HEWLETT
PACKARD

Suppression of Interference Effects in Spectroscopy Using an Integrating Sphere

Geraint Owen
Computer Peripherals Laboratory
HPL-96-69
May, 1996

spectroscopy,
thin film

Interference effects occur in the optical spectroscopy of thin film samples, and they can obliterate absorption spectra, especially if these are weak. A novel solution to this problem is proposed: it involves placing the sample inside an integrating sphere and then collecting both reflected and transmitted light simultaneously. The effectiveness of this technique has been demonstrated experimentally, and absorption dips as weak as 2.4×10^{-4} have been measured. A further attribute of the method is that some of the light reflected from the walls of the sphere is redirected back towards the sample, thus increasing its absorption by a substantial factor.

1) Introduction

In the optical spectroscopy of thin film samples, interference effects can cause the detector output to vary cyclically as the wavelength λ is varied. An experimental arrangement in which this occurs is shown in Fig. 1, which depicts the measurement of the transmission spectrum of a sample consisting of a glass substrate supporting a 1.3 μm thick film of ZnS doped with Tm. The dopant absorbs at λ_0=792 nm, the shape of the dip being the Gaussian

$$1-\beta\,\exp-\{(\lambda-\lambda_0)/w\}^2 .$$

The 1/e half width w is 5.5 nm. Samples with different doping densities were available, and for these, the strength of the absorption dip β varied between 2×10^{-4} and 3×10^{-3}. Because the absorption signal was weak, wavelength modulation was used to obtain a derivative signal which was amplified with low noise by a lock-in amplifier. The resulting absorption feature had a shape

$$\tfrac{2\beta}{w^2}(\lambda_0-\lambda)\exp-\{(\lambda-\lambda_0)/w\}^2 :$$

i.e. a minimum followed by a maximum.

Figure 2a shows the detector output that was obtained with a heavily doped sample: it is dominated by the cyclical thin film interference signal to such an extent that the Tm absorption feature is obscured.

The cause of this effect is light specularly reflected from interfaces #1 and #2. This may amount to much less than 1% of the light flux transmitted by the sample, but this is more than sufficient to obliterate weak spectra. This effect will occur unless the coherence length of the light beam is very much less than the thickness of the film, that is, unless

$$\tfrac{\lambda^2}{\Delta\lambda} << t \qquad (1)$$

where t is the film thickness (see Fig. 1), λ is the "average" wavelength of the light in the beam and $\Delta\lambda$ is its bandwidth (in terms of wavelength). With λ =0.8 μm and $\Delta\lambda$ =2 nm, $\tfrac{\lambda^2}{\Delta\lambda}$ =320 μm. Thus, if the sample has a thickness on the order of 0.1 mm or less, this effect may be present. Interference effects are also observed in reflection spectra, and inequality (1) applies to these also. Although the problem has been described here in terms of a single layer film, it is equally troublesome with multi-layer films.

Well-known palliatives include roughening at least one face of the thin film, using polarized light and inclining the specimen at the Brewster angle to the incoming beam, or depositing the film to be tested as a wedge [1]. In this case, the first two techniques were tried and found not to work sufficiently well, whilst the third was impracticable.

Integrating spheres are used currently in spectroscopy, not for the purpose of nullifying interference effects, but rather for the purpose of collecting light that would otherwise be scattered outside the acceptance region of the detector [2], [3]. This involves placing the sample at a port so that either the transmitted or reflected light is collected in the sphere (depending upon whether a transmission or reflection spectrum is to be measured). In the method described here, the sample is placed <u>inside</u> the sphere so that both reflected <u>and</u> transmitted light are collected simultaneously.

2) Principle of the method

Figure 3 shows a hypothetical experiment in which transmission and reflection spectroscopy are carried out simultaneously on a <u>lossless</u> sample. Detector D_1 measures the transmitted light flux, and D_2 the reflected light flux. Assume for the time being that D_1 and D_2 have identical sensitivities at all wavelengths, and that the sample creates no scattering whatever.

