

VARIABLE ANGLE POWER REFLECTION SPECTROSCOPY FROM SURFACE LIQUID FILMS

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ABSTRACT

A new technique of power reflection spectroscopy from surface liquid films is developed for variable angles of incidence in sigma and pi polarisation. For a surface film of highly absorbing liquid on a pure Al substrate the reflectivity is analysed through the use of the admittance function. Power reflection profiles are obtained for various film depths and are shown to be distinctly and usefully dependent on angle of incidence and the polarisation of the incoming radiation. The profiles are especially interesting in pi polarisation near the Brewster angle.

INTRODUCTION

This letter introduces a new technique of analytical spectroscopy based on variable angle reflectivity of radiation incident upon inhomogeneous condensed matter. If electromagnetic radiation is directed at the surface of this layered system it is reflected from the surface and buried layers. Spectral analysis of the reflected radiation provides a new method of investigation which has two major advantages over conventional power absorption spectroscopy:

- i) The reflected spectrum is dependent on the angle of incidence providing much more information per experiment by varying this angle;
- ii) The reflected radiation has a different frequency dependence in pi and sigma polarisation.

There has been little attempt to exploit these advantages for systems of interest because the implementation of Maxwell's equations for inhomogeneous media is much more difficult than for homogeneous systems such as

molecular liquids, where the Beer Lambert law is applicable. In this letter we look at an inhomogeneous layered system consisting of a thin liquid film on a pure aluminium substrate. By solving the equations governing the reflection of electromagnetic radiation from the surface layer and interface of the liquid layer with the aluminium a great deal of new information is obtained theoretically which could be useful in direct spectral analysis of the surface liquid film by reflectivity of laser radiation under carefully controlled conditions. For a given power absorption profile in the surface liquid film the use of the admittance method [1-4] produces power reflection profiles in sigma and pi polarisation which depend intricately on the angle of incidence and depth of the surface liquid film. This provides a considerable amount of new information which is not available in conventional power absorption. To our knowledge this is the first time that the Maxwell equations have been solved for a system consisting of a surface liquid film on an aluminium metal substrate. By simply reflecting a tunable laser beam from this surface and analysing [5] the reflected radiation a new and useful spectroscopic technique can be developed experimentally for films of thickness down to a few angstroms. This technique could also be of use for the spectral, contactless, analysis of low dimensional materials.

#### THEORETICAL METHODS

The electric and magnetic field vectors  $\vec{E}$  and  $\vec{H}$  of angular frequency  $\omega$  obey the following differential equations in an inhomogeneous medium of relative permittivity  $\hat{\epsilon}$  (usually a complex function), and a relative permeability of  $\mu = 1$ :

$$\Delta \vec{E} + (\omega^2/c^2)\hat{\epsilon}\vec{E} - \text{grad div } \vec{E} = \vec{Q} \quad (1)$$

$$\Delta \vec{H} + (\omega^2/c^2)\hat{\epsilon}\vec{H} + (1/\epsilon)(\text{grad } \hat{\epsilon} \times \text{rot } \vec{H}) = \vec{Q} \quad (2)$$

It is assumed that the system is infinite in directions  $x$  and  $y$  and inhomogeneous only in axis  $z$ :

$$\hat{\epsilon} = \hat{\epsilon}(z). \quad (3)$$

The interfaces in the system are parallel to plane  $(x,y)$  and the inhomogeneous layer is on a homogeneous substrate of infinite thickness. In this system the dependence of the field vector on  $z$  will be treated separately for  $\sigma$  and  $\pi$

polarisation. In  $\pi$  polarisation the electric field is parallel to the plane of incidence, and for  $\sigma$  polarisation perpendicular. The  $\sigma$  polarisation corresponds to the transverse electric (TE) mode, with  $\underline{E}$  in direction  $y$  and the  $\pi$  polarisation to the transverse magnetic (TM) with  $\underline{H}$  in direction  $y$ . The transverse field components  $E_y$  and  $H_y$  then obey the following differential equations

$$\frac{\partial^2 E_y}{\partial z^2} + \frac{\omega^2}{c^2} (\hat{\epsilon} - \sin^2 \phi_0) E_y = 0 \quad (4)$$

$$\frac{\partial}{\partial z} \left( \frac{1}{\hat{\epsilon}} \frac{\partial H_y}{\partial z} \right) + \frac{\omega^2}{c^2} \left( 1 - \frac{\sin^2 \phi_0}{\hat{\epsilon}} \right) H_y = 0 \quad (5)$$

