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Blackett Laboratory

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INFRARED OPTICAL CONSTANTS OF VOLATILE LIQUIDS

Stella Cacoullis

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To My Parents

Abstract

The complex refractive index of a number of liquids has been measured for a wavelength range extending from 2 microns up to 13 microns. Complex refractive index can be defined as $m = n - ik$, where the two optical constants - refractive index (n) and absorptive index (k) - are functions of wavelength.

The thesis deals with two basic classes of liquid - those that are stable at or around room temperature (i.e. 20°C - 25°C) and volatile liquids, that is liquids that rapidly evaporate at room temperature.

The optical constants of liquids which are not considered to be volatile are found by a combination of two experimental methods - free liquid surface reflectometry and transmission measurements. Three non volatile liquids are presented; water, polyethylene glycol 300 and polyethylene glycol 600.

The design and operation of an air tight optical cell is described. This has been specifically developed for the measurement of volatile liquids but is also effective in the measurement of liquids containing regions of large absorptive index. The optical constants of aqueous ammonium sulphate, 1,1,2 trichlorotrifluoroethane, trichlorofluoromethane and acetone have been measured using the closed cell system.

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INTRODUCTION

The importance of knowing the optical constants of solids, liquids and gases has long been acknowledged, the wavelength dependent optical constants are the fundamental quantities that determine the macroscopic optical properties of matter. The two sets of quantities most commonly referred to by the phrase *optical constants* are the *complex dielectric function* and the *complex refractive index*, these two complex functions are not independent, therefore, either can be used to describe the intrinsic optical properties of a material. Our work concentrates entirely on the complex refractive index, this comprises two components, the refractive index (n) and the absorptive index (k). The optical behaviour of a material with respect to electromagnetic radiation is completely determined by its optical constants - they explain the shiny quality of a metal, the transparency of glass, the cloudy white colour of milk and many other visual qualities.

The need to know the optical properties of a variety of substances has long been vital to many branches of science and industry: geology, atmospheric and space physics, environmental science, the defence industry, chemistry and the paint industry to name but a few. It is for this reason that the pursuit of finding the optical constants of previously unreported materials, developing new methods of measurement and refining existing experimental techniques continues.

This thesis begins with some work on optical definitions, the formulae required to calculate complex refractive indexes, and a brief review of the different techniques for the measurement of bulk liquids already in existence. The measurement of the optical constants of non volatile liquids (i.e. liquids that are stable at or around room temperature) is dealt with initially, this involves acquiring values of n and k at suitable wavelength intervals for a wavelength range extending from 2 microns to 13 microns. The two methods used to extract the refractive and absorptive index of the liquid - free liquid surface reflectometry and transmission using variable path length cells - are described at length and the results for two

polyethylene glycols, peg 300 and peg 600, are presented and discussed. Optical constants, measured by us, for distilled water are also presented, and compared with values taken from a number of literature sources.

The second part of the thesis is concerned with the design of a closed optical cell arrangement which can be used in the reflectometer system as an alternative to the free liquid surface arrangement. Clearly this has particular application when a volatile liquid is to be measured. These optical cells are covered with infrared transmitting windows, two substrates have been used, amorphous carbon coated germanium and ytterbium oxide coated zinc selenide. The transmission properties of the coated windows have been measured and are presented, a study of the optical properties of uncoated germanium and uncoated zinc selenide is also included.

The final stage of the thesis includes the measurement of aqueous ammonium sulphate which was chosen from a literature survey because of its large absorption peak. The closed cell system's ability to reproduce large absorptive indexes was tested using a near saturated ammonium sulphate solution. The n and k values of several volatile liquids have been found using the closed cell arrangement, namely trichlorofluoromethane, 1,1,2 trichlorotrifluoroethane and acetone. Finally there is a discussion on the capability of the closed cell system in measuring volatile liquids and liquids with regions of very large absorption.

CHAPTER ONE

Introductory Theory and Review of Optical Constant Measurement

1.1 Defining Optical Constants

Mention was made in the general introduction of the optical constants that describe the intrinsic optical properties of a material. The two sets of quantities referred to by the more general term *optical constants* are the real and imaginary parts of the *complex refractive index*, and the real and imaginary parts of the *complex dielectric function*.

1.1.1 Complex Refractive Index

From Maxwell's equations a plane, homogeneous, three dimensional wave is of the form (Lipson and Lipson, 1969 and Bayvel and Jones, 1981):

$$\underline{E} = E_0 \exp i [2\pi(\hat{x} \cdot \underline{z}) / \lambda - (2\pi\nu t)] \quad (1.1)$$

where: $\underline{E}$ is the electrical field vector

and: $\underline{E}_0 = \hat{x} E_0$ (i.e. unit vector x magnitude)

$\hat{x}$ is a unit vector

$\underline{z}$ is a position vector

λ is the wavelength of radiation in the medium

t is time

By comparison with the non-absorbing case (i.e. from Snell's law), we can define a complex refractive index

$$m = \lambda_0 / \lambda \quad (1.2)$$

where λ_0 is the wavelength in vacuo.

Therefore substituting for λ in equation (1.1):

$$E = E_0 \exp 2\pi i [m(\hat{x} \cdot \underline{z}) / \lambda_0 - (2\pi\nu t)] \quad (1.3)$$

and putting $m = n + ik$ gives:

$$E = E_0 \exp\{-2\pi k(\hat{x} \cdot \underline{z}) / \lambda_0\} \exp[2\pi i(n(\hat{x} \cdot \underline{z}) / \lambda_0 - (\nu t))] \quad (1.4)$$

Thus from equation (1.4) the phase of the wave is

$$2\pi[n(\hat{x} \cdot \underline{z}) / \lambda_0 - (\nu t)] \quad (1.5)$$

from which the phase velocity is given by

$$c / n \quad (1.6)$$

i.e. n is the "normal" Snell's law refractive index. The oscillatory part of the wave function is multiplied by a damping or absorbing factor, in which the imaginary part of the complex refractive index, k , is related to the attenuation of the radiation in the medium. Since intensity is proportional to the square of the electric field amplitude, from equation (1.4)

$$I = I_0 \exp -[4\pi k d / \lambda_0] \quad (1.7)$$

where I denotes the intensity of the beam having traversed a distance, d (see also appendix A), it is correct to say that all materials have a complex refractive index, but in some materials, in certain wavelength regions the imaginary component of the complex index is so small it can be considered negligible.

1.1.2 The Complex Dielectric Function

The complex dielectric function is defined as (Bohren and Huffman, 1983):

$$\epsilon = \epsilon' + i\epsilon'' \quad (1.8)$$

The complex dielectric function and complex refractive index are not independent, the two quantities are linked by the following equations:

$$n = \{[(\epsilon'^2 + \epsilon''^2)^{1/2} + \epsilon'] / 2\}^{1/2} \quad (1.9)$$

$$k = \{[(\epsilon'^2 + \epsilon''^2)^{1/2} - \epsilon'] / 2\}^{1/2} \quad (1.10)$$

and conversely:

$$\epsilon' = n^2 - k^2 \quad (1.11)$$

$$\epsilon'' = 2nk \quad (1.12)$$

It is perhaps appropriate at this stage to state that the term *optical constants* is somewhat misleading since the quantities referred to are not constants, in the accepted sense, at all but are, often strongly, wavelength dependent.

1.1.3 Notation in Formulae

There are a variety of different notations for complex refractive index, which can give rise to ambiguity. The following are commonly encountered:

$n + ik$, $n - ik$, $n' + in''$, $n(1 + ik)$.

This thesis adheres to convention by using the letter k to denote absorptive index. This should not be confused with the propagation constant, which is, unfortunately, also represented by k .

1.1.4 Reflection and Transmission at a Plane Boundary

The real and imaginary parts of the complex refractive index can be used to derive

formulae which describe reflection and transmission at plane interfaces (Bohren and Huffman, 1983 and A.E. Martin, 1966).

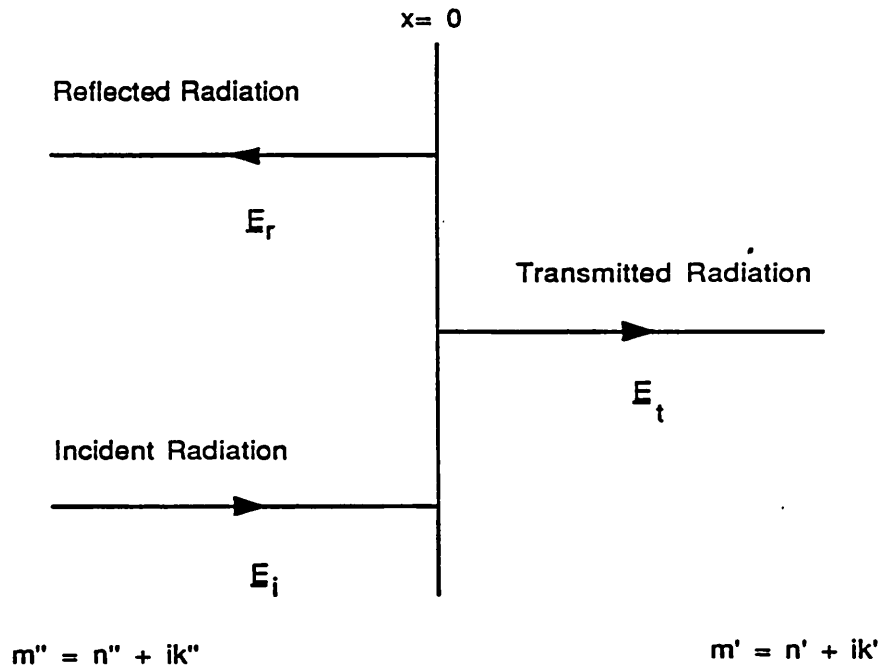


Fig. 1.1 Reflection and Transmission at a Plane Boundary

Fig.1.1 considers a plane wave propagating in a medium of complex refractive index, $m'' = n'' + ik''$, which is normally incident on a medium with complex refractive index, $m' = n' + ik'$. The amplitudes of the incident, transmitted and reflected electric fields are given by E_i , E_t and E_r respectively. Plane wave solutions to the Maxwell equations on both sides of the boundary, $x = 0$ are:

$$E_t \exp \{ i\omega[(m'x / c) - t] \} \quad (x > 0) \quad (1.13)$$

$$E_i \exp \{ i\omega[(m''x / c) - t] \} + E_r \exp \{ -i\omega[(m''x / c) + t] \} \quad (x < 0) \quad (1.14)$$

across the interface $x = 0$ (Duffin, 1980)

$$E_i + E_r = E_t \quad (1.15)$$

and using one of Maxwell's equations for plane waves

$$\mathbf{k} \times \mathbf{E}_0 = \omega \mu \mathbf{H}_0 \quad (1.16)$$

and (1.15), assuming $\mu_1 = \mu_2$

$$E_i - E_r = (m' / m'') E_t \quad (1.17)$$

Solving equations (1.15) and (1.17) for E_r and E_t :

$$E_r = \tilde{r} E_i \quad (1.18)$$

$$E_t = \tilde{t} E_i \quad (1.19)$$

where the amplitude reflection and transmission coefficients are:

$$\tilde{r} = (1 - m) / (1 + m) \quad (1.20)$$

$$\tilde{t} = 2 / (1 + m) \quad (1.21)$$

$$\text{and } m' / m'' = m = (n_1 + i k_1) / (n_2 + i k_2) \quad (1.22)$$

is the complex index of medium 1 relative to medium 2. The intensity reflectance R for normally incident light, defined as the ratio of reflected to incident intensity, is:

$$R = |\tilde{r}|^2 = |(1 - m) / (1 + m)|^2 \quad (1.23)$$

Therefore substituting for m and applying the complex conjugate condition:

$$|a / b|^2 = a a^* / b b^* \quad (1.24)$$

$$R = [(n_1 - n_2)^2 + (k_1 - k_2)^2] / [(n_1 + n_2)^2 + (k_1 + k_2)^2] \quad (1.25)$$

For the special case where medium 2 is air, $n_2 = 1$ and k tends to zero, therefore, equation (1.25)

reduces to the more familiar form:

$$R = [(n_1 - 1)^2 + k_1^2] / [(n_1 + 1)^2 + k_1^2] \quad (1.26)$$

1.2 A Review of the Bulk Measurement Techniques

Infrared optical constants cannot be measured directly but are derived from basic measurements (e.g. reflection and transmission), applied to theoretical formulae (such as the Fresnel formula).

Materials that conform to the description *bulk matter* include large crystals, glassy or amorphous solids, and homogeneous liquids.

The development over the years of stabler light sources, more reliable detectors and even automated systems has made optical measurements, over wide wavelength ranges, quicker and more efficient. In the case of liquids a considerable number of reference sources exist, particularly for those materials which occur naturally as atmospheric aerosols.

In a sense, the method employed to analyse a liquid largely depends on the magnitude of the absorptive index, but the techniques used are generic variations of one of the following experimental methods.

1.2.1 Method One - Measuring Refraction Angles

By direct measurement of refraction angles. For instance the angle of minimum deviation of a prism using a hollow prism filled with the liquid sample, n is then obtained directly using Snell's law. This method is of limited use since it requires the sample to have a low absorptive index i.e. $k < 10^{-5}$.

1.2.2 Method Two - Specular Reflectance and Transmittance

By measurement of specular reflectance and transmittance of liquids at near normal incidence, over a wide range of frequencies, k can be found directly from the transmission and n from the corresponding reflectance since $R = f(n, k)$. The sample must be sufficiently transparent for measurable transmission, but not as transparent as in case 1. This technique

breaks down however, in regions of high absorption which prevent measurement of k .

1.2.3 Method Three - The Kramers - Kronig Analysis

An alternative to case 2 is to confine the measurements made to those of near normal incident reflectance. The phase shift of the reflected radiation is found using a Kramers - Kronig (K - K) analysis which links, by means of an integral relationship, the phase shift at a wavelength with the corresponding reflectance (see chapter 2 for details). This technique is highly appropriate to samples of high absorptive index, but it requires measurements over an extensive range, and extrapolations into regions where measurements cannot be made. It should also be noted that this method is not especially suited to regions of low absorption.

This normal incidence method has been employed by a large number of research groups. Rhine et al (1974) for work on aqueous solutions of alkali halides, Adams and Downing (1986) in work on H_2SO_4 , HNO_3 and H_2O mixtures, and by Tyler and Querry (1978) on ZnCl_2 solutions. Downing et al (1977) used this method to carry out measurements on ammonium sulphate, one of the most abundant aerosols in the earth's stratosphere.

A modified derivation of the K - K integral is the subtractive Kramers - Kronig analysis (Ahrenkiel, 1971), this uses the phase shift at one value inside the wavelength range studied. This appears to offer greater convergence than the conventional integral when reflectance data are available over a limited range. The method is used by Pinkley, Sethna and Williams (1978) in studies on hydrocarbons and Sethna and Williams (1979) to measure optical constants of alcohols in the infrared. Values of n and k are determined using K - K phase shift analysis of the measured reflectances, and linear extrapolations of reflectances outside the frequency range covered in their experiments.

Most, if not all, of the work outlined in method three uses distilled water as the standard liquid when reflectance measurements are made, the absolute reflectance values for water taken from reference sources. Basic problems can arise here since moderate errors in the measured reflectance spectra can propagate, due to the integral relationship, to quite a dramatic degree in the phase shift. Attention was drawn to this problem by Rhine et al in their paper on alkali halides, they cite a critical survey by Irvine and Pollack (1968) which revealed many inconsistencies in published results, and emphasised the importance of further

quantitative studies in this area. In his thesis on infrared constants of powders and liquids, Dolan (1987) extensively covers the subject of the optical constants of water in the literature. He has made suitable corrections to reflectance tables which have been used in subsequent work in this thesis (chapter 2). The question of optical constants of water in the literature is also addressed in this thesis in chapter 2.

1.2.4 Method four - Inverting the Fresnel Formulae

Another method frequently applied to bulk materials involves the measurement of reflectances of light of two polarizations at one angle of incidence, or alternatively, one polarization at two angles. The results are then found from the Fresnel formulae (Bohren and Huffman, 1983), by graphical (Simon, 1961) or computational (Boeckner, 1929) means.

Interestingly enough, this form of making optical constant measurements was attempted in the early days of the project at Imperial College. A large glancing angle of incidence falling onto the liquid surface was found to be the most suitable, and two states of polarization were used at this angle. However, polarization gave rise to a beam of low intensity which was further reduced by aperture stops to prevent spreading on the liquid surface caused by the oblique angle used. Since only about ten percent of the signal is reflected from a liquid surface the intensity of the beam finally arriving at the detector was extremely small (surface contamination of the liquid and poor polarization can also seriously degrade the final result). This resulted in a series of values with extremely large associated errors. This and more particularly the great degree of difficulty in setting up the experiment resulted in its being abandoned at an early stage.

1.2.5 Method Five - Ellipsometry

Ellipsometric techniques in which amplitude ratios and phase shifts, for reflected light, are measured directly have also been implemented (Azzam and Bashara, 1977, Azzam, 1982, and Hunderi, 1972). This method is in contrast to the previous method in which the phase change is obtained indirectly. Properly used ellipsometry provides a means for accurately determining the optical constants of a clean surface, but it is a difficult technique to apply over large wavelength regions because of the need for suitable analysers and retarders.

1.2.6 Method Six - Attenuated Total Reflection

It is worth mentioning a major refinement of the *simple* reflectance technique - attenuated total reflection (Fahrenfort, 1963, Crawford et al, 1978, and Palik and Holm, 1978). This is based on the observation that an increase in sensitivity is achieved if the liquid sample is in contact with a transparent material of high refractive index. A further improvement results if the beam of incident radiation strikes the reflecting surface obliquely. The incident beam in regions of absorption is attenuated by an amount dependent on n , k and the oblique angle of incidence. By a careful choice of suitable incident angles the condition can be found for which R is extremely sensitive to small changes in n and k . Again, it is necessary to make measurements at, for example, two angles so that n and k can be found by the solution of a pair of simultaneous equations for R in terms of n and k .

An extensive study of a number of organic liquids, in the infrared using A.T.R. has been made by Goplen, Cameron and Jones (1980).

Undoubtedly A.T.R. offers a very sensitive reflection based approach, but it is misleading to assume that it is an entirely trouble free, straight forward method. The high sensitivity is achieved at some expense, requirements, such as knowing the incident angles to within 10' of arc and the collimation of the beam to be better than this, are difficult to obtain. The selection of the two optimal angles is also critical. Because of the high sensitivity small errors in beams or angles produce large errors in k . The choice of window materials is very important to the operation of the A.T.R. technique.

1.2.7 Method Seven - Different Windows Technique

The choice of window materials is also vital to the method developed by Libov and Bakshiev (1964), they investigated the optical constants of the liquids CHCl_3 and CCl_4 by applying the method of measuring the near normal reflection coefficient R at the boundary of the liquid with various transparent media of high refractive index indexes. The work carried out by us on volatile liquids and the optical cell (refer to chapter 3) is based on the same methods as the Libov and Bakshiev investigations. The cell Libov and Bakshiev used to carry out their work is shown schematically in figure 1.2. The body of the cell is moulded from teflon

and the window is made in the form of a wedge so that the beam of radiation reflected from surface AB is eliminated from the system, the reflection from the liquid / window interface, CD, need only be considered.

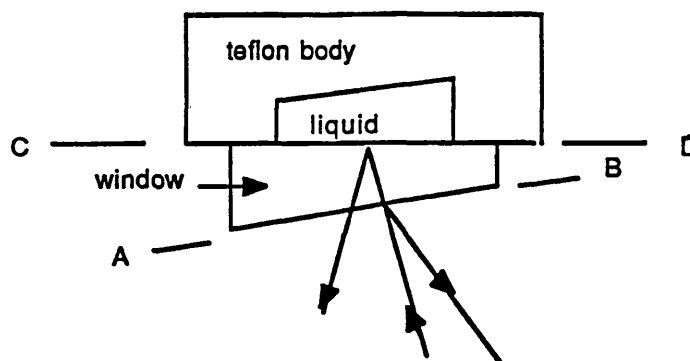


Fig. 1. 2 The Optical Cell Developed by Libov and Bakshiev

Once again, to calculate values of n and k for a wavelength, it is necessary to solve a corresponding pair of general reflection coefficient equations containing the unknowns, n and k . This was done by a graphical method. For the purposes of increasing the reliability of their results, Libov and Bakshiev obtained three independent reflectance measurements at the window / liquid boundary by using three window materials NaCl, CsI and KRS - 5. The authors note that for a 1% - 5% error in the determination of R the n and k values can attain corresponding errors of between 10% and 20%, depending on the part of the spectrum involved.

1.2.8 Concluding Remarks on Bulk Techniques

Even the most perfunctory of investigations of the bulk techniques outlined above, reveals that no one method is superior over *all* wavelengths. In practice, measurements of optical constants are either confined to a restricted wavelength range, or a combination of the described methods is used to cover a more extensive wavelength range.

CHAPTER TWO

The Optical Constants of Non-Volatile Liquids

2.1 Experimental Determination of Optical Constants

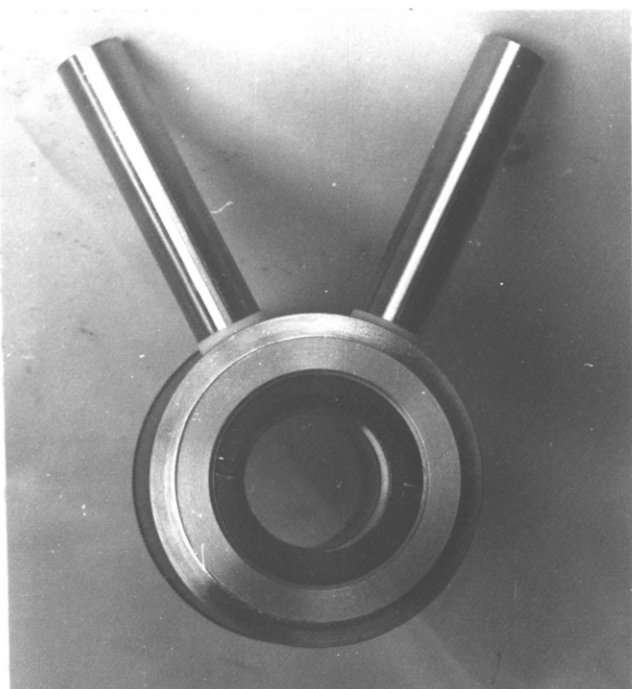
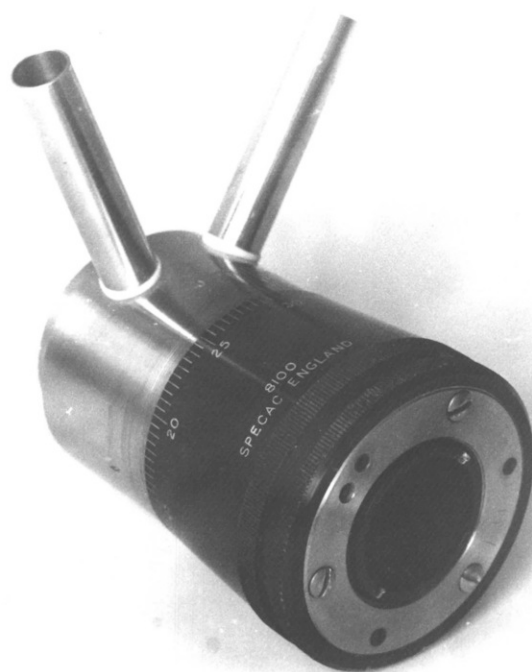
Determining optical constants is not necessarily a simple task, even in the case of homogeneous, non volatile materials at room temperature. Particular problems occur in spectral regions of very high absorption (orders greater than 10^{-2}).

The passage of radiation through a material involves, to some degree, three types of radiation loss mechanism (Bohren and Huffman, 1983) namely loss due to reflection, loss due to absorption and loss due to scattering. The radiant flux contained in the incident beam is, therefore, gradually diminished as the beam traverses the material. For our purposes we make the assumption that the liquids under test are optically homogeneous, so scattering effects can be neglected.

Following a number of precedents the experimental processes used to ascertain the optical constants of the liquid are transmission, from which the absorptive index can be found (chapter one) and near normal reflection, which can be substituted into an inverted Fresnel equation with the absorptive index to yield the refractive index (for proof see chapter one).

2.2 Transmission Measurements with a Variable Path Length Cell

Transmission experiments, from which the absorptive index can be inferred, were carried out using variable path length cells acquired from the Specac Company. A variety of these types of cells exist, some designed to operate at high temperatures and/or pressures, and others at variable temperatures. In this case the simpler type of cell is used (i.e. without a temperature jacket or thermocouple) for operation at room temperature and pressure. Photographs of the cell are shown in photograph plate 2A. The individual components of the basic cell are illustrated in fig 2.1 and fig 2.2. The variable path length cell is of stainless steel and consists of two main parts; the body (labelled 1 in both fig 2.1 and 2.2) and the sleeve (2). In operation two windows trap the liquid in the hollow core of the assembled cell. The flanged



Photograph Plate 2A: Three Views of a Variable Path Length Cell

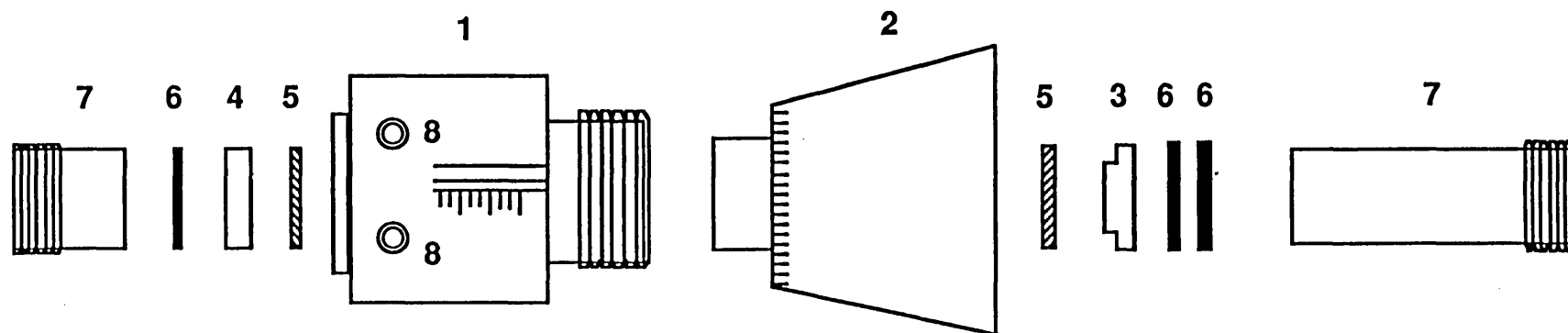


Fig 2.1: The Individual Components of the Variable Path Length Cell.

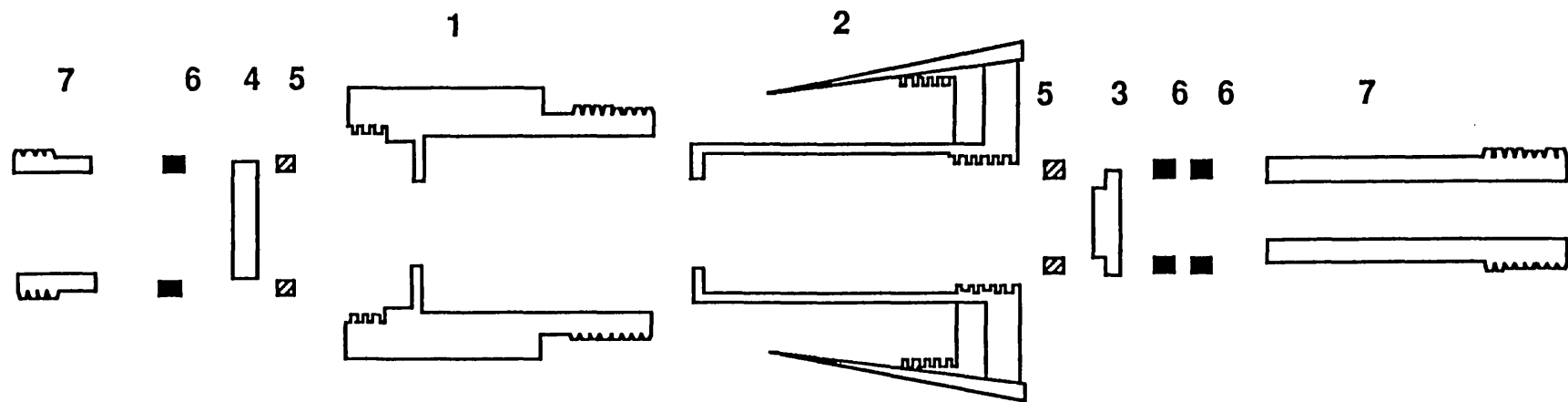


Fig 2.2 : Cross sectional view of the variable path cell components.

window (3) is inserted into the sleeve and the flat window (4) into the body of the cell. The windows are cushioned by P.T.F.E. rings (5) and neoprene gaskets (6) and retained by teflon sealing rings (7), the object is to produce an air tight seal since liquid leakage is highly undesirable. The sleeve is then screwed onto the main body of the cell.

The path length (and hence the thickness of the body of the liquid) is varied by means of a screw arrangement whereby the flanged window rotates with respect to the flat window as the cell spacing is adjusted. The sleeve (2) has a graduated scale with 100 divisions, rotation through one division changes the path length by 0.005 mm. The scale on the main body of the cell is graduated in 0.5 mm divisions up to 15 mm. Therefore a complete revolution of the flanged window is equivalent to a path length change of 0.5 mm.

Two pairs of windows are used to cover the required wavelength range of 0.5 to 16 microns. A pair (one flanged, one plane) of sapphire windows cover the region extending from 0.5 microns to about 5 microns. In practice, depending on the nature of the liquid in the cell, the signal often drops quite sharply at around 5 microns due to a drop in transmission through the sapphire windows. At this point a pair of germanium windows are used to replace the sapphire pair. The high refractive index of the germanium windows will give rise to a high reflectance from the window faces, which reduces the available incident signal. To overcome this problem both faces of the germanium windows have been coated with an amorphous carbon (ARG 4 - trade name of Barr and Stroud Ltd.) antireflection film.

Prior to operation the cell is flushed with the liquid to be tested, this ensures that any possible contaminants are removed. When introducing the liquid into the cell it is important to prevent the introduction of air bubbles into the liquid, these could act as scattering sites and give rise to spurious results. The following procedure is designed to ensure air is kept out of the liquid. A longer than required path length is set and the liquid is syringed slowly into the cell through one of the reservoir ports (8) until the liquid fills the cell and emerges in the second reservoir port. The cell is slowly wound down to the required path length setting and P.T.F.E. plugs inserted into the reservoir ports.

To make a measurement the cell is placed in a source of radiation of wavelength, λ , and the intensity of the transmitted beam, I_1 , is measured for a set path length, d_1 . A second path length is set, d_2 , and a second transmitted intensity reading, I_2 , taken at this same

wavelength , λ . The Lambert - Bouguer law (see appendix A),

$$I = I_0 c e^{-4\pi k d / \lambda} \quad (2.1)$$

where : I is the transmitted intensity

I_0 is the incident intensity

c is a constant related to window effects

k is the absorptive index

d is the set path length of the liquid

is applied to give :

$$I_1 = I_0 c e^{-4\pi k d_1 / \lambda} \quad (2.2)$$

and

$$I_2 = I_0 c e^{-4\pi k d_2 / \lambda} \quad (2.3)$$

By equating (2.2) and (2.3) k can be found.

$$k = [\lambda / 4\pi (d_1 - d_2)] \log_e(I_2 / I_1) \quad (2.4)$$

The main advantage of setting two path lengths at each wavelength is that any window effects such as reflectance or absorption can be neglected since c is eliminated in the final calculation of k .

It should be stated that the thicknesses of the various windows used (all sapphire windows are 3 mm in thickness, all germanium windows are 4 mm thick) and the range of wavelengths used are such that the conditions required to produce discernible interference effects, at any wavelength, are not satisfied (see chapter three, section 3.5.1). However, it is necessary to consider also the liquid gap and ascertain whether this will be a source of observable interference fringes. For observable interference fringes the coherence length

must be much greater than the optical path difference of the beams of radiation (Born and Wolf, 1980). In this case the optical path difference is $2nt$, where, n is the refractive index of the liquid and t is the thickness of the liquid gap. The coherence length is defined as the ratio of the square of the average wavelength of the source to the range of wavelengths produced by it ($\lambda^2/\delta\lambda$). The coherence length and optical path difference is found at different wavelengths and for different values of thickness, t , for an average n value of 1.5 and the results shown in table 2.1. From these general case calculations it is clear to see that the condition for observable interference fringes is satisfied for the small path length of 0.005 mm (this is the minimum path thickness of the V.P.L.C.s and, therefore, carries a large associated error (see later)). However, the small path lengths are required because of the heavy absorption of the liquid, it is therefore highly likely that heavy attenuation prevents the production of strong interference fringes on the absorption spectra of the sample liquid, hence, interference bands are not observed on the sample spectra presented in this chapter.

wavelength (microns)	d (mm)	$\lambda^2/\delta\lambda$ (m)	$2nt$ (m)
2	5	2×10^{-4}	1.5×10^{-2}
2	0.005	2×10^{-4}	1.5×10^{-5}
13	5	1.3×10^{-3}	1.5×10^{-2}
13	0.005	1.3×10^{-3}	1.5×10^{-5}

Table 2.1: A Range of Optical Path Differences and Coherence Lengths
for the Variable Path Length Cell.

2.2.1 The Limitations of the Variable Path Length Cell

The method of finding k by transmission using a variable path length cell (V.P.L.C.) might appear straightforward, however, several difficulties arise which curtail extensive use of the cells.

As expected the most obvious limitation of the variable path length cells is when

absorption becomes too high ($> 10^{-2}$), and the transmitted signal cannot be detected due to this excessively heavy absorption. The gaps in certain wavelength regions of high absorption that subsequently occur can be interpolated using a Kramers - Kronig dispersion analysis, this is discussed in section 2.5. The converse situation also presents problems, that is when k is too low ($< 10^{-5}$). In this instance the difficulty lies in setting suitably large path lengths since the attenuation in the liquid is so small, this is covered in section 2.3.

What then of the intermediate region of $10^{-4} < k < 10^{-2}$? It is easy to imagine this region to be easily measureable. Experimental work, however, revealed worrying inconsistencies that prompted further study. In short, although the vernier scale in theory allowed path length as small as 0.005 mm to be set under experimental conditions attempts to repeat a value at small path lengths resulted in large inconsistencies between the absorptive indexes obtained. In an attempt to pinpoint the cause (or causes) of these inconsistencies, and so assign a suitable experimental uncertainty a number of possible sources of error were considered:

2.2.1.1 Instrumental "Drift"

Instrumental change or changes in the intensity of the source of the incident beam can automatically be discounted as a possible source of discrepancy. Taking two readings at one wavelength, consecutively, rather than performing a full range scan at one path length setting, should nullify any effect of random change.

2.2.1.2 The Influence of Temperature

It has long been known that the intermolecular structure of a liquid changes with temperature so changes in the IR spectrum with temperature will occur, such as shifts in the absorption band positions and changes in the optical constants. Hale et al (1972) made a study of the influence of temperature on the optical constants of water. They measured the normal incidence reflectance of a free water surface in air at 5°C, 27°C and 70°C in the spectral region 2 - 28 microns and used Kramers - Kronig analysis (see later) to determine the corresponding n and k values. The temperature of the sample was maintained to $\pm 1^\circ\text{C}$ by thermal baths. However, in our case the measurements are made at room temperature and the temperature changes would be fluctuations during the course of a full range experiment. The temperature of the housing containing the V.P.L.C. was monitored during experiment and found to vary by no more than $\pm 2^\circ\text{C}$ of the temperature at the start of the experiment. It was, therefore,

concluded that the measurements made by us would not be affected discernably by ambient temperature changes. Any gradual temperature change would, in any case, be nullified by setting two path lengths at each wavelength.

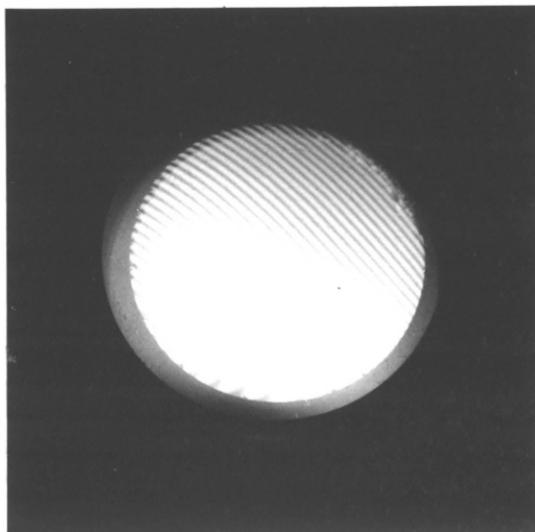
2.2.1.3 Sample Contamination

It is more difficult to detect and quantify the effect impurities will have on the absorptive index values of a sample. In their review of infrared properties of water and ice spheres, Irvine and Pollack (1968) make the comment that in small cell thicknesses, $\Delta t < 10$ microns, the presence of a contaminant in the comparatively small volume of sample can lead to a spurious increase in the k value. In the V.P.L.C. arrangement it is possible that impurities from different samples measured earlier can remain in the screw threads of the body and sleeve of the cell and dissolve in the liquid during experiment. Cleaning each component of the dismantled cell with a solvent, such as acetone, no doubt reduces the chances of impurity.

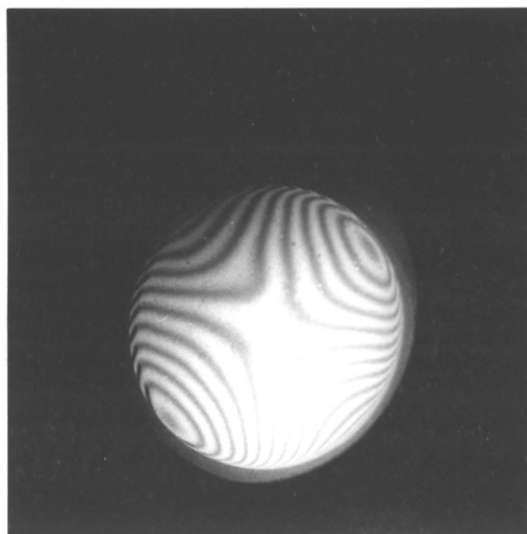
2.2.1.4 Errors due to Variable Path Length Cell Components

Errors in the k values of the liquids can be introduced by faults in the window surfaces in contact with the liquid (tilts, bulges, damaged coatings), wedge effects in the liquid caused by misalignment of the two main sections of the cell (body and sleeve), or vernier scale errors.

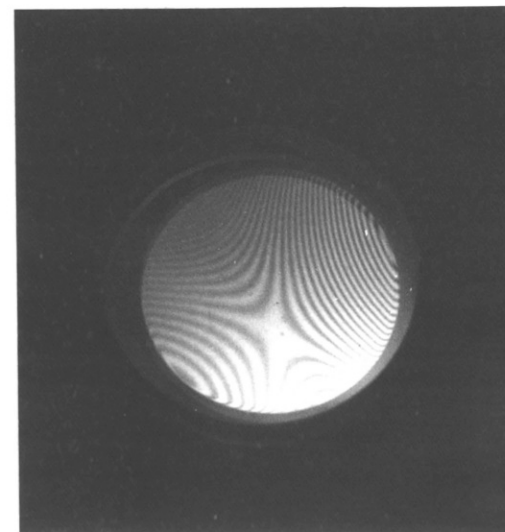
In the report by Irvine and Pollack (introduced in section 2.2.1.3) the point is made that for small path lengths (they consider *small* to be 10 microns or less) curvature in the substrate/sample boundaries, for whatever reason, creates ambiguity in the setting of the path length. Small changes in thickness can lead to large changes in the value of k , for large k . The sapphire windows of the variable path length cells have been studied using a Twyman and Green interferometer (Longhurst, 1973) in the visible. The fringe patterns obtained showed evidence of wedge effects, and some astigmatism in the windows. By placing the windows on an optical flat, and illuminating with a sodium lamp (Malacara, 1978), it is possible to study the interference fringes due to one face of the window in isolation rather than the combined interference effect of both faces given by the Twyman and Green. This has been carried out and the more interesting of the interference fringe patterns obtained are shown in photograph plate 2B for a series of sapphire window faces. Photograph 2Bi is of a tilt fringe pattern, with some irregularity at one edge of the window. The wedge variation across the



i



ii



iii

Photograph Plate 2B: Interference Fringes for Sapphire Surfaces

diameter of the window is of the order of 8 microns. The pattern in 2Bii is of the astigmatism given by axial curvatures of opposite signs. In the worst case the variation of thickness from the flat part of the saddle in the centre of the window to the edge of the window is less than 2 microns. Photograph 2Biii is a combination of astigmatism and some tilt, the variation from flat region to the edge of the window is about 5 microns for the worst case. The aberrations in the three surfaces demonstrates the problems of trying to measure path lengths of the order of a few microns with windows that are not suitably *flat*.

It is virtually impossible to study the effect of the liquid gap when the cell is assembled, since any attempt to isolate the liquid gap requires a compensator plate in the secondary arm of the interferometer to counteract the effect of the windows. Another approach was that of developing a simple mathematical model to assess the errors generated by wedge effects in the liquid. The problems of developing a suitable model, however, proved to be overwhelming. To begin with the incident beam is focussed down onto the cell, the focal point is not defined but will vary according to the path length set, it may fall outside the liquid body for small path lengths. The intensity of the incident beam is in any case not Gaussian. A degree of refraction will occur in the windows which may need to be accounted for. A further complication occurs in considering how the liquid *wedge* changes for different path length settings. The geometry of the model becomes complex in the case of the wedge position when there is a rotation through a *fraction* of a revolution rather than a full or even a half revolution.