Figure 4a depicts the output of D_1, and 4b the output of D_2. The oscillating "spectra" are the results of thin film interference. Figure 4c shows the sum of the outputs of D_1 and D_2. Note that the spectrum of Fig. 4c is completely free of interference effects, and its shape is determined only by variation of the light source's output with wavelength. That the combined spectrum of Fig. 4c shows no interference effects follows directly from the principle of conservation of energy: for a lossless sample, any light which is not reflected must be transmitted and *vice versa.*)

In practice, this hypothetical experiment could not be made to work perfectly as it is shown in Fig. 3. There are two reasons for this: real samples invariably scatter, and no two detectors have identical spectral sensitivities. These two difficulties can be overcome by placing the sample within an integrating sphere, and using a single detector, as is shown in Fig. 5. Since the sample is almost completely enclosed by the highly reflective sphere, nearly all transmitted and reflected light, including scattered light, is collected. Since only one detector is used, the problem of two imperfectly matched detectors does not arise.

So far, this argument has been applied to a lossless sample. In the case of a weakly absorbing specimen, it is to be expected that nearly complete suppression of interference effects should still occur, making weak absorption features much more visible.

3) Experimental Verification

The spectrum shown in Fig. 2b was measured with the same sample as that used for Fig. 2a, but this time with the sample completely enclosed by an integrating sphere. In all other respects, the experimental conditions were identical, except that the vertical scale is more sensitive in Fig. 2b than in Fig. 2a by a factor of 3.

Comparing Figs. 2a and 2b, it is clear that the cyclical interference signal has been suppressed by placing the sample inside the integrating sphere. In addition, the Tm absorption feature is now evident in the vicinity of 792 nm. (It may seem surprising that no trace of this feature was seen in Fig. 2a. For discussion of this point, see Section 4.) The particular sample used in this experiment had an absorption factor β of about 3×10^{-3}.

A separate experiment was performed to verify that the feature at 792 nm really was due to Tm absorption. The spectra in Fig. 6 were all measured between 750 and 830 nm with a vertical scale a further factor of 3.3 more sensitive than in Fig. 2b. In Fig. 6a, the spectrum of the Tm doped sample in the integrating sphere is again shown, but measured under the new conditions. In Fig. 6b the sample was replaced by a similar one in which the ZnS was undoped, and as expected, the Tm feature is now absent. The spectrum of Fig. 6c was measured with no sample in the integrating sphere.

4) Absorption Gain

When the sample is placed inside the integrating sphere, it is irradiated not only with direct light from the source, but also by indirect light reflected from the sphere walls. This increases the absorption of light by the sample, providing an "absorption gain". An estimate of the magnitude of this effect may be made as follows.

If the flux entering the sphere is F, the surface area of the sphere is A_s and the reflectivity of its walls is ρ, then, neglecting the effects of ports, the radiance at the walls is

$$N = \frac{F\rho}{\pi A_s(1-\rho)}$$

(For a description of the theory of the integrating sphere, see, for example, reference [4]). If the area of the sample (assumed to be lamellar) is A, then the reradiated flux F' incident on it is $2\pi AN$. (The factor of 2 appears because the lamella has two surfaces -- front and back.) Thus

$$\frac{F'}{F} = 2\frac{A}{A_s}\frac{\rho}{1-\rho}$$

Under the conditions of the experiments reported here, the area of the sample was 2 cm^2, and the surface area of the (7.5 cm diameter) integrating sphere was 180 cm^2. A reasonable estimate of the reflectivity of the walls is 99%[4]. Substituting these values gives F'/F = 2.2. Thus, the integrating sphere increases the energy incident on the sample by a factor, which in this particular case, may be as large as 3.2.

The absorption gain effect helps to explain why the Tm absorption feature in Fig. 2b appears to be so much stronger than in Fig. 2a. (On the basis of the difference in vertical scale factors, which is only 3, the feature ought to be weakly visible in Fig. 2a, whereas it is not.) An additional effect that enhances the absorption feature in Fig. 2b is that both reflected and transmitted light are being collected, whereas in Fig. 2a, reflected light is lost.

