

Examination of O₂

In this first part, we will calculate the spectra of a diatomic molecule using IQMol and QChem and predict the spectra using the simple harmonic oscillator solution to the Schrödinger Equation. We will get a first glimpse as to why certain vibrations are IR inactive.

- 1) Open IQMol and follow slides 2 – 8 in the IQMol tutorial to create an O₂ molecule
 - a. Select O from the Build Element menu
 - b. Hold Alt and click in the viewer to add O atoms
 - c. Click on one of the O atoms and drag to the other to make a bond
 - d. Click on the minimize energy button to make a good initial guess for the geometry of the molecule
- 2) Follow slides 13 – 20 in the IQMol tutorial and do a geometry relaxation and vibrational frequency calculation of O₂ using QChem Servers:
 - a. Select Calculation -> QChem Setup
 - b. Add a second job by clicking on the big green '+' sign
 - c. Select 'Job 1' and input the following options:
 - i. Calculate: Geometry
 - ii. Method: B3LYP
 - iii. Basis: 6-31G
 - iv. Multiplicity: 3
 - v. Check the unrestricted box
 - d. Select 'Job 2' and input the following options:
 - i. Calculate: Frequency
 - ii. Method: B3LYP
 - iii. Basis: 6-31G
 - e. Make sure that Server says QChem and click 'Submit'. You will be prompted to give a name to your job.
- 3) **While that calculation is running, calculate the wavenumber associated with the transition between the ground state and the first excited state of the vibration in O₂ ($k = 1142 \text{ N m}^{-1}$), what is the predicted wavenumber of an excitation from the ground state to the first excited state.**
- 4) Once the QChem calculation ends you will be prompted. Save the output in a new directory. It should then open the output file.
 - a. Click on the arrow beside your completed job to open a drop down menu.
 - b. Click the arrow beside frequencies to present all the calculated frequencies. They will be presented in cm^{-1} . You can animate your O₂ molecule by double clicking on the wavenumber.
 - c. **Compare the wavenumber you calculated to the one found by QChem. Why do you think they differ?**
 - d. Double click on the word 'Frequencies'
 - i. A new window will open. From here you can view a spectrum of all the vibrations.

- e. **Look at the spectrum. How many peaks are there? Look at the table with all the vibrational modes and the intensities. Confirm the number of peaks which should appear in the spectrum by the intensity of each peak. Explain the results.**

Examination of CH₄ and CH₃D

In this second part, we will examine the spectra of methane and deuterated methane, to see that different vibrations have different excitation energies and further examine why certain vibrations are IR inactive. We will also see the effect on changes in mass on the vibrational frequencies.

- 5) Following the procedure outlined in slides 9 and 10 of the IQMol Tutorial and create a CH₄ molecule.
- 6) Setup a Geometry optimization and frequency calculation similar to the O₂ molecule using the following options:
 - a. Select Calculation -> QChem Setup
 - b. Add a second job by clicking on the big green '+' sign
 - c. Select 'Job 1' and input the following options:
 - i. Calculate: Geometry
 - ii. Method: B3LYP
 - iii. Basis: 6-31G
 - iv. Multiplicity: 1
 - d. Select 'Job 2' and input the following options:
 - i. Calculate: Frequency
 - ii. Method: B3LYP
 - iii. Basis: 6-31G
 - iv. In the bottom left panel there is a menu called "Frequencies". Select it and check the "Isotopic Analysis" box. Over in the "Generated Input File" pane a "\$isotopes" section appears. Make the section say (note where there are spaces):

\$isotopes

1 0

1

5 2.01410

\$end

Setup

Advanced

Job Section

Job 2

Edit

Calculate

Frequencies

Charge

0

Method

B3LYP

Multiplicity

1

Basis

6-31G

ECP

None

Exchange

HF

Correlation

None

SCF Control

Wavefunction Analysis

Frequencies

☐ Raman Frequencies
 ☒ Isotopic Analysis
 ☐ Project Out Translational And Rotational Degrees Of Freedom
 ☐ Compute Anharmonic Corrections