2.2.1.5 Assigning Errors to Variable Path Length Cell Measurements

In general, assuming the sample is *clean*, the greatest inconsistencies will occur for k values found by smaller path lengths (according to the comments of Irvine and Pollack). By a series of simple experiments it was possible to devise a rough error scheme for the k values which was related to the thickness of the liquid. Distilled water was the sample liquid and all three variable path length cells acquired by I.C. from the Specac Company were used. At the same wavelength (4 microns was chosen) the k value (chosen so that it is of average magnitude) at a number of path length setting (covering as much of the vernier scale) was recorded. Clearly the absorptive index chosen could not be too large since all the path settings would be confined to the 0.005 - 0.01 mm region of the scale. The standard deviation in k was

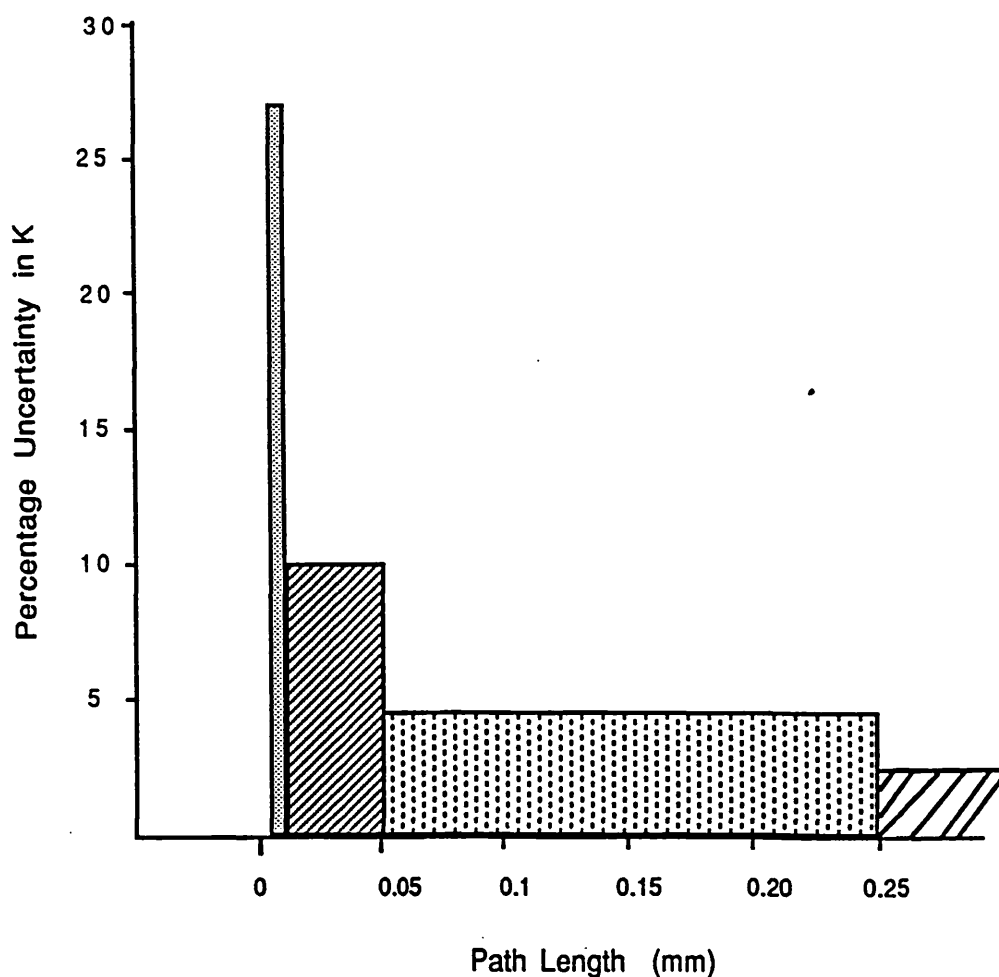


Fig 2.3: The Error Associated with Variable Path Length Cell Measurements.

calculated for different path differences. The percentage uncertainty in the absorptive index for varying cell thicknesses is shown in table 2.2 and in fig 2.5. Although it is a rough analysis which neglects a number of other factors it is clear that a smaller path length, and by implication a high k value, has a large degree of uncertainty whereas a large thickness yields a more accurate absorptive index.

It is perhaps important to note that although three variable path length cells were used the results from all three cells were quite random in nature i.e. no one cell gave consistently better agreement (or indeed worse agreement) for repeated k values. The conclusion that can be drawn from this observation is that large errors do not arise because of a specific fault in one particular cell, but simply because of the limitations imposed on us by having to use small

path lengths. Whilst it is true that only one make and type of cell was used there is nothing to suggest that any other transmission cell of a basically similar design would not suffer the same intrinsic limitations.

Δt (mm)	percentage uncertainty
0.005 - 0.01	27
0.01 - 0.05	10
0.05 - 0.25	5
> 0.25	2.4

Table 2.2: Percentage Uncertainty as a Function of V.P.L.C. Thickness.

2.3 Transmission Measurements with Fixed Length Cells

In wavelength regions where k is small ($k < 10^{-5}$) transmission measurements are carried out with fixed length cells instead of variable path length cells. This is because little absorption occurs in the liquid so to detect any discernable absorption requires greater thicknesses in the liquid sample and the variable path length cells cannot provide the large path lengths required. The fixed length cells are effectively hollow glass tubes of 5 , 10 , 15 and 25 centimetres in length which are filled with the liquid which is to be studied. At a wavelength , λ , a fixed length cell is placed in the path of a collimated beam and the transmitted intensity is recorded, but in this instance to acquire a second intensity reading at the same wavelength the fixed cell is replaced by a cell of a different length and a second measurement made. As in the variable path length cell case the Lambert - Bouguer law is used to create two equations which can be solved for the absorptive index. In practice the fixed length cells have been used in the visible to near infrared region extending from 0.5 microns to about 2 microns. The absorptive index values found in this region can be of the order of 10^{-6} - 10^{-7} , so by virtue of their small magnitude they have associated errors of the order of 50%

(poor collimation leads to large errors when k is very small). They can in any case be considered negligible in our calculation of the corresponding refractive index.

2.4 Reflectance Measurements

The refractive index of a liquid is found indirectly using reflectometry Fig 2.4 shows a schematic diagram of the reflectometer designed, by P.J. Chandley, for free liquid surface measurements. A more detailed diagram of the reflectometer sample stage is shown in fig 2.5 and in photograph plate 2C. Fig 2.4 shows the incoming beam of monochromatic radiation from the monochromator (via the filter which cuts out higher orders of the wavelength) impinging on the first plane mirror and directed upwards to one of two concave mirrors of large radius of curvature. From here the beam is focussed onto the free liquid surface at a *near normal* angle of incidence. A reflected component is then directed upwards onto the second of the concave mirrors and down onto a plane beam steering mirror. The beam then strikes a collecting mirror and is focussed onto the window of the detector.

The sample stage (fig 2.5) holds the two stainless steel dishes into which the sample liquid and reference liquid are placed. The sample stage is symmetrical about the central line XX and the two arms are inclined as shown at an angle of 5° to the horizontal. The sample dishes are themselves machined with a horizontal base and the top sloped at 5° so that when placed into the recesses of the sample stage the liquid surface is normal to the incident beam whilst the base of the dish is inclined so as to turn out the beam transmitted through the bulk of the liquid. In practice, however, the incline was found to be insufficient and unwanted reflectances occurring at the base of the dishes were redirected into the system. By placing neutral density glass filters in the base, supported on metal shoes (to further increase the angle), the base reflectance can be completely steered out of the system. It was discovered, by chance, that the inclusion of the metal shoes made the removal of the neutral density filters a great deal easier when dismantling the cell at the end of an experimental session. It is for this reason that the metal shoes were included in the design of the closed optical cell (chapter three).

The reflectometry system is partially automated so the actual process of obtaining the

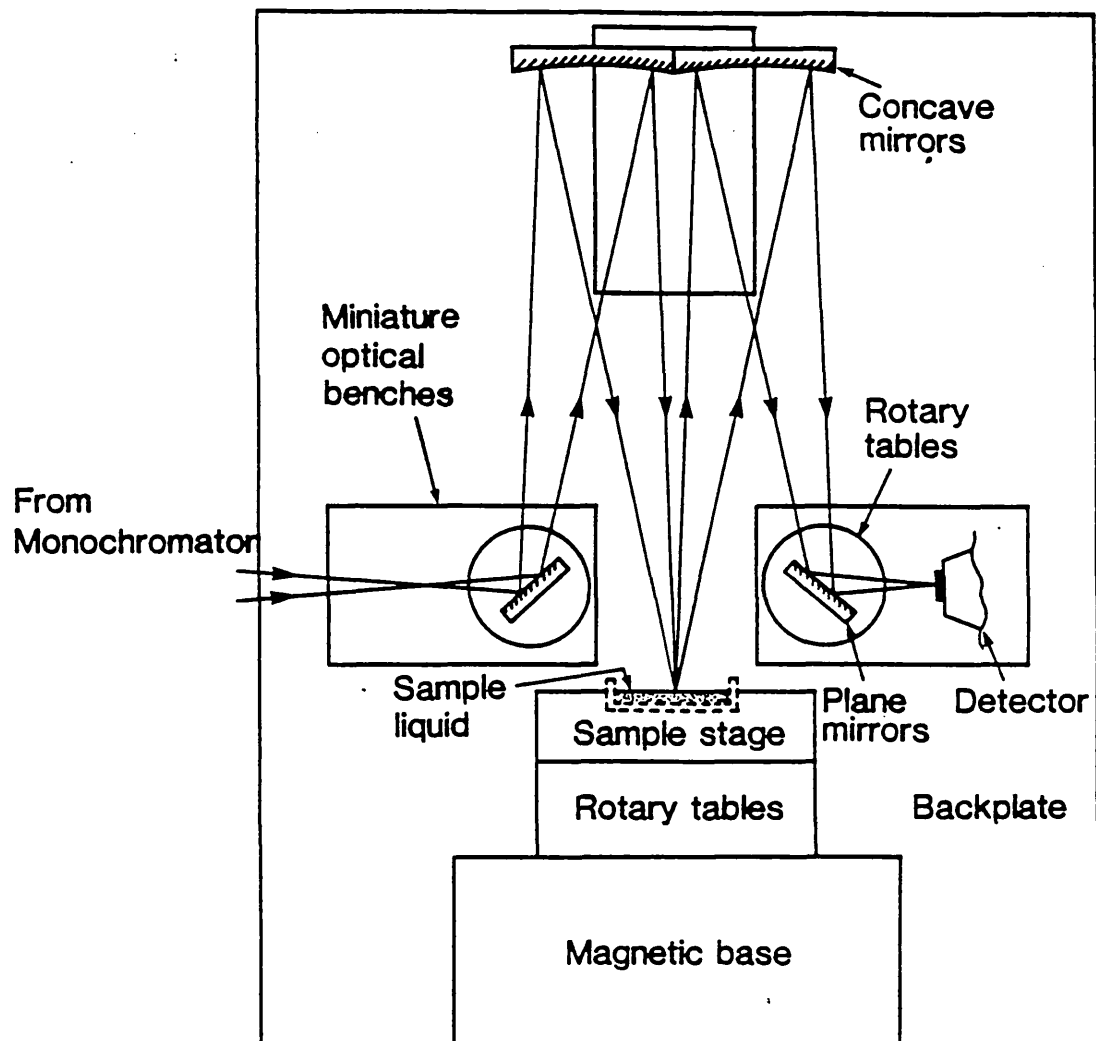


Fig 2.4: The Reflectometer

(Illustrated by Neal Powell, Imperial College, London)

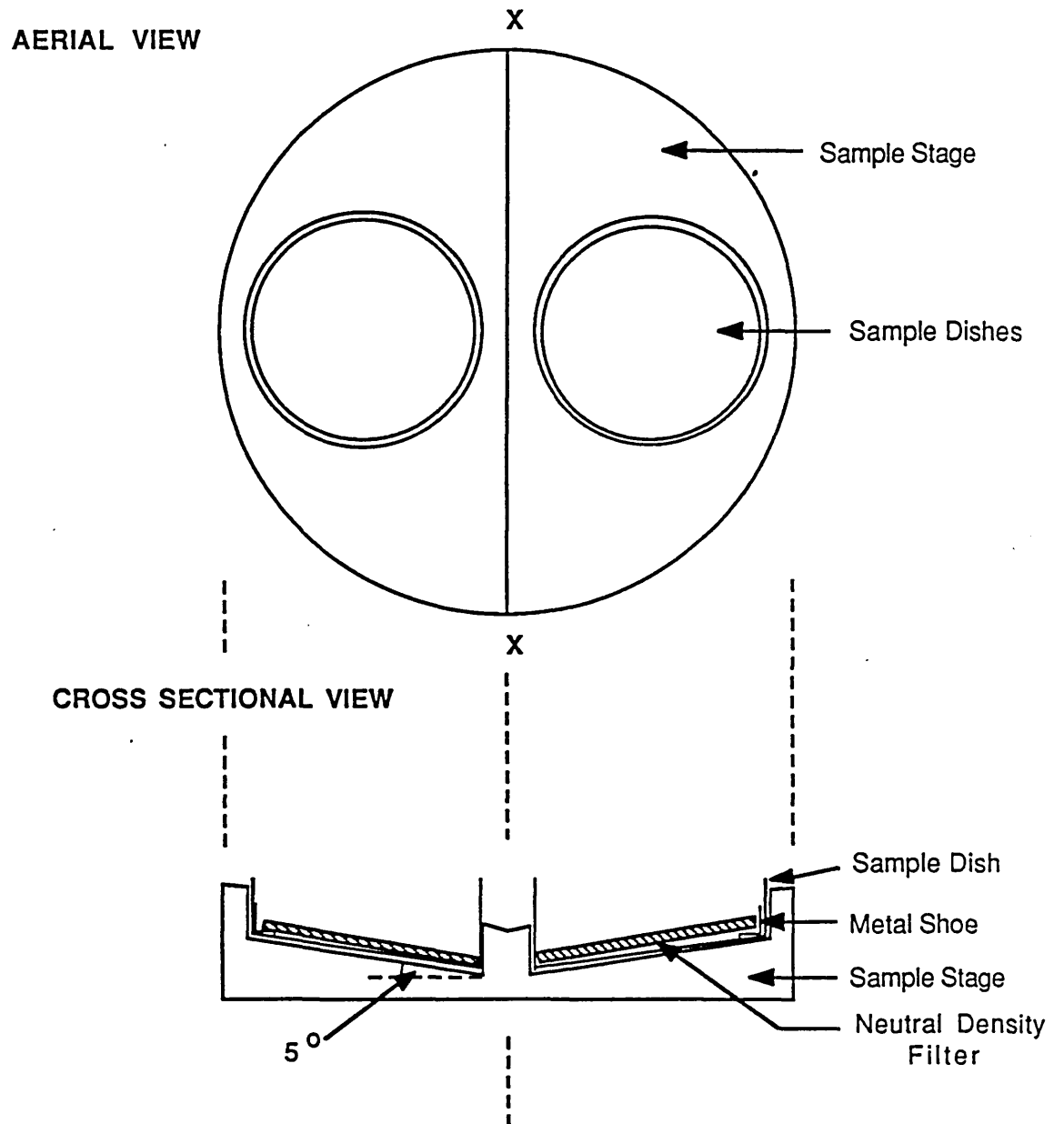
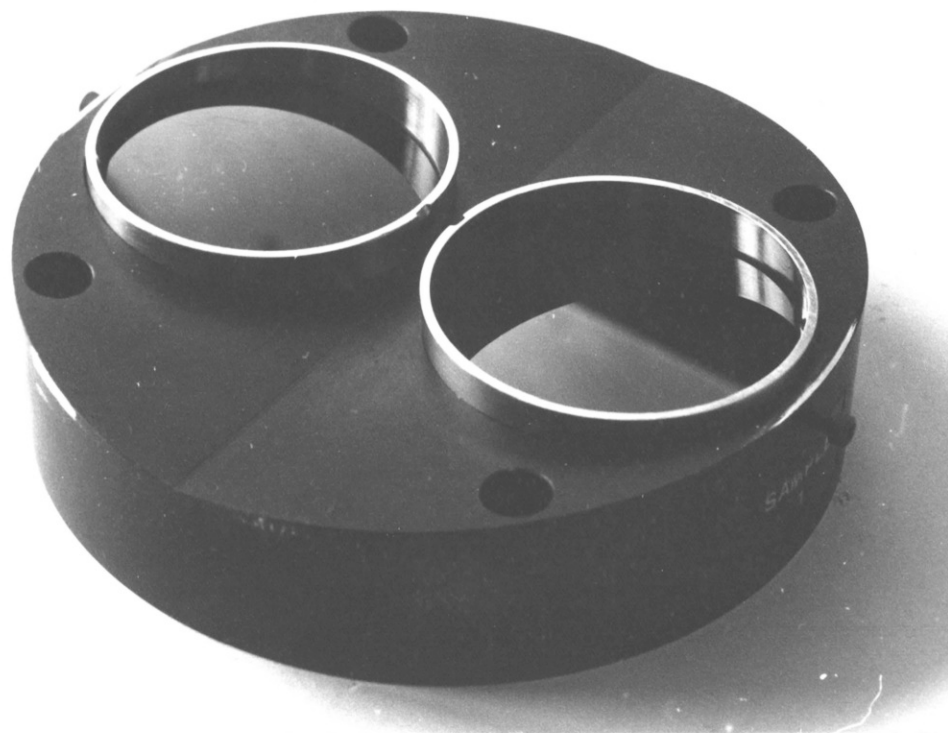


Fig 2.5: The Reflectometer Sample Stage.



Photograph Plate 2C: The Reflectometer Sample Stage for Free Liquid
Surface Measurements

reflectance at each wavelength, for a 0.34 - 16.0 microns range, is quicker than gathering the data manually. At each wavelength the sample stage positions the dish containing the liquid under test so that the incoming beam of radiation is reflected from the liquid surface and the reflected signal recorded. The sample stage then rotates until the dish containing the *reference* liquid, distilled water, is in position and the reflected signal recorded again.

The absolute reflectance of the sample liquid, R_s , is obtained by comparing the measured signal of the sample liquid, G_s , with that of the water, G_{water} . By multiplying the quotient of the measured signals with the absolute reflectance of the distilled water, R_{water} , the absolute reflectance of the sample liquid can be obtained according to

$$R_s(\lambda) = [G_s(\lambda) / G_{\text{water}}(\lambda)] \times R_{\text{water}}(\lambda) \quad (2.5)$$

The symbol (λ) indicates that the signals are wavelength dependent. The calculations are carried out according to a program which accesses the stored standard reflectances of distilled water and the values of R_s are printed.

The absolute reflectance of the liquid sample, R_s , together with the absorptive index, k , which was measured independently by transmission (see section 2.2) can be substituted into the specialized (normal incidence) form of the Fresnel equation (see chapter one)

$$R_s = [(n - 1)^2 + k^2] / [(n + 1)^2 + k^2] \quad (2.6)$$

By inverting equation (2.6) the refractive index of the sample liquid, n , can be extracted. Although equation (2.6) is for the normal case we are in reality working with an incident beam at a *near normal* angle of incidence. However, the approximation to the normal incidence case is justifiable and has been verified in appendix P.

2.5 Kramers - Kronig Dispersion Analysis

It soon becomes obvious when making transmission measurements as described in section 2.2 that there are a number of regions in the infrared for which a k value cannot be

found using the variable path length cells. This occurs in regions where the absorption is so great that even at minimum path lengths the incident beam is completely (or almost completely) absorbed by the liquid and no emergent signal recorded. The effect of not being able to measure an absorptive index is that the corresponding refractive index cannot be calculated. This follows from the Fresnel equation (2.6) discussed in section 2.4. In short any gaps in the absorptive index measurements are translated into corresponding refractive index gaps too. A possible solution to this problem is the application of the Kramers - Kronig dispersion analysis.

The class of mathematical relations known as Kramers - Kronig or dispersion relations link a variety of physical properties by means of an integral formula. Although the integral formulae are not developed from physical reasoning they are based on the assumptions of linearity and causality (Cannit et al, 1969). The dispersion relations have been derived by a number of authors such as Bohren and Huffman (1980), Wooten (1972), and Dolan (1987). Dolan's analysis and application to the liquid diethylene glycol (digol) is particularly relevant to the work carried out in this project.

The particular integral required in this case links the reflectance, R , with the phase change undergone on reflection, $\theta(\lambda_0)$ at λ_0 for a known wavelength λ

$$\theta(\lambda_0) = \frac{\lambda_0}{\pi} \int_0^{\infty} \frac{\log_e [(R(\lambda) / R(\lambda_0))] d\lambda}{\lambda^2 - \lambda_0^2} \quad (2.7)$$

In chapter one the reflection coefficient was expressed as :

$$\tilde{r} = (1 - m) / (1 + m) \quad (1.20)$$

$$\text{where } \tilde{r} = (R)^{1/2} \quad (2.8)$$

but $\tilde{r}$ can also be expressed in terms of its amplitude (modulus) and the phase θ

$$\tilde{r} = r e^{i\theta} \quad (2.9)$$

Therefore, expressing the reflection coefficient as an explicit function of n and k (by substituting $m = n + ik$ into equation (1.20) and equating real and imaginary parts),

$$\tilde{r} = \{ (1 - n^2 - k^2) / [(1 + n)^2 + k^2] \} - i \{ 2k / [(1 + n)^2 + k^2] \} \quad (2.10)$$

from which it can be shown that,

$$n = (1 - R) / (1 + R + 2 R^{1/2} \cos \theta) \quad (2.11)$$

$$k = -2 R^{1/2} \sin \theta / (1 + R + 2 R^{1/2} \cos \theta) \quad (2.12)$$

To apply the Kramers - Kronig theorem to near normal incidence reflectance measurements it is necessary to integrate from zero to infinity. This cannot, of course, be achieved in practice, instead, the reflectance of the liquid sample is measured over as wide a wavelength range as possible. Suitable extrapolations are then made to allow the evaluation of the integral in equation (2.7) in the ranges extending from the minimum measured wavelength to zero and the maximum measured value to infinity. By finding θ , the phase change on reflection, the n and k values of the liquid can be derived from equations (2.11) and (2.12).

There are a number of difficulties associated with applying the Kramers - Kronig analysis outlined above, the most apparent is that of finding suitable extrapolations for the reflectance regions lying outside the measured range. This problem, and other complications connected to the dispersion analysis, has been covered by M.B. Dolan (1987) and the analysis program developed by him has been used to interpolate results for the samples presented in section 2.6.

2.6 Experimental Results

The reflectance and transmission techniques (and where relevant dispersion analysis) described above have been used to produce the optical constants of the polyethylene glycols presented in section 2.6.2. But, because of its unique function as the standard in our measurements, it is necessary to examine the properties of water first.

2.6.1 A Study of the Properties of Water

Water features a great deal in the experimental work carried out in this project, it is used as the liquid standard in our work, so we are required to know its absolute reflectance for the measurements described in section 2.4. The optical constants are also needed when water is used as the standard in the closed cell system described in chapter three. Its choice as a standard to calibrate other liquids is from a purely practical point of view a natural choice, it is resistant to chemical attack, stable, homogeneous and easily obtainable. Perhaps it is for these reasons and its atmospheric abundance that its optical constants are so well documented in the literature, another important reason it was chosen for the work in this project.

A number of references exist in the literature, but the results of Hale and Querry (1973) are considered to be definitive - this is probably because they made a very extensive review of the literature. The absorptive indexes, from forty - eight articles and books spanning 81 years, were plotted for a region extending from 0.2 microns to 200 microns. Significant discrepancies occurred at many wavelengths between the different k values, but the best visual fit to the plotted data was obtained by manually drawing a smooth curve through the points. Hale and Querry weighted the curve in favour of data for water at 25°C and in favour of data reported by authors who in Hale and Querry's judgement used careful experimental procedures. Values of the refractive index were computed by Hale and Querry by applying a subtractive Kramers - Kronig analysis to the absorptive index spectrum.

The results produced by Hale and Querry have been used in a comparative study with the results obtained from experimental measurements by us. Two other references have been used to highlight differences between the optical constants of water measured by different researchers, they are the results of Irvine and Pollack (1968) and those of Zolotarev et al (1969).

(1969).

Irvine and Pollack published results from a critical review of the existing literature on the optical properties of water for the 0.2 - 200 microns region. They tabulated measured values of both k and the Lambert coefficient acquired from about thirty different literature sources. Taking the only four reports available at the time on measurements of the reflectance of water, they collated values for the reflectance measured at near normal incidence for a free water surface. Substituting these reflectance values and the k values into the generalized Fresnel equation (as in equation (2.6)) they were able to obtain values for the refractive index.

Zolotarev et al presented values for the optical constants of water throughout the wavelength region 1 - 10^6 microns. They calculated n and k from measurements of reflectance and the absorption coefficient that they made on water at 25°C in the 2 - 50 microns region and measurements on the internal reflectance spectra in the 2 - 10 microns region. Their measurements and data collated from thirteen other papers available at the time provided k values covering the 1 micron to 10^6 microns spectral range. The refractive index was then obtained from a Kramers - Kronig analysis of the absorptive index spectrum.

2.6.1.1 The Reflectance Data for Water

The absolute reflectance data used in the calculation of absolute reflectances for the liquids under test (see section 2.4) have been measured by M.B. Dolan (1987). He measured the reflectances of water directly using the reflectometer arrangement with water in one arm of the sample stage and an aluminium mirror in the other arm which served as the reflectance standard. The absolute reflectance of the aluminium mirror was measured by means of a Strong reflectometer (Strong, 1938). The reflectance values for water found by M.B. Dolan using this method are shown in fig 2.6.

It may appear, from the method described above, that water is not required as the standard, that it could be replaced by an aluminium mirror standard. So that equation 2.5 would be replaced by:

$$R_s(\lambda) = [G_s(\lambda) / G_{Al}(\lambda)] \times R_{Al} \quad (2.13)$$

where now: G_{Al} is the reflected signal from the aluminium mirror

In a practical situation the reflectance (80% - 98% of the incident beam is reflected) of the mirror is very much greater than that of a liquid, this means that the intensity of the incident radiation must be reduced, otherwise the mirror reflects so much of the beam that an overload occurs at the detection system. However, at the same wavelength the liquid gives a much lower reflection the accuracy of which will be affected by a high level of noise. The accuracy of the reflectometry depends on the comparison of a material with a standard with a reflectance of the same order of magnitude. It is for this reason that water is used so prolifically as a standard liquid in experimental work of this kind.

2.6.1.2 The Optical Constants of Water

The absorptive index of distilled water has been measured using variable path length cells in the spectral range 2 -13 microns, the technique has been described in section 2.2. The k values and reflectances (see section 2.6.1.1) were substituted into the near normal incidence form of the Fresnel equation (equation (2.6)) to yield the corresponding refractive index values. The absorptive and refractive indexes are shown graphically in fig 2.7, the data tables in appendix K. Wavelength regions in which the n and k values have been interpolated using Kramers - Kronig analysis are indicated by an asterisk in the data tables.

The n and k curves were plotted on common axes with n and k curves taken from the review by Hale and Querry, the graphs are shown in fig 2.8. There appears to be good agreement between the curves plotted from Hale and Querry's work and curves found by us in the case of both the refractive index and the absorptive index. The absolute difference between the refractive indexes found by us and those of Hale and Querry and between our absorptive index values and Hale and Querry's are presented in fig 2.9. These two graphs illustrate that pronounced discrepancies occur in the absorption band regions, 2.7 - 3.0 microns and at about 6.1 microns. It is understandable that the greatest variation between different data sources will occur at or around the absorption peaks. This is where, due to the rapid changes, the measurements are more difficult to make and as a consequence have a greater associated error. So for the refractive index curves at 2.8 microns the relative percentage variation is about 2%, at 3.2 - 3.5 microns and 6.7 - 7.4 microns it is 1%. There is also a variation of 1% - 2% at 12.5 - 13.0 microns. The percentage difference is much greater in the absorptive index curves. For the k values the relative percentage discrepancy between our

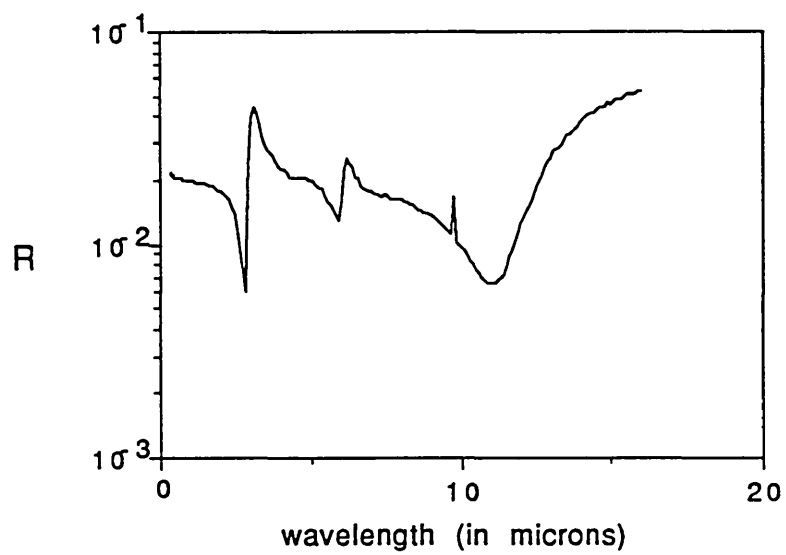


Fig 2.6: Reflectance values for Distilled Water.

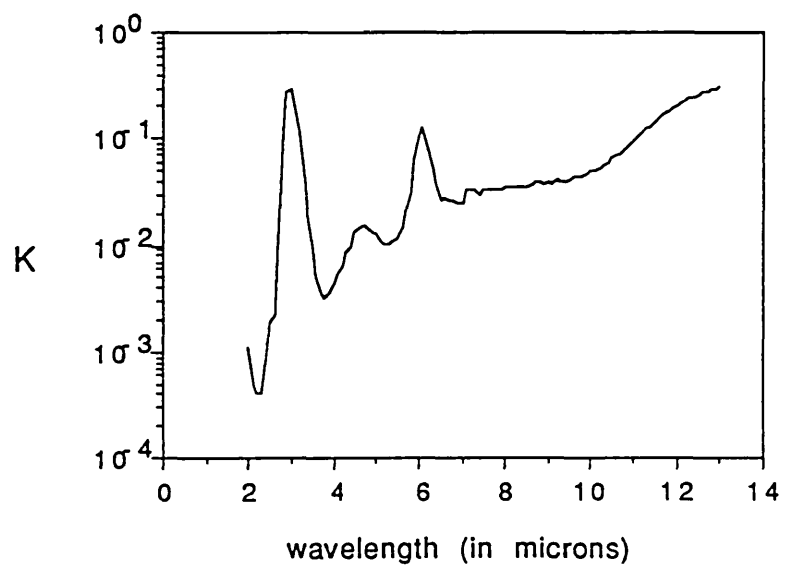
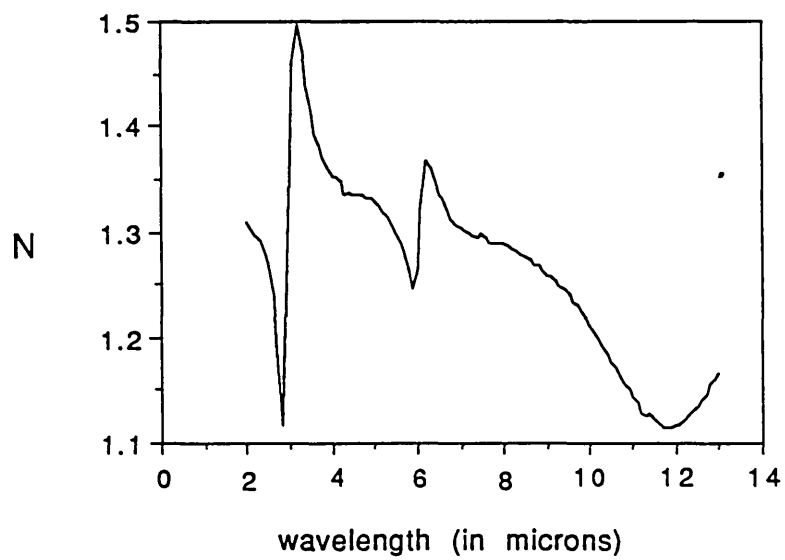


Fig 2.7 N and K values for Distilled Water.

wavelength (microns)	Hale and Querry	Irvine and Pollack	Zolotarev et al
2.2	1.296	1.293	1.278 (1.4)
2.4	1.279	1.276	1.255 (1.9)
2.6	1.242	1.180 (5.3)	1.225 (1.4)
2.7	1.188	1.134 (4.8)	1.150 (3.3)
2.8	1.142	1.232 (-7.3)	1.110 (2.9)
2.9	1.201	1.310 (-8.3)	1.204
3.0	1.371	1.351 (1.5)	1.362
3.1	1.467	1.426 (2.9)	1.470
3.2	1.478	1.509 (-2.1)	1.494 (-1.1)
3.3	1.450	1.470 (-1.4)	1.456
3.4	1.420	1.449 (-2.0)	1.428
3.5	1.400	1.423 (-1.6)	1.400
3.6	1.385	1.402 (-1.2)	1.385
6.0	1.265	1.313 (-3.7)	1.276
6.1	1.319		1.322
6.2	1.363		1.360
6.3	1.357		1.343 (1.0)
11.5	1.126	1.145 (-1.7)	
12.0	1.111	1.160 (-4.2)	1.114
12.5	1.123	1.190 (-5.6)	
13.0	1.146	1.220 (-6.1)	1.135 (1.0)

Table 2.3: Refractive Index Values for Water taken from the work of Hale and Querry (1973), Irvine and Pollack (1968) and Zolotarev et al (1969). The numbers in brackets indicate (relative) percentage variation from Hale and Querry's values.

wavelength (microns)	Hale and Querry	Irvine and Pollack	Zolotarev et al
2.0	1.1e-3	1.082e-3 (1.7)	
2.2	2.89e-3	2.80e-3 (3.1)	3.2e-4 (800)
2.4	9.56e-4	8.02e-4 (19.2)	8.2e-4 (16.6)
2.6	3.17e-3	2.048e-3 (54.8)	2.2e-3 (44.1)
2.7	0.019	0.005049 (276)	0.0160 (18.8)
2.8	0.115	0.09361 (22.9)	0.1570 (-26.8)
2.9	0.268	0.2435 (10.1)	0.2920 (-8.2)
3.0	0.272	0.2586 (5.2)	0.2780 (-2.2)
3.1	0.192	0.1828 (5.0)	0.2030 (-5.4)
3.2	0.0924	0.09422 (-1.9)	0.0760 (21.6)
3.3	0.0368	0.04333 (-15.1)	0.0350 (5.1)
3.4	0.0195	0.01888 (3.3)	0.0185 (5.4)
3.5	0.0094	0.00930 (1.1)	0.0085 (10.6)
3.6	0.00515	0.00567 (-9.2)	0.0050 (3.0)
7.0	0.0320	0.03443 (-7.1)	
7.1	0.0320		
7.2	0.0321		
7.3	0.0322		
7.4	0.0324		
7.5	0.0326	0.03456 (-5.7)	
7.6	0.0328		
7.7	0.0331		
7.8	0.0335		
7.9	0.0339		
8.0	0.0343	0.03603 (-4.8)	

Table 2.4: Absorptive Index Values for Water taken from the work of Hale and Querry (1973), Irvine and Pollack (1968) and Zolotarev et al (1969).

The numbers in brackets indicate (relative) percentage variation from Hale and Querry's value.

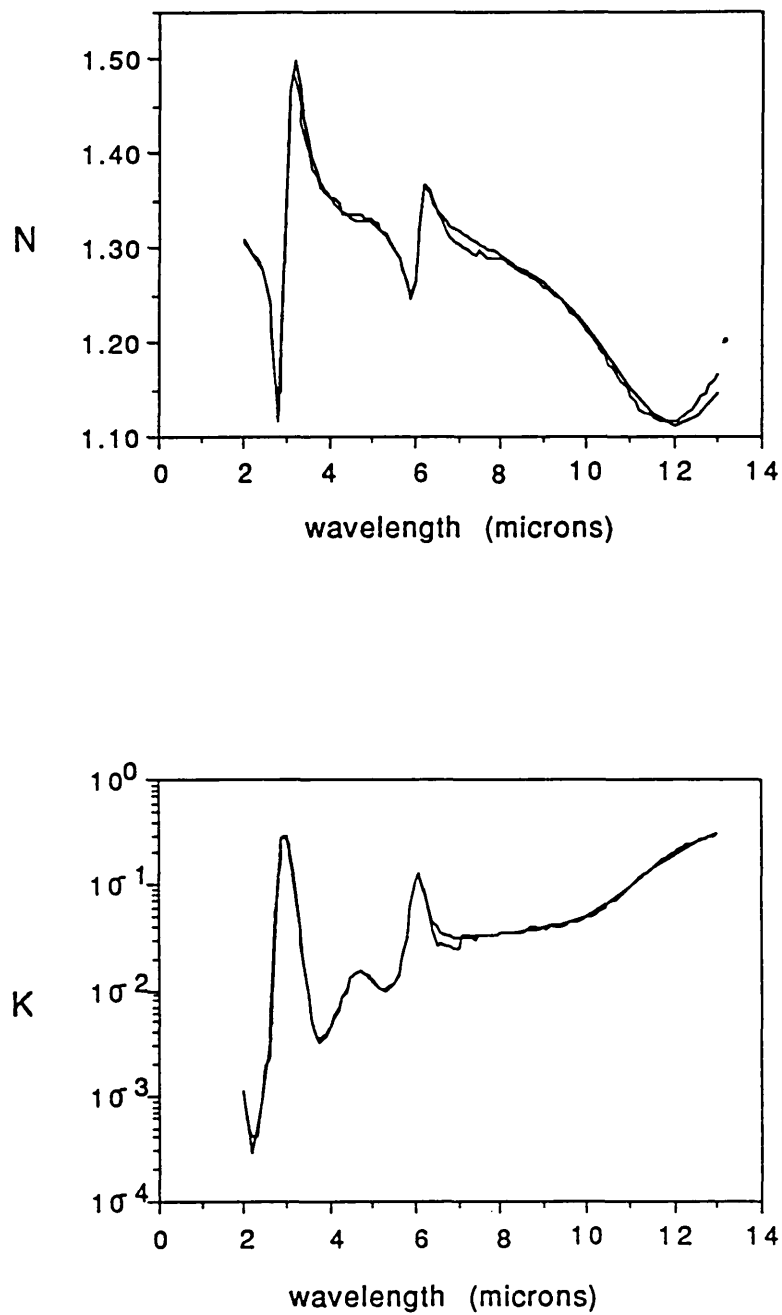


Fig 2.8 The n and k values for water compared with values found by Hale and Querry (1973). In both the n and k case the curves appear to be superimposed.

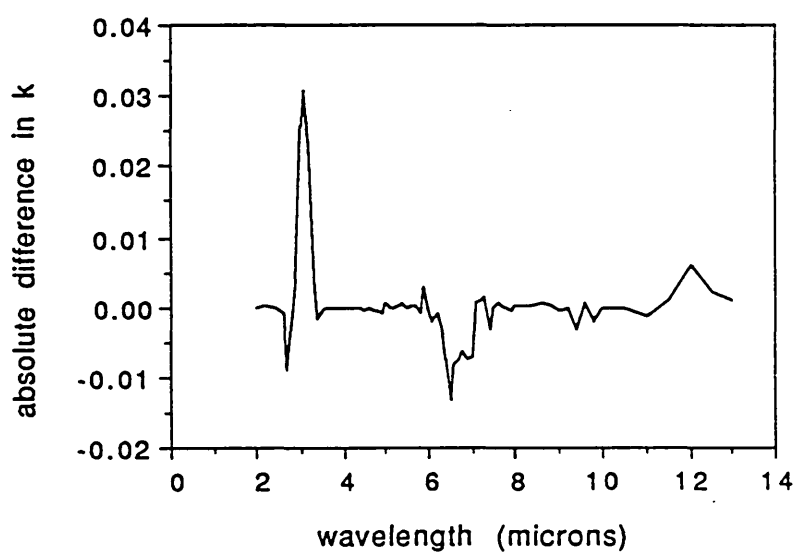
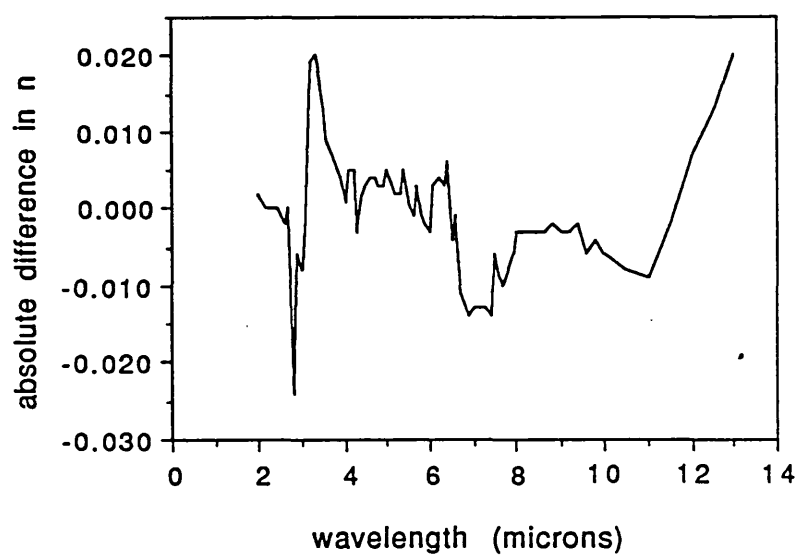


Fig 2.9 The absolute difference in n and k values for water determined by us and those taken from Hale and Querry.

