

Educational experiment package Volume 2

Molecular spectroscopy

Overview

Thermo Fisher Scientific is proud to offer a variety of educational experiments for use with our Fourier transform infrared (FTIR) spectrometer systems. These experiments were written to enable use of FTIR spectrometers in educational curricula. Our Educational Experiment Package provides a ready-to-use introduction to the world of FTIR spectroscopy.

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Experiment 1

Using FTIR spectroscopy to illustrate isomer concepts

Objective

To illustrate the concept of isomers (molecules with the same molecular formula, but different structural or spatial arrangements of the atoms) and how they can be differentiated.

Materials Required

- FTIR spectrometer (Thermo Scientific™ Nicolet™ iS20 FTIR Spectrometer is recommended)
- Sampling Accessory
 - ATR Accessory OR
 - Transmission cell
- o-Xylene, m-xylene, and p-xylene
- Acetone (HPLC grade) as a cleaning agent

Introduction

Traditional laboratory approaches to studying isomerism relies on physical properties to differentiate isomeric compounds. These techniques usually include refractive index and density. However, some isomers have similar physical properties. In addition, most modern industrial laboratories today do not utilize these techniques. They require a faster and more definitive methodology that is offered by FTIR spectroscopy.

Discussion

The specific isomers chosen for this experiment are xylenes, also known as dimethylbenzenes, with the molecular formula $C_6H_4(CH_3)_2$. These isomers are difficult to differentiate based on physical properties. Unfortunately, UV-Visible spectroscopy cannot provide sufficient insights to allow an analyst to discriminate between the isomers. However, xylenes are excellent candidates for infrared spectroscopic discrimination. In this laboratory, you will be given three unlabeled samples, one of each xylene isomer. Physical (and optionally, UV-Visible) properties of the isomers may be investigated or drawn from reference sources to demonstrate that this information alone is not enough to differentiate the isomers. The infrared (IR) spectra will be acquired to see how simple IR makes identification of the three isomers.

Experimental

These instructions are specific to ATR data collection. The modifications for transmission are straightforward, and left to the instructor.

Ensure the ATR accessory is inserted properly in the spectrometer. Initially, clean the crystal with acetone and allow it to dry. Set the experimental parameters to collect

32 scans with a 4 cm^{-1} resolution over the spectral range from 4000 to 650 cm^{-1} (or to the lowest frequency allowed by the spectrometer and accessory combination). Collect a background spectrum. Clean the crystal thoroughly between samples; you can use the initial background or collect new ones before each sample, as desired. Add sufficient sample to cover the crystal – one drop is enough for a single bounce ATR. Save or print out your spectra for use in the interpretation and to turn in to your instructor.

Questions

Draw the molecular structure of the three xylene isomers used in this experiment:

Ortho-Xylene	Meta-Xylene	Para-Xylene

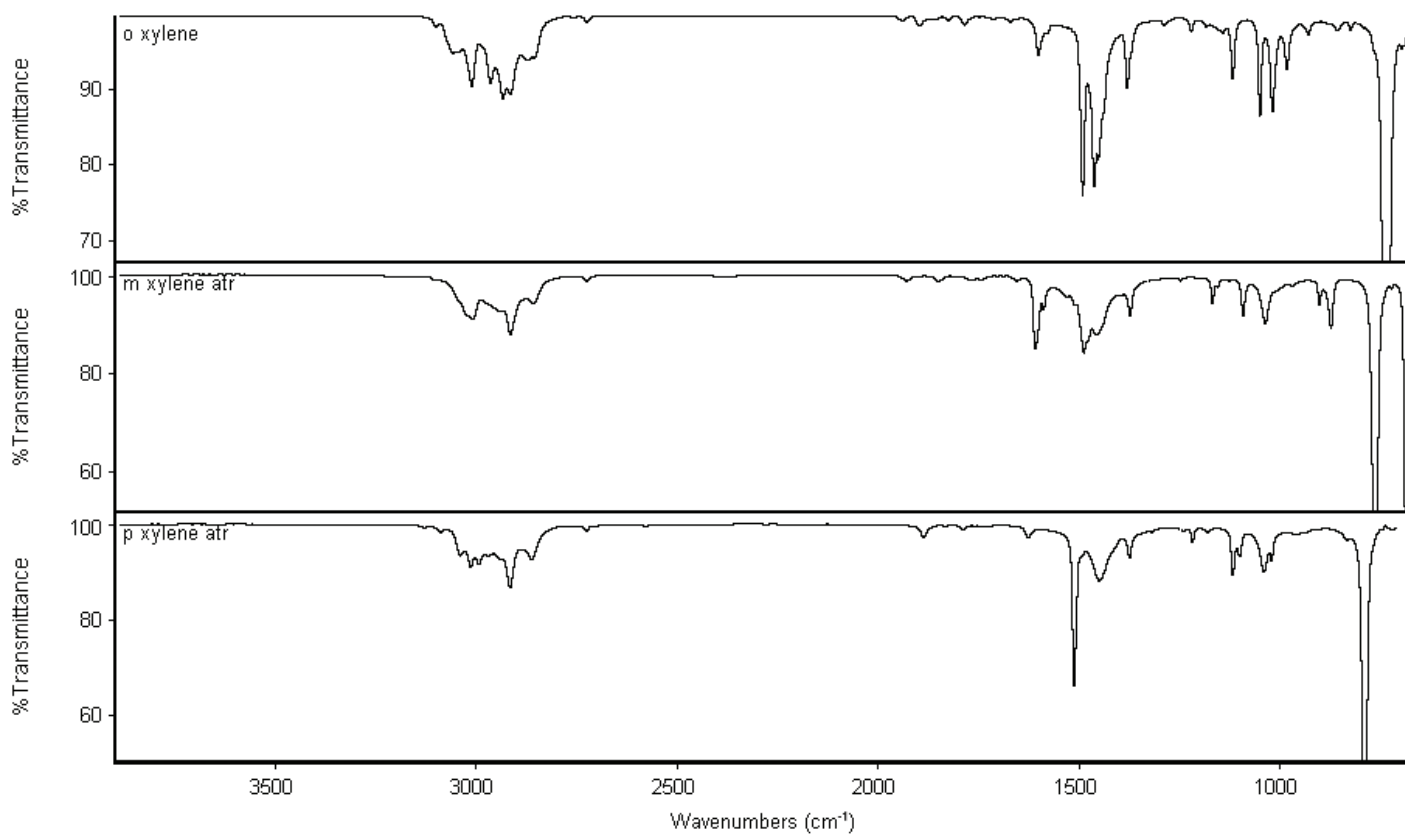
Measure or look up in a reference table the information below for each xylene isomer. Note that most of the measurements are very similar, making it difficult to differentiate the isomers on the basis of these tests.

