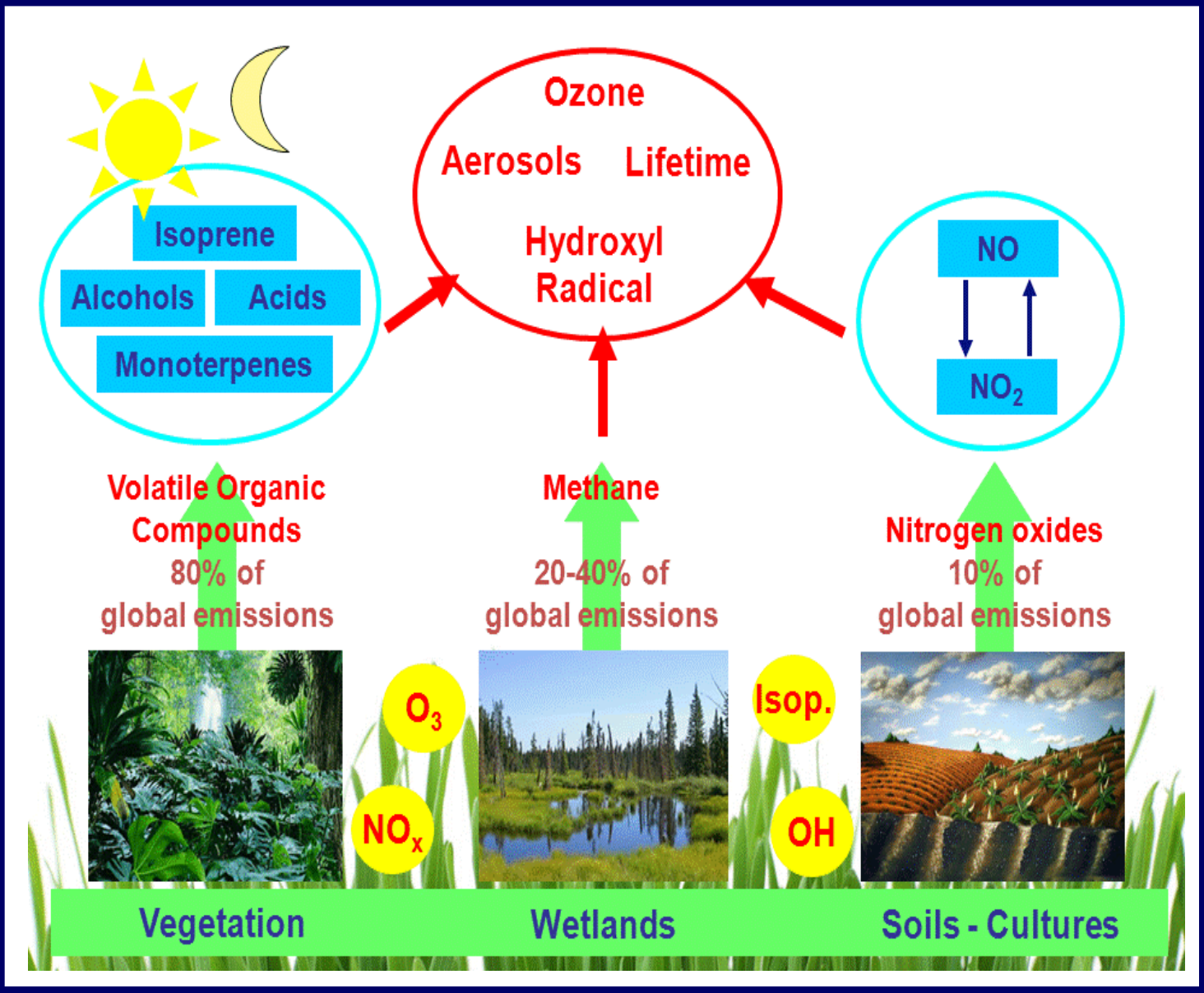

Climate Change and the Underrated Forest

Autumn 2015

The **Scholars** Programme

Tutor Name: Dr S. Allpress

Pupil Name_____

The Scholars Programme – Autumn 2015 – Pupil Feedback Report

Grade	Marks	What this means
1st	70+	Performing to an excellent standard A-level
2:1	60-69	Performing to a good standard at A- level
2:2	50-59	Performing to an excellent standard at GCSE level
3rd	40-49	Performing to a good standard at GCSE level
Workings towards a pass	0-39	Workings towards a pass
Did not submit	DNS	No assignment received by The Brilliant Club

Lateness	
Any lateness	10 marks deducted
Plagiarism	
Some plagiarism	10 marks deducted
Moderate plagiarism	20 marks deducted
Extreme plagiarism	Automatic fail

Name of PhD Tutor	Dr S. Allpress		
Title of Assignment			
Name of Pupil			
Name of School			
ORIGINAL MARK / 100		**FINAL MARK / 100**	
DEDUCTED MARKS		**FINAL GRADE**	

If marks have been deducted (e.g. late submission, plagiarism) the PhD tutor should give an explanation in this section:

Learning Feedback Comment 1 - *Enter Key Learning Priority Here*	
What you did in relation to this Key Learning Priority	**How you could improve in the future**
Learning Feedback Comment 2 – *Enter Key Learning Priority Here*	
What you did in relation to this Key Learning Priority	**How you could improve in the future**
Learning Feedback Comment 3 – *Enter Key Learning Priority Here*	
What you did in relation to this Key Learning Priority	**How you could improve in the future**
Resilience Comment	
How you showed learning resilience during the course	**How you could build learning resilience in the future**

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Course Rationale

Global warming and climate change are a constant news item in modern life. However these stories focus on the man-made causes and the legislation put in place to combat the change. However, the role of vegetation fails to be considered; are they contributing to the problem or preventing the situation from becoming much worse. How can scientist examine the emissions from plant sources? What reactions occur between these emissions and other atmospheric species? This course is aimed at students with an interest in chemistry and environmental science and looks into one of the biggest issues of the 21st century.

The initial tutorial will introduce the basic concepts of chemistry and atmospheric processes, such as structure and reactivity of molecules – including transition states, common atmospheric oxidants (molecules that provide a source of oxygen) and the role of aerosols. Once the students are confident with these initial concepts, they will apply this knowledge with the context of my thesis; through presentation of my data, pupils will discover how we establish the reactivity within a molecule, how this influences how the reaction occurs, how we establish the appropriate transition state for a chemical process and based on all of this which are likely to be the most abundant reaction products.