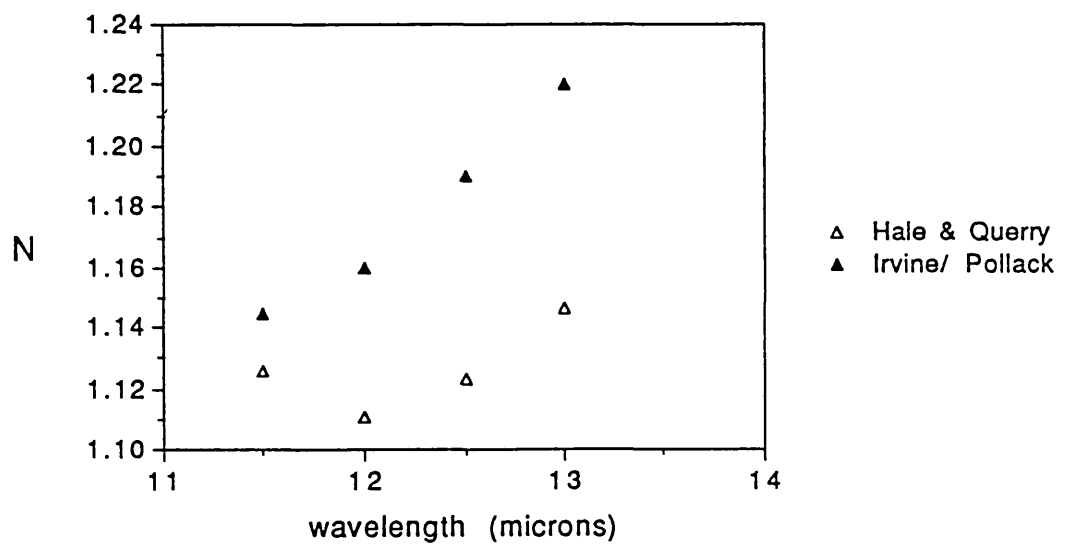
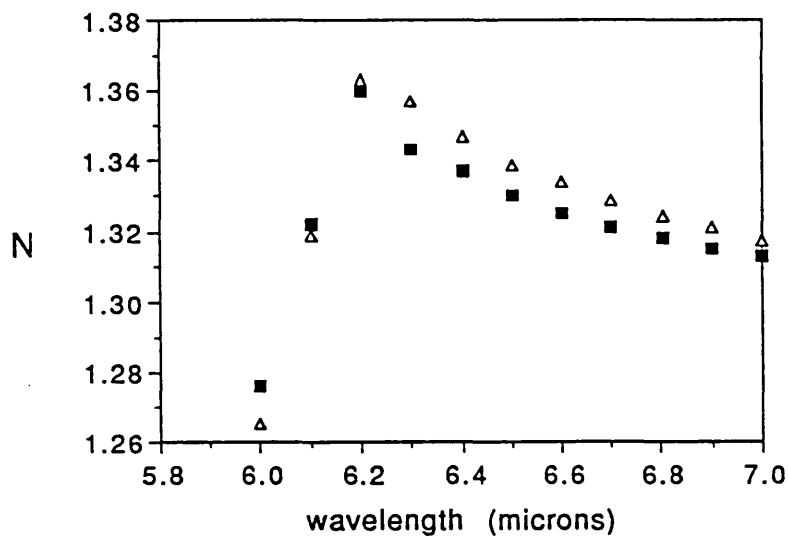
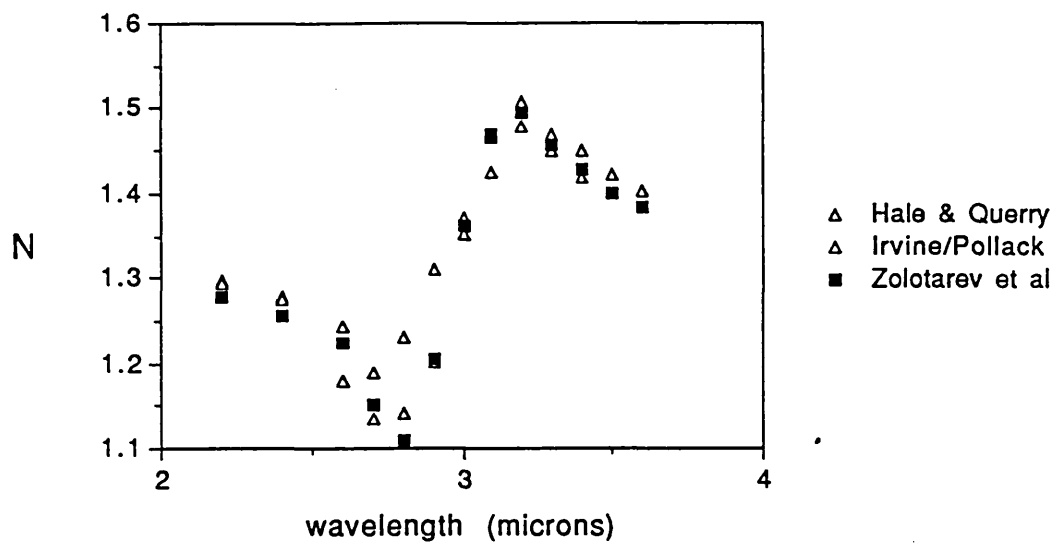


Fig 2.10 Scatter plots for the refractive index of water
(taken from literature sources).

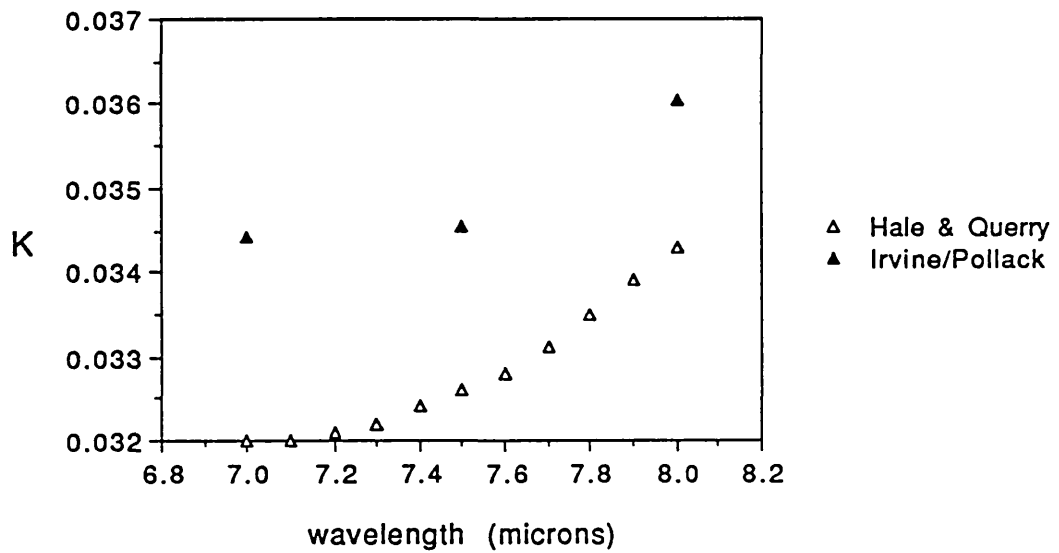
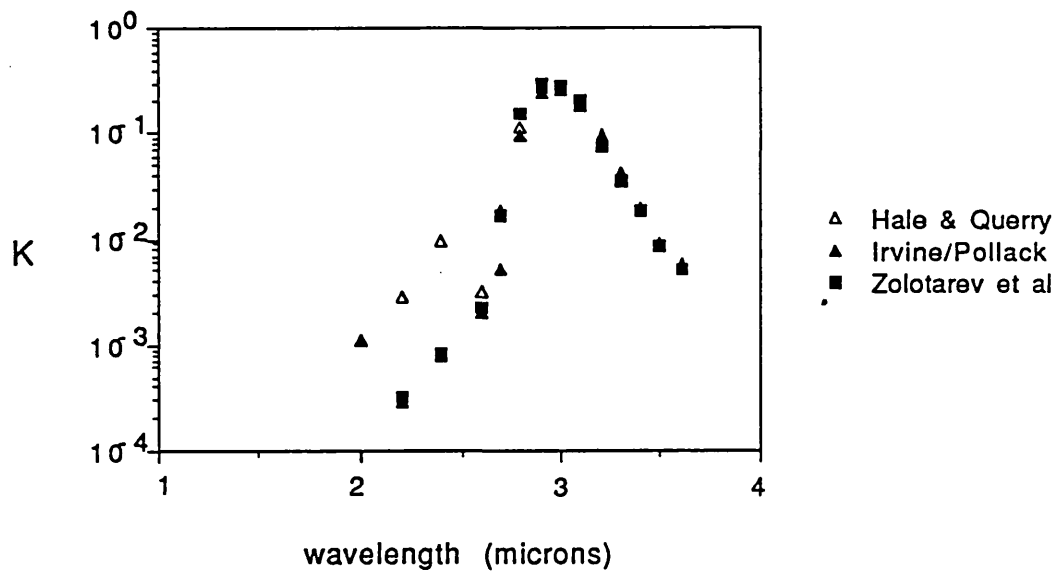


Fig 2.11 : Scatter plots for the k value of water
(all data taken from literature sources).

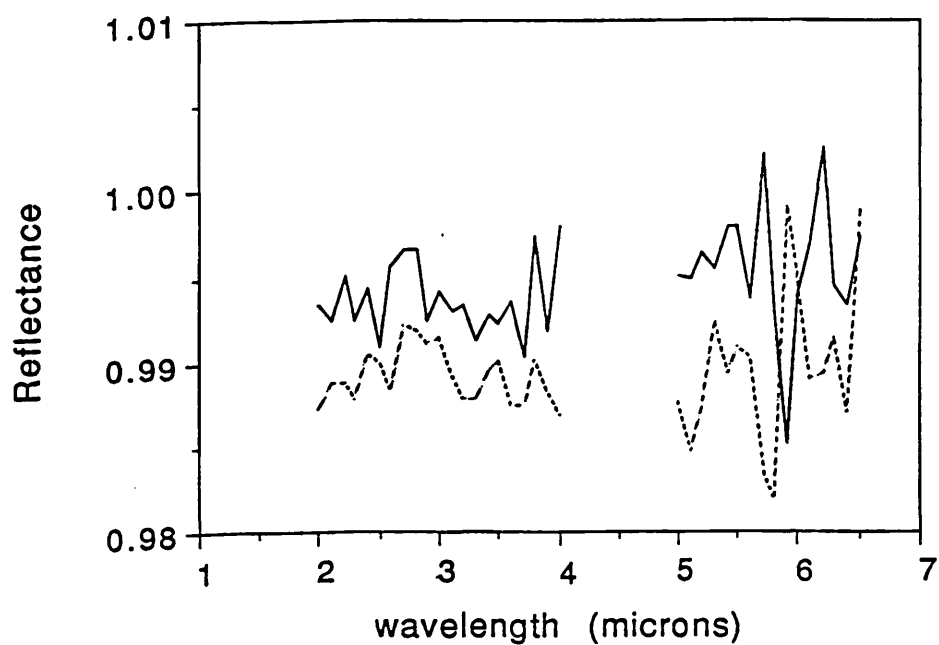


Fig 2.12 : The variation in reflectance of distilled water samples.

The solid line curve indicates the Aldrich water as sample case, and the broken line the case where B.D.H. water is used.

results and those of Hale and Querry at 2.0 - 3.2 microns fluctuates between 0 and 50%, and at 6.4 - 7.0 microns it is of the order of 20% - 30%. However, comparisons drawn between n and k values of several literature sources (Hale and Querry (1973), Irvine and Pollack (1968) and Zolotarev et al (1969)) shows that a spread of values exists. This is illustrated in fig 2.10 for refractive index values and fig 2.11 for absorptive index values and in table 2.3 and table 2.4.

From this cursory study of the water data it is easy to appreciate how difficult the task is of trying to decide on *correct* values for the optical constants of water. Further complications arise when the question of how water from different geographical sources will behave.

2.6.1.3 Distilled Water taken from Different Sources

A short investigation was carried out to determine whether distilled water from different geographical sources (and hence by different purification processes) would have perceptible differences in reflectance. Water was acquired from two sources, Aldrich Chemical Company Limited (glass filtered water sample) and B.D.H. Chemicals Limited (deionised). The two water samples were each treated as *sample* liquids and were placed, in turn, in the sample arm of the reflectometer, with water from Imperial College (I.C.) acting as the *standard water* sample. If there were no differences between I.C. water and Aldrich water, or I.C. water and B.D.H. water, then the relative reflectance ratios ($G_{\text{Aldrich}} / G_{\text{I.C.}}$ and $G_{\text{B.D.H.}} / G_{\text{I.C.}}$) should be exactly 1.00. Allowing for a 1% experimental uncertainty in the reflectance any value lying outside threshold values of 0.99 and 1.01 can be considered to be significant. Fig 2.12 illustrates the results of reflectance measurements made in the absorption band regions (where any differences would be more apparent). It can be seen that the curves do fall outside the lower error band at certain wavelengths. This, albeit preliminary, examination demonstrates that a water sample does not have a reflectance which can be taken to be a comprehensive (or *absolute*) standard.

The optical constants of water measured by us at I.C. (using I.C. water) have been used to subsequently calculate the optical constants of the sample liquids presented in this thesis (in the following section and in chapter three).

2.6.2 The Optical Constants of Polyethylene Glycols (pegs)

Polyethylene glycols (also called polyoxyethylenes, polyglycols or polyether glycols) are a group of condensation polymers of ethylene glycol with the general formula

$\text{HOCH}_2(\text{CH}_2\text{OCH}_2)_n\text{CH}_2\text{OH}$. Their average molecular weights vary from 200 to 6000. Properties vary with molecular weight from clear liquids of low viscosity to waxy, milky solids. The results from work on two pegs, peg 300 and peg 600, have been presented in this thesis. Peg 300 is a clear, slightly viscous liquid at room temperature it has a melting temperature of -10°C . Peg 600, on the other hand, has a melting temperature of $+22^\circ\text{C}$, so it is only just liquid at room temperature, it is as a consequence a great deal more viscous.

The optical constants for the sample peg 300 are illustrated graphically in fig 2.13 and tables of data appear in appendix L. n and k values for peg 600 appear in fig 2.14 and corresponding tables of data also in appendix L. The techniques used to acquire the optical constants have been outlined above - transmission using fixed and variable path length cells, and reflectometry. For both samples Kramers - Kronig dispersion analysis has been used to interpolate n and k values in regions where high absorption has prevented direct measurement. Both pegs naturally have the same characteristic n and k spectral profiles, which includes the large absorption band at 10 microns.

2.6.3 A Cautionary Note: Evaporation and Hygroscopicity

Any free liquid surface technique exposes the liquid under test to the risk of evaporation, or depending on the liquid, it may take up moisture from the atmosphere. The effect of these two processes should be considered when using the free liquid surface reflectometer. We first study the problem of evaporation. Any free liquid surface is susceptible to evaporation and despite the fact that the measurements are carried out at moderate temperatures of 20°C - 24°C (that change very little over the course of an experimental run), in a closed environment, inevitably some evaporation will occur. Up to 50% of the volume of a liquid can be removed from one arm of a sample stage without a serious change (i.e. one that exceeds the assigned error in reflectance) in the reflectance values obtained. However, it is unlikely that a liquid that would evaporate heavily would be used in a free surface measurement (it would be more suited to closed cell measurement).

A potentially more serious problem is that of hygroscopicity. The sample liquids in the reflectometry system are in open dishes and sit on sample stages adjacent to open dishes of distilled water. The degree of uptake of moisture is governed to an extent by the temperature

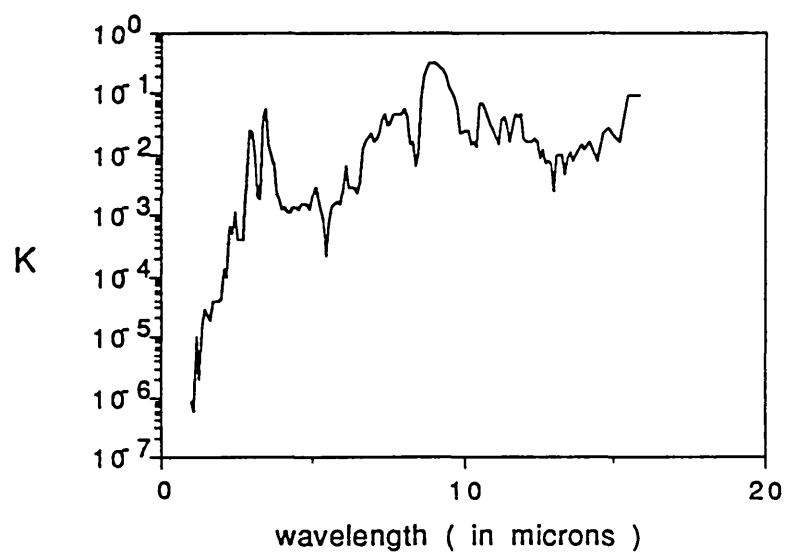
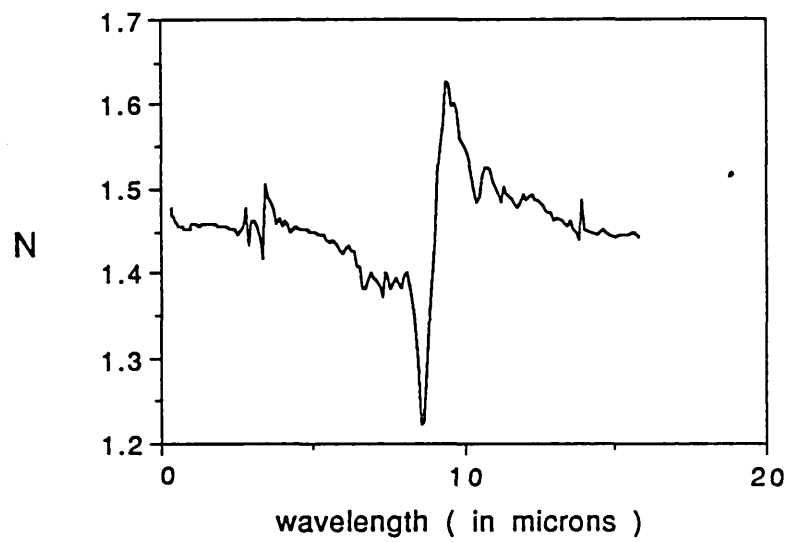


Fig 2.13 N and K values of peg 300.

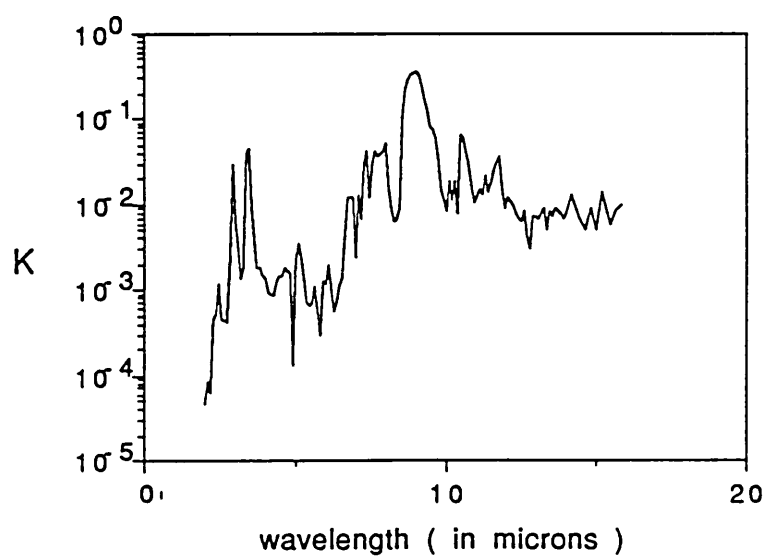
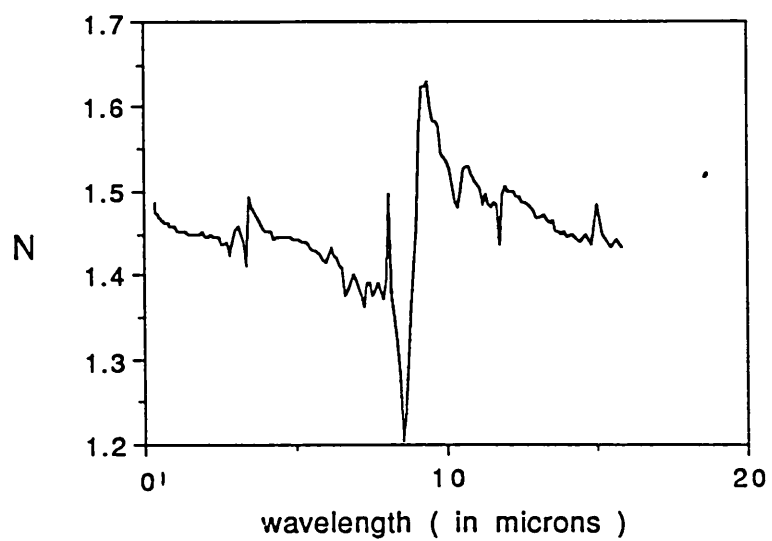


Fig 2.14 N and K values of peg 600

and humidity of the liquid's surroundings, but if the liquid has a tendency to take up water there is no way of preventing the process of uptake occurring by, for example, using dessicants in the sample stage environment. But how does the uptake of water affect the reflectance values?

The effect on the pegs was studied since they are hygroscopic to a degree. Since the ability to pick up water from the atmosphere is related to vapour pressure (vapour can take up water more efficiently than, for example, solid) the greater the peg number the less hygroscopic the liquid will be. Therefore, digol (or diethylene glycol) will be more hygroscopic than peg 300, which in turn will be more hygroscopic than peg 600. Measurements carried out on a sample of peg 300 that had been allowed to stand for 24 hours showed a drop in reflectance when compared to reflectance measurements made on a fresh sample. However, the change in reflectance is within the assigned experimental error and shows a negligible difference when converted into the corresponding refractive index. To make a full range of reflectance measurements on a liquid sample takes of the order of 4 - 6 hours, therefore, the change in reflectance of liquids like peg 300 and peg 600 would be within the associated experimental errors. Reflectance values for a sample of peg 300 that had been standing for 4 weeks were also found in the water band region of 2.5 - 3.0 microns. The corresponding refractive index values changed by 1% - 2% around the water absorption peak at 2.8 microns, and at the peak the discrepancy in the n value was 6%. However, a test sample would never be exposed for as long as 4 weeks (even if it were not hygroscopic it would be likely to absorb other contaminants), but as a cautionary measure a sample should not be exposed for longer than 24 hours. If a more hygroscopic liquid is to be measured then the sample liquid should be discarded from the sample dish at suitably regular intervals and replaced by fresh liquid taken directly from the source container. Another alternative is to measure the liquid in the closed cell system (see chapter three) in which case the liquid is protected from the atmosphere and cannot take up moisture.

2.7 The Complete Experimental Arrangement

Clearly to carry out the reflectance and transmission measurements it is necessary to

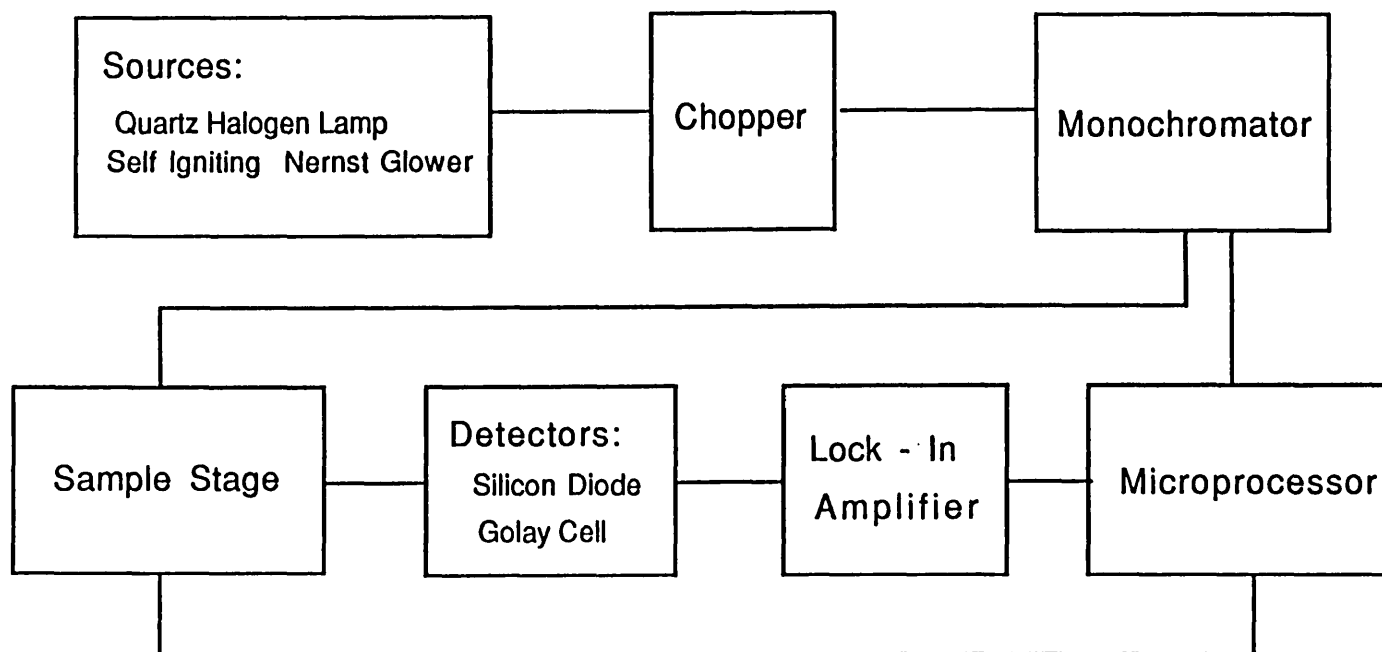


Fig 2.15 : General Experimental Arrangement.

have a source of monochromatic radiation and some means of measuring the amount of light reflected or transmitted, and this process must be repeated over a continual wavelength range from 0.34 microns up to 16 microns. Fig 2.15 is a representation of the peripheral experimental equipment used in making all the measurements in this project. This general arrangement was assembled by my predecessor, P.J. Chandley in 1979, and was subsequently partly automated by P.J. Chandley and M.B. Dolan. Although the equipment used and the general arrangement is fairly standard for this type of work a great deal of modification has been carried out. A brief description of the equipment appears here, a fuller explanation is included in M.B. Dolan's thesis.

A stable power supply is connected to a quartz halogen source (for the wavelength region below 3.9 microns), or a Nernst self igniting heater (for 3.9 - 16 microns). Both light sources were chosen for their ability to provide a stable output over a wide wavelength range and are housed in a fan cooled box. The source signal is chopped at a frequency of 9.3 Hz, Chandley (1982) modified a standard chopper to reduce the phase jitter that was occurring at the comparatively low frequency. The light source illuminates the entrance slit of a blazed grating Czerny Turner type double monochromator (Longhurst, 1973). The monochromator has a built on wavelength drive. The beam emerges from the monochromator and enters the sample box. The sample box houses the various pieces of equipment, reflectometer or transmission cells, during experiment. The equipment housed within the sample box is isolated from background radiation and the layer of polystyrene on the walls of the box prevents large fluctuations in temperature of the liquid environment. The box itself is mounted on an air cushioned cast iron table which provides a vibration free surface on which the equipment can be secured by means of magnetic bases. A filter wheel inside the box blocks second or third order harmonics in the incident light beam. The beam is transmitted or reflected and then steered by mirrors onto a collecting mirror which focusses the beam onto a detector. Two detectors are used to cover the spectral range, a silicon photodiode detects signals below 1 micron and a Golay cell (Martin, 1966) the signal from 1 micron to 16 microns. The Golay cell contains a gas, of low thermal conductivity, within a chamber which responds readily to infrared radiation. A rise in temperature in the gas produces a corresponding rise in pressure and a distortion of a mirror membrane in contact with the gas. To prevent changes in ambient

temperature from affecting the detector a fine leak is provided which connects the detector chamber with a ballasting reservoir of gas on the other side of the mirror membrane. In the absence of a changing radiation signal the pressures on both sides of the mirror membrane are equal and the membrane remains flat. The distortion of the mirror membrane caused by a changing radiation signal is converted into a voltage which is fed into an amplifier, and an analogue to digital converter. The final output is fed into a microprocessor which controls the automated equipment, such as the wavelength drive, filter wheel and reflectometer sample stage.

It is perhaps appropriate at this stage to state that the collection of experimental data over a complete spectral range can, depending on the nature of the liquid, take from one to two days. This at first sight may seem to be excessively prolonged when compared with the operation of a conventional spectrophotometer, but this is counterbalanced with the increased accuracy obtained.

CHAPTER THREE

The Volatile Liquid Cell Technique

3.1 Introduction to Volatile Liquid Measurements

Having investigated the optical properties of a variety of stable state (non volatile) liquids using the system described in chapter two, we considered the problem of adapting the *free surface* arrangement of the reflectometer to the measurement of *volatile* liquids. Since these liquids are characterized by their transition from liquid to vapour state at or around room temperatures, they are naturally unsuitable for use in any free liquid surface arrangement. This chapter deals with the optical cells designed to accommodate the liquids under test and the formulae used to extract the optical constants of the liquids. Also presented are the results of a study of the optical properties of the I.R. materials chosen for the cell windows.

3.2 the Volatile Liquid Cell

It proved necessary to produce an optical cell to contain the volatile liquid under test, for economical and practical reasons it was designed to be compatible with the existing reflectometry arrangement. The cell which was subsequently produced is shown schematically in fig. 3.1.

The incident and reflected beams are, in practice, at near normal angles but are shown with large angles for the sake of clarity. The body of the cell, in which the liquid is placed, is machined from stainless steel. The body of the cell contains a reservoir opening through which liquid is introduced into the cell (this is not illustrated), when the cell is filled the reservoir port is plugged with a P.T.F.E. stopper. The window, which has parallel faces and is of 3 mm thickness, is cushioned by P.T.F.E. rings at the liquid surface, P.T.F.E. is chosen because of its resistance to chemical attack. It is important to ensure that the liquid in the cell is in direct contact with the window, there must be no air gap between the liquid and window. A rubber ring separates the window from the anodised dural ring nut that holds it down. A neutral

density filter rests on a metal shoe in the bottom of the dish and turns out any unwanted signal that may be reflected from the base.

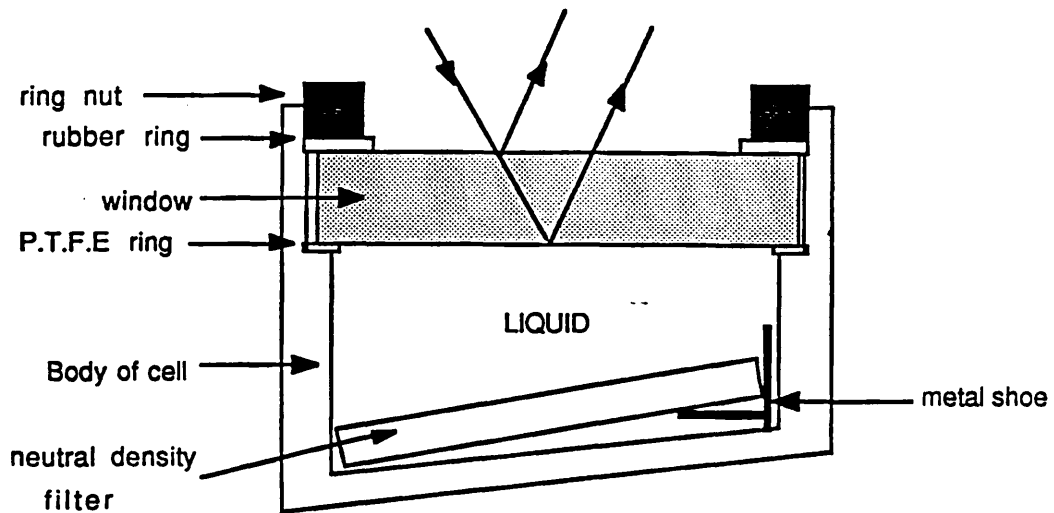


Fig 3.1 The Optical Cell

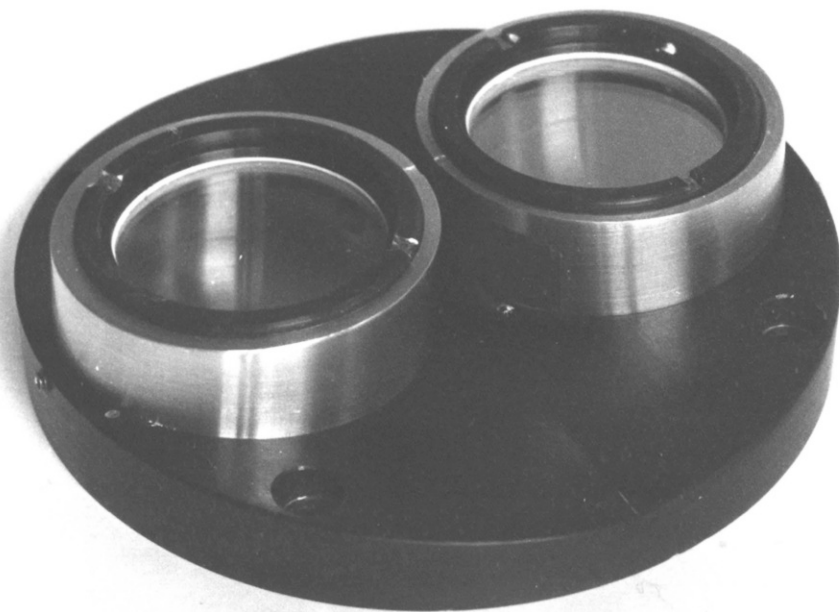
3.2.1 Experimental Technique Used

The experimental procedure used in the measurement of liquids in the closed cell is much the same as in the free surface case (described in chapter 2). The obvious difference is the introduction of windows to cover the test liquid and water dishes. Therefore the sample stage shown in fig 2.5 in chapter 2 is replaced by a modified sample stage, this is shown in photograph plate 3A. This holds an optical cell (of the type shown in fig. 3.1) in each arm, one for the liquid under test and the other for the liquid standard - distilled water.

A technique was developed which requires two different experimental arrangements for each wavelength covered although maintaining the same general procedure as in the free liquid case where a relative reflectance ratio is obtained using a liquid standard i.e.

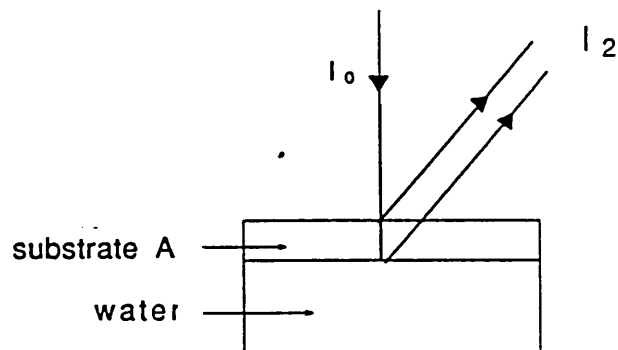
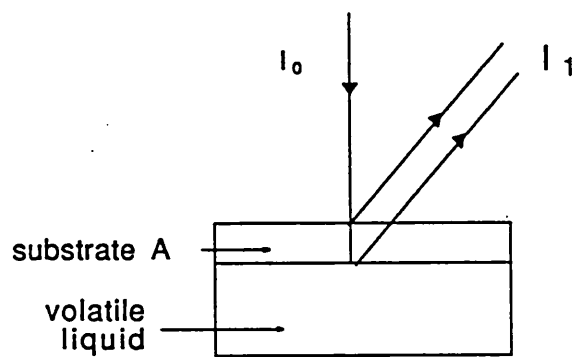
$$R_{\text{relative}} = \text{Signal}_{\text{test liquid}} / \text{Signal}_{\text{standard liquid}} \quad (3.1)$$

The two basic arrangements are illustrated in a simplified form in fig. 3.2. This shows the arrangement where the liquid under test and the distilled water are covered by separate



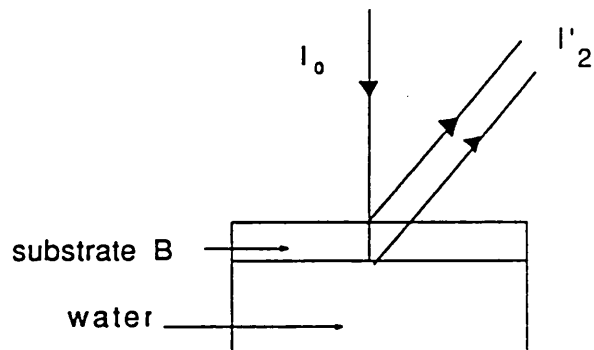
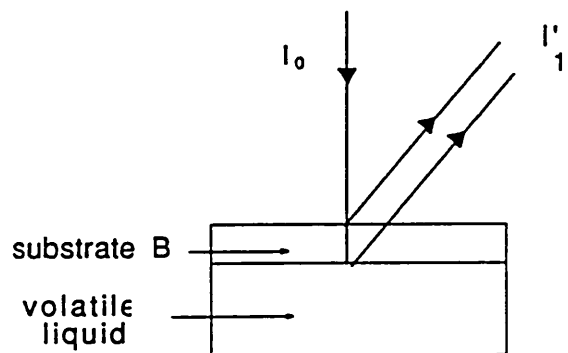
Photograph Plate 3A: The Reflectometer Sample Stage For Closed
Cell Measurements

Arrangement with substrate A:



Relative Reflectance, $R_A = I_1 / I_2$ (3.2.i)

Arrangement with substrate B:



Relative Reflectance, $R_B = I'_1 / I'_2$ (3.2.ii)

Fig. 3.2 The Volatile Liquid Arrangement

windows made of a substrate A. A relative reflectance is then found, R_A , from the ratio of the two intensity readings I_1 (a combination of the reflectance of the air/window surface and the reflectance of the window/test liquid surface) and I_2 (made up from the reflectance of the window/air surface and the window/water surface) (equation 3.2.i) the second arrangement the test liquid and distilled water are each covered with windows made from a substrate B, of a different refractive index. A relative reflectance value, R_B , is found from the intensity ratio of I_1' and I_2' (equation 3.2.ii).

3.2.2 Isolating the Optical Constants of the Volatile Liquid

Clearly adding windows to the reflectometry system creates a generally more complex reflectance arrangement. However, if we consider reflectance at the window/test liquid interface in the substrate A case - RS_A and the window/test liquid interface reflectance for substrate B - RS_B and applying the Fresnel equation (chapter one) :

From substrate A arrangement

$$RS_A = [(n_s - n_A)^2 + (k_s - k_A)^2] / [(n_s + n_A)^2 + (k_s + k_A)^2] \quad (3.3)$$

From substrate B arrangement

$$RS_B = [(n_s - n_B)^2 + (k_s - k_B)^2] / [(n_s + n_B)^2 + (k_s + k_B)^2] \quad (3.4)$$

Where : n_s and k_s are the optical constants of the test liquid

n_A and k_A are the optical constants of substrate A

n_B and k_B are the optical constants of substrate B

In theory we acquire, at each wavelength, a pair of simultaneous equations (3.3) and (3.4) which can be solved for n_s and k_s , the optical constants of the liquid under investigation. Again the special (normal incidence angle) form of the Fresnel equation is used, the justification for using this form, despite the fact that the incident beam is not at the normal

angle, is covered in appendix P.

It is clear that RS_A in equation (3.3) must first be extracted from the general reflectance R_A in equation (3.2.i). The same applies to the substrate B case, in which RS_B from equation (3.4) must be isolated from the general reflectance R_B found in equation (3.2.ii). It should also be noted that to solve the simultaneous equations (3.3) and (3.4) the optical constants of the substrate A, n_A and k_A , and the optical constants of the substrate B, n_B and k_B , are required. The mathematical steps showing how the optical constants of the test liquid are extracted from the initial input of experimental values will be outlined in section 3.4. The mathematical process also includes a number of *background values* such as the optical constants of the window substrates A and B discussed above. A detailed discussion of these values and how they were measured is contained in section 3.5.

3.3 The Windows of the Optical Cells

So far the window materials have been referred to rather anonymously as substrate A and substrate B. Clearly the window of an optical cell is a very important part of the equipment and it is not an exaggeration to say it determines how effectively the system will operate over the complete wavelength range. Therefore, the choice of infrared glasses for the windows was made very carefully from a fairly wide range of materials. The somewhat unusual way in which the windows are being used requires that they satisfy the following basic properties.

- a) They should transmit over as wide a wavelength range as possible. Since we are covering a region extending from 2 to 13 microns it would be more practical to choose a window material that is able to transmit effectively over the whole wavelength range.
- b) The window of a cell is essentially acting as a "stopper" to contain the liquid and is, naturally, in direct contact with the liquid. The substrate has, therefore, to be resistant to chemical attack from a variety of liquids. In between uses the cell needs to be dismantled and cleaned with a variety of solvents, so it is vital that the windows are resilient to general cleaning and handling.
- c) The accuracy of the value of the reflectance from the substrate/liquid interface depends on the magnitude of the signal reflected from this interface, therefore the refractive index of the

window material needs to be significantly different to that of the liquid. If the refractive index of the liquid under test is considered to be in the region of 1.3 to 1.6 then, for example, a window with a higher refractive index will provide a distinct reflectance boundary for the incoming signal, thereby minimising the losses due to transmission in the liquid.

d) The high refractive index required by condition (c), however, implies a high reflectance from the air/substrate interface which in turn means a large loss of signal. This can be prevented to a large degree by applying an anti-reflection coating to this surface. The substrate must, therefore, be suitable for thin film coating. Although the coating will not be in direct contact with the liquid a degree of resilience is necessary, in case of leakage during experiment, and to withstand general cleaning.

The two window materials finally chosen are germanium with an amorphous carbon dual band coating, and zinc selenide with an ytterbium oxide A.R. coating. A further study of the windows is included in section 3.5.

