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

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Experiment Overview

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_2molecular 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.

Aims and Objectives

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 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 aims of the practical are:

- To develop competency in the measurement of emission spectra;
- To measure and record the discrete molecular transitions in C_2, CH and OH from a mixed hydrocarbon/oxygen flame;
- To explore the chemistry by which these species are produced;
- To analyse the spectrum of C_2 in terms of quantum theory of electrons and vibrations of a diatomic molecule;
- 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;
- To relate the bond order of C_2 to theories of bonding, e.g. molecular orbital theory, valence bond theory.

Level of Experiment

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).

Keyword Descriptions of the Experiment

Domain
physical chemistry

Specific Descriptors
flames, emission spectroscopy, force constant, bond order

Course Context and Prerequisite 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.

Time Required to Complete

Prior to Lab: 1 hour
In Laboratory: 4 - 6 hours (see also other comments, below)
After Laboratory: 1 - 2 hours

Experiment History

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.

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:

 "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**).

 "The Identification of Molecular Spectra", R. W. B. Pearse and A. G. Gaydon (Chapman and Hall, **1976**).

 "The Spectra and Structure of Simple Free Radicals" G. Herzberg (Cornell University Press, **1971**).

 "Spectra of Diatomic Molecules" G. Herzberg. 2nd ed. (Van Nostrand Company, **1957**).

 "The Spectroscopy of Flames" A. G. Gaydon (Wiley, **1957**).

- *"Flames, Their Structure, Radiation and Temperature"* A. G. Gaydon and H. G. Wolfhard. 4th ed. (Chapman and Hall, 1979).

- *"Fundamentals of Molecular Spectroscopy"* C. N. Banwell and E. M. McCash. 4th ed. (McGraw-Hill, **1997**)./ol>

The technical reference sections of product catalogs published by optics manufacturers, including Newport, Oriel, Melles Griot, etc, are of tremendous use. Note that extracts from some useful references are included in the downloadable documentation on the Related Documents page.