

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

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**Abstract:** Computational and atmospheric chemistry are two important branches of contemporary chemistry. With the present topical nature of climate change and global warming, it is more crucial than ever that students are aware of and exposed to atmospheric chemistry, with an emphasis on how modeling may aid in understanding how atmospherically relevant chemical compounds interact with incoming solar radiation. Nonetheless, computational and atmospheric chemistry are underrepresented in most undergraduate chemistry curricula. In this manuscript, we describe a simple and efficient method for simulating the electronic absorption spectral profiles of atmospherically relevant molecules that may be utilized in an undergraduate computer laboratory. The laboratory results give students hands-on experience in computational and atmospheric chemistry, as well as electronic absorption spectroscopy.

**Keywords:** Computational Chemical Education, Atmospheric Chemistry, Undergraduate Computational Skills, Curriculum Development, Photochemistry, Spectroscopy.

## 1. INTRODUCTION

Climate change is one of the most significant challenges faced by modern society. The influx of harmful anthropogenic pollutants has led to an increase in the average global temperature. The consequences of such increases in temperatures are most notable observed in the Arctic regions, where melting of polar icecaps lead to rising sea levels. As a results, forefront scientific research into climate change and its implications for global warming have significantly increased in recent years.<sup>1–4</sup>

Despite its importance, little emphasis is given to atmospheric chemistry in many undergraduate chemistry programs. Students are therefore unaware of the vital link between fundamental chemical concepts taught in undergraduate chemistry and their importance in the life-sustaining chemistry of the atmosphere. To date, some studies have focused on implementing atmospheric and environmental research into undergraduate chemistry curricula.<sup>5–13</sup> Much of this research provides hands-on practical experiences in atmospheric sciences and attempts to make students aware of the experimental tools for atmospheric measurements.

Computational chemistry is another field of chemistry that students have little exposure to at the undergraduate level – despite its importance in aiding in the interpretation of experimental results. Several computational chemistry packages such as Gaussian<sup>14–16</sup> and Spartan<sup>17</sup> offer user friendly interfaces that allow the user to draw structures and calculate properties such as their optimized geometries, vibrational and electronic absorption spectra and electronic charge distributions, etc. Such projects are routinely implemented into undergraduate chemistry laboratory classes.<sup>18–25</sup> Given the COVID-19

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pandemic, recent educational research has focused on the design of computational-based exercises for implementation into distance learning laboratories.<sup>26–29</sup> Such studies are important in identify how science may be conveyed at a distance and may be translated to students with disabilities or part-time students. Computational chemistry-based research is particularly suitable for these scenarios.

Atmospheric modelling incorporates both Atmospheric and Computational Chemistry and may be used to model global levels of pollutants, trace gases, and atmospherically relevant products from a given emission source. Advanced modelling techniques such as STOCHEM provide highly detailed information on the global distribution of atmospherically relevant intermediates as well their most likely origins.<sup>30</sup> Such techniques are based on experimental or theoretical kinetic models and are therefore far advanced for implementation into an undergraduate setting.

Modelling may also be used to simulate the electronic absorption spectra of atmospherically relevant molecules.<sup>31–33</sup> Recently, we have used the nuclear ensemble model to model the electronic absorption spectra of various Criegee intermediates, which are a class of carbonyl oxides formed via alkene ozonolysis in the troposphere and are implicated in promoting the oxidizing capacity of troposphere.<sup>31</sup> Others have also used the nuclear ensemble method to model the electronic absorption spectra of other atmospherically relevant molecules.<sup>32,34–39</sup>

In this manuscript, we report a versatile computational chemistry laboratory that may be easily implemented into undergraduate general and organic chemistry laboratories. This laboratory will make use of the nuclear ensemble method of simulating electronic absorption profiles. Students will compute the electronic absorption spectra of CO<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>O, O<sub>3</sub>, NO<sub>3</sub>, and NO<sub>2</sub>. They will be asked to compare their results with the experimentally measured spectrum of these molecules, which is well-known for systems and can be found at The MPI-Mainz UV/VIS Spectral Atlas of Gaseous Molecules of Atmospheric Interest.<sup>40</sup> The students will then compare their results to the tropospherically relevant solar irradiance and will be asked to comment on the extent to which the spectrum of a given molecule overlaps with the solar irradiance spectrum. Students will elaborate on the implications that this observation has on the removal of the molecule of interest by tropospherically relevant solar radiation.