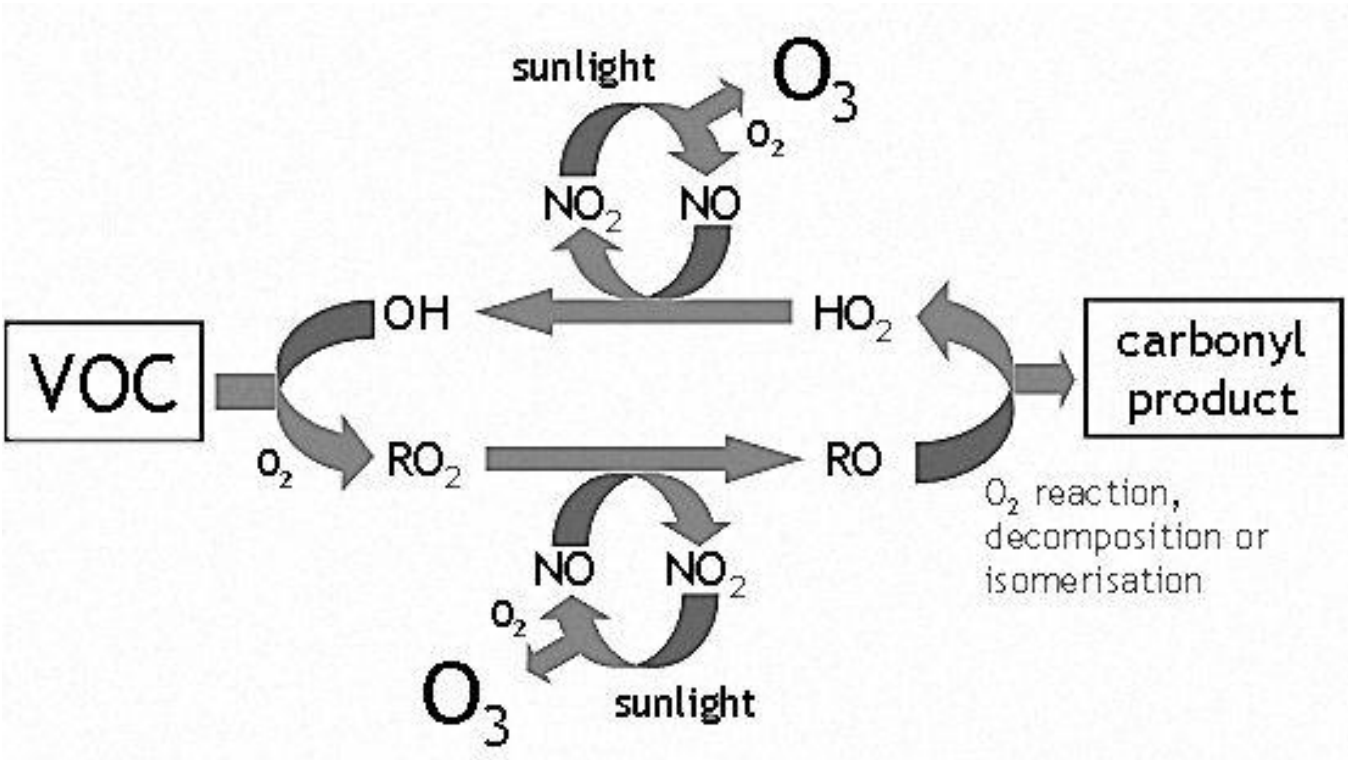
Mark Scheme

Key Skill	1st	2.1	2.2
Scientific Understanding	☐ The student can recognise that IR spectroscopy absorbs radiation to examine bond vibration, with examples ☐ The student can explain in detail the working of a mass spectrometer and explore the at least two particular techniques ☐ Can give clear indications as to why we use computational techniques, with at least one specific example ☐ The student can define a basis set and explain how we can manipulate them to improve accuracy using examples	☐ The student can recognise that IR spectroscopy absorbs radiation to examine bond vibration ☐ The student can explain in detail the working of a mass spectrometer and explore the one particular technique ☐ Can give clear indicate as to why we use computational techniques ☐ The student can define a basis set and explain how we can manipulate them to improve accuracy	☐ The student can explain the general concepts of infrared spectroscopy ☐ The student can describe the basic working of a mass spectrometer without an attempt to explore a specific technique ☐ Give a basis suggestion to the uses of computational chemistry ☐ The student is able to explain a basis set but fails to analyse how we can manipulate them for specific situations
Effective Communication	☐ Students construct a coherent argument ☐ Answers fully address the requirements of the question ☐ Students can recognise the links between the key techniques ☐ Clear sense of direction throughout the discussion leading to an appropriate conclusion ☐ Students include appropriate vocabulary ☐ <5 spelling, punctuation and grammar errors	☐ Students construct a logical argument ☐ Answers address most of the requirements of the question ☐ Students can recognise some links between the key techniques ☐ Clear sense of direction throughout most of the discussion leading to an appropriate conclusion ☐ Students mostly include appropriate vocabulary ☐ <15 spelling, punctuation and grammar errors	☐ Students cannot communicate the argument clearly ☐ Answers address some of the requirements of the question ☐ Students are unable to establish the links between the key techniques ☐ Appropriate conclusion for the attempted discussion ☐ Students attempt to use the appropriate vocabulary ☐ >15 spelling, punctuation and grammar errors
Critical Analysis of Chemical Techniques	☐ The student is able to distinguish the advantages and limitations of IR and analyse the consequence of this ☐ The student is able to distinguish the advantages and limitations of MS and analyse the consequence of this	☐ The student is able to describe the advantages and limitations of IR but fails to explore the consequences ☐ The student is able to describe the advantages and limitations of MS but fails to explore the consequences	☐ The student is able to list the advantage and limitations of IR but fails to explore the consequences ☐ The student is bale to list the advantages and disadvantages of MS but fails to explore the consequences
Effective Use of Sources	☐ The pupil has consulted at least 10 reliable sources ☐ The sources are properly cited in the text ☐ All sources are properly presented in the bibliography	☐ The pupil has consulted at least 10 sources, however they may not all be reliable ☐ The sources are all cited in the text, but not all correctly ☐ All sources are present in the bibliography, but not properly	☐ The pupil has consulted at least 5 sources, however they may not all be reliable ☐ The sources are not all cited in the text ☐ The bibliography is incomplete

Glossary of Keywords and Abbreviations

Anthropogenic Emission: Emissions that relating to or resulting from the influence of humans
Atomic Orbital (AO): A mathematical function describing the wave like behaviour of an electron or a pair of electrons in an atom **Basis Set:** the mathematical representation of molecular orbitals within a molecule
Biogenic Emission: Emissions that come from natural sources, e.g. vegetation
Double bond: A chemical bond between two chemical elements involving 4 bond electrons rather than the usual 2
Electrons (e^-): A subatomic particle, with a negative elementary electrical charge
Energy Maxima: The structure of the greatest energy on the potential energy surface
Energy Minima: The structure of lowest energy on the potential energy surface
Fragmentation Pattern: The dissociation of unstable molecular ions formed from the molecules through an ionisation chamber of a mass spectrometer
Hydroxyl Radical: The neutral form of the hydroxide ion (HO^-), with an unpaired electron $OH^\bullet$
Infrared Radiation (IR): Radiation with a wavelength from ~800 nm to 1 mm
Isoprene: The simplest terpene with the molecular formula C_5H_8
Mass Spectrometry (MS): An analytical technique used to identify the amount and type of chemicals present in a molecule by measuring the mass-to-charge (m/z) ratio
Molecular Orbitals (MO): A mathematical function describing the wave like behaviour electrons in a molecule
Monoterpene: Consist of 2 isoprene units with the molecular formula $C_{10}H_{16}$
Nitrate Radical: The neutral form of the nitrate ion (NO_3^-), with an unpaired electron $NO_3^\bullet$
Organic Chemistry: The scientific study of structure, properties and reactions of matter containing carbon
Oxidant: A molecule that provides a source of oxygen
Ozone: With the chemical formula O_3, exists as part of the Earth's atmosphere
Potential Energy Surface (PES): Describes the energy of a system in terms of certain parameters, normally the position of the atoms
Reaction Coordinate: Representation of the progression of a reaction pathway
Sesquiterpene: Consists of 3 isoprene units with the molecular formula $C_{15}H_{24}$
Terpene: Large and diverse class of organic compounds, produced by a variety of plants and some insects. They are constructed from multiples of the isoprene unit, $(C_5H_8)_n$, where n is the number of isoprene units
Saddle Point: A stationary point on the potential energy surface that is not an energy minima or maxima
Spectroscopy: Investigation and measurement of spectra produced when matter interacts with or emits electromagnetic radiation
Transition State (TS): State corresponding to the highest energy along the reaction coordinate. It has more free energy than the reactant or product, thus is the least stable state
Troposphere: The lowest portion of the Earth's atmosphere, up to 20 km from the Earth's surface
Vibration: Motion occurring when atoms in a molecule are in a periodic motion

Tutorial 1 – What on *air* is going on?!



What is the Purpose of Tutorial 1?

- Introduction to myself and the course
- Introduction to the link between molecular structure and reactivity
- Introduction to atmospheric chemistry including the common atmospheric oxidants
- To combine the structural reactivity and atmospheric oxidants to determine transition state structure

Tutorial 1 – Outline:

<u>Introduction</u>

1. What do you understand by the term climate change?

Molecular Structure

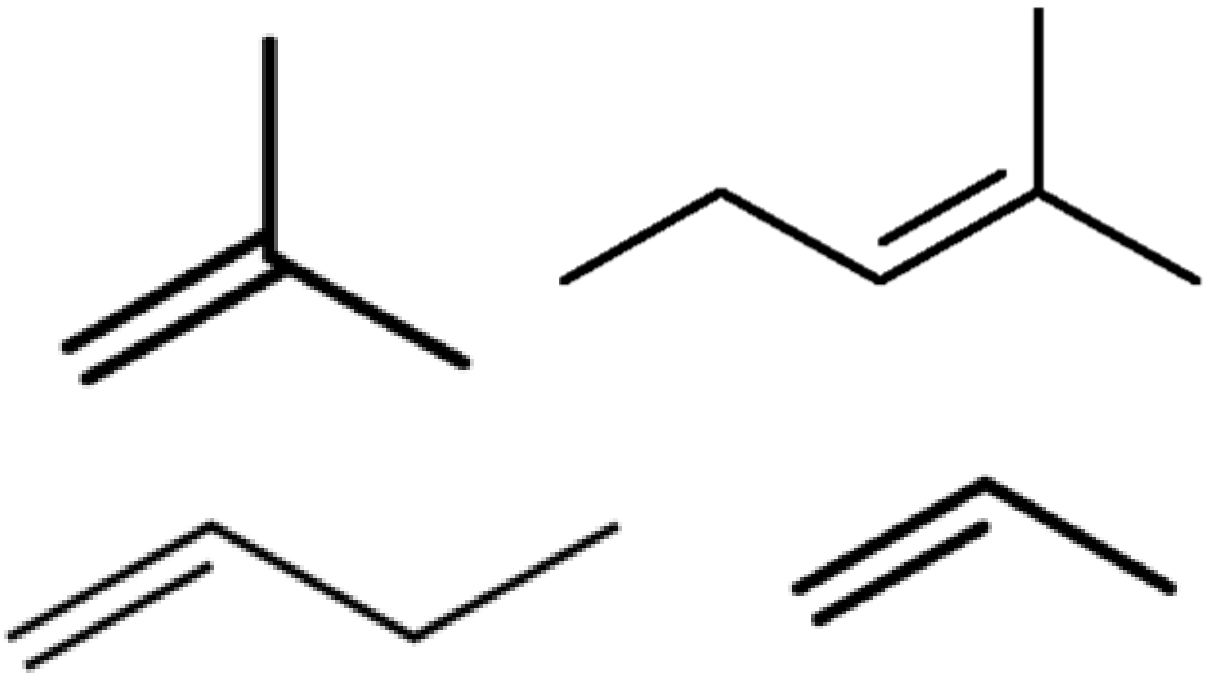
2. Draw in the correct number of bonds for an alkane, an alkene and an alkyne (*Hint*: how many bonds does C have?)

