Aust. J. Ed. Chem., 2004, 64,

An IR investigation of the CO dipole direction and other properties: An APCELL experiment[1]

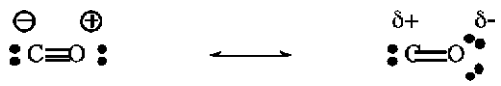
Kieran F. Lim (林百君)

School of Biological and Chemical Sciences, Deakin University, Geelong, Victoria 3217, Australia, lim@deakin.edu.au

Introduction

Spectroscopy is a direct probe of molecular properties. The novelty of this experiment is the placement of a near-standard Fourier-transform infrared (FT-IR) spectroscopy in an applied context of relevenace to physical chemistry, toxicology and organometallic chemistry.

For many years, there was disagreement about the direction of the carbon monoxide (CO) molecular dipole, which had major implications for how CO acts as a poisonous gas (in its binding to haemoglobin), or as a ligand in organometallic complexes.



I **II**

Neither Lewis structure is very satisfactory. Structure **I** is a zwitterion, which obeys the "octet rule", but places the negative charge on the more electropositive atom, and vice versa. Structure **II** minimises the formal charge, but does not obey the "octet rule". Structures **I** and **II** predict opposite directions for molecular dipole.

Structures **I** and **II** also differ in their bond order. In this laboratory exercise, infrared (IR) spectroscopy is used to determine the bond order of CO, and hence infer the direction of the molecular dipole, as follows:

The vibrational transitions are used to estimate the harmonic frequency. The bond order can be determined from the frequency-bond-order relationship.

The vibrational transitions are used to determine the anharmonicity and harmonic frequency. The bond dissociation energy can be determined from the harmonic frequency and the anharmonicity. The bond order can be determined from the bond-strength-bond-order.

The rotational fine structure of the vibrational transitions is used to determine the rotational constant, $\tilde{B}_e$, and hence the molecular bond length, r_e. The bond order can be determined from the bond-length- bond-orderrelationship. This laboratory exercise enables three related but *independent* measures of the bond order of CO and hence infer the direction of the molecular dipole from the Lewis structures **I** and **II**.

Educational Template

Section 1 - Summary of the Experiment

1.1 Experiment Title

An IR investigation of the CO dipole direction and other properties.

1.2 Description of the Experiment

The infrared absorption spectra of gaseous carbon monoxide and atmospheric air (background containing carbon dioxide and water vapour) are recorded. The carbon monoxide spectrum is analysed in terms of molecular vibrations and rotations, various molecular properties and parameters, including the carbon-oxygen bond length, are determined from the spectrum.

The novel feature of this exercise is that the spectroscopic information are used to discuss the CO bond order, molecular dipole direction and other properties. An unusual feature is that the first overtone is measured (*1,2*), in addition to the fundamental vibrational transition.

This laboratory exercise illustrates that spectroscopy is a direct probe of molecular properties, which have practical applications. (Spectroscopy is not just an academic exercise in quantum theory.) The observed gas-phase spectra provide direct evidence of quantisation and the bond order. This exercise is the only occasion when students make a measurement of any molecular bond length in the Deakin University undergraduate chemistry program. It is one of the few occasions where a bond binding energy (the "bond strength") is determined. Furthermore, this laboratory exercise gives students the opportunity to gain "hands-on" experience with a Fourier-transform infrared (FT-IR) spectrometer, which is a common analytical technique in industrial and forensic laboratories.

1.3 Course Context and Students' Required Knowledge and Skills

This laboratory exercise is part of the Spectroscopy unit, which is a compulsory unit (subject) at the start of the third year. All students would have completed either a semester-long unit (subject) on spectroscopy, or a semester-long unit (subject) on analysis of biological molecules, in second year.

In addition, students who are majoring in chemistry would have completed a semester-long unit (subject) on "physical

[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.

chemistry", including numerical analysis using Microsoft Excel, in second year. Explicit *detailed* knowledge of quantum mechanics is not required.

However, there is also a substantial number of non-chemistry-major students who have weaker numerical analysis skills than the chemistry-major students. Some of these students have difficulty with the *language* of physical chemistry, which is a mixture of scientific English and mathemathics. This difficulty is reflected in the student feedback of Section 3 (Student Learning Experience), which shows that many students had difficulty with:

- *comprehending* that they had to fit an equation and
- fitting quadratic curves to experimental data.

