The emission spectroscopy of C_2 produced in a hydrocarbon/oxygen flame: An APCELL experiment[1]

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Introduction

Small hydrocarbon radicals are important as intermediates in combustion processes, including the disposal of household and chemical waste by incineration, in engines, and in energy generation. Moreover, their introduction into the environment plays a significant role in atmospheric chemistry. During combustion, of the more abundantly produced hydrocarbon radicals, C_2 is a species that can be readily generated in a simple natural gas/oxygen flame and is amenable to study at the undergraduate level. Its bright emission allows for ready spectral identification with equipment commonly found in most undergraduate laboratories. By monitoring the production of C_2 in various regions of a flame, students can begin to explore the chemistry of combustion. In addition, by recording and analysing the electronic emission spectrum of C_2, students can gain insight into the structure and bonding of a radical molecule, which is quite different to stable molecules most usually encountered in the undergraduate laboratory.

In this experiment, students begin by observing the emission spectra of atomic species generated in relatively intense discharge lamps prior to studying C_2 molecular emission from a flame. As such, they become familiar with data collection and interpretation strategies in a relatively straightforward manner. Having mastered these skills, students have the competence and confidence to record molecular emission spectra of less luminous species present in a flame. During a one-afternoon laboratory session, the normal expectation is that students will record the emission spectrum of C_2. Students subsequently perform spectral analyses to determine molecular constants in various vibronic states of the radical and use these results to gain insight into the nature of the chemical bond (*i.e.* changes in bond length upon electronic excitation). Noting the relative abundance of C_2 in various regions of the flame also provides students with insight into the chemistry of the combustion process.

Important aims of this exercise are to reinforce (i) the notion of quantised energy levels in atoms (electronic) and molecules (rotational, vibrational and electronic,) and (ii) the spectroscopic concept of transitions occurring between these levels. Students also develop competency in recording and interpreting emission spectra as well as developing generic skills associated with graphical and mathematical analysis (particularly non-linear least squares fitting), self-evaluation of results and critical thinking.

Educational Template

Section 1 - Summary of the Experiment

1.1 Experiment Title

The Emission Spectroscopy of C_2 Produced in a Hydrocarbon/Oxygen Flame.

1.2 Description of the Experiment

Spectroscopy provides a means to examine places and things that are not readily accessible. For example, spectroscopy is the tool with which we can determine the composition of stars. It also tells us which species in Earth's atmosphere protect us from UV radiation, or contribute to the greenhouse effect. Spectroscopy also provides us a window to examine the microscopic world of atoms and molecules. Measurement of spectra and knowledge of spectroscopic theory provides us with the ability to determine the shape and size of molecules, the bonds that hold them together and their reactivity. In this experiment students use spectroscopy to examine both of these applications: they measure the free radical species present in a flame and use this information to enquire into the chemistry of combustion. Detailed analysis of the C_2 spectrum by the students, using quantum theory that is taught in most undergraduate physical chemistry syllabi, allows the structure and bonding of this free radical to be inferred.

In this experiment, the electronic emission spectra of small, diatomic, radicals produced in a hydrocarbon/oxygen flame are recorded and the C_2 spectrum is analysed. The experiment begins by having the students observe the emission spectra of atomic species generated in relatively intense discharge lamps. In this way, they become familiar with data collection and interpretation strategies in a relatively straightforward manner. They then move on to study emission spectra of less luminous species present in a flame where they identify common radical species such as C_2, CH and/or OH.

The experiment is designed to be run in one afternoon (4-6 hours) for Level II or Level III undergraduates (depending upon individual curriculum requirements).

The aims of the practical are:

1. To develop competency in the measurement of emission spectra;
2. To measure and record the discrete molecular transitions in C_2, CH and OH from a mixed

[1] The complete documentation for this experiment is freely available on the APCELL web site [www.apcell.org]. It includes the educational template, a set of student notes, demonstrator notes and technical notes to allow ready implementation into a new laboratory.

hydrocarbon/oxygen flame;
3. To explore the chemistry by which these species are produced;
4. To analyse the spectrum of C_2 in terms of quantum theory of electrons and vibrations of a diatomic molecule;
5. To use the parameters of the analysis to provide the force constant of C_2 in both ground and excited state, and hence infer the bond order of C_2 in each state;
6. To relate the bond order of C_2 to theories of bonding, e.g. molecular orbital theory, valence bond theory.

