A THEORETICAL ESTIMATION OF POWDER REFLECTION SPECTROSCOPY AS AN ANALYTICAL TECHNIQUE

J.R. CUNDEF
Chemistry Department, University College of Wales, Aberystwyth, SY23 3EB, Wales.
(Received 3 October 1979)

ABSTRACT

The potential of powder reflection spectroscopy is investigated theoretically in the following areas:

(i) Reflection from liquid crystals, melts and conducting media;
(ii) Molecular suspensions;
(iii) Semiconductors;
(iv) Gas/solid and liquid/solid interfaces.

There are significant advantages in each area of application, especially where the angle of incidence \( \theta \) can be varied through the Brewster angle range. Measurements near the Brewster angle are especially interesting.

INTRODUCTION

In this paper we aim to explore theoretically the potential advantages of reflection spectroscopy in several fields of application where the technique of absorption is restricted by the nature of the sample or of the experiment. For example, studies of reactions at gas-solid and gas-liquid interfaces may be carried out with advantage by reflection a beam from the solid surface. In addition, the technique of reflection has the added advantage that both the real and imaginary parts of \( \chi^{(2)} \) are measured simultaneously, here \( \chi \) in the complex susceptibility.

The paper is developed as follows. Firstly we recall briefly the fundamental equations of reflection spectroscopy. The next section deals with the advantages of reflection radiation from polycrystalline material, where loss measurements require the use of very thin samples and often
blocking electrodes with associated Maxwell-Wagner losses. In section 5 we apply the method to lossy material such as aqueous biomacromolecular suspensions studied at low frequencies. Lastly we emphasize the use of the technique at gas/solid and gas/liquid interfaces.

Section 1

The measurement of power absorption coefficient or dielectric loss in absorption spectroscopy is replaced by that of the power reflection coefficient \( R \), which is the ratio of reflected intensity to incident intensity. If the incidence angle, \( \theta \), is zero, i.e. if the incident radiation is normal to the reflecting surface, then the emerging beam is unpolarized. In general, however, \( R \) has two components \( R_\parallel \) and \( R_\perp \).

If the direction of vibration of the radiation is taken with respect to the plane of incidence the component of the radiation vibrating parallel to this plane is denoted by the subscript \( \parallel \), and that vibrating perpendicular to by \( \perp \). The reflective power for each component is defined in terms of \( \theta \) and the refracting angle by Fresnel's formulae:

\[
\begin{align*}
r_\parallel &= \frac{\sin^2(\theta-\phi)\sin^2(\phi)}{\sin^2(\theta-\phi)} \\
r_\perp &= \frac{\tan^2(\theta-\phi)}{\tan^2(\phi)}
\end{align*}
\]

(1)

The angles \( \theta \) and \( \phi \) are connected by Snell's law:

\[
\sin \theta = n \sin \phi
\]

where \( n \) is the refractive index of the substance under investigation.

In general, from Maxwell's equations:

\[
\begin{align*}
\varepsilon_0 \mu_0 &= \varepsilon_\infty / \kappa \quad \text{and} \quad \varepsilon_0 \mu_0 &= \varepsilon_\infty / \kappa
\end{align*}
\]

\( \kappa \) is the complex dielectric. It follows that if \( \varepsilon_\infty = n^2(1-\kappa) \)

\[
\begin{align*}
\varepsilon' &= \frac{\varepsilon_0 \varepsilon_n}{\mu_0} \\
\varepsilon'' &= \frac{\varepsilon_0}{n^2} \kappa
\end{align*}
\]
where:

\[
\alpha = \left[ \left( \cos^2 \left( \frac{1}{2} \theta \right) \sin^2 \theta \right) \left( \cos^2 \left( \frac{1}{2} \theta \right) - \sin^2 \theta \right) \right]^{1/2}
\]

\[
\sin^2 \theta = \frac{1}{2} \left( \frac{1}{2} \left( \cos^2 \left( \frac{1}{2} \theta \right) - \sin^2 \theta \right) + \cos \theta \right)
\]

The apparent complexity of these relations is no obstacle with available computers.

