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Diffuse Reflectance Spectroscopy—Important Developments

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Abstract. Effect of front surface reflectance is incorporated into standard Kubelka-Munk theory of diffuse reflection. A method of obtaining the absorption coefficient independent of scattering coefficient is presented.

Key words: FTIR, diffuse reflectance, reststrahlen effect.

In the last decade diffuse reflectance spectroscopy (DRS) has been established as one of the simplest and most powerful spectroscopic techniques. Theoretical aspects of the technique have been developed long ago [1]. The works of Griffiths and others [2] have acknowledged the usefulness of DRS in the field of chemical spectroscopy. It was not, however, until after the introduction of the "Praying Mantis" model of the diffuse reflection attachment (DRA), designed and marketed by Harrick [3] and compatible with virtually every spectrometer, that the technique became widely accepted by the workers in the field.

Theoretical descriptions of DRS are dominated by the Kubelka-Munk (KM) theory. In practice a special case of the KM theory describing the diffuse reflection of an infinitely thick sample is most often employed.

The most general solution to KM model can be written as [4]

$$\begin{aligned} I_+(x) &= I_+(0)\left[\mathrm{ch}\, \alpha x - \frac{\kappa + s}{\alpha}\mathrm{sh}\, \alpha x\right] + I_-(0)\frac{s}{\alpha}\mathrm{sh}\, \alpha x, \\ I_-(x) &= I_-(0)\left[\mathrm{ch}\, \alpha x - \frac{\kappa + s}{\alpha}\mathrm{sh}\, \alpha x\right] - I_+(0)\frac{s}{\alpha}\mathrm{sh}\, \alpha x, \end{aligned} \tag{1}$$

where $I_+(x)$ and $I_-(x)$ are the components of radiation traveling in the positive and negative direction, respectively, of the X-axis. The X-axis is perpendicular to the front surface of the sample, directed toward the inside of the sample, and with the origin at the front surface. κ and s are the absorption and scattering coefficients, respectively, and

$$\alpha = \sqrt{\kappa(\kappa + 2s)}. \tag{2}$$

If the sample thickness increases without limits, both $I_+(\infty)$ and $I_-(\infty)$ must vanish. That requirement establishes the relationship

$$\frac{I_-(0)}{I_+(0)} = \frac{s}{s + \kappa + \alpha}, \tag{3}$$

a well-known result of KM theory.

If one neglects the reflection occurring at the front surface of the sample, then $I_+(0)$ is incident and $I_-(0)$ is reflected radiation, and (3) gives the diffuse reflectance of the sample. It is important to note that (3) states that for very weakly absorbing samples, diffuse reflectance becomes extremely sensitive to small changes in the absorption coefficient.

When one takes the front surface reflection into account, (3) is replaced by the correct expression

$$R_{\text{tot}}^{\infty} = R_s + (1 - R_s)^2 \frac{s}{\alpha + \kappa + s - R_s \cdot s}, \tag{4}$$

where R_s represents the reflectivity of the front surface of the sample.

Since R_s represents the specular reflection from the microscopic crystal faces of the powder grains, it will be an increasing function of κ. The second term in (4) represents modified diffuse reflectance (3) multiplied by the quenching term $(1 - R_s)^2$. R_{diff}^{∞} is a decreasing function of κ. For small values of κ, R_s is practically insensitive to small changes in κ, thus the second, decreasing term in (4) prevails. As κ increases, R_s becomes very sensitive to κ and starts to increase sharply. This causes R_{tot}^{∞} to first decrease as κ increases, and then to sharply increase as κ increases above some critical value κ_c. One can clearly see that a single measurement of the diffuse reflectivity of a sample is insufficient to determine the spectrum of κ. In addition, the inversion of a strong absorption peak described above and known as "reststrahlen effect", additionally complicates spectral analysis. Eq. (4) also quantitatively explains why diluting the sample in a non-absorbing matrix (such as KBr powder) helps remove the "reststrahlen effect" from the spectrum. This will happen when the combined absorption coefficient of the mixture, by dilution, is brought below the critical value κ_c everywhere within the spectral region of interest.

Ideally, one would like to obtain the information on the absorption coefficient of the sample without any interferences from the scattering coefficient and from front surface reflection. This can be done in the following way. From (1) and appropriate boundary conditions, and for a special case of very thin sample placed on a mirror, one finds

$$\kappa d = \frac{(1 - R)(1 - R_s)}{1 - 3R_s + (1 + R_s)R}, \tag{5}$$

where R is measured reflectance, and d is sample thickness. By taking the spectrum of the same sample but of different thickness one can express

$$R_s = \frac{(1 - \zeta) + R_2 - \zeta R_1}{3(1 - \zeta) - R_2 + \zeta R_1}, \tag{6}$$

where

$$\zeta = \frac{d_1}{d_2}\frac{1 - R_1}{1 - R_2}. \tag{7}$$

By using the result (6) for R_s and inserting it into (5), the desired goal is accomplished. In the case where the scattering power of the sample itself is insufficient to scatter the radiation isotropically, one can replace the mirror with a transparent window having a metalized bottom face and ground top face. The calculations indicated above can be easily handled by the computer that controls FTIR spectrometers.

A typically low energy level of DRS, and particularly for the above described method, can be considerably improved by using the collecting hemisphere accessory[1] [3]. This is a hemispherical shell with a highly reflecting inside surface placed above the sample and centered onto the sampling point. It has openings to allow the focusing optics to project the IR beam onto the sampling point and to allow the collecting optics of a DRA to collect the diffusely reflected radiation that would be collected if the collecting hemisphere was not present. It would, however, refocus all otherwise uncollected radiation back exactly to the sampling point of DRA giving it another chance to be captured by the collecting optics of the DRA. This unipoint multiple sampling characteristic generally considerably improves the energy throughput, the spectral contrast, and signal-to-noise ratio of the spectrum. It also converts DRA into a highly sensitive micro-sampling attachment.

References

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[1] Patent pending