Electronics And Instrumentation

8th Semester

Subject: Analytical Instrumentation
Subject code: BT 808

Unit-2

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Infrared and Raman spectroscopy

The roots of infrared spectroscopy go back to the year 1800, when WILLIAM HERSCHEL discovered the infrared region of the electromagnetic spectrum. Since 1905, when WILLIAM W. CO- BLENTZ ran the first infrared spectrum vibration spectroscopy has become an important analytical tool in research and in technical fields. In the late l960s, infrared spectrometry was generally believed to be a dying instrumental technique that was being superseded by nuclear magnetic resonance and mass spectrometry for structural determination, and by gas and liquid chromatography for quantitative analysis. However, the appearance of the first research- grade Fourier transform infrared (FT-IR) spectrometers in the early 1970s initiated a renaissance of infrared spectrometry. After analytical instruments (since the late 1970s) and routine instruments (since the mid 1980s), dedicated instruments are now available at reasonable prices. With its fundamental multiplex or Fellgett's advantage and throughput or Jacquinot's advantage, FT-IR offers a versatility of approach to measurement problems often superior to other techniques. Furthermore, FT-IR is capable of extracting from samples information that is difficult to obtain or even inaccessible for nuclear magnetic resonance and mass spectrometry. Applications of modern FT-IR spectrometry include simple, routine identity and purity examinations (quality control) as well as quantitative analysis, process measurements, the identification of unknown compounds, and the investigation of biological materials. Raman and infrared spectra give images of molecular vibrations which complement each other; i.e., the combined evaluation of both spectra yields more information about molecular structure than when they are evaluated separately. The 1990s witnessed a tremendous growth in the caes and utilization of Raman scattering measurements. The parallel growth of Fourier transform Raman (FT-Ranianj with charge-coupled device (CCD) based dispersive instrumentation has provided the spectroscopist with a wide range of choice in instrumentation. There are clear strengths and weaknesses that accompany both types of instrumentation. While

FT-Raman systems virtually eliminate fluorescence by using near-IR laser sources, this advantage is paid for with limited sensitivity. On the other hand, fluorescence interferences always play a role in dispersive measurements with higher sensitivity. As an alternative to infrared spectroscopy, Ra- man spectroscopy can be easier to use in some cases; for example, whereas water and glass are strong infrared absorbers they are weak Raman scatterers, so that it is easy to produce a good- quality Raman spectrum of an aqueous sample in a glass container.

Computer-Aided Spectral Interpretation

After his first experiences 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 com- pounds or as many as are available because, in similarity search, the retrieval of an excessive number of closely similar references for a particular 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 .