The reflection from a surface of a polarized beam of radiation is a method which is potentially more revealing than absorption spectrometry, especially since both \( R_x \) and \( R_y \) can be measured throughout the range of \( \theta \), the incident angle. At the Brewster angle, which we define by

\[
\tan \theta_B = \frac{\lambda}{2\pi}
\]

where \( \lambda \) is the wavelength of light, the complex refractive index \( n \) is real, and the extinction coefficient \( k \) is zero, some interesting effects are revealed by the theoretical model we develop in the following sections. If these were investigated experimentally, a new source of spectral information would be utilized.

**Section 2**

**Reflection from Salts and Conducting Media**

For an ionic crystal, the dielectric permittivity is

\[
\varepsilon = 1 + \varepsilon_{\text{elec}}
\]

where \( \varepsilon_{\text{elec}} \) is the susceptibility due to the distortion of the electron distribution by the electromagnetic field and \( \varepsilon_{\text{ion}} \) arises from ionic displacements during lattice vibrations. It is usual to define a high frequency or 'optical' dielectric constant by the relation

\[
\varepsilon = 1 + \varepsilon_{\text{elec}}
\]
to develop theoretical expressions for the reflection spectrum from an ionic lattice we may follow the classical Born analysis of an isotropic (cubic) ionic, lossy lattice, with the equation of motion:

\[ \dddot{X} + 2\gamma \ddot{X} + \frac{k_B T}{m} \dot{X} = e^{2\text{int}} \]

(7)

Here \( \gamma \) is a damping constant, defined by:

\[ \frac{1}{\gamma} = \frac{1}{\gamma_1} + \frac{1}{\gamma_2} \]

(8)

where \( \gamma_i \) is the mass of ions type 1 and \( \gamma_2 \) that of type 2. \( e \) is a relative displacement of the ionic coordinates, \( \gamma \) is a damping factor to allow for the loss process, and \( \nu_0 \) is the frequency of the optical lattice mode.

It follows that:

\[ \nu = \frac{e^{2\text{int}}}{\frac{2\gamma k_B T}{m}} \]

(9)

\[ \nu_0 = \frac{e^{2\text{int}}}{\frac{2\gamma k_B T}{m}} \]

(10)

where \( \nu \) is the frequency of the unit cell. If the primitive cell contains more than one intra-atomic active frequency, each (8) and (9) can be generalized to account for such frequencies. The ionic charges, \( z_i \), are replaced by an effective charge:

\[ e^{2\text{int}} \]

where \( \frac{e^{2\text{int}}}{\frac{2\gamma k_B T}{m}} \) is the equilibrium value of the derivative of the lattice moment with respect to the mass-weighted normal coordinate \( \nu_0 \). In general, therefore, eqns (8) and (9) take the form:

\[ \frac{1}{\gamma} = \frac{1}{\gamma_1} + \frac{1}{\gamma_2} \quad \frac{e^{2\text{int}}}{\frac{2\gamma k_B T}{m}} \quad \frac{e^{2\text{int}}}{\frac{2\gamma k_B T}{m}} \]

(11)
In the case of eqs (10) to (13) we can make some relevant data from a paper by Theogmich, Frenkel, and Tsang, on reflection of light from lithium niobate single crystals at infrared frequencies, and concentrate particularly on the $S_2$ component near the Brewster angle:

$$i = \tan^{-1} \left( k_x \frac{\sin \theta}{k_y} \right)$$

(13)

The experimental reflection data from about 30 cm$^{-1}$ to 2000 cm$^{-1}$ can be reproduced almost perfectly by eqs (10) and (11) for an incidence angle of $i = 2\theta$ for $S_2$ polarization for both $S_2$ and $S_3$ symmetry species present in the crystal. The theoretical spectra for the $S_2$ species are reproduced in fig (1). However, using now the value of $\omega = 2$ listed by those authors we may investigate theoretically the effect of varying the incidence angle $i$ on the bands and band intensities. Determination with the actual experimental data that provides us with a means of investigating the point of breakdown of the hands of the model used. In $S_2$ polarization near the Brewster angle the bands and intensities are changed significantly, but dramatically so in $P_2$ polarization (fig.1(a)) where the attenuation is heavy, of course, but not complete. A powerful, polarized, incident, tunable laser beam reflected at the Brewster angle in $P_2$ polarization could be detected to build up the type of information illustrated theoretically in fig.1(b). Note that new peaks and troughs appear in the spectrum near $G_y$ as a result of the fundamental equations of reflectivity which are derived from Maxwell's equations in the relevant context. Also, at very high frequencies the $S_2$ attenuation increases steadily to a peak (fig.1(c)) which could be used for the purposes of characterisation provided the attenuation problems could be met.

