

LAB #5: VIBRATIONAL SPECTROSCOPY OF CHCl₃ AND CCl₄**Abstract**

The vibrational normal modes of liquid chloroform (CHCl₃) and carbon tetrachloride are examined with both infrared and Raman spectroscopy. The change in symmetry in the carbon tetrachloride versus the chloroform and the effect on the normal modes will be examined and the spectra collected will be compared to literature spectra/values.

Related Reading

Shoemaker, Garland, and Nibler, "Experiments in Physical Chemistry", 6th Ed. (Handout in class) and Gundogdu et al, *J Chem Phys*, 125, 174503 (2006) (sent via e-mail)

Background

See Shoemaker, et al. for the theory on Raman spectroscopy, the normal modes for various molecular types, and the valence-force model.

Procedure

The IR and Raman spectra of chloroform and carbon tetrachloride will be collected.

1. IR spectra: Using the ATR attachment of the Bruker Tensor 27 FT-IR spectrophotometer (in the NMR room), collect the spectra of both liquid chloroform and liquid carbon tetrachloride. Follow the directions for collecting a IR spectra of liquid organics.
2. Raman spectra: Using the Raman Systems R-3000 Raman spectrophotometer (in Nobel 107, the p chem lab), collect the spectra of both liquid chloroform and liquid carbon tetrachloride. Directions for use:
 - a. Power on the laptop computer and the Raman system (but not the laser, yet). You want to choose the user RSI on the computer.
 - b. Open the software: RSIScan.
 - c. Take the small vial with the sample and insert it into the sample holder (i.e., remove the black cover, place the vial into the chamber, replace the cover, and move the laser box so it is fully inserted).
 - d. In the software, go to View: Show Control.
 - e. Turn on the laser by turning the key on the control box.
 - f. To collect the spectra, click on the icon as shown below. (The black version of the icon collects a background scan.)



- g. Label the peaks by clicking on the label peaks button at the top of the screen.
- h. Print the spectra (prints entire screen to the GSI lab, you may want to adjust the view of the screen prior to printing).

Lab Report

This should serve as a very general guide for this lab report. This guide lists some items I'd include in the results and discussion section of the report; there are likely some things on in this list that should be included as well. You need only to write the results and discussion section as usual.

Results:

1. IR and Raman spectra
2. Table including peak position (in cm^{-1} or rel. cm^{-1}), peak identification ($\nu_{\#}$), intensities, and literature values
3. Normal modes (assigned to the peaks) for both CCl_4 and CHCl_3 (Note: there are 4 modes for CCl_4 but 6 for CHCl_3). Draw out the modes (as in Table 1 of the handout) and assign them a $\nu_{\#}$. (WebMO calculations may help you.)

Discussion:

1. Use the valence force model to find k and k_{δ}/l^2 and determine if the stretch-stretch, stretch-bend and bend-bend interactions are important terms in potential energy of CCl_4 and CHCl_3 .
2. Compare and contrast the IR and Raman spectra for both CCl_4 and CHCl_3
3. Compare and contrast the two Raman spectra (i.e., compare CCl_4 and CHCl_3)
4. Error sources and any differences between the literature values and experimental (remember we only looked at the Stokes lines)
5. Discussion on overlap of ν_3 and $\nu_1 + \nu_4$

Some good literature sources/resources/tips:

1. NIST webbook (type in compound name/formula & find vibrational energy link)
2. SDDBS (spectral database)... easiest way to access is to google SDDBS
3. Gundogdu, K., et al., *J. Chem. Phys.* 2006, **125**, pg. 174503. (This doesn't have values for CHCl_3 or CCl_4 , but does identify the normal modes of CDCl_3 which may be helpful as you assign the normal modes of CHCl_3 .) This was/will be sent via email.
4. WebMO can be used to help you assign the normal modes (think about the type of calculation you'd need to do...). You should be able to use your username and password from last semester.

References

1. Gundogdu, K., et al., *J. Chem. Phys.* 2006, **125**, pg. 174503
2. Shoemaker, Garland, and Nibler, "Experiments in Physical Chemistry", 6th Ed.