Vibrational Spectrum of SO_2

Introduction

SO_2, a bent triatomic molecule, possesses three degrees of vibrational freedom. In this experiment you will learn about normal vibrations in polyatomic molecules, the simple valence force model of describing those modes, and the contributions of those degrees of freedom to the heat capacity of SO_2 gas by the use of statistical mechanics.

Procedure

The experiment is described in Shoemaker, *et al*, 4th Ed., pp. 418-427 (or 5th Ed. p 446). This text may be found on the Chem 366 reserve shelf in the chemistry library or in lab. Barrow's *Introduction to Molecular Spectroscopy* is also helpful on understanding the spectrum of a polyatomic molecule like SO_2. A more advanced discussion is presented in Herzberg III, and in Wilson, Decius, and Cross, "Molecular Vibrations."

You will use a Perkin-Elmer Model 283B infrared spectrophotometer that is capable of scanning from 200 to 4000 cm^{-1} or the Nicolet Magna Fourier transform infrared spectrometer scanning from 400 to 4000 cm^{-1}. Be sure to use a cell that has windows transparent to at least 500 cm^{-1} so that the low frequency bending vibration ν_2 can be observed. CsI windows satisfy this requirement. As noted in Shoemaker *et al.,* you will have to scan the spectrum several times at several different pressures of SO_2. Given that you are using a glass gas-handling line, you may wish to skip using any SO_2 pressures above 1 atmosphere. Use your judgement on what pressures you want to use.

Report

Carefully note the rotational fine structure on each band. In addition to a P and an R branch observed in a diatomic like HCl, it is possible for some vibrational transitions to possess a Q branch ($\Delta J = 0$) as well. Determine the type of transition for which a Q branch is allowed in the fundamental, and then use this information along with the band positions to assign the observed overtone and combination bands.

Report the infrared band frequencies you observe with their assignments. Also report the force constants, and the values of C_v at 298 and 500 K that you calculate from your spectroscopic measurements using statistical mechanics. If you wish you may write a computer program to calculate C_v over this temperature range. Compare the values of C_v obtained using statistical mechanics with the thermodynamically determined values (see Shoemaker *et al.*).

Note the magnitude of the SO_2 rotational spacings and compare them with the vibrational energy level differences. Prepare a schematic energy-level diagram of the transitions you observe.

Safety Note

The instructor will demonstrate the proper handling of the vacuum system. Be sure to wear goggles at all times when using reduced-pressure equipment. Please be careful not to drop, scratch, leave fingerprints on, or otherwise damage the moisture sensitive CsI cell-windows. They are very expensive!

References

1. D.P. Shoemaker, C.W. Garland, J.I. Steinfeld, and J.W. Nibler, *Experiments In Physical Chemistry*, 4th Edition (McGraw-Hill Book Co., New York, 1981). Later editions are ok.

2. E. Bright Wilson, Jr., J.C. Decius, and Paul C. Cross, *Molecular Vibrations* (Dover Publications, Inc., New York, 1955).

3. G.M. Barrow, *Introduction to Molecular Spectroscopy*, (McGraw-Hill, New York, 1962).

4. G. Herzberg, *Infrared and Raman Spectroscopy* (Van Nostrand Reinhold, New York, 1945).

Jan-91 JT, March-96 BK

Directions for using the Nicolet Magna 550 FTIR in the Chem 366 SO_2 Experiment

Note: an updated version of these directions is provided near the FTIR.

1. Put the evacuated gas cell into the sample compartment. Let it purge for 2 or 3 min. while you do steps 2-4.

2. Start Omnic (not Omnic 1.0 or 1.1, but the most recent version of Omnic) If Omnic is already running open a new window under "windows."

3. Under "file," "open parameter" file open "dtgs4.prm"

4. Choose "collect" "collect set-up"
   Change the resolution to 0.5 cm^{-1} (OK on aperture change)
   Make sure it says 'collect background before every sample'

5. Choose "collect" "optical bench set-up"
   change spectral range to 7000 to 400 cm^{-1}

6. "Collect" "Collect background"

7. Save this background in chem 366 subdirectory

8. Fill your cell, put it in place, and let it purge 2-3 min while you do the next step

9. Choose "collect" "collect set-up" and change to "use saved background.
   Use "browse" to choose your background file.

10. When taking spectra from here on, use "collect" "collect sample"
    After the first (highest pressure) sample, you can revert to saving only 4000 to 400 cm^{-1}

11. Save the sample files in chem 366 subdirectory

12. Play with options: expanding, labeling peaks, and printing.

13. Spectra may be printed using any of the networked printers:

    lw-chemistry-210
    lw-chemistry-216
    lw-morley-149 (often the best)
    lw-morley-246b

14. At the very end, go into the file manager, make your own subdirectory within the chem 366 directory and move your files into your subdirectory.

March-96 BK