

Experiment 13 Qualitative Analysis with Infrared Spectrophotometer

Introduction

Infrared is the portion of the electromagnetic spectrum that extends beyond the visible into the microwave region (Fig. 1). It is measured in units of frequency or wavelength. In the infrared, frequency is usually expressed in wavenumber units, or reciprocal centimeter. Wavelength is expressed in microns (10^{-6} m), abbreviated μ . Frequency, f , and wavelength, λ , are related by the equation $f\lambda = C$, where frequency is defined as cycles per second and C is the velocity of light (3×10^8 cm/sec). A wavenumber unit, ν , is defined as the reciprocal of wavelength ($\nu = 1/\lambda$). The product of ν and C gives the frequency in cycles/sec. The infrared region extends from approximately 0.75μ to almost 1 mm, but the segment most often used by the chemist is from 4000 to 650 cm^{-1} , (2.5 to $15.4\mu\text{m}$) termed the “fundamental” region. The low frequency region from 650 cm^{-1} to the microwave region is often called the far infrared, whereas that from 4000 cm^{-1} to the visible is often called the near infrared or overtone region.

All molecules are made up of atoms held together by chemical bonds. These atoms vibrate with respect to each other, the bonds acting much like springs connecting the atoms. Each molecule has its own specific set of vibrational frequencies, but different molecules have different sets of vibrations. The frequencies of these vibrations are in the same range as the infrared frequencies of electromagnetic radiation.

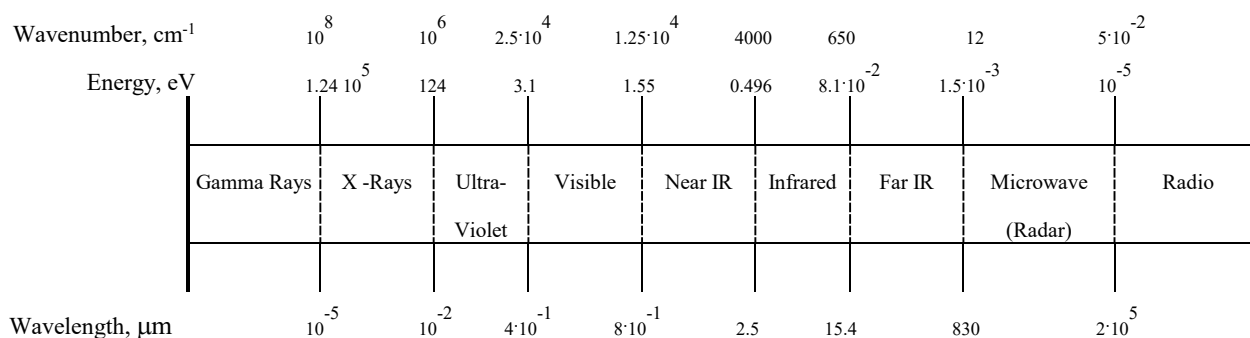


Fig. 1 The electromagnetic spectrum.

Infrared analysis gives the scientist a permanent, step-by-step record of his work, providing him and his organization with evidence of dates on which he reached various stages, a record which can be invaluable in patent applications. In carrying out a complex synthesis, he can determine the identity and purity of reagents, follow stepwise changing in all materials, determine percent yields, and can check back at any stage. Furthermore, there is no fear of having insufficient sample to proceed to the next stage, since **infrared analysis is nondestructive** and the sample is recoverable.

Since the infrared spectrum of a chemical compound is perhaps its most characteristic physical

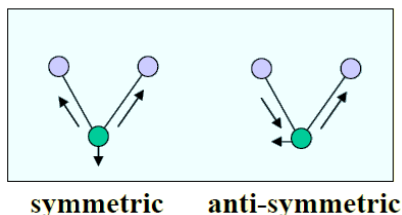
property, infrared finds extensive application in “fingerprinting” or identifying materials. By matching the infrared spectrum of an unknown with that of a known material, proof of identity is established.

Molecular vibrations can be divided into stretching vibrations and bending vibrations:

1. Stretching Vibration:

Symmetric Stretching: Atoms move simultaneously in the same direction.

