

Supporting Information

Simulating Electronic Absorption Spectra of Atmospherically Relevant Molecules: A Systematic Assignment for Enhancing Undergraduate STEM Education

Information omitted due to double-blind review

S1. Pre-laboratory assignment

1. Write mathematical expressions to:
 - a. Describe the energy (E) of a photon of frequency ν ;
 - b. Convert the frequency ν of a photon into wavelength;
 - c. Describe the absorbance of a sample;

Answers: a. $E = h\nu$, b. $\lambda = c / (\nu)$, c. $A = \epsilon l c$

2. During this experiment you will compute and plot the UV absorption spectra of various atmospheric molecules. What will the x-axis and y-axis of your plot be?

Answers: x-axis = λ (nm); y-axis = absorption (arb. u)

3. The excitation energy of a molecule is 5.00 eV. Perform the following conversions:
 - a. 5.00 eV = _____ nm
 - b. 5.00 eV = _____ cm^{-1}
 - c. 5.00 eV = _____ J

Answers: 248 nm; 40325 cm^{-1} ; 8.01E-19

4. A molecule has a vertical excitation energy of E and an oscillator strength of f . What is the relationship between oscillator strength and the absorption cross section?

Answers: see eq. 1 in the main text

5. A molecule is photoexcited to its first excited state; the vertical excitation energy to this state is 5.00 eV and an oscillator strength is 0.250. Using Excel (or analogous program), plot the absorption 'stick' spectrum.

Answers: Make two columns in excels; x-axis is the energy and y-axis is the oscillator strength. Plot as bar plot

6. Using the data and plot in question 5., add a Lorentzian shape function with broadening factor of 0.5 eV to plot a UV absorption spectrum of the molecule.

Answers: input the expression of the Lorentzian shape function in Excel, and set d to 0.5 eV, excitation energy as 5.0 eV and f as 0.250.

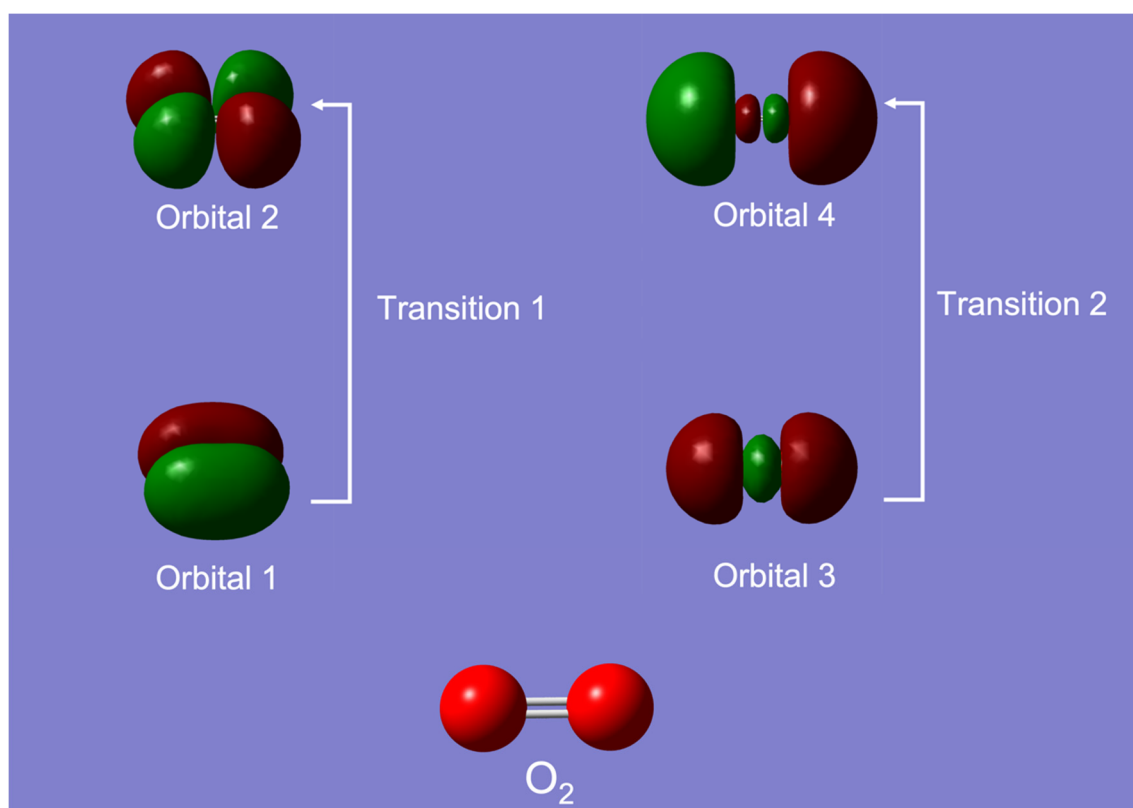
7. Consider the molecule O_2 . Write its ground state electronic configuration. What is the spin of O_2 in its electronic ground state?

