Power Reflection Spectroscopy near the Brewster Angle
Molecular Dynamics of Liquids

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Power reflection spectroscopy has been investigated theoretically for potential use with dipolar liquids as a means of evaluating the molecular dynamics and interactions. Calculations have been made with and without a dynamic internal field correction. This does not affect in any way the major features of the spectra in any polarization at various values of $\phi$, the incidence angle. Near a Brewster angle ($\phi_B = \tan^{-1} n_2$, where $n_2$ is the high frequency permittivity), the reflectivity $r$ displays a high frequency peak, typically in the mid-infrared. This brings the study of librational molecular dynamics within range of conventional spectrometers, provided that the problem of amplification and detection of the reflected $\pi$ radiation can be overcome.

In principle, reflection spectroscopy provides us with information simultaneously both about the real and imaginary parts of the complex refractive index $\alpha^2 = \alpha^2 + i\beta^2$, where $\alpha^2$ is the complex dielectric permittivity of the surface under investigation. However, the fundamental equations of reflection spectroscopy are complicated and for this reason the absorption technique tends to be used almost exclusively, for example in the infrared. The computers available now remove this disadvantage. It is the purpose of this paper to show that measurements of the reflectivity ($R$) in the far- and mid-infrared is an additional useful source of molecular dynamical information which has as yet remained untapped. If we define by $\alpha_0$ the real part of $\alpha^2$ at static frequencies and by $\beta_0$ that at frequencies just past the f.f.r. Poley absorption, then polarized reflectivity measurements very near the incident Brewster angle $\phi_B = \tan^{-1} n_2$ are particularly rewarding; below we explain why. Effectively, our calculations show that the Debye and Poley features in $\alpha^2$ of dipolar liquids are shifted with higher frequencies using $\phi_B$ in $\pi$ polarization, thus bringing the former within range of the f.f.r. Michelson interferometer. And shifting the latter up into the mid-infrared ($\approx 200-1000$ cm$^{-1}$), bringing it within range of conventional grating spectrometers and making its measurement a routine matter gives sufficiently sensitive signal amplification. The paper is developed as follows. First, we specify our reflectivity equation. Secondly, a brief description is given of the molecular dynamical models used and the internal dynamical-field correction. We use linearised Mori 3 variable theory for the orientational autocorrelation function $\langle \phi(t) \cdot \omega(0) \rangle$, where $\phi$ is the molecular dipole moment. This model has been extensively tested by Evans et al. and has been adopted by Lebo et al. to incorporate the idea of dielectric friction introduced by Nee and Zwanzig and Scaife. This is the "dynamical equivalent" of the Onsager reaction field. Finally, we illustrate some theoretical spectra at various incident angles, $\phi$, (normal, Brewster and glancing) and discuss the implications.

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FUNDAMENTAL EQUATIONS OF POWER REFLECTION
SPECTROSCOPY

These are discussed fully by Brügel for infrared spectroscopy and in many fundamental
texts. However, we reproduce some here for convenience. Define the
reflective power $R(\phi)$ as the ratio of the energy reflected to that incident. Here
$\phi$ is the wavenumber in cm$^{-1}$. The direction of vibration of the radiation is taken
with respect to the plane of incidence. The component vibrating parallel to this
plane is denoted by $\pi$ and that perpendicular by $\sigma$. The reflective powers $r_\pi$ and $r_\sigma$
are then given by Fresnel's formulae and Snell's law, so that with polarised radiation:

\[
r_\pi = \frac{\sin^2(\phi - \chi)}{\sin^2(\phi + \chi)} \quad r_\sigma = \frac{\tan^2(\phi - \chi)}{\tan^2(\phi + \chi)} \quad \sin \phi = n^2 \sin \chi.
\]

Writing

\[
n^2 = n(1 - ic)
\]

it follows that

\[
r_\pi = \frac{a^2 + b^2 - 2a \cos \phi + b^2 \cos^2 \phi}{a^2 + b^2 - 2a \cos \phi + b^2 \cos^2 \phi},
\]

\[
r_\sigma = \frac{a^2 + b^2 - 2a \sin \phi + b^2 \sin^2 \phi}{a^2 + b^2 - 2a \sin \phi + b^2 \sin^2 \phi} \tan \phi + \sin \phi \tan \phi \tan^2 \phi,
\]

where

\[
a^2 + b^2 = \frac{[(\sin^2(1 - \kappa^2) - \sin^2 \phi) + (\sin^2(1 - \kappa^2) - \sin^2 \phi) + 4n^2\kappa^2]}{\sin^2(1 - \kappa^2) - \sin^2 \phi + (\sin^2(1 - \kappa^2) - \sin^2 \phi) + 4n^2\kappa^2}.
\]

