ROYAL SOCIETY OF CHEMISTRY

PAPER

Check for updates

Practical atmospheric photochemical kinetics for undergraduate teaching and research

James D'Souza Metcalf, †ab Ruth K. Winkless, †a Abbie Robinson,a Stuart C. Smith, ‡c Andrew R. Rickard ad and Terry J. Dillon*a

Including practical atmospheric chemistry in the undergraduate syllabus presents numerous challenges: most research grade equipment is too complex and expensive, and can require extensive safety training for students to use independently and efficiently. Herein we report an undergraduate analytical project that can be effectively performed in teaching laboratories equipped with standard UV-vis spectrometers, centred around an important application of photochemical kinetics in atmospheric research. Carbonyl containing compounds in dilute cyclohexane solutions may be considered as in a "quasi-gas-phase" environment. Measurements of absorption spectra in such solutions can therefore provide useful information into the atmospheric photochemistry of carbonyl compounds – a critically understudied aspect of atmospheric kinetics. We have delivered this course for two years and found that a project centred around collecting, processing, and understanding the atmospheric implications of these spectra is accessible to a range of student abilities and is an excellent tool for introducing the wider concepts and impacts of atmospheric chemistry.

Sustainability spotlight

Achieving a truly sustainable and environmentally responsible chemical industry requires a thorough consideration of the degradation of chemicals across all environmental domains. The atmospheric photooxidation of organic compounds has huge implications for human health (SDG 3) and the environment (SDGs 13 and 15) as it is the primary source of pollutants such as ozone, nitrogen dioxide and organic aerosol, particularly in many urban environments. In this work we seek to address the lack of practical, lab-based activities addressing this critical topic at undergraduate level and thus engage learners in this vital area of sustainable chemistry. A particular benefit of our approach is its minimal equipment requirements, making it accessible to a wide range of institutions and settings (SDG 4).

Introduction

Air quality is a globally critical issue, with the World Health Organization estimating that 99% of the population live in areas where air pollution poses a risk to health.[1] The atmospheric photooxidation of Volatile Organic Compounds (VOCs) is known to form harmful secondary pollutants including ozone, formaldehyde and airborne particulate matter,[2–5] with such air pollutants being responsible for an estimated 400 000 excess deaths in Europe alone.[6] Therefore, in order to control our exposure to harmful airborne pollution, a detailed understanding both of emission profiles and the chemical transformations VOCs undergo once emitted is required.[7,8]

Current research on fundamental atmospheric photochemistry typically utilizes techniques such as laser photolysis, flow tubes and atmospheric simulation chambers.[7,8] Such experiments require significant expenditure and specialized technical knowledge to design, assemble, characterize, maintain and analyse data. They can also carry safety risks which are often deemed unacceptable for undergraduate researchers (*e.g.* the use of high-powered lasers and/or light sources operating in the UVC region). While development of *in silico* teaching tools has proven effective in engaging students with the study of atmospheric chemistry (for recent examples see Hua *et al.*[9] and Peng *et al.*[10]), the aforementioned technical complexity means integrating experimental work into practical teaching remains challenging. A teaching lab experiment reported by Roberts *et al.*[11] has sought to address these challenges, using Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) spectroscopy to monitor atmospherically relevant alkene ozonolysis chemistry *in situ*. This experiment serves as a powerful tool to explore core kinetic and spectroscopic concepts such as the

a Wolfson Atmospheric Chemistry Laboratories, Department of Chemistry, University of York, Heslington, York, YO10 5DD, UK. E-mail: terry.dillon@york.ac.uk

b Green Chemistry Centre of Excellence, Department of Chemistry, University of York, Heslington, York, YO10 5DD, UK

c Department of Chemistry, University of York, Heslington, York, YO10 5DD, UK

d National Centre for Atmospheric Science, Department of Chemistry, University of York, Heslington, York, YO10 5DD, UK

† These authors contributed equally.

‡ Now at: Department of Chemistry, Durham University, Lower Mount Joy, Durham, DH1 3LE, UK.

pseudo first-order approximation and the Beer–Lambert Law in the context of a key atmospheric reaction class. It is, however, reliant on a custom-built flow cell setup including an ozone generator and measures reactions in a thin film of involatile liquid spread over the ATR detector. While this experimental setup is representative of heterogeneous reactions (*e.g.* on aerosol surfaces), it is not applicable to homogeneous atmospheric chemistry in general.

Herein we describe a combined practical and modelling experiment that allows undergraduate students to estimate atmospheric photolysis rates from their own experimentally determined parameters. Our approach is built around affordable and ubiquitous UV-vis spectroscopy, cheap and readily available chemicals and open-access datasets which can be readily processed using any available spreadsheet software. This experiment is flexible and has successfully been deployed as a core part of undergraduate research projects, summer studentships, secondary school work-experience internships and in our own research to generate novel, publication-quality kinetic data.[12]

Pedagogical objectives

We expect students who carry out this project to achieve the following objectives:

(1) Understand the fundamentals of how UV light interacts with simple organic carbonyls, being able to relate this to gas-phase photochemistry and UV-vis spectroscopy.

(2) Apply kinetic models of atmospheric photolysis to their own experimental data to estimate photolysis rates under different atmospheric conditions.

(3) Recognize the significance of these reactions to the atmosphere and environment, demonstrating critical thinking in the evaluation of the relative environmental impacts of different emissions.

(4) Present and critically discuss scientific findings as reports, presentations and by participating in workshops using appropriate vocabulary, data visualization and scientific writing.

(5) Undertake laboratory work independently, managing their own time and having some input into their project direction.