If now the admittance function is defined as:

$$\hat{j}(z) = - \left( \frac{\mu_0}{\epsilon_0} \right)^{\frac{1}{2}} \frac{H_t(z)}{E_t(z)} \quad (6)$$

then according to the boundary conditions of Maxwell's equations  $H_t$  and  $E_t$  the transverse components are continuous so  $\hat{j}(z)$  is a continuous function of  $z$  in the system, unless  $E_t = 0$  when the admittance function becomes infinite. The interaction of laser radiation with the inhomogeneous system then can be described with the following differential equations in the admittance function

$$d\hat{j}_{TE}/dz = -(i\omega/c) [\hat{\epsilon} - \sin^2 \phi_0 - \hat{j}_{TE}^2] \quad (7)$$

$$d\hat{j}_{TM}/dz = -(i\omega/c) [(1 - \sin^2 \phi_0/\hat{\epsilon})\hat{j}_{TM}^2 - \hat{\epsilon}] \quad (8)$$

These equations can be solved using the method of Hild and Crofcsik [3,4] and this method is described fully for epitaxial semiconductors in a recent paper by Hild and Evans. [6] Particularly interesting and significant effects were found in epitaxials near the Brewster angle [5,6] and it is shown in this letter that this is also the case for absorbing liquid films on an aluminium substrate.

#### OPTICAL COEFFICIENTS FOR THE ALUMINIUM SUBSTRATE

The optical properties of metallic aluminium have recently been investigated thoroughly [7] from the far infra red to the ultra-violet, and it can be estimated that the permittivity of metallic aluminium up to about  $200 \text{ cm}^{-1}$  is approximately constant at 1.5 and that the dielectric loss is approximately constant at about 320,000. Therefore it is convenient to look

in the far infra red region at the inhomogeneous system represented by a highly absorbing liquid film on metallic aluminium substrate, e.g. a well polished aluminium mirror. For a constant permittivity and dielectric loss the Brewster angle is also constant, and for aluminium substrate is, in the far infra-red:

$$\phi_B = \tan^{-1} 320,000^{\frac{1}{2}} = 89.8987^{\circ}$$

This means that in pi polarisation the reflectivity spectrum becomes extremely sensitive to angle of incidence a few minutes of arc above the parallel. With a laser beam directed at the surface liquid film at this glancing angle it is shown in this letter that low angle reflectivity of this nature is able, in pi polarisation, to detect and characterise a surface liquid film only one angstrom in thickness. This method therefore has obvious potential in looking at surface low dimensional materials, monolayers and interfaces between materials.

#### ILLUSTRATIVE RESULTS

These are given for the dielectric loss and permittivity of fig. (1) and for various depths of surface liquid layer and angle of incidence  $\phi$ .

In fig. (2) the depth is 0.1 mm. The static permittivity of the surface liquid film is set at  $\epsilon_0 = 70.0$  and the infinite frequency permittivity at 3.5. For an angle of incidence at  $62^{\circ}$  in fig (2) detailed power reflectivity fingerprints ( $R_{\sigma}$  and  $R_{\pi}$ ) are observable both in sigma and pi polarisation which are very significantly different in appearance from the conventional absorption curves of fig (1). the  $\sigma$  and  $\pi$  spectra cover the full

