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| Exercise  QS2 |

# Quantum Mechanics AND SPECTROSCOPY:

# VIBRATION-ROTATION SPECTRUM

## Aims

(a) To record the infrared absorption spectrum of carbon monoxide in the vapour phase.

(b) To determine spectroscopic parameters of CO, by analyzing a large amount of data, and compare these with literature values.

(c) Determine molecular structure from spectroscopic parameters.

## SKILLS USED IN THIS EXERCISE

* Measuring gas-phase infrared spectra using an **authentic research** instrument (FTIR).
* Peak-picking using FTIR software and export of data to third party software.
* Interpretation of FTIR spectra and data analysis using **Python**.
* Writing an introduction and abstract.

## INTRODUCTION

For a *diatomic molecule* A–B, the harmonic vibrational frequency is given by

where: *c* is the velocity of light (in units of cm s-1);

*k* is the force constant (N m–1) of the A–B bond;

the reduced mass ** (kg) is expressed in terms of the masses *mA* and *mB* of atom A and atom B,

The general anharmonic oscillator is described by energy levels (with respect to the minimum of the potential) obeying an expansion in , where is the vibrational quantum number

The fundamental vibrational frequency ** (in cm–1) is given by:

Where the anharmonicity is small (typically ~10 cm1), the fundamental vibrational frequency is close to .

Diatomic molecules may also rotate, and exhibit a set of energy levels which depend on the angular momentum quantum number . The rotation-vibration energy levels are given by

Where the rotational constant, , depends slightly on the vibrational quantum number,

The equilibrium rotational constant, is related to the equilibrium bond length, ,

Where the factor of converts energy to cm. Thus, must be used in units of cm s. Now, when a molecule such as CO absorbs an infrared photon, angular momentum must be conserved. As such, the angular momentum of the molecule must change. This gives rise to two types of transition: those that *increase* the angular momentum, and those that *decrease* the angular momentum.

The set of transitions that *increase* the angular momentum are called the *R*-branch, and these transitions generally lie to *higher* energy than the vibrational band origin. The set of transitions that *decrease* the angular momentum are called the *P*-branch, and these transitions generally lie to *lower* energy than the vibrational band origin.



**Figure 1 – The vibration-rotation transitions of a diatomic molecule.**

Denoting the upper state angular momentum quantum number and the lower state angular momentum quantum number , a general formula may be written for the vibration-rotation transition.

For the fundamental vibration transition,

Now, the energies of the *R*-branch and *P*-branch may be written

Conveniently, if we introduce a dummy quantum number, for the P-branch and for the *R*-branch, we obtain

for both branches, which allows us to analyze them simultaneously.

You will measure the wavenumber of these transitions, assign them, and then analyze the data to determine the parameters , , and thus , the equilibrium bond length!

### Risk Assessment and Health and Safety Information

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|  | ***Risk*** | ***Safety precautions*** |
| **Apparatus** |  |  |
| FTIR spectrometer | No significant risks. |  |
| Glass cells | Breakage, cuts from broken glass. | Check cells for cracks or sharp edges; notify lab. attendant |
| **Chemicals** | **See MSDS** | **Wear safety glasses.**  **Do not ingest any chemical.** |
| Carbon Monoxide | Toxic if inhaled. | Do not open the IR cell! Amount in cell is small. Cylinder is stored remotely. CO detector mounted on lab bench. |
| **Other hazards** | None identified |  |
| **Control measures** | Eye protection to be worn at all times. | |

**Overall Risk assessment:** Significant risk that may be effectively controlled.

**Risk assessment by:** Prof. Timothy Schmidt

**Date:** 9 March 2017

**References**

1. Engel, T. and Reid, P., *Physical Chemistry*, Pearson New International Edition, Pearson 2014.

## procedure

***Do not spend more than 1h on data acquisition. The apparatus is needed for experiment QS4 (~1h into lab session).***

The instrument used for this experiment is an FTIR spectrometer. Vapour phase spectra are to be recorded and you are therefore provided with a gas cell prefilled with carbon monoxide. **DO NOT OPEN THE CELL.** The cell has two short side arms which are closed with glass taps. Its windows are made of KBr and are easily damaged by water vapour. As such, ***the cell******must be kept in its desiccator when not in use***; the windows must not be touched with fingers as this transfers considerable amounts of moisture to them. The cell is held in a metal cradle which slides directly into the clip of the sample beam of the spectrophotometer. In this single beam FTIR instrument the spectrum the empty chamber may be recorded as a background. We are interested in the structure of the CO fundamental vibrational band, which should not be affected too much by the exact background.

When finished, store the cell in the desiccator provided.

## RESULTS

Concentrate on the structure in the 2150cm-1 region of the spectrum (zoom in using **xmin** and **xmax**). Ensure that the resolution is sufficient to discern the individual rotational lines, else you will have to repeat the acquisition. To aid your analysis, the first line in the *R*-branch should be located near 2147 cm-1.