Scientific background

Much of atmospheric chemistry is concerned with modelling the atmospheric processing of VOC emissions to understand their sources, fates, and the associated environmental and air quality impacts. Such models rely on accurate knowledge of VOC photochemistry under different atmospheric conditions. Several oxidative breakdown routes are available to VOCs upon emission into the atmosphere (Fig. 1). Most atmospheric degradation is initiated by reaction with the OH radical, which is frequently responsible for the largest fraction of VOC reactivity and as such it is by far the best understood. Decades of research has led to a number of comprehensive databases of kinetic data of VOC + OH radical reactions being available[13,14]

along with effective structure – reactivity predictive methods for rate constants.[15–18]

Photolysis is also a key breakdown pathway for carbonyl-containing compounds. In contrast to OH radical reactivity, the available data on carbonyl photolysis is sparse. Due to the lack of reliable data most atmospheric models are forced to make significant assumptions, for example the Master Chemical Mechanism (MCM)[19] assumes that the photolysis rate parameters of many carbonyl species can be necessarily equated to those of a small number of representative carbonyl compounds[20,21] (see SI, S5).

Photolysis rates (*j*-values) can vary significantly between structurally similar compounds, due to their dependence on multiple parameters as described in eqn (1):

$$j = \int F(\lambda,\theta)\sigma(\lambda)\varphi(\lambda)\mathrm{d}\lambda \tag{1}$$

Calculation of photolysis rate: *j* is the first order photolysis rate coefficient, *F* is photon flux (in quanta $cm^{-2}\ s^{-1}\ nm^{-1}$), λ is wavelength, θ is solar zenith angle, σ is the gas-phase absorption cross section (in cm^{2}) and φ is quantum yield to photolysis. σ and φ have additional dependencies (temperature and temperature and pressure respectively) however these are beyond the scope of this work.

In an atmospheric context $F(\lambda)$ is the spectrum of solar light (actinic flux), which is widely available from both measurements and models. Quantum yields have only been reliably measured for a relatively small set of carbonyl compounds as experiments are technically complex and estimating them *via* purely theoretical methods remains complex, computationally expensive and extremely specialized.[22]

Gas-phase absorption cross sections are simpler to measure, but this is still not straightforward given the inherent difficulties in handling and controlling the gas-phase concentration of semi-volatile compounds. Few apparatuses are available worldwide, and none are feasible to implement in a teaching laboratory setting. Estimation of gas-phase cross sections *via* theoretical methods such as Time-Dependent Density Functional Theory (TD-DFT) is notoriously difficult[22] and whilst significant progress has been made towards the development of user-friendly tools for non-specialists,[23] the current state-of-the-art remains computationally expensive and requires specialist knowledge.

It has long been known that absorption cross sections measured dilute in perfluoroalkanes closely resemble those measured in the gas phase, owing to the relative lack of solvent interaction with the n → π* excitation of an oxygen lone pair electron to the lowest unoccupied molecular orbital of the C=O chromophore, which is almost always the most important transition for carbonyl photolysis in the atmosphere.[24,25] In order to facilitate the adoption of a non-fluorinated solvent system in this investigation, experimental measurements of UV absorption cross-sections in a range of polar and non-polar solvents were made (Fig. 2). In keeping with Woodward–Fieser rules, spectra are significantly red-shifted by hydrogen bond donor (protic) solvents (methanol and water) and thus unsuitable for quasi-gas phase measurements, with the hydrogen
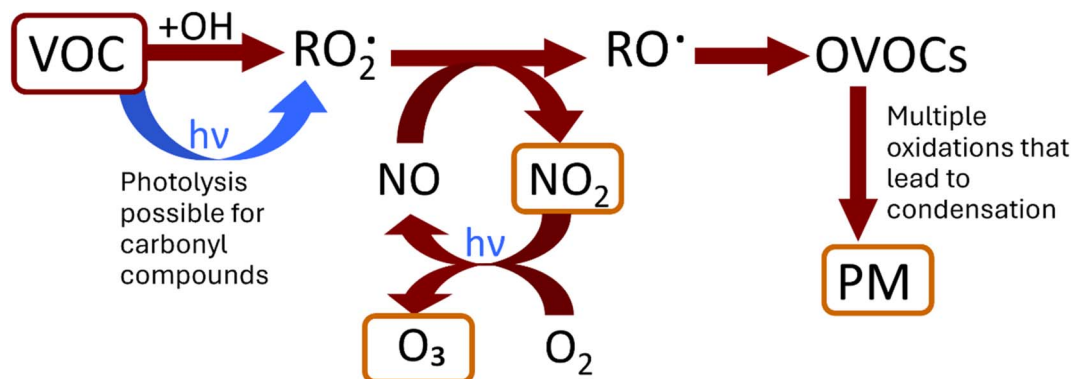
Fig. 1 The various photochemical oxidation routes available to VOCs in the atmosphere. Both radical abstraction and photolysis reactions lead to organic peroxyl radicals, which undergo further reactions to form particulate matter (PM), NO_2 and O_3, all of which are harmful to human health and the environment. OVOCs = oxygenated volatile organic compounds, PM = particulate matter, 'hv' indicates a photolysis-initiated process.

bond donor only (aprotic) solvent diethyl ether showing a much milder effect.[26] In our experience spectra taken in cyclohexane are generally within 20% of the true gas phase values consistently across all wavelengths (no peak shift seen), providing a student friendly and sustainable medium for quasi-gas-phase absorption cross section measurements. Alkane solvents also remove the possibility of unwanted secondary reactivity such as hydrolysis or hemiacetal formation by alcohol or water and aldehydes or ketones or the hydrolysis/transesterification of esters.

Therefore, in practice this means that solution-phase UV-vis spectroscopy, an accessible technique for almost all teaching laboratories be used to measure quasi-gas phase absorption cross-sections, and in combination with standard assumptions regarding quantum yield and open-source actinic flux models used to estimate photolysis rates for a range of atmospherically important carbonyl compounds.

Experimental

The procedure, derived from one we routinely use in our research, takes part in 3 stages:
(1) Acquisition of spectra.
(2) Data analysis and determination of cross sections.
(3) Evaluation of atmospheric impact.