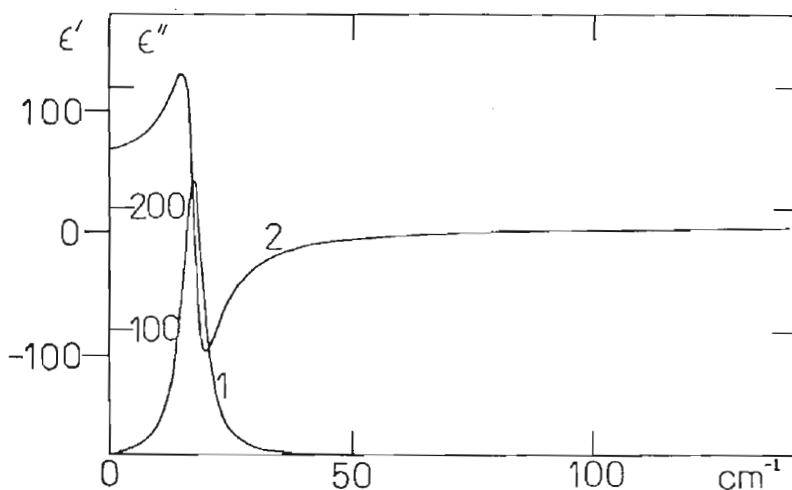


Fig. 1 The basic dielectric loss (1) and permittivity (2) used for the surface liquid film to generate the power reflectivity curves of figs. (2) to (4).

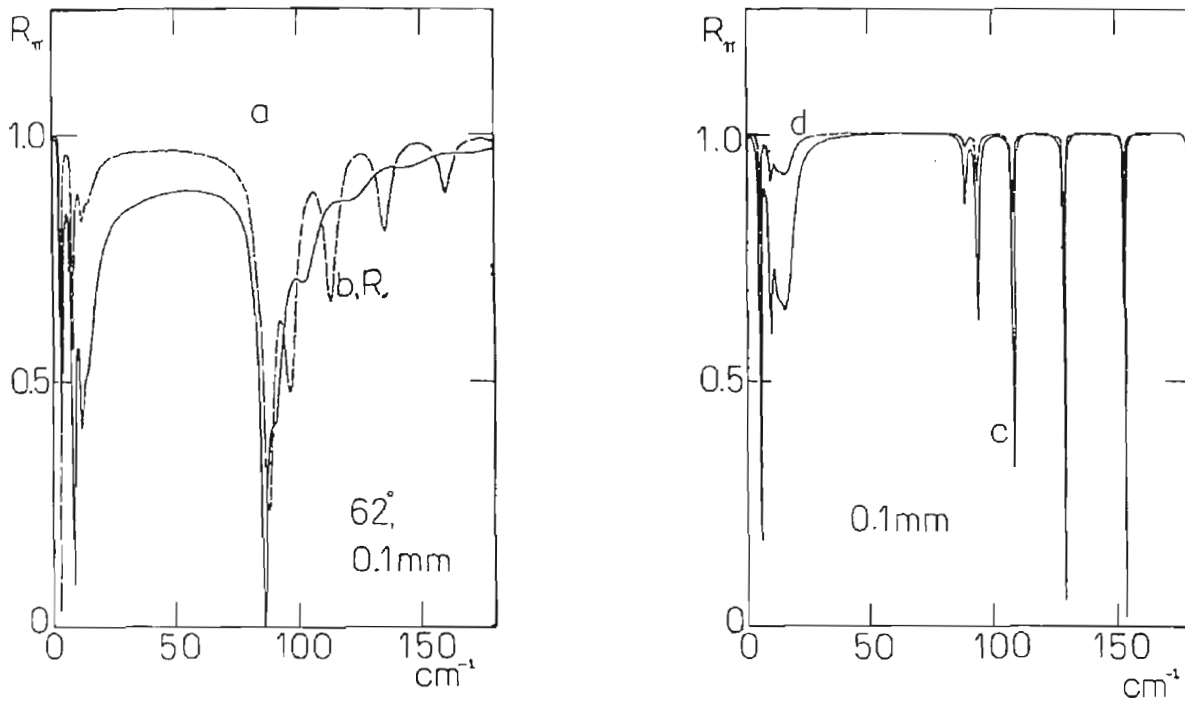


Fig. 2 Reflectivity on an aluminium substrate. Film depth =  $1.0 \times 10^{-2}$  cm.

