Electronics And Instrumentation

8th Semester

Subject: Analytical Instrumentation
Subject code: BT 808

Unit-2

Computer-Aided Spectral Interpretation

An interpreting vibrational spectra the spectroscopist soon realizes the limited capacity of the human brain to store and selectively retrieve all required spectral data.Powerful micro- and personal computers are now available together with fast and efficient software systems to help the spectroscopist to identify unknown compounds. IR Mentor is a program that resembles an interactive book or chart of functional group frequencies. Although the final interpretation remains in human hands, this program saves the spectroscopist time by making tabular correlation information available in computer form, and, moreover, it is also an ideal teaching tool. To facilitate the automated identification of unknown compounds by spectral comparison numerous systems based on library search, e.g., SPECTACLE , GRAMS/32], or those offered by spectrometer manufacturers, are used. These systems employ various algorithms for spectral search j441, and the one that uses full spectra according to the criteria of LOWRY and HUPPLER is the most popular. The central hypothesis behind library search is that if spectra are similar then chemical structures are similar .

In principle, library search is separated into identity and similarity search systems. The identity search is expected to identify the sample with only one of the reference compounds in the library. If the sample is not identical to one of the reference compounds the similarity search presents a set of model compounds similar to the unknown one and an estimate of structural similarity. The size and contents of the library are crucial for a successful library search system, especially a similarity search system. A smaller library with carefully chosen spectra of high quality is more useful than a comprehensive library containing spectra of all known chemical compounds or as many as are available because, in similarity search, the retrieval of an excessive number of closely similar references for a articular sample only increases output volume without providing additional information . A critical discussion of the performance of library search systems is presented by CLERC. While library search systems are well-established, invaluable tools in daily analytical work, expert systems (i.e., computer programs that can interpret spectral data) based on artificial neural networks **(ANNs)** are more and more emerging.

Applications of Vibrational Spectroscopy

1.Infrared Spectroscopy

Transmission Spectroscopy

Transmission spectroscopy is the simplest sampling technique in infrared spectroscopy, and is generally used for routine spectral measure ments on **all** kinds of samples. It requires only simple accessories, such as infrared-transparent windows [e.g., potassium bromide, sodium chloride, or thallium

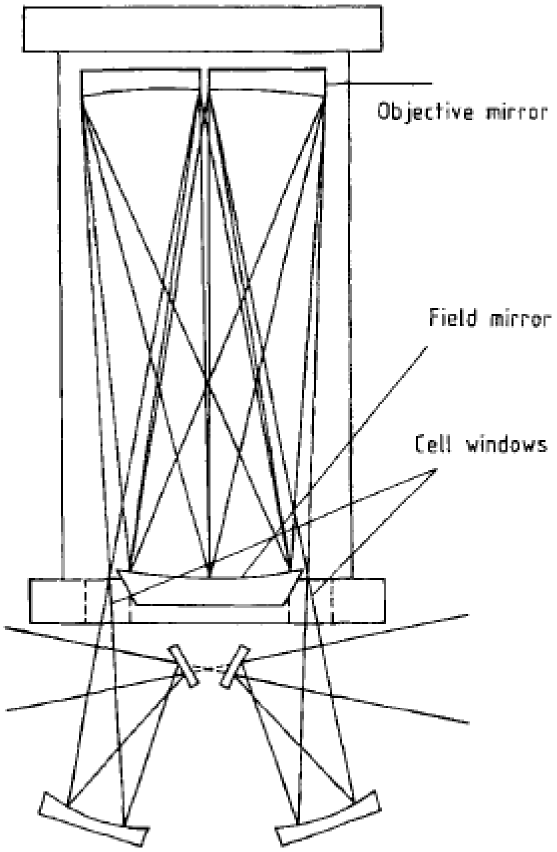

Figure . Optical diagram of a White gas cell **(A** mode) showing eight passes, to change the path length only one objective mirror is rotated, the rotation is nonlinear and is very small a1 long path lengths. For B mode operation, the light beam enters and exits on one and the same side of the field mirror, the objective mirrors are coupled and are rotated together linearly over the entire operational range (Reproduced by permission of Harrick Scientific Corporation, Ossining. NY 10562) bromoiodide (KRS-5)] for gases and liquids, or a sample holder for solids. The sample is placed in the light beam of an infrared spectrometer, and the intensity of the incident beam is compared with that transmitted by the sample. According to the fundamental relation governing the absorption of radiation as a function of transmittance (see Section 17.3.2), parameters that can be determined in transmission spectroscopy are the thickness or the concentration of the sample. The thickness can range from micrometers for solids and liquids to even kilometres for gas samples.

