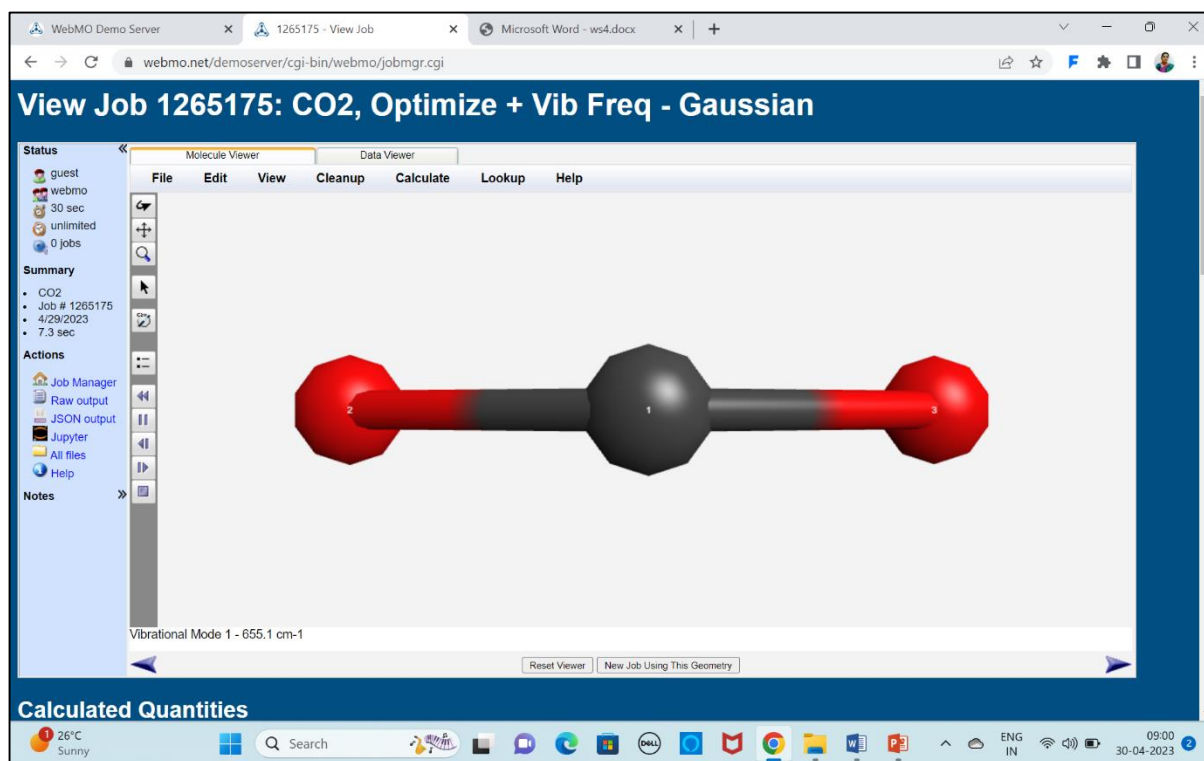
### Calculated Quantities

25°C Mostly sunny | Search | 08:42 30-04-2023

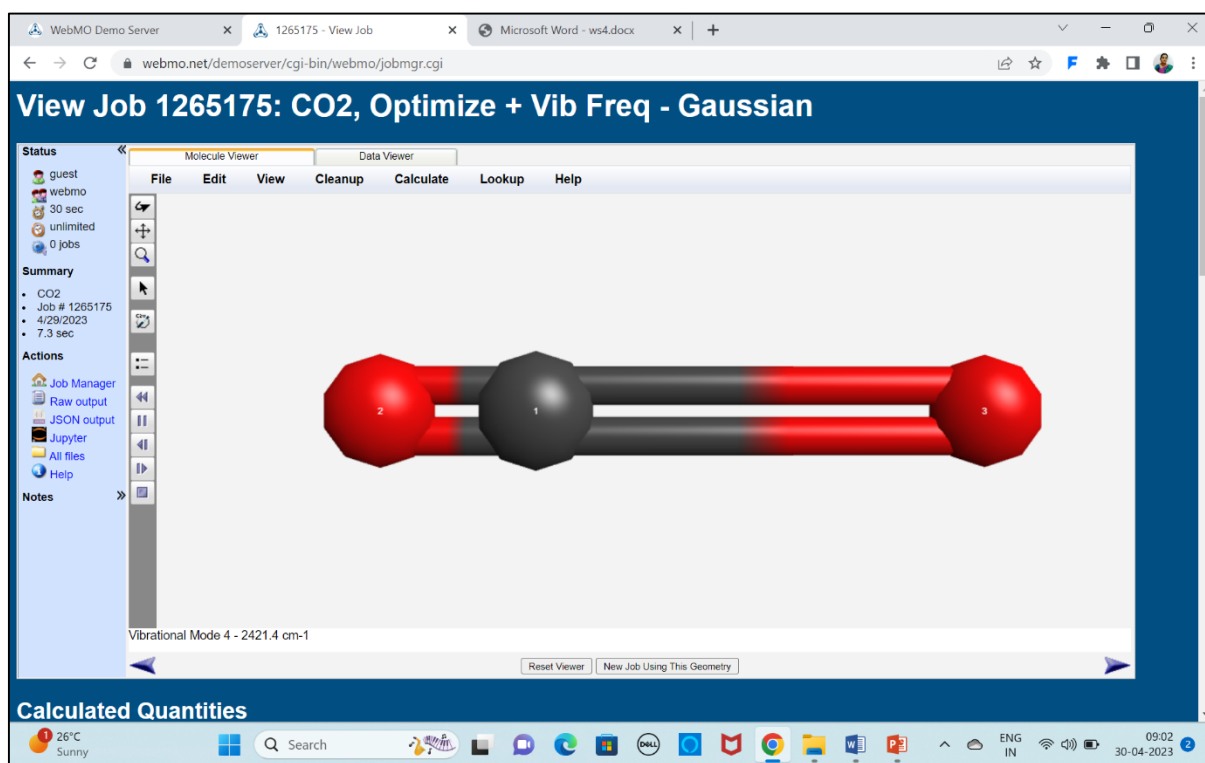
## 7. Assigning the peaks in the simulated FTIR spectra, for the types of Vibrations