- a)  $R_{\pi}$  at  $\phi = 62^{\circ}$ .
- b)  $R_{\sigma}$  at  $\phi = 62^{\circ}$
- c)  $R_{\pi}$  at  $\phi = 89.5^{\circ}$
- d)  $R_{\pi}$  at  $\phi_B = 89.8987^{\circ}$

scale from unit to zero giving plenty of opportunity for spectral analysis of the surface liquid layer. For  $\phi$  just below the Brewster angle (fig. (2)) the  $R_{\pi}$  spectrum has "inverted" at low frequencies and the high frequency full scale fringes have sharpened and are well defined. In  $\sigma$  polarisation (not shown) the reflectivity at low frequency, in great contrast, is dominated completely at this angle by that of the Al substrate (0.997). Nothing is therefore observable in  $R_{\sigma}$  except some residual high frequency fringes, which appear in a different frequency pattern to those illustrated in fig. (2(c)) at  $R_{\pi}$ .

At the Brewster angle of  $\phi = 89.8987^{\circ}$  (fig. (2(d))) the  $R_{\pi}$  spectrum has shifted up scale and is approaching the value of 1.0000 for all  $\bar{\nu}$  expected at  $\phi = 90.0000^{\circ}$ , when the radiation does not, of course, enter the sample, being precisely parallel to the surface of the liquid. For this depth of liquid layer the spectrum does not change dramatically in shape near the Brewster angle, but the fringes are "dampened" from full scale