Alkane	**Alkene**	**Alkyne**

3. Using '*dots and crosses*' draw in the electron distribution for each of these systems

Alkane	**Alkene**

4. Can you identify the most reactive site in the following structures?



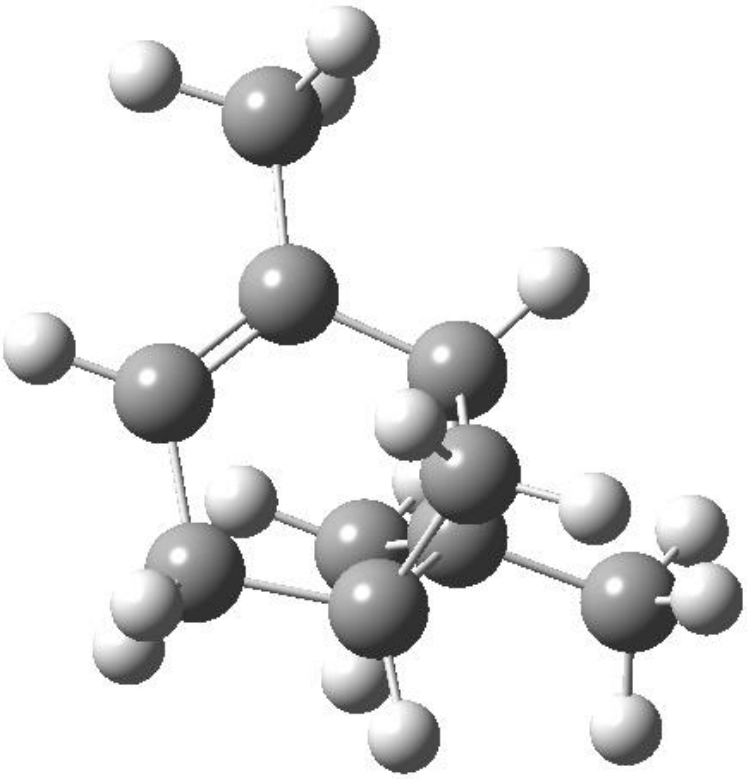
Atmospheric Oxidation

5. What do you understand by the term oxidation?

Atmospheric Oxidant	Time of Dominance
OH radicals (OH·)	
Ozone (O_3)	
NO_3 radicals (NO_3·)	

Oxidation Reactions

6. On the below structure indicate in which position an atmospheric oxidant may bond to the double C=C bond



7. The below structures contain multiple sites of the same bond saturation, can you determine which site is more reactive towards the addition of ozone (O_3)?

Terpinolene	**Linalool**	**Limonene**

8. Why?

Tutorial 1 – Baseline Test

The homework assignment for the first tutorial is a baseline test to see your initial level of attainment in this subject area. The assignment will test for some or all of the subject specific skills that are required later in the final assignment. However, it is shorter than the final assignment and will be an introduction to the subject as well as a challenge!

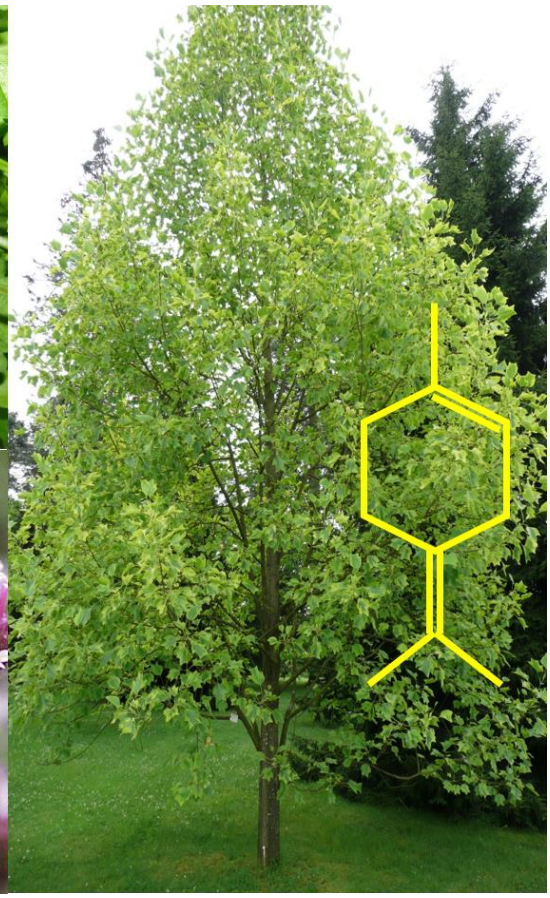
Do not worry too much about doing 'well' or 'badly' on the baseline test, it takes into account the fact that you may not be familiar with the subject area. It is designed to help you and your PhD tutor identify where you are at the start of the programme and to help you measure your progress along the way.

1. Explain what you understand by the term *atmospheric chemistry*, using specific examples where appropriate
   Consider:
   - Your definition of atmospheric chemistry (not a dictionary definition)
   - Are there any examples that help explain your definition, such as the greenhouse effect? Can you think of any other examples?
   - Can you use scientific evidence to explain your examples?
2. Describe what a transition state is and its role within a reaction. You may include a diagram to assist with you answer
   Consider:
   - Your definition of a transition state (not a dictionary definition)
   - Can you draw a reaction profile including the reactants and products of a reaction? Where does the transition state fit into this?
   - How can transition states help explain the energy involved in a reaction?

This baseline test is to establish your initial level of understanding in this subject area. When answering these questions please refer to the '*Effective Communication'* section of the mark scheme (Page 5) to practice the delivery of your ideas. I would expect no more than 1 side (A4) of writing for each of these questions, using:

- Type up you assessment
- Times New Roman font
- Size 12 font, 1.5 line spacing, Justified alignment
- All sources to be referenced in a bibliography at the end (Tips on referencing in Appendix 4)

Tutorial 2 – Atmospheric emissions – are humans solely to blame?



What is the Purpose of Tutorial 2?

- Introduction to biogenic emissions
- Learn how to establish transition state structures

Tutorial 2 – Outline:

<u>Tutorial 1 Revision</u>

In your own words define

a. Anthropogenic emissions

---

b. Biogenic emissions

Terpenes

2. What are terpenes?

3. Where do they come from?

4. Where might the students have come across them before?

5. Why are they important?

Examples of Biogenic Emissions

Isoprene

	C: H: O: Molecular Formula:

Monoterpenes e.g Myrcene

	C: H: O: Molecular Formula:

Sesquiterpene e.g. *β*-caryophyllene

	C: H: O: Molecular Formula:

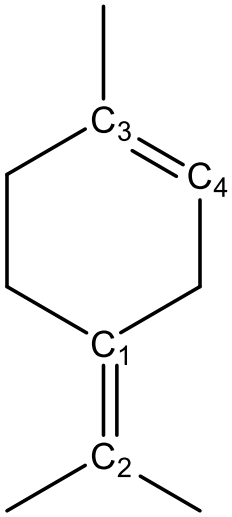
Terpenoid e.g. Linalool

	C: H: O: Molecular Formula:

6. Do these examples comply with the $(C_5H_8)_n$ rule?
7. Based on the work in Tutorial 1, can you identify the most reactive double C=C bond in these structures *(Circle your answer)*

Transition State Structure

7. Thinking about the reactivity of the double C=C bonds, where is the oxidant (O_3) most likely to react with terpinolene? *(Please tick your answer)*



☐ C_1=C_2
☐ C_3=C_4

8. If the O_3 were to react at the other double C=C bond, would the energy require be higher or lower? Why?

Tutorial 2 – Homework:

