Marking Scheme - CHEM1030 Quantum Chemistry Practical B: Equilibrium geometry and vibrational spectrum of sildenafil

Feature	Maximum mark out of 100
Introduction: objectives and problem setting	5
Introduction: description of methods	10
Molecule drawing in GaussView	5
Energy and gradient convergence plots	10
Bond length plot (X-ray against PM6)	5
Bond length accuracy discussion	15
Vibrational mode classification	10
Vibrational mode and IR spectrum accuracy discussion	15
Report: quality of writing	10
Report: quality of typesetting	5
Report: quality of references	10

Introduction: objectives and problem setting [5 points]

The introduction should contain the following statements or their equivalents:

1. The objective of the work is to determine the minimum energy geometry of sildenafil and to use that geometry to determine its vibrational frequencies.
2. The work starts from a schematic drawing of the sildenafil molecule and proceeds in two stages: energy minimisation and calculation of vibrational frequencies.
3. Some of the resulting vibrational modes are classified and some of the vibrational frequencies are compared to the experimental data.

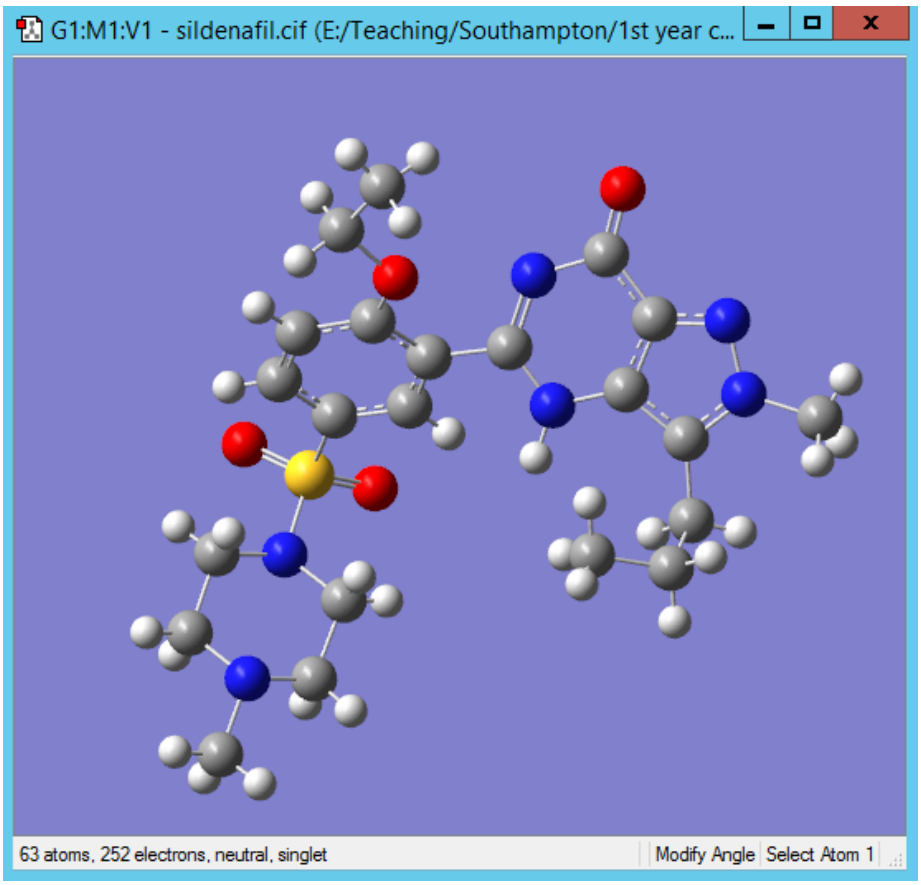
Introduction: description of methods [10 points]

The introduction should contain the following statements or their equivalents:

1. The software package used is Gaussian09, with its graphical user interface called GaussView.
2. The method used for the calculation of energies is PM6, which is a semi-empirical method that differs from the full quantum mechanical treatment in that it replaces complicated integrals with empirical parameters that are derived from experimental databases.
3. Geometry optimisation is performed using a variant of the gradient descent algorithm: at each point in the optimisation process, the gradient of the energy with respect to nuclear coordinates is calculated and the program makes a step down that gradient until a minimum of the energy is located.
4. The vibrational frequencies for the resulting geometry are calculated by computing a matrix of second energy derivatives with respect to atomic coordinates and calculating eigenvalues of that matrix, which are related to the vibrational frequencies as described in the handout.