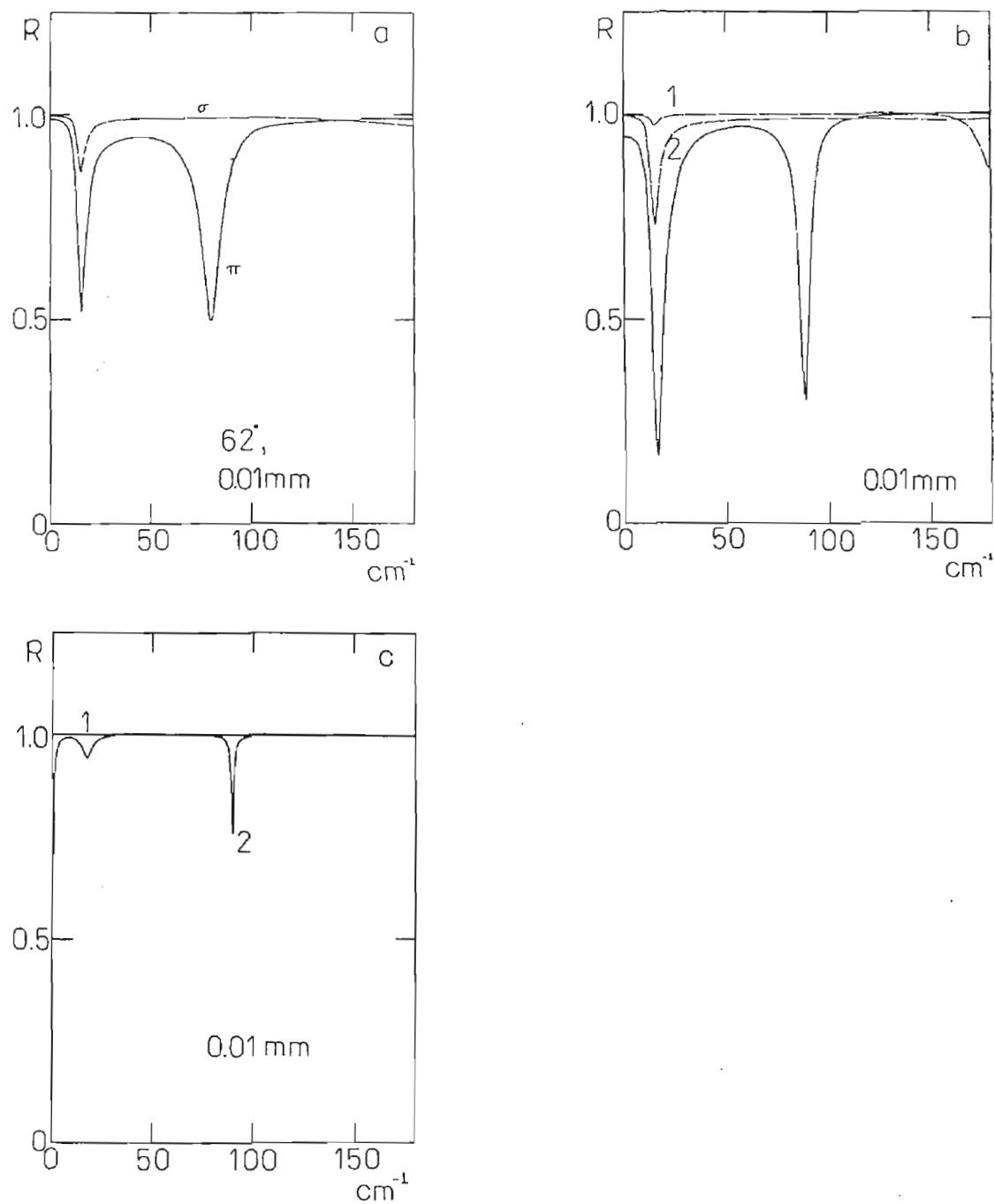


Fig. 3 As for fig (2), film depth =  $1.0 \times 10^{-3}$  cm.

- a) - - - -  $R_{\sigma}$ ; -  $R_{\pi}$  at  $\phi = 62^{\circ}$   
 b) (1) - - - -  $R_{\sigma}$ ; -  $R_{\pi}$  at  $\phi = 85.000^{\circ}$   
 (2) - - - -  $R_{\sigma} = R_{\pi}$  at  $\phi = 0^{\circ}$   
 c) - (1)  $R_{\sigma}$ ; - (2)  $R_{\pi}$  at  $\phi = 89.8987^{\circ}$

(fig. 2(c)) to about quarter scale for about 30 arc minutes change in angle. The amplitude of the spectrum is therefore extremely sensitive to angle of incidence near the parallel.

For a surface liquid depth of  $100,000 \text{ \AA}$  the reflectivity spectra are completely different in appearance (fig. (3)) from those of fig (2). At  $\phi = 62^\circ$  (fig. (3a) there are no interference fringes visible because they have become widely separated in frequency. The minima of the  $R_\pi$  peaks correspond exactly with the frequency in fig. (1) of the maximum of the dielectric loss ( $17.5 \text{ cm}^{-1}$ ) and the frequency ( $76.0 \text{ cm}^{-1}$ ) at which the permittivity cuts the abscissa for the second time, negative to positive. Fig. 3(b) contrasts the  $R_\pi$  and  $R_\sigma$  profiles at  $\phi = 0$  (normal incidence) and  $\phi = 85^\circ$  (low angle of incidence). At  $\phi = 0$ ,  $R_\sigma = R_\pi$  and the reflectivity consists of one inverted peak at  $17.5 \text{ cm}^{-1}$ . At  $\phi = 85^\circ$  in great contrast the  $R_\sigma$  profile is dominated by the aluminium substrate, and the  $17.5 \text{ cm}^{-1}$  feature is barely visible. In  $R_\pi$  two features are clearly visible, at  $17.5 \text{ cm}^{-1}$  and  $76 \text{ cm}^{-1}$ , and are almost full scale. Therefore it would be much more useful to study the  $R_\pi$  profile at  $\phi = 85.0000^\circ$ . Fig. 3(c) illustrates  $R_\sigma$  and  $R_\pi$  at the Brewster angle  $\phi = 89.8987^\circ$ . The  $R_\pi$  profile has shifted upscale, as in fig. 2(d) but now there is visible in fig. 3(c) a clear change of shape in because there has appeared around zero frequency a new spike. Therefore the  $R_\pi$  spectrum now consists of three clear features, but the  $R_\sigma$  spectrum in great contrast is simply a constant very close to 1.000 for all  $\bar{\nu}$  and tells us nothing at all.

There is no space here for further illustration, but for a surface liquid depth of  $10,000 \text{ \AA}$  the  $R_\pi$  profile becomes dominated entirely by a single full scale feature at  $76 \text{ cm}^{-1}$  which appears only as the angle of incidence is increased from zero (normal incidence). At normal incidence this  $76 \text{ cm}^{-1}$  spike vanishes completely, thus showing how much information is lost by restricting the experimental investigation to normal incidence. In this case it loses everything that there is to observe. As the incidence angle is increased to  $85^\circ$  the  $76 \text{ cm}^{-1}$   $R_\pi$  feature is broadened and flattens to half scale, and the original  $17.5 \text{ cm}^{-1}$  feature becomes just visible as a shallow, broad trough. However as the incidence angle is increased to the Brewster angle there is a great change in the appearance of the spectrum in  $R_\pi$ . The high frequency spike again becomes much sharper and to full scale, but is shifted to  $89 \text{ cm}^{-1}$ . Additionally a pronounced zero frequency spike changes the aspect at low frequency, the original  $17.5 \text{ cm}^{-1}$  feature having completely disappeared.