Part 1

Decide upon a terpene or terpenoid form the list below

- Linalool
- β-caryophyllene
- Isoprene
- Limonene
- α-pinene
- Terpinolene

Part 2

Create a research profile on your terpene, including:

- skeletal structure
- molecualr formula
- biogenic sources
- global emissions
- reactivity of double bonds (if applicable)
- atmopsheric reaction products

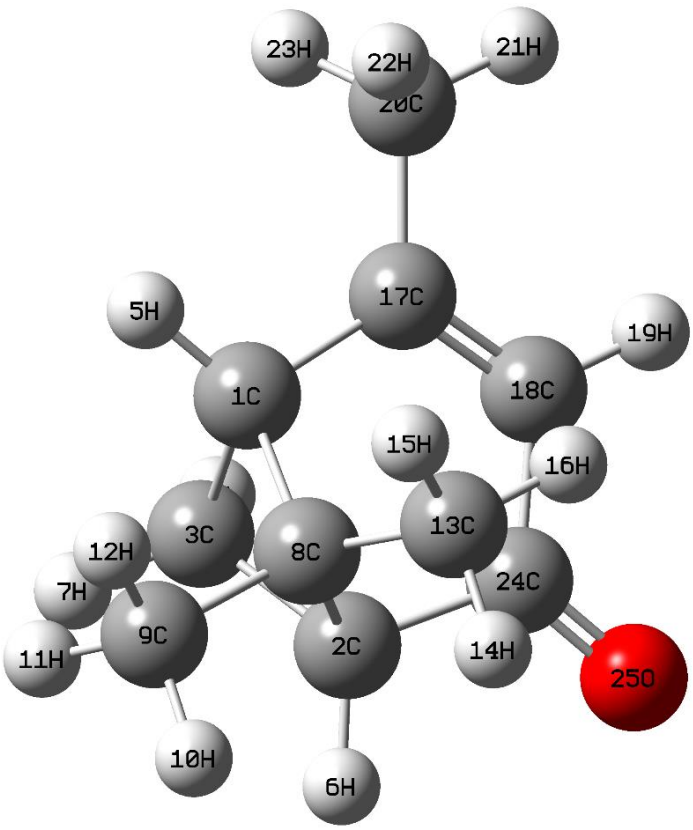
Part 3

Investigate any previous work completed on your terpene, including:

- Infrared Spectroscopy
- Mass Spectrometry
- Computational Chemistry

Research profiles should be presented as a poster, including both text and images. All images must be explained and any research should be referenced. Arial is the suggested font for posters, however if you prefer another that is fine. References should be located at the bottom of the poster (see Appendix 4 for referencing advice)

Tutorial 3 – Seeing the invisible



What is the Purpose of Tutorial 3?

- Using a variety of presentations and computer programmes to:
  - Introduction to computational chemistry
  - Understand how chemist can use this technique to differentiate between transition states and reactants/products

Tutorial 3 – Outline:

<u>Introduction to Computational Chemistry</u>

1. What is computational chemistry?

---

2. Why do we use it?

How do we consider electrons?

3. What is a basis set?

---

4. How can we manipulate these basis sets to better model reality?

Energy minima and maxima

5. What are the differences between energy minima and maxima?

---

6. What important aspects differentiate transition state calculations?

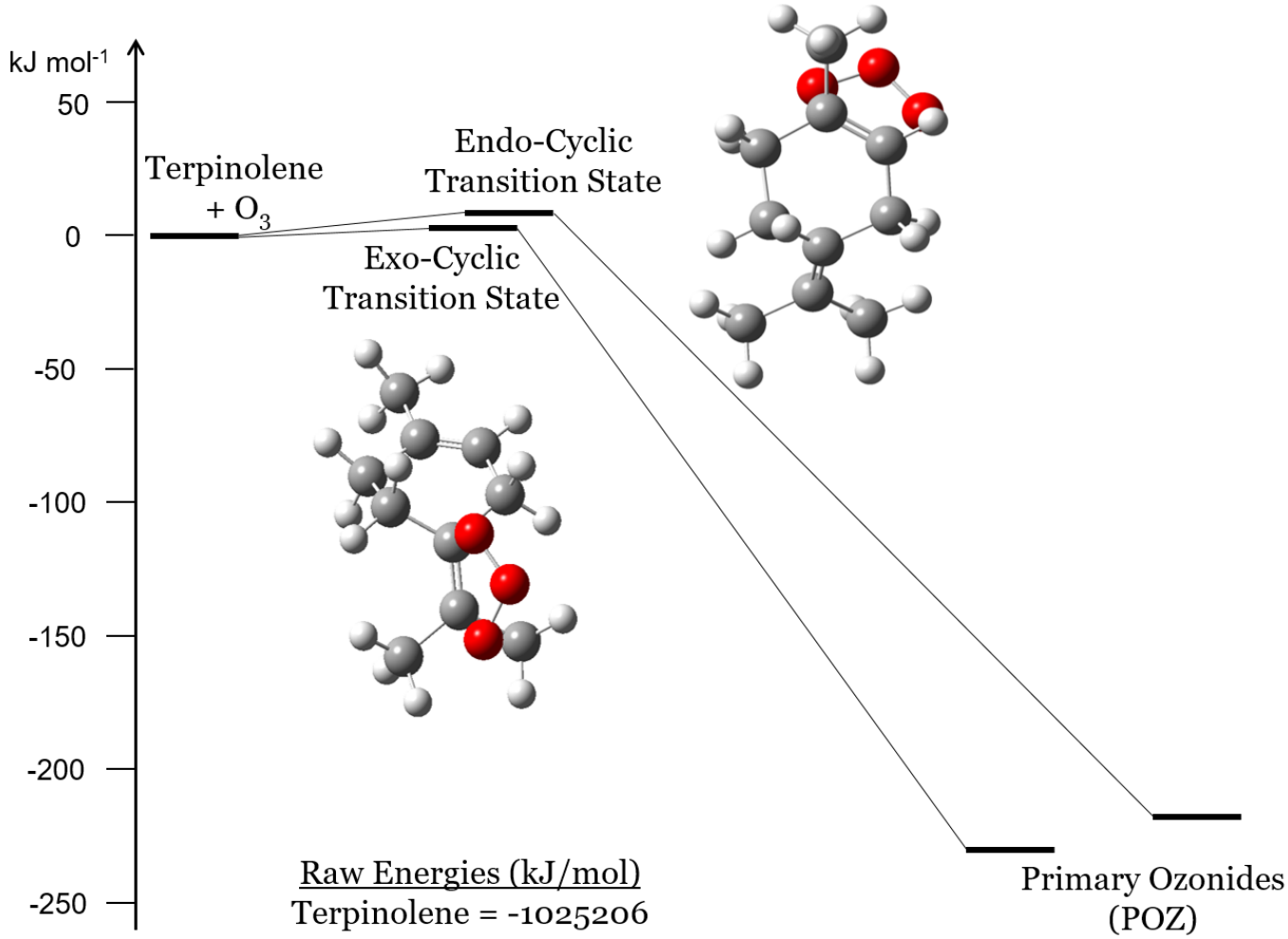
Tutorial 3 – Homework:

Using the diagram below, can you identify which is the more abundant transition state for the given reaction pathway?

Part 1 Calculate the energy barrier for
- endo-cyclic transition state
- exo-cyclic transition state