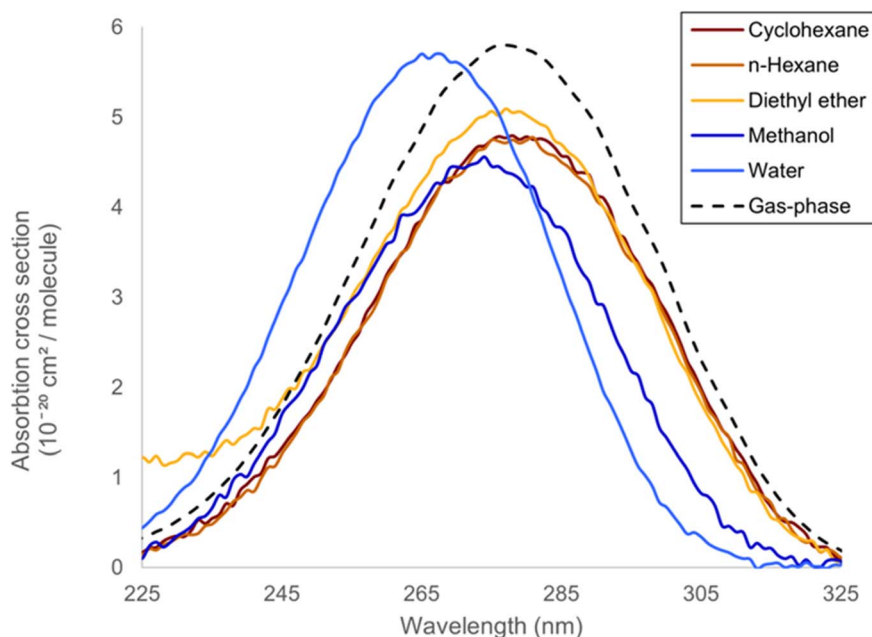**Fig. 2** Absorption cross section spectra of butanone taken in a range of solvents, compared to a gas phase spectrum from the literature.[27] In general terms, hydrogen-bond donor solvents (ethanol, methanol) blue shift carbonyl peaks significantly, hydrogen-bond acceptor solvents (diethyl ether) show a much smaller solvent effect. Non-hydrogen-bonding solvents (hexane, cyclohexane) give the most representative spectra.

In settings where students have multiple compounds to analyse there is flexibility to complete each stage for all compounds before proceeding, complete all analysis one compound at a time or some combination of both, depending on resource availability. Figures in this section are derived from a worked example evaluation of butanone (methyl ethyl ketone, MEK), which we often use as a model carbonyl compound when training new project students. The full worked example, including raw data, evaluation spreadsheets and suggested points for discussion are included in the SI.

Acquisition of spectra

Students conducted experiments in the University of York's Teaching Laboratories, with access to standard volumetric glassware, shared fume hoods and bench space as well as small samples of carbonyl compounds of interest and solvent quantities of cyclohexane (typical measurements were taken at 0.05–0.005 M concentrations from 10–100 mL stock solutions, requiring several hundred mL solvent per experiment). Spectra were acquired at 1 nm resolution using quartz cuvettes on Thermo Scientific GENESYS 180 UV-vis spectrophotometers. Students typically had some familiarity with these instruments from taught lab sessions in earlier years of their course. However, assistance from technicians and postgraduate demonstrators were freely available.

For each sample carbonyl, three spectra at a minimum of three concentrations were measured. Time allowing, a larger number of spectra, typically five were taken to improve precision. Students were given an initial indication of the appropriate concentration range for the spectrometer (around 0.010 M) but were expected to independently ensure that all measurements they used were within the linear concentration-absorption range of the instrument (on most instruments linearity can be achieved in an absorbance range of 0.1 and 1.0, as a minimum, although higher-end instruments are often more forgiving). A check for such linearity is included in our data processing workflow (*vide infra*). It should be reinforced to students that accurate knowledge of the actual concentration of their samples is key, rather than spurious focus on obtaining points at round numbers (*i.e.* 0.10, 0.20 0.30) or achieving even spacing between points. To produce robustly interpretable data, concentrations should be as accurate as possible, with a 2-sigma error in concentration of 10% suggested as a minimum. We find that this is generally attainable for students using standard micropipetting technique and medium sized (25 or 50 mL) volumetric flasks; weighing carbonyl compounds directly into volumetric flasks can also be a useful approach if the compound of interest is of a lower volatility.

To introduce students to the experiment, a postgraduate student familiar with the technique guided the group through an initial experiment with butanone, ensuring that they were familiar with the techniques and equipment used. No techniques were new to the students as both production of stock solutions and use of the spectrometers were covered in previous laboratory sessions in earlier years, so this acted as a practical revision session and a chance for students to ask questions

about the project. The success criterion for this session was for students to accurately record a minimum of three (ideally five) spectra across an appropriate concentration range. An example of this, is shown in Fig. 3.

For the rest of the course, students were expected to plan their own experiment time, making measurements of their assigned or chosen compounds whilst supervised by trained postgraduate student demonstrators with extensive experience in laboratory experimental chemistry, albeit not necessarily in atmospheric chemistry.

Among the most prominent sources of experimental uncertainty in this experiment is spectral noise, which is particularly problematic at low concentrations close to the signal-to-noise limit of the instrument, and at longer wavelengths where actinic flux is high and errors are particularly sensitive when propagated through the following calculations. It is therefore crucial that a good baseline is achieved on spectrometers before spectra are taken. Spectrometers should be turned on well in advance of use to allow the temperatures of the light sources to stabilize, after which their baselines should be thoroughly calibrated. It may also be appropriate to manually subtract a measured solvent blank from spectra depending on the stability of specific instruments. Time allowing, it is also beneficial to average several spectra taken at each concentration.