VCI Quanta

0

Generated Input File:

```

H      0.1145732      0.4800080      0.2598970
H      0.4860763     -0.8462580     -0.4402726
H      0.4880618     -0.2611938      1.4286999
$end

$rem
BASIS = 6-31G
GUI = 2
JOB_TYPE = Optimization
METHOD = B3LYP
SCF_CONVERGENCE = 8
UNRESTRICTED = 1
$end

@@@
!
$molecule
read
$end

$rem
BASIS = 6-31G
GUI = 2
ISOTOPEs = 1
JOB_TYPE = Frequency
METHOD = B3LYP
SCF_CONVERGENCE = 8
$end

$isotope
1 0
1
5 2.01410
$end

```

Server

QChem

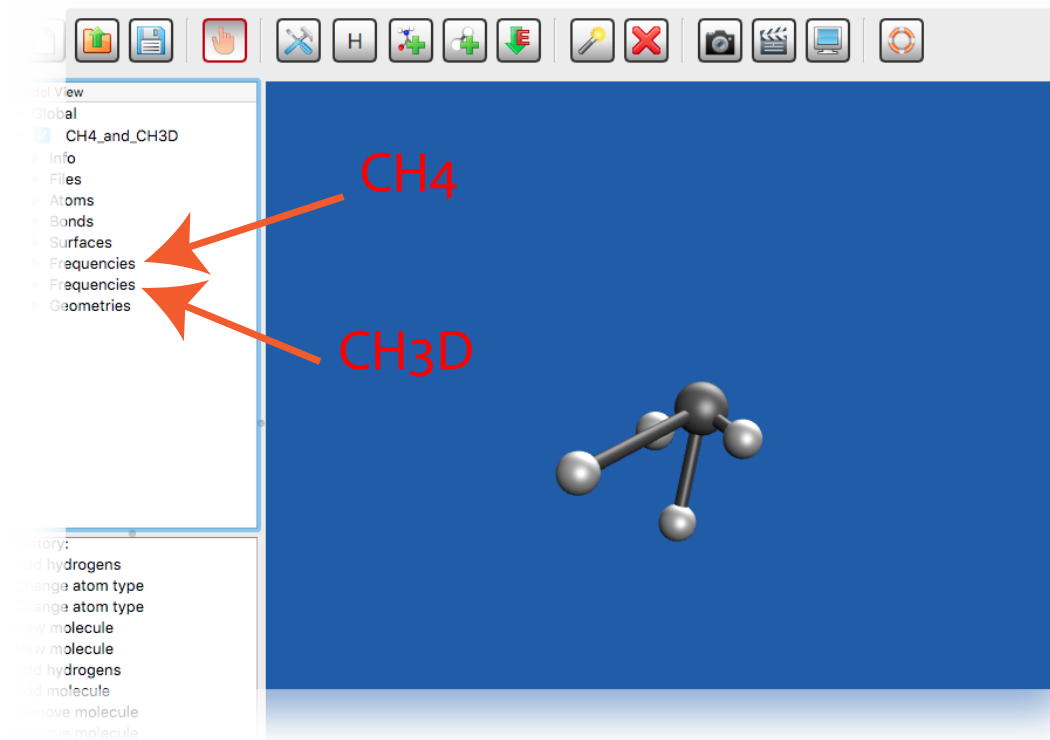
Reset

Cancel

Submit

hydrogens

- e. This sets up the calculation to make CH_4 and CH_3D as well as calculate the vibrational spectrum of both. Make sure that Server says QChem and click 'Submit'. You will be prompted to give a name to your job.
- 7) Once the optimization is complete, save the output in a new directory. There will be two Frequencies menus on the left panel. The top one is for CH_4 and the bottom one will be for CH_3D .