For many applications, it is not necessary to know the value of the absorption gain (for example, when relative measurements are made on a series of samples all of which are approximately the same size and shape). However, if it is necessary to know the value of the gain, it may be measured by taking two spectra of the sample, one with the sample in the path of the direct beam from the source, and the other with the sample out of the direct beam, but still inside the integrating sphere. In the first case, the flux incident on the sample will be $F+F'$, and in the second it will be F', so the ratio of incident fluxes is $(F+F')/F' = 1+F/F'$. Thus the absorption gain can be calculated from the ratio of the magnitudes of a particular absorption dip measured with the sample in and out of the direct beam.

5) Summary

It has been demonstrated that placing a weakly absorbing thin film sample inside an integrating sphere suppresses the interference signal which could otherwise dominate the measured absorption spectrum. A further advantage of the technique is that absorption effects are enhanced, since light reflected off the sphere walls is re-absorbed by the sample. The sample discussed so far in this paper had an absorption factor on the order of of 10^{-3}, but useful results have been obtained with samples whose absorption factors were well below 1×10^{-3} . (See Fig. 7 for examples.)

Acknowledgments

The author would like to acknowledge Gerd Mueller and Regina Mach for many useful discussions and for providing samples.

References

[1] See, e.g. Nelson L. Alpert, William E. Keiser and Herman A. Szymanski, *Theory and Practice of Infrared Spectroscopy* (Plenum Press, New York, 1970) Ch. 7 p. 337.
[2] James E. Stewart, Infrared Spectroscopy (Marcel Dekker, New York, 1970) Sec. 16-III.
[3] Arthur W. Springsteen, *A Guide to Reflectance Spectroscopy* (Labsphere Techguide).
[4] John W.T. Walsh, *Photometry* (Dover, New York, 1965) Ch. VIII p. 258.
[5] Arthur W. Springsteen, James Leland and Trudy M. Ricker, *A Guide to Reflective Coatings and Materials* (Labsphere Techguide).

Figure Captions

Figure 1: The measurement of a transmission spectrum of a thin sample. For the measurements described in this paper, the thin film consisted of Tm doped ZnS, and its thickness t was 1.3 μm.

Figure 2: (a) A transmission derivative spectrum of a Tm doped ZnS sample made with the configuration of Fig. 1. The wavelength was swept from 700 to 900 nm. The 3 mV marker refers to the input to the lock-in amplifier. (b) A derivative spectrum of the same sample, but this time measured with the sample inside an integrating sphere. Note that the sensitivity is greater by a factor of 3 than in (a). The feature in the vicinity of 760 nm is a grating artifact. (See Fig. 6.)

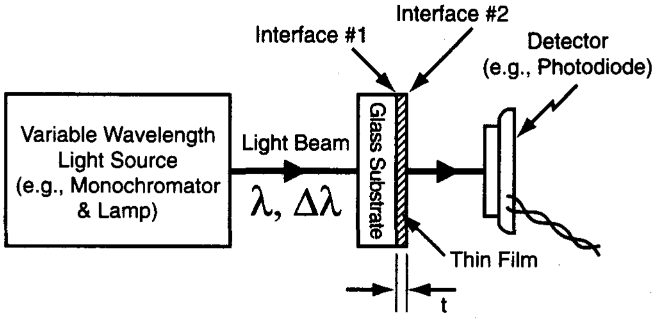
Figure 3: An arrangement for simultaneous transmission and reflection spectroscopy, using two detectors D_1 and D_2.

Figure 4: The separate outputs of D_1 and D_2 are shown in (a) and (b) respectively. The sum of these outputs is shown in (c).