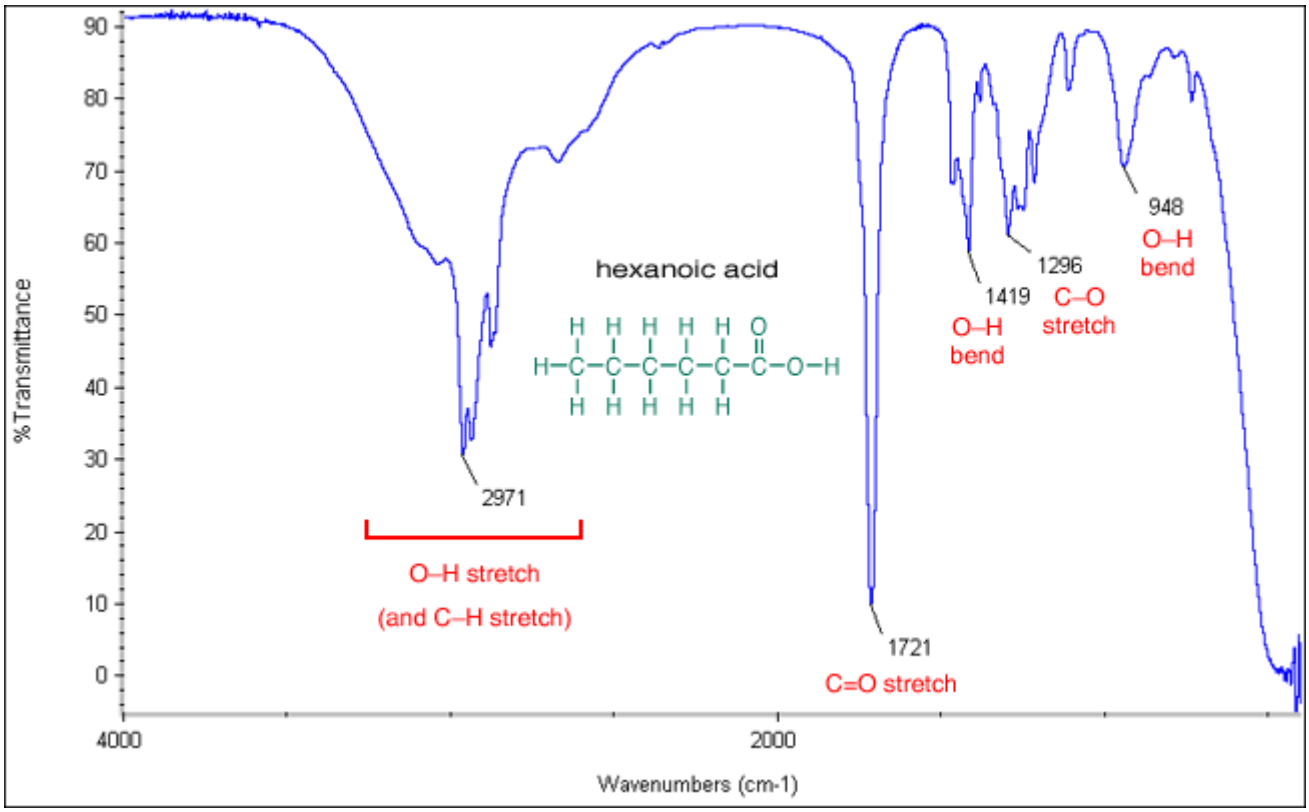
Part 2 Convert the these units into kcal/mol
- Use the conversion table in Appendix 1
- How do these values compare to those you found in Homework 2?

Part 3 Which is the most abundant transiton state?
- Consider
  - the energy barrier
  - molecular strcuture



Raw Energies (kJ/mol)
Terpinolene = -1025206
O_3 = -591829
Endo-Cyclic Transition State = -1617026
Exo-Cyclic Transition State = -1617032

Tutorial 4 – Good vibrations



What is the Purpose of Tutorial 4?

- Using a variety of presentations and computer programmes to:
  - How does infrared spectroscopy work?
  - How can we utilise this technique for analysis of atmospheric chemistry?

Tutorial 4 – Outline:

<u>Introduction to infrared spectroscopy</u>

1. What is it?

---

2. Why do we use it?

---

3. How do we use IR?
    a. Solids

b. Liquids

c. Gases

4. What does the spectrum tell us?

(Characteristic infrared vibrational frequencies are shown in Appendix 2)

How do we utilise this technique to monitor atmospheric chemistry?

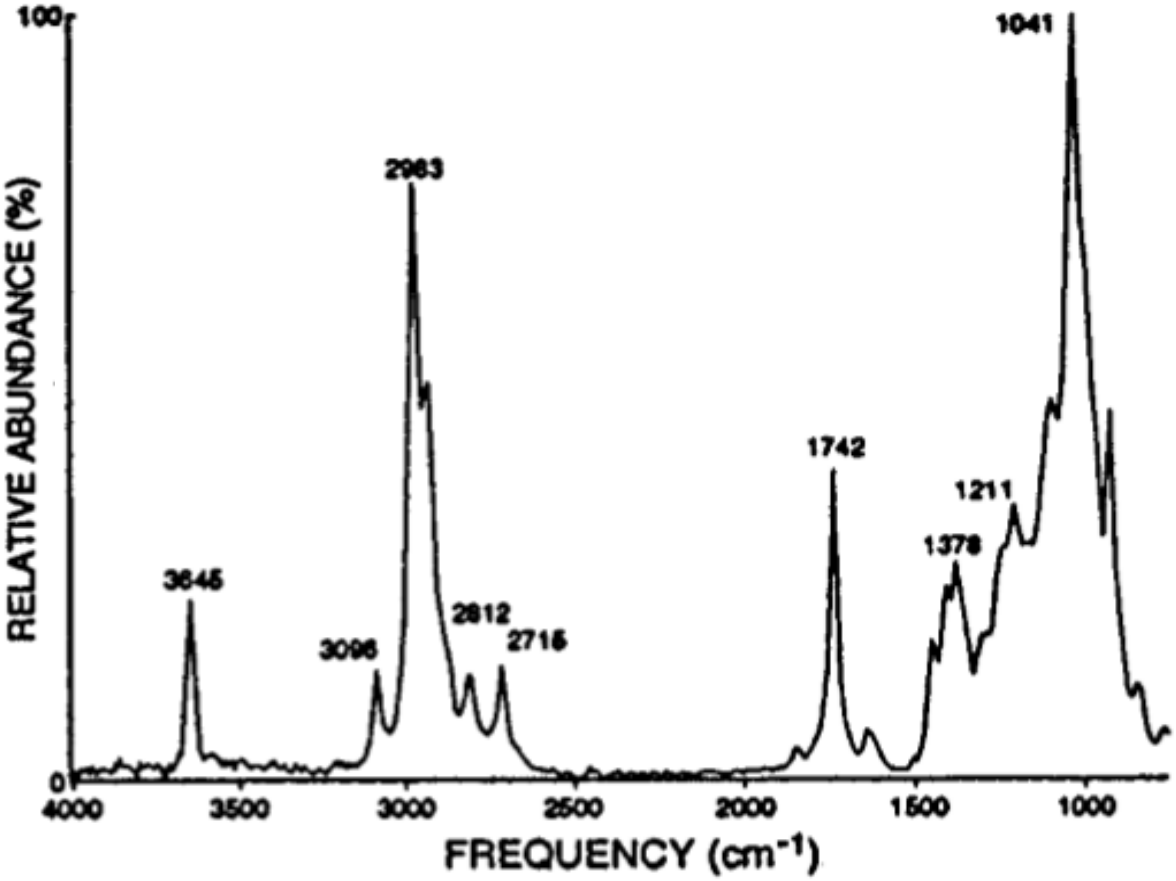
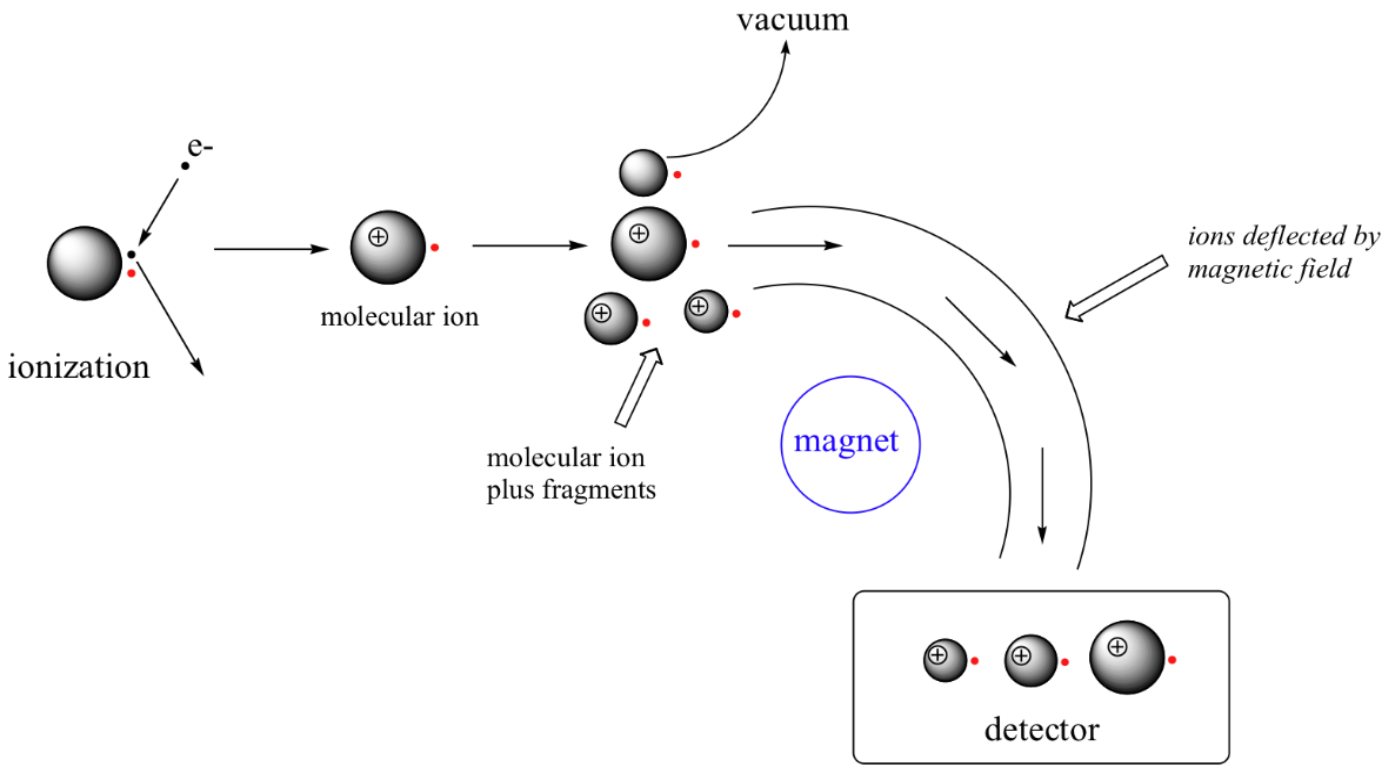


