

contribution to the spectrum of the transmission and internal reflection component. The resulting spectra have an appearance more similar to that of the transmittance spectra than bulk reflectance spectra. If sample dilution is not feasible, the spectra may still be improved by using an optical geometry that employs a low incident angle and an offline collection angle.

The DR spectrum of a dilute sample of “infinite depth” (i.e., up to 3 mm) is usually calculated with reference to the diffuse reflectance of the pure diluent to yield the reflectance,  $R_{i\bar{A}}$ .  $R_{i\bar{A}}$  is related to the concentration of the sample,  $c$ , by the Kubelka–Munk (K–M) equation:

$$f(R_{i\bar{A}}) = (1 - R_{i\bar{A}})^2 / 2R_{i\bar{A}} = 2.303 ac/s \quad (6.1)$$

where  $a$  is the absorptivity and  $s$  is the scattering coefficient. The scattering coefficient depends on both particle size and degree of sample packing. Thus, the K–M function can be used for accurate quantitative analysis, provided the particle size and packing method are strictly controlled. For good diffuse reflectors, plots of the K–M function,  $f(R_{i\bar{A}})$ , are analogous to absorbance plots for transmission spectra. Care must be taken in applying the K–M equation when  $R_{i\bar{A}}$  is much less than about 30%, because deviations from linearity can occur when the sample concentration is high.

A modification of the aforementioned DR model is the *praying mantis model*, where the preferred offline type incorporates two 6:1 90-degree off-axis ellipsoidal mirrors. One of the ellipsoids focuses the incident beam on the sample, whereas the second collects the radiation diffusely reflected by the sample. Both ellipsoidal mirrors are tilted forward; therefore, the specular component is deflected behind the collecting ellipsoid and permits the collection of primarily the diffusely reflected component. Another advantage of the “praying mantis” design is the ability to expand the available sampling area indefinitely by rotating the ellipsoids and positioning the sampling point above the optical plane. This accessory may also be used for specular reflectance at a 41.50-degree angle of incidence. This is achieved by tilting the sample angle as the alignment mirror. Specular sample holders are available for this purpose. Although diffuse reflection spectroscopy primarily measures the spectrum of the bulk, it can be very sensitive to the nature of the sample, for example, powders with a high surface area. Thus, it is valuable for catalysis and oxidation studies. In this application, it is important to measure the spectrum under controlled atmospheres and at high or low temperatures. The “praying mantis” model has a large sampling space between the ellipsoids for additional accessories, such as vacuum chambers. This cell is specially designed to conduct diffuse reflection spectroscopy studies in controlled atmospheres at high (up to 750°C) or low (liquid nitrogen) temperatures and under vacuum or high pressure (e.g., up to 1500 psi).

## 6.9.8 X-Ray Powder Diffraction

X-rays are part of the electromagnetic spectrum lying between the ultraviolet and gamma rays, and they are expressed in angstrom units (Å). Diffraction is a scattered phenomenon, and when X-rays are incident on crystalline solids, they are scattered in all directions. Scattering occurs as a result of the radiation wavelength being in the same order of magnitude as the interatomic distances within the crystal structure. X-rays are extensively used to characterize a crystal. In [Figure 6.8](#), the relationship