3.3.1 A Short Note - The Window/Water Interface

It is perhaps appropriate at this stage to examine the reason for covering the water standard with a window, after all it is not (at room temperature or under the conditions we apply) a volatile liquid so it does not, strictly speaking, require a window to contain it. It is in theory perfectly reasonable to carry out experimental work using an arrangement which has the test liquid covered with a window and the water in an open cell of the type used in the free liquid surface arrangement in chapter 2. However, covering the water with a window of the same material as that covering the test liquid ensures that the reflected signal from both arms is of the same order, which leads to more accurate reflectance ratios, and the whole system is more "balanced" or symmetrical. But the most important reason for using a window is the increase in sensitivity achieved at the liquid surface which is produced by contact with the higher index material.

3.4 Finding the Optical Constants of a Volatile Liquid - The Input Data

This section sets out the initial data involved in the programs used to produce the

optical constants of the liquid under test, that is the experimentally measured input data which includes the "background values" briefly referred to in section 3.2.2.

3.4.1 The Experimental Reflectances Data File

From the experimental arrangement illustrated in fig. 3.2 a set of relative reflectance values R_A (from equation 3.2.i) and R_B (from equation 3.2.ii) are produced for the 2-13 microns wavelength range, where substrate A is the carbon coated germanium window and B the ytterbium oxide coated zinc selenide windows. These values are stored as a separate data file for the particular liquid under study.

3.4.2 The "Background Constants" Data Files

The need for background values in the calculation of the optical constants of a liquid has been briefly introduced in section 3.2.2. The following sections outline the full range of background readings made, and describe the experimental methods employed to find most of these values. Whilst, of course, the experimental reflectances described in section 3.4.1 are different for different liquid samples the background constants are valid for any liquid to be measured.

3.4.2.1 The Water Constants

The values of refractive index, n_w , and absorptive index, k_w , of the distilled water standard have been discussed in chapter 2 and tables of the constants used are presented in appendix K.

3.4.2.2 Reflectance Data for Uncoated Germanium and Uncoated Zinc Selenide

Sample windows of uncoated germanium and uncoated zinc selenide, were supplied by Davin Optical and their reflectances measured for the 2 to 13 microns using the technique described in 3.5.3. The reflectances found experimentally, at each wavelength, are the slab reflectances of the windows, RUG_s for germanium and RUZ_s for zinc selenide. A program that takes RUG_s and RUZ_s values as the input data and calculates the single surface reflectances, the refractive indexes and any absorptive indexes for the window material has been developed and

the formulae used are outlined in 3.6.1.

3.4.2.3 Reflectance Data for the A.R. Coated Germanium and A.R. Coated Zinc Selenide Windows.

The experimental arrangement described in 3.5.3. is also used to find the slab reflectance values of the four A.R. coated windows used (i.e. two carbon coated germanium windows, RA_1 and RA_2 , and two ytterbium oxide coated zinc selenide windows, RB_1 and RB_2). Again a series of reflectance values are found for the wavelength region covered, i.e. at each wavelength there will be four reflectances representing the four windows. In theory the two values RA_1 and RA_2 should be the same since they are the reflectances of two "identically" coated germanium windows and similarly for the two coated zinc selenide windows RB_1 and RB_2 . However, differences in the reflectance values were noted during measurement. The four slab reflectances are converted into single surface reflectances using the formulae outlined in 3.6.2.

3.4.2.4 Transmission Data for Uncoated Germanium and Uncoated Zinc Selenide.

The external transmission values for the uncoated germanium and uncoated zinc selenide windows, TUG and TUZ respectively, have been found using the experimental arrangement described in 3.5.4. The transmission values are used to find the refractive indexes of the Ge and ZnSe.

3.5 Making Measurements on Coated and Uncoated Windows.

The following sections describe how the reflectance and transmission measurements are made on the coated and uncoated windows. The question of any possible interference effects is also briefly considered.

3.5.1 Discounting Interference (Fabry Perot) Effects in the Windows

It is maybe necessary at this point to establish that interference is not occurring in either the germanium or zinc selenide windows for the wavelength range covered (2-13 microns) and for this we refer to Bohren and Huffman (1983). In the text they derive an

expression for the slab transmittance

$$T_{\text{slab}} = (1 - R)^2 / (R^2 e^{-\alpha d} + e^{\alpha d} - 2R \cos \zeta) \quad (3.5)$$

Where: d is the slab thickness

α is the absorption coefficient

and: $\zeta = 4\pi n d / \lambda$

n is the refractive index of the slab

λ is the wavelength of the incident radiation.

A derivation of the equation will not be carried out here since the expression is not directly relevant to our work - a simpler model being sufficiently accurate. However, the equation is quoted to highlight the presence of the oscillatory term $\cos \zeta$ which could be a source of interference bands. Maxima occur when

$$\zeta = 2\pi p \quad (p\lambda = 2nd) \quad p=1,2,3... \quad (3.6)$$

If a maximum occurs at a wavelength λ , neighbouring maxima occur at $\lambda + \Delta\lambda$
where (Hariharan, 1985):

$$\Delta\lambda = \lambda^2 / 2nd \quad (3.7)$$

The *monochromatic* beam is in reality a finite though narrow spread of wavelengths. If the wavelength bandwidth is $\delta\lambda$, interference bands are observable only if $\delta\lambda \ll |\Delta\lambda|$. If we assign 1% to $\delta\lambda$ (monochromator's literature specifies this value). For the germanium and zinc selenide windows of 3 mm thickness, we note that the bandwidth $\delta\lambda$ is considerably greater than $\Delta\lambda$ for all wavelengths between 0.3 - 16 microns, therefore the condition for interference is not satisfied.

3.5.2 Reflectance Measurements using an Aluminium Mirror Standard.

The reflectance measurements described in the following section use a reflectometry arrangement with an aluminium mirror as the standard. The values of absolute reflectance for Al were taken from Palik (1985). The reflectance of the aluminium mirror used during experiment was checked against the values given in Palik at a number of wavelengths using a Strong reflectometer (Dolan, 1987) and found to be in good agreement.

3.5.3 Experimental Arrangement for Window Reflectance Measurements.

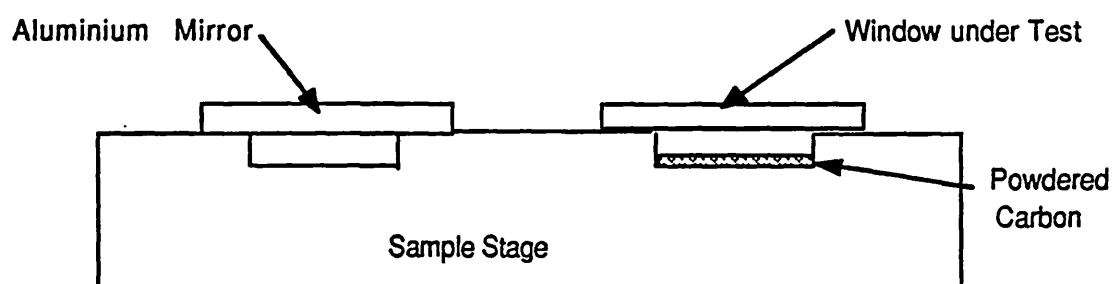


Fig 3.3 The Sample Stage used for Window Reflectance Measurements.

The reflectometer described in chapter 2 and illustrated in fig 2.4 is used to determine the reflectances of the windows (coated and uncoated), but the sample stage used in the free surface measurements is replaced by the sample stage illustrated in fig. 3.3. This shows the aluminium mirror supported in one arm of the stage, and the window under test in the other arm. A roughened layer of powdered carbon is placed in the recess below the window to ensure that any signal from the area below the substrate is heavily scattered and does not re-enter the system to be detected. It should be noted, however, that the window is not in contact with the carbon powder layer, there being an air gap between the window's lower surface and the carbon powder surface.

As in liquid sample reflectance measurements a near normal incident beam is directed onto the sample, and then onto the standard, hence two reflectance intensity readings are made at each wavelength in the range of interest, one from the aluminium mirror surface,

and the other from the window under test. The reflected signal is directed onto a collecting mirror which throws the focussed beam onto a Golay cell (see chapter 2) the signal is recorded in millivolts by a lock-in amplifier. The absolute reflectance of the window is given by:

$$R_{\text{slab}} = (I_{\text{slab}} / I_{\text{Al}}) \cdot R_{\text{Al}} \quad (3.8)$$

Where: I_{slab} is the intensity of the reflected signal from the window

I_{Al} is the intensity of the reflected window from the Al mirror

R_{Al} is the absolute reflectance of the Al mirror taken from Palik.

3.5.4 Experimental Arrangement for Window Transmission Experiments.

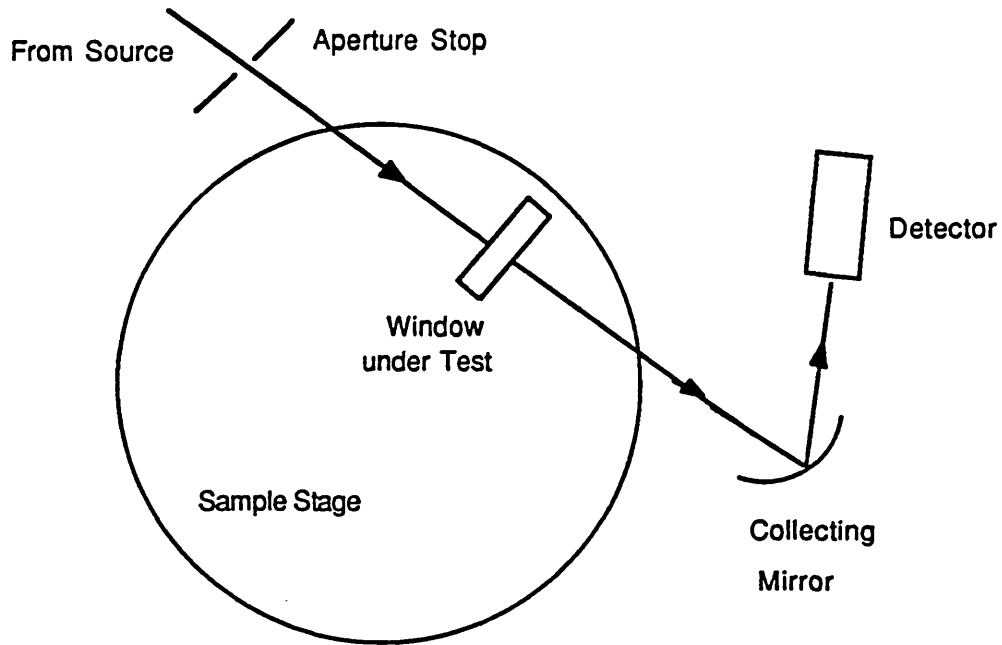


Fig 3.4 Experimental Arrangement to Measure Transmission in Windows.

Fig 3.4 represents the salient features of the experimental arrangement for measuring the transmission of a window. The external transmission of a window is found by comparing

the intensity of a collimated beam in air with the intensity produced when the window under test is placed in the path of the collimated beam. Therefore at some wavelength, λ , the transmission, with the window in place (as in fig 3.4), is recorded. The turntable sample stage is then rotated so that the window is entirely clear of the beam of radiation and a second reading, the transmission in air, is taken. In both the *window* and *air* positions the emerging signal is collected by a concave mirror and directed onto the Golay detector. The transmission of the window is given by the ratio of the slab to air intensities:

$$T_{\text{slab}} = I_{\text{slab}} / I_o \quad (3.9)$$

3.6 Finding the Optical Constants of a Volatile Liquid - The Formulae

The processing of the measured input data introduced in 3.4 to give the optical constants of the volatile liquid under investigation can very roughly be divided into two main parts. The first part of the calculation involves work on the optical properties of the windows that cover the liquid during experiment. The second part is the actual calculation of n_s and k_s for the volatile liquid.

Due to the rather large number of variables used in the analysis a summary of the symbols used is included here.

R_A ... experimental reflectance for germanium (substrate A) found from arrangement illustrated in fig 3.2.

R_B ... experimental reflectance for zinc selenide (substrate B) found from arrangement illustrated in fig 3.2.

n_A, k_A ... optical constants of germanium (substrate A).

n_B, k_B ... optical constants of zinc selenide (substrate B).

α' ... absorption coefficient of germanium.

α'' ... absorption coefficient of zinc selenide.

n_w, k_w ... optical constants of distilled water.

n_s, k_s ... optical constants of volatile liquid.

RUG_s ... slab reflectance of uncoated germanium.

RUZ_s ... slab reflectance of uncoated zinc selenide.

RUG ... single surface reflectance of uncoated germanium.

RUZ ... single surface reflectance of uncoated zinc selenide.

TUG ... external transmission of uncoated germanium.

TUZ ... external transmission of uncoated zinc selenide.

RA_1 ... slab reflectance of 1st coated germanium window.

RA_2 ... slab reflectance of 2nd coated germanium window.

RB_1 ... slab reflectance of 1st coated zinc selenide window.

RB_2 ... slab reflectance of 2nd coated zinc selenide window.

RG_1 ... reflectance of A.R. coated Ge surface - 1st window.

RG_2 ... reflectance of A.R. coated Ge surface - 2nd window.

RZ_1 ... reflectance of A.R. coated ZnSe surface - 1st window.

RZ_2 ... reflectance of A.R. coated ZnSe surface - 2nd window.

RW_{Ge} ... reflectance of germanium/distilled water interface.

RW_{ZnSe} ... reflectance of zinc selenide/distilled water interface.

RS_A ... reflectance of germanium/volatile liquid (substrate A/volatile liquid) interface.

RS_B ... reflectance of zinc selenide/volatile liquid (substrate B/volatile liquid) interface.

For the General Case:

λ ... wavelength of radiation.

d ... thickness of window.

n, k ... optical constants of window.

α ... absorption coefficient of window material.

R_1, R_2 ... single surface reflectances.

R_w ... reflectance at water/window interface.

3.6.1 Calculating Single Surface Reflectance, Refractive and Absorptive Index for an Uncoated Window

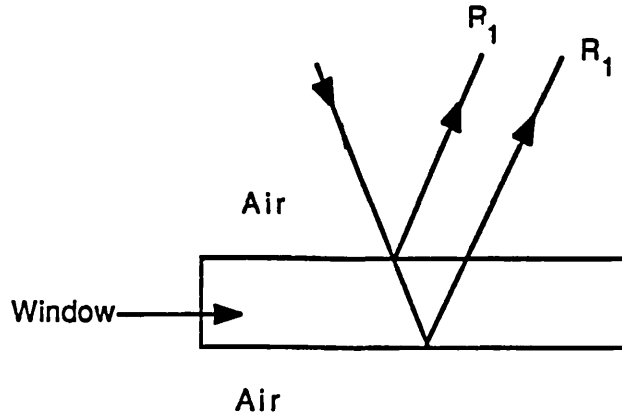


Fig 3.5 General Case Reflectance for an Uncoated Window

As a starting point for the calculation we consider the general case equations for slab reflectance and slab transmission (equations B5 and B6 in appendix B):

$$R_{\text{slab}} = R_1 + \{[(1 - R_1)^2 R_1 e^{-2\alpha d}] / [1 - R_1^2 e^{-2\alpha d}]\} \quad (3.10)$$

$$T_{\text{slab}} = [(1 - R_1)^2 e^{-\alpha d}] / [1 - R_1^2 e^{-2\alpha d}] \quad (3.11)$$

Where, R_{slab} has been found using the experimental technique outlined in 3.5.3, and T_{slab} using the technique outlined in 3.5.4. R_1 is the reflectance at a single surface (see fig. 3.5), in this case both surfaces of the windows undergo the same reflectance (i.e. $R_1 = R_2$). The absorption coefficient of the substrate and the window thickness are denoted by α and d respectively.

(3.10) and (3.11) can be equated to give:

$$\alpha = (1/d) \log_e [T_{\text{slab}} R_1 / (R_{\text{slab}} - R_1)] \quad (3.12)$$

and taking

$$\alpha = \frac{1}{d} \log_e \left[\frac{(1 - R_1)^2}{2 T_{slab}} + \left[R_1^2 + \left(\frac{(1 - R_1)^2}{2 T_{slab}} \right)^2 \right]^{1/2} \right]$$

... (3.13)

(see appendix B for proof), equating with (3.12) and rearranging produces:

$$R_1^2(2 - R_{slab}) + R_1(R_{slab}^2 - T_{slab}^2 - 2R_{slab} - 1) + R_{slab} = 0 \quad (3.14)$$

which is a quadratic in the unknown, R_1 , the single surface reflectance. A Newton-Raphson one dimensional iteration (Stark, 1970) is used to solve for R_1 . An iterative process is very convenient to employ in this case since it is clear the root of the equation, R_1 , must lie between 0 and 1. R_1 is then substituted into equation (3.13) to yield a value for α . This absorption coefficient, α , is then converted into an absorptive index, k , for the window using the simple relationship:

$$\alpha = 4\pi k d / \lambda \quad (3.15)$$

The Fresnel equation (1.26) verified in chapter one is rearranged in terms of the refractive index, n :

$$n = \{ (1 + R_1) \pm [(1 + R_1)^2 - (1 - R_1)^2(1 + k^2)]^{1/2} \} / (1 - R_1) \quad (3.16)$$

(taking +ve solution)

and R_1 and k are substituted to find the refractive index of the window material. Therefore, we are able to find the single surface reflectances of germanium (RUG) and, in the same way, the single surface reflectance of zinc selenide (RUZ). In addition the optical constants of germanium (n_A, k_A), at each wavelength, and the optical constants of zinc selenide (n_B, k_B)

can also be found.

It should be noted that the absorptive index of the zinc selenide is calculated to be generally negligible throughout the 2-13 microns wavelength range (see later).

3.6.2 Converting the Coated Window Slab Reflectances into Coated Surface Reflectances

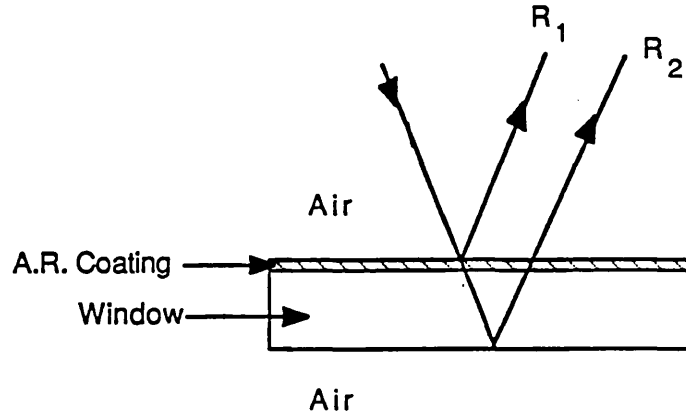


Fig 3.6 General Case Reflectance for an A.R. Coated Window

It is necessary to convert the slab reflectances for the coated windows (RA_1 , RA_2 for the two A.R. coated Ge windows and RB_1 , RB_2 for the A.R. coated ZnSe windows) into single surface reflectances for the coated surfaces. To do this we use the general equation defined in appendix B,

$$R_{\text{slab}} = R_1 + \{[(1 - R_1)^2 e^{-2\alpha d} R_2] / [1 - e^{-2\alpha d} R_1 R_2]\} \quad (3.17)$$

but in this case the reflectance of the slab, R_{slab} , is the slab reflectance for a coated window found using the experimental arrangement described in section 3.5.3 (i.e. RA_1 , RA_2 , RB_1 , RB_2). R_1 is the reflectance of the A.R. coated surface, the unknown in this case. R_2 is the reflectance from the uncoated surface (fig 3.6) which has been calculated for Ge (RUG) and ZnSe (RUZ). Four A.R. coating reflectance values are found, two pertaining to the coated Ge windows (RG_1 , RG_2) and two to the ZnSe windows (RZ_1 , RZ_2).

3.6.3 Finding the Reflectance of the Window / Water Interface

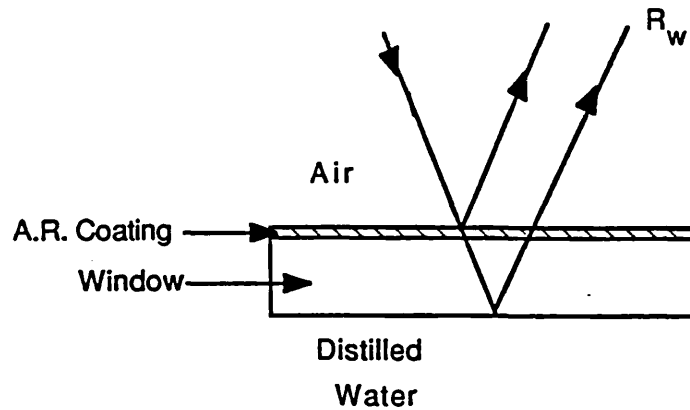


Fig 3.7 General Case Reflectance from the Window/ Water Interface

Turning now to the experimental arrangement illustrated in fig 3.2, it is necessary to isolate the reflectance of the the water/uncoated germanium interface, and likewise the water/uncoated zinc selenide interface. By studying the general case of an uncoated window in an air/ water *sandwich* it is possible to express the reflectance from the window/water interface, R_w in terms of the Fresnel equation (see equation (1.25), chapter one):

$$R_w = [(n_w - n)^2 + (k_w - k)^2] / [(n_w + n)^2 + (k_w + k)^2] \quad (3.18)$$

Where, n , k are the optical constants of the window material and, n_w , k_w are the optical constants of the distilled water, all of which have been found by independent methods (see previous sections). Therefore, the Ge/water reflectance ($R_{W_{Ge}}$) and ZnSe/water reflectance ($R_{W_{ZnSe}}$) can be extracted.

3.6.4. Applying the General Formulae to the Two Substrates

3.6.4.1 Formulae for the Germanium Windows (Substrate A) Arrangement

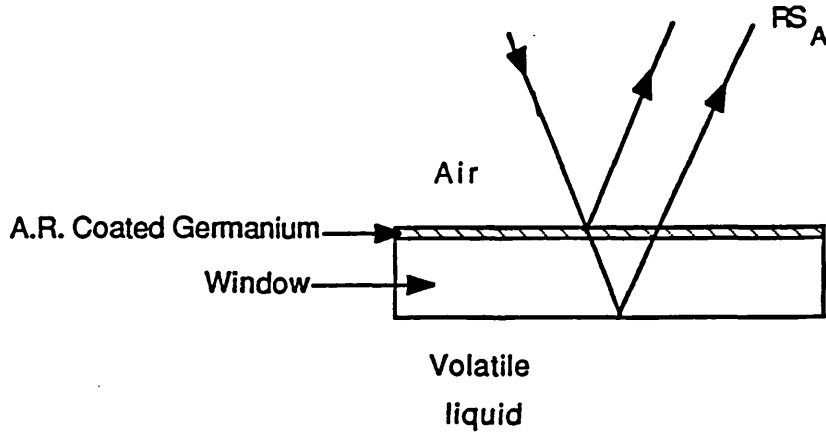


Fig 3.8A The Volatile Liquid/Germanium Window Interface.

We consider the arrangement in fig 3.2 for the substrate A, which is in this case A.R. coated germanium. Rearranging Equation (3.2.i) gives

$$R_A I_2 = I_1 \quad (3.19)$$

But since the definition of reflectance is the ratio of the reflected intensity to the incident intensity

$$I_1 = I_0 R A_1 \quad (3.20)$$

and

$$I_2 = I_0 R A_2 \quad (3.21)$$

Expressing the slab reflectances, $R A_1$ and $R A_2$, in terms of the general equation (3.17) and substituting back into equation (3.19) gives:

$$R_A \left\{ R G_2 + \frac{[(1 - R G_2)^2 e^{-2\alpha'd} R W_{Ge}]}{[1 - e^{-2\alpha'd} R G_2 R W_{Ge}]} \right\} = R G_1 + \frac{[(1 - R G_1)^2 e^{-2\alpha'd} R S_A]}{[1 - e^{-2\alpha'd} R G_1 R S_A]} \quad (3.22)$$

From which it is possible to extract the reflectance of the germanium/volatile liquid interface, RS_A , shown in fig 3.8A.

3.6.4.2 Formulae for the Zinc Selenide (Substrate B) Windows Arrangement

By following the procedure in section 3.6.4.1 but for the zinc selenide arrangement (substrate B in fig 3.2) beginning with the rearrangement of equation (3.2.ii) to give:

$$R_B \Gamma_2 = \Gamma_1 \quad (3.23)$$

from which we get:

$$R_B \left\{ RZ_2 + \left[\frac{(1 - RZ_2)^2 e^{-2\alpha''d} RW_{ZnSe}}{1 - e^{-2\alpha''d} RZ_2 RW_{ZnSe}} \right] \right\} = RZ_1 + \left[\frac{(1 - RZ_1)^2 e^{-2\alpha''d} RS_B}{1 - e^{-2\alpha''d} RZ_1 RS_B} \right] \quad (3.24)$$

and therefore the reflectance of the zinc selenide/ volatile interface, RS_B , shown in fig 3.8B can be found.

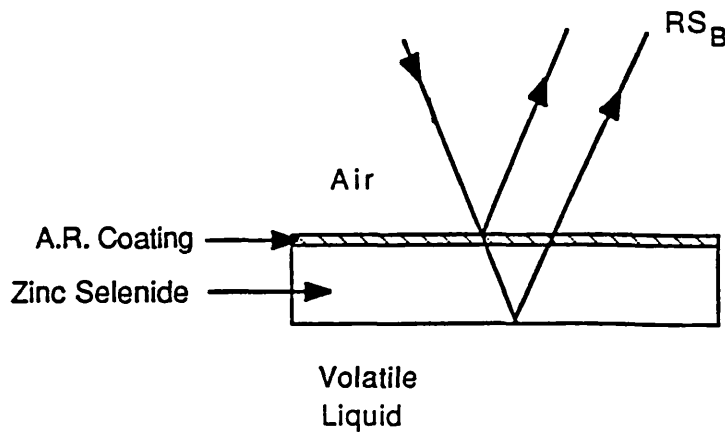


Fig 3.8B The Volatile Liquid / Zinc Selenide Window Interface.

3.6.5 Concluding Remarks - Solving the Fresnel Equations

Isolating the two interface reflectances, RS_A and RS_B , allows the solution of the two Fresnel equations set out in section 3.2.2, i.e.

$$RS_A = [(n_s - n_A)^2 + (k_s - k_A)^2] / [(n_s + n_A)^2 + (k_s + k_A)^2] \quad (3.3)$$

and

$$RS_B = [(n_s - n_B)^2 + (k_s - k_B)^2] / [(n_s + n_B)^2 + (k_s + k_B)^2] \quad (3.4)$$

to give the optical constants of the liquid under study, n_s and k_s .

The solution of the equations is rather difficult, due to the nature of the Fresnel equation and also because of the difference in magnitude between n_s and k_s in certain wavelength regions. This problem will be returned to in the next chapter.

3.7 A Study of the Optical Glasses. Germanium and Zinc Selenide

Germanium and zinc selenide, by virtue of their high transmission and general toughness, have become popular materials in infrared technology. As a consequence a significant amount of work has been carried out on their optical properties and a number of literature sources exist. It may seem needless, therefore, to make measurements on the uncoated windows when the optical constants can be obtained from these literature sources. However, the data in the literature did not cover in detail the increments of wavelength used in our work and whilst a polynomial could be applied to interpolate the results this would not take into account any regions of absorption that may exist. Any values of absorption quoted in the literature were for a few discrete wavelengths only and it was difficult to conclude what would happen to the absorption over the entire wavelength range covered, particularly at the transmission cut-off wavelengths of the substrates.

The case of the A.R. coated windows is somewhat different. Uncoated substrates were forwarded to Barr and Stroud of Dumbartonshire for coating. At the time the thin film coatings used were rather unique in that the dual band carbon coating for the germanium windows was not yet a production item, and the ytterbium oxide coating deposited on the zinc selenide windows had previously only ever been used to coat zinc sulphide windows. The measurement of the reflectance and transmission of the coated windows, therefore, proved to be an interesting exercise.

The following sections describe curves compiled from transmission measurements made on uncoated and coated windows, refractive index measurements for uncoated windows and absorptive index measurements for germanium. For comparison, curves have also been plotted using data from several reference sources:

3.7.1 Reference Sources - Germanium and Zinc Selenide

The following reference sources were used to plot refractive index and transmission curves to allow comparison with the experimental curves compiled by us.

(i) Palik (1985)

The n values for germanium contained in this reference (see appendix D) are an amalgamation of *best* results from a number of sources. The values for the 2 to 13 microns region are made up from the values found by Briggs (1950), Icenogle et al (1976), Edwin et al (1978), and Barnes and Piltch (1979). Briggs's data for the 1.8 to 2.6 microns region is within 0.25% of the 1970's measurements and are included since they "have stood the test of time". Icenogle et al carried out measurements for a series of temperatures and wavelengths between 2.5 and 13 microns. Their n values were assigned an error of approximately 6×10^{-4} . Perhaps the most interesting of all is the data of Edwin et al, they reported values for 8 to 14 microns, but two different experimental arrangements, in separate labs were used on the same Ge crystal sample. The differences between the two lab results were between 1×10^{-4} and 3×10^{-4} . Barnes and Piltch (1979) used the data of Icenogle et al to evaluate the coefficients of a temperature dependent Sellmeier-type equation

$$n^2 = A + B\lambda^2/(\lambda^2 - C) + D\lambda^2(\lambda^2 - E) \quad (3.25)$$

Using the temperature-dependent values of n , they calculated the following values for the coefficients:

$$A = -6.040 \times 10^{-3}T + 11.05128$$

$$B = 9.295 \times 10^{-3}T + 4.00536$$

$$C = -5.392 \times 10^{-4}T + 0.5999034$$

$$D = 4.151 \times 10^{-4}T + 0.09145$$

$$E = 1.51408T + 3426.5$$

The expression has been evaluated for a temperature of 18°C in Palik, and these values included in the table of n values. The Sellmeier equation is able to give an accuracy of 0.025% or better over the spectral range 2.5 - 14 microns.

(ii) Li (1984)

Recommended values for the refractive index of C.V.D. (Chemical Vapour Deposition) zinc selenide were compiled by Li using a dispersion equation based on the data of Feldman et al (1979) (see appendix G):

$$n^2(\lambda, t) = E(t) + A(t)/(\lambda^2 - \lambda_u^2) + B(t)/(\lambda^2/\lambda_I^2 - 1) \quad (3.26)$$

where: λ is in microns

$$t = (T - 293) \text{ K}$$

$$\lambda_u = 0.29934 + 1.004 \times 10^{-4}t \text{ (microns)}$$

$$\lambda_I = 48.38 + 6.29 \times 10^{-3}t \text{ (microns)}$$

$$E(t) = 9.01536 + 1.44190 \times 10^{-3}t + 3.32973 \times 10^{-7}t^2 \\ - 1.08159 \times 10^{-9}t^3 - 3.88394 \times 10^{-12}t^4$$

$$A(t) = 0.24482 + 2.77806 \times 10^{-5}t + 1.01703 \times 10^{-8}t^2 \\ - 4.51746 \times 10^{-11}t^3 + 4.18509 \times 10^{-13}t^4$$

$$B(t) = 3.08889 + 1.13495 \times 10^{-3}t + 2.89063 \times 10^{-7}t^2 \\ - 9.55657 \times 10^{-10}t^3 - 4.76123 \times 10^{-12}t^4$$

Li attaches an uncertainty of ± 0.0004 in the n values for the entire wavelength region. The values quoted are also valid for crystalline samples (Rogers, 1986).

(iii) The Schott Polynomial

The Schott dispersion equation,

$$n^2 = A_0 + A_1\lambda^2 + A_2\lambda^{-2} + A_3\lambda^{-4} + A_4\lambda^{-6} + A_5\lambda^{-8} \quad (3.27)$$

is used by many manufacturers to generate n values for a number of optical glasses (see appendix H for tables). Refractive index values for zinc selenide have been generated by us using coefficients again obtained from Schott. The calculation was performed in two parts; firstly the n values for the 1 - 5 microns region were calculated using five coefficients only

$$A_0 = 5.926782$$

$$A_1 = -0.001361628$$

$$A_2 = 0.2389668$$

$$A_3 = 0.06303920$$

$$A_4 = -0.06595582$$

the sixth term of the equation is neglected since it causes a breakdown in the polynomial at the extreme ends of the wavelength range. The n values for 5 - 13 microns are found using a second set of coefficients, they are

$$A_0 = 5.954322$$

$$A_1 = -0.001535743$$

$$A_2 = -1.279735$$

$$A_3 = 37.25938$$

$$A_4 = -405.0421$$

$$A_5 = 1569.464$$

(iv) Adams (1983)

Comparatively little absorptive index data exists for uncoated germanium. Indeed Palik's review is forced to include data from Stierwalt and Potter (1962) obtained at 50°C, because no room temperature data was available at the time. Adam's in his paper on standardising specifications for optical grade germanium and silicon blanks gives recommended maximum absorption coefficients for a number of wavelengths in the infrared at room temperatures (see appendix E). These *spot* values have been converted to k values for

comparison with our measured data.

3.7.2 Uncoated Germanium Windows

Fig 3.9 shows the transmission curve for uncoated germanium measured experimentally using the method described in section 3.5.4 (transmission tables in appendix C). A second curve is shown which has been plotted using transmission values derived from refractive index values from Palik (see section 3.7.1(i)), i.e. using the generalized Fresnel equation (1.26), assuming $k = 0$, and substituting in the refractive indexes' from Palik's review, n_{Palik} (tables in appendix D):

$$R_{\text{Palik}} = (n_{\text{Palik}} - 1)^2 / (n_{\text{Palik}} + 1)^2 \quad (3.28)$$

Therefore the reflectance R_{Palik} can be found and also the transmission, T_{Palik} from:

$$R_{\text{Palik}} = (1 - T_{\text{Palik}}) / (1 + T_{\text{Palik}}) \quad (3.29)$$

However, plotting Palik's curve without taking account of any possible absorption in the substrate is clearly an erroneous assumption, since the curves diverge dramatically with increasing wavelength. The absorption band at 11.8 microns is consistent with absorption features detected by Bishop (1987), in separate work. It also seems to agree with the absorptions seen beyond 11.7 microns reported by Savage (1985).

Fig 3.10 shows refractive index curves for uncoated germanium. The curve labelled 2 is the experimental measurements curve plotted using data found by the method outlined in section 3.6.1 (see appendix C for tables). Curve 1 is plotted from the n values taken from Palik.

Absorptive index curves for germanium are shown in fig 3.15, the full line curve represents values found using the method in section 3.6.1 (see appendix C) and the broken line those of Adams mentioned in section 3.7.1 (iv). There is some discrepancy up to 12 microns, this is not surprising when one takes into account the relatively small magnitude of the k values (of the order of 10^{-6}) and the fact that Adam's data is a collection of *recommended* values. What is perhaps more surprising is the apparent agreement between the two curves in the 12 - 13

microns range.

Initially the small, but rather sharp, absorption peak at 11.8 microns which appears in the experimental transmission curve in fig 3.9 gave cause for concern, since it was felt it may have been a slightly shifted (due to a 1% bandwidth) oxygen absorption band. Interstitial oxygen is known to give a sharp side band at 11.7 microns, see fig 3.17 (Kaiser and Thurmond, 1961). It appears as a broader shaped band in the absorptive index curve in fig 3.15. The k values in the 11.0 - 12.4 microns region are converted into absorption coefficients (α) (see appendix C, table C3), using the simple relationship quoted in appendix A,

$$\alpha = 4\pi k / \lambda \quad (3.30)$$

where α is in cm^{-1} , for the 11.0 - 12.4 microns range, these are shown graphically in fig 3.16. When a comparison is drawn between this curve and the curves from the work of Kaiser and Thurmond (fig 3.17), it is felt that the peak in fig 3.16 corresponds in shape and magnitude to the peak which arises due to the lattice absorption alone (fig 3.17 A).

3.7.3 Uncoated Zinc Selenide Windows

Fig 3.11 is a graph of transmission curves for uncoated zinc selenide (tables in appendix F). The experimental curve is compiled from values measured using the arrangement covered in section 3.5.4. The other curve (denoted by a broken line) is plotted using transmission values converted from the refractive index values presented in Li's review (see 3.7.1(ii)). The transmission is calculated by using equations like (3.28) and (3.29), shown in section 3.7.2, i.e. (see appendix G for tables)

$$R_{\text{ZnSe}} = (n_{\text{ZnSe}} - 1)^2 / (n_{\text{ZnSe}} + 1)^2 \quad (3.31)$$

and

$$R_{\text{ZnSe}} = (1 - T_{\text{ZnSe}}) / (1 + T_{\text{ZnSe}}) \quad (3.32)$$

Again the assumption is made that $k = 0$, but in this case it would appear to be a valid assumption since the two curves in fig 3.11 do not undergo any divergence.

The corresponding refractive index curves for zinc selenide are shown in fig 3.12. The experimental curve 1 is constructed using results found from the method described in section 3.6.1 (n data in appendix F). Also plotted on the same graph are two *theoretical* curves (labelled 2), one is a plot of Li's n values (see section 3.7.1 (ii) and appendix G) and the other is of n values generated by a Schott dispersion polynomial (section 3.7.1 (iii) and appendix H). These two curves appear almost completely superimposed.

3.7.4 Transmission Curves for ARG6 Coated Germanium Windows

Fig 3.13 is a graph of the transmission curves for the two ARG6 (amorphous carbon) coated germanium windows (tabular data presented in appendix I). Ideally, an A.R. coating that was effective from 2 microns up to 13 microns was required, in practise the the most suitable coating available appeared to be a dual band coating. The ARG6 coating was designed for dual band performance in the 3 - 5 microns and 8 - 12 microns wavebands, the so called *atmospheric windows*. From the curves it is possible to see that, despite the fact that only one face of each window has been coated, the profiles of the curves have regions of *maximum* transmission at 3 - 5 microns and 8 - 12 microns. Between the two peaks is the slight drop in the intermediate 5 - 8 microns range. However, since we are covering a range which extends from 2 microns up to 13 microns the marked drop in transmission in the 2 - 3 microns and 12 - 13 microns is less welcome.

3.7.5 Transmission Curves for Ytterbium Oxide Coated Zinc Selenide Windows

Once again the aim was to apply a coating to one surface of each window which allows a consistently high transmission over the full wavelength range of 2 - 13 microns, since this was not available the next best thing would be, as in the case of the germanium windows, a dual band coating. However, a dual band coating was not commercially available for zinc selenide so an A.R. coating which could mimic a dual band coating as effectively as possible was chosen. Consequently ytterbium oxide was used resulting in the oddly shaped transmission curves in fig 3.14 (see appendix J for transmission data). The lower refractive

index of the zinc selenide means there is a lower reflection loss at the window surfaces, and it is possible to see from fig 3.14, when the substrate is coated the reflection does not fall below 70%.