The complexity of these relations is no obstacle using a convenient microprocessor
or main frame system. The $\pi$ and $\sigma$ polarised reflectivities may now be real-
ised to the molecular dipole autocorrelation function $\langle \phi(t) \cdot \mu(0) \rangle$ through the link

\[
\alpha = \frac{\alpha}{\alpha - \beta} = \alpha(1 - ic)^\beta.
\]

Here $c$ and $c'$ are the dielectric permittivity and loss, related to the infrared power
absorption coefficient $(\alpha)$ by

\[
\alpha = 2\pi\epsilon_0\omega/n
\]

with

\[
n = \frac{[\{e^{\alpha^2 + \omega^2} + e^{-\alpha^2 - \omega^2}\}]}{[\{e^{\alpha^2 + \omega^2} + e^{-\alpha^2 - \omega^2}\}]}.
\]

It remains now to model $\epsilon^*$ with a statistical dynamical mechanism designed to
produce the experimentally known $\tau$ features in dipolar liquids using a few equili-
brum averages. The shape and frequency dependence of $r_\pi$ and $r_\sigma$ for various $\phi$
may then be calculated and evaluated.

MOLECULAR DYNAMICAL MODELS

It is advantageous to use molecular dynamical models to illustrate various aspects of
reflection spectroscopy in the virtual total absence of the required reflection data at
far-infrared frequencies for intensely absorbing liquids at incident angles away
from the normal. The more sophisticated of these can be relied upon to describe
satisfactorily the major features of absorption spectra and therefore serve as indicators.
We have used two recent models, that of Lobo et al.\textsuperscript{3, 4} and that of Evans et al.,\textsuperscript{5} both with inertial and memory effects rebuilt. It is shown elsewhere\textsuperscript{6} that the former corresponds to the latter with internal field considerations added. These do not produce spectral features not already present in the version by Evans et al. We remark in passing that this means that the features labelled by Lobo et al. and Ascarelli\textsuperscript{7} as "plasmons" can be described by autocorrelation functions and cannot be attributed to collective electrodynamic oscillations.

In the following section we calculate reflection spectra from model fittings of known absorption spectra in the far infrared. The parameters \(K_0(0), K_1(0)\) and \(\gamma\) used in these fittings are explained fully in the literature.\textsuperscript{8, 9} We present some illustrative spectra and discuss the relative merits of power absorption and reflection spectroscopy.

**Illustrations of \(r_1\) and \(r_2\)**

The spectra are conveniently presented as \(\log_{10} \alpha_0\) against \(-\ln R\) (or against \(R\)) in fig. 1-14 for various \(K_0, K_1, \gamma\). The possibility of varying \(\phi\) in the experimental set-up and using \(\pi\) and \(\pi\) polarisation widens the range of data attainable in terms of number of spectral parameters. By using the same spectrometer, therefore, a much

![Graph showing \(r_1\) and \(r_2\) vs. \(-\ln R\)](image-url)

*Fig. 1. Theoretical absorption and reflection for liquid HCl: --- power absorption coefficient, \(\alpha_0\), Evans three variable theory \textsuperscript{10} (see table 1). (...) The same for the theory of Lobo et al.\textsuperscript{3} Power reflection coefficient, \(R\) at normal incidence (\(\phi = 0\)): \(\odot\), Evans theory; \(\circ\), Lobo et al. \(\varepsilon_0 = 28.6, \varepsilon_0 = 1.89\).*
Fig. 2.—(a) Nitromethane liquid. $-\ln R$ from Evans three variable theory, $R = r_0$ polarisation (see text). Reflection at a glancing angle of $\theta = 3.55^\circ$. Parameters quoted by Aucarel.$^7$

$d_0 = 25; r_0 = 3$. (b) $-\ln r_0$ against $\log_{10} n$. 
more rigorous testing of analytical theories is possible in using both reflection and absorption techniques. Reflection spectroscopy also has practical advantages when dealing with opaque absorbers, such as biological material or semiconductors.