Next we investigate the possibility of characterising the dielectric relaxation processes of electrolyte solutions using reflection of radiation
(a) Calculated reflection spectra for lithium potassium sulphate in polarization, using eqns. (10) and (11) with the parameters of Hirokata et al.

\[ \theta = 2\theta_f \]

\[ \theta = \theta_0 \pm \frac{1}{2} \theta_0 \]

Refined: \( \theta_0 \) side

(b) The curve in (a) polarization.

Refined: \( \theta_0 \) side

(c) High frequency part of Fig. (1a)
over a broad span of frequencies. In these media the complex permittivity is expressed in the corrected form:

$$\varepsilon = \varepsilon' - i\varepsilon'' = \varepsilon'' - i \varepsilon'$$

(13)

where \( \varepsilon \) is the conductivity, a real quantity. The Debye/Palke/Sheahan effect, however, produces a complex conductivity so that, strictly, \( \varepsilon' \) should also be corrected for the effect. Moreover the form of eqn. (13) already implicitly assumes that the micropolar behaviour of the solution allows this kind of separation of terms. This is by no means clear, but for our present purposes we take eqn. (13) as an useful empiricism. In eqn. (13) \( \varepsilon \) is the absolute permittivity of free space.

In investigating conducting solutions electrically there is the problem of measuring a complex permittivity characterized by a very high loss tangent when working with the low frequency end of the spectrum (i.e. below 100 MHz). On top of this it is not possible to obtain the response of bulk liquid without involving simultaneously that of the solution-electrode interface. Below 100 MHz the conventional methods involve bridges of the Scheiner type, for example, \( \varepsilon' \) being proportional to the cell capacity, \( \varepsilon'' \) to the cell conductance, after due correction for transmission line effects, eddy currents, and electrode polarization. The relevant corrections are often complicated and difficult to apply. Recently, however, there has been a renewed interest in these systems because of their importance in areas of biological activity. Above about 100 MHz the accuracy in \( \varepsilon' \) may be poor from conventional methods because it is calculated after the difference between the large number of measurements on fused salts such as sodium nitrate are particularly prone to this drawback. Finally, time-domain and sweep-frequency methods have not improved matters significantly.

The very simple behaviour of a liquid of radiation from such free-molecular conducting liquid surfaces may be of use in nucleating
Figure (2)

Low frequency reflectivity in conducting media in \( S_e \) polarization at the greater angle.

---

Three variable Mori model of the orientational autocorrelation function.

---

Internal field correction to the Mori model as used by Lobo et al.

\[ (1) \quad \sigma = 10^{-6} \text{ cm}^{-1} \]

\[ (3) \quad \sigma = 10^{-5} \text{ cm}^{-1} \]

**Ordinate:** \(-\log \theta_s\)  
**Abscissa:** \( \log (\sigma) \)
the conventional methods when these prove of unascertifiable accuracy. In principle, the more conducting the medium, the easier it becomes to detect the reflected radiation. Fig. (5) is a theoretical estimate of the $\beta$ component at the Brewster angle using two models 12 of the molecular motion, with and without an internal field correction. One is a Mori three variable approximation applied directly to the orientational autocorrelation function, the internal field being accounted for by the method of Lobe. 11 Robinson and Rodrigues, who used dielectric friction as envisaged by 15 Scaife 12, by Lee and Tammann. 14 Fig. (1) shows that even at the heavily attenuating Brewster angle of incidence, the lower the frequency and the higher the conductivity the easier it becomes to measure the reflectivity $R_1$ (or $R_\pi$) and thereby the complex refractive index. Real and imaginary parts are, of course, measured simultaneously. At frequencies lower than about 100 MHz, the experimental difficulties are as follows:

(1) Control of polarization;
(2) Control of beam direction;
(3) Detection.

At 100 MHz and into the microwave region conventional waveguide techniques could be adopted straightforwardly. The necessary apparatus for work at far infra-red frequencies (300) is already available, designed by Birnboim. 15 Typical theoretical reflection coefficients in this region are illustrated in Figs (5) and (6). The variation of incident angle, $\phi$, proving particularly useful when characterising limits state molecular dynamics with theoretical models.