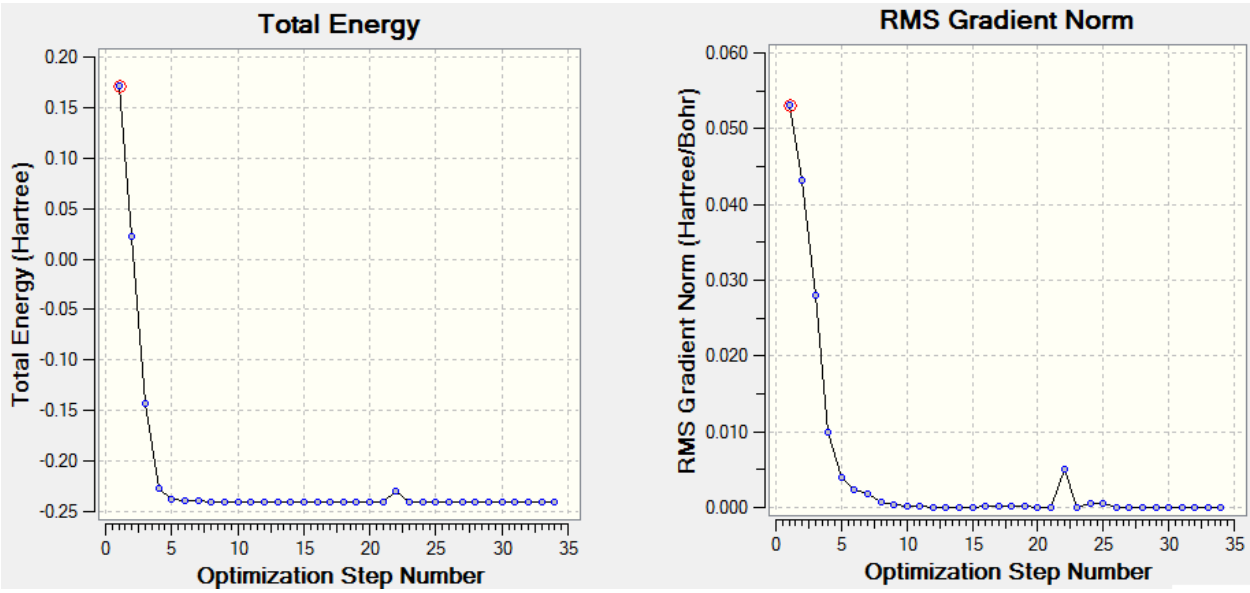
Molecule drawing in GaussView [5 points]

A picture similar to the following should be included



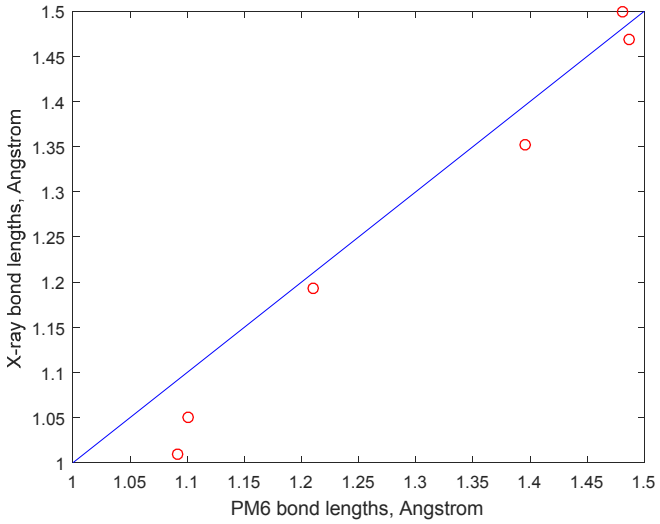
Energy and gradient convergence plots [10 points]

Pictures similar to the following should be included



Bond length plot

A few bond lengths should be extracted from the optimized geometry and the X-ray crystallography data provided. The bond lengths from the PM3 optimization should be plotted against the bond lengths from the X-ray data to produce a plot that looks similar to the following:



Bond length accuracy discussion [15 points]

Students are expected to observe that

1. The agreement between PM6 and X-ray data is not particularly good.
2. The error is most likely to be on the PM6 side because of its approximate nature.
3. The disagreement is of the order of 5% of the bond length.
4. Any applications that require bond lengths to precision greater than about 10% should be using more sophisticated methods than PM6.
5. For the purposes of rough geometry optimization, PM6 is adequate.