The goal of the laboratory is to expose students to computational chemistry, spectroscopy, photochemistry, and atmospheric chemistry, as well as getting them to make the vital link between the atmospheric lifetime of various atmospherically relevant molecules and their removal by solar irradiation. In the next section, we outline the pedagogical goals that we expect from the implementation of this laboratory.

## 2. PEDAGOGICAL GOALS

### *Course Approach*

Our current chemistry curriculum at UL Lafayette exposes undergraduate students to fundamental concepts in chemistry, aligning with the standards set by the American Chemical Society. Many of these concepts translate to atmospheric chemistry, which is an essential field concerned with sustaining life on Earth. Despite this, practical atmospheric chemical studies are largely limited to lecture courses, with very little exposure at the laboratory level.

Atmospheric chemistry involves a myriad of interconnected reaction that have positive and detrimental effects on the environment. Computational chemistry provides essential tools for quantifying the reaction mechanisms of diverse ranges of chemistry. Such computational methods, in particular quantum chemical methods, have been used to great success for describing the complex chemistry of the atmosphere.<sup>41–44 45</sup>

The laboratory experiment designed in this manuscript provides first-hand account of both computational and atmospheric chemistry – in a self-contained manner. This simulation-based laboratory may be implemented into undergraduate General, Organic or

Physical Chemistry laboratories as a single session in a straightforward manner. Implementation of this laboratory will ensure that students are sufficiently exposure to how fundamental organic and physical chemistry is relevant to sustaining the chemistry of our atmosphere and therefore life on Earth. The students will be asked to complete a pre-laboratory assignment that cover topics associated with atmospheric chemistry and photochemistry. During the pre-laboratory lecture, the instructor emphasizes the importance of photochemistry and how it relates to the myriad of chemical processes relevant to our atmosphere. The instructor will then outline the concept of quantum chemistry and methods such as time-dependent density functional theory that may be used to simulate electronic absorption spectra of molecules.

#### *Pedagogical Aims and Learning Outcomes*

Prior to or alongside the General Chemistry Laboratory, students complete the General Chemistry II lecture course and are exposed to concepts such as chemical kinetics which is relevant to atmospheric chemistry. More relevant to the purpose of this study, the General Chemistry I lecture course at UL Lafayette includes a unit comprising three modules and covers fundamentals of electronic structure of atoms and their electronic absorption spectra, as well as electronic and molecular structure of simple molecules. The module-level objectives within this unit are designed to enable students to recognize and understand concepts surrounding electronic and molecular structure as well as light – matter interactions. In particular, the pedagogical aims(*vide infra*) of the current experiment align with the following module- and course-level objectives for General Chemistry I, which constitute the required background and pre-requisite knowledge for this activity:

1. Define and calculate the wavelength, frequency and energy of electromagnetic radiation
2. Describe the concepts of excitation and relaxation of an electron
3. Define the basic concepts of quantum numbers, shells, subshells, orbitals, electronic charge distribution, and their relative energies
4. Write electronic configuration in simple atoms and molecules
5. Correlate electronic configuration of a molecule to its shape

As the current experiment requires students to compute optimised structures and electronic excitations, its implementation in General Chemistry courses could provide students at introductory chemistry level with hands-on experience in exploring principles and concepts pertinent to learning objectives 1 – 5, outlined above.

Furthermore, the general chemistry laboratory course at UL Lafayette includes one experiment on UV/Vis spectroscopy (in aqueous solution) of a metal complex (spectrophotometric analysis of Cu(II) tetraammonia complex); in this laboratory session, students are expected to measure the UV/Vis absorption spectrum of the complex and relate the measured absorbance to both its absorptivity coefficient at set wavelengths (e.g.  $\lambda=610$  nm) and its concentration in the aqueous solution. The computer-based experiment presented in this work could complement this or similar experiments as it provides a more fundamental, molecular approach to exploring molecular spectroscopy and illustrating the link between absorption of light and electronic excitation in simple molecules.

The use of electronic spectroscopy also finds common use in organic chemistry, especially in the context of photoinduced organic reactions – such as the Paterno-Buchi reaction. Students undertaking organic chemistry courses should be equipped with a good background knowledge of electronic structure and spectroscopy to ensure that they

acquire a solid and well-rounded experience surrounding principles of the (photo)reactivity of organic molecules. In this context, the current experiment could represent a useful, hands-on activity for consolidating such knowledge. Furthermore, if implementation into organic or physical chemistry laboratories is planned, this laboratory will provide students with practical knowledge of various concepts in mechanistic chemical reactivity and photochemistry, and how they extend and apply to atmospheric chemistry.