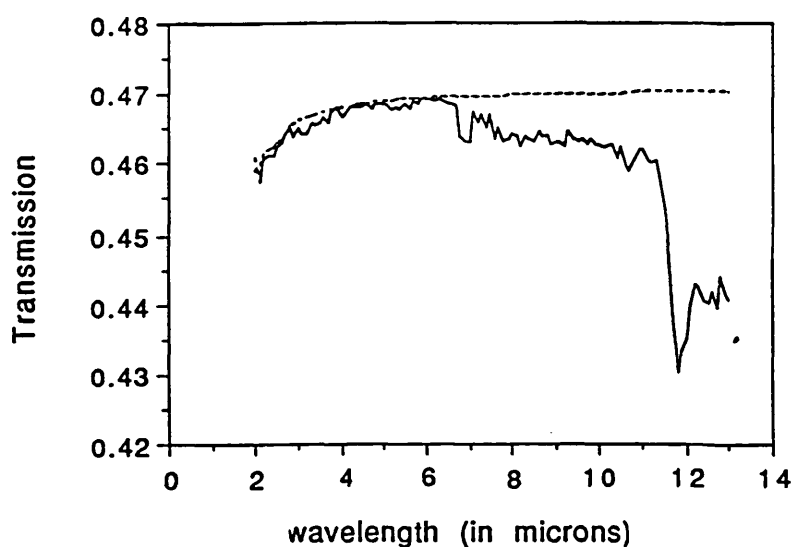


Fig 3.9 Transmission Curves for Uncoated Germanium.
 _____ experimental measurements curve, associated relative error is 0.5%
 ----- Palik

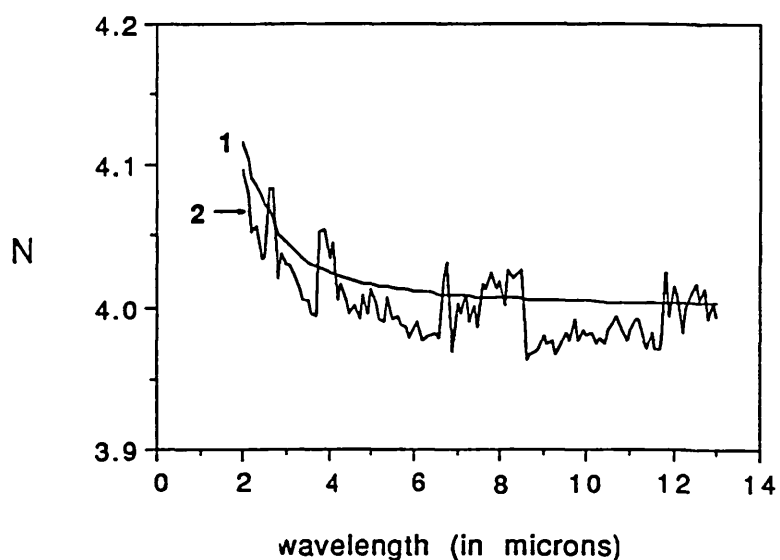


Fig 3.10 Refractive Index Curves for Uncoated Germanium.
 1 Palik
 2 experimental results, associated relative error is 0.8%

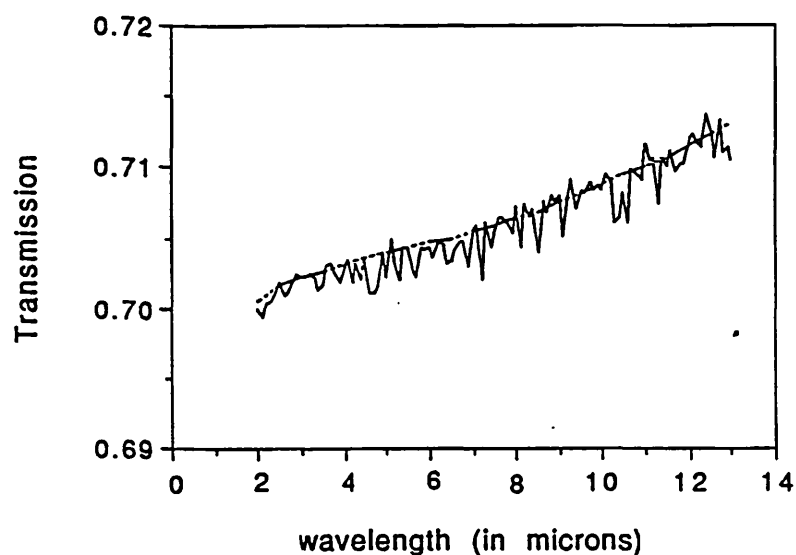


Fig 3.11 Transmission Curves for Uncoated Zinc Selenide.
 — experimental measurements, associated relative error is 0.5%
 - - - - - Li

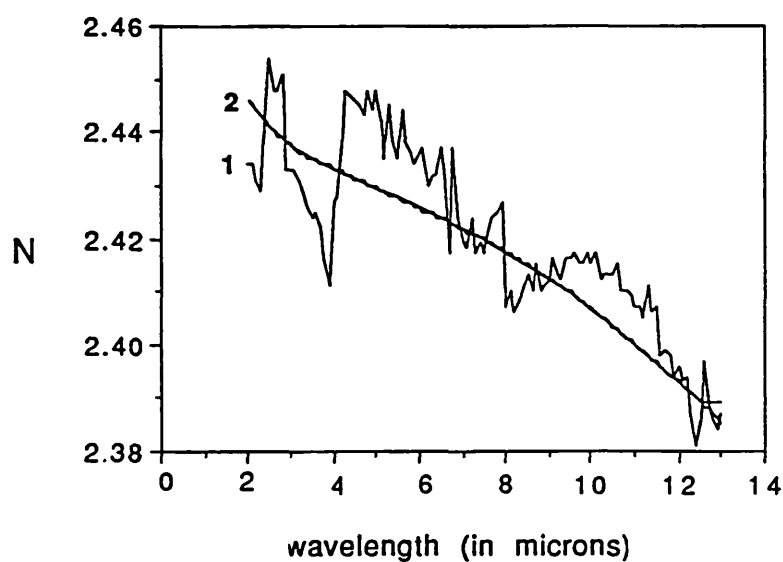


Fig 3.12 Refractive Index Curves for Uncoated Zinc Selenide.
 1 experimental measurements curve, associated relative error is 0.5%
 2 Schott, Li (curves are superimposed)

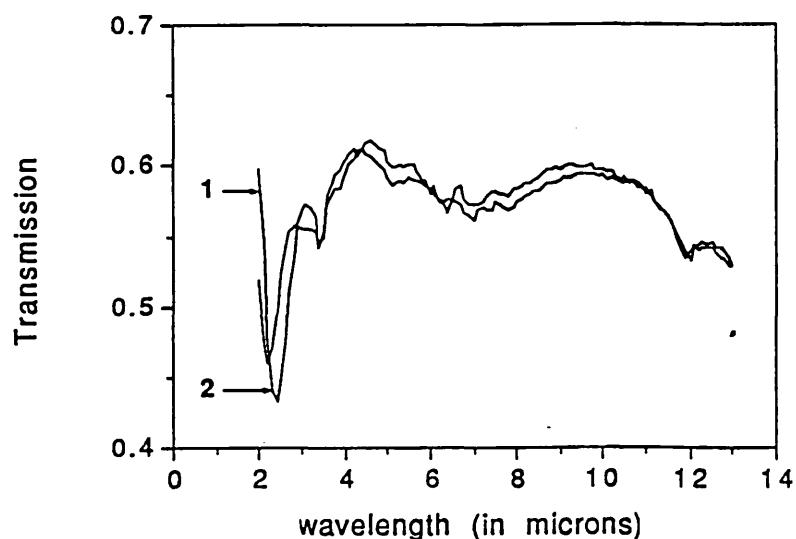


Fig 3.13 Transmission Curves for ARG6 coated Germanium Windows.

1 first coated window

2 second coated window

Relative error in transmission is 0.5%

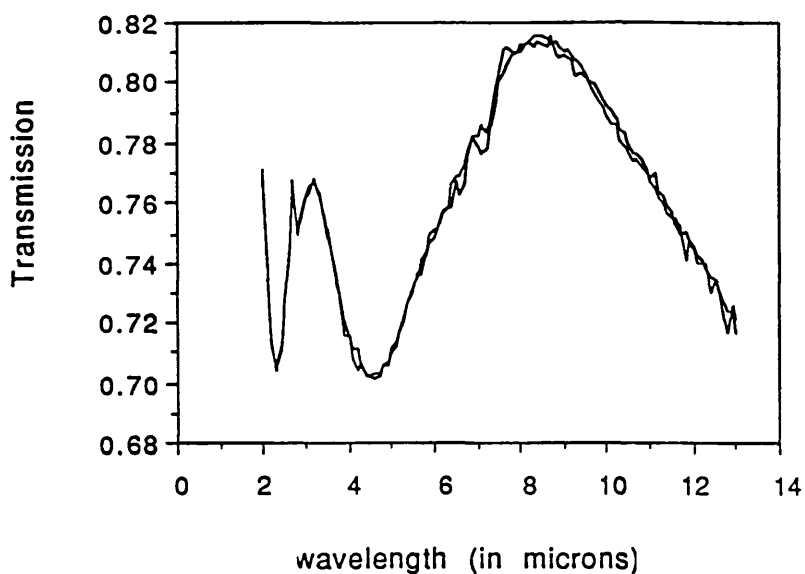


Fig 3.14 Transmission Curves for Ytterbium Oxide Coated Zinc Selenide Windows.

(the two curves appear almost completely superimposed)

Relative error in transmission is 0.5%

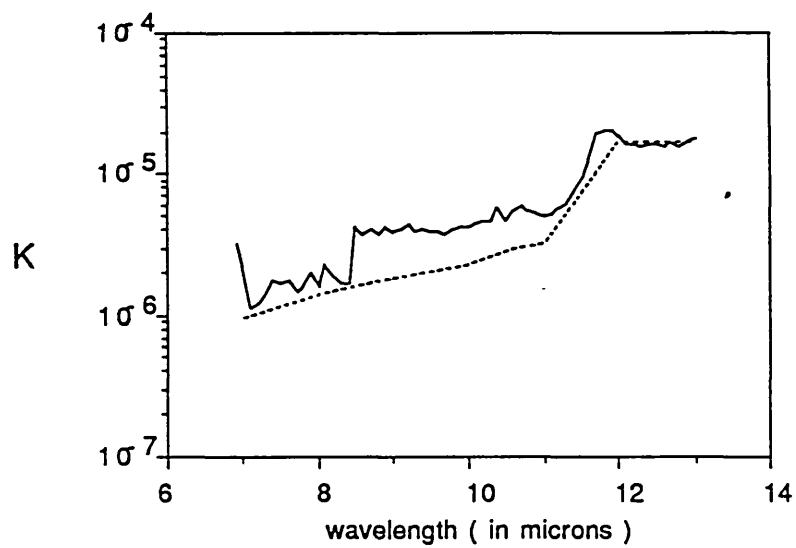


Fig 3.15 Absorptive Index Curves for Uncoated Germanium.
 — experimental values (see appendix C for error details)
 ---- Adams

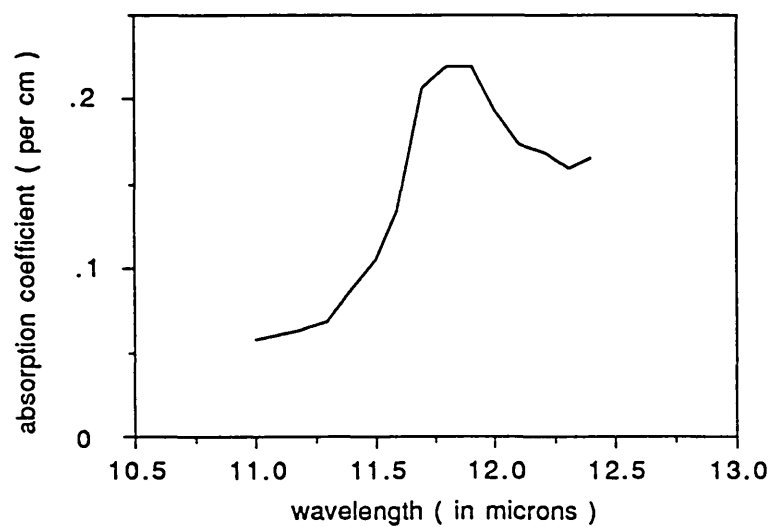


Fig 3.16 Absorption Coefficient Curve for Uncoated Germanium.

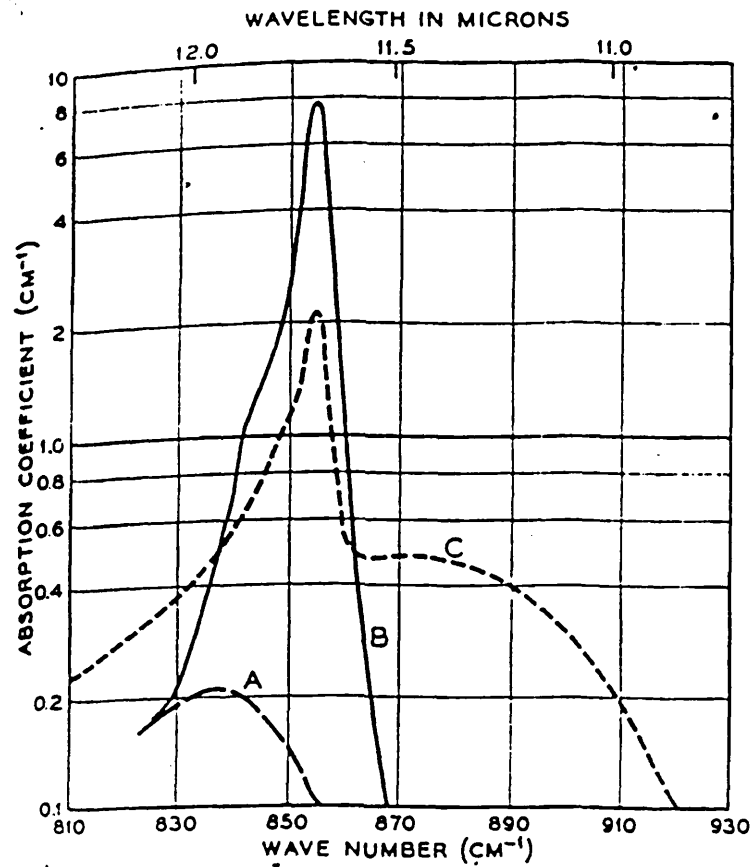


Fig 3.17 Absorption Coefficient Curve for Germanium from the work of Kaiser and Thurmond (1961).

Absorption of oxygen doped Ge before annealing (B) and after (C) at 610 c for 66 hours. Curve (A) shows a small lattice absorption of oxygen free Ge.

CHAPTER FOUR

The Optical Constants of Volatile Liquids

4.1 Introduction

The last chapter dealt mainly with the steps taken to arrive at the two Fresnel equations

$$RS_A = [(n_s - n_A)^2 + (k_s - k_A)^2] / [(n_s + n_A)^2 + (k_s + k_A)^2] \quad (3.3)$$

$$RS_B = [(n_s - n_B)^2 + (k_s - k_B)^2] / [(n_s + n_B)^2 + (k_s + k_B)^2] \quad (3.4)$$

which contain the optical constants of the volatile liquid. Since the reflectances RS_A and RS_B , the optical constants of substrate A, n_A , k_A , and of substrate B, n_B , k_B are all measured values, there are only two unknowns, n_s and k_s . It would seem, at first hand, a simple matter to solve the two equations simultaneously for n_s and k_s . However, this is not the case and the problems encountered in the solution of these equations are discussed in this chapter.

To test the performance of the closed cell system a (non volatile) liquid whose optical constants have previously been found (using free liquid surface reflectometry and transmission) is measured in this closed system. The liquid chosen as a *check* for the volatile liquid system is peg (polyethylene glycol) 300, which, because of its relatively low molecular weight is less viscous, and therefore easier to work with, than the heavier pegs. The optical constants found are displayed in the following sections and compared with the optical constants found by the free surface methods described in chapter two.

Also contained in this chapter are the results from measurements made on several volatile liquids and the absorption band of a near saturated solution of ammonium sulphate. Finally, there is a discussion of the applicability of the closed cell system, its strengths and weaknesses and a brief look at the possible future development of volatile liquid measurement.

4.2 Methods of Solving for n_s and k_s

There are a number of mathematical methods of obtaining the optical constants of the liquid, n_s and k_s , from the two equations (3.3) and (3.4). The most obvious way of solving two non linear simultaneous equations is by using an iterative technique such as the two dimensional Newton-Raphson method (Stark, 1970). Because of the physical nature of the equations it is a straightforward matter to find the two initial optical constant *guesses* with which to initiate the iteration. Another alternative is to manipulate the equations so that, by equating, k_s is eliminated and the remaining equation is expressed in terms of one unknown only, that is n_s . It is then possible to find k_s by re-substitution of n_s .

The latter technique has been implemented in this case, a more detailed outline of the solution of the two Fresnel equations follows.

By rearranging equation (3.3) it is possible to obtain

$$k_s^2 + 2[(RS_A + 1)/(RS_A - 1)] k_A k_s + F_A = 0 \quad (4.1)$$

where

$$F_A = n_s^2 + 2[(RS_A + 1)/(RS_A - 1)] n_A n_s + n_A^2 + k_A^2 \quad (4.2)$$

and similarly from equation(3.4)

$$k_s^2 + 2[(RS_B + 1)/(RS_B - 1)] k_B k_s + F_B = 0 \quad (4.3)$$

where

$$F_B = n_s^2 + 2[(RS_B + 1)/(RS_B - 1)] n_B n_s + n_B^2 + k_B^2 \quad (4.4)$$

applying the quadratic formula to equation (4.1) gives

$$k_s = -[(RS_A + 1)/(RS_A - 1)] k_A \pm \{[(RS_A + 1)/(RS_A - 1)]^2 k_A^2 - F_A\}^{1/2} \quad \text{.....(4.5)}$$

and similarly for equation (4.3)

$$k_s = -[(RS_B + 1)/(RS_B - 1)] k_B \pm \{[(RS_B + 1)/(RS_B - 1)]^2 k_B^2 - F_B\}^{1/2}$$

.....(4.6)

Equating (4.5) and (4.6) eliminates k_s and further simplification and squaring reduces the equation to:

$$(F_A - F_B)^2 + 4 \{[(R_A + 1)/(R_A - 1)] k_A - [(R_B + 1)/(R_B - 1)] k_B\} \\ \times \{[(R_A + 1)/(R_A - 1)] F_B k_A - [(R_B + 1)/(R_B - 1)] F_A k_B\} = 0$$

.....(4.7)

Recalling that F_A and F_B are both functions of the variable n_s (from equations (4.2) and (4.4)) equation (4.7) is an equation in terms of one unknown only, therefore a quadratic solution (for which the negative root was found to give the correct solution) was used to find the refractive index of the liquid, n_s . The refractive index, can then be substituted into equation (4.5) or equation (4.6) to yield the corresponding absorptive index, k_s . The positive root in equations (4.5) and (4.6) gives the correct solution for k_s .

4.3 Testing the Volatile Liquid System

It was mentioned in the introduction that peg 300 was used in the volatile liquid arrangement to generate optical constants. These could then be compared with the optical constants for peg 300 found by the free surface reflectometer and variable path length cells (see chapter two). The two arrangements illustrated in fig 3.2 of chapter three are used, with peg 300 in the *volatile liquid* arm of the sample stage. A series of experimental reflectances, RS_A and RS_B , are obtained for the 2-13 microns region which in turn leads to a series of Fresnel equations of the type shown by the general equations (3.3) and (3.4). The resulting refractive index values have been plotted on a common axis with the values obtained from the free liquid surface technique (covered in chapter two) and the spectral curves are shown in fig 4.1, table 4.1 shows data for the refractive index. The profiles produced are generally very

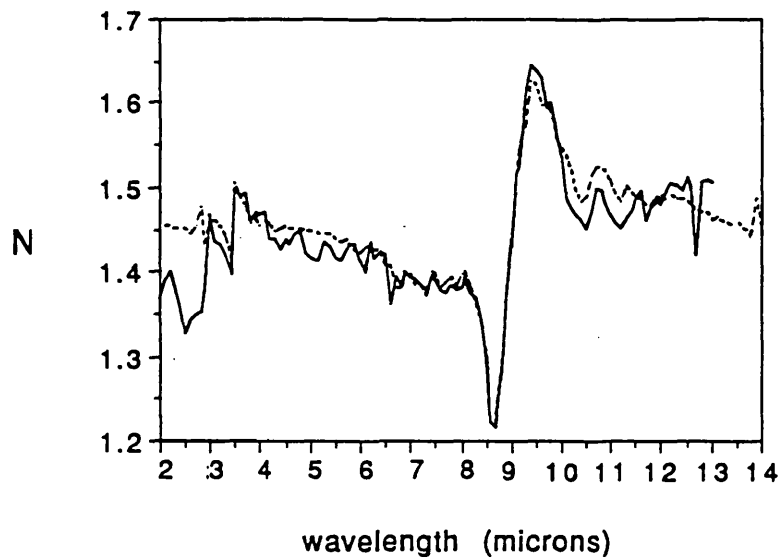


Fig 4.1: Refractive Index Curves for Peg 300.

— VLC curve
 --- free surface
 curve

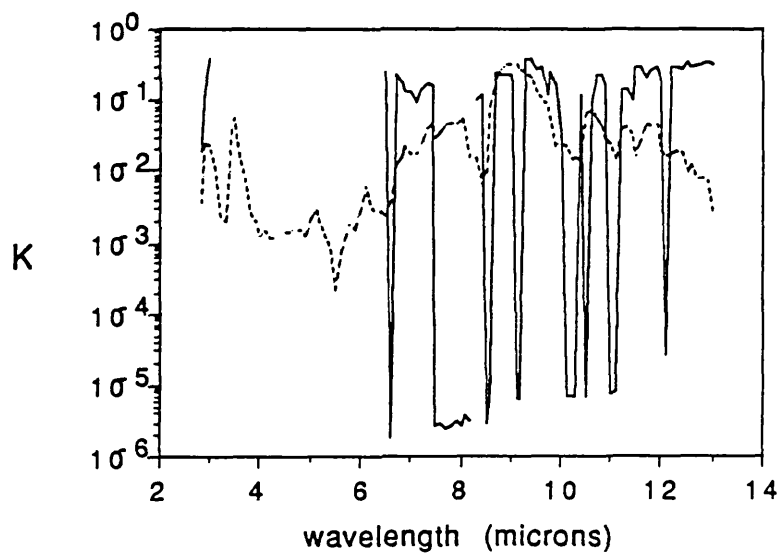


Fig 4.2 : Absorptive Index Curves for Peg 300.

— VLC curve
 --- free surface
 curve

wavelength (microns)	n	wavelength (microns)	n
2	1.369 [6.4]	5.0	1.416 [2.3]
2.1	1.391 [4.6]	5.1	1.414 [2.3]
2.2	1.401 [3.9]	5.2	1.414 [2.2]
2.3	1.389 [4.6]	5.3	1.435 [0.8]
2.4	1.360 [6.8]	5.4	1.430 [1.1]
2.5	1.328 [9.4]	5.5	1.418 [1.4]
2.6	1.343 [7.6]	5.6	1.414 [1.6]
2.7	1.349 [7.8]	5.7	1.425 [0.9]
2.8	1.354 [9.1]	5.8	1.432 [-0.07]
2.9	1.377 [3.9]	5.9	1.433 [-0.5]
3.0	1.469 [-0.6]	6.0	1.413 [0.7]
3.1	1.436 [1.8]	6.1	1.400 [2.1]
3.2	1.433 [1.5]	6.2	1.436 [-0.3]
3.3	1.421 [1.5]	6.3	1.415 [0.7]
3.4	1.396 [1.4]	6.4	1.424 [0.07]
3.5	1.499 [0.4]	6.5	1.420 [-0.9]
3.6	1.491 [-0.07]	6.6	1.361 [3.3]
3.7	1.492 [-1.0]	6.7	1.393 [-0.9]
3.8	1.461 [-0.3]	6.8	1.385 [-0.3]
3.9	1.472 [-0.6]	6.9	1.398 [0.1]
4.0	1.467 [-0.8]	7.0	1.396 [-0.07]
4.1	1.472 [-0.7]	7.1	1.385 [0.4]
4.2	1.440 [1.3]	7.2	1.386 [-0.07]
4.3	1.439 [0.7]	7.3	1.379 [-0.5]
4.4	1.425 [1.9]	7.4	1.394 [0.5]
4.5	1.440 [1.0]	7.5	1.390 [0.7]
4.6	1.431 [1.5]	7.6	1.379 [0.3]
4.7	1.446 [0.4]	7.7	1.374 [1.0]
4.8	1.449 [0.07]	7.8	1.384 [0.7]
4.9	1.422 [1.8]	7.9	1.379 [0.2]

Table 4.1: Refractive Index Values for peg 300 found by
Volatile Liquid Chamber Technique.

Figures in brackets denote percentage (relative) variation from
the free surface n value.

wavelength (microns)	n	wavelength (microns)	n
8.0	1.380 [1.2]	11.0	1.466 [2.9]
8.1	1.393 [0.5]	11.1	1.458 [2.4]
8.2	1.375 [0.8]	11.2	1.453 [2.1]
8.3	1.369 [-0.5]	11.3	1.463 [2.7]
8.4	1.342 [-0.4]	11.4	1.474 [1.4]
8.5	1.275 [1.7]	11.5	1.486 [0.4]
8.6	1.222 [0.08]	11.6	1.495 [-0.5]
8.7	1.215 [0.7]	11.7	1.462 [1.3]
8.8	1.274 [0.4]	11.8	1.479 [-0.1]
8.9	1.363 [0]	11.9	1.489 [-0.3]
9.0	1.429 [0.6]	12.0	1.481 [0.9]
9.1	1.519 [-0.1]	12.1	1.492 [-0.3]
9.2	1.525 [1.6]	12.2	1.506 [-0.9]
9.3	1.610 [-2.0]	12.3	1.502 [-1.1]
9.4	1.646 [-1.2]	12.4	1.495 [-0.6]
9.5	1.639 [-0.9]	12.5	1.512 [-2.0]
9.6	1.629 [-1.8]	12.6	1.504 [-1.5]
9.7	1.596 [0.3]	12.7	1.421 [3.7]
9.8	1.602 [-0.6]	12.8	1.507 [-2.3]
9.9	1.567 [-0.4]	12.9	1.510 [-2.5]
10.0	1.537 [0.7]	13.0	1.507 [-3.0]
10.1	1.488 [3.2]		
10.2	1.474 [3.0]		
10.3	1.469 [2.0]		
10.4	1.462 [1.6]		
10.5	1.450 [2.8]		
10.6	1.473 [2.9]		
10.7	1.498 [1.9]		
10.8	1.497 [1.9]		
10.9	1.483 [2.6]		

Table 4.1: Refractive Index Values for peg 300 found by
Volatile Liquid Chamber Technique.

Figures in brackets denote percentage (relative) variation from
the free surface n value.

wavelength (microns)	k	wavelength (microns)	k
2.8	.0196	9.7	.123
2.9	.132	9.8	.247
3.0	.392	9.9	.157
3.6	.079	10.0	.0334
3.9	.191	10.4	.122
4.1	.141	10.6	.102
4.3	.207	10.7	.216
4.8	.119	10.8	.220
5.3	.227	10.9	.153
5.4	.0823	11.2	.148
5.8	.0879	11.3	.139
5.9	.310	11.4	.104
6.0	.203	11.5	.281
6.2	.213	11.6	.283
6.7	.230	11.7	.206
6.8	.173	11.8	.262
6.9	.127	11.9	.286
7.0	.137	12.0	.232
7.1	.091	12.2	.291
7.2	.144	12.3	.297
7.3	.166	12.4	.268
7.4	.153	12.5	.335
8.3	.105	12.6	.288
8.4	.119	12.8	.325
8.7	.249	12.9	.343
8.8	.219	13.0	.305
8.9	.217		
9.0	.220		
9.3	.378		
9.4	.374		
9.5	.275		
9.6	.283		

Table 4.2: Absorptive Index Values for peg 300 found by Volatile Liquid Chamber Technique.

similar and there appears to be remarkably good agreement between the two curves in the absorption band. The figures in brackets in table 4.1 represent the (relative) percentage difference in the refractive index compared to the refractive index derived from the free liquid surface measurements (shown in appendix L). The greatest variation occurs in the 2.0 - 2.9 microns , in particular the region from 2.5 microns to 2.8 microns where the variation lies between 7.6% - 9.4%. There are two possible explanations for this disagreement, firstly it occurs around a water band, where the reflectance of the water standard will be changing rapidly and so greater errors in measurement will inevitably occur (when bearing in mind the 1% bandwidth). A secondary cause of the discrepancy may be the rapid changes in the AR coatings of the germanium and zinc selenide in the 2 microns to 3 microns range, perhaps because they are operating at the limits of their transmission efficiency. By referring to the transmission curves shown in fig 3.9 and fig 3.11, it is possible to see this fluctuation for both the ARG6 (germanium) coating and ytterbium oxide (zinc selenide) coating. This change in transmission is particularly pronounced in the ARG6 case, here the transmission is falling (in the case of one window) from around 0.598 to 0.430 then rising to 0.570, in an interval of 1 micron (from 2 - 3 microns). Again this rapid change over a comparatively small spectral range may give rise to variation in the subsequent refractive index value.

Fig 4.2 is a comparison of the absorptive index data for peg 300 found by the volatile liquid chamber system and the absorptive index data for the same liquid found by variable path length cell and where necessary Kramers - Kronig dispersion analysis (see chapter two for details). Table 4.2 contains the absorptive index data found by the volatile liquid chamber technique. It is apparent that there is poor agreement between the two curves with the variation between the values found from the two different techniques as high as two orders of magnitude in some regions. The reason for this alarming disagreement is discussed in the following section.

4.3.1 Problems in the Solution of the Absorptive Index

To fully appreciate the problems associated with solving the Fresnel equations (3.3) and (3.4) for the absorptive index it is best to test the behaviour of the two equations by the substitution of a range of optical constants to *find* the corresponding interface reflectances. A

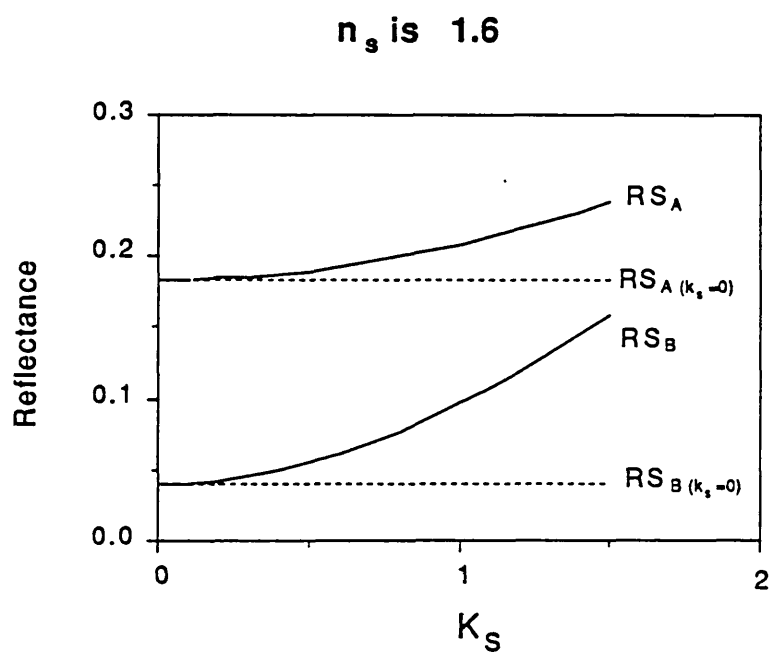
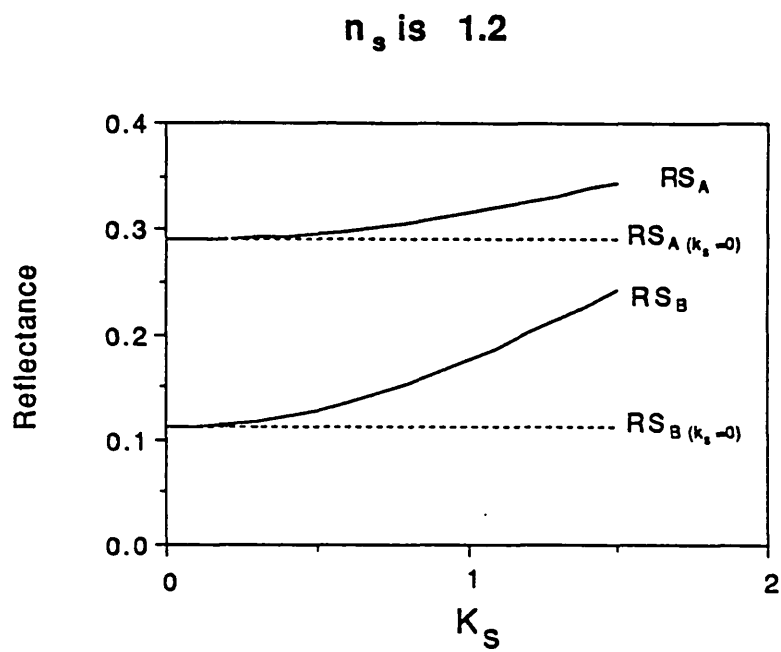


Fig 4.3: Reflectance Curves for a Range of k_s values..

k_s	RS_A	RS_B
0.00	.2899	.1111
0.001	.2899	.1111
0.005	.2899	.1111
0.01	.2899	.1111
0.02	.2900	.1111
0.03	.2900	.1112
0.04	.2900	.1112
0.05	.2900	.1113
0.06	.2900	.1114
0.07	.2901	.1115
0.08	.2901	.1116
0.09	.2902	.1117
0.1	.2902	.1118
0.2	.2910	.1139 [2.5]
0.3	.2923	.1172 [5.5]
0.4	.2941 [1.5]	.1220 [9.8]
0.5	.2965 [2.3]	.1279
0.6	.2993 [3.2]	.1351
0.8	.3064 [5.7]	.1529
1.0	.3153 [8.8]	.1748
1.1	.3204	.1870
1.2	.3258	.2000
1.3	.3317	.2137
1.4	.3379	.2279
1.5	.3445	.2426

Table 4.3 : Generated Reflectance Values for a Range of k_s values,
 n_s is fixed at 1.2.

k_s	RS_A	RS_B
0.00	.1837	.0400
0.001	.1837	.0400
0.005	.1837	.0400
0.01	.1837	.0400
0.02	.1837	.0400
0.03	.1837	.0401
0.04	.1837	.0401
0.05	.1837	.0402
0.06	.1838	.0402
0.07	.1838	.0403
0.08	.1838	.0404 [1.0]
0.09	.1839	.0405 [1.3]
0.1	.1839	.0406 [1.5]
0.2	.1847	.0424 [6.0]
0.3	.1860 [1.3]	.0455 [13.8]
0.4	.1878 [2.2]	.0495
0.5	.1901 [3.5]	.0548
0.6	.1929 [5.0]	.0611
0.8	.2000 [8.9]	.0769
1.0	.2090	.0965
1.1	.2140	.1075
1.2	.2195	.1193
1.3	.2254	.1317
1.4	.2317	.1448
1.5	.2383	.1584

Table 4.4 : Generated Reflectance Values for a Range of k_s values,
 n_s is fixed at 1.6.

series of test values for n_s and k_s were substituted into the Fresnel equations, and values obtained for the corresponding RS_A and RS_B values. The optical constants of the window materials, n_A , k_A , n_B , k_B were set to 4.0, 3.5×10^{-5} , 2.4 and 0 respectively (which are average values for the optical constants of germanium and zinc selenide, the two substrates used in all our experiments). RS_A and RS_B were calculated for k_s from 0 to 1.5, for $n_s = 1.2$ (roughly a *minimum* refractive index value) and for $n_s = 1.6$ (an approximately *maximum* refractive index value). The resulting curves are shown in fig 4.3, the dashed lines represent RS_A and RS_B for the case when k_s is set to 0. It is clear that as the absorptive index, k_s , increases in magnitude the curve diverges from the $k = 0$ line, particularly in the RS_B case (that is the zinc selenide case). However, for k_s values below 0.35 all the curves lie close to the $k_s = 0$ states. In practical terms this suggests that in the analysis any k value below 0.35 should have a large associated error, if k_s can be extracted at all. The data used to produce the curves, is shown in tables 4.3 and 4.4. The data corresponding to the case where $n = 1.2$ shows that the values generated for RS_A do not begin to seriously deviate from the $k_s = 0$ value of 0.2899 until around a k_s value of 0.4 when the relative percentage discrepancy (denoted by the figure in brackets) is 1.5%, the discrepancy increases progressively with increasing absorptive index. The values generated for RS_B (for $n_s = 1.2$), show a similar trend although the degree of difference from the $k_s = 0$ value is apparent at a smaller value of k_s . When n_s is set to 1.6 (table 4.4, fig 4.3) the divergence of RS_A and RS_B from the $k_s = 0$ case is slightly more pronounced at a smaller k_s value (i.e. there is a 1.3% variation at $k_s = 0$ for RS_A), but the general pattern is much the same as the $n = 1.2$ case. It should be noted that in the general error analysis carried out on the measurements the uncertainty associated with the interface reflectances, RS_A and RS_B for the substrates germanium and zinc selenide, were calculated to be of the order of 3% and 1.5% respectively.

To summarise, therefore, the Fresnel equations of the form given by equations (3.3) and (3.4) are ill-conditioned equations, that is they are insensitive to *small* values of absorptive index, k_s , and in this case small implies values below 0.35 - 0.4. This explains the serious lack of agreement between the absorptive index curve plotted using data found by the volatile liquid cell arrangement and the curve plotted from transmission measurements, shown in fig 4.2. The experimental uncertainty attached to the absorptive index values for the

various samples presented in the following sections also reflects the problem of finding an absorptive index value less than 0.4 using the closed cell method.

4.4 Experimental Results

4.4.1 Aqueous Ammonium Sulphate

To test the ability of the closed cell system to measure what we take to be *large* absorptive index values it was necessary to identify a liquid with a suitably large absorption peak and consequently make measurements on that liquid. Aqueous ammonium sulphate was chosen since research papers published by Downing et al (1977) and Remsberg (1973) indicated a large absorption peak in the 8 - 9 microns region due to the sulphate ion.

To make up a liquid sample for measurement crystalline ammonium sulphate was dissolved in distilled water at room temperature (23°C) until a saturated solution was obtained (i.e. some ammonium sulphate remained undissolved at the bottom of the solution which implied there was a maximum volume of the sulphate dissolved in the solution). Initially the saturated solution of ammonium sulphate was placed in the volatile liquid cell system and measurements made on it. However, the resulting absorptive index values obtained did not seem to resemble liquid absorption bands and the *n* and *k* spectra bore no resemblance to the spectra presented in the literature. This apparent disagreement was found to be caused by scattering effects. In simplistic terms, the ions in a saturated solution of ammonium sulphate tend to form what is effectively a *pseudo* lattice i.e., when there is very little *free* water in the solution there is no longer a random ionic system, instead the ions pack into more ordered layers (Ratajczak and Orville-Thomas, 1982, and Higgs, 1987). This *regular* lattice or ordered liquid structure, therefore, causes scattering of the incident radiation. To overcome this effect a *near* saturated solution was produced by cooling the saturated solution by a few degrees. Thus causing some of the ammonium sulphate to precipitate out of the solution. The remaining liquid solution is pipetted off and allowed to return to room temperature. Since there is more water present now, the constituent ions are able to move more freely in the solution and scattering should not occur.

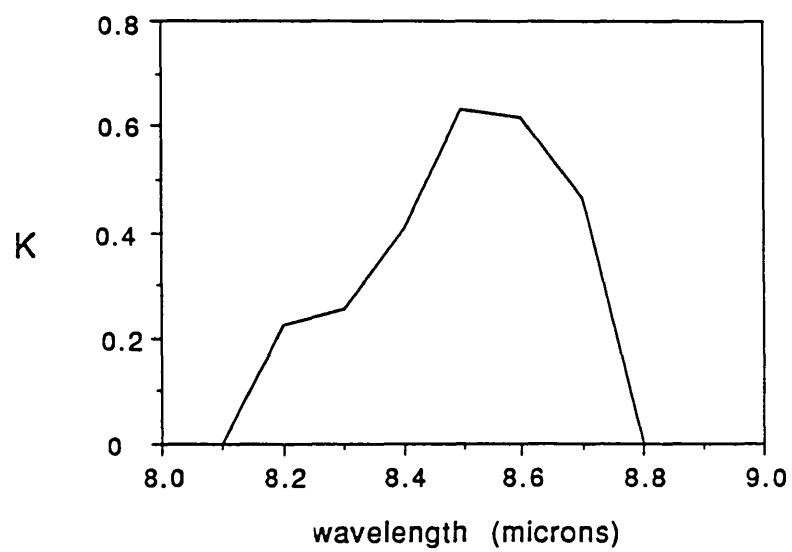
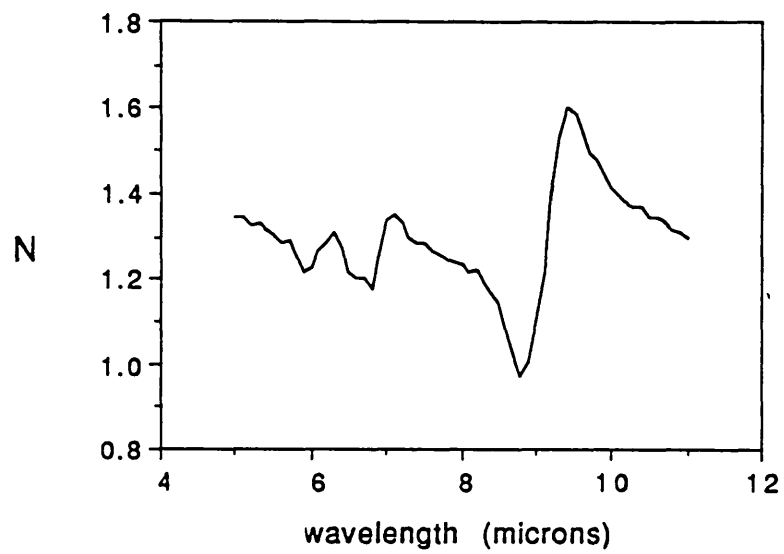


Fig 4.4 : N and k values for near saturated ammonium sulphate solution.

wavelength (microns)	n	wavelength (microns)	n	k
5.0	1.341 (2)	8.0	1.232 (4)	
5.1	1.343	8.1	1.217	
5.2	1.321	8.2	1.220	0.226 (80)
5.3	1.331	8.3	1.188	0.254 (80)
5.4	1.316	8.4	1.169 (4)	0.410 (30)
5.5	1.301	8.5	1.146 (5)	0.632 (10)
5.6	1.283	8.6	1.077	0.618 (10)
5.7	1.288	8.7	1.013	0.464 (25)
5.8	1.261	8.8	0.975	
5.9	1.217	8.9	1.002	
6.0	1.227	9.0	1.108 (4)	
6.1	1.263	9.1	1.215	
6.2	1.286 (4)	9.2	1.391 (3)	
6.3	1.309 (2)	9.3	1.534	
6.4	1.273 (4)	9.4	1.602	
6.5	1.214	9.5	1.583	
6.6	1.199	9.6	1.552	
6.7	1.201 (2)	9.7	1.492	
6.8	1.178	9.8	1.473	
6.9	1.250	9.9	1.440	
7.0	1.332	10.0	1.414	
7.1	1.349	10.1	1.391	
7.2	1.328	10.2	1.372	
7.3	1.299	10.3	1.367	
7.4	1.287	10.4	1.369	
7.5	1.282	10.5	1.344	
7.6	1.262	10.6	1.343	
7.7	1.256	10.7	1.333	
7.8	1.246	10.8	1.319	
7.9	1.238 (4)	10.9	1.310	
		11.0	1.295 (3)	

Table 4.5 : N and k values for a near saturated solution of ammonium sulphate. Figures in brackets denote relative percentage errors.

Measurements were carried out, using the closed cell system, on the near saturated ammonium sulphate solution and the results shown in fig 4.4 and table 4.5. The large absorption peak (k maximum is 0.632) due to a fundamental of the sulphate ion has been reproduced at about 8.5 microns.

The work on aqueous ammonium sulphate indicates that the closed cell system can be used for measuring samples with large absorption peaks and the associated uncertainty (shown in table 4.5) is reduced for large k values.

4.4.2 Acetone

Perhaps the first liquid that springs to mind when one thinks of classically volatile liquids is the solvent acetone (CH_3COCH_3). Measurements were carried out with acetone in the closed cell system which allowed us to assess the effectiveness of the optical cells in containing a reasonably volatile liquid. Acetone has a boiling point of 55.5°C and a vapour pressure of 3.6 P.S.I.A. at 20°C (Gallant and Railey, 1984). The refractive index and absorptive index spectra for acetone are shown in fig 4.5 and the corresponding data tables appear in appendix M (tables M1 and M2). Acetone is a typical non aromatic ketone which, as can be seen from the refractive index spectrum in fig 4.5, shows a large absorption band at 5.8 microns due to the $\text{C}=\text{O}$ functional group (Pouchert, 1981). This is a rather sharp band, in the measurements of acetone by Crawford Jr. et al (1978) using A.T.R. they obtain an absorption peak of less than 0.3 microns in width. The refractive index curve also displays a collection of ketone associated function bands at between 8 microns and 10 microns, these are relatively weak and variable in position.