Common name	o-Xylene
Chemical Name	
Formula Weight	
Refractive index (n_D^{20})	
Density	
UV-Vis λ_{max} , nm	

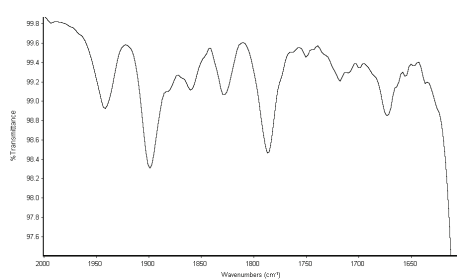
Common name	m-Xylene
Chemical Name	
Formula Weight	
Refractive index (n_D^{20})	
Density	
UV-Vis λ_{max} , nm	

Common name	p-Xylene
Chemical Name	
Formula Weight	
Refractive index (n_D^{20})	
Density	
UV-Vis λ_{max} , nm	

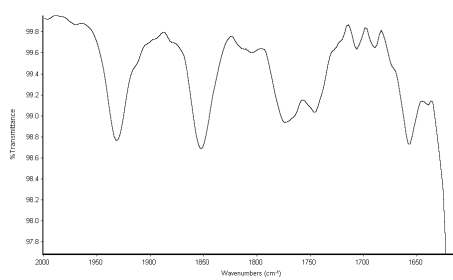
Use the following reference infrared spectra, or spectra from digital libraries, to determine the identity of the three isomer unknown samples. Make particular note of the regions between 1900 and 1700 cm^{-1} as well as 800 to 700 cm^{-1} .



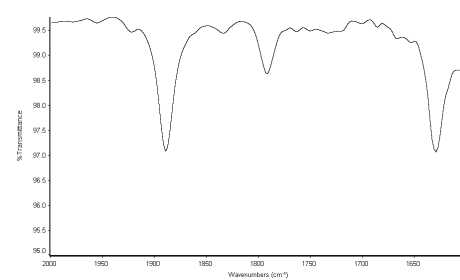
Xylene Isomer Infrared Spectra



o-Xylene, 2000-1600 cm^{-1}



m-Xylene, 2000-1600 cm^{-1}



p-Xylene, 2000-1600 cm^{-1}

Unknown sample #	Xylene isomer name
1	
2	
3	

Experiment 2

Isolation and identification of essential oils from citrus peels*

Objective

To isolate and identify the terpene oil from citrus fruit peels using FTIR spectroscopy.

Materials Required

- FTIR spectrometer (Thermo Scientific™ Nicolet™ iS20 FTIR Spectrometer is recommended)
- Sampling Accessory
 - Transmission cell OR
 - ATR Accessory OR
 - IR transmission card
- Two oranges or other citrus fruit
- Solvent
 - Ethyl acetate OR
 - Dry Ice

Introduction

Terpenes are compounds frequently found in nature. They account for many aromas, such as the “citrus” scent found in oranges and lemons, and other plants and trees. The terpenes can be extracted from fruit peels and its structure elucidated from its infrared spectrum. Terpinolene, one of the basic building blocks for terpenes, is shown in figure 1.

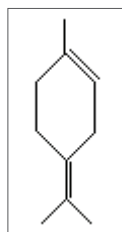
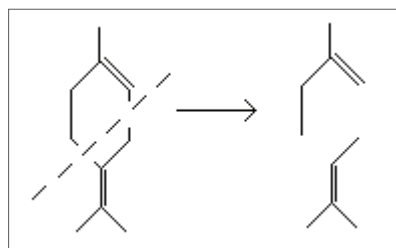


Figure 1. Terpinolene.

Discussion

Terpinolene can be broken down into two, five carbon sub-chains (Equation 1). These fragments are known as isoprene units (Figure 2), named after the similar compound 2-methyl-1,3-butadiene (Figure 3)



Equation 1. Isoprene units from Terpinolene.

more commonly known as isoprene. The isoprene unit is one of nature's most widely used building blocks. Combinations of isoprene units (usually 2, 3 or 4 units) yields a class of compounds known as terpenes.

These isoprene units can arrange into a straight chain (e.g. farnesol, from lily of the valley) or rings (e.g. α -phellandrene, from eucalyptus). Terpenes can also include other functional groups, like alcohols (menthol) or carbonyls (carvone, from spearmint). Isoprene units are usually connected head to

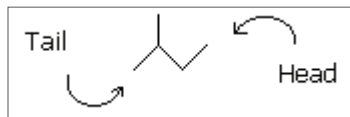


Figure 2. Isoprene unit.

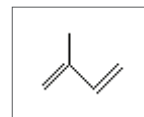


Figure 3. Isoprene (2-methyl-1,3-butadiene).

tail, but also can connect head to head or tail to tail. In some instances isoprene units can be cross-linked as well.

Experimental

Using a scraper, remove just the colored portion of the peel from two oranges, limes, or grapefruits (“zest”). The zest can be rather coarse – do not grind or powder the material.

To perform the ethyl acetate extraction, place the zest into a large (15 mL) centrifuge tube and cover with 10-15 mL of ethyl acetate overnight. The solution should turn from colorless to a golden yellow color. Close examination should reveal the presence of the oils at the bottom of the tube. Remove the ethyl acetate by evaporation, which can be accelerated using heated water. This should leave a yellowish-brown layer or the essential oils.

To perform the CO₂ extraction, place the zest into a 15 mL centrifuge tube. Move to a hood. Fill the tube about 2/3 full with dry ice (using gloves, do not touch the dry ice). Quickly and tightly seal the tube. Place the tube into warm water (still in the hood). This should result in about 3 mL of liquid CO₂ covering the zest, which should last for 2-3 minutes if the tube is sealed. Repeat the procedure three times to ensure good extraction.