In great contrast the  $R_\sigma$  profile is simply total reflection for all  $\bar{\nu}$ .

Therefore as liquid thickness changes the reflectivity fingerprints change significantly and characteristically. Therefore the technique

investigated theoretically here is likely to be of great use in investigating surface films and low dimensional materials. The reflectivity fingerprints for slight changes in the thickness of the liquid film are quite distinct and easily recognisable. These patterns are generated mathematically and therefore entirely consistently from the one simple loss peak of fig. (1).

The equivalent patterns for  $1000 \text{ \AA}$  are again quite distinctly different but are developments of those discussed above. These will be reported in full elsewhere. Note that most of the information is to be found in the arc minutes interval between the Brewster angle and the parallel.

#### SURFACE LIQUID LAYERS OF $100 \text{ \AA}$ AND LESS

In this limit there is room only for about twenty small molecules on rough average from the surface of the liquid to the surface of the aluminium. For  $100 \text{ \AA}$  the dependence of the reflectivity on incidence angle is a development of the pattern for  $1000 \text{ \AA}$  in that the sharp zero frequency feature which made its appearance in fig. (3c) has broadened across the whole spectrum for  $100 \text{ \AA}$  which is in the process of transition to one composed of a feature centred

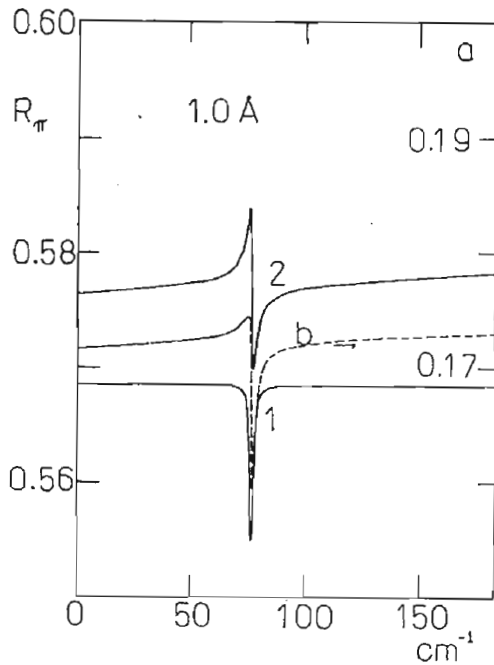


Fig. 4 Surface film depth = one angstrom.  
 a) -  $R_{\pi}$  at  $\phi = 89.5^{\circ}$  ; - (2)  $R_{\pi}$  at  $\phi = 89.98^{\circ}$   
 b)  $R_{\pi}$  at  $\phi = 89.90^{\circ}$



around  $76 \text{ cm}^{-1}$  superimposed on a fairly constant background, the level of which in  $R_{\pi}$  is determined by the incidence angle  $\phi$ . At around the Brewster angle there is now the familiar sensitivity of  $R_{\pi}$  on  $\phi$  both in shape and amplitude, so that a  $100 \text{ \AA}$  layer is quite easy to characterise. Note that  $R_{\sigma}$  again gives no information.

For a surface film depth of one angstrom; Fig. (4) illustrates the experimentally detectable change in signature as we sweep through the Brewster angle from  $89.500^{\circ}$  to  $89.980^{\circ}$ . The result at the Brewster angle itself is shown in Fig. (4b) and shows the considerable fall in background level.

#### CONCLUSIONS

These theoretical results show in detail that the use of reflectivity near the Brewster angle in pi polarisation is of original practical importance in the study of surface films and similar materials. The information available per investigation greatly exceeds the data available from conventional power absorption spectroscopy, even if this were to be applicable.

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