SAQ 3.3a

Multiple internal reflectance (MIR) and ATR are similar techniques, but MIR produces more intense spectra from multiple reflections. While a prism is usually used in ATR work, MIR uses specially shaped crystals which cause many internal reflections, typically 25 or more (Figure 3.3c).

3.3.2. Specular Reflectance

In external reflectance incident radiation is focused on to the sample and two forms of reflectance can occur, namely *specular* and *diffuse*.

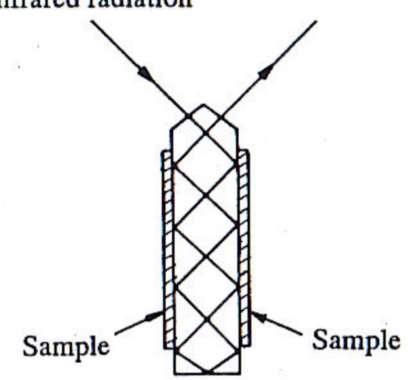

Fig. 3.3c. *A multiple internal reflectance cell*

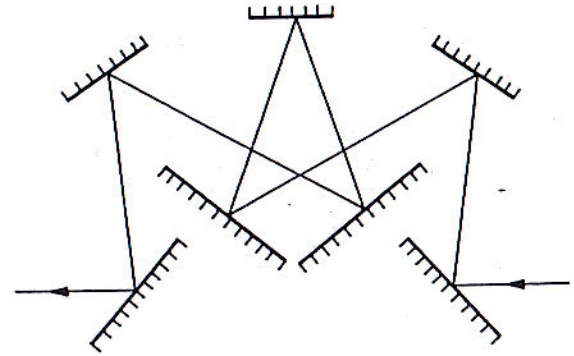

Fig. 3.3d. *Specular reflectance*

External reflectance measures the radiation reflected from a surface. The material must, therefore, be reflective or be attached to a reflective backing. A particularly useful application for this technique is the study of surface coatings such as surface treated metals, paints and polymers.

Specular reflectance occurs when the reflected angle of incident radiation equals the angle of incidence (Figure 3.3d). The amount of light reflected depends on the angle of incidence, the refractive index, the surface roughness and the absorption properties of the sample.

Increased pathlengths through thin coatings can be achieved by using grazing angles of incidence (up to 85°). This gives increased sensitivity. Thicker coatings in the micrometre thickness range are studied using angles of typically 30°.

3.3.3. Diffuse Reflectance

In external reflectance, the energy which penetrates one or more particles is reflected in all directions. This component is called *diffuse reflectance*. In the diffuse reflectance technique, commonly called DRIFT, a powdered sample is mixed with KBr powder. The DRIFT cell reflects radiation to the powder and collects the energy reflected back over a large angle. Diffusely scattered light can be collected directly from a sample or, alternatively, by using an abrasive sampling pad. DRIFT is most useful for sampling powders or fibres. Figure 3.3e

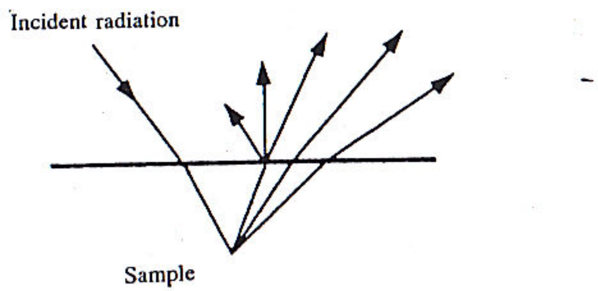

Fig. 3.3e. *Diffuse reflectance*

shows diffuse reflectance from the surface of a sample.

Kubelka and Munk developed a theory describing the diffuse reflectance process for powdered samples, which relates the sample concentration to the scattered radiation intensity. The Kubelka–Munk equation is as follows:

$$\frac{(1 - R_\infty)^2}{2R_\infty} = \frac{c}{k} \quad (3.4)$$

where R_∞ is the absolute reflectance of the layer, c is the concentration and k is the molar absorption coefficient.