Data processing

Students were guided through the analysis of their data according to the predefined workflow laid out in Fig. 4. In cases of limited learner confidence, or in cases where spectra were only collected at 1–2 concentrations a conceptually simpler workflow is also possible, outlined at the end of this section.

Data from the spectrometers was in the form of .txt or .csv files. Students were permitted to process the data in software of their choice, but demonstrations were done using Microsoft Excel, a package available to students through the University
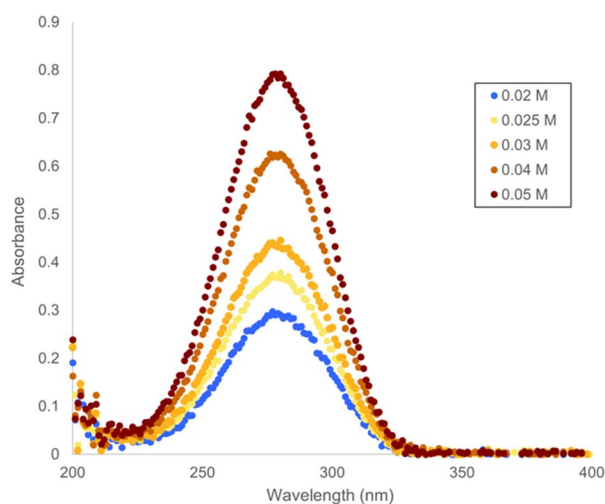

Fig. 3 Absorbance spectra of butanone in the UV region taken at 5 concentrations within the linear range of the instrument.

At each wavelength

Import data → Calculate gradient and correlation coefficient of the linear relationship between Absorbance and Concentration

↓

Calculate molar extinction coefficient from this gradient, by dividing it by path length

↓

Reject values where correlation coefficient is less than 0.9, indication of non-linear Beer-Lambert response

↓

convert to absorption cross section with eqn. 2 → Compare to literature, and to other compounds
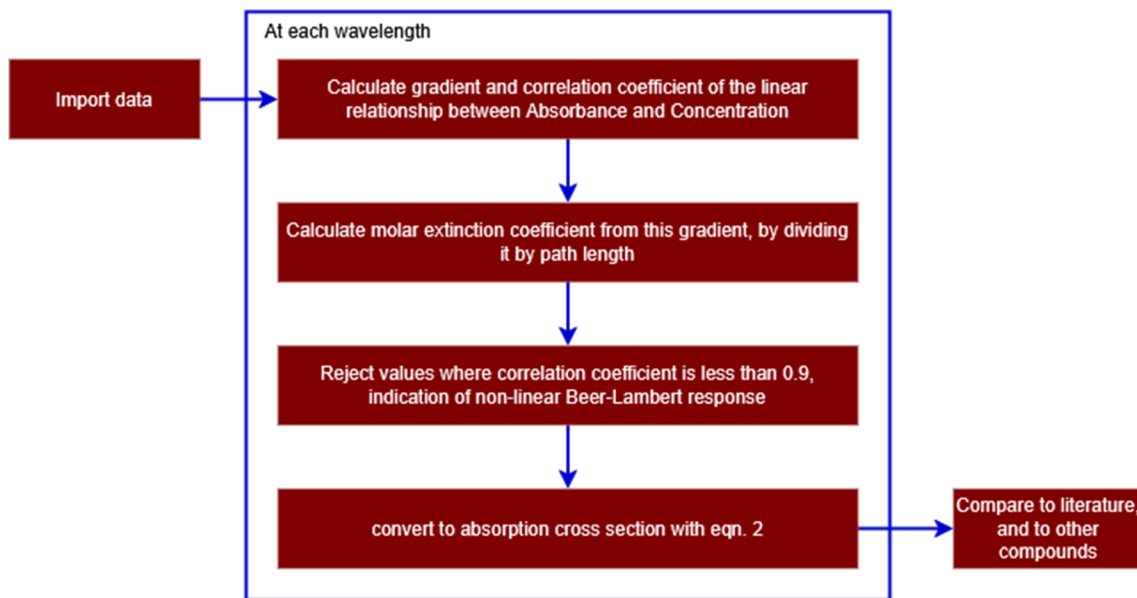
Fig. 4 The workflow used by students to convert measured absorbance spectra to quasi gas-phase absorption spectra.

which they had received prior instruction in using. Analysis is multi-step but straightforward, relying on applying the Beer–Lambert Law (eqn (2)):

$$A(\lambda) = cl\varepsilon(\lambda) \qquad (2)$$

Beer–Lambert Law: $A(\lambda)$ is absorbance at wavelength λ, c is concentration in mol dm^{-3}, l is path length in cm, and $\varepsilon(\lambda)$ is wavelength-dependent molar extinction coefficient in dm^3 mol^{-1} cm^{-1}.

Absorbance can therefore be converted to extinction coefficient using the gradient of the linear relationship between absorbance and concentration. In cases where only one concentration is obtained, the extinction coefficient can be estimated calculated by dividing absorbance by the product of concentration and path length. Theoretically, this should yield the same results, but in practice it is more susceptible to errors arising from noisy or non-zero instrument baselines and so is only advised in cases where the more thorough data analysis methodology is not possible. Worked examples of both processing methods are available in the SI.

Solution phase molar extinction coefficients $\varepsilon(\lambda)$ found from these experiments can then be converted to gas phase absorption cross sections $\sigma(\lambda)$ (in cm^2 per molecule) via eqn (3):

$$\sigma(\lambda) = \varepsilon(\lambda) \times \frac{1000}{N_A} \times \ln 10 \qquad (3)$$

Calculation of gas-phase absorption cross section $\sigma(\lambda)$ in cm^2. $\varepsilon(\lambda)$ is the solution phase molar extinction coefficient in dm^3 mol^{-1} cm^{-1}, and N_A is Avogadro's number.