Figure 1A taken from Shu *et al.* 1997 showing a product from the reaction of linalool and ozone

Tutorial 4 – Homework: Draft Assignment

Establish a plan for your final assignment (Appendix 2) and complete the introduction (below)

Tutorial 5 – Identifying the building blocks



What is the Purpose of Tutorial 5?

- How does mass spectrometry work?
- How can chemists utilise this technique for analysis of atmospheric chemistry?

Tutorial 5 – Outline:

<u>Introduction to mass spectrometry</u>

1. What is it?

---

2. Why do we use it?

---

3. How do we use MS?

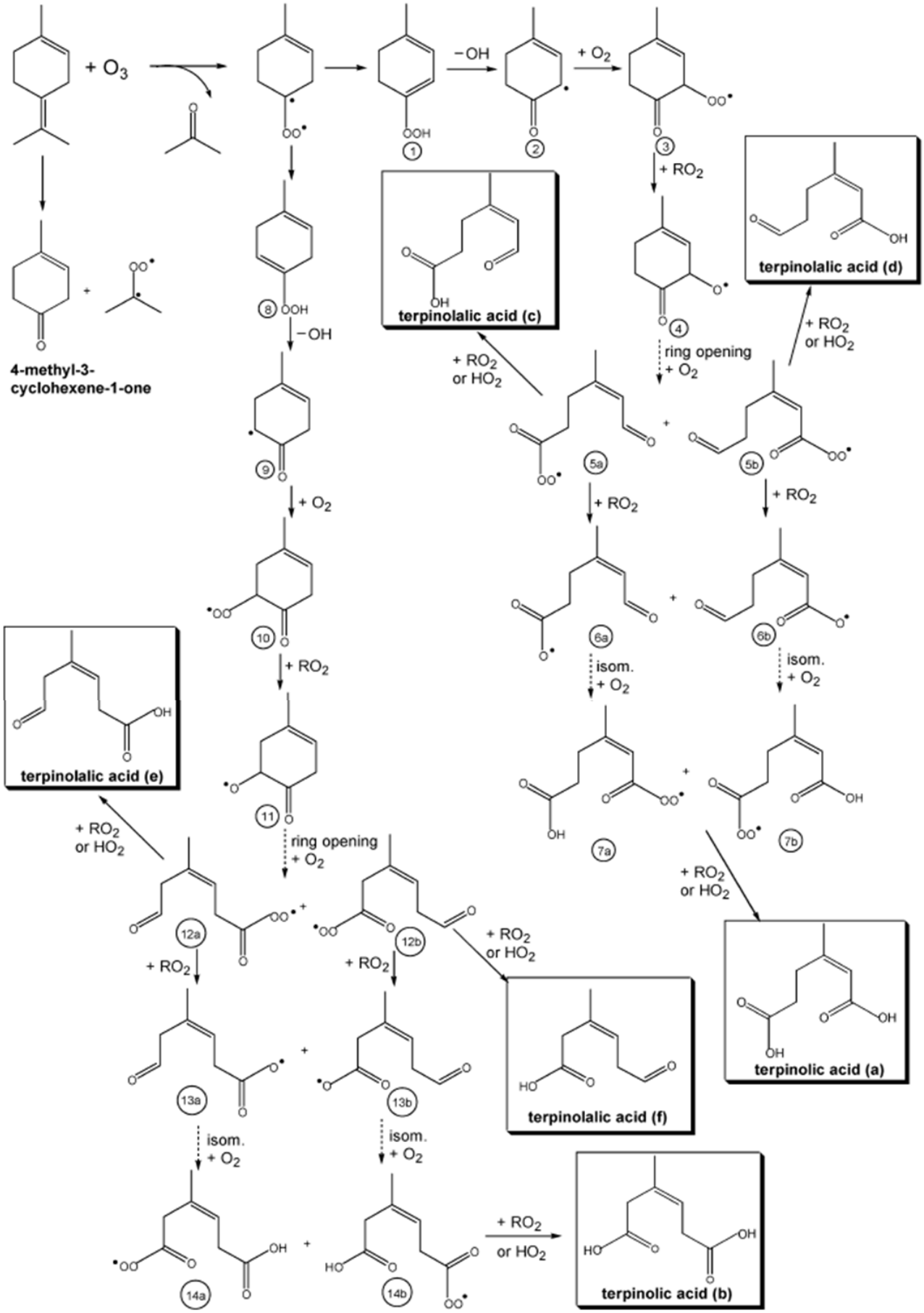
4. What does the spectrum tell us?

Introduce the concept of combined techniques

1. Gas Chromatography – Mass Spectrometry (GC-MS)

2. Time of Flight – Mass Spectroscopy (TOF-MS)

How do we utilise mass spectrometry to monitor atmospheric chemistry?



Scheme 4 taken from Ma and Marston 2009 depicting the possible mechanism for the formation of carboxylic acids identified from the ozonolysis of terpinolene

Tutorial 5 – Homework: Final Assignment

Explore the different techniques chemists can use to analyse atmospheric processes.

Consider:

- Which atmospheric processes are you considering?
- How can we utilise theoretical methods to analyse atmospheric chemistry?
- Which experimental techniques can we use to monitor atmospheric chemistry?
- Do we use these techniques in isolation?
- Give specific (and referenced) examples when considering each of these points

Presentation

- Type up your final assignment
- Essay structure (see Appendix 3)
- 2000 word limit
- Times New Roman font
- Size 12 font, 1.5 line spaced, justified alignment
- All sources to be referenced in a bibliography at the end (Tips on referencing in Appendix 4)

Tutorial 6 – Feedback

What is the Purpose of Tutorial 6?

- Reflect on skills learned on the programme with a view to encouraging resilience
- Receive feedback on final assignment

What are the key questions?

- What strengths have I demonstrated in my work and what areas of development are there left for me to address?
- What steps do I need to take to improve my academic output?

Activity 2 – Marking your own

Using the mark scheme, identify three things you did well and three things you could improve.

What went well?

1.

2.

3.

What could be improved?

1.

2.

3.