Collect the background spectrum of the spectrometer and sampling accessory. Place a drop of the extracted oil on the ATR or transmission accessory, and acquire the infrared spectrum. Your instructor may also give you other essential oils (natural food stores are great sources for these) or other samples to extract. Save or print out the spectra you collect for your analysis and to turn in to your instructor.

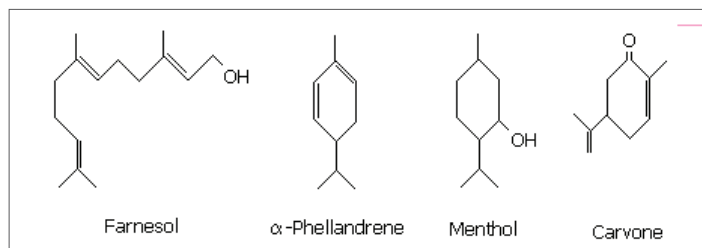


Figure 4. Common Terpenes.

*Contributed by Dr. Kevin Glaeske, Wisconsin Lutheran College, 8800 W. Bluemound Rd., Milwaukee, WI 53226

Questions

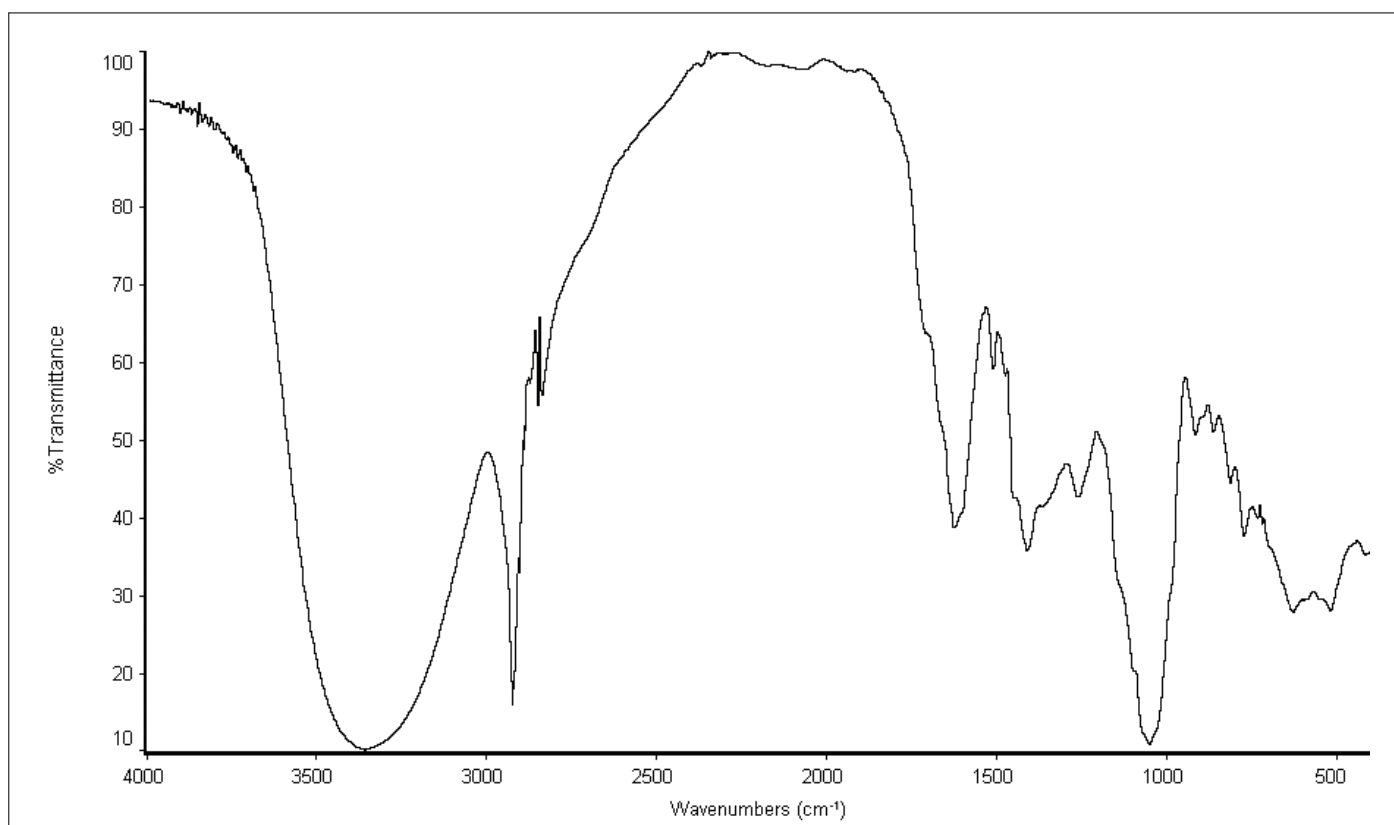
1. When doing the extraction, you saw two layers. What causes these two layers?

2. Why does the terpene move from the citrus peel to the solvent?

3. Compare a commercial sample of the essential oil to your sample. How are they similar or different in appearance? How are they similar or different in smell? What might account for this?

4. Compare your spectrum with a digital library or reference spectrum for limonene and terpinolene. Assign the major peak(s) in this spectrum to the appropriate functional groups. Draw the structures for any terpenes you found, and identify the isoprene substructures.

5. (Optional) The natural terpene carvone comes in two stereoisomeric forms, one found in caraway and one in spearmint. Some people lack an enzyme allowing them to smell the difference. If you have access to these materials, collect their IR spectrum and see if the differences are significant in the IR. Pass the materials around to see if anyone in your class cannot tell the difference (about 1 in 10 cannot). Look up the structures, and add these to your report.



Typical Citrus Peel Extract Spectrum.

Experiment 3

Recycling plastics

Objective

To identify different plastic recyclable classes using infrared spectra.

Materials Required

- FTIR spectrometer (Thermo Scientific™ Nicolet™ iS20 FTIR Spectrometer is recommended)
- ATR accessory
- Various plastic samples, with recyclable category identified
- Acetone (HPLC grade, Aldrich) as a cleaning agent

Introduction

Plastics are an enormous class of materials used in virtually every aspect of our lives. Plastics are polymers, large molecules consisting of chains of smaller molecules. These chains of molecules typically are identifiable by characteristic vibrational peaks in an FTIR spectrum. Identification and classification of polymers is a leading use of FTIR spectroscopy in industry.