Figure 3.3f shows the diffuse reflectance spectrum of a phenylene oxide–styrene copolymer. This copolymer is high melting, insoluble

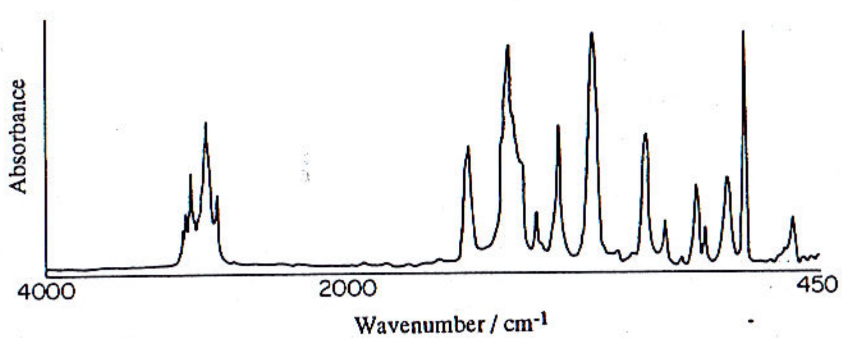

Fig. 3.3f. *A diffuse reflectance spectrum of a phenylene oxide–styrene copolymer*

and hard, but if rubbed with emery paper the powder deposited may be studied by diffuse reflectance.

3.4. OTHER TECHNIQUES

3.4.1. Photoacoustic Spectroscopy

Photoacoustic spectroscopy (PAS) is based on the transfer of modulated infrared radiation to a mechanical vibration. Gaseous, liquid or solid samples can be measured by using PAS and the technique is particularly useful for highly absorbing samples such as rubber or coal. When the modulated infrared radiation is absorbed by a sample, the substance heats and cools in response to the radiation reaching the sample. This heating and cooling pattern is converted into a pressure wave which can be detected by a microphone. Figure 3.4a shows a schematic diagram of a PAS cell.

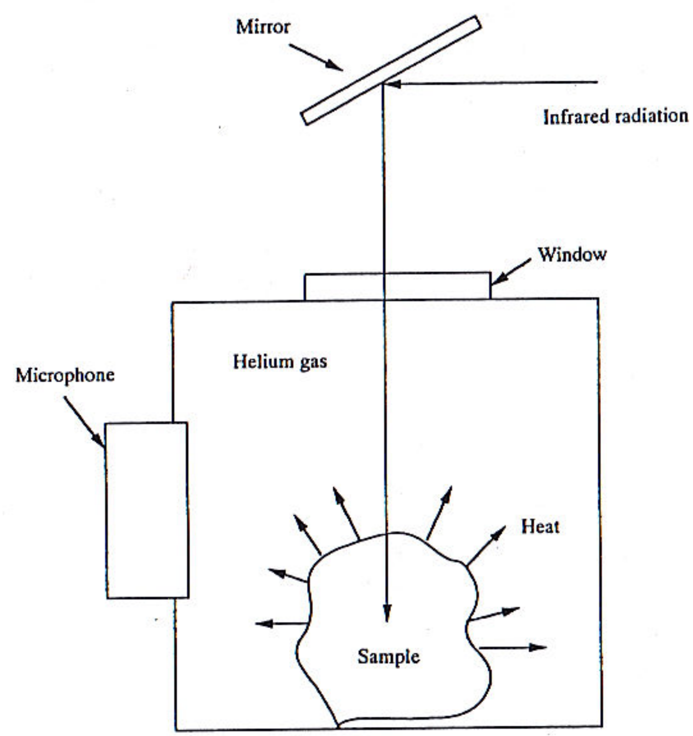

Fig. 3.4a. *Schematic representation of a photoacoustic spectroscopy cell*