During the experiment, students will be asked to calculate the electronic absorption spectra of  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{H}_2\text{O}$ ,  $\text{O}_3$ ,  $\text{NO}_3$ , and  $\text{NO}_2$ . Four ( $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{H}_2\text{O}$  and  $\text{O}_3$ ) out of the six molecules have electronic absorption spectra that are outside of the tropospherically relevant solar irradiance, while the other two ( $\text{NO}_3$  and  $\text{NO}_2$ ) absorb within it. When the electronic absorption spectra are simulated, the students will be asked to compare with measure spectra available in the literature. This will allow students to make the important link between a simulation and how well it is able to model the experimentally derived spectrum.

The pedagogical aims of this experiment are to:

- Expose students to practical photochemistry and electronic absorption spectroscopy at an early stage.
- Making students aware of how important chemical concepts translate to the chemistry of the atmosphere.
- Be able to relate the lifetimes of long-lived greenhouse (and other) gases in Earth's troposphere and their overlap with the tropospherically relevant solar irradiance.
- Be able to discover the reasons for the scarcity of  $\text{NO}_2/\text{NO}_3$  during the day and their higher abundances at night – relating it to the photochemistry.

Furthermore, students will be asked to explore the relationship between the recorded/simulated absorption spectrum of a molecule and its electronic and molecular structure. In particular, at the end of the experiment students will be able to:

- Visualize and analyze molecular orbitals
- Assign electronic transitions
- Relate the character of the electronic excitation to the magnitude of the associated oscillator strength (and/or intensity)
- Compare and contrast spectra simulated with the nuclear ensemble method to those predicted by exclusively computing the vertical excitation energies.

In order to complete the experiment and fulfil its learning objectives, the following computational packages are required:

- GaussView6<sup>14</sup> and Gaussian09<sup>15</sup> and/or Gaussian16<sup>16</sup>
- Newton-X<sup>46</sup>
- Our spectral simulation script which will be made available to interested users by contacting the authors.

GaussView6 and Gaussian09/16 are commercial computational packages; if these are not available, alternative open source computational programs can be used to carry out this experiment. This may include MacMolPlt<sup>47</sup> and Avogadro<sup>48</sup> for drawing and visualizing molecular structure and viewing and analyzing normal mode wavenumbers and molecular orbitals. For computation of optimized structures, normal mode wavenumbers and vertical excitation energies, Psi4<sup>49</sup> and ORCA<sup>50</sup> represent possible alternatives to Gaussian09/16.

### 3. EXPERIMENTAL OVERVIEW

The methodology described in this section provides simulated electronic absorption spectra that have excellent agreement with the experimentally measured spectra.

Furthermore, the methods were selected to return simulated absorption spectra that are computable within a single typical laboratory session (generally 2 – 3 hours). An example pre-laboratory assignment is illustrated in section S1 of the Supporting Information, alongside the answer keys. The pre-laboratory assignment is designed to test the students' understanding of UV spectroscopy and prepare them for the laboratory session, by sampling various, general aspects of this topic. In order to complete the experiment, the students are asked to perform the following steps:

1. Computation of optimized structures and associated vibrational frequencies. This step is performed using the GaussView6 and Gaussian16 computational packages,
2. Generation of initial geometries (Wigner points) and vertical excitation energies to generate the full electronic absorption spectral profile of the selected molecule. This step is performed using our home-written script and is very important since it provides an absorption profile rather than the commonly used (and sometime mis-interpreted) stick spectra,
3. Analysis and interpretation of the simulated spectra, with comparison to the known experimental spectra.