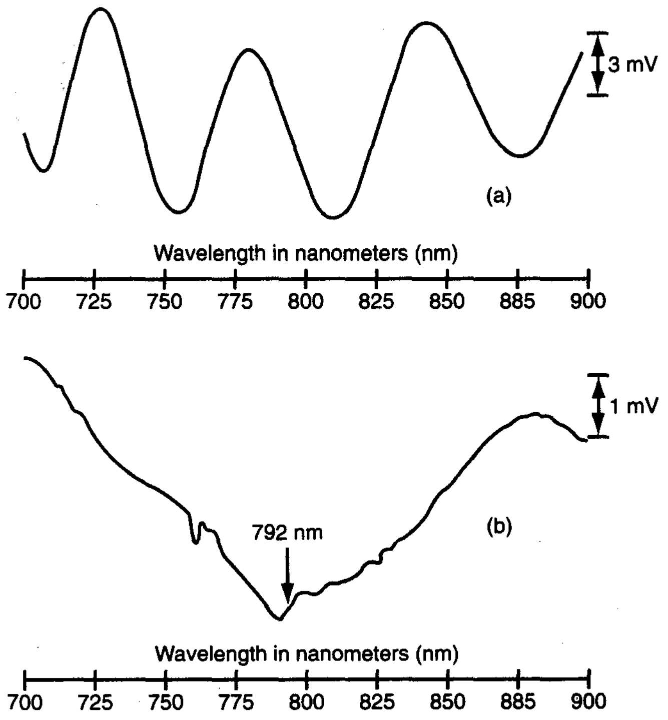
Figure 5: A practical implementation of the idea shown in Fig. 4, using an integrating sphere.

Figure 6: Derivative spectra measured between 750 and 830 nm with (a) a Tm doped ZnS sample, (b) an undoped ZnS sample and (c) no sample. Since it is present in all these spectra, the feature in the vicinity of 760 nm is an artifact of the grating in the monochromator.

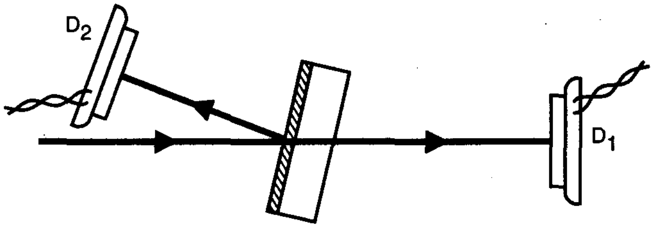
Figure 7: Spectra measured between 776 and 808 nm for two different Tm doped ZnS samples. In (a) the measured absorption factor β was 7.3×10^{-4}. In (b), β was 2.4×10^{-4}. In each case, quantitative results were obtained by fitting the spectrum to the function $y = A + Bx + Cx^2 + Dx\exp(-x/w)^2$ where $x = \lambda - \lambda_0$. The absorption factor β was determined from the calculated value of D. The "baseline" curve has the equation $y = A + Bx + Cx^2$.