The corresponding absorptive index curve (fig 4.5 and appendix M, table M2) however, is a less clearly defined profile. This is due to the closed cell systems inherent inability to extract the smaller absorptive index values (see section 4.3.1), the gaps in the absorptive index curve and in the absorptive index data in appendix M, table M2, indicate regions where the program which calculates the optical constants was unable to produce a k value.

The absorptive index for acetone has also been measured for the 2 - 13 microns region by the transmission method using variable path length cells (see chapter two for

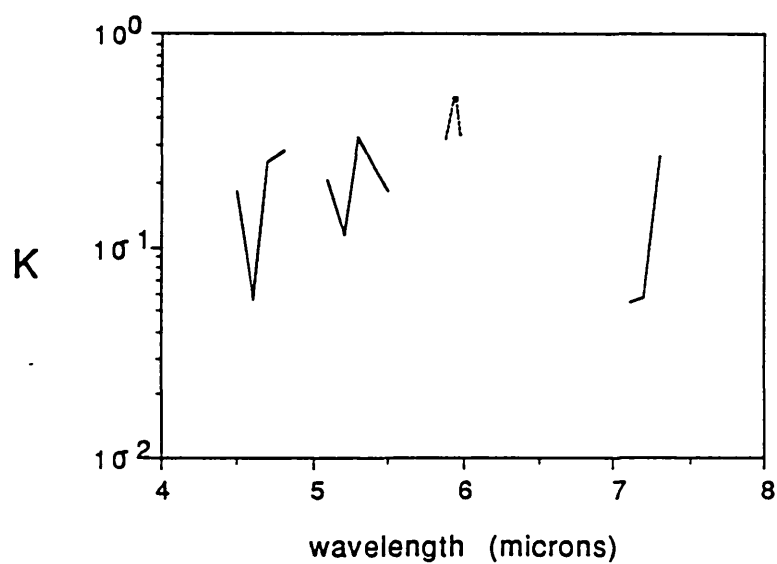
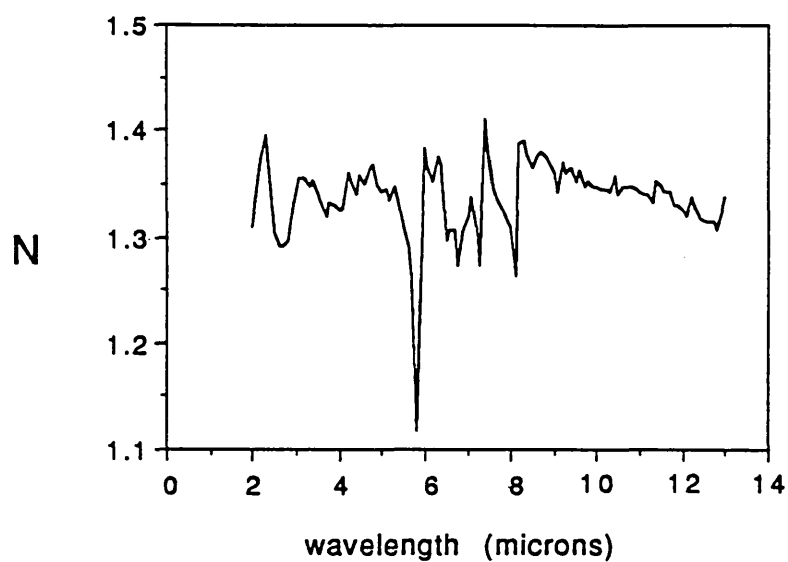


Fig 4.5 : N and K Values for Acetone found
using the Volatile Liquid Cell System.
(See text for further details)

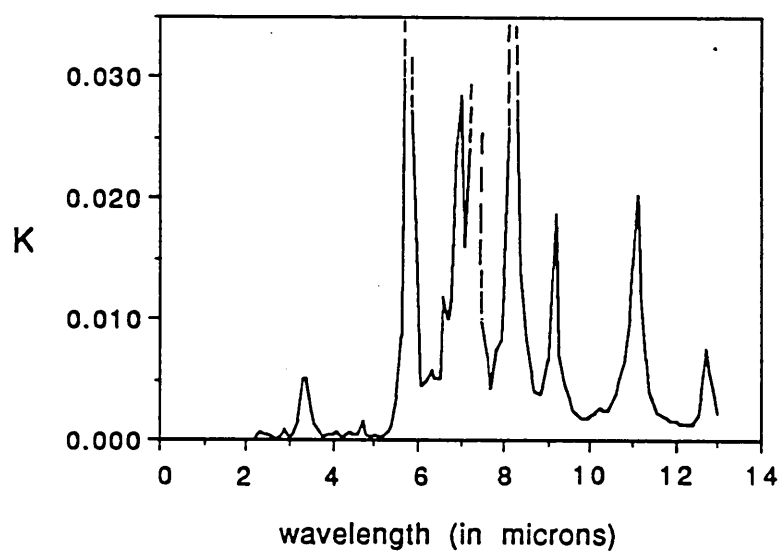


Fig 4.6 : K values for acetone found by transmission measurements using Variable Path Length Cells.
(See text for further details)

details). Although the variable path length cells are not perfectly air tight they contain the acetone sufficiently, thereby allowing experimental measurements to be made. The results of the transmission measurements are shown in appendix O, table O1, and in fig 4.6. This allows a comparison to be made between two distinctly different methods of measuring the absorptive index. Fig 4.6 illustrates the drawback of the transmission method, gaps appear in the absorptive index profile in the wavelength regions where k is too large to be measured using the variable path length cells. These occur at 5.8 microns, 7.3 - 7.4 microns and 8.2 microns and are consistent with the acetone absorption bands reported by Crawford, Jr. et al in their report on the measurement of optical constants by attenuated total reflection. The absorptive index values found by the closed cell technique (appendix M, appendix M2) are in poor agreement with the available transmission k values. However, this is not surprising since the closed cell technique is not suited to finding absorptive index values of the order of 0.4 or less with great accuracy and this is reflected in the large associated errors attached to the k values shown.

In the ideal case the closed cell technique should cover the regions where the transmission technique is unable to produce a value for k because of excessively heavy absorption. This to an extent has been achieved, i.e. the gaps in table O1, appendix O, at 5.8 microns, 7.3 microns and 8.2 microns have been *filled* by the closed cell technique (see table M2, appendix M), and the percentage uncertainty associated with the large absorption peak at 5.8 microns is quite small (5%). However, the gap in the variable path length cell values at 7.4 microns has not been filled by the closed cell measurements, the corresponding gap at 7.4 microns in table M2, appendix M implying the k value was too small to be found by the closed cell technique. This observation suggests that when finding the k value of a liquid, the two techniques, namely transmission measurements and the closed cell measurements, are not necessarily complementary and regions will exist for which a k value cannot be found by either method. This subject will be discussed further in section 4.5.1 and section 4.6.

There is a slightly worrying feature of acetone; at certain spot wavelengths a high k value (i.e. a k value that could not be measured by the variable path length cell method) is predicted by the closed cell technique, i.e. the k values at 4.3 microns, 5.1 microns and 5.3 microns are 0.346, 0.206 and 0.329 respectively. However, referring to the data found by transmission measurements using a variable path length cell, we note that the k values at the

same three wavelengths are respectively, 2.86×10^{-4} , 2.58×10^{-4} and 6.22×10^{-4} . There does not appear to be an absorption band in this region whose rapidly changing absorption would perhaps account for this odd discrepancy, however, the very large percentage uncertainties associated with the closed cell k values indicates that they are very inaccurate, whereas the k values found directly by transmission measurements, at 4.3, 5.1 and 5.3 microns, have a very much smaller associated error of 2.4%.

4.4.3 Freons

Another class of liquids investigated by the closed cell technique were the freons which have widespread application as coolants. Measurements were made on two freons, trichlorofluoromethane (CCl_3F) and 1,1,2 trichlorotrifluoroethane ($\text{C}_2\text{Cl}_3\text{F}_3$), they have boiling points and vapour pressures (at 20°C) of 23.7°C, 13 P.S.I.A. and 47.6°C, 5 P.S.I.A. respectively (Gallant, 1974), both are, therefore, distinctly more volatile than acetone. Trifluoromethane (T.F.M.) and 1,1,2 trichlorotrifluoroethane (T.T.F.E.) are non aromatic halogenated hydrocarbons and both are short molecules, i.e T.F.M. is a single carbon molecule and T.T.F.E. has a structure based on a two carbon chain. When more than one halogen atom is introduced into the molecule it gives rise to a broad range of carbon - halogen stretch absorptions, these occur in the 8 - 13 microns region (Pouchert, 1981). The optical constants for T.T.F.E., found using the volatile liquid arrangement, are shown in fig 4.7 and the optical constants for T.F.M., also found by the closed cell method, are shown in fig 4.9. The corresponding data tables for T.T.F.E. are presented in appendix N (refractive index values in table N1, absorptive index values in table N2), the data tables for T.F.M. are also presented in appendix N (refractive indexes in table N3 and absorptive indexes in table N4). CF_2 and CF_3 groups absorb strongly in the 8 - 9 microns region, which explains the cluster of absorption peaks in the n and k spectra for T.T.F.E. (fig 4.7), since it contains the CF_2 functional group. T.T.F.E. and T.F.M. each have a large characteristic absorption peak around the 12 microns region. Once again the gaps in the absorptive index tables and curves, derived from the closed cell measurements, indicate regions where the k value could not be determined in the analysis due to its comparatively small magnitude.

The absorptive index values of T.T.F.E. have also been measured by transmission using variable path length cells. The resulting data tables appear in appendix O (table O2) and the

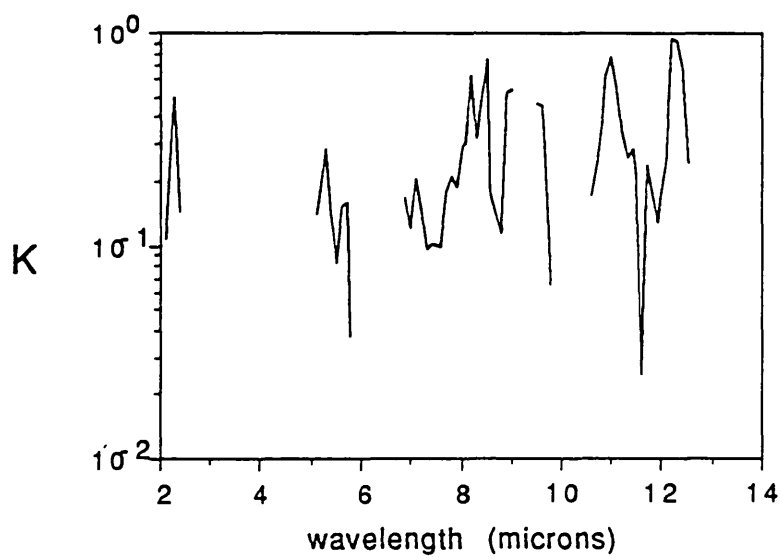
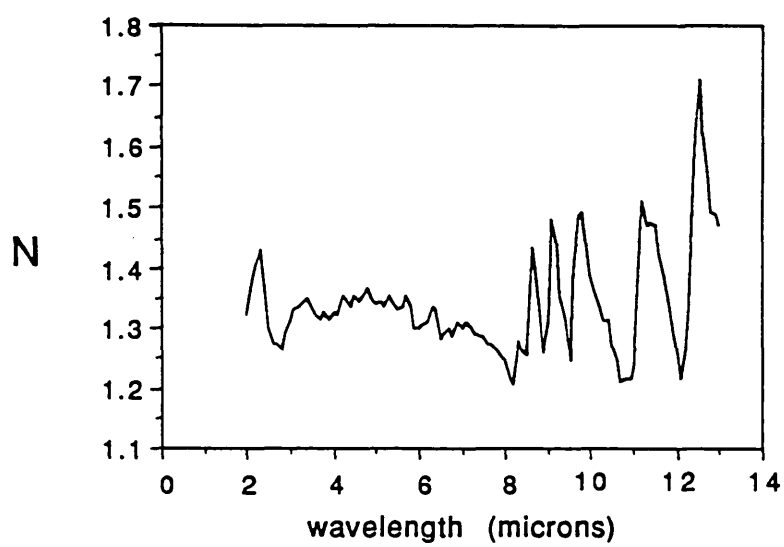


Fig 4.7 : N and K values for T.T.F.E. found using the Volatile Liquid Cell System.

(See text for further details)

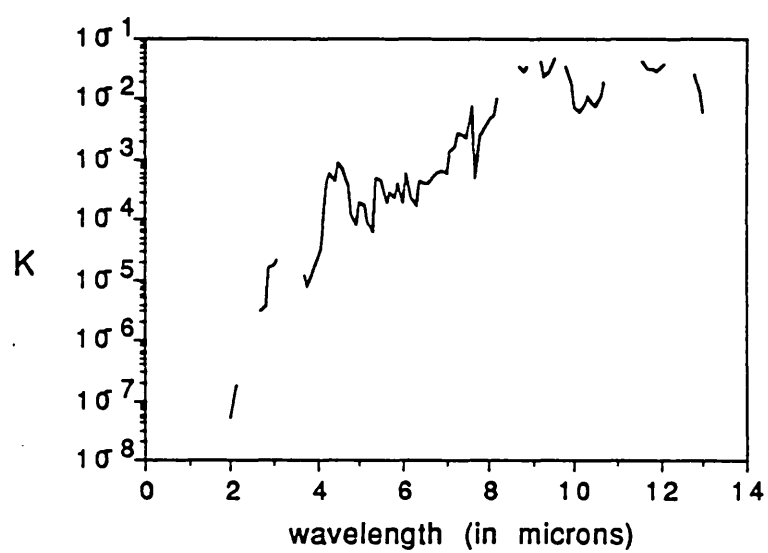


Fig 4.8 : K values T.T.F.E. found by transmission measurements using a variable path length cell.
(See text for further details)

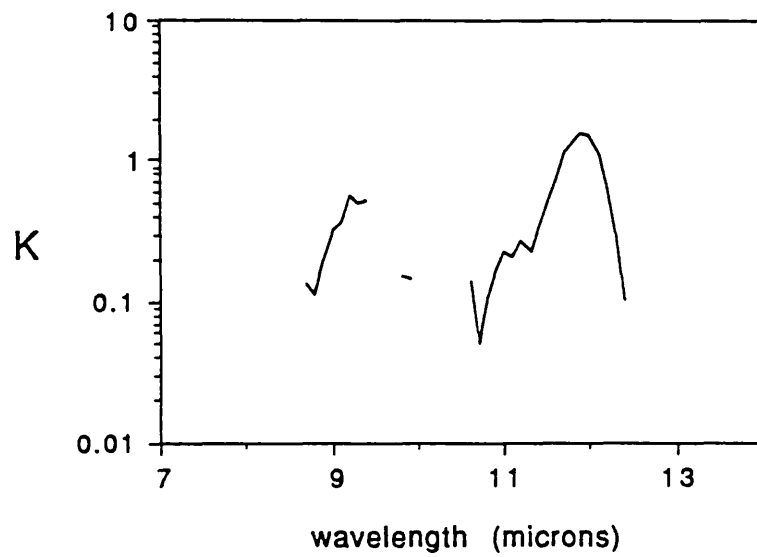
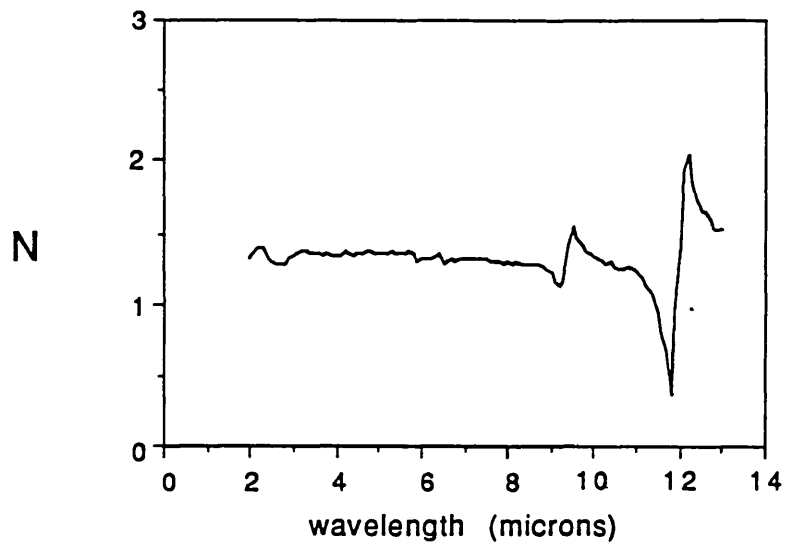


Fig 4.9 : N and K Values for T.F.M. found using the
Volatile Liquid Cell System.
(See text for further details)

corresponding spectral curve in fig 4.8. In this case the gaps that appear in the curve and in the data are due to the k value at that wavelength having too great a magnitude to be detected by transmission. Attempts to measure the absorptive index spectra of T.F.M. by transmission using the variable path length cells were unsuccessful and had to be abandoned since T.F.M. proved far too volatile to be contained by the cells for long enough to allow measurements to be made.

Table O2 (appendix O), the k data found by transmission, indicates that there is very little absorption occurring in the 2 -5 microns region for the sample 1,1,2 T.T.F.E., however, the volatile cell results (table N2, appendix N) show a distinctive sharp peak at 2.2 - 2.3 microns. A comparison of the positions of the large absorption peaks for 1,1,2 T.T.F.E. between the data found by transmission (indicated by gaps in the transmission data shown in appendix O, fig 4.8) and those found by the closed cell method shows a slight shift in peak position in some of the absorption bands. The 8.2 - 8.7 microns, 8.9 - 9.2 microns and 9.5 - 9.8 microns bands are slightly displaced when one set of absorptive index values are compared to the other (i.e. when closed cell results are compared to transmission results). However, this is not surprising, because of the sharpness of the bands, the rapid change of the spectral curves in these regions and the 1% bandwidth limitation.

4.5 Concluding Remarks - the Closed Cell System

4.5.1 Obtaining Optical Constants using the Volatile Liquid Chamber System

In the most general terms it is possible to say the volatile liquid chamber arrangement is a very effective method of measuring the refractive index of a sample liquid, but the extraction of absorptive indexes is more erratic. A more rigorous examination of the results of measurements obtained and of the closed optical cell arrangement in general, however, is required.

The most obvious advantage of the closed cell system is the ability, by virtue of its air tight design, to easily contain volatile liquids. This is a property it shares with many if not all attenuated total reflectance arrangements. Another useful function of the closed cell system is that of providing a stable environment for the measurement of hygroscopic liquids. That is, if

a liquid has a tendency to take up moisture from its surroundings then in, for example, a free liquid surface arrangement the reflectance of the liquid will be changing throughout the course of the experiment (see chapter two). In the closed cell arrangement the test liquid, since it is contained by the air tight cell, is protected from the atmosphere.

Although it was the need to measure volatile liquids that motivated the design of the closed cell arrangement it has proved useful in measurements of very large absorptive index, generally values of 0.4 or more. Values of less than 0.4 cannot always be calculated in the analysis, or if extracted, almost always have rather large associated errors (i.e. 90% - 100%) and hence should not be considered reliable. The volatile liquid cell has proved very effective at finding the refractive indexes of test liquids.

Another, more subtle, advantage of the closed cell technique is unlike the free liquid surface reflectometry method described in chapter two, it is not very dependent on the optical constants of water. In the analysis, because of the nature of the closed cell system, a small change in the refractive index or absorptive index of water makes negligible difference to the optical constants found for the test liquid. This means the effectiveness and overall accuracy of technique is not dominated by the accuracy with which the optical constants of distilled water can be measured, or by the quality of the literature source values used, and the temperature at which they were recorded (see chapter two). This is not true of the conventional free liquid reflectometer arrangement in which the reflectances of water have a great influence on the final result.

4.5.2 Improvements to the Closed Optical Cell

In any new system there is always room for improvement, particularly after initial experiments have been carried out, the closed cell system, though it performed well, is no different in this respect. Since the windows of the cell are in a sense the most important components it is perhaps on this aspect that any changes to the prototype should concentrate. The most obvious improvement that could be made to the windows of the optical cell shown in fig 3.1 would be to replace the plane windows with wedge-shaped substrates. When the cell is assembled, therefore, the wedge would steer the reflectance from the air/window interface out of the system (fig 4.10).

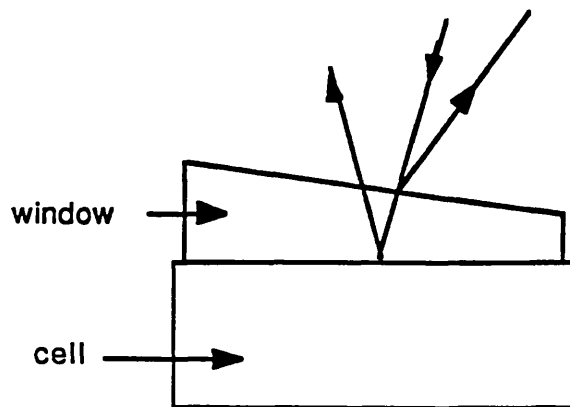


Fig 4.10: Optical Cell with Wedge Window.

This has the advantage of making the calculations, to find the optical constants of the liquid under test, a little simpler since the reflectance of the first surface, the AR coated surface, is neglected. The greater expense and possible difficulty in obtaining and AR coating wedge-shaped substrates would probably be justified by the experimental advantages of having to consider one reflectance only, that of the window/liquid interface, from each optical cell. In the existing optical cells, shown in fig 3.1, the windows are held onto the main body of the cells by a ring nut, and cushioned by a mixture of P.T.F.E. and rubber rings (see chapter 3 for further details). One useful modification would be to integrate the ring nut, and cushioning rings into a single unit into which the window can be placed. This would clearly be convenient in terms of cell assembly and dismantling, but it would be a necessary modification if wedge windows are to be incorporated, since it would prove difficult to use a ring nut, such as in the plane slab case, to retain a wedge-shaped window.

Another potential source of improvement is the window material itself and the coatings applied to the surface in contact with air. The field of infrared optical materials and antireflection coatings is one that is still expanding with the continual development of new substrates, new coatings and new manufacturing processes. The measurement of liquid samples, in the closed cell, using a variety of different window materials and thin film AR

coatings would, no doubt, prove an interesting exercise.

4.6 Summary and Future Developments

The assertion at the start of this thesis that no one measurement technique can capably be applied to cover *all* wavelengths has been reinforced by the work carried out in subsequent chapters. Two factors govern the method of measurement to be applied, the magnitude of the absorptive index of the sample and its volatility. As a method of finding the refractive index of a liquid (indirectly) the free liquid surface reflectometer is naturally unsuitable for a volatile liquid. The transmission method (using variable path length cells) to find the absorptive index directly also has practical limitations, when the k value is above about 0.08 the absorption in the liquid is such that the incident beam is completely absorbed, or the transmitted signal is too small to be measured. In addition it should be noted that liquids with low boiling points (for example trifluoromethane) are not sufficiently contained by the variable path length cells to allow measurements to be carried out. We have further established that the volatile liquid chamber (or closed cell) arrangement is suitably effective in the measurement of refractive index values (of both volatile and non volatile liquids), but is not as practically useful in the measurement of absorptive index values of less than 0.4. Absorptive index values of less than 10^{-4} are also difficult to measure even when the fixed path length cells are used. However, the practical difficulties of measuring small k values (i.e. less than 10^{-4}) do not concern us greatly in our work since an absorption of such a small magnitude can be neglected and will, in any case, make little difference in a Fresnel equation, e.g. if we consider a liquid with a complex refractive index of $1.2 - i10^{-4}$, then the reflectance at the surface, in air, of an incident beam according to Fresnel's equation will be 8.2644648×10^{-3} . However, if the absorptive index component of the complex refractive index is ignored the reflectance is calculated to be 8.2644628×10^{-3} . This difference in the reflectance is too small to be considered significant in our work and would be well within the limits of uncertainty assigned to the experiments.

We have made the observation that the method of measurement employed depends largely on the order of magnitude of the absorptive index to be measured. Table 4.6 is an outline of the k ranges covered and the corresponding technique that would be best employed

to find the k value. In the ideal case the different methods would perfectly complement the full absorptive index range, however, there is a range of k values, $> 0.08 - < 0.4$, which is not covered by any of the three techniques discussed in previous chapters. In this intermediate region the k value becomes too large to be recorded using the variable path length cells, yet it is too small to be accurately extracted by the volatile liquid cell arrangement. One possible solution would be the development of a liquid cell where a thickness of less than 5 microns is possible, the minimum path length setting of the variable path length cells. The inherent problems encountered with the variable path length cells would also prevail in the design and construction of a cell for making intermediate measurements, that is measuring the thickness of the cell and controlling the uniformity of the cell structures such as windows. Indeed, when considering a cell design with a cell thickness of less than 5 microns, these problems are potentially more serious.

k	method of measurement
$< 10^{-5}$	fixed length cells
$10^{-5} - 0.08$	variable path length cells
> 0.4	volatile liquid (closed) cell

Table 4.6: Absorptive Index Ranges and Methods of Measurement

Young and Jones (1969) developed a cell for ultra-thin liquid films for the measurement of strongly absorbing liquids by transmission. The structural design of the cell they produced was based on two potassium bromide plates which had been polished to an optical flatness of about half a fringe per cm for visible light. A uniform film of aluminium was deposited to the required thickness by evaporation on the inner face of one plate such that a rectangular space remains which is to form the liquid cavity. A simplified illustration of the plate is shown in fig 4.10, a side view of the plate shows how the liquid cavity is formed,

although it should be noted that for the sake of clarity the thickness of the deposited film is greatly exaggerated. The two plates are mounted together with an assembly of rubber gaskets and held together by screw threads and wing nuts. The thickness of the evaporated film was determined interferometrically before assembly. On the basis of the even deposition of the film and flatness of the plate, Young and Jones assumed that the thickness of the liquid gap was the same as the thickness of the deposited film. A reservoir cavity allows the introduction of the liquid into the gap between the plates and teflon stoppers ensure the liquid remains in this gap during measurement.

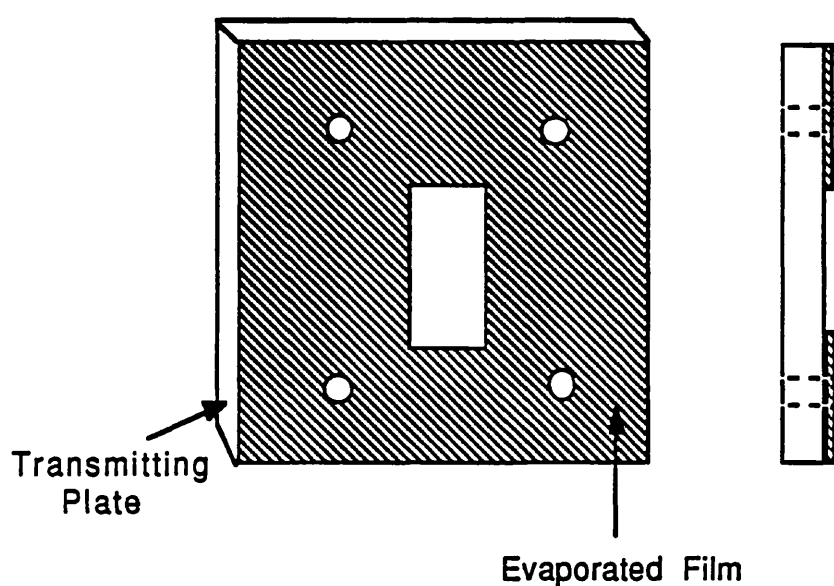


Fig 4.11: Evaporated Film on an Infrared Transmitting Plate
from a Design Devised by Young and Jones (1969).

A number of modifications could be made if this design of cell were to be used in our case, for example the potassium bromide plates could be replaced by germanium or zinc selenide. To reduce reflectances at the window surfaces the inner and outer faces of the assembled cell would require an anti reflection coating. In Young and Jones's method the transmission values obtained require correction due to the effect of reflection losses at the two windows. However, the effects of these reflection losses can be neglected if, as in the variable and fixed length cell cases, two measurements, each of a different thickness, are made at each

wavelength. This would, of course, require two ultra-thin cells with evaporated films of different thicknesses.

Even if the transmitting plates and evaporated film are perfectly plane the possibility of interference due to multiple reflectance would have to be considered, this causes problems when interference fringes are superimposed on the absorption spectra of the liquid under test. Interference effects are appreciable when the difference of the optical path of the interfering beams is much less than the coherence length (Born and Wolf, 1980). Coherence length is defined as (Hariharan, 1985):

$$\Delta l \sim \lambda^2 / \delta\lambda \quad (4.8)$$

Where, λ is the average wavelength of the source and $\delta\lambda$ the range of wavelengths emitted by it. The optical path difference between two rays at normal incidence in a plane parallel film is given by $2nd$ (n is the refractive index of the medium and d it's thickness). Therefore, the condition for observable interference is:

$$2nd \ll \lambda^2 / \delta\lambda \quad (4.9)$$

Equation (4.9) can be used to derive the condition stated, and discussed in chapter three, section 3.5.1, when the interference effects in the windows of the optical cells were considered. In the case of an ultra-thin cell, we consider a cell cavity of 1 micron thickness and a liquid with a refractive index of 1.5 in the cavity, therefore, the optical path difference (given by the left hand side of equation (4.9)) is 3×10^{-6} m. At a wavelength of 2 microns the coherence length (the right hand side of equation (4.9)) is 1×10^{-4} m and at 13 microns the coherence length is 1.3×10^{-3} m. For both these wavelengths (i.e. a minimum and maximum wavelength) the coherence length is greater than the optical path difference, hence, the condition for interference fringes to be observed, given by equation (4.9) is satisfied. Therefore, the absorption spectra of a liquid measured by an ultra-thin cell could suffer from superimposed interference bands which could, in turn, lead to misleading results for absorptive indexes. However, if the liquid in the cell cavity has a large absorptive index heavy

attenuation would prevent effective multiple reflections and if any fringes are present they would be heavily damped. If, however, the liquid is very heavily absorbing the thickness of the cell would have to be further reduced to allow measurable transmission to occur. The internal transmission of a bulk material is given by (Vasko, 1968)

$$T_{\text{int}} = e^{-4\pi k d / \lambda} \quad (4.10)$$

where k is the absorptive index of the sample, d is the thickness of the liquid cavity and λ the wavelength of the incoming beam. Table 4.7 gives the percentage transmission values for a cell thickness of 1 micron (i.e. d is 1 micron in equation (4.10)). The minimum and maximum k values for the range that would be covered by the cells are 0.08 and 0.4. These k values are used together with the minimum and maximum wavelengths of 2 microns and 13 microns in equation (4.10) to calculate the corresponding internal transmissions. There is clearly a great deal of variation over the full wavelength range, for example, at 13 microns with a liquid k value of 0.08 there is very little attenuation (T_{int} is 93%), so multiple reflections could occur giving rise to strong interference effects. At 2 microns the internal transmission for a liquid with a k value of 0.4 is only 8% of the incoming beam, so whilst interference effects would be heavily damped the poor transmission may, in practise, require a shorter path length.

wavelength (microns)	k	T_{int} (%)
2	0.08	61
	0.4	8
13	0.08	93
	0.4	68

Table 4.7: Internal Transmission Values for a Cell Thickness of
1 micron.

It would be imprudent to imply that an ultra-thin cell design would be any easier to apply than any the other methods used, quite apart from interference effects, there are potential difficulties in evaporating an acceptably uniform film onto the window material and in producing windows that are as optically flat as possible. There is then the added difficulty of measuring the thickness of the evaporated film, whether it is done interferometrically or indeed by another method.

Another possible approach to the measurement of k values in the intermediate region of $> 0.08 - < 0.4$ is by the modification of the volatile liquid cell. By choosing window substrates that have refractive indexes which are smaller in magnitude than the germanium and zinc selenide substrates the refractive index component of the Fresnel equations (3.3) and (3.4) can be reduced and so the absorptive index component becomes more significant and can therefore be solved in the analysis. There are a number of possible substrates which could be used, for example CaF_2 (refractive index at 5 microns is 1.40) and KCl (refractive index at 5 microns is 1.47) have the required transmission properties, are chemically inert and have reasonably low refractive indexes. However, the refractive index of the substrate material is now of the order of that of the liquid under test, this means that the window/liquid interface is less distinct and the reflectance from this interface will be reduced in magnitude. It is, of course, this reflectance coefficient which is used in the Fresnel equation to solve the optical constants of the test liquid, a small reflectance would give rise to greater error in the value of k found. The standard of the resulting optical constants, particularly the k value, is dependent on striking the right balance between the refractive index of the window substrates and the reflectance at the interface - a difficult task.

This thesis serves to illustrate the fact that the measurement of optical constants is not as straightforward as it seems, nor is there one method which is clearly superior for all liquids over all wavelengths, in practise a subtle combination of two or more techniques must be applied. The continual interest in the optical properties of liquids, solids and gases by many branches of science and industry will ensure the pursuit of newer and even better methods of measurement of optical constants.

Appendix A

The Lambert - Bouguer Law of Absorption

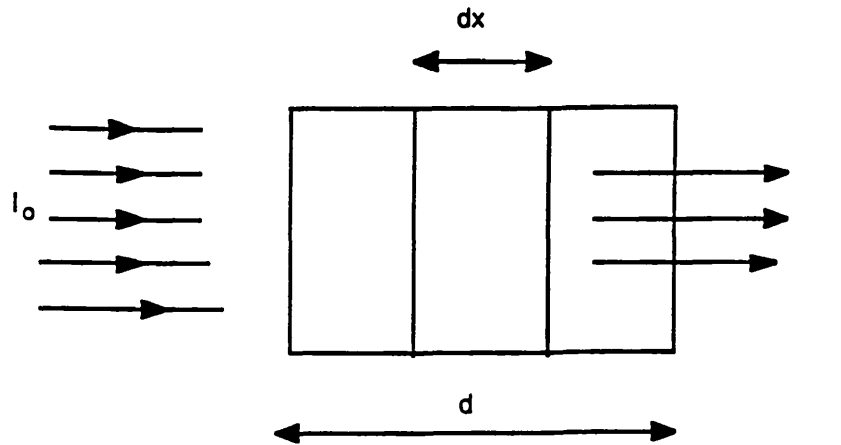


Fig. A 1 A Block of Absorbing Material

Consider a parallel beam of light of incident intensity, I_0 , traversing a small thickness, dx , of a homogeneous material of thickness, d . In the section dx (see fig A1) it will be attenuated by a small amount dI , proportional to the radiation intensity I passing through this section, and is therefore defined by the expression:

$$dI = -\alpha I dx \quad (A1)$$

Where α is the absorption coefficient of the material. Integrating for the full thickness of the material,

$$\int (dI/I) = -\alpha \int dx \quad (A2)$$

therefore,

$$I = I_0 e^{-\alpha d} \quad (A3)$$

α is a function of wavelength, and is related to the absorptive index, k , by the expression

$$\alpha = 4 \pi k / \lambda \quad (\text{A4})$$

Therefore, the Lambert-Bouguer absorption formula affords a simple way of deriving the absorptive index from transmission measurements.

Appendix B

Reflectance, Absorption and Transmission of a Slab

We consider a plane, parallel plate of thickness d , and an absorption coefficient, α . This is illustrated in fig B1, with the reflected and transmitted intensities resulting from an incident beam of intensity I_0 . The radiation is considered to be normally incident on the first surface of the slab, but for the sake of clarity is shown obliquely in the figure, in order to avoid multiple superposition. The reflectivity of the first interface is R_1 and the second interface R_2 . Summing the partial radiation intensities in B1, the following series for the reflected radiation, I_R and the transmitted radiation, I_T , can be obtained:

$$I_R = I_0 R_1 + I_0 (1 - R_1)^2 e^{-2\alpha d} + I_0 (1 - R_1)^2 e^{-4\alpha d} R_1 R_2^2 + \dots \quad (B1)$$

$$I_T = I_0 (1 - R_1) e^{-\alpha d} (1 - R_2) + I_0 (1 - R_1) e^{-3\alpha d} R_1 R_2 (1 - R_2) + \dots \quad (B2)$$

Adding these two infinite series gives

$$R_{\text{slab}} = R_1 + \{[(1 - R_1)^2 e^{-2\alpha d} R_2] / [1 - e^{-2\alpha d} R_1 R_2]\} \quad (B3)$$

$$T_{\text{slab}} = [(1 - R_1)(1 - R_2) e^{-\alpha d}] / [1 - R_1 R_2 e^{-2\alpha d}] \quad (B4)$$

In some cases $R_1 = R_2$, i.e. the two surfaces of the slab are both in contact with the same medium e.g. if the slab is in air or fully submerged in a liquid, and both surfaces are uncoated (or identically coated). In such cases equations (B3) and (B4) reduce to:

$$R_{\text{slab}} = R_1 + \{[(1 - R_1)^2 R_1 e^{-2\alpha d}] / [1 - R_1^2 e^{-2\alpha d}]\} \quad (B5)$$

$$T_{\text{slab}} = [(1 - R_1)^2 e^{-\alpha d}] / [1 - R_1^2 e^{-2\alpha d}] \quad (B6)$$

Equations (B5) and (B6) can be solved for α and R_1 to yield:

$$\alpha = \frac{1}{d} \log_e \left[\frac{(1 - R_1)^2}{2 T_{slab}} + \left[R_1^2 + \left(\frac{(1 - R_1)^2}{2 T_{slab}} \right)^2 \right]^{1/2} \right]$$

... (B7)

$$R_1 = \frac{e^{2\alpha d} + 1}{2(2 - R_1)} \pm \left[\frac{(e^{2\alpha d} + 1)^2}{4(2 - R_1)^2} - \frac{R_1 e^{2\alpha d}}{(2 - R_1)} \right]^{1/2}$$

... (B8)

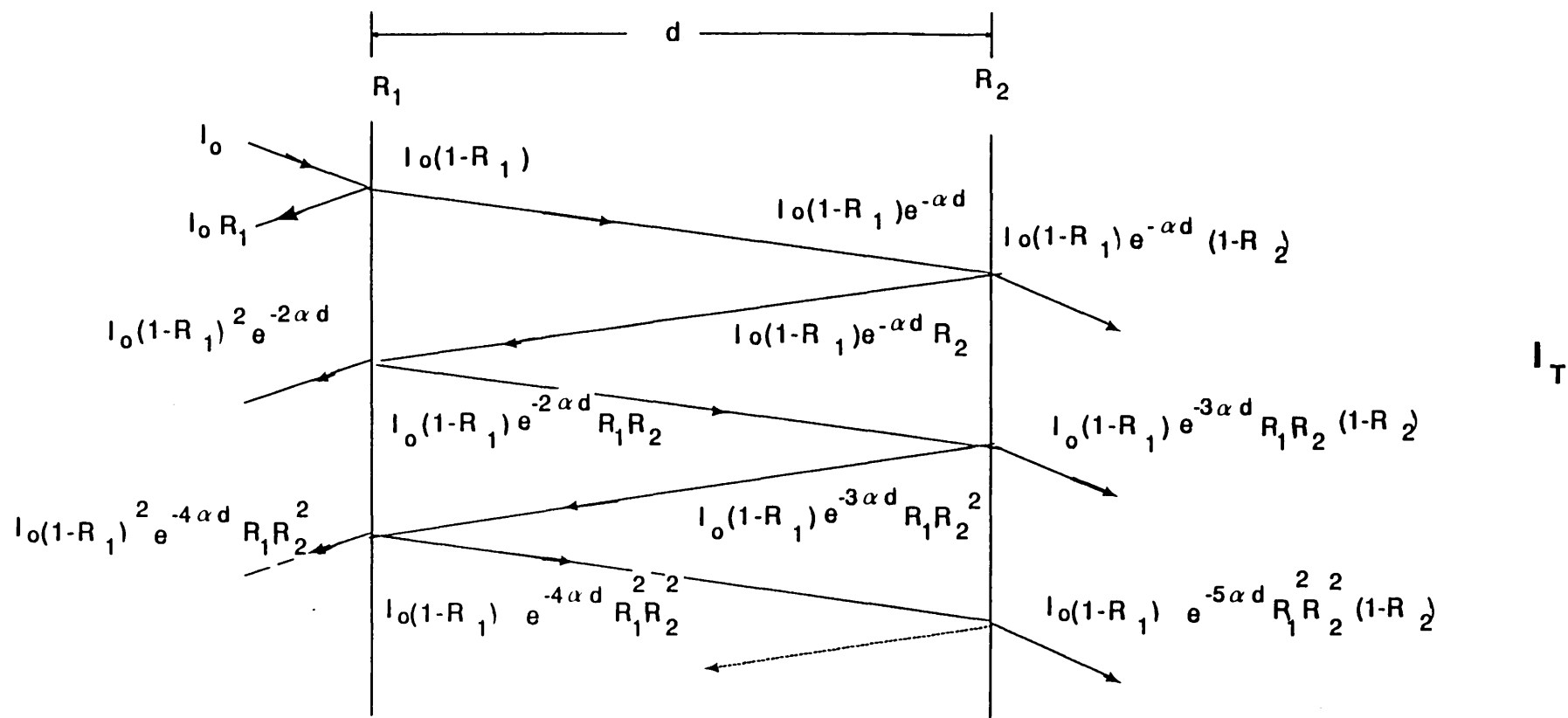


FIG B1 Reflectance, Absorptance and Transmittance of a Plate

APPENDIX C

wavelength (microns)	T	wavelength (microns)	T	wavelength (microns)	T
2.0	.4608	4.8	.4684	7.6	.4636
2.1	.4576	4.9	.4687	7.7	.4650
2.2	.4607	5.0	.4687	7.8	.4633
2.3	.4611	5.1	.4683	7.9	.4637
2.4	.4614	5.2	.4677	8.0	.4642
2.5	.4623	5.3	.4683	8.1	.4641
2.6	.4632	5.4	.4677	8.2	.4626
2.7	.4642	5.5	.4685	8.3	.4639
2.8	.4651	5.6	.4676	8.4	.4635
2.9	.4639	5.7	.4691	8.5	.4632
3.0	.4651	5.8	.4685	8.6	.4649
3.1	.4645	5.9	.4692	8.7	.4638
3.2	.4644	6.0	.4694	8.8	.4641
3.3	.4657	6.1	.4694	8.9	.4629
3.4	.4656	6.2	.4690	9.0	.4630
3.5	.4660	6.3	.4692	9.1	.4632
3.6	.4668	6.4	.4691	9.2	.4623
3.7	.4658	6.5	.4686	9.3	.4647
3.8	.4673	6.6	.4687	9.4	.4635
3.9	.4680	6.7	.4680	9.5	.4632
4.0	.4666	6.8	.4641	9.6	.4637
4.1	.4671	6.9	.4633	9.7	.4628
4.2	.4680	7.0	.4631	9.8	.4636
4.3	.4681	7.1	.4674	9.9	.4627
4.4	.4681	7.2	.4657	10.0	.4628
4.5	.4681	7.3	.4670	10.1	.4625
4.6	.4684	7.4	.4652	10.2	.4629
4.7	.4679	7.5	.4670	10.3	.4627

Table C1 : Experimentally determined transmission values for
uncoated germanium.

