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RESEARCH NOTE

Determination of optical constants by ATR measurements

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SEVERAL recent reports have indicated exact analytical methods for calculating the optical constants from ATR measurements [1–5]. All were based on repeated reflectivity determinations at several incidence angles or polarizations, followed by involved calculations on the results. Simpler approximate methods have a more restricted range of validity [6].

A method is proposed that has several advantages over these. In what follows FAHRENFORT'S notation will be used [7], unless otherwise noted.

The reflectivity R_s for light polarized perpendicularly to the incidence plane is measured in a spectrophotometer where the angle of incidence oscillates about its mean θ with a small amplitude $\Delta\theta$. The photometer output will then contain a steady component proportional to R_s and an a.c. one proportional to ΔR_s. If this is filtered out and sent to a tuned a.c. amplifier reflectivity changes down to 10^{-4} per cent can be measured [8]. If $\Delta\theta \ll \theta - \theta_{\text{crit}}$ then $\Delta R_s/\Delta\theta$ will equal the derivative $\partial R_s/\partial\theta$. This is also true for an imperfectly collimated beam, but then its aperture S_θ must meet the same criterion.

Small k's only give accurately measurable attenuations $(1 - R_s)$ when $\theta - \theta_{\text{crit}}$ is small, thus requiring $\Delta\theta$ and S_θ also to be so. The high values of $\partial R_s/\partial\theta$ in the vicinity of the critical angle, and the high sensitivity with which ΔR_s can be measured, allow very small $\Delta\theta$'s. However, diffraction and imperfections in the optical system place a lower limit on S_θ. For a given value of S_θ and of the accuracy to which $\Delta R_s/\Delta\theta = \partial R_s/\partial\theta$ [and, at the same time $(R_s)_{\text{mean}} = (R_s)_\theta$] must hold, a series expansion using approximate higher order derivatives indicates the minimum $\theta - \theta_{\text{crit}}$. Given this, the angle of incidence, and the number of reflections, R_s may be calculated as a function of k. If, for the sake of accurate measuring, a lower limit is fixed for the attenuation, a minimum value for accurately measurable k's results.

This calculating system can be considered exact for all but extremely small k's, because at all higher values of it the approximations made can be rendered as accurate as desired by keeping $\Delta\theta$ and S_θ small.

The calculating procedure is as follows:

$$F = 2\cos\theta(1 + R_S)/(1 - R_s) \tag{1}$$

$$\frac{\partial F}{\partial\theta} = F' = -\frac{4}{(1 - R_s)^2}\left[(1 - R_s)\sin\theta - \cos\theta\frac{\partial R_s}{\partial\theta}\right] + 2\sin\theta \tag{2}$$

[1] J. FAHRENFORT and W. M. VISSER, *Spectrochim. Acta* **18,** 1103 (1962).
[2] W. N. HANSEN, *Spectrochim. Acta* **21,** 209 (1965).
[3] J. FAHRENFORT and W. M. VISSER, *Spectrochim. Acta* **21,** 1433 (1965).
[4] R. F. POTTER, *J. Opt. Soc. Am.* **54,** 904 (1964).
[5] G. HEILMAN, *Z. Naturforsch.* **16a,** 714 (1961).
[6] W. N. HANSEN, *Spectrochim. Acta* **21,** 815 (1965).
[7] J. FAHRENFORT, *Spectrochim. Acta* **17,** 698 (1961).
[8] N. J. HARRICK, *Phys. Revs.* **125,** 1165 (1962).

This step could be avoided by obtaining a signal proportional to F in the spectrophotometer's circuit before filtering out the a.c. component.

$$a = (F \sin \theta + F' \cos \theta)/(4 \sin \theta + FF'/\cos \theta) \tag{3}$$

$$b^2 = \sin \theta \cos \theta \frac{F - 4a}{F'} - a^2 \tag{4}$$

$$n = [\tfrac{1}{2}(\sin^2 \theta - b^2 + a^2 + [4a^2b^2 + (\sin^2 \theta - b^2 + a^2)^2]^{\frac{1}{2}})]^{\frac{1}{2}} \tag{5}$$

$$k = ab/n^2 \tag{6}$$

The advantages of this procedure are the following:

(a) As all the data needed for calculating n and k are gathered simultaneously, and the equations are fairly simple, an analog device of adequate accuracy and reasonable cost could be made a part of the spectrophotometer for directly recording n and k by on-line computation. To avoid confusing $\partial R_s/\partial \theta$ and $\partial R_s/\partial \lambda$ discontinuous spectral scanning would be useful (a Maltese cross mechanism in the wavelength drive and a switched or point-by-point recorder would be useful).

(b) For highly absorbing samples, the attenuation is high enough for accurate measurement even when $\theta - \theta_{crit}$ is large. ΔR_s also continues to be measurable because of the high sensitivity to it of the system. A fixed θ can thus be used. If 45° is used, simpler equations result, and arbitrarily polarized light may be used, owing to the indentities:

$$R_s = \sqrt{R_p} = (\sqrt{1 + 8R} - 1)/2 = (\sqrt{(1 - P)^2 + 8PR_{pp}} - 1 + P)/2P \tag{7}$$

where R, R_p, and R_{pp} are the reflectivities for unpolarized light, light polarized parallel to the incidence plane, and light having a fraction P of its energy so polarized.

(c) For weakly absorbing samples small values of $\theta - \theta_{crit}$ are required. These are best attained and manitained by using the measured data to control θ through a servo. If the control loop is designed to maintain R_s constant, accuracy is improved and held more constant, and at the same time the measuring range is extended over that provided by a constant $\theta - \theta_{crit}$. Further range increase can be made by providing two values of R_s that may be held constant. An obvious possibility is changing the number of reflections.

(d) Measurements at two values of θ should coincide within the procedure's accuracy unless depth variation of the optical constants exists, which would interact with the variation of the beam's penetration with incidence angle. This is an interesting way to determine the presence of this phenomenon, which invalidates all methods for calculating the optical constants that call for measurements at two widely different angles.

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