

Exercise 4

Infrared Spectroscopy

When it is possible to relate concepts at the microscopic level to the physical world that is visible to us, it is often easier to relate to the concept and attain an understanding of it. This type of reasoning is sometimes carried too far. For example, the atom is sometimes compared to our solar system. The solar system has many shortfalls as a model for the atom. Other models of this type do work better and the first part of this exercise investigates a model for the stretching vibration of bonds. A possible model for bonds could be represented by two masses attached to a spring. For this model, Hooke's Law gives the relationship between the stretching frequency, the masses of the two balls and the force constant (F) of the spring.

$$\nu = (1/2\pi c) (F/\mu)^{1/2} \quad \text{where } \mu = \frac{M_x M_y}{M_x + M_y} = \text{reduced mass with } M_x \text{ and } M_y \text{ representing the masses of the balls on the ends of the spring}$$

- Using the equation above, derive the relationship between the ratio ν_1/ν_2 of the stretching frequencies for two bonds (assuming the stretching force constant is the same for the two bonds) and the masses on the bond.
- Now use the derived equation to determine the ν_1/ν_2 ratio for a C - H bond to a C - D bond assuming the force constants are the same.
- After you have finished the problem immediately above (#2), use the two infrared spectra below to determine the experimental value of ν_1/ν_2 for the ratio of the stretching frequencies of C - H to C - D. Please note that the weak absorptions in the vicinity of 2400 cm^{-1} are due to an inadequate correction for the background absorption of carbon dioxide.
- Compare the result from the model to the experimental value and comment on the validity of the model.
- Are there any other absorptions in the spectra that involve the C - D bond? Explain your answer and if so describe the type of vibration that is responsible for the absorption.
- Does the hydrogen (or deuterium) have a significant effect on the stretching frequency of the C-Cl bond? Explain your answer.
- Is either CHCl_3 or CDCl_3 a good solvent for ir spectroscopy? Explain your answer. Would CCl_4 have any advantages over either chloroform as an ir solvent? Explain your answer.

