EXPERIMENT XI

INFRARED SPECTRUM OF SO_2 (S&G, 5th ed. Expt 36, 6th ed. Expt. 35)

1. Pre-Lab preparation.

The description of this experiment has disappeared from the more recent editions of S&G. Copies of various previous editions of S&G are available in the reserve section of the library, or obtain a copy of the write-up from the instructor, or download a photocopy from the course web site.

A schematic diagram of the vacuum system used to fill the IR gas cell is shown in Fig. 1.

2. Safety

Careful!!

Improper handling of the vacuum line may result in the release of SO_2 which is an irritating and suffocating gas.

Operation of the vacuum line is described below; consult with the instructor if at any time you are unsure or uncomfortable about some of the details of the manipulations.

Liquid nitrogen is used to trap SO_2 gas. There is a risk of frost bite (-190 C) if some liquid nitrogen spills on the skin; wear thick protecting gloves when pouring liquid nitrogen.

Wear your safety goggles at all times.

3. IR spectra

The instrument used in this experiment is a computer controlled BOHEM FT-IR recording spectrophotometer. At the DOS prompt, type on the keyboard the command "S02" which loads the relevant software and sets the spectrophotometer into the proper configuration; make sure that the actual printer attached to the computer is selected. The instructor can brief you on how to use the controlling program (see below page XI-4). Alternatively, the software controlling the instrument can be invoked through a Windows interface (see Addendum below).

Spectra are run for SO_2 at the series of pressures suggested in the text-book (except that the highest pressure used here will be $\approx$ 700 Torr). A spectrum of the empty (evacuated) cell needs to be collected; this spectrum will be used as the "reference spectrum" and can be later subtracted from each spectrum to obtain the "true" SO_2 spectrum. A spectral resolution of 4 cm^{-1} is sufficient for this series of measurements. However, for a better understanding of the observed line shapes, at the lowest pressure record also a spectrum with a resolution of 1 cm^{-1} (check with the instructor on how to

do this); again, the reference spectrum of an evacuated cell must be recorded at this same resolution for later subtraction.

Before leaving the laboratory, fill in the spectrophotometer log-book.

4. Filling the IR gas cell

3.1 GAS-HANDLING LINE

A schematic diagram of the vacuum line used for gas handling is shown in Fig. 1. This line is equipped with greaseless O-ring valves. Make sure you understand how these devices work; if in doubt ask the instructor or your TA.

To prevent corrosive SO_2 from reaching the mechanical vacuum pump, make sure the cold trap is filled with liquid nitrogen. If it needs to be filled, first position the dewar around the trap, then pour in liquid nitrogen from another dewar.

The IR gas cell available is equipped with KBr windows (when not in use, the cell must be stored in a desiccator). Take care to handle the cell by the middle part made of glass. *Do not touch* the KBr plates on the ends; otherwise a permanent record of your fingerprints will be obtained. In this case, the offender will be required to repair the damage by re-polishing the plates. *Do not bring plates in contact with water.* If you do, you will be required to contribute to the purchase of a new plate.

3.2 PROCEDURES TO FILL THE CELL

- Attach the IR gas cell to the vacuum line.
- Evacuate the gas cell and the SO_2 supply line, *i.e.*, A, B, V_2 , C open, and V_1 , V_3, SO_2 bottle shut. The mercury in the manometer should rise up to a certain height, h_0 (mm Hg); this reading corresponds to **zero** pressure in the line. If any amount of gas is present in the line, the new height (h_n mm Hg) of the column of mercury will be lower, and the pressure of the gas in the line expressed in mm Hg is simply $h_0 - h_n$.
- First collect the IR spectrum of the evacuated cell at both 4 cm^{-1} and 1 cm^{-1} resolution as "background" scans and save the corresponding files; these "background" scans are needed for the following scans.
- For the first pressure condition, fill the cell with ≈ 0.8 atm of SO_2 (≈ 600 - 700 Torr, not 900 Torr as indicated in the text book). To do this,
  - Shut A and deliver SO_2 gas into the main manifold by opening gently the SO_2 bottle. As the pressure in the manifold increases, the column of mercury drops. Keep delivering SO_2 until the mercury is near the bottom of the manometer.
  - Shut the SO_2 bottle, then close C, V_2, B, and record the final height of mercury. The cell is now ready for the first IR measurement and can be detached from the line.

- The first filling gives enough gas to obtain the series of pressures in the cell suggested by the text book (approx. 300, 100, 20 and 5 Torr). For the next measurements,
  - Attach the cell to the line.
  - Evacuate the manifold and the length of tubing connecting to the cell, *i.e.* open A and V_2 (keep B, V_1, C and V3 shut) until the mercury rises back to h_0.
  - Shut A and let the gas in the cell expand into the manifold by opening C. The resulting pressure should be larger than what is required.
  - Reduce the pressure in the manifold by opening slowly A until the column of mercury rises to the required height, then close A.
  - Close V_2 and C and proceed to record the IR spectrum with a resolution of 4 cm^{-1}
- Repeat the above steps for each new pressure.
- For the lowest pressure, collect an additional spectrum with a 1 cm^{-1} resolution.