Section 3
Reflection Properties of Biological Systems

The difficulties of making conventionally dielectric measurements on biological systems have been known for many years. These are usually carried out in aqueous media, and static permittivities can reach into the
Figure (1)
Reflectivity spectra: (1) $R_1$; (2) $R_2$ for a dipolar liquid.

--- Mori three variable theory
--- Mori theory corrected for the internal fields using the Method of Lobo et al. $\varphi = 50^\circ$.

 ordinates: $-\log R$; abscissae: $\log (\omega)$
In order of magnitude, Maxwell/Wagner, or interfacial, effects are an added complication because of the size of the molecules under investigation. Generally large dielectric increments can be obtained through effects due to polarization of counterion distribution in the interface between the particle and the surrounding fluid medium. This gives rise to intense absorption at low frequencies (the α process, for example, in the range 1 - 10 kHz). These properties are changed remarkably by the application of an external field, which is, of course, the measuring field in conventional terms. However, if reflectivity methods could be applied in the kHz range (audio frequencies) the applied electric field could be increased in strength to the point of breakdown, or pulsed past this point, the dielectric properties being monitored through the reflection coefficient \( R = \left| R_\text{in} + R_\text{out} \right| \). The reflectivity measurements of the surface of the biological system would usefully complement conventional measurements of the bulk using bridge and capacitance methods. In fig. (5) we illustrate a hypothetical (model) reflectivity curve for a dielectric increment of \( \varepsilon_\infty = 1000, \varepsilon_0 = 5, \delta = \text{one} \text{eV} \). The \( R_\text{in} \) and \( R_\text{out} \) curves are corrected again for internal field effects as in fig. (3). The reflected intensity is sufficient to be measurable provided the incoming and reflected beams can be controlled and detected experimentally. Clearly the higher the dielectric increment the easier it is to reflect a beam from the surface of the material under consideration. This is used to advantage in the next section, where we consider semiconductors and gas-solid interfaces.

Section 3: Semiconductors and Gas-Solid Interfaces

The far infrared absorption of a semiconductor are naturally very intense but provide useful information on a variety of phenomena. These include plasma absorption at low frequencies and absorption by transverse optical lattice modes at higher frequencies, reviewed by Chalmers. These
Figure 3

Low frequency reflectivity for an inhomogeneous species.

- - - Variable part theory and --- Lake theory.

\[ \theta = 180^\circ , \quad \phi = 1 \text{ radian}. \]

\[ \text{Estimate: } \quad \log \tau \quad \text{Estimate: } \quad - \log (\tau). \]

will be observing due to volume resonant if the specimen is in a
dynamic field. These are also detectable features due to localized
changes at interfaces between sites, or due to the excitation of the usual
resonances within species or clusters. However, the specimen's high
efficiency in terms of important resonances such as \( \theta \),
the lifetime of excited states \( \phi \), and the electron - spin relaxation.
the effective mass of the particle of charge \( q \) under linearization. For example, when employing the technique of far infrared cyclotron resonance spectroscopy the particle \( m^* \) will rotate in a circle with a cyclotron frequency \( \omega_c = \frac{qB}{m^*} \), where \( B \) is the applied magnetic field strength. In semiconductors the resonance can arise both from the electrons and the holes, and for both \( m^* \) can differ greatly from \( m_e \).

In plasmas, where electron−ion collisions have the effect of mixing the plasma components and to keep the resistive index real we have for the real and imaginary parts of \( \omega_c \):

\[
\begin{align*}
\omega & = \sqrt{\left( \frac{\mu_e}{\mu_i} \right) \left( \frac{v_0^2}{v_i^2} \right) + \left( \frac{\nu_i}{\nu_0} \right)} \\
\omega_i & = \sqrt{\left( \frac{\mu_e}{\mu_i} \right) \left( \frac{v_0^2}{v_i^2} \right) - \left( \frac{\nu_i}{\nu_0} \right)}
\end{align*}
\]  

(14)

Here \( \nu_i \) in the plasma frequency, given by:

\[
\nu_i = \sqrt{\frac{e^2}{\epsilon_0 m_e}}
\]