Relative uncertainty in transmission is 0.5%.

wavelength (microns)	T
10.4	.4609
10.5	.4624
10.6	.4599
10.7	.4589
10.8	.4604
10.9	.4619
11.0	.4619
11.1	.4606
11.2	.4602
11.3	.4607
11.4	.4581
11.5	.4537
11.6	.4498
11.7	.4377
11.8	.4303
11.9	.4335
12.0	.4354
12.1	.4395
12.2	.4430
12.3	.4425
12.4	.4407
12.5	.4403
12.6	.4417
12.7	.4396
12.8	.4442
12.9	.4413
13.0	.4408

Table C1 : Experimentally determined transmission values for
uncoated germanium.

Relative uncertainty in transmission is 0.5%.

wavelength (microns)	n	wavelength (microns)	n	wavelength (microns)	n
2.0	4.097	4.8	4.009	7.6	4.017
2.1	4.079	4.9	3.996	7.7	4.013
2.2	4.052	5.0	4.013	7.8	4.025
2.3	4.056	5.1	4.004	7.9	4.012
2.4	4.034	5.2	3.992	8.0	4.018
2.5	4.036	5.3	3.989	8.1	4.001
2.6	4.083	5.4	4.007	8.2	4.027
2.7	4.083	5.5	3.992	8.3	4.020
2.8	4.020	5.6	3.993	8.4	4.022
2.9	4.037	5.7	3.988	8.5	4.027
3.0	4.030	5.8	3.986	8.6	3.963
3.1	4.030	5.9	3.979	8.7	3.966
3.2	4.023	6.0	3.986	8.8	3.969
3.3	4.013	6.1	3.990	8.9	3.971
3.4	4.005	6.2	3.977	9.0	3.980
3.5	4.005	6.3	3.981	9.1	3.974
3.6	3.995	6.4	3.980	9.2	3.977
3.7	3.994	6.5	3.983	9.3	3.967
3.8	4.053	6.6	3.979	9.4	3.975
3.9	4.055	6.7	4.022	9.5	3.983
4.0	4.034	6.8	4.031	9.6	3.977
4.1	4.046	6.9	3.968	9.7	3.991
4.2	4.005	7.0	4.004	9.8	3.977
4.3	4.016	7.1	3.995	9.9	3.985
4.4	4.005	7.2	4.009	10.0	3.981
4.5	3.996	7.3	3.990	10.1	3.983
4.6	4.001	7.4	4.001	10.2	3.975
4.7	3.991	7.5	3.986	10.3	3.979

Table C2 : Experimentally determined n values for uncoated germanium.

Relative uncertainty in n values is 0.8%.

wavelength (microns)	n
10.4	3.975
10.5	3.984
10.6	3.990
10.7	3.993
10.8	3.985
10.9	3.977
11.0	3.984
11.1	3.991
11.2	3.991
11.3	3.976
11.4	3.970
11.5	3.983
11.6	3.971
11.7	3.971
11.8	4.024
11.9	3.994
12.0	4.014
12.1	4.009
12.2	3.982
12.3	3.999
12.4	4.008
12.5	4.017
12.6	4.006
12.7	4.013
12.8	3.992
12.9	4.003
13.0	3.994

Table C2 : Experimentally determined n values for uncoated germanium.

Relative uncertainty in n values is 0.8%.

wavelength (microns)	k	wavelength (microns)	k	α cm ⁻¹
6.2	1.09e-6 [>100]	9.1	4.03e-6 [41]	
6.4	1.01e-6	9.2	4.35e-6 [38]	
6.5	1.06e-6	9.3	3.84e-6 [44]	
6.6	1.16e-6	9.4	4.01e-6 [42]	
		9.5	3.82e-6 [45]	
		9.6	3.93e-6 [44]	
6.9	3.24e-6 [38]	9.7	3.74e-6 [47]	
7.0	2.18e-6 [58]	9.8	4.04e-6 [44]	
7.1	1.14e-6 [>100]	9.9	4.14e-6 [43]	
7.2	1.23e-6	10.0	4.29e-6 [42]	
7.3	1.46e-6 [89]	10.1	4.39e-6 [41]	
7.4	1.72e-6 [77]	10.2	4.63e-6 [40]	
7.5	1.65e-6 [81]	10.3	4.59e-6	
7.6	1.75e-6 [78]	10.4	5.67e-6 [33]	
7.7	1.44e-6 [95]	10.5	4.53e-6 [42]	
7.8	1.61e-6 [87]	10.6	5.51e-6 [35]	
7.9	1.97e-6 [72]	10.7	5.86e-6 [33]	
8.0	1.60e-6 [89]	10.8	5.59e-6 [35]	
8.1	2.28e-6 [64]	10.9	5.31e-6 [37]	
8.2	1.89e-6 [78]	11.0	5.02e-6 [39]	.057
8.3	1.66e-6 [89]	11.1	5.34e-6 [37]	.061
8.4	1.70e-6 [85]	11.2	5.61e-6 [36]	.063
8.5	4.16e-6 [89]	11.3	6.19e-6 [33]	.069
8.6	3.62e-6 [43]	11.4	7.92e-6 [26]	.087
8.7	3.95e-6 [40]	11.5	9.58e-6 [22]	.105
8.8	3.75e-6 [42]	11.6	1.24e-5 [17]	.134
8.9	4.18e-6 [38]	11.7	1.93e-5 [11]	.207
9.0	3.84e-6 [42]	11.8	2.06e-5	.219

Table C3 : Experimentally determined k (and some α) values for
uncoated germanium.

Figures in brackets denote percentage (relative)
uncertainty in k value.

wavelength (microns)	k	α cm ⁻¹
11.9	2.07e-5 [11]	.219
12.0	1.85e-5 [12]	.194
12.1	1.67e-5 [14]	.173
12.2	1.63e-5	.168
12.3	1.57e-5 [15]	.160
12.4	1.64e-5 [14]	.166
12.5	1.62e-5	
12.6	1.61e-5 [15]	
12.7	1.71e-5 [14]	
12.8	1.58e-5 [15]	
12.9	1.70e-5 [14]	
13.0	1.80e-5	

Table C3 : Experimentally determined k (and some α) values for uncoated germanium.

Figures in brackets denote percentage (relative) uncertainty in k value.

APPENDIX D

wavelength (microns)	n	wavelength (microns)	n
2.0	4.116	7.0	4.00858
2.1	4.104	7.2	4.00814
2.2	4.092	7.4	4.00773
2.3	4.085	7.6	4.00736
2.4	4.078	7.8	4.00701
2.5	4.072	8.0	4.00668
2.6	4.068	8.2	4.00637
2.8	4.05105	8.4	4.00609
3.0	4.04433	8.6	4.00582
3.2	4.03889	8.8	4.00556
3.4	4.03443	9.0	4.00533
3.6	4.03072	9.2	4.00510
3.8	4.0276	9.4	4.00489
4.0	4.02495	9.6	4.00469
4.2	4.02268	9.8	4.00449
4.4	4.02072	10.0	4.00431
4.6	4.01901	10.5	4.00389
4.8	4.01751	11.0	4.00351
5.0	4.01619	11.5	4.00316
5.2	4.01503	12.0	4.00285
5.4	4.01399	12.5	4.00255
5.6	4.01305	13.0	4.00228
5.8	4.01222		
6.0	4.01146		
6.2	4.01078		
6.4	4.01015		
6.6	4.00958		
6.8	4.00906		

Table D1: N values for uncoated germanium from the review by Palik (1985).

wavelength (microns)	T	wavelength (microns)	T
2.0	.4588	7.0	.4697
2.1	.4600	7.2	.4697
2.2	.4612	7.4	.4698
2.3	.4619	7.6	.4698
2.4	.4626	7.8	.4698
2.5	.4632	8.0	.4699
2.6	.4636	8.2	.4699
2.8	.4653	8.4	.4699
3.0	.4661	8.6	.4699
3.2	.4666	8.8	.4701
3.4	.4670	9.0	.4701
3.6	.4675	9.2	.4701
3.8	.4678	9.4	.4701
4.0	.4680	9.6	.4701
4.2	.4682	9.8	.4702
4.4	.4684	10.0	.4702
4.6	.4686	10.5	.4702
4.8	.4688	11.0	.4703
5.0	.4689	11.5	.4703
5.2	.4691	12.0	.4703
5.4	.4692	12.5	.4703
5.6	.4692	13.0	.4704
5.8	.4693		
6.0	.4694		
6.2	.4695		
6.4	.4695		
6.6	.4696		
6.8	.4696		

Table D2 : Transmission values for uncoated germanium
found from n values given by Palik (assuming
k = 0 in calculation).

APPENDIX E

wavelength (microns)	$\alpha \text{ cm}^{-1}$	k
7.0	0.017	9.47e-7
8.0	0.022	1.40e-6
9.0	0.025	1.79e-6
10.0	0.029	2.31e-6
10.6	0.035	2.95e-6
11.0	0.037	3.24e-6
12.0	0.179	1.71e-5
13.0	0.169	1.75e-5

Table E : Absorption values for uncoated germanium
taken from Adams (1983).

APPENDIX F

wavelength (microns)	T	wavelength (microns)	T	wavelength (microns)	T
2.0	.6999	4.8	.7015	7.6	.7064
2.1	.6994	4.9	.7039	7.7	.7064
2.2	.7003	5.0	.7023	7.8	.7060
2.3	.7005	5.1	.7049	7.9	.7052
2.4	.7013	5.2	.7034	8.0	.7072
2.5	.7018	5.3	.7021	8.1	.7043
2.6	.7009	5.4	.7044	8.2	.7073
2.7	.7011	5.5	.7044	8.3	.7065
2.8	.7020	5.6	.7027	8.4	.7070
2.9	.7025	5.7	.7022	8.5	.7039
3.0	.7023	5.8	.7043	8.6	.7076
3.1	.7023	5.9	.7041	8.7	.7068
3.2	.7025	6.0	.7044	8.8	.7079
3.3	.7022	6.1	.7036	8.9	.7075
3.4	.7013	6.2	.7047	9.0	.7079
3.5	.7016	6.3	.7045	9.1	.7051
3.6	.7030	6.4	.7031	9.2	.7079
3.7	.7031	6.5	.7033	9.3	.7091
3.8	.7026	6.6	.7041	9.4	.7070
3.9	.7019	6.7	.7048	9.5	.7084
4.0	.7029	6.8	.7048	9.6	.7082
4.1	.7033	6.9	.7029	9.7	.7089
4.2	.7019	7.0	.7056	9.8	.7084
4.3	.7032	7.1	.7059	9.9	.7088
4.4	.7020	7.2	.7021	10.0	.7084
4.5	.7035	7.3	.7060	10.1	.7094
4.6	.7010	7.4	.7043	10.2	.7089
4.7	.7011	7.5	.7052	10.3	.7060

Table F1 : Experimentally determined transmission values for
uncoated zinc selenide.

Relative uncertainty in transmission is 0.5%.

wavelength (microns)	T
10.4	.7064
10.5	.7082
10.6	.7061
10.7	.7098
10.8	.7095
10.9	.7092
11.0	.7115
11.1	.7104
11.2	.7106
11.3	.7073
11.4	.7106
11.5	.7101
11.6	.7113
11.7	.7096
11.8	.7102
11.9	.7102
12.0	.7122
12.1	.7124
12.2	.7116
12.3	.7114
12.4	.7136
12.5	.7124
12.6	.7107
12.7	.7134
12.8	.7110
12.9	.7114
13.0	.7104

Table F1 : Experimentally determined transmission values for
uncoated zinc selenide.

Relative uncertainty in transmission is 0.5%.

wavelength (microns)	n	wavelength (microns)	n	wavelength (microns)	n
2.0	2.434	4.8	2.448	7.6	2.422
2.1	2.434	4.9	2.444	7.7	2.424
2.2	2.431	5.0	2.448	7.8	2.425
2.3	2.429	5.1	2.442	7.9	2.427
2.4	2.447	5.2	2.435	8.0	2.407
2.5	2.454	5.3	2.445	8.1	2.410
2.6	2.448	5.4	2.439	8.2	2.406
2.7	2.448	5.5	2.435	8.3	2.408
2.8	2.451	5.6	2.444	8.4	2.410
2.9	2.433	5.7	2.438	8.5	2.413
3.0	2.433	5.8	2.436	8.6	2.410
3.1	2.433	5.9	2.434	8.7	2.415
3.2	2.431	6.0	2.436	8.8	2.410
3.3	2.428	6.1	2.437	8.9	2.411
3.4	2.426	6.2	2.430	9.0	2.412
3.5	2.424	6.3	2.432	9.1	2.416
3.6	2.425	6.4	2.432	9.2	2.413
3.7	2.422	6.5	2.437	9.3	2.412
3.8	2.416	6.6	2.433	9.4	2.416
3.9	2.411	6.7	2.417	9.5	2.416
4.0	2.427	6.8	2.437	9.6	2.417
4.1	2.428	6.9	2.424	9.7	2.415
4.2	2.438	7.0	2.419	9.8	2.415
4.3	2.448	7.1	2.418	9.9	2.417
4.4	2.447	7.2	2.424	10.0	2.415
4.5	2.446	7.3	2.417	10.1	2.417
4.6	2.445	7.4	2.419	10.2	2.412
4.7	2.443	7.5	2.417	10.3	2.413

Table F2 : Experimentally determined n values for zinc selenide.

Relative uncertainty in n values is 0.5% .

wavelength (microns)	n
10.4	2.413
10.5	2.413
10.6	2.415
10.7	2.410
10.8	2.410
10.9	2.409
11.0	2.407
11.1	2.407
11.2	2.405
11.3	2.411
11.4	2.406
11.5	2.407
11.6	2.398
11.7	2.399
11.8	2.398
11.9	2.394
12.0	2.396
12.1	2.393
12.2	2.394
12.3	2.387
12.4	2.381
12.5	2.386
12.6	2.397
12.7	2.388
12.8	2.386
12.9	2.384
13.0	2.387

Table F2 : Experimentally determined n values for zinc selenide.

Relative uncertainty in n values is 0.5% .

APPENDIX G

wavelength (microns)	n
2.0	2.4462
2.5	2.4409
3.0	2.4376
3.5	2.4352
4.0	2.4332
4.5	2.4314
5.0	2.4296
5.5	2.4278
6.0	2.4259
6.5	2.4239
7.0	2.4219
7.5	2.4197
8.0	2.4173
8.5	2.4148
9.0	2.4122
9.5	2.4094
10.0	2.4065
10.5	2.4033
11.0	2.4000
11.5	2.3965
12.0	2.3928
12.5	2.3890
13.0	2.3894

Table G1 : N values for uncoated zinc selenide
taken from the review by Li (1984).

wavelength (microns)	T
2.0	.7005
2.5	.7016
3.0	.7023
3.5	.7027
4.0	.7031
4.5	.7036
5.0	.7040
5.5	.7043
6.0	.7047
6.5	.7050
7.0	.7055
7.5	.7059
8.0	.7065
8.5	.7069
9.0	.7075
9.5	.7081
10.0	.7087
10.5	.7094
11.0	.7100
11.5	.7107
12.0	.7116
12.5	.7123
13.0	.7131

Table G2 : Transmission values for uncoated zinc
selenide found using n values from Li (1984).

APPENDIX H

wavelength (microns)	n	wavelength (microns)	n	wavelength (microns)	n
2.0	2.446	4.8	2.430	7.6	2.419
2.1	2.445	4.9	2.430	7.7	2.419
2.2	2.444	5.0	2.430	7.8	2.418
2.3	2.443	5.1	2.429	7.9	2.418
2.4	2.442	5.2	2.429	8.0	2.417
2.5	2.441	5.3	2.428	8.1	2.417
2.6	2.440	5.4	2.428	8.2	2.416
2.7	2.439	5.5	2.428	8.3	2.416
2.8	2.439	5.6	2.427	8.4	2.415
2.9	2.438	5.7	2.427	8.5	2.415
3.0	2.438	5.8	2.427	8.6	2.414
3.1	2.437	5.9	2.426	8.7	2.414
3.2	2.436	6.0	2.426	8.8	2.413
3.3	2.436	6.1	2.425	8.9	2.413
3.4	2.435	6.2	2.425	9.0	2.412
3.5	2.435	6.3	2.425	9.1	2.412
3.6	2.435	6.4	2.424	9.2	2.411
3.7	2.434	6.5	2.424	9.3	2.411
3.8	2.434	6.6	2.424	9.4	2.410
3.9	2.434	6.7	2.423	9.5	2.410
4.0	2.433	6.8	2.423	9.6	2.409
4.1	2.433	6.9	2.422	9.7	2.408
4.2	2.433	7.0	2.422	9.8	2.408
4.3	2.432	7.1	2.421	9.9	2.407
4.4	2.432	7.2	2.421	10.0	2.407
4.5	2.431	7.3	2.421	10.1	2.406
4.6	2.431	7.4	2.420	10.2	2.405
4.7	2.431	7.5	2.420	10.3	2.405

Table H : N values for uncoated zinc selenide generated using
a Schott polynomial.

wavelength (microns)	n
10.4	2.404
10.5	2.403
10.6	2.403
10.7	2.402
10.8	2.401
10.9	2.401
11.0	2.400
11.1	2.399
11.2	2.399
11.3	2.398
11.4	2.397
11.5	2.397
11.6	2.396
11.7	2.395
11.8	2.394
11.9	2.394
12.0	2.393
12.1	2.392
12.2	2.391
12.3	2.391
12.4	2.390
12.5	2.389
12.6	2.388
12.7	2.388
12.8	2.387
12.9	2.386
13.0	2.385

Table H : N values for uncoated zinc selenide generated using
a Schott polynomial.

APPENDIX I

wavelength (microns)	T	wavelength (microns)	T	wavelength (microns)	T
2.0	.5972	4.8	.6117	7.6	.5717
2.1	.5453	4.9	.6109	7.7	.5696
2.2	.4792	5.0	.6029	7.8	.5680
2.3	.4402	5.1	.5981	7.9	.5699
2.4	.4330	5.2	.5980	8.0	.5734
2.5	.4466	5.3	.6014	8.1	.5755
2.6	.4757	5.4	.5986	8.2	.5773
2.7	.5093	5.5	.6006	8.3	.5787
2.8	.5351	5.6	.6005	8.4	.5808
2.9	.5573	5.7	.5949	8.5	.5818
3.0	.5677	5.8	.5898	8.6	.5855
3.1	.5717	5.9	.5892	8.7	.5873
3.2	.5710	6.0	.5796	8.8	.5873
3.3	.5642	6.1	.5849	8.9	.5882
3.4	.5438	6.2	.5742	9.0	.5889
3.5	.5486	6.3	.5723	9.1	.5902
3.6	.5713	6.4	.5655	9.2	.5915
3.7	.5792	6.5	.5766	9.3	.5912
3.8	.5831	6.6	.5739	9.4	.5925
3.9	.5835	6.7	.5717	9.5	.5932
4.0	.5957	6.8	.5667	9.6	.5927
4.1	.6008	6.9	.5649	9.7	.5930
4.2	.6050	7.0	.5603	9.8	.5930
4.3	.6101	7.1	.5688	9.9	.5911
4.4	.6125	7.2	.5710	10.0	.5921
4.5	.6159	7.3	.5687	10.1	.5900
4.6	.6169	7.4	.5685	10.2	.5904
4.7	.6136	7.5	.5748	10.3	.5891

Table I1 : Transmission values for the first ARG6 coated germanium window.

Relative uncertainty in transmission is 0.5%.

wavelength (microns)	T
10.4	.5871
10.5	.5876
10.6	.5887
10.7	.5883
10.8	.5840
10.9	.5835
11.0	.5800
11.1	.5812
11.2	.5747
11.3	.5704
11.4	.5673
11.5	.5634
11.6	.5579
11.7	.5502
11.8	.5436
11.9	.5397
12.0	.5322
12.1	.5408
12.2	.5439
12.3	.5454
12.4	.5432
12.5	.5447
12.6	.5412
12.7	.5405
12.8	.5387
12.9	.5347
13.0	.5272

Table I1 : Transmission values for the first ARG6 coated germanium window.

Relative uncertainty in transmission is 0.5%.

wavelength (microns)	T	wavelength (microns)	T	wavelength (microns)	T
2.0	.5183	4.8	.5998	7.6	.5791
2.1	.4717	4.9	.5962	7.7	.5799
2.2	.4594	5.0	.5905	7.8	.5773
2.3	.4703	5.1	.5850	7.9	.5832
2.4	.4977	5.2	.5873	8.0	.5842
2.5	.5223	5.3	.5896	8.1	.5861
2.6	.5430	5.4	.5880	8.2	.5870
2.7	.5538	5.5	.5920	8.3	.5877
2.8	.5565	5.6	.5894	8.4	.5896
2.9	.5568	5.7	.5893	8.5	.5909
3.0	.5540	5.8	.5870	8.6	.5947
3.1	.5541	5.9	.5850	8.7	.5968
3.2	.5553	6.0	.5834	8.8	.5969
3.3	.5534	6.1	.5794	8.9	.5980
3.4	.5417	6.2	.5762	9.0	.5977
3.5	.5521	6.3	.5738	9.1	.5990
3.6	.5780	6.4	.5749	9.2	.6014
3.7	.5873	6.5	.5750	9.3	.6012
3.8	.5937	6.6	.5828	9.4	.5993
3.9	.5959	6.7	.5863	9.5	.5988
4.0	.6053	6.8	.5755	9.6	.5990
4.1	.6078	6.9	.5715	9.7	.6004
4.2	.6113	7.0	.5713	9.8	.5974
4.3	.6062	7.1	.5723	9.9	.5970
4.4	.6115	7.2	.5744	10.0	.5965
4.5	.6083	7.3	.5784	10.1	.5956
4.6	.6067	7.4	.5814	10.2	.5949
4.7	.6034	7.5	.5807	10.3	.5915

Table I2 : Transmission values for the second ARG6 coated
germanium window.

Relative error in transmission is 0.5%.

wavelength (microns)	T
10.4	.5899
10.5	.5905
10.6	.5876
10.7	.5887
10.8	.5879
10.9	.5828
11.0	.5826
11.1	.5786
11.2	.5748
11.3	.5691
11.4	.5674
11.5	.5620
11.6	.5604
11.7	.5474
11.8	.5380
11.9	.5334
12.0	.5393
12.1	.5426
12.2	.5397
12.3	.5418
12.4	.5414
12.5	.5418
12.6	.5375
12.7	.5347
12.8	.5346
12.9	.5289
13.0	.5291

Table I2 : Transmission values for the second ARG6 coated
germanium window.

Relative error in transmission is 0.5%.

APPENDIX J

wavelength (microns)	T	wavelength (microns)	T	wavelength (microns)	T
2.0	.7695	4.8	.7063	7.6	.8107
2.1	.7315	4.9	.7069	7.7	.8116
2.2	.7126	5.0	.7115	7.8	.8098
2.3	.7043	5.1	.7141	7.9	.8106
2.4	.7106	5.2	.7175	8.0	.8128
2.5	.7233	5.3	.7229	8.1	.8129
2.6	.7444	5.4	.7268	8.2	.8138
2.7	.7671	5.5	.7318	8.3	.8155
2.8	.7500	5.6	.7349	8.4	.8159
2.9	.7555	5.7	.7410	8.5	.8155
3.0	.7628	5.8	.7433	8.6	.8145
3.1	.7655	5.9	.7496	8.7	.8132
3.2	.7674	6.0	.7509	8.8	.8142
3.3	.7638	6.1	.7516	8.9	.8117
3.4	.7583	6.2	.7569	9.0	.8103
3.5	.7516	6.3	.7587	9.1	.8110
3.6	.7451	6.4	.7666	9.2	.8081
3.7	.7362	6.5	.7693	9.3	.8072
3.8	.7317	6.6	.7689	9.4	.8057
3.9	.7207	6.7	.7731	9.5	.8020
4.0	.7147	6.8	.7771	9.6	.8005
4.1	.7113	6.9	.7826	9.7	.7994
4.2	.7109	7.0	.7827	9.8	.7975
4.3	.7059	7.1	.7864	9.9	.7938
4.4	.7032	7.2	.7838	10.0	.7921
4.5	.7025	7.3	.7882	10.1	.7902
4.6	.7018	7.4	.7985	10.2	.7876
4.7	.7020	7.5	.8022	10.3	.7844

Table J1 : Transmission values for the first ytterbium oxide
coated zinc selenide window.
Relative error in transmission is 0.5%.

wavelength (microns)	T
10.4	.7833
10.5	.7796
10.6	.7765
10.7	.7765
10.8	.7746
10.9	.7711
11.0	.7681
11.1	.7705
11.2	.7637
11.3	.7624
11.4	.7596
11.5	.7571
11.6	.7531
11.7	.7498
11.8	.7505
11.9	.7477
12.0	.7455
12.1	.7421
12.2	.7409
12.3	.7383
12.4	.7353
12.5	.7344
12.6	.7312
12.7	.7260
12.8	.7239
12.9	.7233
13.0	.7168

Table J1 : Transmission values for the first ytterbium oxide
coated zinc selenide window.

Relative error in transmission is 0.5%.

wavelength (microns)	T	wavelength (microns)	T	wavelength (microns)	T
2.0	.7709	4.8	.7059	7.6	.8032
2.1	.7321	4.9	.7055	7.7	.8060
2.2	.7148	5.0	.7097	7.8	.8093
2.3	.7041	5.1	.7119	7.9	.8106
2.4	.7120	5.2	.7163	8.0	.8098
2.5	.7244	5.3	.7209	8.1	.8130
2.6	.7457	5.4	.7262	8.2	.8141
2.7	.7649	5.5	.7299	8.3	.8122
2.8	.7511	5.6	.7372	8.4	.8137
2.9	.7543	5.7	.7364	8.5	.8132
3.0	.7623	5.8	.7427	8.6	.8118
3.1	.7628	5.9	.7469	8.7	.8157
3.2	.7682	6.0	.7484	8.8	.8096
3.3	.7629	6.1	.7513	8.9	.8087
3.4	.7574	6.2	.7580	9.0	.8097
3.5	.7484	6.3	.7583	9.1	.8088
3.6	.7452	6.4	.7581	9.2	.8063
3.7	.7338	6.5	.7676	9.3	.8024
3.8	.7302	6.6	.7629	9.4	.8032
3.9	.7161	6.7	.7666	9.5	.8017
4.0	.7154	6.8	.7750	9.6	.7999
4.1	.7073	6.9	.7828	9.7	.7962
4.2	.7043	7.0	.7789	9.8	.7940
4.3	.7071	7.1	.7760	9.9	.7919
4.4	.7026	7.2	.7778	10.0	.7890
4.5	.7026	7.3	.7842	10.1	.7860
4.6	.7030	7.4	.7921	10.2	.7857
4.7	.7036	7.5	.8008	10.3	.7804

Table J2 : Transmission values for the second ytterbium oxide
coated zinc selenide window.
Relative error in transmission is 0.5%.

wavelength (microns)	T
10.4	.7791
10.5	.7775
10.6	.7739
10.7	.7745
10.8	.7718
10.9	.7702
11.0	.7675
11.1	.7645
11.2	.7621
11.3	.7591
11.4	.7567
11.5	.7549
11.6	.7547
11.7	.7518
11.8	.7408
11.9	.7465
12.0	.7441
12.1	.7401
12.2	.7397
12.3	.7396
12.4	.7300
12.5	.7342
12.6	.7304
12.7	.7212
12.8	.7165
12.9	.7257
13.0	.7208

Table J2 : Transmission values for the second ytterbium oxide
coated zinc selenide window.

Relative error in transmission is 0.5%.

APPENDIX K

wavelength (microns)	n ±1%	k	%age error in k	wavelength (microns)	n ±1%	k	%age error in k
2.0	1.308	1.1e-3	2.4	4.8	1.333	.0146	10
2.1	1.302	5.0e-4	10	4.9	1.331	.0129	10
2.2	1.296	4.0e-4	10	5.0	1.330	.0129	10
2.3	1.290	4.0e-4	10	5.1	1.325	.0111	10
2.4	1.279	1.0e-3	2.4	5.2	1.319	.0101	10
2.5	1.267	1.9e-3	2.4	5.3	1.314	.0102	10
2.6	1.240	2.3e-3	2.4	5.4	1.310	.0109	10
2.7	1.188	.0101	2.4	5.5	1.299	.0113	10
2.8*	1.118	.115		5.6	1.288	.0145	10
2.9*	1.195	.272		5.7	1.280	.0207	10
3.0*	1.363	.298		5.8	1.261	.0320	2.4
3.1*	1.465	.223		5.9	1.246	.0653	10
3.2*	1.497	.115		6.0*	1.262	.106	
3.3*	1.470	.0405		6.1*	1.322	.129	
3.4	1.438	.0180	10	6.2*	1.367	.0870	
3.5	1.413	9.0e-3	5	6.3*	1.360	.0529	
3.6	1.394	5.2e-3	5	6.4	1.353	.0377	30
3.7	1.381	3.5e-3	5	6.5	1.335	.0263	30
3.8	1.370	3.2e-3	5	6.6	1.333	.0274	10
3.9	1.361	3.6e-3	5	6.7	1.318	.0262	10
4.0	1.352	4.6e-3	2.4	6.8	1.312	.0263	10
4.1	1.351	5.4e-3	2.4	6.9*	1.307	.0247	
4.2	1.347	6.6e-3	4.5	7.0*	1.304	.0249	
4.3	1.335	8.4e-3	4.5	7.1	1.301	.0325	10
4.4	1.336	.0100	4.5	7.2	1.299	.0333	10
4.5	1.335	.0129	5	7.3	1.296	.0335	10
4.6	1.334	.0147	2.4	7.4	1.293	.0291	10
4.7	1.334	.0152	10	7.5	1.298	.0324	10

Table K: Optical Constants of Distilled Water
 * denotes wavelengths where K-K has been used,
 the error in k values found by K-K is ± 0.01 .

wavelength (microns)	n ±1%	k	%age error in k	wavelength (microns)	n ±1%	k	%age error in k
7.6	1.293	.0333	10	10.4	1.185	.0616	10
7.7	1.289	.0333	5	10.5	1.177	.0662	10
7.8	1.289	.0333	5	10.6	1.171	.0709	10
7.9	1.288	.0335	5	10.7	1.167	.0733	10
8.0	1.288	.0344	5	10.8	1.157	.0815	10
8.1	1.286	.0348	5	10.9	1.151	.0877	10
8.2	1.283	.0353	5	11.0	1.144	.0957	10
8.3	1.280	.0359	5	11.1	1.138	.105	10
8.4	1.278	.0363	5	11.2	1.129	.117	10
8.5	1.276	.0351	5	11.3	1.126	.126	10
8.6*	1.272	.0377		11.4	1.127	.129	10
8.7*	1.269	.0388		11.5	1.124	.143	10
8.8*	1.267	.0388		11.6	1.120	.157	10
8.9	1.263	.0384	10	11.7	1.116	.168	10
9.0	1.259	.0393	10	11.8*	1.116	.180	
9.1	1.257	.0384	10	11.9*	1.116	.193	
9.2	1.252	.0414	10	12.0*	1.118	.205	
9.3	1.248	.0406	10	12.1*	1.118	.216	
9.4	1.245	.0401	10	12.2*	1.124	.229	
9.5	1.239	.0420	10	12.3*	1.125	.238	
9.6	1.233	.0459	10	12.4*	1.130	.250	
9.7	1.229	.0459	10	12.5*	1.136	.261	
9.8	1.225	.0457	27	12.6*	1.142	.271	
9.9	1.217	.0460	27	12.7*	1.146	.280	
10.0	1.212	.0505	10	12.8*	1.155	.290	
10.1	1.205	.0512	10	12.9*	1.161	.300	
10.2	1.198	.0535	10	13.0*	1.166	.306	
10.3	1.192	.0554	10				

Table K: Optical Constants of Distilled Water

* denotes wavelengths where K-K has been used,
the error in k values found by K-K is ± 0.01 .

APPENDIX L

wavelength (microns)	n	wavelength (microns)	n	wavelength (microns)	n
.34	1.476	.62	1.456	.90	1.452
.35	1.473	.63	1.455	.91	1.451
.36	1.470	.64	1.455	.92	1.452
.37	1.469	.65	1.455	.93	1.452
.38	1.470	.66	1.455	.94	1.451
.39	1.469	.67	1.455	.95	1.451
.40	1.468	.68	1.454	.96	1.451
.41	1.466	.69	1.454	.97	1.451
.42	1.465	.70	1.454	.98	1.451
.43	1.465	.71	1.454	.99	1.451
.44	1.464	.72	1.454		
.45	1.463	.73	1.454		
.46	1.463	.74	1.454		
.47	1.463	.75	1.453		
.48	1.462	.76	1.454		
.49	1.461	.77	1.453		
.50	1.460	.78	1.453		
.51	1.459	.79	1.453		
.52	1.459	.80	1.453		
.53	1.458	.81	1.453		
.54	1.458	.82	1.453		
.55	1.457	.83	1.453		
.56	1.457	.84	1.453		
.57	1.457	.85	1.453		
.58	1.457	.86	1.452		
.59	1.456	.87	1.452		
.60	1.456	.88	1.452		
.61	1.456	.89	1.452		

Table L1 : Refractive Index Values for Peg 300.

Relative error in n is 0.5%.

wavelength (microns)	n	k	wavelength (microns)	n	k
1.0	1.458[0.5]	8.81e-7[50]	3.9	1.463[0.5]	1.90e-3[10]
1.1	1.459	5.94e-7	4.0	1.456	1.28e-3[2.4]
1.2	1.457	1.00e-5[30]	4.1	1.462	1.46e-3
1.3	1.456	1.94e-6	4.2	1.458	1.13e-3
1.4	1.458	1.39e-5	4.3	1.449	1.11e-3
1.5	1.459	2.97e-5	4.4	1.452	1.38e-3
1.6	1.459	1.88e-5	4.5	1.454	1.35e-3
1.7	1.458	3.74e-5	4.6	1.452	1.32e-3
1.8*	1.459[1]	3.76e-5	4.7	1.452	1.49e-3
1.9	1.455[0.5]	3.78e-5	4.8	1.450	1.52e-3
2.0	1.456	4.42e-5	4.9	1.448	1.30e-3
2.1	1.455	1.39e-4	5.0	1.448	2.10e-3
2.2	1.456	9.29e-5	5.1	1.447	2.90e-3
2.3	1.453	6.52e-4[2.4]	5.2	1.445	2.01e-3[4.5]
2.4	1.452	5.00e-4	5.3	1.446	1.28e-3[2.4]
2.5	1.453	1.15e-3	5.4	1.446	8.64e-4
2.6	1.445	4.00e-4	5.5	1.438	2.10e-4[4.5]
2.7	1.454	4.12e-4	5.6	1.436	7.64e-4[2.4]
2.8	1.477	3.59e-3	5.7	1.438	1.37e-3
2.9*	1.431[1]	2.51e-2	5.8	1.431	1.80e-3[4.5]
3.0	1.461[0.5]	2.24e-2[30]	5.9	1.426	1.53e-3
3.1	1.462	1.03e-2	6.0	1.423	2.79e-3
3.2	1.455	2.21e-3[2.4]	6.1	1.429	6.28e-3
3.3	1.443	1.88e-3	6.2	1.432	2.99e-3[10]
3.4*	1.415[1]	4.18e-2	6.3	1.425	2.78e-3
3.5*	1.505	5.63e-2	6.4	1.425	2.75e-3
3.6	1.490[0.5]	1.45e-2	6.5	1.407	2.38e-3
3.7	1.477	7.05e-3	6.6	1.406	3.65e-3
3.8	1.457	2.44e-3[4.5]	6.7	1.380	1.18e-2

Table L1 : Optical Constants for Peg 300, number in brackets denotes relative percentage error. An asterisk denotes a wavelength where the optical constants have been interpolated using a Kramers-Kronig analysis. Error in interpolated (K-K) k value is ± 0.01 .

wavelength (microns)	n	k	wavelength (microns)	n	k
6.8*	1.381[1]	1.58e-2	9.7*	1.601[1]	8.68e-2
6.9*	1.400	2.19e-2	9.8*	1.593	5.41e-2
7.0	1.395[0.5]	1.71e-2	9.9	1.561[0.5]	2.29e-2
7.1*	1.390[1]	1.82e-2	10.0	1.548	2.47e-2
7.2*	1.385	2.19e-2	10.1	1.536	2.36e-2
7.3*	1.372	3.85e-2	10.2	1.518	1.44e-2
7.4*	1.401	4.62e-2	10.3	1.498	1.66e-2
7.5*	1.399	3.08e-2	10.4	1.485	1.40e-2
7.6*	1.383	3.51e-2	10.5*	1.490[1]	6.81e-2
7.7*	1.387	4.73e-2	10.6*	1.515	7.16e-2
7.8*	1.394	4.50e-2	10.7*	1.526	5.71e-2
7.9*	1.381	4.79e-2	10.8*	1.525	4.31e-2
8.0*	1.396	5.41e-2	10.9*	1.522	3.06e-2
8.1*	1.400	4.02e-2	11.0	1.508[0.5]	2.46e-2
8.2	1.386[0.5]	1.42e-2	11.1	1.493	1.52e-2
8.3	1.362	1.60e-2	11.2*	1.484[1]	3.79e-2
8.4	1.337	6.64e-3	11.3*	1.503	4.13e-2
8.5	1.297	1.05e-2	11.4*	1.494	3.12e-2
8.6*	1.223[1]	8.79e-2	11.5	1.491[0.5]	1.66e-2
8.7*	1.224	1.93e-1	11.6	1.487	2.82e-2
8.8*	1.279	2.77e-1	11.7	1.481	4.51e-2
8.9*	1.363	3.23e-1	11.8*	1.477[1]	4.05e-2
9.0*	1.438	3.26e-1	11.9*	1.484	4.71e-2
9.1*	1.517	3.07e-1	12.0	1.494[0.5]	1.90e-2
9.2*	1.550	2.61e-1	12.1	1.488	1.60e-2
9.3*	1.577	2.38e-1	12.2	1.492	1.69e-2
9.4*	1.627	1.97e-1	12.3	1.486	1.92e-2
9.5*	1.625	1.30e-1	12.4	1.486	1.73e-2
9.6*	1.599	1.01e-1	12.5	1.482	9.07e-3

Table L1 : Optical Constants for Peg 300, number in brackets denotes relative percentage error. An asterisk denotes a wavelength where the optical constants have been interpolated using a Kramers-Kronig analysis. Error in interpolated (K-K) k value is ± 0.01 .

wavelength (microns)	n	k
12.6	1.481[0.5]	1.19e-2[30]
12.7	1.473	7.61e-3
12.8	1.472	7.83e-3
12.9	1.472	7.35e-3
13.0	1.462	2.49e-3
13.1	1.464	9.55e-3
13.2	1.462	9.73e-3
13.3	1.459	4.72e-3
13.4	1.456	9.31e-3
13.5	1.462	1.11e-2
13.6	1.451	7.84e-3
13.7	1.447	9.97e-3
13.8	1.440	1.15e-2
13.9	1.486	1.42e-2
14.0	1.452	1.22e-2
14.2	1.449	1.58e-2
14.4	1.445	8.27e-3
14.6	1.451	2.23e-2
14.8	1.446	2.65e-2
15.0	1.441	1.93e-2
15.2	1.446	1.59e-2
15.4*	1.444[1]	9.29e-2
15.6*	1.448	9.27e-2
15.8*	1.442	9.76e-2

Table L1: Optical Constants for Peg 300, number in brackets denotes relative percentage error. An asterisk denotes a wavelength where the optical constants have been interpolated using a Kramers-Kronig analysis. Error in interpolated (K-K) k value is ± 0.01 .

wavelength (microns)	n	wavelength (microns)	n	wavelength (microns)	n
.35	1.488	.60	1.463	.85	1.460
.36	1.482	.61	1.462	.86	1.459
.37	1.481	.62	1.463	.87	1.459
.38	1.477	.63	1.462	.88	1.459
.39	1.477	.64	1.462	.89	1.459
.40	1.474	.65	1.463	.90	1.459
.41	1.474	.66	1.463	.91	1.459
.42	1.470	.67	1.462	.92	1.459
.43	1.470	.68	1.462	.93	1.459
.44	1.472	.69	1.461	.94	1.459
.45	1.471	.70	1.461	.95	1.459
.46	1.470	.71	1.461	.96	1.458
.47	1.469	.72	1.461	.97	1.459
.48	1.468	.73	1.461	.98	1.459
.49	1.468	.74	1.461	.99	1.458
.50	1.466	.75	1.460	1.0	1.458
.51	1.466	.76	1.461	1.1	1.451
.52	1.466	.77	1.461	1.2	1.450
.53	1.465	.78	1.460	1.3	1.450
.54	1.464	.79	1.460	1.4	1.450
.55	1.464	.80	1.460	1.5	1.449
.56	1.463	.81	1.459	1.6	1.448
.57	1.464	.82	1.459	1.7	1.448
.58	1.463	.83	1.460	1.8	1.448
.59	1.463	.84	1.460	1.9	1.450

Table L2 : Refractive Index Values for Polyethylene Glycol 600.