Details of steps 1 – 3 are explained in the following text, while the procedure for the experiment is reported in section S2 of the Supporting Information. The instruction provided in this procedure are specific to GaussView6, thus they need to be modified if another computational package is used for this experiment. Using GaussView6,<sup>14</sup> *i.e.* a user-friendly graphical interface, the students will first construct the molecular structure of CO<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>O, NO<sub>2</sub>, NO<sub>3</sub> or O<sub>3</sub>. In this step, it is important to remind students to derive the charge and spin multiplicity of each molecular system prior setting the 'Opt+Freq' calculations running, especially if the experiment is implemented in higher division classes (even though, when using GaussView6, these are typically suggested by default). Subsequently, they will use GaussView6 to setup the calculations for submission to the Gaussian computational package;<sup>51</sup> this allows geometry optimization and, importantly, calculation of the vibrational frequencies. To this aim, it is important that the job type in the Gaussian Calculation Setup is set to 'Opt+Freq'. The method we used in this project is Density Functional Theory (DFT), *i.e.* one of the most commonly used computational methods in many research applications. The functional and basis set selected for the calculations were B3LYP/6-311+G(d,p). After the calculation setup, the students will submit the job so that the Gaussian computational program may optimize the molecular geometry, calculate the vibrational frequencies and prepare an output file which contains all the relevant information. If GaussView is unavailable, open-source alternatives, such as MacMolPlt or Avogadro, may also be used.

Subsequently, a set of initial geometries is generated by sampling the ground state vibrational wavefunction using a Wigner distribution. We opted to use this approach to simulate the spectra of our molecules of interest since it has been previously used to successfully simulate electronic spectra of more complex atmospheric molecules.<sup>32,34–39</sup> Furthermore, it represents a relatively straightforward approach to be implemented in an undergraduate laboratory. To this end, we developed a simple script which can be run using Terminal on a Unix or Linux platform. The script interfaces with the open source package Newton-X<sup>46</sup> to generate the required number of Wigner points based on the previous frequency calculations. In this way, the Gaussian16 output file from the first step above is used to prepare a set of geometries around the equilibrium geometry. The vertical excitation energies and corresponding oscillator strengths are then calculated at each Wigner point to allow generating the full electronic absorption spectrum. The interactive script guides the students by asking a series of questions, to ensure that they provide the required information for the Wigner point generation. The script then prepares the corresponding input files. In particular, the students will be asked to provide the name of the output file containing the frequency calculations and the desired number of Wigner points to be generated. Subsequently, the script will require the students select the desired level of theory (computational method and basis set) to be used to compute the electronic

absorption spectra. Finally, students will be asked to input the number of absorbing or emitting states for which the vertical excitation energy and oscillator strength require computing. In our optimal case, we have used the B3LYP/6-311+G(d,p) level of theory to compute the lowest 10 singlet excited states for closed shell molecules and lowest 10 doublet states for the radical species (NO<sub>2</sub> and NO<sub>3</sub>). Once the level of theory is selected, the script uses the optimized geometry and normal mode displacements to build a  $n$ -point Wigner distribution to model the ground vibrational level of the ground state.<sup>46,52</sup> A preview of the interactive script is given in section S3 of the Supporting Information. Newton-X also allows one to simulate electronic absorption spectra using this method. The additional aspects of our script are that it enables an interactive way of generating the inputs, i.e., that the student is asked to select the level of theory as well as other molecule specific questions. This script is therefore expected to work alongside Newton-X to facilitate implementation of absorption spectra simulations in an undergraduate laboratory setting. As mentioned above, the number of Wigner points ( $n$ ) is inputted by the students while running the script and can be modified at the discretion of the instructor or operator. In this project, we set the number of Wigner points to be 100. The number of Wigner points to be sampled was selected so as to allow completion of the experiment within the typical timeframe of an undergraduate chemistry laboratory session. A smaller or larger number of Wigner points can be selected by the instructor based on the time and resources allocated for the experiment. Figure S4 of the Supporting Information reports a comparison between the UV absorption spectrum of O<sub>3</sub> computed at the TD-B3LYP/6-311+G(d,p) level of theory, when sampling 50, 100 and 150 Wigner points. If the required information has been entered correctly and the initial geometries have been successfully generated, the script will output a success message and proceed to submission of jobs for computation of the vertical excitation energies. As part this project, a dedicated queueing script is coupled with the previous script to allow the students to run automatically the jobs in series starting from the first to the  $n$ -Wigner point. At each Wigner geometry, vertical excitation energies and oscillator strengths are calculated at the TD-DFT level is computed. In our present study, we use the TD-B3LYP/6-311+G(d,p) level of theory. After these are computed, the excitation energy dependent photoabsorption cross section  $P(E)$  can then be obtained using equation 1,

$$P(E) = \frac{\pi e^2}{2m_e c \epsilon_0} \sum_{j=1}^M \left[ \frac{1}{N_{TOT}} \sum_{N=1}^{N_{TOT}} f_{ij}^N g(E - \Delta E_{ij}^N, \delta) \right] \quad (1)$$

where  $g$  is a Lorentzian line shape function given by equation 5,

$$g(E - \Delta E_{ij}^N, \delta) = \frac{h\delta}{2\pi} \left( (E - \Delta E_{ij}^N)^2 + \left(\frac{\delta}{2}\right)^2 \right)^{-1} \quad (2)$$

$f_{ij}$  is the oscillator strength.