1.3 Course Context and Students' Required Knowledge and Skills

The experiment develops practical skills related to the underlying principles of atomic and molecular spectroscopy that is presented in most second and third year lecture courses and extends the application of these principles to combustion chemistry. Students should have a basic knowledge of quantised energy levels in atoms (electronic) and molecules (rotational, vibrational and electronic). Ideally, students should also have an understanding of the spectroscopic concepts of transitions between these levels and the relationship with the electromagnetic spectrum. However, this is not considered essential as students can learn these concepts as part of the experiment.

1.4 Time Required to Complete

Prior to Lab	1 hour
In Laboratory	4-6 hours
After Laboratory	1-2 hour

1.5 Acknowledgments

The experiment has evolved over several years at Adelaide, Sydney and Griffith Universities. Professor A. E. W. Knight at Griffith University implemented the earliest incarnations of the experiment that we are aware of in the early 1980's. The Submitters, at Adelaide and Sydney Universities, have jointly developed more recent modifications and refinements over the last five years.

1.6 Other Comments

Times Required:

The practical involves background reading in order to answer preliminary questions. The required apparatus has been set-up in advance for immediate data collection during laboratory time. Spectral analysis and subsequent interpretation of results with respect to combustion chemistry is also performed during laboratory time. Students are required to write their practical report outside of the formal laboratory session.

Equipment and apparatus required:

This experiment can be established using equipment commonly found in most physical chemistry laboratories, including:

- Na, H and D discharge lamps;
- Methane/Oxygen flame source, e.g. Bunsen burner or preferably a glassblowers torch;
- Dark room (Optional. This experiment has been performed successfully in a fully lit laboratory.)

To observe emission spectra:

- Hand-held spectroscope;
- Bench-top spectroscope.

To record emission spectra (if required, for example, if a bench-top spectroscope is not available. The accompanying student notes refer to the use of a bench-top spectroscope.):

- Various quartz focusing lenses;
- Dispersing monochromator (e.g. f/10) with photomultiplier tube (or a dispersing CCD system);
- Power supply for photomultiplier tube (e.g. Fluke 4128);
- Signal amplifier or Picoammeter (we use a Kiethley 410A picoammeter).
- A means of displaying spectrum. This could be:
  - Chart recorder, but it then is more difficult to compare simulated spectra;
  - Computer with D/A converter;
  - Data logger (with computer to upload data);
  - Digital oscilloscope connected to computer (e.g. GPIB) with appropriate software.

(We have used a chart recorder, digital scope and D/A converter, which all do the job just fine. We plan to test data loggers because students often have experience with these, even from high school).

To analyse spectra:

- Scientific data analysis/graphical packages (e.g. Excel and Kaleidagraph or Origin)

Safety aspects:

The flame is hot. If used in an enclosed space (e.g. dark room) the fumes should be removed via an appropriate exhaust fan. High voltages (~2000 V) are also used to drive the photomultiplier tube, if used.

References:

Good reference books include:

1. "*Building Scientific Apparatus: A practical guide to design and construction*", J. H. Moore, C.C. Davis and M. A. Coplan. 2nd ed. (Addison-Wesley Publishing Company, **1989**).
2. "*The Identification of Molecular Spectra*", R. W. B. Pearse and A. G. Gaydon (Chapman and Hall, **1976**).
3. "*The Spectra and Structure of Simple Free Radicals*" G. Herzberg (Cornell University Press, **1971**).
4. "*Spectra of Diatomic Molecules*" G. Herzberg. 2nd edition (Van Nostrand Company, **1957**).
5. "*The Spectroscopy of Flames*" A. G. Gaydon (Wiley, **1957**).
6. "*Flames, Their Structure, Radiation and Temperature*" A. G. Gaydon and H. G. Wolfhard. Fourth Edition (Chapman and Hall, **1979**).
7. "*Fundamentals of Molecular Spectroscopy*" C. N. Banwell and E. M. McCash. 4th ed. (McGraw-Hill, **1997**).

The technical reference sections of product catalogs published by optics manufacturers, including Newport, Oriel, Melles Griot, etc, are of tremendous use.