Discussion

Many plastic parts and containers are stamped or embossed with a code indicating the type of plastic present in the piece. Table 1 shows the numbers and scientific names of these plastics. Each of these are homopolymers, made from one monomer linked together in long chains. Co-polymer materials, like acrylonitrile butadiene styrene (ABS), are not readily recyclable because of the different chemistry of each monomer.

Polymers absorb energy in the infrared range of the spectrum at one or more characteristic frequencies, representing a vibration of a group of similar bonds. This allows analysts to identify the type of plastic present in a sample. This is the basis of this experiment. The spectra of different plastics will be acquired, and then the identity of the plastic determined. This will then be compared to the expected identity of the plastics (from the recycling code).

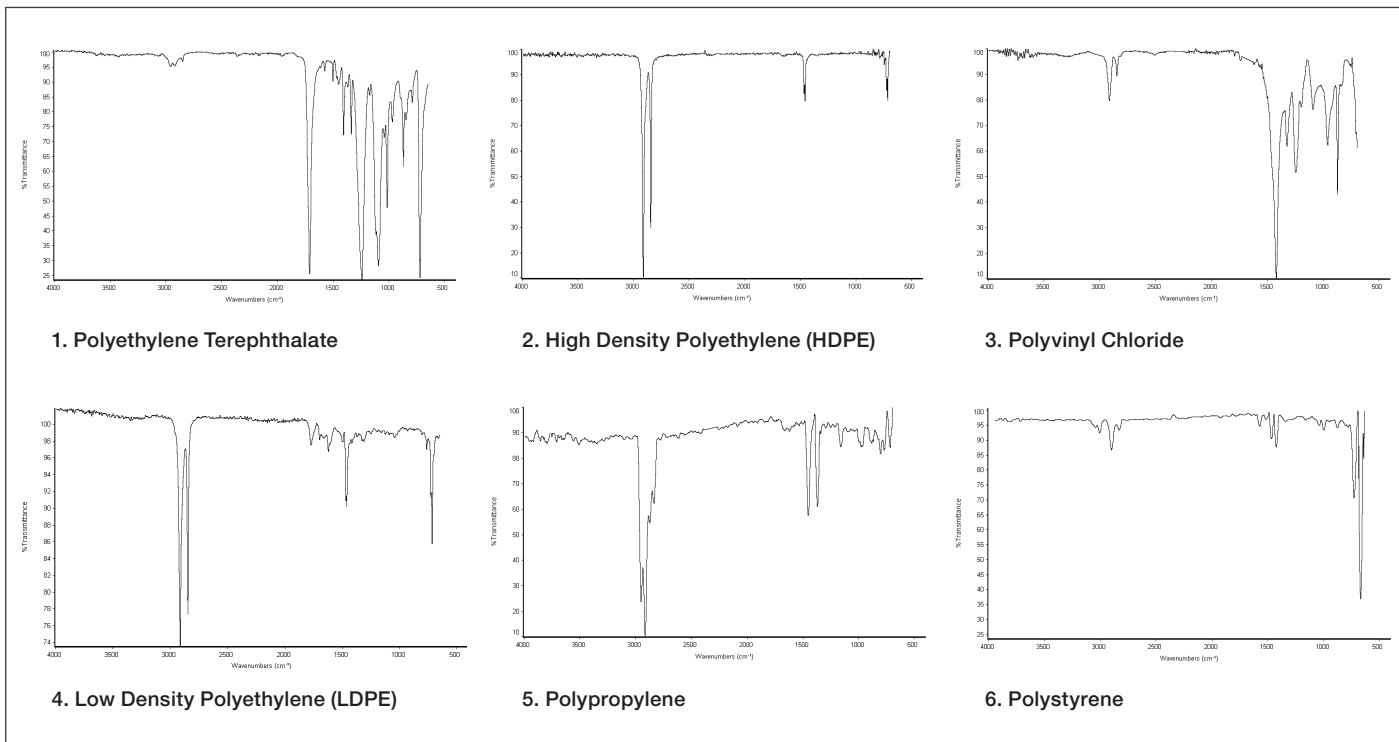
Codes for plastic recycling

1	Polyethylene Terephthalate (PET)
2	High Density Polyethylene
3	Polyvinyl Chloride (PVC)
4	Low Density Polyethylene
5	Polypropylene
6	Polystyrene
7	Other

Table 1.

Experimental

Gather several plastic samples from the instructor. Clean the ATR crystal with acetone and allow it to dry between samples (some plastics have residues from their production or from their use). Collect background spectra between each sample (with no sample on the crystal) for highest spectral quality. If no ATR is available, collect the spectra by slicing very thin layers of the plastic and then mounting them on an infrared sampling card or NaCl window for transmission sampling. This is difficult, because the absorptions are quite strong. Collect the background and sample spectrum of each material using the following experimental parameters: resolution of 4 cm^{-1} , 32 scans, $4000\text{ to }650\text{ cm}^{-1}$ spectral range. Save or print out your spectra for use in the interpretation and to turn in to your instructor. Identify the plastic type of each sample by using the reference spectra for each plastic type provided. Category 7, "Other", can be variable, and are not recyclable. Identification of a class 7 plastic would be indicated if none of the other class spectra match your sample.



Questions

1. Identify the unknown samples you received.

Unknown sample #	Plastic code #
1	
2	
3	
4	
5	
6	

2. Notice that the spectra from #2 and #4, both polyethylene plastics, are similar. Do you think the IR spectrum is sufficiently diagnostic to separate them? Research what the differences are between these two plastic types and suggest another way that a chemist could tell which plastic type an unknown sample would be:

3. Other than the plastics categories that are commonly recycled, plastics are known by many trademarked names that we use in everyday life. Identify at least two other common polymers that are not considered in this experiment.

4. Collect two physically different plastic samples with the same recycle code number. Run both samples and compare the spectra. Explain your findings.

Experiment 4

Rotational-vibrational spectrum of HCl gas*

Objective

To illustrate how experimental evidence obtained from the infrared spectrum of HCl gas can be shown to support a theoretical model developed from basic assumptions; and, secondarily, to obtain physical parameters of the HCl molecule including: rotational constant B_e , coupling constant α_e , forbidden transition frequency ν_o , moment of inertia I_e , and interatomic distance r_e .