This conversion accounts for difference in both concentration units (mol dm^{-3} vs. molecules per cm^3), and difference in convention for measuring absorbance (log$_{10}$ vs. ln scales) between the liquid and gas phases. The resulting cross-section

spectra can then be compared to true gas-phase spectra from literature sources (Fig. 5).

Once experimental data have been collected and processed, comparisons to literature gas phase spectra provides an opportunity to compare and contrast, discuss and reflect on results. Several databases are available which provide suitable data for this from such as those from the IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation,[13] the NASA JPL Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies[28] and the MPI-Mainz UV/VIS Spectra Atlas of Gaseous Molecules of Atmospheric Interest.[27] Previous undergraduate student work has consistently indicated that quasi-gas-phase spectra taken in cyclohexane are reasonably similar
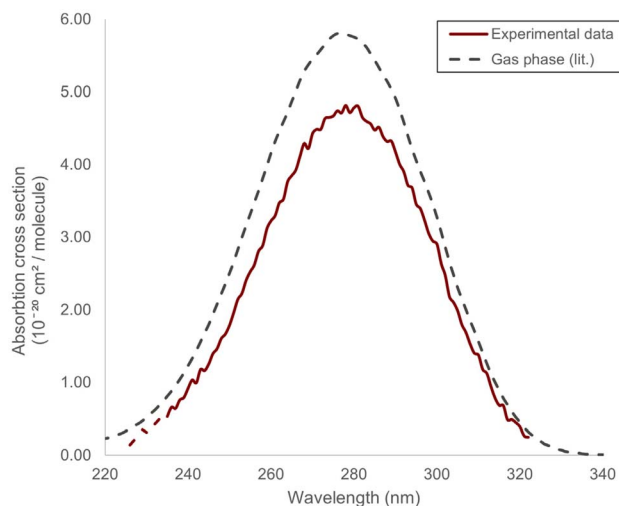

Fig. 5 A quasi-gas phase UV absorbance cross section spectrum for butanone calculated from student data according to our methodology, compared to a literature gas phase spectra.[27]

to their gas phase counterparts. In particular, ketone spectra measured this way consistently give values of $\sigma(\lambda)$ within 20% of the true gas phase spectra (Table 1).

Atmospheric implications

To understand the potential atmospheric significance of their absorption cross section measurements, the students calculate an estimation of photolysis rate using eqn (1). To calculate $F(\lambda, \theta)$, students were directed to use the free online Quick-TUV calculator,[31] a radiative transfer modelling tool that calculates an actinic flux spectrum from a provided solar zenith angle (θ), developed by the US National Centre for Atmospheric Research Atmospheric Chemistry Observation and Modelling (NCAR ACOM) institute. The desired data can be attained by setting the model to "actinic flux, spectral (quanta s^{-1} cm^{-2} nm^{-1})" and selecting the wavelength range(s) and solar zenith angle(s) of interest.

The significance of the estimated photolysis rates can be assessed through comparisons of relative photolytic losses between molecules, and comparisons to other loss pathways, such as reaction with OH radical. In a workshop, students were guided through how to calculate OH reactivity rates from an average atmospheric OH concentration of 10^6 molecules per cm^3 (ref. 32) and rate constants which are available in public databases from IUPAC[13] and EUROCHAMP 2020.[14,33] By comparing OH loss rates and photolysis rates, students can determine which route is primarily responsible for the degradation of their compound(s) of interest and estimate the atmospheric lifetime of the VOC. As a further step, air quality metrics may be calculated for each compound. One such metric is the photochemical ozone creation potential ($POCP_E$) which may be estimated based on molecular structure, k-value and potential for photolysis.[34] Combining this with research or discussion on the sources of emission of their compound helps students contextualize their work in wider atmospheric and environmental chemistry.

Implementation and feedback

This experiment is scalable and flexible, enabling its facile deployment to a range of settings from short teaching lab activities to postgraduate research projects.[12] We have most commonly employed this activity as part of undergraduate summer research studentships and as part of a final-year

research project for BSc students, the details of which we outline below. As atmospheric chemistry is a major research area at the University of York[35,36] it provides a vital route for incorporating this into our taught curriculum beyond lectures.

Undergraduate research project structure

This content was developed to run as a final year group project for BSc students studying chemistry at the University of York. The project is designed as a "capstone module" that comes at the end of the students' course with the stated aim of allowing students to "experience independent project work" whilst "planning and conducting the project in collaboration with an academic supervisor".[37] The project is worth one third of students' final year grade, equivalent to 20% of their overall degree. The module allows for 2 days of work a week for 18 weeks, with introductory workshops on project planning run centrally by the department for all project students. Within this framework, we typically incorporate a series of workshops and presentation sessions to develop students' experimental, data analysis, presentation and scientific discussion skills. During laboratory sessions, students had open access to teaching labs, including fume cupboard space and spectrometers, and were encouraged to manage their own time between lab work and data analysis. Timetabled activities occur at fixed points during this time as outlined in the SI.

Within the group project, individual sub-projects that are of interest to our research were chosen by students (e.g., long chain aldehydes which are present in cooking emissions,[38,39] novel carbonyl-containing "green" solvents,[12] trends arising from branching in ketones, and evaluating other solvents that provide the same quasi gas phase effects). Large numbers of carbonyl compounds could justifiably be of interest due to the general lack of measurements and measurement redundancy in the available cross-section data. We find that having multiple distinct but related sub-projects provides a fertile environment for engagement between students in the discussion groups and workshops, and that students are easily able to influence the direction of their projects to emphasize topics of their own interest. In the past this has included investigating the influence of solvent polarity and hydrogen bonding on $\sigma(\lambda)$, attempting to correlate spectral features ($\sigma(\lambda)$, λ_{max} etc.) to more fundamental chemical and physical parameters calculated via ab initio theoretical calculation such as DFT (e.g., dipole moment), and considering indoor photolysis by UVC air cleaning devices and their potential health implications.