Use the peak-picking code to determine the positions of all significant features in the spectrum.

Make a spreadsheet of your band positions, together with an assignment of lower and upper-state quantum numbers, *J*ʺ and *J*ʹ. Do this for both the *R-* and *P-*branches. To ensure that no mistake is made, discuss with your demonstrator which is the first line in the *R* (*J”* = 0) and *P-*branches (*J”* = 1) [why is there no *P*-branch line for *J”* = 0?].

Plot the line positions *vs* *J*ʺ for both the *R-* and *P-*branches, as scattered data. Ensure that the plots are smooth, and free from bumps and wiggles. Now, fit expressions for the wavenumbers of the *R-* and *P-*branches using the **Solver** routine in **Excel**. An example for a portion of the *R*-branch is shown in the picture above. Enter ***all*** of the data you have and fit it globally using **, *B*1 and *B*0 as variables. You might find it instructive to use a single formula for both the *R*- and *P*-branches,



Plot the modelled positions on the same graph as the data as a smoothed line for each branch.

**Paste this plot in your lab book.**

If you want a challenge, try finessing the model by augmenting *F*(*J*) with a term -*DJ2(J+1)2*. Any extra parameters will improve the fit, but you can decide if they are necessary. The term *D* accounts for centrifugal distortion of the molecule. At high rotational quantum numbers the bond gets stretched and the effective rotational constant goes down. *D* is therefore related to the stiffness of the bond, *D* = 4*B*3/e2. How does your fitted *D* compare to this value? You could reduce the number of parameters by simply using this formula for *D*.

**ANALYSIS**

An error analysis can be performed by taking “combination differences” of transitions which either terminate or originate on the same level.

Plot against *J”*. It should be linear, with a slope of 4*B*1 (confirm this algebraicly). Use LINEST to calculate the error in the slope. One quarter of this error is the error in *B*1. The error in the intercept will allow an estimate of the error in ** (confirm this algebraicly).

Similarly, plot against *J”*. It should be linear, with a slope of 4*B*0 (confirm this algebraicly). Use LINEST to calculate the error in the slope. One quarter of this error is the error in *B*0. An error analysis of the nonlinear fit performed using Solver is beyond the scope of this course. Discuss with your demonstrator how this might be done!

**Include answers to these questions in your lab book together with all (annotated) spectra and plots.**

1. Tabulate the determined spectroscopic parameters, with estimates of their error, **in your lab book.** From the information in the Introduction section of these notes, determine *r*1 and *r*0, the average bond lengths in these vibrational states. Include these in the Table, with error estimates (they will be the same percentage error as the rotational constants).
2. Make a plot of *Bv* *vs* (*v* + 0.5), and thus determine *Be*, *re* and *e*. **Add these spectroscopic constants to your Table in your lab book.**

**DISCUSSION**

1. Compare your determined spectroscopic constants to those listed at

<http://physics.nist.gov/PhysRefData/MolSpec/Diatomic/Html/Tables/CO.html>

and

<http://webbook.nist.gov/cgi/cbook.cgi?Formula=co&NoIon=on&Units=SI&cDI=on>

For the latter, you are interested in the X1+ electronic state (the electronic ground state). What is your percentage difference in *Be* and *B0*? What about other constants?

1. Does the rotational constant increase or decrease with *v*? How does *rv* vary with *v*? Explain this in terms of the Morse oscillator model.
2. From the tabulated values of *e* and *exe*, respectively 2169.81358 and 13.28831 cm-1, one can estimate **, the fundamental vibrational frequency. How does this compare with your determined vibrational band origin (with error)?
3. In 1970, intense radiation of frequency 115.267 GHz was discovered emanating from the Orion Nebula. Assuming that this is due to the *J* = 1 → 0 transition of a diatomic molecule excited by the cosmic microwave background, determine its rotational constant. Identify the molecule and its vibrational state.
4. Challenge: Account for any discrepancy of the observation with spectroscopic constant from literature, assuming that these Nobel Prize-winning astronomers had calibrated their spectrometer properly).

### LAB BOOK WRITE-UP

Ensure that your lab book is complete.

***Before leaving the laboratory, submit your lab book to a demonstrator for stamping and signing off.***

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### PRE – LABORATORY QUESTIONS (PASTE INTO LAB BOOK)

1. Calculate the reduced mass in amu and kg for CO.
2. Calculate the rotational constant *B* (cm-1) for CO if its bond length is 1.20 Å.
3. Calculate the frequency (Hz) you would expect for the pure rotational transition from *J* = 1 → 0 for the rotational constant in Question 2.
4. Derive expressions for the wavenumber of *R*-branch and *P*-branch transitions.
5. How long should you spend on collecting your data?