Answers: triplet

8. Consider the OH radical. Write its ground state electronic configuration. What is the spin of OH in its electronic ground state?

Answers: doublet

9. Below are the selected molecular orbitals of O_2 . Electronic promotions to a two different excited states are also shown. Label the orbitals and electronic transitions according to the orbital character and predict whether the transitions will be associated with high or low oscillator strengths, assuming that all transitions are spin-allowed.



Answers: Orbital 1 = π , Orbital 2 = π^* , Orbital 3 = σ , Orbital 4 = σ^* ,
Transition 1 = $\pi^* \leftarrow \pi$ (high), Transition 2 = $\sigma^* \leftarrow \sigma$ (high)

10. The solar actinic flux at sea level is provided to you as part of this experiment. Describe the profile of the solar irradiations, including peak, wavelength range and dips, and provide a rational for such features.

Answers: See Fig. 1 and associated description in 'Result and discussion' of the main text

11. Which of the following molecule is more likely to undergo photolysis if exposed to sunlight at sea level? Motivate your answer.

- Molecule A; $\lambda_{\max} = 550 \text{ nm}$, $\epsilon_{\max} = 10 \text{ M}^{-1} \text{ cm}^{-1}$
- Molecule B; $\lambda_{\max} = 550 \text{ nm}$, $\epsilon_{\max} = 1.0 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$

- c. Molecule C; $\lambda_{\text{max}} = 250 \text{ nm}$, $\epsilon_{\text{max}} = 10 \text{ M}^{-1} \text{ cm}^{-1}$
d. Molecule D; $\lambda_{\text{max}} = 250 \text{ nm}$, $\epsilon_{\text{max}} = 1.0 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$

Answers: Molecule B; its λ_{max} is in the visible and the ϵ_{max} is large.

S2. Laboratory Manual

Experiment

Simulating Electronic Absorption Spectra of Atmospherically Relevant Molecules; role of Solar Photolysis in Atmospheric Lifetimes.

Procedure

Part I: Optimization and computation of the normal mode wavenumbers

1. Open GaussView (see desktop)
2. Using the 'element fragment tool' in GaussView (look for the ^{12}C icon), draw the structure of CO_2 . Use the appropriate tools in GaussView (if required) to adjust the guess geometry (adjust bond angle, bond length etc.).
3. Prepare your input file by:
 - i. Selecting 'calculate' from the tool bar
 - ii. Select 'Gaussian Calculation Setup'
 - iii. Select 'JobType: Opt and Freq'
 - iv. In Method select: 'Ground State/ DFT/ Default Spin/ B3LYP/ Basis Set: 6-311+G(d,p)'
 - v. Check that the charge and spin are correctly set (0 and Singlet, respectively)
4. Now your calculation input is set up. To run it, click on 'edit', save your file, close it and submit your job.
5. When the job is terminated, a window will pop up. Open the .log output file.
6. The optimized geometry will be displayed, as the output file is opened. Select 'results' in the tool bar and click on 'Summary'. This will display the results.
7. Make sure no imaginary frequency is computed. If so, contact the instructor for advice and further directions.
8. Repeat steps 1 – 7 for CH_4 , H_2O , O_3 , NO_2 , and NO_3 . For all these molecules, the charge is 0, but the spin multiplicity will be singlet for CH_4 , H_2O and O_3 , and doublet for NO_2 and NO_3 .

Part II: Vertical excitation energies and oscillator strengths

9. Using the optimized geometry of CO₂ computed in Part I compute the vertical excitation energy and oscillator strengths to the lowest 10 singlet (doubles for NO₂ and NO₃) excited states by selecting
 - a. 'Energy' in 'JobType'
 - b. In Method select: 'TD-SCF/DFT/ Default Spin/ B3LYP/ Basis Set: 6-311+G(d,p)'. Compute 10 states by changing default 6 to 10 under 'Solve for More States'.
 - c. Check that charge and spin multiplicity are correct.
10. Now your calculation input is set up. To run it, click on 'edit', save your file, close it and submit your job.
11. When the job is terminated, a window will pop up. Open the .log output file.
12. To visualize the stick spectrum click on 'Result' and select 'UV-Vis'. The stick spectrum (with Gaussian shape function overlapped) will be displayed.
13. Repeat 9 – 12 for all other molecules.
14. Open the checkpoint files and select 'MO editor' to view the molecular orbitals (look for green and red *p* orbital icon)
15. Open the output file: scroll down to the results sections; you may search for the key words 'Excitation energies and oscillator strengths'.
16. Use the information in the output file and the molecular orbital viewer assign the electronic promotions (or states) as $\pi^* \leftarrow \pi$, $\pi^* \leftarrow n$, $\sigma^* \leftarrow \sigma$ etc.