Materials Required

- FTIR spectrometer with 1.0 cm^{-1} or better resolution (Thermo Scientific™ Nicolet™ iS20 FTIR Spectrometer is recommended)
- Gas sample cell with KBr windows, 50 mm minimum pathlength
- HCl gas source

Introduction

Infrared spectroscopy is a powerful tool for gaining information about the physical properties of many molecules. The heteronuclear diatomic molecule HCl serves as an excellent molecule for illustrating this capability.

Discussion

A valid theoretical model for the physical behavior of any system must account for what is observed. Rotational and vibrational motions of diatomic molecules have energies falling in the infrared region of the electromagnetic spectrum. Only molecules having a permanent dipole such as HCl are capable of generating infrared spectra. A valid theory for the physical behavior of HCl must, therefore, predict the various features of its infrared spectrum.

Development of a theory for the physical behavior of HCl can only begin once the important characteristics of the HCl infrared spectrum have been identified. Before continuing, it is, therefore, recommended that the infrared spectrum of HCl gas be obtained (see Experimental), and that time be given to study the spectrum and identify its key characteristics (see Question 1). These observations will guide in understanding the development of the theory.

The simplest theoretical model assumes that the vibrational motion of the HCl molecule can be approximated by a quantum-mechanical harmonic oscillator. The quantized

energy levels of a harmonic oscillator are given by $T_{\text{vib}}(v) = h\nu(v + \frac{1}{2})$, where v is the vibrational quantum number ($v = 0, 1, 2, \dots$), ν is the vibrational frequency in Hz (s^{-1}), and h is Planck's constant, $6.62608 \times 10^{-34}\text{ J s}$. Probability of energy transitions involving states other than the ground ($v = 0$) and first excited states ($v = 1$) is low for HCl under normal conditions. This model thus predicts essentially a single infrared spectral band for HCl. However, several closely spaced bands are observed in the actual spectrum, suggesting that a more complex model is needed.

A more sophisticated theory assumes, in addition to regarding HCl as a harmonic oscillator, that the HCl molecule has a rotational mode of motion that can be modeled by a quantum-mechanical rigid rotor. It is also assumed that change in the rotational energy changes the total energy, but has no effect on the vibrational energy, and vice versa. The quantized energy levels of a rigid rotor are given by $T_{\text{rot}}(J) = J(J + 1)Be$ where J is the rotational quantum number ($J = 0, 1, 2, \dots$) and Be , called the rotational constant, is given by $Be = \frac{h^2}{2I_e}$. The constant h is equal to $h/2\pi$ where h is Planck's constant. I_e is the equilibrium moment of inertia for the molecule, given by $I_e = \mu r_e^2$, where μ is the reduced mass ($\mu = \frac{m_A m_B}{m_A + m_B}$), m_A and m_B are masses of the atoms in the rotor and r_e is the equilibrium interatomic distance. The total energy in this model is, therefore, given by

$$T_{\text{tot}} = T_{\text{rot}}(J) + T_{\text{vib}}(v), \text{ or, } T_{\text{tot}} = J(J + 1)Be + h\nu(v + \frac{1}{2})$$

Figure 1 illustrates energy levels for the ground and first excited vibrational states ($v = 0, 1$) for this model. Note that several rotational states accompany each vibrational state, and that the energy difference between vibrational states is much greater than that of the rotational states within a given vibrational state. For HCl, quantum mechanical selection rules allow only those energy transitions which give $\Delta J = \pm 1$. Thus, a vibrational energy transition from ground state ($v = 0$) to first excited state ($v = 1$) must be accompanied by a transition from J in the ground state to $J \pm 1$ in the excited state. Those transitions which result in J to $J + 1$ are termed "R-branch", and those which result in J to $J - 1$ are termed "P-branch." Thus, a vibrational state transition from $v = 0$ to $v = 1$ is predicted to give rise to a spectrum consisting of several closely spaced bands, each band corresponding to a different J to $J \pm 1$ rotational transition. In harmony with this prediction, a spectrum of several closely spaced bands is observed.

*Contributed by Dr. Mitch Menzmer, Southwestern Adventist University

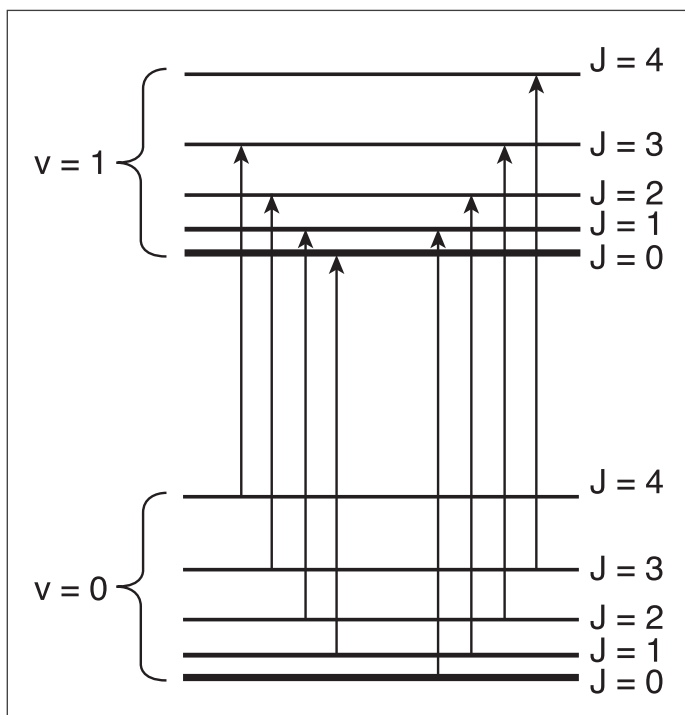


Figure 1. Energy levels for the rigid-rotor harmonic oscillator.