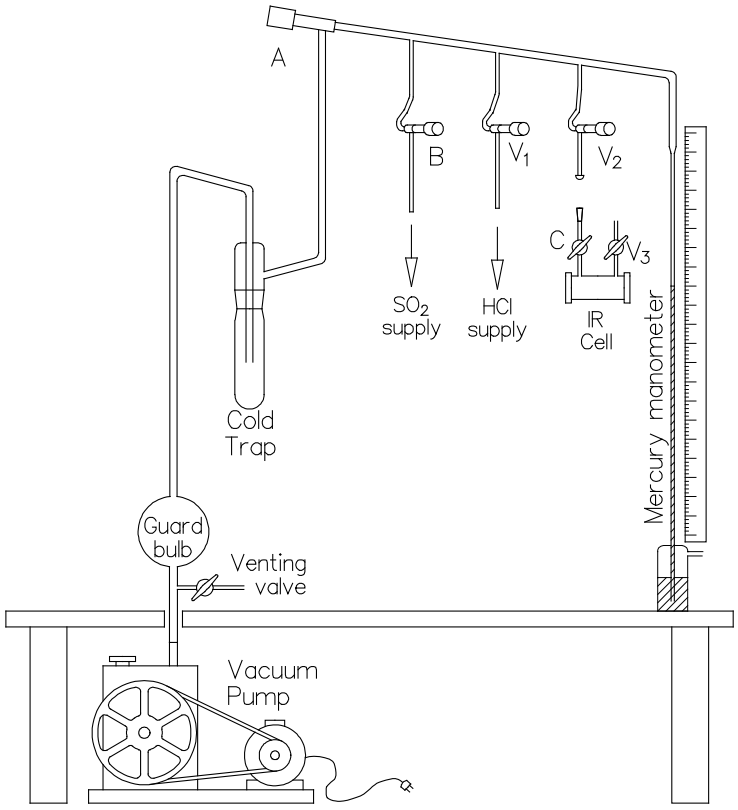

Figure 1. Apparatus used to fill the IR gas cell at various pressures.

5. Vacuum line shut-down

When all your data have been collected and before leaving the lab, the cold trap has to be emptied of trapped SO_2.

Do the following:

- Vent to the air the gas cell and return it to the desiccator,
- Empty the cold trap, *i.e.*,
  - remove the liquid nitrogen dewar,
  - switch off the rotary vacuum pump,
  - vent the vacuum line by turning open the vent valve next to the guard bulb,
  - twist *gently* the glass trap out of the vacuum line (use a heat gun if necessary to soften the grease at the glass joint) and place it in the fume hood to let the trapped SO_2 evaporate safely.

6. Important notes for data processing, analysis and discussion

If the spectra were collected using the DOS-Bomem interface, each spectrum will have to be manipulated to subtract the spectrum of the evacuated cell used as reference. If the "Bomem-Easy" windows interface was used, this background subtraction is done automatically during the data taking.

Then, for each of the pressure get a print out of the corresponding spectrum on which only the vibrational frequencies have been marked (see below). In addition, at the lowest pressure, zoom in on the ≈ 1150 cm^{-1} absorption band and obtain a print out of this band alone at both resolutions in order to illustrate the effect of resolution on the band shape.

To locate properly the position of the vibrational frequencies, you should first have to understand, at least qualitatively, that the band-shapes observed are due to unresolved rotational transitions; read the theory on rotation-vibration spectrum of HCl/DCl in S&G. Also, there are two types of absorption band-shape to be found, depending on whether the pure vibrational transition is forbidden or partially allowed. In one type, the absorption band displays two "bumps"; the pure vibrational frequency is located in the gap between the "bumps". In the second type, in addition to the two "bumps", the absorption band displays a little spike in between the "bumps" which locates the pure vibrational frequency. In each case explain clearly in your *Experimental* or *Results* section, why the features described above can be used to locate the vibrational frequencies. Prepare a table of all the measured frequencies obtained at the different pressures, and then decide which data are best suited for reporting the values of the vibrational frequencies (and associated uncertainties). In your discussion comment on the effect of pressure on your observed spectra and explain why collecting the spectra with a resolution of 4 cm^{-1} is sufficient (actually more appropriate) for the present purpose.

What are the main applications of IR spectroscopy and why?

Addendum

Information on the Windows program used to manipulate the FT-IR data.

Background must be collected first.

To collect background

- Collect / Background Scanning / Ok Scan Background (remember to set parameters)

To collect spectrum

- Collect / Scanning / Ok Scan (remember to set parameters)
- Background is automatically subtracted, choose "keep open in memory" when prompted

To manipulate display

- "drag" out a box of interest and click inside box to zoom in
- Alternatively, View / XY limits (or Ctrl+X)

To mark peak values (cm^{-1})

- Peaks / Sensitivity Setting = 100 (to make insensitive to auto chosen peaks)
- Click on peak position and press Alt+Insert

To Print

- File / Print (make sure that landscape setting is selected before printing)

To Export data

- File / Save As (data must be saved on hard disk first, remember the file location)
- File / Import/Export

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Chem 366W report check list

A report will not be accepted without all the items of this list checked. If a checked item is found missing in the report, the report will be automatically down-graded.

Student Name:_____

Report: Infrared Spectrum of SO_2

Title page.

Correct title of the experiment ☐
Student Name & student ID ☐
Partner name (*if applicable*)_____
Date of performance of experiment ☐
Abstract ☐
Introduction and theory ☐
Experimental
Changes from text description mentioned (*if applicable*) ☐
Sample ID, ser no, stock solution …etc recorded (*if applicable*) ☐
Results
Results as Tables ☐
Graphs
Size, at least ½ page ☐
Axis labelled ☐
Axis labels have units ☐
Axis scales are sensible ☐
Only significant figures ☐
Uncertainties quoted ☐
Raw data provided (*electronic form, if applicable*) ☐
Calculations
Sample calculation provided ☐
Error analysis ☐
Sample error calculation provided ☐
Discussion
Comments on results ☐
Questions in text book and in manual answered ☐
Comparison with literature value(s) ☐
Conclusion ☐

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