1.4 Time Required to Complete

Prior to Lab	1.5 hours reading and pre-lab exercise
In Laboratory	2 hours laboratory and 2 hours computer laboratory for analysis of results
After Laboratory	2-3 hours report writing

1.5 Acknowledgments

Infrared rovibrational diatomic spectroscopy experiments are a standard part of the physical chemistry curriculum in many universities. There are several examples of HCl and CO spectroscopy experiments in textbooks and chemical education journals. For many years, Deakin University had an HCl infrared experiment, investigating the fundamental vibrational transition. The original source is unconfirmed, but is suspected to be a standard literature experiment (*3*).
The course of several years, the author modified the experiment by monitoring student learning and feedback from students and technical staff (*4,5*):

- introducing the pre-lab simulation exercise using an Excel spreadsheet (*6*);
- changing from HCl to CO gas (technical staff were concerned that leakage of HCl — although unlikely — might damage the FTIR instrument);
- introducing the analysis of the first overtone (*1,2*);
- introducing the extension exercise on quantum calculations; and
- introducing the contextual background of the CO dipole and implications for ligand-metal binding.

When developing this exercise, the author was unaware of the paper by Mina-Camilde *et al.* (*1*), which describes an almost identical exercise, but *without* the contextual background of the CO dipole and implications for ligand-metal binding. Professor Mark Spackman (UNE, Armidale) has a computer laboratory exercise on quantum calculations on CO, which provided the idea of the extension exercise here. The author thanks Associate Professor Bryce Williamson (University of Canterbury, NZ) for discussions about his CO_2 experiment, which has lead to the extension exercise in this laboratory exercise. The author thanks Ms Jeanne Lee (李静宁)(Loyola College, Watsonia) for encouraging and helpful discussions.

1.6 Other Comments

There are occupational health and safety issues associated with this exercise. Carbon monoxide is an odourless, colourless, flammable, toxic gas.

Suggestions of alternative (safe!) gases, which could be used for this exercise, would be *extremely* welcome!

The gas cell is the one piece of equipment that is most at risk of breakage. Commercial 10 cm gas cells cost in excess of AUD $600. Specifications and detailed designs for much cheaper "home-made" cells are given in the literature (*7,8*).
The assessment criteria for this laboratory exercise, have been published previously in the description of another exercise from Deakin University (*9,10*).
The teaching-and-learning assessment described in this paper has been approved (EC 29-2002) by the Deakin University Human Research Ethics Committee.

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

Students should understand that each rovibrational spectrum in this exercise corresponds to a "single peak" in the more extended IR spectra, which are encountered in the typical synthetic laboratory.	Students will measure and compare wide-range IR spectra (similar to those in a typical synthetic laboratory) with spectra focusing on a particular vibrational transition (similar to those in physical chemistry texts).	Students will be able to communicate the understanding that a particular vibrational transition with rotational fine structure looks like a single vibrational "peak" when the scale of the spectrum is changed.

Students should appreciate that molecular energy levels are quantised.	These fundamental concepts underpin the entire exercise. Students will measure and compare IR spectra.	Students will be able to communicate the understanding that most of the spectrum has near-zero absorbance except where the photon energy matches quantised *changes* in molecular energy.
Students should understand that absorption of a photon results in a transition from a lower-energy level to a higher-energy level. The quantised *changes* in molecular energy result in spectral peaks. The increase in molecular energy corresponds to the absorbed photon's energy.		
Students should understand that symmetry constraints ("selection rules") determine which energy gaps can correspond to an "allowed" transition.	Students will analyse spectra using relationships derived using the "selection rules".	Reasonable results are obtained only when the assigned quantum numbers for the spectral transitions obey the "selection rules".
Students must understand that solution of the Schrödinger Equation predicts formulas for the vibrational and rotational energies of simple molecules. Hence, these formulas, coupled with the selection rules, will predict the photon energies of the various allowed transitions.		
Students should be able to relate spectroscopic information and concepts to bonding and reactivity concepts in other parts of the chemistry syllabus.	Students will use bond-order relationships to predict the bond order on CO and the direction of the molecular dipole. Students will be asked to apply this knowledge to bonding and reactivity concepts in other parts of the chemistry syllabus.	Students will be able to rationalise and predict metal-ligand binding in other parts of the chemistry syllabus using spectral information, and be able to communicate this understanding.
Students should be able to exercise judgement about what is (or is ***not***) relevant in the context of the exercise, judgement about what is (or is ***not***) significant in the context of the exercise, and judgement about what is (or is ***not***) important in the context of the exercise.	Students must decide what to include or omit from a formal written report. They are given the demonstrator's assessment and feedback *pro forma*. They are encouraged to seek help from the demonstrator.	There must be sufficient data, details and discussion in the main body of the report, so that a student (classmate) who has done everything as the student writer, except this exercise (or this unit), can understand the report.