Fig. 1 illustrates \( r_s \) and \( r_d \) at normal incidence for the very intensely absorbing liquid HCl, with the tabulated values of \( K_s, K_i \), and \( \gamma \) used by Lobo et al. At normal incidence (\( \phi = 0 \)) the \( R \) and \( x \) features (the Polye absorption) peak at the same frequency. The low frequency shoulder in \( R \) at \( r_s = r_d \) for \( \phi = 0 \), being the Debye loss peak in \( \epsilon' \), is not represented. The effect of the internal field correction is to decrease the intensity, but not to introduce any extra spectral feature. This is always true for all values of \( \phi \), \( K_s, K_i \), and \( \gamma \) in fig. 1-14.

The features labelled as \( " \) plasmons \( " \) by Lobo et al. and Ascarielli \( " \) may easily be reproduced in \( r_s \) and \( r_d \) without any internal field (fig. 2), with a glancing angle of \( \phi = 1.55 \) rad. These, unfortunately, have little or no physical significance since the values of \( K_s, K_i \), and \( \gamma \) chosen for reflectivity data by Ascarielli \( " \) (table 1) do not correctly reproduce the observed \( x \) and \( \epsilon' \) features (fig. 3). Similarly, the values chosen by Lobo et al. for water (see table 1) are unrealistic, especially the case \( \epsilon_k = 1 \), which emphasized the \( " \) plasmon \( " \) peaks.

In what follows we have therefore taken the \( K_s, K_i \), and \( \gamma \) values used by Evans and Evans \( " \) to describe \( \epsilon' \) and \( x \) in various dipolar liquids and also the nematic mesophase of \( p \)-dimethoxybenzylidene \( p' \)-n-butylniamine (MBA) as bases for the

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![Graph](image)

**Fig. 3.** Nitromethane liquid, \( \epsilon(\omega) \) and dielectric loss \( \delta(\omega) \) for the Ascarielli parameters. (1) \( \delta(\omega), \gamma = 10^{10} \text{ s}^{-1} \); (2) \( \epsilon(\omega), \gamma = 10^{10} \text{ s}^{-1} \); (3) \( \epsilon(\omega), \gamma = 10^{10} \text{ s}^{-1} \).
Table 1.—Parameters $K_e$, $K_i$ and $\gamma$ used in fig. 1-14

<table>
<thead>
<tr>
<th>fig.</th>
<th>$K_e(0)$/$10^6$ cm$^{-1}$</th>
<th>$K_i(0)$/$10^6$ cm$^{-1}$</th>
<th>$\gamma$/$10^4$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>313.8</td>
<td>313.5</td>
<td>45.5</td>
</tr>
<tr>
<td>2</td>
<td>11.8</td>
<td>29.5</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>11.8</td>
<td>29.5</td>
<td>1 and 10</td>
</tr>
<tr>
<td>4-8</td>
<td>1.43</td>
<td>15.0</td>
<td>6.0</td>
</tr>
<tr>
<td>9, 10</td>
<td>8.96</td>
<td>206.0</td>
<td>14.7</td>
</tr>
<tr>
<td>11</td>
<td>11.8</td>
<td>29.5</td>
<td>1</td>
</tr>
<tr>
<td>12</td>
<td>313.8</td>
<td>313.8</td>
<td>45.5</td>
</tr>
<tr>
<td>13, 14</td>
<td>1.12</td>
<td>208.0</td>
<td>2.4</td>
</tr>
</tbody>
</table>

Calculation of $r_e$ and $r_i$. (In the meantime this work has been greatly extended by Reed 72 to many hundreds of other specimens and has been reviewed.) A set of $r_e$ and $r_i$ curves (for tabulated $(K_e, K_i, \gamma)$) is illustrated in fig. 4-7 for various angles $\phi$. The set of $(K_e, K_i, \gamma)$ used represents "large angled jumps" motion such as that in a pseudo-spherical molecule in a relatively low-density liquid environment (or a highly compressed gas), but reflection $\phi$ of course ruled out in this case experimentally. The features in $r_e$ and $r_i$ are different for different $\phi$, which is in itself very useful, but near the Brewster angle, $\theta_B = \tan^{-1} \frac{1}{2}$ (fig. 6), and for a few degrees either side of $\theta_B$, the behavior of $r_e$ becomes more interesting, in that an extra peak appears theoretically in the mid-infrared which could be used experimentally to investigate the molecular dynamics in a novel manner. Also, for the first time we set in the mid-infrared peak a fair difference between the $z$ peaks, but not in the $x$ peaks (but

Fig. 4.—$K$ plotted against $\log z$ for a dynamical model of "large angled jumps". Parameters tabulated: $\phi = 0$, $\theta_B = 35$° (---) From theoretical ($\cdots$) Labo et al. $\alpha = 25$, $\gamma = 3$. 

\begin{figure}[h]
\centering
\includegraphics[width=0.7\textwidth]{fig4}
\caption{K plotted against \log z for a dynamical model of "large angled jumps". Parameters tabulated: $\phi = 0$, $\theta_B = 35$° (---) From theoretical ($\cdots$) Labo et al. $\alpha = 25$, $\gamma = 3$.}
\end{figure}
Fig. 5.—As for fig. 4; \( \phi = 0.5 \) rad (29.64°). (-----) Lobo et al.; (1) \( h_1 \); (2) \( h_2 \); (3) average. (-----) Exirn three variable, average.