The relative error in n values is 0.5%.

wavelength (microns)	n	k	wavelength (microns)	n	k
2.0	1.446[0.5]	4.60e-5[30]	4.6	1.446[0.5]	1.50e-3
2.1	1.446	8.11e-5	4.7	1.445	1.77e-3
2.2	1.448	6.36e-5	4.8	1.444	1.53e-3
2.3	1.446	4.41e-4[2.4]	4.9	1.441	1.32e-4
2.4	1.444	5.15e-4	5.0	1.441	2.20e-3
2.5	1.445	1.14e-3	5.1	1.441	3.45e-3
2.6	1.436	4.55e-4	5.2	1.439	2.52e-3
2.7	1.438	4.15e-4	5.3	1.440	1.32e-3
2.8	1.422	2.35e-3	5.4	1.440	7.22e-4
2.9*	1.441[1]	2.90e-2	5.5	1.433	6.58e-4
3.0	1.456[0.5]	6.13e-3[10]	5.6	1.429	6.87e-4
3.1	1.457	3.18e-3[4.5]	5.7	1.430	1.13e-3
3.2	1.449	1.40e-3	5.8	1.424	2.86e-4[4.5]
3.3	1.438	1.79e-3	5.9	1.416	1.28e-3
3.4*	1.409[1]	3.88e-2	6.0	1.412	1.17e-3[10]
3.5*	1.493[1]	4.60e-2	6.1	1.424	2.03e-3
3.6	1.481[0.5]	9.46e-3[30]	6.2	1.433	1.11e-3
3.7	1.469	1.86e-3	6.3	1.424	5.50e-4
3.8	1.460	1.86e-3[2.4]	6.4	1.419	7.02e-4
3.9	1.456	1.45e-3	6.5	1.409	1.08e-3[30]
4.0	1.450	1.36e-3	6.6	1.406	1.34e-3
4.1	1.453	9.63e-4	6.7	1.376	4.48e-3
4.2	1.451	8.53e-4	6.8*	1.382[1]	1.26e-2
4.3	1.442	8.91e-4	6.9*	1.400[1]	1.19e-2
4.4	1.444	1.31e-3	7.0	1.394	2.38e-3
4.5	1.446	1.42e-3	7.1	1.386	1.32e-2

Table L2 : Refractive and Absorptive Indexes For P.E.G. 600.

The figures in brackets refer to relative percentage error. Wavelengths marked with an asterisk indicate that the optical constants have been found using K-K, for these wavelengths the error in the k value is ± 0.01 .

wavelength (microns)	n	k	wavelength (microns)	n	k
7.2	1.375[0.5]	6.73e-3[30]	9.8*	1.576[1]	3.42e-2
7.3*	1.362[1]	2.97e-2	9.9	1.545[0.5]	1.50e-2
7.4*	1.392[1]	4.28e-2	10.0	1.535	8.40e-3
7.5	1.392[0.5]	1.26e-2	10.1	1.524	1.85e-2
7.6*	1.374[1]	3.06e-2	10.2	1.507	1.15e-2
7.7*	1.381	4.24e-2	10.3	1.488	1.85e-2
7.8*	1.390	3.81e-2	10.4	1.479	7.83e-3
7.9*	1.372	4.42e-2	10.5*	1.498[1]	6.72e-2
8.0*	1.392	5.43e-2	10.6*	1.524	6.17e-2
8.1	1.497[0.5]	1.69e-2	10.7*	1.528	4.42e-2
8.2	1.376	9.08e-3	10.8*	1.527	3.04e-2
8.3	1.349	6.37e-3	10.9	1.519[0.5]	1.67e-2
8.4	1.322	6.85e-3	11.0	1.511	1.07e-2
8.5	1.279	9.06e-3	11.1	1.503	1.52e-2
8.6*	1.202[1]	9.96e-2	11.2	1.485	1.35e-2
8.7*	1.234	2.14e-1	11.3	1.496	2.17e-2
8.8*	1.292	2.83e-1	11.4	1.485	1.43e-2
8.9*	1.361	3.29e-1	11.5	1.479	1.79e-2
9.0*	1.457	3.56e-1	11.6	1.487	2.47e-2
9.1*	1.568	3.25e-1	11.7*	1.482[1]	3.10e-2
9.2*	1.624	2.40e-1	11.8*	1.435	3.82e-2
9.3*	1.625	1.73e-1	11.9	1.497[0.5]	1.53e-2
9.4*	1.630	1.25e-1	12.0	1.505	8.97e-3
9.5*	1.600	8.52e-2	12.1	1.498	1.21e-2
9.6*	1.582	7.41e-2	12.2	1.498	9.70e-3
9.7*	1.583	6.02e-2	12.3	1.492	7.77e-3

Table L2 : Refractive and Absorptive Indexes For P.E.G. 600.

The figures in brackets refer to relative percentage error. Wavelengths marked with an asterisk indicate that the optical constants have been found using K-K, for these wavelengths the error in the k value is ± 0.01 .

wavelength (microns)	n	k
12.4	1.493[0.5]	6.72e-3[30]
12.5	1.488	6.20e-3
12.6	1.488	8.64e-3
12.7	1.483	4.20e-3[10]
12.8	1.479	3.01e-3
12.9	1.478	7.26e-3
13.0	1.469	7.57e-3
13.1	1.469	6.91e-3
13.2	1.470	8.94e-3
13.3	1.465	5.22e-3
13.4	1.461	8.59e-3
13.5	1.464	7.60e-3
13.6	1.450	9.38e-3
13.7	1.452	8.75e-3
13.8	1.447	7.97e-3
13.9	1.450	6.83e-3
14.0	1.446	7.99e-3
14.2	1.447	1.37e-2[30]
14.4	1.440	6.97e-3
14.6	1.447	5.13e-3
14.8	1.436	9.21e-3
15.0	1.484	4.97e-3
15.2	1.447	1.40e-2
15.4	1.434	6.09e-3
15.6	1.442	8.65e-3
15.8	1.434	1.00e-2

Table L2 : Refractive and Absorptive Indexes For P.E.G. 600.
The figures in brackets refer to relative percentage error.

APPENDIX M

wavelength (microns)	n	wavelength (microns)	n
2.0	1.309 (2)	5.0	1.343 (2)
2.1	1.351	5.1	1.344
2.2	1.372 (3)	5.2	1.335
2.3	1.395 (4)	5.3	1.346
2.4	1.340 (5)	5.4	1.336
2.5	1.305 (4)	5.5	1.311
2.6	1.290	5.6	1.290
2.7	1.290 (3)	5.7	1.263
2.8	1.295	5.8	1.117 (3)
2.9	1.317 (2)	5.9	1.213
3.0	1.342	6.0	1.384 (2)
3.1	1.355	6.1	1.366
3.2	1.355	6.2	1.353 (4)
3.3	1.348	6.3	1.374 (2)
3.4	1.351	6.4	1.368 (4)
3.5	1.340	6.5	1.297
3.6	1.333 (3)	6.6	1.307
3.7	1.318	6.7	1.307 (2)
3.8	1.333 (2)	6.8	1.274
3.9	1.330	6.9	1.306 (4)
4.0	1.325	7.0	1.318
4.1	1.327	7.1	1.336
4.2	1.360	7.2	1.308
4.3	1.352	7.3	1.273
4.4	1.339	7.4	1.412 (3)
4.5	1.357	7.5	1.379
4.6	1.349	7.6	1.345 (4)
4.7	1.365	7.7	1.338
4.8	1.367	7.8	1.326
4.9	1.346	7.9	1.314

Table M1 : Refractive Index Values for Acetone.

The figure in brackets represents the relative percentage uncertainty in the n value.

wavelength (microns)	n	wavelength (microns)	n
8.0	1.310 (4)	11.0	1.342 (3)
8.1	1.264	11.1	1.339
8.2	1.387 (3)	11.2	1.339
8.3	1.390	11.3	1.331
8.4	1.377	11.4	1.353
8.5	1.364	11.5	1.347
8.6	1.378	11.6	1.341
8.7	1.379	11.7	1.343
8.8	1.375	11.8	1.329
8.9	1.369	11.9	1.330
9.0	1.360	12.0	1.324
9.1	1.341	12.1	1.320
9.2	1.370	12.2	1.337
9.3	1.361	12.3	1.330
9.4	1.365	12.4	1.317
9.5	1.351	12.5	1.313
9.6	1.363	12.6	1.314
9.7	1.346	12.7	1.314
9.8	1.351	12.8	1.307
9.9	1.348	12.9	1.323
10.0	1.347	13.0	1.338
10.1	1.345		
10.2	1.345		
10.3	1.343		
10.4	1.358		
10.5	1.340		
10.6	1.348		
10.7	1.347		
10.8	1.346		
10.9	1.344		

Table M1 : Refractive Index Values for Acetone.

The figure in brackets represents the relative percentage uncertainty in the n value.

wavelength (microns)	k
4.3	.346 (90)
4.4	
4.5	.185 (>100)
4.6	.056 (>100)
4.7	.253 (>100)
4.8	.283 (>100)
5.0	
5.1	.206 (90)
5.2	.115 (>100)
5.3	.329 (95)
5.4	.237 (>100)
5.5	.180 (>100)
5.6	
5.7	
5.8	.492 (5)
6.3	.172 (>100)
6.4	
6.9	.195 (90)
7.0	
7.1	.055 (>100)
7.2	.058 (>100)
7.3	.268 (60)
7.4	
8.1	
8.2	.183 (>100)

Table M2 : Absorptive Index Values for Acetone.

The figure in brackets represents the relative percentage uncertainty in the k value.

APPENDIX N

wavelength (microns)	n	wavelength (microns)	n
2.0	1.323 (2)	5.0	1.342
2.1	1.381	5.1	1.345
2.2	1.404 (3)	5.2	1.338
2.3	1.430 (4)	5.3	1.355
2.4	1.343	5.4	1.345
2.5	1.299	5.5	1.334
2.6	1.272	5.6	1.335
2.7	1.272 (3)	5.7	1.352
2.8	1.264	5.8	1.338
2.9	1.290 (2)	5.9	1.300
3.0	1.313	6.0	1.301 (2)
3.1	1.331	6.1	1.306
3.2	1.338	6.2	1.309 (4)
3.3	1.345	6.3	1.338 (2)
3.4	1.349	6.4	1.331 (4)
3.5	1.334	6.5	1.284
3.6	1.325 (3)	6.6	1.290
3.7	1.314	6.7	1.300 (2)
3.8	1.326 (2)	6.8	1.289
3.9	1.313	6.9	1.308 (4)
4.0	1.326	7.0	1.302
4.1	1.322	7.1	1.308
4.2	1.355	7.2	1.299
4.3	1.351	7.3	1.292
4.4	1.338	7.4	1.287
4.5	1.356	7.5	1.288
4.6	1.346	7.6	1.273
4.7	1.359	7.7	1.272
4.8	1.366	7.8	1.267
4.9	1.344	7.9	1.252

Table N1 : Refractive Index Values for 1,1,2 T.T.F.E.

The figure in brackets represents the relative percentage uncertainty in the n value.

wavelength (microns)	n	wavelength (microns)	n
8.0	1.247 (4)	11.0	1.238 (4)
8.1	1.218	11.1	1.431 (3)
8.2	1.205	11.2	1.510
8.3	1.279	11.3	1.469
8.4	1.263	11.4	1.476
8.5	1.256	11.5	1.472
8.6	1.436 (3)	11.6	1.425
8.7	1.405	11.7	1.386
8.8	1.317 (4)	11.8	1.335
8.9	1.260	11.9	1.304
9.0	1.315	12.0	1.254
9.1	1.481 (3)	12.1	1.216
9.2	1.441	12.2	1.269 (4)
9.3	1.354	12.3	1.331 (3)
9.4	1.318 (4)	12.4	1.599
9.5	1.249	12.5	1.710
9.6	1.395 (3)	12.6	1.623
9.7	1.486	12.7	1.546
9.8	1.494	12.8	1.493
9.9	1.422	12.9	1.486
10.0	1.385	13.0	1.472
10.1	1.357		
10.2	1.334		
10.3	1.316		
10.4	1.316		
10.5	1.274		
10.6	1.249		
10.7	1.211 (4)		
10.8	1.214		
10.9	1.215		

Table N1 : Refractive Index Values for 1,1,2 T.T.F.E.

The figure in brackets represents the relative percentage uncertainty in the n value.

wavelength (microns)	k	wavelength (microns)	k
2.0		7.3	.096 (>100)
2.1	.107 (>100)	7.4	.100 (>100)
2.2	.349 (61)	7.5	
2.3	.489 (39)	7.6	.098 (>100)
2.4	.143 (>100)	7.7	.175 (>100)
2.5		7.8	.213 (80)
4.3	.282 (>100)	7.9	.187 (>100)
4.4		8.0	.291 (100)
4.5	.160 (>100)	8.1	.302 (100)
4.6		8.2	.620 (20)
4.7	.198 (>100)	8.3	.315 (70)
4.8	.252 (>100)	8.4	.498 (15)
4.9		8.5	.745 (5)
5.0		8.6	.178 (70)
5.1	.142 (>100)	8.7	
5.2		8.8	.114 (>100)
5.3	.287 (>100)	8.9	.519 (25)
5.4	.142 (>100)	9.0	.546 (15)
5.5	.083 (>100)	9.1	
5.6	.151 (>100)	9.5	.469 (15)
5.7	.158 (>100)	9.6	.452 (15)
5.8	.037 (>100)	9.7	.135 (>100)
5.9		9.8	.066 (>100)
6.2		9.9	
6.3	.149 (>100)	10.4	.200 (90)
6.4		10.5	
6.9	.168 (>100)	10.6	.171 (>100)
7.0	.120 (>100)	10.7	.243 (80)
7.1	.204 (80)	10.8	.407 (15)
7.2	.149 (>100)	10.9	.619 (10)

Table N2 : Absorptive Index Values for 1,1,2 T.T.F.E.

The figure in brackets represents the relative percentage uncertainty in the k value.

wavelength (microns)	k
11.0	.773 (5)
11.1	.552 (10)
11.2	.333 (15)
11.3	.257 (40)
11.4	.284 (35)
11.5	.218 (50)
11.6	.025 (>100)
11.7	.236 (45)
11.8	
11.9	.127 (>100)
12.0	.174 (90)
12.1	.249 (70)
12.2	.940 (2)
12.3	.917 (2)
12.4	.692 (5)
12.5	.242 (30)
12.6	
12.7	

Table N2 : Absorptive Index Values for 1,1,2 T.T.F.E.

The figure in brackets represents the relative percentage uncertainty in the k value.

wavelength (microns)	n	wavelength (microns)	n
2.0	1.326 (2)	5.0	1.355 (2)
2.1	1.375	5.1	1.351
2.2	1.397 (3)	5.2	1.351
2.3	1.404 (4)	5.3	1.369
2.4	1.328 (5)	5.4	1.363
2.5	1.296 (4)	5.5	1.348
2.6	1.280	5.6	1.350
2.7	1.285 (3)	5.7	1.372
2.8	1.288	5.8	1.359
2.9	1.313	5.9	1.301
3.0	1.346 (2)	6.0	1.311
3.1	1.363	6.1	1.319
3.2	1.373	6.2	1.316 (4)
3.3	1.376	6.3	1.347 (2)
3.4	1.363	6.4	1.352 (4)
3.5	1.354	6.5	1.283
3.6	1.355 (3)	6.6	1.300
3.7	1.337 (2)	6.7	1.314 (2)
3.8	1.352	6.8	1.294
3.9	1.342	6.9	1.323 (4)
4.0	1.332	7.0	1.321
4.1	1.333	7.1	1.323
4.2	1.377	7.2	1.318
4.3	1.356	7.3	1.315
4.4	1.347	7.4	1.312
4.5	1.365	7.5	1.313
4.6	1.357	7.6	1.296
4.7	1.375	7.7	1.297
4.8	1.377	7.8	1.295
4.9	1.355	7.9	1.289

Table N3 : Refractive Index Values for T.F.M.

The figure in brackets represents the relative percentage uncertainty in the n value.

wavelength (microns)	n	wavelength (microns)	n
8.0	1.296 (4)	11.0	1.217 (4)
8.1	1.285	11.1	1.186
8.2	1.292	11.2	1.142
8.3	1.277	11.3	1.096
8.4	1.281	11.4	1.042
8.5	1.274	11.5	0.942 (5)
8.6	1.276	11.6	0.809 (6)
8.7	1.272	11.7	0.670
8.8	1.262	11.8	0.372 (8)
8.9	1.246	11.9	1.000 (5)
9.0	1.222	12.0	1.389 (4)
9.1	1.174	12.1	1.930 (2)
9.2	1.126 (5)	12.2	2.043
9.3	1.159 (4)	12.3	1.851
9.4	1.416 (3)	12.4	1.726
9.5	1.544	12.5	1.644
9.6	1.469	12.6	1.639
9.7	1.406	12.7	1.594
9.8	1.384	12.8	1.531 (3)
9.9	1.361	12.9	1.532
10.0	1.338	13.0	1.530
10.1	1.319		
10.2	1.306		
10.3	1.289		
10.4	1.290		
10.5	1.258		
10.6	1.234 (4)		
10.7	1.235 (3)		
10.8	1.266		
10.9	1.238		

Table N3 : Refractive Index Values for T.F.M.

The figure in brackets represents the relative percentage uncertainty in the n value.

wavelength (microns)	k	wavelength (microns)	k
2.2	.175 (>100)		
2.3	.235 (80)	10.6	.143 (>100)
		10.7	.051 (>100)
4.3	.112 (>100)	10.8	.106 (>100)
		10.9	.170 (>100)
5.3	.137 (>100)	11.0	.228 (80)
		11.1	.207 (90)
8.7	.136 (>100)	11.2	.277 (70)
8.8	.114 (>100)	11.3	.231 (80)
8.9	.188 (95)	11.4	.353 (50)
9.0	.330 (50)	11.5	.518 (10)
9.1	.365 (45)	11.6	.736 (5)
9.2	.564 (15)	11.7	1.138 (1)
9.3	.512 (15)	11.9	1.584 (1)
9.4	.532 (10)	12.0	1.540 (1)
		12.1	1.085 (1)
9.8	.156 (>100)	12.2	.621 (2)
9.9	.149 (>100)	12.3	.298 (10)
		12.4	.101 (>100)
10.4	.202 (90)		

Table N4 : Absorptive Index Values for T.F.M.

The figure in brackets represents the relative percentage uncertainty in the k value.

APPENDIX O

wavelength (microns)	k	% error in k	wavelength (microns)	k	% error in k
2.0	1.47e-5	10	4.8	3.41e-4	2.4
2.1	5.97e-5		4.9	1.72e-4	
2.2	8.03e-5		5.0	4.78e-4	
2.3	5.93e-4	2.4	5.1	2.58e-4	
2.4	4.02e-4		5.2	2.90e-4	
2.5	3.85e-4		5.3	6.22e-4	
2.6	1.13e-4		5.4	1.19e-3	
2.7	1.11e-4		5.5	3.55e-3	
2.8	5.05e-4		5.6	8.71e-3	
2.9	8.78e-4		5.7	0.0299	
3.0	2.98e-4				
3.1	4.61e-4		5.9	0.0273	27
3.2	1.59e-3		6.0	0.0125	
3.3	5.10e-3	5	6.1	4.44e-3	10
3.4	5.20e-3		6.2	4.82e-3	
3.5	2.46e-3	2.4	6.3	5.87e-3	
3.6	1.34e-3		6.4	5.08e-3	
3.7	5.90e-4		6.5	5.05e-3	
3.8	3.04e-4		6.6	0.0118	27
3.9	4.94e-4		6.7	0.0100	
4.0	3.65e-4		6.8	0.0116	
4.1	6.03e-4		6.9	0.0237	
4.2	2.25e-4		7.0	0.0285	
4.3	2.86e-4		7.1	0.0161	
4.4	5.93e-4		7.2	0.0241	
4.5	5.24e-4		7.5	0.0100	
4.6	4.52e-4		7.6	7.17e-3	10
4.7	1.59e-3		7.7	4.34e-3	

Table O1 : Absorptive index values for acetone measured with variable path length cells. Gaps indicate regions where the transmitted signal could not be detected (i.e. k too large).

wavelength (microns)	k	% error in k	wavelength (microns)	k	% error in k
7.8	7.39e-3	10	10.5	2.93e-3	5
7.9	8.21e-3		10.6	3.72e-3	2.4
8.0	0.0134		10.7	4.80e-3	5
8.1	0.0258		10.8	6.36e-3	
			10.9	9.95e-3	
8.3	0.0282		11.0	0.0144	10
8.4	0.0140		11.1	0.0202	
8.5	8.19e-3		11.2	0.0124	5
8.6	5.38e-3	10	11.3	6.61e-3	
8.7	3.91e-3	5	11.4	3.95e-3	
8.8	3.68e-3	2.4	11.5	2.81e-3	2.4
8.9	4.39e-3	5	11.6	2.27e-3	
9.0	6.78e-3	10	11.7	1.91e-3	
9.1	0.0115	5	11.8	1.75e-3	
9.2	0.0187	10	11.9	1.66e-3	
9.3	6.88e-3		12.0	1.49e-3	
9.4	4.59e-3	5	12.1	1.30e-3	
9.5	3.31e-3		12.2	1.28e-3	
9.6	2.42e-3		12.3	1.28e-3	
9.7	2.04e-3		12.4	1.44e-3	
9.8	1.85e-3		12.5	2.01e-3	
9.9	1.81e-3	2.4	12.6	3.51e-3	
10.0	1.90e-3		12.7	7.60e-3	5
10.1	2.21e-3	5	12.8	5.69e-3	
10.2	2.73e-3	2.4	12.9	3.62e-3	
10.3	2.53e-3		13.0	2.24e-3	
10.4	2.56e-3	5			

Table O1 : Absorptive index values for acetone measured with variable path length cells. Gaps indicate regions where the transmitted signal could not be detected (i.e. k too large).

wavelength (microns)	k	% error in k	wavelength (microns)	k	% error in k
2.0	5.43e-8	50	6.8	6.11e-4	
3.0	1.73e-5	30	6.9	6.62e-4	
4.0	3.25e-5	30	7.0	5.83e-4	
4.2	4.10e-4	5	7.1	1.35e-3	
4.4	4.46e-4		7.2	1.70e-3	
4.6	6.50e-4		7.3	2.66e-3	
4.8	1.27e-4		7.4	2.48e-3	
5.0	1.83e-4		7.5	2.16e-3	10
5.1	1.80e-4		7.6	1.10e-3	30
5.2	9.37e-5		7.7	5.05e-4	
5.3	6.14e-5		7.8	2.52e-3	
5.4	4.59e-4		8.0	4.79e-3	2.4
5.5	4.29e-4		8.1	5.92e-3	
5.6	1.84e-4		8.2	1.06e-2	5
5.7	2.84e-4		8.6		
5.8	2.32e-4		8.7	3.77e-2	30
5.9	3.80e-4		8.8	2.83e-2	
6.0	1.87e-4		8.9	3.41e-2	
6.1	5.79e-4		9.0		
6.2	2.32e-4		9.2	4.27e-2	
6.3	1.79e-4		9.3	2.38e-2	
6.4	4.24e-4		9.4	2.86e-2	
6.5	4.10e-4		9.5	4.79e-2	
6.6	3.91e-4		9.6		
6.7	5.45e-4		9.8	3.55e-2	10

Table O2 : Absorptive Index Values for 1,1,2 Trichlorotrifluoroethane.

Values determined from transmission measurements with a variable path length cell. Gaps indicate wavelength regions where k was too large, and could not be measured.

wavelength (microns)	k	% error in k
9.9	1.92e-2	10
10.0	7.94e-3	
10.1	6.38e-3	
10.2	8.27e-3	
10.3	1.16e-2	
10.4	8.66e-3	
10.5	7.59e-3	
10.6	1.15e-2	
10.7	1.87e-2	
10.8		
11.5		
11.6	4.51e-2	30
11.7	3.37e-2	
11.8	3.11e-2	
11.9	3.06e-2	
12.0	3.67e-2	
12.1	4.12e-2	
12.2		
12.6		
12.8	2.54e-2	
12.9	1.34e-2	
13.0	6.34e-2	10

Table O2 : Absorptive Index Values for 1,1,2 Trichlorotrifluoroethane.

Values determined from transmission measurements with a variable path length cell. Gaps indicate wavelength regions where k was too large, and could not be measured.

APPENDIX P

A Study of the Fresnel Equations at *Near-Normal* Incidence Angles

This by no means constitutes an intensive study of the collection and concentration of the incoming radiation at each surface of the reflectometer. It is instead an attempt to verify that the special form of the Fresnel equation (i.e. for zero angle of incidence) is valid for both the free liquid surface and closed cell case.

A. The Free Liquid Surface Case

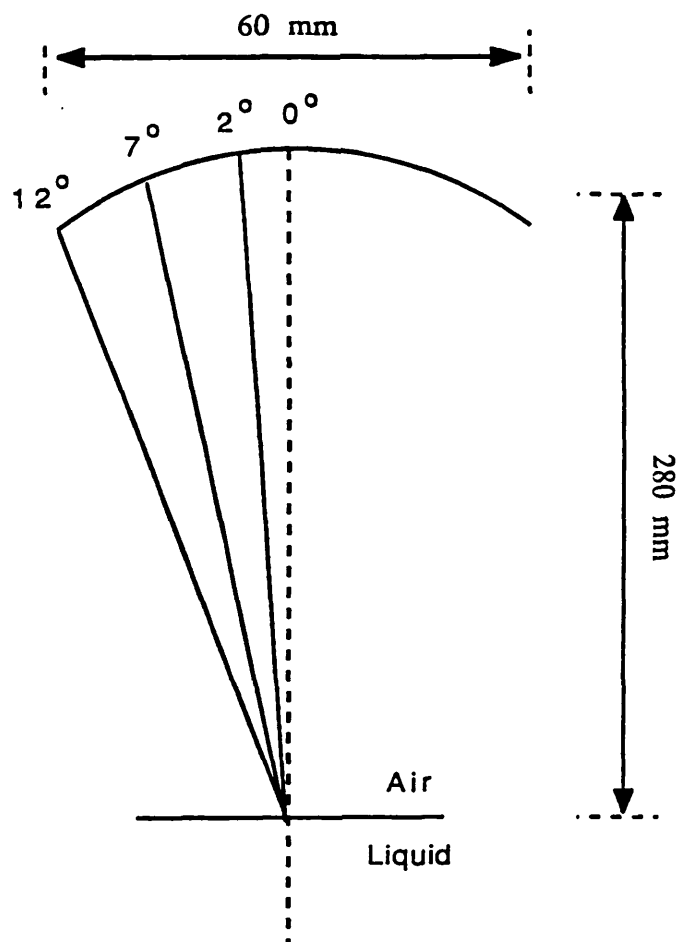


Fig P1 : Angles of Incidence in the Reflectometer System

The reflectance measurements made on the free liquid surface are used together with

the absorptive index to derive the refractive index of the liquid. The special form of the Fresnel equation, equation (P1), for a normal angle of incidence, is used in the calculations of the refractive index.

$$R = [(n - 1)^2 + k^2] / [(n + 1)^2 + k^2] \quad (P1)$$

However, from a practical point of view the angle of incidence cannot be zero. The *mean* angle of incidence (and therefore reflectance) used in the arrangement is 7° , with a convergence angle set at $\pm 5^\circ$. This is illustrated in fig P1, it should be stressed that for the sake of clarity the angles are greatly exaggerated in illustration, the curvature of the mirror is also greatly exaggerated and the distance between the concave mirror and the liquid surface appears reduced in length.

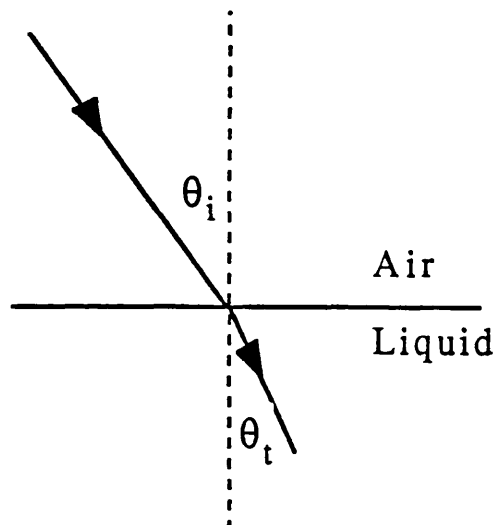


**Fig P2 : Angles at the Media Interface for a Free
Liquid Surface.**

The angles at the interface are shown in fig P2, the reflected component is not shown, θ_t can be determined from Snell's law:

$$\sin \theta_t = \sin \theta_i / m \quad (P2)$$

where m is the complex refractive index and θ_i is the angle of incidence (note $\sin \theta_t$, and hence θ_t , is complex when the liquid medium is absorbing).

The Fresnel formulae for light obliquely incident on a plane boundary (Duffin, 1980) are:

$$r_p = \tan(\theta_i - \theta_t) / \tan(\theta_i + \theta_t) \quad (P3)$$

and:

$$r_s = -\sin(\theta_i - \theta_t) / \sin(\theta_i + \theta_t) \quad (P4)$$

Where r_p is the amplitude reflection coefficient for the electric vector parallel to the plane of incidence and r_s the amplitude reflection coefficient for the electric vector perpendicular to the plane of incidence and the corresponding reflectances are given by:

$$R_p = |r_p|^2 \quad (P5)$$

and:

$$R_s = |r_s|^2 \quad (P6)$$

It is clearly necessary to analyse the effect of using the special form of the Fresnel (and hence setting the angle of incidence to zero) on the refractive index subsequently calculated, the absorptive index is measured independently or when it is large in magnitude it is generated, together with the corresponding refractive index, in a Kramers - Kronig analysis. However, the Kramers - Kronig dispersion technique depends on reflectance input data. In the analysis we envisage the worst possible case, an angle of incidence of 12° (i.e. the entire incident beam is at 12° to the normal). It should be stressed that the condition is, in the practical case, one of the least probable since the beam though not Gaussian, has a Gaussian type profile, therefore at the extreme angle of 12° the intensity will be a minimum (as at the 2°

angle); the greatest intensity of radiation is at 7° . The process of reflection and diffraction causes polarization of the beam, this was found to be in a ratio of 2:3 for the reflectometer arrangement.

The free liquid reflectometer arrangement described in chapter two has a sample dish and a water dish on the sample stage, this design allows the absolute reflectance of the sample liquid to be found by the ratio of the reflected signals obtained from the sample and water, i.e. the ratio of the reflected signals is equal to the ratio of the absolute reflectances of the sample and water (chapter two, equation 2.5). Naturally, the reflected signal from the water surface will also be considered to be at the worst case angle of 12° . In the following analysis we consider a range of sample optical constants and compare the unpolarized reflectance ratios (i.e. the normally incident case calculated using the special form of the Fresnel equation, given by equation (P1)) with the reflectances obtained by considering polarized beams at 12° (calculated using equation (P2) to equation (P6)). Making this comparison allows us to assess the percentage difference between the reflectance of the sample liquid found from the normal case and the reflectance found by the 12° incident angle case, and the subsequent difference in the n value produced. The optical constants of water are of course changing over the spectral range covered, therefore, two representative values of the complex refractive index of water (see chapter two) have been selected to use in the analysis. As previously mentioned the beam is 2:3 polarized which implies it may be one of two cases:

$$R_1 = 1/3 (2R_s + R_p) \quad (P7)$$

or

$$R_2 = 1/3 (R_s + 2R_p) \quad (P8)$$

In practise R_1 was found to lie above the value of the unpolarized reflectance, R , and R_2 lies an equal percentage below the value of R . Table P1 shows the values produced when the n and k values of water are taken to be 1.166 and 0.306 respectively, this low refractive index and high absorptive index combination occurs at 13 microns. A range of dummy optical constants are considered for the liquid under test extending from $1.2 - i 0$ (low n , negligible k value) to $1.2 - i 0.6$ (low n , high k value) and from $1.8 - i 0$ (high n , negligible k) to $1.8 - i 0.6$ (high n and k).

Optical constants of Sample Liquid	Relative %age Difference Between Reflectance at $\theta_i = 0^\circ$ and $\theta_i = 12^\circ$	Relative %age Discrepancy in n when Calculated from $\theta_i = 12^\circ$ Reflectance
1.2 - i 0	0.1	negligible
1.2 - i 0.4	0.2	0.2
1.2 - i 0.6	0.5	2.0
1.8 - i 0	0.8	0.3
1.8 - i 0.4	0.9	0.4
1.8 - i 0.6	1.0	0.6

Table P1: The Percentage Difference in the Refractive Index Between the Normal and 12° Incidence Cases for a Range of Optical Constants.

Complex Refractive Index of Water is $1.166 - i 0.306$.

The second column of table P1 shows the percentage variation of the reflectance for an incident angle of 12° when compared to the reflectance calculated by substituting the optical constants into the form of the Fresnel equation which assumes normal angles of incidence, i.e. equation (P1). This change in the reflectance is then translated into the percentage change in the refractive index value of the liquid under test, and the corresponding percentage discrepancy is shown in the third column of the data table.

It can be seen that, at this worst case angle of incidence, the error introduced into the final n value lies within the experimental limits of the experiment in all but one case. When the complex refractive index of the liquid is $1.2 - i 0.6$ and the complex refractive index of water is $1.166 - i 0.306$ there is a slightly higher variation of 2% in the final n value.

Table P2 again shows the same range of model optical constants and the corresponding variation from the normal case in the reflectance and refractive index if a 12° angle of

incidence is considered. However, in this case the complex refractive index of water is $1.438 - i 0.018$. The shifts in the refractive index values are all found to be within the assigned experimental uncertainty.

Optical constants of Sample	Relative %age Difference Between Reflectance at $\theta_i = 0^\circ$ and $\theta_i = 12^\circ$	Relative %age Discrepancy in n when Calculated from $\theta_i = 12^\circ$ Reflectance
Liquid		
1.2 - i 0	0.4	negligible
1.2 - i 0.4	0.2	0.2
1.2 - i 0.6	0.1	0.5
1.8 - i 0	0.5	0.2
1.8 - i 0.4	0.6	0.3
1.8 - i 0.6	0.6	0.4

Table P2: The Percentage Difference in the Refractive Index Between the Normal and 12° Incidence Cases for a Range of Optical Constants.

Complex Refractive Index of Water is $1.438 - i 0.018$.

B. The Volatile Liquid Chamber Case

The case of the closed cell system is a little different, again the extreme case is taken of the incident beam at 12° , and the polarized radiation is in a ratio of 2:3. However, in the closed cell case there are two interfaces to be considered, the air/AR coated surface and that of the window/liquid surface. Fig P3 shows the incident beam's path through the different media, again, the reflected components are not shown. The thickness of the AR coating has been exaggerated for clarity of illustration. The incident beam, inclined at 12° to the normal,

undergoes refraction at the air/AR coated window interface so that the beam incident at the second interface is inclined at an angle of θ_x . The size of the angle θ_x depends on the window in use, i.e. from Snell's law; for germanium the angle θ_x will be 3° , and for zinc selenide θ_x will be 5° .

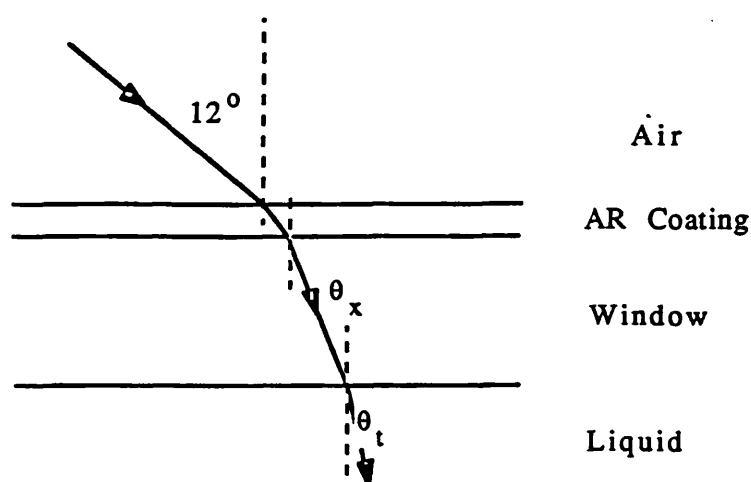


Fig P3 : Angles at the Interfaces for the Closed Cell Case.

In the analysis we make the assumption that in a worst case instance the AR coating is so inefficient that it is effectively not present. Therefore, we carry out a calculation for the first interface as if it is an air/window interface. Firstly for germanium, assuming a refractive index value of 4.0 and neglecting absorption the reflectance for an incident angle of 12° varies by 0.7% from the near-normal incidence value. The reflectance at an air/zinc selenide interface at 12° (assuming zinc selenide has an n value of 2.4 and neglecting absorption) differs by 1% from the near-normal case. The reflectance values of the coated surfaces of the two germanium windows (defined as RG_1 and RG_2 in chapter three) are corrupted by 0.7% in the program designed to calculate the n and k of a liquid in the closed cell system (see chapter three for outline of program). The corresponding coated surface values of the two zinc selenide windows (defined as RZ_1 and RZ_2 in chapter three) are weighted by 1%. The program is then run and n and k values for a test liquid are obtained and compared with n and k values obtained from data that has not been adjusted to represent the 12° incidence case. The

refractive index is found to vary by no more than 0.1% from the near-normal case, table P3 shows the corresponding variation in the k value for a range of absorptive index values generated.

k	%age variation from the near-normal k value
0.1	4
0.25	3
0.3	2
0.37	< 1
0.4	< 0.1

**Table P3: Variation in the k value found by 12° Incidence
Reflectance when Compared to Near-Normal
Reflectance k Values.**

It is clear from the variations shown in table P3 that the relative percentage difference in k found by 12° reflectances compared to the near-normal k value is reduced for increasing absorptive index. In chapter four it was stated that the practical range of the closed cell system began at k values of 0.4 it is therefore important to note that the percentage error in k generated at the maximum convergence angle of 12° is less than 0.1 at absorptive index values of 0.4 and above.

The reflectances at the window/test liquid (and window/water) interfaces are perhaps the most important. The angles of incidence of the beam at these interfaces will be reduced because of the relatively high refractive index of the substrate materials. So, as mentioned earlier, for the worst case analysis starting at 12°, the angle of incidence will fall to 5° in zinc selenide, and 3° in germanium. Once again a comparison between the reflectance found for a

near-normally incident angle and the reflectance for a 12° incident reflectance has been made using a range of dummy optical constants to represent the liquids, and the percentage variation in the reflectance of the 12° incidence calculated when germanium is the substrate in contact with the liquid. The same dummy optical constants are then used in the calculations when zinc selenide is the substrate in contact with the liquid. The results for selected optical constants are shown in table P4.

Optical Constants of Liquid	%age Variation in Reflectance for 12° Incidence	
	Germanium/Liquid	Zinc Selenide/Liquid
0.6 - i 0.8	0.1	0.3
1.1 - i 0.4	0.1	0.4
1.1 - i 0.6	0.1	0.3
1.2 - i 0.6	0.1	0.4
1.2 - i 1.0	0.1	0.2
1.4 - i 0.4	0.1	0.4
1.4 - i 0.8	0.2	0.2
1.9 - i 0.6	0.2	0.2

Table P4: The Difference in the Reflectances of the Substrate/Liquid Interface Between Angles of Incidence of $\theta_i = 0^\circ$ and $\theta_i = 12^\circ$.

Table P4 shows the range of variation between the normal and 12° reflectances is comparatively small i.e. the maximum discrepancy when the substrate is germanium is 0.2% and when the substrate is zinc selenide the maximum discrepancy is 0.4%. But the question remains, how does this discrepancy in the reflectance affect the optical constants of the liquid under investigation calculated in the closed cell technique? To analyse the effect on the n and k values the germanium/liquid reflectances calculated in the program outlined in chapter

three are corrupted by the maximum amount, that is 0.2% and the zinc selenide/liquid interfaces are corrupted by the maximum degree of 0.4%. Specifically, this means that the Ge/test liquid (denoted by RS_A in chapter three) and Ge/water (RW_{Ge}) are weighted by 0.2% and the zinc selenide/test liquid (RS_B) and zinc selenide/water (RW_{ZnSe}) interfaces corrupted by 0.4%. The program is then run with these changes and with the weighted air/substrate reflectances described in earlier sections (and in table P3) to find the overall change in the optical constants of the liquid under test when an angle of incidence of 12° is used.

When all the sources of discrepancy, arising from using an input incident beam of 12° (and assuming no AR coating), are combined the overall variation in the refractive index was found to be not more than 0.4%, which is well within the assigned limits of experimental error. The relative percentage variations in the corresponding k values are shown in table P5.

k	%age Variation in k
0.1	13
0.2	4
0.3	3
0.37	0.8
0.4	0.4

**Table P5: Variation in k when all Errors are Combined
in the 12° Incidence Case.**

It is possible to see that when all the interface discrepancies are combined the percentage difference between the 12° case and normal case for k equal to 0.1 is 13%, and the discrepancy diminishes with increasing k . For k values of about 0.4 - the minimum limit for k in the closed cell technique the error is 0.4%, this is within the assigned experimental variation.

To summarise; the worst case incidence of 12° for the free liquid and closed cell case was considered and the the percentage difference in the optical constants calculated. The conclusion drawn from the results obtained is that it is acceptable to use the near-normal (or special form) of the Fresnel equation for our analysis.

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