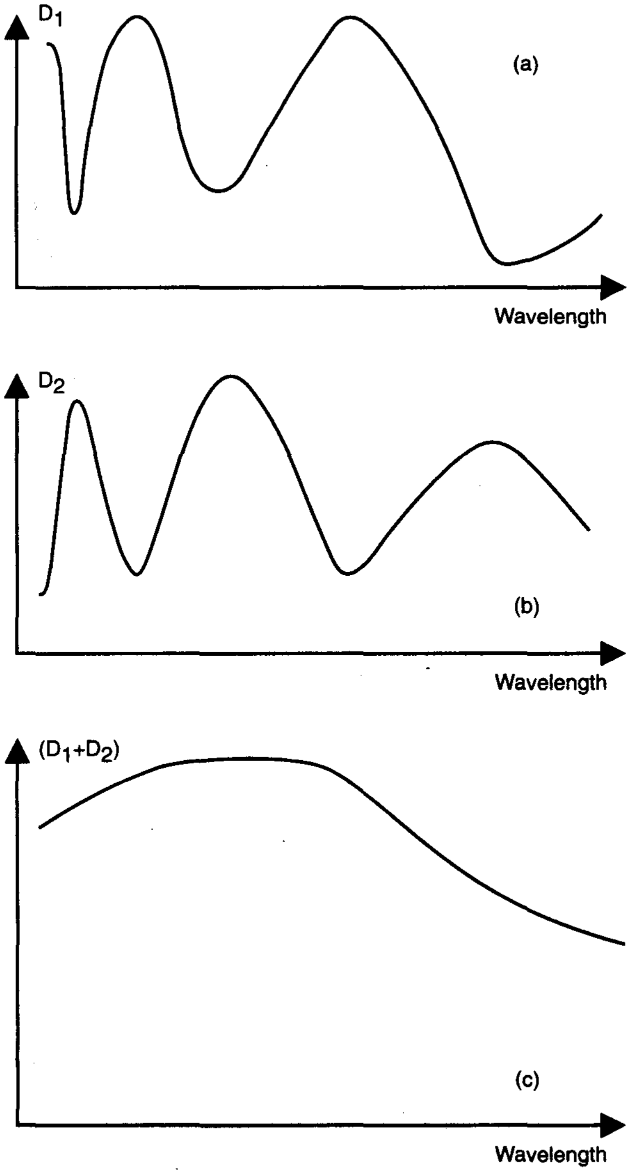
Gerry Owen
Job 1955
Fig1.ai6
4/96



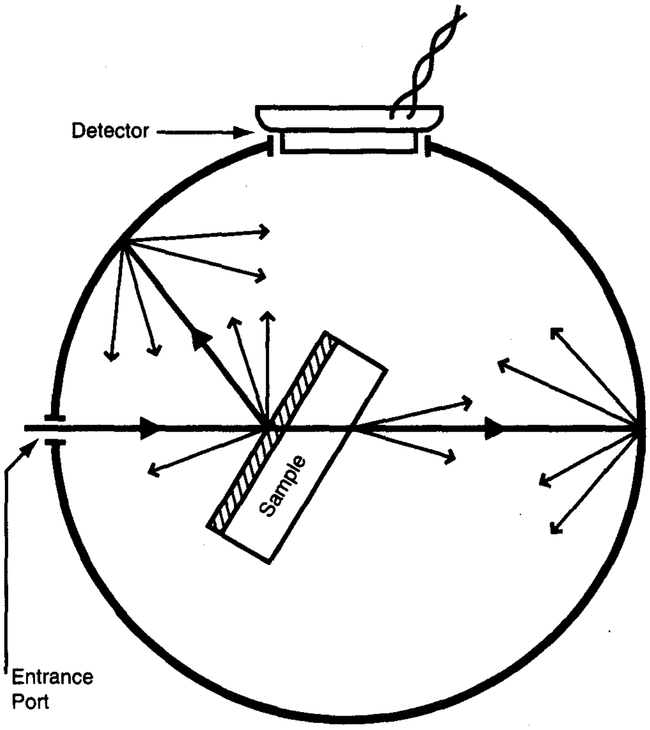
Gerry Owen
Job 1955
Fig2.ai6
4/96



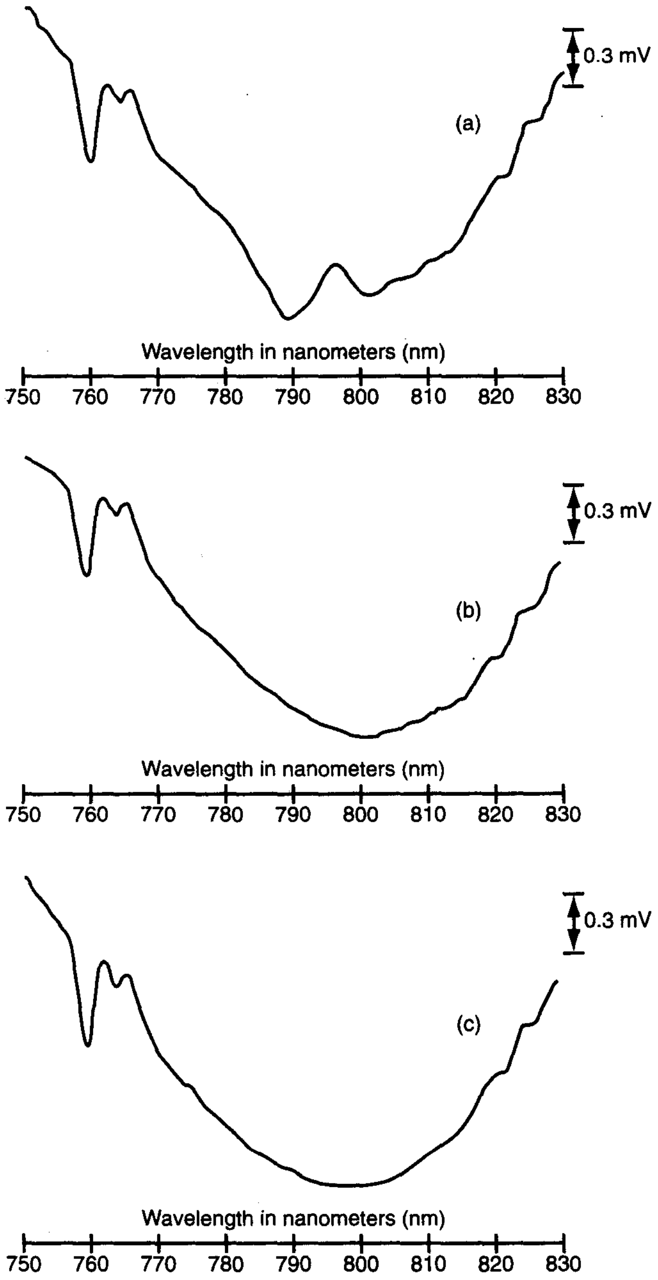
Gerry Owen