Activity 3 – Responding to feedback

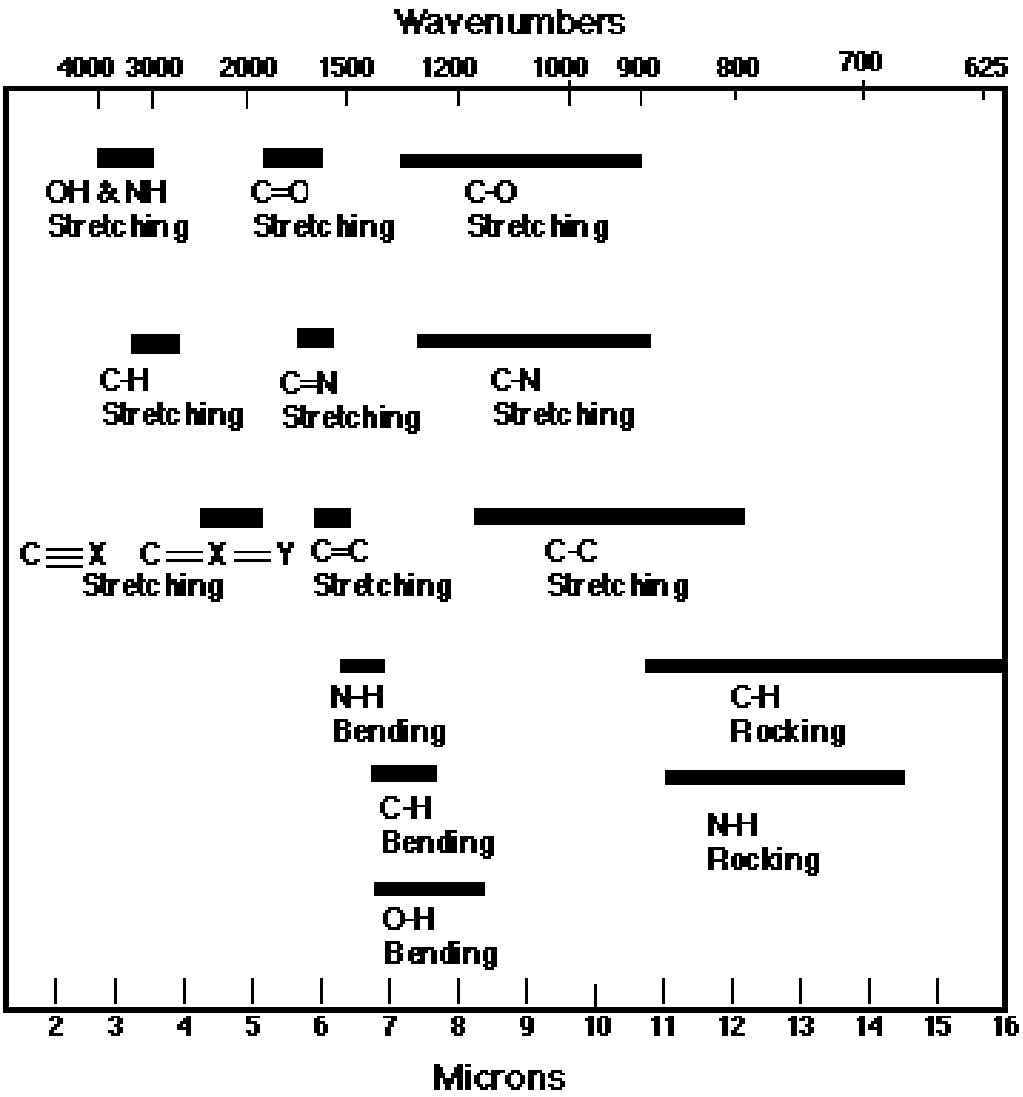
Read through your feedback sheet and highlight on your assignment where you received positive feedback (one colour) and areas for improvement (different colour). You might find it helpful to annotate this with a brief comment or two.

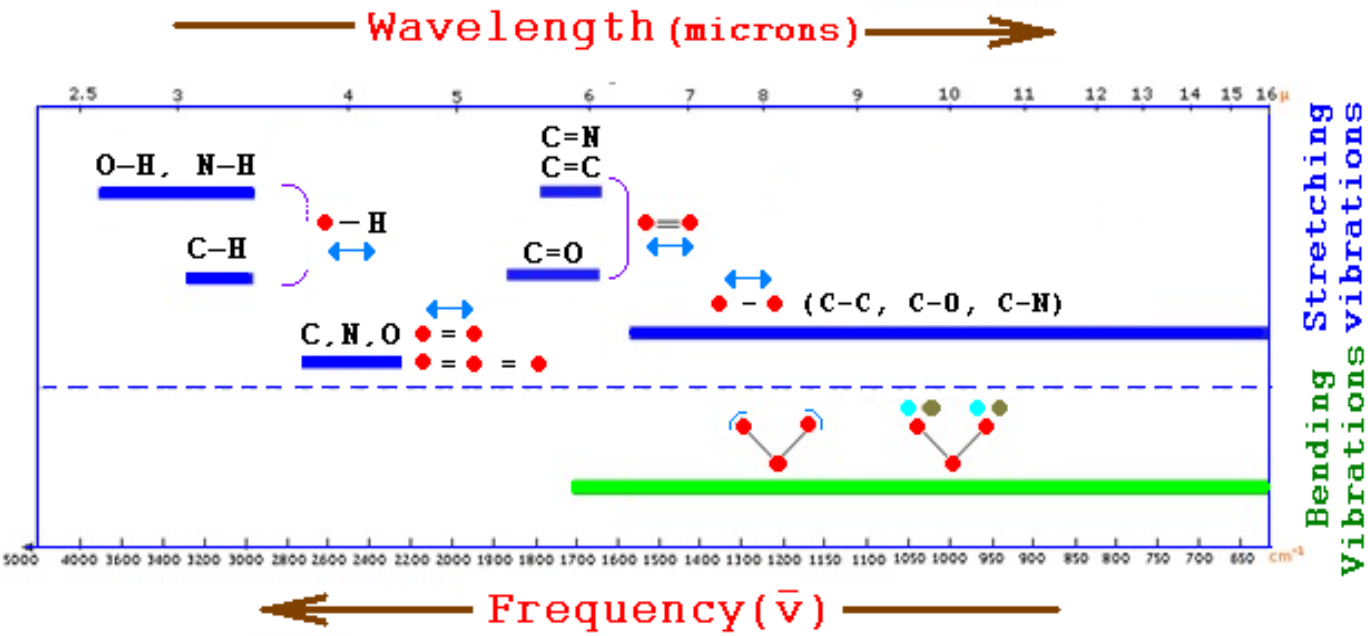
Energy Conversion Table

	hartree	eV	cm^{-1}	kcal/mol	kJ/mol	°K	J	Hz
hartree	1	27.2107	219 474.63	627.503	2 625.5	315 777.	43.60×10^{-19}	$6.57966 \times 10^{+15}$
eV	0.0367502	1	8 065.73	23.060 9	96.486 9	11 604.9	$1.602\ 10 \times 10^{-19}$	$2.418\ 04 \times 10^{+14}$
cm^{-1}	$4.556\ 33 \times 10^{-6}$	$1.239\ 81 \times 10^{-4}$	1	0.002 859 11	0.011 962 7	1.428 79	$1.986\ 30 \times 10^{-23}$	$2.997\ 93 \times 10^{+10}$
kcal/mol	0.001 593 62	0.043 363 4	349.757	1	4.18400	503.228	6.95×10^{-21}	$1.048\ 54 \times 10^{+13}$
kJ/mol	0.000 380 88	0.010 364 10	83.593	0.239001	1	120.274	1.66×10^{-21}	$2.506\ 07 \times 10^{+12}$
°K	0.000 003 166 78	0.000 086 170 5	0.695 028	0.001 987 17	0.008 314 35	1	$1.380\ 54 \times 10^{-23}$	$2.083\ 64 \times 10^{+10}$
J	$2.294 \times 10^{+17}$	$6.241\ 81 \times 10^{+18}$	$5.034\ 45 \times 10^{+22}$	$1.44 \times 10^{+20}$	$6.02 \times 10^{+20}$	$7.243\ 54 \times 10^{+22}$	1	$1.509\ 30 \times 10^{+33}$
Hz	$1.519\ 83 \times 10^{-16}$	$4.135\ 58 \times 10^{-15}$	$3.335\ 65 \times 10^{-11}$	$9.537\ 02 \times 10^{-14}$		$4.799\ 30 \times 10^{-11}$	$6.625\ 61 \times 10^{-34}$	1

To convert from a unit Y in the left hand column to a unit X in the top row, multiply by the table element, For example: 1 hartree = 27.2107 eV