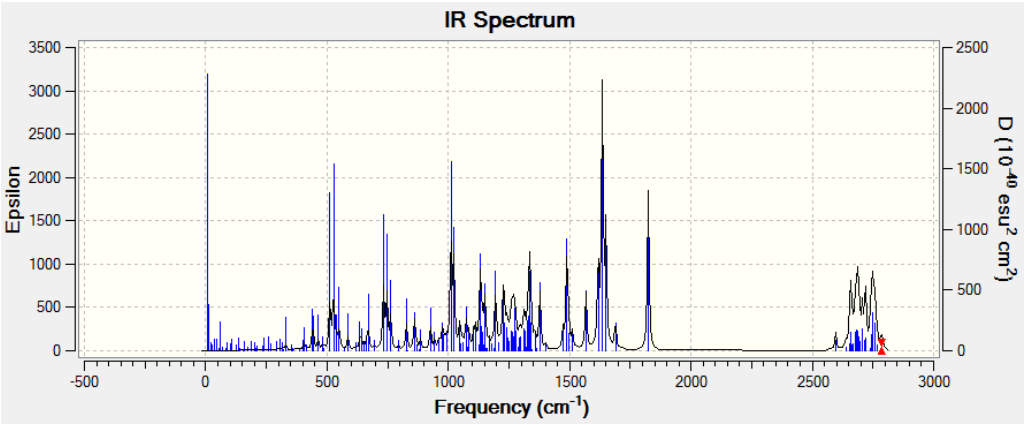
Vibrational mode classification [10 points]

Students are expected to pick a few normal modes (frequencies may differ) and

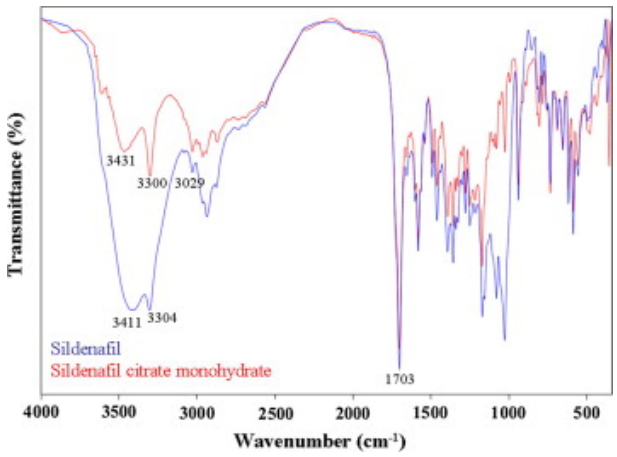
1. Conclude that low frequencies correspond to collective motions of the whole molecule.
2. Conclude that high frequencies correspond to localized vibrations.
3. Include a representative pick of the different normal modes and classify them into stretching, bending, rocking, wagging and twisting types.

Vibrational mode and IR spectrum accuracy discussion [15 points]

A picture similar to the following should be presented.



This picture should be compared to its literature equivalent, for example



the students are expected to observe that:

1. Gaussian plots the X axis in the direction that is opposite to the traditional direction.
2. All high frequencies are massively under-estimated by Gaussian.
3. Low frequencies are reasonably well reproduced.

Report: quality of writing [10 points]

The report should:

1. Be neatly formatted.
2. Not use screenshots of equations instead of correctly entered equations.
3. Use academic English (third person, past tense, neutral and factual).
4. Be written clearly and succinctly.

Report: quality of typesetting [5 points]

Bonus points should be awarded for the use of LaTeX and Origin, as well as for use of consistent, readable and elegant formatting and presentation.

Report: quality of references [10 points]

References should:

1. Only include academic sources (textbooks, peer reviewed journals).
2. Use a consistent referencing style (any style is fine).
3. Not contain any web links.
4. Not include any non-peer-reviewed sources.