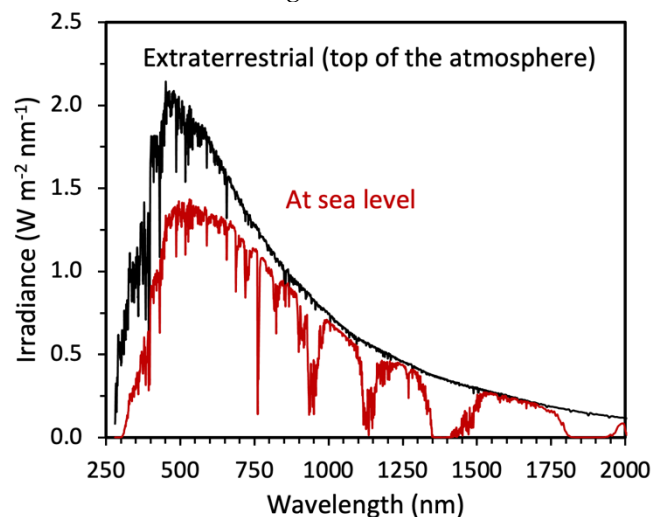
An additional script is then used to obtain the vertical excitation energies and oscillator strengths from each output file. Students are then asked to use equations (1) and (2) to compute the absolute photoabsorption cross sections of the molecules of interest. This functionality is already implemented in Newton-X, which the students may use to calculate the photoabsorption cross section, or they may simply use a spreadsheet program as part of their post-laboratory report to obtain the photoabsorption cross-sections. Interested users can contact the authors to obtain our scripts and for support.

#### 4. RESULTS AND DISCUSSION

This section will outline the results to be obtained from the laboratory session and the learning outcomes that are expected to benefit the students.

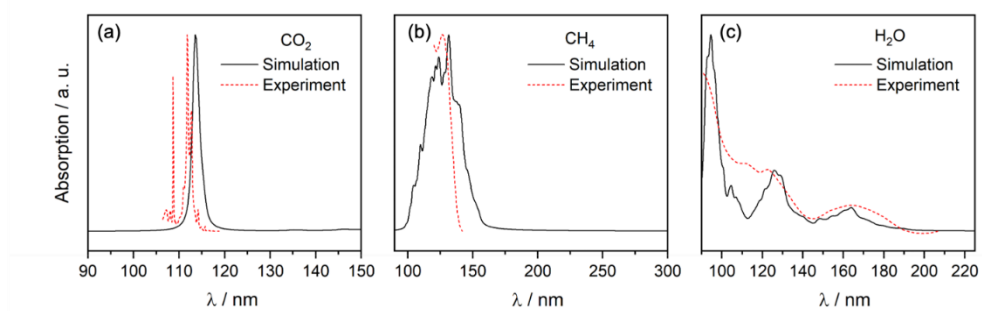
Solar photolysis is a significant source of removing volatile gases from the atmosphere. We therefore start by discussing the tropospheric solar spectrum to decide on the extent to which the absorption profiles of our molecules of interest absorb at and are removed by the fraction of near-UV and Visible solar wavelengths that survive through the

stratosphere. Figure 1 presents the fraction of tropospheric solar flux in the wavelength range 280 – 2000 nm – at the surface of planet Earth. As is evident from Figure 1, no irradiance (the power per unit area per nanometer wavelength of light) is measured at wavelengths shorter than 300 nm. Ozone in our Stratosphere is responsible for the lack of irradiance at such short wavelengths.



**Figure 1.** The solar actinic flux,<sup>53,54</sup> showing the solar flux of a given wavelength present in the troposphere at sea level (red solid line).