Fig. 6.—As for fig. 5; \( \phi = 1.0 \) rad (57.29°). Brewster angle \( \tan^{-1} c_b = 1.047 \) rad (60.00°).
FIG. 7.—As for fig. 5: $\phi = 1.5$ rad (glancing angle).

FIG. 8.—As for fig. 5: $\phi = 1.067$ rad = $\pi \times 10^{-4}$ rad. Plot of $-\ln R$ against $\log_{10} \nu$. (1) $s_0$ (-----) Evans three variables, (- - -) Lobo et al. (2) $r_0$. 
we are not directly concerned with absorption spectroscopy here). This mid-infrared peak has not yet been investigated experimentally. The problem of heavy attenuation (e.g., in \( \epsilon_{m} = -20 \)) could be eased considerably and the noise level could be kept manageable by using intense laser radiation and an incidence angle \( \phi \) close to but not at \( \phi_{m} \). Strictly speaking \( \epsilon_{m} \) is still varying slightly at the upper frequency end of the Poley absorption (the \( \alpha \) peak) so that \( \phi_{m} \) cannot be defined probably better than a few tens of minutes of arc. Measurements with \( \phi \) within a few degrees of this value should produce the mid-infrared feature in \( \epsilon_{m} \). Note (fig. 8) that the \( \epsilon_{m} \) value calculated from both models shows no such feature but retains the peak in the far-infrared (corresponding to \( \alpha \)) and the lower frequency shoulder corresponding to the absorption peak in \( \epsilon' \) at anything from the audio to microwave range. The far-infrared feature of \( \epsilon_{m} \) is also retained in \( \epsilon_{m} \).

A projected experimental set-up would involve an Apollo Instruments far-infrared laser system, tunable over 1500 lines producing monochromatic, polarised radiation a million times more intense than that available from a conventional black-body source (HP-16 high pressure mercury arc).

The same process is illustrated for a 4% w/w solution of CH₃CN in CCl₄ in fig. 9 and \( \phi \). The absorption curves \( \epsilon'' \) and \( \epsilon' \) produced by the tabulated \( (k_{m}, k_{s}, \gamma) \) are illustrated with the experimental absorption data elsewhere.¹²

The theoretical

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**Fig. 9.** As for fig. 8, 4% w/w solution of CH₃CN in CCl₄, best fit of three variable theory to \( \alpha \) and \( \epsilon' \). Lobo et al. results give curves indistinguishable on this scale \( \epsilon_{m} = 3.97; \epsilon_{p} = 1.50; \phi = 1.55 \text{ rad} \). (1) r.h. ordinate scale: \( \epsilon_{m} \); (2) l.h. ordinate scale: \( \epsilon_{m} \).
curves are such that the shoulder and peak observable in fig. 9 are a little too accentuated, but are otherwise a fairly good representation of the measured data. In such a dilute solution the dynamical internal field is negligible, and both models give identical results on the scale of fig. 9 and 10. At a glancing angle of \( \phi = 1.55 \) rad the reflection spectrum is already interesting since the features in \( r_s \) and \( r_p \) fall within the range of Michelson interferometry, which could therefore be used straightforwardly to measure the real and complex parts of \( n^* \) simultaneously. This has been explored for normal incidence by Bunch et al. but not yet for \( \phi \neq 0 \). Near \( \phi = (\tan^{-1} 1.30) \), (fig. 10), the \( r_p \) spectrum is dramatically different, one model being just distinguishable from the other by virtue of the mid-infrared peak in \( -\ln r_s \) at over 600 cm\(^{-1}\), within range of everyday grating instruments.