Student feedback and pedagogical reflection

Qualitative analysis of free-text responses collected from participants in the undergraduate research project revealed several recurring themes that align closely with the stated pedagogical objectives of the module. Though the cohort size ($n = 5$) is limited, the feedback provides meaningful insight into student experiences, highlighting both the perceived value of the project and areas for potential refinement.

One of the most prominent themes to emerge from student feedback was the high value placed on independence in the

Table 1 Scaling factors between student-measured quasi gas-phase cross sections and literature values at maximum absorption for true gas phase spectra[a]

VOC	Scaling factor	Literature σ value/10^{20} cm^2 per molecule
Acetone	0.99 ± 0.0013	4.94 at 274 nm (ref. 29)
Butanone	0.82 ± 0.0007	5.80 at 277 nm (ref. 27)
2-Pentanone	1.14 ± 0.0012	6.13 at 281 nm (ref. 30)
3-Pentanone	1.11 ± 0.0016	6.34 at 279 nm (ref. 27)

[a] Derived from 5 repeats of experiments. Data reported as average $\pm 2\sigma$.
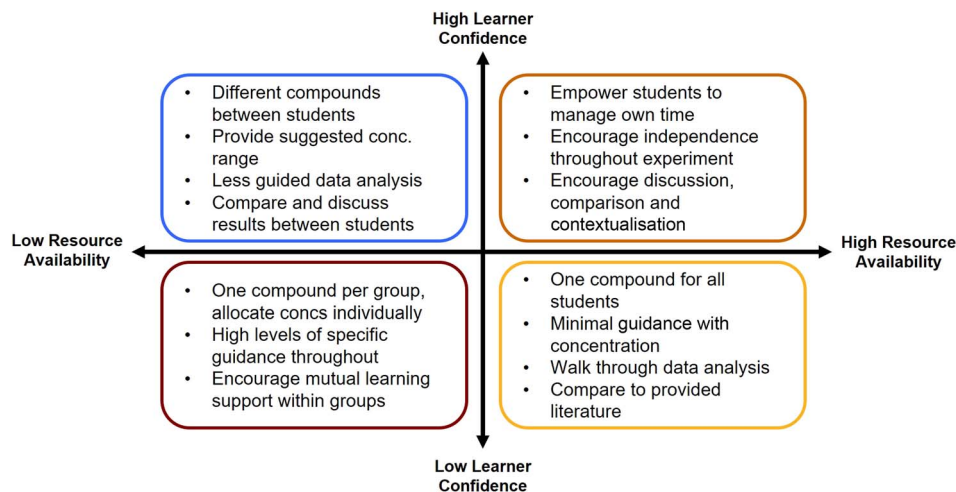
Fig. 6 A visualized framework to guide modifications to the experiment in order to adapt it to different educational settings.

laboratory. Multiple respondents described appreciating the opportunity to work autonomously, to plan and execute their own experiments, and to take ownership of their project direction. Comments such as "I liked being able to work independently in the lab and being responsible for the planning of my own work" indicate that the structure of the project effectively supported students in developing self-reliance – an essential graduate attribute. This autonomy was scaffolded by technical workshops and access to experienced postgraduate demonstrators, allowing students to explore experimental atmospheric chemistry in a low risk yet authentic research environment.

Students frequently referenced the value of data analysis and its connection to real-world applications and impact. For example, one student commented that they found "the data analysis in comparison to literature and its application to real world atmospherics the most valuable." Another reflected on how the project "allowed me to improve in data handling." These responses suggest that the analytical components of the project were not only technically engaging but also pedagogically effective. By situating experimental data within the context of broader environmental implications, the project provided valuable exposure to atmospheric chemistry, a subdiscipline often underrepresented in undergraduate practical courses, with one student noting that the project "gave me an insight into atmospheric study." This aligns with the assertion that the project introduces students to an essential and impactful field of chemistry through accessible practical experimentation.

The workshop sessions embedded throughout the project were highlighted as especially beneficial. Students cited these as being "very useful" and "really helpful for processing data," indicating that structured guidance was a key factor in enabling them to navigate the more technically demanding aspects of the project. This supports the inclusion of a framework of pedagogical interactions within an otherwise open-ended research experience and reinforces the importance of active facilitation in scaffolded inquiry-based learning.

These findings correlated well with the observations of educators delivering the course, who felt that students

demonstrated increasing confidence and autonomy over the duration of the project, becoming proficient in managing experimental design, analysing their results, communicating and discussing their findings. Several students independently extended the scope of their investigations in areas of their choosing—quantifying and attempting to rationalize the effect of new solvents, modifying or extending their assigned set of carbonyl compounds based on their findings or exploring computational chemistry to aid interpretation of their spectra. This observed growth in learner independence underscores the project's success in stimulating authentic research engagement.

Adapting to different educational settings

Whilst we primarily deploy this experiment for undergraduate summer project students or final year undergraduates we believe our methodology could readily be adapted to a much wider range of educational settings from undergraduate teaching labs to postgraduate research projects, the setting in which we first deployed the majority of these techniques.[12] Fig. 6 suggests different adaptations which could be made to the experiment to adapt delivery to different learner profiles and educational settings. Resource availability effectively refers to spectrometer time, although the availability of computers and the time allowed between completion of the experimental section and submission of post-lab components should also be considered. Higher or lower student confidence may be influenced by their year of study, amount of prior lab and data analysis experience and familiarity with atmospheric chemistry from other areas of their course. Whilst resource availability is relatively easily evaluated, care must be taken to accurately build a picture of learner confidence. Evaluation of the efficacy of course delivery relied primarily on in-course feedback (both formal and informal) and teacher observation. We are fortunate to have been running this activity for several years and thus have been able to iterate the details of the course several times based on the aforementioned feedback and quantitative student outcomes. For situations where lower learner confidence might

be anticipated (*e.g.*, teaching laboratories) the prior experience of the learners must be considered both with the practicalities of UV-vis spectroscopy and with the conceptual underpinnings of photolysis and atmospheric chemistry.