Scientific and Practical Skills

Students should be able to operate a FTIR spectrometer.	Students prepare samples and use the spectrophotometer to make measurements.	Students will record spectra of the samples, which are consistent with literature spectra.
Students should be able to transfer gases from gas cylinders to sample cells.		
Students should be able to collate, display and analyse data using a spreadsheet.	Students will use a spreadsheet package to collate, display, and analyse observed data.	Students will obtain linear or quadratic plots, similar to those in textbooks and the scientific literature. The experimentally determined parameters will be in good agreement with literature values.

Generic Skills

Students should be able to work in teams, and to plan and manage their time effectively.	Students must divide tasks between themselves at different stages of the laboratory exercise.	Students will complete the allocated tasks with minimal conflict.
Students must be able to use and interconvert units correctly.	Students should be aware of and convert between energy (units of kJ mol^{-1}), frequency (units of s^{-1}) and wavenumber (units of cm^{-1}) quantities.	The experimentally determined parameters will be in good agreement with literature values.
Students should (further) develop communication and generic skills (*11,12*), including the ability to use appropriate computer programs (*13*). *Note: The semester-long spectroscopy laboratory program at Deakin University is one of a series of laboratory programs specifically intended to foster report-writing skills and use of computer packages (eg word processors and spreadsheets). Students are given the opportunity to submit draft reports for comment. This aspect of the curriculum is not an integral component of the current exercise.*	Students are given the opportunity to submit draft reports for comment. Students are encouraged to consult their demonstrator on the report writing style and use of appropriate computer programs.	Students will present a formal written report, which satisfies the criteria set out on an assessment and feedback *pro forma*.
All of the above knowledge and skills.	By preparing a clear, well-structured formal report, students will organise their knowledge and understanding and to consolidate learning (*14*).	Students demonstrate that their knowledge, skills and understanding … satisfy the stated and implied criteria and they have met [or exceeded] all the other requirements … *Note: This criterion is an extract from the Faculty guidelines on grading and assessment. It is clearly communicated to students during the semester and is the basis for assessment of all laboratory exercises and assignments.*

Section 3 – Student Learning Experience

Explainatory notes to Student Learning Experience

In 2003, almost 30 students completed this laboratory exercise and provided feedback on the Student Learning Experience. Most negative feedback commented on the mathematical analyses (this laboratory exercise requires students to *comprehend* that they had to fit equations to the data and then to perform the fits). The following are anonymous comments, reflecting the range of feedback.

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 it assisted in my knowledge of CO and the reasoning behind its ability to act as two diff. things.

S2: Yes, relationships concerning bond order were understood.

S3: Yes, much better understanding of equations and spectra detail.

S4: Yes, because some research is need to understand the formulae

S5: Yes. The practical helped show how the calculations con be related to obtaining 'real' information about molecules

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

S1: It wasn't except for my goal of passing

S2: CO; relevent in forensics due to its toxicity. Theory quite interesting

S3: Very, want to do well in subject.