Appendix 2: Chart of Characteristic Infrared Vibrations



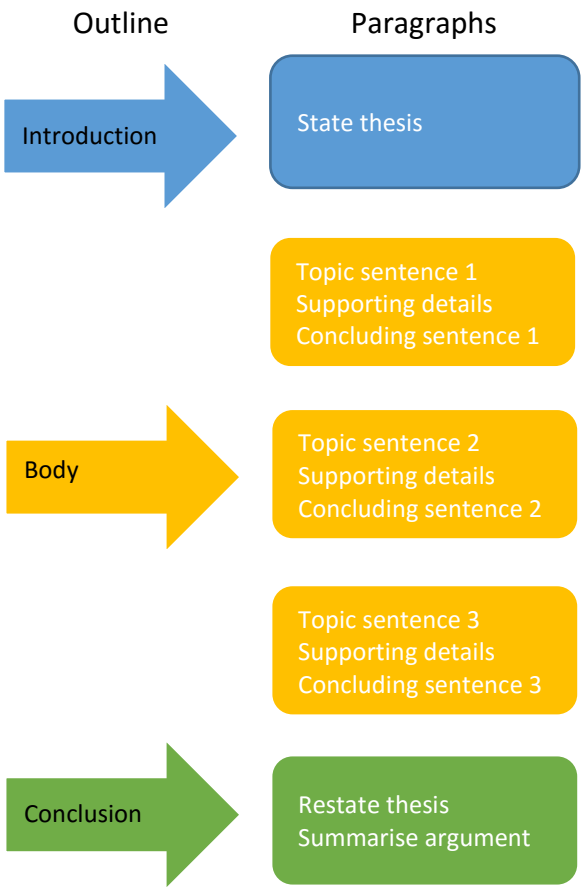


Appendix 3: Planning an essay

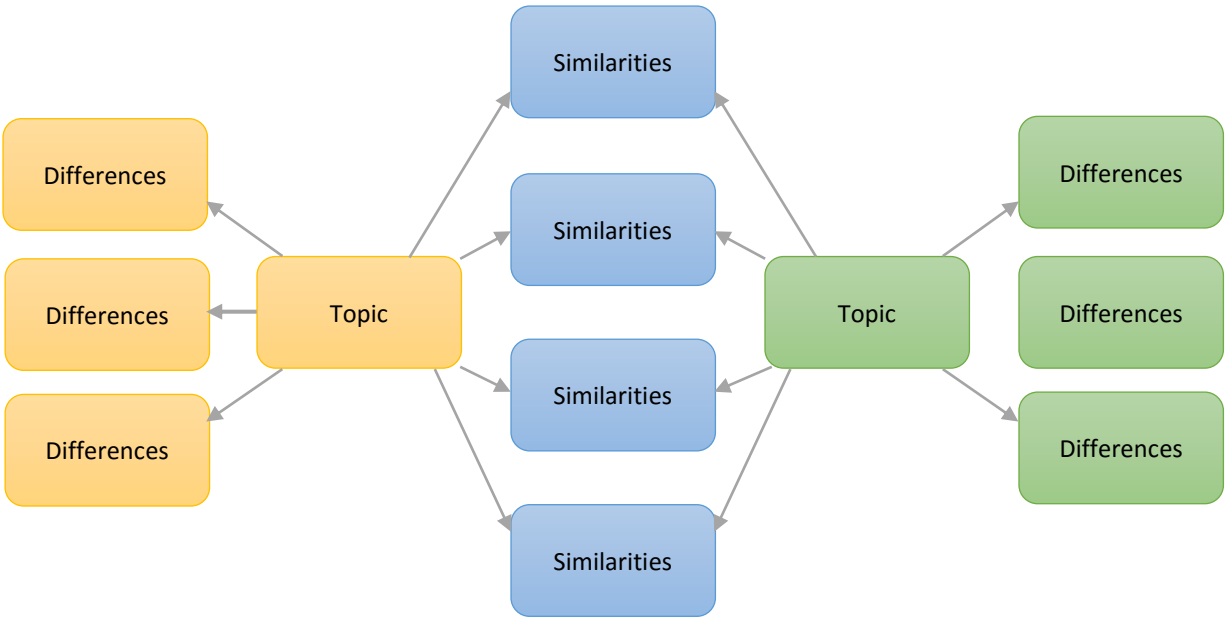
Brainstorming

To start off, and minimise the likelihood of writer's block, a useful exercise is to do a 'brainstorm' of all your ideas in connection with the essay title. You can catch all of your ideas, in no particular order, on a sheet of A4. Once they are down there it will be easier for you to start to review them critically and to see where you need to focus your reading and note taking.

The Basic Essay:



Compare and Contrast:



Appendix 4: Referencing

Journal Articles:

Journal articles should be referenced as:

Authors, *Journal Title*, Year, **Volume**, Page numbers

For example:

- D. J. Stewart, S. H. Almabrok, J. P. Lockhart, O. M. Mohamed, D. R. Nutt, C. Pfrang and G. Marston, *Atmospheric Environment*, 2013, **70**, 227-235.
- R. Winterhalter, R. Van Dingenen, B. R. Larsen, N. R. Jensen and J. Hjorth, *Atmospheric Chemistry and Physics Discussions*, 2003, **3**, 1-39.

Books:

Books should be referenced as:

Authors, *Book Title*, Publisher, Year, Pages (if applicable)

For example:

- M. B. Brown, *Molecular Spectroscopy*, Oxford University Press, New York, 1998.
- J. M. Hollas, *High Resolution Spectroscopy Second Edition*, Wiley, Chichester, 1998.

Websites:

Websites should be referenced as:

Website name, Web address, Date of Access

- Glass-solutions.co.uk, Scientific Glass and Equipment Specialists, http://www.glass-solutions.co.uk/, 2013.
- The Leicester Bearing Co Ltd., http://www.leics-bearings.co.uk/, 2014.

University Applications Guidance

For course choices and careers information:	www.brightknowledge.org.uk
For information and statistics on universities and course:	www.unistats.direct.gov.uk
For comprehensive information on universities, including rankings:	www.thecompleteuniversityguide.co.uk

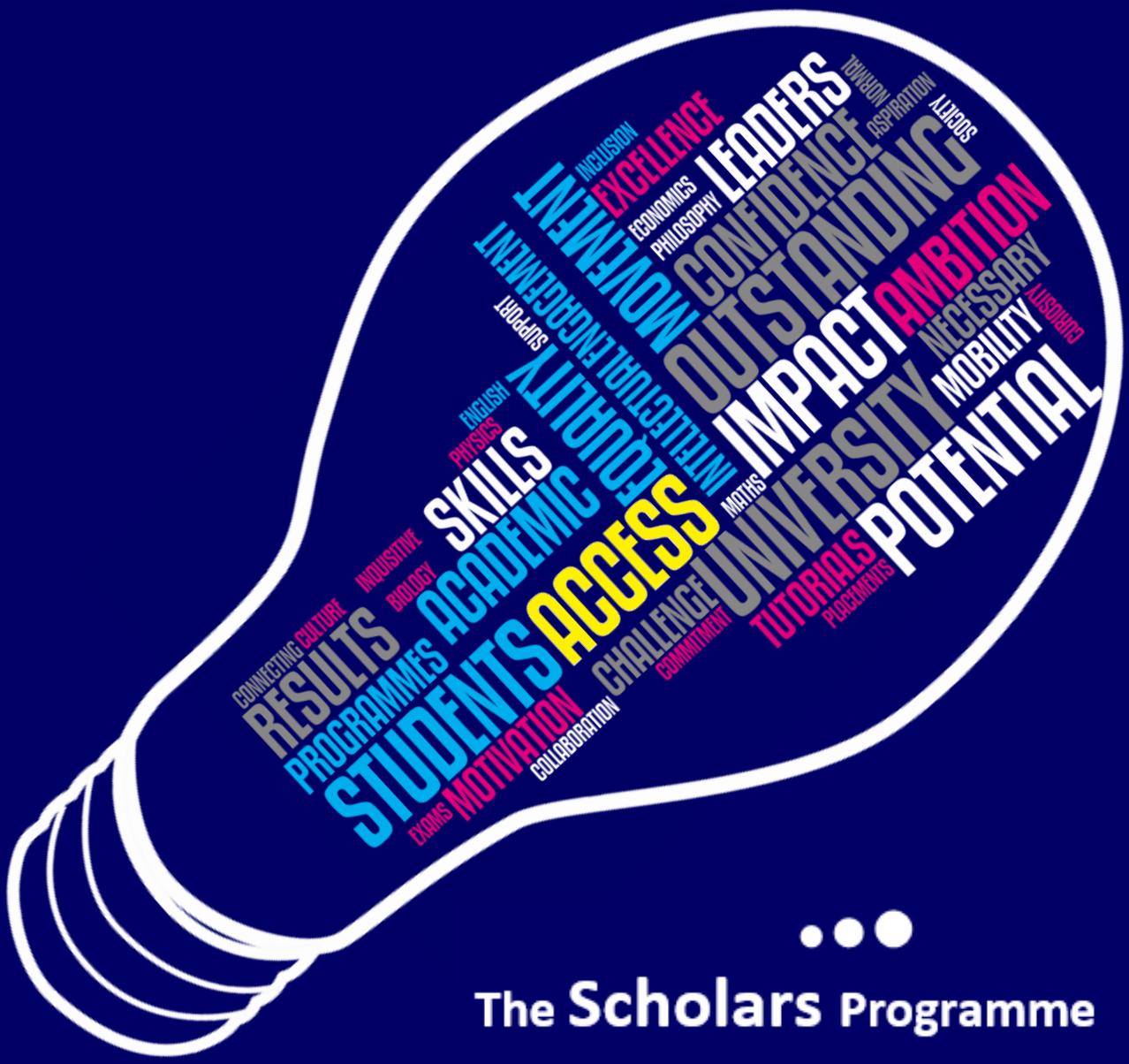
PLEASE NOTE – The Scholars Programme is designed to support the university applications process at your school. The work you complete for the programme should add to your schoolwork rather than detract from it. Please be aware of deadlines and try to manage your workload appropriately. If you are worried about the Scholars Programme interfering with your schoolwork then please speak to your teacher.

Subject Specific Top Tips for Strengthening your Application

What could you read around the subject?

Suggestions of podcasts/videos that can be found online? Are there any age-appropriate, good films on this topic?

What cheap or free events and talks would it be good to attend?



The Scholars Programme