Job 1955
Fig3.ai6
4/96



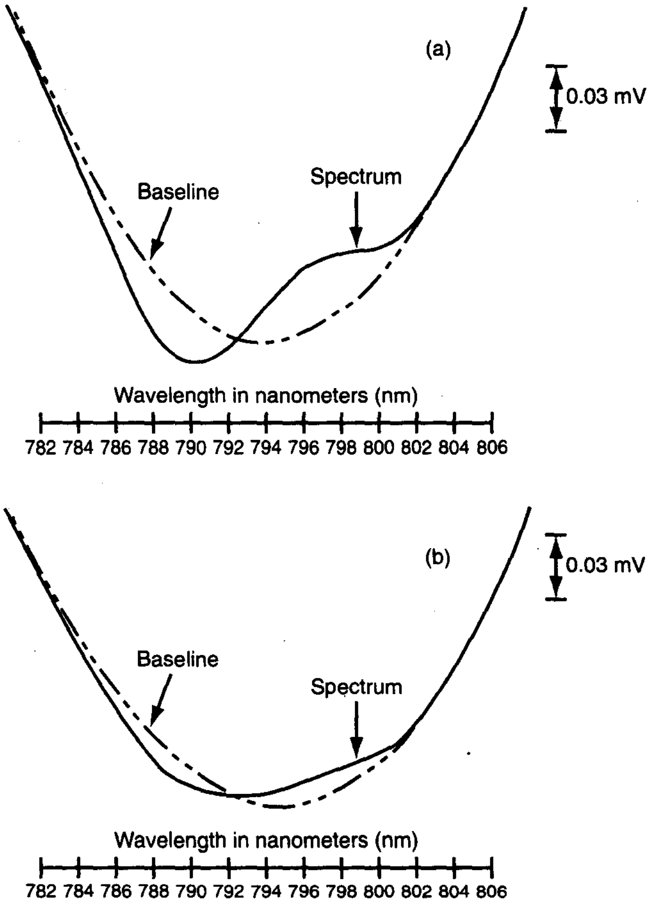
Gerry Owen
Job 1955
Fig4.ai6
4/96



Gerry Owen
Job 1955
Fig5.ai6
4/96



Gerry Owen
Job 1955
Fig6.ai6
4/96



Gerry Owen
Job 1955
Fig7.ai6
4/96