

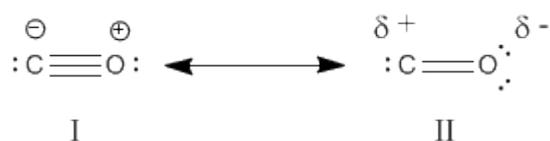
# An IR Investigation of the CO Dipole Direction and Other Properties

by Kieran F. Lim

## Experiment Overview

Spectroscopy is a direct probe of molecular properties. The novelty of this experiment is the placement of a nearstandard Fourier-transform infrared (FT-IR) spectroscopy in an applied context of relevance 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.



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, and hence the molecular bond length. The bond order can be determined from the bond-length- bond-order relationship. 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.

## Aims and Objectives

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 is 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.

## Level of Experiment

This laboratory exercise is part of the Spectroscopy unit, which is a compulsory unit (subject) at the start of the third year.

## Keyword Descriptions of the Experiment

### Domain

physical chemistry

### Specific Descriptors

IR spectroscopy

## Course Context and Prerequisite Knowledge and Skills

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 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 mathematics. 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.

## 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

## Experiment History

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).

Over 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.

## Submission Details

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<sub>2</sub> experiment, which has led to the extension exercise in this laboratory exercise. The author thanks Ms Jeanne Lee (Loyola College, Watsonia) for encouraging and helpful discussions.

## 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.

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