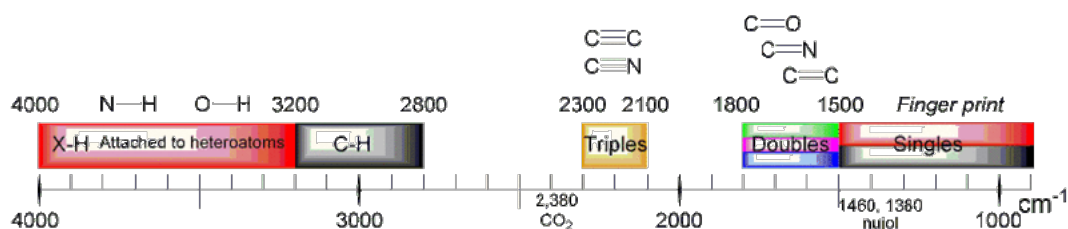


- 8) Open the vibrational frequencies dialogue for CH₄. Describe the vibrational motions that correspond to each of the identified wavenumbers in the spectrum as either stretching or bending.
- 9) There are three normal modes that do not have intensity in the IR spectrum. Explain why this is.
- 10) Open the vibrational frequencies dialogue for CH₃D. Describe the vibrational motions that correspond to each of the vibrational motions in the spectrum as either stretching or bending. Determine which vibrations primarily involves the deuterium, involves both the deuterium and hydrogen, or primarily involves hydrogen (when the vibration animation is off, clicking on a frequency will show pink arrows which will help show which atoms are involved in the vibration). Compare the harmonic frequencies of the CH stretches in CH₄ and the CD and CH stretches in CH₃D. Using

$$\Delta E = \hbar \sqrt{\frac{k}{\mu}}$$

explain the trends that you observe.

- 11) The following figure describes the general ranges one may observe certain types of vibrational spectra. Based on our discussion of CH₄ versus CH₃D, explain why we see N-H/O-H/C-H vibrational modes at larger wavenumbers than CC/CO/CN bonds.



Examination of Anharmonicity

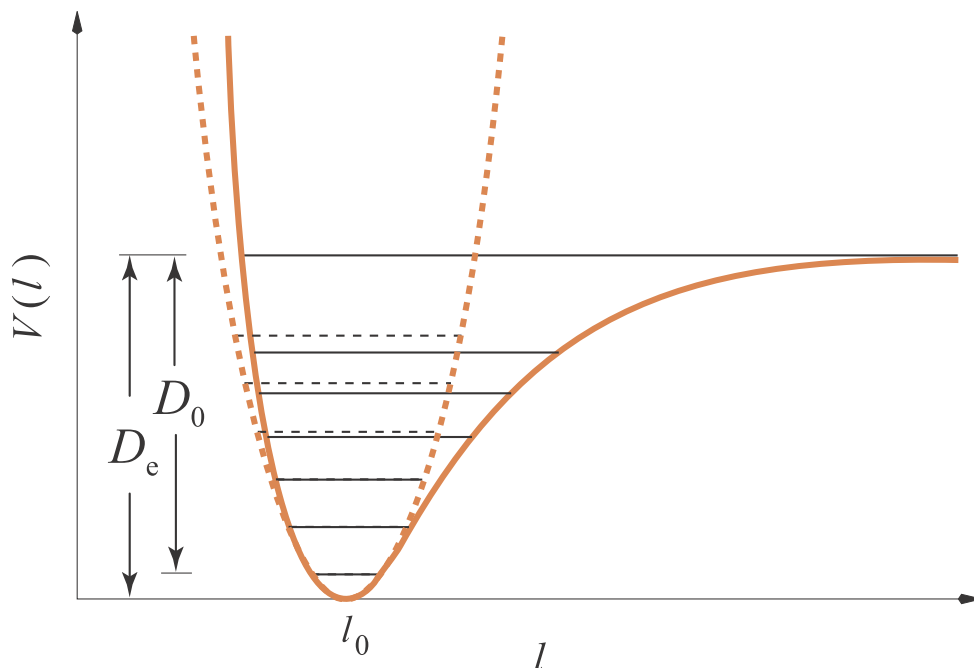
To calculate our predictions of vibrational spectra, we have been assuming a harmonic (parabolic) potential. In reality, the potential which molecules vibrate in is anharmonic where as the spacing increases between two atoms, the potential levels off resulting in the bond breaking. In this final part we will explore the difference between these two potentials.

12) Shown below are plots illustrating how the potential energy, $V(l)$, depends on the bond length, l , for the harmonic (dashed line) and anharmonic (solid line) potential. Also shown are the first 6 harmonic and anharmonic vibrational energy levels. Given that all vibrating bonds are in a potential that has a similar shape to the anharmonic potential, when is it appropriate to apply the harmonic potential to describe almost any system?

13) From the figure it can be seen that the harmonic potential is much tighter than the anharmonic potential. This can be characterized by having a larger spring constant, k . Transition energies between energy levels for the harmonic potential are also consistently larger than for the anharmonic potential. Given that

$$\Delta E = \hbar \sqrt{\frac{k}{\mu}}$$

explain why this is.



14) Using again the figure from 11), based on the discussion from 13), explain why the wavenumber range for C=C is larger than the wavenumber range for C-C vibrations.