The Irradiance reaches a maximum at ca. 500 nm and tails off at wavelengths longer than 1500 nm. The broad “dips” in the irradiance at ca. 950 nm, 1150 nm and 1350 nm are due to near-IR absorptions by tropospheric water vapor. The sharp “dip” at ca. 750 nm is due to near-IR absorption of O<sub>2</sub>. Absorption of IR radiation is insufficient for overcoming the bond dissociation energy of the O-H and O-O bonds in H<sub>2</sub>O and O<sub>2</sub>, respectively. Therefore, H<sub>2</sub>O and O<sub>2</sub> are not removed from the troposphere via solar photolysis. Instead, they are likely to undergo collisional relaxation and subsequent bimolecular chemistry that promotes secondary chemistry in the atmosphere. If, however, the electronic absorption profile of a given molecule overlaps with the solar tropospheric irradiance curve, and its bond dissociation energies are less than or comparable to the excitation wavelength, it will likely undergo removal by solar photolysis. We will now access the electronic absorption spectra of several key molecules that are expected to undergo electronic absorption outside and within the tropospherically relevant solar irradiance.



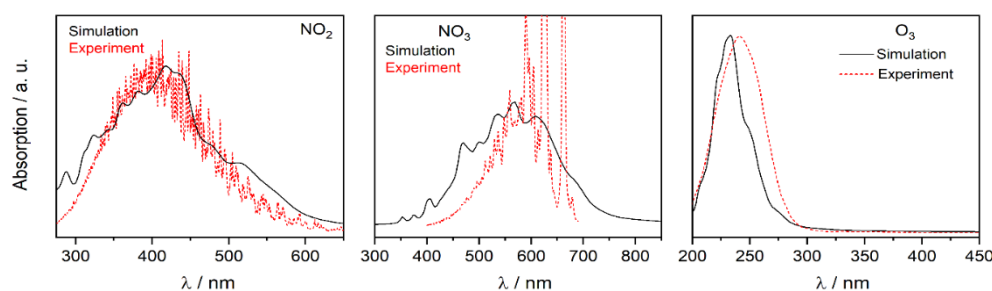
**Figure 2.** Simulated (black) and experimental (red) electronic absorption spectra of (a) CO<sub>2</sub>, (b) CH<sub>4</sub> and H<sub>2</sub>O.

Figure 2 shows the calculated electronic absorption spectra of three key tropospherically relevant molecules CO<sub>2</sub>, CH<sub>4</sub> and H<sub>2</sub>O using the procedure described in the methodology. These molecules are classified as greenhouse gases. The experimentally measured electronic absorption spectra are displayed alongside each simulated absorption profile. The students may be provided with the experimentally measured spectra or asked to

find these by consulting an online database (such as the The MPI-Mainz UV/VIS Spectral Atlas of Gaseous Molecules of Atmospheric Interest).<sup>40</sup> In all cases, the calculated and experimental electronic absorption spectra are in good agreement – reinforcing the level of theory and methodology used to simulate these spectra. By close inspection of figure 2(a), it becomes clear that a second absorption feature is observed in the experimental UV spectrum at  $\lambda < 110$  nm, but it is not reproduced by the simulated electronic spectrum. This is most likely due to the limited number of excited states included in the spectral simulation; computation of vertical excitation energies of additional, higher lying electronic states is expected to return the short-wavelength absorption band observed in the experiment. This was not carried out in the present work as we aim at keeping the computations consistent for all molecules and the simulation easy to complete within the time allocated for a laboratory session. The expected minor differences between the simulated and experimentally measured spectra provide the students with the vital first-hand account of the approximations inherent to quantum chemical methods that lead to such discrepancies between the simulated and experiment results.

Time permitting, the instructor may decide to explore changes in the method and/or basis set or, if the class has been exposed to the essential elements of quantum chemistry, ask students to comment on the differences between the level of theory and the agreement. Students can then gauge which methods and basis sets are the most accurate for a given problem.

In all the molecular systems in Figure 2, the electronic absorption maximum, and its long-wavelength tail, are at shorter wavelengths than the solar spectrum displayed in Figure 1. At this stage students should be able to make the connection between the atmospheric lifetime and their lack of removal via solar photolysis, concluding that they do not absorb within the solar spectrum and therefore survive with long atmospheric lifetimes in the troposphere. Atmospheric lifetimes for  $\text{CO}_2$ ,  $\text{CH}_4$  and  $\text{H}_2\text{O}$  are of the order of 300–1000 years, 9–12 years and a few hours–days, respectively.<sup>55,56</sup> The comparatively shorter lifetime of the latter is attributable to its removal by bimolecular chemistry with atmospherically oxidants (e.g. Criegee intermediates).