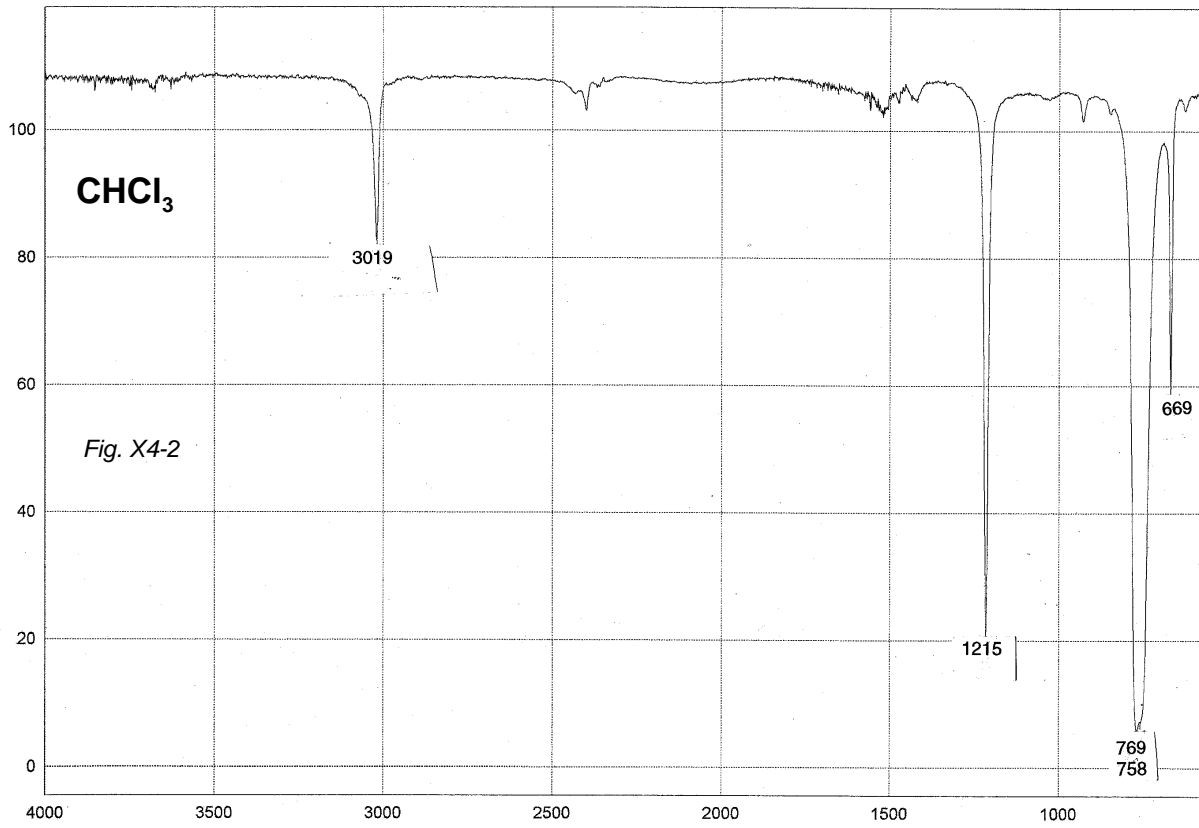
Fig. X4-1



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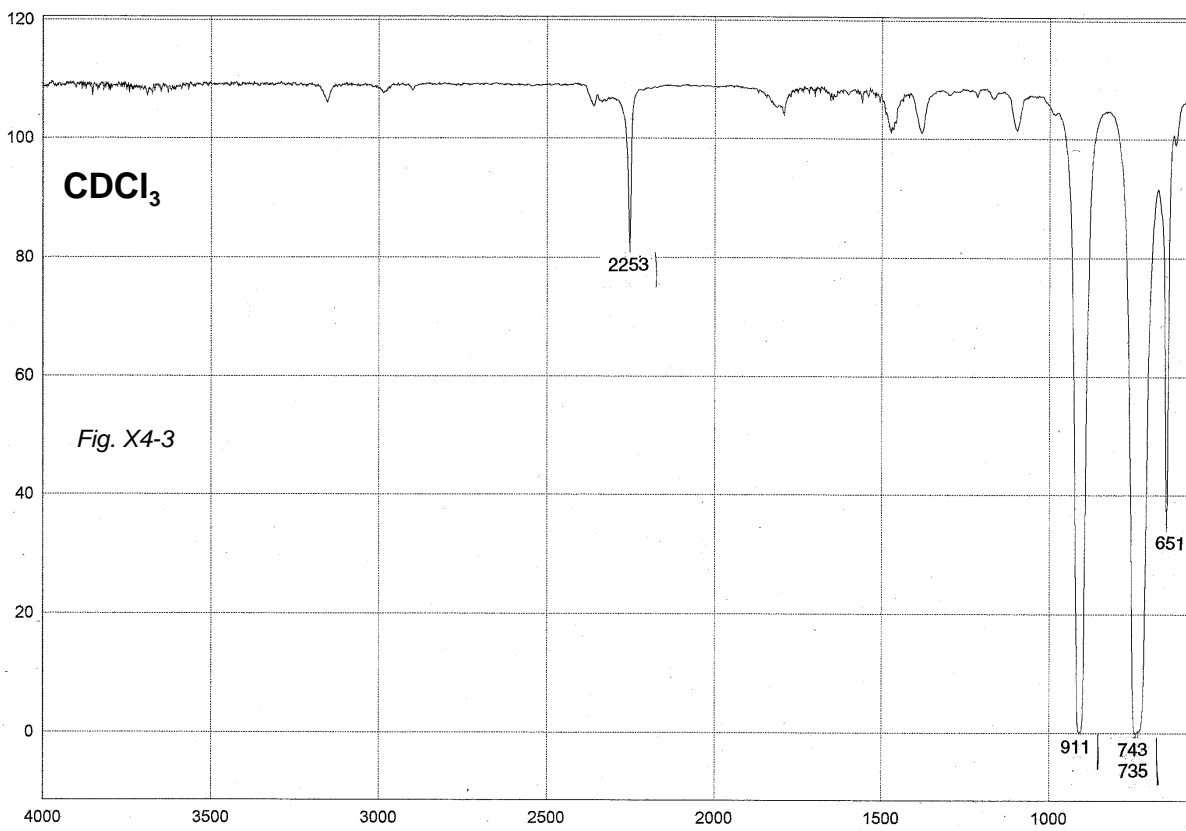
In addition to his pioneering work on insect communication, he coauthored one of the finest books on organic spectroscopy.
<http://www.esf.edu/communications/news/2000/05.02.milt.htm>