Apart from general laboratory gas analysis, gas-phase transmission pectroscopy is used for the characterization of air pollutants as well as the monitoring of stack gas and of air quality in work places. As air quality has become **a** major concern for environmentalists, industrial manufacturers and many others, spectroscopic measurement in the gas phase is receiving increasing attention. However, two major problems must be overcome: absorptions in the gas phase are many times weaker than those in the liquid or solid phase, and the species to be measured usually makes up only a small fraction of the total gas volume. The most popular way of surmounting these problems is to increase the path length by reflecting the beam several times from precisely controlled mirrors. Such multiple-pass gas cells are all based on the White design [49] or variations thereof. Figure 45 shows an optical diagram of a White cell aligned for eight passes. The length of the gas cell and the number of passes employed determines the optical path length, which may vary from centimeters to kilometers. The number of passes is adjusted in four pass increments by rotating one of the objective mirrors. In the A mode of operation, only one objective mirror is rotated, while in the B mode the objective mirrors are coupled and rotated together linearly over the entire operational range to change the path length. To prepare a sample, the gas cell is evacuated, the sample is bled into the cell, and the cell is sealed.

External Reflection Spectroscopy

In external reflection spectroscopy, electromagnetic radiation is reflected at the interface of two materials differing in refractive index or from a smooth surface, a conductor such as metal, a semiconductor, a dielectric, or a liquid. The intensity of light reflected is measured to obtain information about the surface chemistry and structure. The angle of collection is the same as the angle of incidence and is measured from the normal to the surface (Fig.). Small-angle incidence (0, ,usually 10') is called near-normal incidence while that at large angles (02, usually 80") is known as grazing angle incidence. A non destructive method requiring no sample preparation, external reflection spectroscopy comprises two different types of measurements, both being termed specular reflectance. In the first type, the reflection from a smooth mirror like surface, e.g., free-standing film, single crystal face, or surface of an organic material,

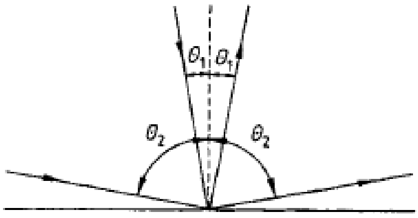

Fig. Near-normal and grazing angle incidence

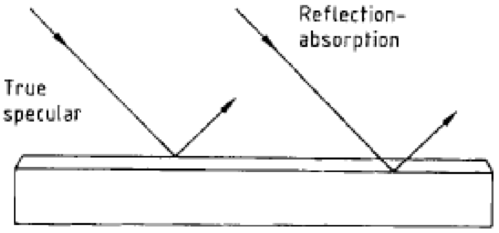

Fig. Types of specular reflection

is referred to as true specular reflection or simply specular reflection . In the second, a film of sample is deposited on a highly reflecting substrate, usually a metal, from which the infrared beam is reflected, the radiation is transmitted through the sample layer, reflected from the substrate surface, and finally transmitted back through the sample. This technique is called reflection - absorption (RA), infrared reflection-absorption spectroscopy (IRRAS), or transflectance.