- Vibrational modes detail show four types of vibrations for the CO<sub>2</sub> molecule
- The four types of vibrations are given with Frequency and IR intensity
- The Vibration at the frequency 655.05 cm<sup>-1</sup> corresponds to two types of bending motion or vibration in the CO<sub>2</sub> molecule
- By clicking on the animate option under Action you can view the animated bending vibrations
- The Vibration at the frequency 1362.35 cm<sup>-1</sup> corresponds to symmetric stretch in the CO<sub>2</sub> molecule with IR intensity as 0.00
- The symmetric stretch of the molecule will not change the dipole moment of the molecule hence we won't get any IR peak for such a vibration as per IR selection rule
- The Vibration at the frequency 2421.40 cm<sup>-1</sup> corresponds to asymmetric stretch in the CO<sub>2</sub> molecule
- Only two peaks are obtained for CO<sub>2</sub> molecule, the strong peak at 2421.40 cm<sup>-1</sup> corresponds to asymmetric stretch and the weak peak at 655.05 cm<sup>-1</sup> corresponds to bending vibrations.
- By clicking on the peaks also we can view the animated vibrations of the molecule

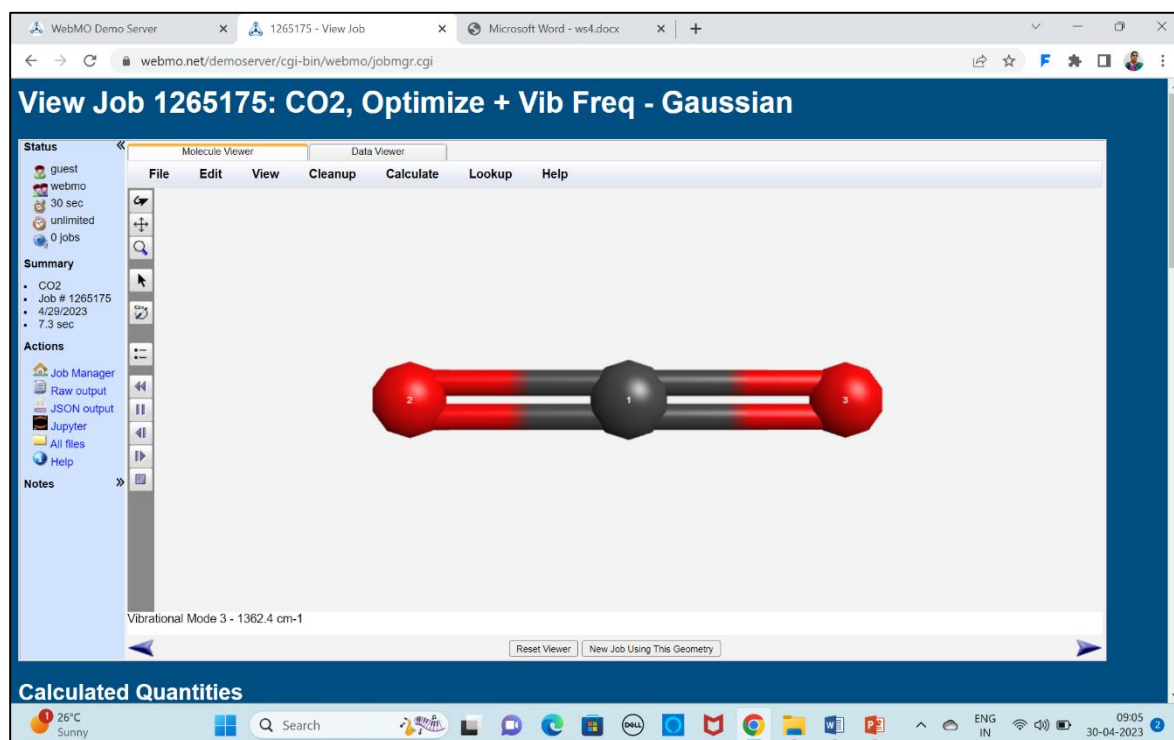
### Bending Vibrations at 655.05 cm<sup>-1</sup> in CO<sub>2</sub> molecule



## Asymmetric stretch at $2421.40\text{ cm}^{-1}$ in $\text{CO}_2$ molecule



Symmetric stretch at  $1362.4\text{ cm}^{-1}$  in  $\text{CO}_2$  molecule (no change in dipole moment- no peak in IR spectra)





#### **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 CO<sub>2</sub> molecule results in 4 types of vibrations
- The four types of vibrations are symmetric stretch, asymmetric stretch and two types bending vibrations
- Among the four types of vibrations the symmetric stretch will not change the dipole moment therefore IR peak corresponding to the symmetric stretch was not obtained
- The two types of bending vibrations will change the dipole moment to the same extent so we get single peak in IR corresponding to both the bending vibrations
- The asymmetric stretch will change the dipole moment drastically therefore we get a strong peak in IR spectrum.

#### **Acknowledgement**

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