S4: Helps me understand rotational and vibrational spectroscopy

S5: This experiment helped clearify some calculations which are required in SBC313 spectroscopy

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: I did find some of the information obtained from the spectra interesting
S2: Yes, CO has a triple bond
S3: Yes, like dealing with molecules that have a biological/biochemical effect
S4: Yes, how molecules move when light is absorbed
S5: Evaluation of data, ie. calculations were 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 I think there is
S2: Yes and no; It is difficult without help and is very time consuming
S3: Yes, not really time during lab work, but enough time during spectra analysis
S4: Deffinately not
S5: Sufficient time for experiment

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

S1: Yes it does particularly the research and understanding the equations
S2: It could
S3: Yes, in obtaining spectra
S4: Yes, to talk through concepts with others
S5: Teamwork is not essential, however very helpful to be able to correlate with teammembers and colleagues

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

S1: Yes I believe that helping each other also assists individual learning
S2: Yes but required additional help
S3: Yes
S4: Yes
S5: Yes, the calculations required further investigation for clearity and better understanding

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

S1: I think some of the equations were quite difficult
S2: NO, can get very confusing more guidelines needed
S3: Yes, computer work, maths skills, etc
S4: Note sure
S5: Students' use of computer software to aid in calculations is potentially improved

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

S1: The unit guide was helpful
S2: Yes & no. Yes calcs were entered
S3: Yes, for literature values and use of eqns
S4: Yes, to understand it
S5: Demonstrators guidance was essential in this experiment as he helped out with some difficult calculations

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

S2: Bad → Why so many calculations. Did not know this was a maths subject
S3: Hard to know where to start in analysing spectra
S4: good – using excel for graphing etc. bad – time to understand and complete tasks
S5: Calculations helped develop problem-solving skills

3.10 What improvements could be made to this experiment?

S1: The explanation of the equations
S4: Try to make it less time consuming
S5: In additon to CO spectrum analysis, further analysis of a diatomic molecule with a single Lewis structure and a single bond could be made

3.11 Other Comments

S4: have a nice day! :)
S5: No

References

1. Mina-Camilde, N.; Manzanares, C.; Caballero, J. F., *J. Chem. Educ.* **1996**, *73*, 804
2. Lim, K. F.; Collins, M. A., *Aust. J. Educ. Chem.* **2003**, *61*, 17.
3. Shoemaker, D. P.; Garland, C. W.; Nibler, J. W., *Experiments in Physical Chemistry;* 6th Ed.; WCB/McGraw-Hill: Boston, 1996.
4. *The Action Research Planner*; 3rd revised Ed.; Kemmis, S.; McTaggart, R., eds.; Deakin University: Geelong (Vic), 1988.
5. Sweeney, A. E.; Bula, O. A.; Cornett, J. W., *J. Res. Sci. Teach.* **2001**, *38*, 408.
6. Lim, K. F., *J. Chem. Educ.* **2005**, *82,* 145
7. Ohno, K.; Matsuura, H.; Tanaka, H., *J. Chem. Educ.* **1997**, *74*, 961
8. Garizi, N.; Macias, A.; Furch, T.; Fan, R.; Wagenknecht, P. S.; Singmaster, K. A., *J. Chem. Educ.* **2001**, *78*, 1665
9. Lim, K. F., Australian Physical Chemistry Enhanced Laboratory Learning (APCELL) Project, *Reaction kinetics. Inhibition of the enzyme o-diphenol oxidase* <http://www.apcell.org/, 2002 (accessed 23 August 2002).
10. Lim, K. F., *Aust. J. Educ. Chem.* **2002**, *59*, 11.
11. AC Nielsen Research Services, *Employer Satisfaction with Graduate Skills: Research Report*; Department of Education, Training and Youth Affairs (Australian Commonwealth Government): Canberra, 2000, <http://www.detya.gov.au/archive/highered/eippubs/eip98-8/execsum.htm> and < http://www.detya.gov.au/highered/eippubs/eip98-8/eip98-8.pdf>.
12. McInnis, C.; Hartley, R.; Anderson, A., *What did you do with your science degree? A national study of employment outcomes for Science degree holders 1990-2000. A study commissioned by the Australian Council of Deans of Science*; Centre for the Study of Higher Education, University of Melbourne: Melbourne, 2001, <http://www.acds.edu.au/ScienceR.doc>.
13. Australian Bureau of Statistics, *Business Use of Information Technology*; Australian Government Publishing Service: Canberra, 1997.
14. Moore, R., *J. Coll. Sci. Teach.* **1993**, *22*, 212.