X4-2



CHCl_3

Fig. X4-2

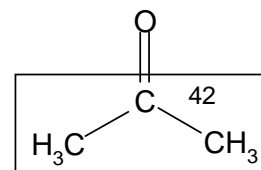
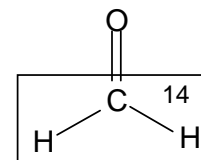


CDCl_3

Fig. X4-3

Group Frequencies (An Internet Exercise)

Based on the Hooke's law exercise above, it might be assumed that the masses for the carbon ends of the carbonyl in formaldehyde and acetone would be 14 and 42 respectively. This would result in significantly different frequencies for the carbonyl stretch. Fortunately this is not the case as carbonyl stretching frequencies for most carbonyls are near 1700 cm^{-1} ($\pm 40\text{ cm}^{-1}$) and therefore relatively independent of the groups attached to the carbonyl carbon. The carbonyl acts as though the masses attached to the bond are simply an oxygen and a carbon. If group frequencies did not exist in the ir, the ir would be relatively useless for the determination of the presence of functional groups. IR would only be useful as a fingerprint for positive identification after the structure had been determined using other techniques. Most absorptions in the ir that occur above 1350 cm^{-1} are relatively independent of the rest of the molecule and are reliably used as group frequencies. A very abbreviated ir correlation chart is included in *Experiment 7*.



Most correlation charts contain a limited number of group frequencies. Commonly left out of the chart are the group frequencies of the thio (-SH) and nitro (-NO₂) groups. This text has purposely left thio and nitro groups out of the experiments. Most compounds that contain thio groups have strong and unpleasant odors. Compounds that contain nitro groups are often toxic and have explosive properties.

1. Do a literature or Internet search to determine the odoriferous gas present in natural gas. The principal component of natural gas is methane. Is methane the odoriferous compound? If not, what is and why has it been added?
2. What compounds are responsible for the essence of skunk?
3. Consider the names of many common explosives (TNT, nitroglycerine, ammonium nitrate). What characteristics are desirable for explosives?
4. Use the SBDS site [http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/cre_index.cgi?lang=eng] (NIMC site,) to determine if there are group frequencies for the thiol (-SH) and nitro (-NO₂) groups. To perform this assignment, inspect the ir spectra of compounds that contain these groups and try to find absorptions that are only present when these groups are present. [Hint: For thiols, search for compounds using the formulas C₄H₁₀S and C₆H₆S. The nitro group is more of a challenge as the absorptions occur close to absorptions for the C-H bending absorptions. You might want to look first at the ir spectra of hydrocarbons to determine which absorptions should be eliminated. Try formulas such as: C₄H₉NO₂, C₆H₅NO₂, C₇H₇NO₂, C₇H₇NO₃. Be sure to consider the effects of conjugation on the position of the nitro absorption. Remember that conjugation of π systems usually lowers the energy of the absorption by about 25 cm^{-1} .]