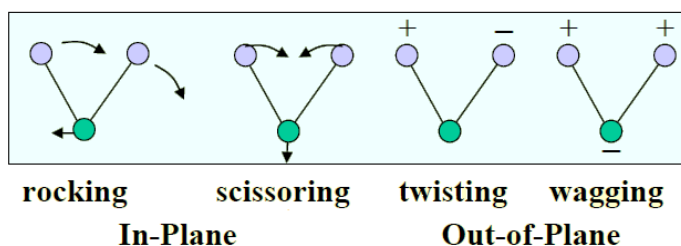
Asymmetric Stretching: Atoms move in opposite directions.



2. Bending Vibration:

In-Plane Bending: Such as scissoring and rocking.

Out-of-Plane Bending: Such as twisting and wagging.



Each functional group has specific absorption frequency ranges. For example:

Hydroxyl Group (-OH): Strong absorption band in the 3200-3600 cm^{-1} range.

Carbonyl Group (-C=O): Strong absorption peak around 1700 cm^{-1} .

Alkenyl Group (-C=C): Absorption in the 1620-1680 cm^{-1} range.

Identifying Functional Groups

Using FT-IR, functional groups in a sample can be identified by recognizing the positions and intensities of absorption peaks. The specific steps are:

1. Obtain the FT-IR Spectrum of the sample.
 2. Identify Major Absorption Peaks and record their wavenumber positions.
 3. Refer to Infrared Spectral Libraries or standard functional group absorption
 4. frequency tables to match the absorption peaks with known functional groups.
- Determine the Functional Groups in the sample and infer its molecular structure.

Instrument

Shimadzu IR Affinity-1 FT-IR

Sample Preparation

1. Read the operational manual for FT- Infrared Spectrophotometer carefully.
2. Prepare solid unknown samples by weighing out about 1~2 mg of unknown sample and mixing with about 99 mg of dried KBr. Mix them and grind them with an agate pestle and mortar . (ask TA for these equipment.)
(註:一組秤 6~8 mg $C_7H_6O_3$ + ~0.396 g KBr)
3. Put the mixture in a metallic cylinder container (die) and try to make a wafer by compressing the mixture with manual hydraulic press. The sample is ready to run.
4. If the film is too thick or the scanning spectrum is not satisfactory, you may readjust the proportions of either sample or KBr.
5. Clean the cells and equipment used.

Results

1. Using the formula provided by TA and the IR spectrum, predict the molecular structure of your unknown.

<<網路參考資料>>

不飽和度 (英文名稱: Degree of unsaturation), 又稱缺氫指數或者環加雙鍵指數 (index of hydrogen deficiency (IHD) or rings plus double bonds), 表示有機物分子不飽和程度的量化指標, 用希臘字母 Ω 表示。不飽和度公式可以估計化合物大約有多少個環、雙鍵、和叁鍵, 但無法給出確切的數目, 而是環和雙鍵以及兩倍叁鍵 (即叁鍵算 2 個不飽和度) 的數目總和。最終結構需要藉助於核磁共振 (NMR), 質譜儀和紅外光譜 (IR) 以及其他的相關資訊來確認。

$$\Omega = (2C + 2 - H + N) / 2$$

其中, C 代表碳原子的數目, H 代表氫和鹵素原子的總數, N 代表氮原子的數目, 氧和其他二價原子對不飽和度計算沒有貢獻, 故不需要考慮氧原子數。這種方法只適用於含碳、氫、單價鹵素、氮和氧的化合物。

若 $\Omega=0$, 說明有機分子呈飽和鏈狀, 分子中的碳氫原子以 C_nH_{2n+2} (此為飽和烴分子式通式) 關係存在。

若 $\Omega=1$, 說明有機分子中含有一個雙鍵或一個環。

若 $\Omega=2$, 說明有機分子中含有兩個雙鍵或一個三鍵或一個雙鍵一個環或兩個環。

若 $\Omega \geq 4$, 說明有機分子中可能含有苯環 (C_6H_6)。

主要官能基的判斷:

在光譜圖上,我們先注意 $\text{C}=\text{O}$ 、 $\text{C}=\text{C}$ 、 $-\text{OH}$ 、 $\text{N}-\text{H}$ 、 $\text{C}-\text{O}$ 、 $-\text{C}\equiv\text{C}$ 以及 NO_2 等振動吸收峰是否存在。這些吸收峰的存在,可驗證酸、醯胺、酯、醛、酮、醇、胺、醚、烯、炔、芳香族以及硝基等主要官能基。下面就此等主要官能基的存在,做一有系統的討論,討論的過程可視為實際由紅外光譜推導分子結構的初步程序。

