UNIT-1 <u>MPHYCC-10</u>

Selection Rules of IR

In order for vibrational transitions to occur, they are normally governed by some rules referred to as selection rules.

An interaction must occur between the oscillating field of the electromagnetic radiation and the vibrational molecule for a transition to occur. This can be expressed mathematically as

$$(\frac{d\mu}{dr})_{req} \neq 0$$

$$\triangle v=+1 \text{ and } \triangle J=+1$$

This holds for a harmonic oscillator because the vibrational levels are equally spaced and that accounts for the single peak observed in any given molecular vibration. For gases J changes +1 for the R branch and -1 for the P branch. $\triangle$J=0 is a forbidden transition and hence a q branch for a diatomic will not be present. For any anharmonic oscillator, the selection rule is not followed and it follows that the change in energy becomes smaller. This results in weaker transitions called overtones, then $\triangle$v=+2$\triangle$ (first overtone) can occur, as well as the 2nd overtone $\triangle$v=+3. The frequencies of the 1st and 2nd overtones provides information about the potential surface and about two to three times that of the fundamental frequency.

For a diatomic, since μ is known, measurement of u_e provides a value for k, the force constant.

$$k=(\frac{d^2V(r)}{dr^2})_{req}$$

where k is the force constant and indicates the strength of a bond.

Influence Factors of IR

Isotope Effects: It's been observed that the effect on k when an atom is replaced by an isotope is negligible but it does have an effect on v due to changes in the new

mass. This is because the reduced mass has an effect on the rotational and vibrational behavior.

Solvent Effects: The polarity of solvent will have an influence on the IR spectra of organic compounds due to the interactions between solvent and compounds, which is called solvent effects. If we place a compound, which contains n, pi and pi* orbitals, into a polar solvent, the solvent will stabilizes these three orbitals in different extent. The stabilization effects of polar solvent on n orbital is the largest one, the next larger one is pi* orbital, and the effects on pi orbital is the smallest one. The spectra of n→pi* transition will shift to blue side, which means it will move to shorter wavelengths and higher energies since the polar solvent causes the energy difference between n orbital and pi* orbital to become bigger. The spectra of pi→pi* transition will shift to red side, which means it will move to longer wavelengths and lower energies since the polar solvent causes the energy difference between n orbital and pi* orbital to become smaller.

Advantages of IR

High Scan Speed: Infrared spectroscopy can get information for the whole range of frequency simultaneously, within one second. Therefore, IR can be used to analyze a substance that is not very stable and finish the scan before it start to decompose.

High Resolution: The resolution of general prism spectrometer is only about 3cm^{-1}, but the resolution of infrared spectrometer is much higher. For example, the resolution of Grating infrared spectrometer could be $0.2\ \text{cm}^{-1}$, the resolution of FT infrared spectrometer could be $0.1\text{-}0.005\ \text{cm}^{-1}$.

High Sensitivity: With Fourier Transform, the infrared spectrometer doesn't need to use the slit and monochromator. In this way, the reflection specularity will be increased and the loss of energy in the analysis process will be decreased. Therefore the energy that reaches the detector is large enough and even very small amount of analytes could be detected. Nowadays, the infrared spectroscopy could detect the sample as small as 1-10 grams.

Wide Range of Application: Infrared spectroscopy could be used to analyze almost all organic compounds and some inorganic compounds. It has a wide range of application in both qualitative analysis and quantitative analysis. Also, the

sample of Infrared spectroscopy doesn't have phase constraints. It could be gas, liquid or solid, which has enlarged the range of analytes a lot.

Large Amount of Information: Infrared Spectra could give us lots of structural information of the analytes, such as the type of compound, the functional group of compound, the stereoscopic structure of compound, the number and position of substituent group and so on. Depending on the available information form the functional part and the fingerprint part, infrared spectroscopy has become a great method to identify different kinds of compounds.

Non-Destructive: Infrared Spectroscopy is non-destructive to the sample.

Disadvantages of IR

Sample Constraint: Infrared spectroscopy is not applicable to the sample that contains water since this solvent strongly absorb IR light.

Spectrum Complication: The IR spectrum is very complicated and the interpretation depends on lots of experience. Sometimes, we cannot definitely clarify the structure of the compound just based on one single IR spectrum. Other spectroscopy methods, such as (Mass Spectrometry) MS and (Nuclear Magnetic Resonance) NMR, are still needed to further interpret the specific structure.

Quantification: Infrared spectroscopy works well for the qualitative analysis of a large variety of samples, but quantitative analysis may be limited under certain conditions such as very high and low concentrations.