Using the rigid-rotor-harmonic-oscillator model, the energy transitions accompanying each spectral band can be predicted based on

$$\Delta T = T_{\text{tot}}(v = 1, J') - T_{\text{tot}}(v = 0, J)$$

or

$$\Delta T = J'(J' + 1)B_e + 3/2 hv - [J(J + 1)B_e + 1/2 hv] \quad (1)$$

where the primed variable is the rotational state in the $v = 1$ vibrational level, and the unprimed variable the rotational state in the $v = 0$ vibrational state. For the R-branch ($\Delta J = +1$), $J' = J + 1$ and equation (1) simplifies to

$$\Delta T_R = hv + 2(J + 1)B_e \quad (2.1)$$

For the P-branch ($\Delta J = -1$), $J' = J - 1$ and equation (1) simplifies to

$$\Delta T_P = hv - 2JB_e \quad (2.2)$$

Energy spacing between the bands can be calculated by substituting either equation (2.1) or (2.2) into $T_{\text{spacing}} = \Delta T_{\text{high}}(J) - \Delta T_{\text{low}}(J)$, where “high” and “low” refer to the relative energies of adjacent spectral bands, and J is the lower energy-state value for the transition associated with a given band. For the R-branch, J values increase with increasing energy and thus $J_{\Delta T\text{-high}} = J_{\Delta T\text{-low}} + 1$. For the P-branch, J values increase with decreasing energy and thus $J_{\Delta T\text{-high}} = J_{\Delta T\text{-low}} - 1$. Using either equation (2.1) or (2.2) for calculating T_{spacing} , it can be shown that $T_{\text{spacing}} = 2B_e$. That is, spacing between all adjacent bands is predicted by the harmonic-oscillator-rigid-rotor model to be constant. Careful observation of the actual spectrum, however,

will show that the spacing varies, becoming smaller with increasing energy (wavenumber, cm^{-1}). This departure from prediction requires a change in the model.

Another theoretical treatment assumes the rotational motion of HCl is non-rigid rather than rigid, and that the vibrational motion is anharmonic rather than harmonic. In a non-rigid rotor, the bond length is expected to stretch as it rotates due to centrifugal force. This effect, in turn, impacts the vibrational motion. However, the centrifugal effect is important only for high J values and the effect can be ignored.

An effect similar to the centrifugal effect, and which will be considered, occurs due to the change in interatomic distance during vibration. In the harmonic-oscillator-rigid-rotor model, it was assumed that rotational and vibrational energies were strictly partitioned; that is, changing the energy of one form of motion changed only the total energy, but had no effect on the energy of the other form of motion. However, as the length of the HCl bond oscillates during vibration, the moment of inertia also oscillates (recall: $I_e = \mu r_e^2$), which in turn affects the rotational energy through the rotational constant B_e (recall: $B_e = h^2/2I_e$). In other words, molecular rotation and vibration are inter-related and the rotational constant is actually a variable dependent upon the vibrational state of the molecule. This phenomenon is called vibrational-rotational coupling and can be accounted for by using $B_v = B_e - \alpha_e(v + 1/2)$ in place of B_e to give $T_{\text{rot}} = J(J + 1)[B_e - \alpha_e(v + 1/2)]$, which can be rearranged to give $T_{\text{rot}} = J(J + 1)B_e - \alpha_e(v + 1/2)J(J + 1)$. where α_e is termed the coupling constant.

In the anharmonic model, the vibrational states for a diatomic molecule are represented by a Morse potential (Figure 2), for which vibrational energy levels become more closely spaced at higher levels. Added to the vibrational energy term is a correctional term taking into account the affect of anharmonicity: $T_{\text{vib}} = hv(v + 1/2) - hv\chi_e(v + 1/2)^2$, where χ_e is termed the anharmonicity constant.

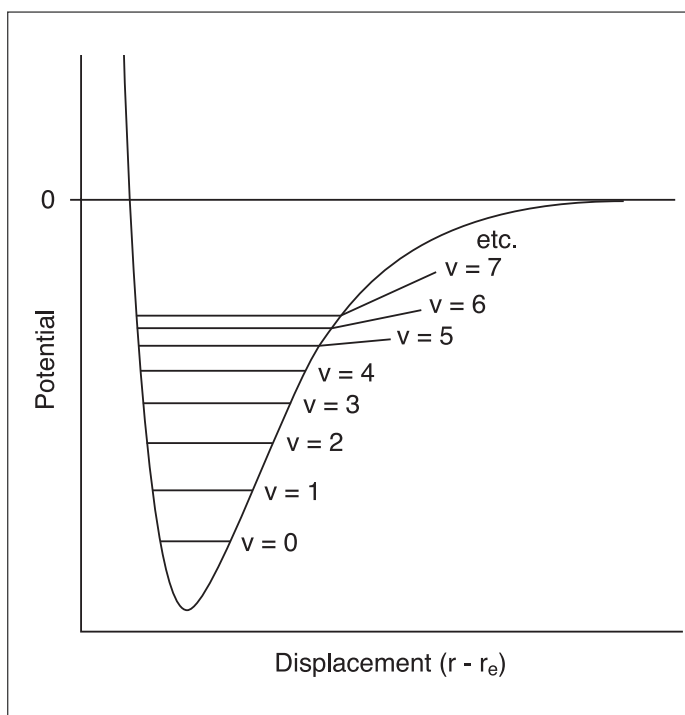


Figure 2. Morse-potential anharmonic oscillator.

Finally, the total vibrational and rotational energy of the HCl molecule can thus be calculated as $T_{\text{tot}} = J(J + 1)B_e + hv(v + \frac{1}{2}) - hv\chi_e(v + \frac{1}{2})^2 - \alpha_e(v + \frac{1}{2})J(J + 1)$.

Energy transitions accompanying each spectral band can be predicted based on

$$\Delta T = T_{\text{tot}}(v = 1, J') - T_{\text{tot}}(v = 0, J) \quad (3)$$

The resulting R- and P-branch formulas for the energies of each spectral band are:

$$\Delta T_R = hv_0 + 2B_e - 3\alpha_e + 2(B_e - 2\alpha_e)J - \alpha_e J^2 \quad (4.1)$$

$$\Delta T_P = hv_0 - 2(B_e - \alpha_e)J - \alpha_e J^2 \quad (4.2)$$

where $hv_0 = hv(1 - 2\chi_e)$. Based on selection rules, the transition $\Delta J = 0$ for $v = 0$ to $v = 1$ is forbidden. Spectral position for the forbidden transition (denoted $h\nu_0$) can also be predicted from the T_{tot} equation by substituting $J' = J$ in equation (3). There should be no spectral band corresponding to this energy.