Section 2 – Educational Analysis

Learning Outcomes *What will students learn?*	**Process** *How will students learn it?*	**Assessment** *How will staff know students have learnt it?* *How will students know they have learnt it?*

Theoretical and Conceptual Knowledge

The students will use theoretical aspects of spectroscopy taught in lectures to analyse spectra, extract molecular constants, calculate molecular properties, compare them with literature values and interpret the results	Students in pairs or small groups perform data analysis, with occasional guidance provided by a demonstrator. Comparison with literature results will allow the students to self-evaluate their spectral analyses.	During the experiment, interaction with a demonstrator will indicate that students are proceeding on the right path. Students are expected to write and submit a report detailing the results of their data analyses, including a discussion of a comparison with literature values.
Students will gain insight into the chemistry of combustion processes occurring in a simple hydrocarbon/ oxygen flame.	Students will identify radical species produced in various regions of a flame, and discuss possible mechanisms of formation of identified species. Information about flame chemistry is available in the reference material.	During the experiment, the demonstrator will query the students on flame chemistry. In the written report, students will discuss the combustion process. An intelligent mechanism for the production of the observed radical(s) will allow staff to assess the students' understanding of flame chemistry.
The students will make their own inference on the bonding of C_2, which is not intuitively obvious. They will test whether their inference makes sense compared with theories of bonding.	From extraction of the force constants from their own experimental data, the students can infer the bond order of C_2 in both ground and excited electronic states (both are approx. double bonds). The students should discover that molecular orbital theory, in facts, predicts not only a double bond for C_2 in both states, but that both states should be triplets (which is information the students are given).	The demonstrator should query the student about the value of their calculated force constants. During the laboratory hours the demonstrator should also check that the students remember at least that molecular orbital theory exists! The answers to the discussion questions concerning bonding in the practical should be written up in the report.

Scientific and Practical Skills

Experimentally, students will learn the procedure and aspects of observing emission spectra.	Student pairs perform the experiment with occasional guidance provided by a demonstrator. When they observe discrete atomic lines from the discharge lamps they will know, themselves, that they have mastered this technique.	The successful observation of spectral transitions will be the indication that the students have mastered the necessary observation skills required of this experiment.
Students will learn to assign a spectrum, by indicating the emitting species and also the quantum levels involved in the emission.	Assignment of the spectrum is done by reference to the literature.	Correct assignment of the spectrum is integral to the successful completion of the prac. Students are specifically requested to confirm their assignments with a demonstrator before progressing. In this way they will get immediate feedback on the skills in assigning a previously unknown spectrum.

Students will gain proficiency in non-linear least squares fitting of their experimental data to a fairly complicated 5-parameter model.	Students will use Microsoft Excel (or any other appropriate software) to perform a non-linear least squares fit. Successful extraction of the 5 molecular parameters will provide immediate feedback that they have mastered this skill.	Successful extraction of the 5 molecular parameters.
Students will learn to question what the numerical value of their results means in terms of fundamental chemical ideas. Specifically, in this experiment they infer a bond order and then question whether this bond order seems sensible.	By employing one or more theories of bonding, the students can examine whether their numerical values make sense in terms. Specifically, molecular orbital theory provides a bond order with which they can rationalise their own inferences.	Correct application of m.o. theory and more importantly being able to connect the ideas of m.o. theory to their own experiment.

Generic Skills

The ability to work in a group and coordinate activities will be one of the key generic skills learnt.	Group members are required to divide up tasks in a fair, equitable and transparent manner.	The demonstrator's interaction with the students will allow their progress to be effectively gauged. Peer and demonstrator evaluation will assess this component of the practical exercise.
The ability to compare results with literature values and to reflect upon the significance of these results.	Discussion with a demonstrator is vital to encourage the students to think about their results and what they mean.	Student discussion and evaluation (oral and/or written) of the quality of their data will indicate their level of understanding.
Students will enhance effective communication by having to submit a written report.	Written communication skills will be developed as the report is prepared.	The required written report will evaluate this aspect.

Section 3 – Student Learning Experience

3.1 Did this experiment help you to understand the theory and concepts of the topic? If so, how, or if not, why not?

S1: Yes, application of theory learnt in lectures.
S2: No. Covered these principles before and I understood them.
S3: Yes. We get to observe the flames by ourselves and then extract the data and then manipulate them.
S4: At the start it didn't but then I got the background and it started to make sense.
S5: Yes, made understanding the parameters clearer.
S6: At then end of the course, I finally do.
S7: In terms of the background theory, not really because we did the experiment before the lectures but I did learn that the different bands responded to different transitions of vibrational states.
S8: The presence of the vibrational parameters were not completely explained, ie we did not know what each parameter meant.
S9: Yes, it demonstrated vibrational energy levels and how to determine the energy of the states.