**Figure 3.** Simulated (black) and experimental (red) electronic absorption spectra of (a)  $\text{NO}_2$ , (b)  $\text{NO}_3$  and (c)  $\text{O}_3$ .

Figure 3 presents three further atmospherically relevant molecules  $\text{NO}_2$ ,  $\text{NO}_3$  and  $\text{O}_3$ . Again, their simulated electronic absorption spectra are given in black, while the experimentally measured spectra are given in red. In all cases, the simulated and experimental electronic absorption spectra are in good agreement. Again, the instructor may decide to change the level of theory to show how method and basis set impacts the spectral profile. In the case studies presented in Figure 3,  $\text{NO}_2$  and  $\text{NO}_3$  absorb in the range 300 – 600 nm, covering the near UV and mid-visible spectrum, and at wavelengths that are well within the solar irradiance that reaches the surface of earth. The students will then be expected to recognize that both  $\text{NO}_2$  and  $\text{NO}_3$  absorb within the tropospheric relevant solar spectral range. In the case of  $\text{O}_3$ , students will be expected to analyze the absorption spectrum of ozone and relate it to the anticipated stratospheric absorption of near- and mid-UV radiation. From this, they will rationalize the absence of such near-/mid-UV



wavelengths in the tropospheric solar spectrum at sea level based on the absorption spectrum of  $O_3$ . This latter observation should be connected to the activity of  $O_3$  in the stratosphere in blocking harming UV-radiation from penetrating into the troposphere, thus offering protection to life to the surface.

The students should also be able to appreciate the comparably shorter day-time lifetimes of  $NO_2$ , and  $NO_3$  (2-11 hours),<sup>57</sup> connecting their daytime removal to their inherently high solar photolysis rate constants, which manifest from their absorption within the tropospheric solar spectrum.

Taken together,  $CO_2$ ,  $H_2O$  and  $CH_4$  are case studies that are designed to show the student that UV-excitation in the troposphere does not contribute to their tropospheric removal, leading to elevated atmospheric lifetimes and their potent activities as greenhouse gases. In contrast,  $O_3$ ,  $NO_2$  and  $NO_3$  are examples which are selected to illustrate how the optical properties of certain atmospheric species can limit their lifetime due to solar photolysis or to block harmful UV-radiation from reaching the surface of earth.

## 5. CONCLUSIONS

In this study we devise a simple and efficient method for simulating the electronic absorption spectra of atmospherically relevant gas molecules which may be implemented into an undergraduate teaching laboratory. The method allows for the computation of spectral profiles, which distinguishes it from the simple yet unreliable approach of calculating vertical excitation energies from optimized ground state minima, which only provide stick spectra.

Once the laboratory session is completed, the participating students should have a realization of the ways in which chemical and physical properties extend to topical issues such as climate science. In particular, the laboratory is designed to expose students to available methods for the simulation of electronic absorption spectra, as well as to provide students with the essential knowledge of how tropospheric solar photolysis leads to removal of trace gases from the atmosphere. The laboratory is especially suitable for exposing students to two underrepresented (but important) fields in chemistry: computational and atmospheric chemistry. The laboratory is therefore expected to bridge the gap between the undergraduate and graduate level chemistry.

The computational exercise presented in this work could be implemented in introductory or general chemistry class as well as physical chemistry laboratories to allow students to explore concepts of molecular and electronic structure through a hand-on activity. For instance, the experiment allows students to visually investigate optimal geometries of simple molecules, beyond the pen and paper approach typically offered in general chemistry lecture courses (e.g., Lewis Dot structures and fundamentals of electronic structure), and provides them with a 3D visualization of molecular orbitals in simple molecules. Furthermore, the experiment may serve to reinforce or facilitate the introduction of basic concepts of ground/excited state configurations of a molecule, vibrational motion and electronic excitation, which may be particularly important for higher division classes such as physical chemistry courses. The experiment can be implemented into organic chemistry classes as it is or by adapting it to include the simulation of UV spectra of atmospherically relevant organic species (e.g., chlorofluorocarbons or hydrochlorofluorocarbons). Finally, it is important to remember that UV spectroscopy often features in both organic and physical chemistry as a mean to investigate the occurrence, mechanisms and kinetics of chemical reactions and computational modelling of ground and excited state properties may aid interpretation of mechanisms of (photo)chemical reactions when experiments are not available; introducing students to the applications of computational chemistry may be beneficial for their future studies or careers.

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