Energy spacing between the bands can now be calculated by substituting either equation (4.1) or (4.2) into $T_{\text{spacing}} = \Delta T_{\text{high}}(J) - \Delta T_{\text{low}}(J)$. As before, "high" and "low" refer to the relative energies of adjacent spectral bands, and J is the lower energy-state value for the transition associated with a given band. Recall: for the R-branch, $J_{\Delta T\text{-high}} = J_{\Delta T\text{-low}} + 1$ and for the P-branch, $J_{\Delta T\text{-high}} = J_{\Delta T\text{-low}} - 1$.

For the R-branch it can be shown that

$$T_{\text{spacing}} = -ae(2J_{\Delta T\text{-low}} + 5) + 2B_e \quad (5.1)$$

For the P-branch it can be shown that

$$T_{\text{spacing}} = ae(2J_{\Delta T\text{-low}} - 3) + 2B_e \quad (5.2)$$

From the first term on the right side in both equation (5.1) and (5.2), it can be seen that the spacing between spectral bands is predicted to vary with changing rotational energy (through change in J) – in agreement with what is observed. Satisfied at this point that the current model is qualitatively accurate in many important respects, information from the spectrum can thus be used together with the theoretically derived equations to calculate for the HCl molecule, values of the constants B_e , α_e , and ν_0 as well as moment of inertia I_e , and interatomic distance, r_e .

Experimental

Preparation of the sample should be carried out in an exhaust hood. Gloves and safety glasses should be worn.

An HCl gas sample can be prepared either from a compressed gas cylinder of HCl, or generated by reaction between slightly moistened NaCl(s) and concentrated sulfuric acid.

If the sample is being prepared using compressed HCl gas, seek technical assistance in becoming completely familiar with the operation of the regulator before attempting to prepare a sample. A piece of flexible tubing is attached to the output of the regulator, and a Pasteur pipet inserted in the open end of the tubing. The regulator will be used to control the release of HCl gas through the pipet and into the sample chamber.

If the HCl is prepared from NaCl and sulfuric acid, a separatory funnel (125 mL) is mounted to a 500 mL suction flask with an airtight seal. The flask/funnel apparatus should be securely mounted to a ring-stand. Attach 3' section of flexible tubing to the sidearm of the suction flask, with a Pasteur pipet secured in the open end. A screw clamp can be used to pinch off the tubing, or it may be pinched closed by hand by simply doubling over a section of the tubing. If the sample is prepared from a gas cylinder, the regulator will be used to control the flow of the gas and pinching off the hose will not be necessary.

The gas sample holder should have KBr windows mounted in it and should be flushed with dry inert gas before using. It is important to prevent any moisture from contacting the KBr windows, as this will readily dissolve them.

For this reason, do not allow bare fingers or hands to come in contact with the KBr windows. Be familiar with the placement of the sample container in the sample compartment of the instrument. Exhaust hood should be on. If HCl is generated by reaction, place an even layer of approximately 2 mm of NaCl(s) on the bottom of the suction flask. Lightly moisten the NaCl(s) by sprinkling with 2-3 mL of water. Put the separatory funnel in place, making sure it forms a tight seal with the flask. Make sure the separatory funnel stopcock is snug, but will still move readily. With the separatory funnel stopcock closed, add about 15 mL of concentrated sulfuric acid to the funnel. With the top off of the separatory funnel, allow a few milliliters of the sulfuric acid to pour into the suction flask, and close the stopcock. Vapor should fill the flask within a few seconds. Moist litmus can be used to indicate when HCl is exiting the tip of the Pasteur pipet. If the reaction is not sufficiently vigorous to supply a continuous stream of HCl gas, pinch off the flexible tubing to allow a small amount of pressure to build (separatory funnel stopcock must be closed), or allow more sulfuric acid into the flask. Use caution when forcing a buildup of pressure. When there is a good flow of HCl gas out the end of the Pasteur pipet tip, carefully insert the tip of the Pasteur pipet into the side-arm of the sample container and open the flexible tubing, allowing HCl gas to fill the chamber. In the case of the gas cylinder, insert the tip of the Pasteur pipet into the sidearm and slowly open the regulator to allow gas to fill the sample container. Stopper the side-arm of the sample container and quench the NaCl-sulfuric acid reaction by carefully removing the separatory funnel and slowly adding water; or, if compressed gas was used, close the regulator on the gas cylinder.

Place the sample container in the sample compartment in the instrument, and obtain the spectrum in the region between about 2500 and 3000 cm^{-1} . The spectrum should be Transmission vs. wavenumber (ν), which correlates linearly with energy according to: $\nu (\text{cm}^{-1}) = E/hc$, where energy is in joules, h is Planck's constant and c is the speed of light ($2.9979 \times 10^{10} \text{ cm s}^{-1}$).

Calculations

1. Identify the transitions in Figure 1 as belonging to either R or P band, subscripted with the initial J state (e.g., R(0), R(1), etc.). Correlate the transitions in the figure with the bands in the R- and P-branches on the spectrum. Sketch an arrow on Figure 1 corresponding to the ground state forbidden transition.
2. Equation (5.1) and (5.2) are linear in form. Thus, a plot of T_{spacing} vs. $2J_{\Delta T\text{-low}} + 5$ for the R-branch, or of T_{spacing} vs. $2J_{\Delta T\text{-low}} - 3$ for the P-branch, will result in slope equal in magnitude to α_e and intercept equal to $2B_e$. In order to obtain α_e and $2B_e$ from slope and intercept of a single line across both the R- and P-branches, the independent variable must be converted to a single form. This can be accomplished by substitution using the variable k , where $k = -J_{\Delta T\text{-low}}$ for the P-branch and $k = J_{\Delta T\text{-low}} + 1$ for the R-branch. In effect, this substitution increases by one all of the J-value labels of the bands in the R-branch, and converts all the J-value labels to negative values in the P-branch. The resulting values of k form a continuous number-line, with the exception of a zero value. Graphically,

J:	...	3	2	1	(ν_0)	0	1	2	3	...
k:	...	-3	-2	-1	(ν_0)	1	2	3	4	...

Making the appropriate substitution into equations (5.1) and (5.2) will give in either case: $T_{\text{spacing}} = -\alpha_e(2k + 3) + 2B_e$. Plot of T_{spacing} vs. $2k + 3$ will thus give slope = $-\alpha_e$ and intercept = $2B_e$.