3.2 How is this experiment relevant to you in terms of your interests and goals?

S1: N/A.
S2: Not relevant.
S3: Quite relevant.
S4: Do the experiment. Get the degree. Helped in making a decision with Honours.
S5: Increased my interest in the topic.
S6: Not more than any other.
S7: Not really relevant since I am not going to pursue this for a job in the future.
S8: Not very relevant as flame emission is quite a basic experiment.
S9: I found it interesting but it isn't relevant theory wise.

3.3 Did you find this experiment interesting? If so, what aspects of this experiment did you find of interesting? If not, why not?

S1: Not really.
S2: Yes. Using the hand held spectroscope was fun.
S3: Yes, quite interesting.
S4: Yes – refer to 3.9
S5: Yes, actual hands-on experience.
S6: Yes – visual. That always helps.
S7: The hand-held spectroscopes were a waste of time but the actual flame emission part was quite interesting.
S8: The function of the telescope was quite interesting.
S9: Simply finding out how much energy is required to excite a molecule vibrationally was interesting.

3.4 Can the experiment be completed comfortably in the allocated time? Is there time to reflect on the tasks while performing them?

S1: Yes.
S2: Yes.
S3: No. Need more time (6 hours).
S4: Yeah, very easy.
S5: Yes.
S6: Yes.
S7: If you are the second group yes, but the first group not really as you have to do all the little things to the spectrometer to see the bands clearly and this takes quite a lot of time.
S8: Plenty of time.
S9: If work is completed efficiently the time was enough but if the task is found to be hard to understand there may not be enough time.

3.5 Does this experiment require teamwork and if so, in what way? Was this aspect of the experiment beneficial?

S1: Yes, to try and get the equipment to work.
S2: Yes. Trying to work out how to actually work the bench top spectrometer and checking bands with each other.
S3: Yes.
S4: Yes – Laurence & I work well as a team.
S5: Yes, a scribe & someone to find the lines.
S6: Teamwork is always good – but if you have Grant in your group there isn't as much teamwork.
S7: Yes, so one can use the spectrometer & the other take the results.
S8: No, the experiment could quite easily be done by one person. The only teamwork needed is to collaborate results.
S9: Yes, someone to record the wavelengths & someone to measure using the spectrometer.

3.6 Did you have the opportunity to take responsibility for your own learning, and to be active as learners?

S1: Yes.
S2: No.
S3: Yes.
S4: Had to. Demonstrator wasn't here all the time. Made me do it & then understand it.
S5: Yes.
S6: Yes.
S7: Yes, as not much help was given by demonstrators as they were busy so had to take it upon yourself to understand what was going on.
S8: Yes!
S9: Yes.

3.7 Does this experiment provide for the possibility of a range of student abilities and interests? If so, how?

S1: No comment.
S2: No
S3: Yes, the ability to extract data and manipulate them.
S4: It shows chemistry isn't just making & destroying molecules.
S5: Yes.
S6: It's something different.
S7: No comment.
S8: Not as such. The chemistry is quite simple and not very broad.
S9: It requires understanding of theories before the calculations can be completed. Thus, for those who have trouble with the theory will have trouble with the calc's.

3.8 Did the laboratory notes, demonstrators' guidance and any other resources help you in learning from this experiment? If so, how?

S1: Yes, the notes explained the theory.
S2: No.
S3: Yes, they do because they help us to understand the theory.
S4: When a demonstrator isn't there the notes are hard to understand.
S5: Yes – how to work the equipment.
S6: No comment.
S7: Yes they were quite clear but the notes on how to use the spectrometer could have been a little more clearer.
S8: Yes, to determine the values of the vibrational parameters.
S9: Yes, learning how to use equipment provided a different explanation to the lab manual.

3.9 Are there any other features of this experiment that made it a particularly good or bad learning experience for you?

S1: No comment.
S2: No.
S3: They're all good learning experiences. Extract data then manipulate them to get important parameters.
S4: It was good just to see something different, eg. Colours in the fluoro etc.
S5: No comment.
S6: No.
S7: No, not really besides slightly burning myself.
S8: The hand-held spectrometer was very inaccurate as the wavelength changed as the spectrometer moved around.
S9: No comment.

3.10 What improvements could be made to this experiment?

S1: No comment.
S2: ?
S3: Longer time (say, 6 hours).
S4: No comment.
S5: Maybe try more than one molecule.
S6: No comment.
S7: Get rid of the hand-held spectroscope part.
S8: Make the equipment a little more user friendly.
S9: Not using the hand-held spectrometer!

3.11 Other Comments

No comment from any of the students.