With the (albeit unrealistic) values of \( (K_0, K_1, \gamma) \) used by Ascarelli for nitro- methane the Brewster peak in \( r_s \) appears theoretically at 1602 cm\(^{-1}\) (fig. 11), and with the (equally unrealistic) set used by Lobo et al. for HCl at over 3000 cm\(^{-1}\) (fig. 12) into the near infrared. The true position of these peaks could be found by using the measured far-infrared/microwave values of \( \alpha, \epsilon', \alpha' \) and \( \eta \), and inserting into the fundamental reflectivity equations for \( r_s \) near the Brewster angle defined by \( \tan^{-1} n \) just above the Poley band in \( n \).
Fig. 11.—Plot of $-\ln R$ against $\log_{10} \omega$ for liquid methane at $\phi = \tan^{-1} 0.4$. (1) $r_1$; (2) $r_2$; Evans 3 variable theory.

Fig. 12.—$A$ for $\phi$. for fig. 11, liquid HC. (1) $r_1$ (-----) Evans 3 variable, (-----) Leth et al. (2) $r_2$. 

$\log_{10} \omega$ (rad s$^{-1}$)
Fig. 13.—Plot of $-\log R$ against $\log A$, isotropic MBBA, theoretical h.c. $\phi = 0$; $n_0 = 25$; $\epsilon_0 = 3$ as test parameters. (---) Three variable theory. (---) Lobo et al.

Fig. 14.—As for fig. 13; $\phi = \tan^{-1} \sqrt{2}$ (0.001); plot of $-\log R$ against $\log A$. (1) $r_2$: (---) EXC; three variable; (---) Lobo et al. (2) $r_2$: theories indistinguishable on this scale.
The true power of Brewster angle reflection spectroscopy may be illustrated by reference to fig. 13 and 14, where the \(K_1, K_2, \phi \) parameters are those used by Evans and Evans \(^6\) for the isotropic and nematic phases of MBBA. At normal incidence the reflection spectrum is featureless except for an absorption at \(\phi = 60^\circ, \omega = 13.2 \) near the Brewster angle, however, (fig. 14) a secondary peak in \(r_s\) appears at \(484 \text{ cm}^{-1}\), which is shifted away from the value derived from the model of Lobe et al. The features in the far-infrared are considerably modified and \(r_s\) retains the same overall form. Given sufficient amplification, therefore, reflection spectroscopy will be rewarding for the relatively heavy absorber.

**DISCUSSION**

In this section we summarise the implications of using power reflection far- and mid-infrared spectroscopy to study the molecular motions in bulk dopant liquids and surfaces of any kind which are properly prepared.

(i) The variation of incident angle \(\phi\) produces a variety of spectral bandshapes which can be used to complement absorption spectroscopy of heavily attenuating fluids and solids.

(ii) Near the Brewster incident angle, \(\phi = \tan^{-1} \phi \), there appear in \(r_s\) extra features in the mid- and near-infrared region which bring the study of the Poley/Debye process within range of tunable infrared lasers and grating spectrometers, provided the amplification system is sensitive enough to overcome the heavy attenuation.

(iii) The two models of molecular motion used to produce (i) and (ii) are versions of the same theory with and without internal field corrections and there are no features in one which are not present in the other. The split seen by Ascarelli in the grazing spectrum of nitromethane cannot therefore be explained in terms of collective hydrodynamic plasmons but is merely a natural consequence of the fundamental equations of reflection spectroscopy. The Evans three variable theory \(^9\) contains no electrodynamic field corrections yet reproduces all the features inherent in the Lobo theory. \(^9\) Therefore it follows that there are no plasmons, since the former theory is strictly one of autocorrelations alone. Ascarelli used a grating angle \(\phi\) to pick up an assumed coupling between the reflected electromagnetic wave and longitudinal "plasmon". By reference to fig. 1-14, however, it can be seen by direct calculation that there is no special structure as the grating angle which is not there near the normal angle. The really interesting region for \(r_s\) is that around the Brewster angle.

(iv) The concept of Brewster angle reflection spectroscopy is not limited to the far-infrared and lower frequency but could be applied to interferometry to shift structure normally seen in the mid-infrared up to visible frequencies, and so on. The study of gas-solid surface variations and the other phenomena of surface science in this way could be useful, always providing that the attenuation problems could be handled with sufficiently sensitive amplifiers and detectors. Probably the most useful feature of Brewster angle reflection spectroscopy is that of shifting structure away from the "difficult" far-infrared region into the mid-infrared and near-infrared.

I thank S.R.C. for extensive financial support and Dr. G. J. Evans for valuable discussions.

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BREWSTER REFLECTION SPECTROSCOPY

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* J. Birch, N.P.L. internal report.
* G. J. Davies, Post Office internal report.

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