(一) 首先檢查 $\text{C}=\text{O}$ 官能基是否存在

$\text{C}=\text{O}$ 官能基若存在,光譜 $1820\text{--}1640\text{ cm}^{-1}$ 有一非常強之吸收峰。在檢查吸收峰時,請注意其強度,以避免與 $\text{C}=\text{C}$ 之吸收峰混淆。

(二) 若 $\text{C}=\text{O}$ 官能基存在

(1) 醛(Aldehydes): 若為醛,光譜 2850 和 2750 cm^{-1} 附近有二弱的 CH 吸收峰。一般烷、烯、炔類 $\text{C}-\text{H}$ 頻率高於 2850 cm^{-1} 。

(2) 酸(Acids): 若為酸,光譜 $3400\text{--}2400\text{ cm}^{-1}$ 附近有一個寬的 $\text{O}-\text{H}$ 吸收峰,其寬度較醇與酚的 $\text{O}-\text{H}$ 吸收峰還要寬。

(3) 醯胺(Amides): 醯胺,光譜 3500 cm^{-1} 附近有一中等強度較銳的 $\text{N}-\text{H}$ 吸收。

(4) 酯(Esters): 若為酯,光譜 $1300\text{--}1000\text{ cm}^{-1}$ 有吸收峰,而在 $3400\text{--}2400\text{ cm}^{-1}$ 沒有吸收峰。

(5) 酸酐(Anhydrides): 若為酸光譜 1810 和 1760 cm^{-1} 附近有 2 個 $\text{C}=\text{O}$ 吸收峰。

(6) 酮(Ketones): 以上五點皆不存在,則為酮類。

(三) 若 $\text{C}=\text{O}$ 官能基不存在,即 $1800\text{--}1640\text{ cm}^{-1}$ 無強吸收峰,則做下列檢查。

(1) 醇(Alcohols)、酚(Phenols): 若為醇或酚應有下列二吸收峰:

a. 光譜 $3600\text{--}3300\text{ cm}^{-1}$ 有寬且強的 $\text{O}-\text{H}$ 吸收峰。

b. 光譜 $1300\text{--}1000\text{ cm}^{-1}$ 有強的 $\text{C}-\text{O}$ 吸收峰。

(2) 胺(Amines): 若為胺,光譜 3500 cm^{-1} 附近有一中等強度較銳的 $\text{N}-\text{H}$ 吸收峰。

(3) 醚(Ethers): 若為醚,則無 $\text{O}-\text{H}$ 吸收峰,在 $1300\text{--}1000\text{ cm}^{-1}$ 有 $\text{C}-\text{O}$ 吸收峰。

(四) 烯與芳香族(Alkenes and aromatic compounds):

(1) 烯與芳香族在大於 3000 cm^{-1} $=\text{C}-\text{H}$ 有吸收峰。

(2) 若為烯類光譜 1650 cm^{-1} 附近有一弱的 $\text{C}=\text{C}$ 吸收峰。

(3) 若為芳香族,光譜 $1650\text{--}1450\text{ cm}^{-1}$ 、有一中等強度 $\text{C}=\text{C}$ 吸收峰。通常在 1470 、 1500 、 1580 以及 1600 附近有 4 個吸收峰代表可能有苯環。

(五) 三鍵官能基:

(1) 腈(Nitriles): 若為腈,光譜 2250 cm^{-1} 附近有一個中等強度且尖銳的 $-\text{C}\equiv\text{N}$ 吸收峰。

(2) 炔(Alkynes): 若為炔,光譜 2150 cm^{-1} 附近有一弱而銳的 $-\text{C}\equiv\text{C}$ 吸收峰。若為末端 $-\text{C}\equiv\text{C}-\text{H}$, 則在 3300 cm^{-1} 附近有 CH 吸收峰。

(六) 硝基(Nitro group): 若有硝基,光譜 $1600\text{--}1500\text{ cm}^{-1}$ and $1390\text{--}1300\text{ cm}^{-1}$ 有兩個強吸收峰。

(七) 烷類(Alkanes): 若為烷類,則無以上吸收峰。在 3000 cm^{-1} 有 CH 的吸收峰,在 1450 cm^{-1} 和 1375 cm^{-1} 附近有簡單吸收峰。

儀器設定:

Scan wavenumber :

blank:

結果: (1)請在圖上標示可能的官能基，並繪出可能的結構式。