(15)

and \( \epsilon_0 \) is the lattice dielectric constant. As \( v \rightarrow 0 \) we have

\[
\begin{align*}
\omega & \approx \frac{\mu_e v_0^2}{\mu_i v_i^2} \\
\omega_i & \approx \frac{\nu_i}{\nu_0}
\end{align*}
\]

The Lorentz angle is therefore given by \( \theta_L = \frac{\omega_i}{\omega} \). This has suggested an apparatus for reflectivity measurements in the far infrared of semiconductors at normal incidence \( (\delta = 0) \). From the measured reflectivity spectrum and its measured minimum, the plasma frequency can be calculated, and \( H_0 \) calculated for a given \( m^* \).

It is clear that reflectivities at both polarizations over a range of \( \delta \) will be a source of extra information, especially when considering bandstructure theories more complicated than \( m_e \) and \( m_i \). Some reflectivity curves from eqs (15) to (16) are illustrated in fig (4). Hence, near the Lorentz angle, the spectrum is significantly different in the \( \omega \) polarization and is therefore a useful source of information on bandstructure behaviour.
Figure 5

Reflection spectra from eqns (15) and (16) for various values of p

\[ 1.1 \quad 15 \]

\[ 0.5 \]

50 150
really in this paper as consider qualitatively some possibilities of applying reflection spectroscopy to the study of gas-solids interactions. Recently Klein and co-workers have developed a theory of the many-body chemical dynamics relevant to this problem by adopting a continued fraction formalism similar to that of Veri. The formal perturbation is of wide applicability in that it reduces the general multi-body problem to one of determining experimentally a vastly smaller number of equilibrium thermodynamic state energies.

In the simplest case the equation of motion governing the system is a generalized Langevin equation:

\[ \ddot{X}(t) = - \frac{\partial W}{\partial X}(X, \dot{X}) + \zeta \dot{X}(t) + \int_0^t g(t-s) \dot{X}(s) \, ds \]  

where \( X \) and \( \dot{X} \) and \( \zeta \) and \( g \) are respectively the coordinates and momenta of the incident gas particle and struck surface atom; \( W(X, \dot{X}) \) is the atom-solved potential energy function. Eq. (17) is the collective equation of motion and the bath bath response function \( W(t) \) is that in the absence of the gas atom. This is rigorous only if the gas is perfectly harmonic, but is otherwise an approximation. The potential energy function \( W(X, \dot{X}) \) can include the static influence of the bathed solid atoms as well. It can depend on the equilibrium position of all atoms in the solid. The damping kernel \( \zeta(t) \) contains the following effects:

(1) The influence of the nuclear motion of all bathed solid atoms on the dynamics of the primary system
(2) Any influence of intermolecular degree of freedom, such as electronic or spin, on atomic motion.
(3) Anharmonicities in the primary system motion.

The influence of gas-solids motions on an infra-red spectrum such as that of fit (3) could be detected by reflection spectroscopy provided
\( \rho(t) \) of eqn. (13) were replaced by such as the relative ionic displacement of eqn. (7), so that the correlation function \( \rho(t) \rho(0) \) could be transformed into an observable infrared reflection spectrum, using an approach of the continued fraction expansion of eqn. (18). The measurement of laser radiation reflected from the reacting surface would be relatively straightforward.

**Discussion**

In this paper we have briefly considered the advantages of using reflection spectroscopy to investigate the dielectric properties of media which present problems when using conventional absorption or bridge techniques. These problems consist of intense absorption, electrode interface effects, Maxwell-Dragoe loci, bridge instabilities, etc., which could be remedied using the 'non-contact' technique of reflection spectroscopy. The latter is especially interesting in \( \varepsilon_r \) polarization near the Brewster angle of incidence provided the problems of attenuation would be overcome. In heavily absorbing media such an aqueous biocellular suspension the low frequency measurement of reflectivity, if experimentally feasible, could usefully complement the conventional bridge technique.

At far infrared frequencies, on the other hand, reflection measurements on semiconductors are already possible, which in principle provide useful information on charge carrier density and behaviour near the plasma edge. Extension of theoretical techniques to band structure analysis in semiconductors would benefit from measurements using a variety of incident angles.

**Acknowledgements**

'Thanks are acknowledged for financial support, and Dr. G. J. Brown for assistance with this work.'