Internal Reflection Spectroscopy

Internal reflection spectroscopy, also known as attenuated total reflectance (ATR) or multiple internal reflectance (MIR), is a versatile, non destructive technique for obtaining the infrared spectrum of the surface of a material or the spectrum of materials either too thick or too strongly absorbing to be analyzed by standard transmission spectroscopy. The technique goes back to newron who, in studies of the total reflection of light at the interface between two media of different refractive indices, discovered that an evanescent wave in the less dense medium extends beyond the reflecting interface. Internal reflection spectroscopy has been developed since 1959, when it was reported that optical absorption spectra could conveniently be obtained by measuring the interaction of the evanescent wave with the external less dense medium . In this technique, the sample is placed in contact with the internal reflection element (IRE), the light is totally reflected, generally several times, and the sample interacts with the evanescent wave resulting in the absorption of radiation by the sample at each point of reflection. The internal reflection element is made from a material with a high refractive index; zinc selenide (ZnSe), thallium iodide thallium bromide (KRS-S), and germanium (Ge) are the most commonly used. To obtain total internal reflection the angle of the incident radiation 0 must exceed the critical angle (Ic [%I. The critical angle is defined as:

$$\theta_c = \sin^{-1} \frac{n_2}{n_1}$$

where *n,* is the refractive index of the internal reflection element and *n2* is the refractive index of the sample. What makes ATR a powerful technique is the fact that the intensity of the evanescent wave decays exponentially with the distance from the surface of the internal reflection element. As the effective penetration depth is usually a fraction of a wavelength, total internal reflectance is generally insensitive to sample thickness and so permits thick or strongly absorbing samples to be analyzed. The depth of penetration dp, defined as the distance required for the electrical field amplitude to fall to e-I of its value at the interface, is given by:

$$d_p = \frac{\lambda_1}{2\pi(\sin^2\theta - n_{21}^2)^{1/2}}$$

where 2, = *A h l* is the wavelength in the denser medium, and nZ1= *n2/nl*i s the ratio of the refractive index of the less dense medium divided by that of the denser .

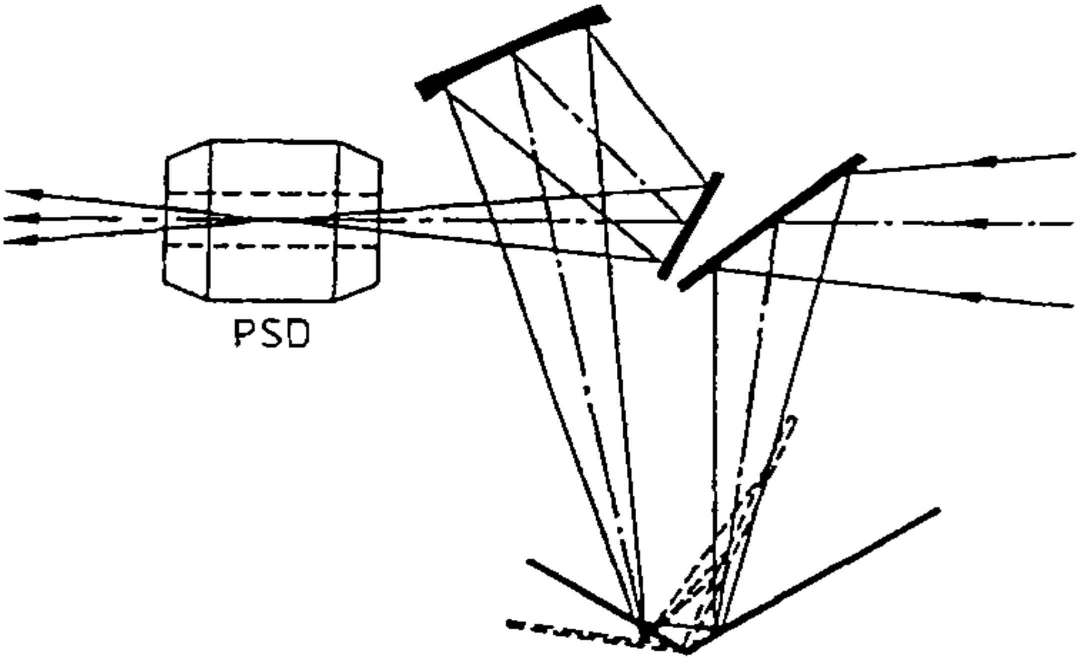

Figure . Ray diagram of the versatile reflection attachment (VRA) with single diamond polarizer (PSD)