Conclusion

An experiment has been designed that allows upper-division undergraduate students to gain experience with experimental atmospheric chemistry, whilst building skills with UV-vis spectroscopy and data analysis. This methodology provides an accessible, low-cost route to inclusion of an underrepresented field into teaching labs and undergraduate research projects. Pleasingly, end-of-project feedback indicates that students engaged with and felt improvement in areas aligned with our stated pedagogical goals. We hope that this work will provide a useful and adaptable resource to the atmospheric chemistry community and effectively empower students to engage with experimental atmospheric chemistry, kinetics and organic photochemistry.

Author contributions

This work was conceived and developed by TJD and ARR and delivered by TJD, ARR, RKW and JDM. The manuscript and supporting content were written by JDM, RKW and SCS with input from all authors. The UV-vis spectra used in the manuscript and supporting content were collected by AR.

Conflicts of interest

There are no conflicts of interest to declare.

Data availability

The data supporting this article have been included as part of the SI. The main document (S1–7) includes information on course structure and project implementation in teaching labs, points for discussion with students and supplemental technical points regarding the scientific background of the activity. Also included as seperate files are slides from group workshops (S8) and worked examples of processed spectra (S9). See DOI: https://doi.org/10.1039/d5su00681c.

Acknowledgements

References

1 Ambient (outdoor) air pollution, https://www.who.int/news-room/fact-sheets/detail/ambient-(outdoor)-air-quality-and-health, accessed 16 January 2025.

2 D. J. Jacob, *Introduction to Atmospheric Chemistry*, Princeton University Press, Princeton, N.J, Online-Ausg, 1999.

3 R. P. Wayne, *Chemistry of Atmospheres: an Introduction to the Chemistry of the Atmospheres of Earth, the Planets, and Their Satellites*, Oxford Univ. Press, Oxford, 3 edn, 2000.

4 B. J. Finlayson-Pitts and J. N. Pitts, *Chemistry of the Upper and Lower Atmosphere: Theory, Experiments, and Applications*, Academic Press, San Diego, 2000.

5 P. J. Ziemann and R. Atkinson, Kinetics, products, and mechanisms of secondary organic aerosol formation, *Chem. Soc. Rev.*, 2012, **41**, 6582.

6 J. Lelieveld, K. Klingmüller, A. Pozzer, U. Pöschl, M. Fnais, A. Daiber and T. Münzel, Cardiovascular disease burden from ambient air pollution in Europe reassessed using novel hazard ratio functions, *Eur. Heart J.*, 2019, **40**, 1590–1596.

7 J. B. Burkholder, J. P. D. Abbatt, I. Barnes, J. M. Roberts, M. L. Melamed, M. Ammann, A. K. Bertram, C. D. Cappa, A. G. Carlton, L. J. Carpenter, J. N. Crowley, Y. Dubowski, C. George, D. E. Heard, H. Herrmann, F. N. Keutsch, J. H. Kroll, V. F. McNeill, N. L. Ng, S. A. Nizkorodov, J. J. Orlando, C. J. Percival, B. Picquet-Varrault, Y. Rudich, P. W. Seakins, J. D. Surratt, H. Tanimoto, J. A. Thornton, Z. Tong, G. S. Tyndall, A. Wahner, C. J. Weschler, K. R. Wilson and P. J. Ziemann, The Essential Role for Laboratory Studies in Atmospheric Chemistry, *Environ. Sci. Technol.*, 2017, **51**, 2519–2528.

8 B. Ervens, A. Rickard, B. Aumont, W. P. L. Carter, M. McGillen, A. Mellouki, J. Orlando, B. Picquet-Varrault, P. Seakins, W. R. Stockwell, L. Vereecken and T. J. Wallington, Opinion: Challenges and needs of tropospheric chemical mechanism development, *Atmos. Chem. Phys.*, 2024, **24**, 13317–13339.

9 A. K. Hua, P. S. J. Lakey and M. Shiraiwa, Multiphase Kinetic Multilayer Model Interfaces for Simulating Surface and Bulk Chemistry for Environmental and Atmospheric Chemistry Teaching, *J. Chem. Educ.*, 2022, **99**, 1246–1254.

10 Z. Peng and J. L. Jimenez, KinSim: A Research-Grade, User-Friendly, Visual Kinetics Simulator for Chemical-Kinetics and Environmental-Chemistry Teaching, *J. Chem. Educ.*, 2019, **96**, 806–811.

11 J. E. Roberts, G. Zeng, M. K. Maron, M. Mach, I. Dwebi and Y. Liu, Measuring Heterogeneous Reaction Rates with ATR-FTIR Spectroscopy To Evaluate Chemical Fates in an Atmospheric Environment: A Physical Chemistry and Environmental Chemistry Laboratory Experiment, *J. Chem. Educ.*, 2016, **93**, 733–737.

12 C. Mapelli, J. K. Donnelly, Ú. E. Hogan, A. R. Rickard, A. T. Robinson, F. Byrne, C. R. McElroy, B. F. E. Curchod, D. Hollas and T. J. Dillon, Atmospheric oxidation of new

"green" solvents – Part 2: methyl pivalate and pinacolone, *Atmos. Chem. Phys.*, 2023, **23**, 7767–7779.

13 IUPAC, Task Group on Atmospheric Chemical Kinetic Data Evaluation, https://iupac.aeris-data.fr/, accessed 8 October 2024.

14 Gas Phase Rate Constants – Eurochamp Data Center, https://data.eurochamp.org/data-access/gas-phase-rate-constants/#/, accessed 24 February 2024.

15 M. E. Jenkin, R. Valorso, B. Aumont, A. R. Rickard and T. J. Wallington, Estimation of rate coefficients and branching ratios for gas-phase reactions of OH with aliphatic organic compounds for use in automated mechanism construction, *Atmos. Chem. Phys.*, 2018, **18**, 9297–9328.