Make a table of ν vs. R(J) and P(J), where J is the lower state for the transition. In an adjacent column, convert J values to k . Calculate T_{spacing} in wavenumbers using $T_{\text{spacing}} = \Delta T_{\text{high}}(k + 1) - \Delta T_{\text{low}}(k)$ where "high" and "low" refer to the relative energies of adjacent spectral bands. Enter these values in a column adjacent to the values of k , where k is for the lower-wavenumber band in the adjacent pair. Make a plot of $T_{\text{spacing}} (\text{cm}^{-1})$ vs. $2k + 3$. After discarding outliers, obtain the slope and intercept from a best-fit line through the points of the plot. From the slope and intercept, obtain α_e and B_e in wavenumbers. Calculate the values of α_e and B_e in joules.

3. Using values of J near or equal to zero, obtain $\tilde{\nu}_0$ as the average of three values of ν_0 calculated from either equation (4.1) or (4.2). This frequency corresponds to the forbidden transition. Also calculate $\tilde{\nu}_0$ in joules.
4. Beginning with α_e and B_e in joules, calculate the equilibrium moment of inertia (I_e) and interatomic distance (r_e) for HCl.
5. Compare the physical constants and values obtained with those reported in the literature.

Questions

1. Make a list of characteristics describing the infrared spectrum of HCl. Formulate these as a series of questions.

2. Beginning with $T_{\text{tot}} = J(J + 1)B_e + hv(v + \frac{1}{2})$, show how $T_{\text{spacing}} = 2B_e$ is derived for both R- and P-branches of the rigid-rotor harmonic oscillator.

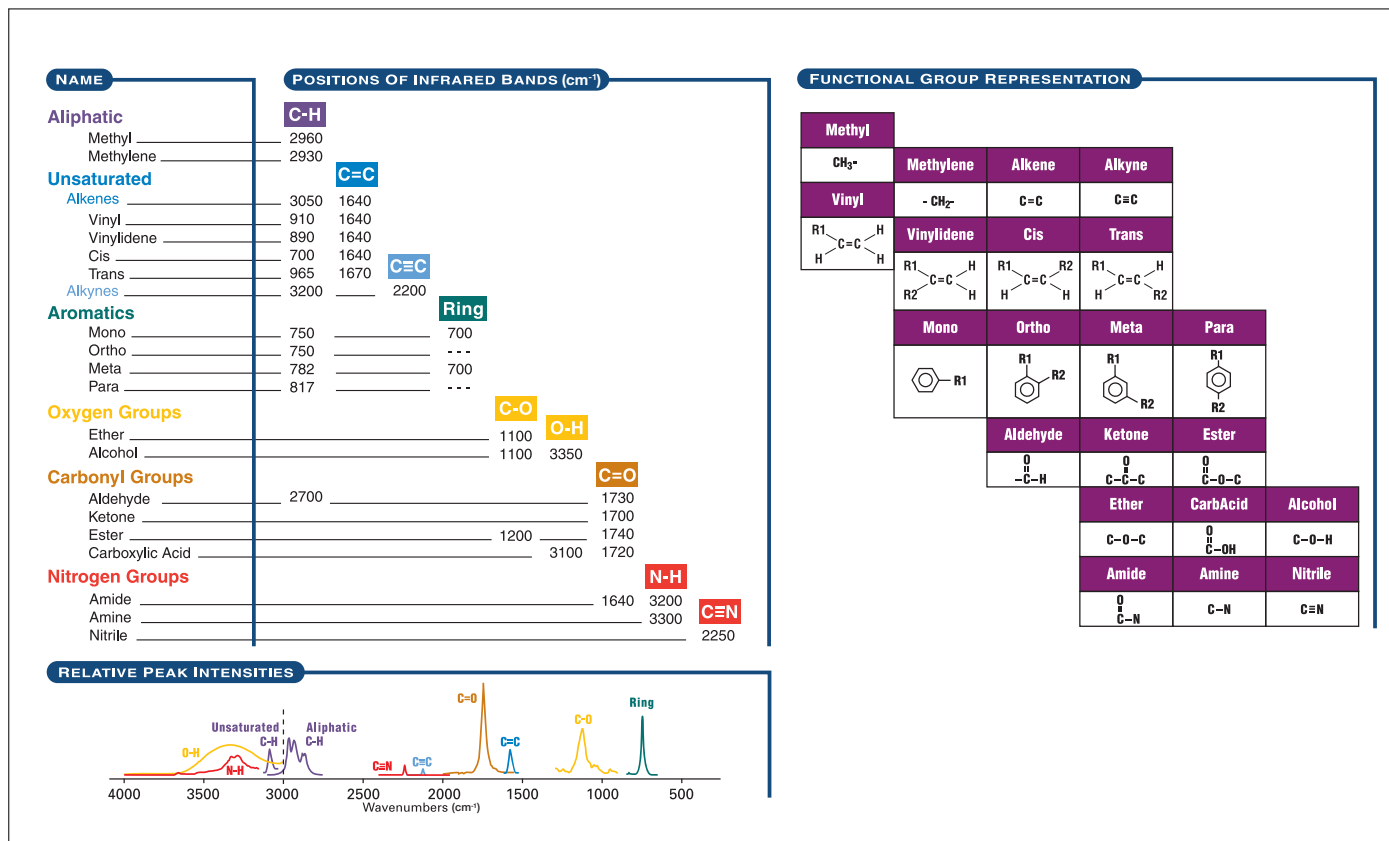
3. Beginning with $T_{\text{tot}} = J(J + 1)B_e + hv(v + \frac{1}{2} - hvx_e(v + \frac{1}{2} - a_e(v + \frac{1}{2})J(J + 1)))$, show how T_{spacing} is derived for both R- and P-branches for a non-rigid rotor anharmonic oscillator. The magnitude of the coupling constant reflects the degree of coupling. For both R- and P-branches, what value of T_{spacing} is approached as a_e approaches zero?

4. What is the energy difference between the ground and first excited vibrational states ($J = 0$ for both states), for HCl?

5. As a result of having read the discussion and completed the calculations, describe how the theoretical model at each stage of development accounts and/or fails to account for what is observed. Which of the observations from Question 1 can be accounted for by the final version of the theoretical model?

6. Optional: The fine structure splitting observed in the HCl spectrum is due to isotope effects from the natural abundances of Cl35 and Cl37. Relative peak areas for each isotope will approximate the relative natural abundance of each form. Calculate the relative peak areas for each isotope and compare to the theoretical value.

Basic organic functional group reference chart



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