Part III: Simulating the absorption spectrum

17. Create a new folder and name it CO₂
18. Create a new file containing the optimized geometry of CO₂. The file structure should specify the number of atoms in the molecule (3) in the first line, have line 2 blank and display the cartesian coordinates of the molecules (in Angstrom) from line 3 – 5.
19. Place the file containing the computed frequencies of CO₂ in this folder.
20. Call the spectral simulation script
21. Prepare your initial geometries by answering the questions prompted by the script: specifically compute 100 points at B3LYP/6-311+G(d,p) for 10 states.
22. Call the queueing script to run your jobs.
23. Call the analysis script to collect the computed vertical excitation energies and oscillator strengths
24. Using Excel (or analogous program) plot the simulated absorption spectrum as directed by the instructor.

Discussion. In your post-laboratory report, include a discussion of the following points:

1. What are the principles underlying the absorption of light by molecules?

2. What atmospheric species have a UV absorption spectrum which overlaps with the solar spectrum? Which electronic transitions are primarily responsible for such overlap? Motivate your answers.
3. What are the possible implications of the absorption of the UV light by certain molecular species in term of their chemistry in the troposphere?
4. Comment on the agreement between the experimentally measured spectra and the simulated one.

S3. Preview of the interactive script.

A preview of the input file and possible responses is illustrated below. Students will be expected to prepare their input files by simply answering the questions prompted by the script. After the points have been generated, the students can use a queueing script to run the prepared input files in series for a more efficient use of their laboratory time. The script can be obtained by contacting the authors of this study.

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Name of file containing input geometry? Geometry.xyz

Number of Atoms? 3

Number of Wigner points? 100

Name of Gaussian log file containing Frequencies? Frequencies.log

Level of theory; b3lyp/6-311+G(d,p)

Number of absorbing/emitting states? 10

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Simulated spectrum of O₃ computed at the TD-B3LYP/6-311+G(d,p) by sampling 50, 100 and 150 Wigner points (10 singlet states)

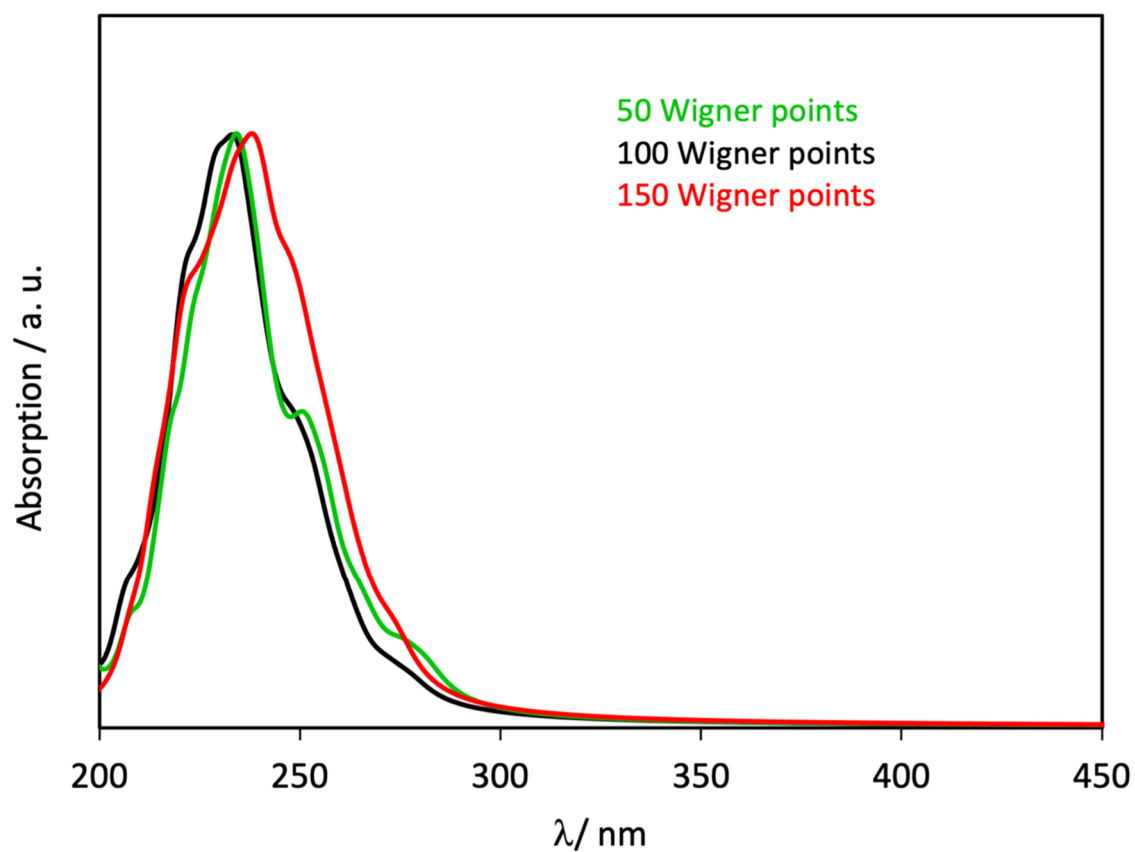


Figure S1: Dependence of the simulated UV absorption spectra to the number of Wigner points sampled.