16 M. E. Jenkin, R. Valorso, B. Aumont, A. R. Rickard and T. J. Wallington, Estimation of rate coefficients and branching ratios for gas-phase reactions of OH with aromatic organic compounds for use in automated mechanism construction, *Atmos. Chem. Phys.*, 2018, **18**, 9329–9349.

17 M. R. McGillen, L. Michelat, J. J. Orlando and W. P. L. Carter, The use of the electrotopological state as a basis for predicting hydrogen abstraction rate coefficients: a proof of principle for the reactions of alkanes and haloalkanes with OH, *Environ. Sci.: Atmos.*, 2024, **4**, 18–34.

18 A. Shiroudi, T. Kurtén and J. Czub, Mechanistic insights and atmospheric implications of the degradation reaction of 3-methoxy-1-propanol by reaction with hydroxyl radicals and identification of the end products in the presence of O2/NO, *Sci. Rep.*, 2025, **15**, 1038.

19 MCM, https://www.mcm.york.ac.uk/MCM/, accessed 13 June 2025.

20 M. E. Jenkin, S. M. Saunders and M. J. Pilling, The tropospheric degradation of volatile organic compounds: a protocol for mechanism development, *Atmos. Environ.*, 1997, **31**, 81–104.

21 S. M. Saunders, M. E. Jenkin, R. G. Derwent and M. J. Pilling, Protocol for the development of the Master Chemical Mechanism, MCM v3 (Part A): tropospheric degradation of non-aromatic volatile organic compounds, *Atmos. Chem. Phys.*, 2003, **3**, 161–180.

22 B. F. E. Curchod and A. J. Orr-Ewing, Perspective on Theoretical and Experimental Advances in Atmospheric Photochemistry, *J. Phys. Chem. A*, 2024, **128**, 6613–6635.

23 D. Hollas and B. F. E. Curchod, AtmoSpec –A Tool to Calculate Photoabsorption Cross-Sections for Atmospheric Volatile Organic Compounds, *J. Phys. Chem. A*, 2024, **128**, 8580–8590.

24 K. Nakashima, K. Uchida-Kai, M. Koyanagi and Y. Kanda, Solvent Effects on the Intensities of Forbidden Bands of Molecules. Absorption Spectra of Acetone and Cyclopentanone, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 415–419.

25 K. N. Rowell, S. H. Kable and M. J. T. Jordan, Structural Effects on the Norrish Type I α-Bond Cleavage of Tropospherically Important Carbonyls, *J. Phys. Chem. A*, 2019, **123**, 10381–10396.

26 I. Fleming and D. Williams, *Spectroscopic Methods in Organic Chemistry*, Springer International Publishing, Cham, 2019.

27 J. F. Brewer, D. K. Papanastasiou, J. B. Burkholder, E. V. Fischer, Y. Ren, A. Mellouki and A. R. Ravishankara, Atmospheric Photolysis of Methyl Ethyl, Diethyl, and Propyl Ethyl Ketones: Temperature-Dependent UV Absorption Cross Sections, *J. Geophys. Res.: Atmos.*, 2019, **124**, 5906–5918.

28 JPL Data Evaluation, https://jpldataeval.jpl.nasa.gov/, accessed 20 June 2025.

29 T. Gierczak, J. B. Burkholder, S. Bauerle and A. R. Ravishankara, Photochemistry of acetone under tropospheric conditions, *Chem. Phys.*, 1998, **231**, 229–244.

30 R. D. Martinez, A. A. Buitrago, N. W. Howell, C. H. Hearn and J. A. Joens, The near U.V. absorption spectra of several aliphatic aldehydes and ketones at 300 K, *Atmos. Environ. Part A*, 1992, **26**, 785–792.

31 ACOM, Quick TUV, https://www.acom.ucar.edu/Models/TUV/Interactive_TUV/, accessed 17 January 2025.

32 J. Lelieveld, S. Gromov, A. Pozzer and D. Taraborrelli, Global tropospheric hydroxyl distribution, budget and reactivity, *Atmos. Chem. Phys.*, 2016, **16**, 12477–12493.

33 M. R. McGillen, W. P. L. Carter, A. Mellouki, J. J. Orlando, B. Picquet-Varrault and T. J. Wallington, Database for the kinetics of the gas-phase atmospheric reactions of organic compounds, *Earth Syst. Sci. Data*, 2020, **12**, 1203–1216.

34 M. E. Jenkin, R. G. Derwent and T. J. Wallington, Photochemical ozone creation potentials for volatile organic compounds: Rationalization and estimation, *Atmos. Environ.*, 2017, **163**, 128–137.

35 U. of York, Atmospheric chemistry, https://www.york.ac.uk/chemistry/research/atmospheric-chemistry/, accessed 19 January 2025.

36 U. of York, Wolfson Atmospheric Chemistry Laboratories - Research, University of York, https://www.york.ac.uk/chemistry/research/wacl/, accessed 20 June 2025.

37 BSc Research Project (CHE00033H) 2024-25 - Module Catalogue, Student home, University of York, https://www.york.ac.uk/students/studying/manage/programmes/module-catalogue/module/CHE00033H/2024-25, accessed 27 June 2025.

38 H. L. Davies, C. O'Leary, T. Dillon, D. R. Shaw, M. Shaw, A. Mehra, G. Phillips and N. Carslaw, A measurement and modelling investigation of the indoor air chemistry following cooking activities, *Environ. Sci.: Processes Impacts*, 2023, **25**, 1532–1548.

39 A. Kumar, C. O'Leary, R. Winkless, M. Thompson, H. L. Davies, M. Shaw, S. J. Andrews, N. Carslaw and T. J. Dillon, Fingerprinting the emissions of volatile organic compounds emitted from the cooking of oils, herbs, and spices, *Environ. Sci.: Processes Impacts*, 2025, **27**, 244–261.